Supporting Information

Photochemical Domino Reaction Driven C-H/S-H Functionalization of Bioactive Molecules to Access Xanthene Scaffolds

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1. General Experimental Detail

All reagents and starting materials were purchased from commercially available suppliers (Alfa Aesar, Sigma Aldrich, or Avra Synthesis) and used without further purification. Thin Layer Chromatography (TLC) was executed utilizing silica gel 60 F_{254} (Merck) plates. The TLC spots were visualized with ultraviolet light using the Optima Ultraviolet Fluorescence Analysis Cabinet of model OSI-072 and/or *p*-anisaldehyde with heat as a revealing agent. Proton nuclear magnetic resonance spectra (^{1}H NMR spectra) were obtained on Bruker 500 MHz FT-NMR spectrometers and 400 MHz Bruker FT-NMR in $CDCl_3$ and DMSO-d_6 solvents. ^{13}C NMR spectra were recorded at 126 MHz and 101 MHz. Chemical shifts (δ) are reported in parts per million (ppm) relative to the standard TMS signal and *J* values are given in Hz. Multiplicity is indicated as follows: s (singlet); bs (broad singlet); d (doublet); t (triplet); q (quartet); m (multiplet); dd (doublet of doublets), etc. TOF and quadrupole mass analyzer types are used for the HRMS measurements. IR spectra were recorded using a Perkin-Elmer Spectrum 65 FT-IR Spectrometer in KBr mode in the range of 400-4000 cm^{-1}.

2. Optimization studies for the present work

We commence our studies to establish conditions for the domino multicomponent reactions driven C-H functionalization of indoles for accessing xanthenes embedded with diverse functionalities. In this regard, a three-component reaction between equimolar amount of 2-hydroxybenzaldehyde **1a**, 5,5-dimethyl-cyclohexane-1,3-dione **2a**, and indole **3a** was considered as the representative example. It was carried out in the presence of different catalysts, solvents, light, temperature, etc. Initially, the execution of the reaction in absence of any catalyst failed to yield the desired product (**Entry 1, Table S1**). Then, we moved our attention to examine the reaction by introducing various kinds of base catalysts, acid catalysts, and hydrogen bond donor catalysts in the presence of different reaction conditions. The presence of bases including K_2CO_3, Na_2CO_3, piperidine, DBU, and DABCO was found to be not likely involved in the formation of the desired product (**Entry 2-7, Table S1**).

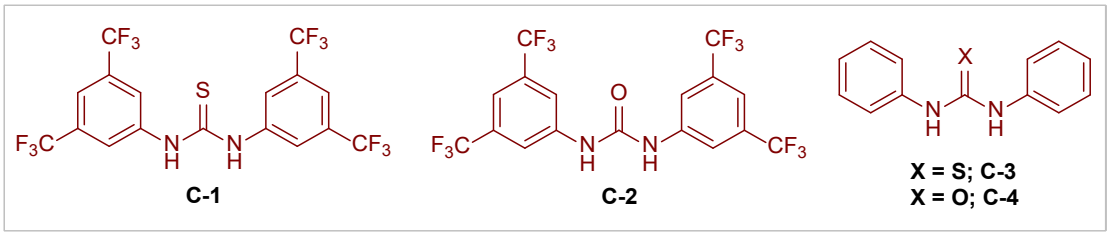
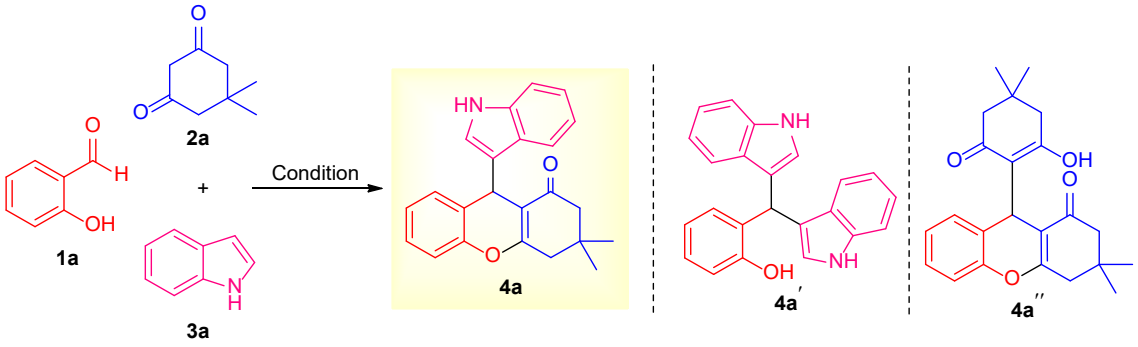


Figure S1: Different organocatalysts used in this study.

Table S1: Optimization studies of catalysts in different reaction conditions [a]



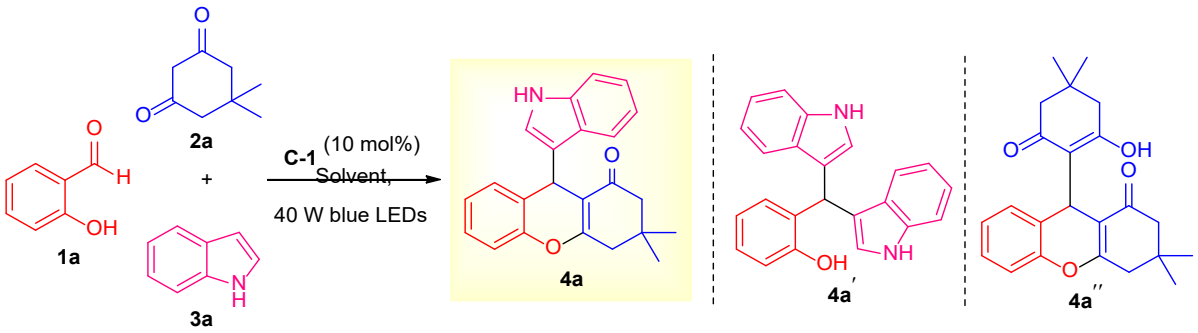
Entry	Catalyst (10 mol%)	Condition	Time[b]	Yield (%)[c]		
				4a	4a′	4a″
1	Catalyst-free	reflux	4 h	-	25	31
2	K_2CO_3	reflux	4 h	0	Trace	55
3	Na_2CO_3	reflux	4 h	0	Trace	45
4	Piperidine	reflux	4 h	0	35	54
5	DBU	reflux	4 h	15	0	35
6	DABCO	reflux	4 h	20	0	42
7	$ZnCl_2$	reflux	6 h	55	15	-
8	$Sc(OTf)_3$	reflux	6 h	59	10	Trace
9	H_3PO_3	reflux	6 h	45	5	-
10	$Ag(OTf)_2$	reflux	6 h	61	10	Trace
11	L-proline	80 °C	4 h	80	0	Trace
12	-	Visible light	12 h	0	15	21
13[d]	**C-1**	**Visible light**	**12 h**	**90**	**0**	**0**
14	**C-1**	Dark	12 h	0	Trace	18
15	**C-1**	50 °C	12 h	16	Trace	32
16[d]	**C-2**	Visible light	12 h	13	Trace	23
17[d]	**C-3**	Visible light	12 h	78	10	-
18[d]	**C-4**	Visible light	12 h	0	5	Trace

[a] Reaction condition: 2-hydroxybenzaldehyde **1a** (0.5 mmol), 5,5-dimethyl-cyclohexane-1,3-dione **2a** (0.5 mmol), and indole **3a** (0.5 mmol) in different catalytic systems with CH_3CN (2 mL) in different reaction conditions. [b] Progress of the reaction was monitored by TLC. [c] Yield of the referred products. [d] Irradiation was done under 40 W blue LEDs in the presence or absence of oxygen at room temperature.

The effect of different acid catalysts such as $ZnCl_2$, $Sc(OTf)_3$, H_3PO_3, and $Ag(OTf)_2$ was examined and found to slightly afford **4a** along with the side products **4a′** and **4a″** (**Entry 8-10, Table S1**). The introduction of L-proline at 80 °C affords the desired product **4a** in 80% yield (**Entry 11, Table S1**). Having this information in hand, we next performed the model reaction by emerging a variety of urea and thiourea catalysts in the presence or absence of visible light and under reaction conditions. To our delight, the reaction carried out in the absence of any catalyst and in the presence of light leads to the formation of side products **4a′** and **4a″** rather than the desired product **4a** (**Entry 12**, **Table S1**). Pleasingly, the reaction in the presence of 10 mol% of **C-1** under 40 W blue LED irradiation in CH_3CN delivered the desired product **4a** in 90% yield with diminished yield of **4a′** and **4a″** (**Entry 13, Table S1**). In the presence of **C-1** and the absence of light, the reaction again failed to yield **4a** (**Entry 14, Table S1**). Heating to 50 °C in CH_3CN, only a trace amount of **4a** was observed (**Entry 15, Table S1**). Moreover, changing the catalytic system from **C-1** to *N, N*-diphenyl urea **C-2**, the reaction was found to not proceed even after 12 hours of irradiation (**Entry 16, Table S1**). This result demonstrated the essential role of sulfur in the reaction. Alternatively, the reaction in the presence of **C-3** also provided a 78% yield of **4a** (**Entry 17, Table S1**), while diphenyl urea **C-4** again proved to be unreactive for this reaction (**Entry 18, Table S1**). The excellent result with thiourea is presumably attributed to the higher acidity of the catalyst upon exposure to light imparted by sulfur atom over oxygen in urea.

After ascertaining the catalytic system, the proficiency of the solvent system for the reaction was also examined (**Table S2**). In this regard, the reaction was initially performed in solvent-free conditions in order to demonstrate the essential role of solvent for this reaction (**Entry 1, Table S2**). To our pleasure, the reaction failed to provide the desired product under solvent-free conditions. Indeed, the reaction executed in various solvents including acetonitrile, dichloroethane, 1,4-dioxane, and THF again proved to be ineffective in the absence of light (**Entry 2-6, Table S2**). Gratifyingly, the best result was obtained when we conducted the reaction in acetonitrile in the presence of 10 mol% of **C-1** under 40 W blue LED irradiation, delivering the product **4a** in excellent yield (**Entry 10, Table S2**). However, the yield of **4a** was dramatically reduced to 82% with <5% of **4a′** upon switching the catalyst loading to 5 mol% (**Entry 13, Table S2**). While dropping the loading of catalyst **C-1** resulted in a drastic variation in the product yield, the same with increased loading of **C-1** seems to not affect the yield of **4a** (**Entry 14, Table S2**). Among different visible light sources scrutinized including 40 W blue LEDs, 60 W white CFLs, 30 W white LEDs, and 18 W green LEDs, 40 W blue LED has been proven to be very effective for the reaction (**Entry 16-18, Table S2**).

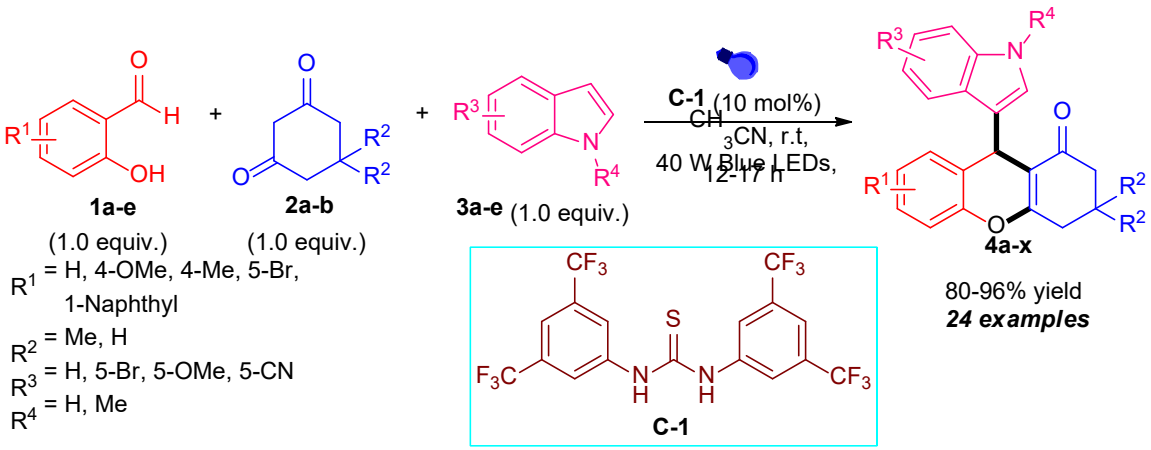
Table S2: Evaluation of solvent systems and catalyst loading [a]



Entry	**C-1** loading (X mol%)	Solvents	Light source	Yield (%)[b]		
				4a	**4a′**	**4a″**
1	10 mol%	Solvent-free	40 W Blue LEDs	-	-	-
2	10 mol%	CH_3CN	-	-		18
3[c]	10 mol%	CH_3CN	-	16	-	32
4	10 mol%	DCE	-	-		
5	10 mol%	1,4-dioxane	-	-		21
6	10 mol%	THF	-	-		19
7	10 mol%	1,4-dioxane	40 W Blue LEDs	85	-	-
8	10 mol%	DCM	40 W Blue LEDs	55	15	-
9	10 mol%	DCE	40 W Blue LEDs	68	-	<5
10	**10 mol%**	**CH_3CN**	**40 W Blue LEDs**	**90**	**-**	**-**
11	10 mol%	Toluene	40 W Blue LEDs	34	10	21
12	10 mol%	THF	40 W Blue LEDs	65	8	-
13	5 mol%	CH_3CN	40 W Blue LEDs	82	<5	-
14	15 mol%	CH_3CN	40 W Blue LEDs	92	-	-
15[d]	10 mol%	CH_3CN	40 W Blue LEDs	90	-	-
16	10 mol%	CH_3CN	60 W White CFL	90	-	-
17	10 mol%	CH_3CN	30 W White LEDs	85	<5	-
18	10 mol%	CH_3CN	18 W Green LEDs	58	10	

[a] Reaction condition: 2-hydroxybenzaldehyde **1a** (0.5 mmol), 5,5-dimethyl-cyclohexane-1,3-dione **2a** (0.5 mmol), and indole **3a** (0.5 mmol) in the presence of **C-1** with different loading (5-15 mol%) in different solvent systems (2 mL) under various visible-light sources at room temperature. [b] Yield of the referred products. [c] Run at 50 °C. [d] Run in the presence or absence of oxygen.

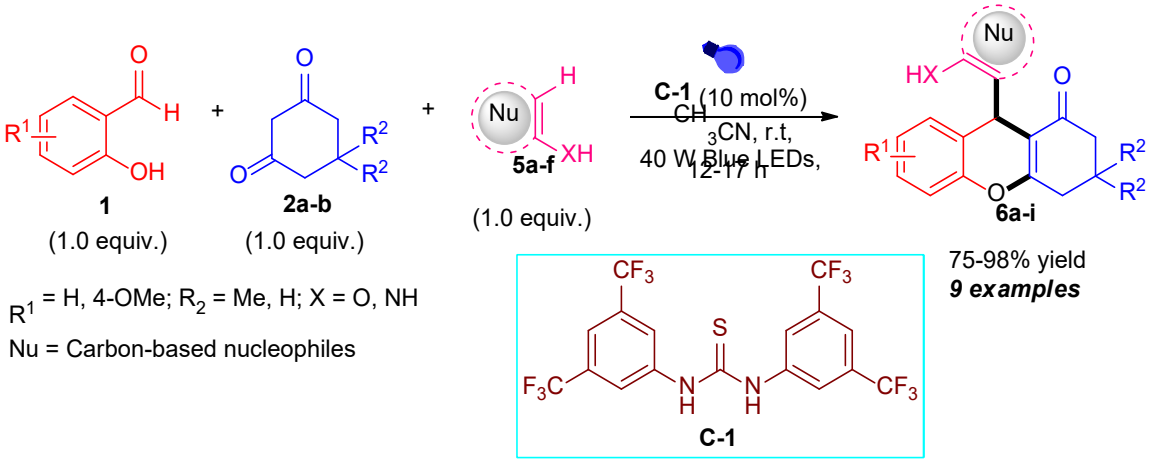
3. General procedure for the synthesis of 4a-4x



Scheme S1: General procedure for photochemical synthesis of product **4**.

An oven-dried 10 mL glass vial was charged with substituted 2-hydroxybenzaldehyde **1** (0.5 mmol), cyclohexane-1,3-diones **2** (0.5 mmol), indoles **3** (0.5 mmol) and **C-1** (10 mol%) in CH_3CN (2 mL) at room temperature. The reaction vial was then subjected to 40 W blue LED (λ = 450 nm) irradiation with continuous stirring for the optimized time (**Scheme S1**). The formation of the products was confirmed by visualizing the complete conversion of the starting material with the help of thin layer chromatography (TLC). Once the starting material was consumed, the solvent was removed under reduced pressure, and water was added to the mixture and extracted three times in EtOAc. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, and passed through a pad of celite to trap any particulate impurities and concentrated *in vacuo*. The residue was purified either by washing with 10% EtOAc/hexane or by column chromatography using hexane/EtOAc as the eluent.

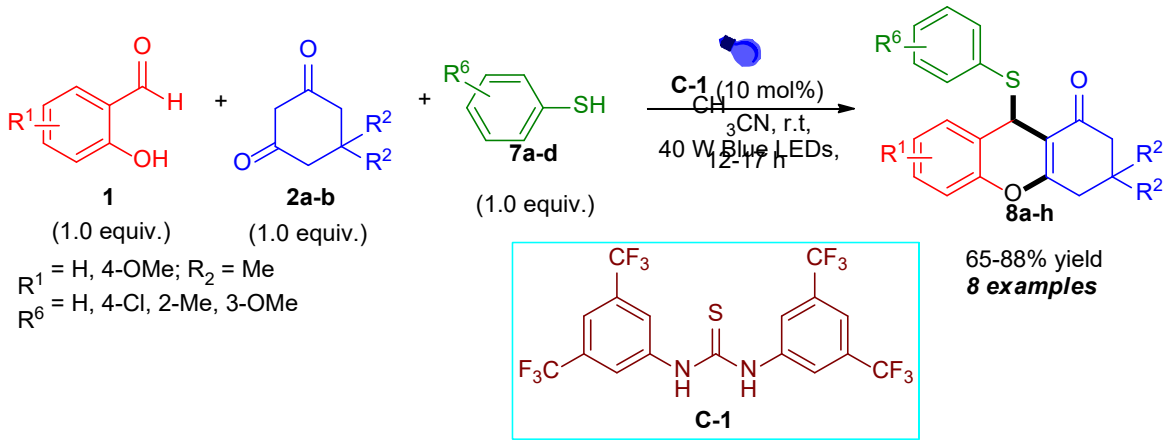
4. General procedure for the synthesis of 6:



Scheme S2: General procedure for photochemical synthesis of product **6**.

An oven-dried 10 mL glass vial was charged with substituted 2- hydroxybenzaldehyde **1a-1b** (0.5 mmol), cyclic-1,3-diketones **2a-2b** (0.5 mmol), nucleophiles **5a-5f** (0.5 mmol) and Schreiner's thiourea **C-1** (10 mol%) in CH_3CN (2 mL) at room temperature. The reaction vial was then subjected to 40 W blue LED (λ = 450 nm) irradiation with continuous stirring for the optimized time (**Scheme S2**). The progress of the reaction was monitored by thin layer chromatography (TLC). After complete consumption of the starting material, the solvent was removed under reduced pressure, and water was added to the reaction mixture. The mixture was subjected to either base aqueous wash and filtered off or extracted with ethyl acetate, washed with brine, dried over anhydrous Na_2SO_4, and isolated by column chromatography.

5. General procedure for the synthesis of 8:



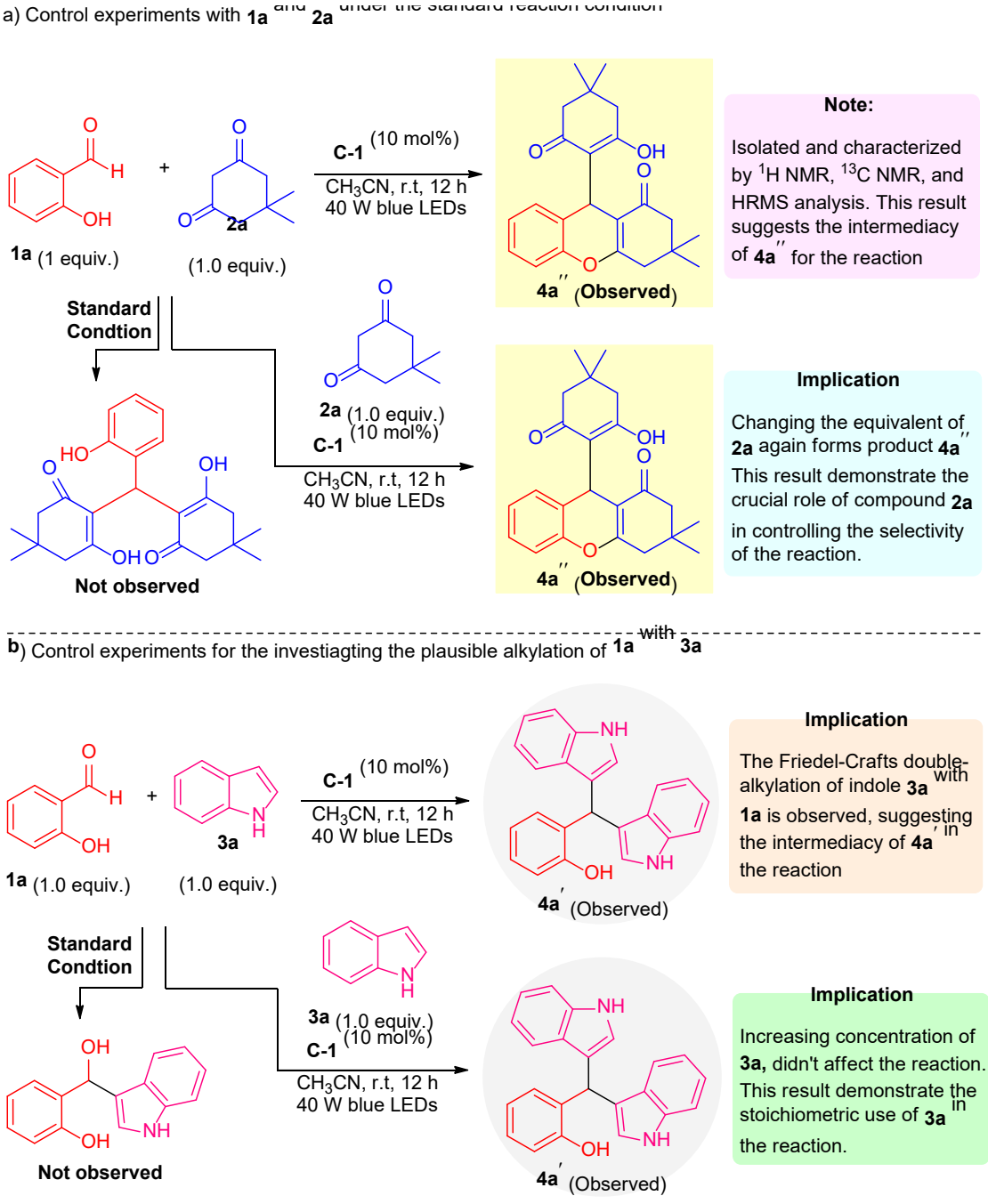
Scheme S3: General procedure for photochemical synthesis of product **8**.

An oven-dried 10 mL glass vial was charged with substituted 2- hydroxybenzaldehyde **1a-1b** (0.5 mmol), cyclic-1,3-diketones **2a-2b** (0.5 mmol), thiophenols **7a-7d** (0.5 mmol) and Schreiner's thiourea **C-1** (10 mol%) in CH_3CN (2 mL) at room temperature. The reaction vial was then subjected to 40 W blue LED (λ = 450 nm) irradiation with continuous stirring at 36 °C for the optimized time (**Scheme S3**). The completion of the reaction was scrutinized by TLC. After completion of the reactions, the solvent was removed under reduced pressure, water was added to the mixture and extracted three times in EtOAc. The combined organic layer was washed with brine, and dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The products **8a-8d** were isolated directly without using column chromatography and the remaining products were purified using column chromatography.

6. Mechanistic Investigation

6.1. Control experiments

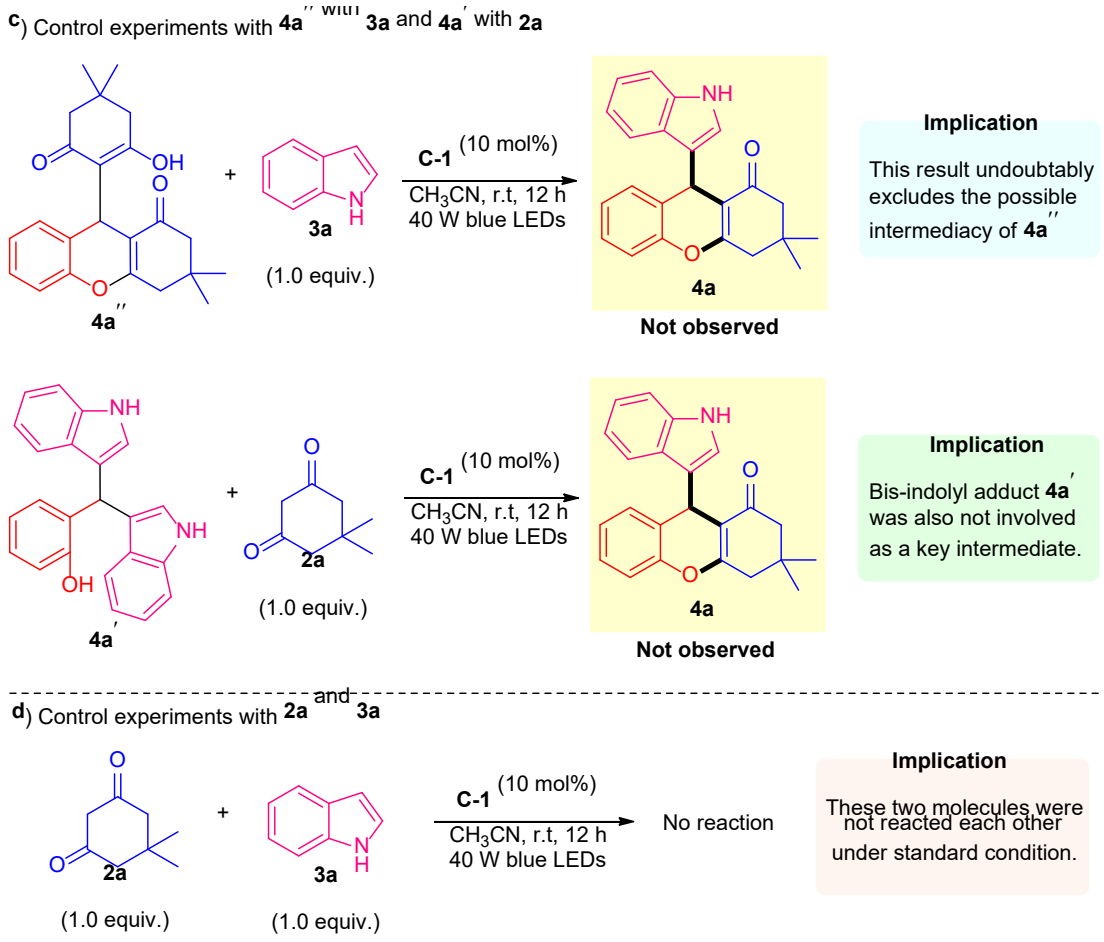
To validate the mechanism of the reaction, diverse sets of control experiments were conducted. Execution of the reaction between equimolar amounts of **1a** and **2a** under standard conditions leads to the formation of **4a″** rather than the possible double acylation tetraketone product (**Scheme S4a**). Also, increasing the concentration of **2a** did not affect the reaction.



Scheme S4: Control experiments for key active intermediacy.

Conversely, the control experiments performed for one equivalent of **1a** and one equivalent of **3a** resulted in the formation of double alkylation product **4a′** whereas no mono-alkylated product was observed (**Scheme S4b**). These results suggested the possible intermediacy of **4a″** and **4a′** for the formation of **4a**.

For further confirmation of the initiation of these two intermediates **4a″** and **4a′** in the reaction, we next performed another series of control experiments (**Scheme S5**). Initial reactions involving **4a″** and **3a** under identical conditions failed to yield the expected product **4a**. A similar result was also obtained for the reaction involving **4a′** and **2a**. Although, the preliminary observations indicate the intermediacy of **4a″** and **4a′**, however, these results completely exclude the possible intermediacy of these two compounds. Furthermore, **2a** and **3a** failed to react with each other.



Scheme S5: Control experiments for isolated adduct **4a′** and **4a″** with **3a** and **2a.**

6.2. ^{1}H NMR & ^{19}F NMR spectroscopic investigation

To gain more insight into the reaction mechanism, ^{1}H NMR & ^{19}F NMR spectroscopic analysis of **C-1**, 2-hydroxybenzaldehyde **1a**, and the corresponding 1:1 reaction mixture of **1a** and catalyst **C-1** before irradiation and after irradiation was performed using $CDCl_3$ as the solvent. The results are summarized in **Figure S2**. The stacked and superimposed ^{1}H NMR and NOSEY of the selected section of all the individual components and their reaction mixtures were disclosed in **Figure S3**, **Figure S4**, and **Figure S5**. The ^{19}F NMR analysis of the selected compounds is depicted in **Figure S6**.

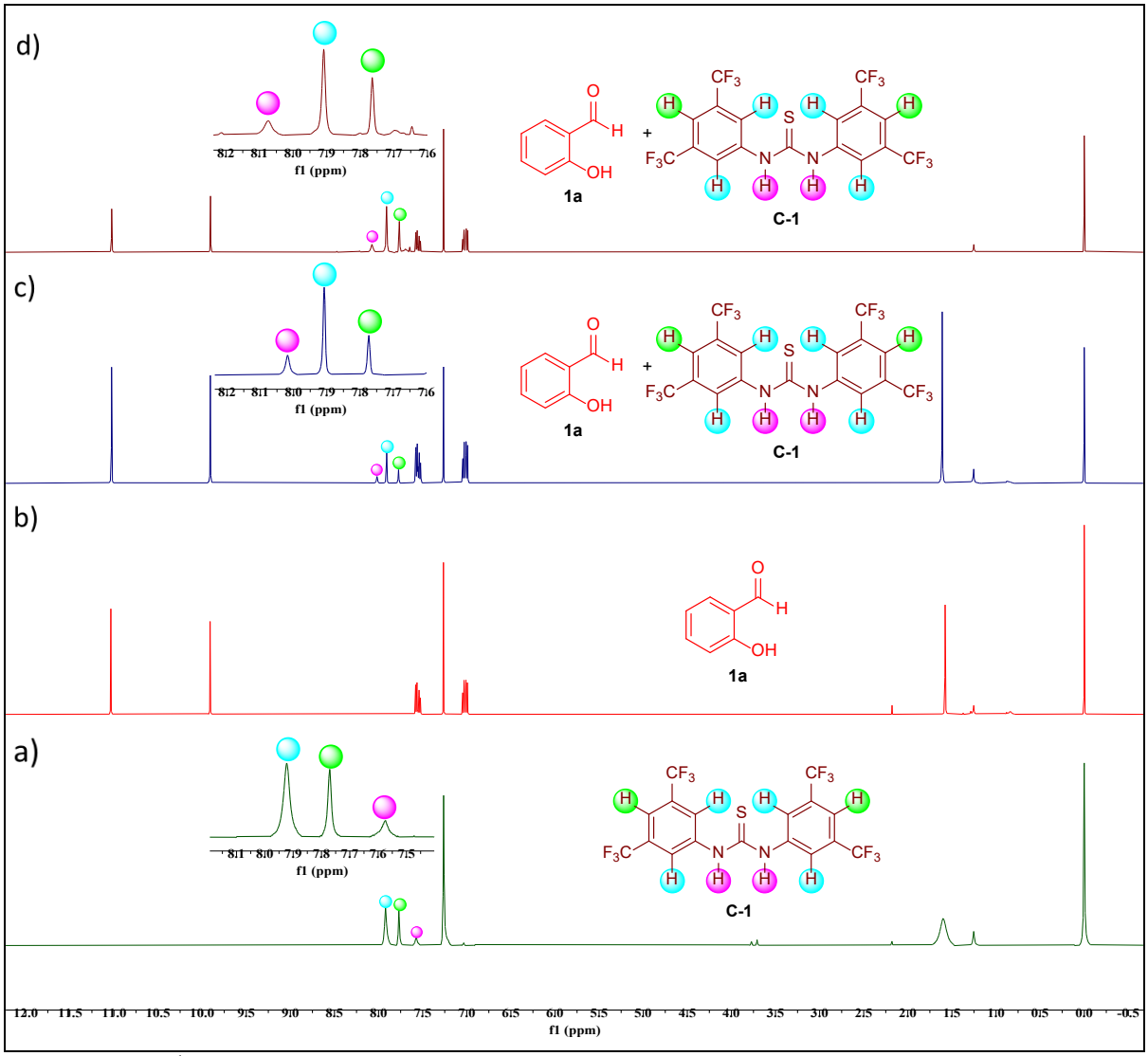


Figure S2: ^{1}H NMR (500 MHz, $CDCl_3$) spectra of **a**) **C-1** (0.01 mmol), **b**) 2-hydroxybenzaldehyde **1a** (0.001 mmol), **c**) 1:1 mixture of **1a** and **C-1** before irradiation, **d**) reaction mixture after irradiation.

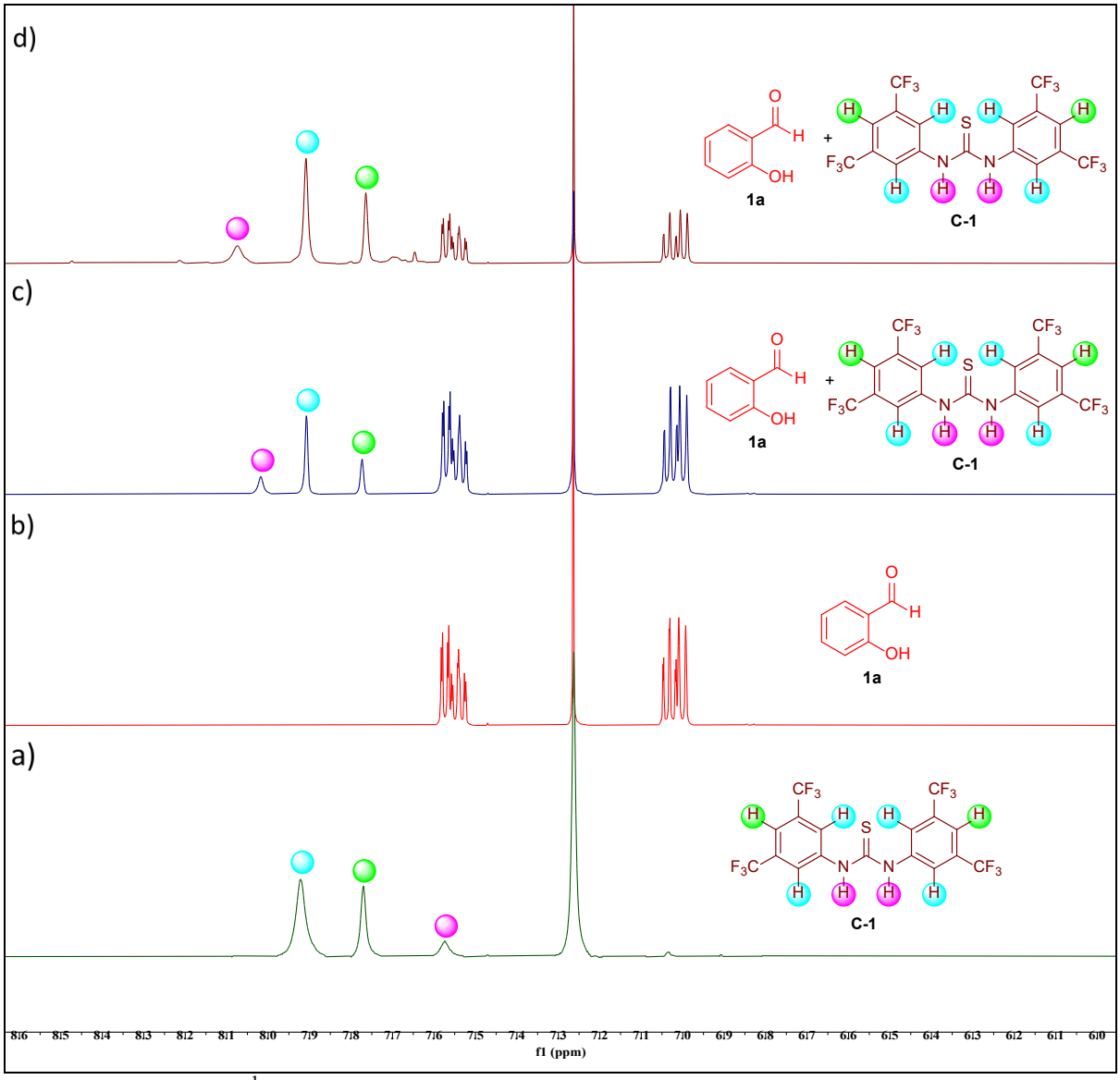


Figure S3: Stacked ^{1}H NMR (500 MHz, $CDCl_3$) (δ = 6.0 ppm to 8.6 ppm) of **a**) **C-1** (0.01 mmol), **b**) 2-hydroxybenzaldehyde **1a** (0.01 mmol), **c**) 1:1mixture of **1a** and **C-1** before irradiation, **d**) reaction mixture of **1a** and **C-1** after irradiation.

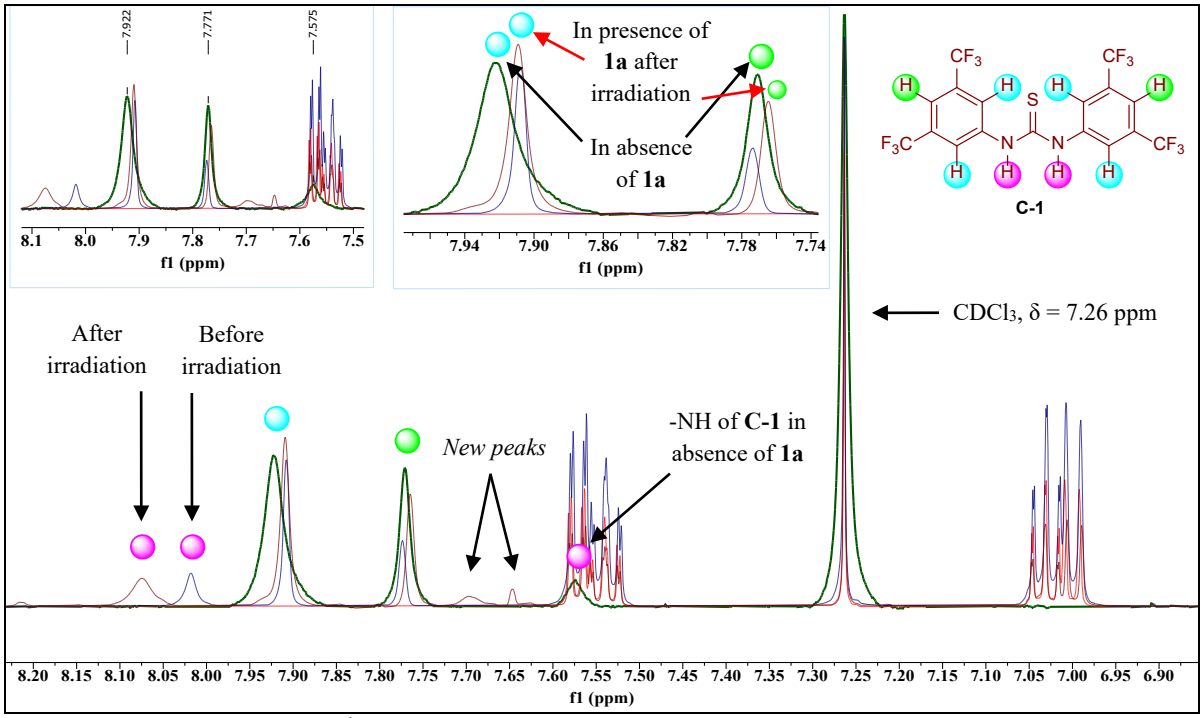


Figure S4: Superimposed ^{1}H NMR (500 MHz, $CDCl_3$) (δ = 6.90 ppm to 8.20 ppm) spectra of **C-1** before and after the addition of **1a**.

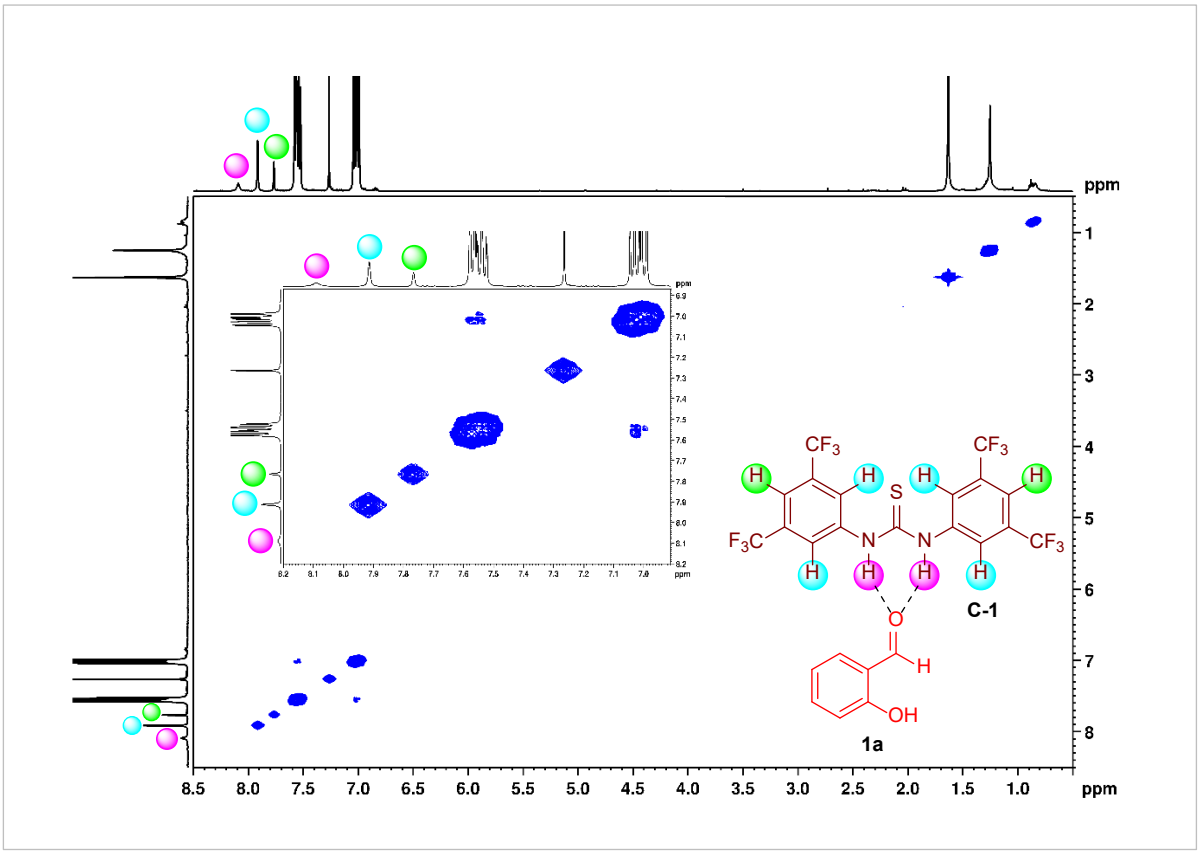


Figure S5: Sections of the NOSEY spectra of 1:1 mixture of **C-1** and 2-hydroxybenzaldehyde **1a**.

Note: The initial ^{1}H NMR spectrum of **C-1** showed a signal at 7.58 ppm for -NH protons and two sets of aromatic signals at 7.77 ppm and 7.92 ppm.[1-3] The introduction of 2-hydroxybenzaldehyde **1a** to the solution of **C-1** leads to significant changes in the chemical shift of **C-1**. The chemical shift value for NH proton which appeared at 7.58 ppm shifted downfield to 8.02 ppm before irradiation and 8.08 ppm after irradiation. The aromatic signals at 7.77 ppm shifted to 7.76 ppm before irradiation and 7.75 ppm after irradiation. Another signal at 7.92 ppm shifted upfield to 7.90 ppm before and after irradiation. This result demonstrates the possible complex formation between **C-1** and **1a** through hydrogen bonding interaction. The NOSEY spectra of a mixture of **C-1** and **1a** showed no correlation between the aromatic signals of **1a** to **C-1** due to the absence of NOE cross peaks.

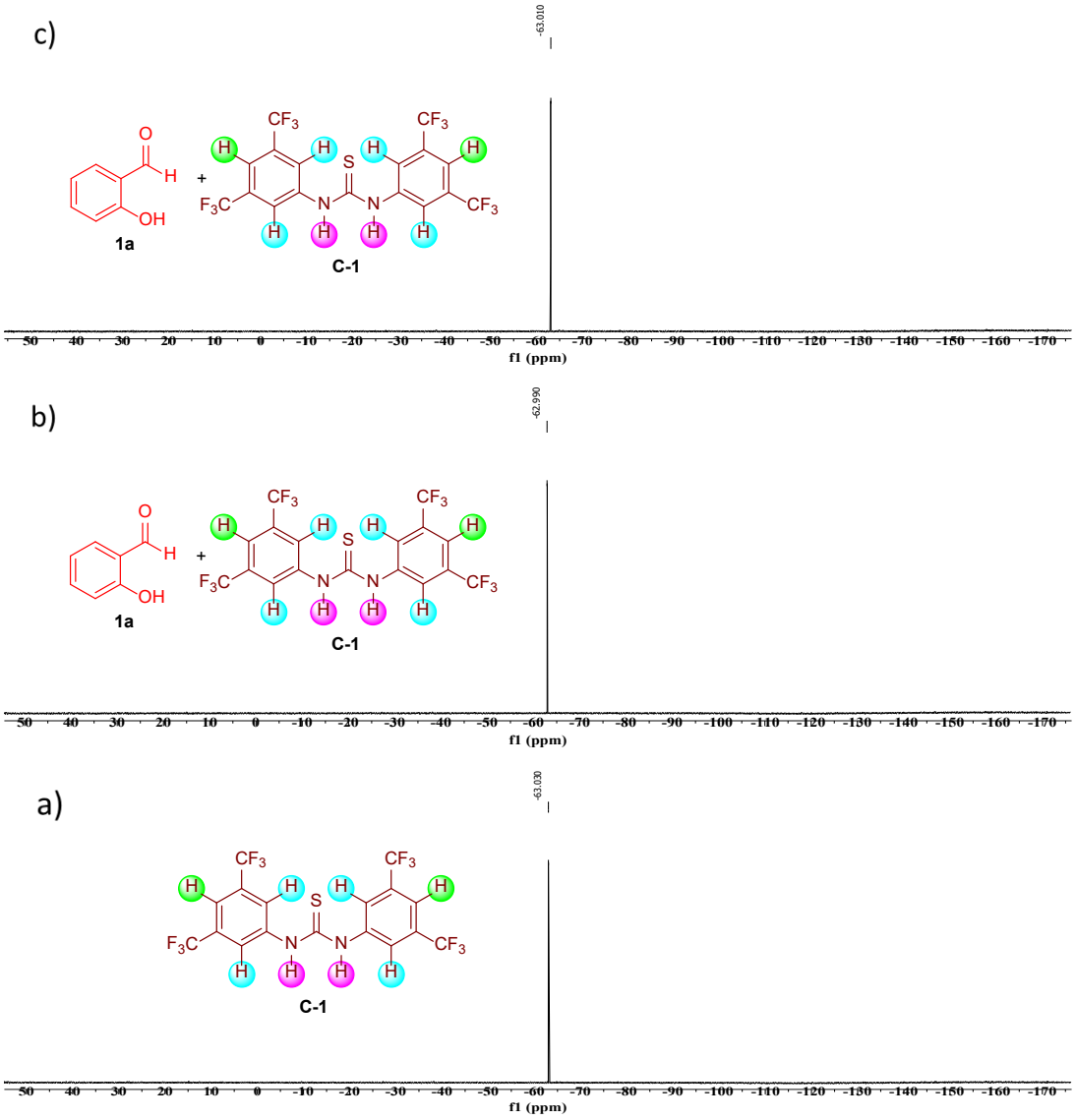


Figure S6: ^{19}F NMR (471 MHz, $CDCl_3$) spectra of **a**) **C-1**, **b**) reaction mixture (**C-1** + **1a**) before irradiation, **c**) reaction mixture after irradiation

We also performed the ^{1}H NMR analysis for 5,5-dimethyl-cyclohexane-1,3-dione **2a** and **C-1**.

