Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Coumarin Derivatives as Dual Photo/Thermal initiators for Free Radical Polymerization and 3D Printing

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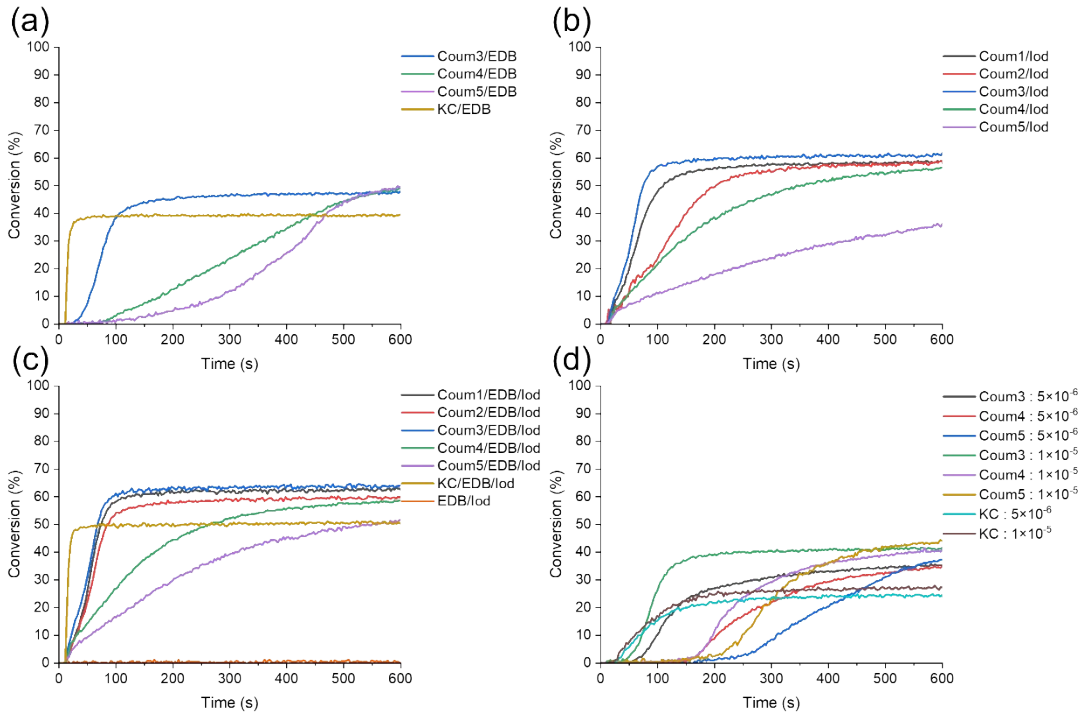


Figure S1. (a), (b), and (c) Photopolymerization kinetics of TMPTA in two- (PIs/EDB, PIs/Iod) and three-component (PIs/EDB/Iod) PISs containing 1×10^{-6} mol·g^{-1} in TMPTA of PIs in a plastic mold (thickness = 1.4 mm) irradiated using a 405 nm LED under air conditions; (d) Photopolymerization kinetics of TMPTA in single-component (PIs) PISs containing different molar content of PIs in a plastic mold (thickness = 1.4 mm) irradiated by a 405 nm LED under air conditions. EDB and Iod (1×10^{-5} mol·g^{-1} in TMPTA). The irradiation starts at t = 10 s.

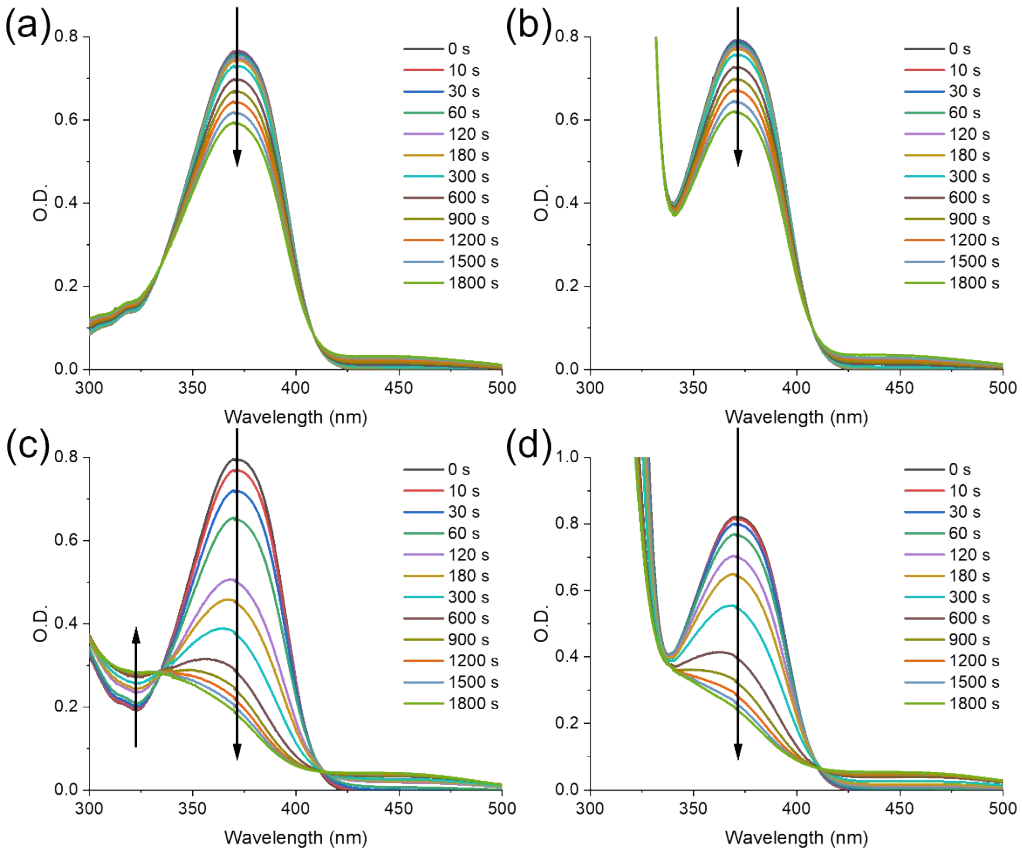


Figure S2. Steady state photolysis of (a) Coum2, (b) Coum2/EDB, (c) Coum2/Iod, and (d) Coum2/EDB/Iod in acetonitrile when exposed to 405 nm LED.

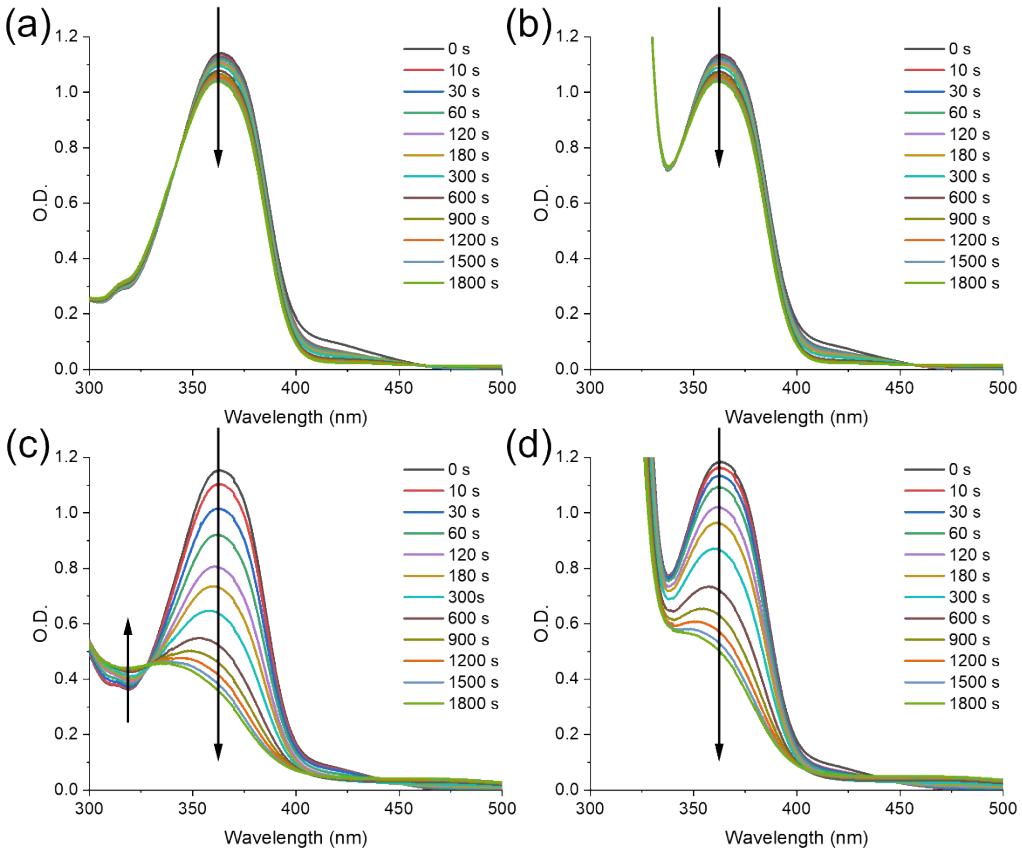


Figure S3. Steady state photolysis of (a) Coum3, (b) Coum3/EDB, (c) Coum3/Iod, and (d) Coum3/EDB/Iod in acetonitrile when exposed to 405 nm LED.

