

Supporting information

Unlocking the Potential of Ketocoumarins: Efficient Photosensitizers for Sustainable Light Driven Hydrogen Evolution

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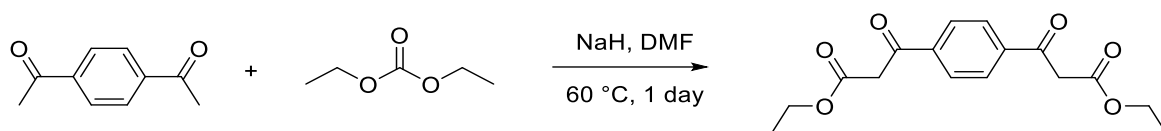
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1. Synthetic procedures

All solvents and chemicals were purchased in commercial grade (Acros, Alfa Aeser, Deutero, Eurisotop, Fisher, Grüssing, Merck, Roth, Sigma Aldrich, TCI and VWR) and unless otherwise stated, used as obtained. The progress of all reactions was monitored by thin-layer chromatography (*Merck* 60 F254). Column chromatography was performed with Macherey-Nagel silica gel 60 (grain size 0.04-0.063 nm). NMR spectra were recorded on a Bruker Avance 300 and a Bruker Avance 400. ^1H and $^{13}\text{C}\{^1\text{H}\}$ spectra were referenced to residual solvent signals (CDCl_3) and. Mass spectrometry was carried out with a Finnigan MAT SSQ710 (EI), Finnigan MAT95XL (ESI) and a Thermo Fisher UHPLC-Orbitrap Q-Extractive plus (APCI).

1.1. Synthesis of diethyl 3,3'-(1,4-phenylene)bis(3-oxopropanoate)

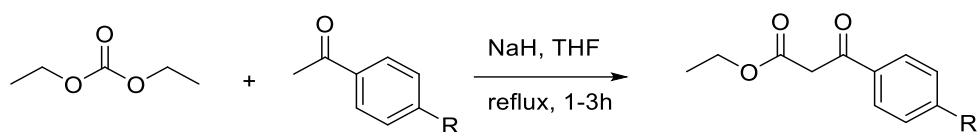


Synthesis was performed following procedure by Patel et al¹: 1,4-diacetylbenzene (1 g, 6.2 mmol) was dissolved in 10 mL of dry DMF and NaH (0.89 g, 37 mmol, 6 eq) was added carefully to the solution. The mixture was stirred at room temperature for 10 minutes, after that Diethyl carbonate (4.37 g, 4.48 mL, 37 mmol, 6 eq) was added and the mixture was heated to 60°C for 1 day. After 1 day solvent was removed under vacuum and the compound was purified with flash column chromatography (hexane:ethyl acetate 6:1) to give 1.13 g of white solid (yield: 60%)

^1H NMR (300 MHz, $\text{DMSO}-d_6$) (1:0.4 mixture of keto-monoenol : dienol tautomers) δ 12.55 (s, 0.4H), 8.09 (s, 4H), 8.04 (s, 1.6H), 6.11 (s, 0.4H), 4.28 (s, 4H), 4.26 – 4.20 (m, 1.4H), 4.13 (q, $J = 7.1$ Hz, 4.8H), 1.29 (t, $J = 7.1$ Hz, 1.4H), 1.18 (t, $J = 7.1$ Hz, 7.3H).

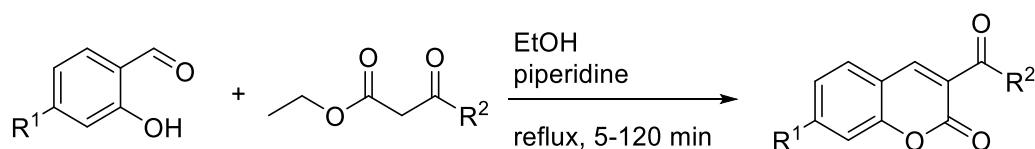
^{13}C NMR (75 MHz, $\text{DMSO}-d_6$) (mixture of keto-monoenol : dienol tautomers) δ 193.38, 172.42, 168.62, 167.45, 139.24, 137.12, 128.74, 126.36, 89.37, 60.69, 60.53, 45.78, 45.65, 14.06, 13.95.

1.2. General protocol for the synthesis of β -ketoesters



Synthesis was performed following procedure by Kumar et al²: A 4¹-acetophenon derivative (1 eq) was dissolved in dry THF and sodium hydride was added carefully (3 eq). After stirring for 10 minutes, Diethyl carbonate was added to the solution (4 eq) and the mixture was heated to reflux temperature for 1-3 hours, meanwhile the colour usually changed to yellow-brownish. The reaction was monitored by TLC (15 % ethyl acetate in hexane) and when the reaction was done, water was added, THF was removed under vacuo and the crude product was extracted with ethyl acetate. The product was purified with flash column chromatography (hexane:ethyl acetate 6:1) to give the final product.

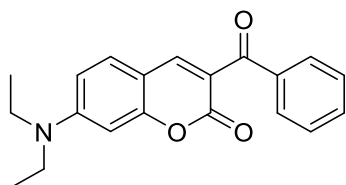
1.3. General protocol for the synthesis of ketocoumarins



(4-Diethylamino)salicylaldehyde or (4-Methoxy)salicylaldehyde (typical starting weight: 1 gram) was refluxed in ethanol (25 mL) in 1:1 molar ratio (in case of **12a**, **12b**, **13a**, **13b** in 2:1 molar ratio) with the appropriate β -ketoester for 5-120 minutes with piperidine (0,5 ml). The reaction time depended on the starting salicylaldehyde: with (4-Methoxy)salicylaldehyde, it took only 5 minutes and the product already precipitated from the hot solution. (4-Diethylamino)salicylaldehyde the reaction time took up to two hours (followed by TLC) and the product often precipitated only from the cooled down solution. After the reaction was done as proven by TLC, the reaction mixture was cooled down, filtered and the precipitate washed with cold ethanol. No further purification steps were needed. The clarity of the product was verified by NMR and HRMS analysis.

2. Analysis of ketocoumarins

2.1. 3-benzoyl-7-(diethylamino)-2H-chromen-2-one (1a)



Yield: 0.75 g; 45%

^1H NMR (300 MHz, $\text{DMSO-}d_6$) δ 8.25 (s, 1H), 7.80 – 7.72 (m, 2H), 7.66 – 7.56 (m, 2H), 7.48 (t, J = 7.6 Hz, 2H), 6.77 (dd, J = 9.0, 2.5 Hz, 1H), 6.58 (d, J = 2.4 Hz, 1H), 3.47 (q, J = 7.0 Hz, 4H), 1.13 (t, J = 7.0 Hz, 6H).

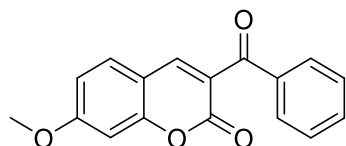
^{13}C NMR (75 MHz, $\text{DMSO-}d_6$) δ 192.17, 158.97, 157.76, 152.39, 147.61, 137.75, 132.69, 131.56, 129.06, 128.33, 116.74, 109.77, 107.27, 96.17, 44.35, 12.32.

HRMS: m/z calcd for $\text{C}_{20}\text{H}_{19}\text{NO}_3\text{Na}^+$ $[\text{M}+\text{Na}]^+$: 344.1257 found: 344.1257

λ_{max} (MeOH): 431 nm

ϵ_{max} (MeOH): 45800 $\text{M}^{-1}\text{cm}^{-1}$

2.2. 3-benzoyl-7-methoxy-2H-chromen-2-one (1b)



Yield: 1.05 g; 57%

^1H NMR (300 MHz, $\text{DMSO-}d_6$) δ 8.38 (s, 1H), 7.87 (d, J = 7.0 Hz, 2H), 7.78 (d, J = 8.7 Hz, 1H), 7.67 (t, J = 7.4 Hz, 1H), 7.52 (t, J = 7.7 Hz, 2H), 7.09 (d, J = 2.4 Hz, 1H), 7.02 (dd, J = 8.7, 2.5 Hz, 1H), 3.89 (s, 3H).

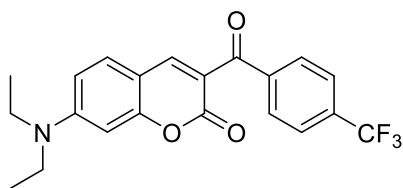
^{13}C NMR (75 MHz, $\text{DMSO-}d_6$) δ 191.91, 164.14, 158.29, 156.52, 146.38, 136.59, 133.54, 131.20, 129.42, 128.63, 122.28, 113.18, 111.82, 100.60, 56.23.

HRMS: m/z calcd for $\text{C}_{17}\text{H}_{12}\text{O}_4\text{Na}^+$ $[\text{M}+\text{Na}]^+$: 303.0628 found: 303.0634

λ_{max} (MeOH): 347 nm

ϵ_{max} (MeOH): 41200 $\text{M}^{-1}\text{cm}^{-1}$

2.3. 7-(diethylamino)-3-(4-(trifluoromethyl)benzoyl)-2H-chromen-2-one (2a)



Yield: 1.32 g; 65%

$^1\text{H NMR}$ (300 MHz, $\text{DMSO-}d_6$) δ 8.38 (s, 1H), 7.92 (d, $J = 8.1$ Hz, 2H), 7.83 (d, $J = 8.2$ Hz, 2H), 7.65 (d, $J = 9.1$ Hz, 1H), 6.80 (dd, $J = 9.0, 2.4$ Hz, 1H), 6.60 (d, $J = 2.4$ Hz, 1H), 3.49 (q, $J = 7.0$ Hz, 4H), 1.14 (t, $J = 7.0$ Hz, 6H).

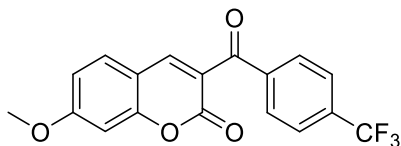
$^{13}\text{C NMR}$ (75 MHz, $\text{DMSO-}d_6$) δ 191.38, 159.09, 158.16, 152.86, 148.82, 141.92, 132.06, 129.47, 125.21, 125.16, 115.42, 110.03, 107.52, 96.16, 44.43, 12.33.

HRMS: m/z calcd for $\text{C}_{21}\text{H}_{18}\text{F}_3\text{NO}_3\text{Na}^+$ $[\text{M}+\text{Na}]^+$: 412.1131 found: 412.1130

λ_{max} (MeOH): 435 nm

ϵ_{max} (MeOH): 41700 $\text{M}^{-1}\text{cm}^{-1}$

2.4. 7-methoxy-3-(4-(trifluoromethyl)benzoyl)-2H-chromen-2-one (2b)



Yield: 2.05 g; 90%

$^1\text{H NMR}$ (300 MHz, $\text{DMSO-}d_6$) δ 8.51 (s, 1H), 8.05 (d, $J = 8.0$ Hz, 2H), 7.88 (d, $J = 8.2$ Hz, 2H), 7.83 (d, $J = 8.7$ Hz, 1H), 7.10 (d, $J = 2.4$ Hz, 1H), 7.03 (dd, $J = 8.7, 2.4$ Hz, 1H), 3.90 (s, 3H).

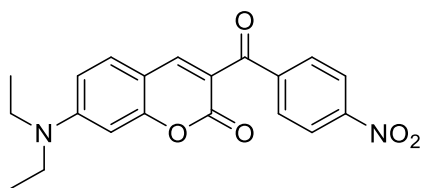
$^{13}\text{C NMR}$ (75 MHz, $\text{DMSO-}d_6$) δ 191.30, 164.59, 158.31, 156.89, 147.99, 140.46, 131.61, 129.95, 125.52, 125.47, 121.29, 113.36, 111.89, 100.61, 56.29.

HRMS: m/z calcd for $\text{C}_{18}\text{H}_{11}\text{F}_3\text{O}_4\text{Na}^+$ $[\text{M}+\text{Na}]^+$: 371.0502 found: 371.0498

λ_{max} (MeOH): 354 nm

ϵ_{max} (MeOH): 35200 $\text{M}^{-1}\text{cm}^{-1}$

2.5. 7-(diethylamino)-3-(4-nitrobenzoyl)-2H-chromen-2-one (3a)



Yield: 1.72 g; 91%

$^1\text{H NMR}$ (300 MHz, $\text{DMSO-}d_6$) δ 8.42 (s, 1H), 8.28 (d, $J = 8.8$ Hz, 2H), 7.95 (d, $J = 8.8$ Hz, 2H), 7.65 (d, $J = 9.1$ Hz, 1H), 6.81 (dd, $J = 9.0, 2.4$ Hz, 1H), 6.60 (d, $J = 2.4$ Hz, 1H), 3.50 (q, $J = 7.0$ Hz, 4H), 1.14 (t, $J = 7.0$ Hz, 6H).

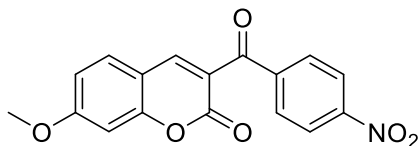
$^{13}\text{C NMR}$ (75 MHz, $\text{DMSO-}d_6$) δ 191.00, 159.16, 158.30, 153.03, 149.19, 149.10, 144.02, 132.23, 129.87, 123.32, 115.01, 110.15, 107.62, 96.17, 44.47, 12.34.

HRMS: m/z calcd for $\text{C}_{20}\text{H}_{18}\text{N}_2\text{O}_5\text{Na}^+$ $[\text{M}+\text{Na}]^+$: 389.1108 found: 389.1115

λ_{max} (MeOH): 446 nm

ϵ_{max} (MeOH): 48300 $\text{M}^{-1}\text{cm}^{-1}$

2.6. 7-methoxy-3-(4-nitrobenzoyl)-2H-chromen-2-one (3b)



Yield: 2.0 g; 94%

$^1\text{H NMR}$ (300 MHz, $\text{DMSO-}d_6$) δ 8.54 (s, 1H), 8.31 (d, $J = 8.7$ Hz, 2H), 8.07 (d, $J = 8.7$ Hz, 2H), 7.83 (d, $J = 8.7$ Hz, 1H), 7.10 (d, $J = 2.4$ Hz, 1H), 7.03 (dd, $J = 8.7, 2.4$ Hz, 1H), 3.90 (s, 3H).

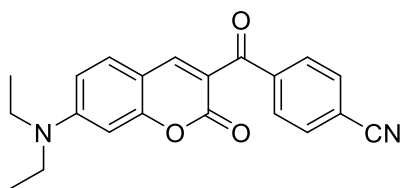
$^{13}\text{C NMR}$ (75 MHz, $\text{DMSO-}d_6$) δ 191.01, 164.75, 158.35, 157.03, 149.79, 148.44, 142.27, 131.75, 130.40, 123.57, 121.02, 113.42, 111.91, 56.32.

HRMS: m/z calcd for $\text{C}_{17}\text{H}_{11}\text{NO}_6\text{Na}^+$ $[\text{M}+\text{Na}]^+$: 348.0479 found: 348.0484

λ_{max} (MeOH): 354 nm

ϵ_{max} (MeOH): 24400 $\text{M}^{-1}\text{cm}^{-1}$

2.7. 4-(7-(diethylamino)-2-oxo-2H-chromene-3-carbonyl)benzonitrile (4a)



Yield: 0.43 g; 77%

$^1\text{H NMR}$ (300 MHz, $\text{DMSO-}d_6$) δ 8.38 (s, 1H), 7.94 (d, $J = 8.6$ Hz, 2H), 7.87 (d, $J = 8.6$ Hz, 2H), 7.64 (d, $J = 9.0$ Hz, 1H), 6.80 (dd, $J = 9.0, 2.4$ Hz, 1H), 6.59 (d, $J = 2.4$ Hz, 1H), 3.49 (q, $J = 7.0$ Hz, 4H), 1.14 (t, $J = 7.0$ Hz, 6H).

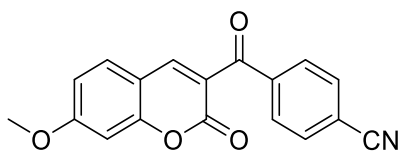
$^{13}\text{C NMR}$ (75 MHz, $\text{DMSO-}d_6$) δ 191.26, 159.12, 158.23, 152.92, 148.95, 142.28, 132.21, 132.13, 129.28, 118.34, 115.18, 114.09, 110.07, 107.58, 96.15, 44.45, 12.34.

HRMS: m/z calcd for $\text{C}_{21}\text{H}_{18}\text{N}_2\text{O}_3\text{Na}^+$ $[\text{M}+\text{Na}]^+$: 369.1210 found: 369.1208

λ_{max} (MeOH): 443 nm

ϵ_{max} (MeOH): 52400 $\text{M}^{-1}\text{cm}^{-1}$

2.8. 4-(7-methoxy-2-oxo-2H-chromene-3-carbonyl)benzonitrile (4b)



Yield: 0.45 g; 92%

$^1\text{H NMR}$ (300 MHz, $\text{DMSO-}d_6$) δ 8.51 (s, 1H), 8.06 – 7.94 (m, 4H), 7.83 (d, $J = 8.7$ Hz, 1H), 7.10 (d, $J = 2.4$ Hz, 1H), 7.04 (dd, $J = 8.7, 2.5$ Hz, 1H), 3.91 (s, 3H).

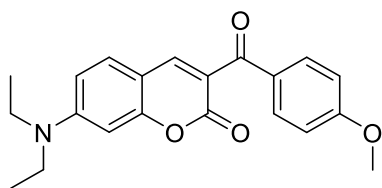
$^{13}\text{C NMR}$ (75 MHz, $\text{DMSO-}d_6$) δ 191.26, 164.64, 158.34, 156.96, 148.17, 140.65, 132.52, 131.65, 129.72, 121.16, 118.20, 115.01, 113.37, 111.92, 100.61, 56.31.

HRMS: m/z calcd for $\text{C}_{18}\text{H}_{11}\text{NO}_4\text{Na}^+$ $[\text{M}+\text{Na}]^+$: 306.0761 found: 306.0763

λ_{max} (MeOH): 354 nm

ϵ_{max} (MeOH): 39100 $\text{M}^{-1}\text{cm}^{-1}$

2.9. 7-(diethylamino)-3-(4-methoxybenzoyl)-2H-chromen-2-one (5a)



Yield: 0.57 g; 58%

$^1\text{H NMR}$ (300 MHz, $\text{DMSO-}d_6$) δ 8.17 (s, 1H), 7.78 (d, $J = 8.9$ Hz, 2H), 7.58 (d, $J = 9.0$ Hz, 1H), 7.02 (d, $J = 8.9$ Hz, 2H), 6.77 (dd, $J = 9.0, 2.4$ Hz, 1H), 6.58 (d, $J = 2.4$ Hz, 1H), 3.84 (s, 3H), 3.47 (q, $J = 7.0$ Hz, 4H), 1.13 (t, $J = 7.0$ Hz, 6H).

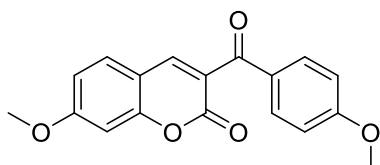
$^{13}\text{C NMR}$ (75 MHz, $\text{DMSO-}d_6$) δ 190.59, 163.11, 159.03, 157.50, 152.08, 146.63, 131.68, 131.22, 130.04, 117.60, 113.69, 109.64, 107.21, 96.21, 55.55, 44.30, 12.33.

HRMS: m/z calcd for $\text{C}_{21}\text{H}_{21}\text{NO}_4\text{Na}^+$ $[\text{M}+\text{Na}]^+$: 374.1363 found: 374.1369

λ_{max} (MeOH): 427 nm

ϵ_{max} (MeOH): $39100 \text{ M}^{-1}\text{cm}^{-1}$

2.10. 7-methoxy-3-(4-methoxybenzoyl)-2H-chromen-2-one (5b)



Yield: 0.81 g; 93%

$^1\text{H NMR}$ (300 MHz, $\text{DMSO-}d_6$) δ 8.31 (s, 1H), 7.88 (d, $J = 8.9$ Hz, 2H), 7.76 (d, $J = 8.7$ Hz, 1H), 7.13 – 6.97 (m, 4H), 3.90 (s, 3H), 3.86 (s, 3H).

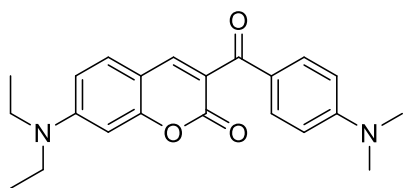
$^{13}\text{C NMR}$ (75 MHz, $\text{Chloroform-}d$) δ 190.17, 163.86, 163.65, 158.35, 156.28, 145.27, 132.01, 130.90, 129.15, 122.90, 113.96, 113.07, 111.83, 100.59, 56.17, 55.64.

HRMS: m/z calcd for $\text{C}_{18}\text{H}_{14}\text{O}_5\text{Na}^+$ $[\text{M}+\text{Na}]^+$: 333.0733 found: 333.0731

λ_{max} (MeOH): 344 nm

ϵ_{max} (MeOH): $44300 \text{ M}^{-1}\text{cm}^{-1}$

2.11. 7-(diethylamino)-3-(4-(dimethylamino)benzoyl)-2H-chromen-2-one (6a)



Yield: 0.31 g; 33%

$^1\text{H NMR}$ (300 MHz, $\text{DMSO-}d_6$) δ 8.05 (s, 1H), 7.67 (d, $J = 9.0$ Hz, 2H), 7.54 (d, $J = 8.9$ Hz, 1H), 6.80 – 6.65 (m, 3H), 6.57 (d, $J = 2.4$ Hz, 1H), 3.46 (q, $J = 7.0$ Hz, 4H), 1.14 (t, $J = 7.0$ Hz, 6H).

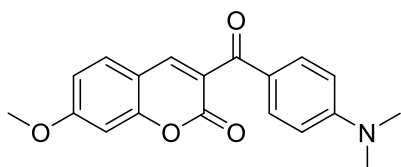
$^{13}\text{C NMR}$ (75 MHz, $\text{DMSO-}d_6$) δ 189.41, 159.07, 157.10, 153.44, 151.63, 145.09, 131.63, 130.73, 124.12, 118.88, 110.59, 109.43, 107.15, 96.24, 44.21, 39.61, 12.31.

HRMS: m/z calcd for $\text{C}_{22}\text{H}_{24}\text{N}_2\text{O}_3\text{Na}^+$ $[\text{M}+\text{Na}]^+$: 387.1679 found: 387.1680

λ_{max} (MeOH): 427 nm

ϵ_{max} (MeOH): 43400 $\text{M}^{-1}\text{cm}^{-1}$

2.12. 3-(4-(dimethylamino)benzoyl)-7-methoxy-2H-chromen-2-one (6b)



Yield: 0.50 g; 60%

$^1\text{H NMR}$ (300 MHz, $\text{DMSO-}d_6$) δ 8.18 (s, 1H), 7.78 – 7.65 (m, 3H), 7.08 (d, $J = 2.4$ Hz, 1H), 7.01 (dd, $J = 8.7, 2.4$ Hz, 1H), 6.73 (d, $J = 9.1$ Hz, 2H), 3.89 (s, 3H), 3.04 (s, 6H).

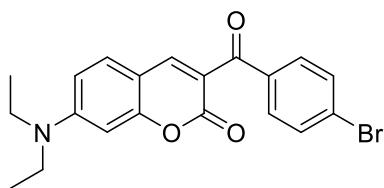
$^{13}\text{C NMR}$ (75 MHz, $\text{DMSO-}d_6$) δ 188.80, 163.45, 158.46, 155.94, 153.77, 143.78, 131.86, 130.54, 123.80, 123.34, 112.93, 111.87, 110.71, 100.58, 56.11, 39.61.

HRMS: m/z calcd for $\text{C}_{19}\text{H}_{17}\text{NO}_4\text{Na}^+$ $[\text{M}+\text{Na}]^+$: 346.1050 found: 346.1051

λ_{max} (MeOH): 358 nm

ϵ_{max} (MeOH): 30900 $\text{M}^{-1}\text{cm}^{-1}$

2.13. 3-(4-bromobenzoyl)-7-(diethylamino)-2H-chromen-2-one (7a)



Yield: 0.55 g; 74%

$^1\text{H NMR}$ (300 MHz, $\text{DMSO-}d_6$) δ 8.30 (s, 1H), 7.70 (s, 4H), 7.62 (d, $J = 9.0$ Hz, 1H), 6.79 (dd, $J = 9.0, 2.4$ Hz, 1H), 6.59 (d, $J = 2.4$ Hz, 1H), 3.49 (q, $J = 7.0$ Hz, 4H), 1.14 (t, $J = 6.9$ Hz, 6H).

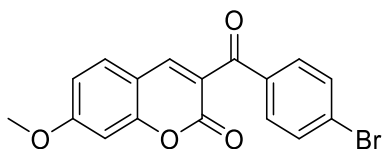
$^{13}\text{C NMR}$ (75 MHz, $\text{DMSO-}d_6$) δ 191.26, 159.03, 157.92, 152.59, 148.15, 137.04, 131.76, 131.32, 130.99, 126.46, 116.08, 109.89, 107.38, 96.16, 44.38, 12.33.

HRMS: m/z calcd for $\text{C}_{20}\text{H}_{18}\text{BrNO}_3\text{Na}^+$ $[\text{M}+\text{Na}]^+$: 422.0362 found: 422.0357

λ_{max} (MeOH): 435 nm

ϵ_{max} (MeOH): 53800 $\text{M}^{-1}\text{cm}^{-1}$

2.14. 3-(4-bromobenzoyl)-7-methoxy-2H-chromen-2-one (7b)



Yield: 0.61 g; 91%

$^1\text{H NMR}$ (300 MHz, $\text{DMSO-}d_6$) δ 8.43 (s, 1H), 7.88 – 7.77 (m, 3H), 7.76 – 7.70 (m, 2H), 7.10 (d, $J = 2.4$ Hz, 1H), 7.03 (dd, $J = 8.7, 2.5$ Hz, 1H), 3.90 (s, 3H).

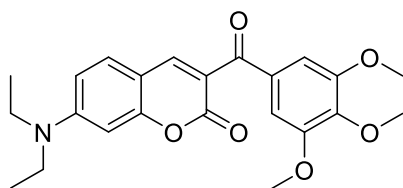
$^{13}\text{C NMR}$ (75 MHz, $\text{DMSO-}d_6$) δ 191.09, 164.32, 158.29, 156.66, 147.06, 135.82, 131.65, 131.33, 127.53, 121.78, 114.53, 113.24, 111.85, 100.60, 56.25.

HRMS: m/z calcd for $\text{C}_{17}\text{H}_{11}\text{BrO}_4\text{Na}^+$ $[\text{M}+\text{Na}]^+$: 380.9733 found: 380.9734

λ_{max} (MeOH): 350 nm

ϵ_{max} (MeOH): 34100 $\text{M}^{-1}\text{cm}^{-1}$

2.15. 7-(diethylamino)-3-(3,4,5-trimethoxybenzoyl)-2H-chromen-2-one (8a)



Yield: 0.44 g; 60%

$^1\text{H NMR}$ (300 MHz, $\text{DMSO-}d_6$) δ 8.22 (s, 1H), 7.61 (d, $J = 9.0$ Hz, 1H), 7.10 (s, 2H), 6.77 (dd, $J = 9.0, 2.4$ Hz, 1H), 6.59 (d, $J = 2.4$ Hz, 1H), 3.80 (s, 6H), 3.75 (s, 3H), 3.48 (q, $J = 7.0$ Hz, 4H), 1.14 (t, $J = 6.9$ Hz, 6H).

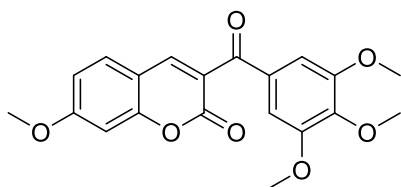
$^{13}\text{C NMR}$ (75 MHz, $\text{DMSO-}d_6$) δ 190.98, 158.79, 157.64, 152.56, 152.25, 147.33, 141.59, 132.85, 131.45, 116.94, 109.66, 107.29, 106.92, 96.20, 60.13, 56.09, 44.32, 12.34.

HRMS: m/z calcd for $\text{C}_{23}\text{H}_{25}\text{NO}_6\text{Na}^+$ $[\text{M}+\text{Na}]^+$: 434.1574 found: 434.1571

λ_{max} (MeOH): 431 nm

ϵ_{max} (MeOH): 51900 $\text{M}^{-1}\text{cm}^{-1}$

2.16. 7-methoxy-3-(3,4,5-trimethoxybenzoyl)-2H-chromen-2-one (8b)



Yield: 0.56 g; 84%

$^1\text{H NMR}$ (400 MHz, $\text{Chloroform-}d$) δ 8.06 (s, 1H), 7.50 (d, $J = 8.6$ Hz, 1H), 7.12 (s, 2H), 6.92 (dd, $J = 8.6, 2.4$ Hz, 1H), 6.88 (d, $J = 2.5$ Hz, 1H), 3.94 (s, 3H), 3.92 (s, 3H), 3.88 (s, 6H).

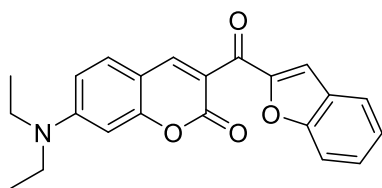
$^{13}\text{C NMR}$ (101 MHz, $\text{Chloroform-}d$) δ 190.98, 164.75, 158.90, 157.21, 153.17, 146.21, 143.31, 131.84, 130.50, 123.25, 113.75, 112.03, 107.42, 100.87, 61.12, 56.53, 56.16.

HRMS: m/z calcd for $\text{C}_{20}\text{H}_{18}\text{O}_7\text{Na}^+$ $[\text{M}+\text{Na}]^+$: 393.0945 found: 393.0950

λ_{max} (MeOH): 345 nm

ϵ_{max} (MeOH): 35800 $\text{M}^{-1}\text{cm}^{-1}$

2.17. 3-(benzofuran-2-carbonyl)-7-(diethylamino)-2H-chromen-2-one (9a)



Yield: 0.04 g; 5%

$^1\text{H NMR}$ (300 MHz, $\text{DMSO-}d_6$) δ 8.44 (s, 1H), 7.87 – 7.80 (m, 2H), 7.75 – 7.68 (m, 1H), 7.62 (d, $J = 9.0$ Hz, 1H), 7.58 – 7.47 (m, 1H), 7.42 – 7.33 (m, 1H), 6.81 (dd, $J = 9.0, 2.5$ Hz, 1H), 6.62 (d, $J = 2.4$ Hz, 1H), 3.50 (q, $J = 7.0$ Hz, 4H), 1.15 (t, $J = 7.0$ Hz, 6H).

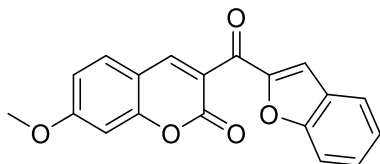
$^{13}\text{C NMR}$ (75 MHz, $\text{DMSO-}d_6$) δ 180.07, 158.46, 157.68, 155.12, 152.64, 151.93, 147.52, 131.76, 128.45, 126.91, 124.04, 123.71, 116.01, 115.76, 112.22, 109.93, 107.11, 96.19, 44.39, 12.34.

HRMS: m/z calcd for $\text{C}_{22}\text{H}_{19}\text{NO}_4\text{Na}^+$ $[\text{M}+\text{Na}]^+$: 384.1206 found: 384.1205

λ_{max} (MeOH): 438 nm

ϵ_{max} (MeOH): 38600 $\text{M}^{-1}\text{cm}^{-1}$

2.18. 3-(benzofuran-2-carbonyl)-7-methoxy-2H-chromen-2-one (9b)



Yield: 0.05 g; 8%

$^1\text{H NMR}$ (300 MHz, $\text{DMSO-}d_6$) δ 8.56 (s, 1H), 7.95 (d, $J = 1.0$ Hz, 1H), 7.83 (d, $J = 7.8$ Hz, 1H), 7.79 (d, $J = 8.7$ Hz, 1H), 7.74 (d, $J = 8.2$ Hz, 1H), 7.56 (t, $J = 8.5$ Hz, 1H), 7.38 (t, $J = 7.5$ Hz, 1H), 7.10 (d, $J = 2.4$ Hz, 1H), 7.03 (dd, $J = 8.7, 2.4$ Hz, 1H), 3.90 (s, 3H).

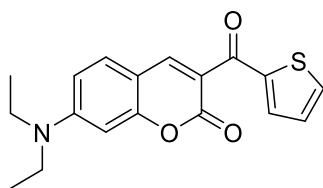
$^{13}\text{C NMR}$ (75 MHz, $\text{DMSO-}d_6$) δ 179.95, 164.42, 157.85, 156.50, 155.48, 151.38, 146.63, 131.42, 129.04, 126.82, 124.27, 123.99, 121.29, 117.50, 113.36, 112.36, 111.65, 100.66, 56.29.

HRMS: m/z calcd for $\text{C}_{19}\text{H}_{12}\text{O}_5\text{Na}^+$ $[\text{M}+\text{Na}]^+$: 343.0577 found: 343.0574

λ_{max} (MeOH): 354 nm

ϵ_{max} (MeOH): 47500 $\text{M}^{-1}\text{cm}^{-1}$

2.19. 7-(diethylamino)-3-(thiophene-2-carbonyl)-2H-chromen-2-one (10a)



Yield: 0.37 g; 44%

$^1\text{H NMR}$ (300 MHz, $\text{DMSO-}d_6$) δ 8.28 (s, 1H), 8.06 (dd, $J = 4.9, 1.2$ Hz, 1H), 7.81 (dd, $J = 3.8, 1.2$ Hz, 1H), 7.59 (d, $J = 8.9$ Hz, 1H), 7.24 (dd, $J = 5.0, 3.8$ Hz, 1H), 6.78 (dd, $J = 9.0, 2.4$ Hz, 1H), 6.59 (d, $J = 2.4$ Hz, 1H), 3.48 (q, $J = 7.0$ Hz, 4H), 1.14 (t, $J = 7.0$ Hz, 6H).

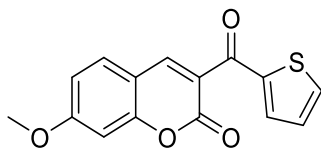
$^{13}\text{C NMR}$ (75 MHz, $\text{DMSO-}d_6$) δ 183.45, 158.57, 157.41, 152.27, 146.48, 143.37, 135.41, 135.19, 131.38, 128.64, 116.87, 109.73, 107.00, 96.18, 44.31, 12.32.

HRMS: m/z calcd for $\text{C}_{18}\text{H}_{17}\text{NO}_3\text{SNa}^+$ $[\text{M}+\text{Na}]^+$: 350.0821 found: 350.0818

λ_{max} (MeOH): 431 nm

ϵ_{max} (MeOH): 44200 $\text{M}^{-1}\text{cm}^{-1}$

2.20. 7-methoxy-3-(thiophene-2-carbonyl)-2H-chromen-2-one (10b)



Yield: 0.65 g; 90%

$^1\text{H NMR}$ (300 MHz, $\text{DMSO-}d_6$) δ 8.43 (s, 1H), 8.14 (dd, $J = 4.9, 1.2$ Hz, 1H), 7.90 (dd, $J = 3.8, 1.2$ Hz, 1H), 7.78 (d, $J = 8.7$ Hz, 1H), 7.27 (dd, $J = 4.9, 3.8$ Hz, 1H), 7.10 (d, $J = 2.4$ Hz, 1H), 7.03 (dd, $J = 8.7, 2.4$ Hz, 1H), 3.90 (s, 3H).

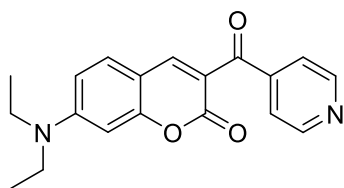
$^{13}\text{C NMR}$ (75 MHz, $\text{DMSO-}d_6$) δ 183.38, 164.07, 157.93, 156.26, 145.36, 142.76, 136.56, 136.47, 131.10, 128.96, 122.06, 113.18, 111.65, 100.60, 56.21.

HRMS: m/z calcd for $\text{C}_{15}\text{H}_{10}\text{O}_4\text{SNa}^+$ $[\text{M}+\text{Na}]^+$: 309.0192 found: 309.0196

λ_{max} (MeOH): 346 nm

ϵ_{max} (MeOH): 36900 $\text{M}^{-1}\text{cm}^{-1}$

2.21. 7-(diethylamino)-3-isonicotinoyl-2H-chromen-2-one (11a)



Yield: 0.55 g; 65%

$^1\text{H NMR}$ (300 MHz, $\text{DMSO-}d_6$) δ 8.80 – 8.67 (m, 2H), 8.42 (s, 1H), 7.67 (d, $J = 9.0$ Hz, 1H), 7.62 – 7.57 (m, 2H), 6.82 (dd, $J = 9.1, 2.4$ Hz, 1H), 6.61 (d, $J = 2.4$ Hz, 1H), 3.51 (q, $J = 7.0$ Hz, 4H), 1.15 (t, $J = 7.0$ Hz, 6H).

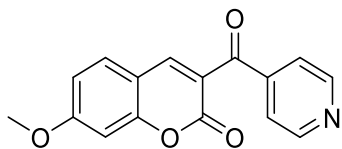
$^{13}\text{C NMR}$ (75 MHz, $\text{DMSO-}d_6$) δ 191.41, 159.01, 158.32, 153.08, 149.98, 149.24, 145.39, 132.29, 121.87, 114.63, 110.14, 107.58, 96.14, 44.47, 12.34.

HRMS: m/z calcd for $\text{C}_{19}\text{H}_{18}\text{N}_2\text{O}_3\text{Na}^+$ $[\text{M}+\text{Na}]^+$: 345.1210 found: 345.1207

λ_{max} (MeOH): 445 nm

ϵ_{max} (MeOH): 56900 $\text{M}^{-1}\text{cm}^{-1}$

2.22. 3-isonicotinoyl-7-methoxy-2H-chromen-2-one (11b)



Yield: 0.58 g; 63%

$^1\text{H NMR}$ (300 MHz, $\text{DMSO-}d_6$) δ 8.83 – 8.72 (m, 2H), 8.56 (s, 1H), 7.86 (d, $J = 8.7$ Hz, 1H), 7.79 – 7.68 (m, 2H), 7.12 (d, $J = 2.4$ Hz, 1H), 7.05 (dd, $J = 8.7, 2.4$ Hz, 1H), 3.92 (s, 3H).

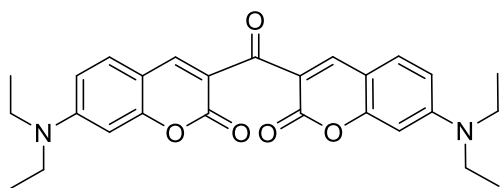
$^{13}\text{C NMR}$ (75 MHz, $\text{DMSO-}d_6$) δ 191.61, 164.81, 158.22, 157.06, 150.35, 148.67, 143.70, 131.82, 122.09, 120.61, 113.43, 111.88, 100.60, 56.33.

HRMS: m/z calcd for $\text{C}_{16}\text{H}_{11}\text{NO}_4\text{Na}^+$ $[\text{M}+\text{Na}]^+$: 304.0580 found: 304.0587

λ_{max} (MeOH): 357 nm

ϵ_{max} (MeOH): 36500 $\text{M}^{-1}\text{cm}^{-1}$

2.23. 3,3'-carbonylbis(7-(diethylamino)-2H-chromen-2-one) (12a)



Yield: 0.92 g; 77%

$^1\text{H NMR}$ (300 MHz, $\text{DMSO-}d_6$) δ 8.28 (s, 2H), 7.62 (d, $J = 9.0$ Hz, 2H), 6.77 (dd, $J = 9.0, 2.4$ Hz, 2H), 6.57 (d, $J = 2.4$ Hz, 2H), 3.47 (q, $J = 7.0$ Hz, 8H), 1.13 (t, $J = 7.0$ Hz, 12H).

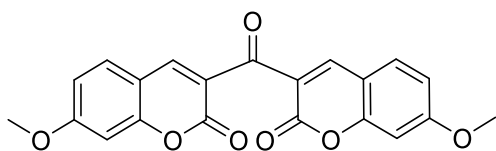
$^{13}\text{C NMR}$ (75 MHz, $\text{DMSO-}d_6$) δ 187.43, 159.53, 157.51, 152.30, 145.58, 131.62, 118.99, 109.81, 107.50, 96.20, 44.35, 12.33.

HRMS: m/z calcd for $\text{C}_{27}\text{H}_{28}\text{N}_2\text{O}_5\text{Na}^+$ $[\text{M}+\text{Na}]^+$: 483.1890; found: 483.1895

λ_{max} (MeOH): 462 nm

ϵ_{max} (MeOH): 82400 $\text{M}^{-1}\text{cm}^{-1}$

2.24. 3,3'-carbonylbis(7-methoxy-2H-chromen-2-one) (12b)



Yield: 1.07 g; 86%

$^1\text{H NMR}$ (300 MHz, $\text{DMSO-}d_6$) δ 8.56 (s, 2H), 7.87 (d, $J = 8.7$ Hz, 2H), 7.11 (d, $J = 2.4$ Hz, 2H), 7.05 (dd, $J = 8.7, 2.5$ Hz, 2H), 3.90 (s, 6H).

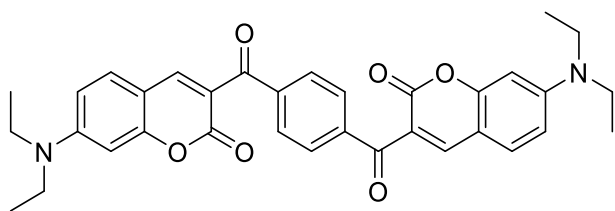
$^{13}\text{C NMR}$ (75 MHz, $\text{DMSO-}d_6$) δ 187.43, 164.62, 158.86, 156.63, 146.20, 131.78, 122.86, 113.58, 111.93, 100.67, 56.32.

