Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

One-pot synthesis of functionalized 4-hydroxy-3-thiomethylcoumarins: Detection and discrimination of Co^{2+} and Ni^{2+} ions

Ajaz A. Dar,[a] Sameer Hussain,[a] Debasish Dutta,[a] Parameswar K. Iyer*[a] and Abu T. Khan*[a,b]

[a]Department of Chemistry, Indian Institute of Technology Guwahati, Guwahati 781 039, India

[b]Aliah University, IIA/27, New Town, Kolkata-700 156, West Bengal, India

*E-mail: atk@iitg.ernet.in; pki@iitg.ernet.in

Experimental

All the reagents were of analytical reagent (AR) grade and were used as purchased without further purification. Melting points were recorded in an open capillary tube and are uncorrected. Fourier transform infrared (FT-IR) spectra were recorded as neat liquid or KBr pellets. ^{1}H and ^{13}C NMR spectra were recorded on Varian 400 MHz NMR spectrometer TMS as internal reference; chemical shifts (δ scale) are reported in parts per million (ppm). ^{1}H NMR Spectra are reported in the order: multiplicity, coupling constant (J value) in hertz (Hz) and no. of protons; signals were characterized as s (singlet), d (doublet), dd (doublet of doublets), t (triplet), m (multiplet). Mass spectra were recorded using ESI/APCI mode (Q-TOF type Mass Analyzer). Column chromatographic separations were performed using silica gel (60-120 mesh). Metal salts were used as their perchlorates. HPLC grade DMSO and Milli-Q water was used in all the experiments. UV-visible absorption spectra were obtained using a Perkin-Elmer Lambda 25 spectrophotometer. Fluorescence emission spectra were recorded on Horiba Fluoromax-4 spectrofluorometer using 10 mm path length quartz cuvette and a slit width of 3 nm at room temperature. The X-ray crystal structures were determined using a single XRD diffractometer. Complete crystallographic data of **28a**, **Co-Complex** and **Ni-Complex** for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 1038726, 1038805 and 1038804 respectively. Copies of this information may be obtained free of charge from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44-1223-336033, e-mail: deposit@ccdc.cam.ac.uk or via: www.ccdc.cam.ac.uk).

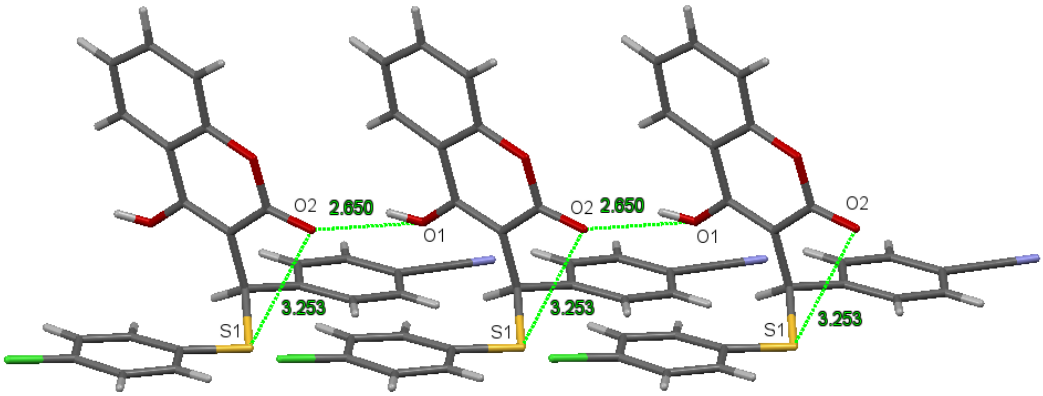
General procedure for the preparation 4-hydroxy-3-thiomethylcoumarins

In 10 mL round bottomed flask, a mixture of aldehyde (1 mmol) and L-proline (0.1 mmol) was dissolved in 3 mL of ethanol and stirred at room temperature. After 10 min of stirring, 4-hydroxycoumarin (1 mmol) and thiol (1.2 mmol) were added either directly if it is a solid or drop-wise through a syringe, in quick succession. The solid products were precipitated out during the reaction after appropriate reaction time. Finally, the solid products were filtered off through a Büchner funnel, thoroughly washed with the mixture of ethanol and hexane (2:8) to remove unreacted starting material and recrystallized in 9:1 mixture of ethanol and chloroform. The following work up procedure was followed for the products in case the solid precipitate did not come out during the reaction time. After completion of reaction as checked by TLC, ethanol was removed under reduced pressure via a rotary evaporator and the crude

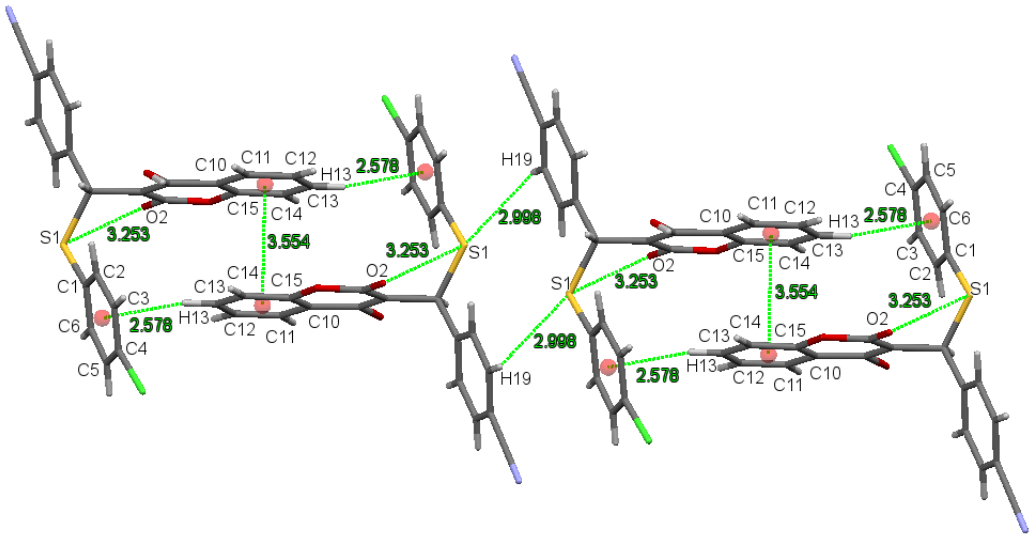
residue was extracted with dichloromethane (2 × 15 mL). The organic layer was washed with water, brine solution (2 x 5 mL) and dried over anhydrous Na_2SO_4. Then, it was concentrated under reduced pressure and the crude residue was passed through a silica gel (60-120 mesh) column with gradient eluents of petroleum ether and ethyl acetate to get the desired pure product.

Synthesis of Cobalt and Nickel complexes:

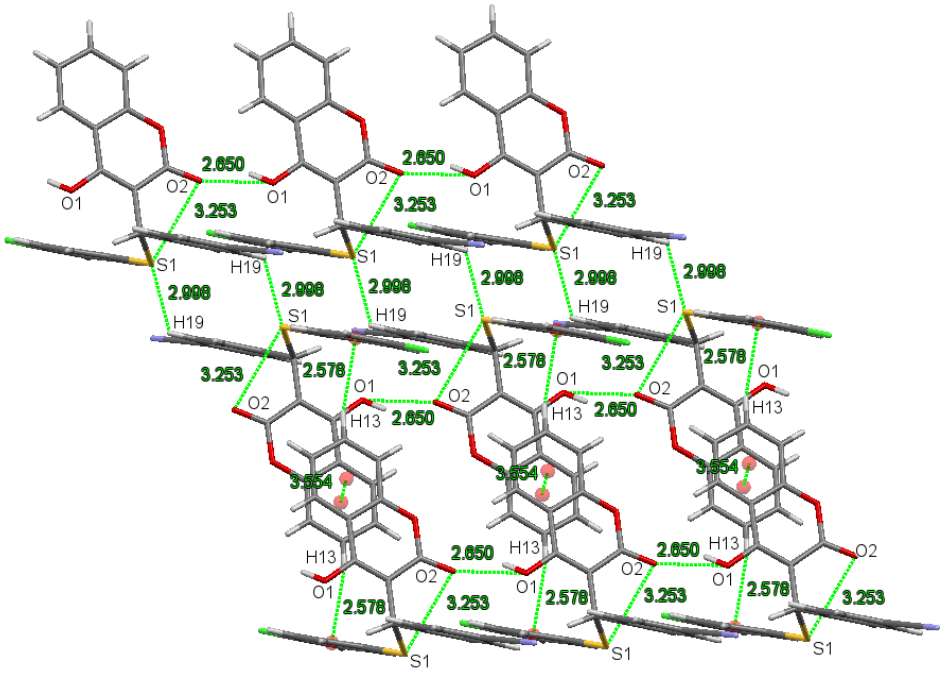
$Co(ClO_4)_2.6H_2O$ or $Ni(ClO_4)_2.6H_2O$ (0.05 mmol) dissolved in 2 ml of methanol was added to a solution of ligand (0.10 mmol) in dichloromethane (2 ml) with stirring under atmosphere oxygen. The resulting solution was allowed to stir for 10 min at room temperature and then filtered. The filtrate obtained were the desired complexes and dried under vacuum. These complexes were characterized by High Resolution Mass spectroscopy (HRMS). For **30a-Co^{2+}** HRMS (ESI): calcd for $C_{34}H_{28}N_2CoO_6S_2$ $[M + H]^+$: 684.0794; Found 684.0793. For **30a-Ni^{2+}** HRMS (ESI): calcd for $C_{34}H_{28}N_2NiO_6S_2$ $[M + H]^+$: 683.0815; Found 683.0815.



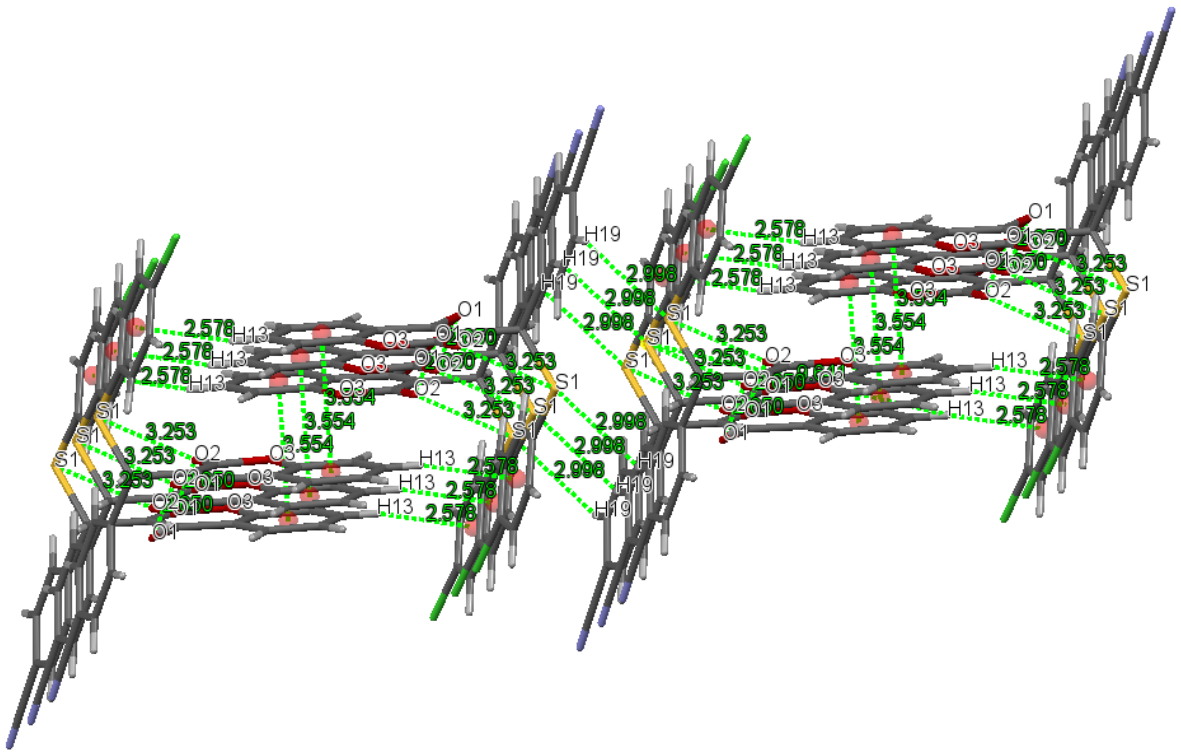
(a)


C10 C11 C12 H13 2.578
C15 C14 C13
O2
S1
3.253
3.554
C1 C2
C6 C3
C5 C4
C13 C14 C15 O2
H13 C12 C11 C10
2.578
3.253
S1
H19
2.998
H19
C10 C11 C12 H13 2.578
C15 C14 C13
O2
3.253
3.554
S1
C13 C14 C15 O2
H13 C12 C11 C10
2.578
3.253
C4 C5
C6
C3 C1
C2
S1

(b)


O1
2.650
O2
3.253
S1
H19
2.998
H13
2.578
3.554

(c)



(d)

Figure S1. (a) Intra-hetero-atomic and intermolecular interaction to form the long chain structure along c-axis. (b) Packing diagram of **28a** forming a 2D sheet viewed along c-axis. (c) Top view (d) Side view of collectively presentation of interactions resulting in the formation of a molecular ladder.

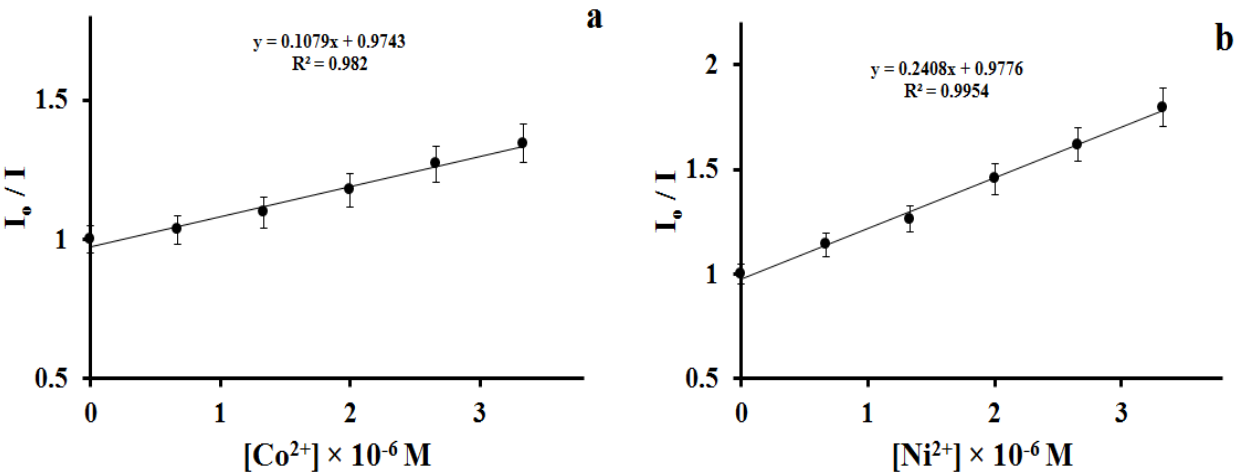


Figure S2. Stern-Volmer plots of ligand **30a** (25 μM) upon addition of (a) Co^{2+} and (b) Ni^{2+} in DMSO/HEPES buffer (9:1, pH=7.4) at room temperature.

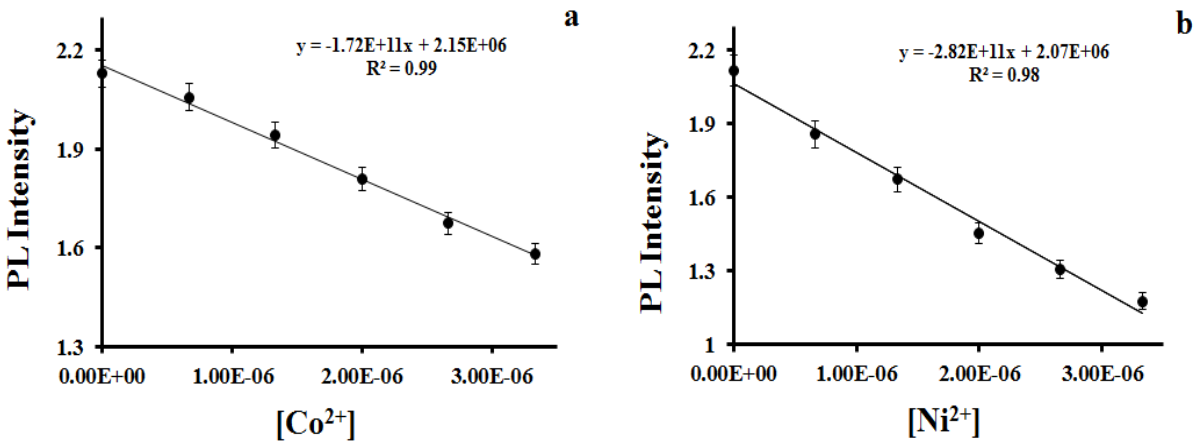


Figure S3. Detection limit plot for (a) Co^{2+} and (b) Ni^{2+} in DMSO/HEPES buffer (9:1, pH=7.4) at room temperature.

LOD for Co^{2+}= 3*12421.5/ 1.72*10^{11}

=0.22μM

LOD for Ni^{2+} = 3*12154.2/2.82*10^{11}

=0.13μM

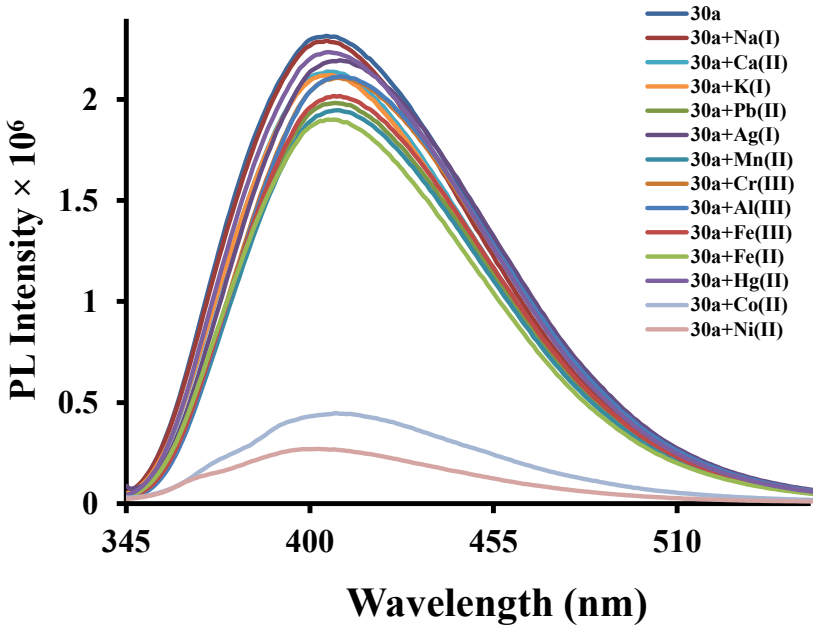


Figure S4. Effect of various metal ions on the emission of **30a** in DMSO/HEPES buffer (9:1, pH=7.4). Concentration of **30a** and each metal ion were 25 μM and 20 μM, respectively.

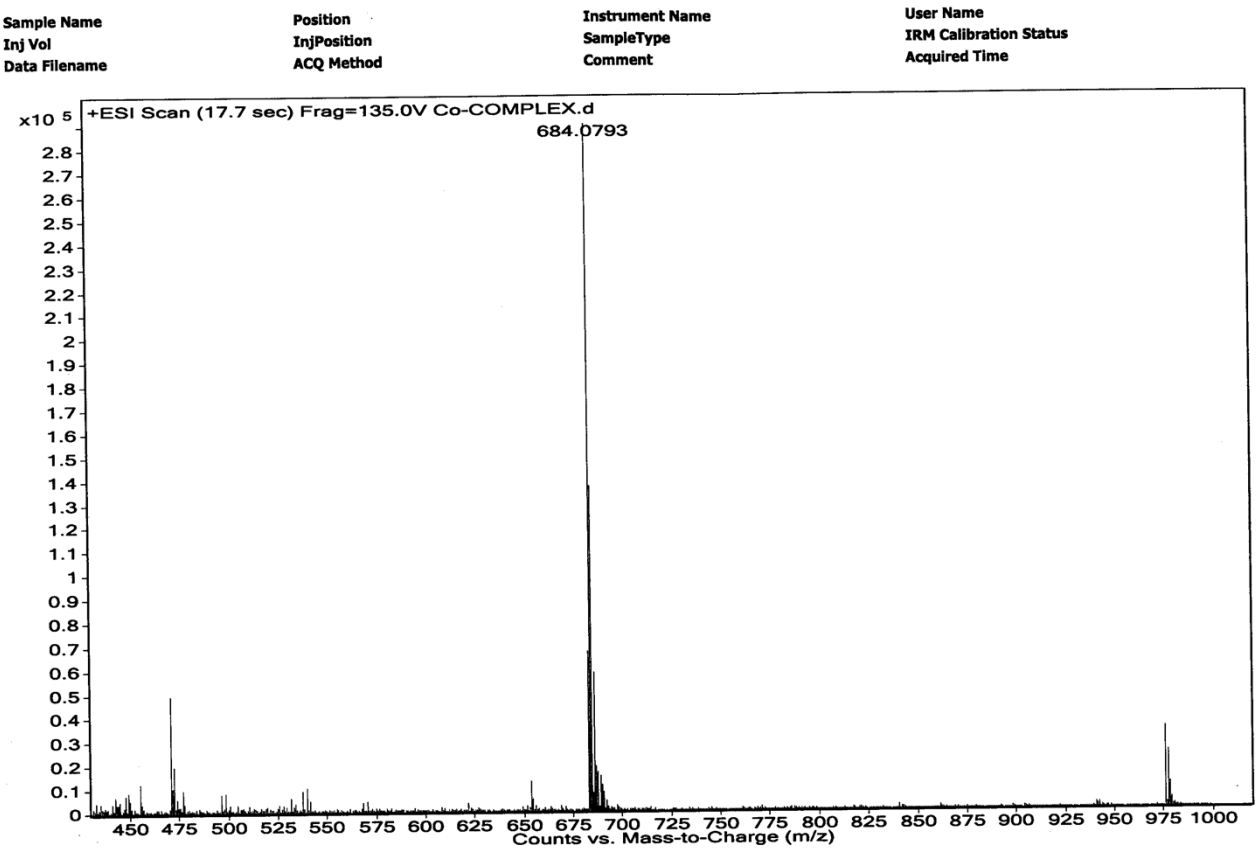


Figure S5. High resolution mass spectrum of **30a**-Co^{2+} complex.

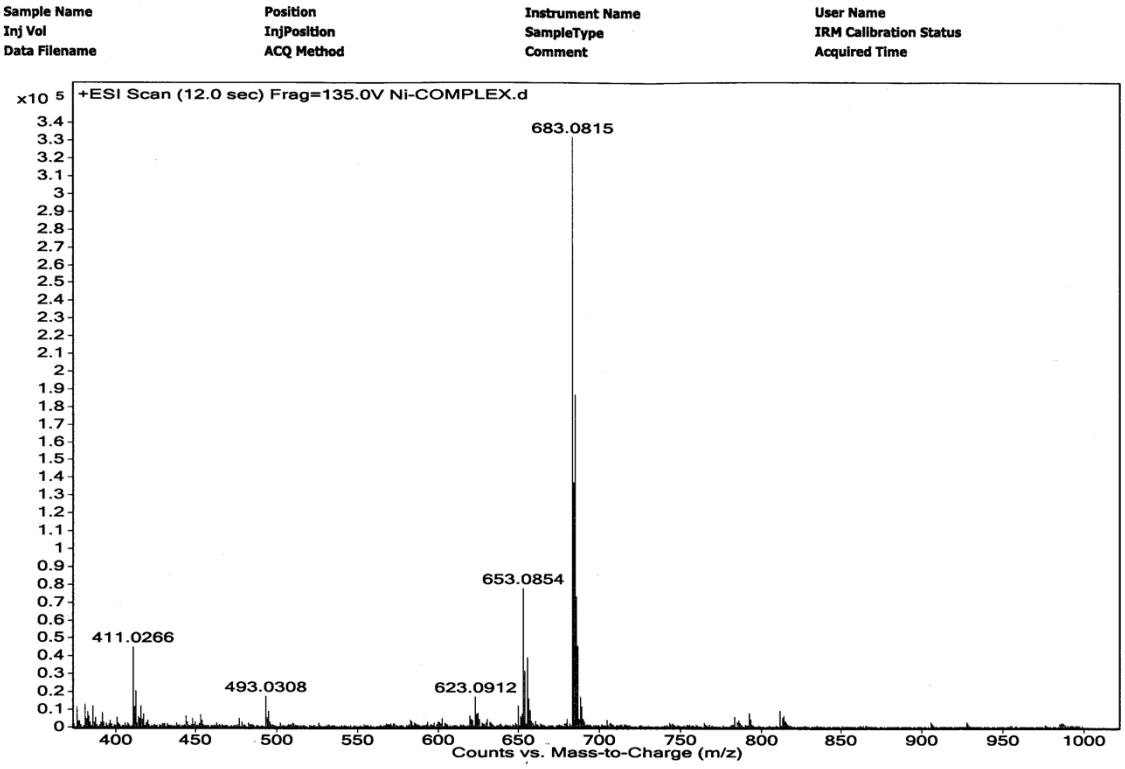


Figure S6. High resolution mass spectrum of **30a**-Ni^{2+} complex.

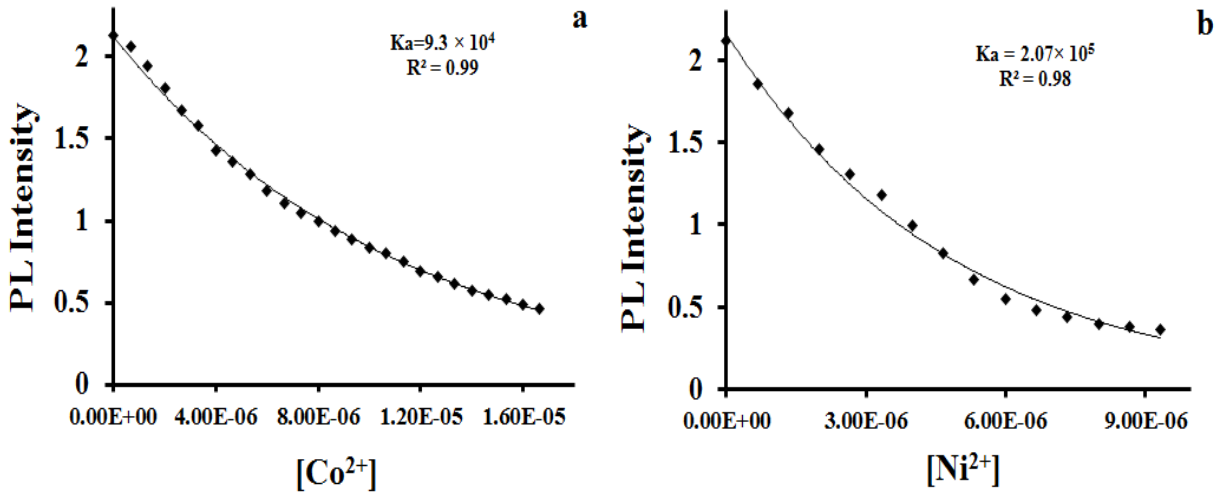


Figure S7. Plot of emission of ligand **30a** *vs* concentration of (a) Co^{2+} and (b) Ni^{2+} in DMSO/HEPES buffer (9:1, pH=7.4).

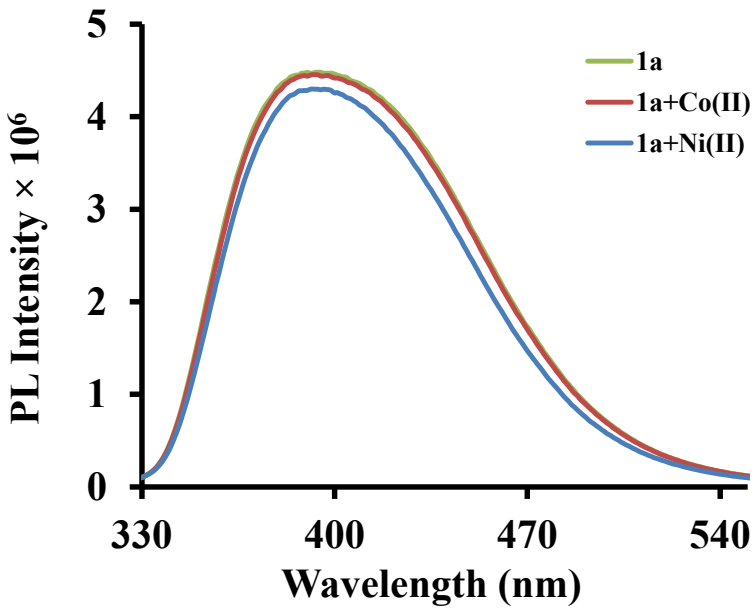


Figure S8. PL Spectra showing the effect of Co^{2+}/Ni^{2+} on the fluorescence emission of ligand **1a** in DMSO/HEPES buffer (9:1, pH=7.4) at room temperature.

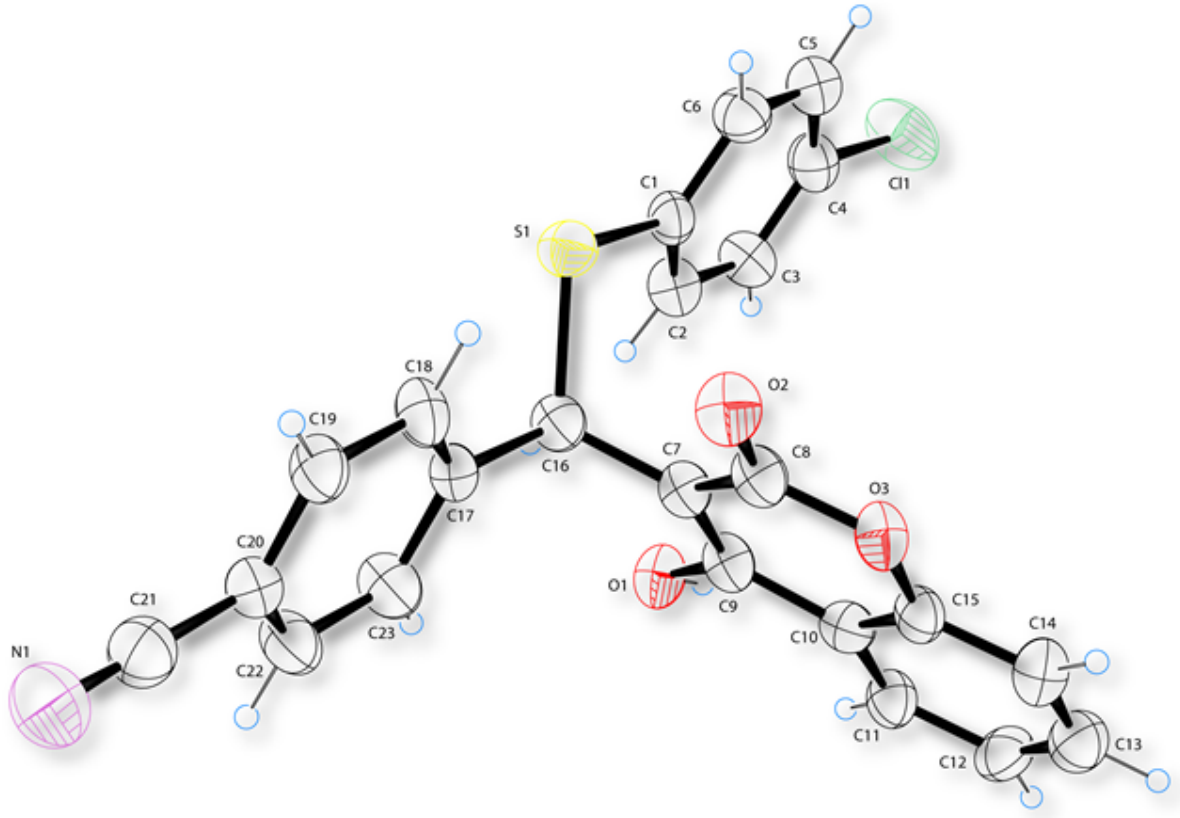


Figure S9. Showing ORTEP diagrams of the molecular structures (30 % probability) of **28a** and the labeling scheme used.

Table S1. Crystal data and structures refinement for the compound **28a** for atomic coordinates, equivalent isotropic displacement parameters and bond angles, please check the CIF.

Parameters	**Compound 28a**
Empirical Formula	C_{23} H_{14} Cl N O_3 S
Formula weight	419.86
Temperature	296 K
Wavelength	0.71073 (Å)
Crystal system	Triclinic
Space group	*P*-1
Radiation source	'fine-focus sealed tube'
Unit cell dimensions	a = 6.8647(11) (Å), α = 112.561(8)°
	b = 10.9002(13) (Å), β = 93.159(14)°
	c = 14.125(2) (Å), γ = 92.253(10)°
Unit cell volume	972.5(3) $Å^3$
Z	2

Density	1.434 g/cm^3
Reflections collected	7641
Independent reflections	3138 [R(int) = 0.0558]
Final R_1 values ($I > 2\sigma(I)$)	0.1338
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.3299
Final R_1 values (all data)	0.2072
Final $wR(F2)$ values (all data)	0.3775
Absorption coefficient, μ/mm	0.329
Radiation type	Mo K\a
Goodness of fit on F^2	1.075
F(0 0 0)	432.0
Theta range for data collection	2.03 to 24.99°
Index ranges	$-8 \leq h \leq 8$, $-12 \leq k \leq 12$, $-16 \leq l \leq 14$
Completeness to theta	24.99° 91.8 %
Number of parameters	263
Number of restraints	0
Refinement method	Full-matrix least-squares on F^2
CCDC number	1038726

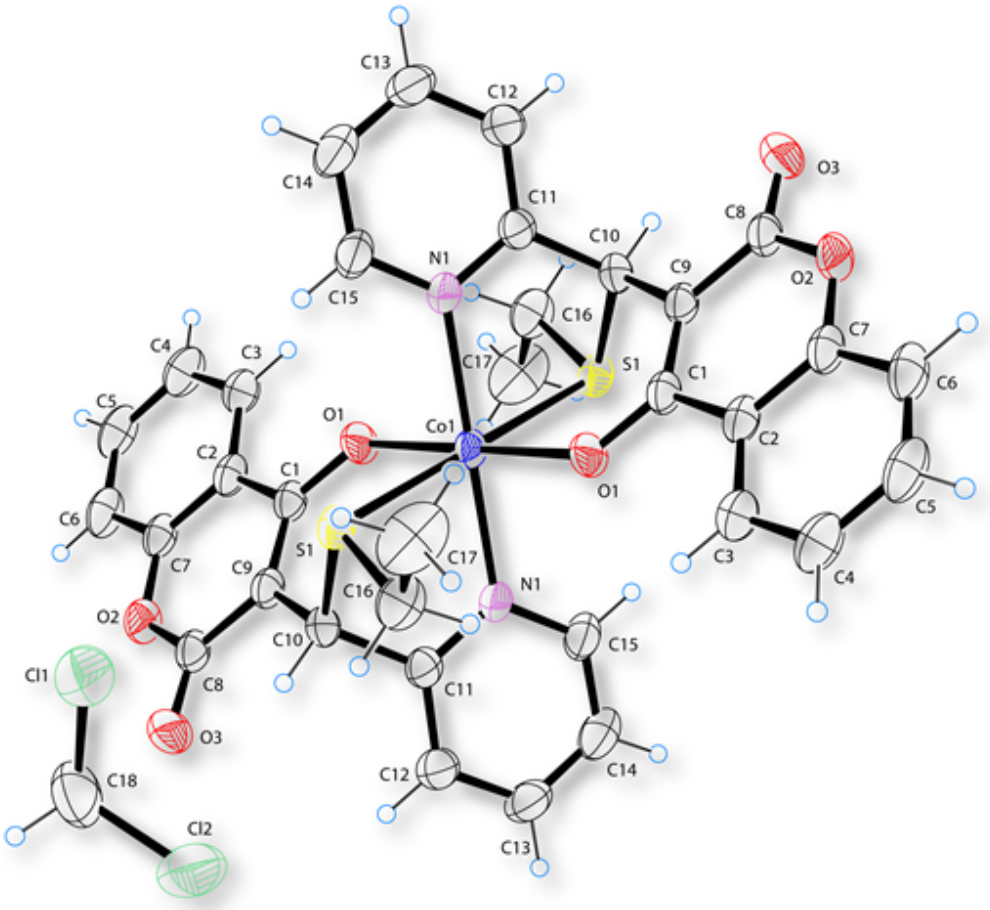


Figure S10. Showing ORTEP diagrams of the molecular structures (30 % probability) of **Co-complex** and the labeling scheme used.

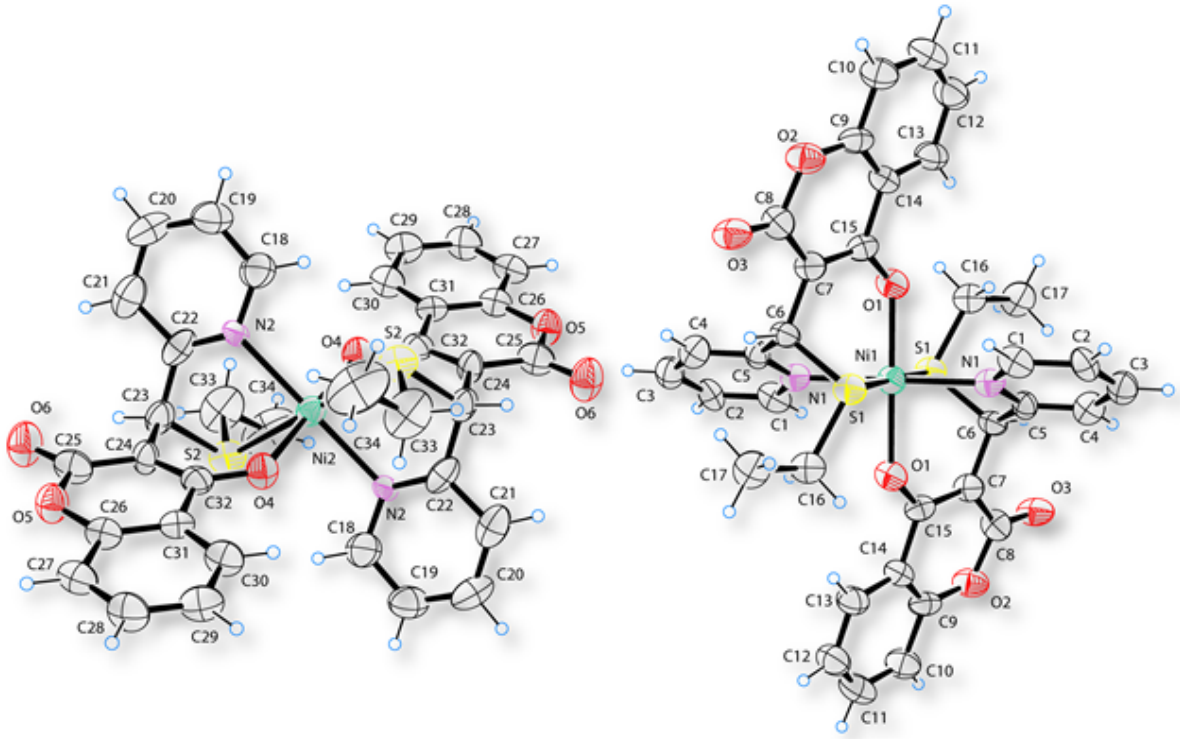


Figure S11. Showing ORTEP diagrams of the molecular structures (30 % probability) of the **Ni-complex** and the labeling scheme used.

Table S2. Crystal data and structures refinement for **Co-Complex** and **Ni-Complex.** For atomic coordinates, equivalent isotropic displacement parameters and bond angles, please check the CIF.

Parameters	**Co Complex**	**Ni Complex**
Empirical Formula	$C_{34}H_{28}N_2O_6S_2Co \bullet 2CH_2Cl_2$	$C_{34}H_{28}N_2O_6S_2Ni$
Formula weight	853.49	683.427
Temperature	296 K	296 K
Wavelength	0.71073 (Å)	0.71073 (Å)
Crystal system	Triclinic	Triclinic
Space group	*P*-1	*P*-1
Radiation source	'fine-focus sealed tube'	'fine-focus sealed tube'

Unit cell dimensions	a = 8.3365(6) (Å), α = 82.838(5)°	a = 8.1460(16) (Å), α = 76.635(17)°
	b = 11.1277(8) (Å), β = 69.409(4)°	b = 11.425(2) (Å), β = 83.429(17)°
	c = 11.2945(8) (Å), γ = 73.262(4)°	c = 17.576(4) (Å), γ = 72.903(17)°
Unit cell volume	938.94(12) Å^3	1519.3(5) Å^3
Z	1	2
Density	1.509 g/cm^3	1.494 g/cm^3
Reflections collected	13358	10908
Independent reflections	3333 [R(int) = 0.0254]	5482 [R(int) = 0.1085]
Final R_1 values ($I > 2\sigma(I)$)	0.0491	0.1013
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.1421	0.1476
Final R_1 values (all data)	0.0615	0.2339
Final $wR(F2)$ values (all data)	0.1553	0.2041
Absorption coefficient, μ/mm	0.900	0.826
Radiation type	Mo K\a	Mo K\a
Goodness-of-fit (GOF) on F^2	0.987	1.102
F(0 0 0)	437.0	708.0
Theta range for data collection	1.91 to 25.25°	2.93 to 25.25°
Index ranges	$-10 \le h \le 10$, $-13 \le k \le 13$, $-13 \le l \le 13$	$-9 \le h \le 9$, $-13 \le k \le 13$, $-21 \le l \le 18$
Completeness to theta	25.25° 98.1 %	25.25° 99.5 %
Number of parameters	233	411
Number of restraints	0	0
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
CCDC number	1038805	1038804

***Spectral data for all products*:**

3-((ethylthio)(phenyl)methyl)-4-hydroxy-2H-chromen-2-one (1a): Yield: (260 mg, 83%); semi-solid; IR (KBr): 3428, 3070, 3030, 2973, 2928, 1707, 1665, 1624, 1572, 1494, 1453, 1404, 1332, 1288, 1250, 1210, 1164, 1107, 1035, 1002, 933, 896, 835, 757, 697 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.34 (t, *J* = 6.8 Hz, 3H), 7.58-7.72 (m, 2H), 5.77 (s, 1H), 7.25-7.30 (m, 5H), 7.44 (d, *J* = 6.0 Hz, 2H), 7.53 (t, *J* = 6.4 Hz, 1H), 7.95 (d, *J* = 7.6 Hz, 1H), 10.85 (s, 1H, OH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.0, 26.8, 45.4, 101.3, 116.0, 116.5, 123.5, 124.2, 127.8 (2C), 128.1, 129.0 (2C), 132.6, 137.9, 152.9, 162.9, 163.6 ppm. HRMS (ESI): calcd for $C_{18}H_{16}O_3S$ $[M + H]^+$: 313.0893; Found 313.0912.

4-hydroxy-3-(phenyl(propylthio)methyl)-2H-chromen-2-one (2a): Yield: (278 mg, 85%); white solid; mp 90-92 °C. IR (KBr): 3455, 3059, 3028, 2964, 2931, 2875, 1707, 1666, 1625, 1572, 1494, 1453, 1404, 1349, 1332, 1281, 1265, 1250, 1209, 1164, 1108, 1035, 933, 896, 834, 798, 757, 736, 697 cm^{-1}. ^{1}H NMR (400 MHZ, $CDCl_3$): δ 1.02 (t, *J* = 7.6 Hz, 3H), 1.64-1.74 (m, 2H), 2.52-2.59 (m, 1H), 2.69-2.75 (m, 1H), 5.71 (s, 1H), 7.28-7.36 (m, 5H), 7.43 (d, *J* = 6.8 Hz, 2H), 7.58 (t, *J* = 7.2 Hz, 1H), 7.96 (d, *J* = 7.6 Hz, 1H), 10.99 (s, 1H, OH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.5, 22.1, 34.7, 45.7, 101.3, 116.1, 116.5, 123.5, 124.1, 127.8 (2C), 128.1, 129.1 (2C), 132.5, 138.1, 153.1, 162.7, 163.5 ppm. HRMS (ESI): calcd for $C_{19}H_{18}O_3S$ $[M + H]^+$: 327.1049; Found 327.1060.

3-((benzylthio)(phenyl)methyl)-4-hydroxy-2H-chromen-2-one (3a): Yield: (285 mg, 76%); White crystalline solid; mp 110-112 °C. IR (KBr): 3086, 3059, 3026, 3000, 1700, 1623, 1570, 1494, 1454, 1385, 1332, 1281, 1243, 1210, 1180, 1164, 1103, 1071, 1036, 1001, 950, 933, 911, 896, 836, 797, 777, 764, 752, 729, 712, 696, 671 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.86 (s, 2H), 5.60 (s, 1H), 7.17 (s, 1H), 7.26-7.37 (m, 11H), 7.57 (t, *J* = 7.6 Hz, 1H), 7.92 (d, *J* = 8.0 Hz, 1H), 10.63 (s, 1H, OH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 37.7,

46.0, 101.5, 116.1, 116.5, 123.6, 124.1, 127.7, 127.9 (2C), 128.2, 128.8 (2C), 128.9 (2C), 129.0 (2C), 132.5, 136.0, 137.6, 153.0, 162.5, 163.3 ppm. HRMS (APCI): calcd for $C_{23}H_{18}O_3S$ $[M + H]^+$: 375.1049; Found 375.1049.

