'Naked-Eye' Colorimetric/Fluorimetric Detection of F^- Ion by Biologically Active 3-((1H-Indol-3-yl)methyl)-4-hydroxy-2H-chromen-2-one Derivatives

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Electronic Supplementary Information (ESI):

1. General Remarks:

1.1. Reagents and instrumentation

All common reagents and solvents were of AR grade, purchased from Sigma Aldrich and Himedia, India and used as received otherwise mentioned. The ^{1}H-NMR and ^{13}C-NMR spectra of compounds were recorded in DMSO-d_6 on a Brüker (500 MHz) spectrometer and chemical shifts were reported as part per million (ppm) in δ scale downfield from TMS (as internal standard). The following abbreviations were used to explain the multiplicities: br = broad, s = singlet, d = doublet, dd = double doublet, dt = doublet of triplet, t = triplet, q = quartrat, m = multiplet. The UV–vis. absorption spectra were recorded on a Shimadzu UV-2450 spectrophotometer and the fluorescent spectra were recorded on a Shimadzu RF-5301 PC Spectrofluorophotometer and Fluoromax–4 Spectrofluorometer with a 3.0 cm standard quartz cell. Melting points were recorded on Optimelt automated melting point system. Quantum yield were obtained by using FLS 980 Fluorescence spectrometer (Edinburgh Instruments). The IR spectra were recorded on a Nicolet 6700 FTIR Thermoscientific in the range 4000–400 cm^{-1} with KBr pellet. Fluorescence life time spectra were obtained by using HORIBA Jobin Yvon, Fluorocube Fluorescence Lifetime System.

1.2. Spectral measurements

^{1}H NMR titration experiments were carried out in the DMSO-d_6 solution (TMS as an internal standard). A 0.01 mol/L solution of the receptor **4a** in DMSO-d_6 was prepared. Then, the increased amount of fluoride anions (1.0 mol/L in DMSO-d_6) was added to the solution above-mentioned and ^{1}H NMR of the host-guest system was measured immediately.

2. General procedure for the synthesis compounds 4a–4n:

A mixture of 4-hydroxycoumarin **1** (1.0 mmol), aldehyde **2** (1.0 mmol) and indole **3** (1.0 mmol) was taken in mortar and mixed thoroughly with pestle and ground at 50–60 °C. The reaction was monitored by thin layer chromatography. After completion of reaction, the reaction mixture was cooled to room temperature and washed with ethanol and dried to obtain pure desired product.

3 Biological activities

3.1. Antibacterial assay

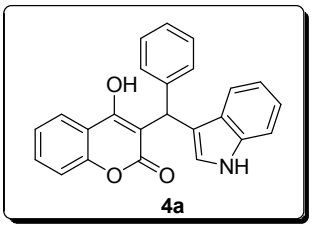
Minimum inhibitory concentration (MIC) is the lowest concentration of an antimicrobial compound that inhibits the visible growth of a microorganism. MIC values of the compounds against bacterial isolates were determined on the basis of micro-well dilution method following National committee for clinical laboratory standards (NCCLS) recommendations.[20] In this method we made stock of chemically synthesized compounds at a concentration of 10 mg/ml in DMSO, which was further converted to working solution of concentration 1.0 mg/ml. Using a micropipette, 100 µl of media into all wells of pre-sterilized microtitre plate was dispensed (experiment was done in triplicate). Two fold serial dilutions (100, 50, 25…, 0.78125 mg/mL) were carried out from the well # 1 to the well # 10 and excess media (100 µl) was discarded from the last well (# 10). Liquid broth culture of test organism was grown to log phase in Luria Bertani broth (LB broth) for 24 h at 37 °C. The optical density of liquid culture was determined at 600 nm and diluted in such a way that each well received 107 cfu/ml of bacterial culture. Appropriate positive and negative control was also included in the study. Positive control contained only microbial cells whereas negative control contained only standard drug solution (Ampicillin and Cefadroxil). All experimental procedures were performed under sterile condition using bio-safety hood and microtitre plates were incubated at 37 °C for 24 h.

3.2. Antifungal assay

MIC of standard antifungal drugs viz. Fluconazole and the synthesized compounds against fungal isolates were determined by the broth micro dilution method as described by the NCCLS, 1997. Liquid broth culture of test organism was grown to a suitable phase in Yeast, Peptone, and D-Glucose (YPD) media for 48 h at 30 °C. The optical density of liquid culture was determined at 600 nm and diluted in such a way that each well received 104 cfu/ml of fungal suspension. The further procedure was similar to above mentioned antibacterial assay.

4. Spectral data of all the compounds:

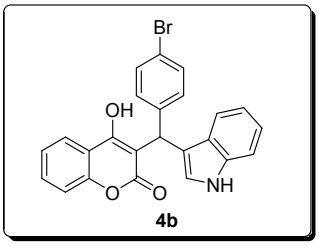
3-((1*H*-Indol-3-yl)(phenyl)methyl)-4-hydroxy-2*H*-chromene-2-one (4a):



4a

Yield: 323 mg (88%) as white solid; MP = 191 °C; IR ν_{max} (KBr, cm^{-1}): 3417, 3345, 2940, 2830, 1689, 1621, 1563, 1417, 1278, 943, 758; ^{1}H-NMR (DMSO-d_6, 500 MHz) δ (ppm): 11.6 (s, broad, D_2O exchangeable, 1H), 10.9 (s, D_2O exchangeable, 1H), 8.02 (d, J = 7.5 Hz, 1H), 7.60 (t, J = 7.0 Hz, 1H), 7.37-7.28 (m, 7H), 7.10–7.03 (m, 4H), 6.90 (t, J = 7.5 Hz, 1H); 6.08 (s, 1H); ^{13}C-NMR [125 MHz (DMSO-d_6)] δ (ppm): 162.2, 160.7, 152.6, 143.1, 136.4, 132.3, 128.6, 128.2, 127.7, 126.1, 124.7, 124.3, 123.9, 121.3, 118.9, 118.7, 116.7, 116.6, 114.6, 111.9, 108.9, 37.5.

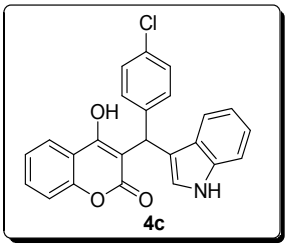
3-((4-Bromophenyl)(1*H*-indol-3-yl)(phenyl)methyl)-4-hydroxy-2*H*-chromene-2-one (4b):



4b

Yield: 378 mg (85%) as white solid; MP = 198 °C; IR ν_{max} (KBr, cm^{-1}): 3447, 3369, 2937, 2827, 1684, 1626, 1550, 1426, 1278, 944, 752; ^{1}H-NMR (DMSO-d_6, 500 MHz) δ (ppm): 10.9 (s, D_2O exchangeable, 1H), 8.02 (d, J = 7.5 Hz, 1H), 7.62 (t, J = 7.5 Hz, 1H), 7.40-7.34 (m, 3H), 7.32-7.27 (m, 5H), 7.12 (s, 1H), 7.06 (t, J = 7.5 Hz, 1H), 6.92 (t, J = 7.5 Hz, 1H), 6.08 (s, 1H); ^{13}C-NMR [125 MHz (DMSO-d_6)] δ (ppm): 161.1, 159.9, 151.6, 141.2, 135.4, 131.3, 129.6, 129.4, 127.0, 126.5, 123.7, 123.2, 122.9, 120.3, 117.9, 117.8, 115.7, 115.6, 113.0, 110.9, 107.6, 35.9.

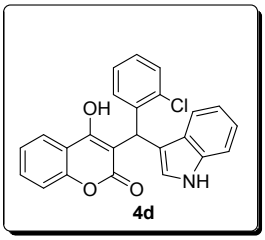
((4-Chlorophenyl)(1*H*-indol-3-yl)methyl)-4-hydroxy-2*H*-chromene-2-one (4c):



4c

Yield: 345 mg (86%) as white solid; MP = 187 °C; IR ν_{max} (KBr, cm^{-1}): 3417, 3321, 2961, 2839, 1673, 1627, 1413, 1278, 756; ^{1}H-NMR (DMSO-d_6, 500 MHz) δ (ppm): 11.7 (s, broad, D_2O exchangeable, 1H), 10.9 (s, D_2O exchangeable, 1H), 8.02 (d, J = 7.5 Hz, 1H), 7.61 (t, J = 7.5 Hz, 1H), 7.42–7.26 (m, 8H), 7.14 (d, J = 2.0 Hz, 1H), 7.06 (t, J = 7.5 Hz, 1H), 6.93 (t, J = 7.5 Hz, 1H), 6.10 (s, 1H); ^{13}C-NMR [125 MHz (DMSO-d_6)] δ (ppm): 162.2, 160.9, 152.6, 142.3, 136.4, 132.4, 130.6, 130.4, 128.0, 127.5, 124.8, 124.2, 123.9, 121.3, 118.9, 118.8, 116.7, 116.6, 114.0, 111.9, 108.6, 36.9.

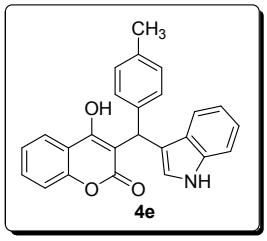
3-((2-Chlorophenyl)(1*H*-indol-3-yl)methyl)-4-hydroxy-2*H*-chromene-2-one (4d):



4d

Yield: 341 mg (85%) as white solid; MP = 181 °C; IR ν_{max} (KBr, cm^{-1}): 3447, 3345, 2960, 2824, 1676, 1624, 1556, 1496, 1428, 1339, 1030, 934, 751; ^{1}H-NMR (DMSO-d_6, 500 MHz) δ (ppm): 11.6 (s, broad, D_2O exchangeable, 1H), 10.9 (s, D_2O exchangeable, 1H), 8.02 (dd, *J* = 1.5, 8.5 Hz, 1H), 7.61 (dt, *J* = 1.5, 8.0 Hz, 1H), 7.39–7.34 (m, 3H), 7.33–7.28 (m, 3H), 7.24 (t, *J* = 7.5 Hz, 2H), 7.16 (t, *J* = 7.5 Hz, 1H), 7.05 (dt, *J* = 1.0, 7.5 Hz, 1H), 6.91 (t, *J* = 7.5 Hz, 1H), 6.10 (s, 1H); ^{13}C-NMR [125 MHz (DMSO-d_6)] δ (ppm): 162.2, 160.7, 152.6, 140.1, 136.5, 135.0, 132.3, 128.8, 128.6, 127.8, 124.7, 124.3, 123.9, 121.3, 119.0, 118.8, 116.8, 116.7, 114.8, 111.9, 109.2, 37.2.

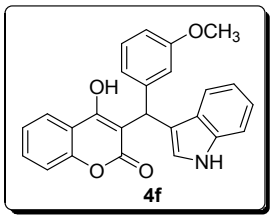
3-((1*H*-Indol-3-yl)(*p*-tolyl)methyl)-4-hydroxy-2*H*-chromene-2-one (4e):



4e

Yield: 90% (343 mg) as white solid; MP = 171 °C; IR ν_{max} (KBr, cm^{-1}): 3457, 3329, 2951, 2828, 1688, 1623, 1564, 1421, 1286, 755; ^{1}H-NMR (DMSO-d_6, 500 MHz) δ (ppm): 11.5 (s, broad, D_2O exchangeable, 1H), 10.9 (s, D_2O exchangeable, 1H), 8.02 (d, *J* = 7.5 Hz, 1H), 7.59 (t, *J* = 7.5 Hz, 1H), 7.41–7.31 (m, 4H), 7.25–7.20 (m, 2H), 7.12 (s, 1H), 7.09–7.04 (m, 3H), 6.91 (t, *J* = 7.5 Hz, 1H), 6.08 (s, 1H), 2.25 (s, 3H); ^{13}C-NMR [125 MHz (DMSO-d_6)] δ (ppm): 162.2, 160.6, 152.6, 140.0, 136.4, 135.0, 132.3, 128.7, 128.5, 127.7, 124.7, 124.2, 123.8, 121.2, 118.9, 118.7, 116.7, 116.6, 114.7, 111.9, 109.1, 37.2, 21.0.

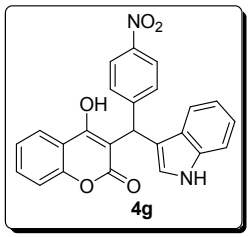
3-((1*H*-Indol-3-yl)(3-methoxyphenyl)methyl)-4-hydroxy-2*H*-chromen-2-one (4f):



4f

Yield: 333 mg (84%) as white solid; MP = 185 °C; IR ν_{max} (KBr, cm^{-1}): 3404, 3342, 2962, 2840, 1700, 1609, 1556, 1495, 1273, 1148, 750; ^{1}H-NMR (DMSO-d_6, 500 MHz) δ (ppm): 11.6 (s, broad, D_2O exchangeable, 1H), 10.9 (s, D_2O exchangeable, 1H), 8.03 (d, *J* = 7.5 Hz, 1H), 7.60 (t, *J* = 7.0 Hz, 1H), 7.42-7.33 (m, 4H), 7.18 (t, *J* = 8.0 Hz, 1H), 7.10 (d, *J* = 2.0 Hz, 1H), 7.06 (t, *J* = 7.5 Hz, 1H), 6.92 (t, *J* = 7.5 Hz, 2H), 6.86 (s, 1H), 6.76 (dd, *J* = 2.0, 7.0 Hz, 1H), 6.08 (s, 1H), 3.66 (s, 3H); ^{13}C-NMR [125 MHz (DMSO-d_6)] δ (ppm): 161.3, 159.7, 151.6, 139.1, 135.5, 134.0, 131.3, 127.8, 127.6, 126.8, 123.8, 123.3, 122.9, 120.3, 118.0, 117.8, 115.8, 115.7, 113.8, 110.9, 108.2, 55.6, 37.0.

