

Supplementary Materials

Coupled Light-Driven *p*-Xylene Oxidation and H₂O₂ Production with Organic Photocatalysts in Propylene Carbonate

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1. Experimental Procedures

1.1. Photocatalysis Experiments

Each reaction was performed in an 8 mL glass vial containing 1 mL of solvent, to which *p*-xylene (or the other substrates employed in this work) and a photocatalyst were added. The solvents used throughout this work were all employed as pure solvents, starting with acetonitrile, followed by acetone and propylene carbonate, with the latter ultimately being chosen as the default solvent for the optimized reaction conditions. Each reaction was carried out at room temperature (~25 °C) and to maintain a stable reaction temperature, a fan is placed at 20 cm from the reaction vials. The vial cap septum was pierced with a needle to promote the entry of air into the reaction mixture. A magnetic stir bar was placed inside the vial, which was then positioned on a magnetic stirrer. On top of the stirrer, a homemade white LED (33 mW/cm²) reactor equipped with several compartments for vials provided uniform white light illumination from below, ensuring consistent exposure for each sample. Unless kinetic assays were being performed, each reaction was allowed to proceed for 24 h under irradiation. Each solution was analyzed by ¹H-NMR in CD₃CN and by gas chromatography. With selected photocatalysts and reaction conditions, the analyses were carried out using the reactors equipped with integrated LEDs at 365 nm, 395 nm, 405 nm, and 450 nm. Images of the photoreactors employed, with white light (left) or LED (right), are reported below.



Figure S1. Images of the photoreactors.



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1.2. ^1H -NMR Analysis

All ^1H NMR analyses were performed in dedicated NMR tubes by adding 200 μL of reaction solution, 300 μL of CD_3CN containing mesitylene as an internal standard for product quantification (mesitylene exhibits a singlet at 2.3 ppm corresponding to the nine protons of its three methyl groups and a singlet at 6.8 ppm due to the three protons of the aromatic ring). Mesitylene was chosen as internal standard because its peaks do not overlap with those of reactants or products. The signals used for product analysis are all located in the aromatic region above 7 ppm. In the case of photocatalytic oxidation of ethanol, dimethylsulfone was used as an internal standard.

1.3. Analysis by Gas Chromatography (GC) and Gas Chromatography Coupled to Mass Spectrometry (GC-MS)

Gas chromatography analyses were initially performed to monitor the composition of the reaction mixtures. For each measurement, an aliquot of the reaction solution was transferred to a GC vial and analyzed without further dilution. The samples were analyzed using a Shimadzu GC-2010 Pro gas chromatograph equipped with a capillary column (SHI-5: 10 m length, 0.10 mm inner diameter, 0.10 μm film thickness). The carrier gas was helium (He) with a column flow rate of 0.57 mL/min. The injector temperature was set to 280 $^\circ\text{C}$ and the detector temperature (FID) to 330 $^\circ\text{C}$. The split injection mode was used with a split ratio of 70.2. The oven temperature program started at 50 $^\circ\text{C}$ (held for 3 min), ramped at 30 $^\circ\text{C}/\text{min}$ to 280 $^\circ\text{C}$ (held for 5 min). Makeup gas was N_2 at a flow rate of 30 mL/min, H_2 at 40 mL/min, and air at 400 mL/min for the FID detector. In the case of GC-MS analysis, an Agilent GC/MSD 6850/5973 instrument was used, equipped with a HP-5 column 30 m length, 0.25 mm inner diameter and 0.25 μm film thickness.

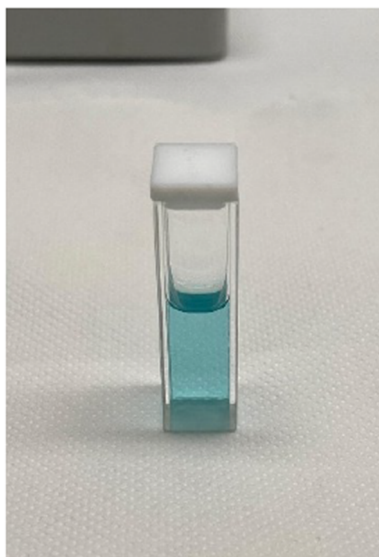
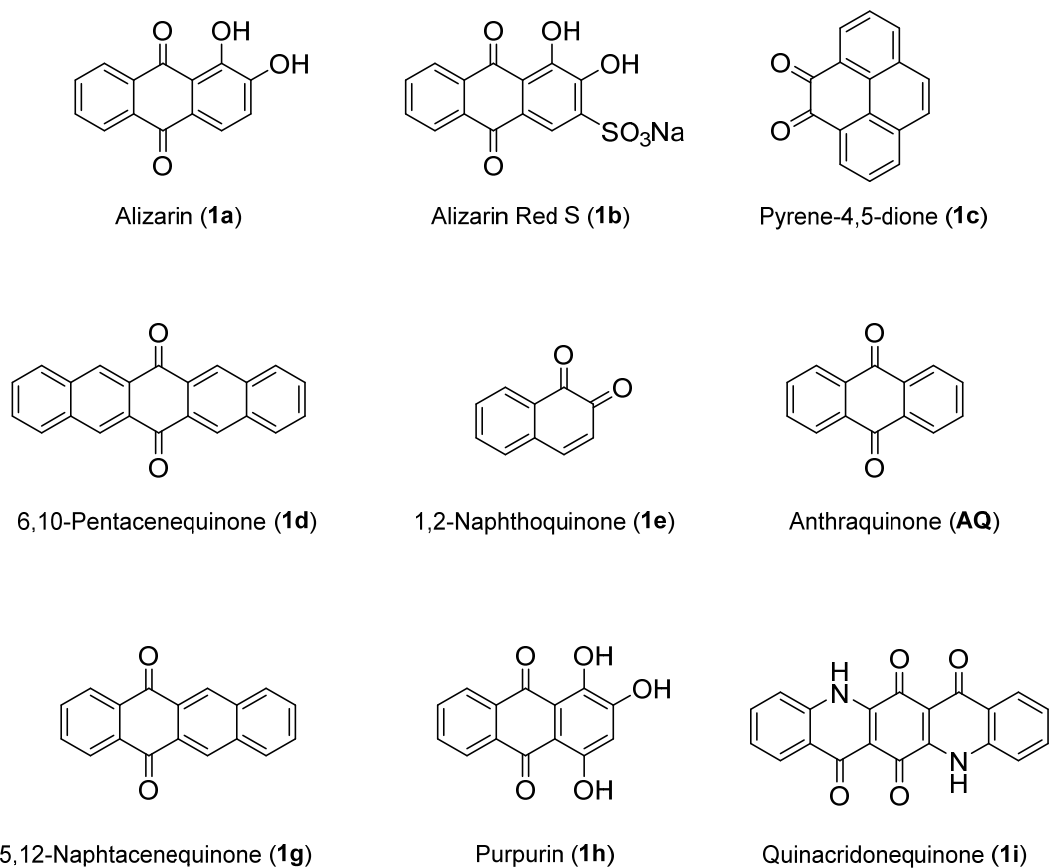


Figure S2. Image of a cuvette used for H_2O_2 quantification; the blue color is associated to the formation of the charge transfer complex from TMB oxidation.

