Ionic liquid mediated Cu-catalyzed cascade *oxa*-Michael-oxidation: efficient synthesis of flavones under mild reaction condition

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Supporting Information

Contents:

1. General Information

Chemicals and solvents were purchased from commercial suppliers and used as received. ^{1}H and ^{13}C NMR spectra were recorded on a AMX500 (500 MHz) spectrometer. Chemical shifts were reported in parts per million (ppm), and the residual solvent peak was used as an internal reference: proton (chloroform δ 7.26), carbon (chloroform δ 77.0) or tetramethylsilane (TMS δ 0.00) was used as a reference. Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublet), bs (broad singlet). Coupling constants were reported in Hertz (Hz). Low resolution mass spectra were obtained on a Finnigan/MAT LCQ spectrometer in ESI mode, and a Finnigan/MAT 95XL-T mass spectrometer in EI mode. All high resolution mass spectra were obtained on a Finnigan/MAT 95XL-T spectrometer. For thin layer chromatography (TLC), Merck pre-coated TLC plates (Merck 60 F254) were used, and compounds were visualized with a UV light at 254 nm. Further visualization was achieved by staining with iodine, or ninhydrin followed by heating using a heat gun. Flash chromatography separations were performed on Merck 60 (0.040-0.063 mm) mesh silica gel. The enantiomeric excesses of products were determined by chiral phase HPLC analysis. Optical rotations were recorded on Jasco DIP-1000 polarimeter.

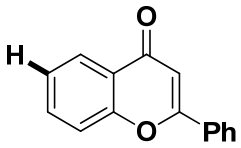
2. General Procedure for Preparation of Chalcone.

To a solution of o-hydroxyacetophenone (3 mmol) and benzaldehyde (4.5 mmol) in 4 ml of ethanol in a 100 mL round bottom flask, sodium hydroxide (6.3M, 0.5 mL) was added dropwise. The reaction was stirred at room temperature for 2 to 3 hours until a thick orange mixture was formed, and was cooled in the refrigerator overnight. The reaction mixture was quenched with 8 mL of ice-cold water and acetic acid (approximately 6 mL) was added slowly with stirring until acidic. The yellow solid separated was filtered and washed with ice-cold water. The chalcone (**1a** to **1aa**) was pure for use without further purification steps.

3. General Procedure for Synthesis of Flavone.

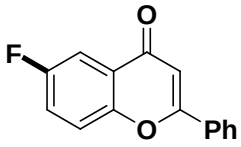
Chalcone **1** (0.2 mmol) and copper (I) iodide (0.04 mmol) were dissolved in 2 mL of N,N-dimethylacetamide (DMA) in a reaction flask with stirring at 130 °C in the open. After 16 hours, the reaction mixture was cooled and the solvent was evaporated. The crude product was purified by column chromatography, hexane: ethyl acetate (12:1) eluent to afford the pure flavone (**2**) as white solid. The flavones were characterized by their ^{1}H NMR and ^{13}C NMR.

4. Analytical Data

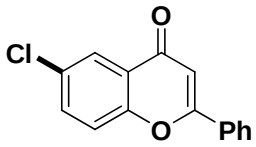


2-phenyl-4H-1-Benzopyran-4-one (2a): ^{1}H NMR (300MHz, $CDCl_3$, TMS): δ = 8.23 (dd, *J* = 7.9,

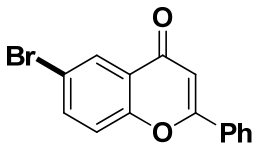
1.3 Hz, 1H), 7.98 – 7.87 (m, 2H), 7.69 (m, 1H), 7.59 – 7.47 (m, 4H), 7.40-7.35 (m, 1H), 6.82 (s, 1H). ^{13}C NMR (300 MHz, $CDCl_3$) δ = δ 178.34, 163.29, 156.15, 133.68, 131.66, 131.51, 128.94, 126.18, 125.59, 125.13, 123.86, 117.99, 107.47. HRMS (ESI) calcd for $C_{15}H_{10}O_2$ (M + H+) 223.0754, found 223.0761.



6-fluoro-2-phenyl-4H-1-Benzopyran-4-one (2b): ^{1}H NMR (300MHz, $CDCl_3$, TMS): δ = 7.96 – 7.84 (m, 3H), 7.66 – 7.48 (m, 4H), 7.48 – 7.38 (m, 1H), 6.82 (s, 1H). ^{13}C NMR (300 MHz, $CDCl_3$) δ = 163.70, 131.78, 131.55, 129.09, 126.32, 122.06, 121.72, 120.20, 120.09, 110.81, 110.50, 106.91. HRMS (ESI) calcd for $C_{15}H_9FO_2$ (M + H+) 241.0659, found 241.0654.

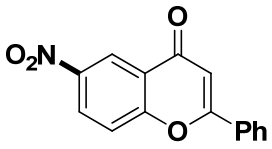


6-chloro-2-phenyl-4H-1-Benzopyran-4-one (2c): ^{1}H NMR (300MHz, $CDCl_3$, TMS): δ = 8.17 (d, *J* = 2.6 Hz, 1H), 7.99-7.83 (m, 2H), 7.67-7.60 (m, 1H), 7.56 – 7.49 (m, 4H), 6.81 (s, 1H). ^{13}C NMR (300 MHz, $CDCl_3$) δ = 177.13, 163.67, 154.52, 133.94, 131.85, 131.33, 131.17, 129.08, 126.29, 125.13, 124.84, 119.78, 107.40. HRMS (ESI) calcd for $C_{15}H_9ClO_2$ (M + H+) 257.0364, found 257.0370.

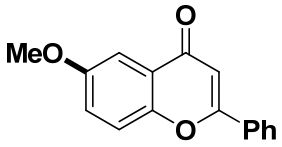


6-bromo-2-phenyl-4H-1-Benzopyran-4-one (2d): ^{1}H NMR (300MHz, $CDCl_3$, TMS): δ = 8.36 (d, *J*

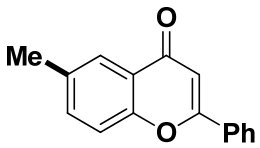
= 2.4 Hz, 1H), 7.98-7.84 (m, 2H), 7.78 (dd, *J* = 8.9, 2.4 Hz, 1H), 7.58 – 7.51 (m, 3H), 7.47 (d, *J* = 8.9 Hz, 1H), 6.83 (s, 1H). ^{13}C NMR (300 MHz, $CDCl_3$) δ = 163.59, 131.86, 131.41, 129.12, 128.40, 126.33, 120.03, 118.67, 107.68, 107.58. HRMS (ESI) calcd for $C_{15}H_9BrO_2$ (M + H+) 300.9859, found 300.9851.



6-nitro-2-phenyl-4H-1-Benzopyran-4-one (2e): ^{1}H NMR (300MHz, $CDCl_3$, TMS): δ = 9.11 (d, *J* = 2.8 Hz, 1H), 8.60-8.53 (m, 1H), 7.99-7.90 (m, 2H), 7.73 (d, *J* = 9.2 Hz, 1H), 7.65 – 7.52 (m, 3H), 6.89 (s, 1H). ^{13}C NMR (300 MHz, $CDCl_3$) δ = 164.13, 132.36, 130.78, 129.29, 128.13, 126.43, 122.51, 119.81, 107.88. HRMS (ESI) calcd for $C_{15}H_9NO_4$ (M + H+) 268.0604, found 268.0614.

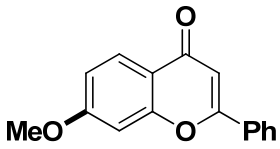


6-methoxy-2-phenyl-4H-1-Benzopyran-4-one (2f): ^{1}H NMR (300MHz, $CDCl_3$, TMS): δ = 7.88 (dd, *J* = 6.1, 2.7 Hz, 2H), 7.57 – 7.44 (m, 5H), 7.25 (m, 1H), 6.78 (s, 1H), 3.87 (s, 3H). ^{13}C NMR (300 MHz, $CDCl_3$) δ = 178.23, 163.09, 156.95, 151.02, 131.82, 131.43, 128.97, 126.17, 124.51, 123.74, 119.46, 106.78, 104.79, 55.87. HRMS (ESI) calcd for $C_{16}H_{12}O_3$ (M + H+) 253.0859, found 253.0870.

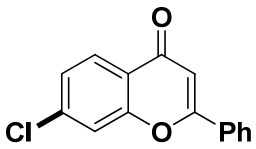


6-methyl-2-phenyl-4H-1-Benzopyran-4-one (2g): ^{1}H NMR (300MHz, $CDCl_3$, TMS): δ = 7.99 (d, *J*

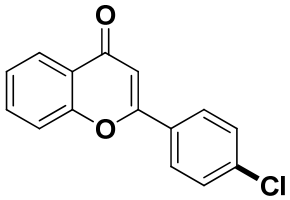
= 0.6 Hz, 1H), 7.95 – 7.81 (m, 2H), 7.54 – 7.40 (m, 5H), 6.78 (s, 1H), 2.44 (s, 3H). ^{13}C NMR (300 MHz, $CDCl_3$) δ = 178.52, 163.37, 154.52, 135.23, 135.05, 131.78, 131.53, 128.98, 126.26, 124.99, 123.45, 117.81, 107.28, 20.90. HRMS (ESI) calcd for $C_{16}H_{12}O_2$ (M + H+) 237.0910, found 237.0910.



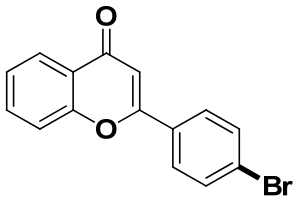
7-methoxy-2-phenyl-4H-1-Benzopyran-4-one (2h): ^{1}H NMR (300MHz, $CDCl_3$, TMS): δ = 8.13 (d, *J* = 8.5 Hz, 1H), 7.95 – 7.85 (m, 2H), 7.58 – 7.48 (m, 3H), 7.00 – 6.94 (m, 2H), 6.76 (s, 1H), 3.93 (s, 3H). ^{13}C NMR (300 MHz, $CDCl_3$) δ = 177.81, 164.33, 163.31, 158.05, 131.67, 131.53, 129.00, 127.01, 126.19, 114.61, 107.22, 100.35, 55.85. HRMS (ESI) calcd for $C_{16}H_{12}O_3$ (M + H+) 253.0859, found 253.0873.



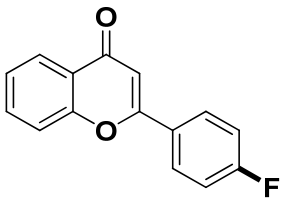
7-chloro-2-phenyl-4H-1-Benzopyran-4-one (2i): ^{1}H NMR (300MHz, $CDCl_3$, TMS): δ = 8.14 (d, *J* = 8.5 Hz, 1H), 7.93 – 7.84 (m, 2H), 7.60 – 7.50 (m, 4H), 7.37 (dd, *J* = 8.5, 1.9 Hz, 1H), 6.79 (s, 1H). ^{13}C NMR (300 MHz, $CDCl_3$) δ = 177.44, 163.48, 156.29, 139.72, 131.79, 131.31, 129.07, 127.04, 126.22, 126.03, 122.46, 118.14, 107.71. HRMS (ESI) calcd for $C_{15}H_9ClO_2$ (M + H+) 257.0364, found 257.0354.



2-(4-chlorophenyl)-4H-1-Benzopyran-4-one (2j): ^{1}H NMR (300MHz, $CDCl_3$, TMS): δ = 8.30 – 8。20 (m, 1H), 7.90 – 7.81 (m, 2H), 7.73 – 7.64 (m, 1H), 7.61 – 7.39 (m, 4H), 6.76 (s, 1H). ^{13}C NMR (300 MHz, $CDCl_3$) δ = 178.12, 162.08, 156.05, 137.80, 133.82, 130.12, 129.28, 127.43, 125.64, 125.29, 123.80, 117.95, 107.56. HRMS (ESI) calcd for $C_{15}H_9ClO_2$ (M + H+) 257.0364, found 257.0361.

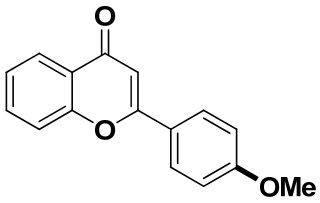


2-(4-bromophenyl)-4H-1-Benzopyran-4-one (2k): ^{1}H NMR (300MHz, $CDCl_3$, TMS): δ = 8.20 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.81 – 7.46 (m, 6H), 7.45 – 7.30 (m, 1H), 7.45 (m, 1H), 6.77 (s, 1H). ^{13}C NMR (300 MHz, $CDCl_3$) δ = 178.07, 163.91, 156.49, 140.36, 133.98, 133.90, 133.39, 131.85, 130.81, 130.45, 130.36, 128.32, 127.60, 126.49, 125.71, 125.31, 124.83, 124.15, 123.83, 121.82, 120.53, 118.26, 118.17, 113.39, 112.78, 112.45. HRMS (ESI) calcd for $C_{15}H_9BrO_2$ (M + H+) 300.9859, found 300.9872.

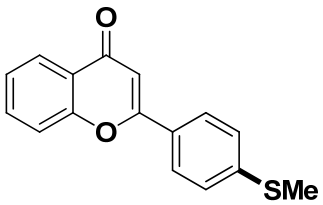


2-(4-fluorophenyl)-4H-1-Benzopyran-4-one (2l): ^{1}H NMR (300MHz, $CDCl_3$, TMS): δ = ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = 8.21 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.99 – 7.85 (m, 2H), 7.75 – 7.65 (m, 1H), 7.54 (d, *J* = 8.5 Hz, 1H), 7.41 (m, 1H), 7.30 – 7.10 (m, 2H), 6.75 (d, *J* = 2.1 Hz, 1H). ^{13}C NMR (300 MHz, $CDCl_3$) δ = 178.23, 166.39, 163.03, 162.35, 156.12, 133.79, 128.51, 128.39, 127.95, 127.91,

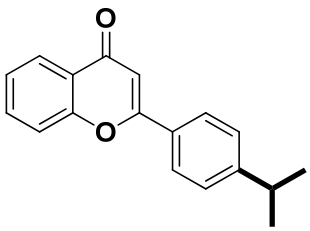
125.69, 125.28, 123.82, 117.96, 116.39, 116.10, 107.32. HRMS (ESI) calcd for $C_{15}H_9FO_2$ (M + H+) 241.0659, found 241.0661.



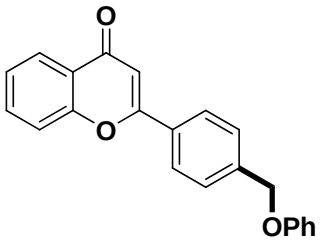
2-(4-methoxyphenyl)-4H-1-Benzopyran-4-one (2m): ^{1}H NMR (300MHz, $CDCl_3$, TMS): δ = 7.88 (d, *J* = 8.9 Hz, 2H), 7.71 – 7.65 (m, 1H), 7.64 – 7.50 (m, 1H), 7.46 – 7.36 (m, 1H), 7.02 (d, *J* = 8.9 Hz, 3H), 6.74 (s, 1H), 3.89 (s, 3H). ^{13}C NMR (300 MHz, $CDCl_3$) δ = 178.37, 163.40, 162.39, 156.17, 133.53, 127.98, 125.65, 125.05, 124.02, 123.93, 117.93, 114.45, 106.18, 55.48. HRMS (ESI) calcd for $C_{16}H_{12}O_3$ (M + H+) 253.0859, found 253.0857.



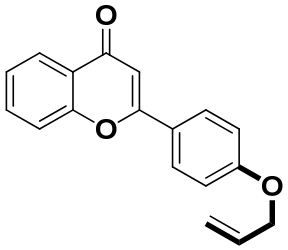
2-(4-methylthiophenyl)-4H-1-Benzopyran-4-one (2n): ^{1}H NMR (300MHz, $CDCl_3$, TMS): δ = 8.19 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.82 – 7.77 (m, 2H), 7.74 – 7.53 (m, 1H), 7.51 (d, *J* = 7.9 Hz, 1H), 7.38 (m, 1H), 7.32 – 7.27 (m, 2H), 6.74 (s, 1H), 2.51 (s, 3H). ^{13}C NMR (300 MHz, $CDCl_3$) δ = 178.20, 162.89, 156.03, 143.93, 133.58, 127.63, 126.33, 125.63, 125.53, 125.06, 123.84, 117.90, 106.62, 14.84. HRMS (ESI) calcd for C16H12SO_2 (M + H+) 269.0631, found 269.0636.



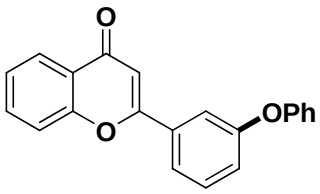
2-(4-isopropylphenyl)- 4H-1-Benzopyran-4-one (2o): ^{1}H NMR (300MHz, $CDCl_3$, TMS): δ = 8.22 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.87 – 7.82 (m, 2H), 7.75 – 7.64 (m, 1H), 7.56 (m, 1H), 7.44 – 7.35 (m, 3H), 6.80 (s, 1H), 2.96 (septet, *J* = 6.9 Hz, 1H), 1.29 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (300 MHz, $CDCl_3$) δ = 178.43, 163.61, 156.22, 153.03, 133.61, 129.26, 127.14, 126.36, 125.63, 125.08, 123.95, 118.01, 107.00, 34.10, 23.67. HRMS (ESI) calcd for $C_{18}H_{16}O_2$ (M + H^+) 265.1223, found 265.1233.



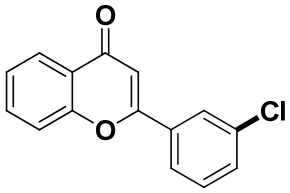
2-(4-(benzyloxy)phenyl)- 4H-1-Benzopyran-4-one (2p): ^{1}H NMR (300MHz, $CDCl_3$, TMS): δ = 8.21 (d, *J* = 7.9 Hz, 1H), 7.85 (d, *J* = 8.5 Hz, 2H), 7.66 (t, *J* = 7.9 Hz, 1H), 7.57 – 7.48 (m, 1H), 7.45 – 7.35 (m, 6H), 7.07 (d, *J* = 8.5 Hz, 2H), 6.74 (s, 1H), 5.13 (s, 2H). ^{13}C NMR (300 MHz, $CDCl_3$) δ = 178.36, 163.32, 161.51, 156.14, 136.15, 133.53, 128.67, 128.21, 127.98, 127.42, 125.62, 125.05, 124.19, 123.87, 117.90, 115.29, 106.17, 70.15. HRMS (ESI) calcd for $C_{22}H_{16}O_3$ (M + H^+) 329.1172, found 329.1174.



2-(4-(ethenyloxy)phenyl)- 4H-1-Benzopyran-4-one (2q): ^{1}H NMR (300MHz, $CDCl_3$, TMS): δ = 8.20 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.89 – 7.82 (m, 2H), 7.70 -7.61 (m, 1H), 7.56 – 7.48 (m, 1H), 7.42 – 7.35 (m, 1H), 7.06 – 6.97 (m, 2H), 6.74 (s, 1H), 6.10 – 6.01 (m, 1H), 5.48 – 5.40 (m, 1H), 5.39 -5.27 (m, 1H), 4.68 – 4.55 (m, 3H). ^{13}C NMR (300 MHz, $CDCl_3$) δ = 178.40, 163.56, 161.43, 156.12, 133.63, 132.43, 132.11, 128.01, 125.58, 125.10, 123.92, 123.69, 118.18, 117.91, 115.14, 114.27, 105.95, 68.88. HRMS (ESI) calcd for $C_{18}H_{14}O$ (M + H+) 279.1016, found 279.1019.

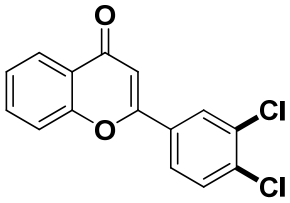


2-(3-phenoxyphenylphenyl)- 4H-1-Benzopyran-4-one (2r): ^{1}H NMR (300MHz, $CDCl_3$, TMS): δ = 8.22 (m, 1H), 7.71 – 7.62 (m, 2H), 7.57 – 7.35 (m, 7H), 7.20 -7.10 (m, 2H), 7.08 – 7.03 (m, 2H), 6.77 (s, 1H). ^{13}C NMR (300 MHz, $CDCl_3$) δ = 178.33, 162.61, 158.08, 156.73, 156.14, 133.80, 133.51, 130.38, 129.98, 125.64, 125.25, 124.00, 123.87, 121.51, 120.84, 119.22, 118.06, 116.22, 107.86. HRMS (ESI) calcd for $C_{21}H_{14}O_3$ (M + H+) 315.1016, found 315.1021.

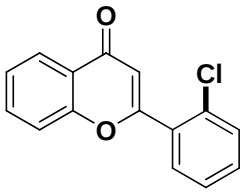


2-(3-chlorophenyl)- 4H-1-Benzopyran-4-one (2s): ^{1}H NMR (300MHz, $CDCl_3$, TMS): δ = 8.25 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.97 – 7.91 (m, 2H), 7.77 -7.68 (m, 1H), 7.58 – 7.50 (m, 3H), 7.44 (m, 1H), 6.89 (s, 1H). ^{13}C NMR (300 MHz, $CDCl_3$) δ = 178.48, 163.55, 156.28, 133.83, 131.75, 131.65, 129.05, 126.33, 125.72, 125.27, 118.09, 107.54. HRMS (ESI) calcd for $C_{15}H_9ClO_2$ (M + H+) 257.0364, found

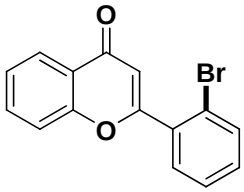
257.0368.



2-(3,4-dichlorophenyl)- 4H-1-Benzopyran-4-one (2t): ^{1}H NMR (300MHz, $CDCl_3$, TMS): δ = 8.23 (dd, *J* = 8.0, 1.4 Hz, 1H), 8.04 (d, *J* = 2.1 Hz, 1H), 7.78 – 7.71 (m, 2H), 7.65 -7.77 (m, 2H), 7.49 -7.40 (m, 1H), 6.79 (s, 1H). ^{13}C NMR (300 MHz, $CDCl_3$) δ = 178.07, 160.92, 156.09, 136.00, 134.13, 133.71, 131.66, 131.12, 128.08, 125.79, 125.58, 125.28, 123.82, 118.06, 108.14. HRMS (ESI) calcd for $C_{15}H_8C_{l2}O_2$ (M + H+) 290.9974, found 290.9979.

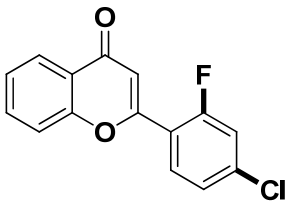


2-(2-chlorophenyl)- 4H-1-Benzopyran-4-one (2u): ^{1}H NMR (300MHz, $CDCl_3$, TMS): δ = 8.23 (dd, *J* = 8.0, 1.4 Hz, 1H), 8.08 – 8.02 (m, 1H), 7.78 -7.81 (m, 2H), 7.63 – 7.57 (m, 2H), 7.49 -7.43 (m, 1H), 6.79 (s, 1H). ^{13}C NMR (300 MHz, $CDCl_3$) δ = 178.07, 162.59, 156.54, 133.87, 132.87, 131.87, 131.74, 130.76, 130.59, 127.05, 125.70, 125.29, 123.79, 118.15, 112.96. HRMS (ESI) calcd for $C_{15}H_9ClO_2$ (M + H+) 257.0364, found 257.0370.

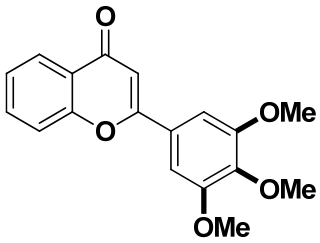


2-(2-bromophenyl)- 4H-1-Benzopyran-4-one (2v): ^{1}H NMR (300MHz, $CDCl_3$, TMS): δ = 8.25 (d,

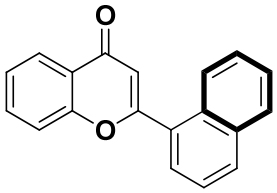
J = 7.9 Hz, 1H), 7.70 (t, *J* = 7.9 Hz, 3H), 7.59 – 7.40 (m, 5H), 6.58 (s, 1H). ^{13}C NMR (300 MHz, $CDCl_3$) δ = 178.13, 175.11, 163.97, 163.01, 133.95, 131.88, 130.85, 127.63, 125.77, 125.36, 118.21, 112.83. HRMS (ESI) calcd for $C_{15}H_9BrO_2$ (M + H+) 300.9859, found 300.9862.