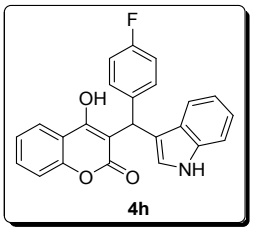
3-((1*H*-Indol-3-yl)(4-nitrophenyl)methyl)-4-hydroxy-2*H*-chromen-2-one (4g):



4g

Yield: 350 mg (85%) as white solid; MP = 199 °C; IR ν_{max} (KBr, cm^{-1}): 3454, 3324, 2940, 2824, 1688, 1623, 1413, 1339, 1243, 1108, 754; ^{1}H-NMR (DMSO-d_6, 500 MHz) δ (ppm): 11.0 (s, broad, D_2O exchangeable, 1H), 8.12,(dd, *J* = 11.0 Hz, 1H),8.04 (dd, *J* = 1.0, 7.5 Hz, 1H) 7.63 (dt, *J* = 1.5, 8.5 Hz, 1H), 7.50 (d, *J* = 8.5 Hz, 2H), 7.41–7.36 (m, 3H), 7.33 (d, *J* = 8.0 Hz, 1H), 7.20 (d, *J* = 2.0 Hz, 1H), 7.08 (dt, *J* = 0.5, 7.5 Hz, 1H), 6.94 (dt, *J* = 1.0, 8.0 Hz, 1H), 6.21 (s, 1H); ^{13}C-NMR [125 MHz (DMSO-d_6)] δ (ppm):162.3, 161.4, 153.7, 152.9, 146.1, 136.4, 132.5, 129.7, 127.4, 125.0, 124.3, 124.0, 123.3, 121.5, 119.0, 118.8, 116.7, 116.6, 113.3, 112.1, 108.1, 37.5.

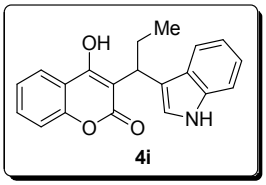
3-((4-Fluorophenyl) (1*H*-indol-3-yl) methyl)-4-hydroxy-2*H*-chromen-2-one (4h):



4h

Yield: 338 mg (88%) as pinkish white solid; MP = 191 °C; IR ν_{max} (KBr, cm^{-1}): 3452, 3354, 2980, 2841, 1622, 1552, 1469, 1382, 1195, 749; ^{1}H-NMR (DMSO-d_6, 500 MHz) δ (ppm): 11.6 (s, broad, D_2O exchangeable, 1H), 10.9 (s, D_2O exchangeable, 1H), 8.02 (d, *J* = 7.5, Hz, 1H), 7.60 (t, *J* = 7.0 Hz, 1H), 7.42–7.27 (m, 6H), 7.13–7.02 (m, 4H), 6.90 (t, *J* = 7.5 Hz, 1H), 6.08 (s, 1H); ^{13}C-NMR [125 MHz (DMSO-d_6)] δ (ppm): 162.2, 162.0, 160.8, 160.0, 152.7, 139.2, 136.5, 132.3, 130.5, 130.4, 127.6, 124.7, 124.2, 123.9, 121.3, 118.9, 118.8, 116.7, 116.6, 114.8, 114.7, 114.6, 111.9, 108.8, 37.0.

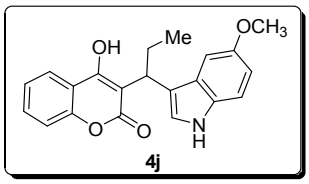
3-(-1-(1*H*-Indol-3-yl)propyl)-4-hydroxy-2*H*-chromen-2-one (4i):



4i

Yield: 303 mg (95%) as white solid; MP = 166 °C; IR ν_{max} (KBr, cm^{-1}): 3434, 3329, 2962, 2820, 1633, 1552, 1413, 1217, 1143, 1100, 747; ^{1}H-NMR [500 MHz (DMSO-d_6)] δ (ppm): 11.4 (s, broad, D_2O exchangeable, 1H), 10.8 (s, D_2O exchangeable, 1H), 8.01(dd, *J* = 1.5, 8.0 Hz, 1H), 7.57 (dt, *J* = 1.5, 8.5, Hz, 1H), 7.47 (d, *J* = 8.0, Hz, 1H), 7.34 (t, *J* = 7.5 Hz, 1H), 7.33–7.28 (m, 2H), 7.26 (d, *J* = 2.0 Hz, 1H), 6.99 (dt, *J* = 0.5, 7.5 Hz, 1H), 6.88 (dt, *J* = 0.5, 7.5 Hz, 1H), 4.58 (dd, *J* = 1.0, 9.0 Hz, 1H), 2.40–2.37 (m, 1H), 2.36–2.34 (m, 1H), 0.95 (t, *J* = 5.0, 3H); ^{13}C-NMR [125 MHz (DMSO-d_6)] δ (ppm): 161.7, 160.2, 152.5, 136.3, 131.9, 127.6, 124.1, 123.8, 123.3, 121.0, 118.7, 118.6, 116.7, 116.5, 111.8, 108.4, 79.62, 33.8, 24.6, 13.1.

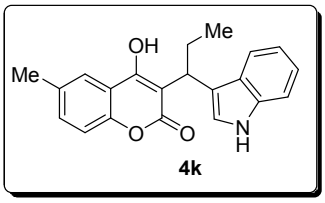
4-Hydroxy-3-(1-(5-methoxy-1*H*-indol-3yl)propyl)-2*H*-chromen-2-one (4j):



4j

Yield: 328 mg (94%) as white solid; MP = 171 °C; IR ν_{max} (KBr, cm^{-1}): 3467, 3342, 2981, 2830, 1660, 1631, 1556, 1469, 1382, 1217, 1152, 1108, 778; ^{1}H-NMR [500 MHz (DMSO-d_6)] δ (ppm): 11.4 (s, broad, D_2O exchangeable, 1H), 10.6 (s, D_2O exchangeable, 1H), 8.02 (dd, *J* = 1.5, 8.0 Hz, 1H), 7.57 (dt, *J* = 1.5, 8.5 Hz, 1H), 7.34 (dt, *J* = 1.0, 8.0 Hz, 1H), 7.31 (dd, *J* = 1.0, 8.5 Hz, 1H), 7.22 (d, *J* = 2.0, 1H) 7.18 (d, *J* = 9.0 Hz, 1H), 7.0 (d, *J* = 2.5 Hz, 1H), 6.66 (dd, *J* = 2.5, 8.5 Hz, 1H) 4.53 (dd, *J* = 6.0, 9.5 Hz, 1H), 3.36 (s, 3H), 2.42–2.33 (m, 1H), 2.18–2.08 (m, 1H), 0.93 (t, *J* = 7.0, 3H); ^{13}C-NMR [125 MHz (DMSO-d_6)] δ (ppm): 161.7, 160.2, 153.1, 152.4, 132.0, 131.4, 127.8, 124.1, 124.0, 123.7, 116.6, 116.4, 116.1, 112.3, 110.6, 108.1, 101.0, 55.6, 33.8, 24.3, 13.0.

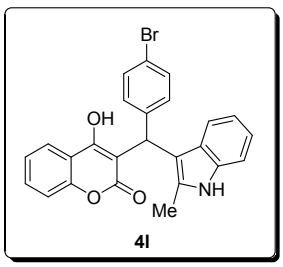
3-(1-(1*H*-Indol-3yl)propyl)-4hydroxy-6-methyl-2*H*-chromen-2-one (4k):



4k

Yield: 90% (300 mg), as white solid, MP: 179 °C; IR ν_{max} (KBr, cm^{-1}): 3430, 3340, 2967, 2841, 1675, 1621, 1563, 1447, 1391, 1286, 1211, 1157, 1113, 800, 753; ^{1}H-NMR (DMSO-d_6, 500 MHz) δ (ppm): 11.4 (s, broad, D_2O exchangeable, 1H), 10.6 (s, D_2O exchangeable, 1H), 8.02 (dd, *J* = 1.5, 8.0 Hz, 1H), 7.65 (d, *J* = 8.0 Hz, 1H), 7.54 (dt, *J* = 1.5, 9.0 Hz, 1H), 7.33–7.29 (m, 2H), 7.10 (d, *J* = 8Hz, 1H), 6.90 (t, *J* = 1.0 Hz, 1H), 6.84 (t, *J* = 6.5, 1H), 4.51 (dd, *J* = 7.0, 3.5 Hz, 1H), 2.65 (S, 3H), 2.37–2.30 (m, 1H), 2.29–2.25 (m, 1H), 0.95 (t, *J* = 7.0 Hz, 3H); ^{13}C-NMR [125 MHz (DMSO-d_6)] δ (ppm): 161.6, 160.1, 152.3, 136.1, 131.8, 127.4, 123.9, 123.6, 123.2, 120.9, 118.6, 118.4, 116.5, 116.3, 111.6, 108.2, 79.4, 33.6, 24.4, 21.0, 12.9.

3-((4-Bromophenyl)(2-methyl-1*H*-indol-3yl)methyl)-4hydroxy-2*H*-chromen-2-one (4l):

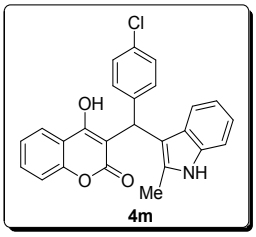


4l

Yield: 368 mg (80%) as white solid; MP = 167 °C; IR ν_{max} (KBr, cm^{-1}): 3443, 3354, 2962, 2832, 1671, 1608, 1485, 1402, 1351, 1310, 1121, 1070, 766, 617; ^{1}H-NMR (DMSO-d_6, 500 MHz) δ (ppm): 10.8 (s, D_2O exchangeable, 1H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.19 (d, *J* = 8.0 Hz, 2H) 6.90 (t, *J* = 7.0 Hz, 2H), 6.81 (d, *J* = 7.5, 2H), 6.70 (t, *J* = 7.0, 2H), 5.90 (s, 1H), 2.09 (s, 3H); ^{13}C-NMR [125 MHz (DMSO-d_6)] δ (ppm):

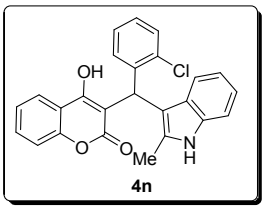
166.1, 162.4, 154.0, 135.5, 133.1, 132.7, 131.6, 131.3, 131.2, 128.5, 124.3, 123.6, 120.1, 119.1, 118.8, 118.5, 116.8, 116.2, 112.0, 110.9, 91.5, 38.5, 12.4.

3-((4-Chlorophenyl)(2-methyl-1*H*-indol-3yl)methyl)-4hydroxy-2*H*-chromen-2-one (4m):



Yield: 341 mg (82%) as white solid; MP = 161 °C; IR ν_{max} (KBr, cm^{-1}): 3456, 3383, 2970, 2840, 1596, 1395, 1191, 1121, 1078, 1017, 746, 610; ^{1}H-NMR (DMSO-d_6, 500 MHz) δ (ppm): 10.79 (s, D_2O exchangeable, 1H), 7.32 (d, *J* = 8.5 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 6.90 (t, *J* = 7.0 Hz, 2H), 6.80 (d, *J* = 8.0 Hz, 2H), 6.70 (t, *J* = 7.0 Hz, 2H), 5.91 (s, 1H), 2.08 (s, 3H); ^{13}C-NMR [125 MHz (DMSO-d_6)] δ (ppm): 166.1, 162.4, 153.9, 143.8, 135.5, 133.1, 132.6, 131.6, 130.9, 130.7, 129.7, 128.5, 128.3, 124.3, 123.6, 120.1, 118.8, 118.5, 116.8, 116.2, 112.1, 110.8, 91.4, 38.4, 12.3.

3-((2-Chlorophenyl)(2-methyl-1*H*-indol-3yl)methyl)-4hydroxy-2*H*-chromen-2-one (4n):



Yield: 336 mg (81%) as white solid; MP = 162 °C; IR ν_{max} (KBr, cm^{-1}): 3423, 3385, 2965, 2841, 1604, 1395, 1315, 1243, 1191, 1121, 1065, 826, 747; ^{1}H-NMR (DMSO-d_6, 500 MHz) δ (ppm): 10.7 (s, broad, D_2O exchangeable, 1H), 7.82 (d, *J* = 7.5 Hz, 1H), 7.64 (t, *J* = 7.0 Hz, 1H), 7.43(d, *J* = 7.5 Hz, 1H), 7.36 (t, *J* = 9.0 Hz, 1H), 7.31–7.19 (m, 4H), 6.89 (t, *J* = 7.0 Hz, 1H), 6.80–6.65 (m, 3H), 6.05 (s, 1H), 2.0 (s, 3H); ^{13}C-NMR [125 MHz (DMSO-d_6)] δ (ppm): 166.1, 162.4, 153.9, 143.8, 135.5, 133.1, 132.7, 131.6, 130.9, 130.7, 129.7, 128.5, 128.3, 124.3, 123.6,120.1, 118.8, 118.5, 116.8, 116.2, 112.1, 110.8, 91.4, 38.4, 12.4.

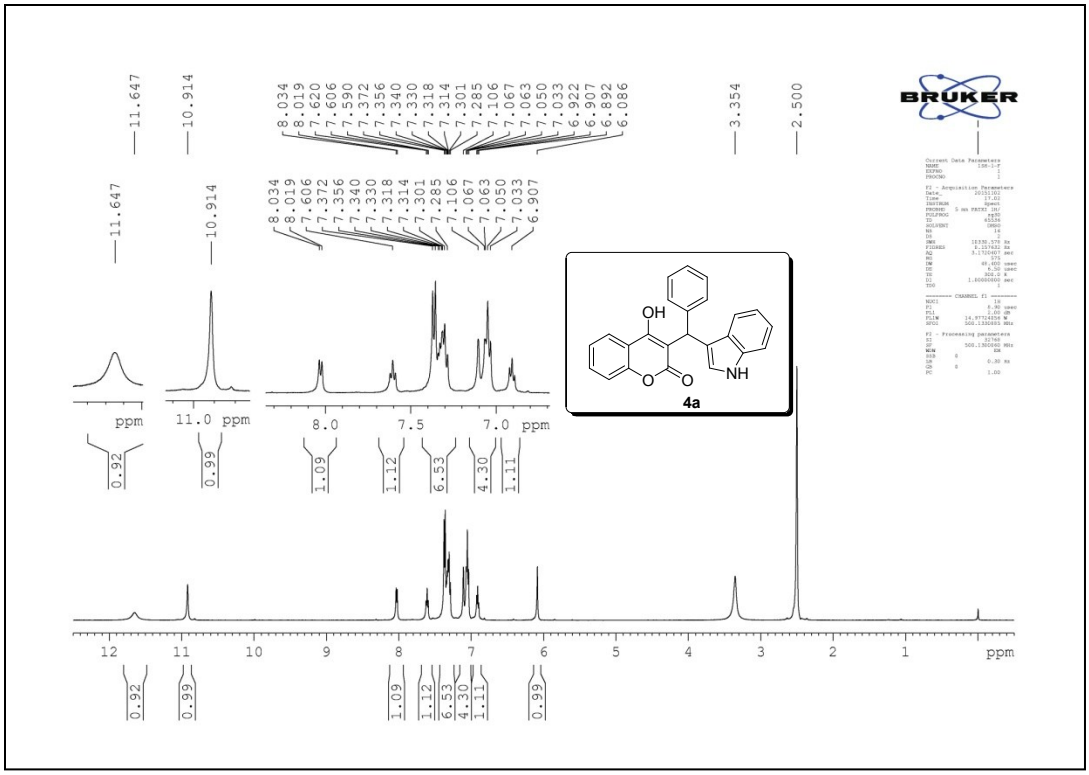


Figure S1. ^{1}H NMR spectra of **4a** in DMSO-d_6.

