Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Sunlight-driven photoinitiating systems for photopolymerization and application in direct laser writing

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Other materials

The different monomers i.e. trimethylolpropane triacrylate (TMPTA) and 3,4-epoxycyclohexane)methyl 3,4-epoxycyclohexylcarboxylate (EPOX) were all purchased from Sartomer (France). The benchmark commercial photoinitiator 2-isopropylthioxanthone (ITX) used for comparison was obtained from Lambson Ltd (United Kingdom). Ethyl 4-dimethylaminobenzoate (EDB) used as the electron donor and *bis*(4-*tert*-butylphenyl)iodonium hexafluorophosphate (Iod) as the electron acceptor were purchased from Lambson Ltd.

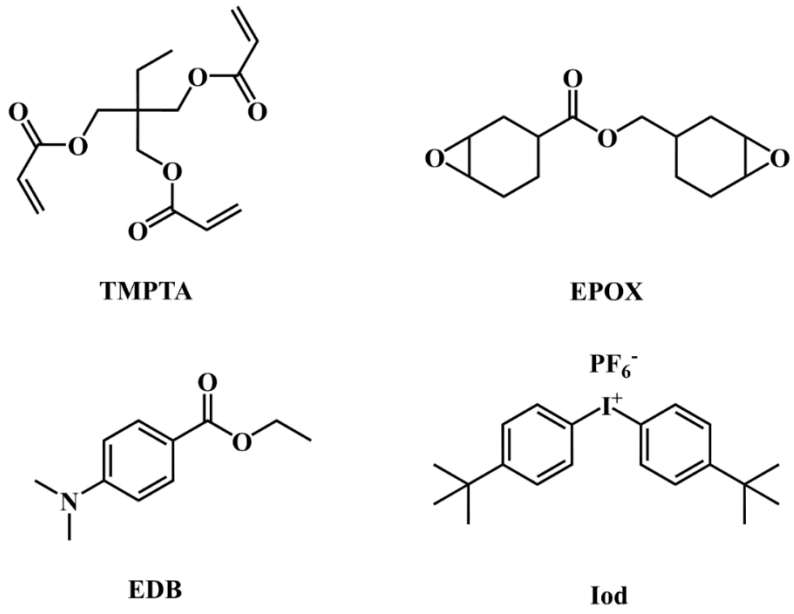


Figure S1. Chemical structures of additives and monomers used in this study.

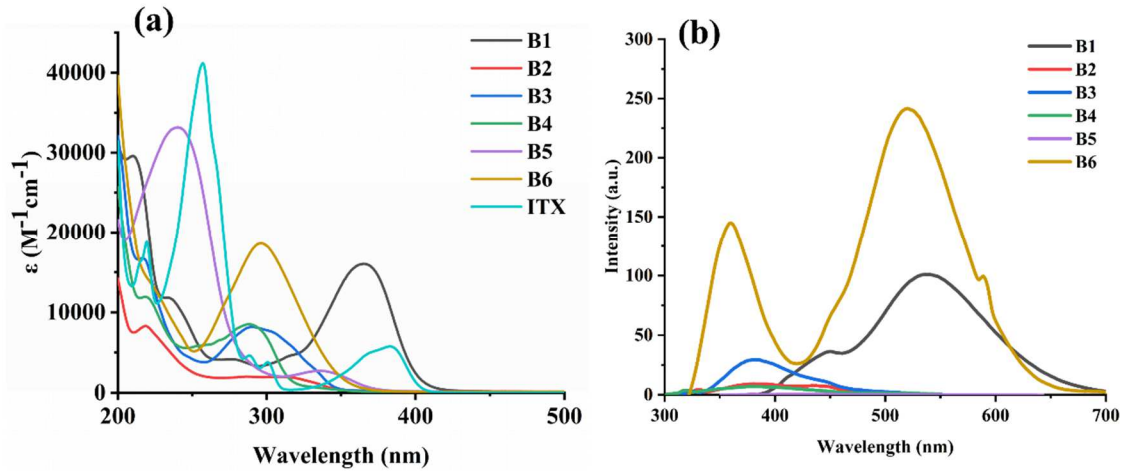


Figure S2. **(a)** UV-visible absorption spectra of dyes in acetonitrile (B1-B6 and ITX)**; (b)** Fluorescence spectra of dyes (5×10^{-5} M) in acetonitrile.

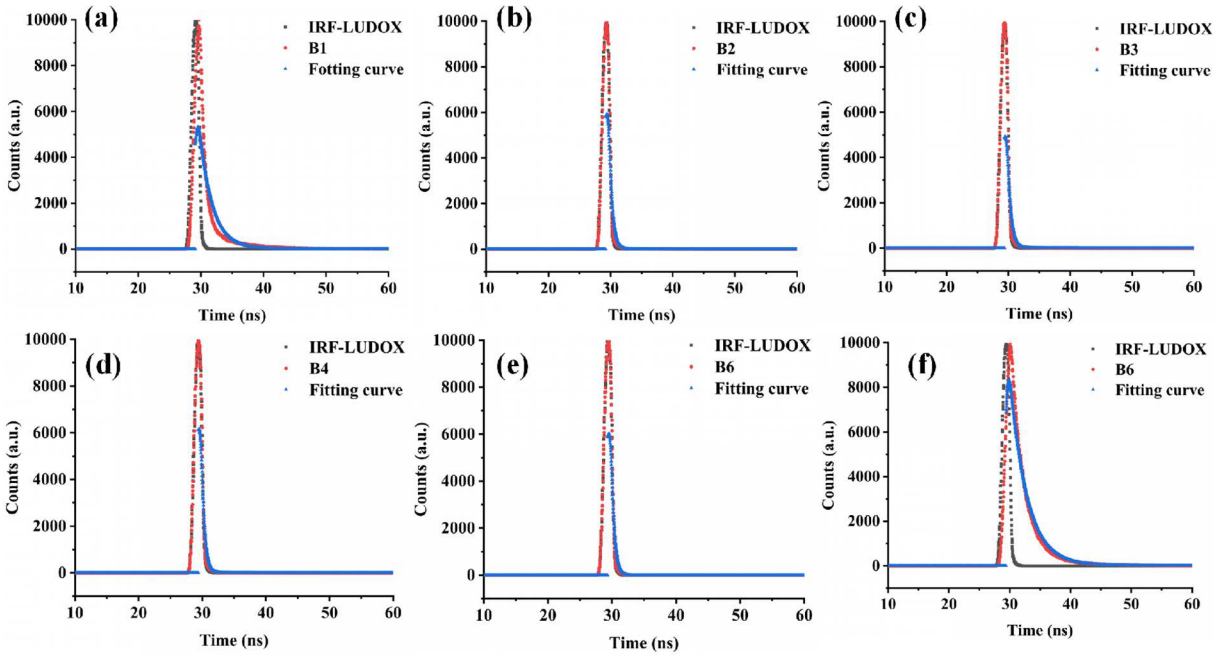


Figure S3. Fluorescence decay curves of dyes (5×10^{-5} M) in acetonitrile.

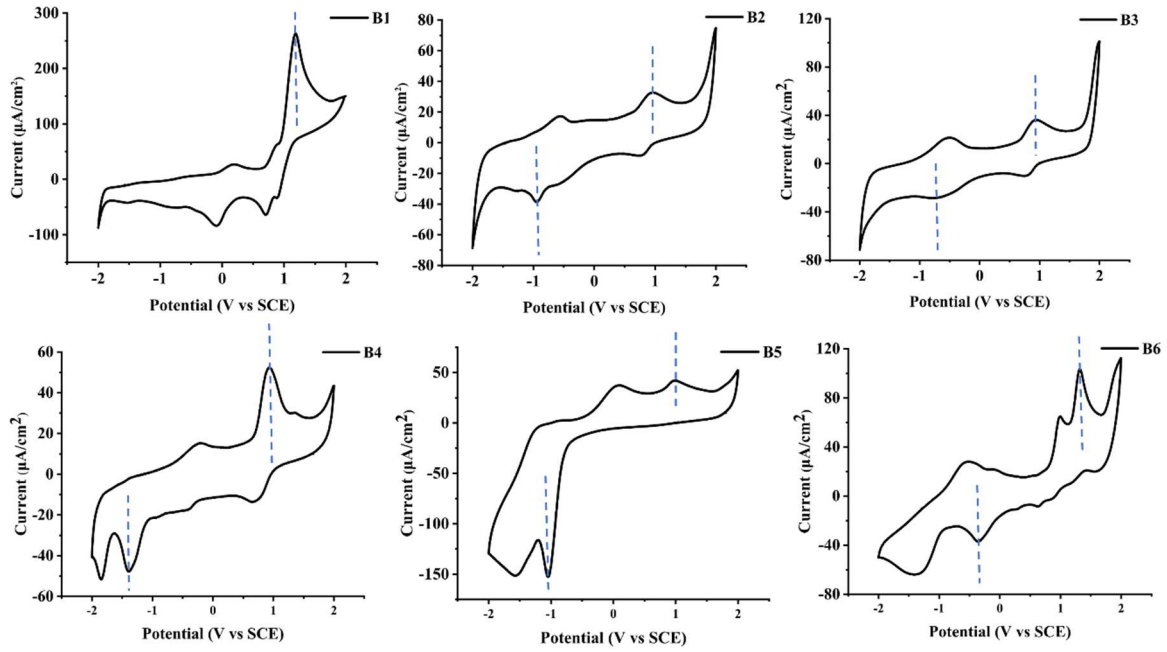


Figure S4. Cyclic voltammetry of electrochemical reactions of the dyes in acetonitrile solvent against saturated calomel electrode (SCE) under N_2 saturated solution.

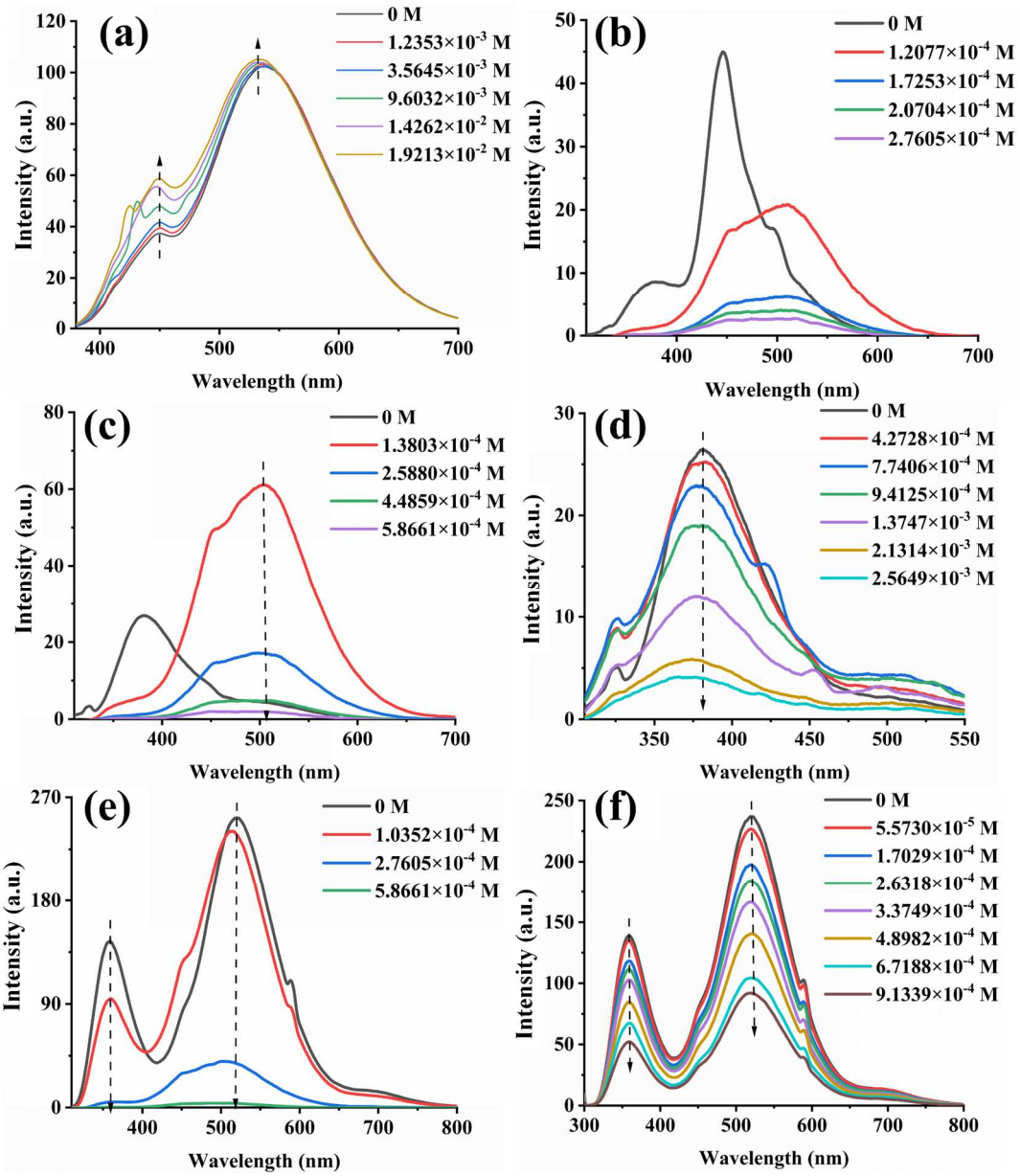


Figure S5. Fluorescence quenching of (a) dye-B2 and EDB, (b) dye-B2 and Iod, (c) dye-B3 and EDB, (d) dye-B3 and Iod, (e) dye-B6 and EDB, (f) dye-B6 and Iod in acetonitrile.

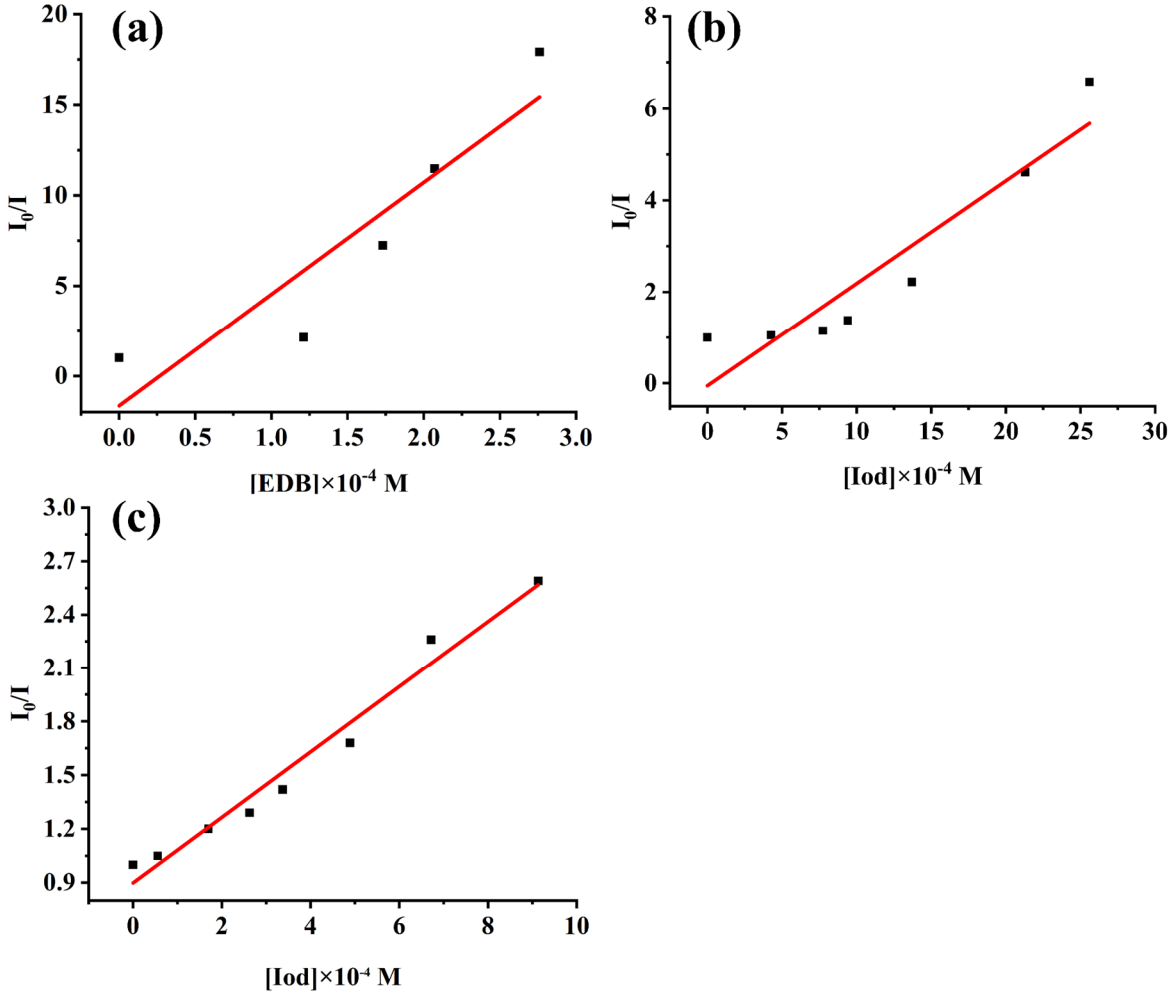


Figure S6. Stern – Volmer treatment for fluorescence quenching of the (a) dye-2/EDB; (b) dye-3/Iod; (c) dye-6/Iod.