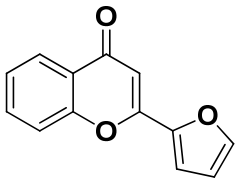
2-(4-chloro-2-fluorophenyl)-4H-1-Benzopyran-4-one (2w): ^{1}H NMR (300MHz, $CDCl_3$, TMS): δ = 8.24 (d, *J* = 7.9 Hz, 1H), 7.90 (t, *J* = 8.3 Hz, 1H), 7.74 (m, 1H), 7.55 (d, *J* = 8.3 Hz, 1H), 7.48 – 7.42 (m, 1H), 7.37 – 7.27 (m, 2H), 6.92 (s, 1H). ^{13}C NMR (300 MHz, $CDCl_3$) δ = 178.15, 161.96, 158.52, 157.65, 157.59, 156.19, 138.27, 138.13, 133.97, 129.72, 129.70, 125.72, 125.39, 125.18, 123.74, 119.89, 117.89, 117.55, 112.48, 112.33. HRMS (ESI) calcd for $C_{15}H_8ClFO_2$(M + H+) 275.0270, found 275.0277.



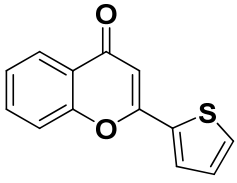
2-(3,4,5-trimethoxyphenyl))-4H-1-Benzopyran-4-one (2x): ^{1}H NMR (300MHz, $CDCl_3$, TMS): δ = 8.23 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.74 – 7.38 (m, 1H), 7.58 (d, *J* = 7.9 Hz, 1H), 7.44 (m, 1H), 7.14 (s, 2H), 6.78 (s, 1H), 3.96 (s, 6H), 3.93 (s, 3H). ^{13}C NMR (300 MHz, $CDCl_3$) δ = 178.33, 162.25, 156.20, 153.58, 133.72, 127.00, 125.71, 125.27, 123.90, 118.03, 107.38, 61.03, 56.34. HRMS (ESI) calcd for $C_{18}H_{16}O_5$ (M + H+) 313.1071, found 313.1078.



2-(1-naphthalenyl)- 4H-1-Benzopyran-4-one (2y): ^{1}H NMR (300MHz, $CDCl_3$, TMS): δ = 8.32 (d, *J* = 7.9 Hz, 1H), 8.13 (m, 1H), 8.01 (d, *J* = 8.1 Hz, 1H), 7.99-7.93 (m, 1H), 7.80 – 7.68 (m, 2H), 7.56 - 7.40 (m, 5H), 6.69 (s, 1H). ^{13}C NMR (300 MHz, $CDCl_3$) δ = 178.28, 156.73, 133.97, 133.71, 131.58, 130.53, 130.35, 128.03, 127.46, 126.57, 125.85, 125.43, 125.05, 124.83, 123.85, 118.24, 112.92. HRMS (ESI) calcd for $C_{19}H_{12}O_2$ (M + H+) 273.0910, found 273.0911.

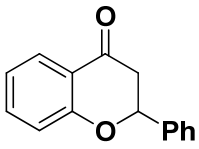


2-(2-furanyl)-4H-1-Benzopyran-4-one (2z): ^{1}H NMR (300MHz, $CDCl_3$, TMS): δ = 8.18 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.67 – 7.63 (m, 1H), 7.60 (d, *J* = 0.9 Hz, 1H), 7.49 – 7.43 (m, 1H), 7.37 (m, 1H), 7.12 – 7.09 (m, 1H), 6.70 (s, 1H), 6.59 – 6.56 (m, 1H). ^{13}C NMR (300 MHz, $CDCl_3$) δ = 177.70, 155.70, 155.07, 146.28, 145.72, 133.64, 125.64, 125.09, 124.11, 117.80, 112.99, 112.45, 105.38. HRMS (ESI) calcd for $C_{13}H_8O_3$ (M + H+) 213.0546, found 213.0547.



2-(2-thienyl)- 4H-1-Benzopyran-4-one (2aa): ^{1}H NMR (300MHz, $CDCl_3$, TMS): δ = 8.17 (m, 1H), 7.72 – 7.61 (m, 2H), 7.57 – 7.52 (m, 1H), 7.50 – 7.47 (m, 1H), 7.37 (m, 1H), 7.17 – 7.13 (m, 1H), 6.66 (s, 1H). ^{13}C NMR (300 MHz, $CDCl_3$) δ = 177.82, 159.10, 155.85, 135.02, 133.76, 130.35, 128.51,

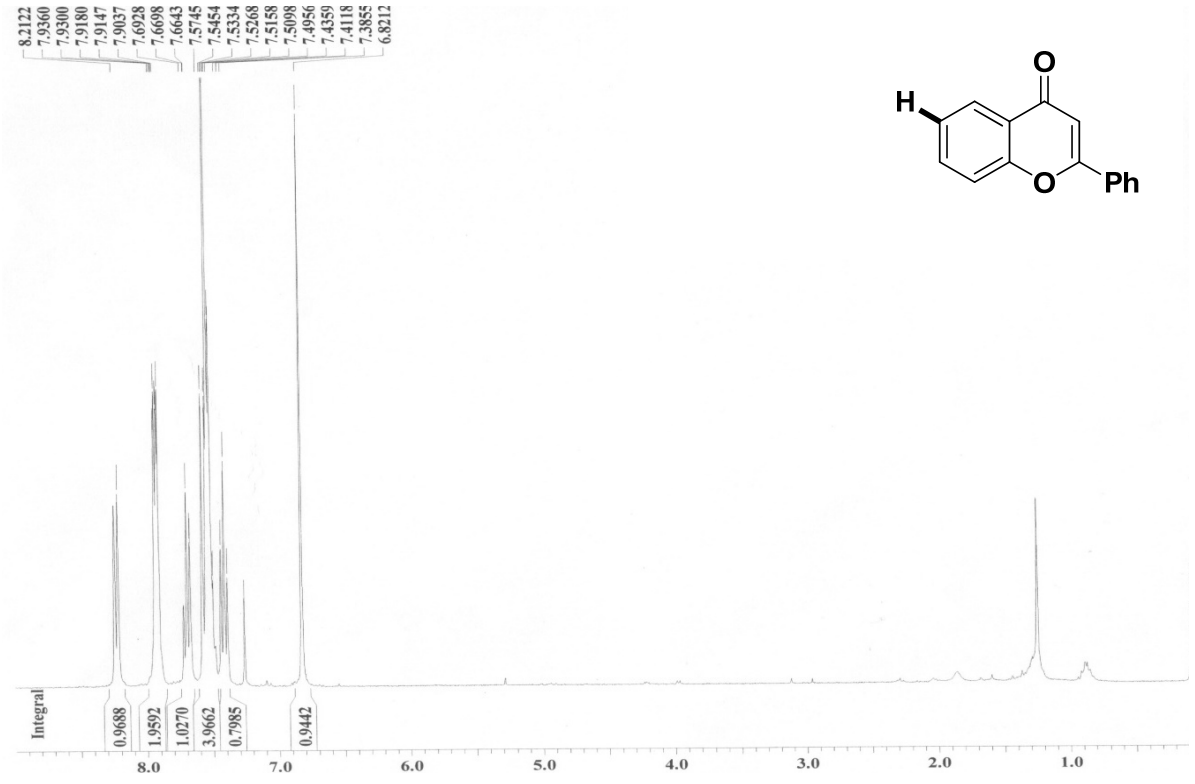
128.47, 125.61, 125.25, 123.80, 117.87, 106.00. HRMS (ESI) calcd for $C_{14}H_{19}NO_3$ (M + H^+) 229.0318, found 229.0322.

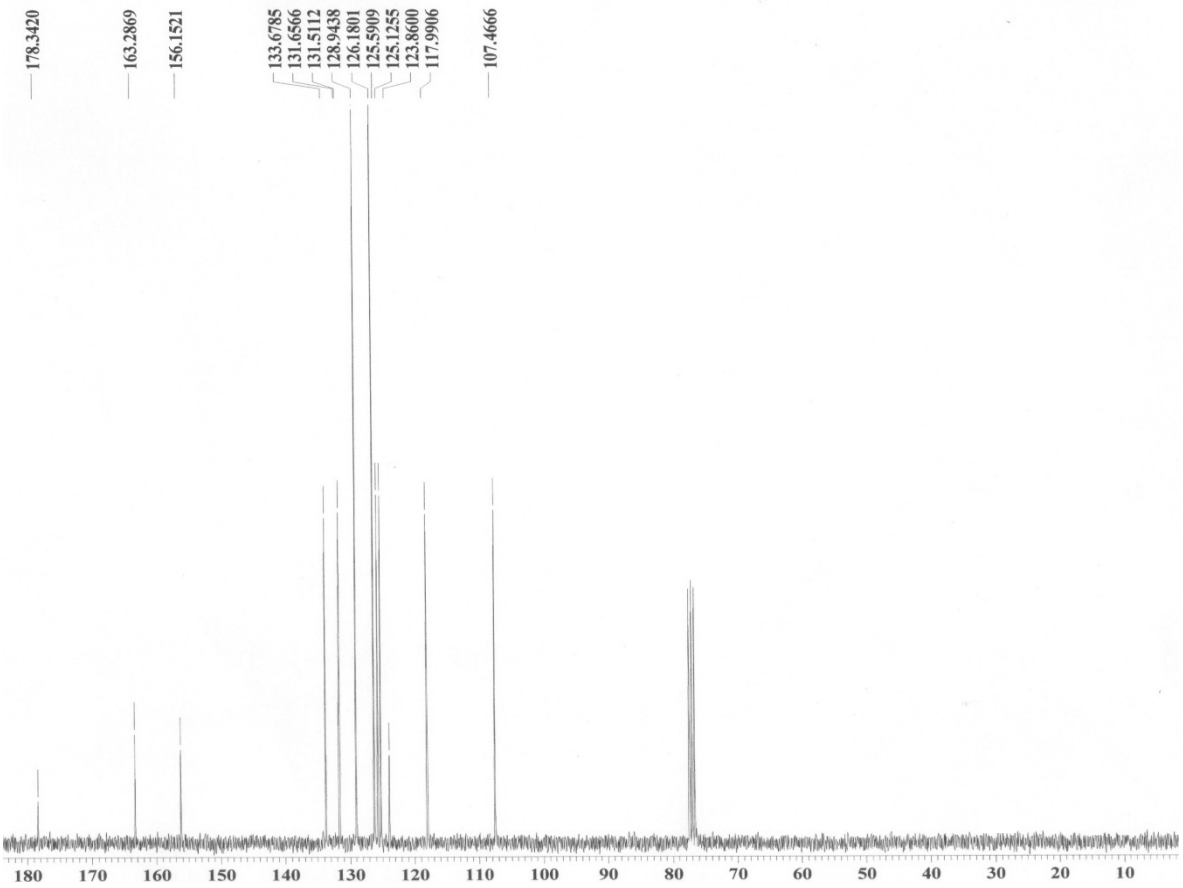


2-phenyl-2,3-dihydrochromen-4-one (2a'): ^{1}H NMR (300MHz, $CDCl_3$, TMS): δ = 7.95 (m, 1H), 7.55-7.37 (m, 6H), 7.09-7.04 (m, 2H), 5.53 – 5.49 (m, 1H), 3.14 – 3.09 (m, 1H), 2.91 (dd, 1H, *J* = 16.9, 3.0 Hz). ^{13}C NMR (300 MHz, $CDCl_3$) δ = 191.95, 161.53, 138.71, 136.18, 128.83, 128.75, 127.03, 126.12, 121.60, 120.91, 118.11, 79.57, 44.64. HRMS (ESI) calcd for $C_{15}H_{12}O_2$ (M + H^+) 225.0910, found 225.0915

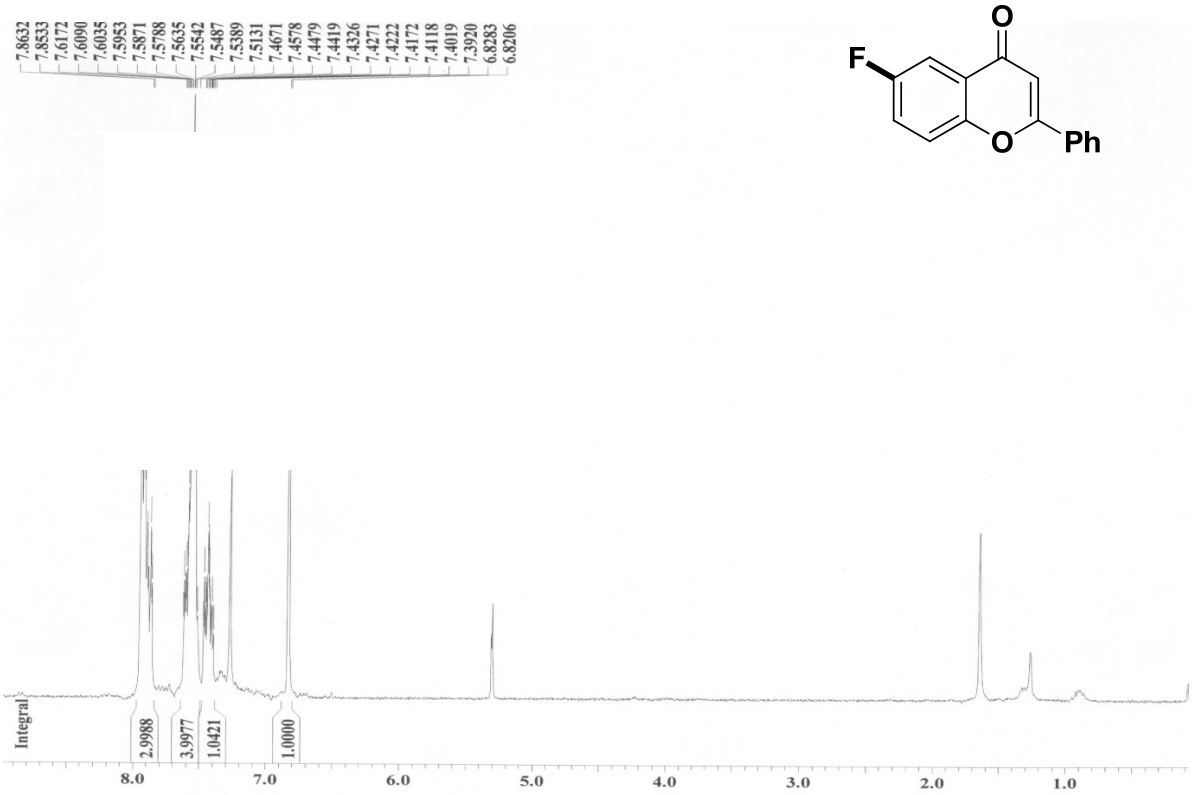
5. NMR Spectra

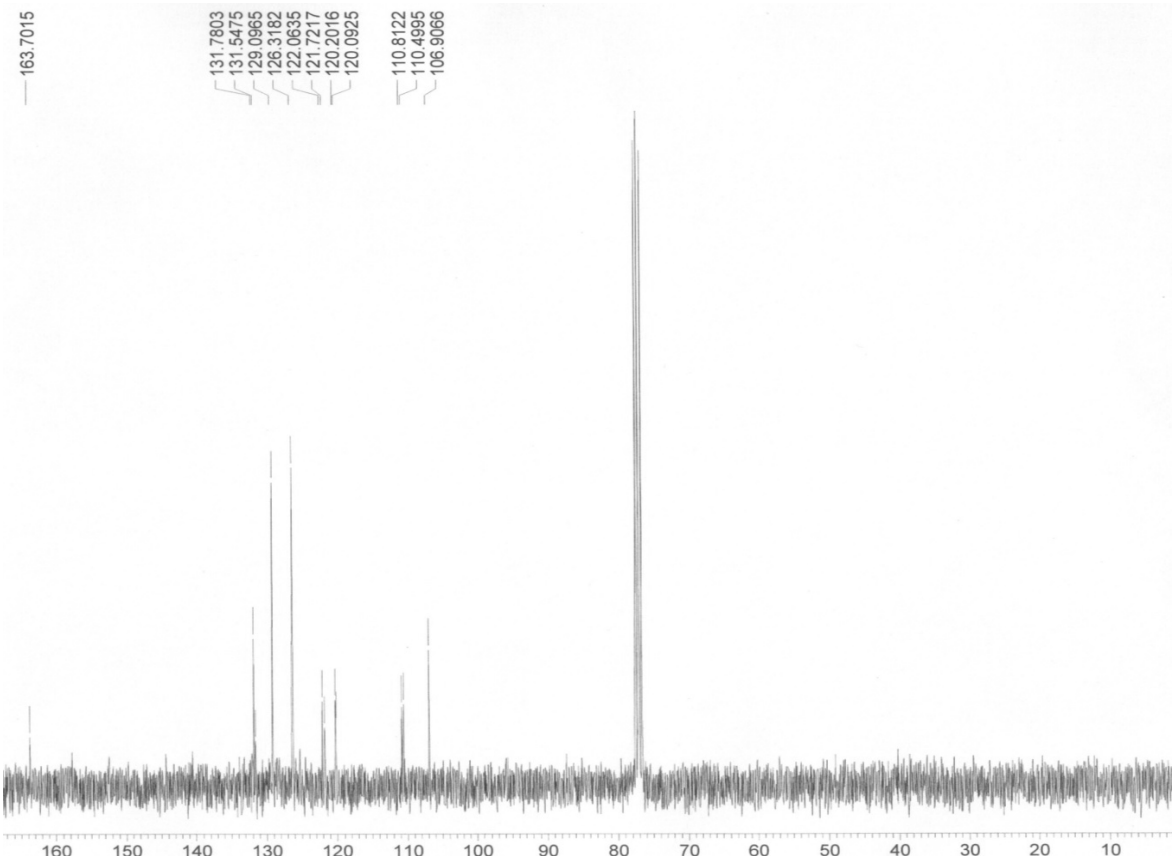
2-phenyl-4H-1-Benzopyran-4-one (2a)



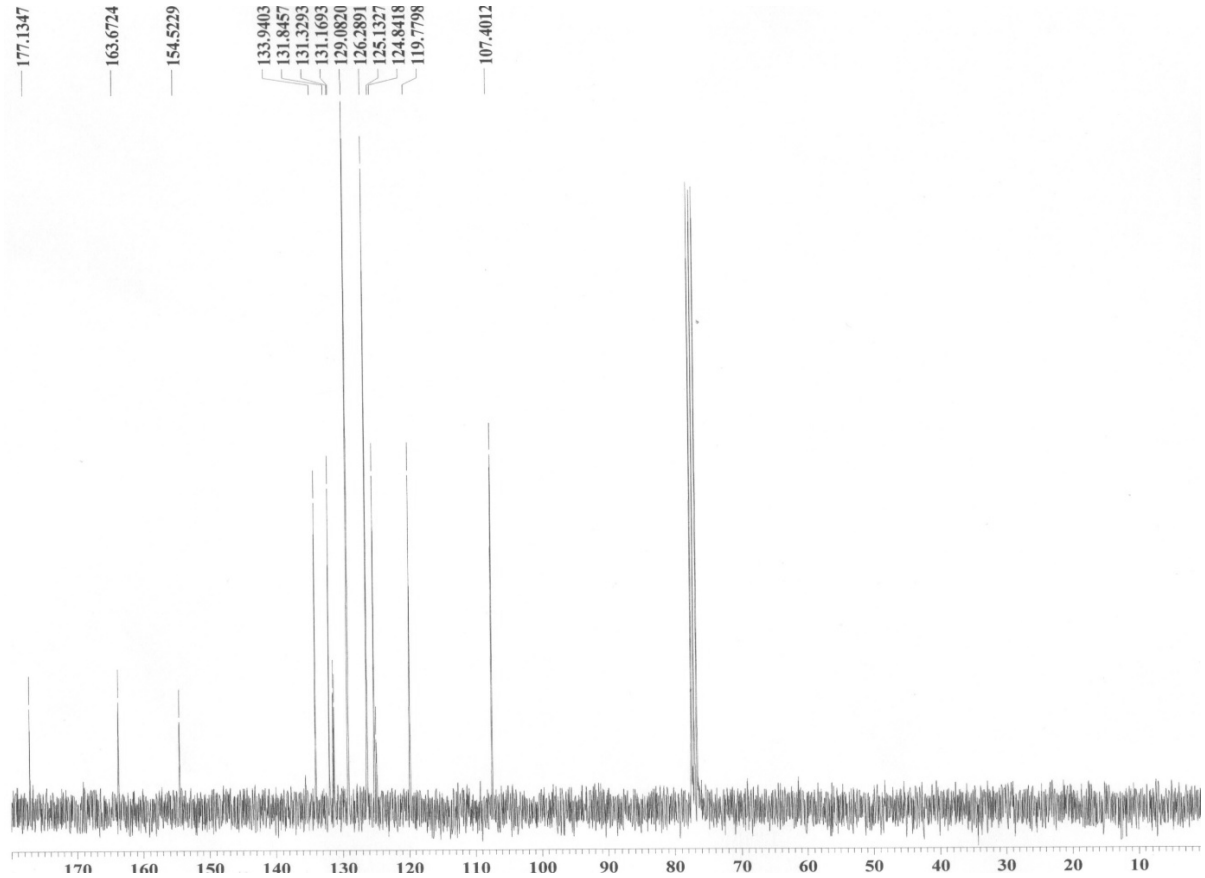


6-fluoro-2-phenyl-4H-1-Benzopyran-4-one (2b)

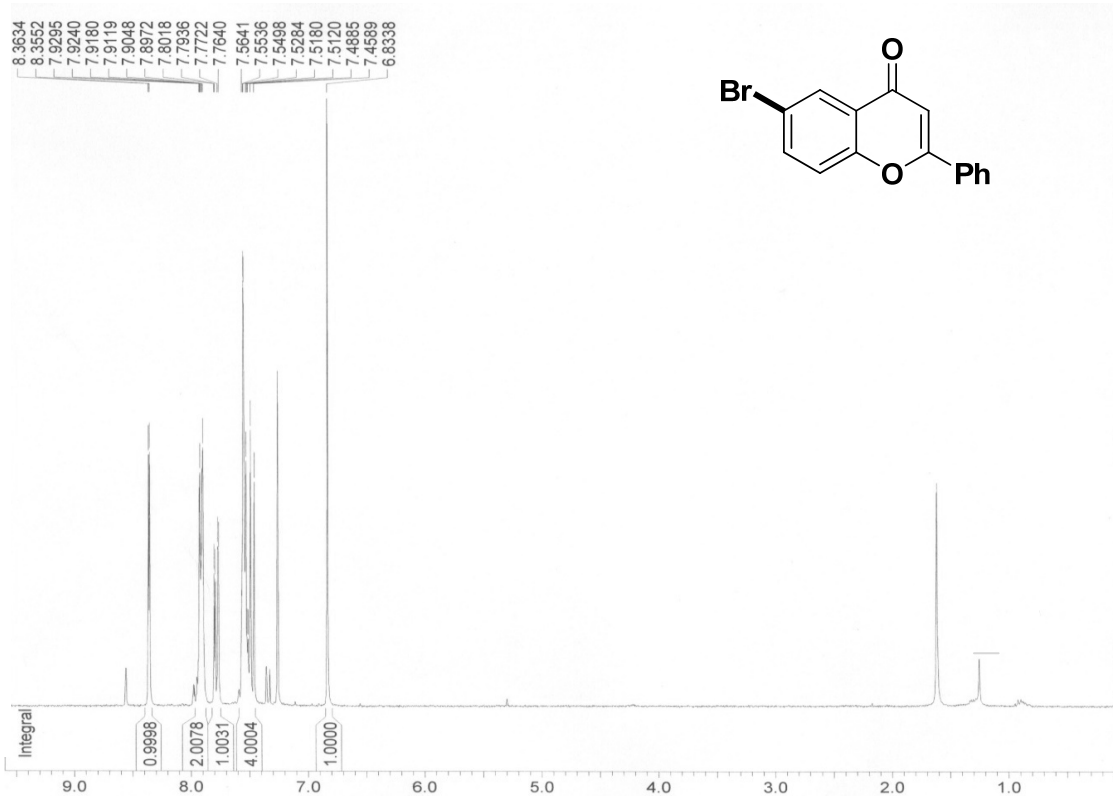


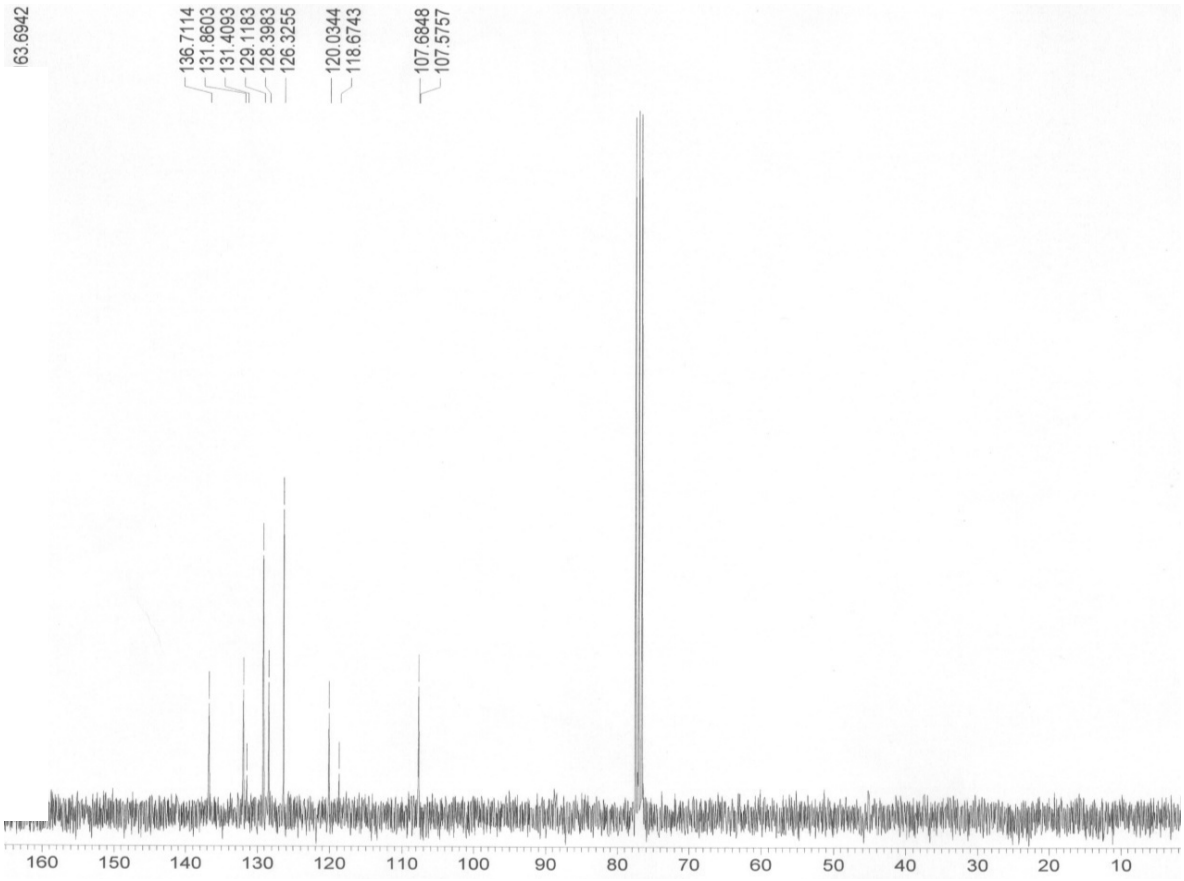


6-chloro-2-phenyl-4H-1-Benzopyran-4-one (2c)

