Supporting Information

Palladium-Catalyzed Coupling of *N*-Tosylhydrazones and *β*-Bromostyrene Derivatives: New Approach to 2*H*-Chromenes

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1. General

All the palladium-catalyzed reactions were performed under argon atmosphere in a flame-dried reaction flask. All solvents were distilled under nitrogen atmosphere prior to use. 1,4-Dioxane and toluene were dried over Na with benzophenone-ketyl intermediate as indicator, and acetonitrile was dried over CaH_2. For chromatography, 200-300 mesh silica gel (Qingdao, China) was employed. ^1H and ^{13}C NMR spectra were recorded at 400 MHz and 100 MHz with Bruker ARX 400 spectrometer. Chemical shifts are reported in ppm using tetramethylsilane as internal standard. IR spectra were recorded with a Nicolet 5MX-S infrared spectrometer. LRMS were obtained on an Agilent 5975C inert 350 EI mass spectrometer. HRMS were obtained on a Bruker Apex IV FTMS by ESI or GCT CA127 Micronass UK by EI.

2. Preparation of *N*-Tosylhydrazones

Typical procedure for converting salicylaldehydes to the corresponding *N*-tosylhydrazones: salicylaldehyde (4.88 g, 40 mmol) was dissolved in methanol (30 mL), then $TsNHNH_2$ (7.44 g, 40 mmol) was added to the reaction mixture. The resulting mixture was heated to 60 ^oC, and stirring was continued for 5 h. After the reaction was cooled to room temperature, the precipitates were filtered and washed by petroleum ether, and then kept in desiccator under vacuum to afford pure product **1a** (9.98 g, 86%). The yields for other tosylhydrazones were about 73-88%. The reactions were usually carried out overnight and were monitored by TLC.

3. Preparation of (*E*)-2-(Bromovinyl)styrenes[1,2]

Compounds **2a-2e**, **2g-2i, 2m** were prepared according to the procedure described in ref. 1. The yields were about 53-67%.

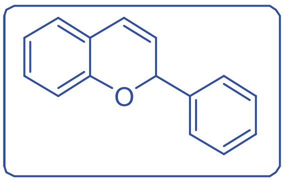
Compounds **2f**, **2j-l** were prepared according to the procedure described in ref. 2. The yields were about 58-86%.

4. General Procedure of Palladium-Catalyzed Reductive Coupling

Under an argon atmosphere, $Pd_2(dba)_3{\cdot}CHCl_3$ (5.2 mg, 0.005 mmol, 2.5 mol%), $PCy_3{\cdot}HBF_4$ (11.1 mg, 0.03 mmol, 15 mol%), *N*-tosylhydrazones (0.4 mmol) and K_2CO_3 (82.8 mg, 0.6 mmol) are successively added to a flame-dried 25 mL Schlenk flask. The reaction flask was degassed three times with argon and dry dioxane (2.0 mL) was added using a syringe. Then (*E*)-2-(bromovinyl)styrenes (0.2 mmol) were added by syringe. Note that (*E*)-2-(bromovinyl)styrene in a solid form was added to the reaction flask prior to K_2CO_3. The reaction was heated at 100 ºC with stirring for about 12 h, then cooled to room temperature and filtered through a short path of neutral alumina with petroleum ether/ethyl acetate (5:1, 30 mL) as eluents. Solvent was then removed in *vacuo* to leave a crude mixture, which was purified by silica gel column chromatography to afford the pure product.

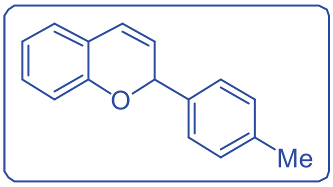
5. Characterization data

2-phenyl-2*H*-chromene (3a)[3-6]



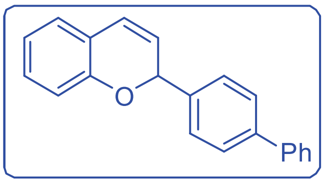
The title compound was prepared *via* the general procedure. After purification by silica gel column chromatography (petroleum ether, PE), the product was isolated as a colorless oil (38 mg, 91%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45-7.43 (m, 2H), 7.37-7.30 (m, 3H), 7.11-7.07 (m, 1H), 6.99 (d, *J* = 7.2 Hz, 1H), 6.87-6.83 (m, 1H), 6.78 (d, *J* = 8.0 Hz, 1H), 6.51 (d, *J* = 10.0 Hz, 1H), 5.90-5.89 (m, 1H), 5.78 (dd, *J* = 10.0 Hz, 3.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.1, 140.8, 129.4, 128.6, 128.3, 126.9, 126.5, 124.8, 123.9, 121.2, 121.1, 115.9, 77.1.

2-(*p*-tolyl)-2*H*-chromene (3b)[3,6]



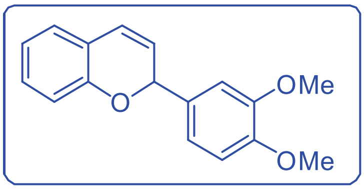
The title compound was prepared *via* the general procedure. After purification by silica gel column chromatography (PE), the product was isolated as a colorless oil (39 mg, 88%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.32 (m, 2H), 7.19-7.15 (m, 2H), 7.10-7.06 (m, 1H), 6.98 (dd, *J* = 8.0 Hz, 1.6 Hz, 1H), 6.86-6.82 (m, 1H), 6.76 (d, *J* = 8.0 Hz, 1H), 6.51 (dd, *J* = 10.0 Hz, 1.6 Hz, 1H), 5.87-5.86 (m, 1H), 5.77 (dd, *J* = 10.0 Hz, 3.6 Hz, 1H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.1, 138.1, 137.8, 129.3, 129.2, 127.0, 126.5, 124.9, 123.9, 121.3, 121.0, 115.9, 77.0, 21.1.

2-[(1,1'-biphenyl)-4-yl]-2*H*-chromene (3c)



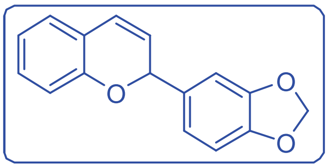
The title compound was prepared *via* the general procedure. After purification by silica gel column chromatography (PE), the product was isolated as a colorless solid (41 mg, 71%); mp 103-104 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60-7.56 (m, 4H), 7.53-7.51 (m, 2H), 7.45-7.41 (m, 2H), 7.36-7.31 (m, 1H), 7.14-7.09 (m, 1H), 7.02 (dd, *J* = 7.2 Hz, 1.6 Hz, 1H), 6.89-6.85 (m, 1H), 6.80 (d, *J* = 8.0 Hz, 1H), 6.56 (dd, *J* = 10.0 Hz, 1.6 Hz, 1H), 5.97-5.95 (m, 1H), 5.83 (dd, *J* = 10.0 Hz, 3.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.1, 141.3, 140.7, 139.7, 129.4, 128.7, 127.5, 127.4, 127.3, 127.1, 126.6, 124.6, 124.1, 121.3, 121.2, 116.0, 76.8; HRMS (ESI, *m/z*): calcd for $C_{21}H_{17}O$ $[M+H]^+$ 285.1274, found 285.1271; LRMS (EI, *m/z*): 284 (M^+, 93), 283 (100), 252 (19), 207 (46), 152 (61); IR (film): 1486, 1209, 1108, 954, 748 cm^{-1}.

2-(3,4-dimethoxyphenyl)-2*H*-chromene (3d)[7]



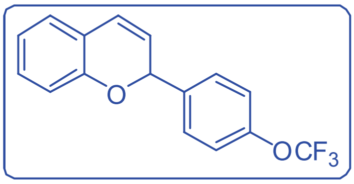
The title compound was prepared *via* the general procedure. After purification by silica gel column chromatography (PE:EA = 60:1), the product was isolated as a colorless oil (23 mg, 42%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13-7.08 (m, 1H), 7.03-6.97 (m, 3H), 6.89-6.83 (m, 2H), 6.77 (d, *J* = 8.4 Hz, 1H), 6.54 (dd, *J* = 10.0 Hz, 1.6 Hz, 1H), 5.87-5.85 (m, 1H), 5.78 (dd, *J* = 10.0 Hz, 3.2 Hz, 1H), 3.87 (s, 3H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.1, 149.2, 149.1, 133.2, 129.4, 126.5, 124.9, 124.1, 121.3, 121.1, 119.7, 116.0, 110.9, 110.4, 77.1, 55.9, 55.8.

2-[4-(3,4-methenedioxy)phenyl]-2*H*-chromene (3e)



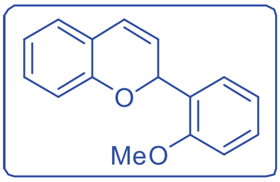
The title compound was prepared *via* the general procedure. After purification by silica gel column chromatography (PE:EA = 60:1), the product was isolated as a colorless oil (27 mg, 53%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12-7.09 (m, 1H), 7.00 (dd, *J* = 7.2 Hz, 1.6 Hz, 1H), 6.95 (d, *J* = 1.6 Hz, 1H), 6.90 (dd, *J* = 8.0 Hz, 1.6 Hz, 1H), 6.87-6.83 (m, 1H), 6.79-6.74 (m, 2H), 6.53 (dd, *J* = 10.0 Hz, 1.2 Hz, 1H), 5.93 (d, *J* = 1.6 Hz, 2H), 5.81 (dd, *J* = 3.2 Hz, 2.0 Hz, 1H), 5.75 (dd, *J* = 10.0 Hz, 3.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.9, 147.9, 147.7, 134.6, 129.4, 126.5, 124.6, 124.1, 121.2, 121.1, 120.8, 116.0, 108.1, 107.8, 101.1, 76.9; HRMS (ESI, *m/z*): calcd for $C_{16}H_{13}O_3$ $[M+H]^+$ 253.0859, found 253.0860; LRMS (EI, *m/z*): 252 (M^+, 100), 221 (28), 205 (21), 165 (92); IR (film): 1502, 1484, 1249, 1226, 1038, 794 cm^{-1}.

2-[4-(trifluoromethoxy)phenyl]-2*H*-chromene (3f)[5]



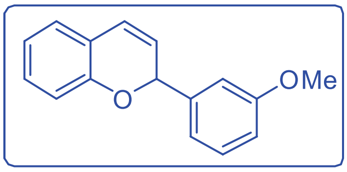
The title compound was prepared *via* the general procedure. After purification by silica gel column chromatography (PE:EA = 100:1, EA = ethyl acetate), the product was isolated as a colorless oil (39 mg, 85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48-7.45 (m, 2H), 7.21-7.18 (m, 2H), 7.13-7.09 (m, 1H), 7.01 (dd, *J* = 8.0 Hz, 1.6 Hz, 1H), 6.89-6.85 (m, 1H), 6.78 (d, *J* = 8.0 Hz, 1H), 6.54 (dd, *J* = 10.0 Hz, 1.6 Hz, 1H), 5.91-5.89 (m, 1H), 5.76 (dd, *J* = 10.0 Hz, 3.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.8, 149.0, 139.4, 129.6, 128.4, 126.6, 124.3, 124.1, 121.4, 121.1, 121.0, 120.4 (q, *J* = 257.0 Hz), 116.0, 76.1.

2-(2-methoxyphenyl)-2*H*-chromene (3g)[4]



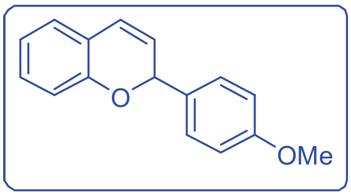
The title compound was prepared *via* the general procedure. After purification by silica gel column chromatography (PE:EA = 100:1), the product was isolated as a colorless oil (29 mg, 61%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (dd, *J* = 7.6 Hz, 1.6 Hz, 1H), 7.30-7.22 (m, 1H), 7.12-7.07 (m, 1H), 6.99-6.88 (m, 3H), 6.86-6.79 (m, 2H), 6.46 (dd, *J* = 10.0 Hz, 1.6 Hz, 1H), 6.35-6.33 (m, 1H), 5.78 (dd, *J* = 10.0 Hz, 3.2 Hz, 1H), 3.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.7, 153.5, 129.3, 129.2, 129.1, 127.6, 126.4, 124.9, 123.2, 121.2, 120.9, 120.7, 115.8, 110.5, 71.5, 55.4.

2-(3-methoxyphenyl)-2*H*-chromene (3h)[6]



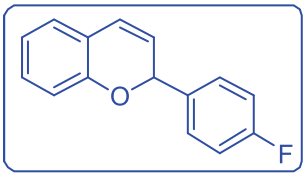
The title compound was prepared *via* the general procedure. After purification by silica gel column chromatography (PE:EA = 100:1), the product was isolated as a colorless oil (28 mg, 59%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.30-7.24 (m, 1H), 7.13-7.08 (m, 1H), 7.04-6.99 (m, 3H), 6.88-6.84 (m, 2H), 6.79 (d, *J* = 8.0 Hz, 1H), 6.52 (dd, *J* = 9.6 Hz, 1.6 Hz, 1H), 5.90-5.87 (m, 1H), 5.79 (dd, *J* = 9.6 Hz, 3.2 Hz, 1H), 3.78 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 159.8, 153.1, 142.4, 129.7, 129.4, 126.6, 124.8, 124.0, 121.3, 121.2, 119.2, 116.0, 113.8, 112.561, 77.0, 55.2.

2-(4-methoxyphenyl)-2*H*-chromene (3i)[3-6]



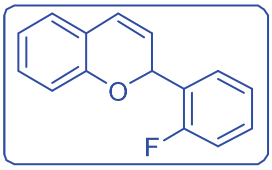
The title compound was prepared *via* the general procedure. After purification by silica gel column chromatography (PE:EA = 100:1), the product was isolated as a colorless oil (35 mg, 74%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.38-7.36 (m, 2H), 7.10-7.06 (m, 1H), 7.00 (dd, *J* = 7.6 Hz, 1.6 Hz, 1H), 6.90-6.82 (m, 3H), 6.75 (d, *J* = 8.0 Hz, 1H), 6.53 (dd, *J* = 10.0 Hz, 1.6 Hz, 1H), 5.85 (dd, *J* = 3.2 Hz, 2.0 Hz, 1H), 5.77 (dd, *J* = 10.0 Hz, 3.2 Hz, 1H), 3.78 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 159.7, 153.0, 132.8, 129.3, 128.6, 126.4, 124.8, 123.9, 121.3, 121.0, 116.0, 113.9, 76.7, 55.2.

2-(4-fluorophenyl)-2*H*-chromene (3j)[3-5]



The title compound was prepared *via* the general procedure. After purification by silica gel column chromatography (PE:EA = 100:1), the product was isolated as a colorless oil (31 mg, 67%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.44-7.40 (m, 2H), 7.13-7.09 (m, 1H), 7.07-6.99 (m, 3H), 6.89-6.84 (m, 1H), 6.77 (d, *J* = 8.0 Hz, 1H), 6.55 (dd, *J* = 10.0 Hz, 1.6 Hz, 1H), 5.89-6.88 (m, 1H), 5.77 (dd, *J* = 10.0 Hz, 3.6 Hz, 1H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 162.6 (d, *J* = 245.3 Hz), 152.8, 136.6 (d, *J* = 3.3 Hz), 129.5 128.9 (d, *J* = 8.3 Hz) , 126.6, 124.4, 124.2, 121.3, 121.2, 116.0, 115.5 (d, *J* = 21.5 Hz), 76.3.

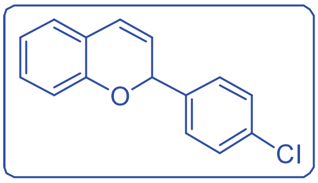
2-(2-fluorophenyl)-2*H*-chromene (3k)



The title compound was prepared *via* the general procedure. After purification by silica gel column chromatography (PE:EA = 100:1), the product was isolated as a colorless oil (39 mg, 87%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.53-7.48 (m, 1H), 7.31-7.25 (m, 1H), 7.14-7.04 (m, 3H), 7.00 (dd, *J* = 7.2 Hz, 1.6 Hz, 1H), 6.89-6.84 (m, 1H), 6.80 (d, *J* = 8.0 Hz, 1H), 6.52 (dd, *J* = 10.0 Hz, 1.6 Hz, 1H), 6.27 (dd, *J* = 3.2 Hz, 1.6 Hz, 1H), 5.77 (ddd, *J* = 10.0 Hz, 3.6 Hz, 0.8 Hz, 1H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 159.5 (d, *J* = 245.9 Hz), 153.1, 129.9 (d, *J* = 8.3 Hz), 129.5, 128.6

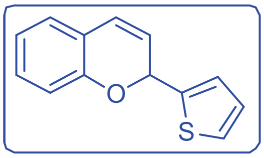
(d, *J* = 2.7 Hz), 128.0 (d, *J* = 13.5 Hz), 126.7, 124.3 (d, *J* = 3.6 Hz), 124.2, 123.6, 121.3, 121.0, 115.9, 115.6 (d, *J* = 21.3 Hz), 70.8 (d, *J* = 3.5 Hz); HRMS (ESI, *m/z*): calcd for $C_{15}H_{12}FO$ $[M+H]^+$ 227.0867, found 227.0863; LRMS (EI, *m/z*): 226 (M^+, 80), 225 (100), 207 (10), 196 (32), 131 (74); IR (film): 1485, 1455, 1226, 1045, 752 cm^{-1}.

2-(4-chlorophenyl)-2*H*-chromene (3l)[5]



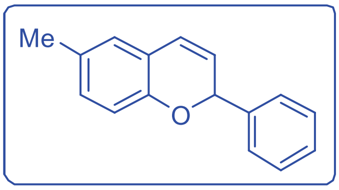
The title compound was prepared *via* the general procedure. After purification by silica gel column chromatography (PE:EA = 100:1), the product was isolated as a colorless oil (34 mg, 69%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.36 (m, 2H), 7.33-7.31 (m, 2H), 7.13-7.08 (m, 1H), 7.00 (dd, *J* = 7.6 Hz, 1.6 Hz, 1H), 6.89-6.84 (m, 1H), 6.77 (d, *J* = 8.0 Hz, 1H), 6.54 (dd, *J* = 9.6 Hz, 1.6 Hz, 1H), 5.87 (dd, *J* = 3.6 Hz, 1.6 Hz, 1H), 5.75 (dd, *J* = 9.6 Hz, 3.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.8, 139.2, 134.1, 129.5, 128.7, 128.4, 126.6, 124.3, 124.2, 121.3, 121.1, 115.9, 76.2.