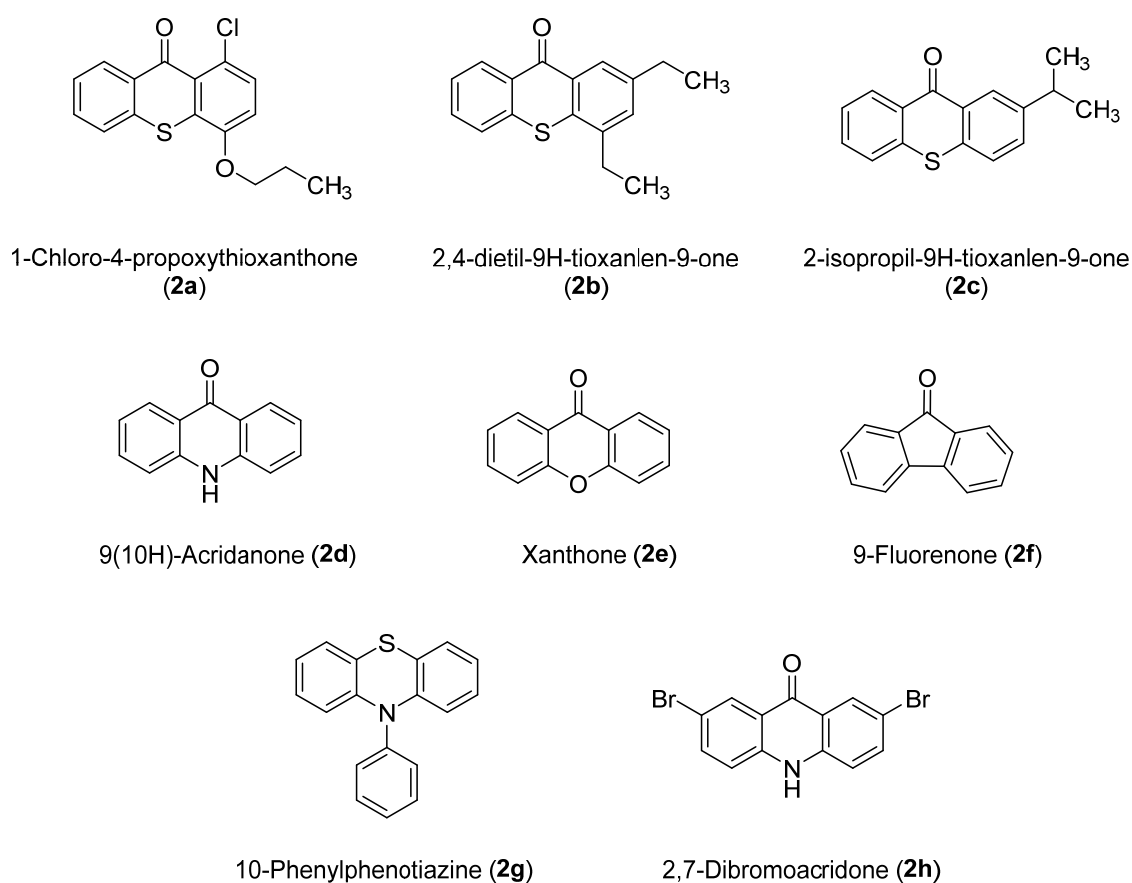
1.4. H_2O_2 Quantification

Two stock solutions were prepared for the analyses: a solution with 2 mg of 3,3',5,5'-tetramethylbenzidine (TMB) in DMSO and a solution with 0.9 mg of Horseradish Peroxidase (HRP) in 50 mL of acetate buffer. A cuvette with a 1 cm optical path was used for UV-Vis analyses, to which 2 mL of HRP solution, 80 μL of TMB solution and 1 μL of the reaction solution were added for each analysis (total volume = 2.081 mL; see a representative image of a cuvette on the right of the page). Each UV-Vis spectrum was subtracted from the respective baseline consisting of just the two initial HRP and TMB stock solutions (without the addition of 1 μL of the reaction solution).

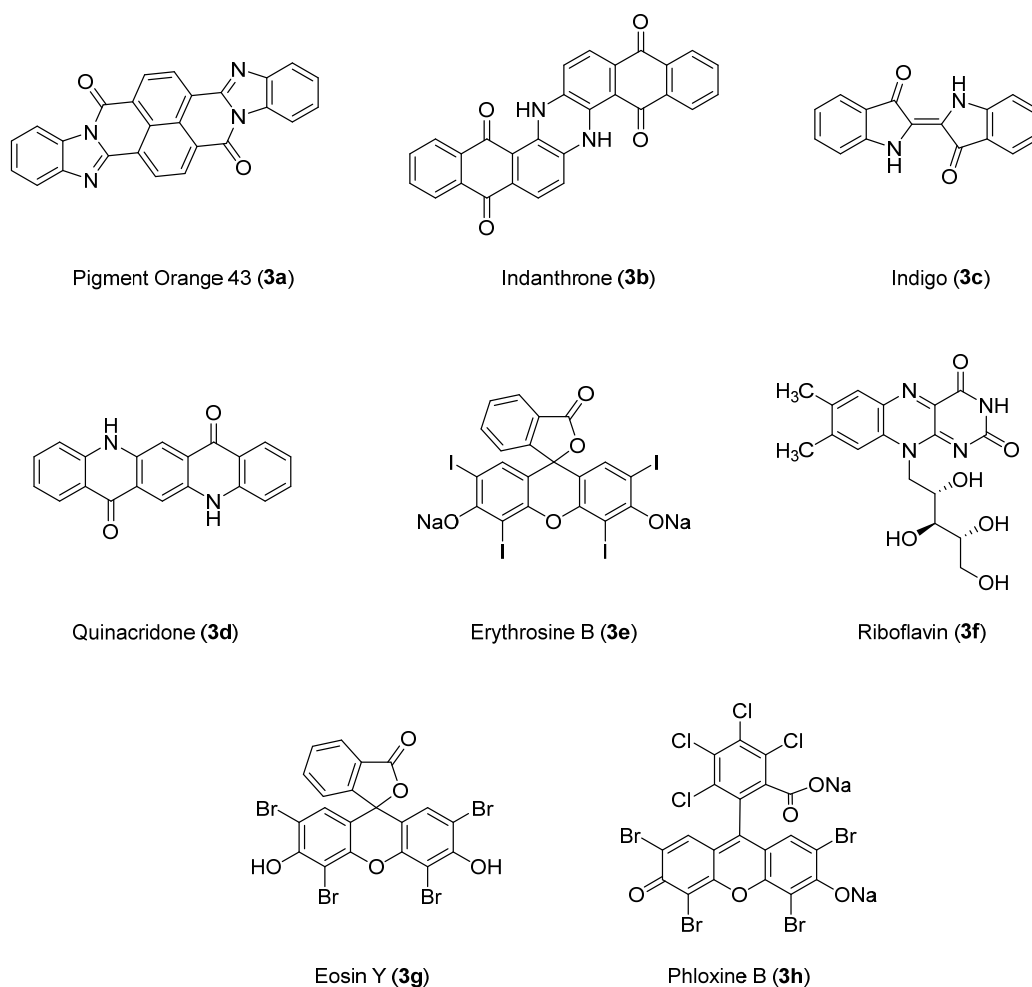
In this system, the oxidation of TMB by H_2O_2 catalyzed by HRP leads to the formation of a blue charge-transfer complex ($\lambda_{\text{max}} \approx 652 \text{ nm}$, $\epsilon^{652} = 3.9 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$) in 1:1 stoichiometry with respect to H_2O_2 . Consequently, from the UV-Vis absorption spectra of the blue compound, it is possible to determine the concentration of the blue charge-transfer complex by measuring the absorption peak at 652 nm, which directly corresponds to the amount of H_2O_2 formed during the reaction. The error used is based on an estimate of 5% resulting from technical replicates (2/3 for each solution).



Scheme S1. Quinoid photocatalysts employed in the present work.



Scheme S2. Organic photocatalysts employed in the present work.



Scheme S3. Pigments and dyes employed in the present investigation.

Table S1. Oxidation of *p*-xylene (80 mM) using catalysts **1c** (1 mM) and **AQ** (1 mM), in acetonitrile, propylene carbonate and acetone, under white light (33 mW cm⁻²), in air atmosphere, at room temperature, 24 h. The other photocatalysts investigated provided negligible activity in these conditions.

Entry	Photocatalyst	Products Yield ^[a] (%)			
		<i>p</i> -MBA	<i>p</i> -TALD	<i>p</i> -TA	TPA
Solvent: acetonitrile					
1	1c	-	2	-	-
2	AQ	2	8	-	-
Solvent: propylene carbonate					
3	1c	-	1	-	-
4	AQ	1	5	-	-
Solvent: acetone					
5	1c	-	-	-	-
6	AQ	2	6	-	-

^[a] *p*-MBA, *p*-TALD, *p*-TA and TPA indicated *p*-methylbenzyl alcohol, *p*-tolualdehyde, *p*-toluic acid and terephthalic acid, respectively.

Table S2. Oxidation of *p*-xylene (80 mM) using catalysts **AQ** in propylene carbonate, at room temperature, 24 h, using different photocatalyst's concentration, atmosphere and light.

Entry	Atm	Products Yield (%)			
		<i>p</i> -MBA	<i>p</i> -TALD	<i>p</i> -TA	TPA
AQ (1 mM), white LED					
1	Air	1	5	-	-
2	O ₂	3	12	1	-
AQ (2 mM), white LED					
3	Air	2	8	-	-
4	O ₂	3	16	2	-

Table S2. Cont.

Entry	Atm	Products Yield (%)			
		<i>p</i> -MBA	<i>p</i> -TALD	<i>p</i> -TA	TPA
AQ (2 mM), LED 365 nm					
5 ^[a]	Air	5	28	4	-
6 ^[b]	O ₂	4	25	3	-
AQ (2 mM), LED 395 nm					
7 ^[c]	Air	8	39	13	1
8 ^[d]	O ₂	2	25	30	2
AQ (2 mM), LED 405 nm					
9 ^[e]	Air	8	44	21	1
10 ^[f]	Air	5	16	3	
11 ^[g]	Air	2	4	<1	

^[a] 37% conversion; ^[b] 32% conversion; ^[c] 61% conversion; ^[d] 59% conversion; ^[e] 75% conversion. ^[f] 240 mM *p*-xylene. ^[g] 800 mM *p*-xylene.

Table S3. Products yield (%) from oxidation of para-xylene (80 mM) using catalysts AQ (2 mM) in different solvents, irradiated with LED 405 nm, at room temperature, 24 h.

Entry	Solvent	Products Yield (%)			
		<i>p</i> -MBA	<i>p</i> -TALD	<i>p</i> -TA	TPA
1 ^[a]	Propylene carbonate	8	44	21	1
2	[BMIM][PF ₆]	4	3	-	-
3	[BMIM][BF ₄]	13	6	1	-
4 ^[b]	Dimethyl carbonate	4	24	19	2

^[a] 74% conversion; ^[b] 50% conversion.

Table S4. Literature systems reporting photochemical oxidation of *p*-xylene. TON = turnover number; TOF = turnover frequency; QY = quantum yield.

