

Supporting Information (SI)

Iodine-PEG as Unique Combination for the Mild and Efficient Metal-Free Synthesis of Flavonoids Through Iodonium-Triiodide Ion-Pair Complexation

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Experimental

General Information

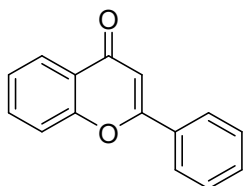
All the chemicals were purchased from Sigma Aldrich and were used as received. The compounds synthesized by the general procedure described below and were characterised by mass spectrometry and ^1H and ^{13}C NMR spectra recorded on 600 MHz JEOL NMR spectrometer in either CDCl_3 or DMSO-d_6 with TMS as an internal reference at Central University of Punjab, Bathinda (^1H NMR: TMS at 0.00 ppm, CDCl_3 at 7.26 ppm, DMSO-d_6 at 2.5 ppm; ^{13}C NMR: CDCl_3 at 77.16 ppm, DMSO-d_6 at 39.52 ppm). The spectroscopic data of all the synthesized compounds are consistent with the reported datas¹.

General Synthetic Procedure for (3a-3v)

A mixture of 2-Hydroxyacetophenone (1 equiv.), respective benzaldehyde (1 equiv.) and iodine (1 equiv.) was taken in a sealed tube in PEG-400 as solvent and heated at 140 °C for 4 to 7 hours. The completion of the reaction was checked by thin-layer chromatography. On completion of the reaction, it was cooled to room temperature, iodine was quenched by 10 % sodium thiosulphate solution and extracted with ethyl acetate. The crude product was purified on silica gel by column chromatography using pet. ether/ethyl acetate (3:1 to 6:1) as eluent to give the desired product (70-84 % yield).

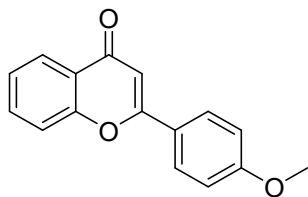
Characteristic Data of the Products

2-phenyl-4H-chromon-4-one (3a).



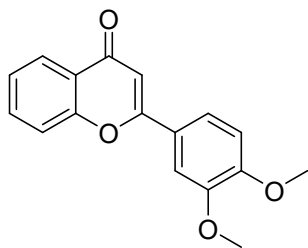
Off-white solid, 76 % yield. M.pt.: 96-98 °C. ^1H NMR (600 MHz, CDCl_3) δ 6.84 (s, 1H), 7.41-7.44 (m, 1H), 7.51-7.55 (m, 3H), 7.58 (dd, J = 8.4, 1.2 Hz, 1H), 7.69-7.72 (m, 1H), 7.94 (dd, J = 7.8, 1.8 Hz, 2H), 8.24 (dd, J = 12.0, 6.0 Hz, 1H); ^{13}C NMR (150 MHz, CDCl_3) δ 107.6, 118.1, 124.0, 125.2, 125.7, 126.3, 129.0, 131.6, 131.8, 133.7, 156.3, 163.43, 178.4. MS (EI, m/z): 222.

2-(4-methoxyphenyl)-4H-chromen-4-one (3b).



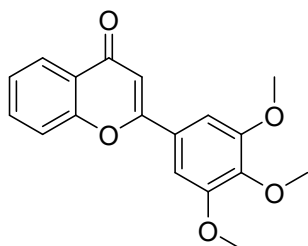
A white solid, 74 % yield. M.pt.: 156-158 °C. ^1H NMR (600 MHz, CDCl_3) δ 3.89 (s, 3H), 6.75 (s, 1H), 7.03 (dd, $J=6.6, 1.8$ Hz, 2H), 7.40-7.42 (m, 1H), 7.55 (dd, $J=8.4, 1.2$ Hz, 1H), 7.67-7.70 (m, 1H), 7.89 (dd, $J=6.6, 1.8$ Hz, 2H), 8.23 (dd, $J=8.4, 1.8$ Hz, 1H); ^{13}C NMR (150 MHz, CDCl_3) δ 55.5, 106.2, 114.4, 117.9, 123.9, 124.0, 125.0, 125.6, 128.0, 133.5, 156.2, 162.4, 163.4, 178.4. MS (EI, m/z): 252.

2-(3,4-dimethoxyphenyl)-4H-chromen-4-one (3c).



A yellowish solid, 78 % yield. M.pt.: 150-152 °C. ^1H NMR (600 MHz, CDCl_3) δ 3.97 (s, 3H), 3.99 (s, 3H), 6.77 (s, 1H), 7.00 (d, $J=8.4$ Hz, 1H), 7.42 (dd, $J=15.0, 7.2$ Hz, 2H), 7.57 (d, $J=8.4$ Hz, 2H), 7.68-7.71 (m, 1H), 8.23 (dd, $J=7.8, 0.6$ Hz, 1H); ^{13}C NMR (150 MHz, CDCl_3) δ 56.0, 56.1, 106.5, 108.8, 111.1, 118.0, 120.0, 123.9, 124.2, 125.1, 125.6, 133.6, 149.3, 152.0, 156.2, 163.3, 178.3. MS (EI, m/z): 282.

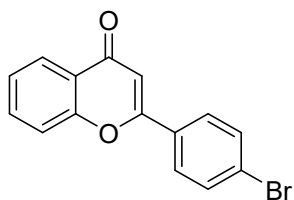
2-(3,4,5-trimethoxyphenyl)-4H-chromen-4-one (3d).



A yellowish solid, 81 % yield. M.pt.: 174-176 °C. ^1H NMR (600 MHz, CDCl_3) δ 3.94 (s, 3H), 3.97 (s, 6H), 6.78 (s, 1H), 7.14 (s, 2H), 7.42-7.45 (m, 1H), 7.60 (dd, $J=8.4, 0.6$ Hz, 1H), 7.72 (m, 1H),

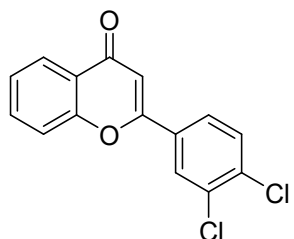
8.24 (dd, $J = 7.8, 1.8$ Hz, 1H); ^{13}C NMR (150 MHz, CDCl_3) δ 56.3, 61.0, 103.6, 107.4, 118.0, 123.9, 125.3, 125.7, 127.0, 133.7, 141.2, 153.6, 156.2, 163.2, 178.4. MS (EI, m/z): 312.

2-(4-bromophenyl)-4H-chromen-4-one (3e)



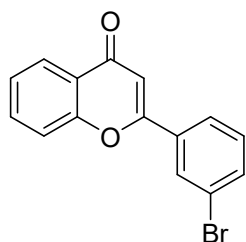
Off-white solid, 71 % yield. M.pt.: 178-180 °C. ^1H NMR (600 MHz, CDCl_3) δ 6.81 (s, 1H), 7.44 (m, 1H), 7.57 (dd, $J = 8.4, 0.6$ Hz, 1H), 7.67 (dd, $J = 6.6, 1.8$ Hz, 2H), 7.70-7.73 (m, 1H), 7.80 (dd, $J = 6.6, 1.8$ Hz, 2H), 8.23 (dd, $J = 7.8, 1.2$ Hz, 1H); ^{13}C NMR (150 MHz, CDCl_3) δ 107.7, 118.0, 123.9, 125.4, 125.7, 126.3, 127.7, 130.7, 132.3, 133.9, 156.1, 162.3, 187.3. MS (EI, m/z): 300.

2-(3,4-dichlorophenyl)-4H-chromen-4-one (3f)



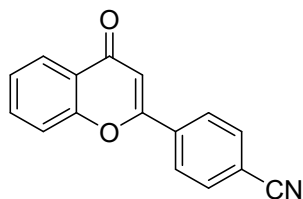
A yellowish solid, 76 % yield. M.pt.: 196-198 °C. ^1H NMR (600 MHz, CDCl_3) δ 6.59 (s, 1H), 7.36 (t, $J = 7.8$ Hz, 1H), 7.44-7.46 (m, 1H), 7.50-7.52 (m, 2H), 7.64 (dd, $J = 7.8, 1.2$ Hz, 1H), 7.70-7.73 (m, 1H), 8.26 (dd, $J = 7.8, 1.8$ Hz, 1H); ^{13}C NMR (150 MHz, CDCl_3) δ 113.1, 118.2, 123.8, 125.5, 125.8, 127.6, 128.9, 131.5, 132.5, 134.0, 134.1, 134.5, 156.5, 162.3, 178.0. MS (EI, m/z): 290.

2-(3-bromophenyl)-4H-chromen-4-one (3g).



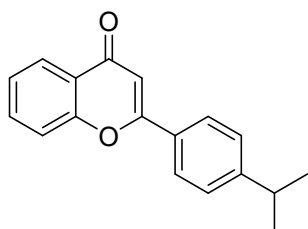
A brownish solid, 78 % yield. M.pt.: 114-116 °C. ¹H NMR (600 MHz, CDCl₃) δ 6.79 (s, 1H), 7.40 (t, J= 7.8 Hz, 1H), 7.42-7.45 (m, 1H), 7.59 (dd, J=8.4, 1.2 Hz, 1H), 7.67 (ddd, J= 6.6, 1.2 Hz, 1H), 7.70-7.73 (m, 1H), 7.83 (ddd, J= 6.6, 1.2 Hz, 1H), 8.08 (t, J= 1.8 Hz, 1H), 8.23 (dd, J= 7.8, 1.8 Hz, 1H); ¹³C NMR (150 MHz, CDCl₃) δ 108.2, 118.1, 123.2, 123.9, 124.8, 125.4, 125.7, 129.2, 130.5, 133.8, 134.0, 134.4, 156.2, 161.7, 178.2. MS (EI, m/z): 300.

4-(4-oxo-4H-chromen-2-yl)benzonitrile (3h).



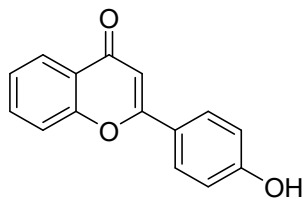
Off white solid, 82 % yield. M.pt.: 218-220 °C. ¹H NMR (600 MHz, CDCl₃) δ 6.87 (s, 1H), 7.45-7.48 (m, 1H), 7.59 (d, J= 8.4 Hz, 1H), 7.73-7.76 (m, 1H), 7.84 (dd, J= 6.6, 1.8 Hz, 2H), 8.05 (dd, J= 6.6, 1.8 Hz, 2H), 8.25 (dd, J= 8.4, 1.8 Hz, 1H); ¹³C NMR (150 MHz, CDCl₃) δ 109.2, 115.0, 117.9, 118.1, 123.9, 125.7, 125.9, 126.8, 132.8, 134.3, 135.9, 156.1, 160.9, 178.0. MS (EI, m/z): 247.

2-(4-isopropylphenyl)-4H-chromen-4-one (3i).



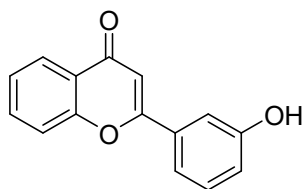
A brownish liquid, 81 % yield. ¹H NMR (600 MHz, CDCl₃) δ 1.30 (d, J= 7.2, 6H), 2.99 (h, J= 6.6 Hz, 1H), 6.80 (s, 1H), 7.38 (d, J= 8.4 Hz, 2H), 7.39-7.42 (m, 1H), 7.56 (d, J= 7.8 Hz, 1H), 7.67-7.70 (m, 1H), 7.86 (dd, J= 6.6, 1.8 Hz, 2H), 8.23 (dd, J= 7.8, 1.8 Hz, 1H); ¹³C NMR (150 MHz, CDCl₃) δ 23.7, 34.1, 107.0, 118.0, 124.0, 125.1, 125.7, 126.4, 127.2, 129.3, 133.6, 153.0, 156.2, 163.6, 178.5. MS (EI, m/z): 264.

2-(4-hydroxyphenyl)-4H-chromen-4-one (3j).



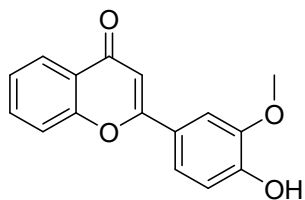
A yellowish solid, 84 % yield. M.pt.: 268-270 °C. ¹H NMR (600 MHz, DMSO) δ 6.87 (s, 1H), 6.95 (d, J= 9.0 Hz, 2H), 7.49 (t, J= 7.2 Hz, 1H), 7.76 (d, J= 7.8 Hz, 1H), 7.80-7.83 (m, 1H), 7.98 (d, J= 8.4 Hz, 2H), 8.04 (dd, J= 8.4, 2.4 Hz, 1H), 10.31 (s, 1H); ¹³C NMR (150 MHz, DMSO) δ 104.7, 115.8, 118.2, 121.4, 123.2, 124.6, 125.2, 128.2, 133.9, 155.4, 160.8, 162.9, 176.7. MS (EI, m/z): 238.

2-(3-hydroxyphenyl)-4H-chromen-4-one (3k)



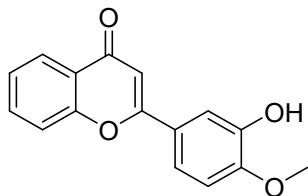
Off white solid, 79 % yield. M.pt.: 206-208 °C. ¹H NMR (600 MHz, DMSO) δ 6.94 (s, 1H), 7.03 (dd, J= 8.4, 2.4 Hz, 1H), 7.39 (t, J= 7.8 Hz, 1H), 7.46 (t, J= 1.8 Hz, 1H), 7.53 (dd, J= 15.6, 7.2 Hz, 2H), 7.78 (d, J= 8.4, 1H), 7.83-7.86 (m, 1H), 8.07 (dd, J= 7.8, 1.2 Hz, 1H), 9.91 (s, 1H); ¹³C NMR (150 MHz, DMSO) δ 106.8, 112.7, 117.1, 118.4, 118.7, 123.2, 124.7, 125.4, 130.1, 132.3, 134.2, 155.5, 157.8, 162.6, 176.9. MS (EI, m/z): 238.

2-(4-hydroxy-3-methoxyphenyl)-4H-chromen-4-one (3l).



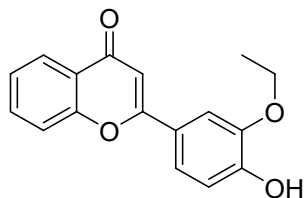
A brownish solid, 82 % yield. M.pt.: 190-192 °C. ¹H NMR (600 MHz, DMSO) δ 3.98 (s, 3H), 6.73 (s, 1H), 7.03 (d, J= 8.4 Hz, 1H), 7.41 (s, 1H), 7.43 (dd, J= 7.8, 0.6 Hz, 1H), 7.48 (dd, J= 8.4, 2.4 Hz, 1H), 7.60 (d, J= 7.8 Hz, 1H), 7.69-7.72 (m, 1H), 8.17 (dd, J= 7.8, 1.2 Hz, 1H), 9.11 (s, 1H); ¹³C NMR (150 MHz, DMSO) δ 56.0, 105.6, 109.3, 115.8, 118.0, 120.3, 122.7, 123.7, 125.0, 125.2, 133.5, 147.9, 150.4, 156.0, 163.7, 178.0. MS (EI, m/z): 268.

2-(3-hydroxy-4-methoxyphenyl)-4H-chromen-4-one (3m).



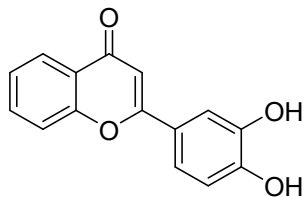
A yellowish solid, 77 % yield. M.pt.: 148-150 °C. ¹H NMR (600 MHz, DMSO) δ 3.96 (s, 3H), 6.70 (s, 1H), 6.99 (dd, J= 6.0, 3.0 Hz, 1H), 7.42 (t, J= 7.2 Hz, 1H), 7.47-7.48 (m, 1H), 7.49 (s, 1H), 7.57 (d, J= 8.4 Hz, 1H), 7.70-7.72 (m, 1H), 8.18 (dd, J= 7.8, 1.2 Hz, 1H), 8.58 (s, 1H); ¹³C NMR (150 MHz, DMSO) δ 55.9, 106.0, 113.0, 113.0, 118.0, 118.5, 123.8, 124.2, 125.0, 125.3, 133.6, 146.8, 150.7, 156.1, 163.5, 178.1. MS (EI, m/z): 268.

2-(3-ethoxy-4-hydroxyphenyl)-4H-chromen-4-one (3n).



A yellow solid, 84 % yield. M.pt.: 150-152 °C. ¹H NMR (600 MHz, DMSO) δ 1.39 (t, J= 6.6 Hz, 3H), 4.18 (q, J= 7.2 Hz, 2H), 6.98 (t, 4.5 Hz, 2H), 7.47-7.50 (m, 1H), 7.59-7.61 (m, 2H), 7.77 (dd, J= 8.4, 0.6 Hz, 1H), 7.80-7.82 (m, 1H), 8.04 (dd, J= 7.8, 1.8 Hz, 1H), 9.84 (s, 1H); ¹³C NMR (150 MHz, DMSO) δ 14.6, 64.1, 105.0, 111.3, 115.7, 118.3, 120.1, 121.8, 123.2, 124.6, 125.1, 133.8, 147.1, 150.6, 155.5, 162.9, 176.8. MS (EI, m/z): 282.

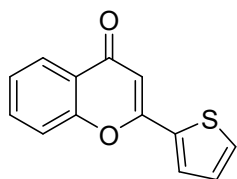
2-(3,4-dihydroxyphenyl)-4H-chromen-4-one (3o).



A brown solid, 81 % yield. M.pt.: 242-244 °C. ¹H NMR (600 MHz, DMSO) δ 6.77 (s, 1H), 6.93 (d, J= 9.0 Hz, 1H), 7.47 (dt, J= 6.6, 1.8 Hz, 2H), 7.5 (d, J= 6.6 Hz, 1H), 7.73 (d, J= 7.8 Hz, 1H), 7.80-7.83 (m, 1H), 8.05 (dd, J= 7.8, 1.2 Hz, 1H), 9.44 (s, 1H), 9.86 (s, 1H); ¹³C NMR (150 MHz,

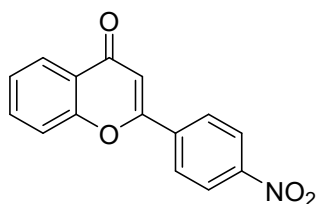
DMSO) δ 104.7, 113.3, 115.9, 118.1, 118.7, 121.8, 123.2, 124.6, 125.2, 133.9, 145.6, 149.3, 155.4, 136.1, 176.6. MS (EI, m/z): 254.

2-(thiophen-2-yl)-4H-chromen-4-one (3t).



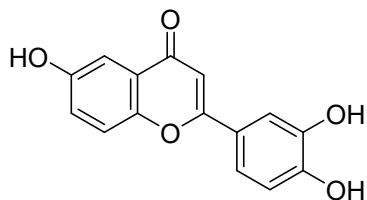
A yellowish solid, 71% yield. M.pt.: 98-100 °C. ^1H NMR (600 MHz, CDCl_3) δ 6.70 (s, 1H), 7.18 (dd, $J=4.2, 1.2$ Hz, 1H), 7.41 (t, $J=8.4$ Hz, 1H), 7.52 (d, $J=9.0$ Hz, 1H), 7.57 (dd, $J=4.2, 1.2$ Hz, 1H), 7.67-7.69 (m, 1H), 7.72 (dd, $J=3.0, 1.2$ Hz, 1H); ^{13}C NMR (150 MHz, CDCl_3) δ 106.2, 117.9, 124.0, 125.2, 125.7, 128.4, 128.5, 130.2, 133.74, 135.2, 155.9, 159.0, 177.8. MS (EI, m/z): 228.

2-(4-nitrophenyl)-4H-chromen-4-one (3u)



A yellowish solid, 74% yield. M.pt.: 244-246 °C. ^1H NMR (600 MHz, CDCl_3) δ 6.91 (s, 1H), 7.47 (t, $J=7.8$ Hz, 1H), 7.61 (d, $J=8.4$ Hz, 1H), 7.76 (t, $J=7.8$ Hz, 1H), 8.12 (d, $J=8.4$ Hz, 2H), 8.25 (d, $J=7.8$ Hz, 1H), 8.39 (d, $J=8.4$ Hz, 2H); ^{13}C NMR (150 MHz, CDCl_3) δ 109.6, 118.1, 123.9, 124.2, 125.7, 125.9, 127.2, 134.3, 137.6, 149.4, 156.2, 160.5, 177.9. MS (EI, m/z): 267.

2-(3,4-dihydroxyphenyl)-6-hydroxy-4H-chromen-4-one (3v)

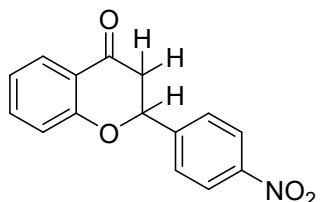


A off white solid, 72% yield. ^1H NMR (600 MHz, CDCl_3) δ 6.67 (s, 1H), 6.90 (d, $J=9.0$ Hz, 1H), 7.23 (dd, $J=6.0, 3.0$ Hz, 1H), 7.31 (d, $J=3.0$ Hz, 1H), 7.41-7.43 (m, 2H), 7.58 (d, $J=9.0$ Hz,

1H), 9.39-9.96 (s, 3H, OH); ¹³C NMR (150 MHz, CDCl₃) δ 104.4, 108.1, 113.7, 116.5, 119.1, 120.0, 122.7, 123.2, 124.7, 146.2, 149.7, 155.2, 163.3, 177.2. MS (EI, m/z): 270.

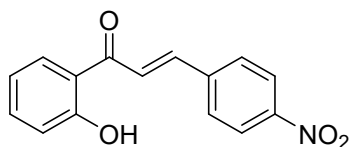
Spectroscopic data of some isolated intermediates/side products

2-(4-nitrophenyl)-chroman-4-one



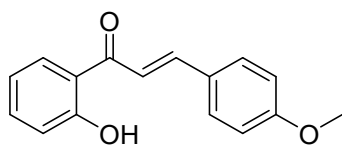
A yellowish solid, ¹H NMR (600 MHz, CDCl₃) δ 2.95 (dd, J= 13.2, 3.6 Hz, 1H), 3.02 (dd, J= 13.2, 3.6 Hz, 1H), 5.61 (dd, J= 9.6, 3.0 Hz, 1H), 7.09-7.11 (m, 2H), 7.55 (td, J= 7.2, 1.2 Hz, 1H), 7.68 (d, J= 9.0, 2H), 7.94 (dd, J= 6.0, 1.8 Hz, 1H), 8.30 (d, J= 8.4 Hz, 2H); ¹³C NMR (150 MHz, CDCl₃) δ 44.6, 78.3, 118.0, 120.9, 122.2, 124.1, 126.8, 127.2, 136.5, 145.8, 148.0, 160.9, 190.6.

(E)-1-(2-hydroxyphenyl)-3-(4-nitrophenyl)prop-2-en-1-one



A yellowish solid, ¹H NMR (600 MHz, DMSO) δ 7.02 (dd, J= 6.0, 2.4 Hz, 2H), 7.58 (t, J= 7.2 Hz, 1H), 7.88 (d, J= 15.6 Hz, 1H), 8.17 (t, J= 13.8 Hz, 3H), 8.22 (d, J= 7.8 Hz, 1H), 8.28 (d, J= 8.4 Hz, 2H), 12.21 (s, 1H, OH); ¹³C NMR (150 MHz, DMSO) δ 118.2, 119.8, 121.5, 124.4, 126.8, 130.5, 131.5, 137.0, 141.4, 141.9, 148.7, 162.1, 193.7.

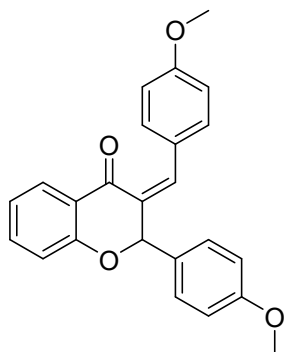
(E)-1-(2-hydroxyphenyl)-3-(4-methoxyphenyl)prop-2-en-1-one



A white solid, ¹H NMR (600 MHz, CDCl₃) δ 3.87 (s, 3H), 6.93 (dd, J= 6.0, 1.2 Hz, 1H), 6.95 (dd, J= 4.8, 1.8 Hz, 2H), 7.02 (dd, J= 7.2, 1.2 Hz, 1H), 7.49 (td, J= 6.6, 1.8 Hz, 1H), 7.54 (d, J= 15.6 Hz, 1H), 7.63 (d, J= 9.0 Hz, 2H), 7.90 (d, J= 12.0 Hz, 1H), 7.92 (dd, J= 4.8, 1.8 Hz, 1H), 12.93 (s,

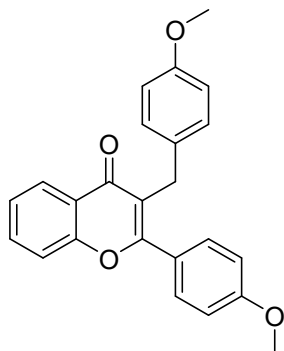
1H, OH); ¹³C NMR (150 MHz, CDCl₃) δ 55.4, 114.5, 117.6, 118.6, 118.7, 120.1, 127.3, 129.5, 130.5, 136.1, 145.3, 162.0, 163.5, 193.7.

(Z)-3-(4-methoxybenzylidene)-2-(4-methoxyphenyl)chroman-4-one



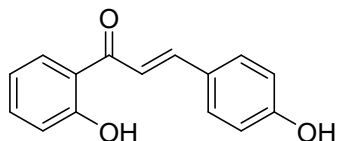
A white solid, ¹H NMR (600 MHz, CDCl₃) δ 3.73 (s, 3H), 3.80 (s, 3H), 6.61 (s, 1H), 6.83 (dd, J= 4.8, 1.8 Hz, 2H), 6.87 (dd, J= 4.8, 1.8 Hz, 2H), 6.89 (dd, J= 7.2, 1.2 Hz, 1H), 6.93-6.95 (m, 1H), 7.24 (dd, J= 4.8, 1.8 Hz, 2H), 7.36-7.38 (m, 1H), 7.39 (dd, J= 8.4, 0.6 Hz, 2H), 7.92 (dd, J= 6.0, 1.8 Hz, 1H), 8.04 (s, 1H); ¹³C NMR (150 MHz, CDCl₃) δ 55.2, 55.4, 77.7, 114.2, 114.4, 118.6, 121.6, 122.3, 126.8, 127.6, 129.1, 130.2, 130.5, 132.2, 135.9, 139.1, 158.8, 159.8, 161.0, 182.7.

3-(4-methoxybenzyl)-2-(4-methoxyphenyl)-4H-chromen-4-one



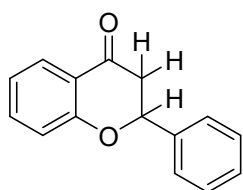
A white solid, ¹H NMR (600 MHz, CDCl₃) δ 3.75 (s, 3H), 3.87 (s, 3H), 3.92 (s, 2H), 6.77 (dt, J= 4.8, 1.8 Hz, 2H), 6.97 (dt, J= 4.8, 1.8 Hz, 2H), 7.07 (d, J= 9.0 Hz, 2H), 7.38-7.40 (m, 1H), 7.46 (d, J= 8.4 Hz, 1H), 7.53 (dt, J= 4.8, 1.8 Hz, 2H), 7.64-7.66 (m, 1H), 8.24 (dd, J= 6.6, 1.2 Hz, 1H); ¹³C NMR (150 MHz, CDCl₃) δ 30.5, 55.2, 55.4, 113.8, 113.9, 117.8, 120.3, 123.0, 124.7, 125.6, 126.1, 129.0, 130.2, 132.4, 133.4, 156.1, 157.8, 161.2, 162.7, 178.3.

(E)-1-(2-hydroxyphenyl)-3-(4-hydroxyphenyl)prop-2-en-1-one



A white solid, ^1H NMR (600 MHz, CDCl_3) δ 6.89 (d, J = 9.0 Hz, 2H), 6.94 (m, 1H), 7.02 (dd, J = 7.2, 1.2 Hz, 1H), 7.48-7.50 (m, 1H), 7.54 (d, J = 15.6 Hz, 1H), 7.59 (d, J = 8.4 Hz, 2H), 7.89 (d, J = 15.6 Hz, 1H), 7.92 (dd, J = 6.6, 1.8 Hz, 1H), 12.92 (s, 1H, OH); ^{13}C NMR (150 MHz, CDCl_3) δ 116.1, 117.8, 118.6, 118.8, 120.20, 127.6, 129.6, 130.8, 136.2, 145.3, 158.3, 136.6, 193.8.