Table S1. Final acrylate function conversions (FCs) of TMPTA for thick sample in the presence of dye/EDB, dye/Iod and dye-EDB/Iod.

Dye(1wt%)+EDB(1wt%)+Iod(1wt%)	FCs (%)	Dye(0.5wt%)+EDB(1wt%)+Iod(1wt%)	FCs (%)	Dye(0.1wt%)+EDB(1wt%)+Iod(1wt%)	FCs (%)	Dye(0.5wt%)+EDB(0.5wt%)+Iod(0.5wt%)	FCs (%)	Dye(0.05wt%)+EDB(0.5wt%)+Iod(0.5wt%)	FCs (%)	Dye(0.05wt%)+EDB(1wt%)+Iod(1wt%)	FCs (%)
ITX	81	ITX	81	ITX	80	ITX	82	ITX	81	ITX	81
B6	80	B6	77	B1	80	B1	65	B1	75	B1	81
B1	62	B1	70	B6	62	B6	61	B5	38	B6	61
EDB+Iod	55	B4	68	2	58	B5	50	B6	19	B3	58
B5	53	B3	64	B3	58	EDB+Iod	3	B4	19	B4	58
B4	-	B2	60	B4	57	B4	-	B3	13	B5	58
B2	0	B5	58	B5	57	B2	0	B2	10	B2	56
B3	0	EDB+Iod	55	EDB+Iod	55	B3	0	EDB+Iod	3	EDB+Iod	55
Dye(1wt%)+EDB(1wt%)	FCs (%)	Dye(1wt%)+Iod(1wt%)	FCs (%)	Dye(0.5wt%)+EDB(1wt%)	FCs (%)	Dye(0.5wt%)+Iod(1wt%)	FCs (%)	Dye(0.5wt%)+EDB(0.5wt%)	FCs (%)	Dye(0.5wt%)+Iod(0.5wt%)	FCs (%)
B5	54	B6	72	B5	54	B6	51	B5	50	B1	63
B6	42	B4	61	B6	34	B1	56	B6	29	B6	56
B1	7	B1	58	B1	7	B2	56	B1	4	B2	52
B4	-	B2	57	B4	-	B4	33	B4	-	B4	18
B2	0	B3	17	B2	0	B3	4	B2	0	B3	3
B3	0	B5	2	B3	0	B5	0	B3	0	B5	0
EDB	0	Iod	0	EDB	0	Iod	0	EDB	0	Iod	0

Table S2. Final acrylate function conversions (FCs) of TMPTA for thin sample in the presence of dye/EDB, dye/Iod and dye-EDB/Iod.

Dye(1wt%)+EDB(1wt%)+Iod(1wt%)	FCs (%)	Dye(0.5wt%)+EDB(1wt%)+Iod(1wt%)	FCs (%)	Dye(0.1wt%)+EDB(1wt%)+Iod(1wt%)	FCs (%)	Dye(0.5wt%)+EDB(0.5wt%)+Iod(0.5wt%)	FCs (%)	Dye(0.05wt%)+EDB(0.5wt%)+Iod(0.5wt%)	FCs (%)	Dye(0.05wt%)+EDB(1wt%)+Iod(1wt%)	FCs (%)
B6	93	B6	92	B6	92	B6	91	ITX	74	B6	92
B5	92	B5	89	B2	92	B5	81	B1	65	B2	92
B2	72	ITX	76	B3	86	ITX	75	EDB+Iod	46	B3	86
B1	60	B2	73	B5	86	B1	64	B2	0	B5	86
ITX	58	B4	68	B4	74	EDB+Iod	46	B3	0	B4	74
B4	45	B1	62	ITX	62	B2	0	B4	0	ITX	62
EDB+Iod	40	B3	57	B1	50	B3	0	B5	0	B1	50
B3	0	EDB+Iod	40	EDB+Iod	40	B4	0	B6	0	EDB+Iod	40
Dye(1wt%)+EDB(1wt%)	FCs (%)	Dye(1wt%)+Iod(1wt%)	FCs (%)	Dye(0.5wt%)+EDB(1wt%)	FCs (%)	Dye(0.5wt%)+Iod(1wt%)	FCs (%)	Dye(0.5wt%)+EDB(0.5wt%)	FCs (%)	Dye(0.5wt%)+Iod(0.5wt%)	FCs (%)
B5	80	B6	93	B5	91	B6	92	B1	62	B2	68
B1	58	B2	93	B1	62	B2	92	B5	50	B1	65
B6	57	B1	92	B2	0	B1	70	B6	39	B4	65
B4	48	B4	92	B3	0	B3	0	B2	0	B6	58
B2	36	B3	25	B4	0	B4	0	B3	0	B3	0
B3	0	B5	0	B6	0	B5	0	B4	0	B5	0
EDB	0	Iod	0	EDB	0	Iod	0	EDB	0	Iod	0

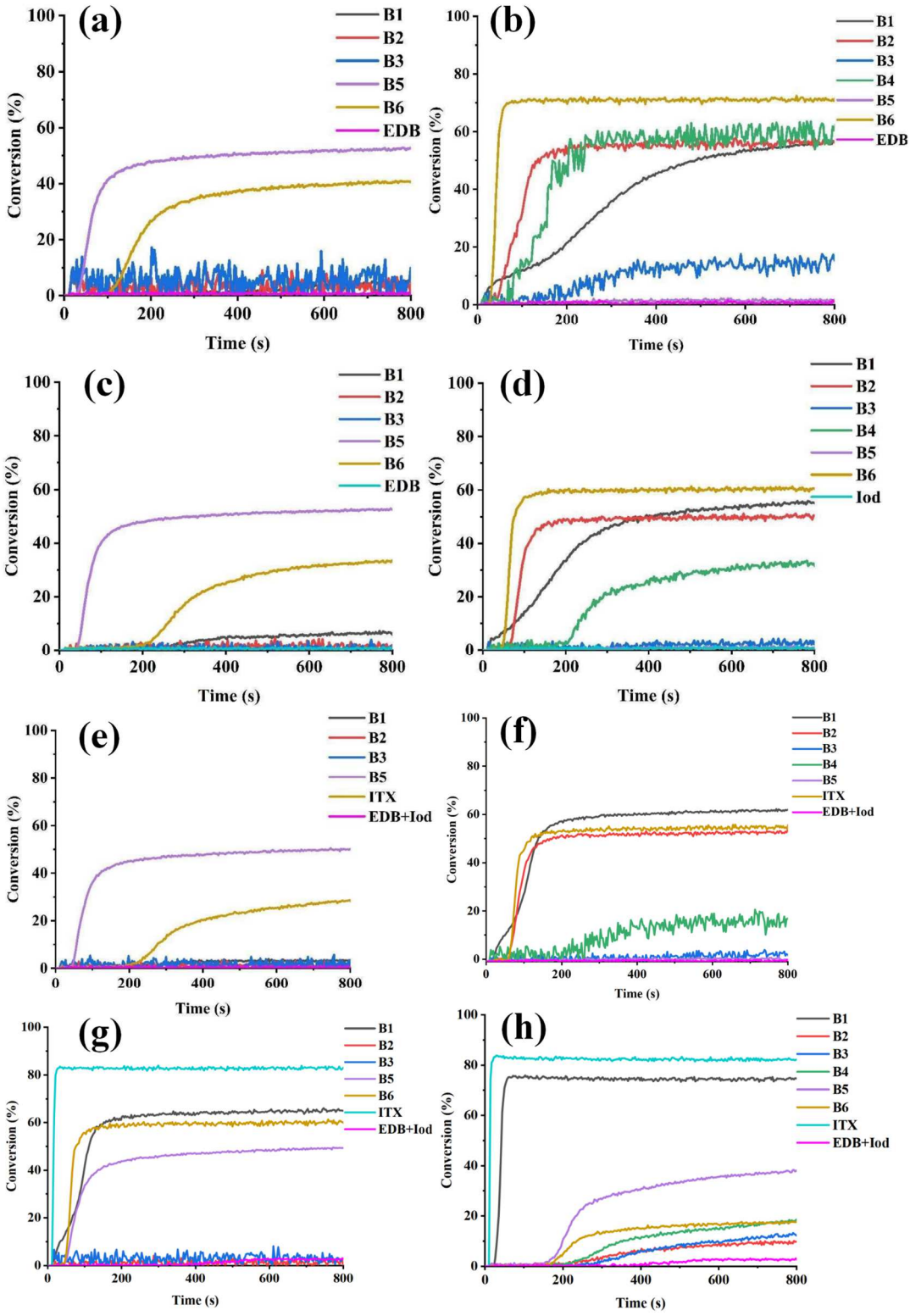


Figure S7. Photopolymerization profiles of TMPTA for thick sample (about 2 mm) upon exposure to LED@405 nm irradiation. (a) dye/EDB 1%/1% w/w; (b) dye/Iod 1%/1% w/w; (c) dye/EDB 0.5%/1% w/w (d); dye/ Iod 0.5%/1% w/w; (e) dye/EDB 0.5%/0.5% w/w ; (f) dye/Iod 0.5%/0.5% w/w ; (g) dye/EDB/Iod 0.5%/0.5%/0.5% w/w/w and (h) dye/EDB/Iod 0.05%/0.5%/0.5% w/w/w. The irradiation starts at t = 10 s.

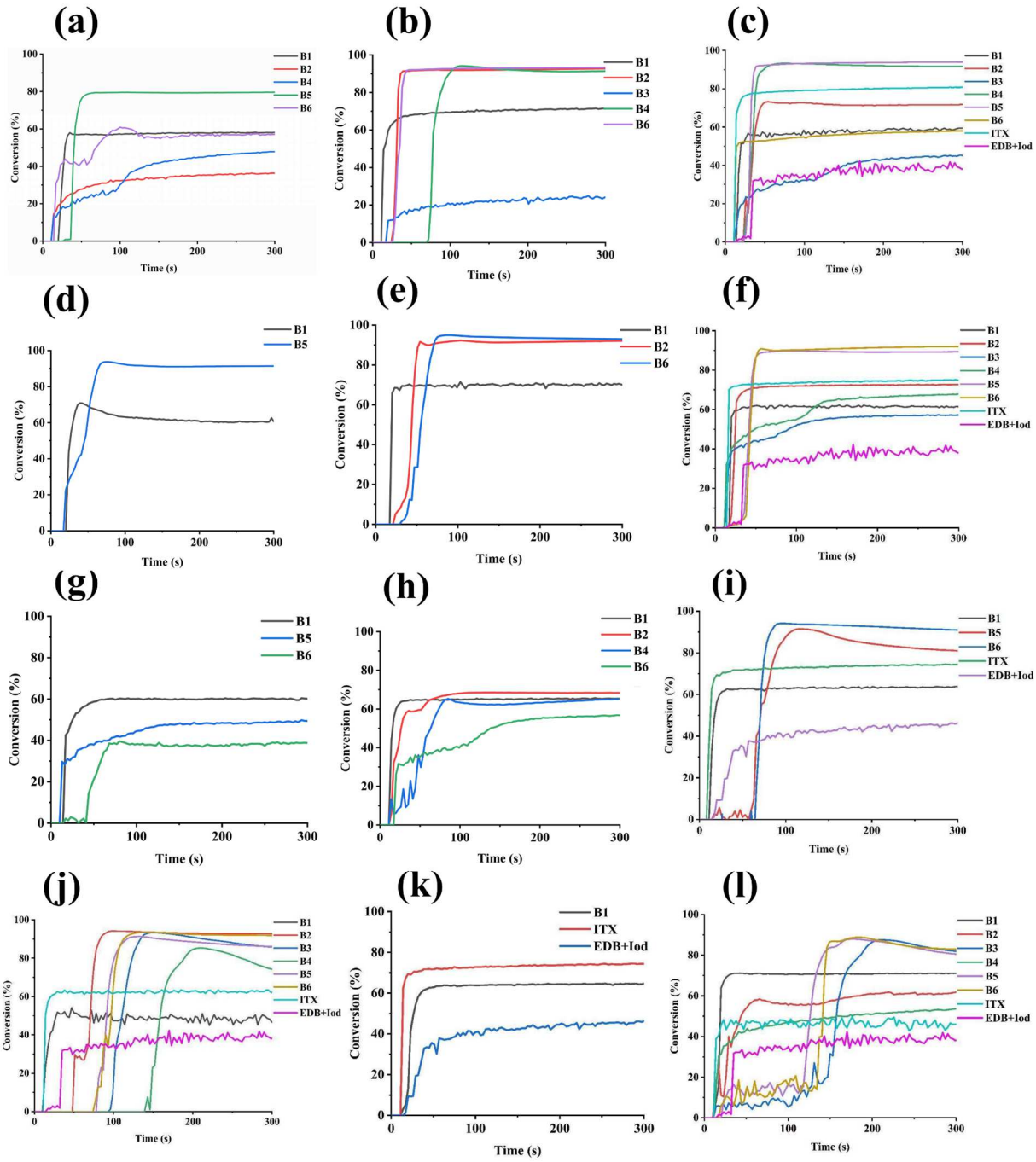


Figure S8. Photopolymerization profiles of TMPTA for thin sample (about 100 microns) upon exposure to LED@405 nm irradiation. (a) dye/EDB 1%/1% w/w; (b) dye/Iod 1%/1% w/w; (c) dye/EDB/Iod 1%/1%/1% w/w/w; (d) dye/EDB 0.5%/1% w/w (e) ; dye/ Iod 0.5%/1% w/w; (f) dye/EDB/Iod 0.5%/1%/1% w/w/w ; (g) dye/EDB 0.5%/0.5% w/w ; (h) dye/Iod 0.5%/0.5% w/w ; (i) dye/EDB/Iod 0.5%/0.5%/0.5% w/w/w ; (j) dye/EDB/Iod 0.1%/1%/1% w/w/w ; (k) dye/EDB/Iod 0.05%/0.5%/0.5% w/w/w ; (l) dye/EDB/Iod 0.05%/1%/1% w/w/w. The irradiation starts at t = 10 s.

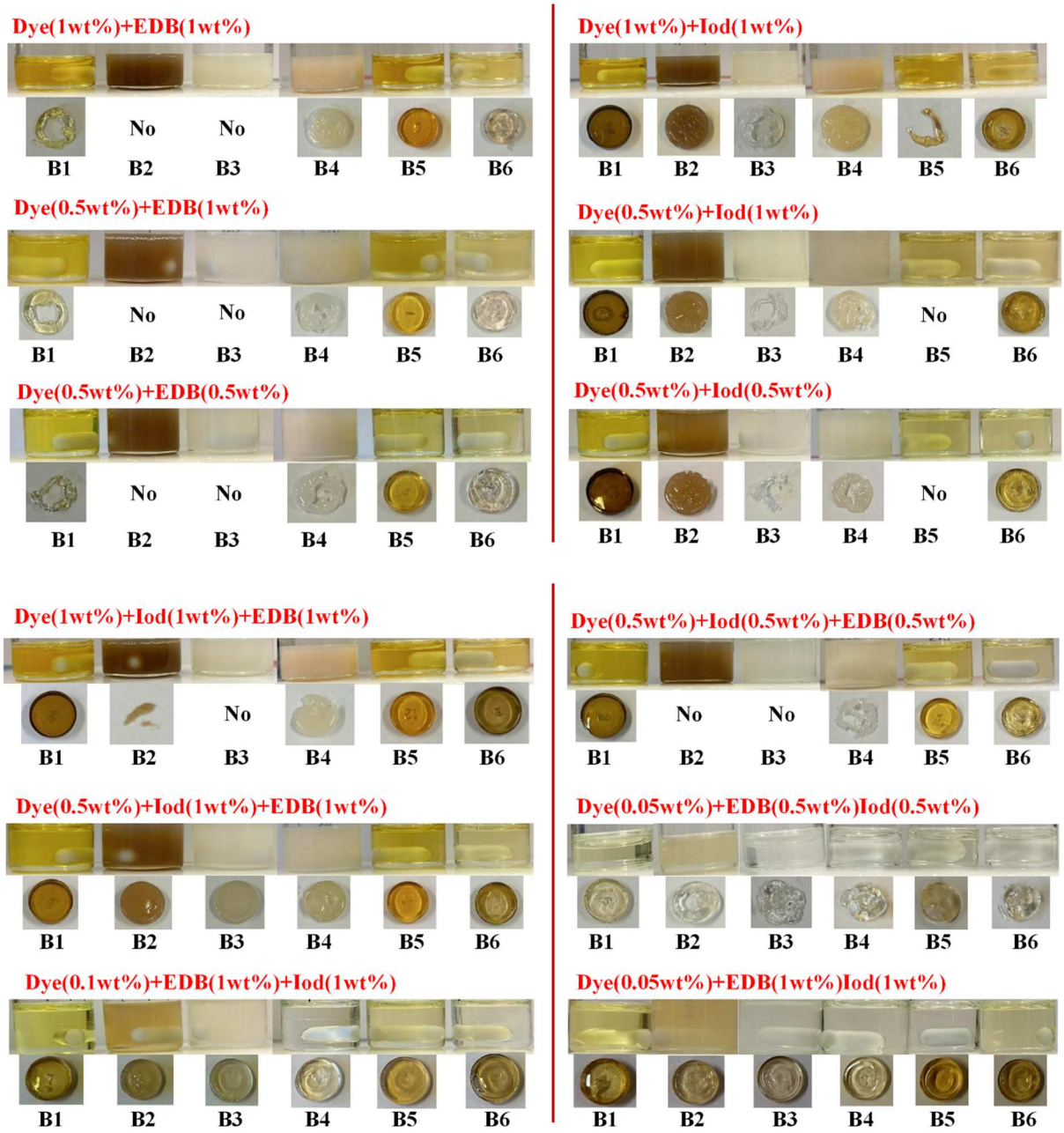


Figure S9. The state of the formulations before and after polymerization.