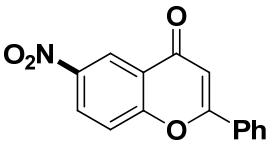


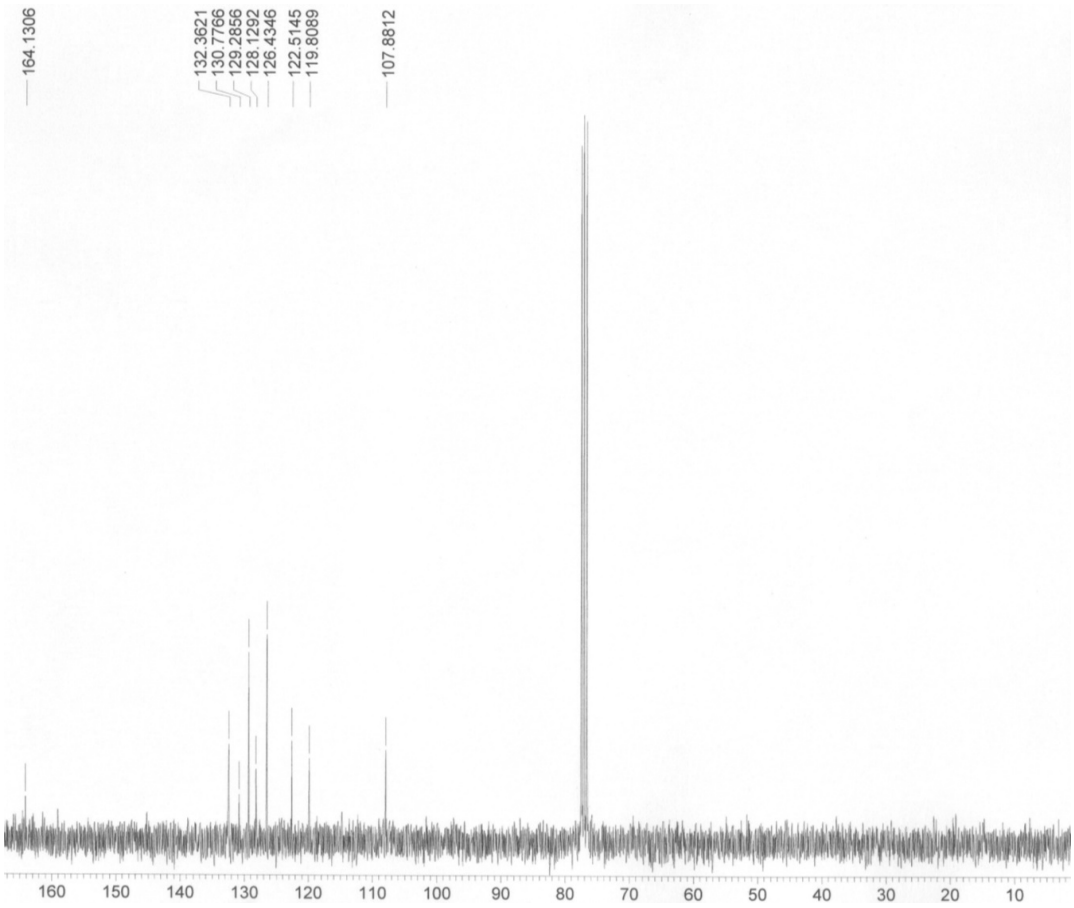
6-bromo-2-phenyl-4H-1-Benzopyran-4-one (2d)



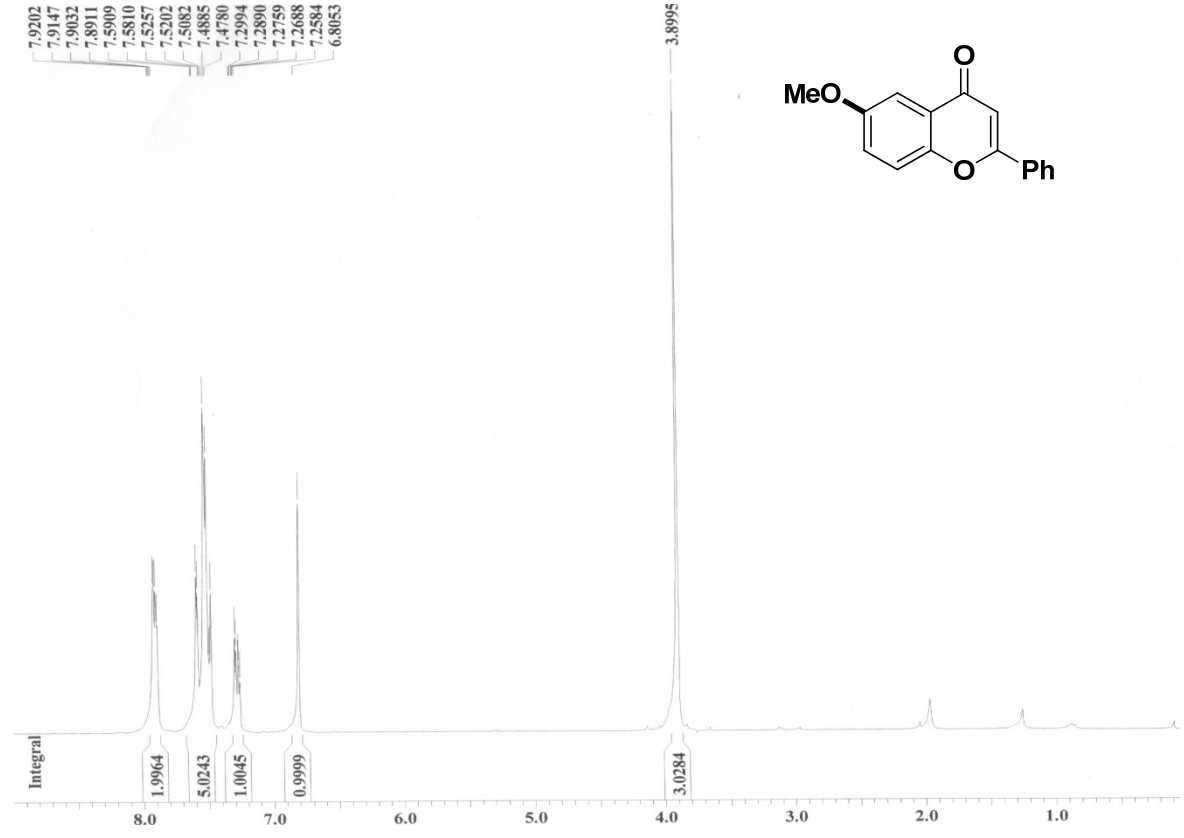


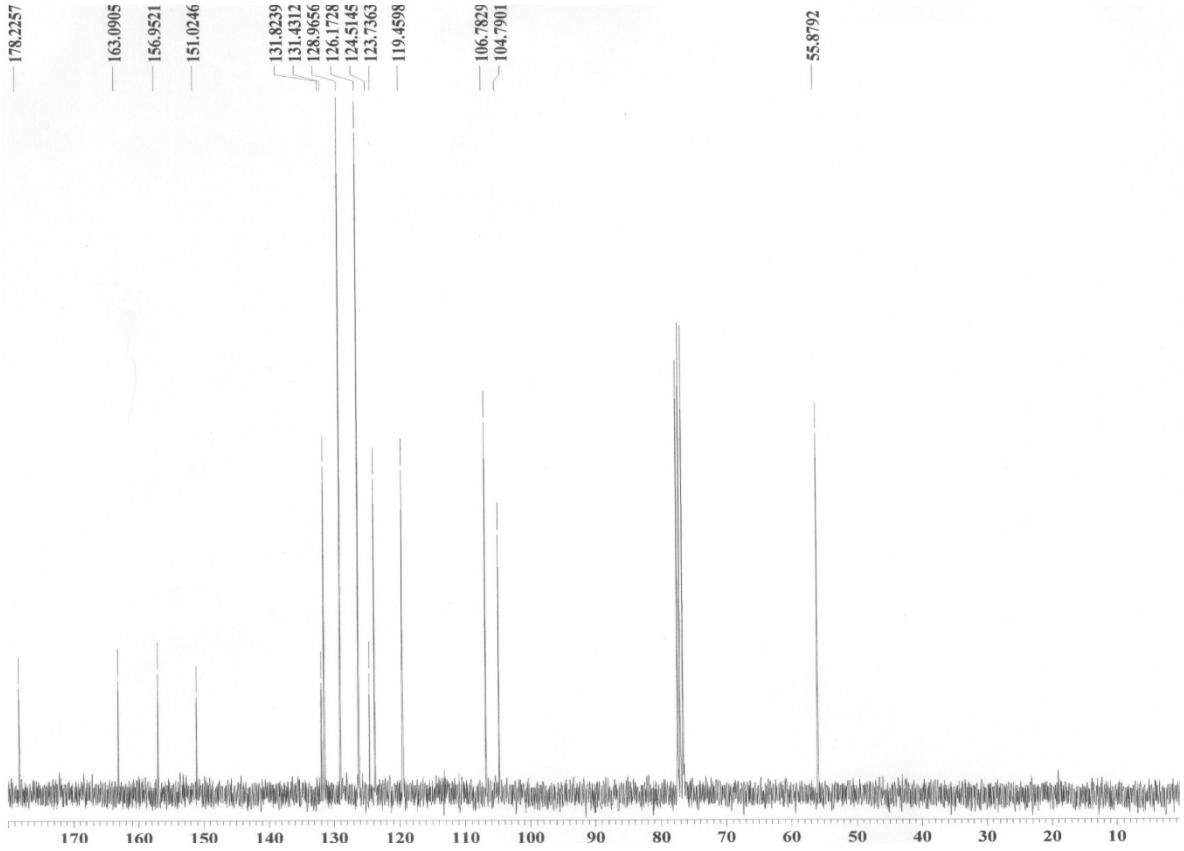
6-nitro-2-phenyl-4H-1-Benzopyran-4-one (2e)



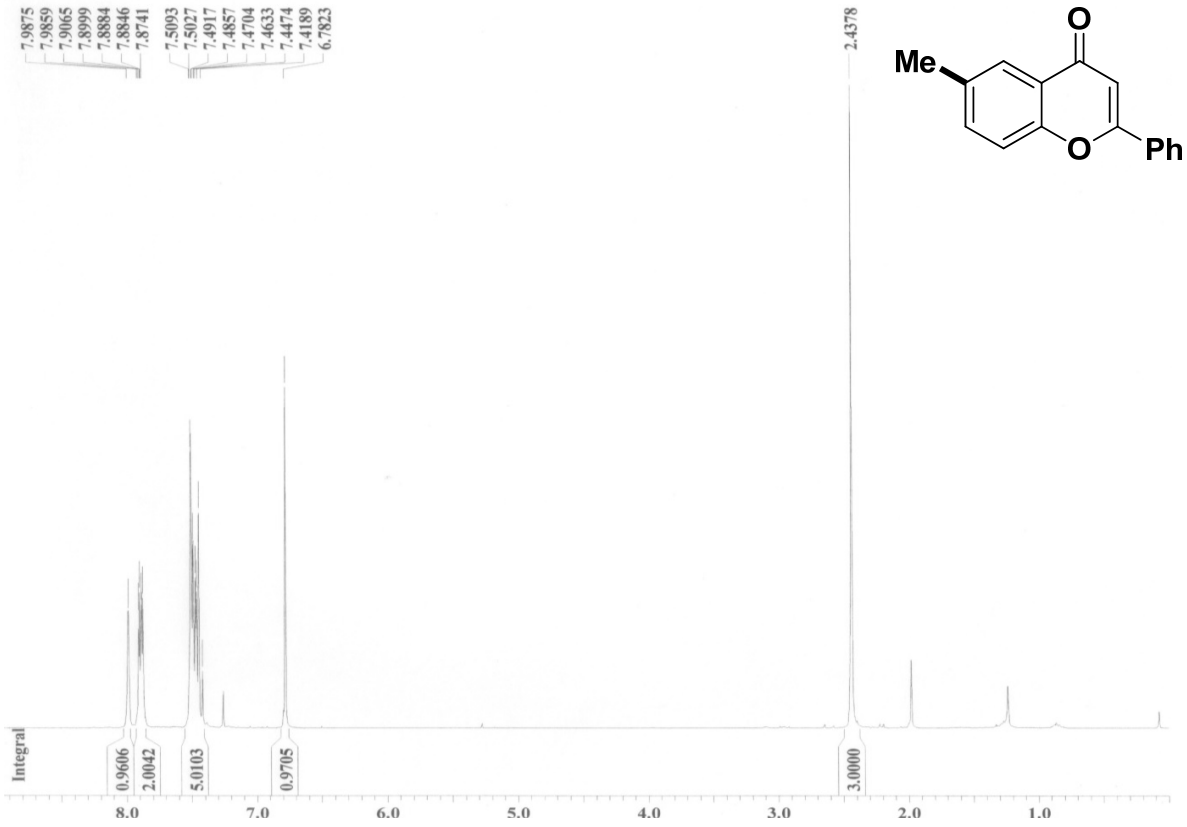


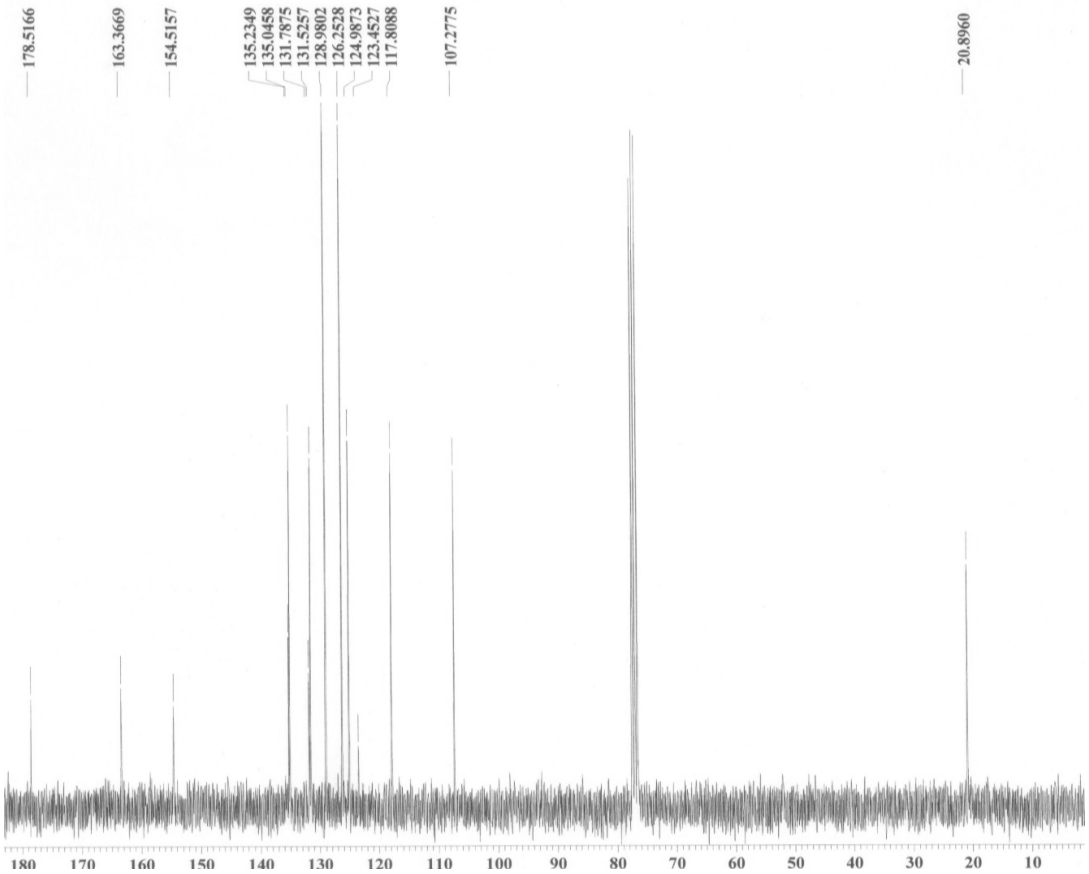
6-methoxy-2-phenyl-4H-1-Benzopyran-4-one
(2f)



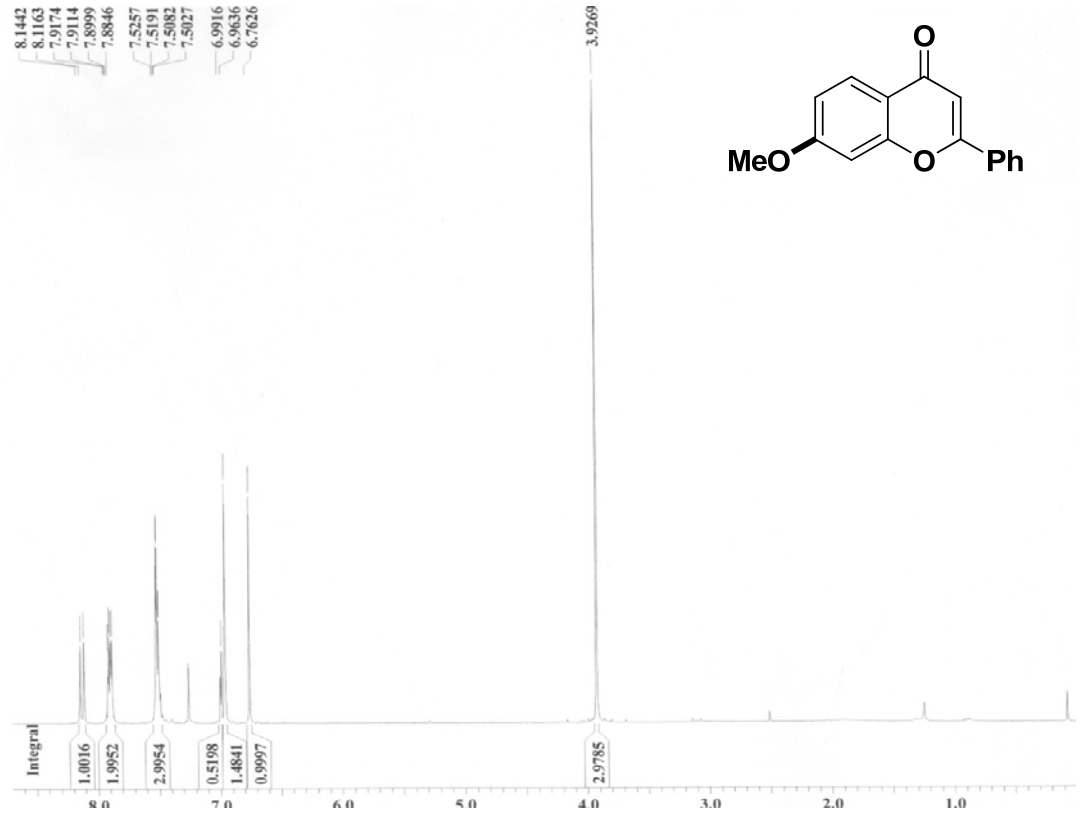


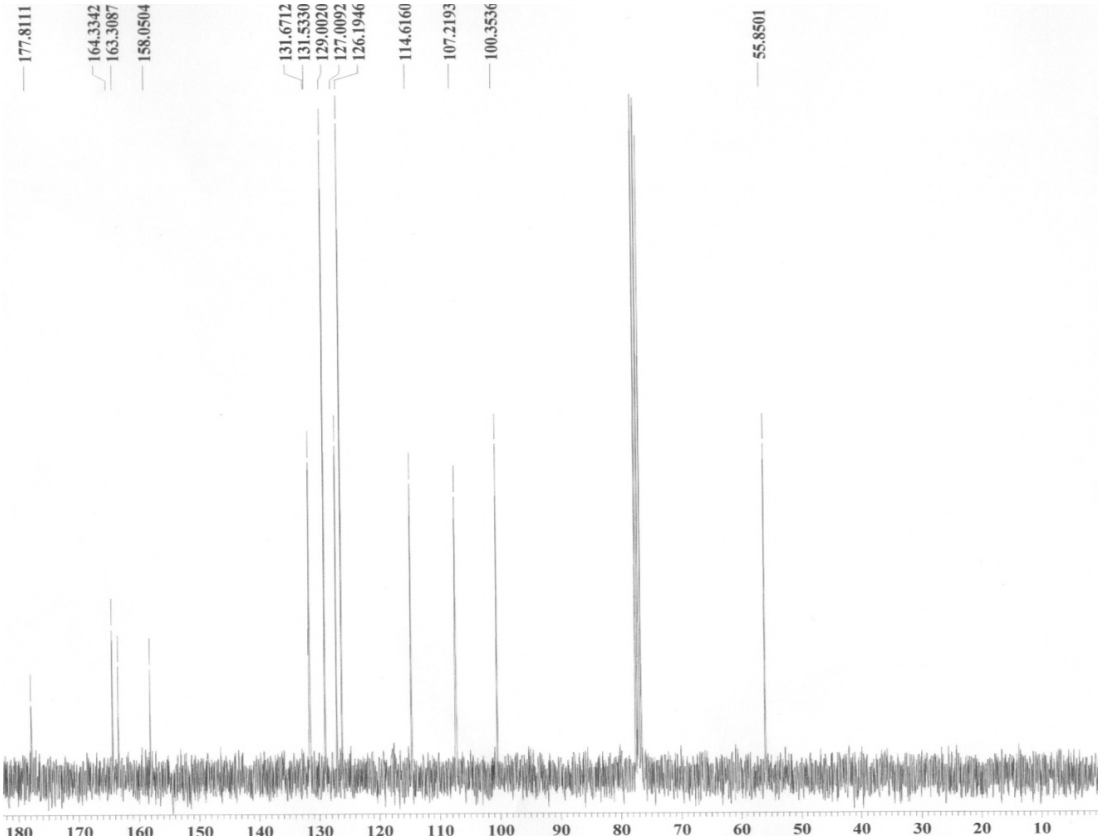
6-methyl-2-phenyl-4H-1-Benzopyran-4-one
(2g)