2-(thiophen-2-yl)-2*H*-chromene (3m)



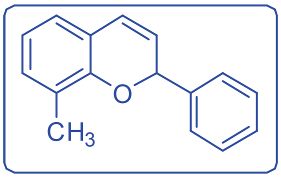
The title compound was prepared *via* the general procedure. After purification by silica gel column chromatography (PE), the product was isolated as a colorless oil (40 mg, 92%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (dd, *J* = 5.2 Hz, 1.2 Hz, 1H), 7.12-7.07 (m, 2H), 7.02 (dd, *J* = 7.2 Hz, 1.2 Hz, 1H), 6.97-6.94 (m, 1H), 6.89-6.84 (m, 1H), 6.78 (d, *J* = 8.0 Hz, 1H), 6.57 (d, *J* = 9.6 Hz, 1H), 6.11-6.09 (m, 1H), 5.90 (dd, *J* = 9.6 Hz, 4.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.4, 143.6, 129.5, 126.7, 126.6, 126.2, 126.0, 124.5, 123.8, 121.4, 121.3, 116.3, 71.6; HRMS (ESI, *m/z*): calcd for $C_{13}H_{11}OS$ $[M+H]^+$ 215.0525, found 215.0524; LRMS (EI, *m/z*): 214 (M^+, 83), 213 (100), 184 (28), 152 (30); IR (film): 1484, 1225, 1197, 1034, 754 cm^{-1}.

6-methyl-2-phenyl-2*H*-chromene (3n)[5]



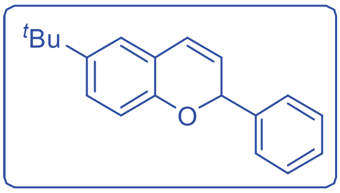
The title compound was prepared *via* the general procedure. After purification by silica gel column chromatography (PE), the product was isolated as a colorless oil (41 mg, 91%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45-7.42 (m, 2H), 7.37-7.27 (m, 3H), 6.90 (dd, *J* = 8.0 Hz, 1.6 Hz, 1H), 6.82-6.80 (m, 1H), 6.69 (d, *J* = 8.0 Hz, 1H), 6.48 (dd, *J* = 10.0 Hz, 1.6 Hz, 1H), 5.87-5.85 (m, 1H), 5.77 (dd, *J* = 10.0 Hz, 3.2 Hz, 1H), 2.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.9, 140.8, 130.3, 129.8, 128.5, 128.2, 127.0, 126.9, 124.9, 124.0, 121.0, 115.6, 77.0, 20.4.

8-methyl-2-phenyl-2*H*-chromene (3o)[8]



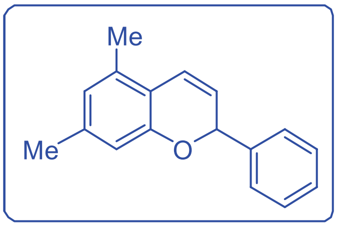
The title compound was prepared *via* the general procedure. After purification by silica gel column chromatography (PE), the product was isolated as a colorless oil (29 mg, 65%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45-7.43 (m, 2H), 7.38-7.29 (m, 3H), 6.97 (d, *J* = 7.2 Hz, 1H), 6.85 (dd, *J* = 7.2 Hz, 0.8 Hz, 1H), 6.78-6.74 (m, 1H), 6.51 (dd, *J* = 9.6 Hz, 2.0 Hz, 1H), 5.94-5.92 (m, 1H), 5.80 (dd, *J* = 9.6 Hz, 3.6 Hz, 1H), 2.15 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.1, 141.2, 130.9, 128.5, 128.0, 126.6, 125.1, 124.4, 124.2, 120.8, 120.4, 76.6, 15.5.

6-(*tert*-butyl)-2-phenyl-2*H*-chromene (3p)[3]



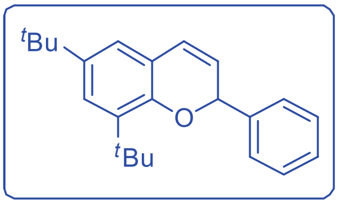
The title compound was prepared *via* the general procedure. After purification by silica gel column chromatography (PE), the product was isolated as a colorless oil (46 mg, 87%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46-7.43 (m, 2H), 7.38-7.30 (m, 3H), 7.13 (dd, *J* = 8.4 Hz, 2.4 Hz, 1H), 7.01 (d, *J* = 2.0 Hz, 1H), 6.73 (d, *J* = 8.4 Hz, 1H), 6.51 (dd, *J* = 9.6 Hz, 2.0 Hz, 1H), 5.90-5.88 (m, 1H), 5.76 (dd, *J* = 9.6 Hz, 3.2 Hz, 1H), 1.28 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.8, 143.8, 141.0, 128.5, 128.2, 126.9, 126.3, 124.7, 124.4, 123.5, 120.5, 115.2, 77.1, 34.0, 31.4.

5,7-dimethyl-2-phenyl-2*H*-chromene (3q)



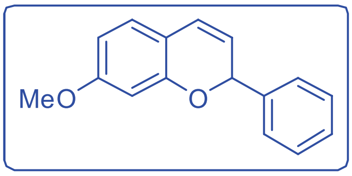
The title compound was prepared *via* the general procedure. After purification by silica gel column chromatography (PE), the product was isolated as a colorless oil (34 mg, 72%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45-7.42 (m, 2H), 7.37-7.29 (m, 3H), 6.68 (dd, *J* = 10.0 Hz, 0.8 Hz, 1H), 6.53 (s, 1H), 6.50 (s, 1H), 5.82-5.80 (m, 1H), 5.77 (dd, *J* = 10.0 Hz, 3.6 Hz, 1H), 2.27 (s, 3H), 2.21 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.2, 140.9, 139.0, 133.9, 128.5, 128.1, 126.9, 123.7, 123.5, 121.1, 117.3, 114.5, 76.4, 21.3, 18.2. HRMS (ESI, *m/z*): calcd for $C_{17}H_{17}O$ $[M+H]^+$ 237.1274, found 237.1281; LRMS (EI, *m/z*): 236 (M^+, 92), 235 (100), 221 (34), 209 (16), 178 (20), 159 (56); IR (film): 1613, 1453, 1282, 1140, 1074, 842, 761, 699 cm^{-1}.

6,8-*di*-tert-butyl-2-phenyl-2*H*-chromene (3r)[3]



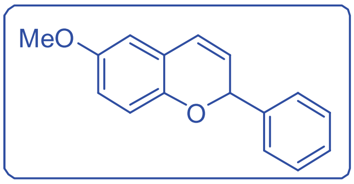
The title compound was prepared *via* the general procedure. After purification by silica gel column chromatography (PE), the product was isolated as a colorless oil (60 mg, 93%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49-7.46 (m, 2H), 7.40-7.30 (m, 3H), 7.19 (d, *J* = 2.4 Hz, 1H), 6.92 (d, *J* = 2.4 Hz, 1H), 6.51 (dd, *J* = 10.0 Hz, 2.0 Hz, 1H), 5.86-5.84 (m, 1H), 5.74 (dd, *J* = 10.0 Hz, 3.2 Hz, 1H), 1.31 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.3, 143.0, 140.8, 136.6, 128.5, 128.0, 126.9, 125.4, 124.9, 124.0, 121.7, 121.5, 76.9, 34.6, 34.2, 31.5, 29.7.

7-methoxy-2-phenyl-2*H*-chromene (3s)[5]



The title compound was prepared *via* the general procedure. After purification by silica gel column chromatography (PE:EA = 100:1), the product was isolated as a colorless oil (32 mg, 66%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46-7.43 (m, 2H), 7.39-7.28 (m, 3H), 6.91 (d, J = 8.4 Hz, 1H), 6.48 (dd, J = 10.0 Hz, 1.6 Hz, 1H), 6.42 (dd, J = 8.4 Hz, 2.4 Hz, 1H), 6.38 (d, J = 2.4 Hz, 1H), 5.88 (dd, J = 3.2 Hz, 2.0 Hz, 1H), 5.65 (dd, J = 10.0 Hz, 3.2 Hz, 1H), 3.73 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.9, 154.4, 140.9, 128.6, 128.3, 127.2, 127.0, 123.6, 121.8, 114.6, 107.0, 101.8, 77.3, 55.3.

6-methoxy-2-phenyl-2*H*-chromene (3t)[9]



The title compound was prepared *via* the general procedure. After purification by silica gel column chromatography (PE:EA = 100:1), the product was isolated as a colorless oil (32 mg, 68%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45-7.42 (m, 2H), 7.38-7.29 (m, 3H), 6.72 (d, J = 8.8 Hz, 1H), 6.66 (dd, J = 8.8 Hz, 2.8 Hz, 1H), 6.58 (d, J = 3.2 Hz, 1H), 6.49 (dd, J = 10.4 Hz, 2.8 Hz, 1H), 5.86-5.82 (m, 2H), 3.74 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.9, 147.0, 140.6, 128.5, 128.2, 126.9, 125.8, 124.1, 121.9, 116.5, 114.4, 111.7, 76.9, 55.6.

8-methoxy-2-phenyl-2*H*-chromene (3u)

The title compound was prepared *via* the general procedure. After purification by silica gel column chromatography (PE:EA = 100:1), the product was isolated as a colorless oil (13 mg, 26%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47-7.45 (m, 2H), 7.37-7.29 (m, 3H), 6.84-6.86 (m, 2H), 6.65 (dd, J = 7.2 Hz, 1.6 Hz, 1H), 6.52 (dd, J = 10.0 Hz, 1.6 Hz, 1H), 5.98-5.96 (m, 1H), 5.85 (dd, J = 10.0 Hz, 3.6 Hz, 1H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.8, 142.0, 140.7, 128.5, 128.2, 126.8, 124.9, 123.7, 122.0, 120.7, 118.9, 112.7, 76.9, 56.1; HRMS (ESI, *m/z*): calcd for $C_{16}H_{15}O_2$ $[M+H]^+$ 239.1067, found 239.1069; LRMS (EI, *m/z*): 238 (M^+, 78), 207 (23), 165 (100), 152 (38); IR (film): 1479, 1268, 1211, 1076, 754, 698 cm^{-1}.

6. References

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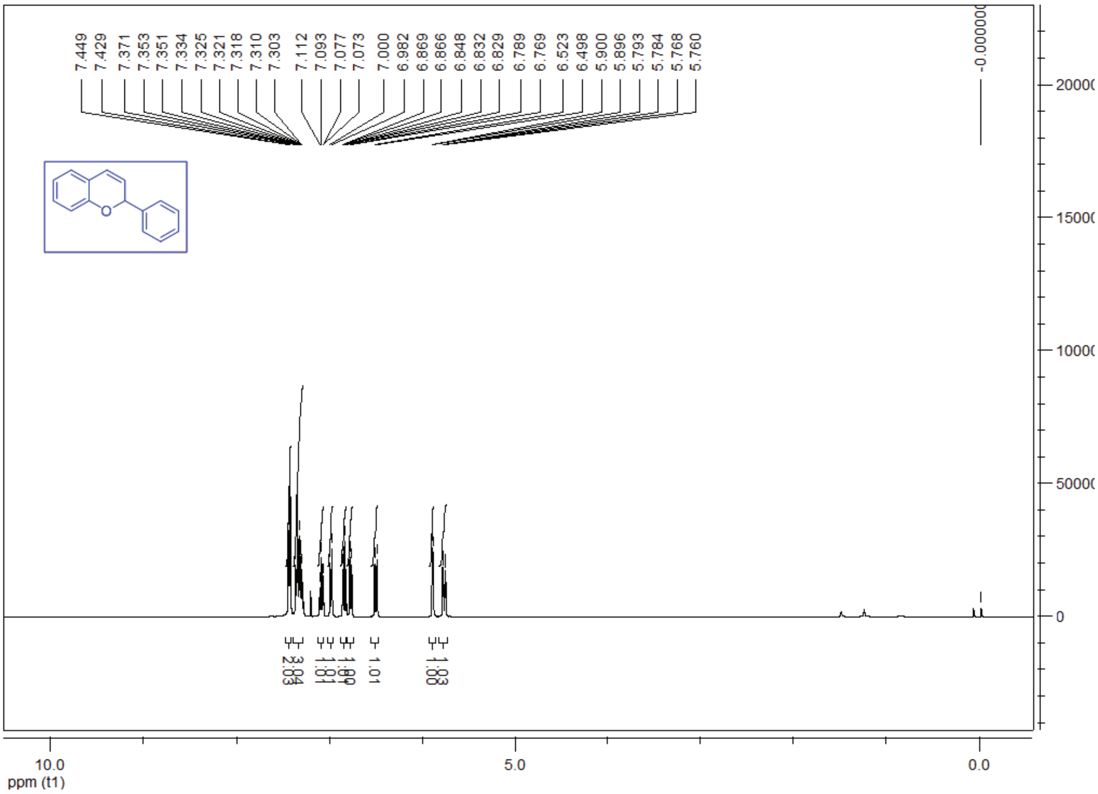
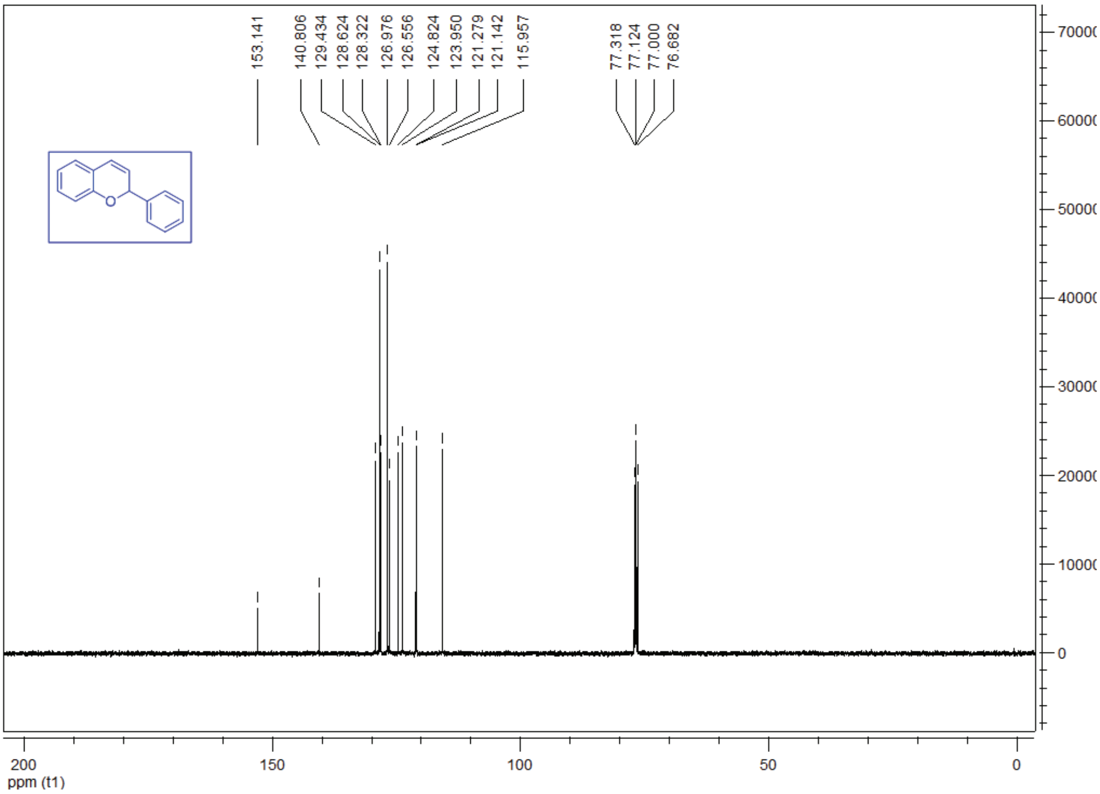
7. ^{1}H NMR and ^{13}C NMR spectra

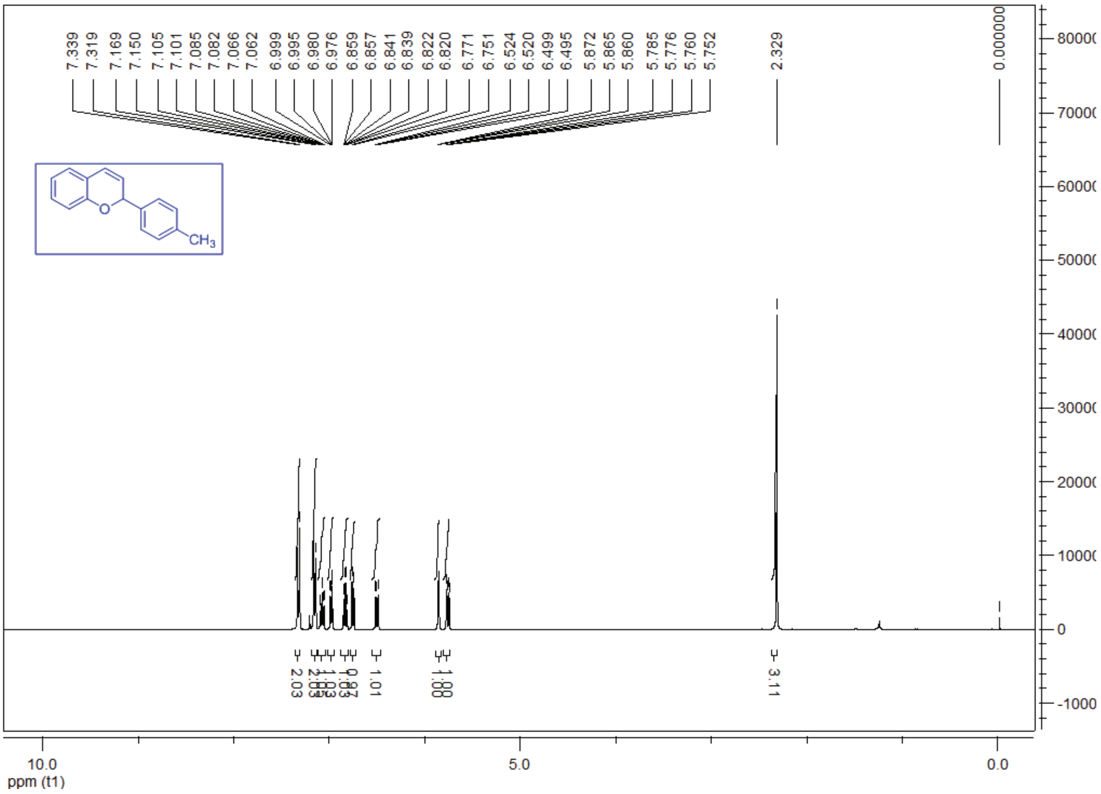
^{1}H NMR, 2-phenyl-2*H*-chromene **(3a)**



