Supporting Information

For

Photocatalytic Aerobic Oxidation of Benzylic Alcohols and Concomitant Hydrogen Peroxide Production

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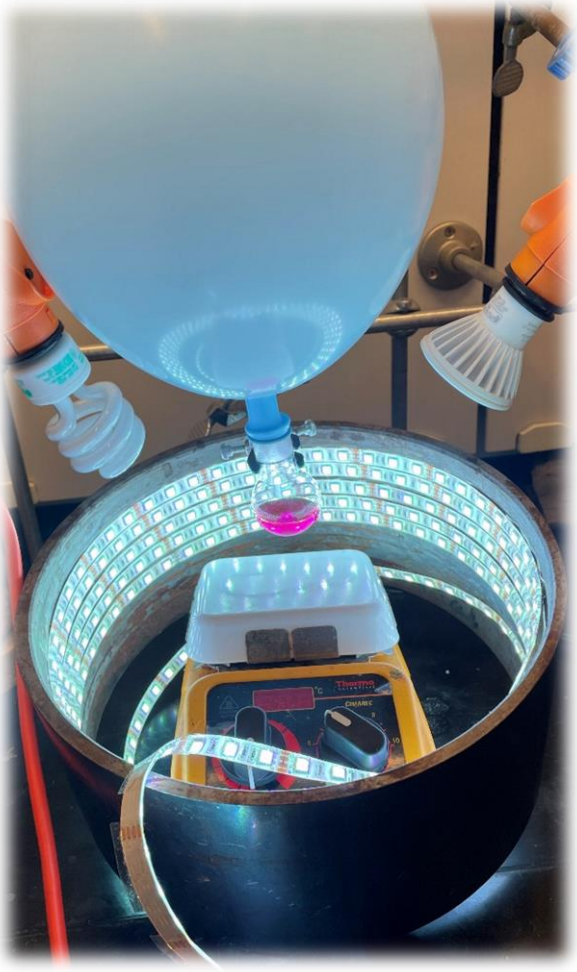
Experimental methodologies

All chemicals used in this study were purchased from Tokyo Chemical Industries (TCI).

Photochemical oxidation of benzyl alcohols

In a 10 mL round bottom flask equipped with a stir bar, benzhydrol (5 mmol) was dissolved in a 5 mL solution of Rose Bengal (1×10^{-4} M) in acetonitrile. Solid NHPI (0.25 mmol) was added to the solution. The flask was sealed with a balloon filled with oxygen gas. The contents of the flask were stirred (1500 rpm) while being irradiated with a ring of white LEDs (Solid Apollo 24 W 16 ft) at room temperature for 72 hours.



Extraction of hydrogen peroxide (H_2O_2)

The reaction mixture (5 mL) was mixed with toluene (5 mL) in a separatory funnel. The organic layer was extracted with water (5 mL).[1] The presence of H_2O_2 was confirmed in the aqueous layer using quantitative peroxide test-strips (MilliporeSigma™ MQuant™).

Quenching experiments

In a 10 mL round bottom flask equipped with a stir bar, benzhydrol (5 mmol) was dissolved in a 5 mL solution of Rose Bengal (1×10^{-4} M) in acetonitrile. Different quenching agents (5 mmol) and solid NHPI (0.25 mmol) were added to the solution for different experiments. The flask was sealed with a balloon filled with oxygen gas. The contents of the flask were stirred (1500 rpm) while being irradiated with a ring of white LEDs at room temperature for 72 hours.[2]

Quantification of products using ^{1}H NMR spectroscopy

500 µL of the reaction mixture was pipetted in a 5 mL round bottom flask and mixed with 500 µL of 1M ethylene carbonate (internal standard) in acetonitrile solution. The acetonitrile was evaporated on a rotary evaporator. The contents of the flask were redissolved in 500 µL of CD_3CN. ^{1}H NMR was performed using a 400 MHz Bruker (b400) spectrometer.

