Supporting Information

Visible-Light Activatable Coumarin-based Phototriggers for Fluorescence Imaging with Ultra-High Photolysis Efficiency

1. Materials and Characterizations

1.1 Materials

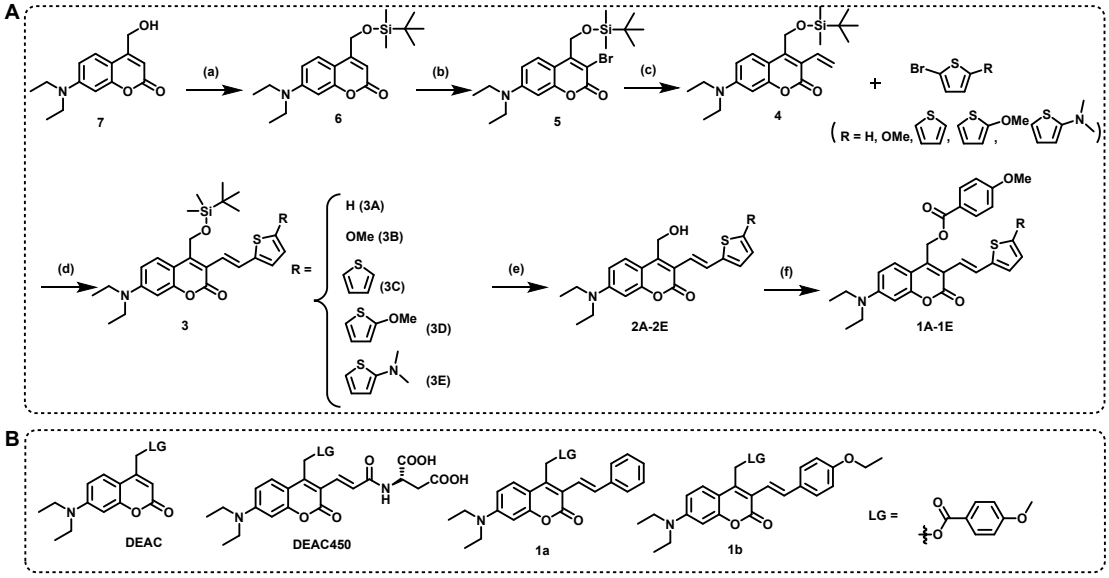
4-Methyl-7-(diethylamino)coumarin (98%, Bide Pharmatech), 2-(Chlorodimethylsilyl)-2-methylpropane (TBDMSCl, 98%, Shanghai Haohong Scientific), N-Bromosuccinimide (NBS, 98%, Bide Pharmatech), Tetrakis(triphenylphosphine) palladium ($Pd(PPh_3)_4$, 98%, Bide Pharmatech), 2,4,6-trivinyl-boroxin pyridine complex (98%, Adamas), 2-bromothiophene derivatives (98%, Bide Pharmatech), Palladium (II) acetate ($Pd(OAc)_2$, 98%, Bide Pharmatech), Lithium chloride (LiCl, 98%, Adamas), P-methoxybenzonic acid (98%, Shanghai Haohong Scientific), Tetrabutylammonium chloride (TBACl, 98%, Bide Pharmatech), Tetrabutylammonium fluoride (TBAF, 98%, Bide Pharmatech), N-Succinimidyl carbonate (DSC, 98%, Shanghai Haohong Scientific), Benzotriazol-1-yl-oxytripyrrolidinophosphonium hexafluorophosphate (PyBOP, 98%, Bide Pharmatech). The other reagents were purchased from Greagent Corp. All reagents applied were GR grade and used as received without further purification.

1.2 Characterizations

Proton and carbon nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance 500 (400 MHz) spectrometer. Deuterated DMSO and $CDCl_3$ were used as the solvents. Chemical shifts were reported in parts per million (ppm), and Me_4Si was used as the internal standard. Mass spectra were recorded on a Micromass GCTTM and a Micromass LCTTM with methanol as the mobile phase. Absorption spectra were recorded on a Shimadzu UV-2550 UV-vis spectrometer. Samples were dissolved in a

mixed solution of methanol/water (9:1) and scanned from 200 to 700 nm. The steady-state fluorescence experiments were performed on a Varian Cary Eclipses fluorescence spectrometer. The reversed-phase HPLC (Agilent 1200 Series) equip ped with a BetaBasic-18 column was used to monitor the photolysis process. A mixture of methanol and water was used as the mobile phase. The intensity of the light source applied was measured using a UV-A type radiation meter manufactured by Photoelectric Instrument Factory of Beijing Normal University.

2. Synthesis of Organic Compounds



Scheme S1. (A) The synthetic routes of PPGs 1A-1E: a) TBDMSCl, DCM, b) NBS, dry DCM, c) $Pd(PPh_3)_4$, 2,4,6-trivinyl-boroxin pyridine complex, 1M K_2CO_3 (aq), DME, d) 2-bromothiophene derivatives, Pd(OAc)2, LiCl, TBACl, NaHCO3, e) TBAF, dry THF; f) P-methoxybenzonic acid, DMAP, EDC. (B) Chemical structures of compounds 1a, 1b, DEAC, DEAC450 applied as control samples.

2.1 General procedures for the synthesis of compounds 4-7

Compounds 5, 6 and 7 were synthesized according to a previous report.[1]

Compound 4: Compound 5 (3 g, 6.8 mmol, 1 eq) was dissolved in ethylene glycol dimethyl ether (60 mL) under argon. K_2CO_3 aqueous solution (1 M, 5 mL), $Pd(PPh_3)_4$

(0.16 g, 0.14 mmol, 0.02 eq), and 2,4,6-trivinyl-boroxin pyridine complex (0.82 g, 3.4 mmol, 0.5 eq) were then added. The resulting mixture was refluxed for 6 hours under magnetic stirring. After reaction, the reaction solution was poured into water and extracted by ethyl acetate. The organic layer was washed with brine for 3 times and dried over Na_2SO_4 anhydrous. After removing the salts by filtration, the solution was concentrated by rotary evaporation under reduced pressure, and the obtained crude product was purified by column chromatography (silica gel, petroleum ether:ethyl acetate (v:v) = 9:1) to receive 4 as a yellow solid with a yield of 86% (2.3 g). ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 7.64 (d, J = 9.2, 1H), 6.75 (m, 2H), 6.51 (d, J = 2.5, 1H), 5.98 (dd, J = 17.5, 2.4, 1H), 5.48 (dd, J = 11.7, 2.4, 1H), 4.86 (s, 2H), 3.43 (q, J = 6.9, 4H), 1.12 (t, J = 7.0, 6H), 0.85 (s, 9H), 0.10 (s, 6H); ^{13}C NMR (101 MHz, DMSO -d_6) δ (ppm): 160.6, 155.2, 150.5, 148.2, 129.7, 127.6, 120.5, 116.2, 109.4, 107.8, 96.8, 58.1, 44.4, 26.1, 18.3, 12.8, -4.8; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{33}NO_3Si$ 388.2230; Found 388.2228 $[M+H]^+$.

2.2 General procedures for the synthesis of compounds 3A-3E

Compound 4 (0.5 g, 1.3 mmol, 1 eq) and 2-bromothiophene derivatives (1.6 mmol, 1.2 eq) were dissolved in DMF (20 mL), and lithium chloride (85 mg, 2.0 mmol, 1.5 eq), sodium bicarbonate (0.17 g, 2.0 mmol, 1.5 eq), and tetrabutylammonium chloride (0.56 g, 1.6 mmol, 1.2 eq) were then added. The solution was purged with Ar for 20 min, Palladium (II) acetate (88 mg, 0.39 mmol, 0.3 eq) was then added to the reaction solution. After heating at 110 °C for 1 h, the reaction solution was cooled to room temperature, poured into water, and extracted with ethyl acetate. The organic layer was washed with brine for three times and dried over anhydrous Na_2SO_4. The solution was filtrated and concentrated by rotary evaporation under reduced pressure. The received crude product was purified by column chromatography (silica gel, petroleum ether:dichloromethane (v:v) = 3:1). Compounds 3A-3E were synthesized through similar procedures, and the structural characterization results are as described as follows:

Compound 3A: Compound 3A was obtained as a yellow solid with a yield of 56% (0.34

g). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.86 (d, J = 15.8, 1H), 7.60 (d, J = 9.1, 1H), 7.20 (d, J = 5.1, 1H), 7.09 (m, 2H), 6.00 (dd, J = 5.1, 3.6, 1H), 6.64 (d, J = 8.8, 1H), 6.51 (s, 1H), 4.89 (s, 2H), 3.42 (q, J = 7.1, 4H), 1.22 (t, J = 7.1, 6H), 0.94 (s, 9H), 0.18 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 161.3, 154.9, 146.4, 143.9, 128.5, 127.6, 126.7, 126.5, 126.3, 125.4, 124.9, 124.5, 120.4, 109.1, 97.4, 58.0, 44.8, 25.9, 18.3, 12.5, -5.0; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{26}H_{35}NO_3SSi$ 470.2107; Found 470.2105 $[M+H]^+$.

Compound 3B: Compound 3B was obtained as a yellow solid with a yield of 53% (0.34 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.72 (d, J = 15.7, 1H), 7.58 (d, J = 9.0, 1H), 6.72 (m, 3H), 6.51 (s, 1H), 6.09 (d, J = 3.9, 1H), 4.87 (s, 2H), 3.90 (s, 3H), 3.42 (q, J = 6.8, 4H), 1.22 (t, J = 8.3, 6H), 0.93 (s, 9H), 0.18 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 165.8, 161.4, 154.7, 149.6, 145.3, 130.7, 128.6, 126.3, 125.6, 117.2, 116.9, 109.0, 104.1, 97.4, 60.0, 58.0, 44.8, 25.8, 18.2, 12.4, -5.1; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{27}H_{37}NO_4SSi$ 500.2213; Found 500.2211 $[M+H]^+$.

Compound 3C: Compound 3C was obtained as an orange solid with a yield of 57% (0.41 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.85 (d, J = 15.7, 1H), 7.60 (d, J = 9.1, 1H), 7.21 (d, J = 0.9, 1H), 7.17 (d, J = 2.6, 1H), 7.08 (d, J = 1.5, 1H), 7.05 (d, J = 10.4, 1H), 7.02 (dd, J = 5.0, 3.7, 1H), 6.97 (d, J = 3.7, 1H), 6.65 (d, J = 7.7, 1H), 6.51 (s, 1H), 4.90 (s, 2H), 3.42 (q, J = 7.0, 4H), 1.22 (t, J = 7.0, 6H), 0.95 (s, 9H), 0.20 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 161.3, 154.9, 146.3, 143.0, 137.6, 136.2, 127.9, 127.2, 126.5, 124.4, 124.2, 123.6, 120.6, 116.4, 109.1, 97.4, 58.0, 44.9, 29.7, 25.9, 12.5, -5.0; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{30}H_{37}NO_3S_2Si$ 552.1984; Found 552.1982 $[M+H]^+$.

Compound 3D: Compound 3D was obtained as an orange solid with a yield of 51% (0.39 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.82 (d, J = 15.7, 1H), 7.59 (d, J = 9.1, 1H), 7.01 (d, J = 9.3, 1H), 6.93 (d, J = 3.8, 1H), 6.88 (d, J = 3.7, 1H), 6.81 (d, J = 3.9, 1H), 6.63 (d, J = 8.1, 1H), 6.50 (d, J = 2.0, 1H), 6.13 (d, J = 4.0, 1H), 4.90 (s, 2H), 3.91 (s, 3H), 3.42 (q, J = 7.1, 4H), 1.21 (t, J = 8.7, 6H), 0.95 (s, 9H), 0.19 (s, 6H); ^{13}C NMR

(101 MHz, $CDCl_3$) δ (ppm): 165.6, 161.3, 154.8, 149.9, 146.1, 141.8, 137.0, 127.7, 127.3, 126.4, 124.0, 122.6, 121.3, 120.0, 116.4, 108.9, 104.5, 97.3, 60.2, 58.0, 44.7, 30.1, 25.8, 12.5, -5.0; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{31}H_{39}NO_4S_2Si$ 582.2090; Found 582.2092 $[M+H]^+$.