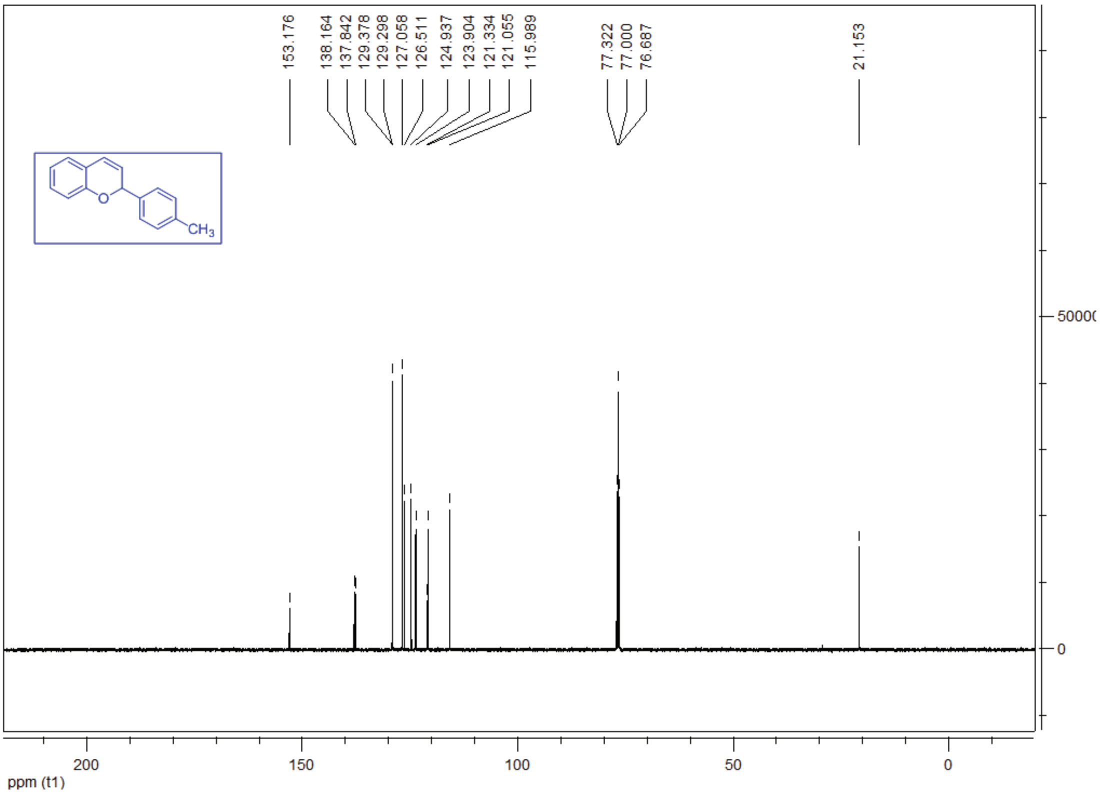
^{13}C NMR, 2-phenyl-2*H*-chromene **(3a)**



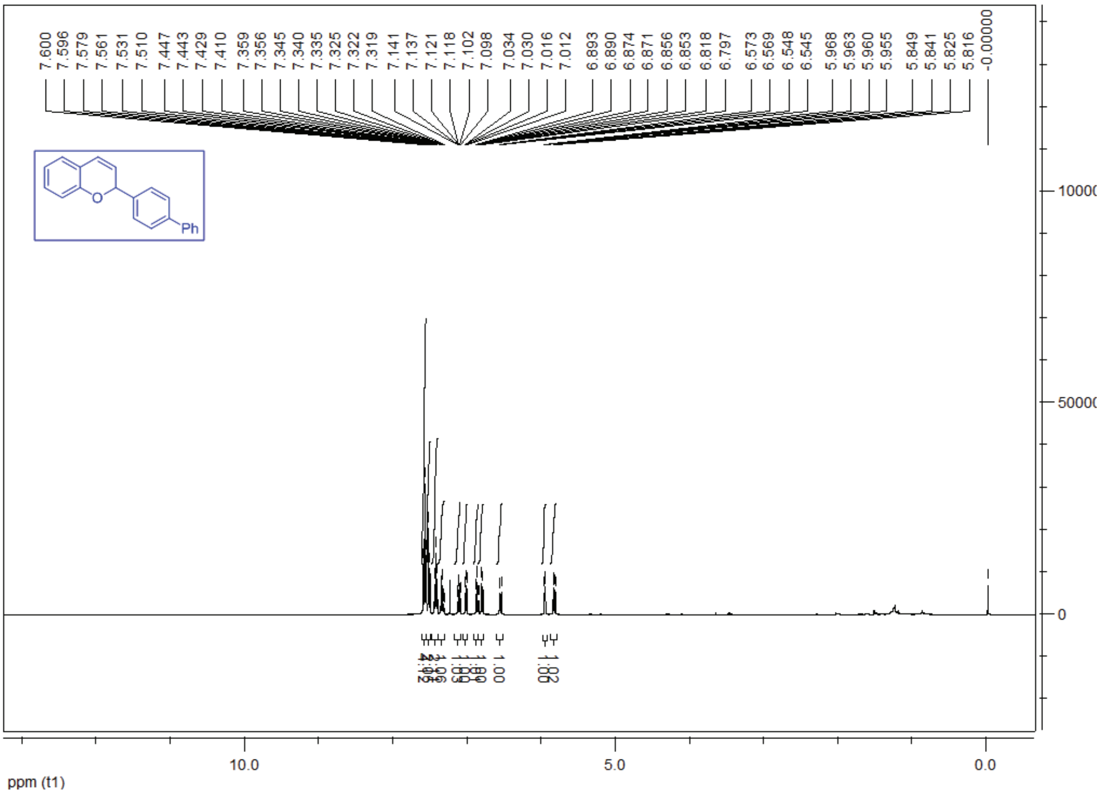
^{1}H NMR, 2-(*p*-tolyl)-2*H*-chromene **(3b)**



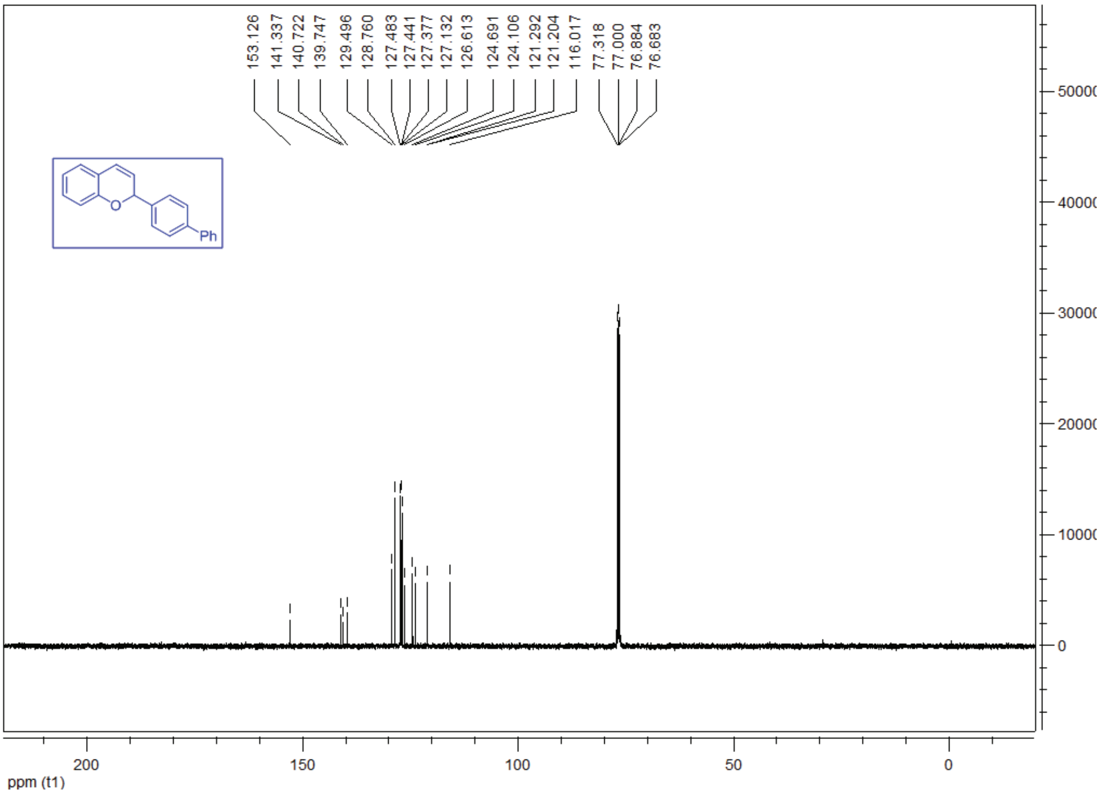
^{13}C NMR, 2-(*p*-tolyl)-2*H*-chromene **(3b)**



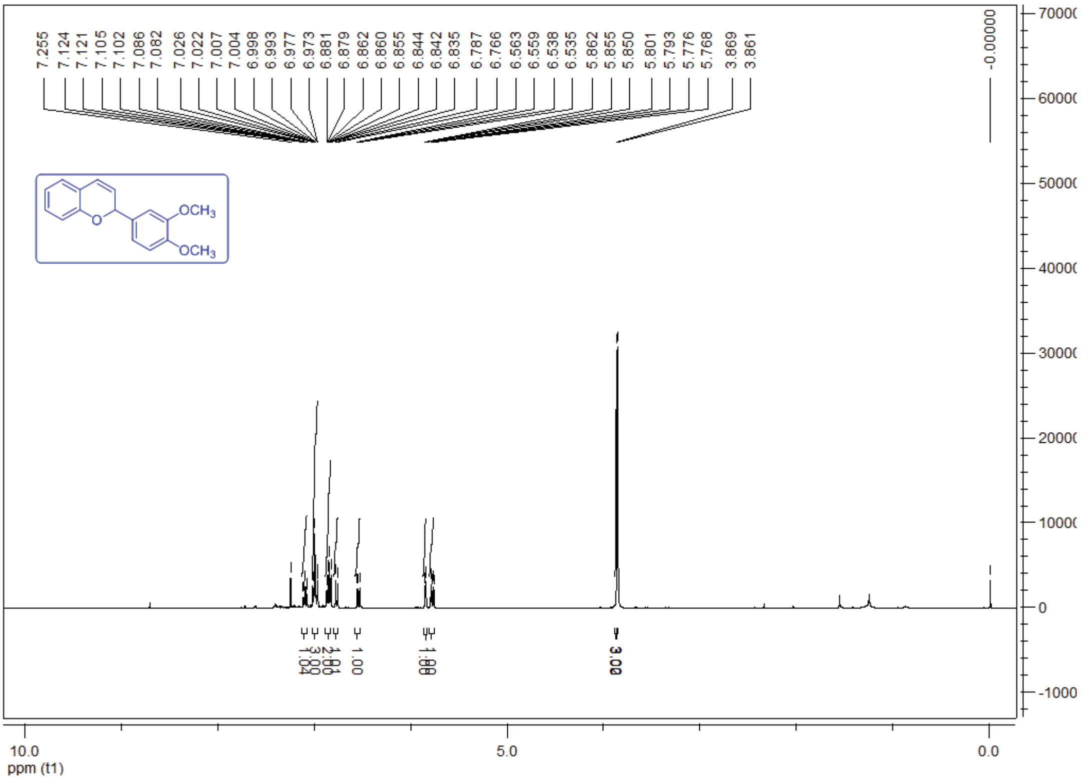
^{1}H NMR, 2-[(1,1'-biphenyl)-4-yl]-2*H*-chromene **(3c)**



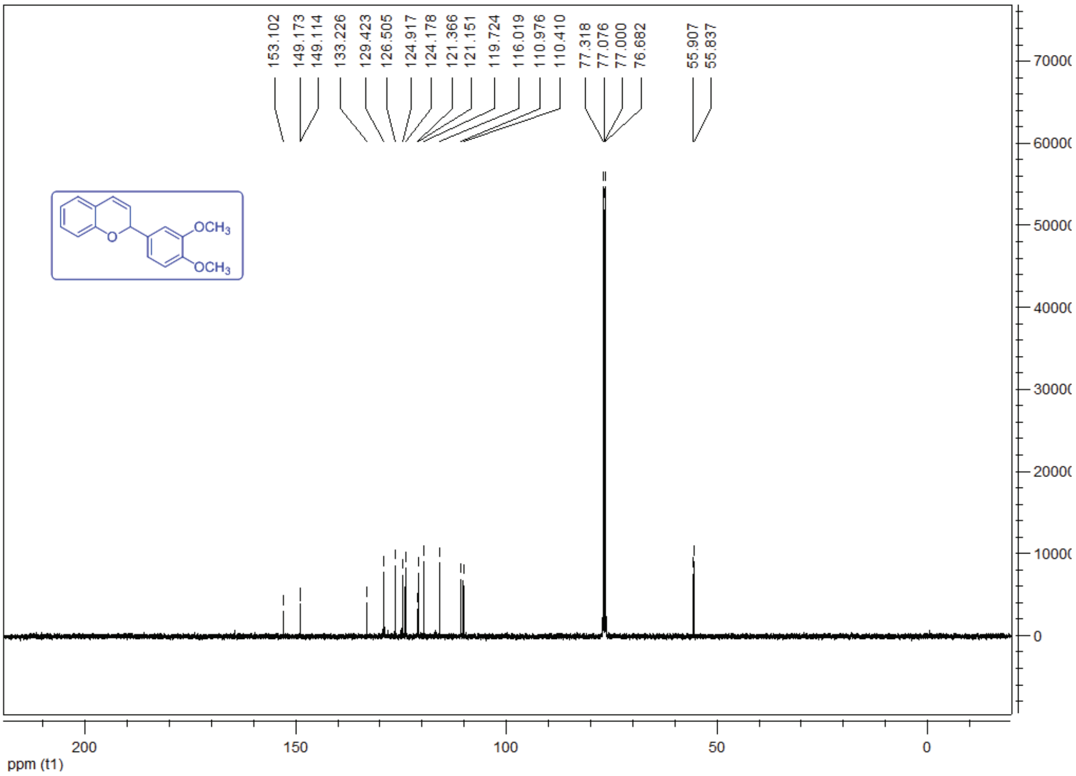
^{13}C NMR, 2-[(1,1'-biphenyl)-4-yl]-2*H*-chromene **(3c)**



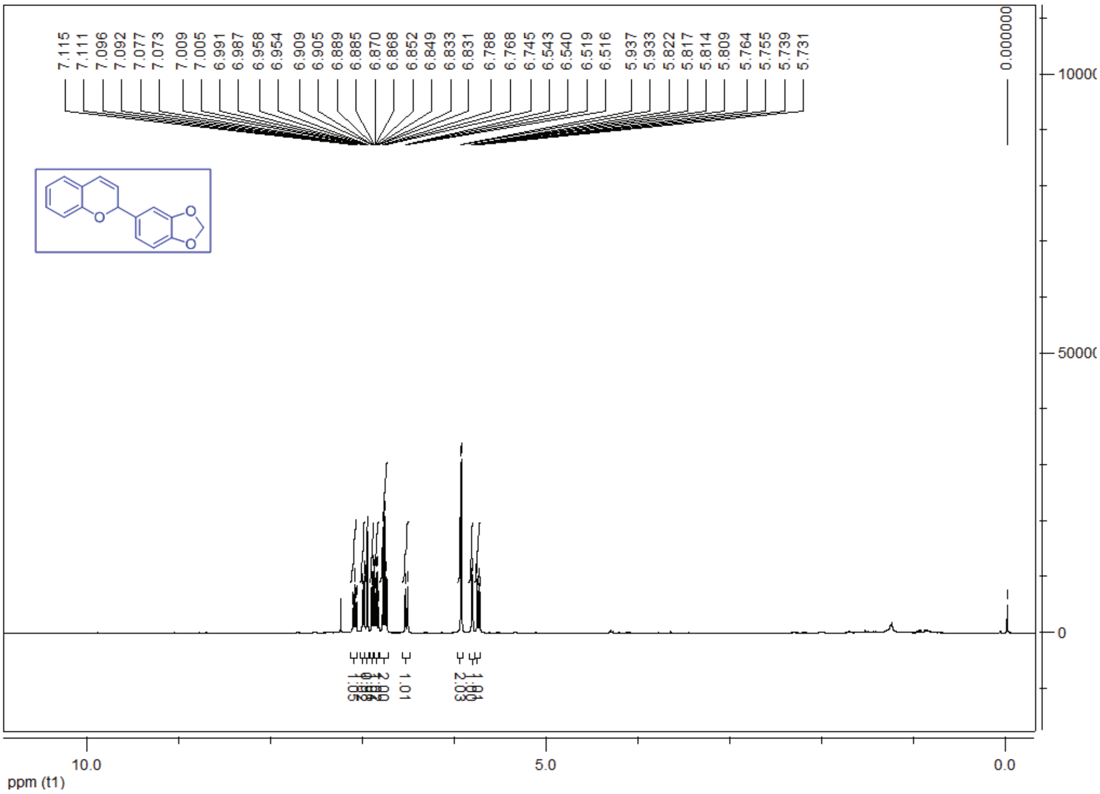
^{1}H NMR, 2-(3,4-dimethoxyphenyl)-2*H*-chromene **(3d)**



