

Multichromophoric Perylene Iridium Triad as a Homogeneous Photocatalyst for the Efficient Synthesis of Tetrahydroquinoline Derivatives

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1. Material and Methods

All chemicals and solvents were purchased from commercial suppliers (Sigma Aldrich, GLR, TCI Chemicals) and used without further purification. *N, N*-dimethylformamide (DMF) and dichloromethane (DCM) were dried over calcium hydride and distilled before use. Toluene was dried over sodium/benzophenone and distilled before use. Silica gel of mesh size 60-120 was used for column chromatography.

The ^1H and ^{13}C NMR spectra were recorded on a 400 MHz Bruker BiospinAvance III FT-NMR spectrometer, respectively with trimethylsilane (TMS) as an internal standard at room temperature. Chemical shift values were reported in parts per million (ppm). The solvent used were deuterated chloroform (CDCl_3) (from Merck, Germany) and dimethyl sulfoxide- d_6 (DMSO- d_6) (from Eurisotop). The high-resolution mass spectra were recorded with Waters QTOF mass spectrometer. The software used for acquiring mass spectra was Flex Control, Bruker (USA) and the software used for analyzing mass spectra was Flex Analysis 3.1.

UV/Vis absorption was recorded at room temperature on a Cary 60 UV/Vis spectrophotometer using a quartz cuvette with 1 cm path length. Fluorescence spectra were recorded on Hitachi F7000 fluorescence spectrophotometer using FL Solutions software. The photoluminescence decay lifetimes were estimated by time-correlated single-photon counting (TCSPC) technique using a Deltaflex Modular Fluorescence Lifetime System (HORIBA Scientific) with nano-LED pulsed diode light source (510 nm).

Cyclic voltammetry measurements were conducted using a computer-controlled CHI6159E electrochemical workstation (CH Instruments, USA) in a conventional three-electrode single-compartment cell. The setup included a glassy carbon working electrode, an Ag/AgCl reference electrode with a 1M KCl solution, and a Pt wire counter electrode, operated at a scan rate of 0.1 V/s. A solution of tetrabutylammonium hexafluorophosphate (TBAHFP, 0.1 M) (Alfa

Aesar) dissolved in pre-dried DCM served as the supporting electrolyte. Prior to each measurement, the solutions were purged with nitrogen for 5 minutes. The concentrations of the prepared samples were approximately 0.1-0.3 mM, and the electrochemical potential was calibrated internally against the ferrocene/ferrocenium (Fc/Fc⁺) redox couple.

2. Synthesis

Synthesis of compound **2**^{S1}

A mixture of 4-amino-2-bromopyridine (200 mg, 1.15 mmol), phenylboronic acid (PhB(OH)₂, 155 mg, 1.27 mmol), Pd(OAc)₂ (10 mg, 0.04 mmol) and H₂O (25 mL) in a two-neck round-bottom flask (100 mL) was stirred under reflux at 100 °C under N₂. Palladium black gradually formed when 100 °C was reached. After being cooled to room temperature, the reaction mixture was basified using 30% NaOH aqueous solution and then extracted with ethyl acetate. The combined organic phase was passed over anhydrous Na₂SO₄ and the solvent was removed under vacuum and the pure product **2** was obtained after column chromatography in a solvent mixture of ethylacetate and hexane (5:95, v/v) with 87% yield.

¹H NMR of compound **2 (400 MHz, DMSO-d₆) δ (ppm):** 8.08 (d, *J* = 8 Hz, 1 H), 7.91-7.89 (m, 2 H), 7.46 -7.41 (m, 2 H), 7.39-7.36 (m, 1 H), 6.99 (d, *J* = 2 Hz, 1 H), 6.45 (dd, *J* = 4 Hz, 1 H), 6.08 (s, 2 H).

Synthesis of compound **4**^{S2}

Compound **3** (50 mg, 0.07 mmol), **NMI** (115 mg, 0.24 mmol) and cesium carbonate (48 mg, 0.14 mmol) were dissolved in DMF and refluxed for 30 h under nitrogen. After cooling to room temperature, the reaction mixture was extracted with chloroform (2×50 mL) and passed over sodium sulphate. The isolation of compound **4** in pure form by column chromatography was challenging due to the strong adherence of the anhydride group of this compound to silica gel.

Although flash column chromatography was employed for purification, it was not possible to obtain compound **4** in pure form. Additionally, due to its limited solubility in organic solvents, acquiring its proton NMR spectra was not feasible. Consequently, the resulting crude compound **4** was used for subsequent reactions.

Synthesis of compound **5**

Compounds **4** (50 mg, 0.07 mmol), **2** (40 mg, 0.23 mmol) and Zn(OAc)₂ (34 mg, 0.18 mmol) were dissolved in 5 mL of pyridine and heated to 100 °C. The reaction mixture was stirred for 48 h. Pyridine was removed under vacuum and the reaction mixture was extracted with chloroform (3 × 50 mL) and dried over sodium sulfate. Then the crude product was subjected to column chromatography on a silica column with chloroform/hexane (95:5, v/v) as the eluent to obtain compound **5** with 60% yield.

¹H NMR of compound 5 (400 MHz, CDCl₃) δ (ppm): 9.46-9.36 (m, 2 H), 8.92-8.89 (m, 1 H), 8.72-8.66 (m, 1 H), 8.61 (t, *J* = 8 Hz, 2 H), 8.55-8.46 (m, 6 H), 8.19-8.12 (m, 2 H), 8.05-8.02 (m, 2 H), 7.96 (s, 1 H), 7.7 (d, *J* = 12 Hz, 1 H), 7.71-7.66 (m, 2 H), 7.49-7.41 (m, 4 H), 7.38-7.33 (m, 4 H), 7.28 (d, *J* = 8 Hz, 2 H), 7.24-7.20 (m, 2 H), 4.38-4.33 (m, 4 H), 3.38 (t, *J* = 8 Hz, 8 H), 1.82-1.78 (m, 4 H), 1.66-1.58 (m, 8 H), 1.53-1.49 (m, 4 H), 1.29-1.25 (m, 24 H), 1.03-0.98 (m, 6 H), 0.84 (t, *J* = 8 Hz, 12 H).

Synthesis of compound **6**

Compound **5** (10 mg, 0.006 mmol) and *p*-toluene sulfonic acid monohydrate (*p*-TsOH·H₂O) (7 mg, 0.03 mmol) were dispersed in 2 mL of toluene. The reaction mixture was stirred at 110 °C for 12 h. After cooling, the precipitate was filtered and washed several times with water and dried. Subsequently, the precipitate was dissolved in the minimum amount of CHCl₃ and to this solution, MeOH was added to obtain the precipitate of the pure product. The red precipitate was collected by filtration and dried to afford the pure product with a yield of 62%.

¹H NMR of compound 6 (400 MHz, CDCl₃) δ (ppm): 9.68-9.60 (m, 2 H), 8.89 (d, *J* = 4 Hz, 1 H), 8.76 (d, *J* = 4 Hz, 2 H), 8.71 (s, 1 H), 8.68 (d, *J* = 8 Hz, 1 H), 8.62-8.58 (m, 2 H), 8.54 (d, *J* = 4 Hz, 1 H), 8.51 (s, 1 H), 8.49-8.46 (m, 2 H), 8.03-8.01 (m, 2 H), 7.76-7.75 (m, 1 H), 7.70-7.65 (m, 2 H), 7.48-7.39 (m, 8 H), 7.36 (s, 1 H), 7.35-7.32 (m, 2 H), 7.29-7.28 (m, 1 H), 7.23-7.20 (m, 2 H), 3.39 (t, *J* = 8 Hz, 8 H), 1.61 (s, 8 H), 1.29-1.25 (m, 24 H), 0.85 (t, 8 Hz, 12 H).

¹³C NMR of compound 6 (100 MHz, CDCl₃) δ (ppm): 164.86, 164.25, 159.53, 156.38, 156.15, 151.07, 143.56, 134.63, 134.50, 133.08, 132.84, 131.77, 131.69, 131.52, 131.48, 130.92, 130.71, 129.48, 129.27, 128.90, 127.40, 127.33, 127.29, 127.23, 126.14, 125.25, 124.21, 123.21, 123.18, 123.14, 122.17, 120.98, 119.99, 116.80, 115.05, 114.99, 53.91, 31.69, 27.21, 26.97, 22.71, 14.12.

MS (MALDI): Calculated for C₁₀₆H₁₀₈ClIrN₆O₁₁ [M+H]: 1848.6767; found 1848.6436

Synthesis of compound Ir-triad 1

Compound **6** (10 mg, 0.006 mmol) was dissolved in 6 mL of dry DCM and purged with nitrogen for half an hour. [Cp*IrCl₂]₂ (6 mg 0.006 mmol) and NaOAc·3H₂O (3 mg, 0.021 mmol) were added and the reaction mixture was stirred for 36 h at room temperature in dark conditions under nitrogen. The crude product was loaded in silica gel column and eluted with a mixture of acetone/DCM (80:20). The pure product was obtained after precipitation with the addition of hexane in the solution of the compound with 58% yield.

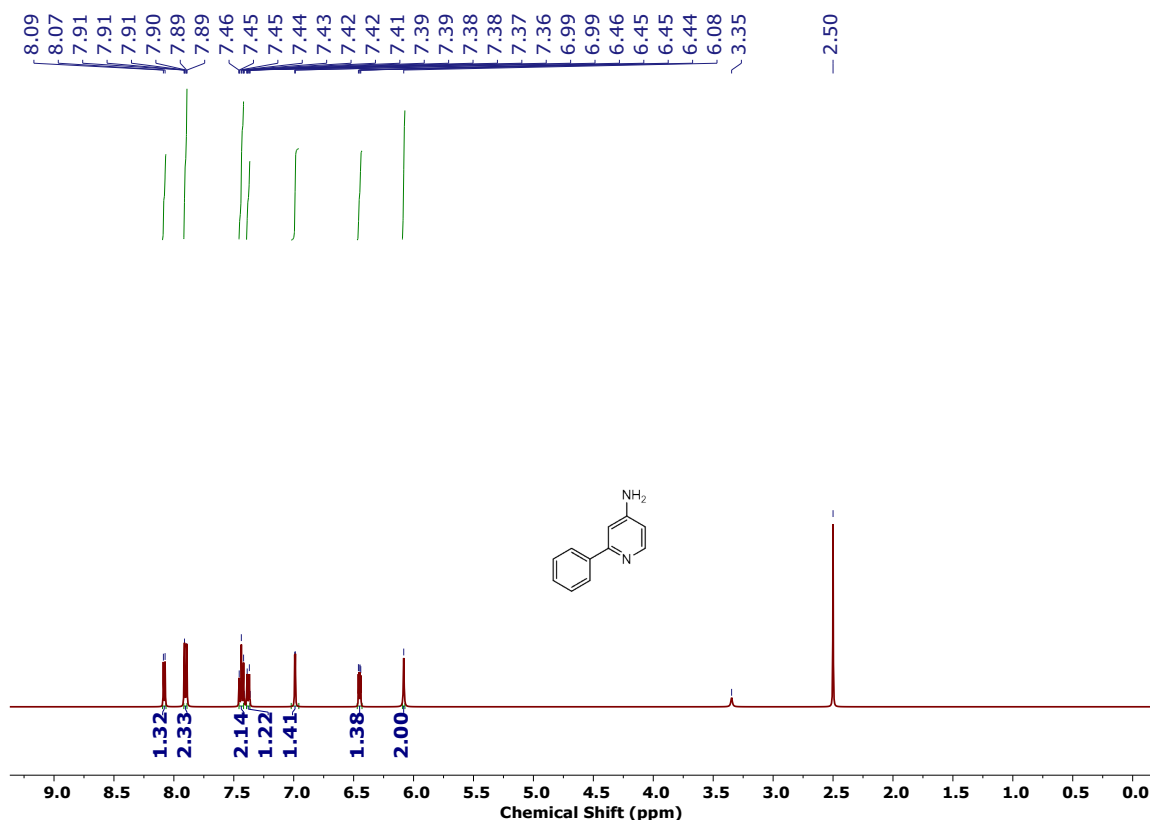
¹H NMR of compound Ir-triad 1 (400 MHz, CDCl₃) δ (ppm): 9.65 (d, *J* = 8 Hz, 1 H), 9.57 (d, *J* = 8 Hz, 1 H), 8.87 (t, *J* = 8 Hz, 1 H), 8.73-8.55 (m, 8 H), 8.53-8.44 (m, 5 H), 7.87-7.83 (m, 2 H), 7.68-7.61 (m, 2 H), 7.42 (t, *J* = 8 Hz, 3 H), 7.36-7.32 (m, 3 H), 7.23-7.16 (m, 4 H), 7.03- 6.96 (m, 1 H), 3.41-3.36 (m, 8 H), 1.72 (s, 15 H), 1.61 (s, 8 H), 1.28-1.25 (m, 24 H), 0.85 (t, *J* = 8 Hz, 12 H).