HRMS: m/z calcd for $\text{C}_{21}\text{H}_{14}\text{O}_7\text{Na}^+$ $[\text{M}+\text{Na}]^+$: 401.0632 found: 401.0628

λ_{max} (MeOH): 376 nm

ϵ_{max} (MeOH): 41700 $\text{M}^{-1}\text{cm}^{-1}$

2.25. 3,3'-terephthaloylbis(7-(diethylamino)-2H-chromen-2-one) (13a)



Yield: 0.64 g; 70%

$^1\text{H NMR}$ (300 MHz, Chloroform-*d*) δ 8.12 (s, 2H), 7.86 (s, 4H), 7.38 (d, $J = 8.9$ Hz, 2H), 6.67 (dd, $J = 9.0, 2.5$ Hz, 2H), 6.54 (d, $J = 2.5$ Hz, 2H), 3.47 (q, $J = 7.1$ Hz, 8H), 1.25 (t, $J = 7.1$ Hz, 12H).

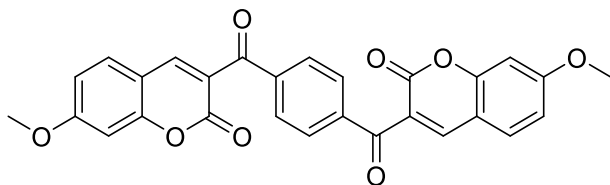
$^{13}\text{C NMR}$ (75 MHz, Chloroform-*d*) δ 191.93, 159.52, 158.34, 152.57, 148.22, 141.08, 131.24, 129.08, 117.39, 110.03, 108.17, 97.36, 45.37, 12.39.

HRMS: m/z calcd for $\text{C}_{34}\text{H}_{32}\text{N}_2\text{O}_6\text{Na}^+$ $[\text{M}+\text{Na}]^+$: 587.2153 found: 587.2146

λ_{max} (MeOH): 440 nm

ϵ_{max} (MeOH): 79300 $\text{M}^{-1}\text{cm}^{-1}$

2.26. 3,3'-terephthaloylbis(7-methoxy-2H-chromen-2-one) (13b)



Yield: 0.69 g; 87%

$^1\text{H NMR}$ (400 MHz, D_2SO_4 , Chloroform-*d*) δ 9.15 (s, 2H), 8.27 (s, 4H), 8.08 (d, $J = 9.2$ Hz, 2H), 7.37 (d, $J = 9.1$ Hz, 2H), 4.21 (s, 6H).

$^{13}\text{C NMR}$ (101 MHz, D_2SO_4 , Chloroform-*d*) δ 197.83, 177.46, 177.42, 168.49, 161.40, 160.27, 160.24, 138.31, 136.20, 132.42, 120.60, 116.39, 106.94, 102.75, 58.75.

HRMS: m/z calcd for $\text{C}_{28}\text{H}_{18}\text{O}_8\text{Na}^+$ $[\text{M}+\text{Na}]^+$: 505.0894 found: 505.0893

λ_{max} (MeOH): 353 nm

ϵ_{max} (MeOH): 36500 $\text{M}^{-1}\text{cm}^{-1}$

3. Light-driven hydrogen evolution catalysis

All solutions were prepared in glovebox under argon atmosphere. All solvents were deoxygenized previously by purging argon through them and kept in glovebox. For the photocatalytic hydrogen evolution, a 0.1 mM stock solution of the catalyst Chlor-bis-(dimethylglyoximato)-(pyridine)-cobalt(III) in THF was prepared. Another stock solution of 50-50% water-methanol mixture containing Ascorbic acid (85 mg/mL), set to pH 4 by adding 27.5 $\mu\text{L}/\text{mL}$ of a 25% aqueous ammonia solution, and dimethylglyoxime (5 mg/mL) was also prepared. 10 μL from the prior and 200 μL from the latter stock solution were transferred into a 5 mL vial loaded with solid ketocoumarin **1-13a/b**. The amount of ketocoumarin in the vials was set to be, that the nominal concentration will be 1 mM when there is a total of 1 mL of solvent in it. To the solutions was added water and methanol to obtain 1 ml total with the respective water/methanol ratio. For each dye 5 measurements were conducted with 10-50% water content in methanol with 10% increments. The vials were sealed with a cap with a septum. Parallely 10 Samples were irradiated for 20 hours with blue or UV LED (New Energy LST1-01G01-RYL1-00 (3.0V, 0.35A) and LST1-01G01-UV01-00 (3.5V, 0.35A)) while vigorously shaking, in a 3D-printed irradiation chamber. Samples were continuously cooled by a fan to prevent overheating from the intense light source. The ambient temperature of the room was set to 20 $^{\circ}\text{C}$. For each data point, the hydrogen content of one vial was measured and then the vial was discarded. Parallely measuring multiple samples with the same conditions confirmed that hydrogen concentration in each vial is within 10% of difference.

For hydrogen measurements 100 μL from the headspace of the vial was injected to a Shimadzu Nexis GC-2030 with a sieve A5 column and BID detector. Obtained hydrogen amount value was compared to values obtained from a 1% hydrogen in synthetic air can. TON is calculated as the mols of hydrogen in gas phase compared to the mols of cobaloxime in the catalytic solution.

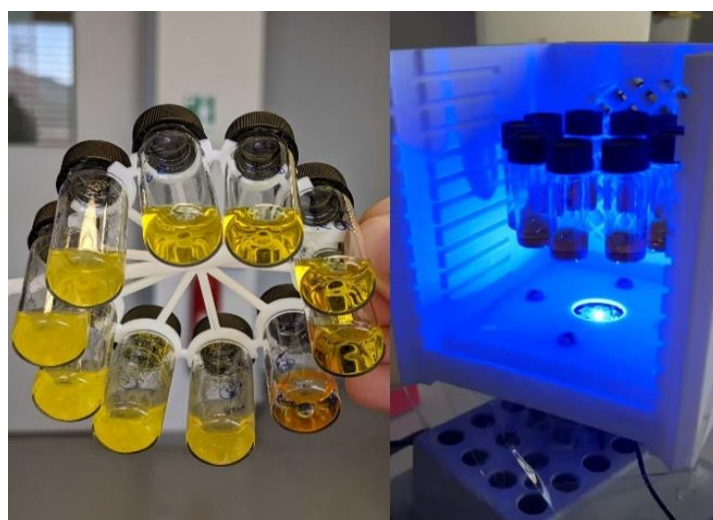


Figure S1: Left: Ketocoumarins before irradiation Right: a glimpse into the photoreactor (with removed wall and lid) used in our experiments.

	water content in methanol						water content in methanol				
	10%	20%	30%	40%	50%		10%	20%	30%	40%	50%
1a	603	1020	715	524	341	1b	1386	1182	1081	1207	1945
2a	751	769	766	403	388	2b	2820	3633	3635	3285	1294
3a	218	269	191	658	671	3b	6	10	0	0	0
4a	647	755	694	819	589	4b	2223	2953	3220	2253	692
5a	815	1171	1028	675	410	5b	1294	1681	2085	1018	283
6a	806	870	815	429	444	6b	389	327	258	266	349
7a	299	278	307	283	197	7b	722	613	447	298	298
8a	1394	2015	3821	1170	1137	8b	1952	2349	2253	1769	1070
9a	995	1150	1027	454	244	9b	2270	2423	2017	1205	354
10a	518	705	972	1049	281	10b	1315	1297	1216	1538	880
11a	0	0	0	0	0	11b	519	950	1296	123	635
12a	543	779	1653	1279	489	12b	3087	3670	3736	3955	1740
13a	1077	632	445	299	140	13b	3325	2888	2064	1120	642

Table S1: Turnover numbers for all ketocoumarins with different water content. Best results are highlighted in pale green.

3.1. Multi-day irradiation measurements

Multi-day measurements were executed by preparing two vials containing 100 μM and two vials containing 1000 μM **8a** with 100 μM cobaloxime in a 70-30% methanol-water mixture (otherwise the same content as described in general procedure). The vials were irradiated parallelly with blue light for multiple days. Hydrogen amounts is an average measured from the two vials. After each measurement the septum cap was removed under argon atmosphere in a glovebox, hydrogen vented out and the vial was resealed with a new, unused septum cap, then the vial was irradiated for another day. After 14 days the solution in the 100 μM **8a** dye started to fade, like it did after 1 day, when the cobaloxime concentration was 1 μM . HPLC measurement was made by sampling one of the vials containing 1000 μM **8a** before irradiation and after 14 days.

	1. day	2. day	3. day	4. day	8. day	9. day	14. day	22. day
100 μM 8a	6.18	2.42	1.33	0.70	1.86	0.29	0.60	0.26
1000 μM 8a	8.23	7.41	3.39	1.84	5.35	0.95	3.00	2.44

Table S2: Amount of hydrogen measured (μmol , average of 2 vials) after each day of irradiation. 100 μM Cobaloxime, 30-70% water-methanol solution with 0.1 M Ascorbic acid and 1 mg/ml dmgH_2 .



Figure S2: Samples before irradiation (left), after 4 days of irradiation (middle), and after 14 days of irradiation (right)

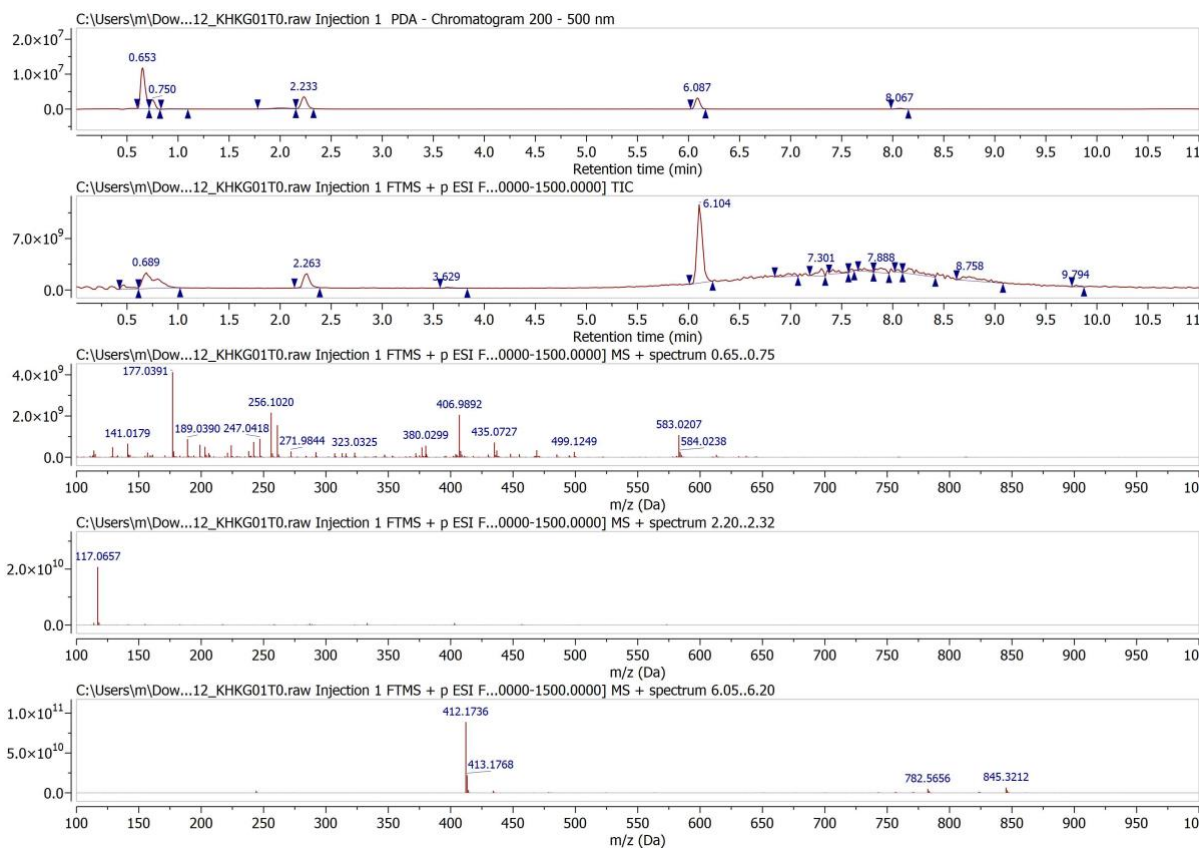


Figure S3: HPLC-HRMS chromatogram *before* 14 days of irradiation of a sample with 1000 μM **8a** and 100 μM cobaloxime. Known peaks: 0.65 min: ascorbic acid (3rd row), 2.23 min: dm gH_2 (4th row), 6.09 min: **8a** (5th row).

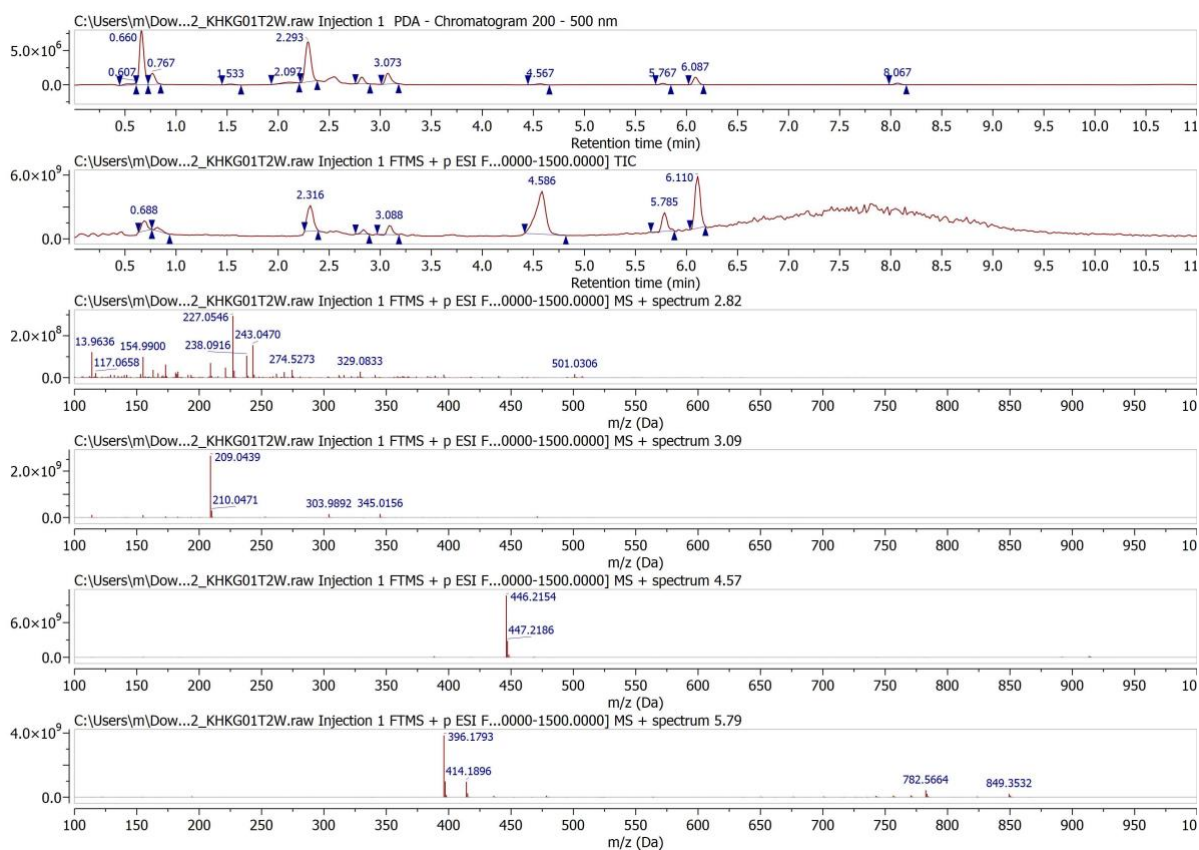


Figure S4 HPLC-HRMS chromatogram *after* 14 days of irradiation of a sample with 1000 μM **8a** and 100 μM cobaloxime. New peaks: 2.82 min M/z: 227.0546, possible elemental composition: $\text{C}_{10}\text{H}_{10}\text{O}_6$ (3rd row); 3.09 min M/z: 209.0439, possible elemental composition: $\text{C}_{10}\text{H}_8\text{O}_5$ (4th row); 4.57 min M/z: 446.2154, possible elemental composition: $\text{C}_{24}\text{H}_{31}\text{NO}_7$ (**8a**+2H+MeOH) (5th row), 5.79 min M/z: 414.1896 and 396.1793, possible elemental composition: $\text{C}_{23}\text{H}_{27}\text{NO}_6$ (**8a**+2H and **8a**+2H-H₂O during ionisation) (6th row)

4. Spectroscopic measurements

Steady state absorption and emission: UV-Vis steady state absorption of all the compounds were recorded in Jasco V-530 spectrophotometer whereas all emission spectra were recorded with a FLS980 spectrometer from Edinburgh Instruments. For all measurements a 1 cm quartz cell was used.

Nanosecond transient absorption: A Nd:YAG laser system from Surelite Continuum generates a 355 nm pulse of 10 Hz with a pulse duration of 10 ns. The 355 nm was converted to the suitable pump wavelength using an optical parametric oscillator (OPO) also from Continuum. The probe beam was generated using a xenon arc lamp. The probe beam after spatial overlapping with the pump was sent to a Acton monochromator from Princeton Instruments which was then detected by a Hamamatsu R928 photomultiplier tube. The amplification and processing of the signal were done using a detection system from Pascher Instruments AB.

Time resolved emission: Time resolved emission were measured using a Hamamatsu streak scope C4334 (Hamamatsu Photonics, Japan) with an excitation wavelength of 410 nm. The instrument response function (IRF) of the set up was obtained by directing the scattered pump light using a glass slide. The IRF recorded was ~400 ps

Graph extraction procedure from literature: The data files from literature were extracted using WebPlotDigitalizer (<https://apps.automeris.io/wpd/>)

Commercially available chemicals: Coumarin 522 dye used as a reference for emission quantum yield ($\Phi_{em.}$) experiments was purchased from Lambda Physik.

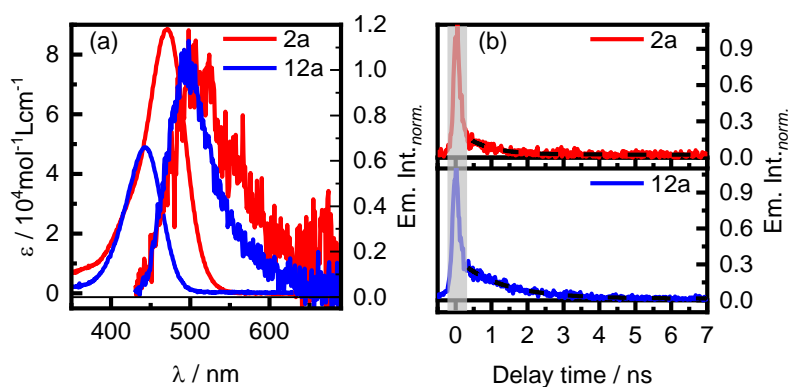


Figure S5 (a) Steady state absorption and emission spectra with 420 nm excitation of **2a** and **12a** in aerated MeOH-H₂O (v-v: 70%-30%). (b) Fluorescence lifetimes of **2a** and **12a** in aerated MeOH-H₂O (v-v: 70%-30%) with 410 nm excitation. The kinetics is averaged between 470 and 530 nm with the light grey highlight showing the instrumental response function (IRF) of ~400 ps.

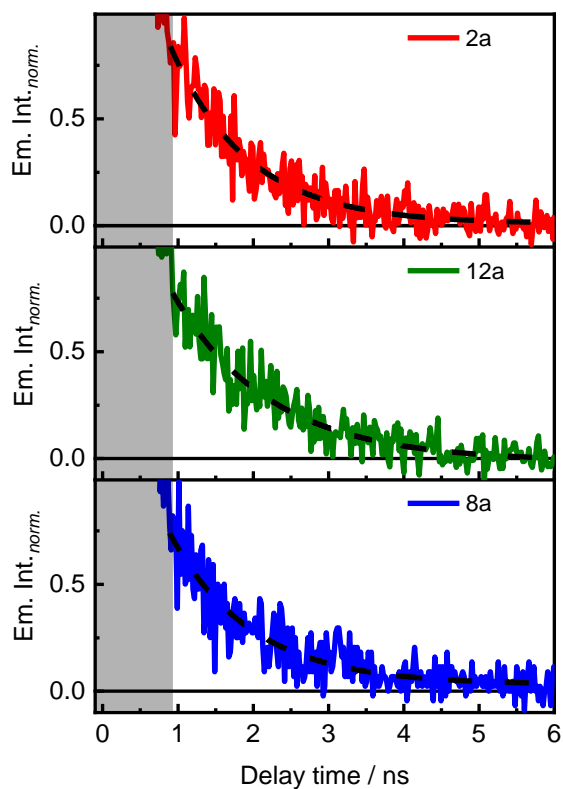


Figure S6 Fluorescence lifetimes of **2a**, **12a** and **8a** in aerated MeOH-H₂O (v-v: 70%-30%) in 100 mM ascorbic acid (AA) with 410 nm excitation. The kinetics is averaged between 470 and 530 nm and the instrument response function (IRF) is ~400 ps. The IRF is excluded from the figure due to high IRF intensity and low emission signal for all the PS. The emission intensity for all PS is instead normalized at 0.5 ns

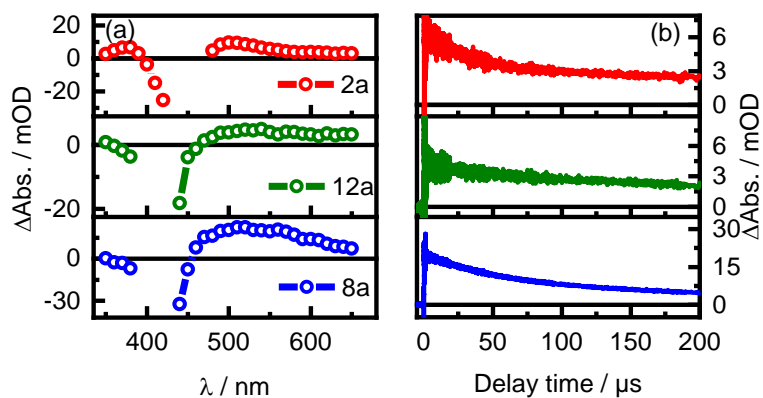


Figure S7 (a) ns-TA spectra with 420nm excitation of **2a**, **12a** and **8a** (averaged between 2 and 5 μ s) in deaerated tetrahydrofuran (THF) with (b) showing their respective TA kinetics (averaged between 500 and 600 nm).

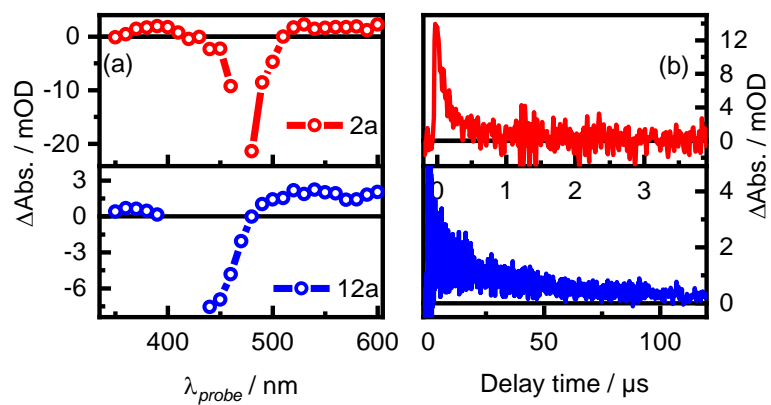


Figure S8 (a) Ns-TA spectra with 470 and 440 nm excitation of **2a** and **12a** (averaged between 2 and 5 μs) respectively in deaerated MeOH-H₂O (v-v: 70%-30%) with (b) showing their respective TA kinetics (averaged between 500 and 600 nm).

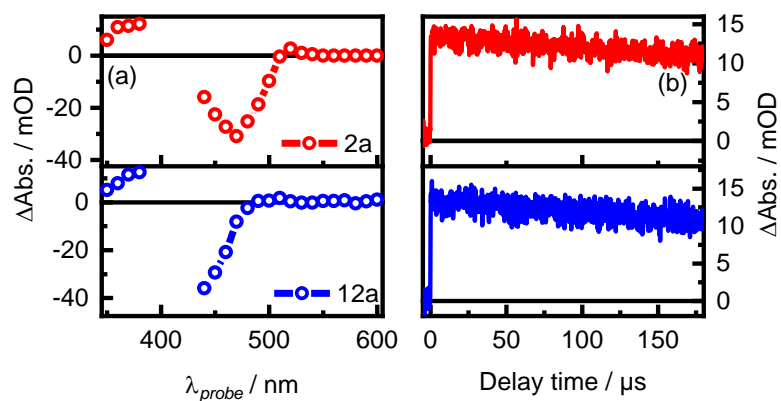


Figure S9 (a) Ns-TA spectra with 430 nm excitation of **2a** and **12a** (averaged between 2 and 5 μs) respectively in deaerated MeOH-H₂O (v-v: 70%-30%) in 100 mM ascorbic acid (AA) with (b) showing their respective TA kinetics (averaged between 340 and 390 nm).

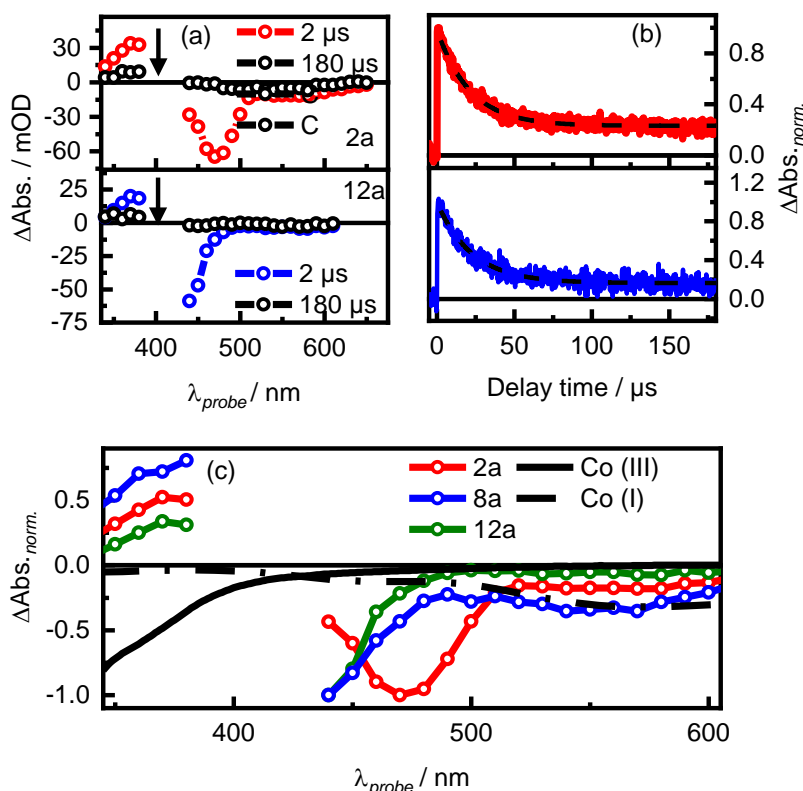


Figure S10 (a) Ns-TA spectra with 430 nm excitation of **2a** and **12a** at 2 and 180 μs in deaerated MeOH-H₂O (v-v: 70%-30%) in 100 mM ascorbic acid (AA) and 100 μM cobaloxime [Co(III)] catalyst with (b) showing their respective TA kinetics (averaged between 340 and 390 nm). (c) Ns-TA spectra of **2a**, **8a** and **12a** at 2 μs delay time in deaerated MeOH-H₂O (v-v: 70%-30%) in 100 mM ascorbic acid (AA) and 100 μM [Co(III)] catalyst showing a negative signal above 500 nm which corresponds to the formation of [Co(I)] during the [Co(I)] formed during the time course of the measurement. See explanation below. Inverted steady state spectra of [Co(III)] (in black) and [Co(I)] (in red) obtained by spectroelectrochemical reduction of [Co(III)]³. The inverted [Co(I)] spectra is extracted using WebPlotDigitalizer(<https://apps.automeris.io/wpd/>)

Formation of [Co(I)] species: A Ground State Bleach above 500 nm with a broad maxima at 550 nm is observed for all PS (Figure 1 and Figure S6). The feature resembles the absorption spectra of [Co(I)] generated by spectroelectrochemical reduction of [Co(III)]³⁻⁵. Surprisingly we observe this feature as a bleach rather than an ESA implying that the formed [Co(I)] could be stable during the experiment, accumulates and gets electronically excited by the pump pulse.

Compound	Φ _{1,4-dioxane} (%)	Φ _{MeOH} (%)	Φ _{MeOH-H₂O} (%)	Φ _{MeOH-H₂O-AA} (%)	τ _{MeOH-H₂O} (ns)	τ _{MeOH-H₂O-AA} (ns)
2a	2.0	0.13	0.07	0.04	0.8	0.8
12a	27.6	0.29	0.15	0.14	1.1	1.1
8a	1.5	0.92	0.54	0.56	1.2	1.2

Table S3 Fluorescence quantum yield (Φ) of the photosensitizers **2a**, **12a** and **8a** evaluated in aerated 1,4-dioxane, MeOH, MeOH-H₂O and MeOH-H₂O-AA with an excitation wavelength of 420 nm. The fluorescence quantum yield is determined by

using a laser dye, Coumarin 522 (C-522) as the standard. Φ_{C-522} in MeOH is 75.7% which is evaluated by using an integrated sphere with an excitation wavelength of 420 nm. For all PS an absorbance between 0.04-0.065 is maintained at the excitation wavelength. Fluorescence emission lifetime (τ) in aerated MeOH-H₂O and MeOH-H₂O-AA is collected with an excitation wavelength of 410 nm. An absorbance of 0.2 for all PS is maintained at the excitation wavelength. AA: Ascorbic acid, [AA]:100 mM. Φ is determined using the equation $\Phi_s = \Phi_r \frac{I_s}{I_r} \cdot \frac{Abs_r}{Abs_s} \cdot \frac{\eta_r^2}{\eta_s^2}$ where Φ_s and Φ_r are the fluorescence quantum yield of the sample and the reference respectively, I_s and I_r are the integrated fluorescence intensity of the sample and the reference respectively, Abs_r and Abs_s are the absorbance at the excitation wavelength of the reference and the sample respectively, η_r and η_s are the refractive indices of the reference and the sample respectively.

5. Apparent quantum yield calculations

All reactions were performed in a modular photoreactor, where photon flux with 1, 4 and 8 holders were already reported. For most experiments we used a 10 holder, so based on their data acquired with actinometry we downscaled their flux to 350 mA with the UV lamp fitted a Gaussian curve on their data and extrapolated their photon flux numbers for X=60 mm (the vial position in the 10 holder).

Position (mm) (X)	Photon flux (Y)
0 (1 holder)	118.6
24 (4 holder)	110.8
46.4 (8 holder)	62.8
-24	110.8
-46.4	62.8

Table S4 Recalibrated photon fluxes for 350 mA UV lamp

Gaussian equation: $Y = 125.4034 * e^{-(X - 3.286935e-7)^2 / (2 * 40.5638^2)}$

Solving for X=60, we get a photon flux of 42 nmol/s for vials in the 10 holder

Initial irradiation experiments for 20h resulted in $42 * 60 * 60 * 20 = 3$ mmol UV photons absorbed per vial. For blue lamp, they reported only values for the 8 holder (111 nmol/s), using the same dropratio from 8 to 10 holder, we get 74 nmol/s blue photons absorbed per vial, so 5.3 mmol during the experiment. This corresponds to the following apparent quantum yield for each photosensitizer system:

dye	H ₂ (nmol)	Quantum Yield (%)	dye	H ₂ (nmol)	Quantum Yield (%)
1a	1020	0.068	1b	1945	0.130
2a	769	0.051	2b	3635	0.242
3a	671	0.045	3b	10	0.001
4a	819	0.055	4b	3220	0.215
5a	1171	0.078	5b	2085	0.139
6a	870	0.058	6b	389	0.026
7a	307	0.020	7b	722	0.048
8a	3821	0.255	8b	2349	0.157
9a	1150	0.077	9b	2423	0.162
10a	1049	0.070	10b	1538	0.103
11a	-	-	11b	1296	0.086
12a	1653	0.110	12b	3955	0.264
13a	1077	0.041	13b	3325	0.222

Table S5 Apparent quantum yield for each photoreaction

6. Electrochemistry

Cyclic voltammetry and differential pulse voltammetry measurements were recorded with a PalmSens4 Potentiostat device. A 0.1 M solution of *n*-Bu₄NPF₆ in dry and deaerated CH₃CN was prepared and the ketocoumarins were dissolved in this to have approximately 0.5 – 2 mM concentration. A silver wire electrode was used as reference electrode, and after measuring the compounds, ferrocene was added as internal standard to be remeasured again. Graphs measured without ferrocene were shifted to the middle point of ferrocene.

	Positive directional DPV		Negative directional DPV			Positive directional DPV		Negative directional DPV	
	E _{red} (V)	E _{ox} (V)	E _{red} (V)	E _{ox} (V)		E _{red} (V)	E _{ox} (V)	E _{red} (V)	E _{ox} (V)
1a	-1.85	0.68	-1.77	0.70	1b	-1.71	1.43	-1.64	1.43
2a	-1.75	0.73	-1.74	0.71	2b	-1.61	1.47	-1.55	1.54
3a	-2.29	0.73	-2.53	0.76	3b	-1.55	1.51	-1.23	1.60
	-1.65		-1.71					-1.63	
	-1.32		-1.28					-2.23	
4a		0.67	-1.61	0.77	4b		1.47	-1.51	1.48
5a	-1.87	0.64	-1.83	0.71	5b	-1.76	1.45	-1.86	
6a	-1.96	0.71	-1.91	0.76	6b	-1.80	0.66	-1.90	
							1.54		
7a	-1.77	0.68	-1.70	0.74	7b	-1.67	1.48	-1.76	
8a	-1.86	0.67	-1.81	0.77	8b	-1.74	1.10	-1.79	
		1.20		1.22			1.72		
9a		0.74	-1.62	0.74	9b	-1.61	1.44	-1.58	
10a	-1.81	0.69	-1.74	0.68	10b	-1.69	1.45	-1.76	
11a	-1.71	0.76	-1.71	0.82	11b	-1.56	1.87	-1.76	
12a	-1.77	0.74	-1.70	0.76	12b	-1.54	1.43	-1.61	1.71
13a		0.72	-1.61	0.77	13b	-1.88	1.41	-1.46	

Table S6 positive and negative directional DPV peaks of ketocoumarin measurements of 0,5-2,0 mM sample concentrations in 0.1 M solution of *n*-Bu₄NPF₆ in dry and deaerated CH₃CN vs. Fc⁺/Fc⁰ with 0.1 V/s scan rate (0.01 V steps, pulse: 0.2 V, 0.02 sec)

7. Photocatalytic activity, absorbance spectrum and electrochemical properties

7.1. 3-benzoyl-7-(diethylamino)-2H-chromen-2-one (1a)

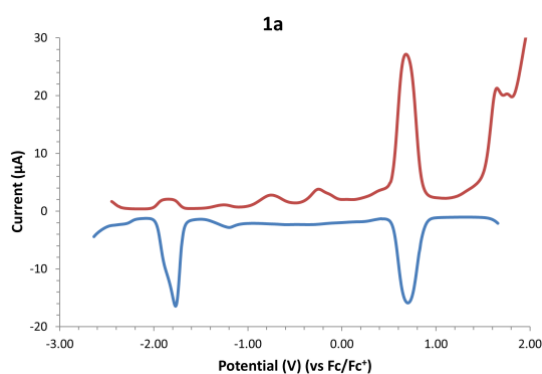
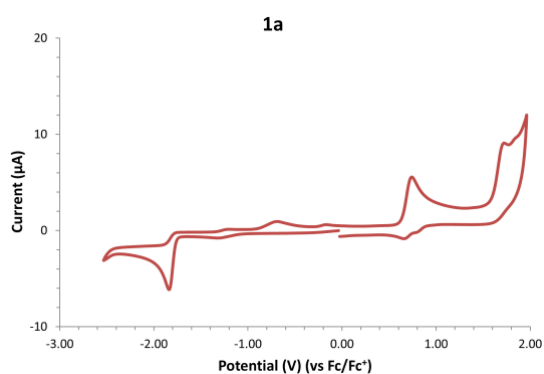
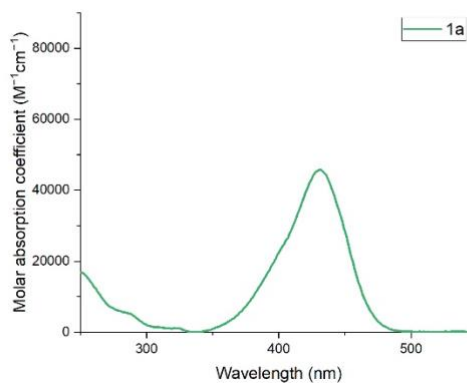
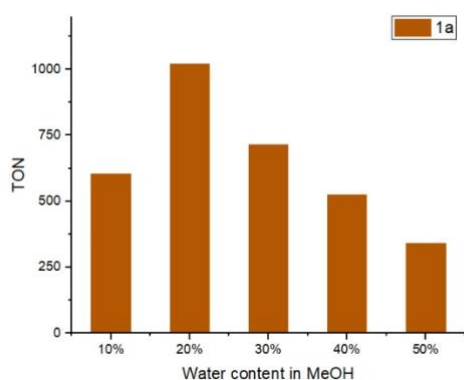
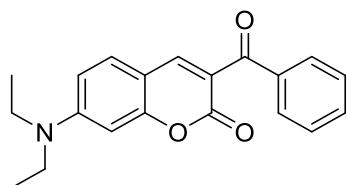


Figure S11 Top left: Turnover numbers of cobaloxime catalyst in different amount of water content in MeOH Top right: absorption spectrum of ketocoumarin **1a** Bottom: cyclic voltammety (left) and differential pulse voltammety (right, red: positive direction, blue: negative direction) measurements (0.1 M solution of $n\text{-Bu}_4\text{NPF}_6$ in dry and deaerated CH_3CN vs. Fc^+/Fc with 0.1 V/s scan rate).

7.2. 3-benzoyl-7-methoxy-2H-chromen-2-one (1b)

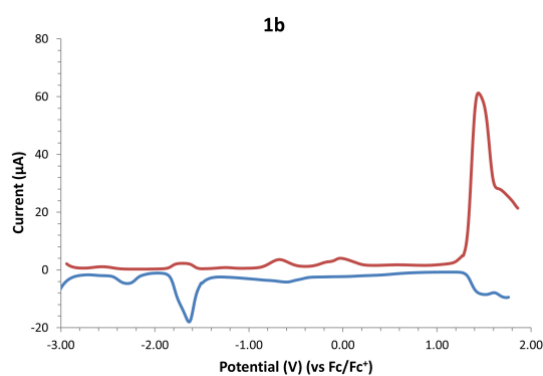
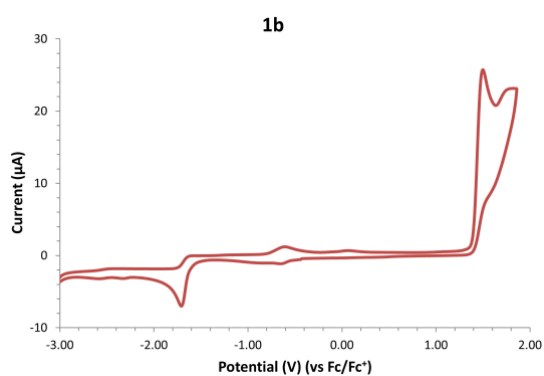
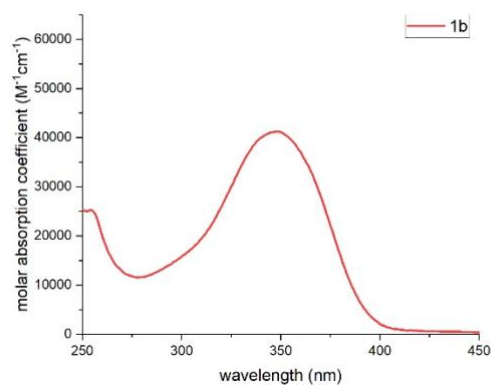
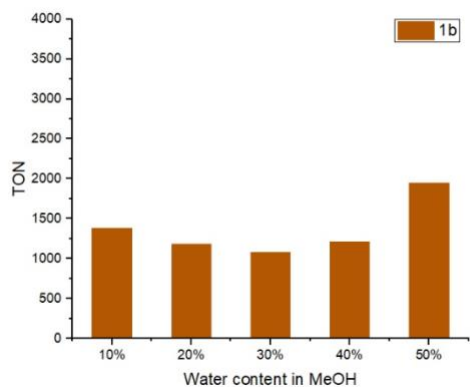
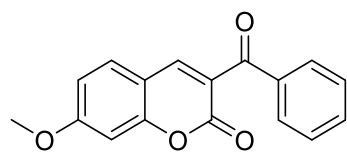


Figure S12 Top left: Turnover numbers of cobaloxime catalyst in different amount of water content in MeOH Top right: absorption spectrum of ketocoumarin **1b** Bottom: cyclic voltammety (left) and differential pulse voltammety (right, red: positive direction, blue: negative direction) measurements (0.1 M solution of $n\text{-Bu}_4\text{NPF}_6$ in dry and deaerated CH_3CN vs. Fc^+/Fc with 0.1 V/s scan rate).