Photocatalyst	Conditions	Main Product, Productivity Selectivity	TON/TOF/QY	Reference and Notes
AQ	405 nm LED Propylene carbonate air	<i>p</i> -TALD 47% y (62% selectivity)	TON 19 TOF 3.2 h ⁻¹ QY ₄₀₅ 0.38%	This work
Acr ⁺ -I	White Light Propylene carbonate air	<i>p</i> -TALD 41% y (51% selectivity)	TON 16 TOF 1.4 h ⁻¹	This work
Acr ⁺ -I	450 nm LED Propylene carbonate air	<i>p</i> -TALD 37% y (46% selectivity)	TON 14 TOF 1 h ⁻¹ QY ₄₅₀ 0.20%	This work
2-carboxyanthraquinone (AQ-COOH)	35 Watt tungsten-bromine lamp Acetone 1 atm O ₂ ^[a]	<i>p</i> -TA (88.2% selectivity) 62.5% yield	TON 8.3 TOF 0.69 h ⁻¹ QY n.r.	superoxide free radicals (O ₂ ^{•-}) and singlet oxygen (¹ O ₂) [1]
Acr ⁺ -Mes	xenon lamp attached with a colour glass filter (λ = 380–500 nm) CH ₃ CN/H ₂ O/H ₂ SO ₄ O ₂ ^[b]	<i>p</i> -TALD (75%), <i>p</i> -MBA (15%) H ₂ O ₂ (74%)	TON 20–200 QY 0.37	simultaneous production of H ₂ O ₂ [2]
TBA ₄ W ₁₀ O ₃₂ (decatungstate)	365 nm CH ₃ CN/HCl (aq.) air in flow ^[c]	TA 93% yield	TON 20 TOF 1.05 h ⁻¹ QY n.r.	HAT by the photocatalyst [3]
TBA ₃ PW ₁₂ O ₄₀ (phosphotungstate)	125 W mercury lamp CH ₃ CN O ₂ ^[d]	<i>p</i> -TALD 17% yield, 67% selectivity	TON 42 TOF 2 h ⁻¹ QY n.r.	oligomeric oxidized by-products [4]
TiO ₂ nanoparticles	365 nm LED CH ₃ CN O ₂ In flow ^[e]	<i>p</i> -xylene to <i>p</i> -MBA and <i>p</i> -TALD at ca 10% <i>p</i> -xylene conversion		superoxide (O ₂ ^{•-}) and peroxide (O ₂ ²⁻) [5]
-	(Hg lamp, 500W, 0–2 Sun) UV irradiation CH ₃ CN, 45° O ₃ flow	84% terephthalic yield	-	ozonization procedure [6]
Fe(pyclen)	White light irradiation CH ₃ CN, air	<i>p</i> -TALD 31% yield, 79% selectivity	QY (405 nm) 0.14% [7]	

^[a] 12 h, 0.5 mmol *p*-xylene in 5 mL acetone, 7.5 mol% photocatalyst. ^[b] After photoirradiation for 80 min. Conditions: [photocatalyst] = 0.2 mM, [substrate] = 4.0 mM, [H₂O] = 0.9 M, [H₂SO₄] = 1.0 mM. ^[c] 19 h, 10 mM *p*-xylene in 20 mL solvent, 0.5 mM photocatalyst. ^[d] 0.25 mM *p*-xylene in 30 h, 0.4 mol% photocatalyst. ^[e] 0.4 mmol of *p*-xylene in 4 mL CH₃CN, 20 mg of catalyst, 4 μL of H₃PO₄, O₂, 25 °C, 1 h.

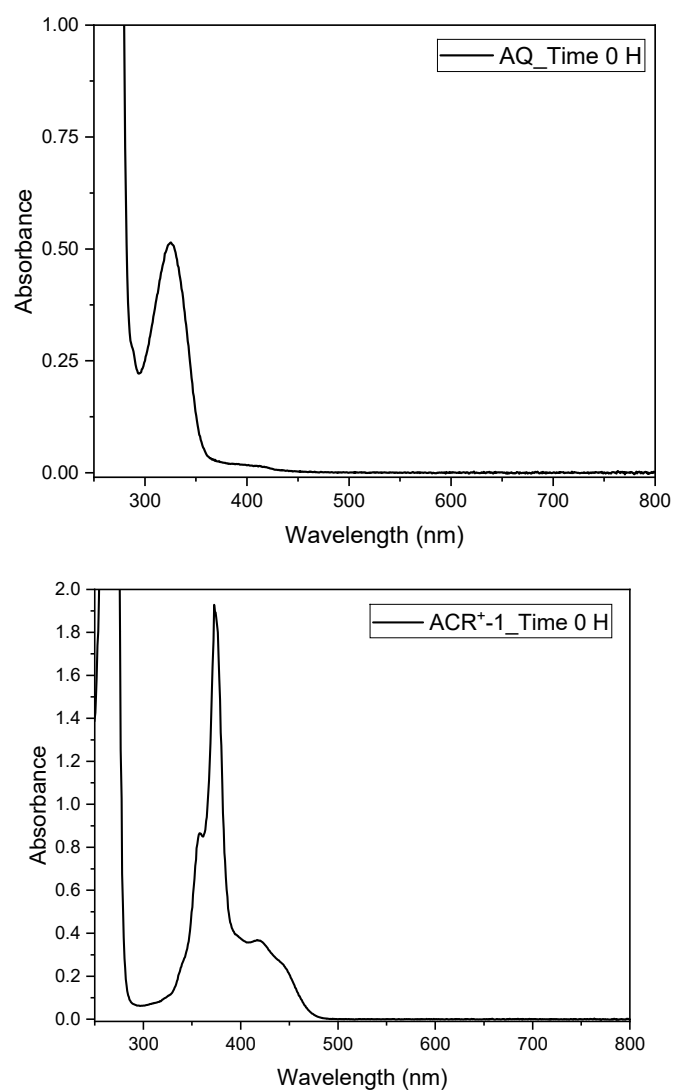


Figure S3. Absorption spectra of 2 mM AQ (**top**) and Acr⁺-1 (**bottom**) in propylene carbonate; 1 mm path cuvette.

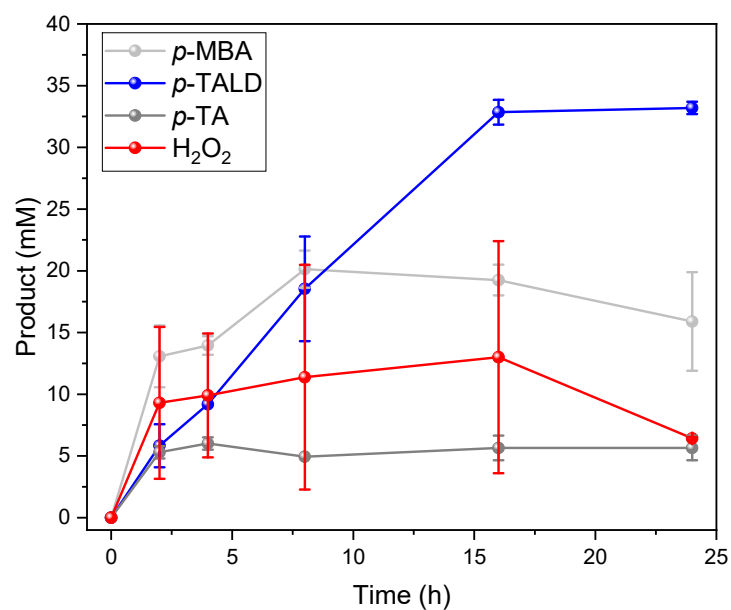


Figure S4. Photocatalytic aerobic oxidation of *p*-xylene (80 mM) in propylene carbonate with Acr⁺-1 (2 mM) under white light irradiation.