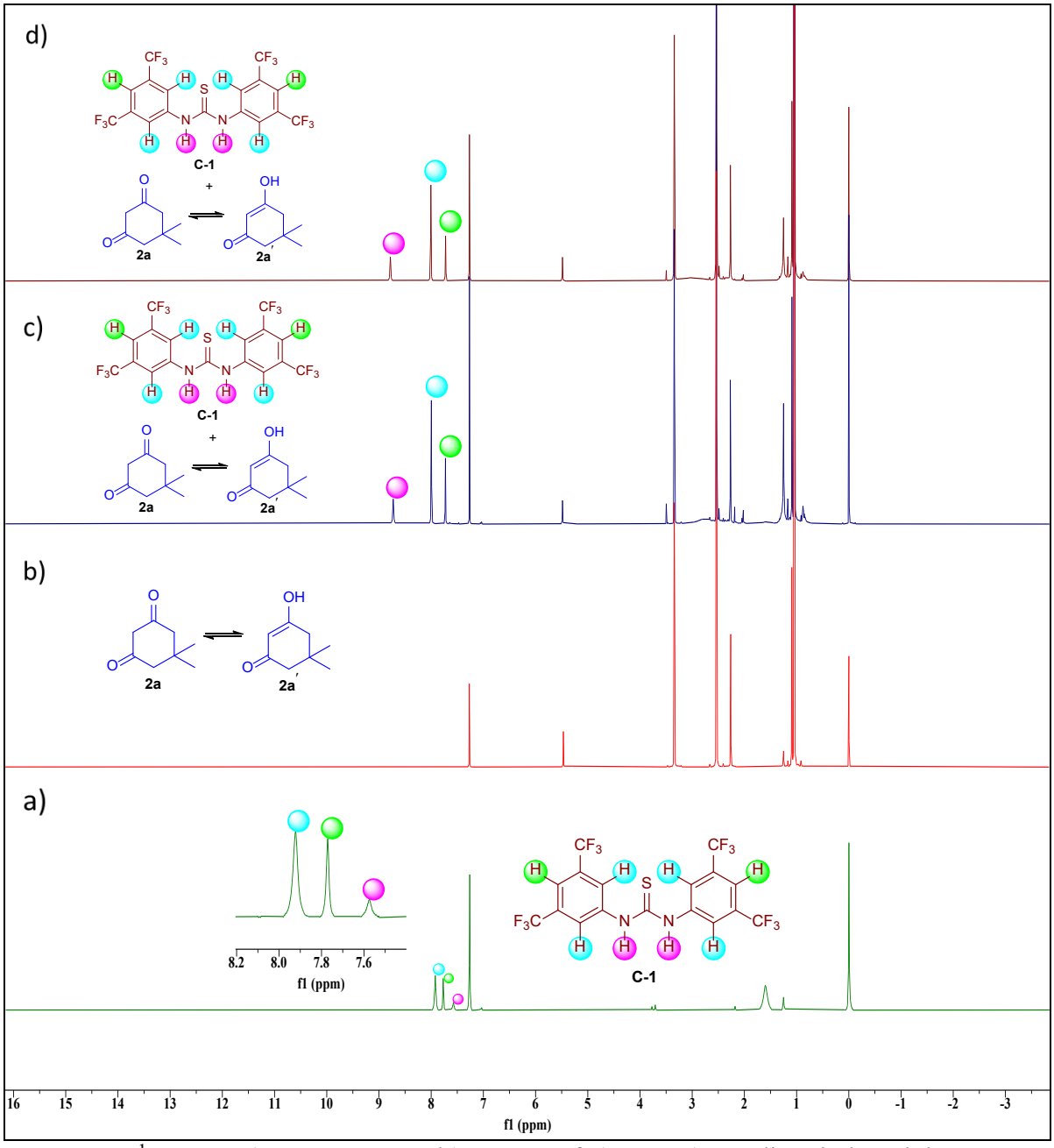
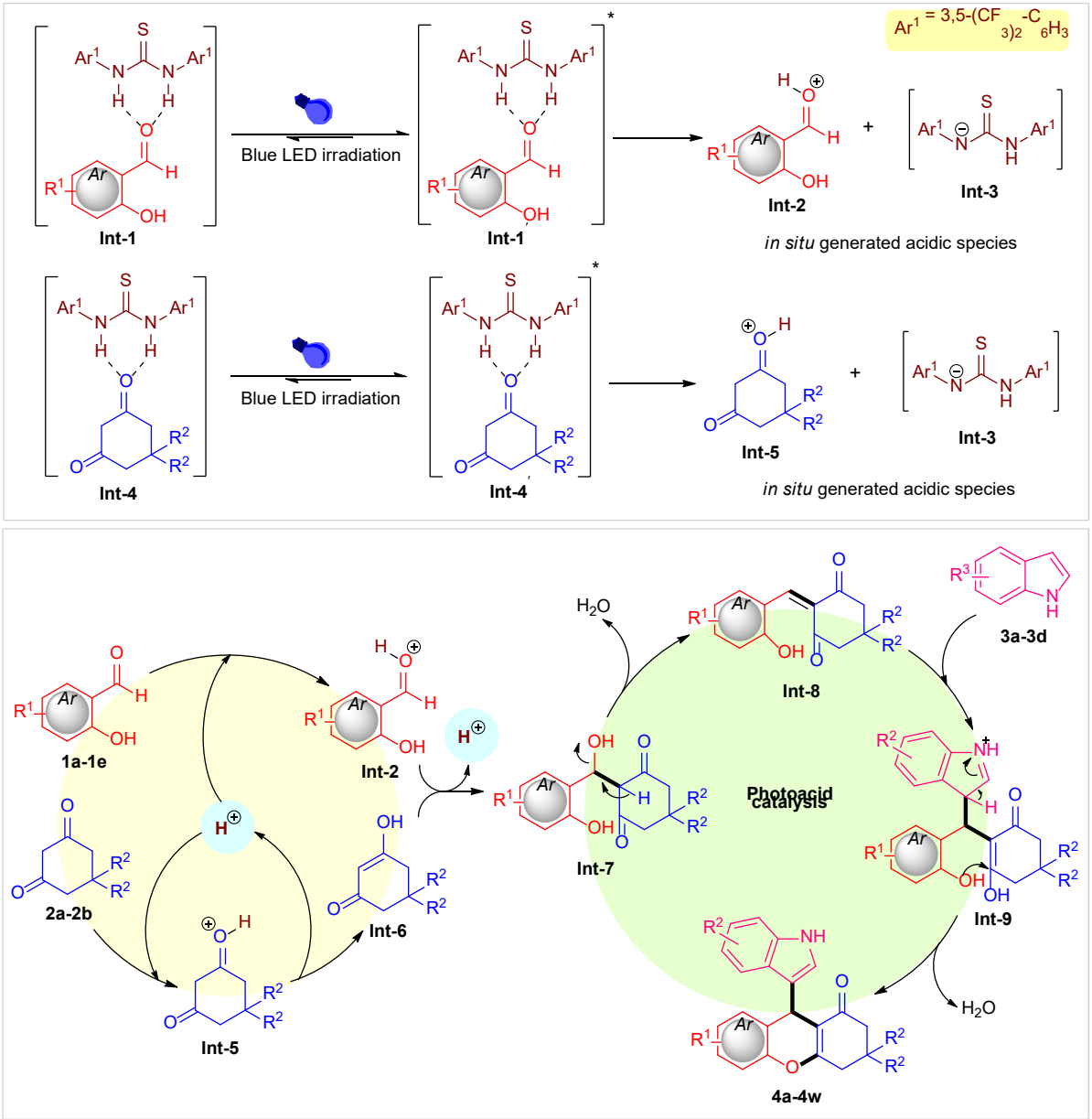


Figure S7: ^{1}H NMR (500 MHz, $CDCl_3$) spectra of **a**) **C-1**, **b**) 5,5-dimethyl-cyclohexane-1,3-dione **2a**, **c**) 1:1 mixture of **C-1** and **2a** before irradiation, **d**) reaction mixture of **C-1** and **2a** after irradiation

Note: While the ^{1}H NMR spectrum of **2a** showed a mixture of two compounds (keto and enol) in $CDCl_3$, the majority of the compound was assigned as keto form of **2a**. In this case, we again observed a large chemical shift for the NH proton of the catalyst (**Figure S7**). The

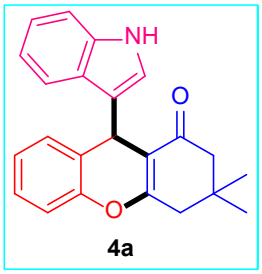
chemical shift value for -NH initially appeared at 7.58 ppm and shifted downfield to 8.73 ppm before irradiation and 8.78 ppm. The aromatic signal at 7.77 ppm shifted upfield to 7.73 ppm before irradiation and 7.72 ppm after irradiation. Another signal at 7.92 ppm shifted downfield to 7.99 ppm before irradiation and 8.0 ppm after irradiation. Based on this result, we again assume the possible formation of a ground state complex between **C-1** and **2a** through hydrogen bonding interaction.[1-3]

6.3. Proposed Reaction Mechanism



Scheme S6: Proposed photoacid catalytic cycle.

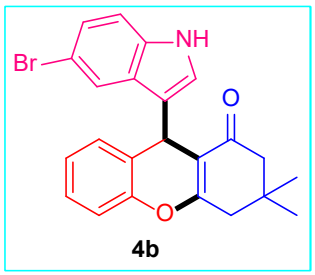
7. Characterization data for the products 4a-4x, 6a-6i, and 8a-8h:



4a

9-(1*H*-indol-3-yl)-3,3-dimethyl-2,3,4,9-tetrahydro-1*H*-xanthen-1-one, 4a:

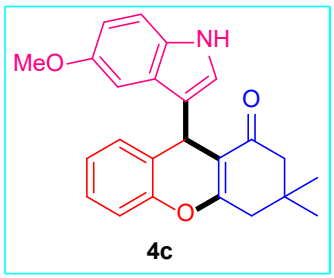
90% yield, white solid. ^{1}H NMR (500 MHz, DMSO-d_6) δ 10.86 (s, 1H), 7.44 (d, J = 8.9 Hz, 1H), 7.31-7.24 (m, 2H), 7.21 – 7.14 (m, 3H), 7.07 – 6.97 (m, 2H), 6.94 – 6.87 (m, 1H), 5.21 (s, 1H), 2.66 (d, J = 1.5 Hz, 2H), 2.29 (d, J = 16.1 Hz, 1H), 2.10 (d, J = 16.1 Hz, 1H), 1.08 (s, 3H), 0.95 (s, 3H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 196.09, 164.21, 149.03, 136.42, 129.80, 127.44, 125.83, 125.24, 124.74, 122.63, 120.79, 119.65, 118.44, 118.34, 116.15, 112.04, 111.57, 50.28, 40.49, 31.68, 28.82, 28.59, 26.77. HRMS (ESI$^+$): m/z calculated for [$C_{23}H_{21}NO_2$ + Na]$^+$: 366.1470; found 366.1472.



4b

9-(5-bromo-1*H*-indol-3-yl)-3,3-dimethyl-2,3,4,9-tetrahydro-1*H*-xanthen-1-one, 4b:

96% yield, white solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.08 (s, 1H), 7.61 (d, J = 1.9 Hz, 1H), 7.26 (dd, J = 8.2, 2.8 Hz, 2H), 7.20 (dd, J = 6.7, 2.1 Hz, 3H), 7.12 (dd, J = 8.6, 1.9 Hz, 1H), 7.05 (ddd, J = 8.2, 6.4, 2.2 Hz, 1H), 5.20 (s, 1H), 2.68 (d, J = 17.5 Hz, 1H), 2.60 (d, J = 17.5 Hz, 1H), 2.29 (d, J = 16.1 Hz, 1H), 2.10 (d, J = 16.2 Hz, 1H), 1.07 (s, 3H), 0.94 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 196.09, 164.30, 148.96, 134.97, 129.85, 127.64, 127.06, 125.52, 124.90, 124.45, 123.26, 120.77, 119.69, 116.23, 113.58, 111.97, 111.16, 50.19, 40.49, 31.70, 28.84, 28.23, 26.57. HRMS (ESI$^+$): m/z calculated for [$C_{23}H_{20}BrNO_2$ + Na]$^+$: 444.0575; found 444.0583.

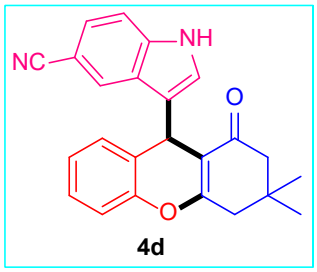


4c

9-(5-methoxy-1*H*-indol-3-yl)-3,3-dimethyl-2,3,4,9-tetrahydro-1*H*-xanthen-1-one, 4c:

92% yield, white solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.73 (s, 1H), 8.25 (d, J = 8.5 Hz, 1H), 7.86 (dd, J = 8.6, 1.8 Hz, 2H), 7.49 – 7.42 (m, 2H), 7.41 – 7.33 (m, 2H), 7.13 (d, J = 8.7 Hz, 1H), 6.85 (d, J = 2.4 Hz, 1H), 6.61 (dd, J = 8.7, 2.5 Hz, 1H), 5.86 (s, 1H), 3.68 (s, 3H), 2.68 (d, J = 17.4 Hz, 1H), 2.59 (d, J = 17.4 Hz, 1H), 2.31 (d, J = 16.2 Hz, 1H), 2.10 (d, J = 16.2 Hz, 1H), 1.04 (s, 3H), 0.82 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 196.16, 163.26, 152.73, 147.06, 131.35, 131.11, 128.66, 126.82, 125.64, 124.74, 123.51, 117.36, 116.89,

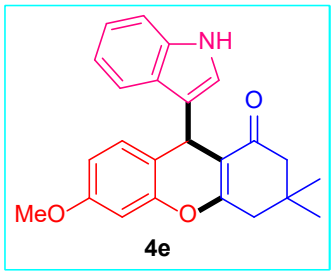
112.34, 112.16, 110.48, 100.21, 55.02, 50.26, 40.24, 31.80, 28.88, 26.48, 25.94. HRMS (ESI$^+$): m/z calculated for [$C_{24}H_{23}NO_3$ + Na]$^+$: 396.1576; found 396.1577.



4d

3-(3,3-dimethyl-1-oxo-2,3,4,9-tetrahydro-1*H*-xanthen-9-yl)-1*H*-indole-5-carbonitrile, 4d:

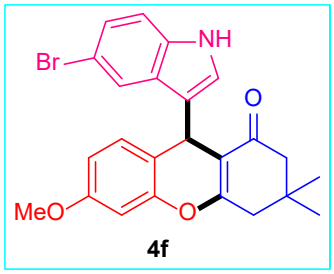
80% yield, white solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.47 (s, 1H), 8.00 (d, J = 1.6 Hz, 1H), 7.47 (d, J = 8.4 Hz, 1H), 7.38 (dd, J = 8.5, 1.6 Hz, 1H), 7.34 – 7.27 (m, 2H), 7.21 (dd, J = 5.9, 1.8 Hz, 2H), 7.05 (ddd, J = 8.2, 6.2, 2.4 Hz, 1H), 5.29 (s, 1H), 2.66 (s, 2H), 2.29 (d, J = 16.1 Hz, 1H), 2.12 (d, J = 16.1 Hz, 1H), 1.07 (s, 3H), 0.94 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 196.13, 164.55, 148.93, 137.98, 129.84, 127.79, 125.56, 125.35, 125.14, 124.98, 124.08, 123.62, 121.14, 120.88, 116.33, 112.97, 111.94, 100.60, 50.18, 40.45, 31.75, 28.71, 27.98, 26.68. HRMS (ESI$^+$): m/z calculated for [$C_{24}H_{20}N_2O_2$ + Na]$^+$: 391.1422; found 391.1424.



4e

9-(1*H*-indol-3-yl)-6-methoxy-3,3-dimethyl-2,3,4,9-tetrahydro-1*H*-xanthen-1-one, 4e:

82% yield, white solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.82 (s, 1H), 7.39 (d, J = 7.9 Hz, 1H), 7.27 (d, J = 8.1 Hz, 1H), 7.17 – 7.09 (m, 2H), 7.06 – 6.95 (m, 1H), 6.92 – 6.84 (m, 1H), 6.73 (d, J = 2.6 Hz, 1H), 6.62 (dd, J = 8.5, 2.6 Hz, 1H), 5.12 (s, 1H), 3.71 (s, 3H), 2.63 (s, 2H), 2.27 (d, J = 16.0 Hz, 1H), 2.08 (d, J = 16.1 Hz, 1H), 1.06 (s, 3H), 0.92 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 196.12, 163.99, 158.44, 149.56, 136.43, 130.36, 125.23, 122.52, 120.71, 119.81, 118.35, 117.72, 112.28, 111.53, 111.48, 100.98, 55.36, 50.28, 40.45, 31.68, 28.79, 28.06, 26.78. HRMS (ESI$^+$): m/z calculated for [$C_{24}H_{23}NO_3$ + Na]$^+$: 396.1576; found 396.1580.

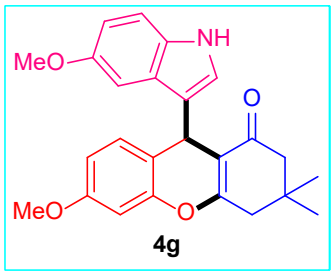


4f

9-(5-bromo-1*H*-indol-3-yl)-6-methoxy-3,3-dimethyl-2,3,4,9-tetrahydro-1*H*-xanthen-1-one, 4f:

90% yield, ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.06 (s, 1H), 7.58 (d, J = 2.0 Hz, 1H), 7.26 (d, J = 8.6 Hz, 1H), 7.20 (d, J = 2.4 Hz, 1H), 7.15 – 7.09 (m, 2H), 6.77 (d, J = 2.6 Hz, 1H), 6.65 (dd, J = 8.5, 2.6 Hz, 1H), 5.12 (s, 1H), 3.72 (s, 3H), 2.66 (d, J = 17.4 Hz, 1H), 2.57 (d, J = 17.5 Hz, 1H), 2.28 (d, J = 16.1 Hz, 1H), 2.09 (d, J = 16.1 Hz, 1H), 1.06 (s, 3H), 0.93 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 196.12, 164.11, 158.59, 149.52, 135.01, 130.41, 127.07, 124.35,

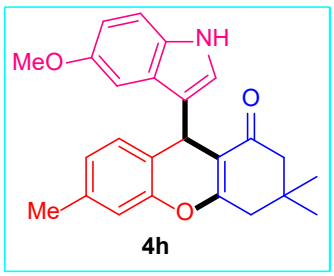
123.20, 120.79, 119.91, 117.40, 113.55, 112.23, 111.68, 111.11, 101.04, 55.40, 50.20, 40.49, 31.68, 28.84, 27.76, 26.57. HRMS (ESI$^+$): m/z calculated for [$C_{24}H_{22}BrNO_3$ + Na]$^+$: 474.0681; found 474.0704.



4g

6-methoxy-9-(5-methoxy-1*H*-indol-3-yl)-3,3-dimethyl-2,3,4,9-tetrahydro-1*H*-xanthen-1-one, 4g:

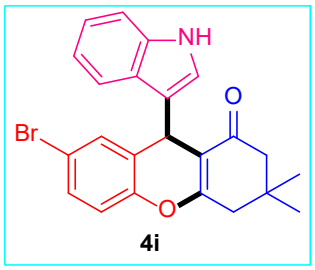
94% yield, white solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.68 (s, 1H), 7.23 – 7.11 (m, 3H), 6.90 (d, J = 2.4 Hz, 1H), 6.76 (d, J = 2.6 Hz, 3H), 6.66 (ddd, J = 14.7, 8.6, 2.5 Hz, 2H), 5.12 (s, 1H), 3.72 (s, 6H), 2.61 (d, J = 4.3 Hz, 2H), 2.28 (d, J = 16.1 Hz, 1H), 2.11 (d, J = 16.1 Hz, 1H), 1.06 (s, 3H), 0.94 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 196.16, 163.98, 158.50, 152.77, 149.76, 131.66, 130.44, 125.56, 123.18, 119.62, 117.72, 112.31, 112.17, 111.50, 110.67, 100.93, 100.36, 55.35, 55.14, 50.30, 40.50, 31.67, 28.88, 28.13, 26.81. HRMS (ESI$^+$): m/z calculated for [$C_{25}H_{25}NO_4$ + Na]$^+$: 426.1681; found 426.1689.



4h

9-(5-methoxy-1*H*-indol-3-yl)-3,3,6-trimethyl-2,3,4,9-tetrahydro-1*H*-xanthen-1-one, 4h:

86% yield, white solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.72 (s, 1H), 7.18 (d, J = 8.8 Hz, 1H), 7.15 (d, J = 2.4 Hz, 1H), 7.08 – 7.03 (m, 2H), 6.98 (dd, J = 8.4, 2.1 Hz, 1H), 6.86 (d, J = 2.4 Hz, 1H), 6.65 (dd, J = 8.8, 2.4 Hz, 1H), 5.11 (s, 1H), 3.69 (s, 3H), 2.65 (d, J = 18.0 Hz, 1H), 2.58 (d, J = 17.5 Hz, 1H), 2.28 (d, J = 16.2 Hz, 1H), 2.15 (s, 3H), 2.08 (d, J = 16.2 Hz, 1H), 1.05 (s, 3H), 0.91 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 196.07, 164.16, 152.74, 147.20, 133.72, 131.59, 129.94, 128.03, 125.50, 125.27, 123.29, 119.28, 115.83, 112.18, 111.82, 110.69, 100.26, 55.12, 50.25, 40.51, 31.67, 28.92, 28.73, 26.73, 20.33. HRMS (ESI$^+$): m/z calculated for [$C_{25}H_{25}NO_3$ + Na]$^+$: 410.1732; found 410.1745.

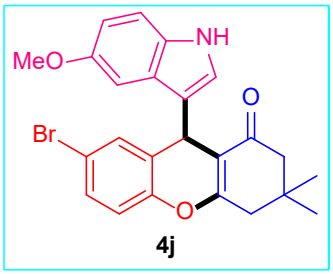


4i

7-bromo-9-(1*H*-indol-3-yl)-3,3-dimethyl-2,3,4,9-tetrahydro-1*H*-xanthen-1-one, 4i:

95% yield, white solid. ^{1}H NMR (500 MHz, DMSO-d_6) δ 11.07 (s, 1H), 7.57 (d, J = 1.9 Hz, 1H), 7.30 – 7.14 (m, 6H), 7.11 (dt, J = 8.6, 1.4 Hz, 1H), 7.07 – 7.01 (m, 1H), 5.18 (s, 1H), 2.67 (d, J = 17.5 Hz, 1H), 2.57 (d, J = 17.4 Hz, 1H), 2.29 (d, J = 16.3 Hz, 1H), 2.08 (d, J = 16.0 Hz, 1H), 1.06 (s, 3H), 0.92 (s, 3H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 196.52, 164.62, 149.12, 135.16,

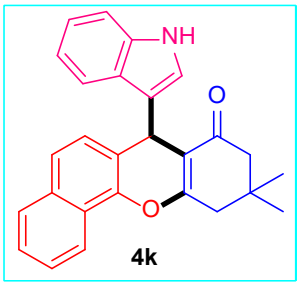
130.02, 127.89, 127.20, 125.60, 125.13, 124.62, 123.48, 120.89, 119.82, 116.41, 113.80, 112.12, 111.36, 50.36, 40.69, 31.85, 29.02, 28.47, 26.67. HRMS (ESI$^+$): m/z calculated for $[C_{23}H_{20}BrNO_2 + Na]^+$: 444.0575; found 444.0583.



4j

7-bromo-9-(5-methoxy-1*H*-indol-3-yl)-3,3-dimethyl-2,3,4,9-tetrahydro-1*H*-xanthen-1-one, 4j:

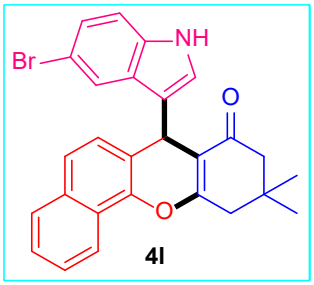
91% yield, white solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.06 (s, 1H), 7.58 (d, J = 2.0 Hz, 1H), 7.26 (d, J = 8.6 Hz, 1H), 7.20 (d, J = 2.4 Hz, 1H), 7.15 – 7.09 (m, 2H), 6.77 (d, J = 2.6 Hz, 1H), 6.65 (dd, J = 8.5, 2.6 Hz, 1H), 5.12 (s, 1H), 3.72 (s, 3H), 2.66 (d, J = 17.4 Hz, 1H), 2.57 (d, J = 17.5 Hz, 1H), 2.28 (d, J = 16.1 Hz, 1H), 2.09 (d, J = 16.2 Hz, 1H), 1.06 (s, 3H), 0.93 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 196.57, 164.56, 159.03, 149.96, 135.45, 130.85, 127.52, 124.80, 123.65, 121.23, 120.35, 117.85, 113.99, 112.67, 112.13, 111.55, 101.48, 55.84, 50.65, 40.94, 32.12, 29.28, 28.20, 27.01. HRMS (ESI$^+$): m/z calculated for $[C_{24}H_{22}BrNO_3 + Na]^+$: 474.0681; found 474.0676.



4k

7-(1*H*-indol-3-yl)-10,10-dimethyl-10,11-dihydro-7*H*-benzo[*c*]xanthen-8(9*H*)-one, 4k:

95% yield, white solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.86 (s, 1H), 8.23 (d, J = 8.4 Hz, 1H), 7.86 (d, J = 8.8 Hz, 2H), 7.45 (t, J = 8.6 Hz, 2H), 7.36 (d, J = 10.3 Hz, 3H), 7.22 (d, J = 7.9 Hz, 1H), 6.93 (t, J = 7.5 Hz, 1H), 6.84 (t, J = 7.7 Hz, 1H), 5.87 (s, 1H), 2.69 (d, J = 17.4 Hz, 1H), 2.59 (d, J = 17.3 Hz, 1H), 2.31 (d, J = 16.3 Hz, 1H), 2.09 (d, J = 15.6 Hz, 1H), 1.05 (s, 3H), 0.80 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 196.17, 163.28, 146.99, 136.16, 131.09, 128.68, 128.47, 126.84, 125.35, 124.80, 124.21, 123.47, 120.57, 118.48, 118.24, 117.73, 117.26, 117.06, 112.51, 111.61, 50.28, 40.25, 31.83, 28.88, 26.41, 25.95. HRMS (ESI$^+$): m/z calculated for $[C_{27}H_{23}NO_2 + Na]^+$: 416.1626; found 416.1639.

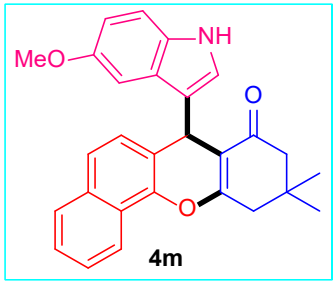


4l

7-(5-bromo-1*H*-indol-3-yl)-10,10-dimethyl-10,11-dihydro-7*H*-benzo[c]xanthen-8(9*H*)-one, 4l:

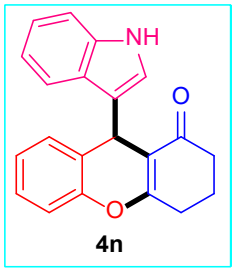
93% yield, white solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.10 (s, 1H), 8.16 (d, J = 8.4 Hz, 1H), 7.87 (dd, J = 8.6, 4.1 Hz, 2H), 7.58 (s, 1H), 7.51 – 7.42 (m, 2H), 7.41 – 7.35 (m, 2H), 7.22 (d, J = 8.5 Hz, 1H), 7.07 (d, J = 9.6 Hz, 1H), 5.85 (s, 1H), 2.67 (d, J = 17.3 Hz, 1H), 2.56 (d, J = 17.3

Hz, 1H), 2.30 (d, J = 16.1 Hz, 1H), 2.11 (d, J = 16.3 Hz, 1H), 1.04 (s, 3H), 0.81 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 196.13, 163.34, 146.99, 134.76, 131.08, 130.95, 128.88, 128.49, 127.16, 126.94, 125.90, 124.86, 123.33, 123.07, 120.80, 117.85, 116.97, 113.57, 112.49, 111.24, 50.18, 40.25, 31.79, 28.79, 26.27, 25.63. HRMS (ESI$^+$): m/z calculated for $[C_{27}H_{22}BrNO_2 + Na]^+$: 494.0732; found 494.0735.



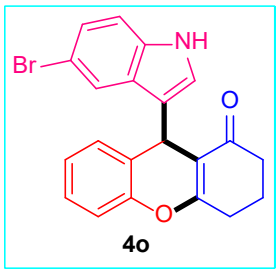
7-(5-methoxy-1*H*-indol-3-yl)-10,10-dimethyl-10,11-dihydro-7*H*-benzo[*c*]xanthen-8(9*H*)-one, 4m:

87% yield, white solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.71 (s, 1H), 8.24 (d, J = 8.4 Hz, 1H), 7.86 (d, J = 9.1 Hz, 2H), 7.50 – 7.43 (m, 3H), 7.41 – 7.36 (m, 2H), 7.35 (d, J = 2.6 Hz, 1H), 7.11 (d, J = 8.8 Hz, 1H), 6.82 (d, J = 2.5 Hz, 1H), 6.59 (dd, J = 8.8, 2.5 Hz, 1H), 5.84 (s, 1H), 3.66 (s, 3H), 2.70 (d, J = 17.3 Hz, 1H), 2.60 (d, J = 17.4 Hz, 1H), 2.32 (d, J = 16.3 Hz, 1H), 2.10 (d, J = 16.0 Hz, 1H), 1.05 (s, 3H), 0.83 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 196.17, 163.27, 152.70, 147.05, 131.32, 131.11, 131.08, 128.67, 128.46, 126.83, 125.61, 124.78, 124.74, 123.51, 117.32, 117.06, 116.89, 112.32, 112.15, 110.45, 100.18, 55.02, 50.26, 40.25, 31.83, 28.89, 26.49, 25.92. HRMS (ESI$^+$): m/z calculated for $[C_{28}H_{25}NO_3 + Na]^+$: 446.1732; found 446.1720.



9-(1*H*-indol-3-yl)-2,3,4,9-tetrahydro-1*H*-xanthen-1-one, 4n:

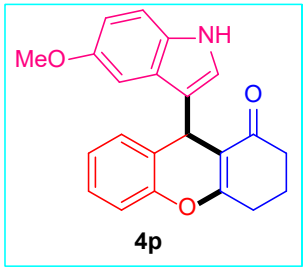
92% yield, white solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.87 (s, 1H), 7.50 (d, J = 7.9 Hz, 1H), 7.34 – 7.28 (m, 2H), 7.17 (dd, J = 5.3, 2.1 Hz, 3H), 7.03 (ddd, J = 9.4, 7.1, 2.0 Hz, 2H), 6.94 (ddd, J = 8.0, 7.0, 1.1 Hz, 1H), 5.24 (s, 1H), 2.83 – 2.64 (m, 2H), 2.39 – 2.22 (m, 2H), 1.99 (dq, J = 13.3, 5.1 Hz, 1H), 1.87 (ddd, J = 20.3, 8.8, 5.2 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 196.24, 166.19, 149.03, 136.48, 129.72, 127.42, 125.96, 125.34, 124.72, 122.73, 120.79, 119.65, 118.54, 118.37, 116.12, 113.21, 111.59, 36.63, 28.53, 27.17, 20.16. HRMS (ESI$^+$): m/z calculated for $[C_{21}H_{17}NO_2 + Na]^+$: 338.1157; found 338.1155.



9-(5-bromo-1*H*-indol-3-yl)-2,3,4,9-tetrahydro-1*H*-xanthen-1-one, 4o:

86% yield, white solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.09 (s, 1H), 7.71 (d, J = 1.9 Hz, 1H), 7.29 (t, J = 8.0 Hz, 2H), 7.23 – 7.12 (m,

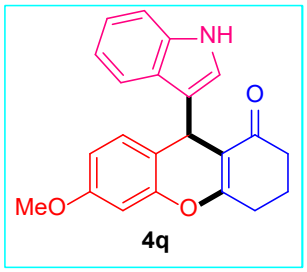
4H), 7.05 (ddd, *J* = 7.6, 6.4, 2.1 Hz, 1H), 5.24 (s, 1H), 2.80 – 2.64 (m, 2H), 2.38 – 2.22 (m, 2H), 1.99 (dq, *J* = 13.2, 5.0 Hz, 1H), 1.94 – 1.83 (m, 1H). ^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ 196.24, 166.25, 148.99, 134.99, 129.70, 127.60, 127.19, 125.69, 124.86, 124.59, 123.30, 120.75, 119.80, 116.18, 113.57, 113.27, 111.26, 36.58, 28.11, 27.17, 20.15. HRMS (ESI$^+$): m/z calculated for [$C_{21}H_{16}BrNO_2$ + Na]$^+$: 416.0262; found 416.0256.



4p

9-(5-methoxy-1*H*-indol-3-yl)-2,3,4,9-tetrahydro-1*H*-xanthen-1-one, 4p:

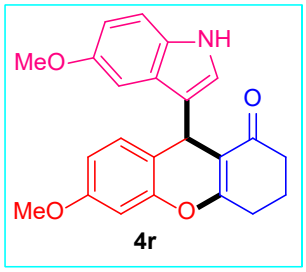
90% yield, white solid. ^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 10.71 (s, 1H), 7.33 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.22 – 7.15 (m, 3H), 7.11 (d, *J* = 2.5 Hz, 1H), 7.05 (ddd, *J* = 7.5, 6.1, 2.3 Hz, 1H), 6.97 (d, *J* = 2.4 Hz, 1H), 6.69 (dd, *J* = 8.8, 2.5 Hz, 1H), 5.22 (s, 1H), 3.73 (s, 3H), 2.84 – 2.64 (m, 3H), 2.39 – 2.24 (m, 3H), 1.99 (dq, *J* = 13.2, 4.9 Hz, 1H), 1.88 (ddd, *J* = 14.4, 10.0, 7.1 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ 196.28, 166.17, 152.91, 149.17, 131.63, 129.76, 127.43, 125.94, 125.62, 124.77, 123.38, 119.39, 116.03, 113.25, 112.18, 110.66, 100.39, 55.20, 36.65, 28.49, 27.17, 20.21. HRMS (ESI$^+$): m/z calculated for [$C_{22}H_{19}NO_3$ + Na]$^+$: 368.1263; found 368.1257.



4q

9-(1*H*-indol-3-yl)-6-methoxy-2,3,4,9-tetrahydro-1*H*-xanthen-1-one, 4q:

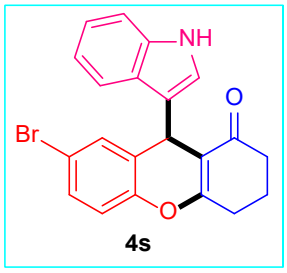
92% yield, white solid. ^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 10.83 (d, *J* = 2.5 Hz, 1H), 7.46 (d, *J* = 7.9 Hz, 1H), 7.30 (d, *J* = 8.0 Hz, 1H), 7.20 – 7.14 (m, 2H), 7.02 (ddd, *J* = 8.2, 7.0, 1.2 Hz, 1H), 6.92 (ddd, *J* = 8.1, 7.0, 1.1 Hz, 1H), 6.75 (d, *J* = 2.6 Hz, 1H), 6.63 (dd, *J* = 8.5, 2.6 Hz, 1H), 5.17 (s, 1H), 3.71 (s, 3H), 2.82 – 2.63 (m, 2H), 2.30 (dddd, *J* = 21.8, 16.7, 11.1, 5.1 Hz, 2H), 1.98 (dq, *J* = 13.3, 5.1 Hz, 1H), 1.87 (dq, *J* = 9.8, 4.9 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ 196.28, 165.98, 158.47, 149.59, 136.50, 130.28, 125.36, 122.62, 120.73, 119.87, 118.47, 118.37, 117.88, 113.49, 111.56, 111.41, 101.01, 55.35, 36.65, 28.03, 27.15, 20.18. HRMS (ESI$^+$): m/z calculated for [$C_{22}H_{19}NO_3$ + Na]$^+$: 368.1263; found 368.1264.



4r

6-methoxy-9-(5-methoxy-1*H*-indol-3-yl)-2,3,4,9-tetrahydro-1*H*-xanthen-1-one, 4r:

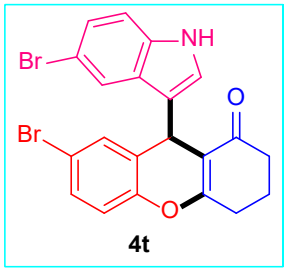
94% yield, white solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.67 (s, 1H), 7.19 (dd, J = 8.8, 4.8 Hz, 2H), 7.09 (d, J = 2.6 Hz, 1H), 6.92 (d, J = 2.5 Hz, 1H), 6.75 (t, J = 3.1 Hz, 1H), 6.66 (ddd, J = 9.9, 8.6, 2.6 Hz, 2H), 5.13 (s, 1H), 3.72 (d, J = 2.0 Hz, 6H), 2.82 – 2.63 (m, 2H), 2.39 – 2.22 (m, 2H), 2.04 – 1.94 (m, 1H), 1.94 – 1.81 (m, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 196.32, 165.98, 158.49, 152.83, 149.72, 131.65, 130.32, 125.63, 123.27, 119.61, 117.87, 113.52, 112.13, 111.46, 110.54, 100.94, 100.43, 55.37, 55.18, 36.66, 27.96, 27.15, 20.22. HRMS (ESI$^+$): m/z calculated for [$C_{23}H_{21}NO_4$ + Na]$^+$: 398.1368; found 398.1374.



4s

7-bromo-9-(1*H*-indol-3-yl)-2,3,4,9-tetrahydro-1*H*-xanthen-1-one, 4s:

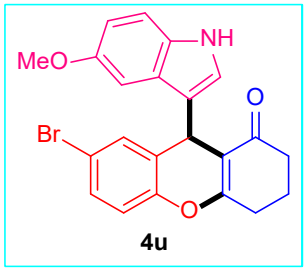
93% yield, white solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.93 (s, 1H), 7.51 – 7.45 (m, 2H), 7.37 – 7.30 (m, 2H), 7.22 (d, J = 2.5 Hz, 1H), 7.14 (d, J = 8.7 Hz, 1H), 7.07 – 7.00 (m, 1H), 6.98 – 6.92 (m, 1H), 5.25 (s, 1H), 2.73 (tdd, J = 21.9, 15.1, 8.6 Hz, 2H), 2.30 (dddd, J = 22.1, 16.7, 11.1, 5.1 Hz, 2H), 1.98 (dq, J = 13.3, 5.0 Hz, 1H), 1.87 (qd, J = 12.2, 5.2 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 196.10, 165.89, 148.20, 136.45, 132.05, 130.26, 128.49, 125.16, 123.04, 120.91, 119.11, 118.71, 118.51, 118.14, 116.17, 112.80, 111.72, 36.58, 28.46, 27.05, 20.11. HRMS (ESI$^+$): m/z calculated for [$C_{21}H_{16}BrNO_2$ + Na]$^+$: 416.0262; found 416.0256.



4t

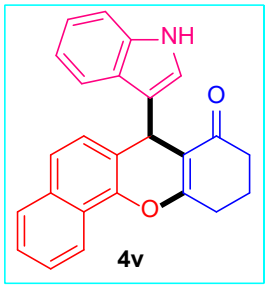
7-bromo-9-(5-bromo-1*H*-indol-3-yl)-2,3,4,9-tetrahydro-1*H*-xanthen-1-one, 4t:

90% yield, white solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.16 (s, 1H), 7.74 (d, J = 2.1 Hz, 1H), 7.49 (d, J = 2.5 Hz, 1H), 7.36 (dd, J = 8.8, 2.5 Hz, 1H), 7.29 (d, J = 8.6 Hz, 1H), 7.21 (d, J = 2.6 Hz, 1H), 7.15 (dd, J = 8.6, 3.3 Hz, 2H), 5.26 (s, 1H), 2.71 (dt, J = 9.7, 5.4 Hz, 2H), 2.39 – 2.21 (m, 2H), 1.99 (dq, J = 13.2, 5.0 Hz, 1H), 1.93 – 1.81 (m, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 196.09, 165.96, 148.20, 134.97, 132.05, 130.42, 128.26, 127.03, 124.87, 123.44, 120.64, 119.30, 118.57, 116.28, 113.68, 112.96, 111.42, 36.53, 28.01, 27.05, 20.10. HRMS (ESI$^+$): m/z calculated for [$C_{21}H_{15}Br_2NO_2$ + Na]$^+$: 493.9367; found 493.9362.



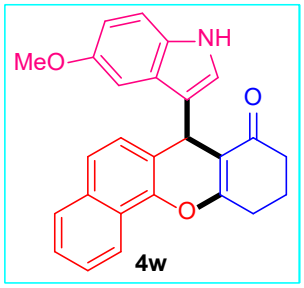
7-bromo-9-(5-methoxy-1*H*-indol-3-yl)-2,3,4,9-tetrahydro-1*H*-xanthen-1-one, 4u:

91% yield, white solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.76 (s, 1H), 7.52 (d, J = 2.4 Hz, 1H), 7.35 (dd, J = 8.7, 2.5 Hz, 1H), 7.21 (d, J = 8.8 Hz, 1H), 7.17 – 7.12 (m, 2H), 6.97 (d, J = 2.4 Hz, 1H), 6.70 (dd, J = 8.8, 2.4 Hz, 1H), 5.23 (s, 1H), 3.73 (s, 3H), 2.83 – 2.63 (m, 2H), 2.39 – 2.23 (m, 2H), 1.99 (dt, J = 13.2, 5.1 Hz, 1H), 1.89 (dq, J = 13.6, 6.6 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 196.12, 165.93, 153.02, 148.35, 132.10, 131.60, 130.22, 128.46, 125.43, 123.61, 118.79, 118.41, 116.18, 112.82, 112.31, 110.80, 100.19, 55.23, 36.58, 28.40, 27.05, 20.15. HRMS (ESI$^+$): m/z calculated for [$C_{22}H_{18}BrNO_3$ + Na]$^+$: 446.0368; found 446.0375.



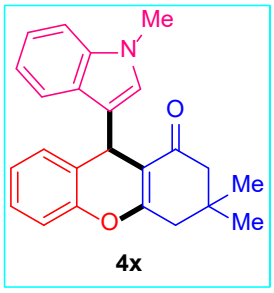
7-(1*H*-indol-3-yl)-10,11-dihydro-7*H*-benzo[c]xanthen-8(9*H*)-one, 4v:

89% yield, white solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.90 (s, 1H), 8.20 (d, J = 8.5 Hz, 1H), 7.88 – 7.82 (m, 2H), 7.51 – 7.32 (m, 5H), 7.26 (d, J = 8.1 Hz, 1H), 6.96 (t, J = 7.5 Hz, 1H), 6.87 (t, J = 7.5 Hz, 1H), 5.91 (s, 1H), 2.73 (q, J = 5.2 Hz, 2H), 2.31 (dddd, J = 21.8, 16.6, 13.3, 4.9 Hz, 2H), 1.94 (dq, J = 14.6, 5.0 Hz, 1H), 1.84 – 1.70 (m, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 196.31, 165.15, 147.05, 136.17, 131.08, 131.04, 128.65, 128.44, 126.82, 125.44, 124.76, 124.21, 123.37, 120.58, 118.58, 118.26, 117.98, 117.37, 116.97, 113.86, 111.61, 36.59, 26.89, 25.85, 20.09. HRMS (ESI$^+$): m/z calculated for [$C_{25}H_{19}NO_2$ + Na]$^+$: 388.1313; found 388.1310.



7-(5-methoxy-1*H*-indol-3-yl)-10,11-dihydro-7*H*-benzo[*c*] xanthen-8(9*H*)-one, 4w:

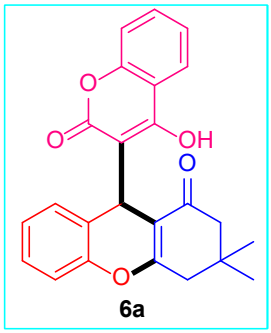
95% yield, white solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.72 (s, 1H), 8.19 (d, J = 8.4 Hz, 1H), 7.90 – 7.82 (m, 2H), 7.50 – 7.42 (m, 2H), 7.38 (ddd, J = 8.0, 6.9, 1.2 Hz, 1H), 7.28 (d, J = 2.5 Hz, 1H), 7.13 (d, J = 8.7 Hz, 1H), 6.85 (d, J = 2.5 Hz, 1H), 6.62 (dd, J = 8.8, 2.5 Hz, 1H), 5.87 (s, 1H), 3.66 (s, 3H), 2.75 (q, J = 5.1 Hz, 2H), 2.33 (dddd, J = 21.9, 16.7, 11.2, 5.0 Hz, 2H), 1.97 (dt, J = 13.5, 5.1 Hz, 1H), 1.79 (tdd, J = 13.1, 5.8, 3.4 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 196.40, 165.21, 152.80, 147.17, 131.35, 131.08, 128.68, 128.47, 126.86, 125.73, 124.78, 123.42, 117.59, 117.24, 116.84, 113.76, 112.15, 110.35, 100.34, 55.03, 36.60, 26.89, 25.80, 20.13. HRMS (ESI$^+$): m/z calculated for [$C_{26}H_{21}NO_3$ + Na]$^+$: 418.1419; found 418.1419.



4x

3,3-dimethyl-9-(1-methyl-1H-indol-3-yl)-2,3,4,9-tetrahydro-1H-xanthen-1-one, 4x:

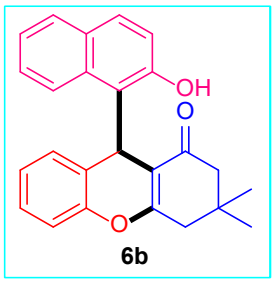
91% yield, white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 (dd, *J* = 8.1, 2.9 Hz, 1H), 7.17 (d, *J* = 6.7 Hz, 3H), 7.14 – 7.05 (m, 3H), 7.02 (d, *J* = 2.9 Hz, 1H), 6.96 (d, *J* = 7.5 Hz, 1H), 5.28 (s, 1H), 3.67 (s, 3H), 2.59 (d, *J* = 17.5 Hz, 1H), 2.52 (d, *J* = 17.3 Hz, 1H), 2.24 (d, *J* = 16.3 Hz, 1H), 2.17 (d, *J* = 18.4 Hz, 1H), 1.09 (s, 3H), 0.95 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.36, 164.21, 149.61, 137.25, 130.19, 127.35, 127.04, 126.16, 125.51, 124.91, 121.16, 119.19, 119.05, 118.83, 116.25, 112.90, 109.24, 50.96, 41.58, 32.65, 32.12, 29.36, 29.11, 27.74.HRMS (ESI$^+$): m/z calculated for $[C_{24}H_{23}NO_2 + H]^+$: 358.1807; found 358.1822.



6a

9-(4-hydroxy-2-oxo-2*H*-chromen-3-yl)-3,3-dimethyl-2,3,4,9-tetrahydro-1*H*-xanthen-1-one, 6a:

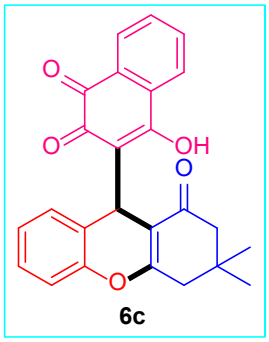
88% yield, white solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.95 (s, 1H), 8.03 (d, *J* = 8.3 Hz, 1H), 7.59 – 7.51 (m, 1H), 7.31 (dd, *J* = 17.9, 8.0 Hz, 2H), 7.22 – 7.15 (m, 1H), 7.12 – 7.01 (m, 3H), 5.48 (s, 1H), 2.60 (d, *J* = 17.3 Hz, 1H), 2.43 (d, *J* = 17.3 Hz, 1H), 2.29 (d, *J* = 16.1 Hz, 1H), 2.08 (d, *J* = 16.0 Hz, 1H), 1.04 (s, 3H), 0.98 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 196.40, 166.22, 159.49, 152.12, 149.99, 131.84, 128.68, 127.82, 124.55, 123.87, 123.33, 116.30, 116.08, 115.80, 109.10, 50.26, 40.66, 31.76, 29.04, 27.40, 26.33. HRMS (ESI$^+$): m/z calculated for $[C_{24}H_{20}O_5 + Na]^+$: 411.1208; found 411.1218.



6b

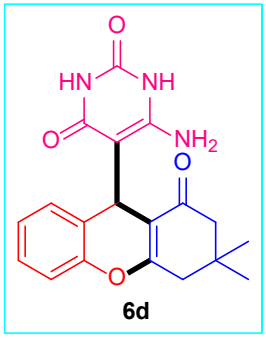
9-(2-hydroxynaphthalen-1-yl)-3,3-dimethyl-2,3,4,9-tetrahydro-1*H*-xanthen-1-one, 6b:

94% yield, white solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.68 (s, 1H), 8.33 (d, *J* = 8.5 Hz, 1H), 7.86 (dd, *J* = 11.6, 7.9 Hz, 2H), 7.49 (t, *J* = 7.6 Hz, 1H), 7.44 – 7.36 (m, 2H), 7.01 (d, *J* = 7.6 Hz, 1H), 6.88 (td, *J* = 7.4, 1.8 Hz, 1H), 6.72 (d, *J* = 8.1 Hz, 1H), 6.61 (t, *J* = 7.4 Hz, 1H), 5.76 (s, 1H), 2.69 (d, *J* = 17.3 Hz, 1H), 2.56 (d, *J* = 16.9 Hz, 1H), 2.34 (d, *J* = 16.1 Hz, 1H), 2.11 (d, *J* = 16.1 Hz, 1H), 1.07 (s, 3H), 0.93 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ 196.21, 164.31, 153.61, 147.27, 131.46, 131.20, 130.89, 130.00, 128.55, 128.41, 127.29, 126.88, 124.82, 123.54, 119.19, 118.15, 117.14, 115.82, 112.90, 50.21, 40.37, 31.89, 29.00, 28.41, 26.23. HRMS (ESI$^+$): m/z calculated for $[C_{25}H_{22}O_3 + H]^+$: 371.1647; found 371.1656.



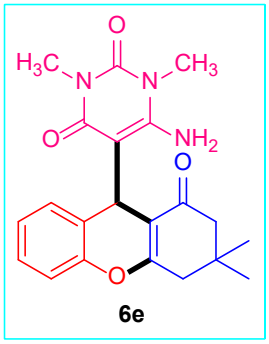
3-(3,3-dimethyl-1-oxo-2,3,4,9-tetrahydro-1*H*-xanthen-9-yl)-4-hydroxynaphthalene-1,2-dione, 6c:

78% yield, white solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.07 (s, 1H), 7.92 (d, J = 7.5 Hz, 1H), 7.85 – 7.62 (m, 4H), 7.17 (t, J = 7.6 Hz, 1H), 7.02 (dd, J = 13.9, 7.3 Hz, 3H), 5.36 (s, 1H), 2.60 (d, J = 17.3 Hz, 1H), 2.39 (d, J = 16.7 Hz, 1H), 2.28 (d, J = 16.0 Hz, 1H), 2.04 (d, J = 16.0 Hz, 1H), 1.04 (s, 3H), 0.97 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 196.07, 183.35, 181.47, 165.57, 154.92, 149.41, 134.75, 133.20, 131.66, 129.78, 128.79, 127.88, 125.59, 124.75, 115.92, 109.67, 50.22, 40.66, 31.72, 29.09, 26.36. HRMS (ESI$^+$): m/z calculated for $[C_{25}H_{20}O_5 + H]^+$: 401.1389; found 401.1397.