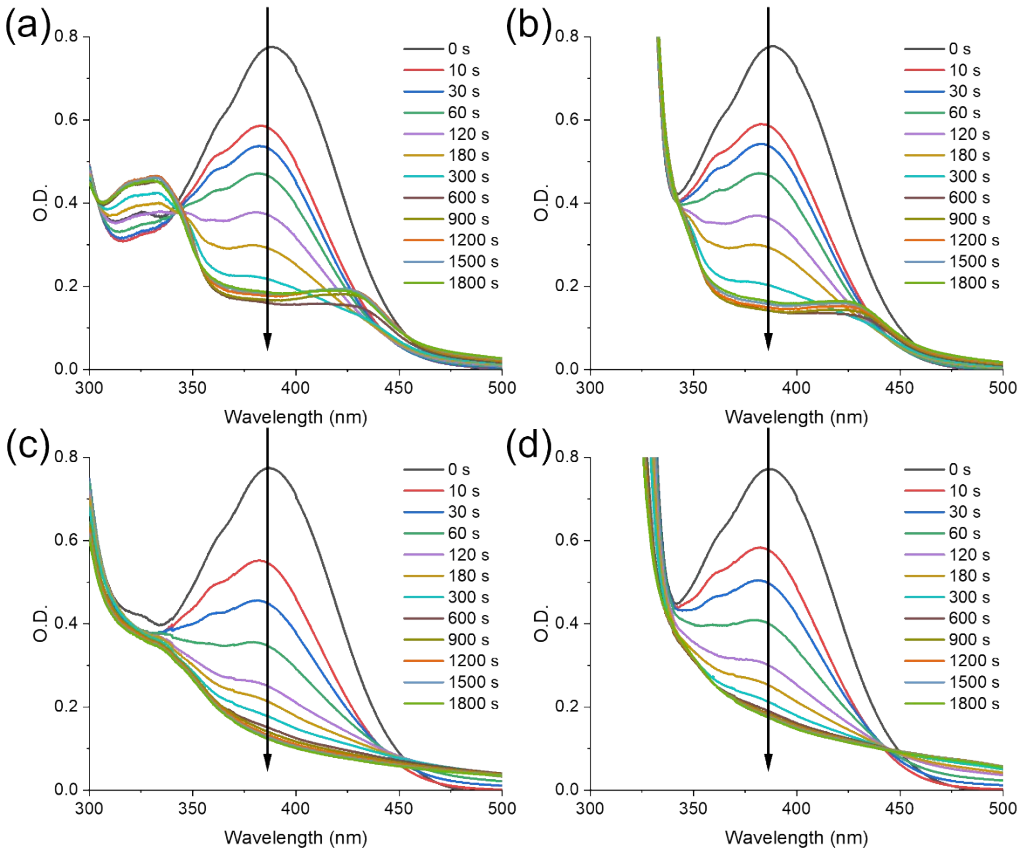


Figure S4. Steady state photolysis of (a) Coum4, (b) Coum4/EDB, (c) Coum4/Iod, and (d) Coum4/EDB/Iod in acetonitrile when exposed to 405 nm LED.

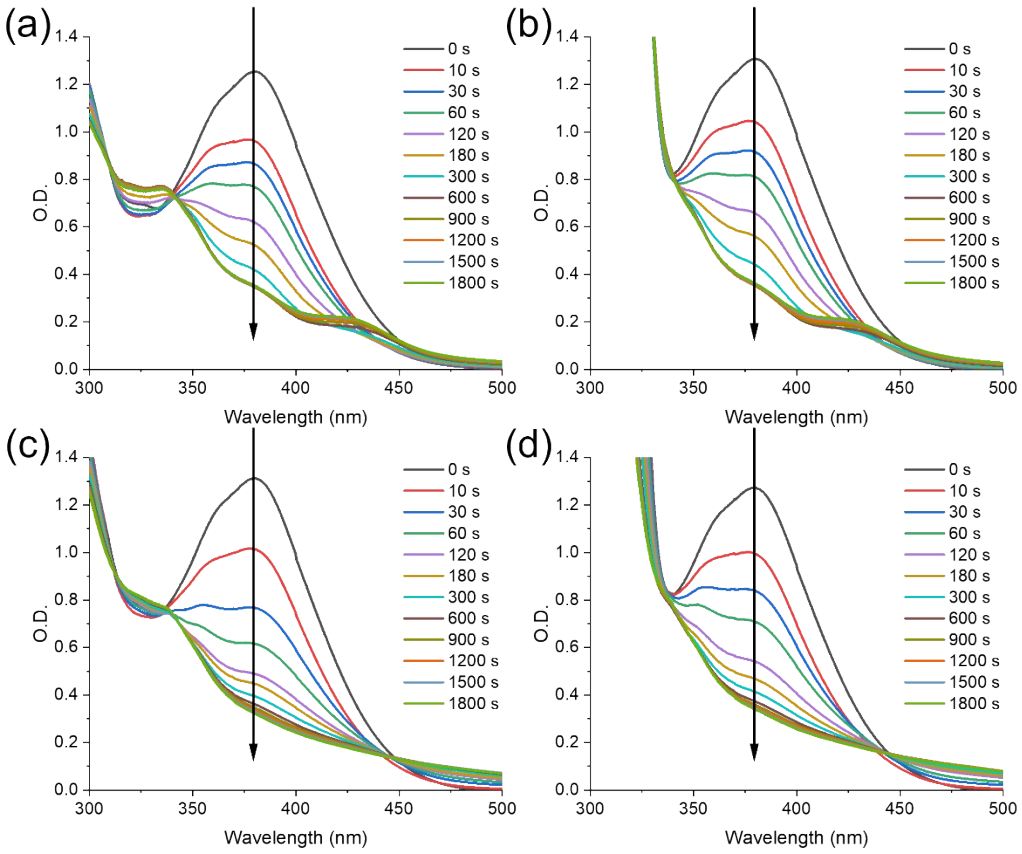


Figure S5. Steady state photolysis of (a) Coum5, (b) Coum5/EDB, (c) Coum5/Iod, and (d) Coum5/EDB/Iod in acetonitrile when exposed to 405 nm LED.

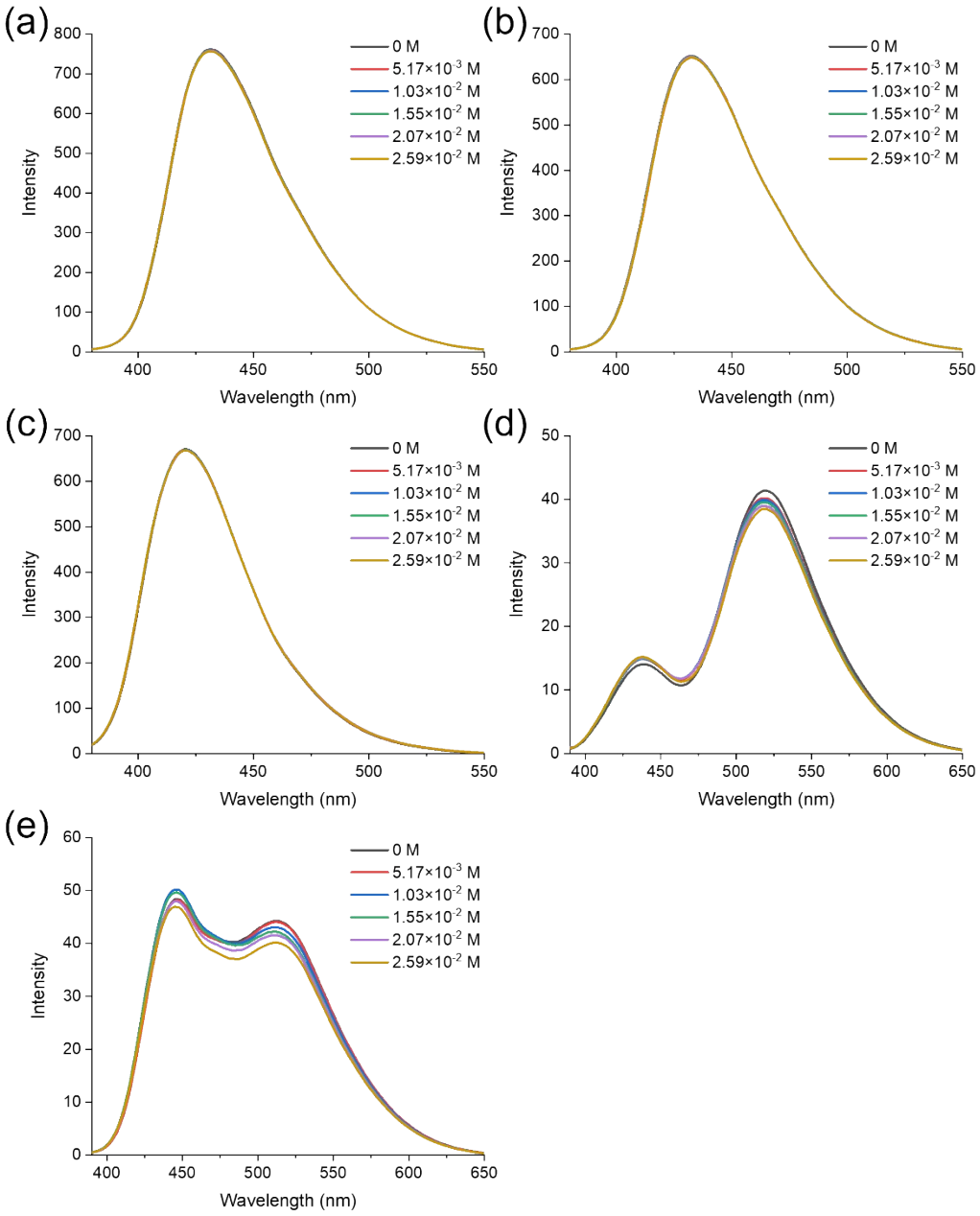


Figure S6. Fluorescence quenching of (a) Coum1, (b) Coum2, (c) Coum3, (d) Coum4, and (e) Coum5 by EDB in acetonitrile.