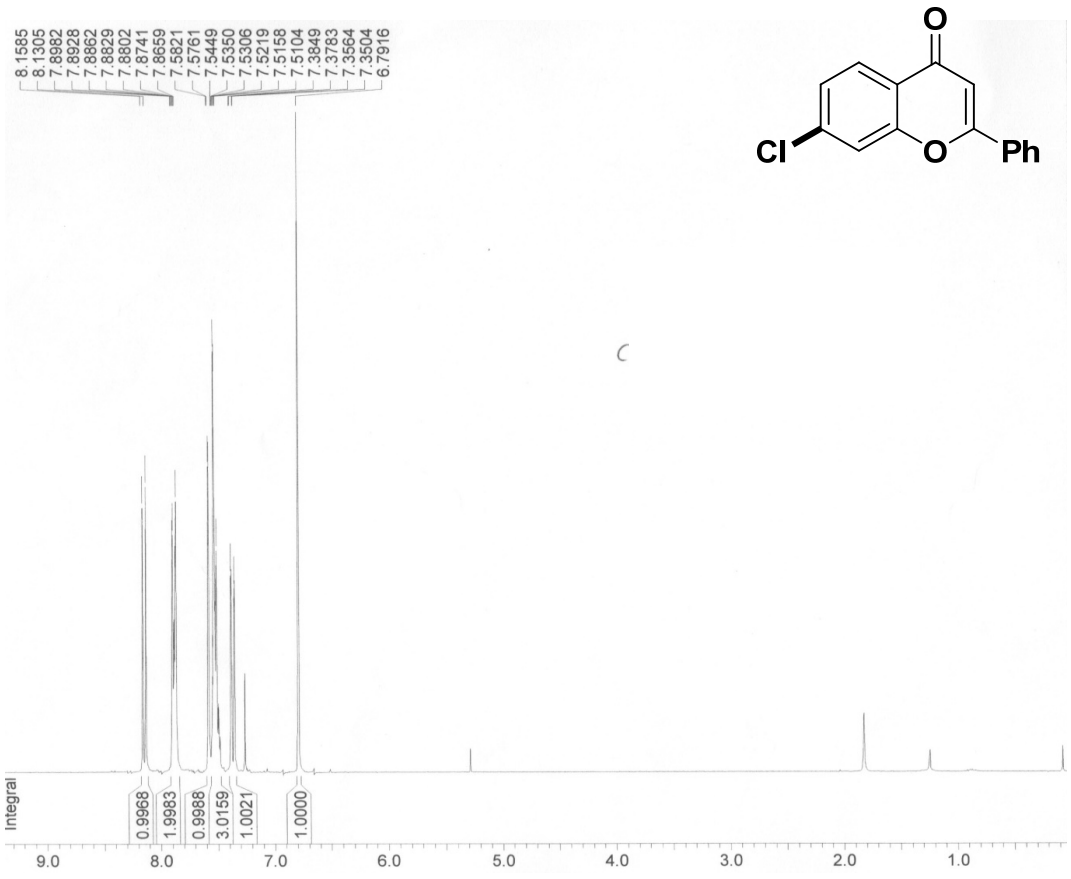


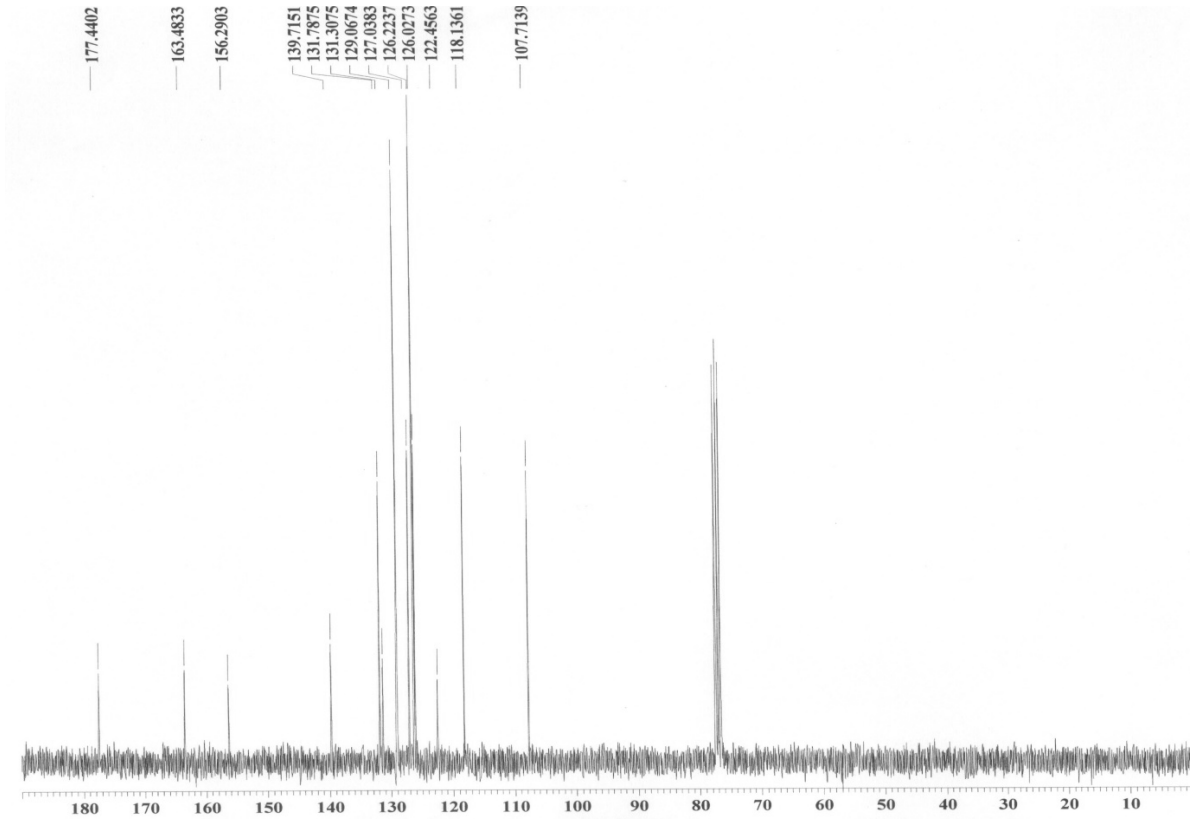
7-methoxy-2-phenyl-4H-1-Benzopyran-4-one (2h)



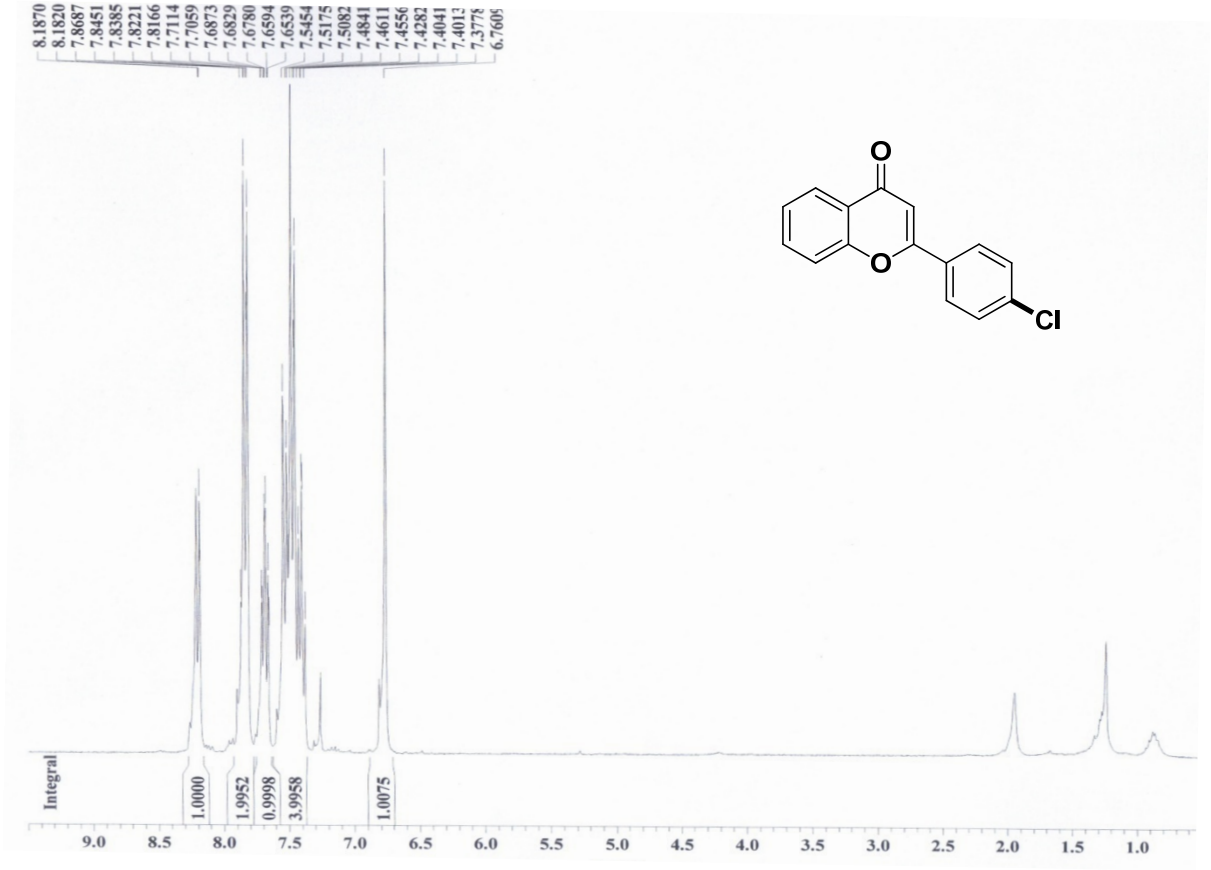


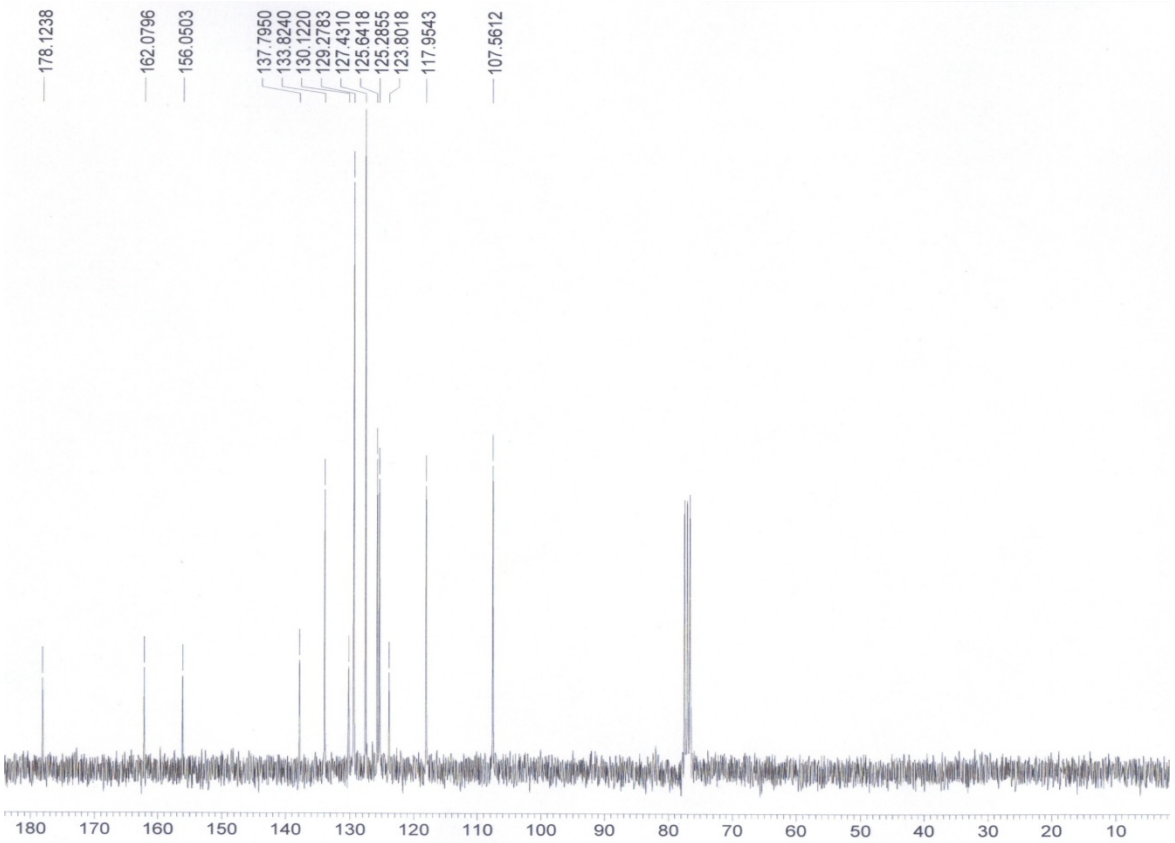
7-chloro-2-phenyl-4H-1-Benzopyran-4-one (2i)



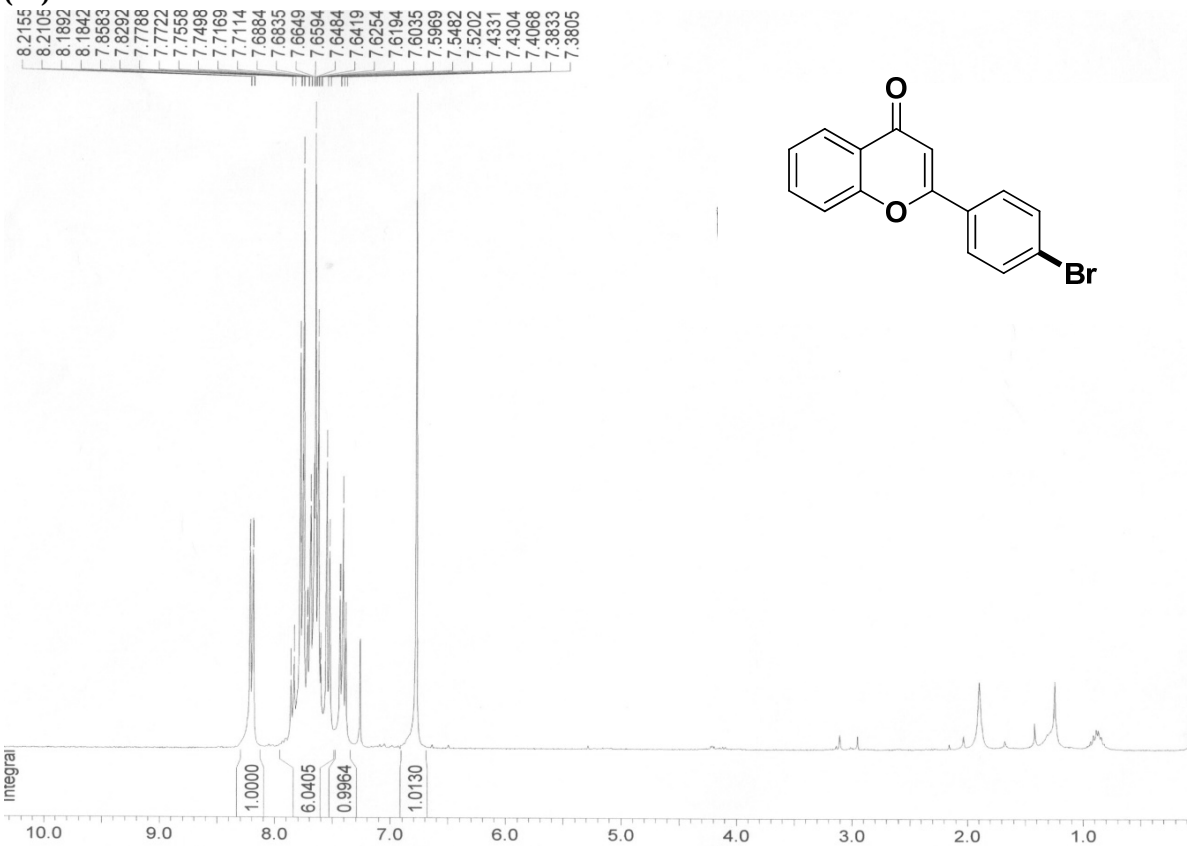


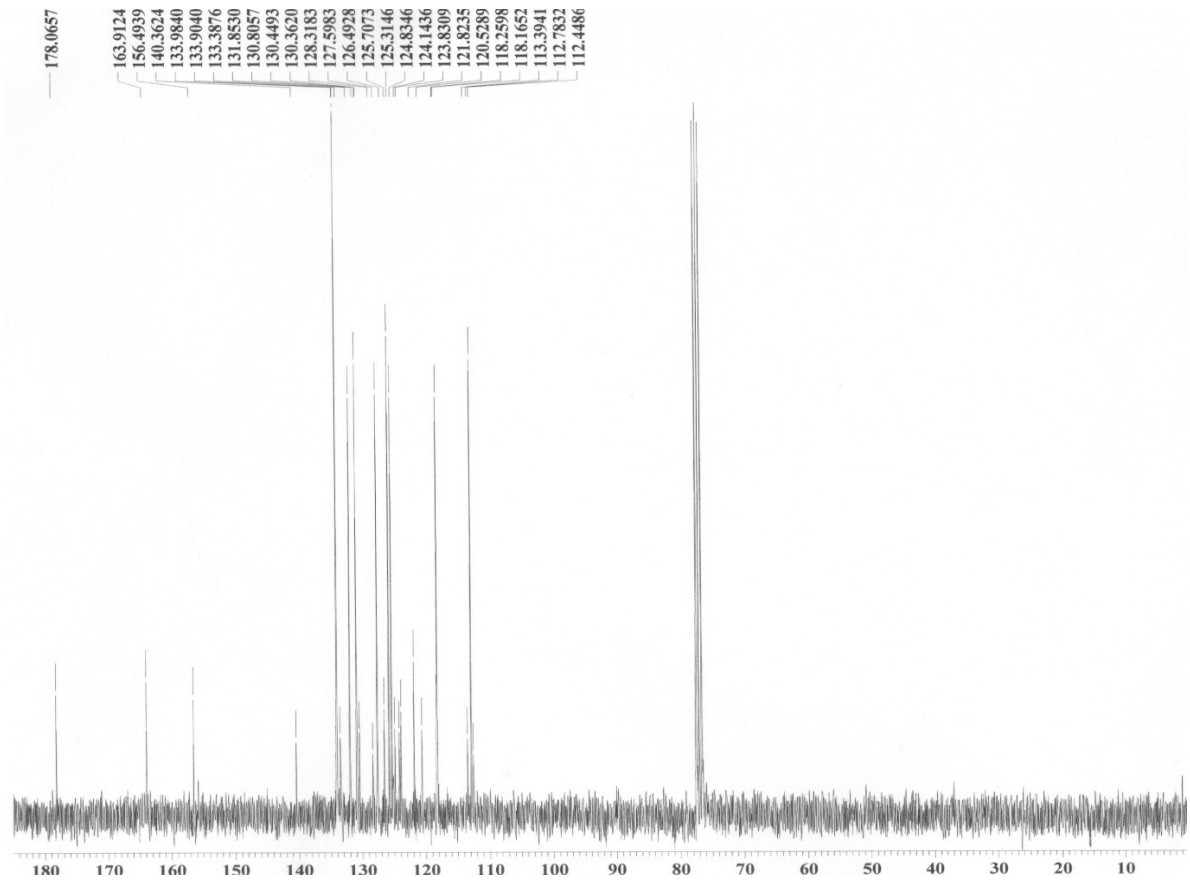
2-(4-chlorophenyl)-4H-1-Benzopyran-4-one
(2j)



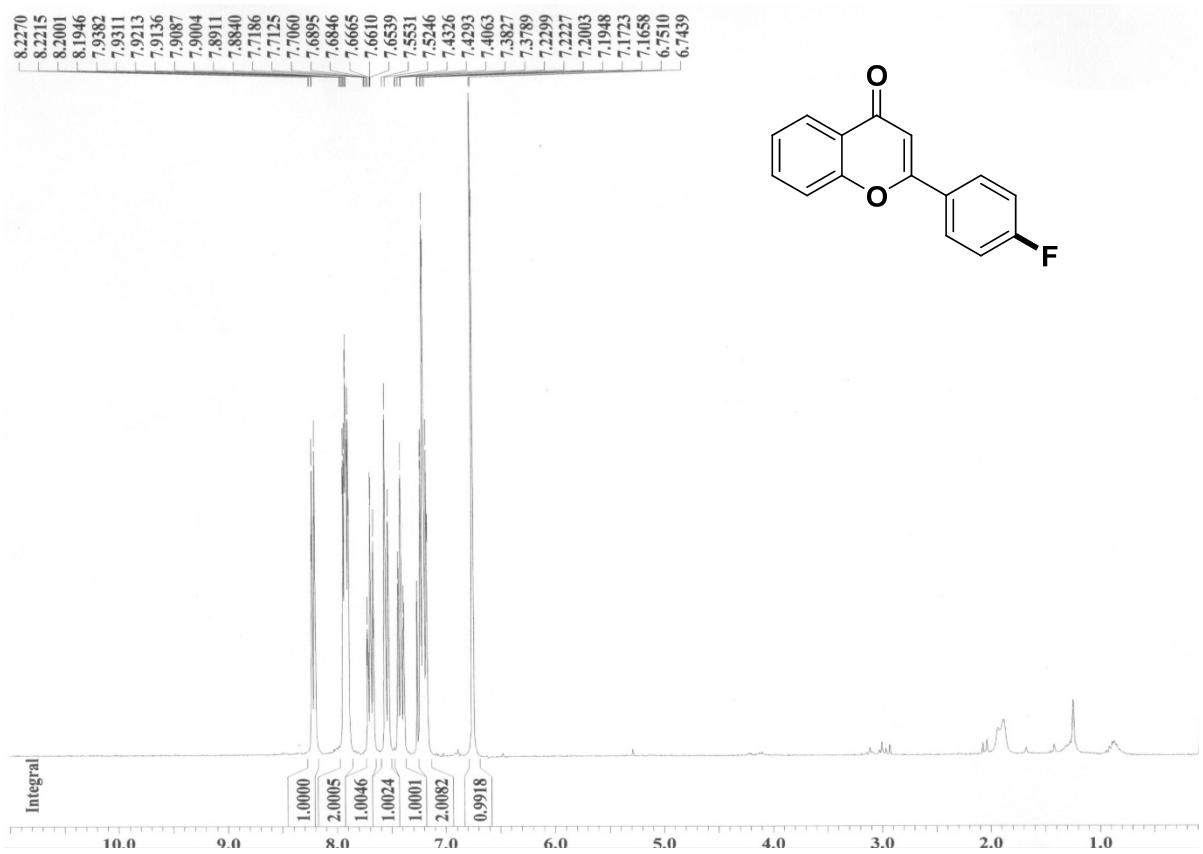


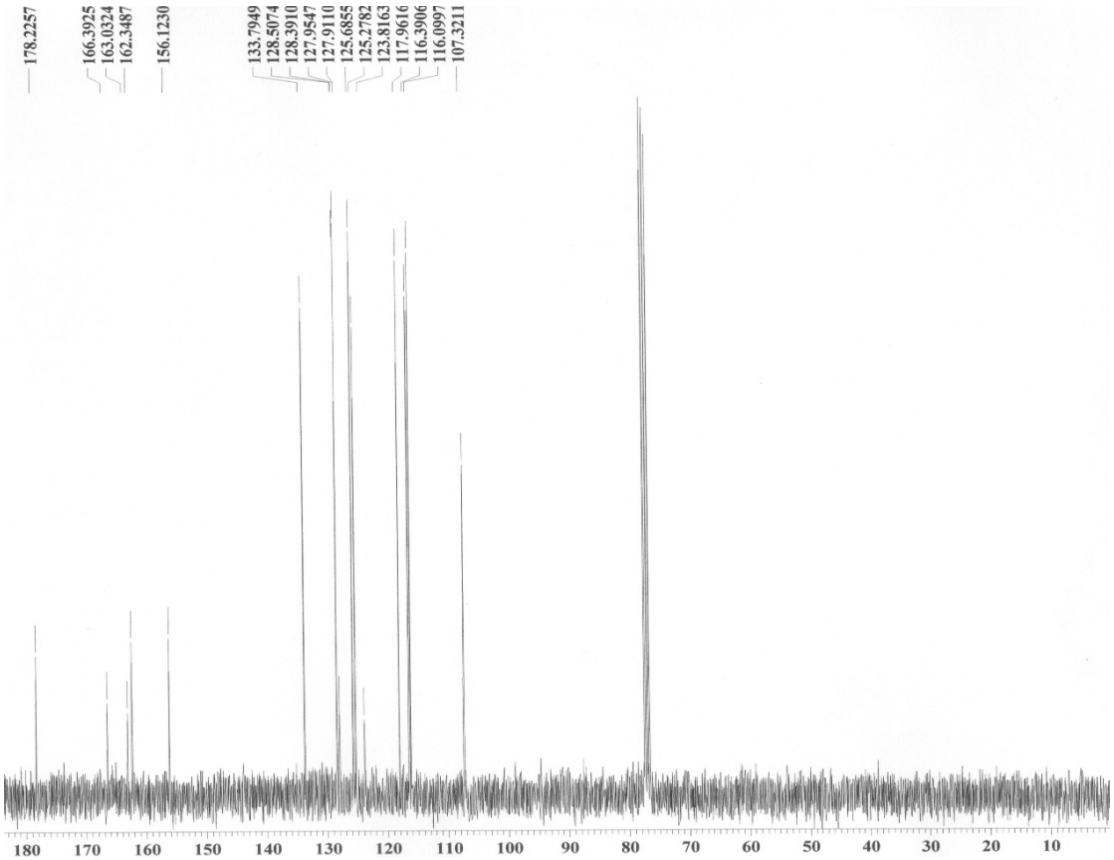
2-(4-bromophenyl)-4H-1-Benzopyran-4-one
(2k)