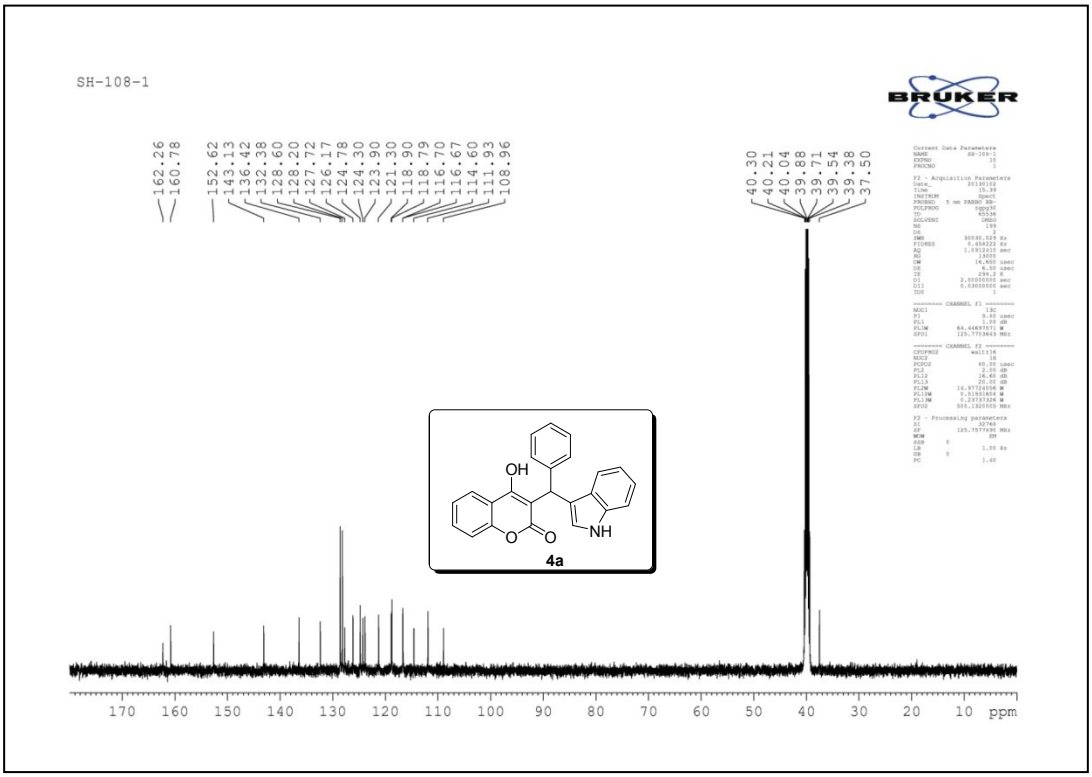


Figure S2. ^{13}C NMR spectra of **4a** in DMSO-d_6.

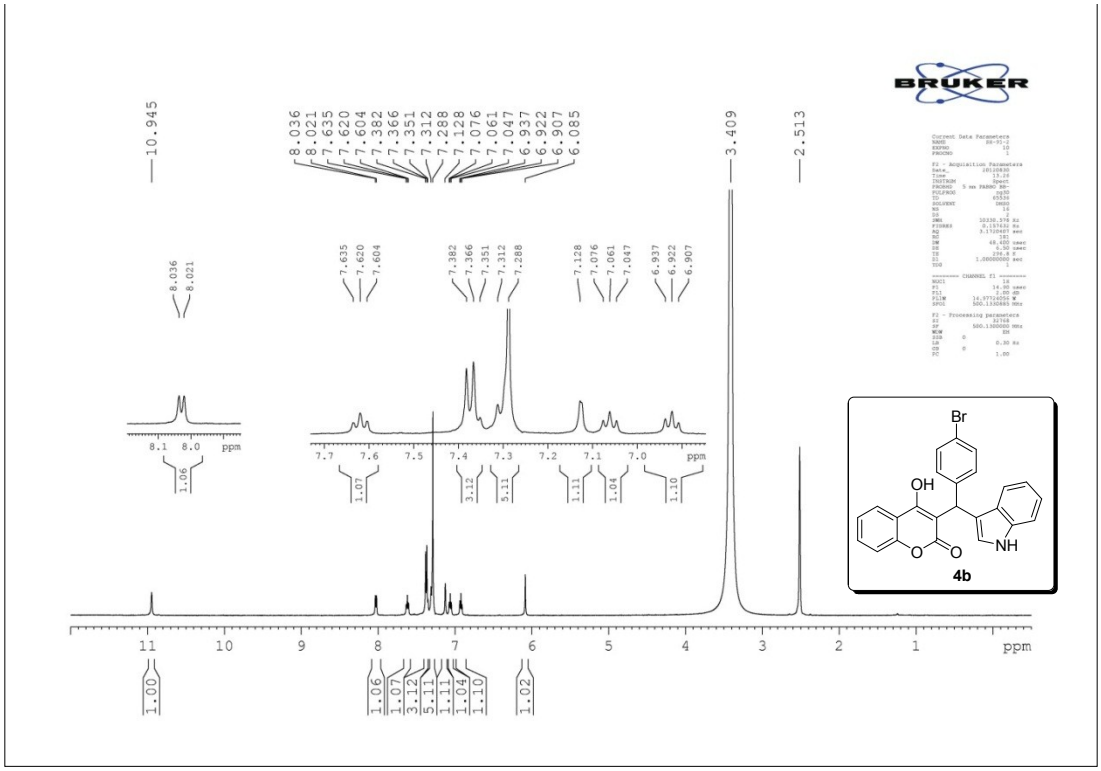


Figure S3. ^{1}H NMR spectra of **4b** in DMSO-d_6.

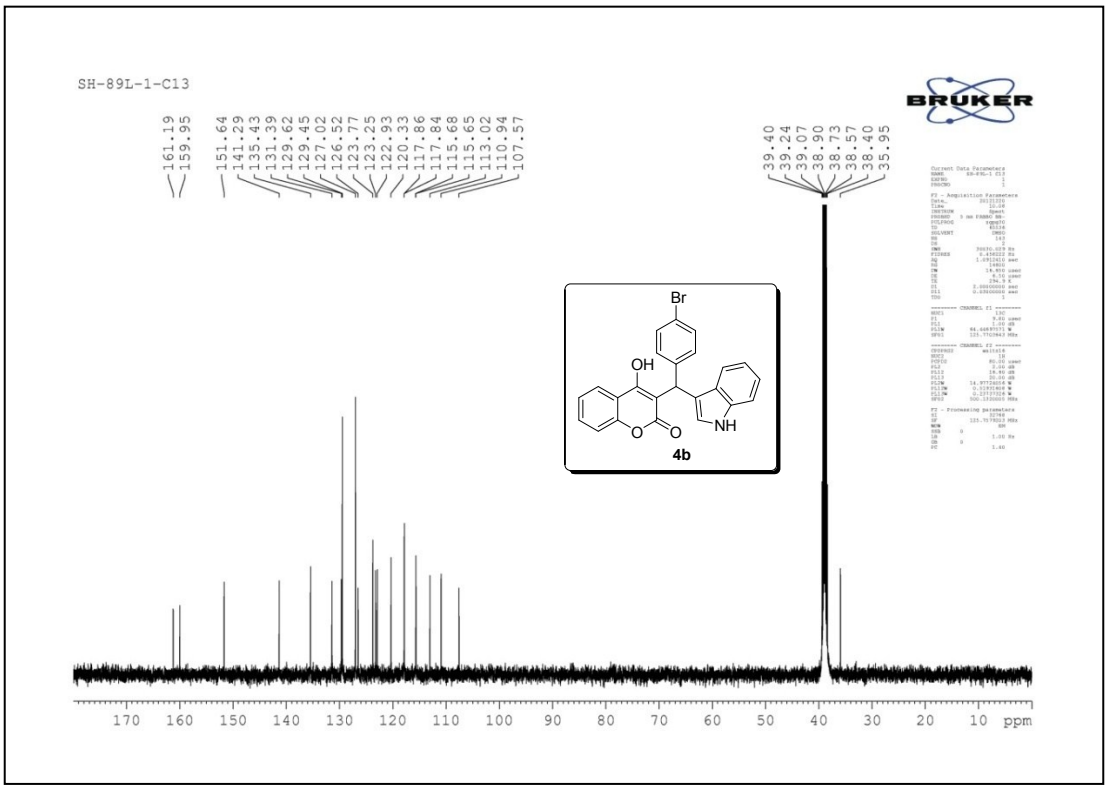


Figure S4. ^{13}C NMR spectra of **4b** in DMSO-d_6.

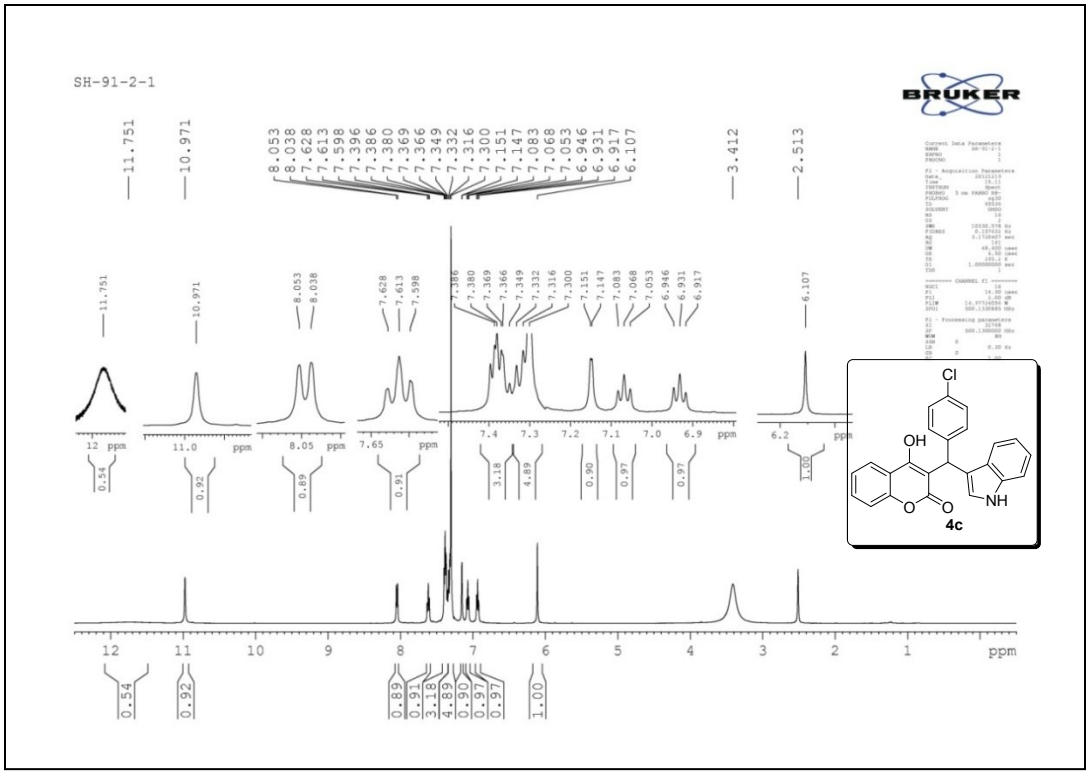


Figure S5. [1]H NMR spectra of **4c** in DMSO-d_6.

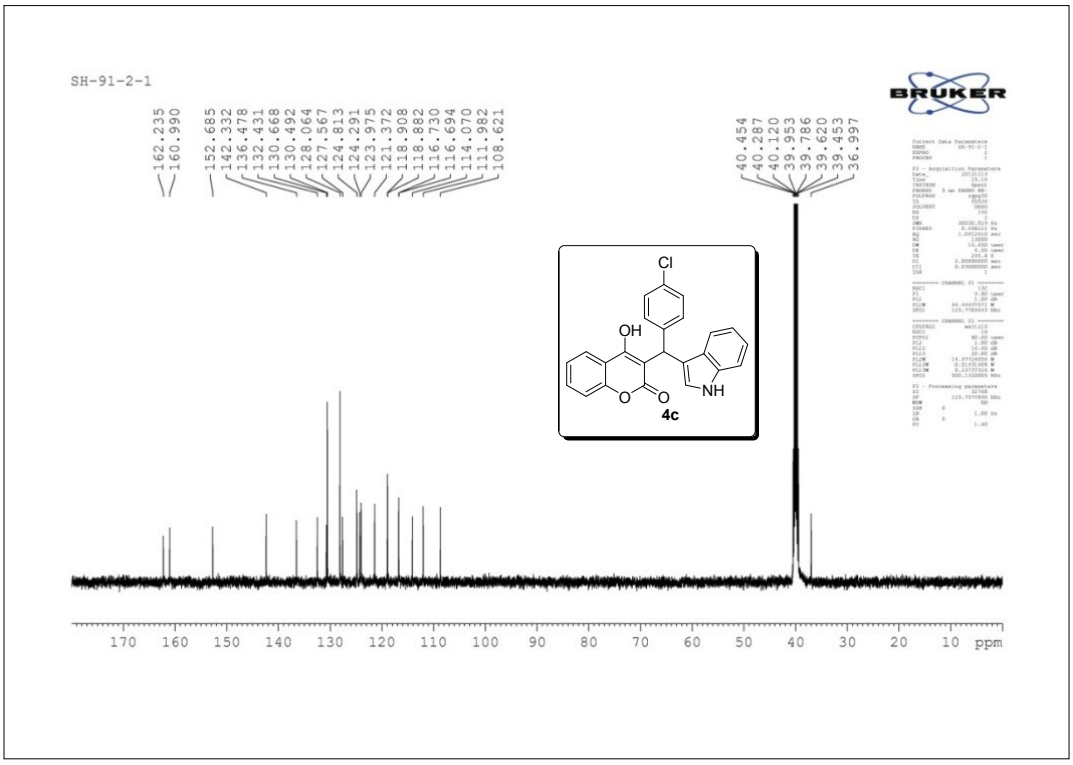


Figure S6. [13]C NMR spectra of **4c** in DMSO-d_6.

