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Supporting Information

Selective Photooxidation Reactions using Water-Soluble Anthraquinone Photocatalysts

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1. Experimental details

1.1 Materials

Sodium anthraquinone-2-sulfonate (SAS, ≥98% by HPLC) and other chemicals with the highest commercial purity were purchased from Sigma-Aldrich or Merck and used as received.

1.2 photooxidation of alkanes and alcohols

The photooxidation reactions were performed by using a homemade light-setup (**Setup 1**, see Figure S10) at 30 ^{o}C under oxygen atmosphere (oxygen balloons). Unless mentioned otherwise, to a 4 mL glass vial 700 uL of MilliQ water (containing 1.0 mM of SAS) and 300 uL of organic substrates were added. The reaction mixture was exposed to visible light bulb (Philips 7748XHP 200W, white light bulb) and continuously stirred at 200 rpm. The distance between the light bulb and reaction vial is 4cm. At intervals, aliquots were taken, extracted/diluted by ethyl acetate (containing 5mM of dodecane or 1-octanol as internal standards), dried over anhydrous $MgSO_4$ and analysed by GC (SHIMADZU) using commercial standard.

The H_2O_2 concentration is quantified by colorimetric assay as described in our previous report.[1] Briefly, 1 mL of mixture containing 100 mg L^{-1} of 4-aminoantipyrine, 100 mg L^{-1} of phenol in 20 mM phosphate buffer (pH 6.0) and peroxidase solution (100 µl, 2.5 U m L^{-1}) were added to the sample solution (100 µL) and the mixture was incubated for 20 min at 30 °C. The absorbance at 550 nm was recorded spectrophotometrically and [H_2O_2] was calculated based on a calibration curve.

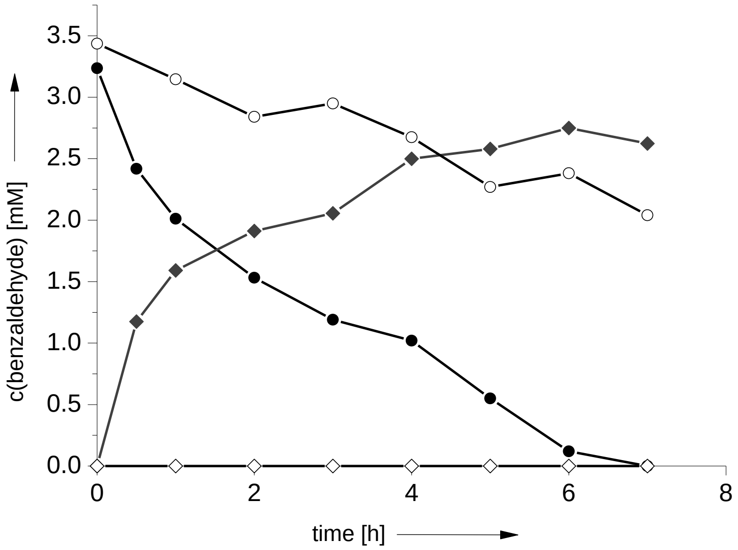


Figure S1. Monoaqueous phase oxidation of toluene (circle) to benzaldehyde (diamond). Conditions: approx. 3 mM of toluene (solid) and 0.1 mM of SAS (3 mol %) in 1.0 mL of water irradiated with visible light (white light bulb, 200W) at 30 °C and under oxygen protection. The control reaction (empty symbol) without SAS was included. The concentration of benzoic acid was only measured at the end of the reaction.

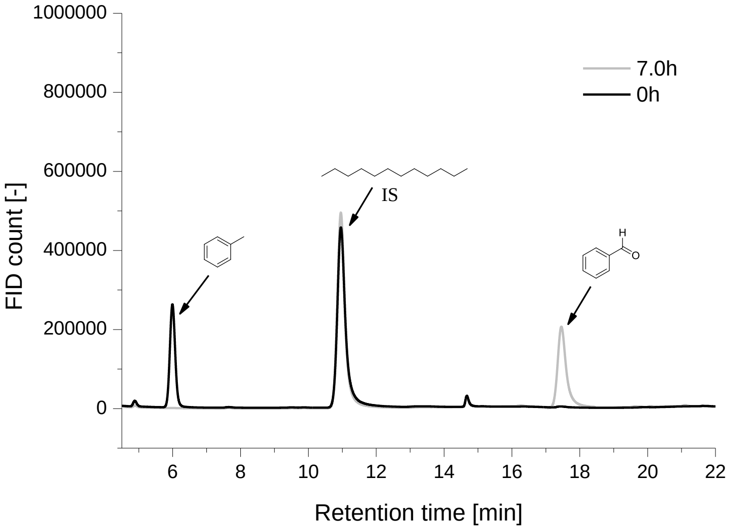


Figure S2. Representative gas chromatograms of the oxidation of toluene to benzaldehyde. Ethyl acetate containing 5 mM of dodecane as inner standard is used for the extraction and GC analysis.