3-(((2-chlorobenzyl)thio)(phenyl)methyl)-4-hydroxy-2H-chromen-2-one (4a): Yield: (319 mg, 78%); White solid; mp 146-148 °C. IR (KBr): 3445, 3062, 2952, 1817, 1684, 1622, 1611, 1572, 1495, 1472, 1442, 1416, 1384, 1331, 1278, 1250, 1237, 1205, 1165, 1146, 1108, 1054, 1038, 1001, 933, 896, 831, 759, 738, 707, 693, 668 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 4.00 (dd, J_1 = 13.2 Hz & J_2 = 13.2 Hz, 2H), 5.66 (s, 1H), 7.06 (d, J = 7.2 Hz, 1H), 7.11 (t, J = 7.6 Hz, 1H), 7.24 (d, J = 7.6 Hz, 2H), 7.28-7.33 (m, 5H), 7.36 (d, J = 7.2 Hz, 2H), 7.56 (t, J = 8.0 Hz, 1H), 7.88 (d, J = 8.4 Hz, 1H), 10.53 (s, 1H, OH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 35.7, 46.4, 101.7, 116.1, 116.5, 123.6, 124.1, 127.1, 128.0 (2C), 128.3, 129.0 (2C), 129.2, 130.0, 131.0, 132.5, 133.9, 134.1, 137.5, 152.9, 162.6, 163.4 ppm. HRMS (ESI): calcd for $C_{23}H_{17}ClO_3S$ $[M + H]^+$: 409.0660; Found 409.0662.

4-hydroxy-3-(((2-hydroxyethyl)thio)(phenyl)methyl)-2H-chromen-2-one (5a): Yield: (198 mg, 60%); White solid; mp 126-128 °C. IR (KBr): 3448, 2929, 2865, 2589, 1670, 1621, 1610, 1569, 1495, 1453, 1426, 1409, 1334, 1309, 1277, 1250, 1206, 1166, 1103, 1071, 1047, 1002, 936, 897, 863, 800, 760, 735, 696 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 2.35 (s, 1H, OH), 2.77-2.89 (m, 2H), 3.89 (s, 2H), 5.82 (s, 1H), 7.28-7.31 (m, 5H), 7.44 (d, J = 7.2 Hz, 2H), 7.56 (t, J = 8.4 Hz, 1H), 7.93 (d, J = 7.6 Hz, 1H), 10.48 (s, 1H, OH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 35.2, 45.7, 60.9, 101.7, 116.1, 116.7, 123.7, 124.3, 127.9 (2C), 128.4, 129.1 (2C), 132.8, 137.8, 153.0, 163.0, 163.6 ppm. HRMS (ESI): calcd for $C_{18}H_{16}O_4S$ $[M + Na]^+$: 351.0662; Found 351.0664.

4-hydroxy-3-(phenyl(phenylthio)methyl)-2H-chromen-2-one (6a):[23] Yield: (249 mg, 69%); White solid; mp 160-161 °C. IR (KBr): 3449, 3050, 3023, 2978, 1652, 1611, 1596, 1561,

1537, 1491, 1479, 1450, 1437, 1420, 1347, 1261, 1230, 1204, 1167, 1155, 1103, 1084, 1027, 997, 925, 848, 756, 740, 720, 690, 666 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 6.18 (s, 1H), 7.23-7.32 (m, 6H), 7.36 (t, *J* = 7.6 Hz, 2H), 7.48 (d, *J* = 7.6 Hz, 2H), 7.52 (d, *J* = 7.2 Hz, 3H), 7.91 (d, *J* = 8.4 Hz, 1H), 10.32 (s, 1H, OH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 49.6, 102.3, 116.0, 116.6, 123.6, 124.1, 128.1 (2C), 128.5, 128.6, 129.2 (2C), 129.6 (2C), 130.9 (2C), 132.1, 132.6, 136.9, 152.8, 162.7, 163.1 ppm. HRMS (ESI): calcd for $C_{22}H_{16}O_3S$ $[M + H]^+$: 361.0893; Found 361.0905.

4-hydroxy-3-(((4-methoxyphenyl)thio)(phenyl)methyl)-2H-chromen-2-one (7a): Yield: (301 mg, 77%); White solid; mp 126-127 °C. IR (KBr): 3434, 3063, 2932, 1686, 1624, 1610, 1590, 1572, 1494, 1453, 1439, 1390, 1330, 1291, 1249, 1210, 1179, 1166, 1110, 1029, 932, 896, 847, 832, 817, 799, 757, 731, 711, 702, 669 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 3.74 (s, 3H), 6.02 (s, 1H), 6.79 (d, *J* = 8.0 Hz, 2H), 7.24 (d, *J* = 9.6 Hz, 1H), 7.31 (t, *J* = 7.6 Hz, 2H), 7.36 (d, *J* = 7.2 Hz, 2H), 7.45 (d, *J* = 7.2 Hz, 2H), 7.50 (d, *J* = 8.0 Hz, 2H), 7.54 (d, *J* = 8.0 Hz, 1H), 7.95 (d, *J* = 8.0 Hz, 1H), 10.48 (s, 1H, OH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 51.4, 55.4, 102.4, 115.3 (2C), 116.2, 116.6, 122.2, 123.6, 124.2, 128.1 (2C), 128.4, 129.2 (2C), 132.5, 134.2 (2C), 137.2, 152.9, 160.4, 162.7, 163.0 ppm. HRMS (APCI): calcd for $C_{23}H_{18}O_4S$ $[M + H]^+$: 391.0999; Found 391.0994.

3-(((4-chlorophenyl)thio)(phenyl)methyl)-4-hydroxy-2H-chromen-2-one (8a): Yield: (297 mg, 75%); White solid; mp 167-169 °C. IR (KBr): 3084, 3022, 2973, 1653, 1611, 1596, 1559, 1540, 1491, 1476, 1451, 1418, 1391, 1341, 1318, 1286, 1229, 1196, 1166, 1152, 1103, 1095, 1080, 1030, 1010, 950, 923, 860, 847, 832, 820, 787, 754, 720, 698, 664 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 6.18 (s, 1H), 7.26 (s, 4H), 7.31-7.37 (m, 3H), 7.41 (d, *J* = 8.4 Hz, 2H), 7.50-7.55 (m, 3H), 7.90 (d, *J* = 6.4 Hz, 1H), 10.04 (s, 1H, OH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 49.7, 102.1, 115.9, 116.7, 123.6, 124.3, 128.1 (2C), 128.7, 129.3 (2C), 129.9

(2C), 130.6, 132.3 (2C), 132.8, 134.8, 136.5, 152.9, 162.8, 163.1 ppm. HRMS (ESI): calcd for $C_{22}H_{15}ClO_3S$ $[M + H]^+$: 395.0503; Found 395.0512.

3-(((2-chlorophenyl)thio)(phenyl)methyl)-4-hydroxy-2H-chromen-2-one (9a): Yield: (281 mg, 71%); White solid; mp 179-180 °C. IR (KBr): 3312, 3064, 1676, 1621, 1568, 1496, 1450, 1431, 1396, 1335, 1299, 1273, 1220, 1191, 1169, 1147, 1105, 1070, 1033, 949, 912, 892, 854, 784, 757, 748, 734, 718, 678 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 6.32 (s, 1H), 7.18 (t, *J* = 4.0 Hz, 2H), 7.25-7.33 (m, 3H), 7.35 (d, *J* = 5.2 Hz, 1H), 7.39 (d, *J* = 7.2 Hz, 2H), 7.44 (d, *J* = 7.6 Hz, 1H), 7.54 (d, *J* = 7.6 Hz, 3H), 7.90 (d, *J* = 7.6 Hz, 1H), 9.97 (s, 1H, OH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 47.5, 101.9, 116.0, 116.6, 123.8, 124.3, 127.9, 128.3 (2C), 128.8, 129.0, 129.4 (2C), 130.4, 130.7, 131.8, 132.7, 134.6, 136.3, 152.9, 162.7, 163.4 ppm. HRMS (ESI): calcd for $C_{22}H_{15}ClO_3S$ $[M + K]^+$: 433.0062; Found 433.0053.

3-(((2-bromophenyl)thio)(phenyl)methyl)-4-hydroxy-2H-chromen-2-one (10a): Yield: (321 mg, 73%); White solid; mp 181-183 °C. IR (KBr): 3321, 3070, 1676, 1622, 1568, 1496, 1449, 1427, 1395, 1335, 1298, 1271, 1220, 1189, 1173, 1147, 1105, 1070, 1017, 911, 891, 853, 784, 756, 732, 719, 678, 647 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 6.33 (s, 1H), 7.09 (t, *J* = 7.6 Hz, 1H), 7.24 (d, *J* = 7.6 Hz, 1H), 7.29 (t, *J* = 7.2 Hz, 1H), 7.32-7.36 (m, 2H), 7.39 (t, *J* = 7.6 Hz, 1H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.56 (t, *J* = 8.0 Hz, 5H), 7.91 (d, *J* = 7.6 Hz, 1H), 9.94 (s, 1H, OH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 47.7, 101.8, 115.9, 116.6, 123.8, 124.2, 124.3, 128.3 (2C), 128.5, 128.8, 128.9, 129.3 (2C), 130.2, 132.7, 133.6, 133.9, 136.2, 152.8, 162.8, 163.4 ppm. HRMS (ESI): calcd for $C_{22}H_{15}BrO_3S$ $[M + H]^+$: 440.9979; Found 441.0000.

4-hydroxy-3-((naphthalen-2-ylthio)(phenyl)methyl)-2H-chromen-2-one (11a): Yield: (312 mg, 76%); White solid; mp 153-155 °C. IR (KBr): 3078, 3052, 1683, 1662, 1622, 1607, 1593, 1567, 1494, 1446, 1399, 1340, 1281, 1228, 1194, 1165, 1148, 1108, 1080, 1029, 943,

916, 894, 860, 850, 839, 813, 777, 758, 738, 717, 697, 647 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.35 (s, 1H), 7.21 (d, *J* = 8.0 Hz, 1H), 7.33-7.38 (m, 3H), 7.45-7.49 (m, 3H), 7.56-7.57 (m, 3H), 7.76-7.78 (m, 4H), 7.90 (d, *J* = 6.4 Hz, 1H), 7.95 (s, 1H) 10.34 (s, 1H, OH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 49.3, 102.3, 116.0, 116.6, 123.6, 124.1, 126.9, 127.0, 127.4, 127.7, 127.8, 127.9, 128.2 (2C), 128.6, 129.3 (2C), 129.5, 129.9, 132.6, 132.8, 133.7, 136.8, 152.8, 162.8, 163.2 ppm. HRMS (ESI): calcd for $C_{26}H_{18}O_3S$ $[M]^+$: 410.0977; Found 410.0983.

4-hydroxy-3-((4-hydroxyphenyl)(phenylthio)methyl)-2H-chromen-2-one (12a): Yield: (272 mg, 72%); White solid; mp 115-117 °C. IR (KBr): 3068, 2606, 2360, 2256, 2126, 1657, 1601, 1566, 1514, 1474, 1452, 1437, 1354, 1311, 1271, 1253, 1217, 1182, 1160, 1114, 1097, 1048, 1024, 995, 907, 841, 791, 764, 740, 688, 675 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.63 (s, 1H, OH), 6.03 (s, 1H), 6.69 (d, *J* = 8.8 Hz, 2H), 7.16-7.24 (m, 7H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.46 (t, *J* = 8.0 Hz, 1H), 7.84 (d, *J* = 8.0 Hz, 1H), 10.34 (s, 1H, OH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$ + DMSO): δ 46.7, 105.5, 114.4 (2C), 115.2, 115.4, 123.0, 125.7, 128.1 (3C), 128.2 (2C), 129.1 (2C), 129.2, 131.2, 135.9, 151.5, 155.7, 160.0, 161.3 ppm. HRMS (ESI): calcd for $C_{22}H_{16}O_4S$ $[M + K]^+$: 415.0401; Found 415.0393.

4-hydroxy-3-((phenylthio)(p-tolyl)methyl)-2H-chromen-2-one (13a): Yield: (251 mg, 67%); White solid; mp 134-136 °C. IR (KBr): 3089, 2919, 2850, 2362, 1695, 1625, 1572, 1514, 1495, 1455, 1439, 1279, 1250, 1205, 1159, 1109, 1037, 931, 897, 762, 756, 748, 711, 692 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.34 (s, 3H), 6.17 (s, 1H), 7.17 (d, *J* = 8.0 Hz, 2H), 7.23-7.31 (m, 5H), 7.42 (d, *J* = 7.6 Hz, 2H), 7.48 (d, *J* = 7.2 Hz, 2H), 7.53 (t, *J* = 8.0 Hz, 1H), 7.92 (d, *J* = 8.0 Hz, 1H), 10.30 (s, 1H, OH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.2, 49.3, 102.5, 116.0, 116.5, 123.6, 124.1, 128.0 (2C), 128.4, 129.6 (2C), 129.9 (2C), 130.8 (2C),

132.3, 132.5, 133.9, 138.4, 152.8, 162.7, 163.0 ppm. HRMS (ESI): calcd for $C_{23}H_{18}O_3S$ [M + H]$^+$: 375.1049; Found 375.1057.

3-(cyclohexyl(phenylthio)methyl)-4-hydroxy-2H-chromen-2-one (14a): Yield: (195 mg, 53%); dark brown semi-solid; IR (KBr): 3418, 2927, 2851, 1704, 1666, 1622, 1570, 1495, 1480, 1449, 1439, 1385, 1330, 1282, 1202, 1170, 1106, 1068, 1025, 959, 897, 760, 689 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.43-1.25 (m, 4H), 1.37-1.45 (m, 1H), 1.59-1.79 (m, 4H), 1.96-2.08 (m, 2H), 4.89 (d, *J* = 6.4 Hz, 1H), 7.15-7.27 (m, 5H), 7.36 (d, *J* = 7.2 Hz, 2H), 7.49 (t, *J* = 8.0 Hz, 1H), 7.82 (d, *J* = 7.6 Hz, 1H), 9.98 (s, 1H, OH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 26.0, 26.2, 26.3, 31.0, 31.1, 42.5, 51.7, 102.7, 116.0, 116.3, 123.3, 123.9, 127.8, 129.3 (2C), 130.7 (2C), 131.8, 132.1, 152.6, 162.5, 163.4 ppm. HRMS (ESI): calcd for $C_{22}H_{22}O_3S$ [M + H]$^+$: 367.1362; Found 367.1383.

(E)-4-hydroxy-3-(1-(phenylthio)but-2-en-1-yl)-2H-chromen-2-one (15a): Yield: (163 mg, 50%); dark brown semi-solid; IR (KBr): 3419, 2978, 2924, 2853, 1711, 1627, 1609, 1573, 1493, 1454, 1438, 1415, 1382, 1327, 1276, 1213, 1187, 1112, 1036, 906, 757, 691, 666 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.47 (d, *J* = 6.8 Hz, 3H), 5.21-5.22 (m, 1H), 5.50 (d, *J* = 9.6 Hz, 1H), 6.49 (d, *J* = 10.0 Hz, 1H), 7.14-7.23 (m, 6H), 7.43 (dd, J_1 = 7.2 Hz & J_2 = 7.6 Hz 2H), 7.69 (d, *J* = 8.4 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 22.0, 74.6, 101.0, 115.4, 116.9 (2C), 118.2, 122.4, 122.9, 124.2, 127.3, 127.7, 129.2, 129.4, 132.3 (2C), 153.3, 159.5, 161.0 ppm. HRMS (ESI): calcd for $C_{19}H_{16}O_3S$ [M + H]$^+$: 325.0893; Found 325.0896.

4-hydroxy-3-(phenyl(p-tolylthio)methyl)-2H-chromen-2-one (16a): Yield: (270 mg, 72%); White solid; mp 134-135 °C. IR (KBr): 3446, 3063, 2920, 1686, 1654, 1620, 1611, 1572, 1561, 1535, 1492, 1453, 1390, 1279, 1229, 1202, 1166, 1103, 1087, 1036, 931, 848, 821, 805, 753, 724, 700 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.27 (s, 3H), 6.10 (s, 1H), 7.08 (d, *J* = 8.8 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 1H), 7.30 (t, *J* = 7.2 Hz, 1H), 7.35 (d, *J* = 8.0 Hz, 2H),

7.38 (d, *J* = 8.4 Hz, 3H), 7.50-7.53 (m, 3H), 7.93 (d, *J* = 8.0 Hz, 1H), 10.45 (s, 1H, OH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.3, 50.3, 102.4, 116.2, 116.6, 123.6, 124.2, 128.1 (2C), 128.4, 128.5, 129.2 (2C), 130.5 (2C), 131.5 (2C), 132.5, 137.1, 139.0, 152.9, 162.7, 163.1 ppm. HRMS (APCI): calcd for $C_{23}H_{18}O_3S$ $[M + H]^+$: 375.1049; Found 375.1048.

4-hydroxy-3-((4-hydroxyphenyl)(p-tolylthio)methyl)-2H-chromen-2-one (17a): Yield: (297 mg, 76%); White solid; mp 144-145 °C. IR (KBr): 3313, 3124, 1665, 1610, 1591, 1571, 1512, 1496, 1455, 1438, 1284, 1272, 1253, 1225, 1177, 1159, 1107, 1059, 1030, 1017, 845, 838, 802, 763, 750, 669 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.26 (s, 3H), 6.02 (s, 1H), 6.76 (d, *J* = 8.4 Hz, 2H), 7.06 (d, *J* = 7.2 Hz, 2H), 7.23 (d, *J* = 8.8 Hz, 1H), 7.31 (d, *J* = 7.6 Hz, 3H), 7.36 (s, *J* = 7.2 Hz, 3H), 7.53 (t, *J* = 8.0 Hz, 1H), 7.93 (d, *J* = 8.0 Hz, 1H), 10.57 (s, 1H, OH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.3, 50.0, 102.6, 116.1, 116.2 (2C), 116.3, 116.6, 123.7, 124.4, 128.2, 128.5, 129.4 (2C), 130.4 (2C), 131.4 (2C), 132.6, 138.9, 152.7, 156.5, 163.5 ppm. HRMS (APCI): calcd for $C_{23}H_{18}O_4S$ $[M + H]^+$: 391.0999; Found 391.0998.

4-hydroxy-3-((4-methoxyphenyl)(p-tolylthio)methyl)-2H-chromen-2-one (18a): Yield: (300 mg, 74%); White solid; mp 142-144 °C. IR (KBr): 3078, 2959, 2837, 1693, 1629, 1604, 1573, 1510, 1493, 1453, 1443, 1364, 1334, 1306, 1279, 1257, 1213, 1180, 1164, 1148, 1111, 1091, 1044, 1033, 936, 896, 837, 817, 807, 792, 765, 749, 739, 701, 690, 671 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.27 (s, 3H), 3.80 (s, 3H), 6.07 (s, 1H), 6.88 (d, *J* = 8.0 Hz, 2H), 7.07 (d, *J* = 7.2 Hz, 2H), 7.24 (d, *J* = 8.4 Hz, 1H), 7.30 (d, *J* = 7.2 Hz, 1H), 7.37 (d, *J* = 7.6 Hz, 2H), 7.43 (d, *J* = 7.6 Hz, 2H), 7.53 (t, *J* = 8.0 Hz, 1H), 7.93 (d, *J* = 8.0 Hz, 1H), 10.46 (s, 1H, OH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.2, 49.7, 55.4, 102.6, 114.5 (2C), 116.1, 116.5, 123.5, 124.1, 128.5, 128.9, 129.3 (2C), 130.4 (2C), 131.4 (2C), 132.4, 138.8, 152.8, 159.6, 162.7, 162.9 ppm. HRMS (APCI): calcd for $C_{24}H_{20}O_4S$ $[M + K]^+$: 443.0714; Found 443.0725.

3-((4-chlorophenyl)(p-tolylthio)methyl)-4-hydroxy-2H-chromen-2-one (19a): Yield: (315 mg, 77%); White solid; mp 138-140 °C. IR (KBr): 3155, 2922, 1892, 1682, 1619, 1567, 1492, 1450, 1393, 1340, 1282, 1199, 1161, 1146, 1108, 1088, 1061, 1013, 896, 815, 804, 765, 754, 733, 680 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.27 (s, 3H), 6.04 (s, 1H), 7.08 (d, *J* = 7.6 Hz, 2H), 7.24 (d, *J* = 8.8 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 3H), 7.37 (d, *J* = 7.6 Hz, 2H), 7.44 (d, *J* = 8.4 Hz, 2H), 7.54 (t, *J* = 8.0 Hz, 1H), 7.93 (d, *J* = 8.0 Hz, 1H), 10.42 (s, 1H, OH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.3, 49.8, 102.1, 116.0, 116.7, 123.7, 124.2, 128.0, 129.4 (2C), 129.5 (2C), 130.5 (2C), 131.6 (2C), 132.7, 134.4, 135.7, 139.2, 152.9, 162.6, 163.2 ppm. HRMS (APCI): calcd for $C_{23}H_{17}ClO_3S$ $[M + K]^+$: 447.0219; Found 447.0221.

3-((4-bromophenyl)(p-tolylthio)methyl)-4-hydroxy-2H-chromen-2-one (20a): Yield: (280 mg, 79%); White solid; mp 143-145 °C. IR (KBr): 3493, 3160, 2961, 2919, 2852, 1682, 1619, 1566, 1493, 1449, 1395, 1339, 1281, 1198, 1161, 1145, 1108, 1061, 1009, 896, 804, 764, 754, 731, 684, 668 cm^{-1}. ^{1}H NMR (400 MHZ, $CDCl_3$): δ 2.28 (s, 3H), 6.03 (s, 1H), 7.09 (d, *J* = 7.6 Hz, 2H), 7.25 (d, *J* = 8.4 Hz, 1H), 7.32 (t, *J* = 7.2 Hz, 1H), 7.38 (d, *J* = 8.0 Hz, 4H), 7.48 (d, *J* = 7.6 Hz, 2H), 7.55 (t, *J* = 7.6 Hz, 1H), 7.93 (d, *J* = 7.6 Hz, 1H), 10.42 (s, 1H, OH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.2, 49.7, 102.0, 115.9, 116.5, 122.4, 123.5, 124.2, 128.0, 129.7 (2C), 130.4 (2C), 131.5 (2C), 132.2 (2C), 132.6, 136.2, 139.1, 152.8, 162.6, 163.1 ppm. HRMS (ESI): calcd for $C_{23}H_{17}BrO_3S$ $[M + H]^+$: 455.0136; Found 455.0144.

3-((4-fluorophenyl)(p-tolylthio)methyl)-4-hydroxy-2H-chromen-2-one (21a): Yield: (271 mg, 69%); White solid; mp 79-80 °C. IR (KBr): 3447, 3071, 2953, 2922, 2858, 1925, 1686, 1624, 1573, 1507, 1494, 1454, 1381, 1279, 1250, 1234, 1211, 1160, 1108, 1040, 1015, 942, 929, 896, 853, 819, 799, 767, 751, 716, 671 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.27 (s, 3H), 6.06 (s, 1H), 7.03 (t, *J* = 8.4 Hz, 2H), 7.08 (d, *J* = 8.4 Hz, 2H), 7.24 (d, *J* = 9.6 Hz, 1H),

7.31 (t, J = 7.6 Hz, 1H), 7.37 (d, J = 8.4 Hz, 2H), 7.48 (dd, J_1 = 8.4 Hz & J_2 = 8.8 Hz, 2H), 7.54 (t, J = 8.0 Hz, 1H), 7.93 (d, J = 8.0 Hz, 1H), 10.47 (s, 1H, OH). ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.2, 49.6, 102.3, 115.9, 116.0, 116.2, 116.6, 123.6, 124.2, 128.1, 129.8, 129.9, 130.4, 131.5, 132.6, 132.9, 133.0, 139.1, 152.8, 161.3, 162.6, 163.1, 163.8 ppm. HRMS (APCI): calcd for $C_{23}H_{17}FO_3S$ $[M + K]^+$: 431.0514; Found 431.0518.

4-hydroxy-3-((4-nitrophenyl)(p-tolylthio)methyl)-2H-chromen-2-one (22a): Yield: (340 mg, 81%); White solid; mp 201-203 °C. IR (KBr): 3471, 3162, 2919, 2847, 1678, 1620, 1566, 1518, 1495, 1451, 1401, 1344, 1280, 1220, 1190, 1166, 1148, 1109, 1072, 1012, 897, 854, 827, 806, 767, 759, 715, 673 cm-1. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.29 (s, 3H), 6.11 (s, 1H), 7.11 (d, J = 7.2 Hz, 2H), 7.26 (d, J = 3.6 Hz, 1H), 7.34 (t, J = 7.6 Hz, 1H), 7.40 (d, J = 7.2 Hz, 2H), 7.58 (t, J = 7.6 Hz, 1H), 7.68 (d, J = 8.0 Hz, 2H), 7.96 (d, J = 8.0 Hz, 1H), 8.21 (d, J = 8.0 Hz, 2H), 10.45 (s, 1H, OH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.3, 50.0, 101.4, 115.9, 116.7, 123.7, 124.3 (2C), 124.4, 127.4, 129.2 (2C), 130.7 (2C), 131.9 (2C), 133.0, 139.7, 144.7, 147.8, 152.9, 162.6, 163.5 ppm. HRMS (APCI): calcd for $C_{23}H_{17}NO_5S$ $[M + H]^+$: 420.0900; Found 420.0901.

3-((2-chlorophenyl)(p-tolylthio)methyl)-4-hydroxy-2H-chromen-2-one (23a): Yield: (254 mg, 62%); White solid; mp 197-199 °C. IR (KBr): 3173, 2964, 2919, 2855, 1668, 1627, 1568, 1496, 1465, 1452, 1437, 1404, 1343, 1292, 1269, 1231, 1192, 1163, 1151, 1114, 1058, 1046, 1034, 1017, 955, 939, 896, 867, 850, 807, 764, 750, 738, 697, 682, 643 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.30 (s, 3H), 6.29 (s, 1H), 7.12 (d, J = 7.6 Hz, 2H), 7.20 (t, J = 7.6 Hz, 1H), 7.25-7.27 (m, 2H), 7.34 (t, J = 8.0 Hz, 2H), 7.46-7.49 (m, 3H), 7.58 (t, J = 8.0 Hz, 1H), 8.00 (d, J = 8.0 Hz, 1H), 11.06 (s, 1H, OH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.3, 49.2, 101.5, 116.2, 116.7, 123.7, 124.2, 127.5, 128.3, 128.7, 129.9, 130.6 (2C), 130.7, 132.0 (2C),

132.7, 134.7, 134.8, 139.5, 153.0, 162.3, 163.8 ppm. HRMS (ESI): calcd for $C_{23}H_{17}ClO_3S$ [M + H]$^+$: 409.0660; Found 409.0667.

4-hydroxy-3-((2-nitrophenyl)(p-tolylthio)methyl)-2H-chromen-2-one (24a): Yield: (273 mg, 65%); White solid; mp 170-172 °C. IR (KBr): 3174, 2919, 2861, 1667, 1630, 1619, 1565, 1525, 1497, 1475, 1451, 1404, 1349, 1292, 1267, 1231, 1212, 1190, 1164, 1150, 1113, 1081, 1059, 1033, 1017, 941, 921, 897, 878, 858, 828, 808, 788, 761, 749, 735, 716, 678 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.23 (s, 3H), 6.60 (s, 1H), 7.06 (d, *J* = 7.6 Hz, 2H), 7.18 (d, *J* = 7.2 Hz, 1H), 7.27 (t, *J* = 7.2 Hz, 1H), 7.38-7.45 (m, 4H), 7.49 (t, *J* = 8.0 Hz, 2H), 7.93 (d, *J* = 8.4 Hz, 1H), 7.97 (d, *J* = 8.0 Hz, 1H), 11.09 (s, 1H, OH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.4, 47.6, 101.3, 116.0, 116.7, 123.8, 124.3, 126.0, 127.5, 129.4, 129.5, 130.7 (2C), 132.5 (2C), 132.6, 132.9, 133.7, 140.0, 148.8, 153.1, 162.2, 163.9 ppm. HRMS (ESI): calcd for $C_{23}H_{17}NO_5S$ [M + H]$^+$: 420.0900; Found 420.0904.

3-((2,4-dimethoxyphenyl)(p-tolylthio)methyl)-4-hydroxy-2H-chromen-2-one (25a): Yield: (305 mg, 70%); White solid; mp 122-123 °C. IR (KBr): 3213, 2919, 2836, 2359, 2332, 1671, 1621, 1606, 1567, 1495, 1457, 1438, 1399, 1345, 1293, 1204, 1191, 1178, 1163, 1102, 1074, 1031, 938, 917, 894, 840, 820, 757, 680 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.27 (s, 3H), 3.79 (s, 3H), 3.95 (s, 3H), 6.16 (s, 1H), 6.44 (d, *J* = 8.0 Hz, 1H), 6.51 (s, 1H), 7.07 (d, *J* = 7.2 Hz, 2H), 7.22-7.32 (m, 3H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.51 (t, *J* = 8.4 Hz, 1H), 7.94 (d, *J* = 7.6 Hz, 1H), 10.77 (s, 1H, OH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.1, 46.0, 55.4, 55.9, 99.3, 102.5, 104.8, 116.3, 118.1, 123.5, 123.9, 129.7, 129.8, 130.1 (2C), 131.3 (2C), 132.1, 132.4, 138.3, 152.6, 158.0, 161.1, 162.5, 162.7 ppm. HRMS (ESI): calcd for $C_{25}H_{22}O_5S$ [M + K]$^+$: 473.0820; Found 473.0827.

4-hydroxy-3-(naphthalen-2-yl(p-tolylthio)methyl)-2H-chromen-2-one (26a): Yield: (336 mg, 79%); White solid; mp 114-116 °C. IR (KBr): 3445, 3052, 2921, 2854, 1693, 1662,

1621, 1567, 1492, 1453, 1395, 1331, 1281, 1207, 1105, 1037, 896, 858, 808, 761, 669 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 2.28 (s, 3H), 6.26 (s, 1H), 7.09 (d, *J* = 7.6 Hz, 2H), 7.25 (s, 1H), 7.32 (t, *J* = 7.6 Hz, 1H), 7.42 (d, *J* = 7.6 Hz, 2H), 7.46-7.47 (m, 2H), 7.54 (t, *J* = 8.0 Hz, 1H), 7.66 (d, *J* = 8.4 Hz, 1H), 7.80-7.86 (m, 3H), 7.89 (s, 1H), 7.97 (d, *J* = 7.6 Hz, 1H), 10.47 (s, 1H, OH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.3, 50.6, 102.4, 116.2, 116.6, 123.7, 124.2, 126.2, 126.5, 126.6, 126.8, 127.8, 128.2, 128.4, 129.1, 130.5 (2C), 131.6 (2C), 132.6, 133.2, 133.5, 134.5, 139.0, 152.9, 162.8, 163.2 ppm. HRMS (APCI): calcd for $C_{27}H_{20}O_3S$ $[M + K]^+$: 463.0765; Found 463.0755.

3-(((4-bromophenyl)thio)(4-methoxyphenyl)methyl)-4-hydroxy-2H-chromen-2-one (27a): Yield: (334 mg, 71%); White solid; mp 230-232 °C. IR (KBr): 3438, 3074, 2837, 2734, 2616, 1670, 1615, 1604, 1564, 1510, 1453, 1353, 1308, 1280, 1258, 1219, 1178, 1162, 1093, 1053, 1034, 1009, 960, 920, 906, 895, 827, 811, 798, 787, 769, 674 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 3.79 (s, 3H), 6.15 (s, 1H), 6.88 (d, *J* = 8.8 Hz, 2H), 7.25-7.28 (m, 1H), 7.32 (d, *J* = 8.4 Hz, 3H), 7.41 (t, *J* = 9.2 Hz, 4H), 7.55 (t, *J* = 8.4 Hz, 1H), 7.89 (d, *J* = 7.6 Hz, 1H), 10.03 (s, 1H, OH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 48.9, 55.5, 102.3, 114.7 (2C), 115.9, 116.7, 122.6, 123.6, 124.3, 128.2, 129.4 (2C), 131.5, 132.2 (3C), 132.7 (2C), 152.8, 159.8, 162.7, 162.9 ppm. HRMS (ESI): calcd for $C_{23}H_{17}BrO_4S$ $[M + K]^+$: 508.9644; Found 508.9628.

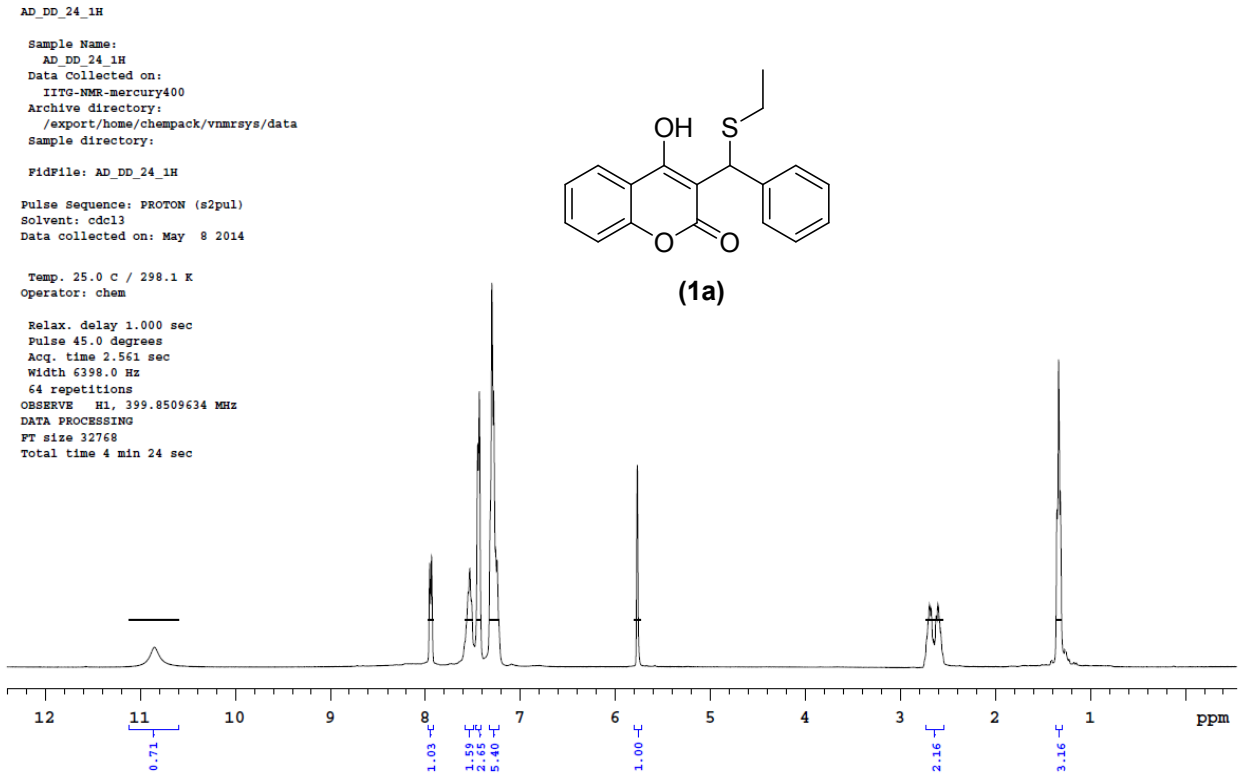
4-(((4-chlorophenyl)thio)(4-hydroxy-2-oxo-2H-chromen-3-yl)methyl)benzonitrile (28a): Yield: (328 mg, 78%); White solid; mp 110-112 °C. IR (KBr): 3157, 2229, 1678, 1621, 1607, 1566, 1498, 1476, 1451, 1395, 1345, 1279, 1221, 1198, 1167, 1149, 1108, 1093, 1076, 1023, 1011, 952, 922, 897, 860, 827, 820, 789, 770, 757, 743, 690 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 6.11 (s, 1H), 7.21-7.23 (m, 3H), 7.29 (t, *J* = 7.6 Hz, 2H), 7.37 (d, *J* = 8.8 Hz, 2H), 7.54 (t, *J* = 8.4 Hz, 1H), 7.60 (s, 3H), 7.90 (d, *J* = 8.0 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$ + DMSO): δ 47.1, 104.7, 109.3, 115.1, 115.4, 117.8, 122.9, 128.0 (5C), 130.7 (3C),

130.8 (2C), 131.4, 134.5, 145.0, 151.6, 160.6, 160.9 ppm. HRMS (ESI): calcd for $C_{23}H_{14}ClNO_3S$ $[M + K]^+$: 458.0015; Found 458.0015.

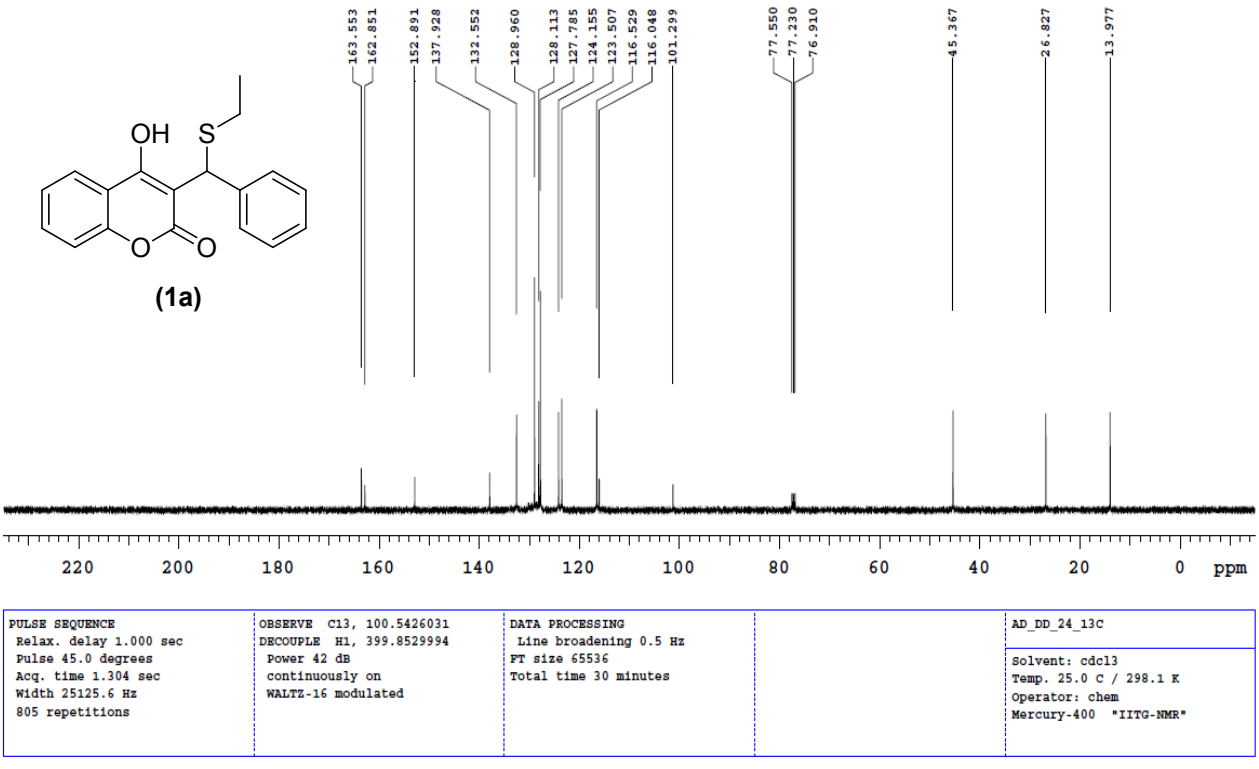
3-((benzylthio)(thiophen-2-yl)methyl)-4-hydroxy-2H-chromen-2-one (29a): Yield: (278 mg, 73%); Light green solid; mp 178-180 °C. IR (KBr): 3235, 3070, 2924, 2854, 1723, 1679, 1664, 1621, 1609, 1551, 1495, 1463, 1450, 1401, 1387, 1339, 1306, 1249, 1212, 1193, 1164, 1110, 1068, 1028, 892, 863, 804, 763, 747, 698 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 3.86 (s, 2H), 5.90 (s, 1H), 6.88 (t, *J* = 4.0 Hz, 1H), 6.98 (d, *J* = 2.4 Hz, 1H), 7.12 (d, *J* = 5.6 Hz, 1H), 7.20 (d, *J* = 4.8 Hz, 1H), 7.24 (t, *J* = 6.0 Hz, 3H), 7.31 (t, *J* = 7.6 Hz, 3H), 7.57 (t, *J* = 7.6 Hz, 1H), 7.87 (d, *J* = 8.0 Hz, 1H), 10.03 (s, 1H, OH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 37.5, 40.8, 102.2, 115.8, 116.4, 123.5, 124.1, 125.7, 126.2, 126.9, 127.6, 128.7 (2C), 128.8 (2C), 132.6, 135.8, 140.6, 152.8, 162.2, 162.9 ppm. HRMS (ESI): calcd for $C_{21}H_{16}O_3S_2$ $[M + K]^+$: 419.0172; Found 419.0172.

3-((ethylthio)(pyridin-2-yl)methyl)-4-hydroxy-2H-chromen-2-one (30a): Yield: (236 mg, 75%); White solid; mp 97-99 °C. IR (KBr): 3446, 3067, 2980, 2970, 2930, 2919, 2872, 2853, 1684, 1630, 1613, 1596, 1578, 1488, 1453, 1434, 1382, 1368, 1329, 1298, 1278, 1263, 1199, 1186, 1165, 1108, 1052, 1034, 1012, 944, 901, 864, 805, 779, 769, 760, 705, 675 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 1.23 (t, *J* = 7.6 Hz, 3H), 2.52-2.57 (m, 2H), 5.87 (s, 1H), 7.26 (d, *J* = 5.6 Hz, 2H), 7.39 (s, 1H), 7.50 (t, *J* = 8.0 Hz, 1H), 7.57 (d, *J* = 7.2 Hz, 1H), 7.89 (t, *J* = 7.6 Hz, 1H), 8.01 (d, *J* = 7.6 Hz, 1H), 8.53 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.6, 26.9, 46.3, 101.9, 116.4, 118.0, 123.7, 124.0, 124.4, 124.5, 132.4, 140.2, 146.2, 152.9, 159.5, 164.1, 165.7 ppm. HRMS (ESI): calcd for $C_{17}H_{15}NO_3S$ $[M + H]^+$: 314.0845; Found 314.0845.

