Electronic Supplementary Information

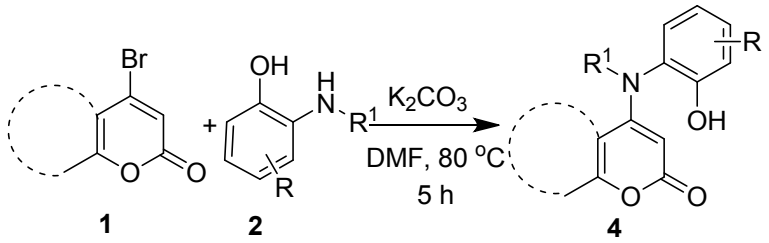
Unexpected C-N bond formation via smiles rearrangement: one pot synthesis of *N*-arylated coumarin/pyran derivatives

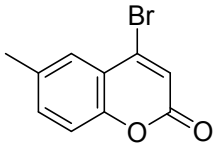
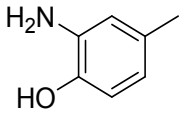
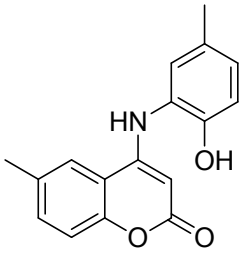
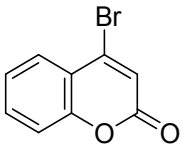
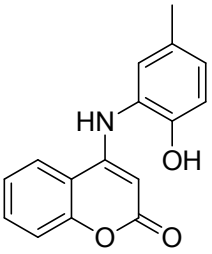
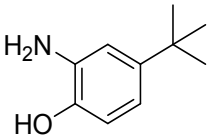
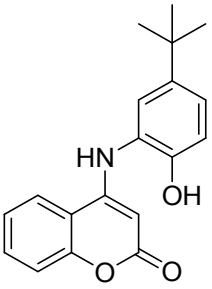
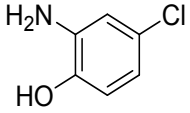
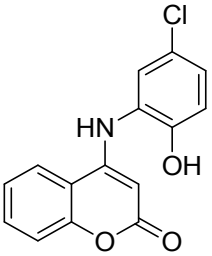
K. Shiva Kumar,* Meesa Siddi Ramulu, N. Praveen Kumar

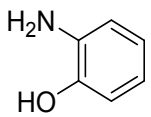
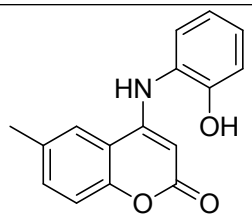
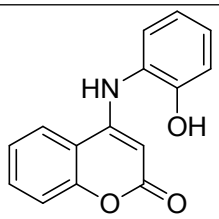
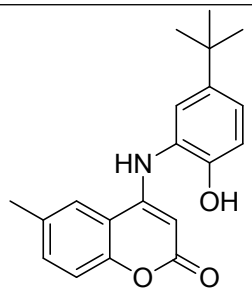
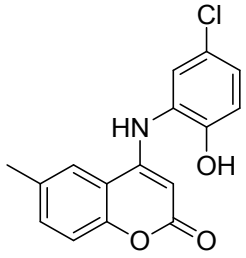
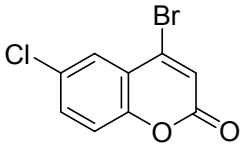
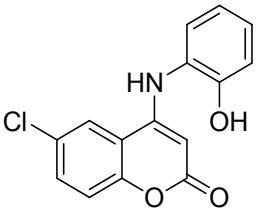
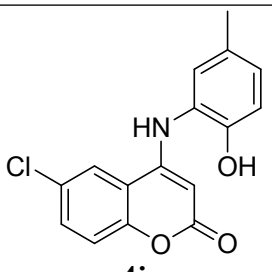
Department of Chemistry, Osmania University, Hyderabad-500 007, India.
E-mail: shivakumarkota@yahoo.co.in; Tel: +91 40 27682337

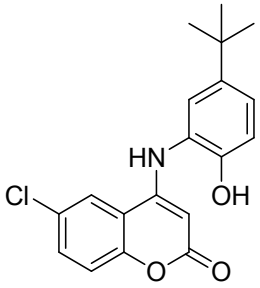
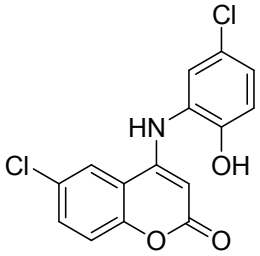
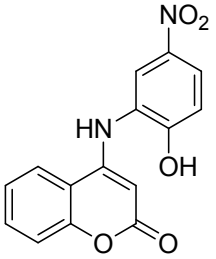
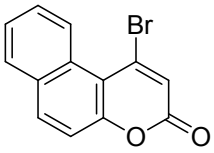
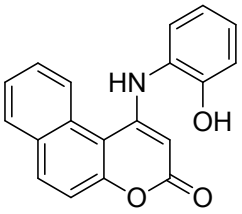
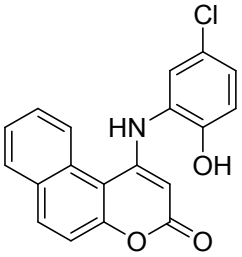
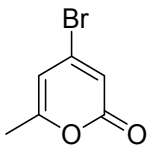
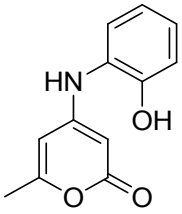
Table of content **Page No**

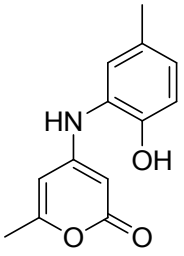
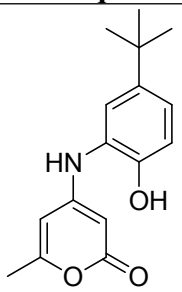
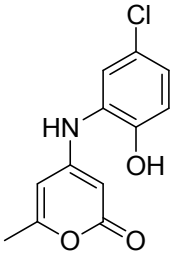
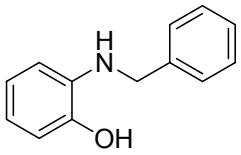
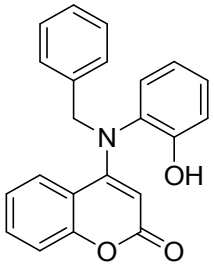
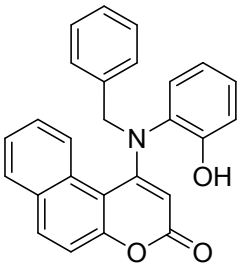
Table 1: K_2CO_3 mediated synthesis of *N*-arylated coumarin/pyran derivatives **4**[a].

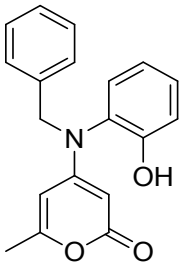
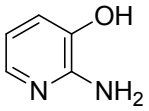
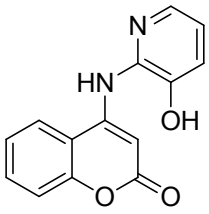


Entry	4-Bromo coumarin/pyran (**1**)	2-Aminophenols (**2**)	*N*-Arylated coumarin/pyran (**4**)	Yield[b]
1	 **1a**	 **2a**	 **4a**	85
2	 **1b**	**2a**	 **4b**	81
3	**1b**	 **2b**	 **4c**	83
4	**1b**	 **2c**	 **4d**	78

5	**1a**	 **2d**	 **4e**	82
6	**1b**	**2b**	 **4f**	85
7	**1a**	**2c**	 **4g**	82
8	**1a**	**2d**	 **4h**	75
9	 **1c**	**2b**	 **4i**	85
10	**1c**	**2a**	 **4j**	86

11	**1c**	**2c**	 **4k**	80
12	**1c**	**2d**	 **4l**	85
13	**1b**	**2e**	 **4m**	81
14	 **1d**	**2b**	 **4n**	80
15	**1d**	**2d**	 **4o**	76
16	 **1e**	**2b**	 **4p**	80

17	**1e**	**2a**	 **4q**	81
18	**1e**	**2c**	 **4r**	86
19	**1e**	**2d**	 **4s**	83
20	**1b**	 **2f**	 **4t**	84
21	**1d**	**2f**	 **4u**	78

22	**1e**	**2f**	 **4v**	80
23	**1b**	 **2g**	 **4w**	78

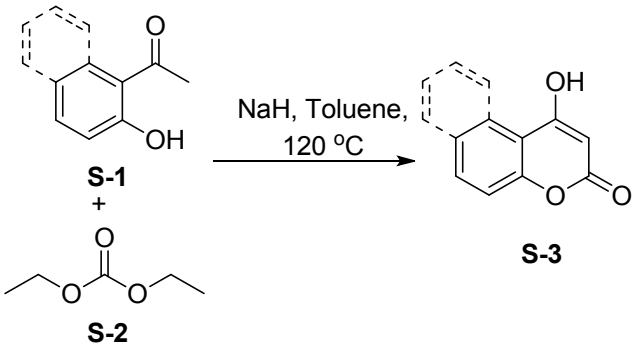
[a]All the reactions were carried out using compound **1a** (1.05 m. mol), **2a** (1.05 m. mol) and 2.63 m. mol. K_2CO_3 in a DMF (3 mL) at 80 °C for 5 h. [b]Isolated yield.

Chemistry

General methods: Unless stated otherwise, solvents and chemicals were obtained from commercial sources and were used without further purification. Reactions were monitored by thin layer chromatography (TLC) on silica gel plates (60 F254), visualizing with ultraviolet light or iodine spray. Flash chromatography was performed on silica gel (230-400 mesh) using hexane and ethyl acetate. ^{1}H and ^{13}C NMR spectra were determined in $CDCl_3$ and DMSO-d_6 solutions by using 400 or 100 MHz spectrometers, respectively. Proton chemical shifts (δ) are relative to tetramethylsilane (TMS, δ = 0.00) as internal standard and expressed in ppm. Spin multiplicities are given as s (singlet), d (doublet), t (triplet) and m (multiplet) as well as b (broad). Coupling constants (*J*) are given in hertz. Infrared spectra were recorded on a FT-IR spectrometer. Melting points were determined using a melting point apparatus and are uncorrected. MS spectra were obtained on a mass spectrometer. HRMS data were recorded by electrospray ionization with a Q-TOF mass analyzer.

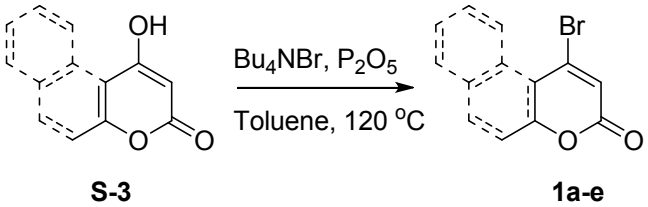
All starting materials 4-bromo coumarin/pyrans [1] (**1a−e**) and 2-(benzylamino)phenol[2] **(2f**) were prepared according to the known procedure.

General procedure for the synthesis of 4-hydroxy pyrans (S-3)[1]:



A solution of S-1 (9 mmol, 1 equiv) in toluene (15 mL) was added dropwise to a dry round-bottom flask containing sodium hydride (60% w/w suspension, 27 mmol, 3 equiv) in toluene (10 mL) at 0° C. The mixture was stirred at the same temperature for 15 min. To this, dropwise addition of diethylcarbonate (13.5 mmol, 1.5 equiv) in toluene (10 mL). Then, the reaction mixture was heated at 120 °C. After completion of the reaction, the reaction mixture was cooled to room temperature. The solvents were removed under reduced pressure and resulting mixture residue was quenched at ice bath temperature by slow addition of water (20 mL) followed by, acidified with 2 N HCl. The solid precipitate was filtered, washed with water, and dried under vacuum to afford the crude substituted 4-hydroxy coumarin which was directly used in the next step.

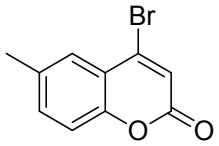
General procedure for the synthesis of 4-bromo pyrans (1a-e)[1]:



To a solution of substituted 4-hydroxy coumarin/pyran (2.00 mmol) in toluene (8 mL) was heated to 120 °C for 10 min and then Bu_4NBr (3.0 equiv) was added in portions wise over 5 min and the reaction mixture was stirred another 10 min to dissolve the starting material completely. P_2O_5 (4.8 mmol) was then added in portions wise over 10 min and the reaction was heated for 5 h until reaction completion. After completion of the reaction, the reaction mixture was cooled to room temperature then washed with a saturated aqueous $NaHCO_3$ solution. Then the reaction mixture was extracted with toluene (3 × 10 mL). dried over anhydrous Na_2SO_4, filtered and

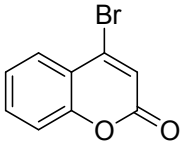
concentrated under reduced pressure. The residue was purified by column chromatography using ethyl acetate – hexane to give the desired product **1**.

4-Bromo-6-methyl-2*H*-chromen-2-one (1a)



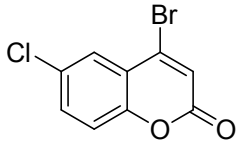
Brown color solid; Yield: 80%; mp: 84-87 °C (lit[1b] 78-80 °C);; R_f = 0.6 (20% EtOAc/*n*-hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (s, 1H), 7.40 (d, J = 8.4 Hz, 1H), 7.23 (d, J = 8.4 Hz, 1H), 6.84 (s, 1H), 2.45 (s, 3H).

4-Bromo-2*H*-chromen-2-one (1b)



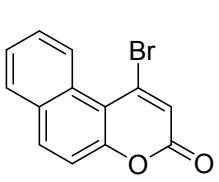
Off white solid; Yield: 89%; mp: 88-90 °C (lit[1b] 75-77 °C); R_f = 0.5 (20% EtOAc/*n*-hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (d, J = 8 Hz, 1H), 7.61 (t, J = 8.4 Hz, 1H), 7.39-7.33 (m, 2H), 6.87 (s, 1H).

4-Bromo-6-chloro-2*H*-chromen-2-one (1c)



Off white solid; Yield: 75%; mp: 120-125 °C; R_f = 0.6 (20% EtOAc/*n*-hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 (d, J = 2.4 Hz, 1H), 7.55 (d, J = 8.8 Hz, 1H), 7.30 (d, J = 8.8 Hz, 1H), 6.90 (s, 1H).

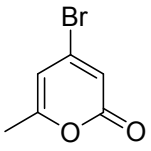
1-Bromo-3*H*-benzo[*f*]chromen-3-one (1d)



Yellow solid; Yield: 86%; mp: 140-143 °C; R_f = 0.5 (20% EtOAc/*n*-hexane); IR: 3068, 1723, 1535, 751 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.58 (d, J = 8.8 Hz, 1H), 8.04 (d, J = 8.8 Hz, 1H), 7.92 (d, J = 7.2 Hz, 1H), 7.70 (t, J= 8.2 Hz, 1H), 7.60 (t, J = 8 Hz, 1H), 7.45 (d, J = 9.2 Hz,

1H), 7.02 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.2, 153.8, 138.6, 135.1, 131.2, 129.4, 129.1, 127.7, 126.2, 124.5, 121.2, 117.1, 112.2; Mass: m/z (CI) 276 (M+1, 100%).

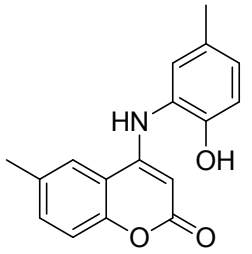
4-Bromo-6-methyl-2*H*-pyran-2-one (1e)



Off white solid; Yield: 82%; mp: 82-85 °C (lit[3] 87-89); R_f = 0.6 (30% EtOAc/*n*-hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.46 (s, 1H), 6.20 (s, 1H), 2.25 (s, 3H).

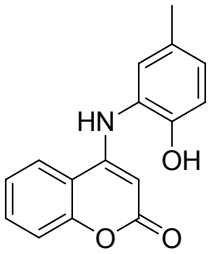
General Procedure for the preparation of 4: A mixture of 4-bromo coumarin/pyran derivatives (**1a-1e**, 1.05 m.mol), an amino phenol (**2a-2e**, 1.05 m.mol) and K_2CO_3 (2.63 m. mol) in DMF (3 mL) was stirred at 90 ^{o}C for 5 h. After completion of the reaction, the mixture was cooled to room temperature, diluted with water (10 mL) and extracted with ethyl acetate (2×20 mL). The organic layers were collected, combined, dried over anhydrous Na_2SO_4 and concentrated under vacuum. The residue obtained was purified by column chromatography using ethylacetate/hexane to give the desired product.

4-((2-Hydroxy-5-methylphenyl)amino)-6-methyl-2*H*-chromen-2-one (4a)



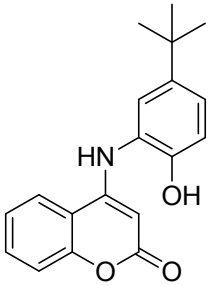
Light brown solid; Yield: 85%; mp: 252-254 °C; R_f = 0.4 (50% EtOAc/*n*-hexane); IR: 3021, 2404, 1215, 741 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.47 (s, 1H, D_2O Ex), 8.89 (s, 1H, D_2O Ex), 8.08 (s, 1H), 7.45 (d, *J*= 8 Hz, 1H), 7.25 (d, *J* = 8 Hz, 1H), 7.01 (d, *J* = 8 Hz, 2H), 6.89 (d, *J* = 7.6 Hz, 1H), 4.73 (s, 1H), 2.41 (s, 3H), 2.24 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 161.7, 152.9, 151.4, 150.4, 132.7, 132.5, 128.7, 128.5, 128.3, 124.1, 122.7, 116.5 (2C), 114.2, 84.0, 20.5, 19.9; Mass: m/z (CI) 282 (M+1, 100%); HRMS (ESI): m/z calcd for $C_{17}H_{16}NO_3$ ($[M + H]^+$) 282.1130, found 282.1131.

4-((2-Hydroxy-5-methylphenyl)amino)-2*H*-chromen-2-one (4b)



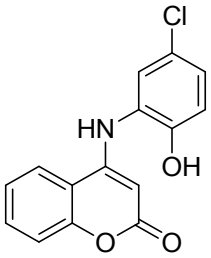
Light brown solid; Yield: 81%; mp: 229-231 °C; R_f = 0.35 (50% EtOAc/*n*-hexane); IR: 3238, 3062, 1633, 1537, 754 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ 9.44 (s, 1H), 8.94 (s, 1H), 8.22 (d, J = 8 Hz, 1H), 7.62 (t, J = 8.4 Hz, 1H), 7.37-7.32 (m, 2H), 7.00 (d, J = 7.6 Hz, 2H), 6.88 (d, J = 8.4 Hz, 1H), 4.72 (s, 1H), 2.22 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 161.5, 153.3, 153.0, 150.4, 132.0, 128.8, 128.6, 128.3, 124.0, 123.4, 122.9, 116.9, 116.6, 114.6, 83.9, 19.9; Mass: m/z (CI) 268 (M+1, 100%); HRMS (ESI): m/z calcd for $C_{16}H_{13}NO_3Na$ ($[M+Na]^+$) 290.0793, found 290.0791.

4-((5-(Tert-butyl)-2-hydroxyphenyl)amino)-2*H*-chromen-2-one (4c)



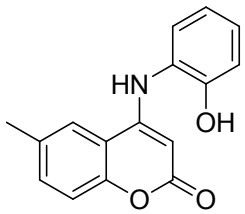
Light yellow solid; Yield: 83%; mp: 170-172 °C; R_f = 0.4 (50% EtOAc/ *n*-hexane); IR: 3412, 3169, 2958, 1660, 1195, 742 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ 9.54 (s, 1H), 9.05 (s, 1H), 8.26 (d, J = 7.6 Hz, 1H), 7.64 (t, J = 7.6 Hz, 1H), 7.40-7.35 (m, 2H), 7.24 (d, J = 7.6 Hz, 1H), 7.18 (s, 1H), 6.95 (d, J = 8.4 Hz, 1H), 4.73 (s, 1H), 1.27 (s, 9H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 161.6, 153.3, 153.0, 150.3, 142.0, 132.0, 125.0 (2C), 123.6, 123.3, 122.9, 116.8, 116.3, 114.6, 83.9, 33.7, 31.2 (3C); Mass: m/z (CI) 310 (M+1, 100%); HRMS (ESI): m/z calcd for $C_{19}H_{20}NO_3$ ($[M + H]^+$) 310.1443, found 310.1441.

4-((5-Chloro-2-hydroxyphenyl)amino)-2*H*-chromen-2-one (4d)



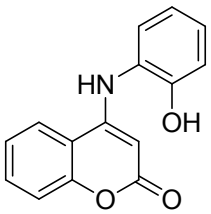
Brown solid; Yield: 78%; mp: 212-214 °C; R_f= 0.4 (50% EtOAc/*n*-hexane); IR: 3234, 3163, 1678, 1257, 744 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ 10.10 (s, 1H, D_2O Ex), 9.07 (s, 1H, D_2O Ex), 8.21 (d, J = 7.6 Hz, 1H), 7.65 (t, J = 7.6 Hz, 1H), 7.41-7.36 (m, 2H), 7.30-7.26 (m, 2H), 7.02 (d, J = 8.4 Hz, 1H), 4.76 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 161.4, 153.2, 152.6, 151.9, 132.1, 128.0, 127.9, 125.8, 123.5, 122.9, 122.3, 118.1, 116.9, 114.4, 84.7; Mass: m/z (CI) 288 (M+1, 100%); HRMS (ESI): m/z calcd for $C_{15}H_{11}NO_3Cl$ ($[M + H]^+$) 288.0427, found 288.0428.

4-((2-Hydroxyphenyl)amino)-6-methyl-2*H*-chromen-2-one (4e)



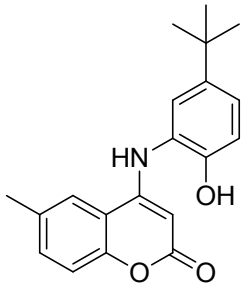
Brown solid; Yield: 82%; mp: 247-249 °C; R_f = 0.35 (50% EtOAc/ *n*-hexane); IR: 3427, 3323, 1658, 1269, 748 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ 9.69 (s, 1H, D_2O Ex), 8.89 (s, 1H, D_2O Ex), 8.06 (s, 1H), 7.43 (d, J = 8.8 Hz, 1H), 7.23 (d, J = 8.4 Hz, 1H), 7.17 (d, J = 8 Hz, 2H), 6.99 (d, J = 7.6 Hz, 1H), 6.88 (t, J = 7.6 Hz, 1H), 4.70 (s, 1H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 161.7, 153.0, 152.8, 151.4, 132.7, 132.5, 128.4, 128.3, 124.5, 122.7, 119.5, 116.7, 116.6, 114.2, 84.0, 20.4; Mass: m/z (CI) 268 (M+1, 100%); HRMS (ESI): m/z calcd for $C_{16}H_{14}NO_3$ ($[M + H]^+$) 268.0974, found 268.0973.

4-((2-Hydroxyphenyl)amino)-2*H*-chromen-2-one (4f)



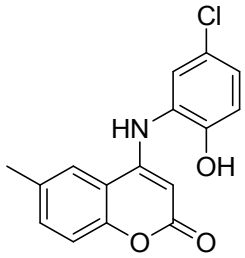
Brown solid; Yield: 85%; mp: 221-222 °C; R_f = 0.3 (50% EtOAc/*n*-hexane); IR: 3380, 3022, 1568, 1216, 762 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ 9.70 (s, 1H), 8.98 (s, 1H), 8.23 (d, J = 8 Hz, 1H), 7.62 (t, J = 8 Hz, 1H), 7.38-7.33 (m, 2H), 7.20 (t, J = 8 Hz, 2H), 6.99 (d, J = 8 Hz, 1H), 6.89 (t, J = 7.6 Hz, 1H), 4.71 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 161.5, 153.3, 153.1, 152.9, 132.0, 128.5, 128.4, 124.4, 123.4, 122.9, 119.5, 116.9, 116.7, 114.6, 83.9; Mass: m/z (CI) 254 (M+1, 100%); HRMS (ESI): m/z calcd for $C_{15}H_{12}NO_3$ ($[M + H]^+$) 254.0814, found 254.0811.

4-((5-(Tert-butyl)-2-hydroxyphenyl)amino)-6-methyl-2*H*-chromen-2-one (4g)



Yellow solid; Yield: 82%; mp: 122-124 °C; R_f = 0.4 (40% EtOAc/*n*-hexane); IR: 3298, 2958, 1666, 1195, 815 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ 9.52 (s, 1H), 8.95 (s, 1H), 8.09 (s, 1H), 7.44 (s, 1H), 7.24-7.17 (m, 3H), 6.94 (s, 1H), 4.72 (s, 1H), 2.41 (s, 3H), 1.27 (s, 9H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 161.7, 152.9, 151.3, 150.3, 142.0, 132.6, 132.5, 124.9 (2C), 123.7, 122.7, 116.6, 116.2, 114.2, 84.0, 33.7, 31.2 (3C), 20.5; Mass: m/z (CI) 324 (M+1, 100%); HRMS (ESI): m/z calcd for $C_{20}H_{22}NO_3$ ($[M + H]^+$) 324.1600, found 324.1594.

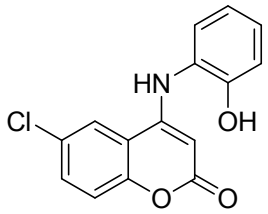
4-((5-Chloro-2-hydroxyphenyl)amino)-6-methyl-2*H*-chromen-2-one (4h)



Off white solid; Yield: 75%; mp: 236-238 °C; R_f = 0.4 (40% EtOAc/*n*-hexane); IR: 3143, 3109, 1674, 1217, 813 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ 10.09 (s, 1H), 8.99 (s, 1H), 8.04 (s, 1H), 7.47 (d, J= 8.4 Hz, 1H), 7.29-7.25 (m, 3H), 7.02 (d, J = 8.4 Hz, 1H), 4.74 (s, 1H), 2.41 (s,

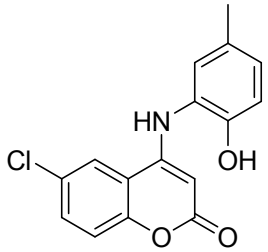
3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 161.6, 152.5, 151.8, 151.3, 132.8, 132.6, 127.9, 127.8, 125.9, 122.7, 122.3, 118.1, 116.6, 114.1, 84.8, 20.4; Mass: m/z (CI) 302 (M+1, 100%); HRMS (ESI): m/z calcd for $C_{16}H_{13}NO_3Cl$ ([M + H]$^+$) 302.0584, found 302.0586.

6-Chloro-4-((2-hydroxyphenyl)amino)-2*H*-chromen-2-one (4i)



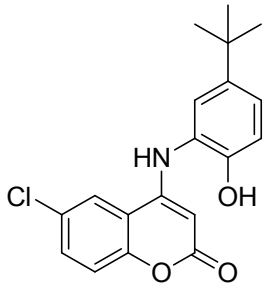
Brown solid; Yield: 85%; mp: 252-254 °C; R_f = 0.4 (50% EtOAc/*n*-hexane); IR: 3320, 3022, 1597, 1215, 768 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.78 (s, 1H), 9.10 (s, 1H), 8.43 (d, J = 2 Hz, 1H), 7.70 (d, J = 8.8 Hz, 1H), 7.42 (d, J = 8.8 Hz, 1H), 7.23 (d, J = 8.4 Hz, 2H), 7.03 (d, J = 8 Hz, 1H), 6.93 (t, J = 7.6 Hz, 1H), 4.78 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 161.0, 152.7, 152.1, 151.9, 131.7, 128.5, 128.4, 127.7, 124.1, 122.6, 119.6, 118.9, 116.8, 116.0, 84.4; Mass: m/z (CI) 288 (M+1, 100%); HRMS (ESI): m/z calcd for $C_{15}H_{11}N\ O_3Cl$ ([M + H]$^+$) 288.0427, found 288.0427.

6-Chloro-4-((2-hydroxy-5-methylphenyl)amino)-2*H*-chromen-2-one (4j)



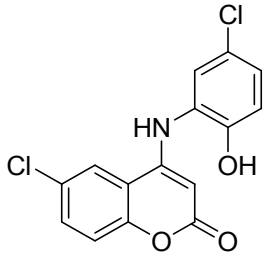
Brown solid; Yield: 86%; mp: 219-221 °C; R_f = 0.4 (50% EtOAc/*n*-hexane); IR: 3299, 3221, 1677, 1233, 768; ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.52 (s, 1H), 9.06 (s, 1H), 8.42 (s, 1H), 7.69 (d, J= 8 Hz, 1H), 7.41 (d, J= 8.8 Hz, 1H), 7.03 (d, J= 8.4 Hz, 2H), 6.92 (d, J= 7.6 Hz, 1H), 4.79 (s, 1H), 2.25 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 161.1, 152.1, 151.9, 150.3, 131.6, 128.9, 128.4 (2C), 127.7, 123.7, 122.6, 118.9, 116.6, 116.0, 84.4, 19.9; Mass: m/z (CI) 302 (M+1, 100%); HRMS (ESI): m/z calcd for $C_{16}H_{13}NO_3Cl$ ([M + H]$^+$) 302.0584, found 302.0582.

4-((5-(Tert-butyl)-2-hydroxyphenyl)amino)-6-chloro-2*H*-chromen-2-one (4k)



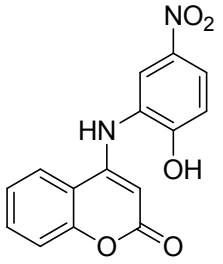
Yellow solid; Yield: 80%; mp: 130-132 °C; R_f = 0.4 (30% EtOAc/*n*-hexane); IR: 3355, 3244, 1656, 1199, 741 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ 9.55 (s, 1H), 9.10 (s, 1H), 8.41 (s, 1H), 7.68 (s, 1H), 7.41 (d, J = 4 Hz, 1H), 7.23-7.18 (m, 2H), 6.94 (d, J = 3.6 Hz, 1H), 4.75 (s, 1H), 1.26 (s, 9H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 161.1, 152.0, 151.9, 150.2, 142.1, 131.6, 127.6, 125.1, 124.8, 123.3, 122.6, 118.8, 116.3, 116.1, 84.5, 33.7, 31.2 (3C); Mass: m/z (CI) 344 (M+1, 100%); HRMS (ESI): m/z calcd for $C_{19}H_{19}NO_3Cl$ ($[M + H]^+$) 344.1053, found 344.1054.

6-Chloro-4-((5-chloro-2-hydroxyphenyl)amino)-2*H*-chromen-2-one (4l)



Brown solid; Yield: 85%; mp: 251-253 °C; R_f = 0.4 (30% EtOAc/*n*-hexane); IR: 3323, 3201, 1637, 1205, 815 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ 10.12 (s, 1H), 9.14 (s, 1H), 8.38 (s, 1H), 7.70 (d, J = 8.4 Hz, 1H), 7.43 (d, J = 8.8 Hz, 1H), 7.30 (t, J = 8.4 Hz, 2H), 7.04 (d, J = 8.4 Hz, 1H), 4.81 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 160.9, 151.9, 151.8, 151.6, 131.8, 128.2, 127.7 (2C), 125.5, 122.6, 122.3, 118.9, 118.2, 115.9, 85.3; Mass: m/z (CI) 322 (M+1, 100%); HRMS (ESI): m/z calcd for $C_{15}H_{10}NO_3Cl_2$ ($[M + H]^+$) 322.0038, found 322.0038.