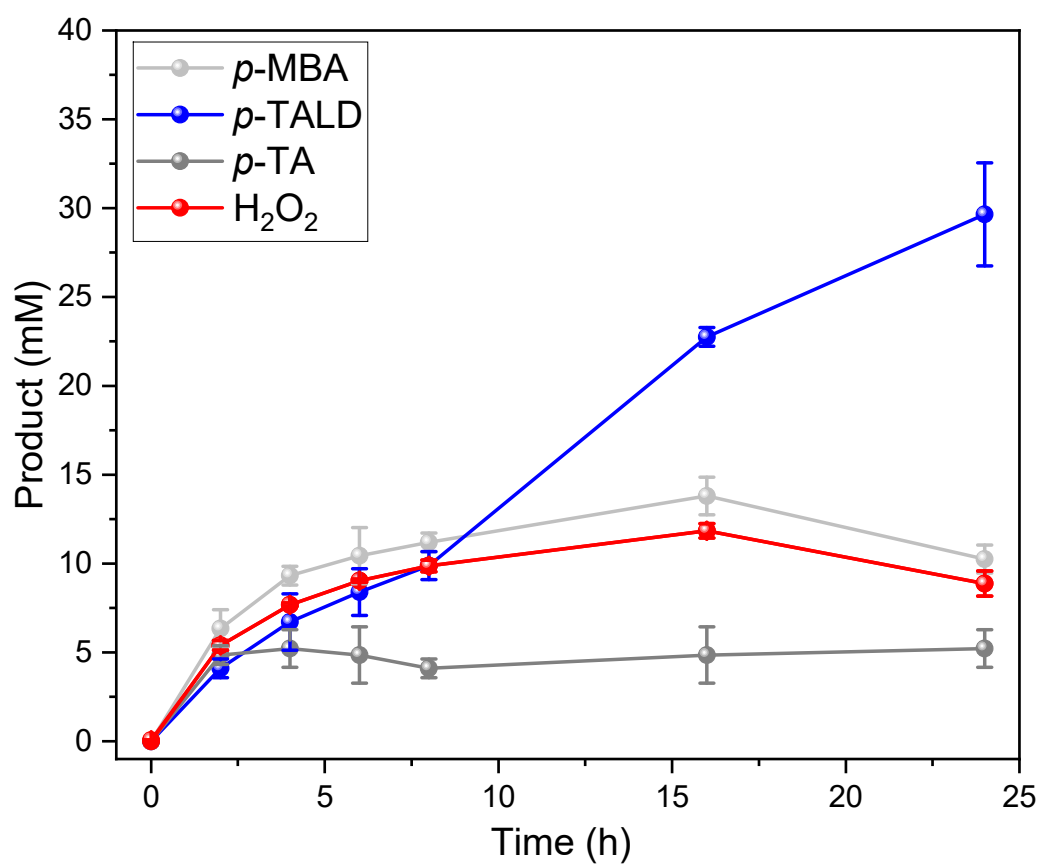


Figure S5. Photocatalytic aerobic oxidation of *p*-xylene (80 mM) in propylene carbonate with Acr⁺-1 (2 mM) under blue light irradiation (LED 450 nm).

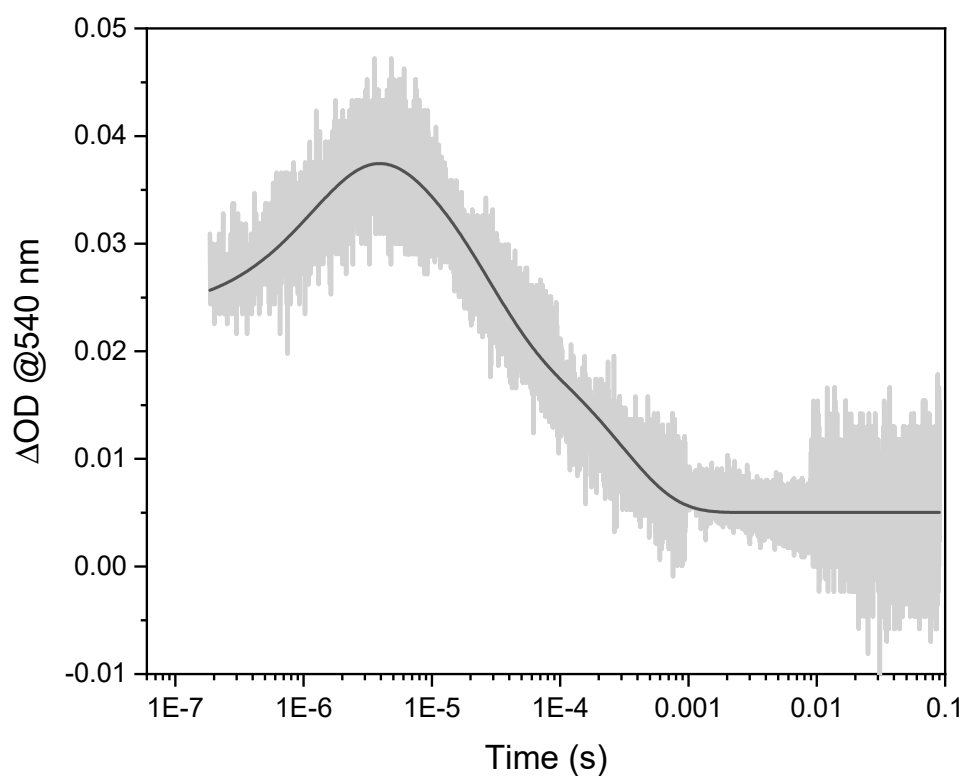


Figure S6. Kinetic profile of the signature at 540 nm under LFP of AQ (1 mM in propylene carbonate, degassed) upon laser excitation at 355 nm.

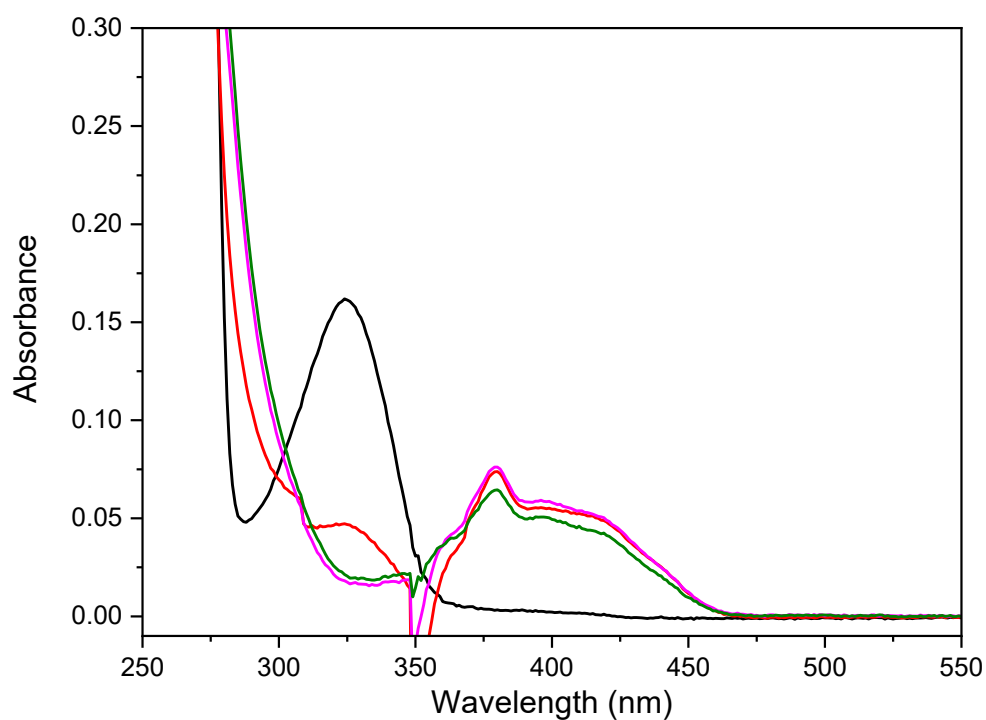


Figure S7. UV-Vis spectrum of a solution of AQ (2 mM in propylene carbonate) under 400 nm LED illumination, in N₂ atmosphere (optical path 1 mm); black trace: before irradiation; colored traces: along 5 min irradiation.

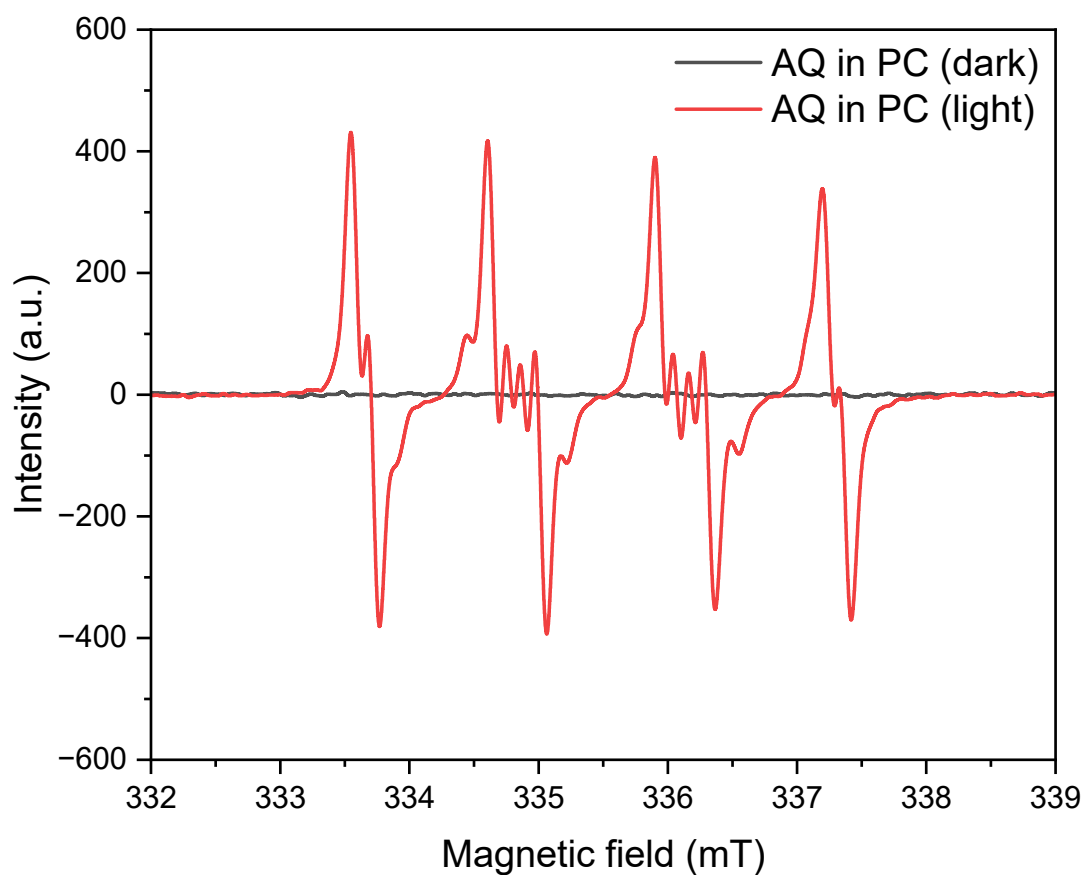


Figure S8. EPR signal obtained upon irradiation of a solution of AQ in propylene carbonate (black trace, AQ 2 mM, aerobic conditions, DMPO 25 mM, 405 nm irradiation).