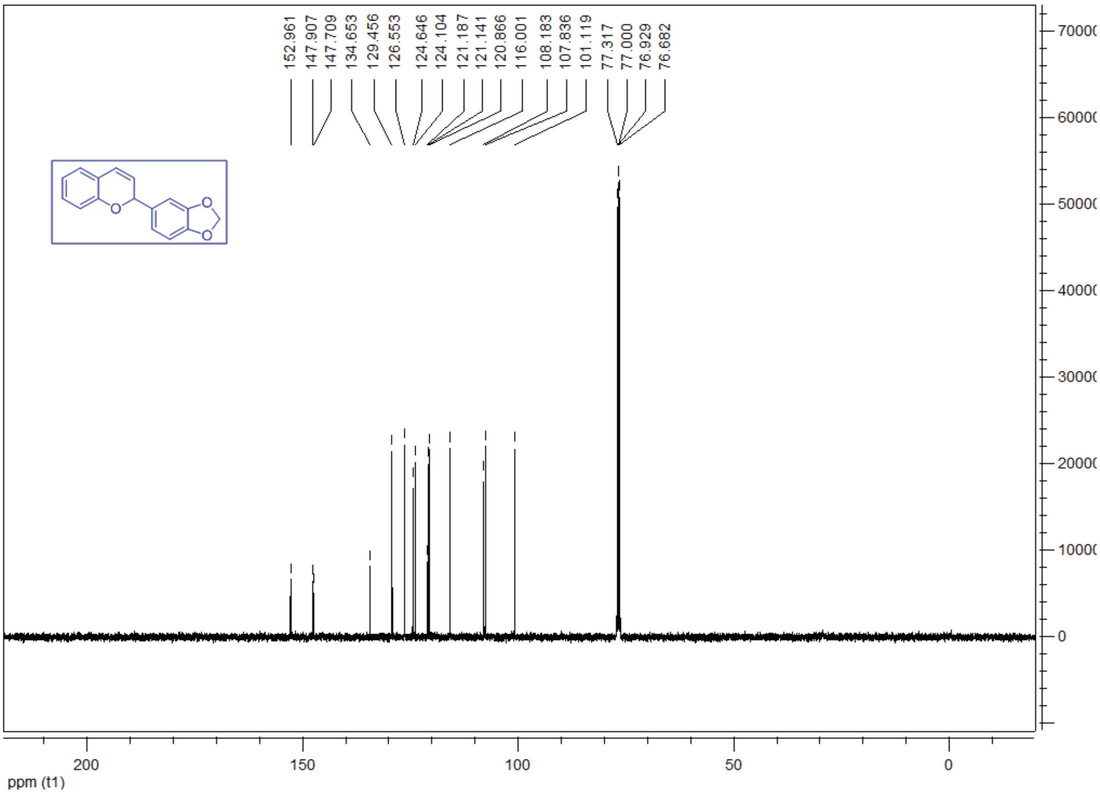
^{13}C NMR, 2-(3,4-dimethoxyphenyl)-2*H*-chromene **(3d)**



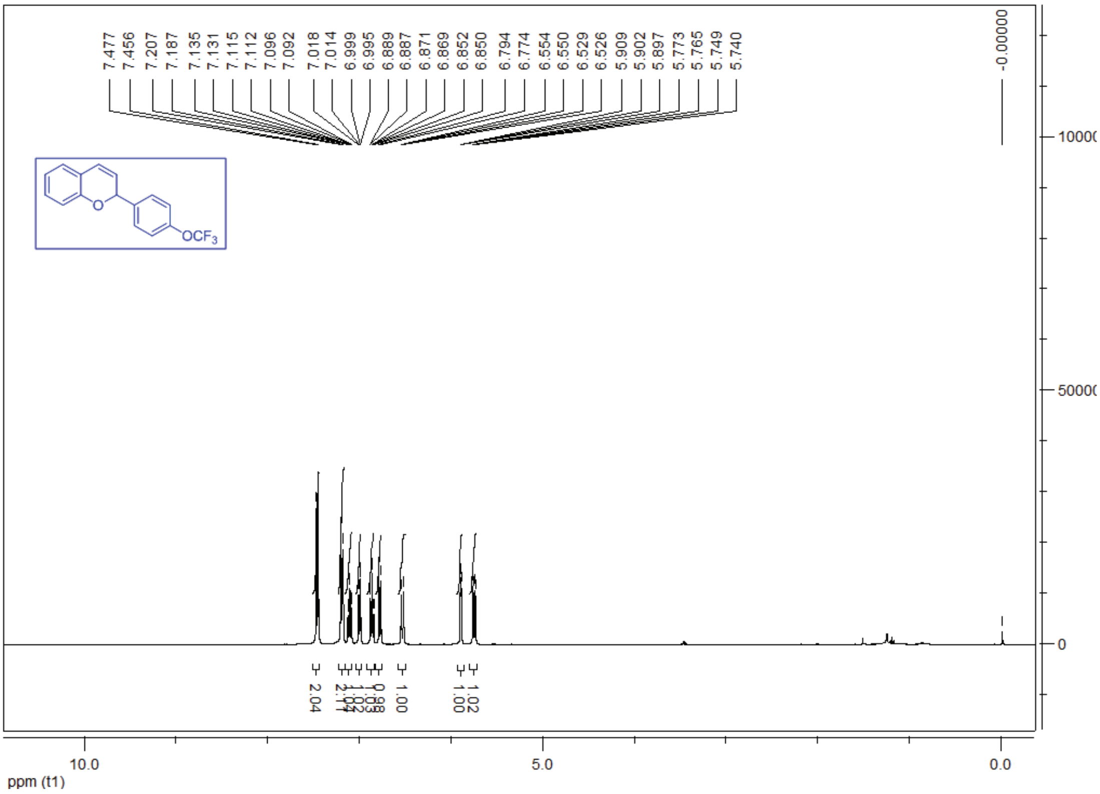
^{1}H NMR, 2-[4-(3,4-methenedioxy)phenyl]-2*H*-chromene **(3e)**



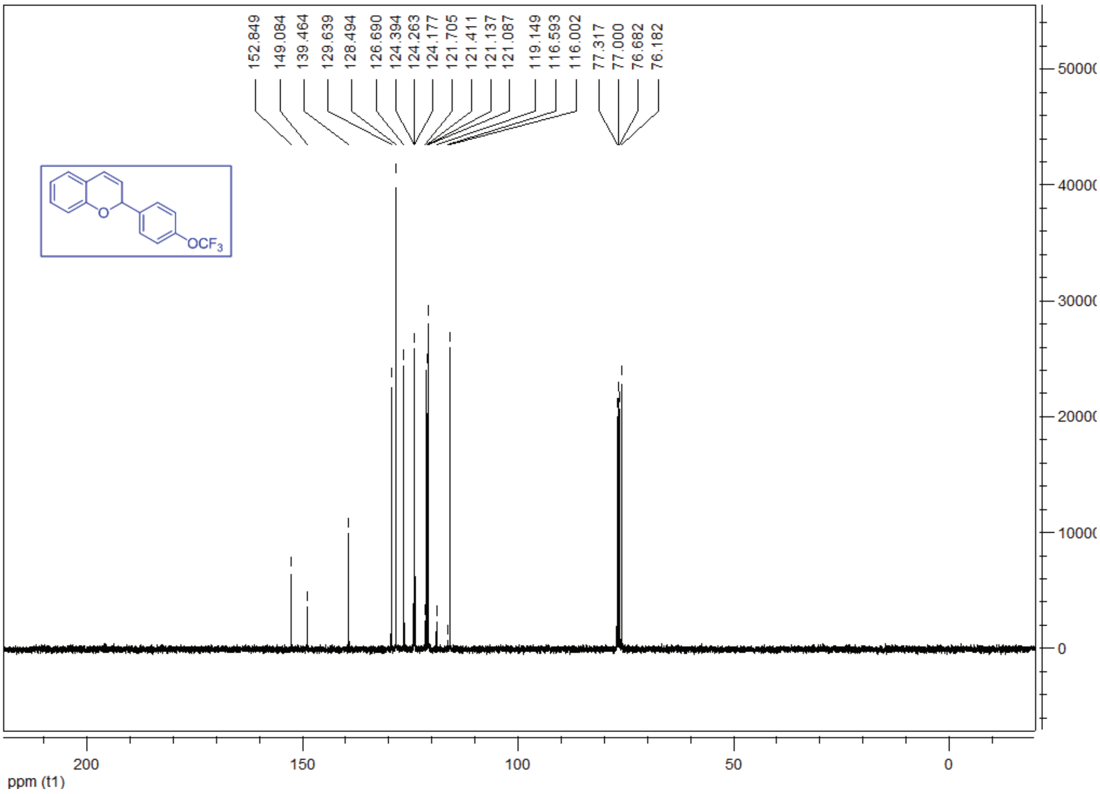
^{13}C NMR, 2-[4-(3,4-methenedioxy)phenyl]-2*H*-chromene **(3e)**



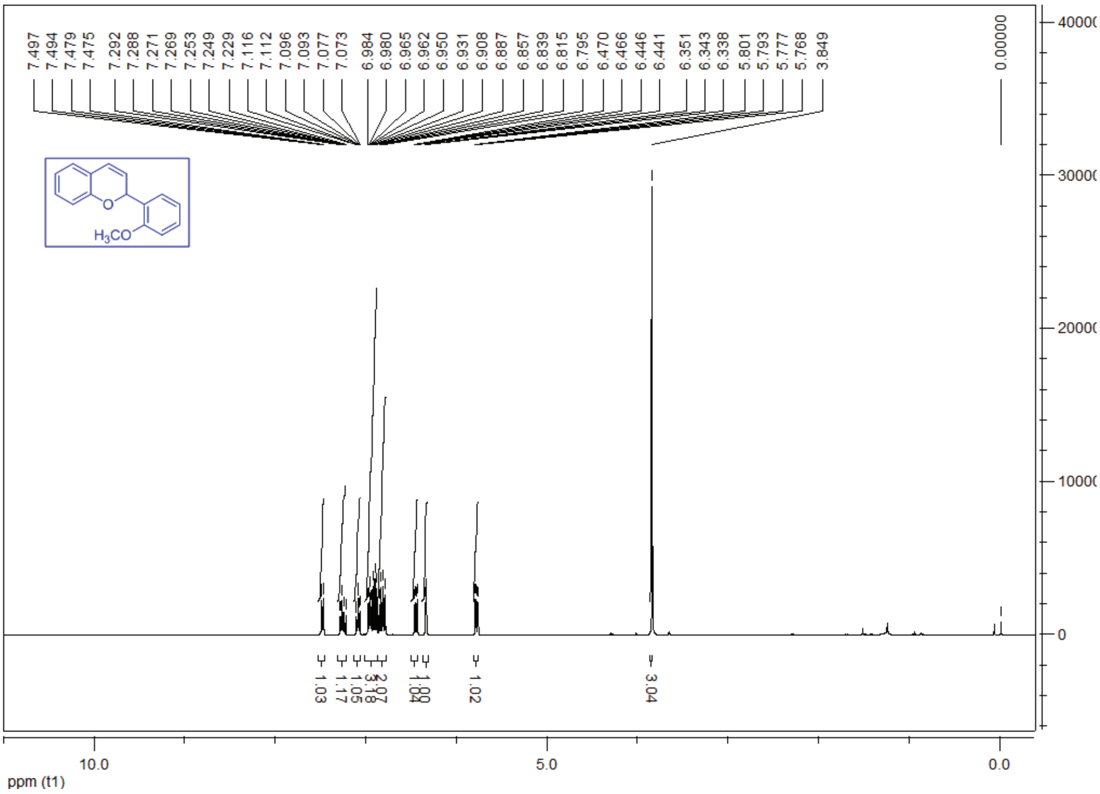
^{1}H NMR, 2-[4-(trifluoromethoxy)phenyl]-2*H*-chromene **(3f)**



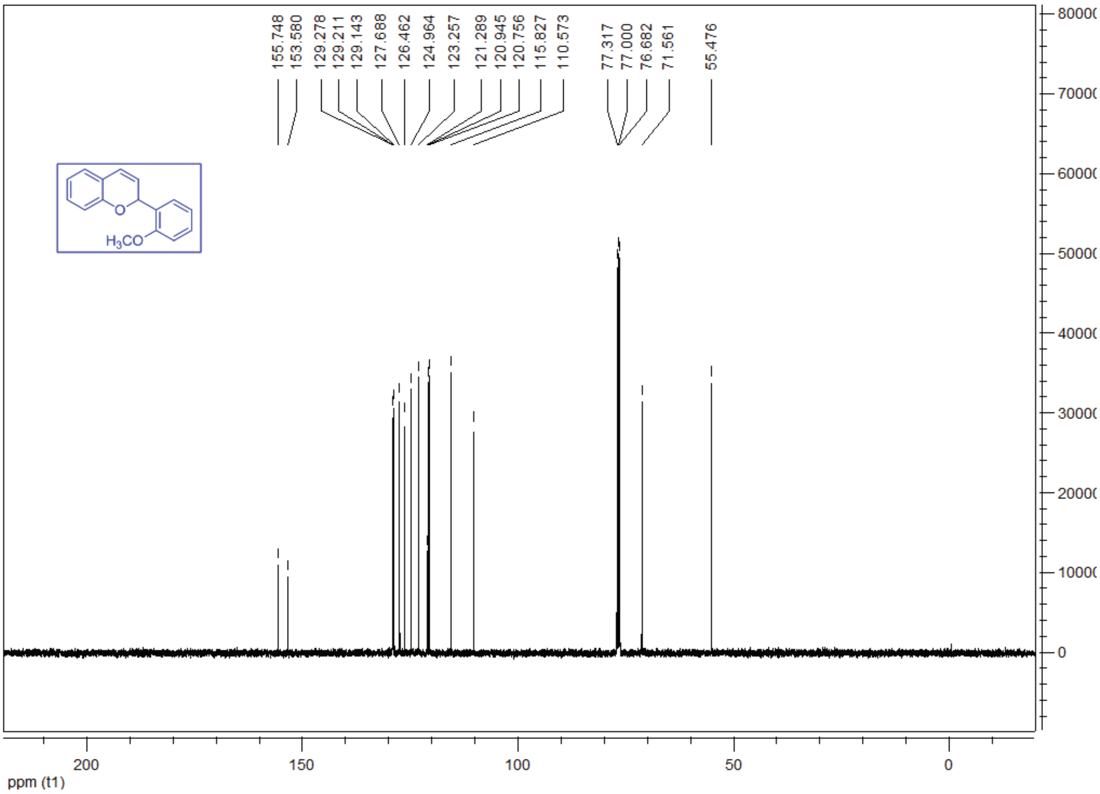
^{13}C NMR, 2-[4-(trifluoromethoxy)phenyl]-2*H*-chromene **(3f)**



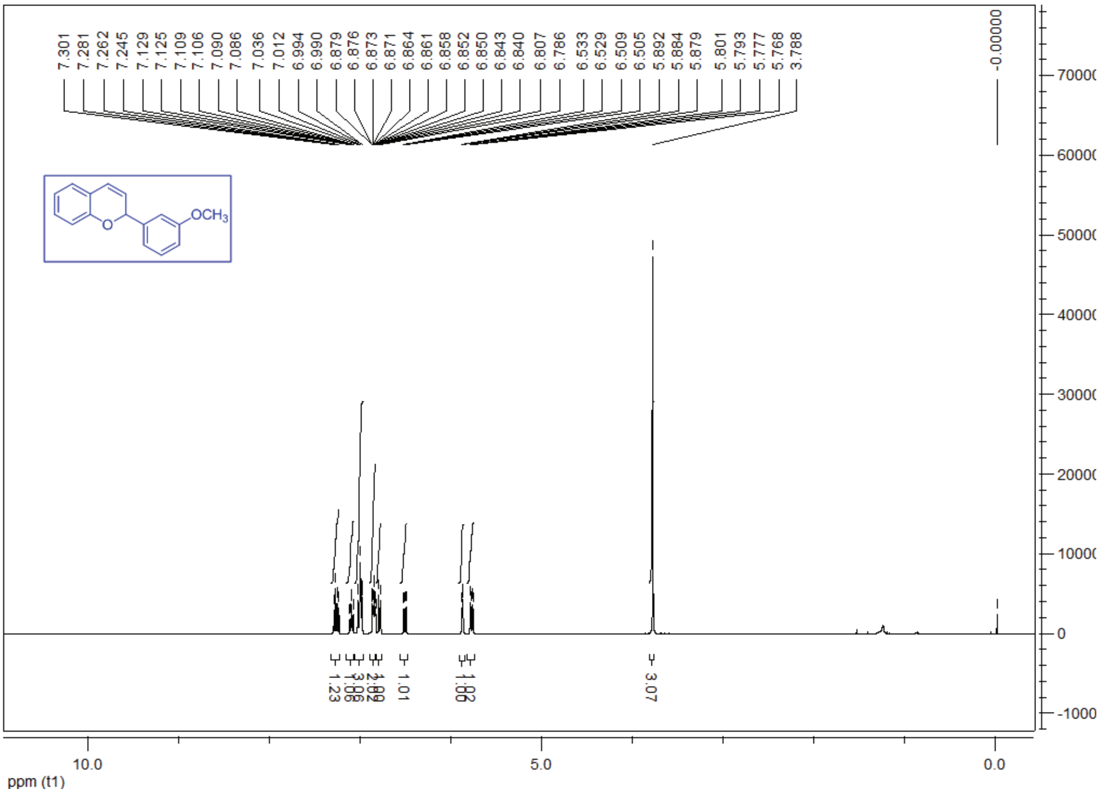
^{1}H NMR, 2-(2-methoxyphenyl)-2*H*-chromene **(3g)**



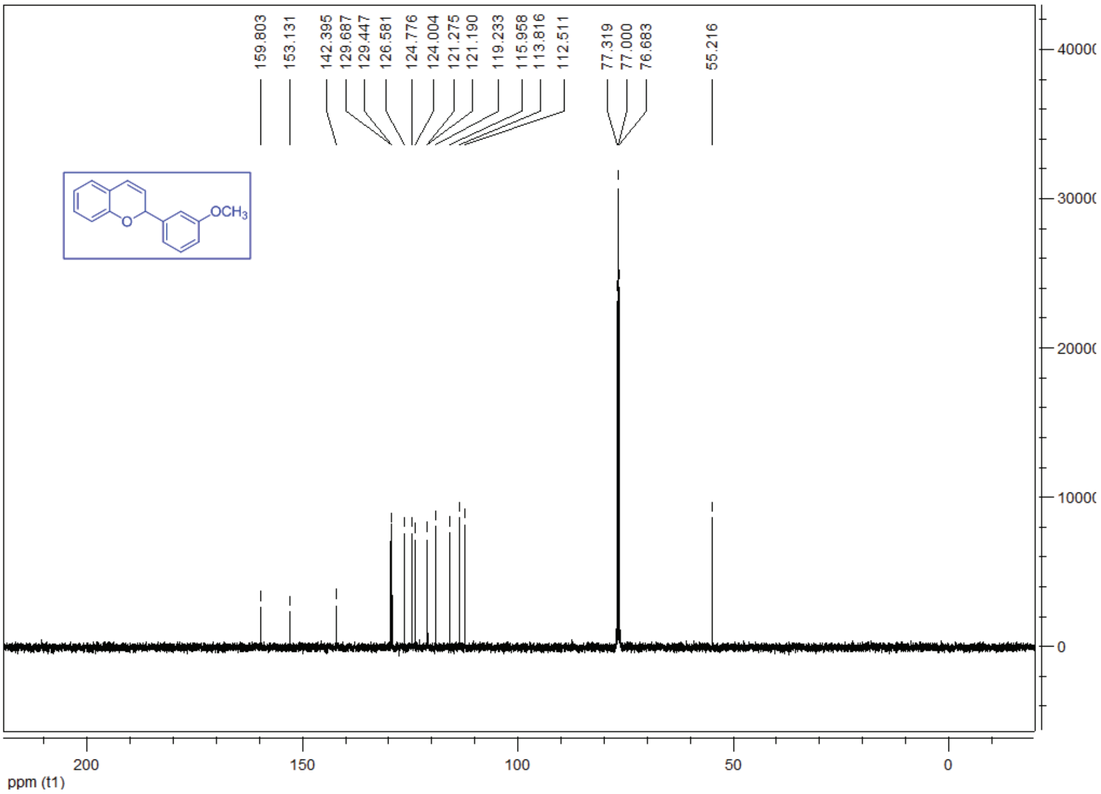
^{13}C NMR, 2-(2-methoxyphenyl)-2*H*-chromene **(3g)**