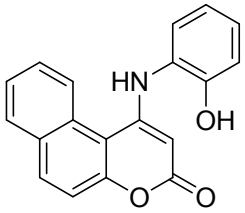
4-((2-Hydroxy-5-nitrophenyl)amino)-2*H*-chromen-2-one (4m)



Chemical Formula: $C_{15}H_{10}N_2O_5$
Exact Mass: 298.0590

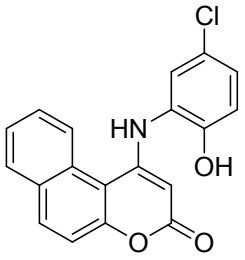
Yellow solid; Yield: 81%; mp: 274-278 °C; R_f = 0.4 (EtOAc); IR: 3245, 3144, 1567, 1245, 741 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ 11.51 (s, 1H), 9.18 (s, 1H), 8.22 (d, J = 6.4 Hz, 1H), 8.17-8.15 (m, 2H), 7.67 (t, J = 6 Hz, 1H), 7.43-7.38 (m, 2H), 7.20 (t, J = 4 Hz, 1H), 4.85 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 161.8, 159.8, 153.7, 152.9, 140.1, 132.7, 125.7, 124.9, 124.8, 124.0, 123.5, 117.4 (2C), 114.9, 86.0; Mass: m/z (CI) 299 (M+1, 100%); HRMS (ESI): m/z calcd for $C_{15}H_{11}N_2O_5$ ($[M + H]^+$) 299.0668, found 299.0679.

1-((2-Hydroxyphenyl)amino)-3*H*-benzo[*f*]chromen-3-one (4n)



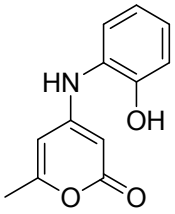
Brown solid; Yield: 80%; mp: 241-243 °C; R_f = 0.3 (50% EtOAc/*n*-hexane); IR: 3347, 3022, 1597, 1215, 760 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ 9.76 (s, 1H), 8.90 (d, J = 8.8 Hz, 1H), 8.72 (s, 1H), 8.17 (d, J = 9.2 Hz, 1H), 8.06 (d, J = 7.6 Hz, 1H), 7.66 (t, J = 7.2 Hz, 1H), 7.59 (t, J = 7.2 Hz, 1H), 7.49 (d, J = 8.8 Hz, 1H), 7.22-7.15 (m, 2H), 7.00 (d, J = 8 Hz, 1H), 6.88 (t, J = 7.2 Hz, 1H), 5.00 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 161.0, 155.8, 153.7, 151.8, 133.3, 130.4, 129.0, 128.3, 127.7, 127.6, 127.0, 125.8, 125.4, 125.0, 119.6, 117.3, 116.6, 108.7, 86.9; Mass: m/z (CI) 304 (M+1, 100%); HRMS (ESI): m/z calcd for $C_{19}H_{14}NO_3$ ($[M + H]^+$) 304.0974, found 304.0972.

1-((5-Chloro-2-hydroxyphenyl)amino)-3*H*-benzo[*f*]chromen-3-one (4o)



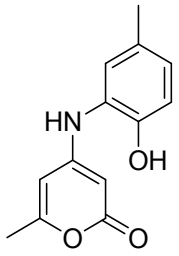
Yellow solid; Yield: 76%; mp: 192-194 °C; R_f = 0.4 (40 % EtOAc/*n*-hexane); IR: 3367, 3188, 1547, 1192, 756 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ 10.16 (s, 1H), 8.90 (d, J = 9.2 Hz, 2H), 8.20 (d, J = 8.8 Hz, 1H), 8.09 (d, J = 8 Hz, 1H), 7.69 (t, J = 7.6 Hz, 1H), 7.62 (t, J = 7.6 Hz, 1H), 7.52 (d, J = 8.8 Hz, 1H), 7.27 (s, 1H), 7.23 (d, J = 8.8 Hz, 1H), 7.02 (d, J = 8.4 Hz, 1H), 5.02 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 160.9, 155.2, 153.8, 150.7, 133.5, 130.5, 129.0, 128.2, 127.8, 127.3, 127.0, 126.1, 125.4, 125.1, 122.4, 117.8, 117.3, 108.7, 88.2; Mass: m/z (CI) 338 (M+1,100%); HRMS (ESI): m/z calcd for $C_{19}H_{13}NO_3Cl$ ($[M + H]^+$) 338.0584, found 338.0591.

4-((2-Hydroxyphenyl)amino)-6-methyl-2*H*-pyran-2-one (4p)



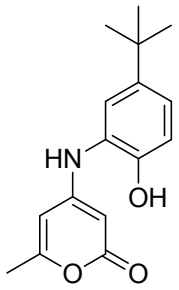
Off white solid; Yield: 80%; mp: 212-214 °C; R_f = 0.3 (EtOAc); IR: 3226, 3022, 1697, 1216, 762 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ 9.73 (s, 1H), 8.65 (s, 1H), 7.11-7.05 (m, 2H), 6.93 (d, J = 8 Hz, 1H), 6.81 (t, J = 7.6 Hz, 1H), 5.94 (s, 1H), 4.74 (s, 1H), 2.10 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 163.4, 160.9, 156.9, 151.6, 127.0, 126.3, 124.9, 119.2, 116.4, 98.5, 80.6, 19.5; Mass: m/z (CI) 218 (M+1, 100%); HRMS (ESI): m/z calcd for $C_{12}H_{12}NO_3$ ($[M + H]^+$) 218.0817, found 218.0817.

4-((2-Hydroxy-5-methylphenyl)amino)-6-methyl-2*H*-pyran-2-one (4q)



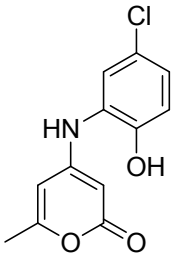
Brown solid; Yield: 81%; mp: 221-223 °C; R_f = 0.4 (EtOAc); IR: 3230, 3064, 1678, 1166, 802 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ 9.45 (s, 1H), 8.59 (s, 1H), 6.88 (t, J= 8.4 Hz, 2H), 6.80 (d, J = 8.4 Hz, 1H), 5.93 (s, 1H), 4.73 (s, 1H), 2.18 (s, 3H), 2.09 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 163.5, 160.8, 156.9, 149.2, 127.9, 127.5, 126.5, 124.5, 116.2, 98.5, 80.6, 20.0, 19.5; Mass: m/z (CI) 232 (M+1, 100%); HRMS (ESI): m/z calcd for $C_{13}H_{14}NO_3$ ($[M + H]^+$) 232.0974, found 232.0970.

4-((5-(Tert-butyl)-2-hydroxyphenyl)amino)-6-methyl-2*H*-pyran-2-one (4r)



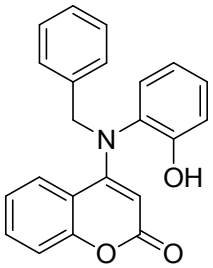
Brown solid; Yield: 86%; mp: 220-224 °C; R_f = 0.4 (EtOAc); IR: 32943, 3223, 1655, 1278, 867 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ 9.55 (s, 1H), 8.70 (s, 1H), 7.09 (t, J = 7.0 Hz, 2H), 6.87 (d, J = 8 Hz, 1H), 5.95 (s, 1H), 4.72 (s, 1H), 2.12 (s, 3H), 1.23 (s, 9H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 163.5, 160.7, 157.0, 149.3, 141.6, 124.1, 123.7, 123.1, 115.9, 98.5, 80.5, 33.7, 31.2 (3C), 19.4; Mass: m/z (CI) 274 (M+1, 100%); HRMS (ESI): m/z calcd for $C_{16}H_{20}NO_3$ ($[M + H]^+$) 274.1443, found 274.1447.

4-((5-Chloro-2-hydroxyphenyl)amino)-6-methyl-2*H*-pyran-2-one (4s)



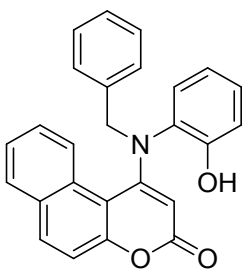
Brown solid; Yield: 83%; mp: 209-211 °C; R_f = 0.4 (EtOAc); IR: 3250, 3105, 1676, 1271, 810 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ 10.14 (s, 1H), 8.80 (s, 1H), 7.19-7.13 (m, 2H), 6.96 (d, J = 8 Hz, 1H), 5.98 (s, 1H), 4.81 (s, 1H), 2.14 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 163.3, 161.1, 156.5, 150.6, 126.6, 126.4, 125.6, 122.1, 117.7, 98.4, 81.4, 19.5; Mass: m/z (CI) 252 (M+1, 100%); HRMS (ESI): m/z calcd for $C_{12}H_{11}NO_3Cl$ ($[M+H]^+$) 252.0427, found 252.0433.

4-(Benzyl(2-hydroxyphenyl)amino)-2*H*-chromen-2-one (4t)



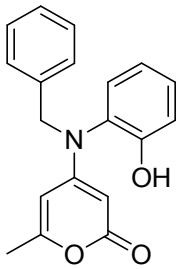
Off white solid; Yield: 84%; mp: 182-184 °C; R_f = 0.5 (50% EtOAc/*n*-hexane); IR: 3187,1661, 1214, 756 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ 10.15 (s, 1H, D_2O Ex), 7.54 (d, J = 7.2 Hz, 2H), 7.42 (t, J = 6.4 Hz, 1H), 7.34-7.23 (m, 4H), 7.10 (t, J = 8.4 Hz, 3H), 6.98 (d, J = 7.6 Hz, 2H), 6.76 (t, J = 7.2 Hz, 1H), 5.67 (s, 1H), 4.95 (s, 2H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 161.6, 155.9, 153.4, 151.8, 136.3, 134.1, 130.4, 128.1(2C), 127.5, 127.1, 126.8, 126.6(2C), 125.3, 122.4, 119.6, 116.8, 116.6, 116.3, 95.1, 57.0; Mass: m/z (CI) 344 (M+1, 100%); HRMS (ESI): m/z calcd for $C_{22}H_{18}NO_3$ ($[M + H]^+$) 344.1287, found 344.1285.

1-(Benzyl(2-hydroxyphenyl)amino)-3*H*-benzo[*f*]chromen-3-one (4u)



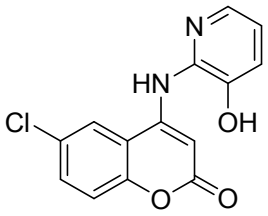
Brown color solid; Yield: 78%; mp: 201-203 °C; R_f = 0.5 (40% EtOAc/*n*-hexane); IR: 3378, 3167, 1633, 1276, 867; ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.54 (s, 1H), 9.05 (d, J = 5.6 Hz, 1H), 8.01 (d, J = 8.8 Hz, 1H), 7.80 (d, J = 4.4 Hz, 1H), 7.71 (d, J = 6.8 Hz, 2H), 7.44 (d, J = 8.8 Hz, 1H), 7.35-7.38 (m, 4H), 7.27 (d, J = 6.4 Hz, 1H), 6.89 (d, J = 7.2 Hz, 1H), 6.81 (d, J = 6.4 Hz, 1H), 6.47 (d, J = 6.8 Hz, 1H), 6.32 (t, J = 6.8 Hz, 1H), 6.02 (s, 1H), 5.02 (s, 2H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 160.6, 157.3, 154.0, 151.2, 137.5, 134.6, 133.1, 129.7, 128.5 (2C), 128.1, 128.0, 127.6 (2C), 127.1, 126.7, 126.3, 125.7, 125.1, 125.0, 119.0, 117.0, 116.8, 110.1, 99.8, 55.0; Mass: m/z (CI) 394 (M+1, 100%); HRMS (ESI): m/z calcd for $C_{26}H_{20}NO_3$ ([M + H]$^+$) 394.1443, found 394.1443.

4-(Benzyl(2-hydroxyphenyl)amino)-6-methyl-2*H*-pyran-2-one (4v)



Off white solid; Yield: 80%; mp: 141-143 °C; R_f = 0.4 (50% EtOAc/*n*-hexane); IR: 3400, 1728, 1232, 744 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.35-7.25 (s, 4H), 7.19 (s, 1H), 7.03-6.96 (m, 2H), 6.60 (t, J = 8 Hz, 2H), 6.31 (s, 1H), 6.16 (s, 1H), 4.97 (s, 1H), 4.34 (s, 2H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 170.4, 163.3, 163.2, 139.9 (2C), 138.1, 128.2 (2C), 127.2, 126.7 (2C), 126.6, 121.3, 115.8, 112.3, 99.9, 89.2, 45.5, 19.3; Mass: m/z (CI) 308 (M+1, 100%); HRMS (ESI): m/z calcd for $C_{19}H_{18}NO_3$ ([M + H]$^+$) 308.1287, found 308.1287.

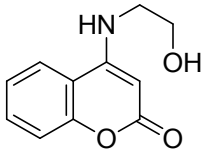
6-Chloro-4-((3-hydroxypyridin-2-yl)amino)-2*H*-chromen-2-one (4w)



Pale yellow solid; Yield: 78%; mp: 256-260 °C; R_f = 0.4 (EtOAc); IR: 3434, 3123, 1721, 1421, 745 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.62 (s, 1H), 8.95 (s, 1H), 8.30 (s, 1H), 7.96 (s, 1H), 7.70 (d, J = 8 Hz, 1H), 7.44 (d, J = 8.8 Hz, 1H), 7.35 (d, J = 7.6 Hz, 1H), 7.15 (d, J = 4.4 Hz, 1H), 6.45 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 161.0, 151.9, 148.1, 145.0, 141.3,

137.8, 131.7, 127.9, 122.8, 122.2, 121.2, 119.0, 116.0, 89.4; Mass: m/z (CI) 289 (M+1, 100%); HRMS (ESI): m/z calcd for $C_{14}H_{10}N_2O_3Cl$ ($[M + H]^+$) 289.0380, found 289.0378.

4-((2-Hydroxyethyl)amino)-2*H*-chromen-2-one (7)

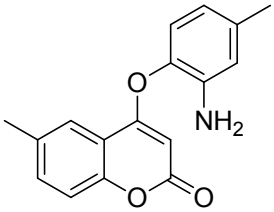


Chemical Formula: $C_{11}H_{11}NO_3$
Exact Mass: 205

Off white solid; Yield: 70%; mp: 182-183 °C; R_f = 0.3 (EtOAc); IR: 3309, 3089, 1658, 1193, 758 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ 8.07 (d, J= 8 Hz, 1H), 7.63-7.57 (m, 2H), 7.32 (t, J= 8 Hz, 2H), 5.21 (s, 1H), 4.87 (t, J = 6 Hz, 1H, D_2O Ex), 3.67-3.63 (m, 2H), 3.38-3.32 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 162.1, 153.4, 152.8, 132.0, 123.4, 122.2, 116.9, 114.2, 81.1, 58.2, 44.7; Mass: m/z (CI) 206 (M+1, 100%); HRMS (ESI): m/z calcd for $C_{11}H_{12}NO_3$ ($[M + H]^+$) 206.0817, found 206.0813.

General Procedure for the preparation of 3a: A mixture of 4-bromo coumarin/pyran derivatives (**1a** 1.05 m.mol), an amino phenol (**2a** 1.05 m.mol) and K_2CO_3 (1.32 m. mol) in DMF (3 mL) was stirred at 60 ^oC for 3 h. After completion of the reaction, the mixture was cooled to room temperature, diluted with water (10 mL) and extracted with ethyl acetate (2×20 mL). The organic layers were collected, combined, dried over anhydrous Na_2SO_4 and concentrated under vacuum. The residue obtained was purified by column chromatography using ethylacetate/hexane to give the desired product.

4-(2-Amino-4-methylphenoxy)-6-methyl-2*H*-chromen-2-one (3a)



Brown solid; Yield: 83%; mp: 158-162 °C; R_f= 0.5 (20% EtOAc/*n*-hexane); IR: 3468, 3365, 1715, 1209, 823 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.83 (s, 1H), 7.42 (d, J = 8.4 Hz, 1H), 7.27 (d, J = 7.2 Hz, 1H), 6.88 (d, J = 8.4 Hz, 1H), 6.69 (s, 1H), 6.62 (d, J = 8 Hz, 1H), 5.49 (s,

1H), 3.63 (s, 2H, D_2O Ex), 2.46 (s, 3H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.3, 162.9, 151.8, 138.0, 137.5, 136.8, 133.9, 133.7, 122.6, 121.5, 119.9, 117.8, 116.6, 114.9, 93.0, 21.0, 20.9; Mass: m/z (CI) 282 (M+1, 100%).

Single crystal X-ray data:

The X-ray data collection was monitored by SMART program (Bruker, 2003). All the data were corrected for Lorentzian, polarization and absorption effects using SAINT and SADABS programs (Bruker, 2003). SHELX-97 was used for structure solution and full matrix leastsquares refinement on F2. Molecular and packing diagrams were generated using ORTEP-3 and Mercury-3.0. Geometrical calculations were performed using SHELXTL (Bruker, 2003) and PLATON.

Crystal data of (7): CCDC 1825038, Single crystals suitable for X-ray diffraction of **7** DCM: EtOAc (1:1). Molecular formula = C_{11} H_{11} N_1 O_3, Formula weight = 205.21, Crystal system = Triclinic, space group = P -1, a = 8.0084(3) Å, b = 8.1626(3) Å, c = 8.5962(3) Å, V = 465.51(3) Å3, T = 296(2) K, Z = 2, Dc = 1.464 Mg/m^3, 7164 Reflections collected, 1801 [R(int) = 0.0751] independent reflections, Goodness of fit = 1.066.

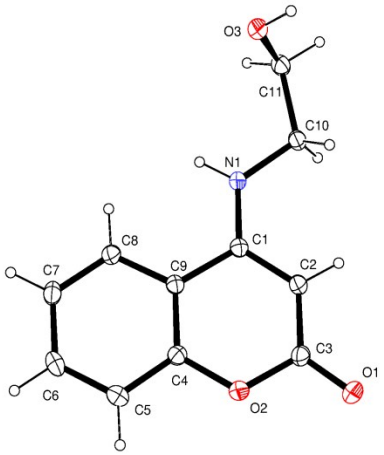


Fig. S-1 X-ray crystal structure of **7** (ORTEP diagram). Thermal ellipsoids are drawn at the 50% probability level.

Reference

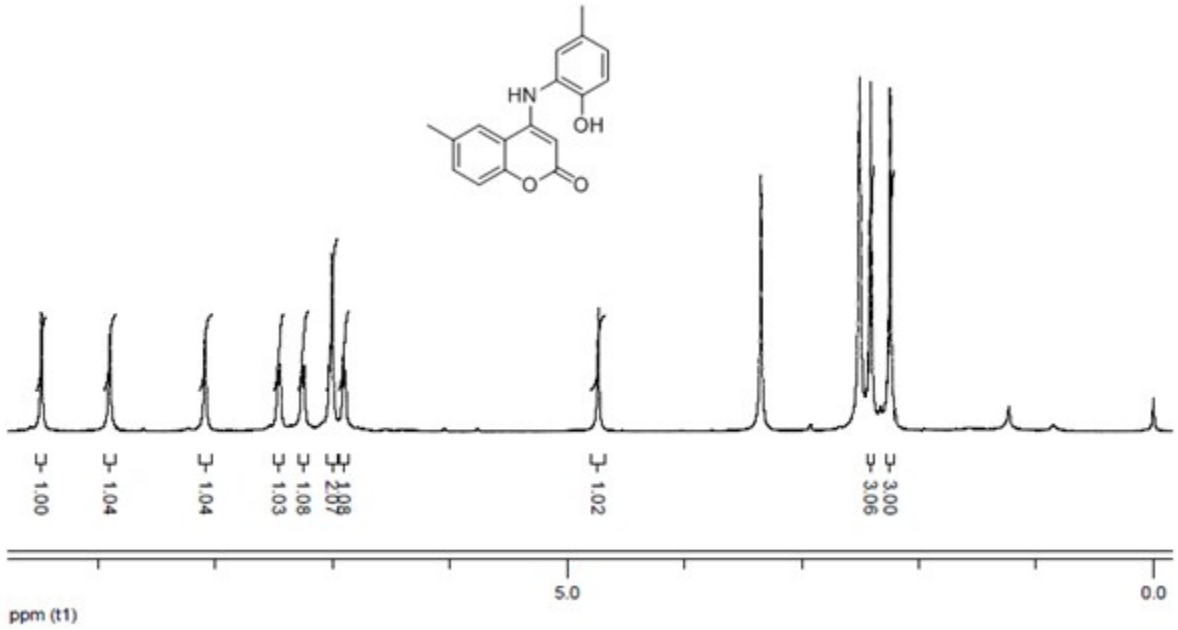
1 (a) C. Cheng, W. W. Chen, B. Xu, M. H. Xu, *Org. Chem. Front*., 2016, **3**, 1111–1115. (b) M. L. N. Rao, V. Venkatesh, D. N. Jadhav, *Eur. J. Org. Chem.* 2010, 3945–3955

2 G. Feng, J. Wu, W. M. Dai, *Tetrahedron*, 2006, **62**, 4635-4642.

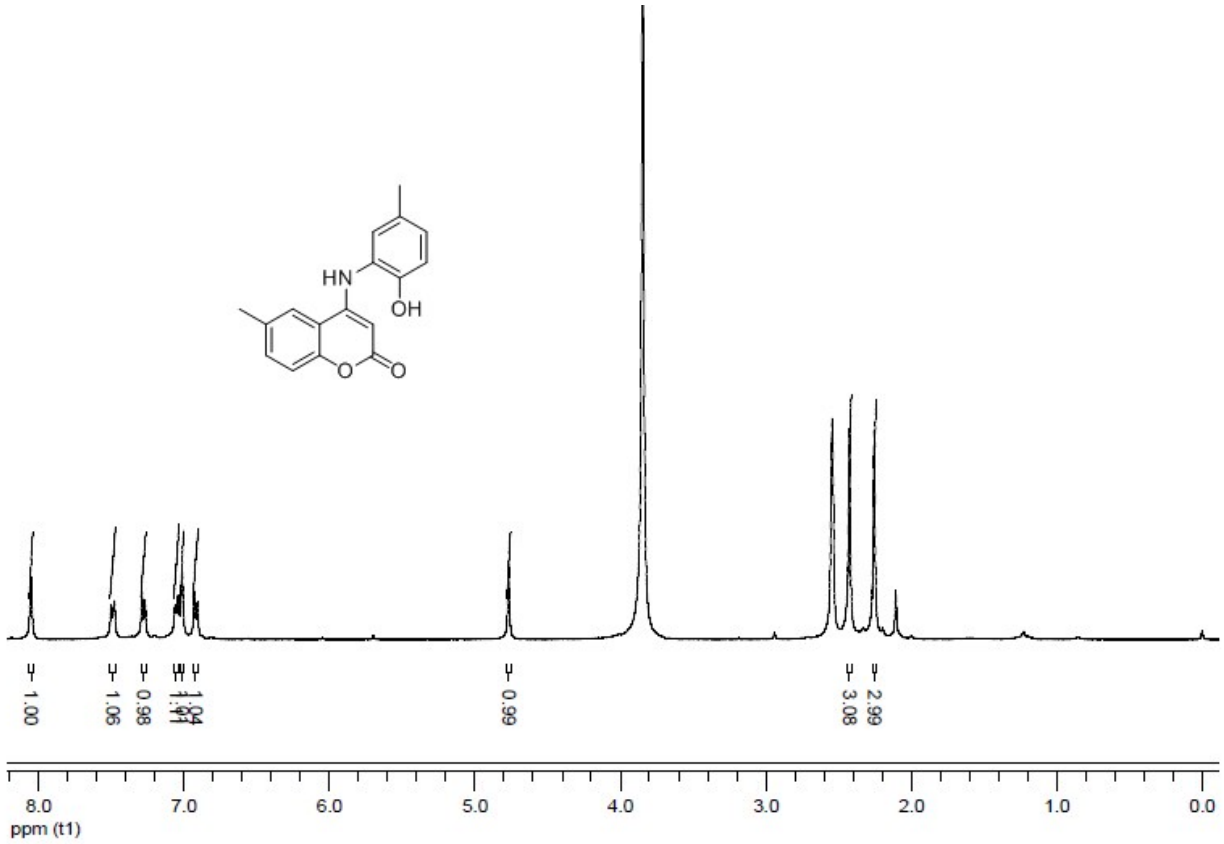
3 M Cervera, M Moreno-mañas, R Pleixats, *Tetrahedron*, 1990, **46**, 7885-7892.

Copies of ^{1}H and ^{13}C NMR spectra

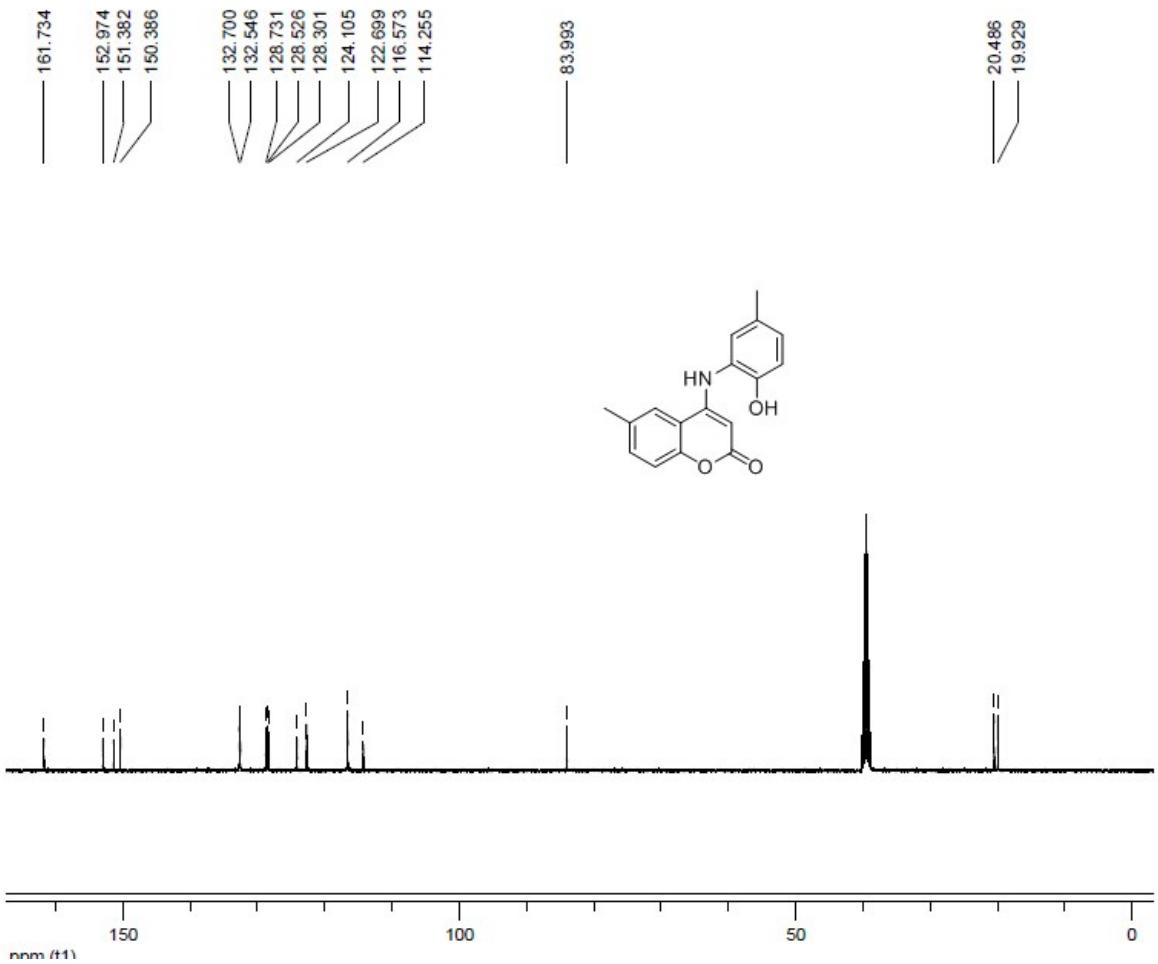
4a ^{1}H NMR (400 MHz, DMSO-d_6)



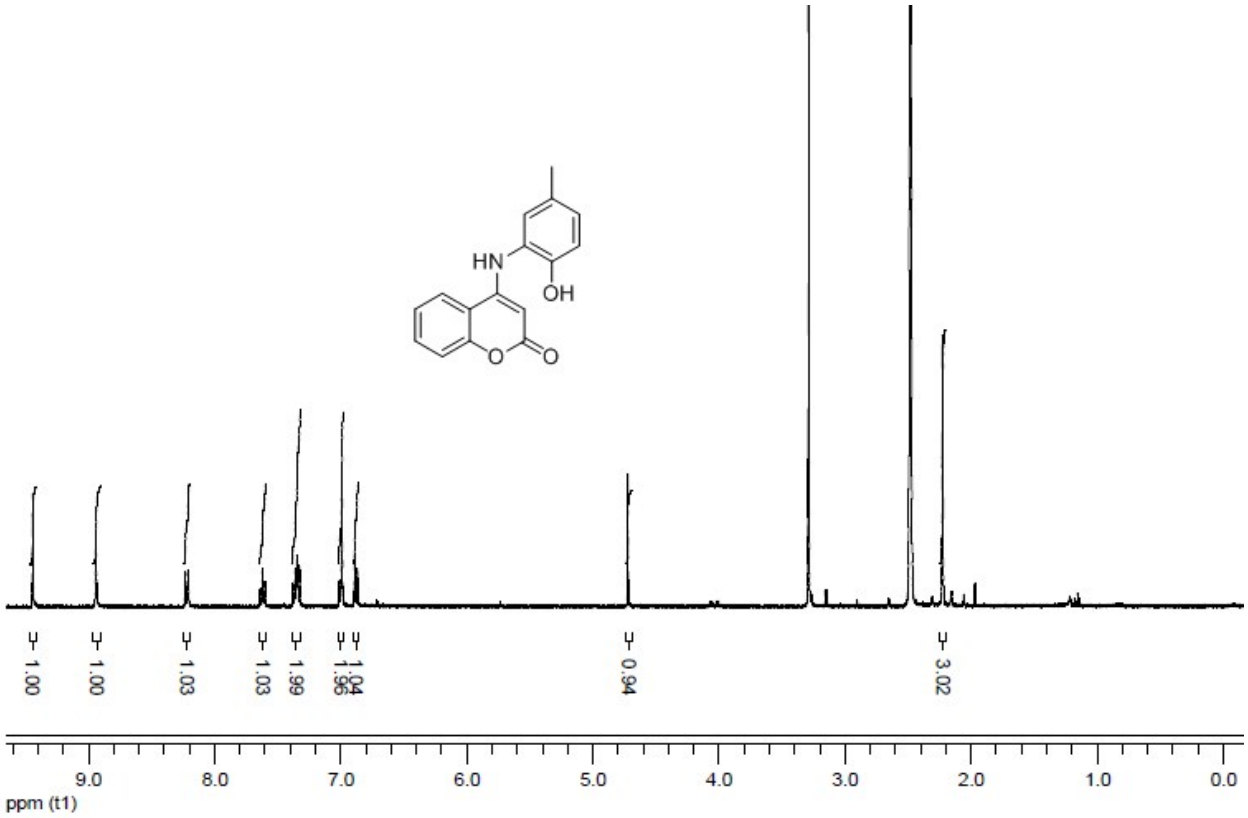
4a ^{1}H NMR (400 MHz, DMSO-D_2O Ex)