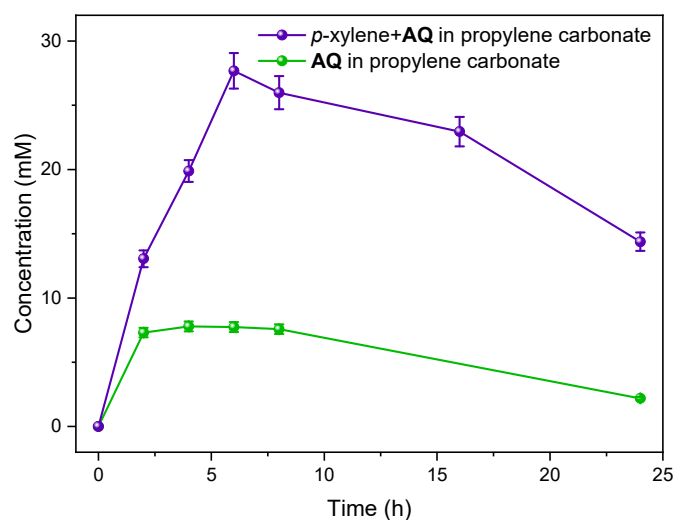


Figure S9. Time profile of H_2O_2 concentration obtained by the oxidation reaction in presence (purple) and absence (green) of *p*-xylene catalyzed by AQ (2 mM), LED 405 nm. Estimated error as semi-dispersion of three repeated trials. For the plot of the data, the absorbance values obtained from the reaction mixtures at $\lambda = 652$ nm for the blue complex are used to quantify the concentration of hydrogen peroxide. The Lambert-Beer law is applied, where the concentration of hydrogen peroxide is calculated from the Abs using the extinction coefficient for the blue complex, given the 1:1 stoichiometry of the reaction.

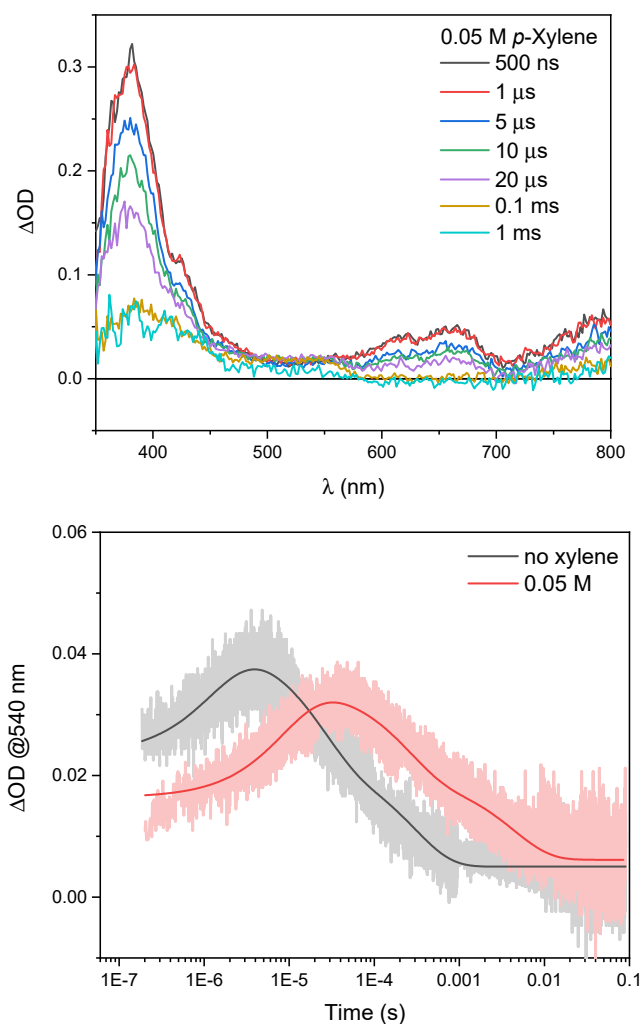


Figure S10. (Top): LFP of AQ (1 mM in propylene carbonate, 50 mM *p*-xylene, degassed) upon laser excitation at 355 nm. **(Bottom):** kinetic profile of the transient absorption at 540 nm (ascribable to $\text{AQ}^{\bullet-}$) with or without *p*-xylene.

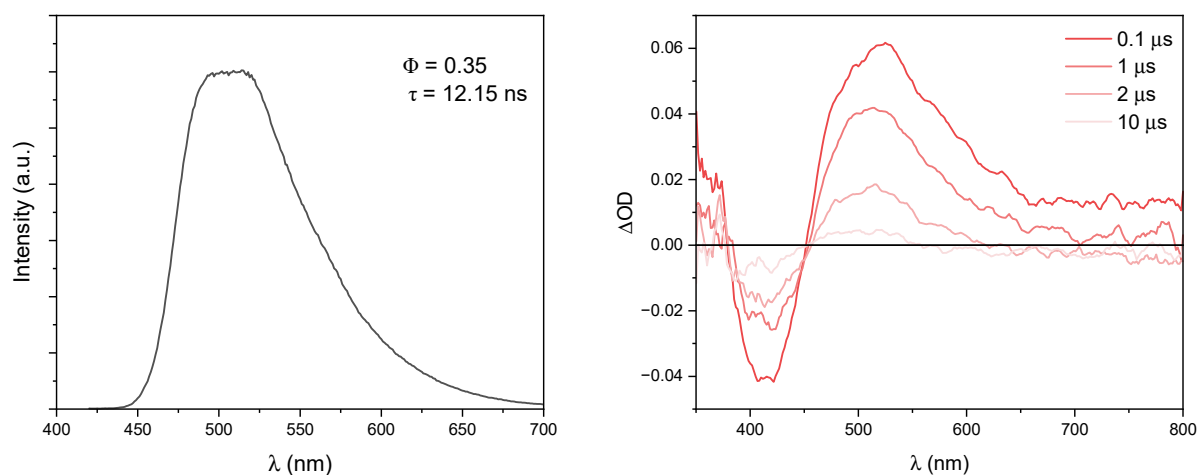


Figure S11. Fluorescence (**left**) and LFP (**right**) of $\text{Acr}^{+}\cdot\text{-1}$ in propylene carbonate. The trace at 10 μ s in LFP is ascribable to persistent neutral radical $\text{Acr}^{\cdot}\text{-1}$.

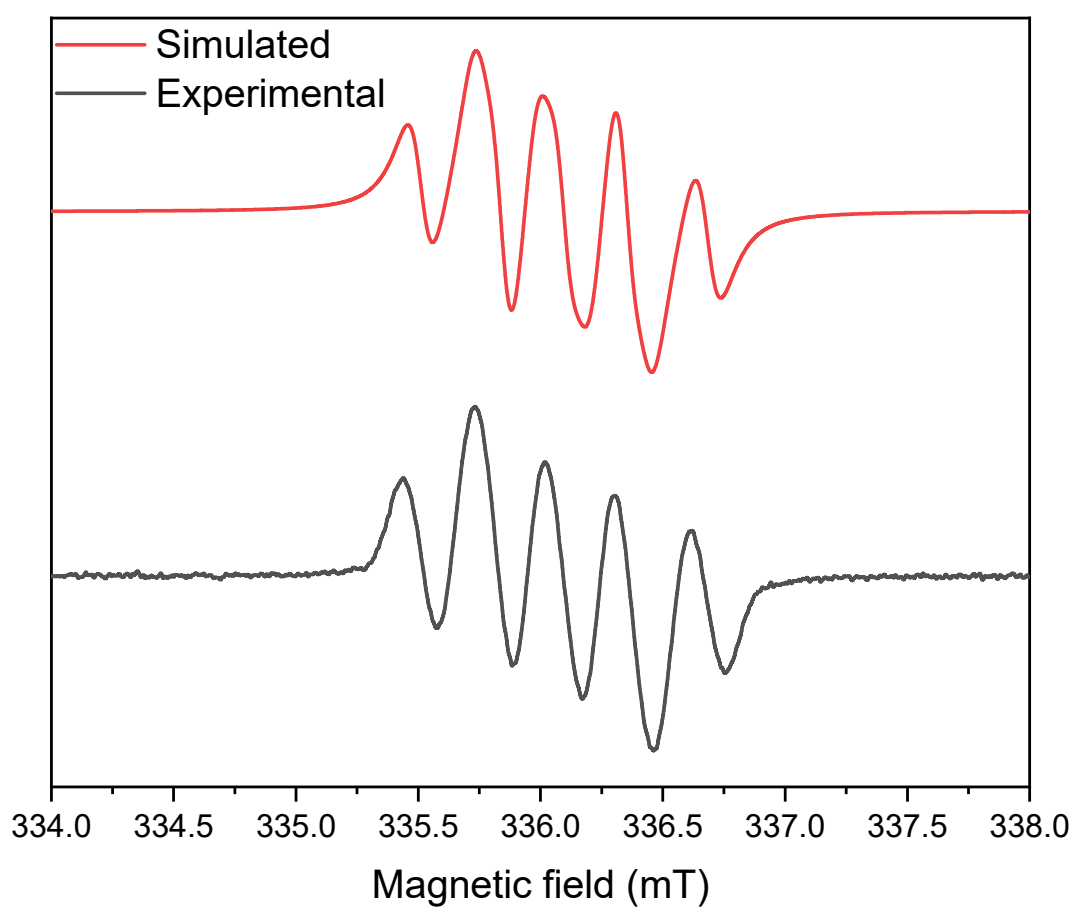


Figure S12. EPR of $\text{Acr}^{+}\cdot\text{-1}$ in propylene carbonate, upon irradiation with blue light.