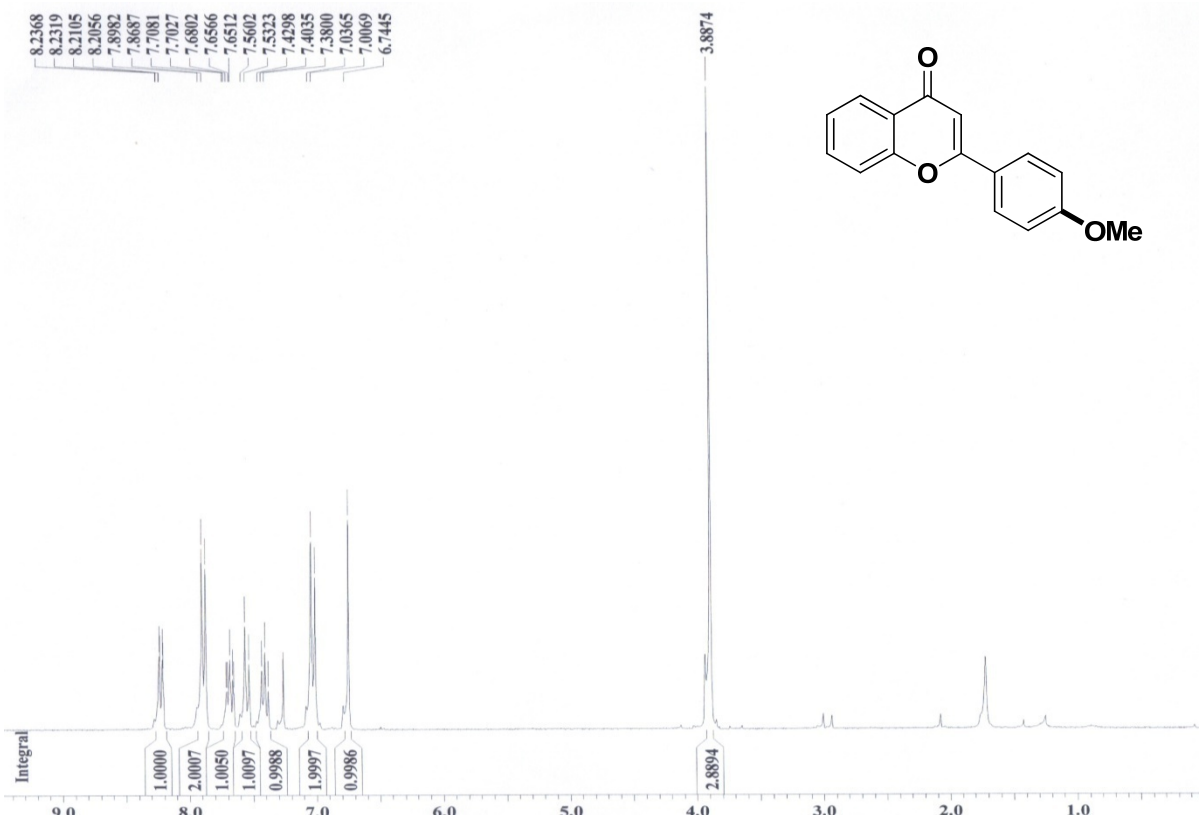


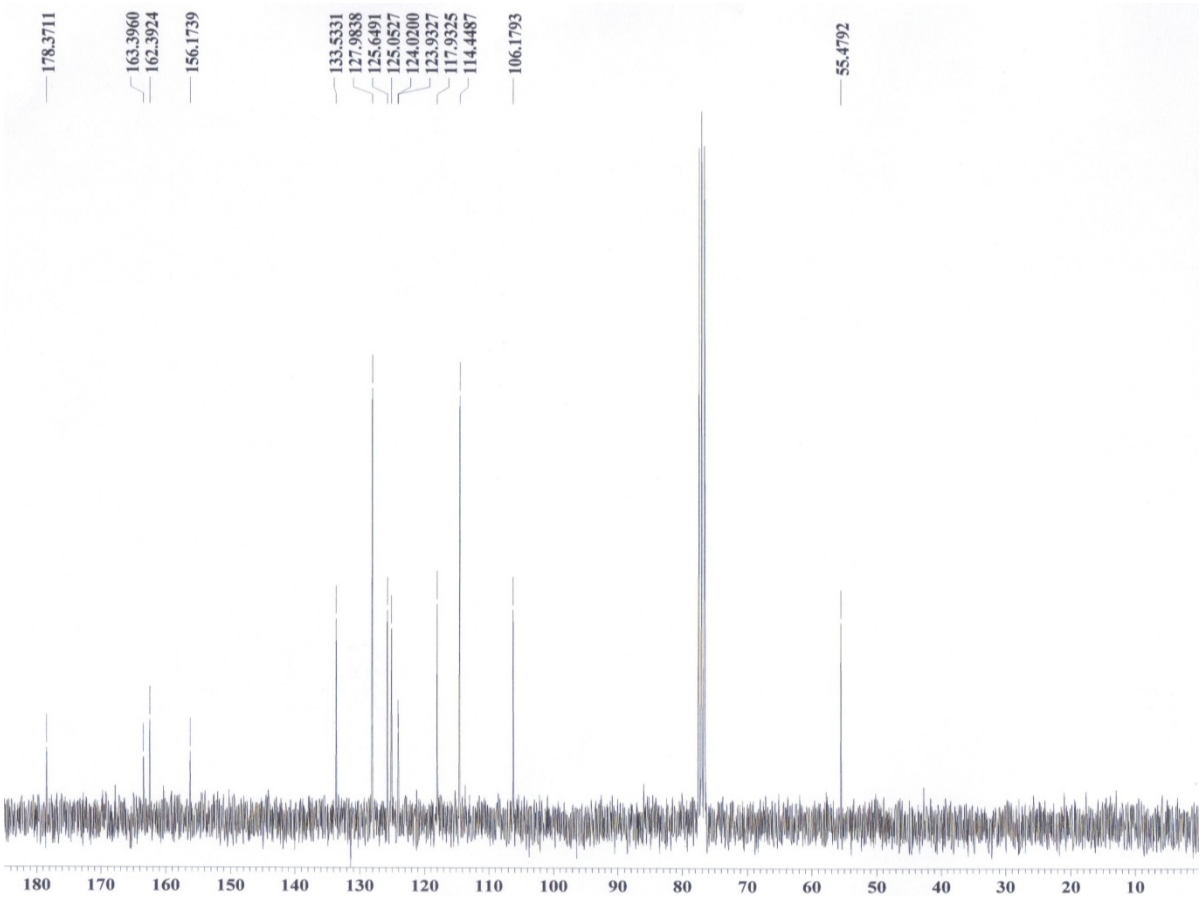
2-(4-fluorophenyl)-4H-1-Benzopyran-4-one (2l)



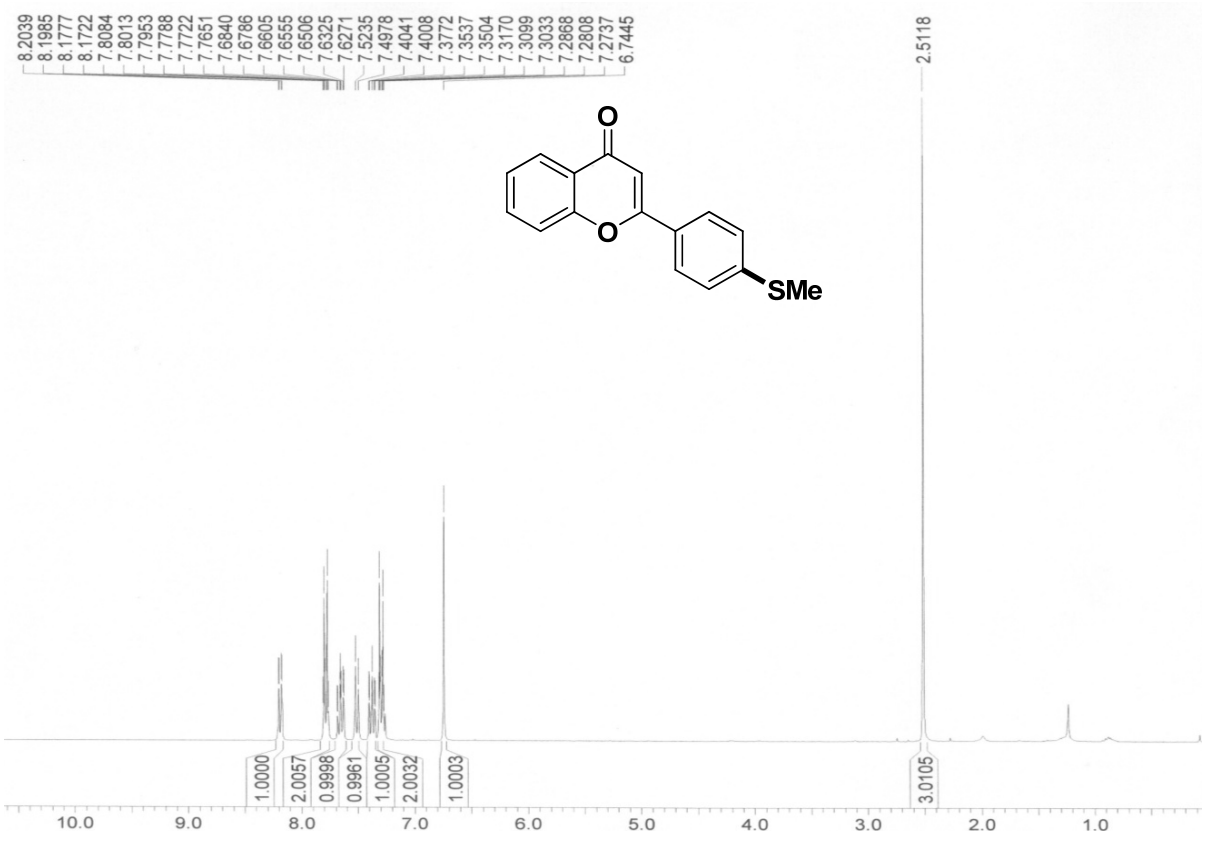


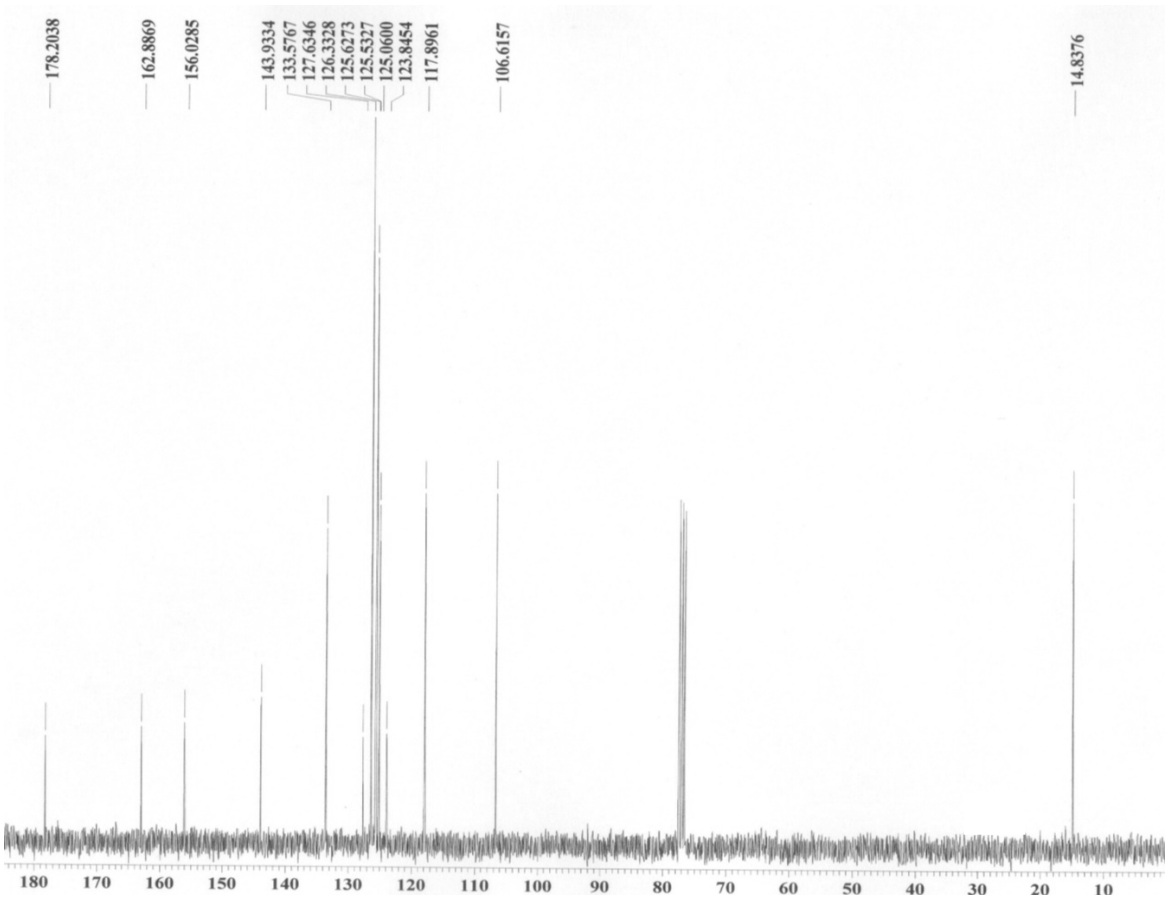
2-(4-methoxyphenyl)-4H-1-Benzopyran-4-one
(2m)



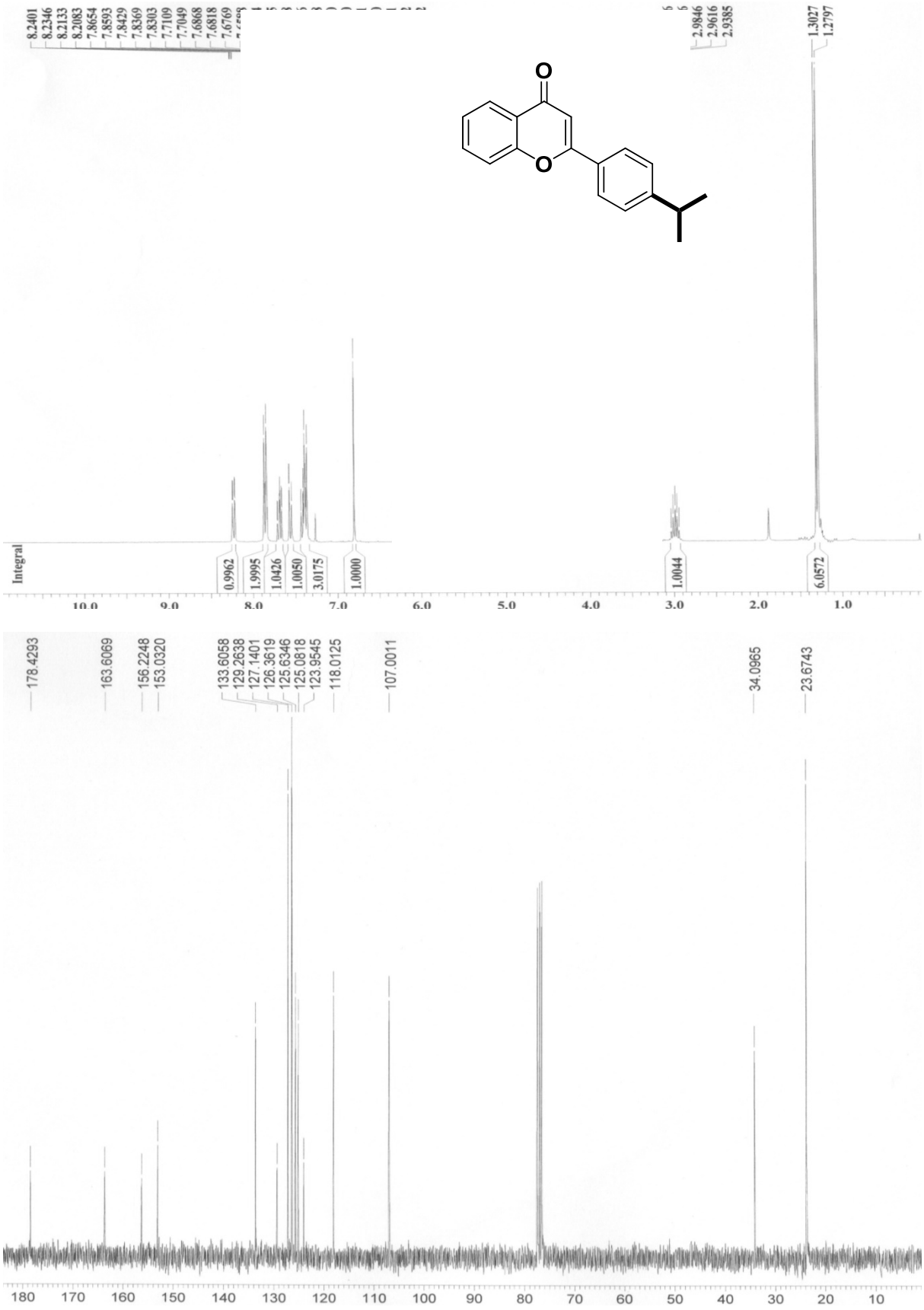


2-(4-methylthiophenyl)-4H-1-Benzopyran-4-one
(2n)

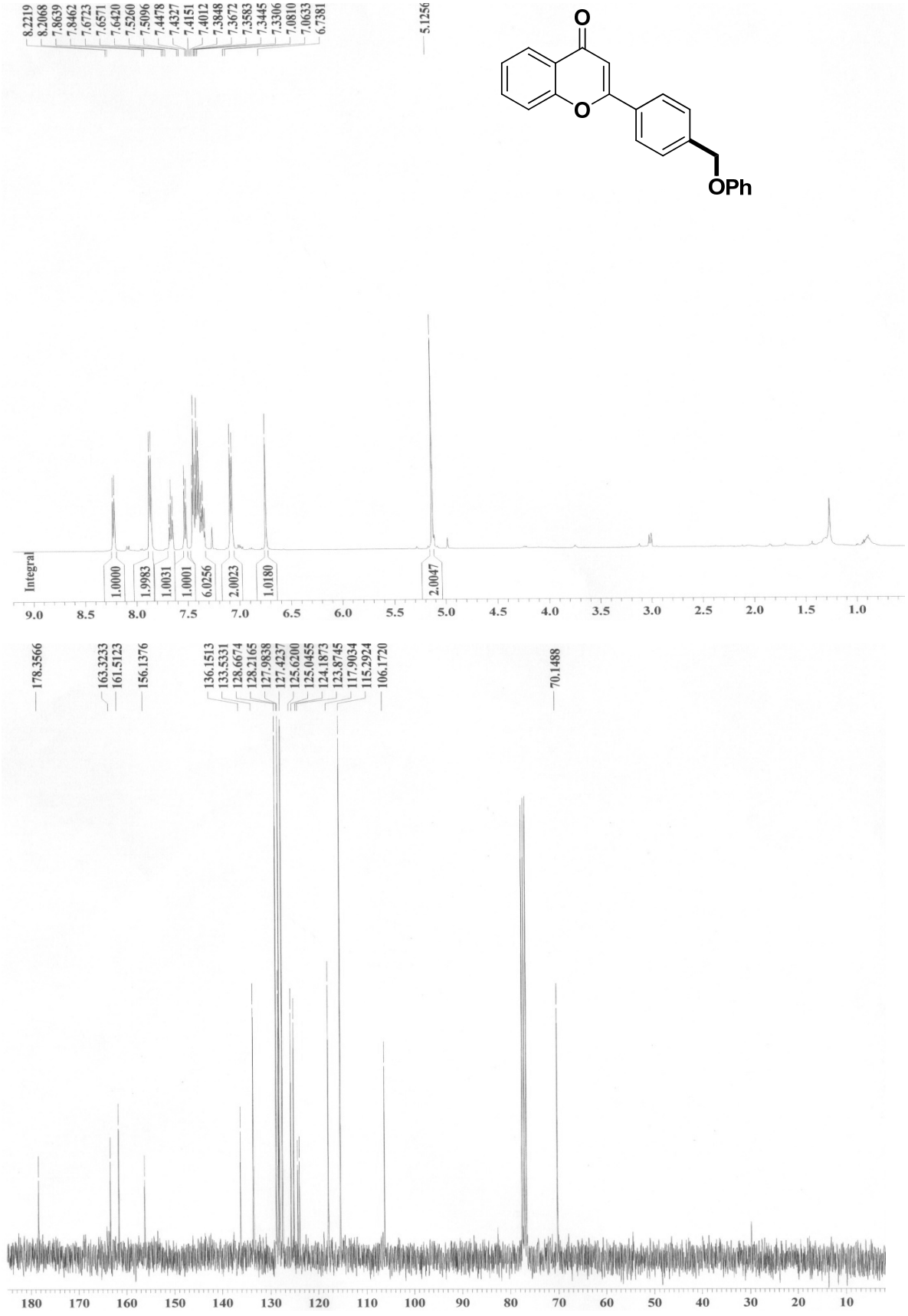




2-(4-isopropylphenyl)-4H-1-Benzopyran-4-one
(2o)

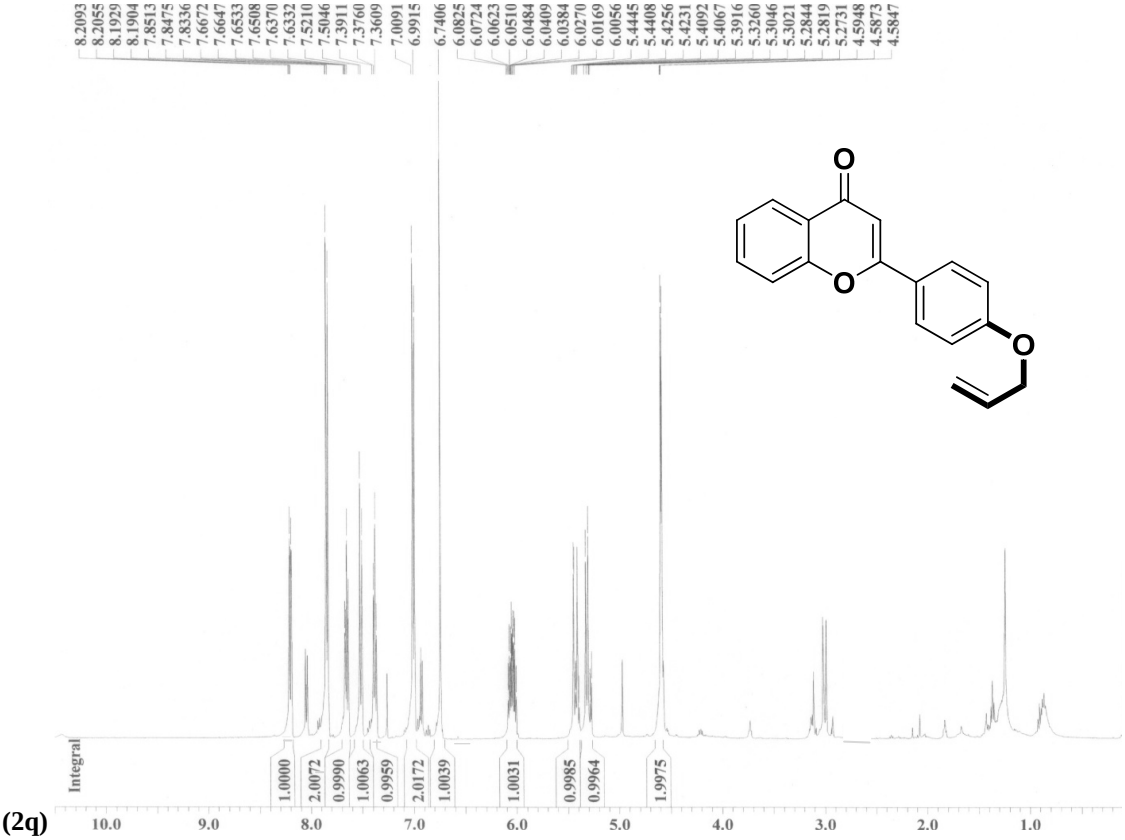


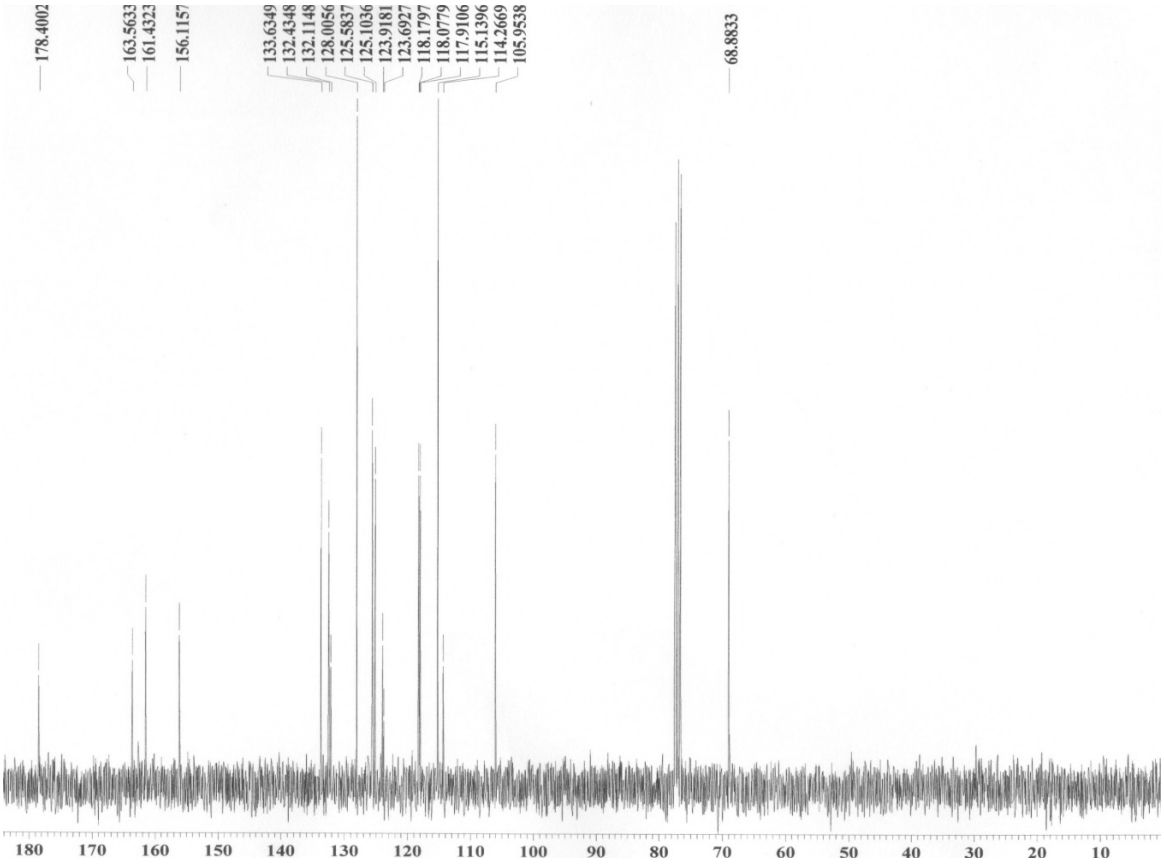
2-(4-(benzyloxy)phenyl)-4H-1-Benzopyran-4-one
(2p)