7.3. 7-(diethylamino)-3-(4-(trifluoromethyl)benzoyl)-2H-chromen-2-one (2a)

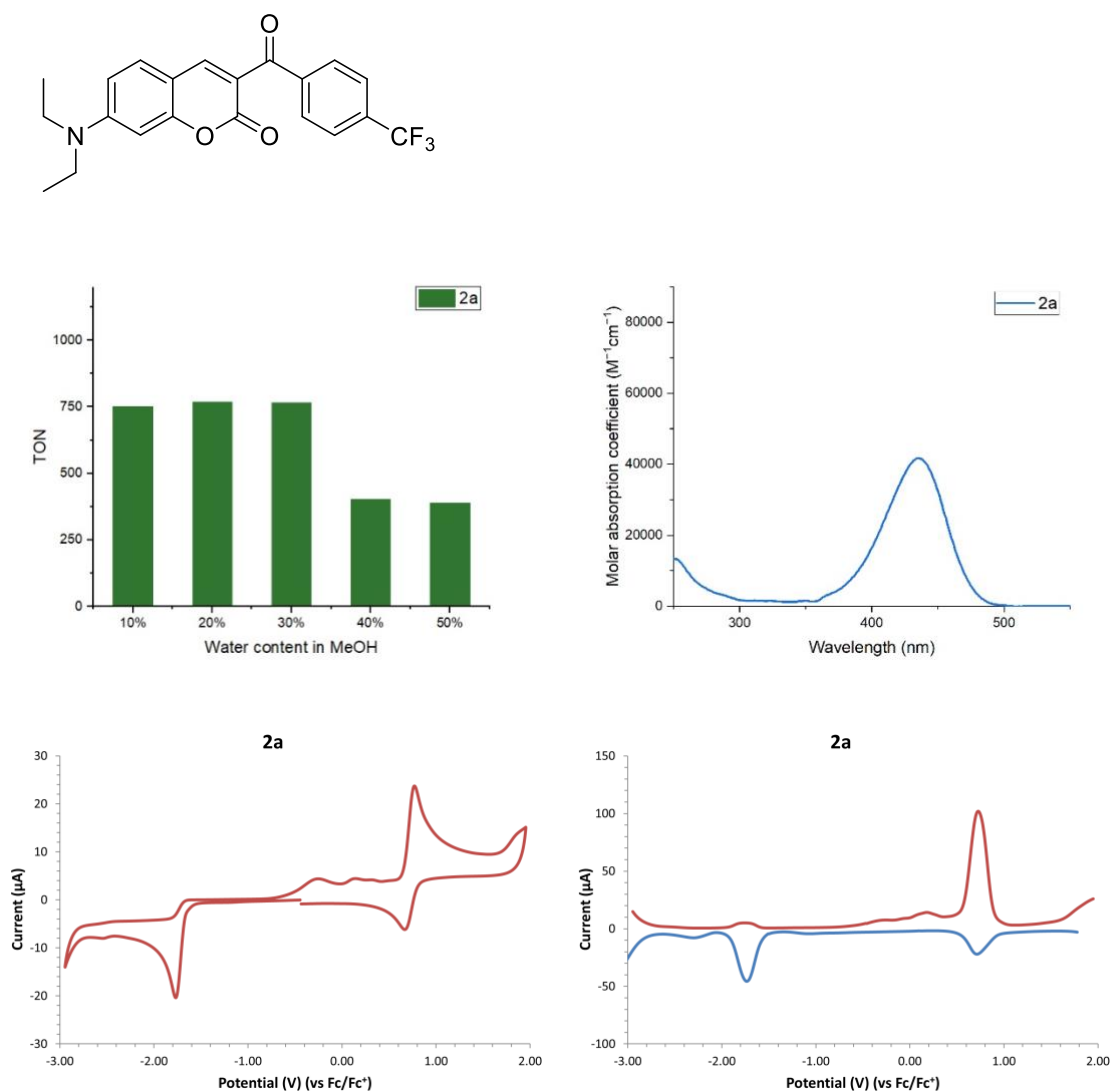


Figure S13 Top left: Turnover numbers of cobaloxime catalyst in different amount of water content in MeOH Top right: absorption spectrum of ketocoumarin **2a** Bottom: cyclic voltammery (left) and differential pulse voltammery (right, red: positive direction, blue: negative direction) measurements (0.1 M solution of $n-Bu_4NPF_6$ in dry and deaerated CH_3CN vs. Fc^+/Fc with 0.1 V/s scan rate).

7.4. 7-methoxy-3-(4-(trifluoromethyl)benzoyl)-2H-chromen-2-one (2b)

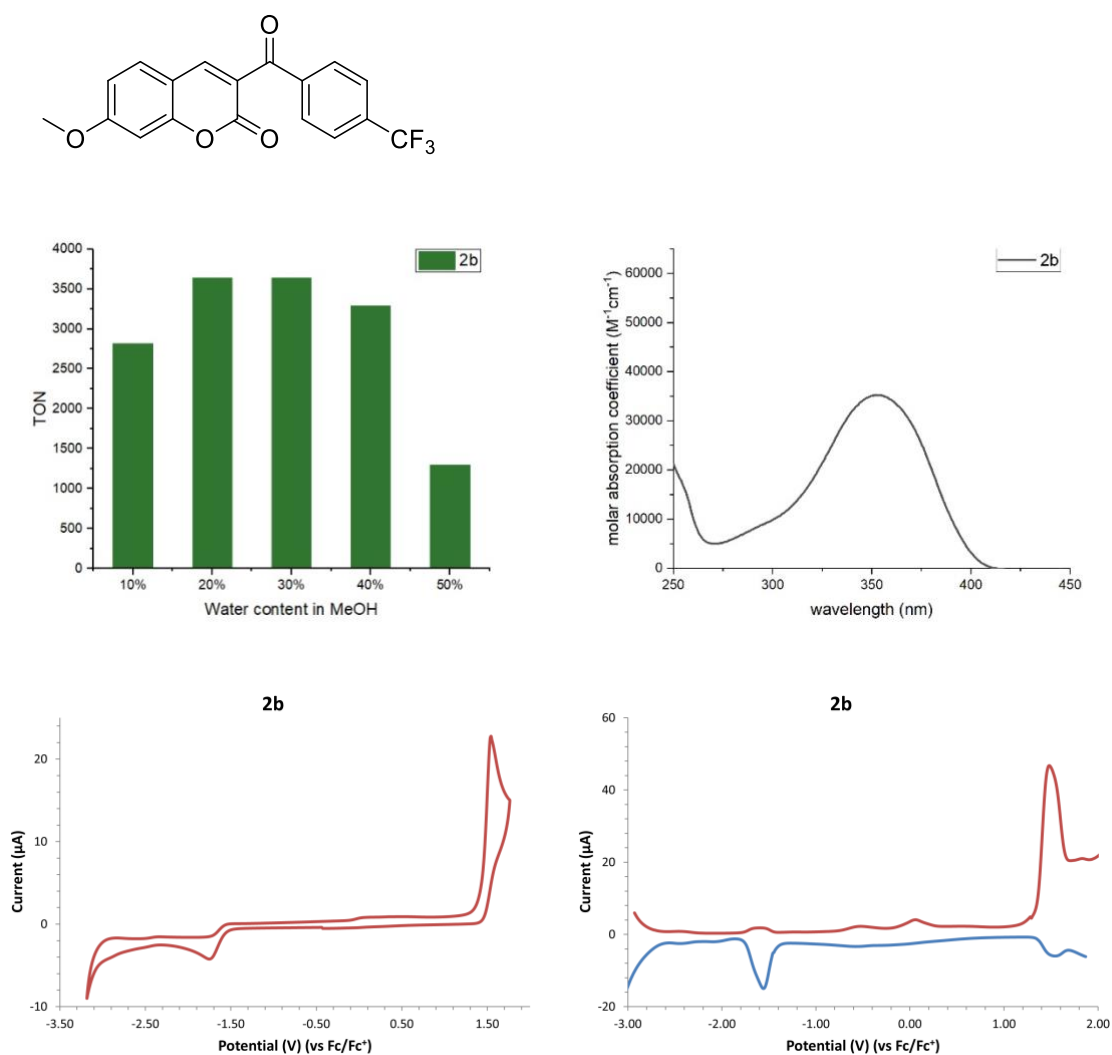


Figure S14 Top left: Turnover numbers of cobaloxime catalyst in different amount of water content in MeOH Top right: absorption spectrum of ketocoumarin **2b** Bottom: cyclic voltammety (left) and differential pulse voltammety (right, red: positive direction, blue: negative direction) measurements (0.1 M solution of n-Bu₄NPF₆ in dry and deaerated CH₃CN vs. Fc⁺/Fc with 0.1 V/s scan rate).

7.5. 7-(diethylamino)-3-(4-nitrobenzoyl)-2H-chromen-2-one (**3a**)

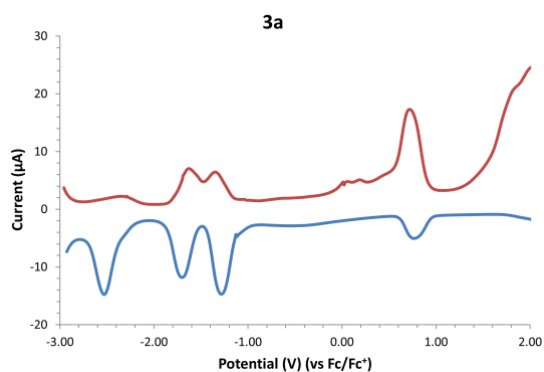
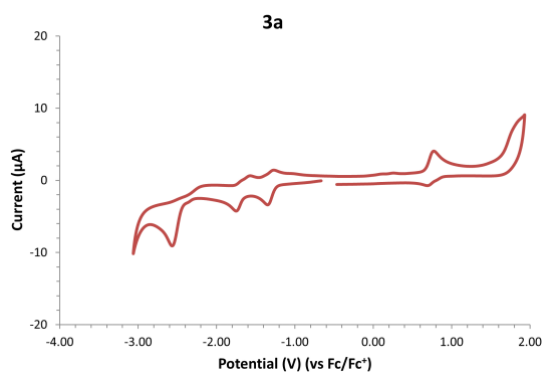
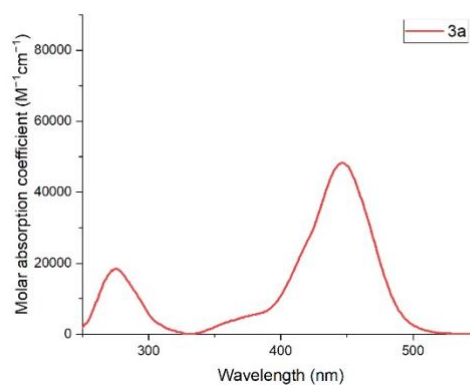
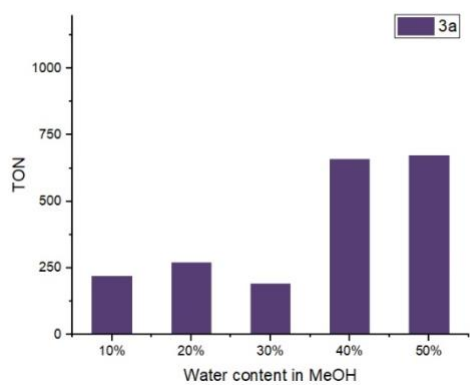
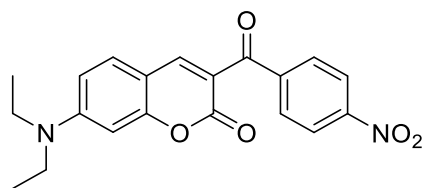


Figure S15 Top left: Turnover numbers of cobaloxime catalyst in different amount of water content in MeOH Top right: absorption spectrum of ketocoumarin **3a** Bottom: cyclic voltammetry (left) and differential pulse voltammetry (right, red: positive direction, blue: negative direction) measurements (0.1 M solution of $n\text{-Bu}_4\text{NPF}_6$ in dry and deaerated CH_3CN vs. Fc^+/Fc with 0.1 V/s scan rate).

7.6. 7-methoxy-3-(4-nitrobenzoyl)-2H-chromen-2-one (3b)

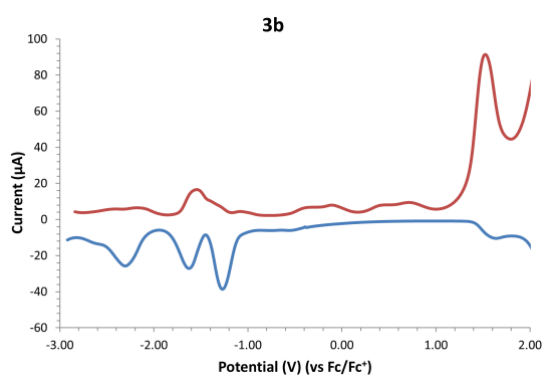
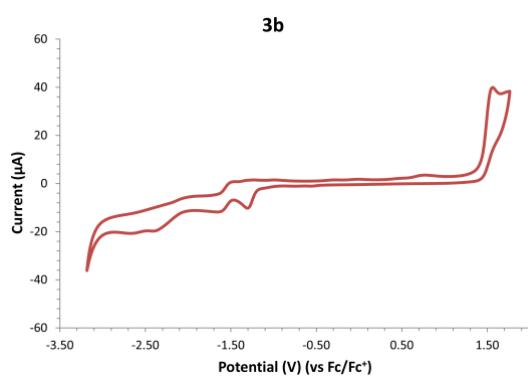
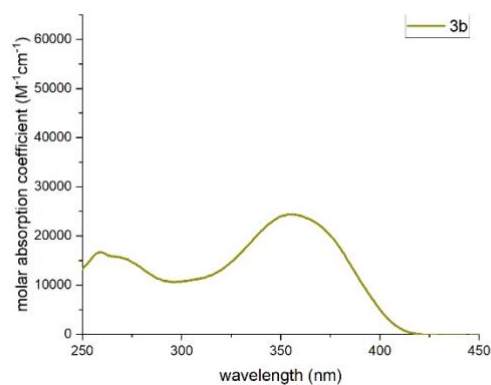
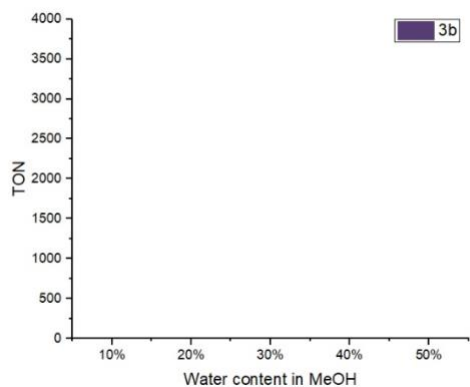
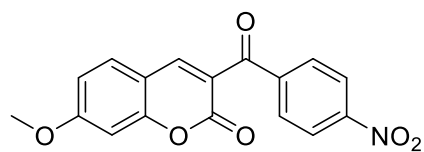


Figure S16 Top left: Turnover numbers of cobaloxime catalyst in different amount of water content in MeOH Top right: absorption spectrum of ketocoumarin **3b** Bottom: cyclic voltammety (left) and differential pulse voltammety (right, red: positive direction, blue: negative direction) measurements (0.1 M solution of $n\text{-Bu}_4\text{NPF}_6$ in dry and deaerated CH_3CN vs. Fc^+/Fc with 0.1 V/s scan rate).

7.7. 4-(7-(diethylamino)-2-oxo-2H-chromene-3-carbonyl)benzonitrile (**4a**)

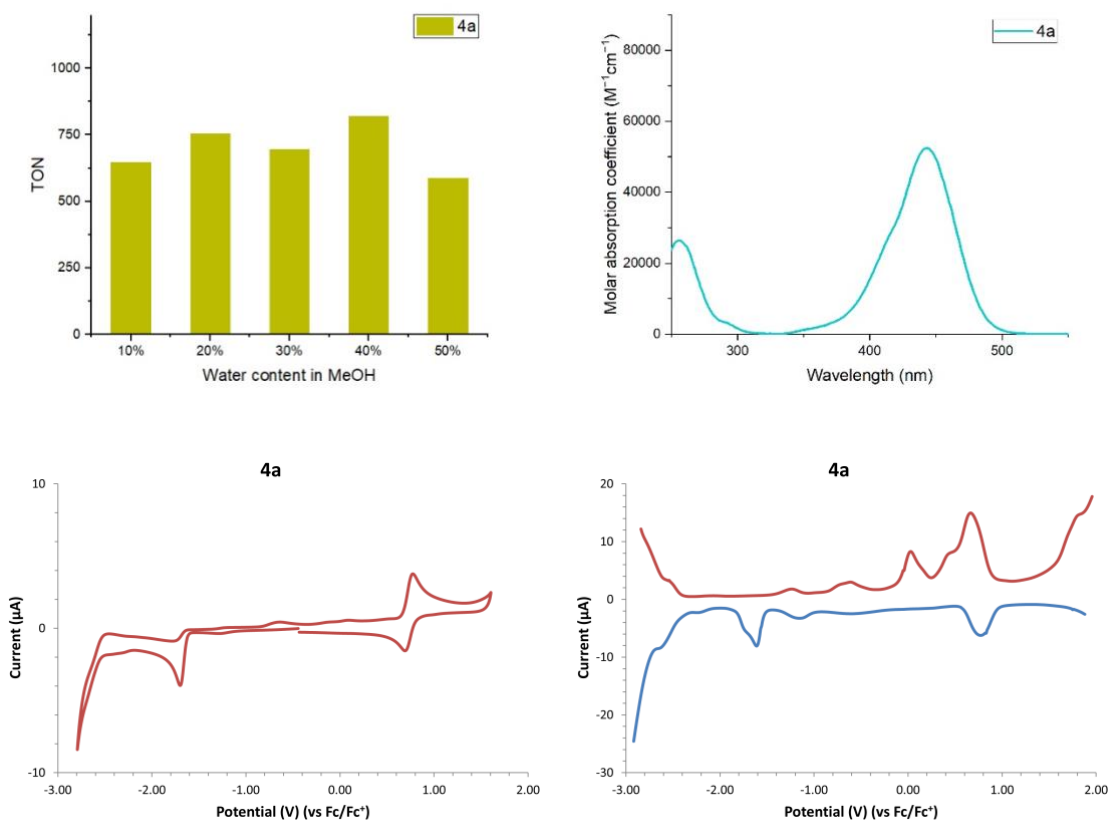
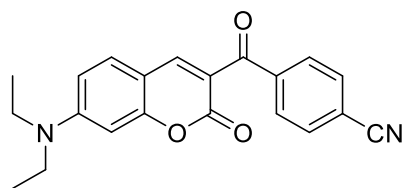


Figure S17 Top left: Turnover numbers of cobaloxime catalyst in different amount of water content in MeOH Top right: absorption spectrum of ketocoumarin **4a** Bottom: cyclic voltammery (left) and differential pulse voltammery (right, red: positive direction, blue: negative direction) measurements (0.1 M solution of $n-Bu_4NPF_6$ in dry and deaerated CH_3CN vs. Fc^+/Fc with 0.1 V/s scan rate).

7.8. 4-(7-methoxy-2-oxo-2H-chromene-3-carbonyl)benzotrile (4b)

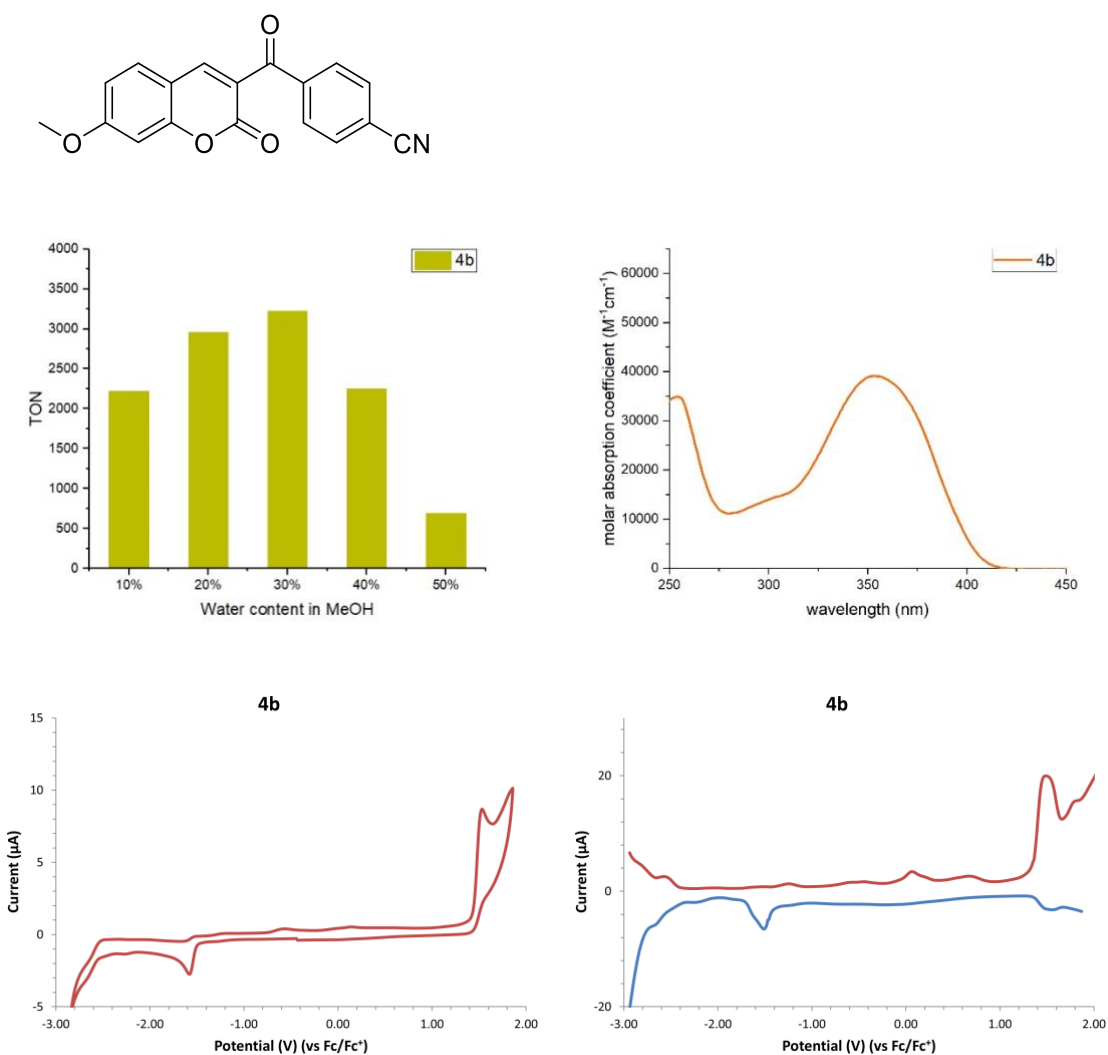


Figure S18 Top left: Turnover numbers of cobaloxime catalyst in different amount of water content in MeOH Top right: absorption spectrum of ketocoumarin **4b** Bottom: cyclic voltammetry (left) and differential pulse voltammetry (right, red: positive direction, blue: negative direction) measurements (0.1 M solution of n-Bu₄NPF₆ in dry and deaerated CH₃CN vs. Fc⁺/Fc with 0.1 V/s scan rate).

7.9. 7-(diethylamino)-3-(4-methoxybenzoyl)-2H-chromen-2-one (5a)

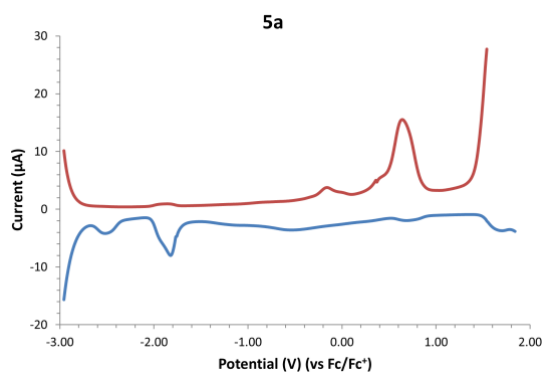
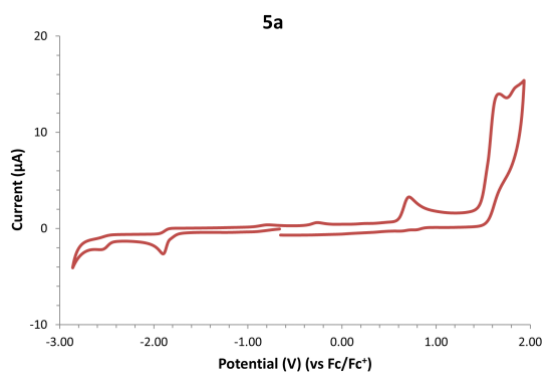
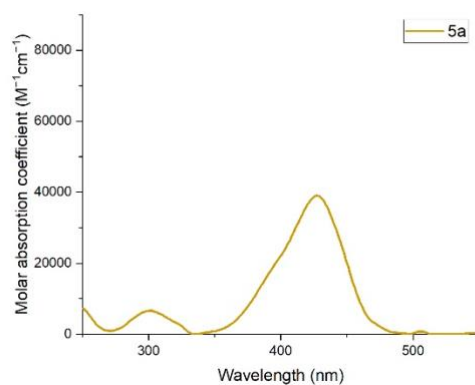
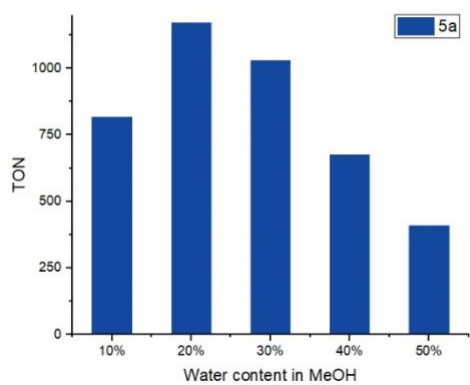
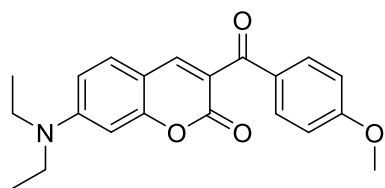


Figure S19 Top left: Turnover numbers of cobaloxime catalyst in different amount of water content in MeOH Top right: absorption spectrum of ketocoumarin **5a** Bottom: cyclic voltammetry (left) and differential pulse voltammetry (right, red: positive direction, blue: negative direction) measurements (0.1 M solution of $n\text{-Bu}_4\text{NPF}_6$ in dry and deaerated CH_3CN vs. Fc^+/Fc with 0.1 V/s scan rate).

7.10. 7-methoxy-3-(4-methoxybenzoyl)-2H-chromen-2-one (**5b**)

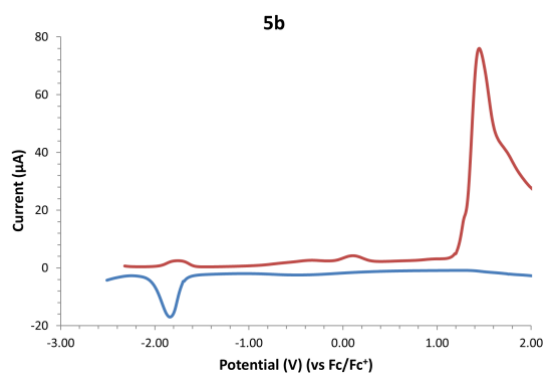
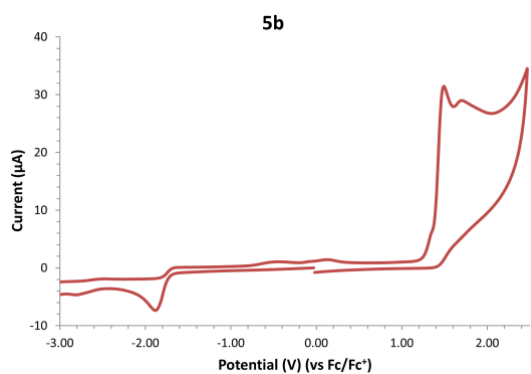
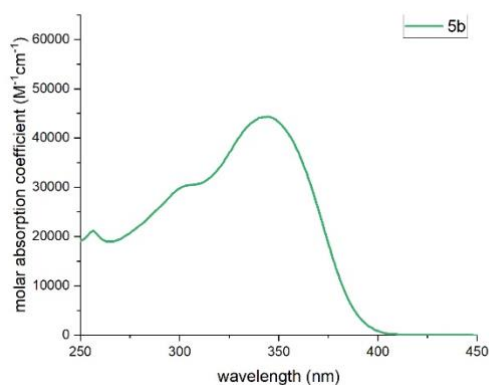
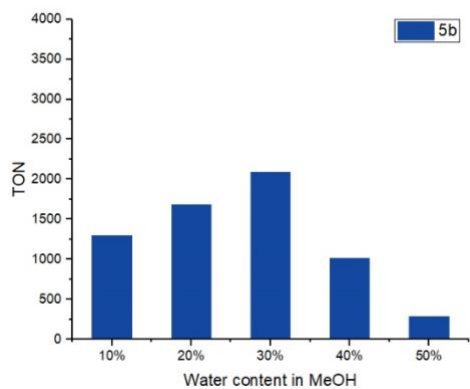
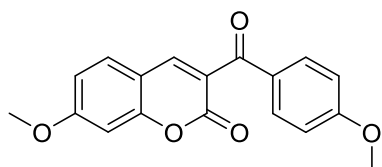


Figure S20 Top left: Turnover numbers of cobaloxime catalyst in different amount of water content in MeOH Top right: absorption spectrum of ketocoumarin **5b** Bottom: cyclic voltammetry (left) and differential pulse voltammetry (right, red: positive direction, blue: negative direction) measurements (0.1 M solution of $n\text{-Bu}_4\text{NPF}_6$ in dry and deaerated CH_3CN vs. Fc^+/Fc with 0.1 V/s scan rate).

7.11. 7-(diethylamino)-3-(4-(dimethylamino)benzoyl)-2H-chromen-2-one (6a)

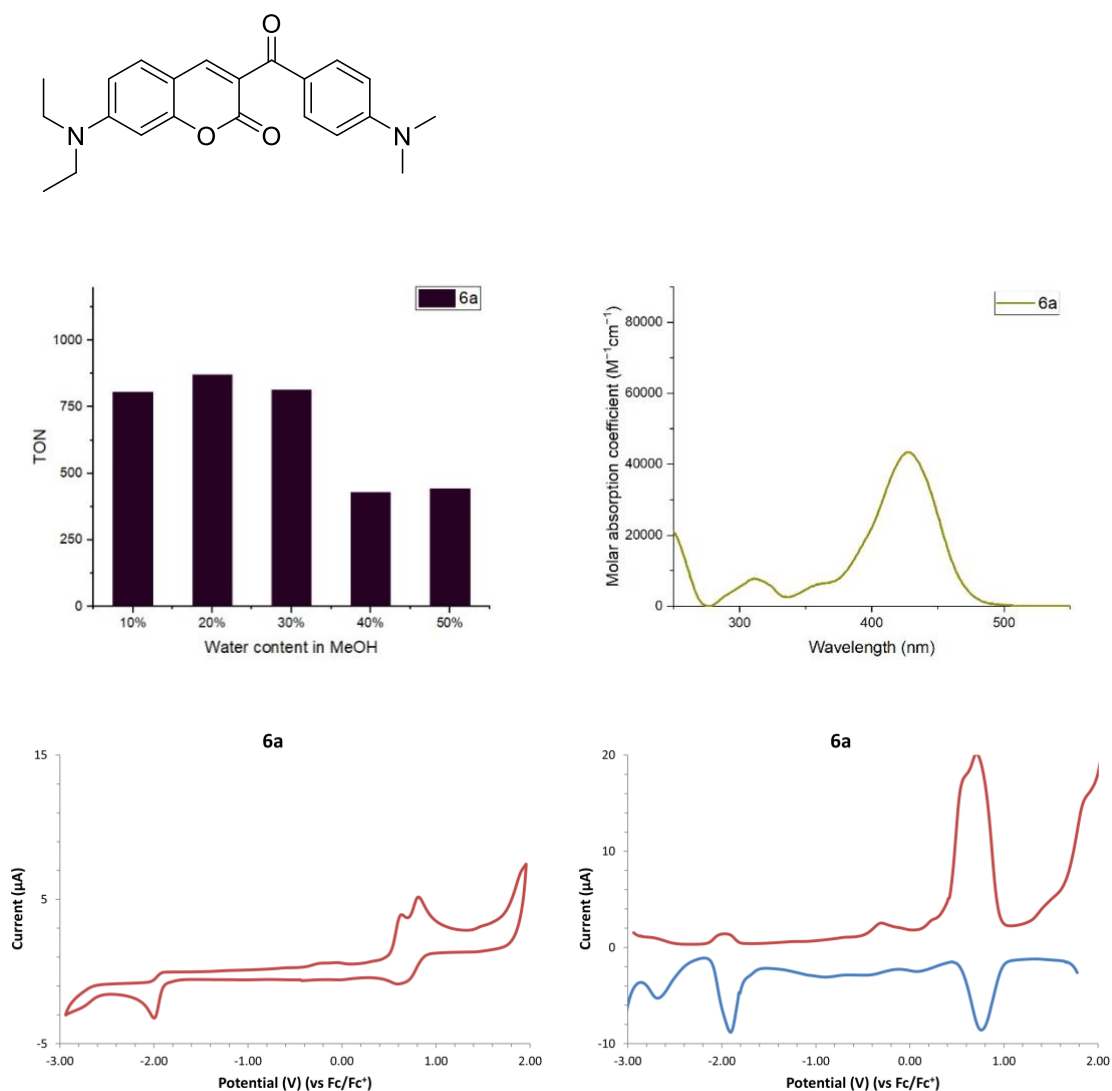


Figure S21 Top left: Turnover numbers of cobaloxime catalyst in different amount of water content in MeOH Top right: absorption spectrum of ketocoumarin **6a** Bottom: cyclic voltammery (left) and differential pulse voltammery (right, red: positive direction, blue: negative direction) measurements (0.1 M solution of n-Bu₄NPF₆ in dry and deaerated CH₃CN vs. Fc⁺/Fc with 0.1 V/s scan rate).

7.12. 3-(4-(dimethylamino)benzoyl)-7-methoxy-2H-chromen-2-one (6b)

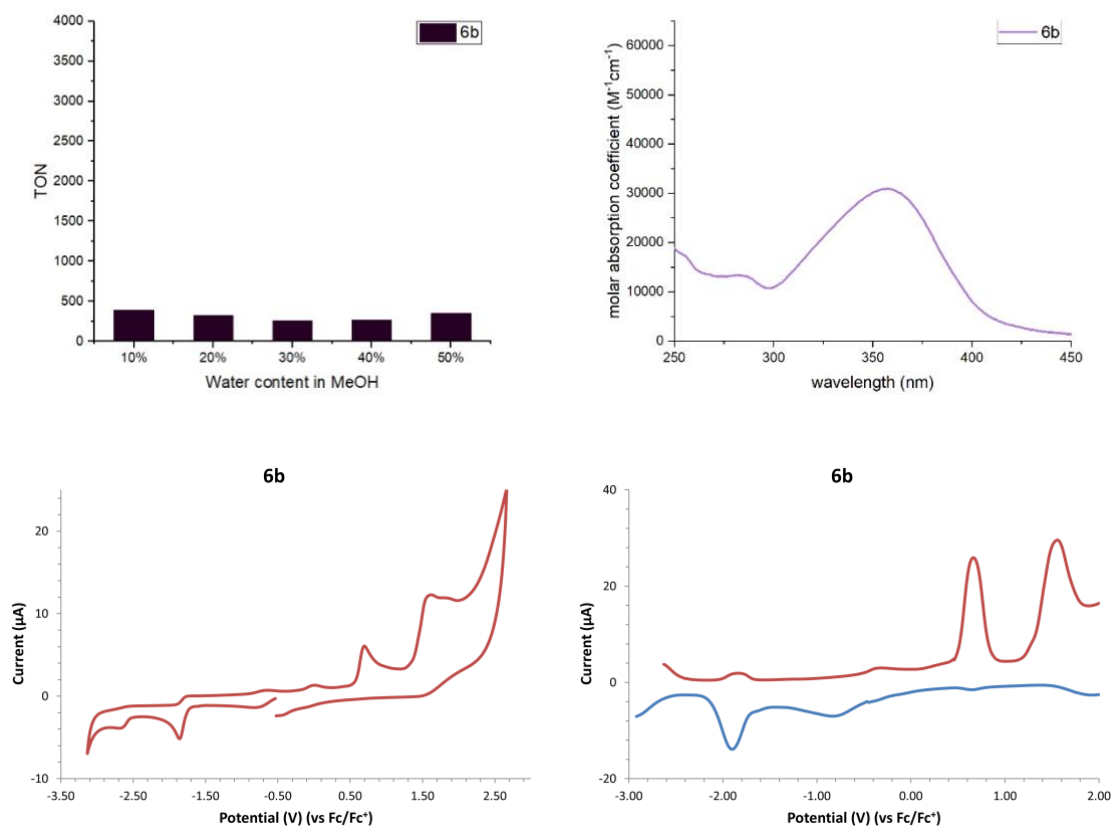
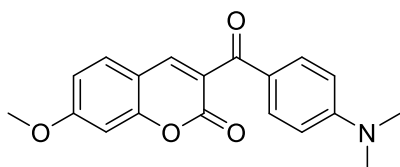


Figure S22 Top left: Turnover numbers of cobaloxime catalyst in different amount of water content in MeOH Top right: absorption spectrum of ketocoumarin 6b Bottom: cyclic voltammery (left) and differential pulse voltammery (right, red: positive direction, blue: negative direction) measurements (0.1 M solution of n-Bu₄NPF₆ in dry and deaerated CH₃CN vs. Fc⁺/Fc with 0.1 V/s scan rate).

7.13. 3-(4-bromobenzoyl)-7-(diethylamino)-2H-chromen-2-one (7a)

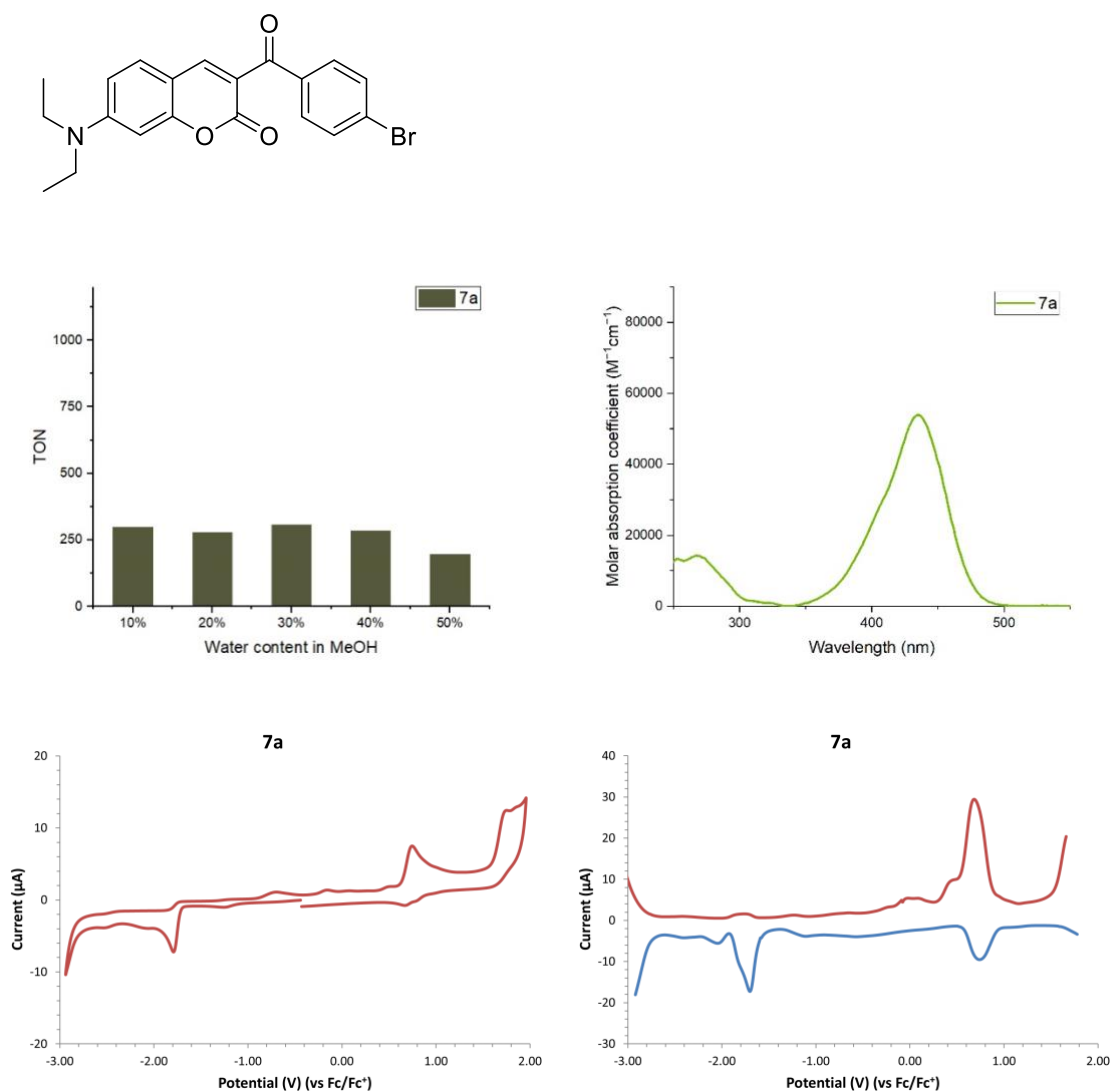


Figure S23 Top left: Turnover numbers of cobaloxime catalyst in different amount of water content in MeOH Top right: absorption spectrum of ketocoumarin **7a** Bottom: cyclic voltammetry (left) and differential pulse voltammometry (right, red: positive direction, blue: negative direction) measurements (0.1 M solution of n-Bu₄NPF₆ in dry and deaerated CH₃CN vs. Fc⁺/Fc with 0.1 V/s scan rate).