Compound 3E: Compound 3E was obtained as a yellow solid with a yield of 53% (0.32 g). ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.96 (d, J = 15.7 Hz, 1H), 7.61 (d, J = 9.1 Hz, 1H), 7.21 (d, J = 5.1 Hz, 1H), 7.13 (d, J = 15.0 Hz, 1H), 7.05 (s, 1H), 6.99 (d, J = 15.7 Hz, 1H), 6.73 (d, J = 8.1 Hz, 1H) , 6.66 (d, J = 7.5 Hz, 1H) , 6.52 (s, 1H), 4.91 (s, 2H), 3.41 (dd, J = 13.9, 6.8 Hz, 4H), 2.94 (s, 6H), 1.21 (t, J = 7.0 Hz, 6H) ,0.94 (s, 9H), 0.20 (s, 6H);^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 163.7, 160.9, 154.6, 150.0, 141.1, 140.2, 138.7, 132.0, 128.6, 128.3, 125.9, 124.2, 121.7, 121.2, 118.7, 113.8, 109.3, 108.7, 102.7, 97.3, 61.2,44.8, 42.7, 30.1,25.8, 12.5, -5.0; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{32}H_{42}N_2O_3S_2Si$ 594.2406; Found 595.2405 $[M+H]^+$.

2.3 General procedures for the synthesis of compounds 2A-2E

To a solution of compound 3A (0.5 mmol, 1 eq) in tetrahydrofuran (20 mL), 1 M TBAF tetrahydrofuran solution (0.6 mmol, 1.2 eq) was added. The mixture was stirred at 0 ℃ for 30 min. Afterwards, the reaction solution was poured into water and extracted with ethyl acetate. The organic layer was washed with brine for three times and dried over anhydrous Na_2SO_4. The solution was filtrated and concentrated by rotary evaporation under reduced pressure. The crude product was purified by column chromatography (silica gel, dichloromethane) to receive compound 2A. Compounds 2A-2E were synthesized through similar procedures, and the structural characterization results are as described as follows:

Compound 2A: Compound 2A was obtained as a yellow solid with a yield of 60% (0.10 g). ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.85 (d, J = 15.8, 1H), 7.64 (d, J = 9.0, 1H), 7.19 (d, J = 4.6, 1H), 7.02 (m, 3H), 6.63 (d, J = 7.7, 1H), 6.47 (s, 1H), 4.95 (s, 2H), 3.41 (q, J = 6.7, 4H), 1.21 (t, J = 6.9, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 161.2, 154.9, 150.1, 145.9, 143.6, 127.9, 127.7, 126.9, 126.2, 124.7, 119.6, 116.4, 109.3,

108.4, 97.5, 57.4, 44.8, 12.5; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{21}NO_3S$ 356.1242; Found 356.1240 $[M+H]^+$.

Compound 2B: Compound 2B was obtained as a yellow solid with a yield of 56% (0.11 g). ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.72 (d, J = 15.6, 1H), 7.63 (d, J = 9.1, 1H), 6.71 (m, 2H), 6.63 (d, J = 7.0, 1H), 6.48 (s, 1H), 6.08 (d, J = 4.0, 1H), 4.92 (s, 2H), 3.90 (s, 3H), 3.40 (q, J = 7.1, 4H), 1.20 (t, J = 7.1, 6H) ; ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 166.0, 161.3, 154.7, 149.7, 144.8, 130.3, 129.1, 126.0, 122.5, 116.3, 109.1, 104.3, 97.6, 60.1, 57.4, 44.8, 12.4; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{23}NO_4S$ 386.1348; Found 386.1346 $[M+H]^+$.

Compound 2C: Compound 2C was obtained as an orange solid with a yield of 53% (0.12 g). ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.77 (d, J = 15.6, 1H), 7.65 (d, J = 9.1, 1H), 7.19 (dd, J = 5.1, 1.1, 1H), 7.15 (dd, J = 3.6, 1.1, 1H), 6.98 (m, 3H), 6.85 (d, J = 3.7, 1H), 6.59 (d, J = 8.9, 1H), 6.38 (d, J = 1.9, 1H), 4.93 (s, 2H), 3.34 (q, J = 7.1, 4H), 1.16 (t, J = 7.1, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 161.4, 154.8, 150.1, 146.2, 142.6, 137.6, 136.3, 127.8, 127.4, 126.3, 124.3, 124.0, 123.6, 119.5, 115.8, 109.3, 97.3, 57.2, 44.7, 12.4; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{24}H_{23}NO_3S_2$ 438.1119; Found 438.1117 $[M+H]^+$.

Compound 2D: Compound 2D was obtained as an orange solid with a yield of 50% (0.12 g). ^1H NMR (400 MHz, DMSO-d_6) δ (ppm): ^1H NMR (400 MHz, DMSO) δ (ppm): 7.80 (d, J = 15.7, 1H), 7.72 (d, J = 9.3, 1H), 7.10 (d, J = 3.8, 1H), 7.05 (d, J = 3.7, 1H), 7.02 (d, J = 9.6, 1H), 6.99 (d, J = 2.2, 1H), 6.75 (dd, J = 9.2, 2.4, 1H), 6.53 (d, J = 2.4, 1H), 6.32 (d, J = 4.0, 1H), 4.72 (d, J = 5.0, 2H), 3.90 (s, 3H), 3.44 (q, J = 6.8, 4H), 1.13 (t, J = 7.0, 6H); ^{13}C NMR (101 MHz, DMSO-d_6) δ (ppm): 165.5, 160.6, 155.0, 150.4, 148.9, 141.6, 136.4, 128.6, 127.7, 126.0, 123.4, 123.0, 122.6, 121.1, 114.6, 109.7, 108.4, 105.5, 96.8, 60.8, 55.9, 44.5, 12.8; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{25}H_{25}NO_4S_2$ 468.1225; Found 468.1223 $[M+H]^+$.

Compound 2E: Compound 2E was obtained as a yellow solid with a yield of 60% (0.22

g). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.94 (d, J = 15.7 Hz, 1H), 7.59 (d, J = 9.1 Hz, 1H), 7.21 (d, J = 5.1 Hz, 1H), 7.13 (d, J = 15.0 Hz, 1H), 7.02 (s, 1H), 6.99 (d, J = 15.7 Hz, 1H), 6.73 (d, J = 8.1 Hz, 1H) , 6.66 (d, J = 7.5 Hz, 1H) , 6.52 (s, 1H), 4.91 (s, 2H), 3.41 (dd, J = 13.9, 6.8 Hz, 4H), 2.94 (s, 6H), 1.23 (t, J = 7.0 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 163.4, 161.0, 154.7, 150.1, 141.2, 140.2,138.6, 132.0, 128.6, 128.4, 125.7, 124.2, 121.6, 121.2, 118.6, 113.7, 109.3, 108.6, 97.2, 61.1,44.7, 42.6, 12.4; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{26}H_{28}N_2O_3S_2$ 481.1541; Found 481.1543 $[M+H]^+$.

2.4 General procedures for the synthesis of compounds 1A-1E

To a solution of compound 2A (0.20 mmol, 1 eq) in dried dichloromethane (20 mL), p-methoxybenzoic acid (0.3 mmol, 1.5 eq), 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (0.4 mmol, 2 eq) and 4-dimethylamino-pyridine (0.04 mmol, 0.2 eq) were added. The mixture was stirred at room temperature for 3 hours under dark condition. After reaction, the reaction solution was concentrated by rotary evaporation under reduced pressure, and the crude product was purified by column chromatography (silica gel, petroleum ether:dichloromethane (v:v) = 3:1).

Compound 1A: Compound 1A was obtained as a yellow solid with a yield of 88% (86 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.00 (d, J = 8.8 Hz, 2H), 7.94 (d, J = 15.8 Hz, 1H), 7.62 (d, J = 9.1 Hz, 1H), 7.18 (dd, J = 14.9, 10.4 Hz, 2H), 7.09 (d, J = 3.4 Hz, 1H), 7.02 - 6.96 (m, 1H), 6.89 (d, J = 8.8 Hz, 2H), 6.63 (dd, J = 9.1, 2.4 Hz, 1H), 6.52 (d, J = 2.4 Hz, 1H), 5.60 (s, 2H), 3.84 (s, 3H), 3.42 (q, J = 7.1 Hz, 4H), 1.21 (t, J = 7.1 Hz, 6H), ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 165.8, 163.7, 160.8, 154.9, 150.2, 143.7, 141.9, 132.0, 128.1, 127.7, 127.0, 126.1, 124.9, 121.7, 119.9, 117.9, 113.7, 109.3, 108.5, 97.4, 58.4, 55.5, 44.8, 12.5; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{28}H_{27}NO_5S$ 490.1610; Found 490.1687 $[M+H]^+$.

Compound 1B: Compound 1B was obtained as a yellow solid with a yield of 86% (89 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.99 (d, J = 5.0, 2H), 7.79 (d, J = 9.7, 1H), 7.60 (d, J = 9.1, 1H), 6.89 (d, J = 0.5, 2H), 6.84 (d, J = 15.6, 1H), 6.72 (d, J = 3.9, 1H),

6.65 (d, J = 6.7, 1H), 6.54 (s, 1H), 6.08 (d, J = 3.9, 1H), 5.57 (s, 2H), 3.89 (s, 3H), 3.84 (s, 3H), 3.41 (q, J = 7.1, 4H), 1.20 (t, J = 7.1, 6H), ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 166.2, 165.8, 163.6, 160.8, 154.5, 140.7, 131.9, 130.4, 129.4, 126.2, 125.9, 121.7, 116.6, 113.7, 109.5, 104.3, 97.6, 60.1, 58.4, 55.4, 45.0, 26.9, 12.4; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{29}H_{29}NO_6S$ 520.1716; Found 520.1796 $[M+H]^+$.

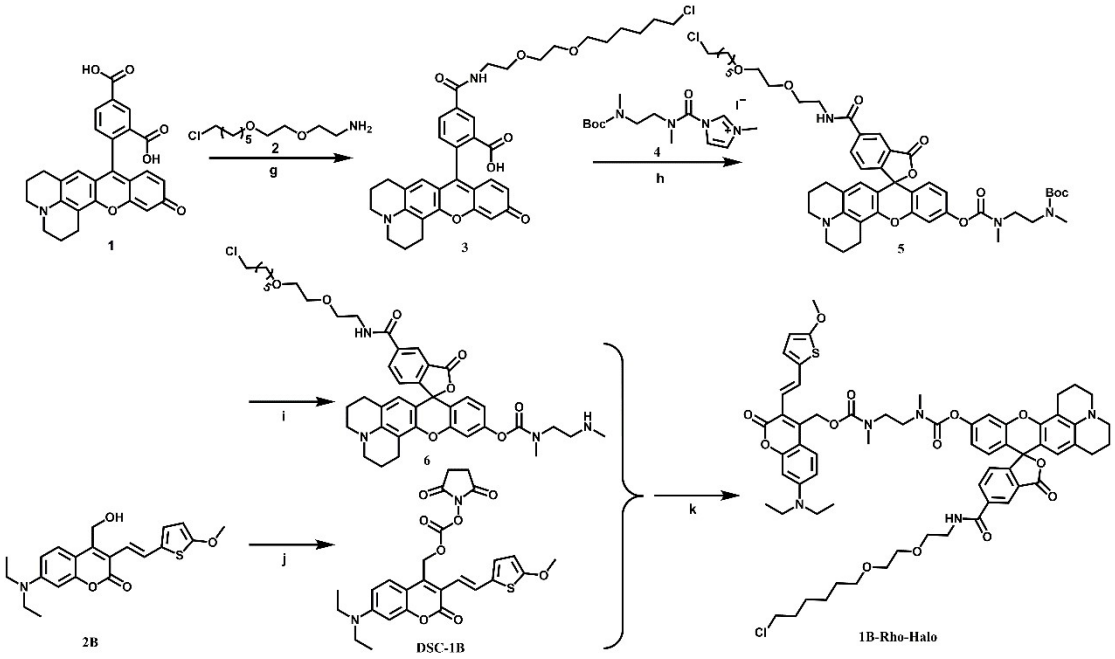
Compound 1C: Compound 1C was obtained as an orange solid with a yield of 89% (0.10 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.01 (d, J = 8.9 Hz, 2H), 7.95 (m, 1H), 7.62 (d, J = 9.2 Hz, 1H), 7.21 (t, J = 5.2 Hz, 1H), 7.17 (d, J = 3.4 Hz, 1H), 7.13 (d, J = 15.7 Hz, 1H), 7.06 (d, J = 3.7 Hz, 1H), 7.03 – 6.95 (m, 2H), 6.89 (d, J = 8.9 Hz, 2H), 6.63 (dd, J = 9.1, 2.3 Hz, 1H), 6.52 (d, J = 2.4 Hz, 1H), 5.61 (s, 2H), 3.83 (s, 3H), 3.41 (q, J = 7.0 Hz, 4H), 1.21 (t, J = 7.1 Hz, 6H), ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 165.9, 163.6, 160.7, 154.9, 150.2, 142.7, 141.9, 137.5, 136.6, 131.9, 128.1, 127.8, 126.1, 124.4, 124.2, 123.7, 121.7, 119.9, 117.6, 113.7, 109.3, 108.5, 97.3, 58.4, 55.5, 44.8, 12.5; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{32}H_{29}NO_5S_2$ 572.1487; Found 572.1564 $[M+H]^+$.