Determination of the presence of hydrogen peroxide using a Ti-porphyrin dye

A 5 M solution of $[TiO(TPyPH)_4]^{4+}$ was prepared by dissolving 34.03 mg of the dye in 1 L of 0.05 M hydrochloric acid. To 250 µL DI water, 250 µL 4.8 M perchloric acid and 250 µL $[TiO(TPyPH)_4]^{4+}$ dye solution was added. The solution was mixed and allowed to stand for 5 minutes at room temperature. This solution was further diluted with 2.5 mL of DI water. The absorbance of this solution was measured. The solution was mixed with a sample of H_2O_2 solution of known concentration, the aqueous extract of the reaction mixture, and a blank.[3] The absorption data for all the solutions were measured using a Shimadzu UV-3600 spectrometer.

Quantification of H_2O_2 by iodometric titration.

A 0.5 mL aliquot of a benzhydrol oxidation reaction at 48 h was extracted using 5 mL of H_2O. 1.2 mmol of potassium iodide and 1 mL of 1 M HCl was added to the aqueous solution. A second solution containing 0.1 M of $Na_2S_2O_3$ in water was titrated into the first solution that was a brown/black color. When the reaction began to lighten 5 drops of a 1 N starch solution was added. The titration continued until reaction became clear yellow. Analysis done in triplicate yielded 9% hydrogen peroxide after 48 hr.

Generation of singlet oxygen without light.[4]

Benzhydrol, 0.93 g (5.0 mmol) was added to 5 ml of acetonitrile and heated to 40 ^{0}C. *N*-hydroxyphthalimide, 0.042 g (0.5 mmol), and Li_2MoO_4, 0.87 g (5 mmol) was added to the solution. The reaction flask was covered using aluminum foil. 2.5 ml (22 mmol) hydrogen peroxide 30% by weight was added in 0.5 ml increments over the course of 5 hours and was stirred for 24 hours. By ^{1}H NMR, 50% conversion to benzophenone was observed after 24 hours of reaction time. The same reaction conditions with no NHPI showed no oxidized products by NMR after 24 hours.

Computational methodologies

All computational modeling was done using Gaussian 09 quantum chemistry package and were run on a HPC cluster.[5] The optimization calculations were done using M06-2X functional and 6-311+G(d) basis sets in PCM acetonitrile solvation model.[6] Normal mode frequency calculations were done on the optimized structures to confirm the convergence to a true stationary point with no imaginary frequencies. Gibbs energy change of the reactions were calculated using Hess' law of constant heat summation.