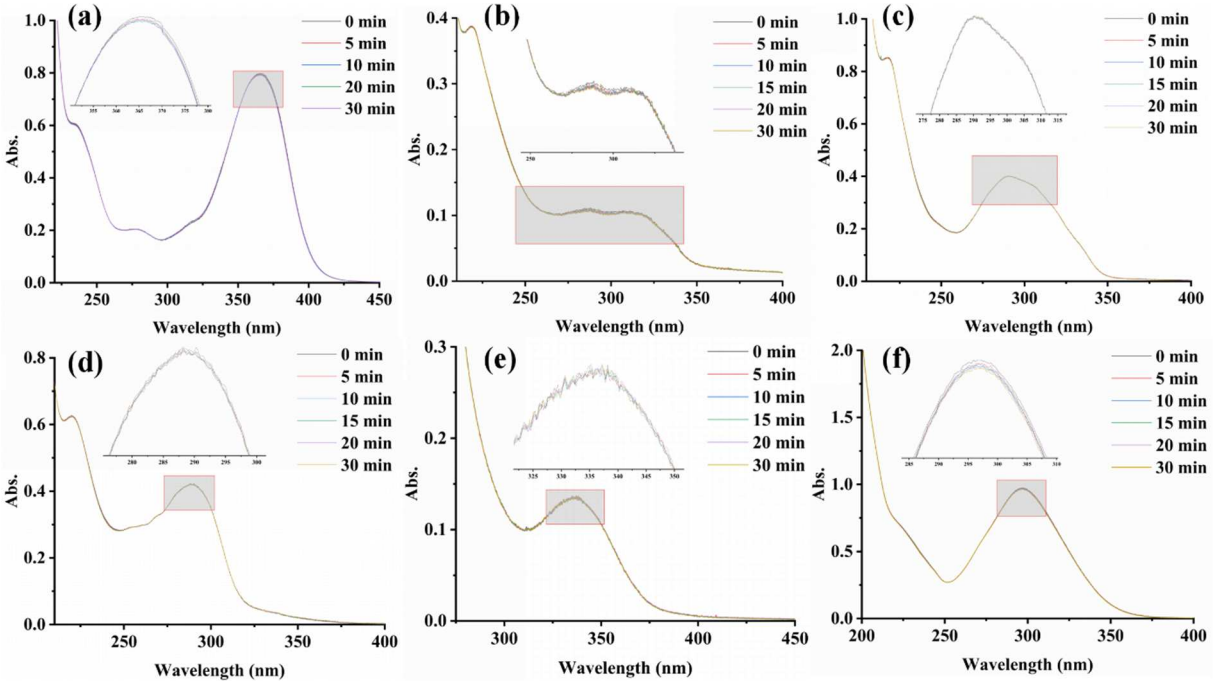


Figure S10. Steady-state photolysis of dye (2.5×10^{-5} M) alone under LED@ 405 nm. (a-f) are dye-B1, B2, B3, B4, B5 and B6 in acetonitrile, respectively.

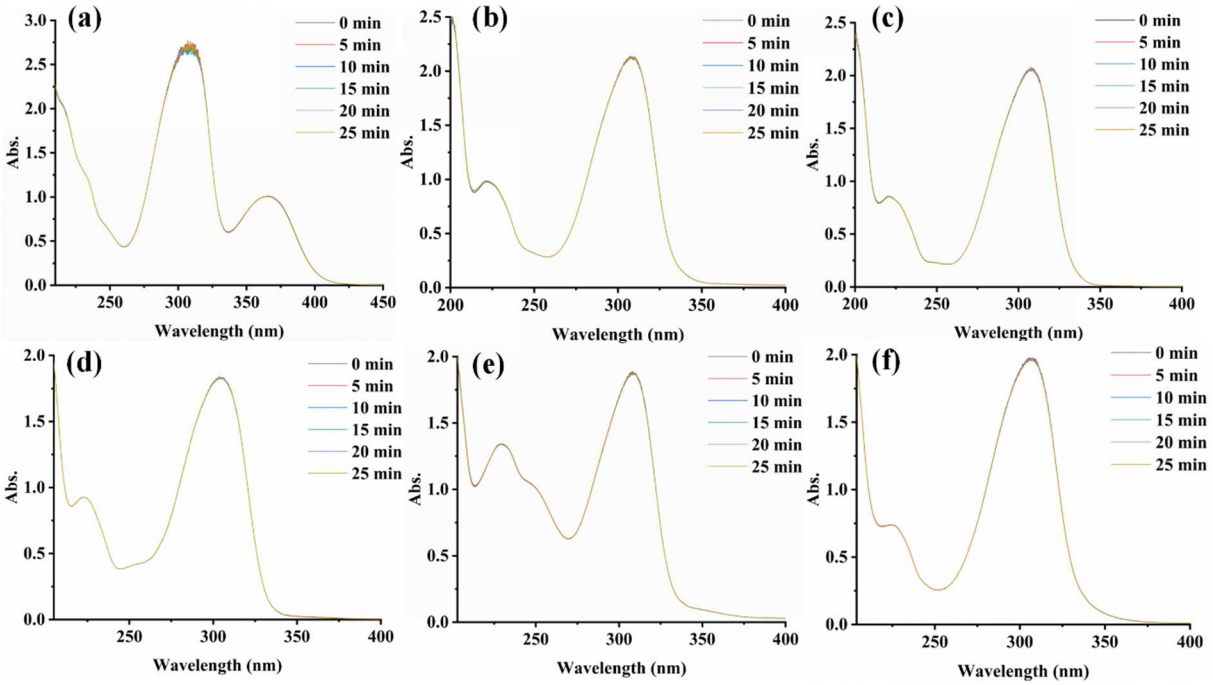


Figure S11. Steady-state photolysis of dye (2.5×10^{-5} M) and EDB (5×10^{-5} M) under LED@ 405 nm. (a-f) are dye-B1, B2, B3, B4, B5 and B6 in acetonitrile, respectively.

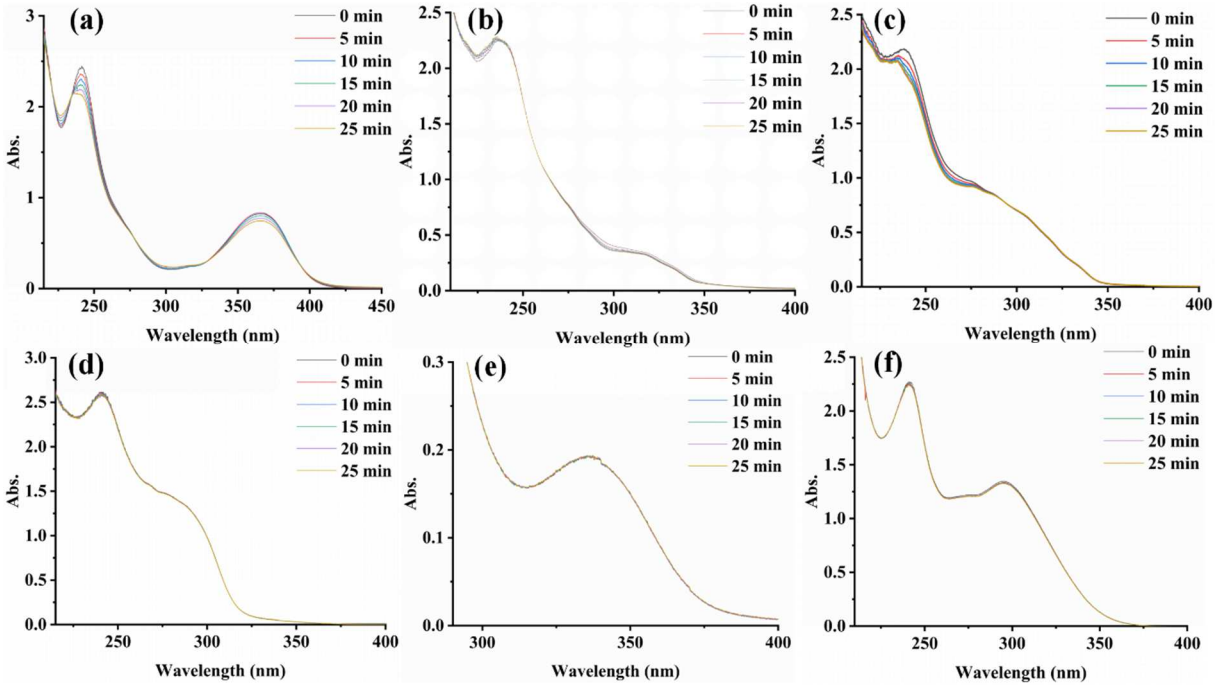


Figure S12. Steady-state photolysis of dye (2.5×10^{-5} M) and Iod (5×10^{-5} M) under LED@ 405 nm. (a-f) are dye-B1, B2, B3, B4, B5 and B6 in acetonitrile, respectively.

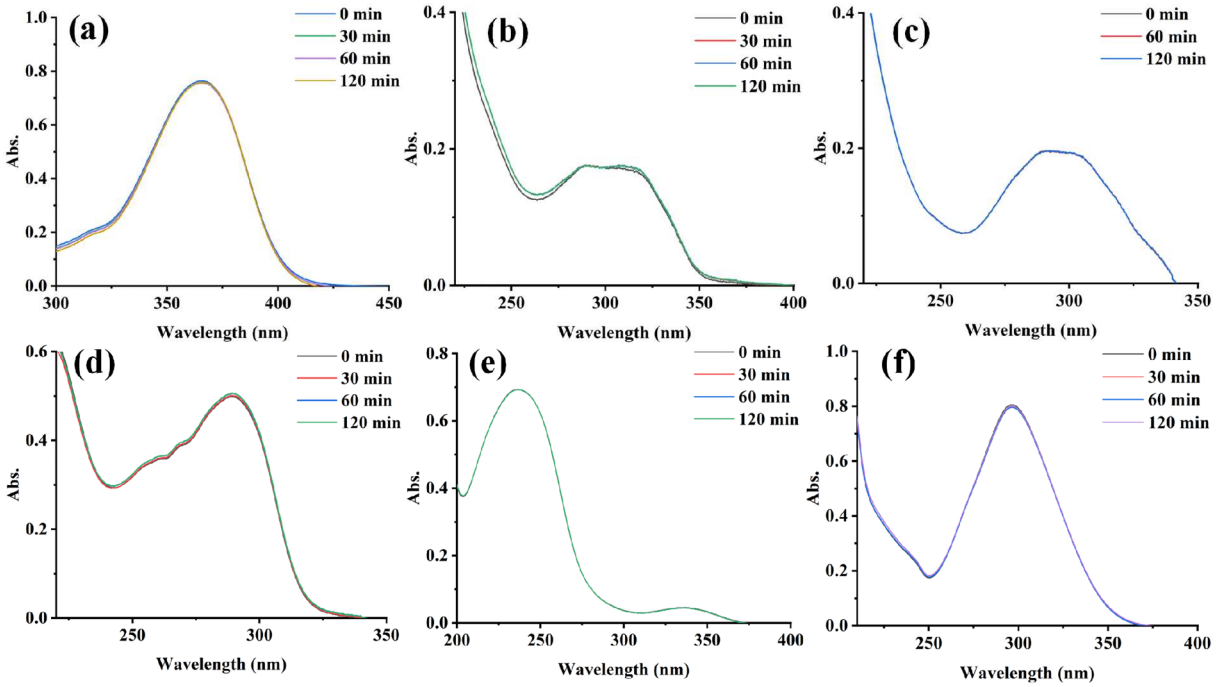


Figure S13. Steady-state photolysis of dye in acetonitrile (the concentration of dye is 2.5×10^{-5} M) under sunlight in the air. (a-f) are dye-B1, B2, B3, B4, B5 and B6 in acetonitrile, respectively.

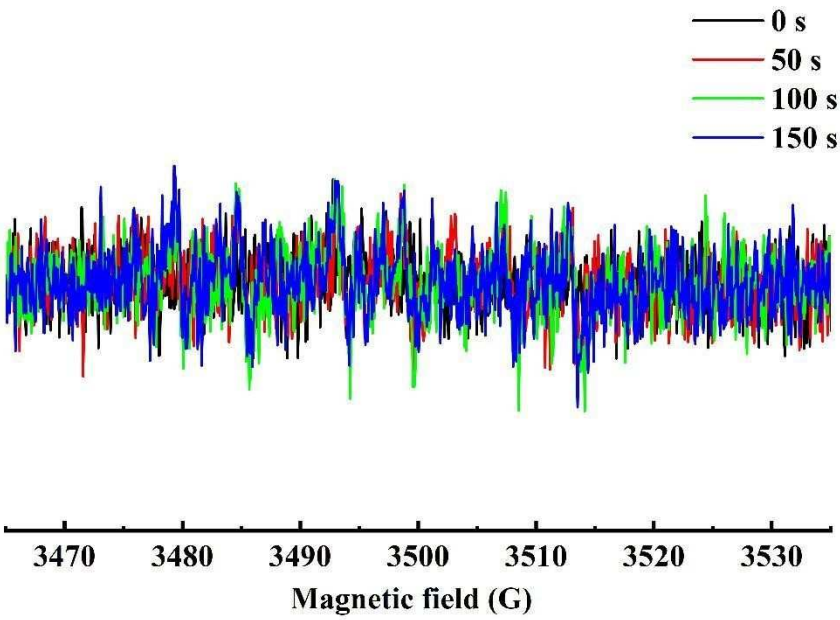
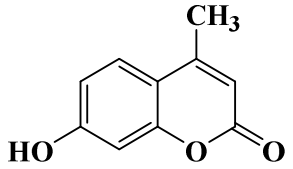


Figure S14. ESR-ST spectra of the radical adducts (in tert-butylbenzene under nitrogen atmosphere), dye-B6/EDB.

General information

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 7-hydroxy-4-methyl-2*H*-chromen-2-one



Chemical Formula: $C_{10}H_8O_3$
Molecular Weight: 176.1710

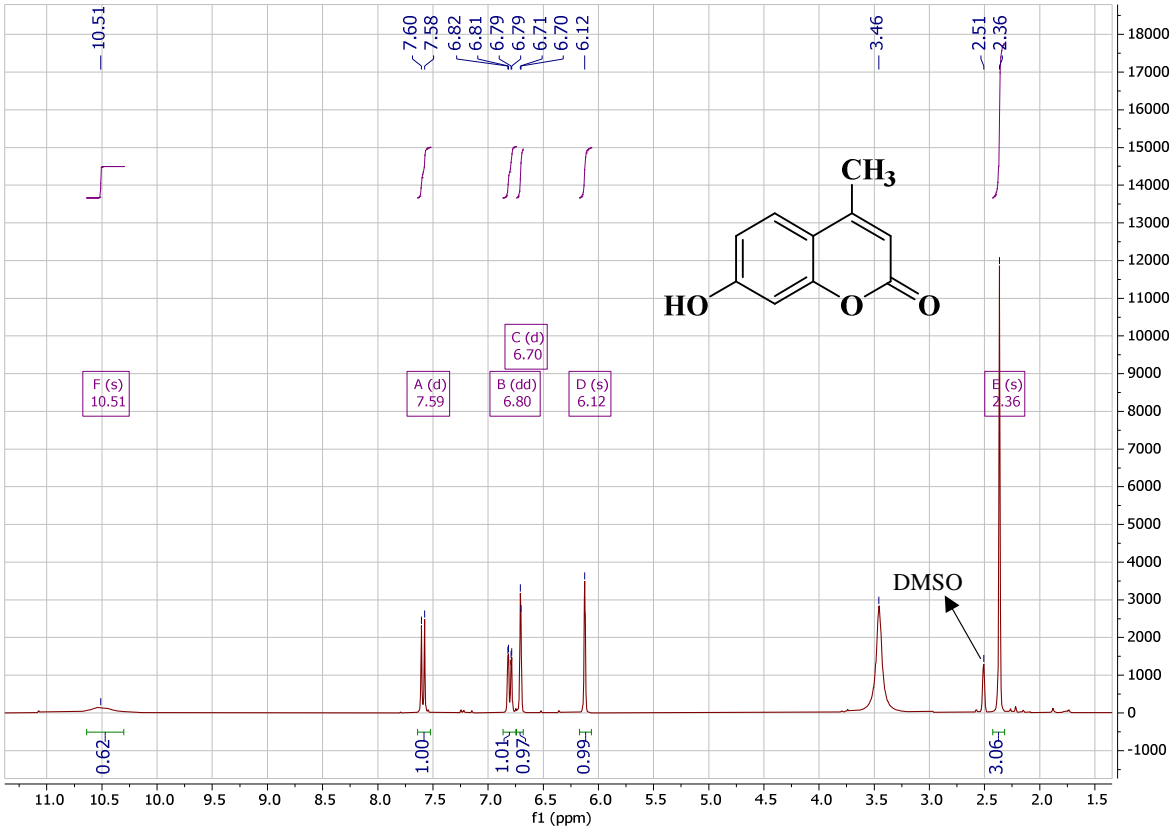
Resorcinol (3.7 g, 33.60 mmol, M = 110.11 g/mol) and ethyl acetoacetate (4.4 mL, 4.53 g, 34.82 mmol, M = 130.14 g/mol, d = 1.030) was added to concentrated sulfuric acid (15 mL) at 5°C with constant stirring and the solution was stirred at room temperature for one hour. The mixture was poured onto ice with vigorous stirring. During that time, a beige solid formed that was filtered off, washed with water until pH = 7 and the solid was dried under vacuum (2.26 g, 61% yield).

