Electronic Supplementary Information for:

Photoredox catalytic organic reactions promoted with broadband visible light-absorbing Bodipy-iodo azaBodipy triad photocatalyst

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1. Experimental Section

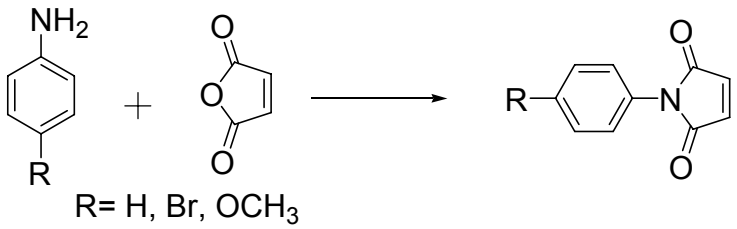
General Information:

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. 15 min before measurement .

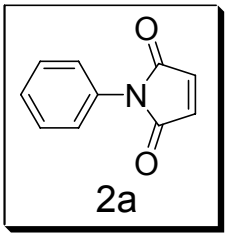
Electron spin resonance (ESR) spectroscopy. ESR spectra were recorded at room temperature using a Bruker ESP-300E spectrometer at 9.8 GHz, X-band, with 100 Hz field modulation. Samples were quantitatively injected into specially made quartz capillaries for ESR analysis in the dark and illuminated directly 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 capillaries. A diode pumped solid state (DPSS) laser (532 nm) irradiate the solution in quartz capillaries 120 seconds.

1.0 For the synthesis of **B-1**-**B-3**, please refer to *Chem. Sci*., 2014, **5**, 489 –500.

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

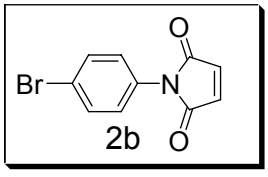


R= H, Br, OCH_3



Synthesis of **2a**

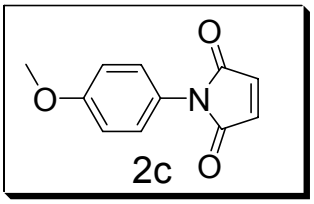
General methods: Phenylamine (0.39g, 4.2 mmol) were dissolved in THF (15 mL). Maleic anhydride (0.49g, 5 mmol) was dissolved in another portion of THF (15 mL). Maleic anhydride solution was dropped into the aniline derivatives slowly, the reaction mixture was stirred for 30 min at room temperature. A lot of precipitation appeared. The precipitation was collected by filtration. The filtrate was dissolved in acetic anhydride (10 mL) and acetic acid-sodium (6 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.



Synthesis of **2b**

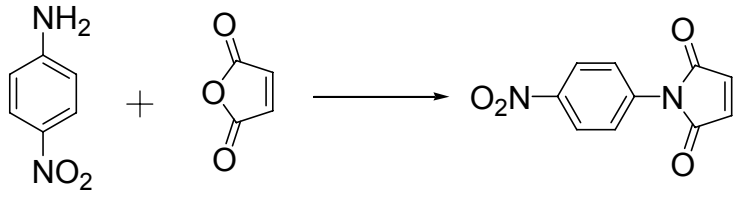
4-bromobenzenamine (0.27g, 1.55 mmol) were dissolved in THF (12 mL). Maleic anhydride (0.2g, 2 mmol) was dissolved in another portion of THF (12 mL). Maleic anhydride solution was dropped into the aniline derivatives slowly, the reaction mixture was stirred for 30 min at room temperature. A lot of precipitation appeared. The precipitation was collected by filtration. The filtrate was dissolved in acetic anhydride (5 mL) and acetic acid-sodium (3 mmol) was added. The mixture was heated at 120°C by microwave irradiation for 30 min. The acetic anhydride solution was poured into water (15 mL), saturated NaOH solution was added to neutralize the mixture. Precipitation appeared and the

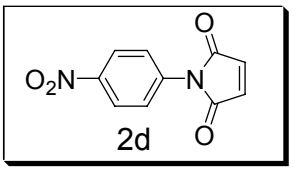
solid was collected by filtration. The precipitates was purified by column chromatography (silica gel, CH_2Cl_2/petroleum ether **= 1/1, v/v**), Yield: 0.3 g (76.8%). M.p. 121.4–121.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.63 (d, J = 9.2 Hz, 2H), 7.27–7.22 (m, 2H), 6.86 (s, 2H). HRMS (ESI$^+$): Calcd $C_{10}H_6NO_2Br$ $[M+H]^+$ m/z = 251.9766. Found m/z = 251.9739.



Synthesis of **2c**

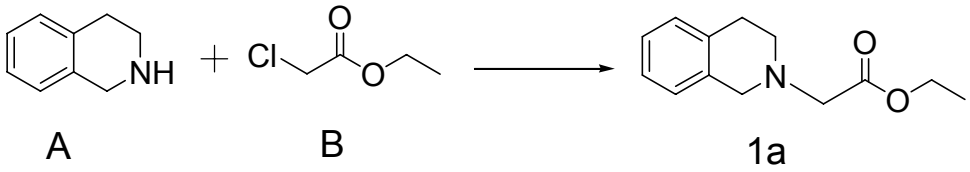
4-methoxybenzenamine (0.15g, 1.27 mmol) were dissolved in THF (10 mL). Maleic anhydride (0.2g, 2 mmol) was dissolved in another portion of THF (10 mL). Maleic anhydride solution was dropped into the aniline derivatives slowly, the reaction mixture was stirred for 30 min at room temperature. A lot of precipitation appeared. The precipitation was collected by filtration. The filtrate was dissolved in acetic anhydride (5 mL) and acetic acid-sodium (3 mmol) was added. The mixture was heated at 120°C by microwave irradiation for 30 min. The acetic anhydride solution was poured into water (15 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: 0.2 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.

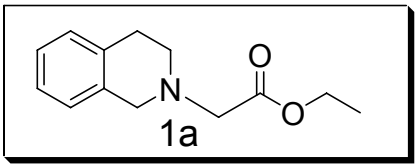




Synthesis of **2d**

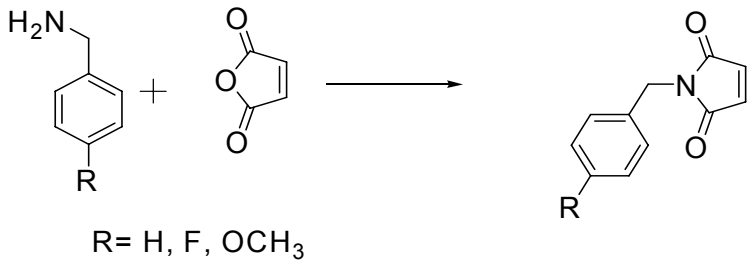
p-nitroaniline (10 mmol) and maleic anhydride (11 mmol) was dissolved in THF (40 mL). The mixture was stirred under reflux for 6 h. Precipitation appeared and the solid was filtrated. The filtrate was dissolved in acetic anhydride (20 mL), then sodium acetate (12 mmol) was added. The mixture was heated 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.



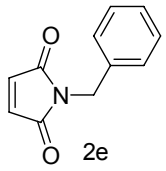


Synthesis of **1a**

A (0.41g, 3.1 mmol), **B** (0.42g, 3.5 mmol) and Na_2CO_3 (10 mmol) was dissolved in THF (30 mL), the mixture was stirred at room temperature for 24 h. When the reaction was completed, the reaction mixture was poured into water (80 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). Yield: 0.5 g (73.8%). Oily product. ^{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.



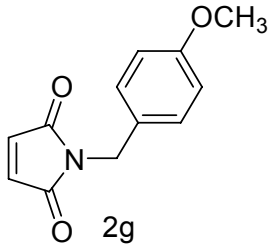
R= H, F, OCH_3



2e

Synthesis of **2e**

Benzylamine (0.54g, 5 mmol) were dissolved in 2 mL $CHCl_3$. Maleic anhydride (0.49g, 5mmol) 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 room temperature. A lot of precipitation appeared. The precipitation was collected by filtration. The filtrate was dissolved in acetic anhydride (5 mL) and acetic acid-sodium (6 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). 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 C10H7NO2 $[M+H]^+$ m/z = 188.0706; Found m/z = 188.0704.

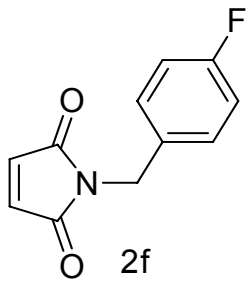


2g

Synthesis of **2g**

4-methoxybenzylamine (0.82g, 6 mmol) were dissolved in 2 mL $CHCl_3$. Maleic anhydride (0.6g, 6mmol) 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 room temperature. A lot of precipitation appeared. The precipitation was collected by filtration. The filtrate was dissolved in acetic anhydride (5 mL) and acetic acid-sodium (6 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

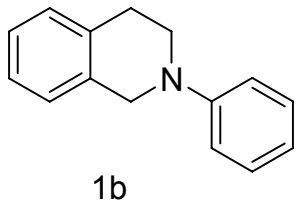
extracted with DCM, dried with Na_2SO_4, filtered, and the solvent was evaporated. The product was purified by silica gel column.(silica gel, CH_2Cl_2). Yield: 0.7 g (53.2%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.30 (d, *J* = 8.5 Hz, 2H), δ = 6.85 (d, *J* = 8.7 Hz, 2H), 6.68 (s, 2H), 4.61 (s, 2H), 3.78 (s, 3H). HRMS (ESI+): Calcd C10H7NO2 [M+H]+ m/z = 218.0812. Found m/z = 218.0818.



2f

Synthesis of **2f**

4-fluorobenzylamine (0.8g, 6.4 mmol) were dissolved in 2 mL $CHCl_3$. Maleic anhydride (0.7g, 7mmol) 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 room temperature. A lot of precipitation appeared. The precipitation was collected by filtration. The filtrate was dissolved in acetic anhydride (6 mL) and acetic acid-sodium (6 mmol) was added. The mixture was heated at 138℃ 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). 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 C10H8FNO2 $[M+H]^+$ m/z = 206.0612; Found m/z = 206.0607.



1b

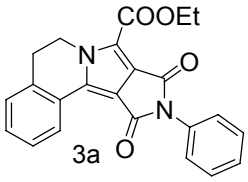
Synthesis of **1b**

A (2 ml, 15 mmol), iodobenzene (1.12ml, 10 mmol) and K_3PO_4 (20 mmol) was dissolved in mixture solution of 1.11ml glycol and 10 ml isopropanol, then add 200mg CuI into the solution under Ar. The mixture was stirred at 90 ℃ for 24 h. When the reaction was completed, the reaction mixture was poured into DCM (80 mL), and suction filtration. The solvent was evaporated under reduced pressure.

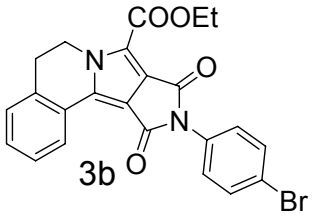
The mixture was purified by column chromatography (silica gel, CH_2Cl_2). Yield: 0.62 g (29.7%). ^{1}H NMR (400 MHz, CDCl3) δ = 7.36–7.31 (2, 4H), 7.23–7.21 (m, 4H), 7.04 (d, *J* =8.3 Hz, 2H), 6.89–6.86 (m, 1H), 4.45 (s, 2H), 3.60 (t, *J* =5.5 Hz, 2H), 3.03 (t, *J* =5.5 Hz, 2H).

The general procedure for oxidation/[3+2] cycloaddition/aromatization tandem reaction with tetrahydroisoquinoline derivatives catalyzed by organic triplet photosensitizers B-1 and B-2

Dissolved **1** (0.15 mmol), photosensitizers (1 mmol%) and **2** (0.1 mmol) into 5 mL dichloroform. 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. NBS (25 mg) is added into reactor. Then another 5 min, remove the solvents, The residue was purified by column chromatography (silica gel, DCM). Yeild: Please refer to table 3.

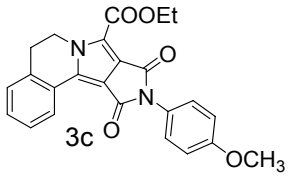


^{1} H NMR (400 MHz, $CDCl_3$) δ = 8.60 (d, *J* = 7.2 Hz, 1H), 7.29–7.51 (m, 8H), 4.79 (t, *J* = 6.9 Hz, 2H), 4.47–4.41 (m, 2H), 3.19 (t, *J* = 6.4 Hz, 2H), 1.47 (t, *J* = 7.2 Hz, 3H). HRMS (EI+): Calcd C23H17N2O4 [M+] m/z = 386.1267. Found m/z = 386.1270. ^{13}C NMR (125 MHz, $CDCl_3$): 163.2, 161.5, 159.5, 128.9, 128.0, 127.5, 125.5, 118.6, 116.3, 61.6, 43.4, 29.7, 28.0, 14.2.

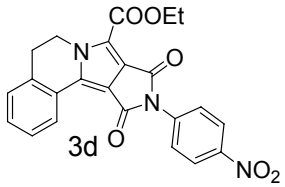


^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.57 (d, *J* = 8.0 Hz, 1H), 7.62 (d, *J* = 8.3 Hz, 2H), 7.43–7.31 (m, 5H), 4.79 (t, *J* =6.0 Hz, 2H), 4.47–4.41 (m, 2H), 3.19 (t, *J* = 8.6 Hz, 2H), 1.47 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (125 MHz,

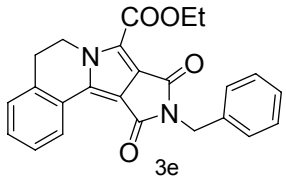
$CDCl_3$): 162.7, 161.2, 159.6, 133.8, 132.1, 130.5, 128.6, 125.3, 125.1, 121.5, 118.8, 115.9, 61.8, 43.6, 29.7, 28.4, 14.2. HRMS (ESI+): Calcd $C_{23}H_{17}N_2O_4NaBr$ $[M+Na]^+$ m/z = 487.0269. Found m/z = 487.0261.



^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.59 (d, *J* = 7.5 Hz, 1H), 7.44–7.29 (m, 5H), 7.01 (d, *J* =9.0 Hz, 2H), 4.78 (t, *J* =5.9 Hz, 2H), 4.46–4.40 (m, 2H), 3.85 (s, 3H), 3.19 (d, *J* = 6.2 Hz, 2H), 1.47 (t, J = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): 163.5, 162.1, 159.9, 159.2, 130.4, 128.6, 127.8, 125.5, 118.9, 116.4, 114.5, 61.8, 55.6, 43.5, 28.5, 14.3.

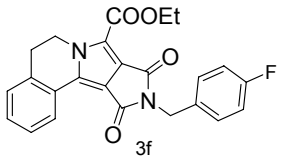


1 H NMR (400 MHz, CDCl3) δ = 8.56 (t, *J* = 7.2 Hz, 1H), 8.36 (d, *J* = 9.2 Hz, 1H), 7.72 (d, *J* = 8.8 Hz, 2H), 7.46–7.40 (m, 2H), 7.33 (d, *J* = 7.2 Hz, 1H), 4.80 (t, *J* =7.2 Hz, 2H), 4.48–4.43 (m, 2H), 3.22 (t, **J** = 6.4 Hz, 2H), 1.50 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 162.3, 160.9, 159.7, 146.5, 138.7, 132.7, 130.9, 128.0, 127.0, 124.3, 119.4, 115.8, 62.0, 43.7, 28.4, 14.4. HRMS (EI+) Calcd for $C_{23}H_{17}N_3O_6$ $[M+]$ m/z = 431.1117. Found m/z = 431.1126.



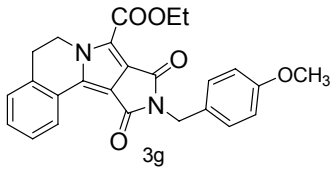
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.54 (d, *J* = 7.7 Hz, 1H), 7.45–7.23 (m, 8H), 4.80–4.70 (m, 4H), 4.45–4.40 (m, 4H), 3.14 (t, *J* =7.2 Hz, 2H), 1.48 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 164.0, 162.4, 159.8,

130.3, 128.6, 128.0, 127.8, 125.7,118.4, 116.7, 61.7, 43.5, 42.0, 28.5, 14.7. HRMS (ESI+): Calcd $C_{24}H_{20}N_2O_4Na$ $[M+Na]^+$ m/z = 423.1315. Found m/z = 423.1317.



3f

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.53 (d, *J* = 7.7 Hz, 1H), 7.44–7.27 (m, 5H), 6.98 (t, *J* =8.7 Hz, 2H), 4.76–4.70 (m, 4H), 4.46–4.41 (m, 2H), 3.14 (t, *J* =6.7 Hz, 2H), 1.48 (d, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): 164.0, 163.5, 162.2, 161.1, 159.5, 132.4, 130.6, 128.0, 125.6, 118.6, 116.5, 115.5, 61.4, 43.1, 41.1, 28.2, 14.1. HRMS (ESI+): Calcd $C_{24}H_{19}FN_2O_4Na$ $[M+Na]^+$ m/z = 441.1221. Found m/z = 441.1219.

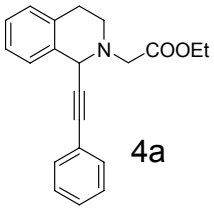


3g

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.53 (d, *J* = 7.5 Hz, 1H), 7.42–7.25 (m, 5H), 6.84 (d, *J* = 6.4 Hz, 2H), 4.73–4.70 (m, 4H), 4.46–4.40 (m, 2H), 3.77 (s, 3H), 1.48 (d, *J* = 7.3 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): 163.9, 162.2, 159.8, 159.1, 130.0, 129.5, 127.6, 125.7, 118.4, 116.7, 113.8, 61.5, 55.4, 43.3, 41.4, 28.4, 14.3. HRMS (ESI+): Calcd $C_{25}H_{22}N_2O_5Na$ $[M+Na]^+$ m/z = 453.1426. Found m/z = 453.1409.

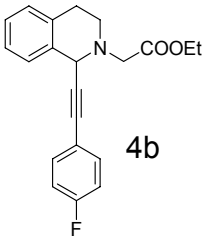
The general procedure for the photocatalytic aerobic oxidation and metal catalyzed alkynylation reactions

To a dry flask were added **B-1** or **B-2** (1 mol%), tetrahydroisoquinoline derivatives (0.1 mmol), acetylene derivatives (5 eq). The reaction mixture was stirred at room temperature (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 completion of the reaction, the solvent was evaporated under reduced pressure. The residue was purified by column chromatography (silica gel, dichloromethane). Yield: please refer to Table 5.



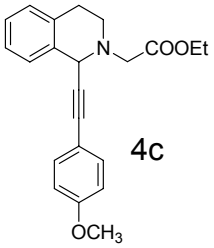
4a

^{1}H NMR (400 MHz, $CDCl_3$): 7.41-7.11 (m, 9H), 5.11 (s, 1H), 4.25-4.20 (m, 2H), 3.74-3.56 (m, 2H), 3.13-2.83 (m, 4H), 1.29 (t, 3H, *J* = 7.2 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): 170.8, 143.9, 133.6, 131.9, 129.1, 128.3, 127.8, 127.2, 126.1, 123.0, 94.6,87.0, 60.9, 56.7,54.9, 46.8, 29.0, 14.4.



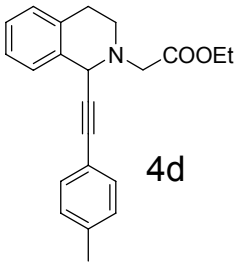
4b

^{1}H NMR (400 MHz, $CDCl_3$): 7.40-7.29 (m, 3H), 7.19-7.14 (m, 3H), 6.99-6.95 (m, 2H), 5. 09 (s, 1H), 4.25-4.20 (m, 2H), 3.73-3.55 (m, 2H), 3.11-2.84 (m, 2H), 1.30(t, 3H, *J* = 7.0Hz). ^{13}C NMR (100 MHz, $CDCl_3$): 170.8, 129.1, 127.8, 127.2, 119.1, 115.7, 86.9, 86.0, 60.6, 56.6, 54.8, 46.6, 29.0, 14.4.



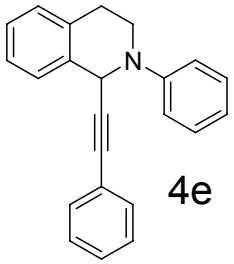
4c

^{1}H NMR (400 MHz, $CDCl_3$): 7.53-7.31 (m, 3H), 7.18-7.12 (m, 3H), 6.81 (d, 2H, *J* = 8.3 Hz), 5.11 (s, 1H), 4.25-4.20 (m, 2H), 3.79 (s, 3H), 3.75-3.57 (m, 2H), 3.15-2.86 (m, 4H), 1.30 (t, 3H, *J* = 7.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): 170.8, 133.4, 129.1, 127.8, 127.2, 126.0, 114.0, 86.8, 85.4, 60.9, 56.8, 55.0, 47.0, 29.9, 29.0, 14.4.



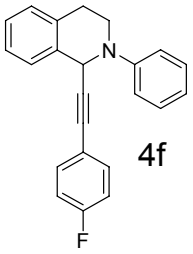
4d

^{1}H NMR (400 MHz, $CDCl_3$): 7.31-7.29 (m, 3H), 7.18-7.07 (m, 6H), 5.11 (s, 1H), 4.25-4.20 (m, 2H), 3.74-3.56 (m, 2H), 3.14-2.85 (m, 4H), 2.33 (s, 1H), 1.29 (t, 3H, J = 7.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): 170.7, 138.4, 131.8, 129.1, 127.9, 127.2, 126.1, 120.2, 87.1, 86.1, 61.1, 56.6, 54.8, 46.4, 28.8, 21.7, 14.2.