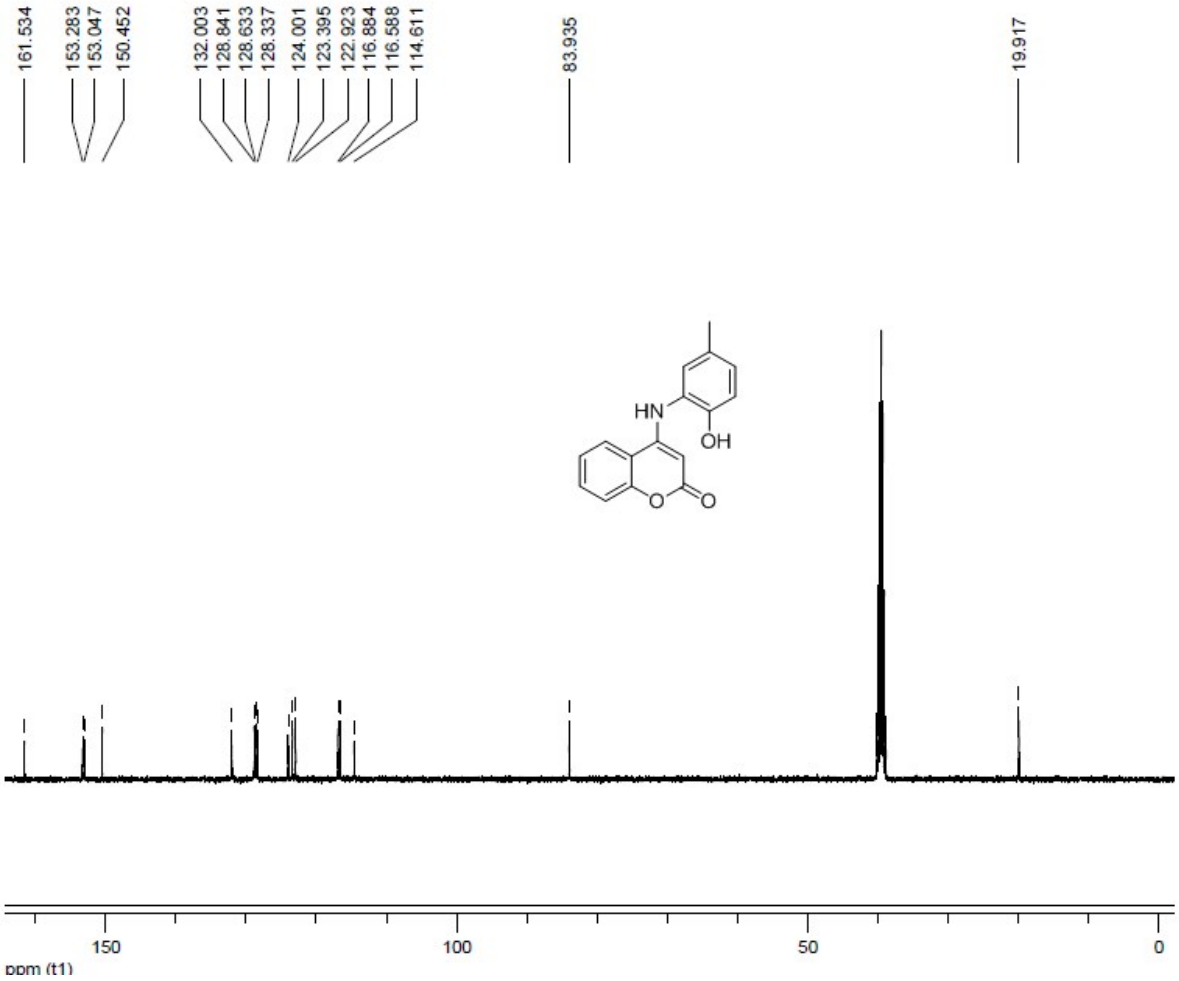
4a ^{13}C NMR (100 MHz, DMSO-d_6)



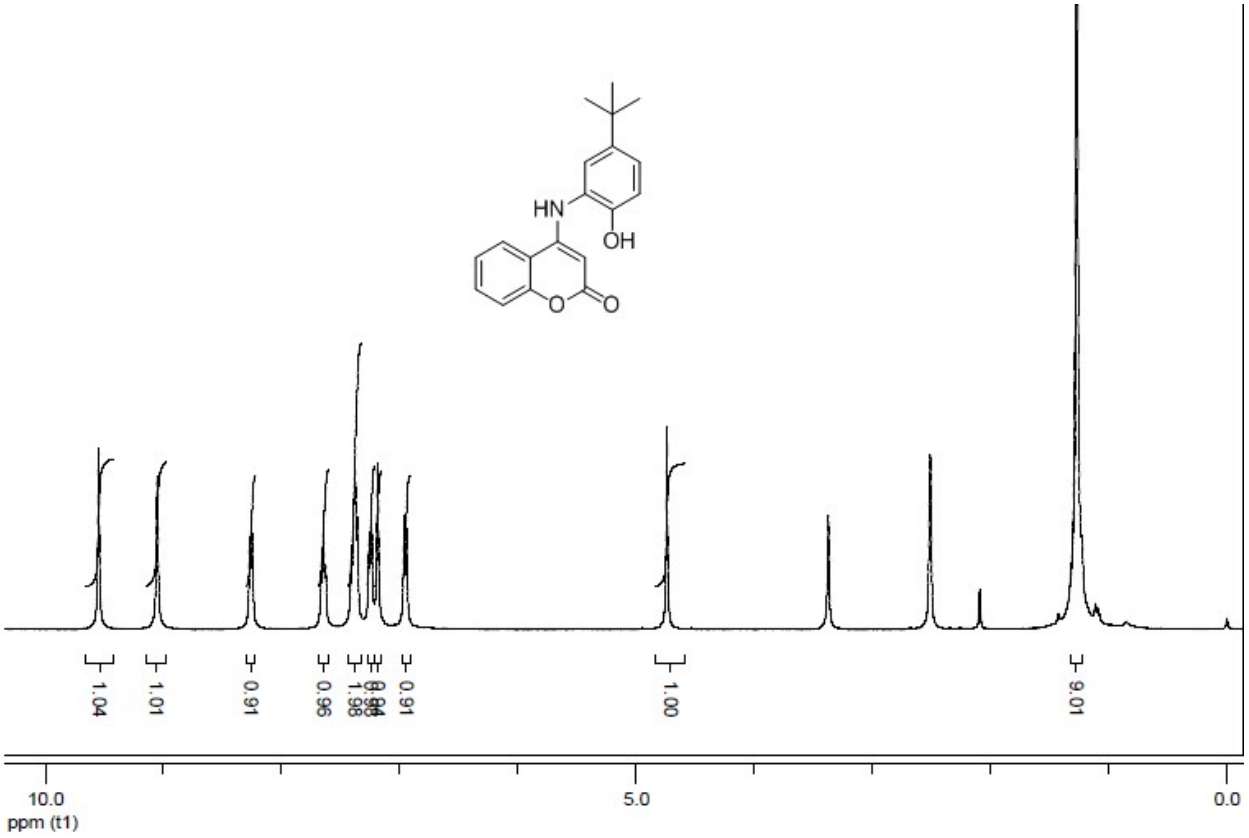
4b ^{1}H NMR (400 MHz, DMSO-d_6)



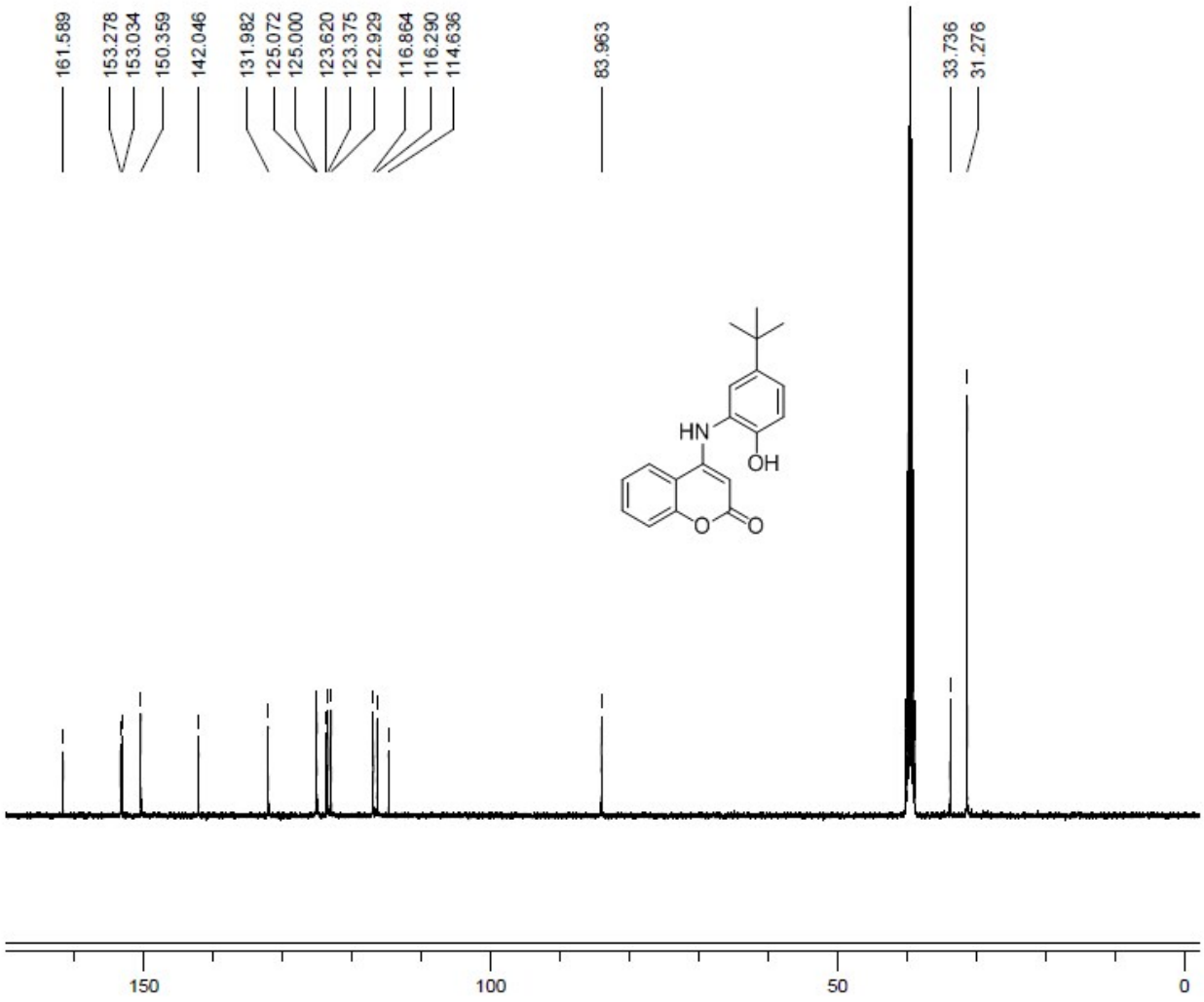
4b ^{13}C NMR (100 MHz, DMSO-d_6)



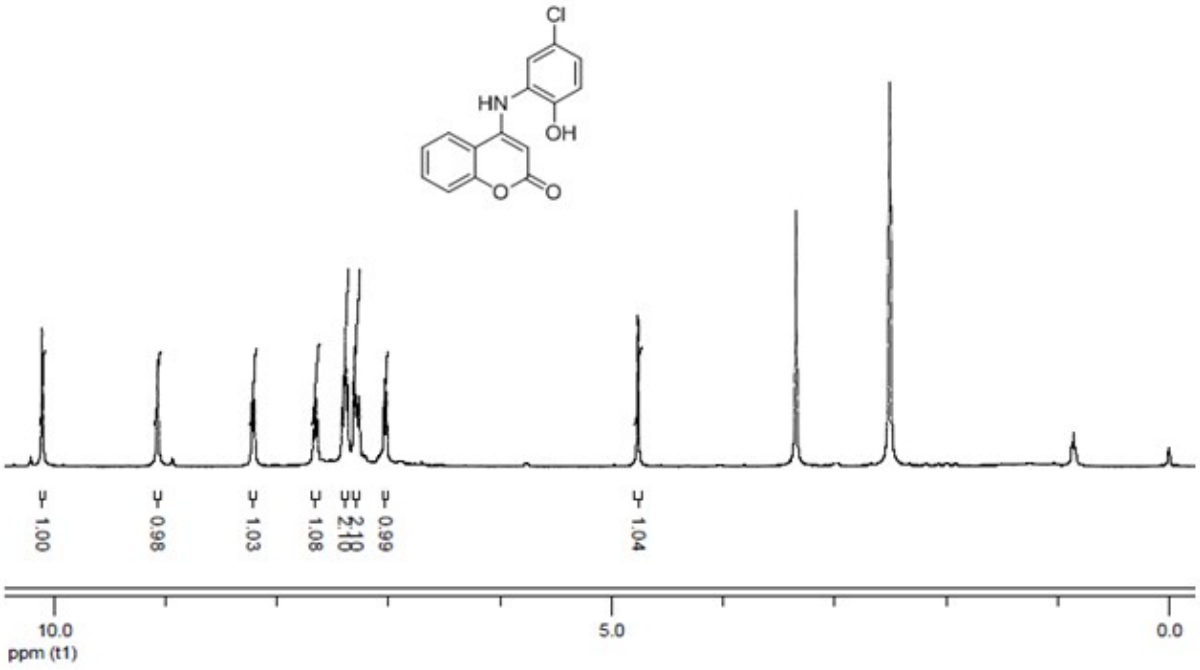
4c ^{1}H NMR (400 MHz, DMSO-d_6)



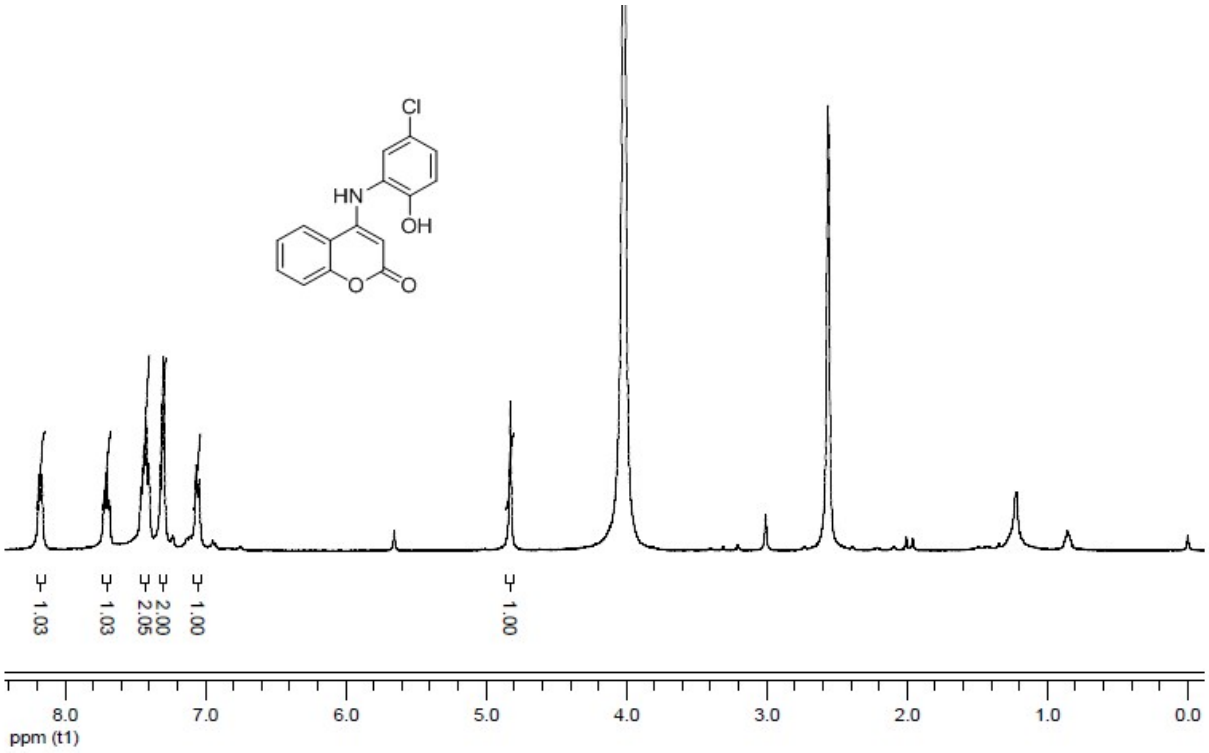
4c ^{13}C NMR (100 MHz, DMSO-d_6)



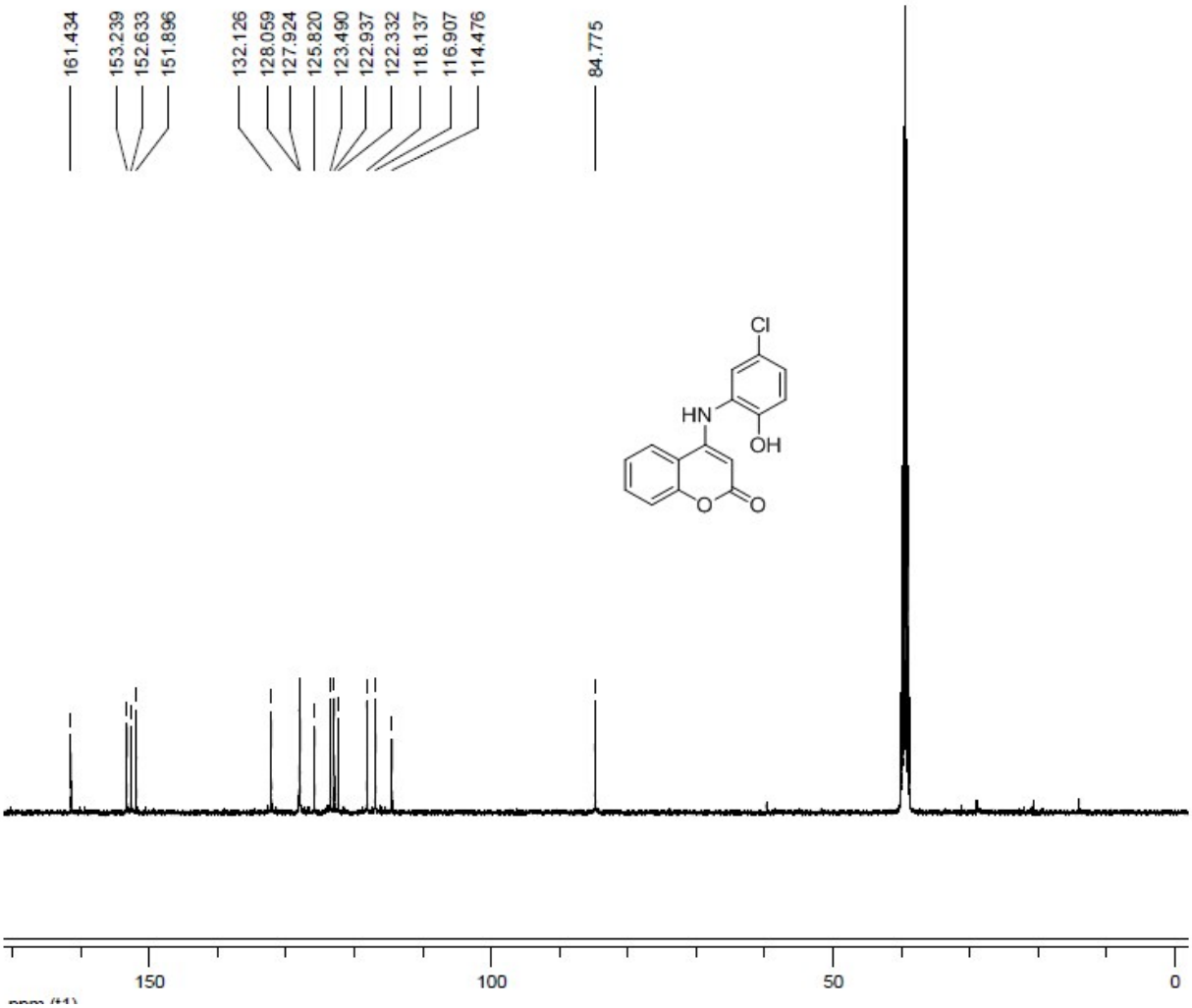
4d ^{1}H NMR (400 MHz, DMSO-d_6)



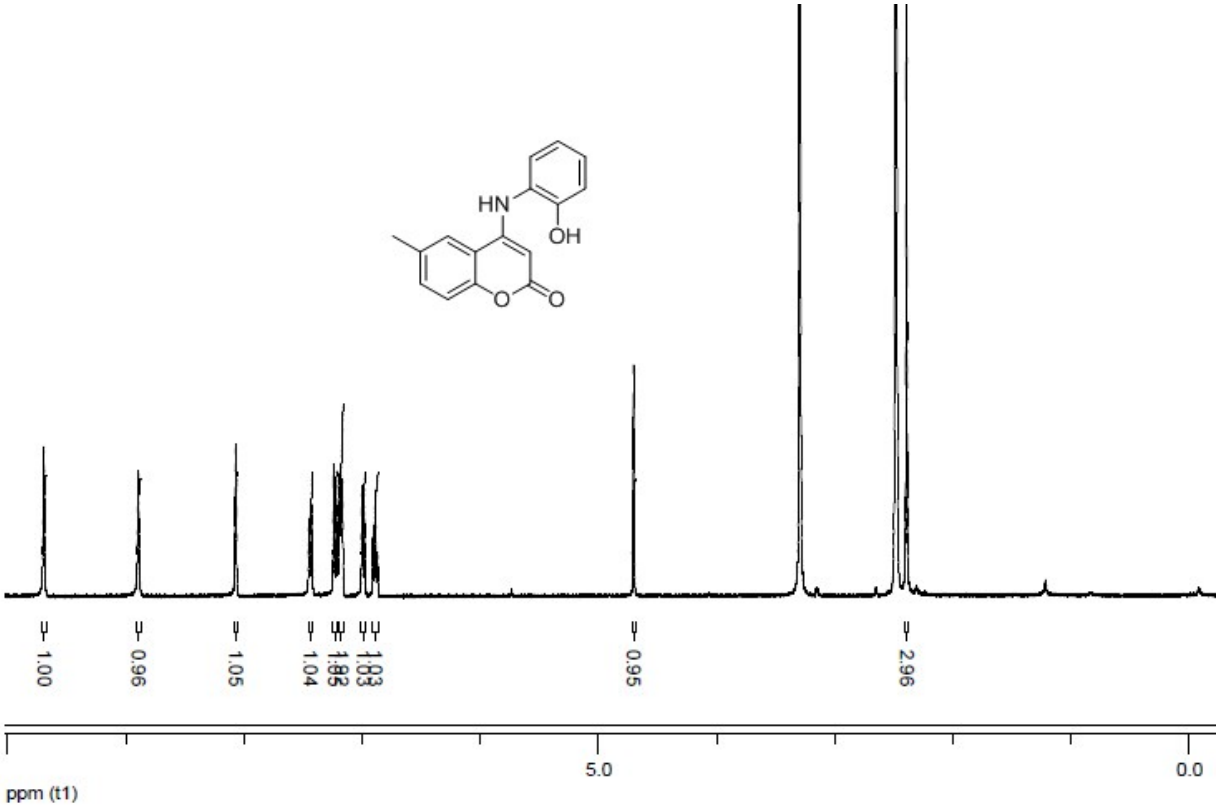
4d ^{1}H NMR (400 MHz, DMSO-D_2O Ex)



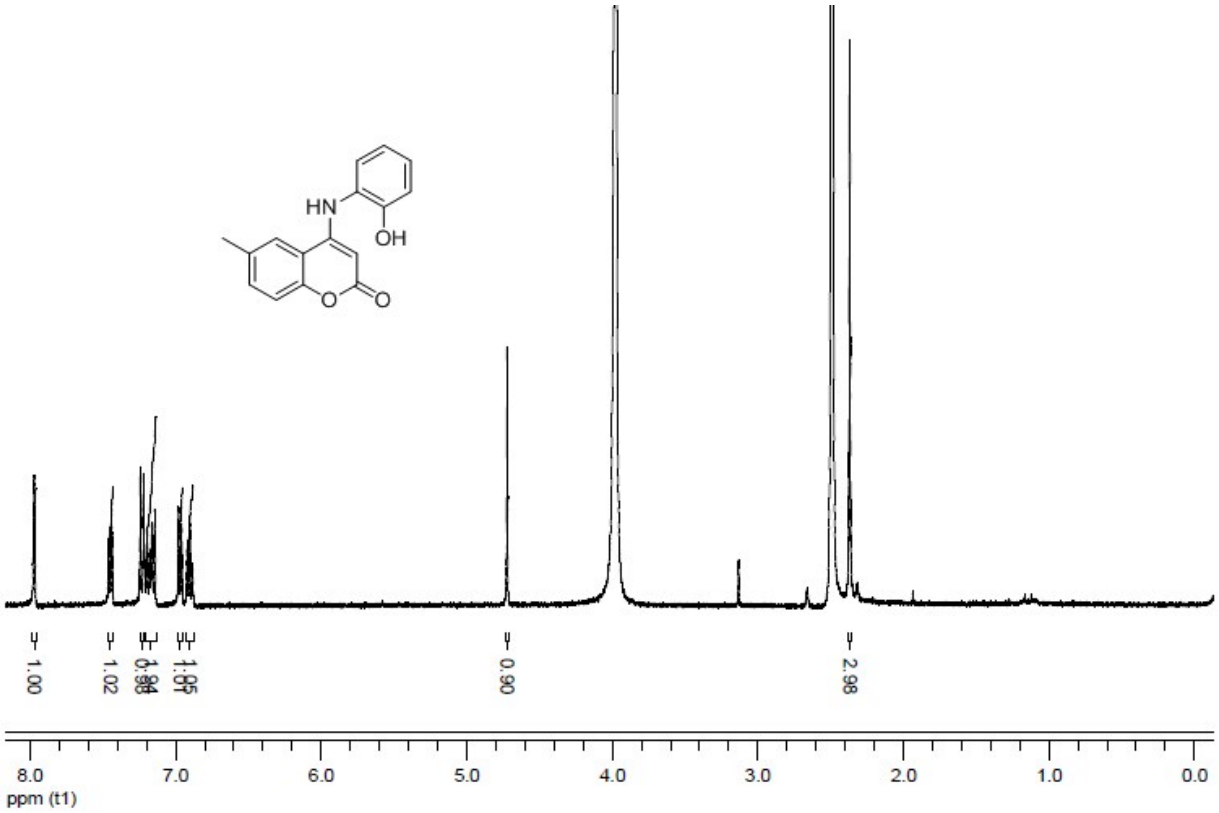
4d ^{13}C NMR (100 MHz, DMSO-d_6)



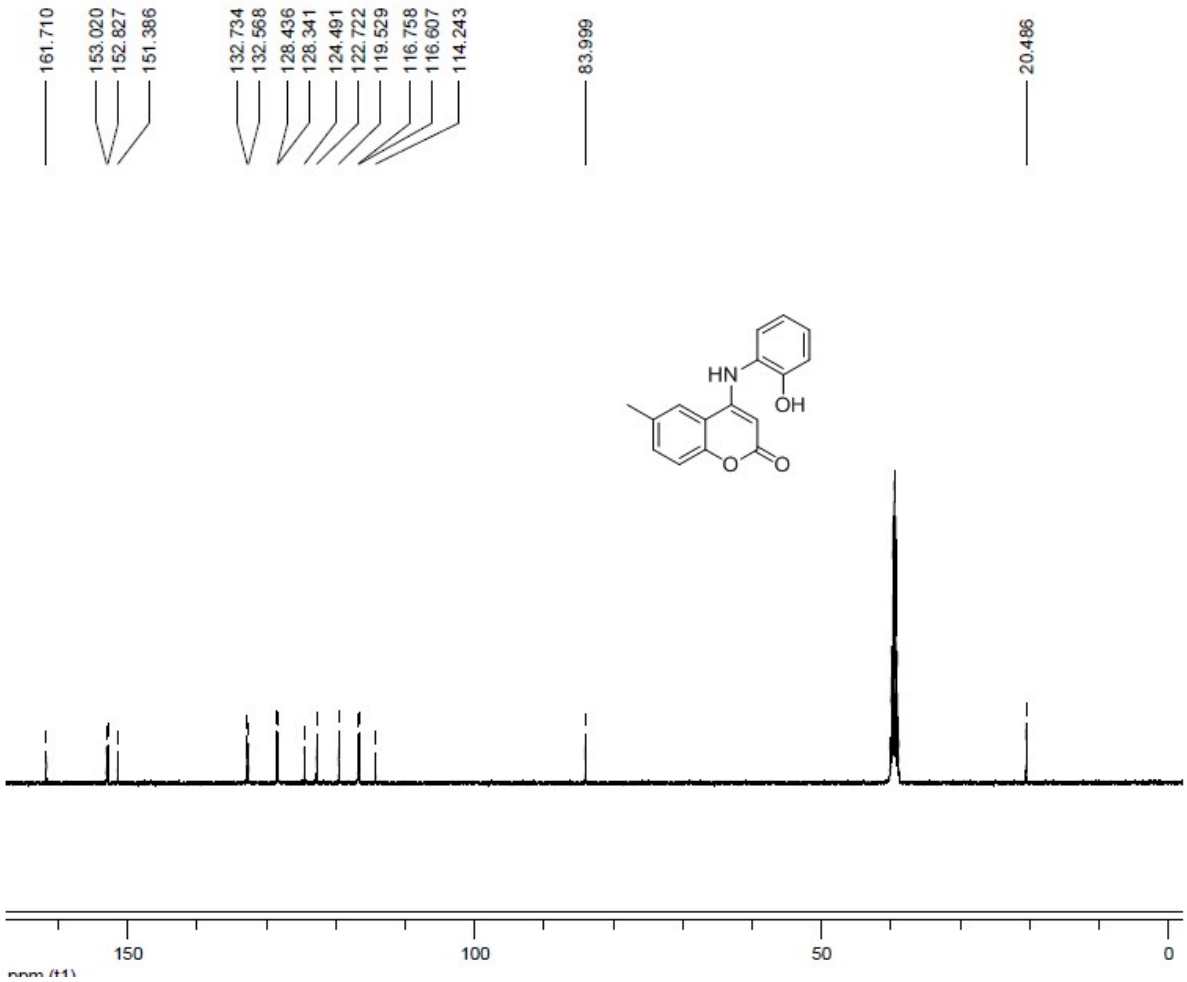
4e ^{1}H NMR (400 MHz, DMSO-d_6)



