

Electronic Supplementary Information for

C₆₀-Bodipy Dyads Triplet Photosensitizers as Organic Photocatalysts for Photocatalytic Tandem Oxidation/[3+2] Cycloaddition Reactions to Prepare Pyrrolo[2,1-*a*]isoquinolines

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Experimental Section

General Information:

Fluorescence spectra were recorded on a Shimadzu RF 5301PC spectrofluorometer. UV-Vis absorption spectra were taken on a HP8453 UV-visible spectrophotometer. The nanosecond time-resolved transient difference absorption spectra were detected by Edinburgh LP920 instruments (Edinburgh Instruments, UK). The signal was buffered on a Tektronix TDS 3012B oscilloscope and was analyzed by the LP900 software. All samples in flash photolysis experiments were deaerated with N₂ for ca. 20 min before measurement.

Electrochemical measurement. Cyclic voltammograms of triplet photosensitizers **B-1 – B-2** ($c = 1.0 \times 10^{-3}$ M) were measured at a scan rate of 0.1 V/s in deaerated CH₂Cl₂. Glassy carbon electrode is working electrode, Ag/Ag⁺ electrode is reference electrode, and Pt electrode is supporting electrode. 0.1 M Tetra-*n*-butylammonium hexafluorophosphate(TBAPF₆) was used as the supporting electrolyte. All scans start in the negative. The experiments were deaerated with N₂ for ca. 15 min before measurement and the gas flow is kept during the measurement.

Electron spin resonance (ESR) spectroscopy. ESR spectra were recorded at room temperature using a Bruker ESP-300E spectrometer at 9.8 GHz, X-band, with 100 Hz field modulation. Samples were quantitatively injected into specially made quartz capillaries for ESR analysis in the dark and illuminated directly in the cavity of the ESR spectrometer. Triplet photosensitizers and superoxide radical anion (O₂^{–•}) or singlet oxygen (¹O₂) scavengers (5,5-dimethyl-1-pyrroline-*N*-oxide (DMPO) or 2,2,6,6-tetramethylpiperidine (TEMP)) in air-saturated CH₂Cl₂ was stirred in the dark , then the solution was injected into the quartz capillary. A diode pumped solid state (DPSS) laser (635 nm) irradiate the solution in quartz capillary 100 seconds.

Measurement of the Singlet oxygen quantum yield (Φ_Δ).¹ The ¹O₂ quantum yields (Φ_Δ) of the **B-2** were calculated with methylene blue (MB) at standard ($\Phi_\Delta = 0.57$ in dichloromethane). The

absorbance of the $^1\text{O}_2$ scavenger 1,3-diphenylisobenzofuran (DPBF) was adjusted around 1.0 in air saturated dichloromethane. Then the photosensitizer was added to cuvette and photosensitizer's absorbance was adjusted around 0.2–0.3. The cuvette was irradiated with monochromatic light at the peak absorption wavelength for 10 seconds. Absorbance was measured for several times after each irradiation. The slope of the graph of absorbance maxima of DPBF at 414 nm versus the photoirradiation time for each photosensitizer were calculated. Singlet oxygen quantum yield (Φ_Δ) were calculated according to the equation:¹

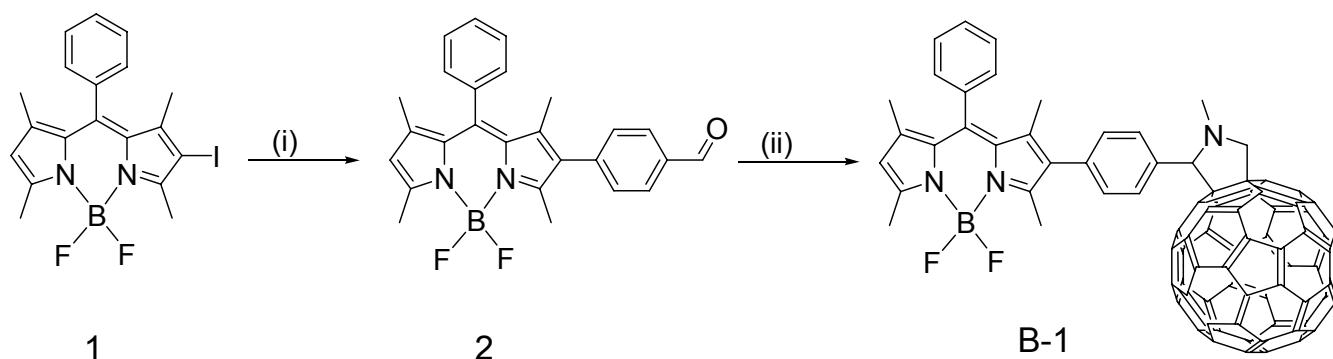
$$\Phi(\text{bod}) = \Phi(\text{ref}) \times \frac{k(\text{bod})}{k(\text{ref})} \times \frac{F(\text{ref})}{F(\text{bod})}$$

where 'bod' and 'ref' designate the "**B-2'** and "MB" respectively. k is the slope of difference in change in absorbance of DPBF (414 nm) with the irradiation time, F is the absorption correction factor, which is given by $F = 1 - 10^{-\text{O.D.}}$ (OD at the irradiation wavelength). The singlet oxygen quantum yield **B-1** were measured with same method, with Bengal rose as the standard ($\Phi_\Delta = 0.80$ in Methanol).

Photocatalytic reactions. The visible-light-induced photocatalytic reactions were carried out as followings, The solution of the triplet photosensitizers (photocatalysts, the substrates) was photoirradiated by using a 35 W xenon lamp (with focusing reflector) through a cut-off filter (0.72 M NaNO₂ aqueous solution, which is transparent for light with wavelength > 385 nm). The reaction was monitored by TLC. After completion of the reaction, the solvent was evaporated under reduced pressure. The residue was purified by column chromatography to give the product as white solid. For the detail reaction conditions, pleaser refer to the following sections.

References

- (1) Cakmak, Y.; Kolemen, S.; Duman, S.; Dede, Y.; Dolen, Y.; Kilic, B.; Kostereli, Z.; Yildirim, L. T. A.; Dogan, L.; Guc, D.; Akkaya, E. U. *Angew. Chem. Int. Ed.* **2011**, *50*, 11937–11941.



Scheme S1. Preparation of the **B-1** and the control compounds. (i) 5 mol% Pd(PPh₃)₄, 3 eq K₂CO₃, in mixed solvent (toluene:ethanol:water, 2/2/1, v/v/v). Refluxed for 8 h. Yield: 85%; (ii) 3.0 eq N-methylglycine, C₆₀, refluxed in toluene for 12 h. 60%.

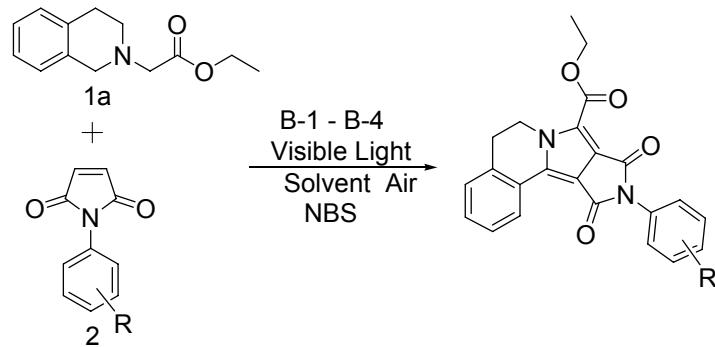
Compound 2. Under Ar atmosphere, Compound **1** (900 mg, 2 mmol), 4-formylphenylboronic acid (900 mg, 6 mmol), anhydrous K₂CO₃ (829 mg, 6 mmol) and 120 mg Pd(PPh₃)₄ were dissolved in mixed solvent of toluene : alcohol : water (2 : 2 : 1, v/v, 50 mL). The mixture was heated at 100 °C for 4 hour. Then the mixture was cooled to rt. The mixture was extract with CH₂Cl₂. The organic layer was dried over anhydrous NaSO₄ and the solvent was evaporated under reduced pressure. The crude product was purified using column chromatography (silica gel, CH₂Cl₂ : petroleum ether = 1:1, v/v) to give **10** as red powder. 738.1 mg, 86.2%. Mp > 250 °C. ¹H NMR (400 MHz, CDCl₃) δ 10.02 (s, 1H), 7.90 (d, 2H, J = 8.0 Hz), 7.51(d, 3H, J = 8.0 Hz), 7.34 (d, 4H, J = 8.0 Hz), 6.05 (s, 1H), 2.60 (s, 3H), 2.54 (s, 3H), 1.40 (s, 3H), 1.31 (s, 3H). TOF HRMS ES⁺: calcd ([C₂₆H₂₃BF₂N₂]⁺) m/z = 428.1872, found m/z = 428.1869.

Preparation of **B-1**.

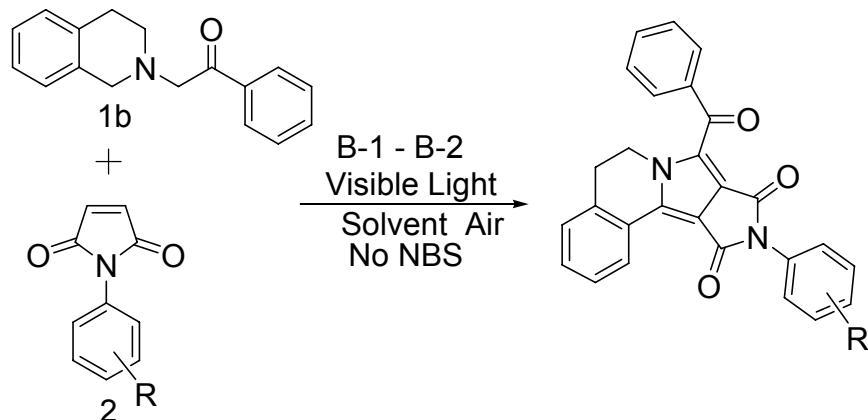
Under Ar atmosphere, compound **2** (95.2 mg, 0.20 mmol), C₆₀ (216.2 mg 0.30mmol) and sarcosine (57mg, 0.25mmol) were suspended in dry toluene (200 mL). The mixture was refluxed for 12 h. After completion of the reaction, the solvent was evaporated under reduced pressure. After removal of the solvent, the residue was purified by column chromatography (silica gel, hexane/CH₂Cl₂ = 1:2, v/v) to give the product of compound **3** as red solid. Yield: 235.4 mg, 72.1% ¹H NMR (400 MHz, CDCl₃) δ =

7.73 (m, 2 H), 7.54–7.45 (m, 4 H), 7.30 (d, 1H, J = 4.0 Hz), 7.20 (d, 2H, J = 8.0 Hz), 5.99 (s, 1 H), 4.99 (s, 1 H), 4.00–3.97 (m, 2 H), 2.86 (s, 3 H), 2.57 (s, 3 H), 2.47 (s, 2 H), 1.37 (s, 3 H), 1.23 (s, 3 H), ppm. HRMS (MALDI): calcd ([C₈₈H₂₈BF₂N₃]⁻) m/z = 1175.2344, found m/z = 1175.2355.

The detail of Oxidation/ [3+2] cycloaddition/ aromatization sequence

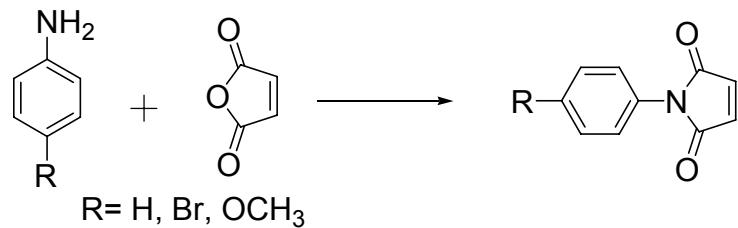


To a dry 10 mL flask were added triplet photosensitizer (1-2 mol%), **1a** (0.6 mmol, 1.2 equiv), **2** (0.5 mmol) and CH₂Cl₂ (5 mL). The reaction mixture was stirred at rt under air atmosphere. The solution was then photoirradiated using a 35 W xenon lamp through a cut off filter (0.72 M NaNO₂ aqueous solution, which is transparent for light > 385 nm). Thin layer chromatography (TLC) was used to monitor the progress of the reaction. After the reaction is completed, 1.2 eqv NBS was added and the mixture was stirred for further 10 min. The solvent was evaporated under reduced pressure. The residue was purified by column chromatography (silica gel, CH₂Cl₂).

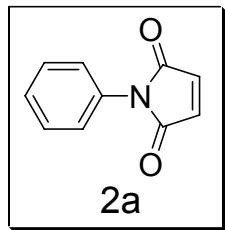


To a dry 10 mL flask were added triplet photosensitizer (1-2 mol%), **1b** (0.6 mmol, 1.2 equiv), **2** (0.5 mmol) and CH₂Cl₂ (5 mL). The reaction mixture was stirred at rt under air atmosphere. The

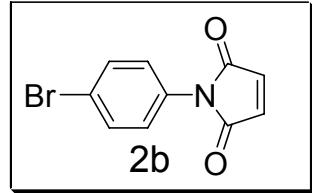
solution was then photoirradiated using a 35 W xenon lamp through a cut off filter (0.72 M NaNO₂ aqueous solution, which is transparent for light > 385 nm). Thin layer chromatography (TLC) was used to monitor the progress of the reaction. After the reaction is completed, the solvent was evaporated under reduced pressure. The mixture was purified by column chromatography (silica gel, CH₂Cl₂).



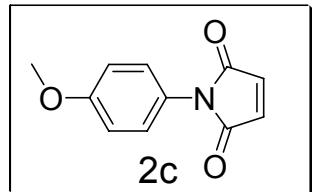
Aniline derivatives (10 mmol) dissolved in THF (20 mL). Maleic anhydride (11 mmol) was dissolved in another portion of THF (20 mL). Maleic anhydride solution was added dropwise into the aniline derivatives THF solution slowly at room temperature. The reaction mixture was stirred for 30 min and a lot of precipitation was produced. The precipitation was collected by filtration. The filtrate was dissolved in 20ml acetic anhydride (20 mL) and sodium acetate (12 mmol) was added. Microwave The mixture was heated at 120°C by microwave irradiation for 30 min. The acetic anhydride solution was poured into water (20 mL), saturated NaOH solution was added to neutralize the mixture. a lot of precipitation appeared and was purified by filtration. The precipitation was purified by column chromatography (silica gel, CH₂Cl₂/petroleum ether = 1/1, v/v).



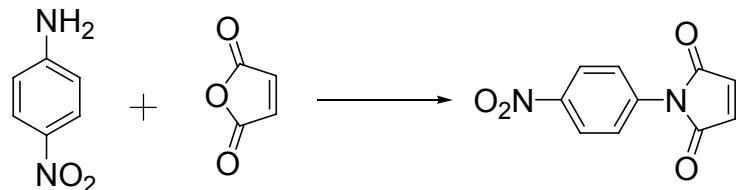
M.p. 82.9–83.2°C. ¹H NMR (400 MHz, CDCl₃) δ = 7.47 (t, J = 7.2 Hz, 2H), 7.37–7.34 (m, 3H), 6.84 (s, 2H). HRMS (ESI⁺): Calcd C₁₀H₇NO₂ [M+H]⁺ m/z = 173.0477. Found m/z = 173.0787.



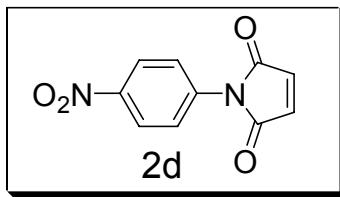
M.p. 121.4–121.8 °C. ^1H NMR (400 MHz, CDCl_3) δ = 7.63 (d, J = 9.2 Hz, 2H), 7.27–7.22 (m, 2H), 6.86 (s, 2H). HRMS (ESI $^+$): Calcd $\text{C}_{10}\text{H}_6\text{NO}_2\text{Br} [\text{M}+\text{H}]^+$ m/z = 251.9766. Found m/z = 251.9739.