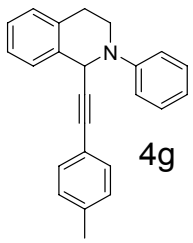
4e

^{1}H NMR (400 MHz, $CDCl_3$): 7.38-7.13 (m, 13H), 6.92-6.88 (m, 1H), 5.65 (s, 1H), 3.68-3.61 (m, 2H), 3.12-2.90 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): 149.7, 135.5, 134.5, 131.8, 129.3, 129.0, 128.2, 126.4, 123.1, 119.7, 116.8, 88.8, 84.9, 78.0, 77.2, 76.9, 52.4, 43.5, 29.0.



4f

^{1}H NMR (400 MHz, $CDCl_3$): 7.40-7.29 (m, 3H), 7.19-7.14 (m, 3H), 6.99-6.95 (m, 2H), 5.09 (s, 1H), 4.25-4.20 (m, 2H), 3.73-3.55 (m, 2H), 3.12-2.84 (m, 4H), 1.29 (t, 3H, J = 7.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): 170.8, 129.1, 127.8, 127.2, 119.1, 115.7, 86.9, 86.0, 60.6, 56.6, 54.8, 46.6, 29.0, 14.4.



^{1}H NMR (400 MHz, $CDCl_3$): 7.45-6.97 (m, 15H), 5.65 (s, 1H), 3,81-3.76 (m, 2H), 3.22-3.04 (m, 2H), 2.37 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): 149.6, 138.4, 134.4, 131.7, 128.9, 127.2, 126.3, 119.6, 116.7, 87.9, 84.9, 52.4, 43.5, 28.9, 21.3.

2. NMR and HRMS spectra

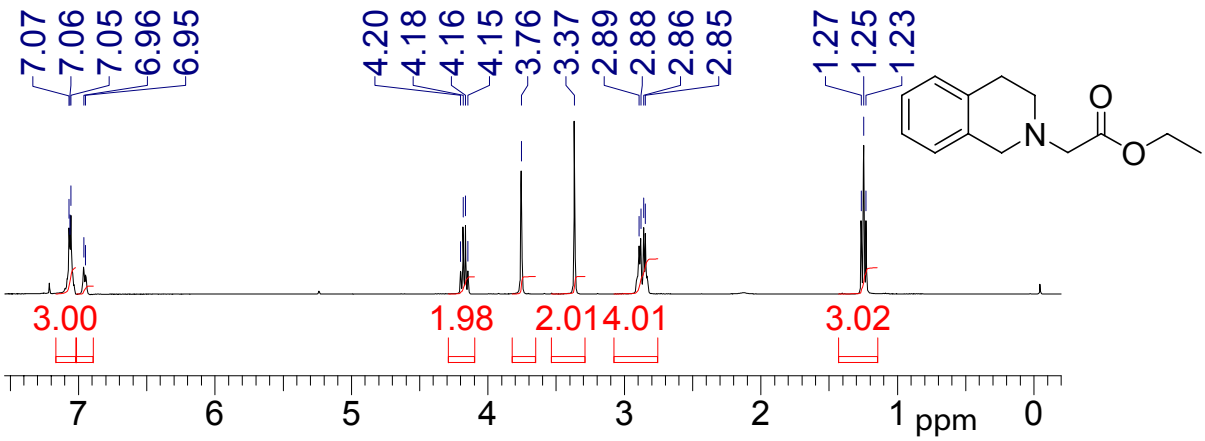


Fig. S1 ^{1}H NMR of **1** (400 MHz. In $CDCl_3$).

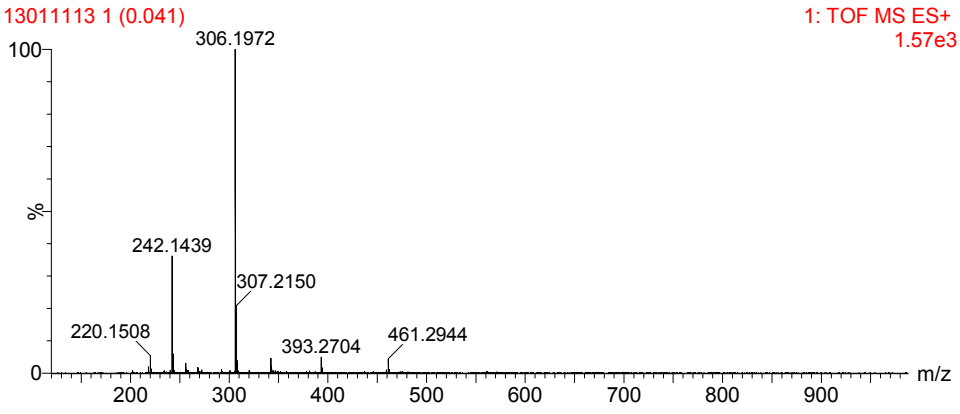


Fig. S2 TOF HRMS ESI+ of **1**.

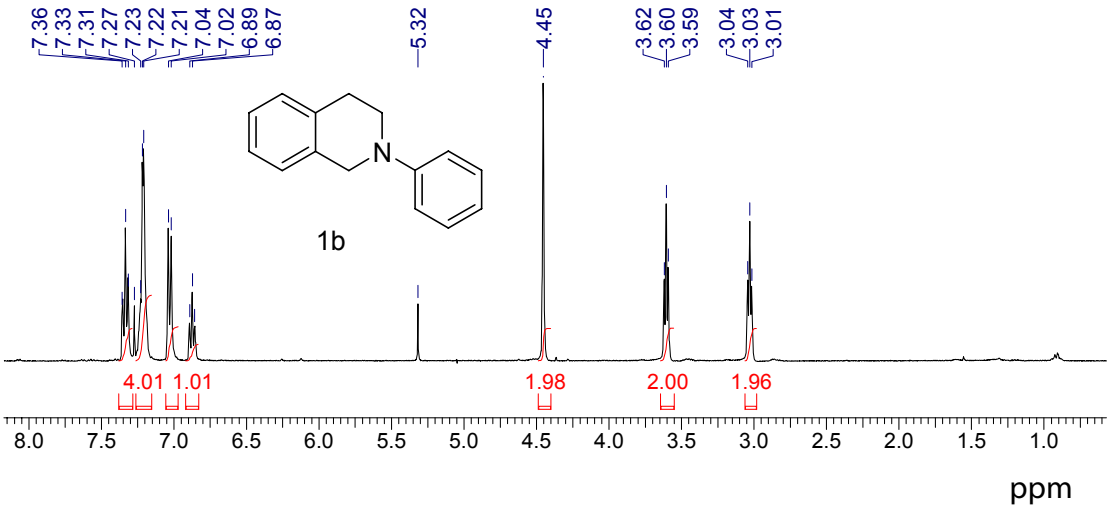


Fig.S3 ^{1}H NMR of **1b** (400MHz.In $CDCl_3$).

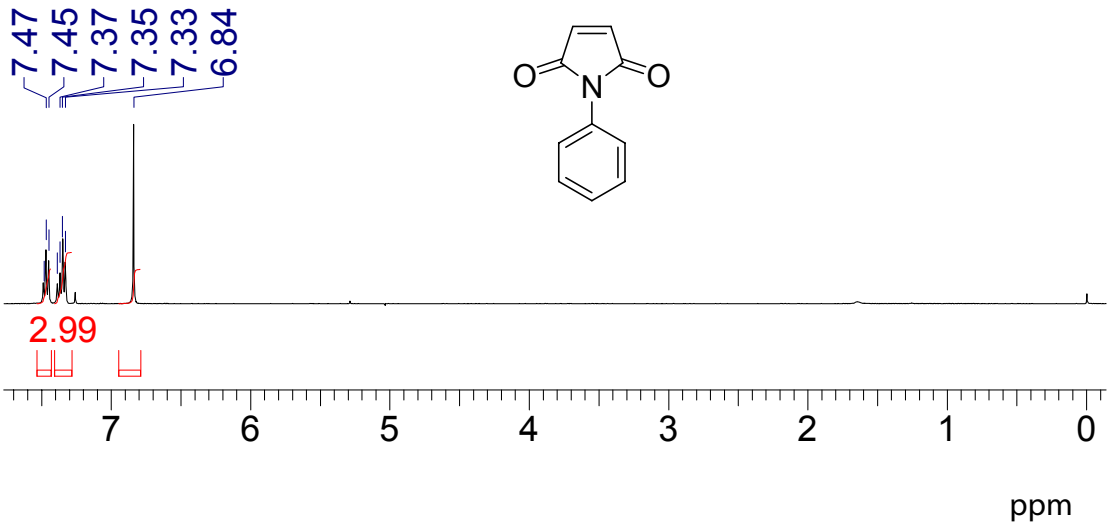


Fig.S4 ^{1}HNMR of **2a** (400MHz. In $CDCl_3$).

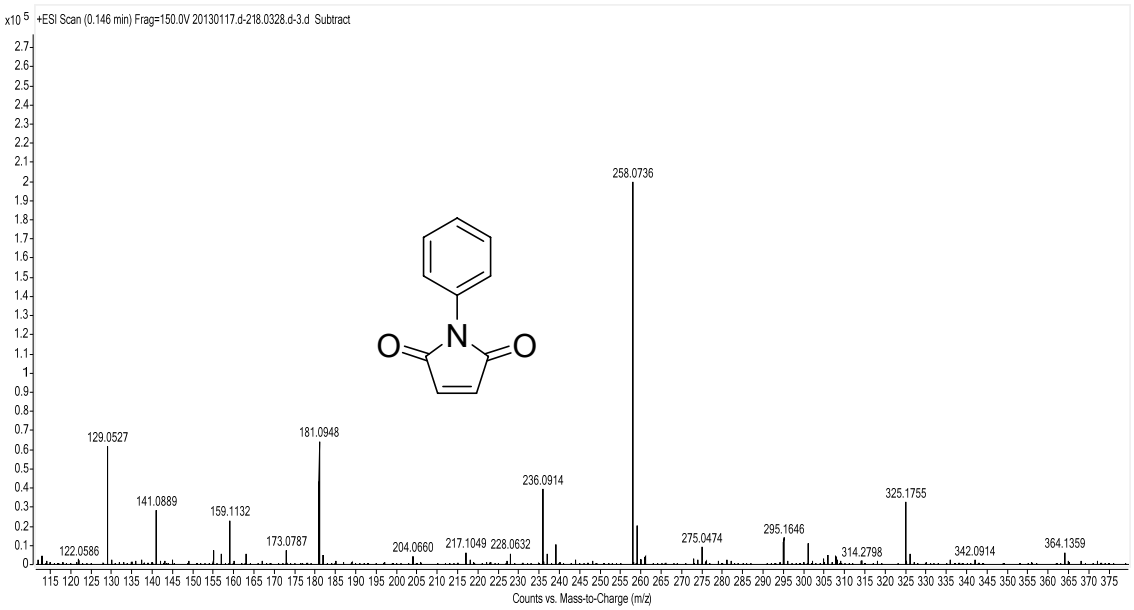


Fig. S5 TOF HRMS ESI+ of **2a**.

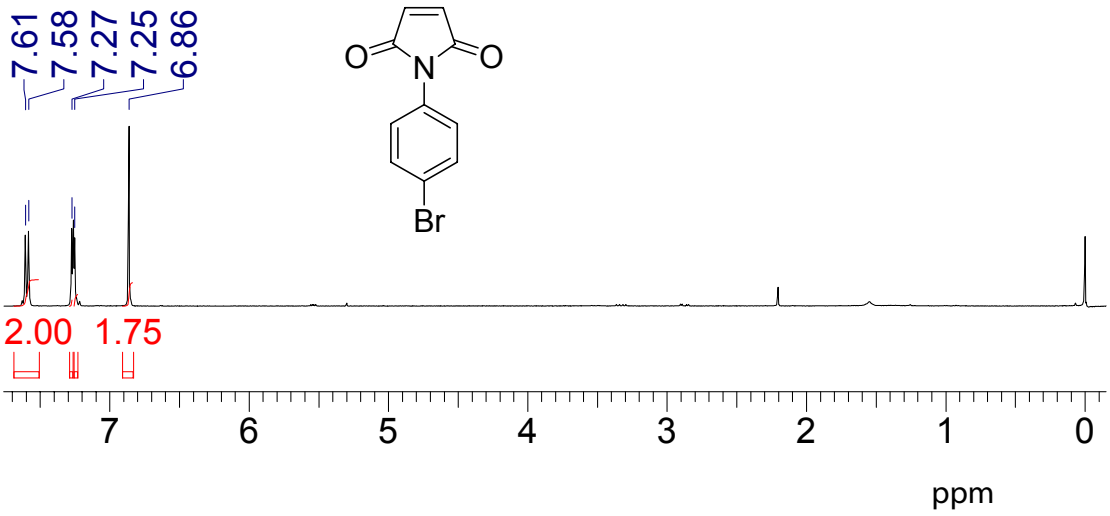


Fig. S6 ^{1}H NMR of **2b** in $CDCl_3$ (400 MHz).

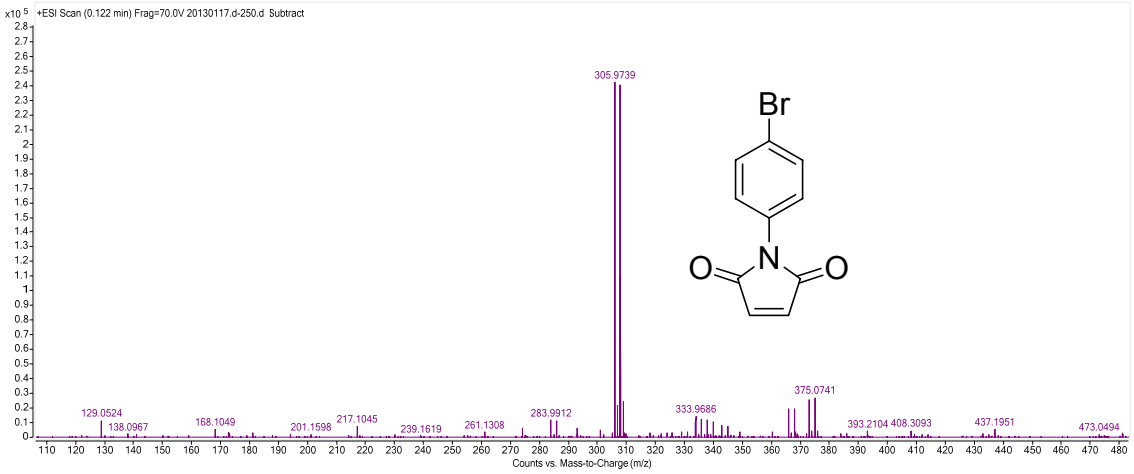


Fig. S7 TOF HRMS ESI+ of **2b**.

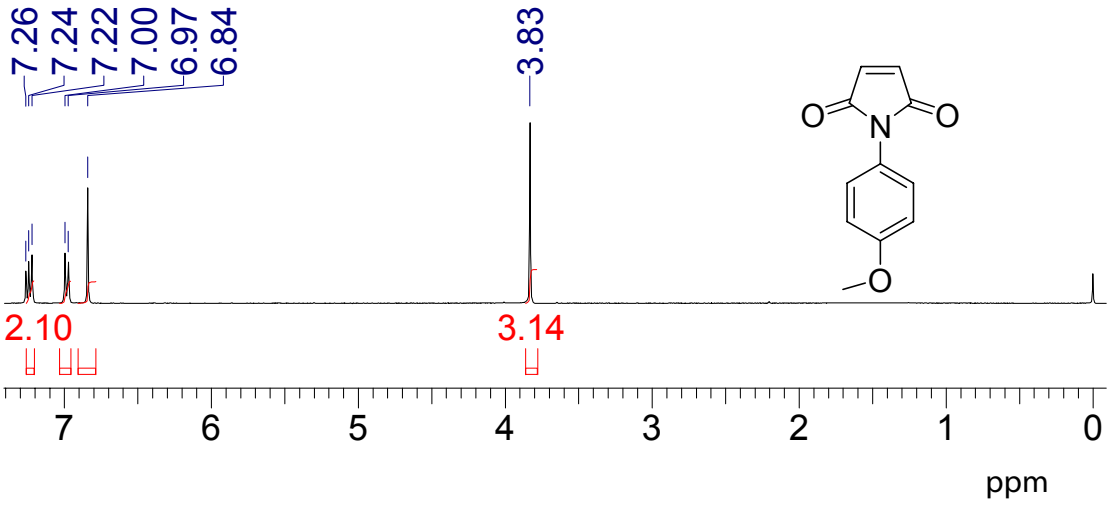


Fig. S8 ^{1}H NMR of **2c** (400 MHz. In $CDCl_3$).

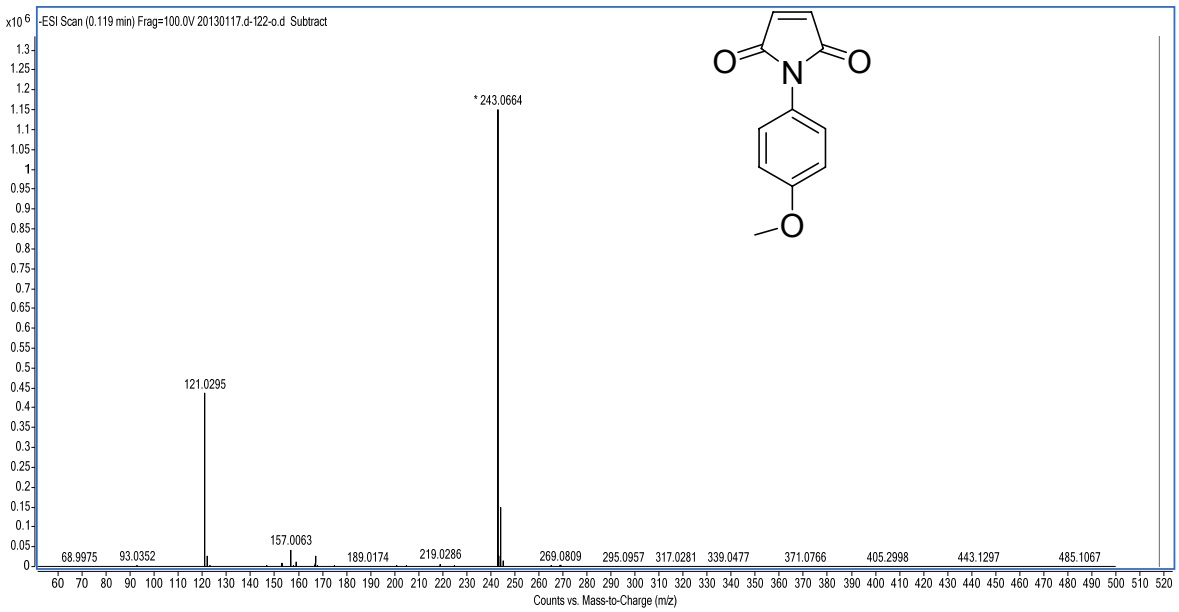


Fig. S9 TOF HRMS ESI+ of **2c**.

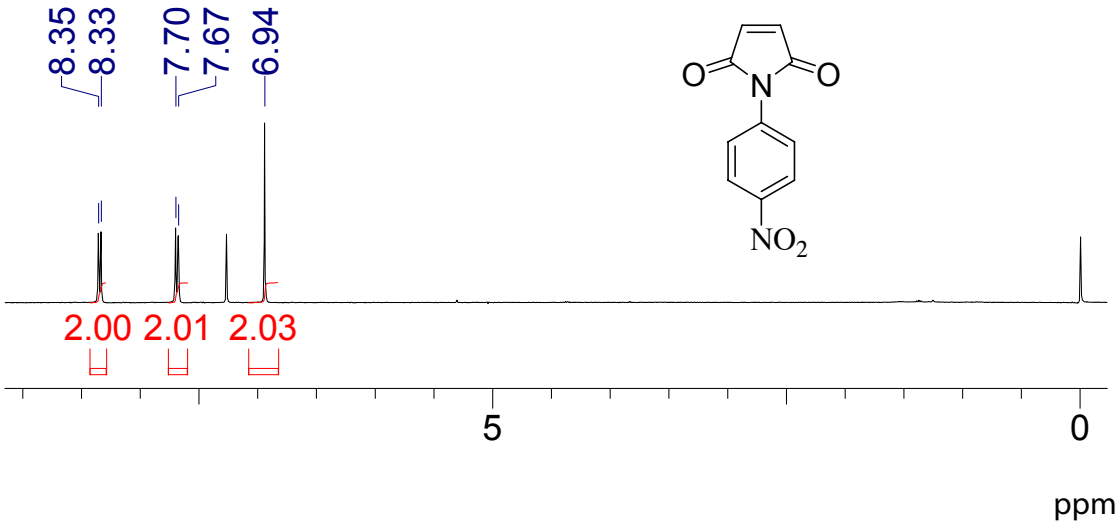


Fig. S10 ^{1}H NMR of **2d** (400 MHz. In $CDCl_3$).