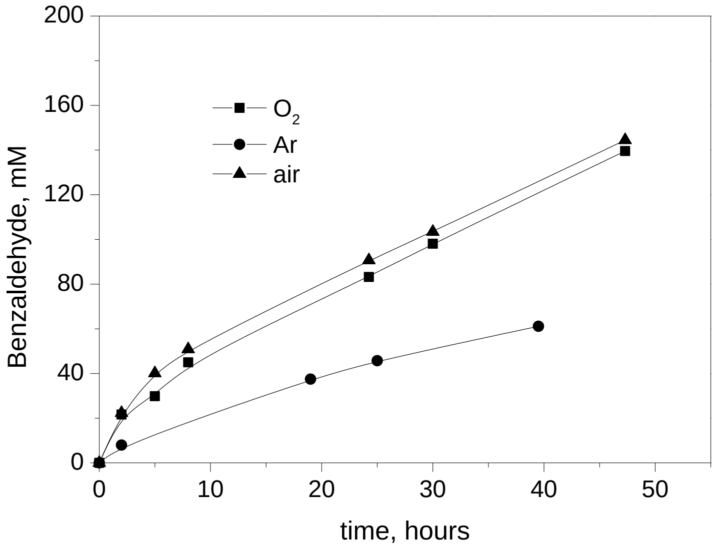


Figure S3. Photooxidation of toluene under different atmosphere.

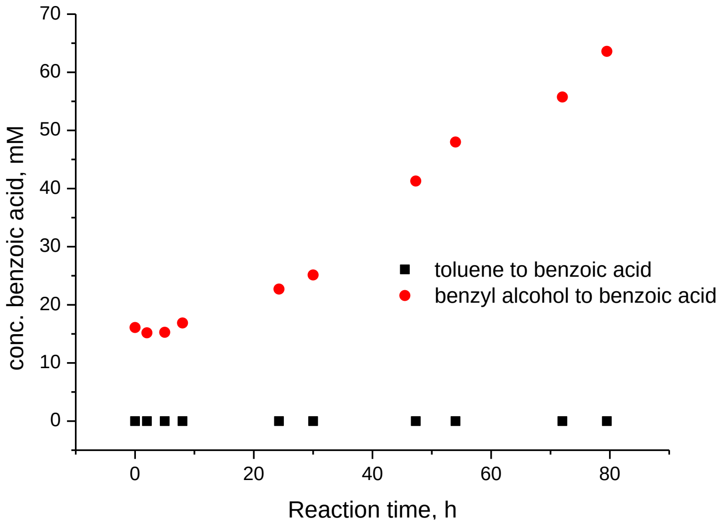


Figure S4. Formation of benzoic acid in the photooxidation of toluene and benzyl alcohol. Conditions: toluene/benzyl alcohol : water ($c(SAS)_{aq}$ = 1 mM)= 3:7, ambient atmosphere, T=30 °C, λ> 400 nm.

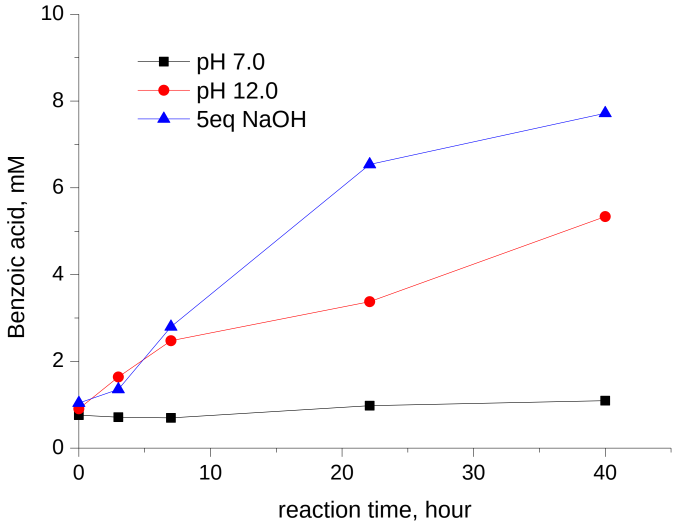


Figure S5. The formation of benzoic acid at different pH (pH 7 and 12, NaPi buffer, 100 mM) or Cannizzaro reaction, starting from the oxidation of benzyl alcohol (200 mM) and 1 mM of SAS in monophase reaction.