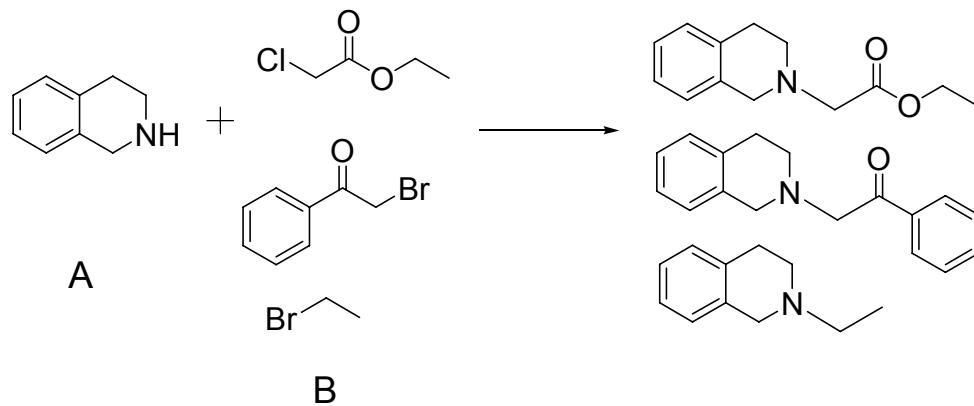
M.p. 147.7–148.2°C. ^1H NMR (400 MHz, CDCl_3) δ = 7.23 (d, J = 4.8 Hz, 2H), 7.00 (d, J = 2.0 Hz, 2H), 6.84 (s, 2H), 3.83 (s, 3H). HRMS (ESI $^+$): Calcd $\text{C}_{11}\text{H}_9\text{NO}_2\text{Na} [\text{M}+\text{Na}]^+$ m/z = 226.0467. Found m/z = 226.0469.



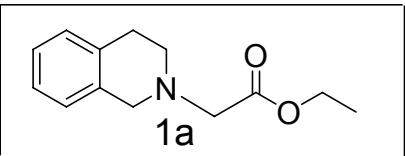
p-nitroaniline (10 mmol) and maleic anhydride (11 mmol) was dissolved in THF (40 mL). The mixture was stirred and refluxed for 6 h, and a lot of precipitation was produced. the precipitation was filtrated. The filtrate was dissolved in acetic anhydride (20 mL) and sodium acetate (12 mmol) was added. The mixture was heated by microwave irradiation at 120°C for 30 min. The mixture was poured into water (20 mL), saturated NaOH solution was added to neutralize the solution. A lot of precipitation appeared and was collected by filtration. The precipitation was purified by column chromatography (silica gel, $\text{CH}_2\text{Cl}_2/\text{petroleum}$ 1/1, v/v).



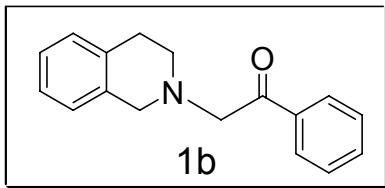
M.p. 170.1–170.7°C. ^1H NMR (400 MHz, CDCl_3) δ = 8.36 (d, J = 9.2 Hz, 2H), 7.68 (d, J = 6.0 Hz, 2H), 6.94 (s, 2H). HRMS (ESI $^+$): Calcd $\text{C}_{10}\text{H}_5\text{N}_2\text{O}_4$ [M-H] $^-$ m/z = 217.0328. Found m/z = 217.0660.



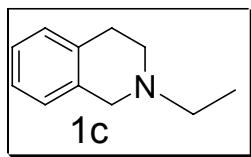
A (10 mmol), **B** (11 mmol) and Na_2CO_3 (20 mmol) were dissolved in THF (50 mL), the mixture was stirred at room temperature for 24 h. After the reaction was completed, the reaction mixture was poured into water (100 mL), and the mixture was extracted with CH_2Cl_2 . The solvent was evaporated under reduced pressure. The crude product was purified by column chromatography (silica gel, CH_2Cl_2).



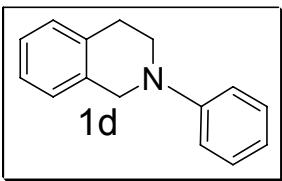
Oily product. ^1H NMR (400 MHz, CDCl_3) δ = 7.08–7.03 (m, 3H), 6.96 (d, J = 5.2 Hz, 1H), 4.20–4.15 (m, 2H), 3.76 (s, 2H), 3.37 (s, 2H), 2.89–2.83 (m, 4H), 1.27–1.23 (m, 3H). HRMS (ESI $^+$): Calcd $\text{C}_{13}\text{H}_{17}\text{NO}_2$ [M+H] $^+$ m/z = 220.1559. Found m/z = 220.1508.



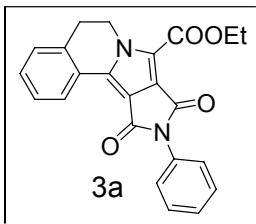
M.P. 60.6–60.8°C. ^1H NMR (400 MHz, CDCl_3) δ = 8.06 (d, J = 7.6 Hz, 2H), 7.58–7.56 (m, 1H), 7.51–7.45 (m, 2H), 7.15 (d, J = 6.8 Hz, 3H), 7.04 (d, J = 6.0 Hz, 1H), 4.12 (s, 2H), 3.95 (s, 2H), 3.04–3.00 (m, 4H). HRMS (ESI $^+$): Calcd $\text{C}_{13}\text{H}_{17}\text{NO}_2$ [M+H] $^+$ m/z = 252.1310. Found m/z = 252.1398.



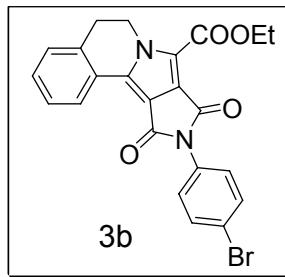
Oily product. ^1H NMR (400 MHz, CDCl_3) δ = 7.12–7.10 (m, 3H), 7.04 (s, 1H), 3.65 (s, 2H), 2.95 –2.92 (m, 2H), 2.77–2.74 (m, 2H), 2.61–2.60 (m, 2H), 1.22–1.19 (m, 3H).



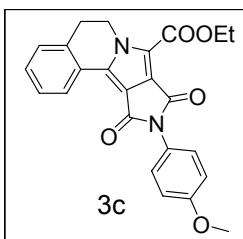
White solid. ^1H NMR (400 MHz, CDCl_3) δ = 7.33–7.32 (m, 4H), 7.22–7.21 (m, 2H), 7.04–7.02 (d, J = 8.0 Hz 2H), 6.96–6.94 (m, 1H), 4.45 (s, 2H), 2.62 –2.59 (m, 2H), 2.03–2.01 (m, 2H).



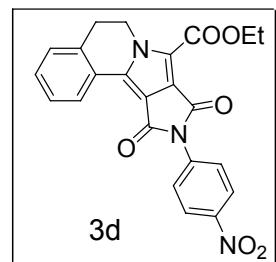
^1H NMR (400 MHz, CDCl_3) δ = 8.60 (d, J = 7.2 Hz, 1H), 7.49 (t, J = 8.0 Hz, 2H), 7.42–7.34 (m, 4H), 7.31 (d, J = 7.2 Hz, 2H), 4.80 (t, J = 6.9 Hz, 2H), 4.47–4.41 (m, 2H), 3.20 (t, J = 6.4 Hz, 2H), 1.47 (t, J = 7.2 Hz, 3H). HRMS (EI $^+$): Calcd $\text{C}_{23}\text{H}_{17}\text{N}_2\text{O}_4$ [M $^+$] m/z = 386.1267. Found m/z = 386.1270.



¹ H NMR (400 MHz, CDCl₃) δ = 8.57 (t, *J* = 6.0 Hz, 1H), 7.62 (d, *J* = 8.8 Hz, 2H), 7.45–7.38 (m, 2H), 7.31 (t, *J* = 4.8 Hz, 2H), 4.80 (t, *J* = 2.8 Hz, 2H), 4.47–4.41 (m, 2H), 3.20 (t, *J* = 7.2 Hz, 2H), 1.49 (t, *J* = 7.2 Hz, 3H).
HRMS (EI⁺): Calcd C₂₃H₁₇N₂O₄Br [M⁺] *m/z* = 464.0372. Found *m/z* = 464.0374.

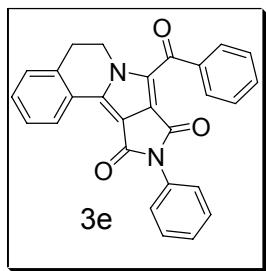


¹ H NMR (400 MHz, CDCl₃) δ = 8.59 (t, *J* = 7.2 Hz, 1H), 7.43–7.36 (m, 2H), 7.29 (t, *J* = 4.0 Hz, 3H), 7.01 (d, *J* = 4.8 Hz, 2H), 4.80 (t, *J* = 6.0 Hz, 2H), 4.46–4.40 (m, 2H), 3.20 (t, *J* = 6.4 Hz, 2H), 1.47 (t, *J* = 7.2 Hz, 3H).
HRMS (EI⁺): Calcd C₂₄H₂₀N₂O₅ [M⁺] *m/z* = 416.1372. Found *m/z* = 416.1373.

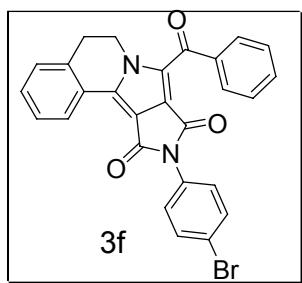


¹ H NMR (400 MHz, CDCl₃) δ = 8.56 (t, *J* = 7.2 Hz, 1H), 8.36 (d, *J* = 9.2 Hz, 1H), 7.72 (d, *J* = 8.8 Hz, 2H), 7.46–7.40 (m, 2H), 7.33 (d, *J* = 7.2 Hz, 1H), 4.80 (t, *J* = 7.2 Hz, 2H), 4.48–4.43 (m, 2H), 3.22 (t, *J* = 6.4 Hz,

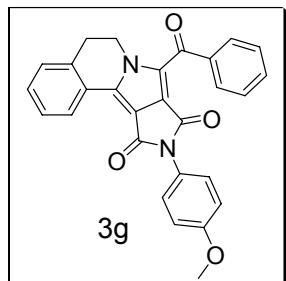
2H), 1.50 (t, $J = 6.8$ Hz, 3H). HRMS (El⁺) Calcd for C₂₃H₁₇N₃O₆ [M⁺] $m/z = 431.1117$. Found $m/z = 431.1126$.



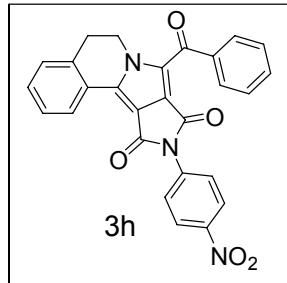
¹ H NMR (400 MHz, CDCl₃) $\delta = 8.15$ (d, $J = 7.6$ Hz, 2H); 8.11 (d, $J = 7.6$ Hz, 1H); 7.64–7.61 (m, 1H); 7.54 (d, $J = 7.8$ Hz, 2H); 7.42 (t, $J = 7.2$ Hz, 2H); 7.22 (d, $J = 7.6$ Hz, 1H); 7.16 (t, $J = 7.6$ Hz, 3H); 7.14 (d, $J = 7.8$ Hz, 2H); 4.06 (d, $J = 6.4$ Hz, 1H); 3.92 (t, $J = 8.0$ Hz, 1H); 2.92–2.87(m, 2H) HRMS (El⁺): Calcd for C₂₃H₁₇N₃O₆ [M⁺] $m/z = 418.1317$; Found $m/z = 418.1315$.



¹ H NMR (400 MHz, CDCl₃) $\delta = 8.14$ (d, $J = 4.0$ Hz, 2H); 8.11 (d, $J = 7.6$ Hz, 1H); 7.65–7.61 (m, 1H); 7.53 (t, $J = 6.4$ Hz, 3H); 7.39 (t, $J = 7.6$ Hz, 1H); 7.22 (d, $J = 7.6$ Hz, 1H); 7.16 (t, $J = 7.6$ Hz, 1H); 7.07 (t, $J = 8.8$ Hz, 2H); 4.05 (d, $J = 8.0$ Hz, 1H); 3.92 (t, $J = 8.4$ Hz, 1H); 2.91–2.88(m, 2H) HRMS (El⁺): Calcd for C₂₇H₁₇N₂O₃Br [M⁺] $m/z = 496.0423$. Found $m/z = 496.0422$.



¹H NMR (400 MHz, CDCl₃) δ = 8.15–8.09 (m, 2H); 7.62–7.52 (m, 1H); 7.52 (d, *J* = 7.6 Hz, 1H); 7.48(t, *J* = 8.0 Hz, 2H); 7.20 (t, *J* = 6.4 Hz, 1H); 7.16 (t, *J* = 7.6 Hz, 1H); 7.07 (t, *J* = 8.6 Hz, 2H); 6.91 (d, *J* = 5.2 Hz, 1H); 6.84 (s, 1H); 4.04 (d, *J* = 8.0 Hz, 1H); 3.92 (t, *J* = 8.4 Hz, 1H); 3.83(s, 3H); 2.91–2.88 (m, 2H) HRMS (El⁺): Calcd for C₂₈H₂₀N₂O₄ [M⁺] *m/z* = 448.1423. Found *m/z* = 448.1434.



¹H NMR (400 MHz, CDCl₃) δ = 8.27 (d, *J* = 8.8 Hz, 1H), 8.14 (d, *J* = 7.6 Hz, 1H), 7.64 (d, *J* = 7.6 Hz, 1H), 7.53 (t, *J* = 7.6 Hz, 2H), 7.43(d, *J* = 8.8 Hz, 2H), 7.38(d, *J* = 8.0 Hz, 1H), 7.22 (t, *J* = 8.8 Hz, 1H), 7.18 (t, *J* = 7.6 Hz, 1H), 7.01 (d, *J* = 7.8 Hz, 1H), 4.11 (d, *J* = 4.2 Hz, 1H), 3.94 (t, *J* = 8.4 Hz, 1H), 2.89–2.81(m, 2H). HRMS (El⁺): Calcd C₂₇H₁₇N₃O₅ [M⁺] *m/z* = 463.1168 Found *m/z* = 463.1164.

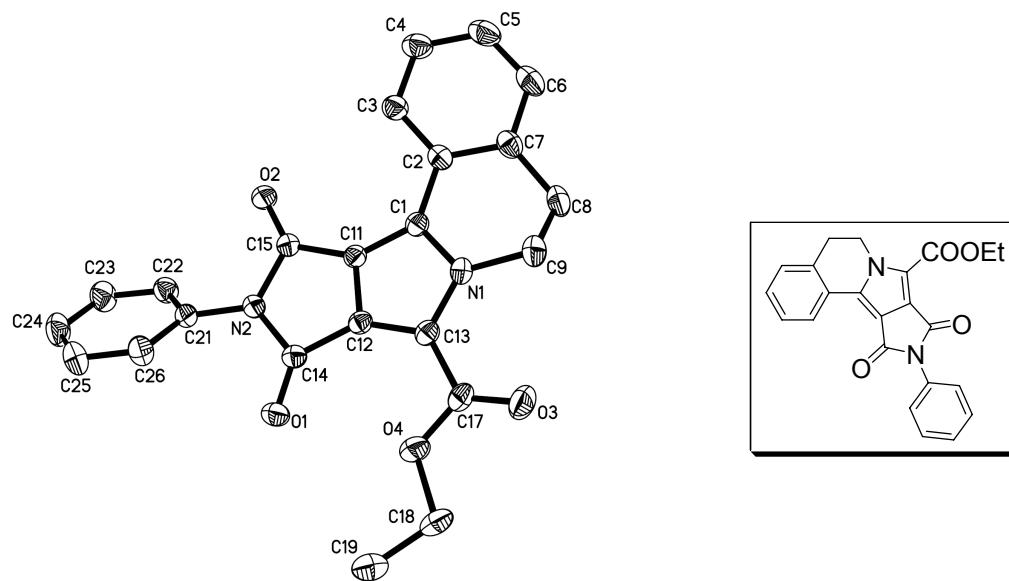


Figure S1. ORTEP view (293 K, 50% probability thermal ellipsoids) of **3a**. Hydrogen atoms are omitted for clarity. Cambridge Crystallographic Data Centre deposition (CCDC) number: 918257.