7.14. 3-(4-bromobenzoyl)-7-methoxy-2H-chromen-2-one (7b)

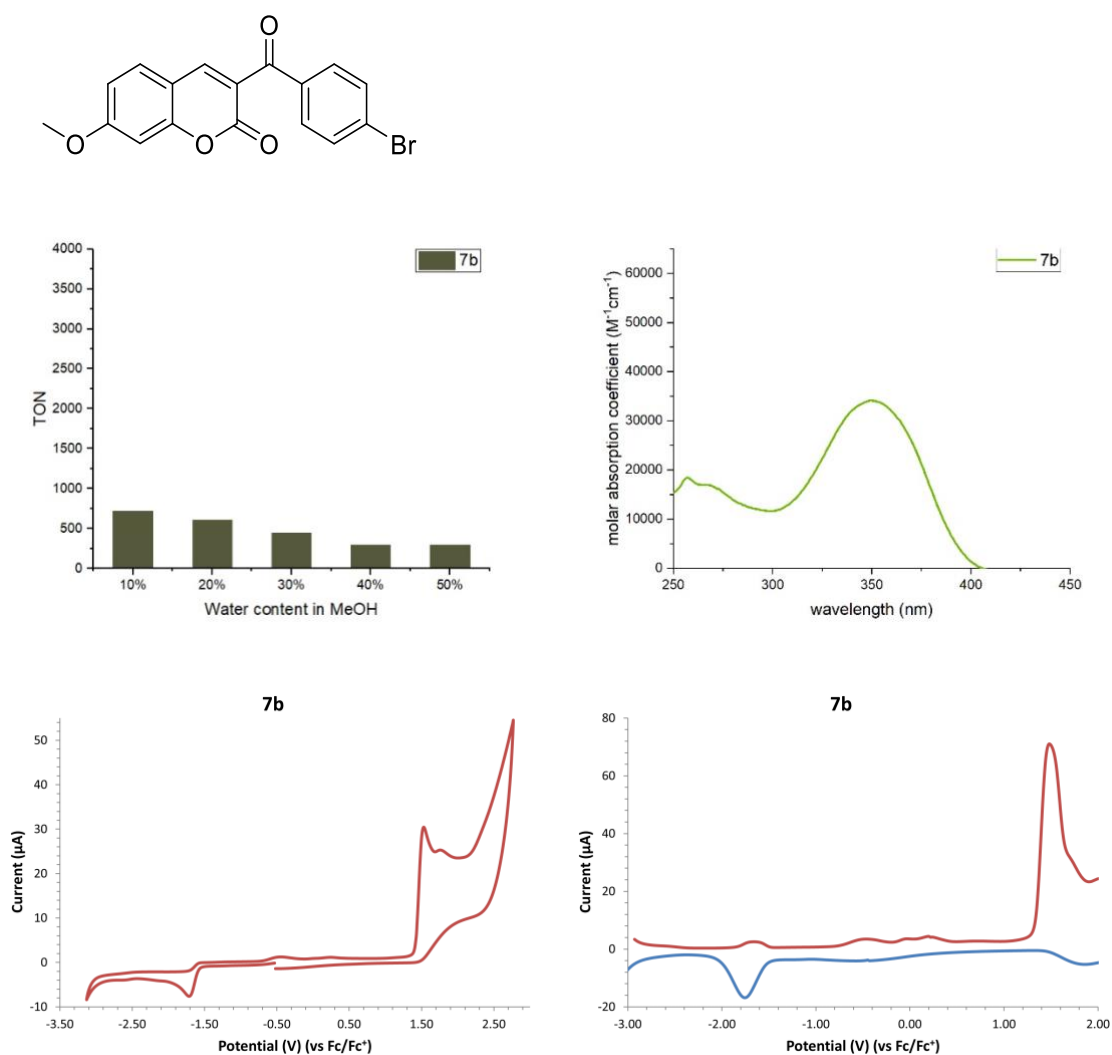


Figure S24 Top left: Turnover numbers of cobaloxime catalyst in different amount of water content in MeOH Top right: absorption spectrum of ketocoumarin **7b** Bottom: cyclic voltammety (left) and differential pulse voltammety (right, red: positive direction, blue: negative direction) measurements (0.1 M solution of n-Bu₄NPF₆ in dry and deaerated CH₃CN vs. Fc⁺/Fc with 0.1 V/s scan rate).

7.15. 7-(diethylamino)-3-(3,4,5-trimethoxybenzoyl)-2H-chromen-2-one (**8a**)

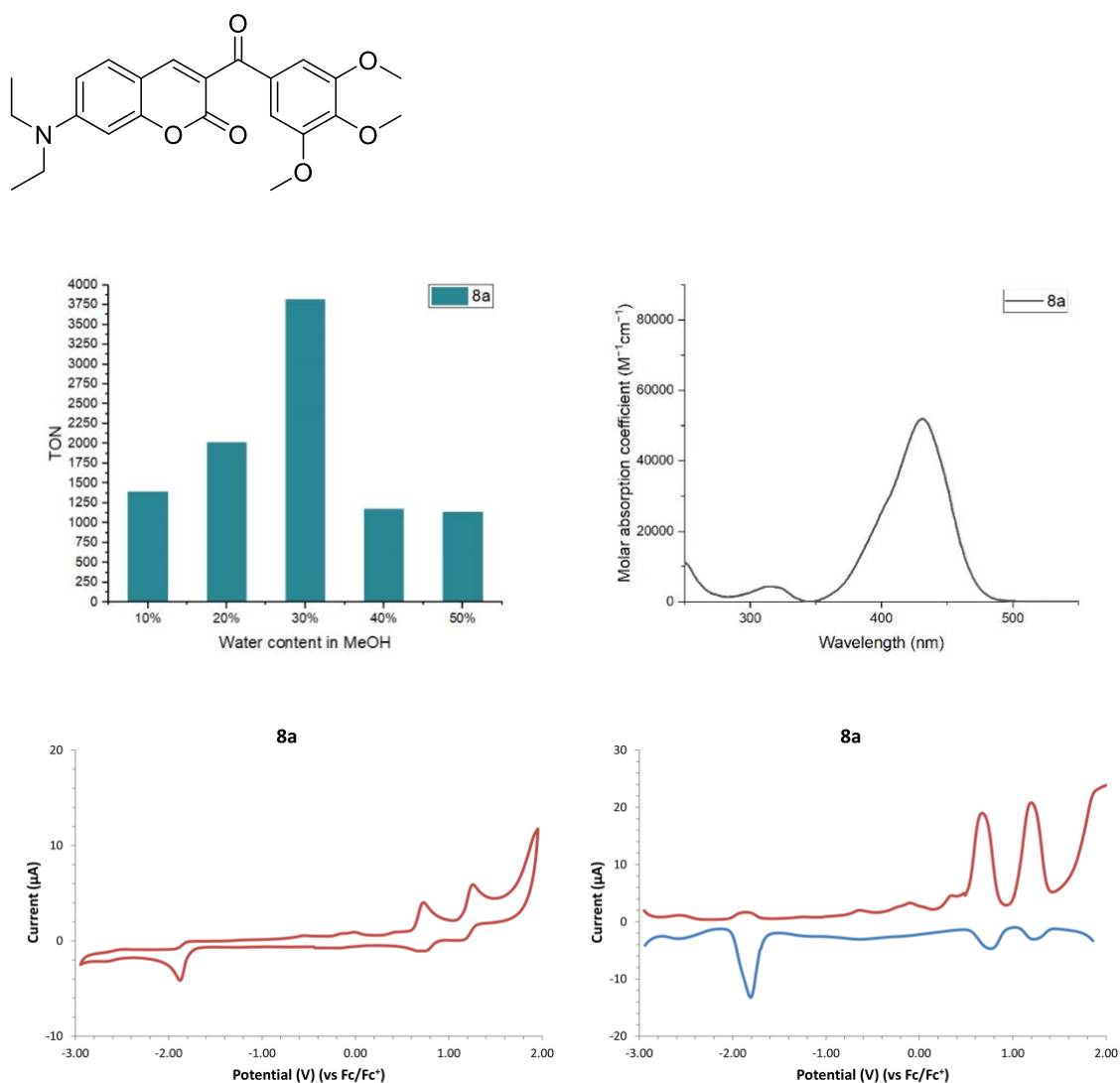


Figure S25 Top left: Turnover numbers of cobaloxime catalyst in different amount of water content in MeOH Top right: absorption spectrum of ketocoumarin **8a** Bottom: cyclic voltammetry (left) and differential pulse voltammetry (right, red: positive direction, blue: negative direction) measurements (0.1 M solution of $n-Bu_4NPF_6$ in dry and deaerated CH_3CN vs. Fc^+/Fc with 0.1 V/s scan rate).

7.16. 7-methoxy-3-(3,4,5-trimethoxybenzoyl)-2H-chromen-2-one (**8b**)

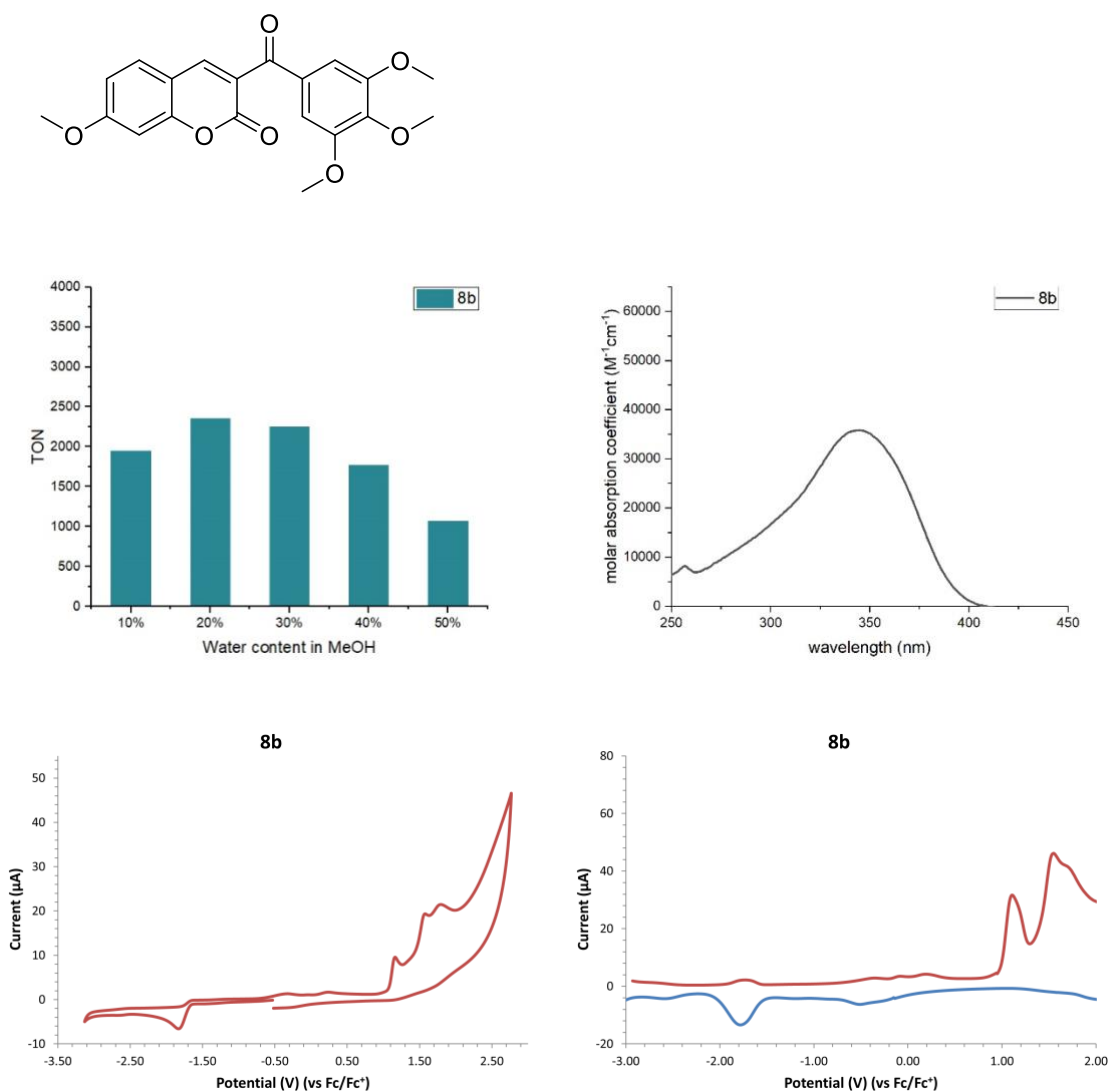


Figure S26 Top left: Turnover numbers of cobaloxime catalyst in different amount of water content in MeOH Top right: absorption spectrum of ketocoumarin **8b** Bottom: cyclic voltammety (left) and differential pulse voltammety (right, red: positive direction, blue: negative direction) measurements (0.1 M solution of $n-Bu_4NPF_6$ in dry and deaerated CH_3CN vs. Fc^+/Fc with 0.1 V/s scan rate).

7.17. 3-(benzofuran-2-carbonyl)-7-(diethylamino)-2H-chromen-2-one (9a)

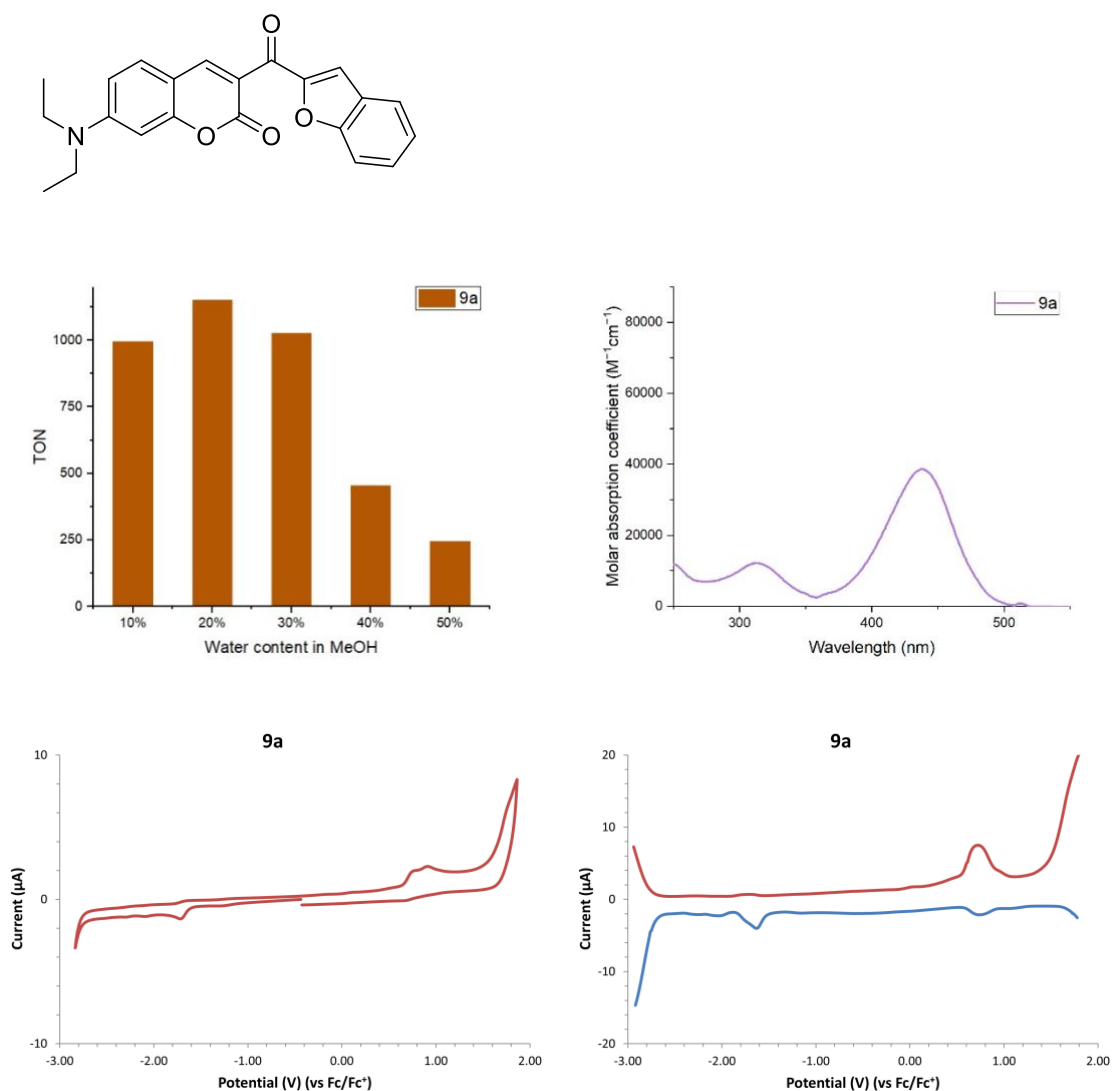


Figure S27 Top left: Turnover numbers of cobaloxime catalyst in different amount of water content in MeOH Top right: absorption spectrum of ketocoumarin **9a** Bottom: cyclic voltammetry (left) and differential pulse voltammetry (right, red: positive direction, blue: negative direction) measurements (0.1 M solution of $n\text{-Bu}_4\text{NPF}_6$ in dry and deaerated CH_3CN vs. Fc^+/Fc with 0.1 V/s scan rate).

7.18. 3-(benzofuran-2-carbonyl)-7-methoxy-2H-chromen-2-one (**9b**)

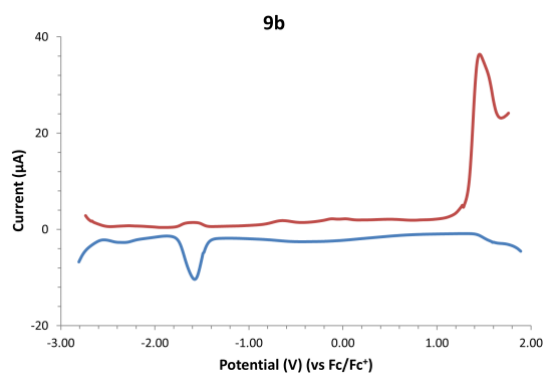
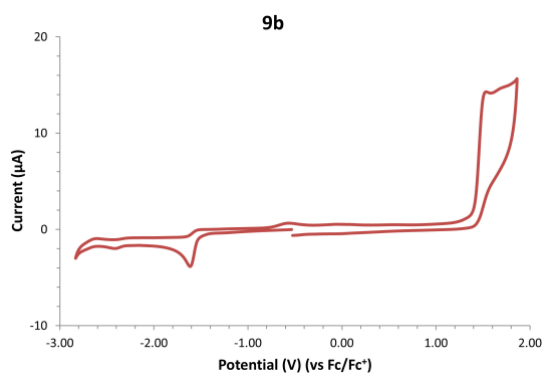
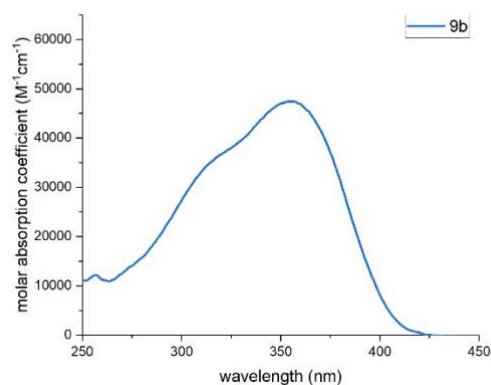
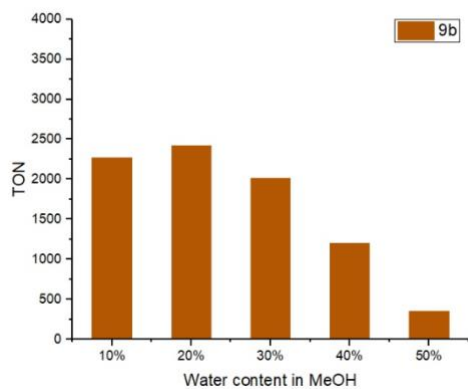
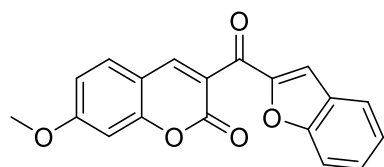


Figure S28 Top left: Turnover numbers of cobaloxime catalyst in different amount of water content in MeOH Top right: absorption spectrum of ketocoumarin **9b** Bottom: cyclic voltammetry (left) and differential pulse voltammetry (right, red: positive direction, blue: negative direction) measurements (0.1 M solution of $n\text{-Bu}_4\text{NPF}_6$ in dry and deaerated CH_3CN vs. Fc^+/Fc with 0.1 V/s scan rate).

7.19. 7-(diethylamino)-3-(thiophene-2-carbonyl)-2H-chromen-2-one (10a)

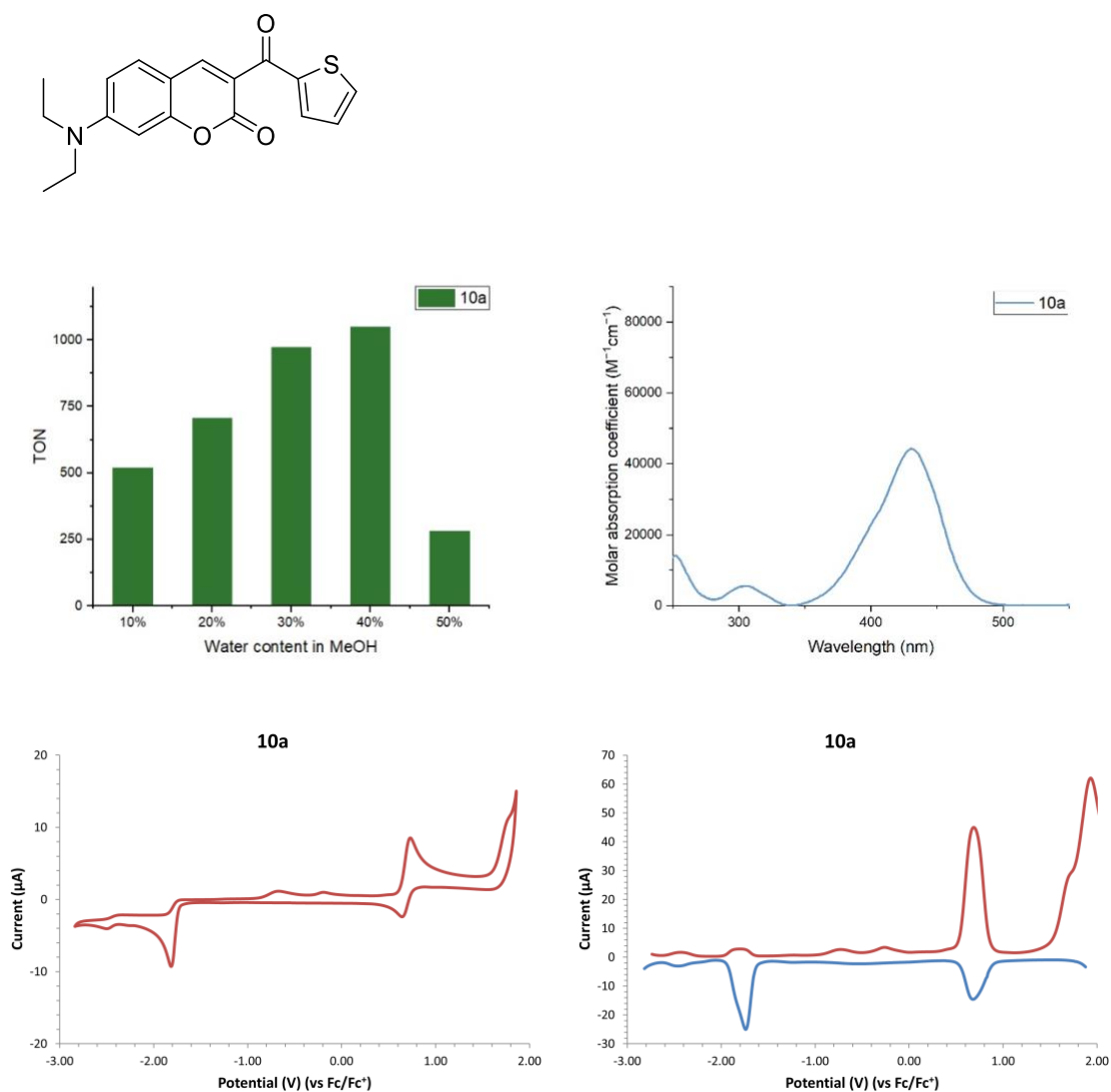


Figure S29 Top left: Turnover numbers of cobaloxime catalyst in different amount of water content in MeOH Top right: absorption spectrum of ketocoumarin **10a** Bottom: cyclic voltammety (left) and differential pulse voltammety (right, red: positive direction, blue: negative direction) measurements (0.1 M solution of n-Bu₄NPF₆ in dry and deaerated CH₃CN vs. Fc⁺/Fc with 0.1 V/s scan rate).

7.20. 7-methoxy-3-(thiophene-2-carbonyl)-2H-chromen-2-one (10b)

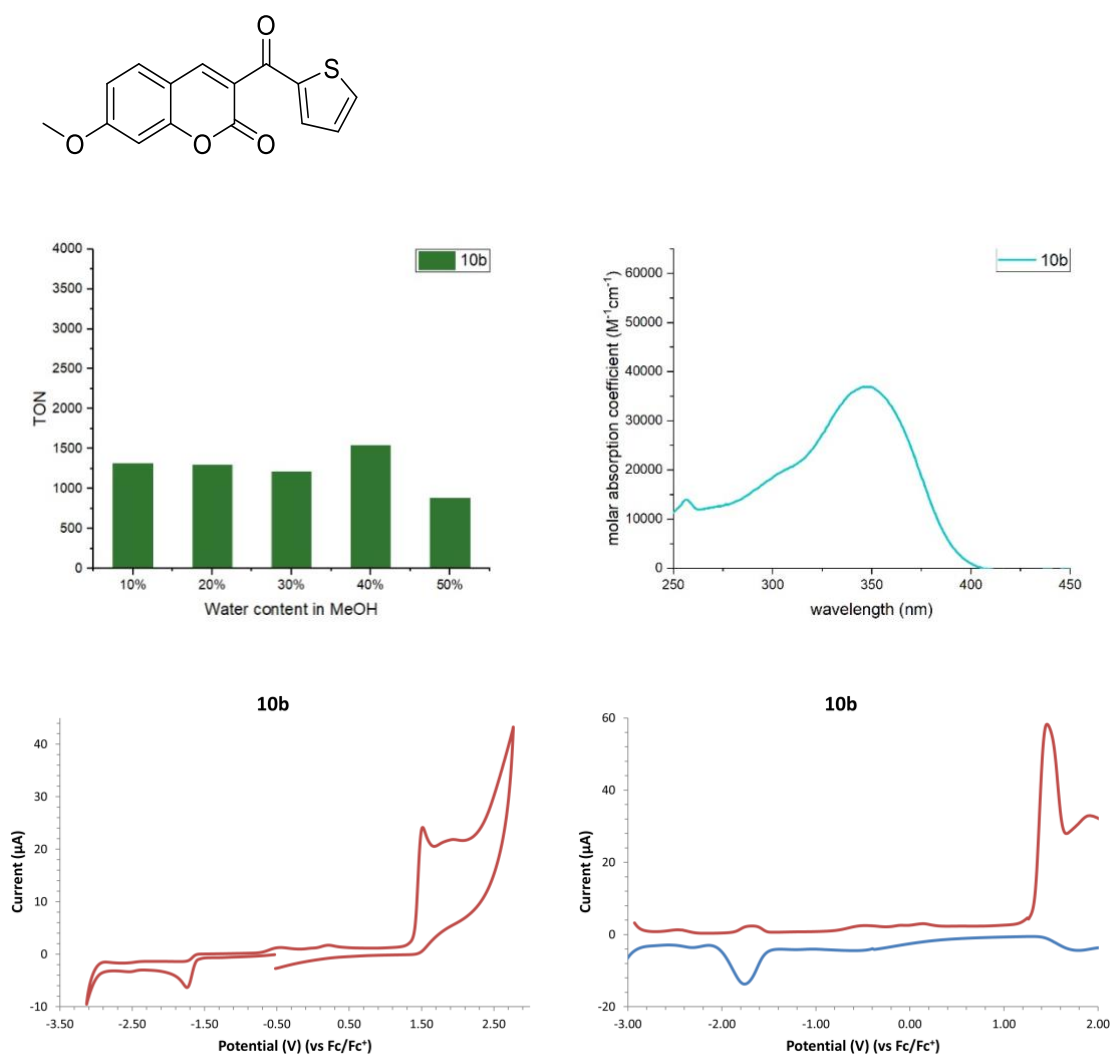


Figure S30 Top left: Turnover numbers of cobaloxime catalyst in different amount of water content in MeOH Top right: absorption spectrum of ketocoumarin **10b** Bottom: cyclic voltammetry (left) and differential pulse voltammetry (right, red: positive direction, blue: negative direction) measurements (0.1 M solution of n-Bu₄NPF₆ in dry and deaerated CH₃CN vs. Fc⁺/Fc with 0.1 V/s scan rate).

7.21. 7-(diethylamino)-3-isonicotinoyl-2H-chromen-2-one (11a)

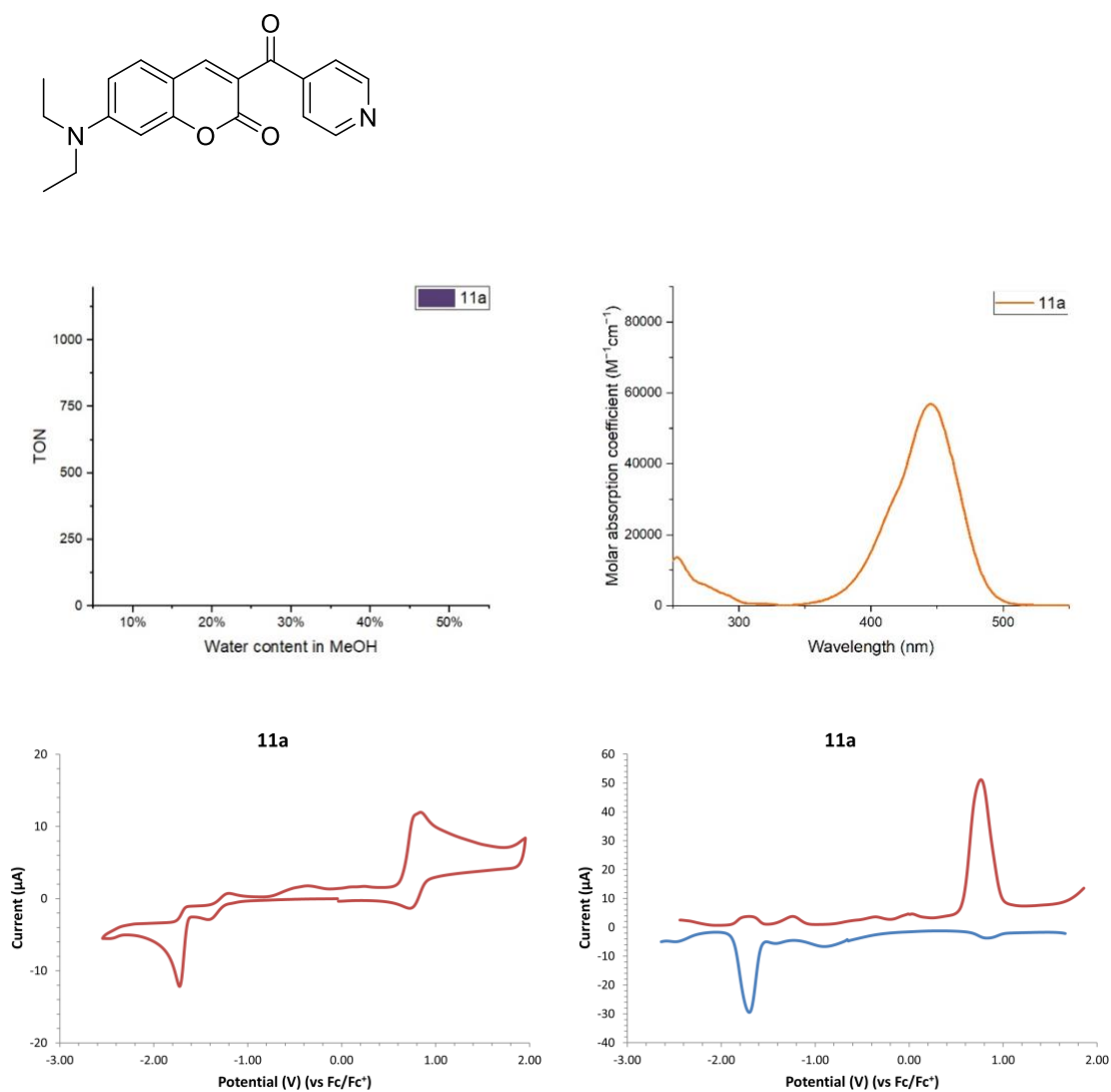


Figure S31 Top left: Turnover numbers of cobaloxime catalyst in different amount of water content in MeOH Top right: absorption spectrum of ketocoumarin **11a** Bottom: cyclic voltammety (left) and differential pulse voltammety (right, red: positive direction, blue: negative direction) measurements (0.1 M solution of $n\text{-Bu}_4\text{NPF}_6$ in dry and deaerated CH_3CN vs. Fc^+/Fc with 0.1 V/s scan rate).

7.22. 3-isonicotinoyl-7-methoxy-2H-chromen-2-one (**11b**)

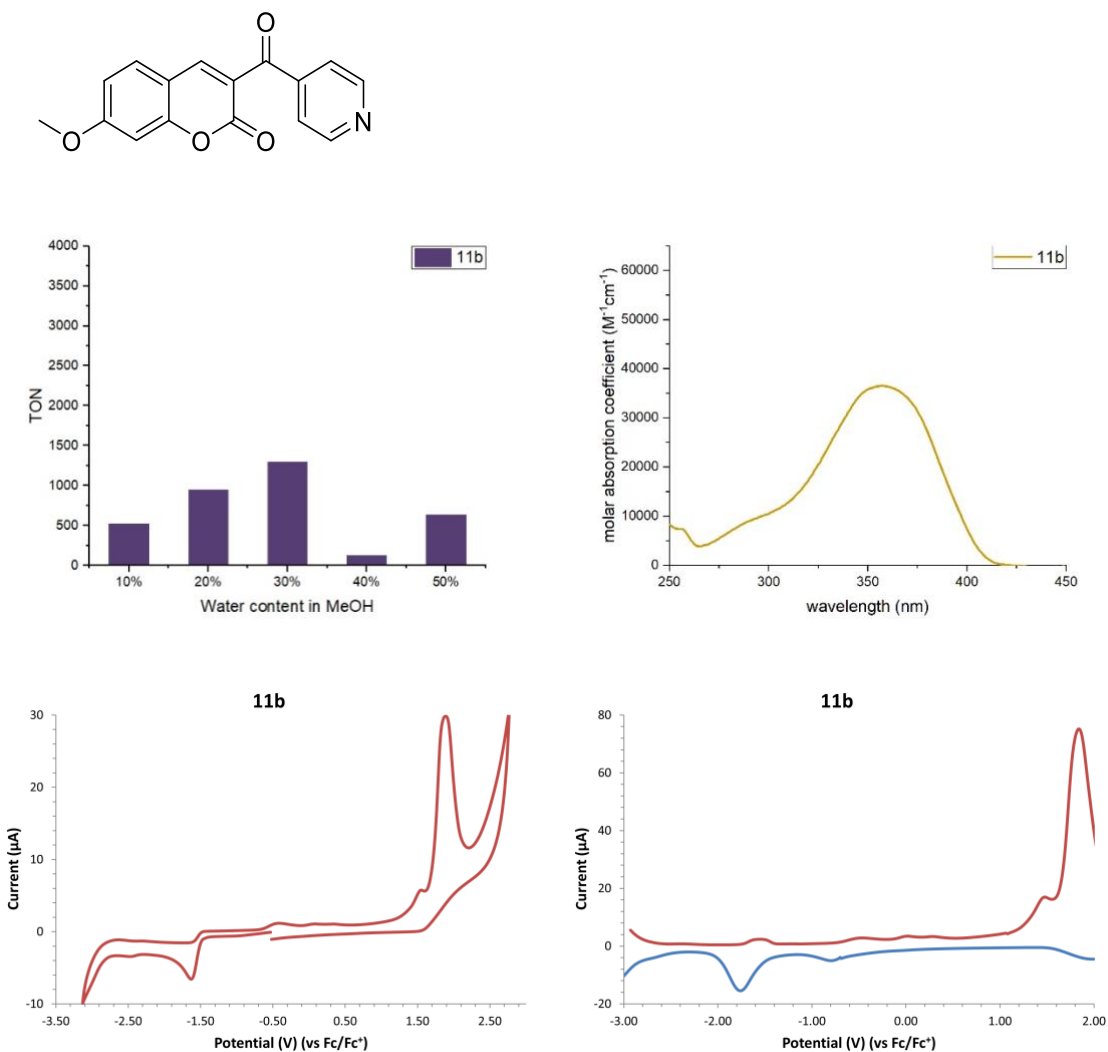


Figure S32 Top left: Turnover numbers of cobaloxime catalyst in different amount of water content in MeOH Top right: absorption spectrum of ketocoumarin **11b** Bottom: cyclic voltammetry (left) and differential pulse voltammetry (right, red: positive direction, blue: negative direction) measurements (0.1 M solution of $n\text{-Bu}_4\text{NPF}_6$ in dry and deaerated CH_3CN vs. Fc^+/Fc with 0.1 V/s scan rate).

7.23. 3,3'-carbonylbis(7-(diethylamino)-2H-chromen-2-one) (**12a**)

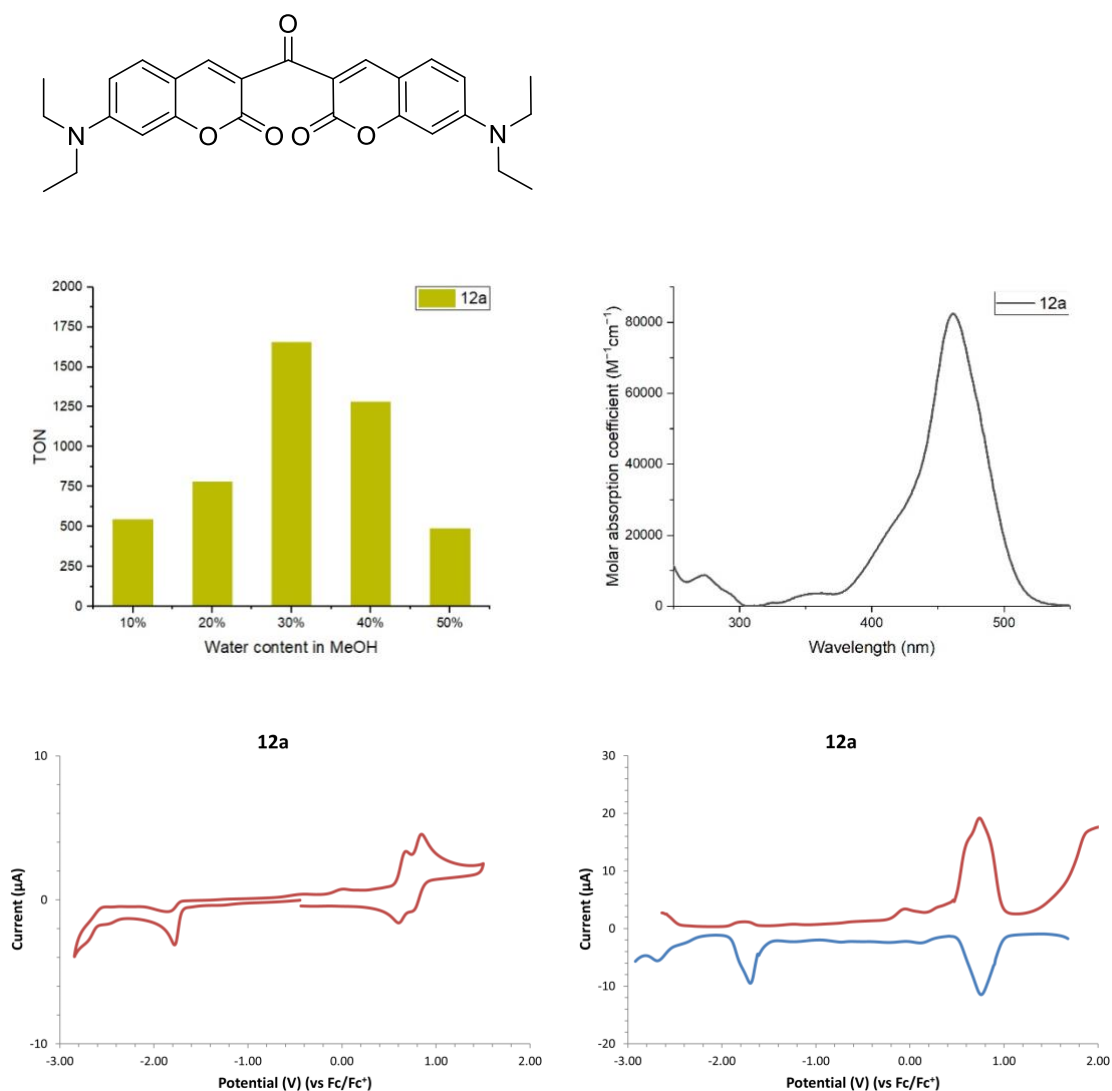


Figure S33 Top left: Turnover numbers of cobaloxime catalyst in different amount of water content in MeOH Top right: absorption spectrum of ketocoumarin **12a** Bottom: cyclic voltammety (left) and differential pulse voltammety (right, red: positive direction, blue: negative direction) measurements (0.1 M solution of $n\text{-Bu}_4\text{NPF}_6$ in dry and deaerated CH_3CN vs. Fc^+/Fc with 0.1 V/s scan rate).