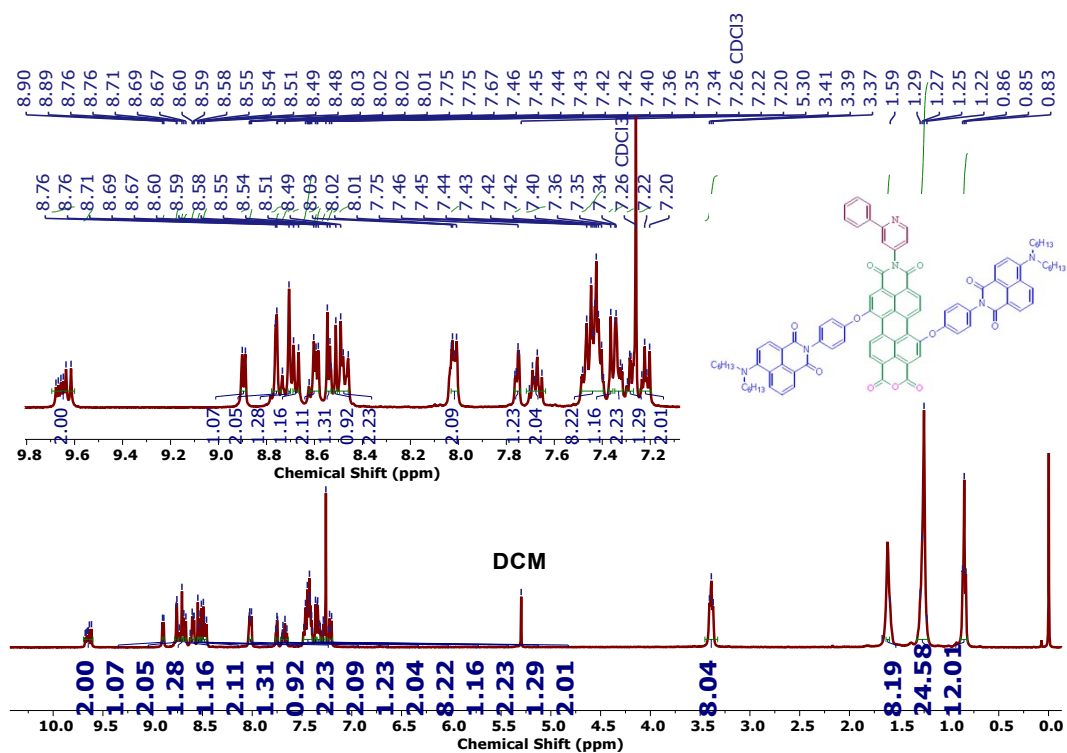
^{13}C NMR of Ir-triad 1 (100 MHz, CDCl_3) δ (ppm): 169.10, 164.88, 164.82, 164.28, 164.22, 164.19, 164.14, 162.74, 162.46, 161.73, 160.26, 156.33, 156.04, 155.12, 152.03, 143.85, 135.94, 134.99, 134.66, 134.41, 134.31, 133.06, 132.80, 131.69, 131.65, 131.62, 131.48, 131.43, 131.40, 131.36, 130.86, 130.82, 129.27, 129.10, 128.96, 127.20, 125.20, 124.60, 123.14, 122.75, 122.32, 120.05, 119.69, 119.55, 119.47, 118.67, 118.57, 116.79, 116.76, 115.01, 114.94, 88.97, 88.92, 53.87, 31.69, 29.84, 27.19, 26.97, 22.72, 14.14, 9.13.

MS (MALDI): Calculated for $\text{C}_{95}\text{H}_{84}\text{N}_6\text{O}_{11}$ $[\text{M}+\text{H}]$: 1485.6276; found 1485.6115.

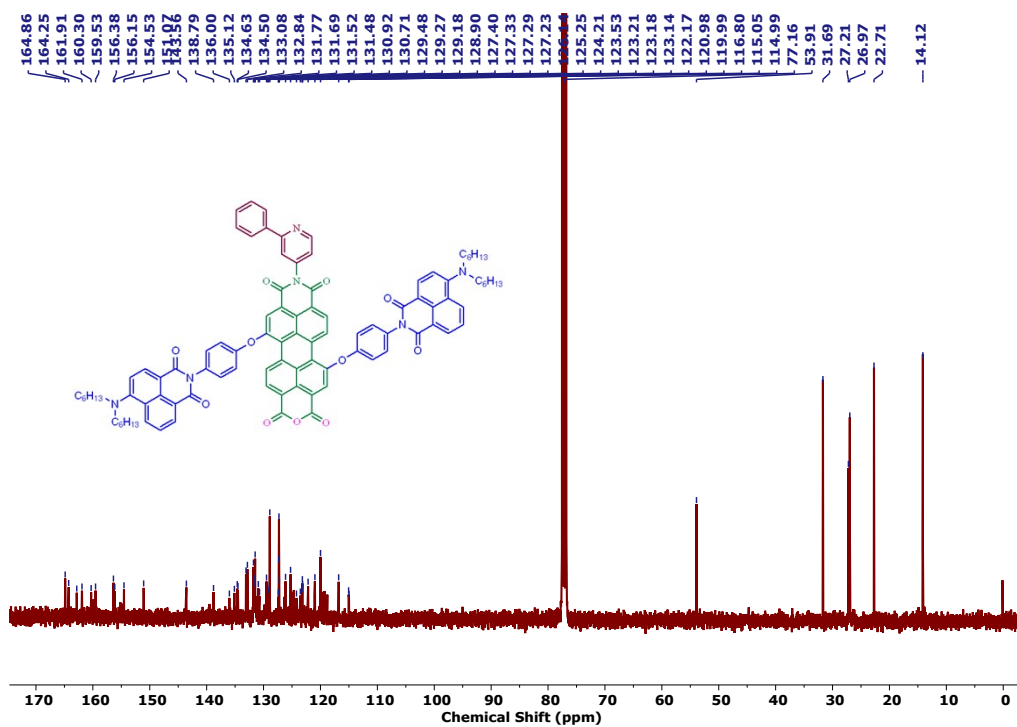
3. ^1H and ^{13}C NMR

^1H NMR of compound 2 in DMSO-d_6 .