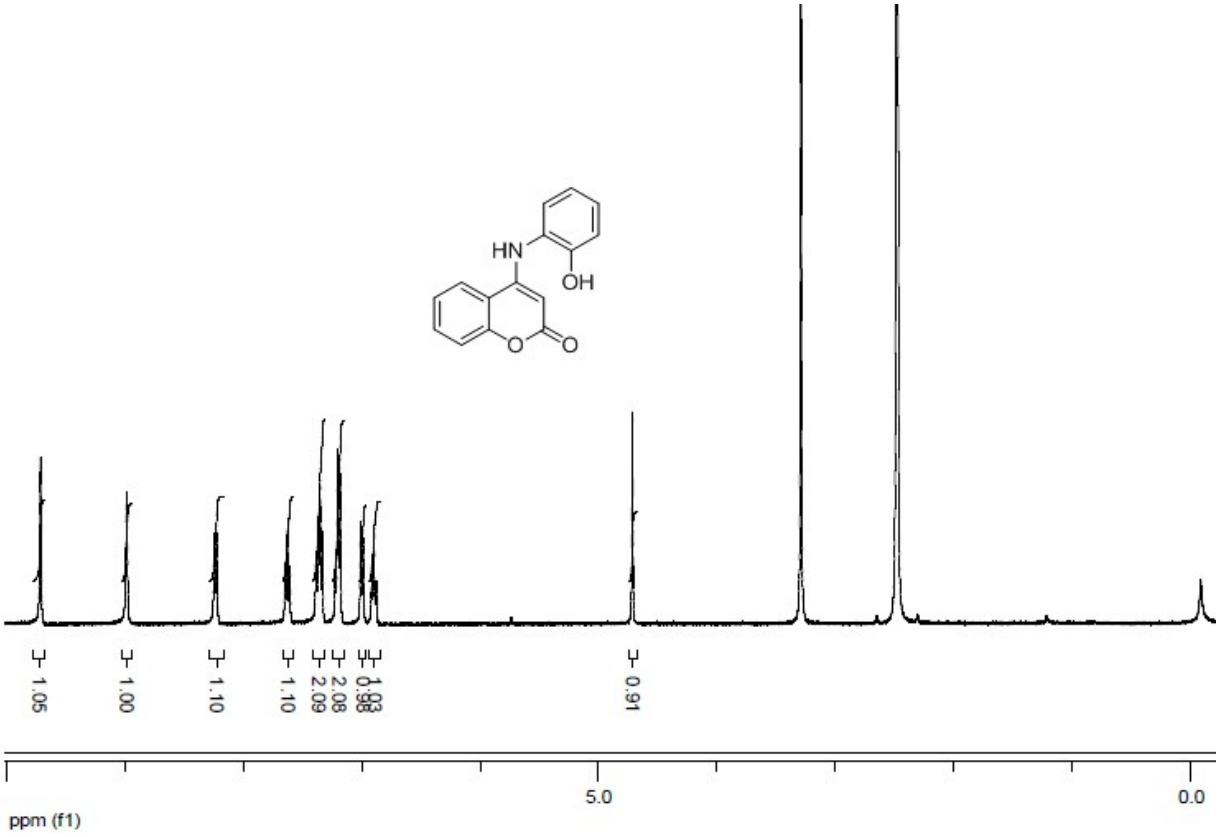
4e ^{1}H NMR (400 MHz, DMSO-D_2O Ex)



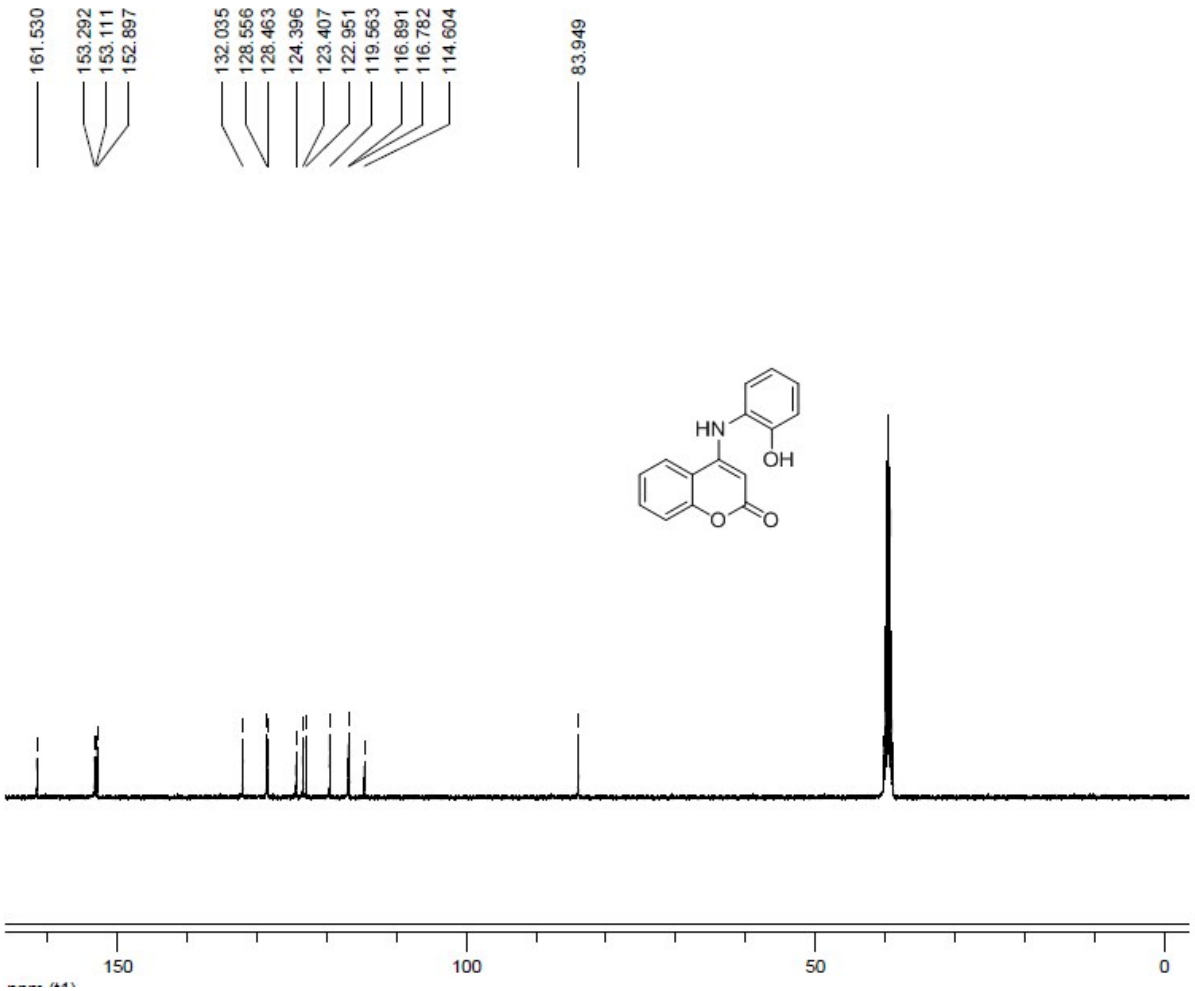
4e ^{13}C NMR (100 MHz, DMSO-d_6)



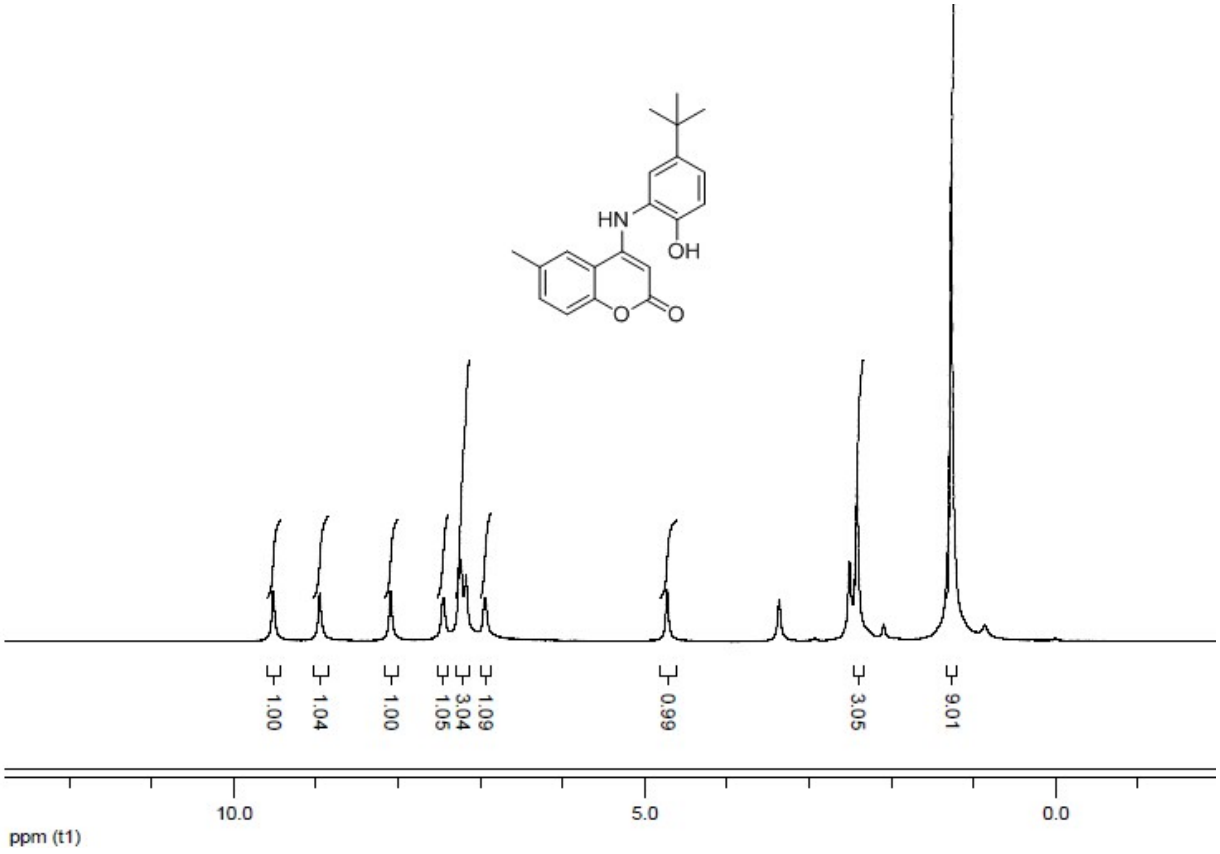
4f ^{1}H NMR (400 MHz, DMSO-d_6)



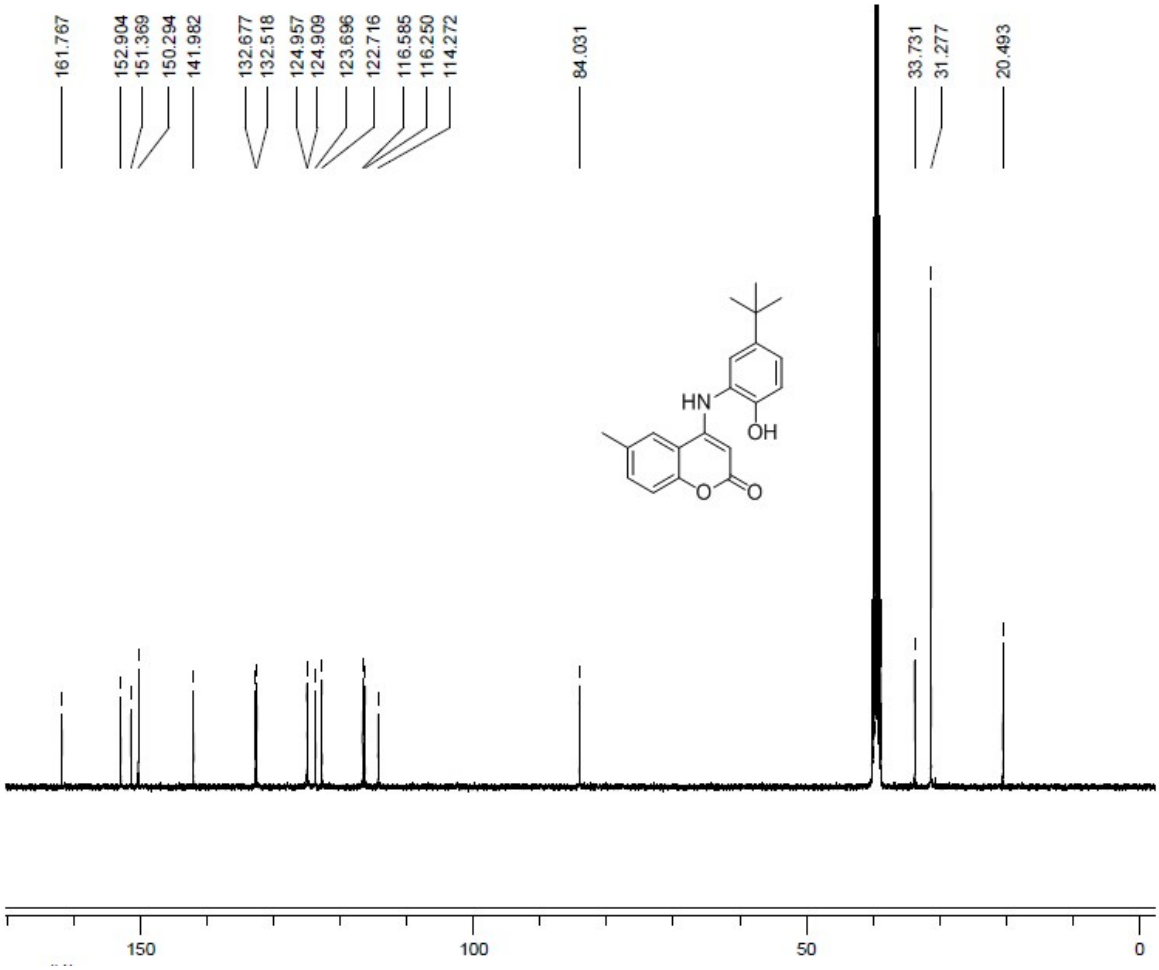
4f ^{13}C NMR (100 MHz, DMSO-d_6)



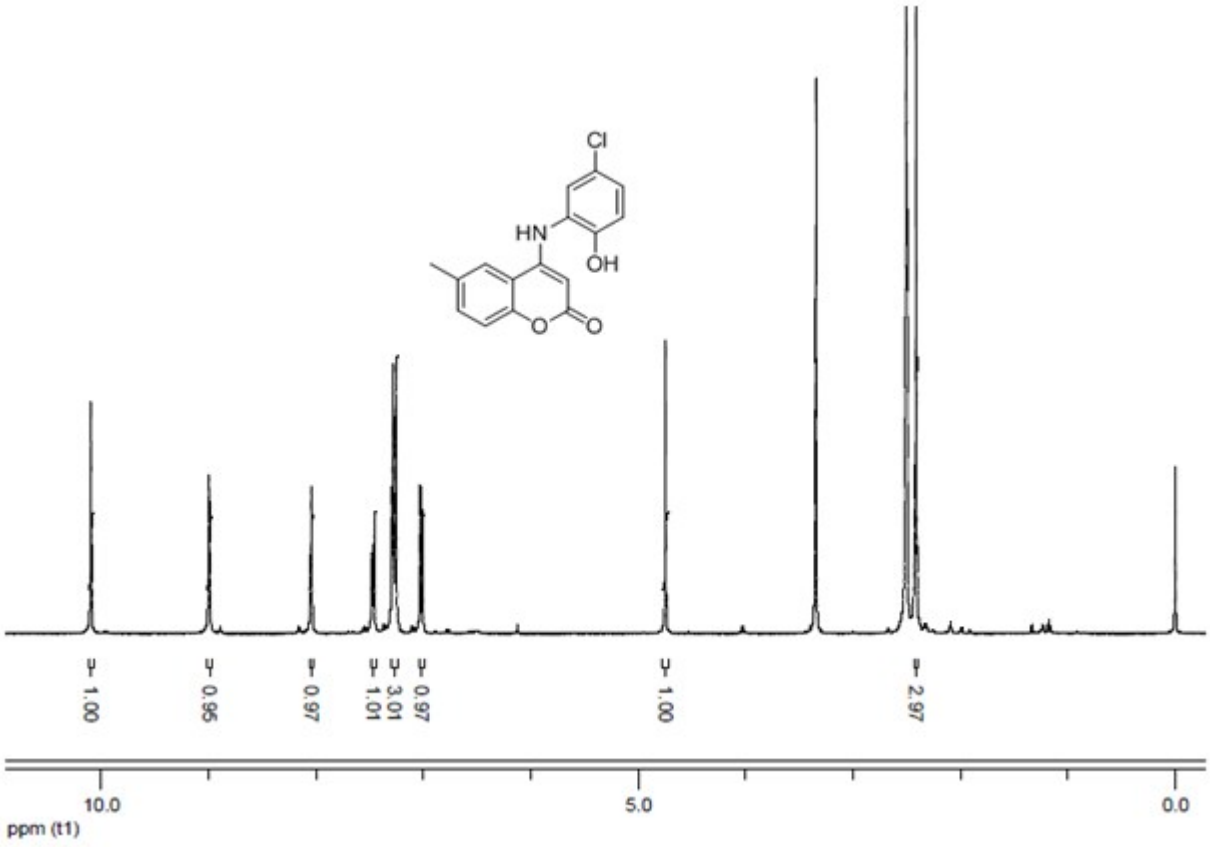
4g ^{1}H NMR (400 MHz, DMSO-d_6)



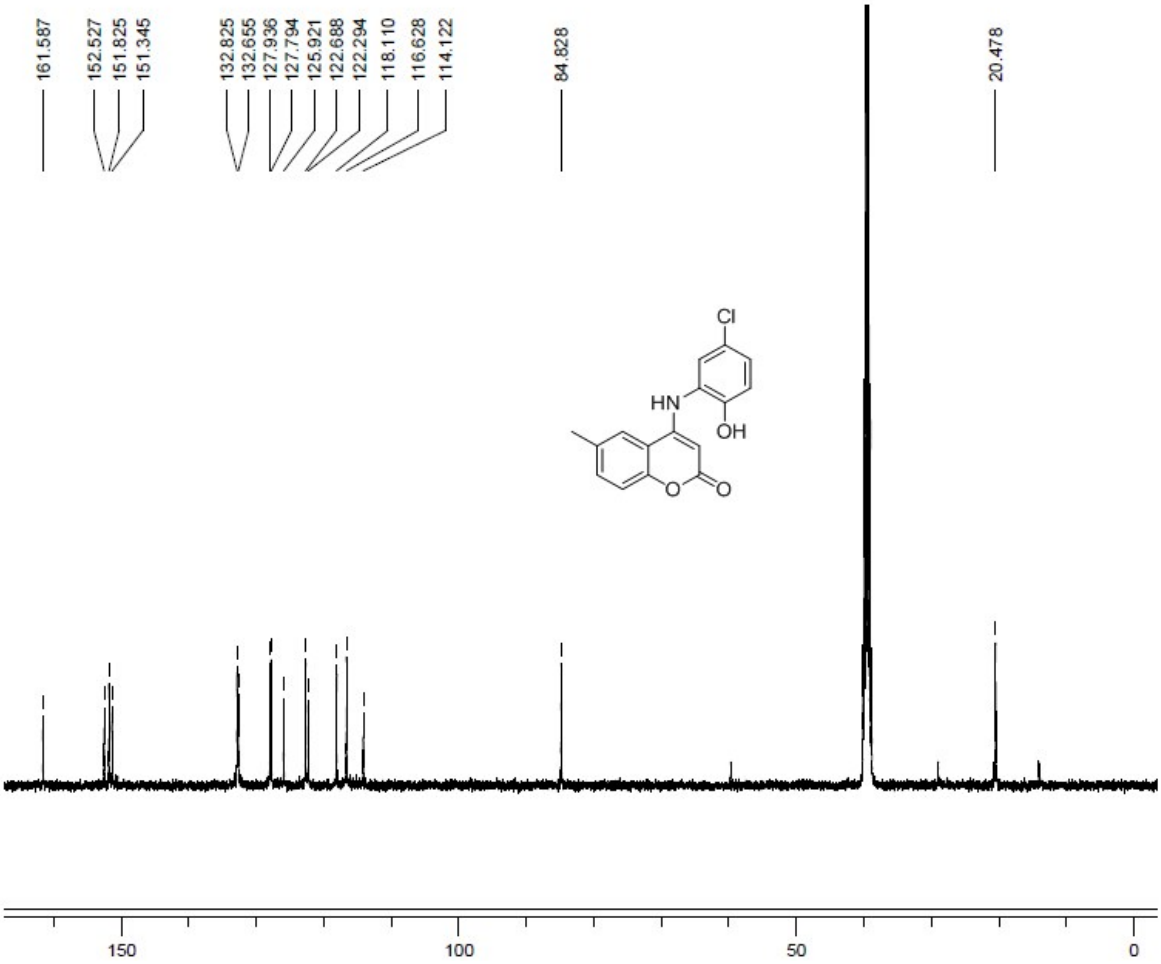
4g ^{13}C NMR (100 MHz, DMSO-d_6)



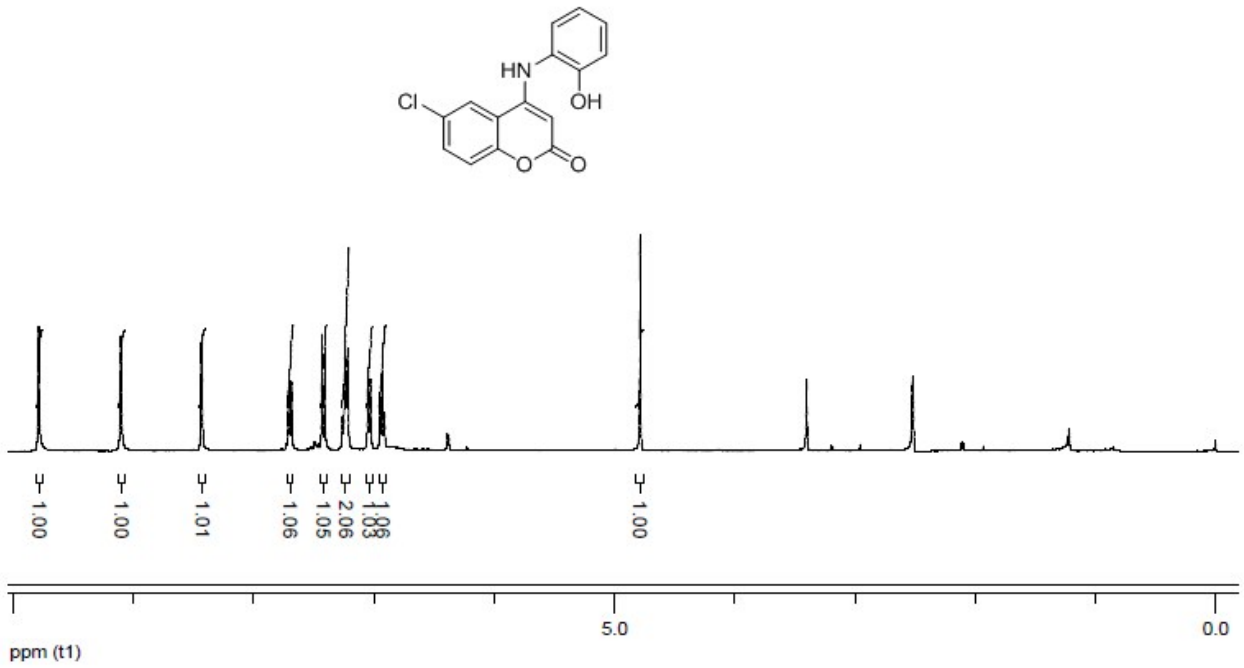
4h ^{1}H NMR (400 MHz, DMSO-d_6)



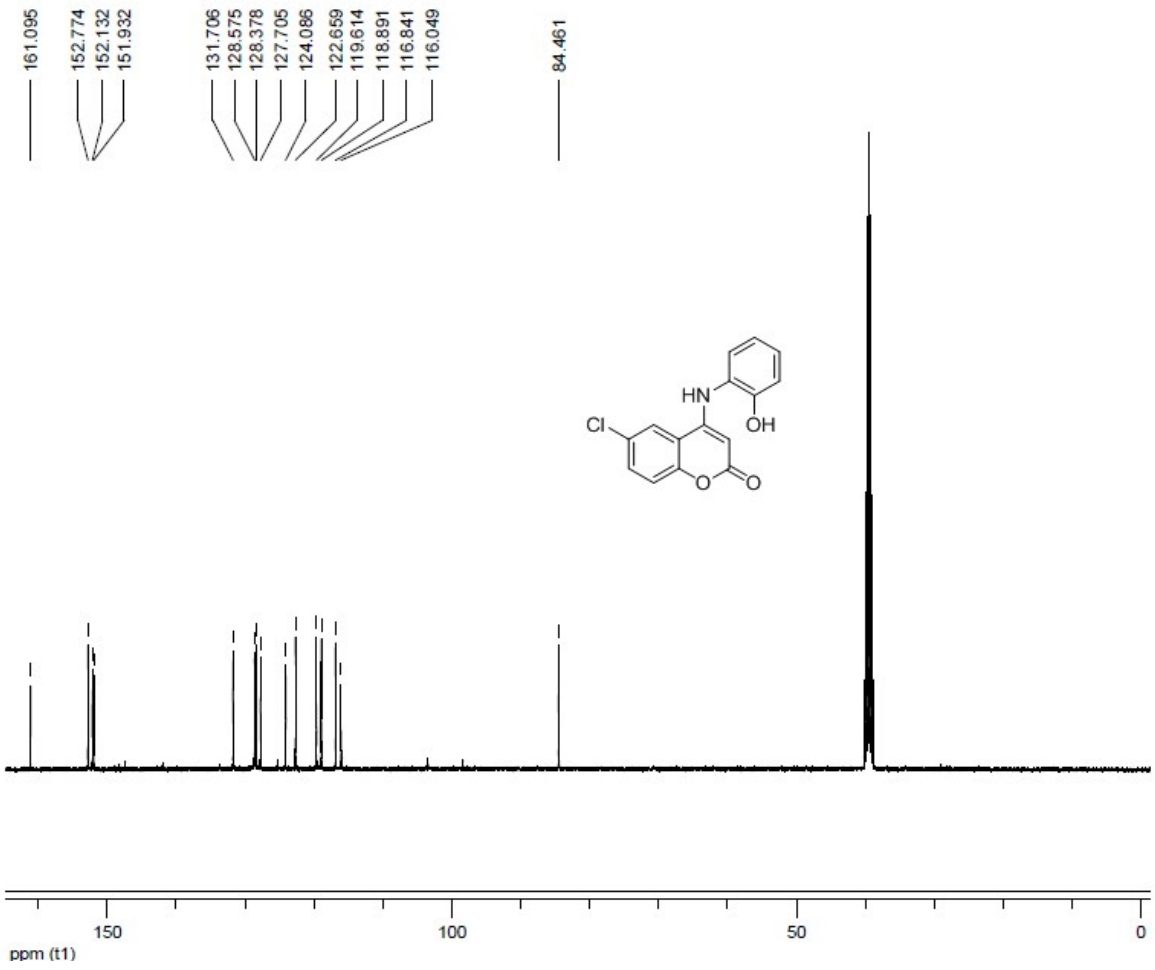
4h ^{13}C NMR (100 MHz, DMSO-d_6)



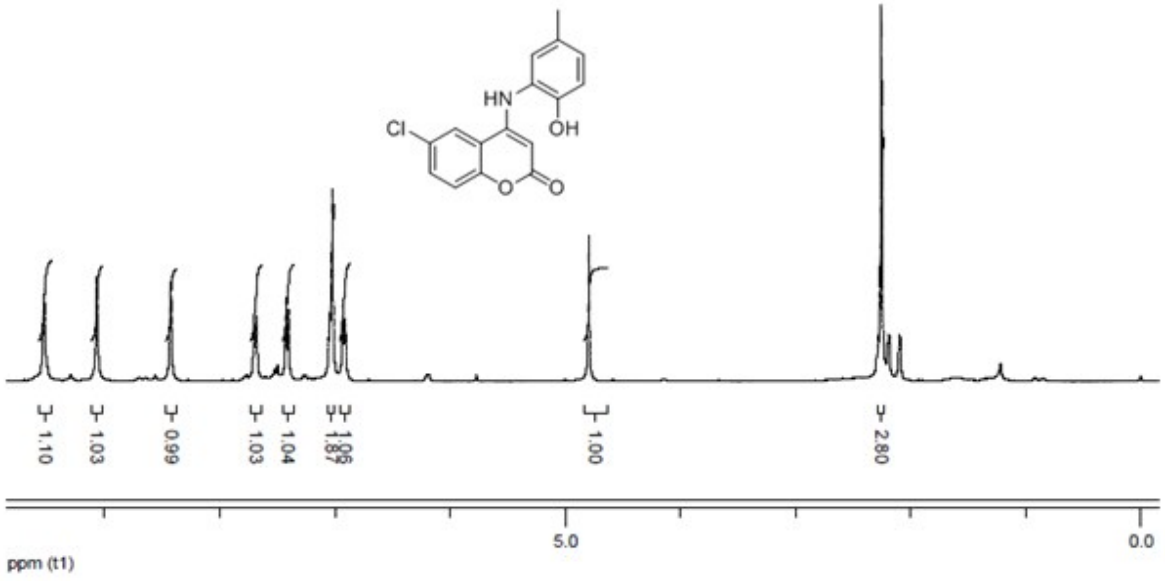
4i ^{1}H NMR (400 MHz, DMSO-d_6)