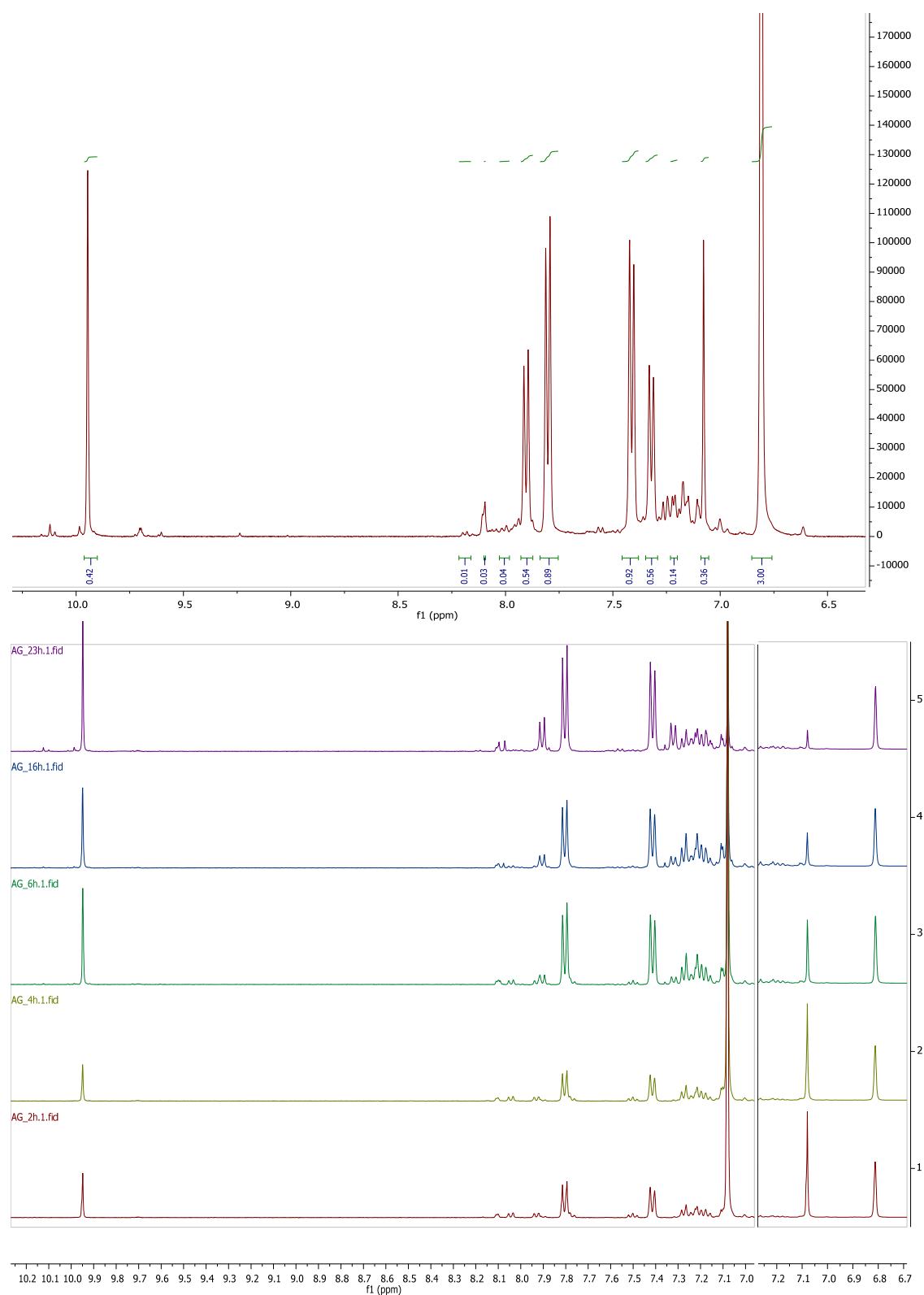


Figure S13. ^1H NMR spectrum of *p*-xylene oxidation reaction. ^1H NMR (400 MHz, CD_3CN) δ 6.8 (s, 3H, mesitylene standard), 7.1 (s, 4H, *p*-xylene), 7.2 (d, 2H, *p*-MBA), 7.3 (d, 2H, *p*-TA), 7.4 (d, 2H, *p*-TALD), 8.1 (s, 4H, TPA), 9.9 (s, 1H, *p*-TALD). Below is represented a kinetic analysis.

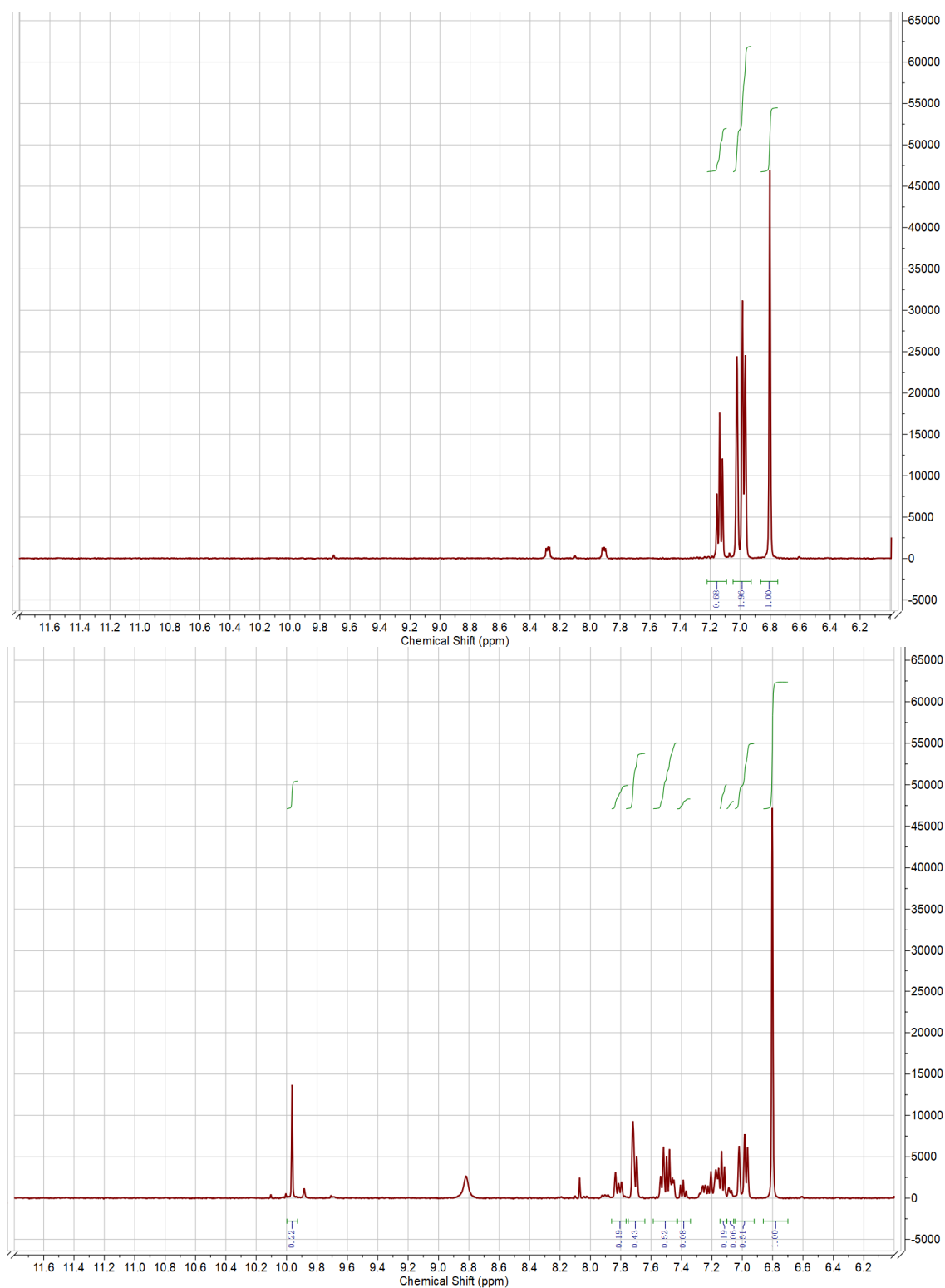


Figure S14. Oxidation of *m*-xylene. NMR analysis before (**top**) and after (**bottom**) 24 h irradiation. For sample preparation, 250 μL of the crude reaction solution was combined with 750 μL of mesitylene. Subsequently, 300 μL of the resulting mixture was transferred to an NMR tube containing 200 μL of CD_3CN . ^1H NMR (400 MHz) δ 6.80 (s, 3H, mesitylene standard), δ 6.96–7.15 (m, 4H, *m*-xylene), 9.95 (s, 1H, *m*-TALD).