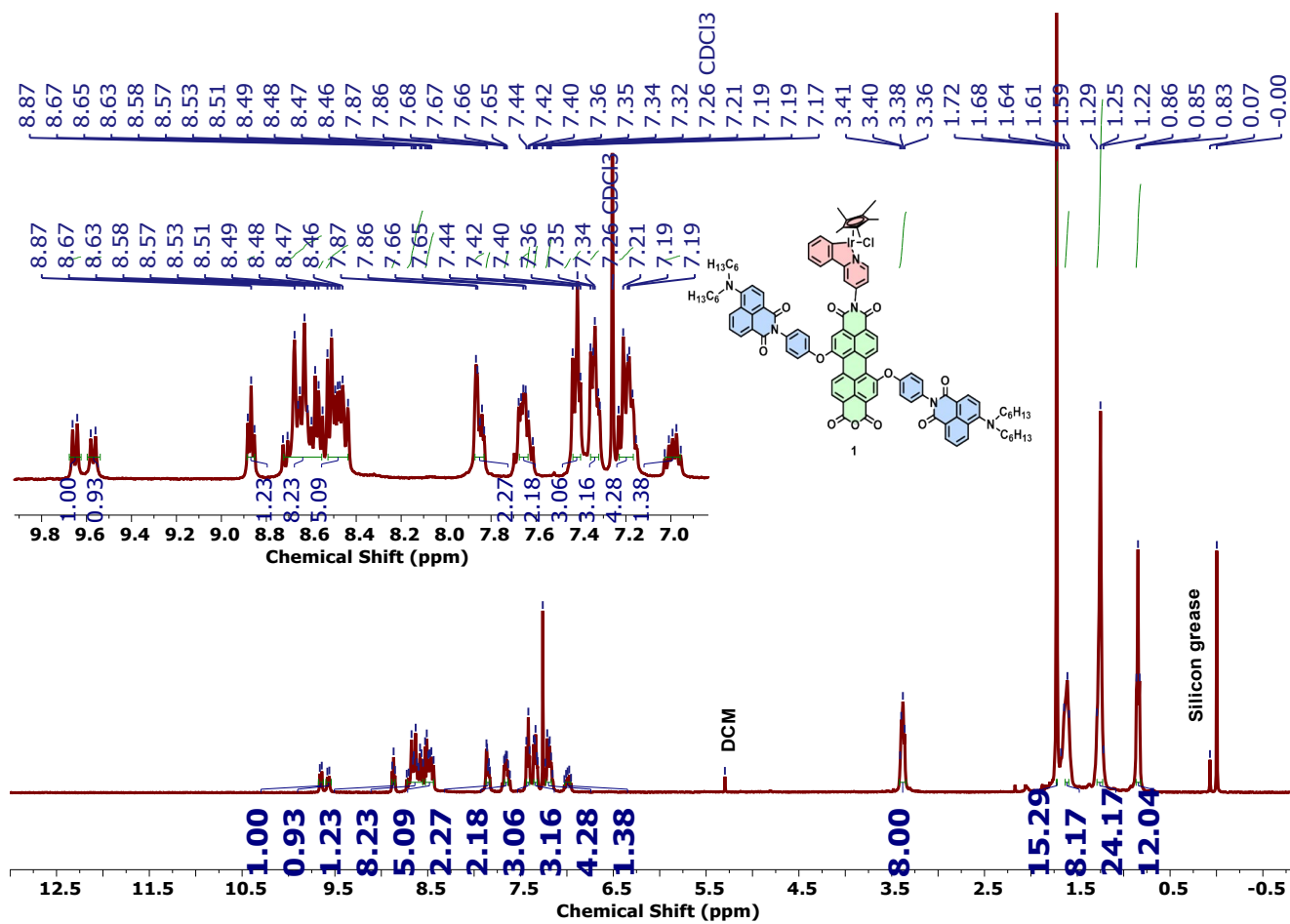




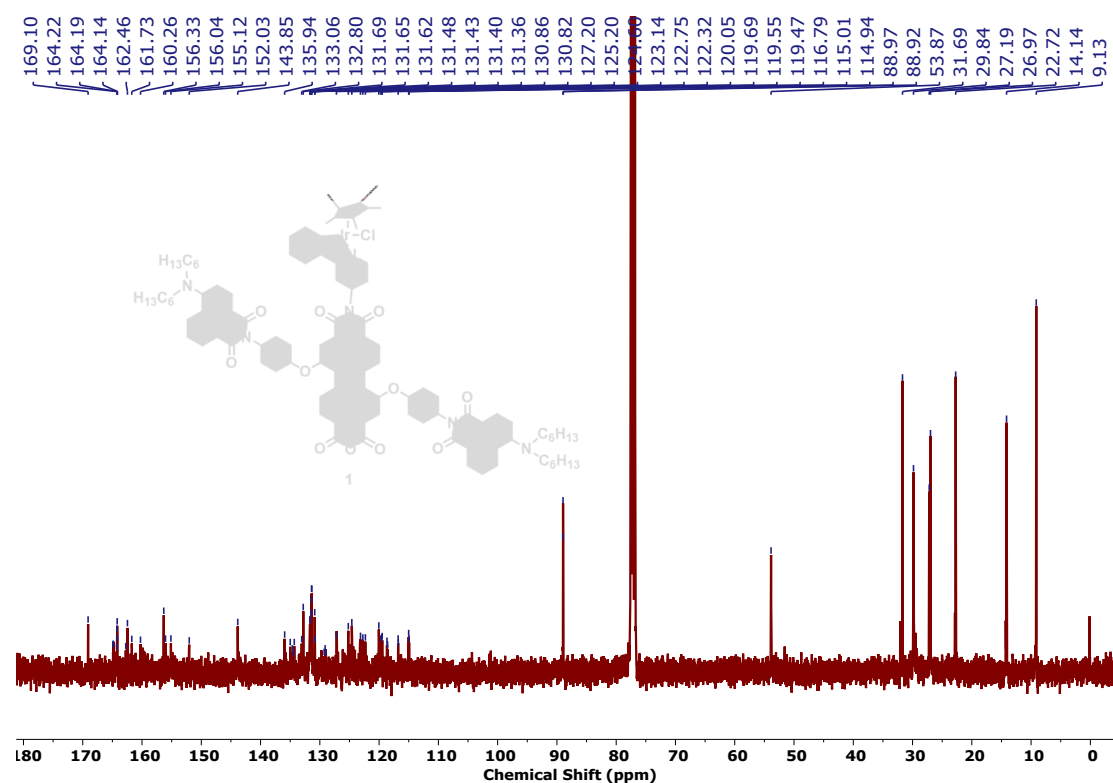
¹³C NMR of compound 6 in CDCl₃



¹H NMR of Ir-triad 1 in CDCl₃



^{13}C NMR of Ir-triad 1 in CDCl_3



4. Photophysical Characterization

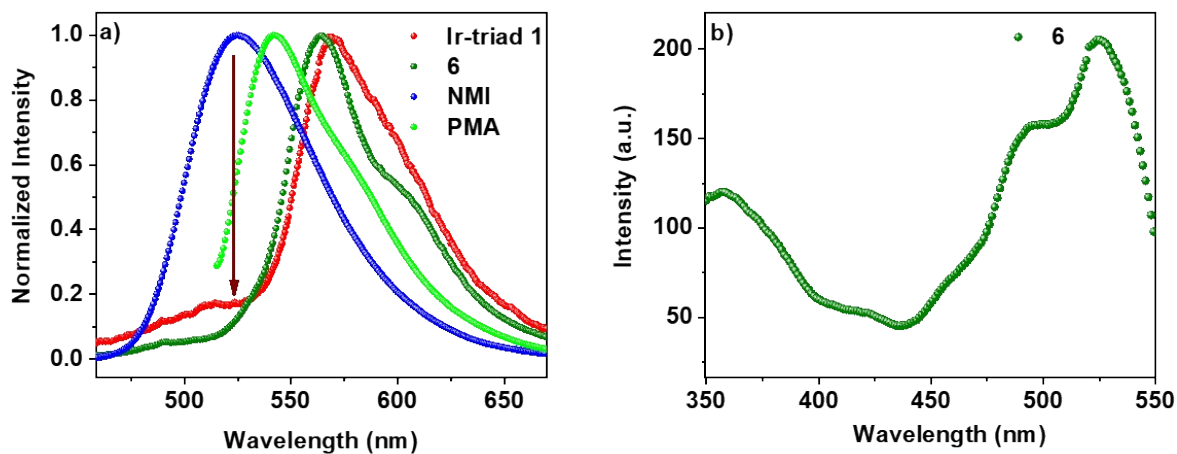


Fig. S1 (a) Emission spectra of **Ir-triad 1**, **6** ($\lambda_{\text{ex}} = 425 \text{ nm}$), NMI ($\lambda_{\text{ex}} = 425 \text{ nm}$) and PMA ($\lambda_{\text{ex}} = 505 \text{ nm}$), (b) Fluorescence excitation spectra of **6** recorded at an emission wavelength of PMI at 565 nm in DCM.

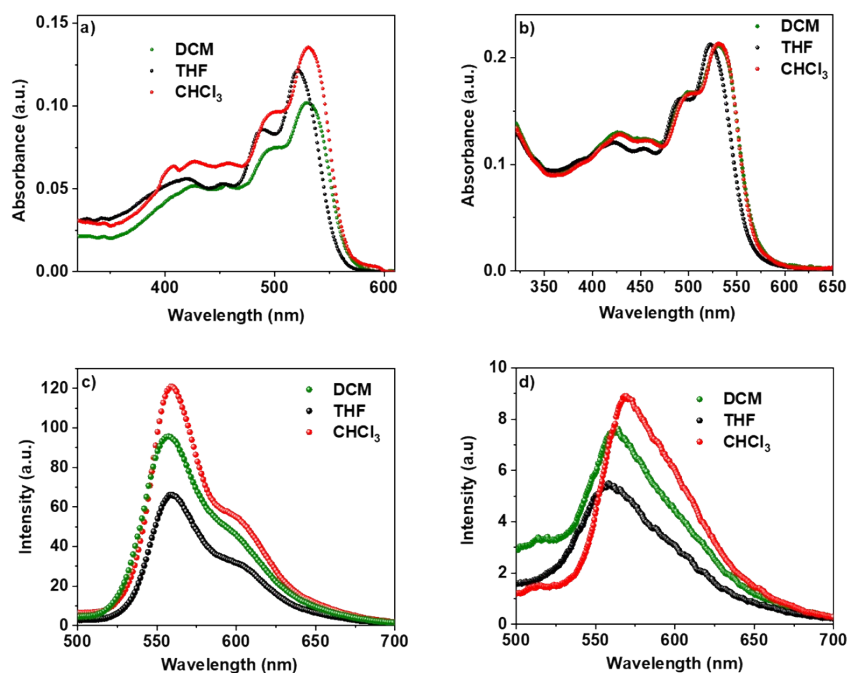


Fig. S2 Absorption spectra of (a) **6** (b) **Ir-triad 1** and emission spectra of (c) **6** and (d) **Ir-triad 1** in solvents of different polarities.

Fluorescence quantum yield

Fluorescence quantum yields of **Ir-triad 1** and **6** were performed using 4',6-Diamidino-2-Phenylindole, dihydrochloride (DAPI) ($\Phi_R = 0.5$) in DMSO and Rhodamine B ($\Phi_R = 0.5$) in ethanol as reference dyes using the following equation S1:^{S3}

$$\Phi = \Phi_R (I/I_R) (A_R/A) (\lambda_{exR}/\lambda_{ex}) (n^2/n_R^2) \quad (S1)$$

where Φ_R is the quantum yield of reference dyes, I and I_R are integrated fluorescence intensities of compounds and reference dyes respectively, A and A_R are the absorbances of the compounds and reference dyes respectively, n and n_R are the refractive index of solvent(s) used for compounds and reference respectively. All the compounds were dissolved in dichloromethane in three different concentrations (10^{-6} M) such that their absorbance was less than or equal to 0.1 and fluorescence spectra were recorded at excitation wavelengths of 425 nm and 532 nm. Absorbance and fluorescence spectra were recorded for three different concentrations of DAPI (excitation wavelength of 360 nm) in DMSO and Rhodamine B (excitation wavelength of 543

nm) at $c \sim 10^{-5}$ - 10^{-6} M. The calculated fluorescent quantum yield values are shown in Table S1.

Table S1 Relative quantum yields of **Ir-triad 1** and **6** using the comparative method and DAPI and Rhodamine B as reference dyes.

Compound	Wavelength	Absorbance	Integrated PL intensity	Quantum Yield	
				Φ_i	Φ_{avg}
NMI	425	0.019	164.751	0.327	0.377
		0.024	223.185	0.377	
		0.038	366.508	0.382	
Ir-triad 1	425	0.0392	8.494	0.0070	0.0071
		0.061	11.560	0.0070	
		0.0789	16.899	0.0074	
	532	0.0597	18.802	0.024	0.025
		0.0899	25.921	0.024	
		0.123	37.880	0.027	
DAPI (DMSO)	360	0.0448	629.732	0.58	
		0.0707	867.144	(Reported) S4	
		0.0828	1086.253	0.0047	
6	425	0.035	5.078	0.0080	0.006
		0.042	9.072	0.0075	
		0.062	13.321	0.0424	
	532	0.067	36.368	0.0412	0.045
		0.095	45.344	0.0536	
		0.109	66.157	0.5	
Rhodamine B (ethanol)	543	0.033	234.7	(Reported) S5	
		0.065	418.247		
		0.105	655.361		

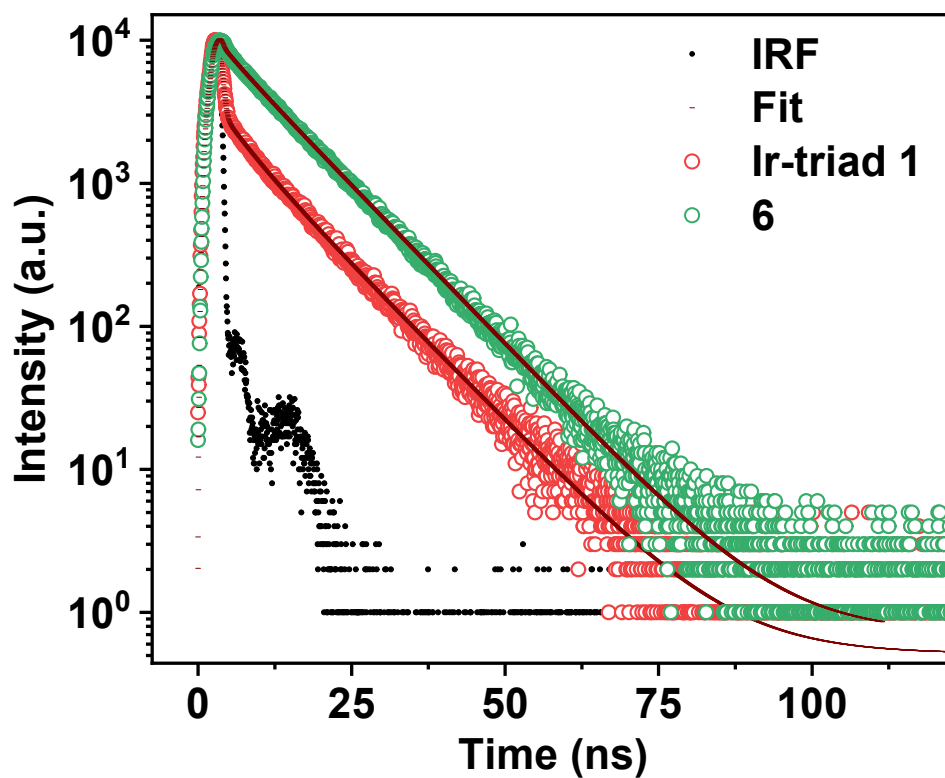


Fig. S3 Fluorescence lifetime decay profiles of **Ir-triad 1** and **6** recorded in DCM.

Table S2 Fluorescence lifetime parameters of **Ir-triad 1** and **6** at 510 nm excitation at different monitoring wavelengths in DCM.

Compound	Excitation Wavelength (nm)	Emission Wavelength (nm)	τ_1 (a_1) (ns)	τ_2 (a_2) (ns)	τ_3 (a_3) (ns)	τ_{avg} (ns)	χ^2
Ir-triad 1	510	569	1.98	4.65	0.13	0.34	1.20
			(0.02)	(0.04)	(0.94)		
6	510	562	1.51	4.57	0.072	0.87	1.20
			(0.02)	(0.17)	(0.81)		

Table S3 Comparison table of photophysical characteristics of literature reported Ir-peryene complexes (Ir complexes attached at peri position of PMI/PDI are only listed).