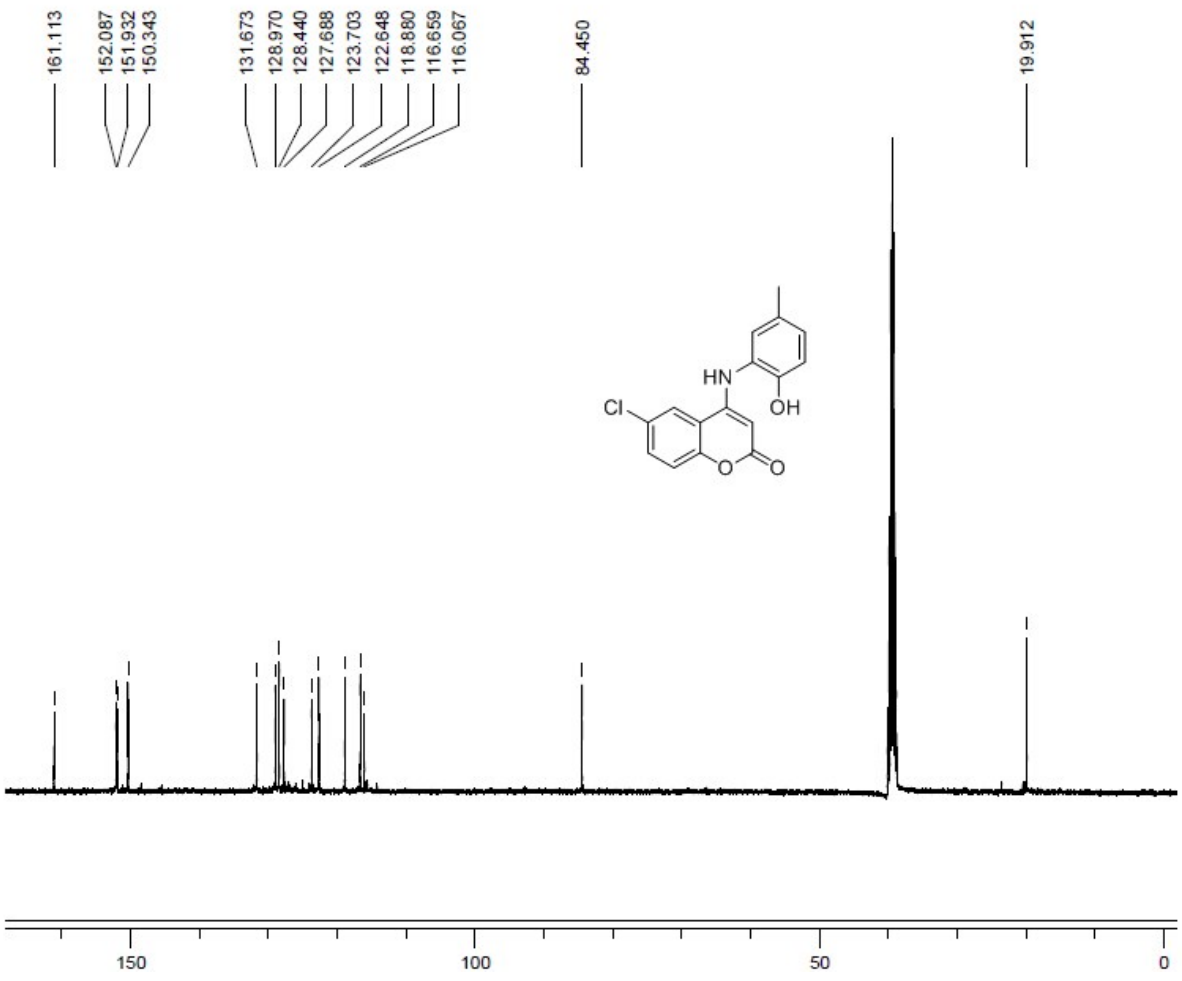
4i ^{13}C NMR (100 MHz, DMSO-d_6)



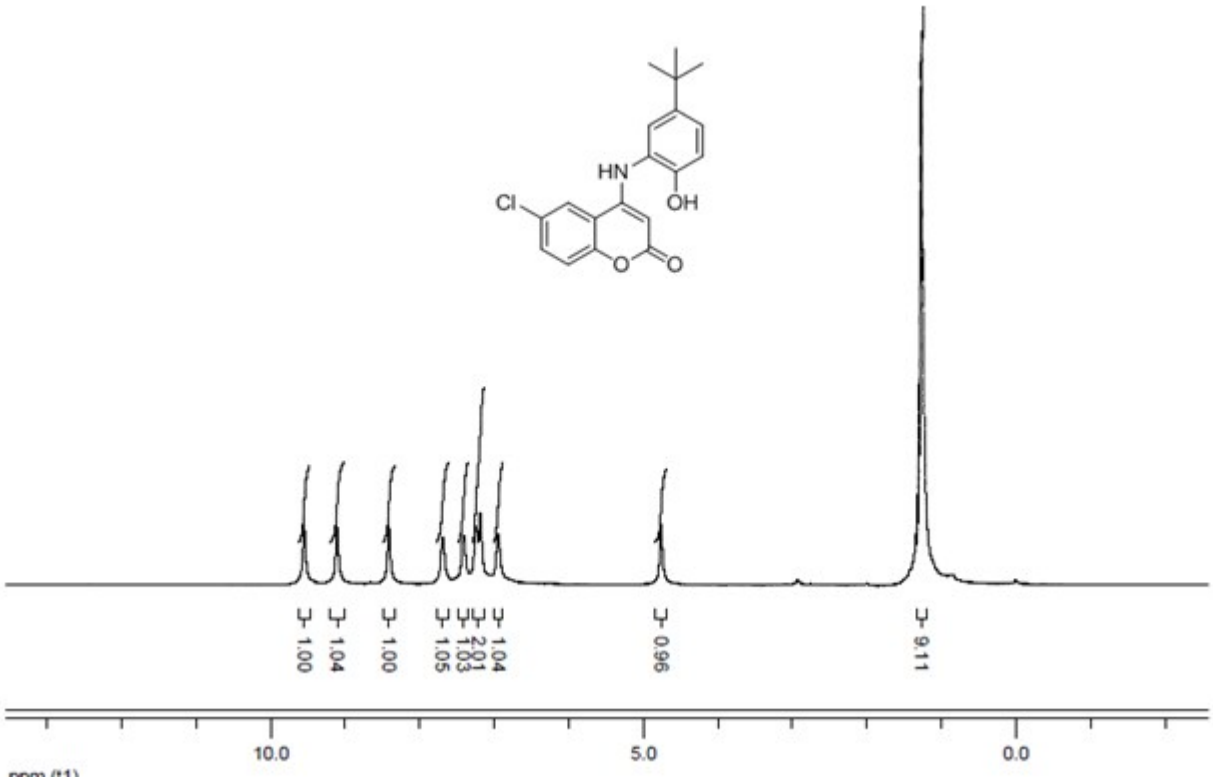
4j ^{1}H NMR (400 MHz, DMSO-d_6)



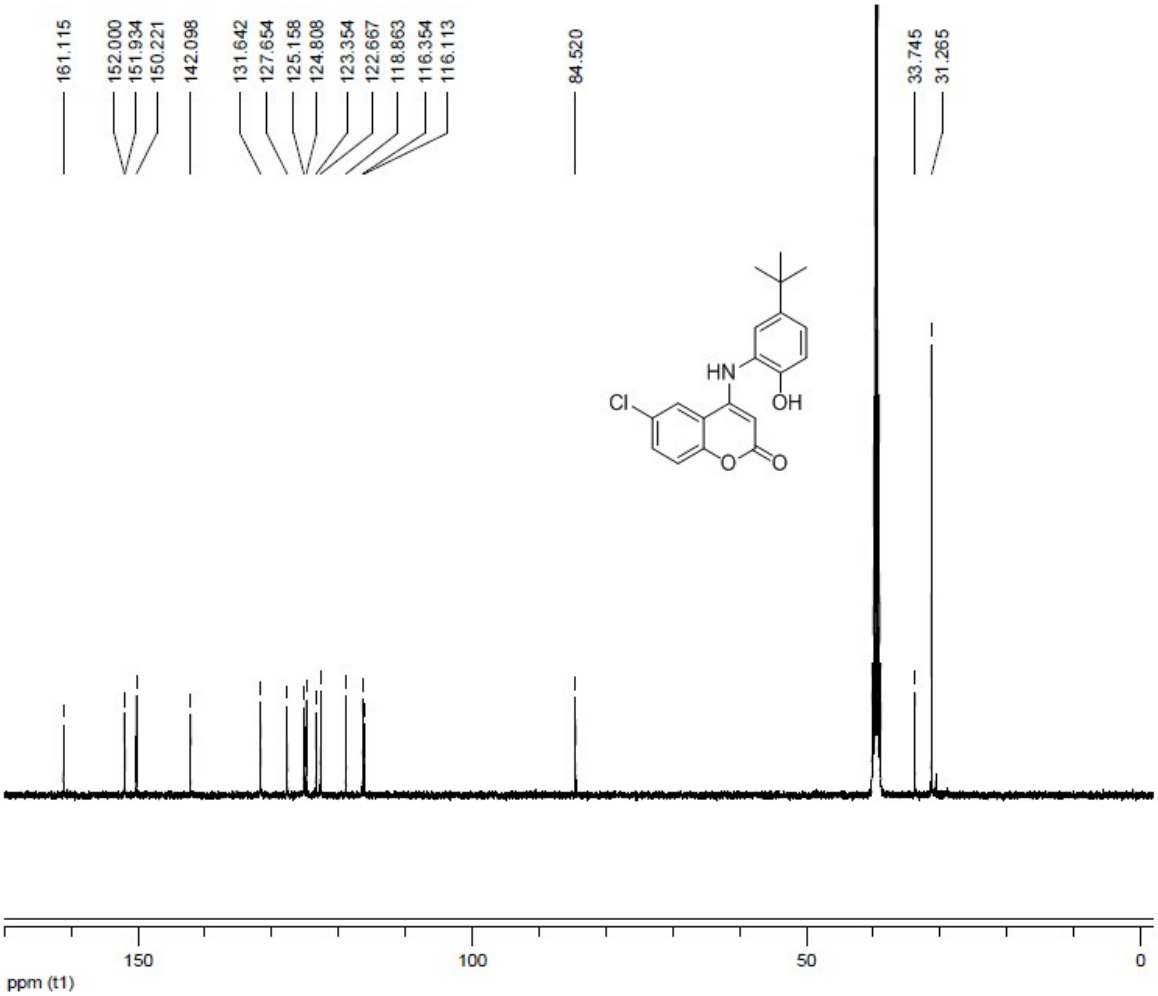
4j ^{13}C NMR (100 MHz, DMSO-d_6)



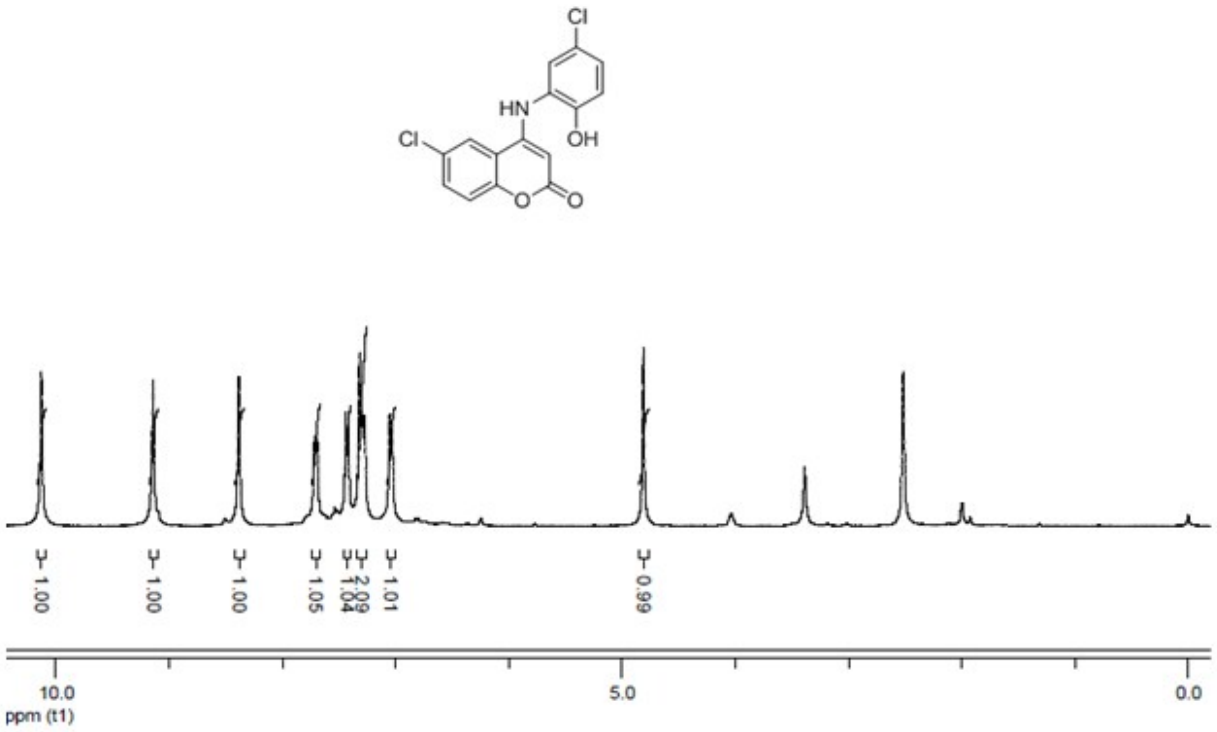
4k ^{1}H NMR (400 MHz, DMSO-d_6)



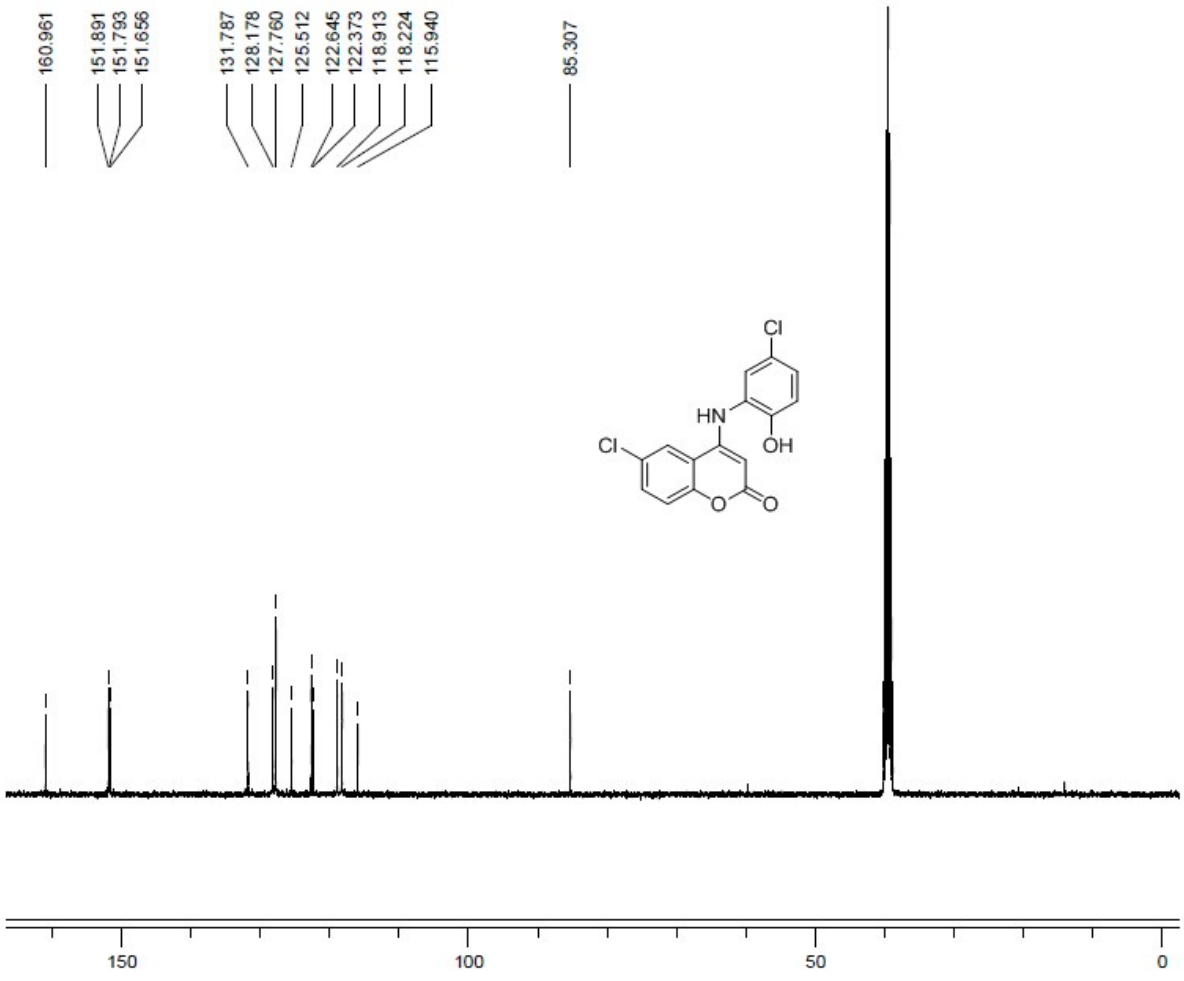
4k ^{13}C NMR (100 MHz, DMSO-d_6)



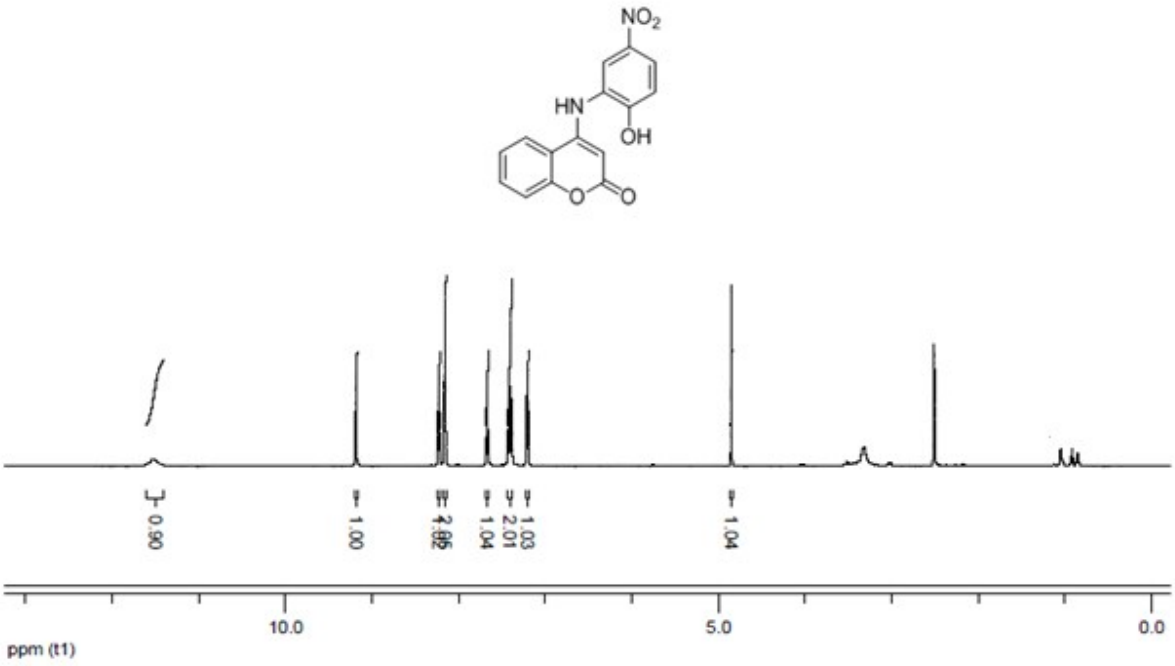
4l ^{1}H NMR (400 MHz, DMSO-d_6)



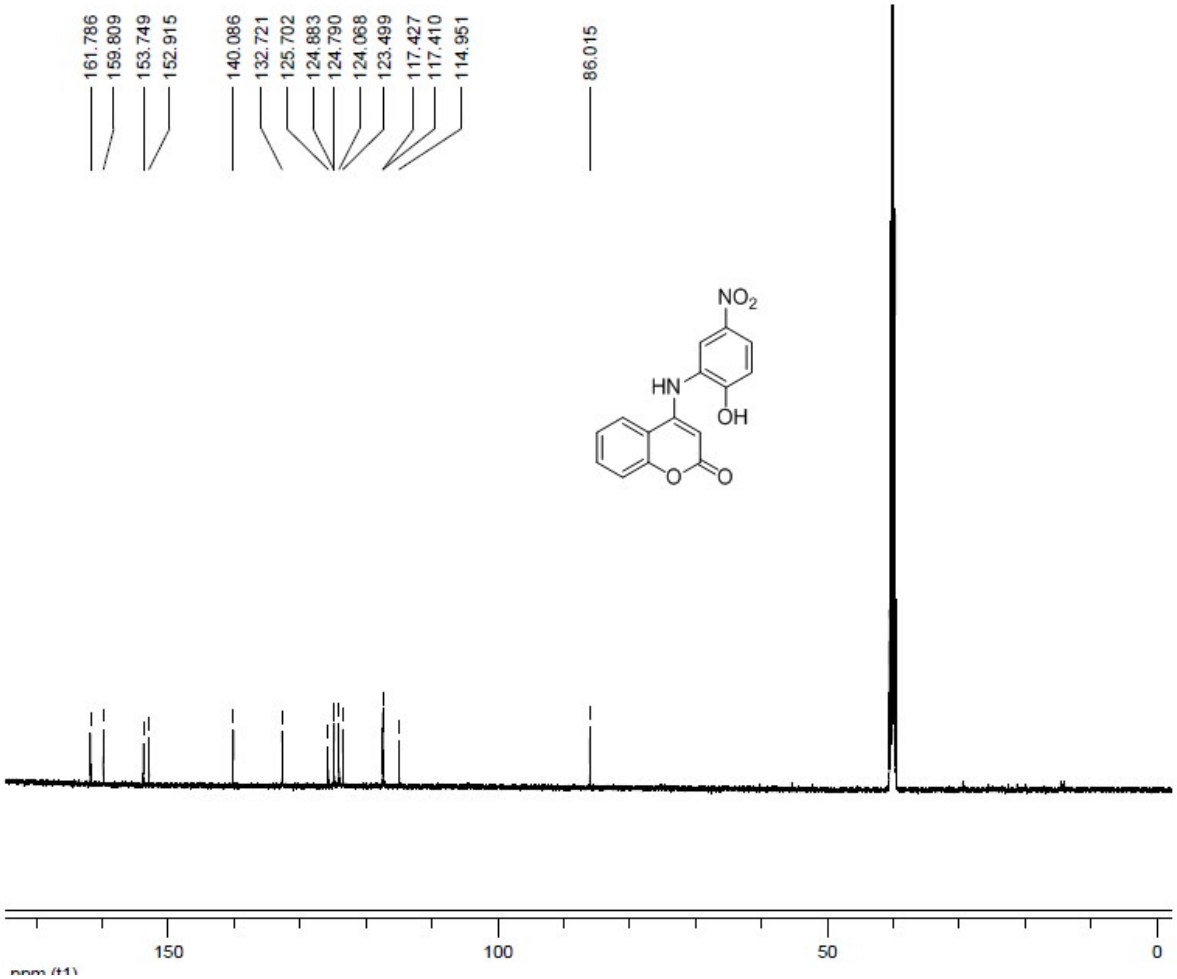
4l ^{13}C NMR (100 MHz, DMSO-d_6)



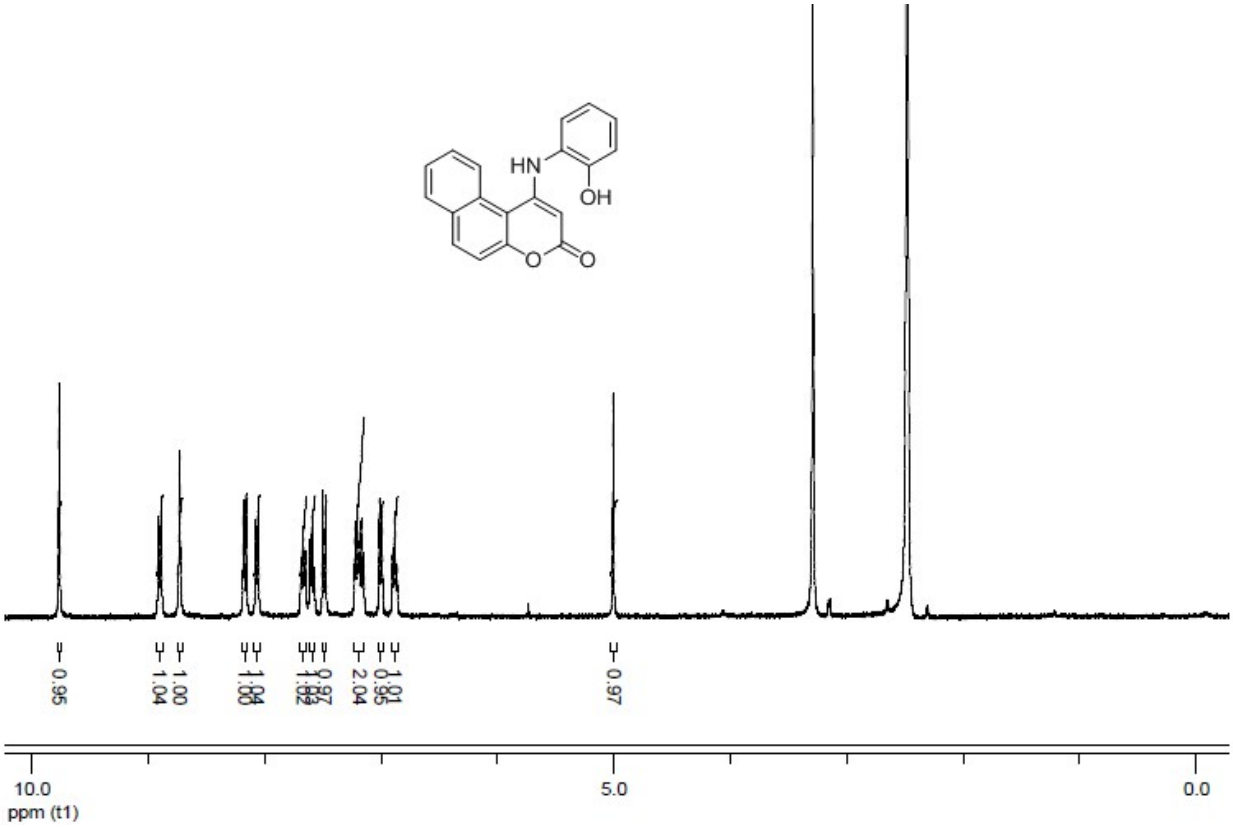
4m ^{1}H NMR (400 MHz, DMSO-d_6)



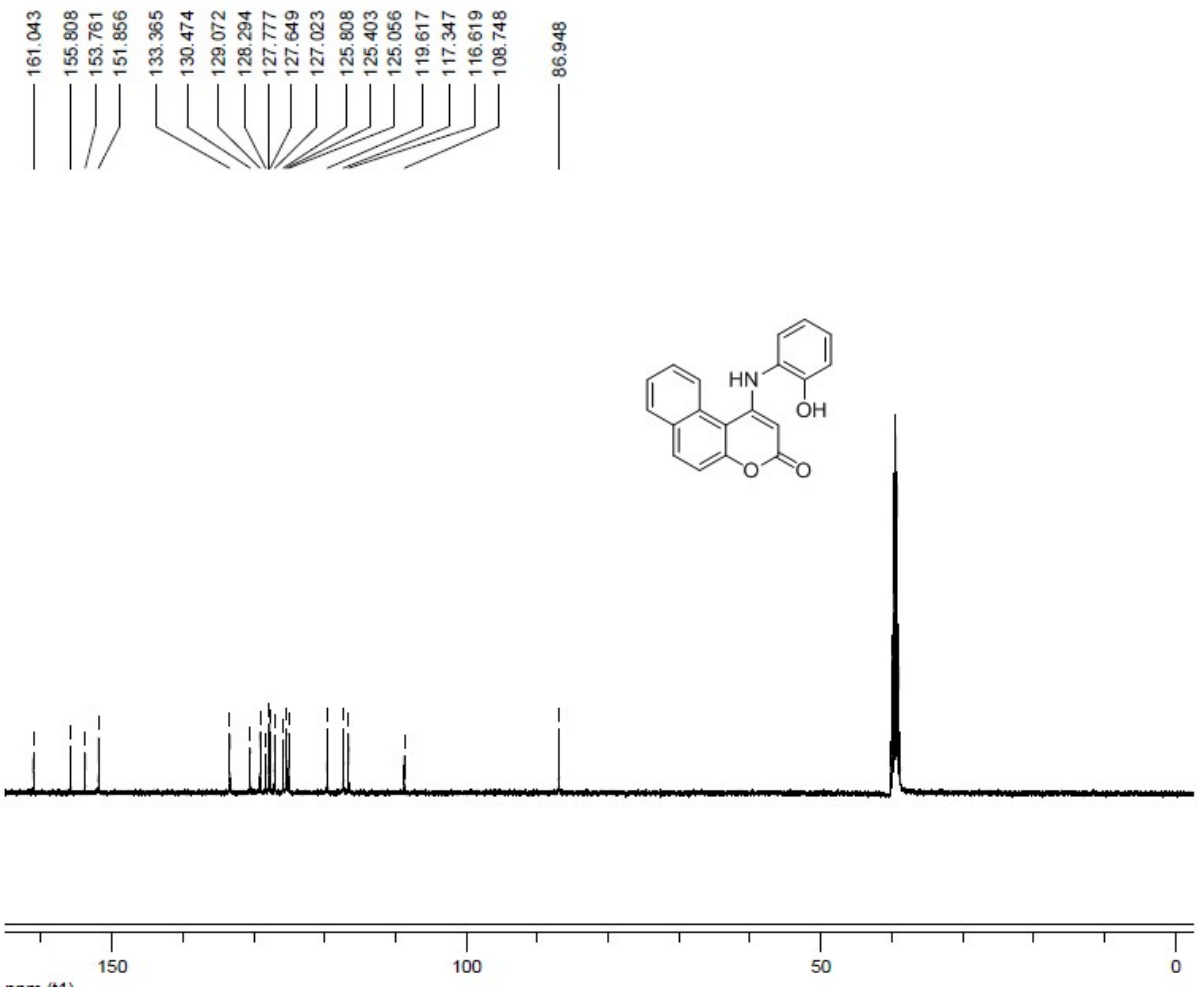
4m ^{13}C NMR (100 MHz, DMSO-d_6)



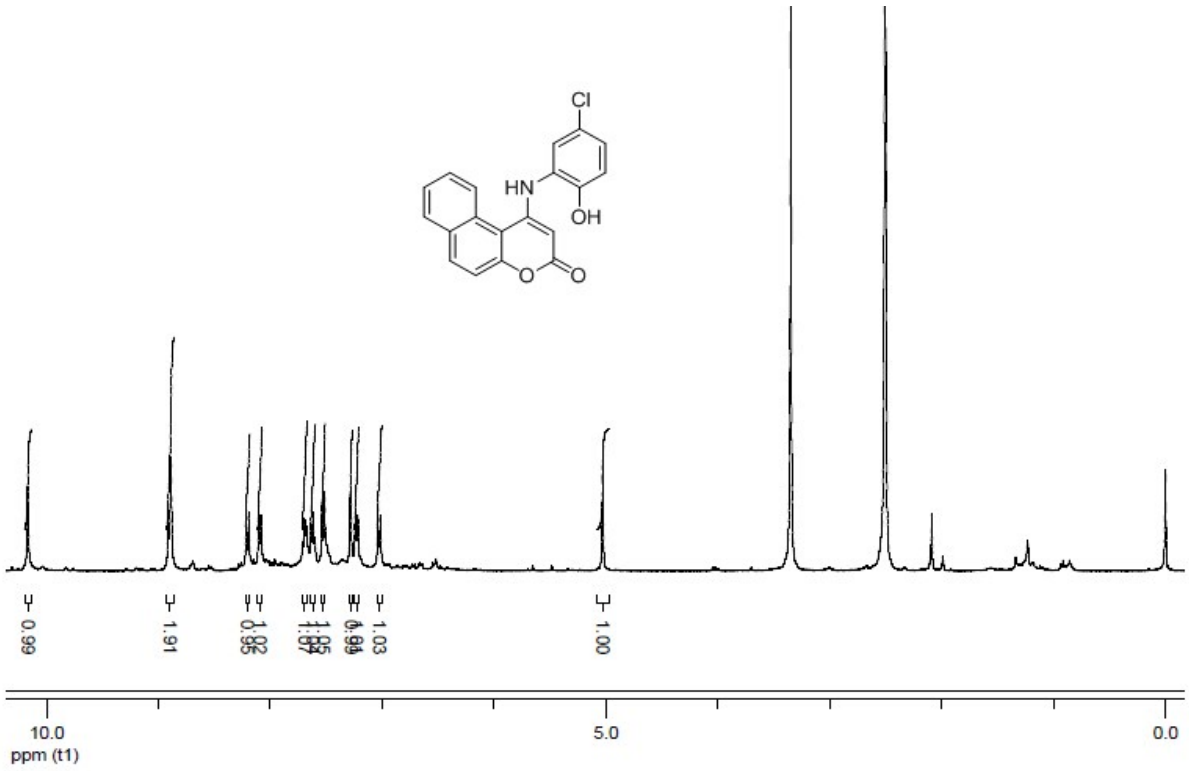
4n ^{1}H NMR (400 MHz, DMSO-d_6)