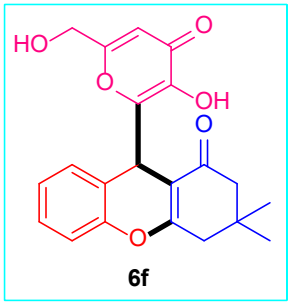
6-amino-5-(3,3-dimethyl-1-oxo-2,3,4,9-tetrahydro-1*H*-xanthen-9-yl)pyrimidine-2,4(1*H*,3*H*)-dione, 6d:

80% yield, white solid. ^{1}H NMR (500 MHz, DMSO-d_6) δ 10.09 (s, 1H), 9.94 (s, 1H), 7.12 (t, J = 7.6 Hz, 1H), 7.06 – 6.97 (m, 2H), 6.95 (d, J = 8.0 Hz, 1H), 6.48 (s, 2H), 4.68 (s, 1H), 2.55 (s, 1H), 2.39 (d, J = 17.3 Hz, 1H), 2.24 (d, J = 16.0 Hz, 1H), 2.10 (d, J = 16.2 Hz, 1H), 1.05 (s, 3H), 0.99 (s, 3H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 196.38, 165.32, 162.58, 151.12, 150.30, 150.11, 128.71, 126.99, 125.21, 123.99, 115.27, 110.06, 90.63, 50.42, 40.65, 31.74, 31.64, 28.96, 26.57. HRMS (ESI$^+$): m/z calculated for $[C_{19}H_{19}N_3O_4 + H]^+$: 354.1454; found 354.1450.



6-amino-5-(3,3-dimethyl-1-oxo-tetrahydro-1*H*-xanthen-9-yl)-1,3-dimethylpyrimidine-2,4(1*H*,3*H*)-dione, 6e:

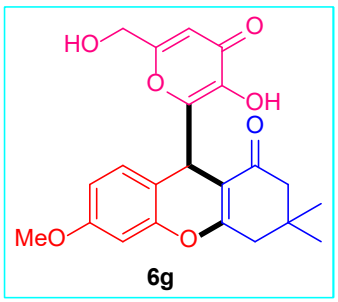
75% yield, white solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.49 (s, 1H), 9.20 (s, 1H), 7.05 – 6.87 (m, 2H), 6.69 (t, J = 8.1 Hz, 2H), 4.97 (s, 1H), 3.46 (s, 3H), 3.12 (s, 3H), 2.66 (d, J = 17.4 Hz, 1H), 2.56 (d, J = 17.4 Hz, 1H), 2.25 (d, J = 16.3 Hz, 1H), 2.08 (d, J = 16.3 Hz, 1H), 1.06 (s, 3H), 0.95 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 195.47, 162.05, 153.97, 151.11, 150.21, 144.65, 132.99, 129.02, 127.24, 119.54, 117.21, 110.91, 89.65, 49.89, 32.11, 30.39, 29.04, 28.61, 27.91, 26.60. HRMS (ESI$^+$): m/z calculated for $[C_{21}H_{23}N_3O_4 + H]^+$: 382.1767; found 382.1768.



6f

9-(3-hydroxy-6-(hydroxymethyl)-4-oxo-4*H*-pyran-2-yl)-3,3-dimethyl-2,3,4,9-tetrahydro-1*H*-xanthen-1-one, 6f:

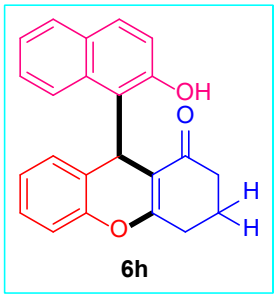
98% yield, white solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.18 (s, 1H), 7.36 (d, J = 7.5 Hz, 1H), 7.29 (td, J = 7.8, 1.8 Hz, 1H), 7.15 (t, J = 7.6 Hz, 2H), 6.23 (s, 1H), 5.59 (t, J = 6.1 Hz, 1H), 5.30 (s, 1H), 4.13 (d, J = 6.0 Hz, 2H), 2.69 (d, J = 16.3 Hz, 1H), 2.49 (d, J = 11.8 Hz, 1H), 2.37 (d, J = 16.0 Hz, 1H), 2.16 (d, J = 16.0 Hz, 1H), 1.10 (s, 3H), 1.07 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 196.05, 173.80, 166.83, 166.52, 151.80, 148.96, 140.71, 129.12, 128.96, 125.47, 121.35, 116.60, 108.87, 107.37, 59.37, 50.03, 40.65, 31.90, 30.94, 29.11, 26.06. HRMS (ESI$^+$): m/z calculated for $[C_{21}H_{20}O_6 + H]^+$: 369.1338; found 369.1342.



6g

9-(3-hydroxy-6-(hydroxymethyl)-4-oxo-4*H*-pyran-2-yl)-6-methoxy-3,3-dimethyl-2,3,4,9-tetrahydro-1*H*-xanthen-1-one, 6g:

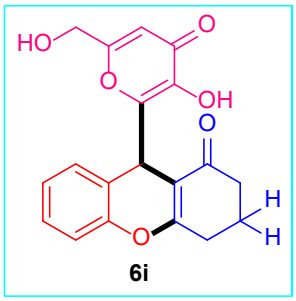
96% yield, white solid. ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.14 (s, 1H), 7.24 (d, J = 8.6 Hz, 1H), 6.76 (dd, J = 8.6, 2.6 Hz, 1H), 6.72 (d, J = 2.6 Hz, 1H), 6.21 (s, 1H), 5.61 (t, J = 6.2 Hz, 1H), 5.22 (s, 1H), 4.15 – 4.08 (m, 2H), 3.74 (s, 3H), 2.70 (d, J = 15.6 Hz, 1H), 2.46 (d, J = 1.6 Hz, 1H), 2.38 (d, J = 16.0 Hz, 1H), 2.16 (d, J = 14.3 Hz, 1H), 1.10 (s, 3H), 1.06 (s, 3H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 196.32, 173.96, 166.86, 166.59, 159.60, 152.25, 149.74, 140.60, 129.77, 113.15, 112.33, 108.93, 107.72, 101.53, 59.46, 55.60, 50.12, 40.73, 31.99, 30.52, 29.17, 26.14. HRMS (ESI$^+$): m/z calculated for $[C_{22}H_{22}O_7 + H]^+$: 399.1444; found 399.1473.



6h

9-(2-hydroxynaphthalen-1-yl)-2,3,4,9-tetrahydro-1*H*-xanthen-1-one, 6h:

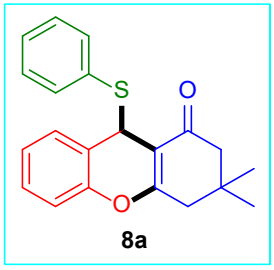
90% yield, white solid. ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.68 (s, 1H), 8.27 (d, J = 8.4 Hz, 1H), 7.87 (dd, J = 12.1, 8.6 Hz, 2H), 7.51 – 7.45 (m, 1H), 7.45 – 7.38 (m, 2H), 6.97 (d, J = 7.5 Hz, 1H), 6.92 – 6.85 (m, 1H), 6.71 (d, J = 8.3 Hz, 1H), 6.65 – 6.58 (m, 1H), 5.77 (s, 1H), 2.81 – 2.72 (m, 2H), 2.43 – 2.33 (m, 1H), 2.34 – 2.26 (m, 1H), 2.05 – 1.97 (m, 1H), 1.92 – 1.82 (m, 1H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 196.77, 166.32, 153.56, 147.28, 131.84, 131.11, 130.89, 129.97, 128.57, 128.42, 127.30, 126.90, 124.84, 123.44, 119.46, 118.20, 117.10, 115.89, 114.26, 36.55, 28.31, 27.06, 20.05. HRMS (ESI$^+$): m/z calculated for $[C_{23}H_{18}O_3 + H]^+$: 343.1334; found 343.1349.



6i

9-(3-hydroxy-6-(hydroxymethyl)-4-oxo-4*H*-pyran-2-yl)-2,3,4,9-tetrahydro-1*H*-xanthen-1-one, 6i:

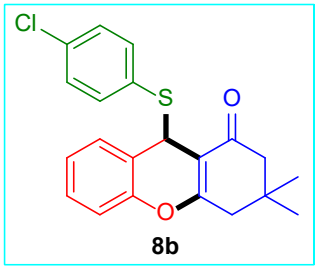
94% yield, white solid. ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.11 (s, 1H), 7.37 – 7.32 (m, 1H), 7.33 – 7.26 (m, 1H), 7.18 – 7.12 (m, 2H), 6.22 (s, 1H), 5.59 (s, 1H), 5.29 (s, 1H), 4.19 (d, J = 15.2 Hz, 1H), 4.14 (d, J = 16.8 Hz, 1H), 2.70 (t, J = 6.2 Hz, 2H), 2.42 – 2.31 (m, 2H), 2.06 – 1.93 (m, 2H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 196.21, 173.82, 168.18, 166.84, 151.62, 148.91, 140.73, 129.05, 128.90, 125.38, 121.29, 116.52, 108.84, 108.40, 59.38, 36.40, 31.12, 27.36, 20.16. HRMS (ESI$^+$): m/z calculated for $[C_{19}H_{16}O_6 + H]^+$: 341.1025; found 341.1045.



8a

3,3-dimethyl-9-(phenylthio)-2,3,4,9-tetrahydro-1*H*-xanthen-1-one, 8a:

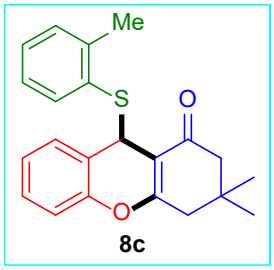
83% yield, brown liquid. ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.38 – 7.30 (m, 2H), 7.23 – 7.16 (m, 4H), 6.95 (dd, J = 7.9, 1.3 Hz, 2H), 6.87 (dd, J = 8.1, 1.3 Hz, 1H), 5.32 (s, 1H), 2.42 – 2.34 (m, 3H), 2.32 (s, 1H), 1.10 (s, 3H), 1.00 (s, 3H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 195.07, 166.12, 150.37, 135.79, 131.11, 129.59, 128.89, 128.49, 127.20, 125.06, 122.04, 115.91, 109.03, 50.24, 40.36, 40.02, 31.83, 27.85, 27.82. HRMS (ESI$^+$): m/z calculated for $[C_{21}H_{20}O_2S + Na]^+$: 359.1082; found 359.1109.



8b

9-((4-chlorophenyl)thio)-3,3-dimethyl-2,3,4,9-tetrahydro-1*H*-xanthen-1-one, 8b:

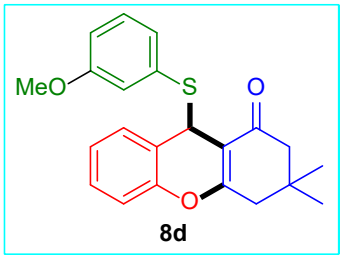
69% yield, brown liquid. ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.39 (dd, J = 7.6, 1.8 Hz, 1H), 7.27 (d, J = 2.0 Hz, 1H), 7.26 (d, J = 2.0 Hz, 1H), 7.23 (dd, J = 8.0, 1.8 Hz, 1H), 7.22 – 7.16 (m, 1H), 6.95 (d, J = 2.0 Hz, 1H), 6.94 (d, J = 2.0 Hz, 1H), 6.91 (dd, J = 8.2, 1.3 Hz, 1H), 5.35 (s, 1H), 2.46 (d, J = 17.3 Hz, 1H), 2.42 – 2.33 (m, 2H), 2.30 (d, J = 15.9 Hz, 1H), 1.10 (s, 3H), 1.00 (s, 3H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 195.11, 166.27, 150.40, 137.42, 134.09, 130.18, 129.64, 129.22, 128.51, 125.21, 121.68, 115.97, 108.94, 50.21, 40.33, 40.22, 31.90, 27.86, 27.76. HRMS (ESI$^+$): m/z calculated for $[C_{21}H_{19}ClO_2S + Na]^+$: 393.0692; found 393.0670.



8c

3,3-dimethyl-9-(o-tolylthio)-2,3,4,9-tetrahydro-1*H*-xanthen-1-one, 8c:

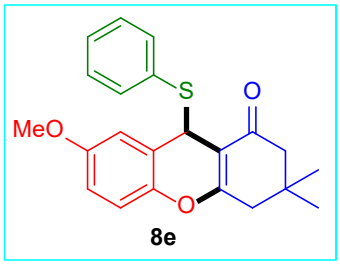
73% yield, brown liquid. ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.28 – 7.18 (m, 3H), 7.16 (d, J = 7.6 Hz, 1H), 7.11 – 7.07 (m, 2H), 7.08 – 7.03 (m, 1H), 7.03 – 6.98 (m, 1H), 5.28 (s, 1H), 2.47 (d, J = 17.3 Hz, 1H), 2.39 (d, J = 21.5 Hz, 2H), 2.33 (d, J = 6.3 Hz, 1H), 1.99 (s, 3H), 1.09 (s, 3H), 1.00 (s, 3H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 194.96, 167.02, 150.17, 142.48, 136.95, 130.08, 129.16, 129.08, 128.51, 127.04, 126.05, 124.89, 122.54, 116.04, 109.18, 50.20, 40.52, 40.02, 31.97, 27.73, 20.32, 19.53. HRMS (ESI$^+$): m/z calculated for $[C_{22}H_{22}O_2S + Na]^+$: 373.1238; found 373.1261.



8d

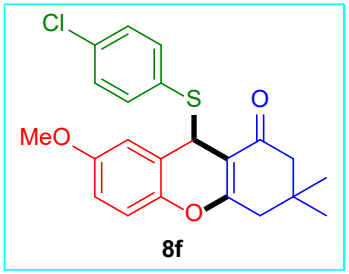
9-((3-methoxyphenyl)thio)-3,3-dimethyl-2,3,4,9-tetrahydro-1*H*-xanthen-1-one, 8d:

65% yield, brown liquid. ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.38 (dd, J = 7.6, 1.8 Hz, 1H), 7.26 – 7.04 (m, 4H), 6.93 – 6.83 (m, 2H), 6.63 (d, J = 7.5 Hz, 1H), 6.40 (t, J = 2.0 Hz, 1H), 5.33 (s, 1H), 3.57 (s, 3H), 2.42 – 2.26 (m, 4H), 1.08 (s, 3H), 1.00 (s, 3H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 195.55, 166.58, 159.28, 150.86, 132.76, 130.12, 129.73, 128.90, 128.32, 125.55, 122.48, 120.29, 116.39, 115.76, 109.53, 55.40, 50.65, 40.83, 40.45, 32.18, 28.44, 28.09. HRMS (ESI$^+$): m/z calculated for $[C_{22}H_{22}O_3S + Na]^+$: 389.1187; found 389.1161.



8e

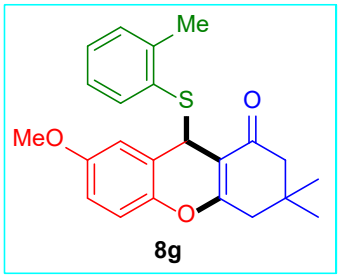
7-methoxy-3,3-dimethyl-9-(phenylthio)-2,3,4,9-tetrahydro-1*H*-xanthen-1-one, 8e: 88% yield, orange liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 (t, J = 7.4 Hz, 1H), 7.27 – 7.23 (m, 2H), 7.07 – 7.04 (m, 2H), 6.88 (d, J = 8.7 Hz, 1H), 6.85 – 6.80 (m, 2H), 5.33 (s, 1H), 3.70 (s, 3H), 2.39 (d, J = 3.4 Hz, 2H), 2.37 – 2.30 (m, 2H), 1.11 (s, 3H), 1.03 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 194.97, 166.43, 156.05, 144.45, 135.68, 131.47, 128.81, 128.53, 122.85, 116.91, 114.94, 112.70, 108.18, 55.44, 50.21, 40.56, 40.40, 31.80, 27.92, 27.67.



8f

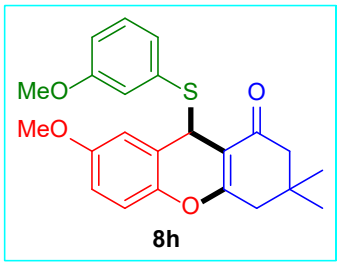
9-((4-chlorophenyl)thio)-7-methoxy-3,3-dimethyl-2,3,4,9-tetrahydro-1*H*-xanthen-1-one, 8f: 79% yield, red liquid. ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.30 – 7.27 (m, 2H), 7.02 – 6.99 (m, 2H), 6.89 – 6.86 (m, 2H), 6.81 (dd, J = 9.0, 2.9 Hz, 1H),

5.33 (s, 1H), 3.70 (s, 3H), 2.43 (d, J = 17.3 Hz, 1H), 2.40 – 2.32 (m, 2H), 2.29 (d, J = 16.0 Hz, 1H), 1.09 (s, 3H), 0.99 (s, 3H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 195.04, 166.54, 156.18, 144.55, 137.41, 134.05, 130.44, 128.53, 122.46, 117.01, 115.16, 112.79, 108.12, 55.50, 50.21, 40.81, 40.39, 31.86, 27.83, 27.76.



8g

7-methoxy-3,3-dimethyl-9-(o-tolylthio)-2,3,4,9-tetrahydro-1*H*-xanthen-1-one, 8g: 85% yield, brown liquid. ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.29 – 7.23 (m, 1H), 7.22 – 7.18 (m, 1H), 7.17 – 7.11 (m, 2H), 6.97 (d, J = 9.0 Hz, 1H), 6.81 (dd, J = 9.0, 3.0 Hz, 1H), 6.41 (d, J = 3.1 Hz, 1H), 5.24 (s, 1H), 3.56 (s, 3H), 2.49 – 2.42 (m, 2H), 2.32 (s, 2H), 2.07 (s, 3H), 1.08 (s, 3H), 1.01 (s, 3H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 194.87, 167.34, 155.82, 144.11, 142.46, 136.91, 131.45, 130.11, 129.10, 126.13, 123.25, 116.98, 114.96, 112.21, 108.29, 55.29, 50.16, 40.54, 40.43, 31.90, 27.97, 27.46, 20.33.



8h

7-methoxy-9-((3-methoxyphenyl)thio)-3,3-dimethyl-2,3,4,9-tetrahydro-1*H*-xanthen-1-one, 8h: 86% yield, red liquid. ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.31 – 7.24 (m, 1H), 7.03 (dd, J = 7.6, 1.8 Hz, 1H), 6.90 – 6.85 (m, 2H), 6.80 – 6.72 (m, 2H), 6.61 (d, J = 2.9 Hz, 1H), 5.35 (s, 1H), 3.60 (s, 6H), 2.44 – 2.32 (m, 2H), 2.30 – 2.20 (m, 2H), 1.07 (s, 3H), 0.99 (s, 3H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 194.82, 166.38, 160.04, 155.73, 144.34, 137.22, 130.56, 123.01, 120.23, 119.84, 116.64, 114.65, 112.72, 111.05, 108.72, 55.41, 55.30, 50.14, 40.54, 38.99, 31.75, 27.95, 27.50.

8. Copies of ^{1}H NMR and ^{13}C NMR spectra for product (4a-4x), (6a-6i), and (8a-8h):

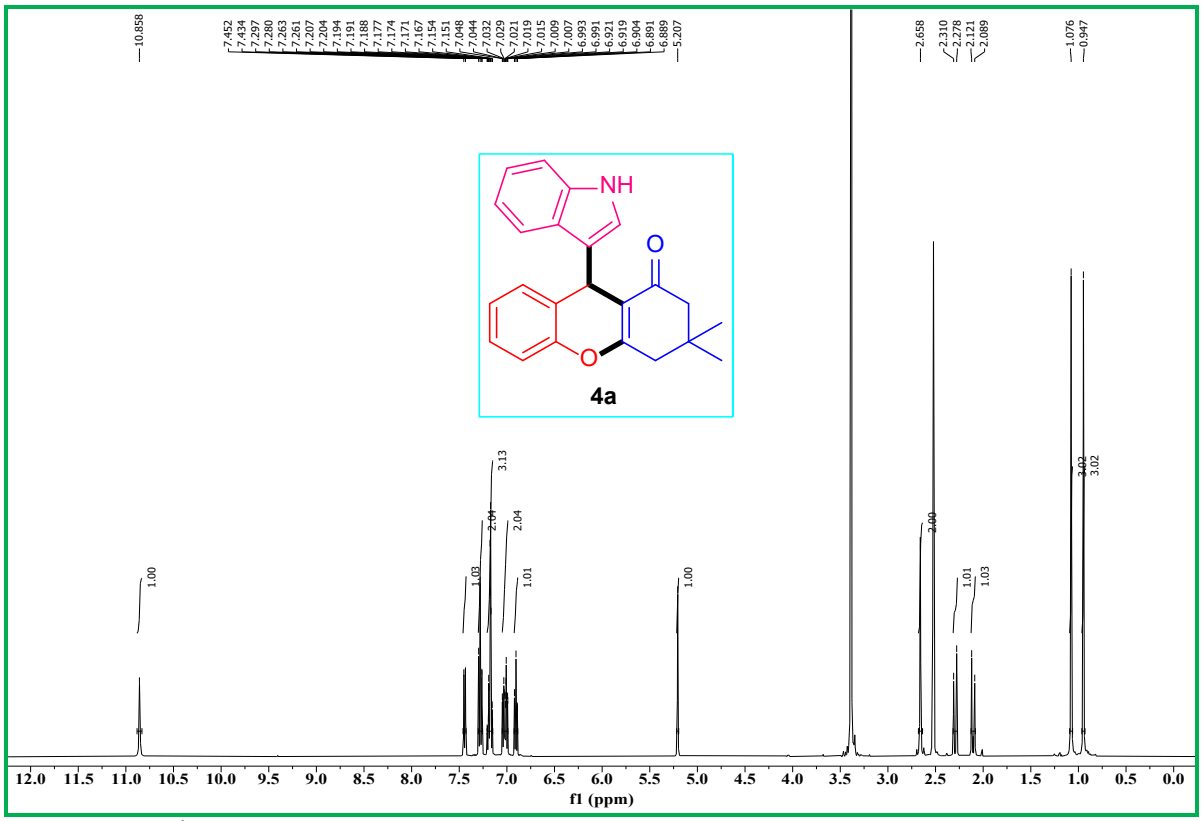


Figure S8: ^{1}H NMR spectrum of 9-(1*H*-indol-3-yl)-3,3-dimethyl-2,3,4,9-tetrahydro-1*H*-xanthen-1-one, 4**a**.

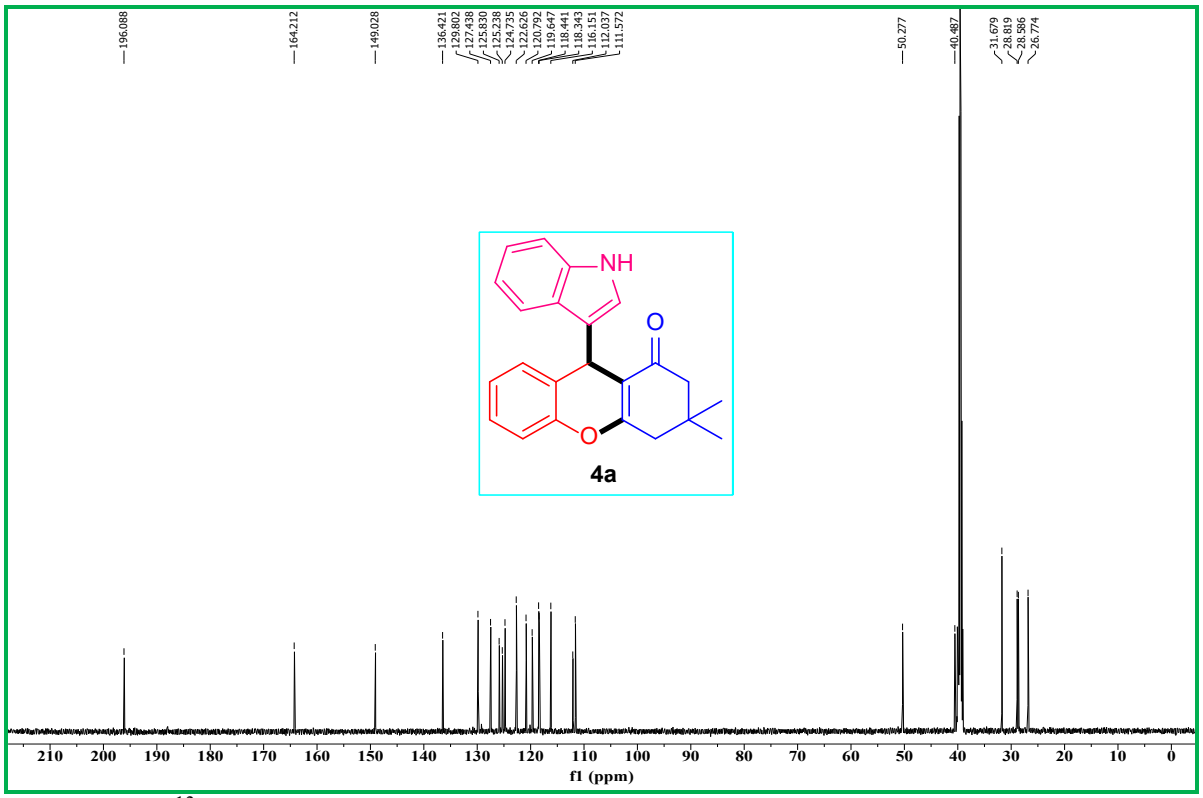


Figure S9: ^{13}C NMR spectrum of 9-(1*H*-indol-3-yl)-3,3-dimethyl-2,3,4,9-tetrahydro-1*H*-xanthen-1-one, **4a**.

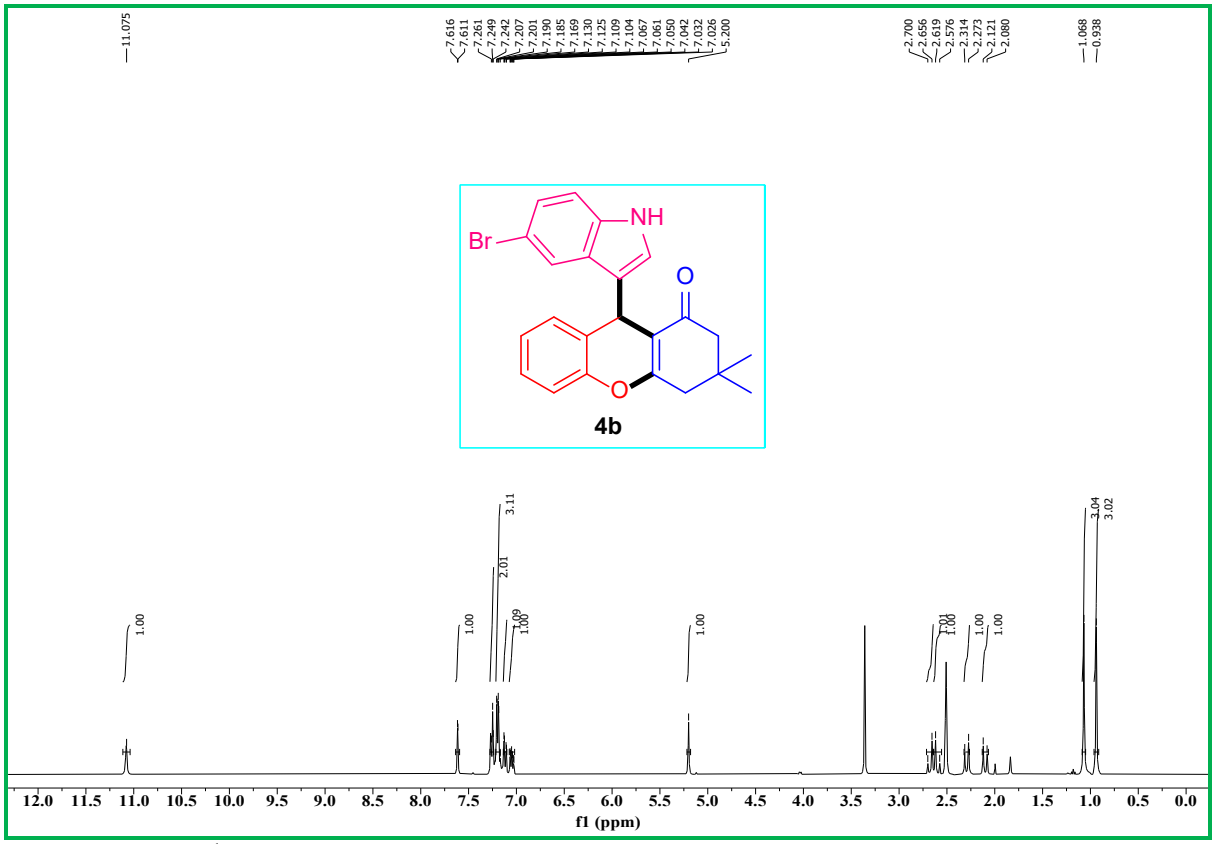


Figure S10: ^{1}H NMR spectrum of 9-(5-bromo-1*H*-indol-3-yl)-3,3-dimethyl-2,3,4,9-tetrahydro-1*H*-xanthen-1-one, **4b**.

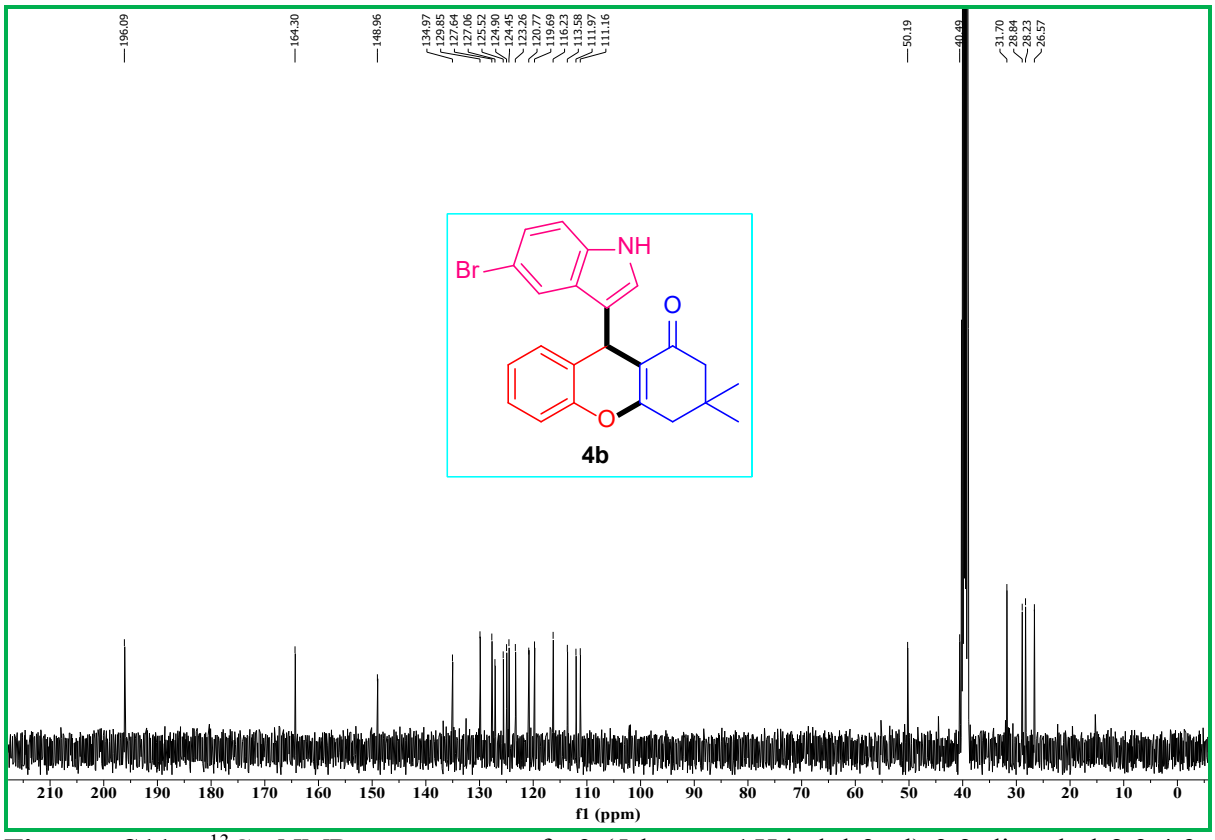


Figure S11: ^{13}C NMR spectrum of 9-(5-bromo-1*H*-indol-3-yl)-3,3-dimethyl-2,3,4,9-tetrahydro-1*H*-xanthen-1-one, **4b**.

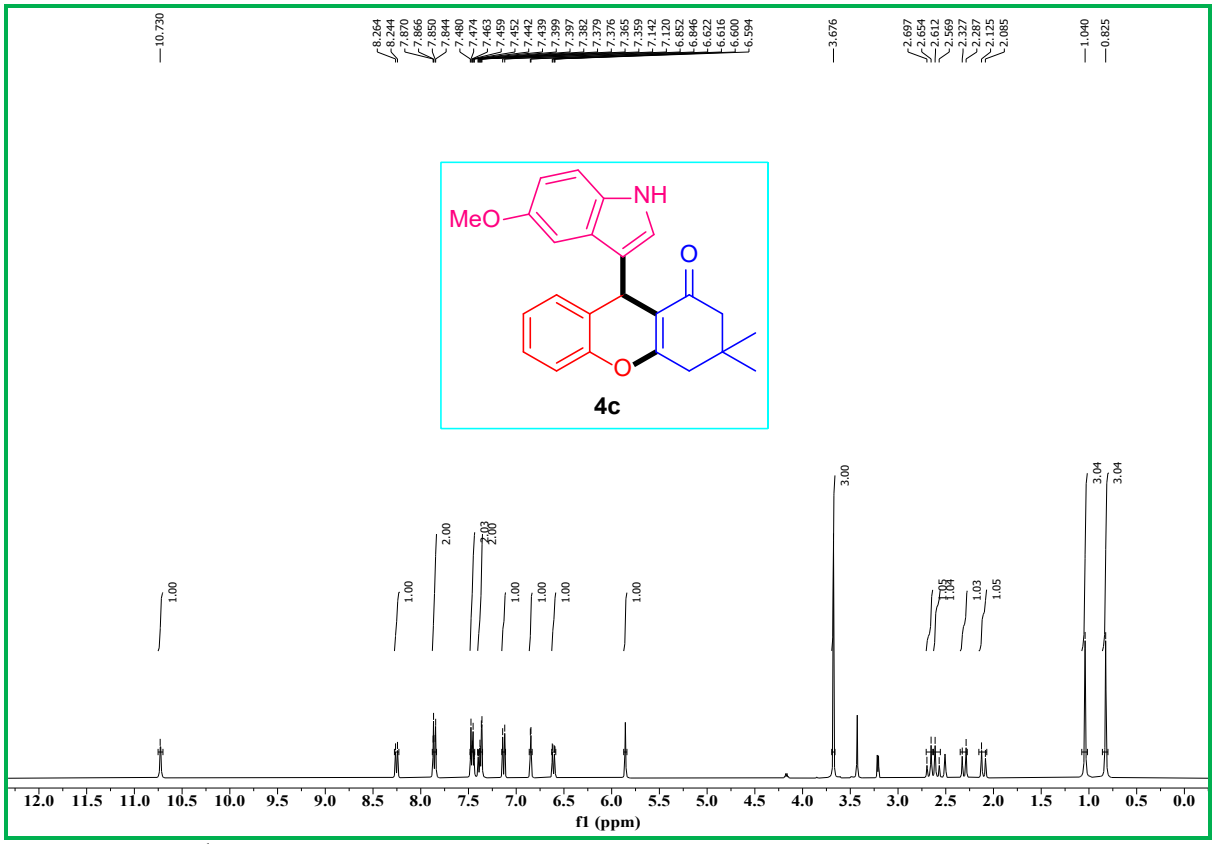


Figure S12: ^{1}H NMR spectrum of 9-(5-methoxy-1*H*-indol-3-yl)-3,3-dimethyl-2,3,4,9-tetrahydro-1*H*-xanthen-1-one, **4c**.

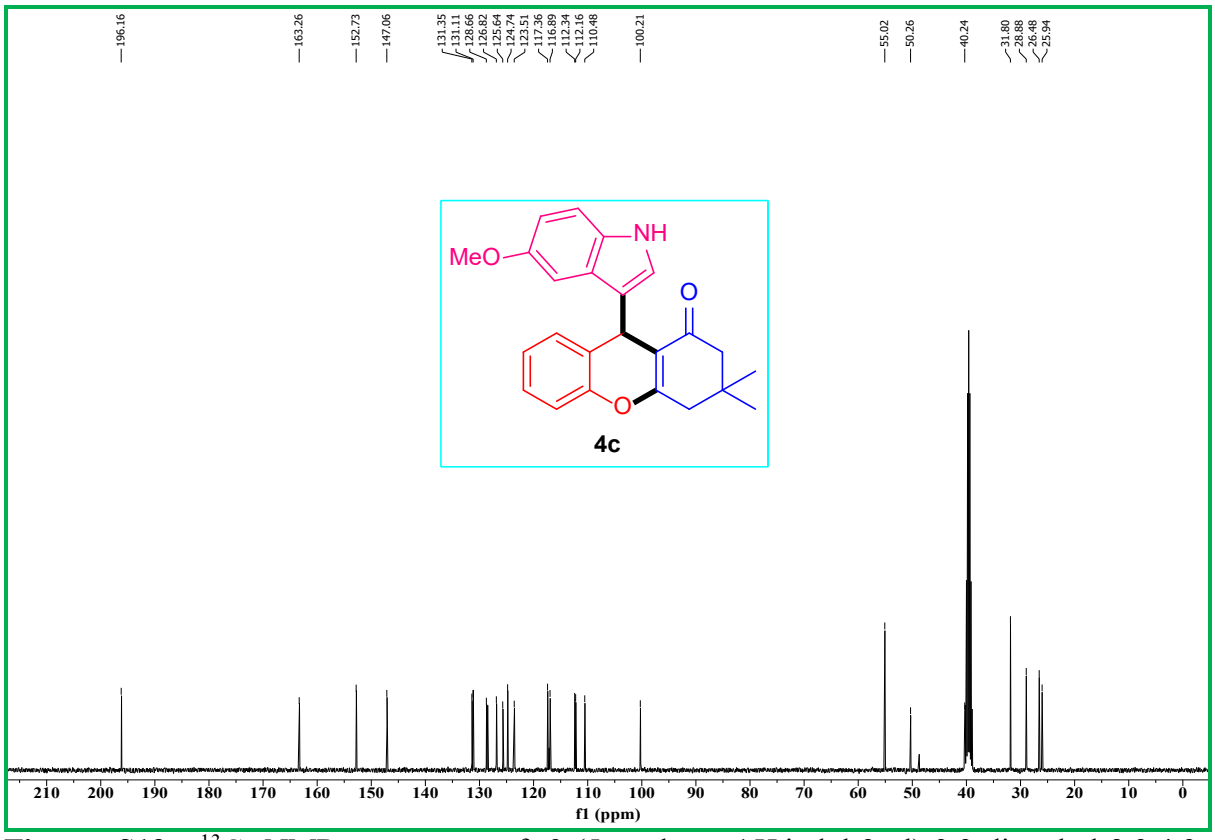


Figure S13: ^{13}C NMR spectrum of 9-(5-methoxy-1*H*-indol-3-yl)-3,3-dimethyl-2,3,4,9-tetrahydro-1*H*-xanthen-1-one, **4c**.

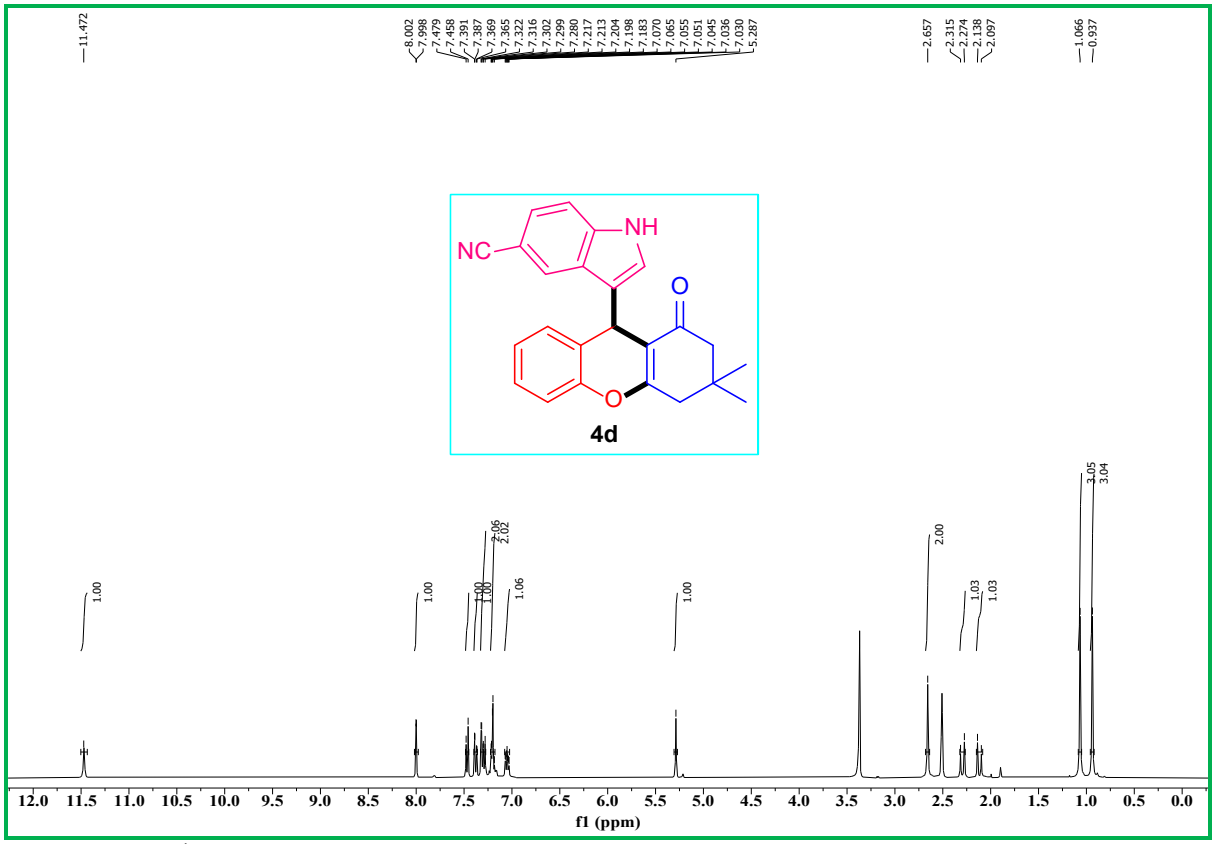


Figure S14: ^{1}H NMR spectrum of 3-(3,3-dimethyl-1-oxo-2,3,4,9-tetrahydro-1*H*-xanthen-9-yl)-1*H*-indole-5-carbonitrile, **4d**.

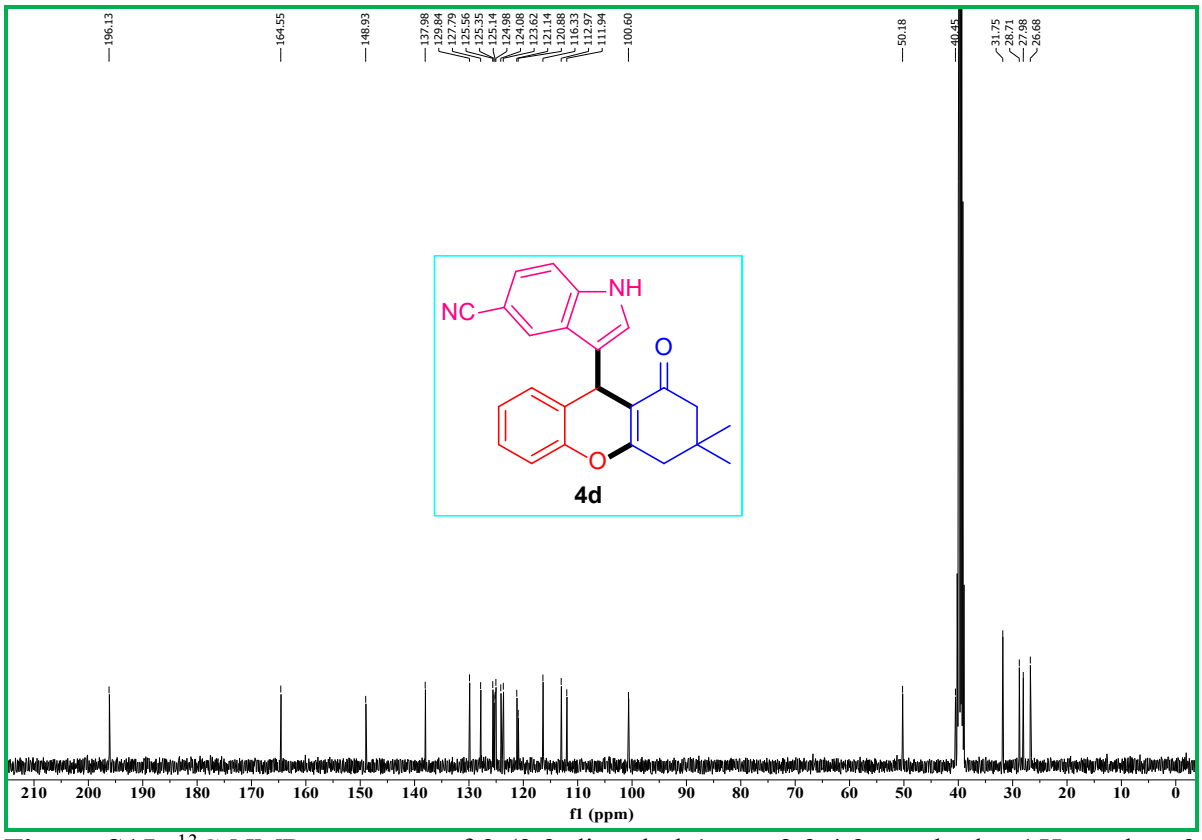


Figure S15: ^{13}C NMR spectrum of 3-(3,3-dimethyl-1-oxo-2,3,4,9-tetrahydro-1*H*-xanthen-9-yl)-1*H*-indole-5-carbonitrile, **4d**.

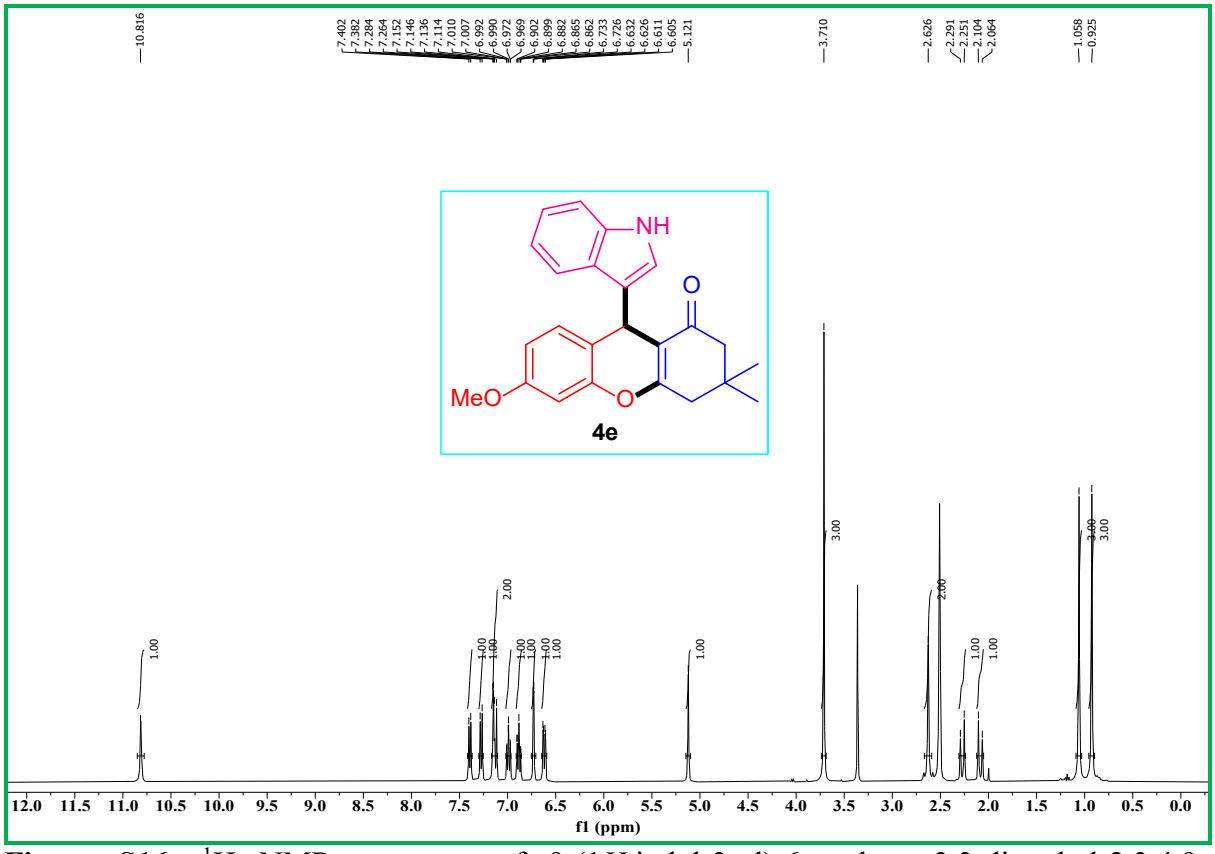


Figure S16: ^{1}H NMR spectrum of 9-(1*H*-indol-3-yl)-6-methoxy-3,3-dimethyl-2,3,4,9-tetrahydro-1*H*-xanthen-1-one, **4e**.