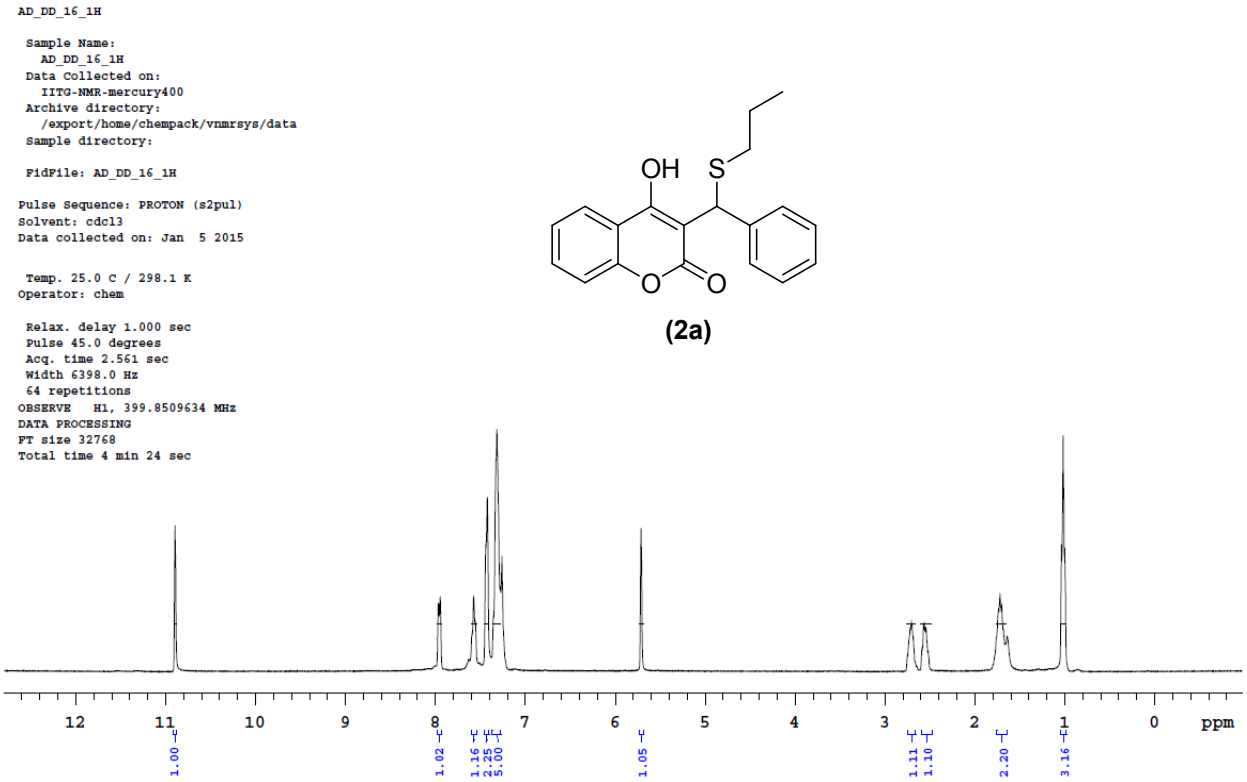
***[1]H NMR (400 MHz, $CDCl_3$)**: 3-((ethylthio)(phenyl)methyl)-4-hydroxy-2H-chromen-2-one* (**1a**)



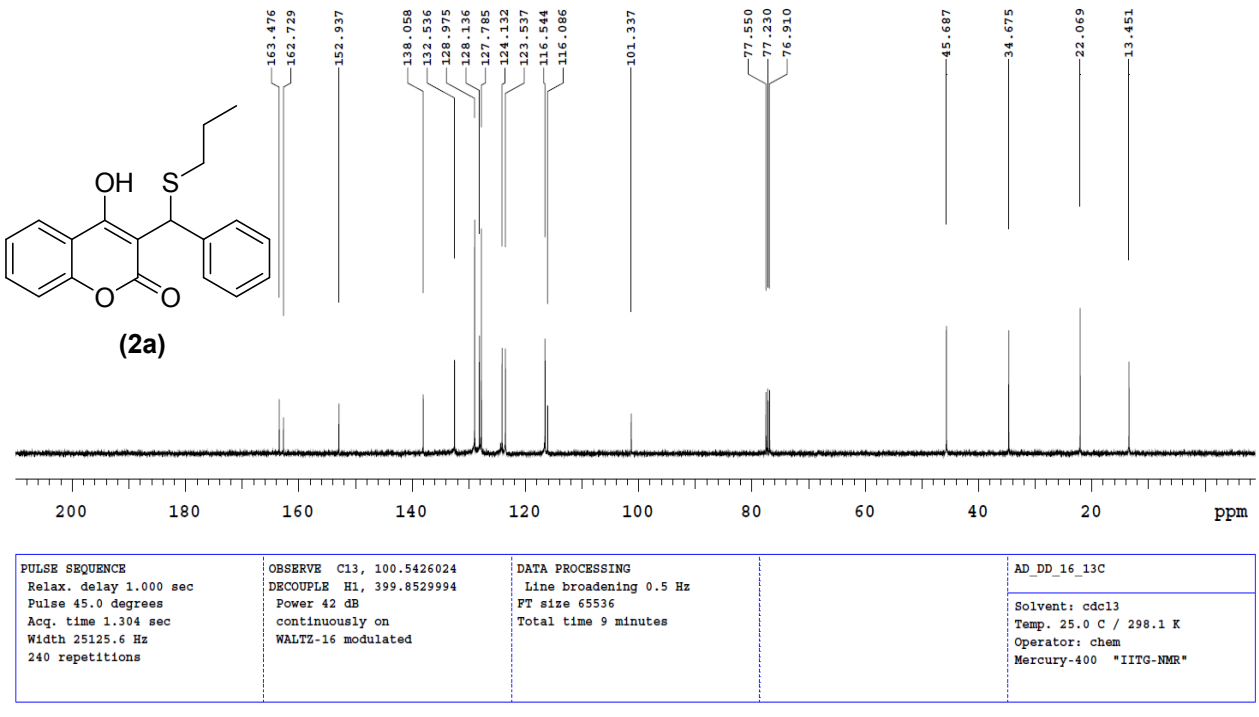
***[13]C NMR (100 MHz, $CDCl_3$)**: 3-((ethylthio)(phenyl)methyl)-4-hydroxy-2H-chromen-2-one* (**1a**)



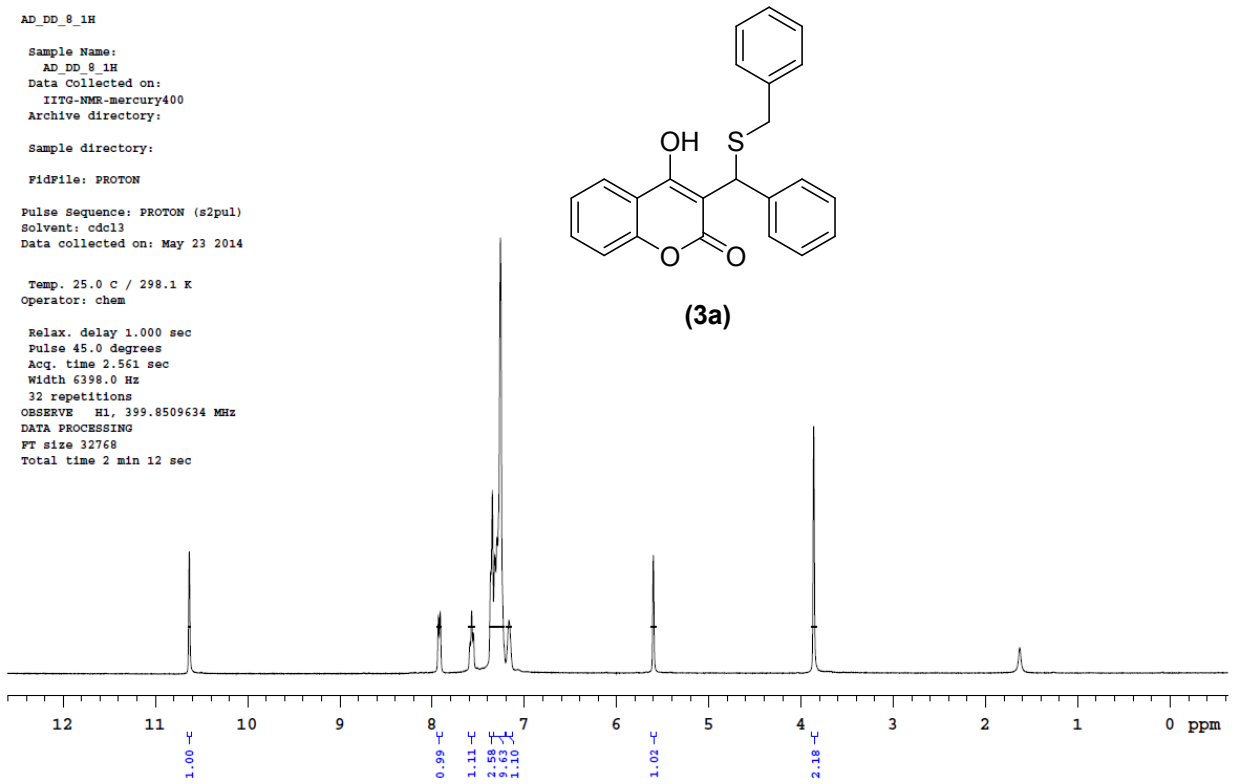
[1]H NMR (400 MHz, CDCl3): *4-hydroxy-3-(phenyl(propylthio)methyl)-2H-chromen-2-one* (**2a**)



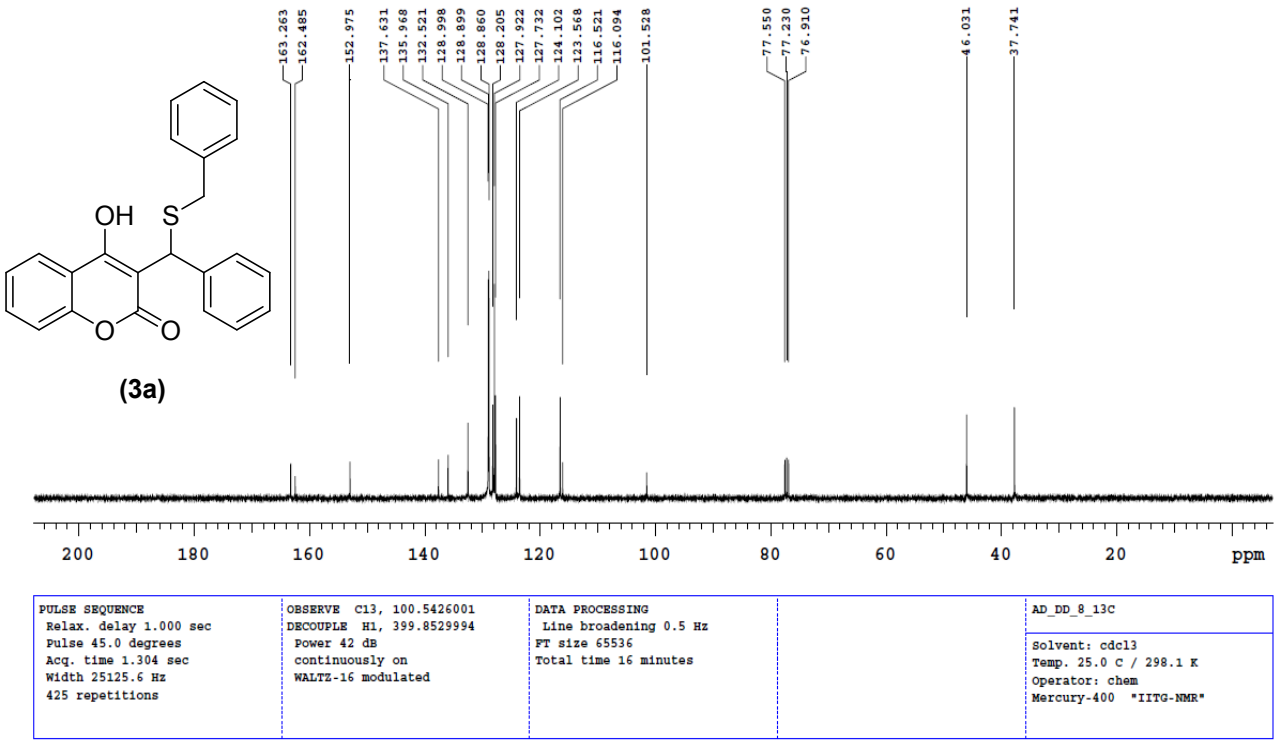
[13]C NMR (100 MHz, CDCl3): *4-hydroxy-3-(((2-hydroxyethyl)thio)(phenyl)methyl)-2H-chromen-2-one* (**2a**)



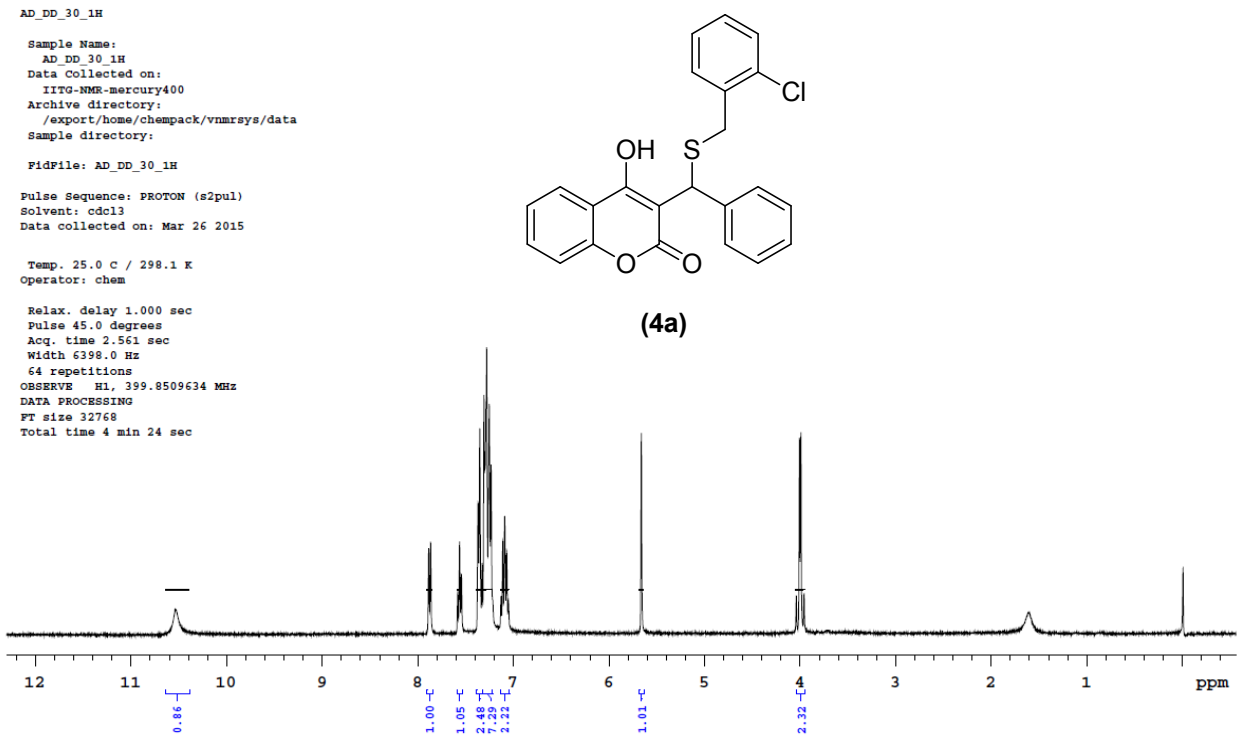
[1]H NMR (400 MHz, CDCl3): *3-((benzylthio)(phenyl)methyl)-4-hydroxy-2H-chromen-2-one* (**3a**)



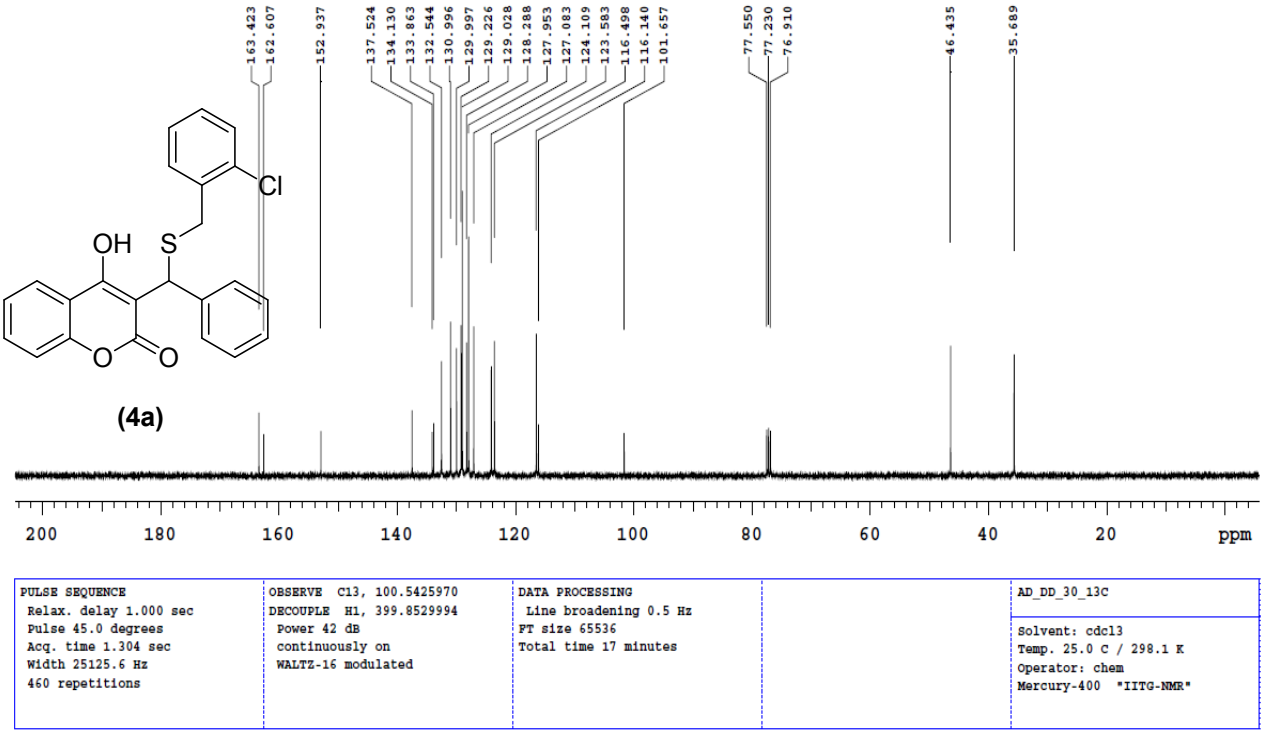
[13]C NMR (100 MHz, CDCl3): *3-((benzylthio)(phenyl)methyl)-4-hydroxy-2H-chromen-2-one* (**3a**)



^{1}H NMR (400 MHz, $CDCl_3$): *3-(((2-chlorobenzyl)thio)(phenyl)methyl)-4-hydroxy-2H-chromen-2-one* (**4a**)

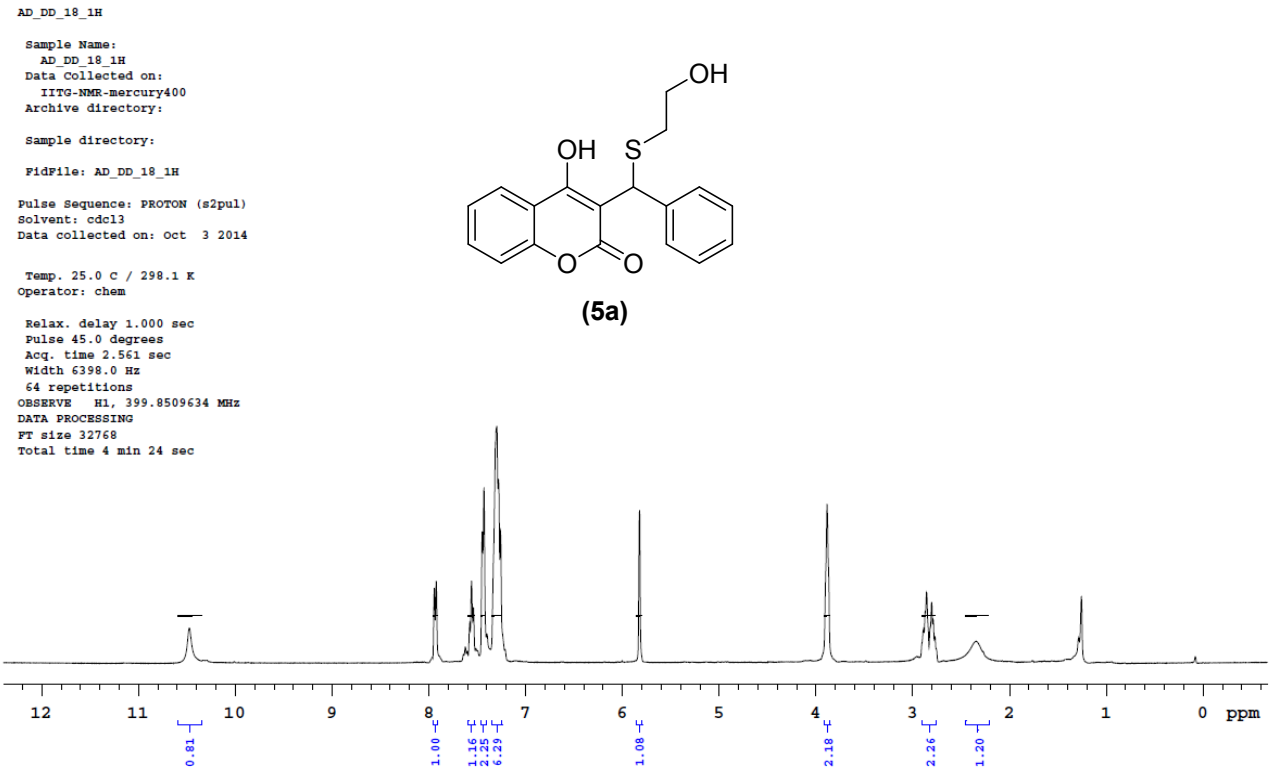


^{13}C NMR (100 MHz, $CDCl_3$): *3-(((2-chlorobenzyl)thio)(phenyl)methyl)-4-hydroxy-2H-chromen-2-one* (**4a**)

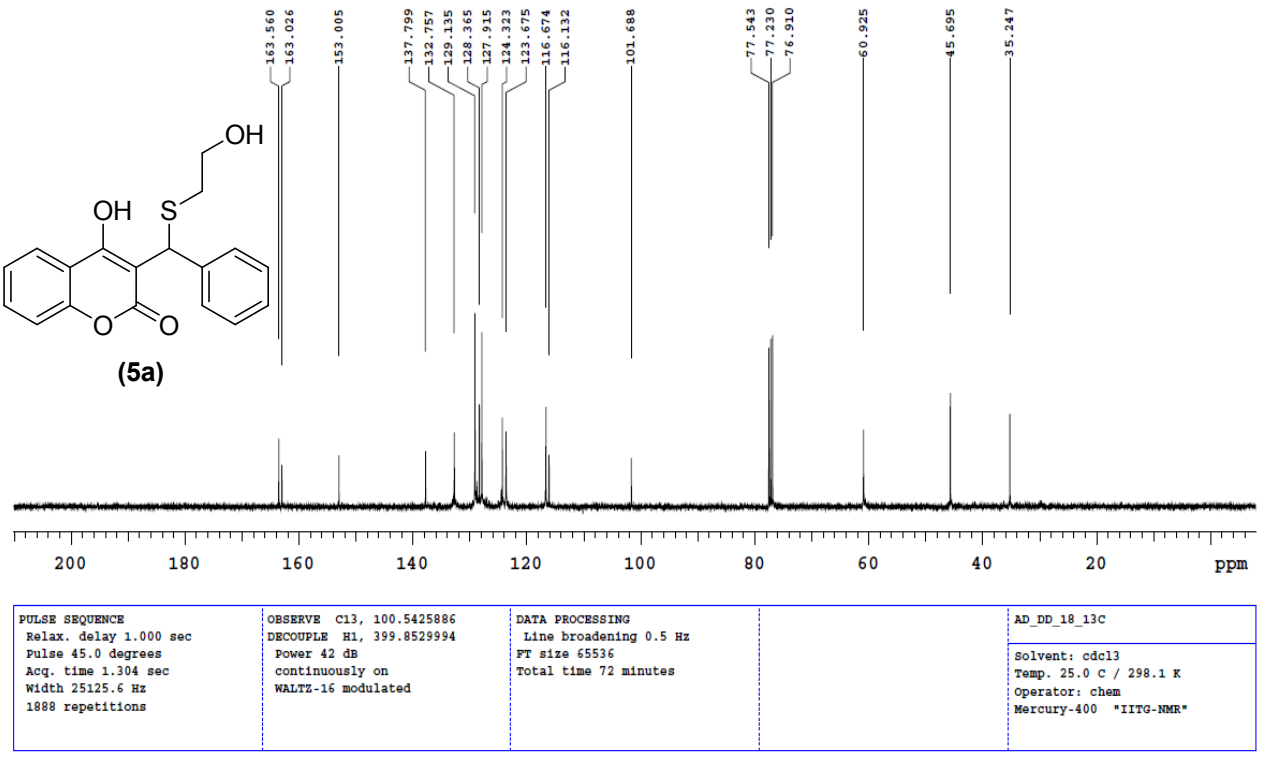


PULSE SEQUENCE Relax. delay 1.000 sec Pulse 45.0 degrees Acq. time 1.304 sec Width 25125.6 Hz 460 repetitions	OBSERVE C13, 100.5425970 DECOUPLE H1, 399.8529994 Power 42 dB continuously on WALTZ-16 modulated	DATA PROCESSING Line broadening 0.5 Hz FT size 65536 Total time 17 minutes		AD_DD_30_13C Solvent: cdcl3 Temp. 25.0 C / 298.1 K Operator: chem Mercury-400 "IITG-NMR"

[1]H NMR (400 MHz, CDCl3): *4-hydroxy-3-(phenyl(propylthio)methyl)-2H-chromen-2-one* (**5a**)



[13]C NMR (100 MHz, CDCl3): *4-hydroxy-3-(phenyl(propylthio)methyl)-2H-chromen-2-one* (**5a**)