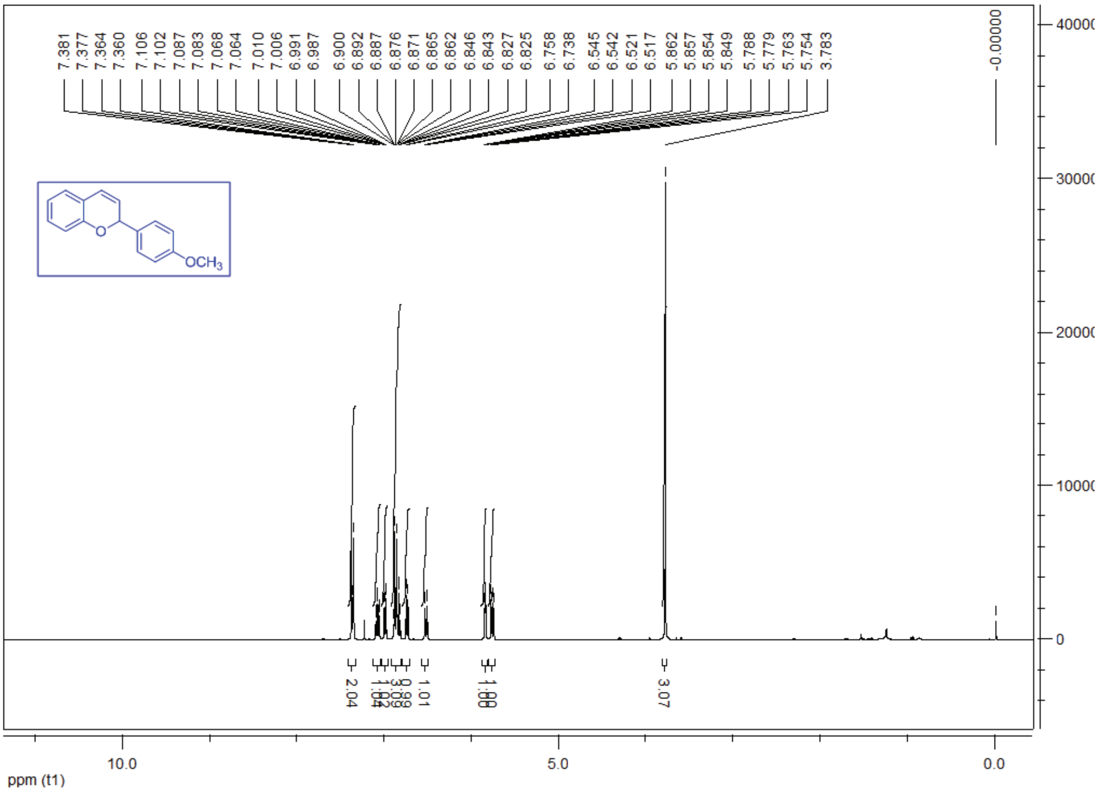
^{1}H NMR, 2-(3-methoxyphenyl)-2*H*-chromene **(3h)**



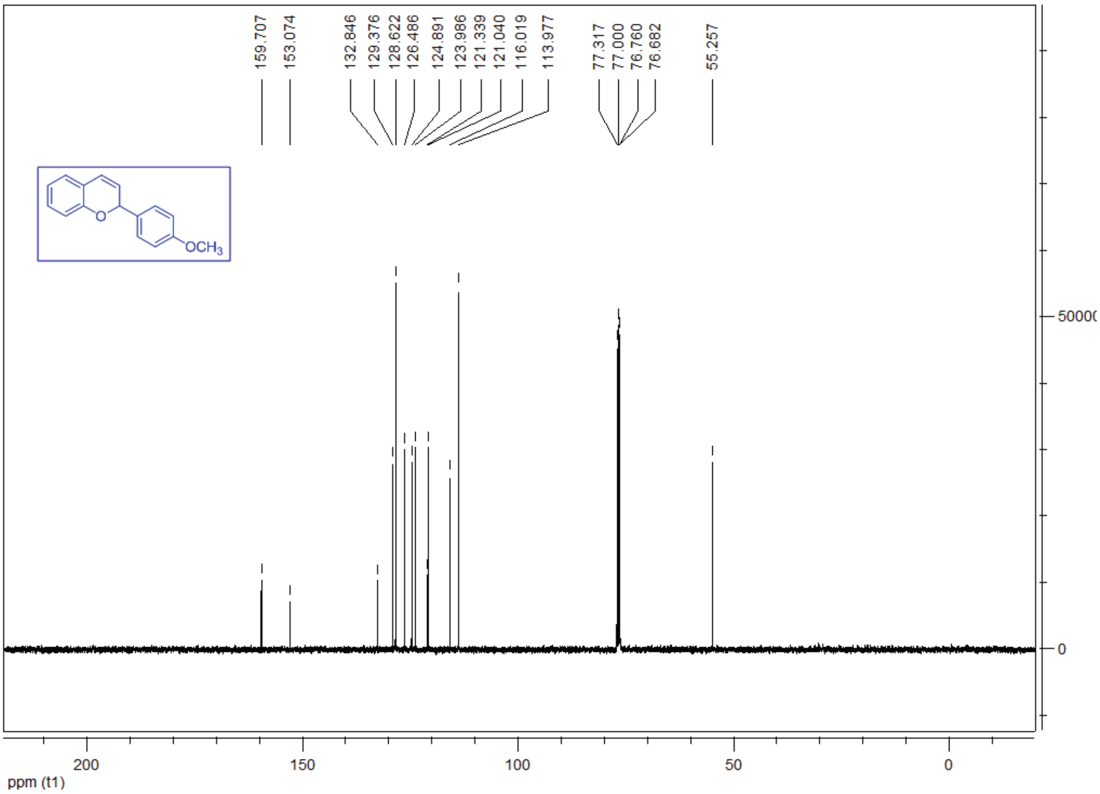
^{13}C NMR, 2-(3-methoxyphenyl)-2*H*-chromene **(3h)**



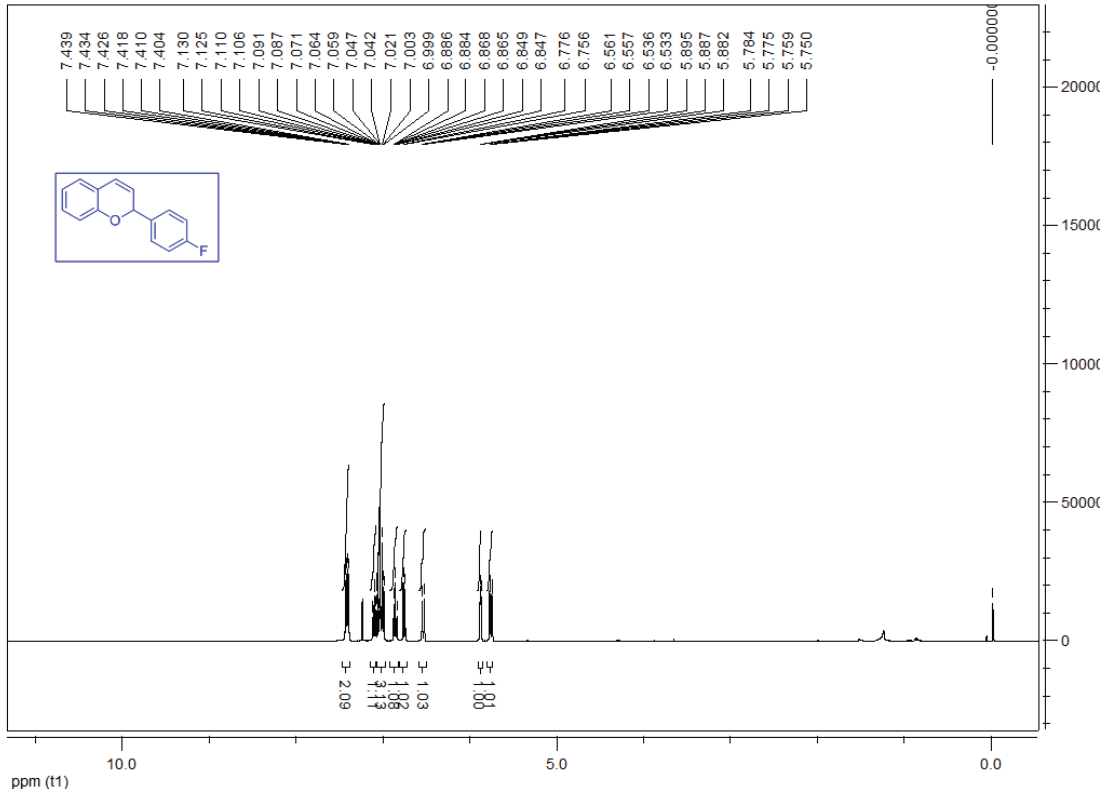
^{1}H NMR, 2-(4-methoxyphenyl)-2*H*-chromene **(3i)**



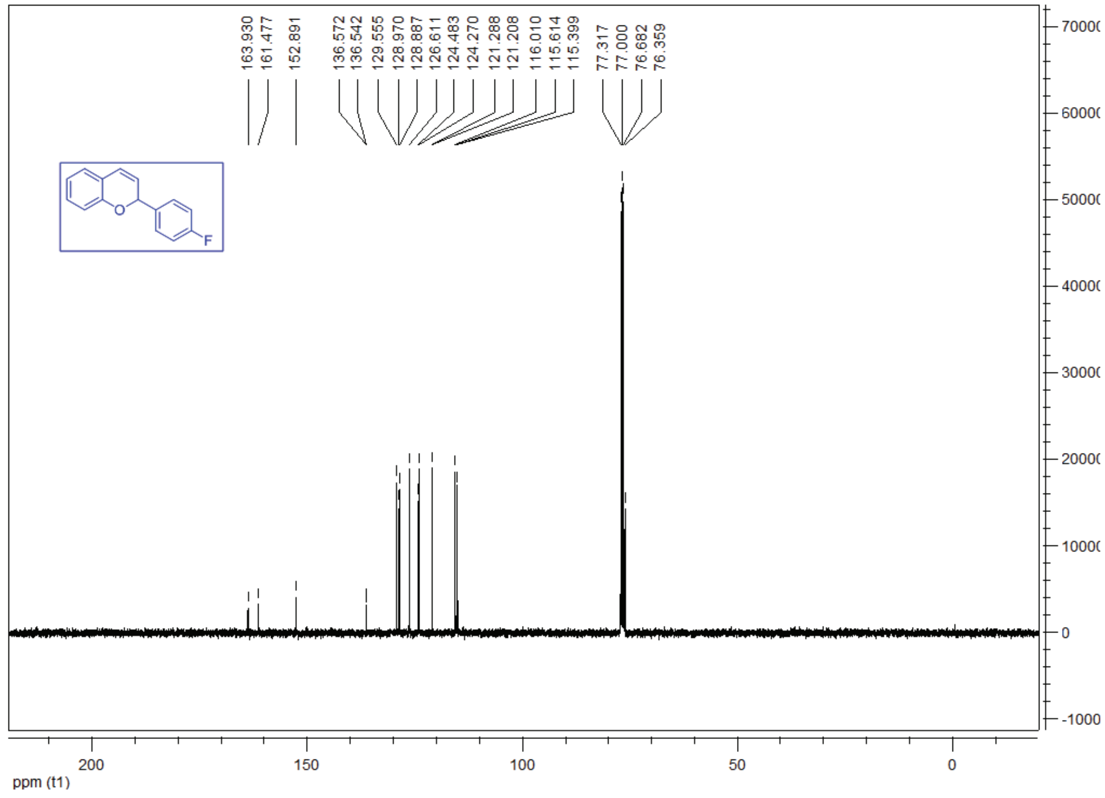
^{13}C NMR, 2-(4-methoxyphenyl)-2*H*-chromene **(3i)**



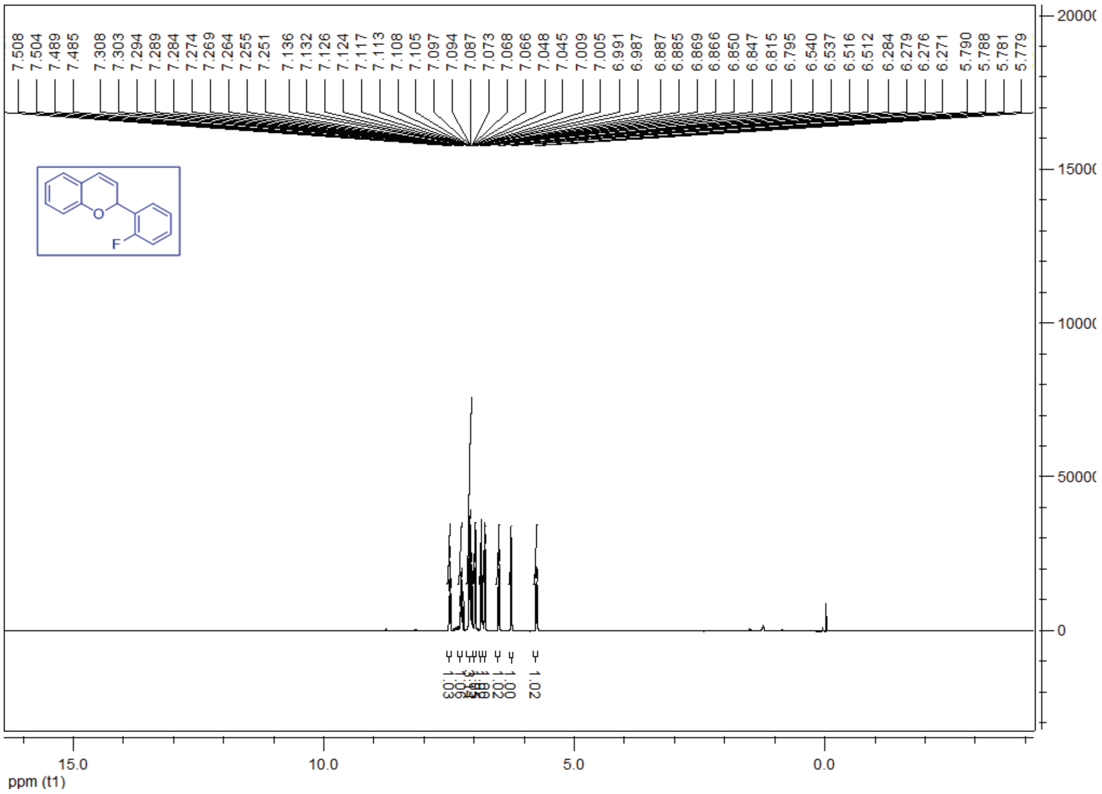
^{1}H NMR, 2-(4-fluorophenyl)-2*H*-chromene **(3j)**



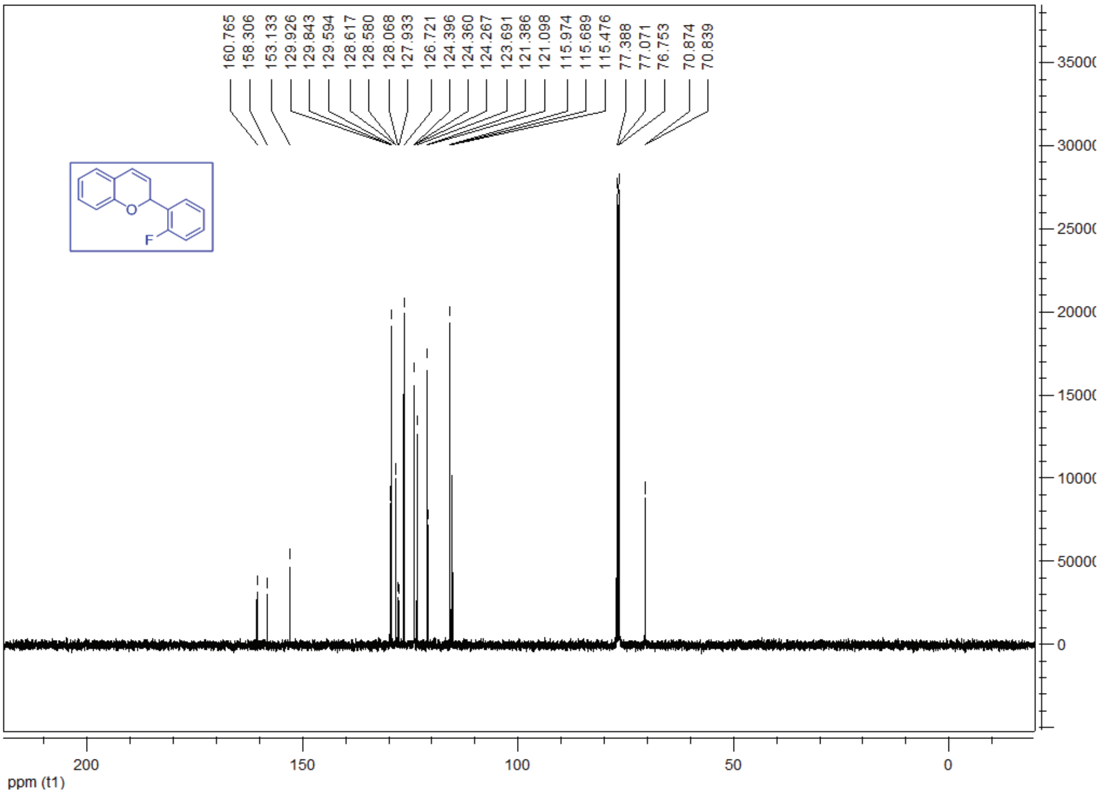
^{13}C NMR, 2-(4-fluorophenyl)-2*H*-chromene **(3j)**