^{1}H NMR Spectrum for aerobic oxidation of secondary benzylic alcohol

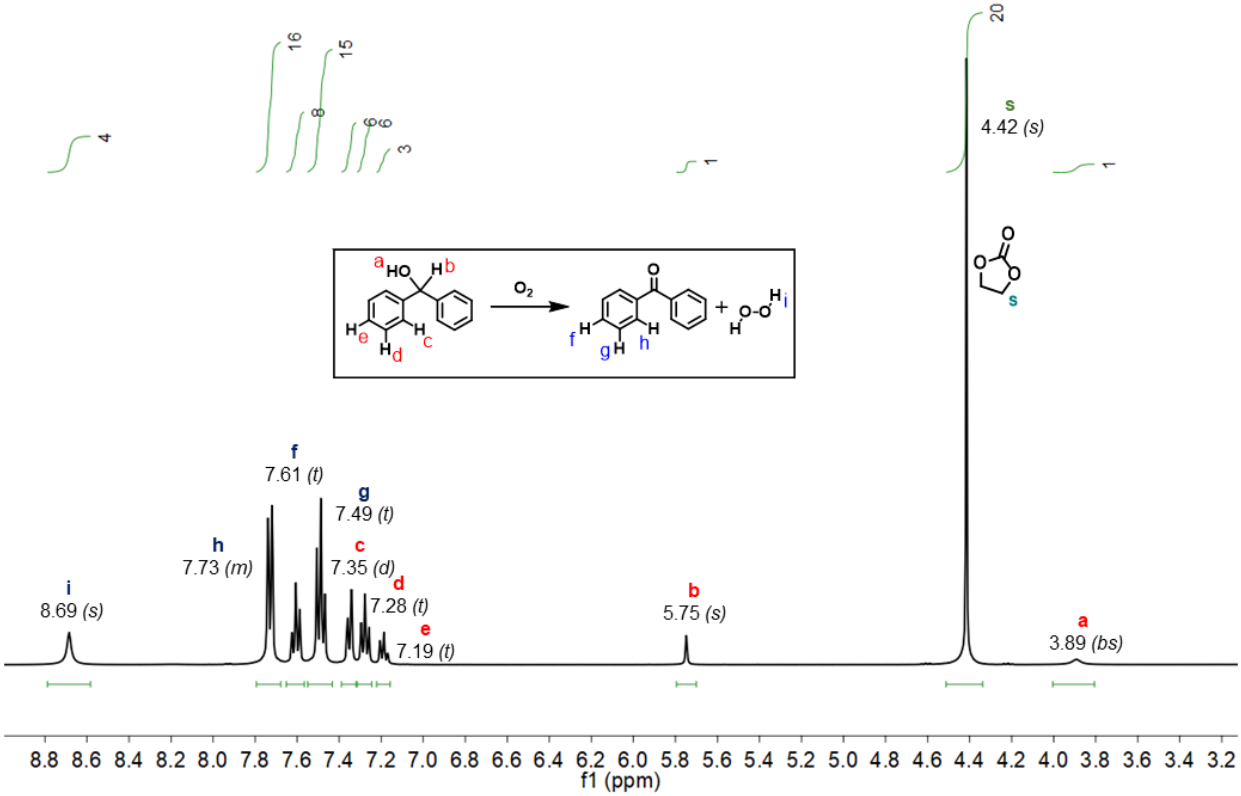


Figure S1. A ^{1}H NMR spectrum acquired in CD_3CN using 400 MHz spectrometer for the reaction mixture of the photochemical aerobic oxidation of benzhydrol in presence of an internal standard (ethylene carbonate, **s**) after 3 days of irradiation time. The peaks indicated using red correspond to the starting material whereas the peaks indicated in blue are for the oxidation products: benzophenone and H_2O_2.