[1]H NMR (400 MHz, CDCl3): *4-hydroxy-3-(phenyl(phenylthio)methyl)-2H-chromen-2-one* (**6a**)

```
AD_DD_9_1H

 Sample Name:
   AD_DD_9_1H
 Data Collected on:
   IITG-NMR-mercury400
 Archive directory:

 Sample directory:

 FidFile: PROTON

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: May 28 2014

 Temp. 25.0 C / 298.1 K
Operator: chem

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 Pulse 45.0 degrees
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 Width 6398.0 Hz
 64 repetitions
OBSERVE   H1, 399.8509634 MHz
DATA PROCESSING
FT size 32768
Total time 4 min 24 sec
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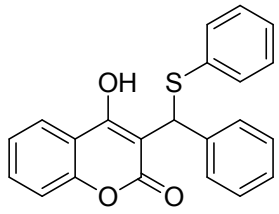
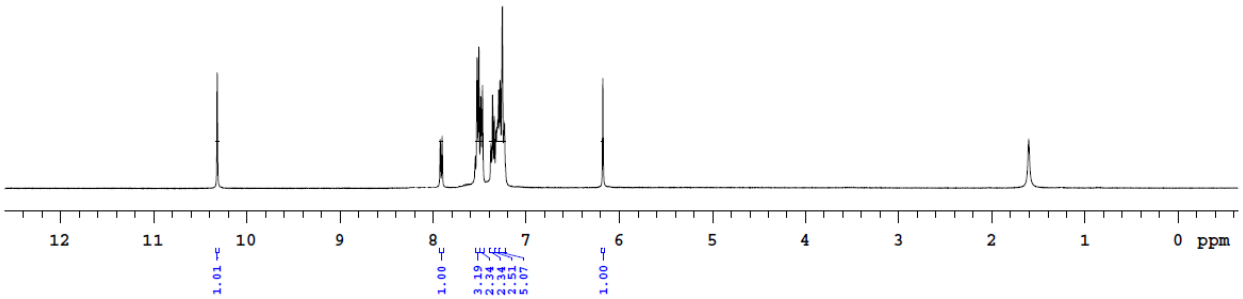
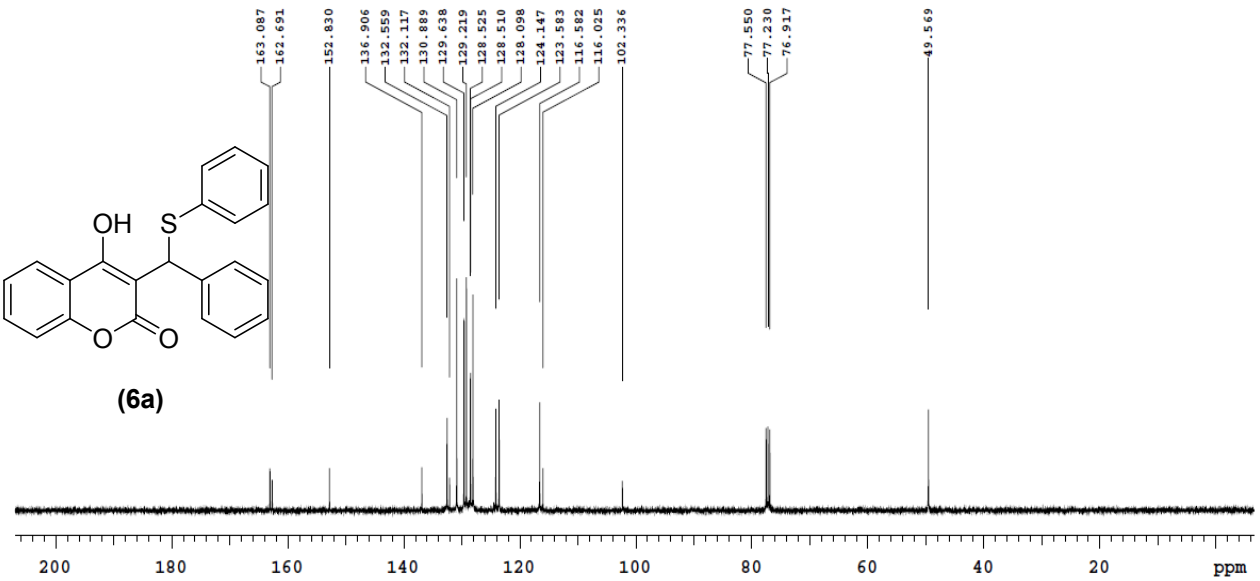


(6a)



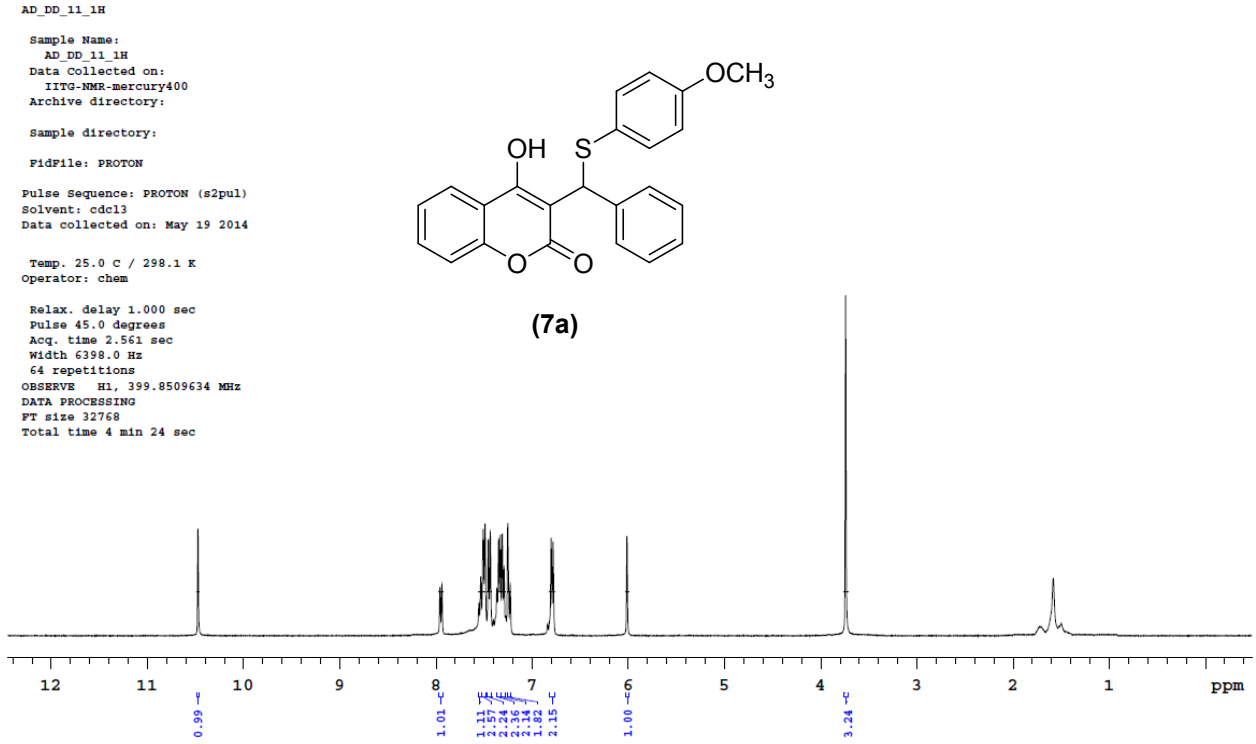
[13]C NMR (100 MHz, CDCl3): *4-hydroxy-3-(phenyl(phenylthio)methyl)-2H-chromen-2-one* (**6a**)



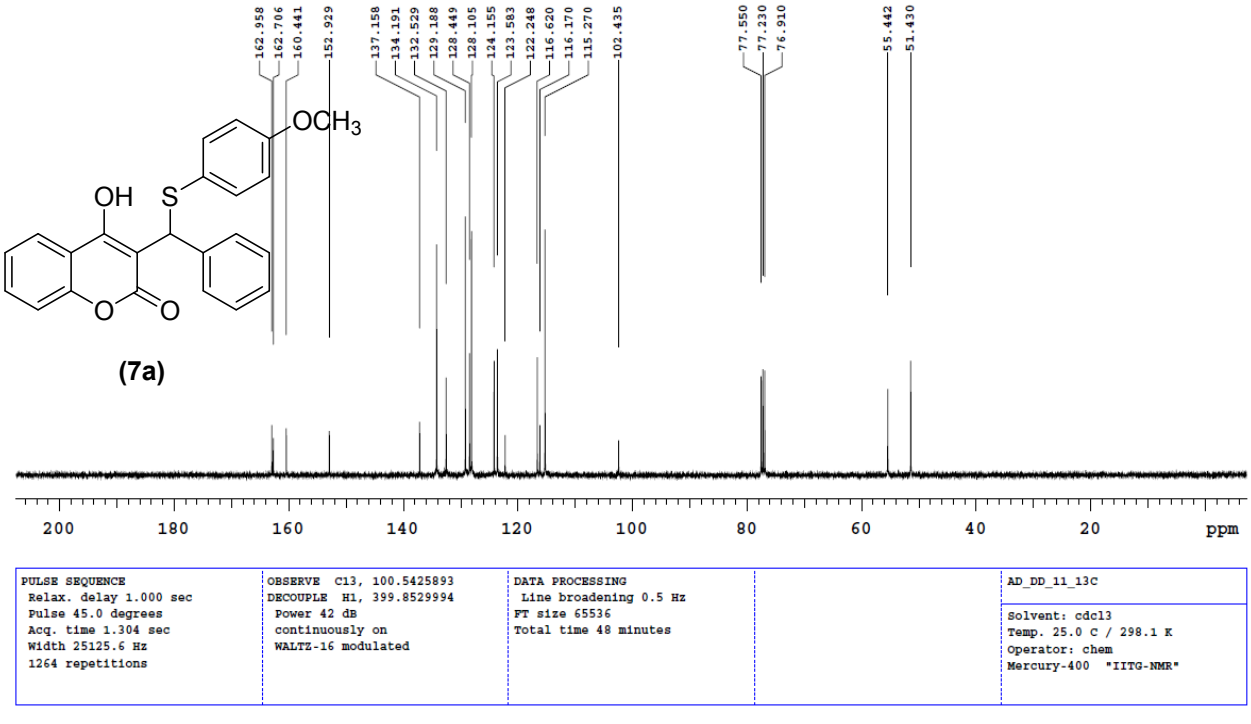
(6a)

PULSE SEQUENCE	OBSERVE C13, 100.5425955	DATA PROCESSING		AD_DD_9_13C
Relax. delay 1.000 sec Pulse 45.0 degrees Acq. time 1.304 sec Width 25125.6 Hz 452 repetitions	DECOUPLE H1, 399.8529994 Power 42 dB continuously on WALTZ-16 modulated	Line broadening 0.5 Hz FT size 65536 Total time 17 minutes		Solvent: cdcl3 Temp. 25.0 C / 298.1 K Operator: chem Mercury-400 "IITG-NMR"

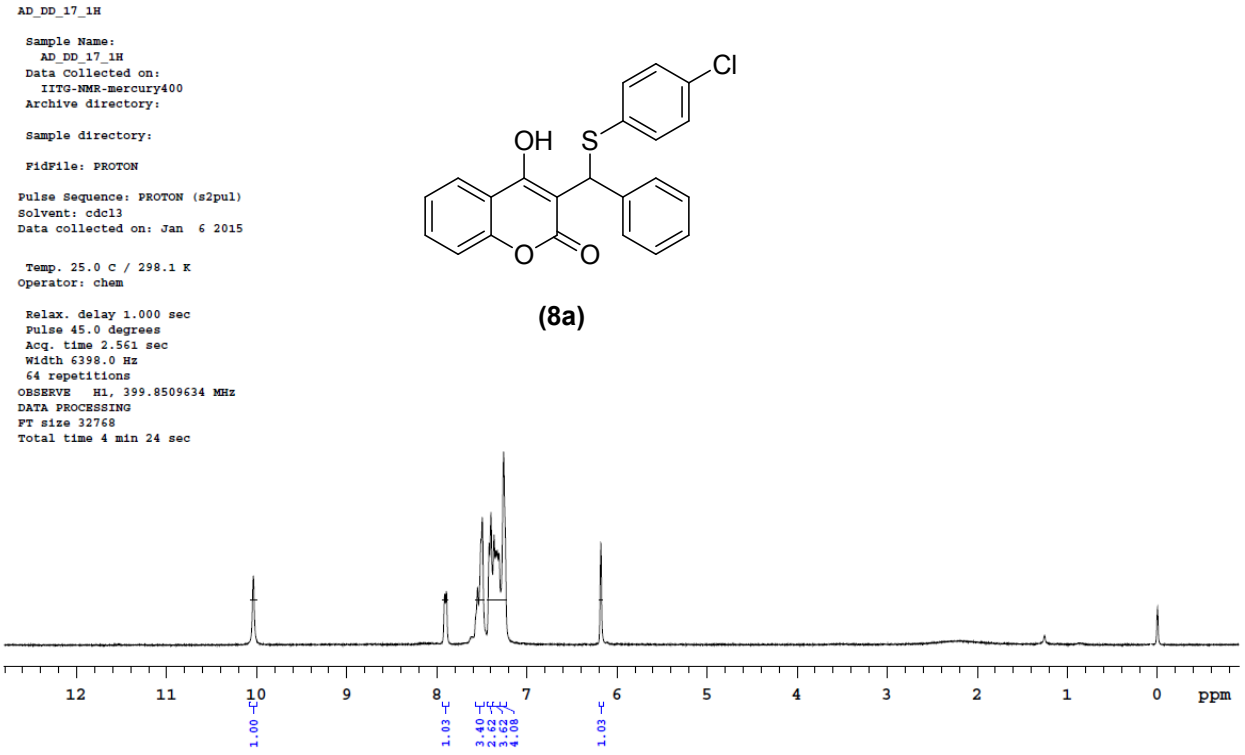
*[1]**H NMR (400 MHz, CDCl$_3$)**: 4-hydroxy-3-(((4-methoxyphenyl)thio)(phenyl)methyl)-2H-chromen-2-one* (**7a**)



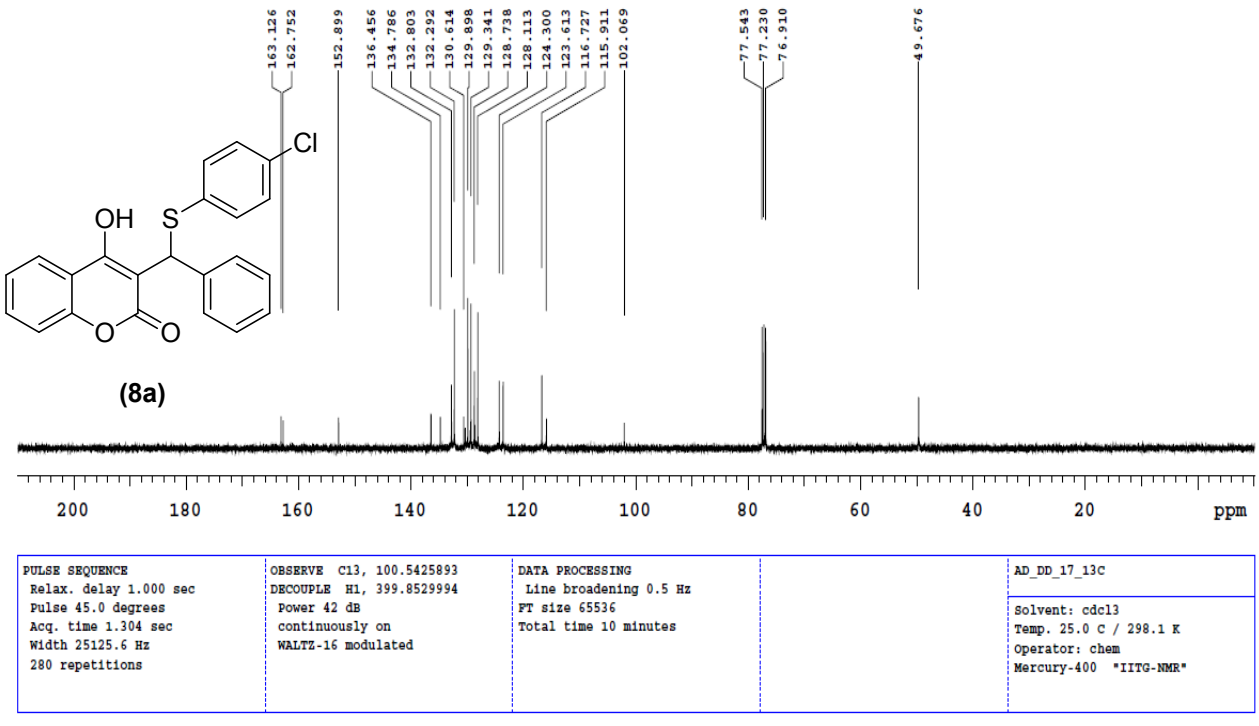
*[13]**C NMR (100 MHz, CDCl$_3$)**: 4-hydroxy-3-(((4-methoxyphenyl)thio)(phenyl)methyl)-2H-chromen-2-one* (**7a**)



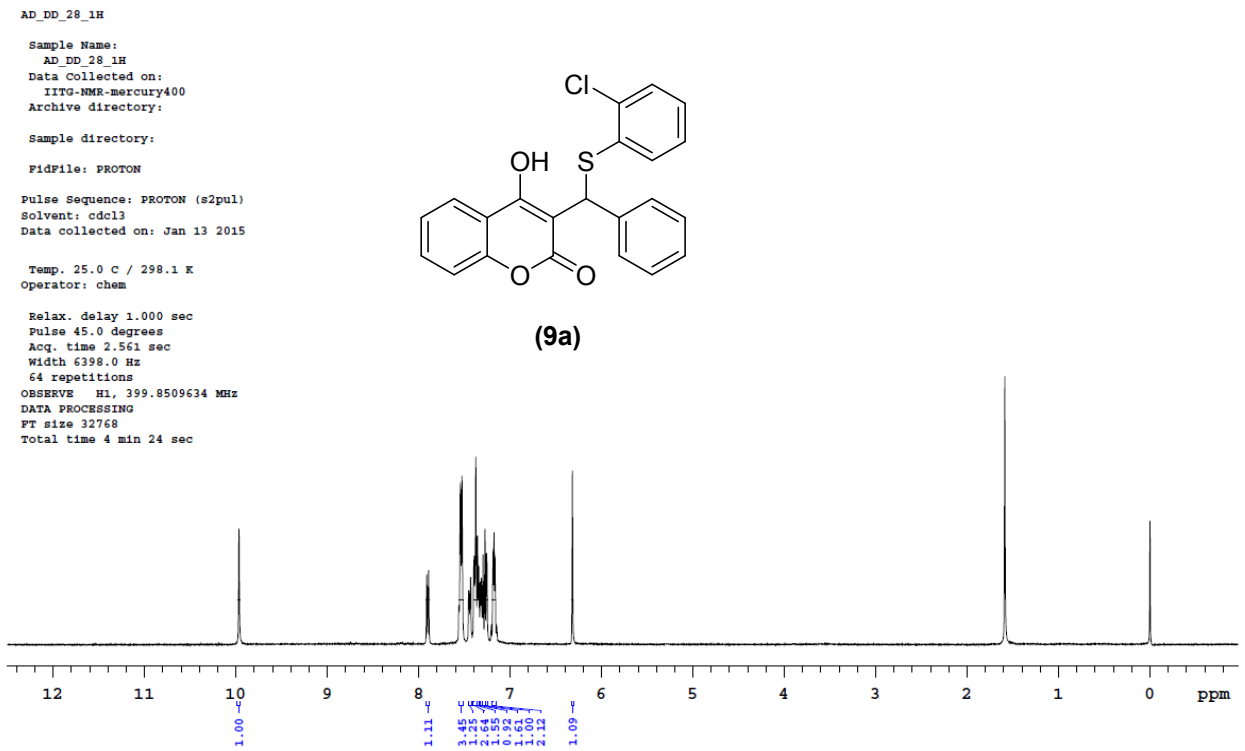
^{1}H NMR (400 MHz, $CDCl_3$): *3-(((4-chlorophenyl)thio)(phenyl)methyl)-4-hydroxy-2H-chromen-2-one* (**8a**)



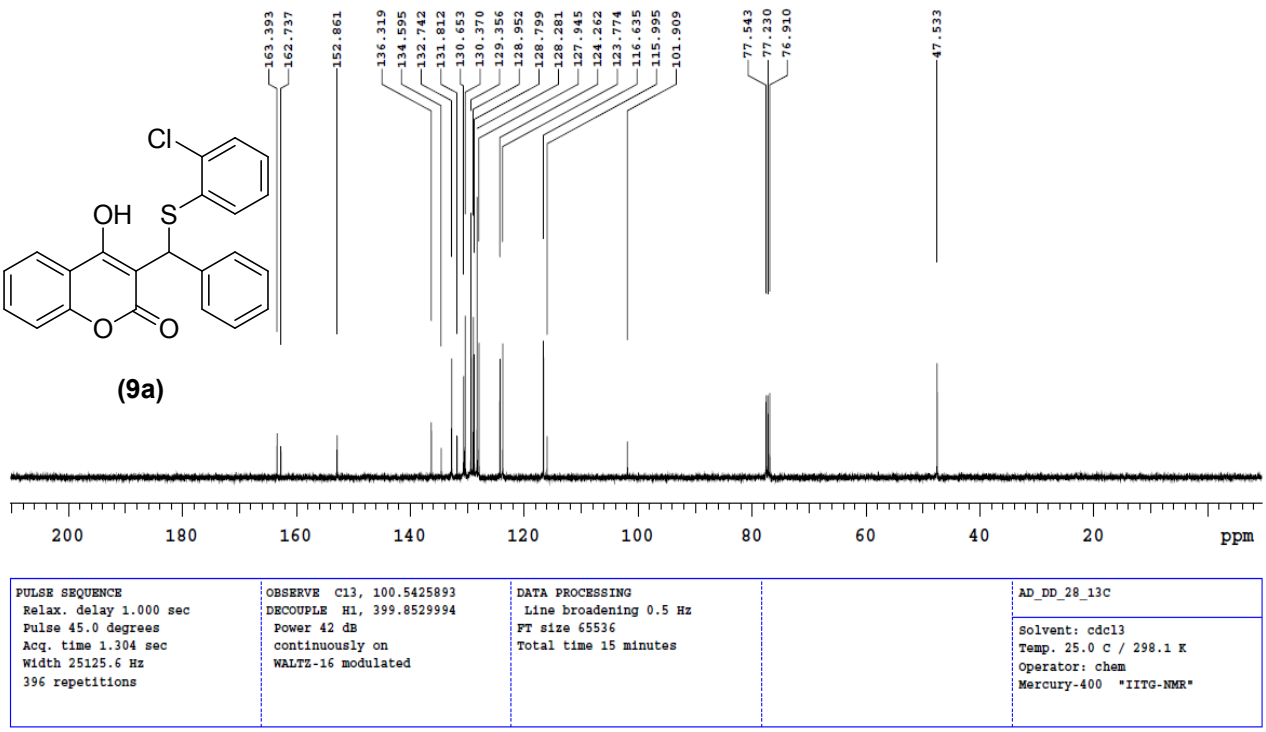
^{13}C NMR (100 MHz, $CDCl_3$): *3-(((4-chlorophenyl)thio)(phenyl)methyl)-4-hydroxy-2H-chromen-2-one* (**8a**)



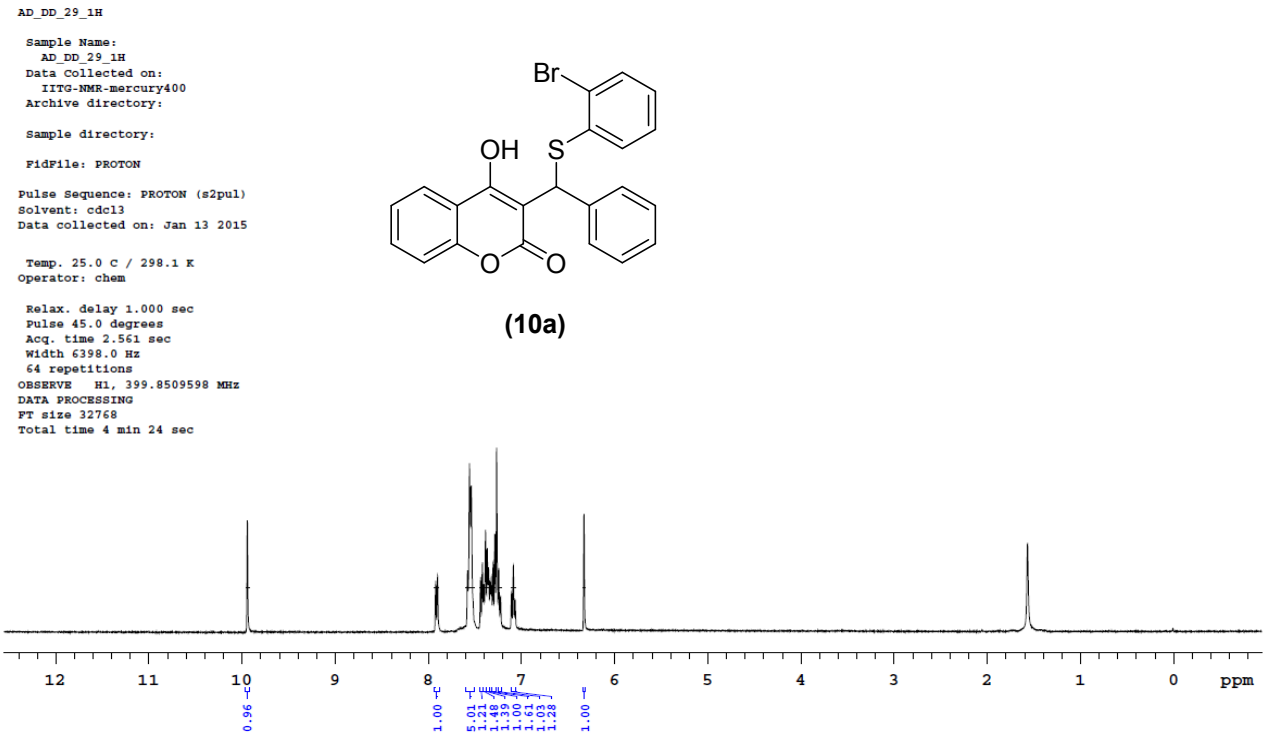
^{1}H NMR (400 MHz, $CDCl_3$): *3-(((2-chlorophenyl)thio)(phenyl)methyl)-4-hydroxy-2H-chromen-2-one* (**9a**)



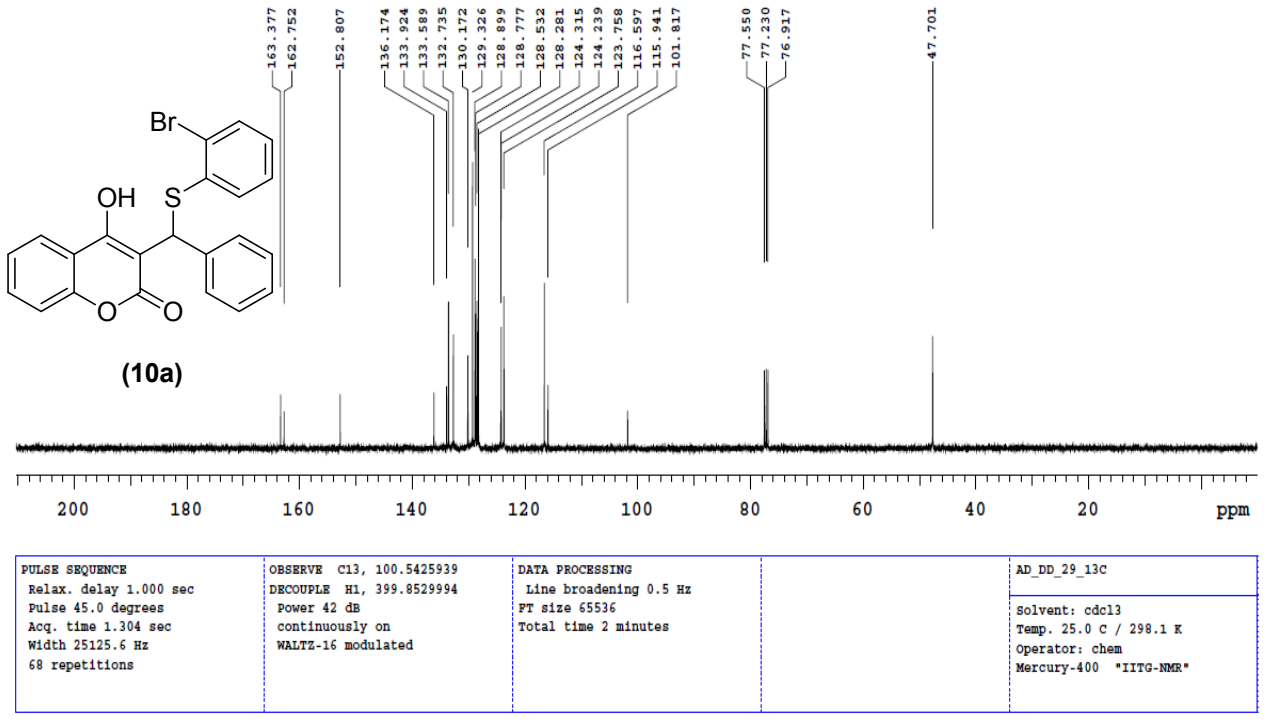
^{13}C NMR (100 MHz, $CDCl_3$): *3-(((2-chlorophenyl)thio)(phenyl)methyl)-4-hydroxy-2H-chromen-2-one* (**9a**)



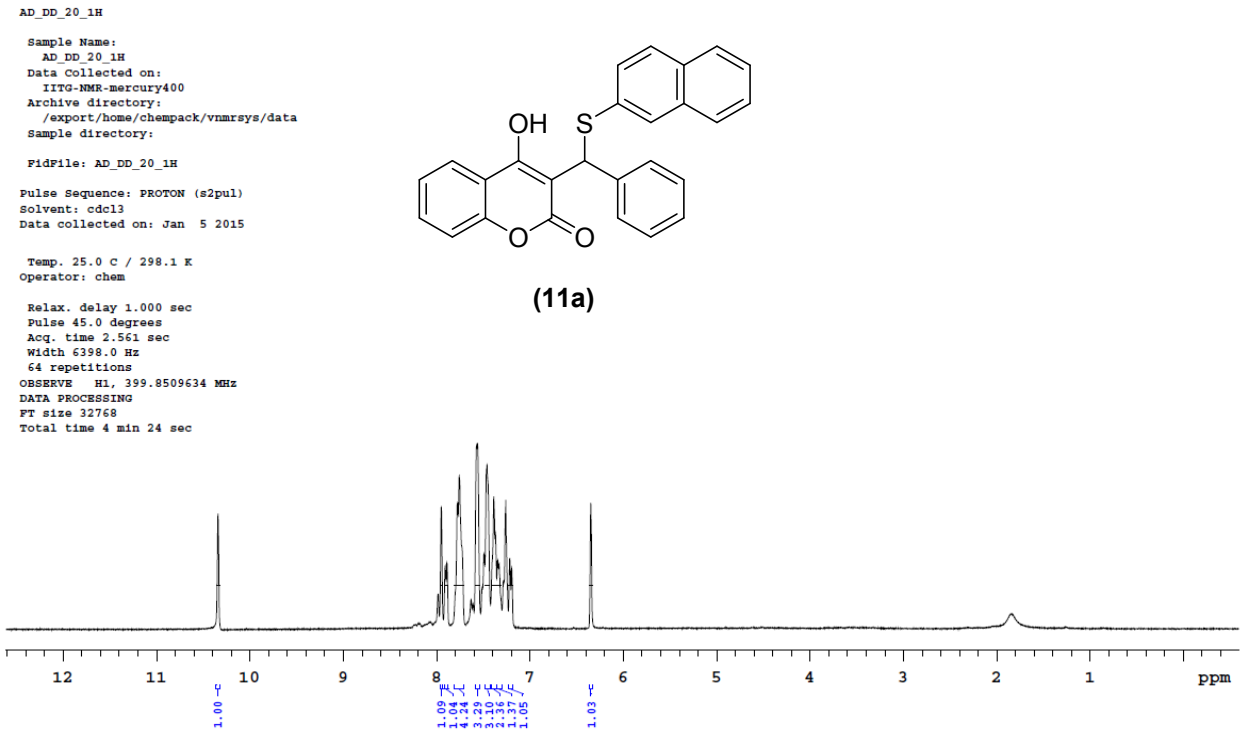
^{1}H NMR (400 MHz, $CDCl_3$): *3-(((2-bromophenyl)thio)(phenyl)methyl)-4-hydroxy-2H-chromen-2-one* (**10a**)



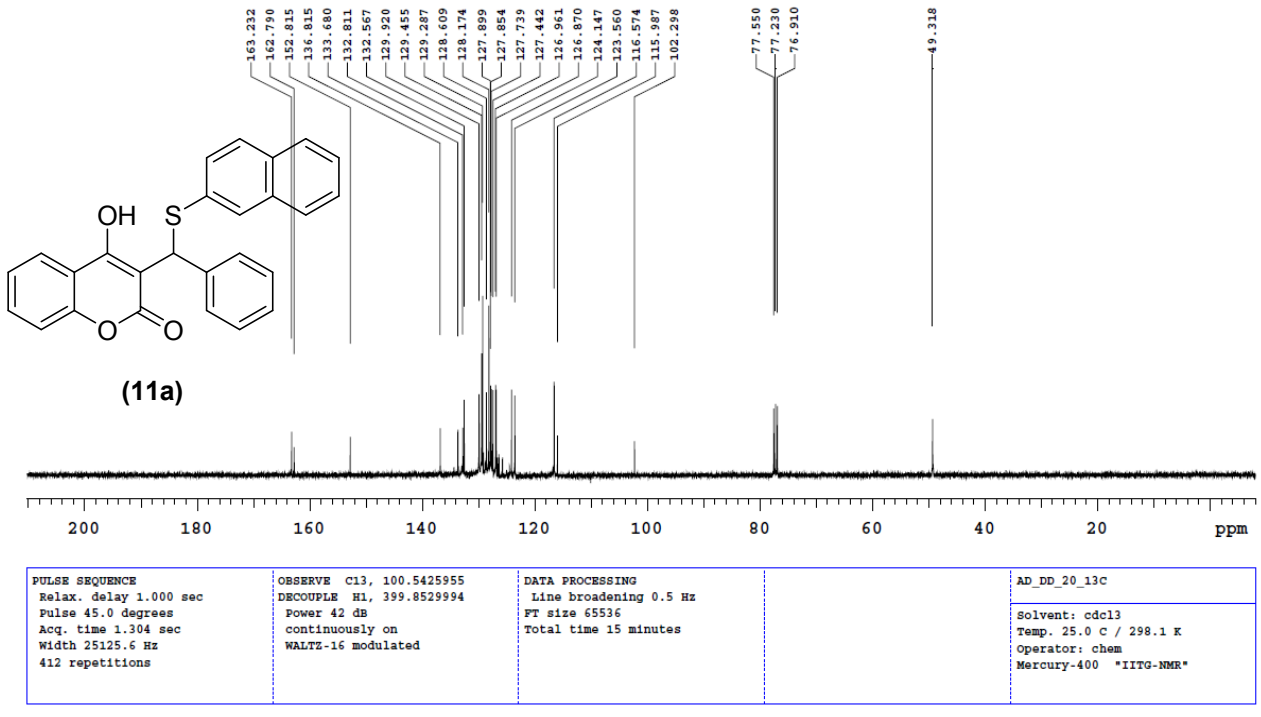
^{13}C NMR (100 MHz, $CDCl_3$): *3-(((2-bromophenyl)thio)(phenyl)methyl)-4-hydroxy-2H-chromen-2-one* (**10a**)