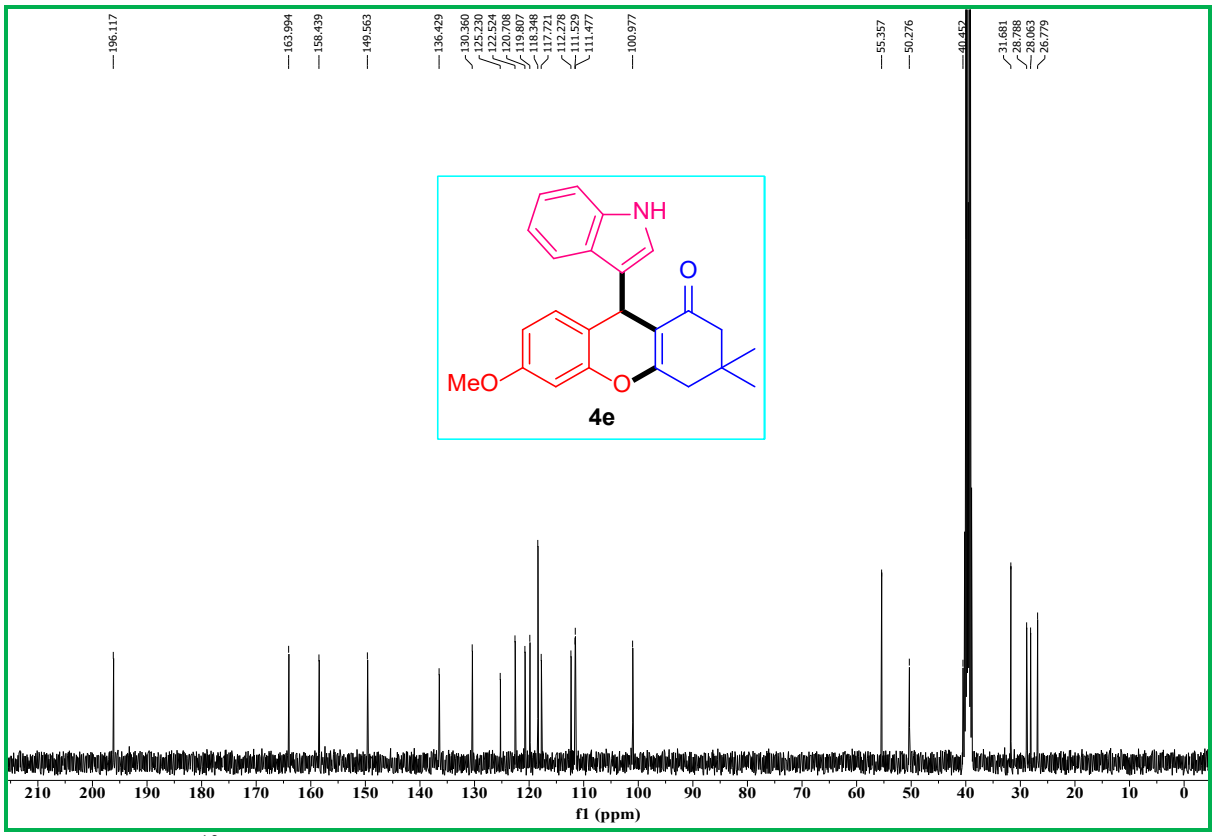


Figure S17: ^{13}C NMR spectrum of 9-(1*H*-indol-3-yl)-6-methoxy-3,3-dimethyl-2,3,4,9-tetrahydro-1*H*-xanthen-1-one, **4e**.

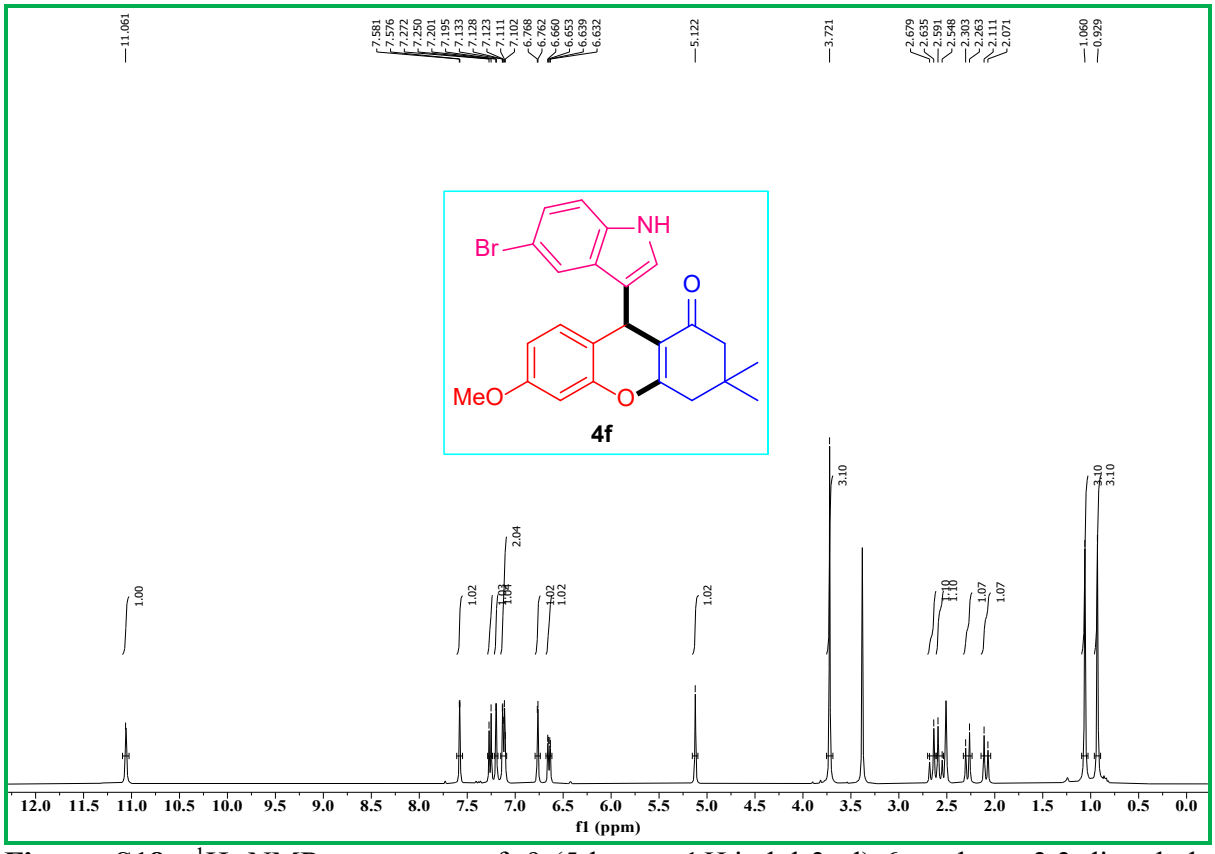


Figure S18: ^{1}H NMR spectrum of 9-(5-bromo-1*H*-indol-3-yl)-6-methoxy-3,3-dimethyl-2,3,4,9-tetrahydro-1*H*-xanthen-1-one,4**f**.

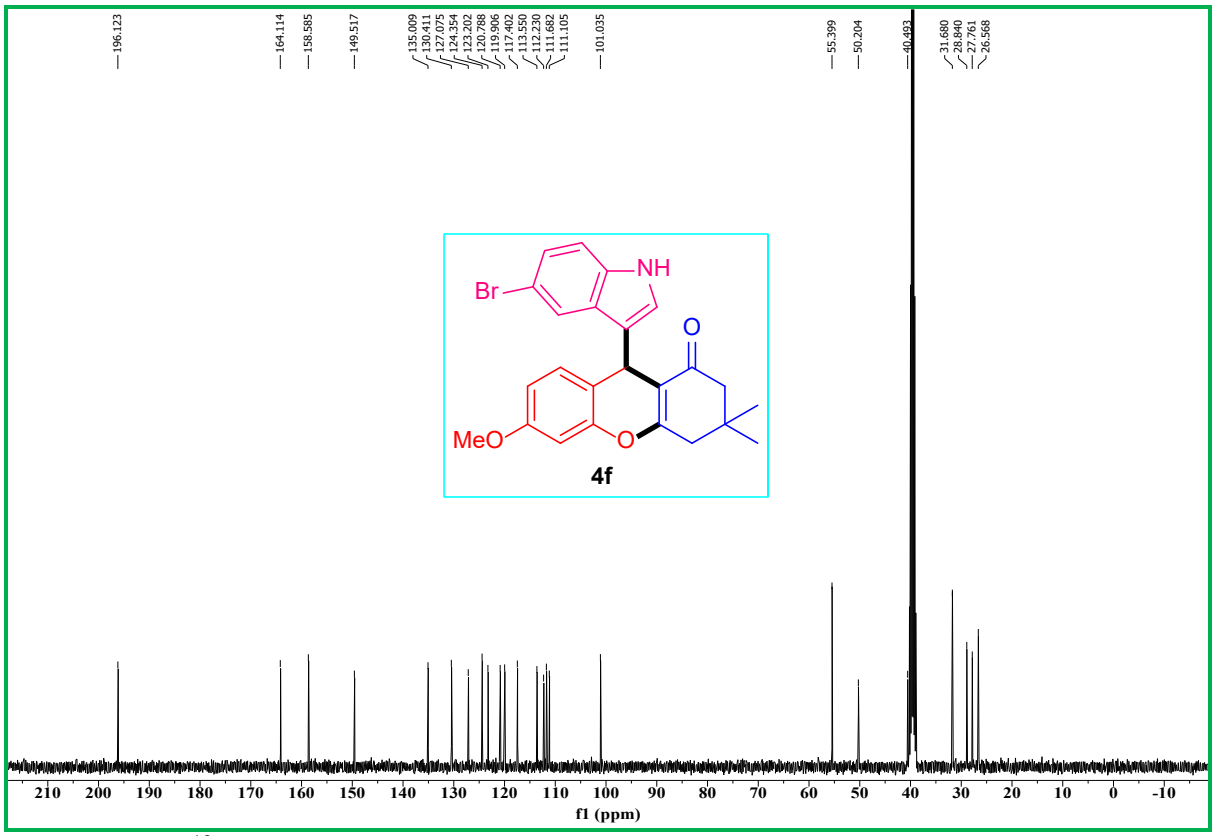


Figure S19: ^{13}C NMR spectrum of 9-(5-bromo-1*H*-indol-3-yl)-6-methoxy-3,3-dimethyl-2,3,4,9-tetrahydro-1*H*-xanthen-1-one, **4f**.

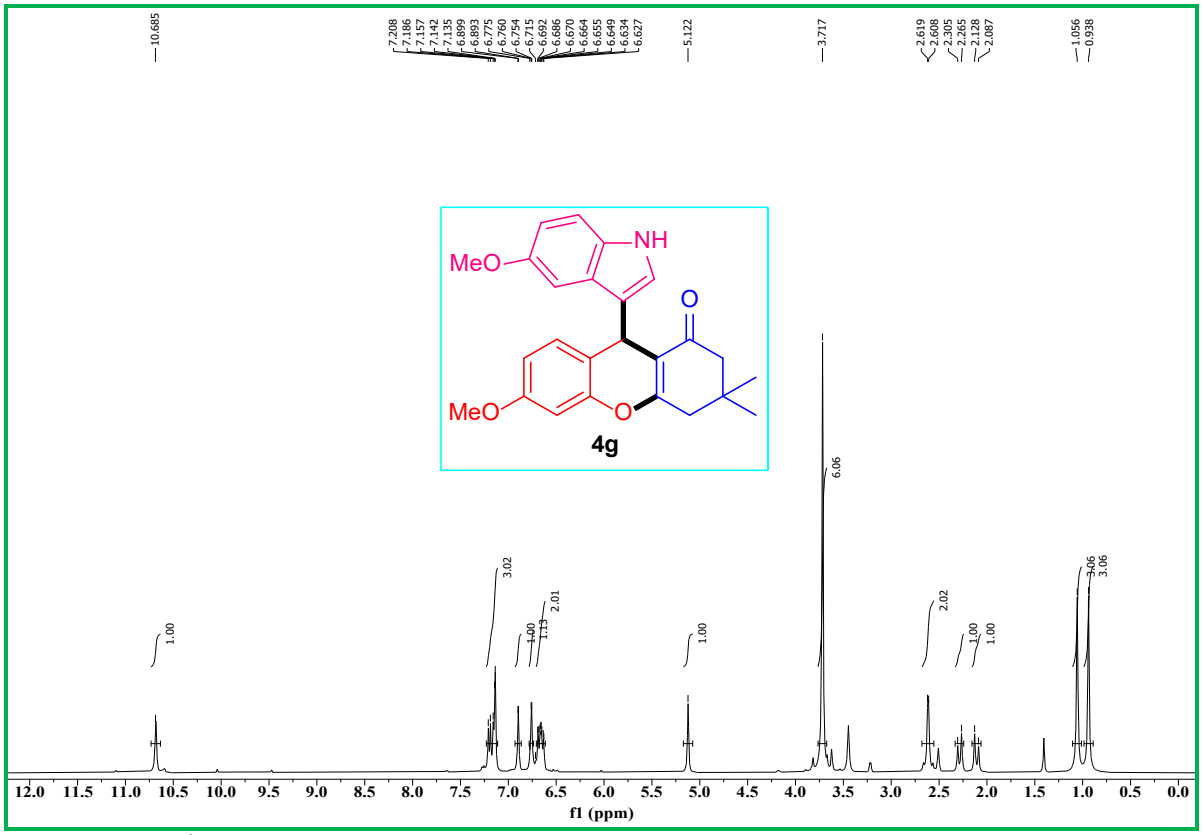


Figure S20: ^{1}H NMR spectrum of 6-methoxy-9-(5-methoxy-1*H*-indol-3-yl)-3,3-dimethyl-2,3,4,9-tetrahydro-1*H*-xanthen-1-one, **4g**.

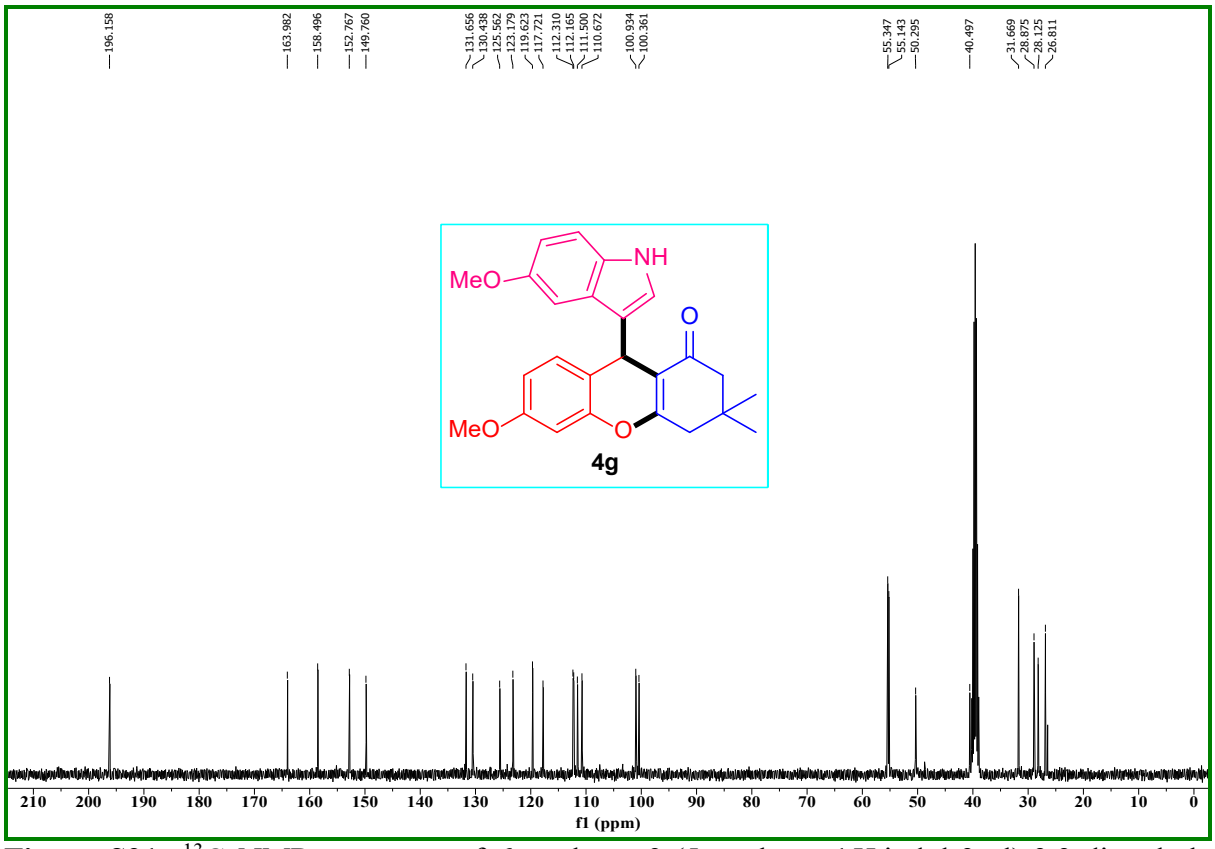


Figure S21: ^{13}C NMR spectrum of 6-methoxy-9-(5-methoxy-1*H*-indol-3-yl)-3,3-dimethyl-2,3,4,9-tetrahydro-1*H*-xanthen-1-one, **4g**.

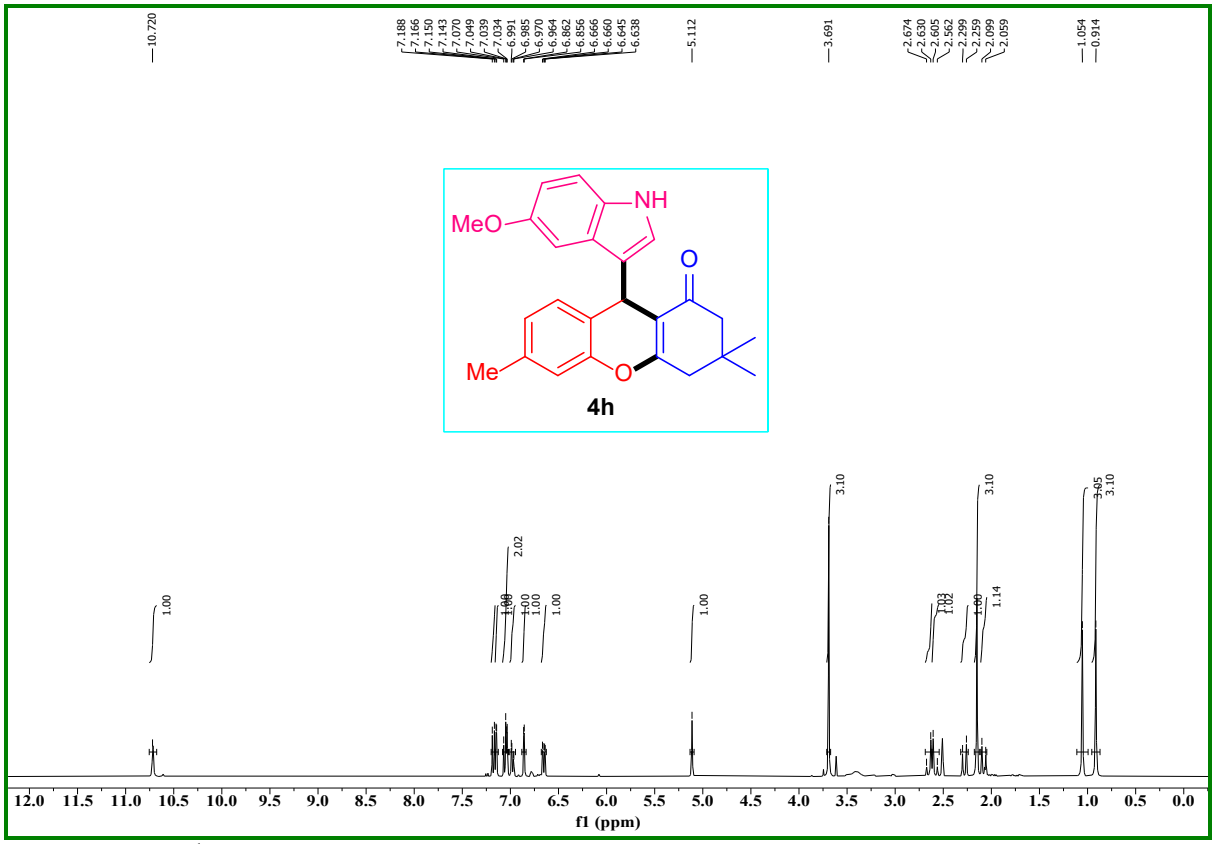


Figure S22: ^{1}H NMR spectrum of 9-(5-methoxy-1*H*-indol-3-yl)-3,3,6-trimethyl-2,3,4,9-tetrahydro-1*H*-xanthen-1-one, 4**h**.

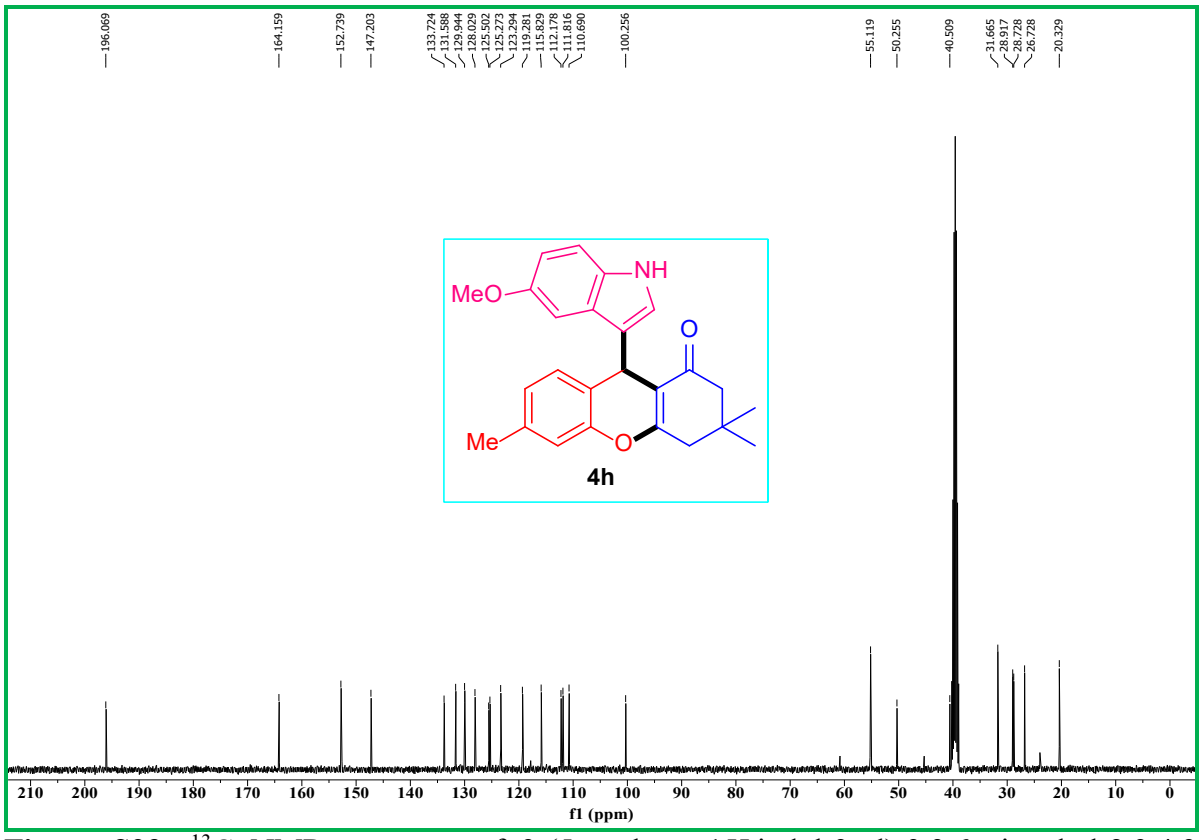


Figure S23: ^{13}C NMR spectrum of 9-(5-methoxy-1*H*-indol-3-yl)-3,3,6-trimethyl-2,3,4,9-tetrahydro-1*H*-xanthen-1-one, **4h**.

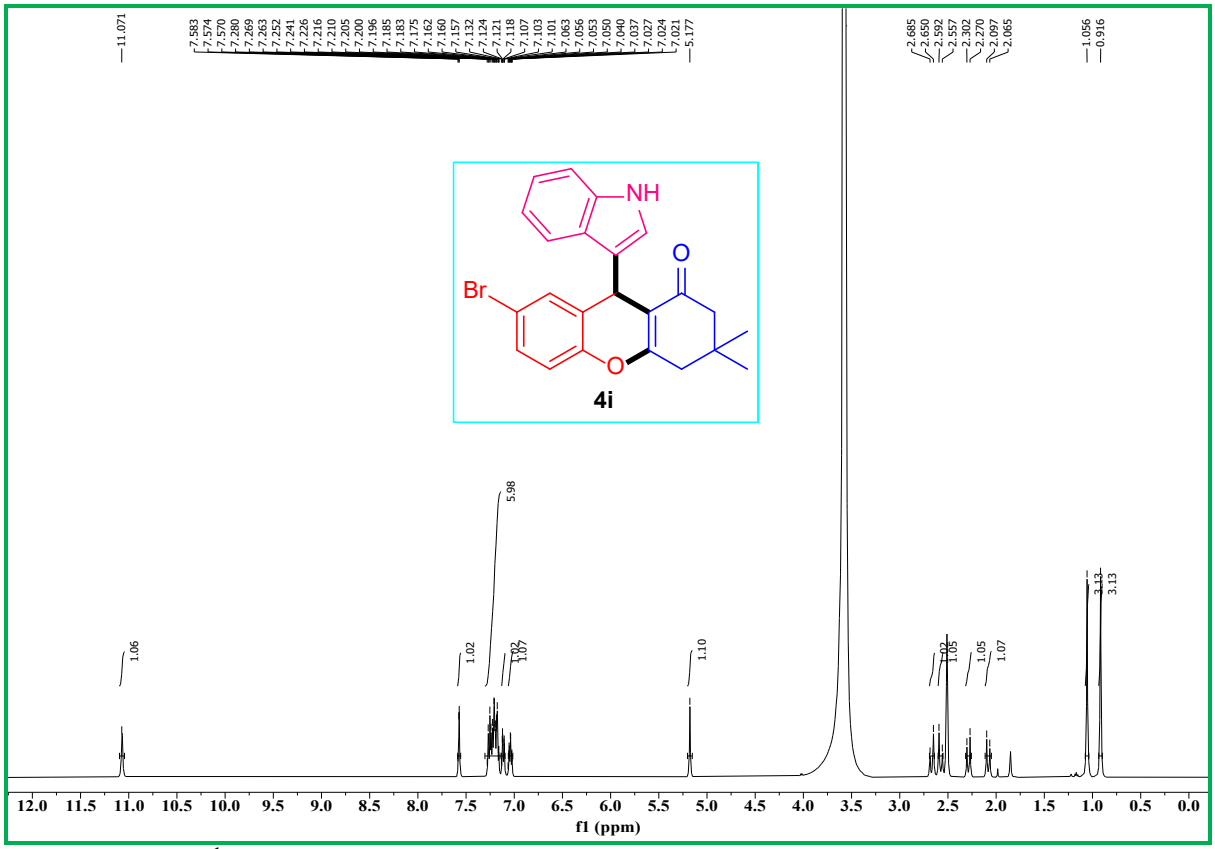


Figure S24: ^{1}H NMR spectrum of 7-bromo-9-(1*H*-indol-3-yl)-3,3-dimethyl-2,3,4,9-tetrahydro-1*H*-xanthen-1-one, **4i**.

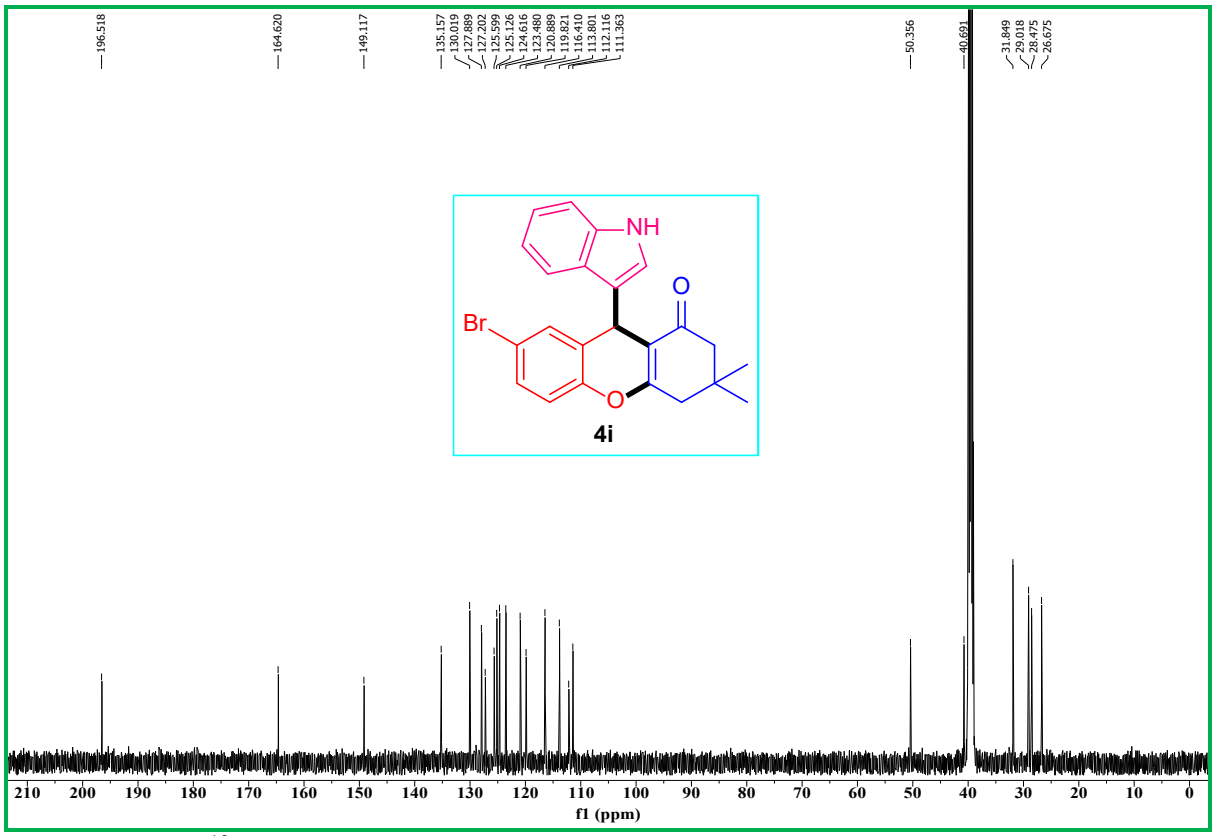


Figure S25: ^{13}C NMR spectrum of 7-bromo-9-(1*H*-indol-3-yl)-3,3-dimethyl-2,3,4,9-tetrahydro-1*H*-xanthen-1-one, **4i**.

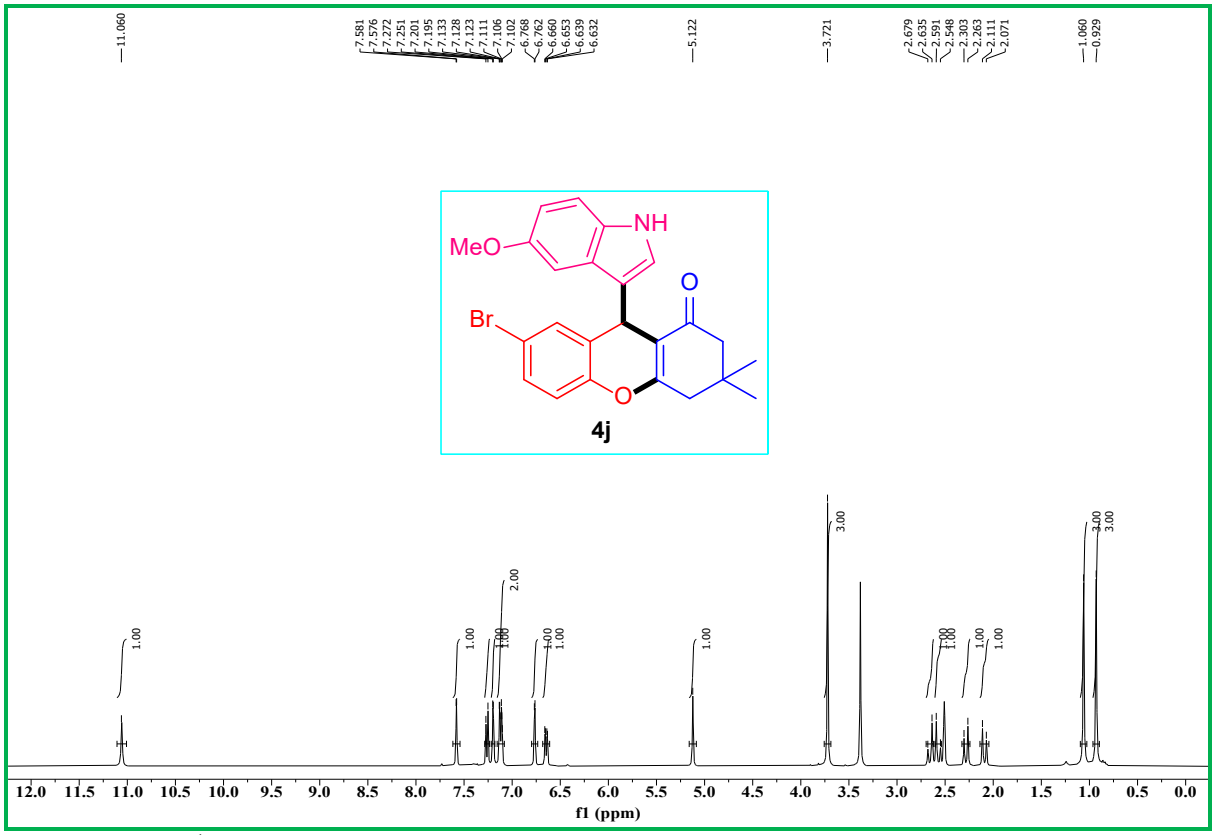


Figure S26: ^{1}H NMR spectrum of 7-bromo-9-(5-methoxy-1*H*-indol-3-yl)-3,3-dimethyl-2,3,4,9-tetrahydro-1*H*-xanthen-1-one, **4j**.

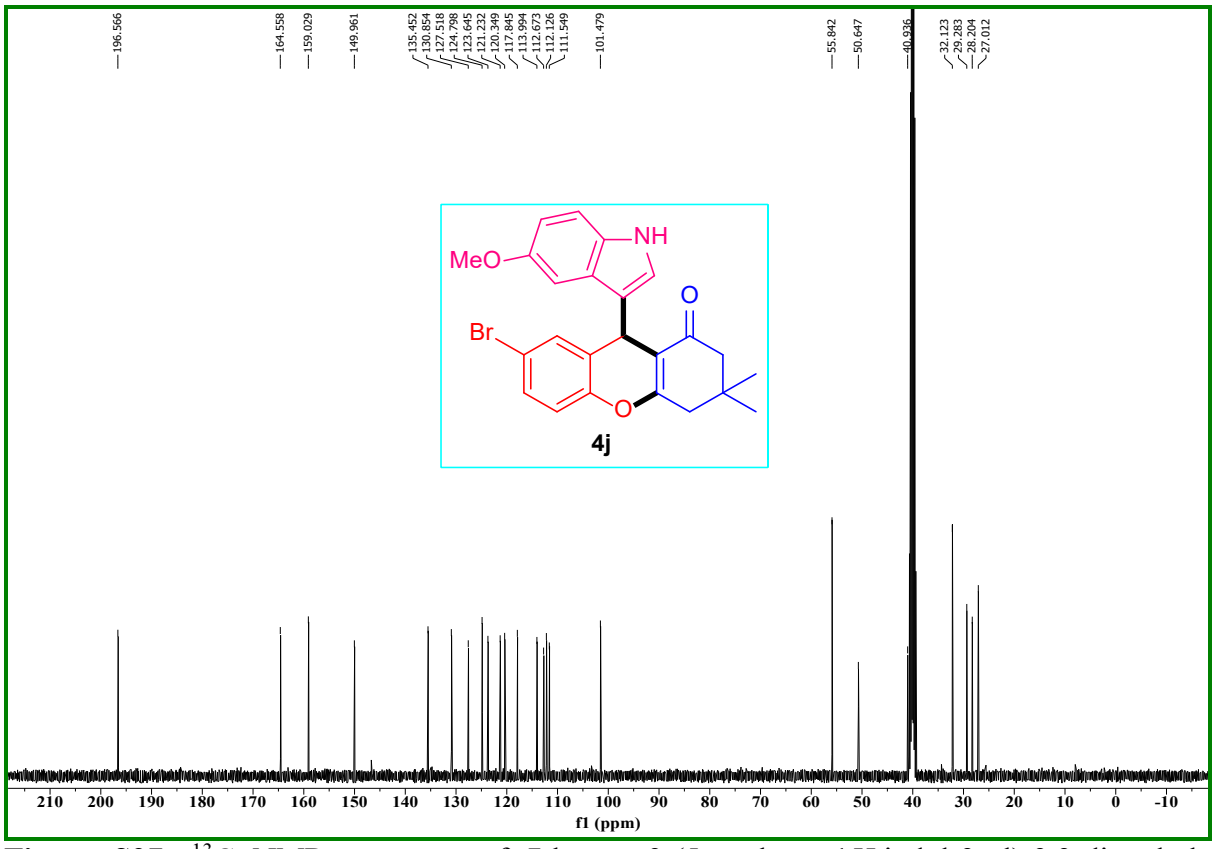


Figure S27: ^{13}C NMR spectrum of 7-bromo-9-(5-methoxy-1*H*-indol-3-yl)-3,3-dimethyl-2,3,4,9-tetrahydro-1*H*-xanthen-1-one, **4j**.

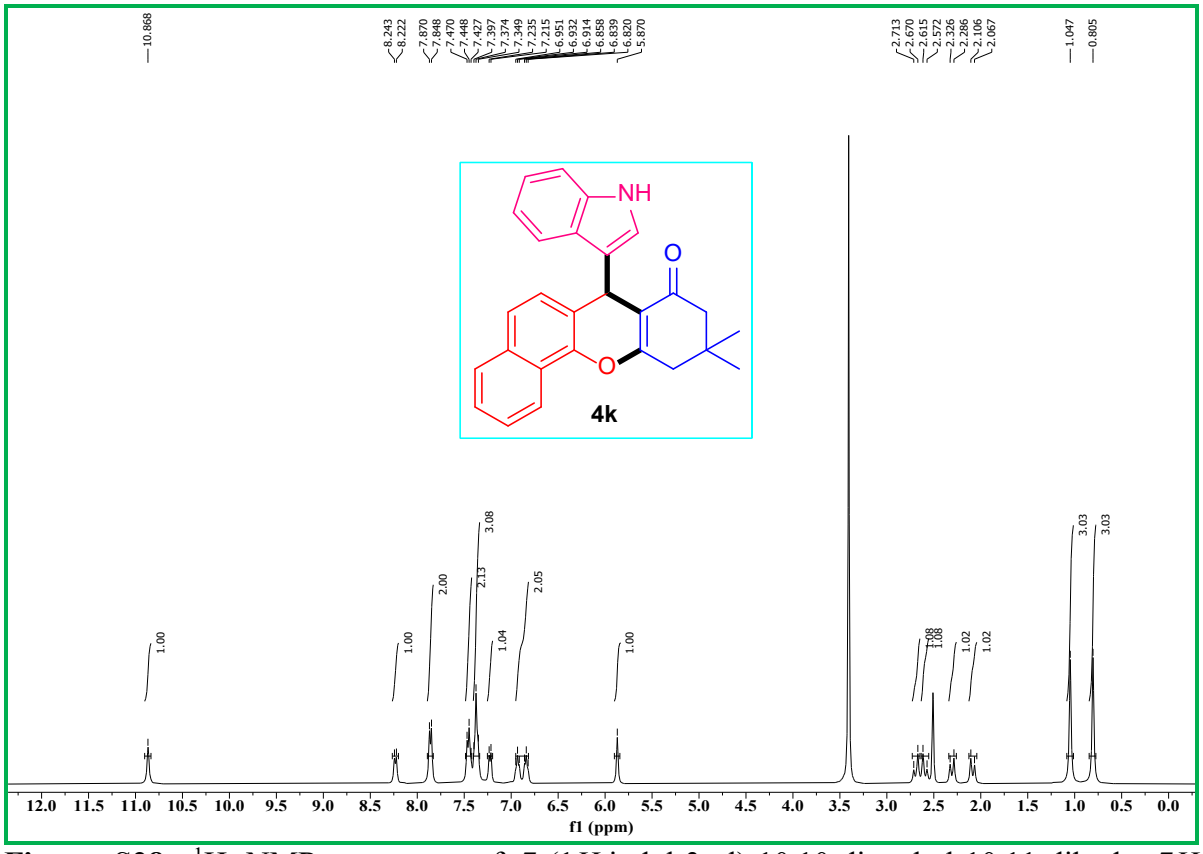


Figure S28: ^{1}H NMR spectrum of 7-(1*H*-indol-3-yl)-10,10-dimethyl-10,11-dihydro-7*H*-benzo[c]xanthen-8(9*H*)-one, **4k**.

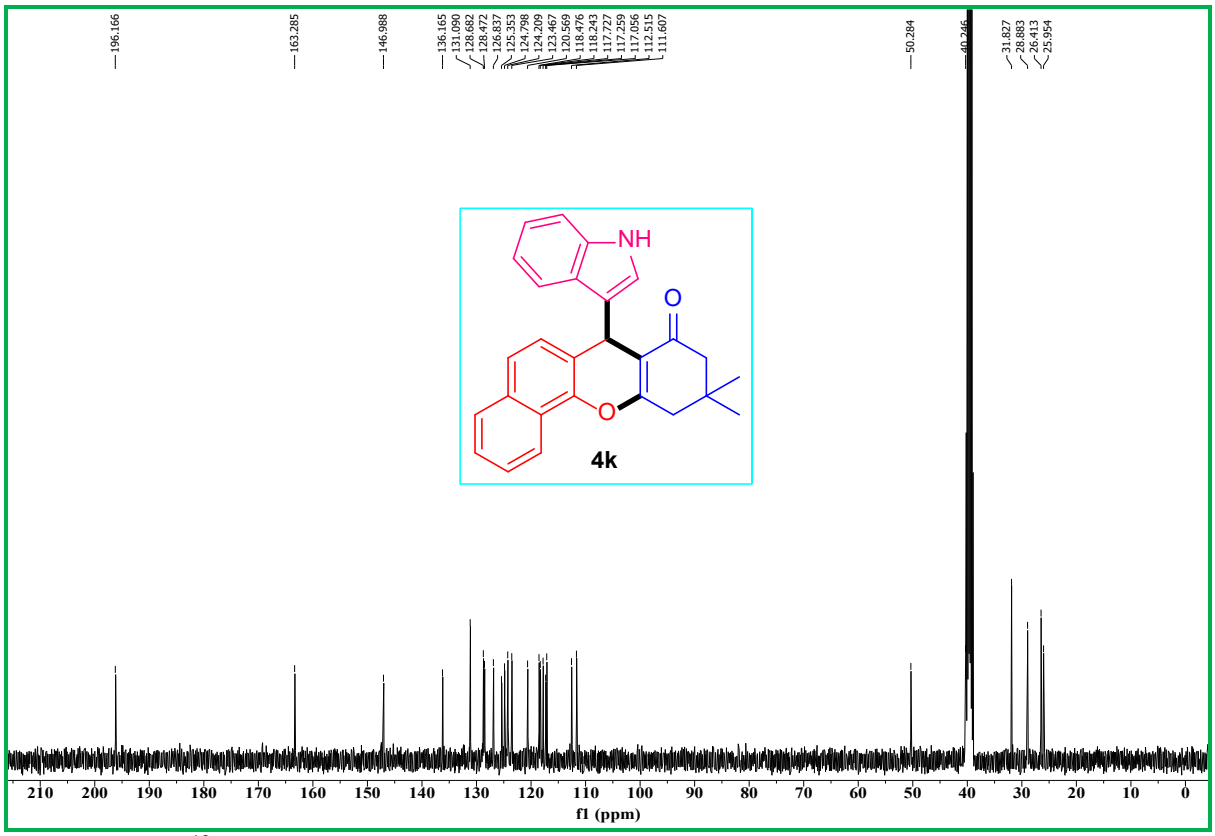


Figure S29: ^{13}C NMR spectrum of 7-(1*H*-indol-3-yl)-10,10-dimethyl-10,11-dihydro-7*H*-benzo[c]xanthen-8(9*H*)-one, **4k**.

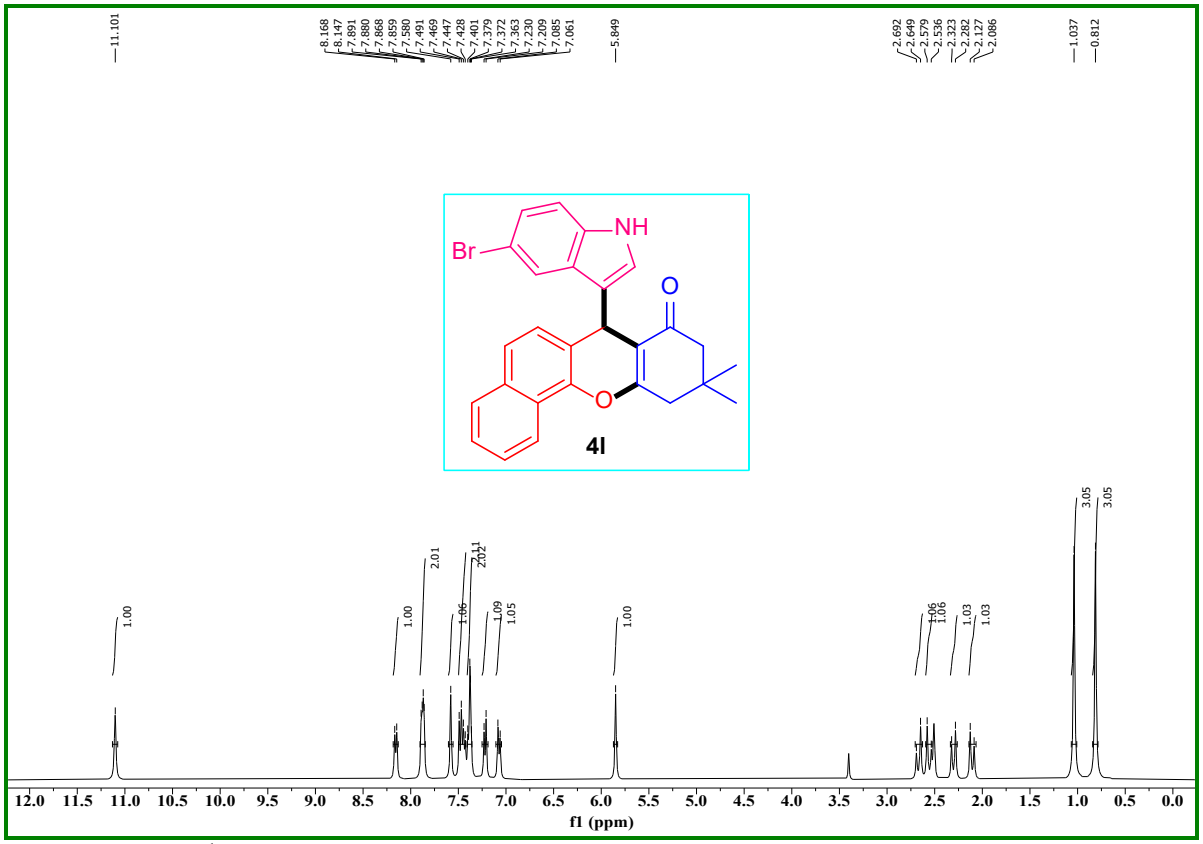


Figure S30: ^{1}H NMR spectrum of 7-(5-bromo-1*H*-indol-3-yl)-10,10-dimethyl-10,11-dihydro-7*H*-benzo[*c*]xanthen-8(9*H*)-one, **4l**.

