Electronic Supplementary Information For

Porous material-immobilized iodo-Bodipy as efficient photocatalyst for photoredox catalytic organic reaction to prepare pyrrolo[2,1-*a*]isoquinoline

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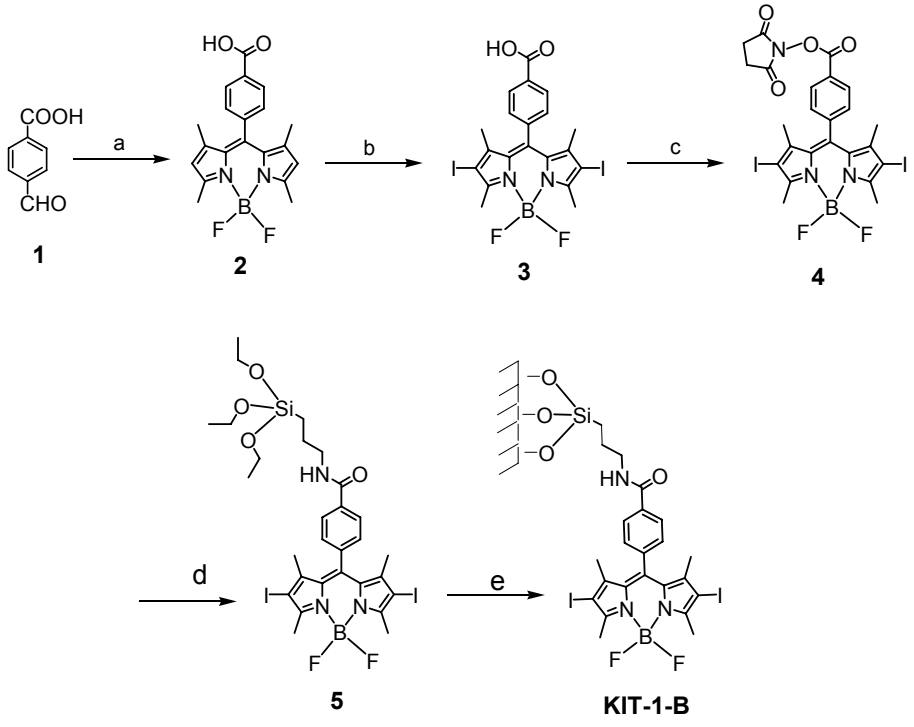
1. Experimental Section

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 N_2 for ca. 20 min before 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 ($O_2^{-\bullet}$) or singlet oxygen ($^1O_2$) scavengers (5,5-dimethyl-1-pyrroline-*N*-oxide (DMPO) or 2,2,6,6-tetramethylpiperidine (TEMP)) in air-saturated CH_3CN was stirred in the dark , then the solution was injected into the quartz capillary. A diode pumped solid state (DPSS) laser (532 nm) irradiate the solution in quartz capillary 120 seconds.



Scheme S1. Preparation of the porous molecular sieve-supported photocatalyst **KIT-1-B**. Key: a) 2,4-dimethylpyrrole, TFA, anhydrous CH_2Cl_2, rt, 20 h; DDQ, $BF_3{\cdot}Et_2O$, 12 h, Yield: 13.5 %; b) iodine, iodic acid, 60 °C, 1 h, Yield: 100 %; c) NHS, EDC·HCl, DCM, rt, 12 h, Yield: 63.8 %; d) Aminopropyltriethoxysilane , anhydrous CH_2Cl_2, rt, 20 h, 22 °C, Yield: 88.9 %; e) **KIT-1**, toluene, 120 °C, 10 h.

Compound 2: 4-carboxybenzaldehyde aldehyde (21.9 mmol, 2.1 g) was added to a 500 mL round-bottom flask. Then dichloromethane (400 mL) was added into the flask. The mixture was degassed by argon for 30 min, 2,4-dimethyl pyrrole (21.9 mmol, 2.1 g) was added. Then two drops of TFA was added and the solution was stirred under Ar for 29 h at room temperature. After addition of a solution of DDQ (9.9 mmol, 2.46 g) in dichloromethane (100 mL) to the reaction mixture, stirring was continued for 4 hours. Then 10 mL of Et_3N and 10 mL of $BF_3{\cdot}OEt_2$ were successively added. After 12 hours, the reaction mixture was treated with water (300 mL). Then the mixture was extracted into the dichloromethane. The organic layer was dried over anhydrous Na_2SO_4. The solvent was evaporated and the residue was purified by silica gel column chromatography (CH_2Cl_2 : MeOH = 30:1, v/v). Red solid was obtained. Yield: 0.5 g (13.5%). ^{1}H NMR (400 MHz, $CDCl_3$): 8.12 (d, 2H, J = 8.0 Hz), 7.55 (d, 2H, J = 8.0 Hz), 6.20 (s, 2H), 2.46 (s, 6H), 1.33 (s, 6H). HRMS (ESI$^-$): *m/z* calcd for $[C_{80}H_{19}BF_2N_2O_2]^-$: *m/z* 367.1429; found: 367.1425.

Compound 3: Compound **2** (0.141 mmol, 0.05 g) and iodine (0.353 mmol, 0.09 g) were added to a 100 mL round-bottom flask and to this solution was added iodic acid (0.282 mmol, 0.05g) dissolved in water (0.5 mL). The reaction mixture was stirred at 60 °C. After 1 hour, all the starting material had been consumed. Saturated $Na_2S_2O_3$ solution was added and the product was extracted into dichloromethane. The solvent was evaporated and the residue was purified by silica gel column chromatography (CH_2Cl_2 : MeOH = 30:1, v/v). Deep red solid was obtained. Yield: 0.1 g (100%). ^{1}H NMR (400 MHz, $CDCl_3$): 8.28 (d, 2H, J = 8.0 Hz), 7.38 (d, 2H, J = 8.0 Hz), 2.65 (s, 6H), 1.36 (s, 6H). HRMS (ESI$^-$): *m/z* calcd for $[C_{20}H_{16}BF_2N_2O_2I_2]^-$: 618.9362; found: 618.9382.

Compound 4: compound **3** (50 mg, 0.081 mmol), EDC·HCl (34.5 mg, 0.18 mmol), *N*-hydroxysuccinimide (20.72 mg, 0.18 mmol) were dissolved in dichloromethane (20 mL). The mixture was stirred at room temperature under Ar. After 10 hours, the solution was washed with distilled water (2 × 50 mL), dried over $MgSO_4$. The solvent was evaporated and the residue was purified by column chromatography (silica gel, CH_2Cl_2). Deep red solid was obtained. Yield: 37.2mg (63.8%). ^{1}H NMR (400 MHz, $CDCl_3$): 8.32 (d, 2H, J = 8.0 Hz), 7.49 (d, 2H, J = 8.0 Hz), 2.97 (d, 4H), 2.65 (s, 6H), 1.36 (s, 6H). HRMS (MALDI): *m/z* calcd for $[C_{24}H_{20}BF_2N_3O_4I_2]^+$: 716.9604; found: 716.9574.

Compound 5: compound **4** (30 mg, 0.042 mmol) was dissolved in dichloromethane (5 mL). Then Aminopropyltriethoxysilane (0.1 mL, 0.42 mmol) was added. The resulting solution was stirred at room temperature under Ar. After 20 hours, The solution was washed with water (3 × 20 mL), dried over $MgSO_4$. The solvent was evaporated and the residue was purified by column chromatography

using (silica gel, CH_2Cl_2) as the eluent. Deep red solid (29.2mg, 88.9%). ^{1}H NMR (400 MHz, $CDCl_3$): 7.98 (d, 2H, *J* = 8.0 Hz), 7.37 (d, 2H, *J* = 8.0 Hz), 3.82–3.88 (m, 4H), 3.70–3.75 (m, 4H), 3.55 (t, 2H), 2.65 (s, 6H), 1.80–1.86 (m, 2H), 1.37 (s, 6H), 3.70–3.75 (m, 4H), 0.88 (t, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): 166.4, 157.4, 145.3, 140.1, 138.0, 136.1, 131.1, 128.2, 86.1, 58.8, 42.5, 32.9, 32.1, 30.2, 29.9, 29.6, 22.9, 18.5, 17.4, 16.3, 14.3, 8.1. HRMS (MALDI): *m/z* calcd for $[C_{29}H_{38}BF_2N_3O_4I_2Si]^-$: 823.0782; found: 823.0742.

Preparation of KIT-1-B: 5 (40 mg, 0.10 mmol) was dissolved in toluene (5 mL). Then 400 mg **KIT-1** was added.[1] The resulting solution was stirred at 120 °C under Ar. After 20 hours, the color of the solution almost disappeared, indicated that all the compound **5** has been attached onto the surface of **KIT-1** (by weight it is ca. 10 %). The mixture was filtered and washed with DCM (5 × 30 mL), Then the red solid was dried in a vacuum drying oven.

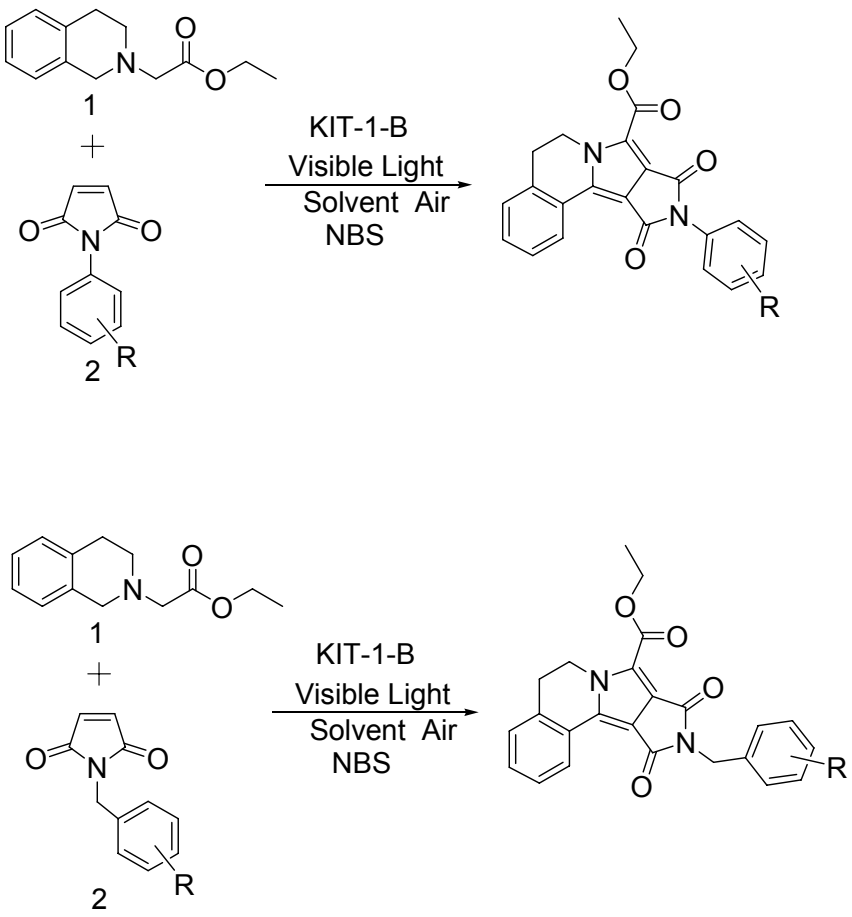
Table S1. Structural characterization of **KIT-1** and the photocatalyst **KIT-1-B**.

Sample	d_{100} [a] (nm)	a_0 [b] (nm)	Pore size [c] (nm)	Wall Thickness [d] (nm)	BET surface area(m^2/g)	Total pore Volume [d] (cm^3g)
KIT-1	5.1	5.9	3.1	2.8	619.0	0.86
KIT-1-B	5.3	6.1	2.7	3.4	445.8	0.59

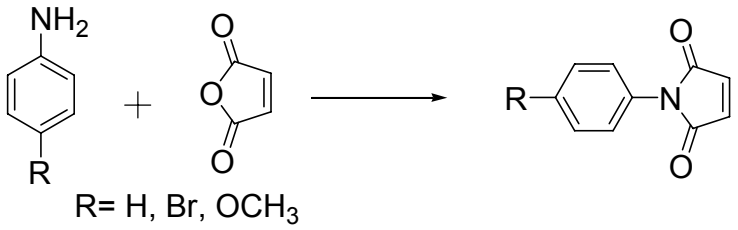
[a] Calculated from XRD analysis. [b] $a_0=2d_{100}/3^{1/2}$. [c] Calculated from adsorption branch of nitrogen isotherms using BJH model. [d] Wall thickness = a_0–pore size. [e] Calculated from the volume adsorbed of P/P_0 at 0.99.

1. **KIT-1** was prepared following the reported method: (*a*) R. Ryoo, J. M. Kim, C. H. Ko, and C. H. Shin. *J. Phys. Chem.*, 1996, **100**, 17718; (*b*) L.-P. Liu, G. Xiong, X.-S. Wang, X.-J. Cheng, *Catal. Lett.*, 2011, **141**, 1136

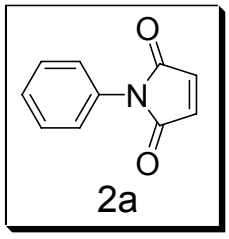
The detail of oxidation/ [3+2] cycloaddition/ aromatization sequence



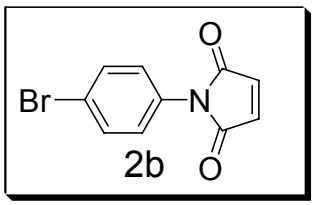
To a dry 10 mL flask were added **KIT-1-B** (10 mg), **1** (0.12 mmol, 1.2 equiv), **2** (0.1 mmol) and CH_3CN (3 mL). The reaction mixture was stirred at rt under air atmosphere. The solution was then irradiated using a 35 W xenon lamp through a cut off filter (0.72 M $NaNO_2$ aqueous solution, which 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 added and the mixture was stirred for further 5 min. Then the solvent was evaporated under reduced pressure. The residue was purified by column chromatography (silica gel, CH_2Cl_2).



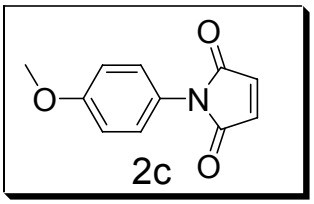
Aniline derivatives (10 mmol) were dissolved in THF (20 mL). Maleic anhydride (11 mmol) was dissolved in another portion of THF (20 mL). Maleic anhydride solution was dropped into the aniline derivatives slowly, the reaction mixture was stirred for 30 min at room temperature. A lot of precipitation appeared. The precipitation was collected by filtration. The filtrate was dissolved in acetic anhydride (20 mL) and acetic acid-sodium (12 mmol) was added. 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. Precipitation appeared and the solid was collected by filtration. The precipitates was purified by column chromatography (silica gel, CH_2Cl_2/petroleum ether = 1/1, v/v).



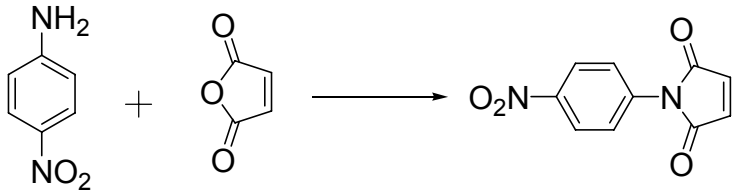
Yield: 0.6 g (82.6%). M.p. 82.9–83.2°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.47 (t, J = 7.2 Hz, 2H), 7.37–7.34 (m, 3H), 6.84 (s, 2H). HRMS (ESI$^+$): Calcd $C_{10}H_7NO_2$ $[M+H]^+$ m/z = 173.0477. Found m/z = 173.0787.



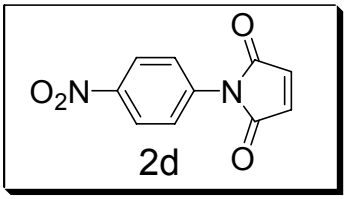
Yield: 0.3 g (76.8%). M.p. 121.4–121.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.63 (d, J = 9.2 Hz, 2H), 7.27–7.22 (m, 2H), 6.86 (s, 2H). HRMS (ESI$^+$): Calcd $C_{10}H_6NO_2Br$ $[M+H]^+$ m/z = 251.9766. Found m/z = 251.9739.



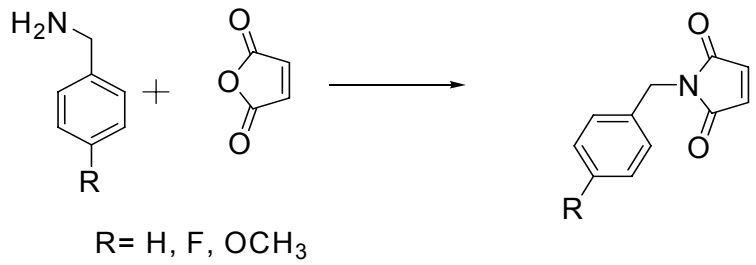
Yield: 0.2 g (77.2%). M.p. 147.7–148.2°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.23 (d, J = 4.8 Hz, 2H), 7.00 (d, J = 2.0 Hz, 2H), 6.84 (s, 2H), 3.83 (s, 3H). HRMS (ESI$^+$): Calcd $C_{11}H_9NO_2Na$ $[M+Na]^+$ m/z = 226.0467. Found m/z = 226.0469.



p-nitroaniline (10 mmol) and maleic anhydride (11 mmol) was dissolved in THF (40 mL). The mixture was stirred under reflux for 6 h. Precipitation appeared and the solid was filtrated. The filtrate was dissolved in acetic anhydride (20 mL), then sodium acetate (12 mmol) was added. The mixture was heated by microwave irradiation at 120°C for 30 min. The acetic anhydride solution was poured into water (20 mL), saturated NaOH solution was added to neutralize the solution. The precipitation was collected by filtration and purified by column chromatography (silica gel, CH_2Cl_2/petroleum 1/1, v/v).

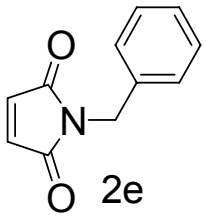


Yield: 0.3 g (62.1%). M.p. 170.1–170.7°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.36 (d, J = 9.2 Hz, 2H), 7.68 (d, J = 6.0 Hz, 2H), 6.94 (s, 2H). HRMS (ESI$^+$): Calcd $C_{10}H_5N_2O_4$ $[M-H]^-$ m/z = 217.0328. Found m/z = 217.0660.



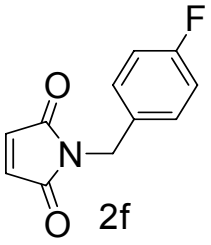
R= H, F, OCH_3

Benzylamine derivatives (10 mmol) were dissolved in $CHCl_3$ (2 mL). Maleic anhydride (10 mmol) was dissolved in another portion of $CHCl_3$ (10 mL). Maleic anhydride solution was dropped into the aniline derivatives slowly, the reaction mixture was stirred for 3 h at rt. A lot of precipitation appeared. The precipitation was collected by filtration. The filtrate was dissolved in acetic anhydride (8 mL) and acetic acid-sodium (12 mmol) was added. The mixture was heated at 138°C for 3 h. The reaction was cooled and quenched with water. Then the aqueous solution was extracted with DCM, dried with Na_2SO_4, filtered, and the solvent was evaporated. The product was purified by silica gel column (silica gel, CH_2Cl_2).



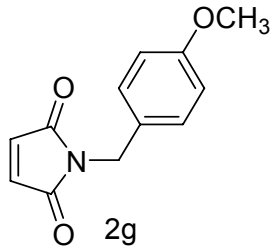
2e

Yield: 0.5 g (53.9%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.33–7.29 (m, 5H), 6.71 (s, 2H), 4.68 (s, 2H). HRMS (ESI$^+$): Calcd $C_{10}H_7NO_2$ $[M+H]^+$ m/z = 188.0706; Found m/z = 188.0704.



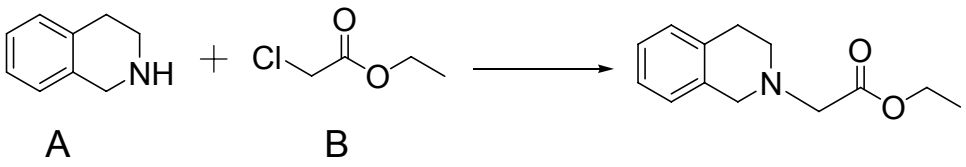
2f

Yield: 0.8 g (40.1%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.34–7.31 (m, 2H), δ = 6.99 (t, J = 8.6 Hz, 2H), 6.70 (s, 2H), 4.63 (s, 2H). HRMS (ESI$^+$): Calcd $C_{10}H_8FNO_2$ $[M+H]^+$ m/z = 206.0612; Found m/z = 206.0607.