Compound 1D: Compound 1D was obtained as an orange solid with a yield of 83% (0.10 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.01 (d, J = 8.9 Hz, 2H), 7.93 (d, J = 15.6 Hz, 1H), 7.61 (d, J = 9.2 Hz, 1H), 7.07 (m, 1H), 6.94 (d, J = 3.7 Hz, 1H), 6.90 (s, 1H), 6.87 (d, J = 5.0 Hz, 2H), 6.81 (d, J = 3.9 Hz, 1H), 6.62 (dd, J = 9.2, 2.5 Hz, 1H), 6.51 (d, J = 2.4 Hz, 1H), 6.11 (d, J = 4.0 Hz, 1H), 5.60 (s, 2H), 3.90 (s, 3H), 3.83 (s, 3H), 3.41 (q, J = 7.0 Hz, 4H), 1.21 (t, J = 7.1 Hz, 6H), ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 165.8, 165.7, 163.7, 160.8, 154.7, 150.1, 141.6, 141.5, 137.5, 131.9, 128.2, 128.0, 126.0, 123.9, 122.6, 121.7, 121.5, 119.4, 117.8, 113.7, 109.3, 108.6, 104.5, 97.3, 60.3, 58.3, 55.4, 44.7, 12.5; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{33}H_{31}NO_6S_2$ 602.1593; Found 602.1670 $[M+H]^+$.

Compound 1E: Compound 1E was obtained as an orange solid with a yield of 86% (0.16 g).^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.01 (d, J = 8.7 Hz, 2H), 7.92 (d, J = 15.6 Hz, 1H), 7.61 (d, J = 9.1 Hz, 1H), 7.03 (d, J = 15.6 Hz, 1H), 6.96 – 6.86 (m, 4H),

6.80 (d, J = 3.3 Hz, 1H), 6.61 (d, J = 9.1 Hz, 1H), 6.51 (d, J = 1.9 Hz, 1H), 5.78 (d, J = 3.5 Hz, 1H), 5.60 (s, 2H), 3.82 (d, J = 11.4 Hz, 3H), 3.41 (dd, J = 13.9, 6.8 Hz, 4H), 2.94 (s, 6H), 1.21 (t, J = 7.0 Hz, 6H), ^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 166.0, 165.7, 163.7, 160.9, 158.9, 155.8, 154.6, 150.0, 141.1, 140.2, 138.7, 132.0, 128.6, 128.3, 125.9, 124.2, 121.7, 121.2, 118.7, 118.2, 113.8, 109.3, 108.7, 102.7, 97.3, 58.4, 55.4, 44.8, 42.7, 29.7, 12.5; HRMS (ESI) m/z: [M+H]+ Calcd for $C_{34}H_{34}N_2O_5S_2$ 615.1919; Found 615.1990 $[M+H]^+$.

2.5 Procedures for the synthesis of compound 1B-Rho-Halo [2]



Scheme S2. The synthetic routes of the photo-activated fluorescent probe 1B-Rho-Halo. g) PyBOP, TEA, DMF; h) DMAP, DIPEA, MeCN, i) TFA, DCM, j) DSC, DIPEA, DCM; k) DIPEA, DCM.

Compound 3: Compound 1 (0.2 g, 0.44 mmol, 1 eq) was dissolved in DMF (5 ml) under argon. Afterwards, Compound 2 (0.12 g, 0.53 mmol, 1.2 eq), PyBOP (0.46 g, 0.88 mmol, 2 eq), and triethylamine (0.12 ml, 0.88 mmol, 2 eq) were added to the solution. The resulting mixture was stirred at room temperature for 1 hour. After reaction, the reaction solution was poured into water and extracted with ethyl acetate. The organic layer was washed with brine and dried over anhydrous Na_2SO_4. After filtration, the solution was concentrated by rotary evaporation under reduced pressure, and the crude

product was purified by column chromatography (silica gel, dichloromethane: methanol (v:v) = 100 : 1) to receive Compound 3 as a red solid with a yield of 86% (0.25 g). ^{1}H NMR (600 MHz, DMSO-d_6) δ (ppm): 8.30 (d, J = 7.8 Hz, 1H), 7.86 (d, J = 7.2 Hz, 1H), 7.80 (d, J = 7.2 Hz, 1H), 7.13 (s, 1H), 6.77 (d, J = 2.4 Hz, 1H), 6.60 (d, J = 9.0 Hz, 1H), 6.40 (d, J = 9.0 Hz, 1H), 3.62 (t, J = 6.0, 2H), 3.47 (m, 4H), 3.38 (m, 4H), 3.25 (m, 4H), 3.05 (m, 2H), 2.86 (t, J = 3.6 Hz, 2H), 2.76 (t, J = 6.6 Hz, 2H), 1.96 (m, 4H), 1.70 (m, 2H), 1.48 (m, 2H), 1.37 (m, 2H), 1.33 (m, 2H); ^{13}C NMR (101 MHz, DMSO-d_6) δ (ppm): 169.5, 167.8, 167.0, 156.5, 151.6, 147.7, 144.8, 143.3, 134.5, 133.6, 132.9, 129.5, 128.8, 127.7, 126.4, 124.6, 116.4, 115.6, 111.7, 105.7, 70.6, 70.2, 51.5, 44.6, 39.6, 31.5, 28.2, 26.7, 25.1, 23.6, 22.0; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{37}H_{41}N_2O_7Cl$ 661.2530; Found 683.2603 $[M+Na]^+$.

Compound 5: A mixture of compound 3 (0.2 g, 0.30 mmol, 1 eq), compound 4 (0.14g, 0.33 mmol, 1.1 eq), DMAP (10.1 mg, 0.09 mmol, 0.3 eq), and DIPEA (0.16 ml, 0.90 mmol, 3 eq) dissolved in 10 ml acetonitrile was refluxed for 30 min. After reaction, the solution was concentrated by rotary evaporation under reduced pressure, and the crude product was purified by column chromatography (silica gel, dichloromethane) to receive Compound 5 as a red solid with a yield of 89% (0.22 g). ^{1}H NMR (600 MHz, DMSO-d_6) δ (ppm): 8.32 (d, J = 9.0 Hz, 1H), 7.88 (d, J = 7.8 Hz, 1H), 7.82 (d, J = 7.8 Hz, 1H), 7.16 (s, 1H), 6.80 (d, J = 2.4 Hz, 1H), 6.62 (d, J = 8.0 Hz, 1H), 6.42 (d, J = 7.2 Hz, 1H), 3.60 (t, J = 6.6, 2H), 3.49 (m, 4H), 3.36 (m, 4H), 3.25 (m, 10H), 3.08 (t, J = 9.0, 2H), 3.07 (m, 2H), 2.90 (t, J = 6.0 Hz, 2H), 2.79 (t, J = 6.6 Hz, 2H), 2.67 (t, J = 9.0, 2H), 1.96 (m, 4H), 1.72 (m, 2H), 1.52 (m, 2H), 1.43 (s, 9H), 1.34 (m, 2H), 1.30 (m, 2H); ^{13}C NMR (101 MHz, DMSO-d_6) δ (ppm): 169.6, 168.0, 167.4, 156.7, 154.3, 151.8, 149.9, 146.6, 144.1, 136.3, 133.7, 132.4, 129.6, 128.9, 127.6, 126.6, 124.0, 116.0, 115.3, 112.6, 105.9, 79.8, 70.8, 70.3, 54.8, 51.9, 48.6, 44.9, 39.9, 36.0, 31.6, 28.8, 28.2, 26.9, 25.3, 23.7, 22.4; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{47}H_{59}N_4O_{10}Cl$ 876.3920; Found 897.3295 $[M+Na]^+$.

Compound 1B-Rho-Halo: Compound 5 (0.2 g, 0.23 mmol, 1 eq) was dissolved in DMF (5 ml) under argon, and 1 mL of trifluoroacetic acid was then added and stirred for 40 min at room temperature. The reaction solution was concentrated by rotary evaporation

under reduced pressure, and the crude product, Compound 6, was directly used in the next step without further purification. In the next step, a mixture of compound 2B (0.093 g, 0.24 mmol, 1 eq), DSC (0.088g, 0.35 mmol, 1.5 eq), and DIPEA (1.2 ml, 0.69 mmol, 3.0 eq) dissolved in 20 ml DCM was stirred at room temperature for 3 hours. After reaction, the solution was concentrated by rotary evaporation under reduced pressure, and the crude product was purified by flash chromatography (silica gel, 100% DCM) to yield DSC-1B as a yellow solid. Finally, compound DSC-1B was dissolved in 10 ml DCM, and compound 6 and DIPEA (1.2 ml, 0.69 mmol, 3 eq) were then added to the solution. The resulting mixture was stirred at room temperature for 1 hour. After reaction, the solution was concentrated by rotary evaporation under reduced pressure, and the crude product was purified by column chromatography (silica gel, dichloromethane: methanol (v:v) = 100:1) to receive 1B-Rho-Halo as a red solid with a yield of 69% (0.19 g). ^{1}H NMR (600 MHz, DMSO-d_6) δ (ppm): 8.29 (d, J = 7.8 Hz, 1H), 8.02 (d, J = 6.0 Hz, 2H), 7.87 (m, 2H), 7.82 (d, J = 7.8 Hz, 1H), 7.56 (d, J = 6.6 Hz, 1H), 7.36 (d, J = 6.6 Hz,2H), 7.21 (d, J = 16.2 Hz,1H), 7.17 (s, 1H), 6.92 (d, J = 9.0 Hz, 2H), 6.80 (d, J = 2.4 Hz, 1H), 6.70 (d, J = 7.8 Hz, 2H), 6.67 (d, J = 7.2 Hz, 1H), 6.62 (m, 2H), 6.40 (d, J = 9.0 Hz, 1H), 5.57 (s, 2H), 3.86 (s, 3H), 3.60 (t, J = 6.0, 2H), 3.47 (m, 4H), 3.42 (q, J = 7.2 Hz, 4H), 3.36 (m, 4H), 3.25 (m, 10H), 3.09 (t, J = 7.8, 2H), 3.05 (m, 2H), 2.88 (t, J = 7.2 Hz, 2H), 2.77 (t, J = 6.0 Hz, 2H), 2.69 (t, J = 7.8, 2H), 1.98 (m, 4H), 1.70 (m, 2H), 1.50 (m, 2H), 1.41 (s, 9H), 1.36 (m, 2H), 1.32 (m, 2H), 1.20 (t, J = 7.2, 6H); ^{13}C NMR (101 MHz, DMSO-d_6) δ (ppm): 169.8, 167.8, 167.6, 166.0, 161.3,156.5, 154.7, 154.3, 151.6, 149.8, 147.9, 144.8, 144.6, 143.1, 134.3, 133.3, 132.7, 130.3, 129.3, 129.1, 128.6, 127.9, 126.3, 126.0, 124.6, 122.6, 116.3, 116.0, 115.6, 111.6, 109.2, 105.5, 104.3, 97.7, 79.8, 70.6, 70.1, 60.1, 57.4, 54.6, 51.7, 48.4, 44.9, 44.7, 39.6, 36.3, 31.3, 28.6, 28.0, 26.7, 25.1, 23.5, 22.2, 12.5; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{64}H_{72}N_5O_{13}SCl$ 1186.4536; Found 1186.4595 $[M+H]^+$.