^{1}H NMR (300 MHz, DMSO) δ 10.51 (s, 2H), 7.59 (d, *J* = 8.7 Hz, 3H), 6.80 (dd, *J* = 8.7, 2.1 Hz, 3H), 6.70 (d, *J* = 2.1 Hz, 3H), 6.12 (s, 3H), 2.36 (s, 9H).

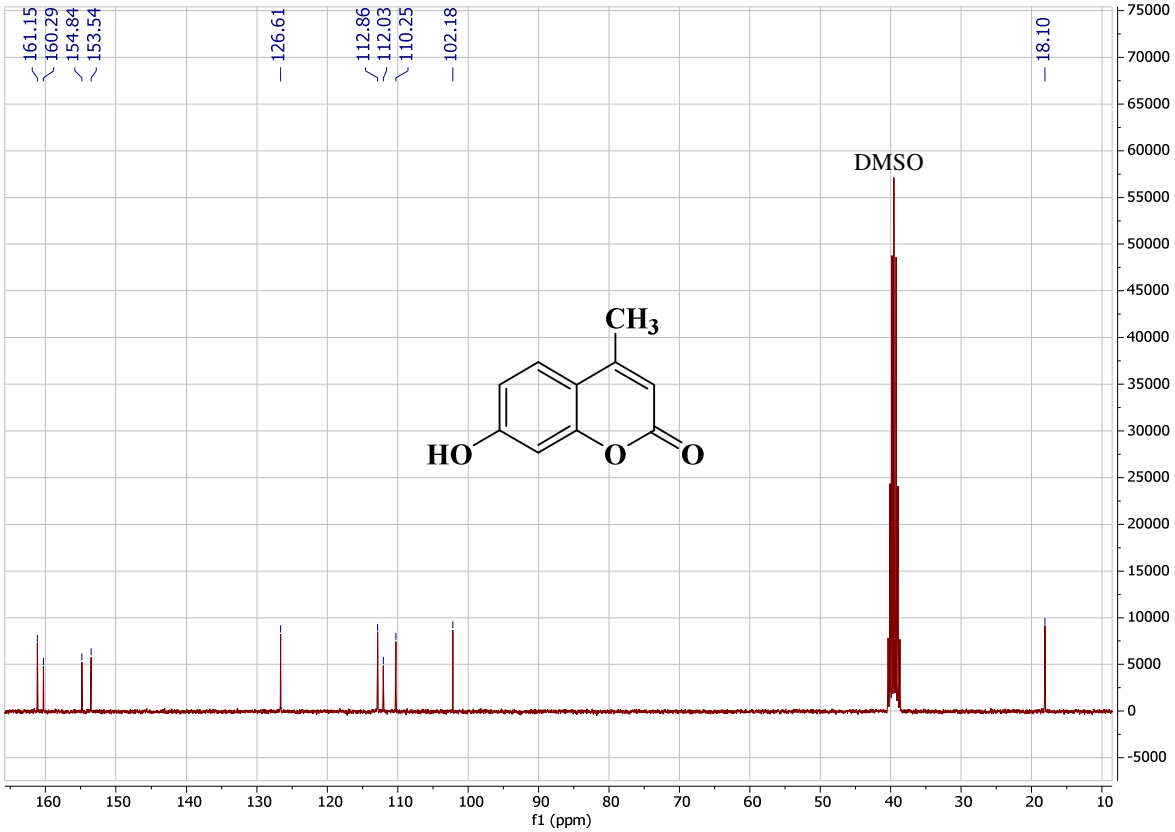
^{13}C NMR (75 MHz, DMSO) δ 161.15, 160.29, 154.84, 153.54, 126.61, 112.86, 112.03, 110.25, 102.18, 18.10.

Analyses were consistent with those previously reported in the literature [Establishing a Flow Process to Coumarin-8-Carbaldehydes as Important Synthetic Scaffolds, Jaroslav Zak, David Ron, Elena Riva, Heather P. Harding, Benedict C. S. Cross, Ian R. Baxendale, Chem. Eur. J. 2012,18, 9901 – 9910].

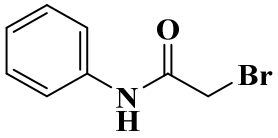
^{1}H NMR spectrum of 7-hydroxy-4-methyl-2*H*-chromen-2-one



^{13}C NMR spectrum of 7-hydroxy-4-methyl-2*H*-chromen-2-one



Synthesis of 2-bromo-*N*-phenylacetamide



Chemical Formula: C_8H_8BrNO
Molecular Weight: 214.0620

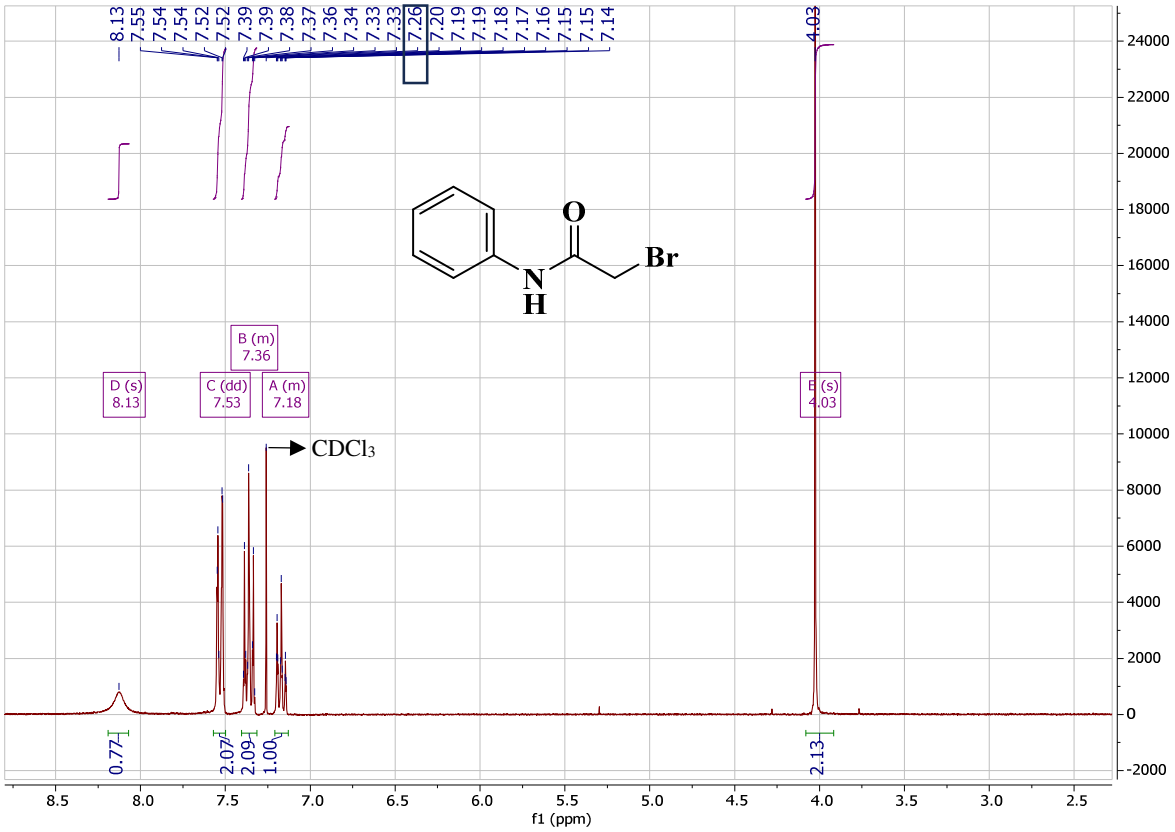
To a solution of aniline (0.91 mL, 0.93 g, 10 mmol, M = 93.13 g/mol, d = 1.022, 1 equiv.) and triethylamine (1.55 mL, 1.13 g, 11 mmol, M = 101.19 g/mol, d = 0.726, 1.1 equiv.) in CH_2Cl_2 at 0°C was added bromoacetyl bromide (0.87 mL, 2.02 g, 10 mmol, M = 201.84 g/mol, d = 2.317, 1 equiv.) dropwise over 15 min and the mixture was stirred continuously for 1 h at room temperature. The mixture was diluted with DCM, washed with diluted HCl and water. The organic phase was dried over magnesium sulfate and the solvent removed under reduced pressure. The residue was suspended in acetone and pentane was added. The solid was filtered off, washed several times with pentane and dried under vacuum (1.95 g, 91% yield).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.13 (s, 1H), 7.57 – 7.50 (m, 2H), 7.40 – 7.31 (m, 2H), 7.21 – 7.13 (m, 1H), 4.03 (s, 2H).

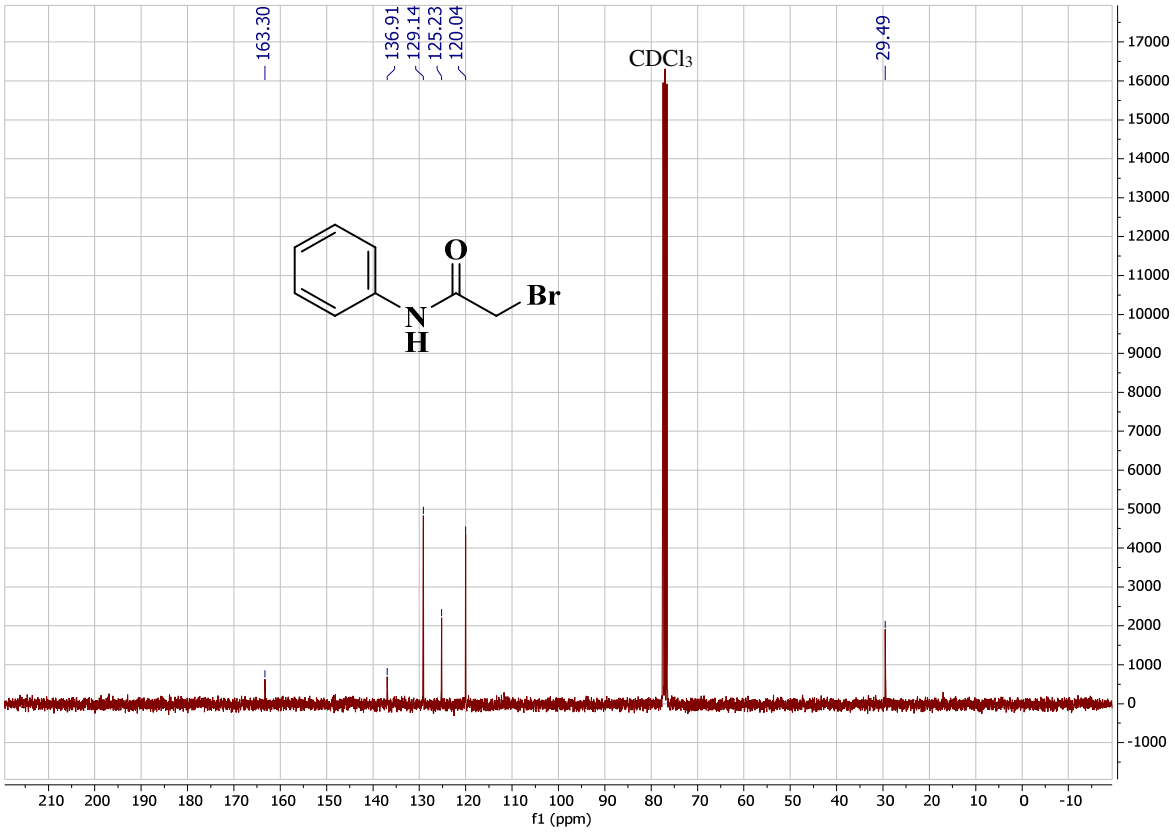
^{13}C NMR (75 MHz, $CDCl_3$) δ 163.30, 136.91, 129.14, 125.23, 120.04, 29.49.

Analyses were consistent with those previously reported in the literature [Antitubercular and Antiparasitic 2-Nitroimidazopyrazinones with Improved Potency and Solubility, Chee Wei Ang, Lendl Tan, Melissa L. Sykes, Neda Abu Gharbiyeh, Anjan Debnath, Janet C. Reid, Nicholas P. West, Vicky M. Avery, Matthew A. Cooper, Mark A. T. Blaskovich, J. Med. Chem. 2020, 63, 15726 – 15751].

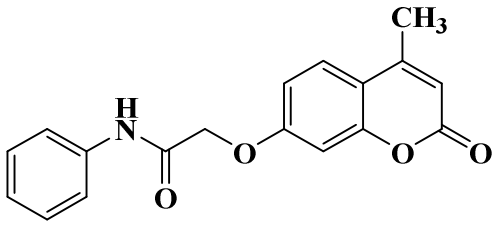
^{1}H NMR spectrum of 2-bromo-*N*-phenylacetamide



^{13}C NMR spectrum of 2-bromo-*N*-phenylacetamide



Synthesis of 2-((4-methyl-2-oxo-2*H*-chromen-7-yl)oxy)-*N*-phenylacetamide



Chemical Formula: $C_{18}H_{15}NO_4$
Molecular Weight: 309.3210

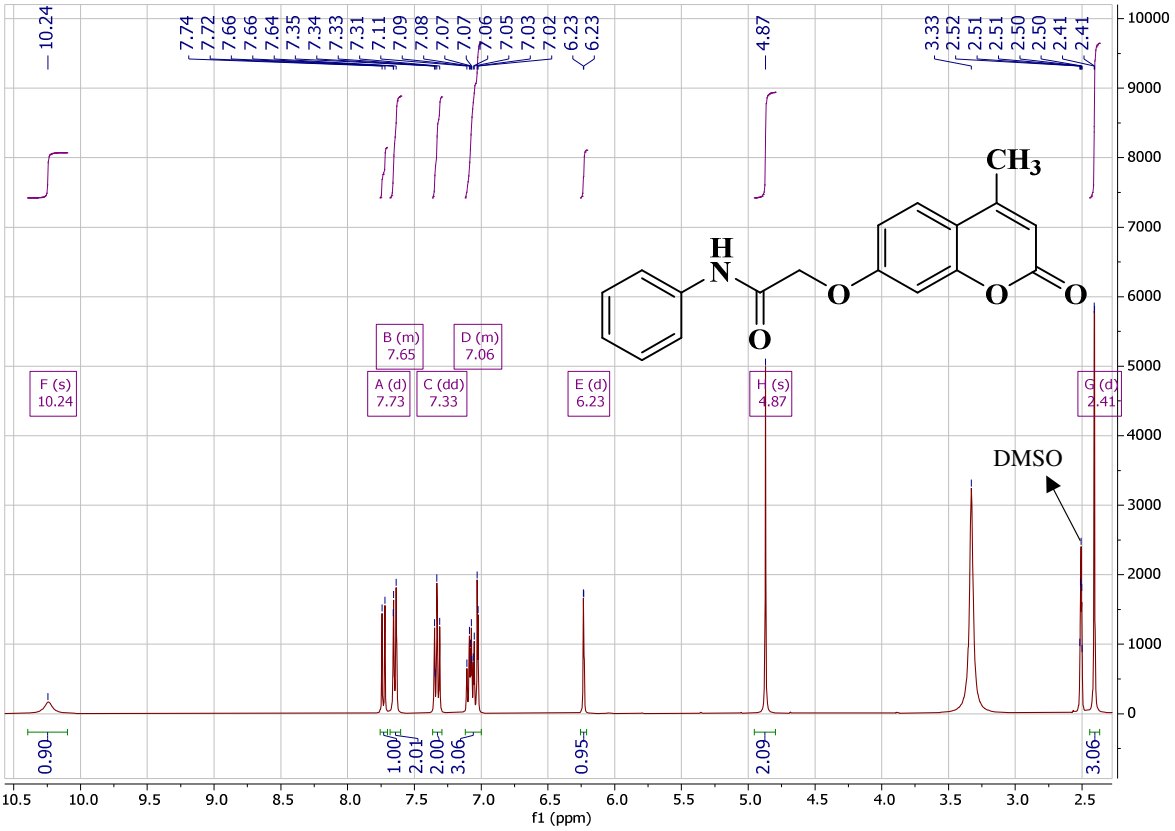
7-Hydroxy-4-methyl-2*H*-chromen-2-one (1.76 g, 10 mmol, M = 176.17 g/mol, 1 eq.) and Cs_2CO_3 (3.91 g, 12 mmol, M = 325.82 g/mol, 1.2 eq.) were suspended in acetonitrile (50 mL) and 2-bromo-*N*-phenylacetamide (2.57 g, 12 mmol, M = 214.06 g/mol, 1.2 eq.) was added. The resulting slurry was stirred at 50°C for two days. During that time, a white precipitate formed. The solvent was partially removed under reduced pressure. The solid was filtered off, washed several times with acetonitrile and dried under vacuum (2.07 g, 67% yield).