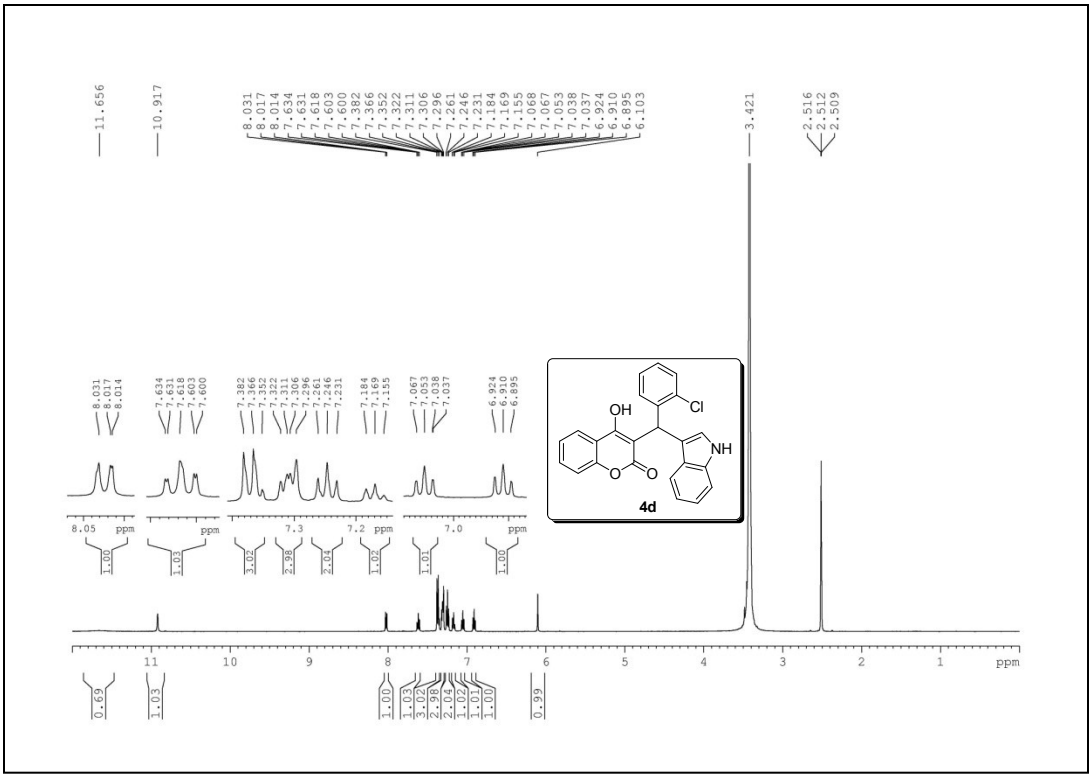


Figure S7. ^{1}H NMR spectra of **4d** in DMSO-d_6.

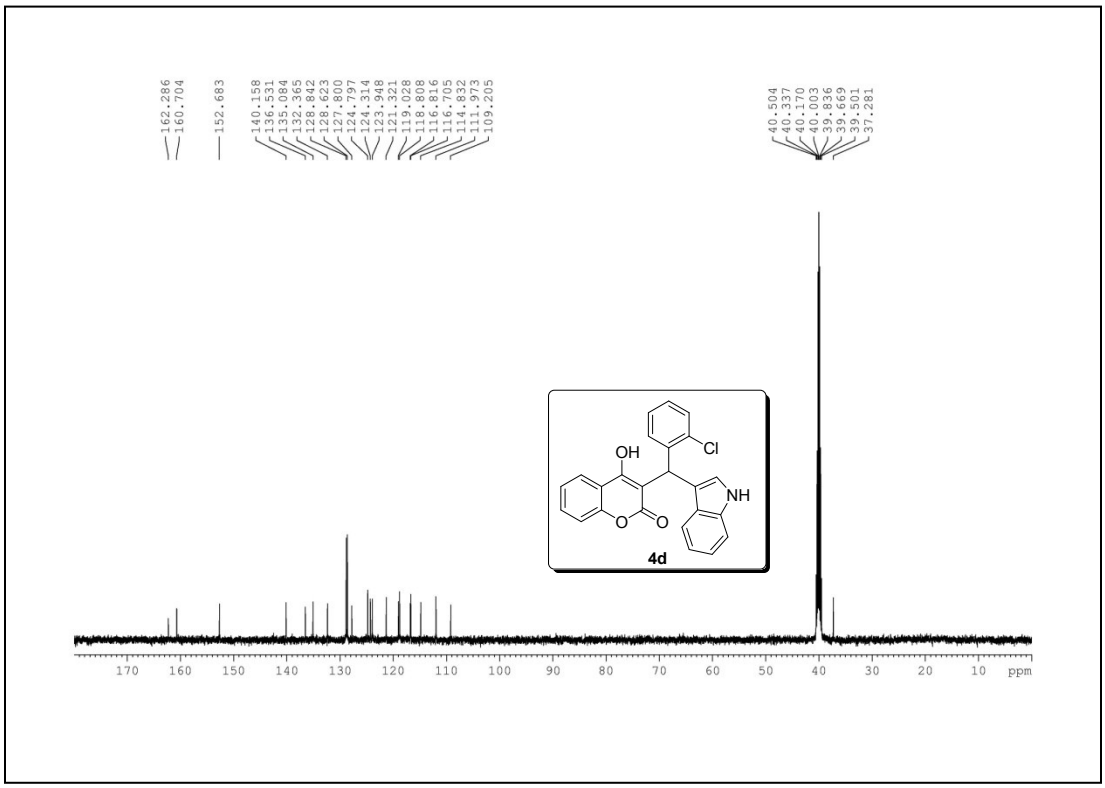


Figure S8. ^{13}C NMR spectra of **4d** in DMSO-d_6.

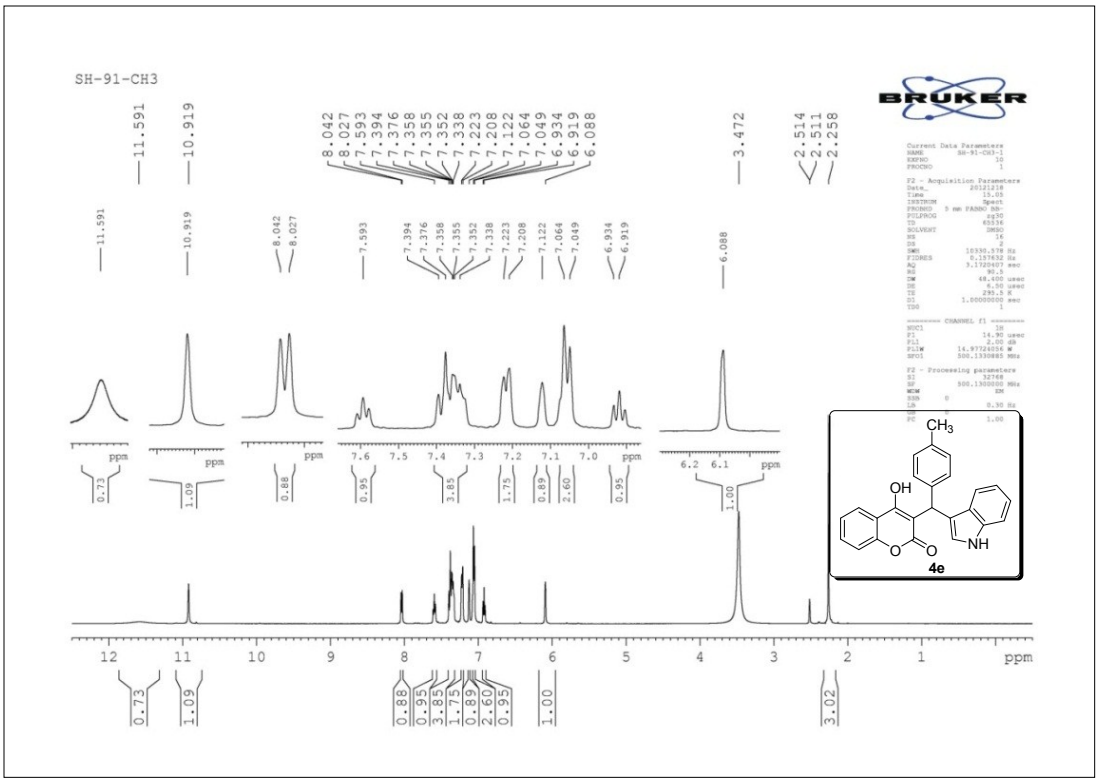


Figure S9. [1]H NMR spectra of **4e** in DMSO-d_6.

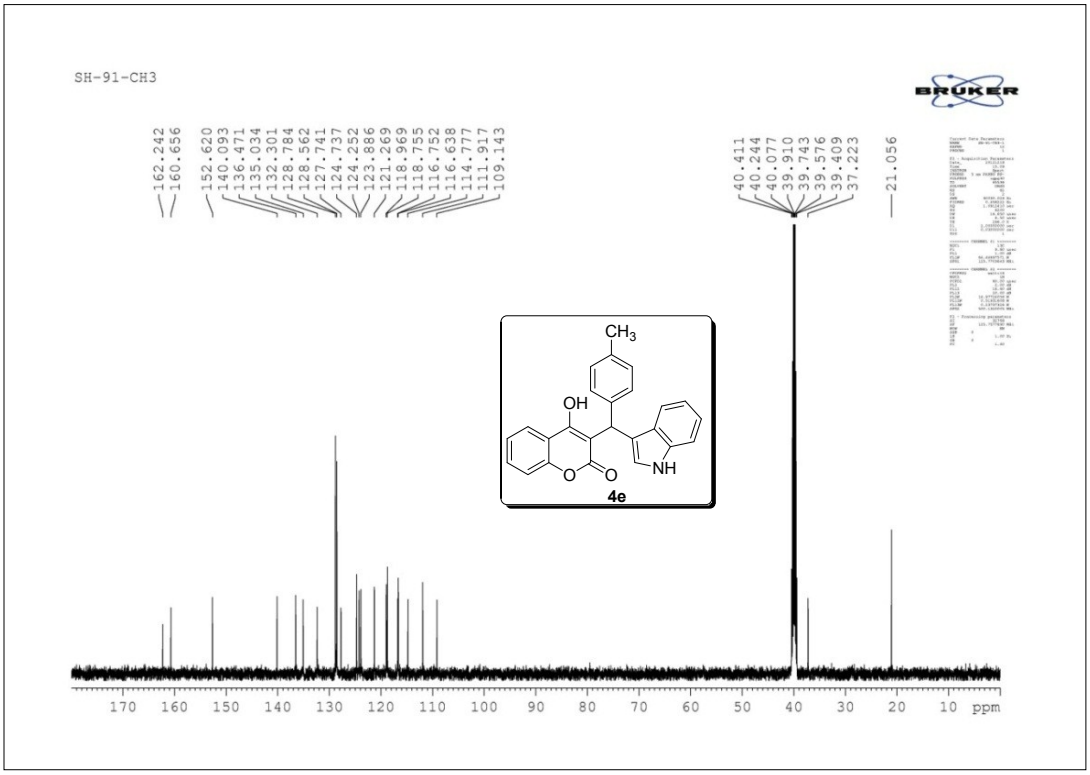


Figure S10. [13]C NMR spectra of **4e** in DMSO-d_6.

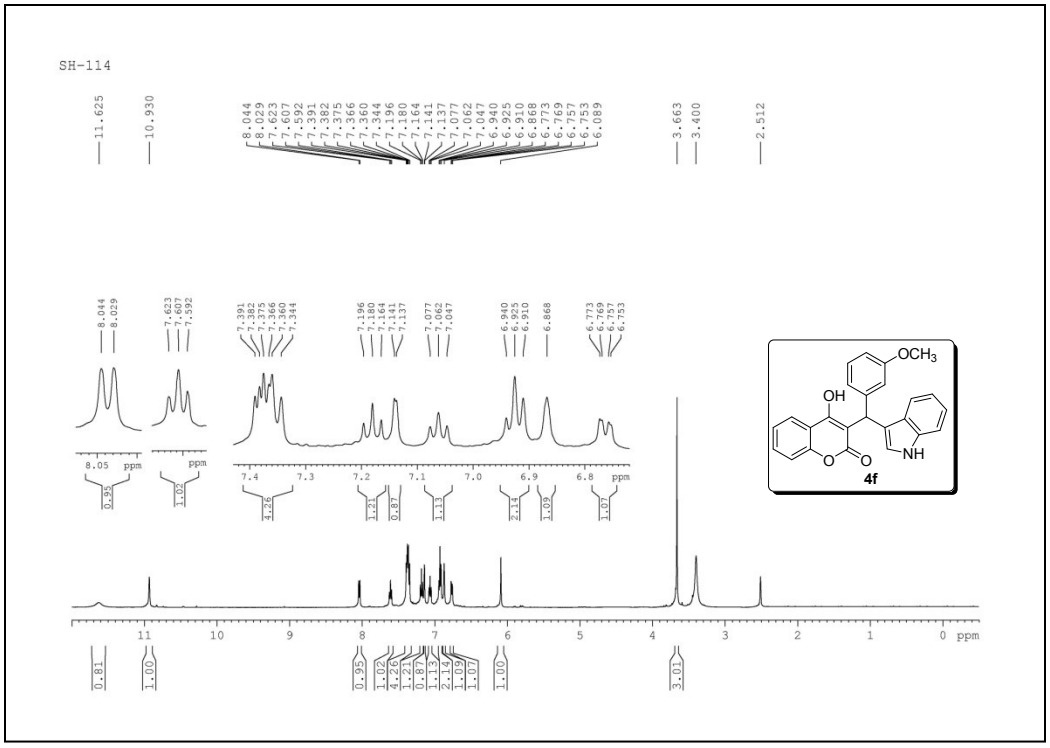


Figure S11. ^{1}H NMR spectra of **4f** in DMSO-d_6.