2-phenylchroman-4-one



A white solid, ^1H NMR (600 MHz, CDCl_3) δ 2.90 (dd, J = 13.8, 3.0 Hz, 1H), 3.09 (dd, J = 13.2, 3.6 Hz, 1H), 5.49 (dd, J = 10.2, 3.0 Hz, 1H), 7.06 (m, 2H), 7.39 (tt, J = 3.6, 1.2 Hz, 1H), 7.44 (m, 2H), 7.49 (dd, J = 7.2, 1.2 Hz, 2H), 7.51 (dt, J = 5.4, 1.8 Hz, 1H), 7.94 (dd, J = 6.6, 1.8 Hz, 1H); ^{13}C NMR (150 MHz, CDCl_3) δ 44.7, 79.6, 118.1, 120.9, 121.6, 126.1, 127.0, 128.8, 128.8, 136.2, 138.7, 161.5, 191.9.

DFT calculations

All the DFT calculations were performed using the ORCA 5.0.3 software.² Density functional theory was employed with PBE0 functional³, dispersion corrections based on tight binding partial charges (D4)⁴ along with Ahlrichs and co-workers balanced polarised double zeta basis set (def2-svp).⁵ RIJCOSX⁶ approximation was used throughout to speed up the calculations. Transition states were calculated by implementing Nudged-Elastic-Band method of Asgeirsson *et al.*⁷ All minima on the potential energy surface were verified by calculating the vibrational frequencies using the same level of theory. Furthermore, for refinement in results, a higher valence polarised triple zeta basis set (def2-tzvp) was employed with PBE0 functional to calculate the single point-energy of the whole system. The solute-solvent interaction is described by the conductor-like polarizable continuum model (CPCM)⁸. The dielectric constant & refractive index of PEG-400 is taken as 11.6 and 54 respectively.

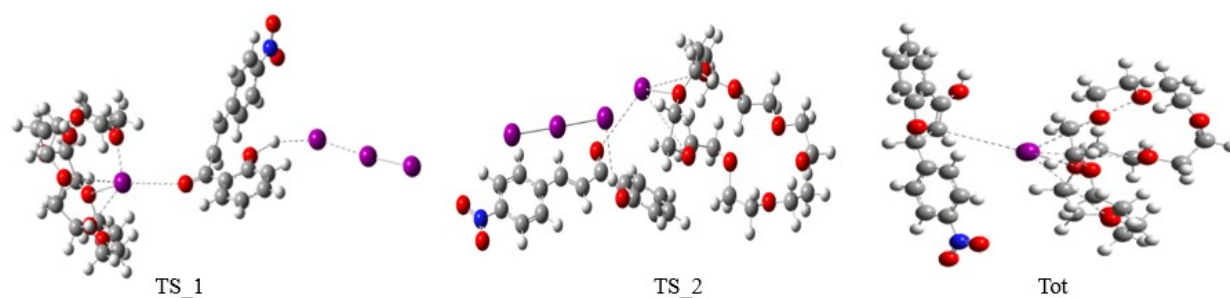
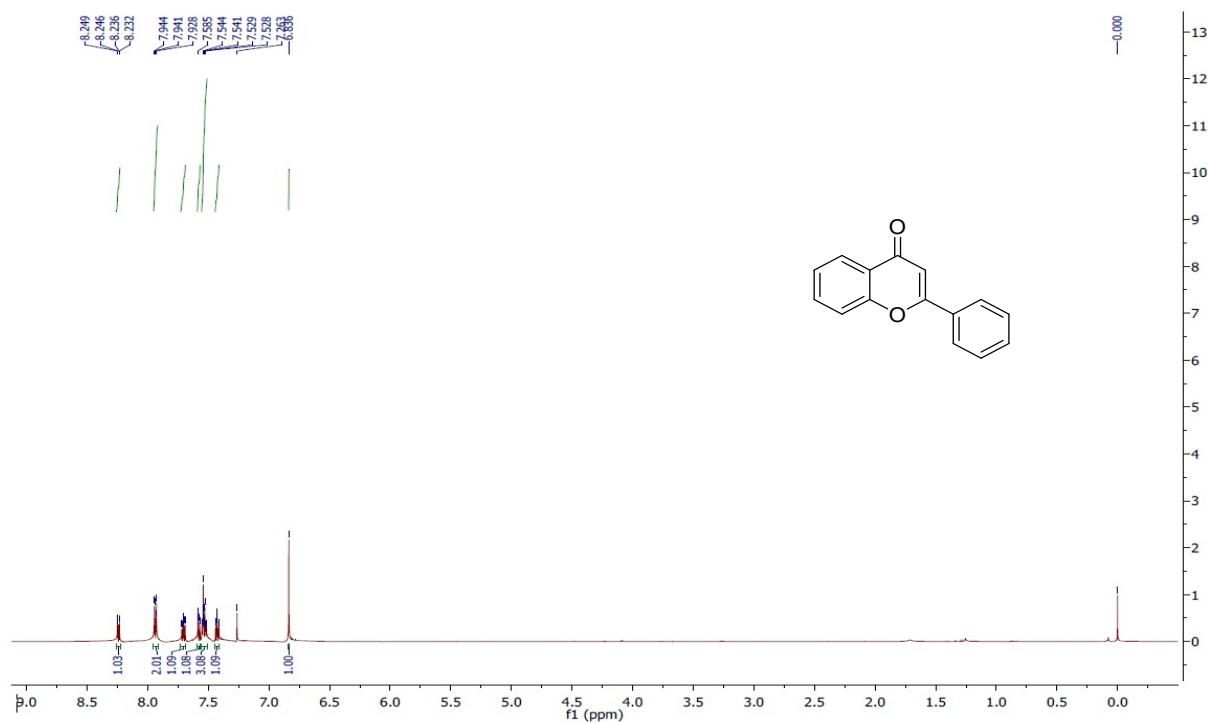


Fig. S1 Interaction diagrams of acetophenone and tautomer with PEG-400, and the interaction of PEG-400 in transition states 1 and 2.

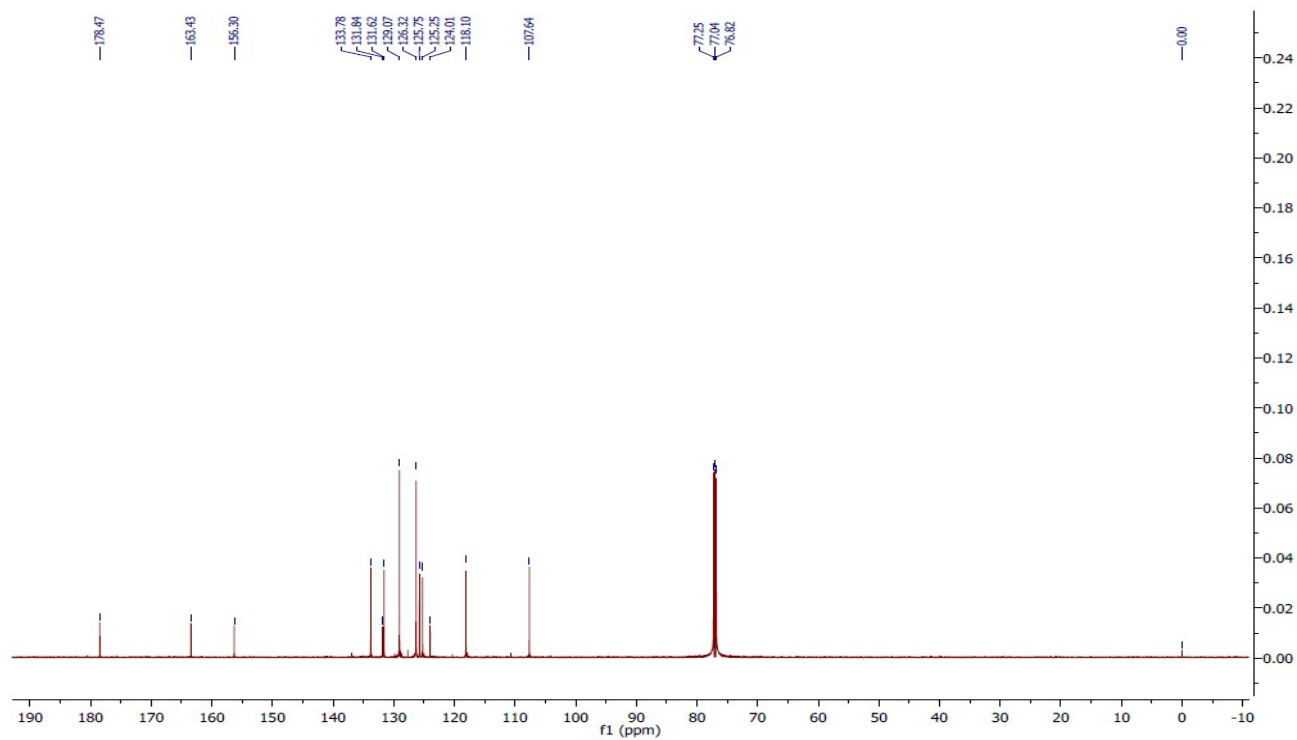
Table: S1 Energies of the various species including starting materials, intermediates, and transition states. (E_{elec} = Electronic energy in gas phase, G^{S} = Gibbs free energy in solvent, H^{S} = Enthalpy in solvent)

Species	E_{elec}	G^{S}	H^{S}
A	-459.787145932339	-459.69504252	-459.62810581
B	-933.109691205920	-932.94527555	-932.84716421
C	-931.928190775293	-931.78145045	-931.68880309
D	-933.132746285290	-932.96457866	-932.86981981
PEG	-1229.39191956	-1229.39191956	-1229.39191956
PEGI	-1527.311172488971	-1526.90311373	-1526.76751762
I_3^-	-893.393896594535	-893.43782180	-893.38404157
TS_1	-1230.174097750667	-1230.02694086	-1229.92264379
TS_2	-3353.862490186070	-3353.28177433	-3353.04872527
II	-1306.559198882304	-1306.42286120	-1306.27986039
III	-1009.513839334502	-1009.32305888	-1009.22064602
IV	-1230.258995954341	-1230.10501402	-1230.00402559
TOT	-933.110141544027	-932.94205030	-932.84707574
I_2	-595.464519981321	-595.50146074	-595.45857235
H_2O	-76.387365438931	-76.39236652	-76.36092331
HI	-298.320747908430	-298.34492113	-298.31093735

¹H NMR Spectra (CDCl₃) of 3a



¹³C NMR Spectra (CDCl₃) of 3a



Mass Spectra of 3a

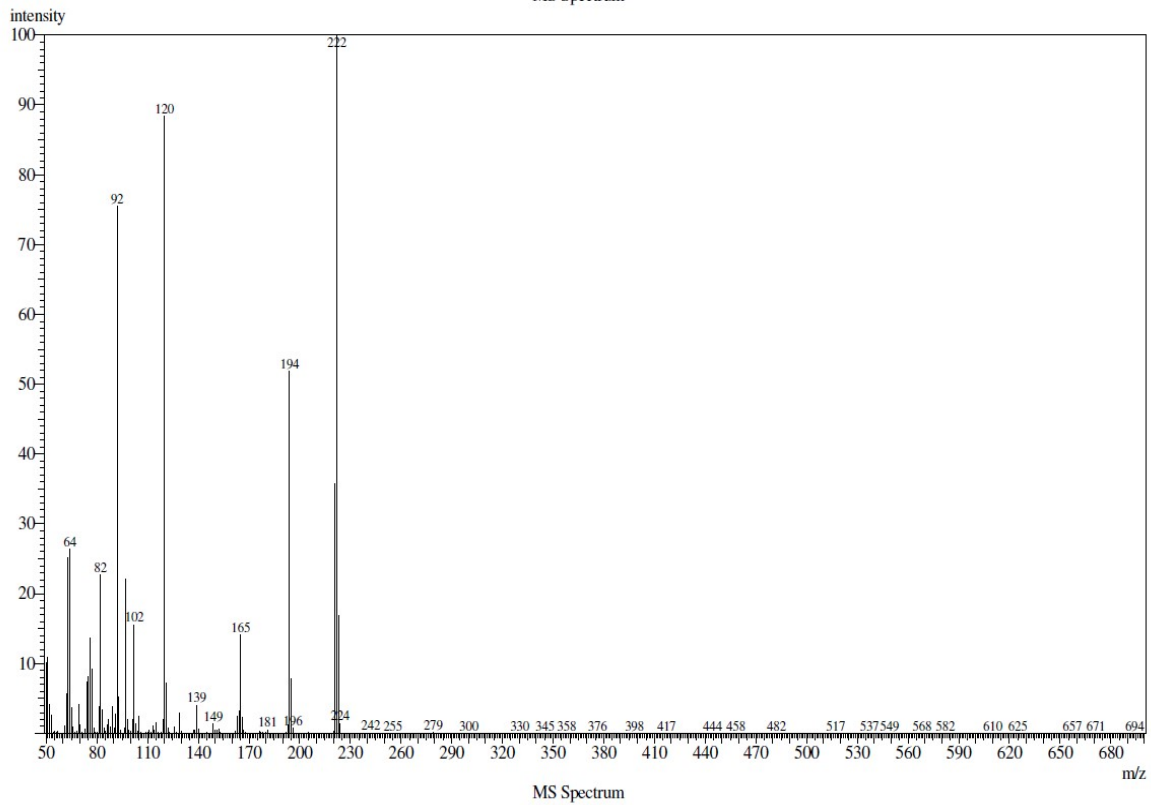
Line#: 1 R.Time: 4.3300(Scan#: 567)

MassPeaks: 386

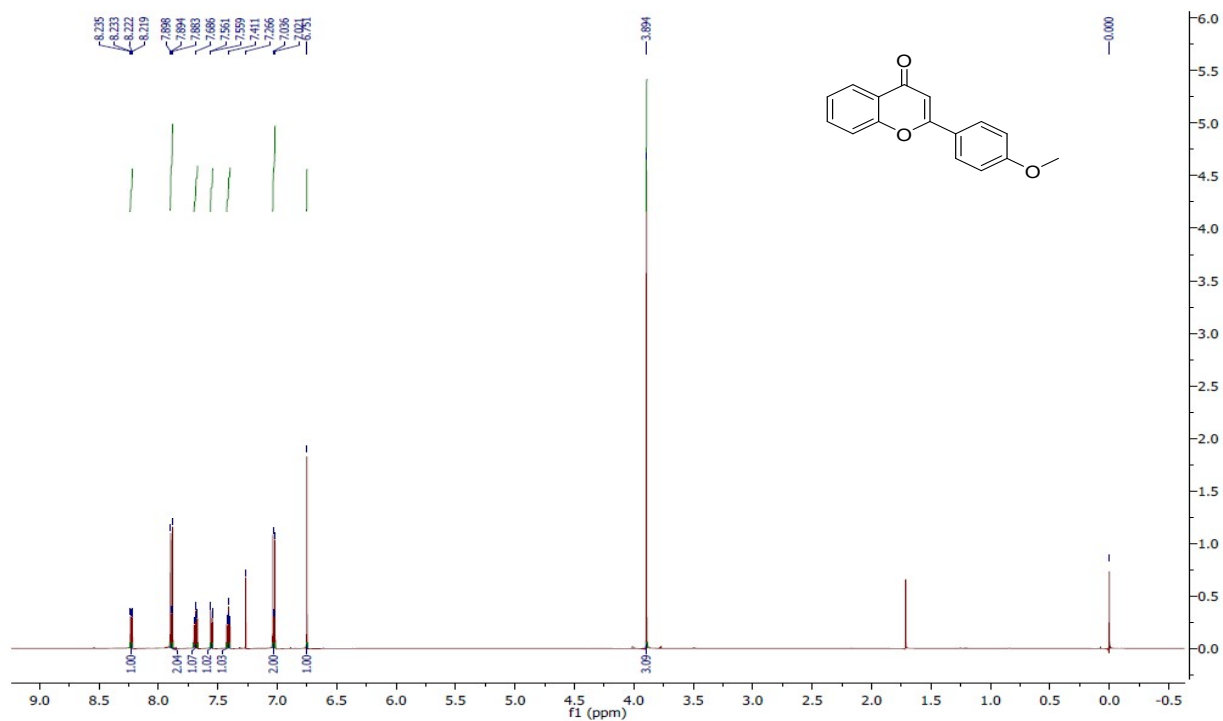
RawMode: Averaged 4.3250-4.3350(566-568) BasePeak: 222.0500(350886)

BG Mode: Calc. from Peak Group 1 - Event 1

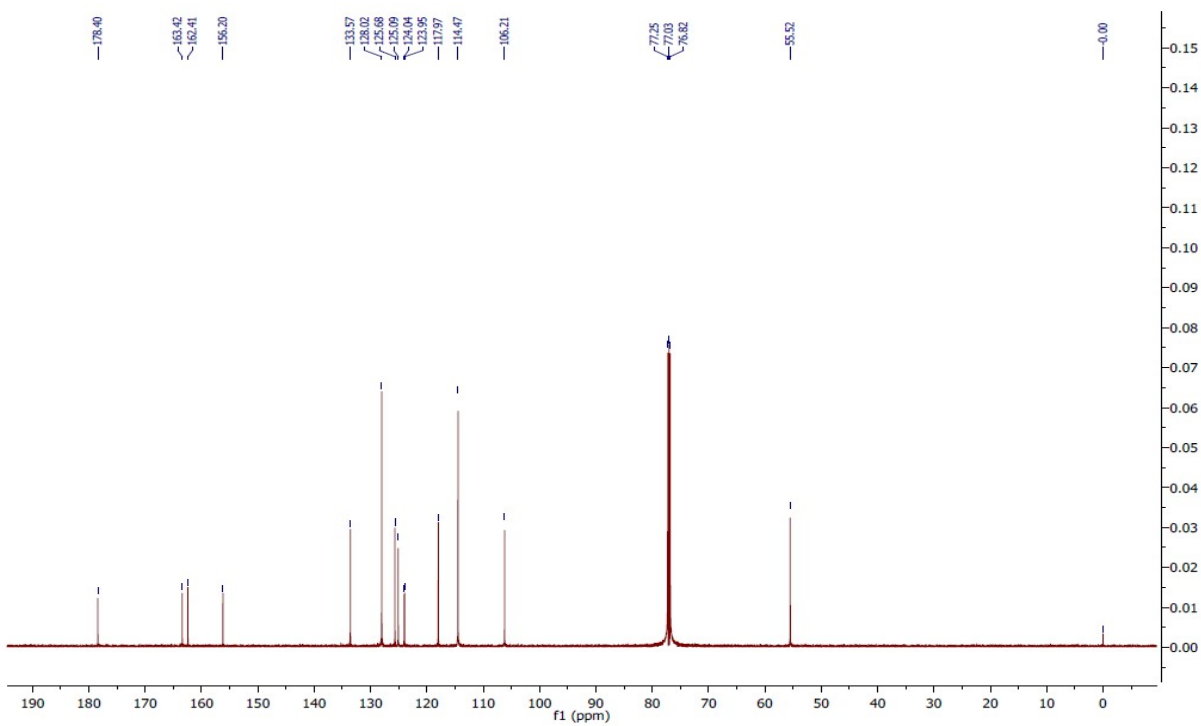
MS Spectrum



¹H NMR Spectra (CDCl₃) of 3b



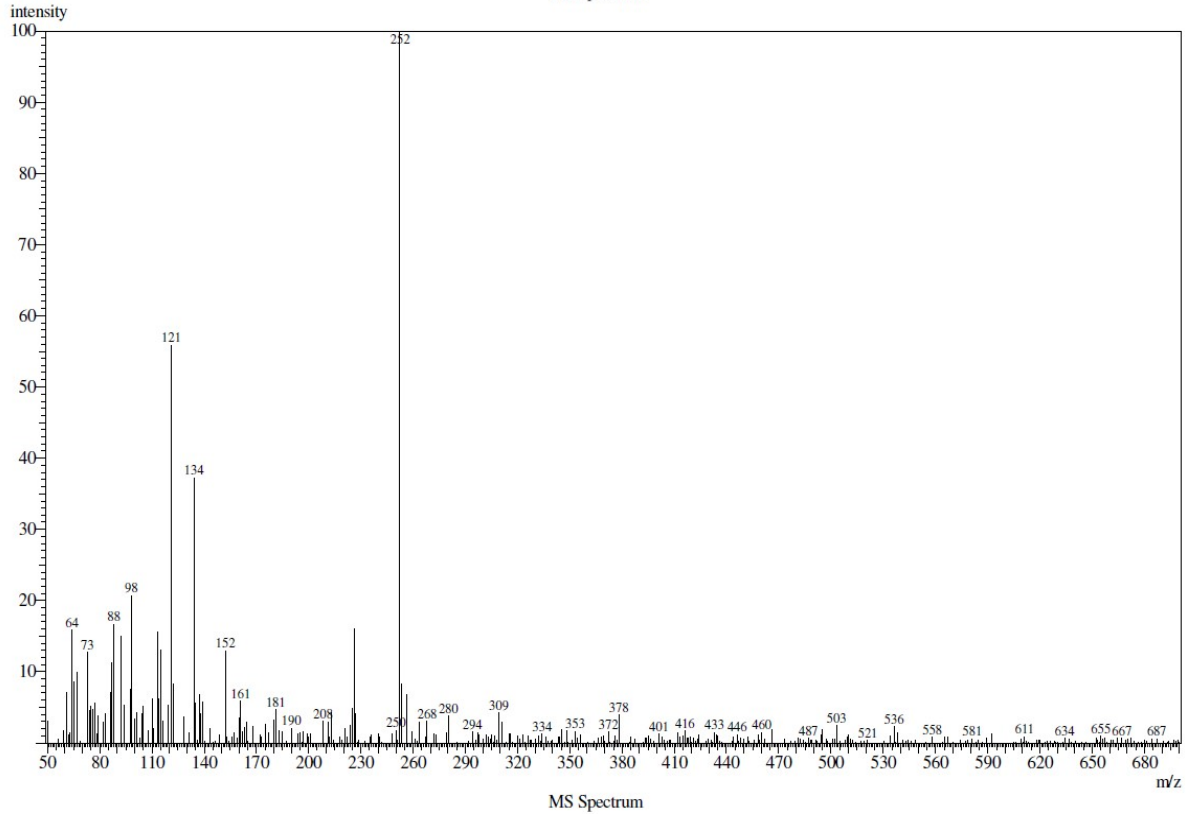
¹³C NMR Spectra (CDCl₃) of 3b



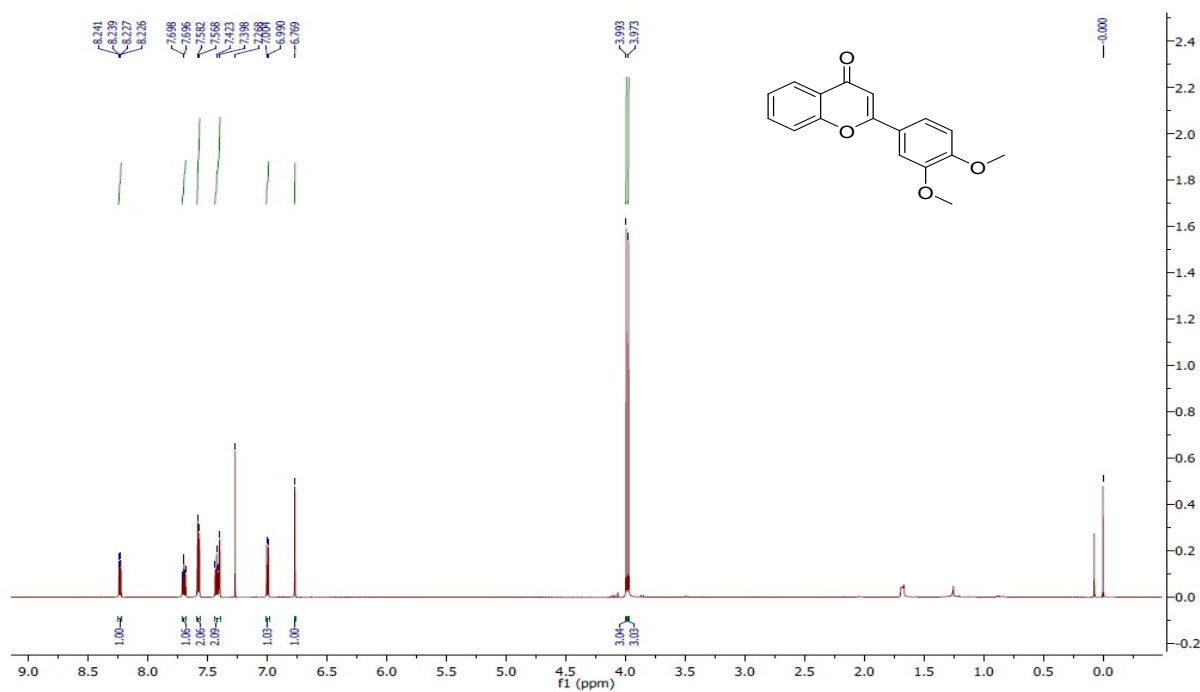
Mass Spectra of 3b

Line#: 1 R.Time: 7.2600(Scan#: 1153)
MassPeaks: 444
RawMode: Averaged 7.2550-7.2650(1152-1154) BasePeak: 254.1000(3728)
BG Mode: Calc. from Peak Group 1 - Event 1

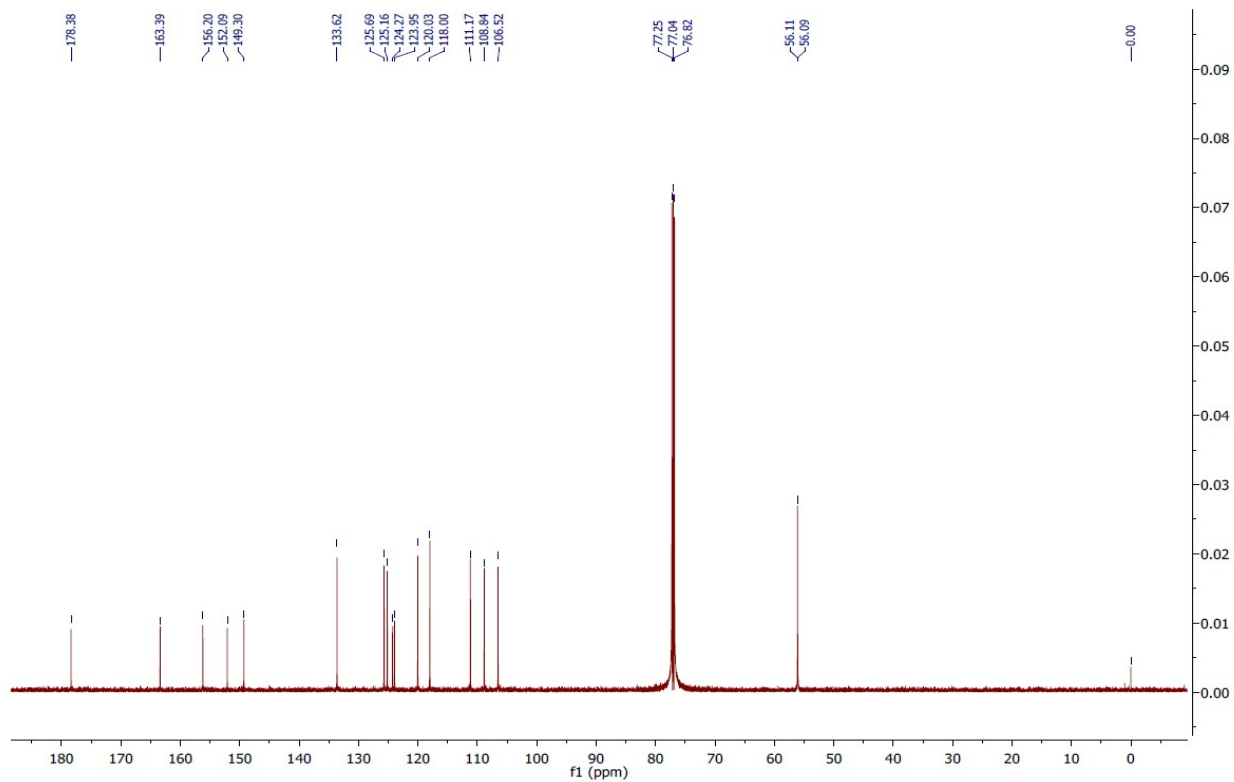
MS Spectrum



¹H NMR Spectra (CDCl₃) of 3c



¹³C NMR Spectra (CDCl₃) of 3c



Mass Spectra of 3c

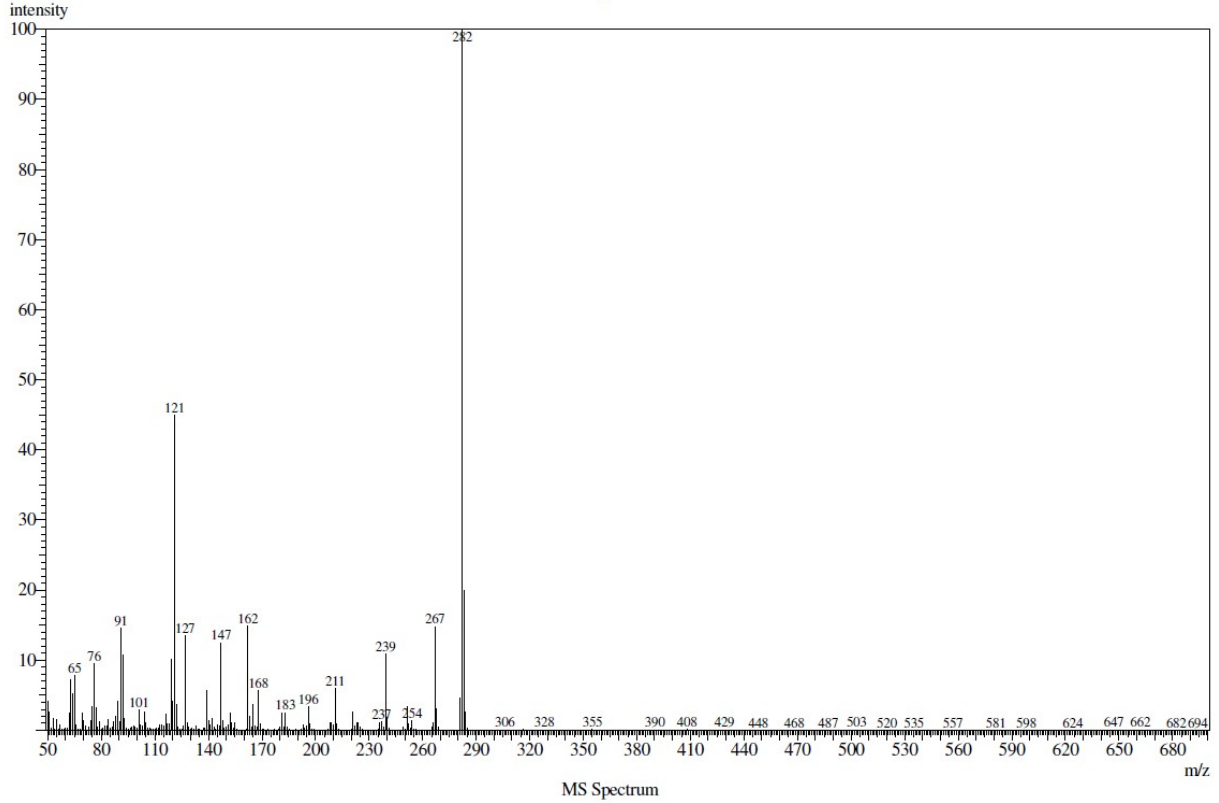
Line#: 1 R.Time:6.6300(Scan#:1027)