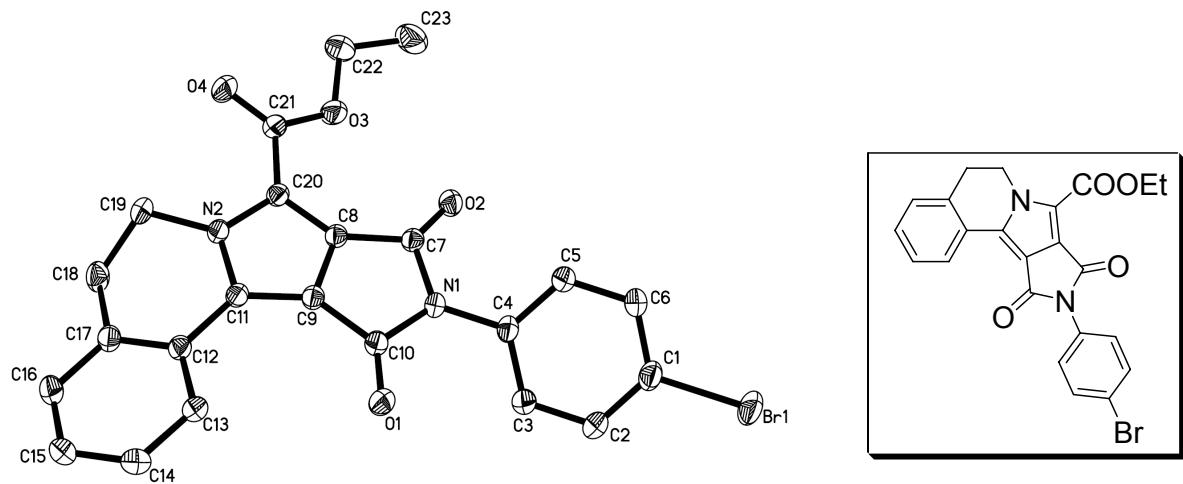


Figure S2. ORTEP view (293 K, 50% probability thermal ellipsoids) of **3b**. Hydrogen atoms are omitted for clarity. Cambridge Crystallographic Data Centre deposition (CCDC) number: 918258.

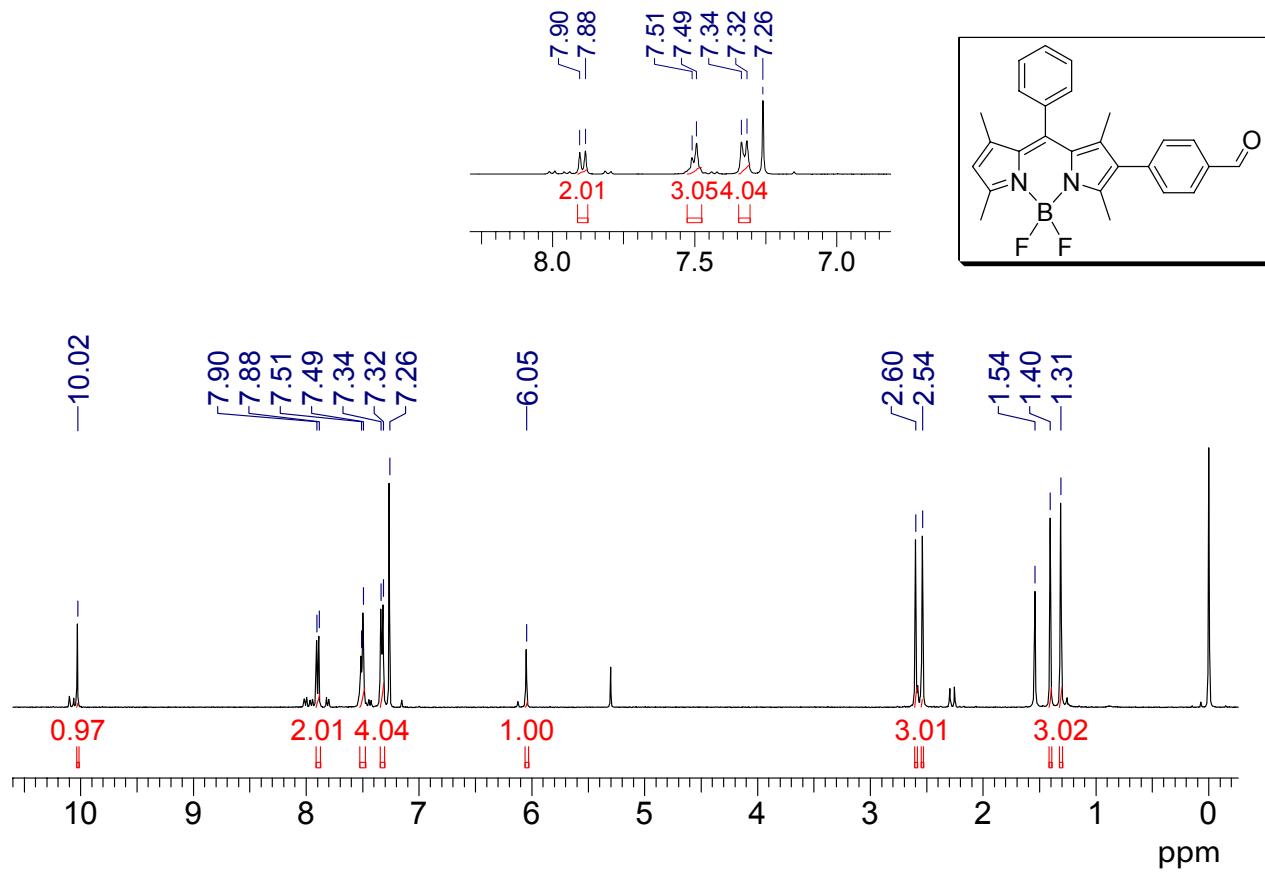


Figure S3. ¹H NMR of **2** in CDCl_3 (400 MHz).

ZCS-2

12071303 12 (0.398) Cn (Cen,4, 50.00, Ht); Sm (SG, 2x3.00); Sb (15,10.00); Cm (12:22)

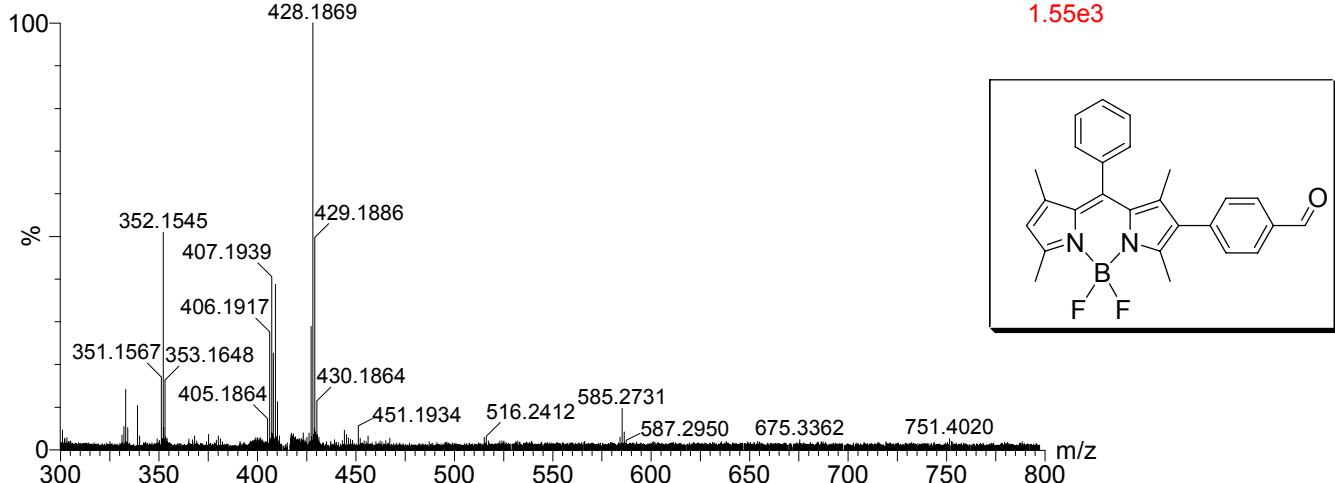


Figure S4. TOF MS EI+ of Compound 2.

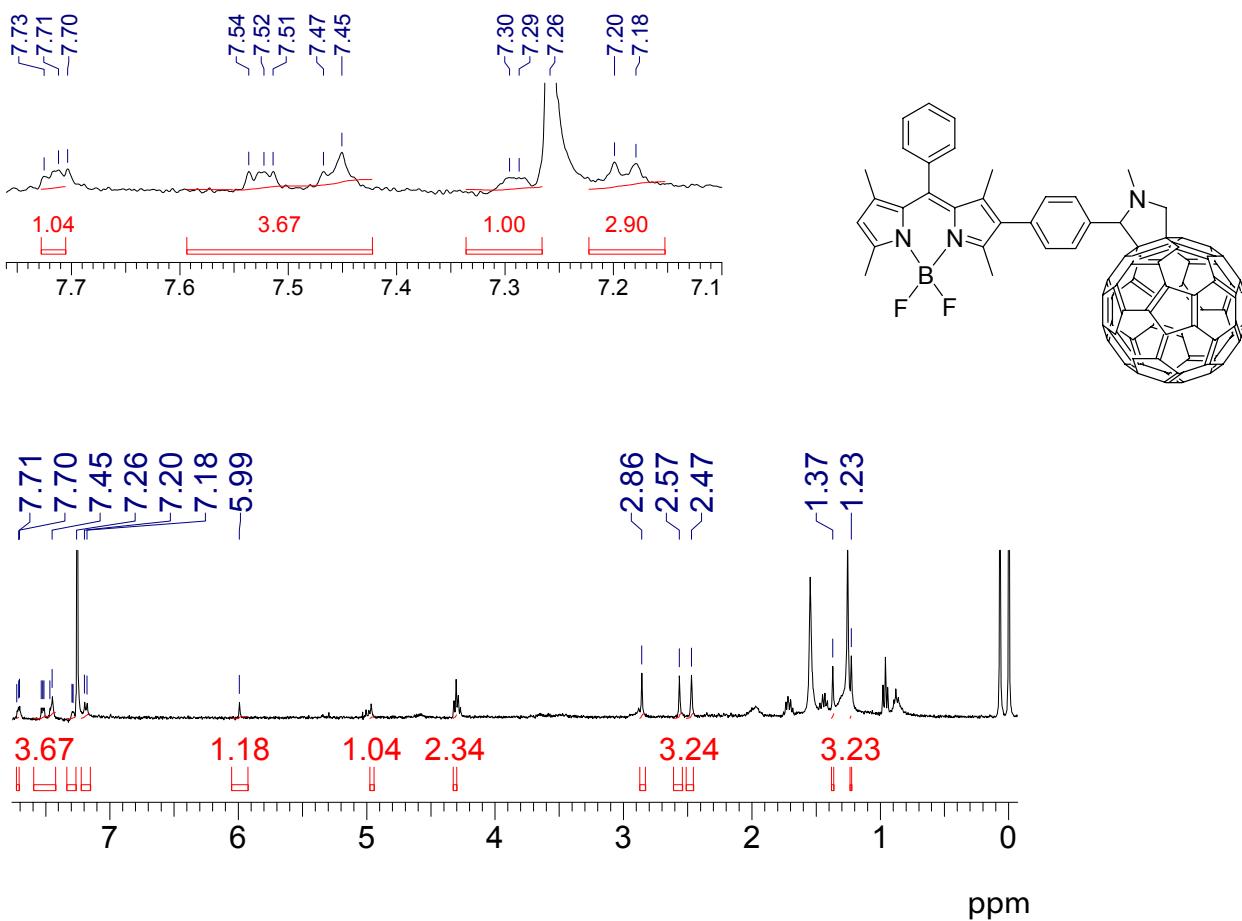


Figure S5. ¹H NMR of B-3 in CDCl₃ (400 MHz).

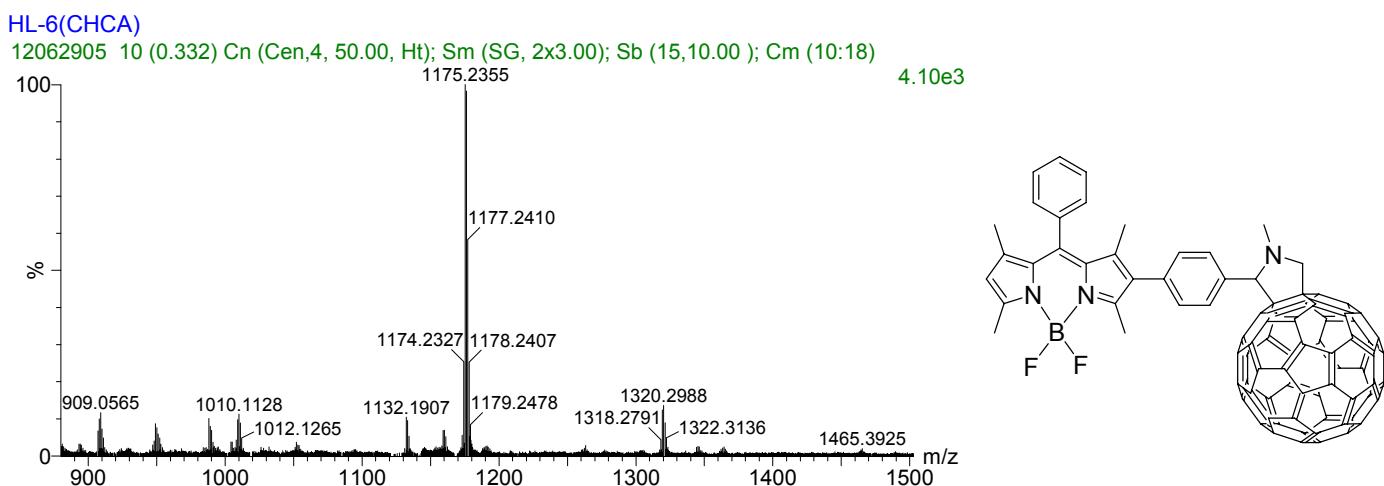


Figure S6. TOF HRMS MALDI of **B-3**.

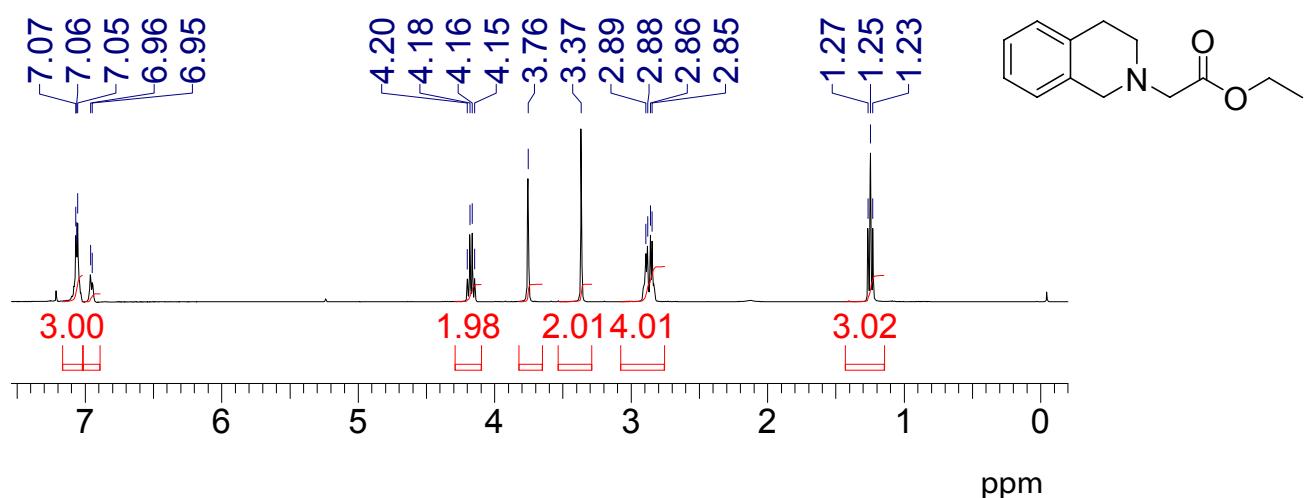


Figure S7. ^1H NMR of **1a** in CDCl_3 (400 MHz).