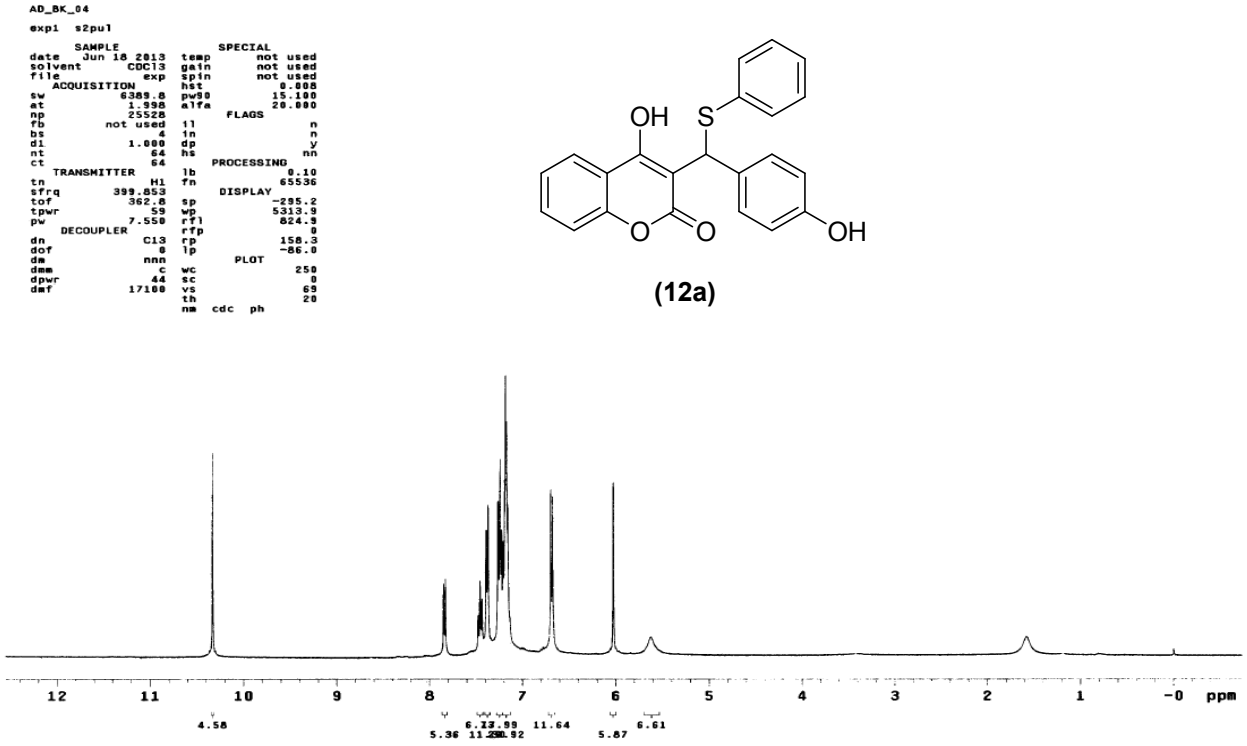
^{1}H NMR (400 MHz, $CDCl_3$): 4-hydroxy-3-((naphthalen-2-ylthio)(phenyl)methyl)-2H-chromen-2-one (**11a**)



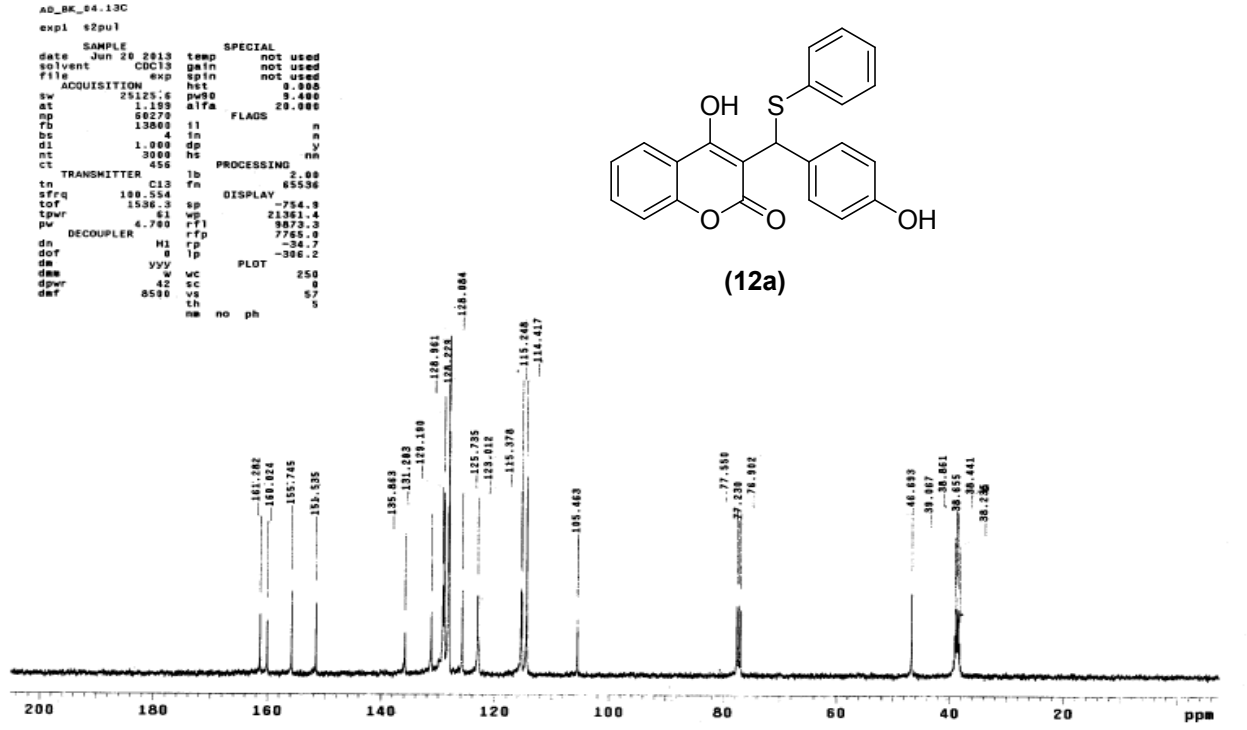
^{13}C NMR (100 MHz, $CDCl_3$): 4-hydroxy-3-((naphthalen-2-ylthio)(phenyl)methyl)-2H-chromen-2-one (**11a**)



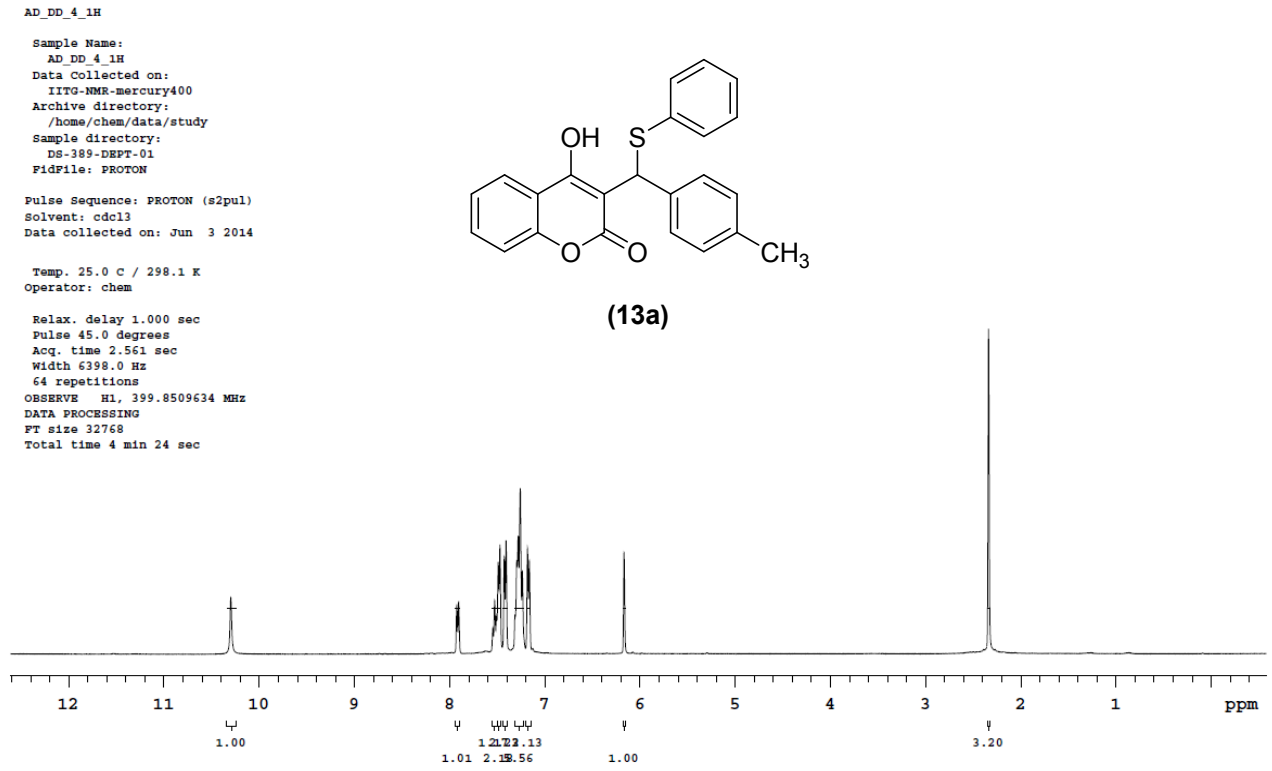
[1]H NMR (400 MHz, $CDCl_3$): *4-hydroxy-3-((4-hydroxyphenyl)(phenylthio)methyl)-2H-chromen-2-one* (**12a**)



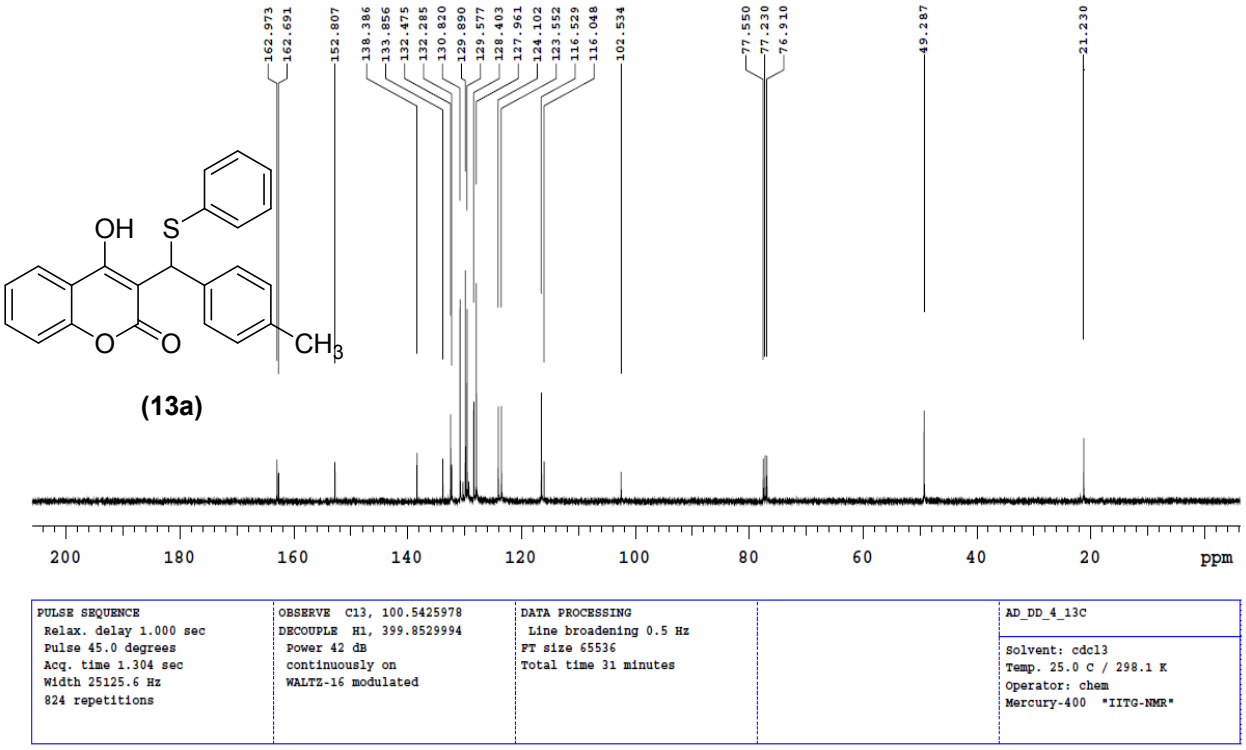
[13]C NMR (100 MHz, $CDCl_3$ + DMSO): *4-hydroxy-3-((4-hydroxyphenyl)(phenylthio)methyl)-2H-chromen-2-one* (**12a**)



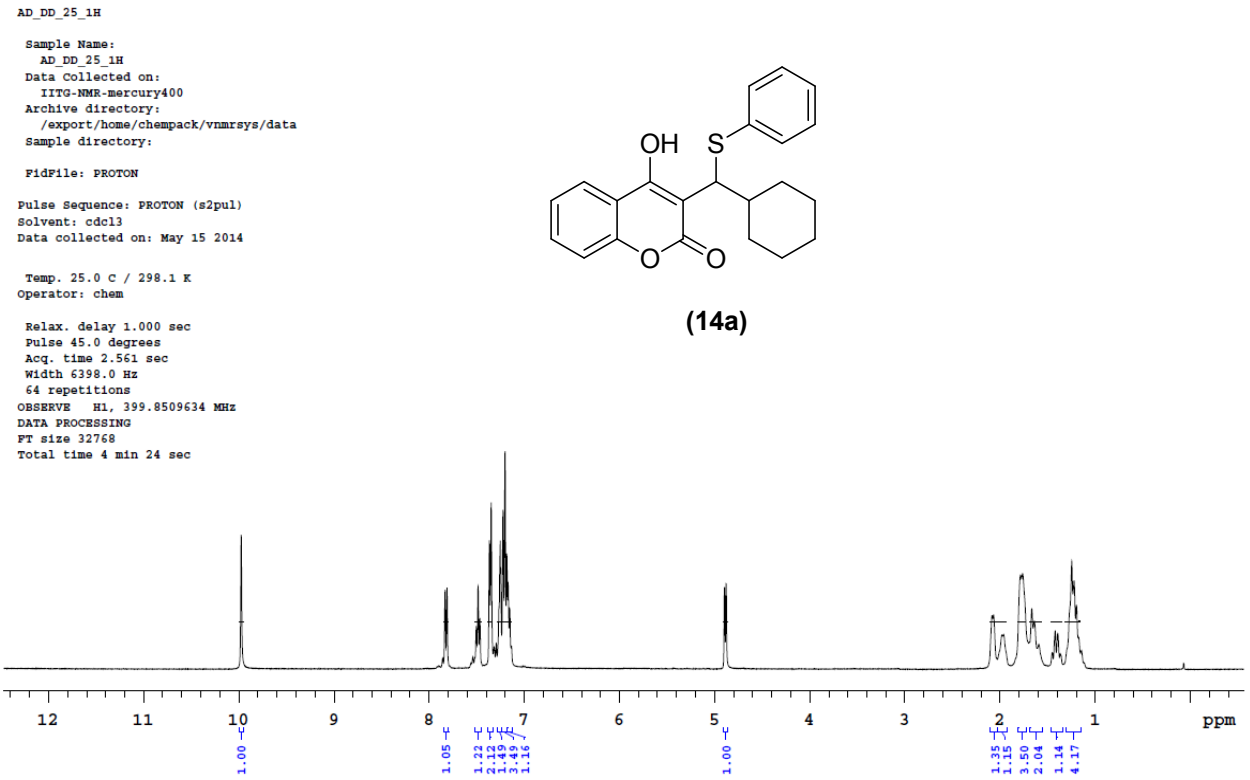
^{1}H NMR (400 MHz, $CDCl_3$): *4-hydroxy-3-((phenylthio)(p-tolyl)methyl)-2H-chromen-2-one* (**13a**)



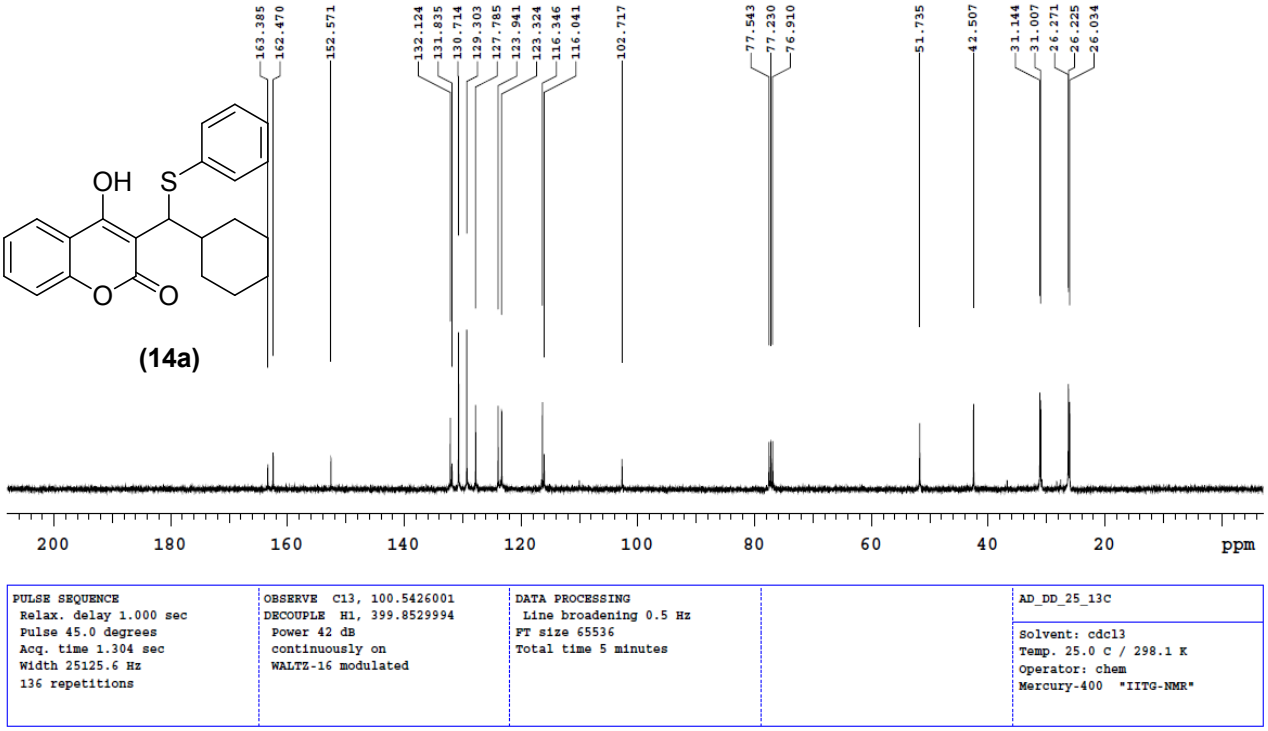
^{13}C NMR (100 MHz, $CDCl_3$): *4-hydroxy-3-((phenylthio)(p-tolyl)methyl)-2H-chromen-2-one* (**13a**)



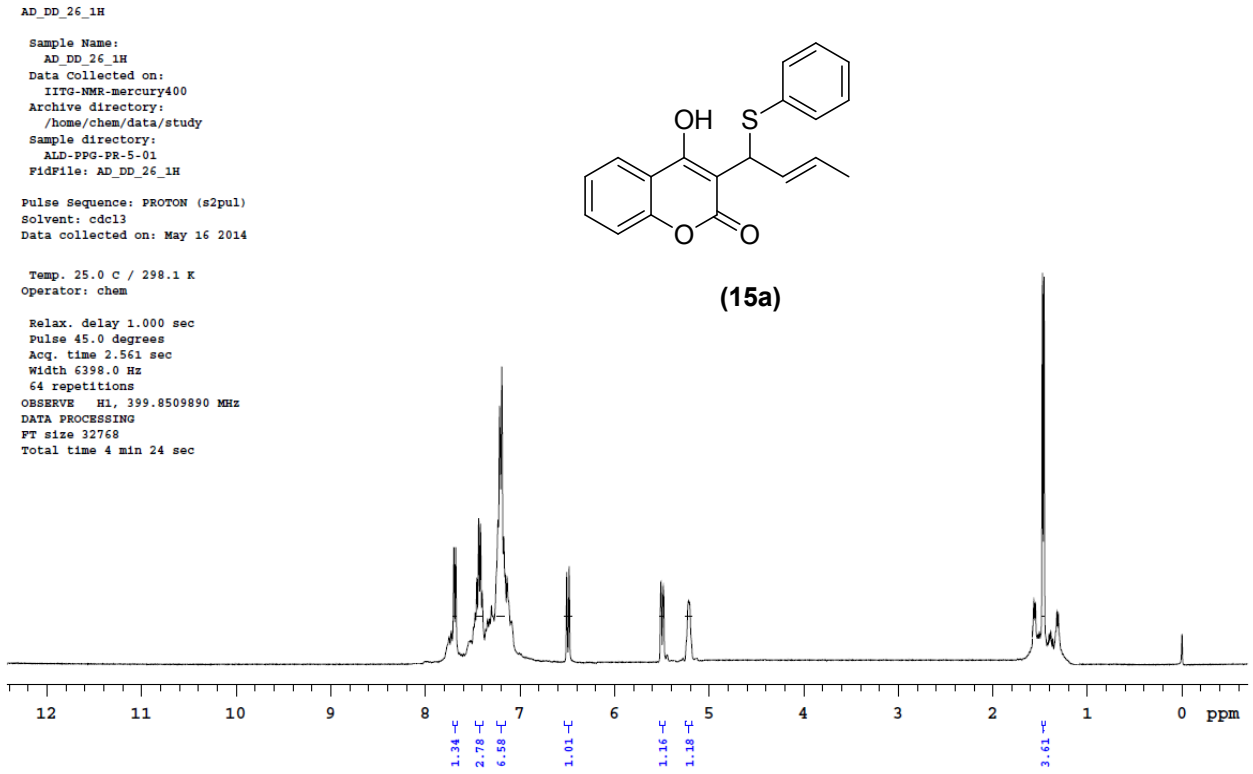
[1]H NMR (400 MHz, CDCl3): *3-(cyclohexyl(phenylthio)methyl)-4-hydroxy-2H-chromen-2-one* (**14a**)



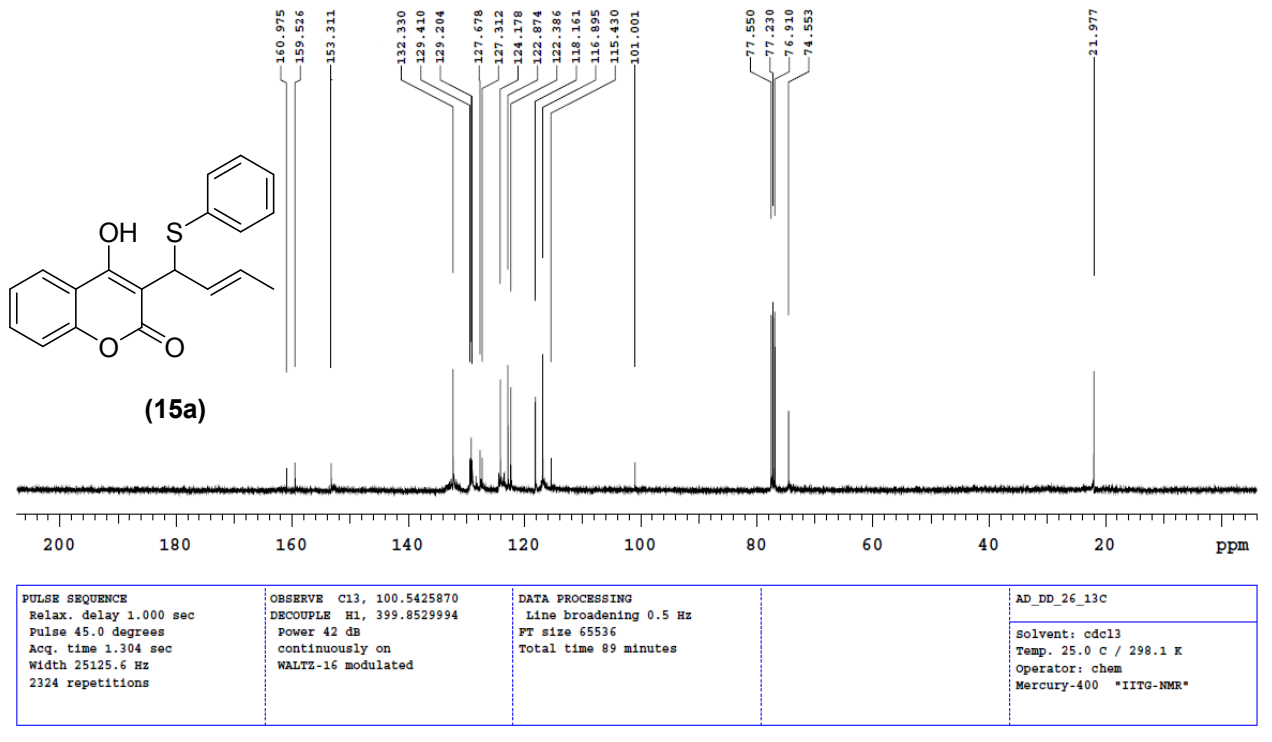
[13]C NMR (100 MHz, CDCl3): *3-(cyclohexyl(phenylthio)methyl)-4-hydroxy-2H-chromen-2-one* (**14a**)



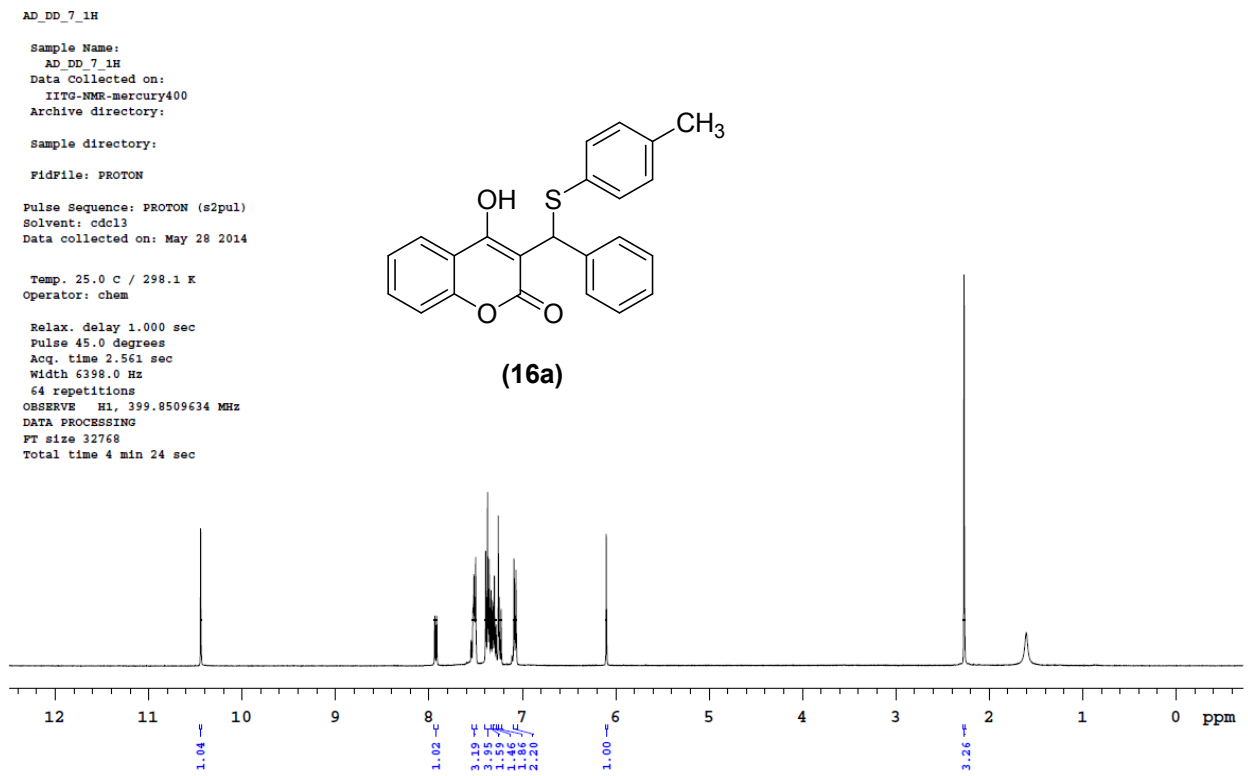
^{1}H NMR (400 MHz, $CDCl_3$): *(E)-4-hydroxy-3-(1-(phenylthio)but-2-en-1-yl)-2H-chromen-2-one* (**15a**)



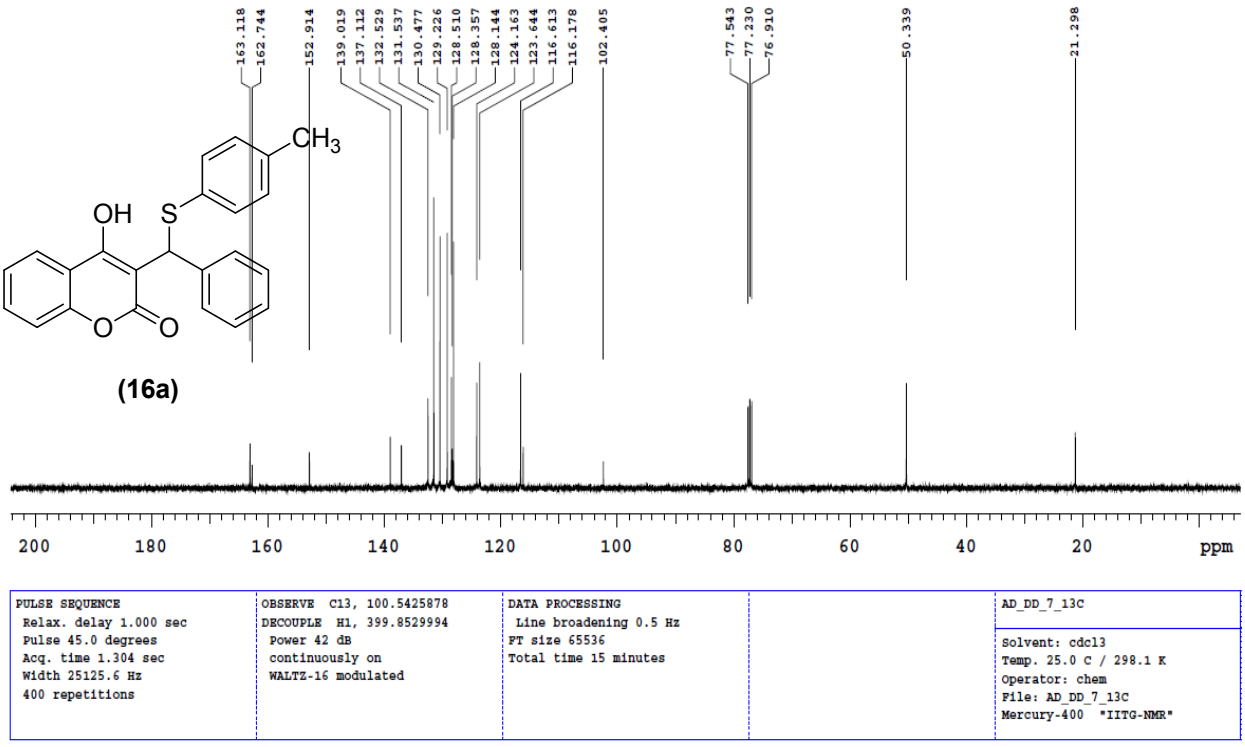
^{13}C NMR (100 MHz, $CDCl_3$): *(E)-4-hydroxy-3-(1-(phenylthio)but-2-en-1-yl)-2H-chromen-2-one* (**15a**)



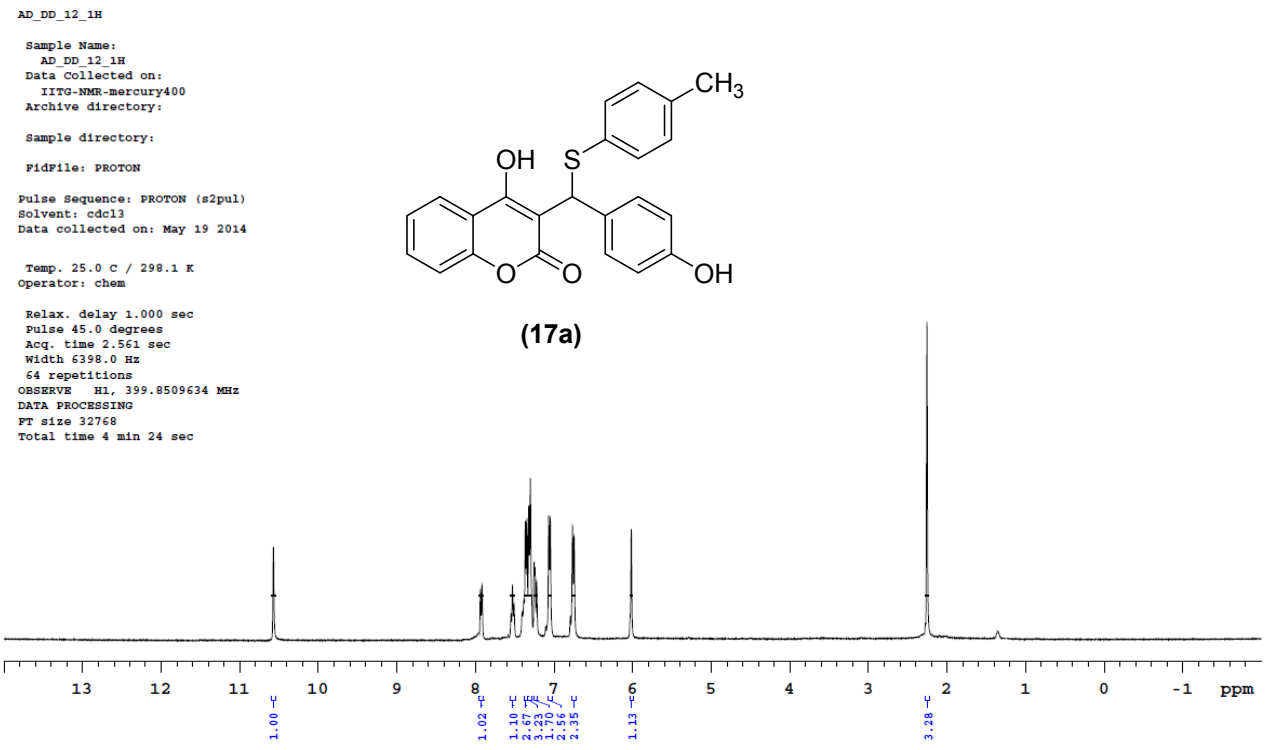
[1]H NMR (400 MHz, CDCl3): *4-hydroxy-3-(phenyl(p-tolylthio)methyl)-2H-chromen-2-one* (**16a**)



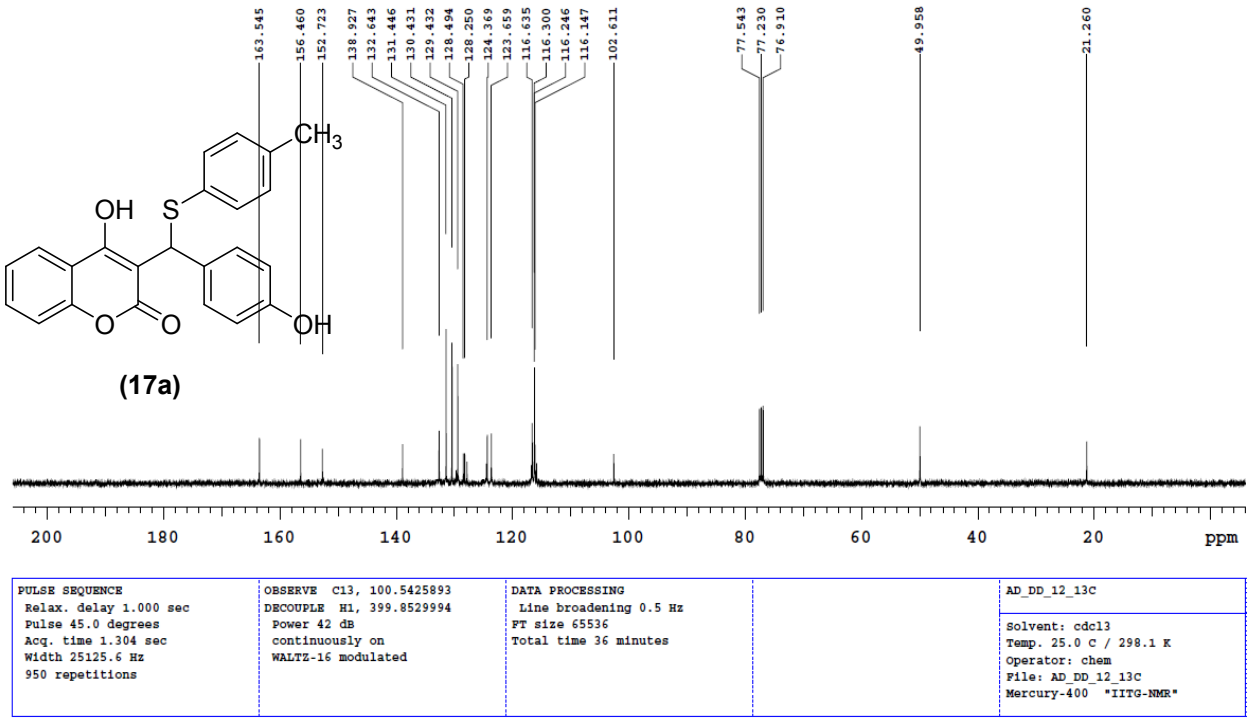
[13]C NMR (100 MHz, CDCl3): *4-hydroxy-3-(phenyl(p-tolylthio)methyl)-2H-chromen-2-one* (**16a**)



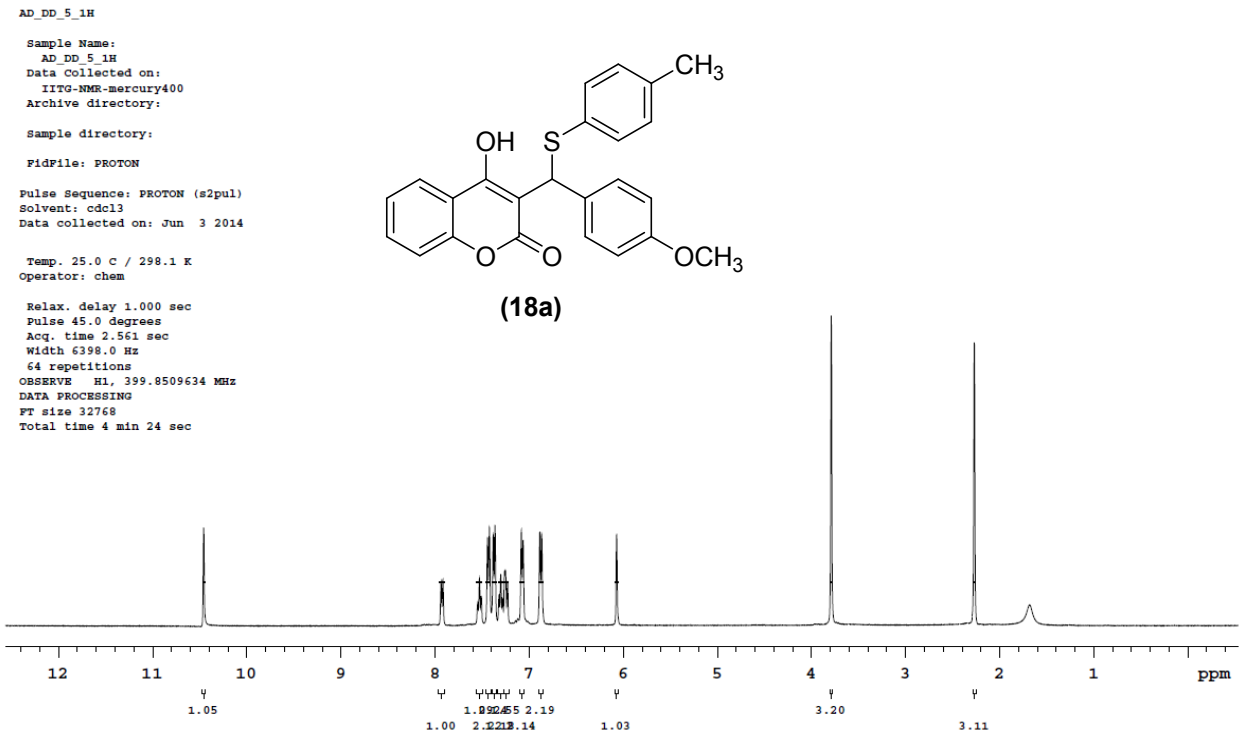
[1]H NMR (400 MHz, CDCl3): *4-hydroxy-3-((4-hydroxyphenyl)(p-tolylthio)methyl)-2H-chromen-2-one* (**17a**)



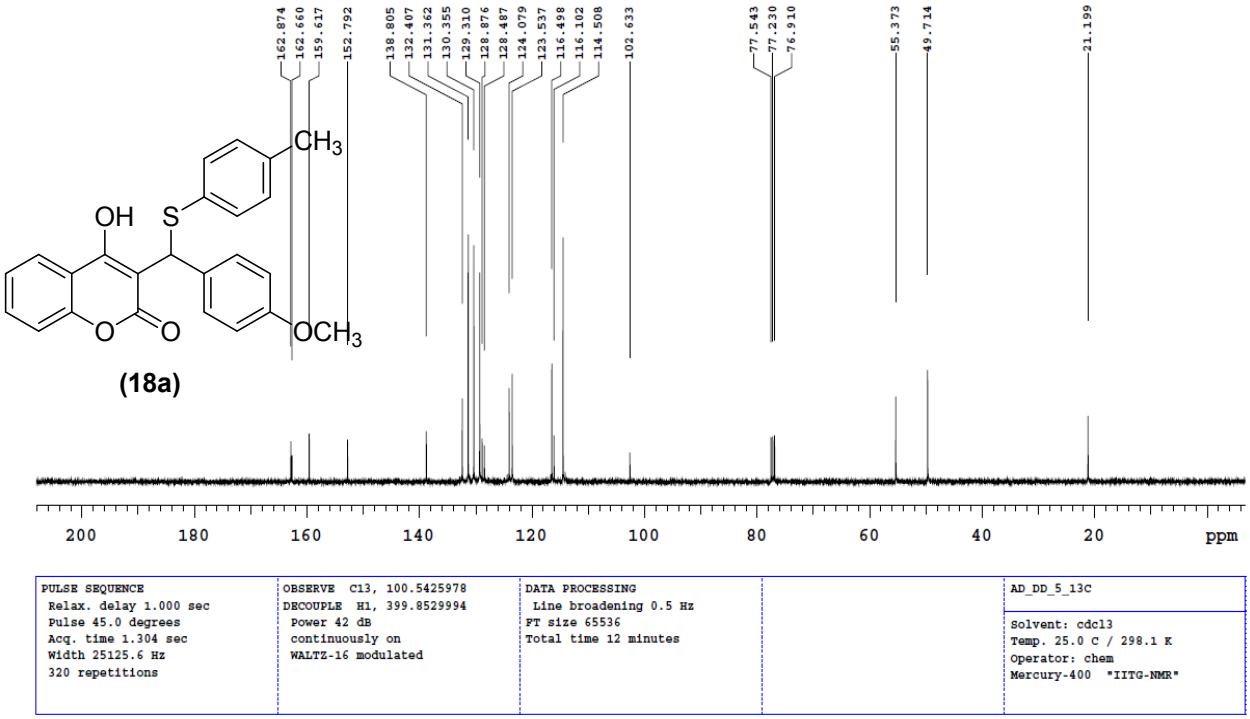
[13]C NMR (100 MHz, CDCl3): *4-hydroxy-3-((4-hydroxyphenyl)(p-tolylthio)methyl)-2H-chromen-2-one* (**17a**)



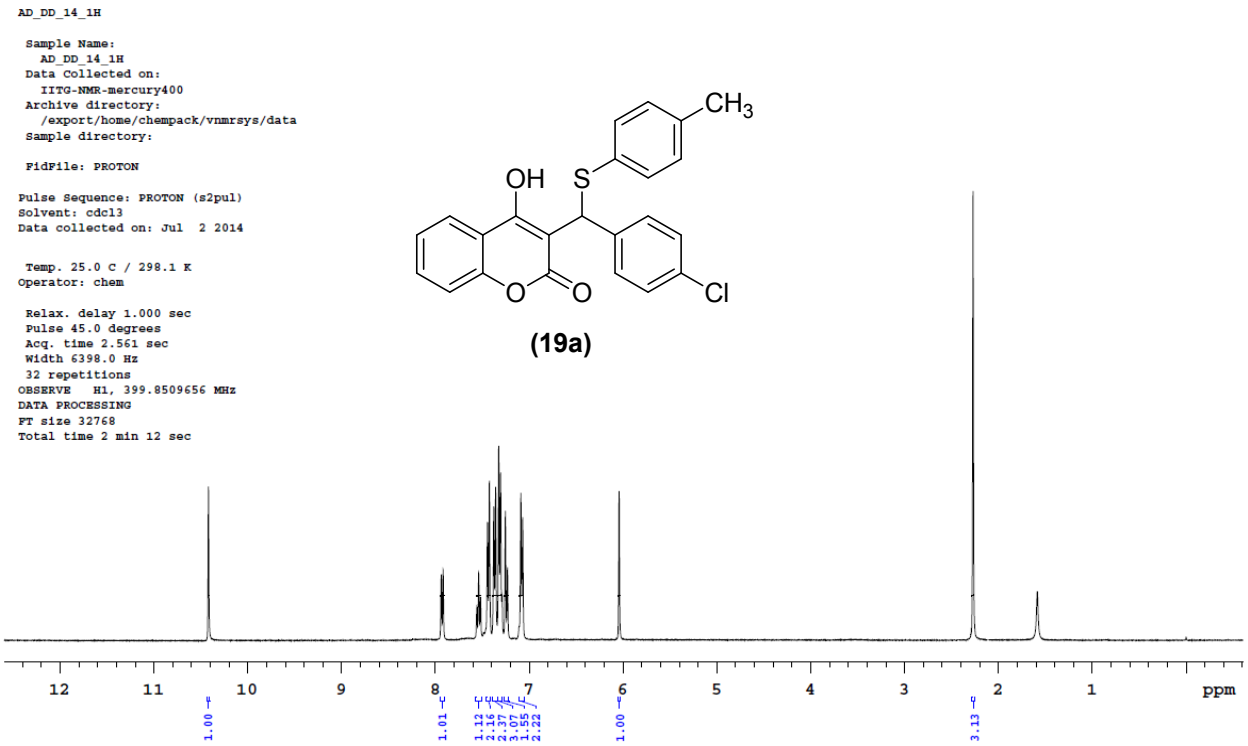
^{1}H NMR (400 MHz, $CDCl_3$): *4-hydroxy-3-((4-methoxyphenyl)(p-tolylthio)methyl)-2H-chromen-2-one* (**18a**)



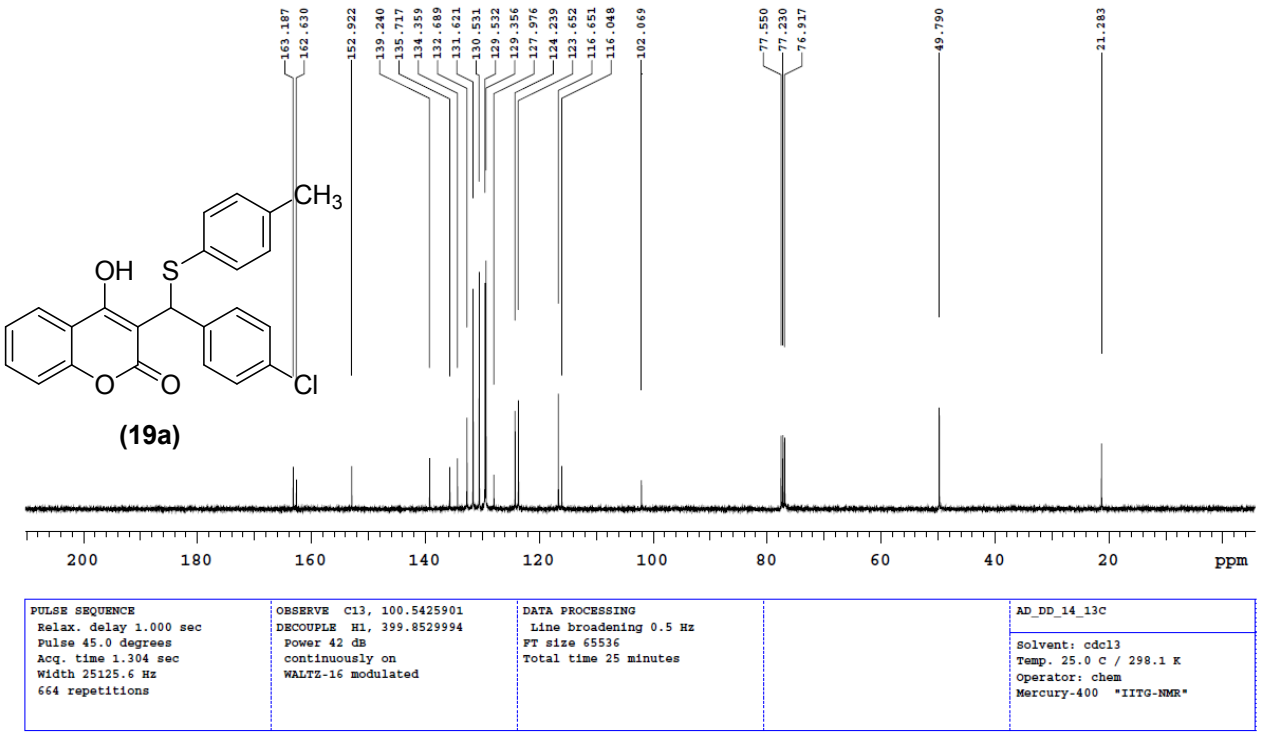
^{13}C NMR (100 MHz, $CDCl_3$): *4-hydroxy-3-((4-methoxyphenyl)(p-tolylthio)methyl)-2H-chromen-2-one* (**18a**)



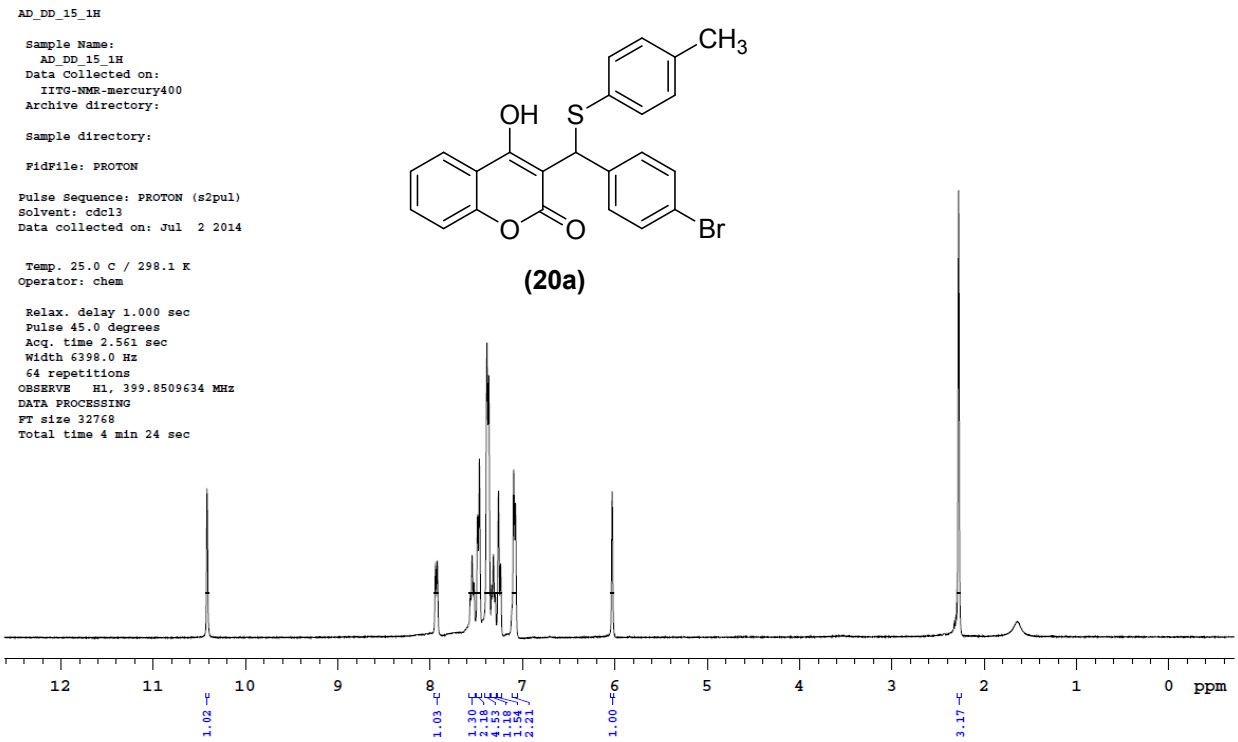
^{1}H NMR (400 MHz, $CDCl_3$): *3-((4-chlorophenyl)(p-tolylthio)methyl)-4-hydroxy-2H-chromen-2-one* (**19a**)