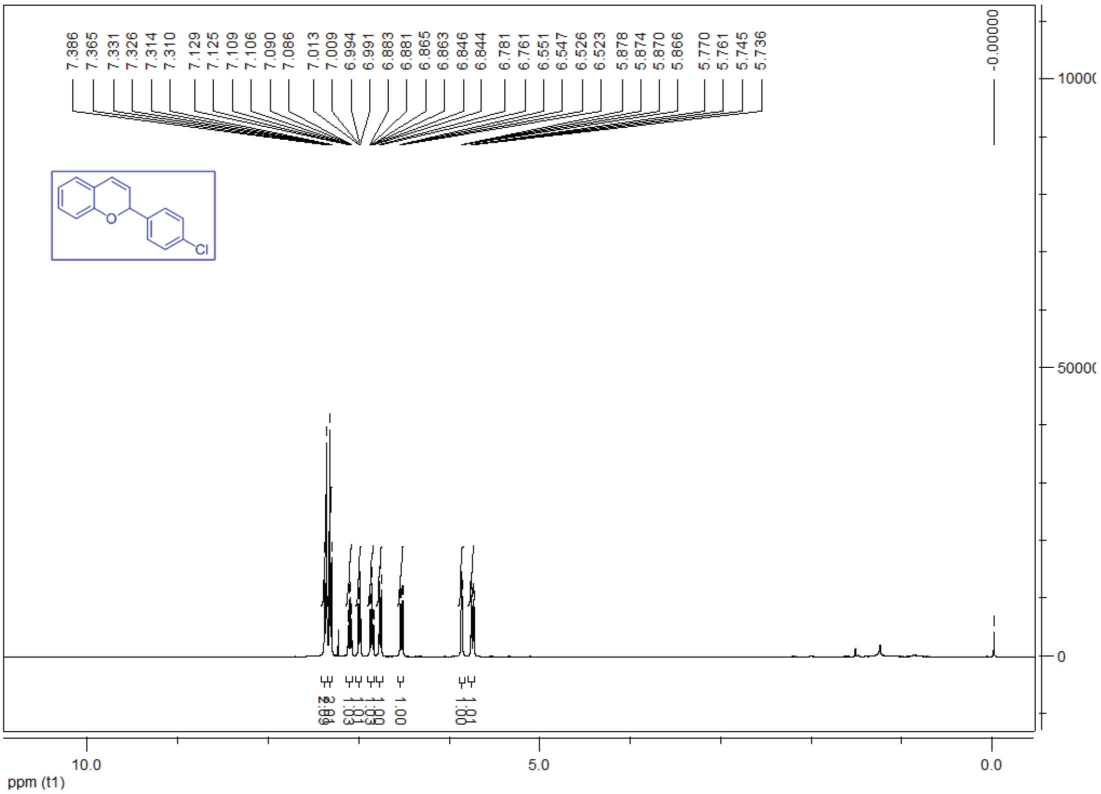
^{1}H NMR, 2-(2-fluorophenyl)-2*H*-chromene **(3k)**



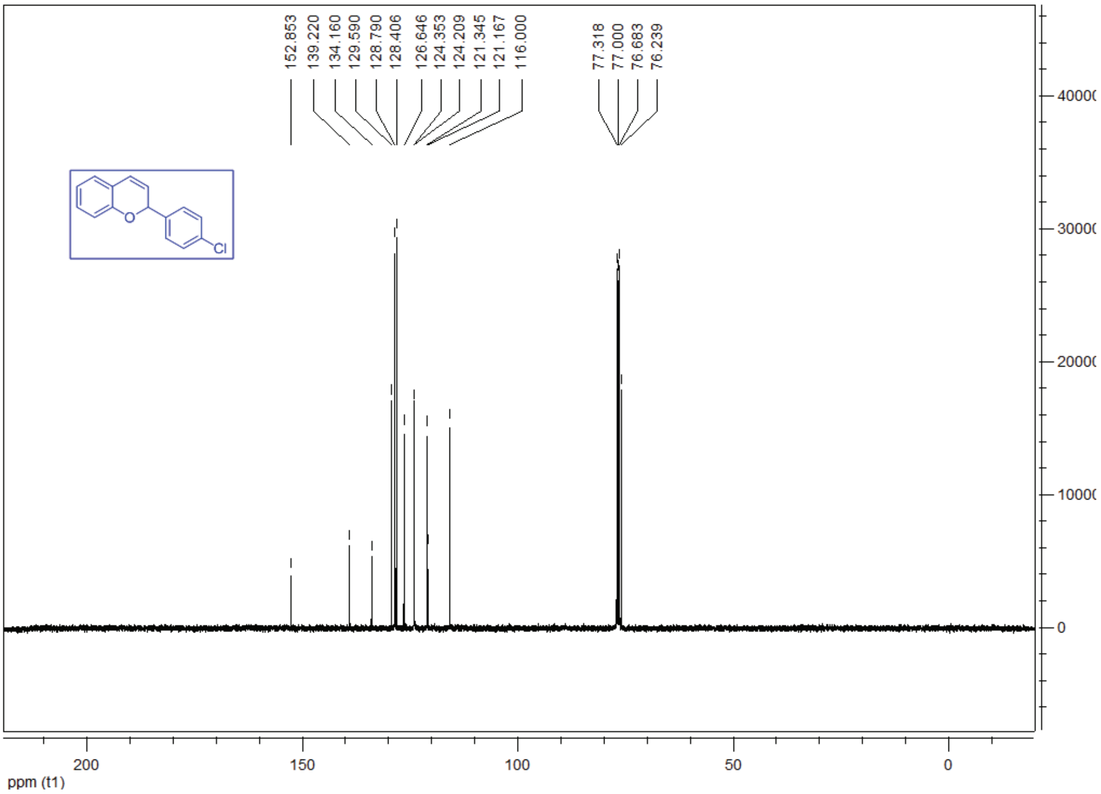
^{13}C NMR, 2-(2-fluorophenyl)-2*H*-chromene **(3k)**



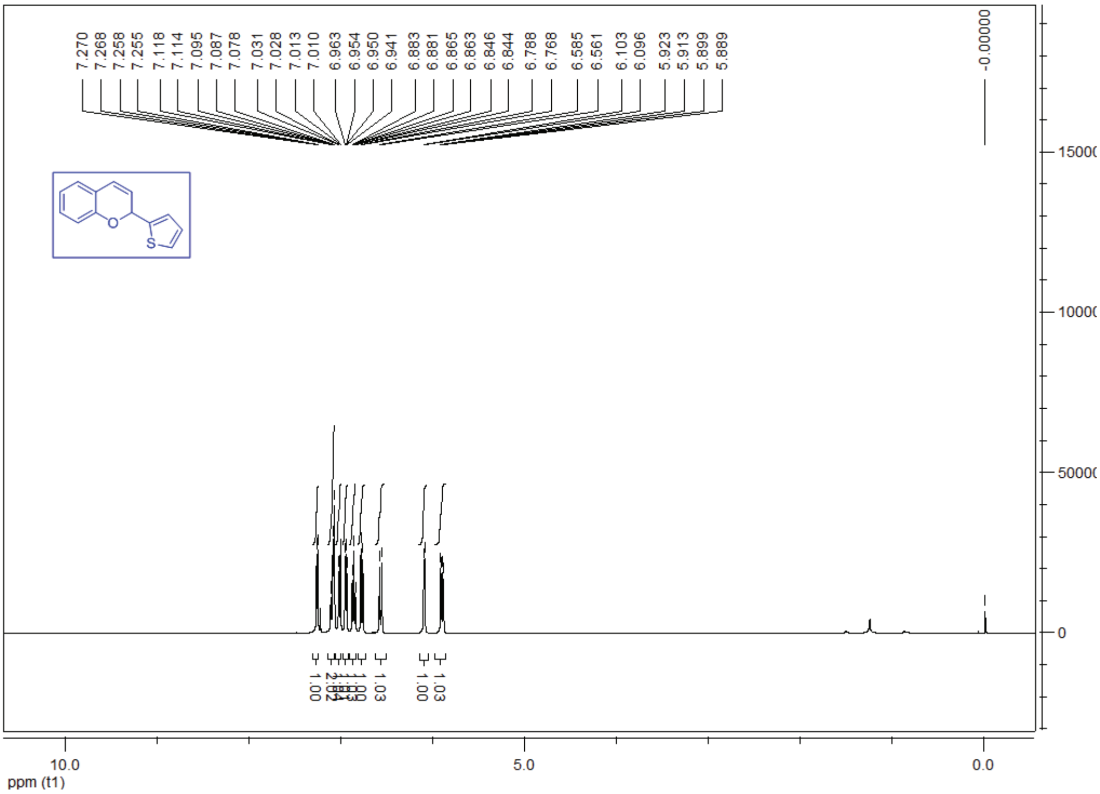
^{1}H NMR, 2-(4-chlorophenyl)-2*H*-chromene **(3l)**



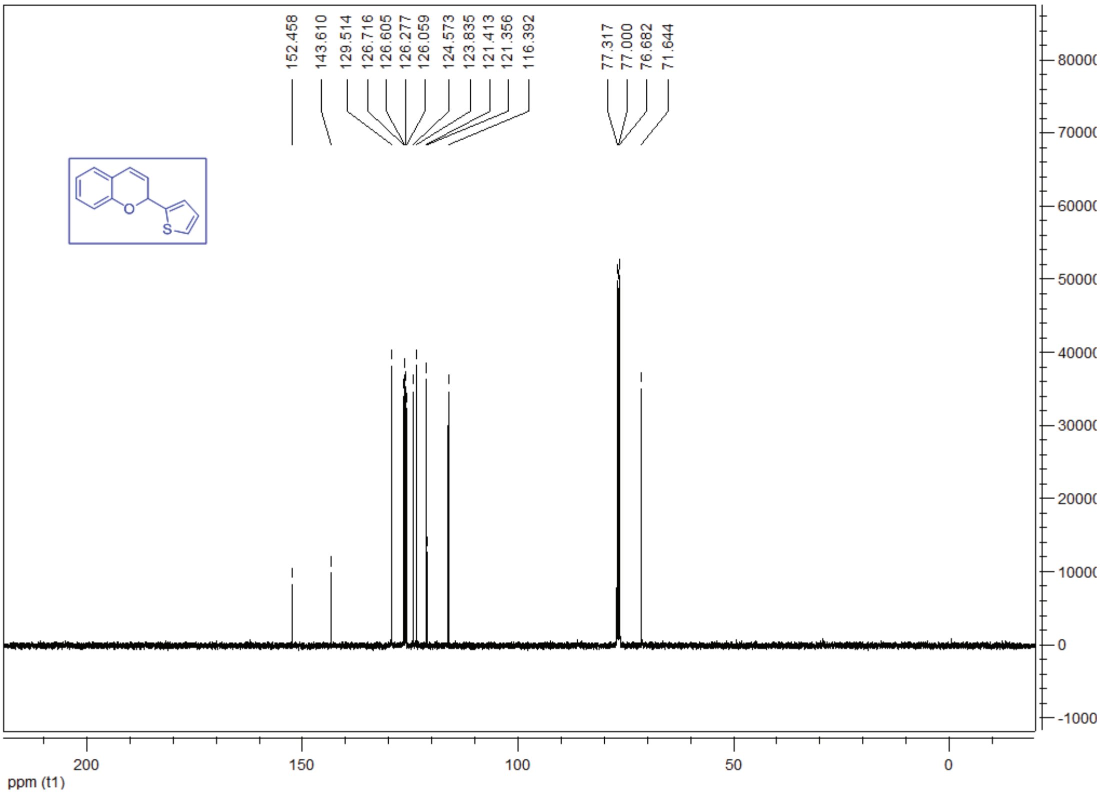
^{13}C NMR, 2-(4-chlorophenyl)-2*H*-chromene **(3l)**



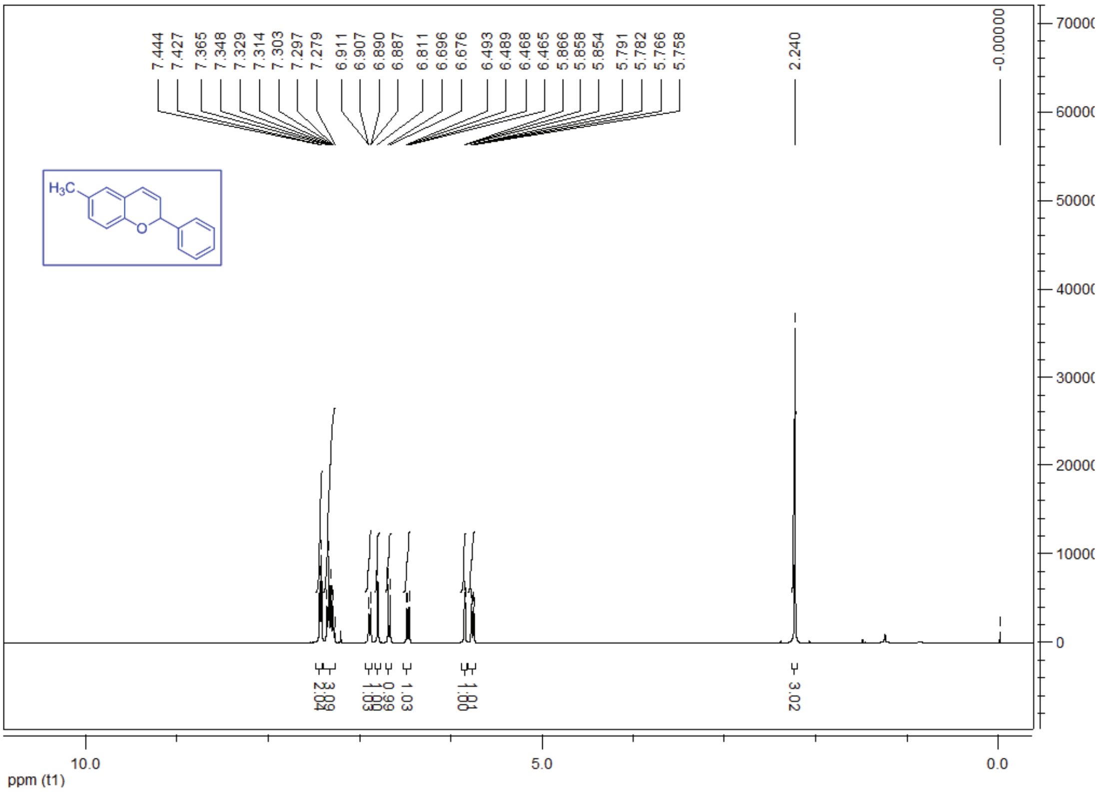
^{1}H NMR, 2-(thiophen-2-yl)-2*H*-chromene **(3m)**



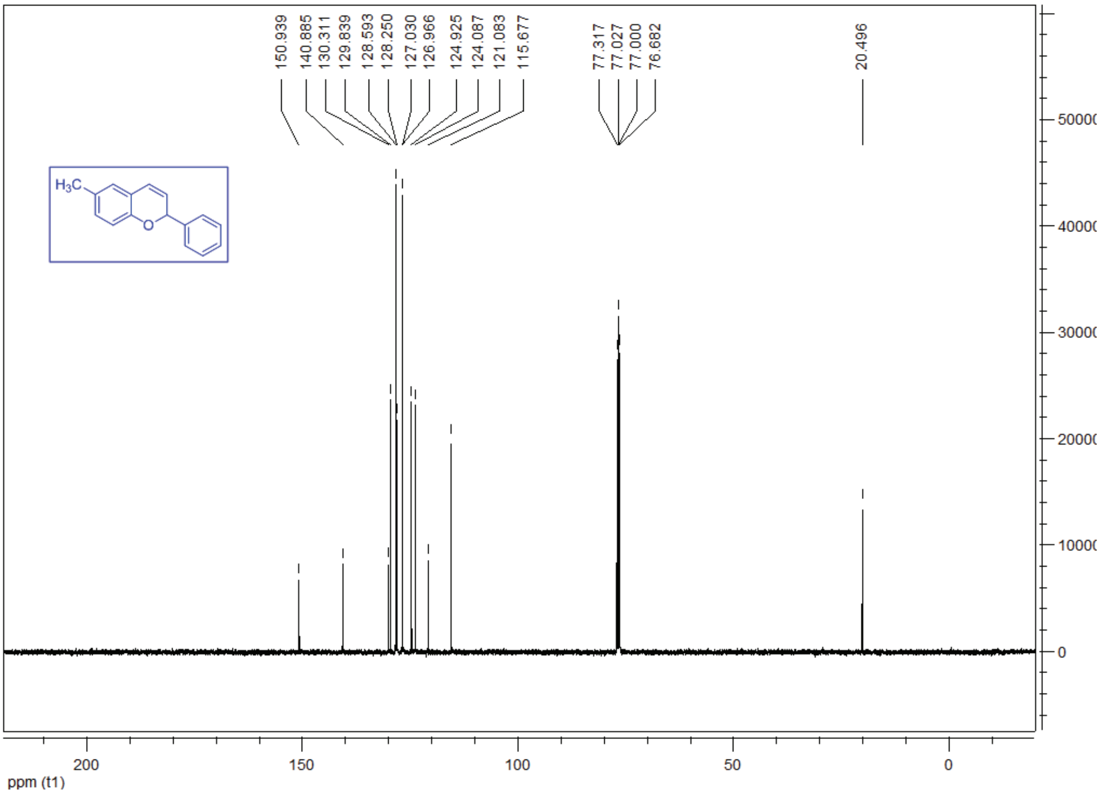
^{13}C NMR, 2-(thiophen-2-yl)-2*H*-chromene **(3m)**