7.24. 3,3'-carbonylbis(7-methoxy-2H-chromen-2-one) (**12b**)

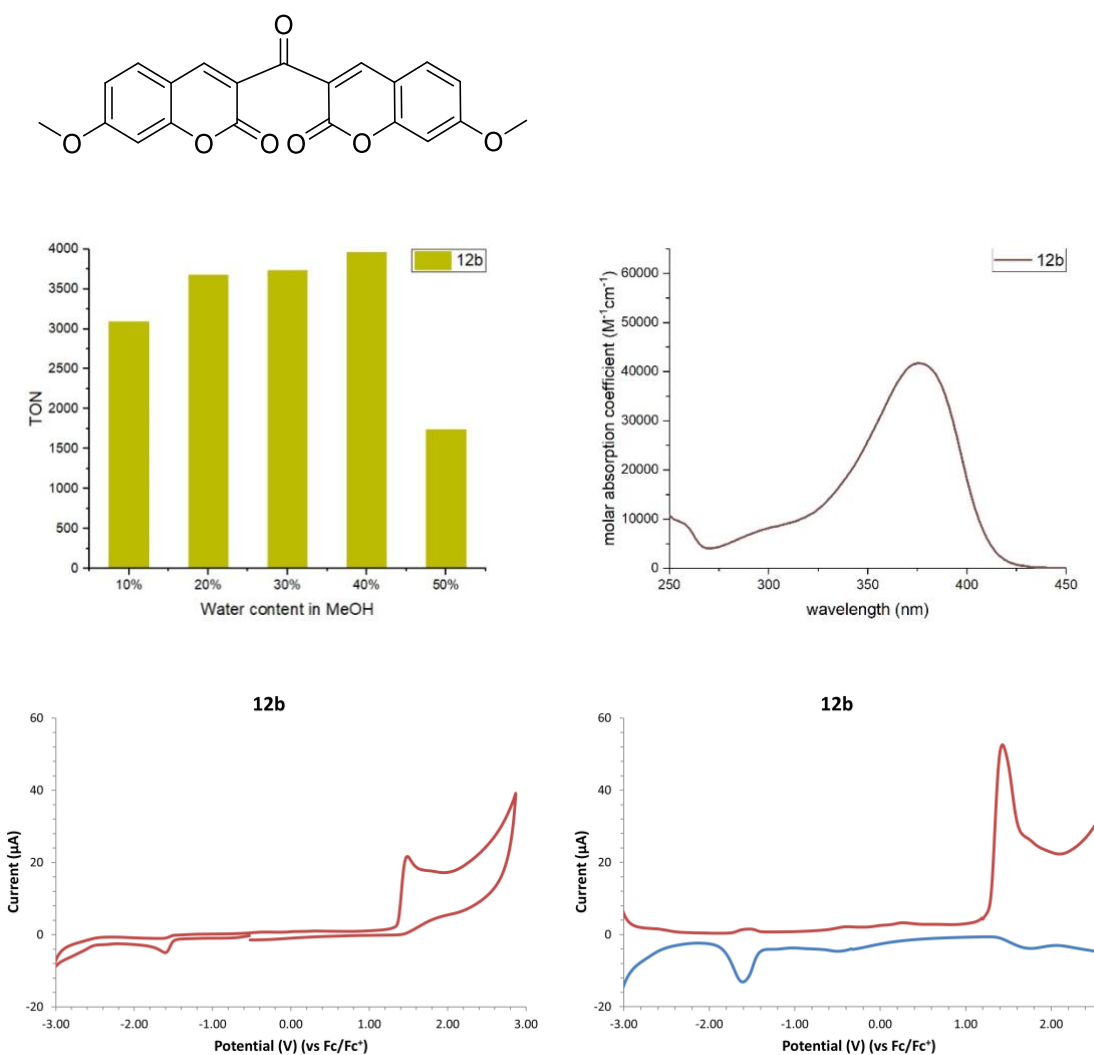


Figure S34 Top left: Turnover numbers of cobaloxime catalyst in different amount of water content in MeOH Top right: absorption spectrum of ketocoumarin **12b** Bottom: cyclic voltammetry (left) and differential pulse voltammetry (right, red: positive direction, blue: negative direction) measurements (0.1 M solution of $n\text{-Bu}_4\text{NPF}_6$ in dry and deaerated CH_3CN vs. Fc^+/Fc with 0.1 V/s scan rate).

7.25. 3,3'-terephthaloylbis(7-(diethylamino)-2H-chromen-2-one) (**13a**)

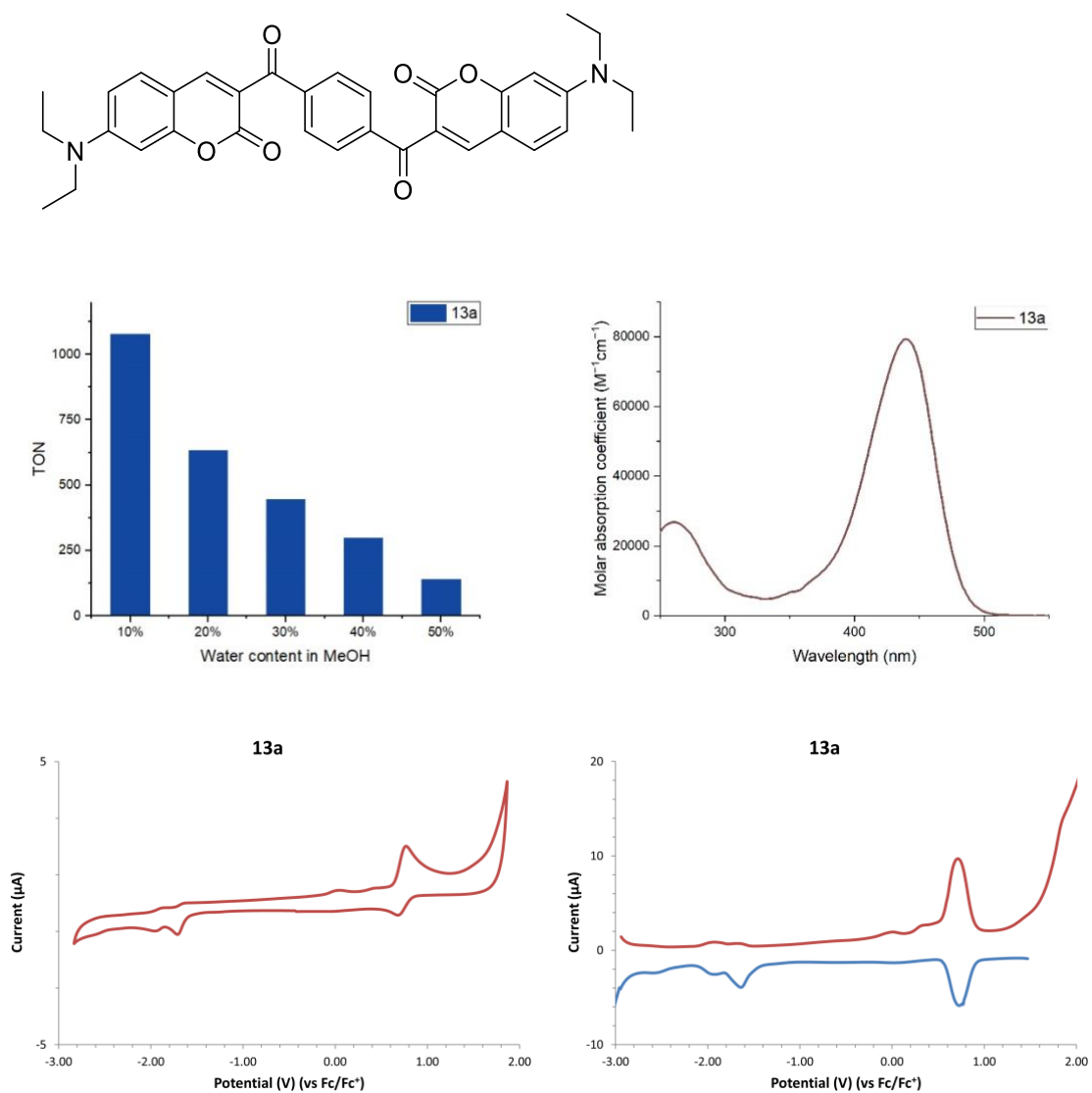


Figure S35 Top left: Turnover numbers of cobaloxime catalyst in different amount of water content in MeOH Top right: absorption spectrum of ketocoumarin **13a** Bottom: cyclic voltammery (left) and differential pulse voltammery (right, red: positive direction, blue: negative direction) measurements (0.1 M solution of $n-Bu_4NPF_6$ in dry and deaerated CH_3CN vs. Fc^+/Fc with 0.1 V/s scan rate).

7.26. 3,3'-terephthaloylbis(7-methoxy-2H-chromen-2-one) (**13b**)

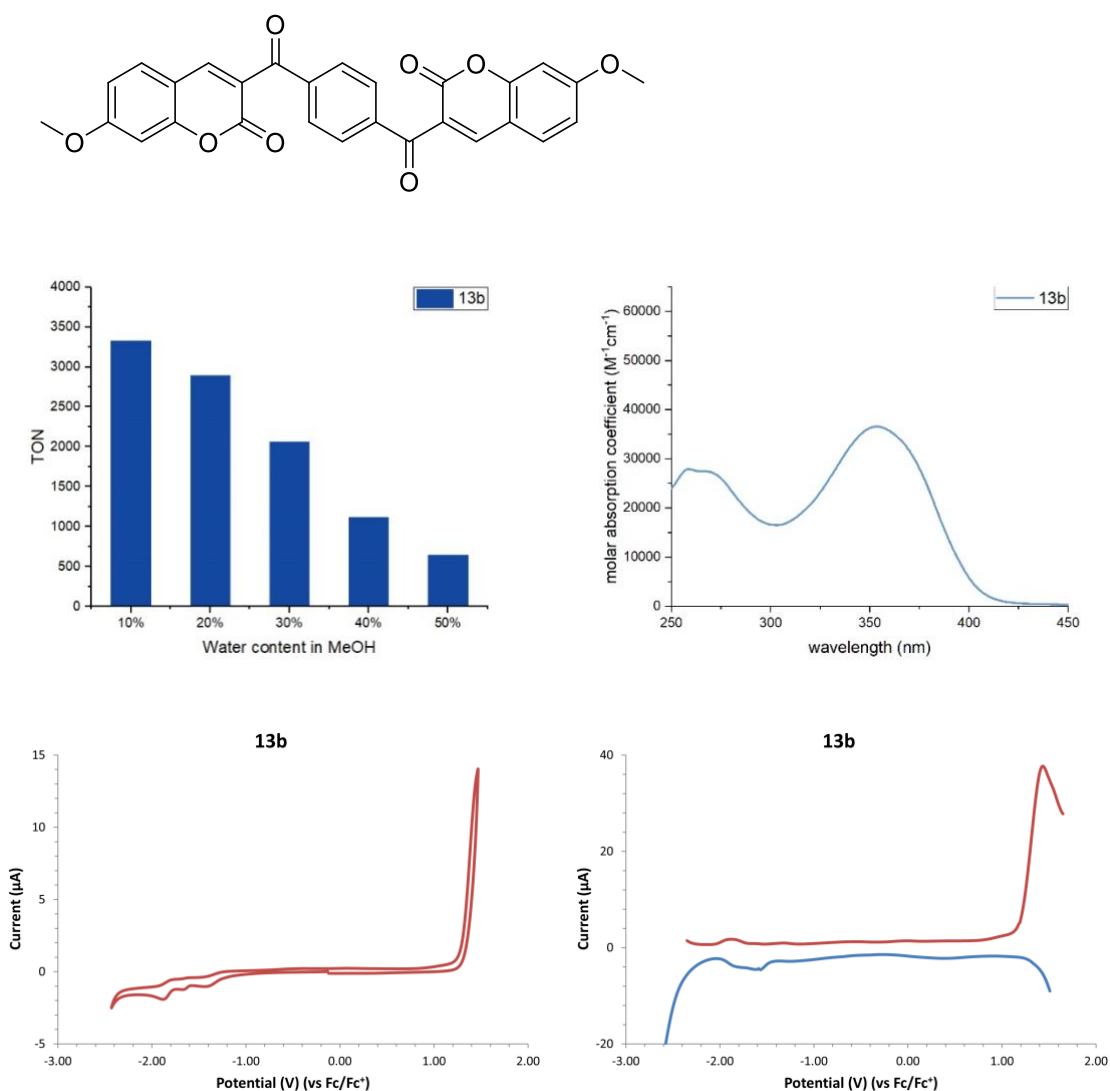


Figure S36 Top left: Turnover numbers of cobaloxime catalyst in different amount of water content in MeOH Top right: absorption spectrum of ketocoumarin **13b** Bottom: cyclic voltammety (left) and differential pulse voltammety (right, red: positive direction, blue: negative direction) measurements (0.1 M solution of n-Bu₄NPF₆ in dry and deaerated CH₃CN vs. Fc⁺/Fc with 0.1 V/s scan rate).

8. NMR Spectra of compounds 1-13a/b

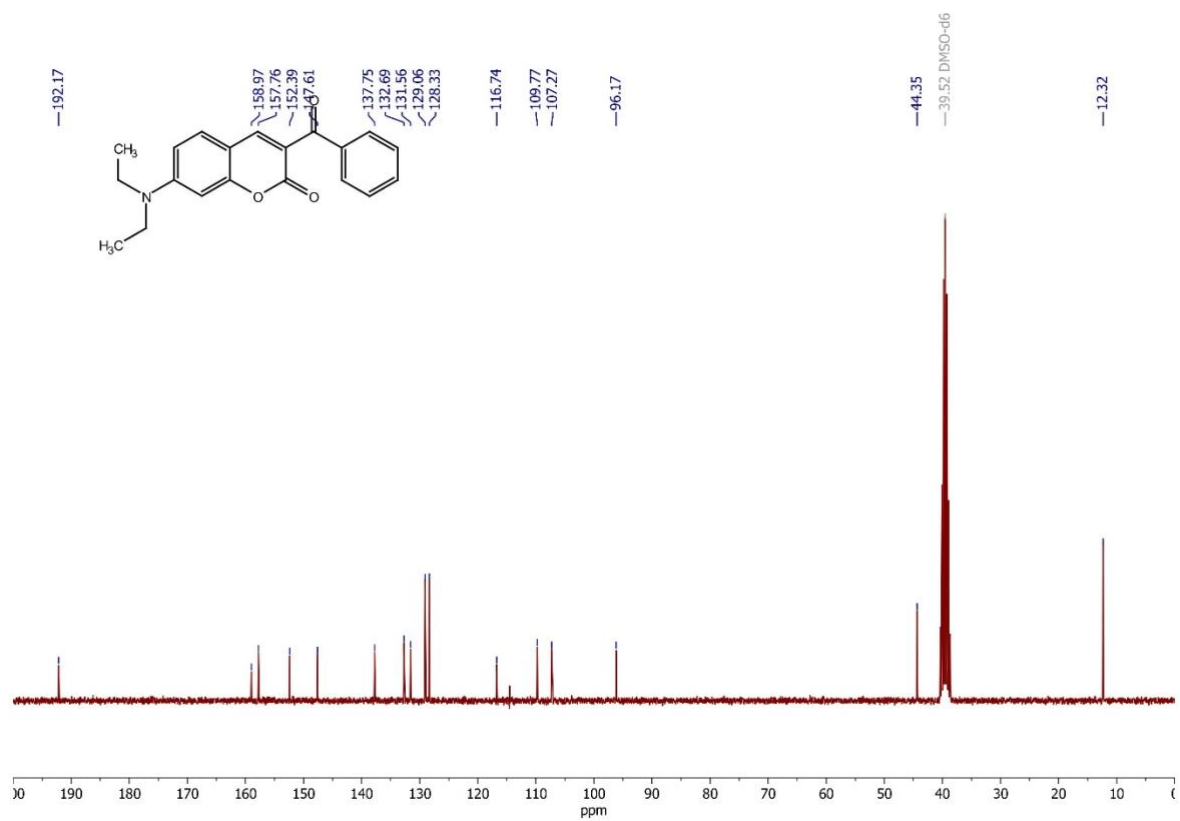
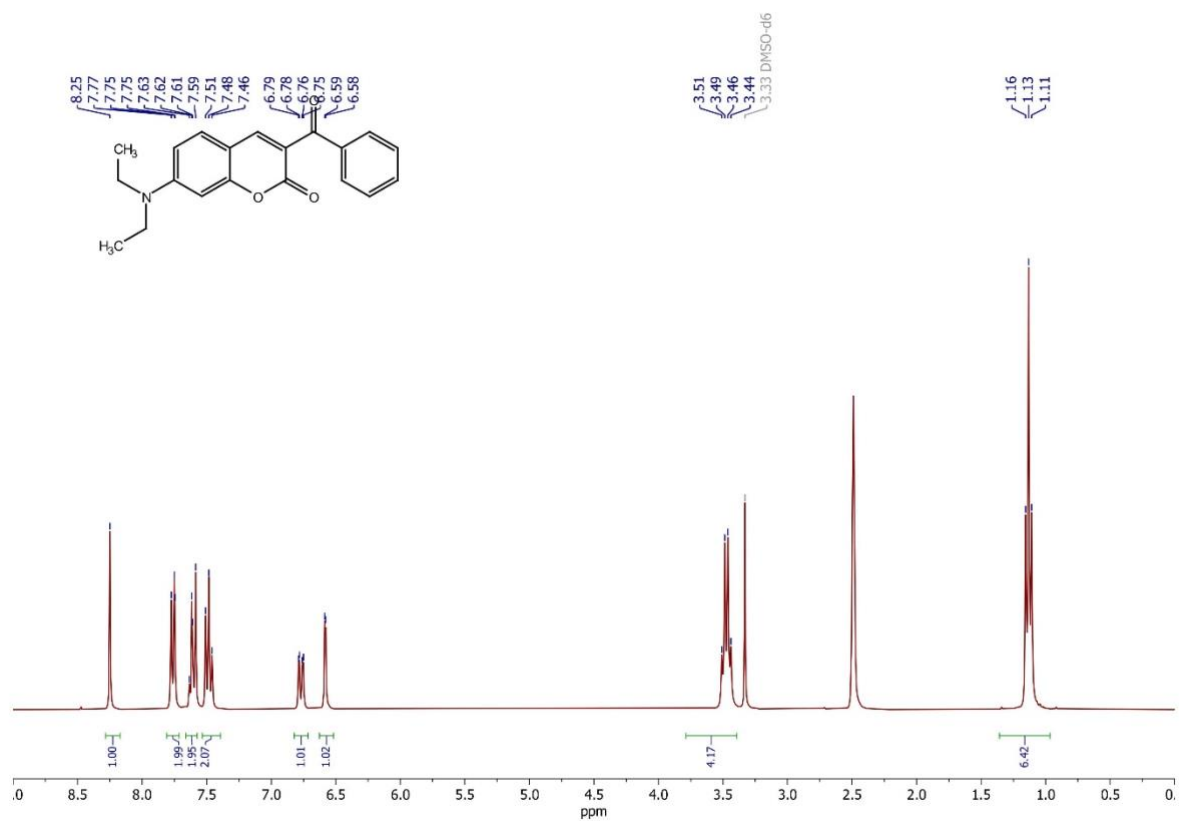


Figure S37: ¹H and ¹³C NMR spectra recorded in DMSO-*d*₆

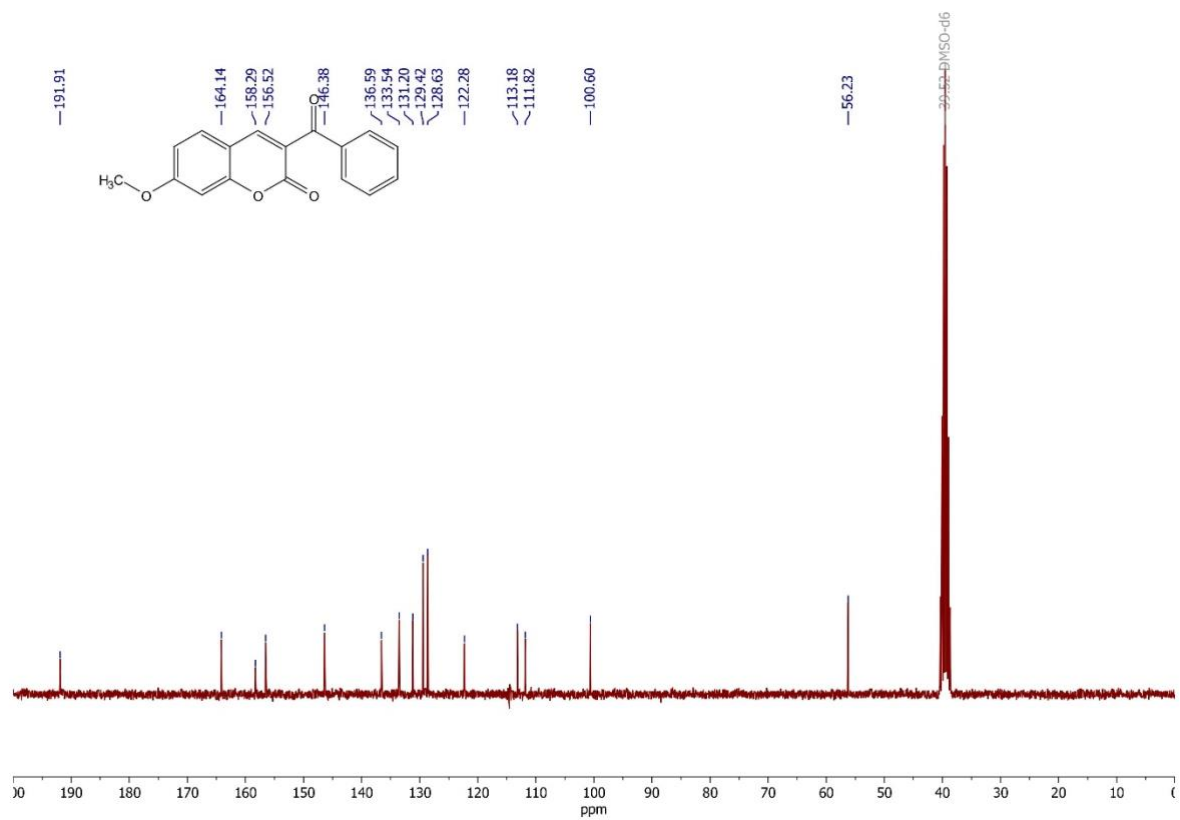
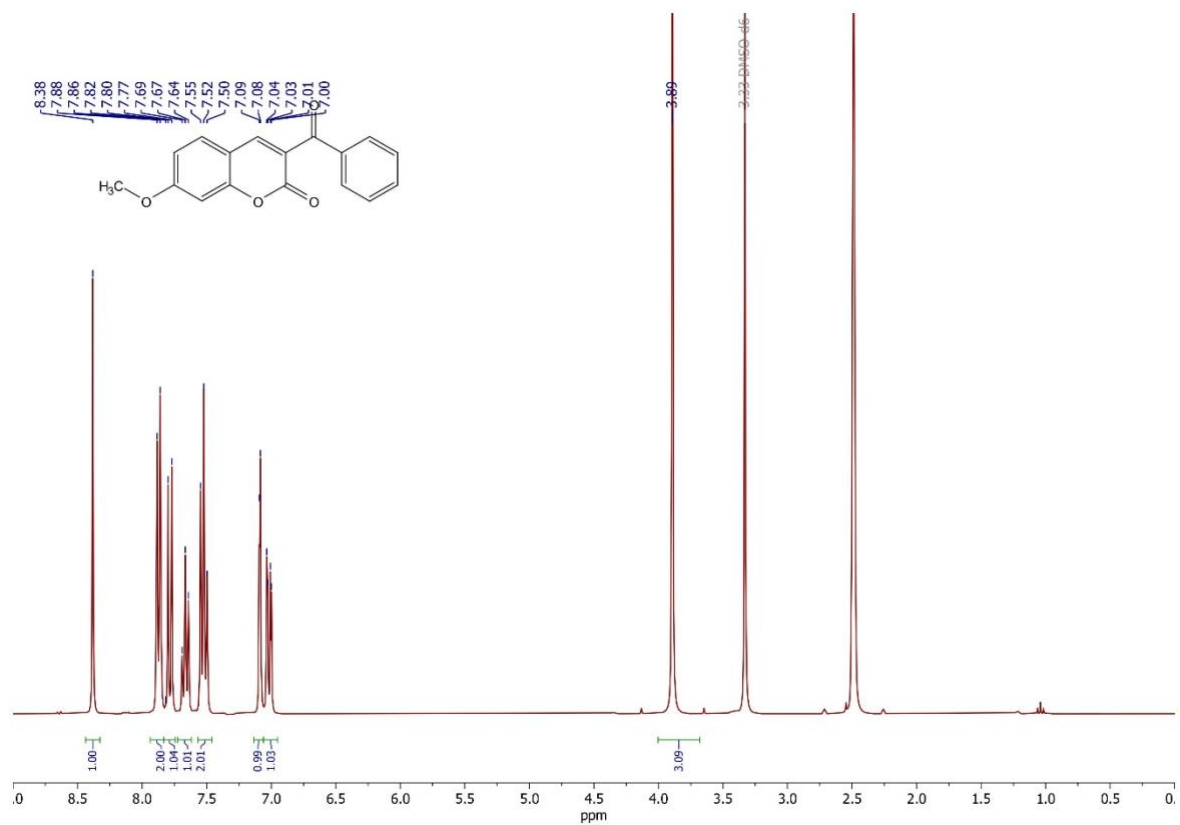


Figure S38: ¹H and ¹³C NMR spectra recorded in DMSO-*d*₆

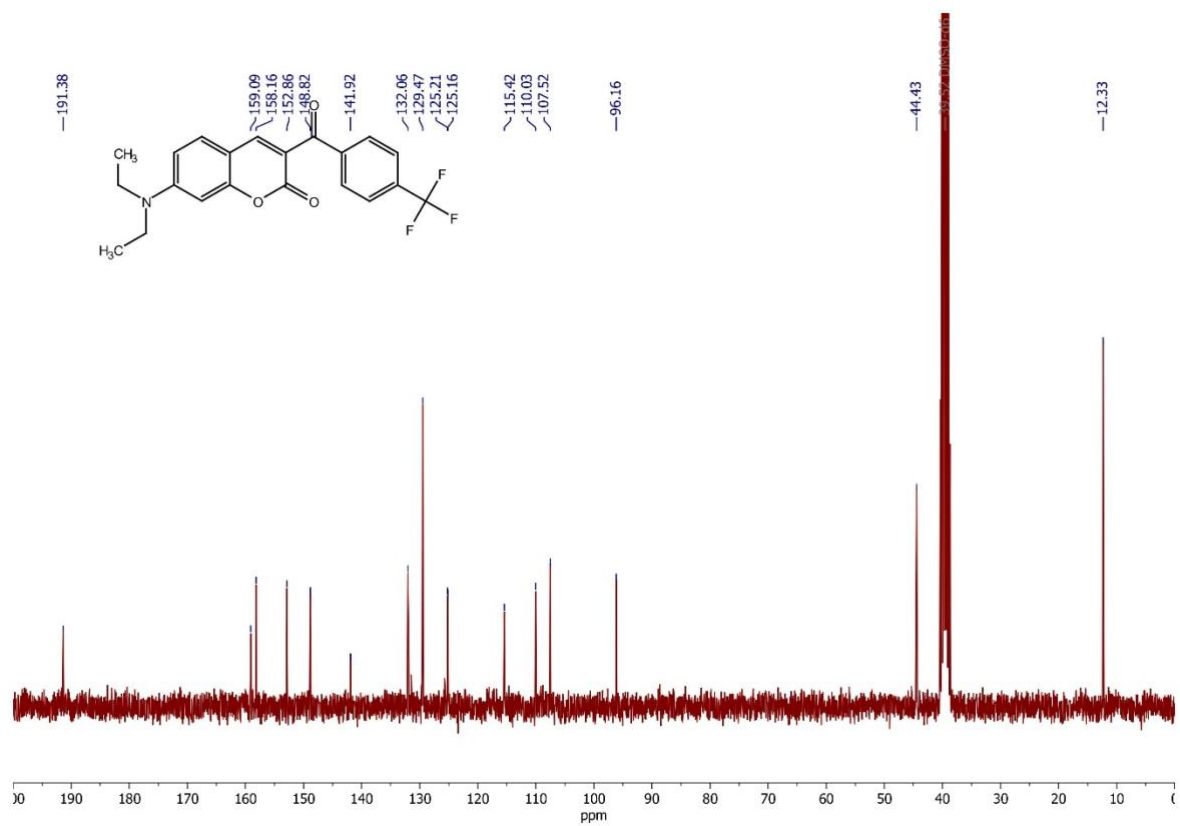
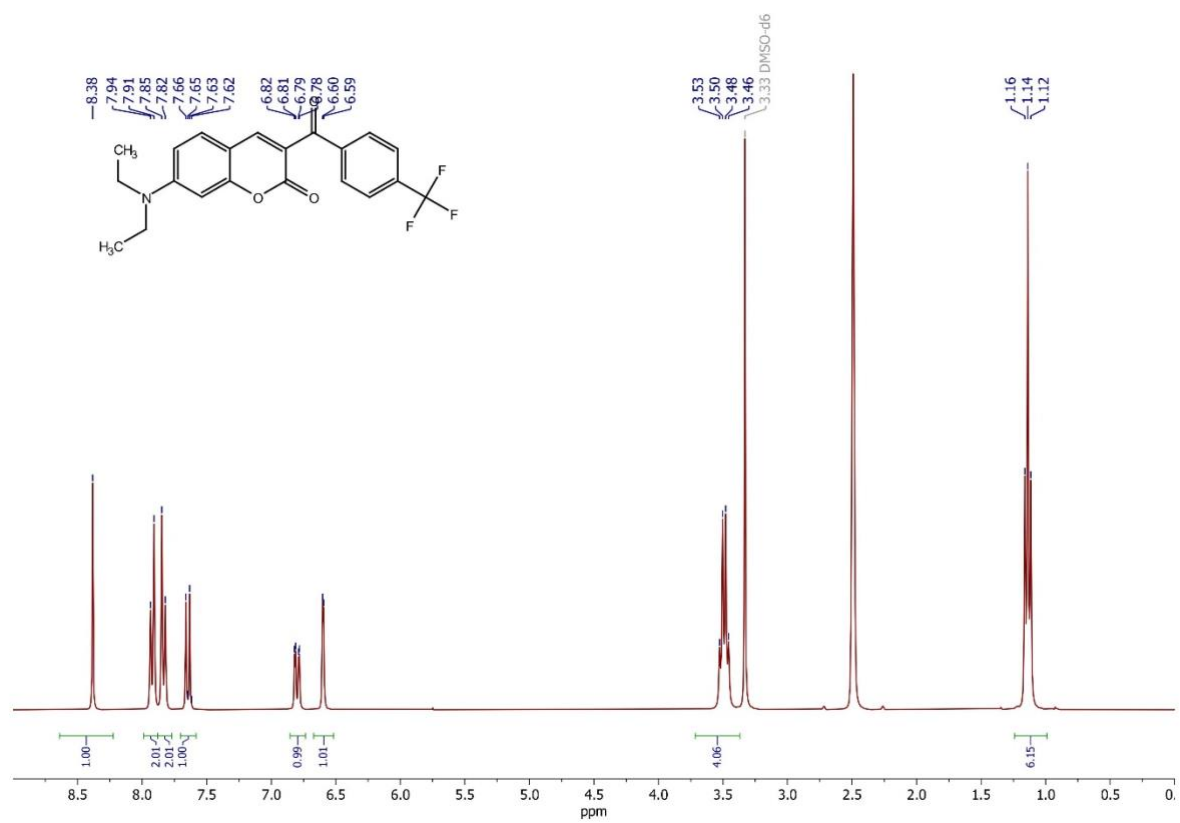


Figure S39: ¹H and ¹³C NMR spectra recorded in DMSO-d₆

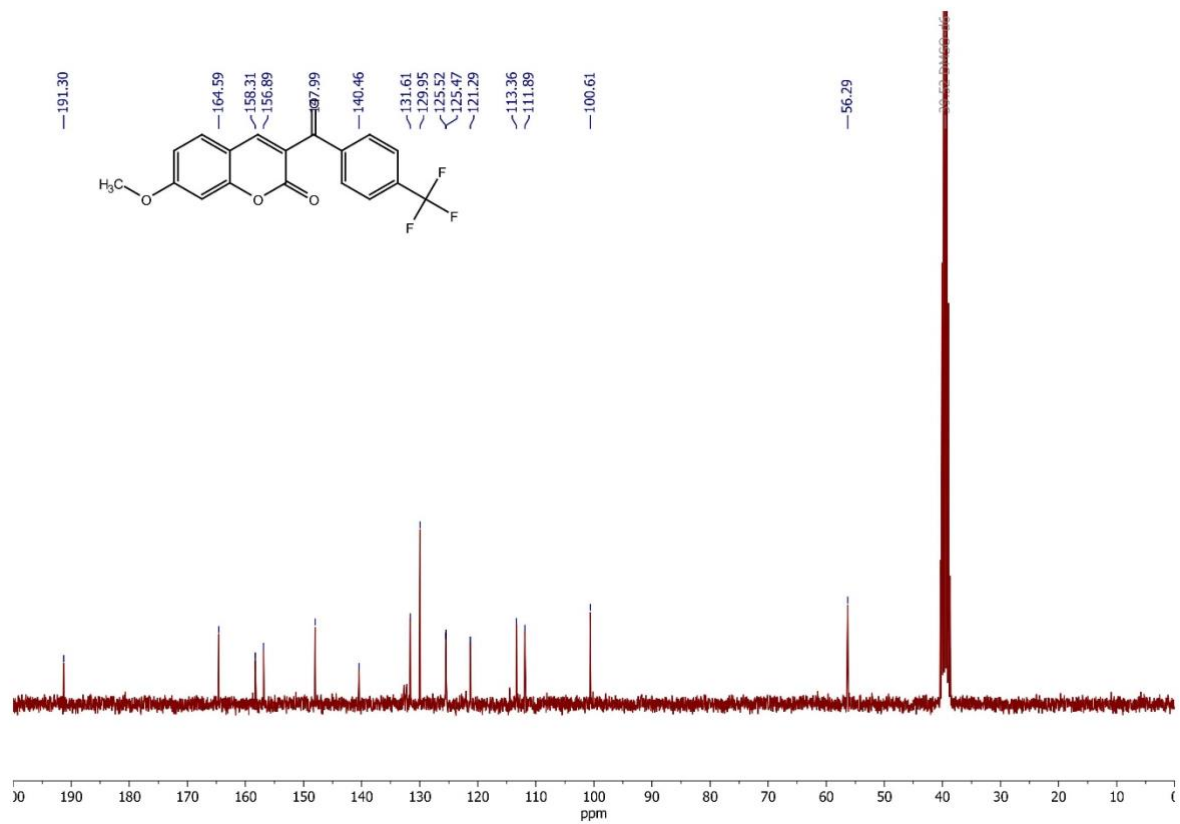
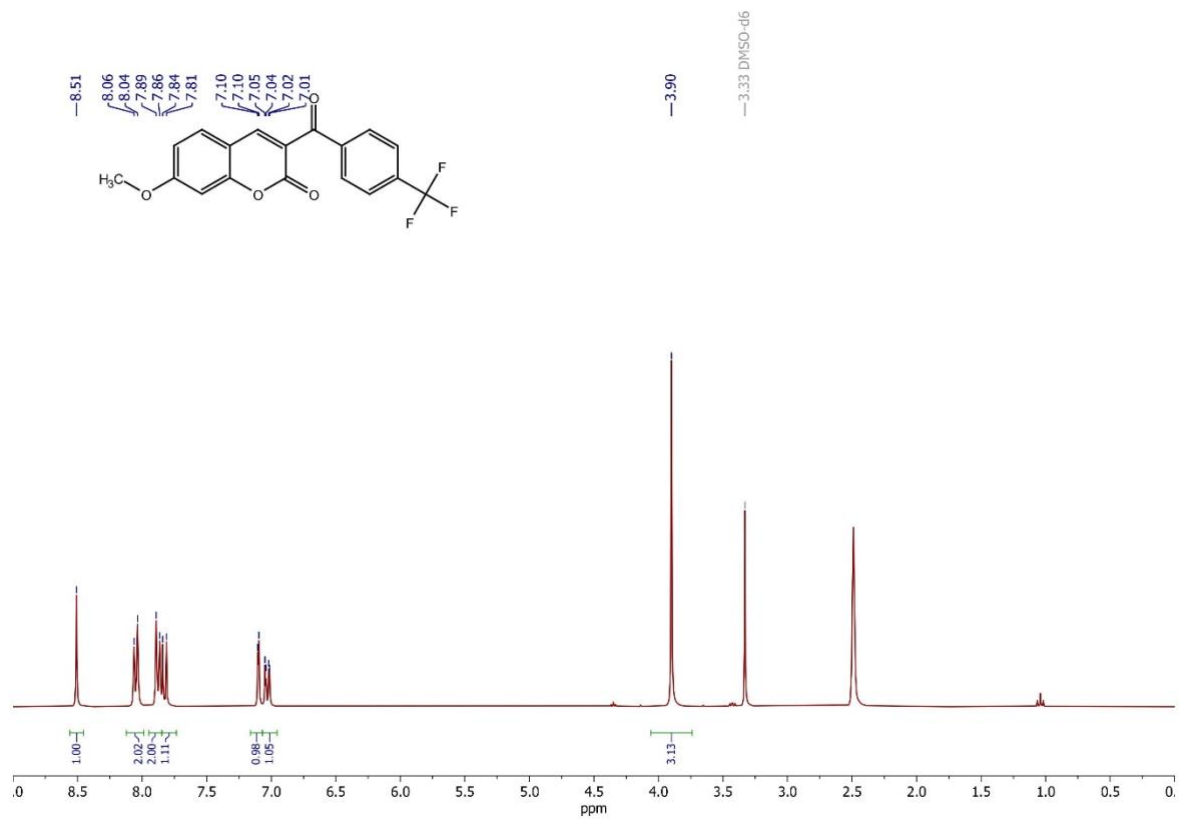


Figure S40: ^1H and ^{13}C NMR spectra recorded in DMSO- d_6

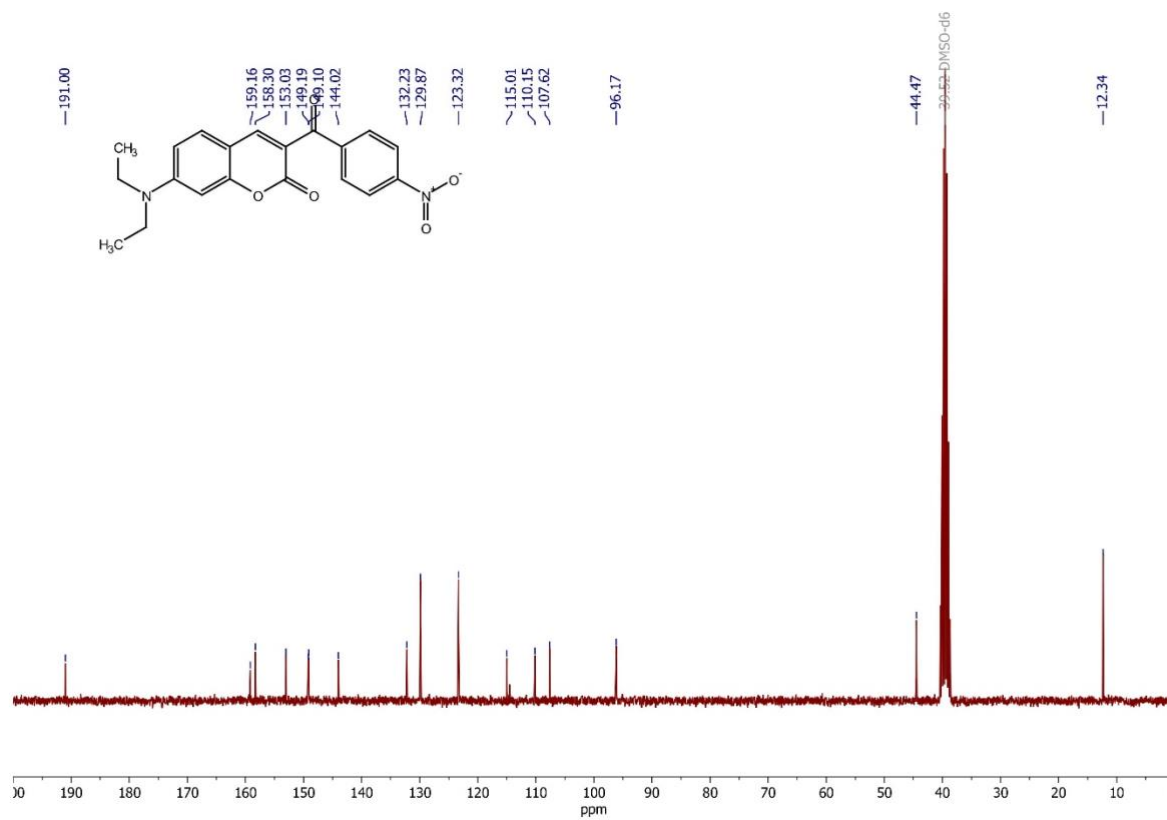
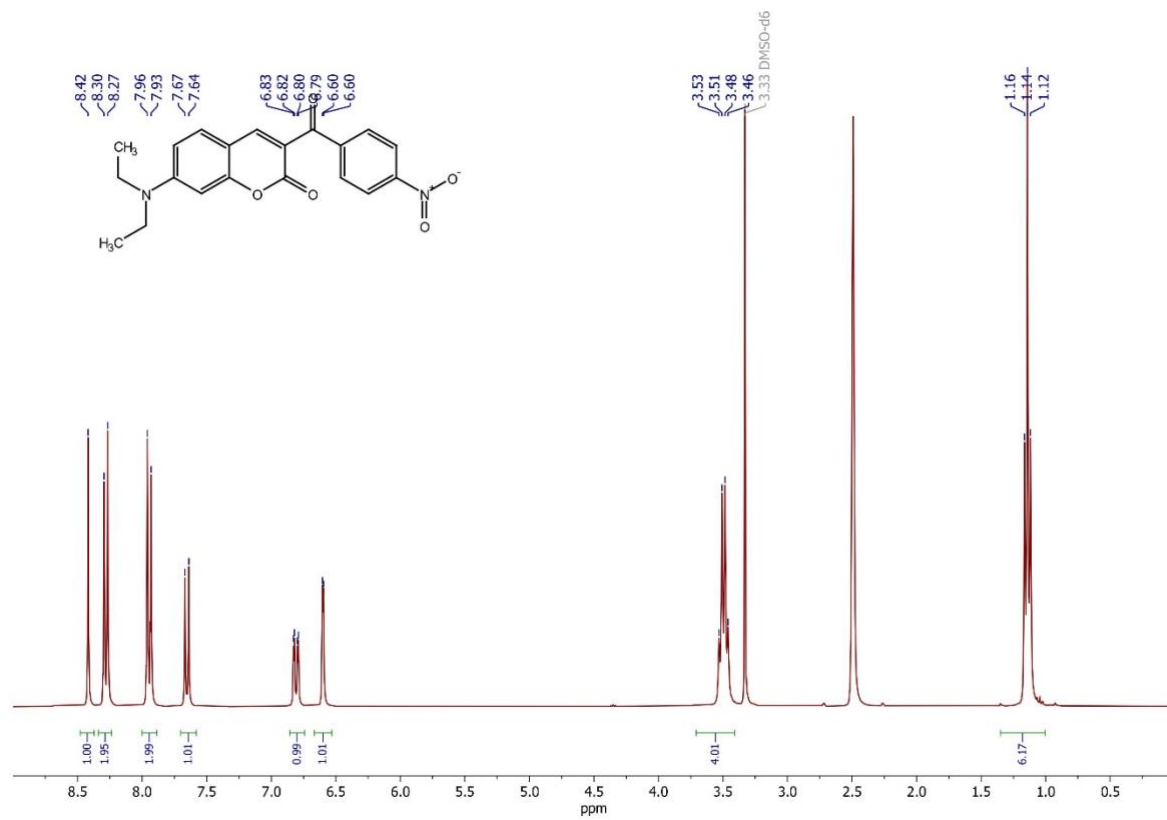