^{1}H NMR (400 MHz, DMSO) δ 10.24 (s, 1H), 7.73 (d, *J* = 8.8 Hz, 1H), 7.68 – 7.60 (m, 2H), 7.33 (dd, *J* = 10.8, 5.1 Hz, 2H), 7.12 – 7.00 (m, 3H), 6.23 (d, *J* = 1.1 Hz, 1H), 4.87 (s, 2H), 2.41 (d, *J* = 1.1 Hz, 3H).

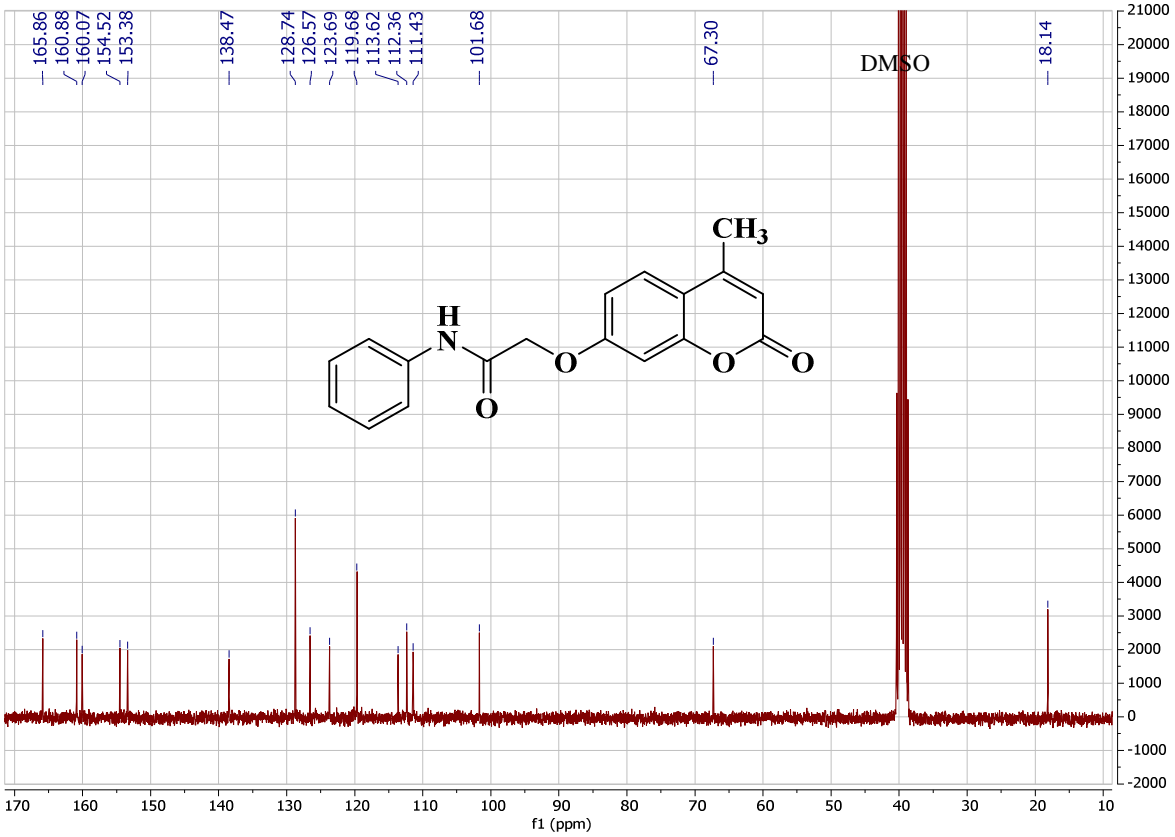
^{13}C NMR (75 MHz, DMSO) δ 165.86, 160.88, 160.07, 154.52, 153.38, 138.47, 128.74, 126.57, 123.69, 119.68, 113.62, 112.36, 111.43, 101.68, 67.30, 18.14.

Analyses were consistent with those previously reported in the literature [Synthesis of 7-Aminocoumarins from 7-Hydroxycoumarins via Amide Smiles Rearrangement, Daniel S. Lippe, Omar Elghawy, Adam M. Zucker, Evan S. K. Yanagawa, Erin Mathews, Yusef G. Ahmed, Paige N.D'Elia, Sabrina Bimson, Ryan R. Walvoord, ACS Omega 2022, 7, 35269 – 35279].

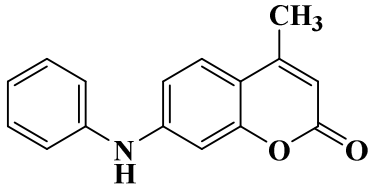
^{1}H NMR spectrum of 2-((4-methyl-2-oxo-2*H*-chromen-7-yl)oxy)-*N*-phenylacetamide



^{13}C NMR spectrum of 2-((4-methyl-2-oxo-2*H*-chromen-7-yl)oxy)-*N*-phenylacetamide



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



Chemical Formula: $C_{16}H_{13}NO_2$
Molecular Weight: 251.2850

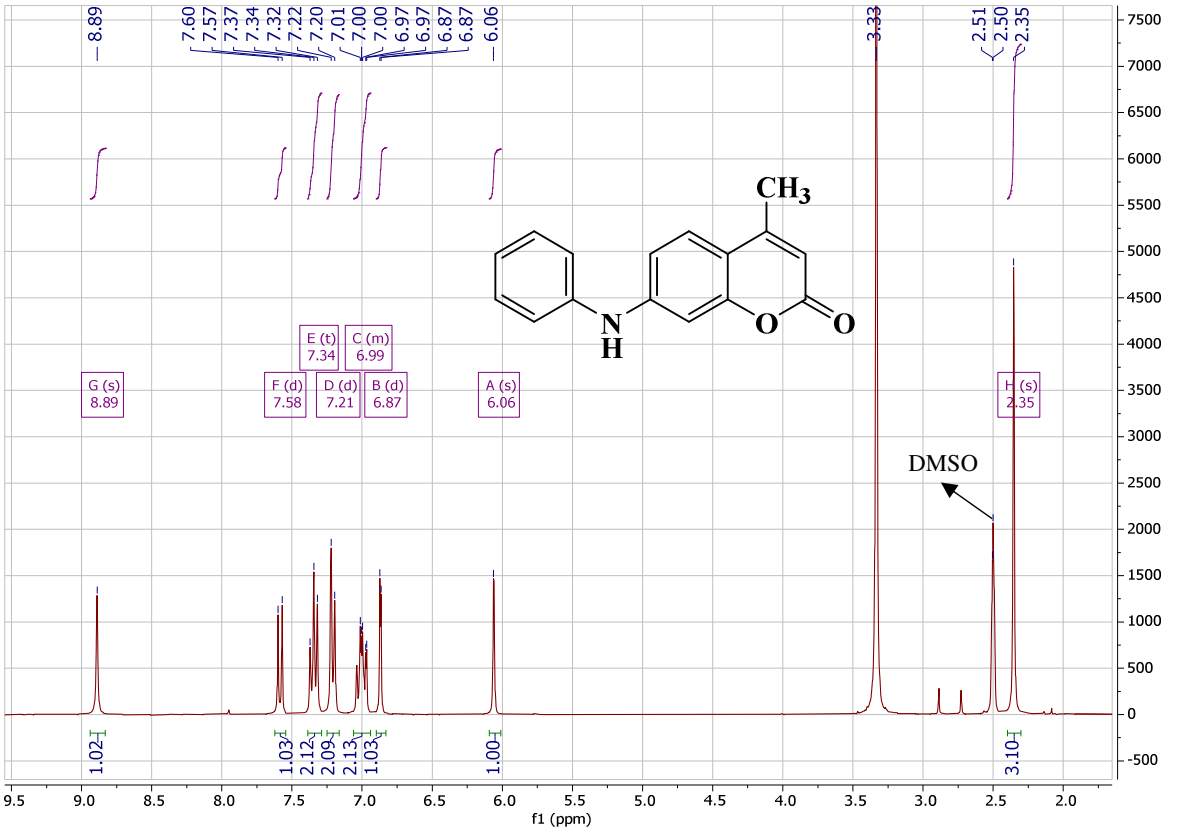
To a solution of 2-((4-methyl-2-oxo-2*H*-chromen-7-yl)oxy)-*N*-phenylacetamide (96 mg, 0.31 mmol, M = 309.32 g/mol) in DMF (3.1 mL, 0.1 M) was added Cs_2CO_3 (121 mg, 0.37 mmol, M = 325.82 g/mol) and the resulting slurry was stirred vigorously for 24 h at 70°C. The mixture was cooled and the solvent was removed under reduced pressure. The resulting solid was washed with 1 M HCl (10 mL) and extracted with DCM several times. The combined organic phases were dried over sodium sulfate, concentrated under reduced pressure. During evaporation, a solid formed. Addition of acetone precipitated a light beige solid that was filtered off, washed several times with acetone and dried under vacuum (32 mg, 41% yield).

^{1}H NMR (300 MHz, DMSO) δ 8.89 (s, 1H), 7.58 (d, *J* = 8.7 Hz, 1H), 7.34 (t, *J* = 7.8 Hz, 2H), 7.21 (d, *J* = 7.6 Hz, 2H), 7.06 – 6.94 (m, 2H), 6.87 (d, *J* = 2.1 Hz, 1H), 6.06 (s, 1H), 2.35 (s, 3H).

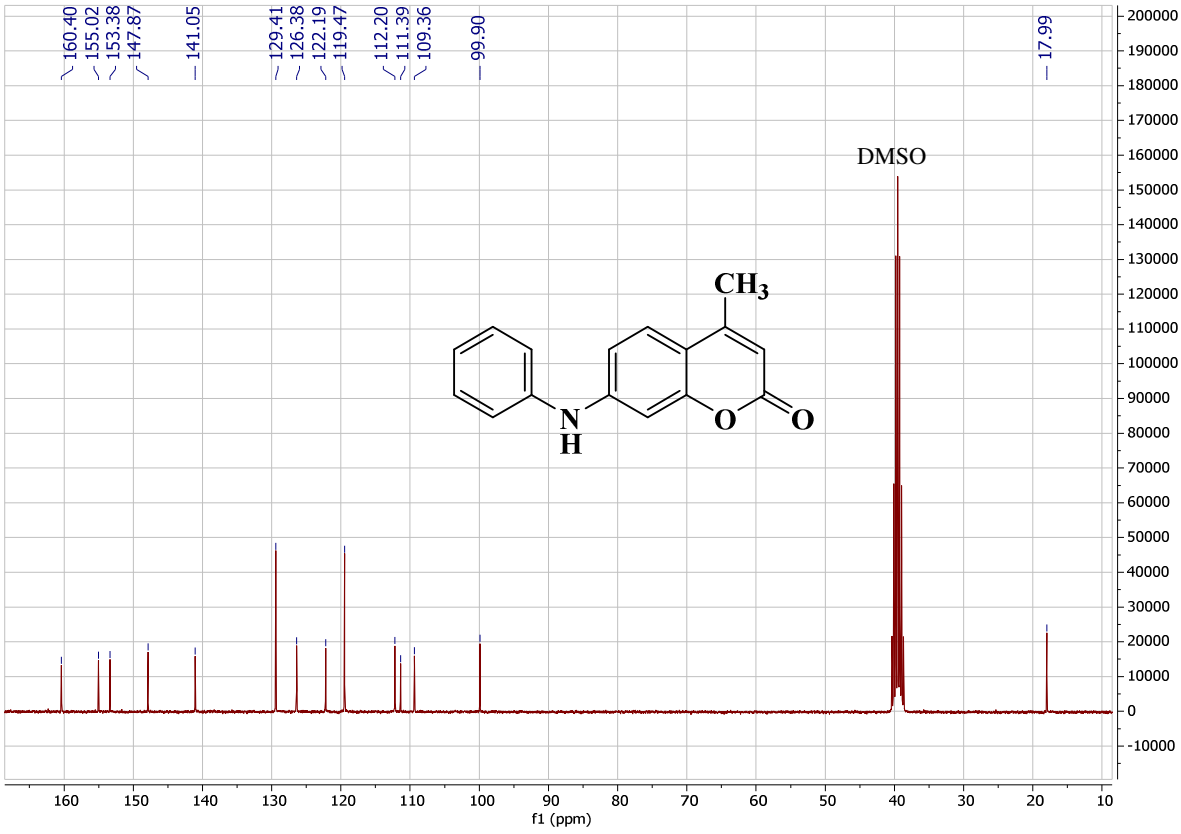
^{13}C NMR (75 MHz, DMSO) δ 160.40, 155.02, 153.38, 147.87, 141.05, 129.41, 126.38, 122.19, 119.47, 112.20, 111.39, 109.36, 99.90, 17.99.

Analyses were consistent with those previously reported in the literature [Synthesis of 7-Aminocoumarins from 7-Hydroxycoumarins via Amide Smiles Rearrangement, Daniel S. Lippe, Omar Elghawy, Adam M. Zucker, Evan S. K. Yanagawa, Erin Mathews, Yusef G. Ahmed, Paige N.D'Elia, Sabrina Bimson, Ryan R. Walvoord, ACS Omega 2022, 7, 35269 – 35279].

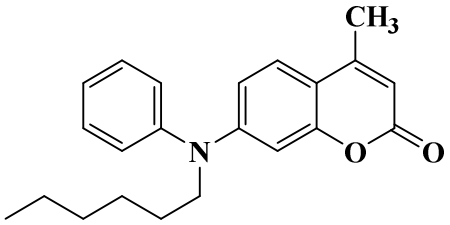
[1]H NMR spectrum of 4-methyl-7-(phenylamino)-2*H*-chromen-2-one



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



Synthesis of 7-(hexyl(phenyl)amino)-4-methyl-2*H*-chromen-2-one **B1**



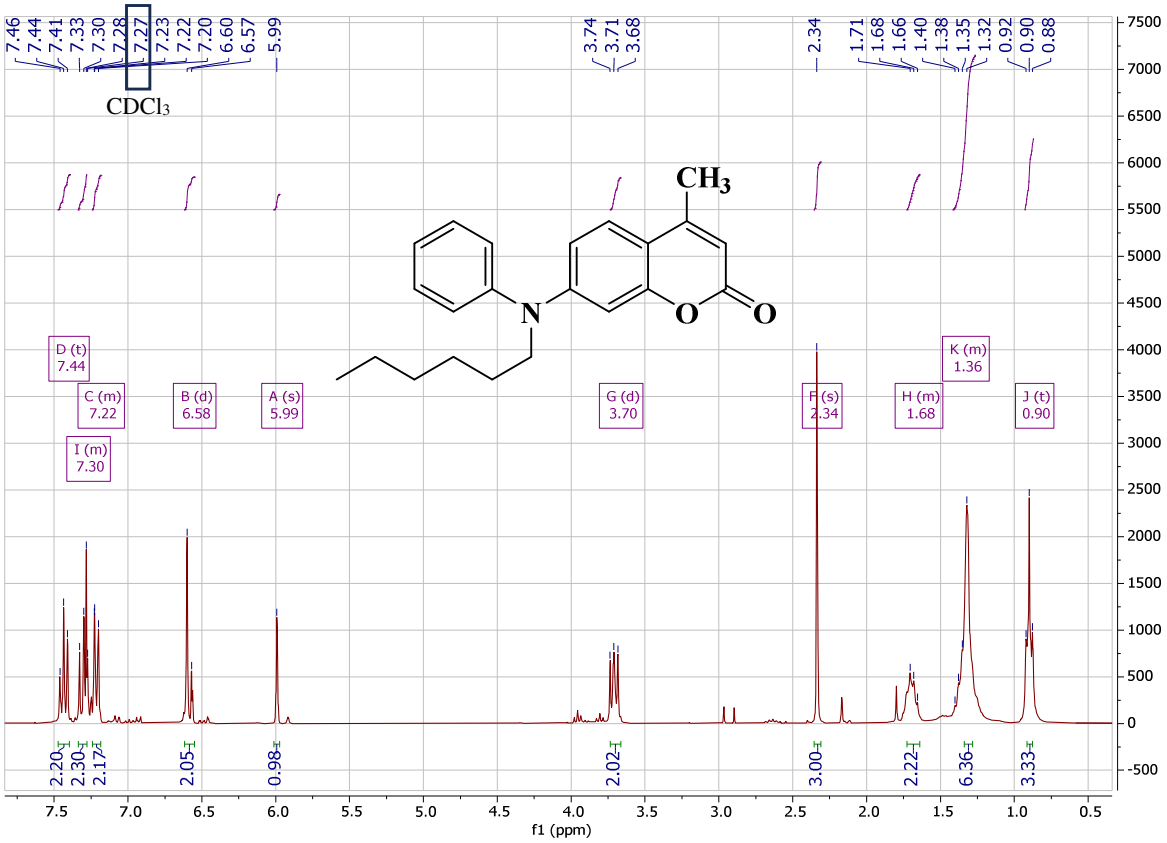
Chemical Formula: $C_{22}H_{25}NO_2$
Molecular Weight: 335.4470

4-Methyl-7-(phenylamino)-2*H*-chromen-2-one (4 g, 15.92 mmol, M = 251.28 g/mol) was suspended in DMF (100 mL) and NaH 90% (0.57 g, 23.88 mmol, M = 24 g/mol) was added at 0°C. The solution was stirred for 5 minutes and iodohexane (5.06 g, 3.52 mL, 23.88 mmol, M = 212.07 g/mol, d = 1.437) was added. The solution was stirred at room temperature overnight. Water was added, followed by chloroform. The organic phase was washed numerous times with water, dried over magnesium sulfate and the solvent removed under reduced pressure. The residue was purified by column chromatography using a gradient of DCM/pentane (4.75 g, 89% yield).