Compound	Ir Catalyst attached at imide site	λ_{abs} (nm)	λ_{em} (nm)	Fluorescence Lifetime	Φ_{F}	Reference
Ir-triad 1	Cp*Ir (ppy)Cl	425, 530	569	0.34 ns	0.007 (425 nm) 0.025 (532 nm)	This work
PDI-Ir (III)1	Cp*Ir (ppy)Cl	553	576	3.9 ps	–	<i>Proc. Natl. Acad. Sci. U. S. A.</i> , 2012, 109 , 15651–15656 (Ref. 6 of paper)
PDI-Ir (III)2	Cp*Ir (ppy)Cl	544	579	1.5 ps	–	<i>Proc. Natl. Acad. Sci. U. S. A.</i> , 2012, 109 , 15651–15656 (Ref. 6 of paper)
PDI-Ir (II) dyad (1)	[Ir(ppy) ₂ (phen)]PF ₆	2.15, 2.31, 2.80 eV	2.00 eV, 619	2.89 ns ($\lambda_{\text{abs}} = 360 \text{ nm}$) 3.0 ns ($\lambda_{\text{ex}} = 550 \text{ nm}$)	0.12 (360 nm) 0.55 (550 nm)	<i>J. Phys. Chem. C</i> , 2009, 120 , 22831–22843 (Ref. 7 of paper)
NDI-PMI-Ir	Cp*Ir (ppy)Cl	480, 506	-	1.5 ps	-	<i>Chem. Sci.</i> , 2013, 4 , 3863–3873 (Ref. 11 of paper)
NMI-PMI-Ir	Cp*Ir (ppy)Cl	542 nm	550	3.4 ps	-	<i>Chem. Sci.</i> , 2013, 4 , 3863–3873 (Ref. 11 of paper)
[(phen)₂Ru (II) (pPDIp)] (PF₆)₂	[(phen) ₂ Ru (II)PF ₆) ₂	450 (MLCT peak), 500, 525	600, 525	10 ps (90%) 3.5 ns (10%) at 532 nm excitation	-	<i>J. Phys. Chem. C</i> , 2016, 120 , 22831–22843 (Ref. 14 of paper)

5. Cyclic Voltammetry

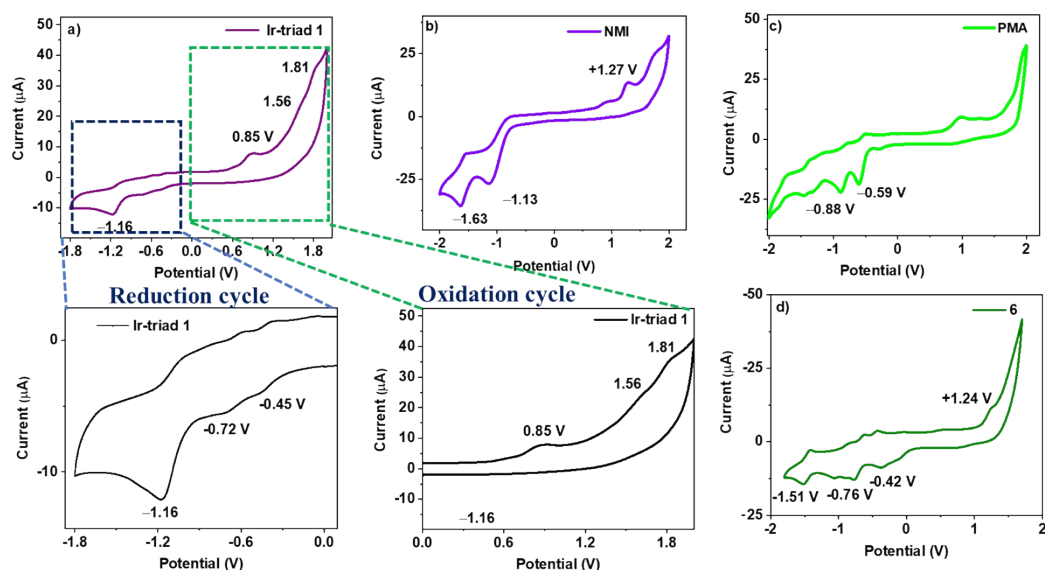


Fig. S4 Cyclic voltammograms of (a) **Ir-triad 1** (b) **NMI** (c) **PMA** (d) **6** in dry DCM with 0.1 M TBAHFP and potentials measured vs Ag/AgCl as reference electrode.

Table S4 Redox properties of **Ir-triad 1**, **6**, **NMI** and **PMA** based on cyclic voltammetry.

Compound	$E_{\text{ox onset}}(\text{V})$	HOMO ^[a] (eV)	$E_{\text{red onset}}(\text{V})$	LUMO ^[b] (eV)	E_{g}^{CV} (eV)	$E_{\text{g}}^{\text{opt}}$ (eV)	λ_{onset} (nm)
Ir-triad 1	0.64	-5.40	-0.47	-4.29	1.11	2.19	566
6	1.09	-5.85	-0.48	-4.28	1.57	2.19	565
NMI	1.4	-5.99	-0.81	-3.96	2.03	2.7	456
PMA	-	-6.56	-0.46	-4.29	2.27	2.31	535

[a] HOMO = $-(E_{\text{ox onset}} + 4.76)$ eV, [b] LUMO = $-(E_{\text{red onset}} + 4.76)$ eV ^{S6}

To assess the feasibility of photoinduced electron transfer (PET), the Gibbs free energy for charge-separation (ΔG_{CS}) was calculated for compound **6** using the Rehm–Weller analysis in equation S2 ^{S7}

$$\Delta G_{\text{CS}} = e[E_{\text{ox}}(\text{NMI}) - E_{\text{red}}(\text{PMA})] - E_{00} - \frac{331}{\epsilon_s} r \quad (\text{S2})$$

where $E_{\text{ox}}(\text{NMI})$ is the first oxidation potential of **NMI**, $E_{\text{red}}(\text{PMA})$ is the first reduction potential of compound **PMA**, E_{00} is the energy of the $S_0 \rightarrow S_1$ excited state, ϵ_s is the dielectric

constant of the solvent used and r refers to the distance between the centers of the donor (**NMI**) and acceptor (**PMA**) segments.

The first oxidation potential of **NMI** = 1.27

The first reduction potential of **PMA** = -0.59

Centre-to-centre distance for compound **6** = 11.38 Å (estimated from the geometry-optimized structure using DFT calculations)

E_{00} = 2.24 eV, ϵ_s for DCM is 8.93

By using these values, ΔG_{CS} was calculated to be -0.41 eV which is an indication of high feasibility of PET.

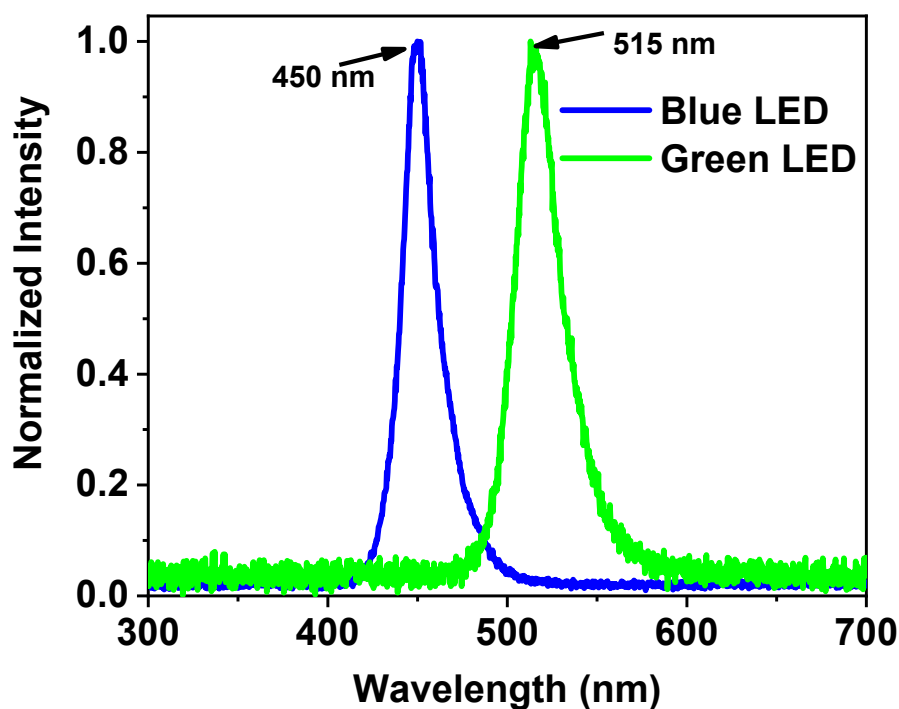


Fig. S5 Spectra of blue and green LED light sources used in photocatalytic reactions.

Fluorescence quenching experiment and Stern-Volmer plot:

The Stern-Volmer relationship (equation S3) was established by taking the ratio of the integrated fluorescence intensities (I_0/I_n) in the absence and presence of a quencher:

$$I_0/I_n = 1 + K_{SV} [Q] \quad (S3)$$

where I_0 is the fluorescence intensity without the quencher (*N,N*-dimethylaniline), I is the fluorescence intensity in the presence of the quencher, $[Q]$ is the concentration of added quencher and K_{SV} is the Stern-Volmer constant. The concentration of **Ir-triad 1** was 3.6×10^{-6} M and the concentration of quencher stock solution was 0.3 M. When the concentration of quencher was increased, the fluorescence intensity of **Ir-triad 1** was gradually decreased. Further, fluorescence intensity change with the quencher's concentration was plotted, and a straight line emerged with K_{SV} of 29 M^{-1} (Fig. S6b).

Further, the quenching rate constant (k_q) was calculated using the following equation

$$K_{sv} = k_q \cdot \tau_0 \quad (\text{S4})$$

where τ_0 denotes the excited state lifetime of **Ir-triad 1**. Accordingly, k_q was calculated to be $8.5 \times 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$.

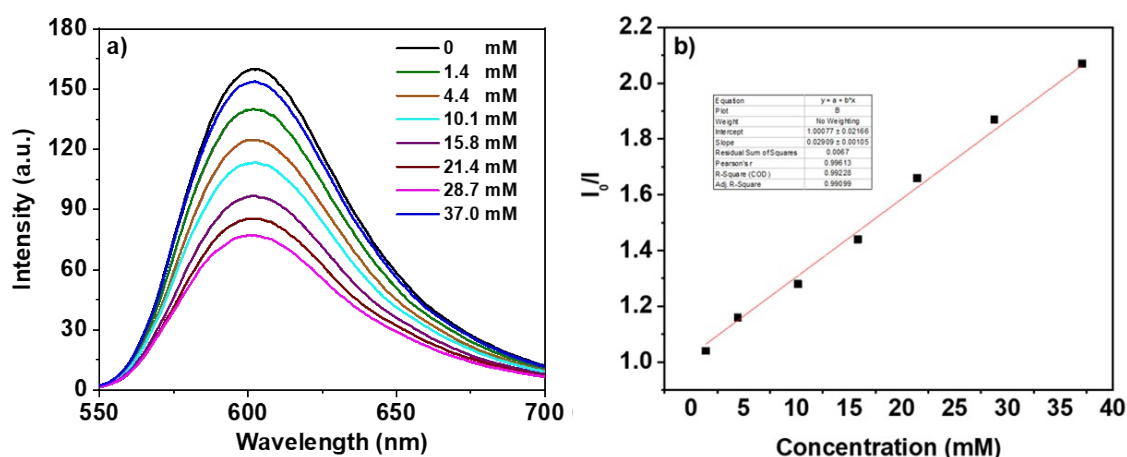


Fig. S6 (a) Fluorescence emission spectra of **Ir-triad 1** ($\lambda_{\text{ex}} = 450 \text{ nm}$) and its intensity quenching by addition of successive aliquots of quencher (*N,N*-dimethylaniline), (b) Stern-Volmer quenching of **Ir-triad 1** showing a linear correlation with increasing quencher concentration.

6. Photocatalysis

General procedures for the synthesis of products

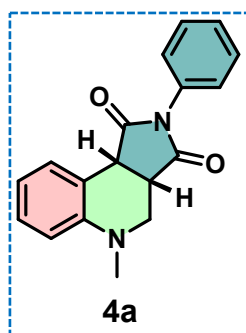
To a 10 mL schlenk tube, *N,N*-dimethylaniline **2a-2b** (0.23 mmol), maleimide **3a-3c** (0.11 mmol), **Ir-triad 1** (5 mol%) and $\text{CH}_3\text{CN}/\text{THF}$ (1:6)) were added. The solution was irradiated under blue LED (450 nm) at room temperature in open air. After 17 h, upon completion of the reaction, the solvent was removed using rotary evaporator. The residue was then subjected to

silica gel chromatography using a hexane/EtOAc (10:1) mixture as the eluent to isolate the desired product (s).

Procedures for the synthesis of 4a using compound 6 as photocatalyst. Substrates *N,N*-dimethylaniline (**2a**, 0.23 mmol) and *N*-phenylmaleimide (**3a**, 0.11 mmol), compound **6** (5 mol%) and CH₃CN/THF (1:6) were taken in 10 mL schlenk tube. The reaction mixture was irradiated under blue LED for 17 h in open air. The obtained residue was then subjected to silica gel chromatography using a hexane/EtOAc (10:1) mixture as the eluent and product **4a** was obtained with 32% yield.

Reaction under green LED (515 nm)

Following the aforementioned procedure, substrates *N,N*-dimethylaniline (**2a**, 0.23 mmol), and *N*-phenylmaleimide (**3a**, 0.11 mmol) were subjected to the reaction under green light for 17 h. The product (**4a**) was obtained with 83% yield.



(3a*S*,9b*R*)-5-methyl-2-phenyl-3a,4,5,9b-tetrahydro-1*H*-pyrrolo[3,4-*c*]quinoline-1,3(2*H*)-dione (4a)

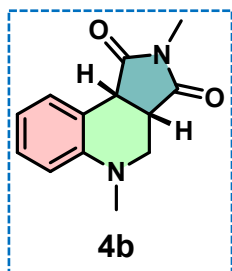
Yield: 32% (using **6** as photocatalyst)

Yield: 82% (using **Ir-triad 1** as photocatalyst and blue LED)

Yield: 83% (using **Ir-triad 1** as photocatalyst and green LED)

¹H NMR of compound 4a (400 MHz, CDCl₃) δ (ppm): 7.53 (d, *J* = 8 Hz, 1 H), 7.43 (t, *J* = 8 Hz, 2 H), 7.36 (d, *J* = 4 Hz, 1 H), 7.28-7.22 (m, 3 H), 6.91 (t, *J* = 8 Hz, 1 H), 6.75 (d, *J* = 8 Hz, 1 H), 4.16 (d, *J* = 12 Hz, 1 H), 3.61 (dd, *J* = 12, 1 H), 3.56-3.52 (m, 1 H), 3.13 (dd, *J* = 8, 4 Hz, 1 H), 2.84 (s, 3 H).