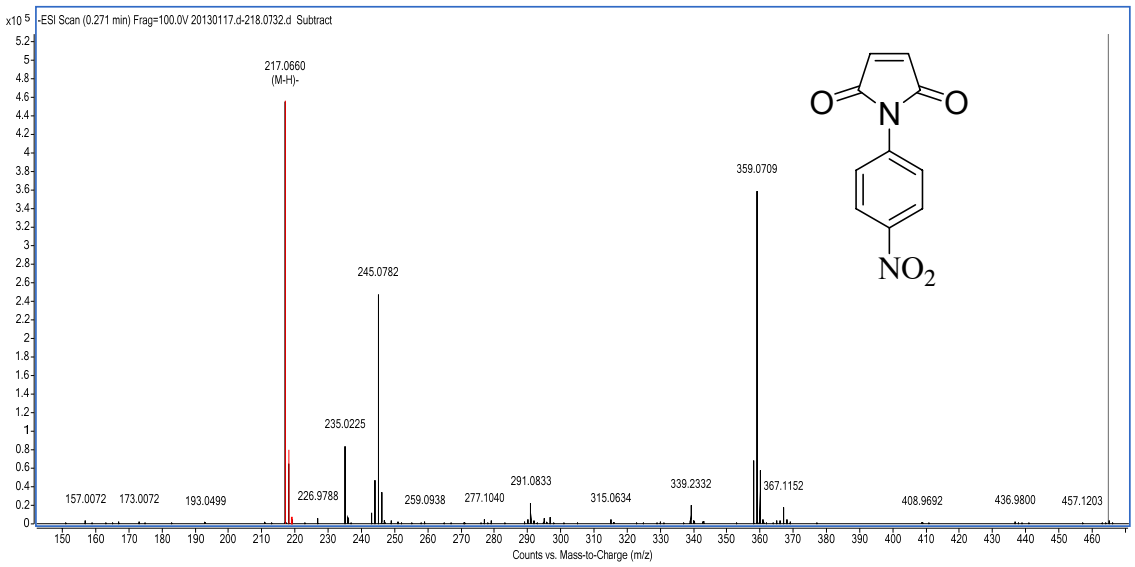


Fig. S11 TOF HRMS ESI+ of **2d**.

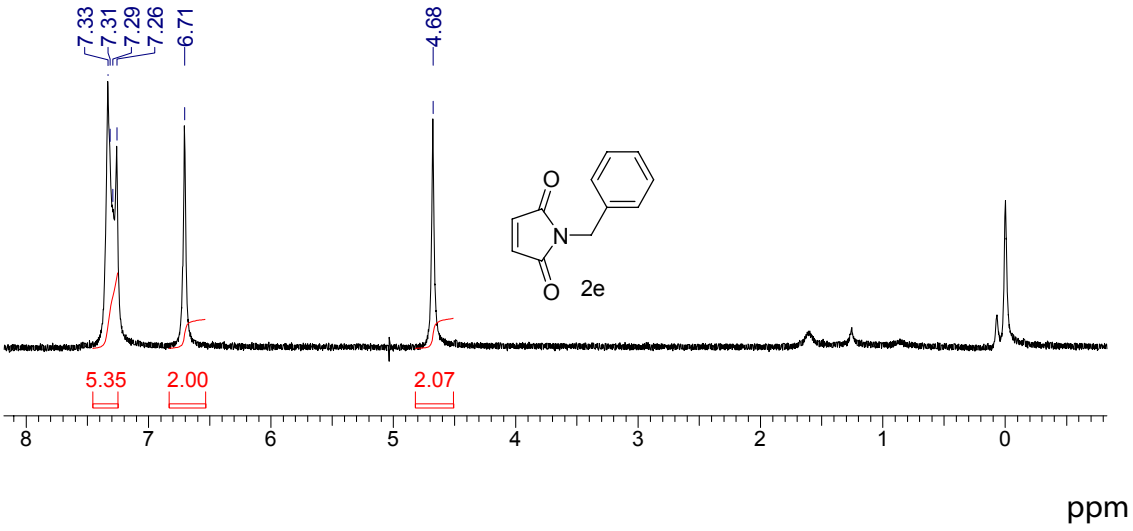


Fig. S12 ^{1}H NMR of **2e** (400 MHz. In $CDCl_3$).

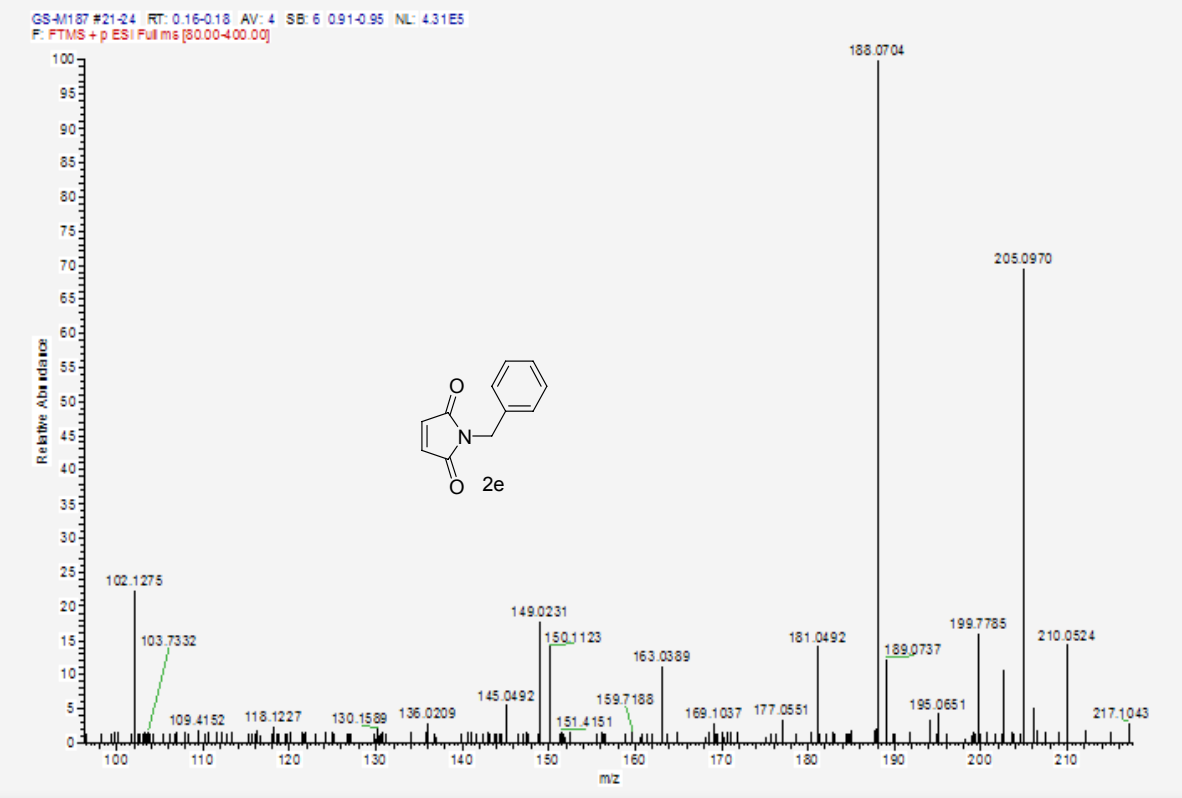


Fig. S13 TOF HRMS ESI+ of **2e**.

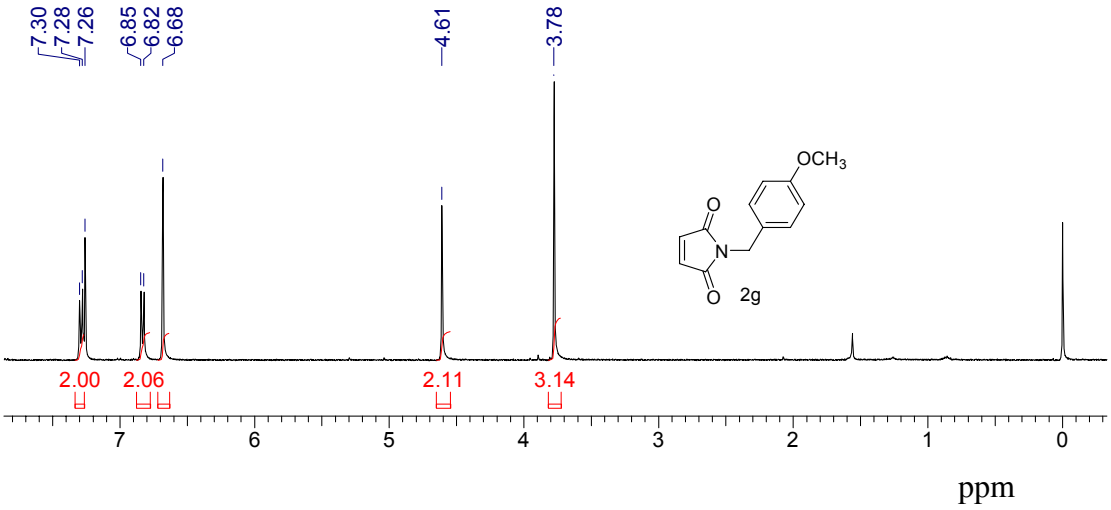


Fig. S14 ^{1}H NMR of **2g** (400 MHz. $CDCl_3$).

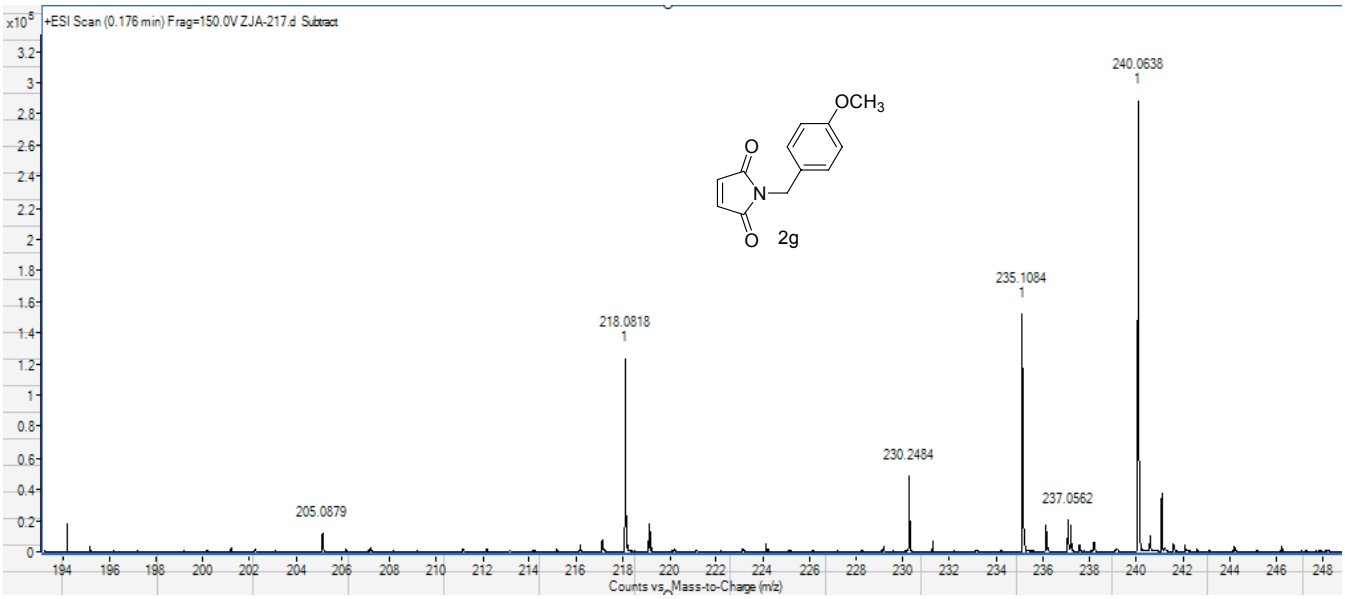


Fig. S15 TOF HRMS ESI+ of **2g**.

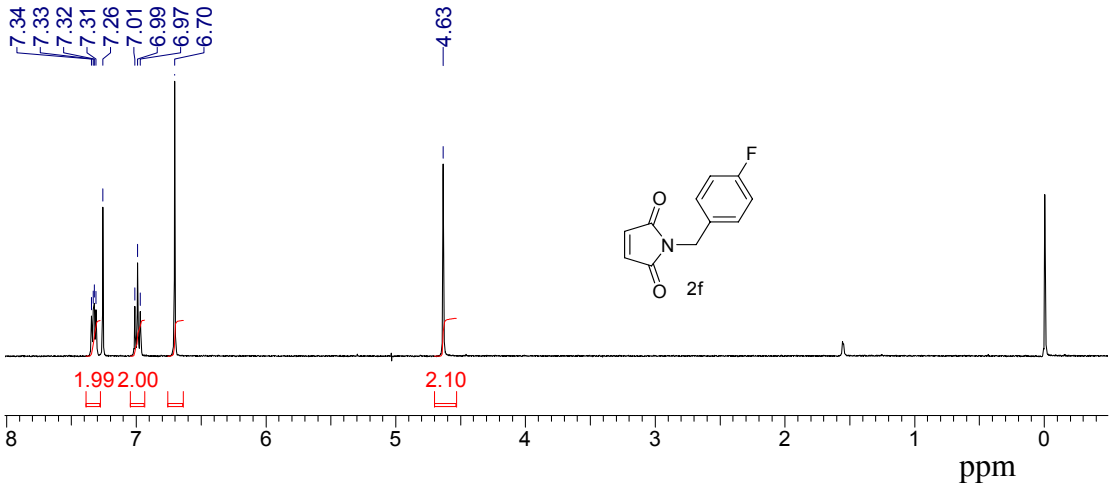


Fig. S16 ^{1}H NMR of **2f** (400 MHz. $CDCl_3$).

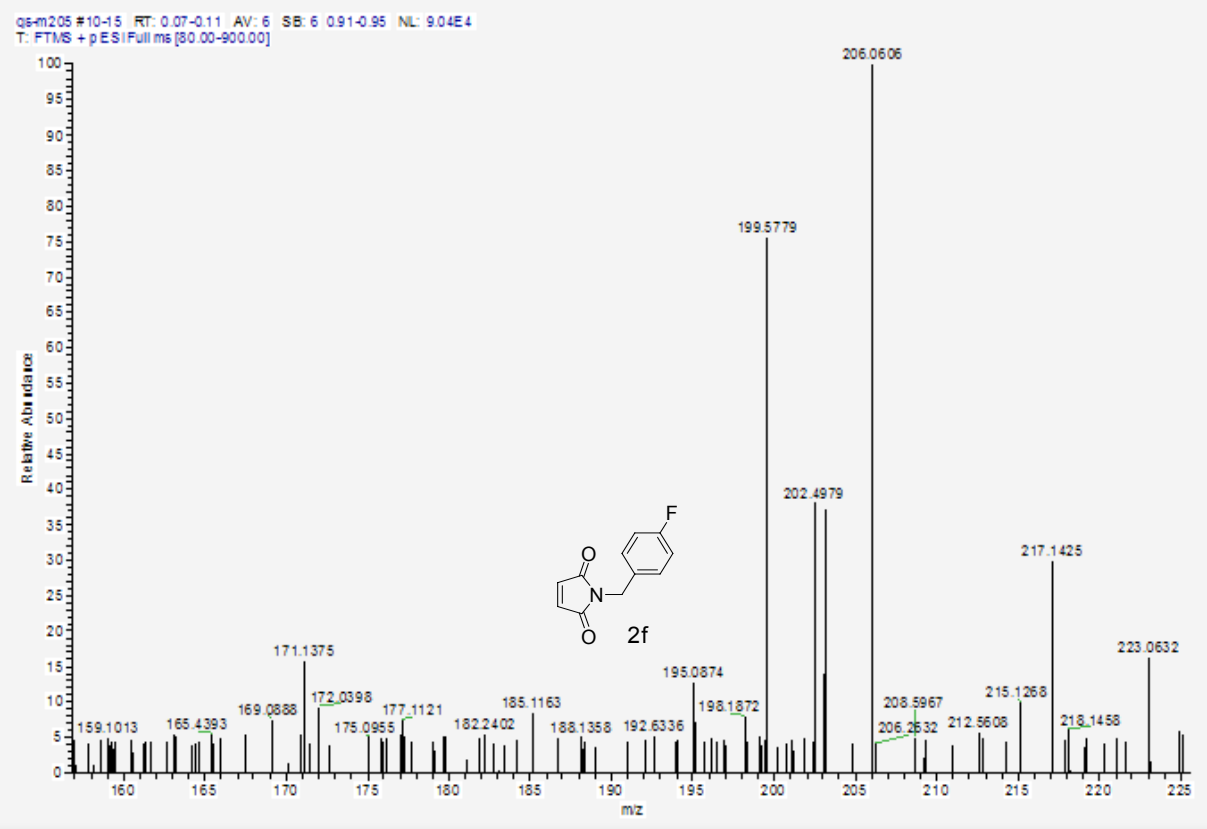


Fig. S17 TOF HRMS ESI^{+} of **2f**.

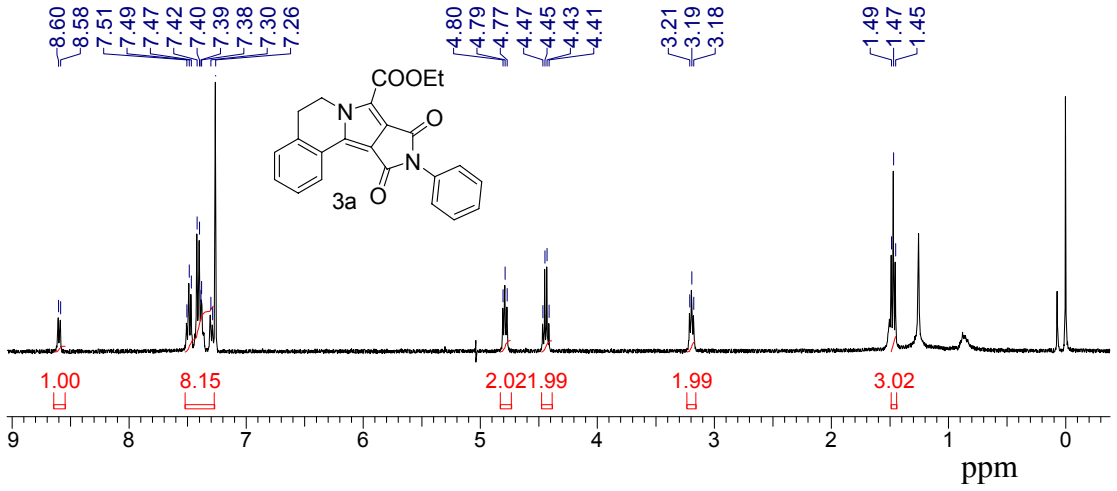


Fig. S18 ^{1}H NMR of **3a** (400 MHz. In $CDCl_3$).

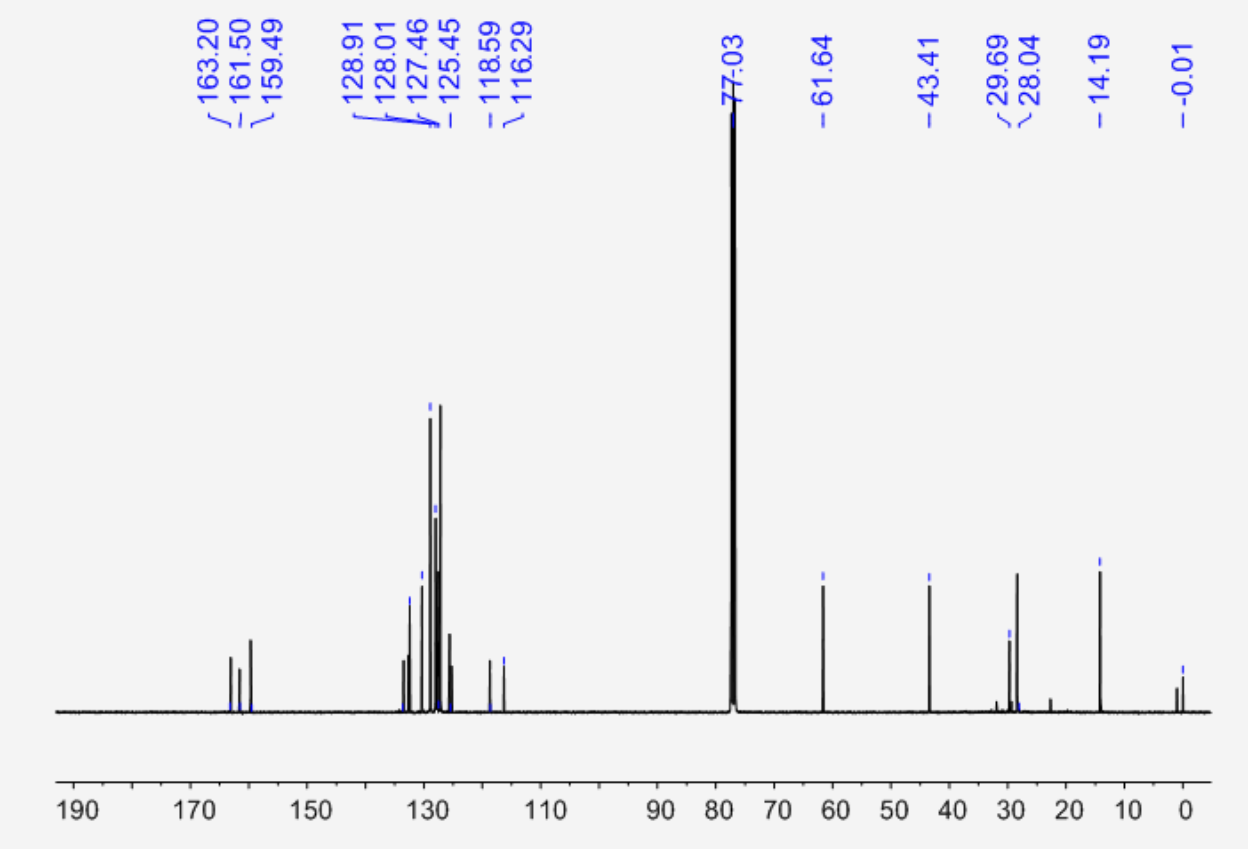


Fig. S19 ^{13}C NMR of **3a** (125 MHz. In $CDCl_3$).