Figure S41: ¹H and ¹³C NMR spectra recorded in DMSO-d₆

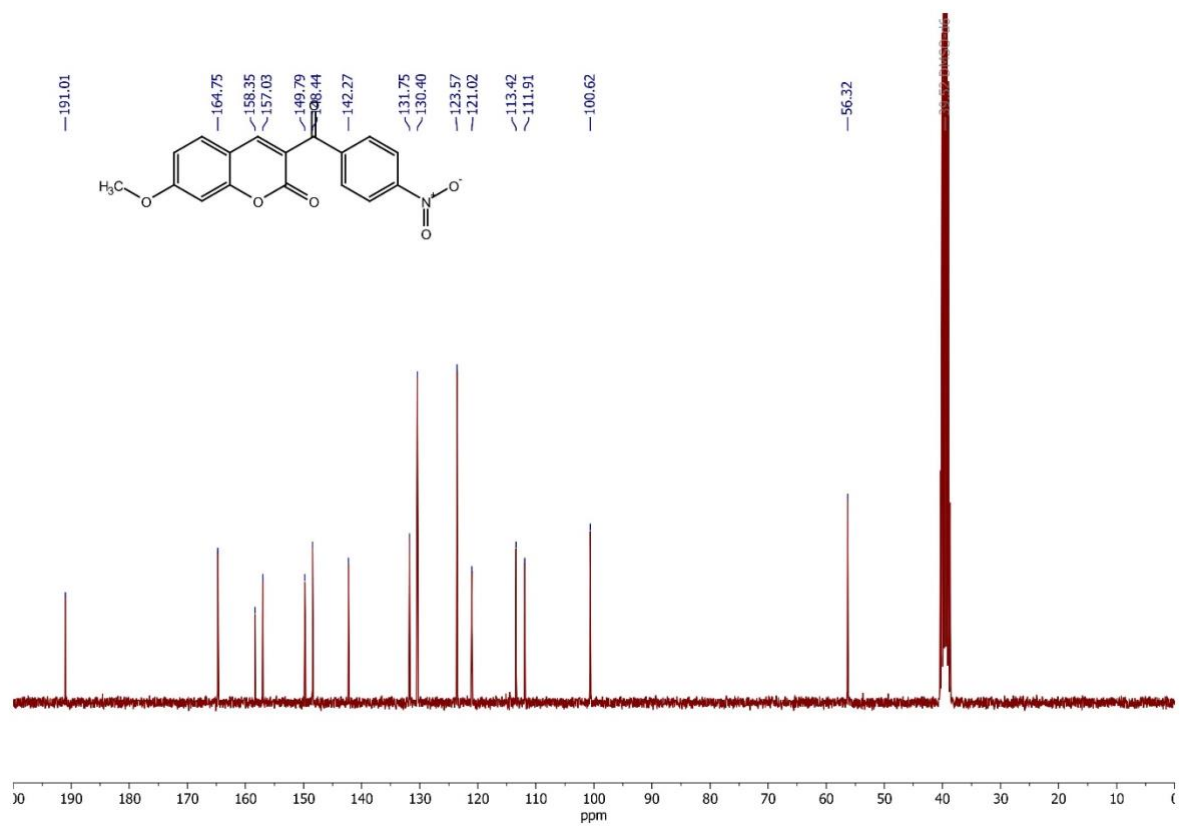
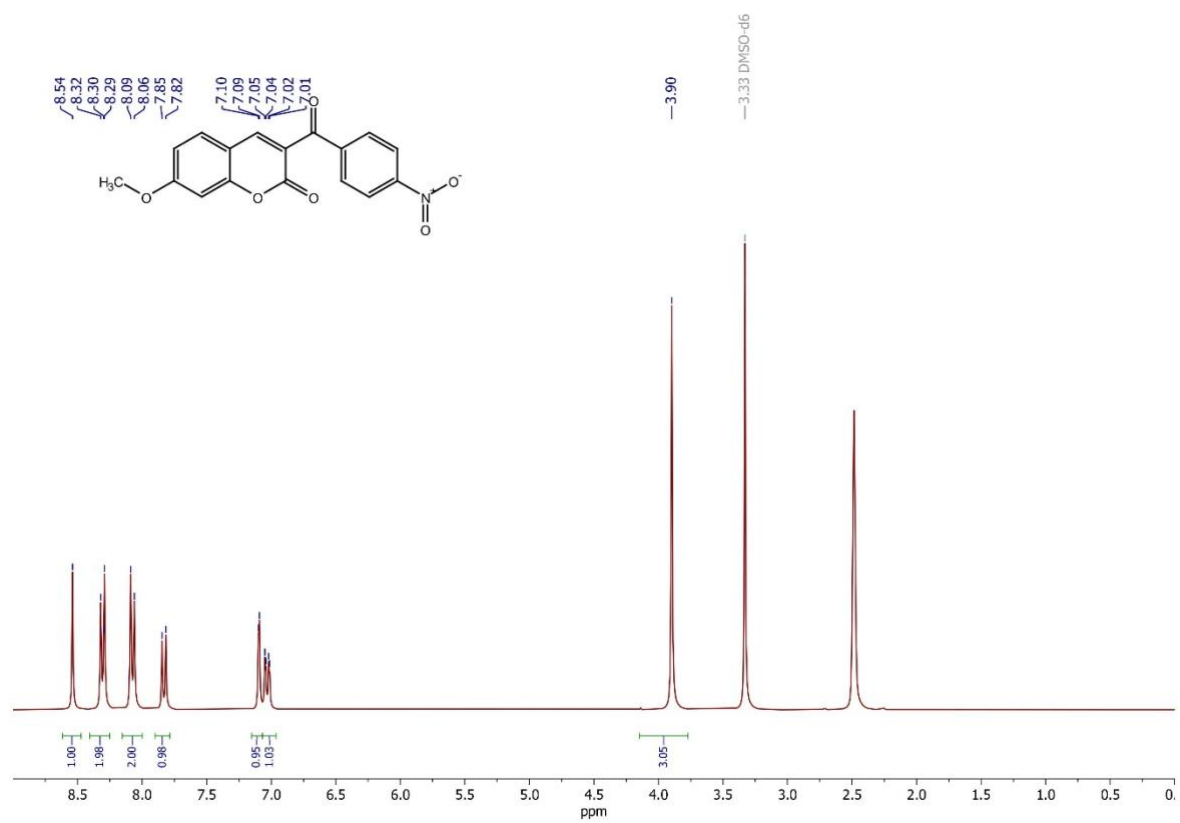


Figure S42: ^1H and ^{13}C NMR spectra recorded in $\text{DMSO-}d_6$

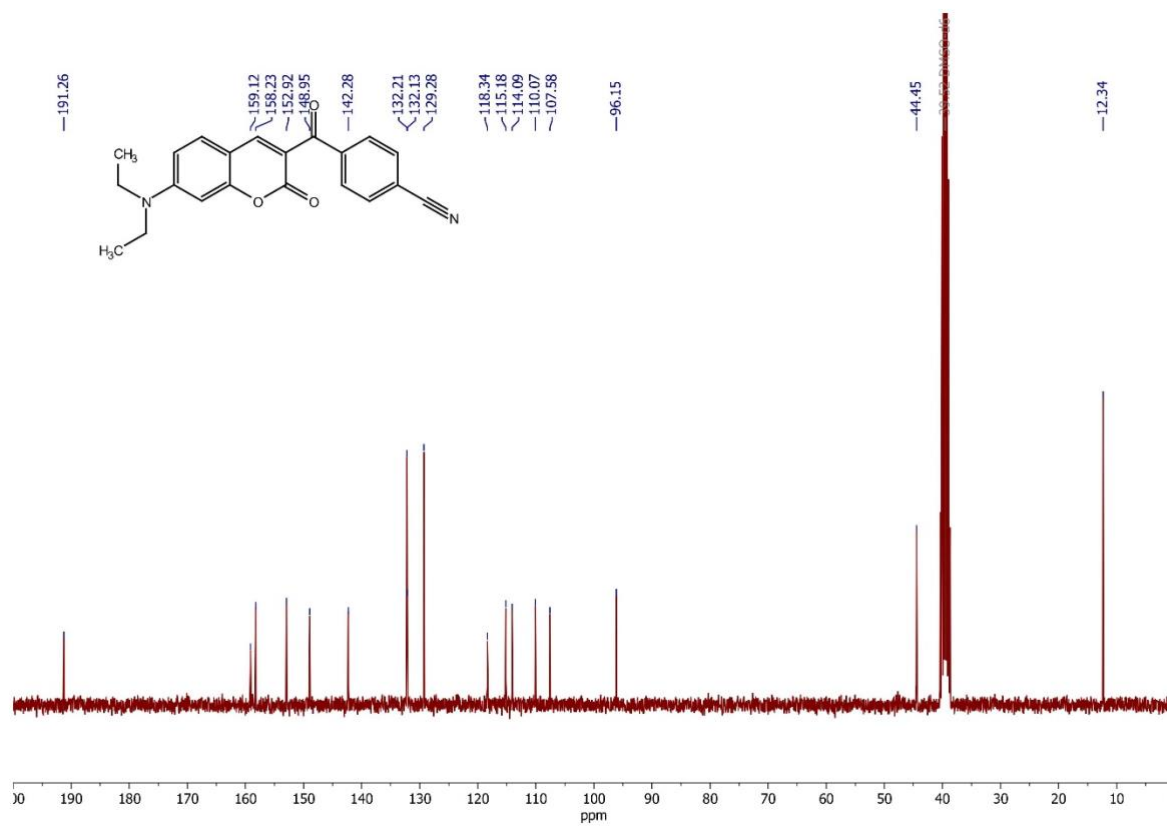
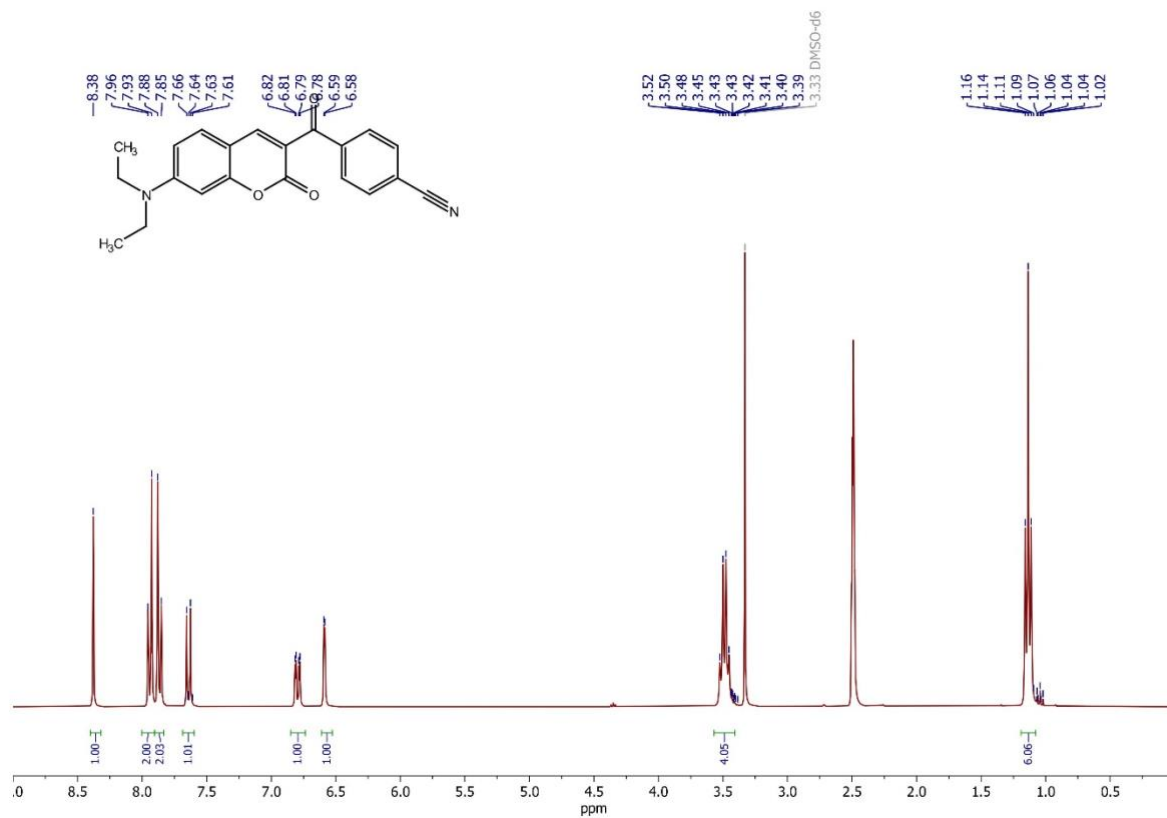


Figure S43: ¹H and ¹³C NMR spectra recorded in DMSO-*d*₆

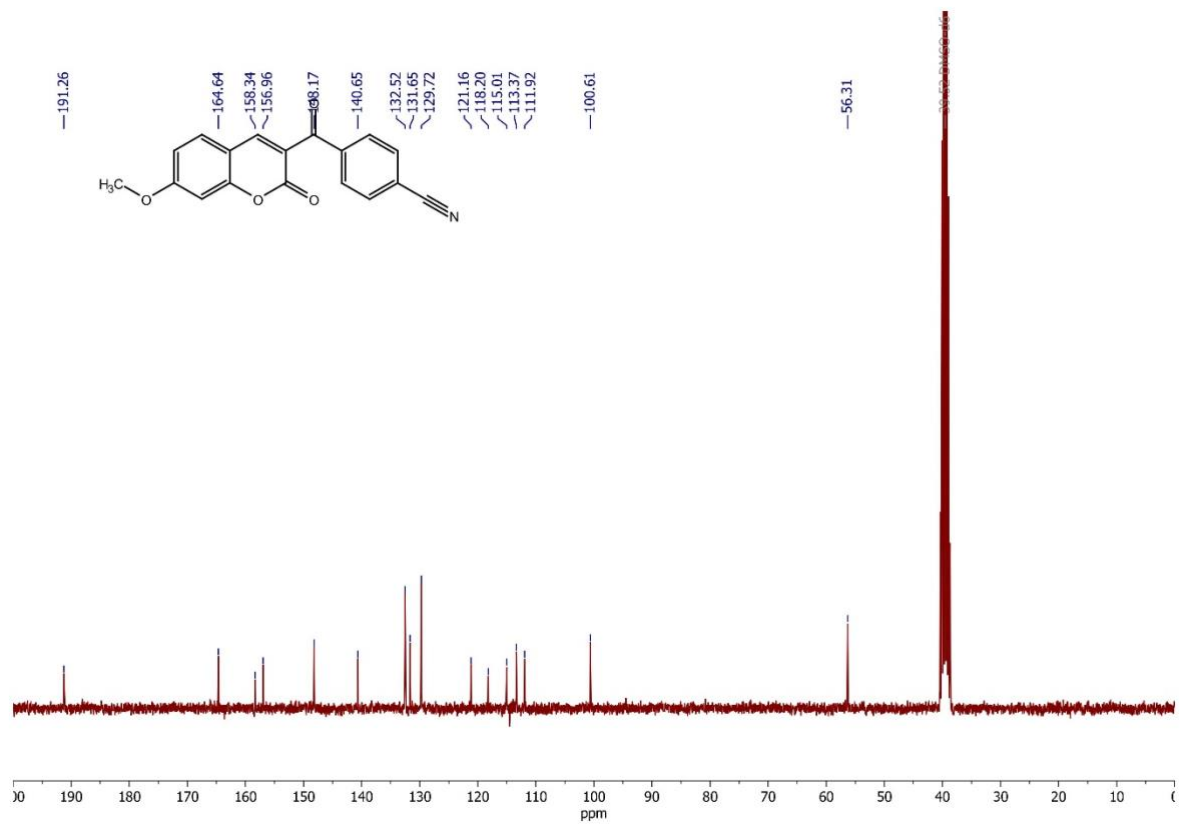
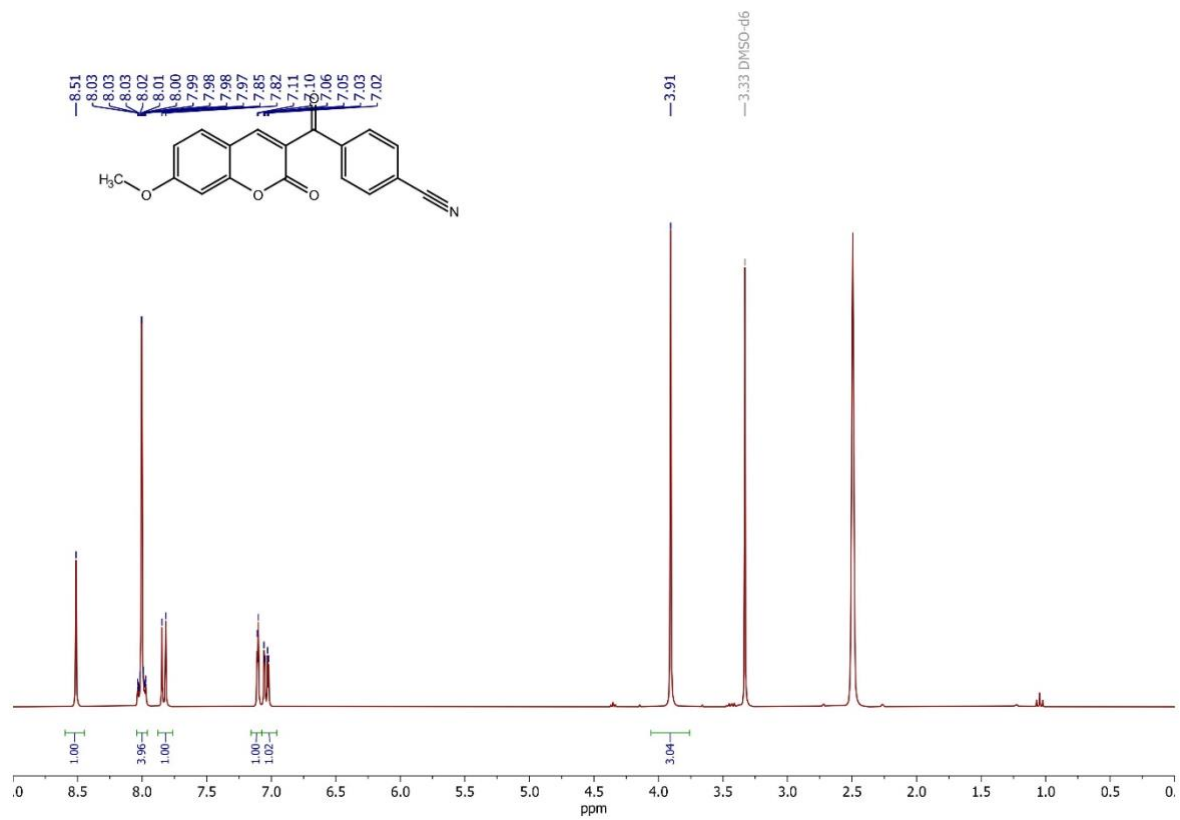


Figure S44: ¹H and ¹³C NMR spectra recorded in DMSO-*d*₆

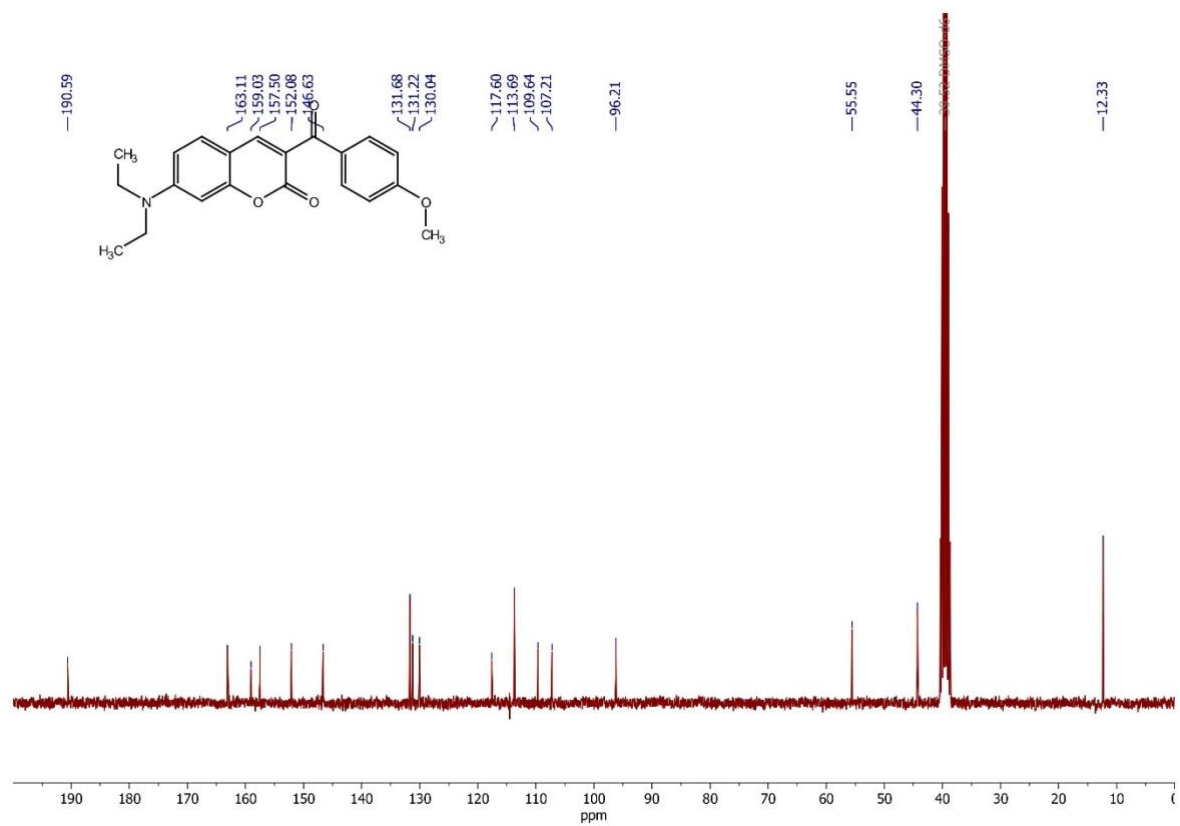
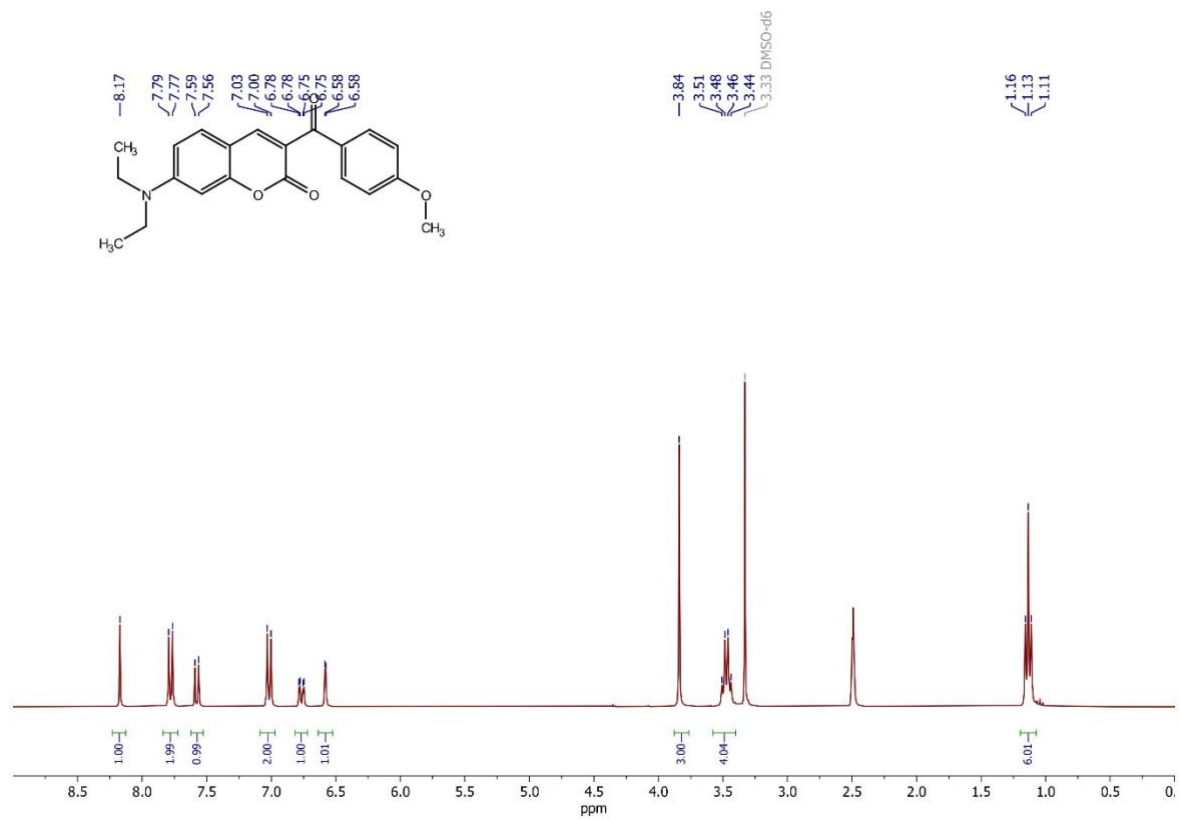


Figure S45: ¹H and ¹³C NMR spectra recorded in DMSO-d₆

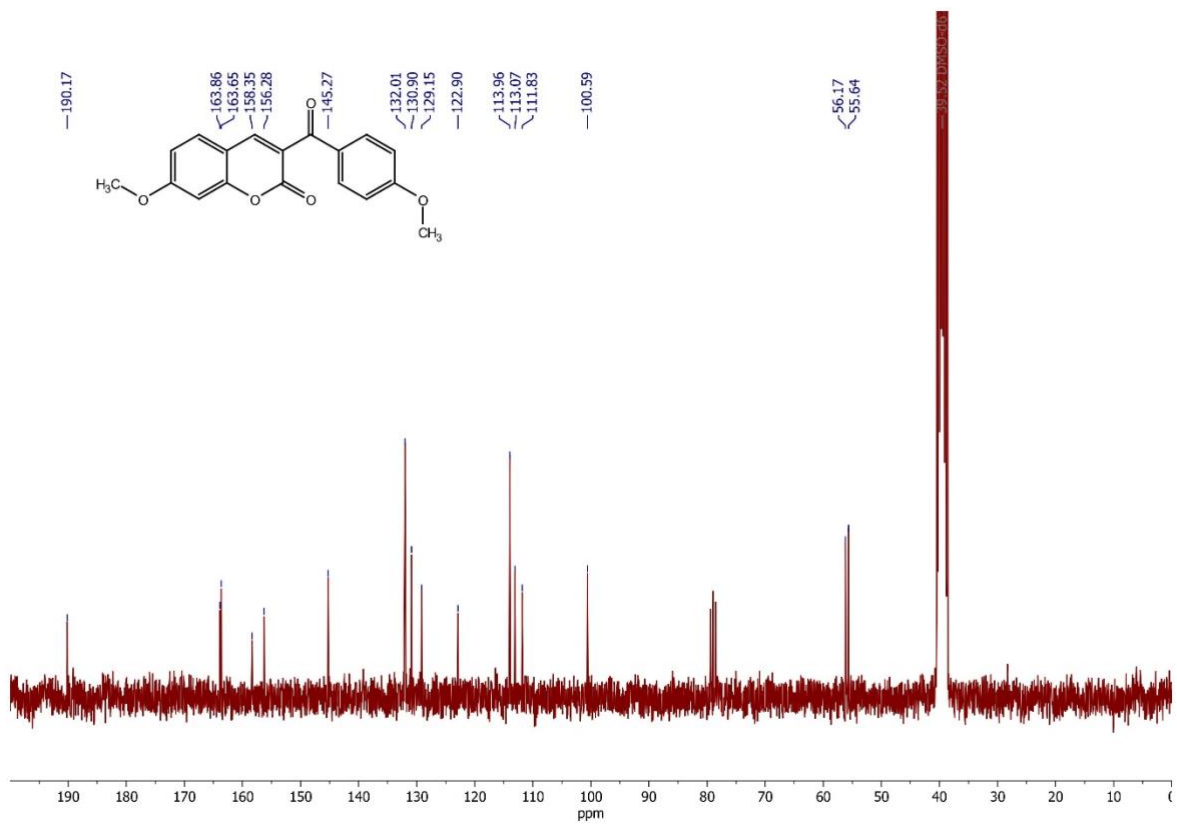
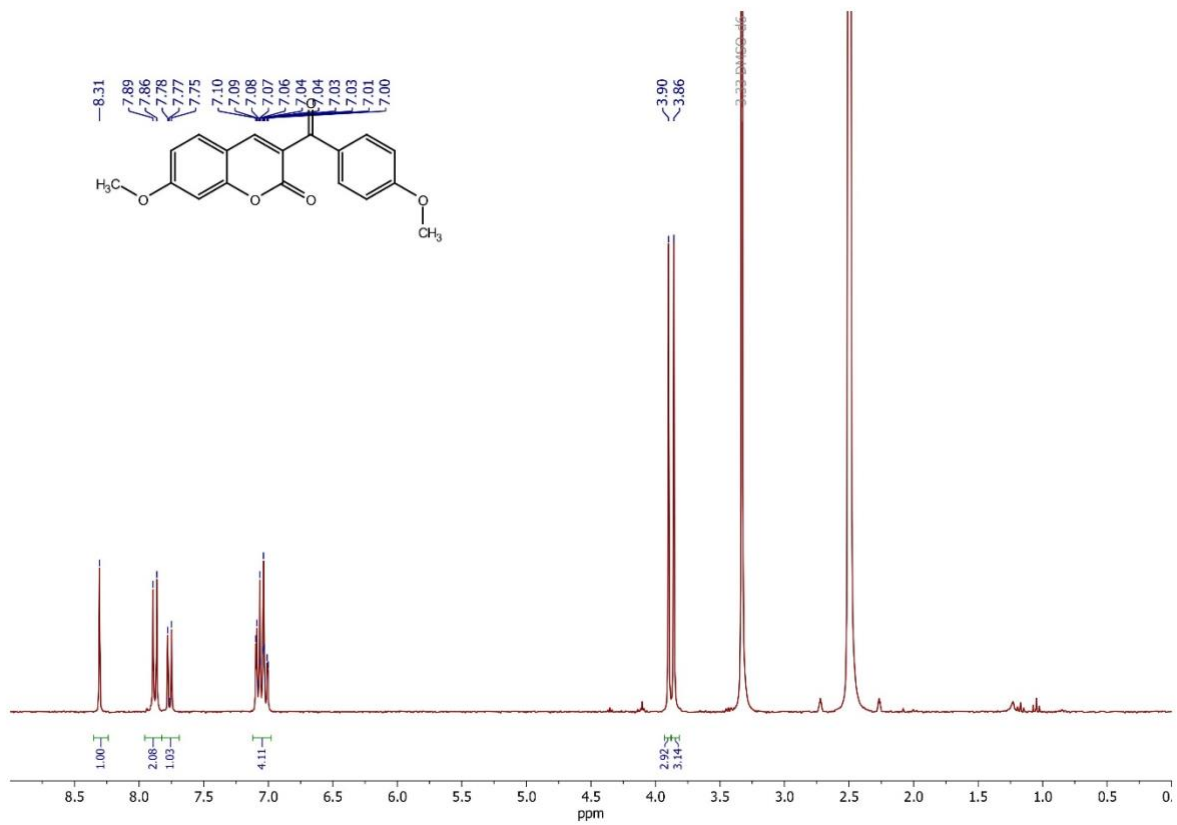


Figure S46: ¹H and ¹³C NMR spectra recorded in DMSO-*d*₆

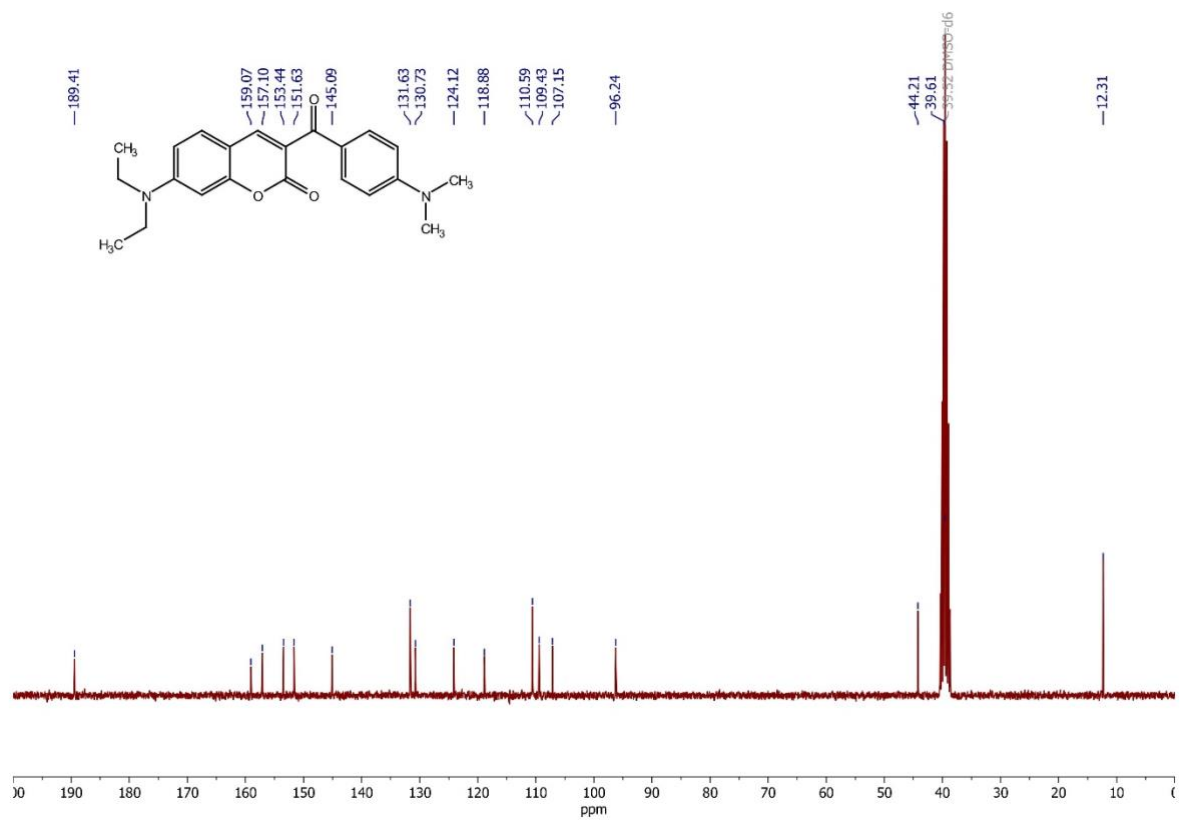
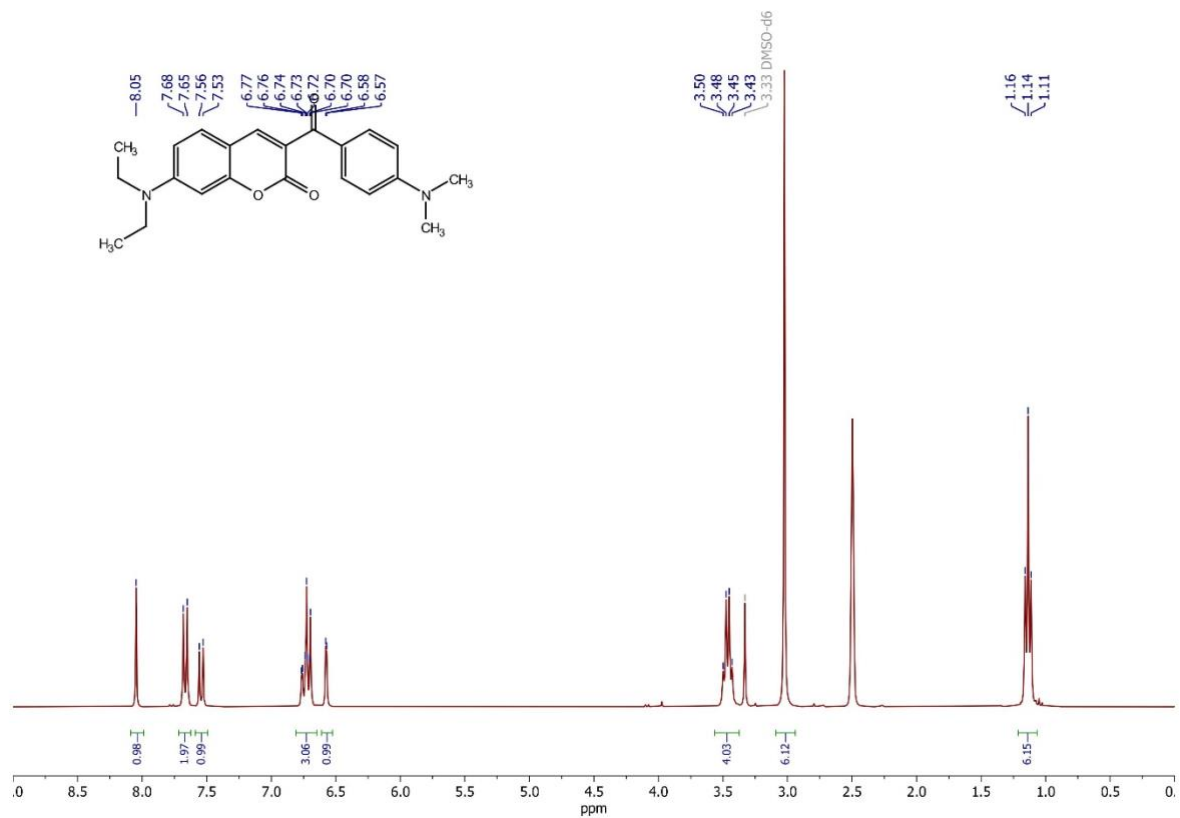