3. Photophysical and photochemical properties

3.1 General procedures for monitoring the photolysis process by UV/Vis spectroscopy

The sample was dissolved in a solvent mixture (methanol/water (v:v) = 9:1) and loaded to a 1 cm cuvette. The sample concentration was adjusted to ensure the optical density (OD) value was within the range of 0.5-1. Under ambient conditions, the sample solution (~2.5 ml) was irradiated by a 450 nm LED light with a light intensity of 10 mW/cm^2, and the UV-Vis absorption spectra of the sample solution irradiated at different time intervals were recorded by a UV-Vis spectrometer.

3.2 General procedures for monitoring the photolysis process by HPLC

The sample was dissolved in a solvent mixture (methanol/water (v:v) = 9:1) with a concentration of 2.5×10^{-5} mol/L. The resulting solution (2.5 mL) was loaded to a 1 cm cuvette and irradiated by a 450 nm LED light with an intensity of 10 mW/cm^2 under ambient conditions. For the 1B and 1b solutions, 450 nm LED light of different light intensities (2, 5, and 10 mW/cm^2) was also applied for irradiation. The sample solution was irradiated at different time intervals. At each time, 50 μL of the solution was injected into a reversed-phase HPLC equipped with a BetaBasic-18 column and a 254 nm absorbance detector for analysis. The mobile phase was methanol/water (9:1), and the flow rate was set at 0.5 mL/min.

3.3 General procedures for monitoring the photolysis process by fluorescence spectroscopy

The sample was dissolved in a solvent mixture (methanol/water (v:v) = 9:1) and loaded to a 1 cm cuvette. The sample concentration was diluted to 5 μM. Under ambient conditions, the sample solution (~3 mL) was irradiated by a 450 nm LED light with a light intensity of 10 mW/cm^2, and the fluorescence spectra of the sample solution irradiated at different time intervals were recorded by a fluorescence spectrometer with 384 nm or 476 nm as exciting wavelength.

3.4 General procedures for characterizing compound storage stability by UV-Vis spectroscopy and HPLC.

The sample was dissolved in DMSO to prepare 1 mM stock solutions. The sample concentration was adjusted to ensure the optical density (OD) value was within the

range of 0.5-1 with mixture solution (methanol/water (v:v) = 9:1). The UV-Vis absorption and HPLC spectra of the sample solution at different storage time intervals were recorded by a UV-Vis spectrometer and HPLC. All these experiments were performed in at ambient light conditions.

3.5 Measurements of photochemical quantum yield (Φ_u)[3]

Definition of Φ_u. The photochemical quantum yield (Φ_u) was calculated according to the following equation:

$$\Phi_u = \frac{N_c}{N_{abs}} \quad (1a)$$

where N_c is the number of photons that directly induce the photolysis, and it is also the number of consumed molecules during photolysis, N_{abs} is the total number of photons absorbed by the compound. N_c and N_{abs} are calculated according to the following equations:

$$N_c = kVN_At \quad (1b)$$

$$N_{abs} = \frac{(I_1 - I_2)St}{h\nu} \quad (1c)$$

where k is reaction rate constant, V is the volume of the sample solution, N_A is Avogadro constant, t is the irradiation time, I_1-I_2 (mW/cm^2) is the light intensity absorbed by the sample solution, S is the irradiation area, h is Planck constant, and ν is the light frequency.

Data collection. Sample was dissolved in a mixed solution of methanol/water (9:1), and the OD value was adjusted to 0.3. 2.5 mL solution was moved to a quartz cuvette, irritated with a LED light (450 nm, 1 mW/cm^2) for 5 s, and examined by HPLC. The peak areas of PPG before (A_0) and after (A_t) photolysis in HPLC spectra was calculated. The reaction rate constant (k) was further calculated according to $\ln(A_0 - A_t) = kt$. Thus, Nc can be calculated based on Equation 1b. The light intensities before (I_1) and

after (I_2) passing through the quartz cuvette containing 2.5 mL sample solution was determined by a light intensity meter. Thus, N_{abs} can be calculated based on Equation 1c (n=3).

3.6 Fluorescence quantum yield

Sample solution with an OD value at the maximum absorption wavelength of 0.05 was loaded into a 1 cm quartz cuvette and detected by a Shimadzu UV-2550 spectrophotometer and a Varian Cary Eclipses fluorescence spectrometer, respectively. Fluorescein solution (Φ_R = 0.95 in 0.1 M NaOH) was applied as the reference. The quantum yield (Φ_S) of the sample solution was calculated according to the following equation:

$$\Phi_S = \Phi_R \left[\frac{I_S}{I_R}\right]\left[\frac{A_R}{A_S}\right]\left[\frac{n_S}{n_R}\right]^2$$

where subscripts, S and R, represent the test sample and reference sample, respectively; *I* represents the emission intensity calculated by peak area integration from fluorescent spectra; Φ represents the quantum yield; *A* represents the absorbance intensity at the excitation wavelength; *n* represents the refractive index.

3.7 Luminol chemiluminescence induced photolysis of Compounds 1B, 1a-1b, DEAC

The sample was dissolved in a mixed solution of methanol/water (9:1) with a concentration of 1.0×10^{-5} mol/L. 600 μL of the solution was loaded to a NMR tube using a pipette. The NMR-tube with the sample solution was placed in a 1 cm cuvette which contained 2.5 ml Luminol luminescence solution (purchased from Golden Clone Biotechnology Corp.). 10 μL horseradish peroxidase (HRP) was added to the luminescent solution in cuvette for luminescence, which further induced the photolysis of the sample. After 10 s, the NMR-tube was taken out from the cuvette, and 20 μL sample solution collected from the NMR-tube was injected into a reversed-phase HPLC equipped with a BetaBasic-18 column and a 254 nm detector for analysis. The flow rate was set at 0.5 mL/min, and the mobile phase was methanol/water (9:1). The above procedures were repeated for 10 times, and the photolysis of the sample solution at

different time (0-100 s) was recorded by HPLC.

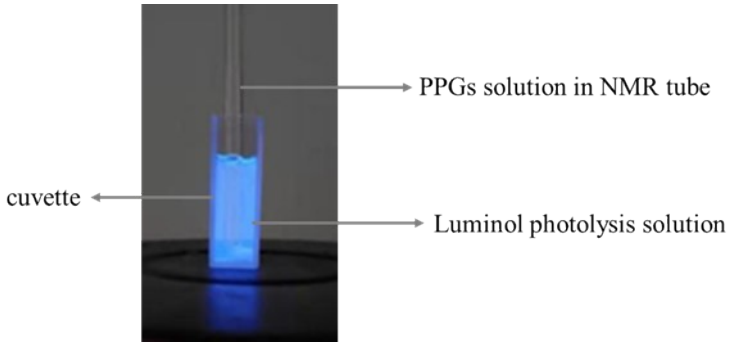


Figure S1. The photolysis reaction of coumarin-based PPGs in Luminol chemiluminescence system.

3.8 Photolysis procedures of compound 1B-Rho-Halo bound to Halo-tag protein

10 μM Halo-tag protein and 2 μM 1B-Rho-Halo in DPBS buffer were incubated for 2 hours. Fluorescence spectra of the solution irradiated by 450 nm LED light (10 mW/cm^2) with different time intervals were recorded by a Varian Cary Eclipses fluorescence spectrometer.

4. DFT Calculations

First-principles calculations were performed to better illustrate the photolysis mechanism. The energy profiles of the photolysis process were determined by density functional theory (DFT) calculations using the Gaussian 09 program package.[4] The structures of the test sample were optimized by the method of B3LYP level with the 6-31G** basis set for all the atoms without symmetry constrains.[5] In addition, the mixed solvent (methanol:water = 9:1) was taken into account by using SMD model[6] in the calculations.

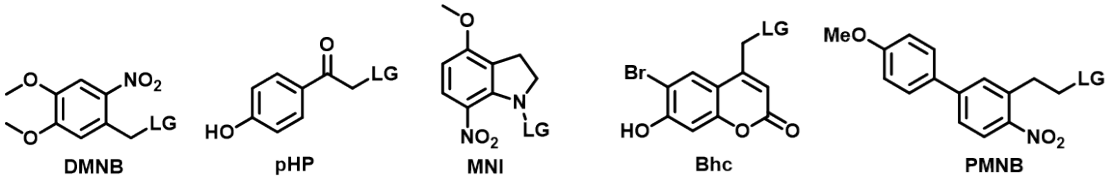
5. Procedures for photoactivation of 1B-Rho-Halo in living cells

Plasmids that can express the fusion Halo-BFP protein (BFP-tag was used for colocalization imaging) were transfected into the nucleus of HEK293T cells and

incubated for 36 hours. A solution of 1B-Rho-Halo in DMSO (1 mM) was prepared and then diluted in DMEM and added in the dish containing transfected HEK293T cells. The concentration of 1B-Rho-Halo in the dish was 2 μM. After incubation for 2 hours, confocal images were taken using a Leica SP8 confocal laser scanning microscope equipped with a HC PL APO CS2×63.0/1.40 OIL objective and HyD detectors. Unless indicated, a 405 nm laser was applied to activate the photo release of 1B-Rho-Halo, while a 561 nm laser was applied to image the nucleus in HEK293T cells. Moreover, a 405 nm laser was used to image the nucleus labeled with BFP-tag for colocalization.

6. Supplementary tables and Figures

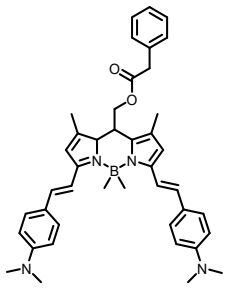
Table S1 Photochemical properties of the PPGs reported in the early studies with the absorption wavelength < 400 nm.



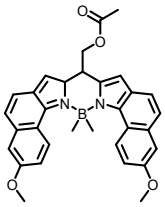
	λ_{max}[a]	ε($M^{-1}cm^{-1}$)	Φ_u	$\varepsilon\Phi_u$ ($M^{-1}cm^{-1}$)	Ref
DMNB	350	2499	0.15	375	[7]
pHP	268	15993	0.086	1375	[8]
MNI	336	4500	0.085	383	[9]
Bhc	375	14600	0.081	1183	[10]
PMNB	317	9900	0.1	990	[11]

[a] Symbols and abbreviations: λ_{max}, absorption maximum (nm); ε_{max}, molar extinction coefficient ($M^{-1}cm^{-1}$); Φ_u, uncaging quantum yield, $\varepsilon_{max}\Phi_u$, uncaging efficiency upon one-photon excitation ($M^{-1}cm^{-1}$).

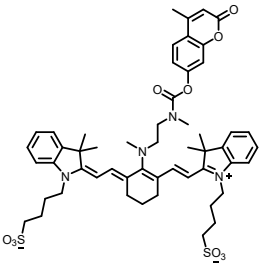
Table S2 Photochemical properties of the reported Bodipy- and Cyanine-based PPGs.



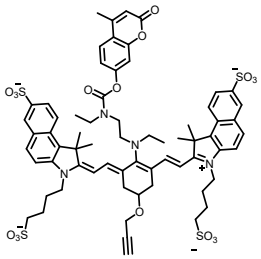
Bodipy 1



Bodipy 2



Cy1

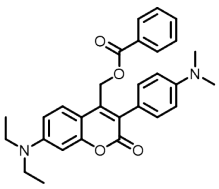


Cy2

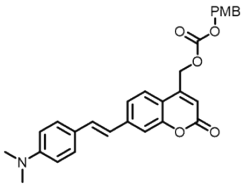
	λ_{max} [a]	ε($M^{-1}cm^{-1}$)	Φ_u	$\varepsilon\Phi_u$ ($M^{-1}cm^{-1}$)	$t_{1/2}$ (min)	Ref
Bodipy 1	689	78000	0.0011	86	/	[12]
Bodipy 2	681	120000	0.038	4560	/	[13]
Cy1	674	52000	/	/	84	[14]
Cy2	732	70000	/	/	90	[15]

[a]Symbols and abbreviations: λ_{max}, absorption maximum (nm); ε_{max}, molar extinction coefficient ($M^{-1}cm^{-1}$); Φ_u, uncaging quantum yield, $\varepsilon_{max}\Phi_u$, uncaging efficiency upon one-photon excitation ($M^{-1}cm^{-1}$). $t_{1/2}$ (min), half-lives of LG release for photolysis process.