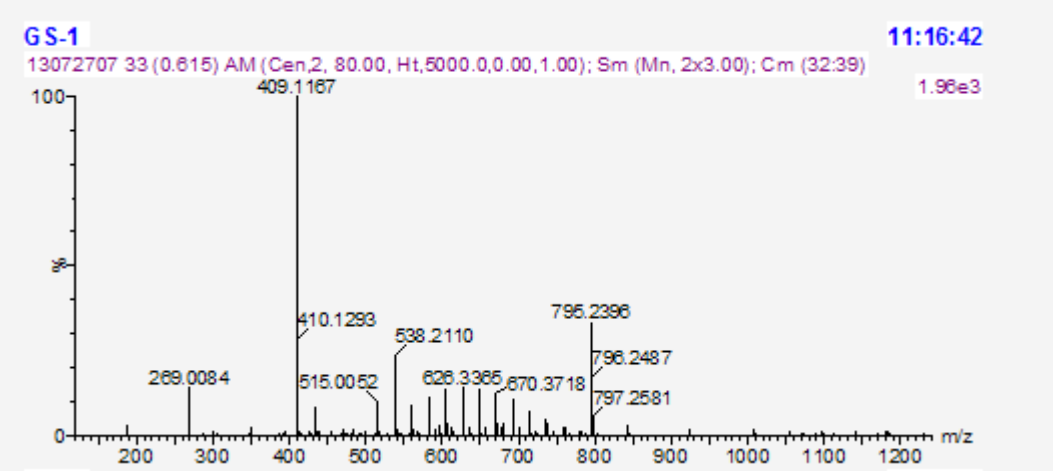


Fig. S20 TOF HRMS ESI^+ of **3a**.

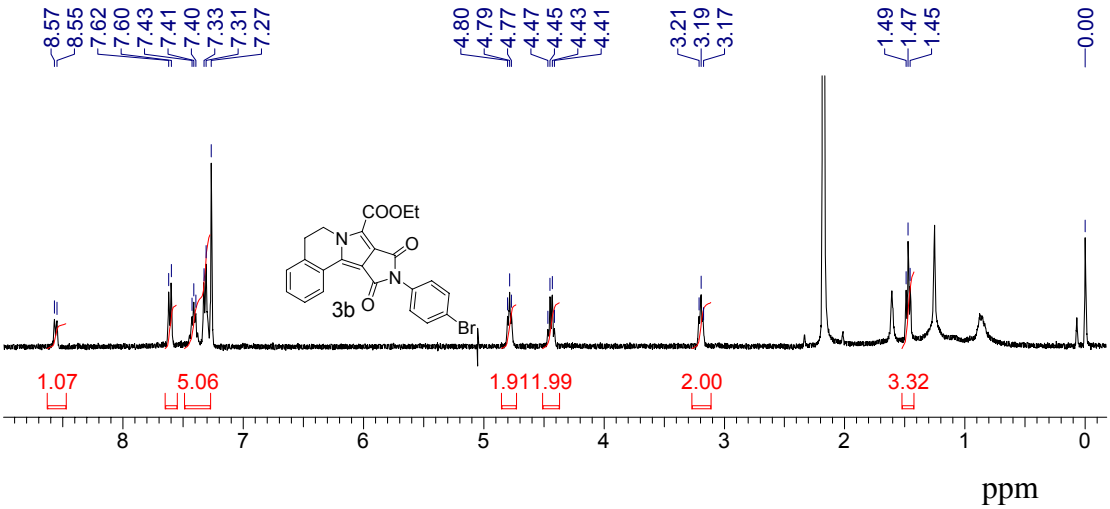


Fig. S21 ^{1}H NMR of **3b** (400 MHz. In $CDCl_3$).

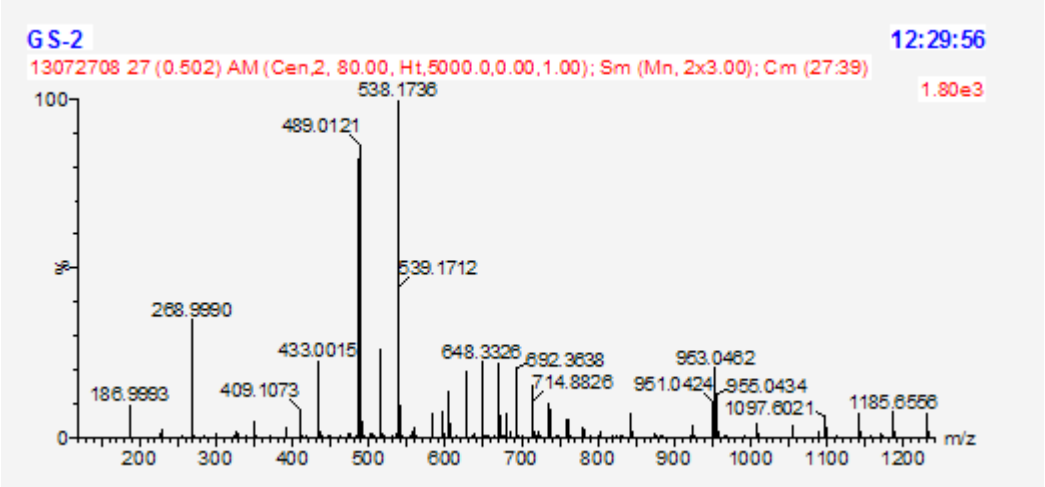


Fig. S22 TOF HRMS ESI+ of **3b**.

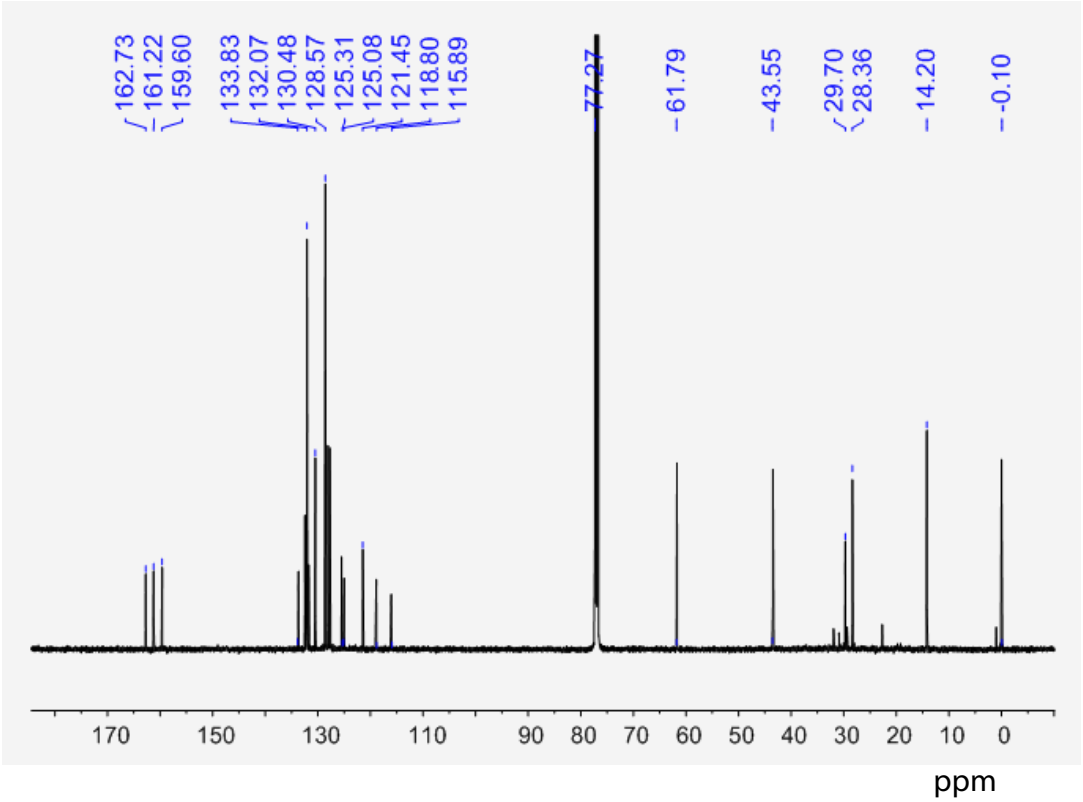


Fig. S23 ^{13}C NMR of **3b** (125 MHz. In $CDCl_3$).

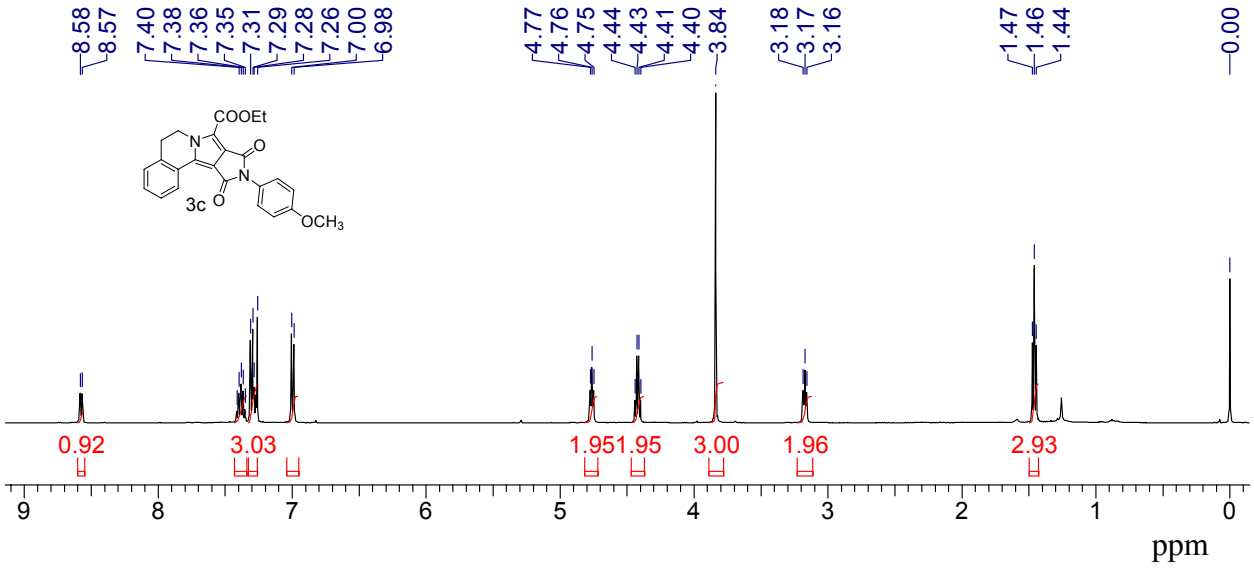


Fig. S24 ^{1}H NMR of **3c** (400 MHz. In $CDCl_3$).

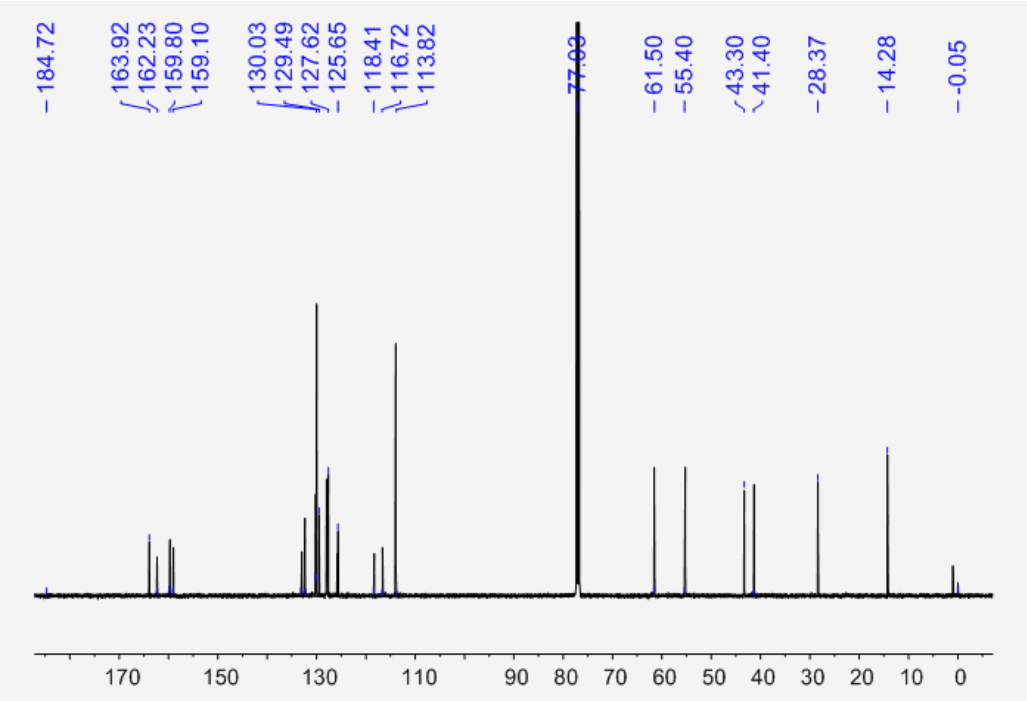


Fig. S25 ^{13}C NMR of **3c** (125 MHz. In $CDCl_3$).

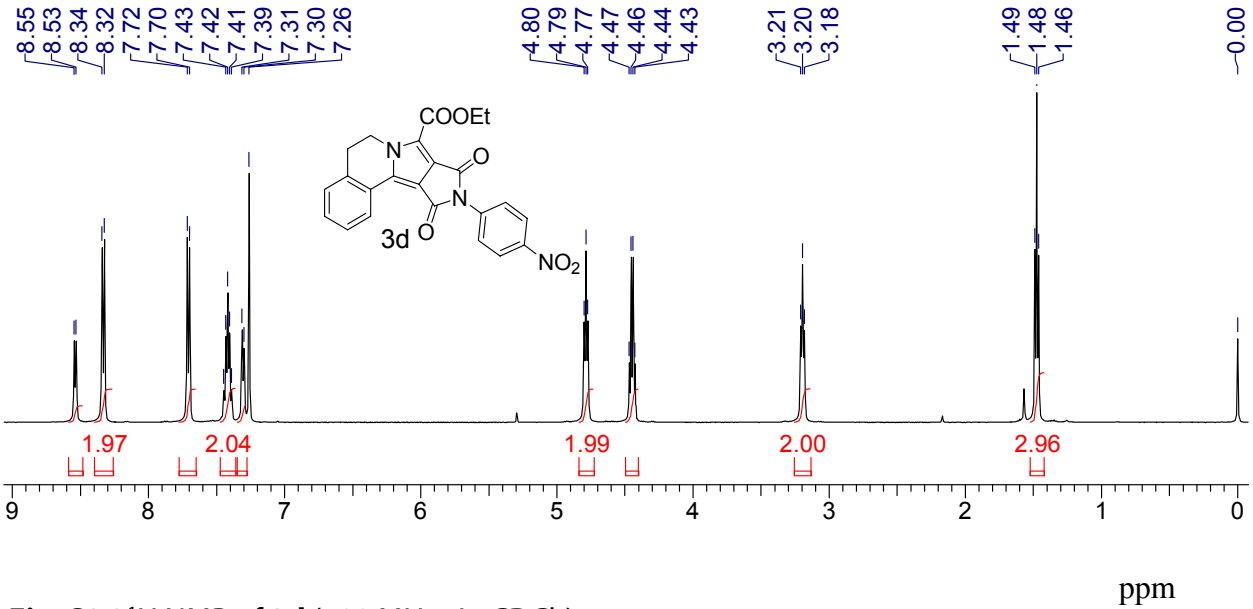


Fig. S26 ^{1}H NMR of **3d** (400 MHz. In $CDCl_3$).

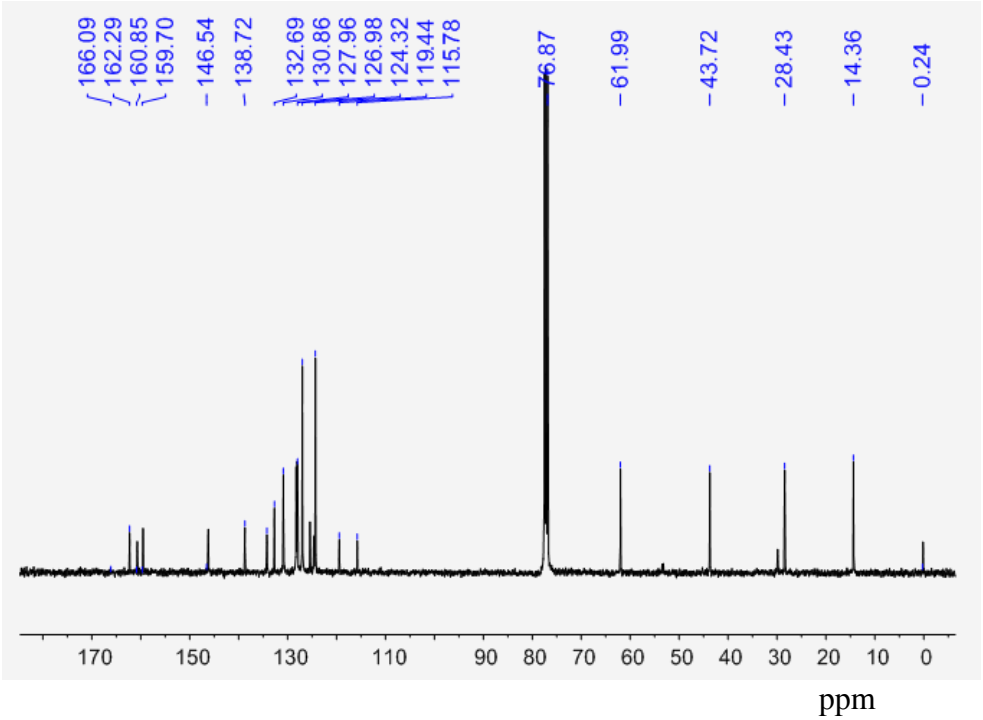


Fig. S27 ^{13}C NMR of **3d** (125 MHz. In $CDCl_3$).

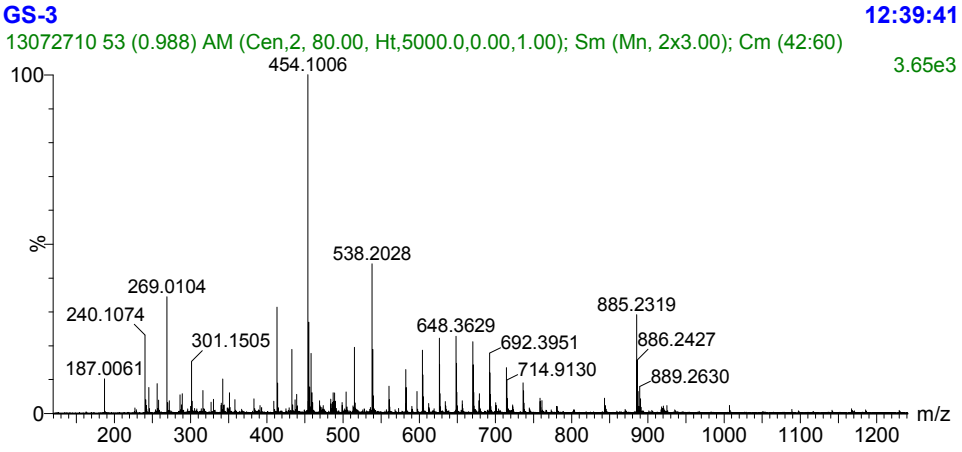


Fig. S28 TOF HRMS ESI+ of **3d**.

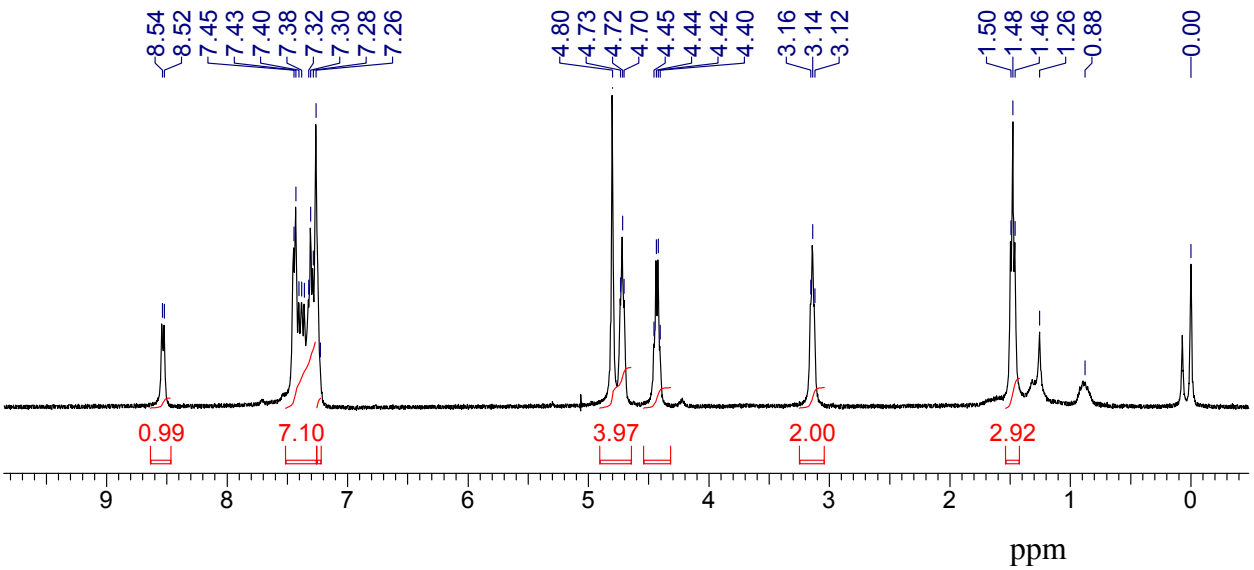


Fig. S29 ^{1}H NMR of 3e (400 MHz. In $CDCl_3$).