Figure S47: ¹H and ¹³C NMR spectra recorded in DMSO-*d*₆

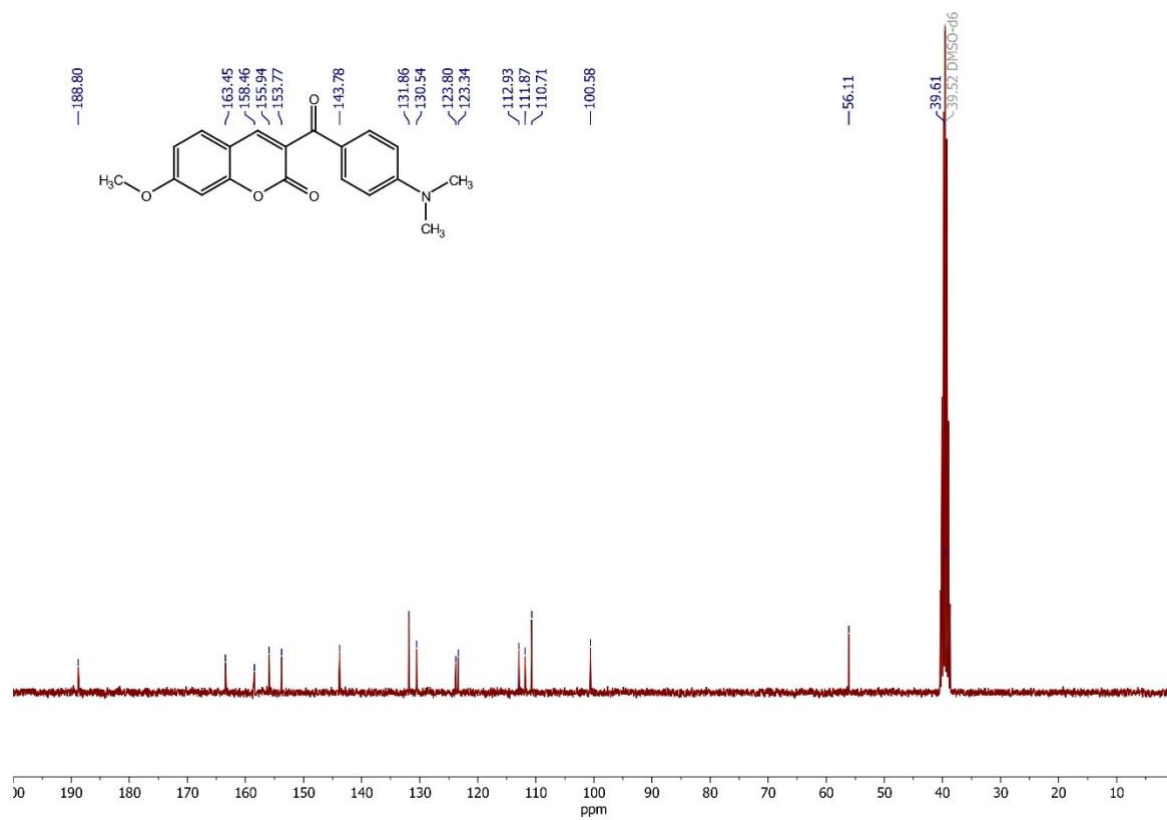
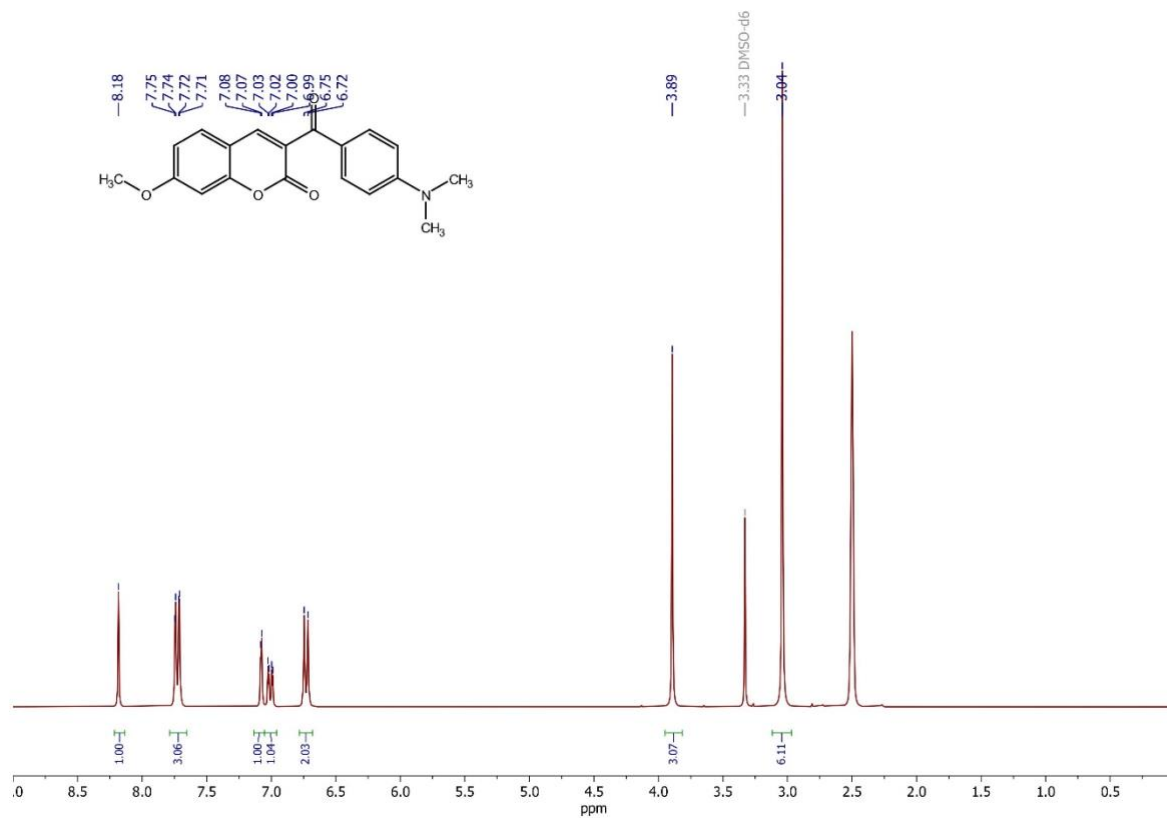


Figure S48: ^1H and ^{13}C NMR spectra recorded in DMSO-*d*₆

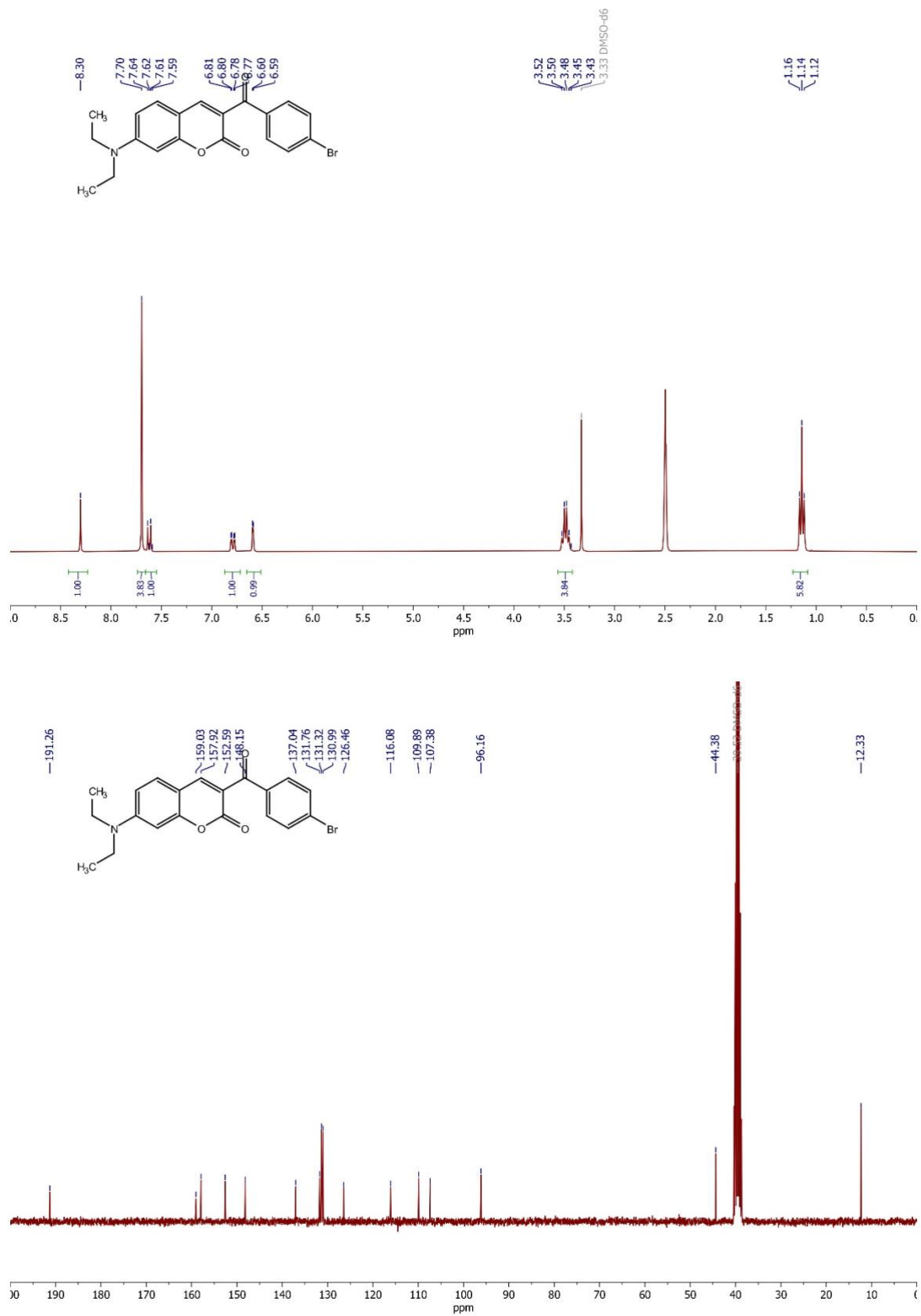


Figure S49: ¹H and ¹³C NMR spectra recorded in DMSO-d₆

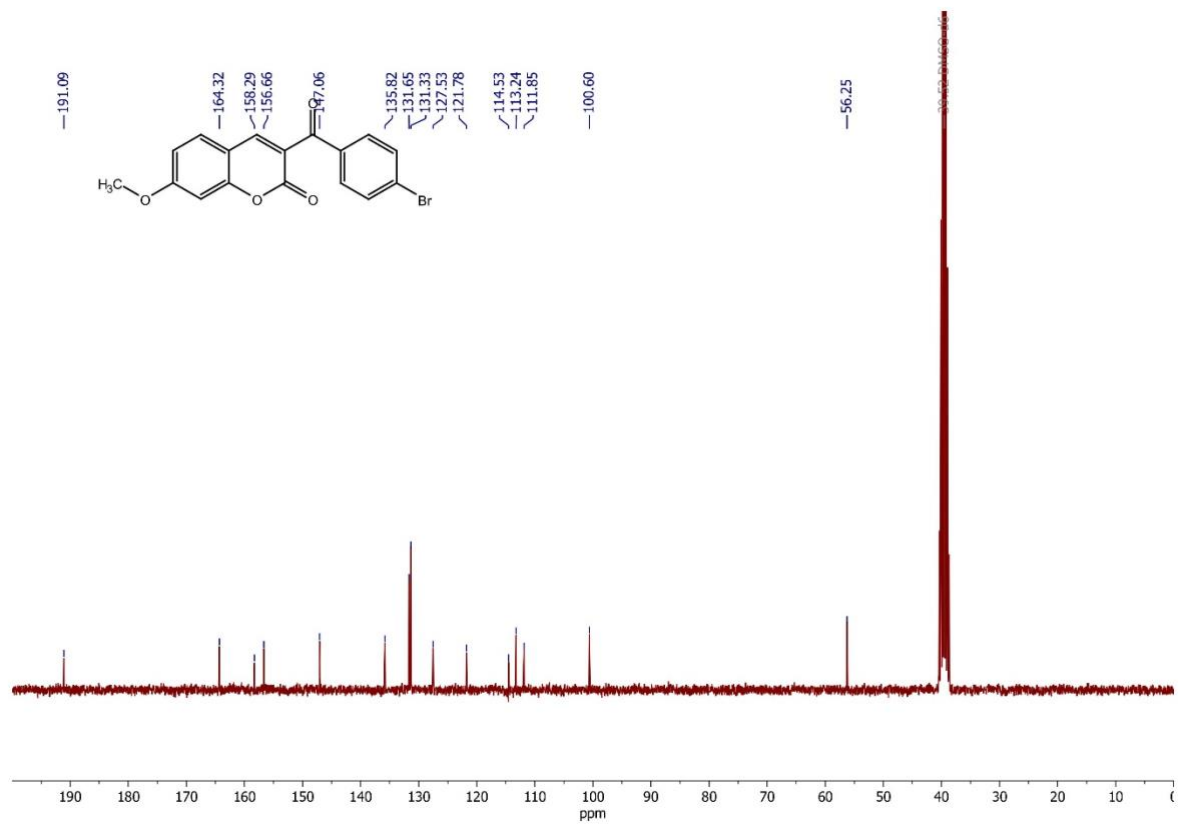
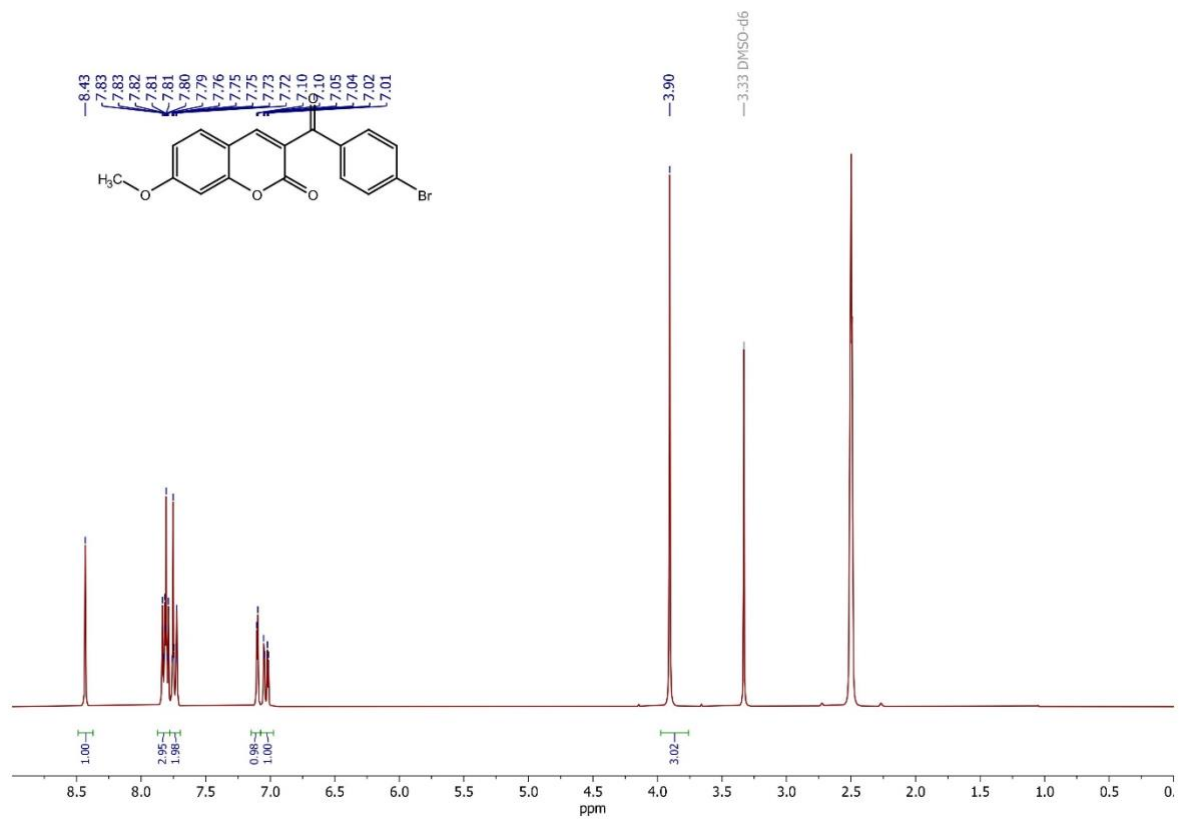


Figure S50: ^1H and ^{13}C NMR spectra recorded in DMSO-*d*₆

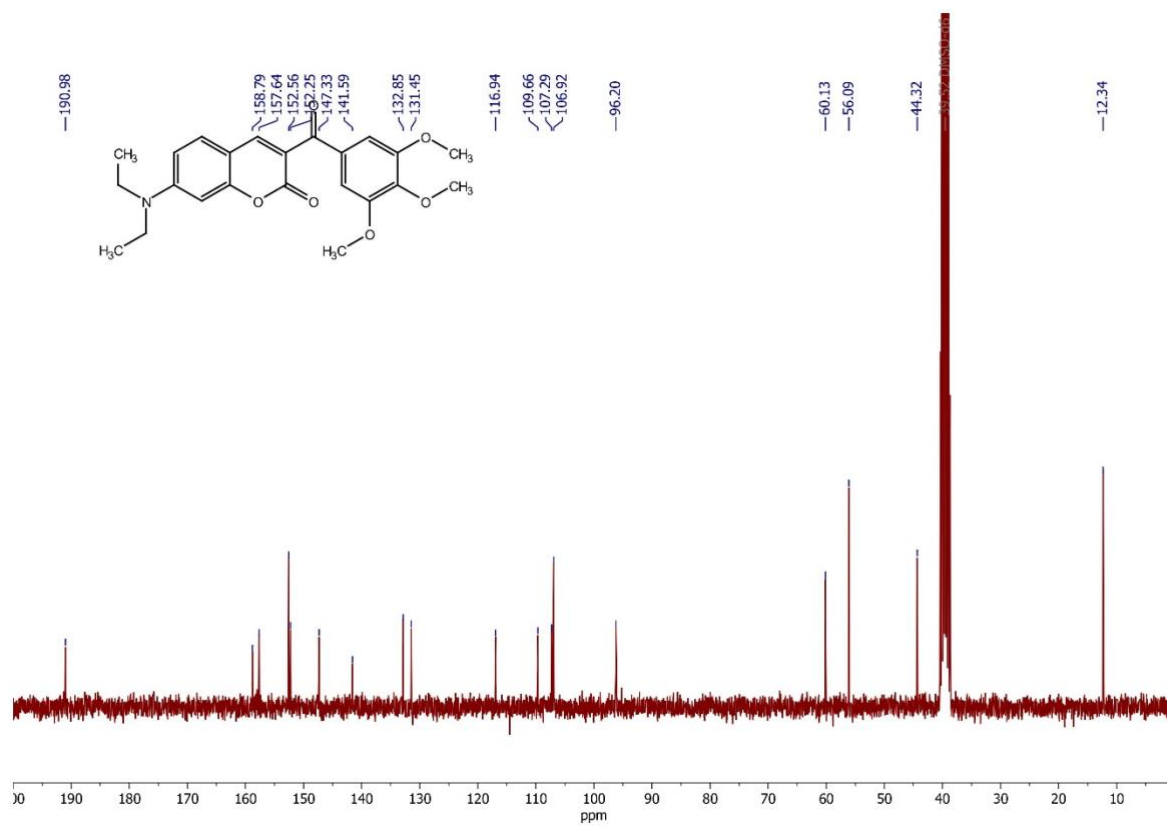
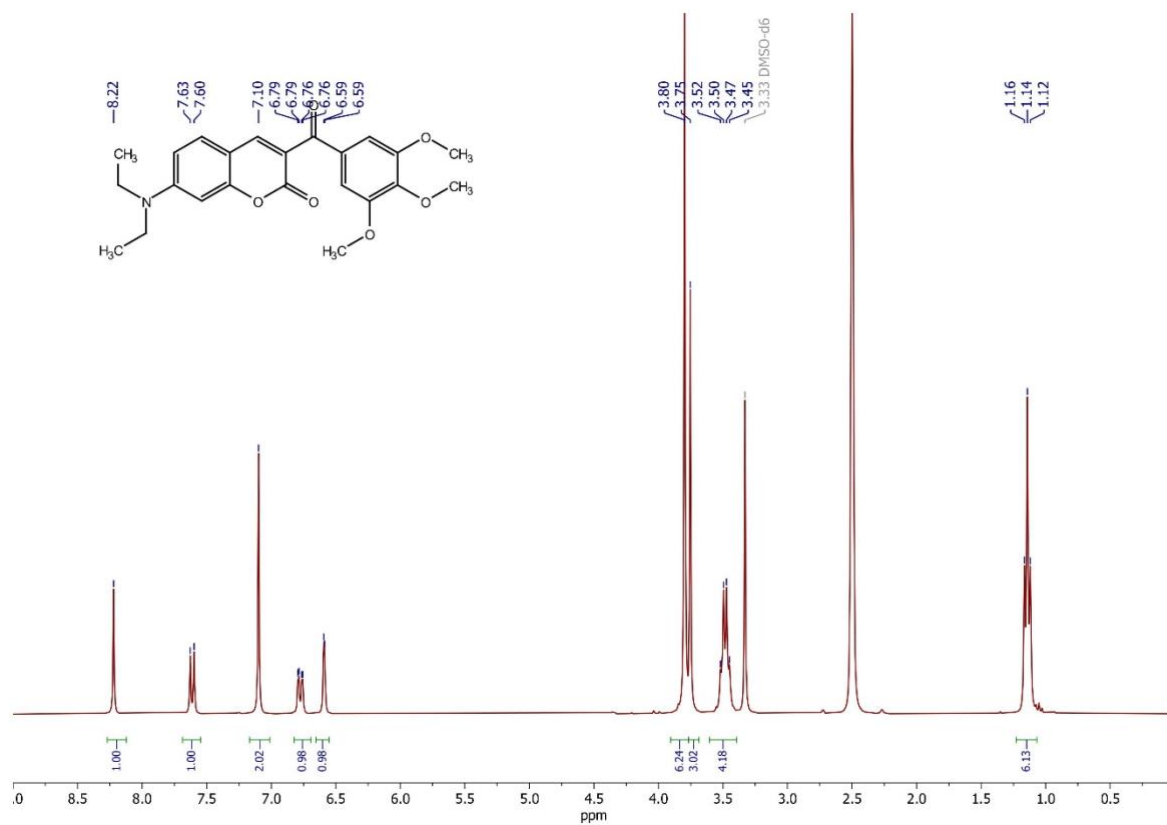


Figure S51: ¹H and ¹³C NMR spectra recorded in DMSO-*d*₆

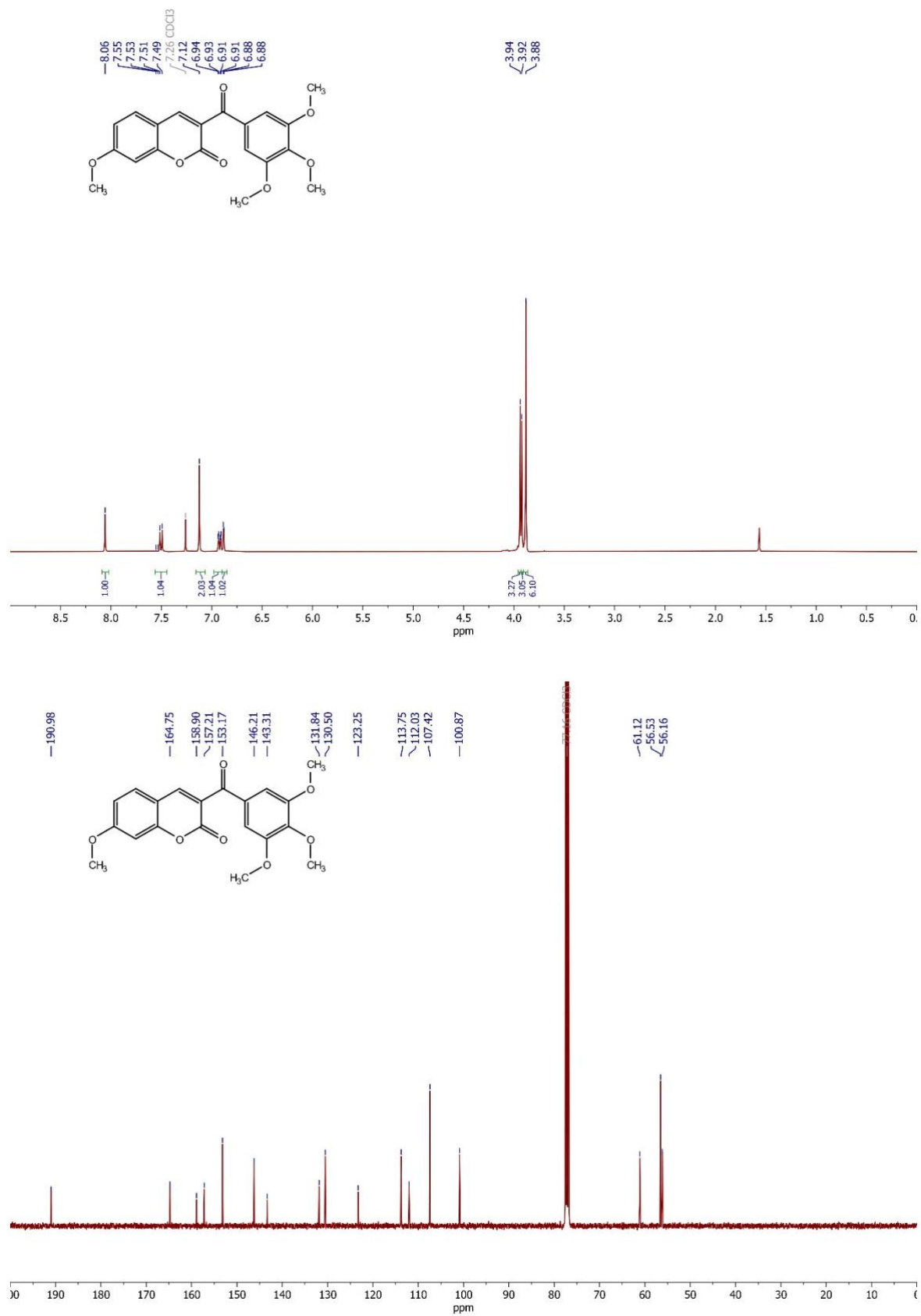


Figure S52: ¹H and ¹³C NMR spectra recorded in DMSO-*d*₆

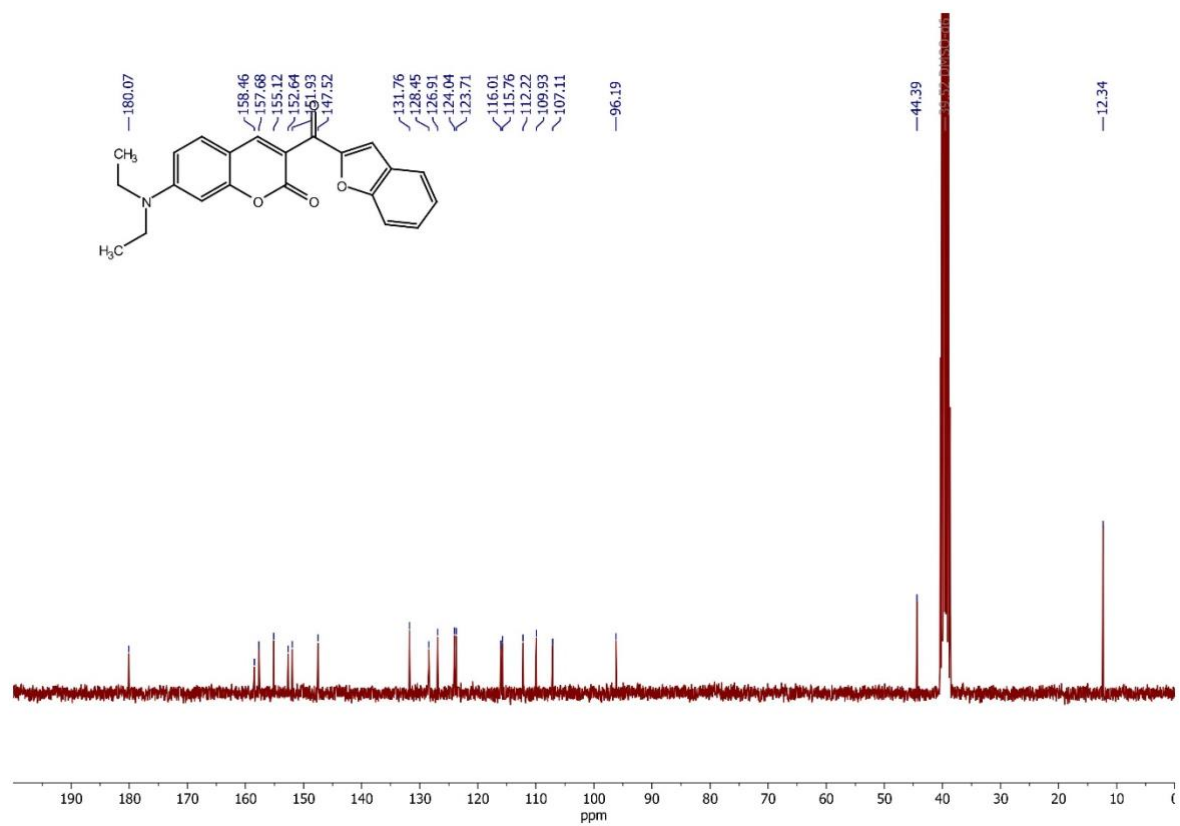
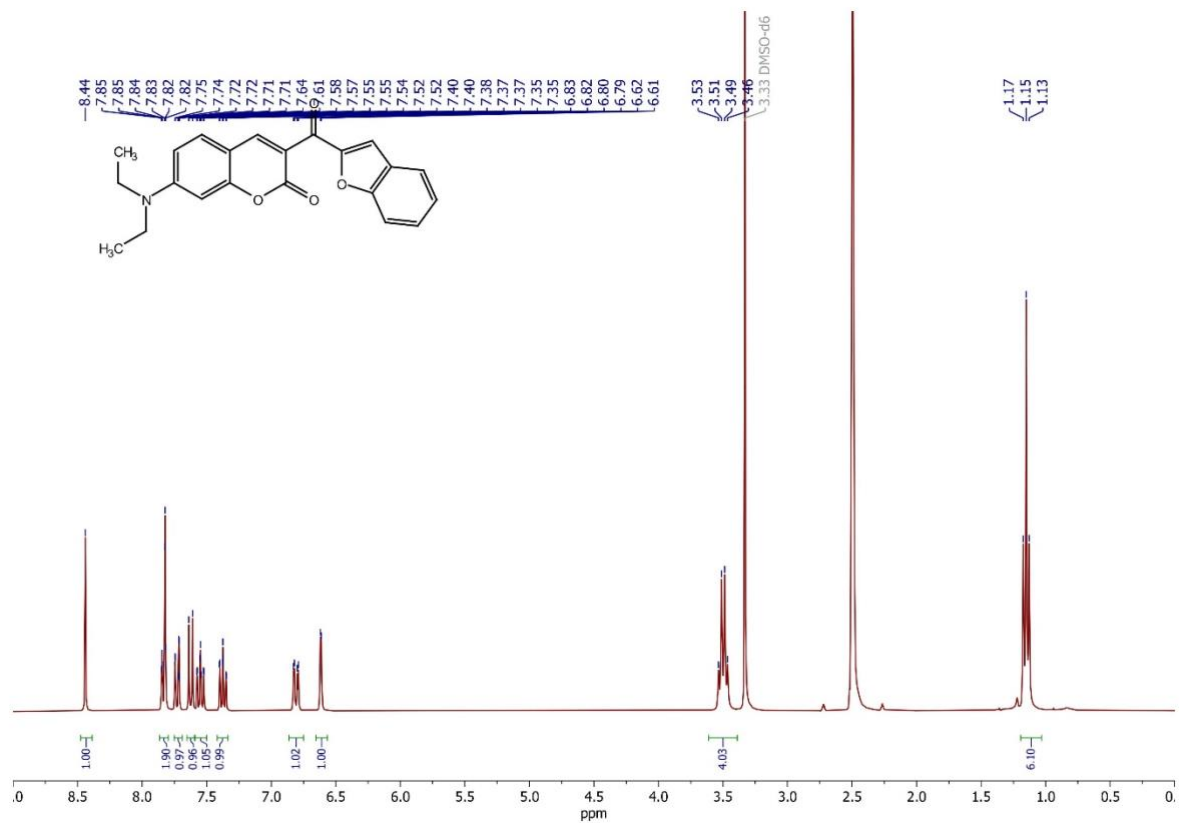


Figure S53: ¹H and ¹³C NMR spectra recorded in DMSO-d₆

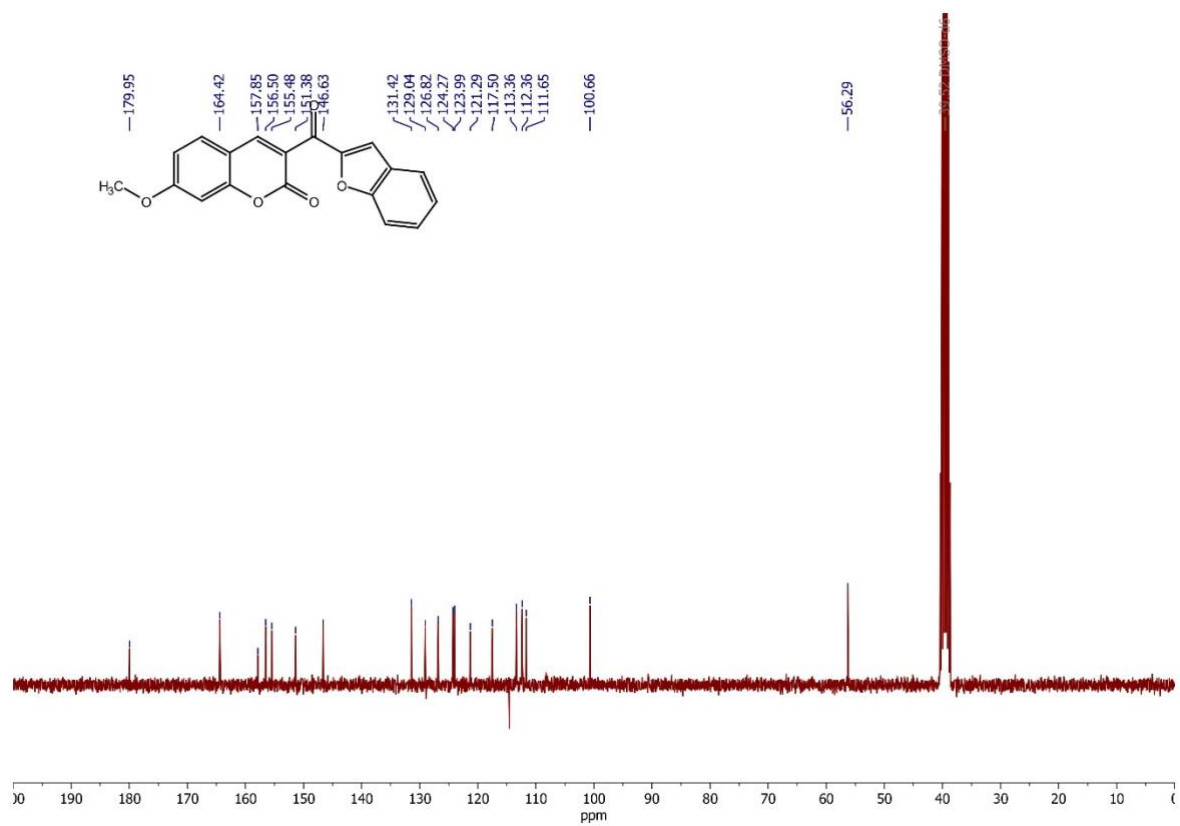
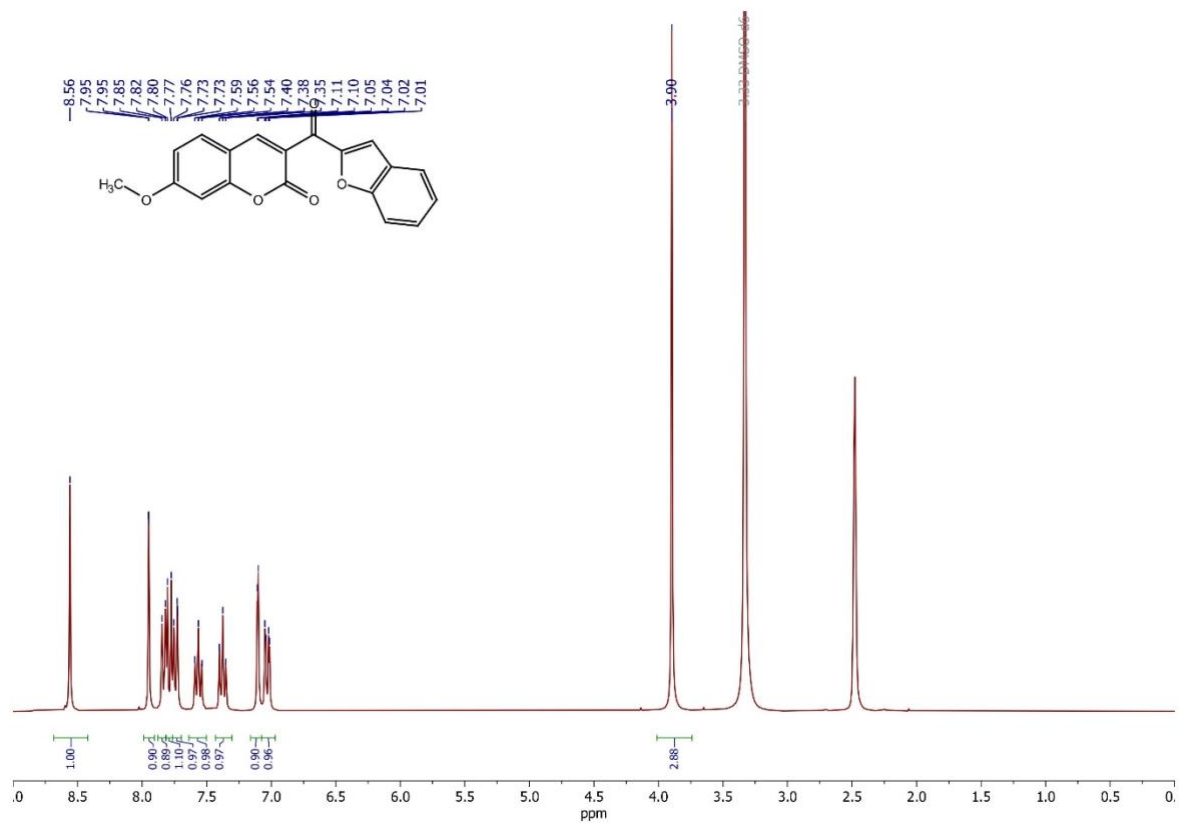


Figure S54: ¹H and ¹³C NMR spectra recorded in DMSO-*d*₆

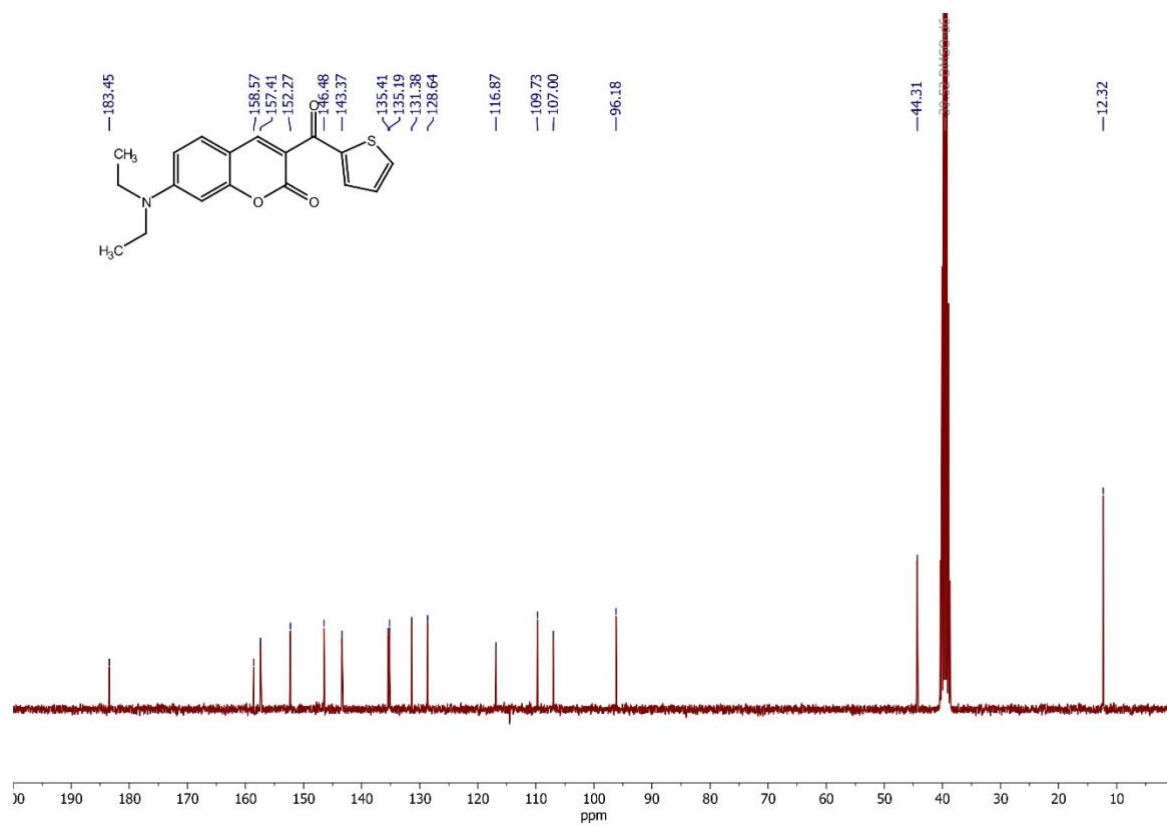
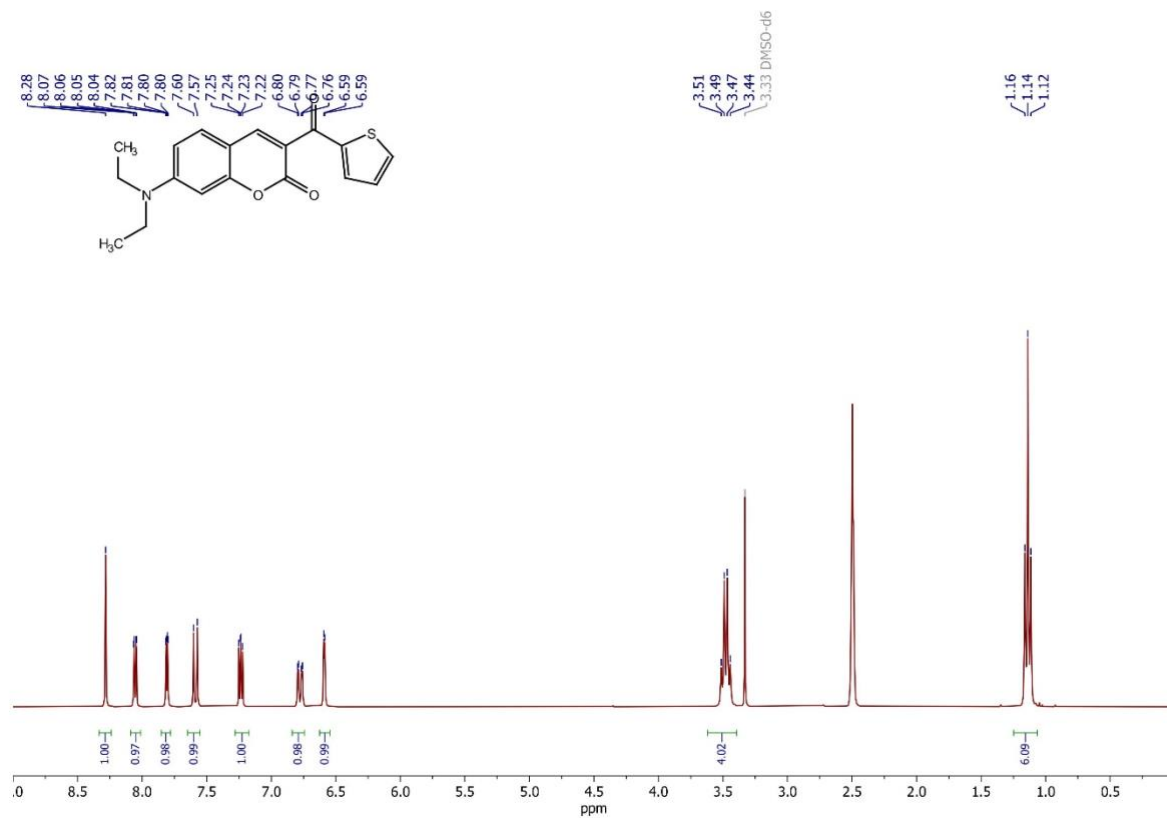