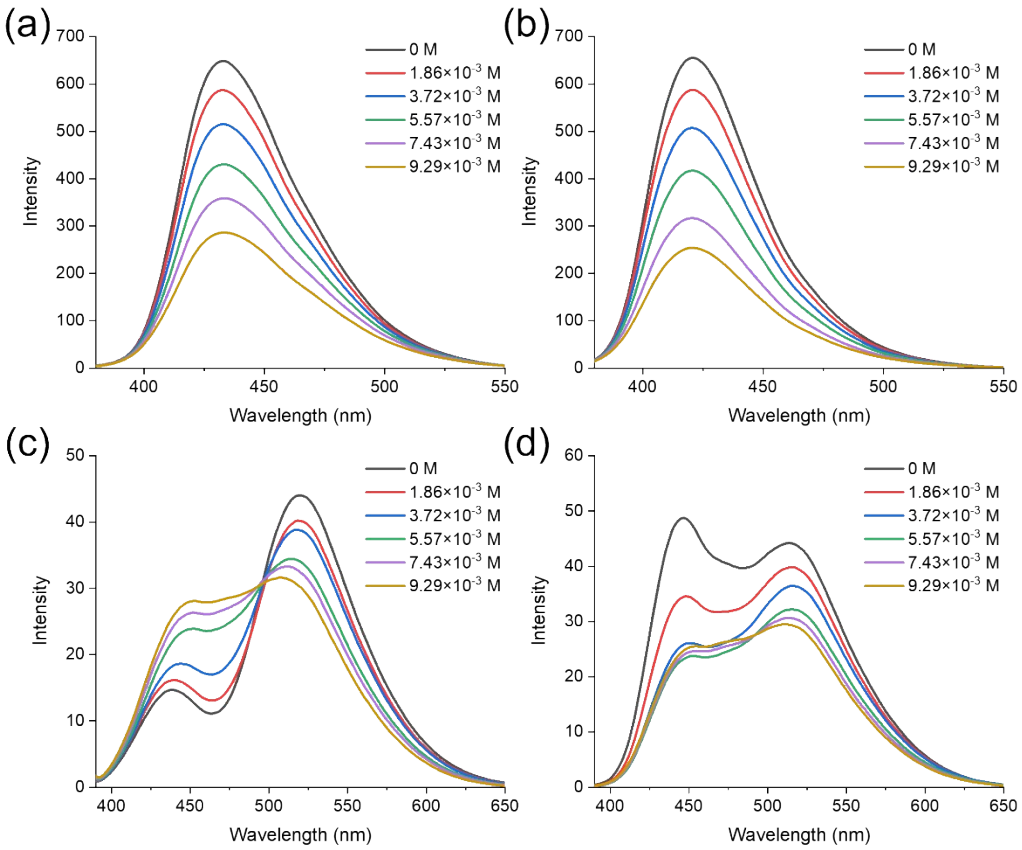


Figure S7. Fluorescence quenching of (a) Coum2, (b) Coum3, (c) Coum4, and (d) Coum5 by Iod in acetonitrile.

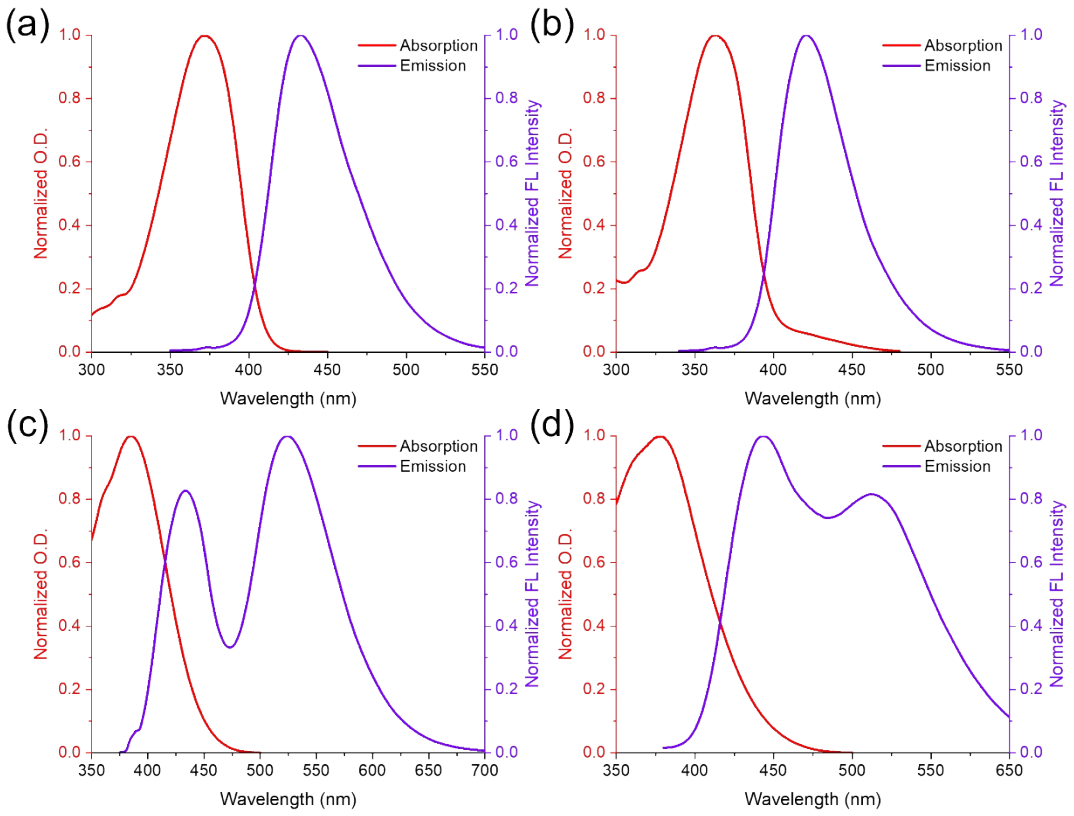


Figure S8. Singlet-state energy determination of (a) Coum2, (b) Coum3, (c) Coum4, and (d) Coum5 in acetonitrile (concentration = 5×10^{-5} M).

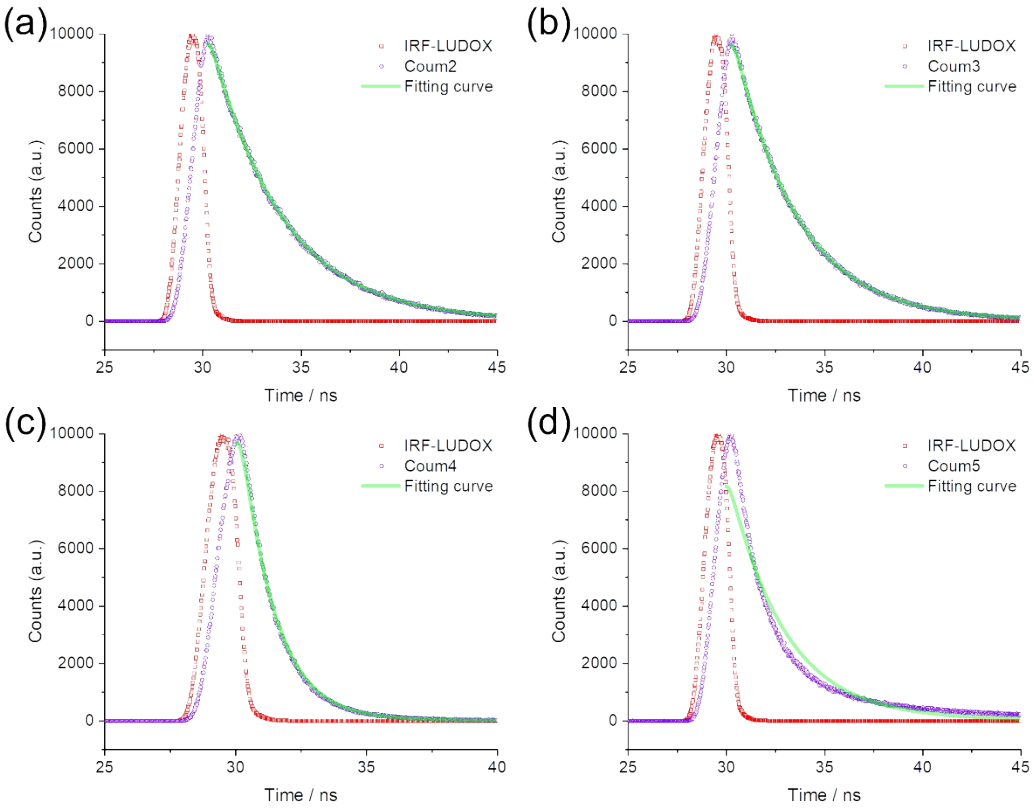


Figure S9. Fluorescence decay curve of (a) Coum2, (b) Coum3, (c) Coum4, and (d) Coum5 in acetonitrile (concentration = 5×10^{-5} M).