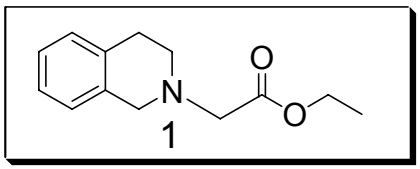
2g

Yield: 0.7 g (53.2%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.30 (d, J = 8.5 Hz, 2H), δ = 6.85 (d, J = 8.7 Hz, 2H), 6.68 (s, 2H), 4.61 (s, 2H), 3.78 (s, 3H). HRMS (ESI$^+$): Calcd $C_{10}H_7NO_2$ $[M+H]^+$ m/z = 218.0812. Found m/z = 218.0818.



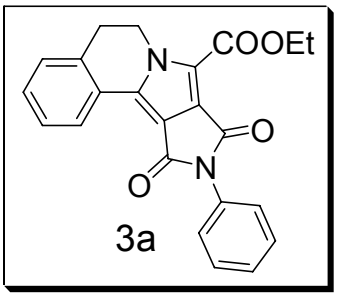
A B

A (10 mmol), **B** (11 mmol) and Na_2CO_3 (20 mmol) was dissolved in THF (50 mL), the mixture was stirred at room temperature for 24 h. When 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 mixture was purified by column chromatography (silica gel, CH_2Cl_2).

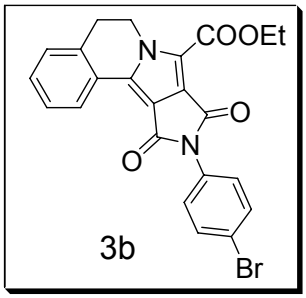


1

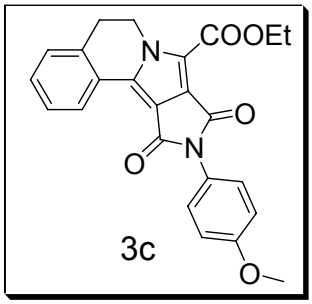
Oily product. Yield: 0.5 g (73.8%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.08–7.03 (m, 3H), 6.96 (d, J = 5.2 Hz, 1H), 4.20–4.15 (m, 2H), 3.76 (s, 2H), 3.37 (s, 2H), 2.89–2.83 (m, 4H), 1.27–1.23 (m, 3H). HRMS (ESI$^+$): Calcd $C_{13}H_{17}NO_2$ $[M+H]^+$ m/z = 220.1559; Found m/z = 220.1508.



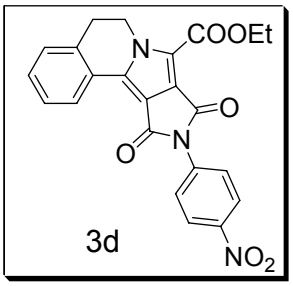
Yield: 30.8 mg (80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.60 (d, J = 7.2 Hz, 1H), 7.29–7.51 (m, 8H), 4.79 (t, J = 6.9 Hz, 2H), 4.47–4.41 (m, 2H), 3.19 (t, J = 6.4 Hz, 2H), 1.47 (t, J = 7.2 Hz, 3H). HRMS (EI$^+$): Calcd $C_{23}H_{17}N_2O_4$ $[M+H]^+$ m/z = 387.1399. Found m/z = 387.1329.



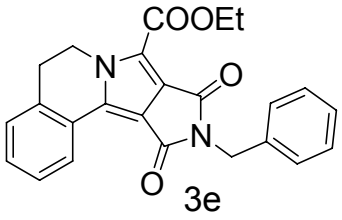
Yield: 35.7 mg (77%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.57 (t, J = 6.0 Hz, 1H), 7.62 (d, J = 8.8 Hz, 2H), 7.42–7.39 (m, 2H), 7.31 (t, J = 4.8 Hz, 2H), 4.78 (t, J =2.8 Hz, 2H), 4.47–4.41 (m, 2H), 3.19 (t, J = 7.2 Hz, 2H), 1.47 (t, J = 7.2 Hz, 3H). HRMS (EI+): Calcd $C_{23}H_{17}N_2O_4Br$ $[M+H]^+$ m/z = 465.0444. Found m/z = 465.0429.



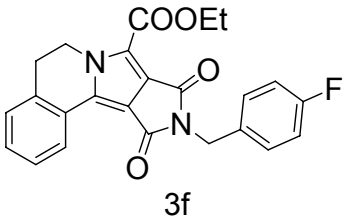
Yield: 31.2 mg (75%). ^{1}H NMR (400 MHz, $CDCl_3$) δ= 8.59 (d, J = 7.0 Hz, 1H), 7.43–7.01 (m, 5H), 7.01 (d, J = 9.0 Hz, 2H), 4.78 (t, J =6.8 Hz, 2H), 4.46–4.40 (m, 2H), 3.84 (s, 3H), 3.18 (t, J =6.8 Hz, 2H), 1.47 (t, J = 7.2 Hz, 3H). HRMS (EI$^+$): Calcd $C_{24}H_{20}N_2O_5$ $[M+H]^+$ m/z = 417.1445. Found m/z = 417.1454.



Yield: 31.0 mg (72%). The compound was verified by comparison with a reported result.[2] HRMS (EI$^+$): Calcd $C_{24}H_{20}N_2O_5$ [M$^+$] m/z = 432.1190. Found m/z = 432.1199.



Yield: 27.2 mg (68%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.54 (d, J = 6.9 Hz, 1H), δ = 7.45–7.29 (m, 8H), 4.80 (s, 2H), δ = 4.72 (d, J = 6.9 Hz, 2H), δ = 4.46–4.40 (m, 2H), δ = 3.14 (d, J = 6.7 Hz, 2H), 1.48 (t, J = 7.2 Hz, 3H). HRMS (ESI$^+$): Calcd $C_{10}H_7NO_2$ [M+H]$^+$ m/z = 401.1496. Found m/z = 401.1487.



Yield: 25 mg (60%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.53 (d, J = 7.5 Hz, 1H), δ = 7.41–7.24 (m, 5H), δ = 6.84 (d, J = 7.6 Hz, 2H), δ = 4.73–4.69 (m, 4H), δ = 4.45–4.40 (m, 2H), δ = 3.76 (s, 3H), δ = 3.13 (t, J = 6.6 Hz, 2H), 1.48 (t, J = 7.0 Hz, 3H). HRMS (ESI$^+$): Calcd $C_{10}H_7NO_2$ [M+H]$^+$ m/z = 419.1402, found m/z = 419.1391; [M+Na]$^+$ m/z = 441.1227, found m/z = 441.1209.

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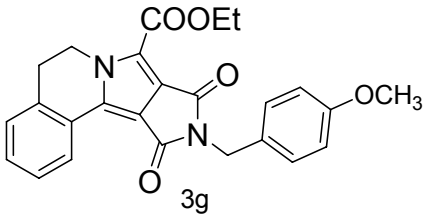
2 L. Huang and J. Zhao, *Chem. Commun.*, 2013, **49**, 3751–3753.



3g

Yield: 22 mg (51%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.53 (d, J = 6.5 Hz, 1H), δ = 7.44–7.35 (m, 8H), δ = 6.98 (t, J = 8.8 Hz, 2H), δ = 4.76–4.70 (m, 4H), δ = 4.45–4.41 (m, 2H), δ = 3.14 (t, J = 6.5 Hz, 2H), 1.48 (t, J = 7.2 Hz, 3H). HRMS (ESI$^+$): Calcd $C_{10}H_7NO_2$ $[M+H]^+$ m/z = 431.1601, found m/z = 431.1591; $[M+Na]^+$ m/z = 453.1426, found m/z = 453.1405.

2. NMR and HRMS spectra

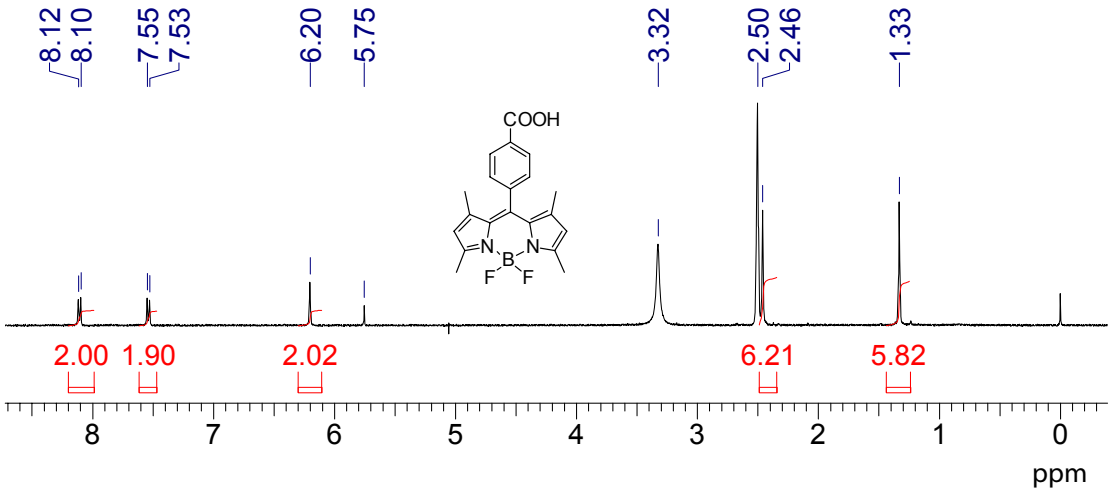


Fig. S1 ^{1}H NMR of **2** (400 MHz. DMSO-d_6).

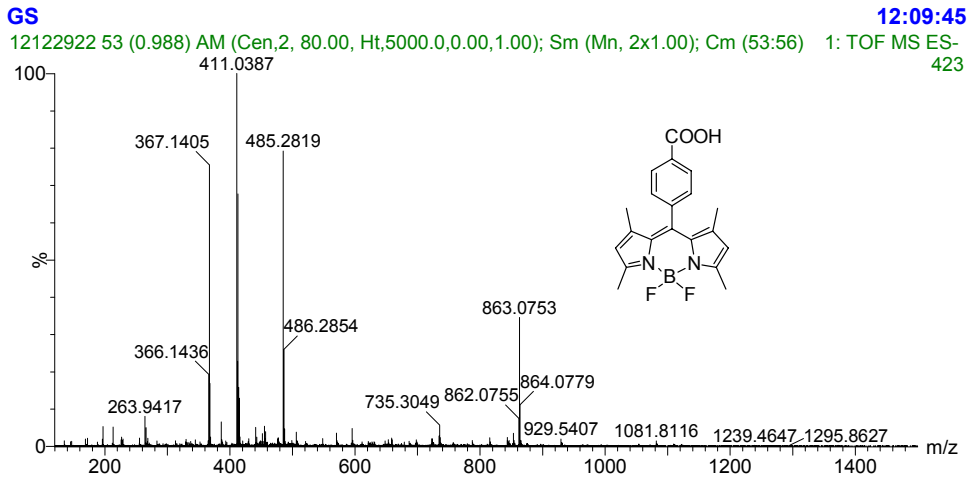


Fig. S2 TOF HRMS ESI⁻ of **2**.

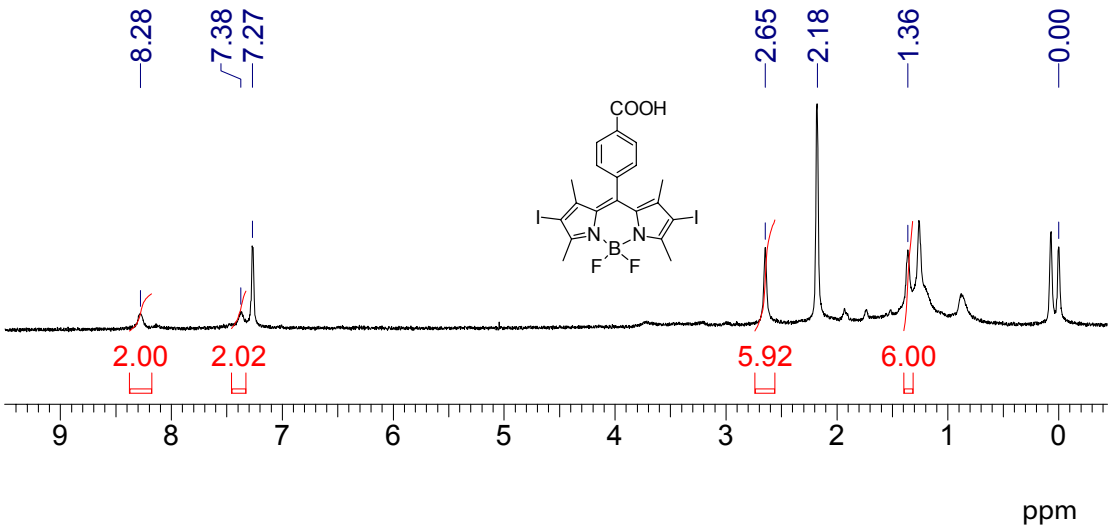


Fig. S3 ^{1}H NMR of **3** (400 MHz. In $CDCl_3$).

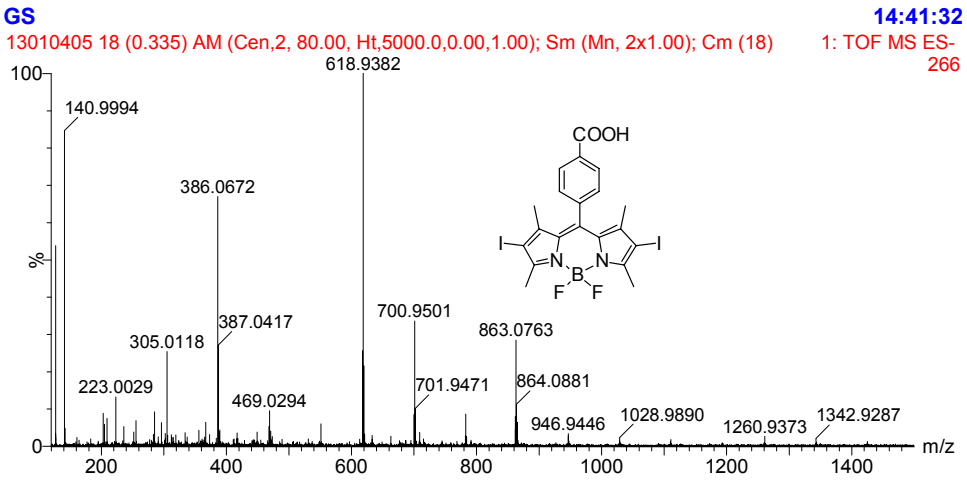


Fig. S4 TOF HRMS ESI$^-$ of **3**.

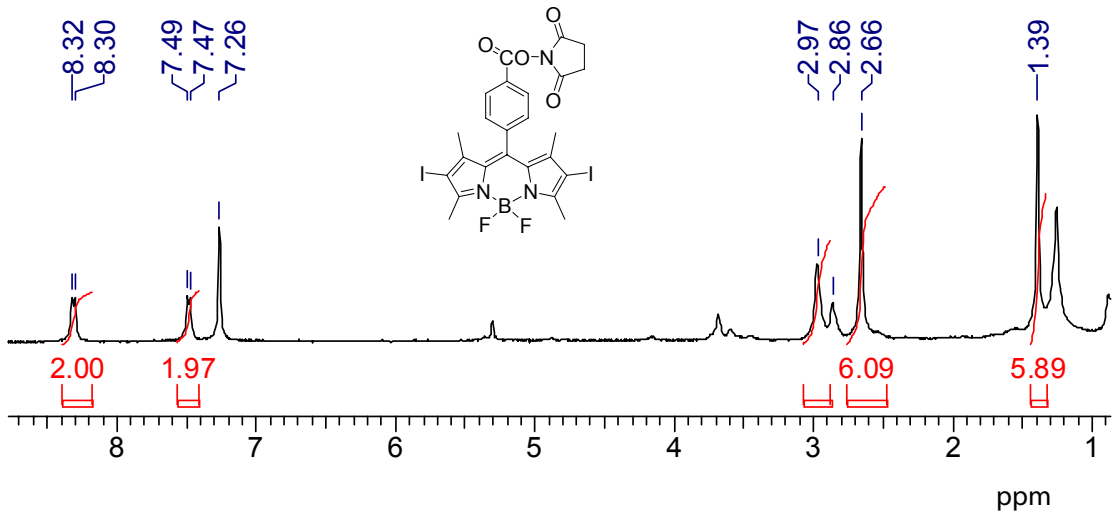


Fig. S5 ^{1}H NMR of **4** (400 MHz, in $CDCl_3$).

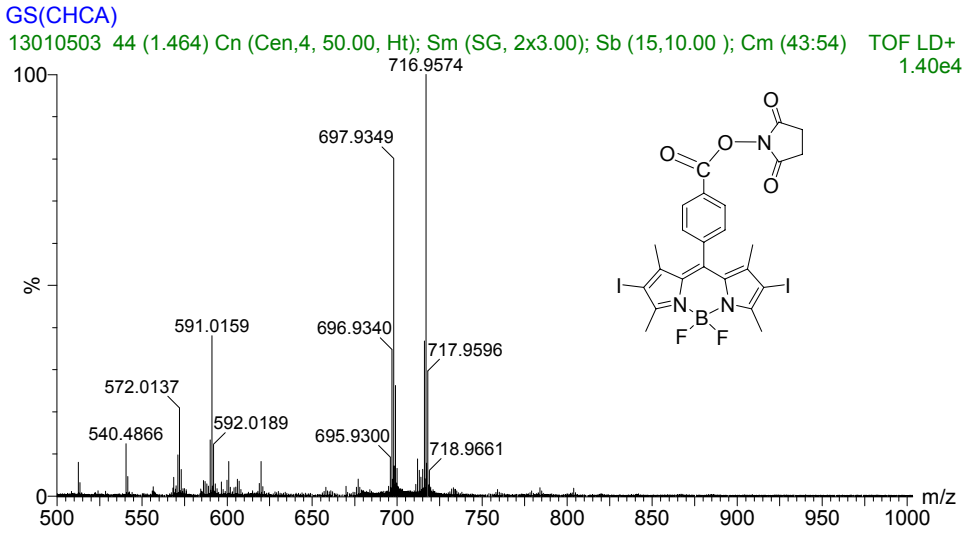


Fig. S6 TOF HRMS (MALDI) ESI of **4**.

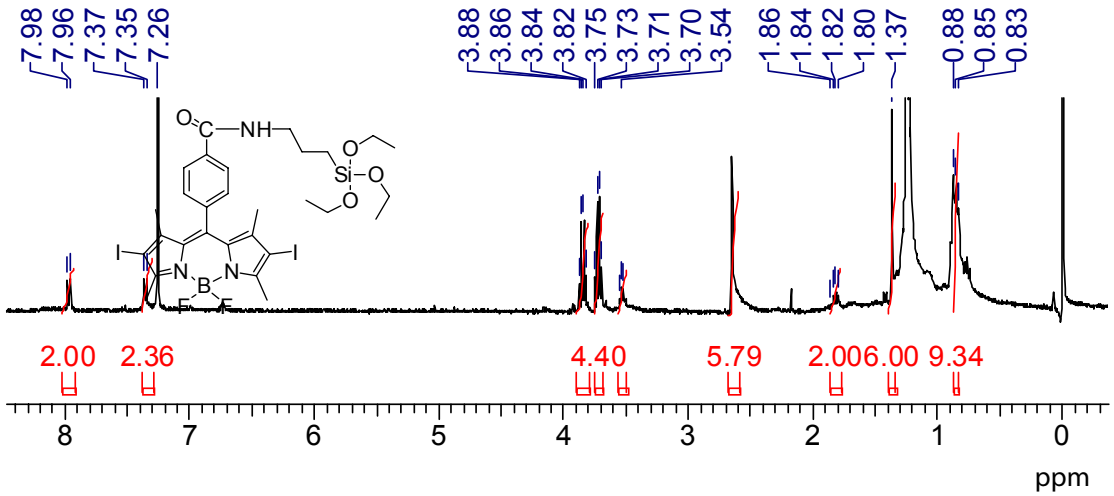


Fig. S7 ^{1}H NMR of **5** (400 MHz. In $CDCl_3$).