MassPeaks:568

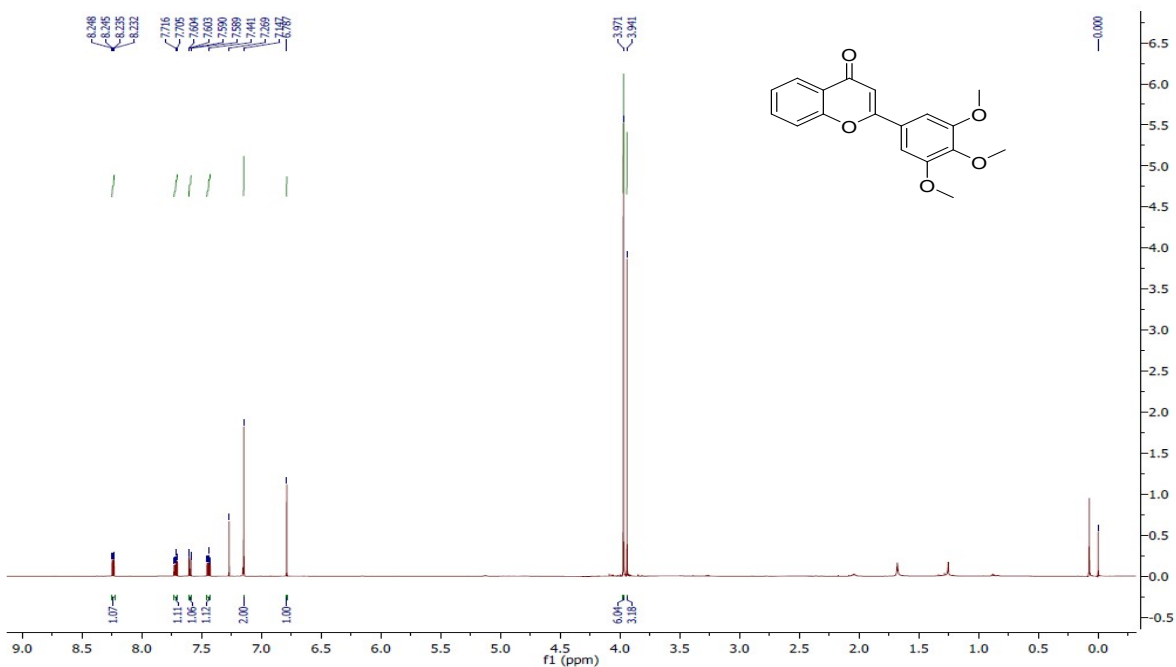
RawMode:Averaged 6.6250-6.6350(1026-1028) BasePeak:282.1500(170587)

BG Mode:Calc. from Peak Group 1 - Event 1

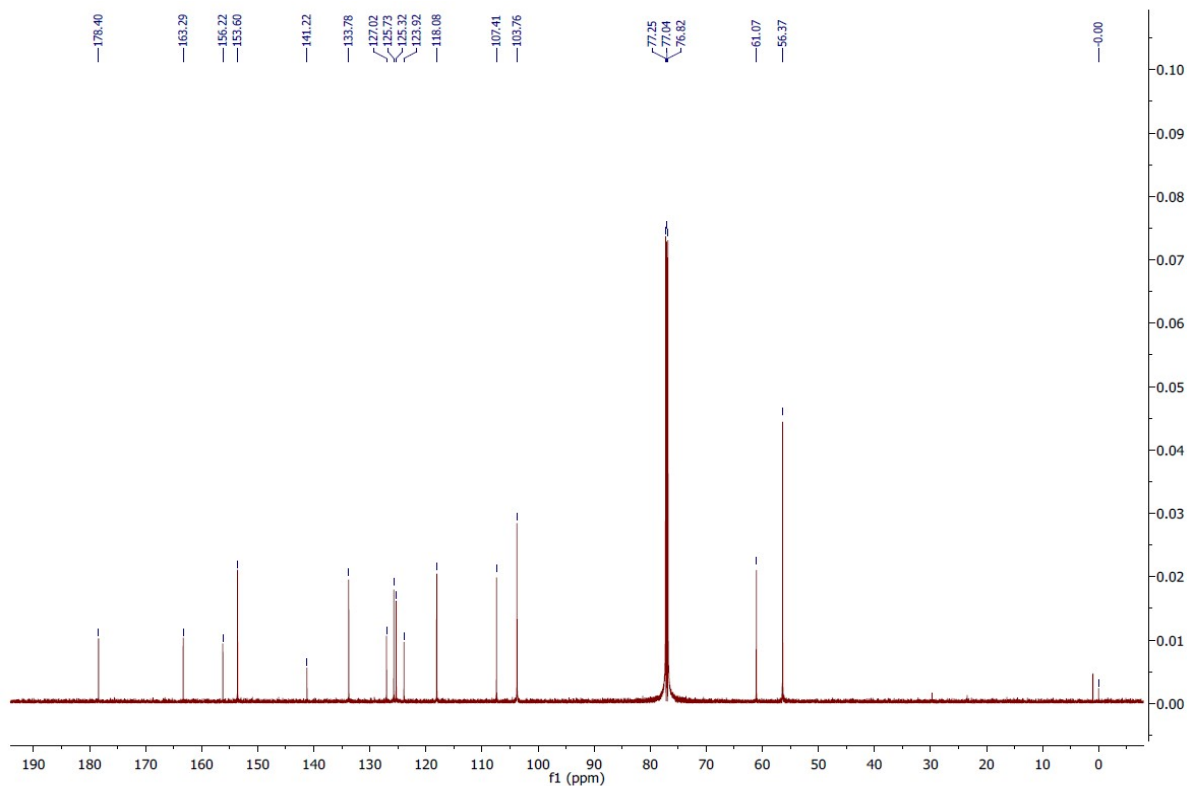
MS Spectrum



¹H NMR Spectra (CDCl₃) of 3d

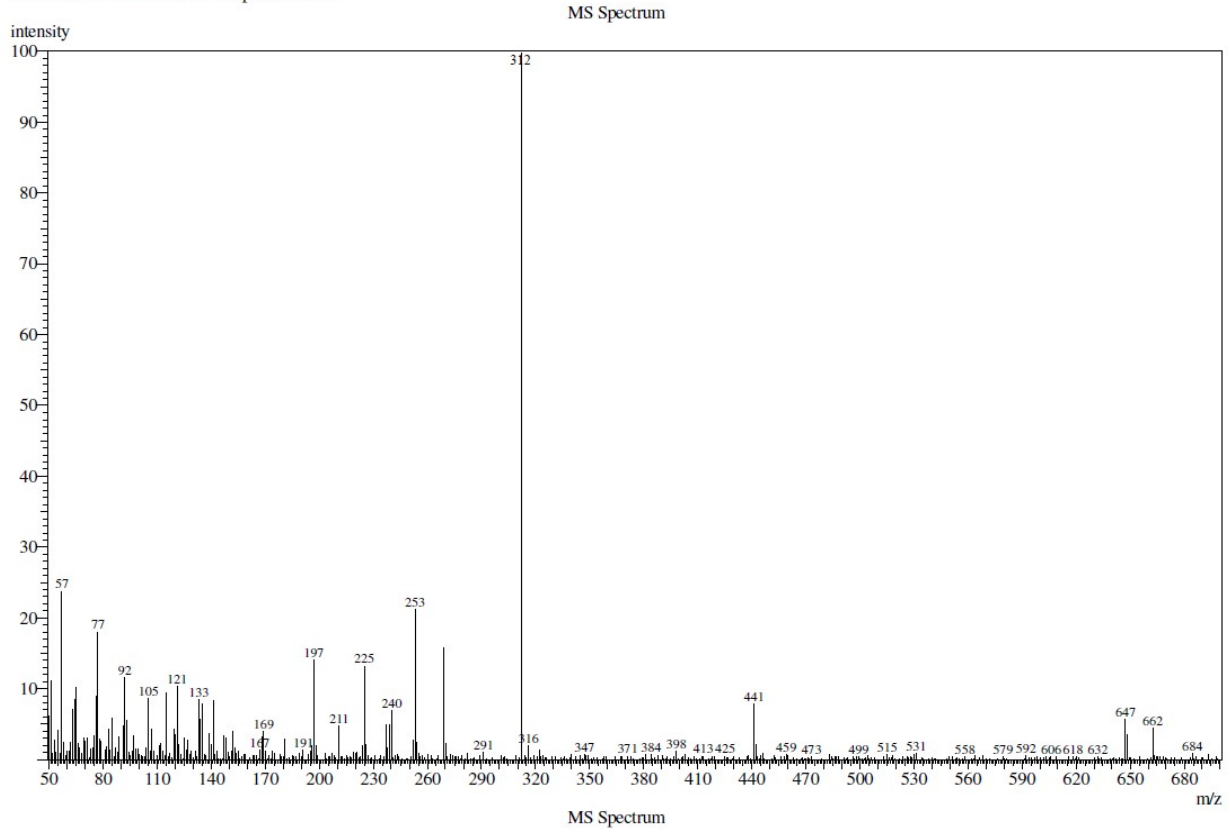


¹³C NMR Spectra (CDCl₃) of 3d

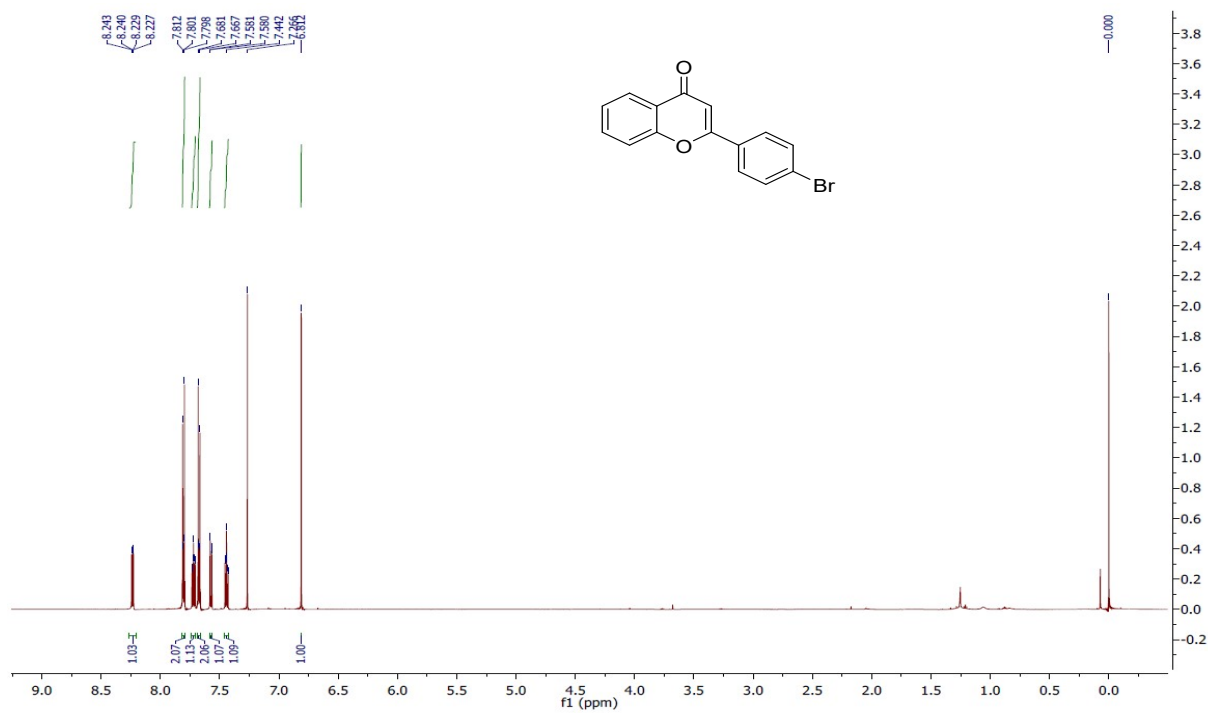


Mass Spectra of 3d

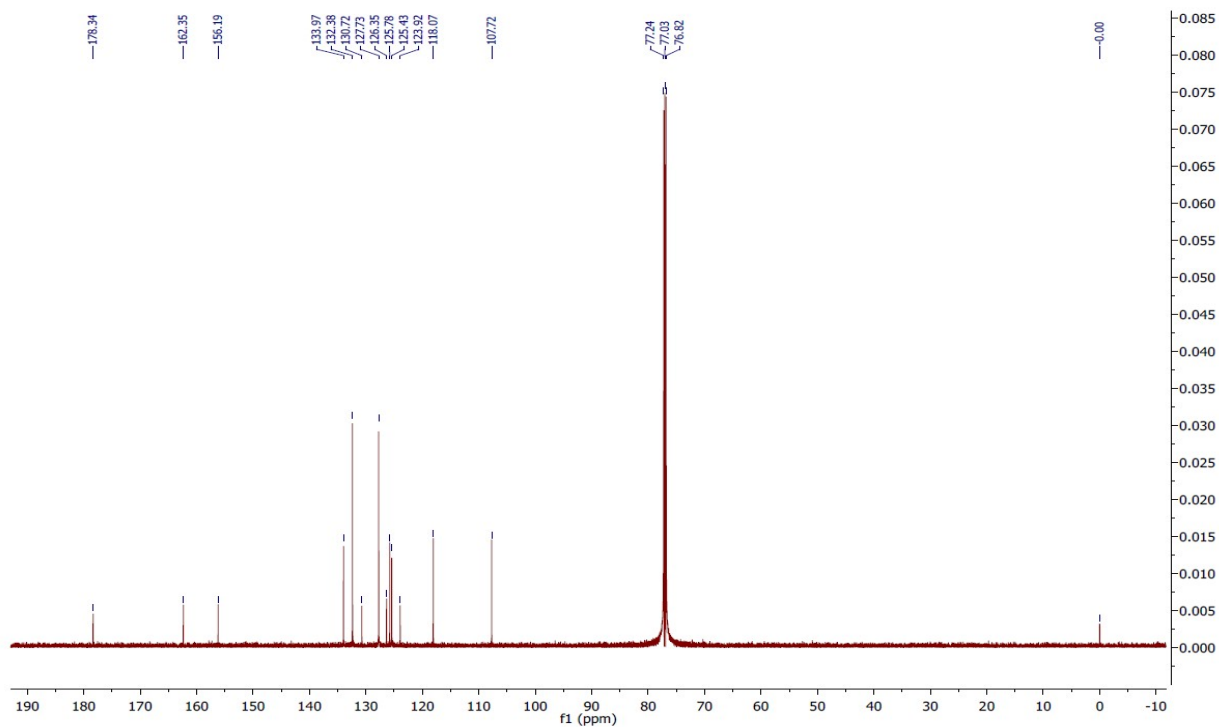
Line#:1 R.Time:4.9150(Scan#:684)
MassPeaks:576
RawMode:Averaged 4.9100-4.9200(683-685) BasePeak:268.1000(5803)
BG Mode:Calc. from Peak Group 1 - Event 1



¹H NMR Spectra (CDCl₃) of 3e



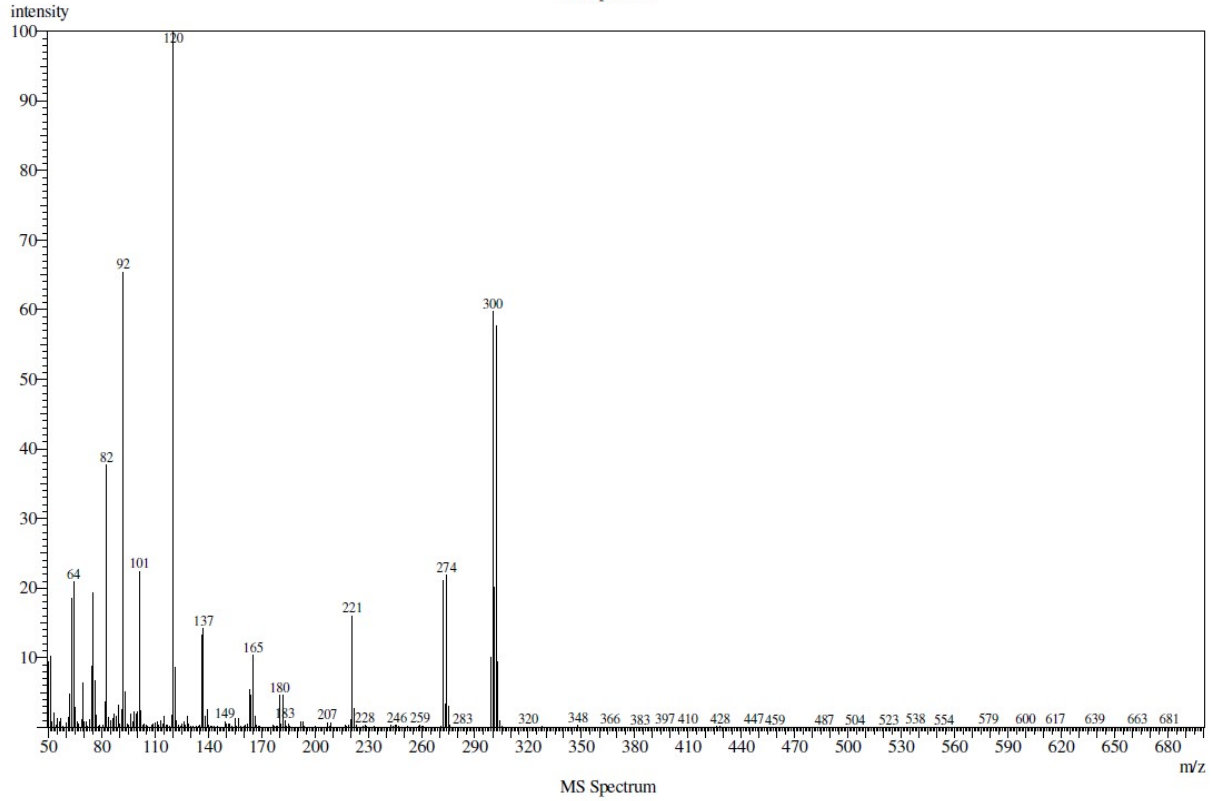
¹³C NMR Spectra (CDCl₃) of 3e



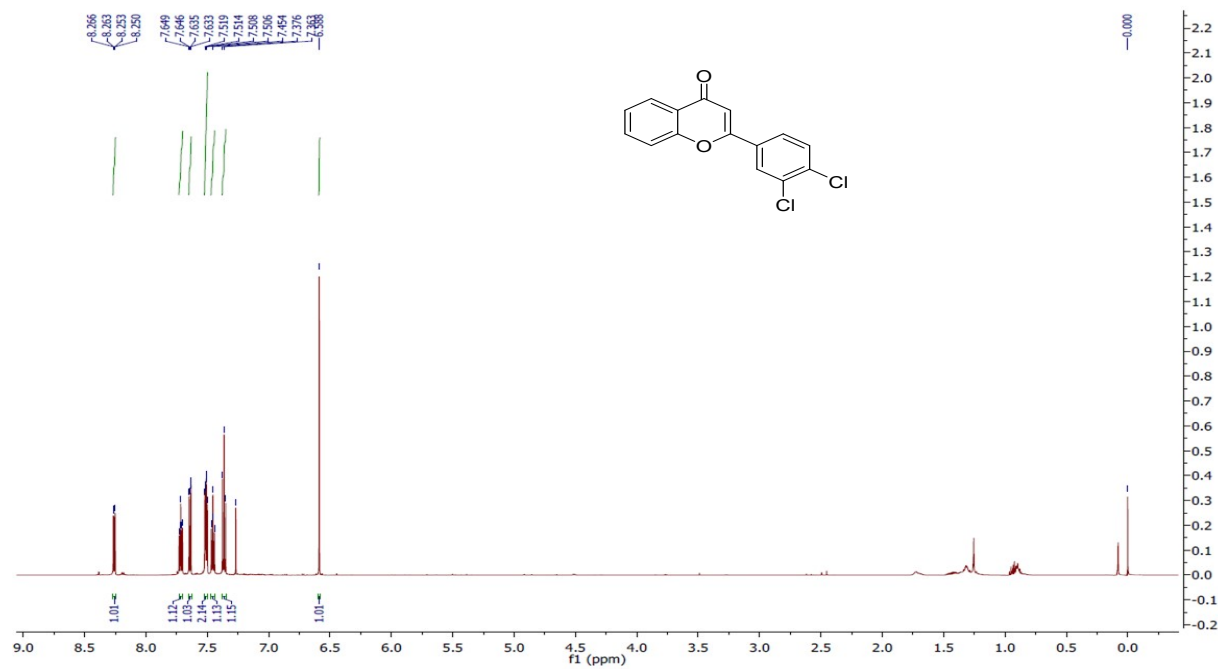
Mass Spectra of 3e

Line#:1 R.Time:5.6050(Scan#:822)
MassPeaks:605
RawMode:Averaged 5.6000-5.6100(821-823) BasePeak:120.1000(114197)
BG Mode:Calc. from Peak Group 1 - Event 1

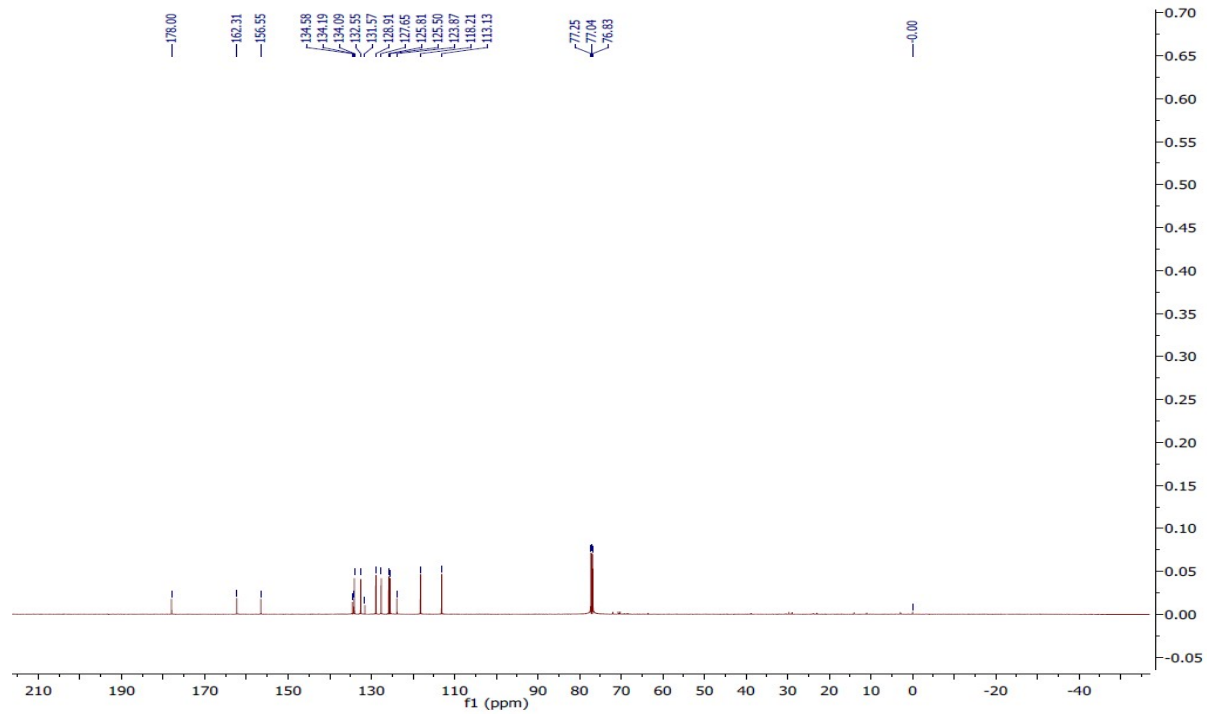
MS Spectrum



¹H NMR Spectra (CDCl₃) of 3f



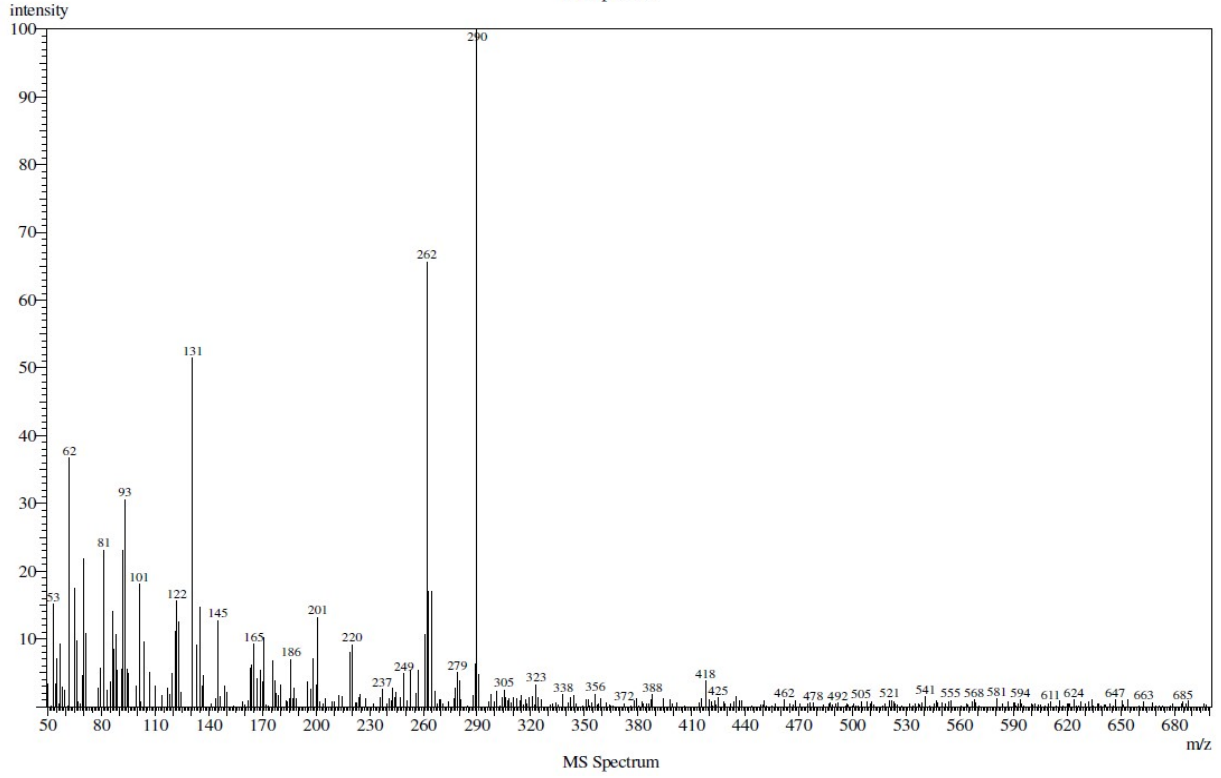
¹³C NMR Spectra (CDCl₃) of 3f



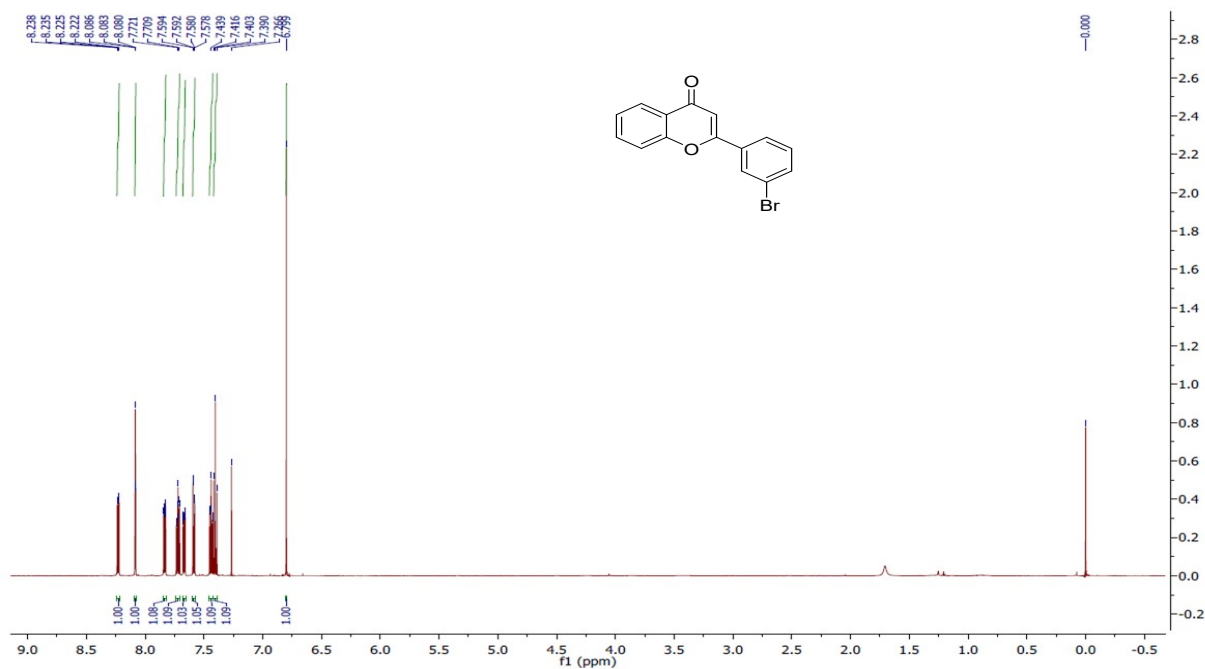
Mass Spectra of 3f

Line#:1 R.Time:5.0100(Scan#:703)
MassPeaks:470
RawMode:Averaged 5.0050-5.0150(702-704) BasePeak:290.0000(3702)
BG Mode:Calc. from Peak Group 1 - Event 1