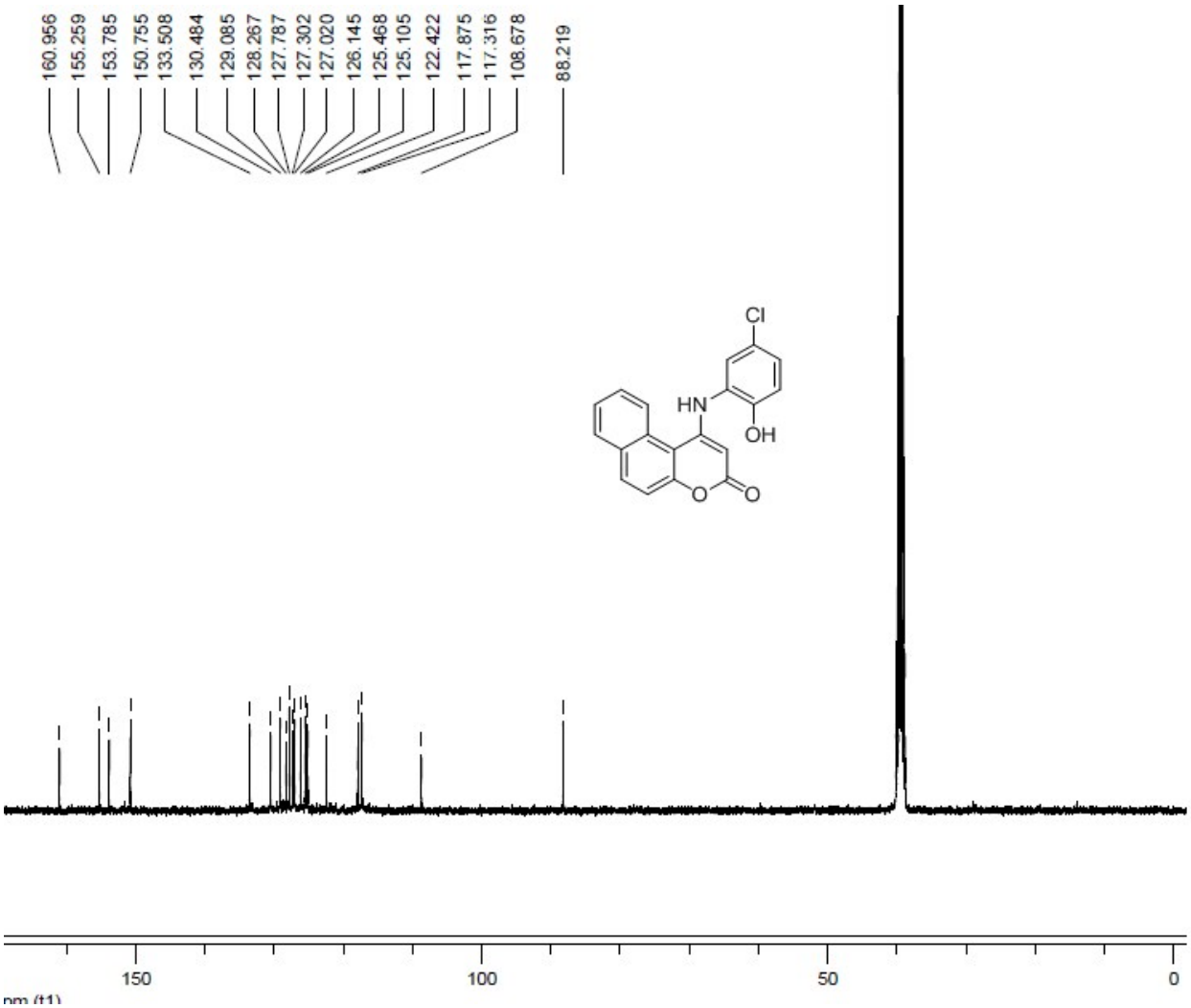
4n ^{13}C NMR (100 MHz, DMSO-d_6)



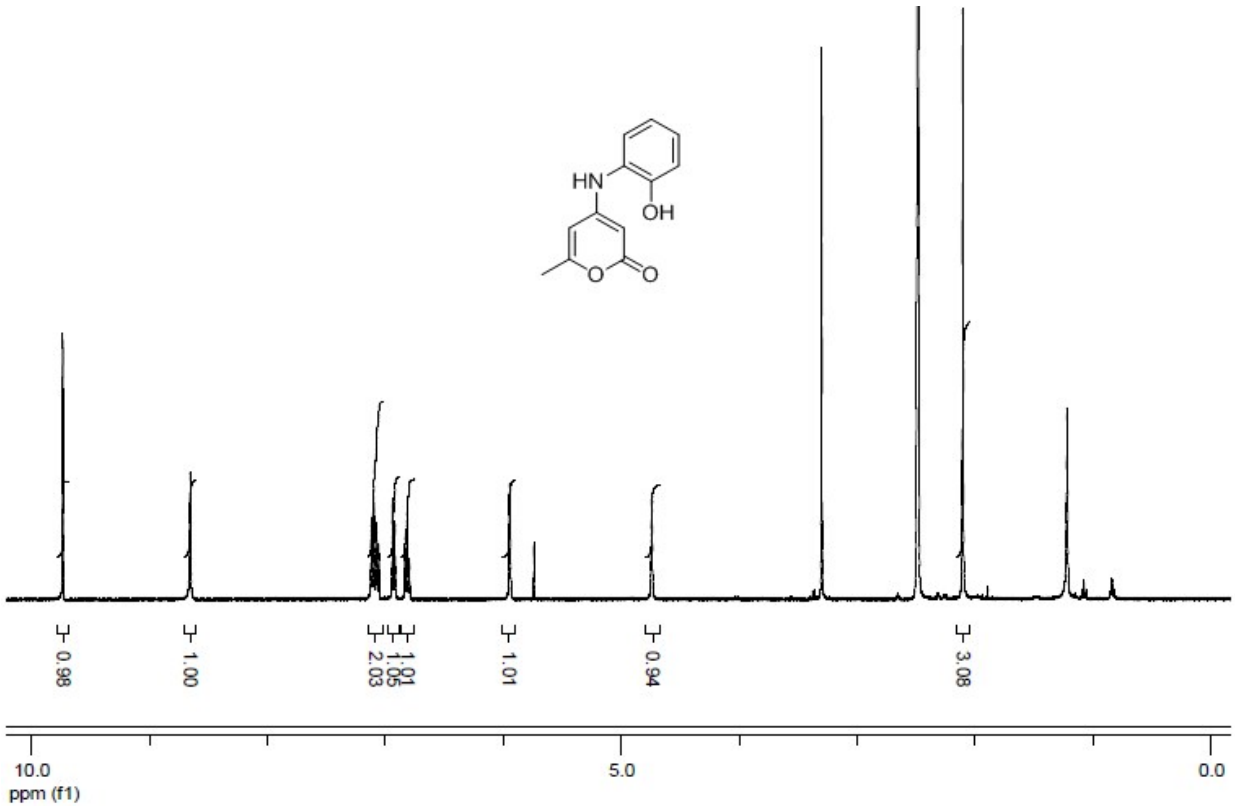
4o ^{1}H NMR (400 MHz, DMSO-d_6)



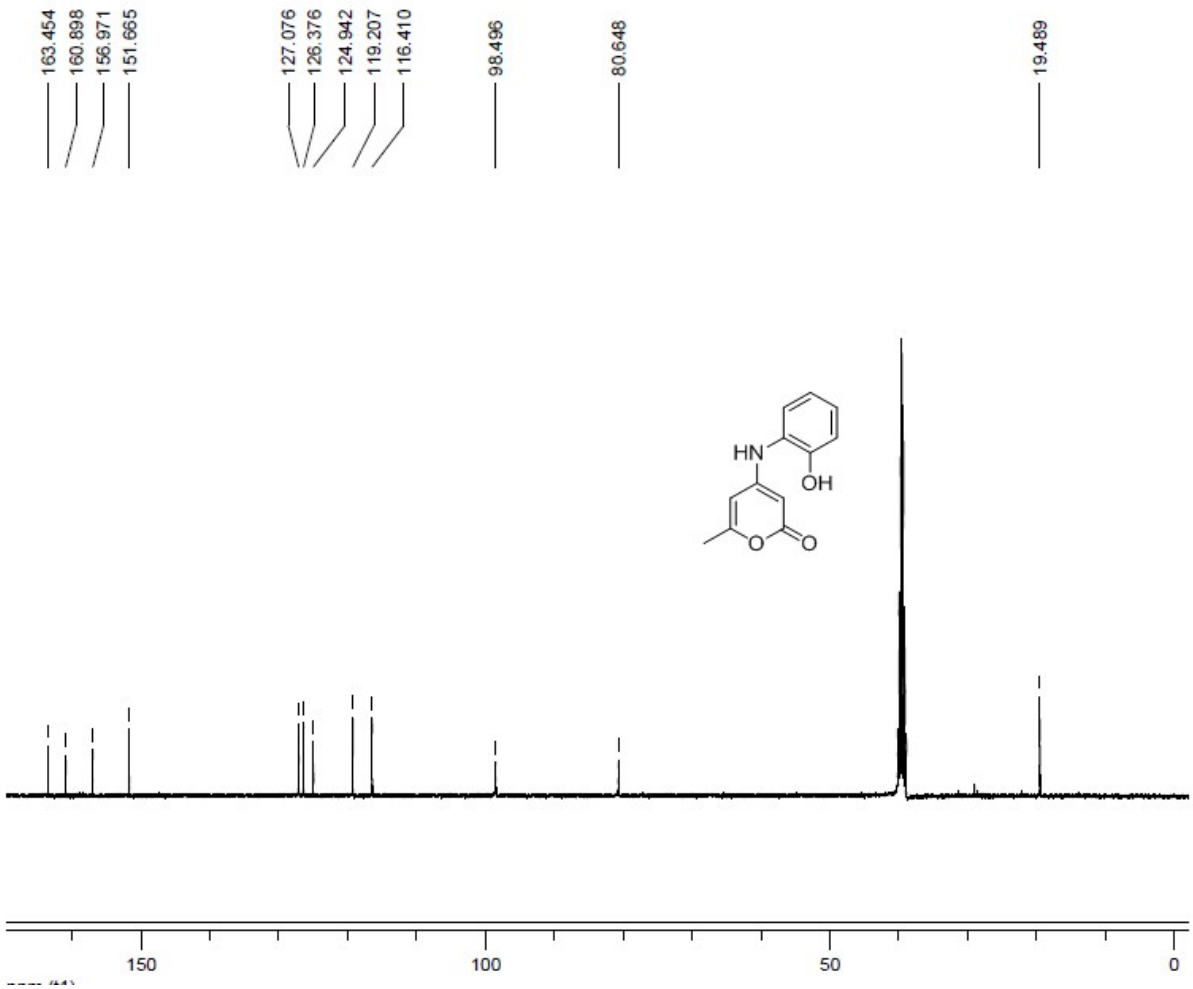
4o ^{13}C NMR (100 MHz, DMSO-d_6)



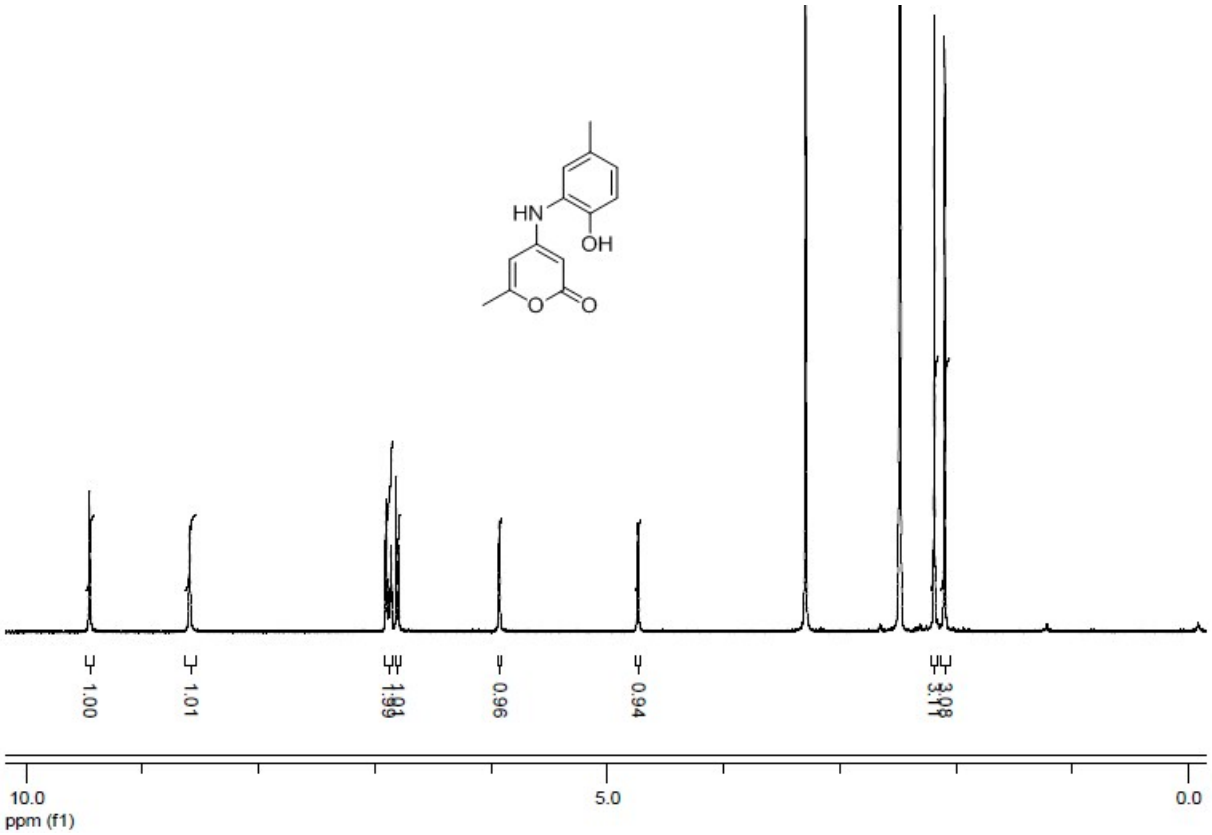
4p ^{1}H NMR (400 MHz, DMSO-d_6)



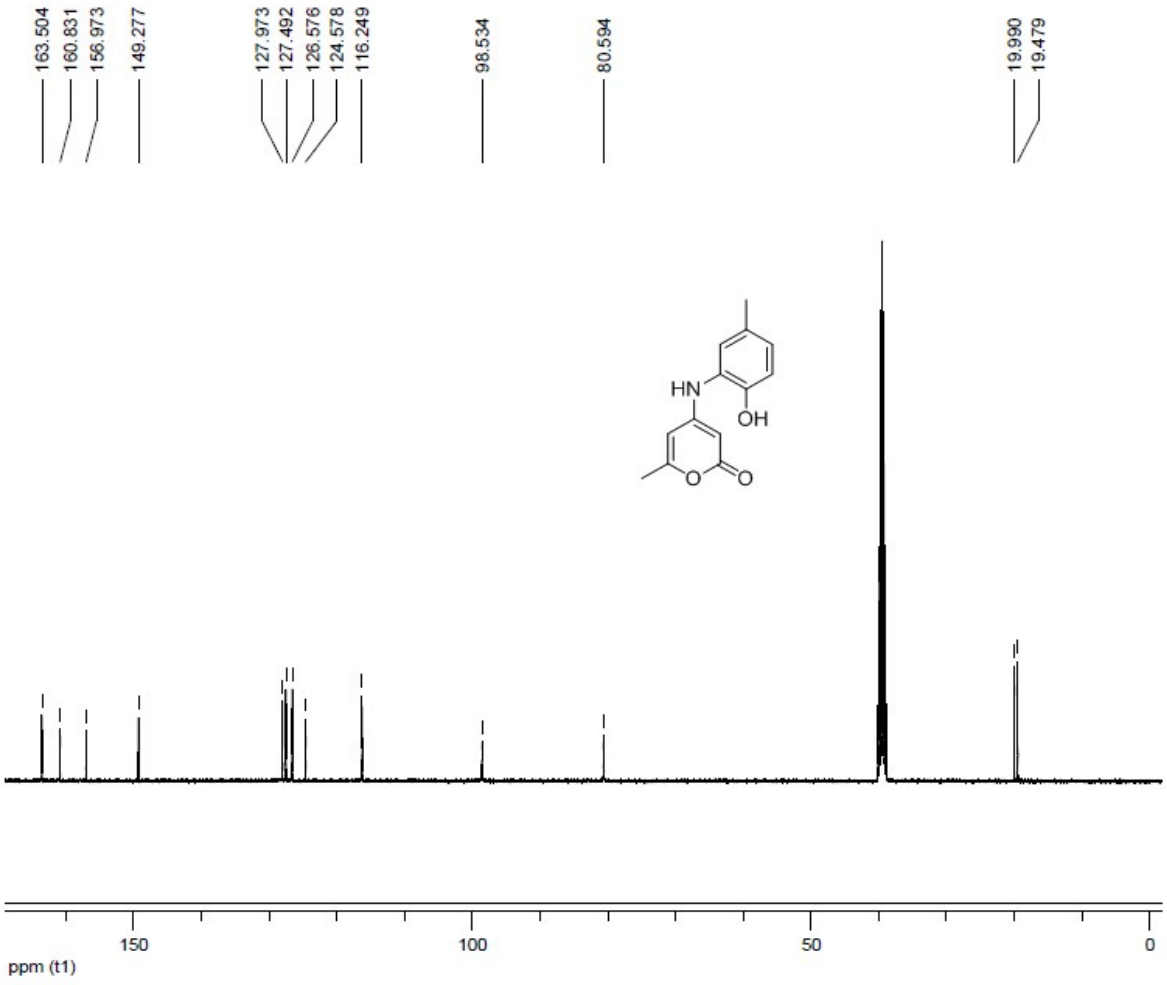
4p ^{13}C NMR (100 MHz, DMSO-d_6)



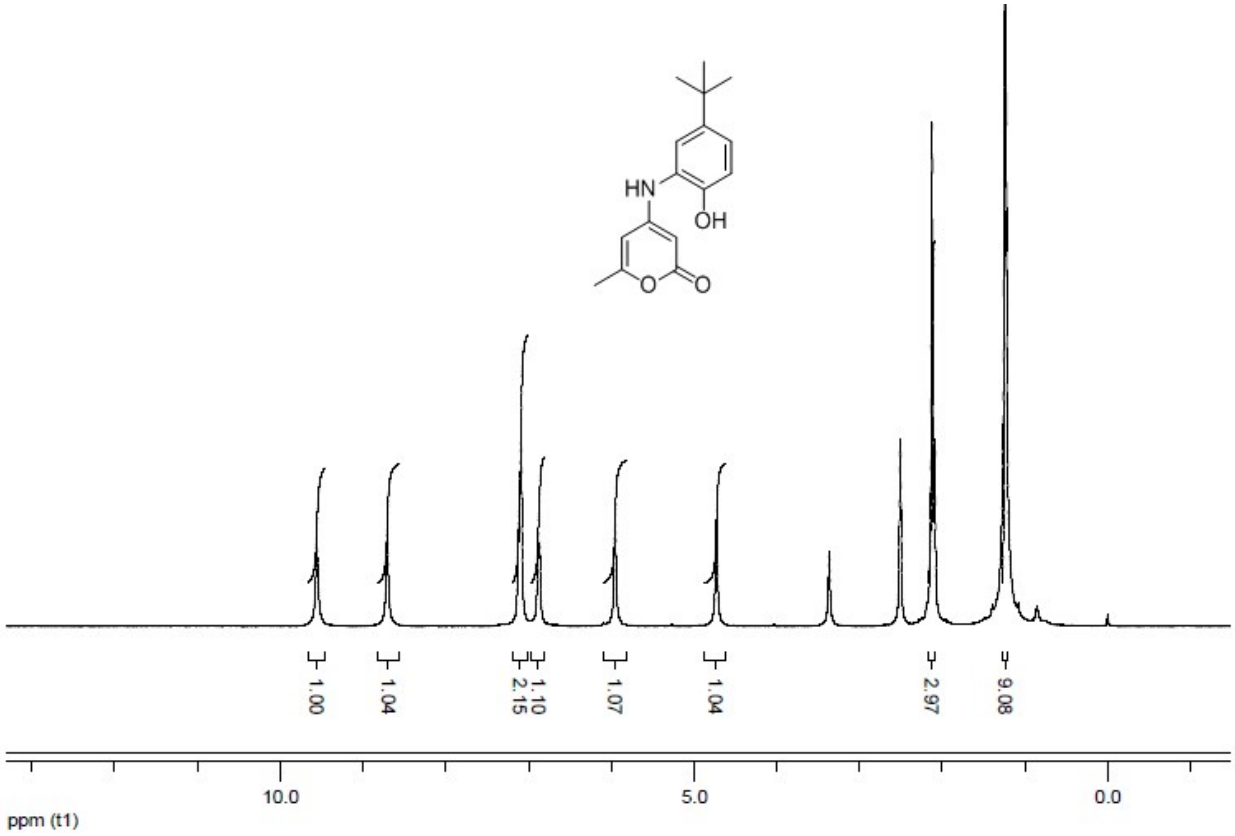
4q ^{1}H NMR (400 MHz, DMSO-d_6)



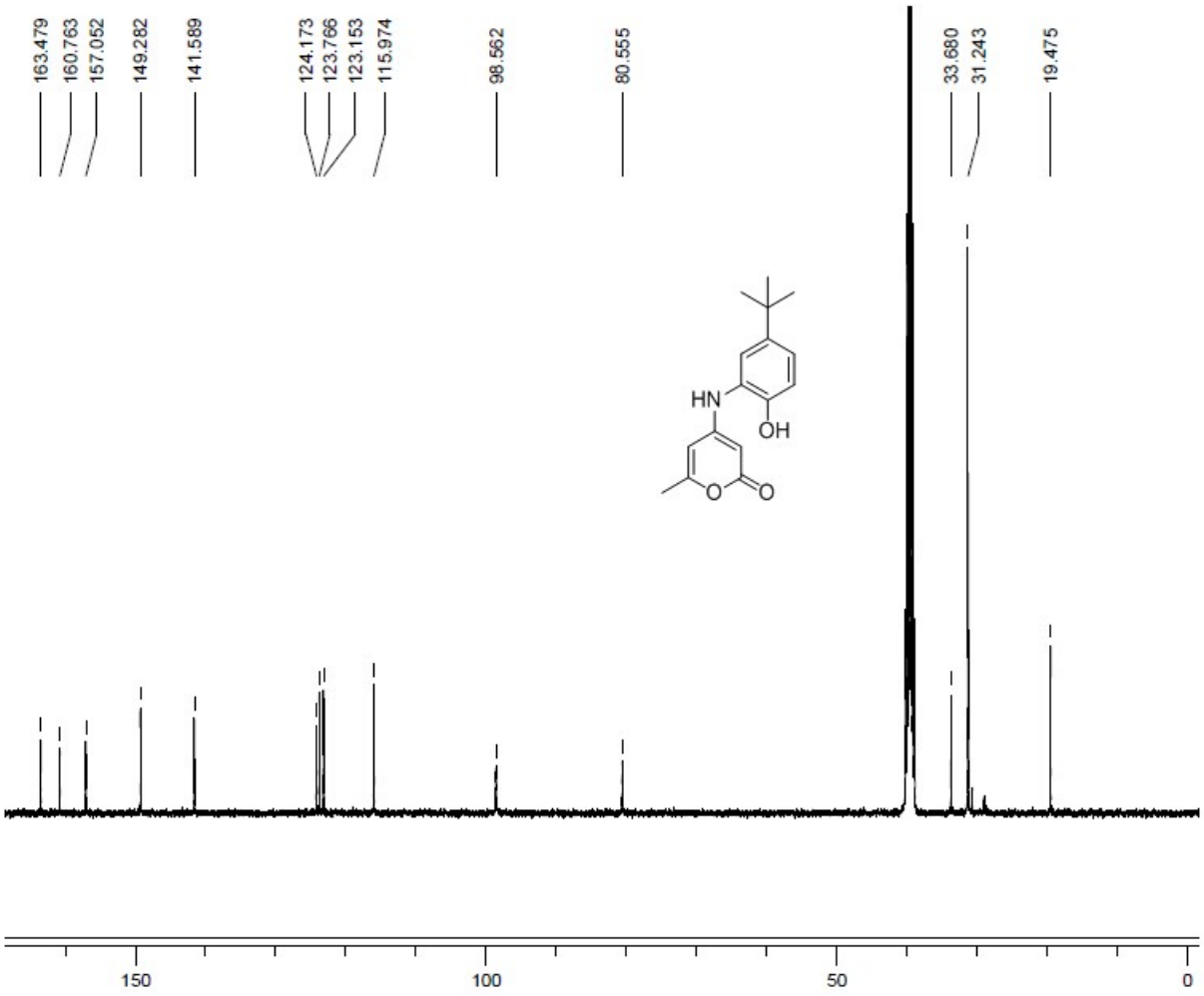
4q ^{13}C NMR (100 MHz, DMSO-d_6)



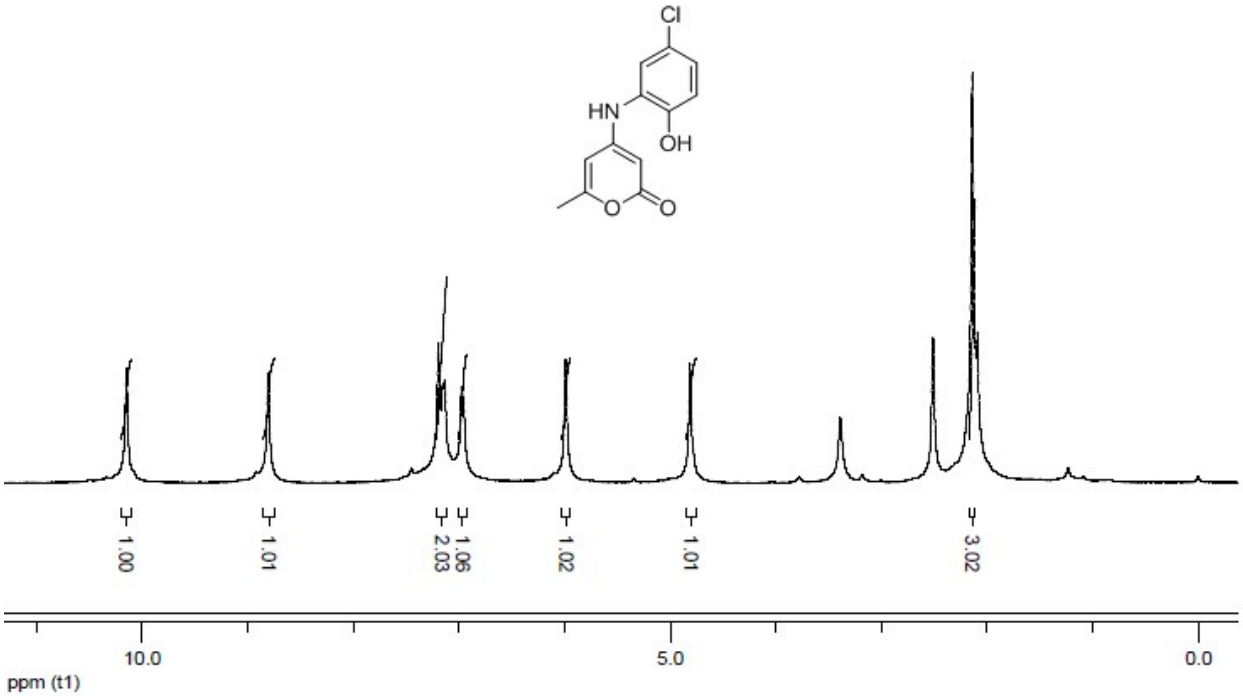
4r ^{1}H NMR (400 MHz, DMSO-d_6)



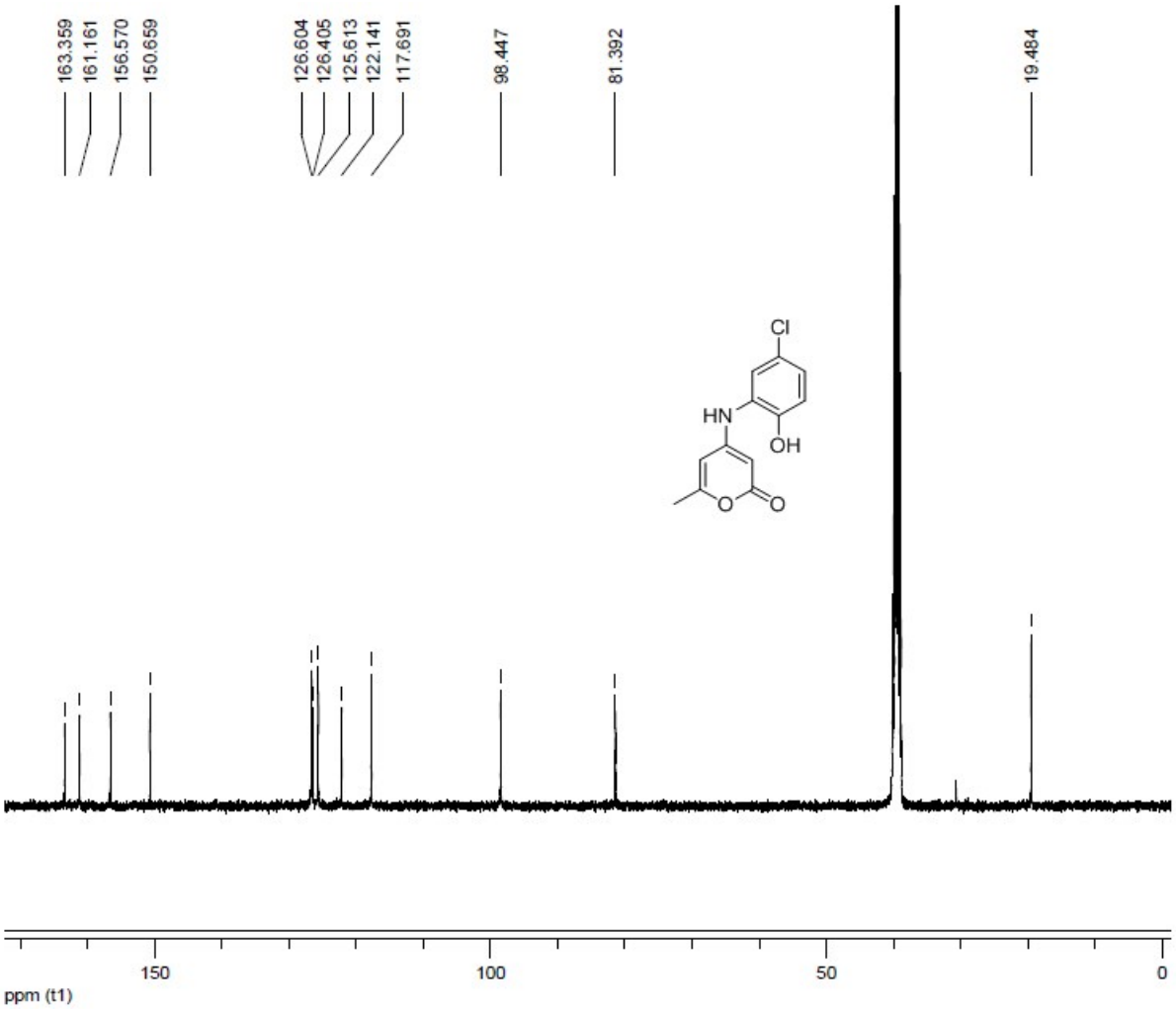
4r ^{13}C NMR (100 MHz, DMSO-d_6)