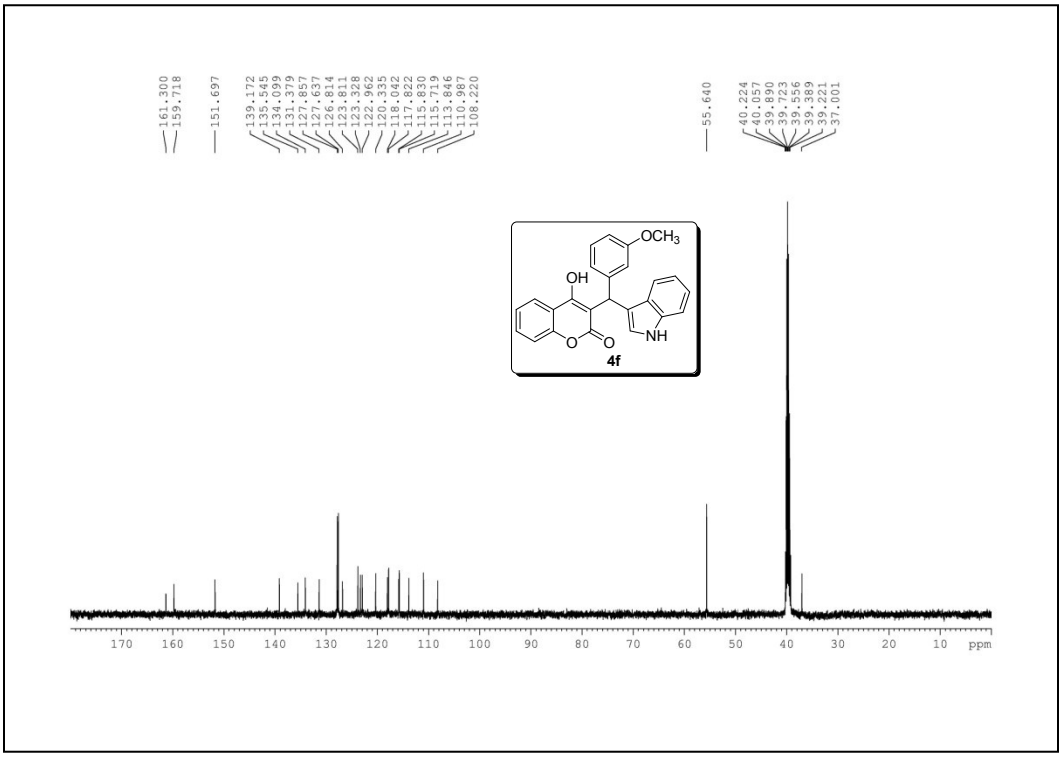


Figure S12. ^{13}C NMR spectra of **4f** in DMSO-d_6.

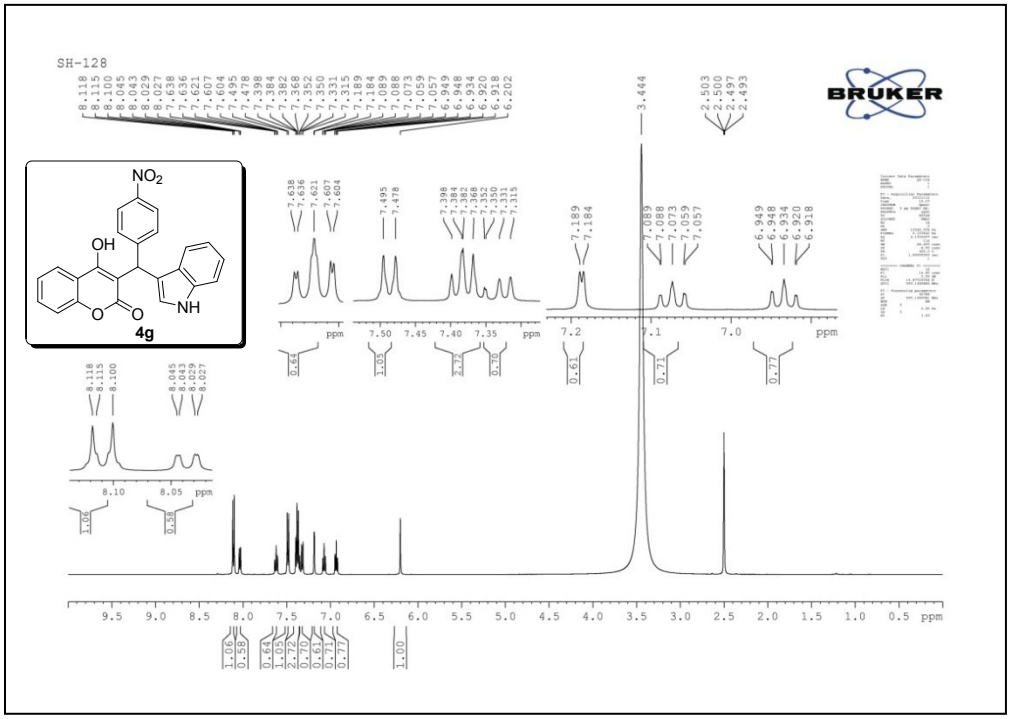


Figure S13. [1]H NMR spectra of **4g** in DMSO-d_6.

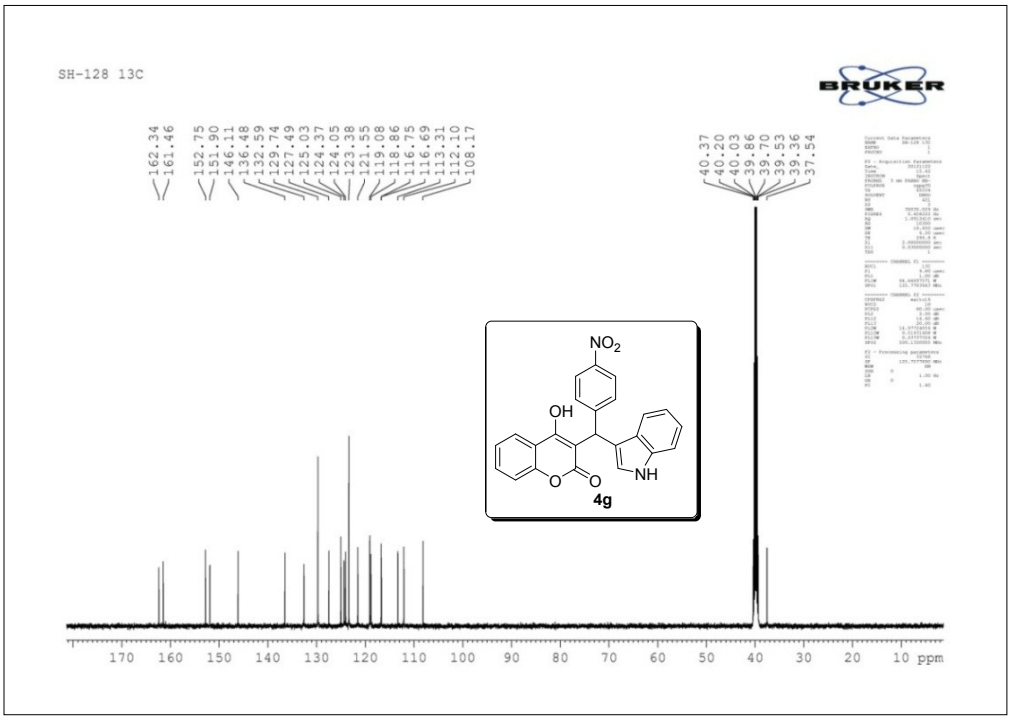


Figure S14. [13]C NMR spectra of **4g** in DMSO-d_6.

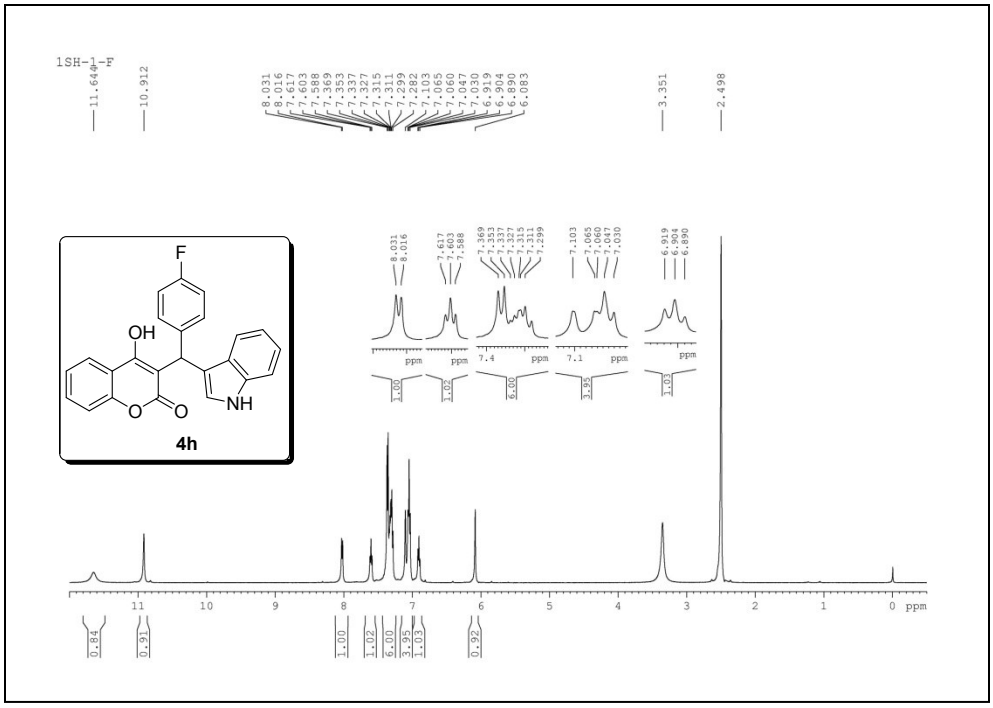


Figure S15. ^{1}H NMR spectra of **4h** in DMSO-d_6.

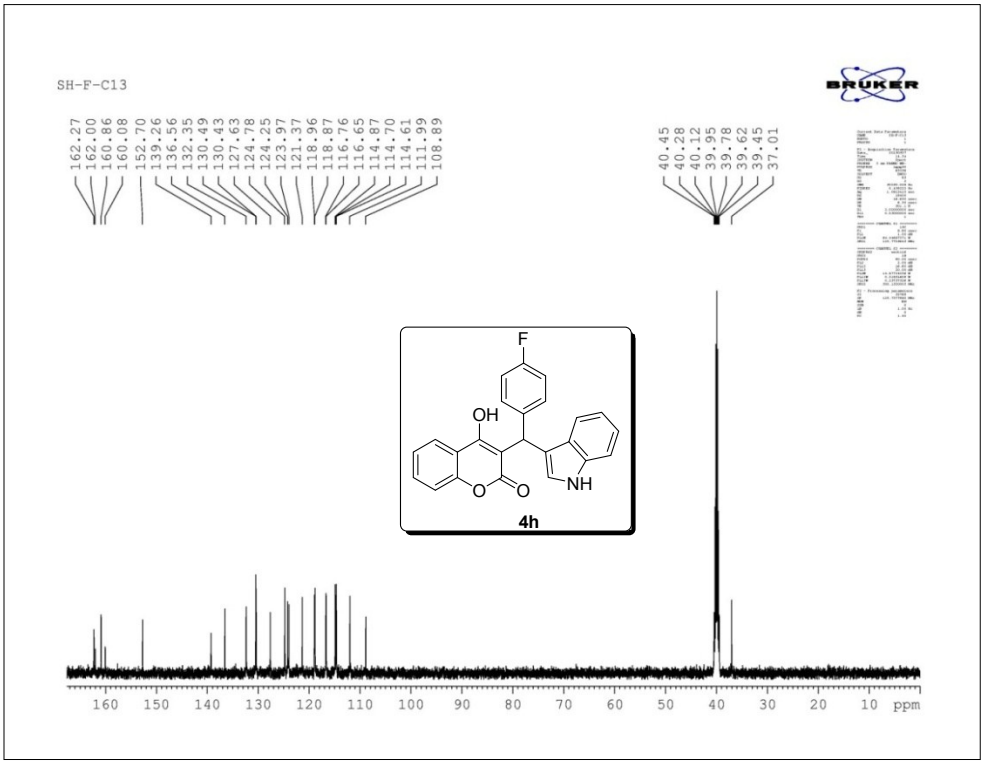


Figure S16. ^{13}C NMR spectra of **4h** in DMSO-d_6.