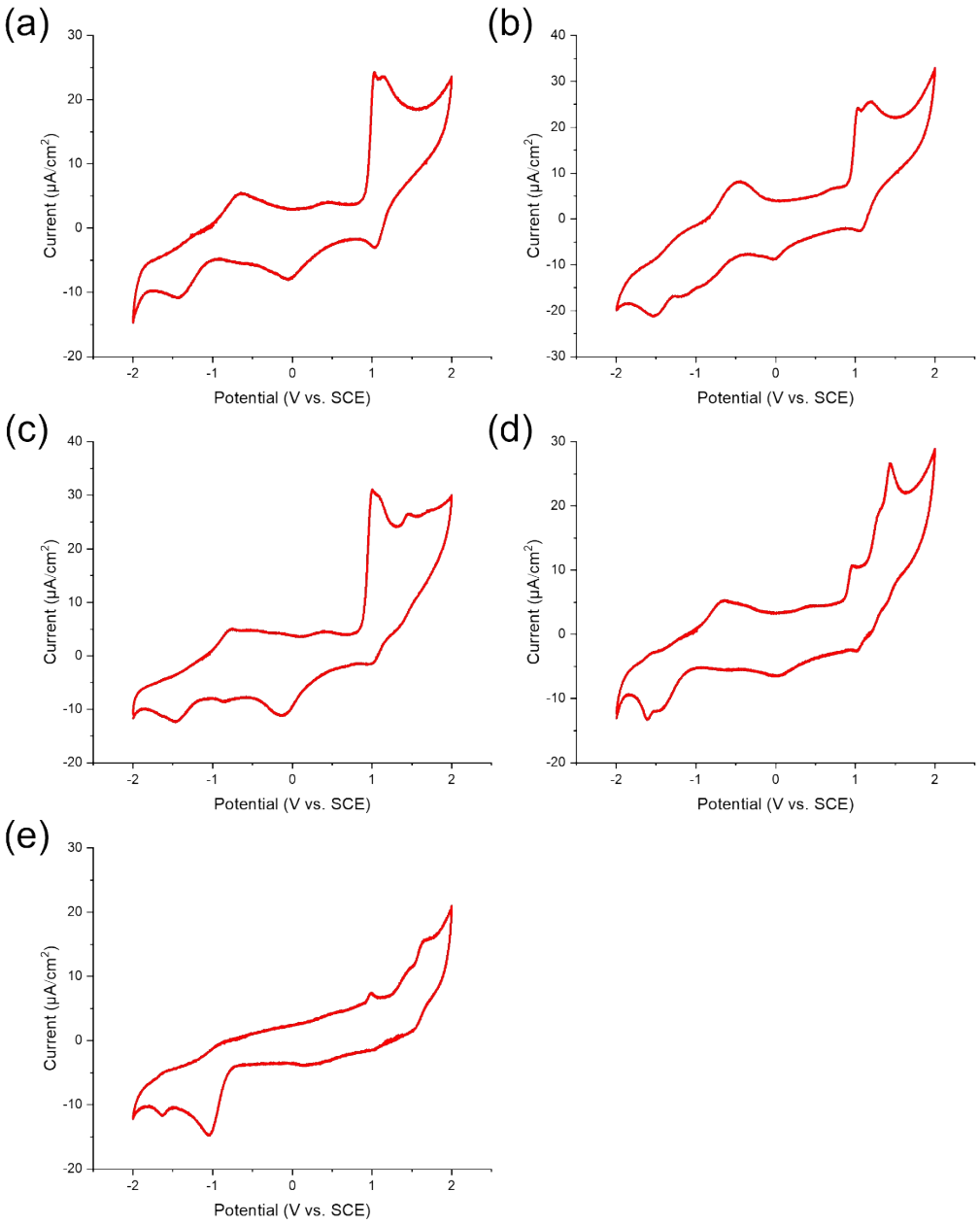


Figure S10. Cyclic voltammograms of electrochemical reactions of (a) Coum1, (b) Coum2, (c) Coum3, (d) Coum4, and (e) Coum5 in acetonitrile solvent against saturated calomel electrode (SCE) under nitrogen saturated solution.

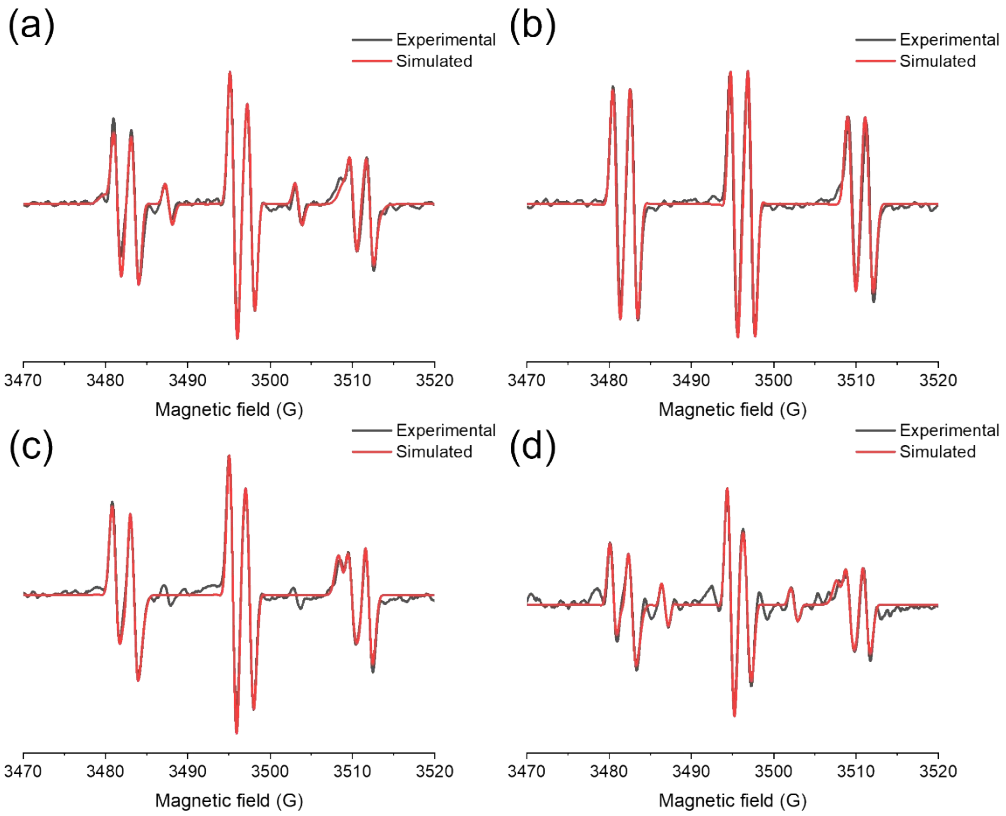


Figure S11. ESR-ST spectra of the radical adducts of (a) Coum2/Iod, (b) Coum3/Iod, (c) Coum4/Iod, and (d) Coum5/Iod in N_2 saturated medium when exposed to the 405 nm LED, with PBN acting as the trapping agent in *tert*-butylbenzene.

Table S1. FCs of TMPTA in two- (PIs/EDB, PIs/Iod) and three-component (PIs/EDB/Iod) PISs containing 1×10^{-6} mol·g^{-1} TMPTA of PIs after 600 s of irradiation by a 405 nm LED under air conditions (for EDB and Iod; the concentration is 1×10^{-5} mol·g^{-1} in TMPTA).

PIs/EDB	FC (%)	PIs/Iod	FC (%)	PIs/EDB/Iod	FC (%)
Coum1/EDB	np	Coum1/Iod	59	Coum1/EDB/Iod	63
Coum2/EDB	np	Coum2/Iod	59	Coum2/EDB/Iod	60
Coum3/EDB	42	Coum3/Iod	62	Coum3/EDB/Iod	64
Coum4/EDB	41	Coum4/Iod	57	Coum4/EDB/Iod	59
Coum5/EDB	44	Coum5/Iod	36	Coum5/EDB/Iod	52
KC/EDB	39	KC/Iod	np	KC/EDB/Iod	50
				EDB/Iod	np

np: no polymerization.

Table S2. FCs of TMPTA in single-component PIs PISs containing different molar contents of PIs after 600s of irradiation by a 405 nm LED under air conditions.

PIs	FC	PIs	FC	PIs	FC	PIs	FC

1×10^{-6} mol·g^{-1}	(%)	2.5×10^{-6} mol·g^{-1}	(%)	5×10^{-6} mol·g^{-1}	(%)	5×10^{-6} mol·g^{-1}	(%)
Coum1	np	Coum1	np	Coum1	np	Coum1	np
Coum2	np	Coum2	np	Coum2	np	Coum2	np
Coum3	np	Coum3	np	Coum3	35	Coum3	42
Coum4	np	Coum4	np	Coum4	35	Coum4	41
Coum5	np	Coum5	np	Coum5	37	Coum5	44
KC	np	KC	np	KC	25	KC	27

np: no polymerization.

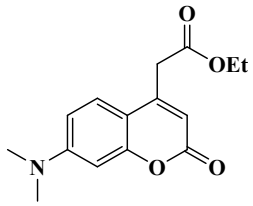
Table S3. Hyperfine coupling constants (hfcs) for the detected spin adduct of PBN in *tert*-butylbenzene of Coums in N_2 saturated medium under the irradiation of 405 nm LED.

Coums	**Radical 1**	**Radical 2**	**PBNox**
Coum1	aN = 14.3 G ; aH = 2.1 G ; (100.0%)		
Coum2	aN = 14.2 G ; aH = 2.1 G ; (64.2%)	aN = 14.8 G ; aH = 2.0 G ; (26.6%)	(9.2%)
Coum3	aN = 14.3 G ; aH = 2.1 G ; (100.0%)		
Coum4	aN = 14.3 G ; aH = 2.1 G ; (61.0%)	aN = 13.8 G ; aH = 1.8 G ; (39.0%)	
Coum5	aN = 14.3 G ; aH = 2.1 G ; (53.2%)	aN = 13.3 G ; aH = 1.6 G ; (40.2%)	(6.6%)

General informations

All reagents and solvents were purchased from Aldrich or Alfa Aesar and used as received without further purification. Mass spectroscopy was performed by the Spectropole of Aix-Marseille University. ^{1}H and ^{13}C NMR spectra were determined at room temperature in 5 mm o.d. tubes on a Bruker Avance 400 or a Bruker Avance 300 spectrometer of the Spectropole: ^{1}H (400 MHz), ^{1}H (300 MHz), ^{13}C (100 MHz), and ^{13}C (75 MHz). All ^{1}H chemical shifts were referenced to the solvent peak $CDCl_3$ (7.26 ppm), DMSO-d_6 (2.49 ppm) and the ^{13}C chemical shifts were referenced to the solvent peak $CDCl_3$ (77.0 ppm).