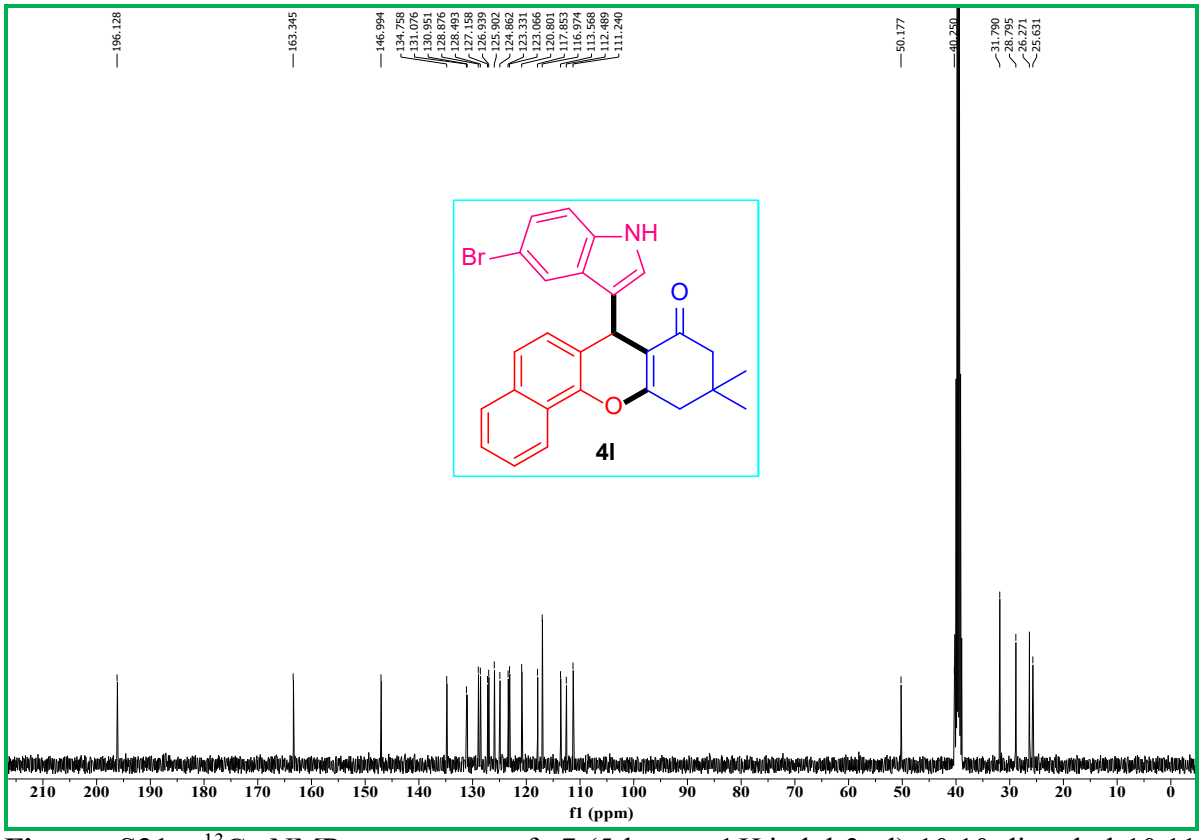


Figure S31: ^{13}C NMR spectrum of 7-(5-bromo-1*H*-indol-3-yl)-10,10-dimethyl-10,11-dihydro-7*H*-benzo[*c*]xanthen-8(9*H*)-one, **4l**.

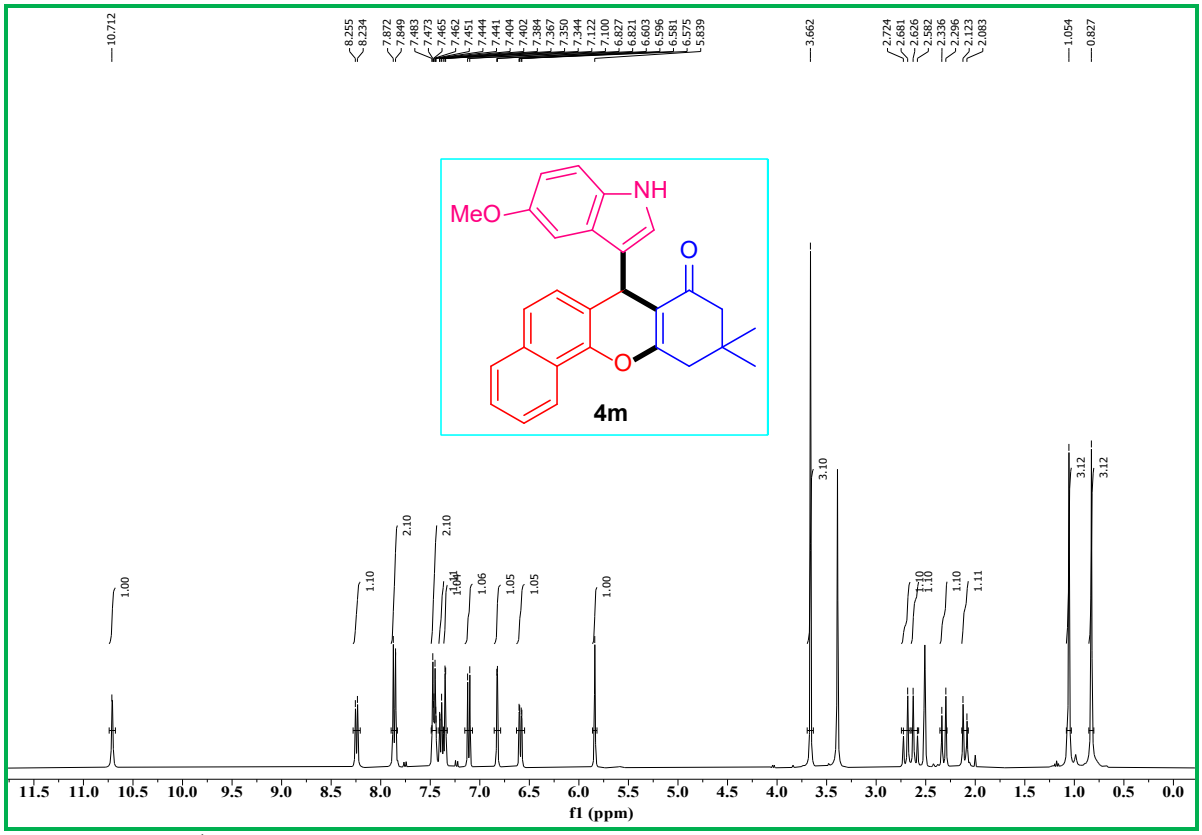


Figure S32: ^{1}H NMR spectrum of 7-(5-methoxy-1*H*-indol-3-yl)-10,10-dimethyl-10,11-dihydro-7*H*-benzo[*c*]xanthen-8(9*H*)-one, **4m**.

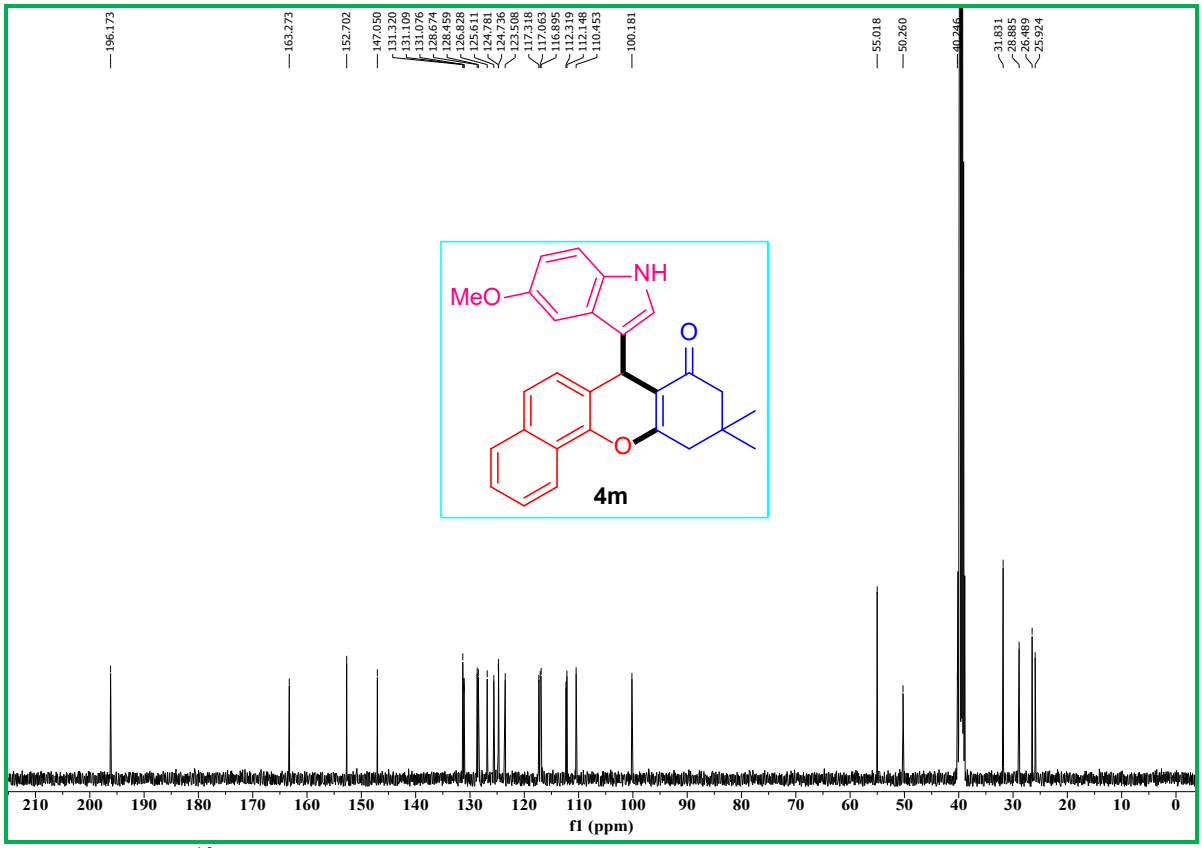


Figure S33: ^{13}C NMR spectrum of 7-(5-methoxy-1*H*-indol-3-yl)-10,10-dimethyl-10,11-dihydro-7*H*-benzo[*c*]xanthen-8(9*H*)-one, **4m**.

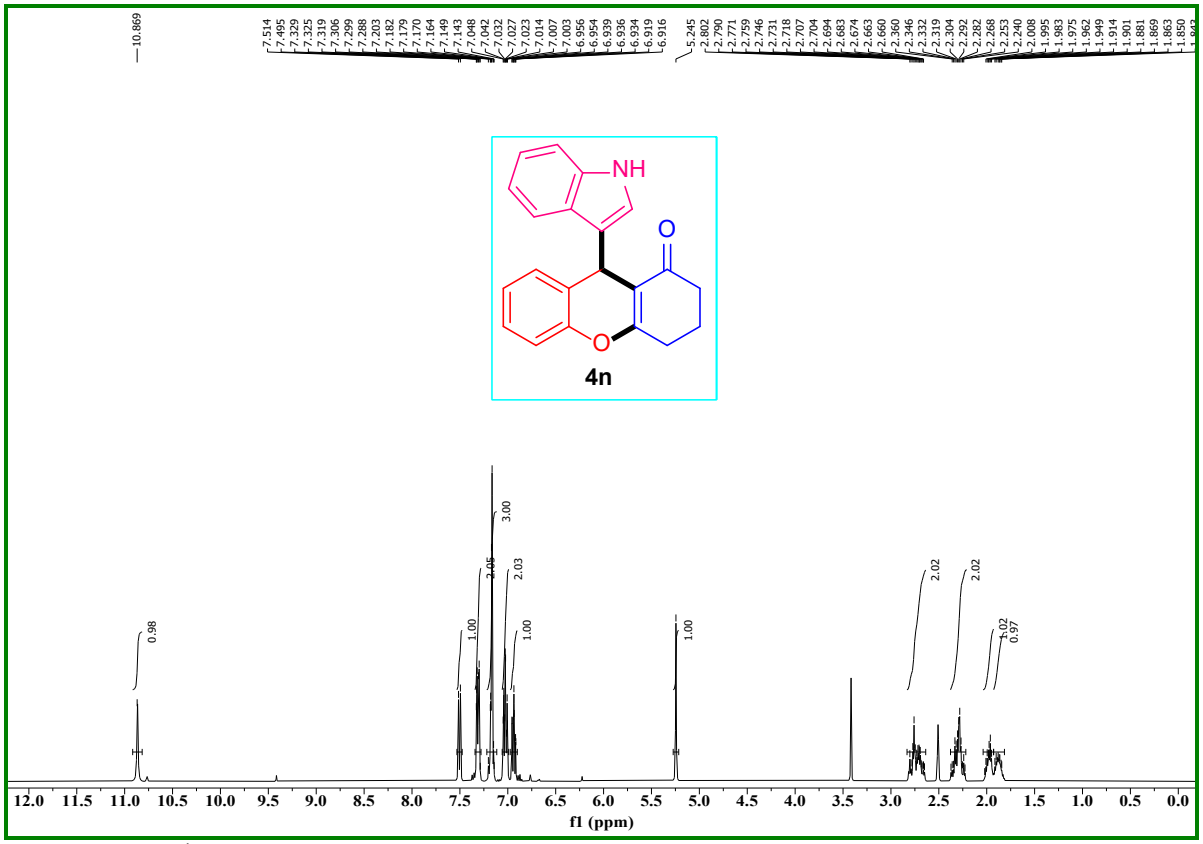


Figure S34: ^{1}H NMR spectrum of 9-(1*H*-indol-3-yl)-2,3,4,9-tetrahydro-1*H*-xanthen-1-one, **4n**.

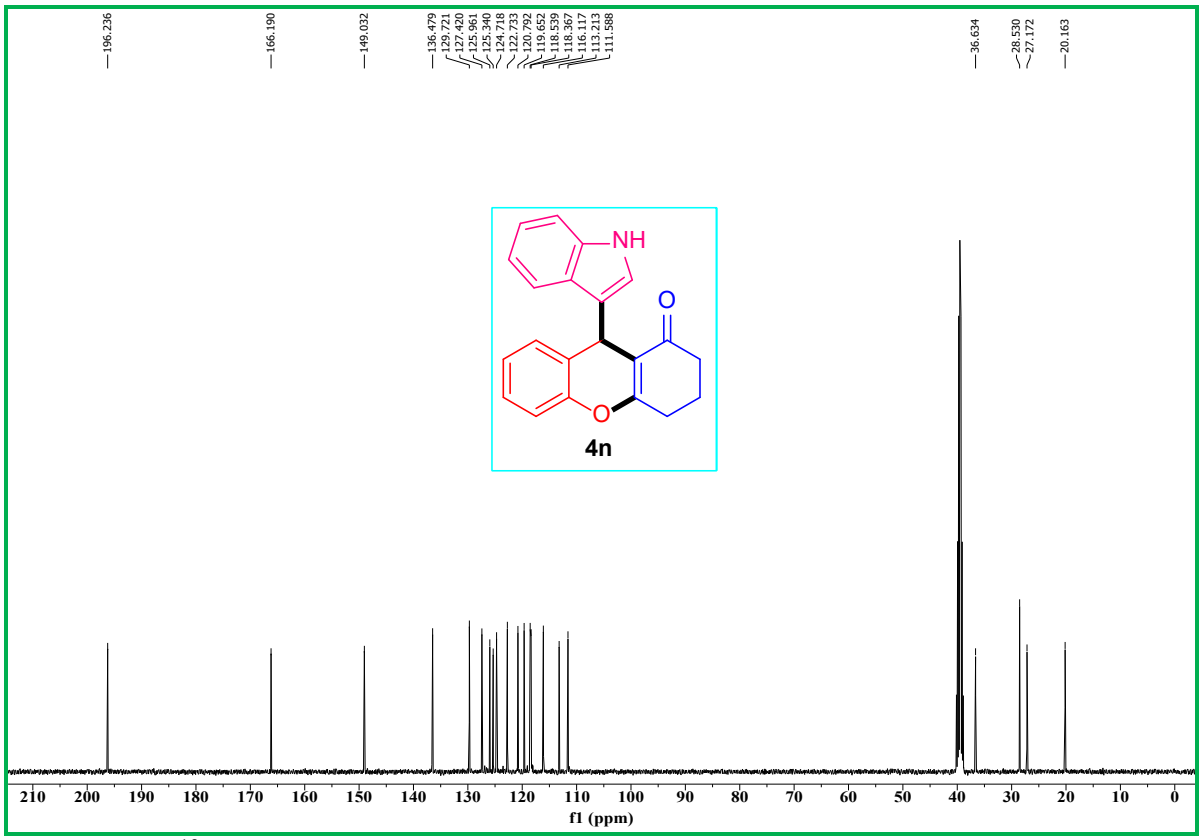


Figure S35: ^{13}C NMR spectrum of 9-(1*H*-indol-3-yl)-2,3,4,9-tetrahydro-1*H*-xanthen-1-one, **4n**.

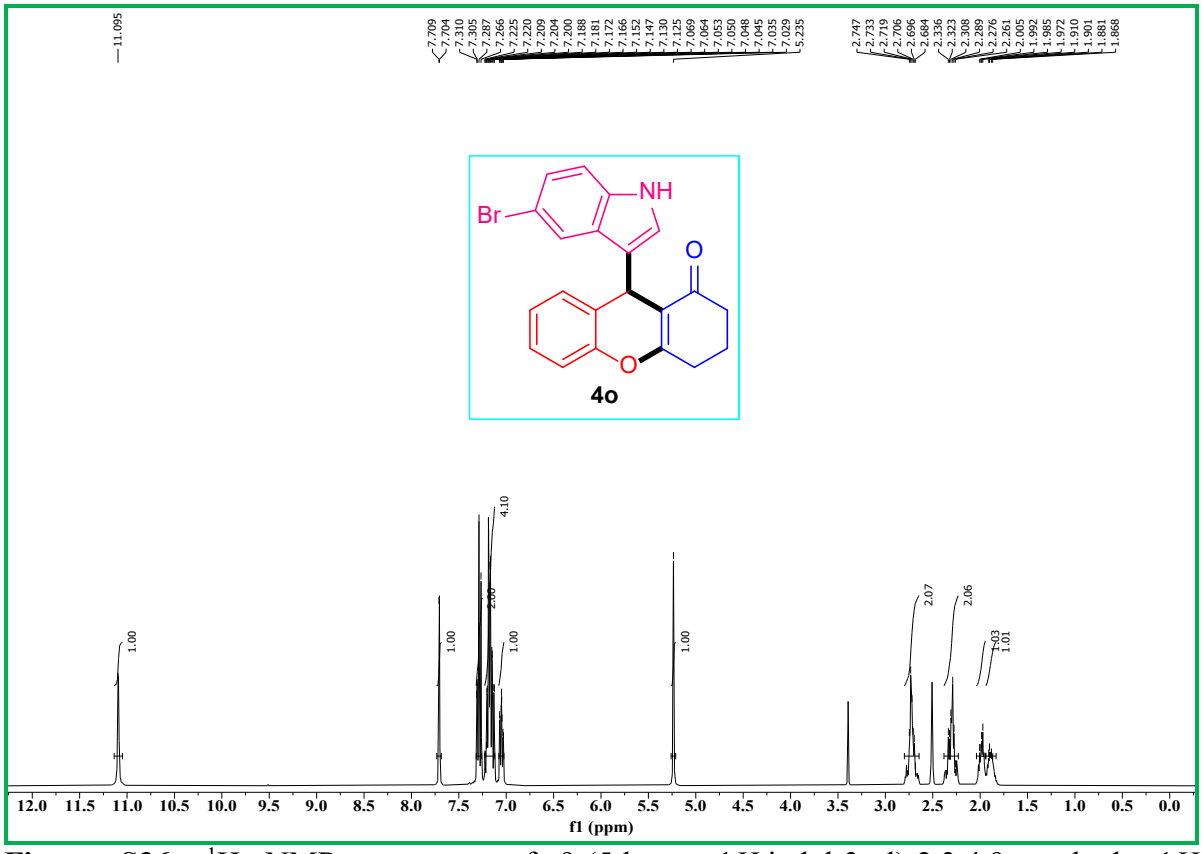


Figure S36: ^{1}H NMR spectrum of 9-(5-bromo-1*H*-indol-3-yl)-2,3,4,9-tetrahydro-1*H*-xanthen-1-one, **4o**.

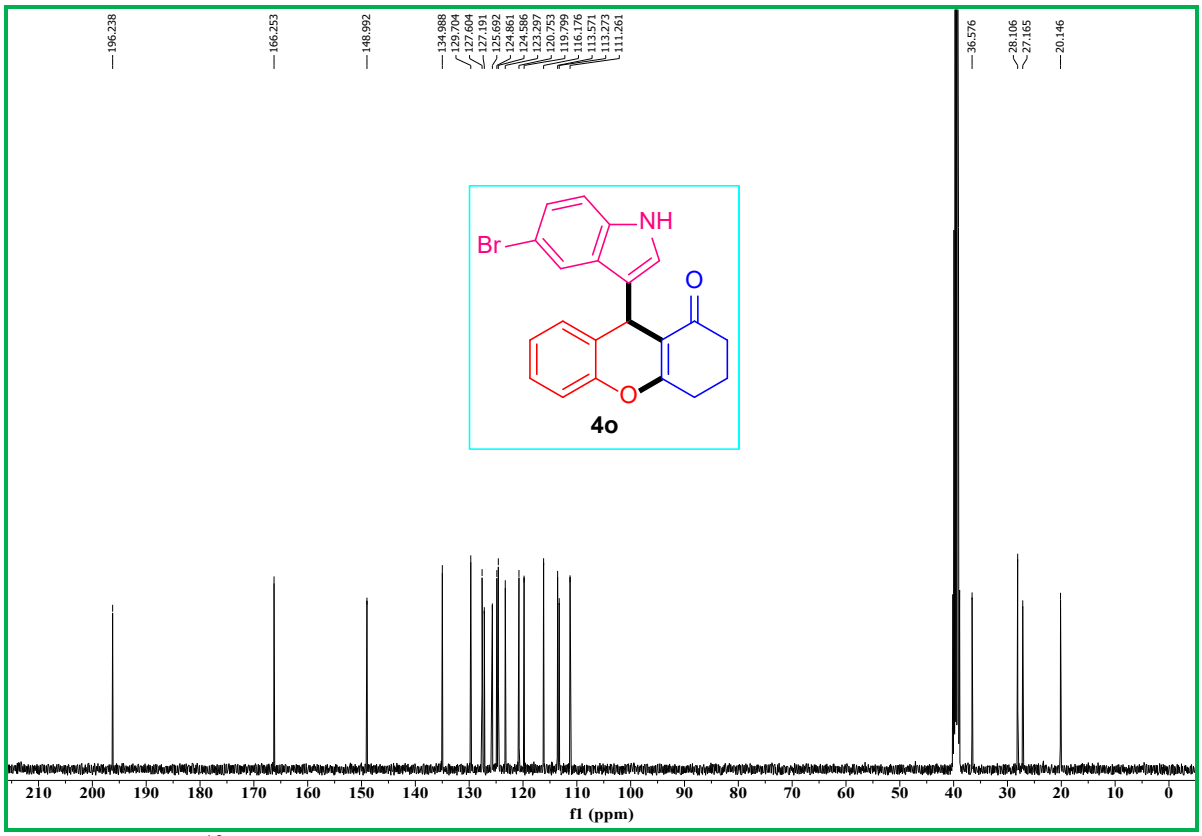


Figure S37: ^{13}C NMR spectrum of 9-(5-bromo-1*H*-indol-3-yl)-2,3,4,9-tetrahydro-1*H*-xanthen-1-one, **4n**.

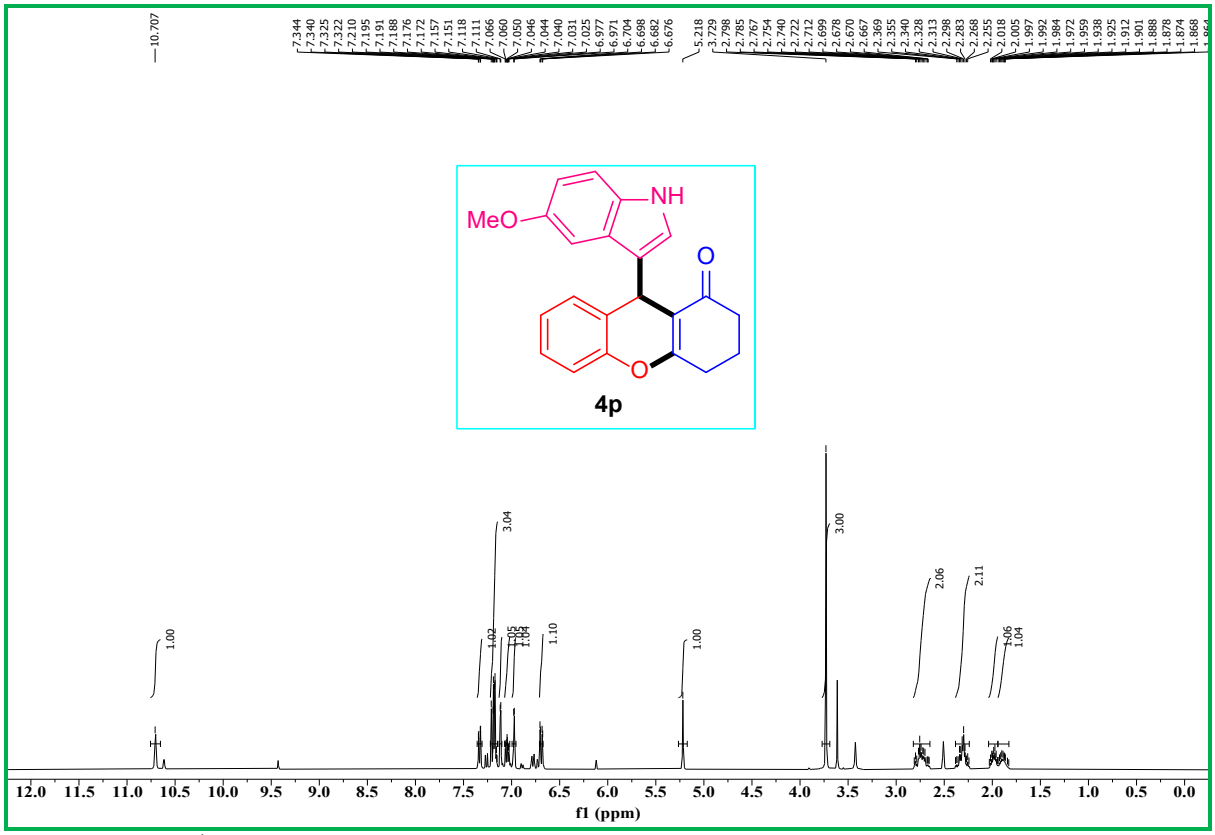


Figure S38: ^{1}H NMR spectrum of 9-(5-methoxy-1*H*-indol-3-yl)-2,3,4,9-tetrahydro-1*H*-xanthen-1-one, **4p**.

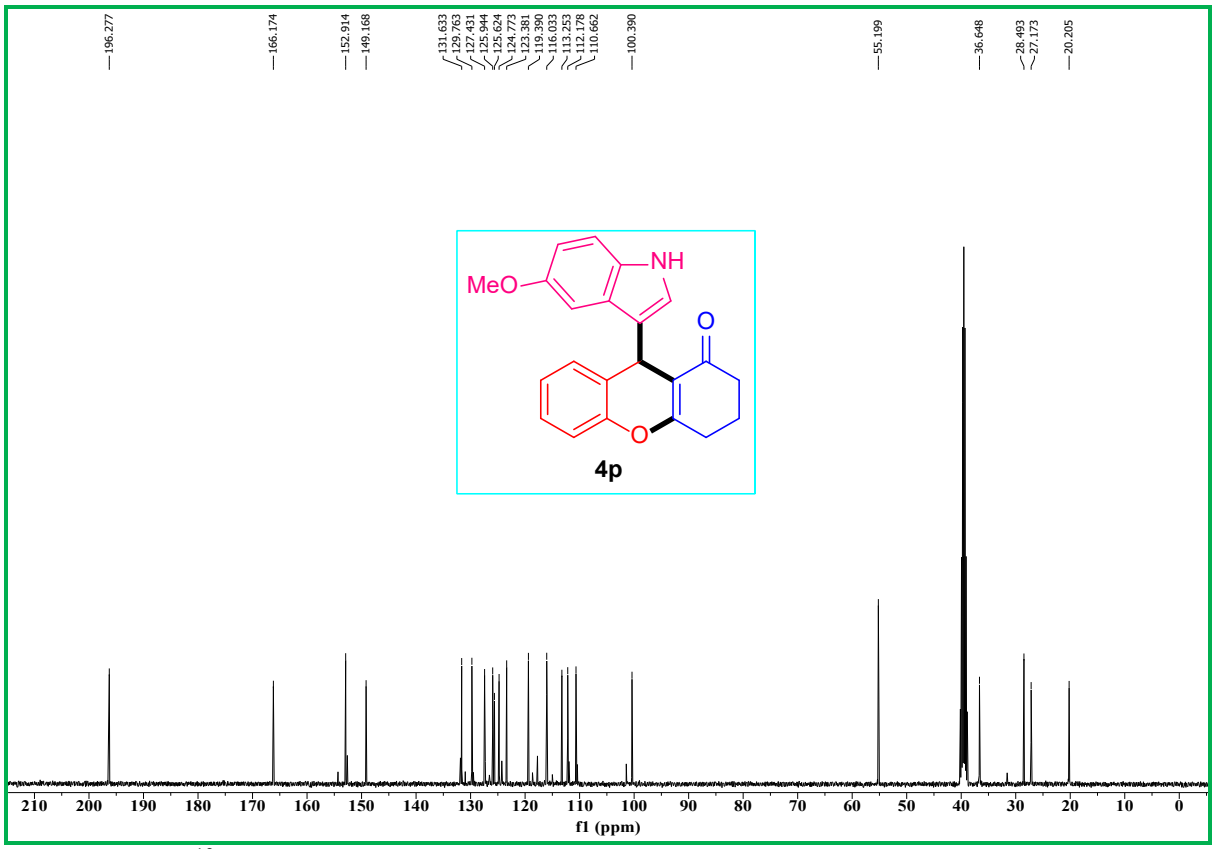


Figure S39: ^{13}C NMR spectrum of 9-(5-methoxy-1*H*-indol-3-yl)-2,3,4,9-tetrahydro-1*H*-xanthen-1-one, **4p**.

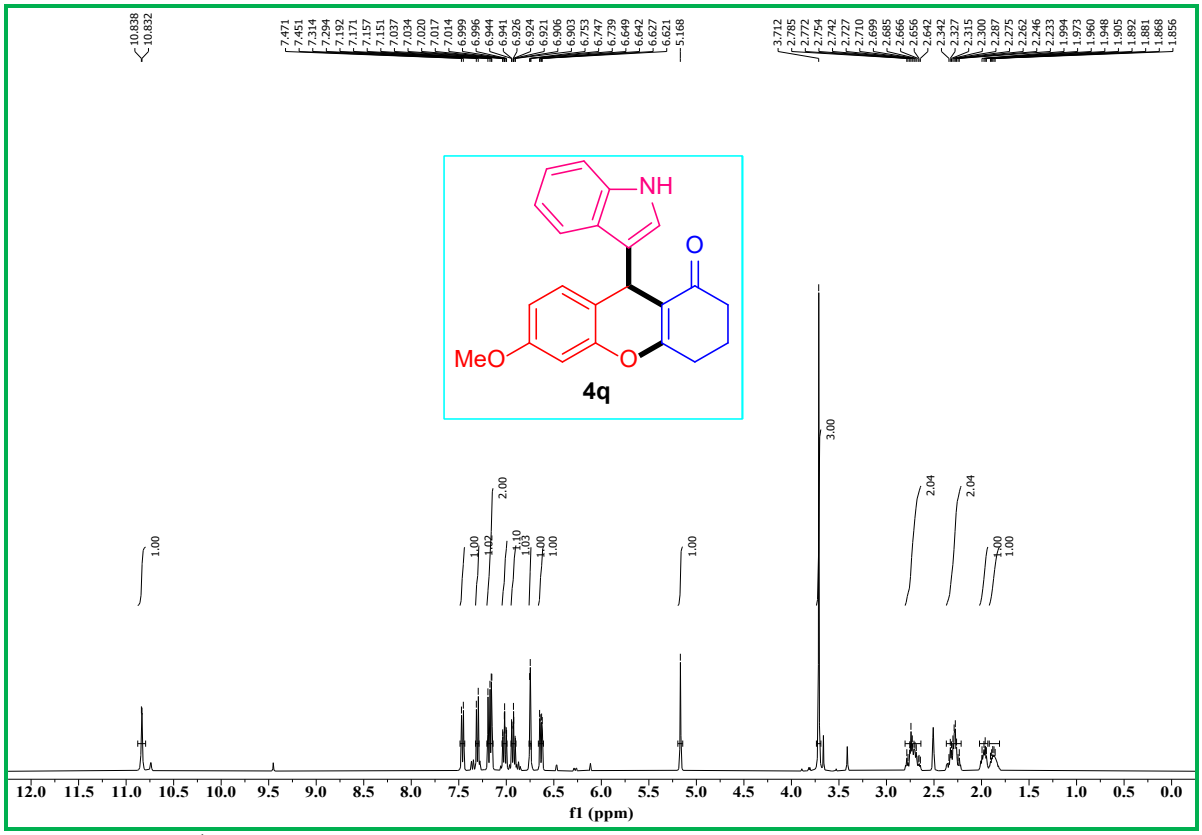


Figure S40: ^{1}H NMR spectrum of 9-(1*H*-indol-3-yl)-6-methoxy-2,3,4,9-tetrahydro-1*H*-xanthen-1-one, **4q**.

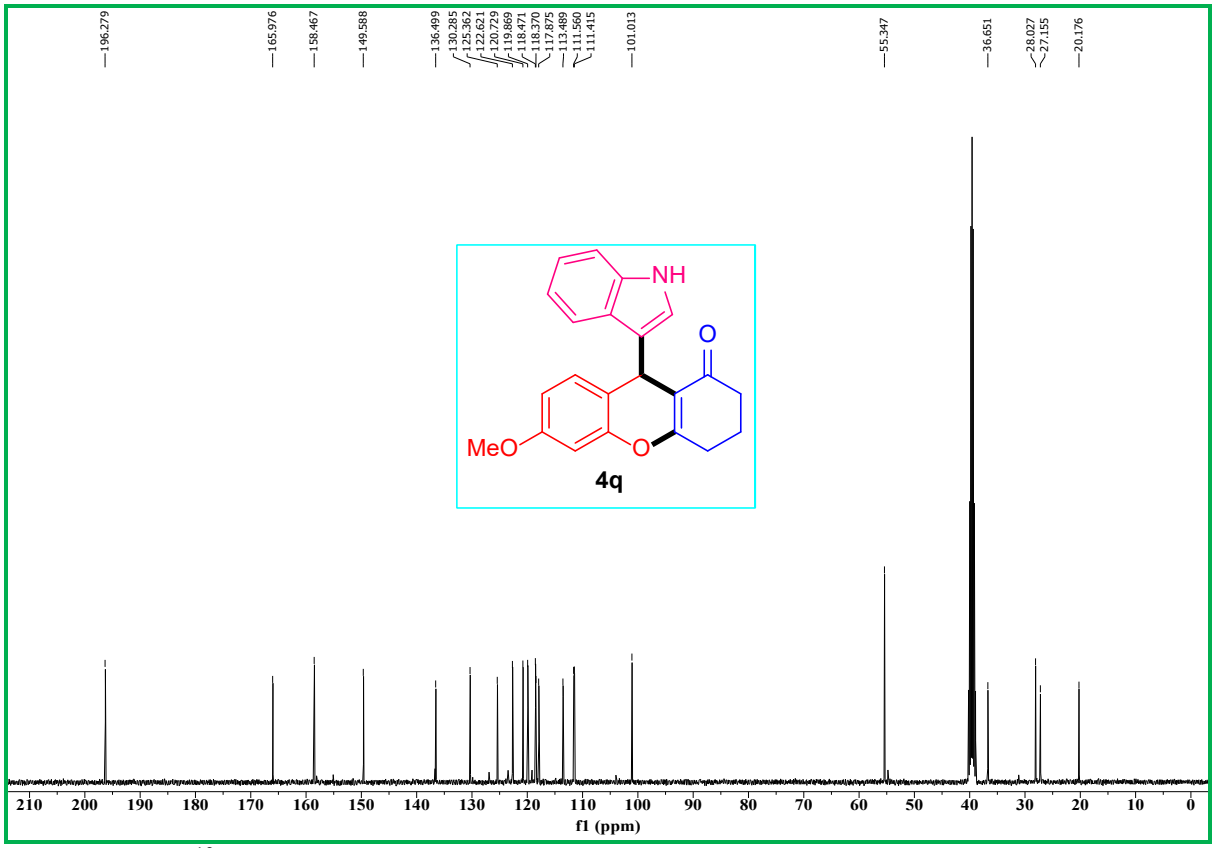


Figure S41: ^{13}C NMR spectrum of 9-(1*H*-indol-3-yl)-6-methoxy-2,3,4,9-tetrahydro-1*H*-xanthen-1-one, **4q**.

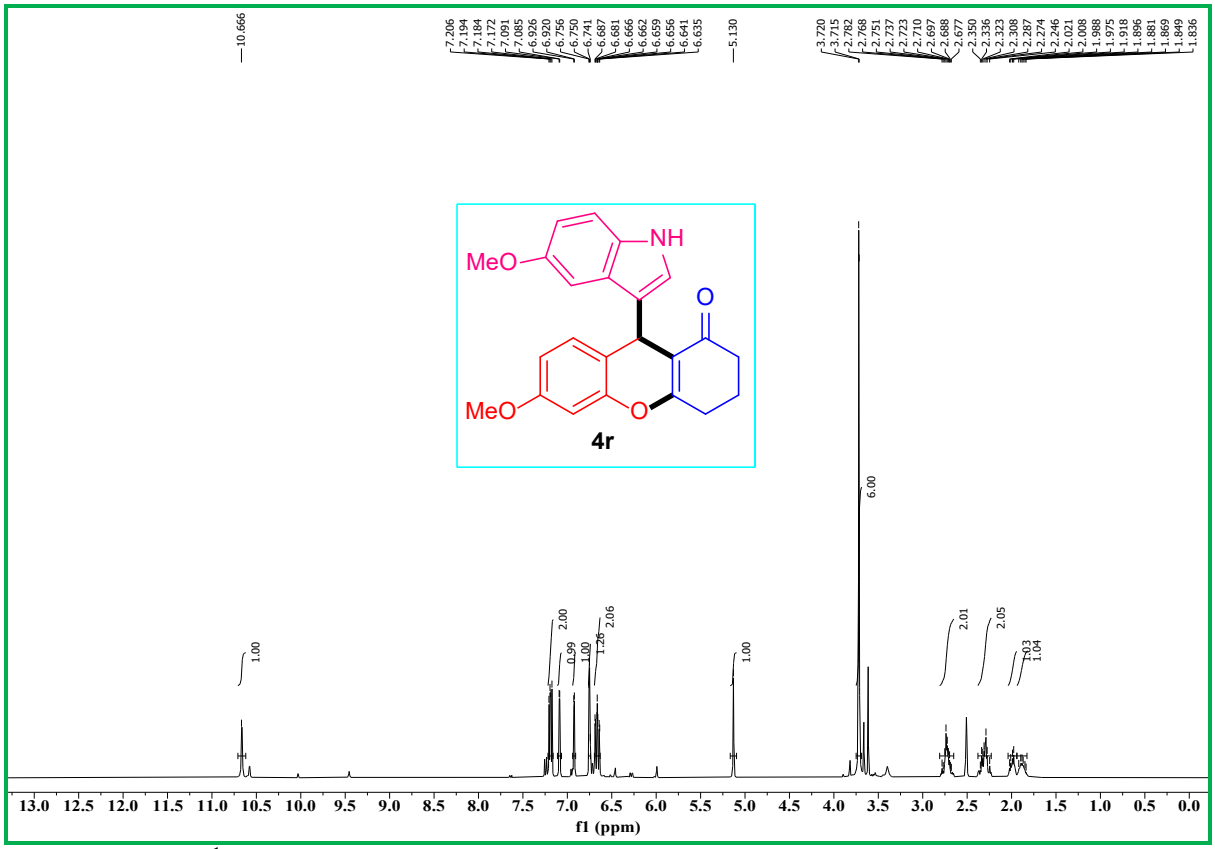


Figure S42: ^{1}H NMR spectrum of 6-methoxy-9-(5-methoxy-1*H*-indol-3-yl)-2,3,4,9-tetrahydro-1*H*-xanthen-1-one, **4r**.

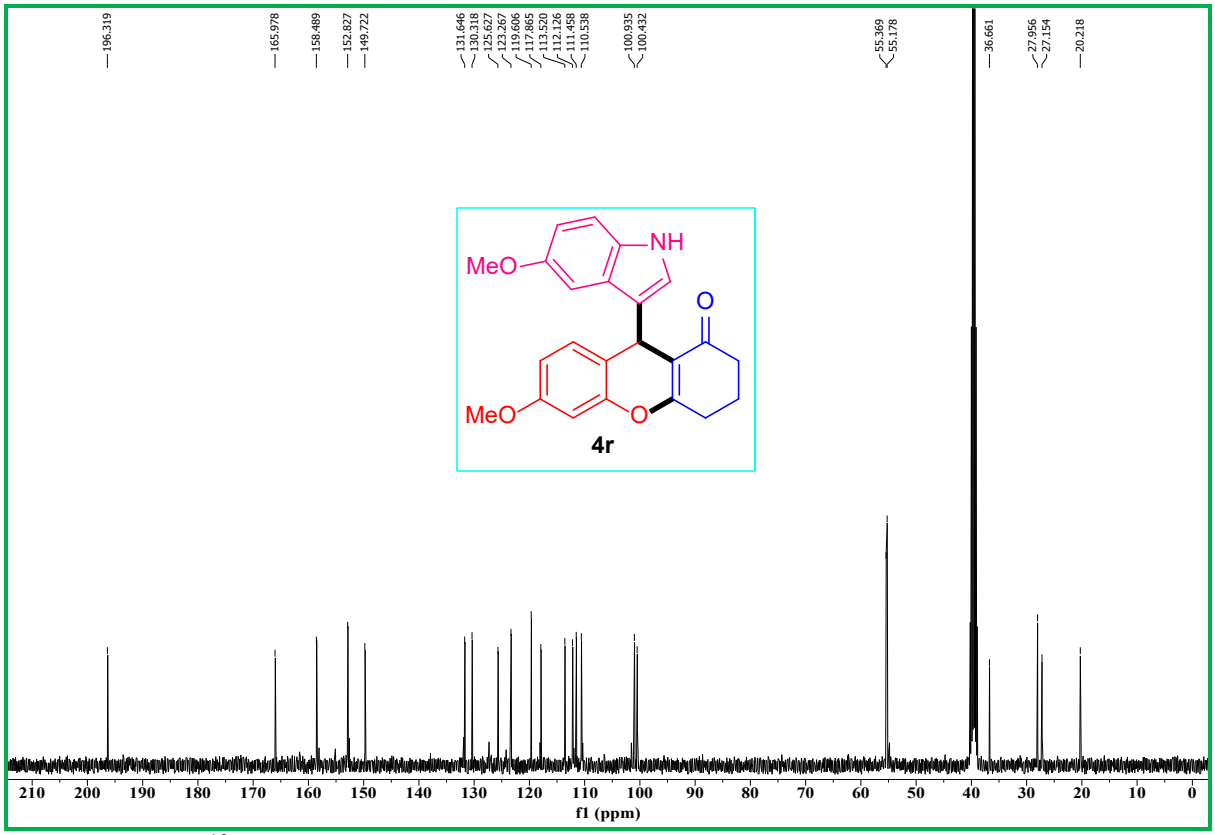


Figure S43: ^{13}C NMR spectrum of 6-methoxy-9-(5-methoxy-1*H*-indol-3-yl)-2,3,4,9-tetrahydro-1*H*-xanthen-1-one, **4r**.

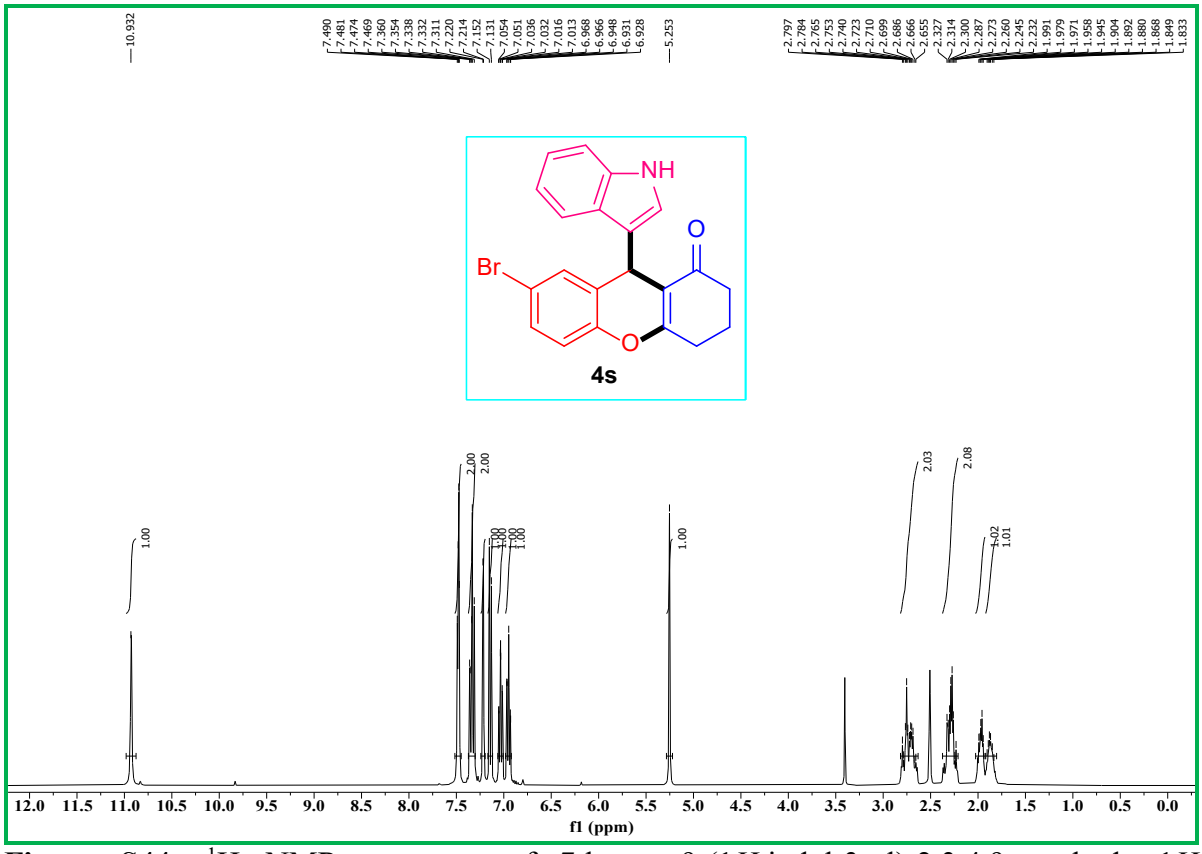


Figure S44: ^{1}H NMR spectrum of 7-bromo-9-(1*H*-indol-3-yl)-2,3,4,9-tetrahydro-1*H*-xanthen-1-one, **4s**.

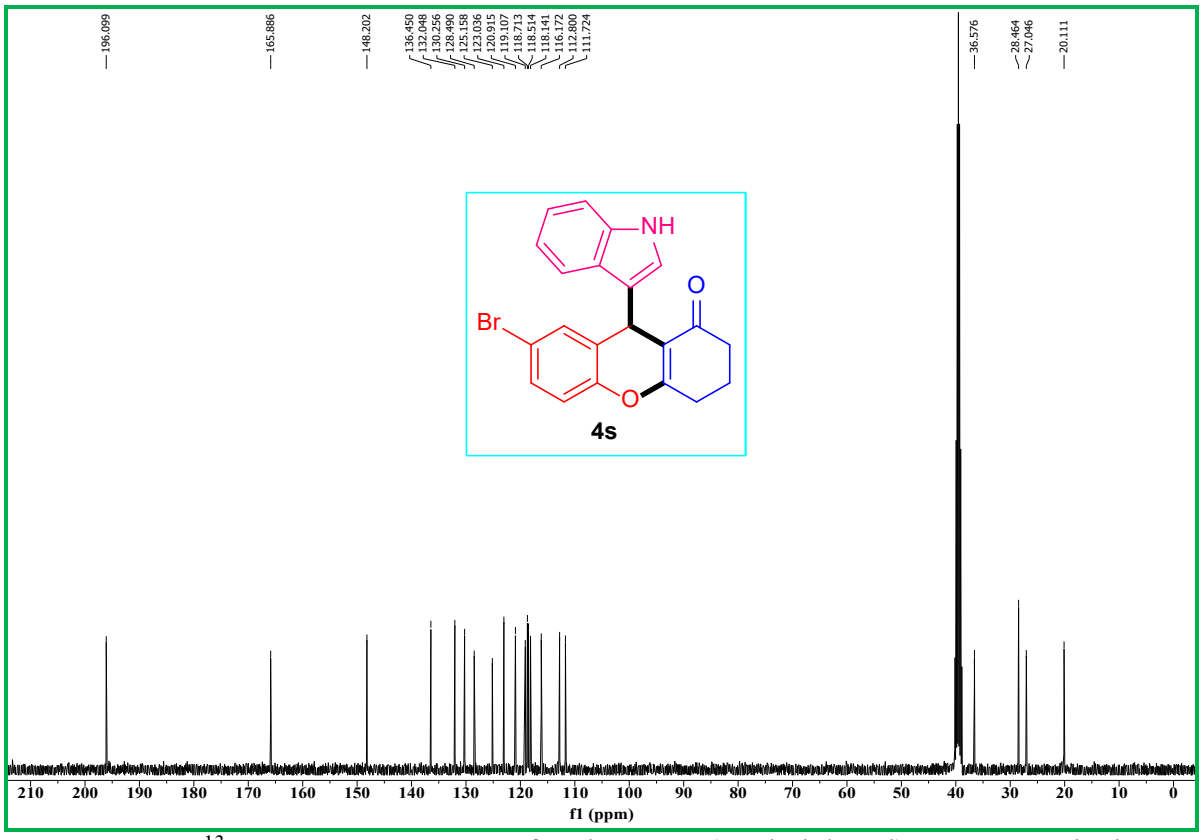


Figure S45: ^{13}C NMR spectrum of 7-bromo-9-(1*H*-indol-3-yl)-2,3,4,9-tetrahydro-1*H*-xanthen-1-one, **4s**.