2-(4-(ethenyloxy)phenyl)-4H-1-Benzopyran-4-one

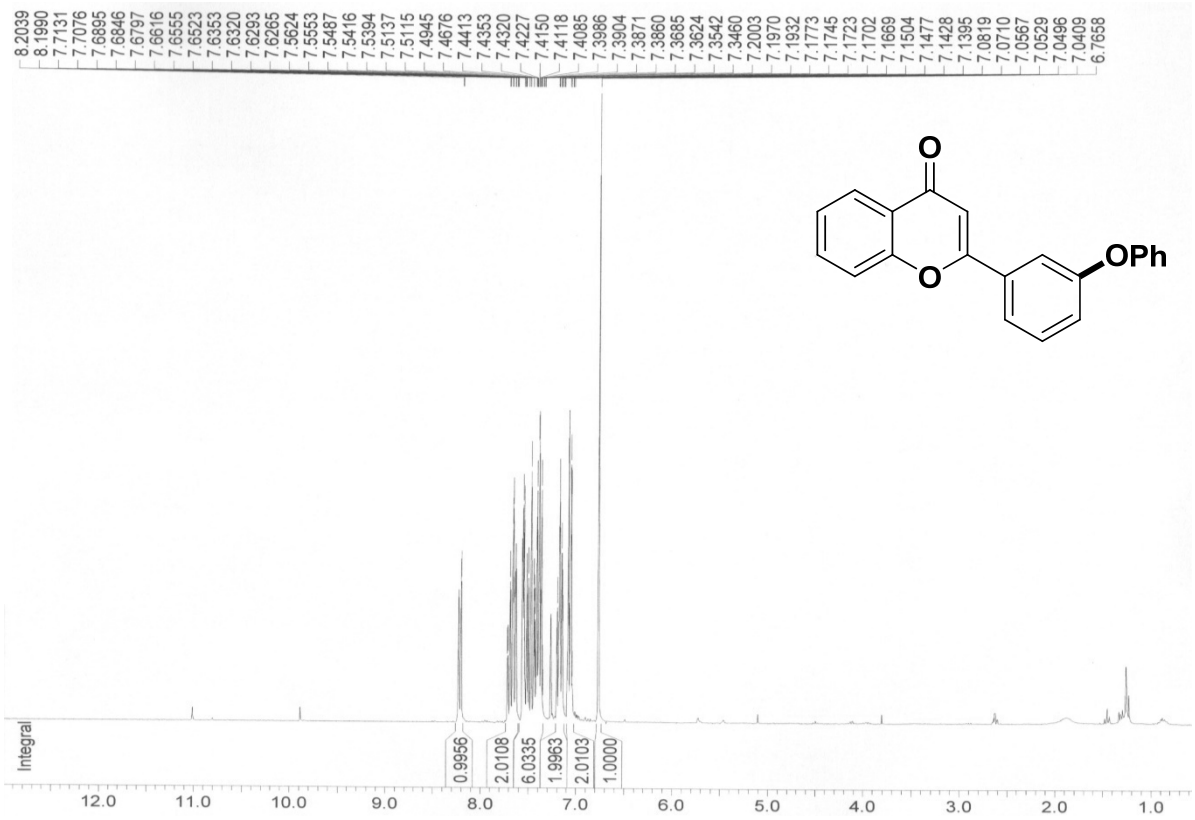
(2q)

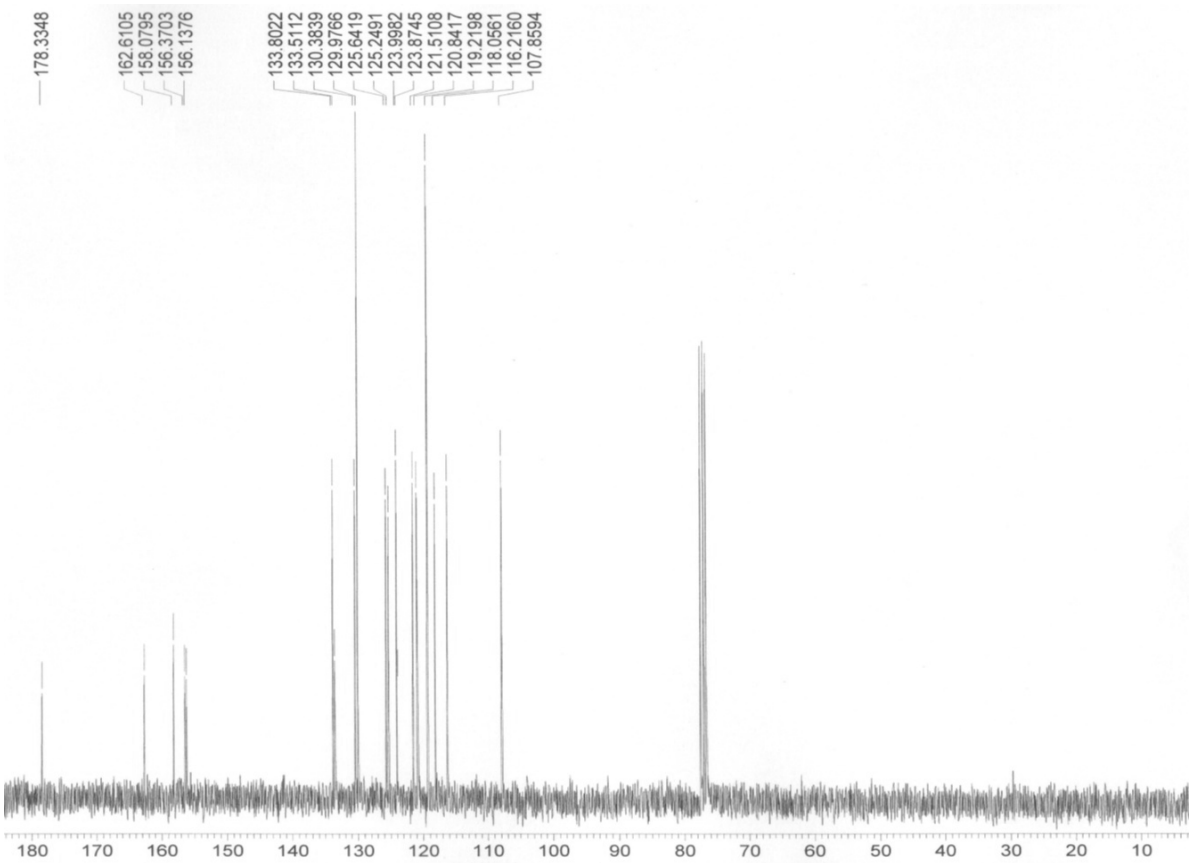




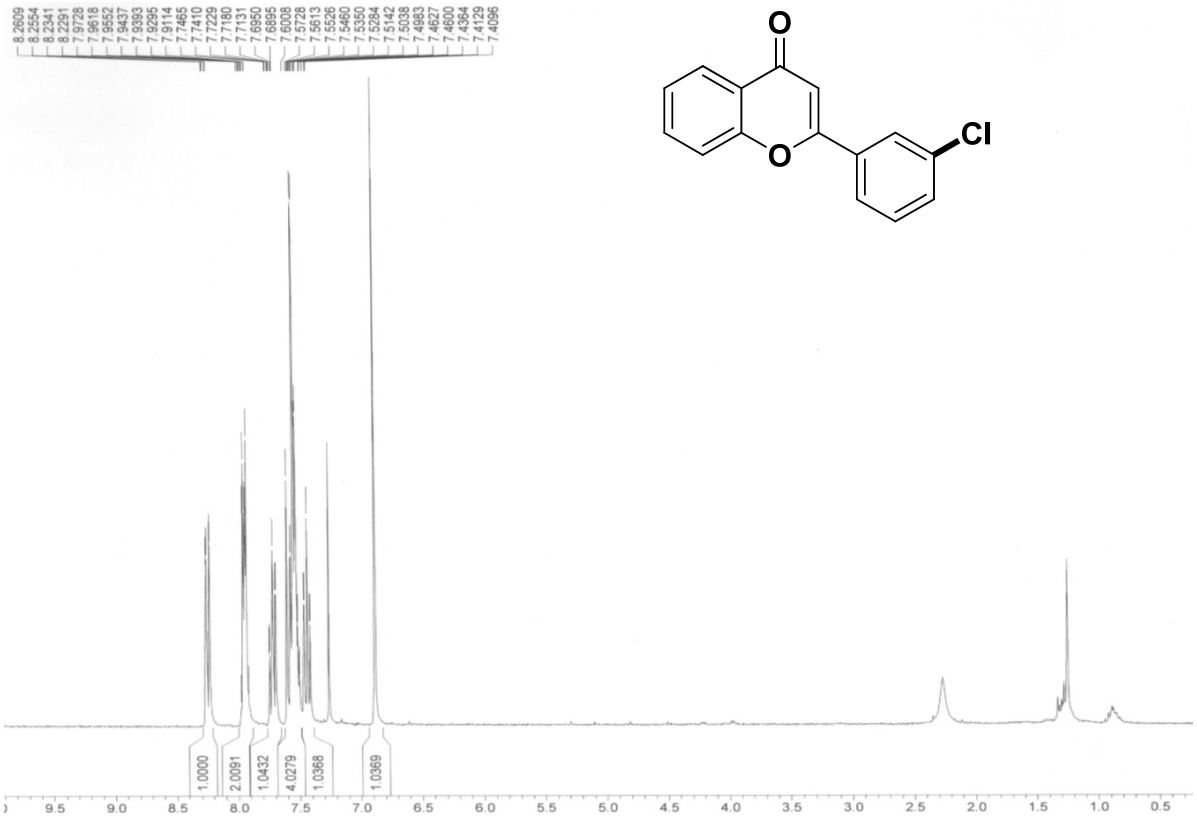
2-(3-phenoxyphenylphenyl)- 4H-1-Benzopyran-4-one

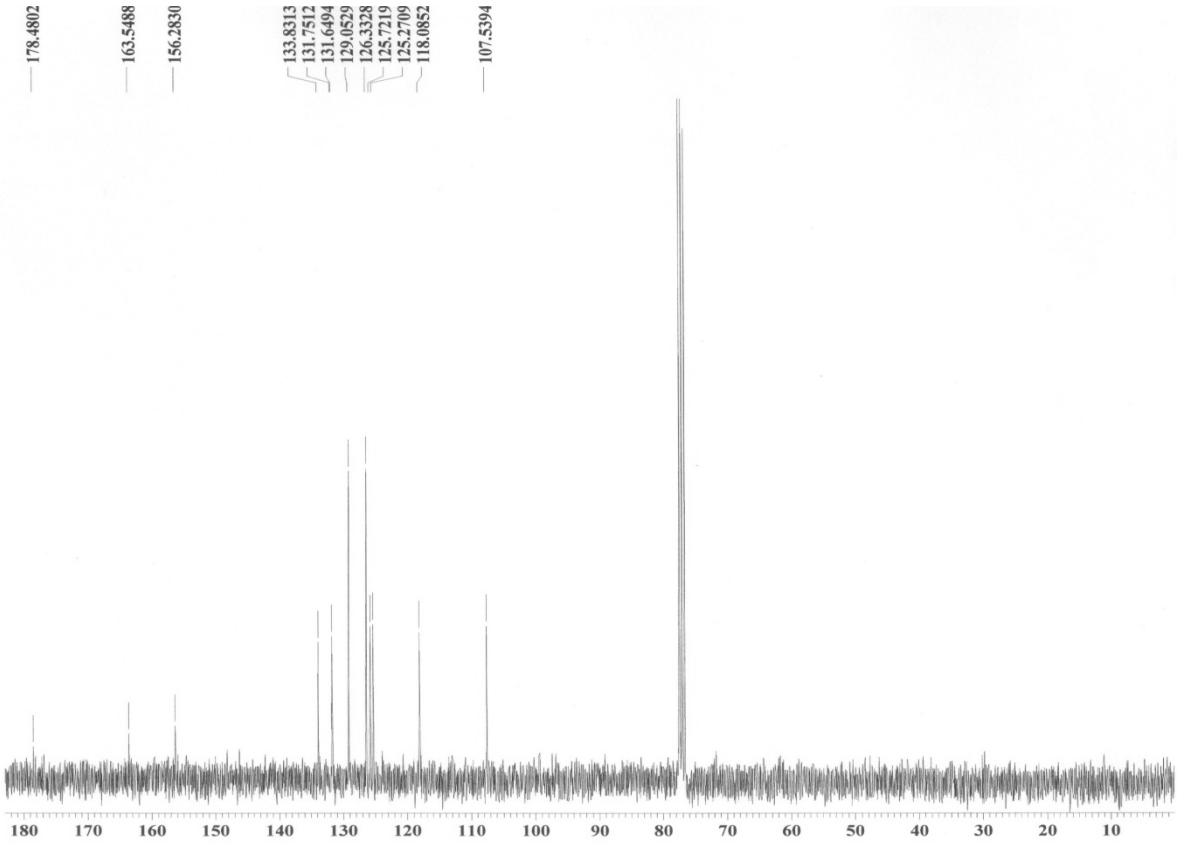
2r)



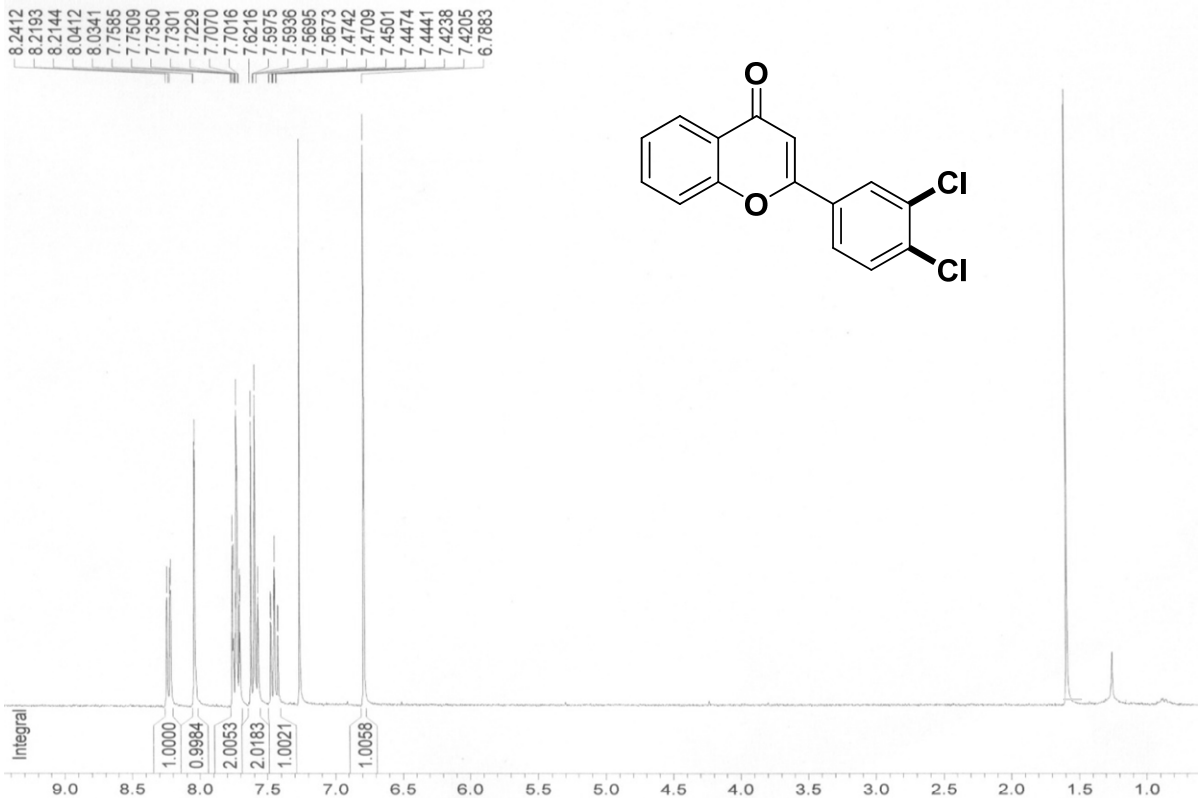


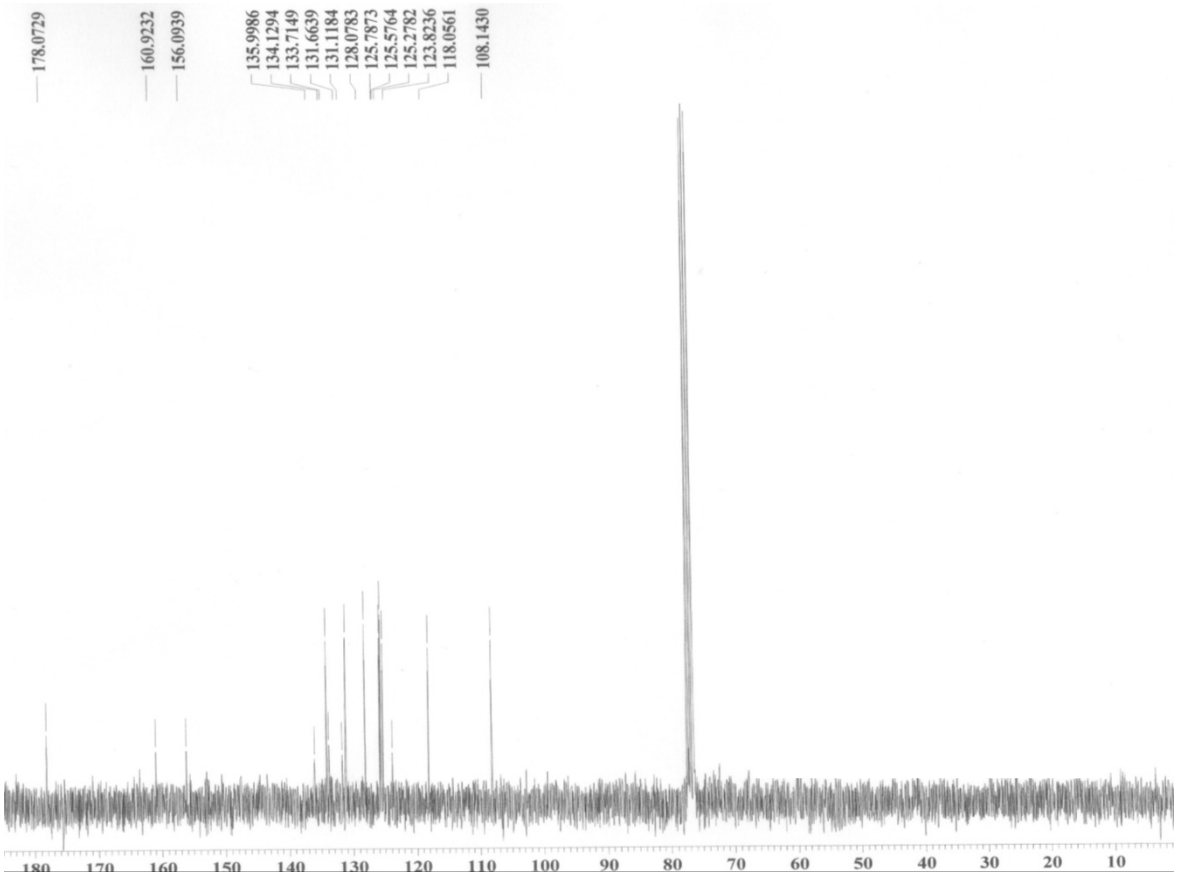
2-(3-chlorophenyl)- 4H-1-Benzopyran-4-one
(2s)



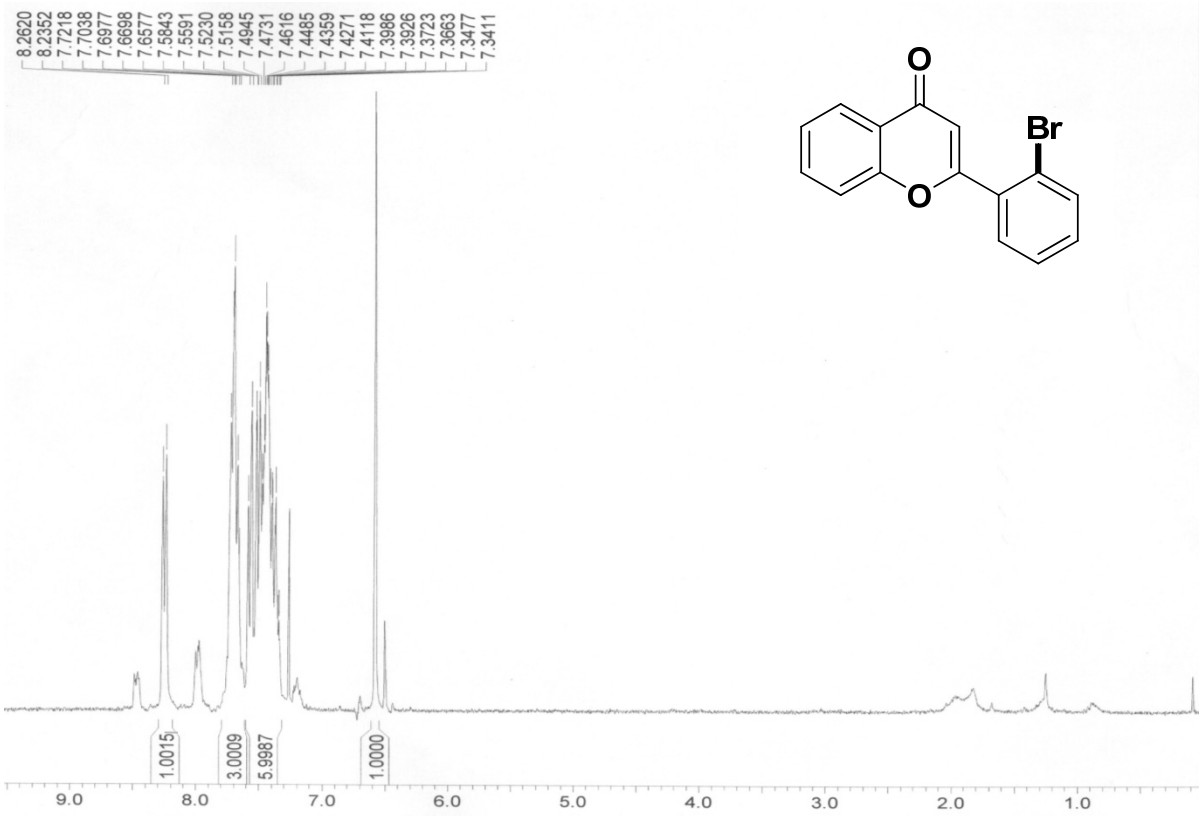


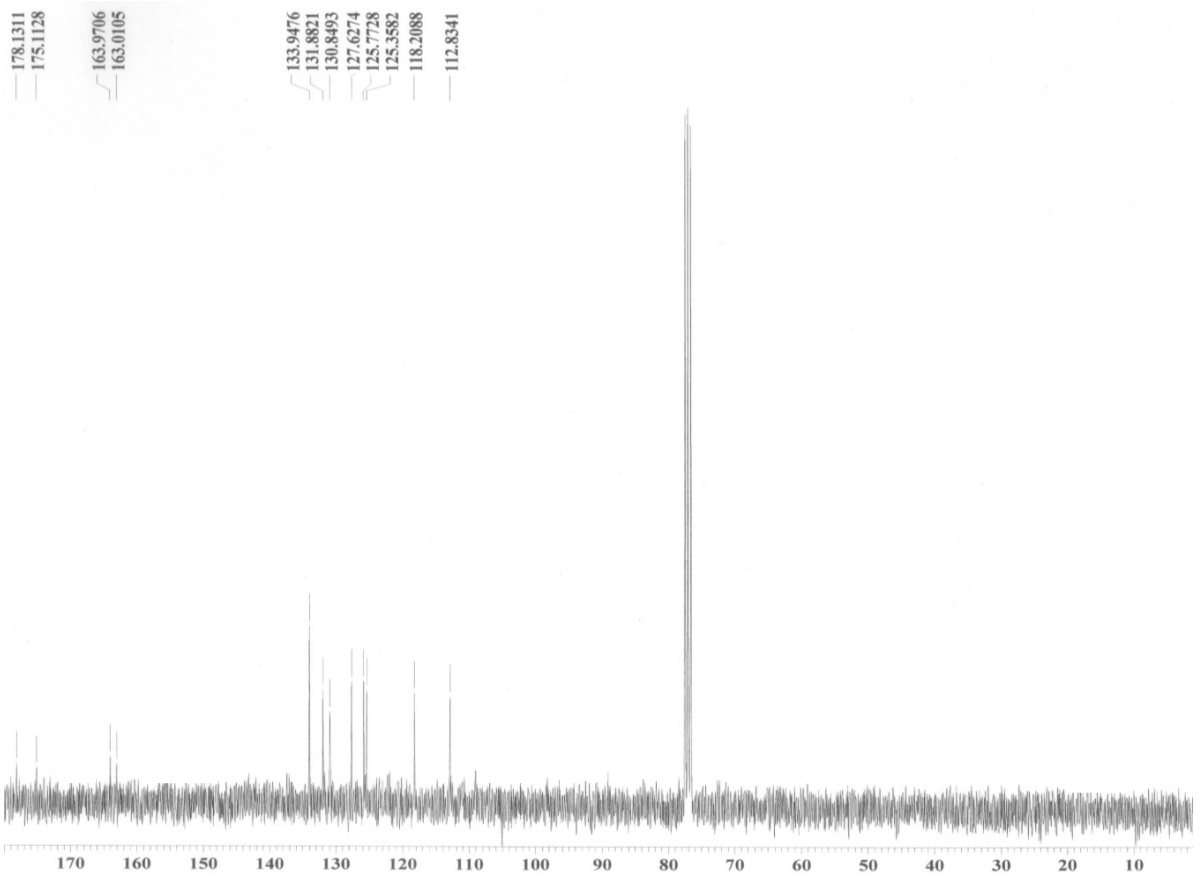
2-(3,4-dichlorophenyl)- 4H-1-Benzopyran-4-one
(2t)