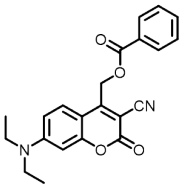
Table S3 Effect of different substitutions on the photochemical properties of coumarin PPGs.



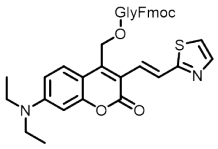
Compound 1



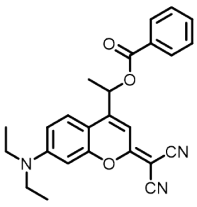
Compound 2



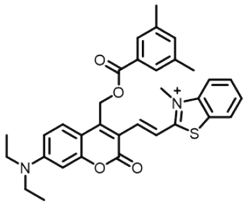
Compound 3



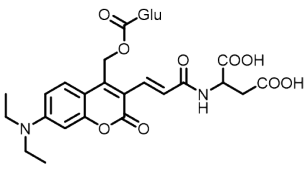
Compound 4



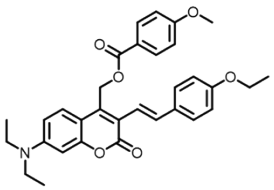
Compound 5



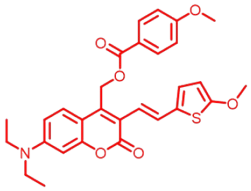
Compound 6



Compound 7 (DEAC450)



Compound 8 (Compound 1b)



Compound 1B (this work)

Name	λ_{max} [nm]	ε_{max} [$\times10^4M^{-1}cm^{-1}$]	Φ_u [%]	$\varepsilon_{max}\Phi_u$ [$M^{-1}cm^{-1}$]	Ref
Compound 1	400	2.9	16	4640	[16]
Compound 2	443	2.6	0.01	2.6	[17]

Compound 3	407	2.9	0.08	23.2	[18]
Compound 4	457	3.6	20	7200	[19]
Compound 5	489	3.2	0.33	106	[20]
Compound 6	538	4	0.14	56	[21]
Compound7	450	4.3	39	16770	[22]
Compound 8	430	3	45	13500	[1]
Compound 1B	**450**	**4.5**	**76**	**34200**	**This work**

[a]Symbols and abbreviations: λ_{max}, absorption maximum (nm); ε_{max}, molar extinction coefficient ($M^{-1}cm^{-1}$); Φ_u, uncaging quantum yield, $\varepsilon_{max}\Phi_u$, uncaging efficiency upon one-photon excitation ($M^{-1}cm^{-1}$).

6. Supplementary Figures

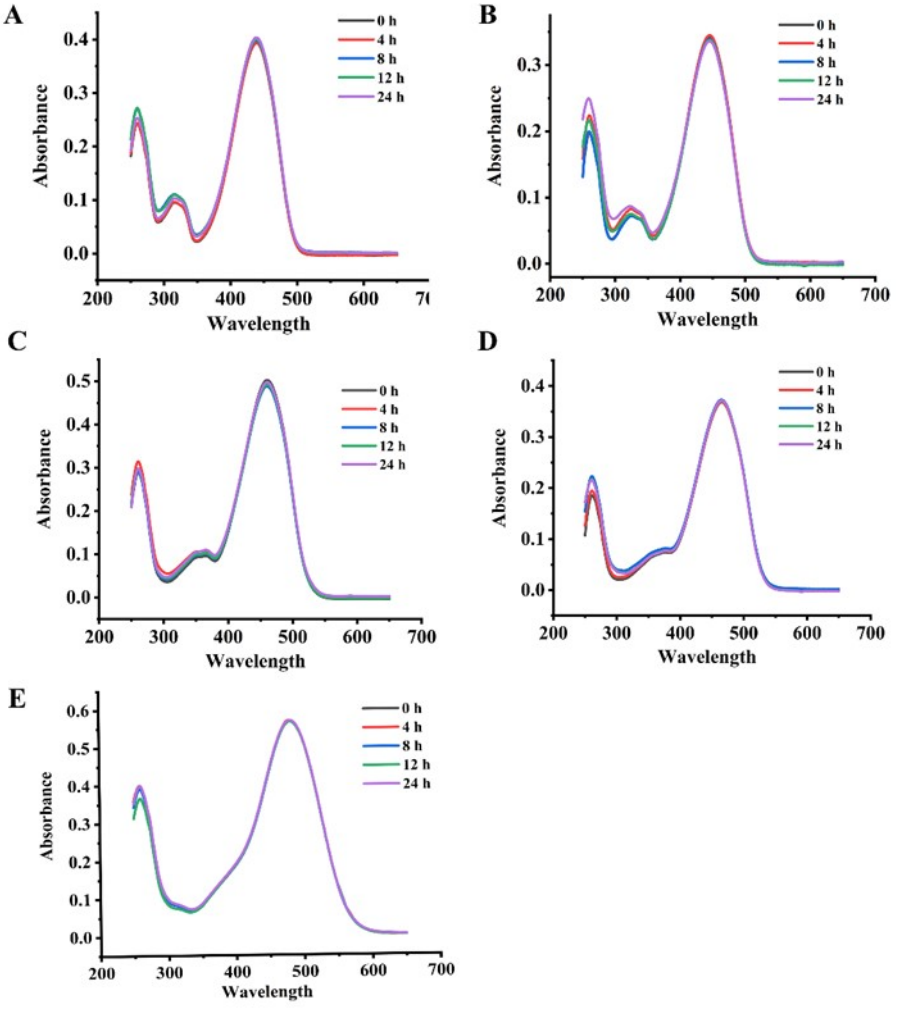


Figure S2. The UV-Vis spectra for compounds with different storage times in at ambient light conditions A) **1A**; B) **1B**; C) **1C**; D) **1D**; E)**1E**.

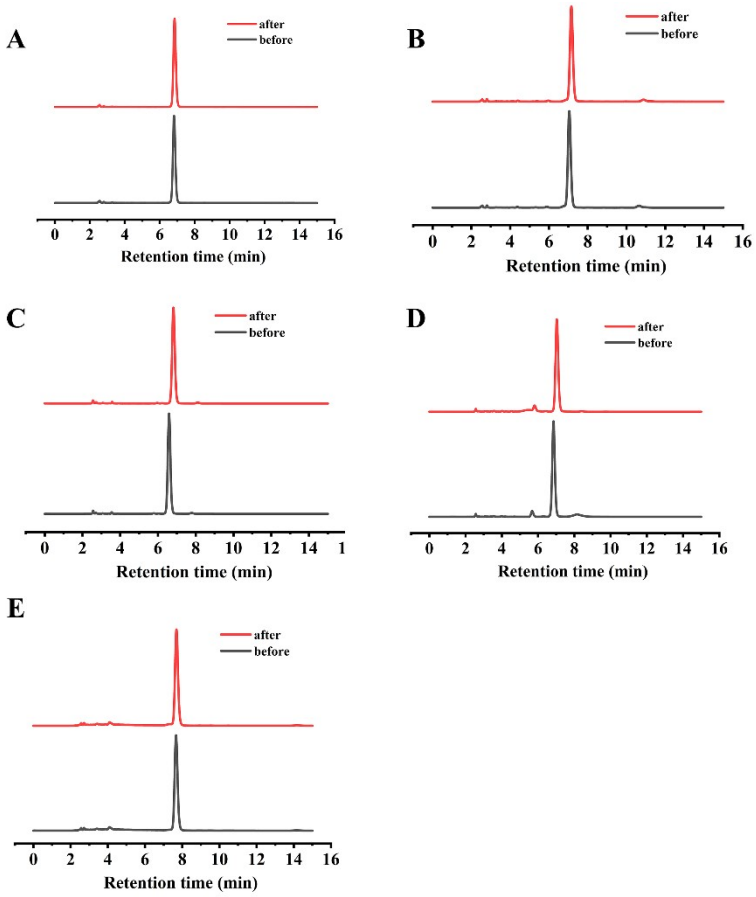


Figure S3. The HPLC spectra of PPG compounds before and after storage under ambient light for 24 h: A) **1A**; B) **1B**; C) **1C**; D) **1D**; E) **1E**.

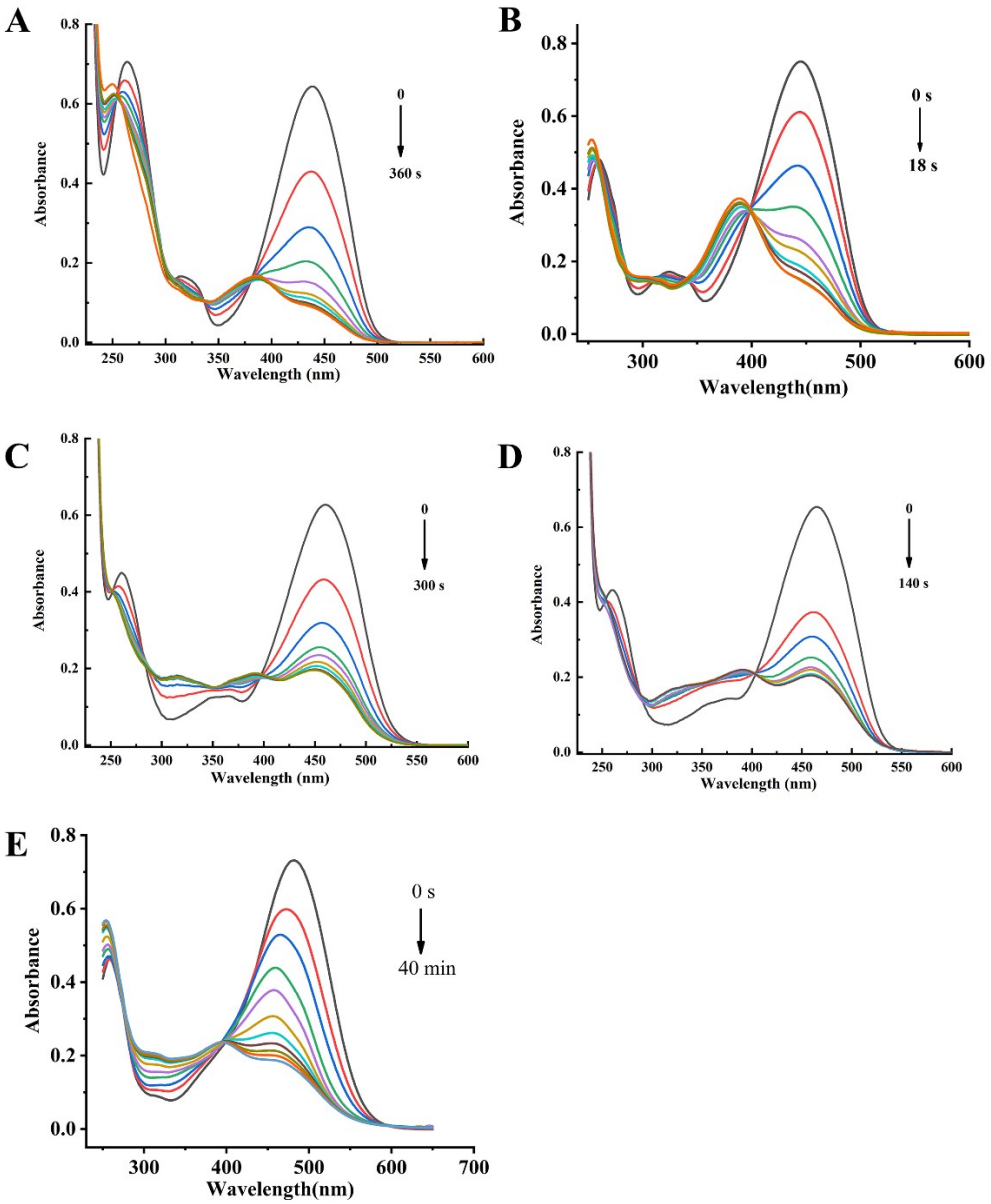


Figure S4. Time course UV-Vis spectra during photolysis for compounds A) **1A**; B) **1B**; C) **1C**; D) **1D** ; E) **1E** in a mixed solution of methanol/water (9:1).