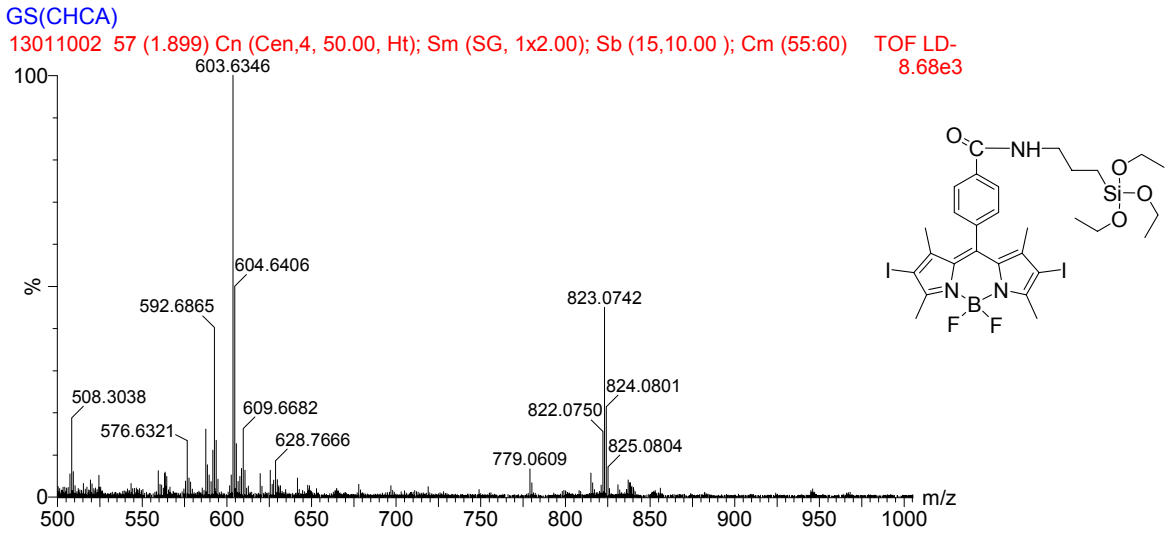


Fig. S8 TOF HRMS (MALDI) ESI of **5**.

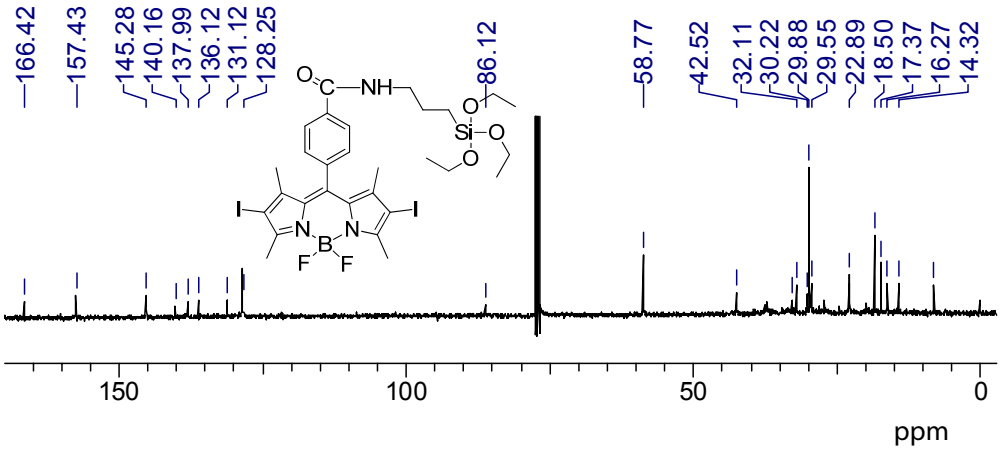


Fig. S9 ^{13}C NMR of **5** (100 MHz. In $CDCl_3$).

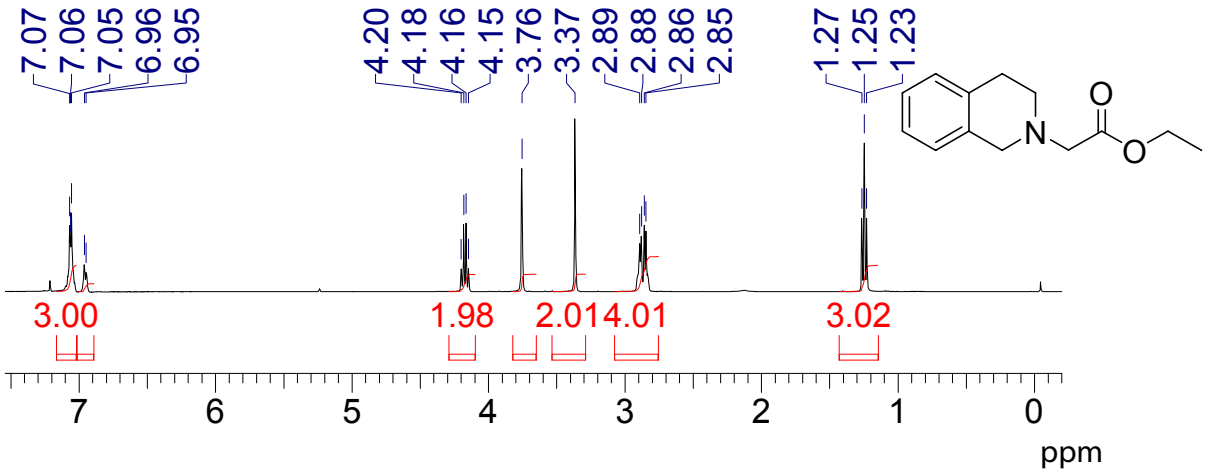


Fig. S10 ^{1}H NMR of **1** (400 MHz. In $CDCl_3$).

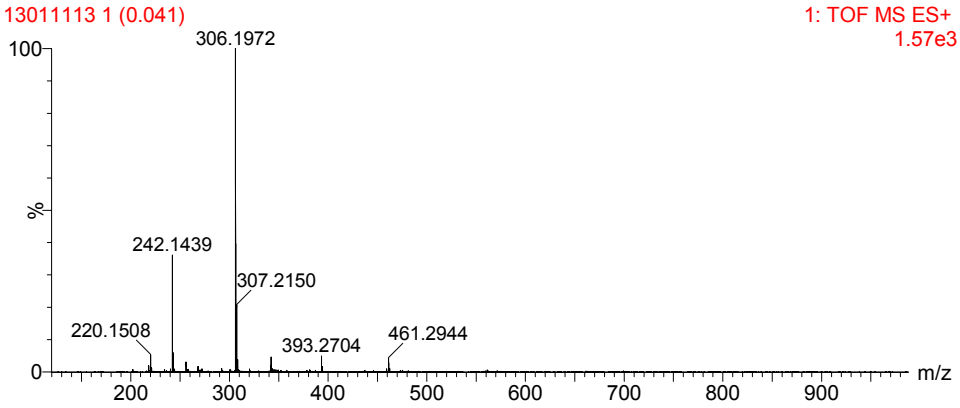


Fig. S11 TOF HRMS ESI^{+} of **1.**

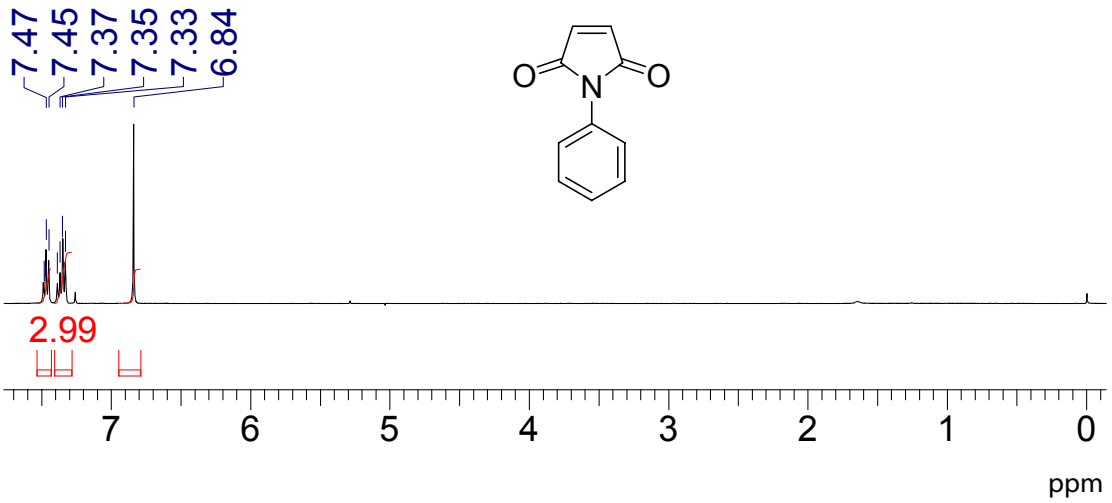


Fig. S12 ^{1}H NMR of **2a** (400 MHz. In $CDCl_3$).

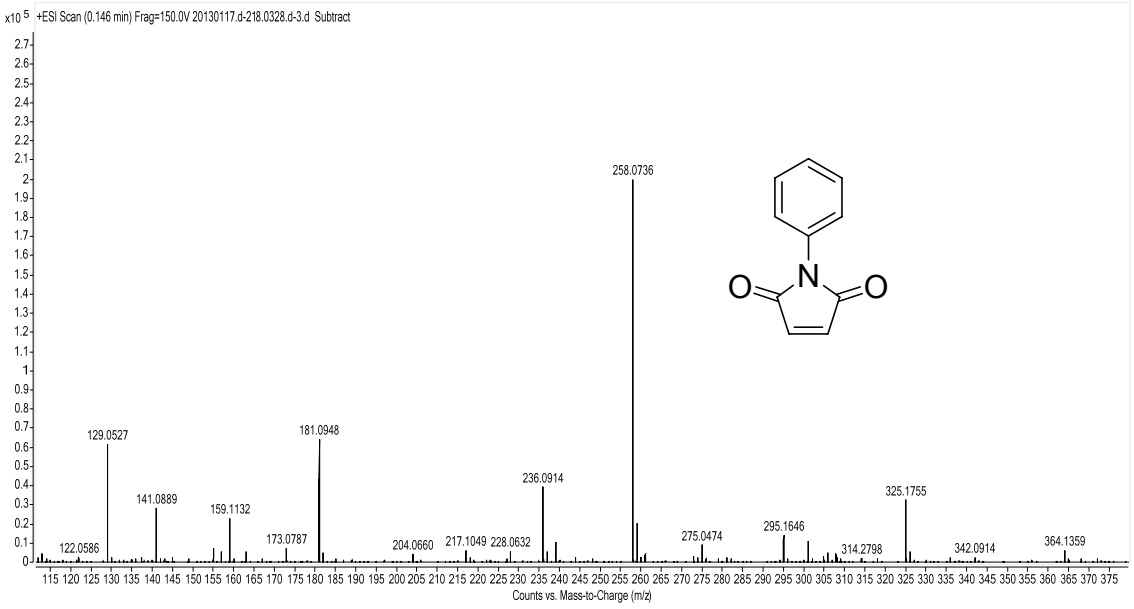


Fig. S13 TOF HRMS ESI^{+} of **2a**.

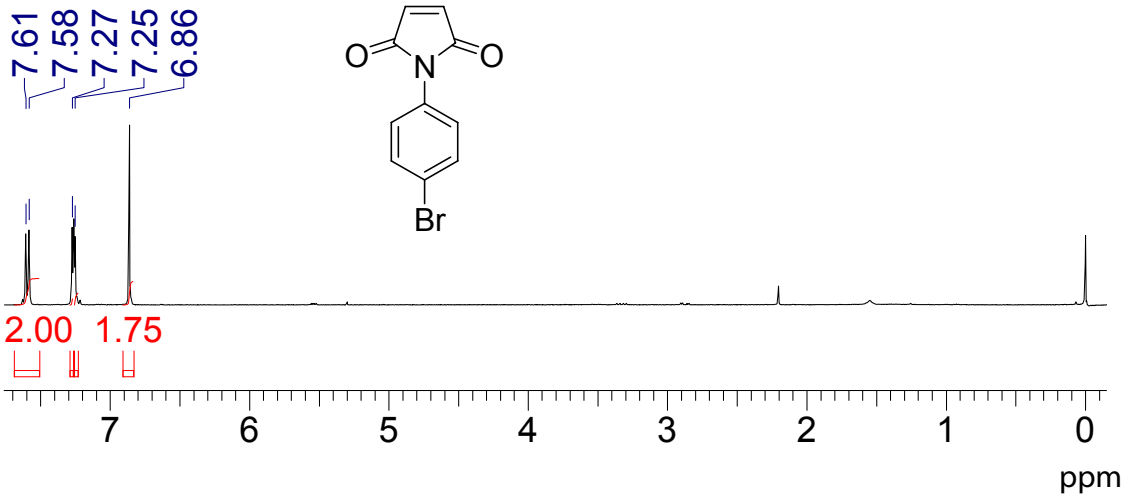


Fig. S14 ^{1}H NMR of **2b** in $CDCl_3$ (400 MHz).

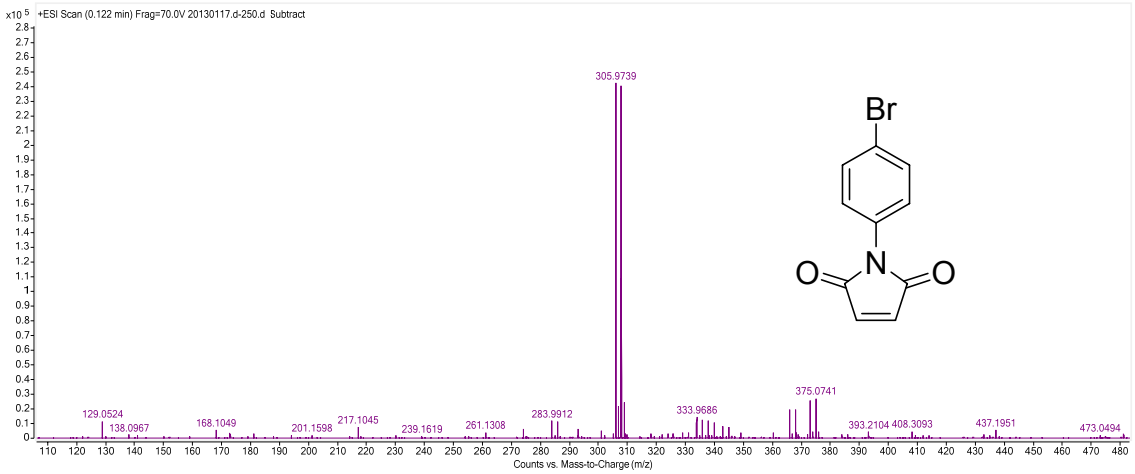


Fig. S15 TOF HRMS ESI^{+} of **2b.**

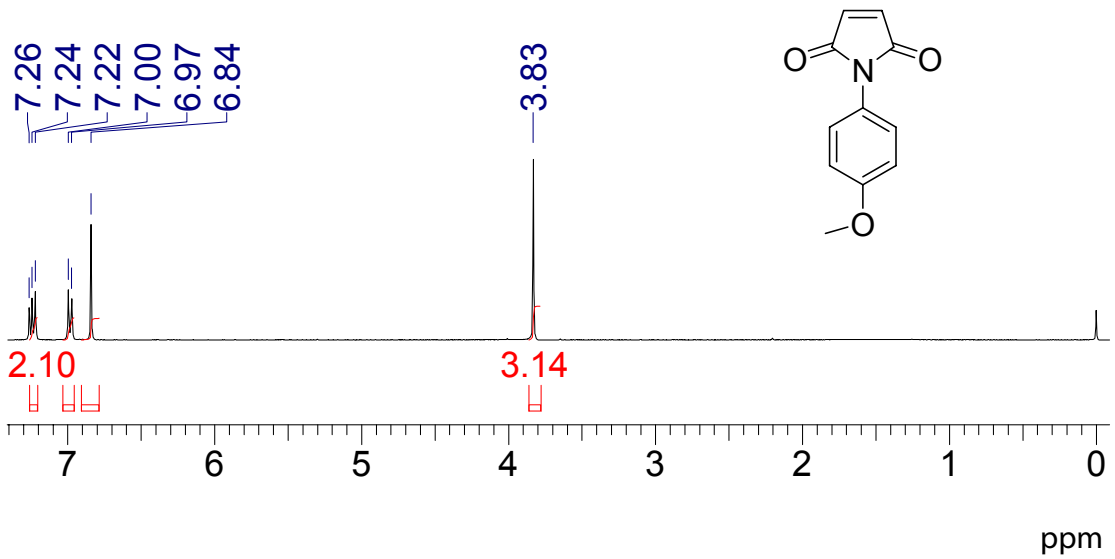


Fig. S16 ^{1}H NMR of **2c** (400 MHz. In $CDCl_3$).

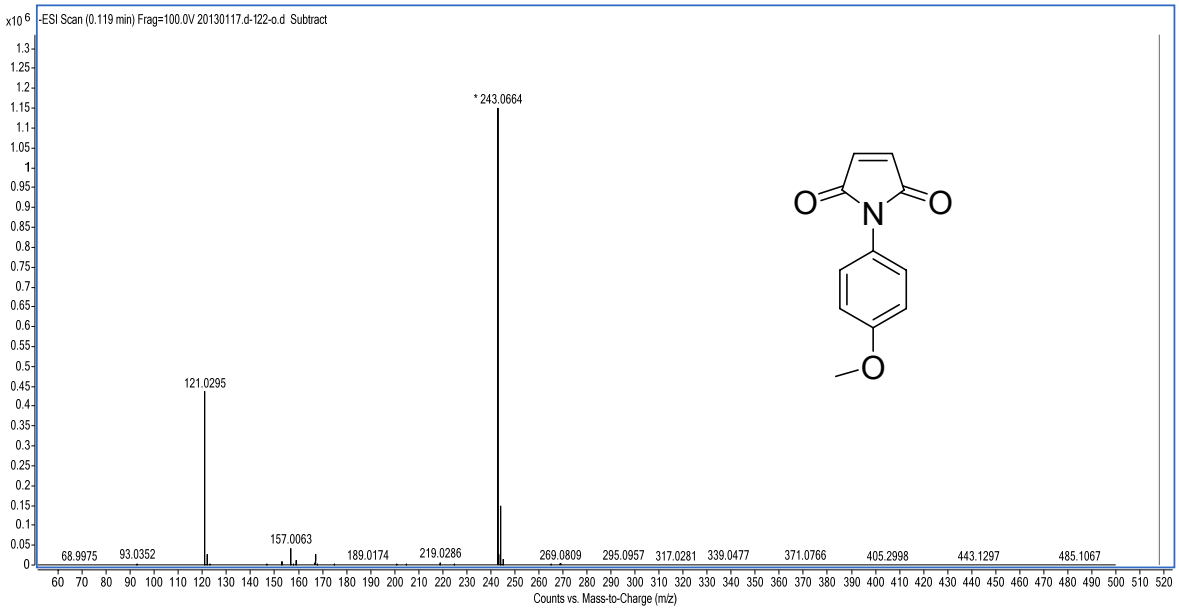


Fig. S17 TOF HRMS ESI^{+} of **2c**.

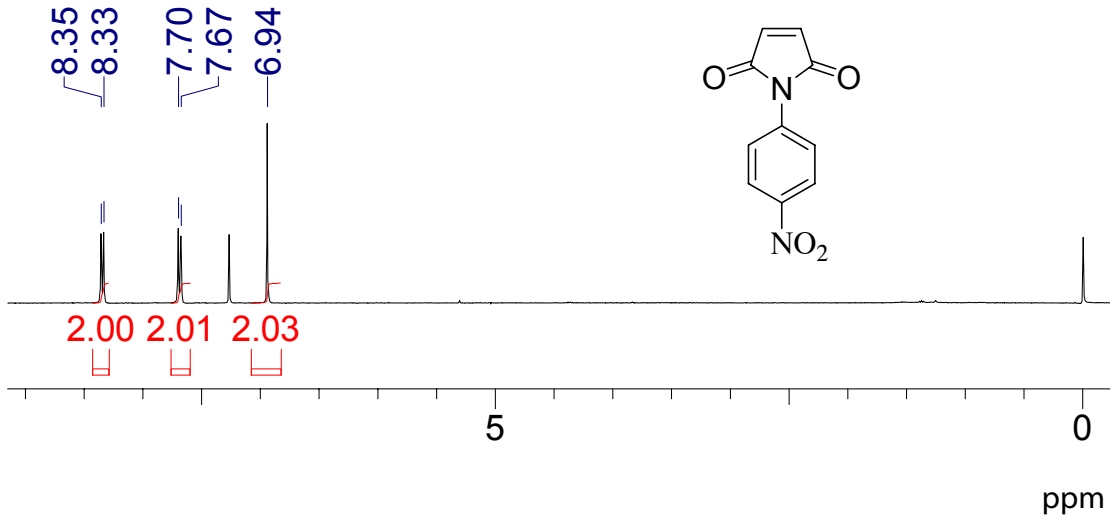


Fig. S18 ^{1}H NMR of **2d** (400 MHz. In $CDCl_3$).