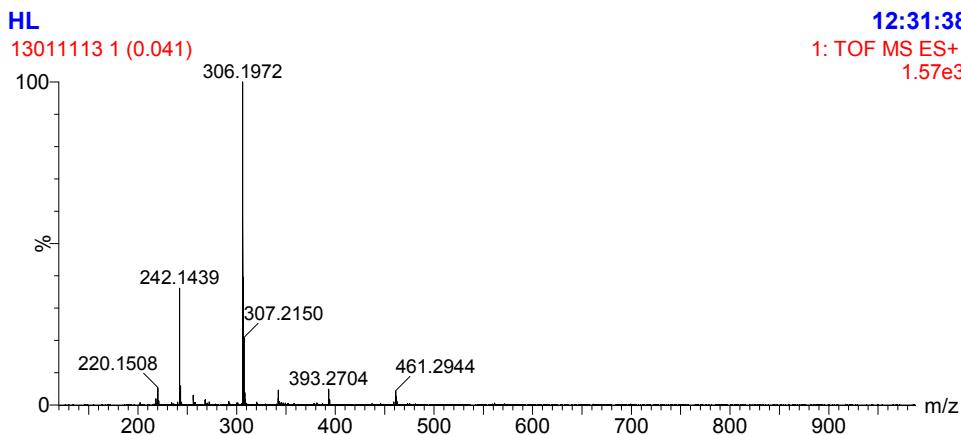


Figure S8. TOF HRMS ESI⁺ of **1a**

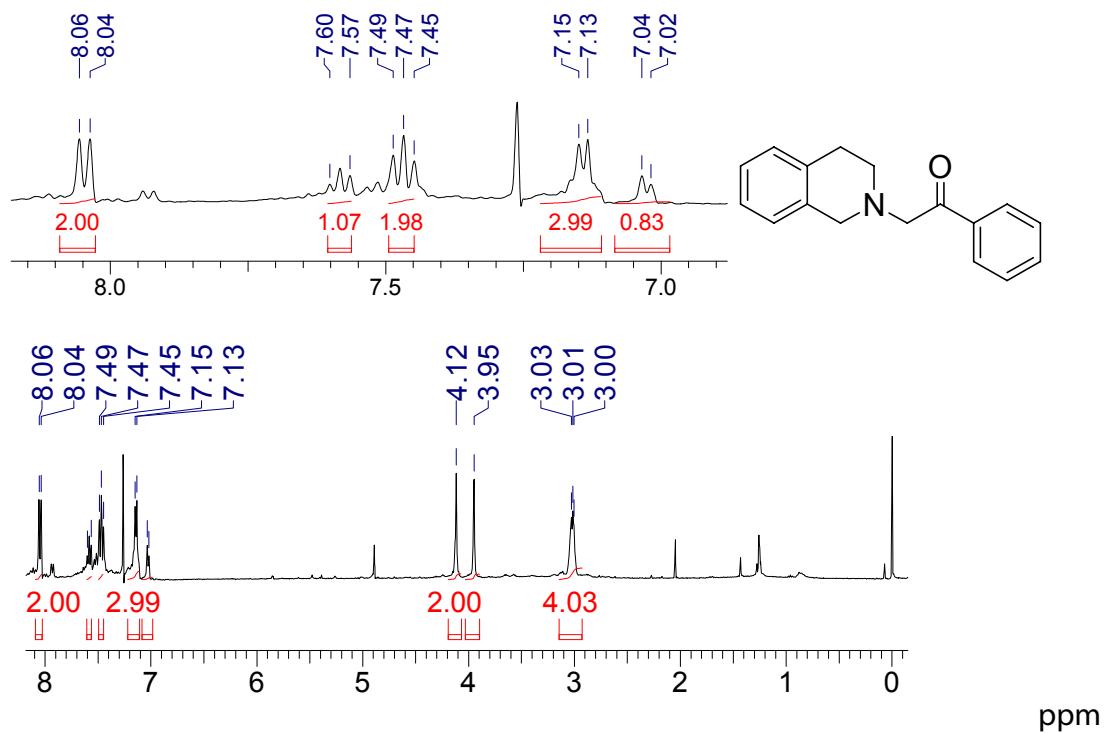


Figure S9. ^1H NMR of **1b** in CDCl_3 (400 MHz).

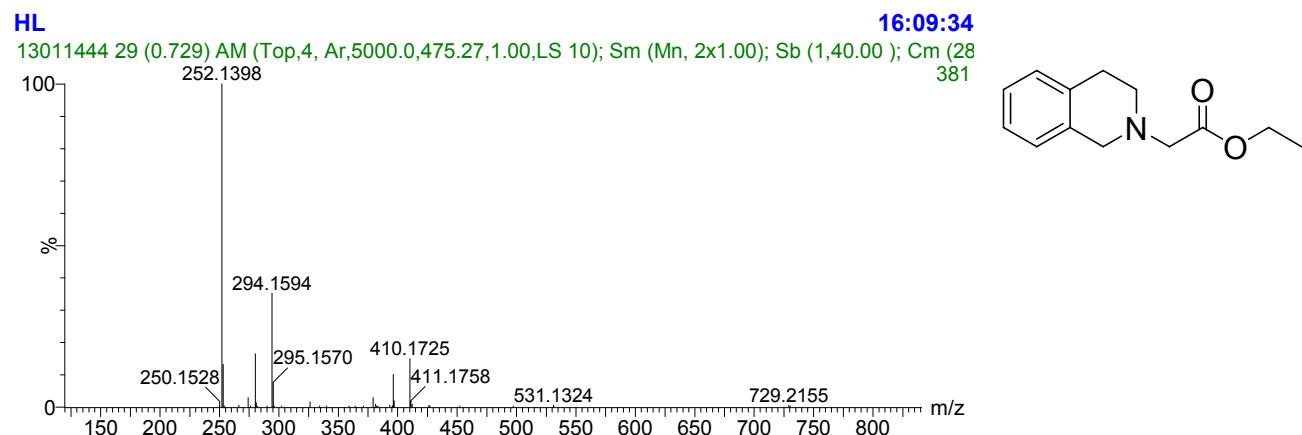


Figure S10. TOF HRMS ESI⁺ of **1b**

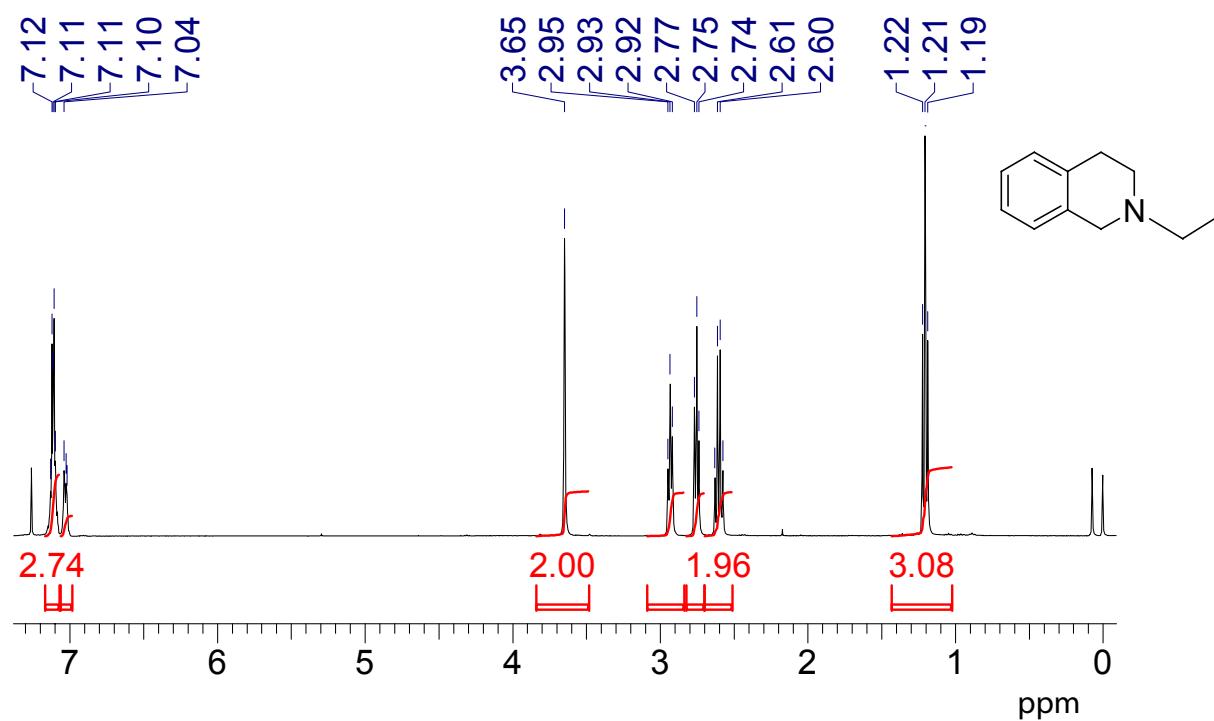


Figure S11. ¹H NMR of **1c** in CDCl₃ (400 MHz).

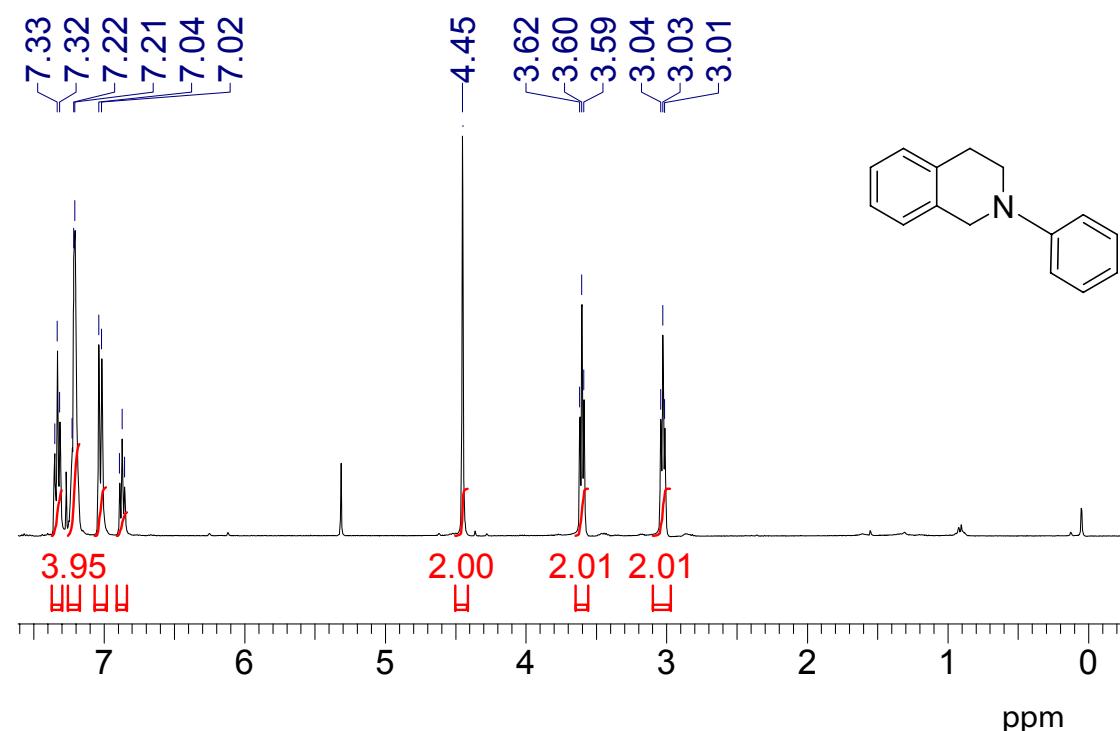


Figure S12. ¹H NMR of **1d** in CDCl₃ (400 MHz).

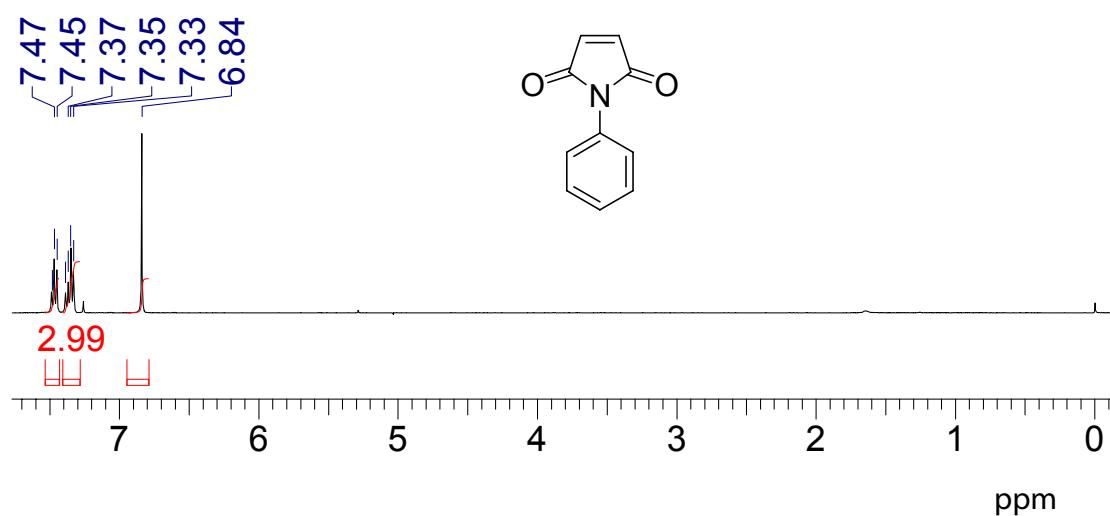


Figure S13. ¹H NMR of **2a** in CDCl₃ (400 MHz).

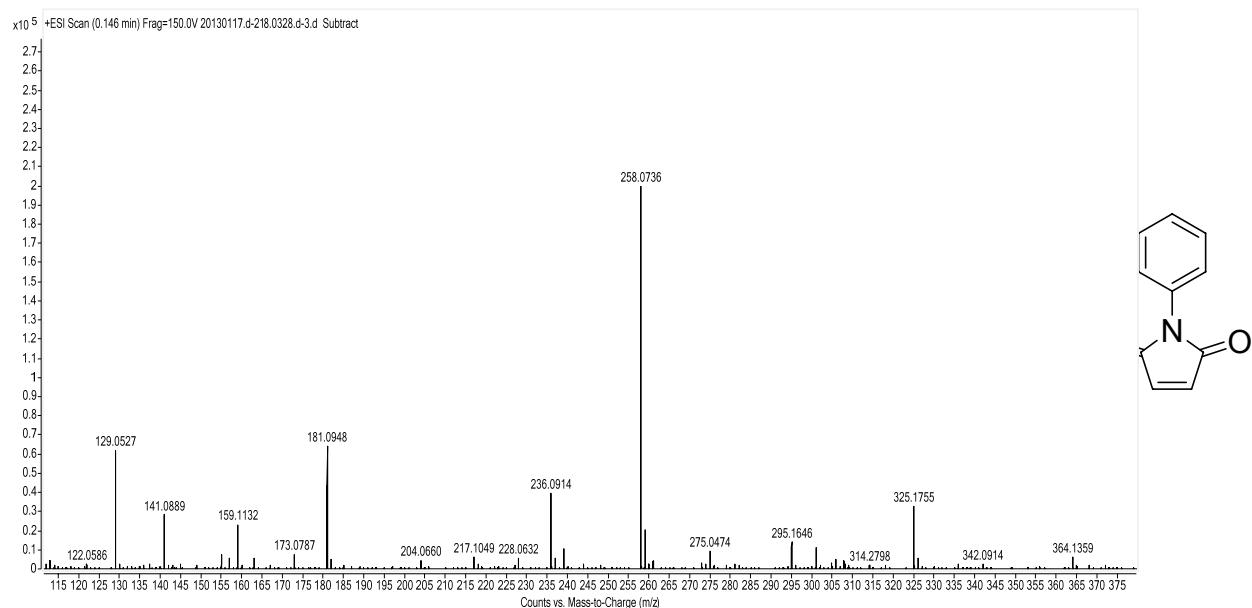


Figure S14. TOF HRMS ESI⁺ of **2a**

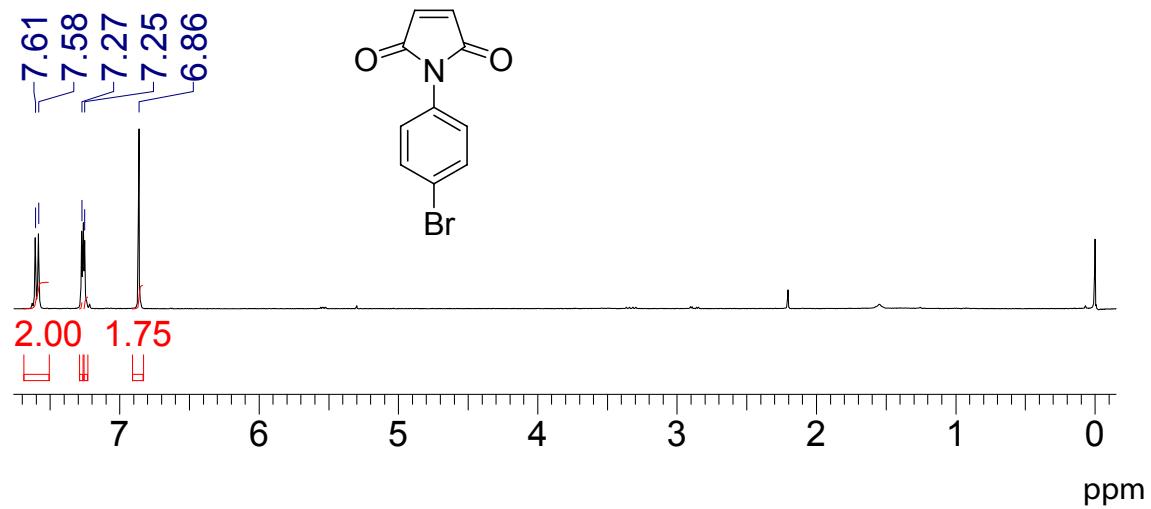


Figure S15. ¹H NMR of **2b** in CDCl₃ (400 MHz).