Synthesis of ethyl 2-(7-(dimethylamino)-2-oxo-2*H*-chromen-4-yl)acetate (Coum1)



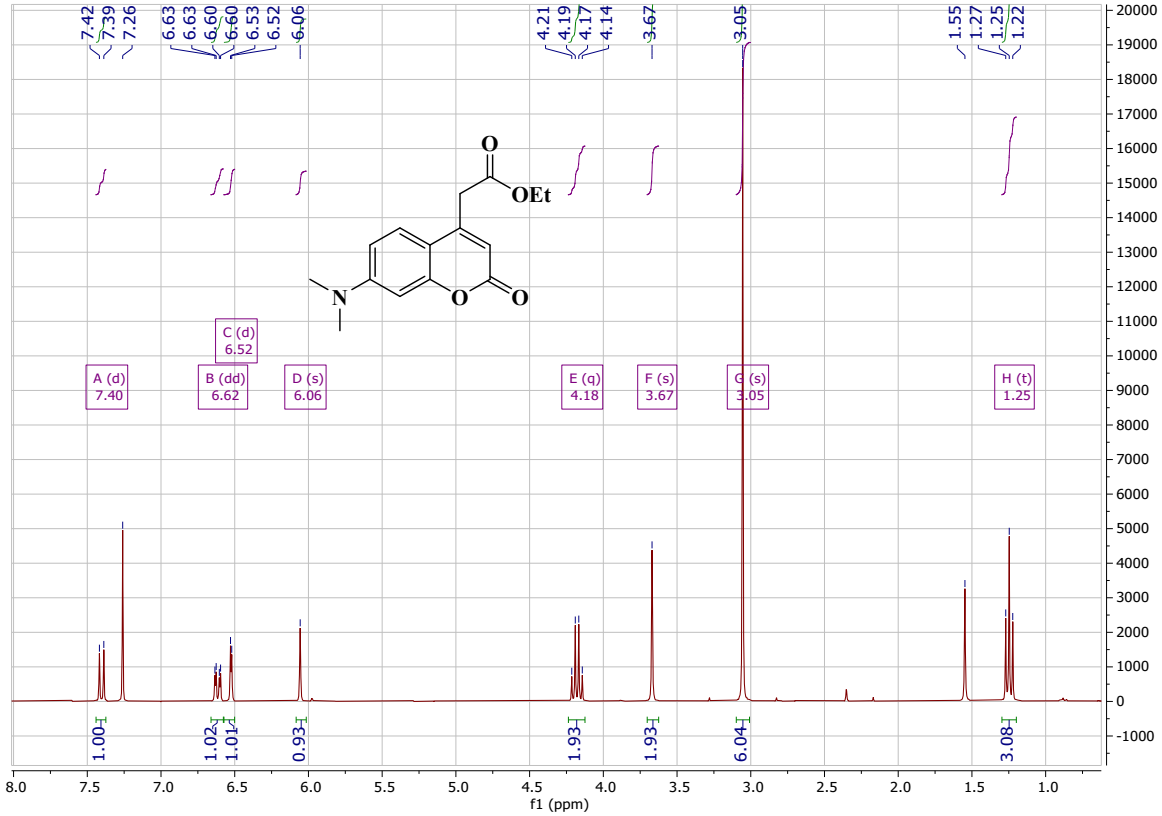
Chemical Formula: $C_{15}H_{17}NO_4$
Molecular Weight: 275.3040

3-Dimethylaminophenol (12 g, 87.5 mmol, M = 137.18 g/mol), diethyl 1,3-acetonedicarboxylate (19.46 g, 17.5 mL, 96.2 mmol, 1.1 eq., M = 202.20 g/mol, d = 1.113) and $ZnCl_2$ (14.31 g, 105 mmol, M = 136.30 g/mol) were dissolved in absolute ethanol (50 mL). The reaction mixture was heated at reflux for 15 h. The reaction mixture was cooled to room temperature and the yellow precipitate formed was filtered. The filtrate was poured into ice-water. The precipitate formed was filtered and air-dried. The product was recrystallized to give ethyl 7-dimethylaminocoumarin as orange needles (14.69 g, 61% yield).

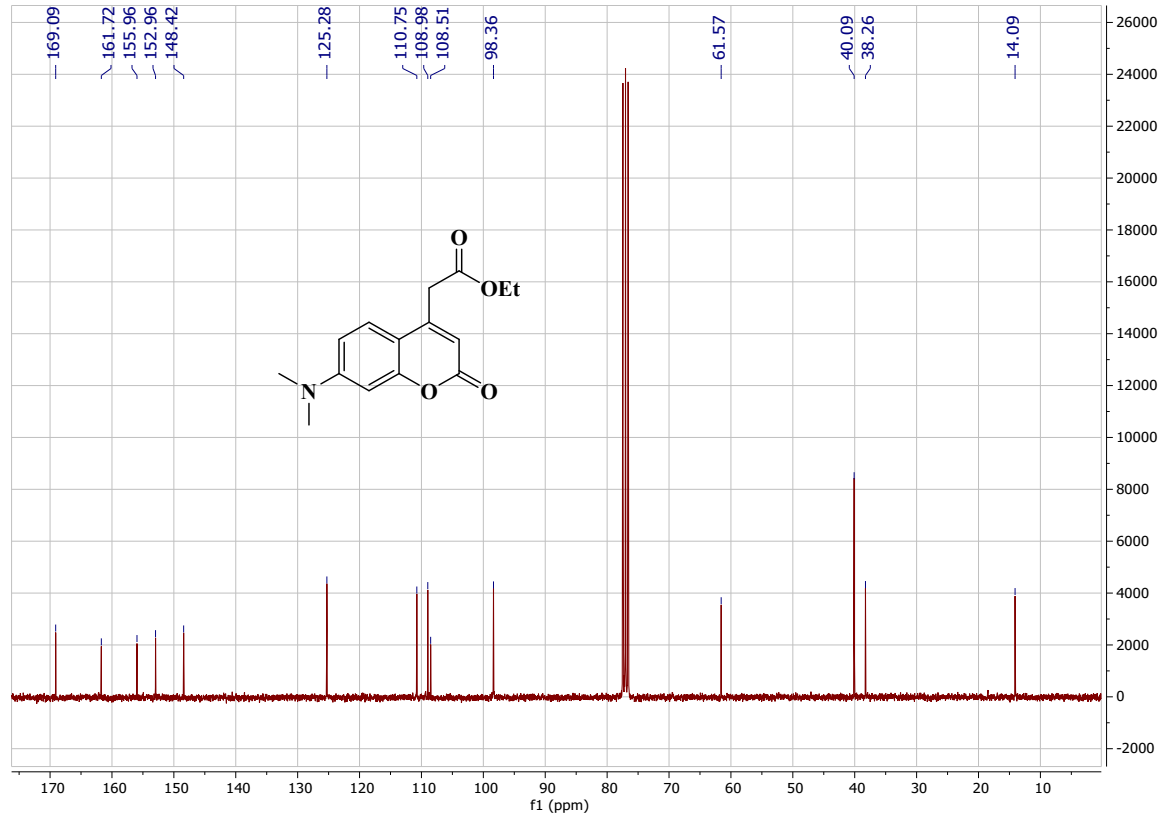
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.9 Hz, 1H), 6.62 (dd, *J* = 9.0, 2.5 Hz, 1H), 6.52 (d, *J* = 2.5 Hz, 1H), 6.06 (s, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.67 (s, 2H), 3.05 (s, 6H), 1.25 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 169.09, 161.72, 155.96, 152.96, 148.42, 125.28, 110.75, 108.98, 108.51, 98.36, 61.57, 40.09, 38.26, 14.09.

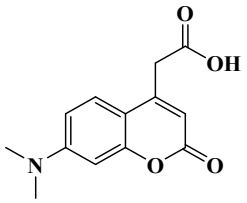
^{1}H NMR spectrum of ethyl 2-(7-(dimethylamino)-2-oxo-2*H*-chromen-4-yl)acetate



^{13}C NMR spectrum of ethyl 2-(7-(dimethylamino)-2-oxo-2*H*-chromen-4-yl)acetate



Synthesis of 2-(7-(dimethylamino)-2-oxo-2*H*-chromen-4-yl)acetic acid (Coum2)



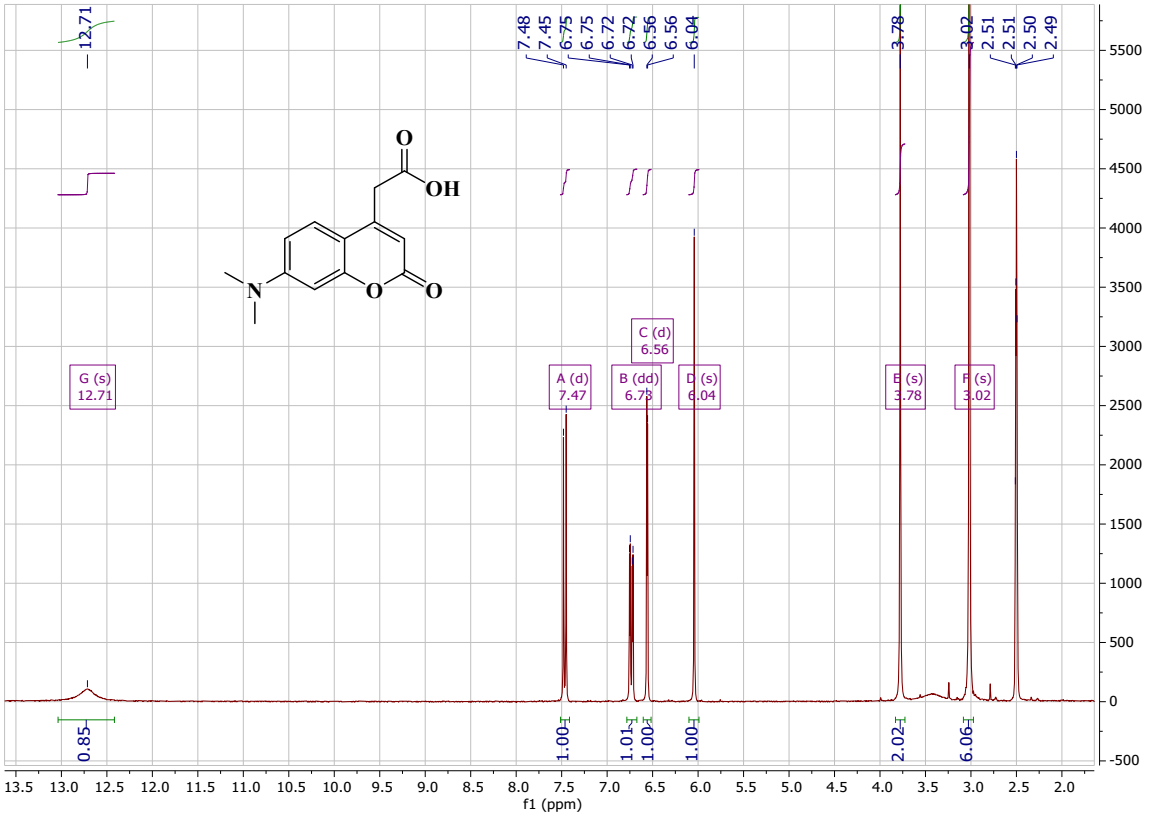
Chemical Formula: $C_{13}H_{13}NO_4$
Molecular Weight: 247.2500

Ethyl 2-(7-(dimethylamino)-2-oxo-2*H*-chromen-4-yl)acetate (10 g, 36.32 mmol, M = 275.30 g/mol) was dissolved in THF/H_2O (3:1) (60 mL). 2M LiOH solution (36.3 mL, 72.64 mmol, 2.0 equiv., 1.74 g, in 35 mL) was added dropwise. The reaction mixture was stirred at room temperature for 30 min. Water (60 mL) was added, the aqueous layer was extracted with Et_2O several times. The aqueous layer was acidified to pH = 2 by a 2 M HCl solution. The precipitate formed was filtered and dried under vacuum to give the acid as a yellow solid (7.27 g, 81% yield).