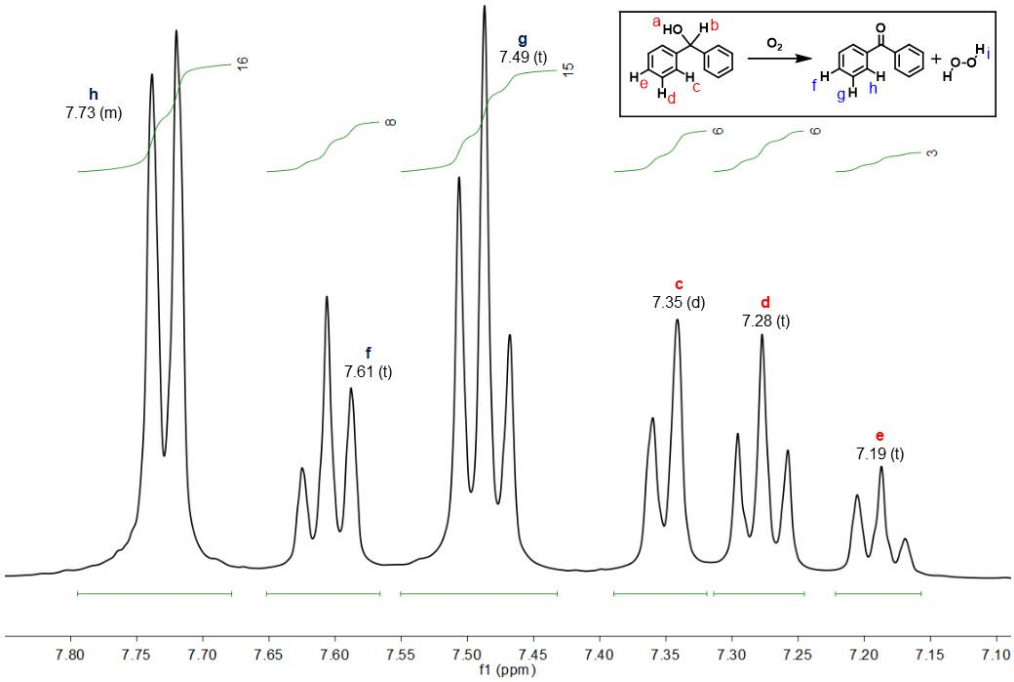


Figure S2. The enlarged image of the aromatic region of previously shown ^{1}H NMR spectrum of the benzhydrol oxidation reaction. The peaks marked as c, d, and e (shown in red) are the aromatic protons of benzhydrol whereas f, g, and h (shown in blue) correspond to the aromatic protons of benzophenone.

^{1}H NMR Spectrum for aerobic oxidation of primary benzylic alcohol

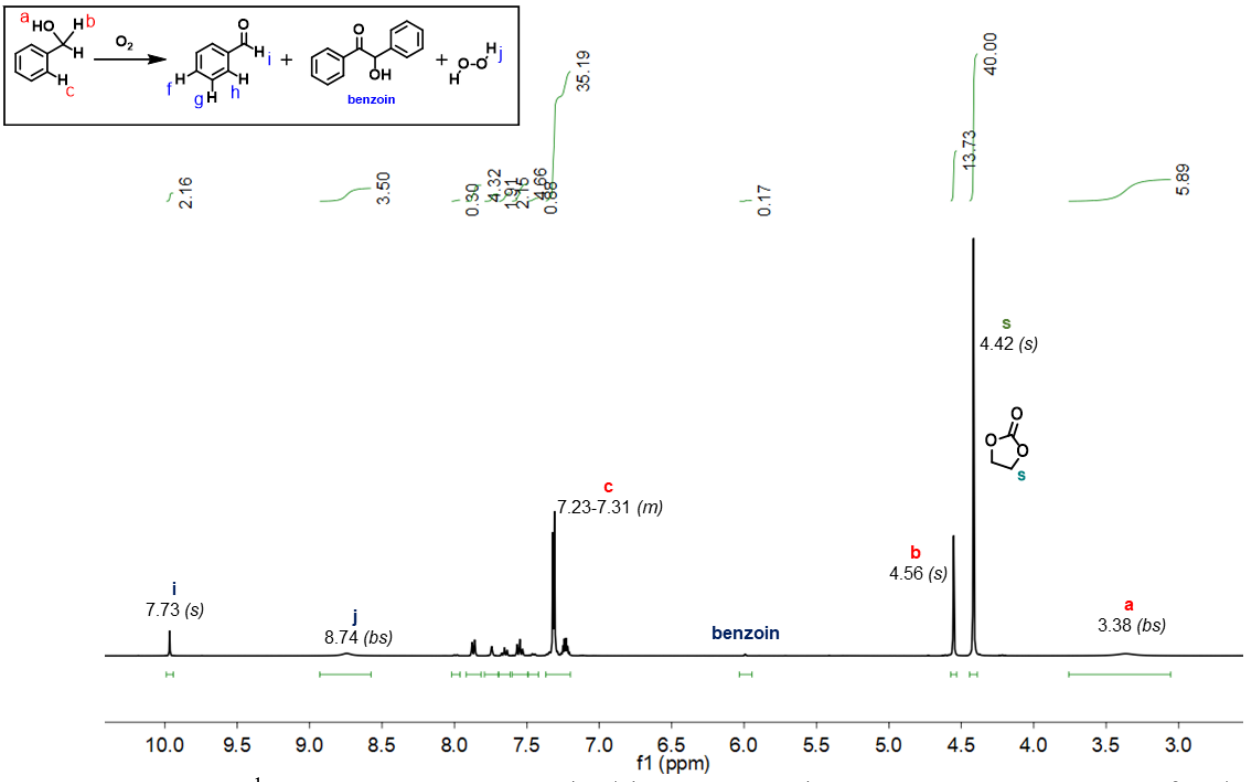


Figure S3. A^{1}H NMR spectrum acquired in CD_3CN using 400 MHz spectrometer for the reaction mixture of the photochemical aerobic oxidation of benzyl alcohol in presence of an internal standard (ethylene carbonate, **s**) after 3 days of irradiation time. The peaks indicated using red correspond to the starting material whereas the peaks indicated in blue are for the oxidation products: benzaldehyde, H_2O_2, and benzoin.