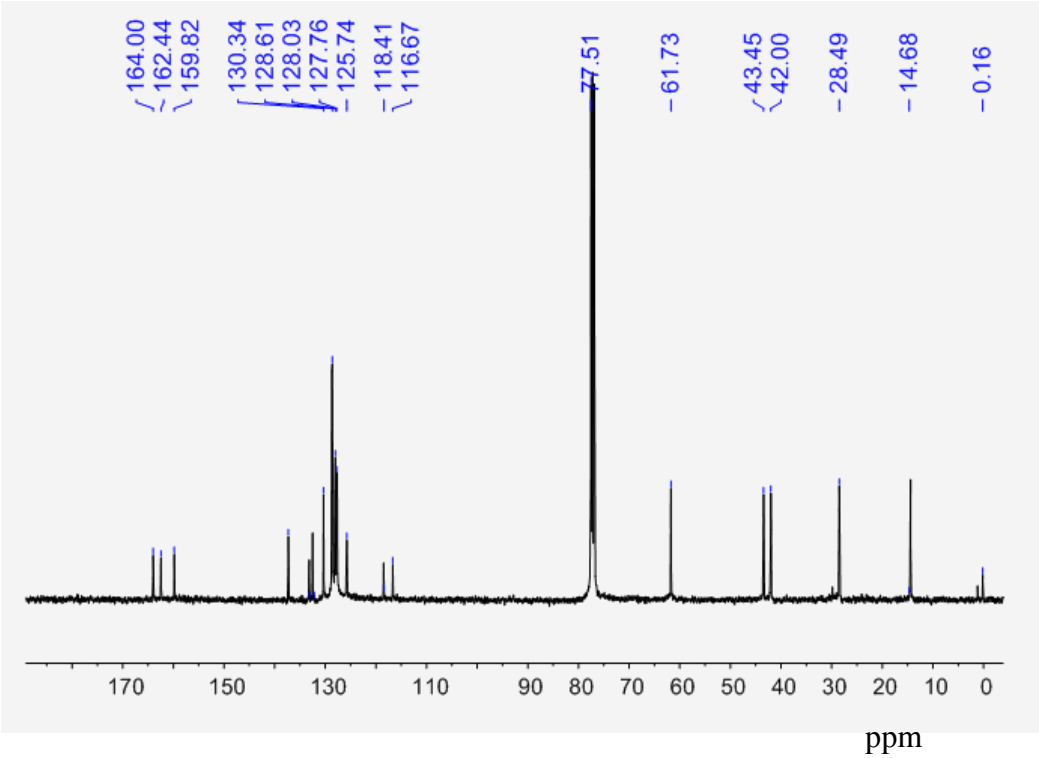


Fig. S30 ^{13}C NMR of **3e** (100 MHz. In $CDCl_3$).

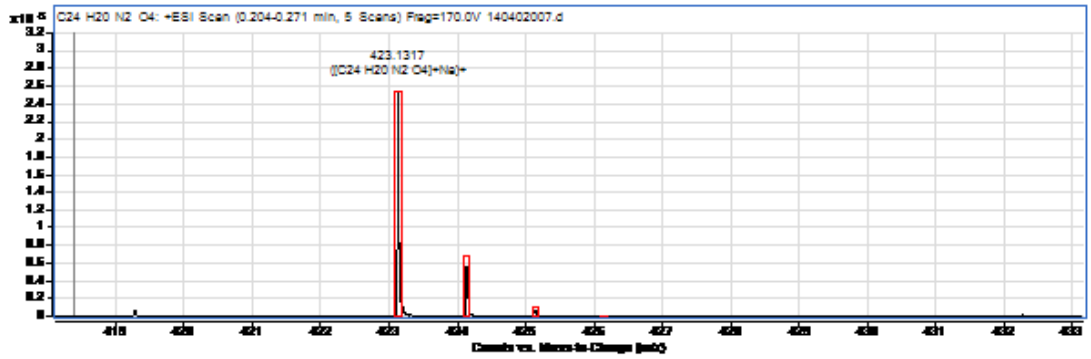


Fig. S31 TOF HRMS ESI$^+$ of 3e.

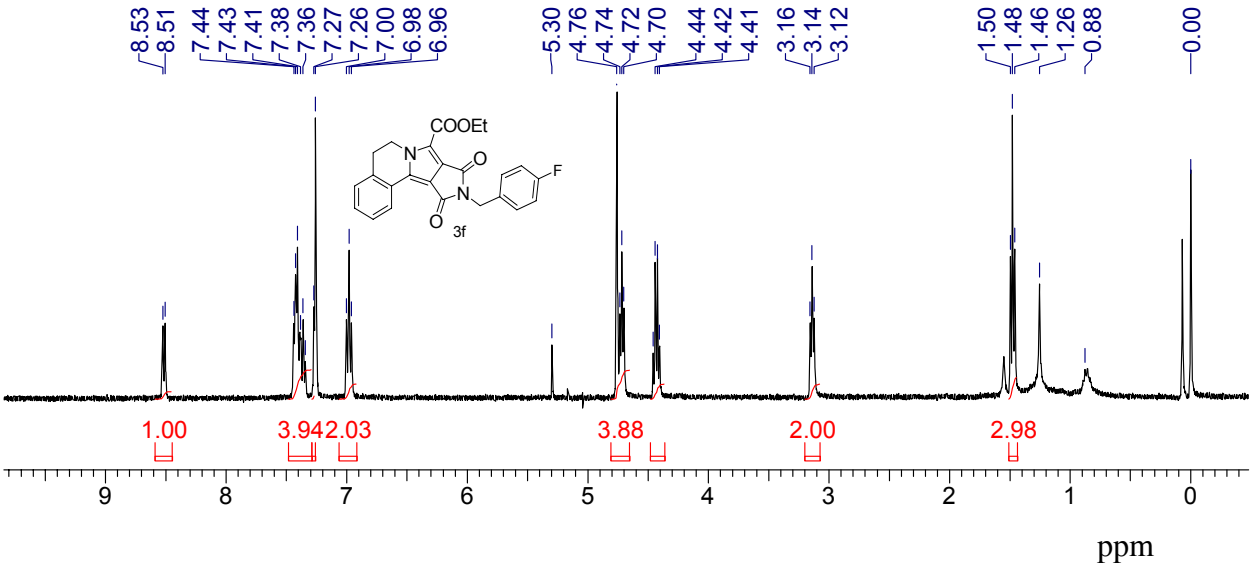


Fig. S32 ^{1}H NMR of **3f** (400 MHz. In $CDCl_3$).

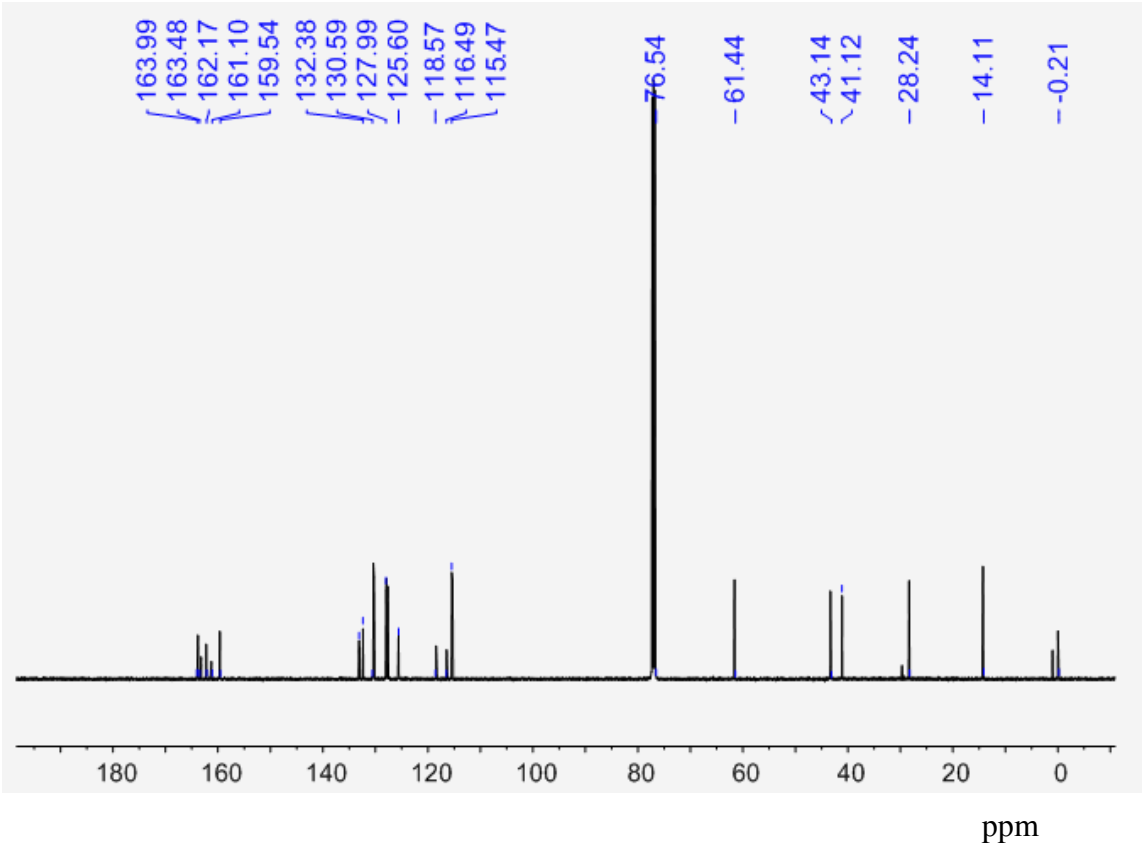


Fig. S33 ^{13}C NMR of **3f** (125 MHz. In $CDCl_3$).

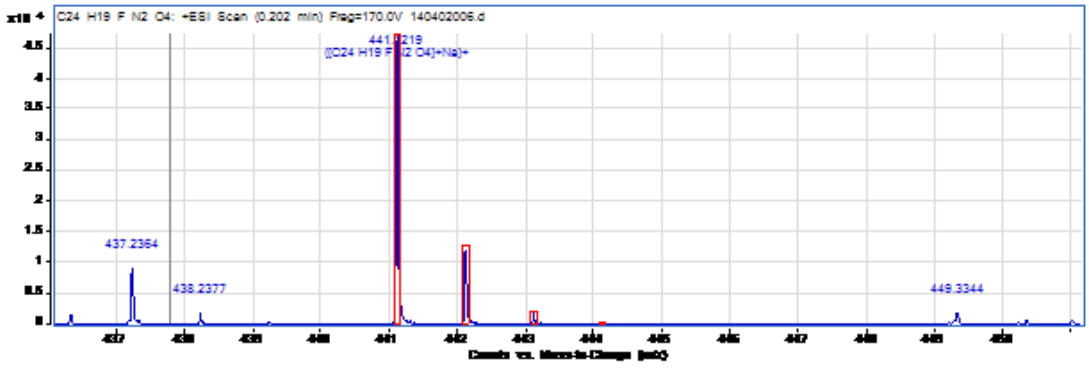


Fig. S34 TOF HRMS ESI$^+$ of **3f**.

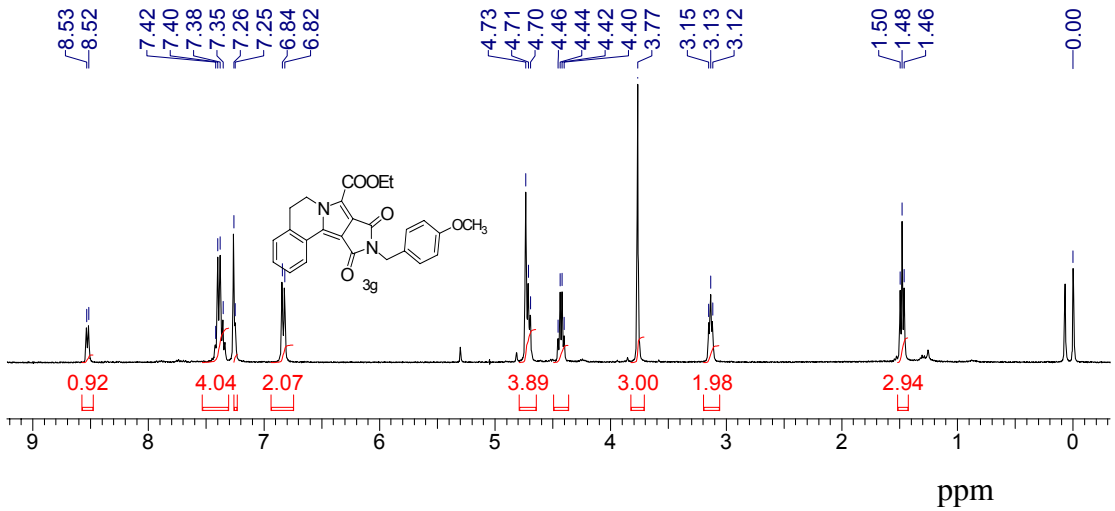


Fig. S35 ^{1}H NMR of 3g (400 MHz. In $CDCl_3$).

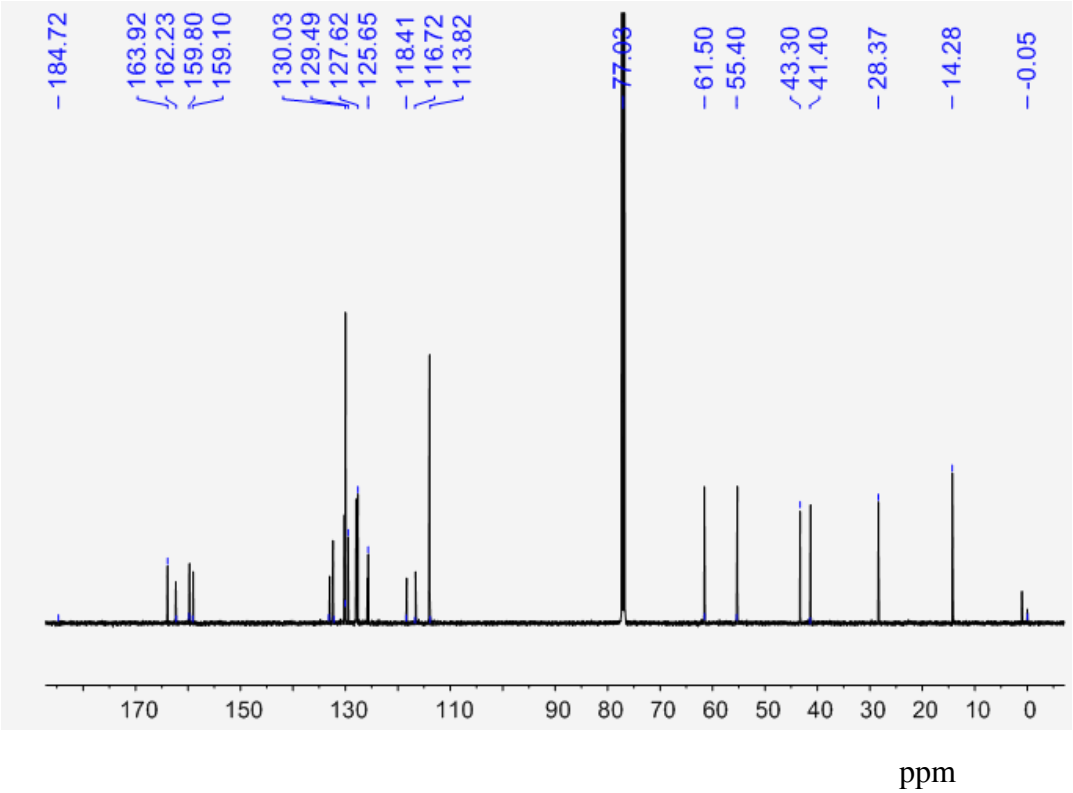


Fig. S36 ^{13}C NMR of **3g** (125 MHz. In $CDCl_3$).

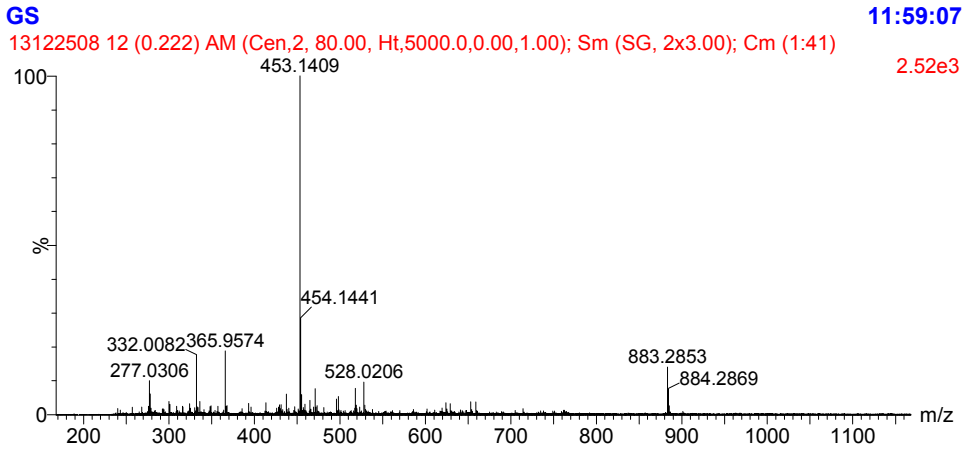


Fig. S37 TOF HRMS ESI^{+} of **3g**.

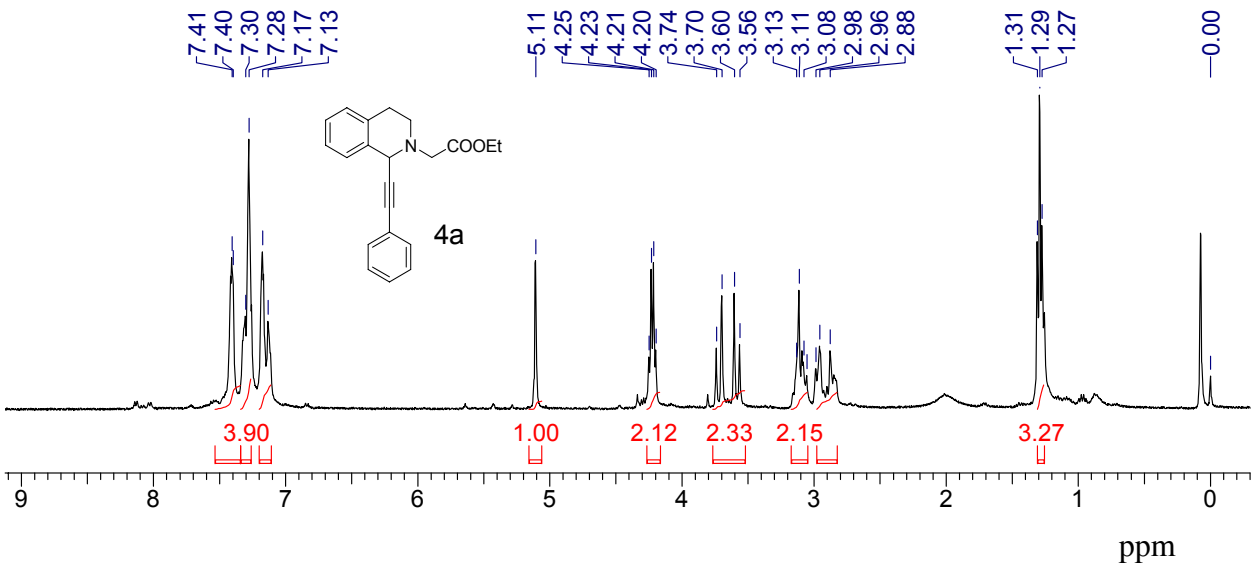


Fig. S38 ^{1}H NMR of **4a** (400 MHz. In $CDCl_3$).

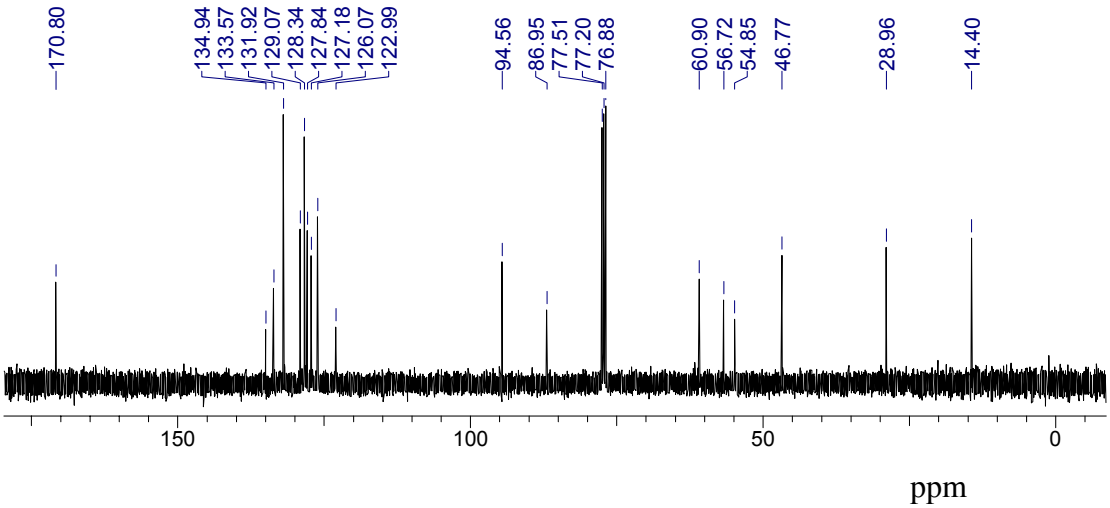


Fig. S39 ^{13}C NMR of **4a** (100 MHz. In $CDCl_3$).