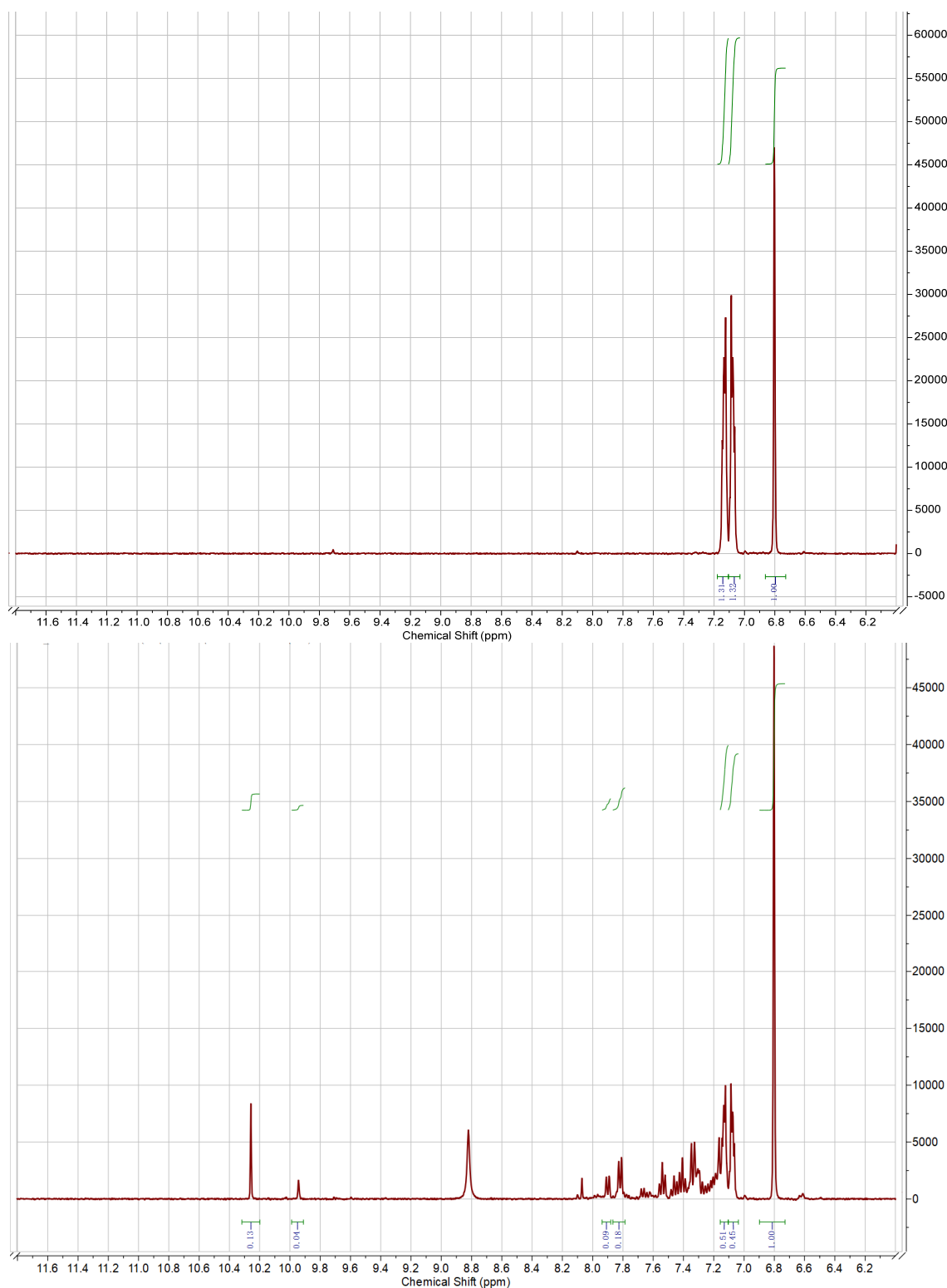


Figure S15. Oxidation of *o*-xylene. NMR analysis before (**top**) and after (**bottom**) 24 h irradiation. For sample preparation, 250 μ L of the crude reaction solution was combined with 750 μ L of mesitylene. Subsequently, 300 μ L of the resulting mixture was transferred to an NMR tube containing 200 μ L of CD₃CN. ¹H NMR (400 MHz) δ 6.80 (s, 3H, mesitylene standard), δ 7.06–7.14 (m, 4H, *o*-xylene), 10.25 (s, 1H, *o*-TALD).

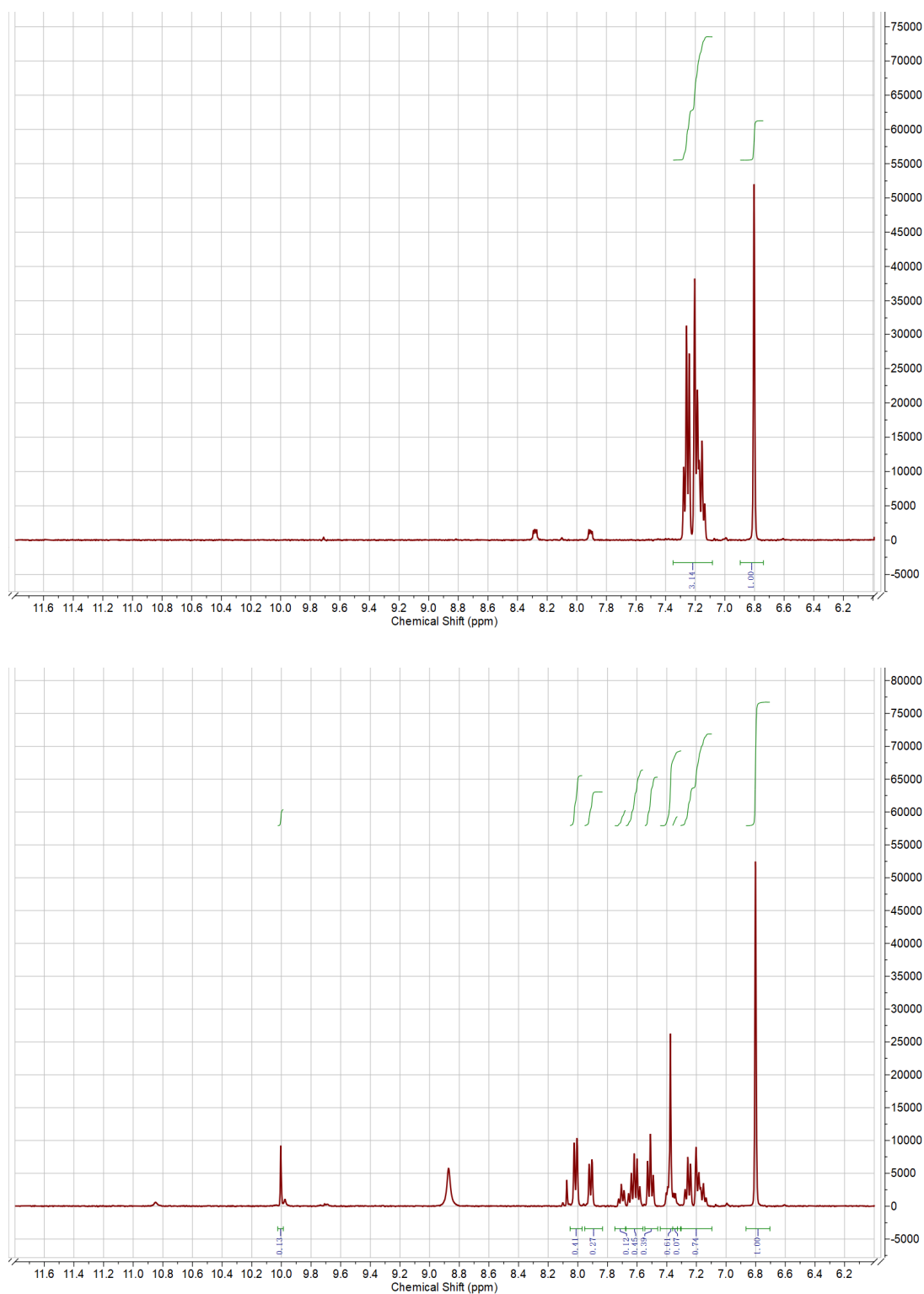


Figure S16. Oxidation of toluene. NMR analysis before (**top**) and after (**bottom**) 24 h irradiation. For sample preparation, 250 μ L of the crude reaction solution was combined with 750 μ L of mesitylene. Subsequently, 300 μ L of the resulting mixture was transferred to an NMR tube containing 200 μ L of CD_3CN . ^1H NMR (400 MHz) δ 6.80 (s, 3H, mesitylene standard), δ 7.13–7.27 (m, 5H, toluene), 10.00 (s, 1H, benzaldehyde).