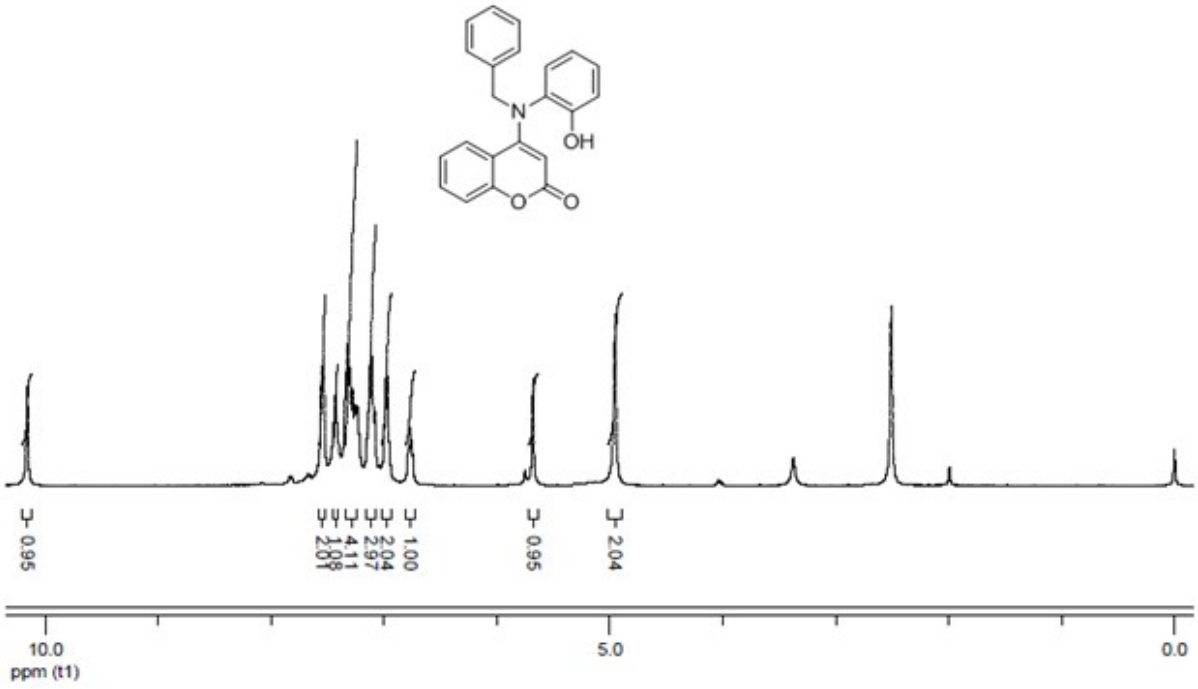
4s ^{1}H NMR (400 MHz, DMSO-d_6)



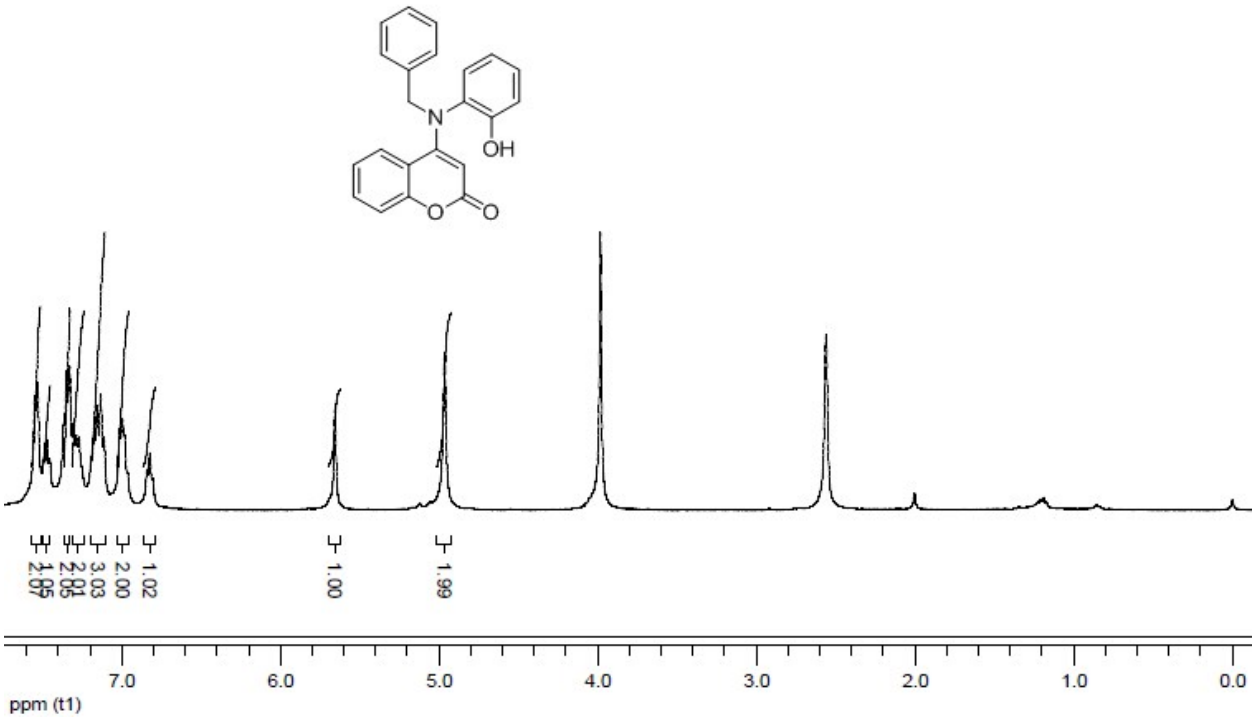
4s ^{13}C NMR (100 MHz, DMSO-d_6)



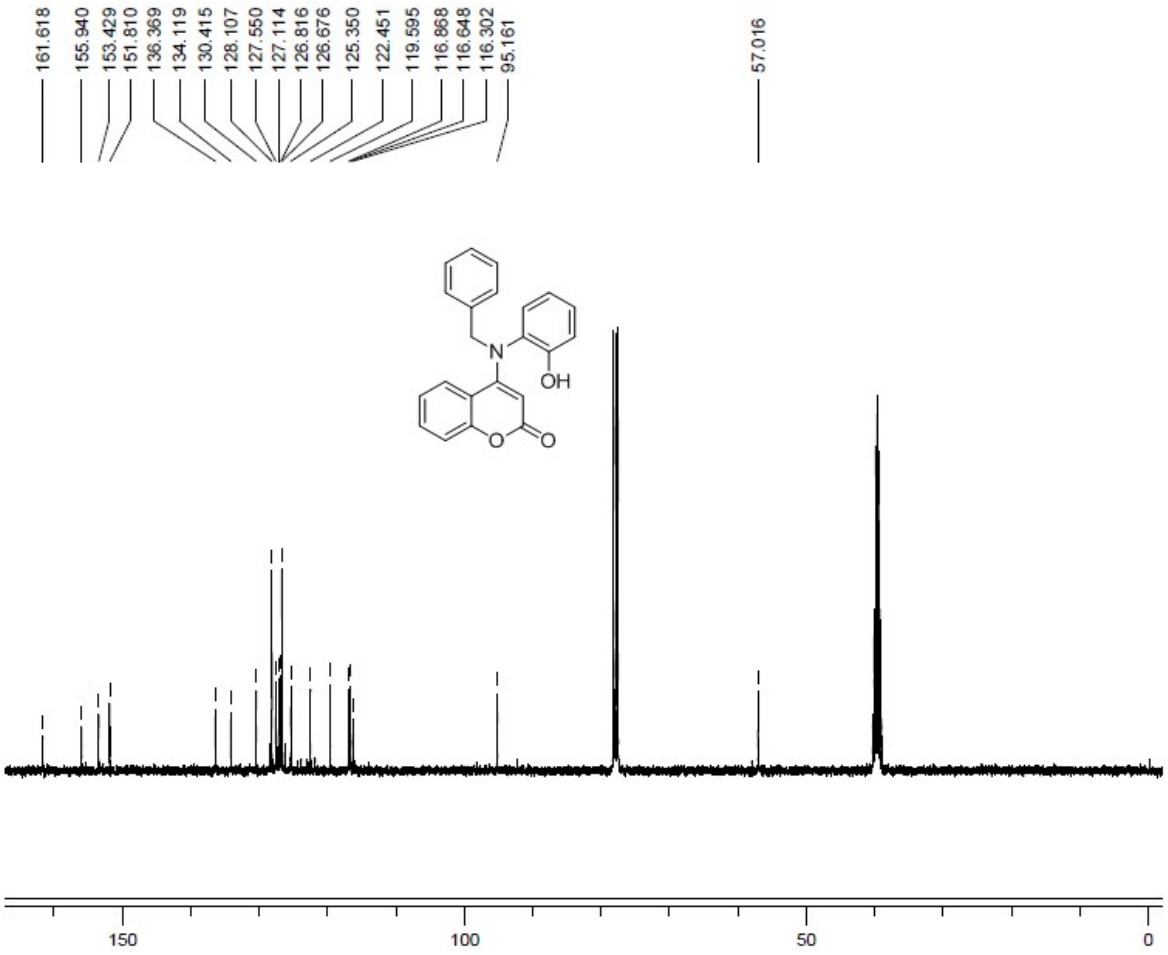
4t ^{1}H NMR (400 MHz, DMSO-d_6)



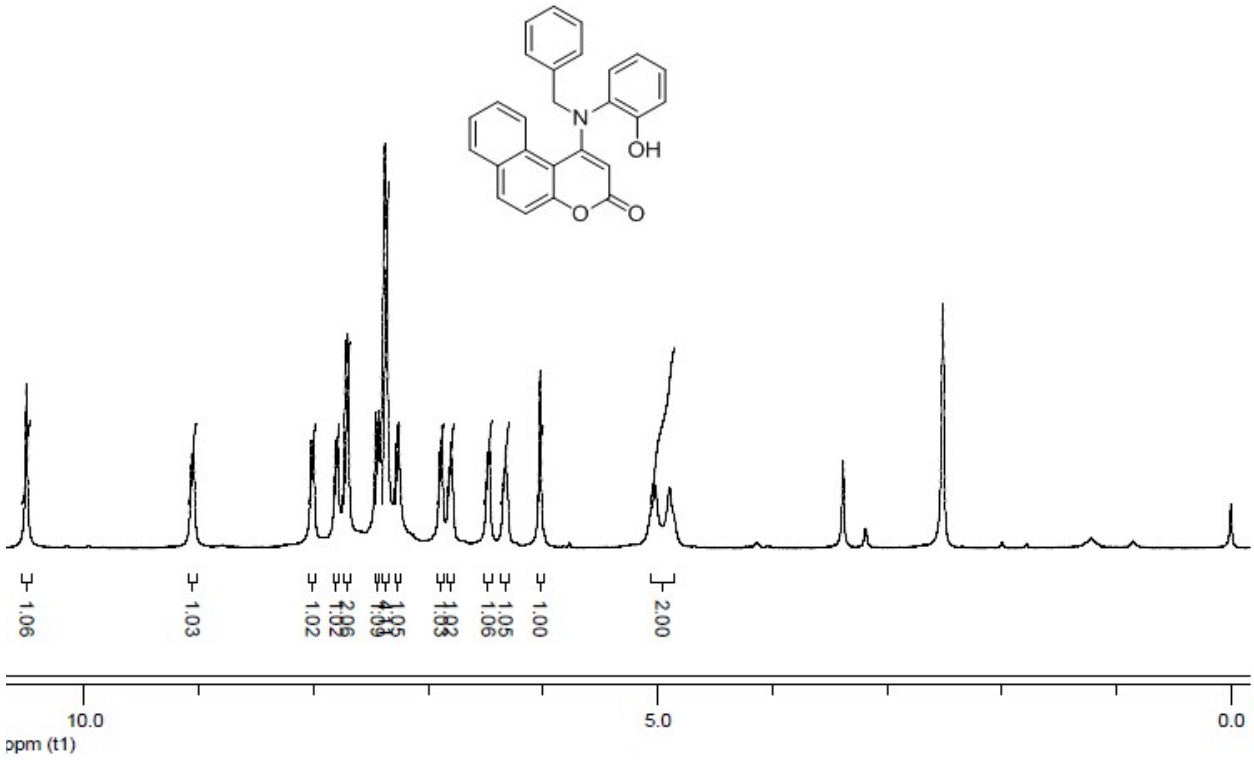
4t ^{1}H NMR (400 MHz, DMSO-D_2O Ex)



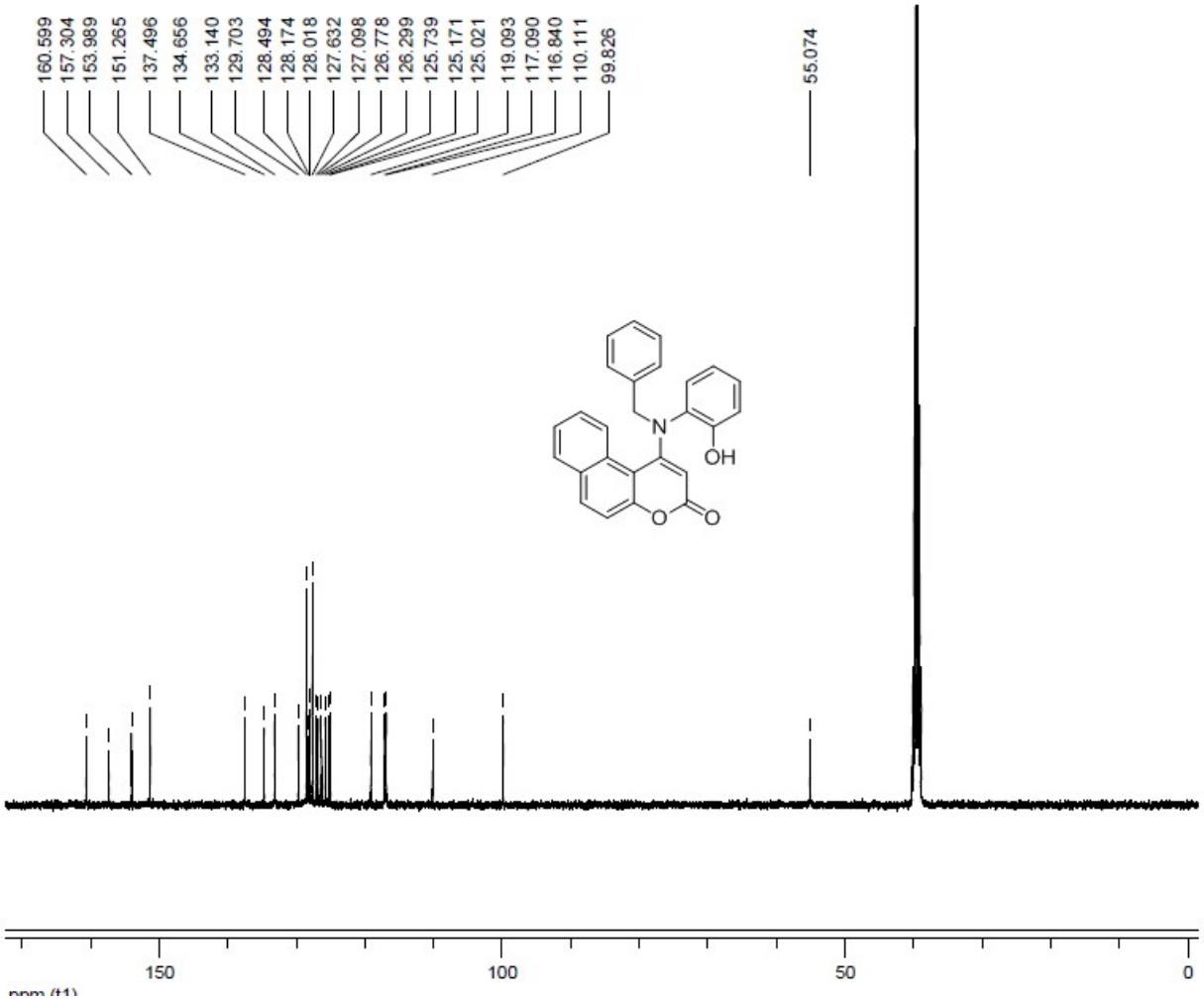
4u ^{13}C NMR (100 MHz, DMSO-d_6)



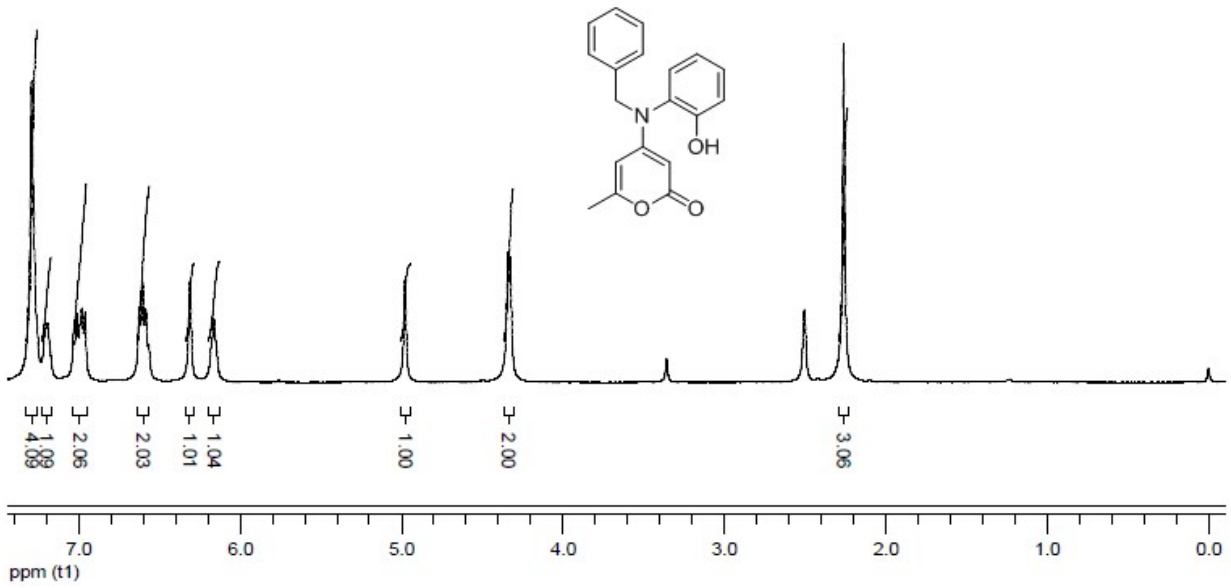
4u ^{1}H NMR (400 MHz, DMSO-d_6)



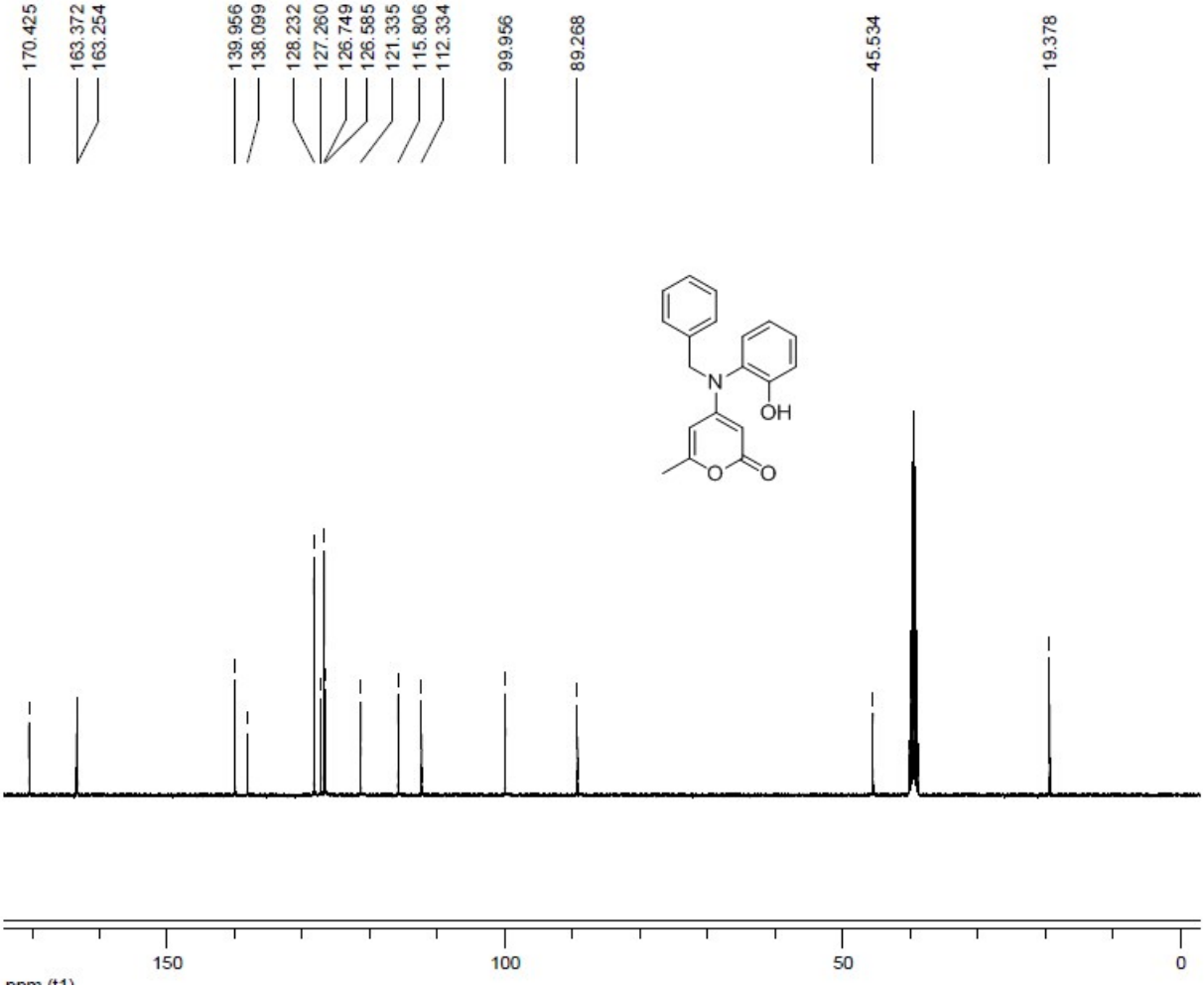
4v ^{13}C NMR (100 MHz, DMSO-d_6)



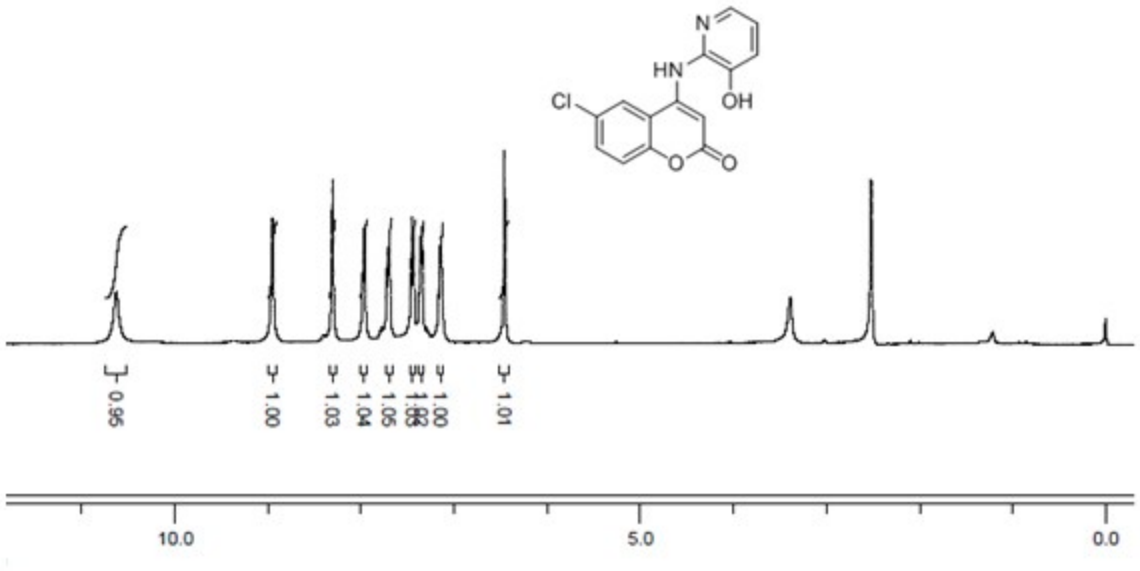
4v ^{1}H NMR (400 MHz, DMSO-d_6)



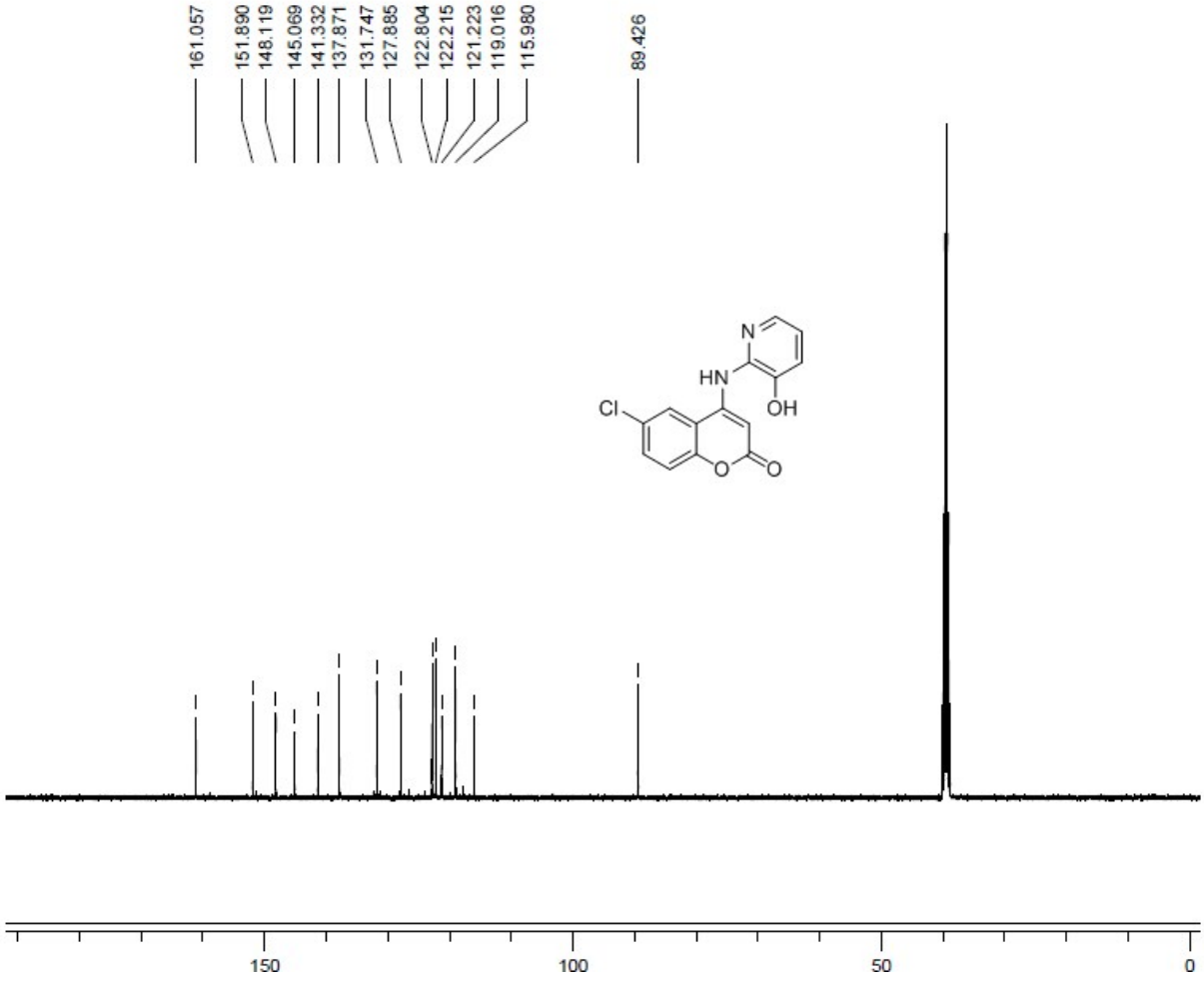
4v ^{13}C NMR (100 MHz, DMSO-d_6)



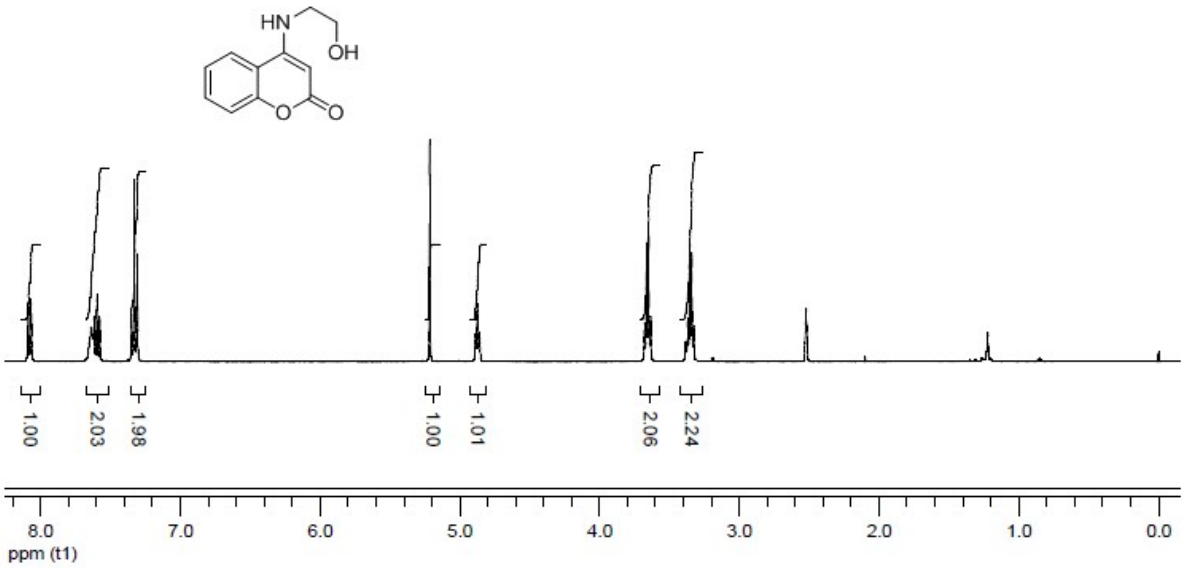
4w ^{1}H NMR (400 MHz, DMSO-d_6)