^{13}C NMR of compound 4a (100 MHz, CDCl_3) δ (ppm): 177.85, 175.92, 148.65, 132.12, 130.47, 129.13, 128.83, 128.65, 126.50, 119.80, 118.67, 112.67, 50.80, 43.72, 42.28, 39.57.

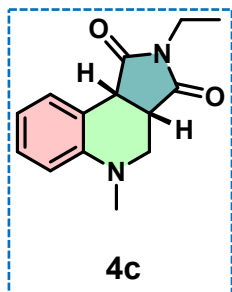


(3a*S*,9b*R*)-2,5-dimethyl-3a,4,5,9b-tetrahydro-1*H*-pyrrolo[3,4-*c*]quinoline-1,3(2*H*)-dione (4b)

Yield: 80%

^1H NMR of compound 4b (400 MHz, CDCl_3) δ (ppm): 7.48 (d, $J = 8$ Hz, 1 H), 7.21 (t, $J = 8$ Hz, 1 H), 6.89 (t, $J = 8$ Hz, 1 H), 6.70 (d, $J = 8$ Hz, 1 H), 4.00 (d, $J = 12$ Hz, 1 H), 3.54 (dd, $J = 12$ Hz, 1 H), 3.38-3.35 (m, 1 H), 3.04 (dd, $J = 8, 4$ Hz, 1 H), 2.99 (s, 3 H), 2.79 (s, 3 H).

^{13}C NMR of compound 4b (100 MHz, CDCl_3) δ (ppm): 178.93, 176.98, 148.56, 130.34, 128.74, 119.78, 118.84, 112.63, 50.63, 43.77, 42.18, 39.54, 29.85.

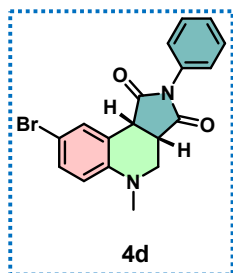


(3a*S*,9b*R*)-2-ethyl-5-methyl-3a,4,5,9b-tetrahydro-1*H*-pyrrolo[3,4-*c*]quinoline-1,3(2*H*)-dione (4c)

Yield: 71%

^1H NMR of compound 4c (400 MHz, CDCl_3) δ (ppm): 7.48 (d, $J = 8$ Hz, 1 H), 7.21 (t, $J = 8$ Hz, 1 H), 6.88 (d, $J = 8$ Hz, 1 H), 6.70 (d, $J = 8$ Hz, 1 H), 3.97 (d, $J = 8$ Hz, 1 H), 3.59-3.48 (m, 3 H), 3.37-3.33 (m, 1 H), 3.02 (s, 1 H), 2.80 (s, 3 H), 1.14 (t, $J = 8$ Hz, 3 H).

^{13}C NMR of compound 4c (100 MHz, CDCl_3) δ (ppm): 178.50, 176.56, 148.44, 130.22, 128.53, 119.60, 118.84, 112.45, 50.65, 43.48, 41.99, 39.40, 34.28, 12.98.

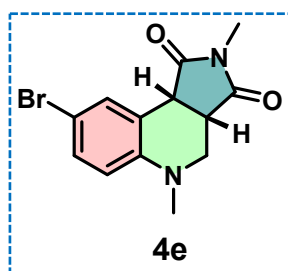


(3a*S*,9b*R*)-8-bromo-5-methyl-2-phenyl-3a,4,5,9b-tetrahydro-1*H*-pyrrolo[3,4-c]quinoline-1,3(2*H*)-dione (4d)

Yield: 83%

¹H NMR of compound 4d (400 MHz, CDCl₃) δ (ppm): 7.65 (d, *J* = 4 Hz, 1 H), 7.44 (t, *J* = 8 Hz, 2 H), 7.39 – 7.30 (m, 2 H), 7.27-7.26 (m, 2 H), 6.61 (d, *J* = 8 Hz, 1 H), 4.11 (d, *J* = 8 Hz, 1 H), 3.61 (dd, *J* = 8, 4 Hz, 1 H), 3.56-3.52 (m, 1 H), 3.11 (dd, *J* = 8, 4 Hz, 1 H), 2.82 (s, 3 H).

¹³C NMR of compound 4d (100 MHz, CDCl₃) δ (ppm): 177.36, 147.62, 132.88, 131.97, 131.61, 129.20, 128.79, 126.44, 120.49, 114.36, 111.85, 50.52, 43.43, 41.93, 39.60.

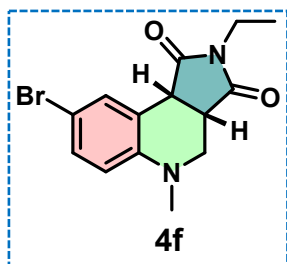


(3a*S*,9b*R*)-8-bromo-2,5-dimethyl-3a,4,5,9b-tetrahydro-1*H*-pyrrolo[3,4-c]quinoline-1,3(2*H*)-dione (4e)

Yield: 76%

¹H NMR of compound 4e (400 MHz, CDCl₃) δ (ppm): 7.59 (s, 1 H), 7.30-7.27 (m, 1 H), 6.56 (d, *J* = 8 Hz, 1 H), 3.95 (d, *J* = 12 Hz, 1 H), 3.52 (dd, *J* = 12, 1 H), 3.38-3.34 (m, 1 H), 3.04-3.02 (m, 1 H), 2.99 (s, 3 H), 2.77 (s, 3 H).

¹³C NMR of compound 4e (100 MHz, CDCl₃) δ (ppm): 178.45, 176.28, 147.56, 132.74, 131.48, 120.69, 114.31, 111.82, 50.38, 43.48, 41.83, 39.56, 25.60.



(3a*S*,9b*R*)-8-bromo-2-ethyl-5-methyl-3a,4,5,9b-tetrahydro-1*H*-pyrrolo[3,4-*c*]quinoline-1,3(2*H*)-dione (4f)

Yield: 79% ¹H NMR of compound 4f (400 MHz, CDCl₃) δ (ppm): 7.59-7.58 (m, *J* = 1 Hz, 1 H), 7.30- 7.27 (m, 1 H), 6.56 (d, *J* = 12 Hz, 1 H), 3.91 (d, *J* = 12 Hz, 1 H), 3.60-3.52 (m, 2 H), 3.50-3.47 (m, 2.7 Hz, 1 H), 3.36-3.30 (m, 1 H), 3.02 (dd, *J* = 8, 4 Hz, 1 H), 2.78 (s, 3 H), 1.14 (t, *J* = 8 Hz, 3 H).

¹³C NMR of compound 4f (100 MHz, CDCl₃) δ (ppm): 178.16, 175.99, 147.57, 132.77, 131.42, 120.84, 114.28, 111.79, 50.54, 43.33, 41.78, 39.56, 34.53, 13.10.

Calculation of excited-state oxidation potential and reduction potential of Ir-triad 1

The excited-state oxidation potential (E_{ox}^*) and reduction potential (E_{red}^*) were calculated using the following equations^{S9}

$$E_{ox}^* = E_{ox} - E_{0,0} \quad (S5)$$

$$E_{red}^* = E_{red} + E_{0,0} \quad (S6)$$

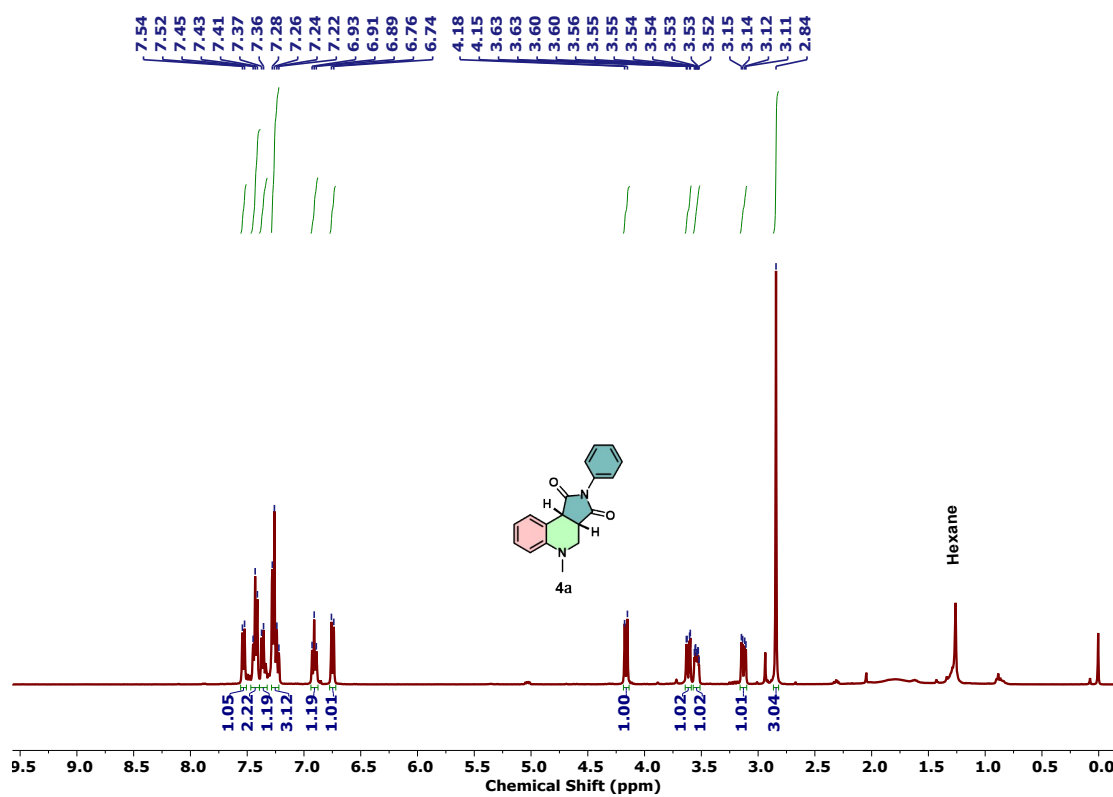
here E_{ox} and E_{red} are the half-oxidation potential and half-reduction potential, respectively, and $E_{0,0}$ is the lowest energy electronic transition between the lowest vibrational states of the ground and the first excited state and calculated by taking the intersection point of normalized absorption and normalized emission spectra.

For Ir-triad 1

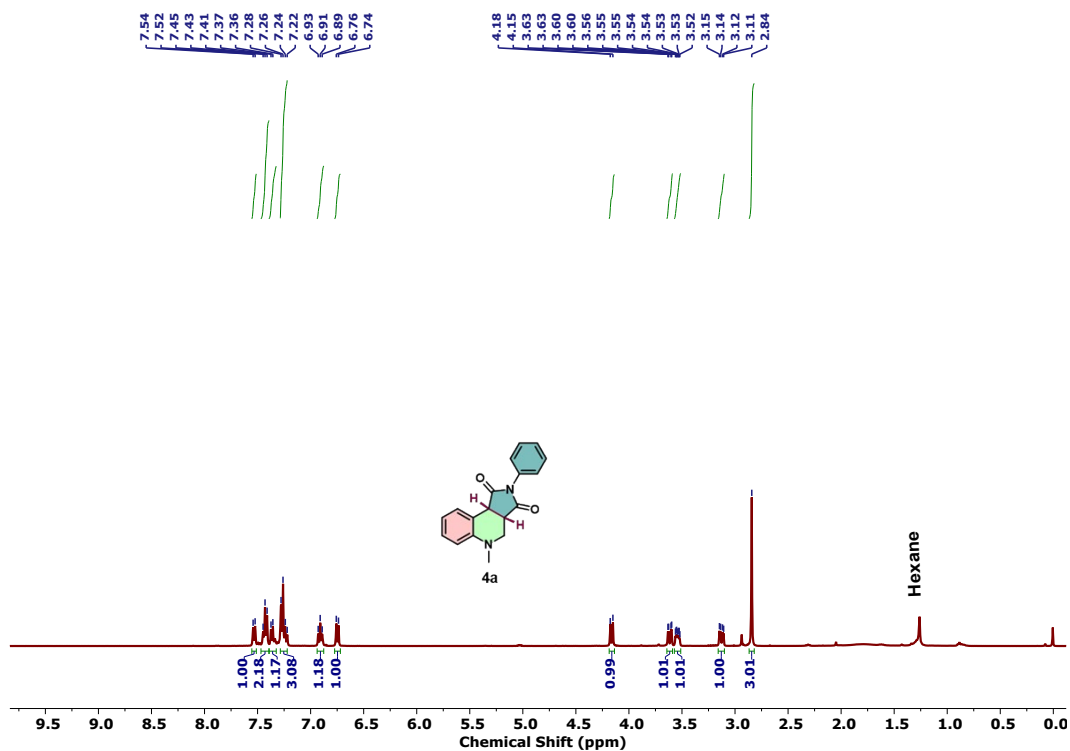
$$E_{ox} = 0.85 \text{ V}, E_{red} = -0.45 \text{ V}, E_{0,0} = 2.24 \text{ eV}$$

Accordingly, E_{ox}^* and E_{red}^* were calculated to be -1.39 V and 1.79 V respectively.