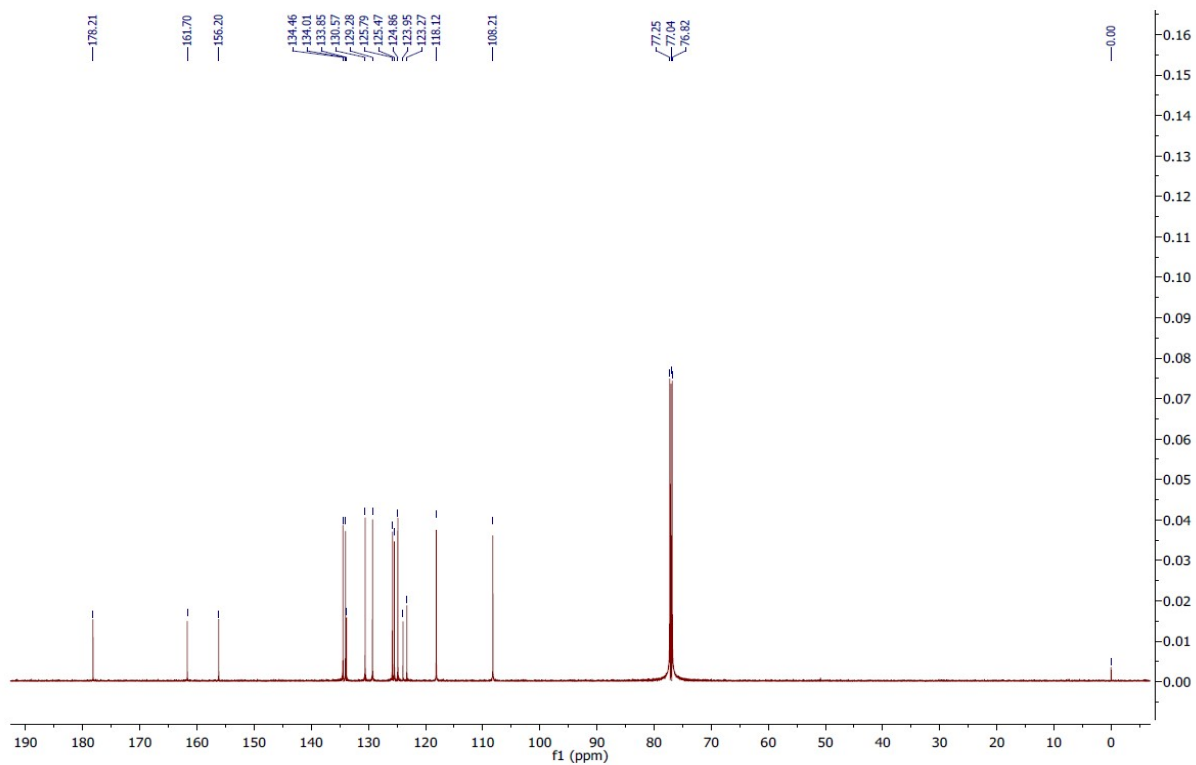
MS Spectrum



¹H NMR Spectra (CDCl₃) of 3g

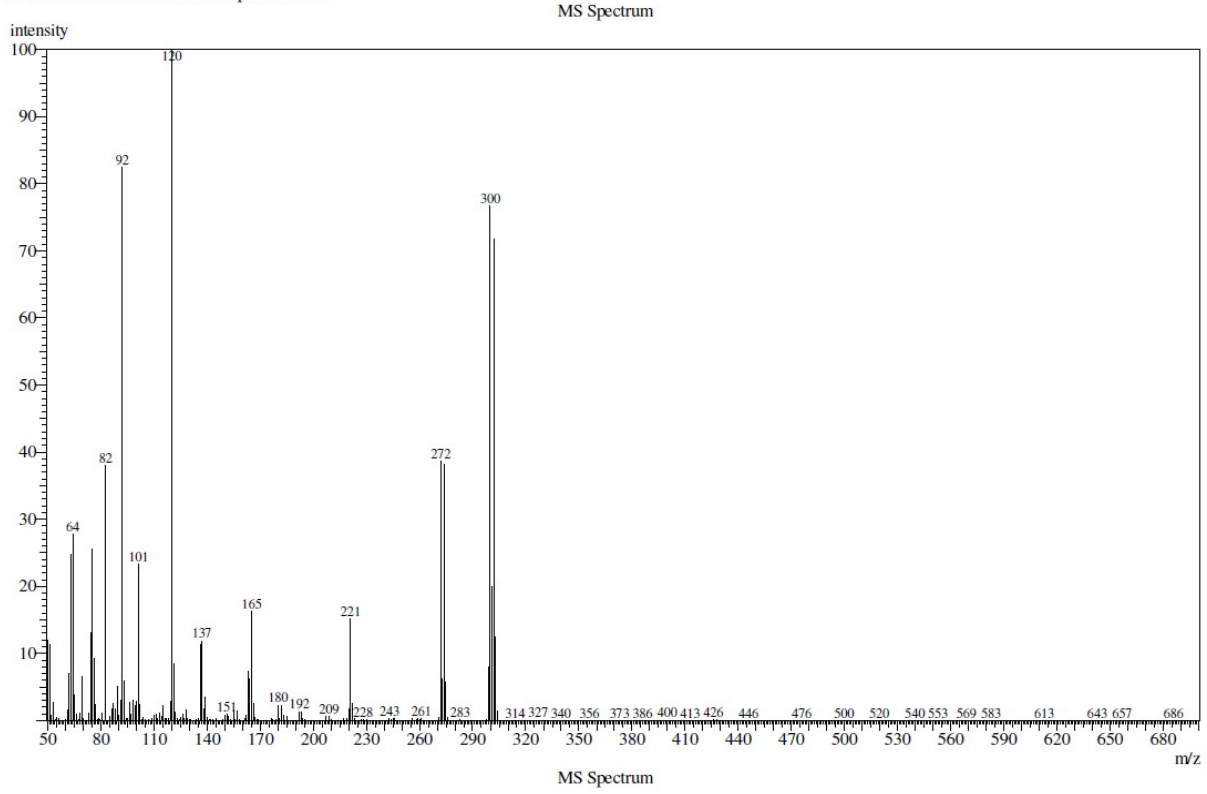


¹³C NMR Spectra (CDCl₃) of 3g

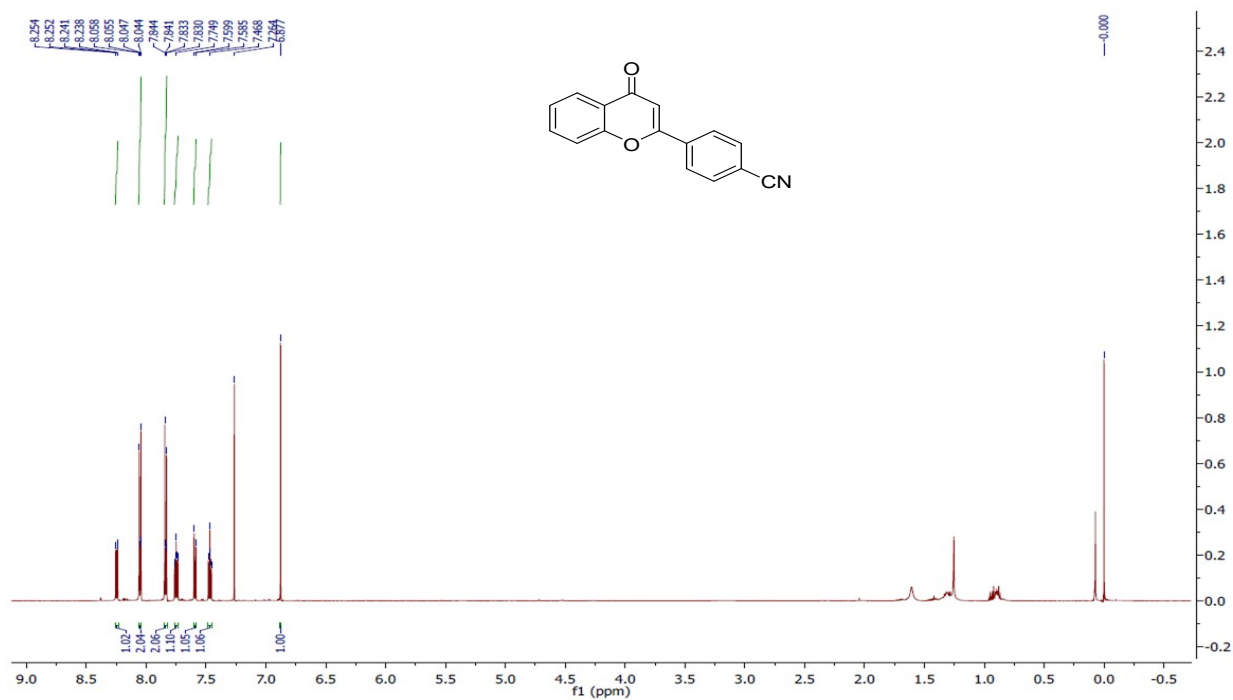


Mass Spectra of 3g

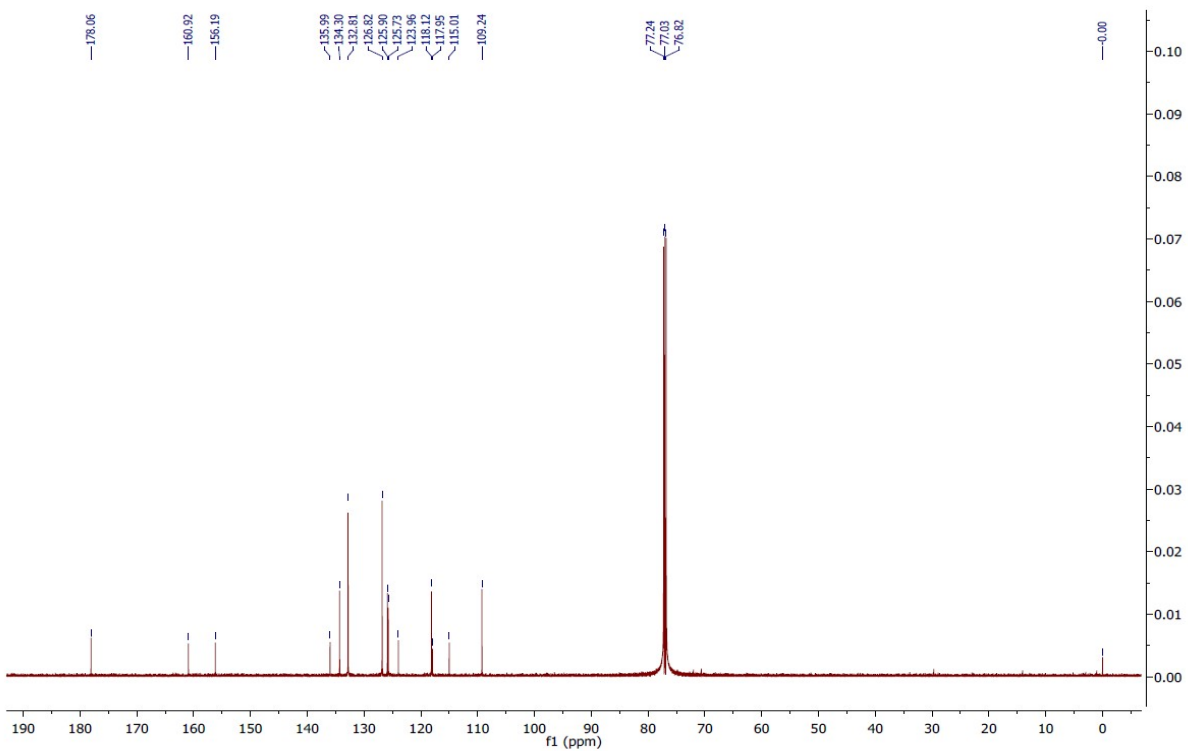
Line#: 1 R.Time: 5.3750(Scan#: 776)
MassPeaks: 577
RawMode: Averaged 5.3700-5.3800(775-777) BasePeak: 120.0500(526009)
BG Mode: Calc. from Peak Group 1 - Event 1



¹H NMR Spectra (CDCl₃) of 3h



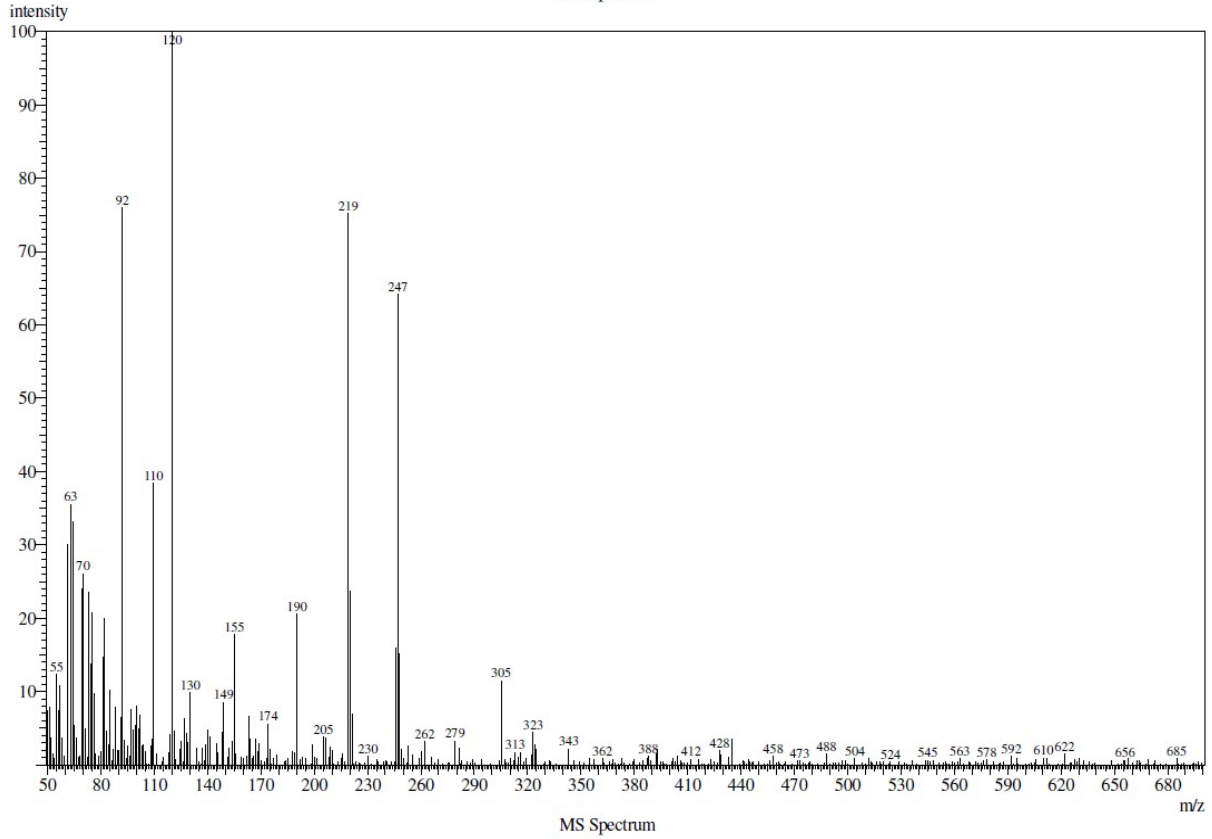
¹³C NMR Spectra (CDCl₃) of 3h



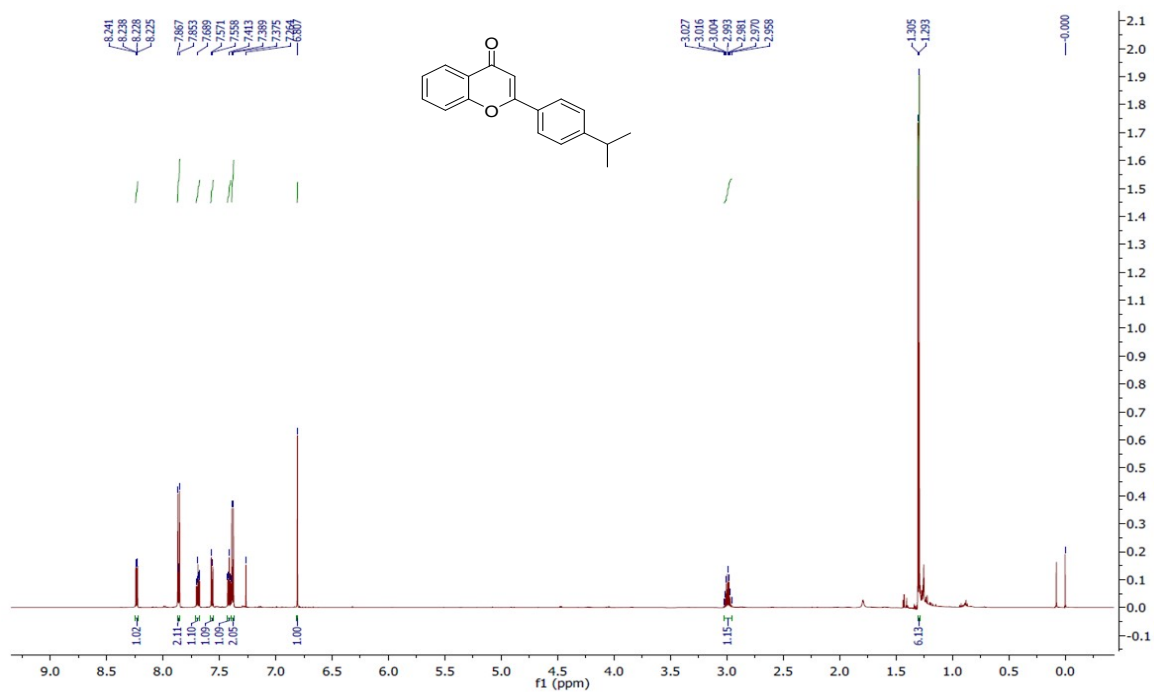
Mass Spectra of 3h

Line#:1 R.Time:3.8750(Scan#:476)
MassPeaks:511
RawMode:Averaged 3.8700-3.8800(475-477) BasePeak:120.0500(4116)
BG Mode:Calc. from Peak Group 1 - Event 1

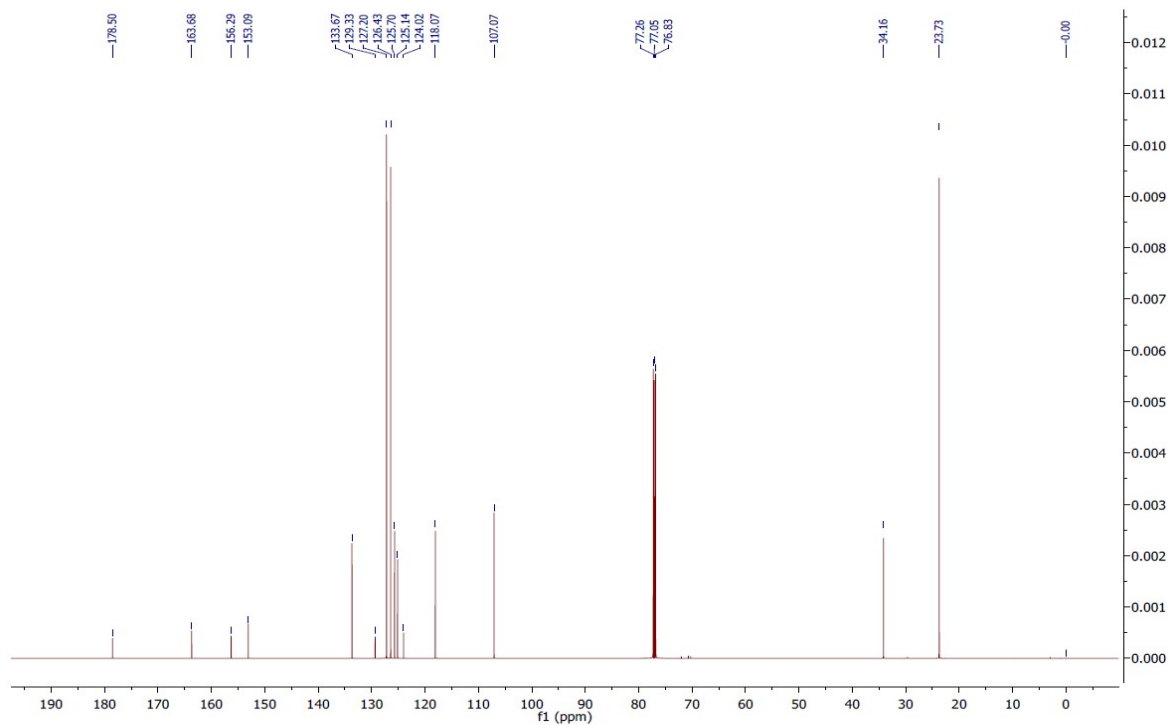
MS Spectrum



¹H NMR Spectra (CDCl₃) of 3i

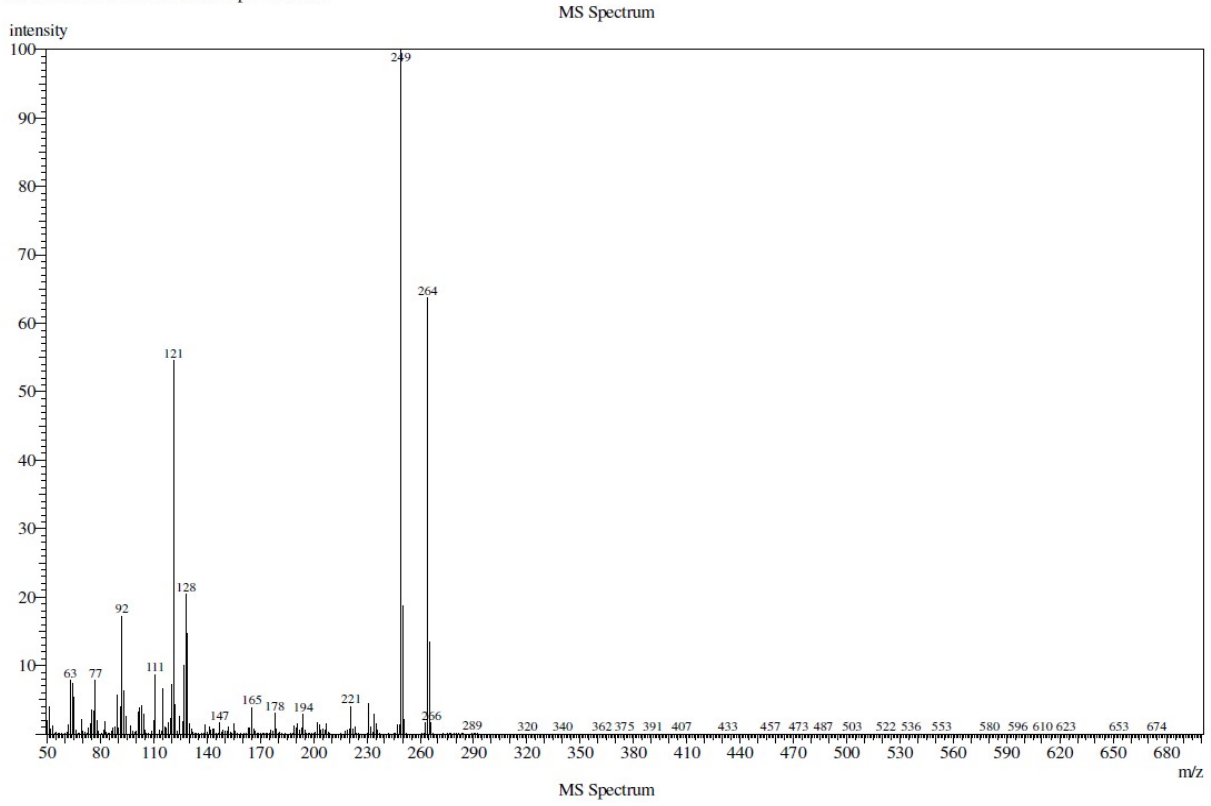


¹³C NMR Spectra (CDCl₃) of 3i

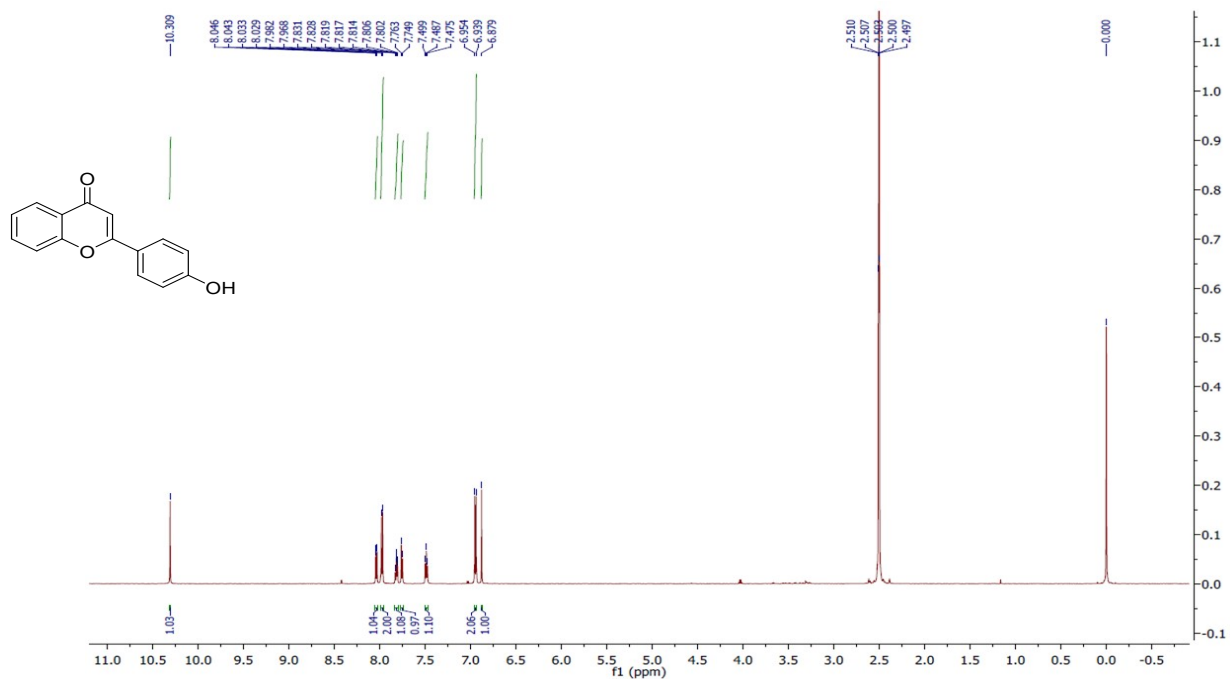


Mass Spectra of 3i

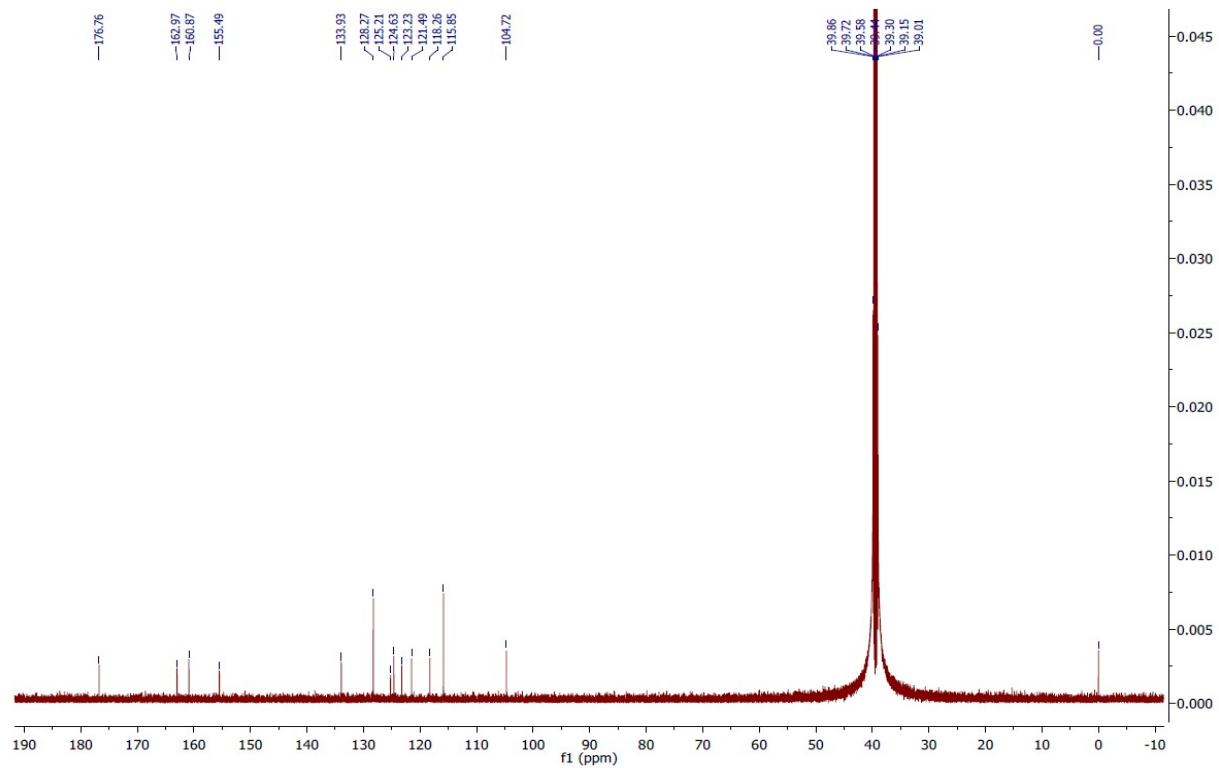
Line#:1 R.Time:5.5700(Scan#:815)
MassPeaks:590
RawMode:Averaged 5.5650-5.5750(814-816) BasePeak:249.0500(2079753)
BG Mode:Calc. from Peak Group 1 - Event 1