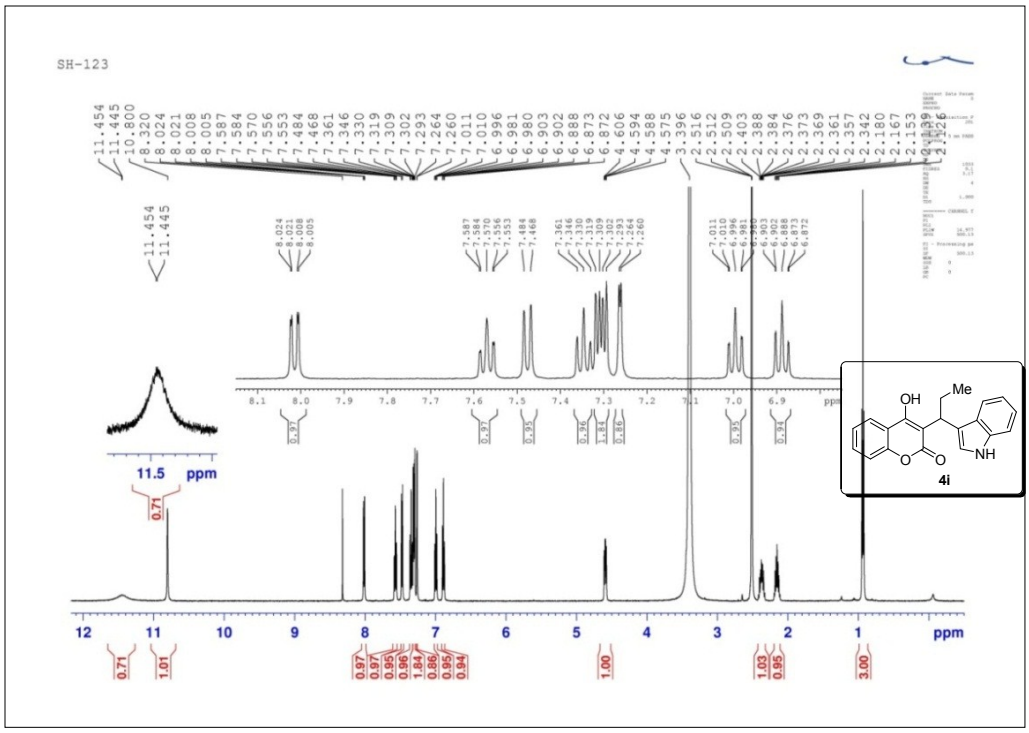


Figure S17. ^{1}H NMR spectra of **4i** in DMSO-d_6.

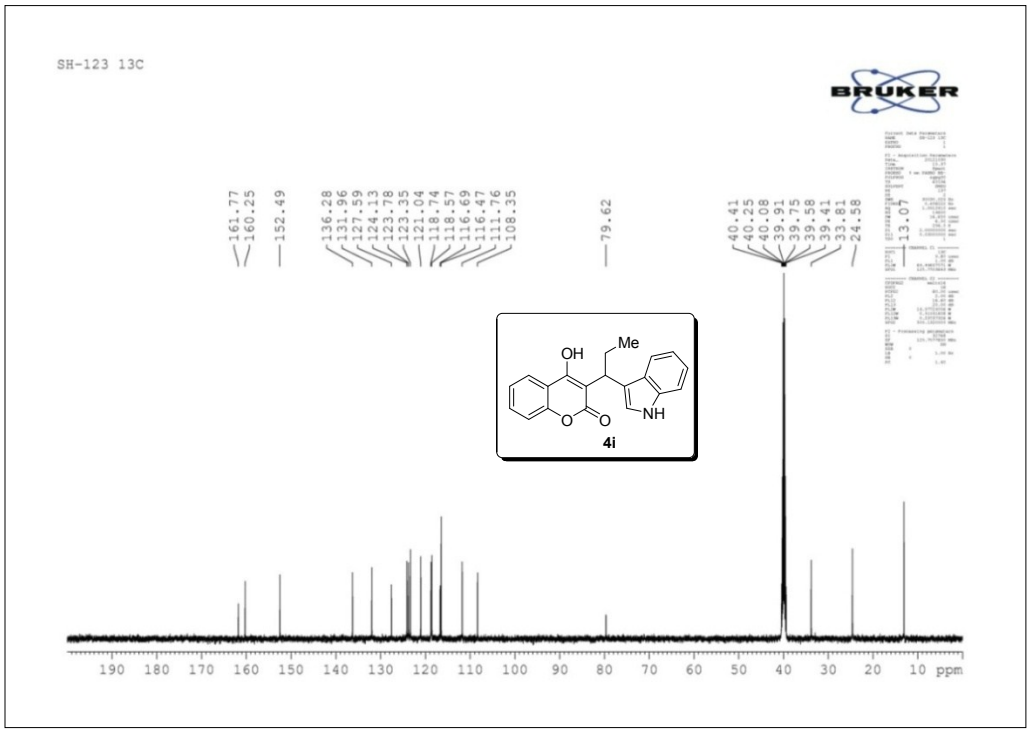


Figure S18. ^{13}C NMR spectra of **4i** in DMSO-d_6.

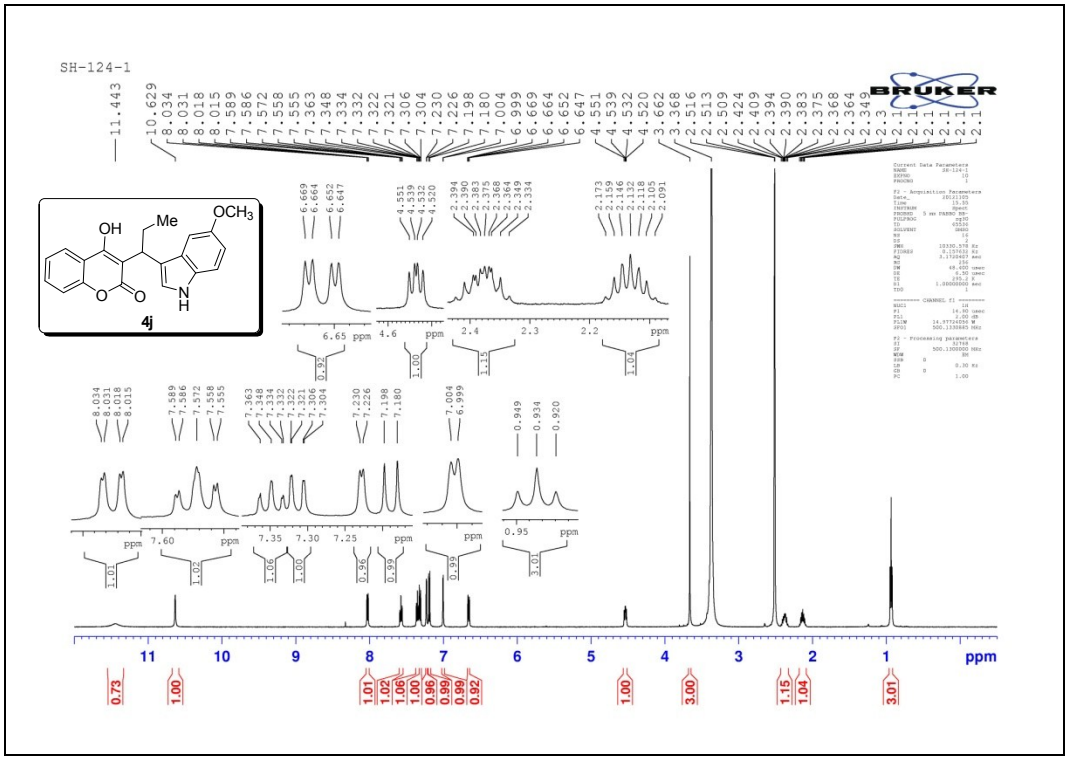


Figure S19. [1]H NMR spectra of **4j** in DMSO-d_6.

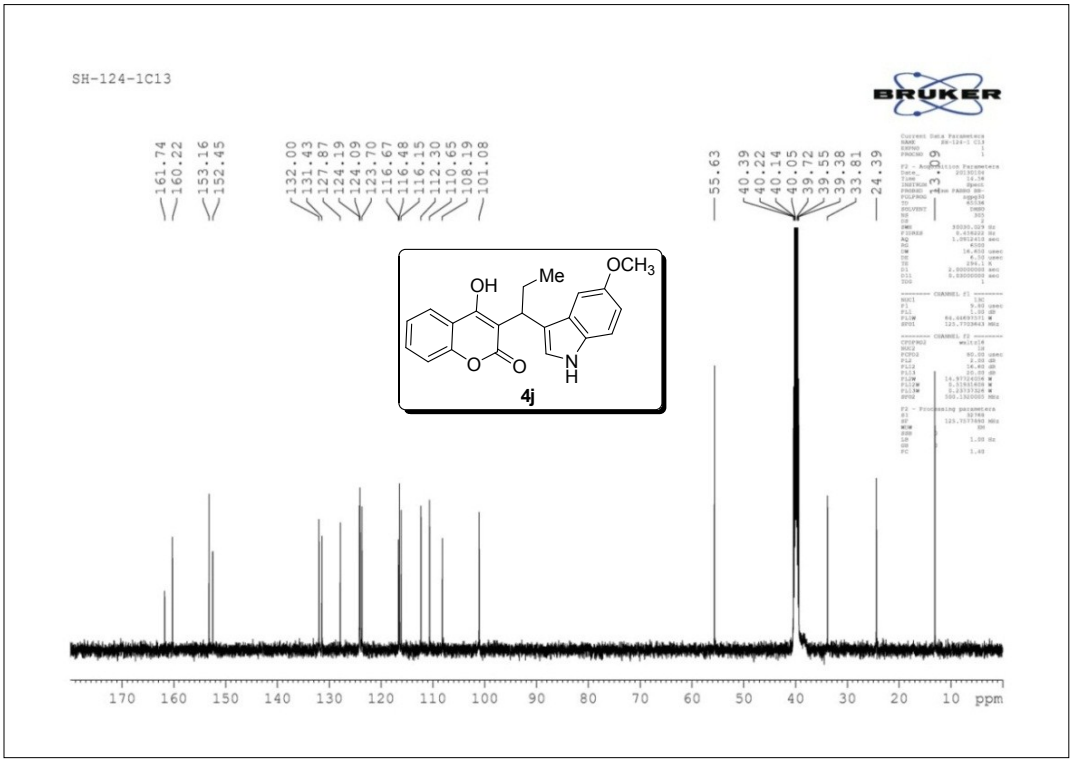


Figure S20. [13]C NMR spectra of **4j** in DMSO-d_6.

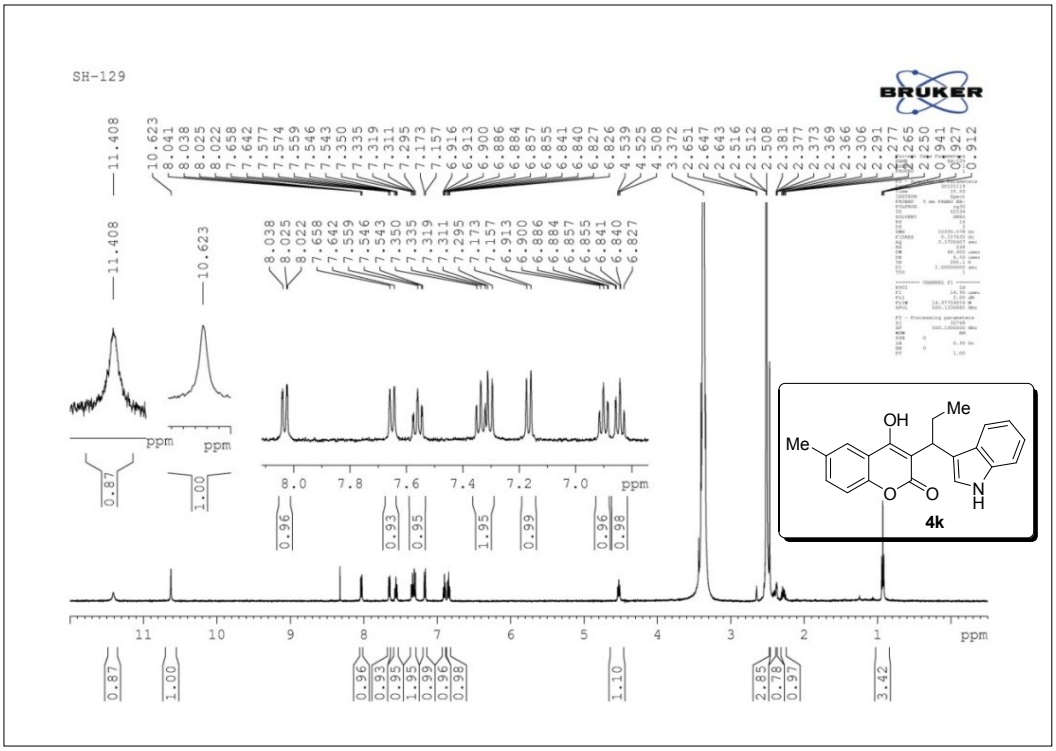


Figure S21. ^{1}H NMR spectra of **4k** in DMSO-d_6.

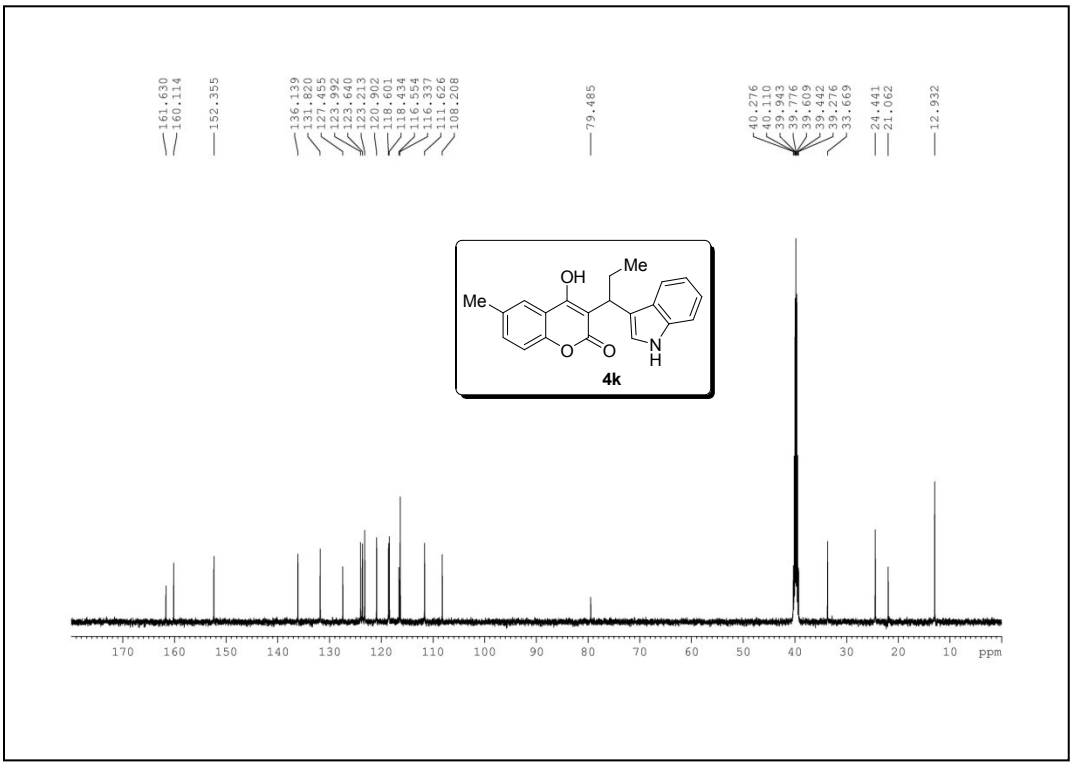


Figure S22. ^{13}C NMR spectra of **4k** in DMSO-d_6.