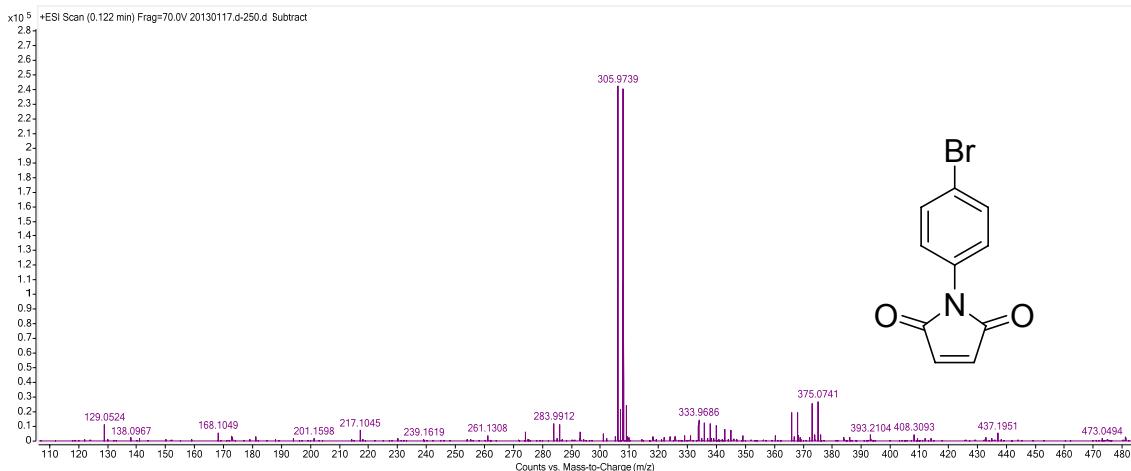


Figure S16. TOF HRMS ESI⁺ of 2b

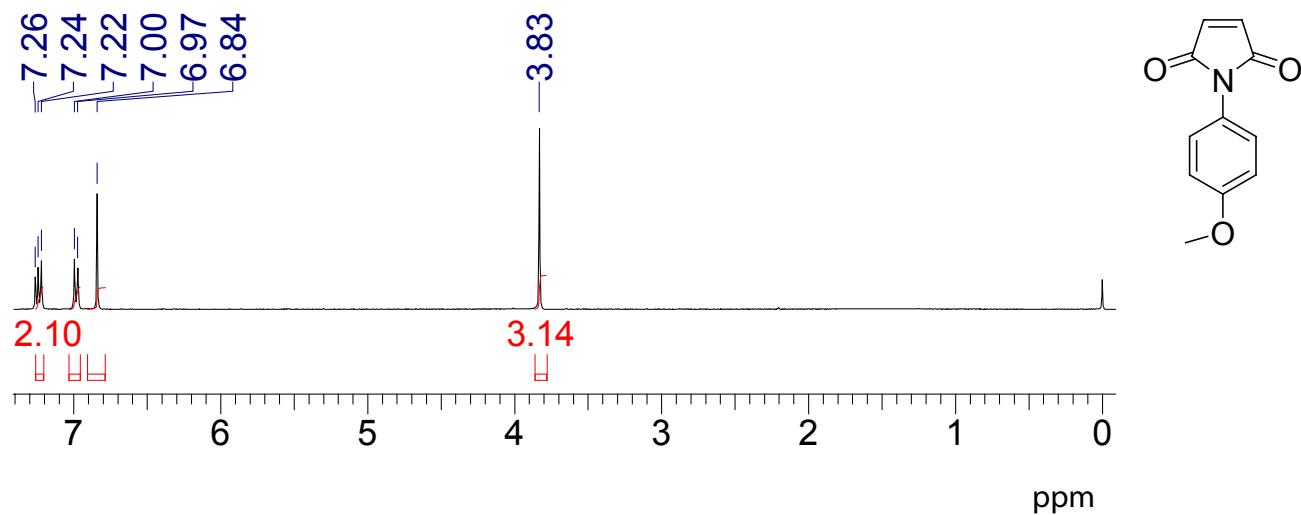


Figure S17. ¹H NMR of 2c in CDCl₃ (400 MHz).

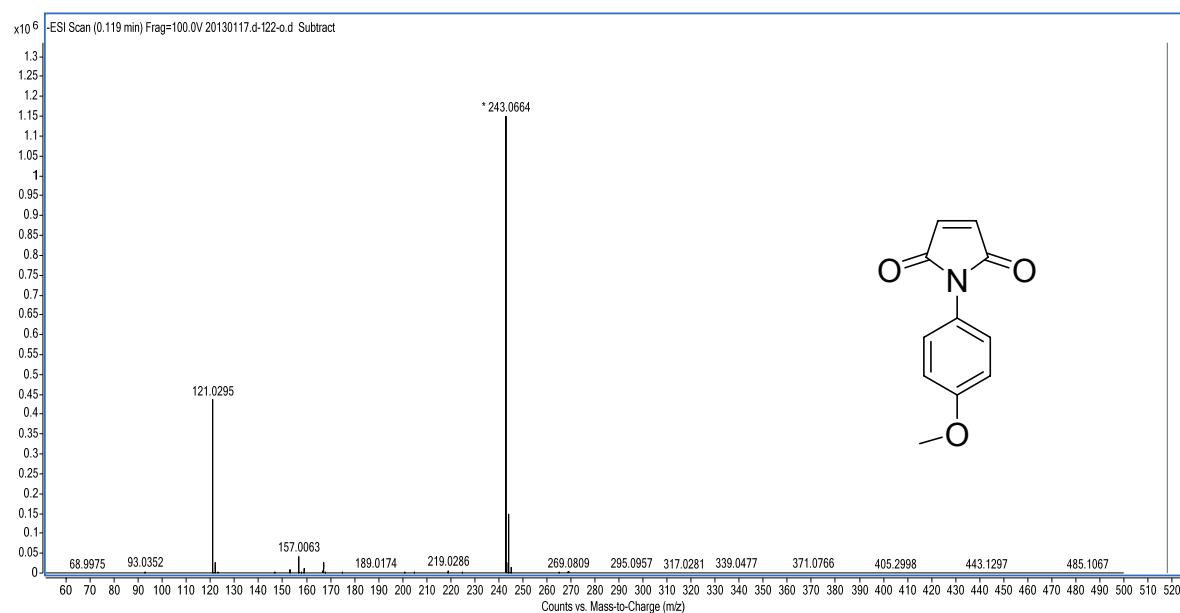


Figure S18. TOF HRMS ESI⁺ of **2c**

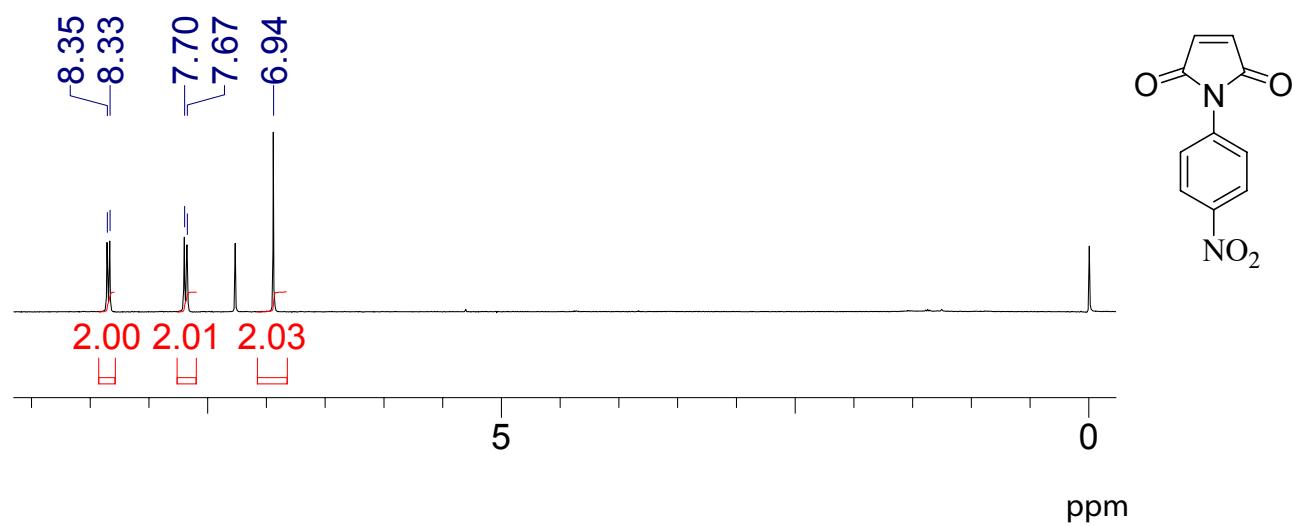


Figure S19. ¹H NMR of **2d** in CDCl_3 (400 MHz).

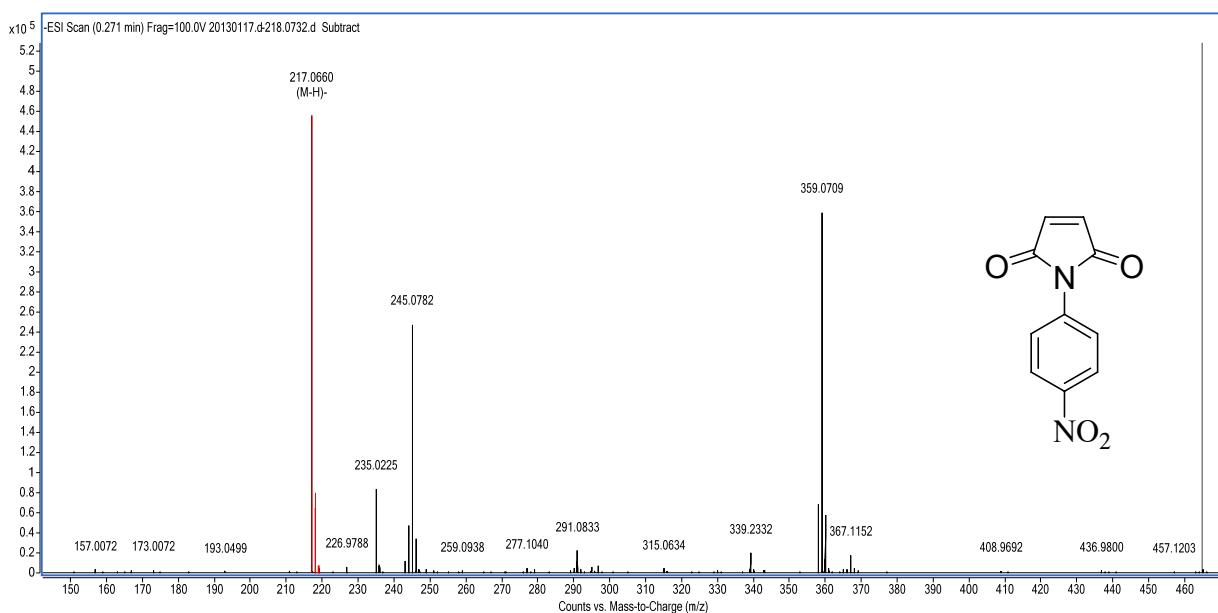


Figure S20. TOF HRMS ESI⁺ of 2d

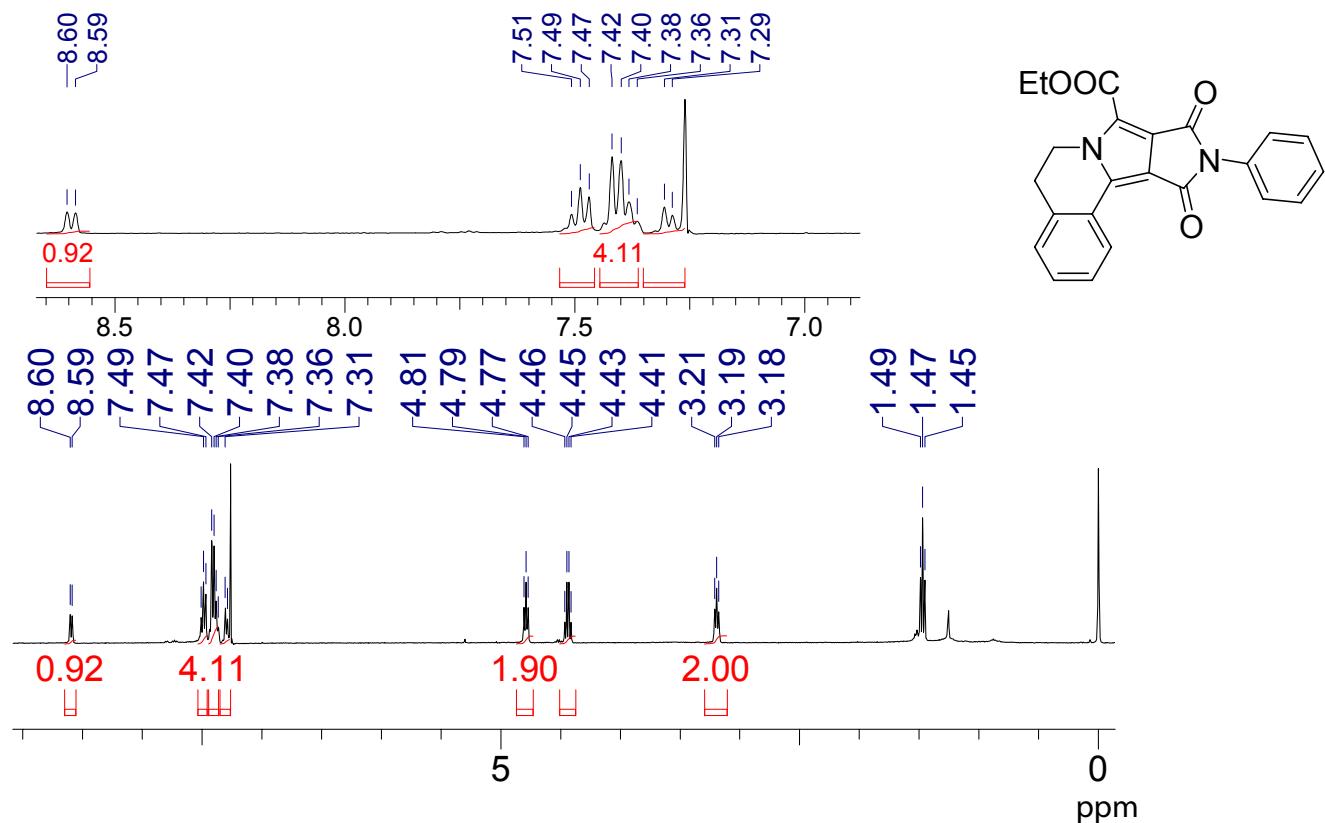


Figure S21. ¹H NMR of 3a in CDCl₃ (400 MHz).

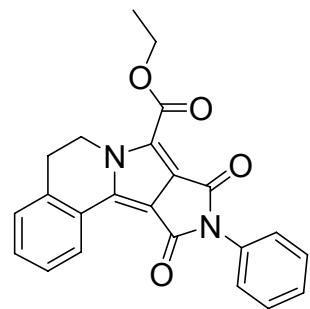
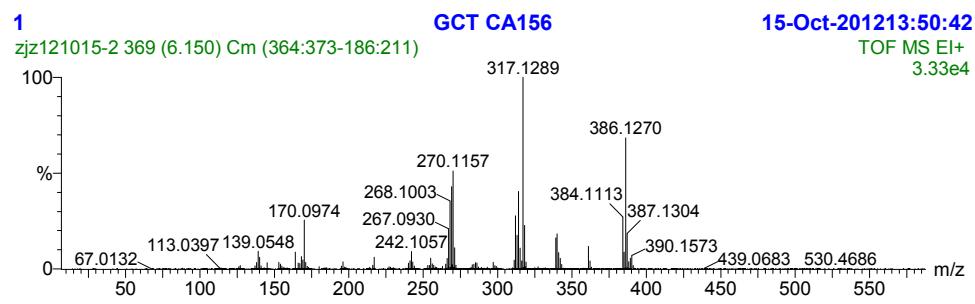


Figure S22. TOF HRMS El⁺ of **3a**.