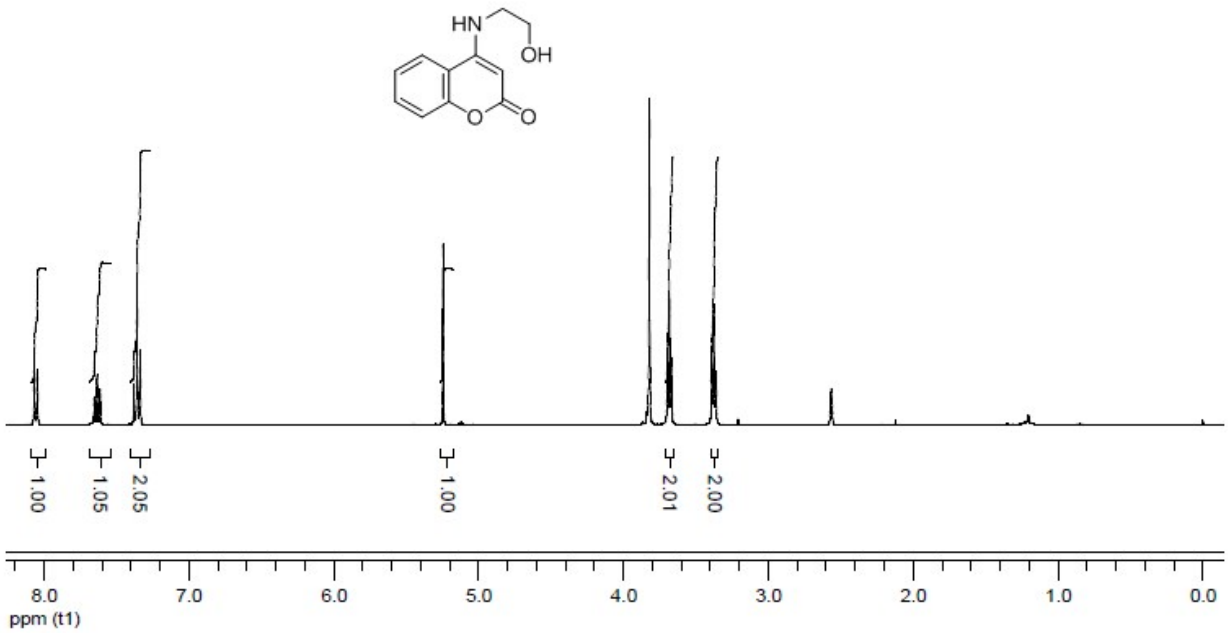
4w ^{13}C NMR (100 MHz, DMSO-d_6)



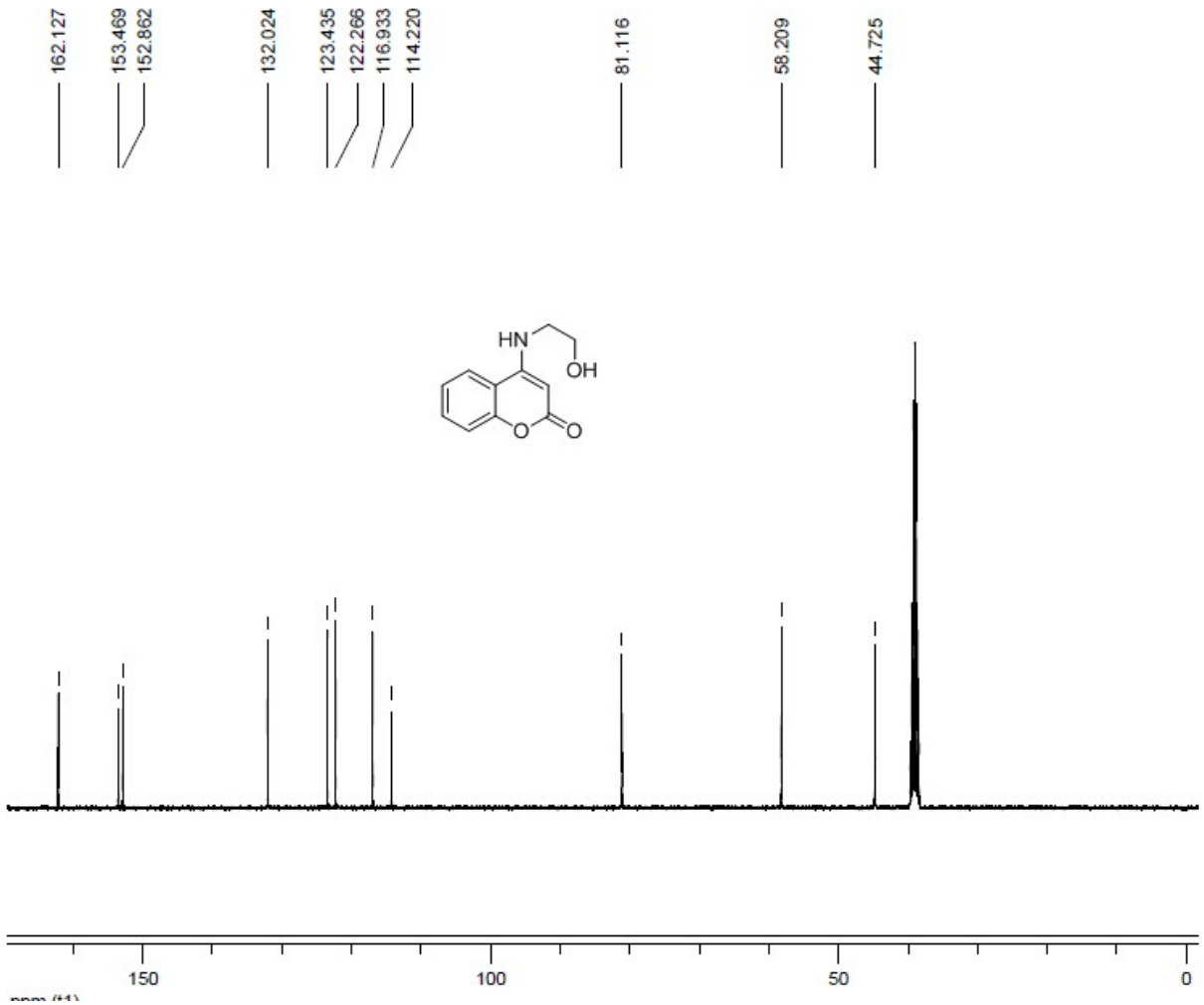
7 ^{1}H NMR (400 MHz, DMSO-d_6)



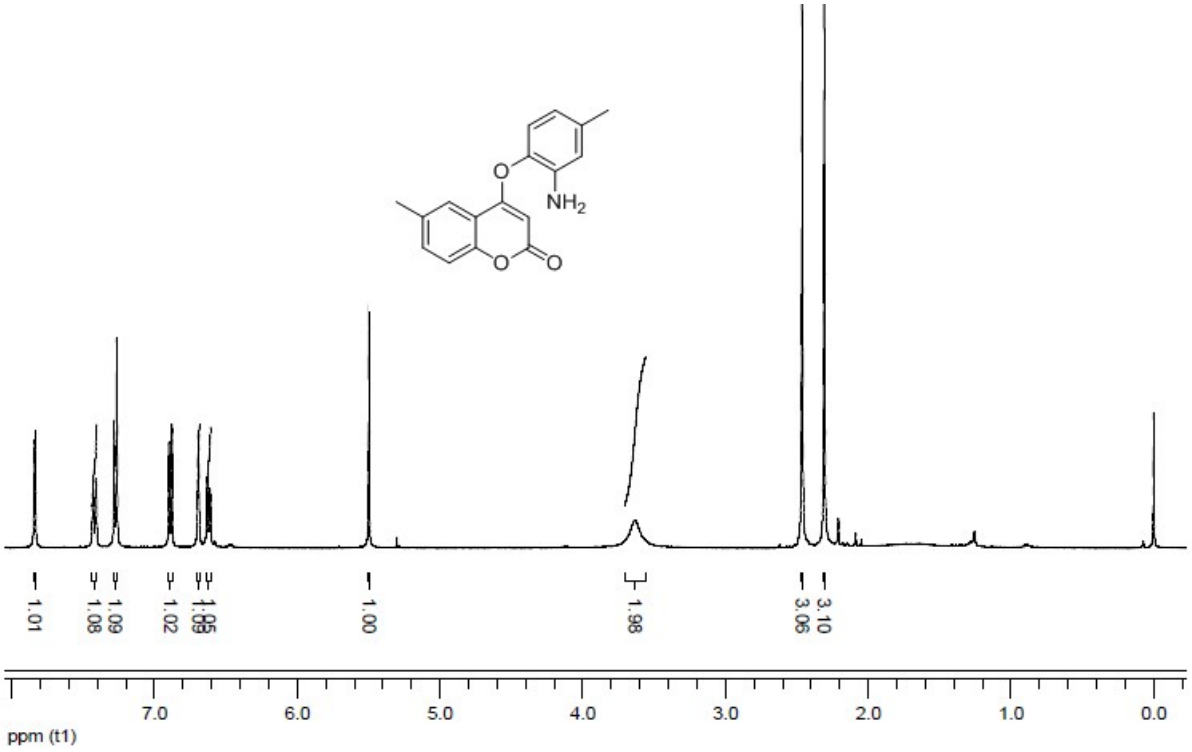
7 ^{1}H NMR (400 MHz, DMSO-D_2O Ex)



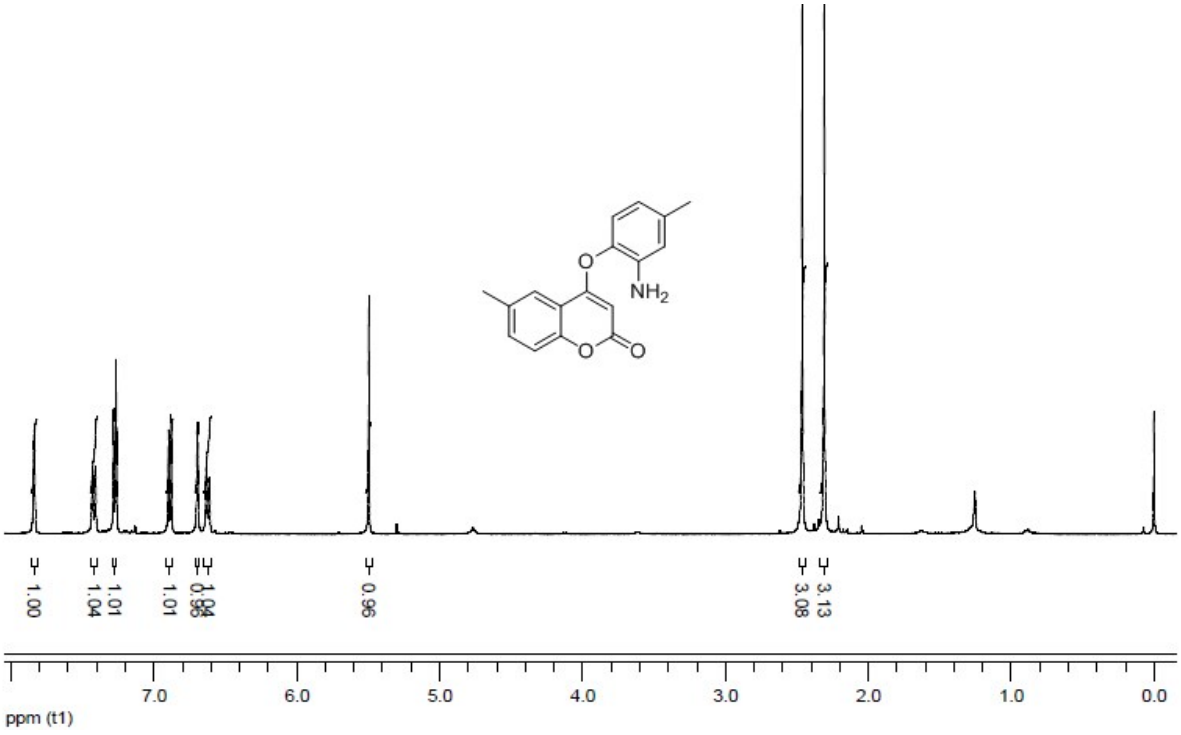
7 ^{13}C NMR (100 MHz, DMSO-d_6) (**7**)



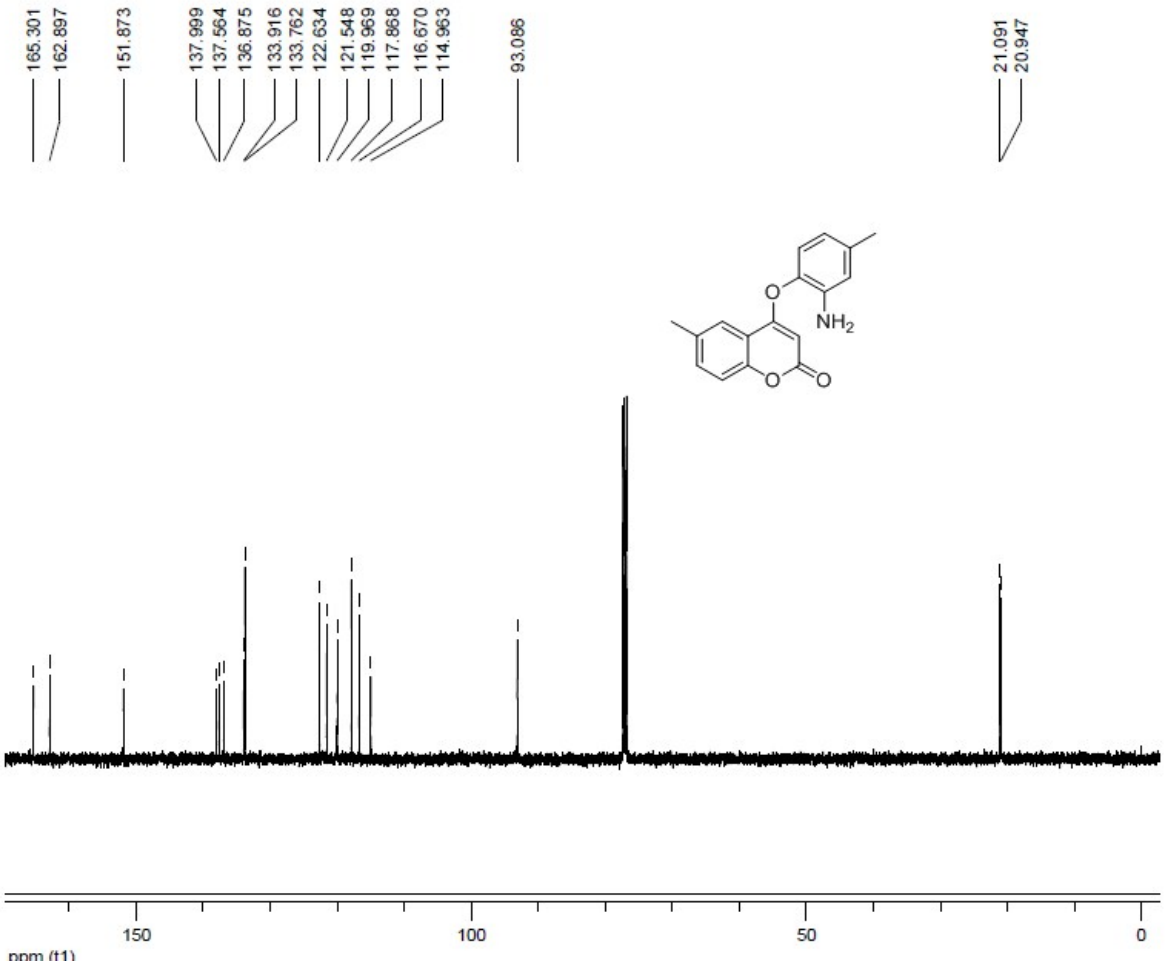
3a ^{1}H NMR (400 MHz, $CDCl_3$)



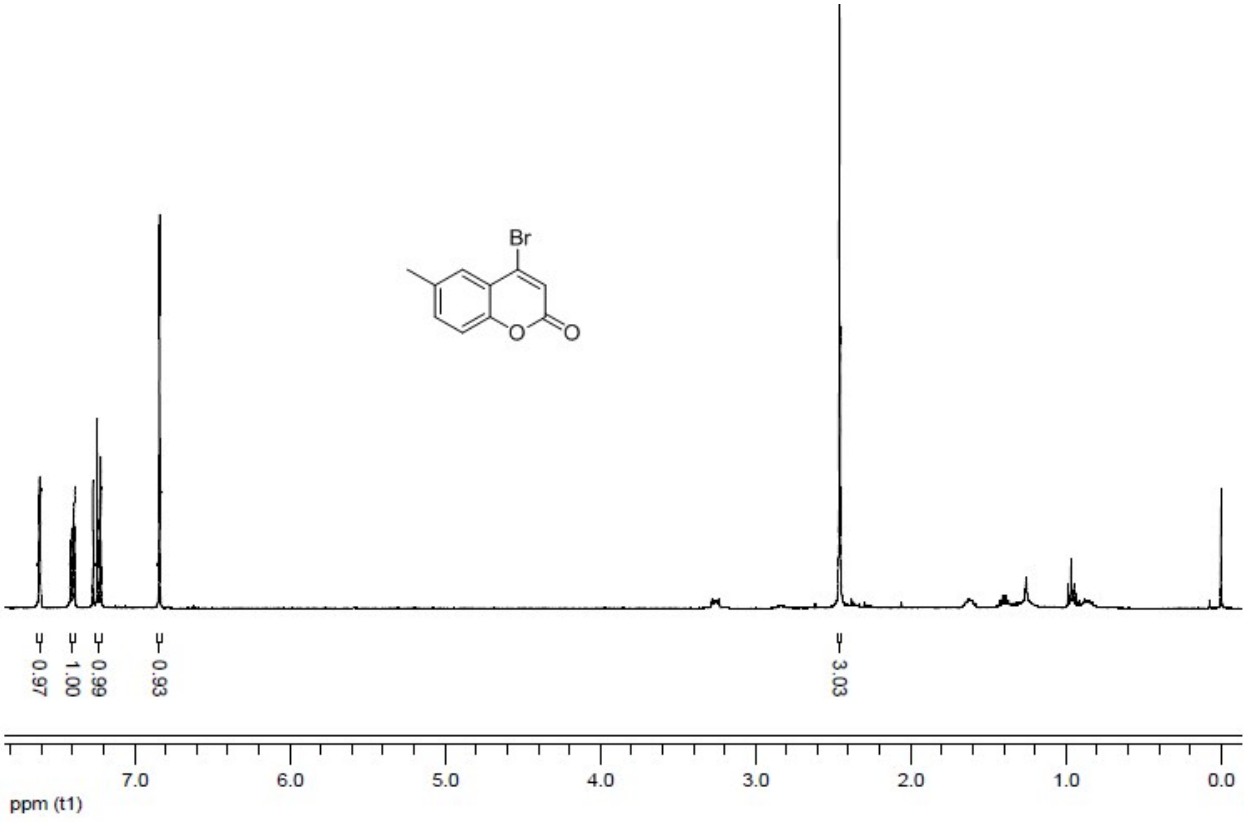
3a ^{1}H NMR (400 MHz, $CDCl_3$-D_2O Ex) **()**



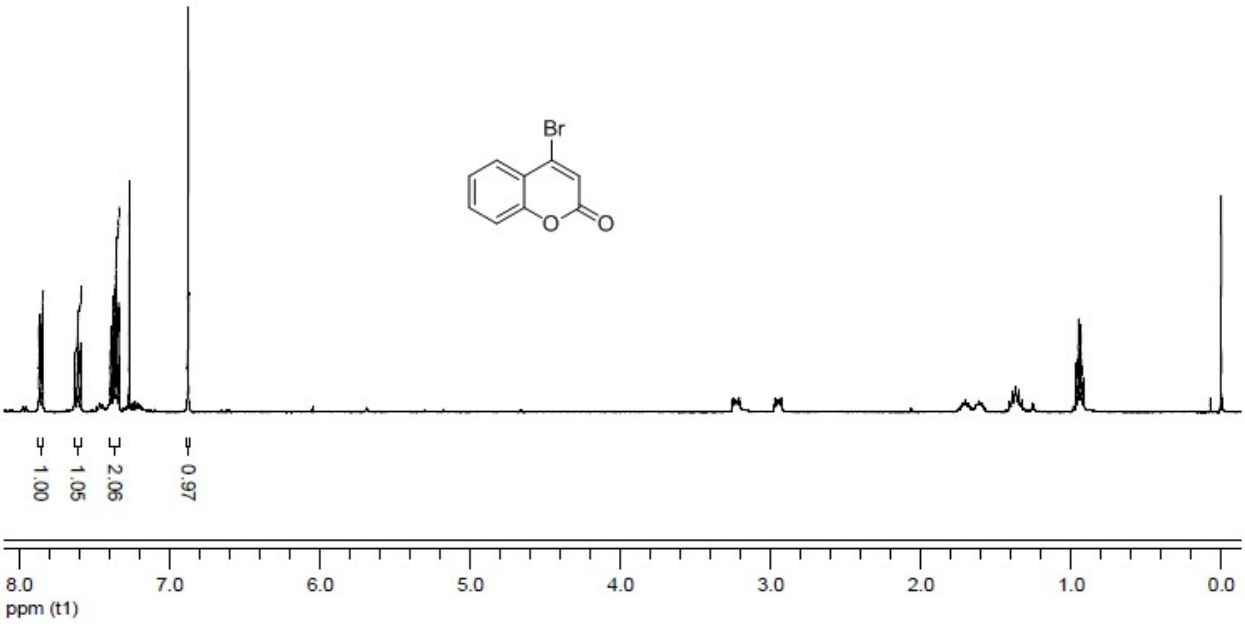
3a ^{13}C NMR (100 MHz, $CDCl_3$)



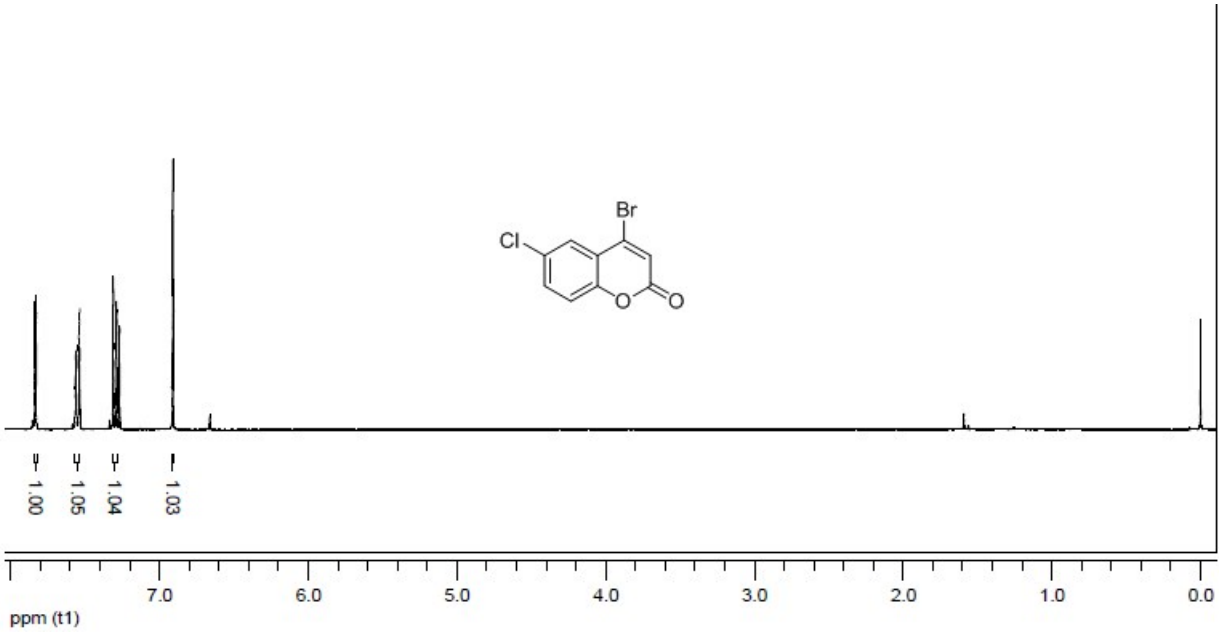
1a ^{1}H NMR (400 MHz, $CDCl_3$)



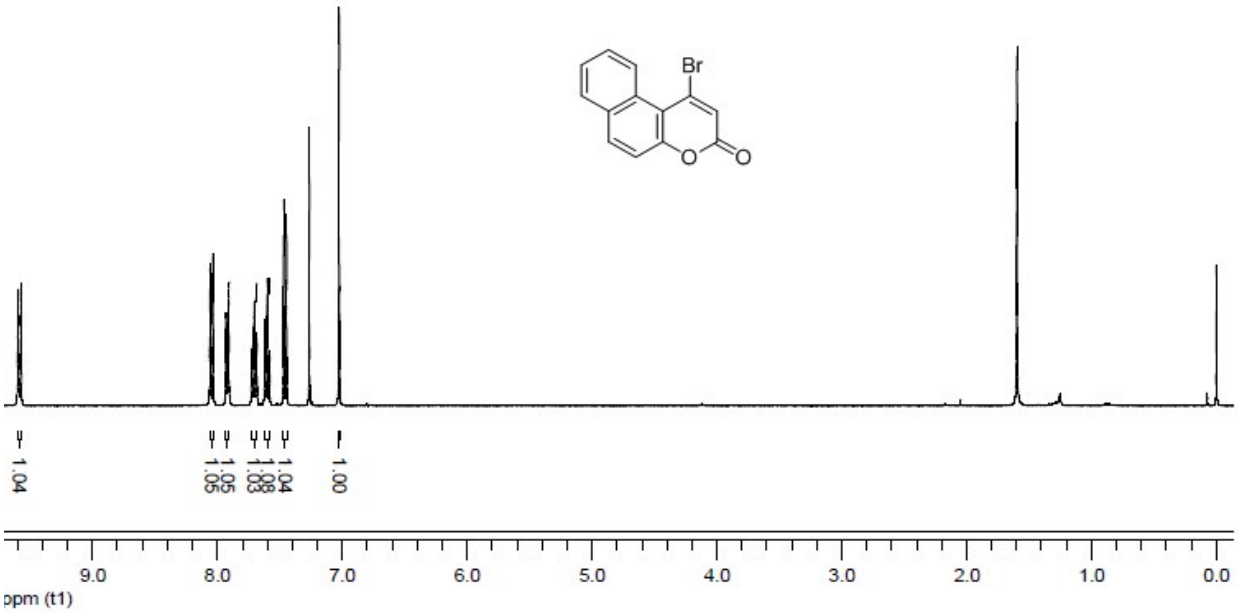
1b ^{1}H NMR (400 MHz, $CDCl_3$)



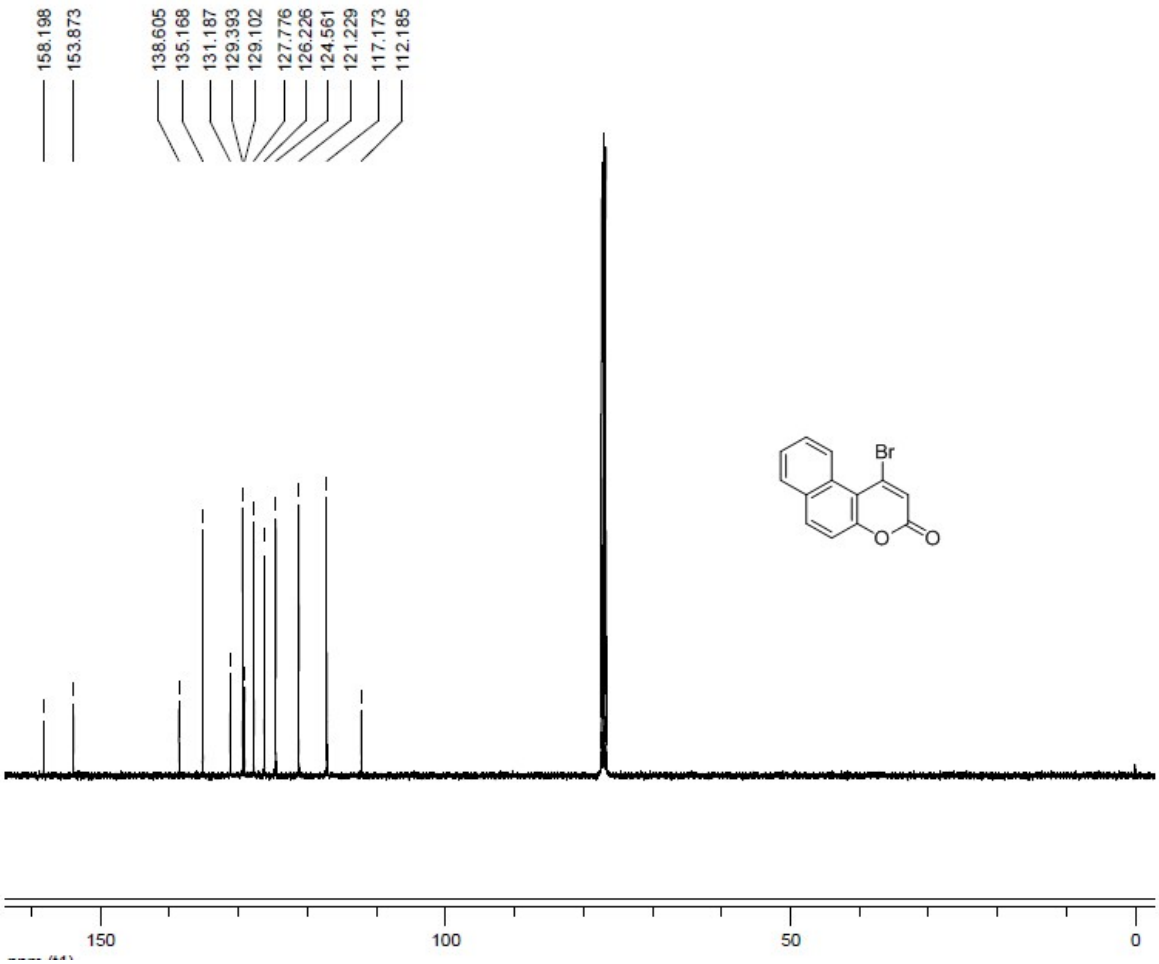
1c ^{1}H NMR (400 MHz, $CDCl_3$)



1d ^{1}H NMR (400 MHz, $CDCl_3$)



1d ^{13}C NMR (400 MHz, $CDCl_3$)



1e ^{1}H NMR (400 MHz, $CDCl_3$)