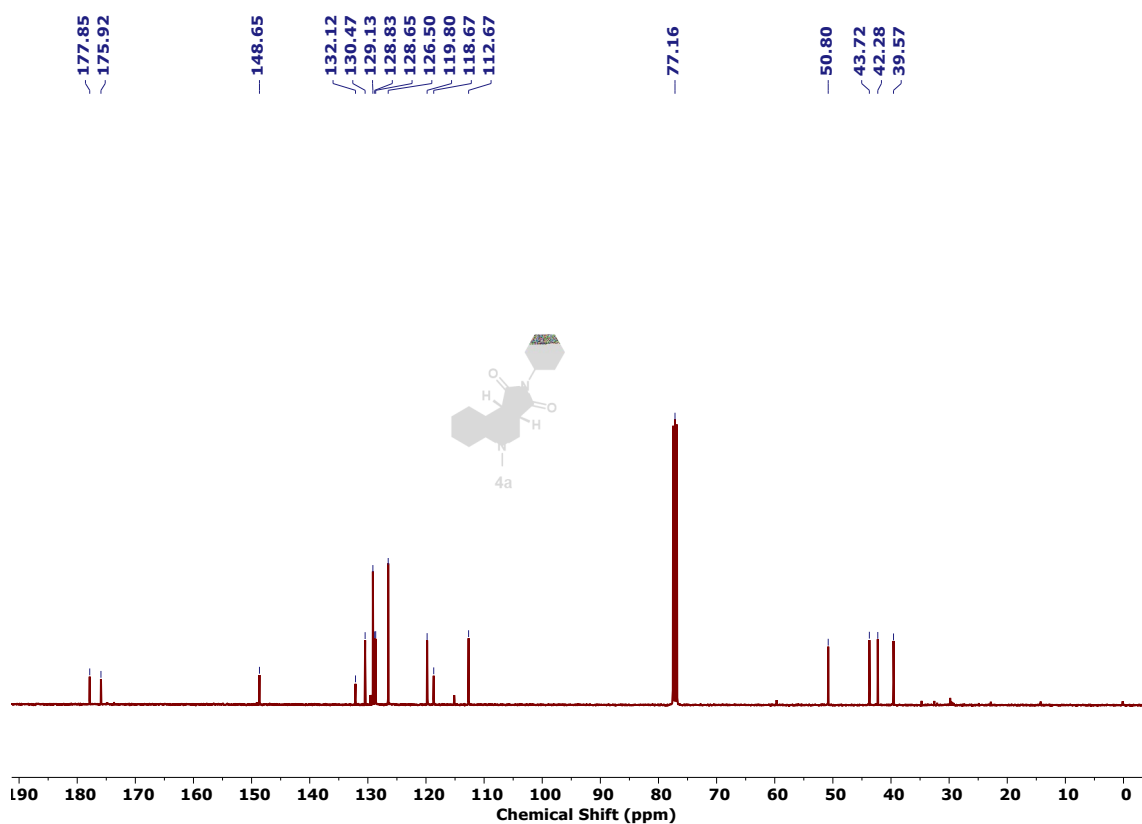
^1H NMR of compound 4a in CDCl_3



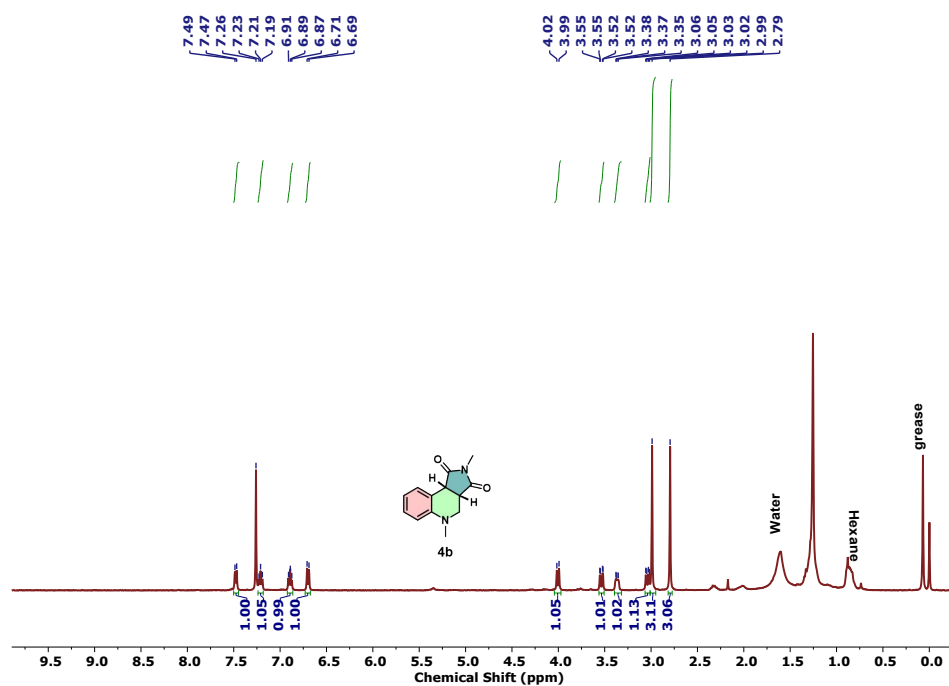
^1H NMR of compound 4a in CDCl_3 using compound 6 as photocatalyst