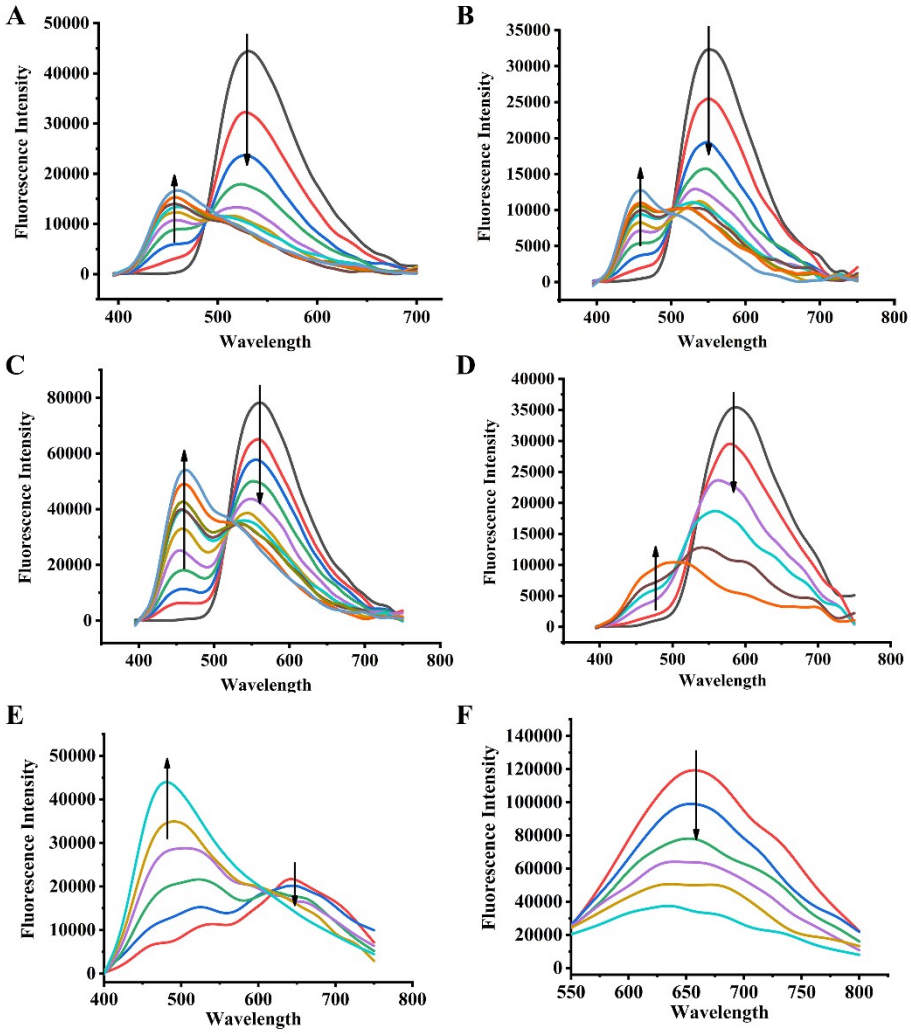


Figure S5. Time course fluorescence spectra during photolysis for compounds with 384 nm as exciting wavelength a) **1A**; b) **1B**; c) **1C**; d) **1D; E)1E** (5 μM) in a mixed solution of methanol/water (9:1). F) Time course fluorescence spectra during photolysis for 1E (5 μM) with 476 nm as exciting wavelength in a mixed solution of methanol/water (9:1).

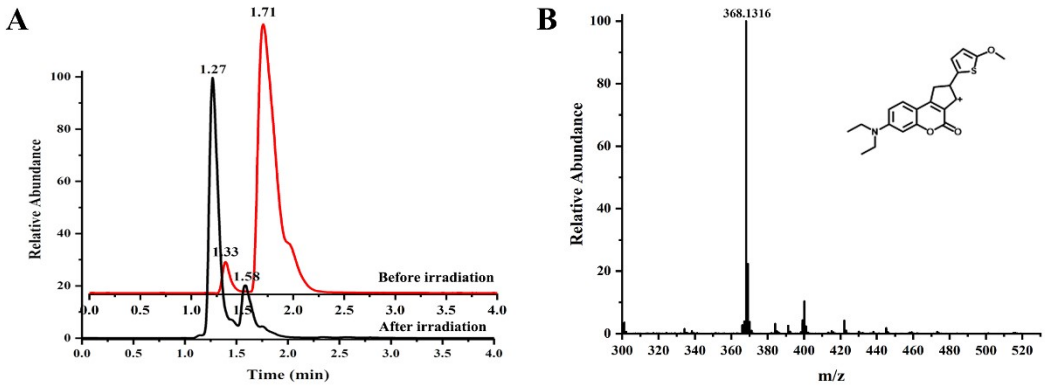


Figure S6. (A) The HPLC-MS spectra of compound 1B before and after irradiation in a mixed solution of methanol/water (9:1) with a light intensity of 10 mW/cm^2. (B) The mass spectrum of the photoproduct after irradiation showing the formation of five-membered ring structure after photolysis.

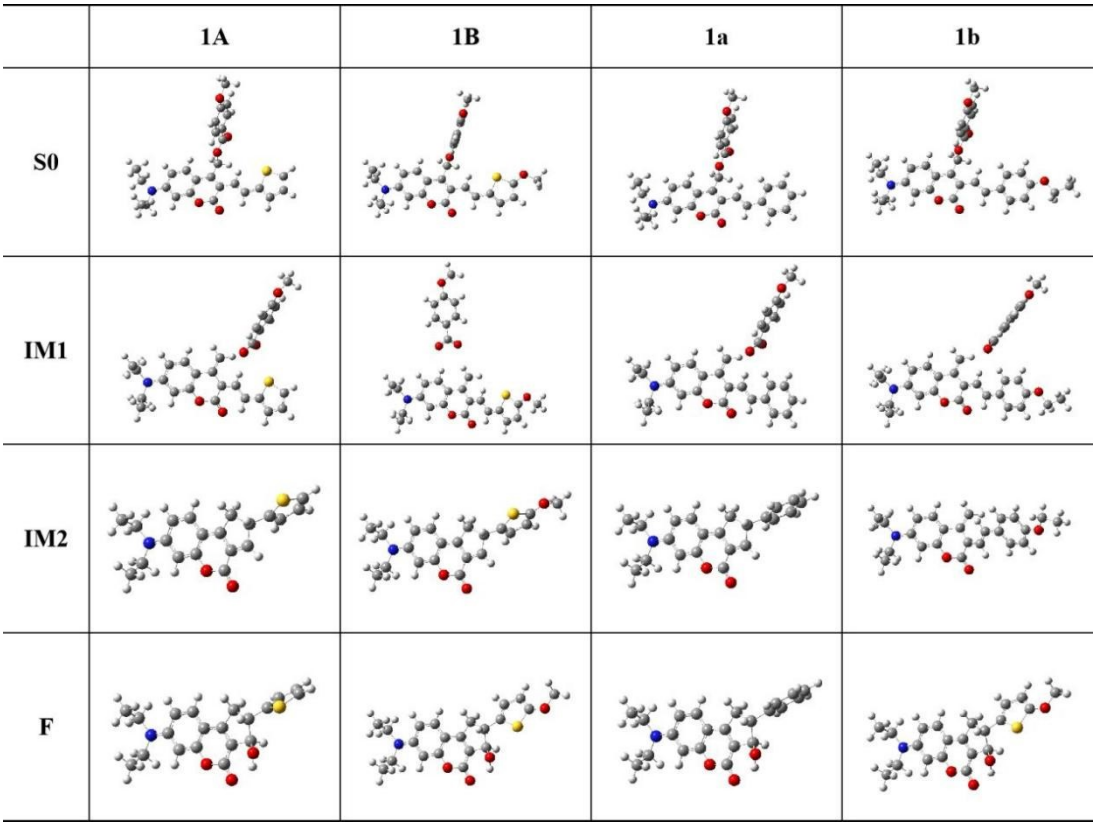


Figure S7. Calculated structures of the key states of compounds 1A, 1B, 1a and 1b.