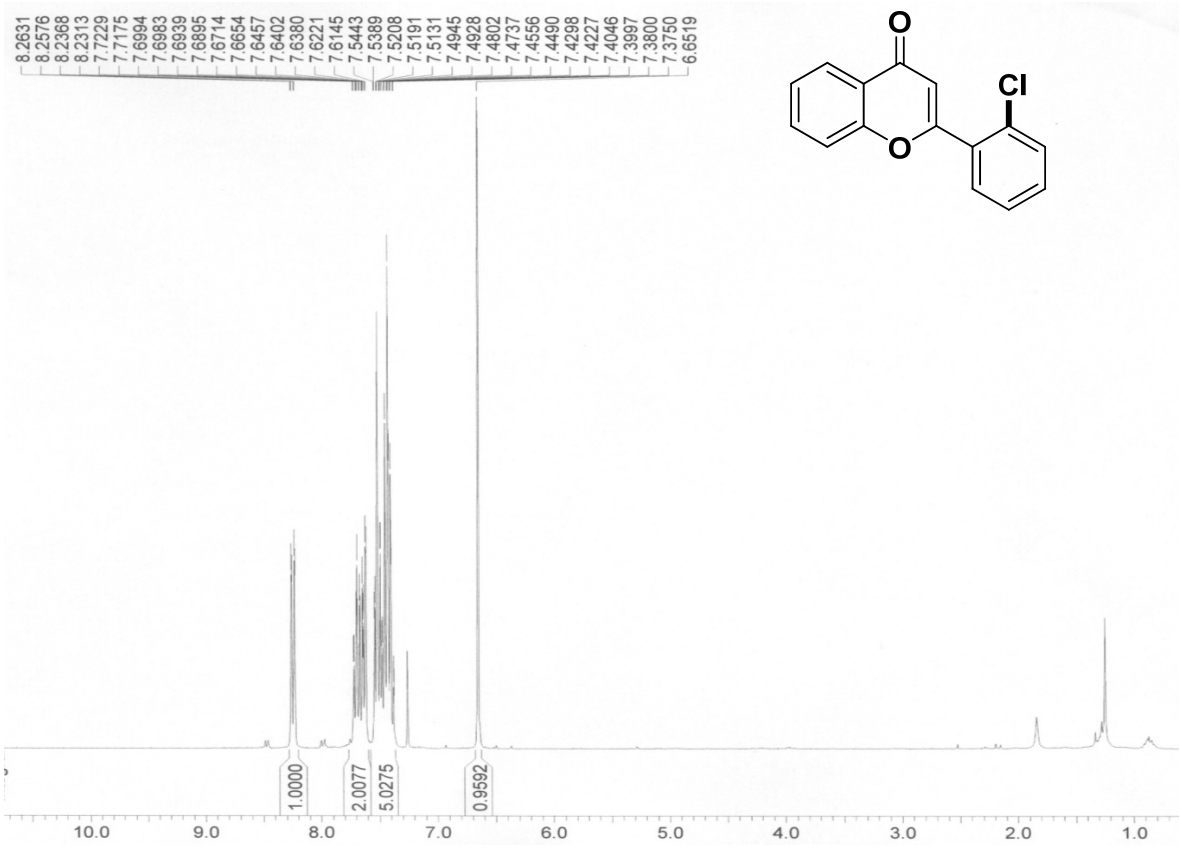


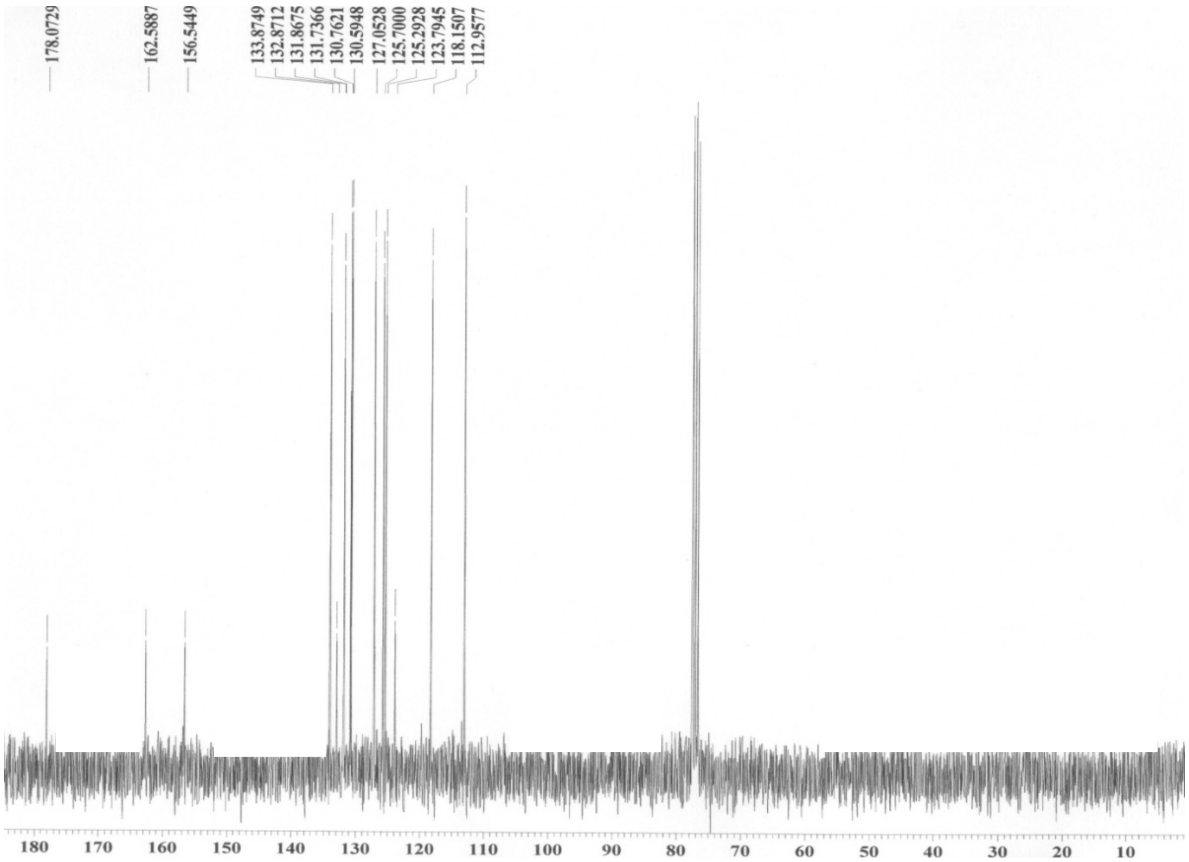
2-(2-bromophenyl)-4H-1-Benzopyran-4-one
(2v)



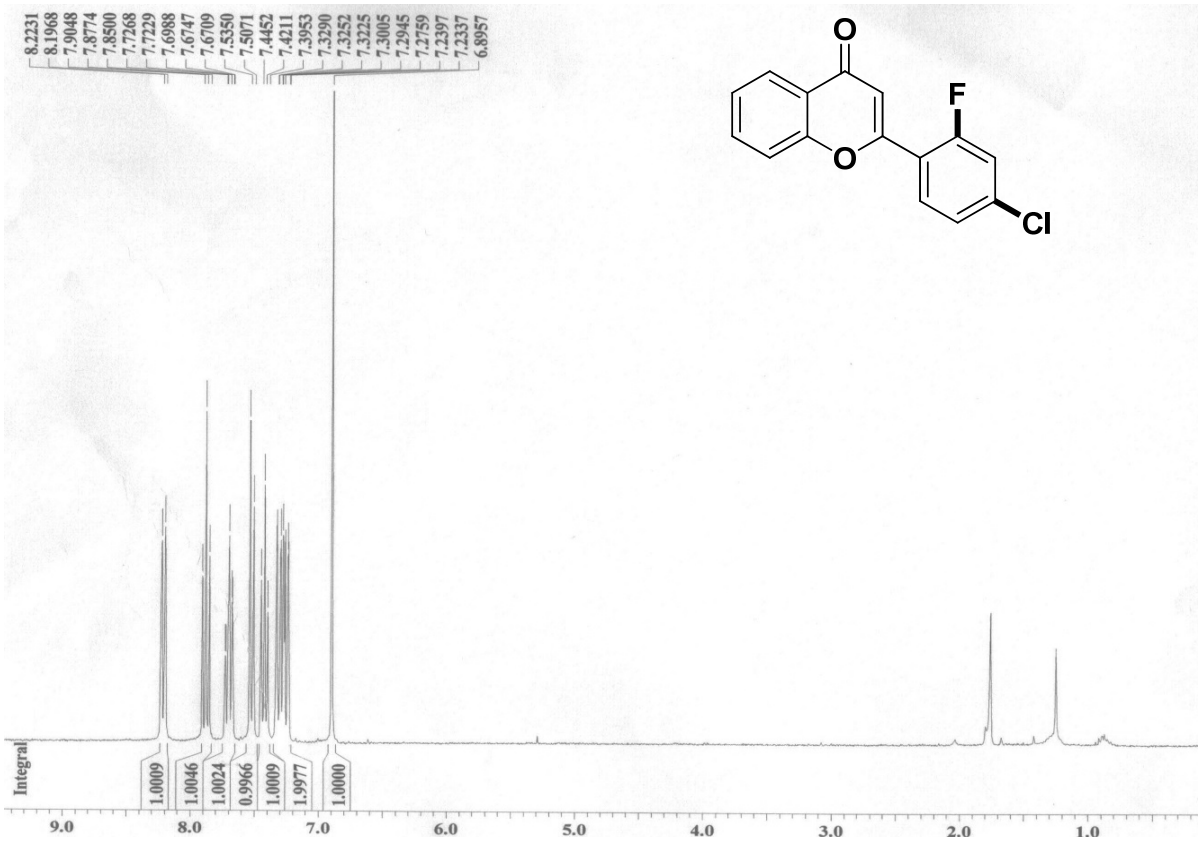


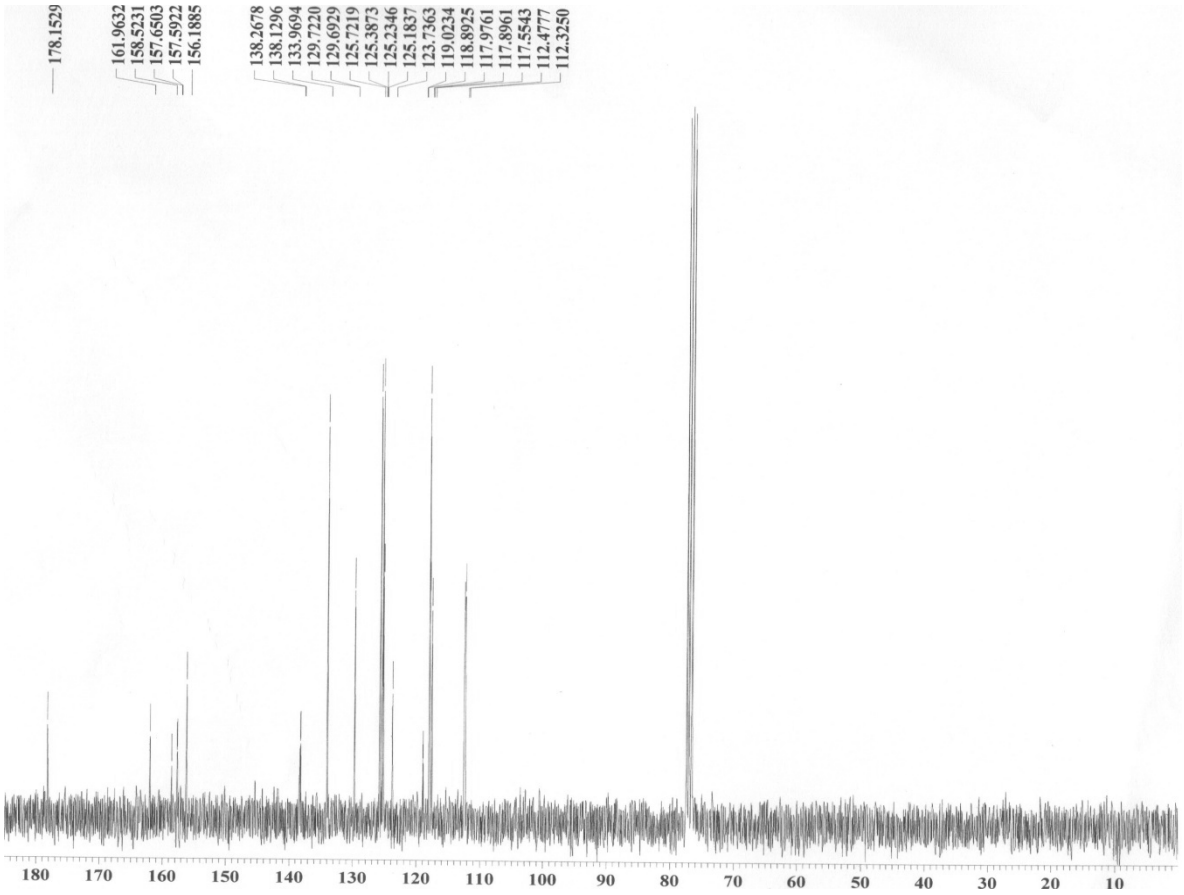
2-(2-chlorophenyl)-4H-1-Benzopyran-4-one
(2u)



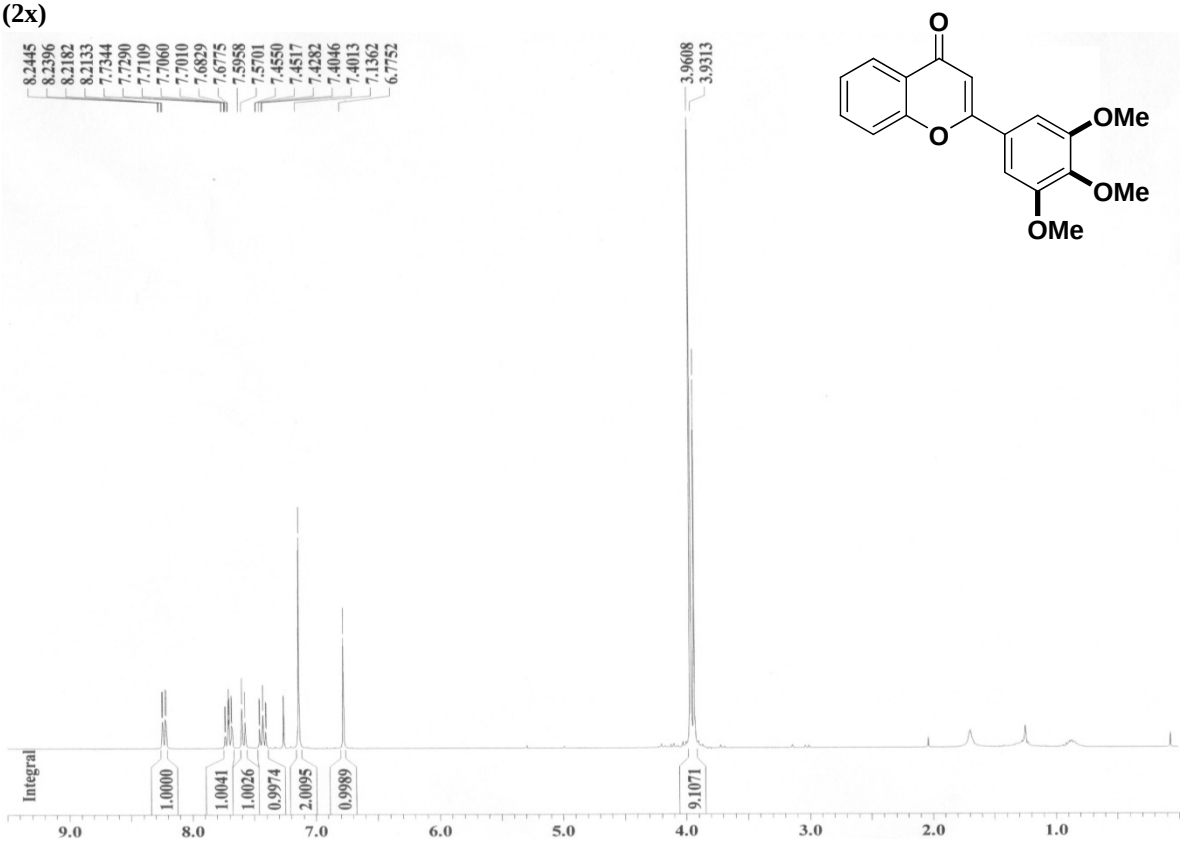


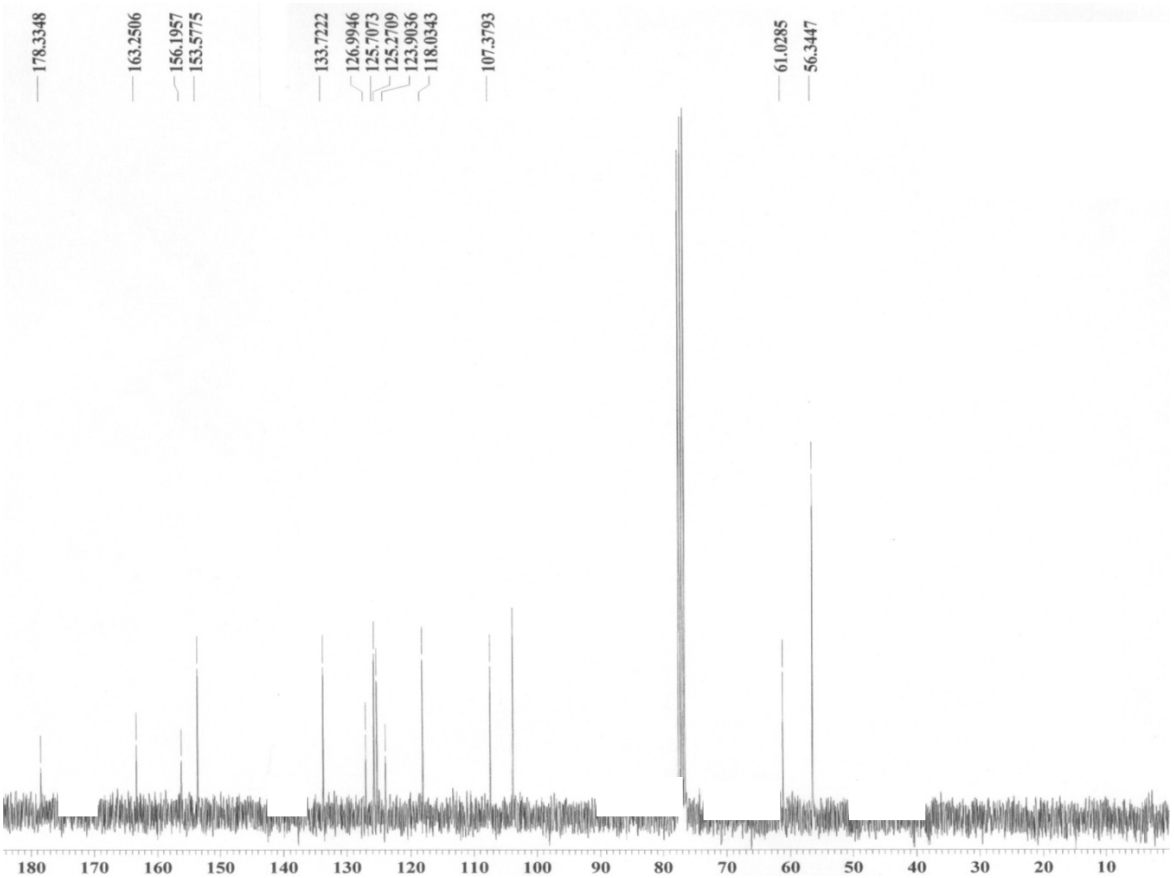
2-(4-chloro-2-fluorophenyl)-4H-1-Benzopyran-4-one
(2w)