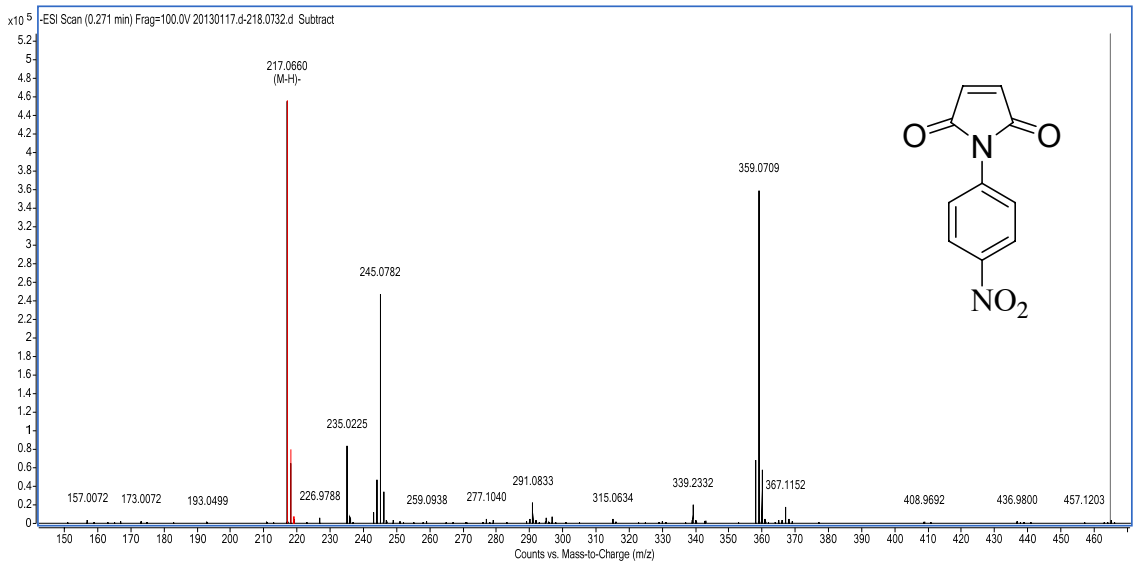


Fig. S19 TOF HRMS ESI^{+} of **2d.**

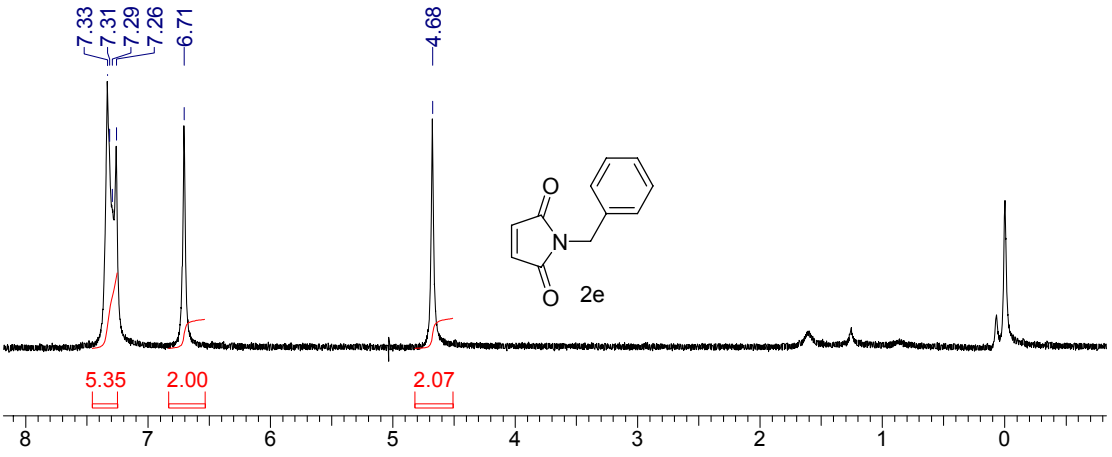


Fig. S20 ^{1}H NMR of **2e** (400 MHz. $CDCl_3$).

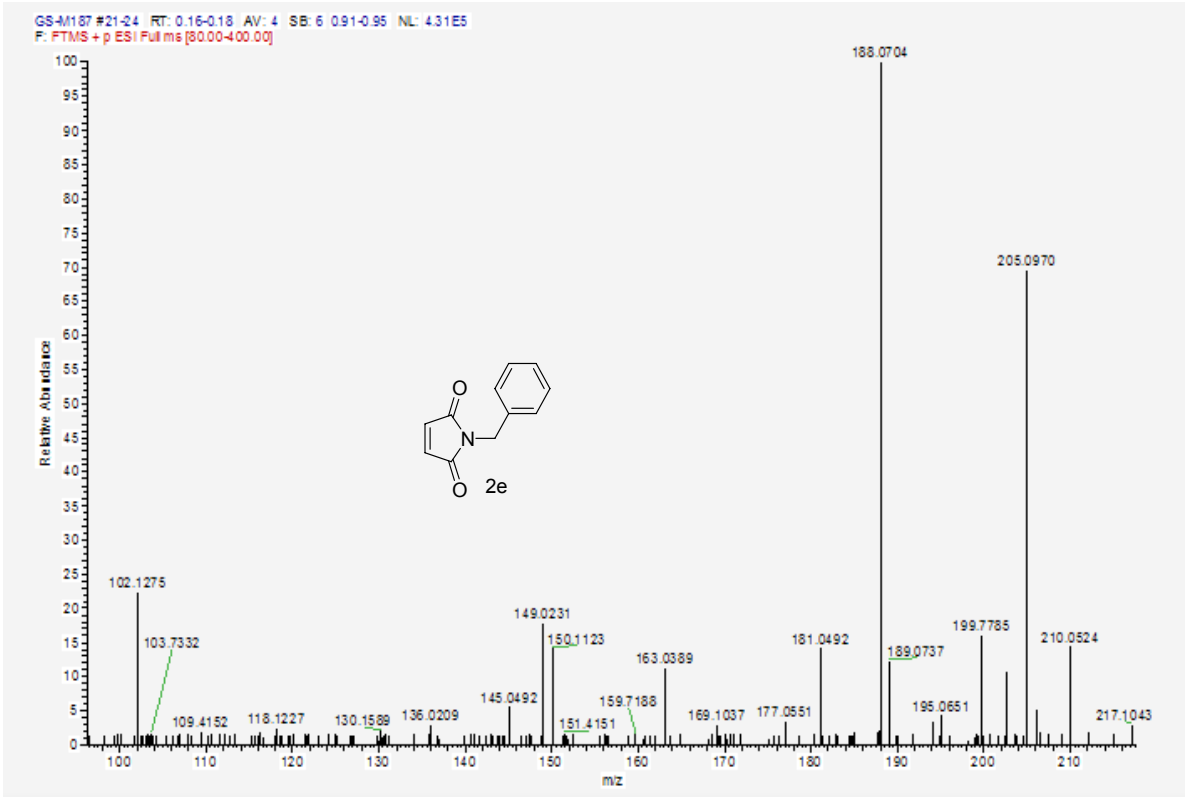


Fig. S21 TOF HRMS ESI^{+} of **2e**.

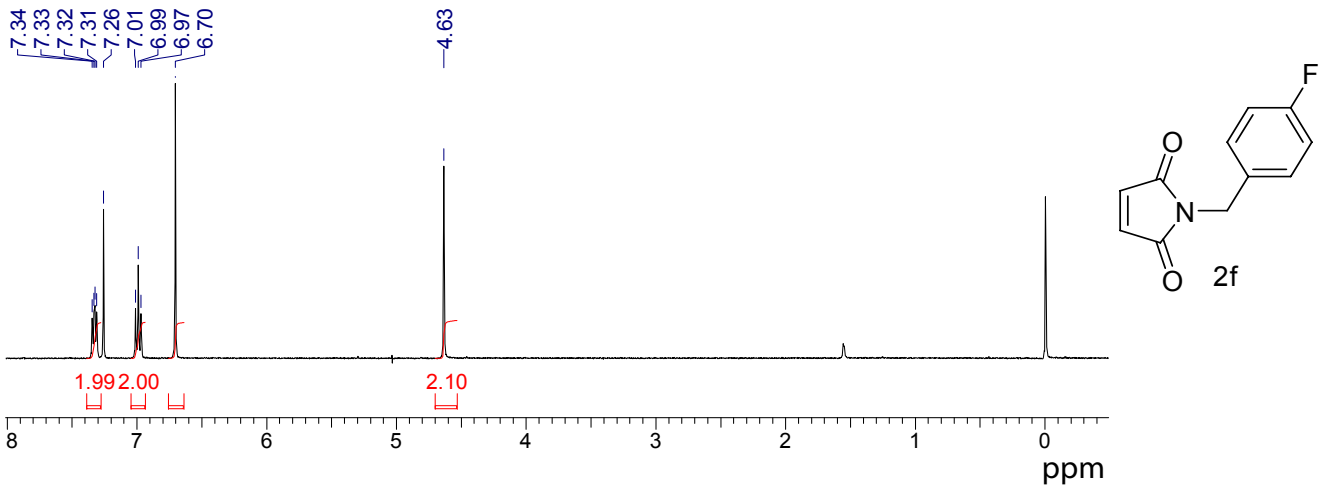


Fig. S22 ^{1}H NMR of **2f** (400 MHz. $CDCl_3$).

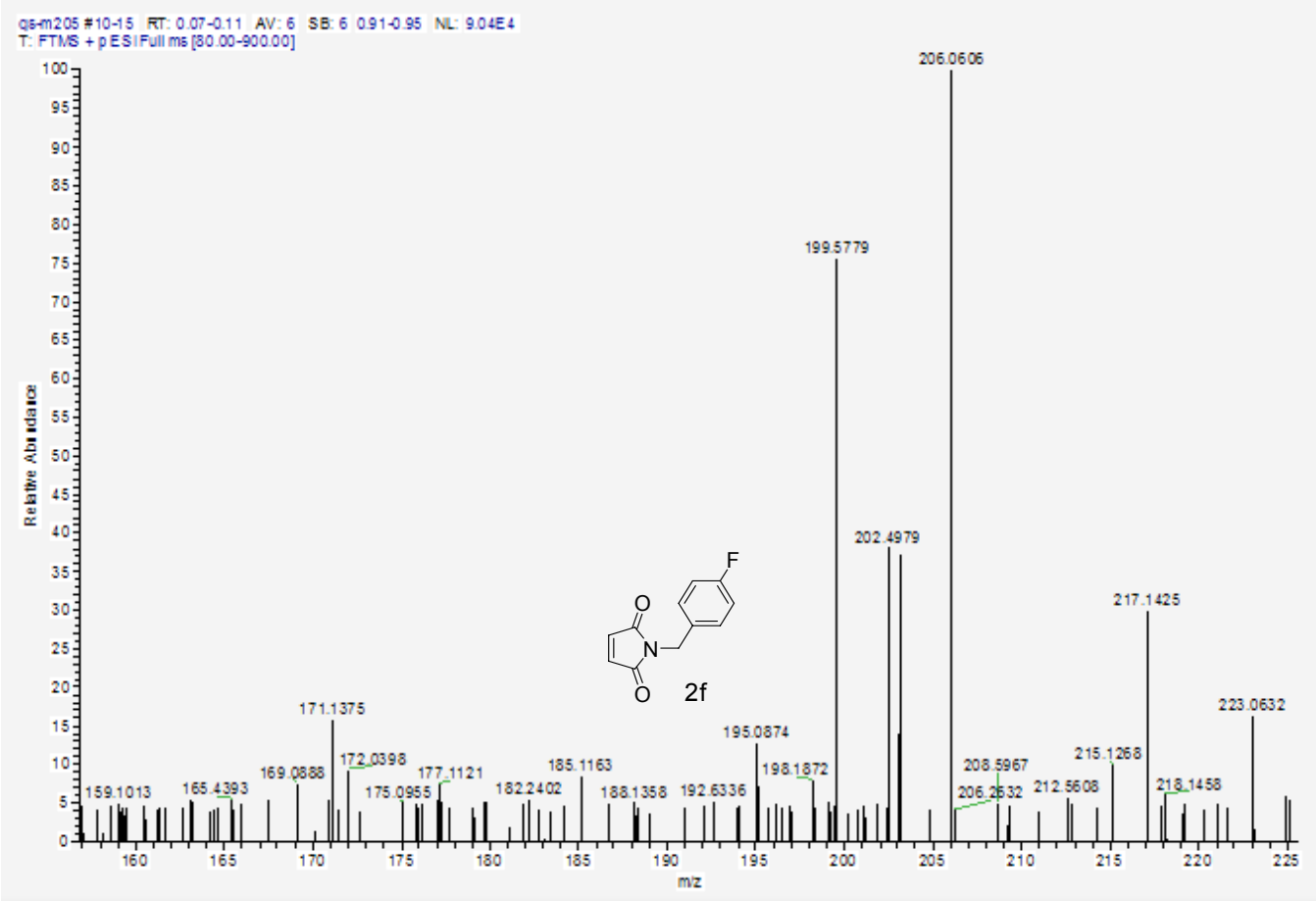


Fig. S23 TOF HRMS ESI^{+} of **2f**.

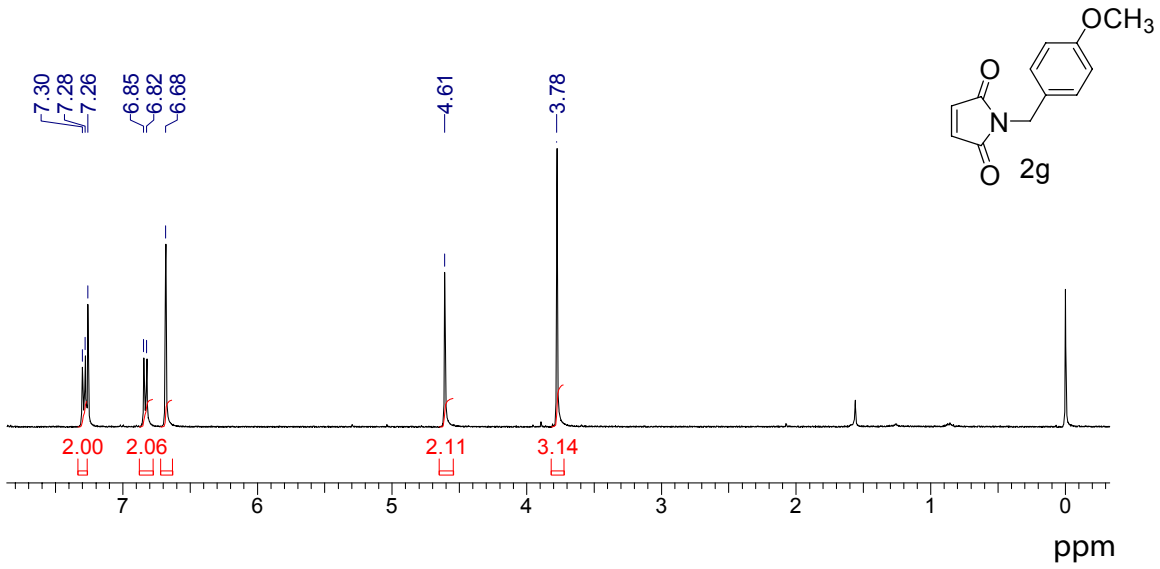


Fig. S24 ^{1}H NMR of **2g** (400 MHz. $CDCl_3$).

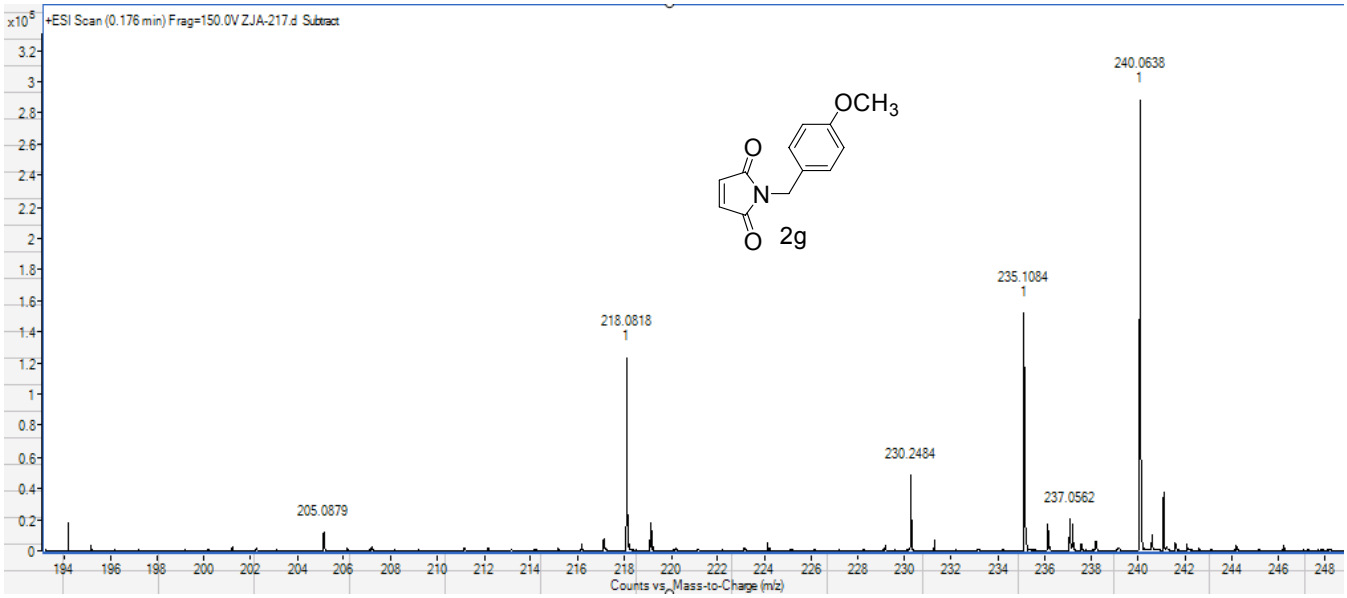


Fig. S25 TOF HRMS ESI^{+} of **2g**.

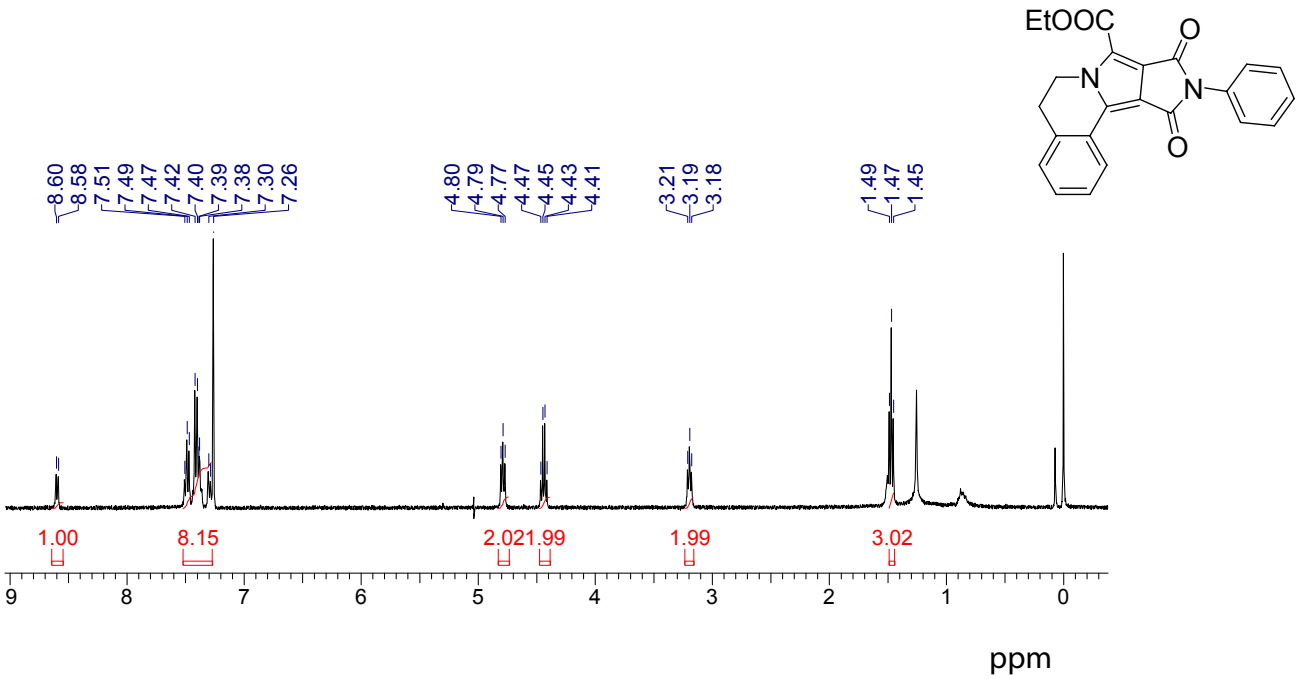


Fig. S26 ^{1}H NMR of **3a** (400 MHz. $CDCl_3$).