7. NMR Spectra of compounds 1A-1E

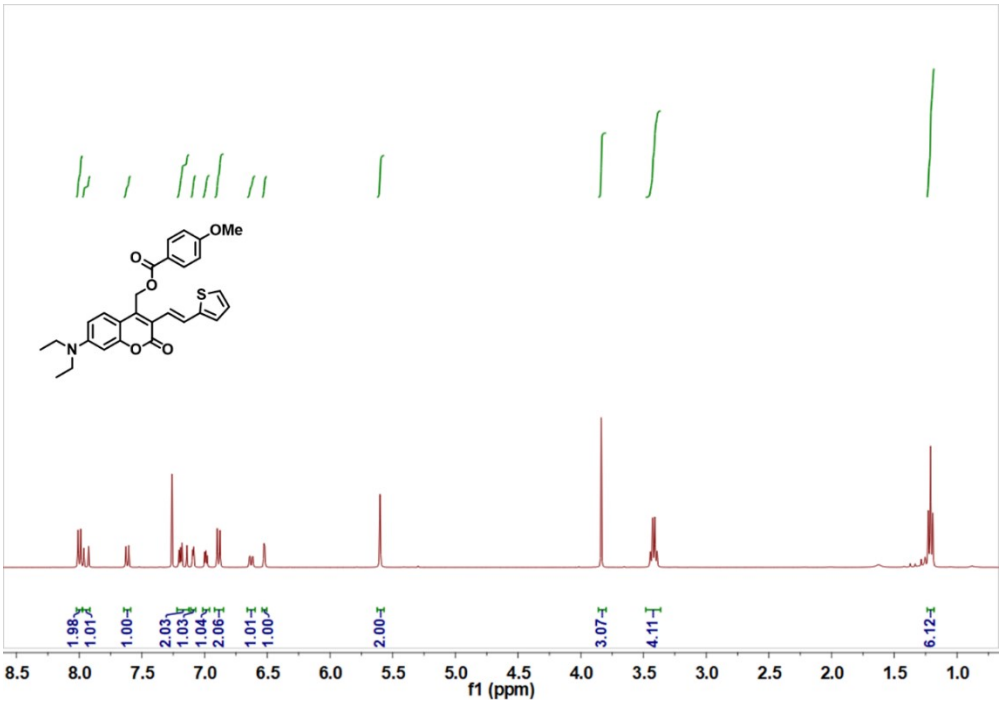


Figure S8. ^{1}H NMR (400 MHz, $CDCl_3$): 1A

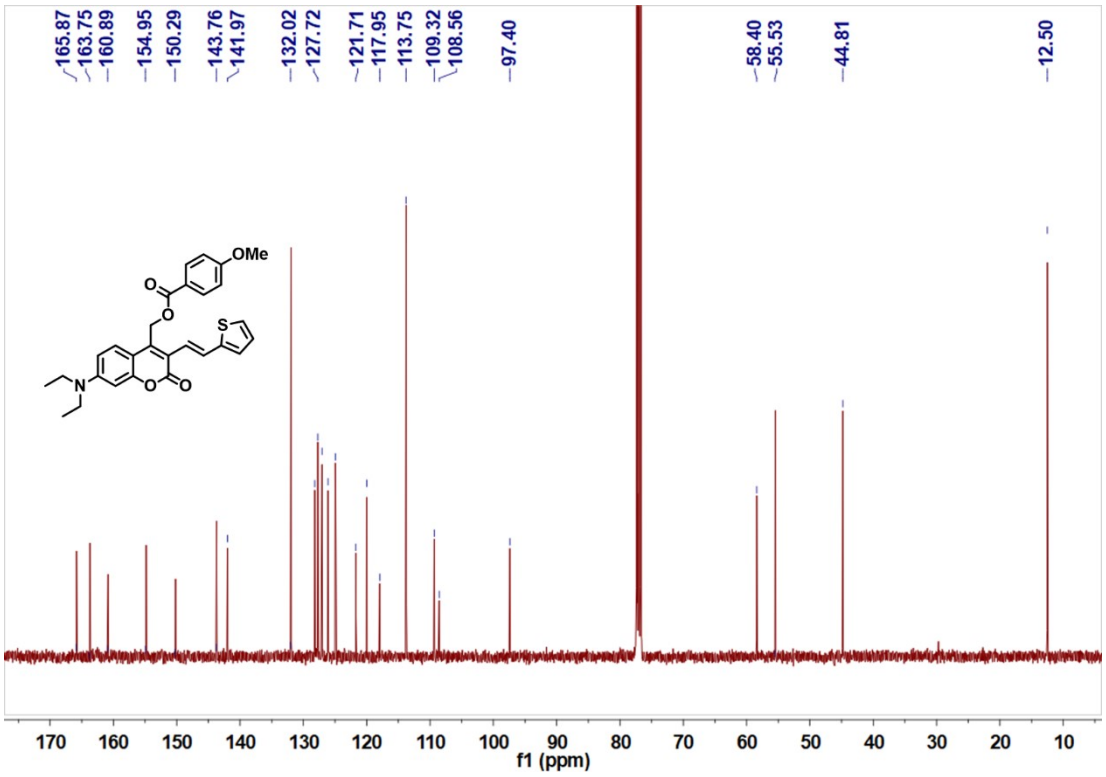


Figure S9. ^{13}C NMR (101 MHz, $CDCl_3$): 1A

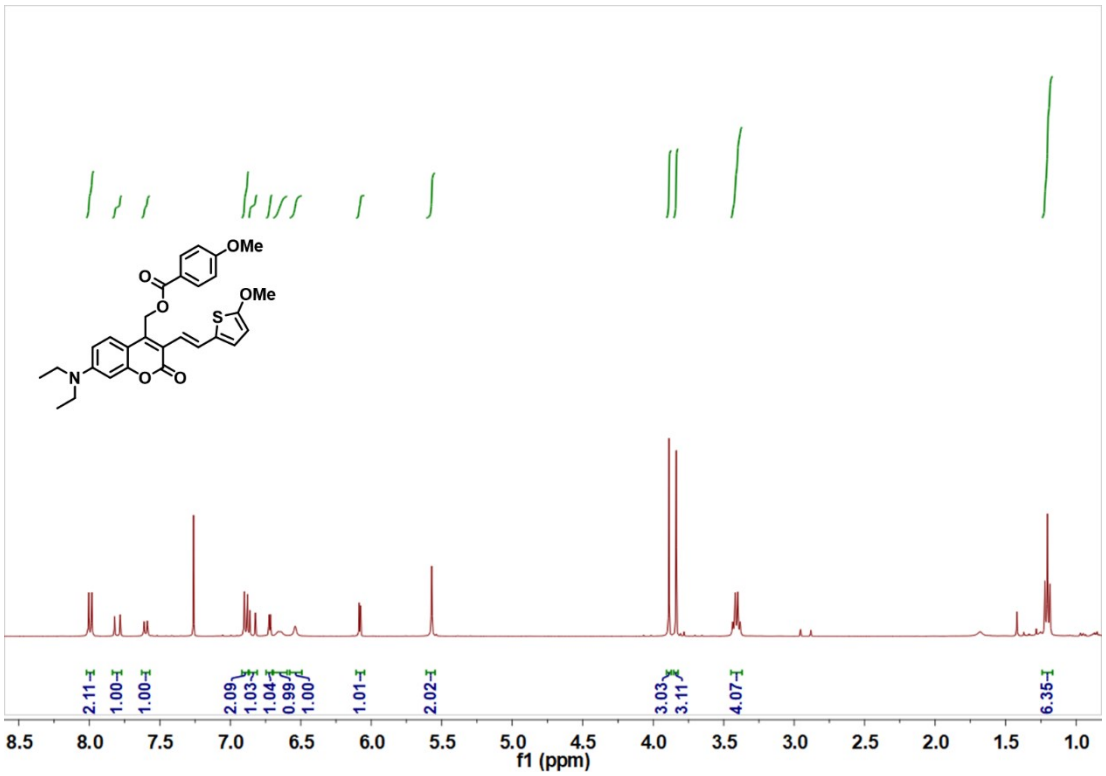


Figure S10. ^{1}H NMR (400 MHz, $CDCl_3$): 1B

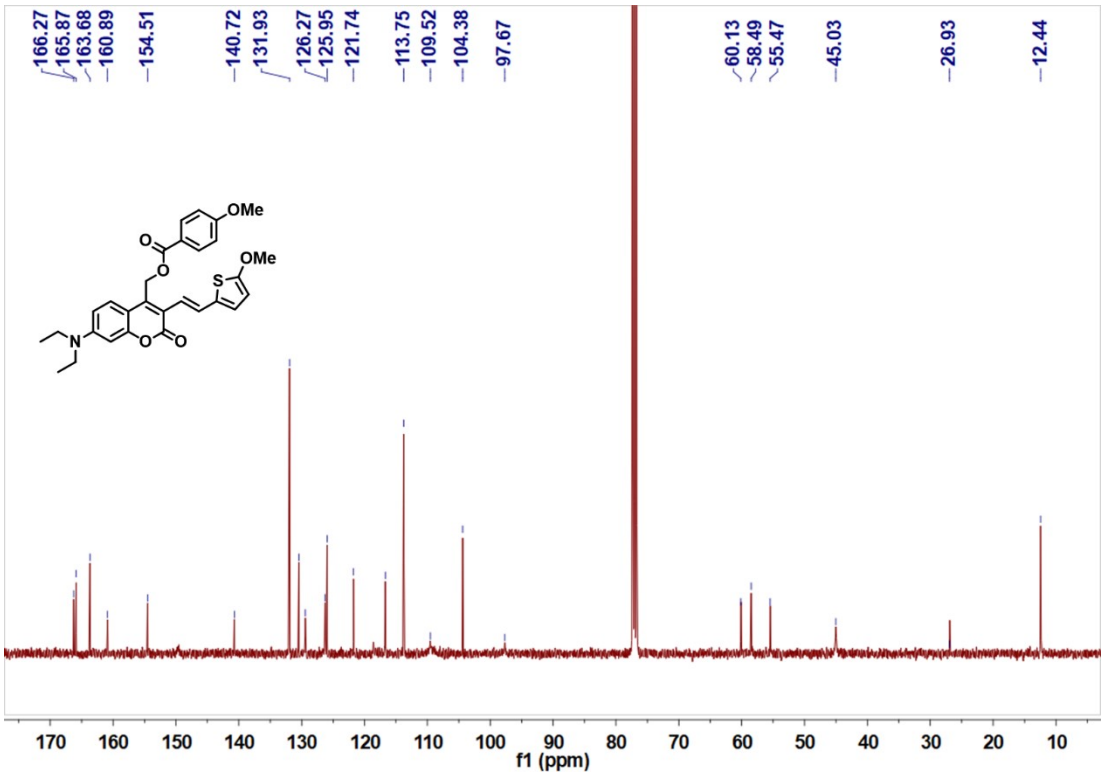


Figure S11. ^{13}C NMR (101 MHz, $CDCl_3$): 1B

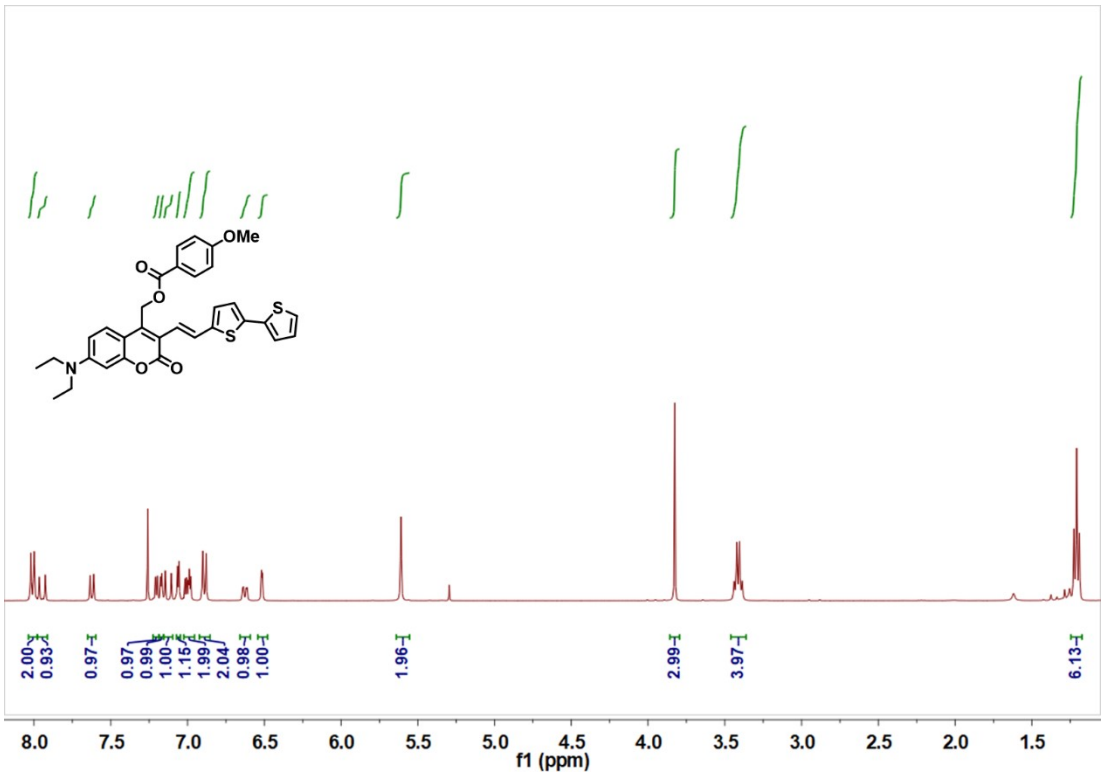


Figure S12. ^{1}H NMR (400 MHz, $CDCl_3$): 1C