Figure S55: ¹H and ¹³C NMR spectra recorded in DMSO-d₆

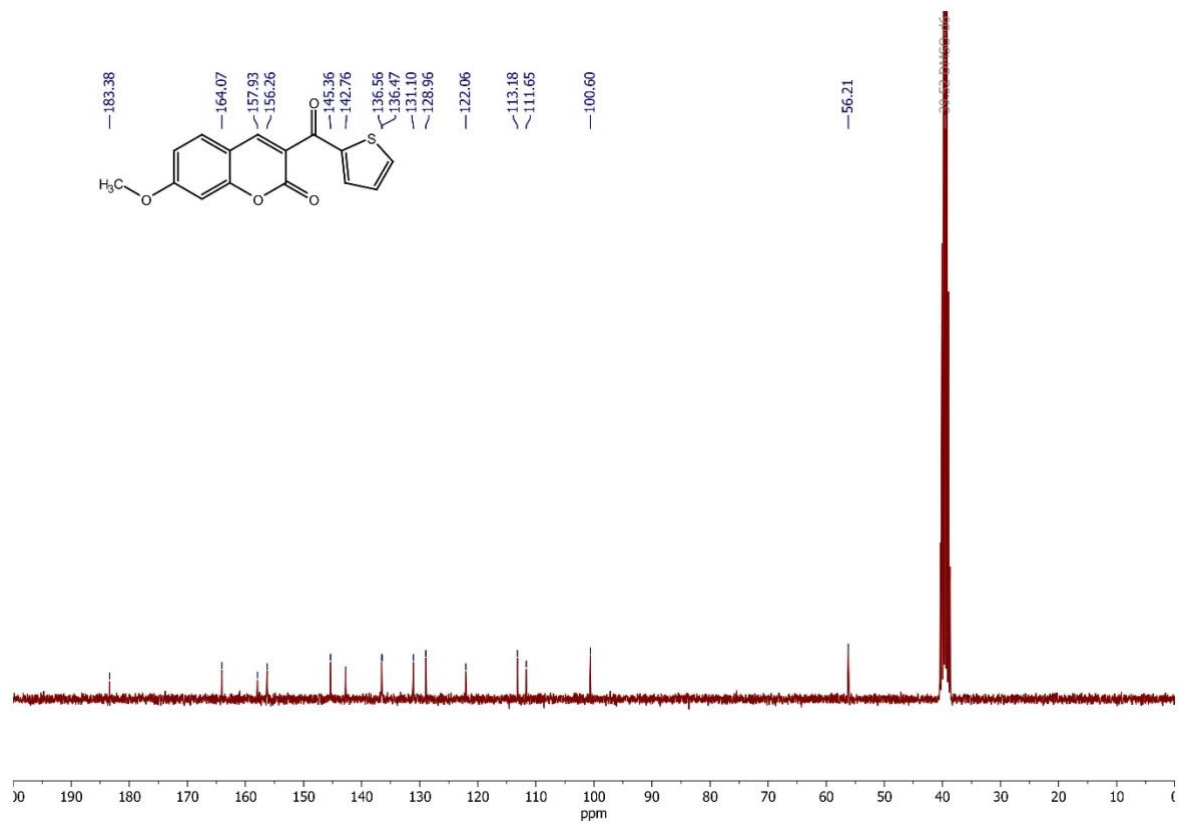
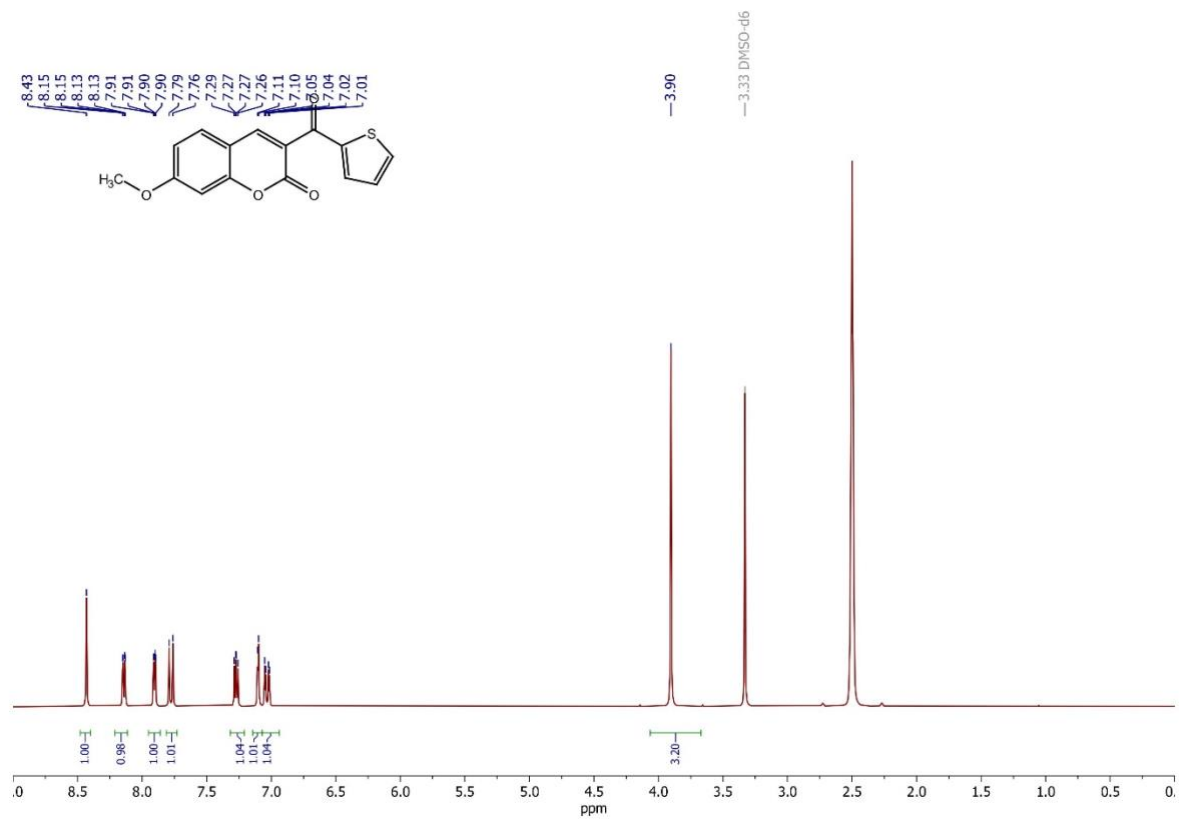


Figure S56: ¹H and ¹³C NMR spectra recorded in DMSO-*d*₆

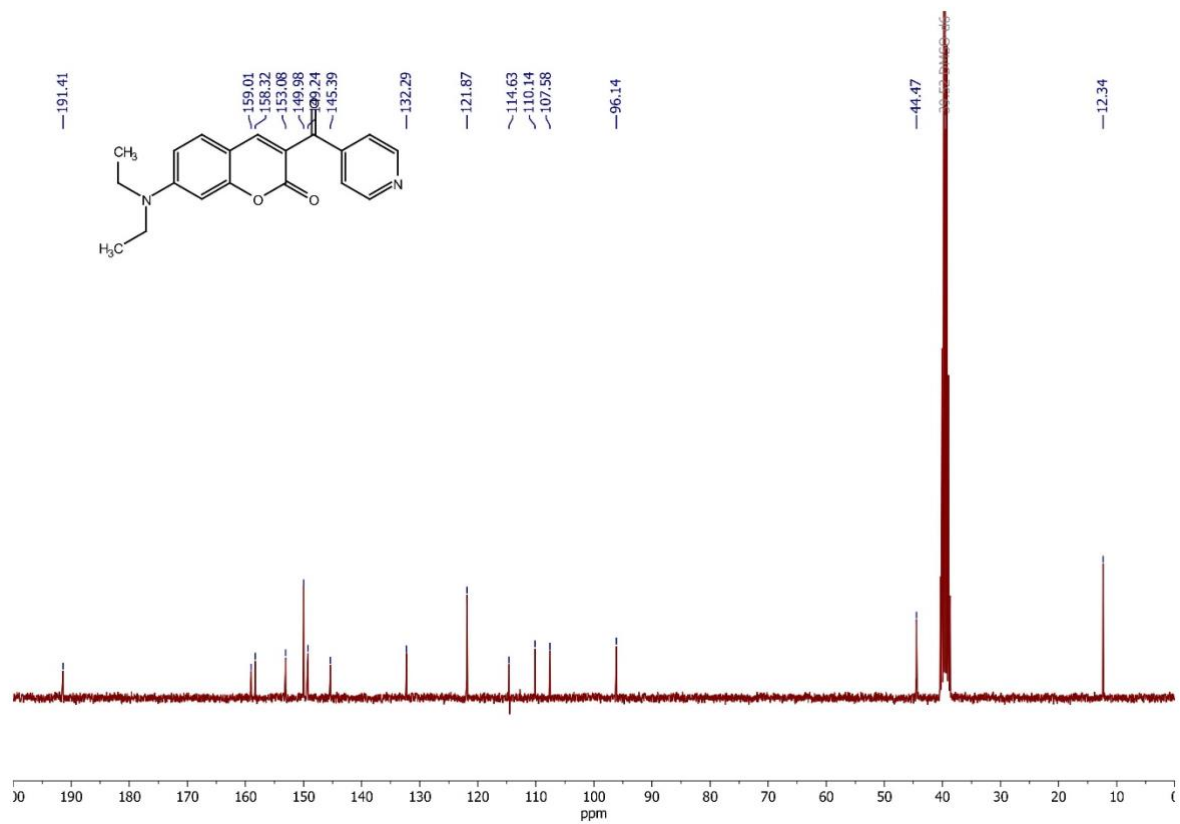
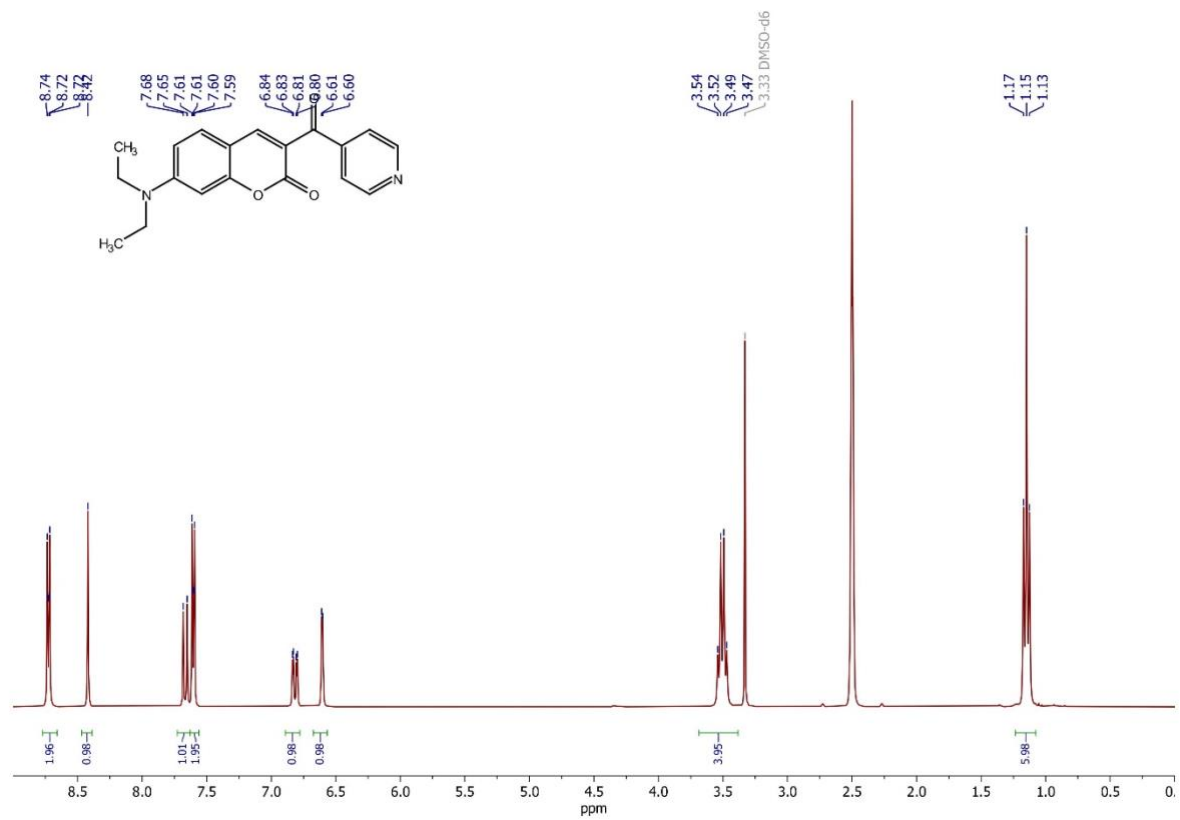


Figure S57: ¹H and ¹³C NMR spectra recorded in DMSO-d₆

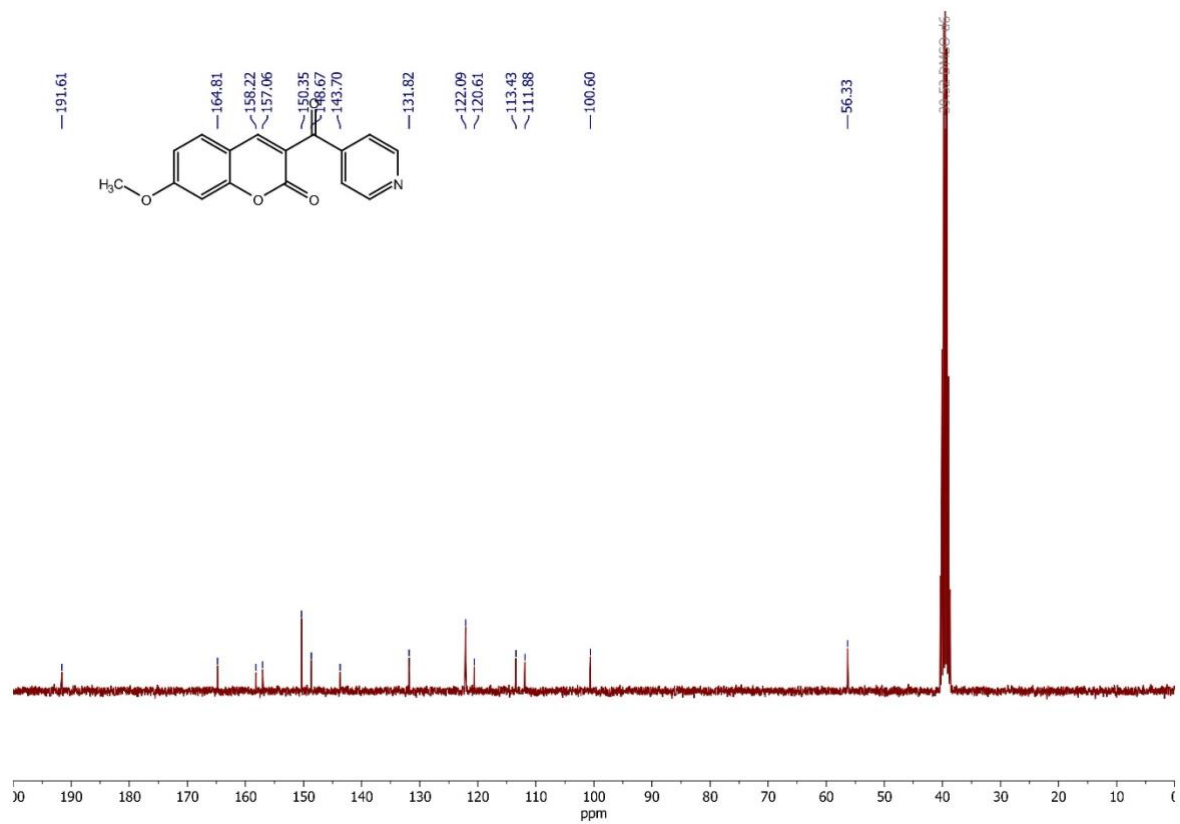
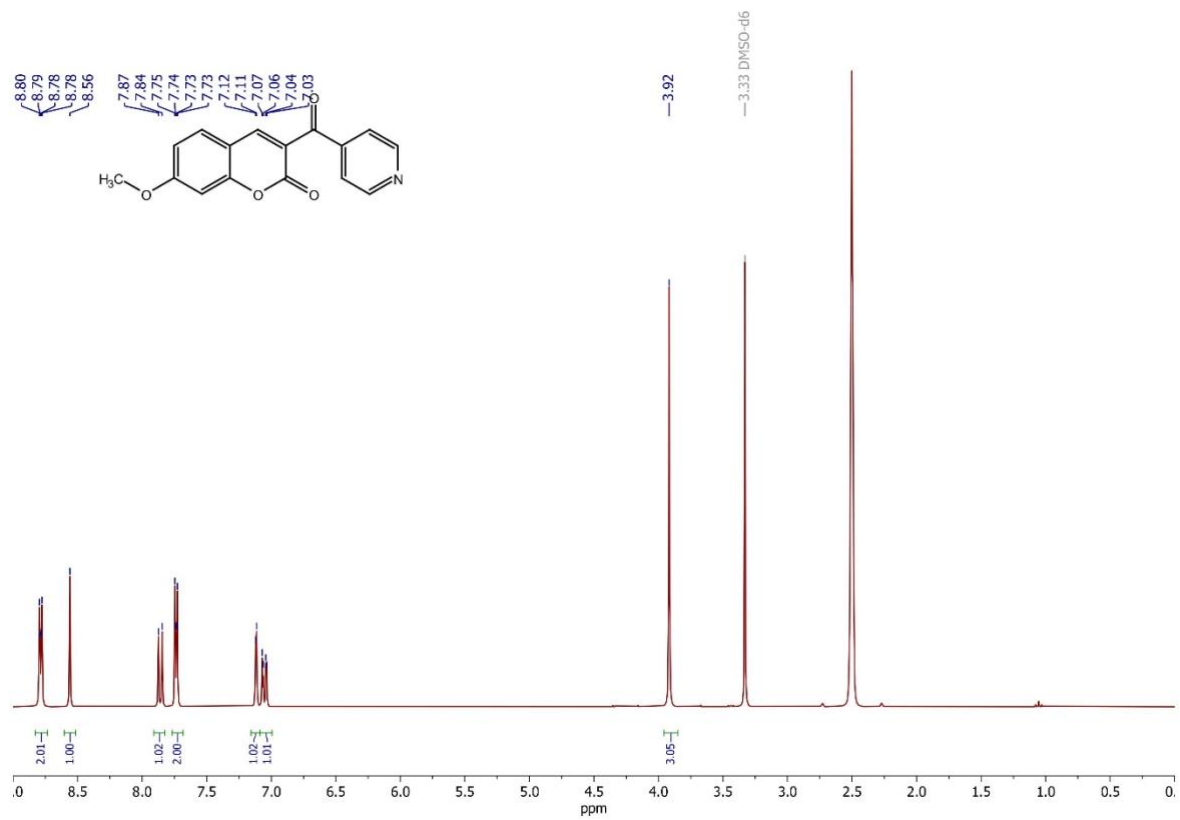


Figure S58: ^1H and ^{13}C NMR spectra recorded in DMSO- d_6

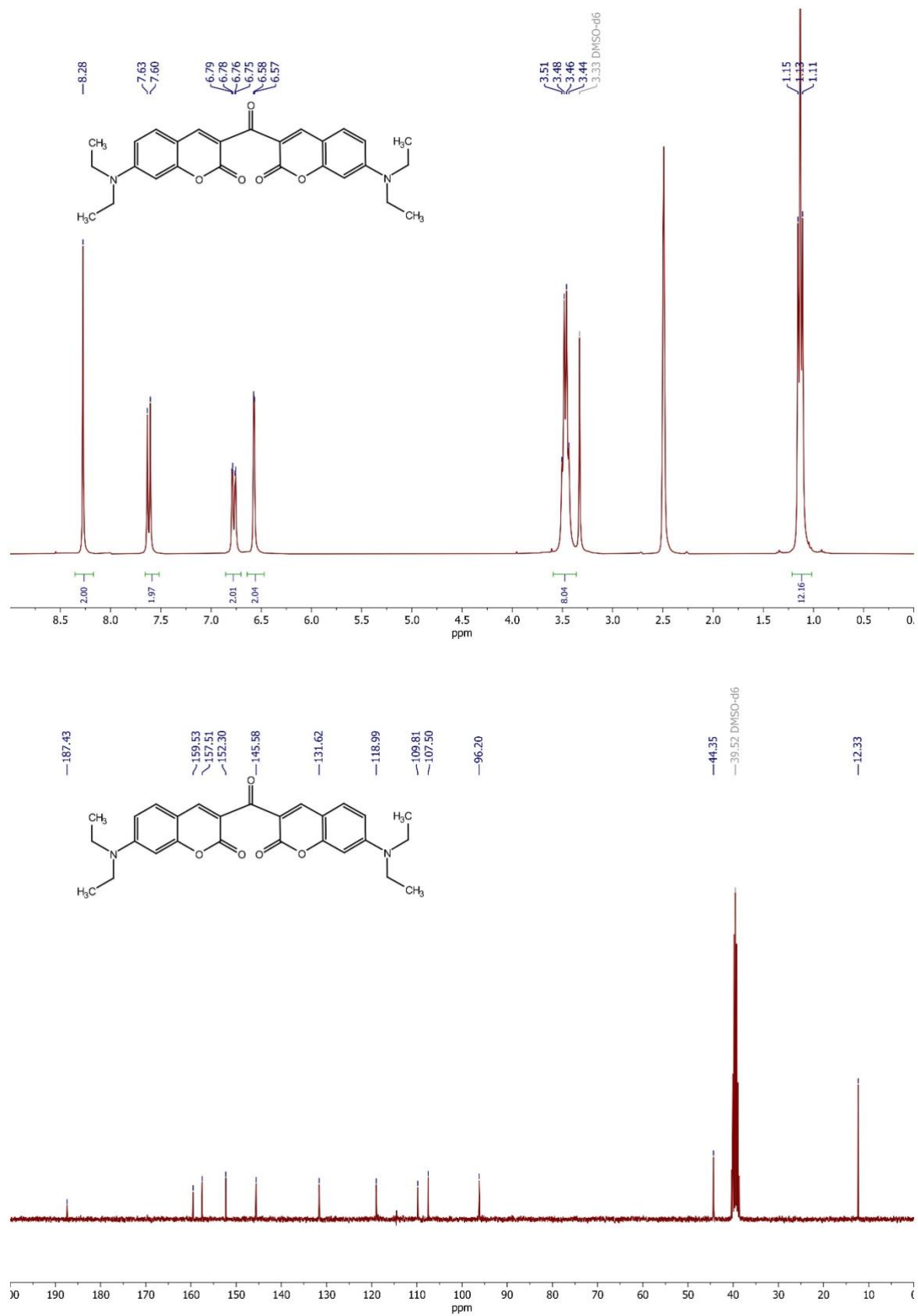


Figure S59: ¹H and ¹³C NMR spectra recorded in DMSO-d₆

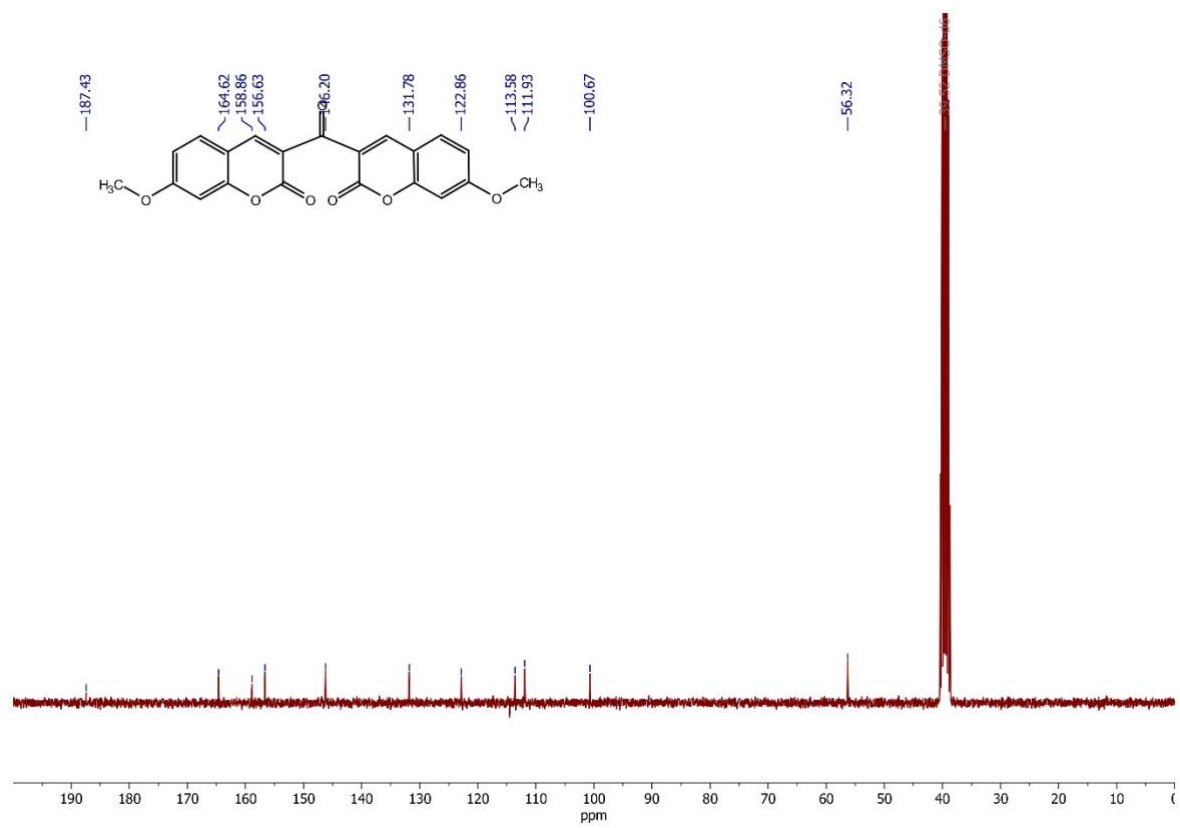
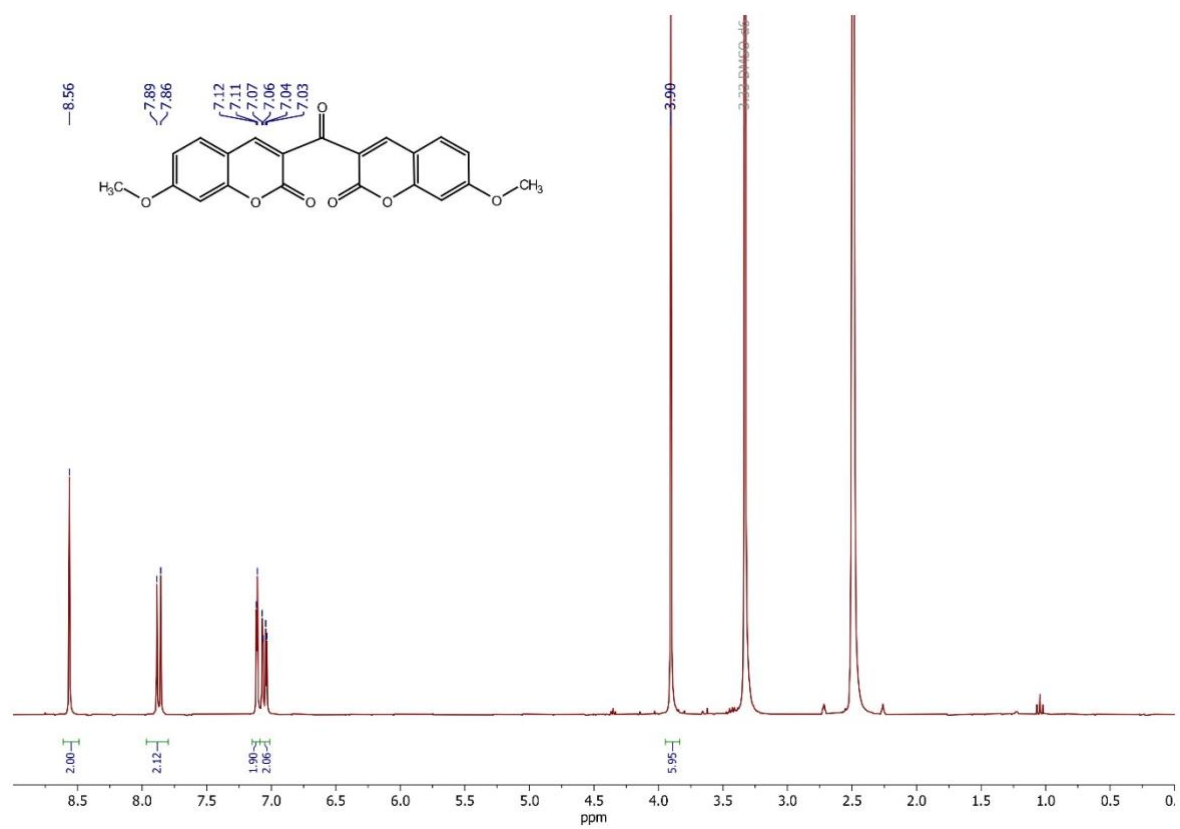


Figure S60: ^1H and ^{13}C NMR spectra recorded in $\text{DMSO-}d_6$

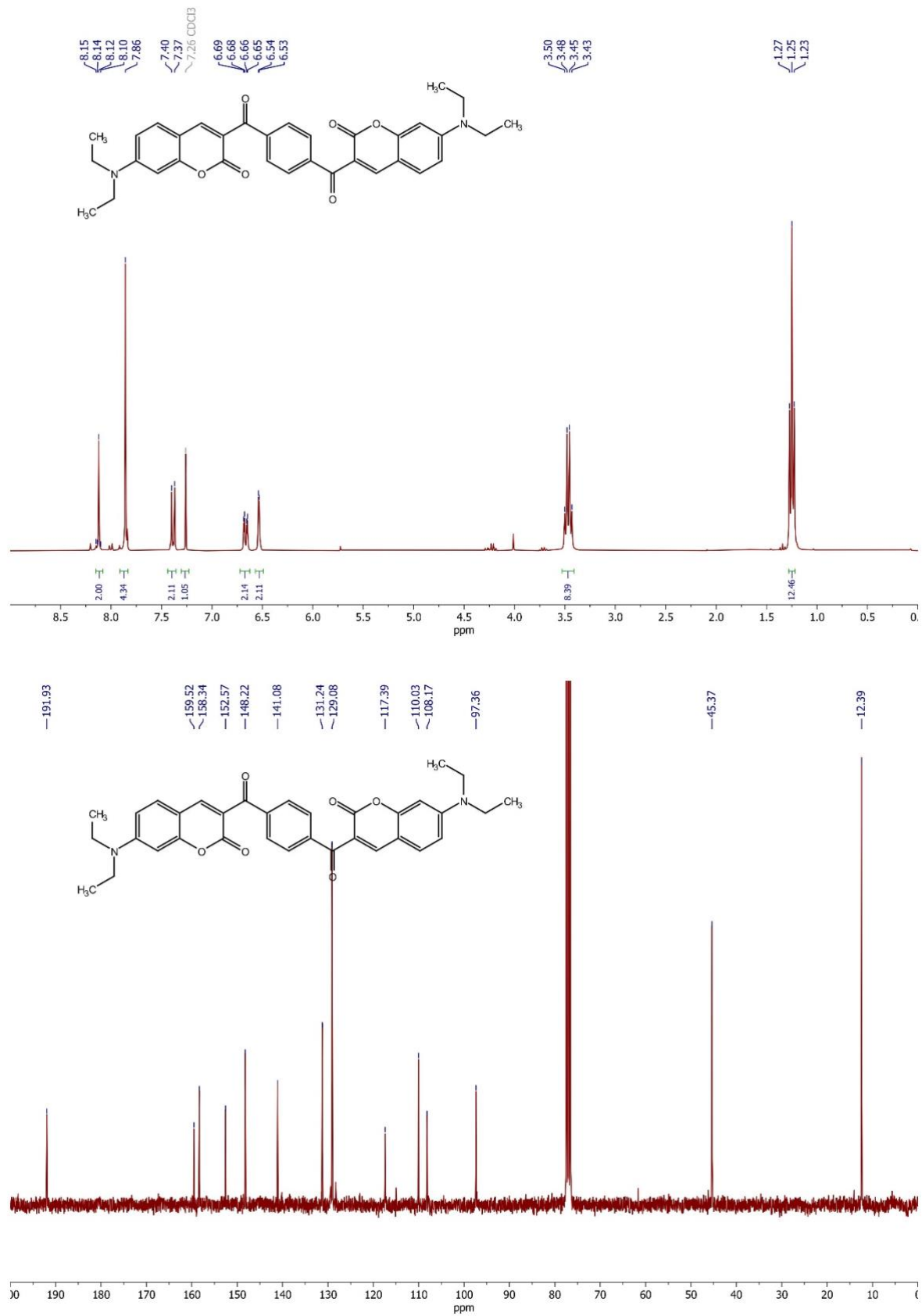


Figure S61: ¹H and ¹³C NMR spectra recorded in DMSO-*d*₆

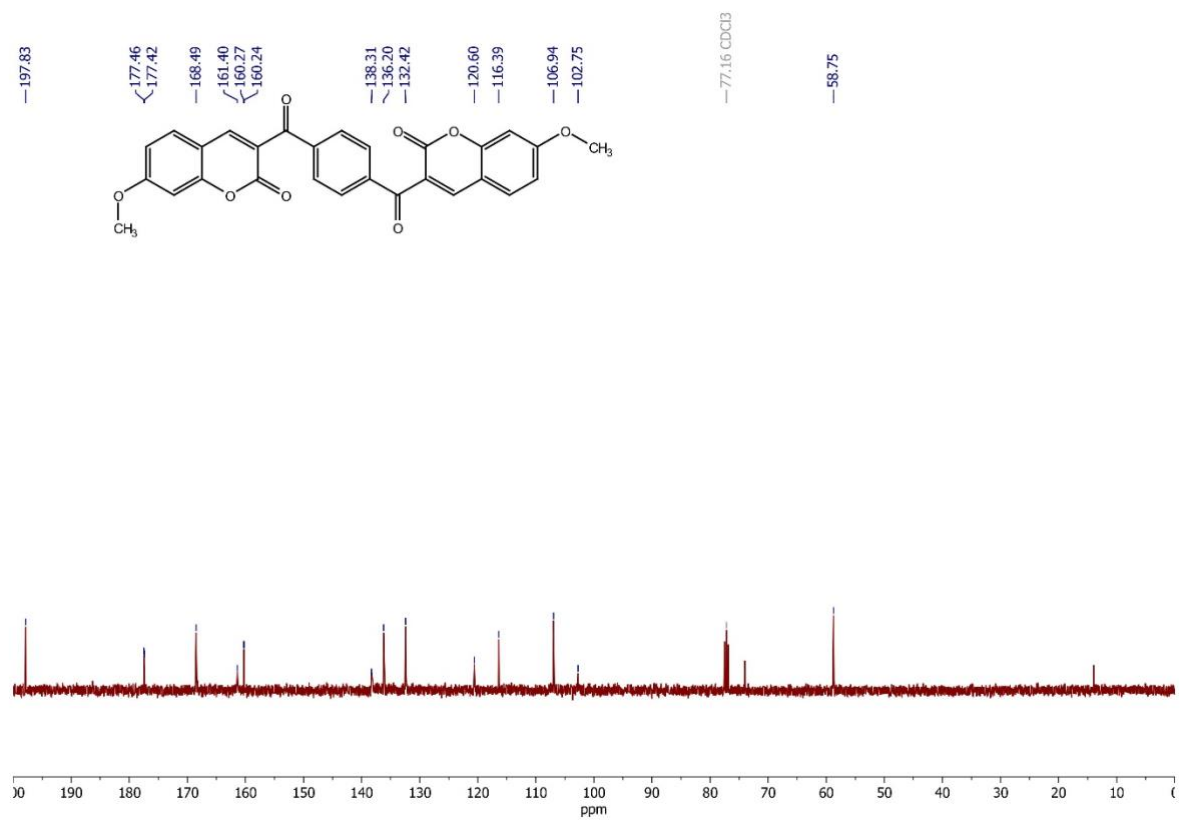
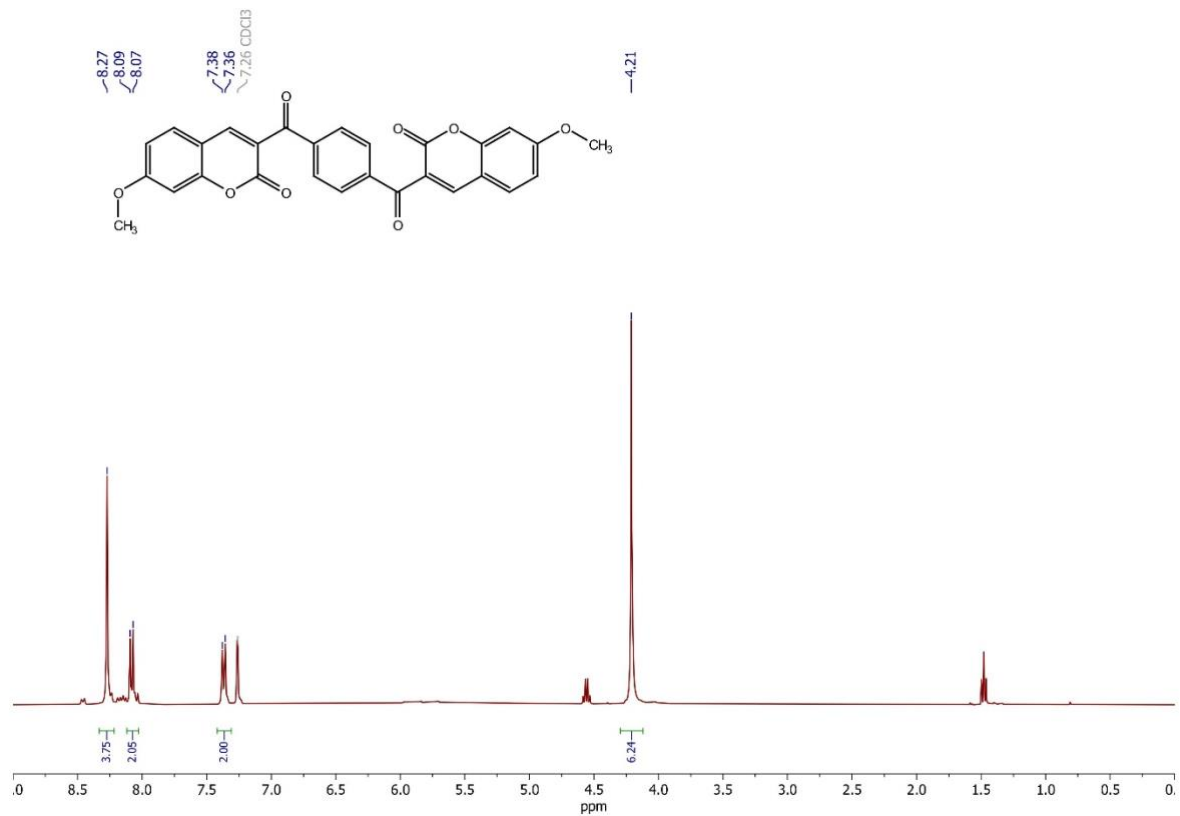


Figure S62: ^1H and ^{13}C NMR spectra recorded in $\text{DMSO}-d_6$

9. References

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