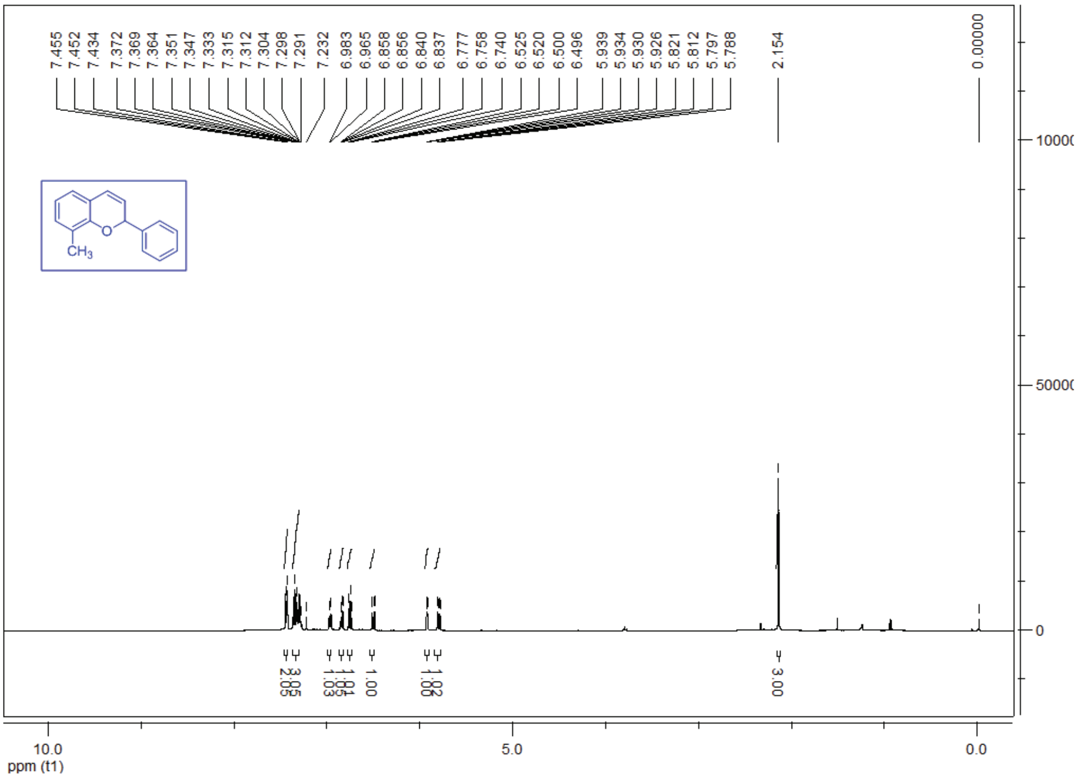
^{1}H NMR, 6-methyl-2-phenyl-2*H*-chromene **(3n)**



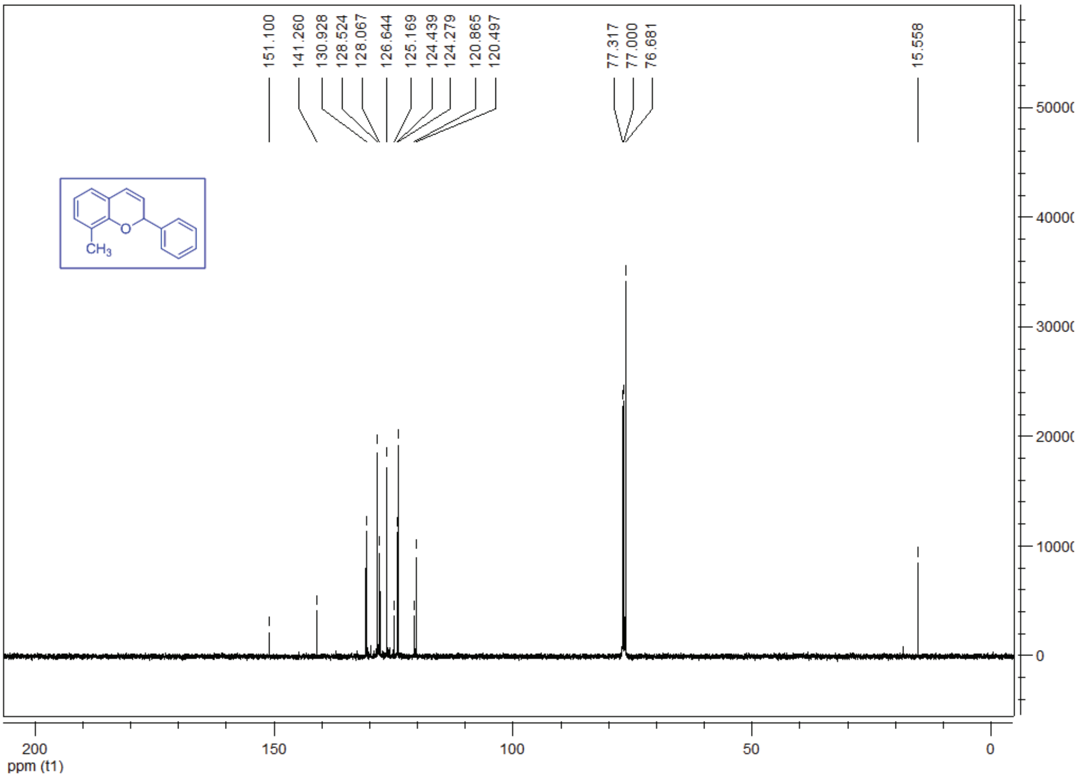
^{13}C NMR, 6-methyl-2-phenyl-2*H*-chromene **(3n)**



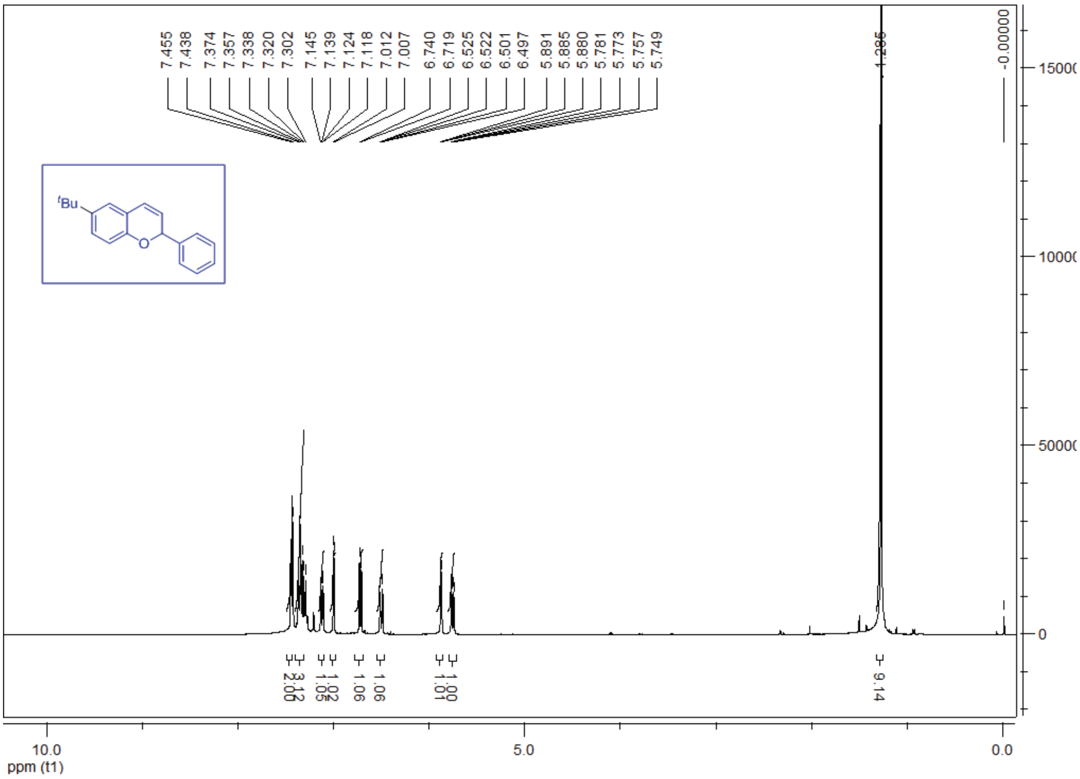
^{1}H NMR, 8-methyl-2-phenyl-2*H*-chromene **(3o)**



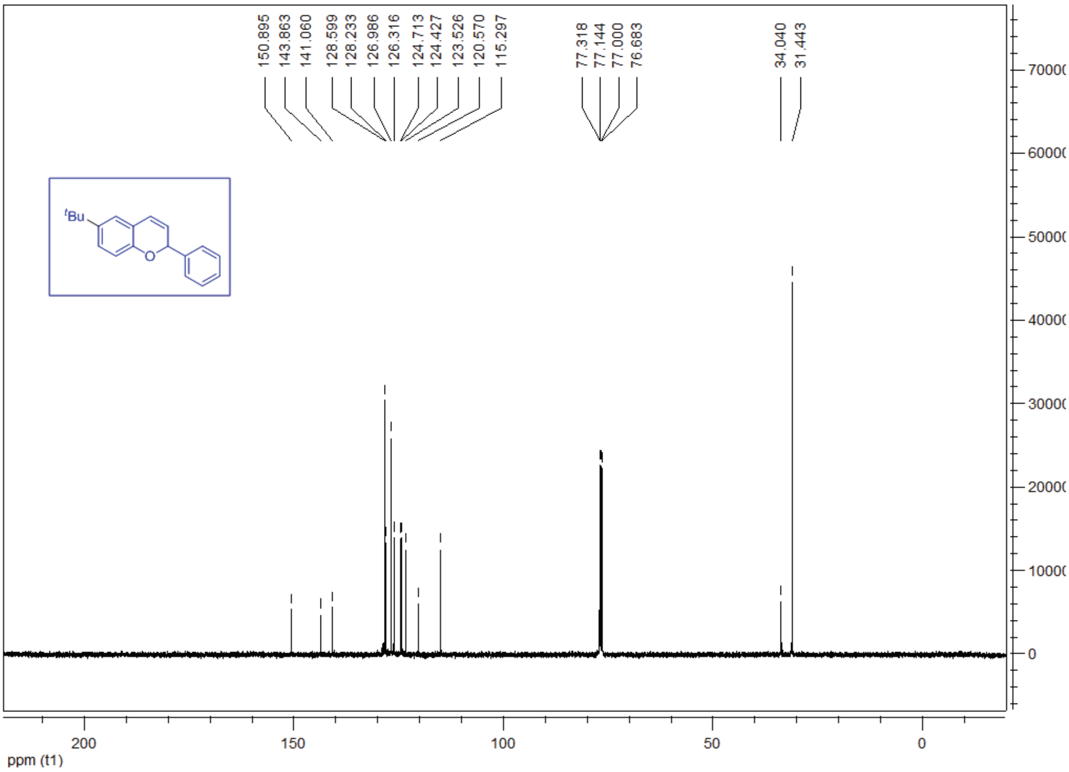
^{13}C NMR, 8-methyl-2-phenyl-2*H*-chromene **(3o)**



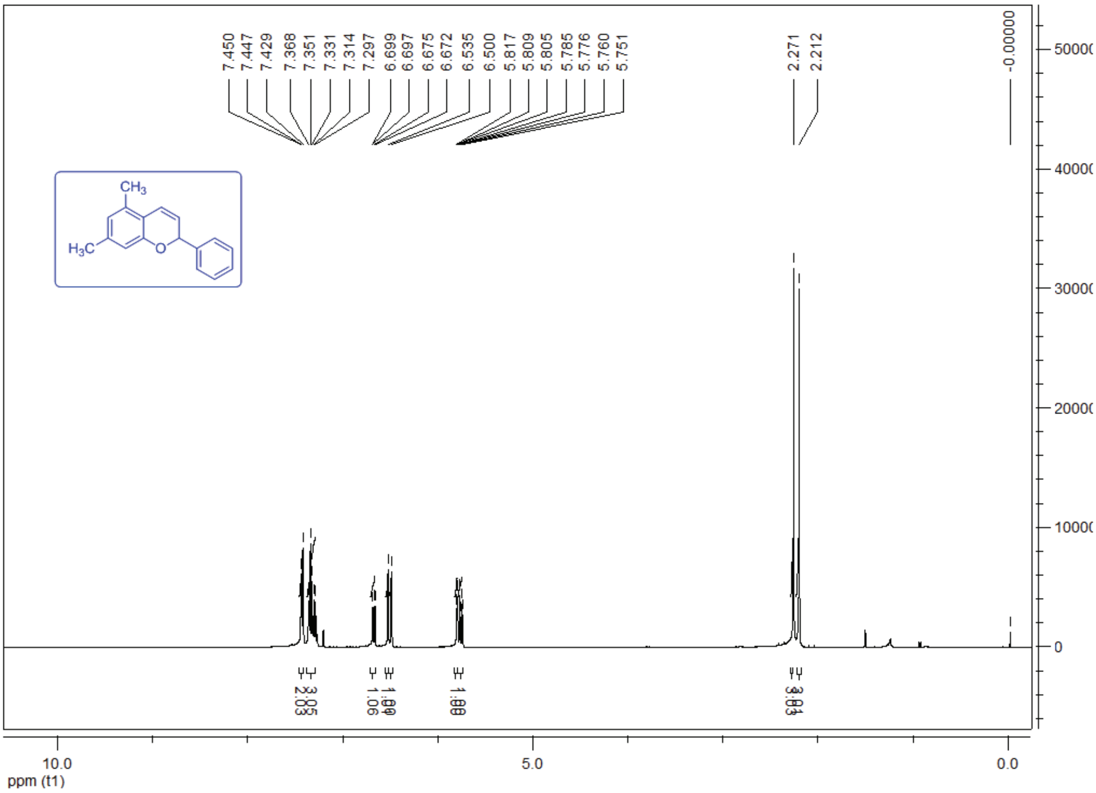
^{1}H NMR, 6-(*tert*-butyl)-2-phenyl-2*H*-chromene **(3p)**



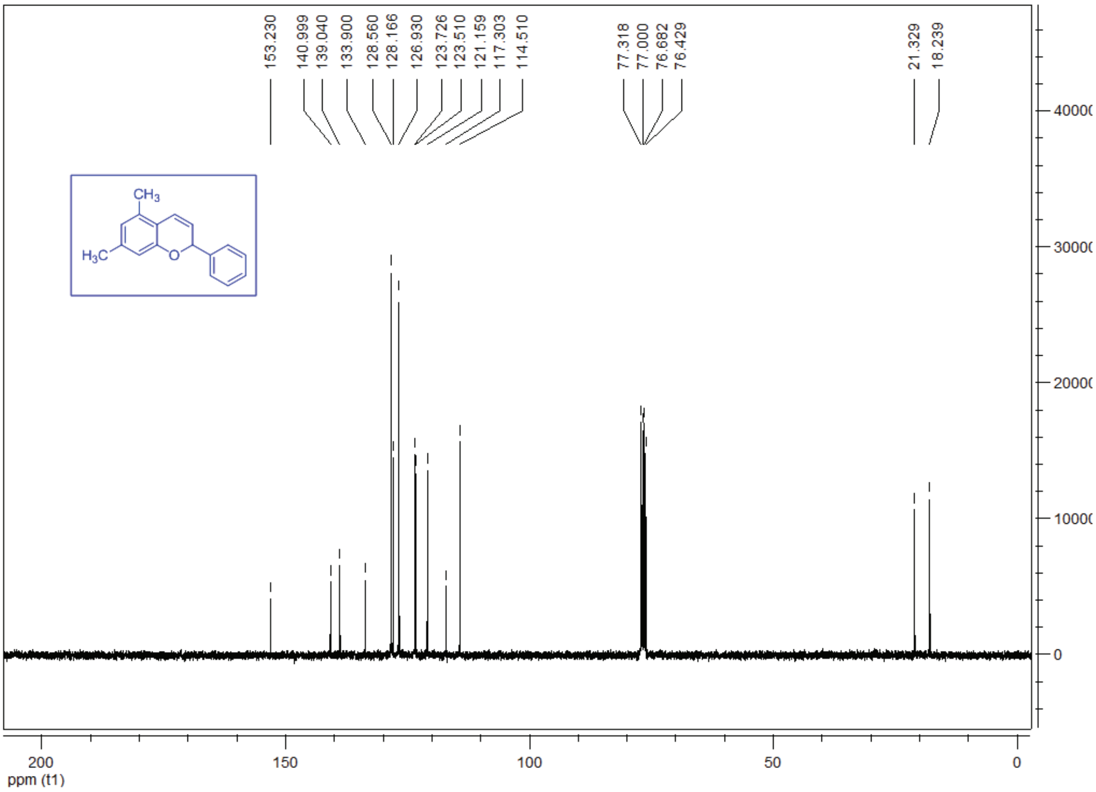
^{13}C NMR, 6-(*tert*-butyl)-2-phenyl-2*H*-chromene **(3p)**



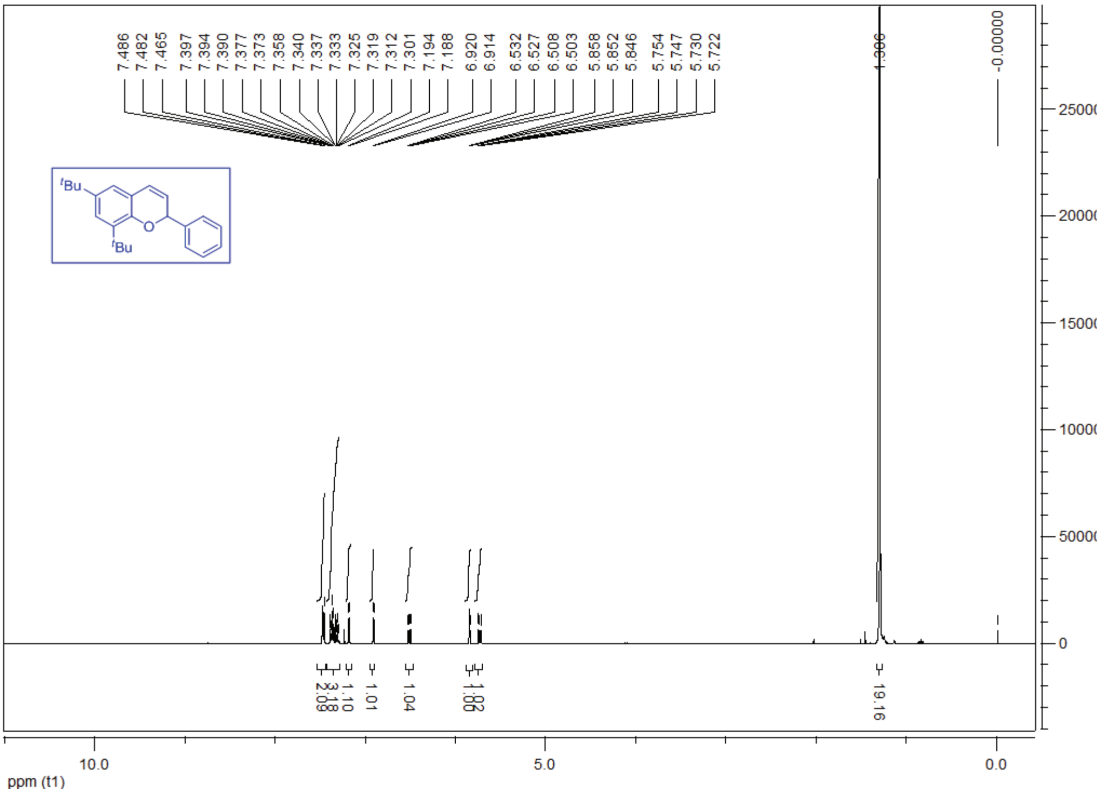
^{1}H NMR, 5,7-dimethyl-2-phenyl-2*H*-chromene **(3q)**