¹H NMR Spectra (DMSO) of 3j

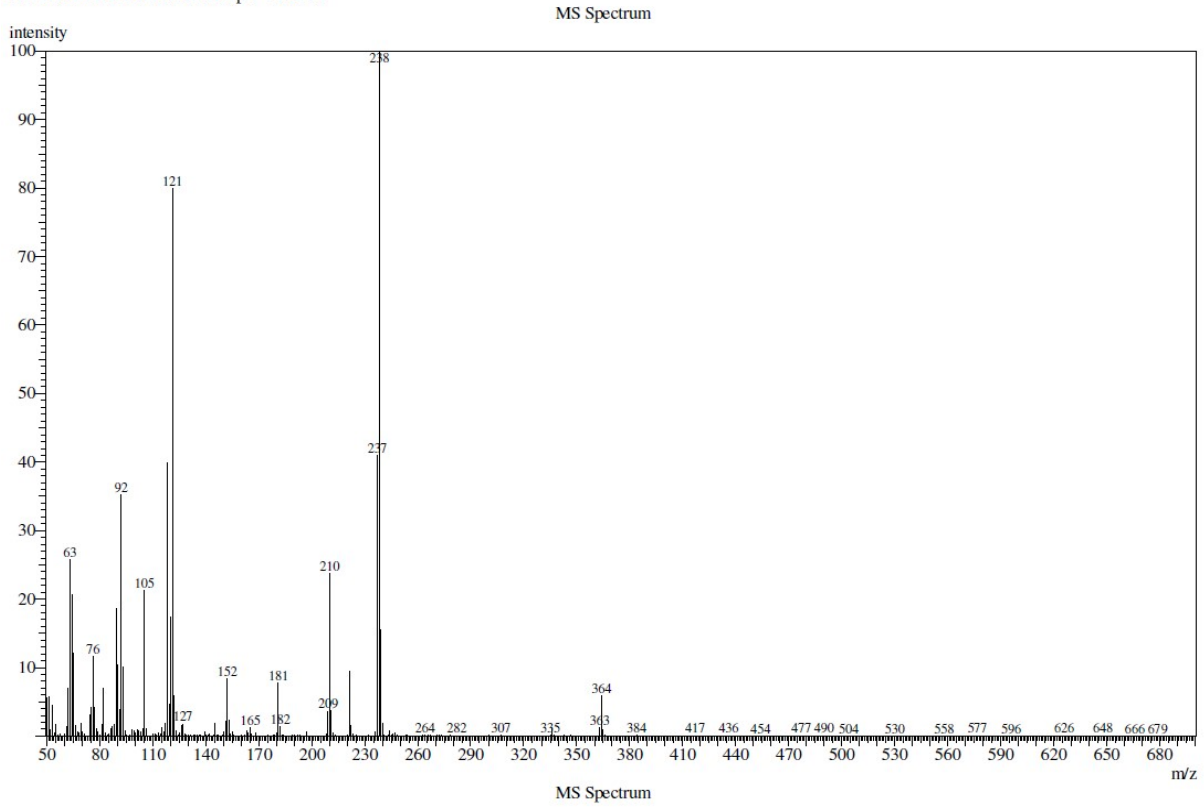


¹³C NMR Spectra (DMSO) of 3j

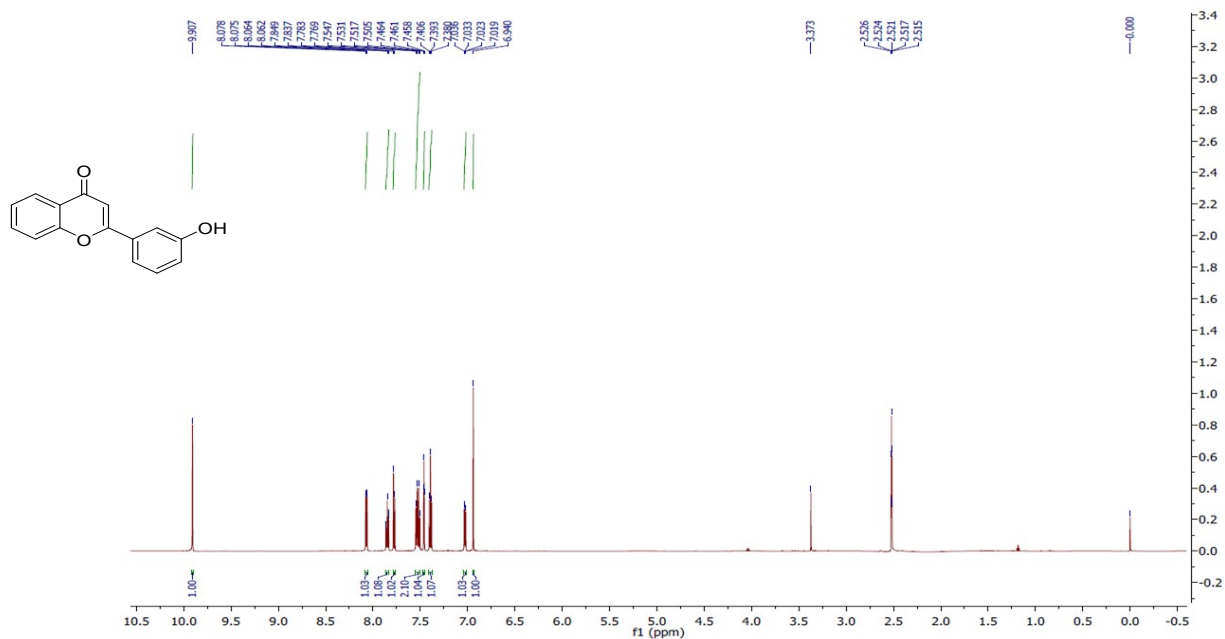


Mass Spectra of 3j

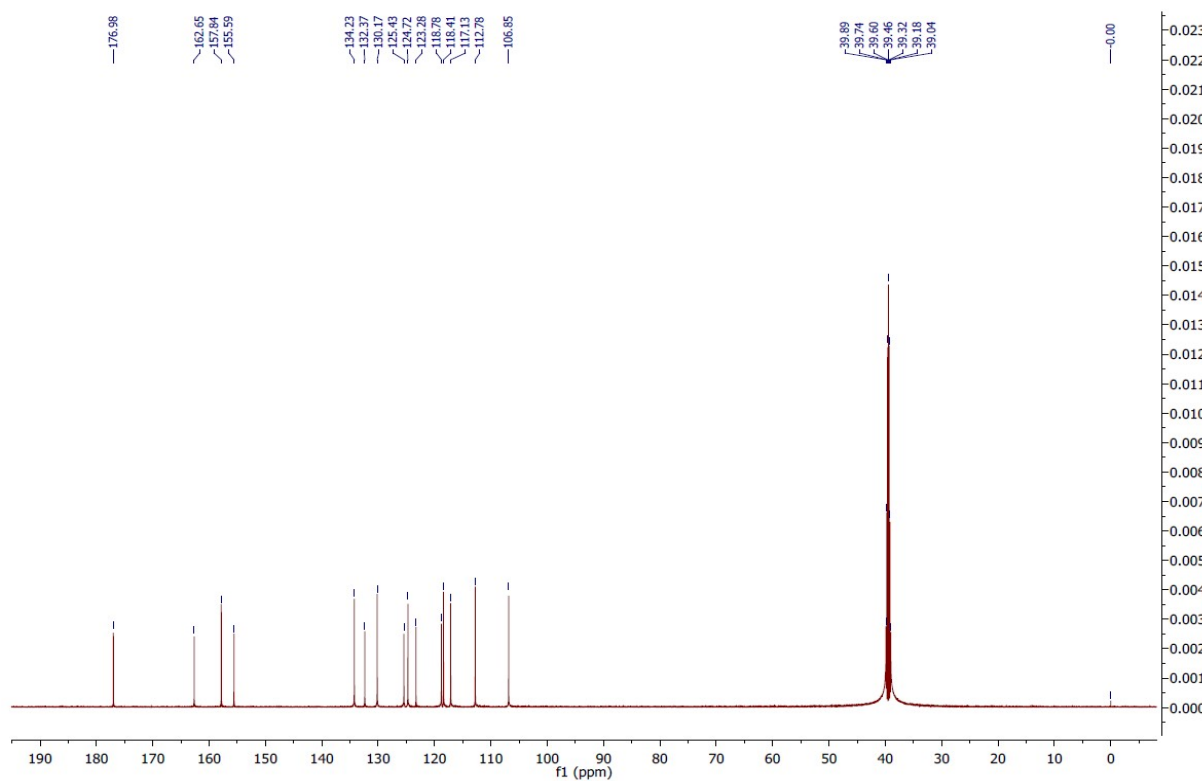
Line#:2 R.Time:8.4100(Scan#:1383)
MassPeaks:542
RawMode:Averaged 8.4050-8.4150(1382-1384) BasePeak:238.1000(175416)
BG Mode:Calc. from Peak Group 1 - Event 1



¹H NMR Spectra (DMSO) of 3k

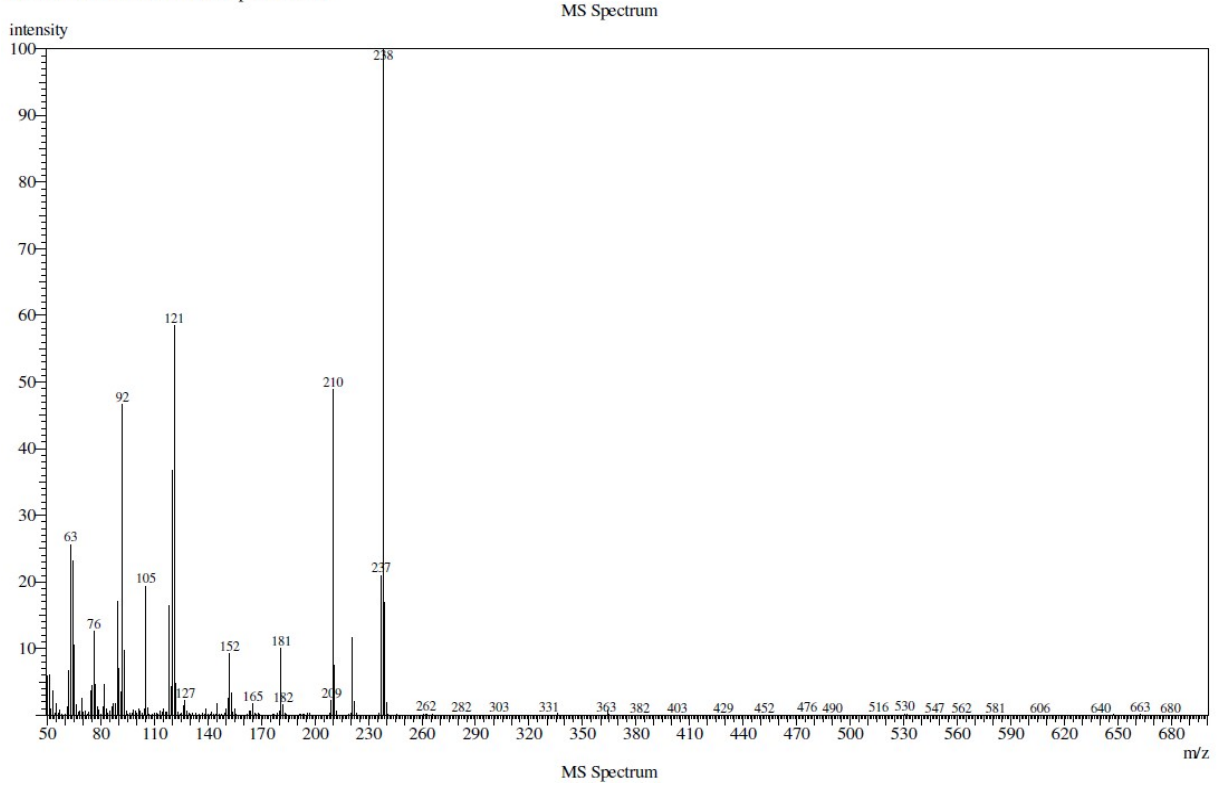


¹³C NMR Spectra (DMSO) of 3k

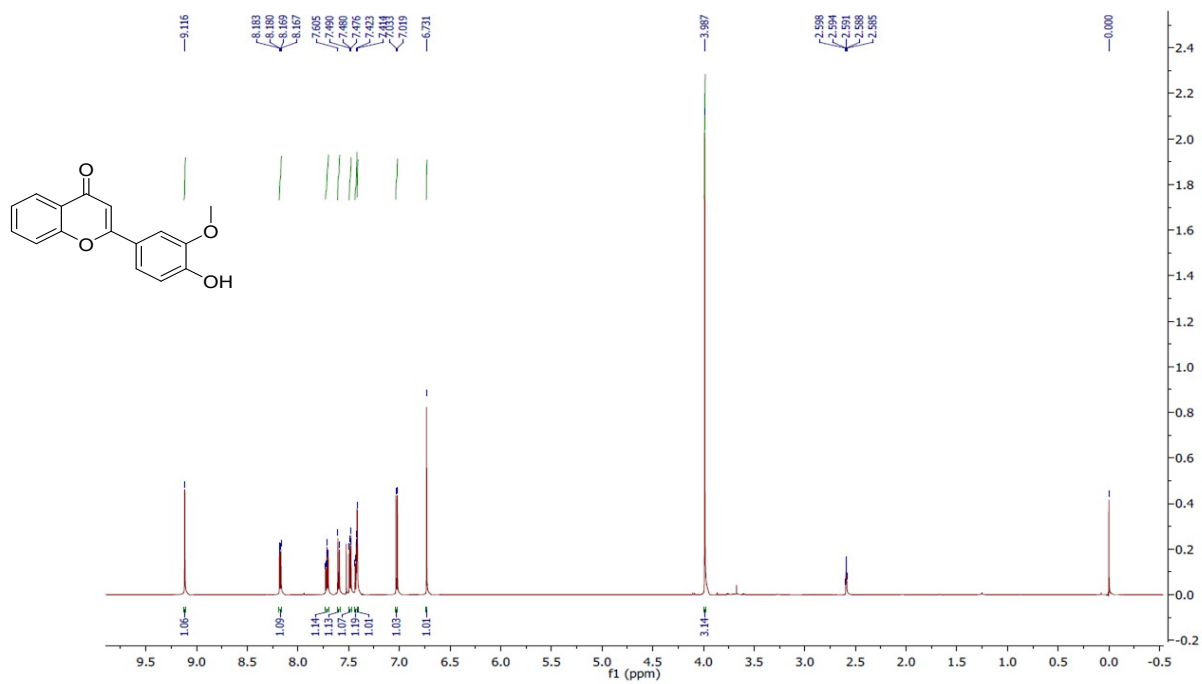


Mass Spectra of 3k

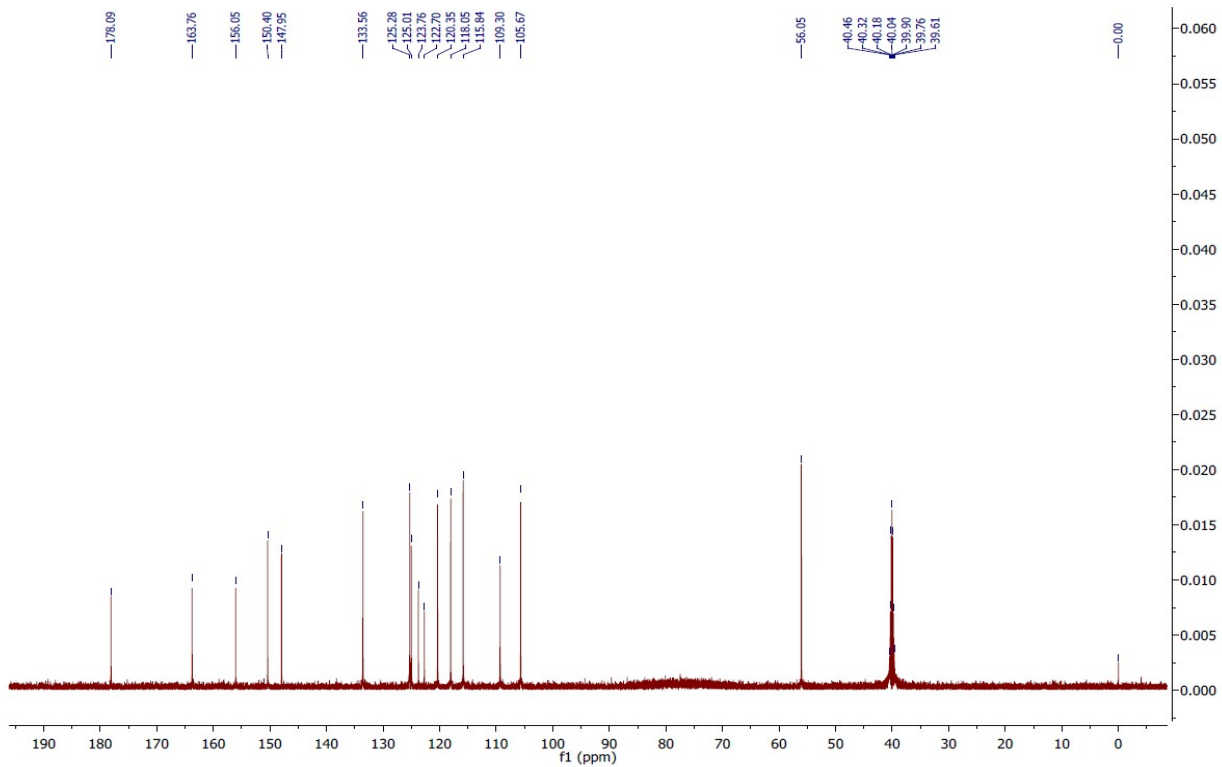
Line#:1 R.Time:6.8700(Scan#:1075)
MassPeaks:627
RawMode:Averaged 6.8650-6.8750(1074-1076) BasePeak:238.1000(452376)
BG Mode:Calc. from Peak Group 1 - Event 1



¹H NMR Spectra (DMSO) of 31



¹³C NMR Spectra (DMSO) of 31



Mass Spectra of 3I

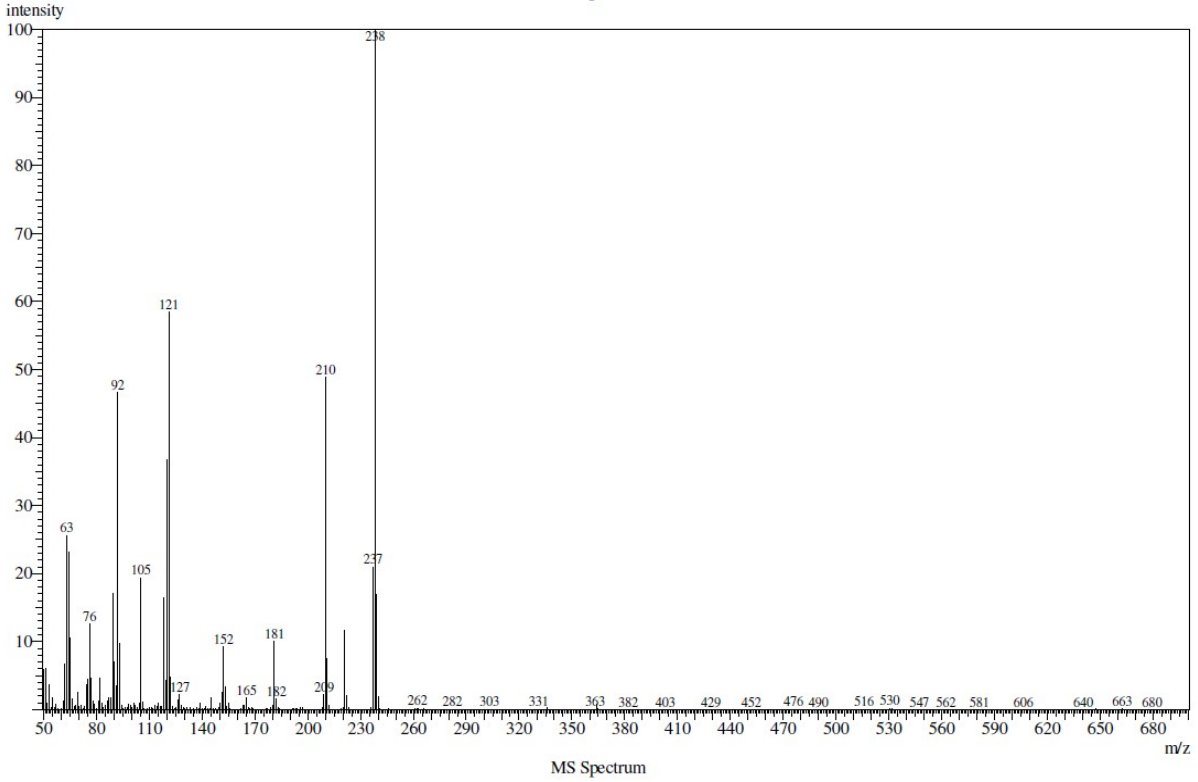
Line#:1 R.Time:6.8700(Scan#:1075)

MassPeaks:627

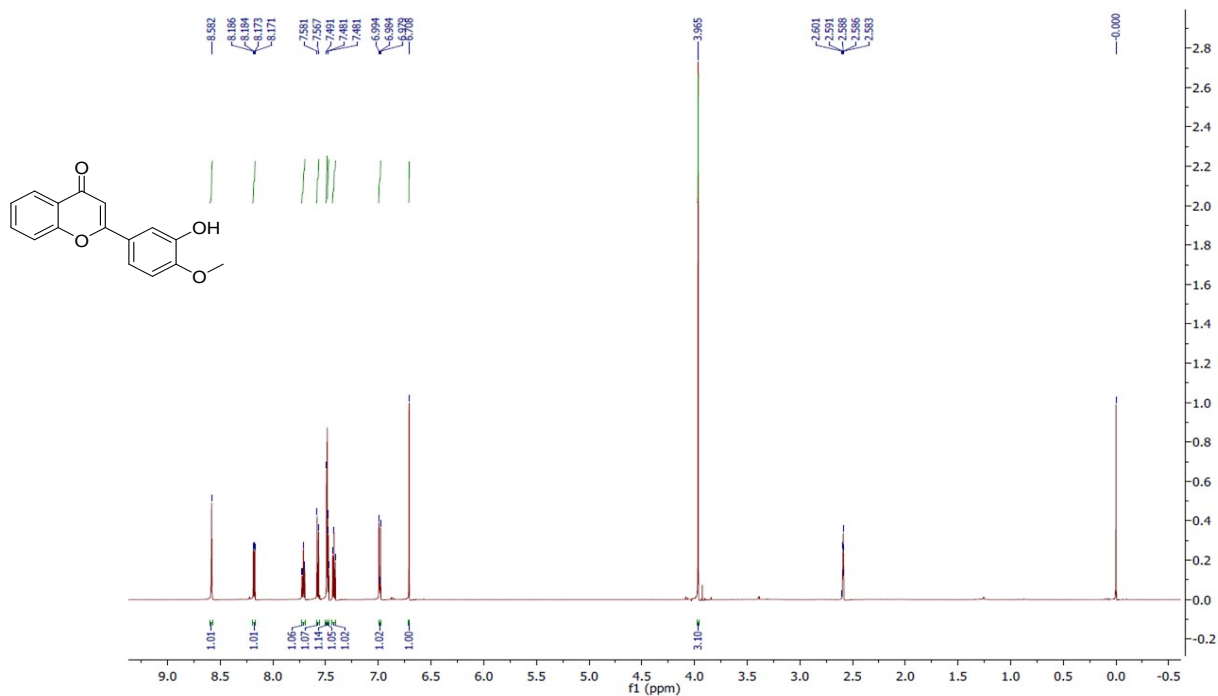
RawMode:Averaged 6.8650-6.8750(1074-1076) BasePeak:238.1000(452376)

