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 ($5 \times 10^{-5}$ 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.

<table>
<thead>
<tr>
<th>Dye(1wt%)+EDB(1wt%)+Iod(1wt%)</th>
<th>FCs (%)</th>
<th>Dye(0.5wt%)+EDB(1wt%)+Iod(1wt%)</th>
<th>FCs (%)</th>
<th>Dye(0.1wt%)+EDB(1wt%)+Iod(1wt%)</th>
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### Table S2. Final acrylate function conversions (FCs) of TMPTA for thin sample in the presence of dye/EDB, dye/Iod and dye-EDB/Iod.

<table>
<thead>
<tr>
<th>Dye(1wt%)+EDB(1wt%)+Iod(1wt%)</th>
<th>FCs (%)</th>
<th>Dye(0.5wt%)+EDB(1wt%)+Iod(1wt%)</th>
<th>FCs (%)</th>
<th>Dye(0.1wt%)+EDB(1wt%)+Iod(1wt%)</th>
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<th>Dye(0.5wt%)+EDB(0.5wt%)+Iod(0.5wt%)</th>
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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-2H-chromen-2-one

![Chemical Structure]

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).

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

\[ ^{13}\text{C NMR (75 MHz, DMSO)} \delta 161.15, 160.29, 154.84, 153.54, 126.61, 112.86, 112.03, 110.25, 102.18, 18.10. \]

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-$2H$-chromen-2-one

$^{13}$C NMR spectrum of 7-hydroxy-4-methyl-$2H$-chromen-2-one
Synthesis of 2-bromo-N-phenylacetamide

\[
\text{Chemical Formula: } \text{C}_8\text{H}_8\text{BrNO}
\]
\[
\text{Molecular Weight: 214.0620}
\]

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\textsubscript{2}Cl\textsubscript{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\textsubscript{3}) \(\delta\) 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\textsubscript{3}) \(\delta\) 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-2H-chromen-7-yl)oxy)-N-phenylacetamide

![Chemical Formula: C_{18}H_{15}NO_{4}  
Molecular Weight: 309.3210](image)

7-Hydroxy-4-methyl-2H-chromen-2-one (1.76 g, 10 mmol, M = 176.17 g/mol, 1 eq.) and Cs₂CO₃ (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).

¹H 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).

¹³C 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)-2H-chromen-2-one

![Chemical structure](image)

Chemical Formula: C₁₆H₁₃NO₂  
Molecular Weight: 251.2850

To a solution of 2-((4-methyl-2-oxo-2H-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 Cs₂CO₃ (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).

¹H 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).

¹³C 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)-2H-chromen-2-one

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

![Chemical Structure]

Chemical Formula: C\textsubscript{22}H\textsubscript{25}NO\textsubscript{2}
Molecular Weight: 335.4470

4-Methyl-7-(phenylamino)-2\textit{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).

\textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}) \(\delta\) 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).

\textsuperscript{13}C NMR (75 MHz, CDCl\textsubscript{3}) \(\delta\) 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-2H-chromen-2-one B1

$^{13}$C NMR spectrum of 7-(hexyl(phenyl)amino)-4-methyl-2H-chromen-2-one B1
Synthesis of 2-bromo-N-(3,5-dinitrophenyl)acetamide B5

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 CH₂Cl₂ 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).

¹H NMR (300 MHz, CDCl₃) δ 8.87 – 8.79 (m, 3H), 8.62 (s, 1H), 4.11 (s, 2H).

¹³C NMR (75 MHz, CDCl₃) 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-2H-chromen-7-yl)oxy)acetamide B2

![Chemical structure](image)

Chemical Formula: C_{18}H_{13}N_{3}O_{8}
Molecular Weight: 399.3150

7-Hydroxy-4-methyl-2H-chromen-2-one (1.76 g, 10 mmol, M = 176.17 g/mol, 1 eq.) and Cs₂CO₃ (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).

\(^1\text{H NMR (400 MHz, DMSO)}\) 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).

\(^{13}\text{C NMR (75 MHz, DMSO)}\) 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 Structure](image)

**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$_2$Cl$_2$ (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$_2$Cl$_2$ (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-benzylophenyl)-2-bromoacetamide

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

\[
\text{Chemical Formula: } C_{24}H_{19}NO_5 \\
\text{Molecular Weight: } 413.4290
\]

7-Hydroxy-4-methyl-2\(H\)-chromen-2-one (1.76 g, 10 mmol, M = 176.17 g/mol, 1 eq.) and Cs\(_2\)CO\(_3\) (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) \(\delta\) 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) \(\delta\) 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-2H-chromen-7-yl)oxy)acetamide B3

$^{13}$C NMR spectrum of $N$-(4-benzoylphenyl)-2-((4-methyl-2-oxo-2H-chromen-7-yl)oxy)acetamide B3
Synthesis of 1-(2-((4-benzoylphenyl)amino)-2-oxoethyl)pyridin-1-ium bromide B4

\[
\text{Chemical Formula: } C_{20}H_{17}BrN_2O_2
\]
\[
\text{Molecular Weight: 397.2720}
\]

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\(_2\)Cl\(_2\) 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) \(\delta\) 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) \(\delta\) 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

\[
\begin{array}{c}
\text{Chemical Formula: } \text{C}_{18}\text{H}_{17}\text{NO} \\
\text{Molecular Weight: } 263.3400
\end{array}
\]

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\(_3\)) \(\delta\) 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