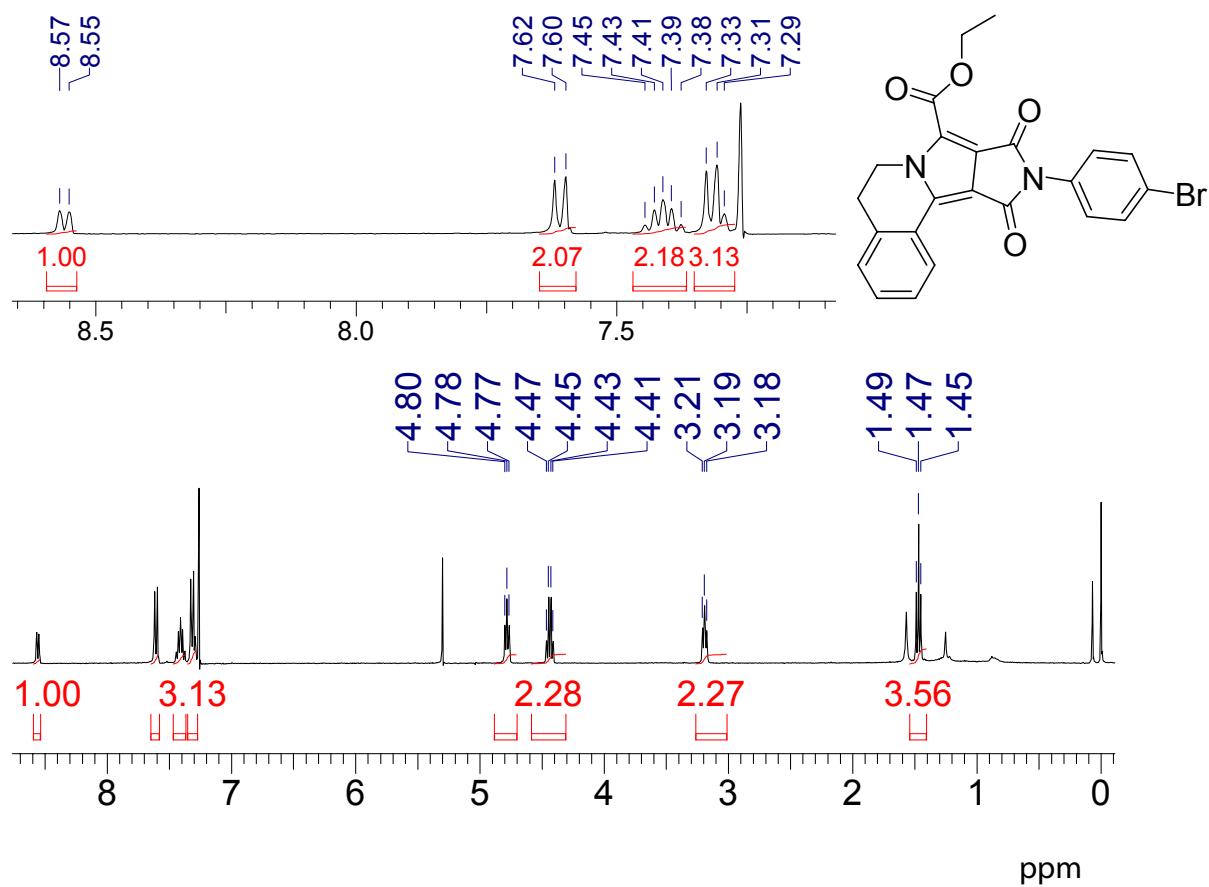


Figure S23. ¹H NMR of **3b** in CDCl₃ (400 MHz).

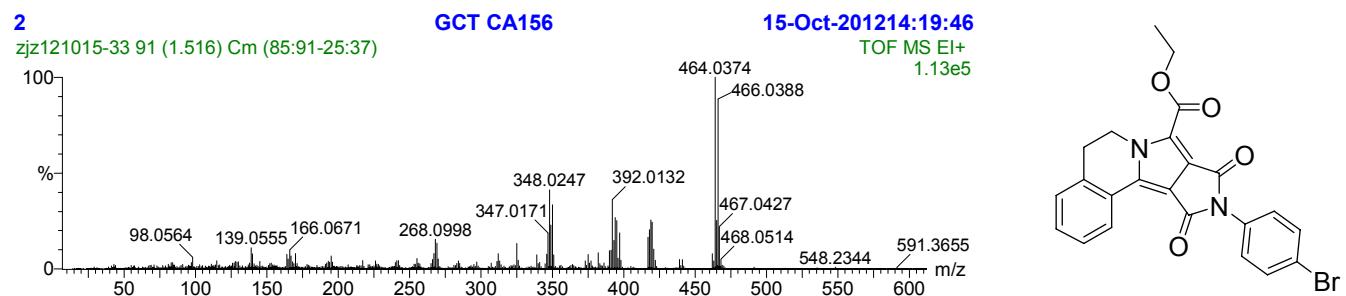


Figure S24. TOF HRMS El⁺ of **3b**.

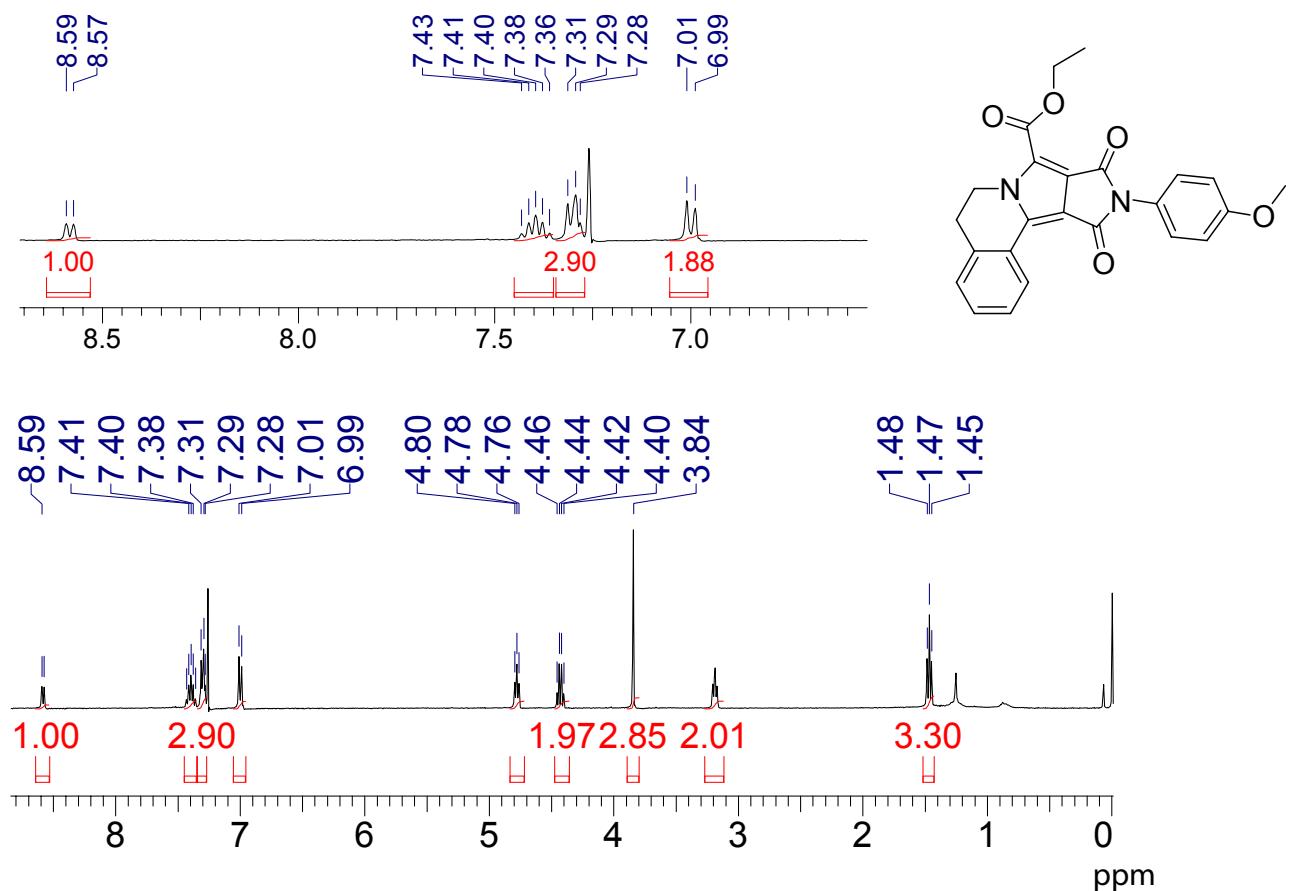


Figure S25. ¹H NMR of **3c** in CDCl₃ (400 MHz).

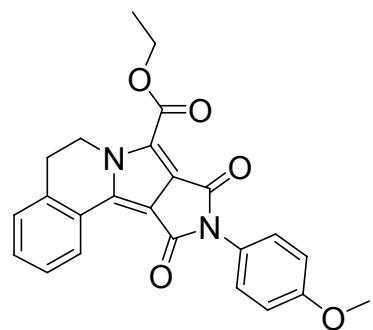
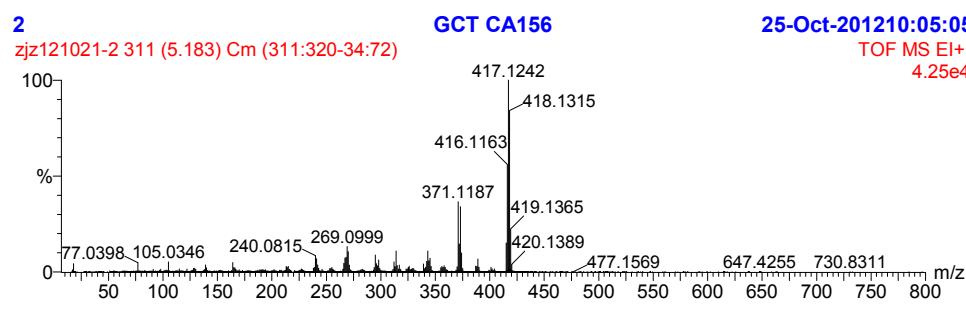


Figure S26. TOF HRMS EI⁺ of **3c**.

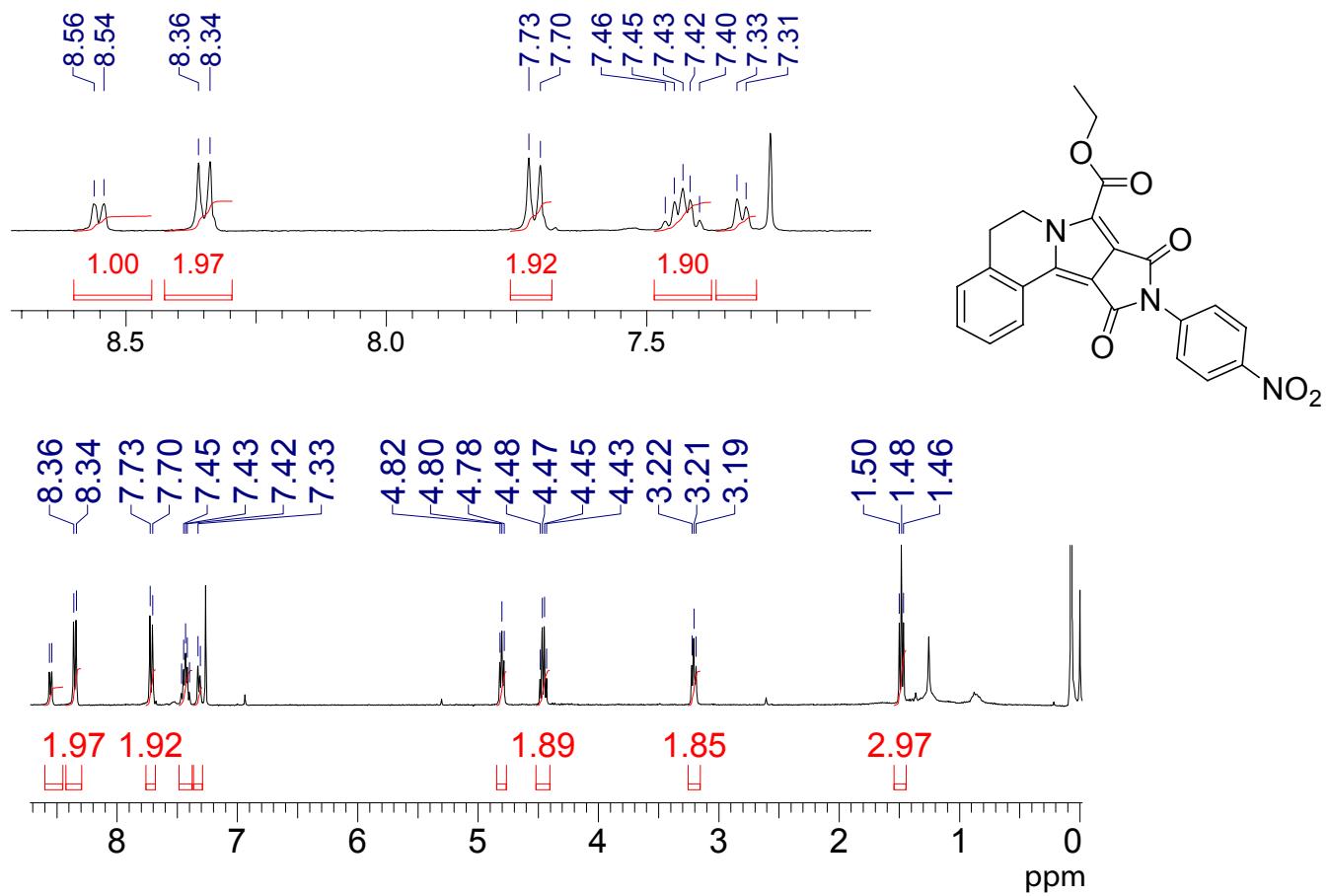


Figure S27. ¹H NMR of **3d** in CDCl₃ (400 MHz).

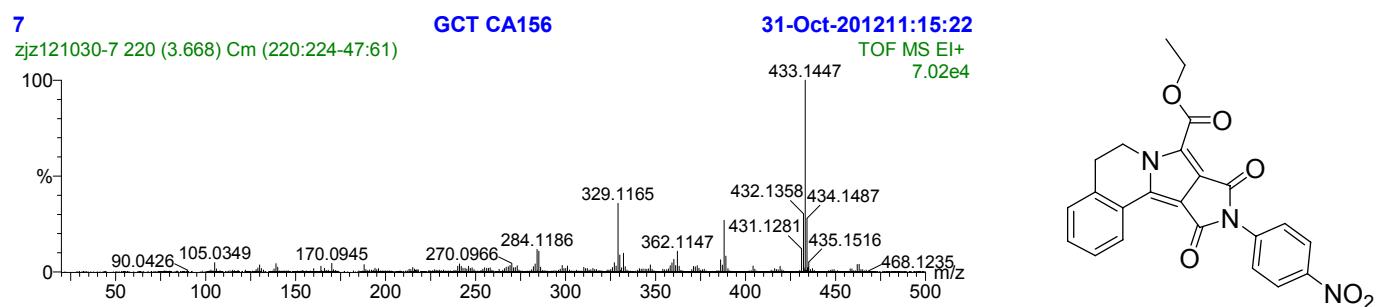


Figure S28. TOF HRMS EI⁺ of **3d**.