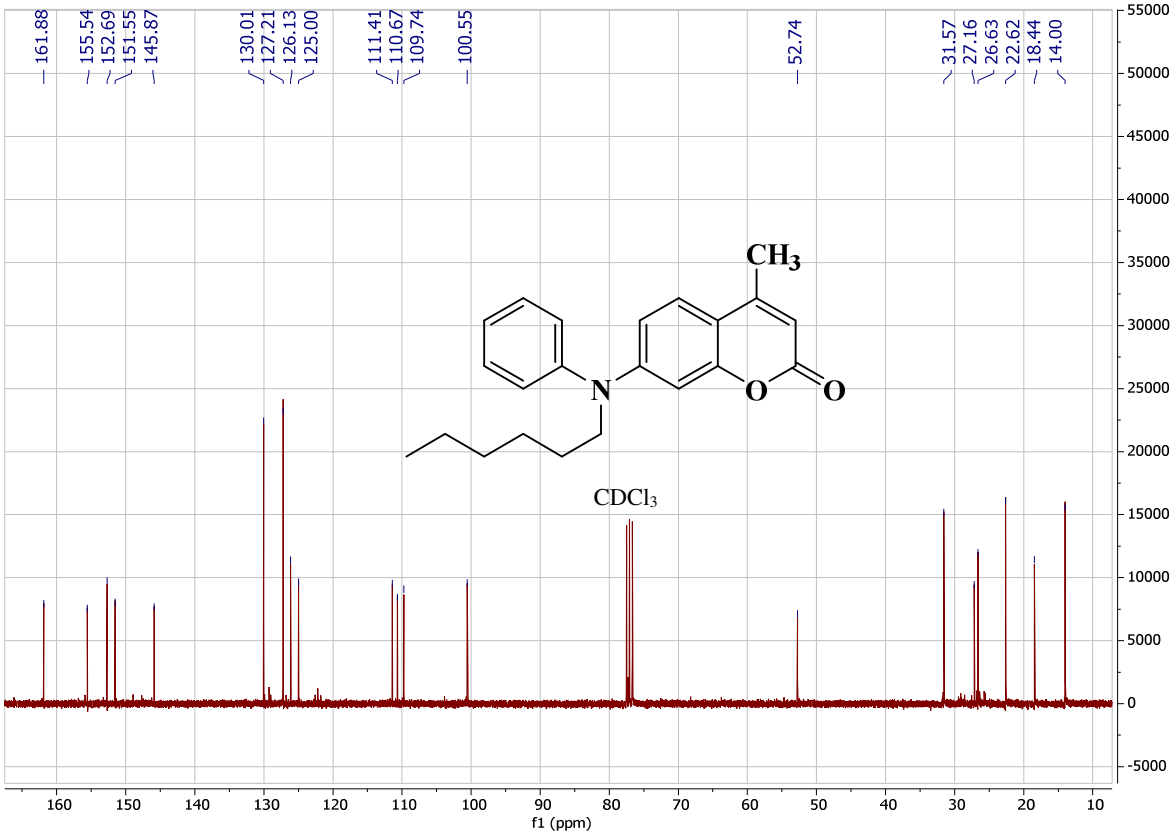
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44 (t, *J* = 7.7 Hz, 2H), 7.34 – 7.28 (m, 2H), 7.24 – 7.18 (m, 2H), 6.58 (d, *J* = 8.9 Hz, 2H), 5.99 (s, 1H), 3.70 (d, *J* = 7.9 Hz, 2H), 2.34 (s, 3H), 1.73 – 1.64 (m, 2H), 1.42 – 1.26 (m, 6H), 0.90 (t, *J* = 6.6 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 161.88, 155.54, 152.69, 151.55, 145.87, 130.01, 127.21, 126.13, 125.00, 111.41, 110.67, 109.74, 100.55, 52.74, 31.57, 27.16, 26.63, 22.62, 18.44, 14.00.

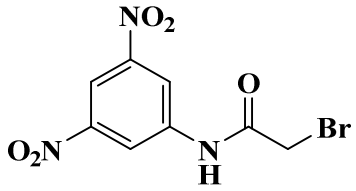
^{1}H NMR spectrum of 7-(hexyl(phenyl)amino)-4-methyl-2*H*-chromen-2-one **B1**



^{13}C NMR spectrum of 7-(hexyl(phenyl)amino)-4-methyl-2*H*-chromen-2-one **B1**



Synthesis of 2-bromo-*N*-(3,5-dinitrophenyl)acetamide **B5**



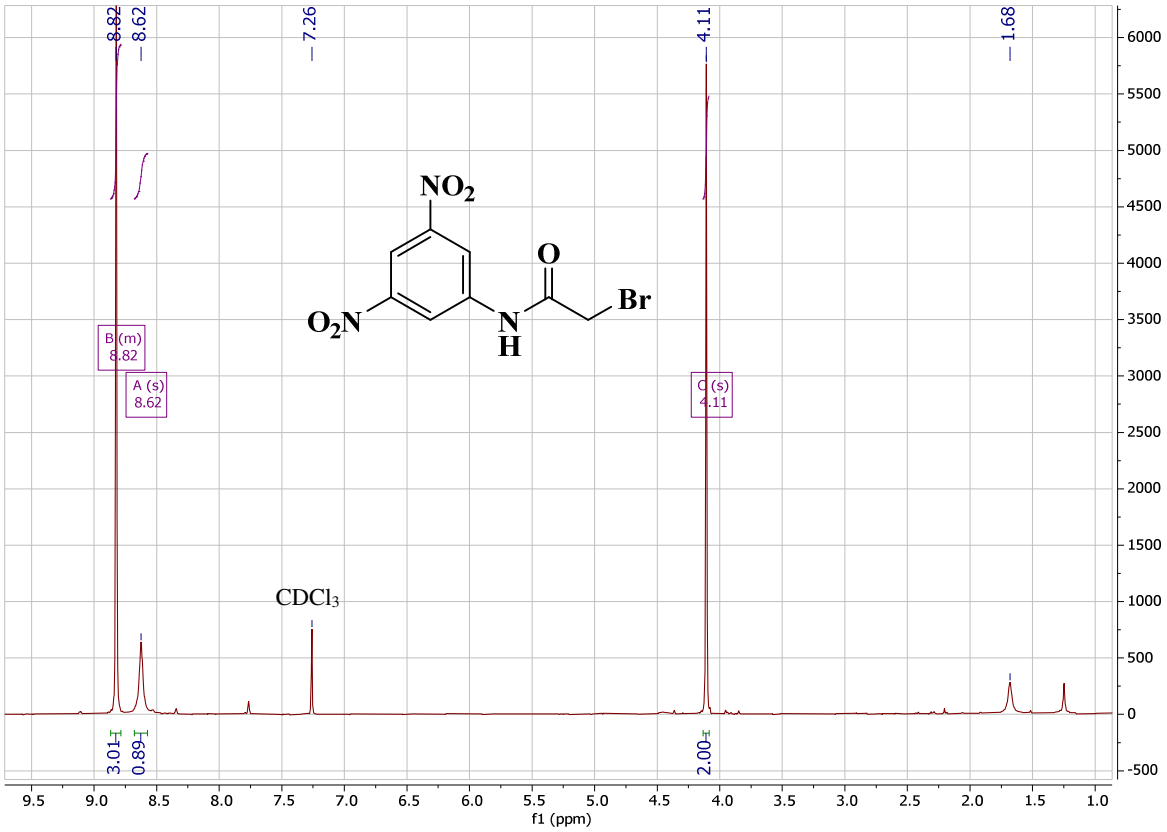
Chemical Formula: $C_8H_6BrN_3O_5$
Molecular Weight: 304.0560

To a solution of 3,5-dinitroaniline (1.83 g, 10 mmol, M = 183.12 g/mol, 1 equiv.) and triethylamine (1.55 mL, 1.13 g, 11 mmol, M = 101.19 g/mol, d = 0.726, 1.1 equiv.) in CH_2Cl_2 at 0°C was added bromoacetyl bromide (0.87 mL, 2.02 g, 10 mmol, M = 201.84 g/mol, d = 2.317, 1 equiv.) dropwise over 15 min and the mixture was stirred continuously for 1 h at room temperature. The mixture was diluted with DCM, washed with diluted HCl and water. The organic phase was dried over magnesium sulfate and the solvent removed under reduced pressure. The residue was suspended in acetone and pentane was added. The solid was filtered off, washed several times with pentane and dried under vacuum (2.67 g, 88% yield).

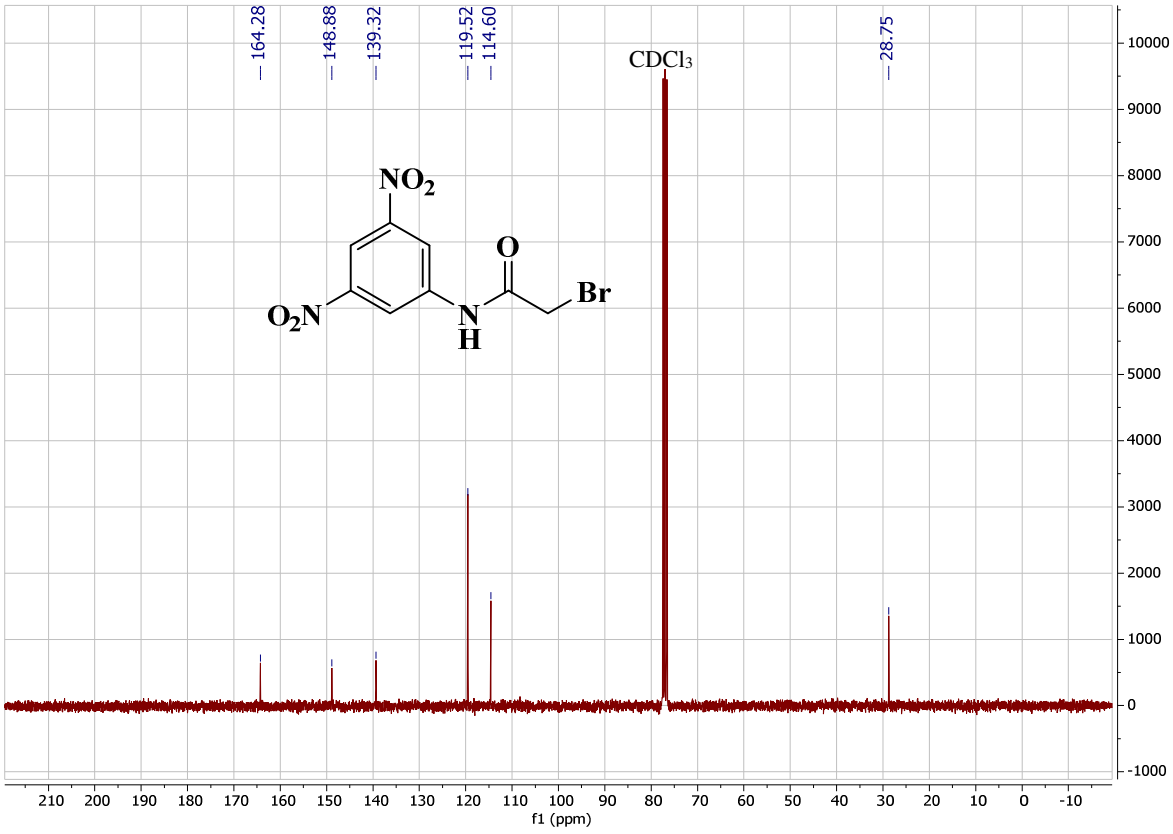
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.87 – 8.79 (m, 3H), 8.62 (s, 1H), 4.11 (s, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 164.28, 148.88, 139.32, 119.52, 114.60, 28.75.

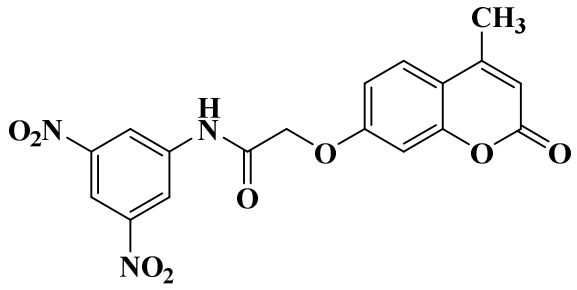
^{1}H NMR spectrum of 2-bromo-*N*-(3,5-dinitrophenyl)acetamide **B5**



^{13}C NMR spectrum of 2-bromo-*N*-(3,5-dinitrophenyl)acetamide **B5**



Synthesis of *N*-(3,5-dinitrophenyl)-2-((4-methyl-2-oxo-2*H*-chromen-7-yl)oxy)acetamide **B2**



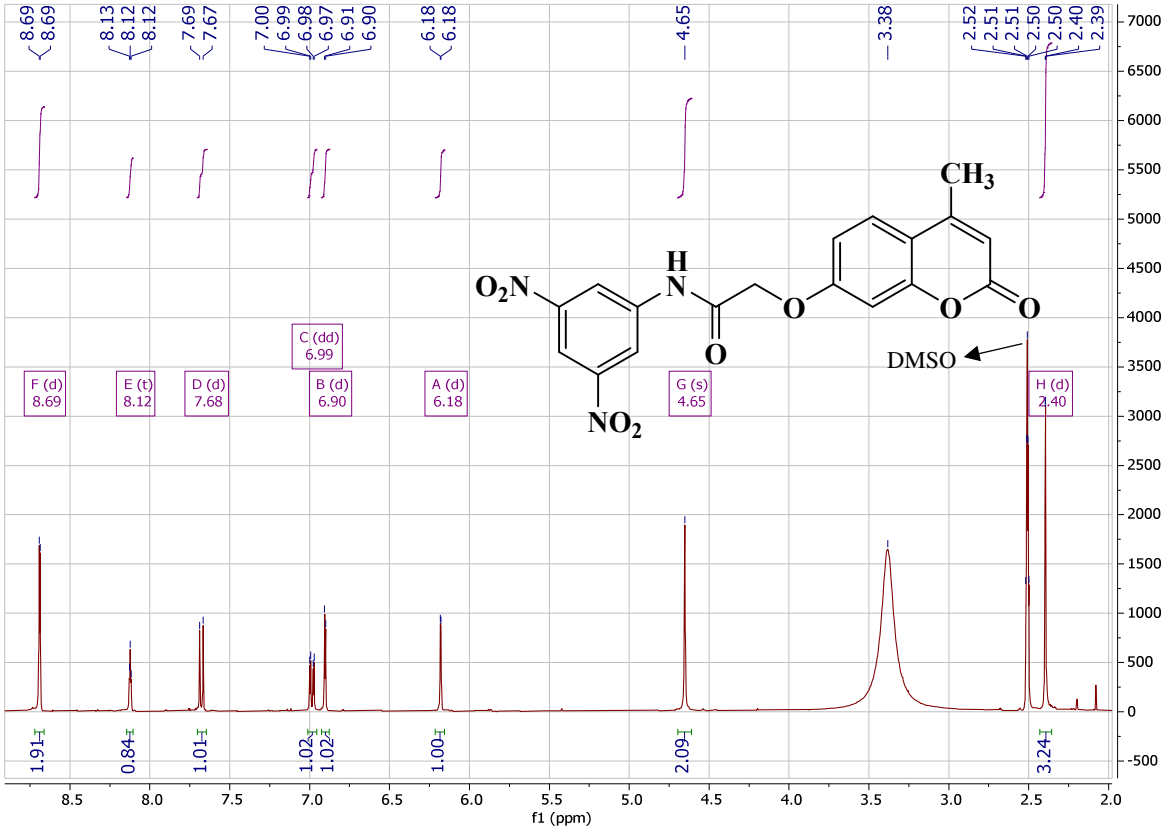
Chemical Formula: $C_{18}H_{13}N_3O_8$
Molecular Weight: 399.3150

7-Hydroxy-4-methyl-2*H*-chromen-2-one (1.76 g, 10 mmol, M = 176.17 g/mol, 1 eq.) and Cs_2CO_3 (3.91 g, 12 mmol, M = 325.82 g/mol, 1.2 eq.) were suspended in acetonitrile (50 mL) and 2-bromo-*N*-(3,5-dinitrophenyl)acetamide (3.65 g, 12 mmol, M = 304.05 g/mol, 1.2 eq.) was added. The resulting slurry was stirred at 50°C for two days. During that time, a white precipitate formed. The solvent was partially removed under reduced pressure. The solid was filtered off, washed several times with acetonitrile and dried under vacuum (2.08 g, 52% yield).