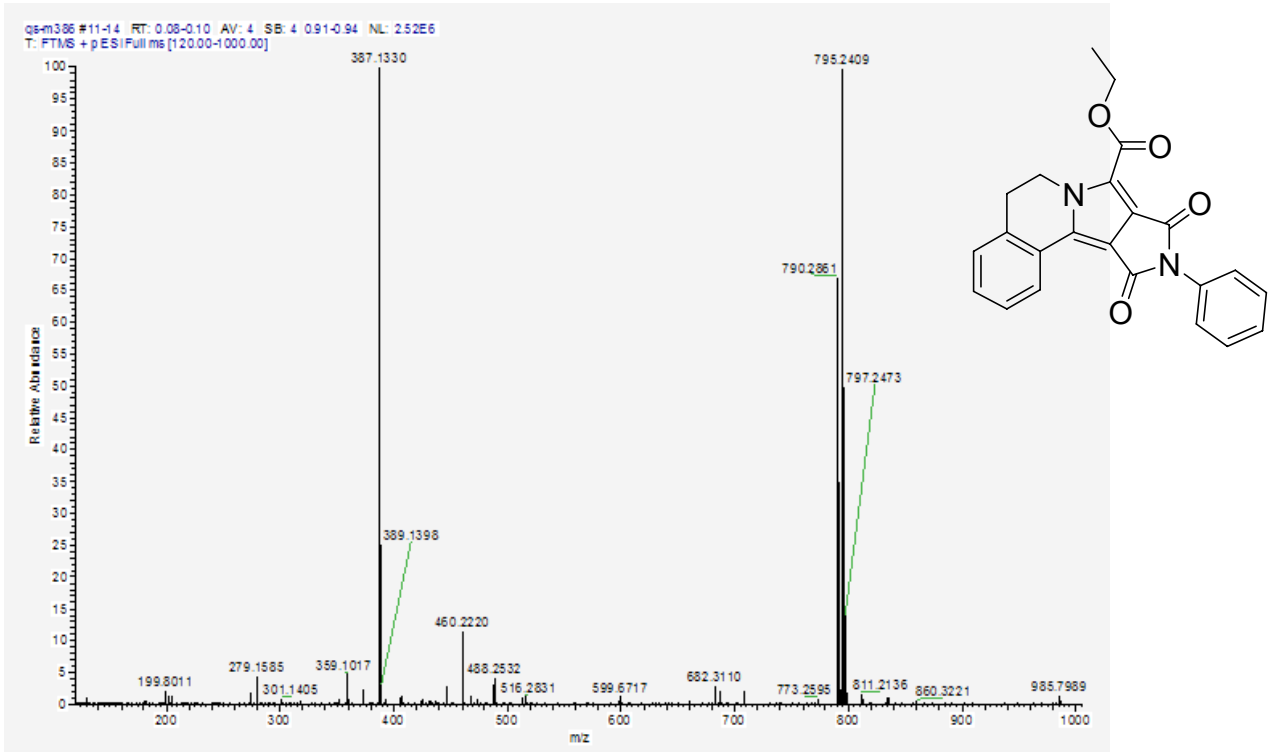


Fig. S27 TOF HRMS EI^{+} of **3a**.

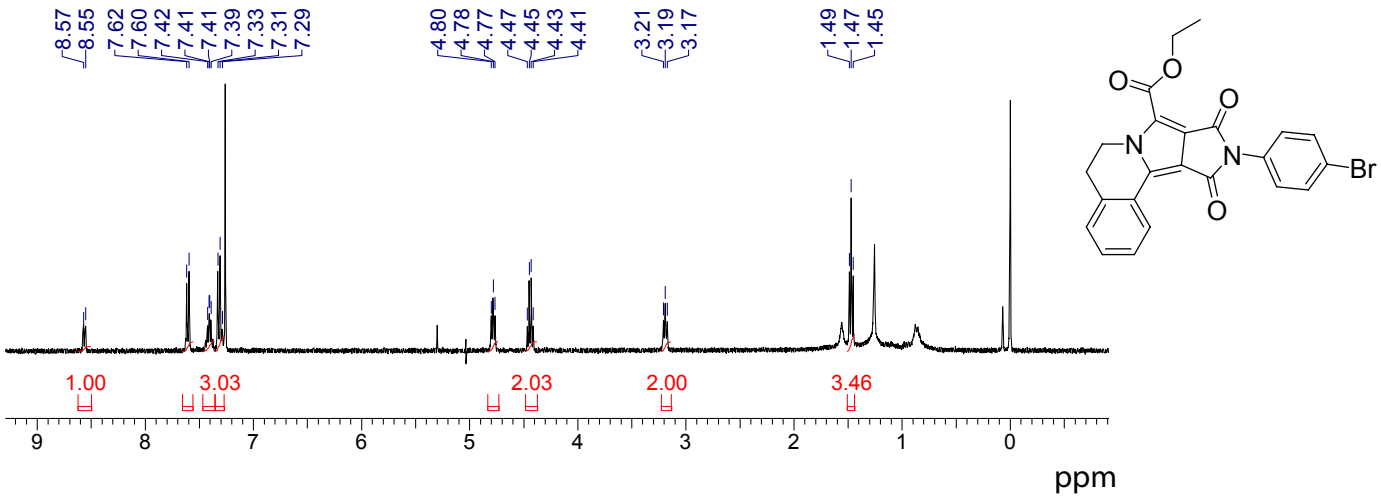


Fig. S28 ^{1}H NMR of **3b** (400 MHz. $CDCl_3$).

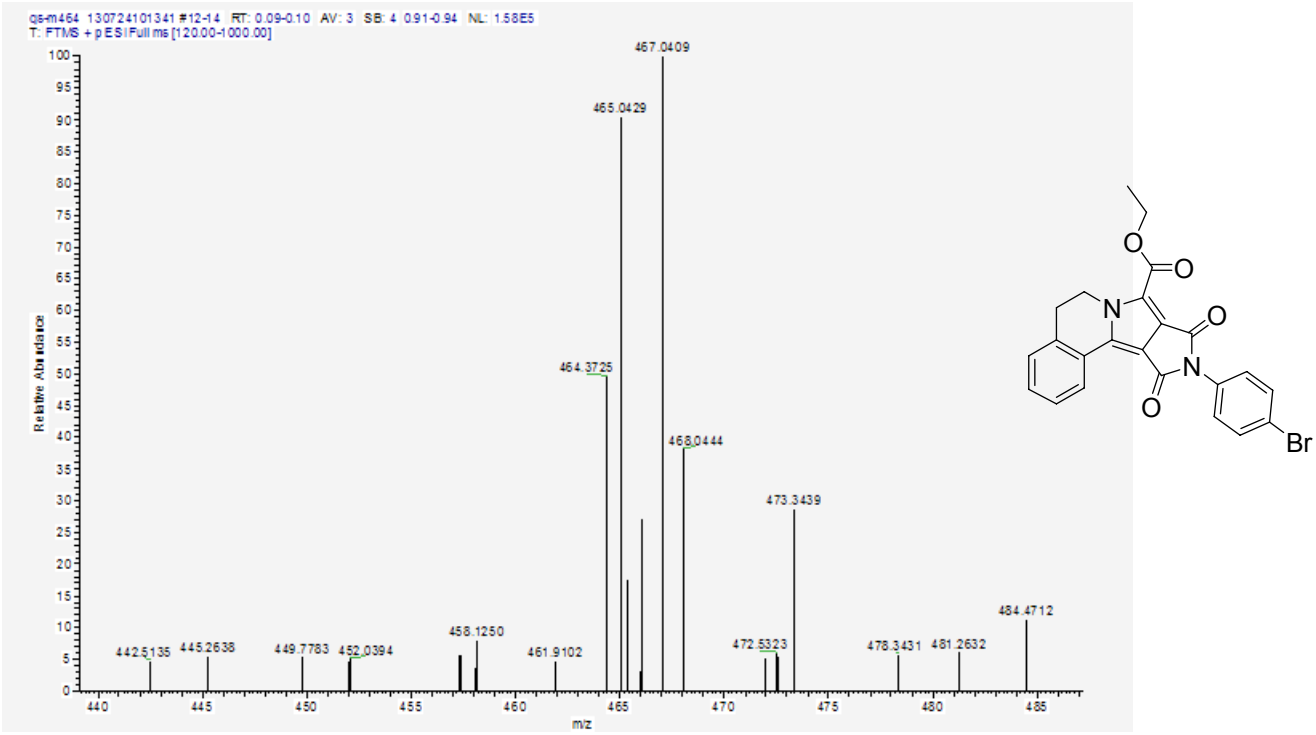


Fig. S29 TOF HRMS EI^{+} of **3b**.

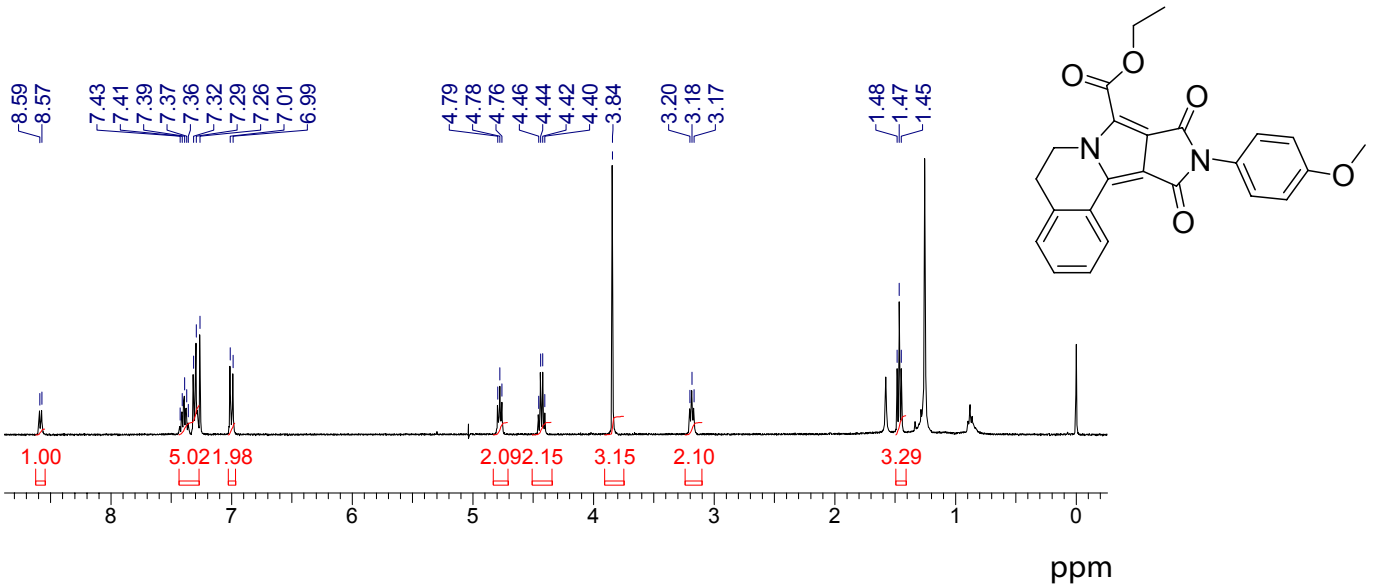


Fig. S30 ^{1}H NMR of **3c** (400 MHz. $CDCl_3$).

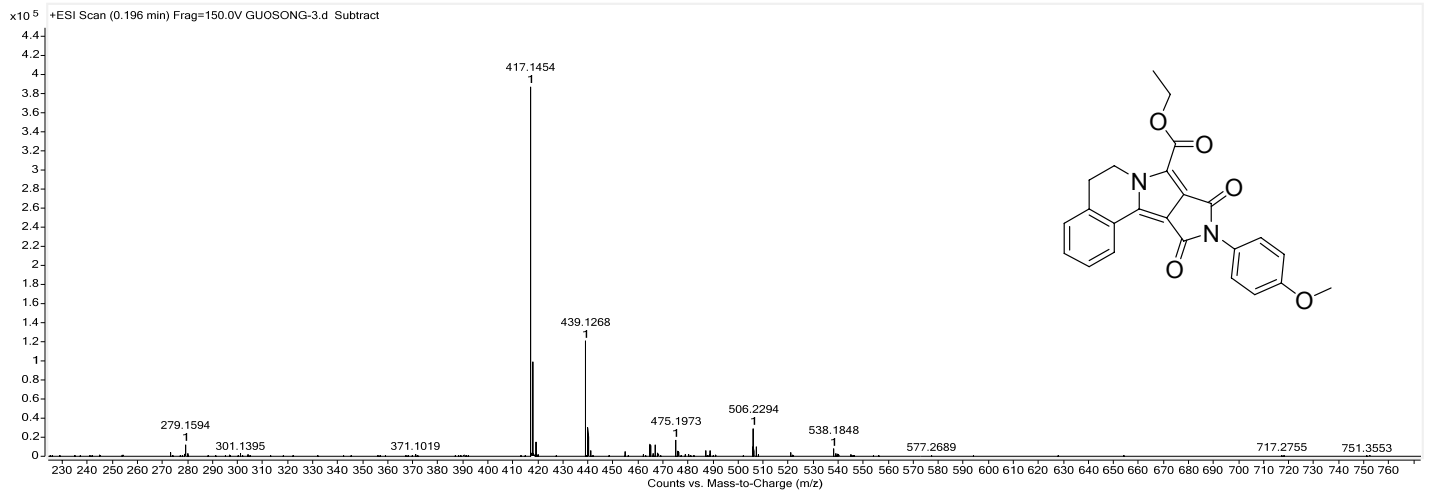


Fig. S31 TOF HRMS EI^{+} of **3c**.

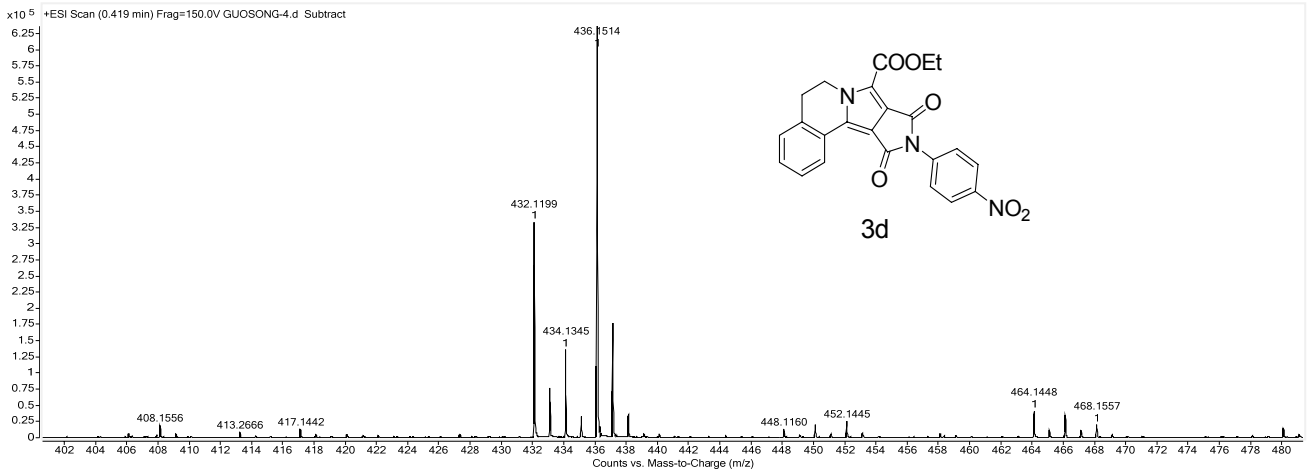


Fig. S32 TOF HRMS EI⁺ of **3d**.

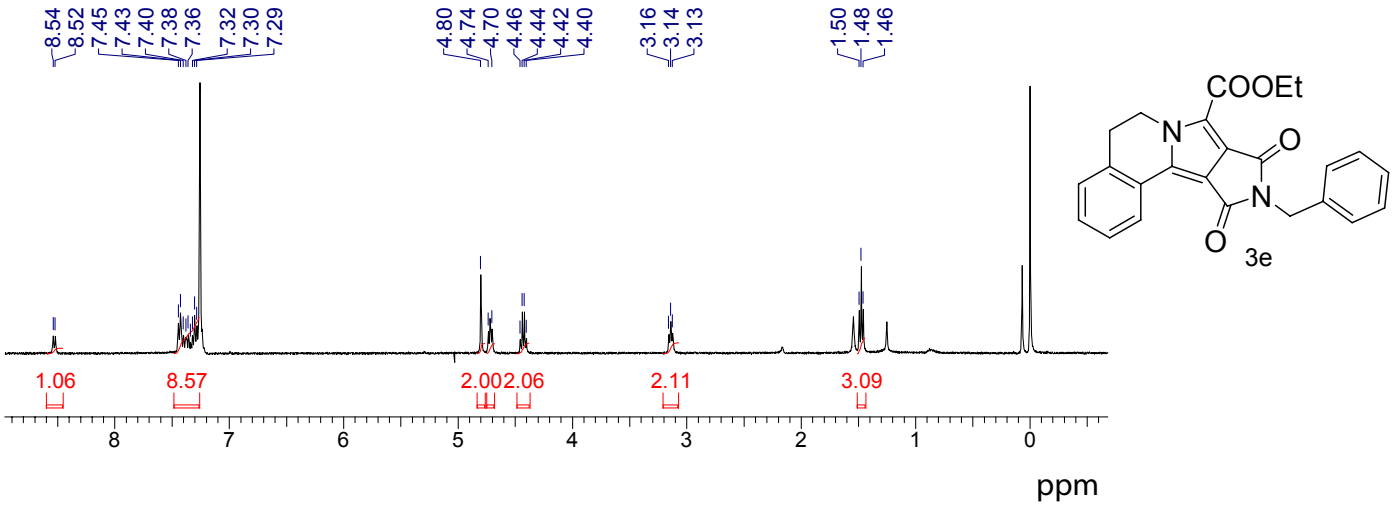


Fig. S33 ^{1}H NMR of **3e** in $CDCl_3$ (400 MHz).

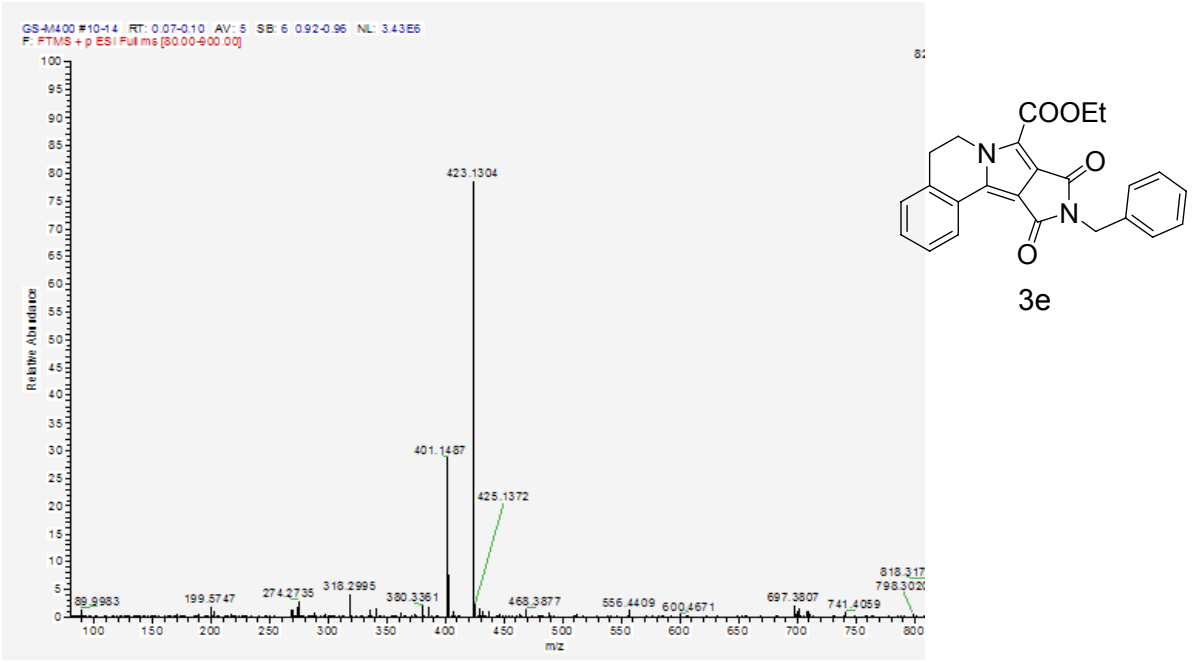


Fig. S34 TOF HRMS EI$^+$ of **3e**.