BG Mode:Calc. from Peak Group 1 - Event 1

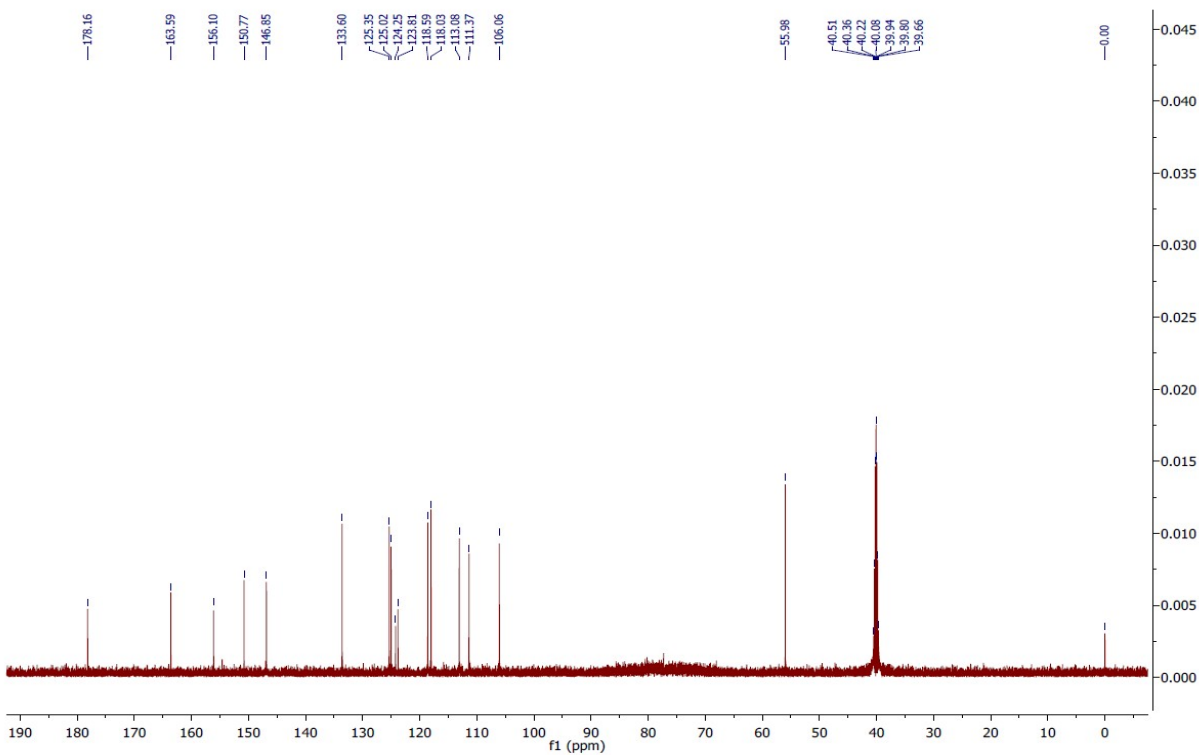
MS Spectrum



¹H NMR Spectra (DMSO) of 3m

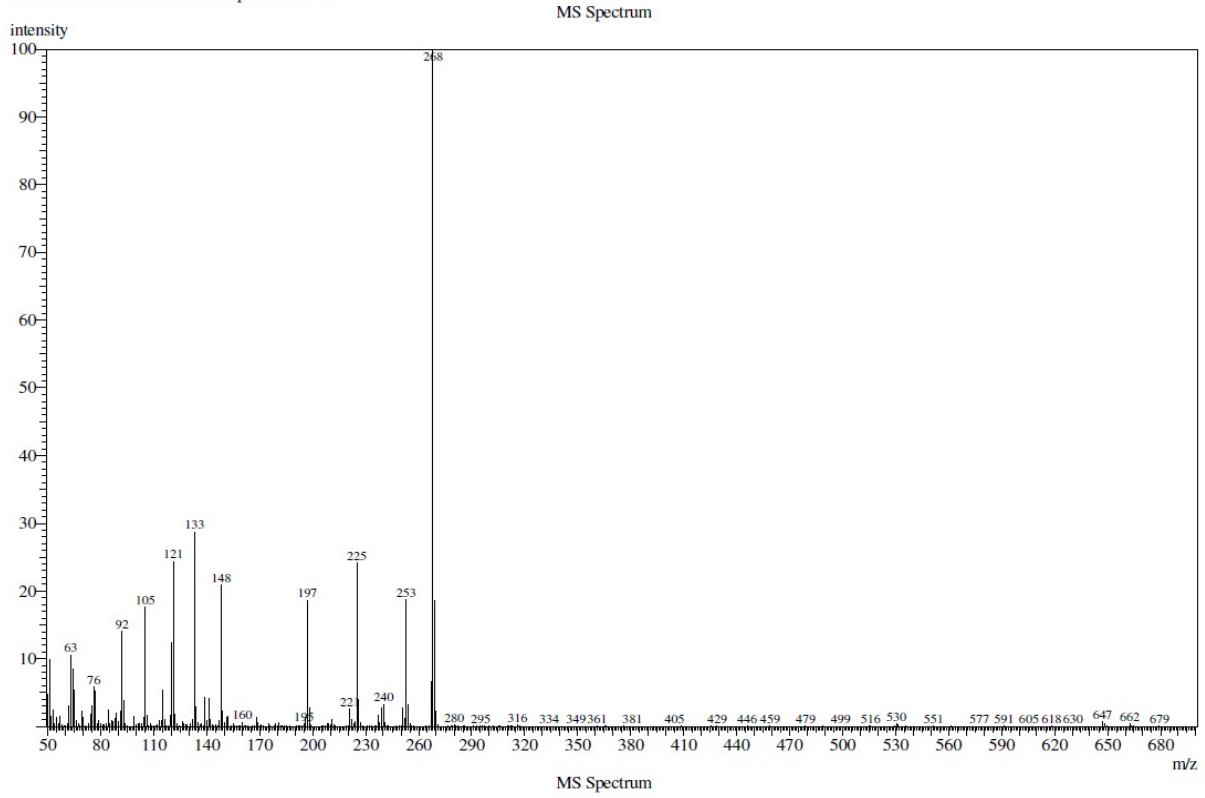


¹³C NMR Spectra (DMSO) of 3m

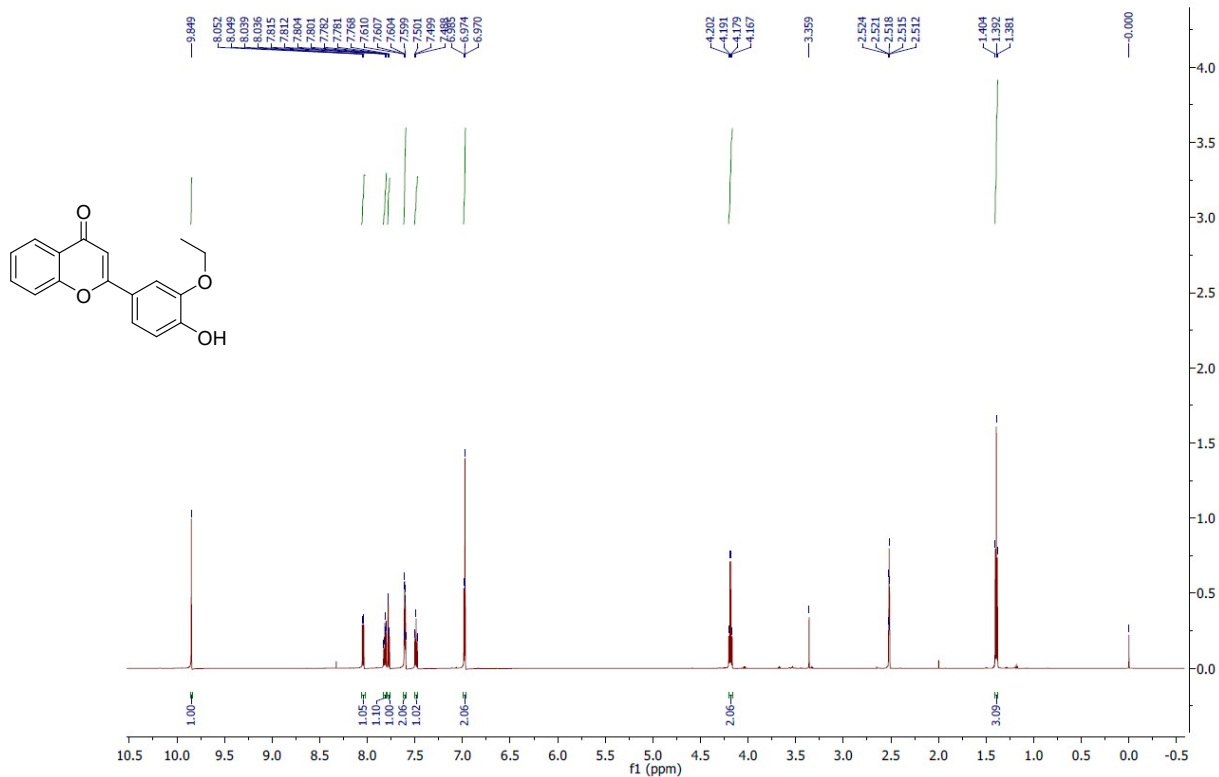


Mass Spectra of 3m

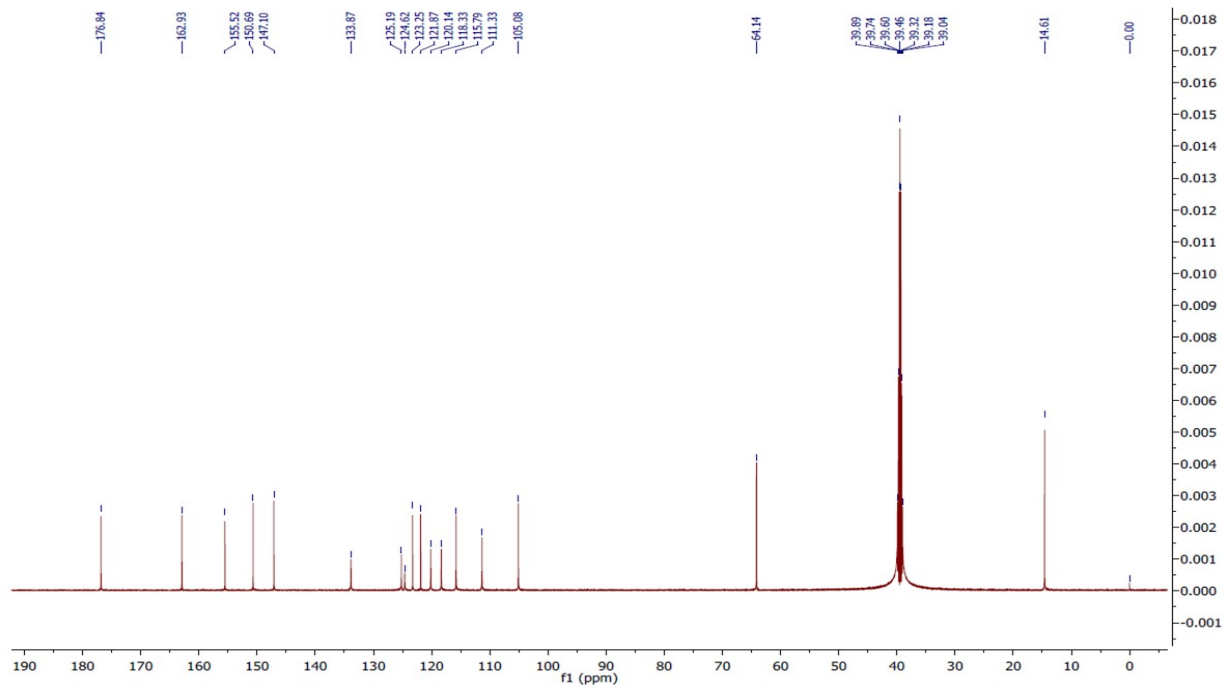
Line#:2 R.Time:6.8550(Scan#:1072)
MassPeaks:501
RawMode:Averaged 6.8500-6.8600(1071-1073) BasePeak:268.0500(188016)
BG Mode:Calc. from Peak Group 1 - Event 1



¹H NMR Spectra (DMSO) of 3n



¹³C NMR Spectra (DMSO) of 3n



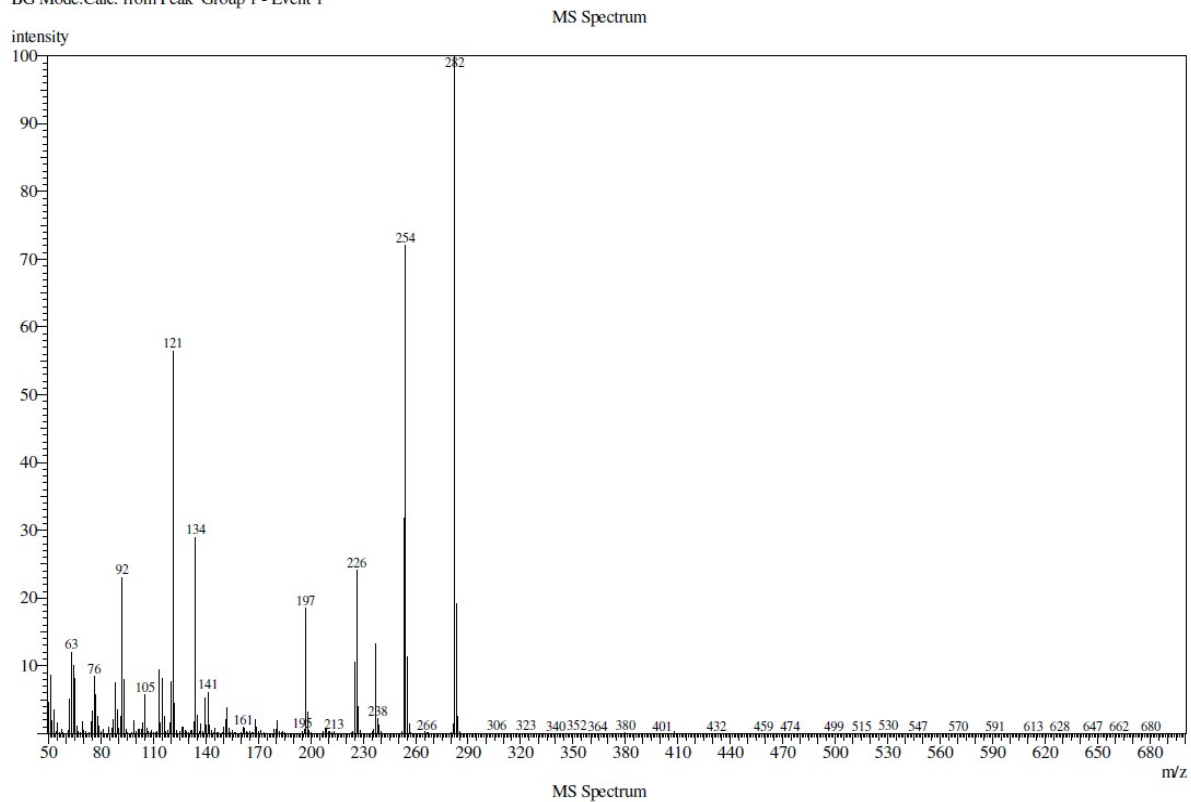
Mass Spectra of 3n

Line#:1 R.Time:7.3800(Scan#:1177)

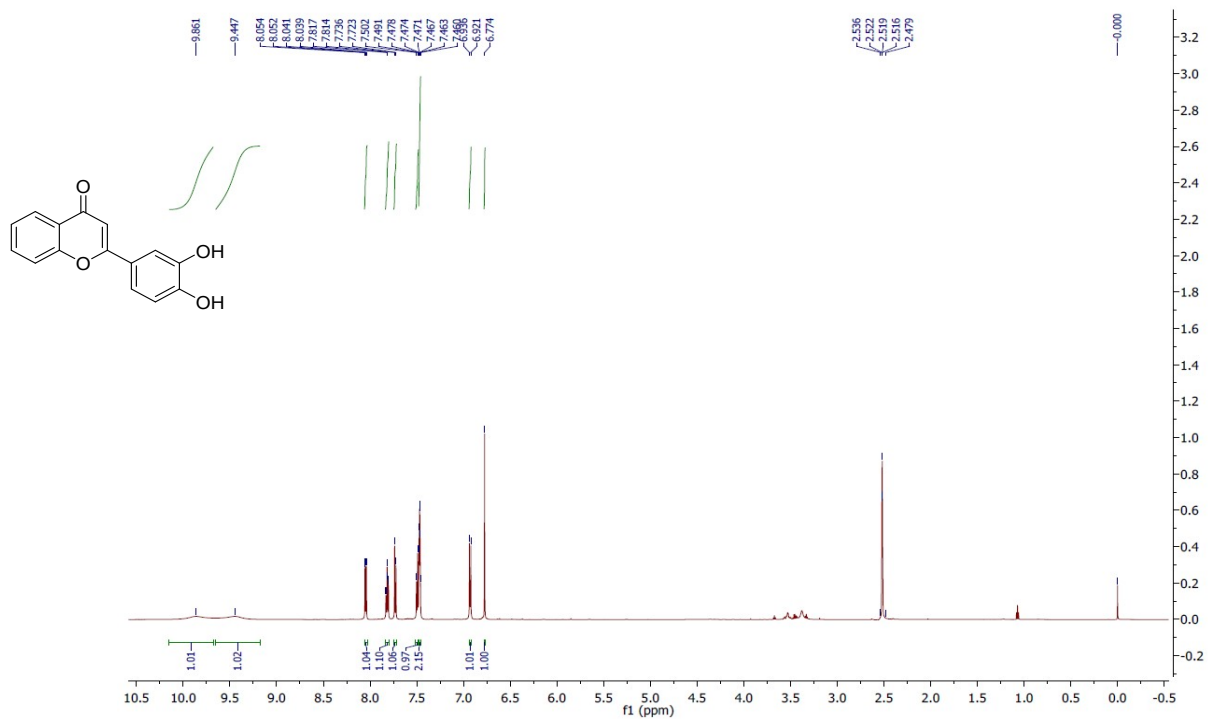
MassPeaks:621

RawMode:Averaged 7.3750-7.3850(1176-1178) BasePeak:282.1500(1742560)

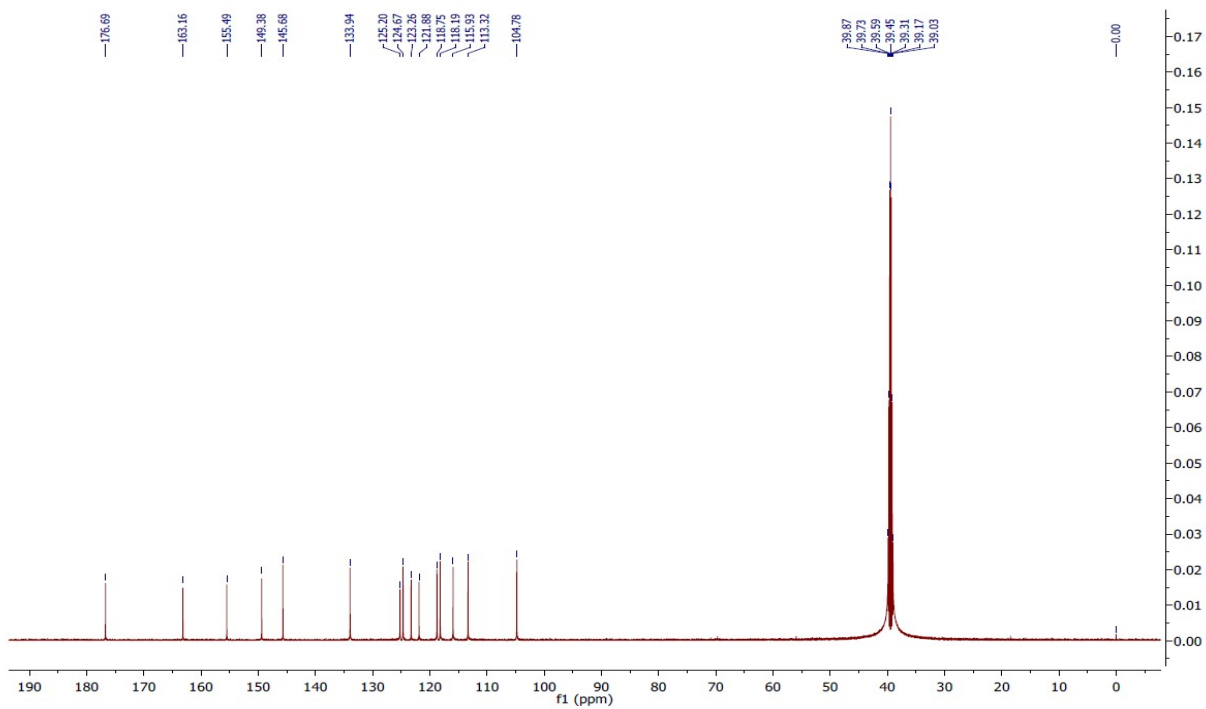
BG Mode:Calc. from Peak Group 1 - Event 1



¹H NMR Spectra (DMSO) of 3o

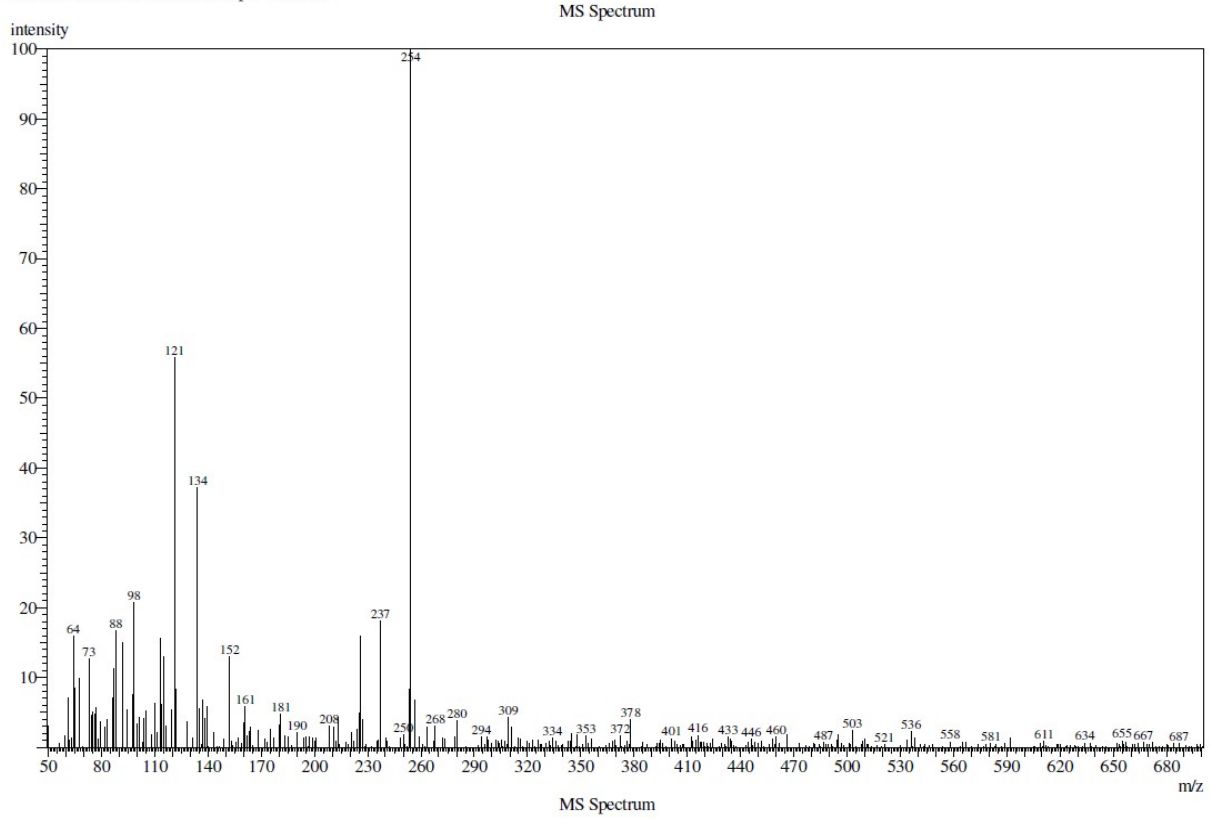


¹³C NMR Spectra (DMSO) of 3o



Mass Spectra of 3o

Line#:1 R.Time:7.2600(Scan#:1153)
MassPeaks:444
RawMode:Averaged 7.2550-7.2650(1152-1154) BasePeak:254.1000(3728)
BG Mode:Calc. from Peak Group 1 - Event 1



Mass Spectra of 3t

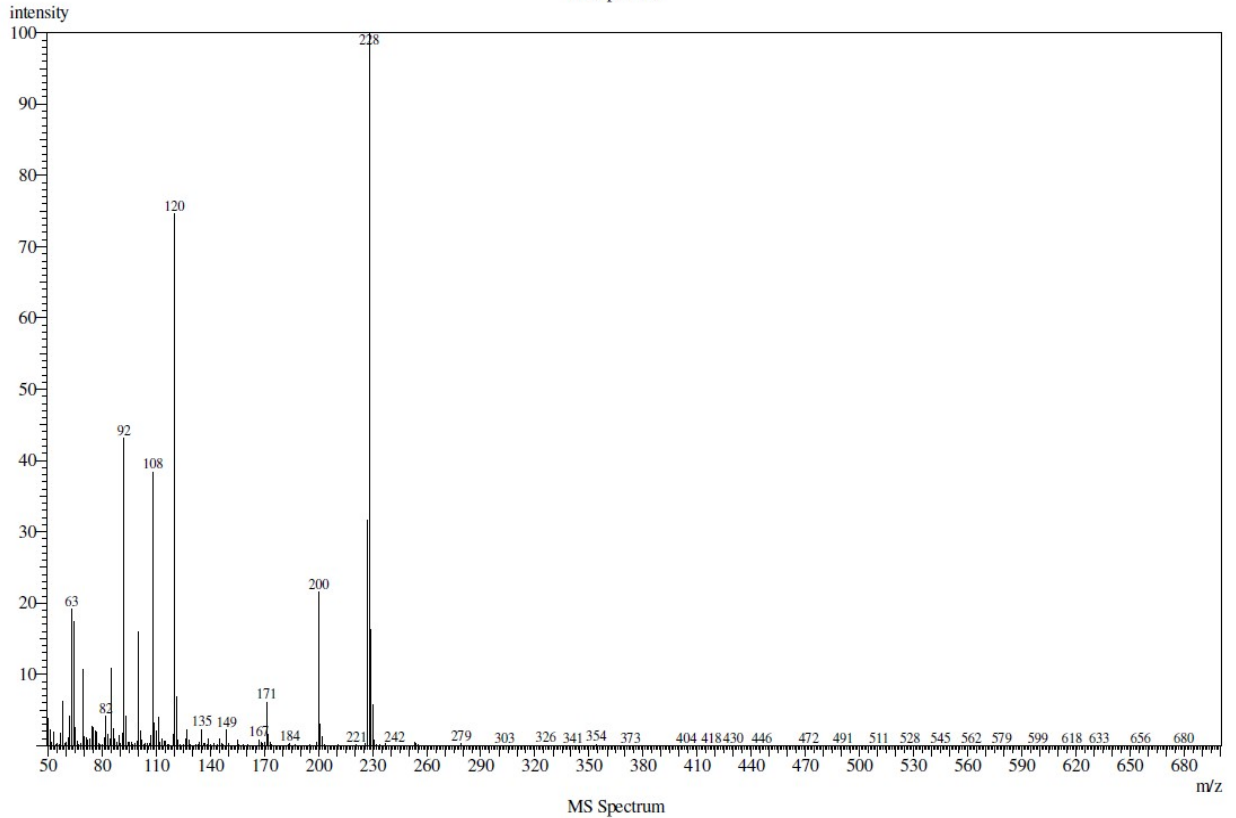
Line#:1 R.Time:2.6850(Scan#:238)

MassPeaks:572

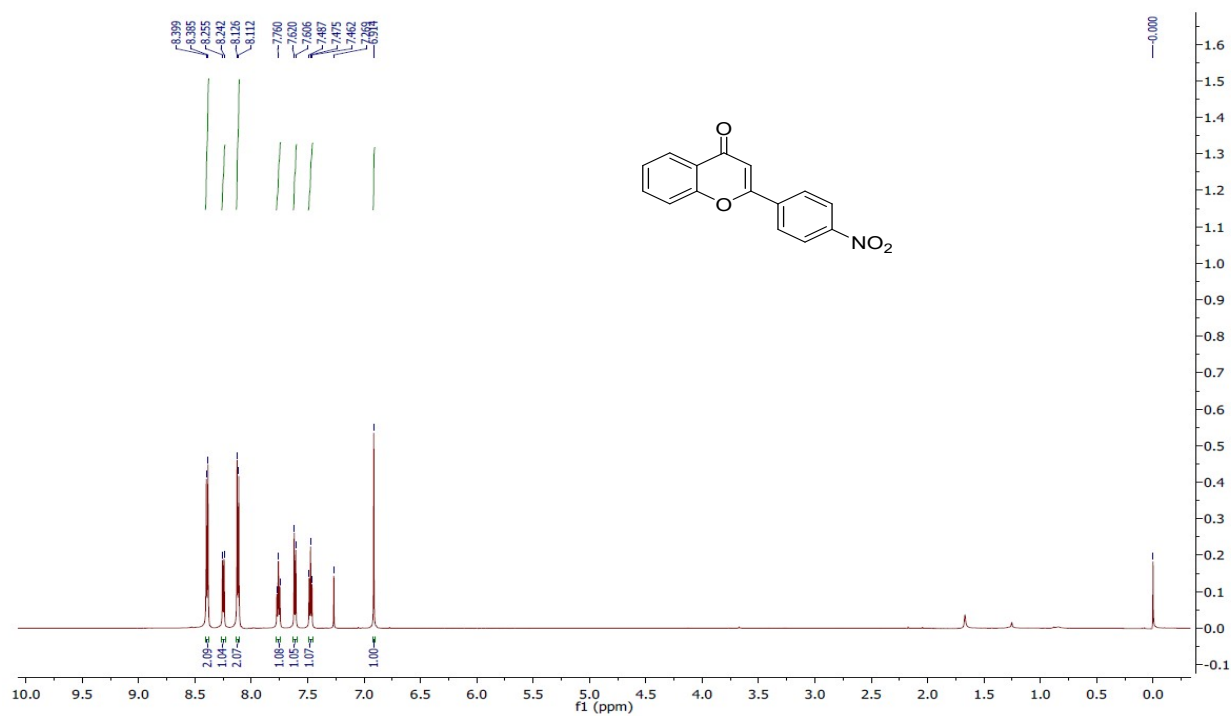
RawMode:Averaged 2.6800-2.6900(237-239) BasePeak:228.0000(882295)