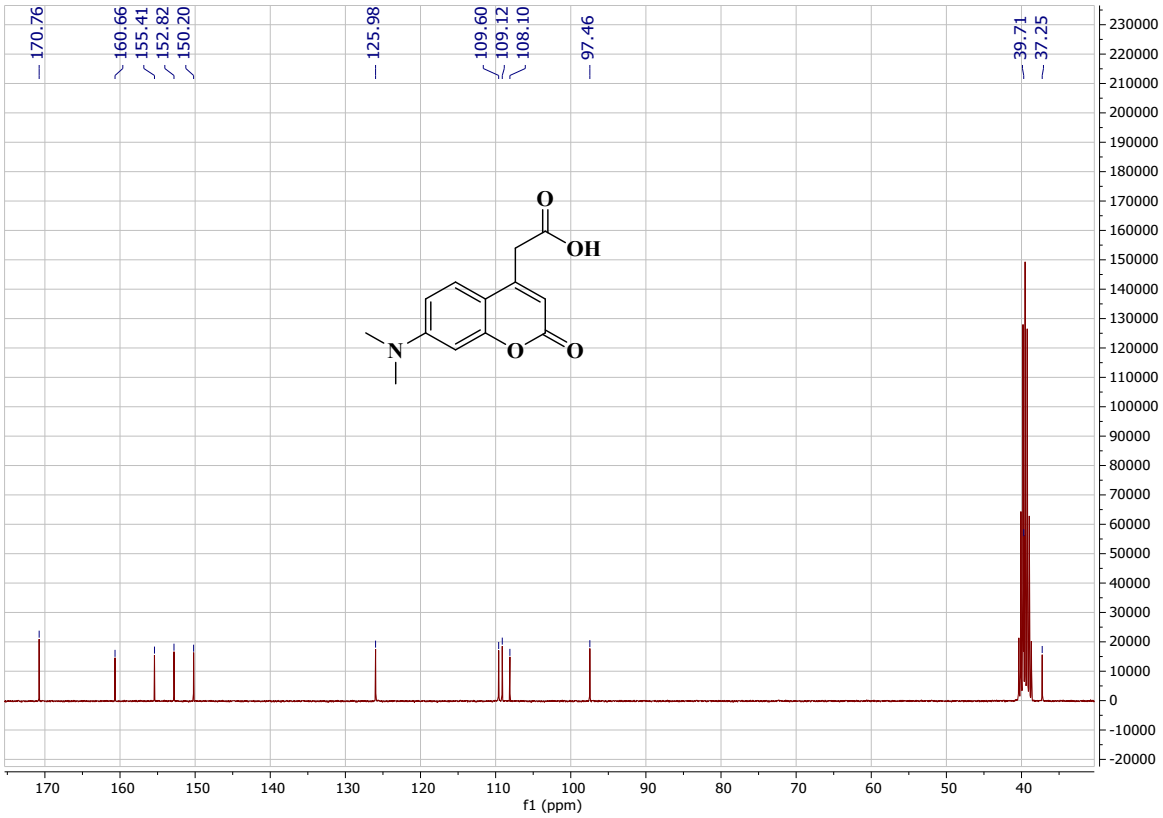
^{1}H NMR (300 MHz, DMSO) δ 12.71 (s, 1H), 7.47 (d, *J* = 9.0 Hz, 1H), 6.73 (dd, *J* = 9.0, 2.5 Hz, 1H), 6.56 (d, *J* = 2.5 Hz, 1H), 6.04 (s, 1H), 3.78 (s, 2H), 3.02 (s, 6H).

^{13}C NMR (75 MHz, DMSO) δ 170.76, 160.66, 155.41, 152.82, 150.20, 125.98, 109.60, 109.12, 108.10, 97.46, 39.71, 37.25.

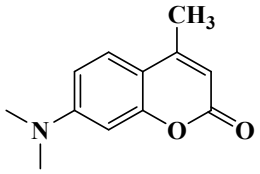
^{1}H NMR spectrum of 2-(7-(dimethylamino)-2-oxo-2*H*-chromen-4-yl)acetic acid



^{13}C NMR spectrum of 2-(7-(dimethylamino)-2-oxo-2*H*-chromen-4-yl)acetic acid



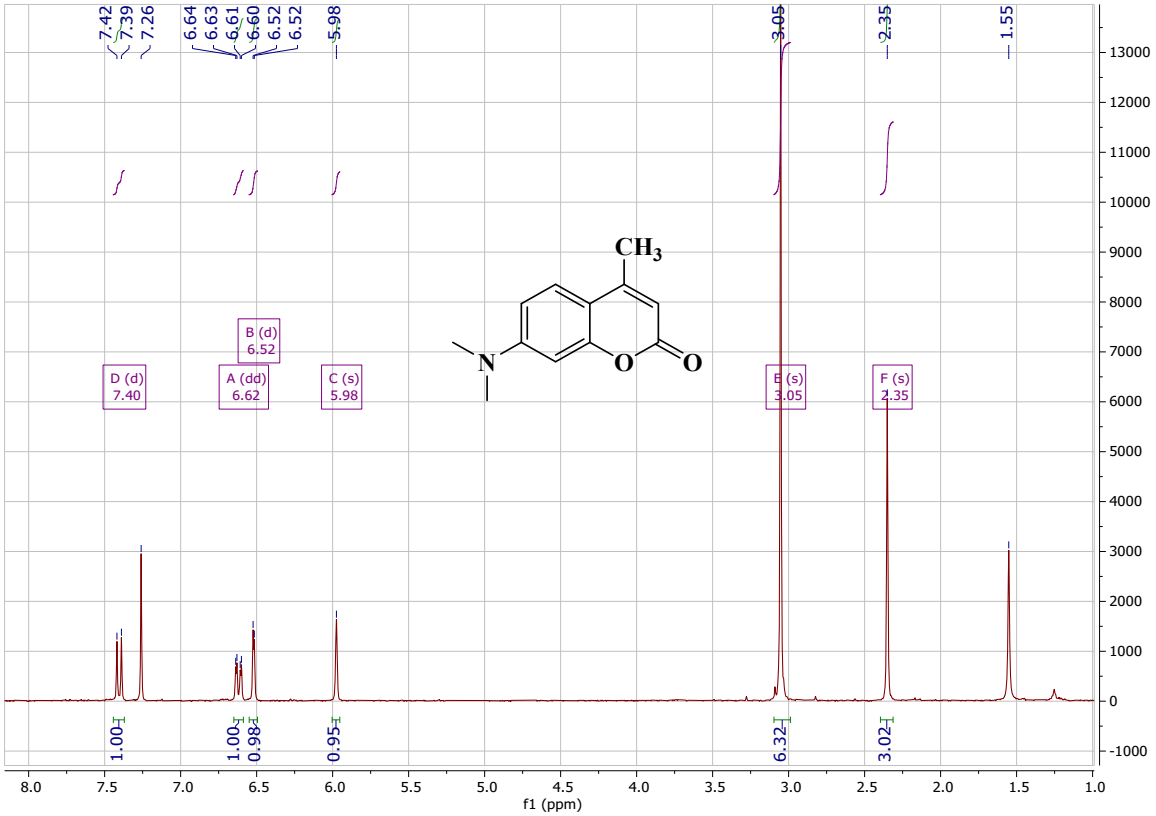
Synthesis of 7-(dimethylamino)-4-methyl-2*H*-chromen-2-one (Coum3)



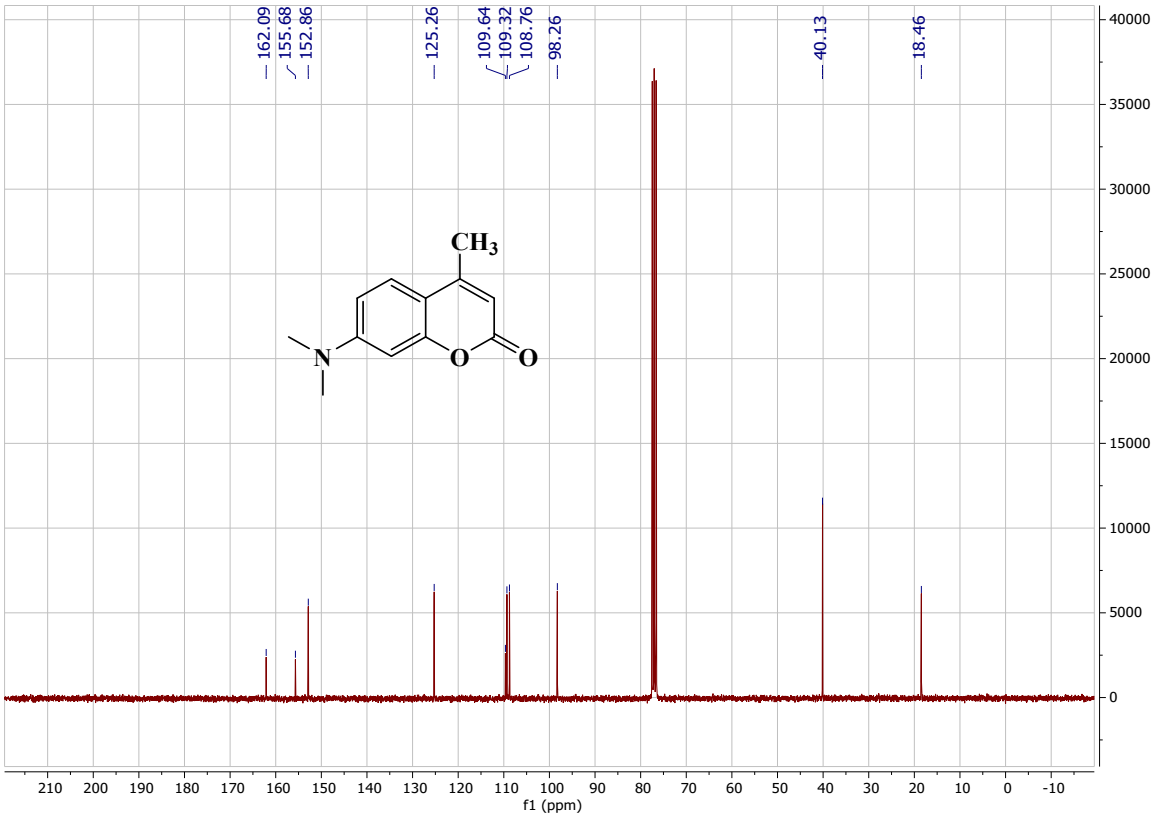
Chemical Formula: $C_{12}H_{13}NO_2$
Molecular Weight: 203.2410

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.9 Hz, 1H), 6.62 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.52 (d, *J* = 2.4 Hz, 1H), 5.98 (s, 1H), 3.05 (s, 6H), 2.35 (s, 3H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 162.09, 155.68, 152.86, 125.26, 109.64, 109.32, 108.76, 98.26, 40.13, 18.46.