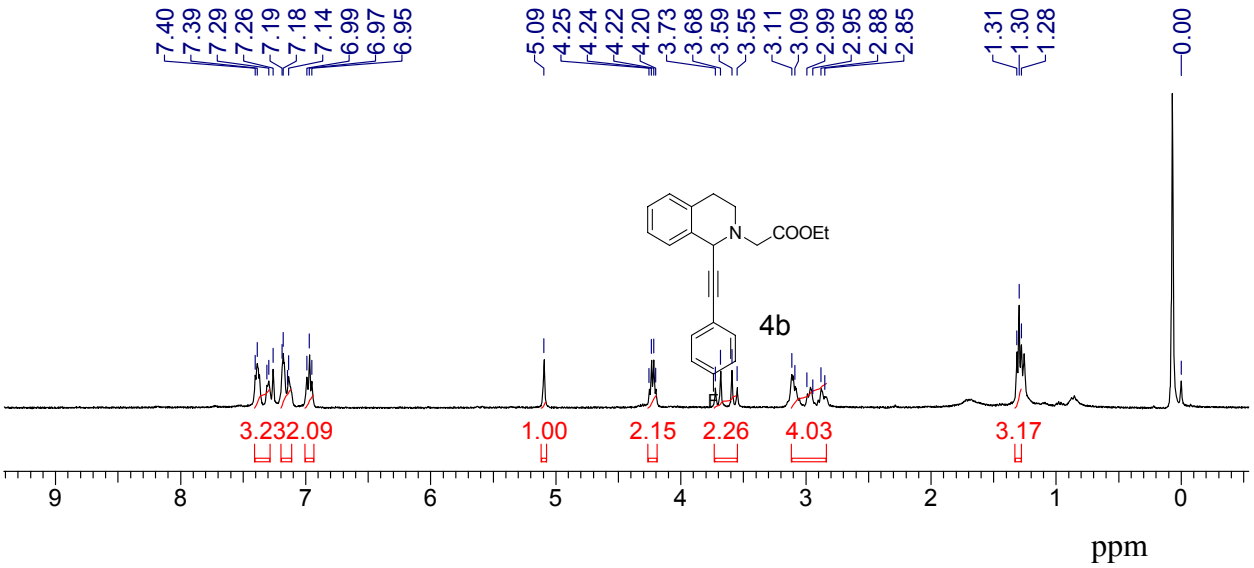


Fig. S40 ^{1}H NMR of **4b** (400 MHz. In $CDCl_3$).

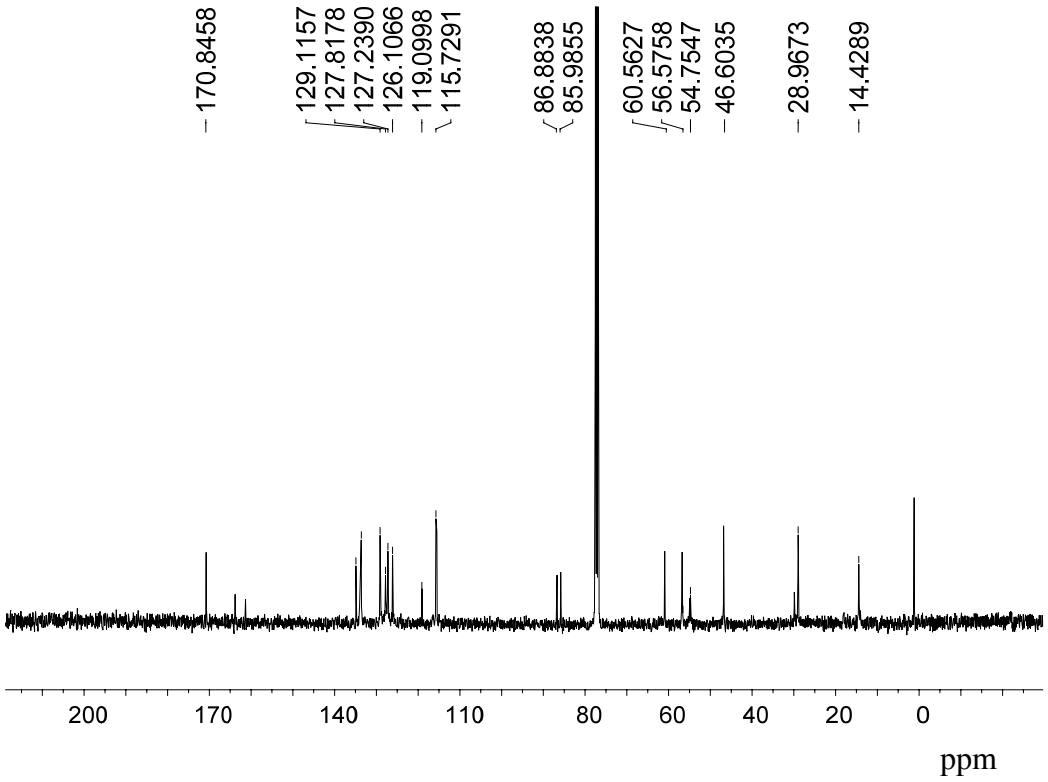


Fig. S41 ^{13}C NMR of **4b** (100 MHz. In $CDCl_3$).

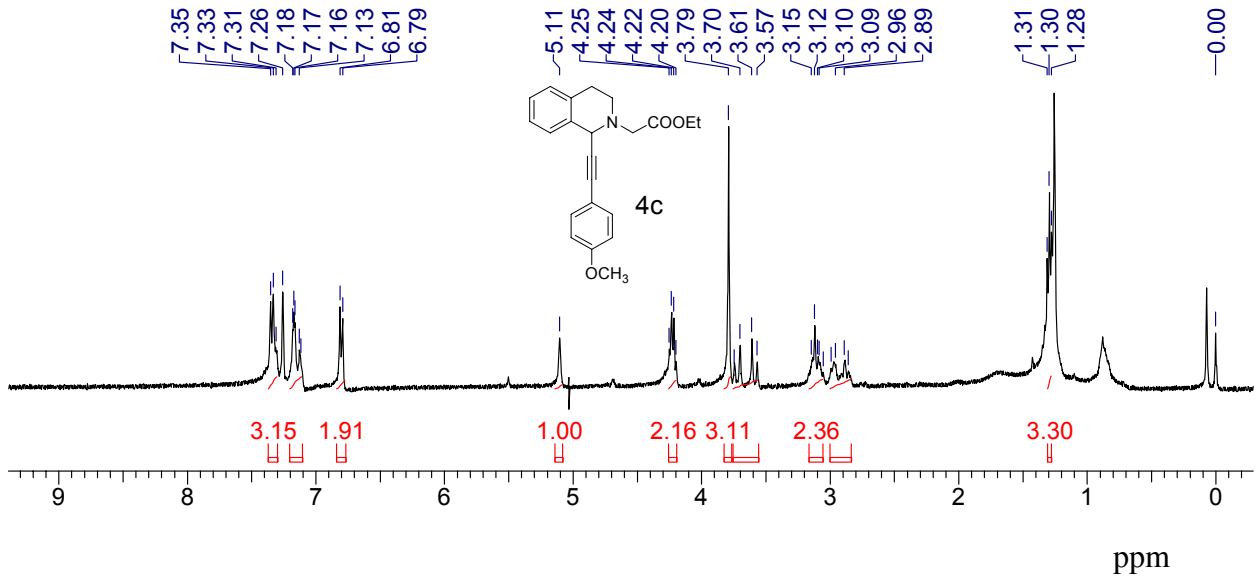


Fig. S42 ^{1}H NMR of **4c** (400 MHz. In $CDCl_3$).

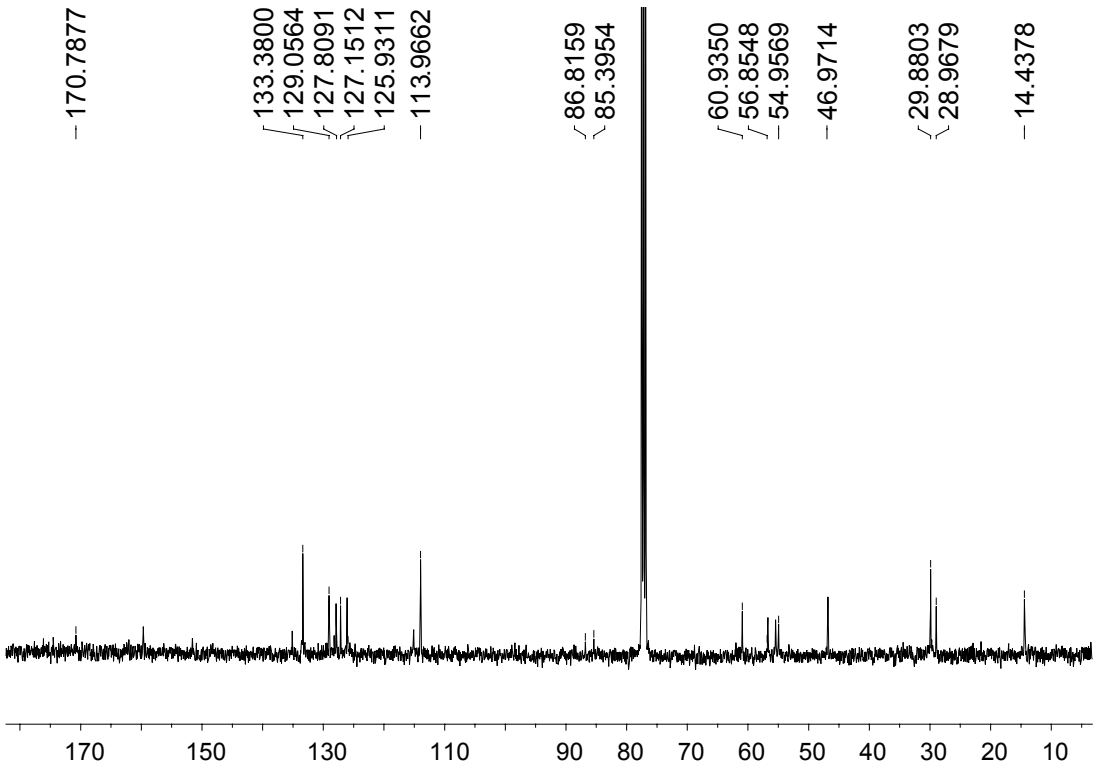


Fig. S43 ^{13}C NMR of **4c** (100 MHz. In $CDCl_3$).

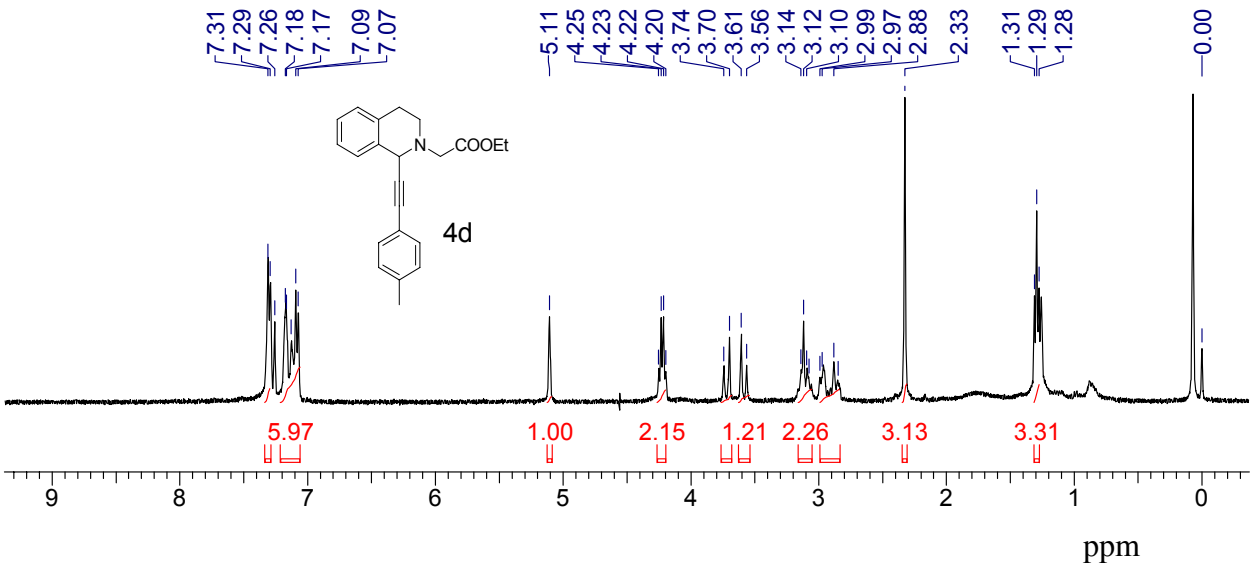


Fig. S44 ^{1}H NMR of **4d** (400 MHz. In $CDCl_3$).

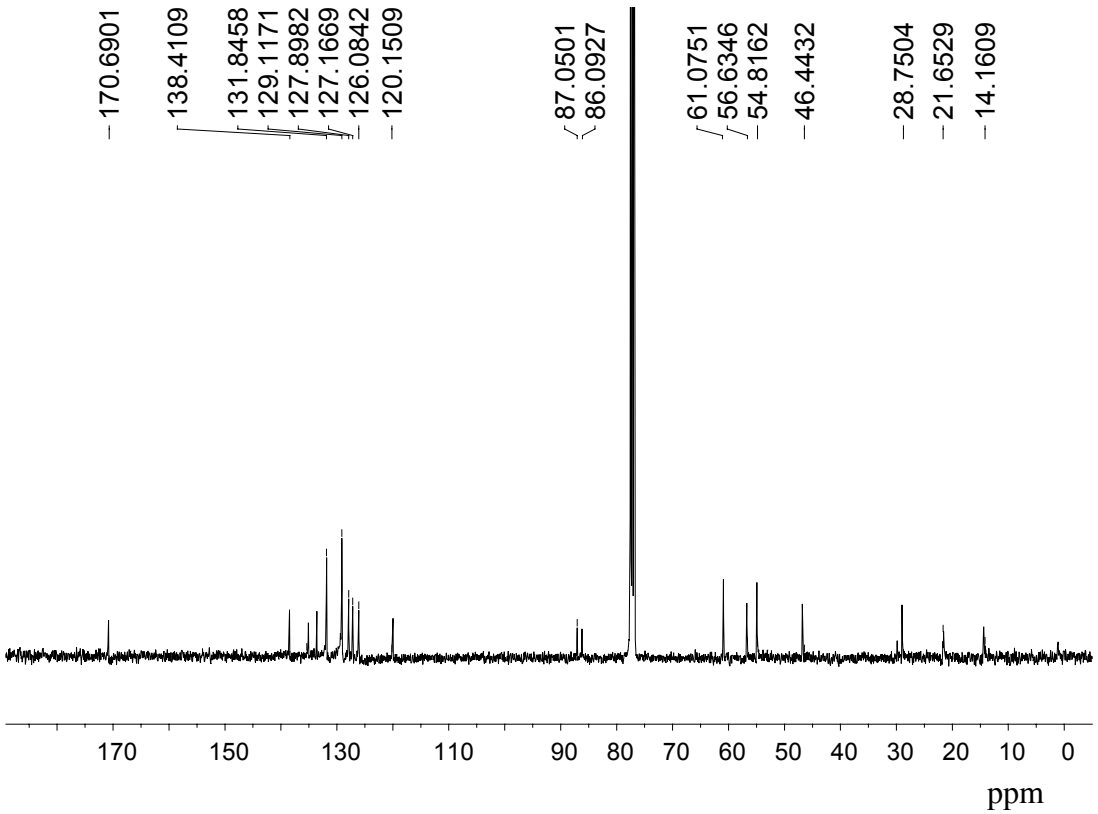


Fig. S45 ^{13}C NMR of **4d** (100 MHz. In $CDCl_3$).

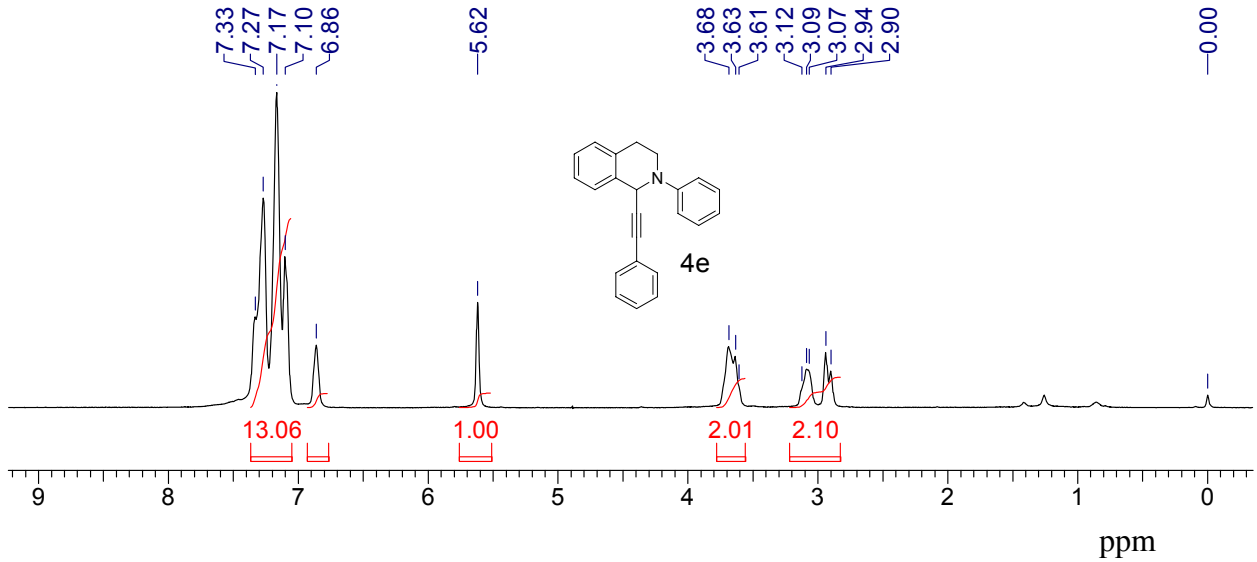


Fig. S46 ^{1}H NMR of **4e** (400 MHz. In $CDCl_3$).

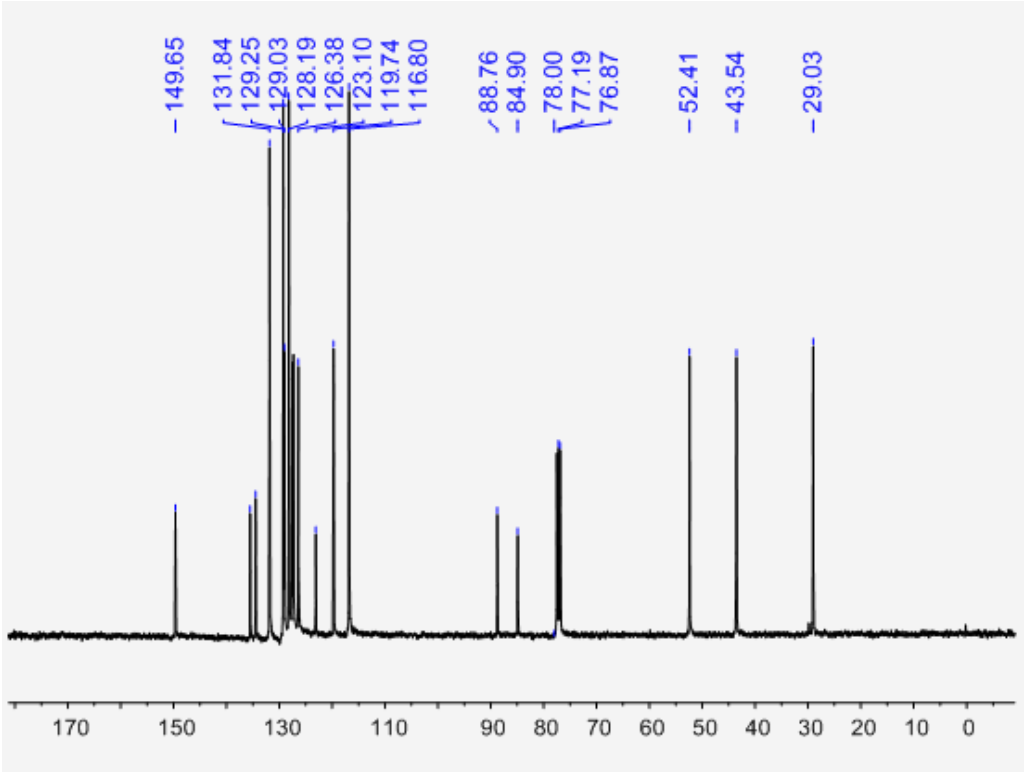


Fig. S47 ^{13}C NMR of **4e** (100 MHz. In $CDCl_3$).

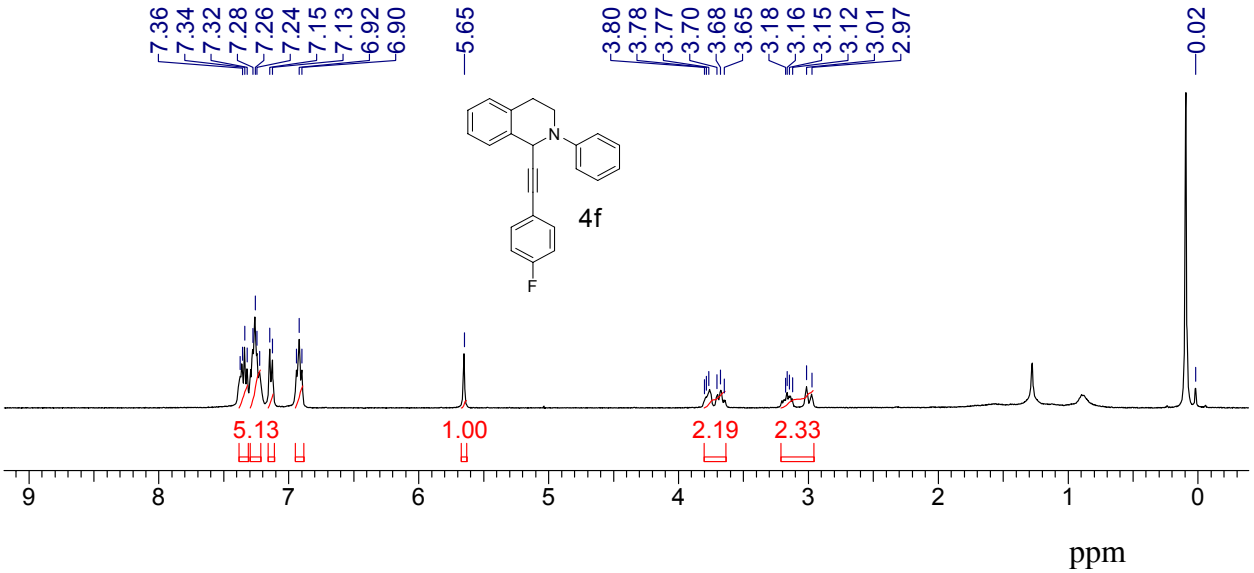


Fig. S48 ^{1}H NMR of **4f** (400 MHz. In $CDCl_3$).