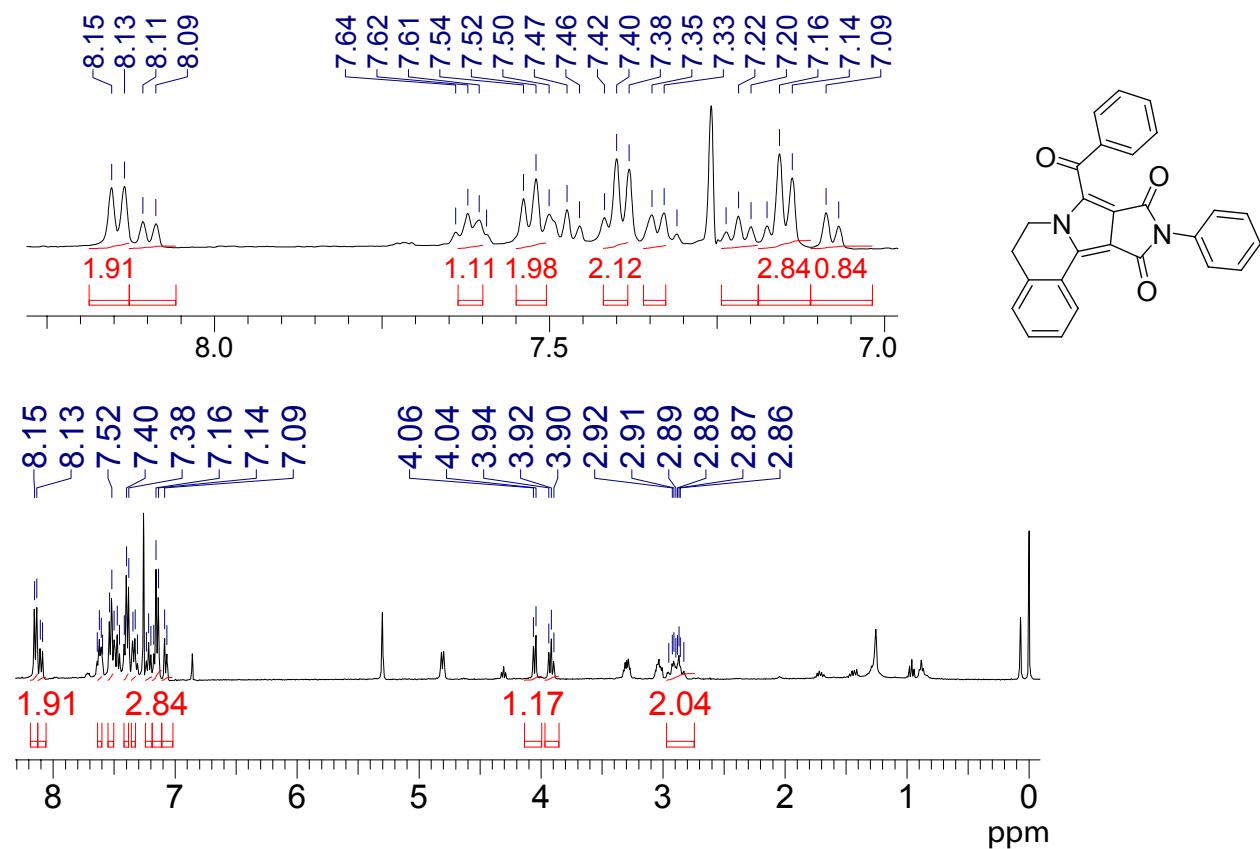


Figure S29. ¹H NMR of **3e** in CDCl₃ (400 MHz).

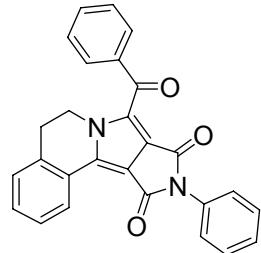
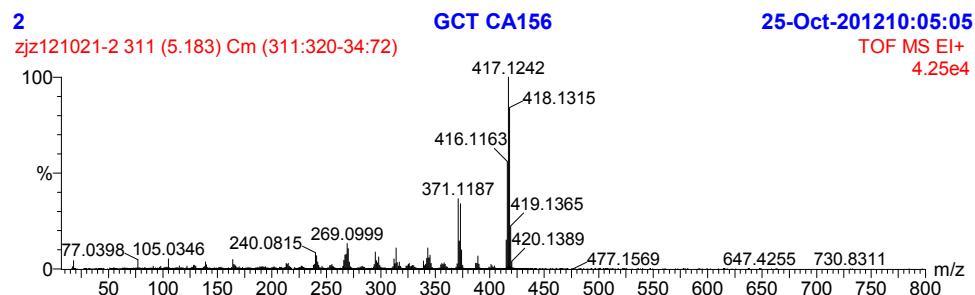


Figure S30. TOF HRMS EI⁺ of **3e**.

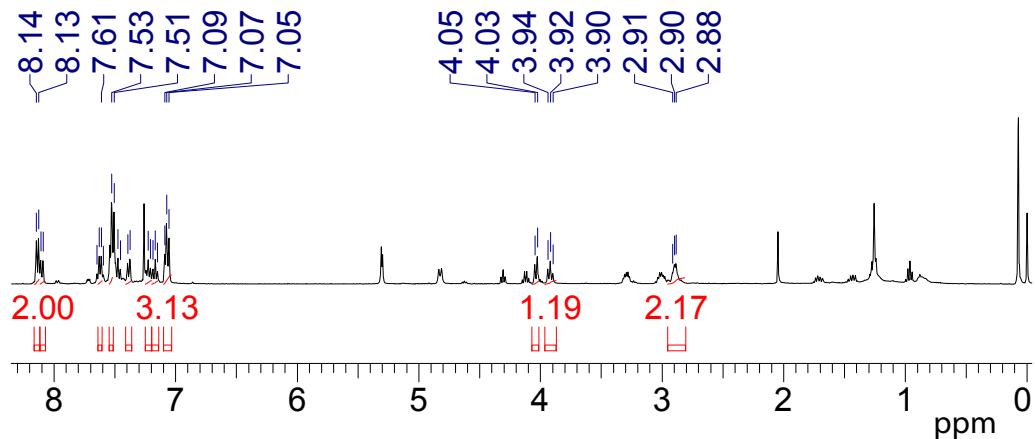
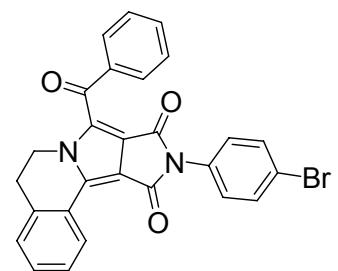
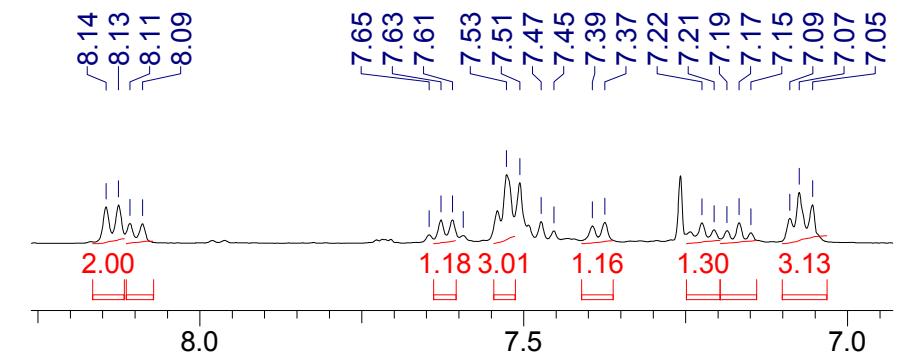


Figure S31. ¹H NMR of **3f** in CDCl₃ (400 MHz).

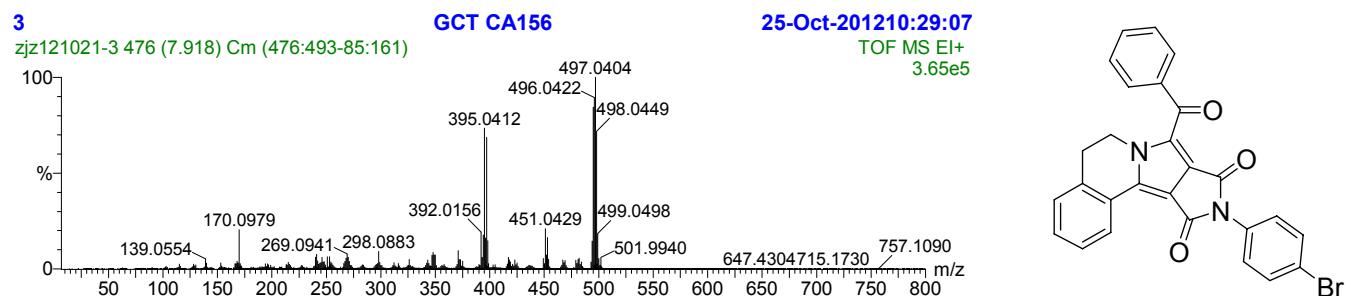


Figure S32. TOF HRMS EI⁺ of **3f**.

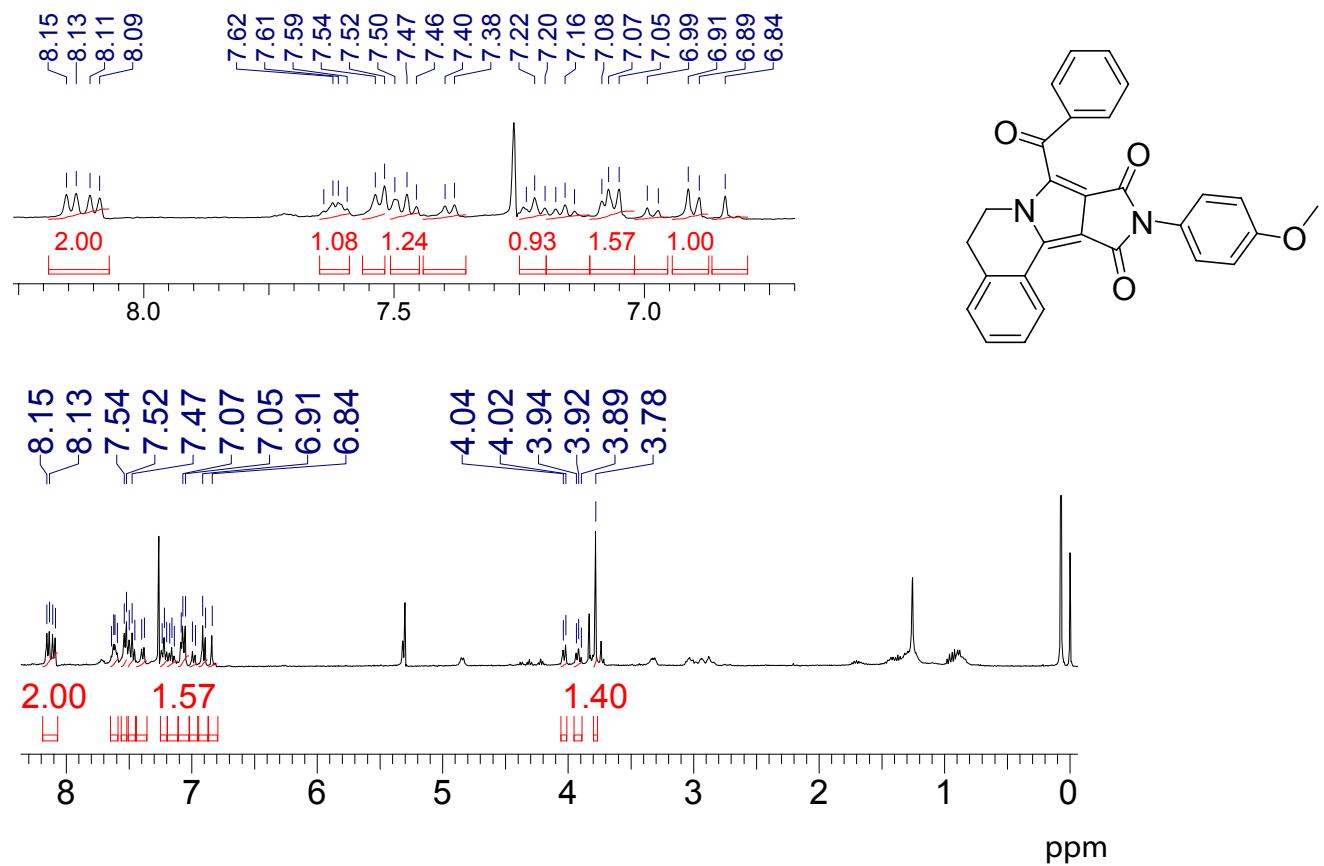


Figure S33. ¹H NMR of **3g** in CDCl₃ (400 MHz).

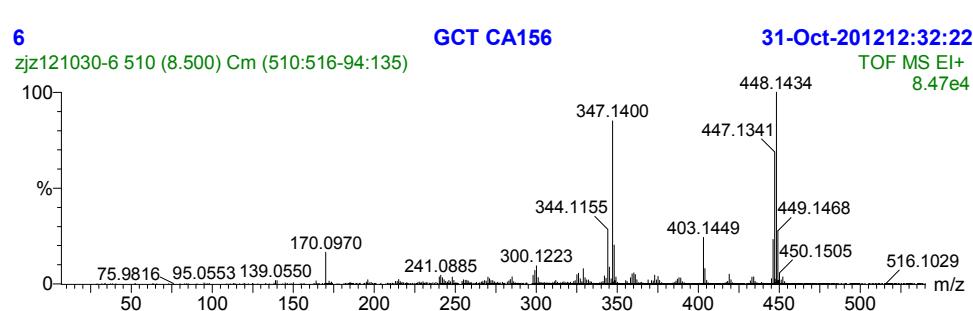


Figure S34. TOF HRMS El⁺ of **3g**.

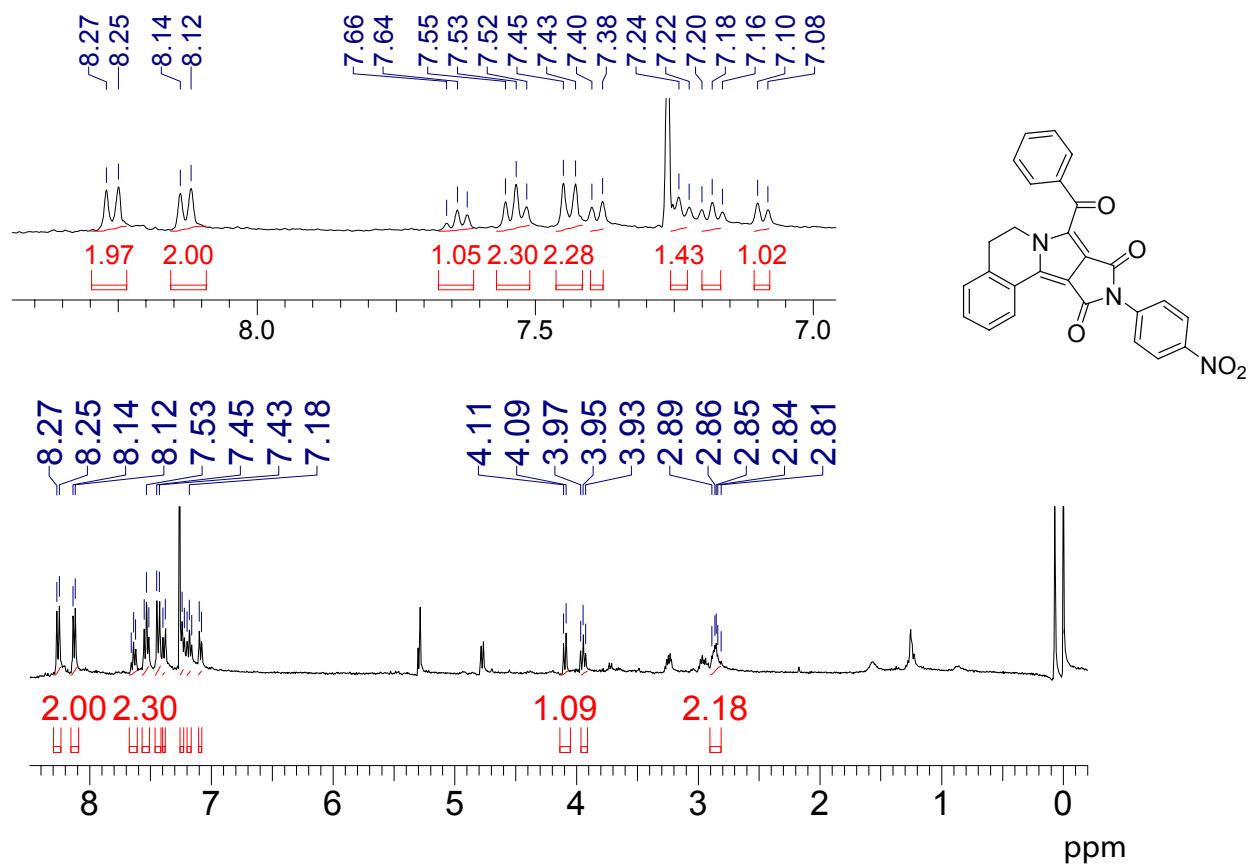


Figure S35. ¹H NMR of **3h** in CDCl₃ (400 MHz).