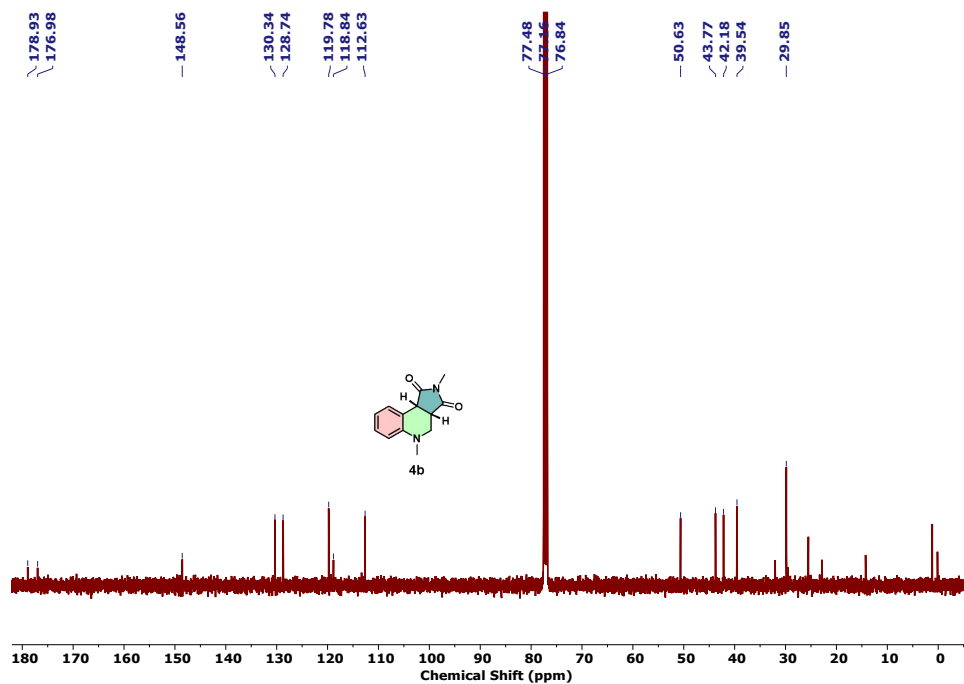
¹³C NMR of compound 4a in CDCl₃



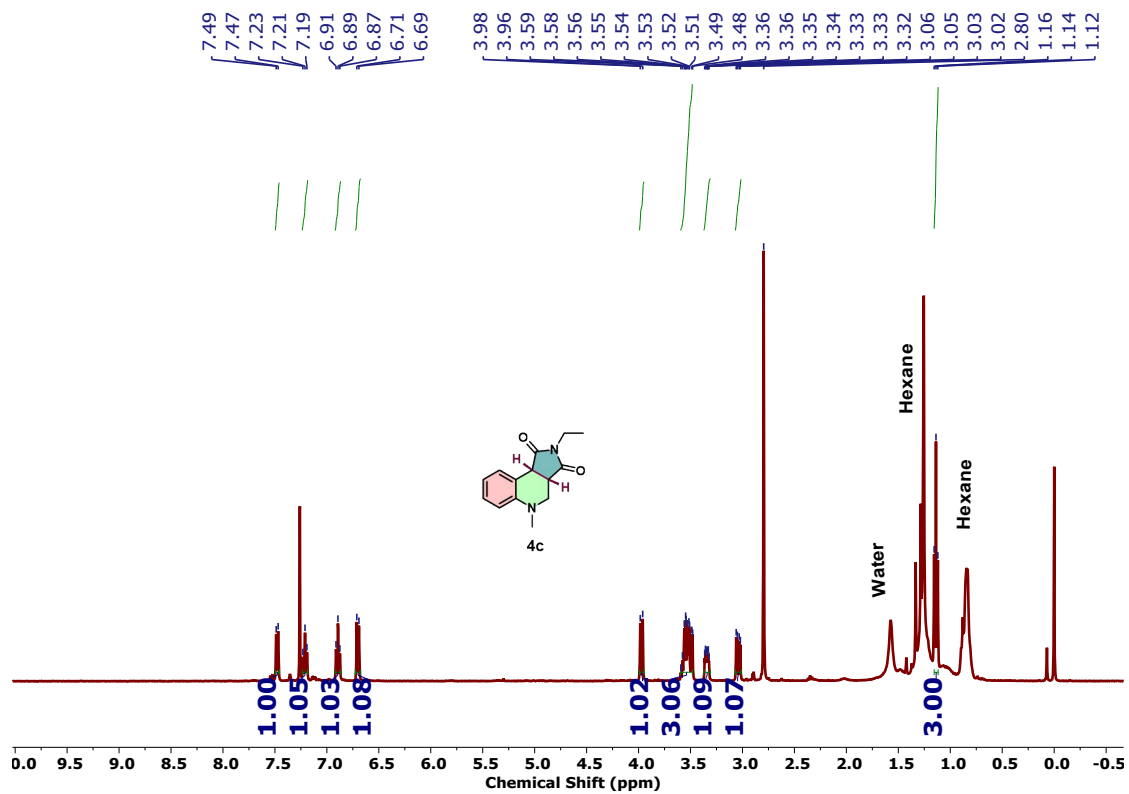
¹H NMR of compound 4b in CDCl₃



^{13}C NMR of compound 4b in CDCl_3

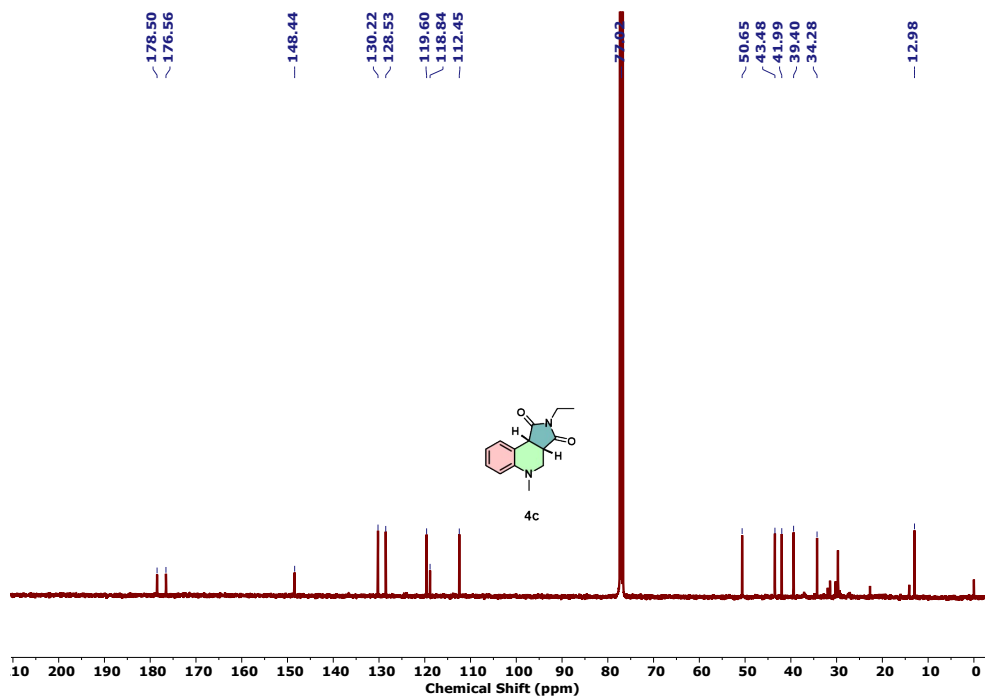


^1H NMR of compound 4c in CDCl_3

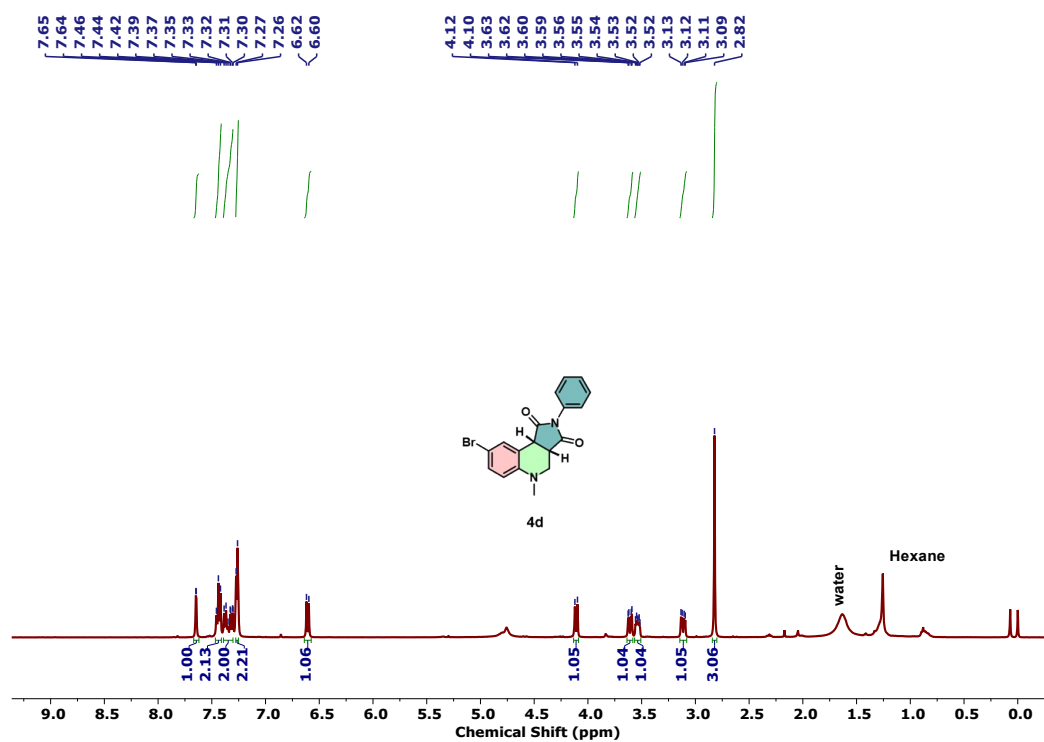


7.49, 7.47, 7.23, 7.21, 7.19, 6.91, 6.89, 6.87, 6.71, 6.69, 3.98, 3.96, 3.59, 3.58, 3.56, 3.55, 3.54, 3.53, 3.52, 3.51, 3.49, 3.48, 3.36, 3.36, 3.35, 3.34, 3.33, 3.33, 3.32, 3.06, 3.05, 3.03, 3.02, 2.80, 1.16, 1.14, 1.12