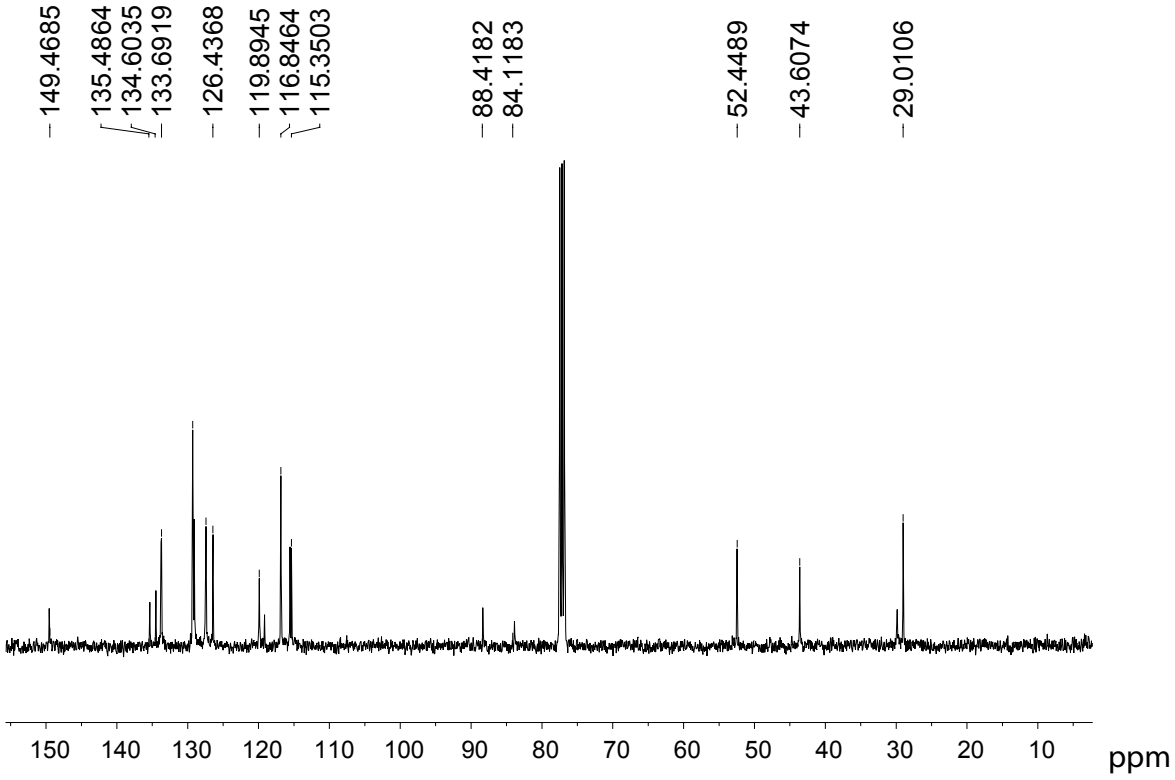


Fig. S49 ^{13}C NMR of **4f** (100 MHz. In $CDCl_3$).

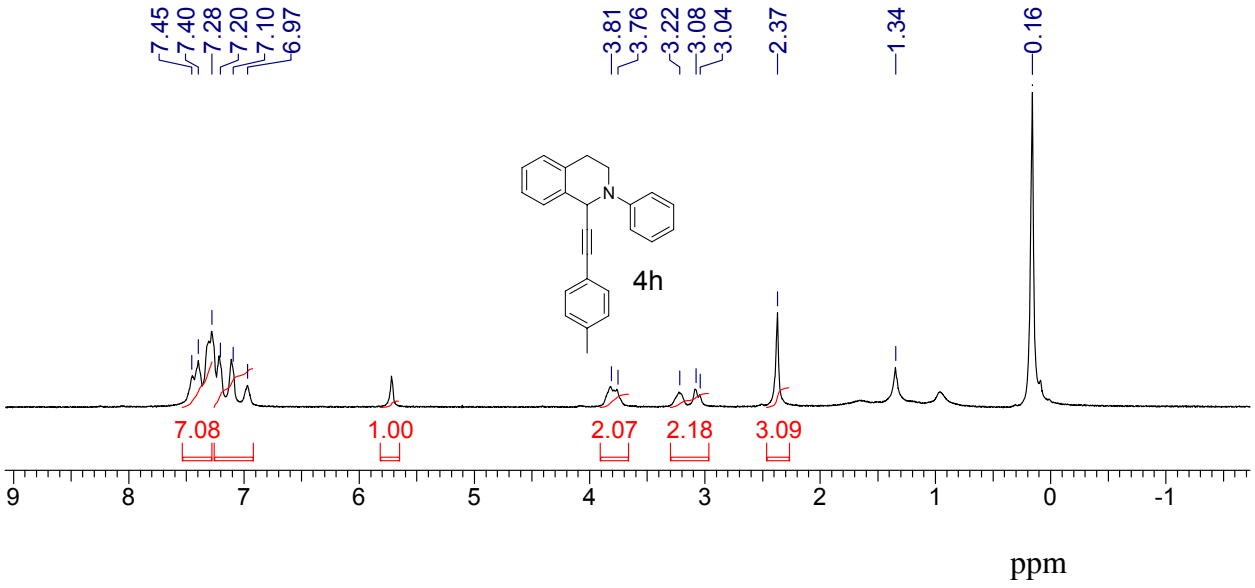


Fig. S50 ^{1}H NMR of **4h** (400 MHz. In $CDCl_3$).

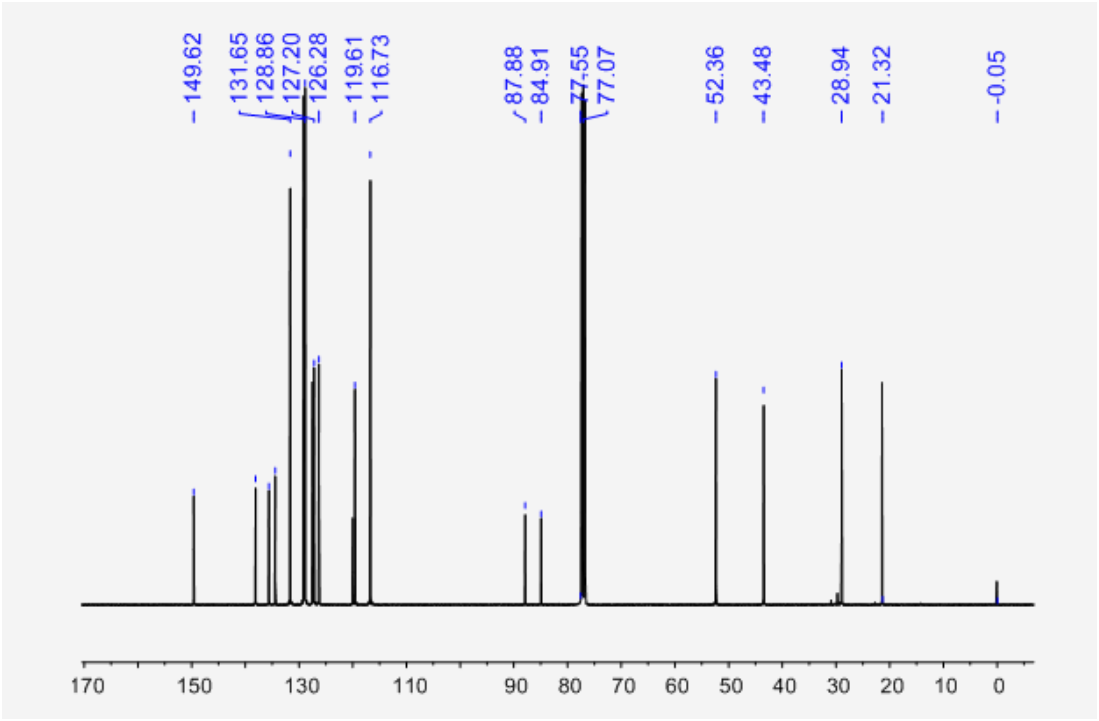


Fig. S51 ^{13}C NMR of **4h** (100 MHz. In $CDCl_3$).

3. Photophysical and photochemistry of B-1 and B-2

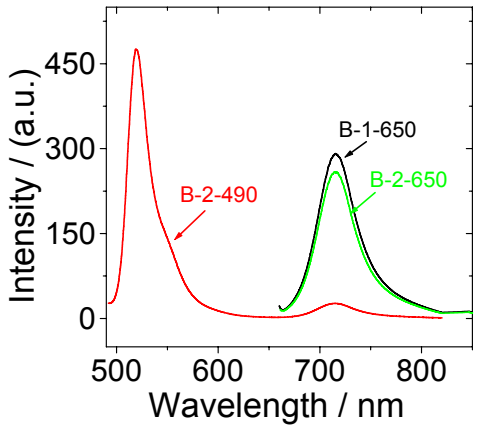


Fig. S52 The fluorescence spectra of the Bodipy dyads. (a) The emission spectra of **B-1** and **B-2**, λ_{ex} = 650 nm; B-2, λ_{ex} = 490 nm; c =1.0×10^{-5} M in toluene, 20 °C.

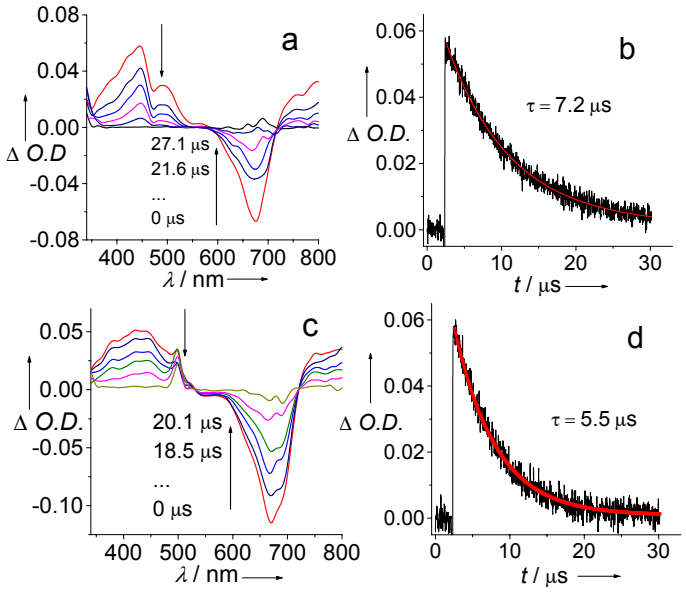


Fig. 53 Nanosecond time-resolved transient difference absorption spectra of (a) **B-1** and (c) **B-2**. The decay curves are (b) **B-1** at 430 nm and (d) **B-2** at 430 nm, respectively. After pulsed excitation at 355 nm (deaerated toluene, 2.0×10^{-5} M, 20 °C).

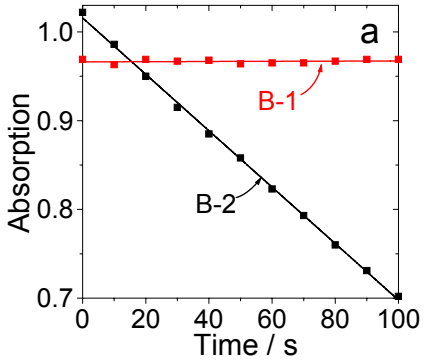


Fig. S54 Comparative singlet oxygen generation experiment. Absorbance decrease of DPBF with time in the presence of photosensitizers: **B-1** and **B-2**. The samples were irradiated with monochromatic light from spectrofluorometer (λ_{ex} = 501nm); c [sensitizers] = 5.0×10^{-4} M. 20 °C.

4. Mechanism of the photocatalytic reaction

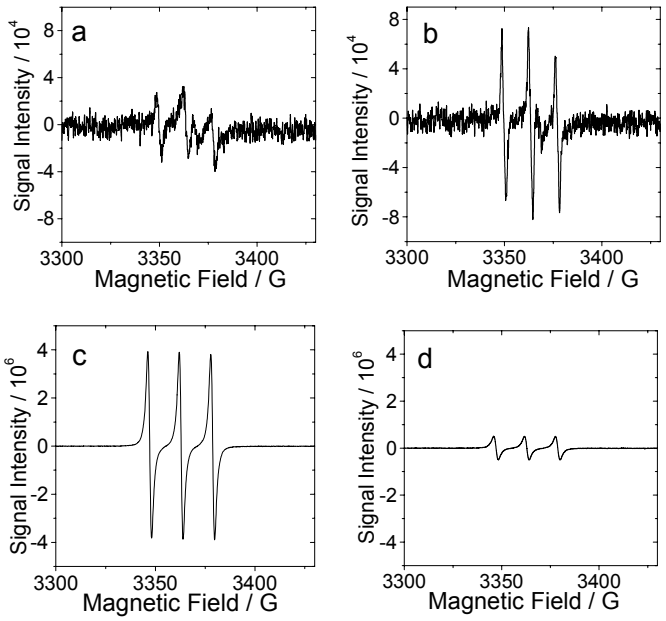
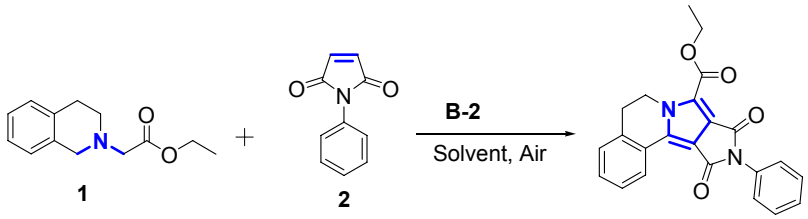


Fig. S55 (a) ESR spectrum of the mixture **B-1** (4.0×10^{-4} M) and DMPO (2.0×10^{-2} M); (b) ESR spectrum of the mixture **B-1** (4.0×10^{-4} M), **1a** (5.0×10^{-2} M) and DMPO (2.0×10^{-2} M); (c) **B-1** (4.0×10^{-4} M), TEMP (0.10M); (d) **B-1** (4.0×10^{-4} M), TEMP (0.10 M), **1a** (5.0×10^{-2} M). In air saturated CH_3CN. All the irradiations were performed with 635 nm continuous laser and the duration is 120 s (210 mW/cm^2). 22 °C.



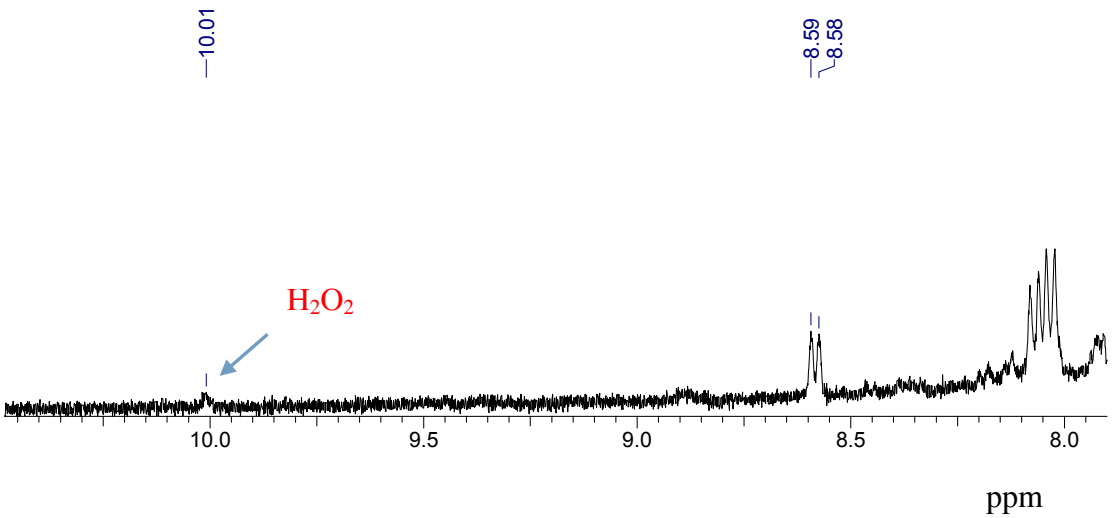


Fig. S56 ^{1}H NMR of reaction solution after 1.5 h irradiation, **B-2**(1mmol%), 300mW/m^2, in CH_2Cl_2, $CDCl_3$ (400 MHz). **1** (0.15 mmol), **2a** (0.10 mmol), **B-2**(1mol%)were mixed in dichloromethane (5.0 mL), the mixture was irradiated with 35 W Xe lamp (λ > 385 nm), R.T.

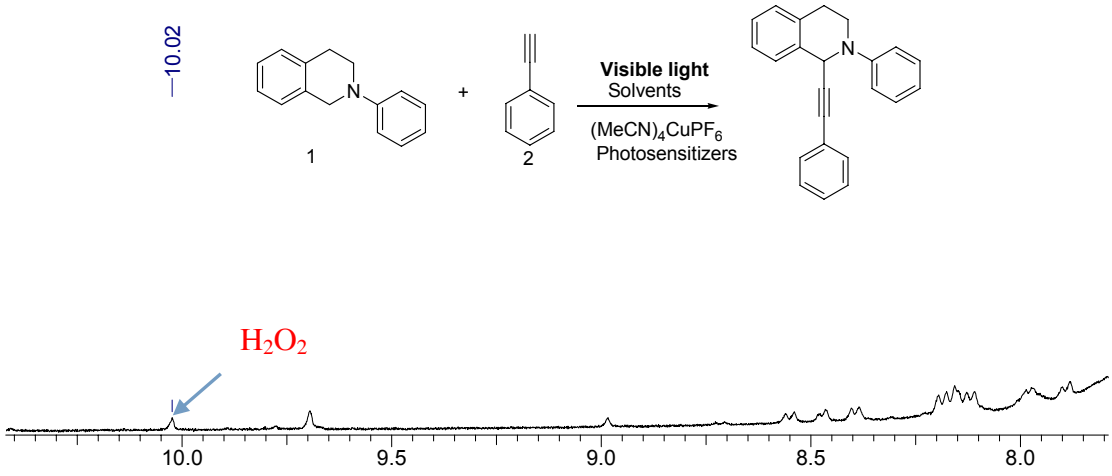
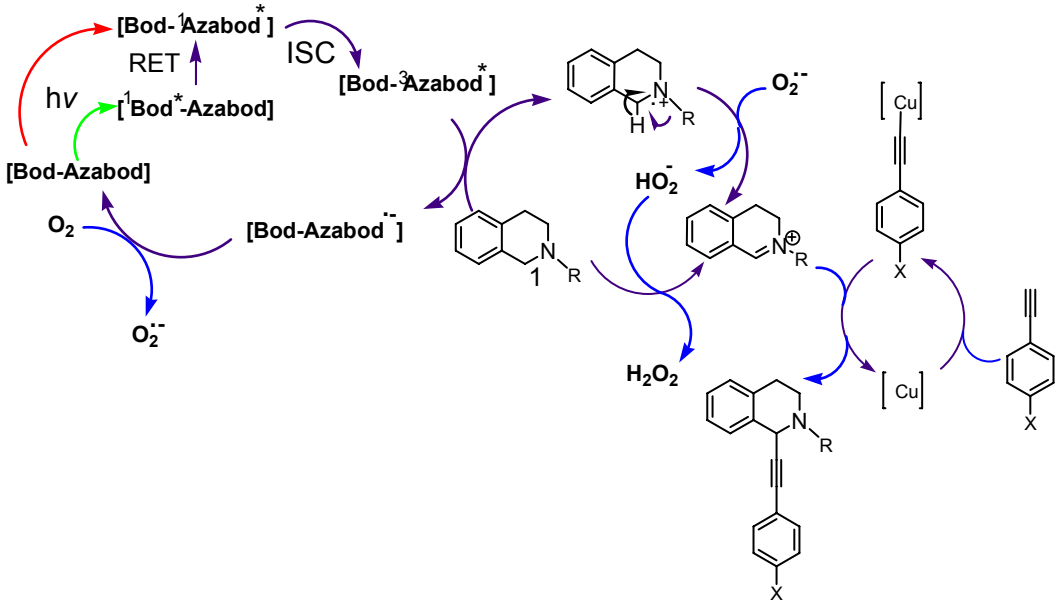


Fig. S57 ^{1}H NMR of reaction solution after 3 h irradiation, **B-2**(1mmol%), 300mW/m^2, in CH_3CN, $CDCl_3$ (400 MHz). **1** (0.10 mmol), **2** (0.80 mmol), $(MeCN)_4CuPF_6$ (10 mol%), B-2 (1mol%)were mixed in CH_3CN (2.0 mL), the mixture was irradiated with 35 W Xe lamp (λ > 385 nm), R.T.

Scheme S1. Proposed Mechanism of the Photoredox catalysis and metal catalysis sequence with the Organic Photocatalysts **B-2**.