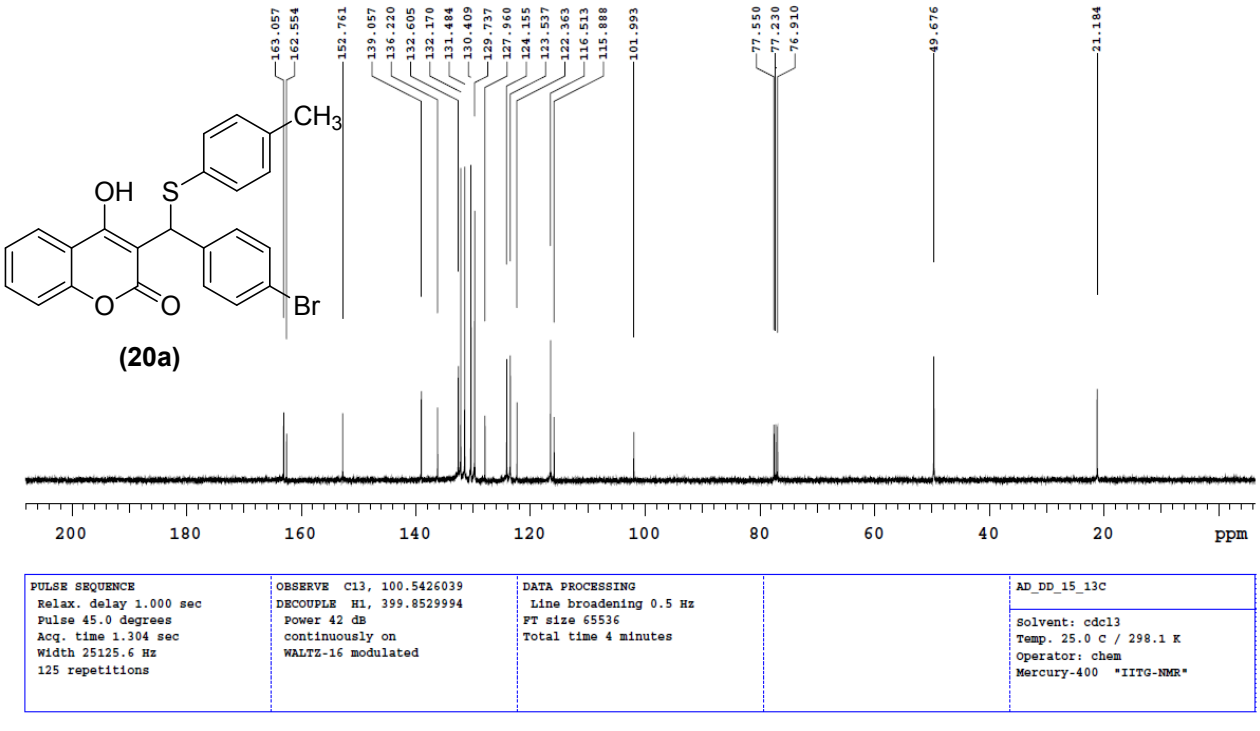
^{13}C NMR (100 MHz, $CDCl_3$): *3-((4-chlorophenyl)(p-tolylthio)methyl)-4-hydroxy-2H-chromen-2-one* (**19a**)



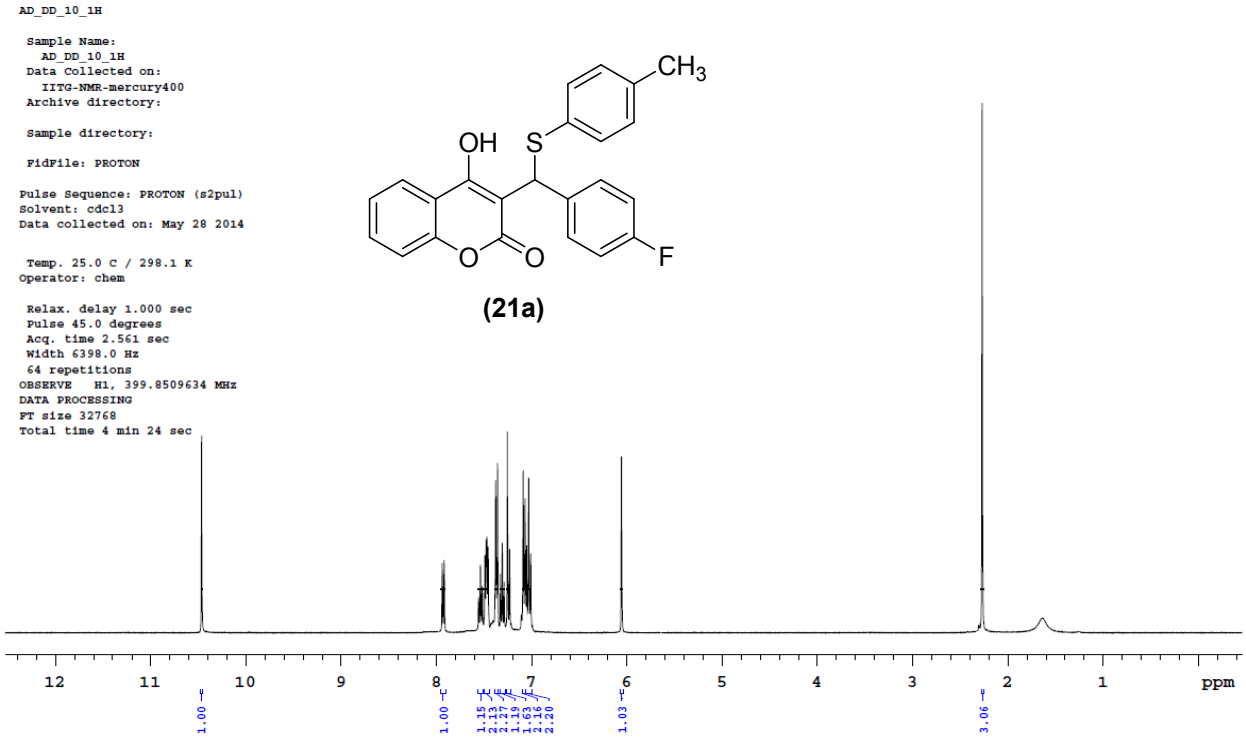
^{1}H NMR (400 MHz, $CDCl_3$): *3-((4-bromophenyl)(p-tolylthio)methyl)-4-hydroxy-2H-chromen-2-one* (**20a**)



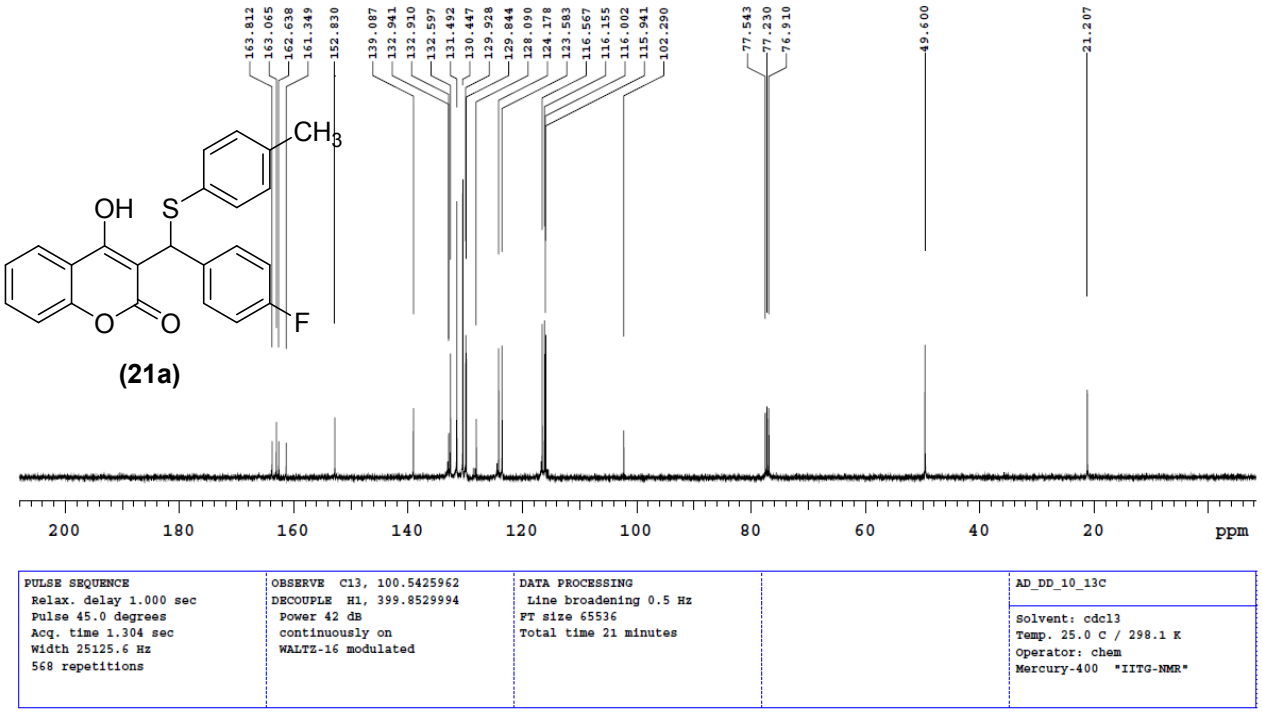
^{13}C NMR (100 MHz, $CDCl_3$): *3-((4-bromophenyl)(p-tolylthio)methyl)-4-hydroxy-2H-chromen-2-one* (**20a**)



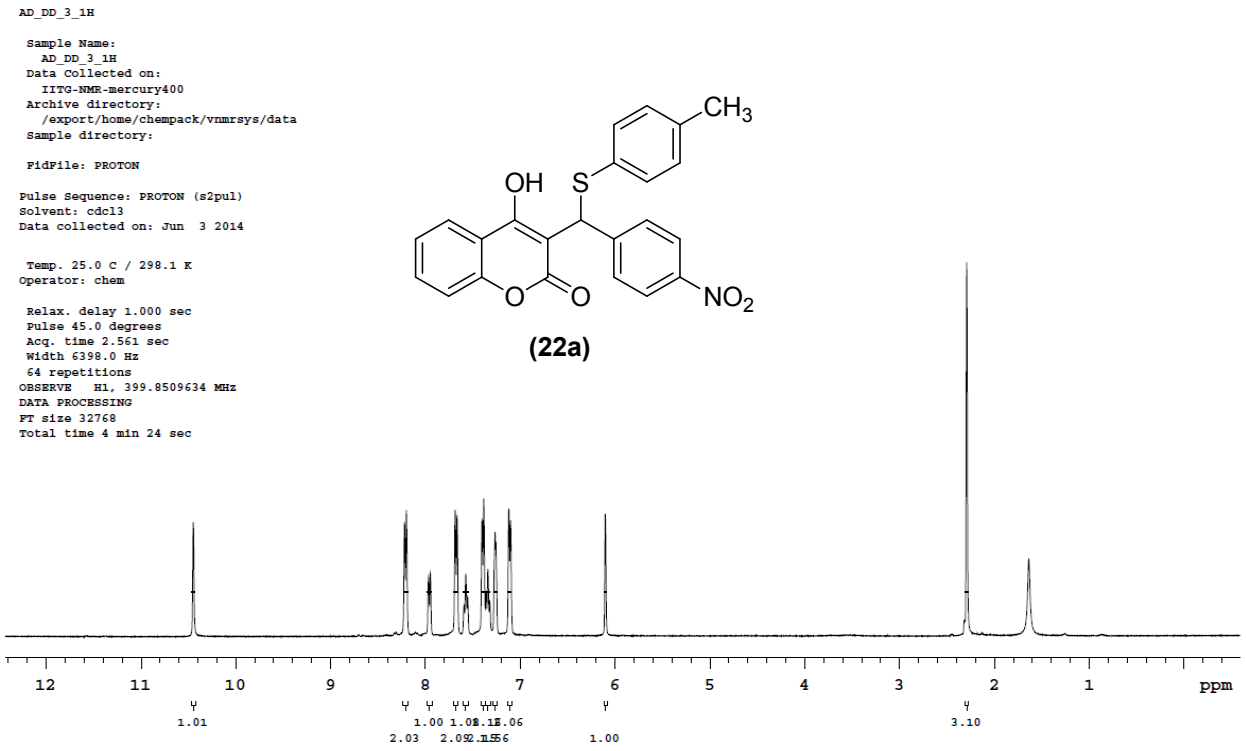
^{1}H NMR (400 MHz, $CDCl_3$): *3-((4-fluorophenyl)(p-tolylthio)methyl)-4-hydroxy-2H-chromen-2-one* (**21a**)



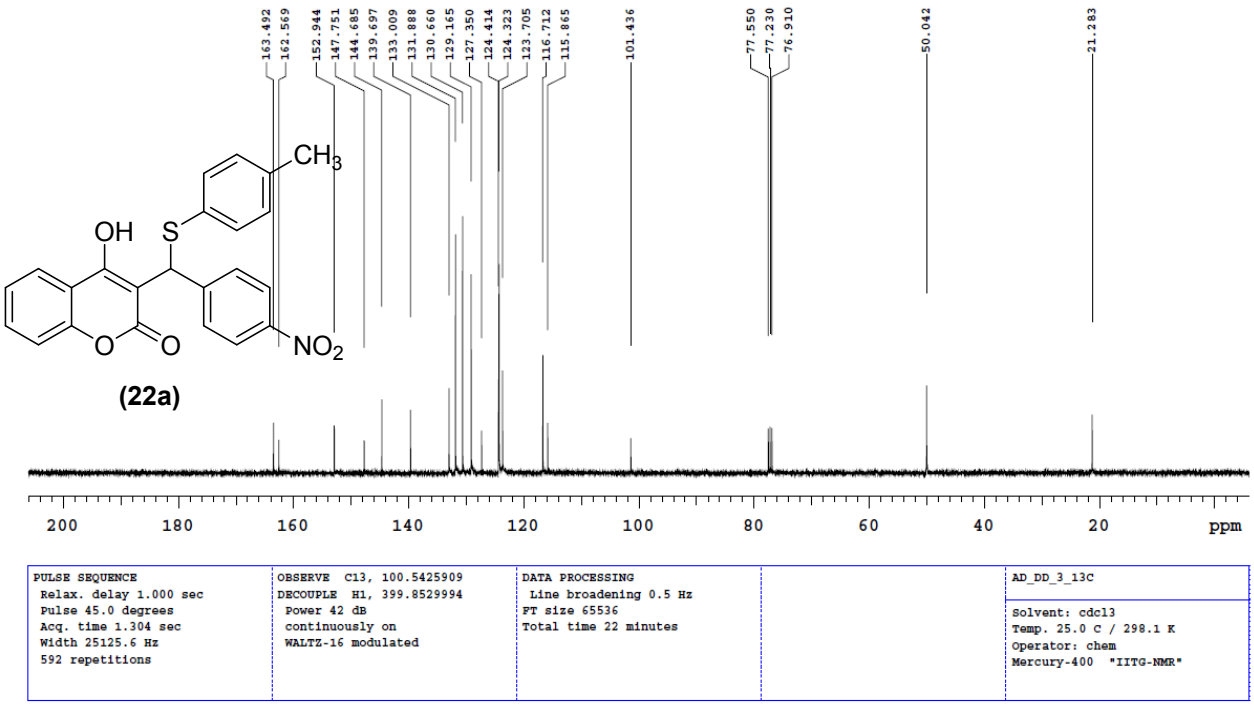
^{13}C NMR (100 MHz, $CDCl_3$): *3-((4-fluorophenyl)(p-tolylthio)methyl)-4-hydroxy-2H-chromen-2-one* (**21a**)



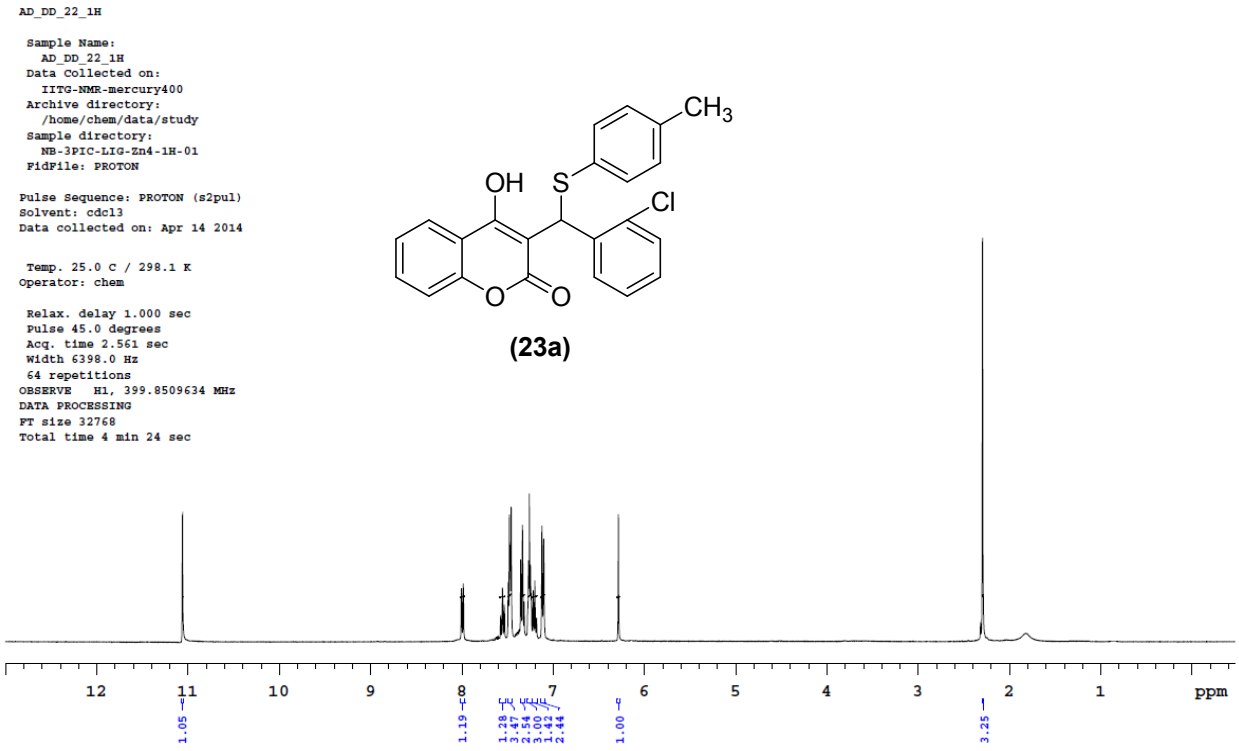
^{1}H NMR (400 MHz, $CDCl_3$): *4-hydroxy-3-((4-nitrophenyl)(p-tolylthio)methyl)-2H-chromen-2-one* (**22a**)



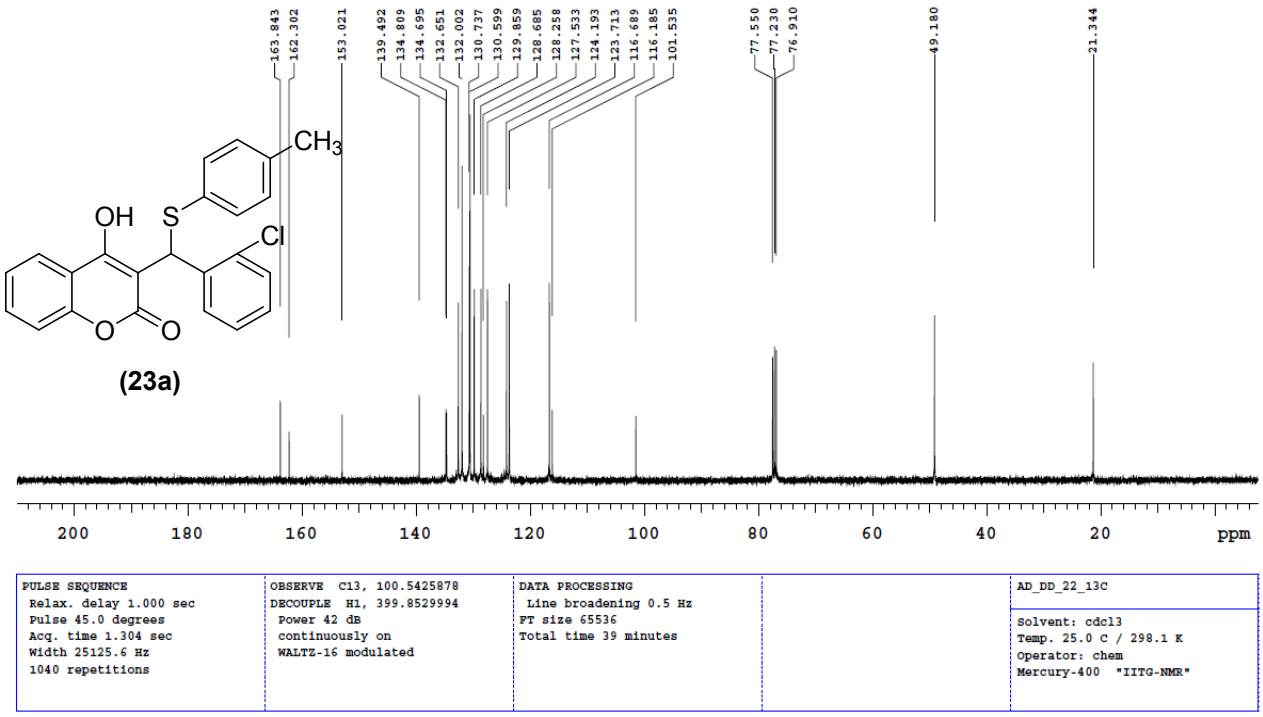
^{13}C NMR (100 MHz, $CDCl_3$): *4-hydroxy-3-((4-nitrophenyl)(p-tolylthio)methyl)-2H-chromen-2-one* (**22a**)



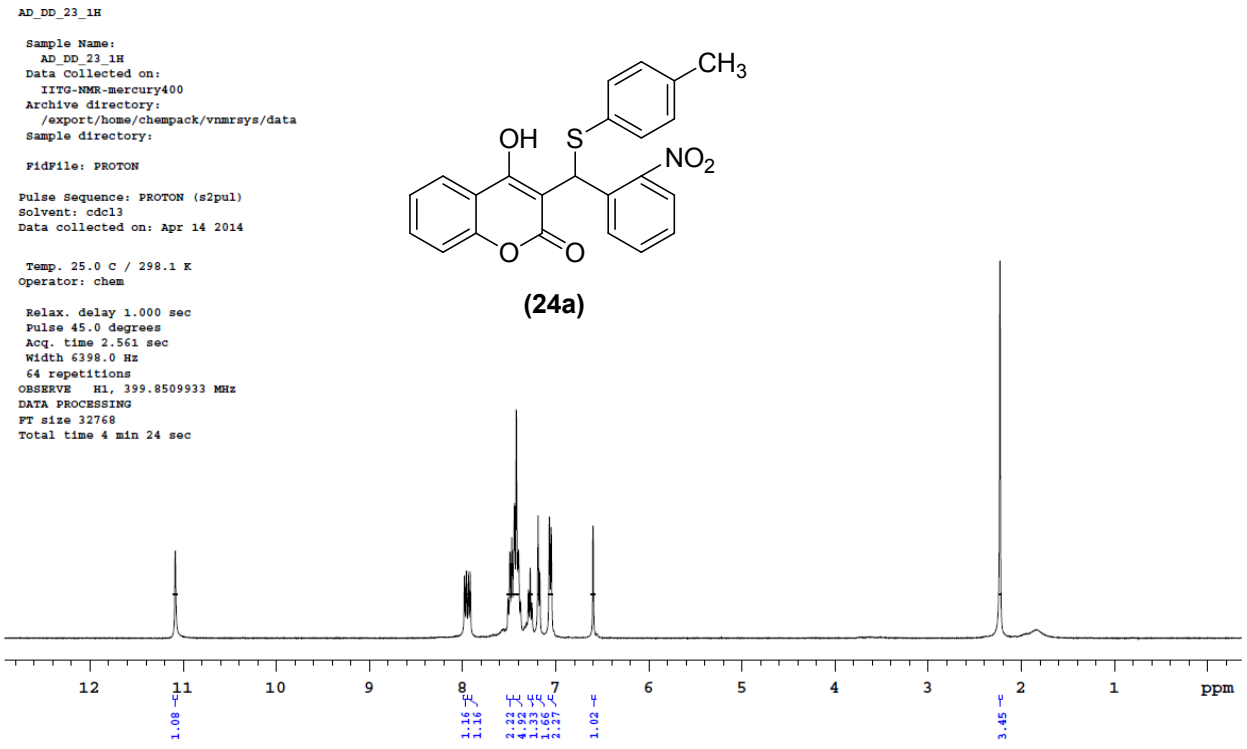
^{1}H NMR (400 MHz, $CDCl_3$): *3-((2-chlorophenyl)(p-tolylthio)methyl)-4-hydroxy-2H-chromen-2-one* (**23a**)



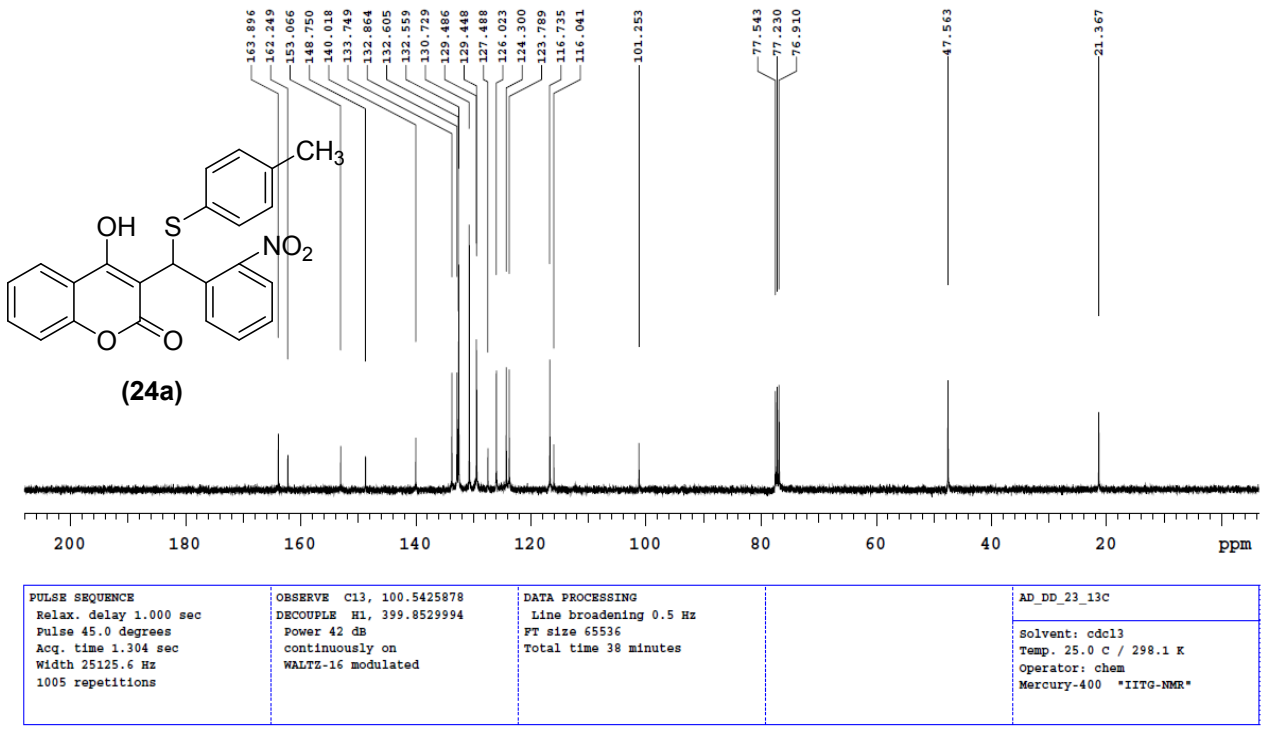
^{13}C NMR (100 MHz, $CDCl_3$): *3-((2-chlorophenyl)(p-tolylthio)methyl)-4-hydroxy-2H-chromen-2-one* (**23a**)



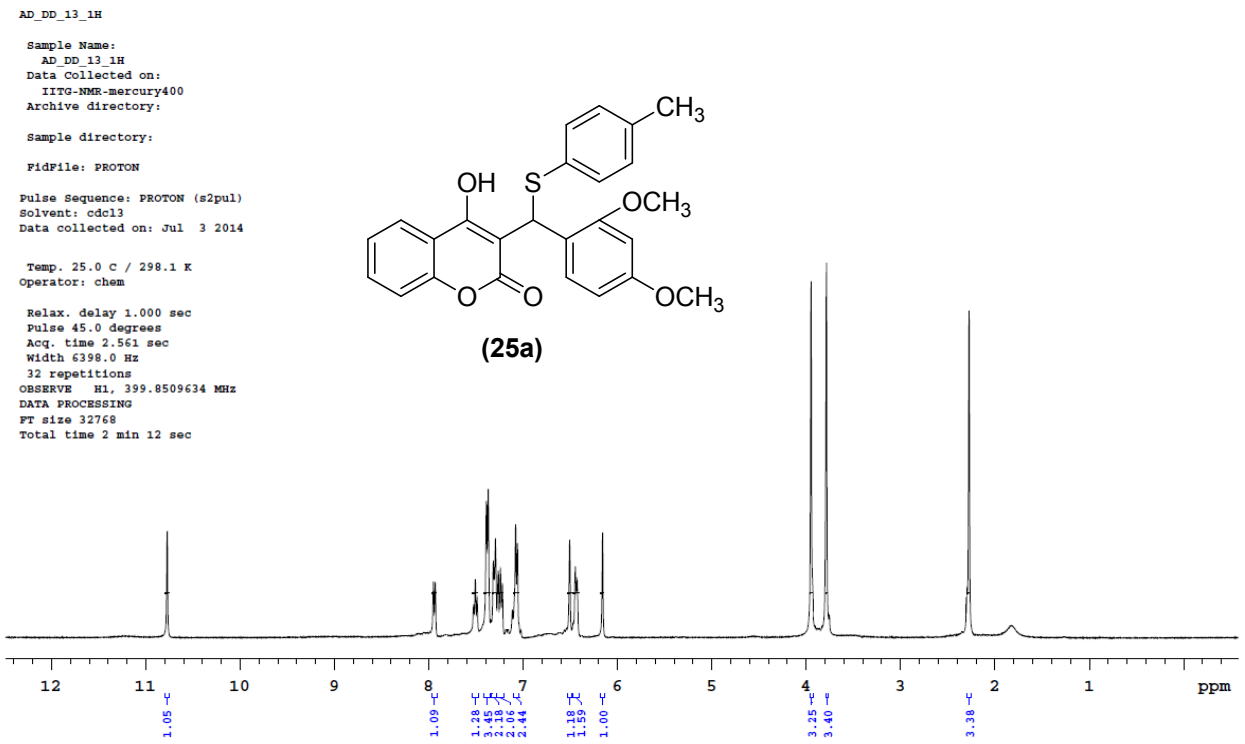
^{1}H NMR (400 MHz, $CDCl_3$): *4-hydroxy-3-((2-nitrophenyl)(p-tolylthio)methyl)-2H-chromen-2-one* (**24a**)



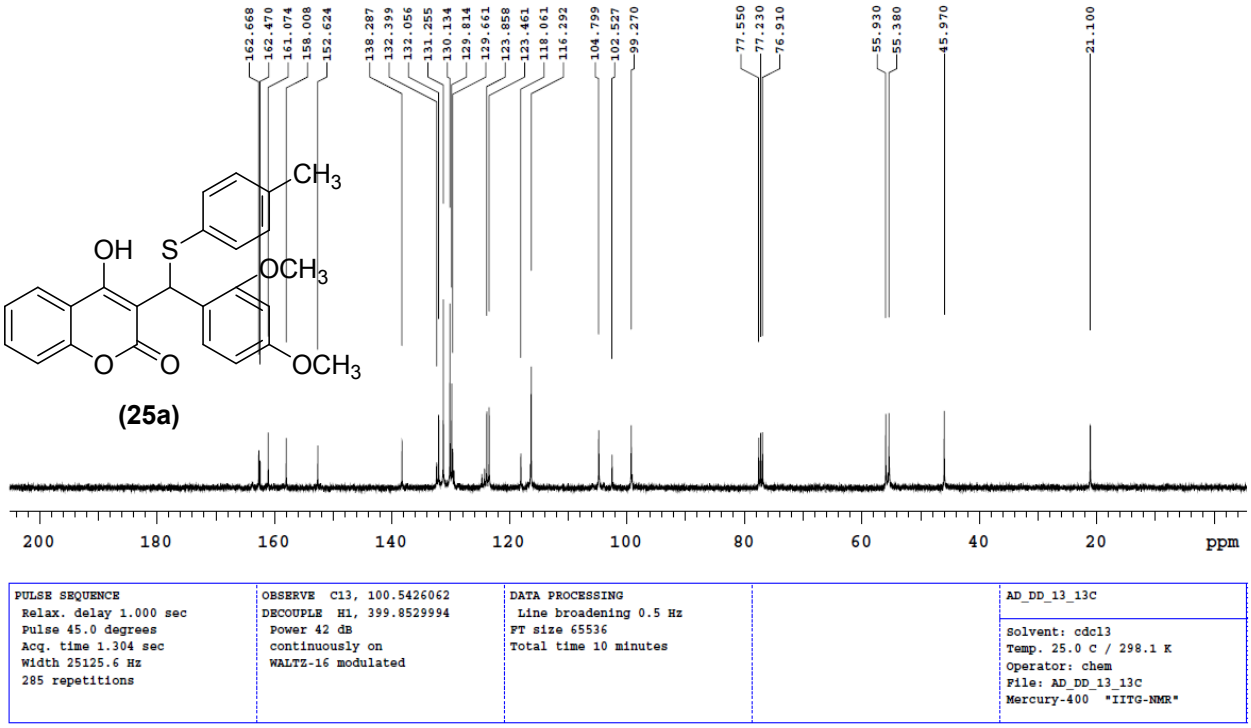
^{13}C NMR (100 MHz, $CDCl_3$): *4-hydroxy-3-((2-nitrophenyl)(p-tolylthio)methyl)-2H-chromen-2-one* (**24a**)



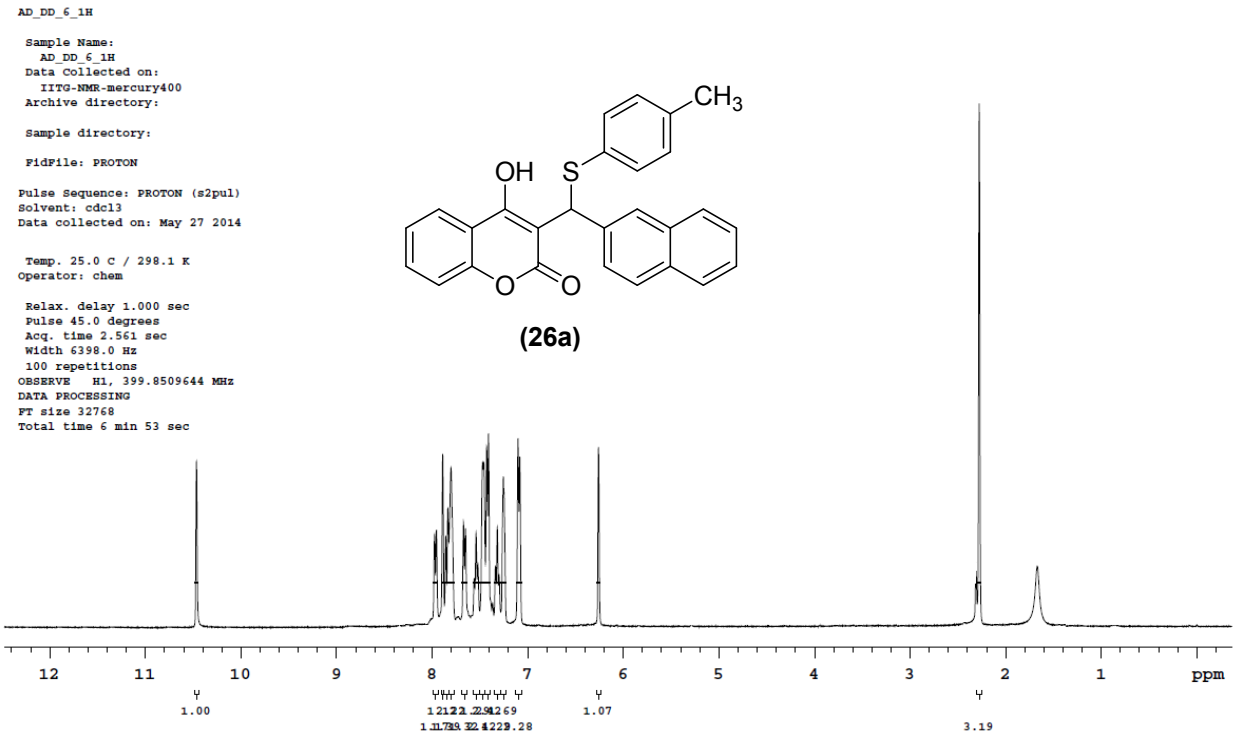
^{1}H NMR (400 MHz, $CDCl_3$): *3-((2,4-dimethoxyphenyl)(p-tolylthio)methyl)-4-hydroxy-2H-chromen-2-one* (**25a**)



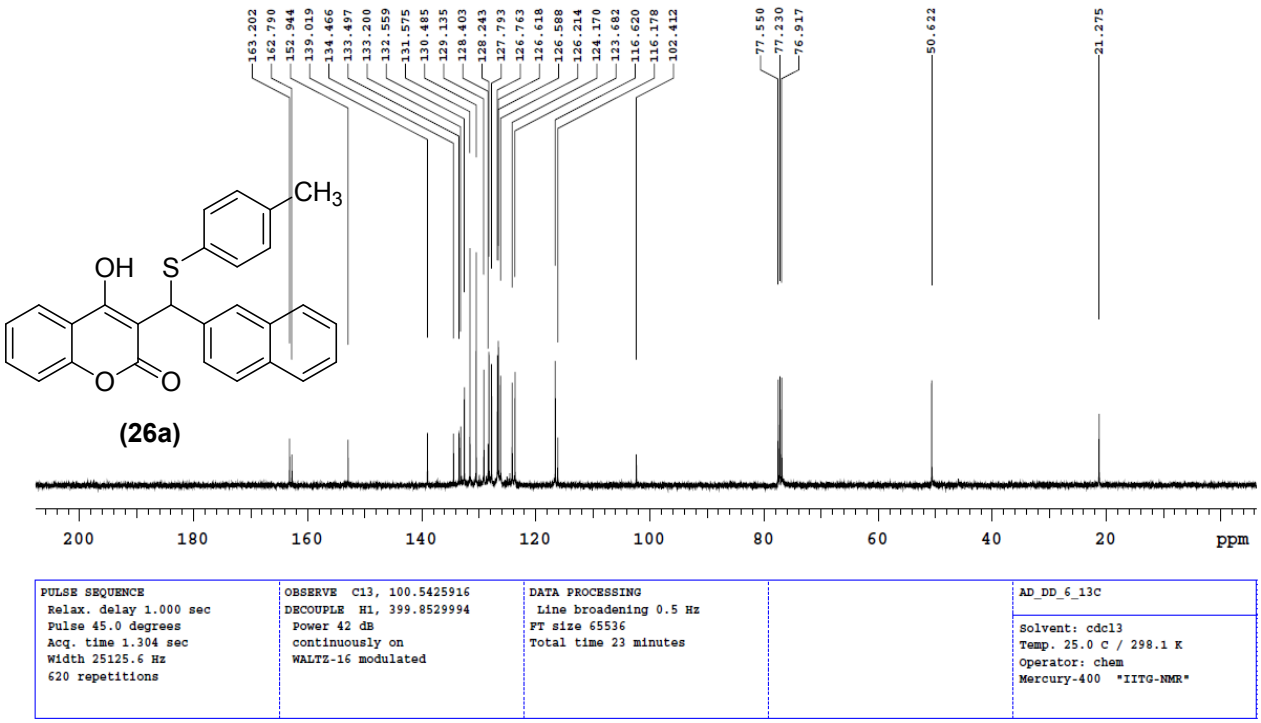
^{13}C NMR (100 MHz, $CDCl_3$): *3-((2,4-dimethoxyphenyl)(p-tolylthio)methyl)-4-hydroxy-2H-chromen-2-one* (**25a**)



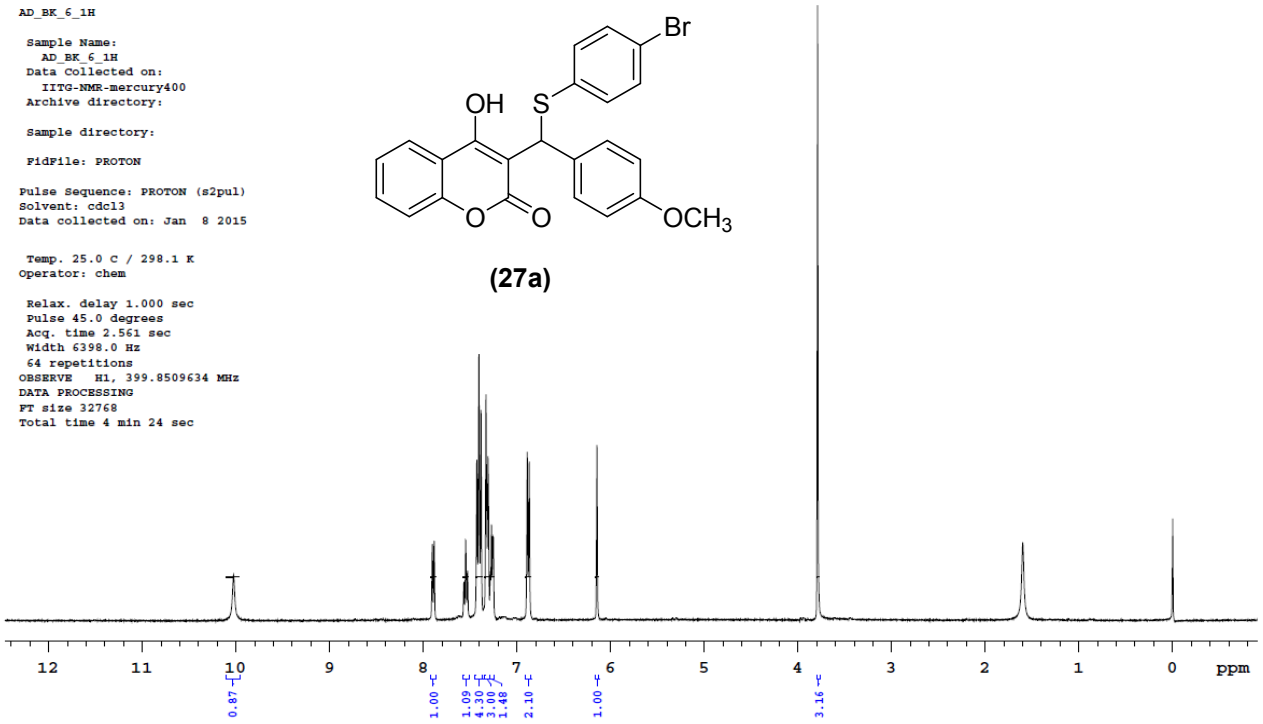
^{1}H NMR (400 MHz, $CDCl_3$): *4-hydroxy-3-(naphthalen-2-yl(p-tolylthio)methyl)-2H-chromen-2-one* (**26a**)



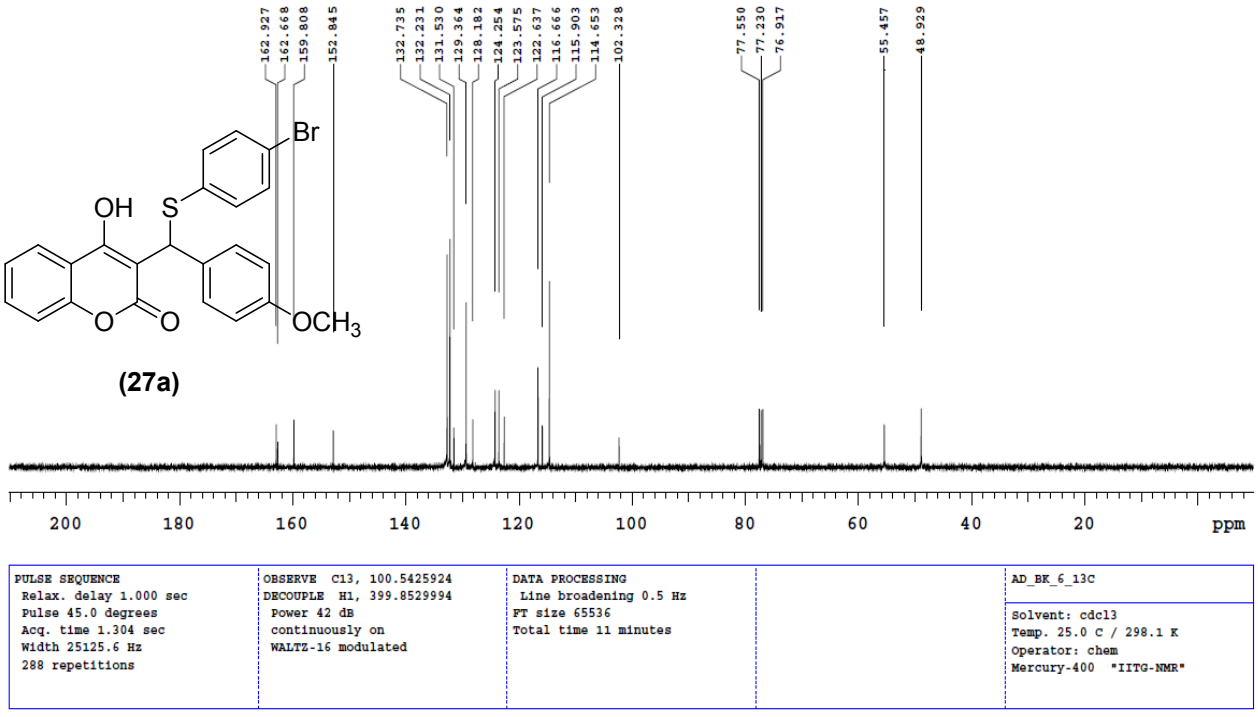
^{13}C NMR (100 MHz, $CDCl_3$): *4-hydroxy-3-(naphthalen-2-yl(p-tolylthio)methyl)-2H-chromen-2-one* (**26a**)



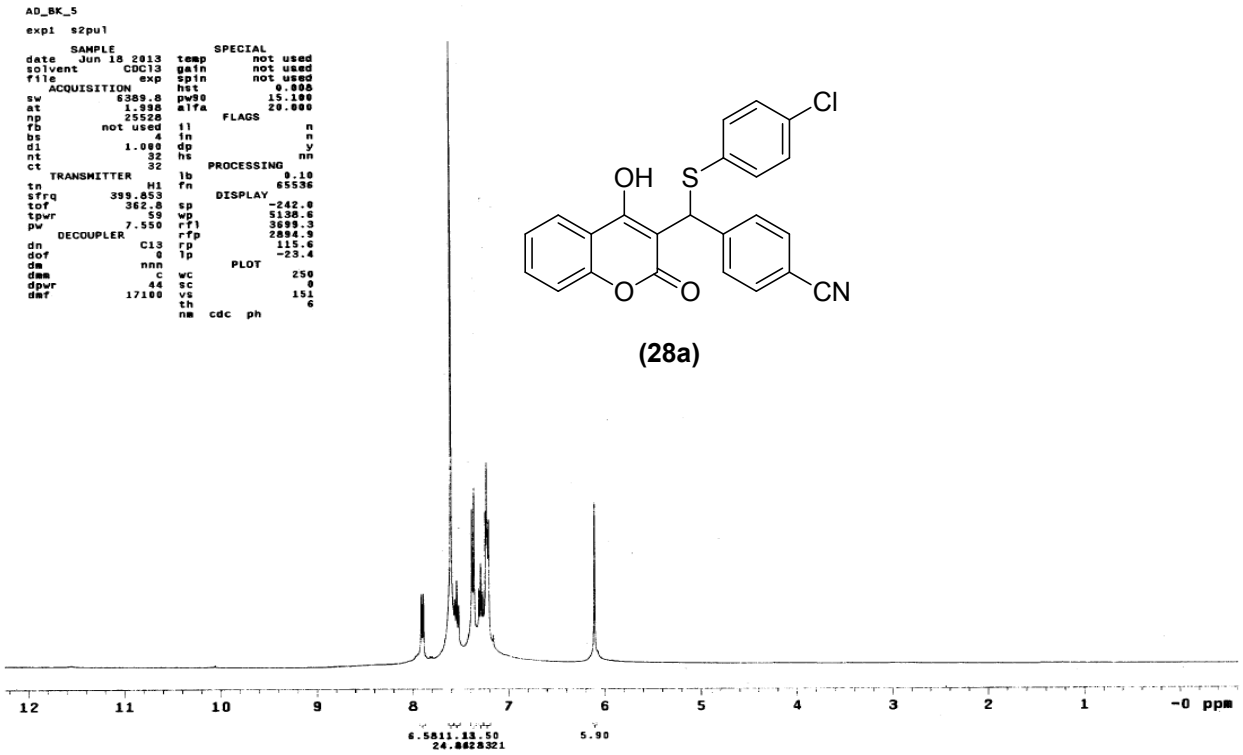
^{1}H NMR (400 MHz, $CDCl_3$): *3-(((4-bromophenyl)thio)(4-methoxyphenyl)methyl)-4-hydroxy-2H-chromen-2-one* (**27a**)



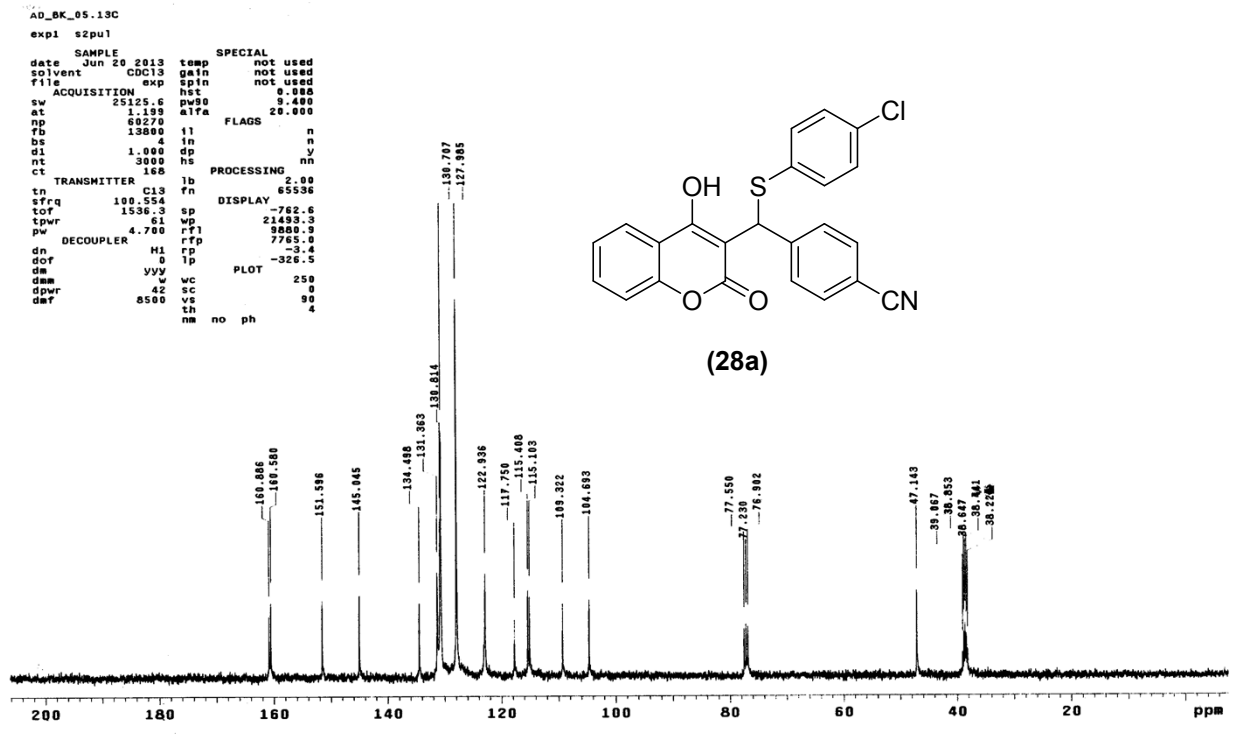