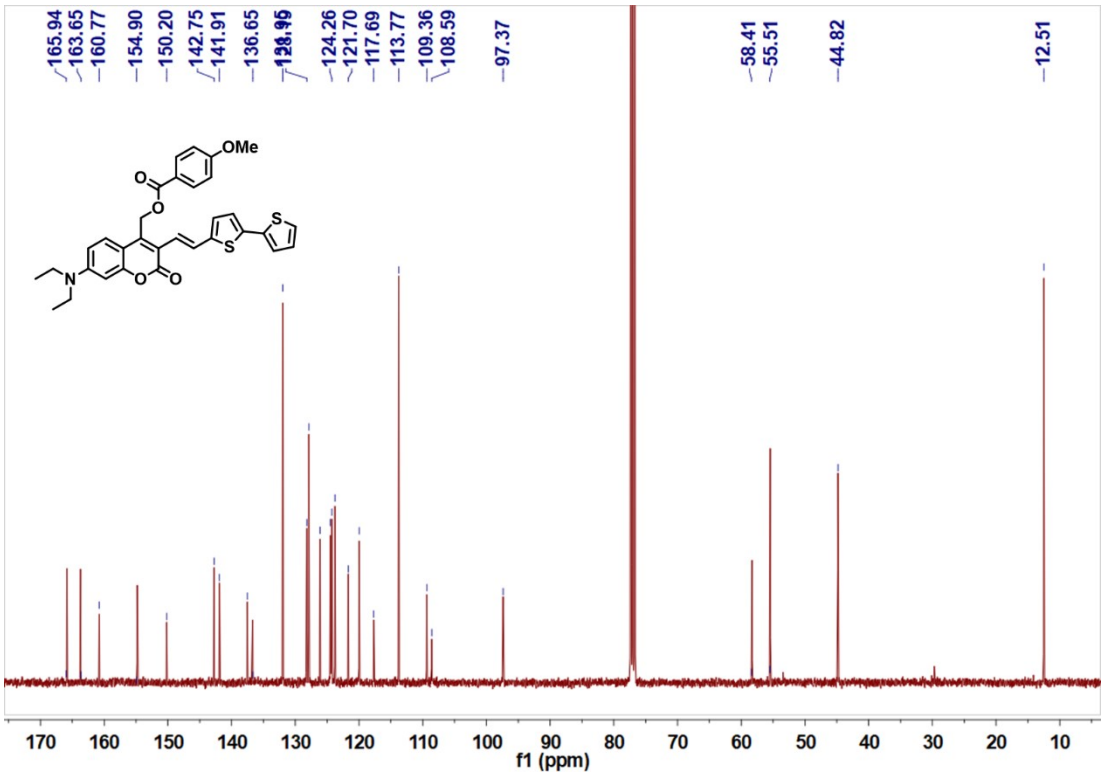


Figure S13. ^{13}C NMR (101 MHz, $CDCl_3$): 1C

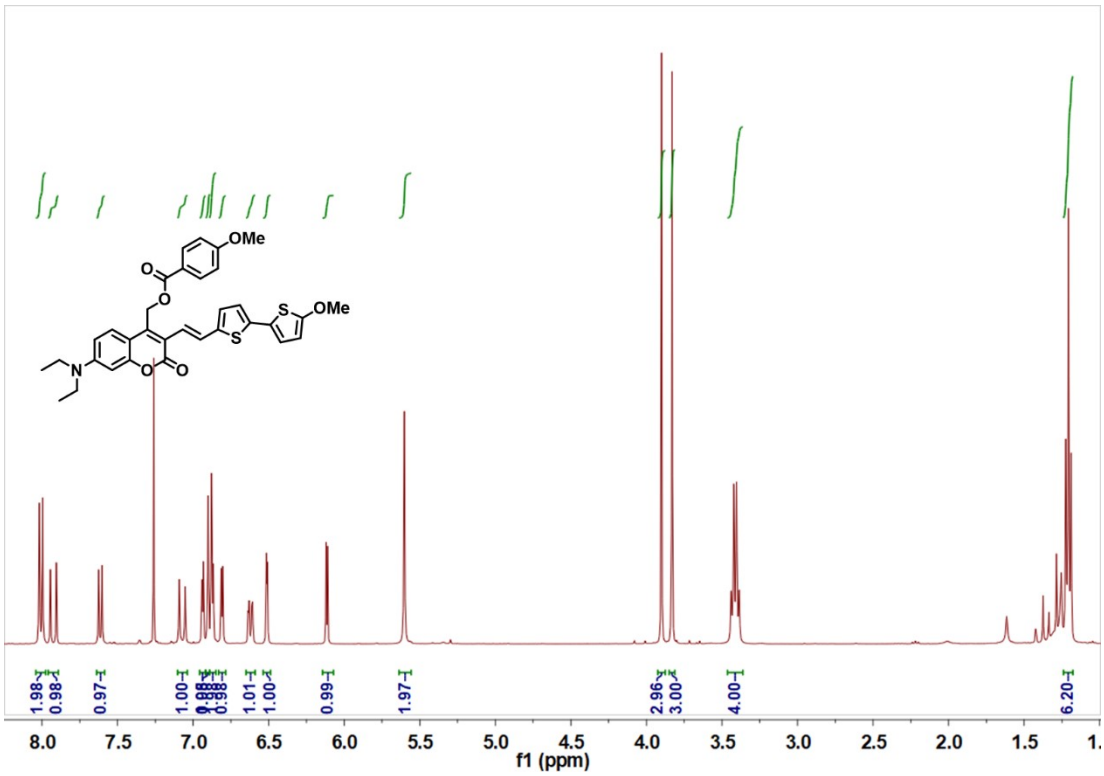


Figure S14. ^{1}H NMR (400 MHz, $CDCl_3$): 1D

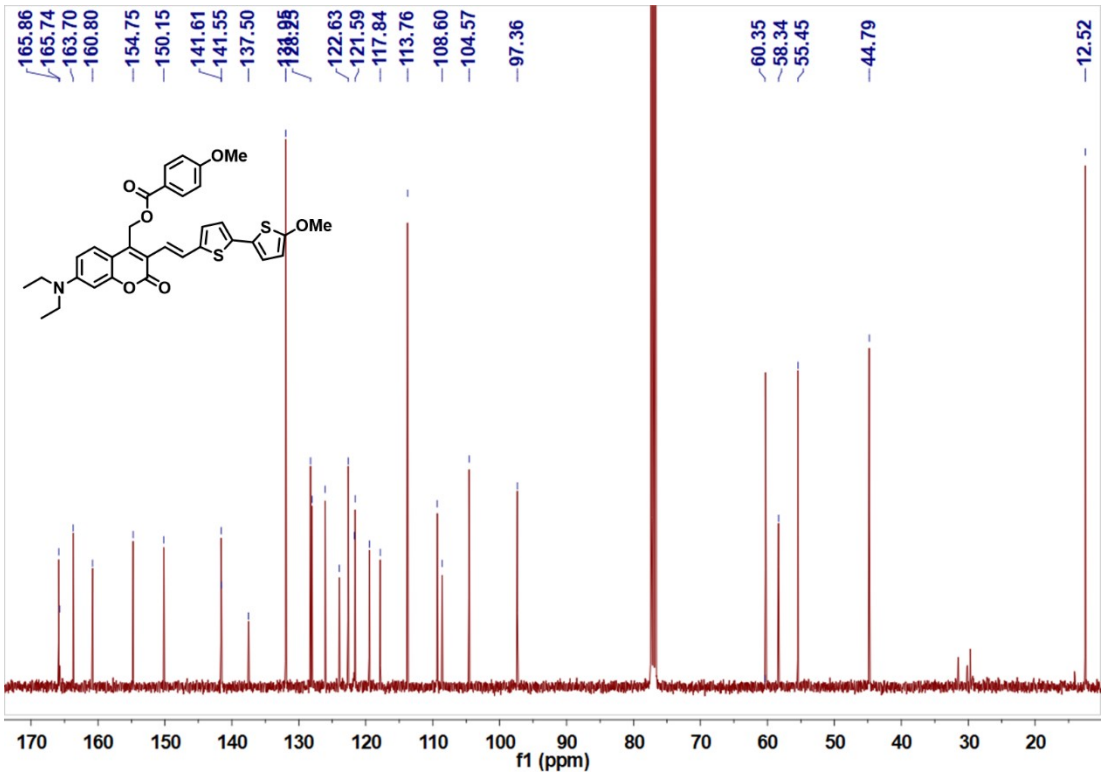


Figure S15. ^{13}C NMR (101 MHz, $CDCl_3$): 1D

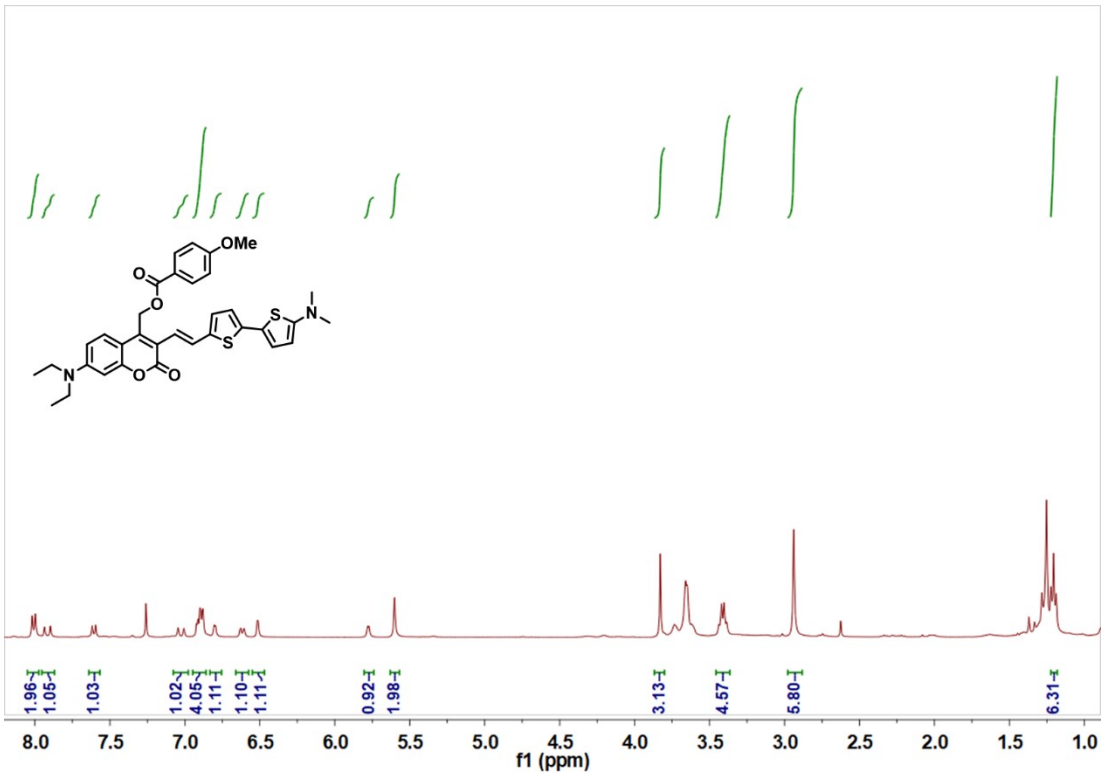


Figure S16. ^{1}H NMR (400 MHz, $CDCl_3$): 1E

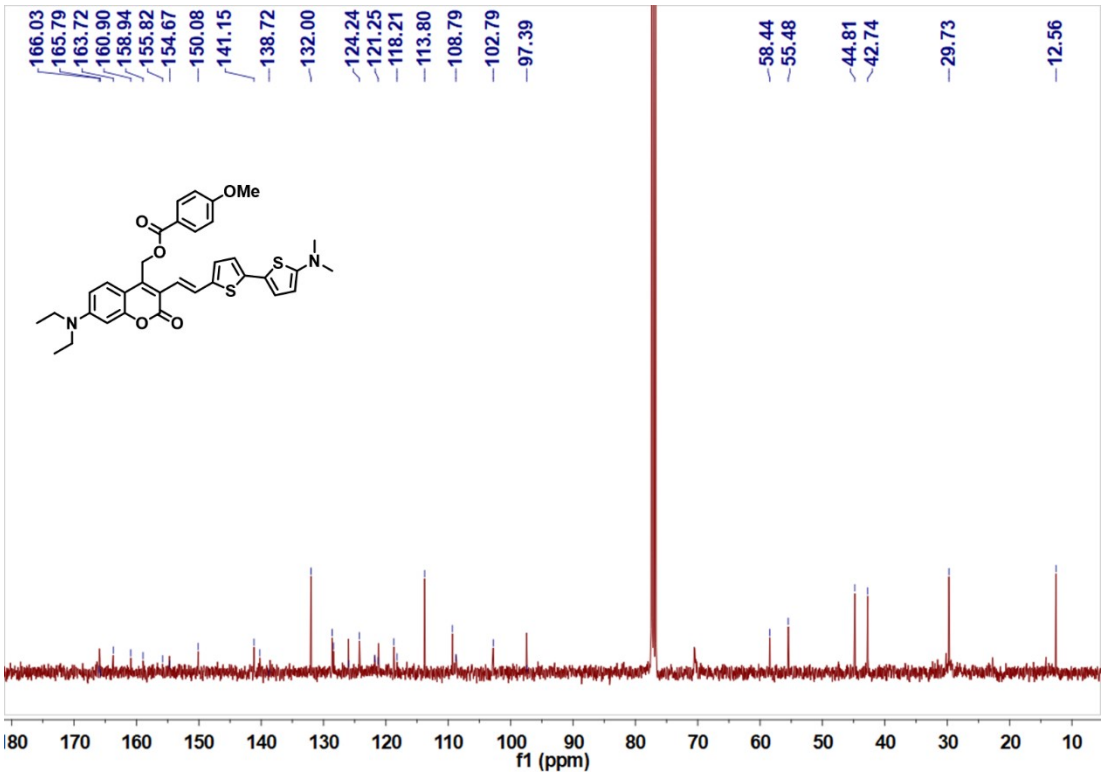


Figure S17. ^{13}C NMR (101 MHz, $CDCl_3$): 1E

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