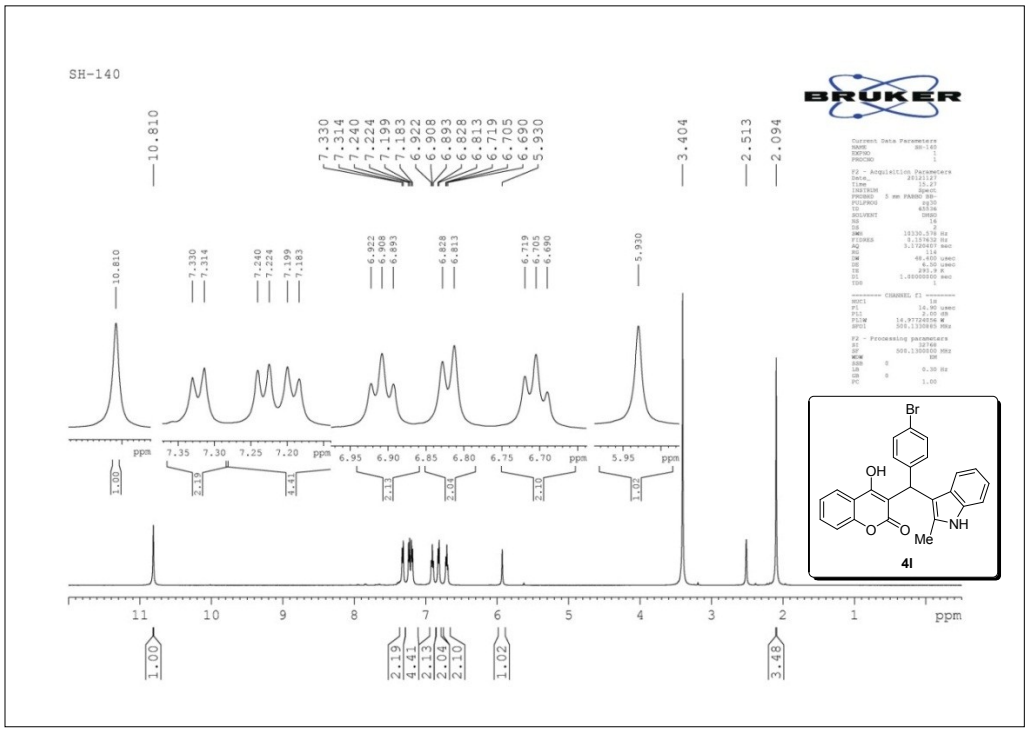


Figure S23. [1]H NMR spectra of **4l** in DMSO-d_6.

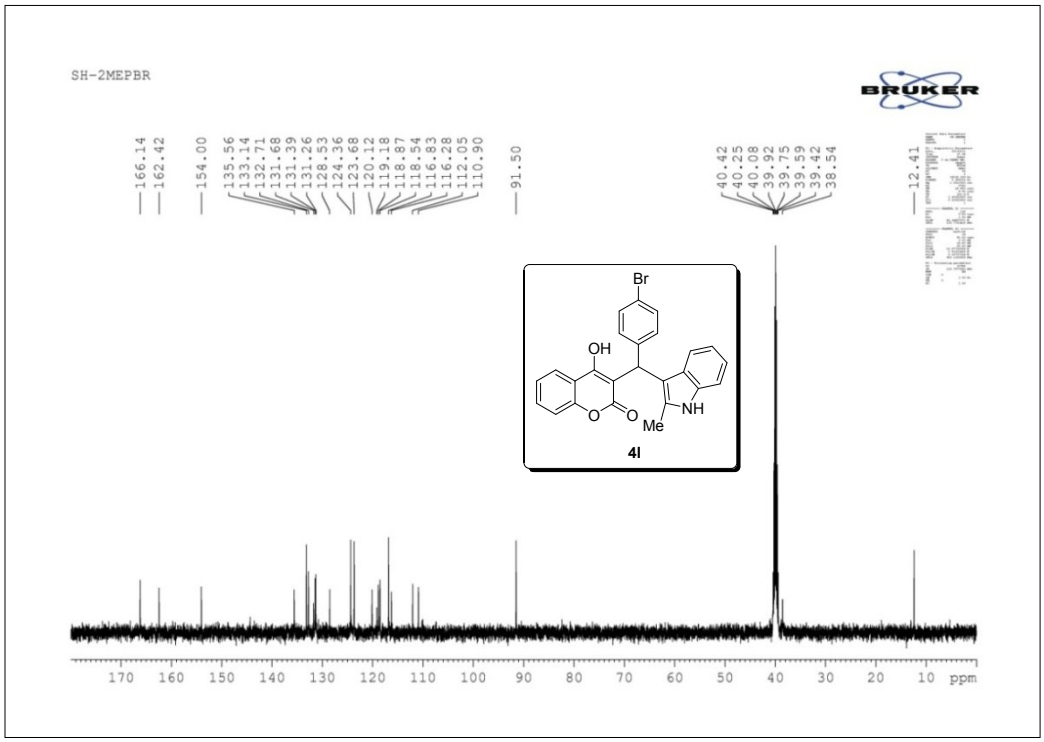


Figure S24. [13]C NMR spectra of **4l** in DMSO-d_6.

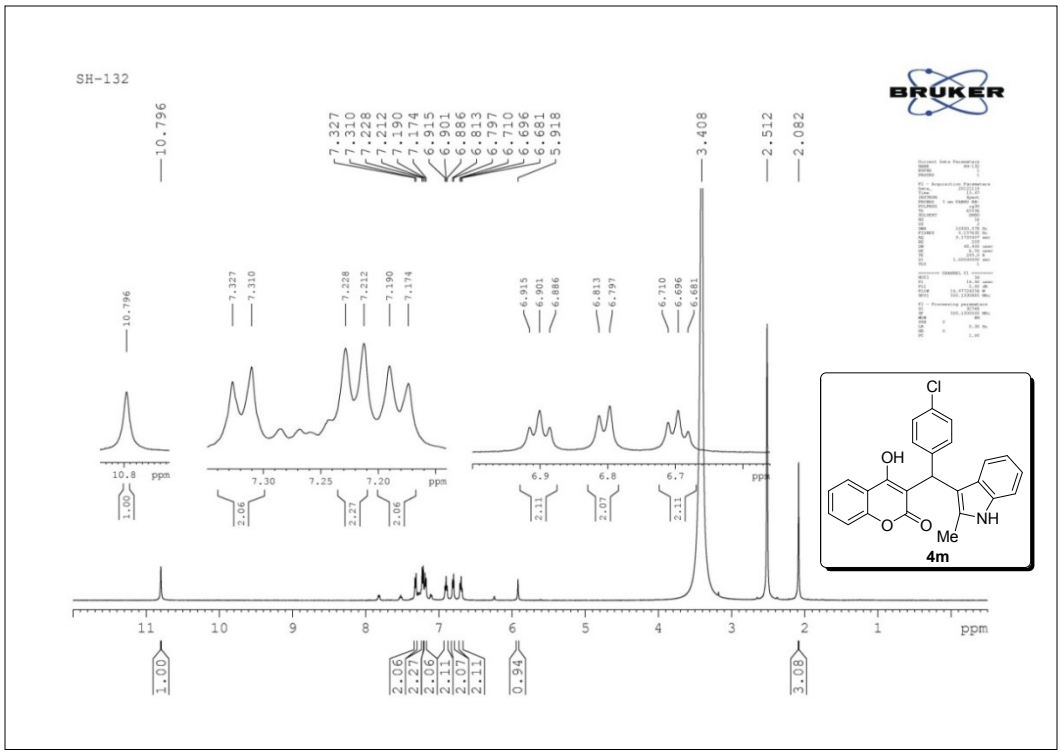


Figure S25. [1]H NMR spectra of **4m** in DMSO-d_6.

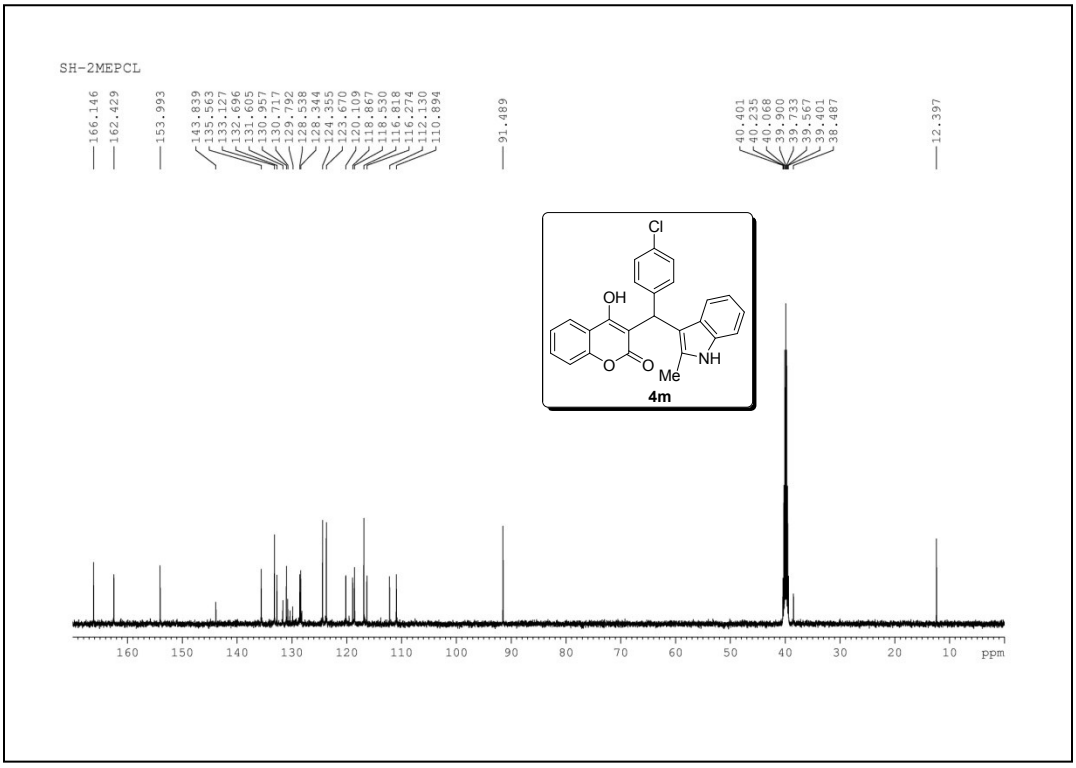


Figure S26. [13]C NMR spectra of **4m** in DMSO-d_6.

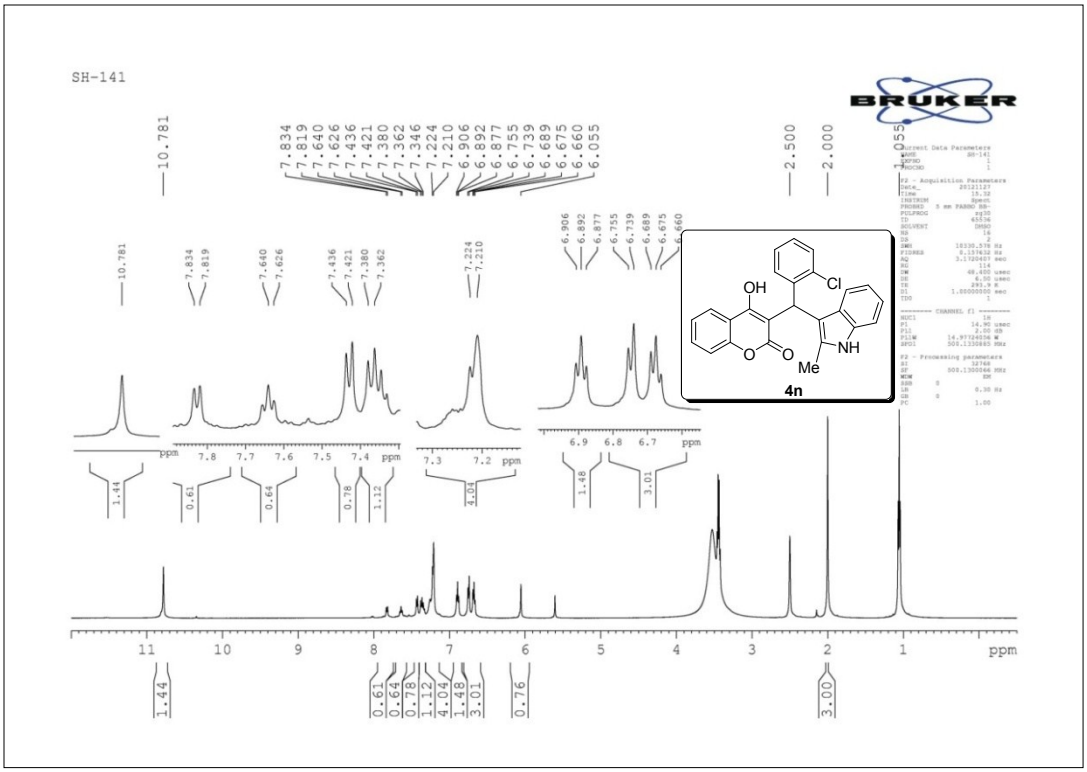


Figure S27. [1]H NMR spectra of **4n** in DMSO-d_6.