^{13}C NMR (100 MHz, $CDCl_3$): *3-(((4-bromophenyl)thio)(4-methoxyphenyl)methyl)-4-hydroxy-2H-chromen-2-one* (**27a**)



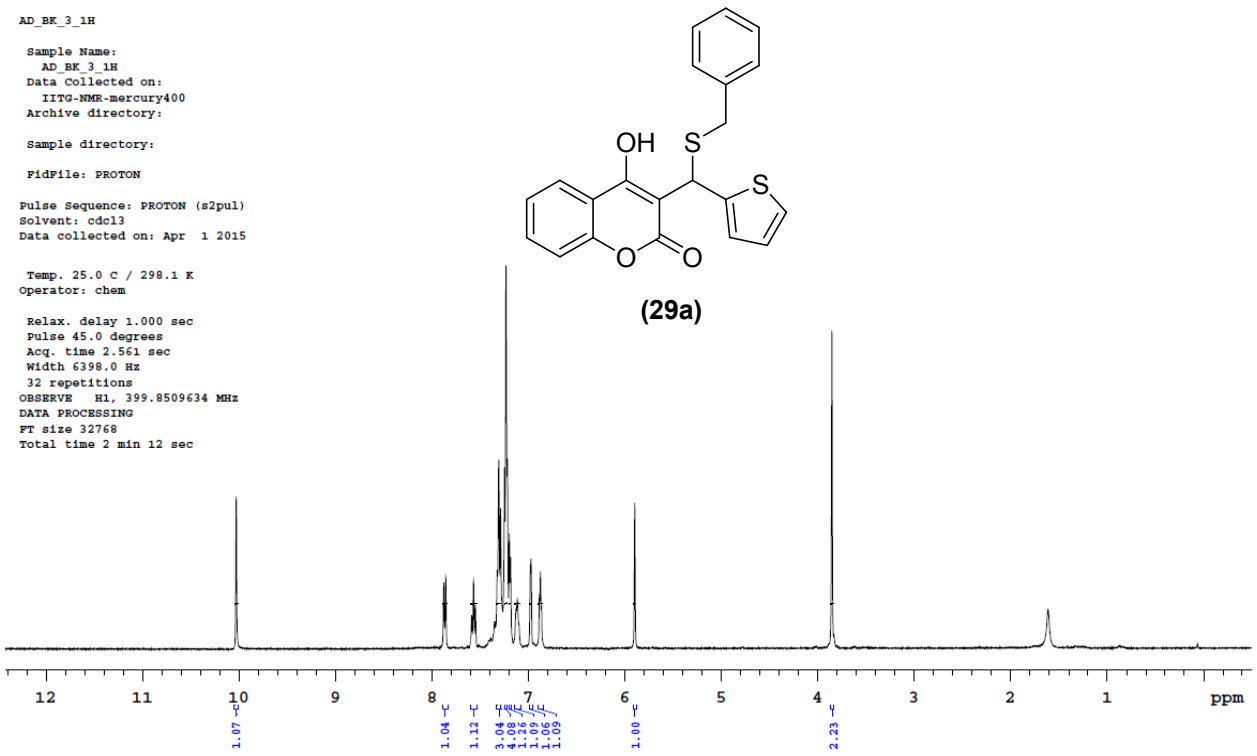
*[1]**H NMR (400 MHz, CDCl$_3$)**: 4-(((4-chlorophenyl)thio)(4-hydroxy-2-oxo-2H-chromen-3-yl)methyl)-benzonitrile* (**28a**)



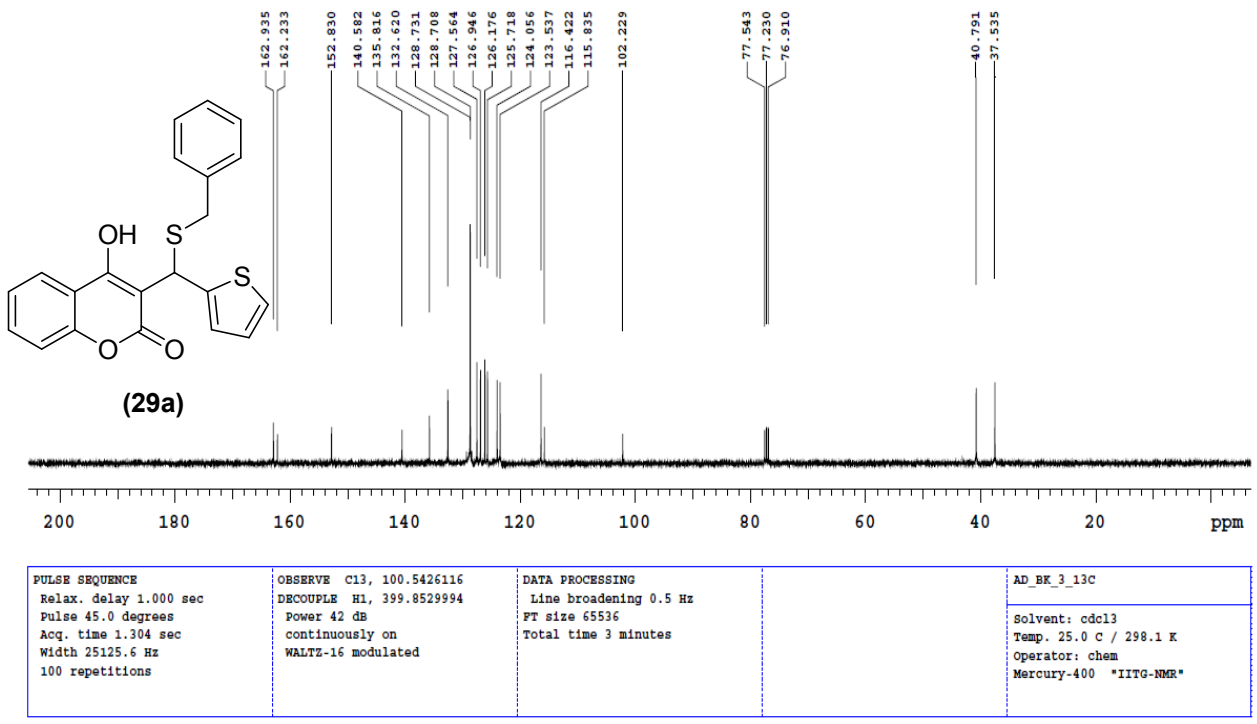
*[13]**C NMR (100 MHz, CDCl$_3$ + DMSO)**: 4-(((4-chlorophenyl)thio)(4-hydroxy-2-oxo-2H-chromen-3-yl)methyl)benzonitrile* (**28a**)



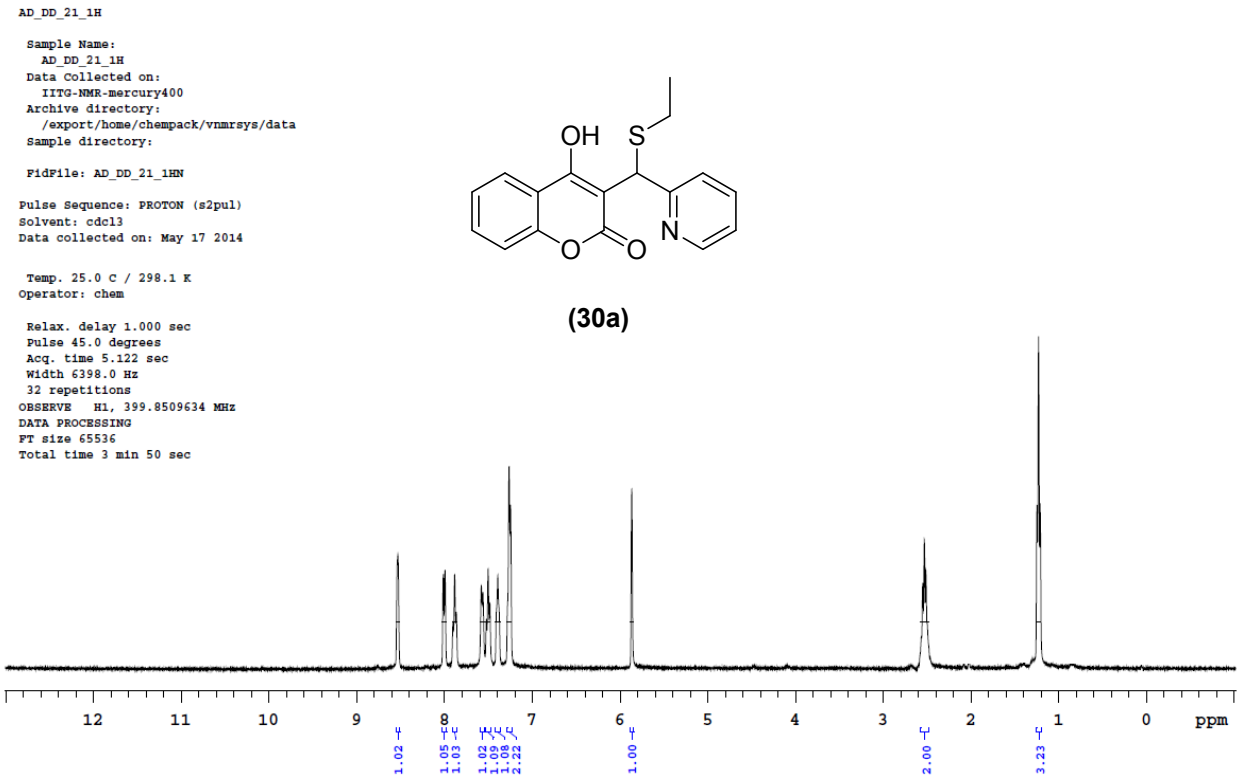
^{1}H NMR (400 MHz, CDCl$_3$): *3-((benzylthio)(thiophen-2-yl)methyl)-4-hydroxy-2H-chromen-2-one* (**29a**)



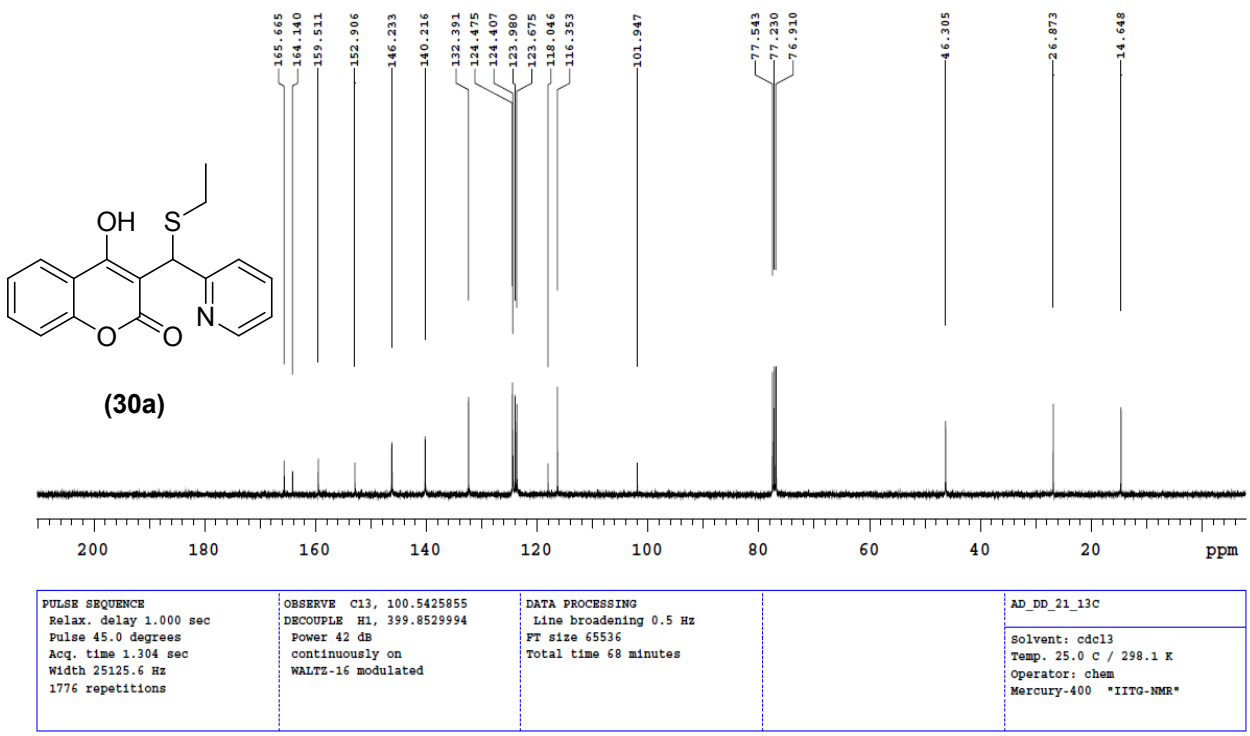
^{13}C NMR (100 MHz, CDCl$_3$): *3-((benzylthio)(thiophen-2-yl)methyl)-4-hydroxy-2H-chromen-2-one* (**29a**)



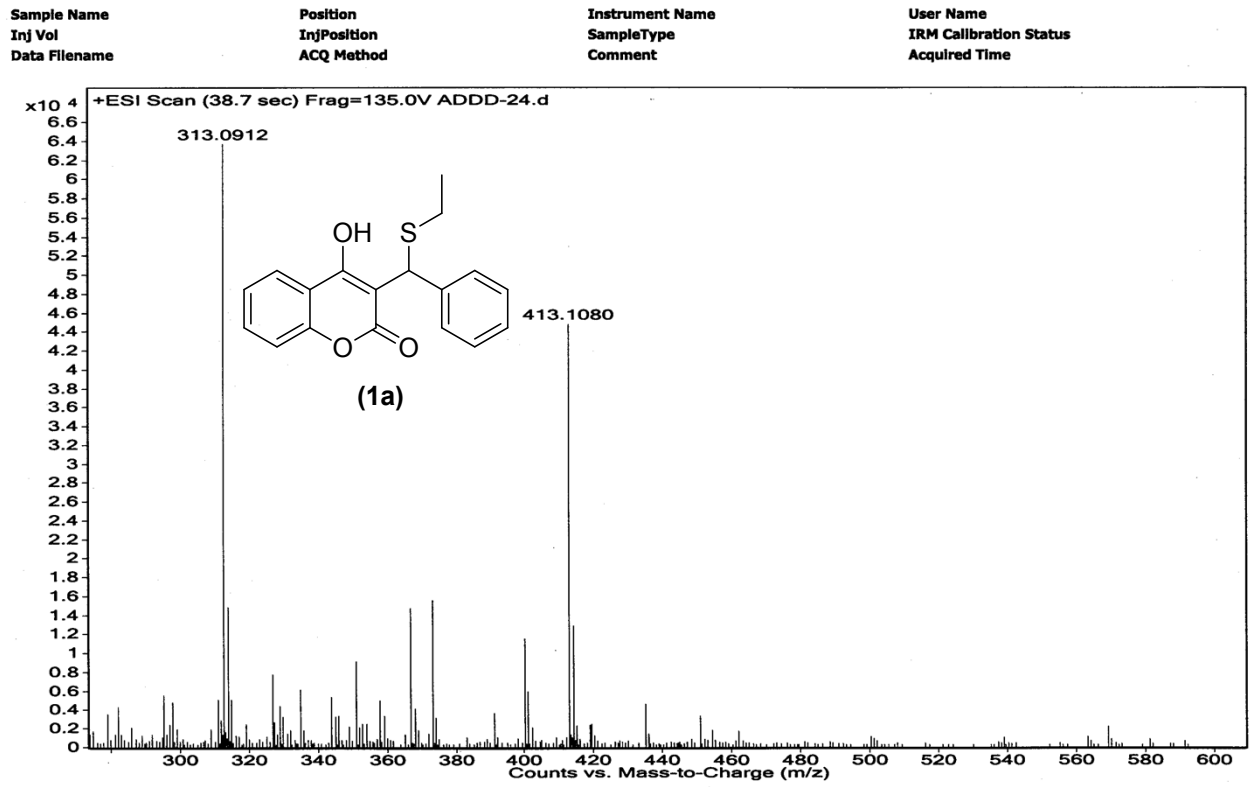
[1]H NMR (400 MHz, CDCl3): 3-((ethylthio)(pyridin-2-yl)methyl)-4-hydroxy-2H-chromen-2-one (**30a**)



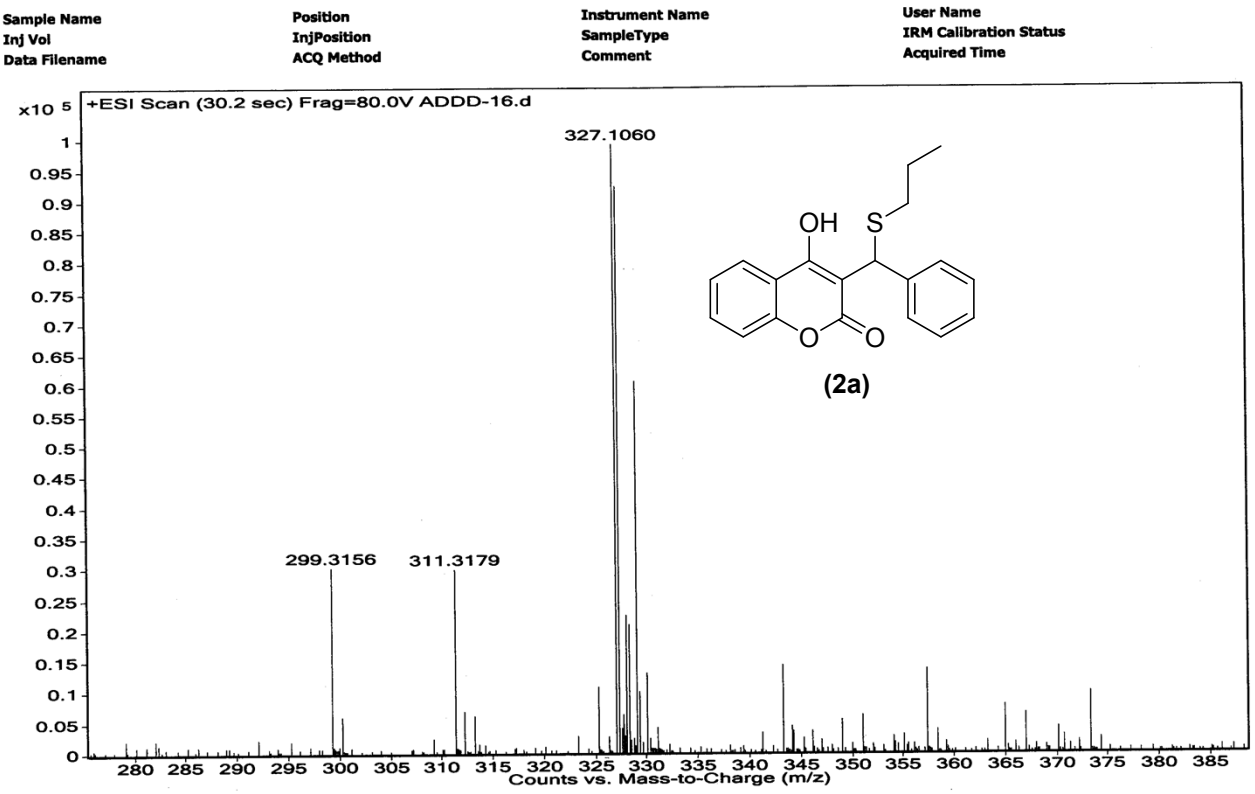
[13]C NMR (100 MHz, CDCl3): 3-((ethylthio)(pyridin-2-yl)methyl)-4-hydroxy-2H-chromen-2-one (**30a**)



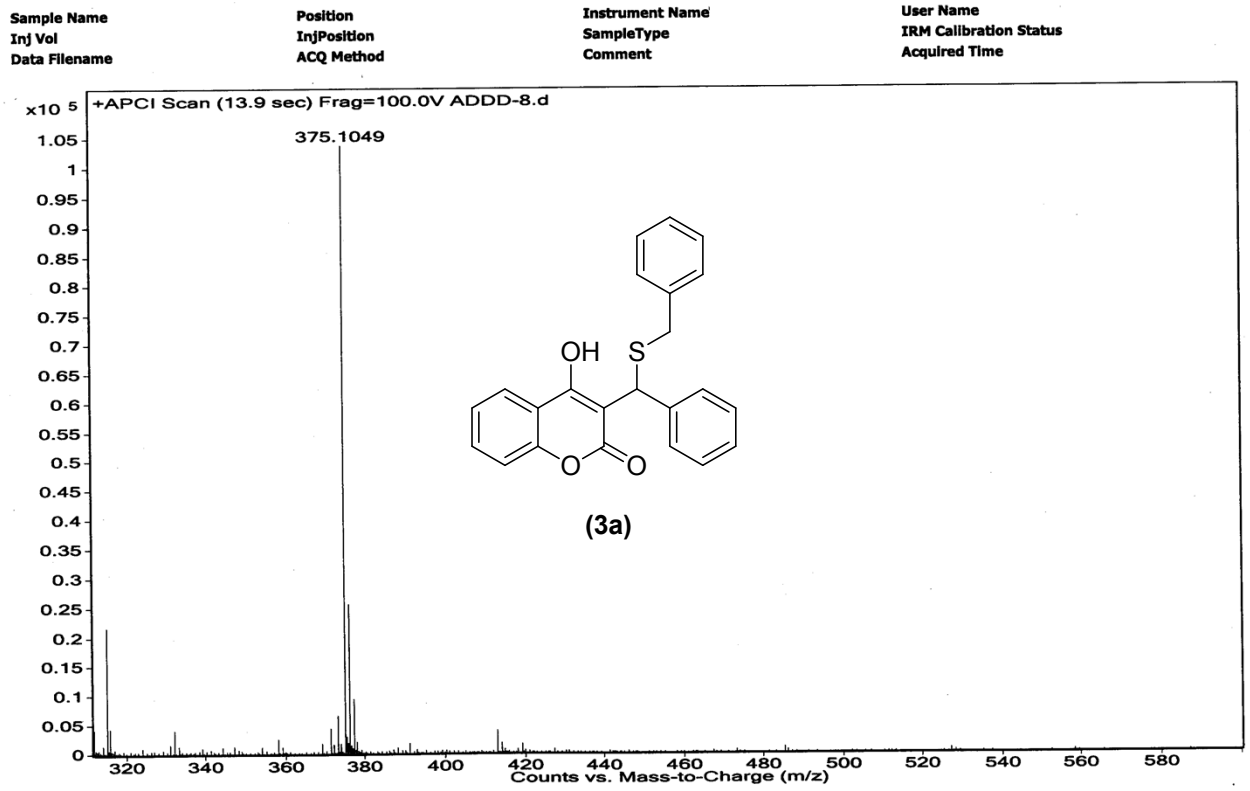
HRMS (ESI) spectra *: 3-((ethylthio)(phenyl)methyl)-4-hydroxy-2H-chromen-2-one* (**1a**)



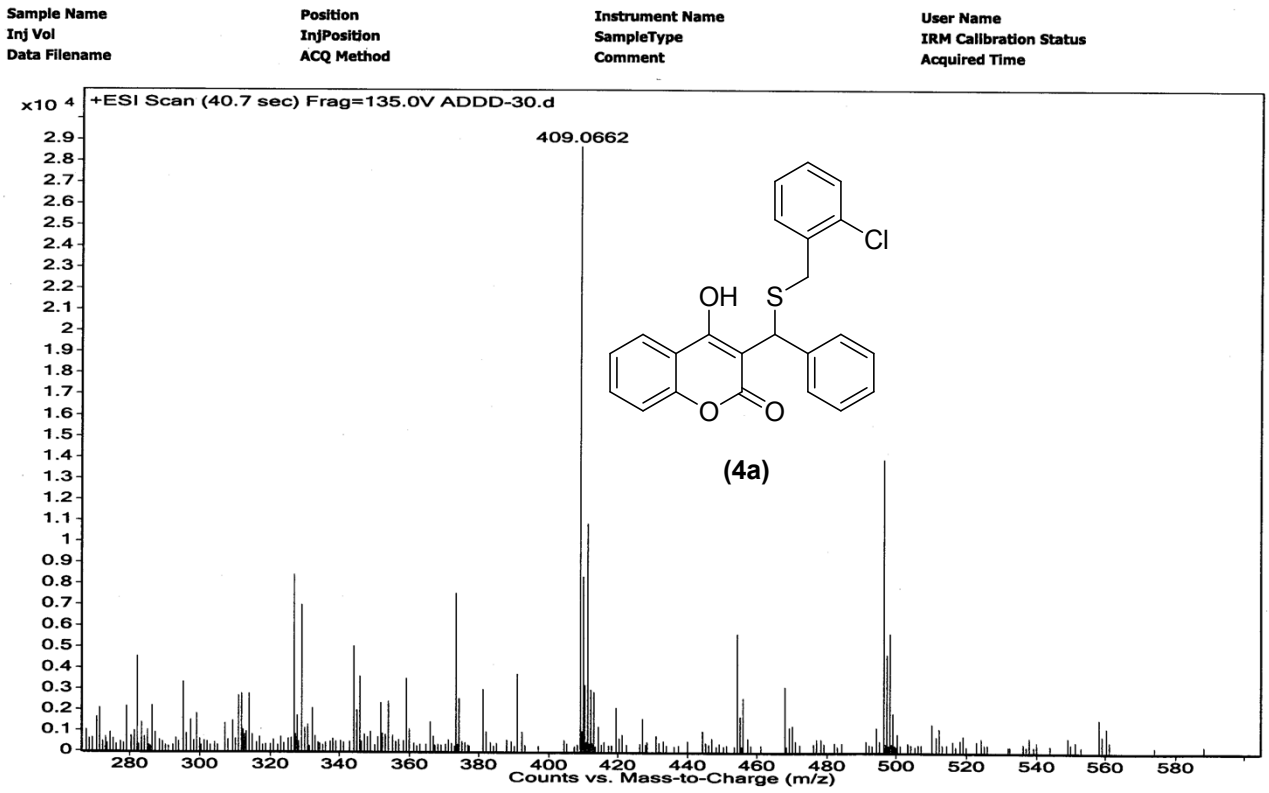
HRMS (ESI) spectra *: 4-hydroxy-3-(phenyl(propylthio)methyl)-2H-chromen-2-one* (**2a**)



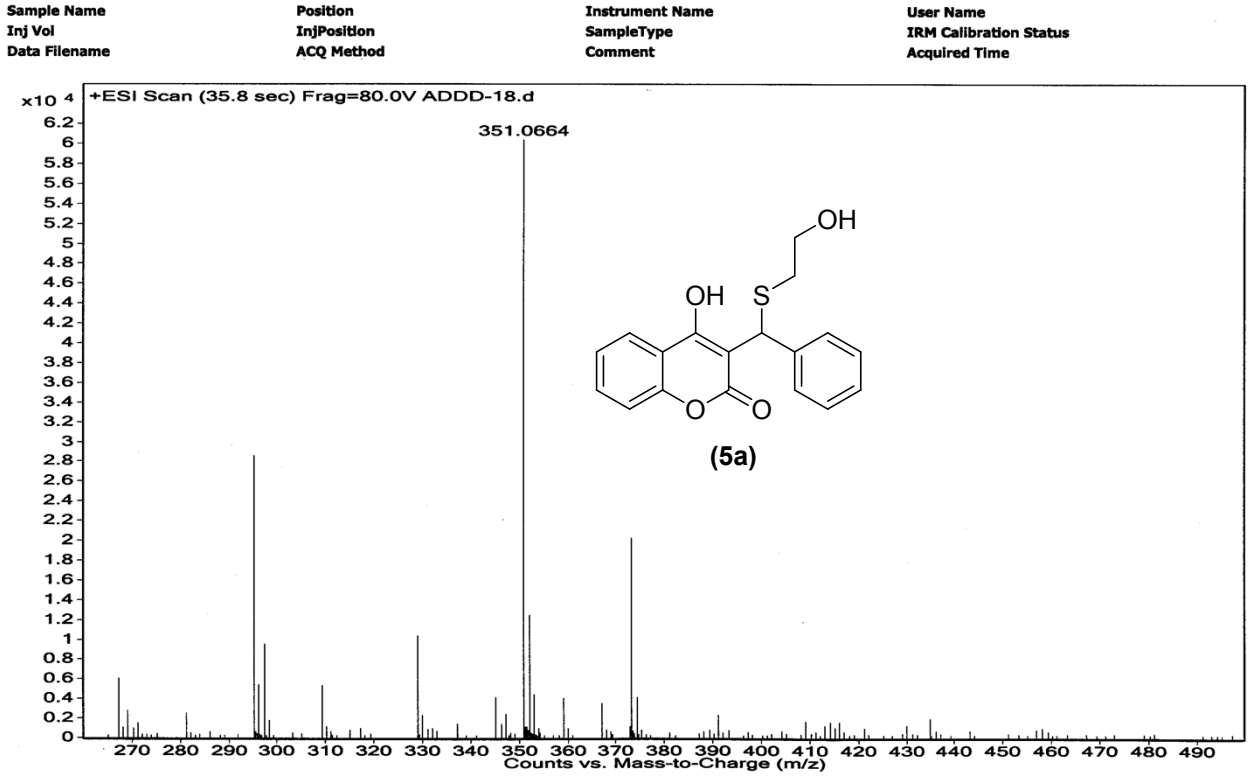
HRMS (APCI) spectra *: 3-((benzylthio)(phenyl)methyl)-4-hydroxy-2H-chromen-2-one* (**3a**)



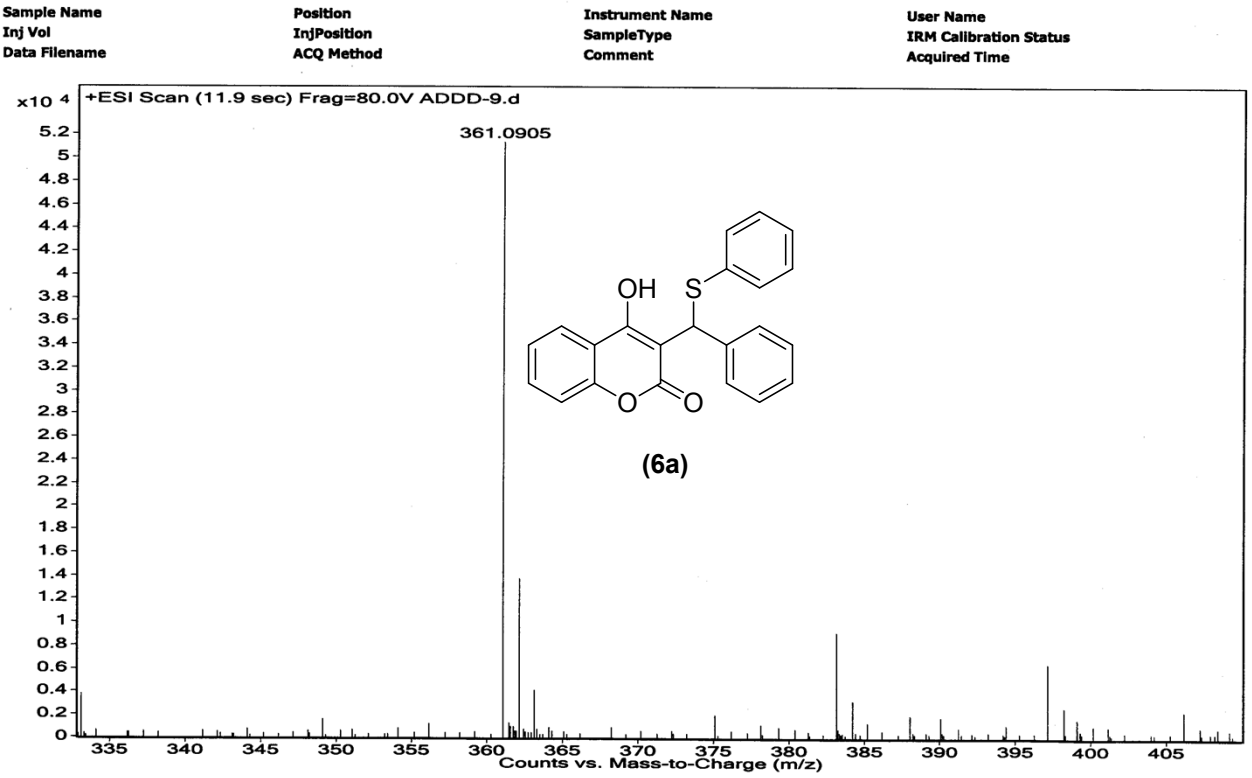
HRMS (ESI) spectra *: 3-(((2-chlorobenzyl)thio)(phenyl)methyl)-4-hydroxy-2H-chromen-2-one* (**4a**)



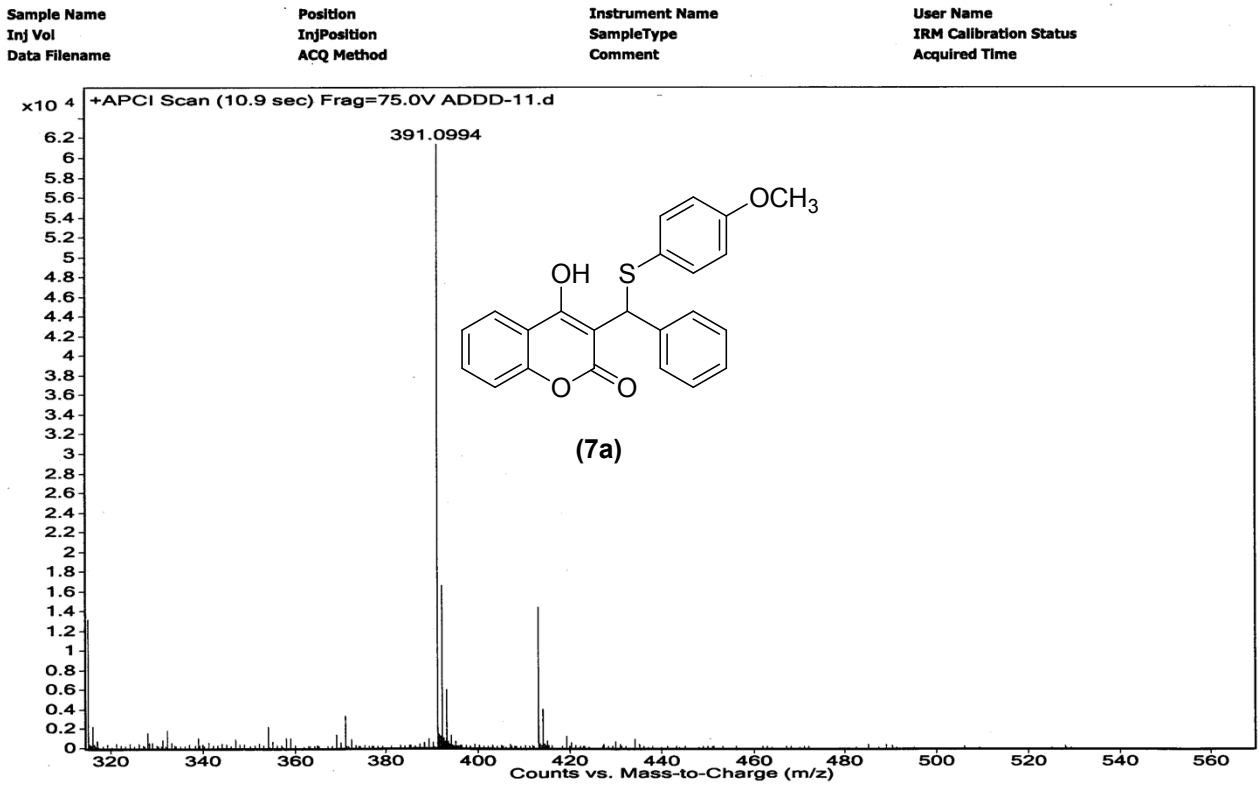
HRMS (ESI) spectra *: 4-hydroxy-3-(phenyl(propylthio)methyl)-2H-chromen-2-one* (**5a**)



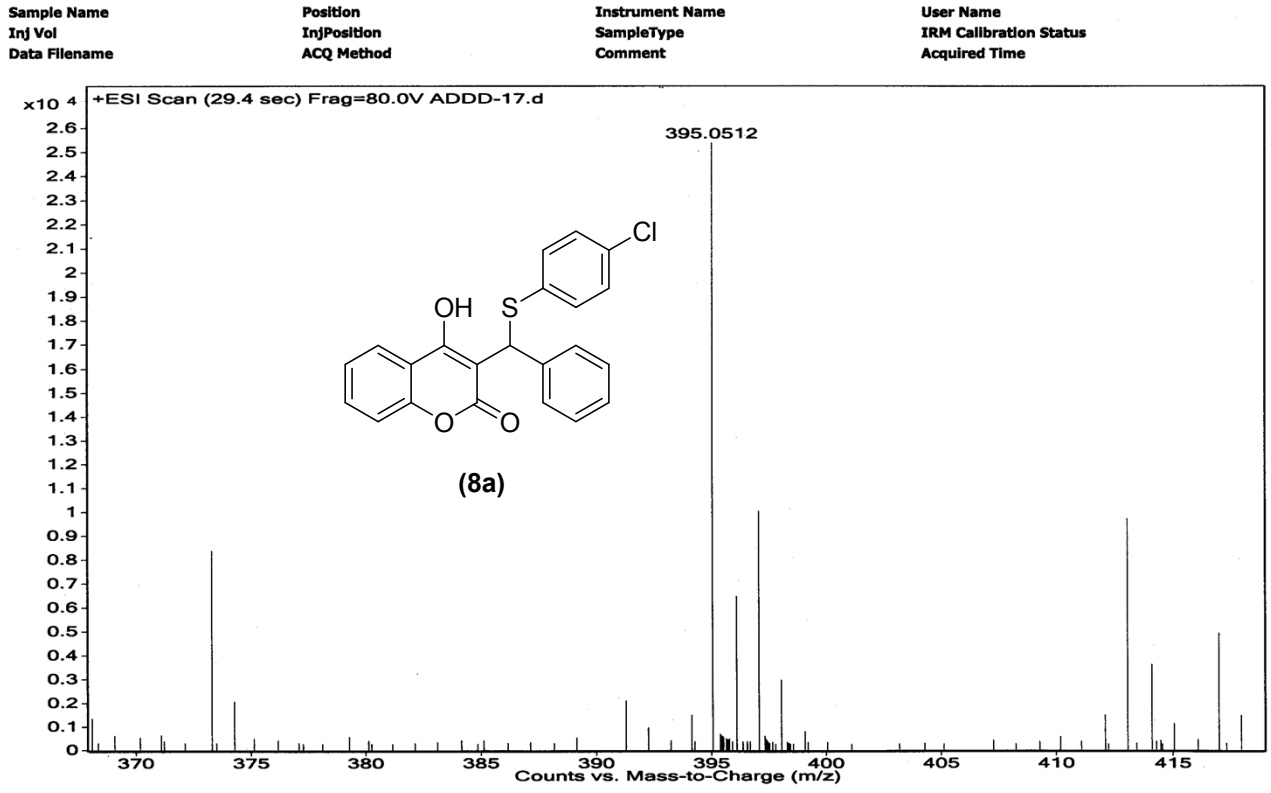
HRMS (ESI) spectra *: 4-hydroxy-3-(phenyl(phenylthio)methyl)-2H-chromen-2-one* (**6a**)



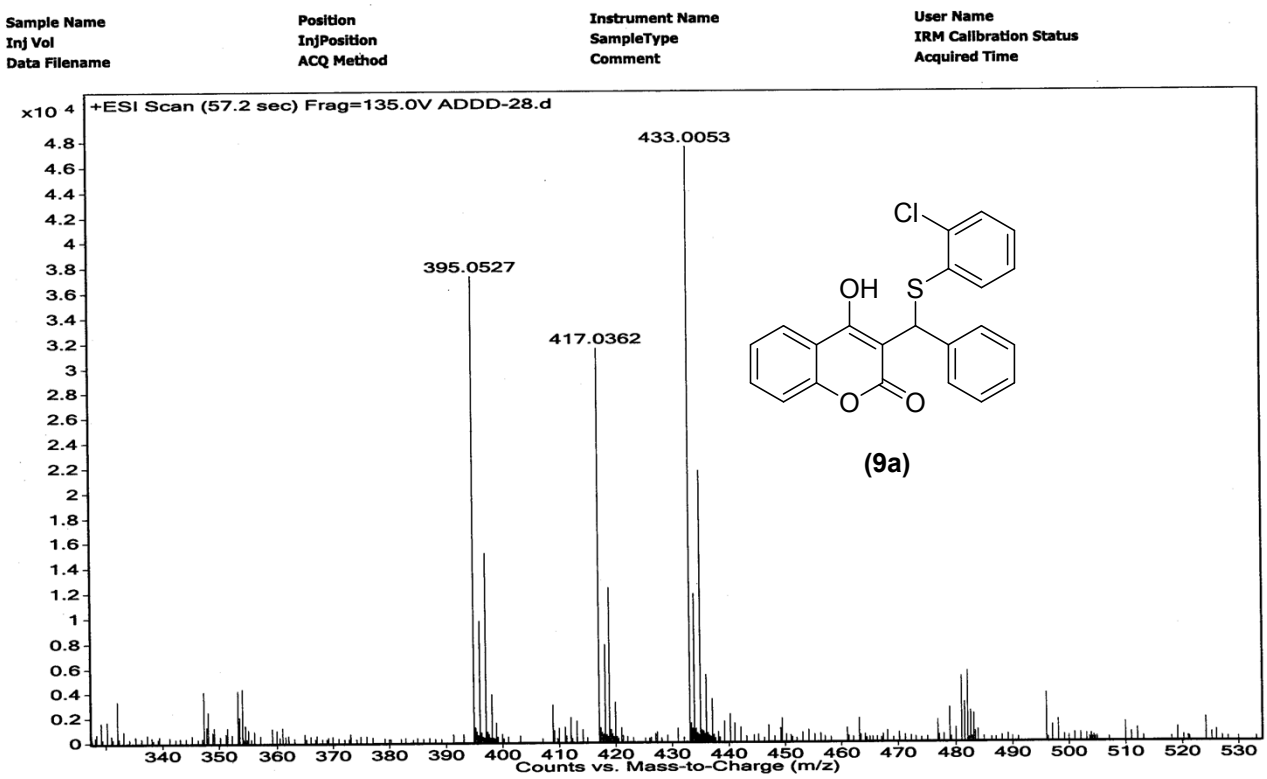
HRMS (APCI) spectra *: 4-hydroxy-3-(((4-methoxyphenyl)thio)(phenyl)methyl)-2H-chromen-2-one* (**7a**)



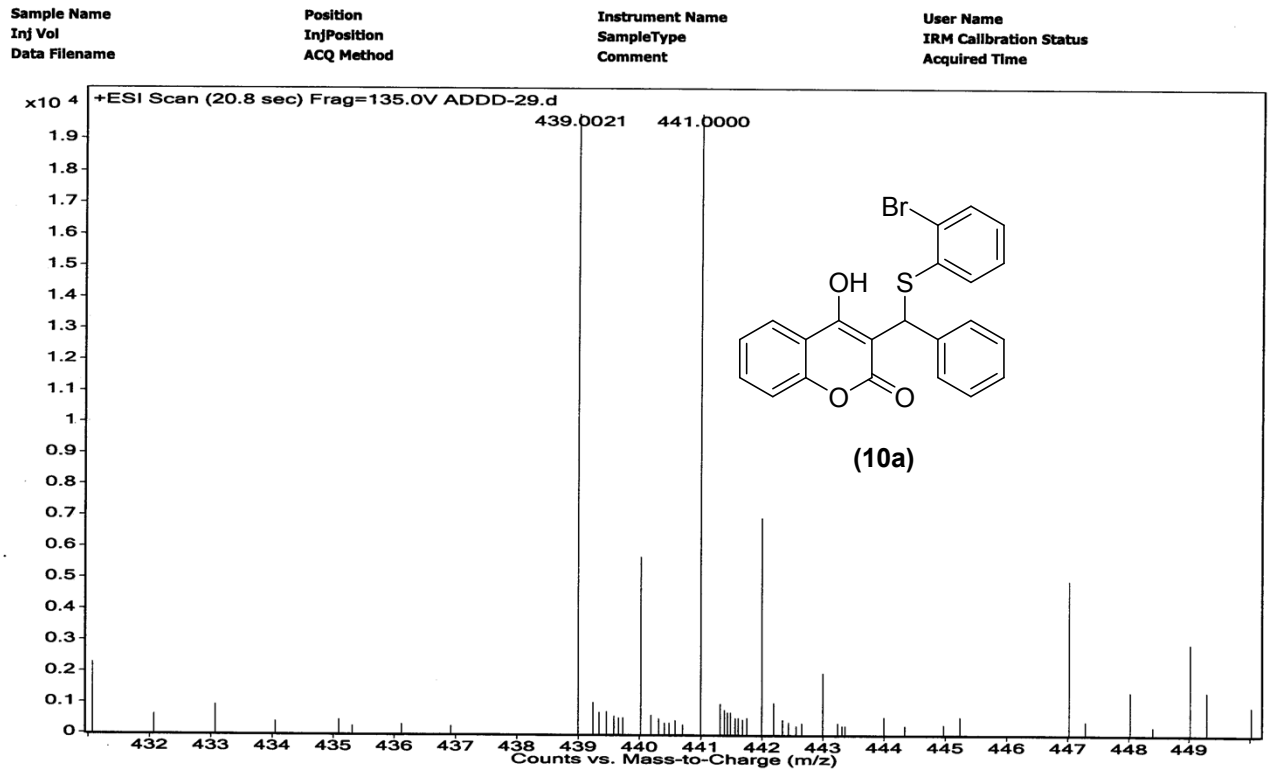
HRMS (ESI) spectra *: 3-(((4-chlorophenyl)thio)(phenyl)methyl)-4-hydroxy-2H-chromen-2-one* (**8a**)



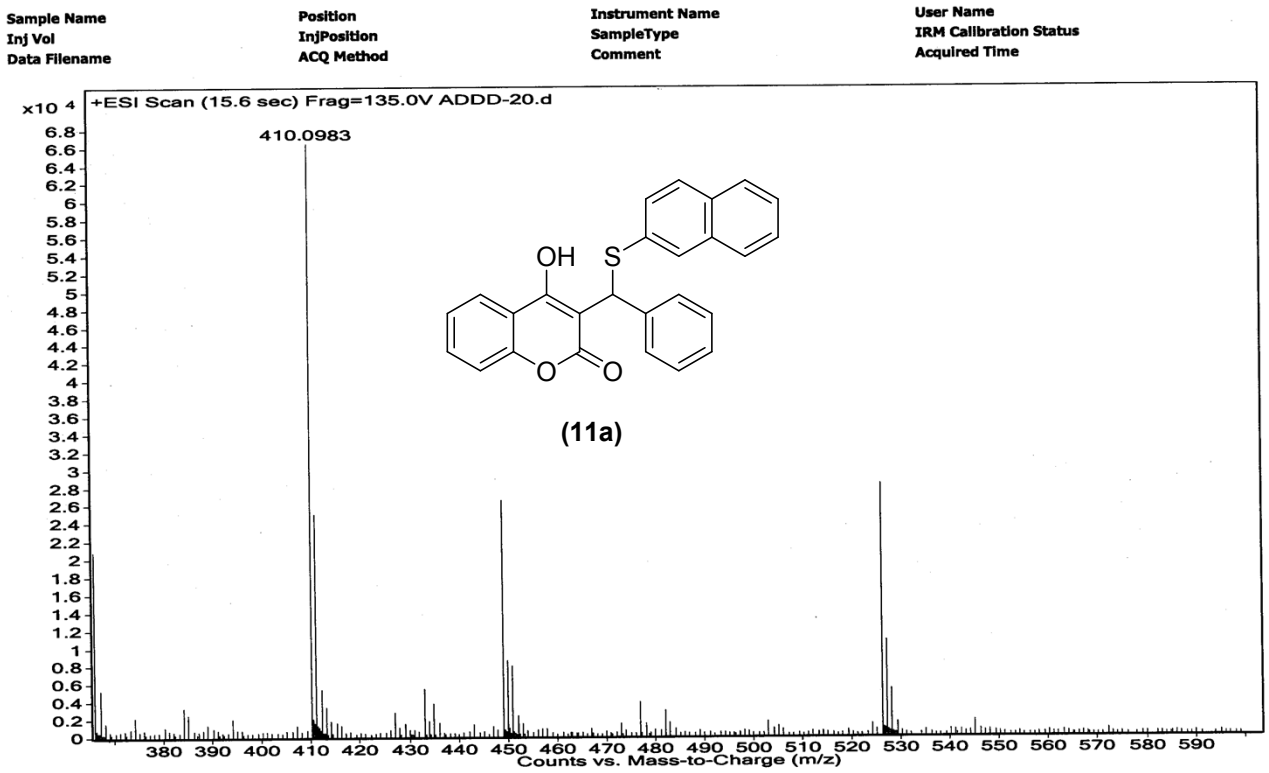
HRMS (ESI) spectra *: 3-(((2-chlorophenyl)thio)(phenyl)methyl)-4-hydroxy-2H-chromen-2-one* (**9a**)



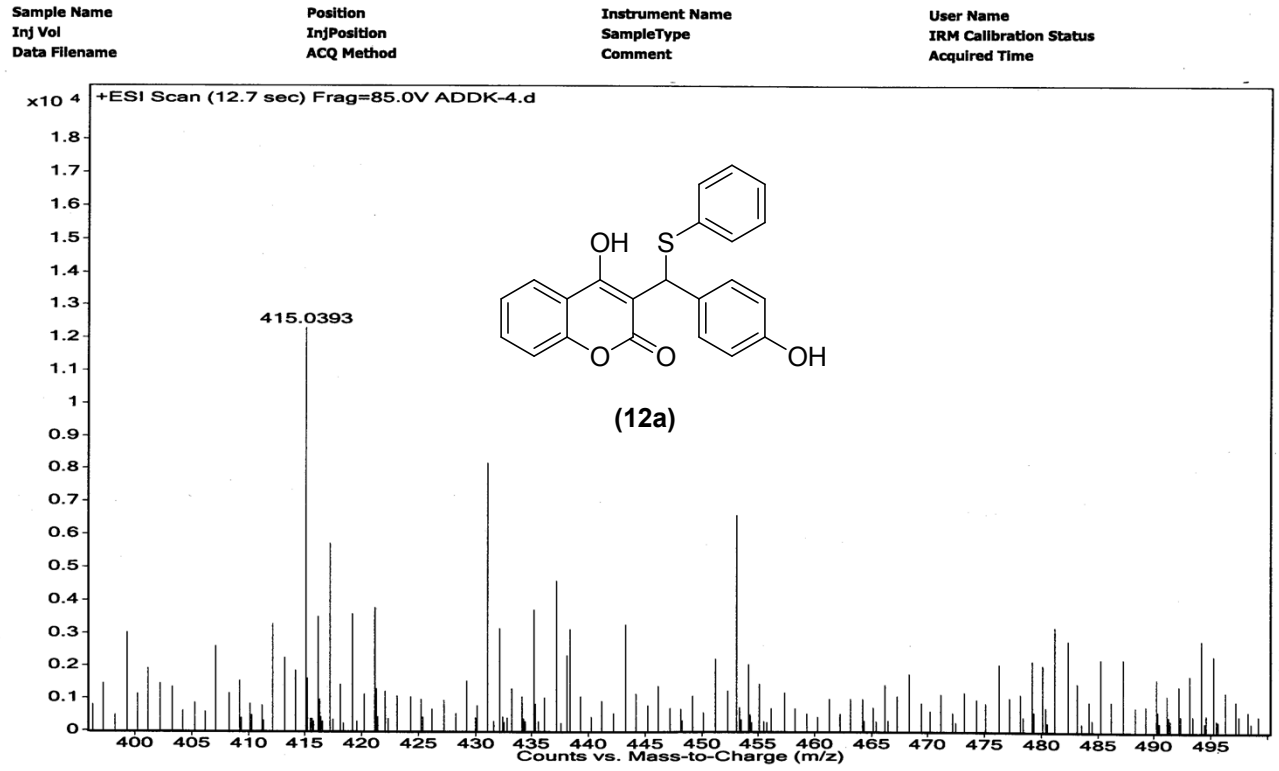
HRMS (ESI) spectra *: 3-(((2-bromophenyl)thio)(phenyl)methyl)-4-hydroxy-2H-chromen-2-one* (**10a**)



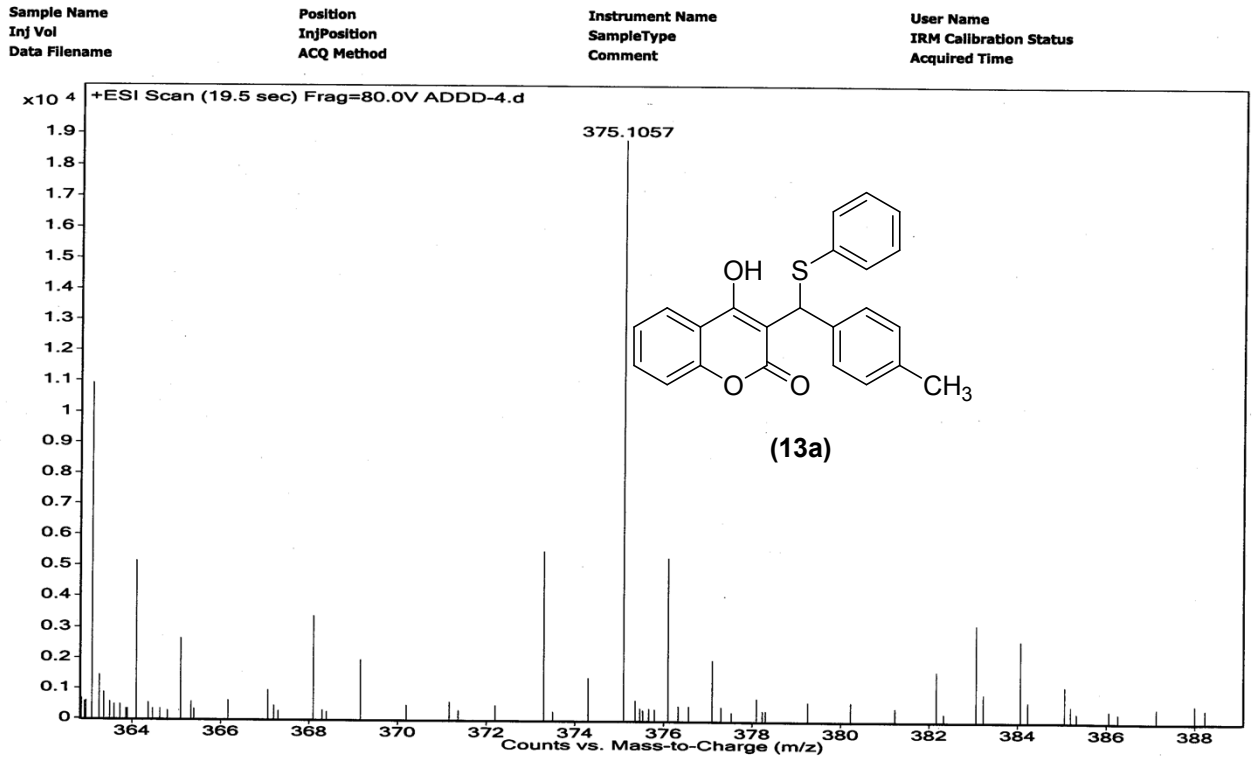
HRMS (ESI) spectra *: 4-hydroxy-3-((naphthalen-2-ylthio)(phenyl)methyl)-2H-chromen-2-one* (**11a**)



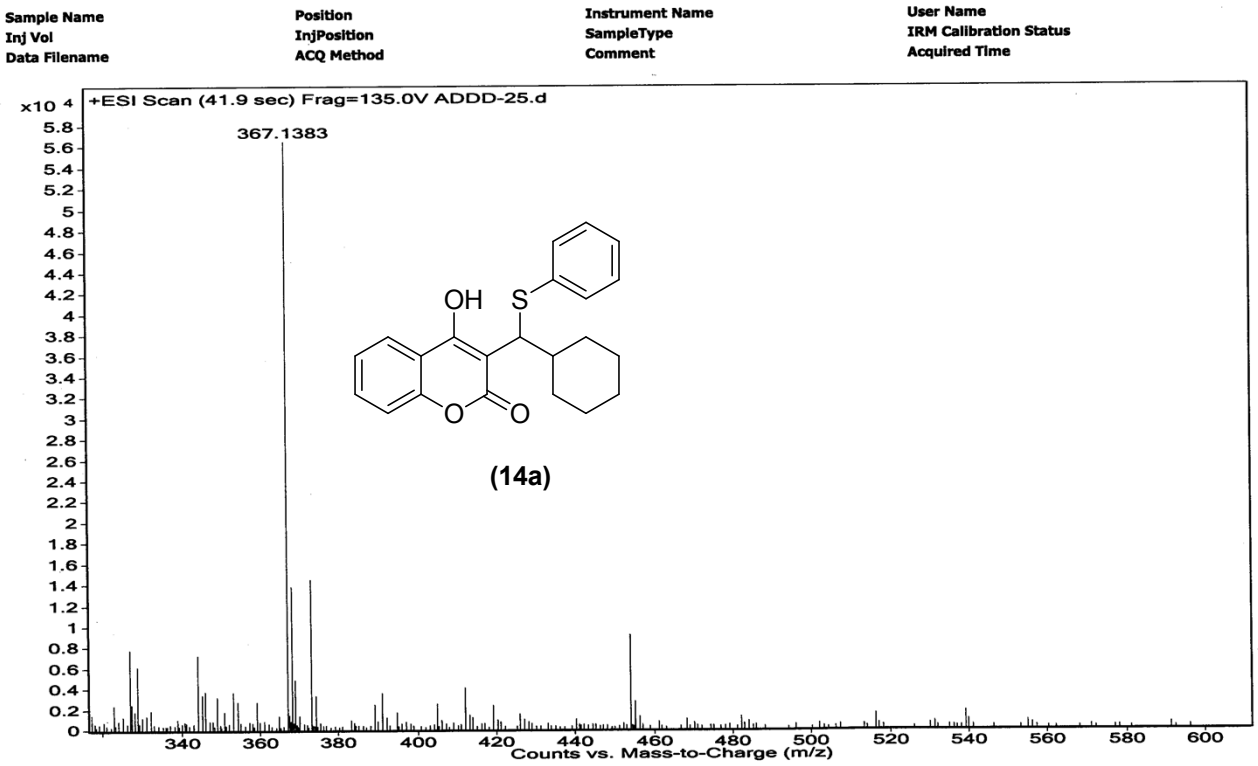