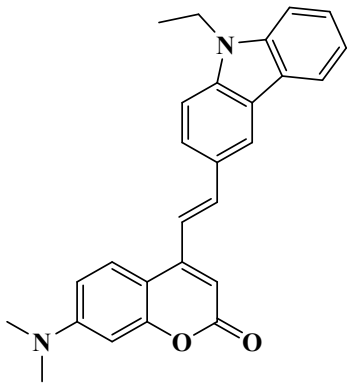
[1]H NMR spectrum of 7-(dimethylamino)-4-methyl-2*H*-chromen-2-one



[13]C NMR spectrum of 7-(dimethylamino)-4-methyl-2*H*-chromen-2-one



Synthesis of 7-(dimethylamino)-4-(2-(9-ethyl-9*H*-carbazol-3-yl)vinyl)-2*H*-chromen-2-one (Coum4)



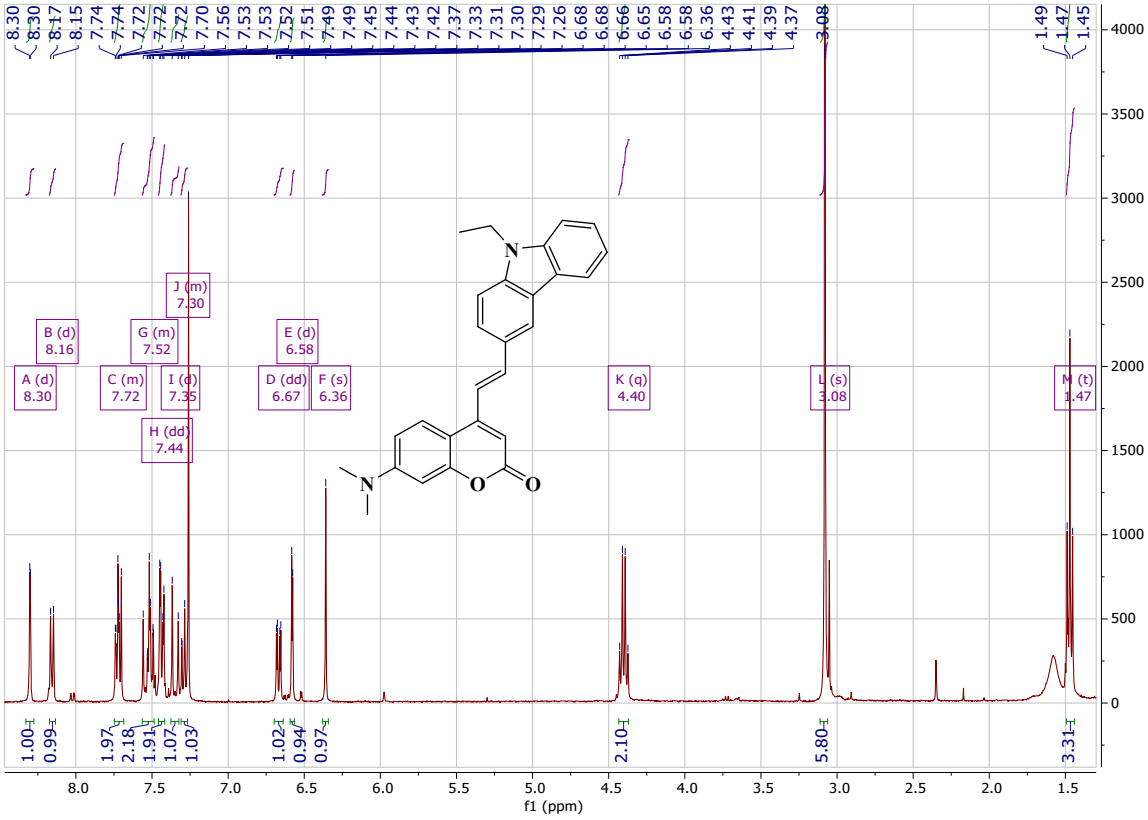
Chemical Formula: $C_{27}H_{24}N_2O_2$
Molecular Weight: 408.5010

2-(7-(Dimethylamino)-2-oxo-2*H*-chromen-4-yl)acetic acid (1 g, 4.04 mmol, M = 247.50 g/mol) and *N*-ethylcarbazole-3-carbaldehyde (0.90 g, 4.04 mmol, M = 223.27 g/mol) were dissolved in ethanol (30 mL), and piperidine (0.5 mL) was added. The solution was stirred at reflux overnight. During that time, the reaction colour changed from colorless to yellow. The solution was cooled to room temperature. A yellow precipitate formed. It was filtered off, washed with ethanol and dried under vacuum (1.22 g, 74% yield).

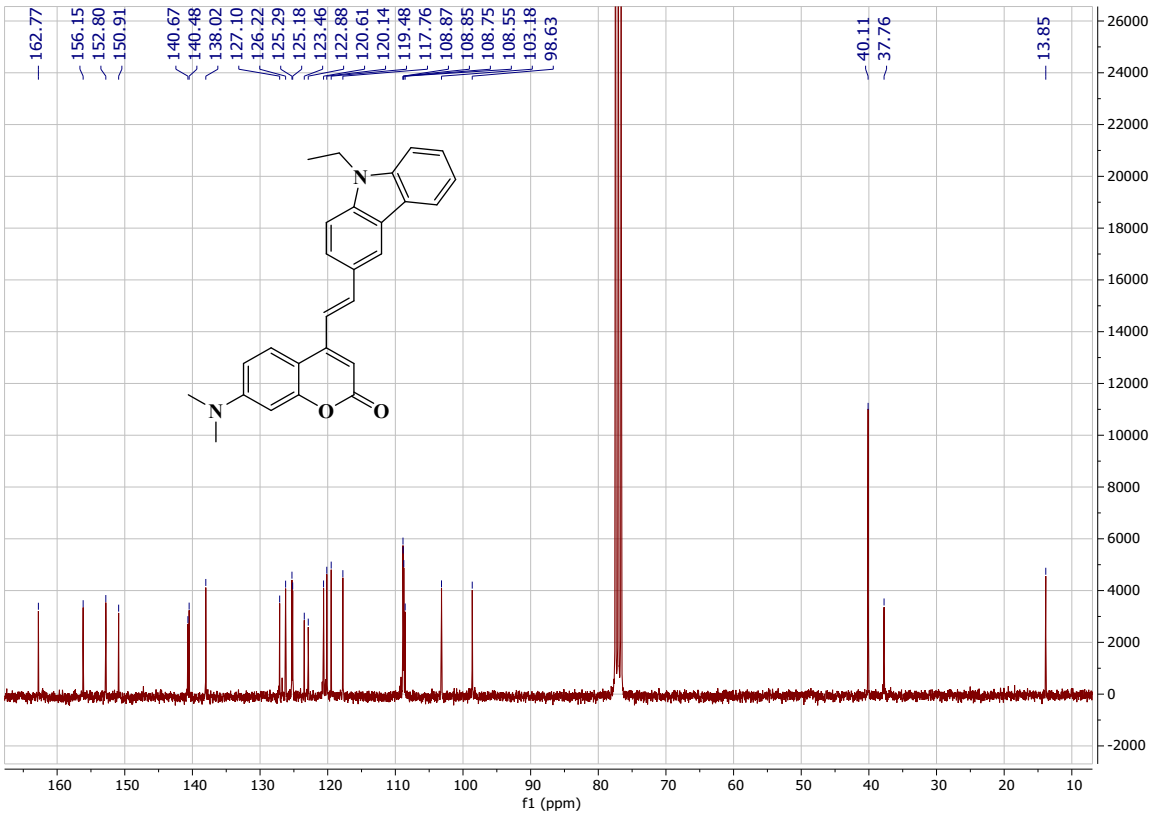
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, *J* = 1.4 Hz, 1H), 8.16 (d, *J* = 7.7 Hz, 1H), 7.75 – 7.69 (m, 2H), 7.56 – 7.49 (m, 2H), 7.44 (dd, *J* = 8.4, 2.6 Hz, 2H), 7.35 (d, *J* = 15.9 Hz, 1H), 7.31 – 7.27 (m, 1H), 6.67 (dd, *J* = 9.0, 2.6 Hz, 1H), 6.58 (d, *J* = 2.5 Hz, 1H), 6.36 (s, 1H), 4.40 (q, *J* = 7.2 Hz, 2H), 3.08 (s, 6H), 1.47 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 162.77, 156.15, 152.80, 150.91, 140.67, 140.48, 138.02, 127.10, 126.22, 125.29, 125.18, 123.46, 122.88, 120.61, 120.14, 119.48, 117.76, 108.87, 108.85, 108.75, 108.55, 103.18, 98.63, 40.11, 37.76, 13.85.