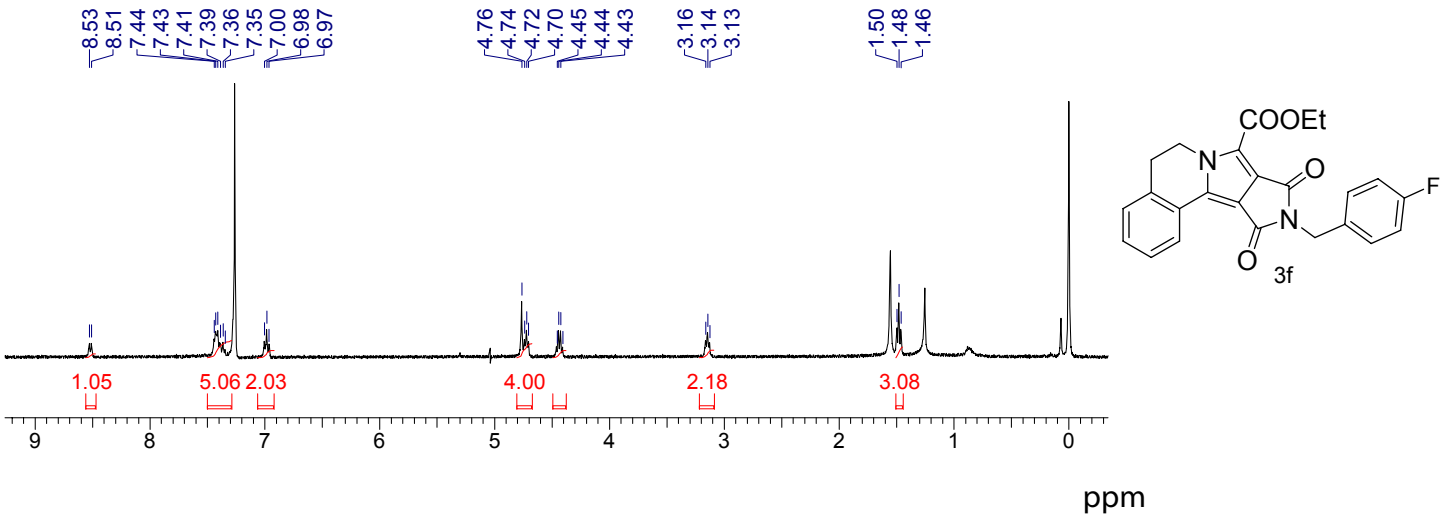


Fig. S35 ^{1}H NMR of **3f** in $CDCl_3$ (400 MHz).

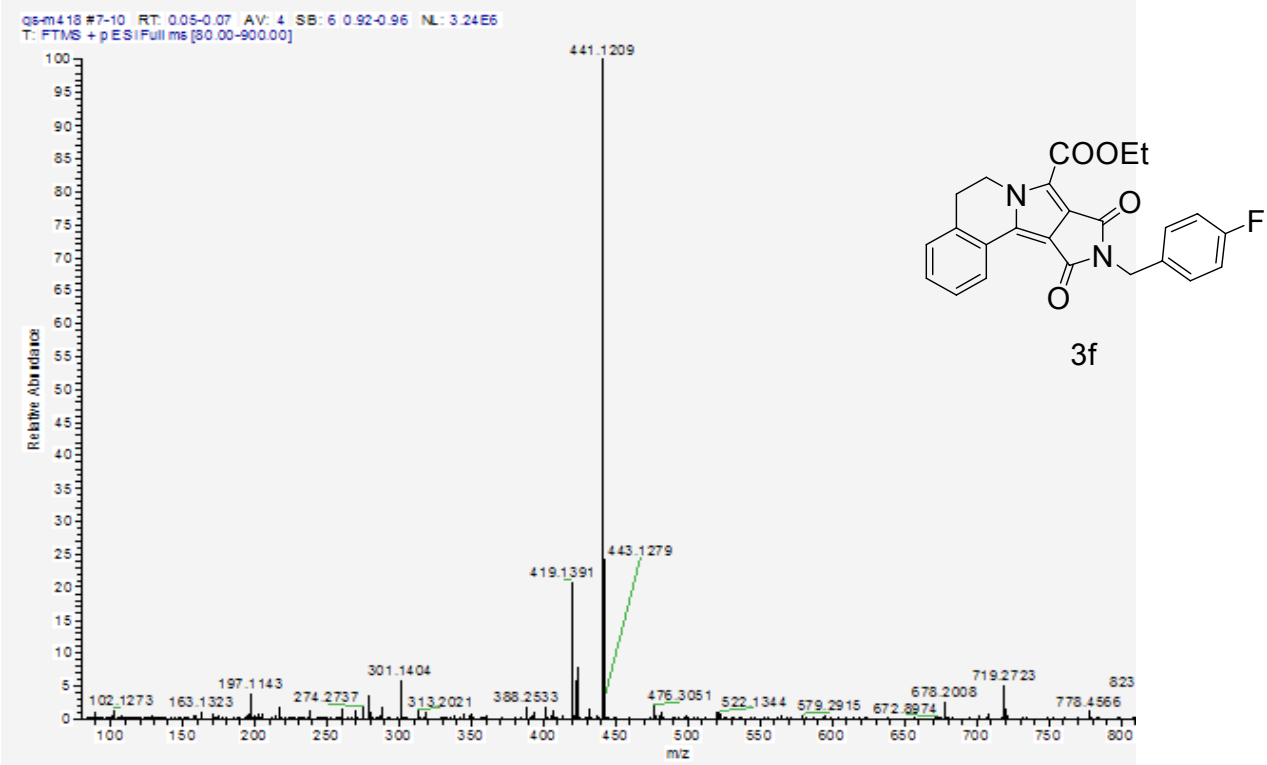


Fig. S36 TOF HRMS ESI$^+$ of **3f**.

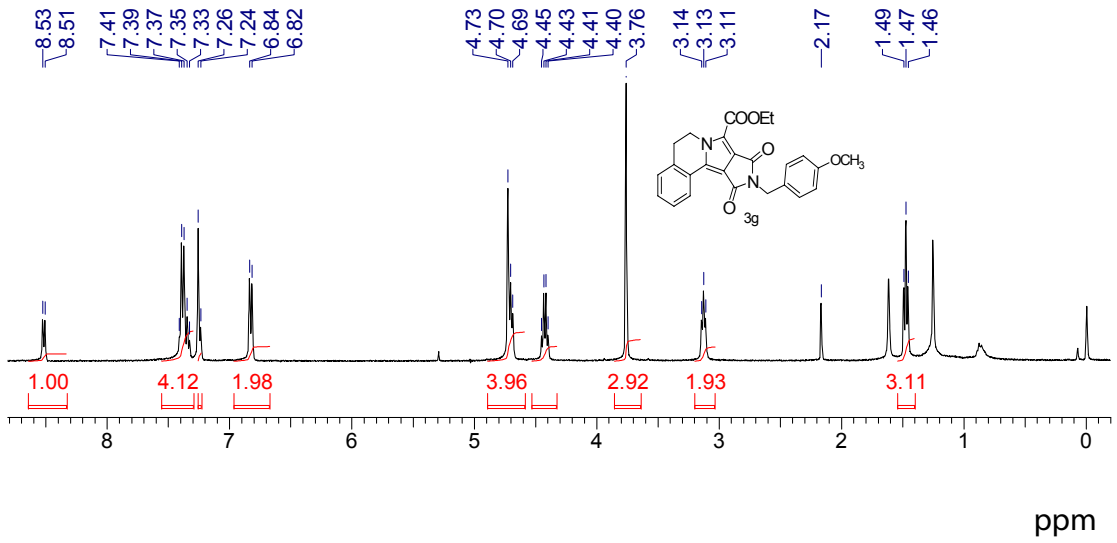


Fig. S37 ^{1}H NMR of **3g** in $CDCl_3$ (400 MHz).

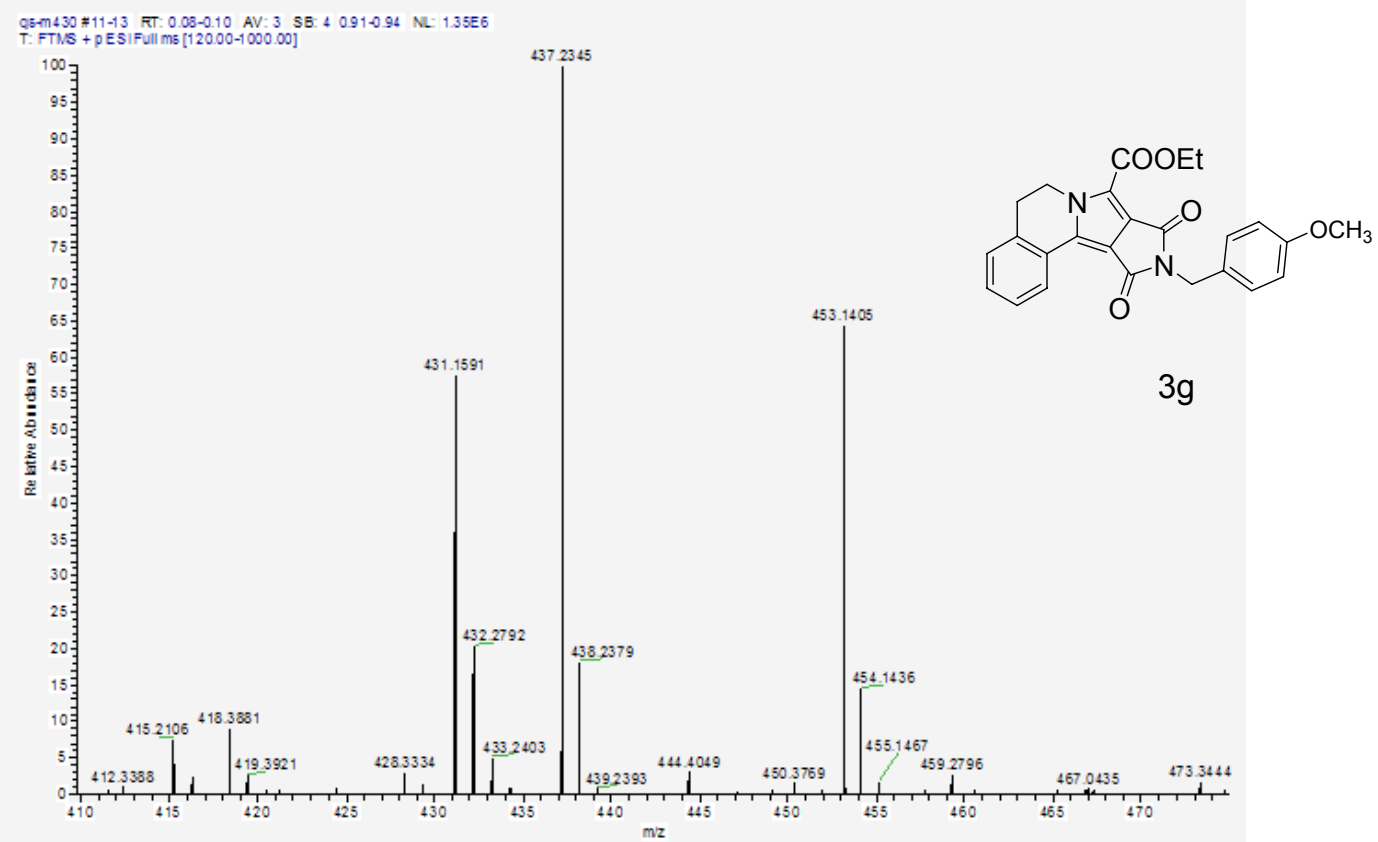


Fig. S38 TOF HRMS ESI+ of **3g**.

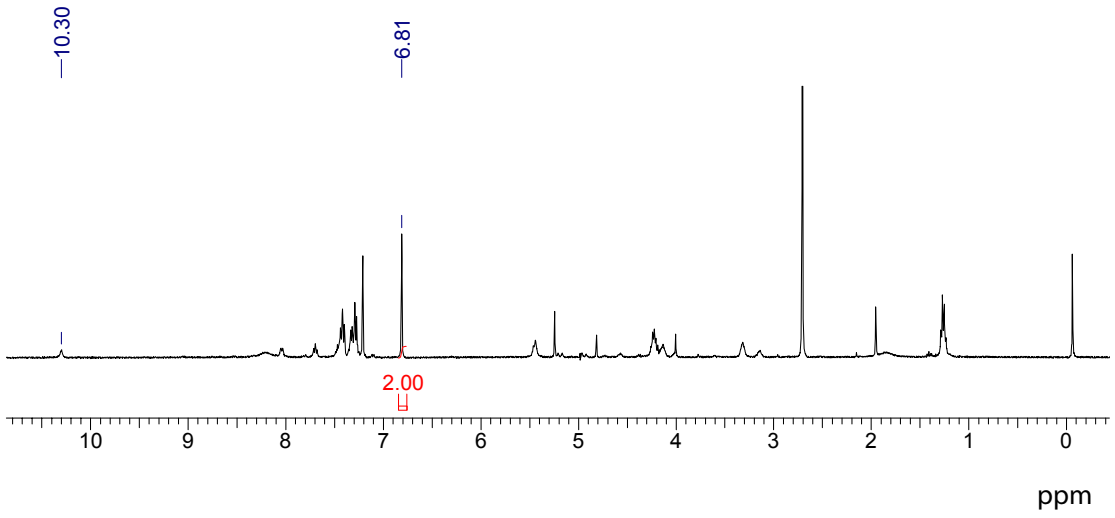


Fig. S39 ^{1}H NMR of reaction solution after 1.5 h irradiation, no catalysis, 100 mw/m^2, (400 MHz, $CDCl_3$). Reaction conditions: **1a** (0.12 mmol), **2a** (0.10 mmol), NBS (1.2 equiv).

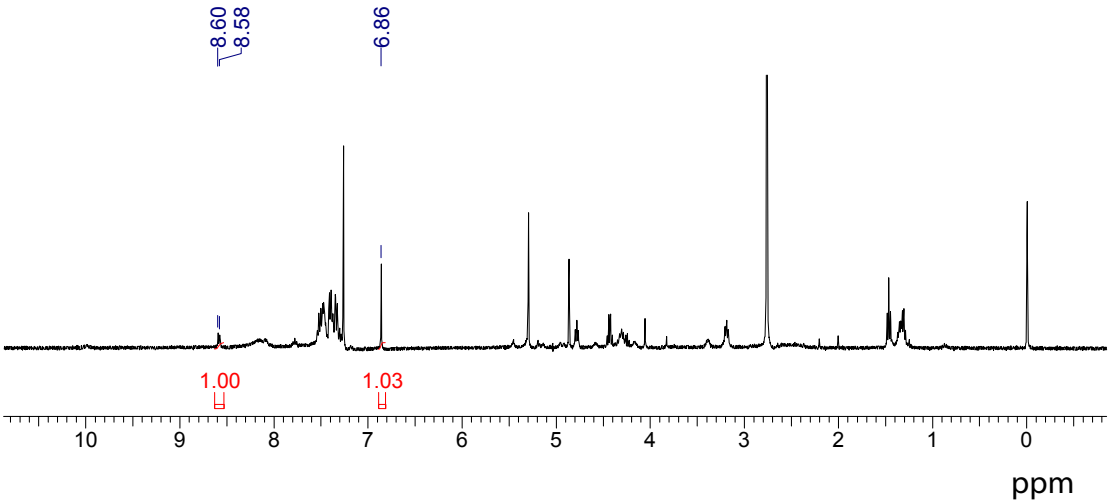


Fig. S40 ^{1}H NMR of reaction solution after 0.5 h irradiation, 10 mg **KIT-1-B**, 100 mw/m^2, in CH_3CN, (400 MHz, $CDCl_3$). Reaction conditions: **1a** (0.12 mmol), **2a** (0.10 mmol), NBS (1.2 equiv).

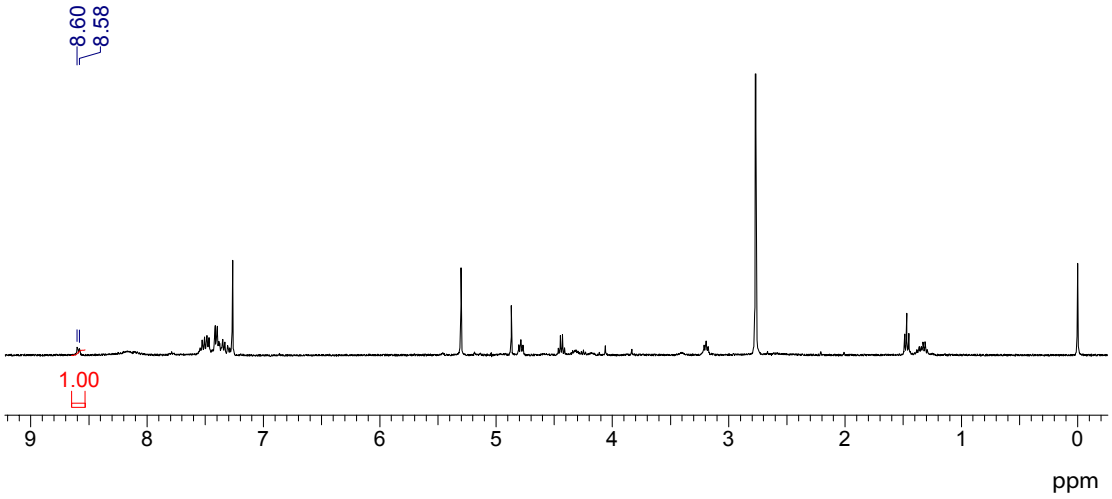


Fig. S41 ^{1}H NMR of reaction solution after 1 h irradiation, 10 mg **KIT-1-B**, 100 mw/m^2, in CH_3CN, (400 MHz, $CDCl_3$). Reaction conditions: **1a** (0.12 mmol), **2a** (0.10 mmol), NBS (1.2 equiv).

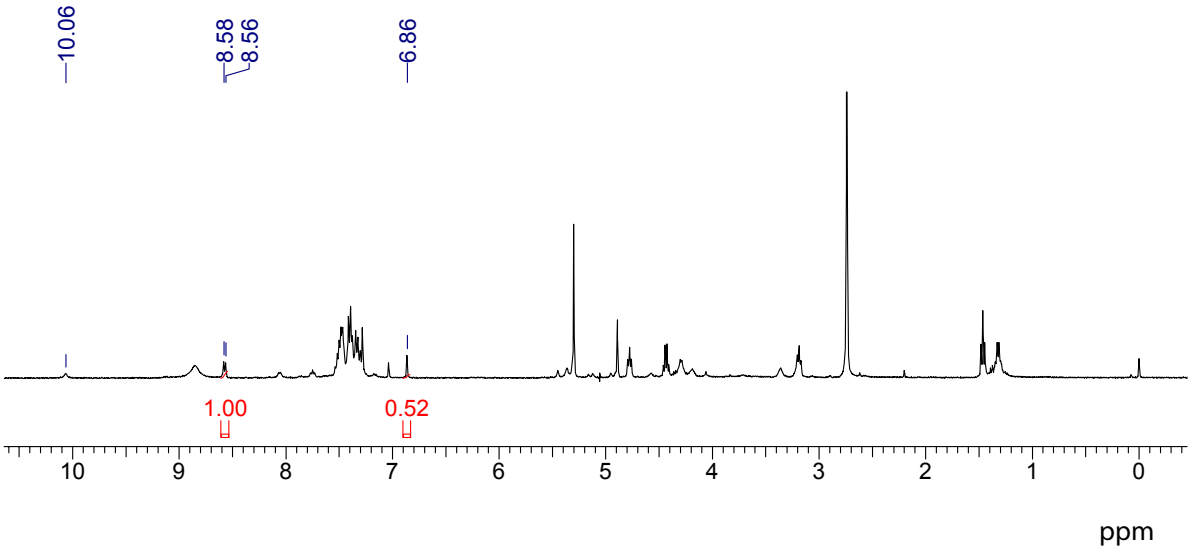


Fig. S42 ^{1}H NMR of reaction solution after 1.5 h irradiation, 10 mg **KIT-1-B**, 200 mw/m^2, in CH_2Cl_2, (400 MHz, $CDCl_3$). Reaction conditions: **1a** (0.12 mmol), **2a** (0.10 mmol), NBS (1.2 equiv).