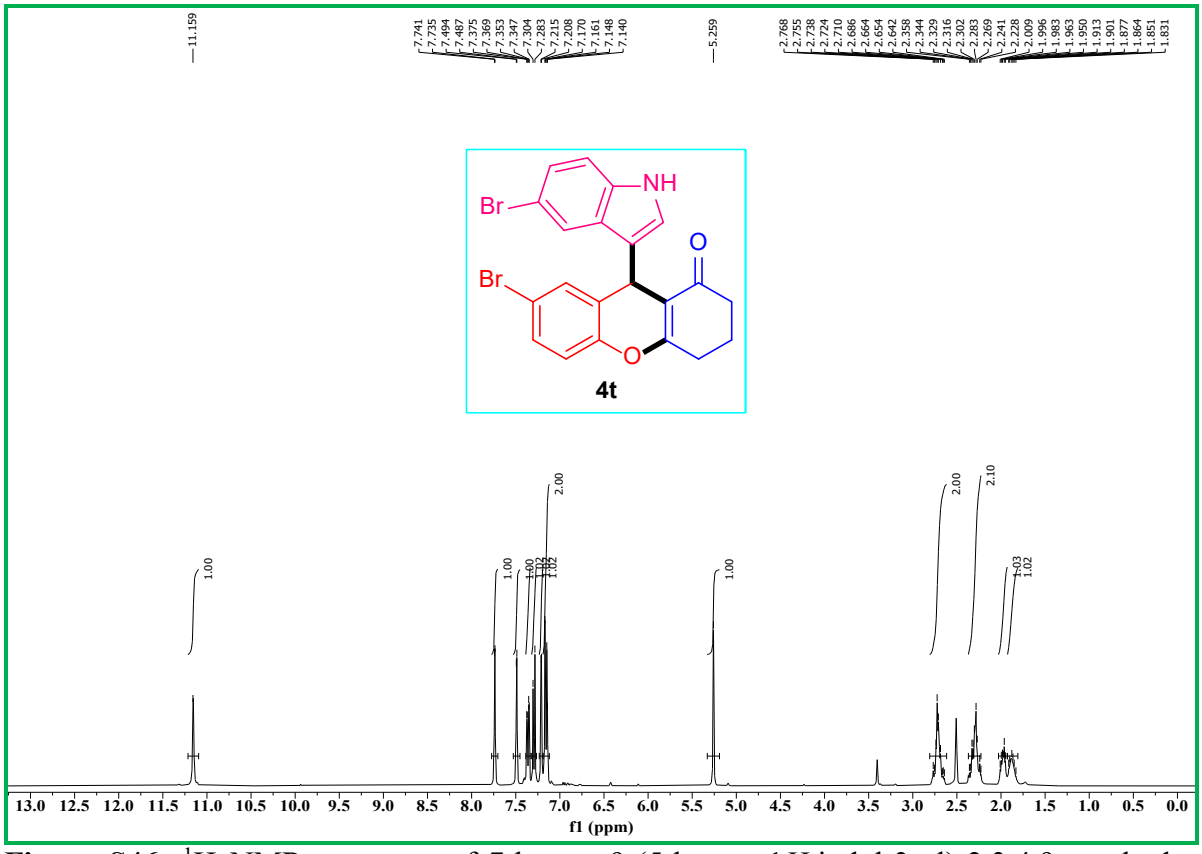


Figure S46: ^{1}H NMR spectrum of 7-bromo-9-(5-bromo-1*H*-indol-3-yl)-2,3,4,9-tetrahydro-1*H*-xanthen-1-one, **4t**.

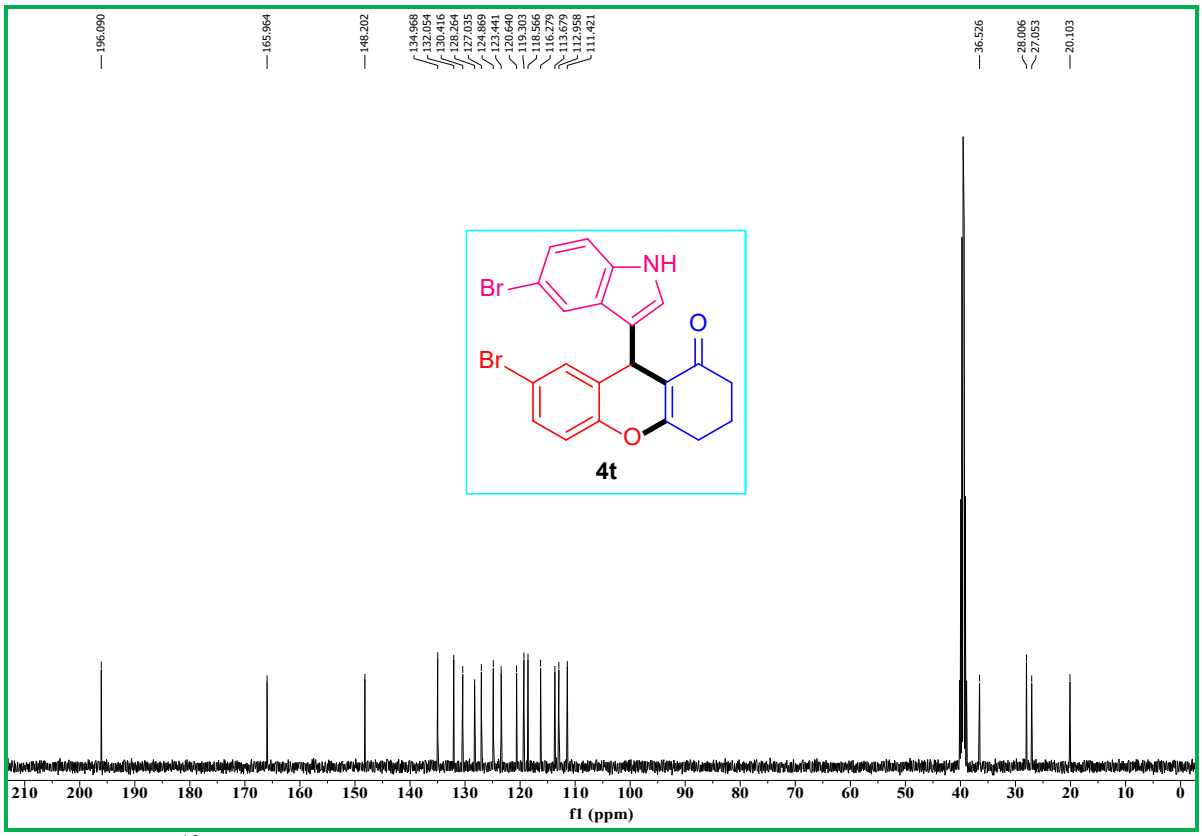


Figure S47: ^{13}C NMR spectrum of 7-bromo-9-(5-bromo-1*H*-indol-3-yl)-2,3,4,9-tetrahydro-1*H*-xanthen-1-one, **4t**.

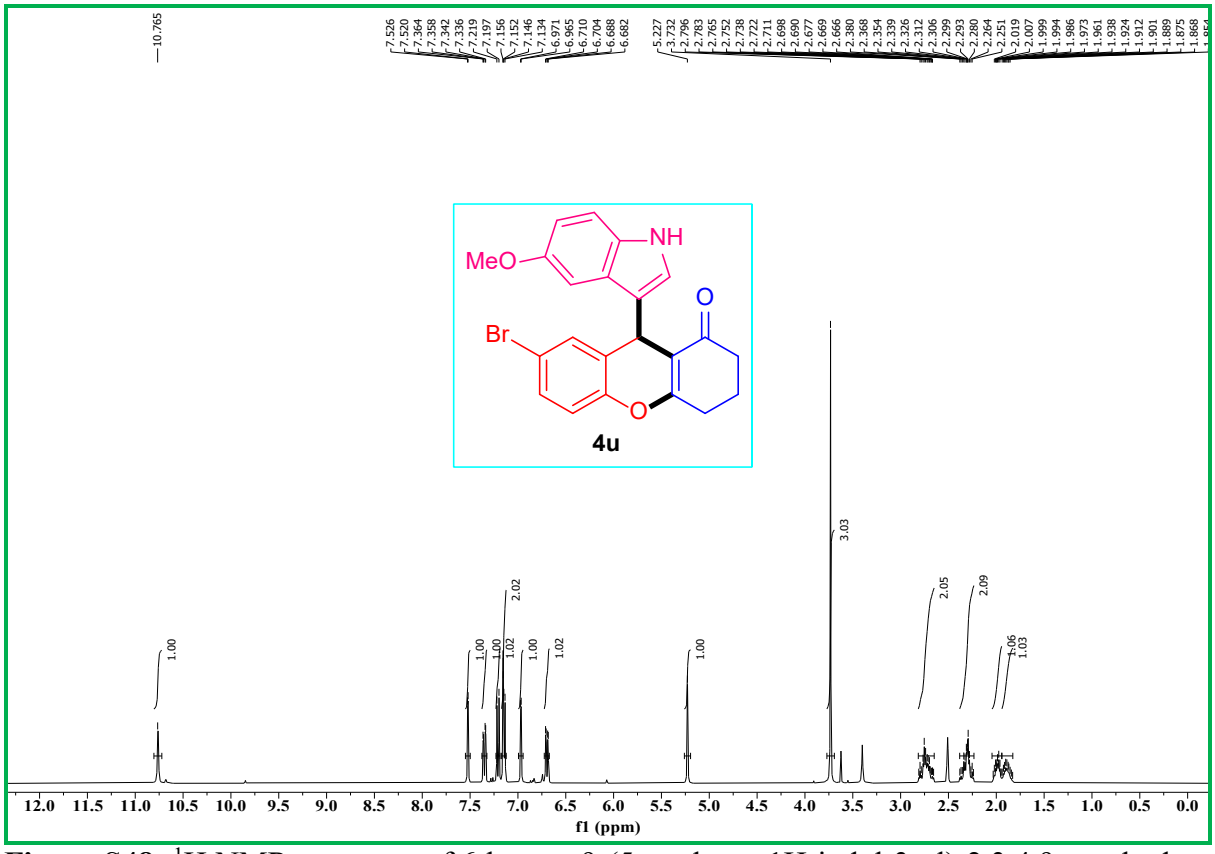


Figure S48: ^{1}H NMR spectrum of 6-bromo-9-(5-methoxy-1H-indol-3-yl)-2,3,4,9-tetrahydro-1H-xanthen-1-one, **4u**.

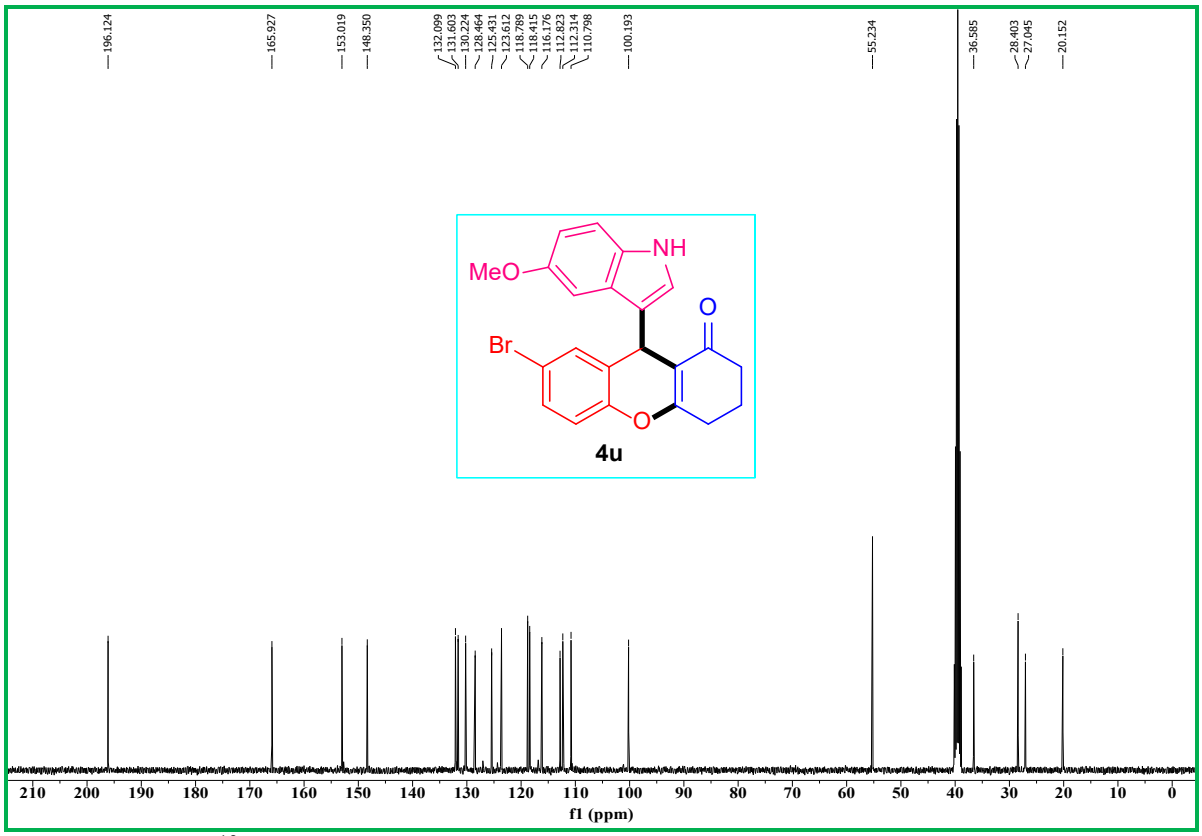


Figure S49: ^{13}C NMR spectrum of 6-bromo-9-(5-methoxy-1H-indol-3-yl)-2,3,4,9-tetrahydro-1H-xanthen-1-one, **4u**.

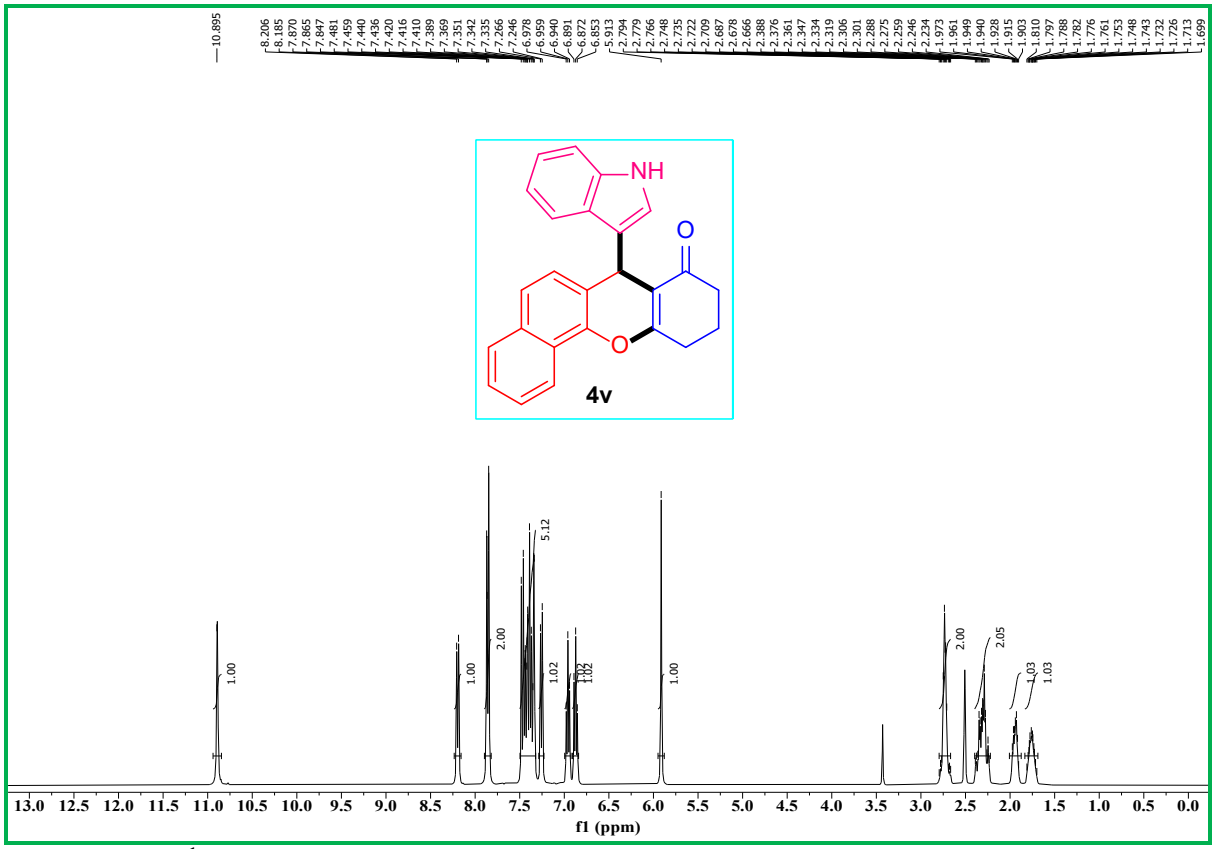


Figure S50: ^{1}H NMR spectrum of 7-(1*H*-indol-3-yl)-10,11-dihydro-7*H*-benzo[*c*]xanthen-8(9*H*)-one, **4v**.

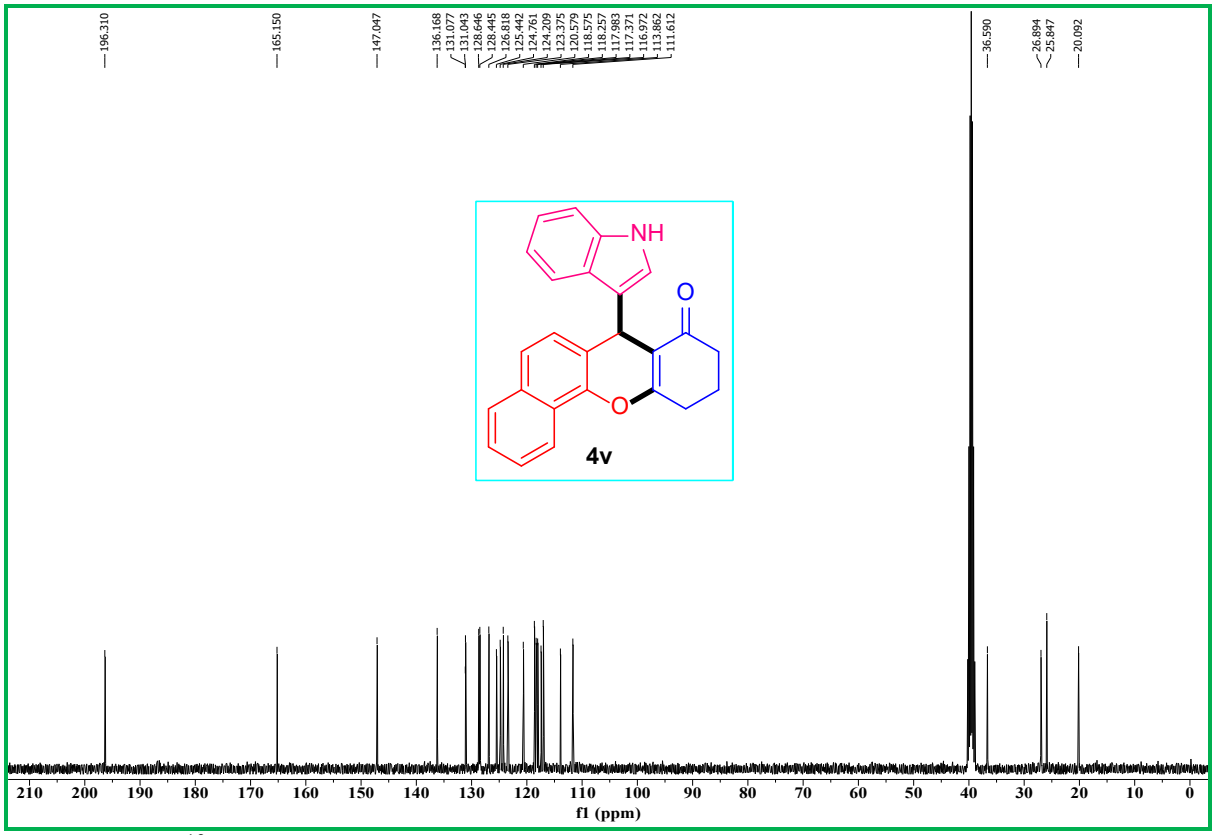


Figure S51: ^{13}C NMR spectrum of 7-(1*H*-indol-3-yl)-10,11-dihydro-7*H*-benzo[*c*]xanthen-8(9*H*)-one, **4v**.

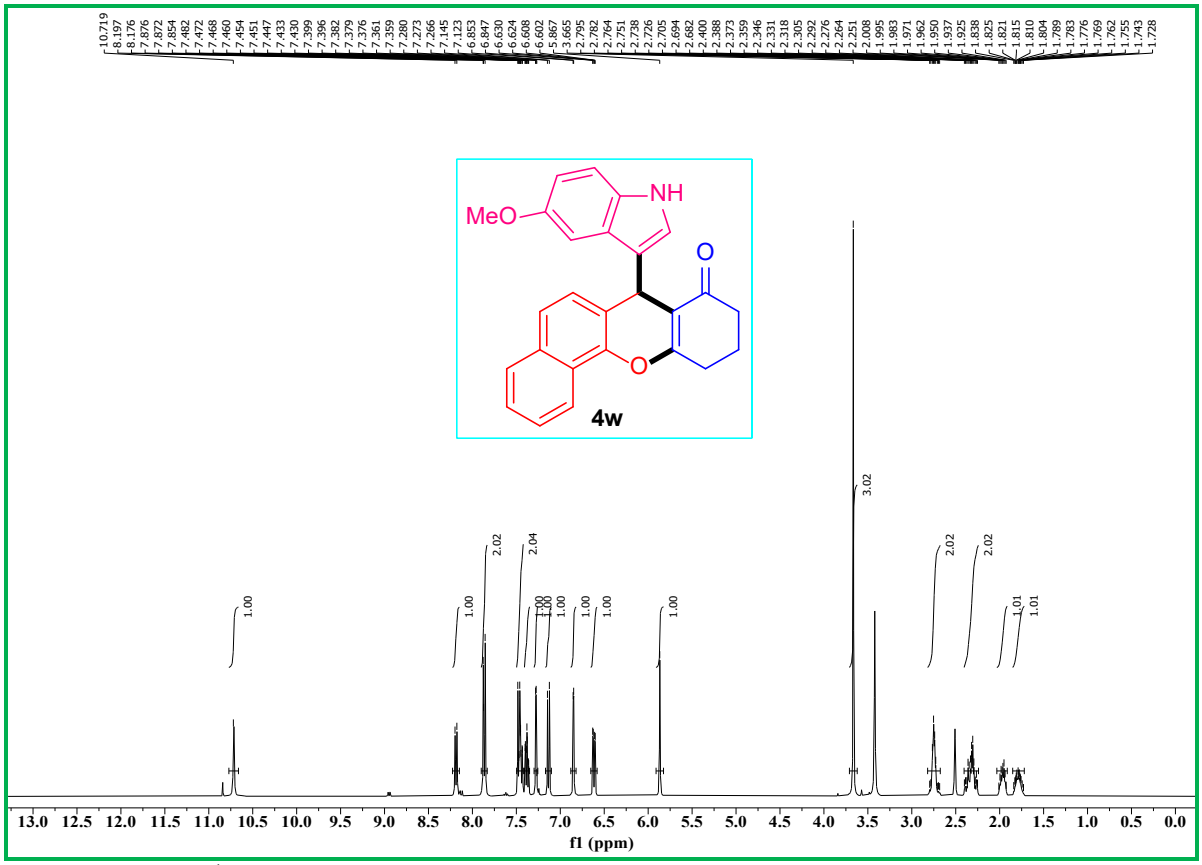


Figure S52: ^{1}H NMR spectrum of 7-(5-methoxy-1*H*-indol-3-yl)-10,11-dihydro-7*H*-benzo[*c*]xanthen-8(9*H*)-one, **4w**.

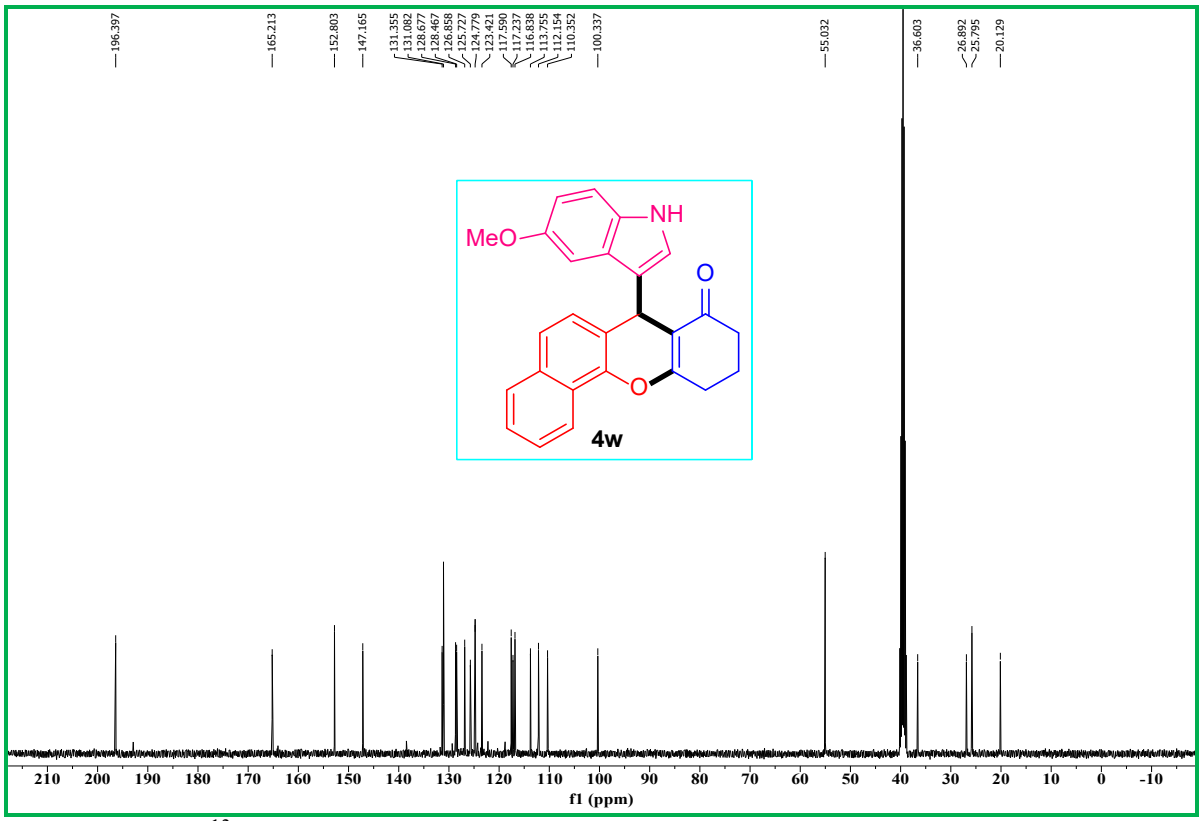


Figure S53: ^{13}C NMR spectrum of 7-(5-methoxy-1*H*-indol-3-yl)-10,11-dihydro-7*H*-benzo[*c*]xanthen-8(9*H*)-one, **4w**.

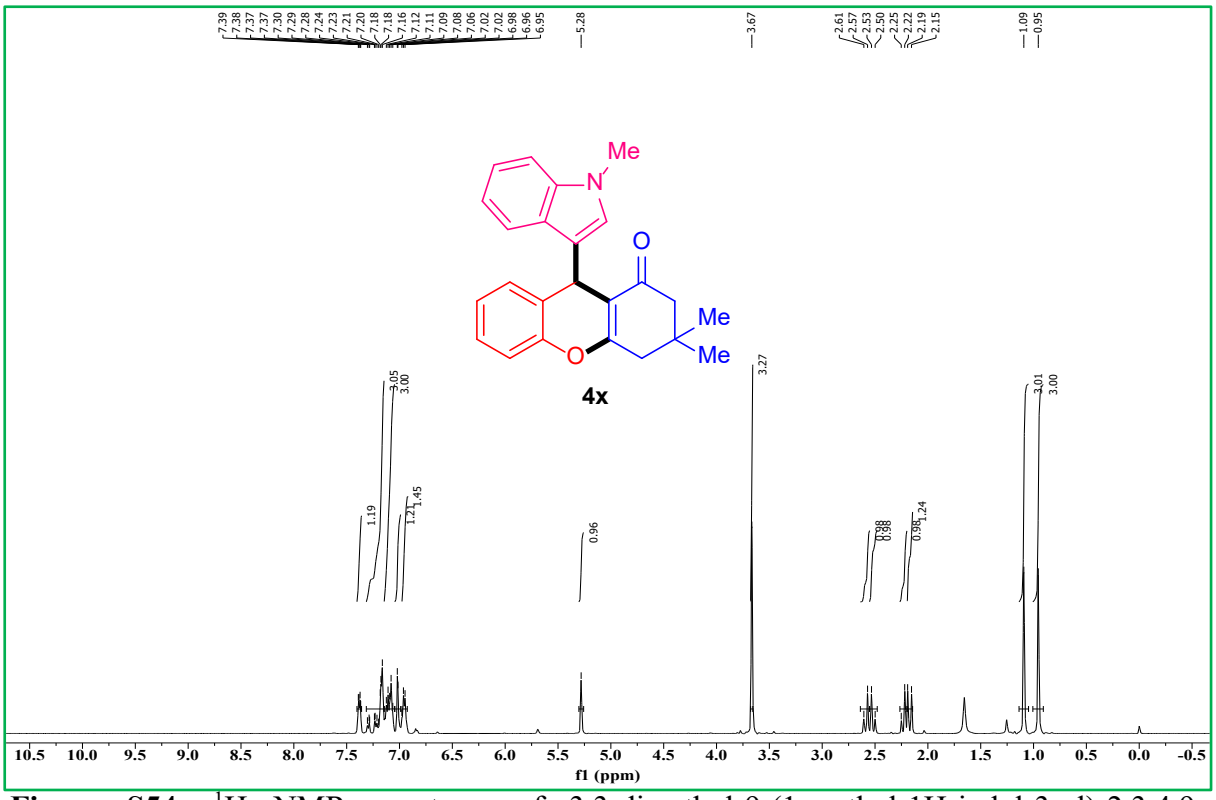


Figure S54: ^{1}H NMR spectrum of 3,3-dimethyl-9-(1-methyl-1H-indol-3-yl)-2,3,4,9-tetrahydro-1H-xanthen-1-one, **4x**.

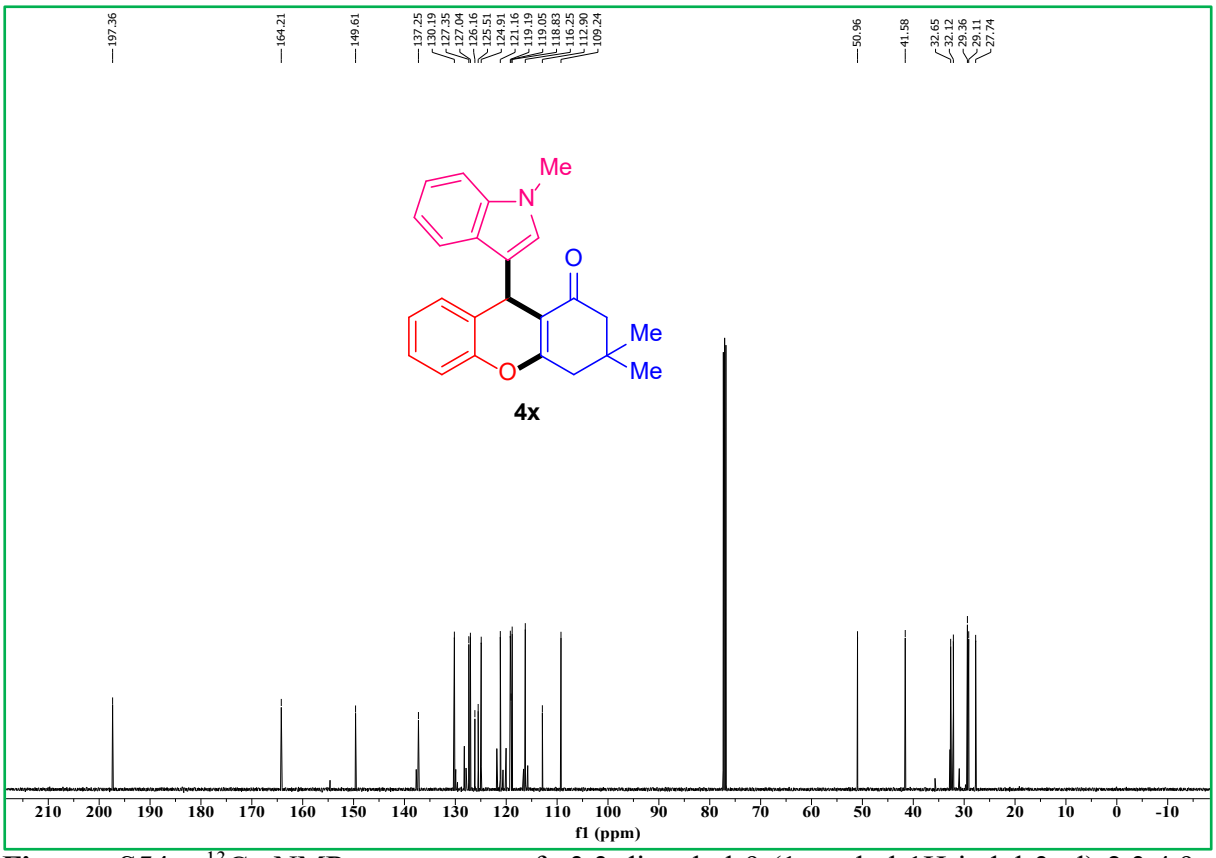


Figure S54: ^{13}C NMR spectrum of 3,3-dimethyl-9-(1-methyl-1H-indol-3-yl)-2,3,4,9-tetrahydro-1H-xanthen-1-one, **4x**.

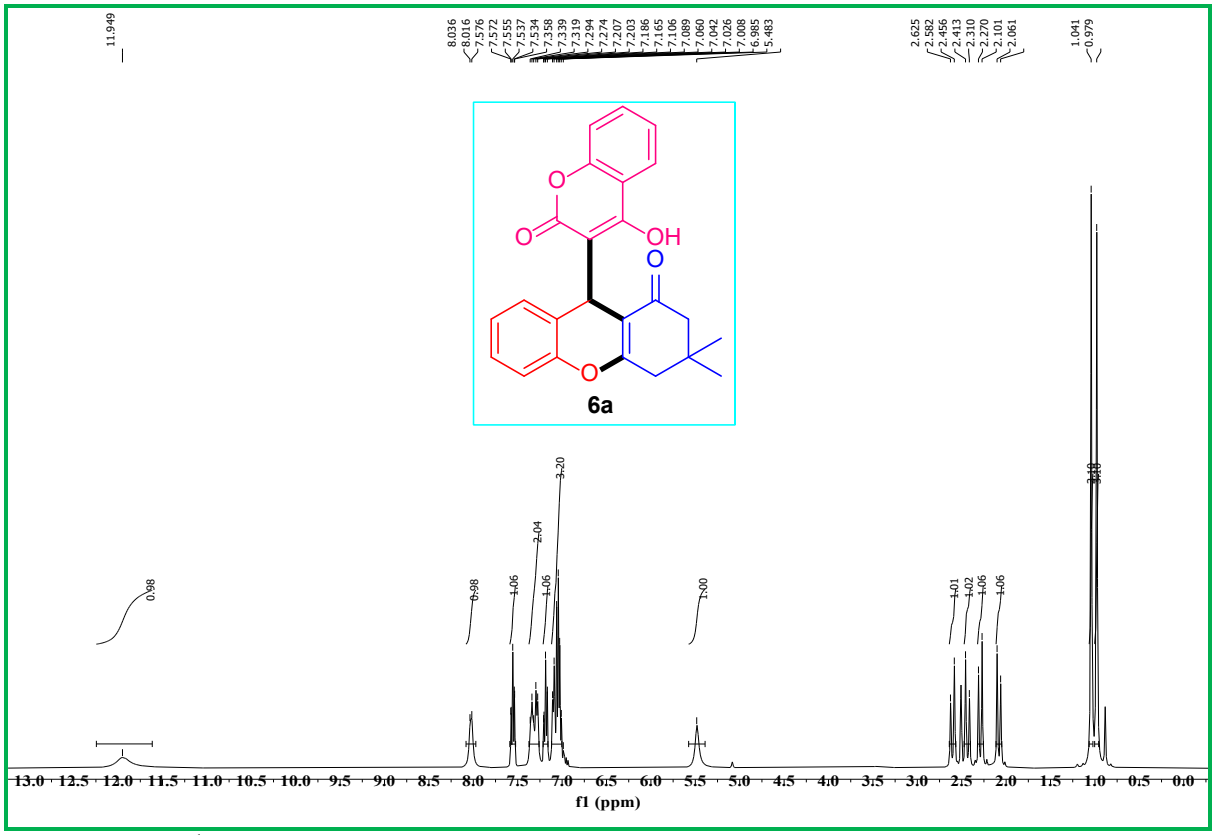


Figure S56: ^{1}H NMR spectrum of 9-(4-hydroxy-2-oxo-2*H*-chromen-3-yl)-3,3-dimethyl-2,3,4,9-tetrahydro-1*H*-xanthen-1-one, **6a**.

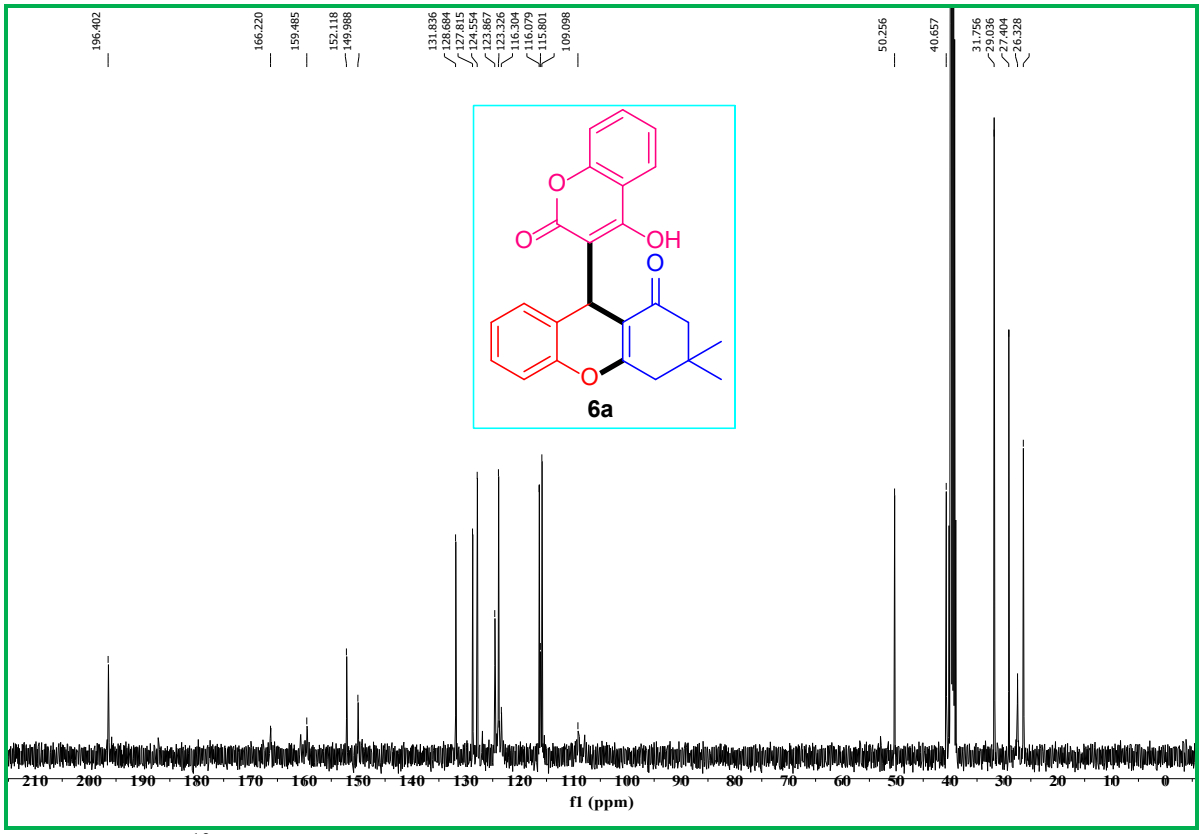


Figure S57: ^{13}C NMR spectrum of 9-(4-hydroxy-2-oxo-2*H*-chromen-3-yl)-3,3-dimethyl-2,3,4,9-tetrahydro-1*H*-xanthen-1-one, **6a**.

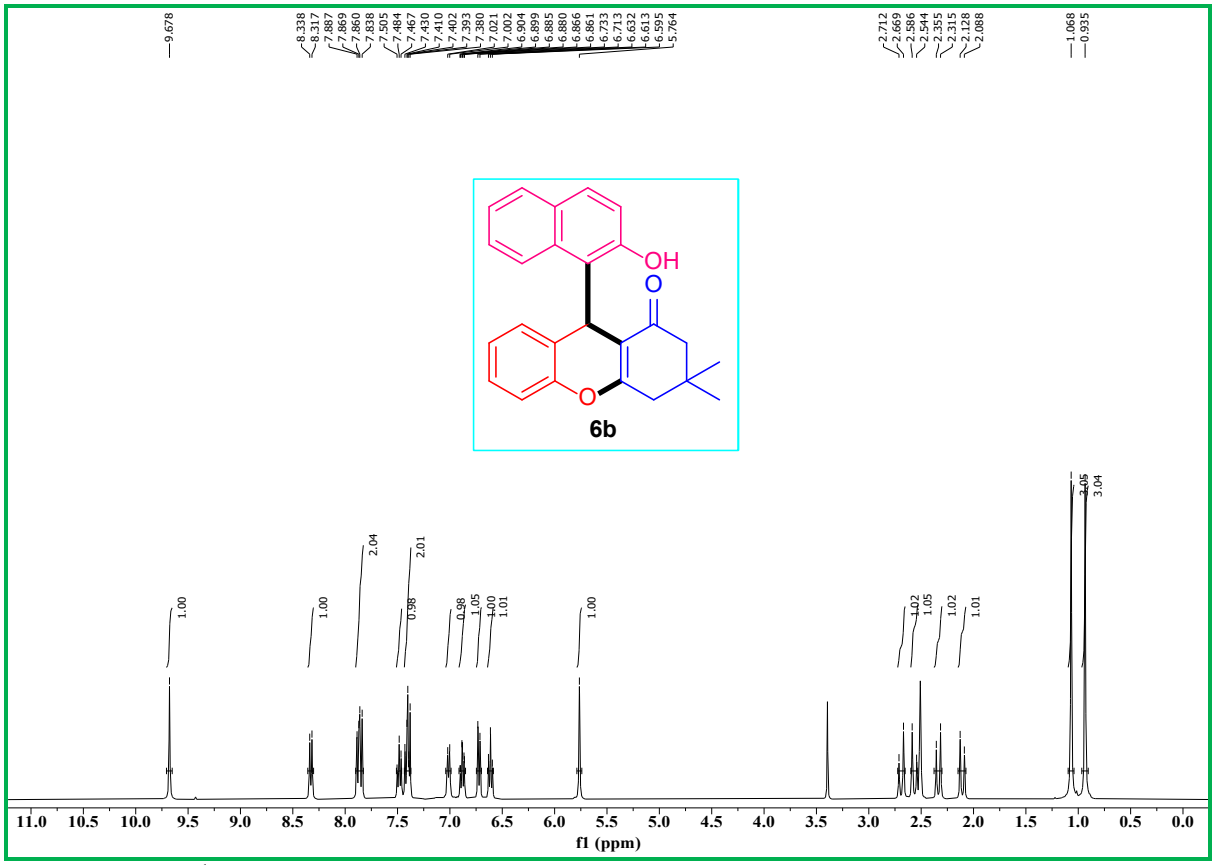


Figure S58: ^{1}H NMR spectrum of 9-(2-hydroxynaphthalen-1-yl)-3,3-dimethyl-2,3,4,9-tetrahydro-1*H*-xanthen-1-one, **6b**.

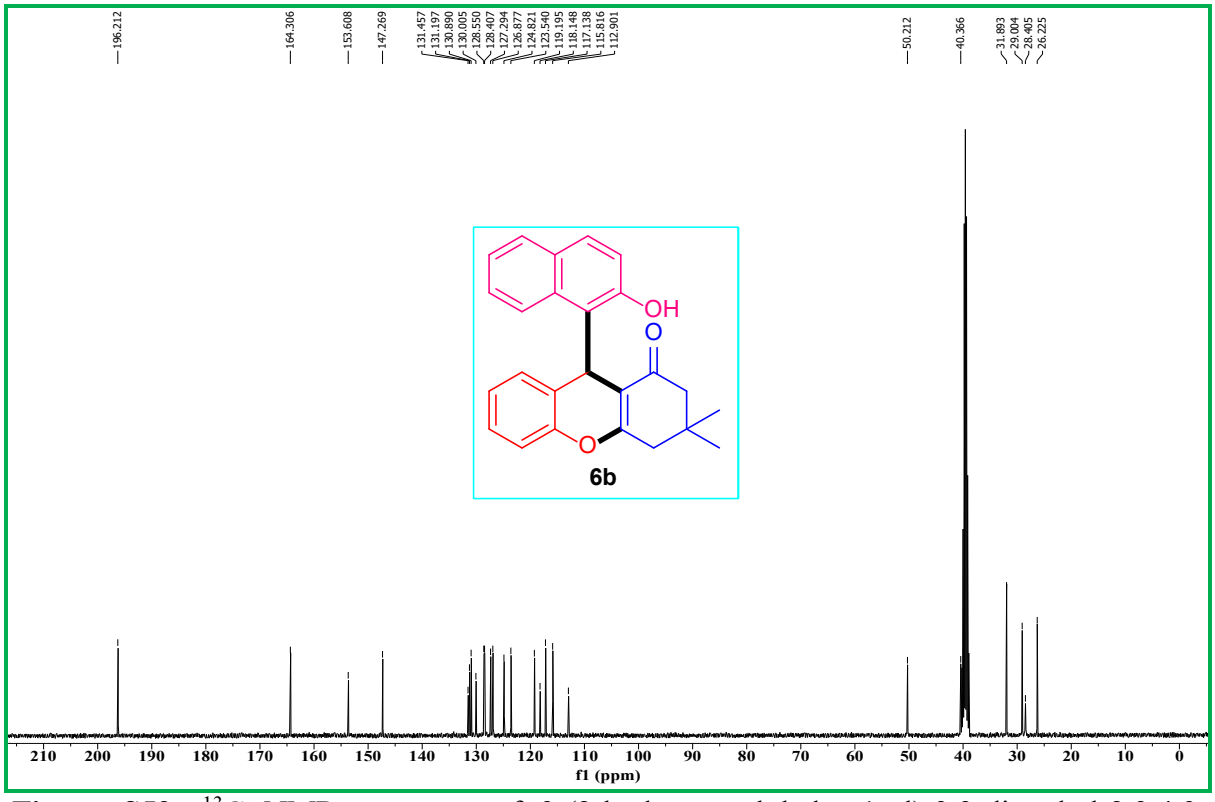


Figure S59: ^{13}C NMR spectrum of 9-(2-hydroxynaphthalen-1-yl)-3,3-dimethyl-2,3,4,9-tetrahydro-1*H*-xanthen-1-one, **6b**.

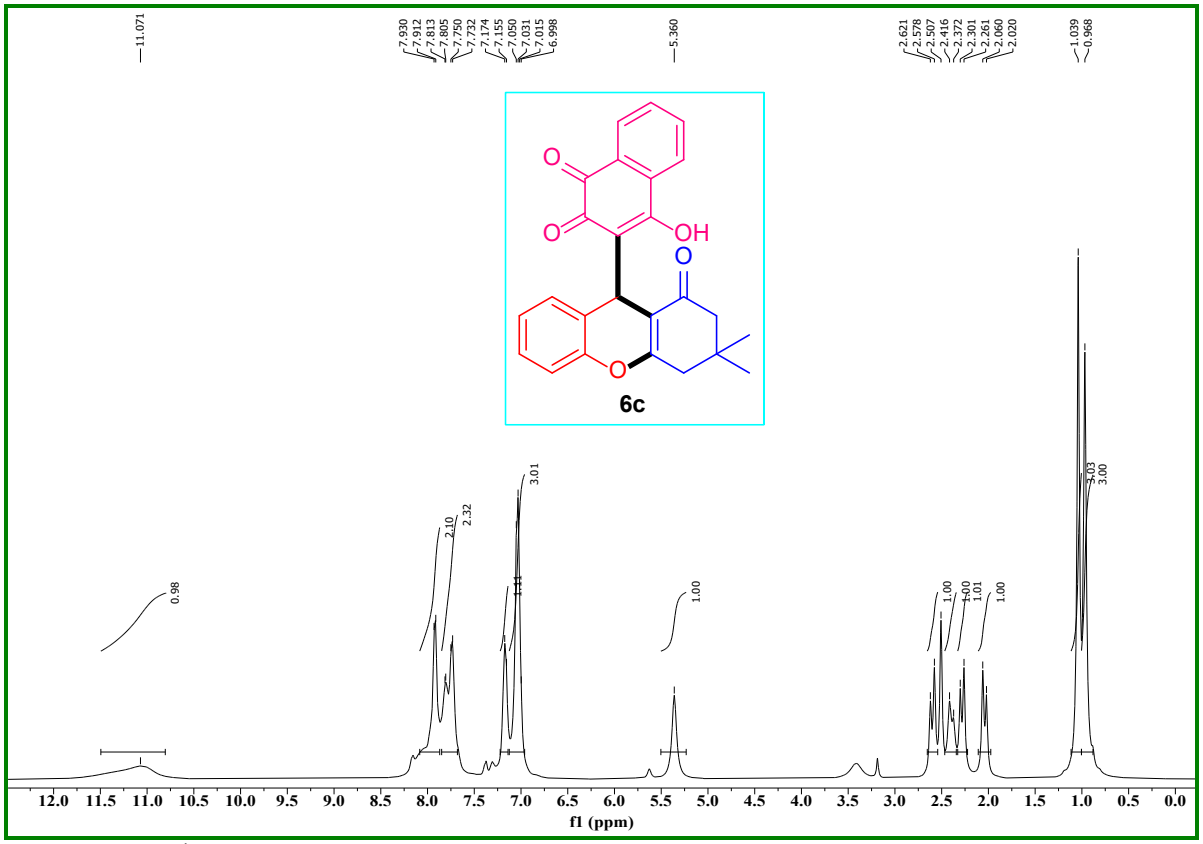


Figure S60: ^{1}H NMR spectrum of 3-(3,3-dimethyl-1-oxo-2,3,4,9-tetrahydro-1*H*-xanthen-9-yl)-4-hydroxynaphthalene-1,2-dione, **6c**.