^{1}H NMR spectrum of 7-(dimethylamino)-4-(2-(9-ethyl-9*H*-carbazol-3-yl)vinyl)-2*H*-chromen-2-one



^{13}C NMR spectrum of 7-(dimethylamino)-4-(2-(9-ethyl-9*H*-carbazol-3-yl)vinyl)-2*H*-chromen-2-one


162.77
156.15
152.80
150.91
140.67
140.48
138.02
127.10
126.22
125.29
125.18
123.46
122.88
120.61
120.14
119.48
117.76
108.87
108.85
108.75
108.55
103.18
98.63
40.11
37.76
13.85
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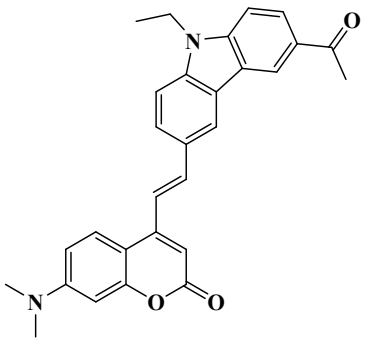
N
O
O
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

Synthesis of 4-(2-(6-acetyl-9-ethyl-9*H*-carbazol-3-yl)vinyl)-7-(dimethylamino)-2*H*-chromen-2-one (Coum5)



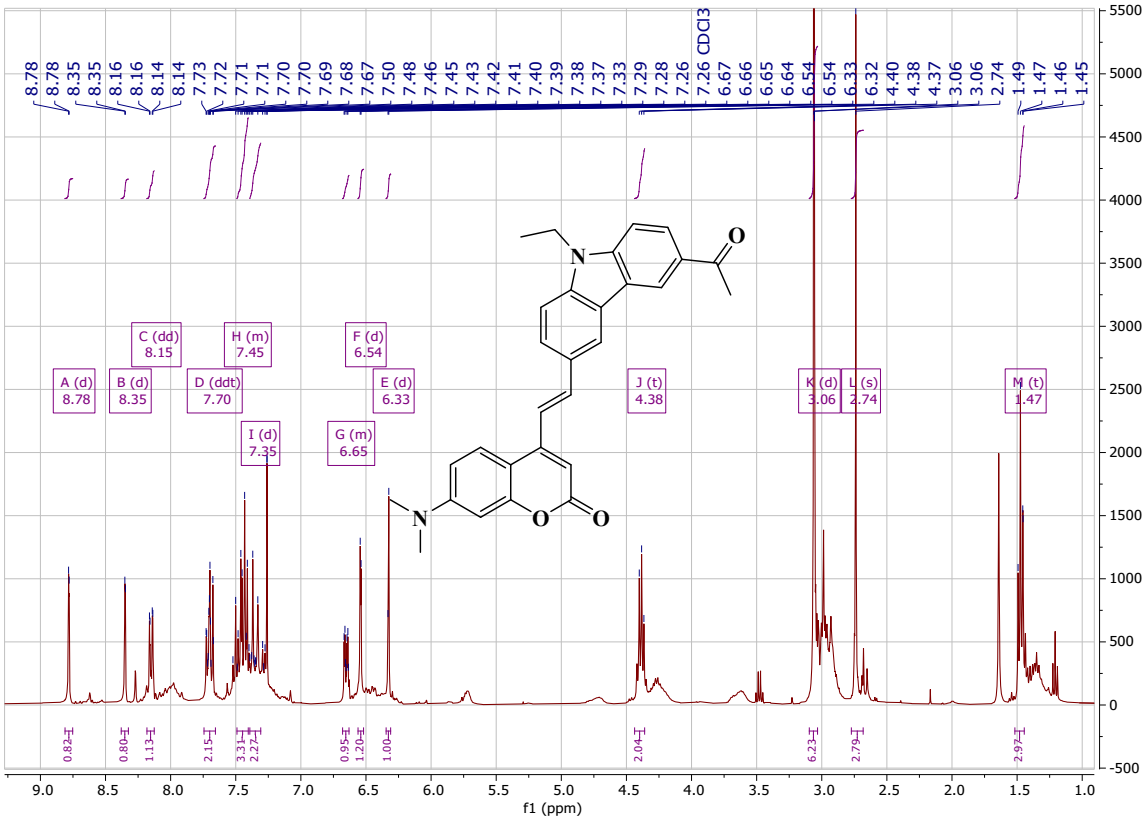
Chemical Formula: $C_{29}H_{26}N_2O_3$
Molecular Weight: 450.5380

7-(Dimethylamino)-4-(2-(9-ethyl-9*H*-carbazol-3-yl)vinyl)-2*H*-chromen-2-one (1.39 g, 3.42 mmol, M = 408.50 g/mol) and acetyl chloride (0.532 g, 0.48 mL, 6.84 mmol, d = 1.104, M = 78.05 g/mol) were dissolved in 10 mL DCM (stabilized with amylene) and the solution was cooled to 0°C. Then, $AlCl_3$ (0.9 g, 6.84 mmol, M = 133.33 g/mol, 1 eq.) were added in one portion and the solution was stirred overnight. The reaction mixture was poured on ice-water. The solution was extracted several times with DCM. The organic phases were combined, dried over magnesium sulfate and the solvent removed under reduced pressure. The residue was filtered on a plug of silicagel using DCM as the eluent. The product was isolated in 84% yield.

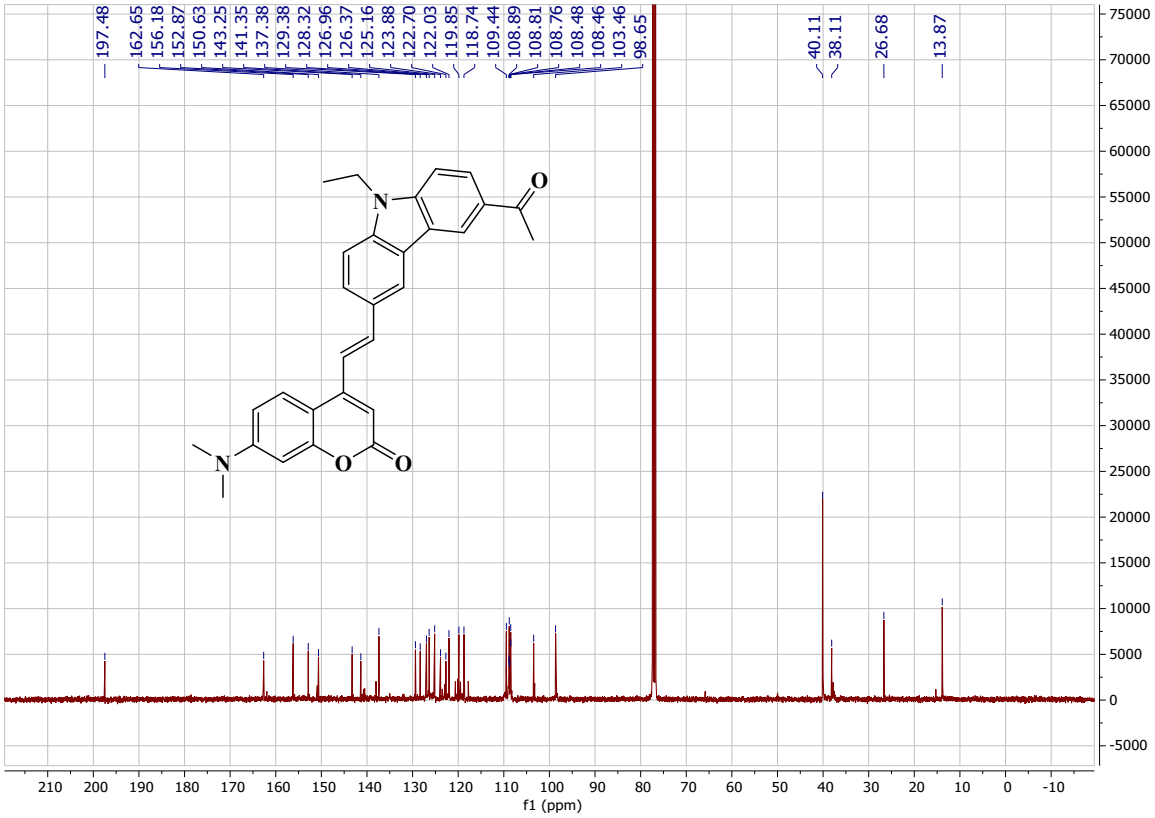
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.78 (d, *J* = 1.7 Hz, 1H), 8.35 (d, *J* = 1.7 Hz, 1H), 8.15 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.70 (ddt, *J* = 10.3, 7.2, 1.6 Hz, 2H), 7.49 – 7.40 (m, 3H), 7.35 (d, *J* = 15.5 Hz, 1H), 6.68 – 6.63 (m, 1H), 6.54 (d, *J* = 2.5 Hz, 1H), 6.33 (d, *J* = 2.4 Hz, 1H), 4.38 (t, *J* = 7.1 Hz, 2H), 3.06 (d, *J* = 1.8 Hz, 6H), 2.74 (s, 3H), 1.47 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 197.48, 162.65, 156.18, 152.87, 150.63, 143.25, 141.35, 137.38, 129.38, 128.32, 126.96, 126.37, 125.16, 123.88, 122.70, 122.03, 119.85, 118.74, 109.44, 108.89, 108.81, 108.76, 108.48, 108.46, 103.46, 98.65, 40.11, 38.11, 26.68, 13.87

^{1}H NMR spectrum of 4-(2-(6-acetyl-9-ethyl-9*H*-carbazol-3-yl)vinyl)-7-(dimethylamino)-2*H*-chromen-2-one



^{13}C NMR spectrum of 4-(2-(6-acetyl-9-ethyl-9*H*-carbazol-3-yl)vinyl)-7-(dimethylamino)-2*H*-chromen-2-one


197.48
162.65
156.18
152.87
150.63
143.25
141.35
137.38
129.38
128.32
126.96
126.37
125.16
123.88
122.70
122.03
119.85
118.74
109.44
108.89
108.81
108.76
108.48
108.46
103.46
98.65
40.11
38.11
26.68
13.87
N
O
N
O
O
f1 (ppm)