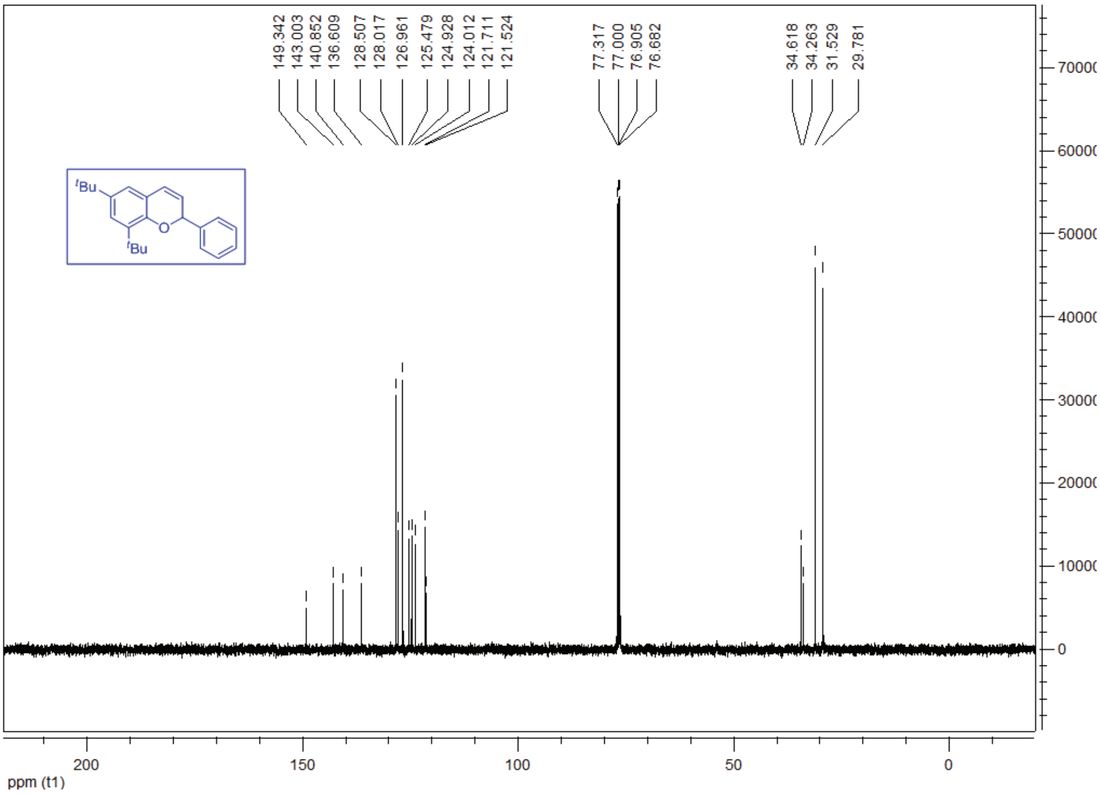
^{13}C NMR, 5,7-dimethyl-2-phenyl-2*H*-chromene **(3q)**



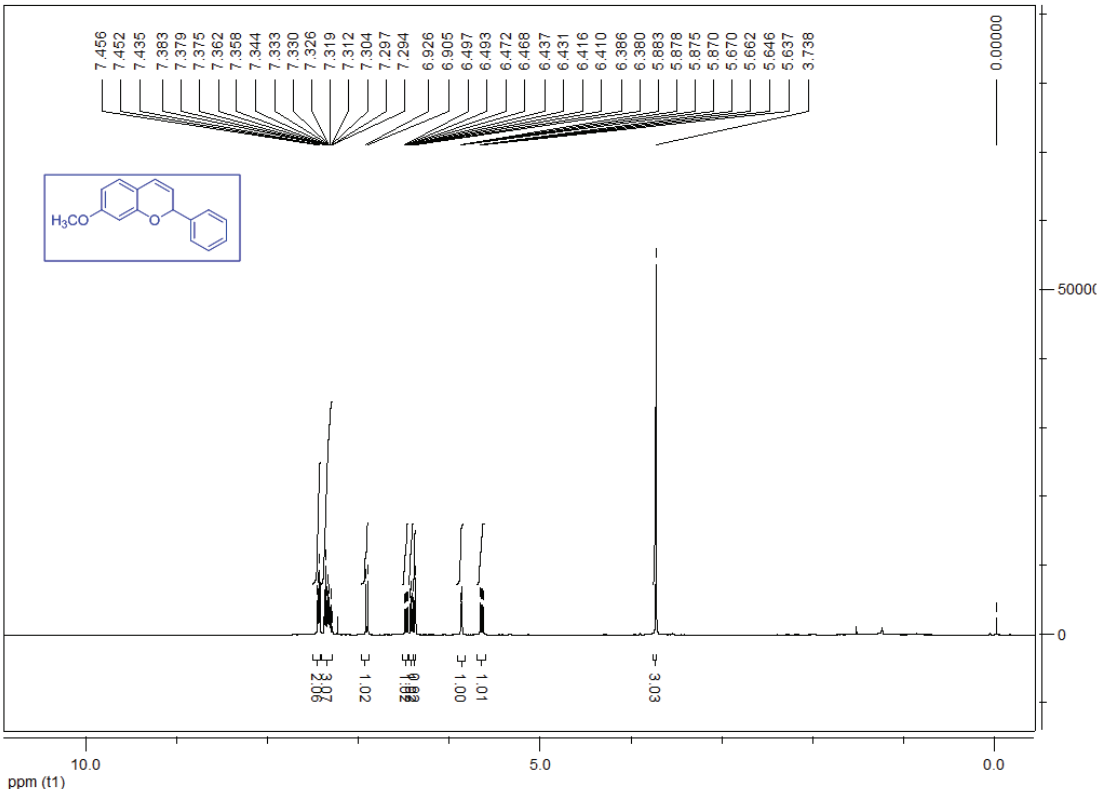
^{1}H NMR, 6,8-*di*-tert-butyl-2-phenyl-2*H*-chromene **(3r)**



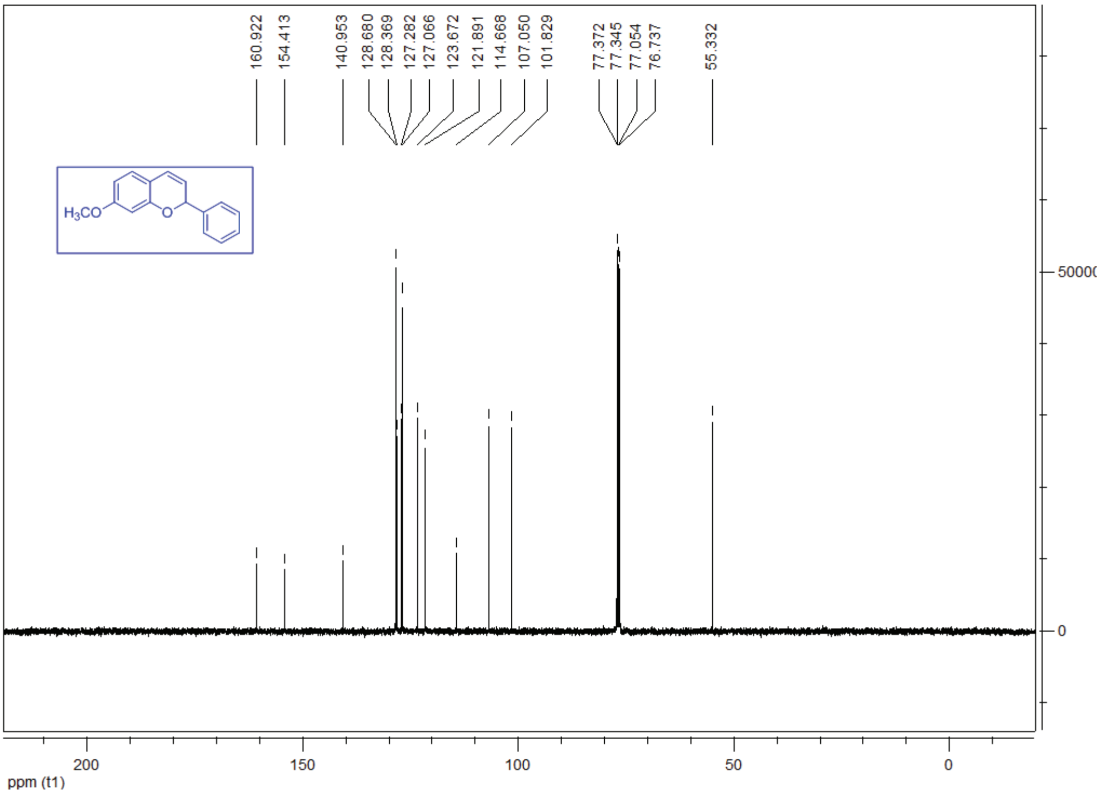
^{13}C NMR, 6,8-*di*-tert-butyl-2-phenyl-2*H*-chromene **(3r)**



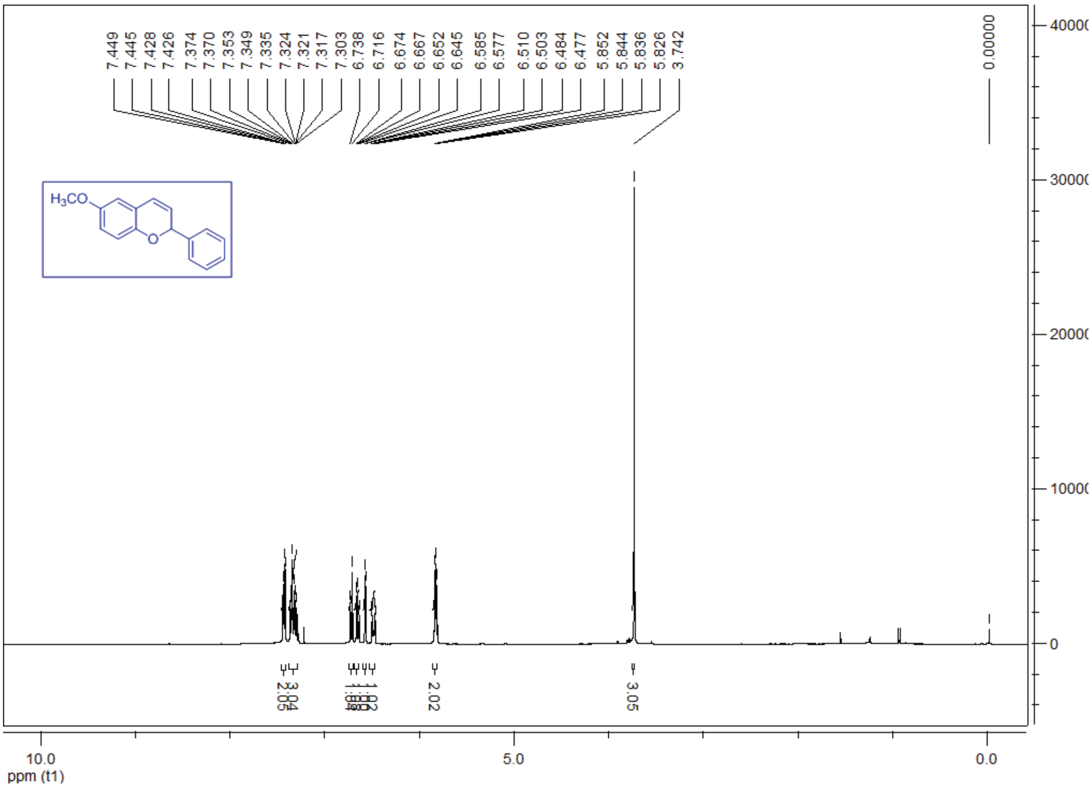
^{1}H NMR, 7-methoxy-2-phenyl-2*H*-chromene **(3s)**



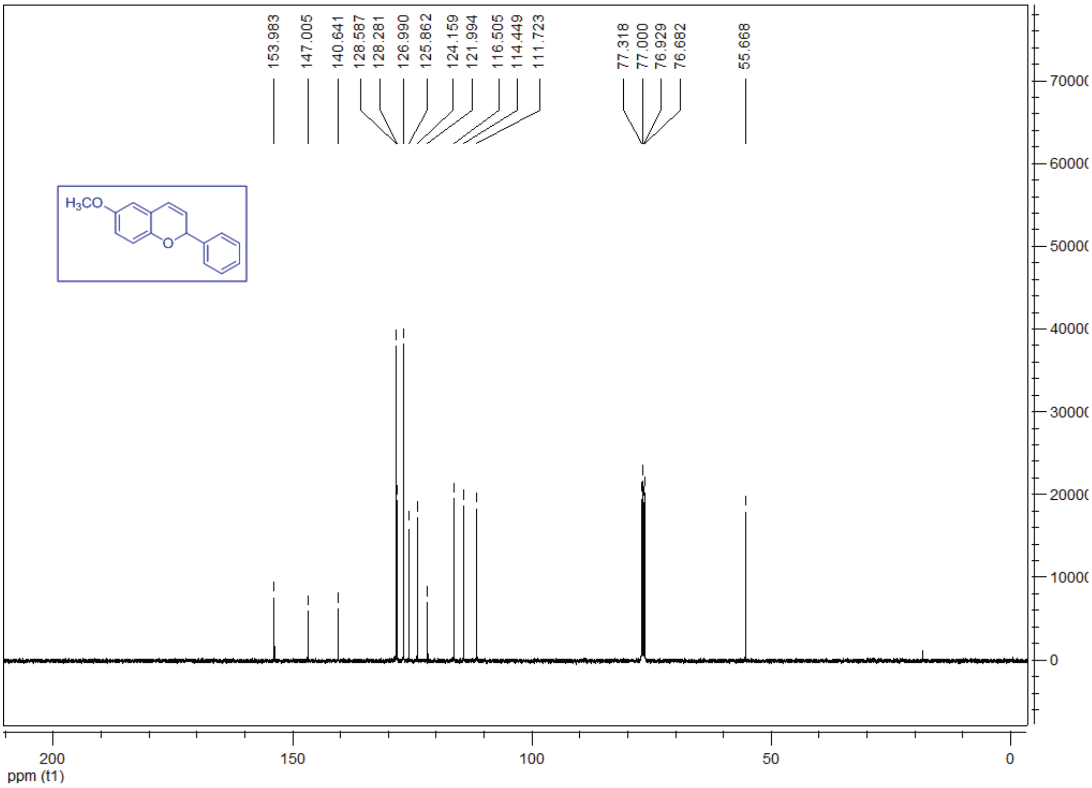
^{13}C NMR, 7-methoxy-2-phenyl-2*H*-chromene **(3s)**



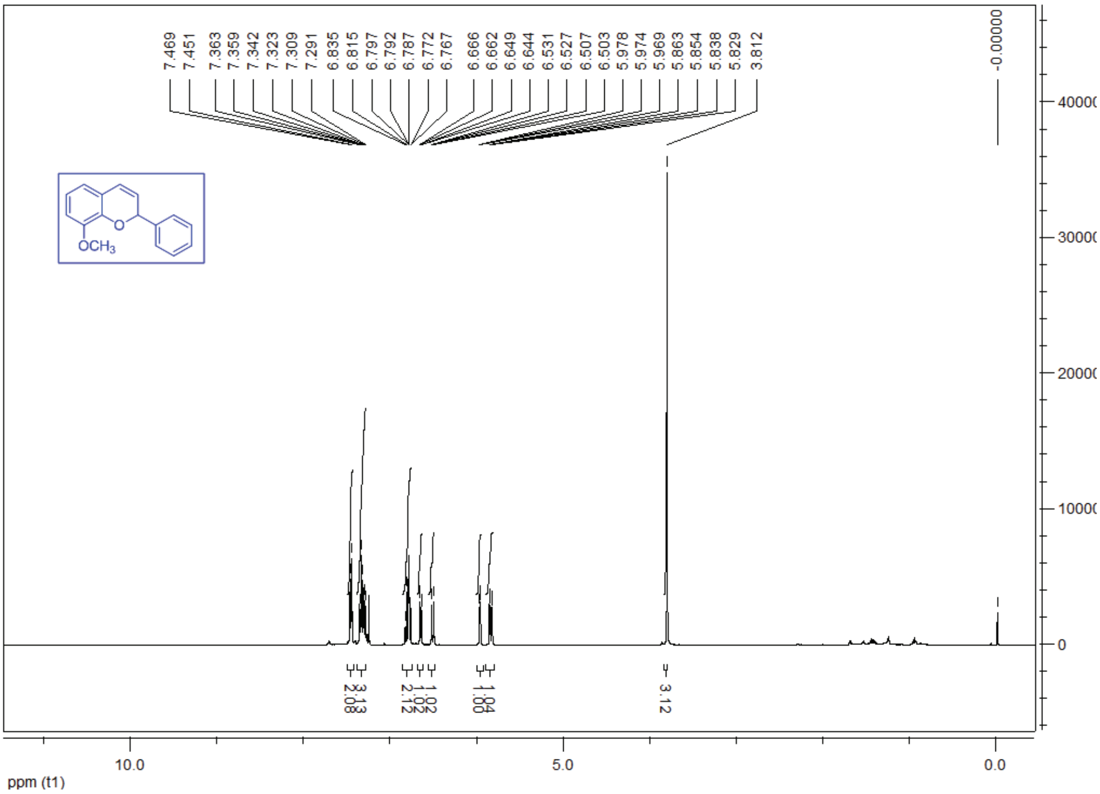
^{1}H NMR, 6-methoxy-2-phenyl-2*H*-chromene **(3t)**



^{13}C NMR, 6-methoxy-2-phenyl-2*H*-chromene **(3t)**



^{1}H NMR, 8-methoxy-2-phenyl-2*H*-chromene **(3u)**



^{13}C NMR, 8-methoxy-2-phenyl-2*H*-chromene **(3u)**