BG Mode:Calc. from Peak Group 1 - Event 1

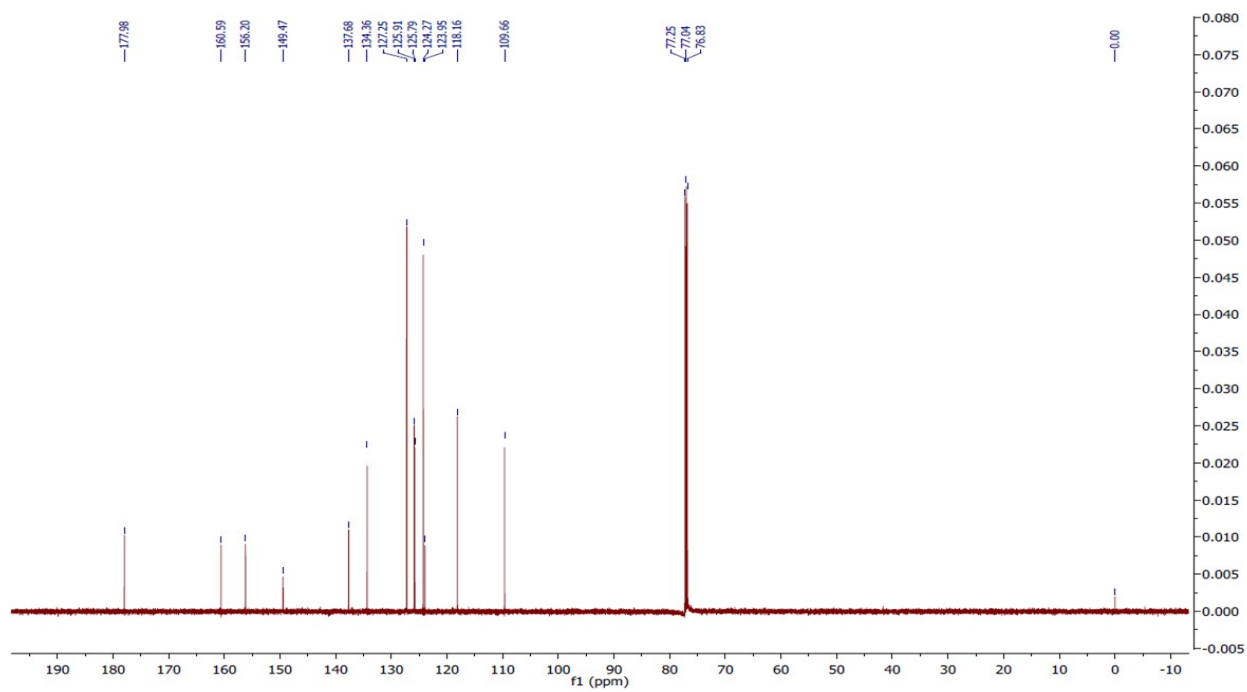
MS Spectrum



¹H NMR Spectra (CDCl₃) of 3u



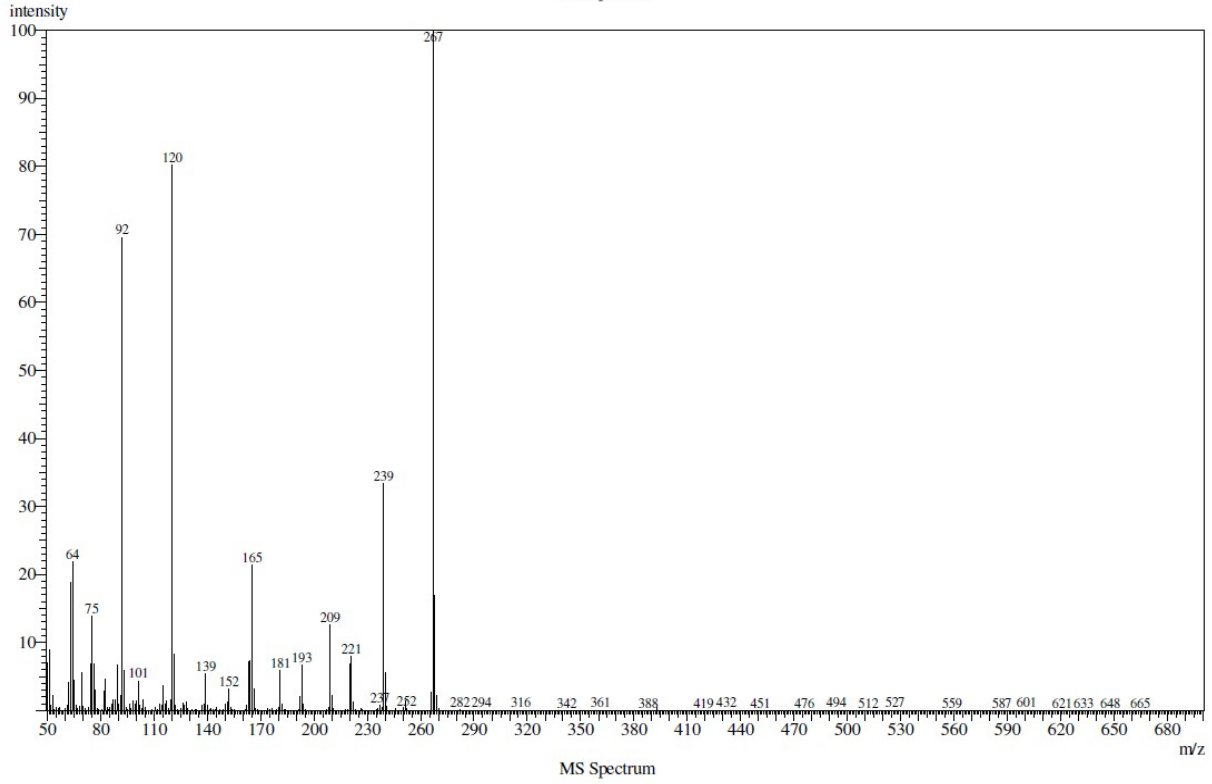
¹³C NMR Spectra (CDCl₃) of 3u



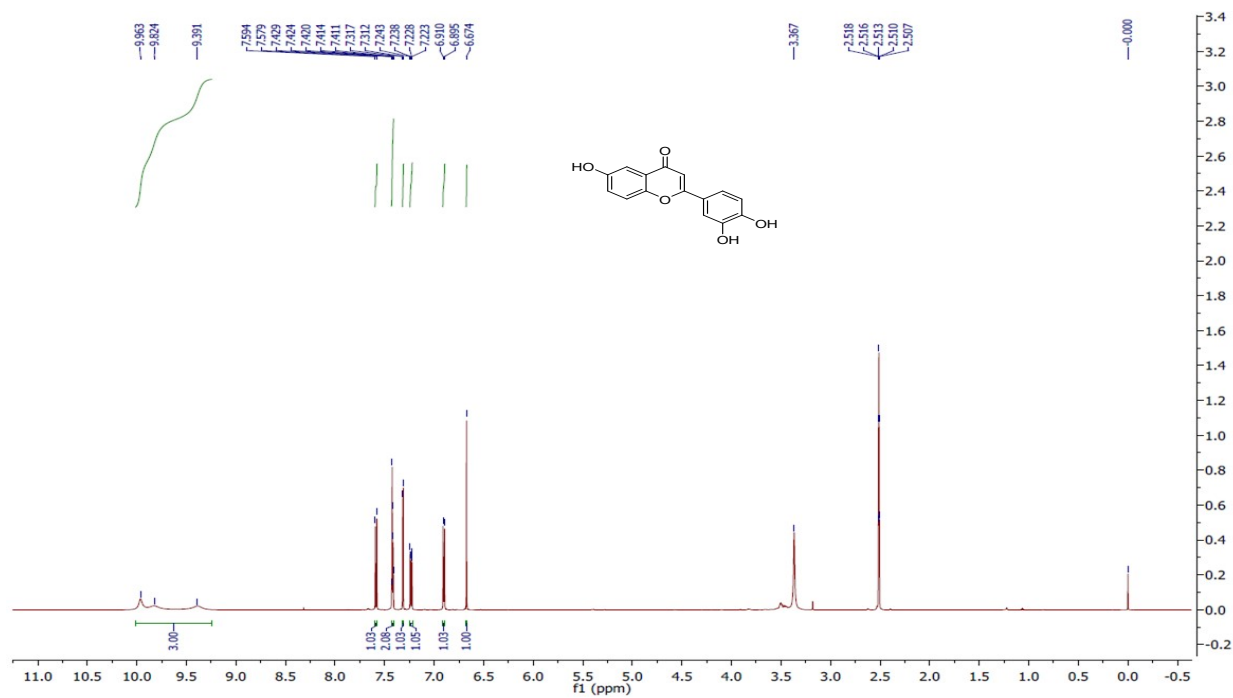
Mass Spectra of 3u

Line#:1 R.Time:6.3650(Scan#:974)
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RawMode:Averaged 6.3600-6.3700(973-975) BasePeak:267.1000(139936)
BG Mode:Calc. from Peak Group 1 - Event 1

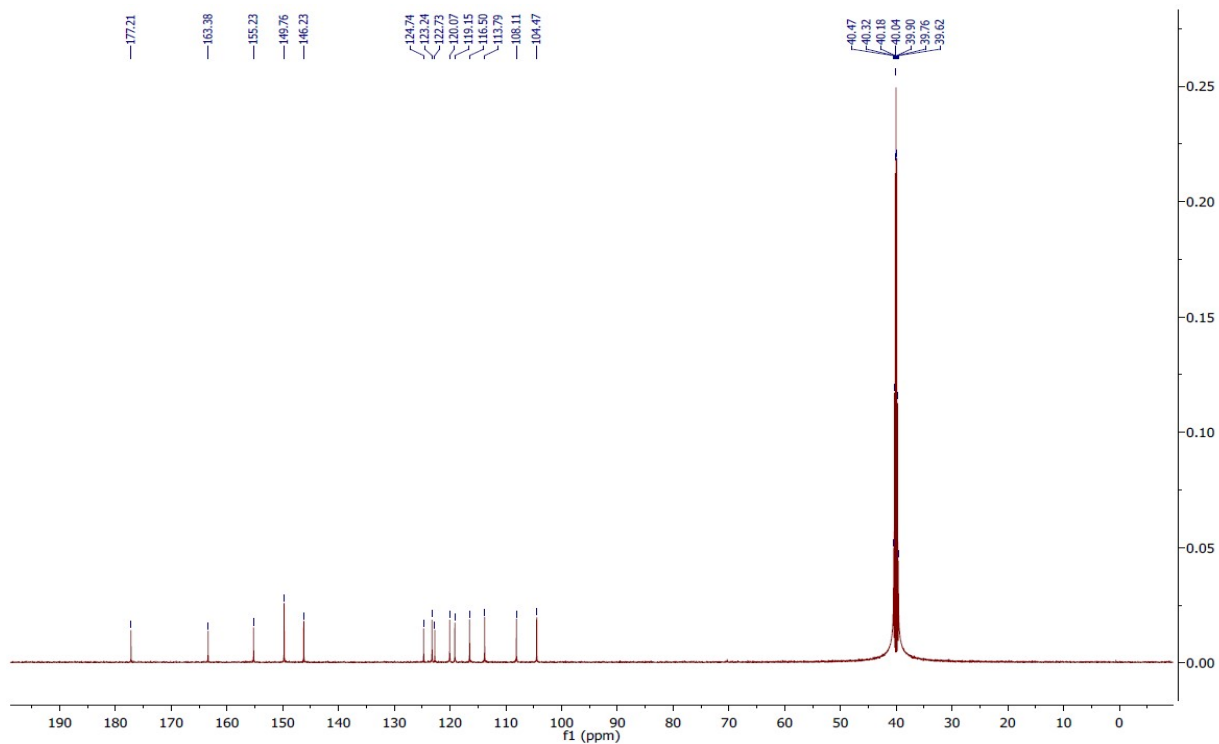
MS Spectrum



¹H NMR Spectra (DMSO) of (3v) (6,3'4'-HOFL)

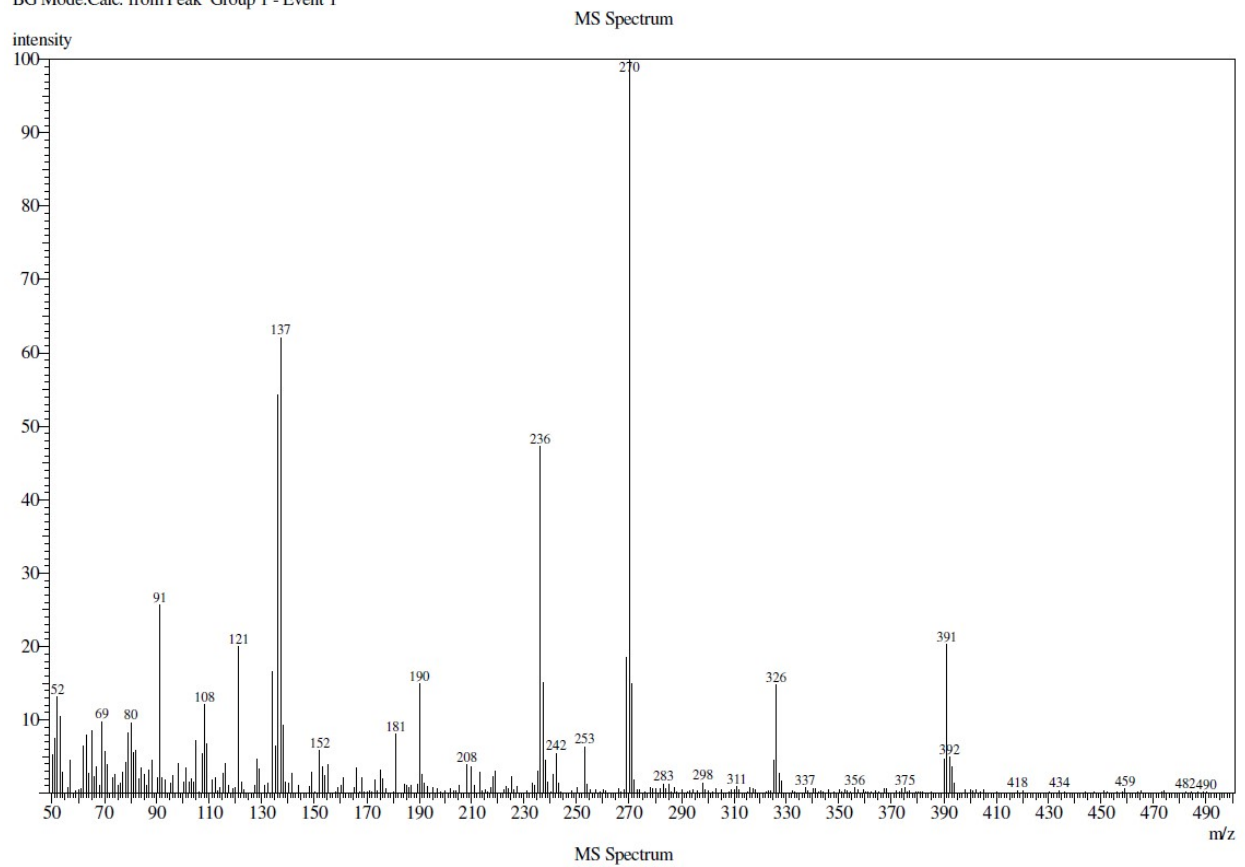


¹³C NMR Spectra (DMSO) of (3v) (6,3'4'-HOFL)



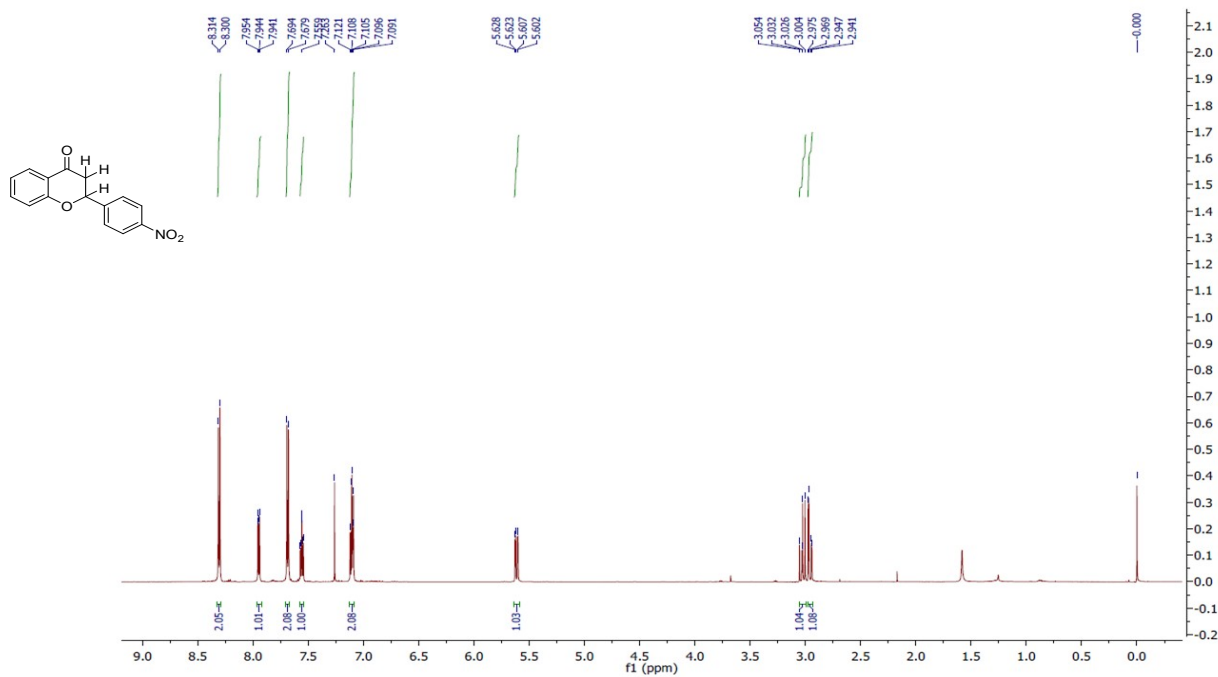
Mass spectra of 3v (6,3'4'-HOFL)

Line#:1 R.Time:8.9800(Scan#:1497)
MassPeaks:580
RawMode:Averaged 8.9750-8.9850(1496-1498) BasePeak:270.1000(14642)
BG Mode:Calc. from Peak Group 1 - Event 1

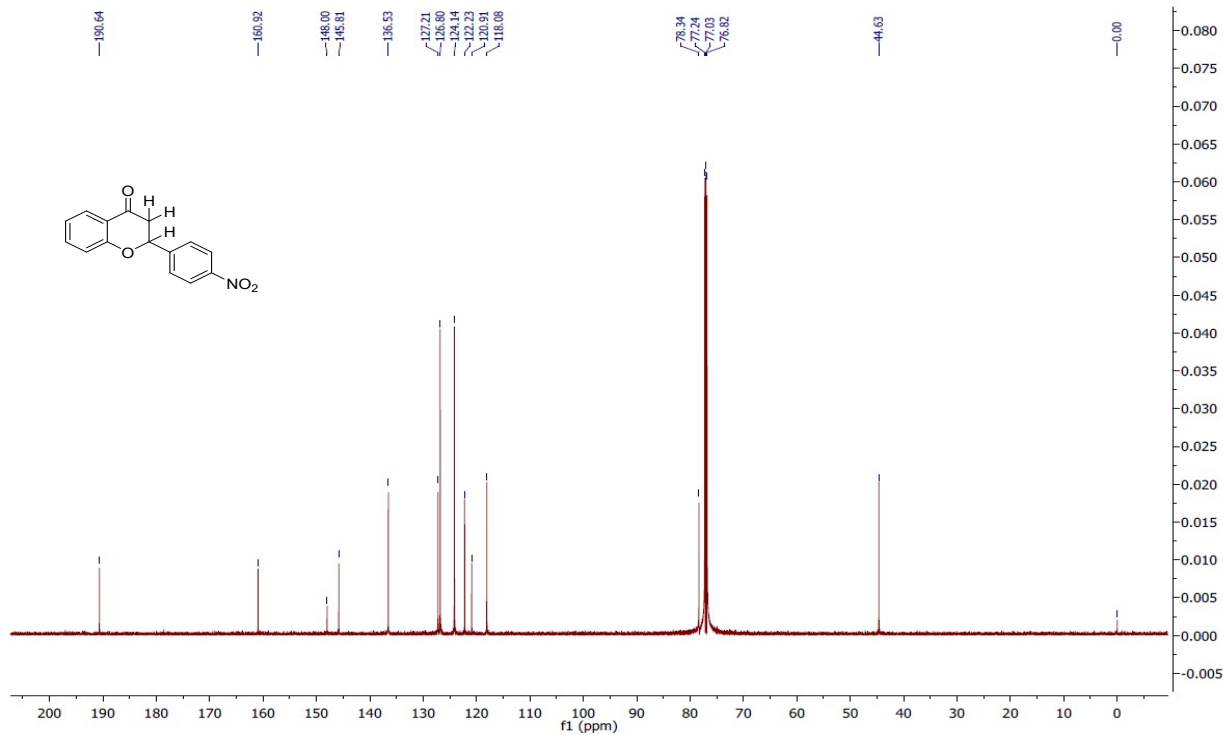


NMR spectra of the identified intermediates.

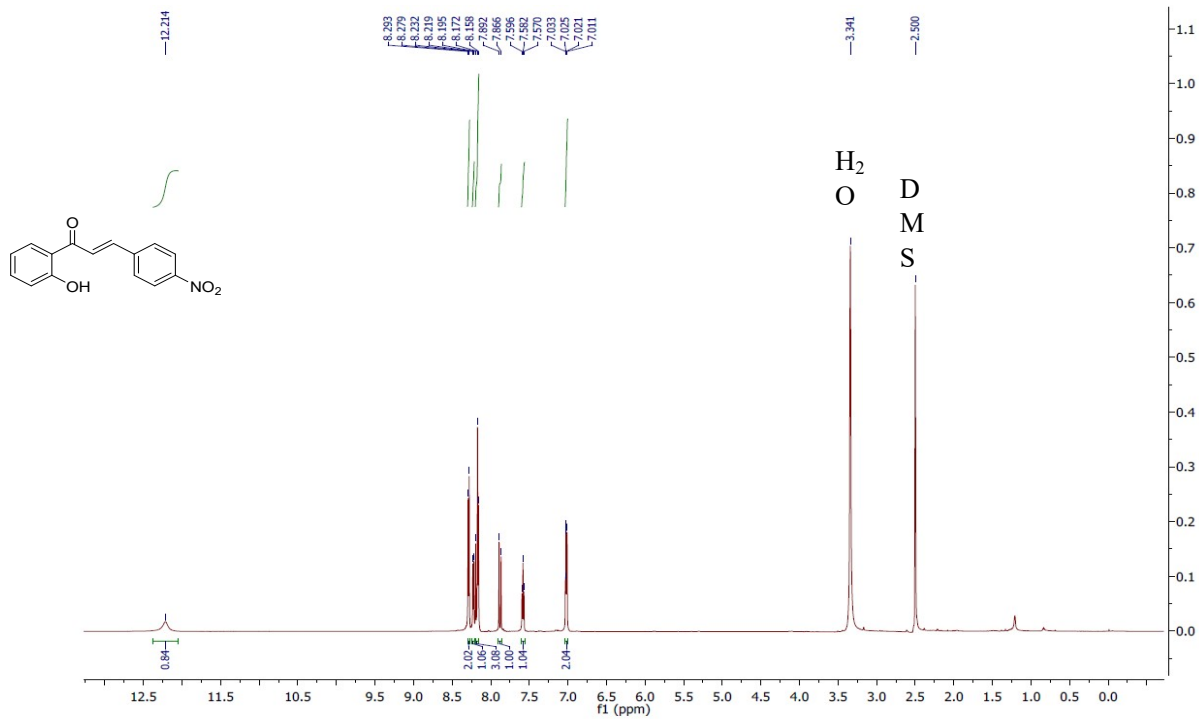
¹H NMR Spectra (CDCl₃) of 2-(4-nitrophenyl)-chroman-4-one



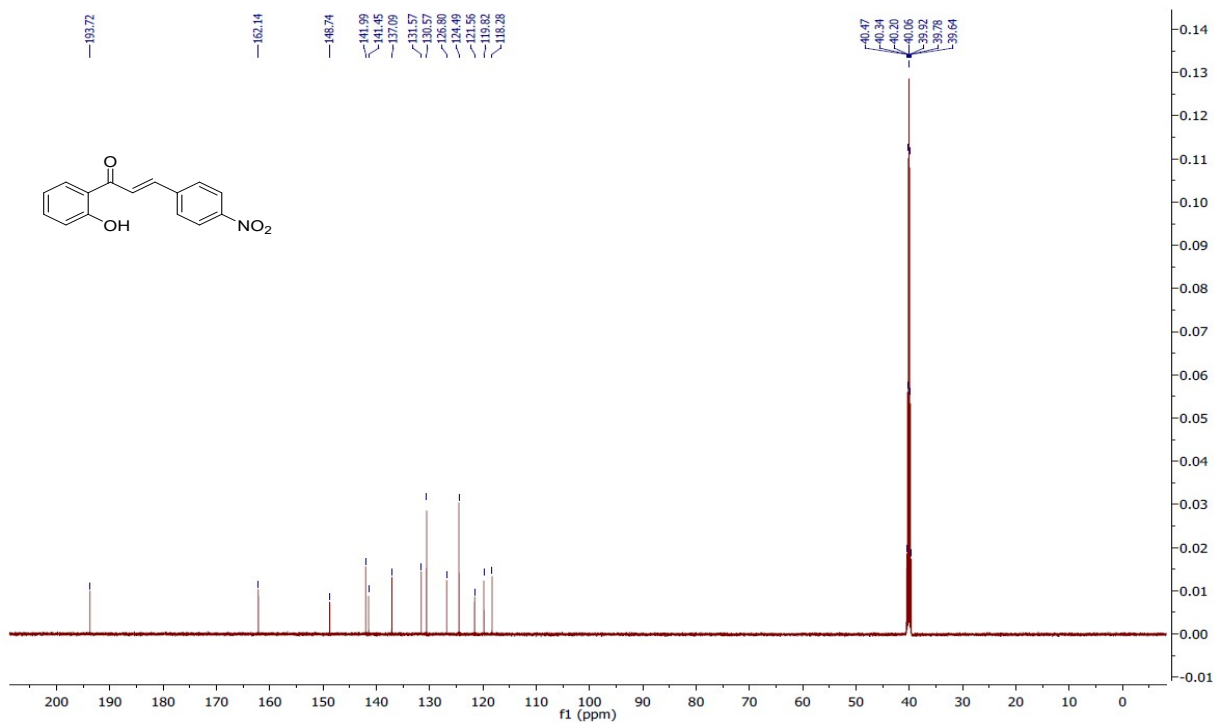
¹³C NMR Spectra (CDCl₃) of 2-(4-nitrophenyl)-chroman-4-one