HRMS (ESI) spectra*: 4-hydroxy-3-((4-hydroxyphenyl)(phenylthio)methyl)-2H-chromen-2-one* (**12a**)



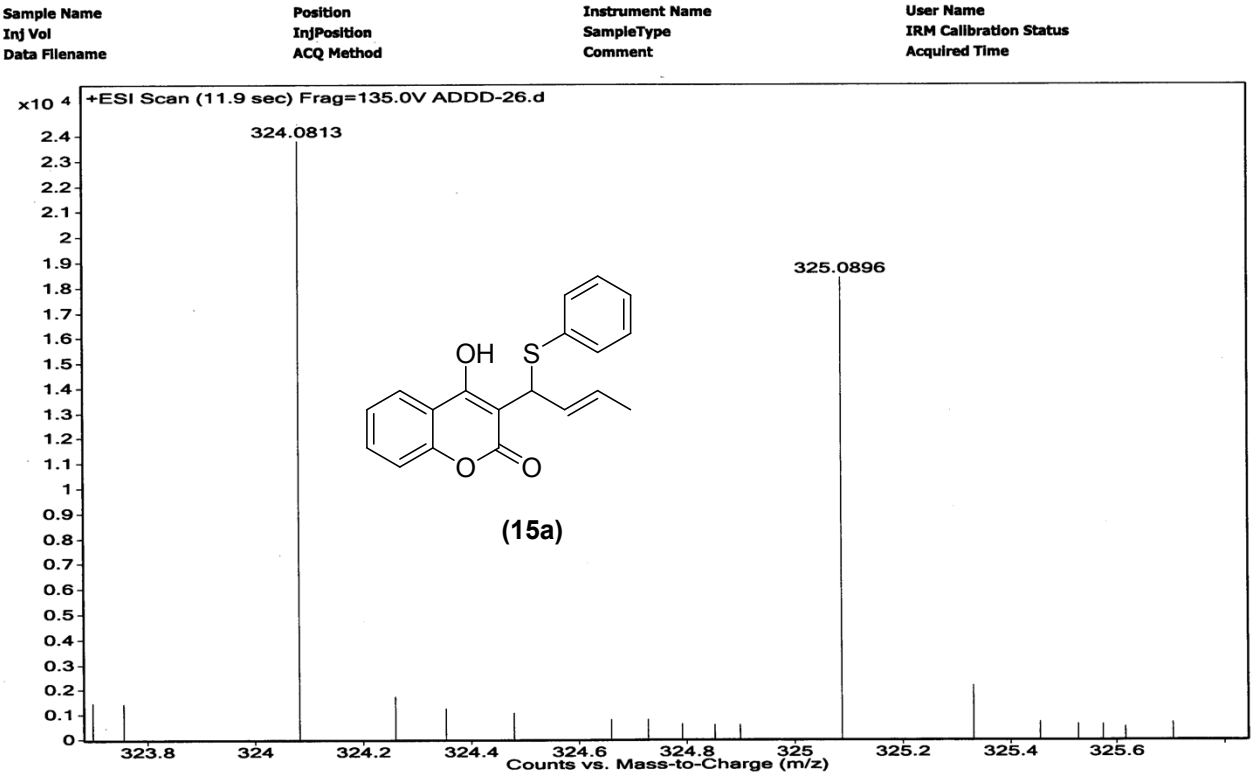
HRMS (ESI) spectra *: 4-hydroxy-3-((phenylthio)(p-tolyl)methyl)-2H-chromen-2-one* (**13a**)



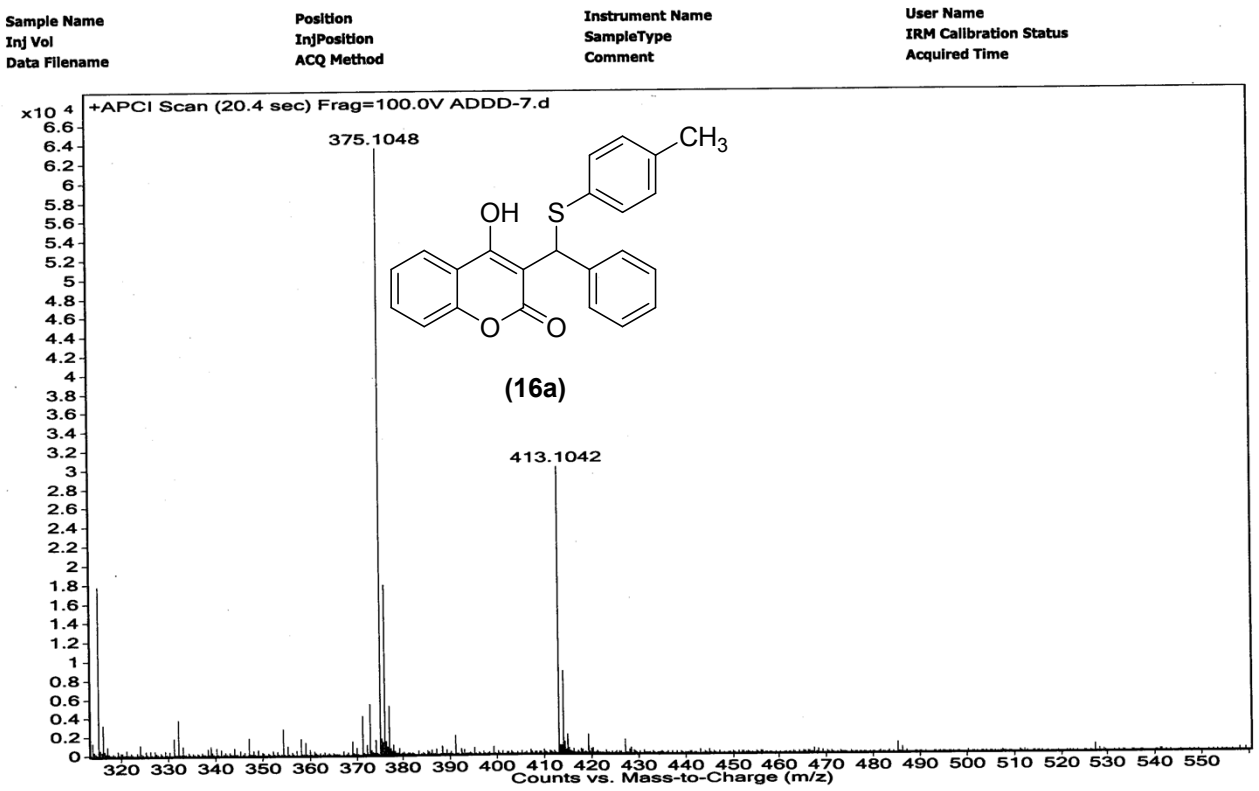
HRMS (ESI) spectra *: 3-(cyclohexyl(phenylthio)methyl)-4-hydroxy-2H-chromen-2-one* (**14a**)



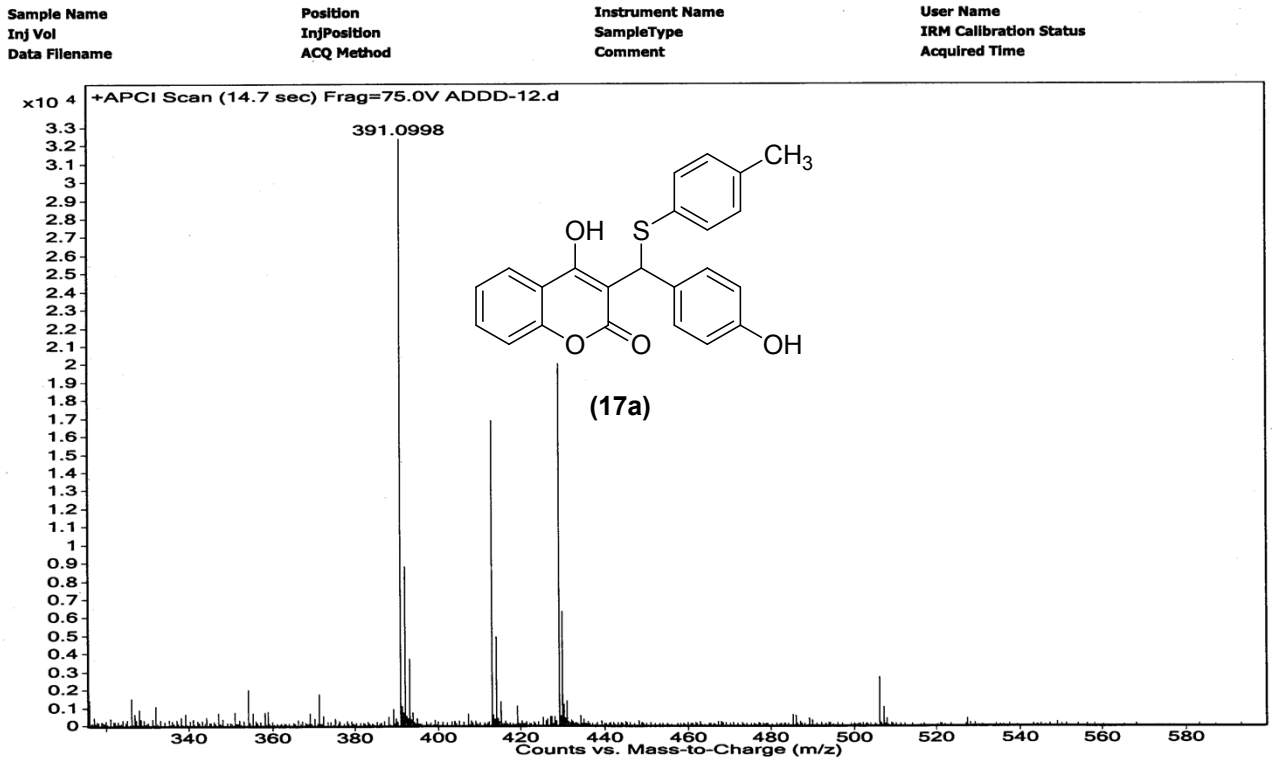
HRMS (ESI) spectra *: (E)-4-hydroxy-3-(1-(phenylthio)but-2-en-1-yl)-2H-chromen-2-one* (**15a**)



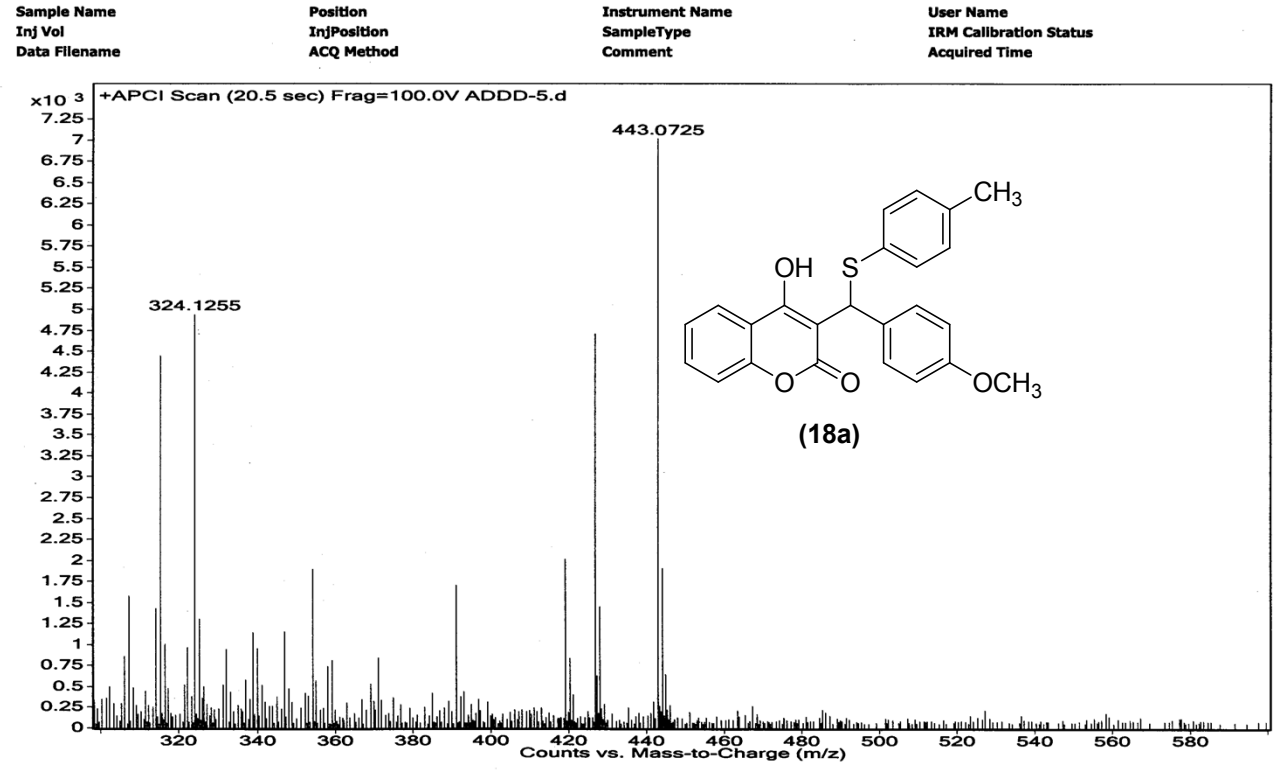
HRMS (APCI) spectra *: 4-hydroxy-3-(phenyl(p-tolylthio)methyl)-2H-chromen-2-one* (**16a**)



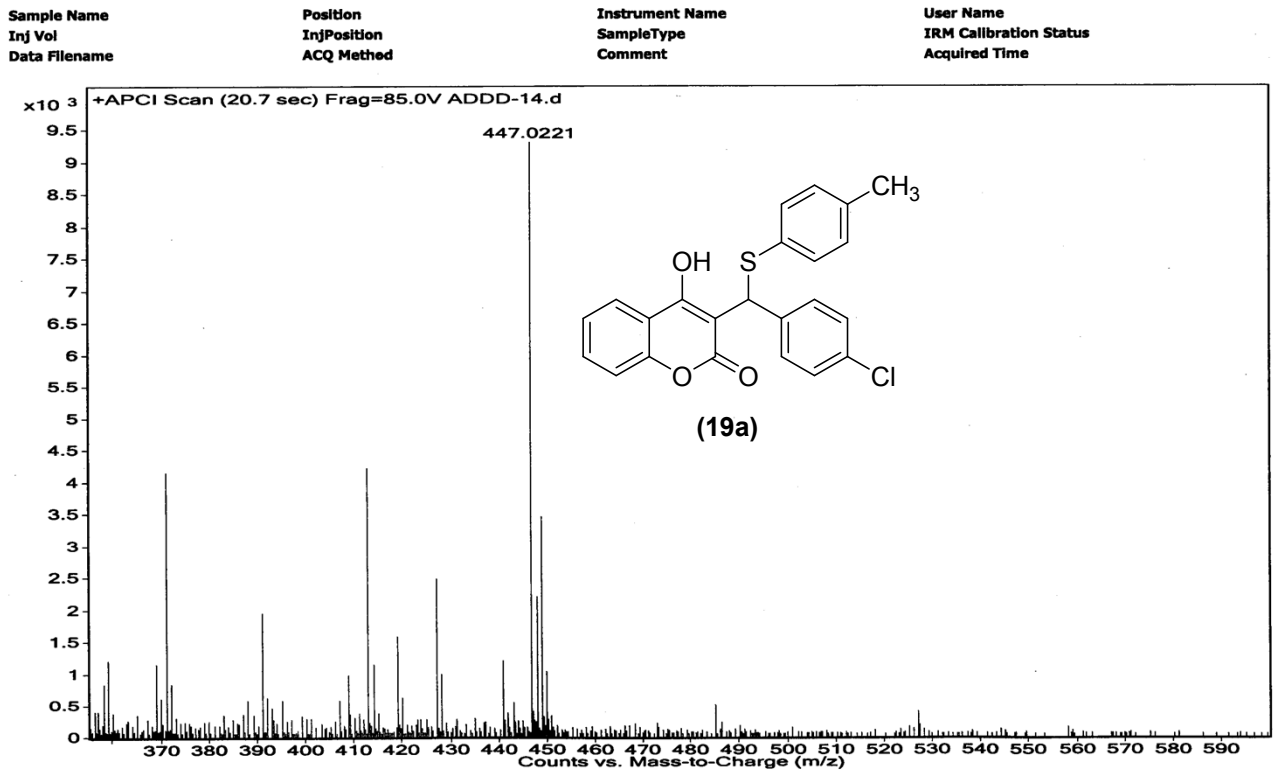
APCI-HRMS spectra *: 4-hydroxy-3-((4-hydroxyphenyl)(p-tolylthio)methyl)-2H-chromen-2-one* (**17a**)



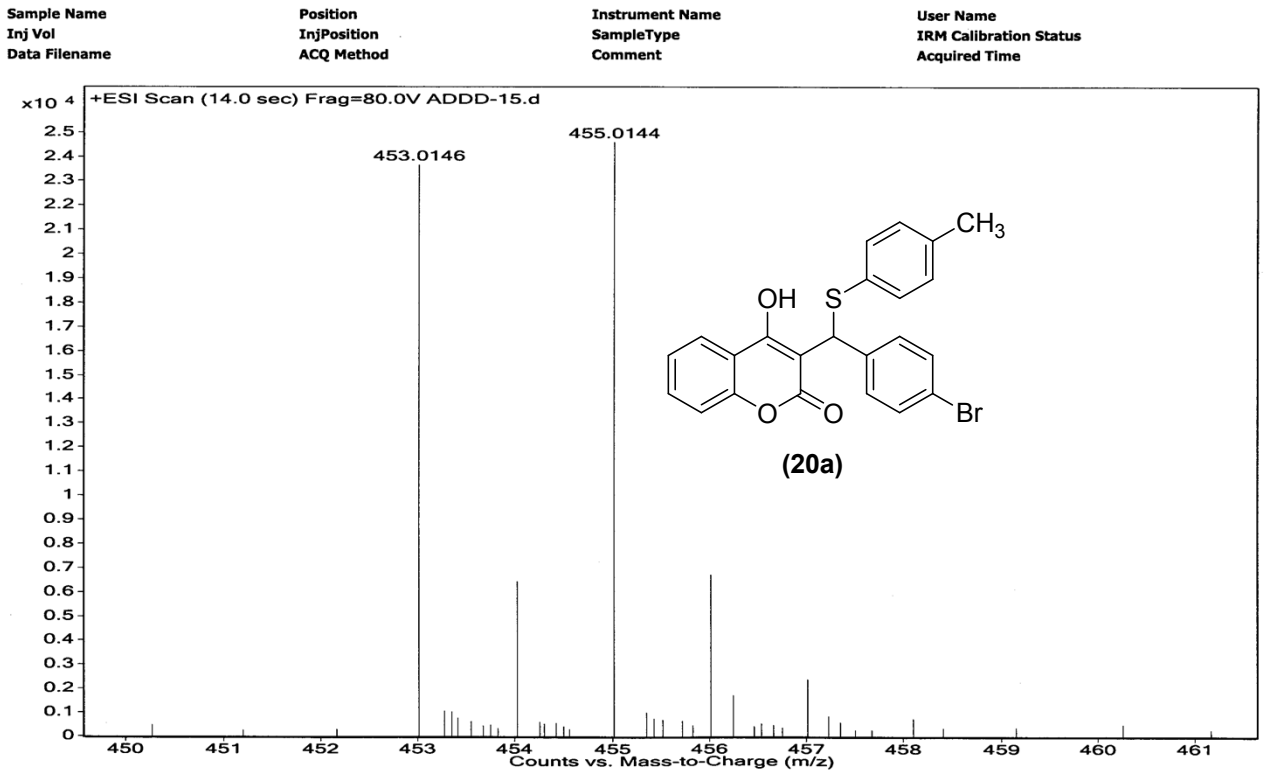
HRMS (APCI) spectra *: 4-hydroxy-3-((4-methoxyphenyl)(p-tolylthio)methyl)-2H-chromen-2-one* (**18a**)



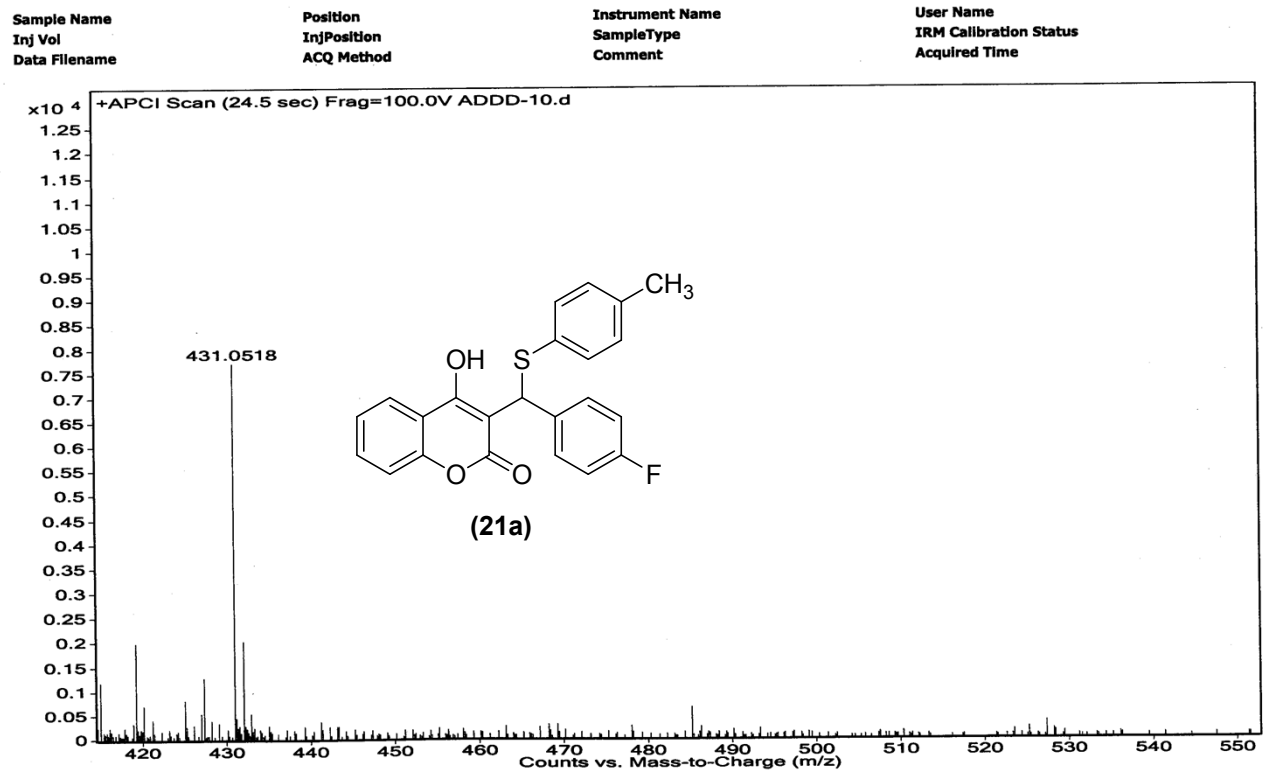
HRMS (APCI) spectra *: 3-((4-chlorophenyl)(p-tolylthio)methyl)-4-hydroxy-2H-chromen-2-one* (**19a**)



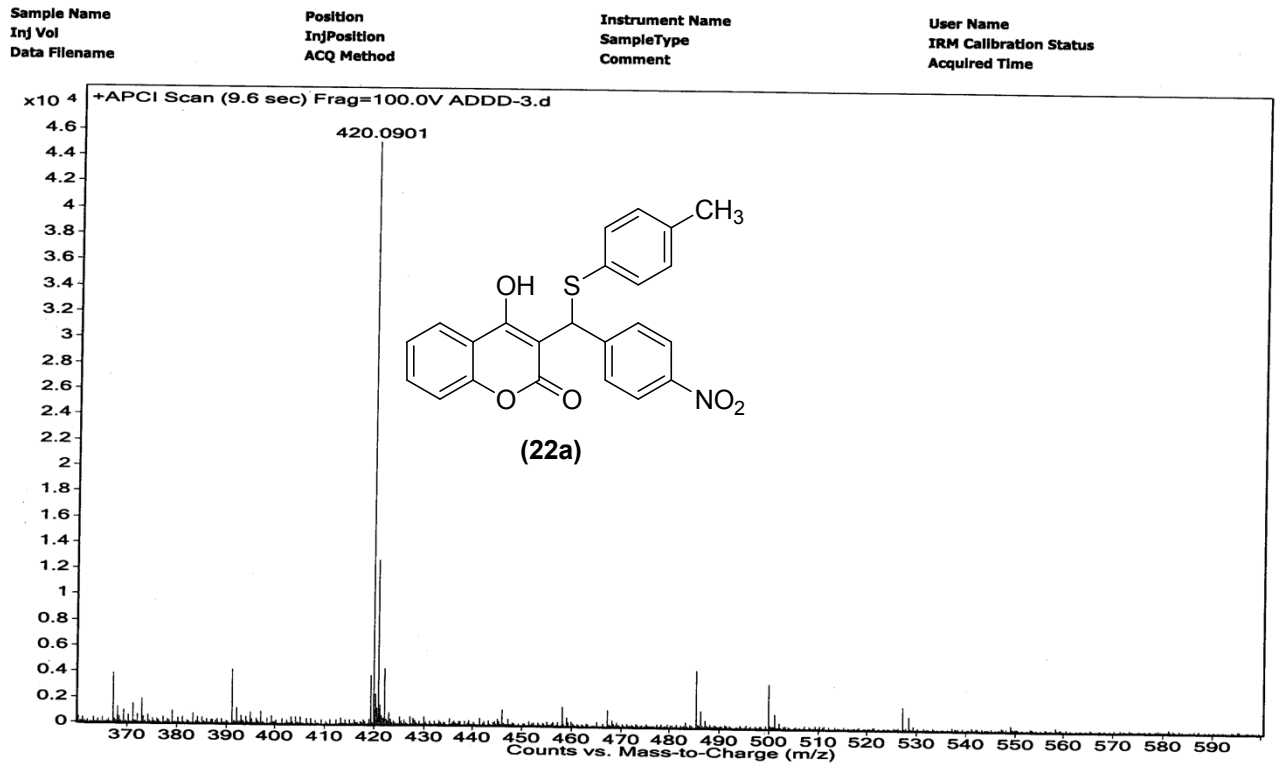
HRMS (ESI) spectra *: 3-((4-bromophenyl)(p-tolylthio)methyl)-4-hydroxy-2H-chromen-2-one* (**20a**)



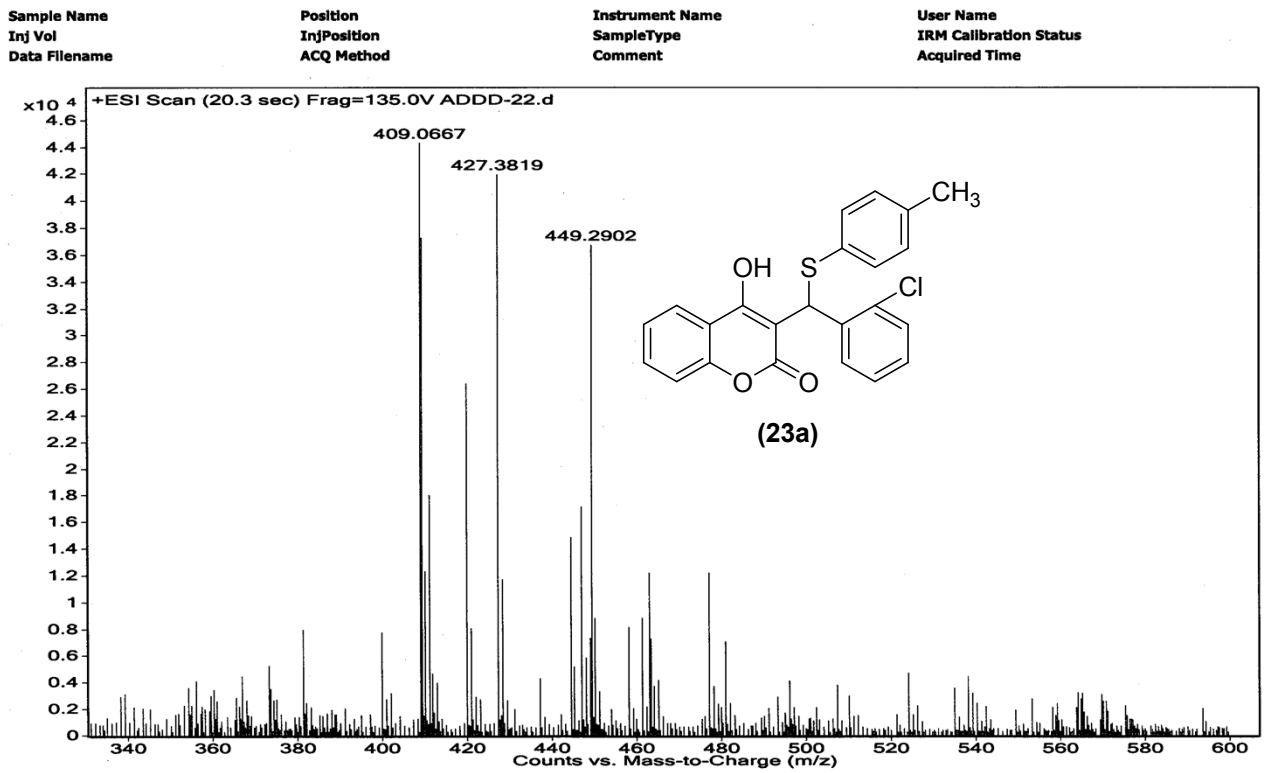
HRMS (APCI) spectra *: 3-((4-fluorophenyl)(p-tolylthio)methyl)-4-hydroxy-2H-chromen-2-one* (**21a**)



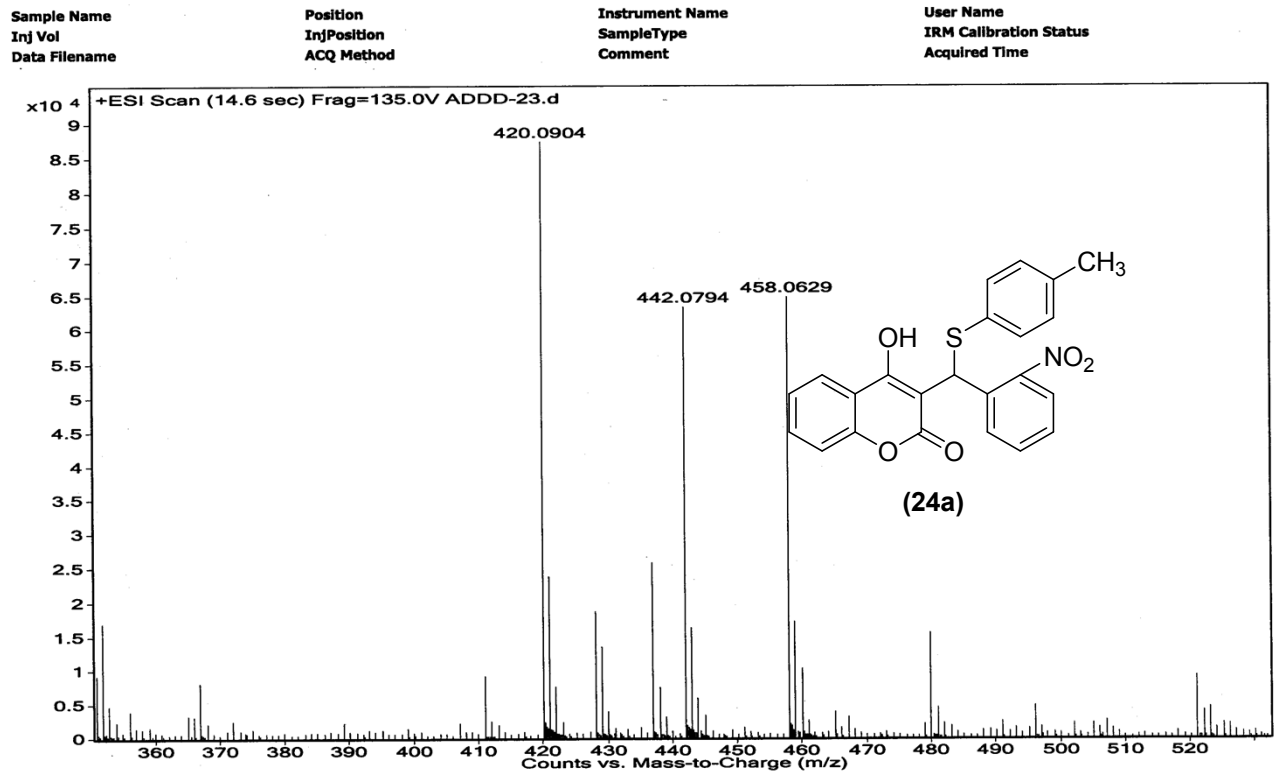
HRMS (APCI) spectra *: 4-hydroxy-3-((4-nitrophenyl)(p-tolylthio)methyl)-2H-chromen-2-one* (**22a**)



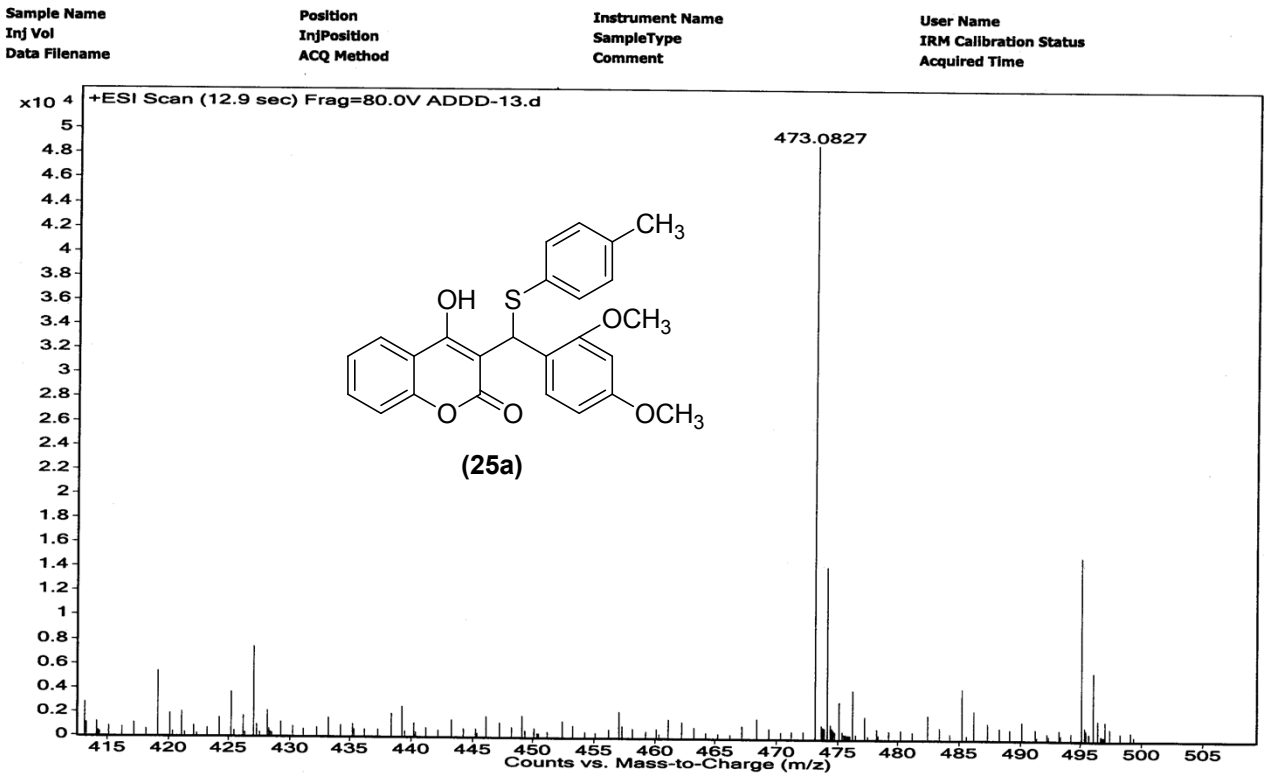
HRMS (ESI) spectra *: 3-((2-chlorophenyl)(p-tolylthio)methyl)-4-hydroxy-2H-chromen-2-one* (**23a**)



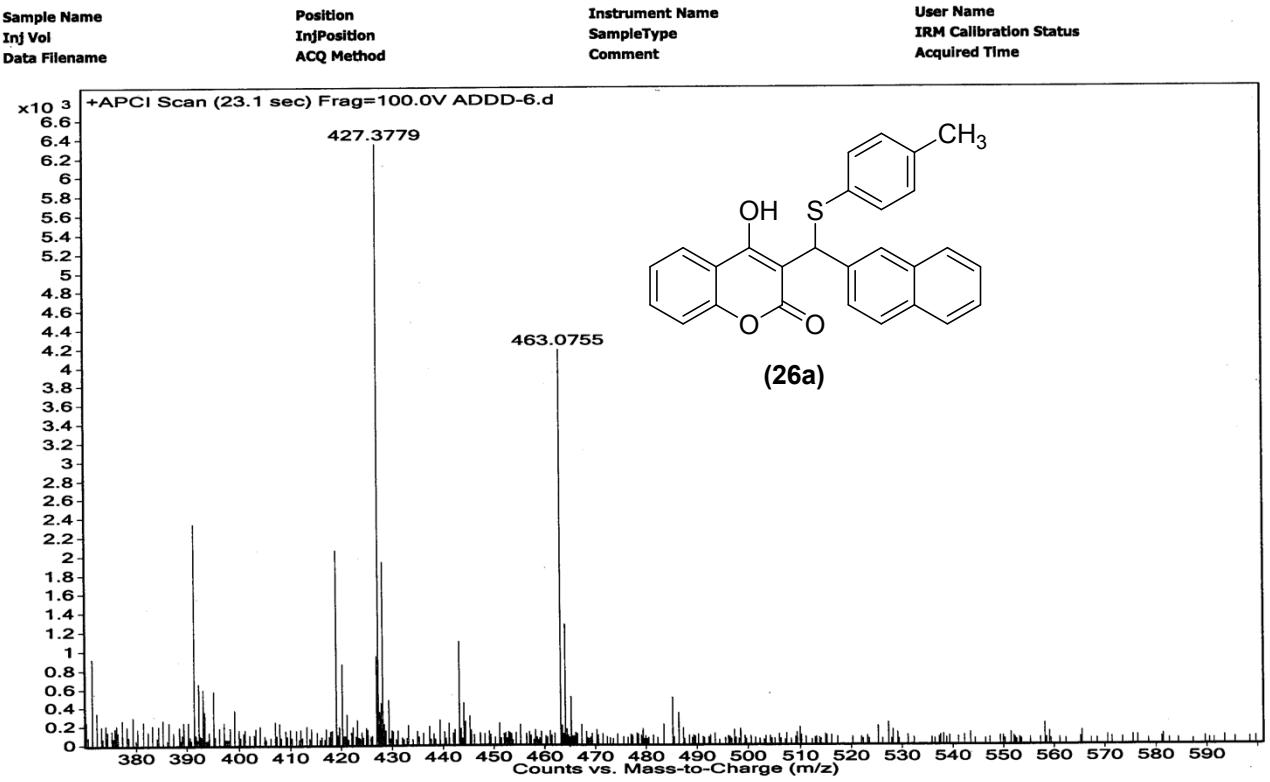
HRMS (ESI) spectra *: 4-hydroxy-3-((2-nitrophenyl)(p-tolylthio)methyl)-2H-chromen-2-one* (**24a**)



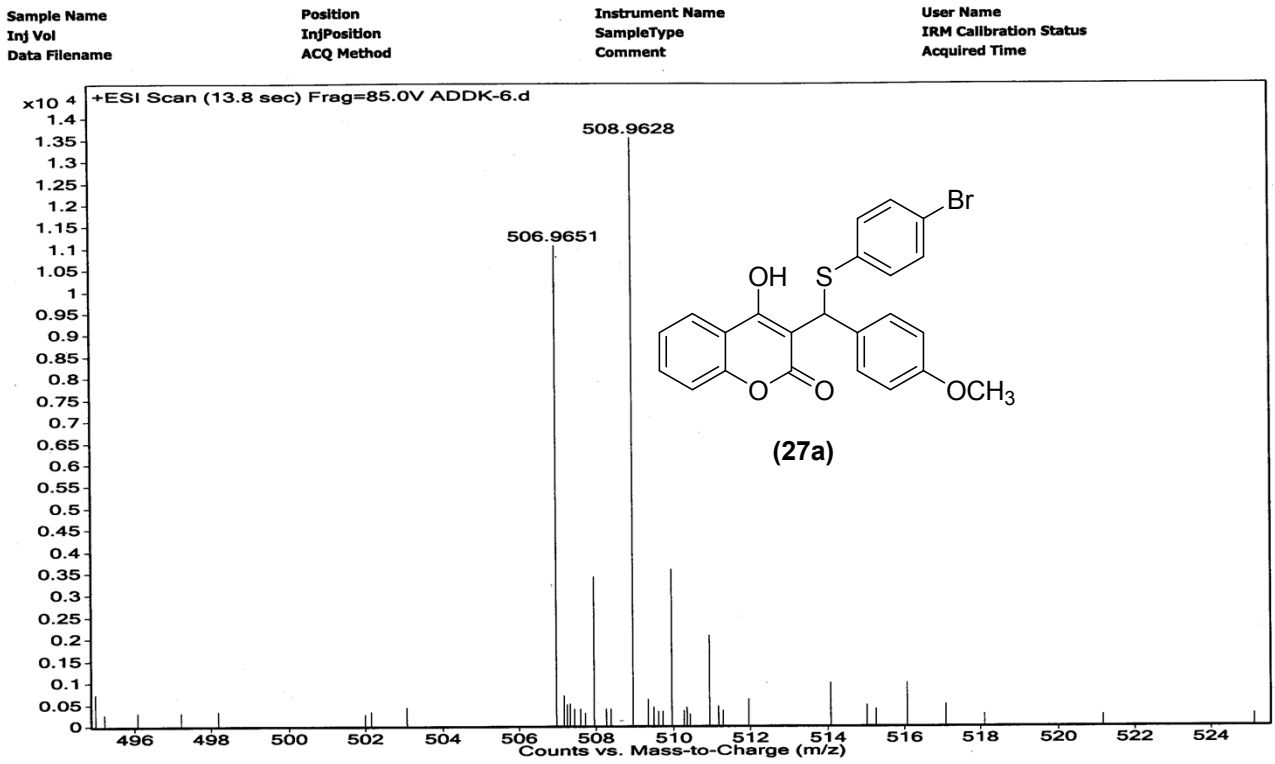
HRMS (ESI) spectra *: 3-((2,4-dimethoxyphenyl)(p-tolylthio)methyl)-4-hydroxy-2H-chromen-2-one* (**25a**)



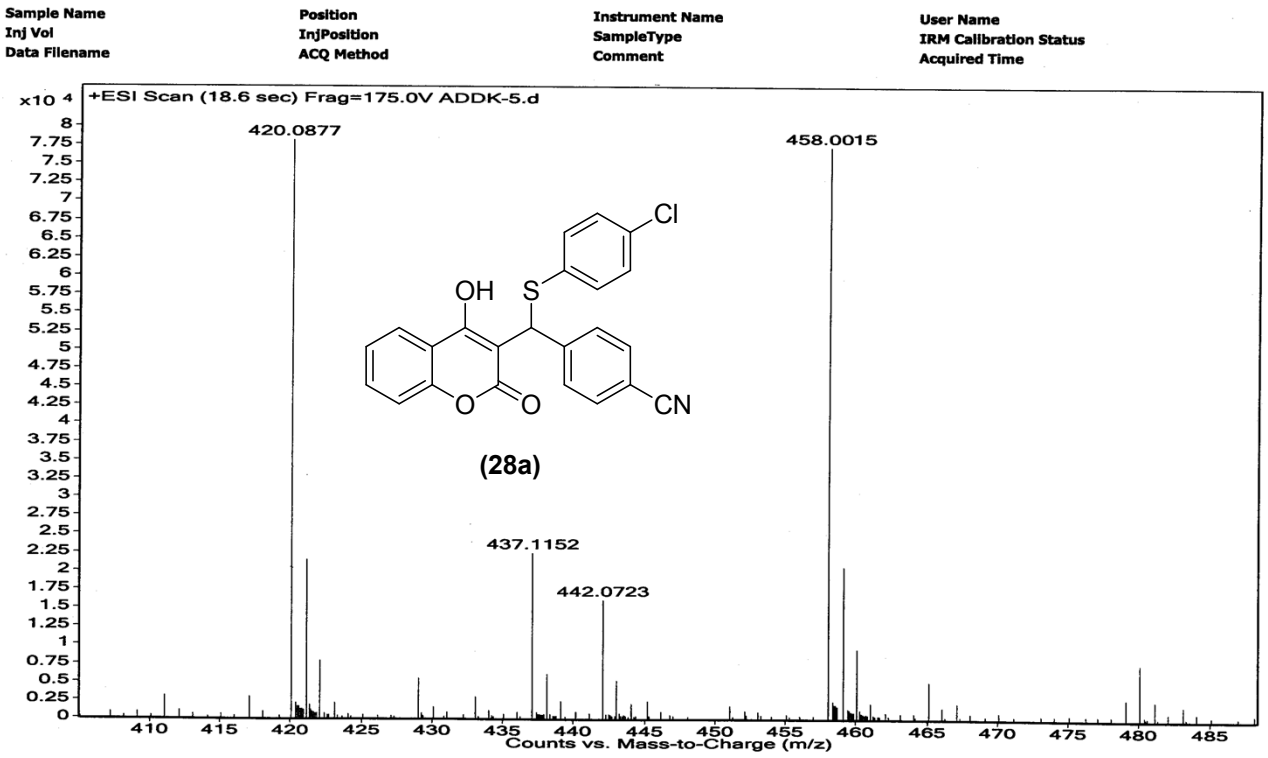
HRMS (APCI) spectra *: 4-hydroxy-3-(naphthalen-2-yl(p-tolylthio)methyl)-2H-chromen-2-one* (**26a**)



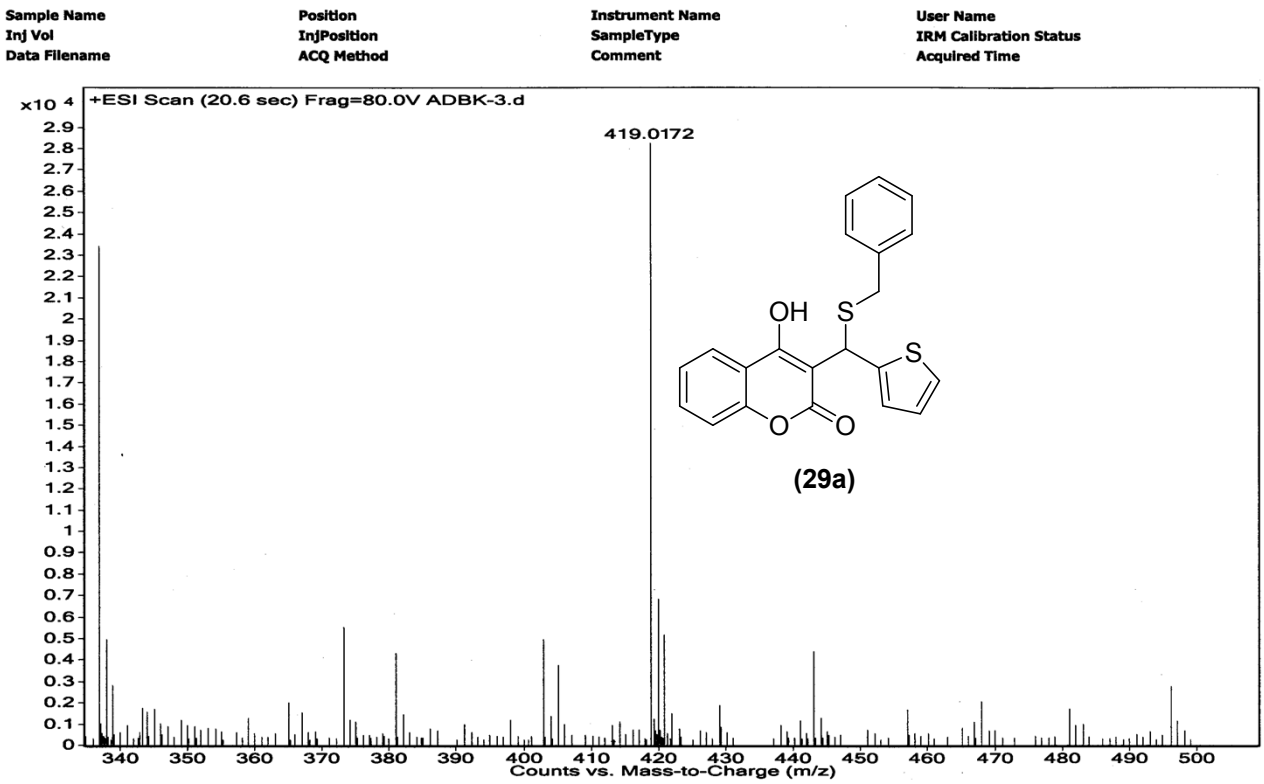
HRMS (ESI) spectra *: 3-(((4-bromophenyl)thio)(4-methoxyphenyl)methyl)-4-hydroxy-2H-chromen-2-one* (**27a**)



HRMS (ESI) spectra *: 4-(((4-chlorophenyl)thio)(4-hydroxy-2-oxo-2H-chromen-3-yl)methyl)benzonitrile* (**28a**)



HRMS (ESI) spectra *: 3-((benzylthio)(thiophen-2-yl)methyl)-4-hydroxy-2H-chromen-2-one* (**29a**)



HRMS (ESI) spectra *: 3-((ethylthio)(pyridin-2-yl)methyl)-4-hydroxy-2H-chromen-2-one* (**30a**)