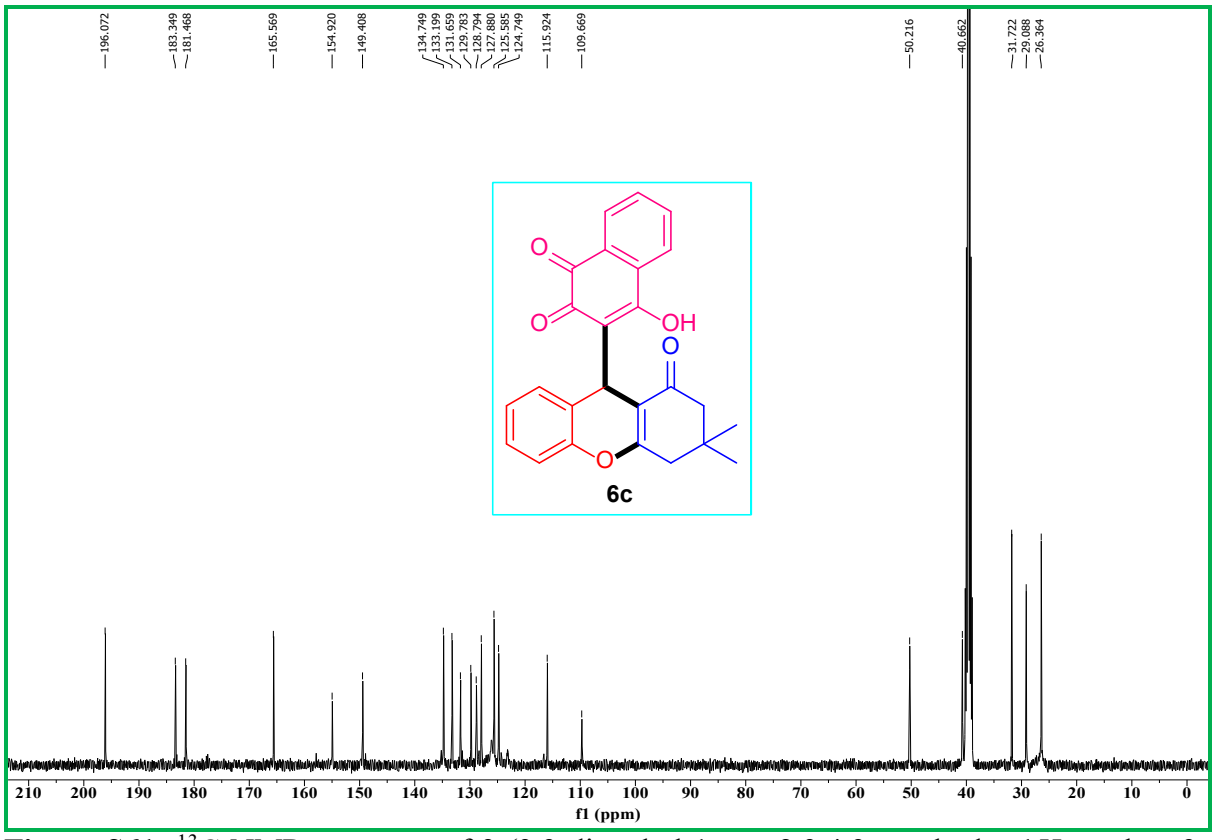


Figure S61: ^{13}C NMR spectrum of 3-(3,3-dimethyl-1-oxo-2,3,4,9-tetrahydro-1*H*-xanthen-9-yl)-4-hydroxynaphthalene-1,2-dione, **6c**.

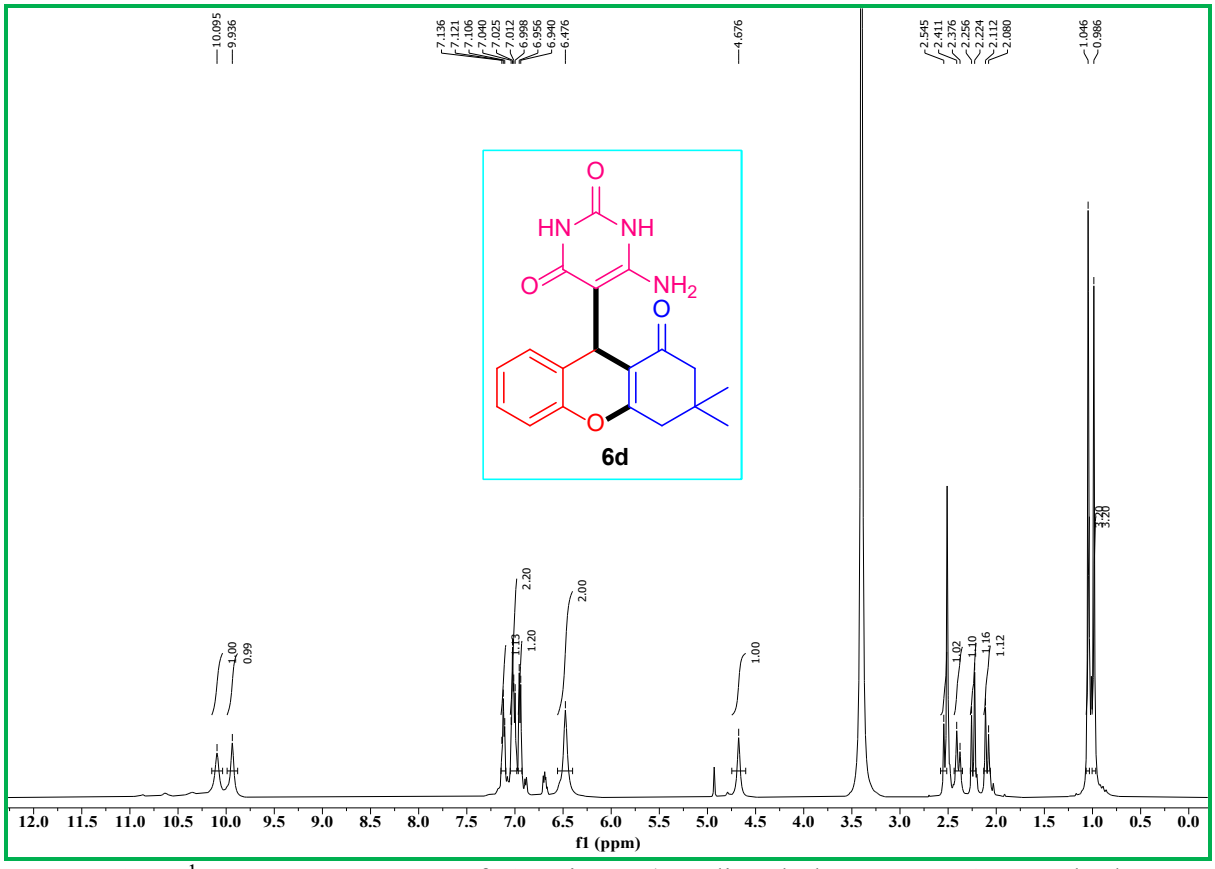


Figure S62: ^{1}H NMR spectrum of 6-amino-5-(3,3-dimethyl-1-oxo-2,3,4,9-tetrahydro-1*H*-xanthen-9-yl)pyrimidine-2,4(1*H*,3*H*)-dione, **6d**.

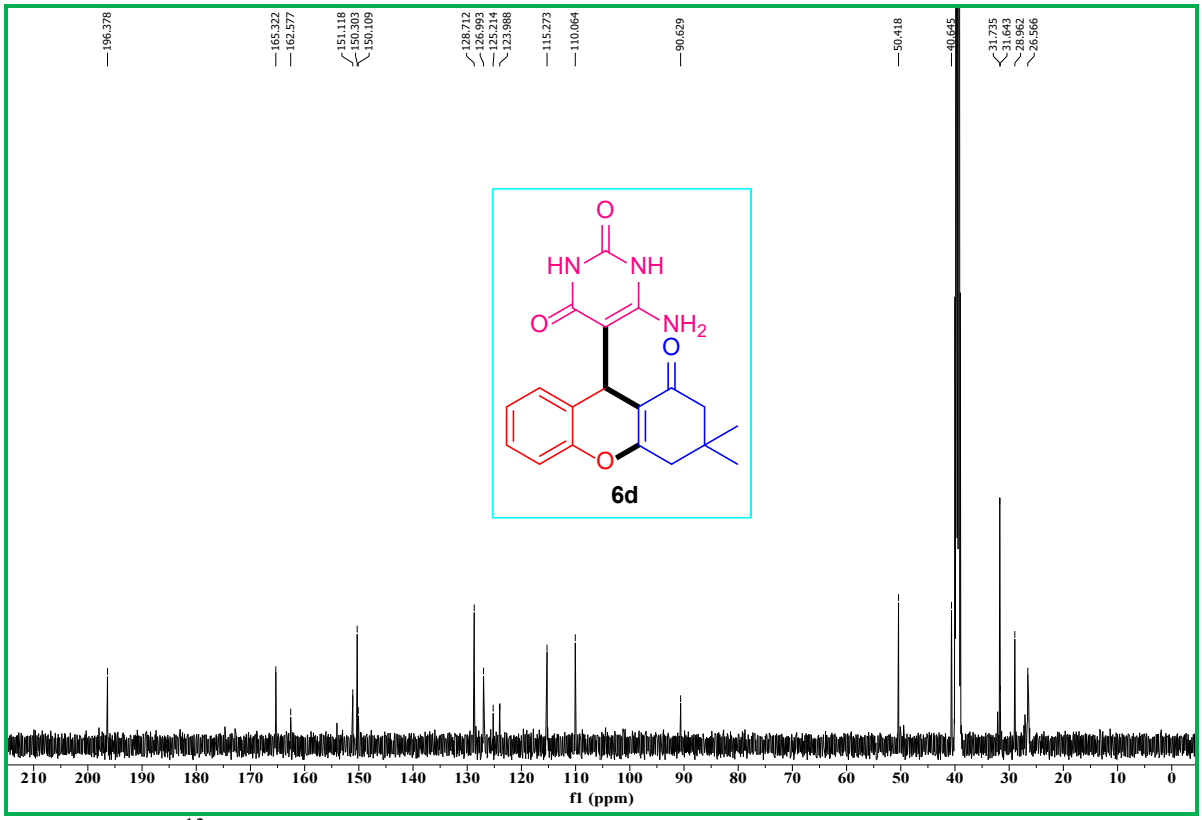


Figure S63: ^{13}C NMR spectrum of 6-amino-5-(3,3-dimethyl-1-oxo-2,3,4,9-tetrahydro-1*H*-xanthen-9-yl)pyrimidine-2,4(1*H*,3*H*)-dione, **6d**.

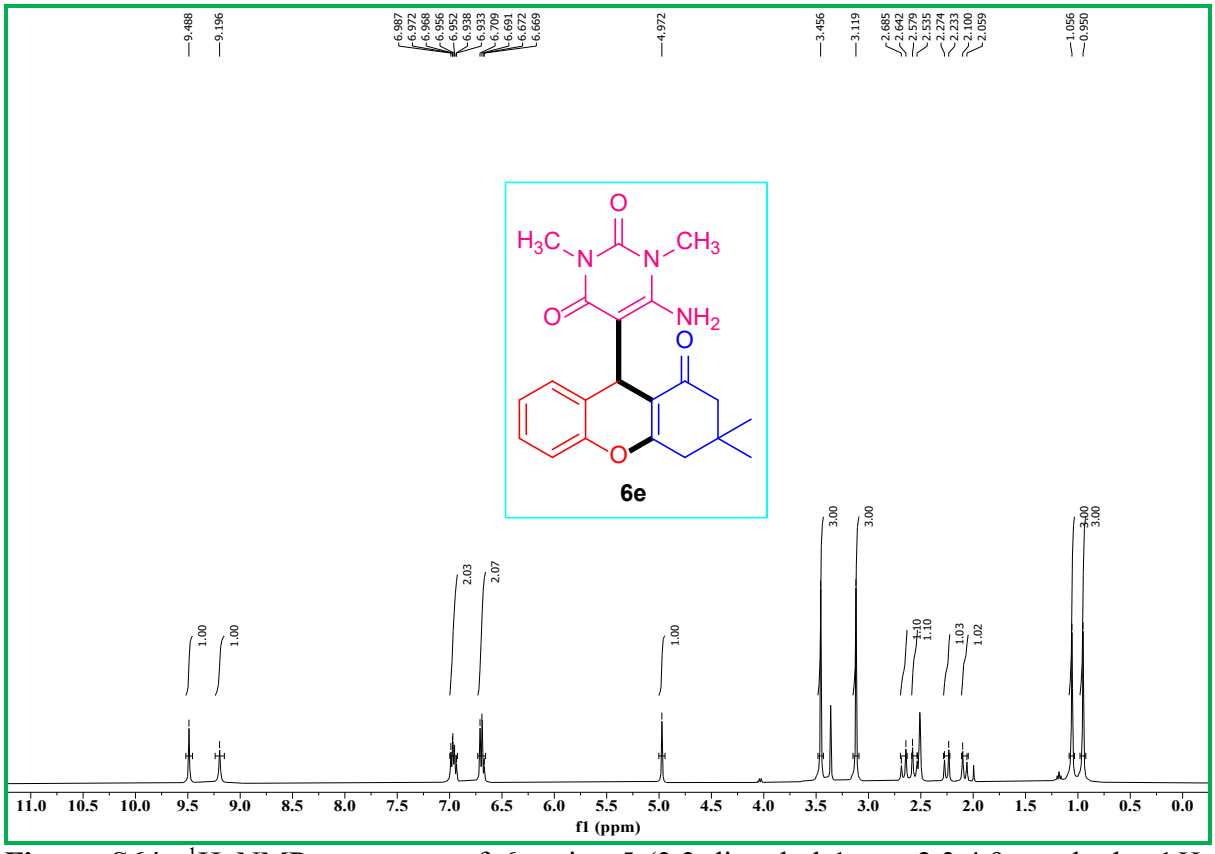


Figure S64: ^{1}H NMR spectrum of 6-amino-5-(3,3-dimethyl-1-oxo-2,3,4,9-tetrahydro-1*H*-xanthen-9-yl)-1,3-dimethylpyrimidine-2,4(1*H*,3*H*)-dione, **6e**.

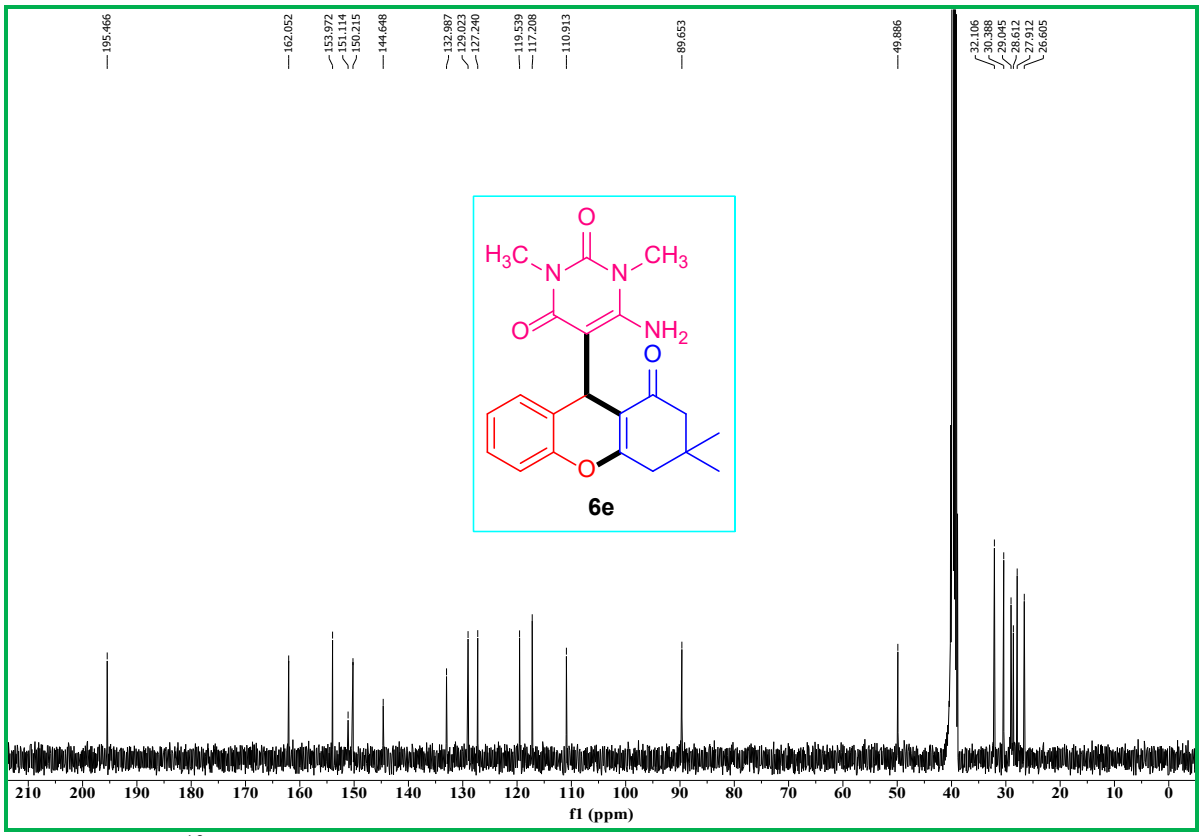


Figure S65: ^{13}C NMR spectrum of 6-amino-5-(3,3-dimethyl-1-oxo-2,3,4,9-tetrahydro-1*H*-xanthen-9-yl)-1,3-dimethylpyrimidine-2,4(1*H*,3*H*)-dione, **6e**.

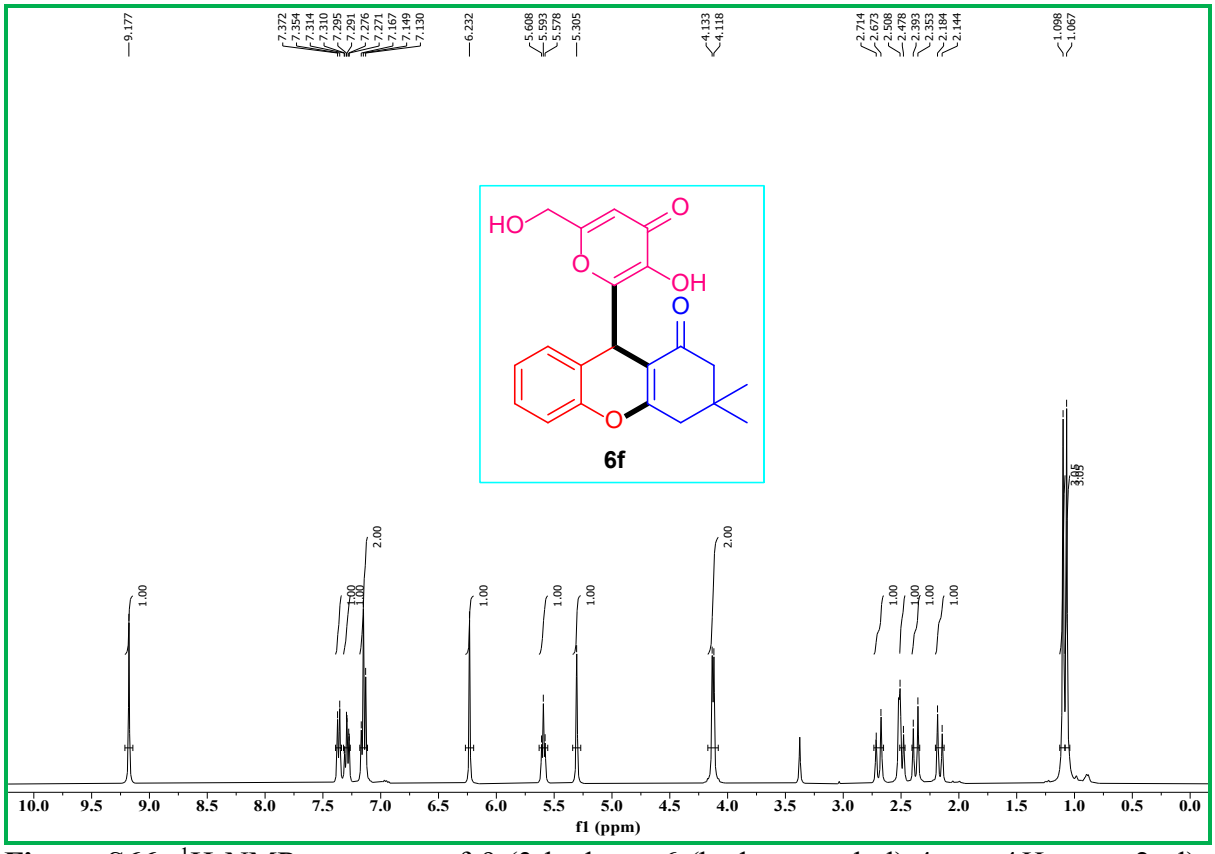


Figure S66: ^{1}H NMR spectrum of 9-(3-hydroxy-6-(hydroxymethyl)-4-oxo-4*H*-pyran-2-yl)-3,3-dimethyl-2,3,4,9-tetrahydro-1*H*-xanthen-1-one, **6f**.

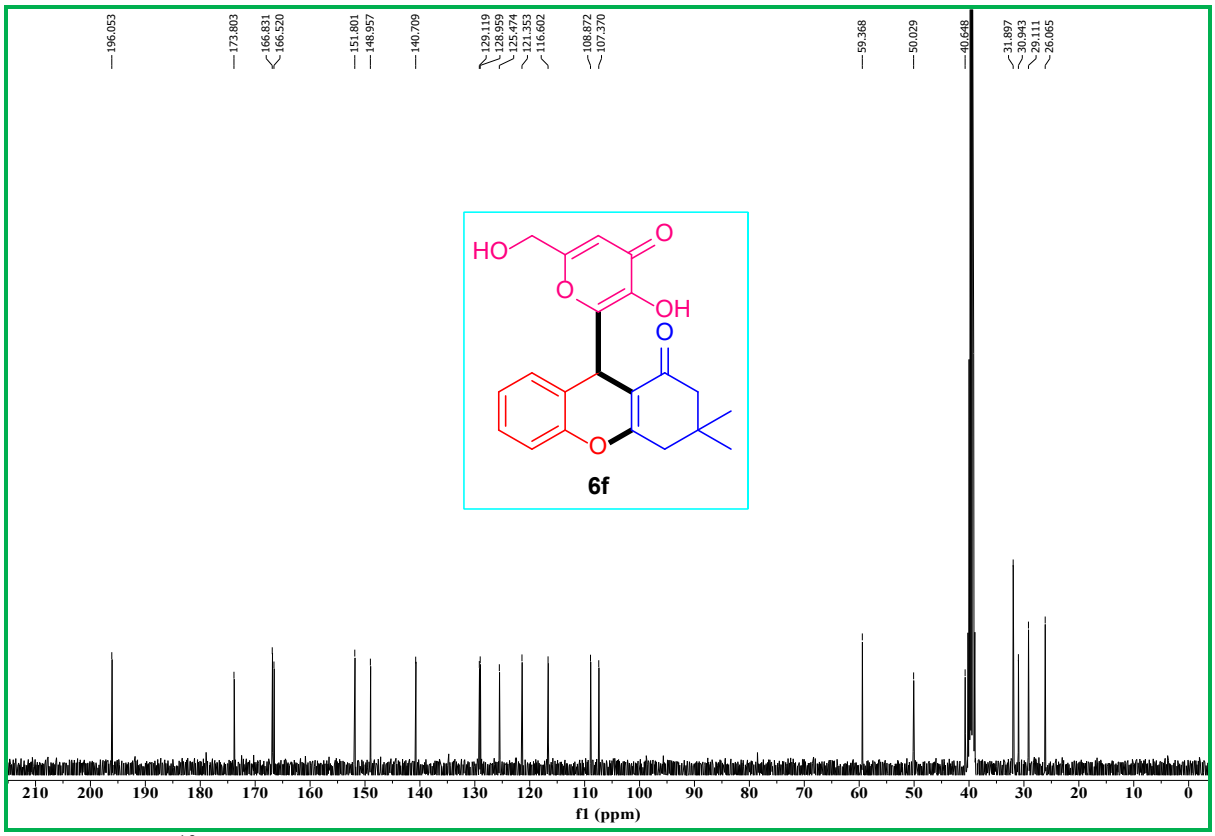


Figure S67: ^{13}C NMR spectrum of 9-(3-hydroxy-6-(hydroxymethyl)-4-oxo-4*H*-pyran-2-yl)-3,3-dimethyl-2,3,4,9-tetrahydro-1*H*-xanthen-1-one, **6f**.

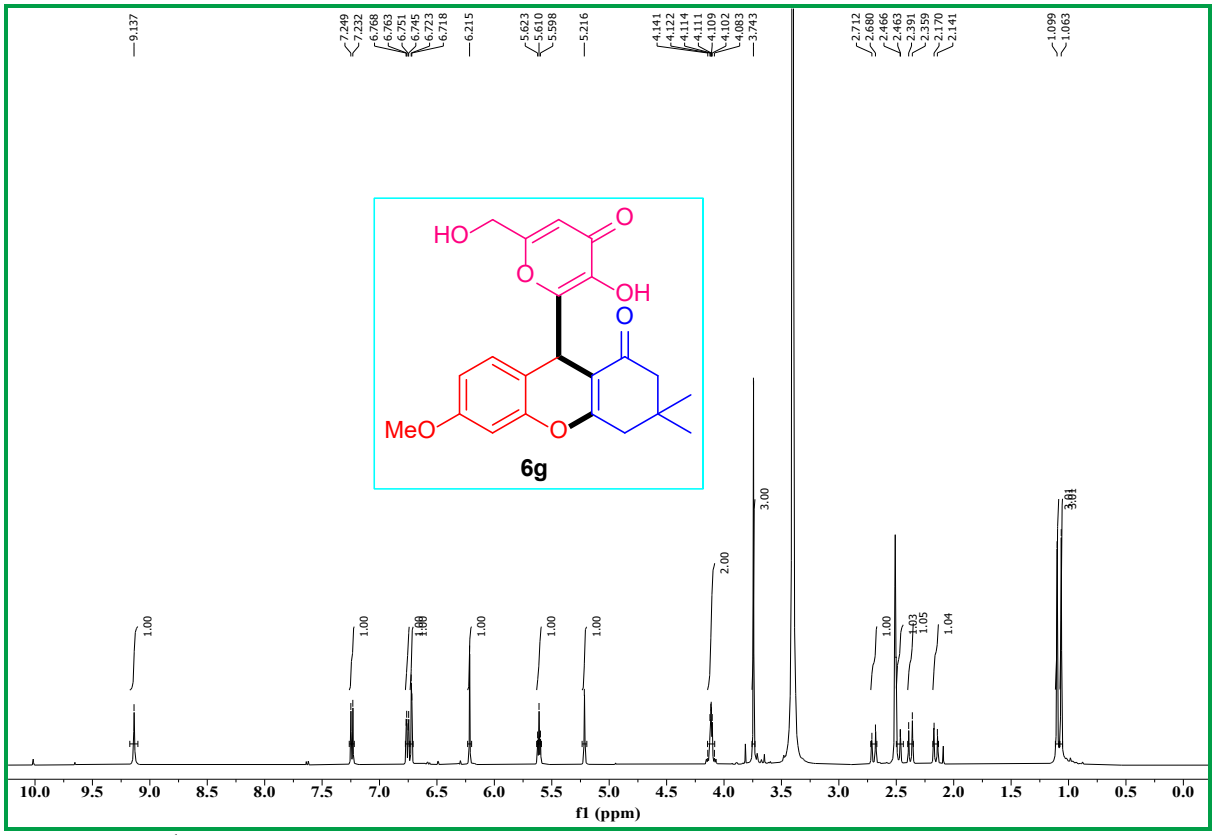


Figure S68: ^{1}H NMR spectrum of 9-(3-hydroxy-6-(hydroxymethyl)-4-oxo-4*H*-pyran-2-yl)-6-methoxy-3,3-dimethyl-2,3,4,9-tetrahydro-1*H*-xanthen-1-one, **6g**.

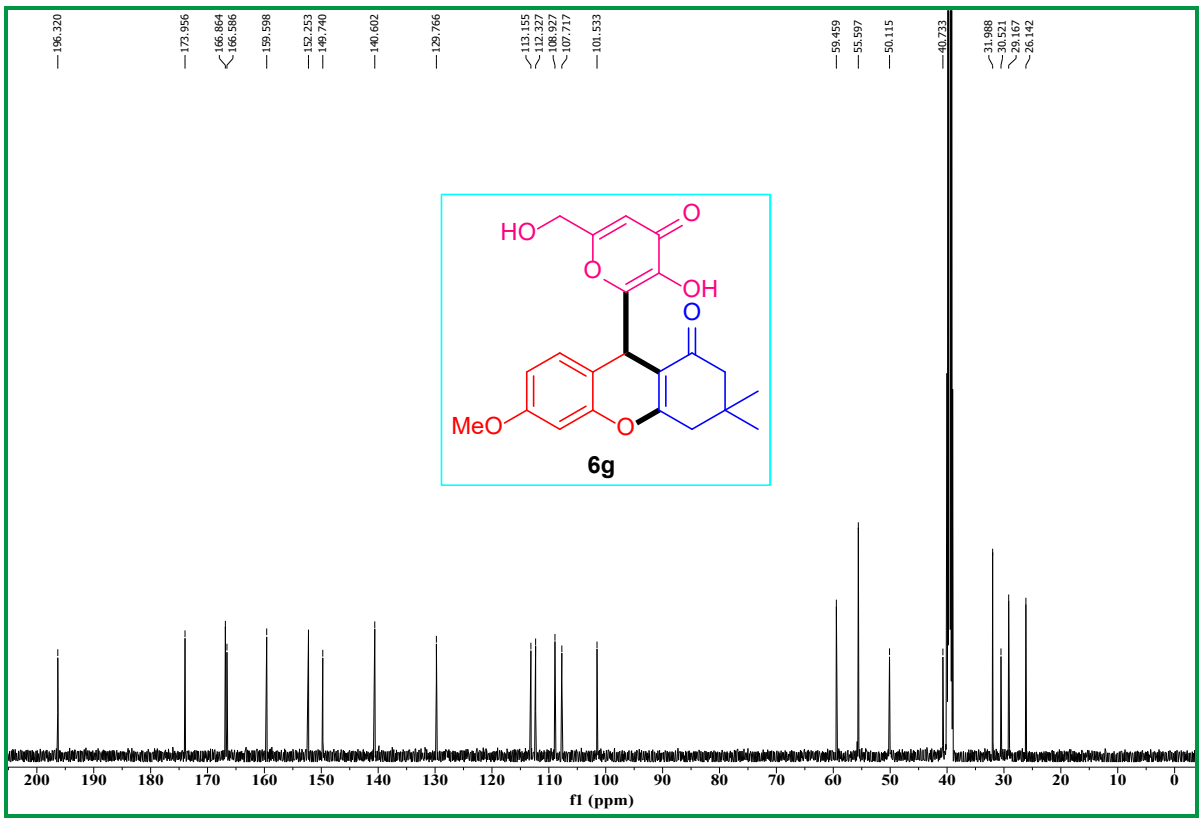


Figure S69: ^{13}C NMR spectrum of 9-(3-hydroxy-6-(hydroxymethyl)-4-oxo-4*H*-pyran-2-yl)-6-methoxy-3,3-dimethyl-2,3,4,9-tetrahydro-1*H*-xanthen-1-one, **6g**.

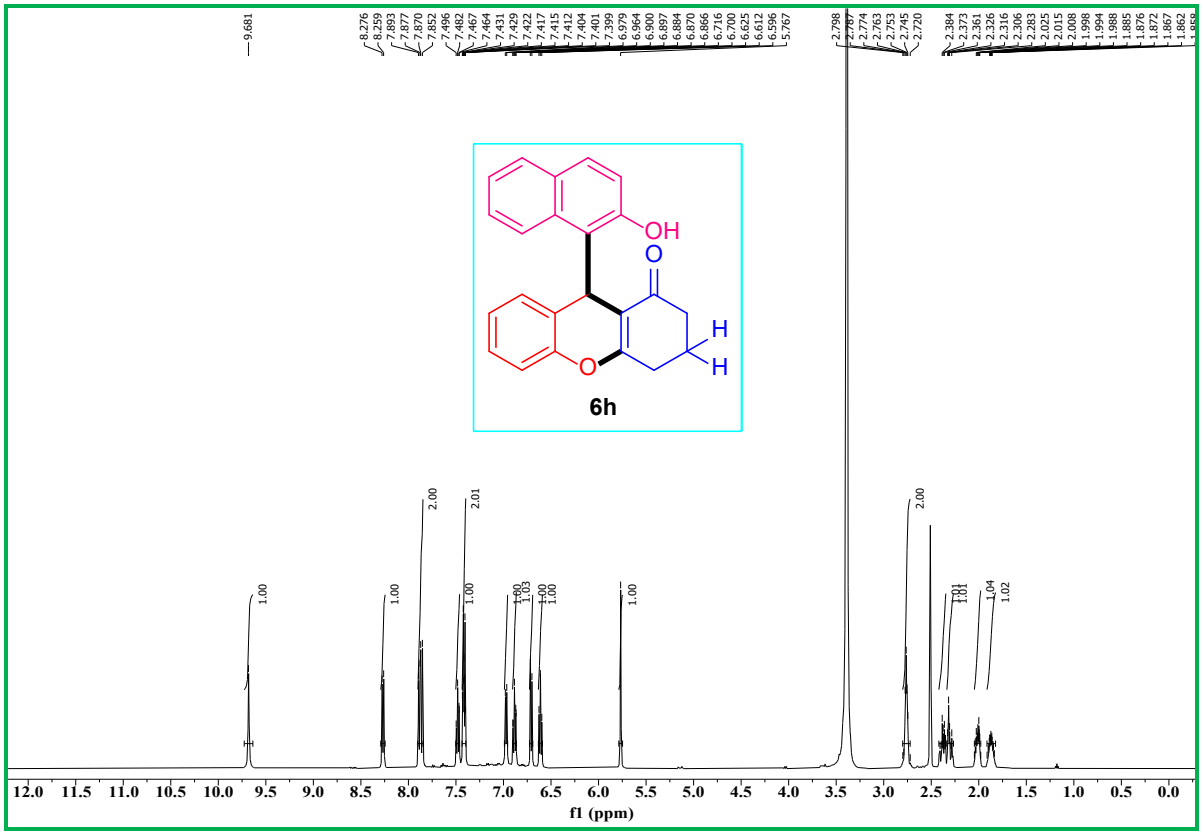


Figure S70: ^{1}H NMR spectrum of 9-(2-hydroxynaphthalen-1-yl)-2,3,4,9-tetrahydro-1*H*-xanthen-1-one, **6h**.

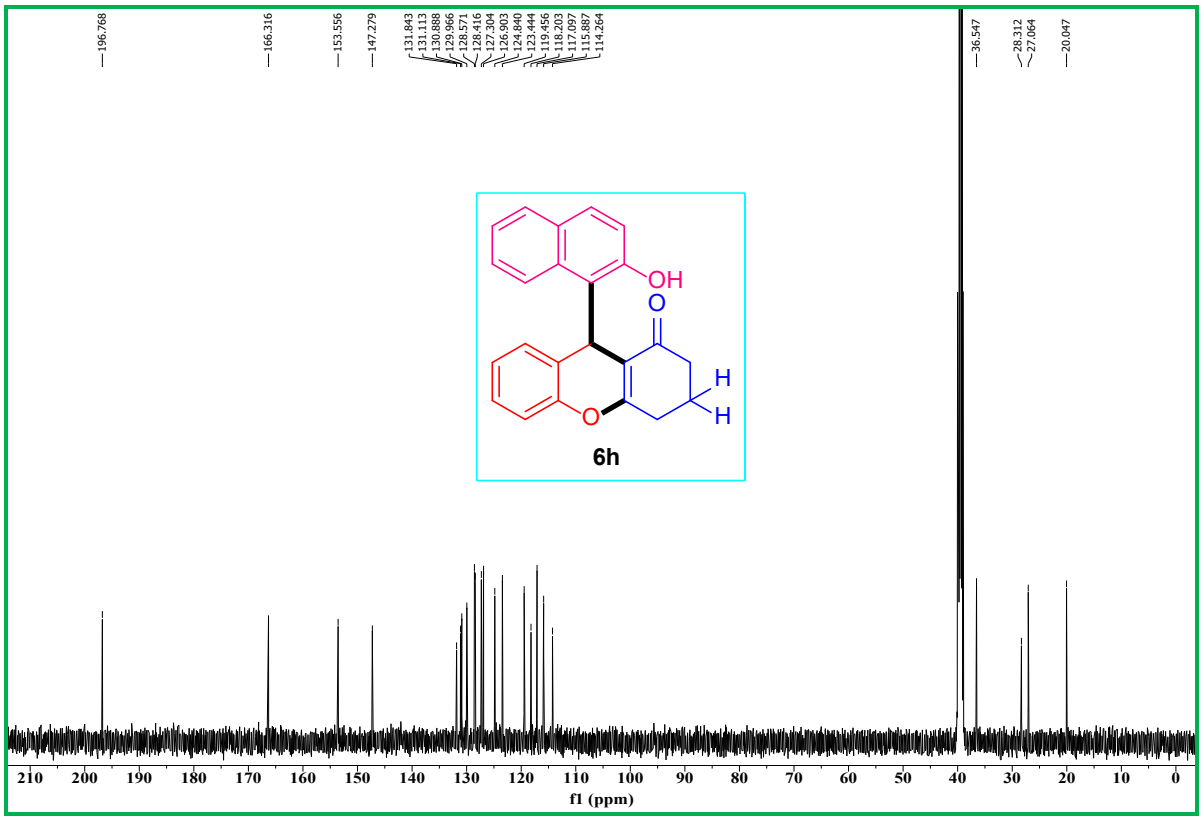


Figure S71: ^{13}C NMR spectrum of 9-(2-hydroxynaphthalen-1-yl)-2,3,4,9-tetrahydro-1*H*-xanthen-1-one, **6h**.

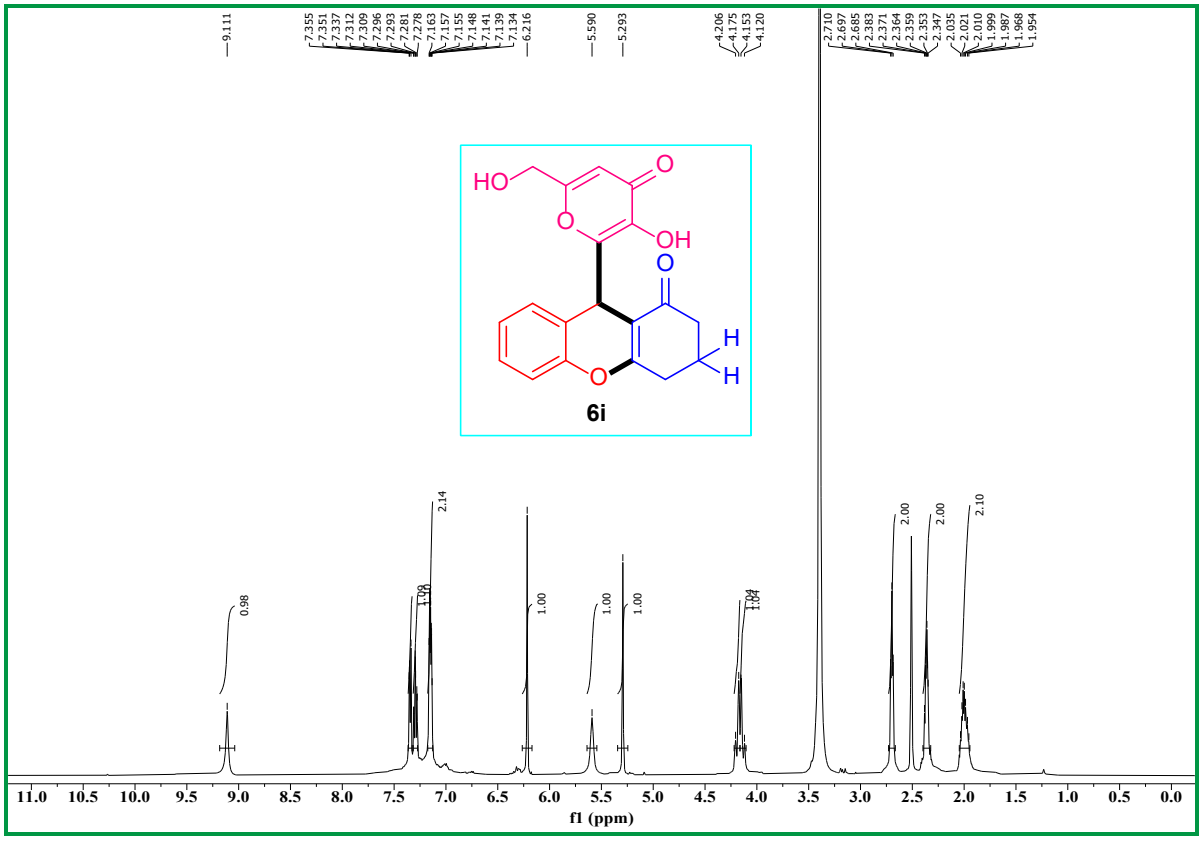


Figure S72: ^{1}H NMR spectrum of 9-(3-hydroxy-6-(hydroxymethyl)-4-oxo-4*H*-pyran-2-yl)-2,3,4,9-tetrahydro-1*H*-xanthen-1-one, **6i**.

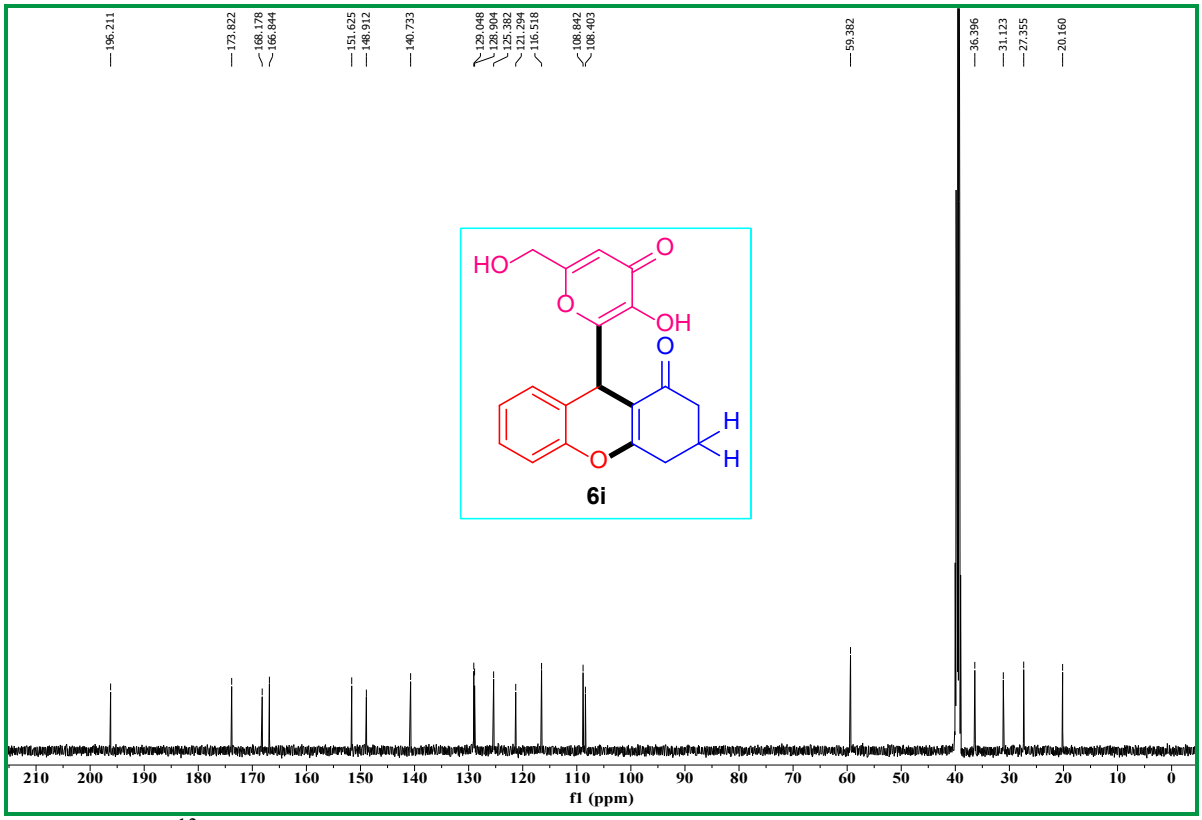


Figure S73: ^{13}C NMR spectrum of 9-(3-hydroxy-6-(hydroxymethyl)-4-oxo-4*H*-pyran-2-yl)-2,3,4,9-tetrahydro-1*H*-xanthen-1-one, **6i**.

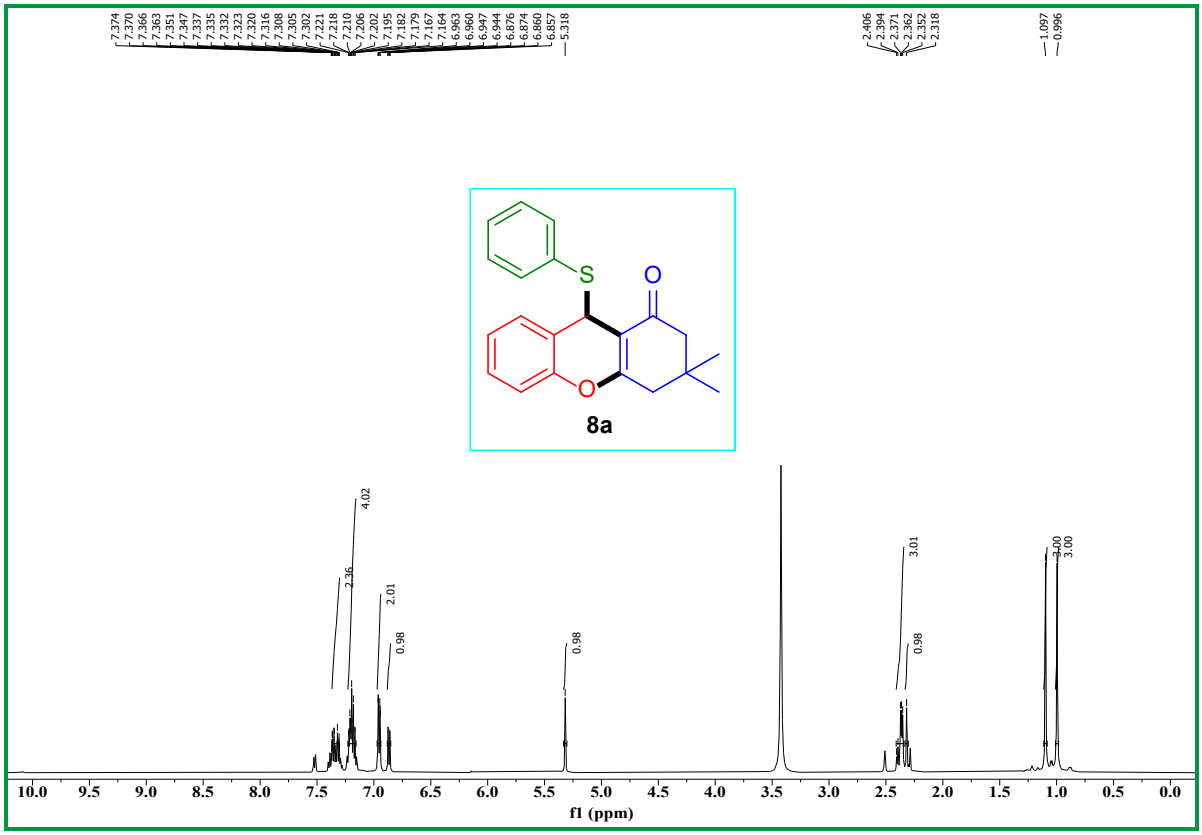


Figure S74: ^{1}H NMR spectrum of 3,3-dimethyl-9-(phenylthio)-2,3,4,9-tetrahydro-1*H*-xanthen-1-one, **8a**.