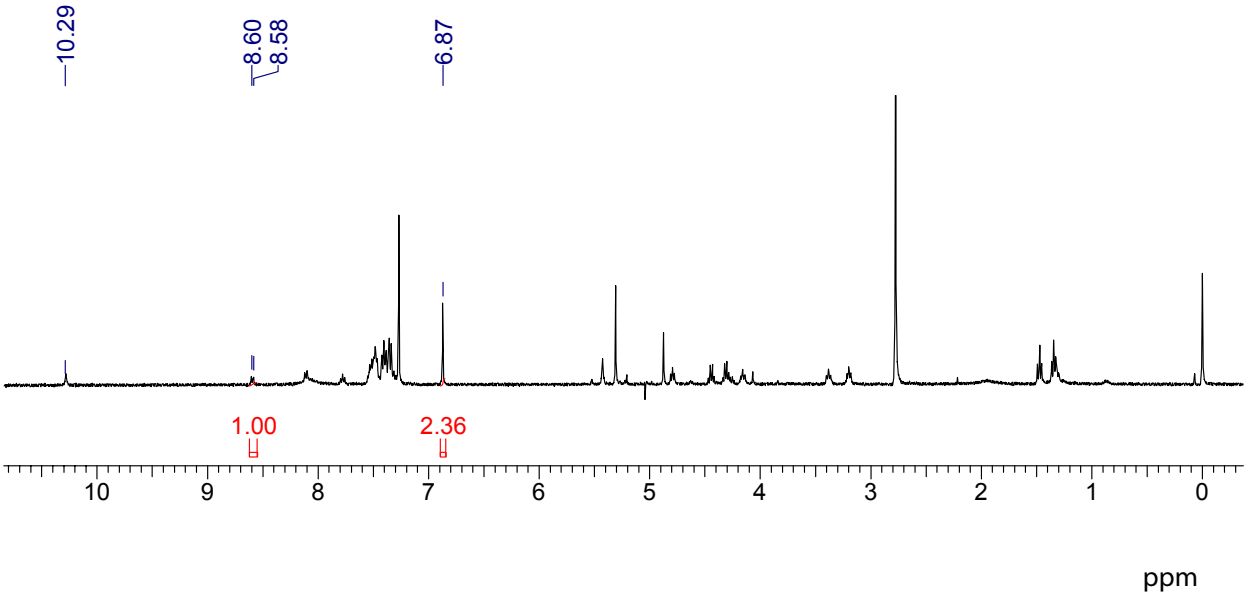


Fig. S43 ^{1}H NMR of reaction solution after 1 h irradiation, 10 mg **KIT-1**, 100 mw/m^2, in CH_2Cl_2, (400 MHz, $CDCl_3$). Reaction conditions: **1a** (0.12 mmol), **2a** (0.10 mmol), NBS (1.2 equiv).

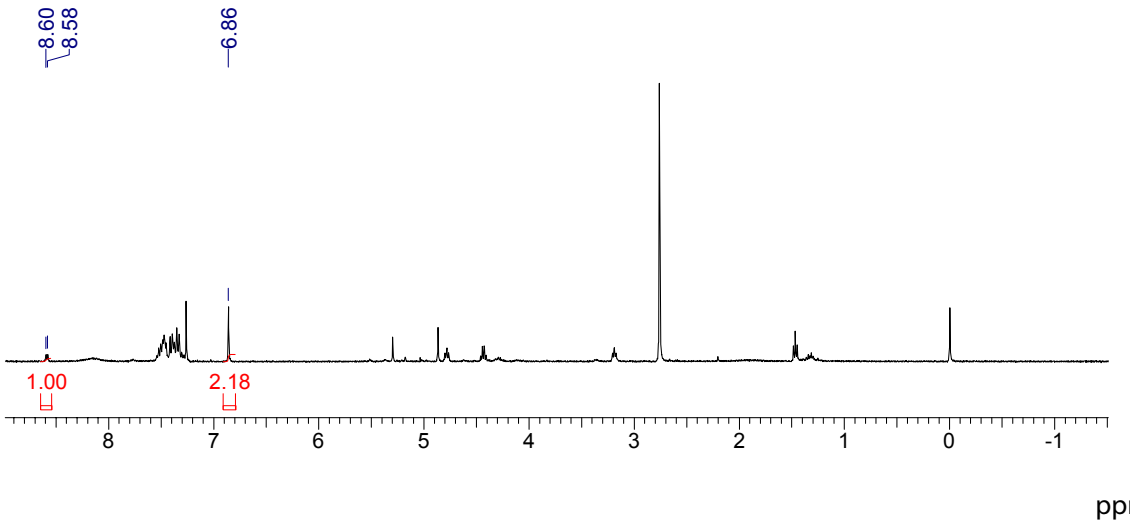


Fig. S44 ^{1}H NMR of reaction solution after 2 h irradiation, 10 mg **KIT-1-B**, 100 mw/m^2, in CH_2Cl_2, (400 MHz, $CDCl_3$). Reaction conditions: **1a** (0.12 mmol), **2a** (0.10 mmol), NBS (1.2 equiv).

3. CharacterizationKIT-1 and KIT-1-B

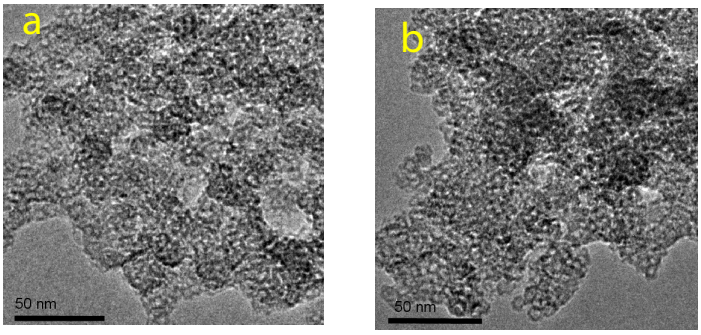


Fig. S45 TEM of (a) **KIT-1**, and (b) **KIT-1-B**.

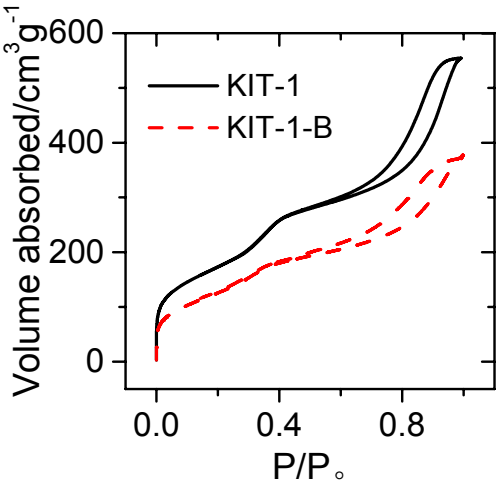


Fig. S46 Nitrogen adsorption-desorption isotherms of **KIT-1** and **KIT-1-B**.

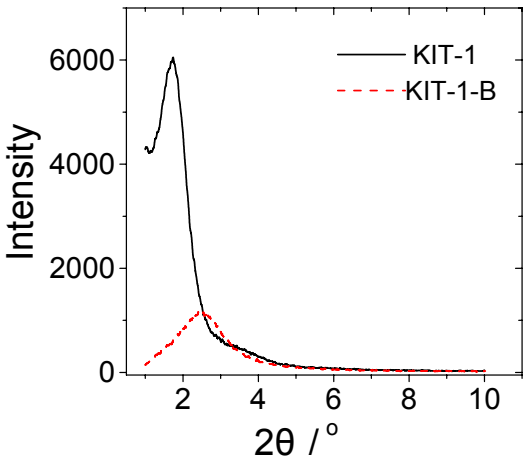


Fig. S47 The XRD patterns of **KIT-1** and **KIT-1-B**.

4. Mechanism of the Photoredox Catalytic Reaction

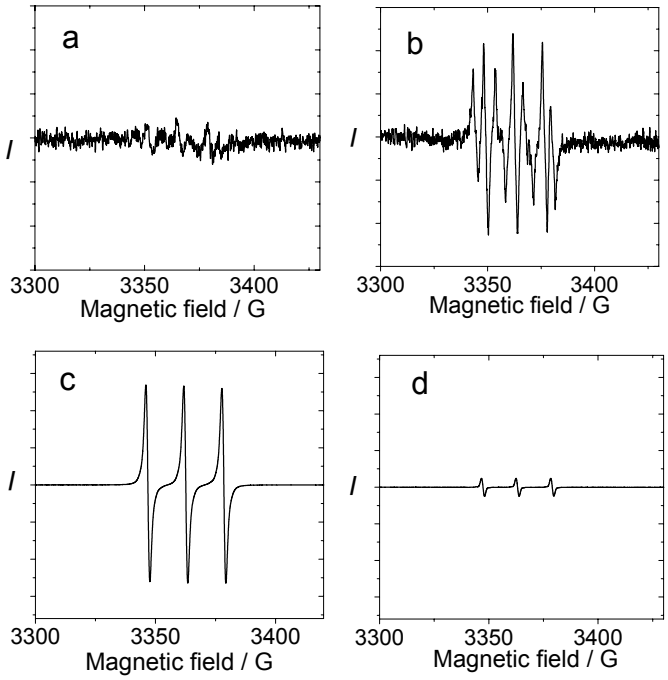


Fig. S48 (a) ESR spectrum of the mixture **KIT-1-B** (2 mg/mL) and DMPO (1.5×10^{-2} M); (b) ESR spectrum of the mixture **KIT-1-B** (2 mg/mL), **1a** (5.0×10^{-2} M) and DMPO (1.5×10^{-2}M); (c) **KIT-1-B** (2 mg/mL), TEMP (0.10M); (d) **KIT-1-B** (2 mg/mL), TEMP (0.10 M), **1a** (5.0×10^{-2} M). In air saturated CH_3CN. All the irradiations were performed with 532 nm continuous laser and the duration is 120 s (210 mW/cm^2). 22 °C.

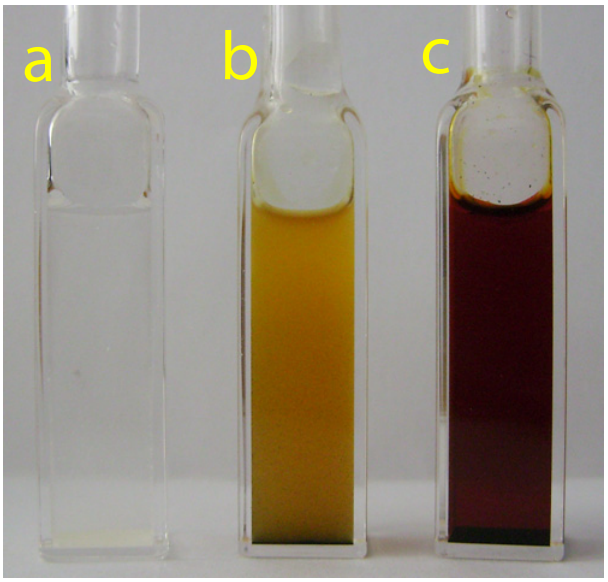
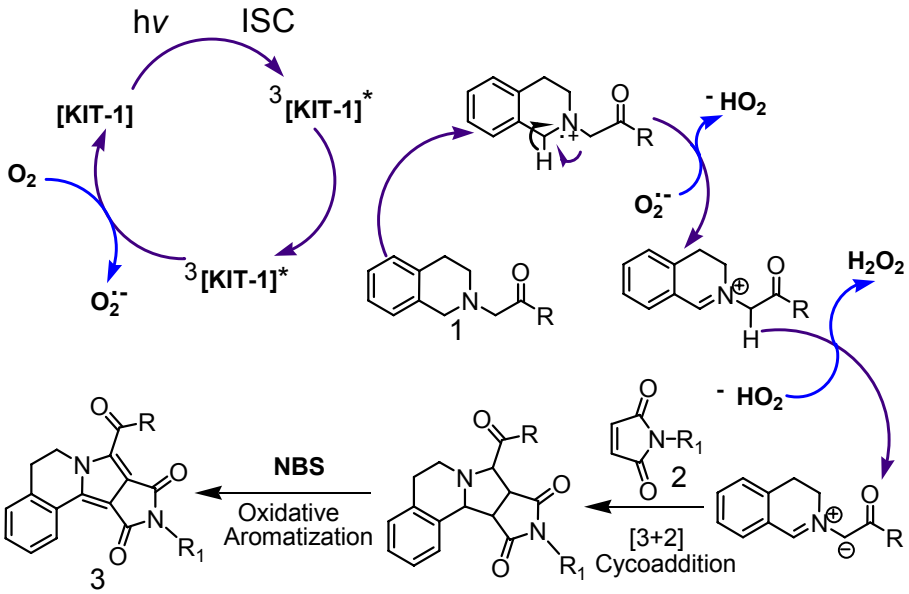


Fig. S49 Detection of the H_2O_2 in the reaction mixture of photoredox catalytic organic reaction to prepare pyrrolo[2,1-*a*]isoquinoline. (a) The picture of KI, aqueous acetic acid and starch. (b) The picture of KI, aqueous acetic acid, starch, and extracting solution of the oxidation/[3+2] cycloaddition reactions. (c) The picture of he picture of KI ,aqueous acetic acid, starch, and the 30% H_2O_2. KI (0.1 M), aqueous acetic acid (0.1 M), starch (2 mg/ml), **KIT-1-B** (10 mg), **1a** (0.12 mmol), **2a** (0.10 mmol), solvent: acetonitrile (3 mL), reaction time: 1 h, 22 °C.



Scheme S1. Proposed photocatalytic oxidation–cycloaddition–aromatization sequence with the organic triplet photosensitizers.

5. Loading and Recycling of the Photocatalyst

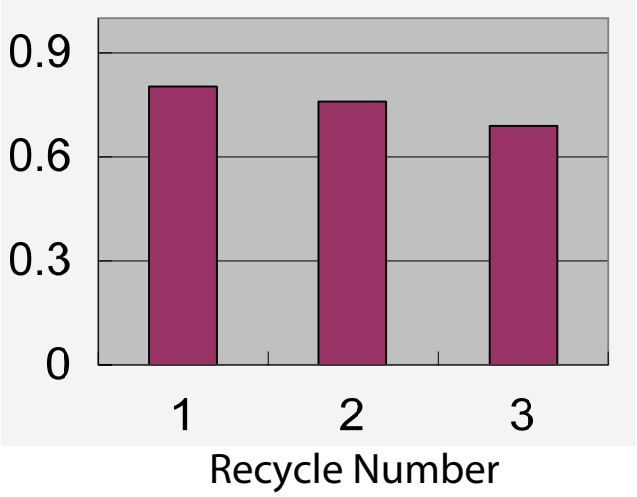
Table S2. Elemental analyses of catalyst and mass fraction of loading(w_L).

Sample	N(%)	C(%)	H(%)	w_L(%)
KIT-1	Trace	Trace	1.947	0
KIT-1-B	0.573	3.629	1.936	9.6
KIT-1-B [a]	0.423	2.832	1.858	7.5

[a] **KIT-1-B** was collected after reaction. Reaction conditions: 1 (0.12 mmol, 26.3mg), 2 (0.10 mmol, 17.3 mg), **KIT-1-B** (10 mg) and NBS (1.2 equiv) were mixed in CH_3CN (3.0 mL), the mixture was irradiated 1 h with 35 W Xe lamp ($\lambda > 385$ nm), 28 °C.

The loading of iodo-Bodipy on the porous material **KIT-1** is 9.6%.

The loading of the organic photocatalyst(Diiodo-Bodipy) on porous material is 0.0013 mmol/10 mg.



Scheme S2. Recycling of the **KIT-1-B** catalyst. Substrates**1a** (0.12 mmol) and **2a** (0.10 mmol) were used, photocatalyst catalysis loading was15 mg, NBS (1.2 equiv), and solvent (3.0 mL). Under air atmosphere, 35 W Xe lamp light irradiation ($\lambda >$385 nm), 20 °C.

6. Comparison of the radiance spectrum of the Xenon lamp used in the photocatalysis and the UV-Vis absorption spectrum of the photocatalyst

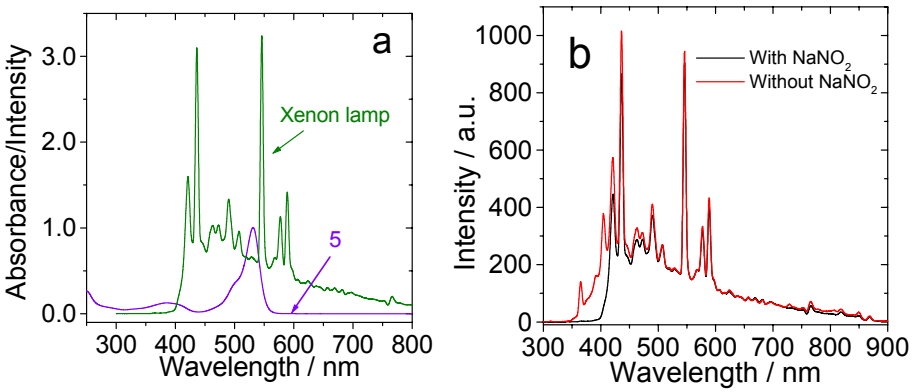
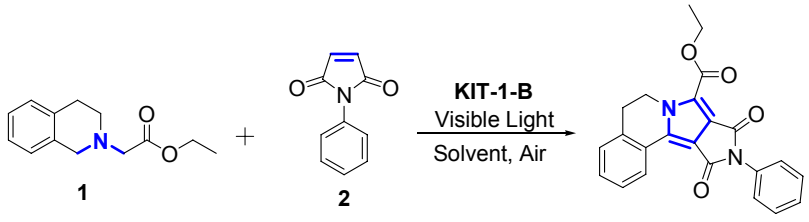


Fig. S50 (a) Comparison of the UV-Vis absorption spectra of 5 and the emission spectra of the 35 W xenon lamp (measured with spectrofluorometer). In CH_3CN, 1.0×10^{-5} M, 20°C. The excitation of xenon lamp with wavelength shorter than 387 nm was blocked by 0.72 M $NaNO_2$ solution. (b) The emission spectrum of the 35 W xenon lamp with and without the $NaNO_2$ solution filter. Xe lamp parameter: 35 W, 8000 K.

7. Heterogeneous catalysis: visible light promoted aerobic oxidation [3+2] cycloaddition run on a large scale [a]



[a] Reaction conditions: **1** (0.96 mmol, 210 mg), **2** (0.8 mmol, 138.4mg), **KIT-1-B** (80 mg) and NBS (1.2 equiv) were mixed in CH_3CN (24.0 mL), the mixture was irradiated with 35 W Xe lamp ($\lambda > 385$ nm), 28 °C. Yield: 82%

8. Comparison of the Photocatalytic activity of the Immobilized and the Un-immobilized Photocatalyst

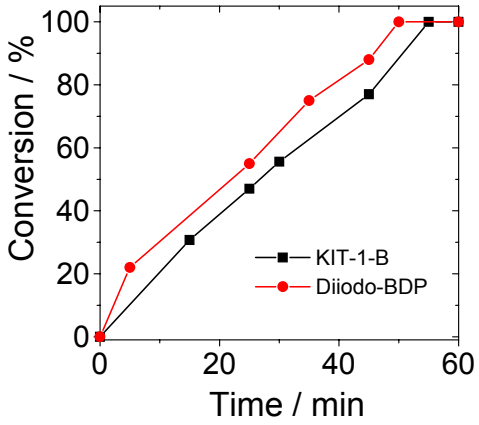
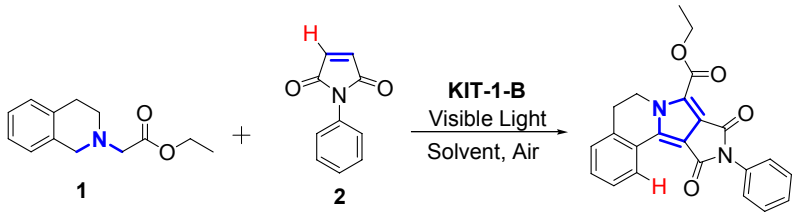


Fig. S51 The conversion of **1** and **2** as a function of reaction time photocatalyzed by the **KIT-1-B** and **2,6-Diiodo-Bodipy** under visible light. Reaction conditions: Reaction conditions: 1 (0.12 mmol), 2 (0.10 mmol), KIT-1-B (10 mg)(or 2,6-Diiodo-Bodipy 0.0013mmol**)** and NBS (1.2 equiv) were mixed in CH_3CN (3.0 mL), the mixture was irradiated with 35 W Xe lamp ($\lambda > 385$ nm), 28 °C.



The two protons used for determination of the reaction yields are highlighted.