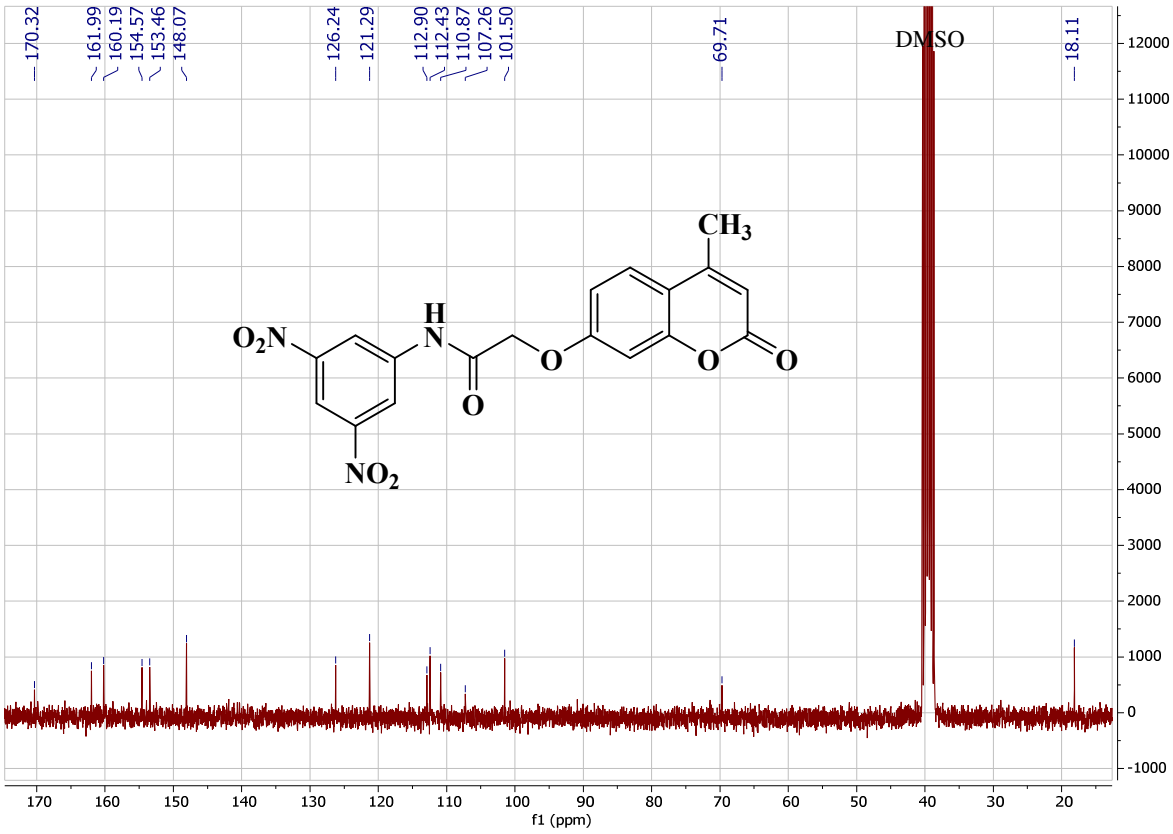
^{1}H NMR (400 MHz, DMSO) δ 8.69 (d, *J* = 2.2 Hz, 2H), 8.12 (t, *J* = 2.1 Hz, 1H), 7.68 (d, *J* = 8.8 Hz, 1H), 6.99 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.90 (d, *J* = 2.5 Hz, 1H), 6.18 (d, *J* = 1.2 Hz, 1H), 4.65 (s, 2H), 2.40 (d, *J* = 1.1 Hz, 3H).

^{13}C NMR (75 MHz, DMSO) δ 170.32, 161.99, 160.19, 154.57, 153.46, 148.07, 126.24, 121.29, 112.90, 112.43, 110.87, 107.26, 101.50, 69.71, 18.11.

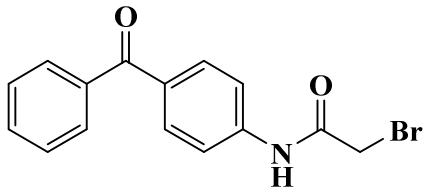
^{1}H NMR spectrum of *N*-(3,5-dinitrophenyl)-2-((4-methyl-2-oxo-2*H*-chromen-7-yl)oxy)acetamide **B2**



^{13}C NMR spectrum of *N*-(3,5-dinitrophenyl)-2-((4-methyl-2-oxo-2*H*-chromen-7-yl)oxy)acetamide **B2**



Synthesis of *N*-(4-benzoylphenyl)-2-bromoacetamide



Chemical Formula: $C_{15}H_{12}BrNO_2$
Molecular Weight: 318.1700

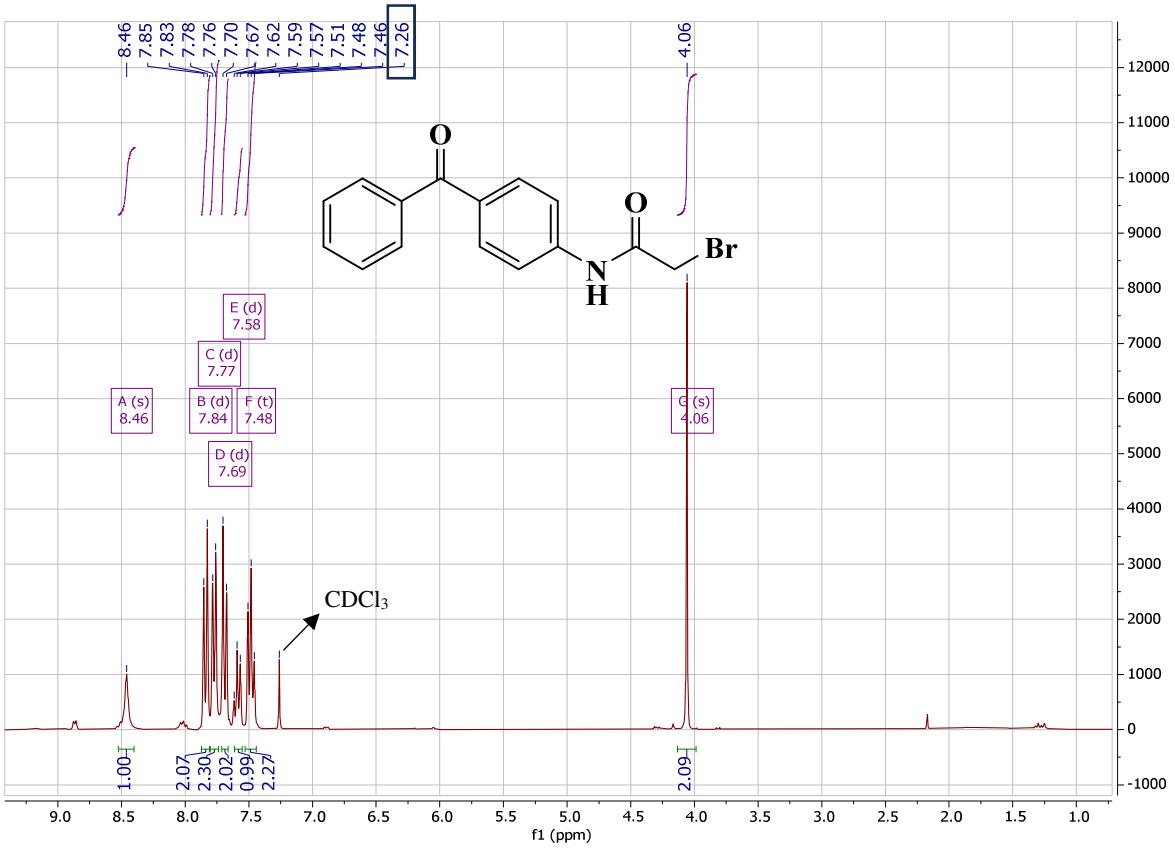
To a solution of 4-aminobenzophenone (1.97 g, 10 mmol, M = 197.23 g/mol, 1 eq.) and bromoacetyl bromide (0.87 mL, 2.02 g, 10 mmol, M = 201.84 g/mol, d = 2.317, 1 eq.) in CH_2Cl_2 (20 mL) was added **at 0°C** pyridine (0.89 mL, 0.87 g, 11 mmol, M = 79.10 g/mol, d = 0.978, 1.1 eq.) in CH_2Cl_2 (10 mL) and the mixture was stirred at room temperature for five hours. The mixture was diluted with DCM, washed with water numerous times in order to remove the pyridinium salt. The organic phase was dried over magnesium sulfate and the solvent removed under reduced pressure. Addition of acetone followed by ether precipitated the undesired product. It was filtered off, washed several times with ether. The filtrate was concentrated under reduced pressure. The product was identified in the filtrate (2.67 g, 84% yield).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.46 (s, 1H), 7.84 (d, *J* = 8.6 Hz, 2H), 7.77 (d, *J* = 7.2 Hz, 2H), 7.69 (d, *J* = 8.6 Hz, 2H), 7.58 (d, *J* = 7.5 Hz, 1H), 7.48 (t, *J* = 7.4 Hz, 2H), 4.06 (s, 2H).

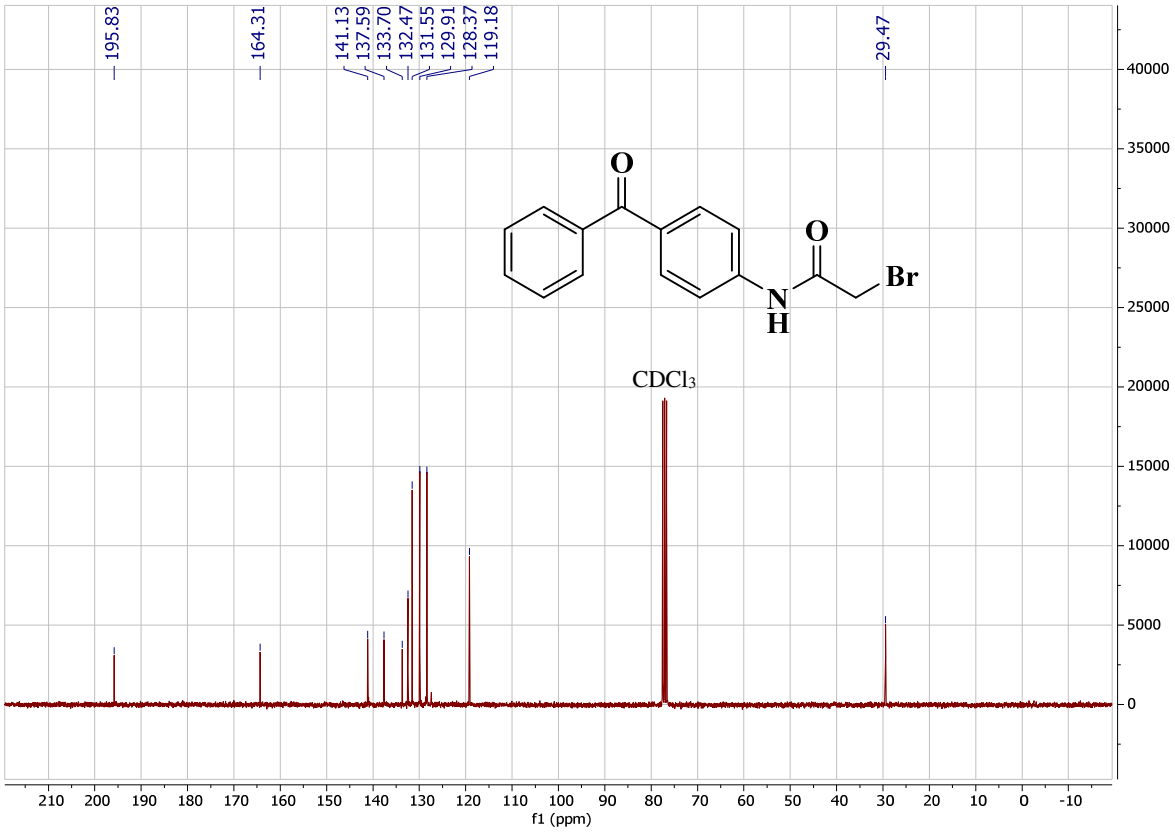
^{13}C NMR (75 MHz, $CDCl_3$) δ 195.83, 164.31, 141.13, 137.59, 133.70, 132.47, 131.55, 129.91, 128.37, 119.18, 29.47.

Analyses were consistent with those previously reported in the literature [Discovery of 2-((4,6-dimethylpyrimidin-2-yl)thio)-*N*-phenylacetamide derivatives as new potent and selective human sirtuin 2 inhibitors, Lingling Yang, Xiaobo Ma, Chen Yuan, Yanying He, Ling Li, Sha Fang, Wei Xia, Tao He, Shan Qian, Zhihong Xu, Guobo Li, Zhouyu Wang, European Journal of Medicinal Chemistry 2017, 134, 230 – 241].

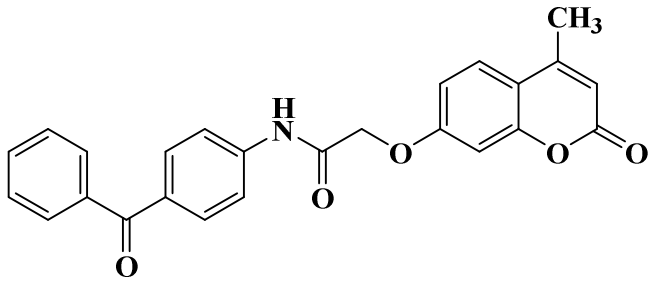
^{1}H NMR spectrum of *N*-(4-benzoylphenyl)-2-bromoacetamide



^{13}C NMR spectrum of *N*-(4-benzoylphenyl)-2-bromoacetamide



Synthesis of *N*-(4-benzoylphenyl)-2-((4-methyl-2-oxo-2*H*-chromen-7-yl)oxy)acetamide **B3**



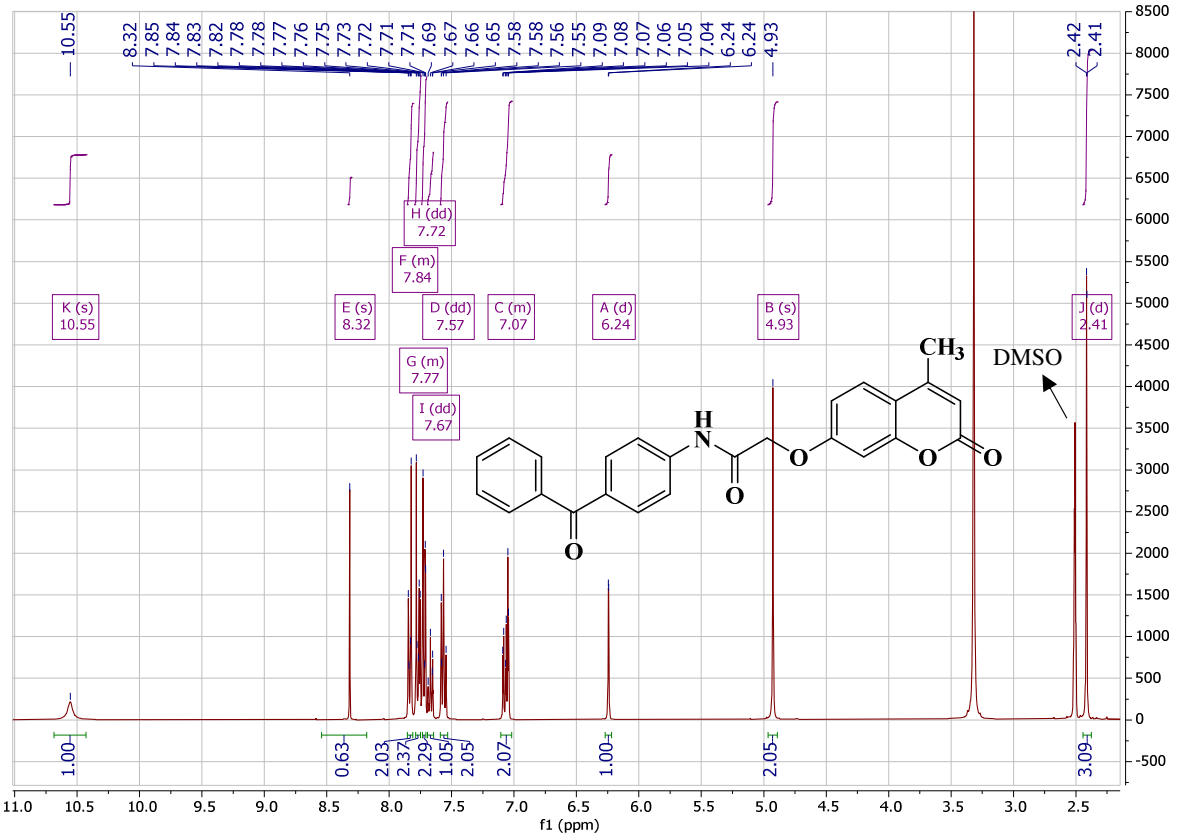
Chemical Formula: $C_{25}H_{19}NO_5$
Molecular Weight: 413.4290

7-Hydroxy-4-methyl-2*H*-chromen-2-one (1.76 g, 10 mmol, M = 176.17 g/mol, 1 eq.) and Cs_2CO_3 (3.91 g, 12 mmol, M = 325.82 g/mol, 1.2 eq.) were suspended in acetonitrile (50 mL) and *N*-(4-benzoylphenyl)-2-bromoacetamide (3.82 g, 12 mmol, M = 318.17 g/mol, 1.2 eq.) was added. The resulting slurry was stirred at 50°C for two days. During that time, a white precipitate formed. The solvent was partially removed under reduced pressure. The solid was filtered off, washed several times with acetonitrile and dried under vacuum. The product was contaminated by a mixture of the closed/opened form of the lactone. The powder was suspended in chloroform and acetone was added. The remaining solid was filtered off. During evaporation of the filtrate, a precipitate formed. It was filtered off, washed several times with ether and dried under vacuum (2.98 g, 72% yield).