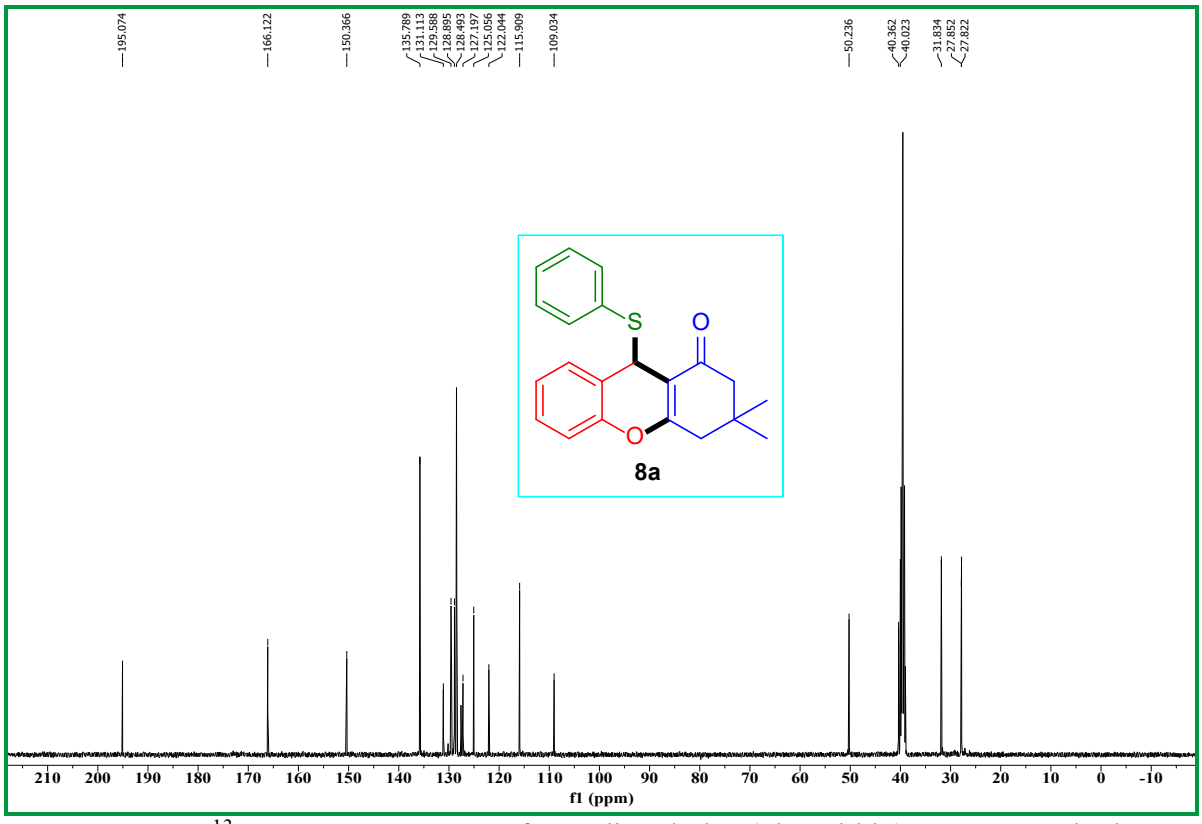


Figure S75: ^{13}C NMR spectrum of 3,3-dimethyl-9-(phenylthio)-2,3,4,9-tetrahydro-1*H*-xanthen-1-one, **8a**.

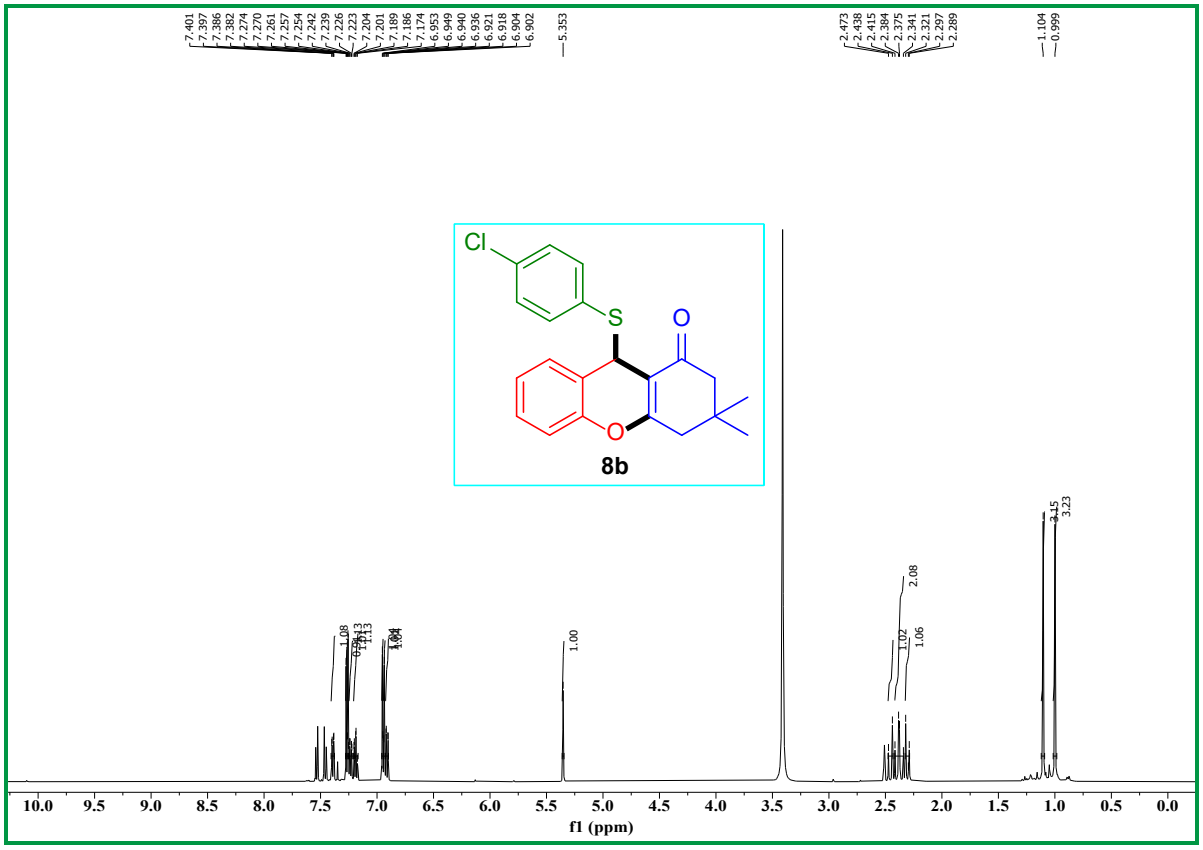


Figure S76: [1]H NMR spectrum of 9-((4-chlorophenyl)thio)-3,3-dimethyl-2,3,4,9-tetrahydro-1*H*-xanthen-1-one, **8b**.

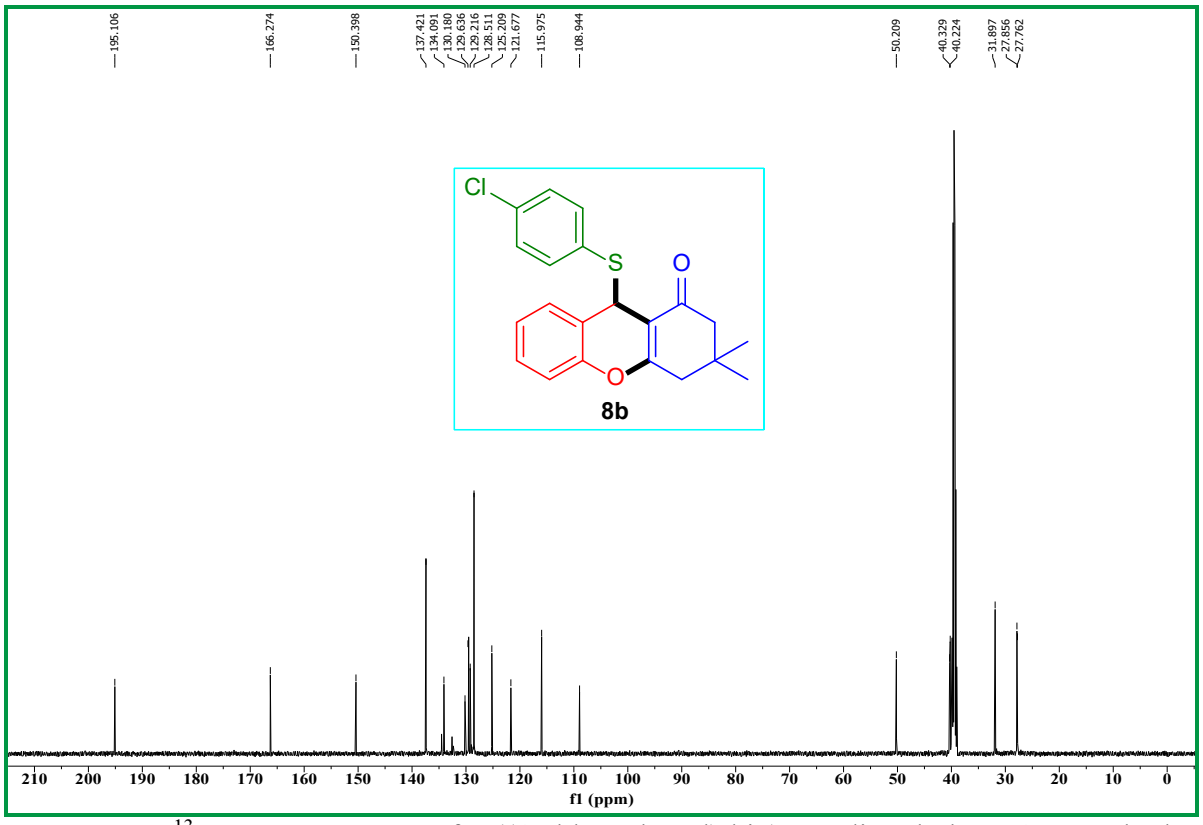


Figure S77: [13]C NMR spectrum of 9-((4-chlorophenyl)thio)-3,3-dimethyl-2,3,4,9-tetrahydro-1*H*-xanthen-1-one, **8b**.

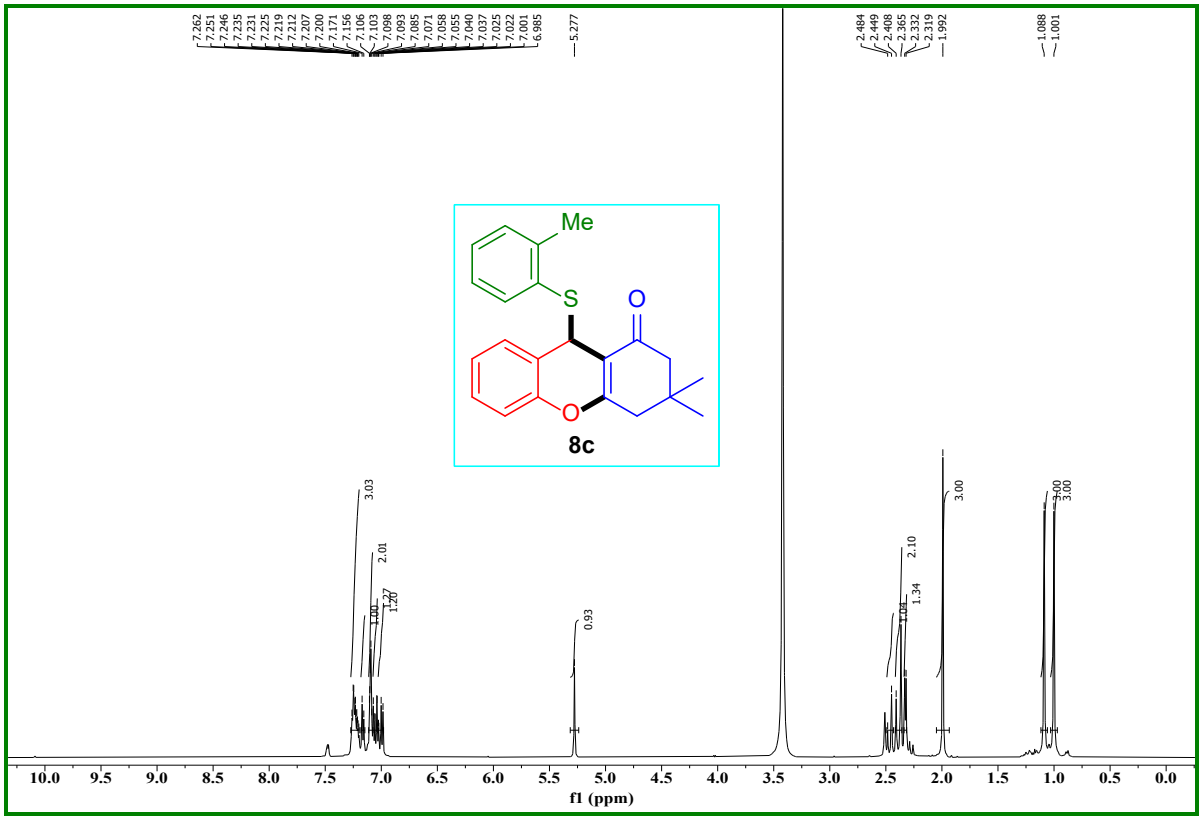


Figure S78: ^{1}H NMR spectrum of 3,3-dimethyl-9-(o-tolylthio)-2,3,4,9-tetrahydro-1*H*-xanthen-1-one, **8c**.

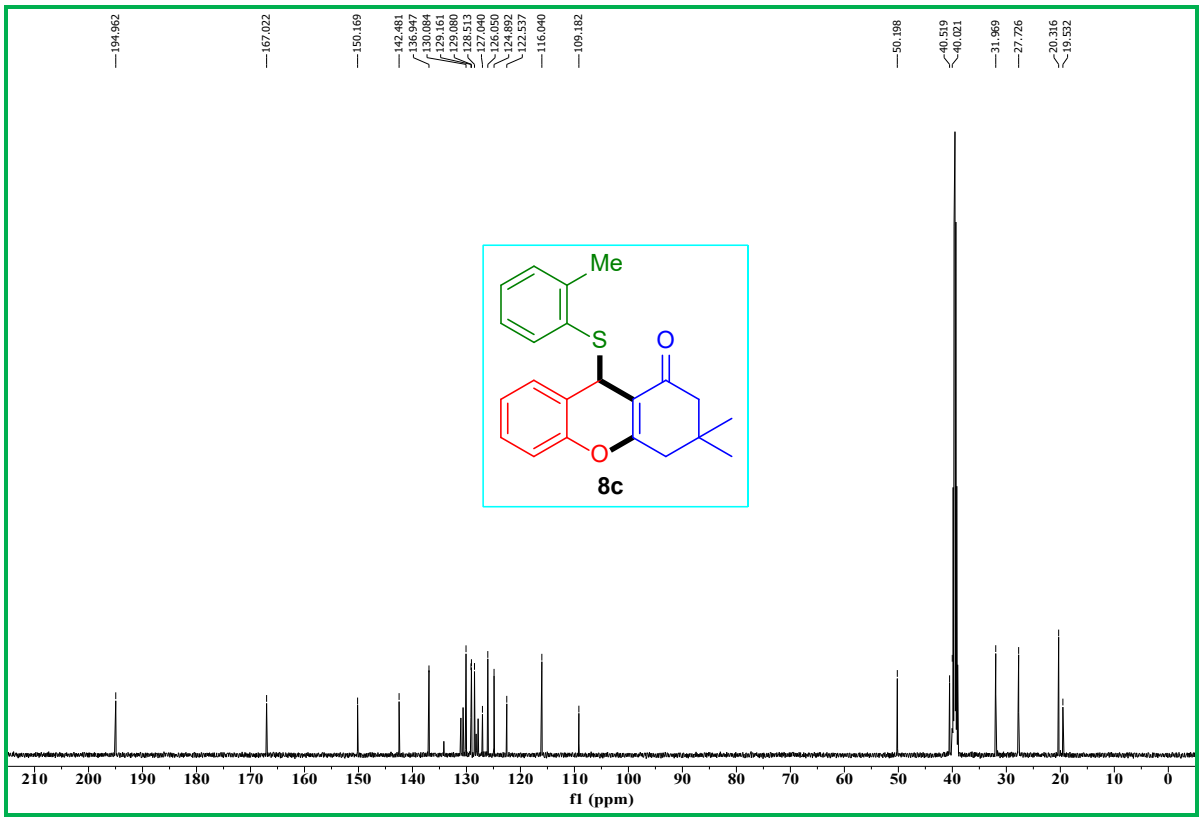


Figure S79: ^{13}C NMR spectrum of 3,3-dimethyl-9-(o-tolylthio)-2,3,4,9-tetrahydro-1*H*-xanthen-1-one, **8c**.

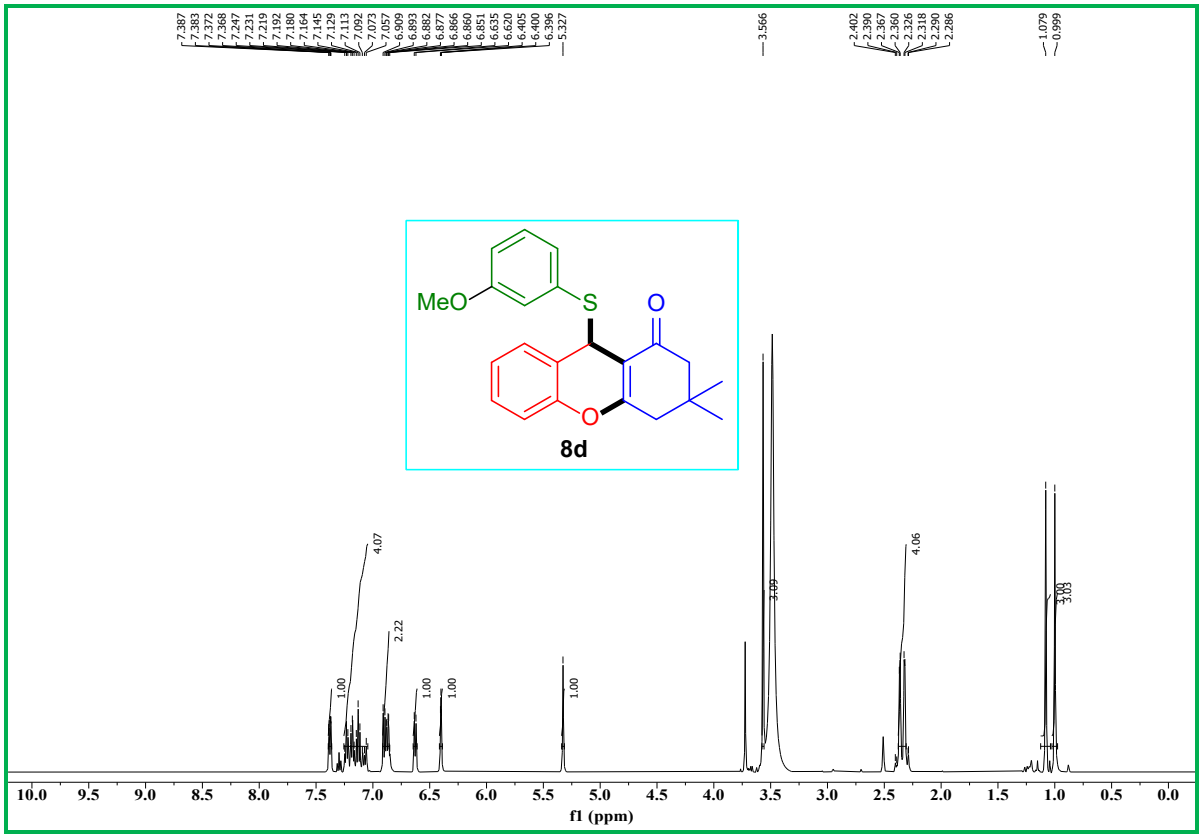


Figure S80: ^{1}H NMR spectrum of 9-((3-methoxyphenyl)thio)-3,3-dimethyl-2,3,4,9-tetrahydro-1*H*-xanthen-1-one, **8d**.

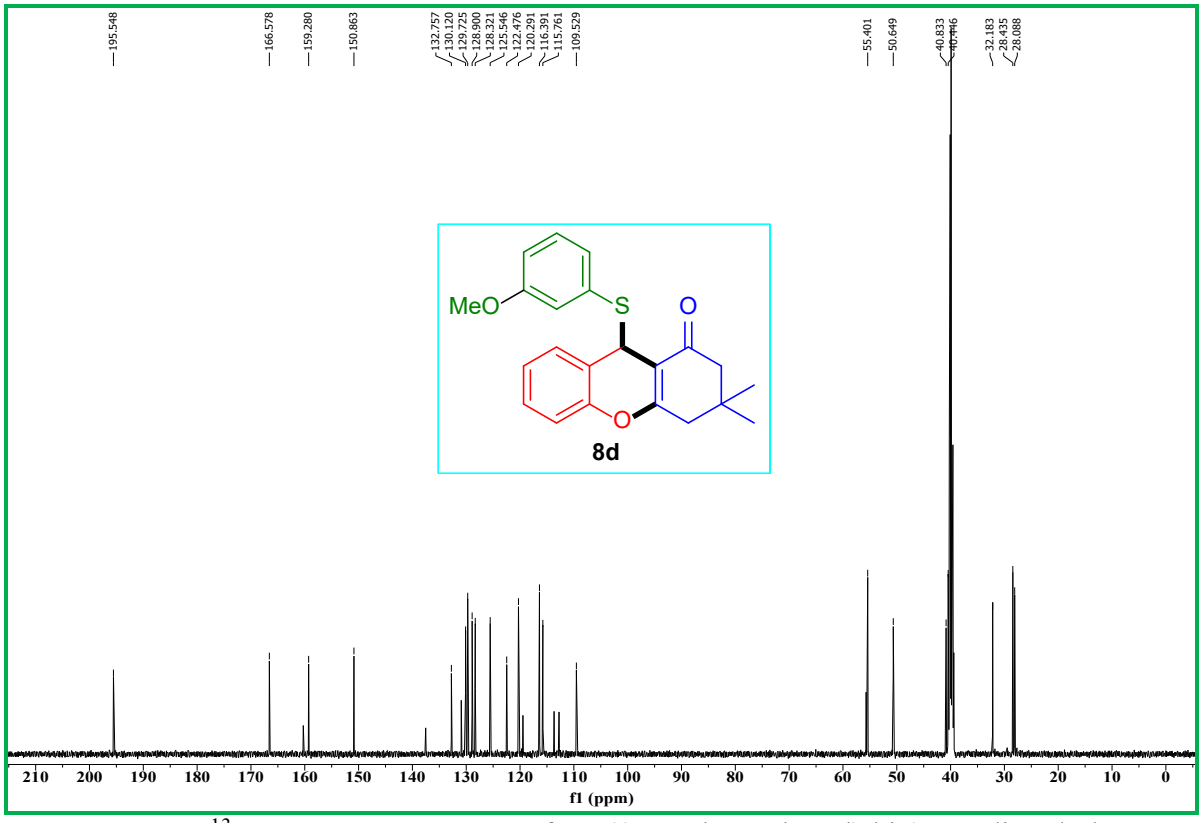


Figure S81: ^{13}C NMR spectrum of 9-((3-methoxyphenyl)thio)-3,3-dimethyl-2,3,4,9-tetrahydro-1*H*-xanthen-1-one, **8d**.

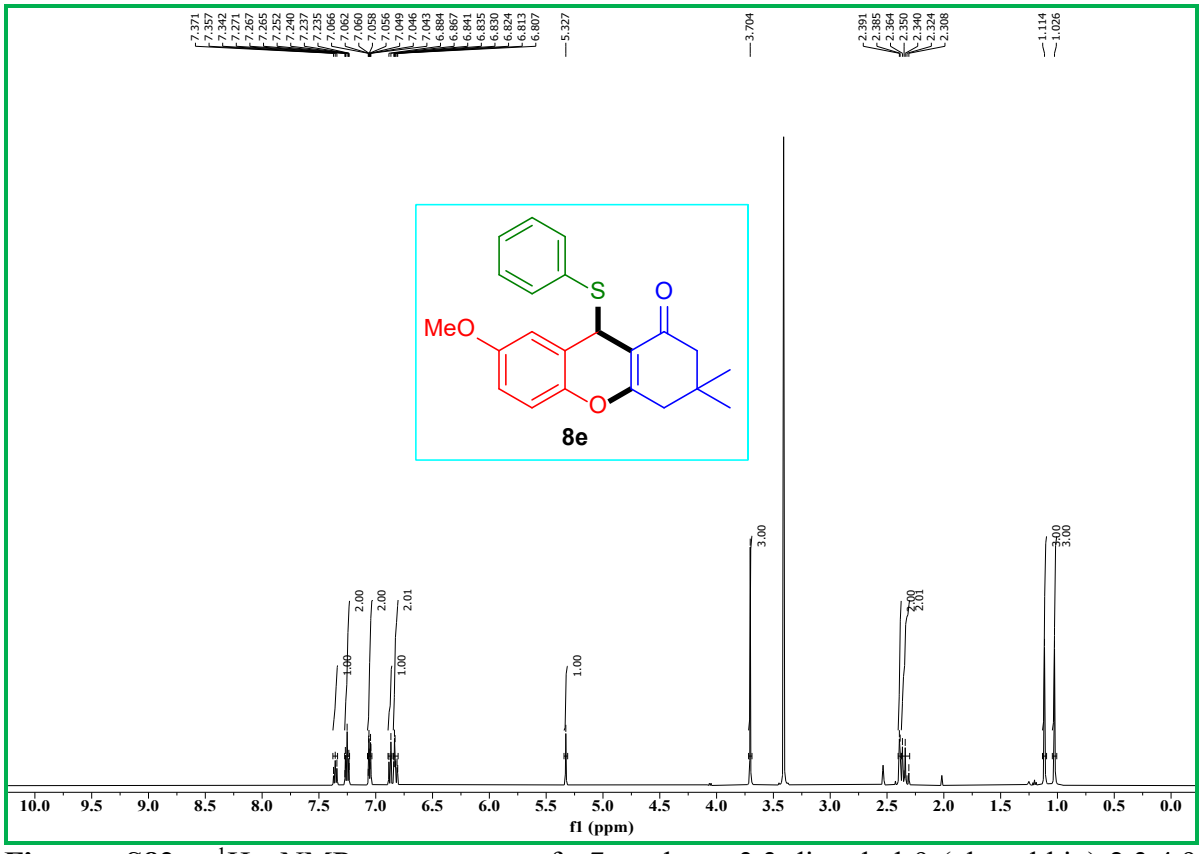


Figure S82: ^{1}H NMR spectrum of 7-methoxy-3,3-dimethyl-9-(phenylthio)-2,3,4,9-tetrahydro-1*H*-xanthen-1-one, **8e**.

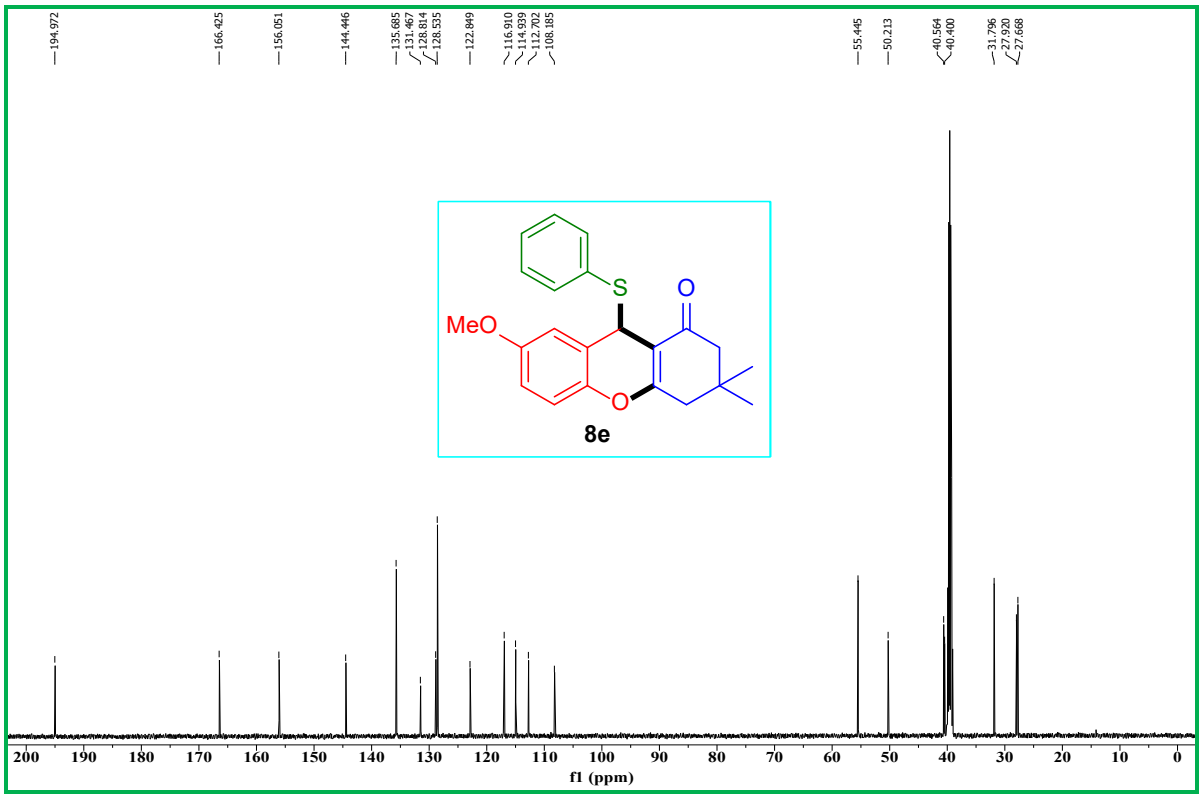


Figure S83: ^{13}C NMR spectrum of 7-methoxy-3,3-dimethyl-9-(phenylthio)-2,3,4,9-tetrahydro-1*H*-xanthen-1-one, **8e**.

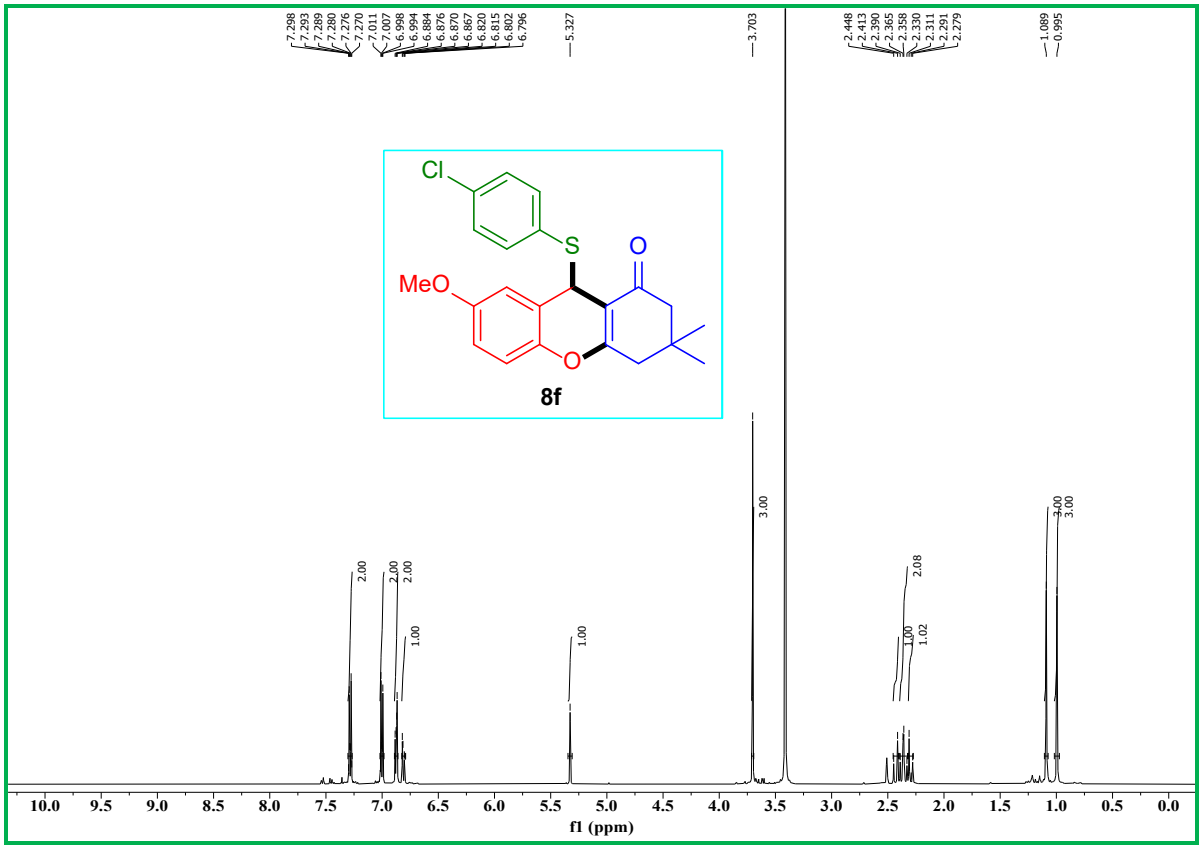


Figure S84: ^{1}H NMR spectrum of 9-((4-chlorophenyl)thio)-7-methoxy-3,3-dimethyl-2,3,4,9-tetrahydro-1*H*-xanthen-1-one, **8f**.

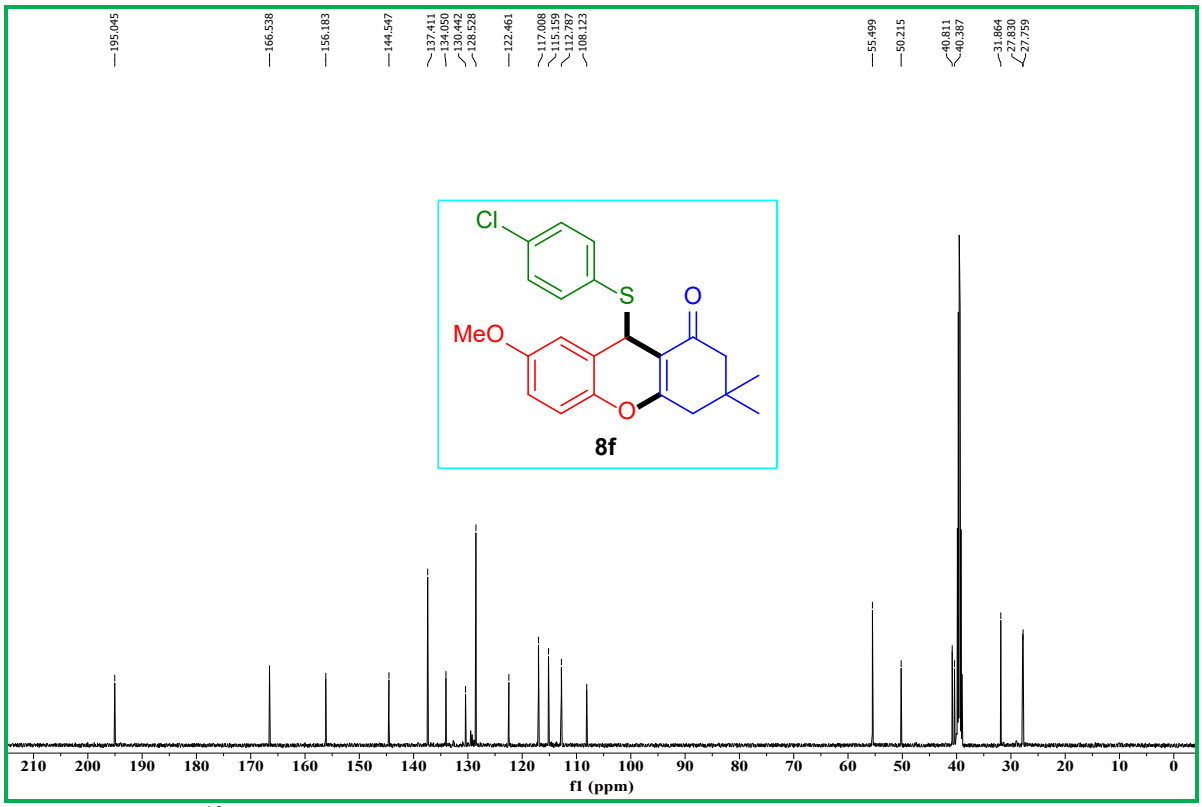


Figure S85: ^{13}C NMR spectrum of 9-((4-chlorophenyl)thio)-7-methoxy-3,3-dimethyl-2,3,4,9-tetrahydro-1*H*-xanthen-1-one, **8f**.

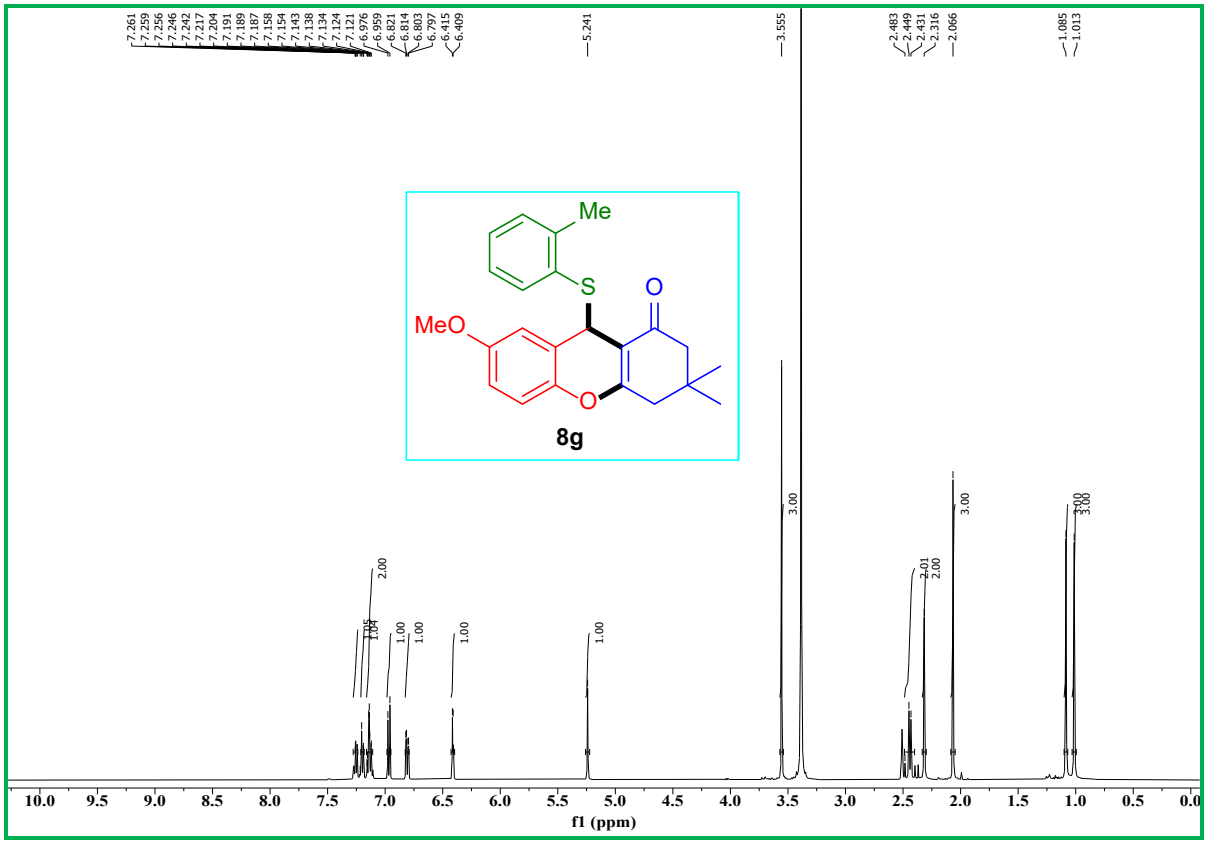


Figure S86: ^{1}H NMR spectrum of 7-methoxy-3,3-dimethyl-9-(o-tolylthio)-2,3,4,9-tetrahydro-1*H*-xanthen-1-one, **8g**.

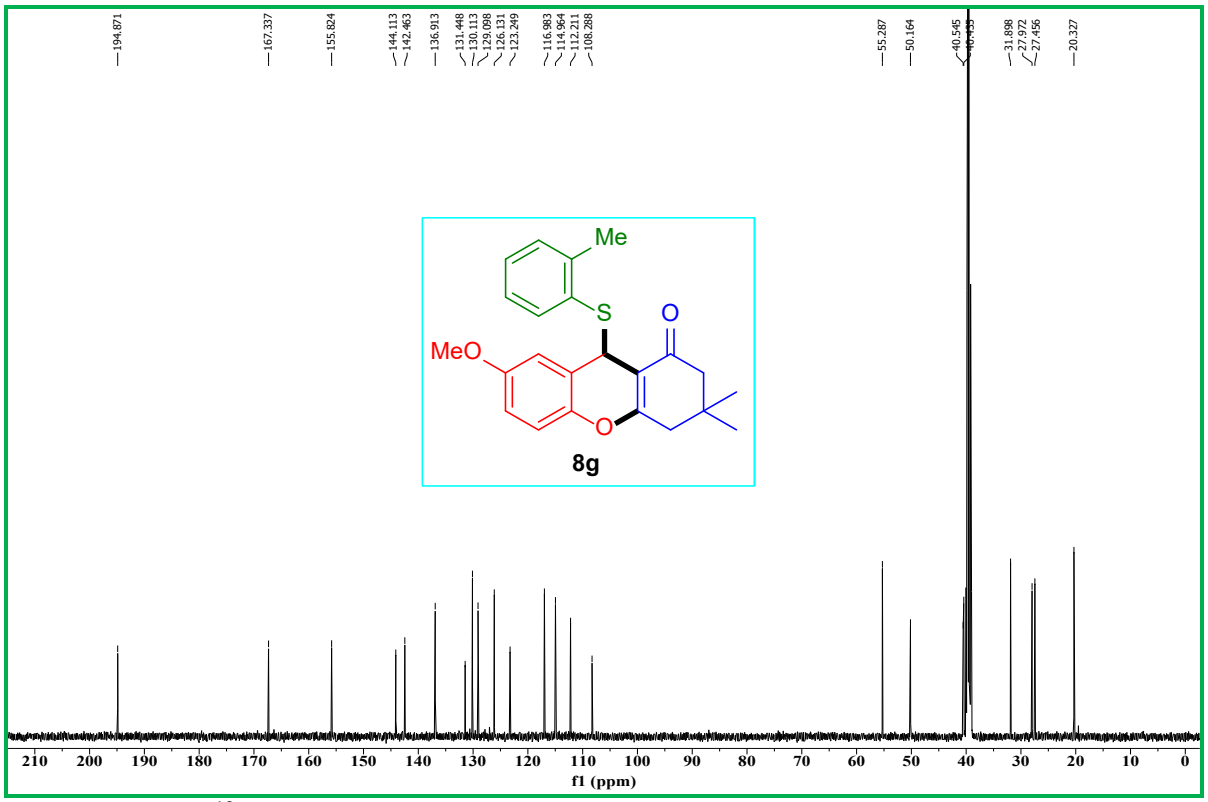


Figure S87: ^{13}C NMR spectrum of 7-methoxy-3,3-dimethyl-9-(o-tolylthio)-2,3,4,9-tetrahydro-1*H*-xanthen-1-one, **8g**.

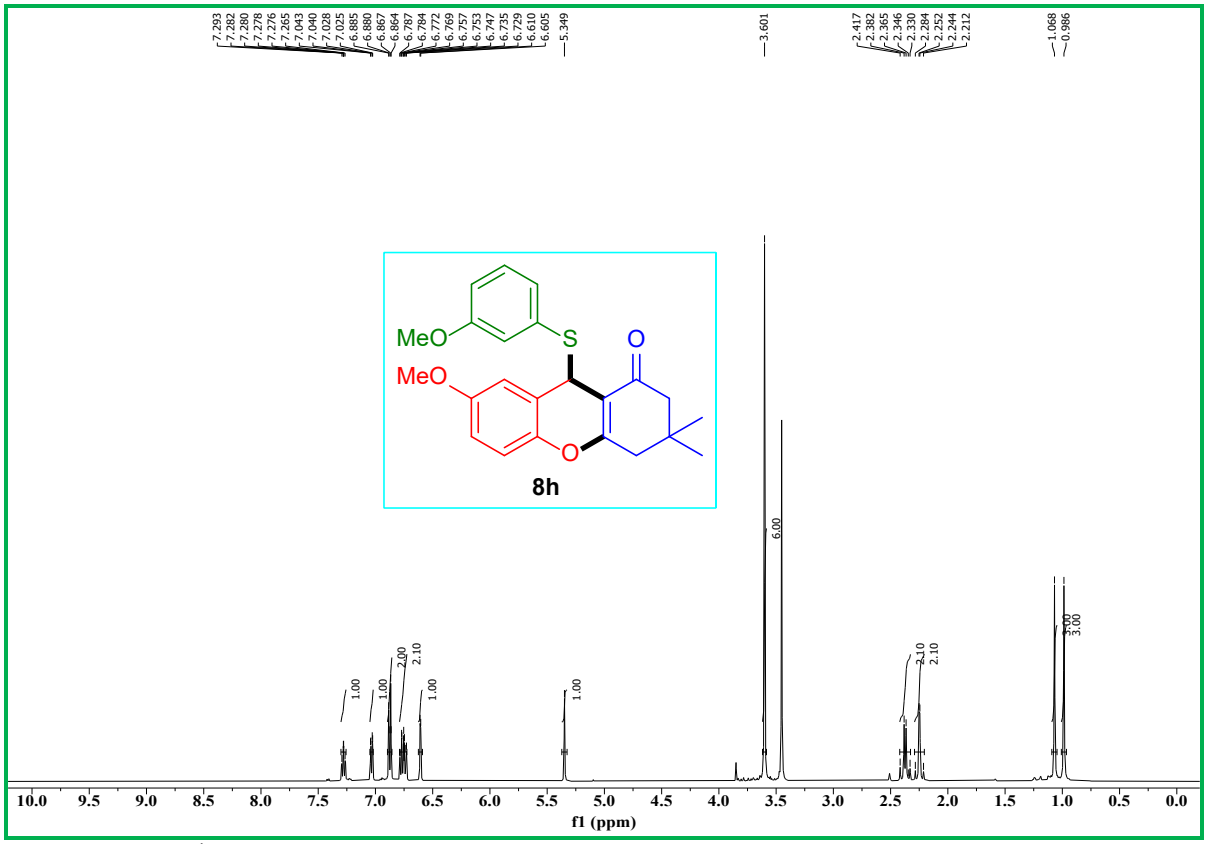


Figure S88: ^{1}H NMR spectrum of 7-methoxy-9-((3-methoxyphenyl)thio)-3,3-dimethyl-2,3,4,9-tetrahydro-1*H*-xanthen-1-one, **8h**.

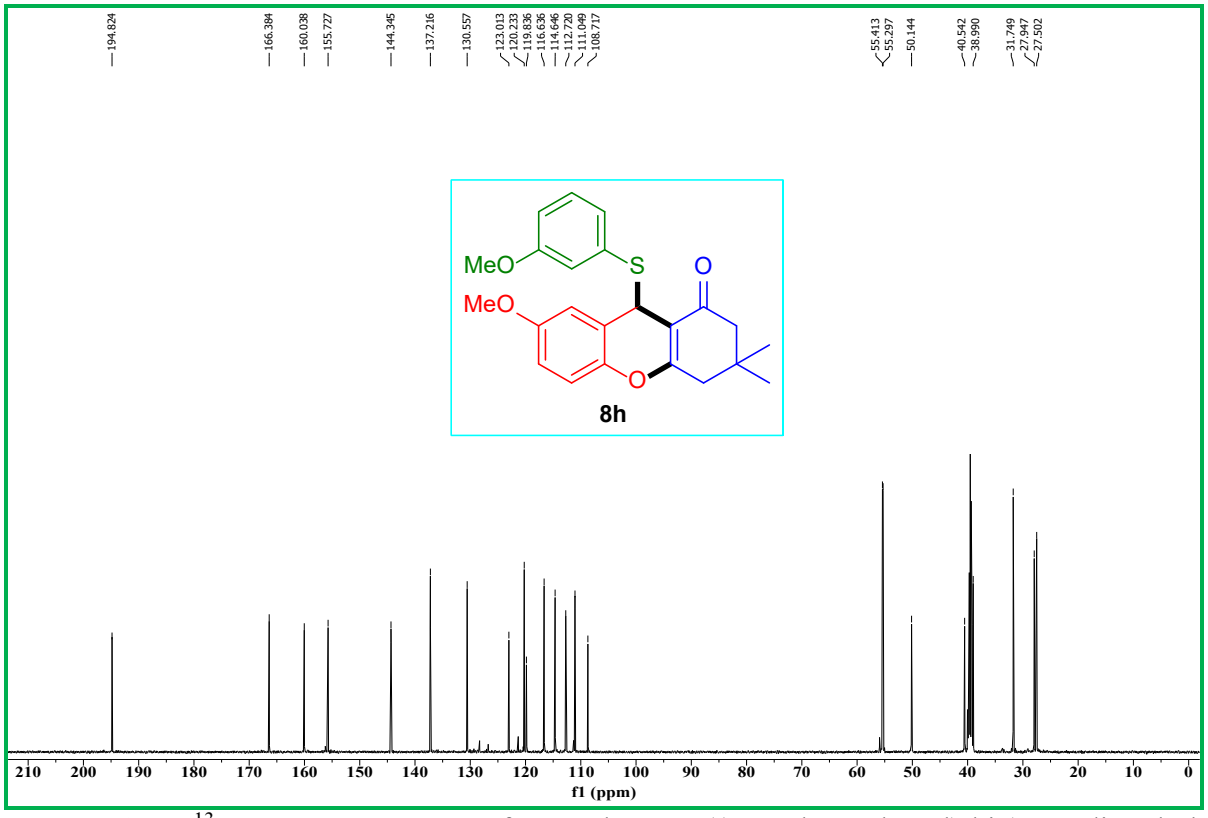


Figure S89: ^{13}C NMR spectrum of 7-methoxy-9-((3-methoxyphenyl)thio)-3,3-dimethyl-2,3,4,9-tetrahydro-1*H*-xanthen-1-one, **8h**.

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1. Spiliopoulou, N.; Nikitas, N. F.; Kokotos, C. G. *Green Chem.* **2020**, *22*, 3539–3545.
2. Lippert, K. M.; Hof, K.; Gerbig, D.; Ley, D.; Hausmann, H.; Guenther, S.; *Eur. J. Org. Chem.* **2012**, *2012*, 5919–5927.
3. Salem, Z. M.; Saway, J.; Badillo, J. J. *Org. Lett.* **2019**, *21*, 8528–8532.