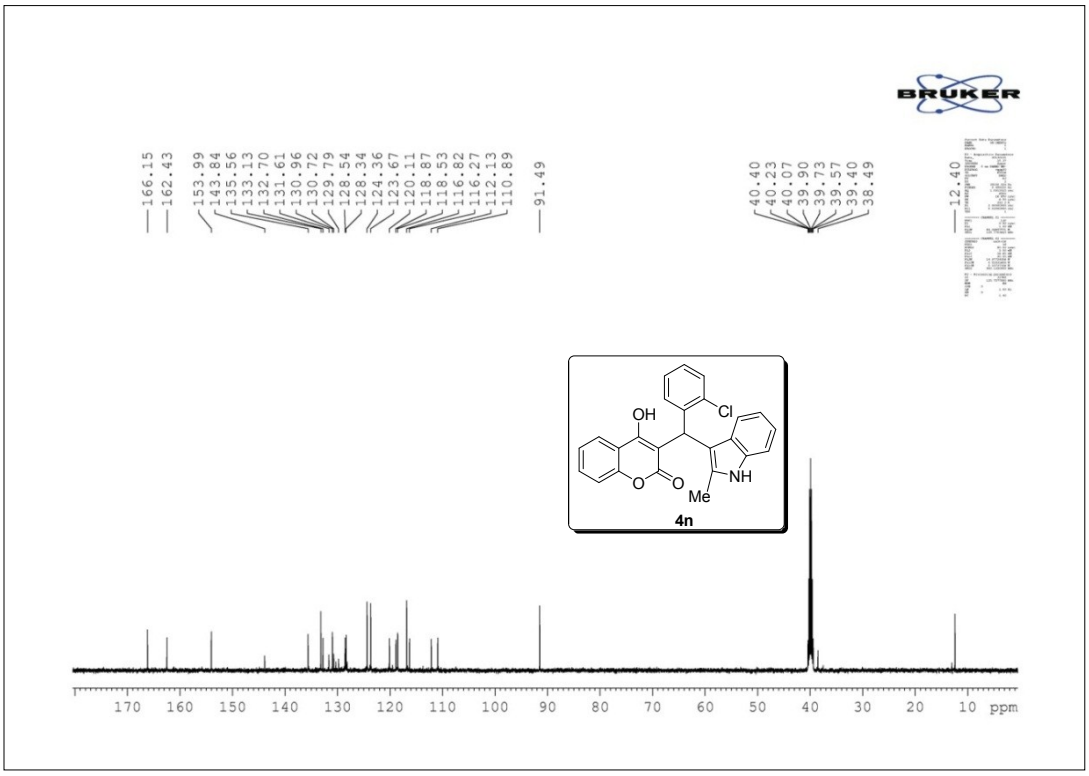


Figure S28. [13]C NMR spectra of **4n** in DMSO-d_6.

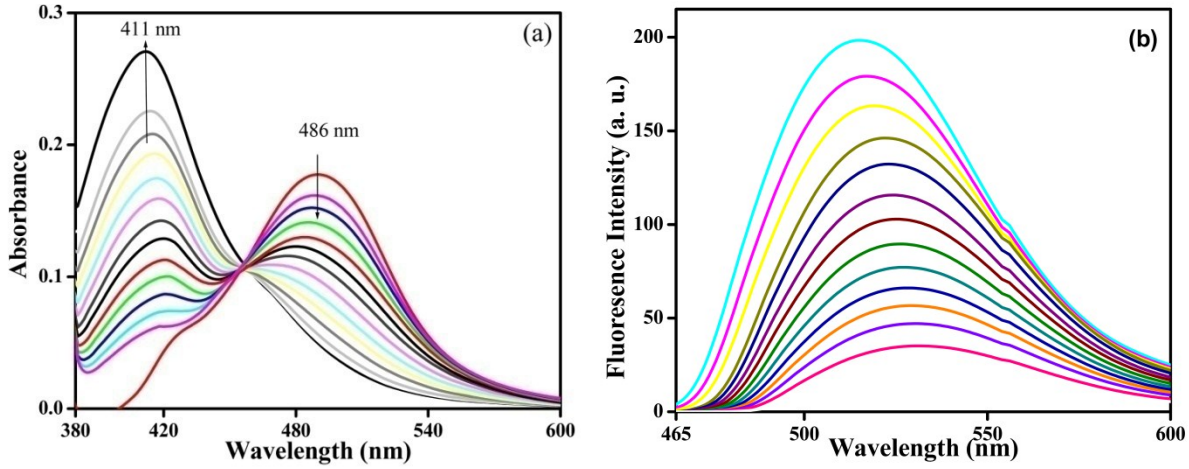


Figure S29. (a) Absorption and (b) fluorescence emission spectral responses of **4a** (1.0×10^{-5} M) towards varying concentrations of strong base TBAOH (0 to 15×10^{-5} M) in CH_3CN. λ_{ex} = 456 nm.

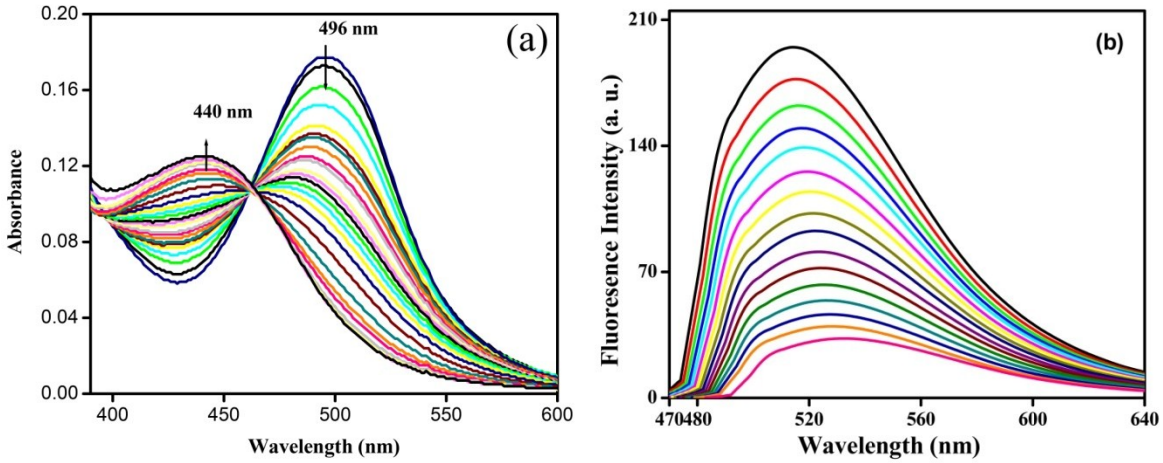


Figure S30. (a) Absorption and (b) fluorescence emission spectral responses of **4a** (1.0×10^{-5} M) towards varying concentrations of F^-ion concentrations (0 to 20×10^{-5} M) in 10 % H_2O in DMSO. λ_{ex} = 462 nm.

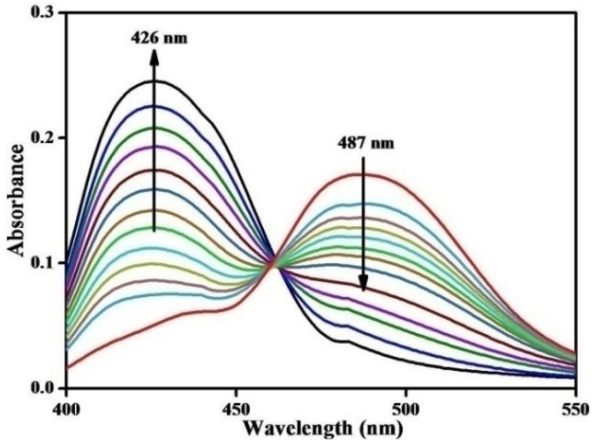
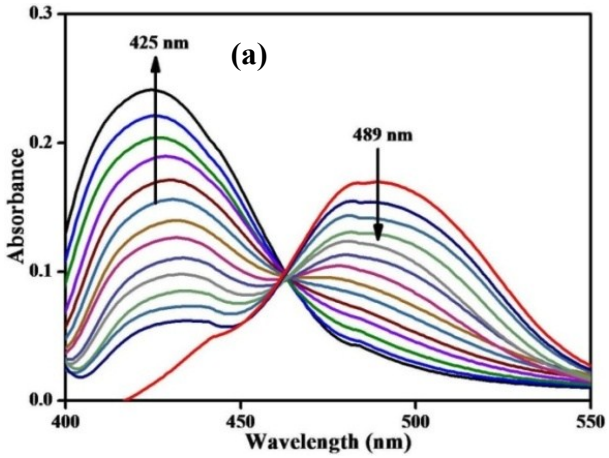


Figure S31. Absorption spectral responses of **4e** (1.0×10^{-5} M) towards varying F^-ion concentrations (0 to 20×10^{-5} M) in CH_3CN.



(b)

Figure S32. Absorption spectral responses of **4f** (1.0×10^{-5} M) towards varying F^-ion concentrations (0 to 20×10^{-5} M) in CH_3CN.

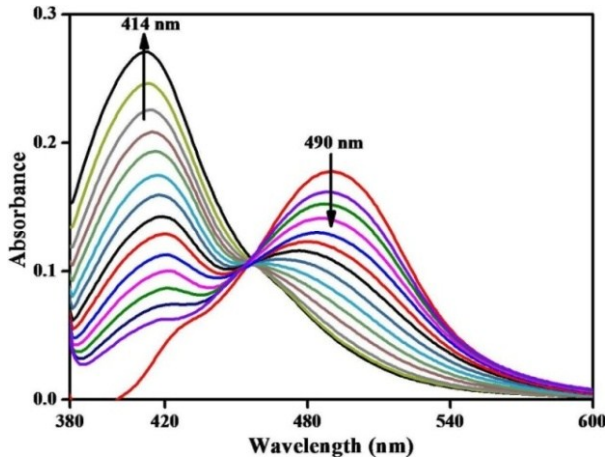


Figure S33. Absorption spectral responses of **4j** (1.0×10^{-5} M) towards varying F^-ion concentrations (0 to 20×10^{-5} M) in CH_3CN.

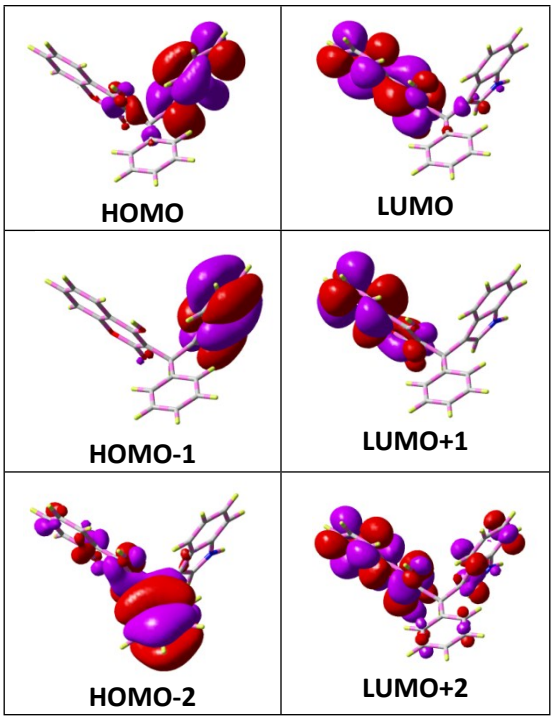


Figure S34. Pictorial view of frontier molecular orbitals of **4a**

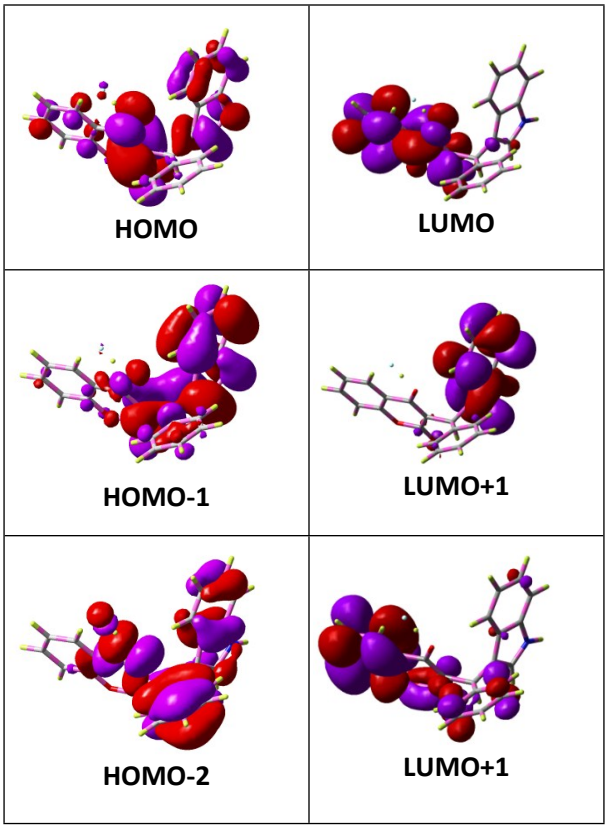


Figure S35. Pictorial view of frontier molecular orbitals of **4a** + F^-.

Table S1. Computed vertical excitation and their orbital contribution using B3LYP/6-31G(d)

Compound	λ_{max}(nm)	Transition state	f	Assignment	ΔE (cm^{-1})
4a	478	$S_0 \longrightarrow S_1$	0.0010	HOMO-4 ⟶ LUMO (15%) HOMO-3 ⟶ LUMO (15%) HOMO-2 ⟶ LUMO (10%) HOMO ⟶ LUMO (52%) HOMO-5 ⟶ LUMO (2%)	20902
4a+F^-	321	$S_0 \longrightarrow S_1$	0.1167	HOMO ⟶ LUMO (94%) HOMO-1 ⟶ LUMO (3%)	31113

Table S2. Colorimetric and fluorimetric properties of **4b-4n** toward F^- ion in CH_3CN.

S. No.	Compound	λ_{max} without Fluoride (nm)	λ_{max} with Fluoride (nm)	λ_{ex} (nm)	λ_{em} without Fluoride (nm)	λ_{em} with Fluoride (nm)
1	**4a**	485	415	455	507	534
2	**4b**	490	424	463	510	538
3	**4c**	490	414	456	508	536
4	**4d**	498	416	461	509	536
5	**4e**	487	426	462	512	539
6	**4f**	489	425	463	513	540
7	**4g**	497	420	462	506	535
8	**4h**	495	432	471	515	542
9	**4i**	472	401	430	490	520
10	**4j**	490	414	456	508	527
11	**4k**	476	401	430	492	525
12	**4l**	509	446	477	515	540
13	**4m**	490	438	460	510	534
14	**4n**	492	440	462	509	536