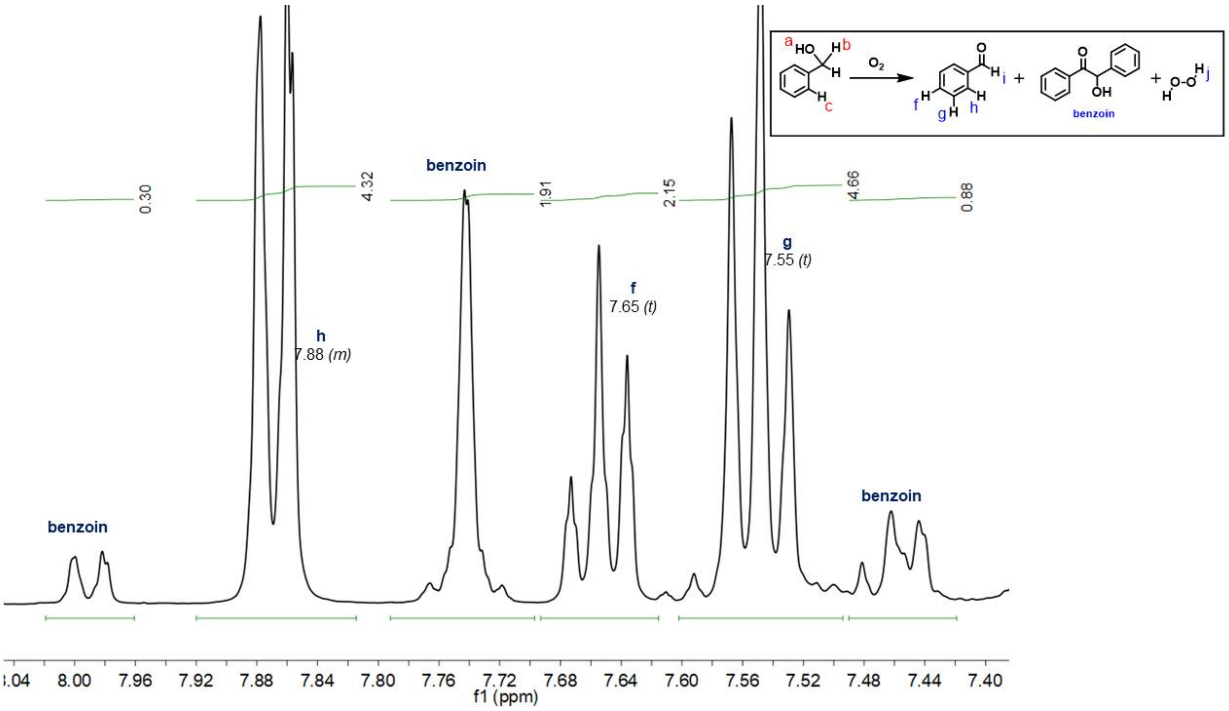


Figure S4. The enlarged image of the aromatic region of previously shown ^{1}H NMR spectrum of the benzyl alcohol oxidation reaction. The peaks marked as f, g, and h (shown in blue) correspond to the aromatic protons of benzaldehyde and the other peaks in correspond to the condensation product, benzoin.