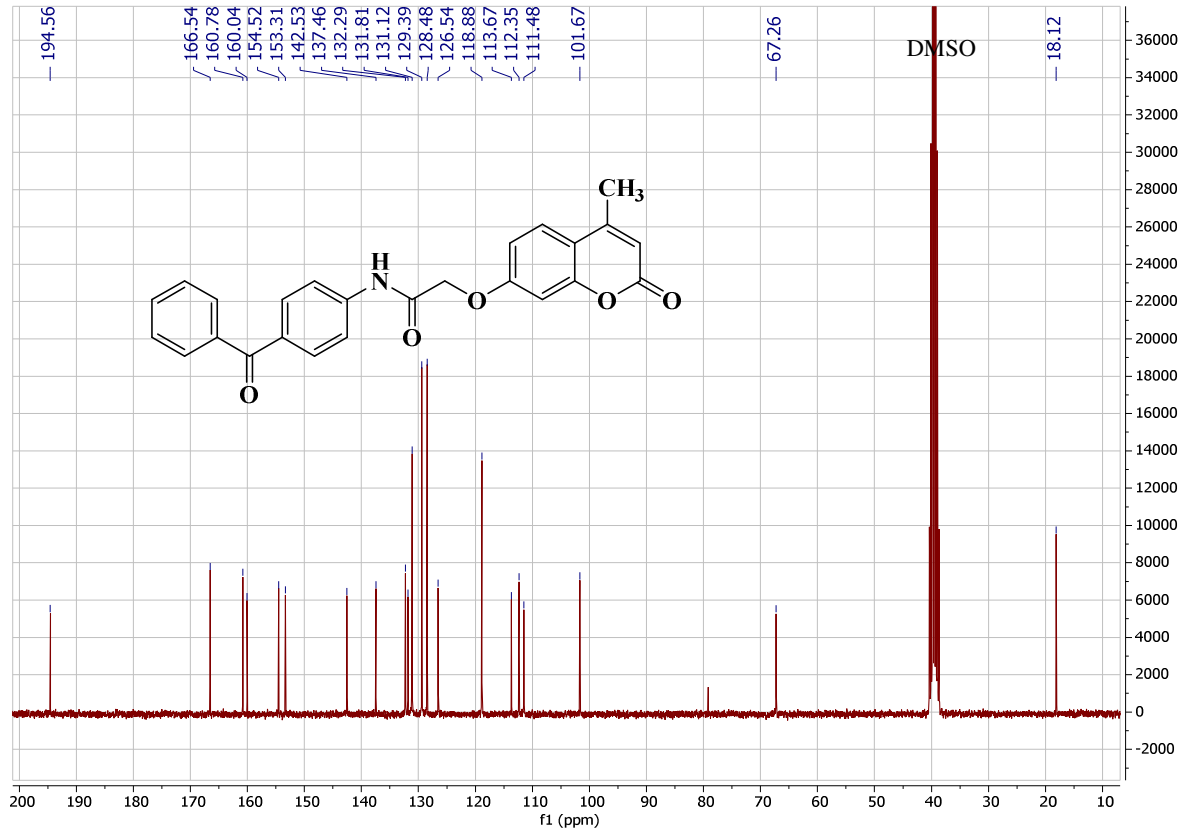
^{1}H NMR (400 MHz, DMSO) δ 10.55 (s, 2H), 8.32 (s, 1H), 7.85 – 7.81 (m, 4H), 7.79 – 7.74 (m, 5H), 7.72 (dd, *J* = 5.2, 3.2 Hz, 5H), 7.67 (dd, *J* = 10.5, 4.4 Hz, 2H), 7.57 (dd, *J* = 10.6, 4.4 Hz, 4H), 7.10 – 7.02 (m, 4H), 6.24 (d, *J* = 1.2 Hz, 2H), 4.93 (s, 4H), 2.41 (d, *J* = 1.1 Hz, 6H).

^{13}C NMR (75 MHz, DMSO) δ 194.56, 166.54, 160.78, 160.04, 154.52, 153.31, 142.53, 137.46, 132.29, 131.81, 131.12, 129.39, 128.48, 126.54, 118.88, 113.67, 112.35, 111.48, 101.67, 67.26, 18.12.

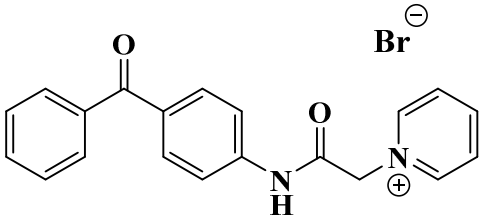
^{1}H NMR spectrum of *N*-(4-benzoylphenyl)-2-((4-methyl-2-oxo-2*H*-chromen-7-yl)oxy)acetamide **B3**



^{13}C NMR spectrum of *N*-(4-benzoylphenyl)-2-((4-methyl-2-oxo-2*H*-chromen-7-yl)oxy)acetamide **B3**



Synthesis of 1-(2-((4-benzoylphenyl)amino)-2-oxoethyl)pyridin-1-ium bromide **B4**



Chemical Formula: $C_{20}H_{17}BrN_2O_2$
Molecular Weight: 397.2720

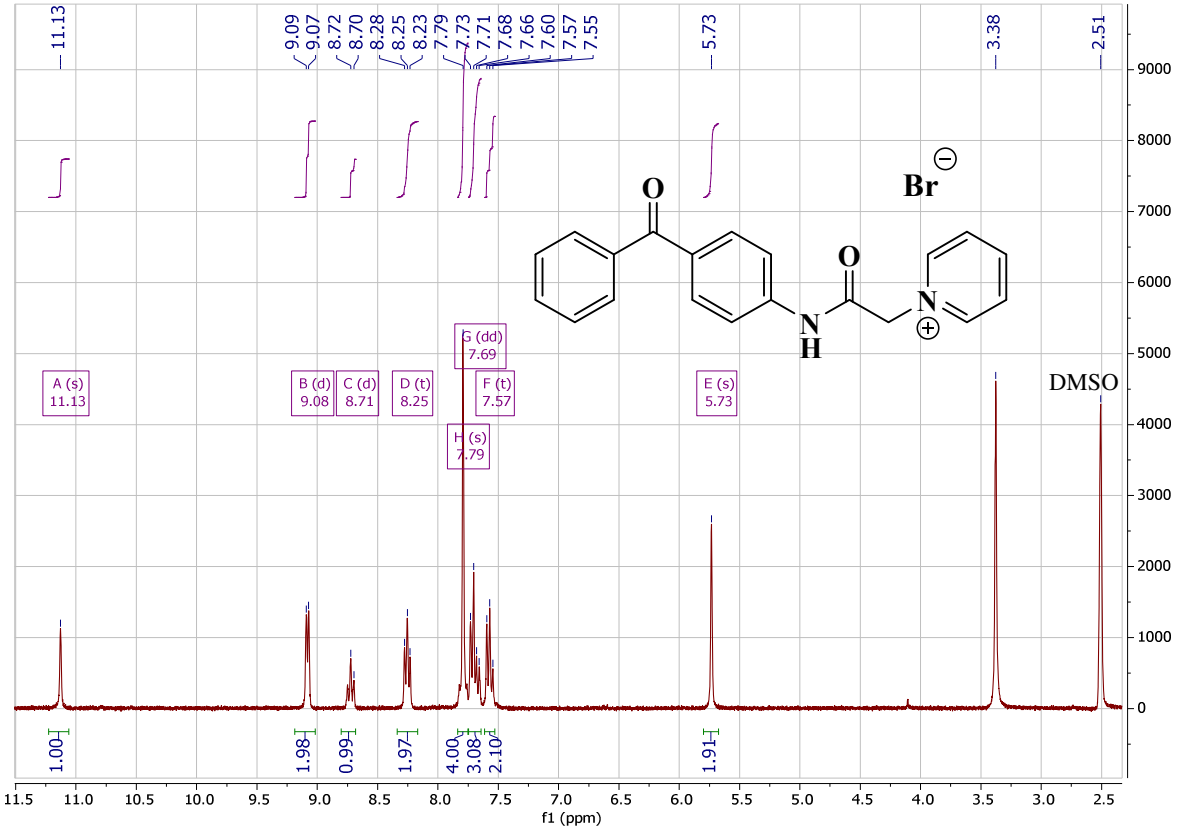
To a solution of 4-aminobenzophenone (1.97 g, 10 mmol, M = 197.23 g/mol, 1 eq.) and pyridine (0.89 mL, 0.87 g, 11 mmol, M = 79.10 g/mol, d = 0.978, 1.1 eq.) in CH_2Cl_2 **at room temperature** was added bromoacetyl bromide (0.87 mL, 2.02 g, 10 mmol, M = 201.84 g/mol, d = 2.317, 1 eq.) dropwise and the mixture was stirred continuously for 8 h at room temperature. The mixture was diluted with DCM, washed with diluted HCl and water. A gel formed. Diluted aq. NaOH was added in order to solubilize the solid. The organic phase was washed with water several times. The organic phase was dried over magnesium sulfate and the solvent removed under reduced pressure. The residue was suspended in diethyl ether and acetone then DCM was added in order to separate the white solid from a sticky pink glue. The white solid was filtered off, washed several times with ether and dried under vacuum. In fact, the product was identified as being the pyridinium salt (1.75 g, 44% yield).

^{1}H NMR (300 MHz, DMSO) δ 11.13 (s, 1H), 9.08 (d, *J* = 6.0 Hz, 2H), 8.71 (d, *J* = 8.0 Hz, 1H), 8.25 (t, *J* = 7.0 Hz, 2H), 7.79 (s, 4H), 7.69 (dd, *J* = 14.4, 6.8 Hz, 3H), 7.57 (t, *J* = 7.4 Hz, 2H), 5.73 (s, 2H).

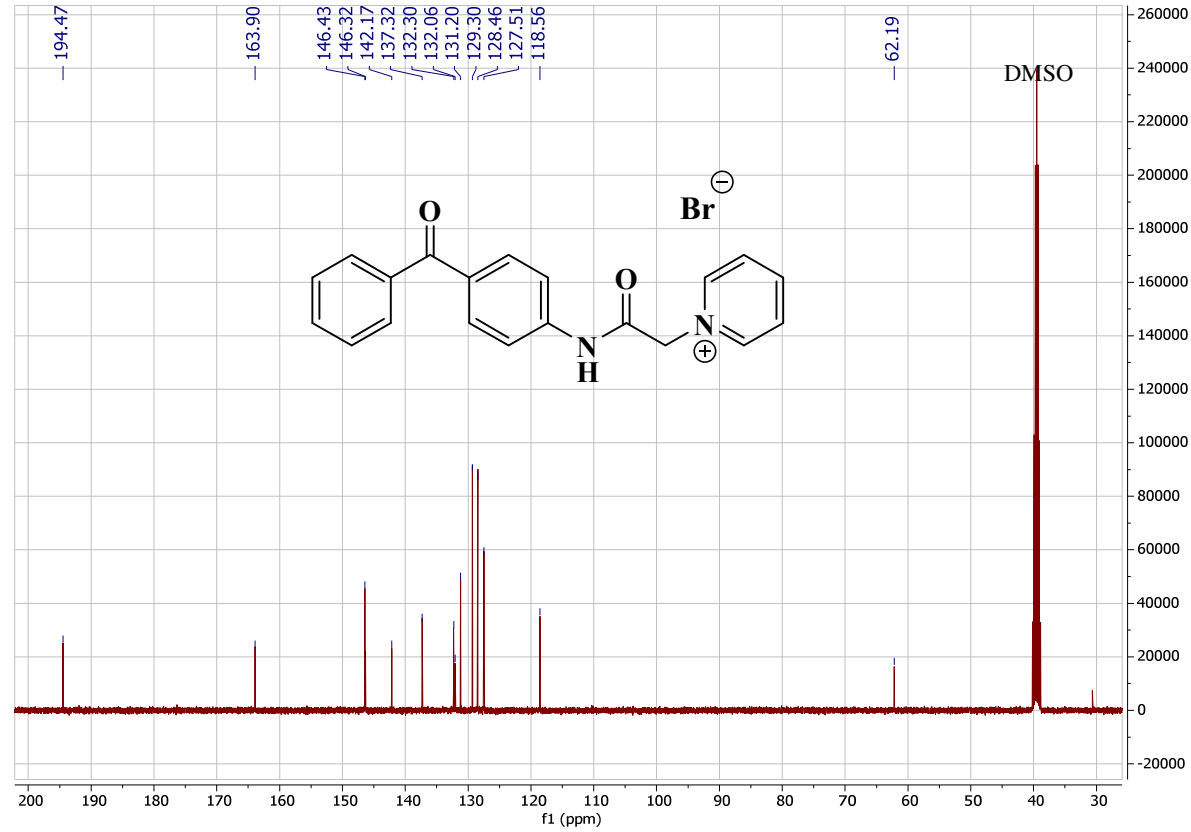
^{13}C NMR (101 MHz, DMSO) δ 194.47, 163.90, 146.43, 146.32, 142.17, 137.32, 132.30, 132.06, 131.20, 129.30, 128.46, 127.51, 118.56, 62.19.

Analyses were consistent with those previously reported in the literature [Design and Synthesis of New Sulfonamides-Based Flt3 Inhibitors, Reem F. Abutayeh, Jehad Almaliti and Mutasem O. Taha, Medicinal Chemistry 2020, 16, 403 – 412].

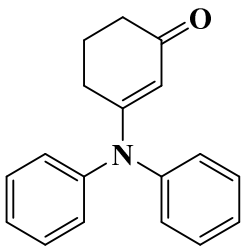
^{1}H NMR spectrum of 1-(2-((4-benzoylphenyl)amino)-2-oxoethyl)pyridin-1-ium bromide **B4**



^{13}C NMR spectrum of 1-(2-((4-benzoylphenyl)amino)-2-oxoethyl)pyridin-1-ium bromide **B4**



Synthesis of 3-(diphenylamino)cyclohex-2-en-1-one **B6**



Chemical Formula: $C_{18}H_{17}NO$
Molecular Weight: 263.3400

Diphenylamine (5.07 g, 30 mmol, M = 169.22 g/mol) and cyclohexane-1,3-dione (3.36 g, 30 mmol, M = 112.13 g/mol) were suspended in AcOH (60 mL) and the mixture was stirred at 100°C under inert atmosphere for 14 days. Although the reaction was still not complete (TLC), the solvent was removed under reduced pressure and the residue was dissolved in a minimum of chloroform and the product chromatographed using chloroform/acetone 95/5 as the eluent (4.58 g, 58% yield).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38 (t, *J* = 7.7 Hz, 4H), 7.28 (s, 2H), 7.20 (d, *J* = 8.1 Hz, 4H), 5.31 (s, 1H), 2.45 – 2.33 (m, 4H), 2.06 – 1.95 (m, 2H).

Analyses were consistent with those previously reported in the literature [Formation of 3-Aminophenols from Cyclohexane-1,3-diones, Damian Szymor-Pietrzak, Muhammad N. Khan, Anaïs Pagès, Ajay Kumar, Noah Depner, Derrick L. J. Clive, Journal of Organic Chemistry 2021, 86, 619 – 631].

^{1}H NMR spectrum of 3-(diphenylamino)cyclohex-2-en-1-one **B6**