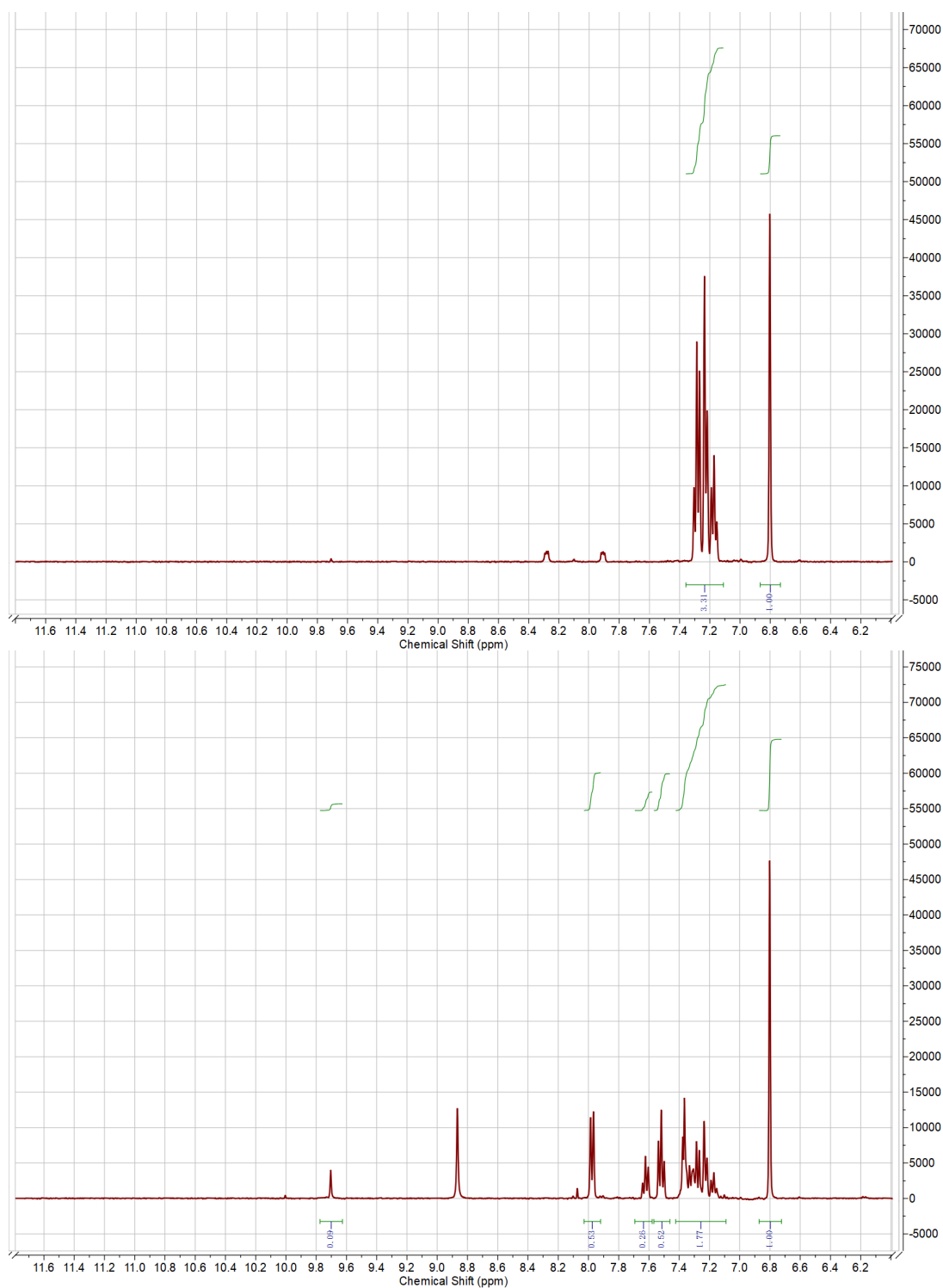


Figure S17. Oxidation of ethylbenzene. NMR analysis before (**top**) and after (**bottom**) 24 h irradiation. For sample preparation, 250 μL of the crude reaction solution was combined with 750 μL of mesitylene. Subsequently, 300 μL of the resulting mixture was transferred to an NMR tube containing 200 μL of CD_3CN . ^1H NMR (400 MHz) δ 6.80 (s, 3H, mesitylene standard), δ 7.14–7.30 (m, 5H, ethylbenzene), 9.70 (s, 1H, acetophenone).

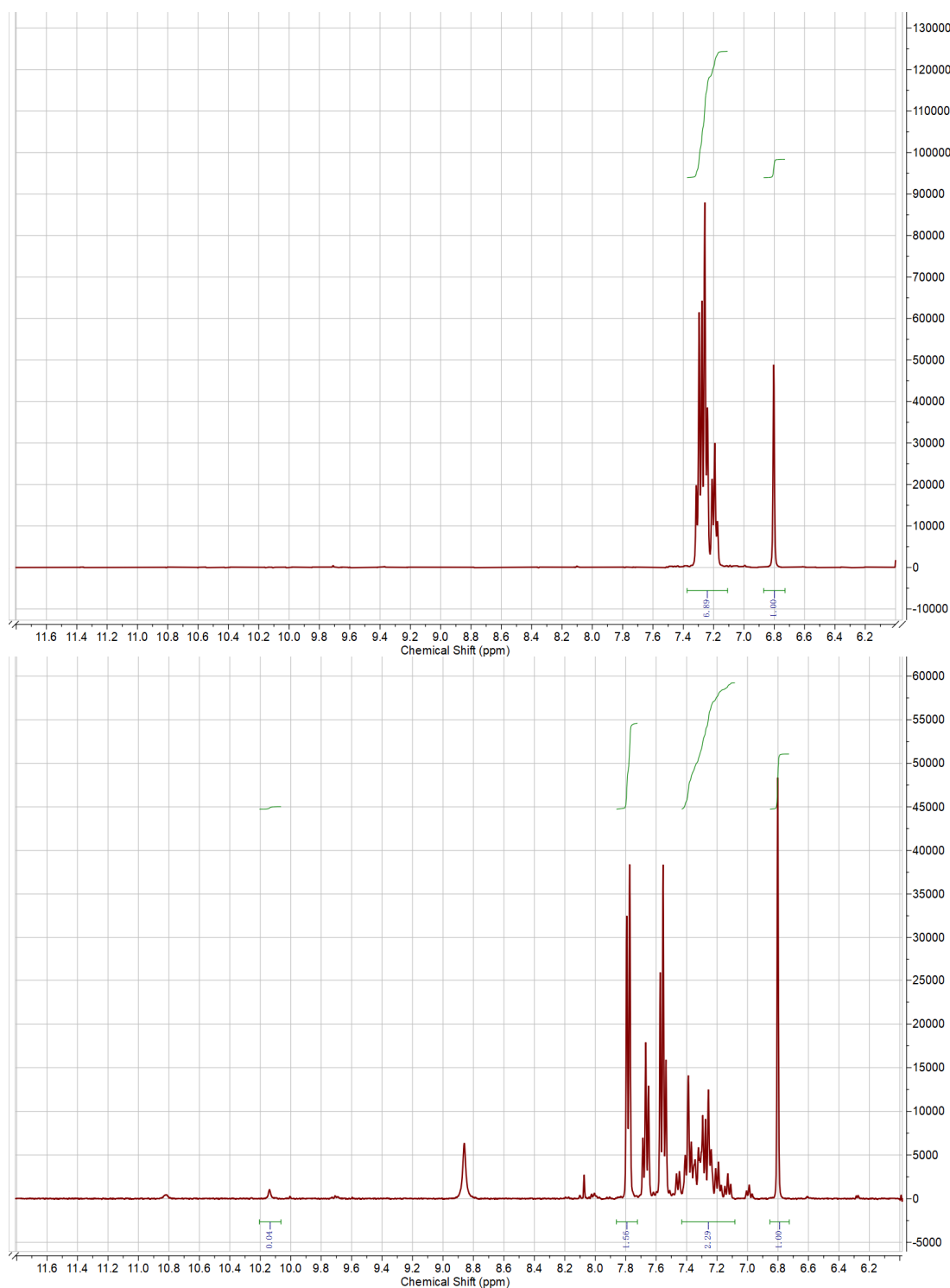
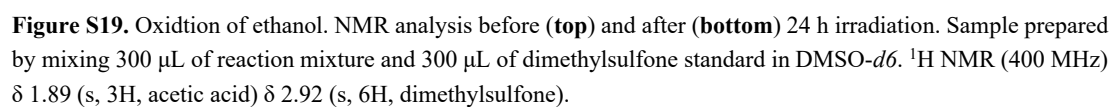


Figure S18. Oxidation of diphenylmethane. NMR analysis before (**top**) and after (**bottom**) 24 h irradiation. For sample preparation, 250 μ L of the crude reaction solution was combined with 750 μ L of mesitylene. Subsequently, 300 μ L of the resulting mixture was transferred to an NMR tube containing 200 μ L of CD_3CN . ^1H NMR (400 MHz) δ 6.80 (s, 3H, mesitylene standard), δ 7.17–7.31 (m, 10H, diphenylmethane), 7.78 (d, 4H, benzophenone).



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