Table S1. Yield of conversion for various alcohols. Reactions were run with 5 mmol alcohol NHPI (5 mol%) catalyst and Rose Bengal, (RB) (1×10^{-4}) in 5 mL acetonitrile (ACN) under white light irradiation at room temperature for 72 hours

Starting material	***72 h Yield***
(E)- Cinnamyl alcohol	5%
(±)-Phenylethyl alcohol	8%
Diphenylmethanol	39%
Phenylmethanol	29%

UV Vis absorption of the Ti-porphyrin dye in presence and absence of hydrogen peroxide

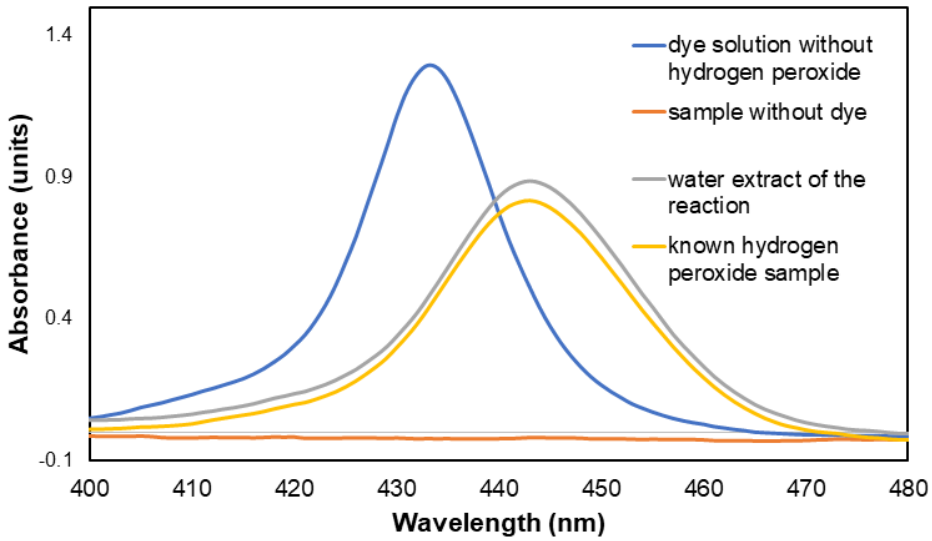


Figure S5. The UV-Vis spectrum of the Ti-porphyrin dye (blue) shows a characteristic absorption band at 432 nm. The characteristic peak is missing in absence of the dye (orange). The water extract of the reaction mixture (grey), and a hydrogen peroxide solution of known concentration (yellow) shows a shift in the absorption peak to 445 nm.[3]

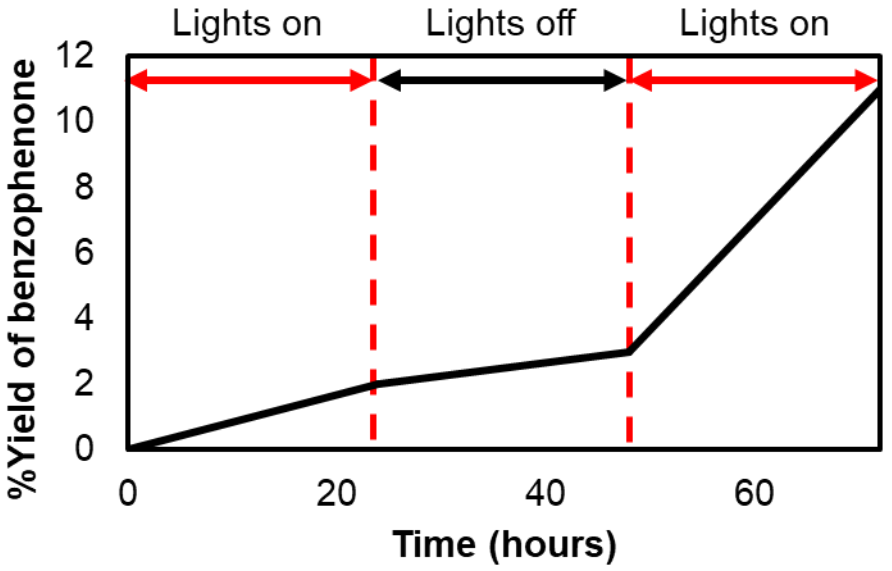


Figure S6. Yield of benzophenone with 1 day of irradiation, followed by 1 day in the dark, and 1 day irradiated. The yields were determined by ^{1}H NMR, reaction contained diphenylmethanol (**1,** 5 mmol), NHPI (5 mol%) Rose Bengal, (1×10^{-4} M) in 5 mL acetonitrile (ACN) under white light irradiation at room temperature.