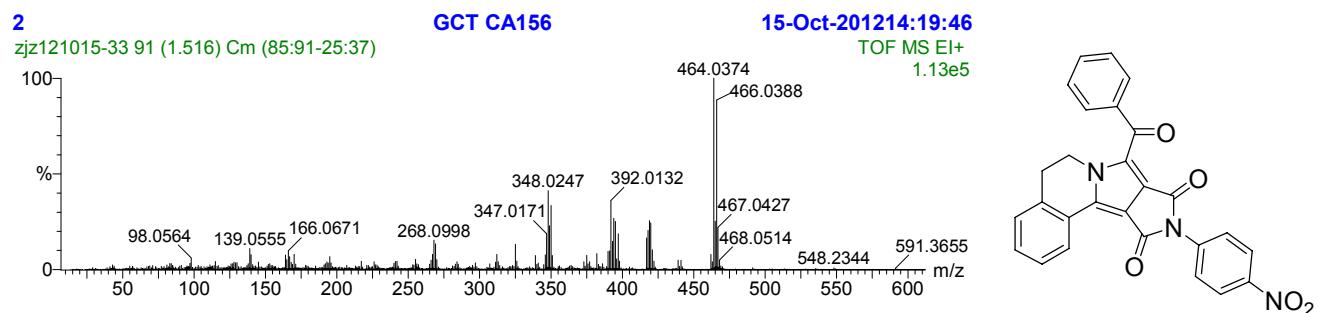


Figure S36. TOF HRMS EI^+ of **3h**.

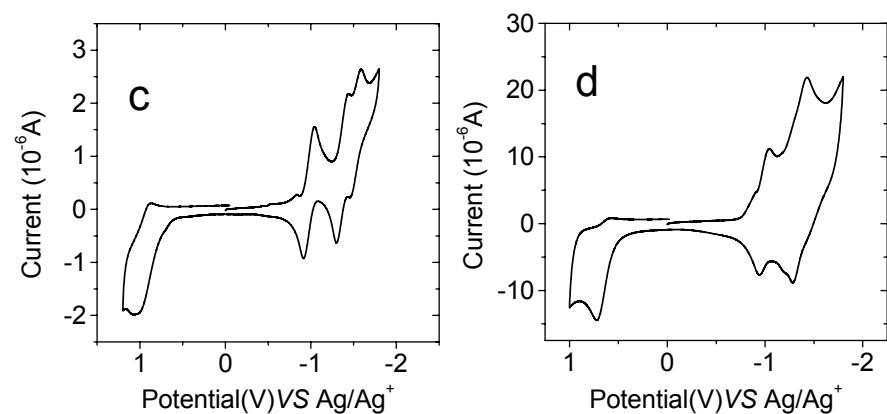


Figure S37. Cyclic voltammograms of **B-1–B-2** (1.0 mM) at a scan rate of 0.1 V/s in DCM at glassy carbon working electrode, supporting electrolyte, 0.1 M TBAPF_6 , all scans start in the negative direction.

Table S1. Redox Potentials of photocatalysts (pc stands for photocatalyst)^a

Photocatalyst	E_{red} (pc/pc ⁻)	E_{ox} (pc ⁺ /pc)	E_{red}^* (pc [*] /pc ⁻)	E_{ox}^* (pc ⁺ /pc [*])	$\Delta E_{0,0}^b$	ΔG^c /eV
B-1	-1.02	1.08	0.68	-1.29	1.56	-0.44 ^d
B-2	-1.02	0.74	0.68	-1.20	1.56	-0.44 ^d

^a Cyclic voltammograms of **B-1**–**B-2** (1.0 mM) at a scan rate of 100 mV/s in DCM. Glassy carbon working electrode, supporting electrolyte is 0.1 M TBAPF₆. All scans start in the negative direction. Potential in V vs. Ag/Ag⁺. ^bΔE_{0,0} refers to the lowest excited energy. ^cΔG was calculated by the Rehm–Weller equation: $\Delta G = \Delta E_{ox} - \Delta E_{red} - \Delta E_{0,0} - e^2/\varepsilon_a$, here ΔE_{ox} and ΔE_{red} versus NHE are oxidative and reductive potentials of 1a (0.61V) and **B-1** – **B-2**. e^2/ε_a is 0.012 V in CH₂Cl₂. $\Delta E_{0,0}$ refers to the lowest excited energy. ^dThe calculation followed a literature method.

Arbogast, J. W.; Foote, C. S.; Kao, M. *J. Am. Chem. Soc.* **1992**, 114, 2277.

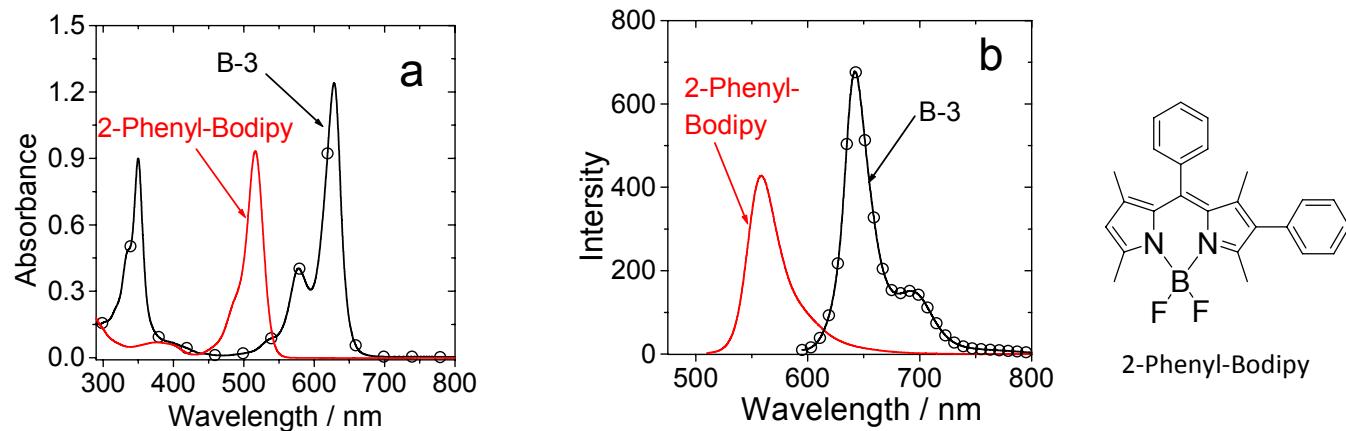


Figure S38. (a) UV/Vis absorption spectra of the **2-phenyl-Bodipy** and **B-3**. (b) Emission spectra of **2-phenyl-Bodipy** and **B-3**, Excited at 505 nm and 590 nm, respectively. In toluene (1.0×10^{-5} M; 25 °C). 2-Phenyl-Bodipy is the control compound of **B-1** in the main text of the paper.

Photophysical properties of **2-phenyl-Bodipy**:

$\varepsilon = 94000 \text{ M}^{-1} \text{ cm}^{-1}$ at 517 nm; $\lambda_{em} = 540 \text{ nm}$, $\Phi_F = 79\%$; $\tau_F = 4.3 \text{ ns}$.

2-Phenyl-Bodipy was also used as triplet photosensitizer for photocatalytic reaction, but no product was observed. This result indicated that the C₆₀-Bodipy dyad is mandatory for the photocatalytic activity.

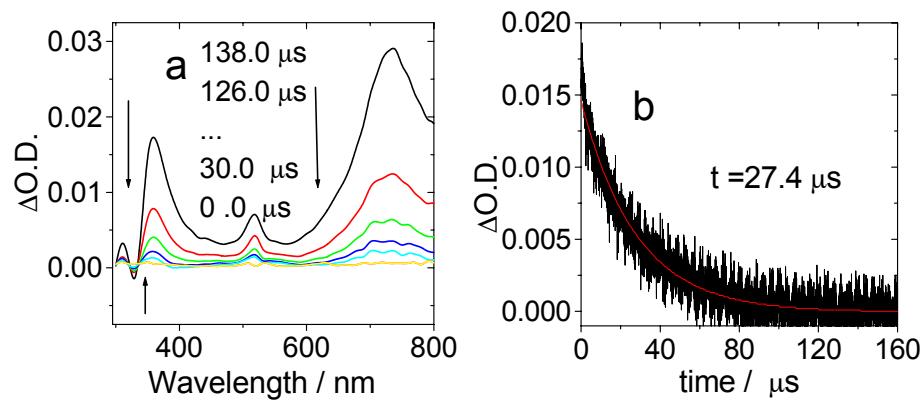


Figure S39. Nanosecond time-resolved transient difference absorption of **B-1**. (a) transient absorption difference spectra and (b) decay trace at 520 nm. In deaerated toluene. $\lambda_{\text{ex}} = 532 \text{ nm}$, 20 °C.

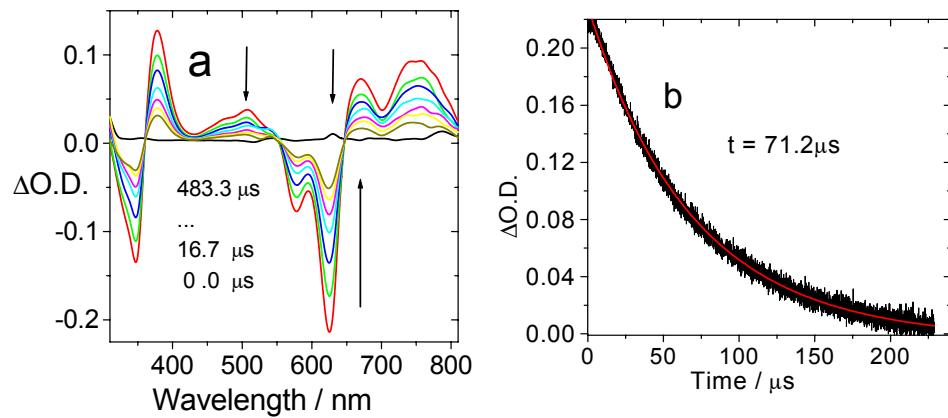


Figure S40. Nanosecond time-resolved transient difference absorption of **B-2**. (a) transient absorption difference spectra and (b) decay trace at 630 nm. In deaerated toluene. $\lambda_{\text{ex}} = 532 \text{ nm}$, 20 °C.

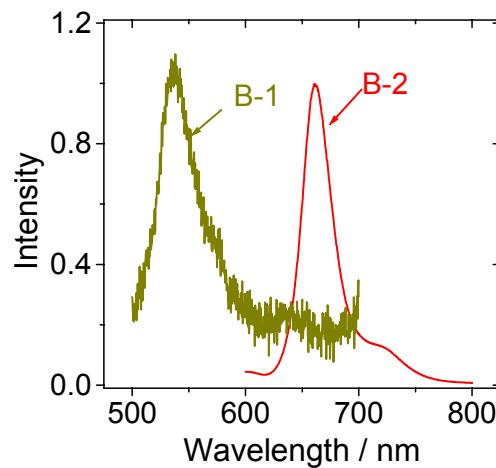


Figure S41. Normalized emission spectra of **B-1** - **B-2** ($\lambda_{\text{ex}} = 490, 590 \text{ nm}$, respectively). In toluene, $1.0 \times 10^{-5} \text{ M}$, 20°C . Note all these emission are weak due to the intramolecular energy transfer from Bodipy units to C_{60} unit in **B-1** and **B-2**.

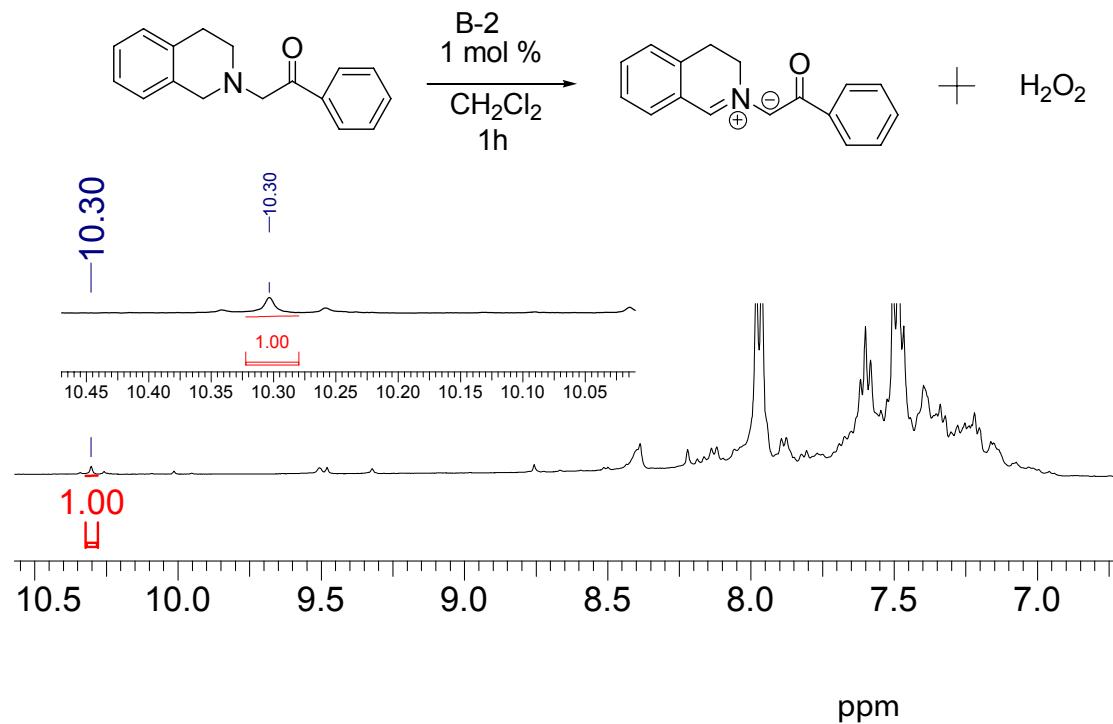


Figure S42. Experimental evidence for the photocatalytic reaction mechanism: the detection of H_2O_2 by ¹H NMR spectroscopy after reaction in DMSO-d₆. The peak at 10.30 ppm is due to H_2O_2 .^a

^a J. H. Park, K. C. Ko, E. Kim, N. Park, J. H. Ko, D. H. Ryu, T. K. Ahn, J. Y. Lee, S. U.Son, *Org. Lett.* **2012**, *14*, 5502–5505.

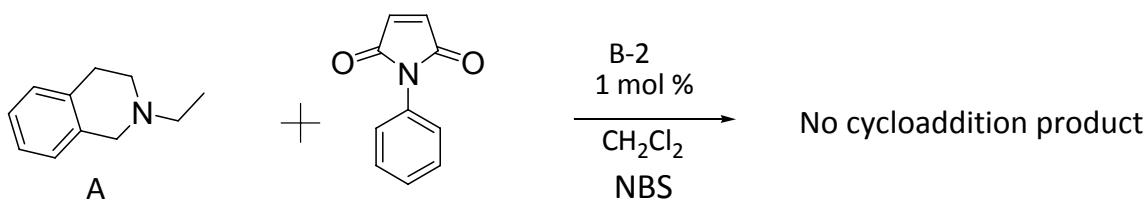


Figure S43. Experimental evidence for the photocatalytic reaction mechanism. Reaction condition: **1c** (0.15 mmol), **2a** (0.10 mmol), **B-2** (1 mol%), NBS (1.2 equiv) in CH_2Cl_2 (5.0 mL) was added after 2 h of photoirradiation. The mixture was irradiated with 35 W Xe lamp ($\lambda > 385$ nm), 20 °C.

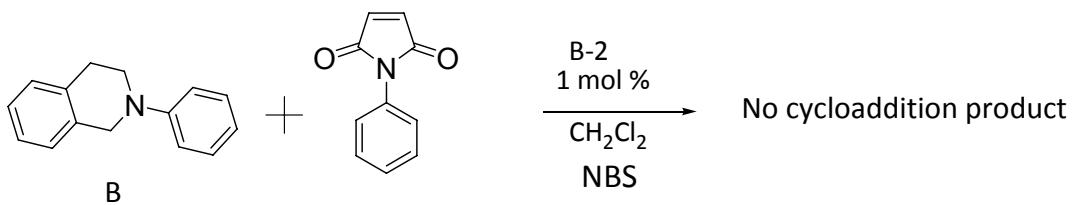


Figure S44. Experimental evidence for the photocatalytic reaction mechanism. Reaction conditions: **1d** (0.15 mmol), **2a** (0.10 mmol), **B-2** (1 mol%), NBS (1.2 equiv) in CH_2Cl_2 (5.0 mL) was added after 2 h of photoirradiation. The mixture was irradiated with 35 W Xe lamp ($\lambda > 385$ nm), 20 °C.