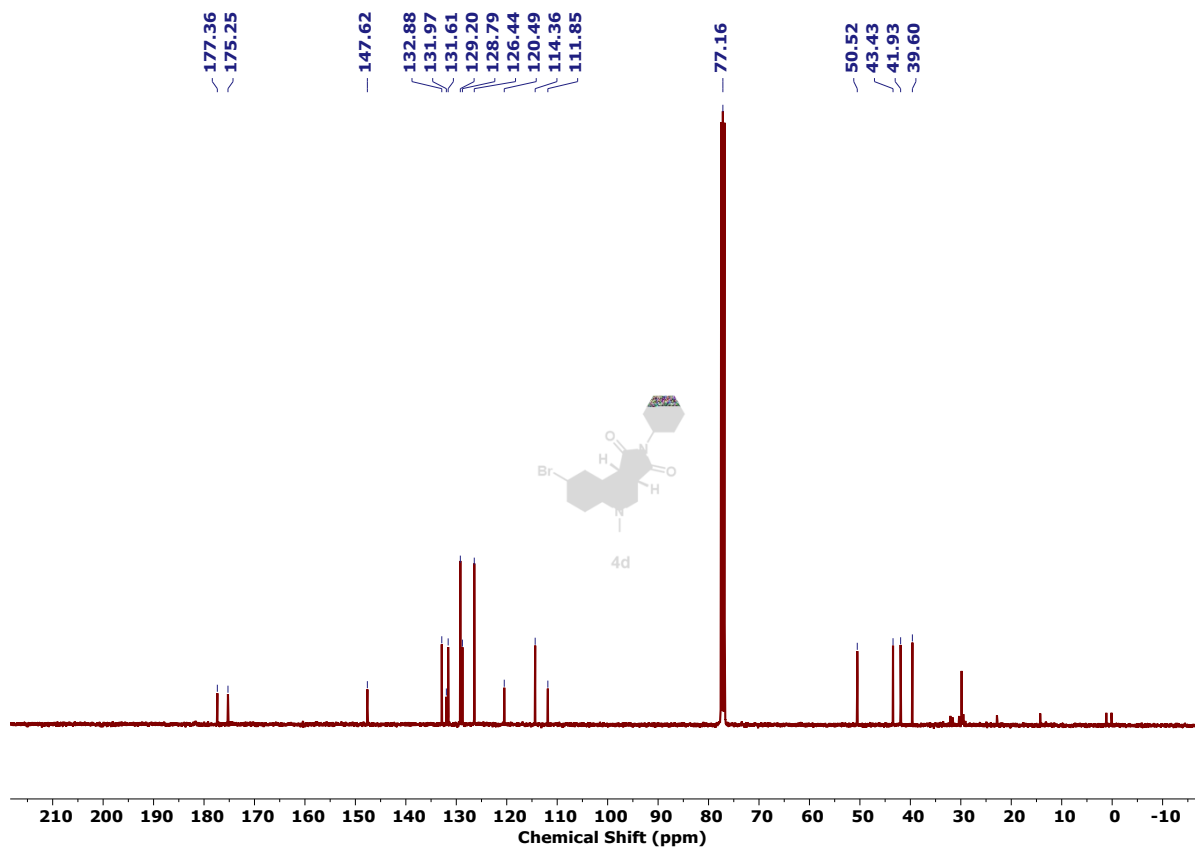
¹³C NMR of compound 4c in CDCl₃



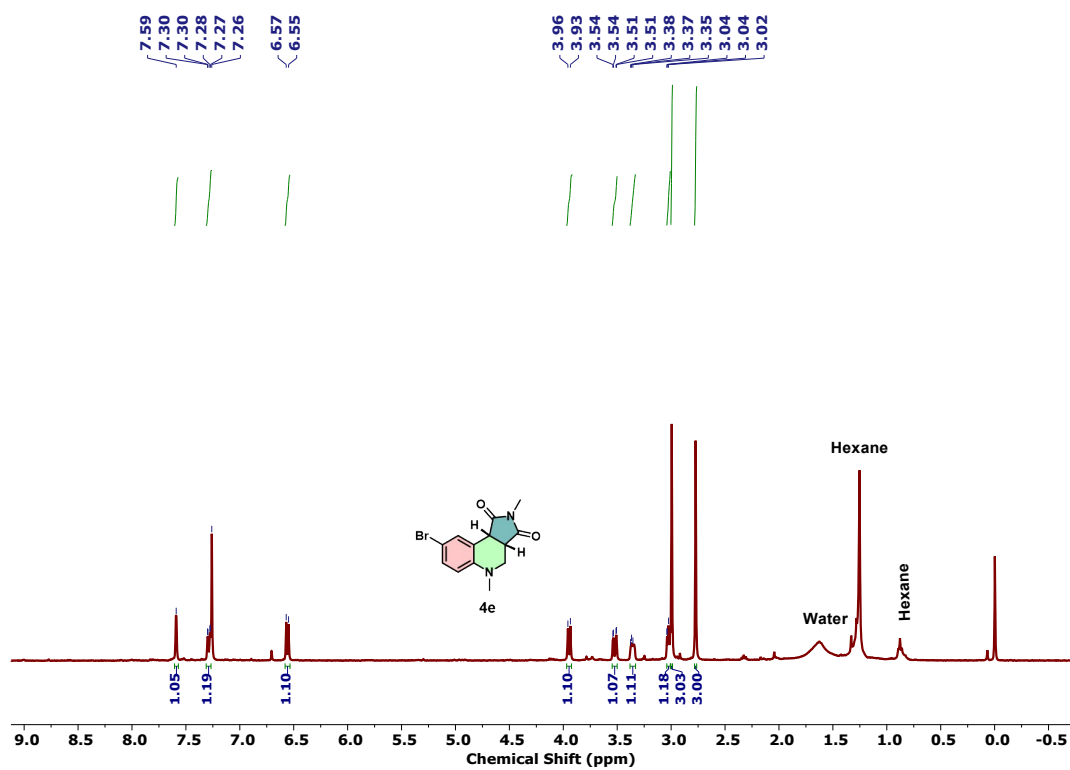
^1H NMR of compound 4d in CDCl_3



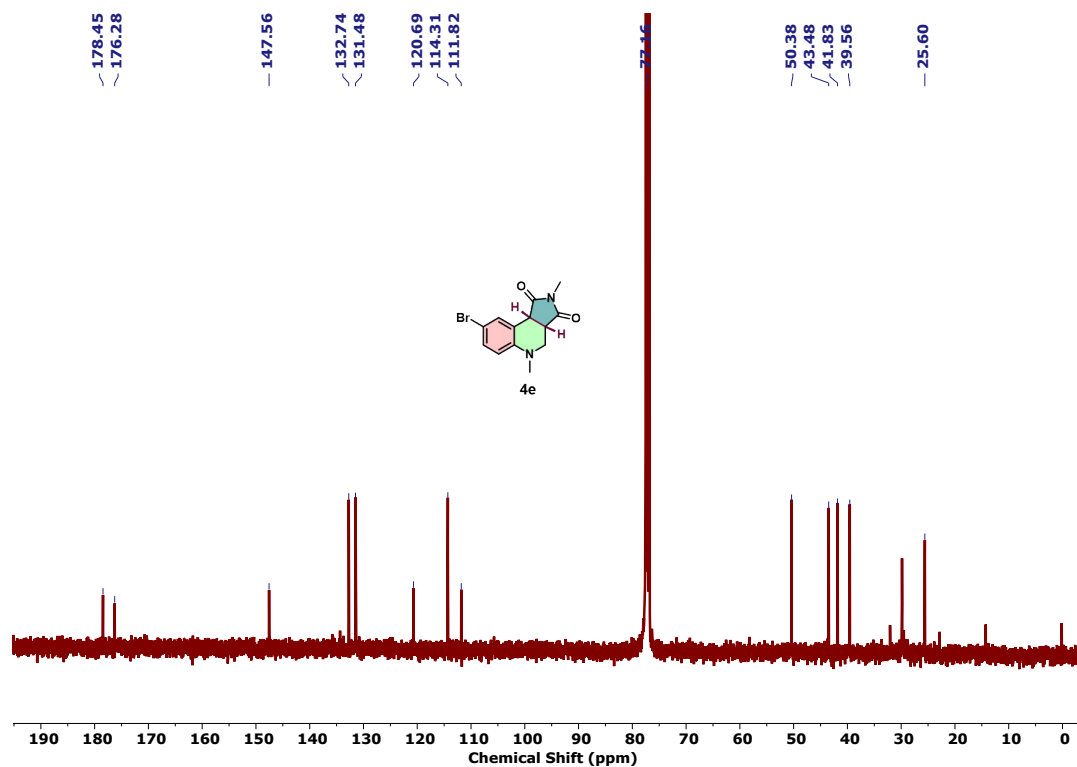
^{13}C NMR of compound 4d in CDCl_3



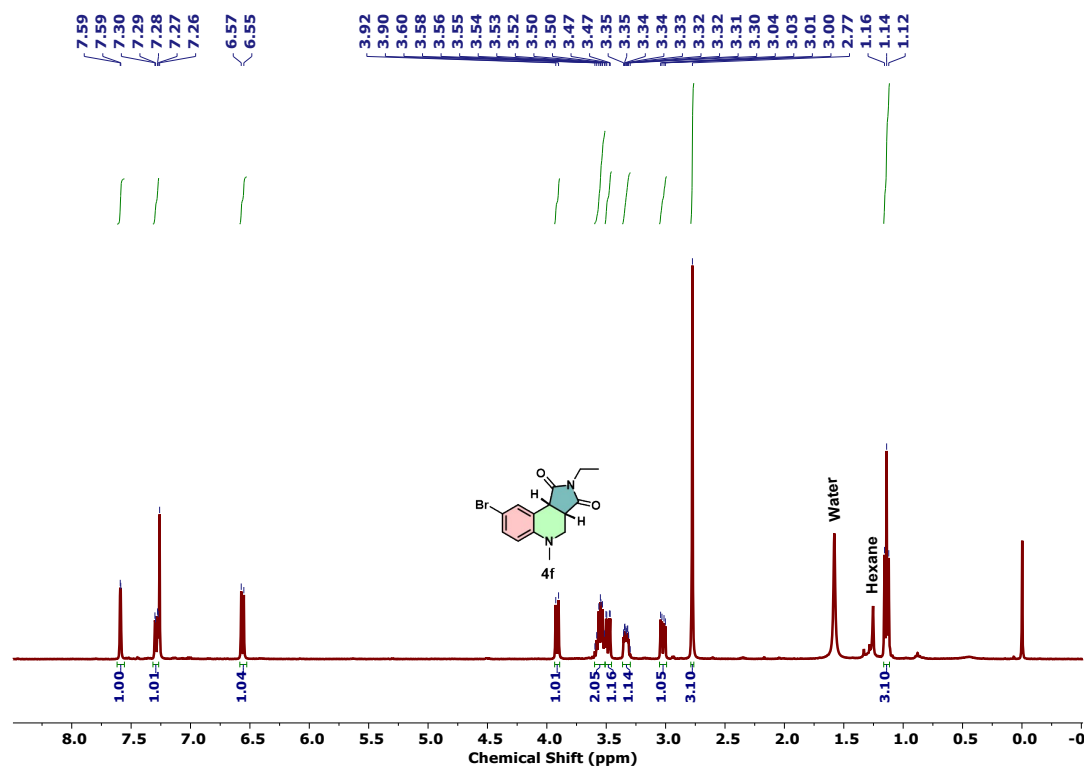
¹H NMR of compound 4e in CDCl₃



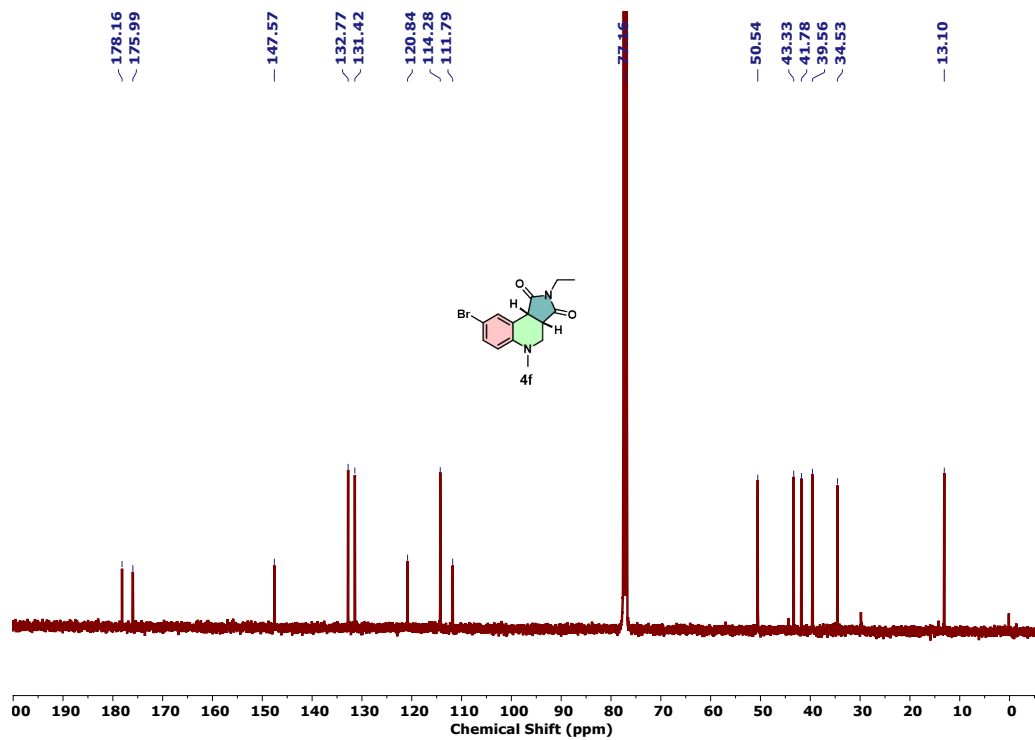
¹H NMR of compound 4e in CDCl₃



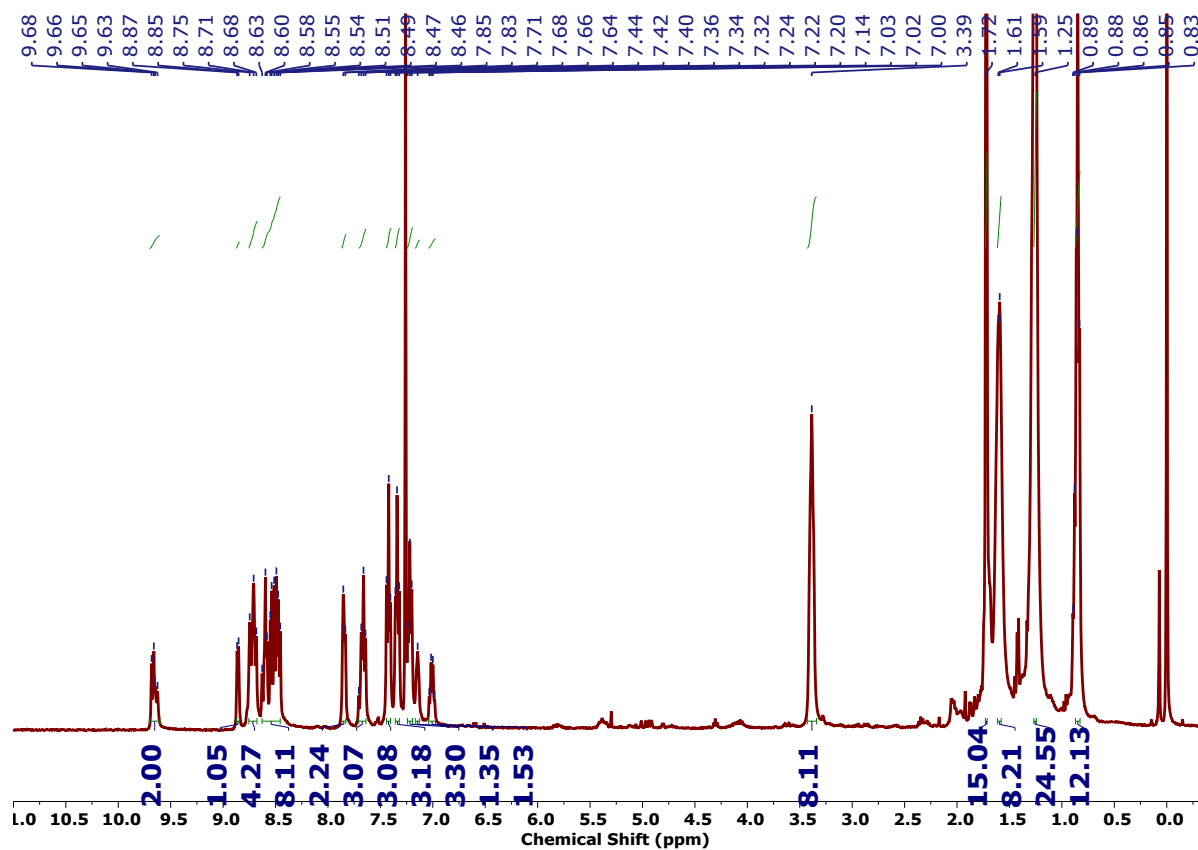
¹H NMR of compound 4f in CDCl₃



¹H NMR of compound 4f in CDCl₃



¹H NMR and absorption spectra of recovered Ir-triad 1 after photocatalysis



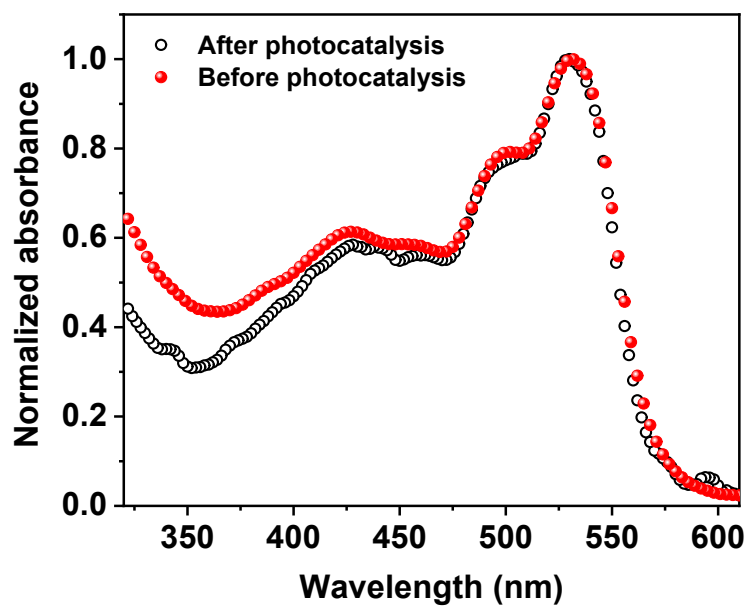
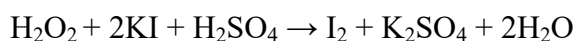


Fig. S7 Absorption spectra of **Ir-triad 1** before and after photocatalysis.

Detection of H₂O₂

The generation of H₂O₂ in the photocatalytic reaction was detected according to the following iodometric reaction:^{S10}



Procedure: After completing the synthesis of compound **4a**, 1 mL aliquot of the filtrate (b) was taken and subsequently, 3 mL of 3.5 M H₂SO₄ solution and 1 mL of 0.1 M KI solution (c) were successively added to the solution (a). This addition led to a change in dark yellow colour with the release of I₂ as indicated in (a). Thus, this reaction demonstrates the generation of H₂O₂, consistent with the mechanistic pathway described in the literature.

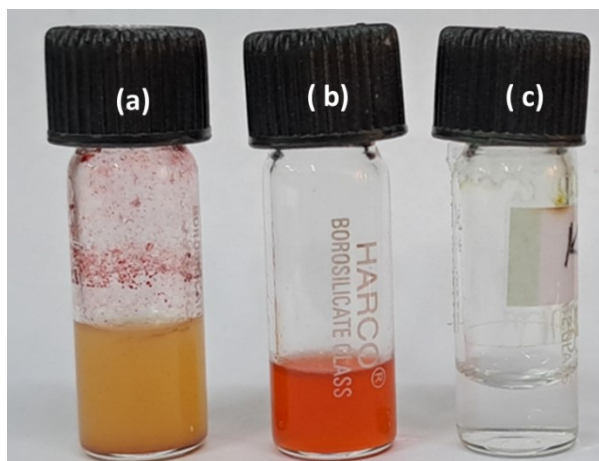


Fig. S8 Iodometric detection of H_2O_2 from the aliquot of the photocatalytic reaction.

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