^{1}H NMR of the secondary alcohol oxidation with respect to time

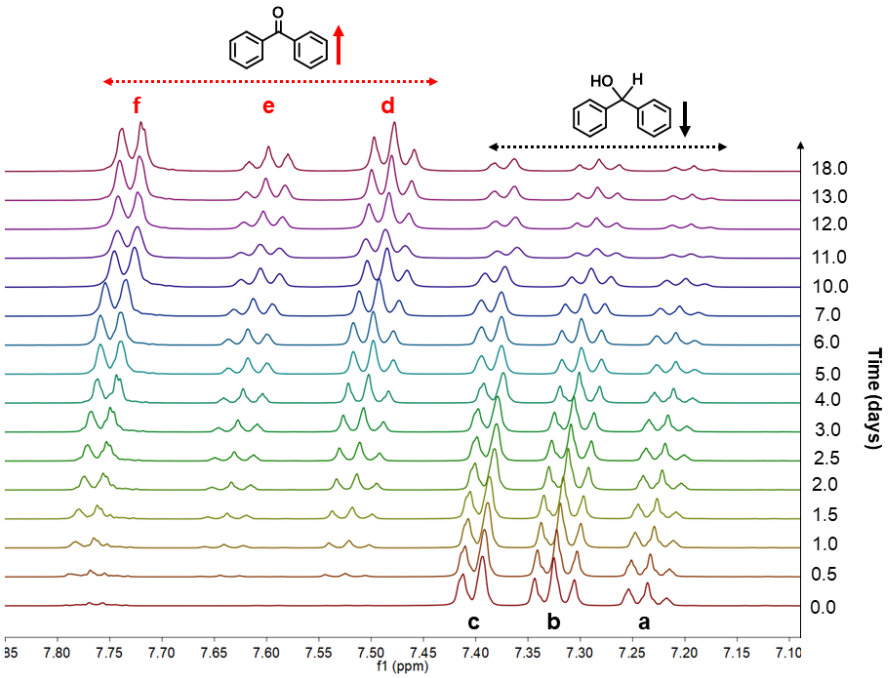
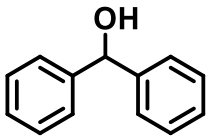


Figure S7. The ^{1}H NMR plot of the aromatic region of the benzhydrol oxidation reaction mixture taken in CD_3CN before irradiation with white light (t = 0 days) through 18 days of irradiation. The peaks a, b, and c (indicated in black) correspond to the starting material and d, e, and f (indicated in red) correspond to the product. The intensities of the peaks a, b, and c decreases over time whereas the intensity of the product peaks: d, e, and f are increasing with the progression of the reaction.

Cartesian coordinates

Benzhydrol (**1**)



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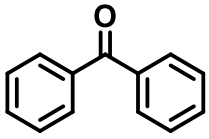
Benzophenone (**3**)



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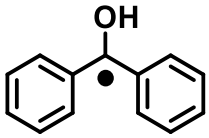
Intermediate 1 (**Int 1**)



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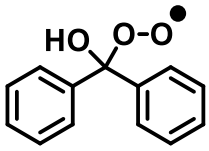
Intermediate 2 (**Int 2**)



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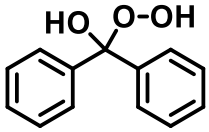

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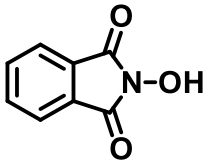
NHPI



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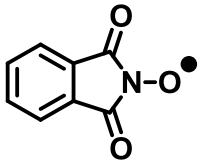
PINO



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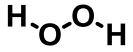
H_2O_2 (**2**)



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References

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