5. Spectrum of the Xenon lamp and the UV-Vis absorption spectrum of the photocatalyst

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

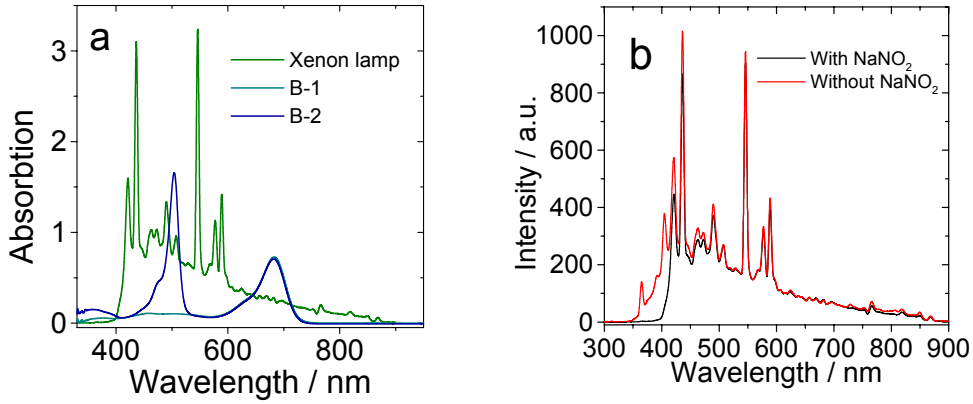
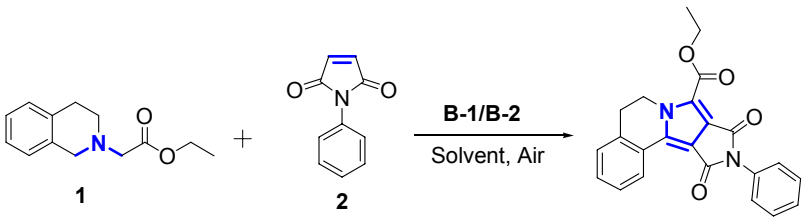


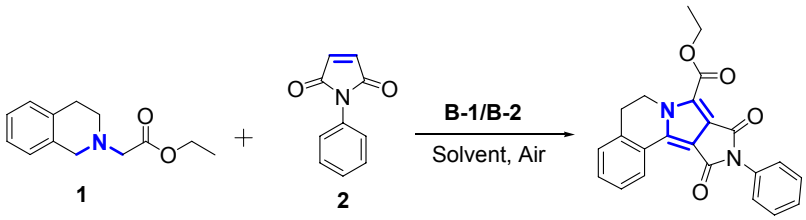
Fig. S58 (a) Comparison of the UV-Vis absorption spectra of **B-1**, **B-2** and the emission spectra of the 35 W xenon lamp (measured with spectrofluorometer). In CH_2Cl_2, 1.0×10^{-5} M, 20°C. The excitation of xenon lamp with wavelength shorter than 387 nm was blocked by 0.72 M $NaNO_2$ solution. (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.

6. Yields of the aerobic oxidation [3+2] cycloaddition photoreactions with B-1 and B-2 as photocatalysts, upon Xe lamp excitation with Band-Pass Filters (450 nm-520 nm) [a]



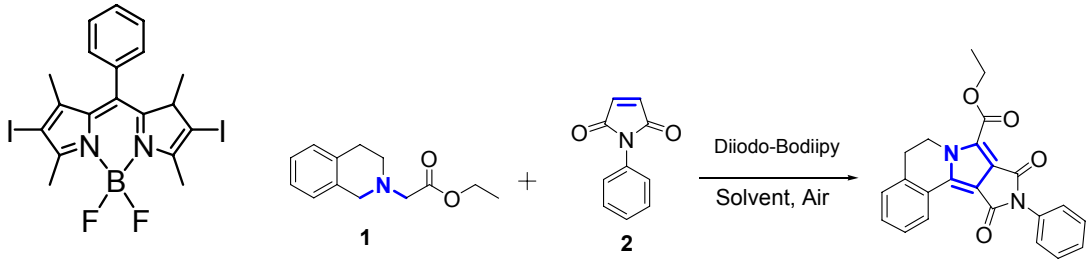
[a] Reaction conditions: **1** (0.15 mmol, 26 mg), **2** (0.1 mmol, 17.3 mg), **B-1**/**B-2** (1mmol%) and NBS (1.2 equiv) were mixed in CH_2Cl_2 (5.0 mL), the mixture was irradiated 2.0 h, 29 °C. Yield: with **B-1**: 41%, with **B-2**: 46%.

7. Sun light promoted aerobic oxidation [3+2] cycloaddition [a]



[a] Reaction conditions: **1** (0.15 mmol, 26 mg), **2** (0.1 mmol, 17.3mg), **B-1**/**B-2** (1mmol%) and NBS (1.2 equiv) were mixed in CH_2Cl_2 (5.0 mL), the mixture was irradiated 1.5 h with solar light (270W/m^2~330W/m^2), 29°C. Yield: B-1:70%, B-2:78%. East longitude:121.536°, Northern latitude: 38.866°, 9:30 a.m.

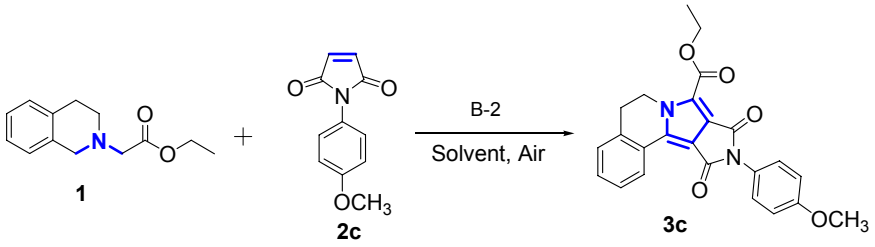
8. Diiodo-Bodipy as photocatalysts, upon Xe lamp excitation for aerobic oxidation [3+2] cycloaddition [a]



1 2

[a] Reaction conditions: **1** (0.15 mmol, 26 mg), **2** (0.1 mmol, 17.3mg), **Diiodo-Bodipy** (1mmol%) and NBS (1.2 equiv) were mixed in CH_2Cl_2 (5.0 mL), the mixture was irradiated 1.5 h, 29 °C. Yield: 79%.

9. B-2 as photocatalysts for reproducing of a previous work [a]



1 2c 3c

[a] Reaction conditions: **1** (0.15 mmol, 26 mg), **2c** (0.1 mmol, 20.3 mg), **B-2** (1mmol%) and NBS (1.2 equiv) were mixed in CH_2Cl_2 (5.0 mL), the mixture was irradiated 1.5 h, 29 °C. Yield: 72 %.

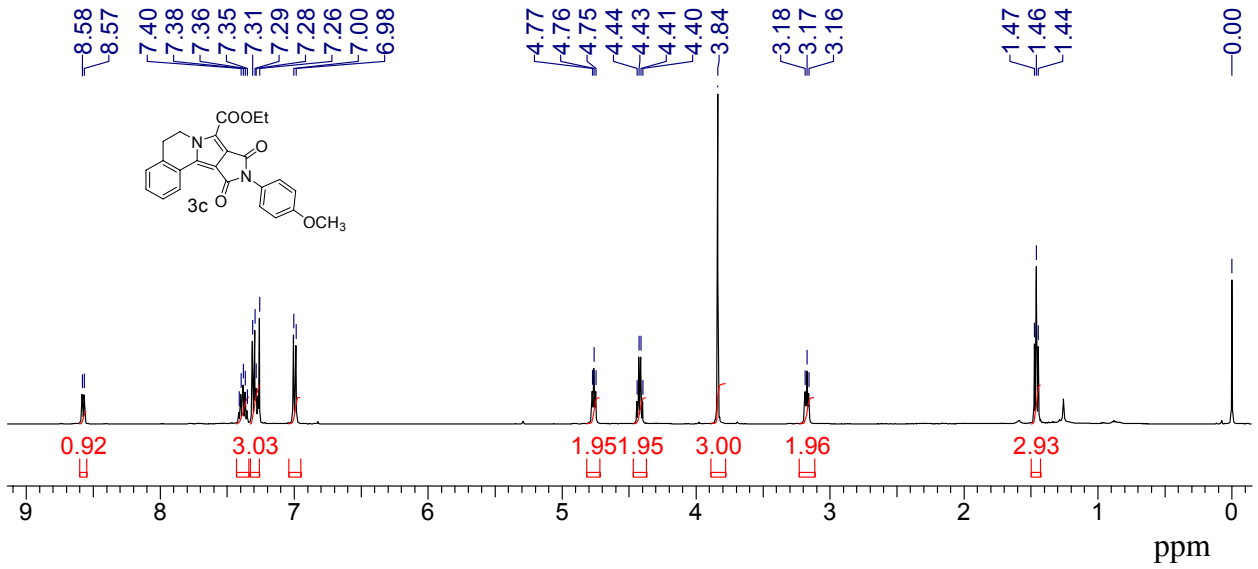
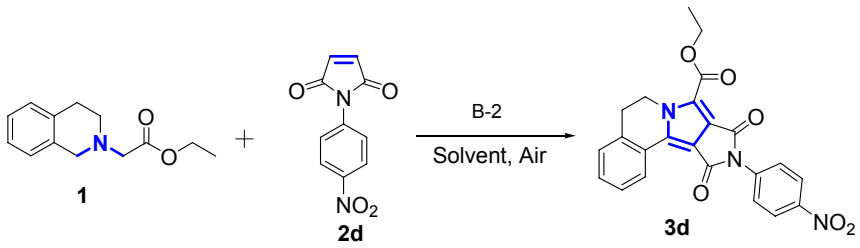


Fig. S59 [1]HNMR of **3c**. Reaction conditions: **1** (0.15 mmol, 26 mg), **2c** (0.1 mmol, 20.3 mg), **B-2** (1mmol%) and NBS (1.2 equiv) were mixed in CH_2Cl_2 (5.0 mL), the mixture was irradiated 1.5 h.



[a] Reaction conditions: **1** (0.15 mmol, 26 mg), **2d** (0.1 mmol, 21.8 mg), **B-2** (1mmol%) and NBS (1.2 equiv) were mixed in CH_2Cl_2 (5.0 mL), the mixture was irradiated 1.5 h, 29 °C. Yield: 78 %.

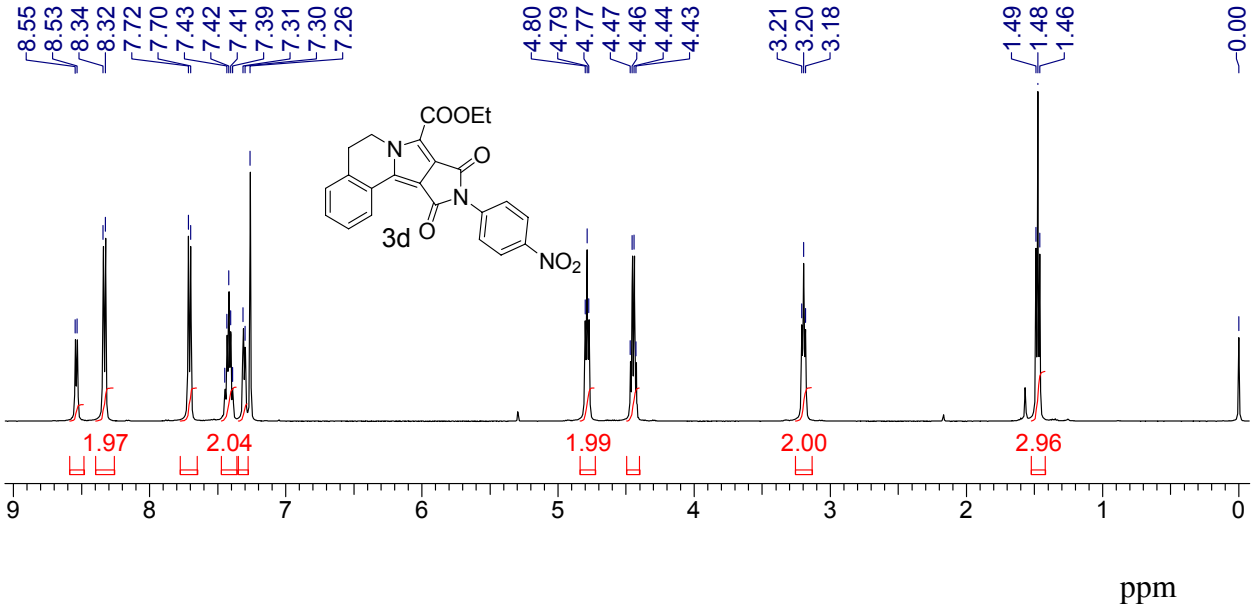
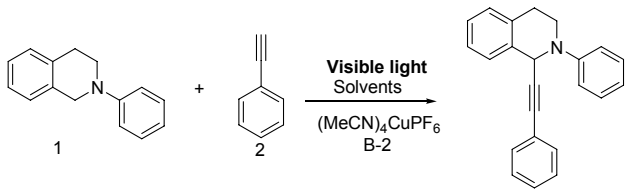


Fig. S60 [1]HNMR of **3d**. Reaction conditions: **1** (0.15 mmol, 26 mg), **2d** (0.1 mmol, 21.8 mg), **B-2** (1mmol%) and NBS (1.2 equiv) were mixed in CH_2Cl_2 (5.0 mL), the mixture was irradiated 1.5 h.



[a] Reaction conditions: 1 (0.10 mmol), 2 (0.8 mmol), photocatalyst catalysis B-2 (1mol%) , air, 35 W Xe light irradiation ($\lambda > 385$ nm), $(MeCN)_4CuPF_6$ (10 mol%), and solvent (3.0 mL), rt. Yield: 77 %.

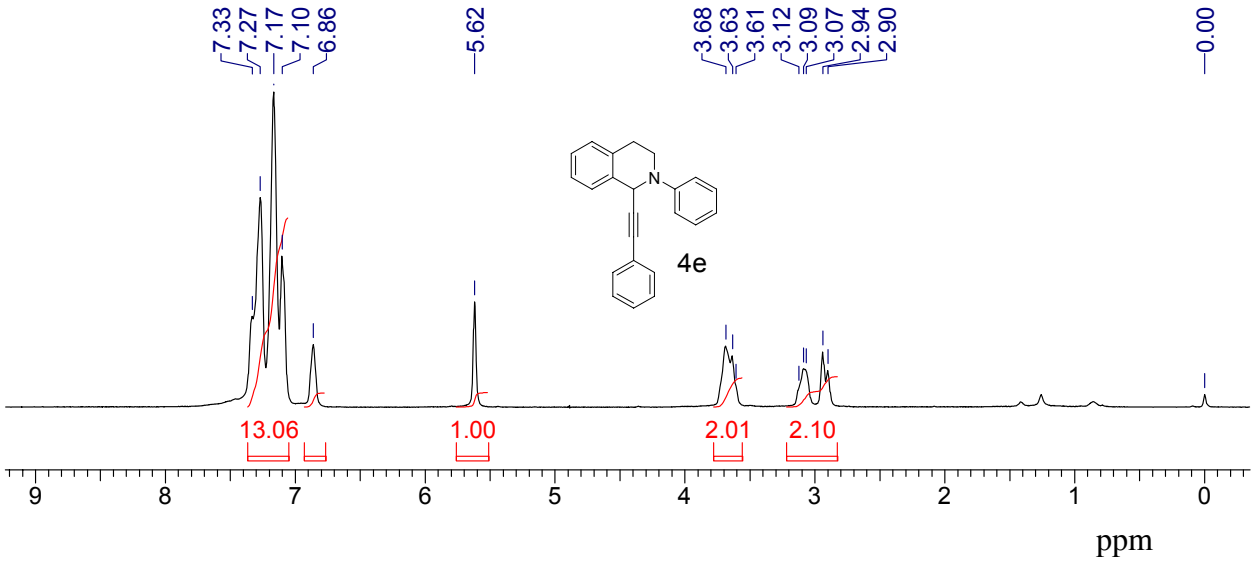
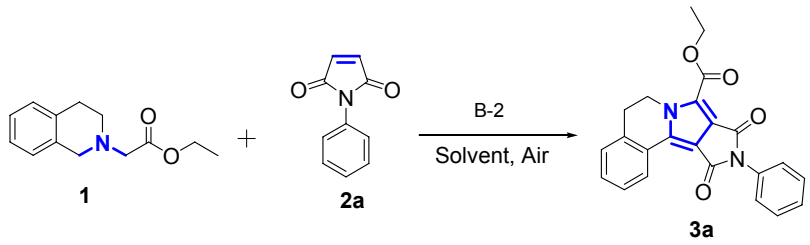


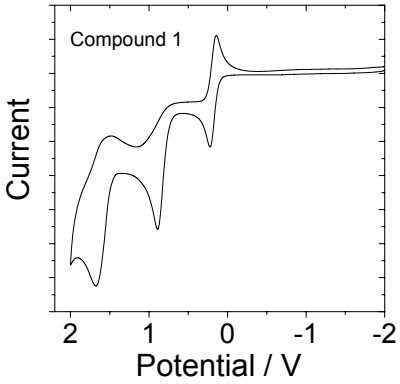
Fig. S61 [1]HNMR of **3d**. Reaction conditions: 1 (0.10 mmol), 2 (0.8 mmol), photocatalyst catalysis **B-2** (1 mol%) , air, 35 W Xe light irradiation ($\lambda > 385$ nm), $(MeCN)_4CuPF_6$ (10 mol%), and solvent (3.0 mL).

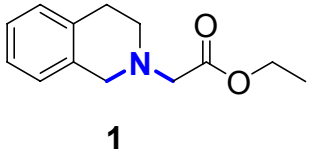
10. The Photocatalytic reaction run on a large scale [a]



[a] Reaction conditions: **1** (0.45 mmol, 78 mg), **2a** (0.3 mmol, 51.9mg), **B-2** (1mmol%) and NBS (1.2 equiv) were mixed in CH_2Cl_2 (7.0 mL), the mixture was irradiated 1.5 h, Yield: 83 %.

11. The data of electrochemistry





1

Fig. S62 Cyclic voltammogram of the dyad photosensitizer compound **1**. Ferrocene (Fc) was used as internal reference ($E_{1/2}$ = +0.40 V (Fc+/Fc) vs. SCE). In deaerated CH_3CN solutions containing 1.0 mM photosensitizers alone, or with the ferrocene, 0.10 M Bu_4NPF_6 as supporting electrolyte, $Ag/AgNO_3$ reference electrode, Scan rates: 0.05 V/s.

Calculation of the free energy changes of the electron transfer

The free energy changes of the electron transfer process (charge separation, CS), can be calculated with the Weller equation (eq. 1 and eq.2).

$$\Delta G^0{}_{\mathrm{CS}} = e[E_{OX} - E_{RED}] - E_{00} + \Delta G_{\mathrm{S}} \qquad \text{(Eq. 1)}$$

$$\Delta G_{\mathrm{S}} = -\frac{e^2}{4\pi\varepsilon_{\mathrm{S}}\varepsilon_0 R_{\mathrm{CC}}} - \frac{e^2}{8\pi\varepsilon_0}\left(\frac{1}{R_D} + \frac{1}{R_{\mathrm{A}}}\right)\left(\frac{1}{\varepsilon_{REF}} - \frac{1}{\varepsilon_S}\right) \qquad \text{(Eq. 2)}$$

Where ΔG_S is the static Columbic energy, which is described by eq. 2. ε = electronic charge, E_{OX} = half-wave potential for mono-electron oxidation of the electron-donor unit, E_{RED} = half-wave

potential for one-electron reduction of the electron-acceptor unit; note herein the anodic and cathodic peak potentials were used because in some cases the oxidation is irreversible therefore the formal potential $E_{1/2}$ cannot be derived; E_{00} = energy level approximated with the fluorescence emission wavelength (for the singlet excited state), or1.20 eV for the T_1 state energy of iodo-Aza Bodipy. ε_S = static dielectric constant of the solvent, R_{CC} = (17.0 Å) center-to-center separation distance determined by DFT optimization of the geometry, R_D is the radius of the BODIPY-based donor, R_A is the radius of the electron acceptor, ε_{REF} is the static dielectric constant of the solvent used for the electrochemical studies, ε_0 permittivity of free space. The solvents used in the calculation of free energy of the electron transfer is CH_3CN ($\varepsilon = 37.5$).

Based on these parameters, for **B-2** in CH_3CN, ΔG_S is calculated as −0.02 eV.

With azaBodipy unit as the electron acceptor and Bodipy part as the electron donor,

Given the electron transfer occurs via the triplet excited state of the azaBodipy,

then $\Delta G(CS) = 1.15 - (-0.22) - 1.2\text{-}0.02 = +0.15$ eV;

Given the electron transfer occurs via the singlet excited state of the Bodipy part,

then $\Delta G(CS) = 1.15 - (-0.22) - 2.4 - 0.02 = -1.05$ eV;

For **1** and iodo-Aza Bodipy

We hypothesis that two molecules should collide each other to carry out electron transfer between the molecules, here R_{CC} = (10.6 Å) center-to-center separation distance determined by DFT optimization of the geometry. ΔGS is calculated as −0.06 eV. 1.20 eV for the T_1 state energy of iodo-Aza Bodipy. Triplet excited state of iodo-Aza Bodipy also were determined by DFT calculation.

Considering the mixture was irradiated with 35 W Xe lamp (λ > 385 nm), 1 was nearly impossible to be excited by Xe lamp. Thus we proposed that electron only could transfer from 1 to triplet excited state of iodo-Aza Bodipy.

With the azaBodipy unit in **B-2** as electron acceptor and T_1 = 1.2 eV,

the $\Delta G(CS) = 1.0 - (-0.22) - 1.2 - 0.06 = -0.04$ eV