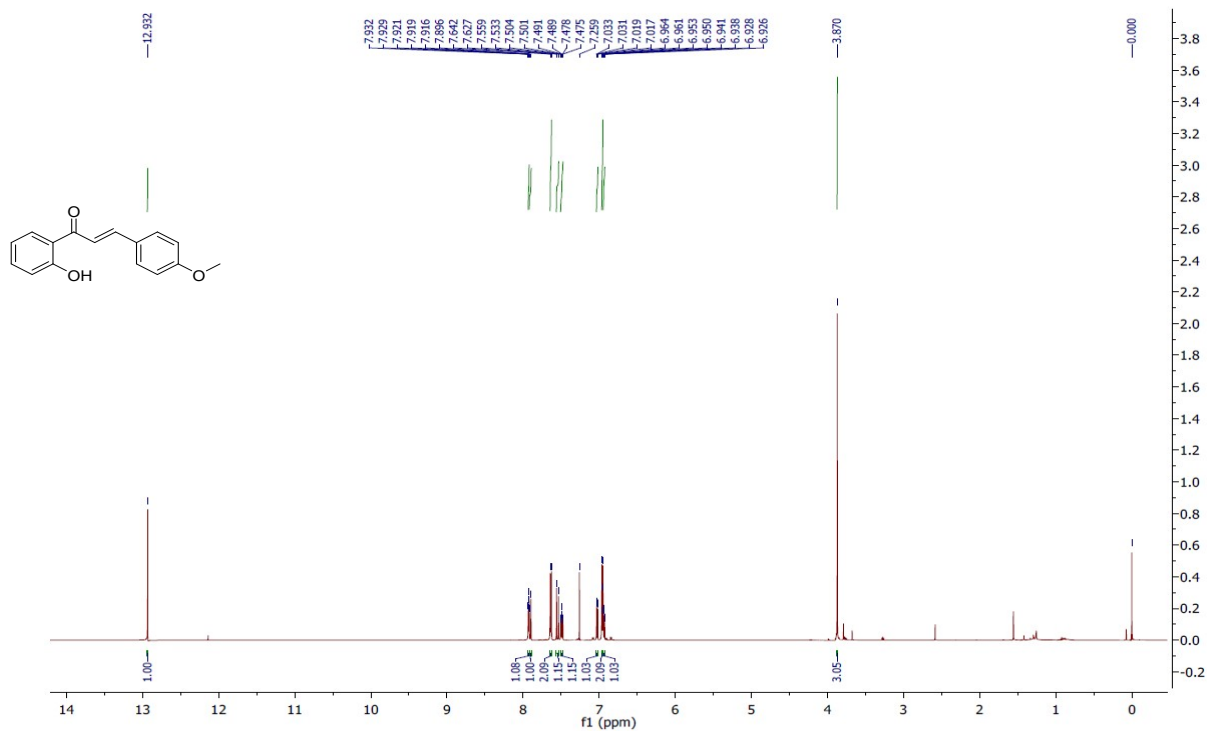
¹H NMR Spectra (DMSO) of (E)-1-(2-hydroxyphenyl)-3-(4-nitrophenyl)prop-2-en-1-one



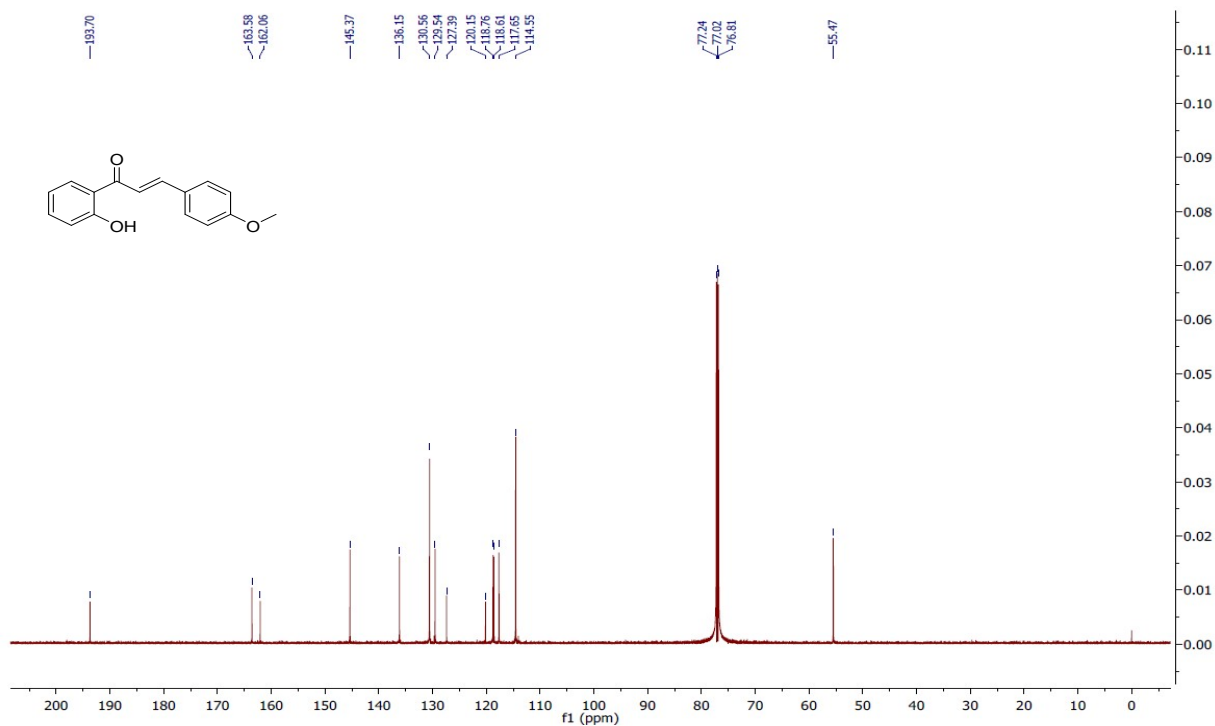
¹³C NMR Spectra (DMSO) of (E)-1-(2-hydroxyphenyl)-3-(4-nitrophenyl)prop-2-en-1-one



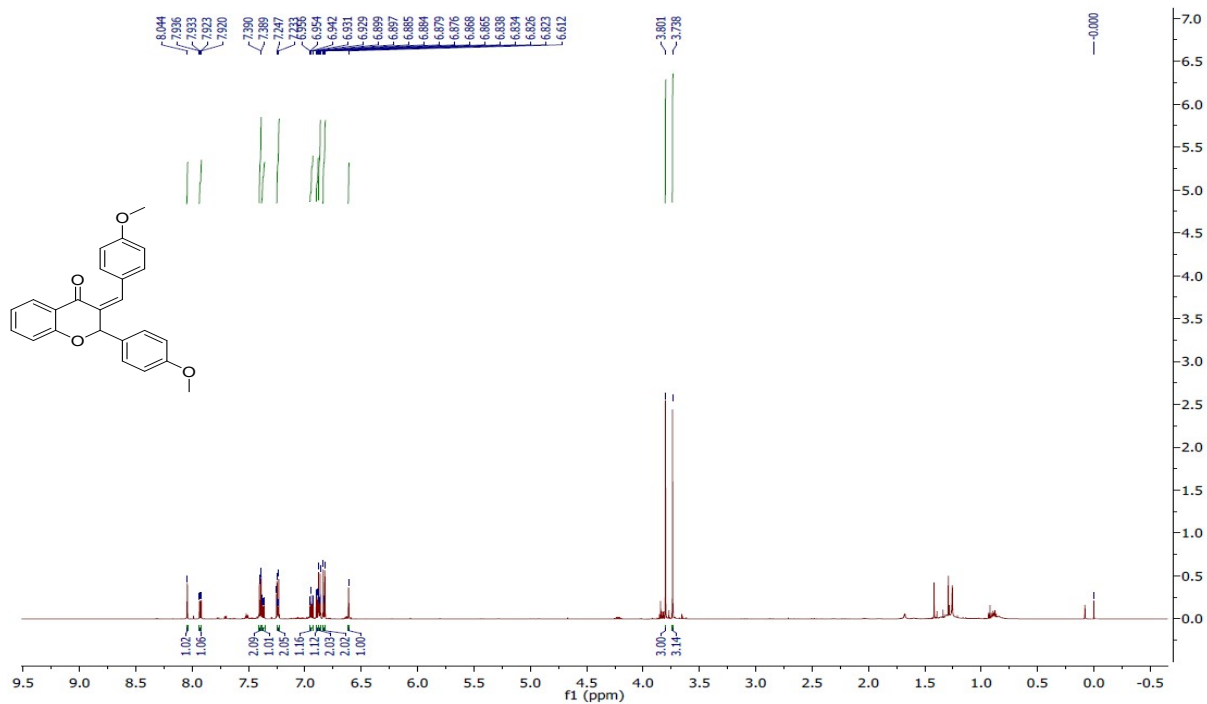
¹H NMR Spectra (CDCl₃) of (E)-1-(2-hydroxyphenyl)-3-(4-methoxyphenyl)prop-2-en-1-one



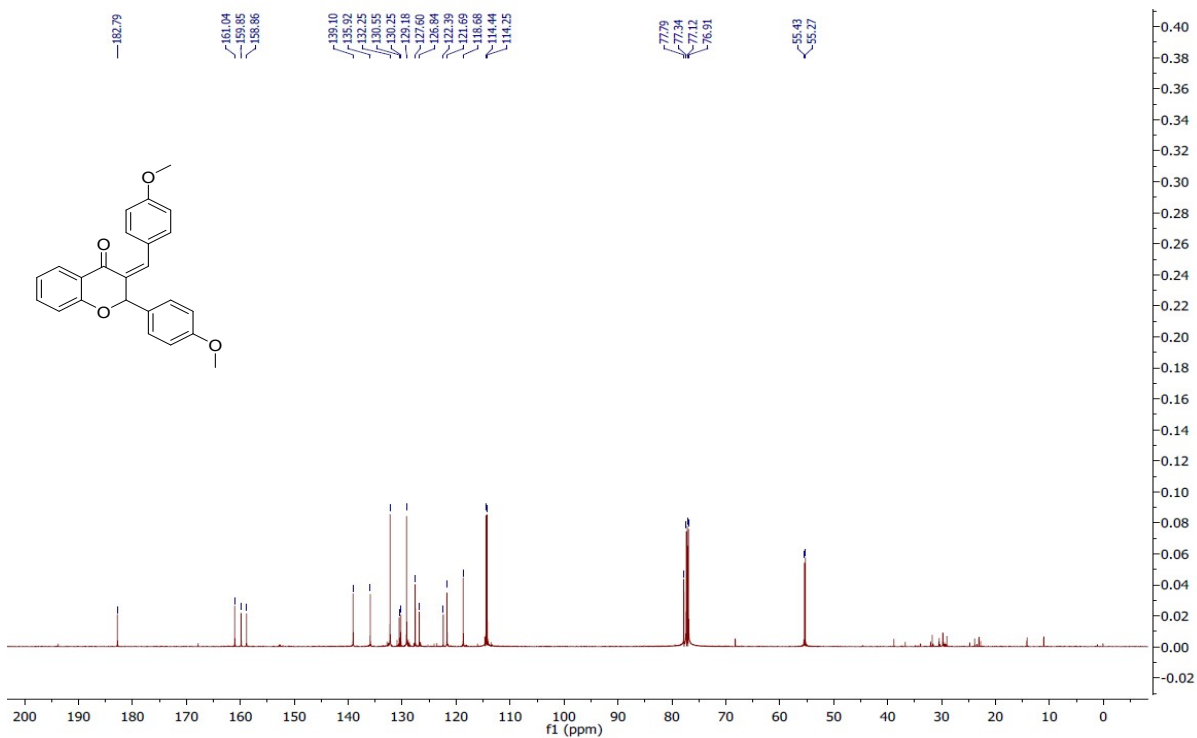
¹³C NMR Spectra (CDCl₃) of (E)-1-(2-hydroxyphenyl)-3-(4-methoxyphenyl)prop-2-en-1-one



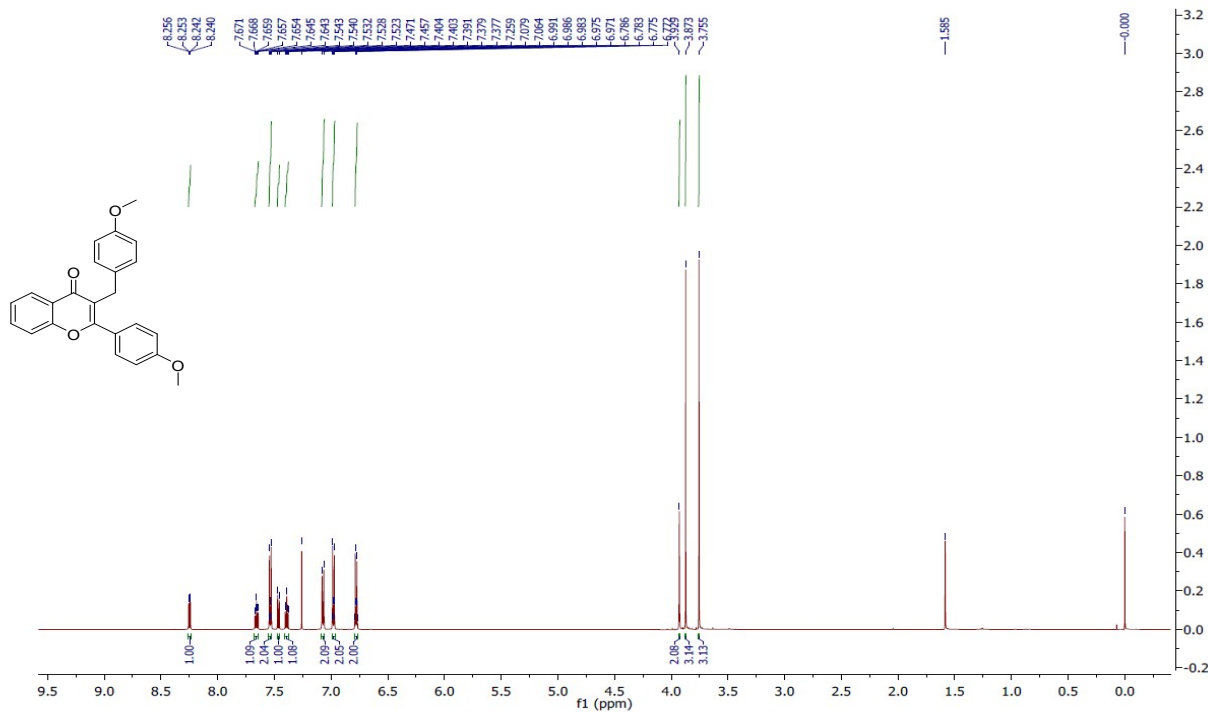
¹H NMR Spectra (CDCl₃) of (Z)-3-(4-methoxybenzylidene)-2-(4-methoxyphenyl)chroman-4-one



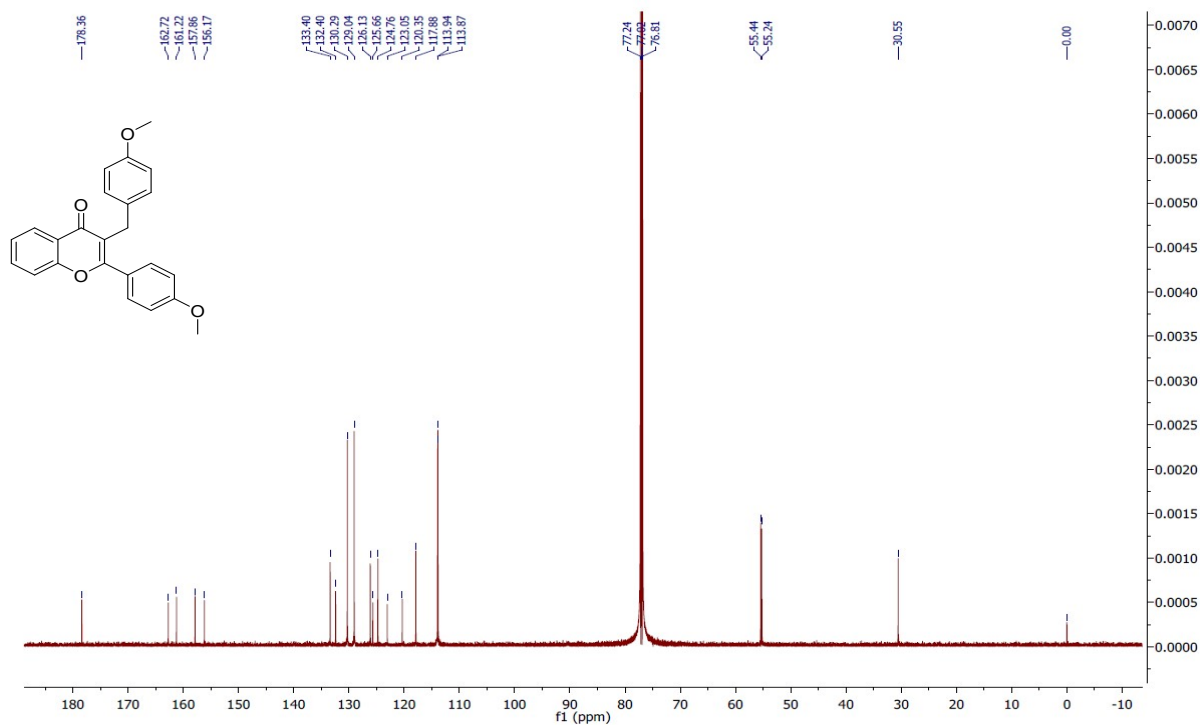
¹³C NMR Spectra (CDCl₃) of (Z)-3-(4-methoxybenzylidene)-2-(4-methoxyphenyl)chroman-4-one



¹H NMR Spectra (CDCl₃) of 3-(4-methoxybenzyl)-2-(4-methoxyphenyl)-4H-chromen-4-one



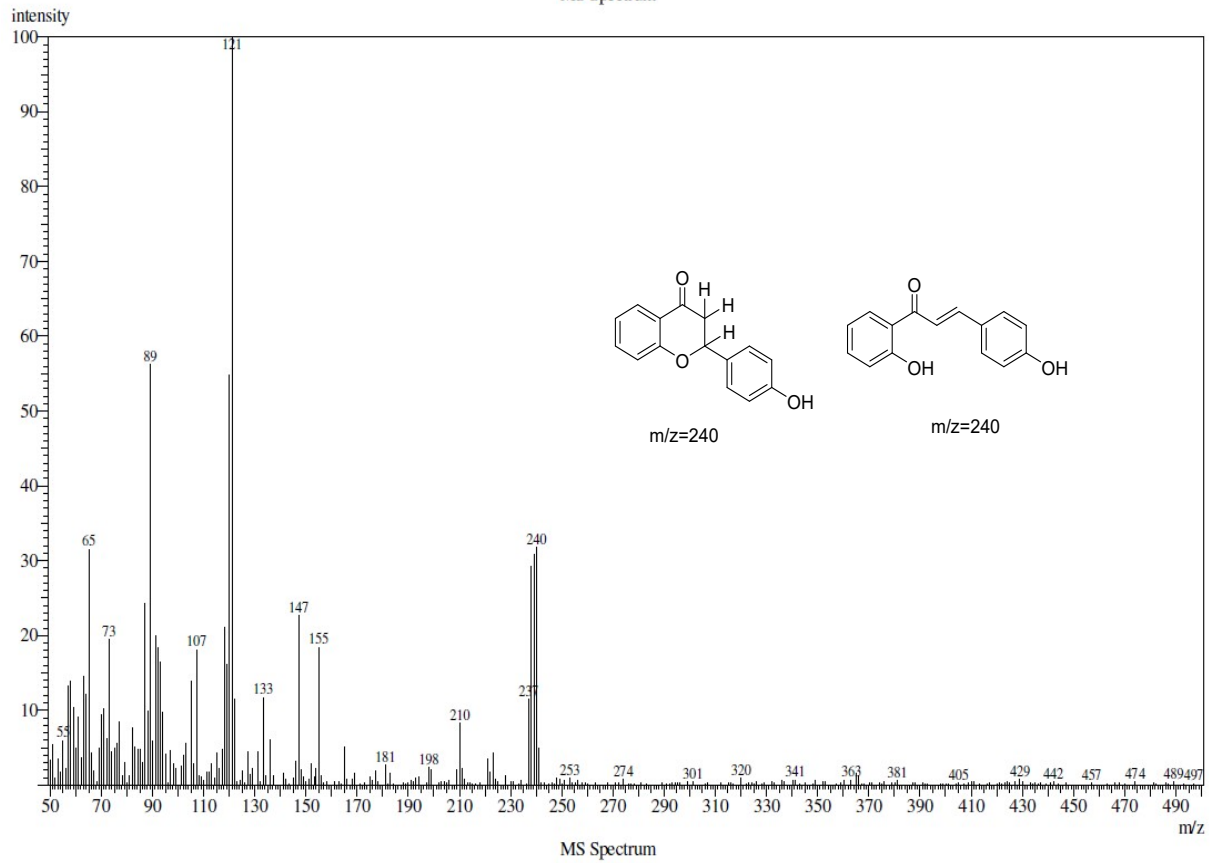
¹³C NMR Spectra (CDCl₃) of 3-(4-methoxybenzyl)-2-(4-methoxyphenyl)-4H-chromen-4-one



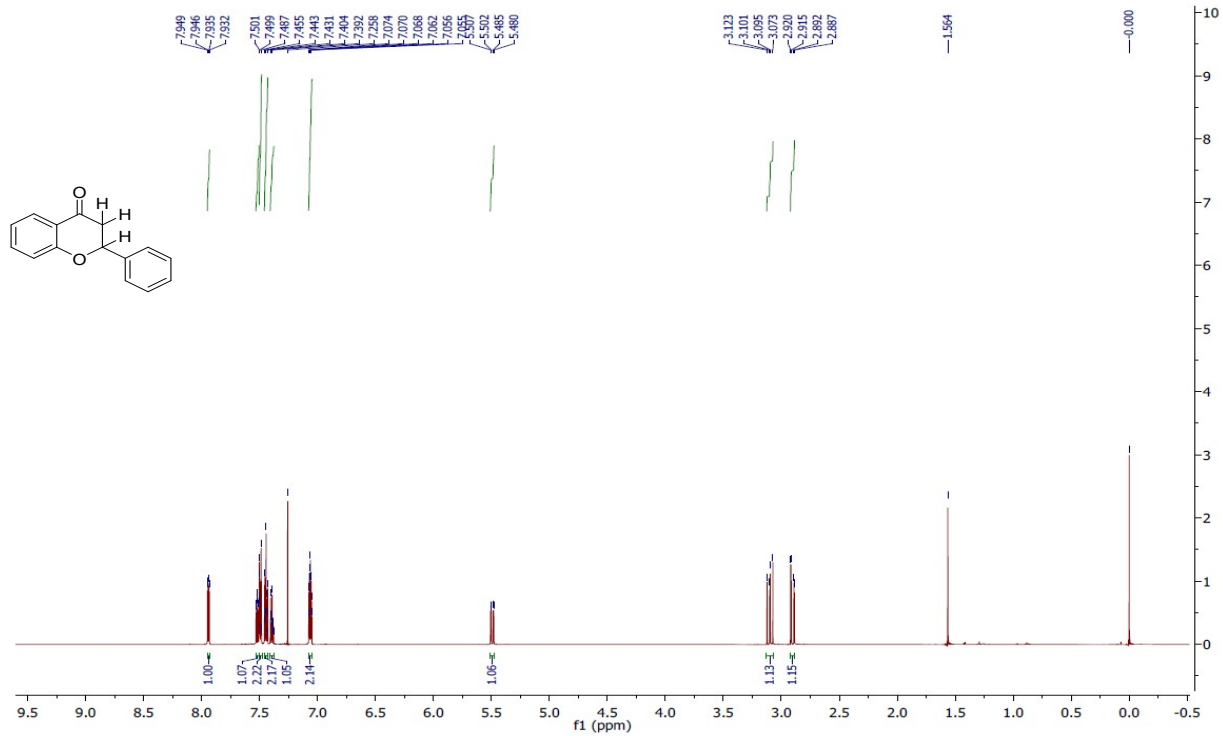
¹H NMR Spectra (CDCl₃) of (E)-1-(2-hydroxyphenyl)-3-(4-hydroxyphenyl)prop-2-en-1-one

Line#:1 R.Time:6.0850(Scan#:918)
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BG Mode:Calc. from Peak Group 1 - Event 1

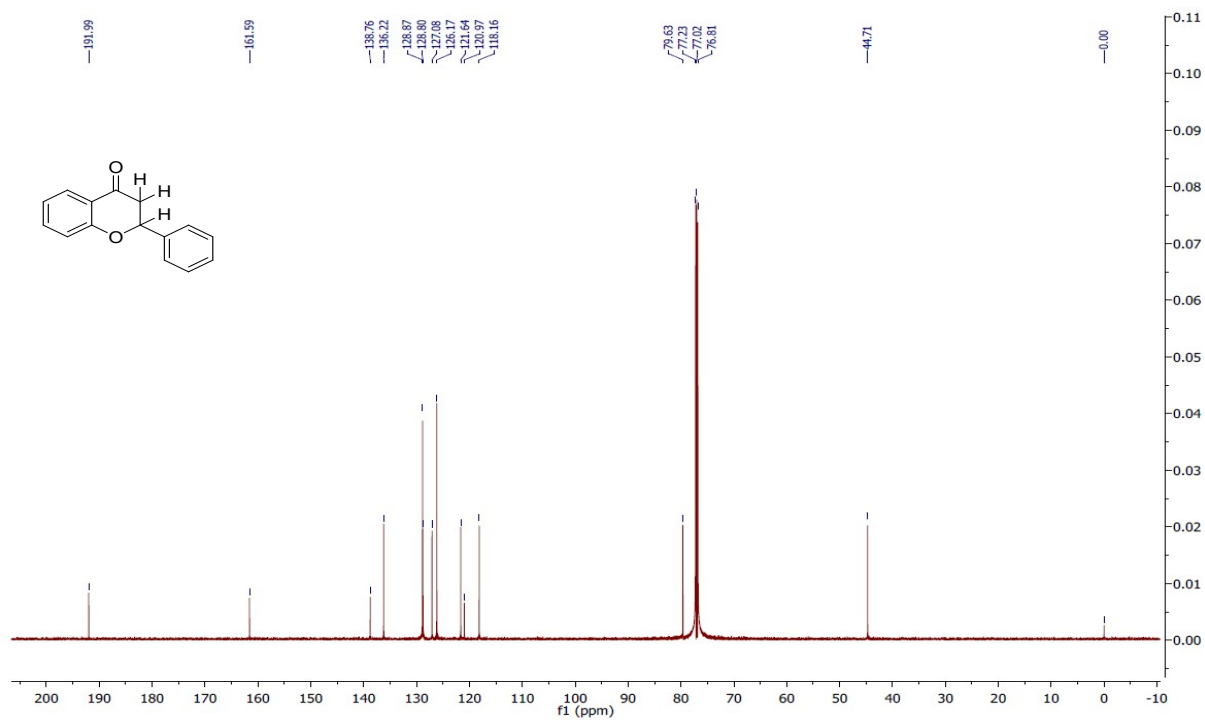
MS Spectrum



¹H NMR Spectra (CDCl₃) of 2-phenylchroman-4-one



¹³C NMR Spectra (CDCl₃) of 2-phenylchroman-4-one



DFT COORDINATES

A

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C	-2.84389372809650	3.23149506378688	0.00898103262741
C	-4.22528088906757	3.29502897774839	-0.00511451589248
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H	-4.73581384214040	4.26017619917412	-0.01404828611279
H	-6.04964223783558	2.12306208637623	-0.01891333298276
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H	-1.42770479977968	-0.42666834548758	0.03856671171502
C	-0.65479872276133	2.11428446147442	0.03464922455412
O	-0.11987058149602	3.20850664996881	0.03511495202056
C	0.20063243385189	0.87279357008053	0.04800861515332
H	0.00775615102108	0.26491163699025	0.94842511038766
H	0.02544680565078	0.25837180497193	-0.85157556146572
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C	-2.96336105548226	1.38607791752323	-1.33683456704448
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C	-0.55690859587299	-0.73644182476405	2.39297121189371
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C	1.90834125928935	-1.11451214535309	1.93686946517855
C	2.47713566390535	-2.00389552056629	1.02136254330224
C	3.60173546902882	-2.74383703705023	1.37005654339096
C	4.14263747095938	-2.57970326732674	2.64043849006956
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H	2.04633219826670	-0.25507979863414	3.92087268267177
H	2.03690708226091	-2.11553039391722	0.03049918068671
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O	5.77743644893030	-4.12861077338870	2.19457605321512
O	5.78729574454441	-3.18869372419196	4.12194913557856
C	0.67115692915116	-0.33174215964495	1.59331347460609
H	-0.38725091685668	-0.65463932037031	3.47312884522182
H	0.84682160164855	0.73396782327451	1.85084998530206

TOT

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C	1.57889878921131	-1.96686258813450	-0.06050564747110
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H	16.12501052471770	0.16495620106564	0.10474214457136
I	15.97285888006031	0.44766483117322	3.73132382084722
I	21.78351176428666	-2.83102827856720	5.62782954775541
I	19.19557670352271	-2.35226667134523	4.14804987678652
I	24.25883544191604	-3.27594844380104	7.02351277183013
H	16.54657421033755	-5.22636518148418	2.40875222067531
H	16.55272736039576	-3.55387930015795	3.09245008065473

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