The yields were determined by ^{1}H NMR spectra, refer to the following section:

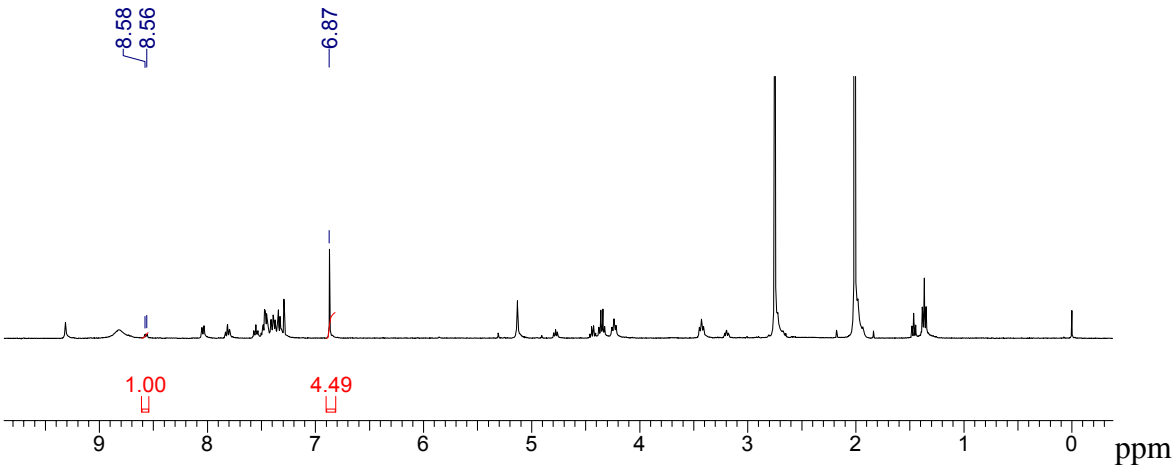


Fig. S52 ^{1}H NMR of reaction solution after 15min irradiation, 10 mg **KIT-1-B**, 100 mw/m^2, in $CH_3CN/CDCl_3$ (400 MHz). Reaction time: 15 min; Yield: 30.7%.

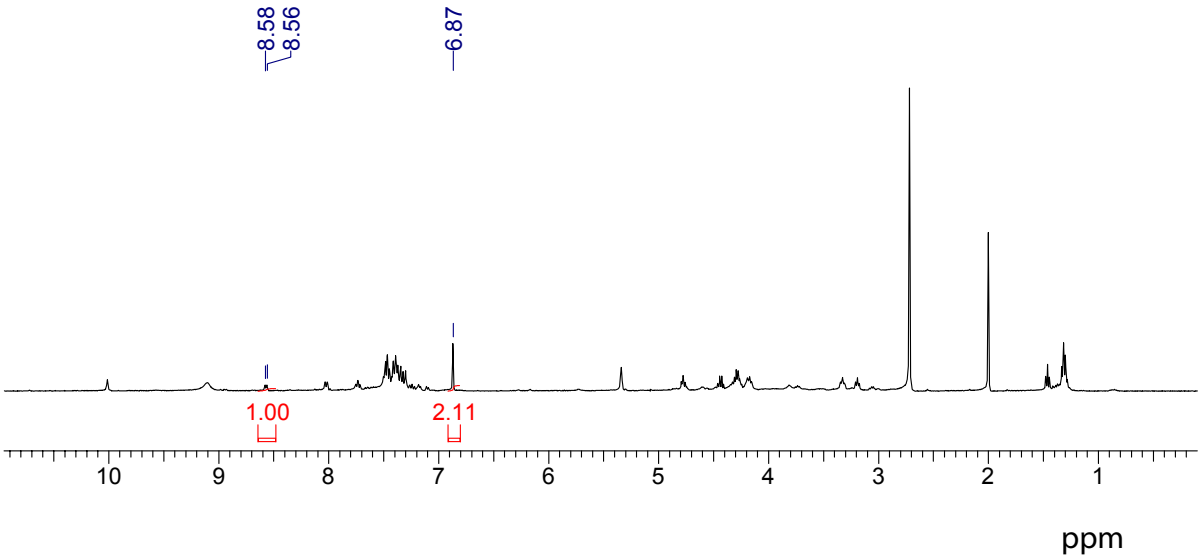


Fig. S53 ^{1}H NMR of reaction solution after 25 min irradiation, 10 mg **KIT-1-B**, 100 mw/m^2, in CH_3CN, $CDCl_3$ (400 MHz). Reaction time: 25 min; Yield: 47 %.

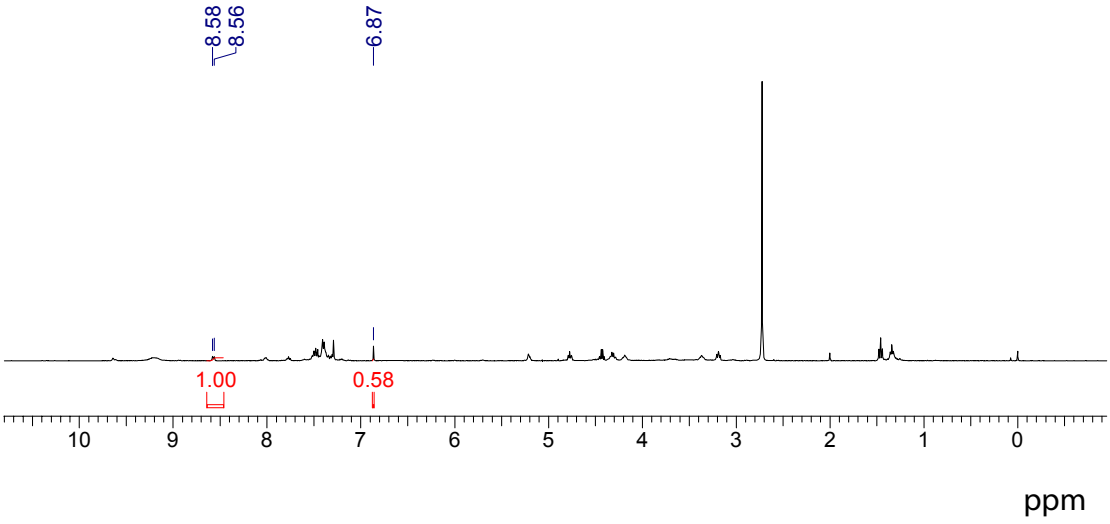


Fig. S54 ^{1}H NMR of reaction solution after 45 min irradiation, 10 mg **KIT-1-B**, 100 mw/m^2, in CH_3CN, $CDCl_3$ (400 MHz). Reaction time: 45 min; Yield: 77 %.

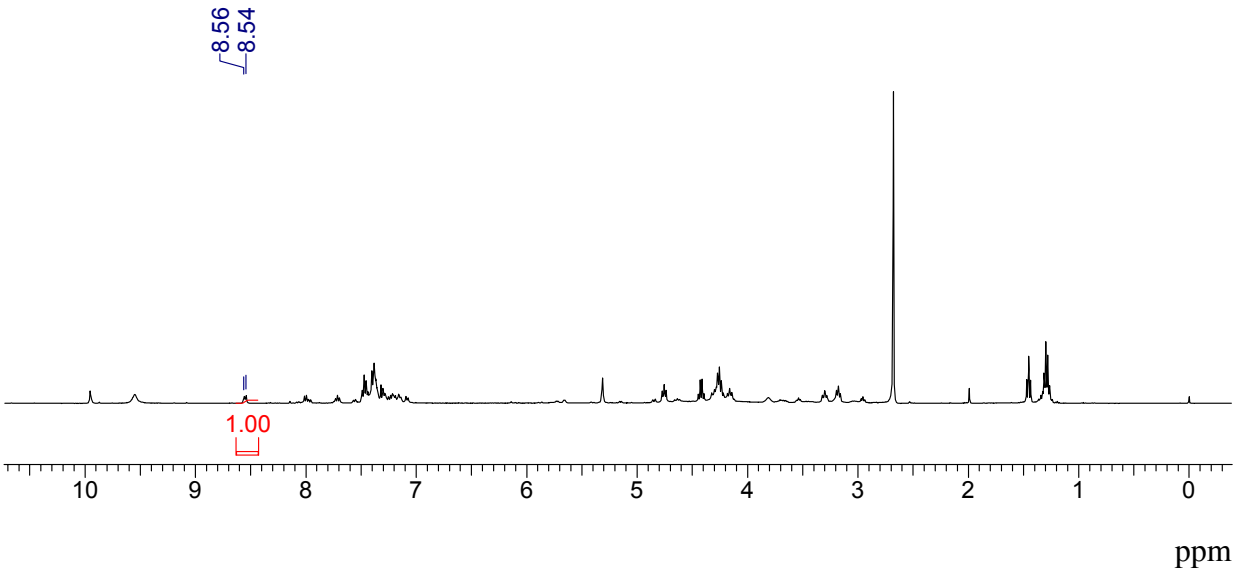


Fig. S55 ^{1}H NMR of reaction solution after 55 min irradiation, 10 mg **KIT-1-B**, 100 mw/m^2, in CH_3CN, $CDCl_3$ (400 MHz). Reaction time: 55 min; Yield: 100 %.

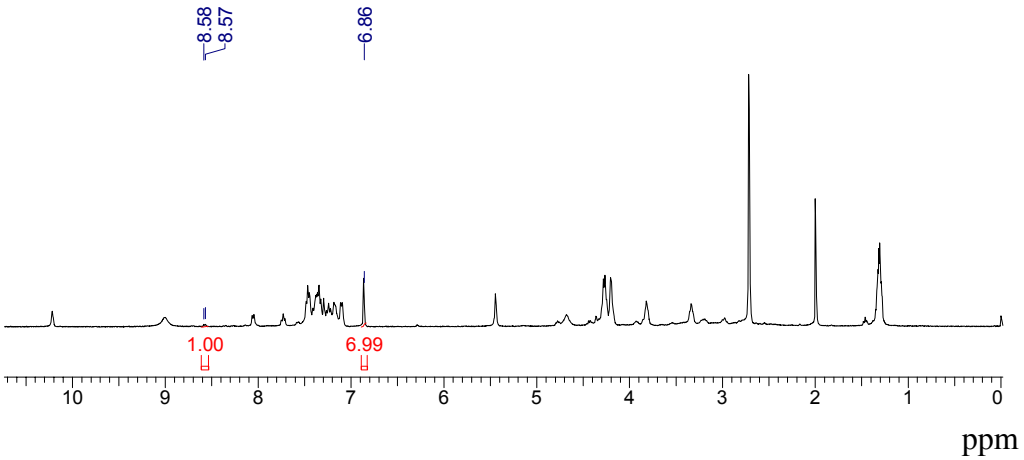


Fig. S56 ^{1}H NMR of reaction solution after 5 min irradiation, 0.0013 mmol, 2,6-**Diiodo-Bodipy**, 100 mw/m^2, in CH_3CN, $CDCl_3$ (400 MHz). Reaction time: 5 min; Yield: 22.2%.

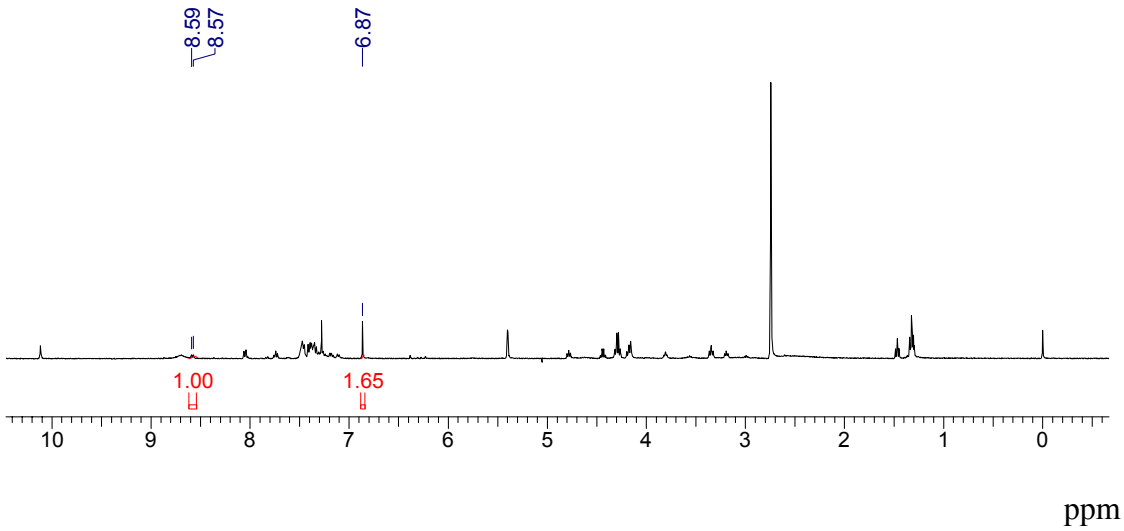


Fig. S57 ^{1}H NMR of reaction solution after 25 min irradiation, **2,6-diiodo-Bodipy (**0.0013 mmol), 100 mw/m^2, in CH_3CN, $CDCl_3$ (400 MHz). Reaction time: 25 min; Yield: 54.8%.

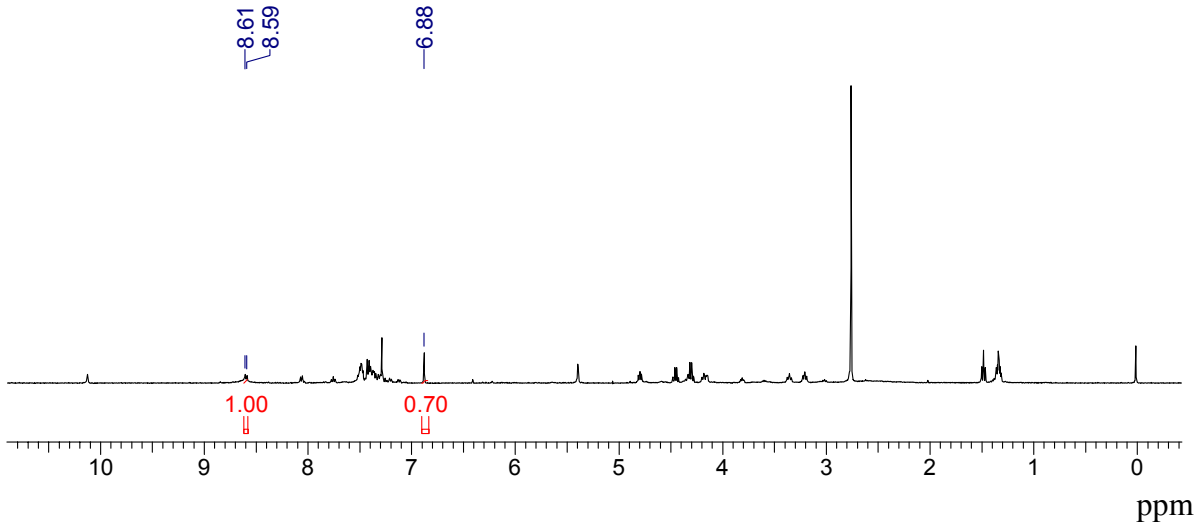


Fig. S58 ^{1}H NMR of reaction solution after 35 min irradiation, **2,6-diiodo-Bodipy (**0.0013 mmol), 100mw/m^2, in CH_3CN, $CDCl_3$ (400 MHz). Reaction time: 35 min; Yield: 74.1%**.**

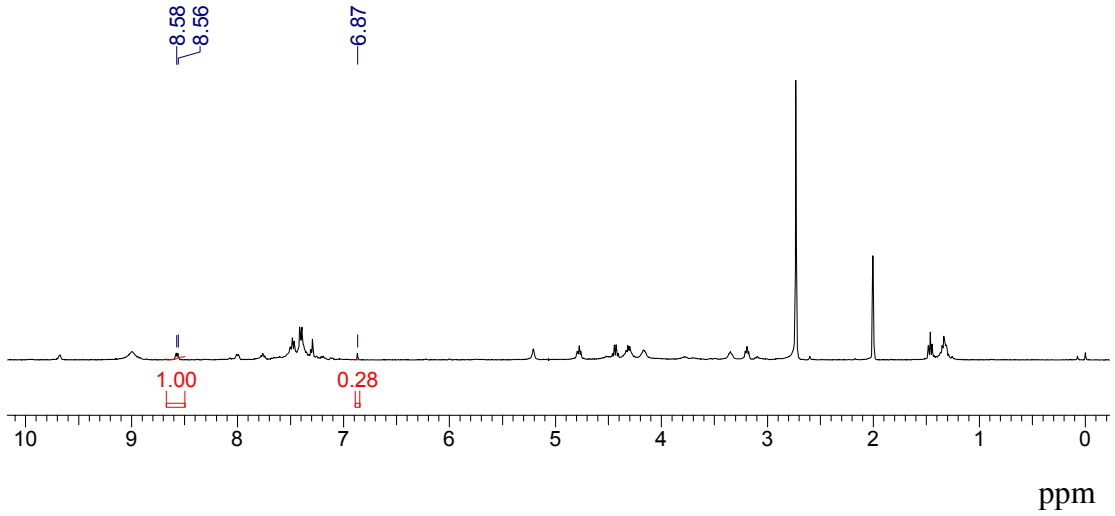


Fig. S59 ^{1}H NMR of reaction solution after 45 min irradiation, **2,6-diiodo-Bodipy** (0.0013 mmol), 100 mw/m^2, in CH_3CN, $CDCl_3$ (400 MHz). Reaction time: 45 min; Yield: 87.7%.

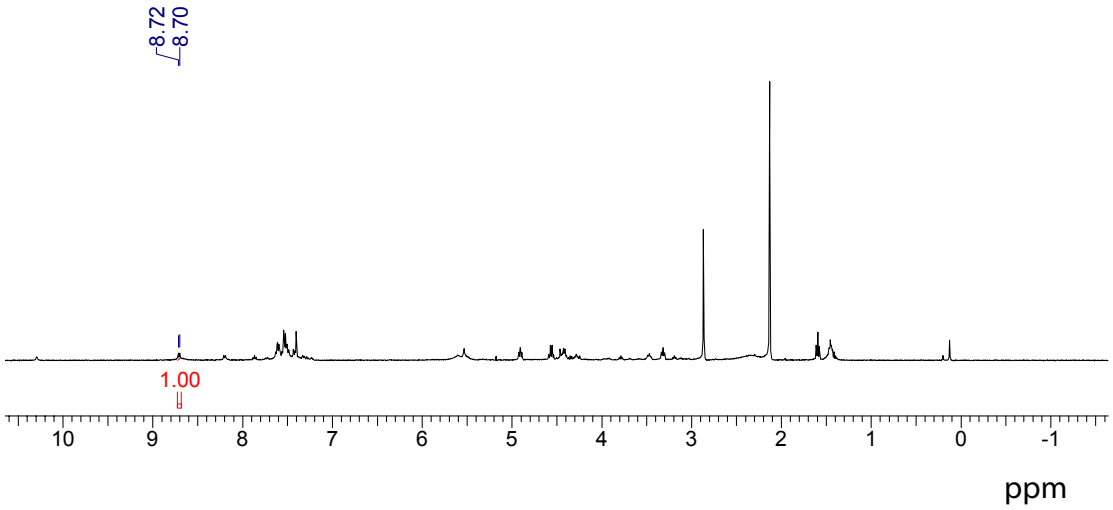


Fig. S60 ^{1}H NMR of reaction solution after 50 min irradiation, **2,6-diiodo-Bodipy (**0.0013 mmol),, 100 mw/m^2, in CH_3CN, $CDCl_3$ (400 MHz). Reaction time: 50 min; Yield: 100%.

9. Triplet Excited State Lifetime of the Photoredox Catalytic Reaction

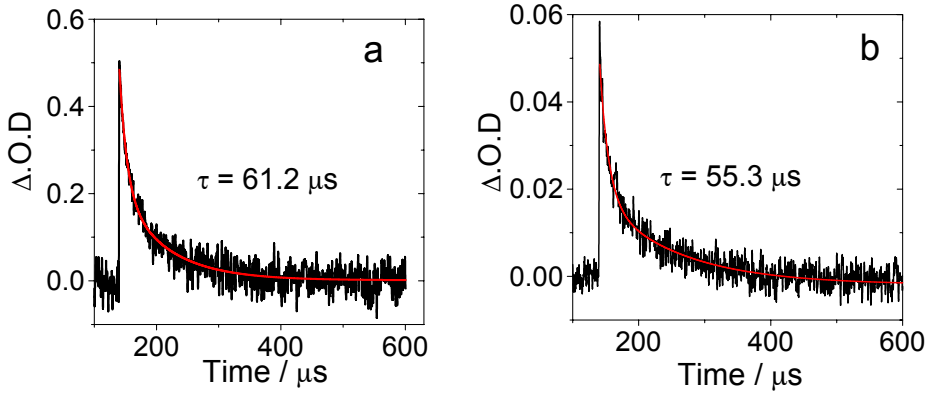


Fig. S61 Triplet excited state lifetime of (a) the un-supported catalyst (compound **5**), decay trace of **5** at 528 nm. In deaerated CH_3CN; and (b) the supported photocatalyst **KIT-1-B**. Decay trace of at 528 nm. Suspension in deaerated CH_3CN. Both materials were excited at 532 nm with pulsed laser. 20 °C.