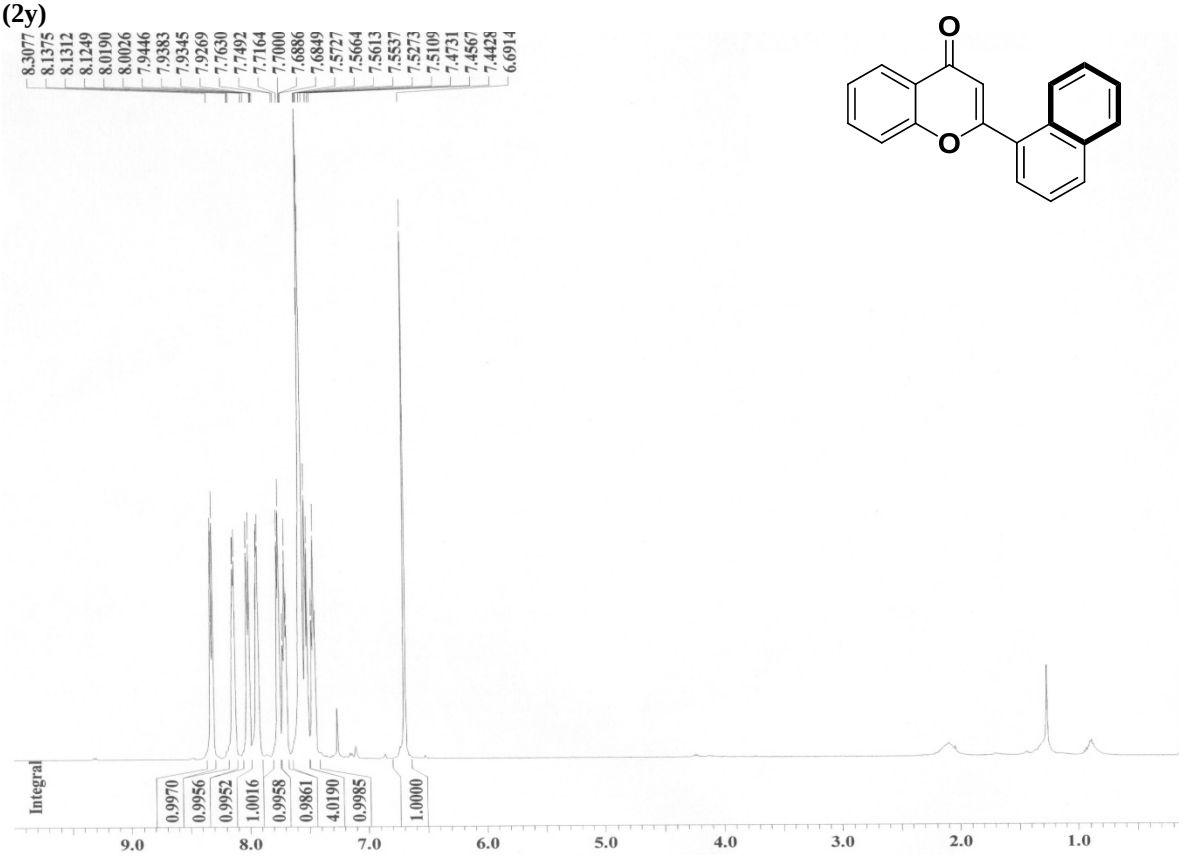


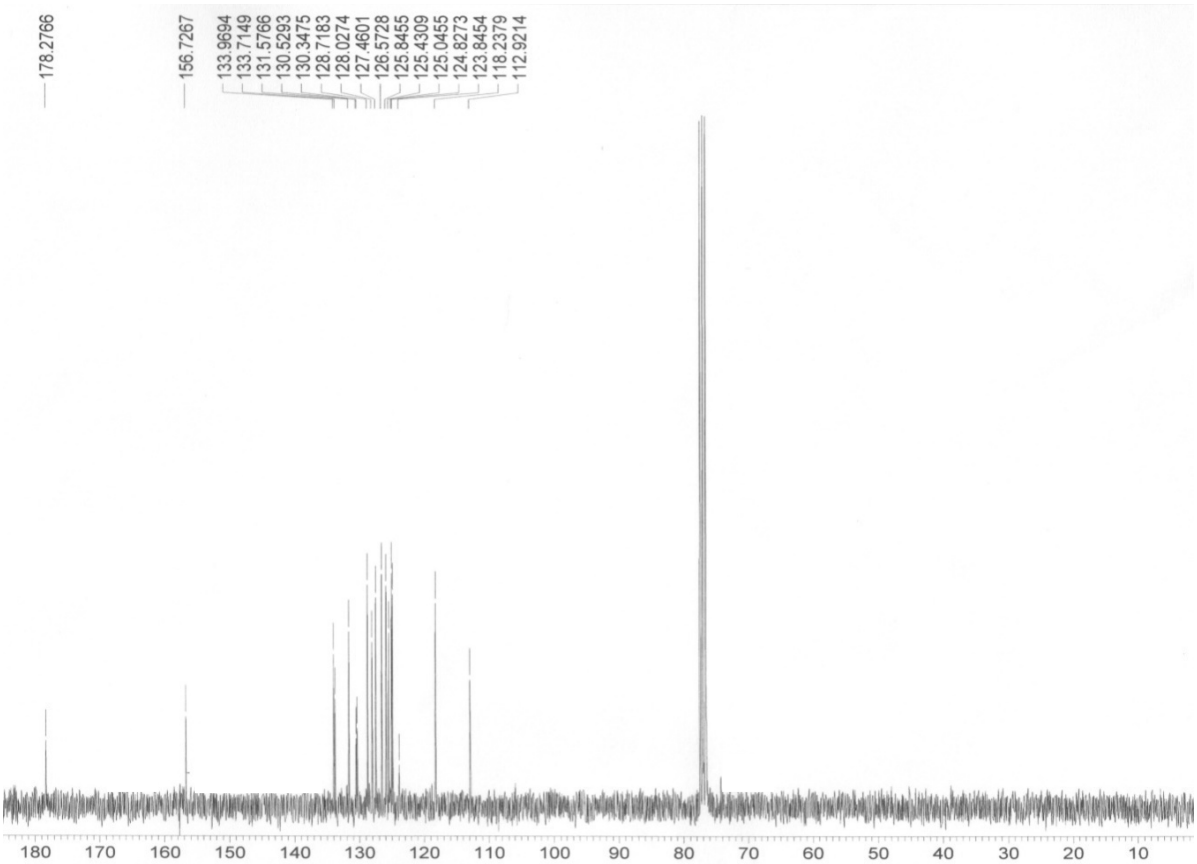
2-(3,4,5-trimethoxyphenyl))-4H-1-Benzopyran-4-one
(2x)



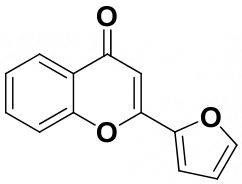


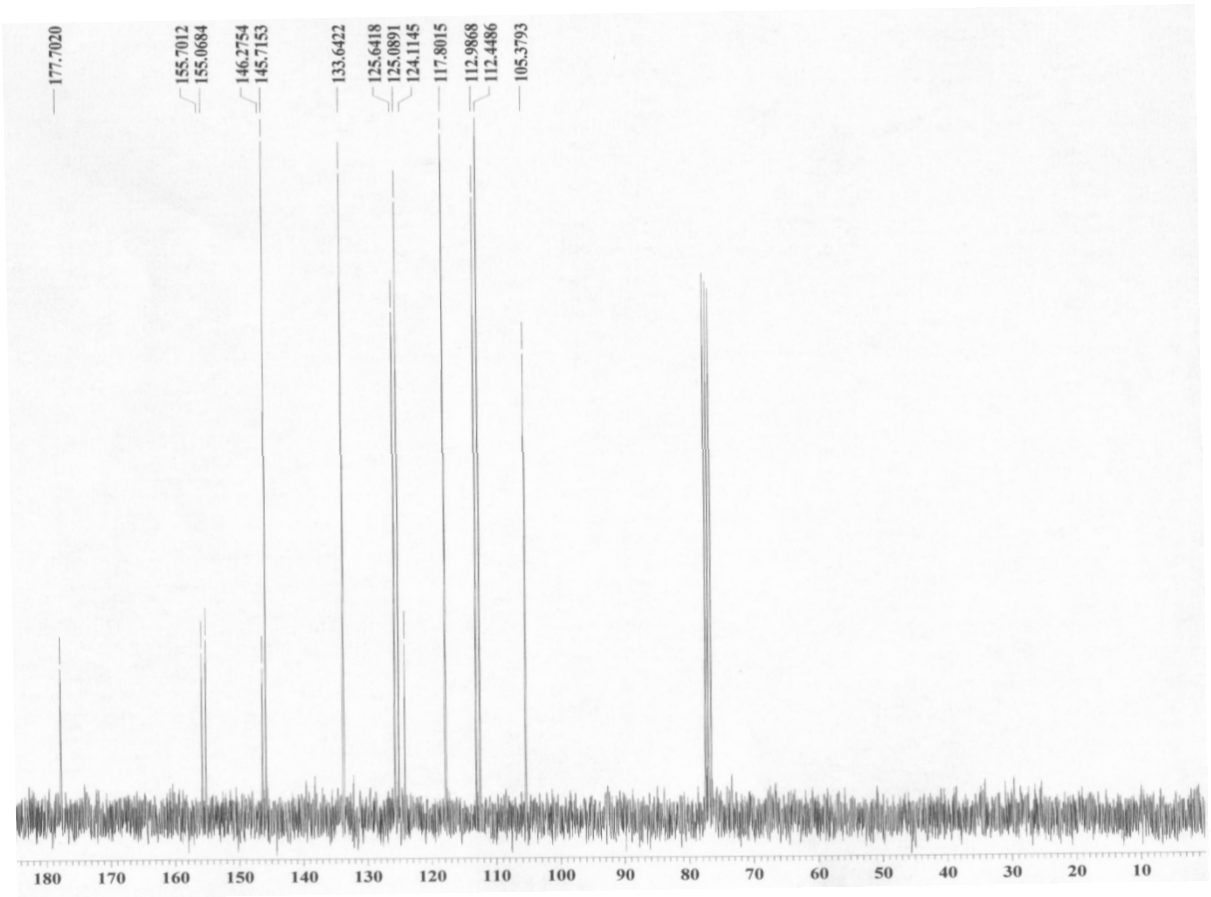
2-(1-naphthalenyl)-4H-1-Benzopyran-4-one
(2y)



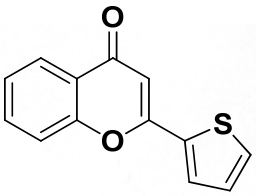


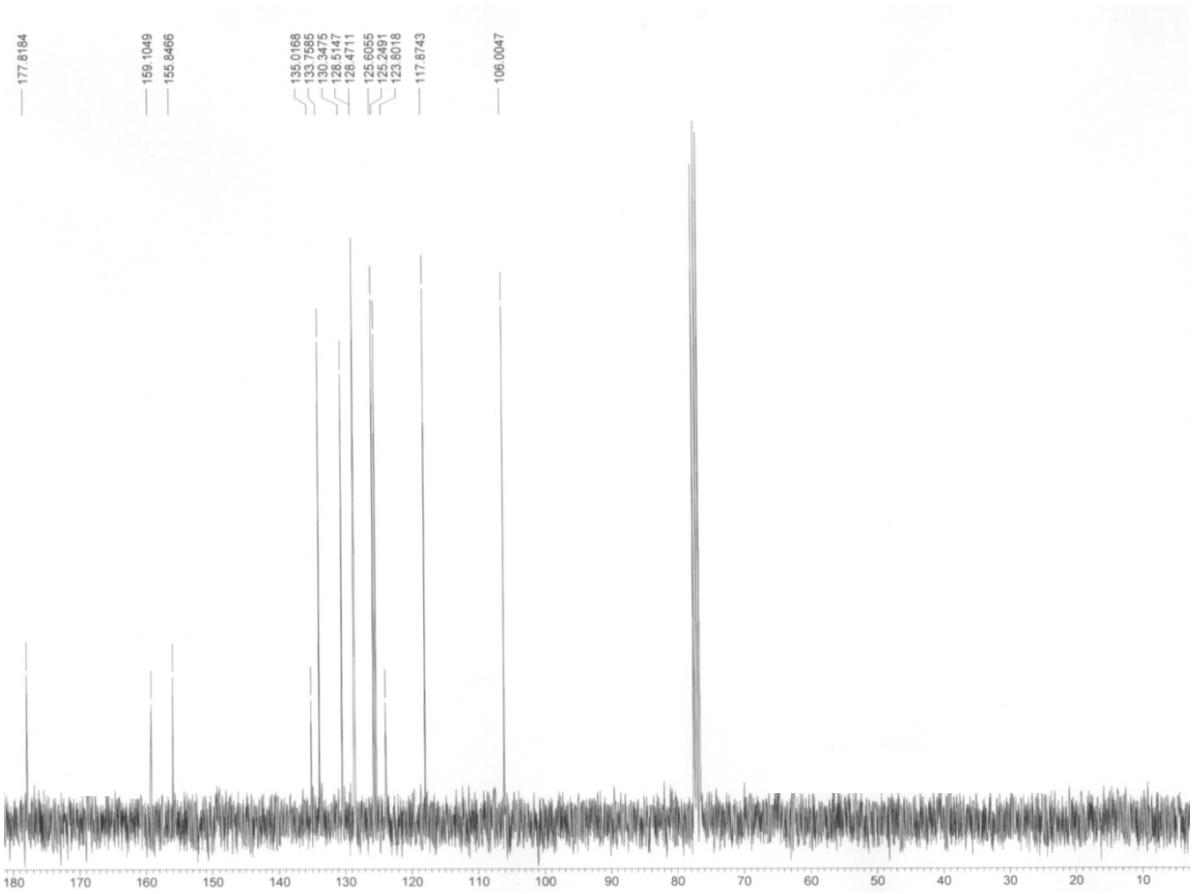
2-(2-furanyl)-4H-1-Benzopyran-4-one
(2z)



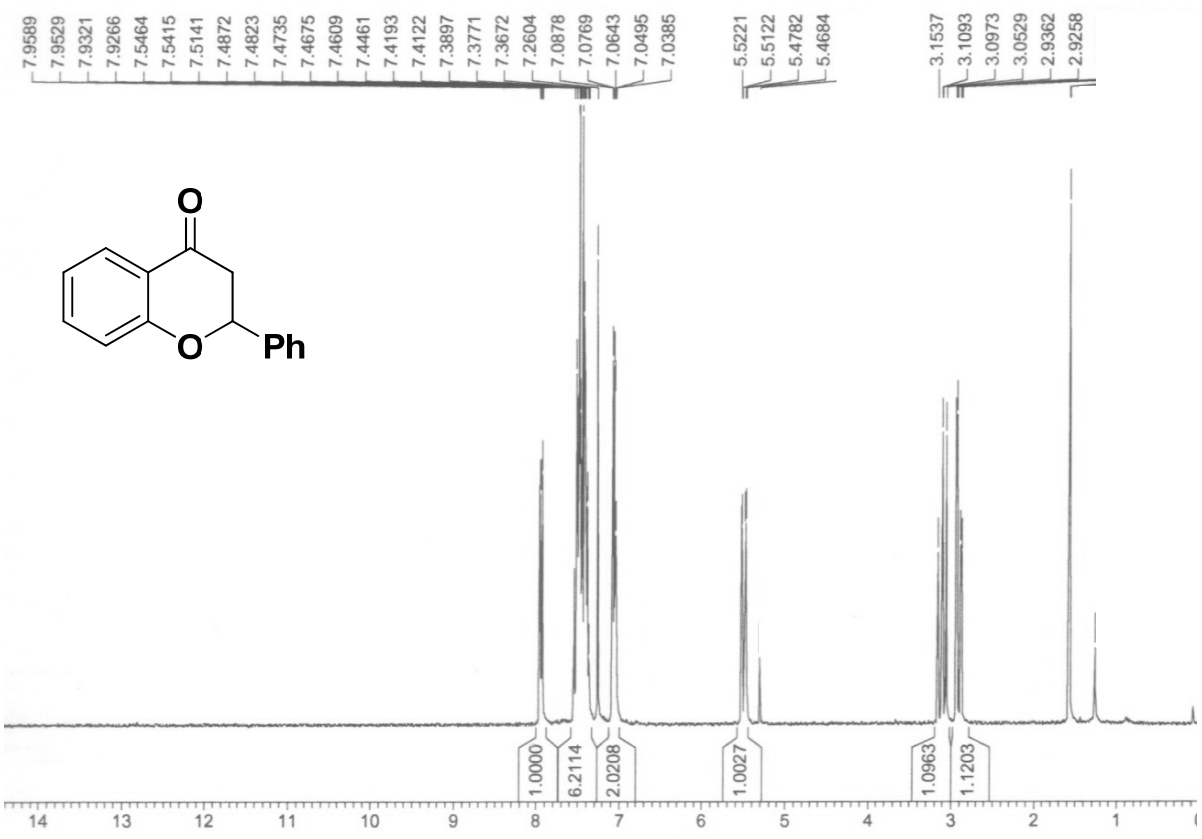


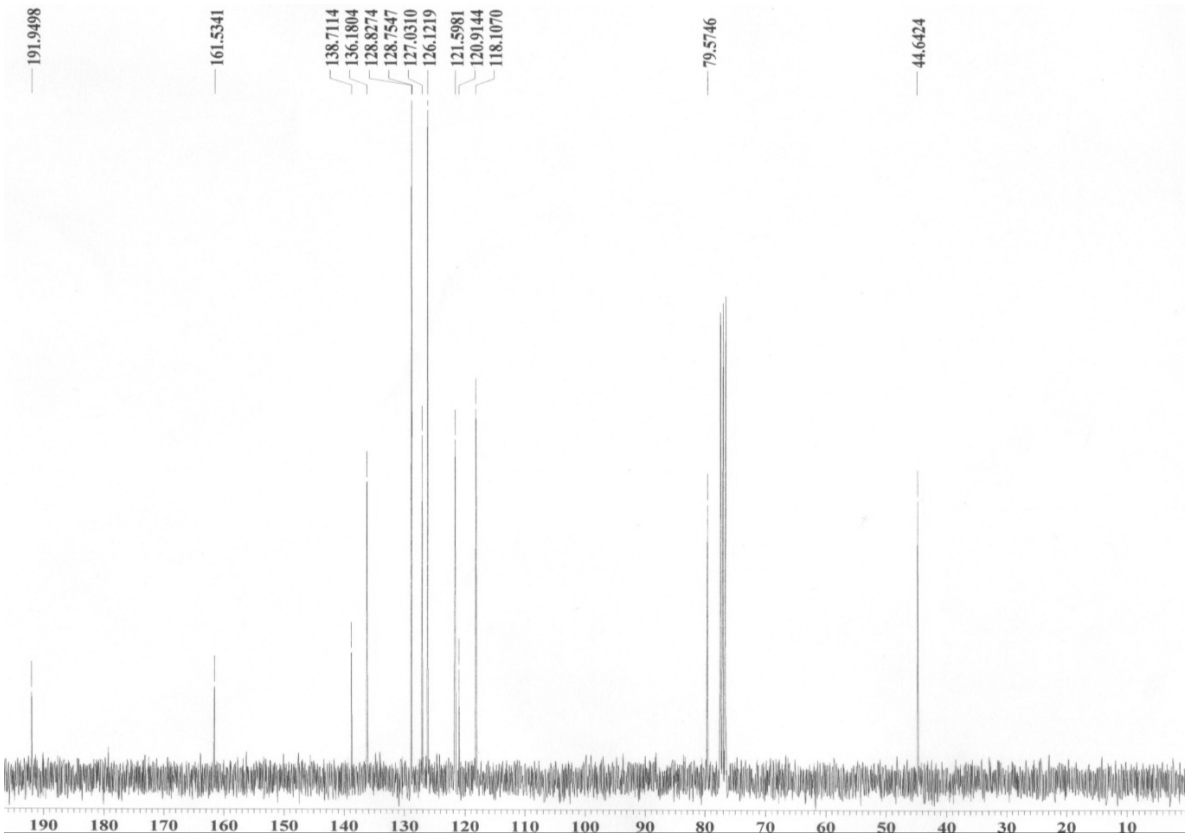
2-(2-thienyl)-4H-1-Benzopyran-4-one
(2aa)





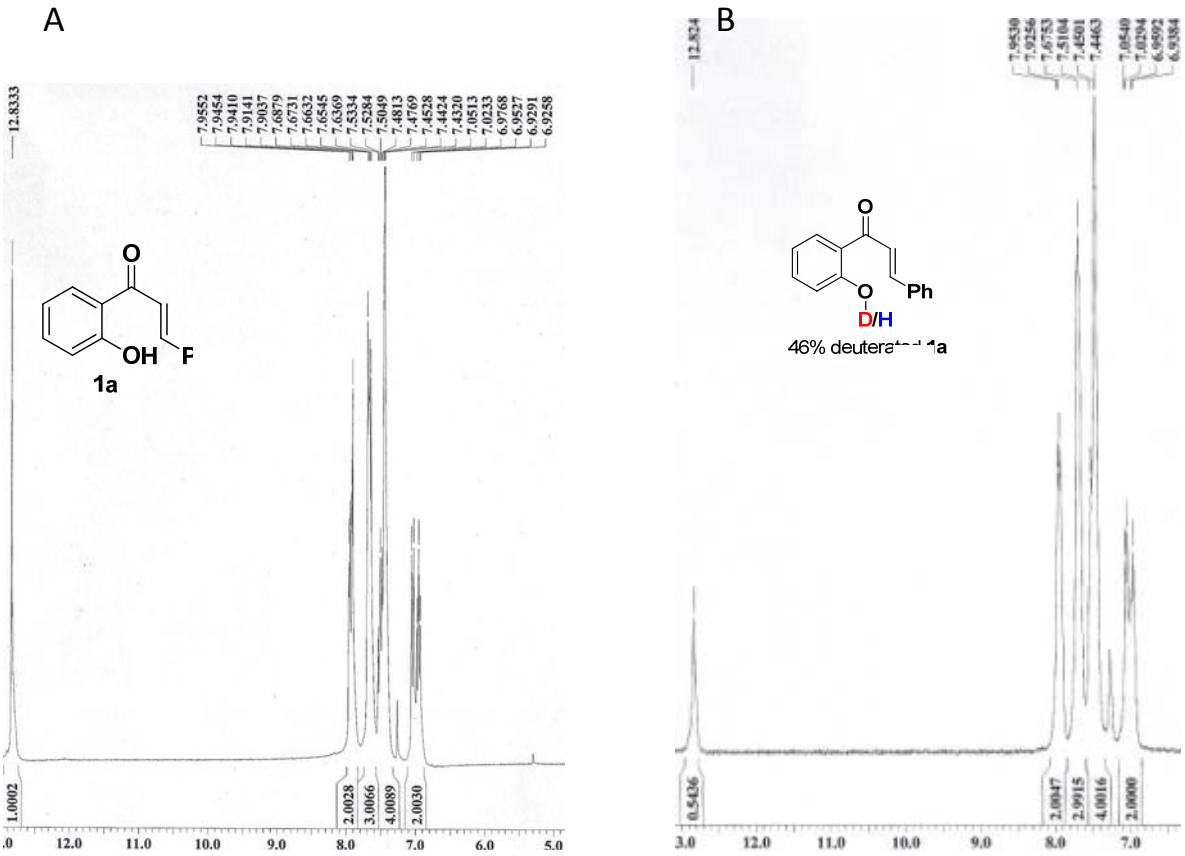
2-phenyl-2,3-dihydrochromen-4-one (2a')





Isotope Experiment

To probe the action of this mechanism, in particular the hydrogen source in the formation of intermediate **2a'** and the subsequent oxidation to product **2a**, deuterated chalcone **1a** was obtained. Deuteration exchange with deuterated water (D_2O) afforded 46% deuteration. The NMR spectra for non-deuterated and deuterated **1a** are shown in Fig 1. A and B. The solvent used was anhydrous DMF instead of DMA to minimise proton exchange with any labile H_2O proton that could be present in DMA. Flavone **2a** with 30% deuteration was isolated after 16 hours (Fig 1. D).



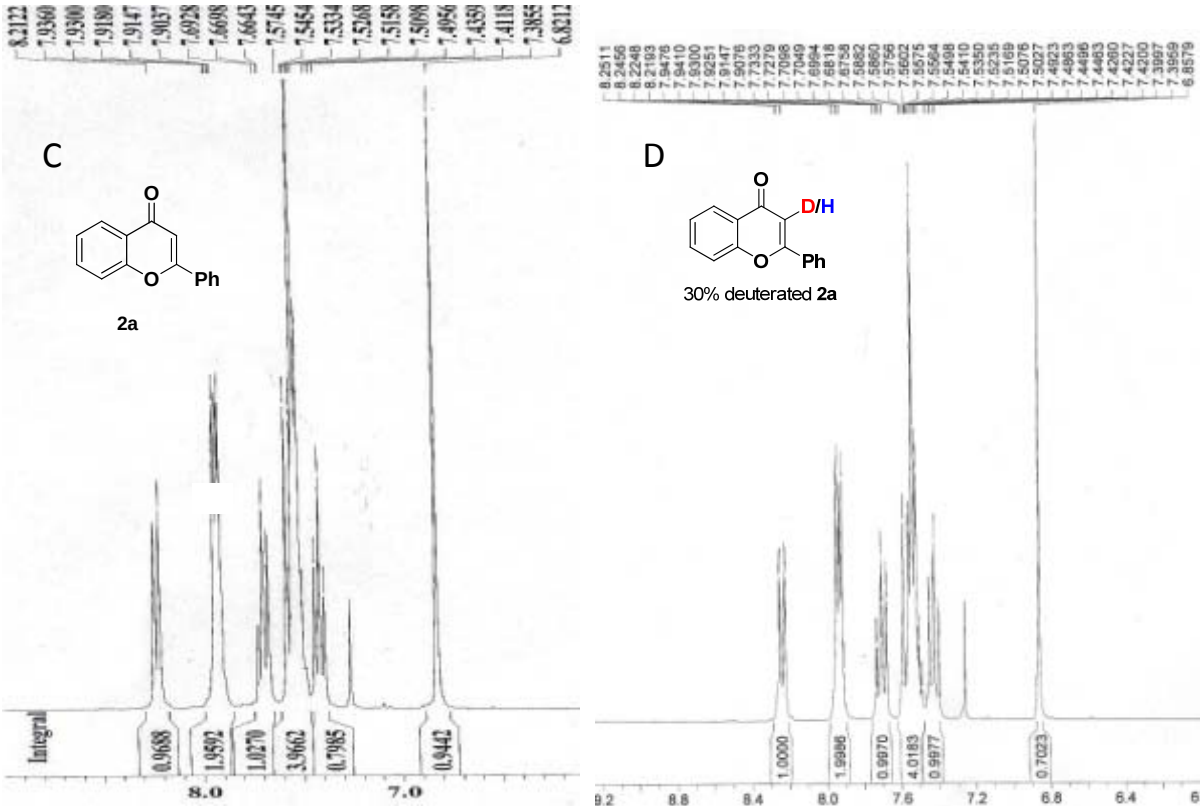


Fig 1. NMR spectra for (A) non-deuterated chalcone **1a**, (B) deuterated chalcone **1a**, (C) non-deuterated flavone **2a** and (D) deuterated flavone **2a**