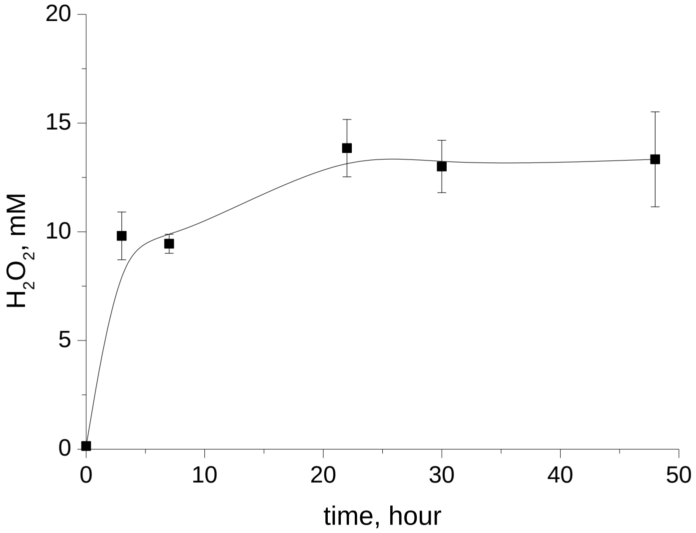


Figure S6. H_2O_2 concentration during the oxidation of toluene to benzaldehyde. Conditions: toluene : water (c(SAS)aq = 1 mM)= 3:7, ambient atmosphere, T=30 oC, hv > 400 nm.

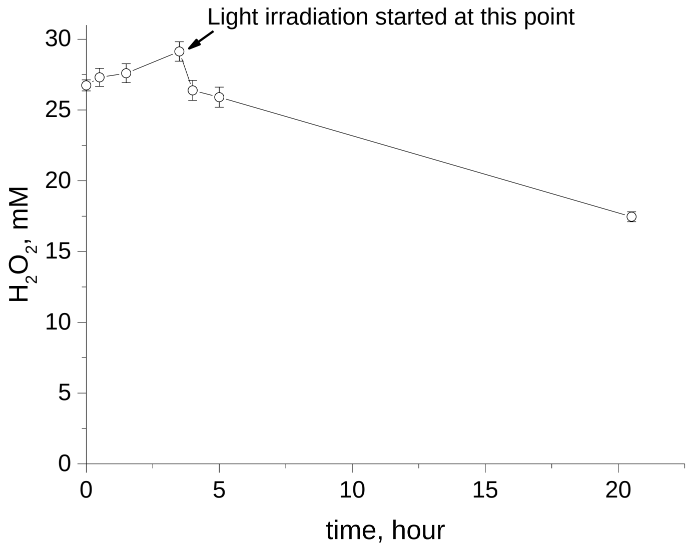


Figure S7. Influence of SAS on H_2O_2-decomposition under light irradiation, starting from approx. 25 mM of H_2O_2 and 1mM of SAS in solution.

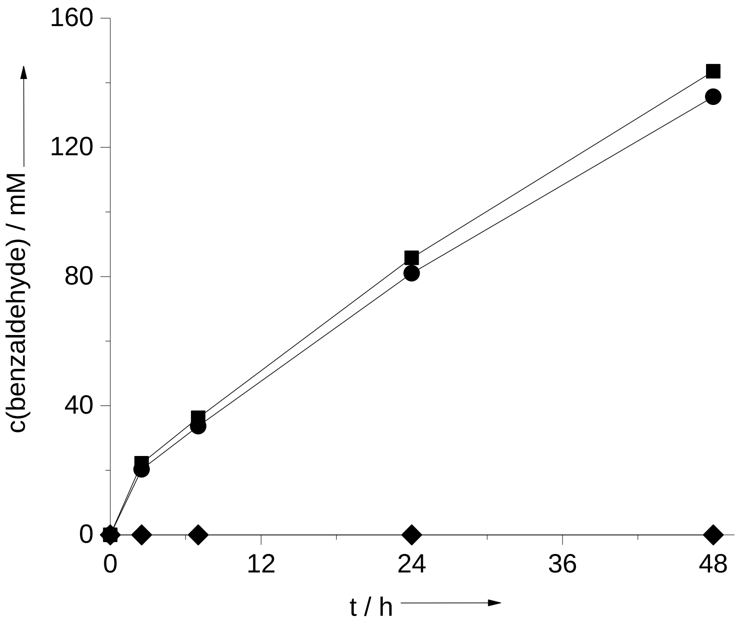


Figure S8. Control reactions excluding the role of H_2O_2: direct addition of H_2O_2 (100 mM) to aqueous phase in the dark (◆), direct addition of catalase (600 U) (●) or H_2O_2 (100 mM) (■) into aqueous phase and the reaction mixture was irradiated afterwards. Conditions: toluene : water (c(SAS)aq = 1 mM) = 3:7, ambient atmosphere, T = 30 °C, $\lambda > 400$ nm.

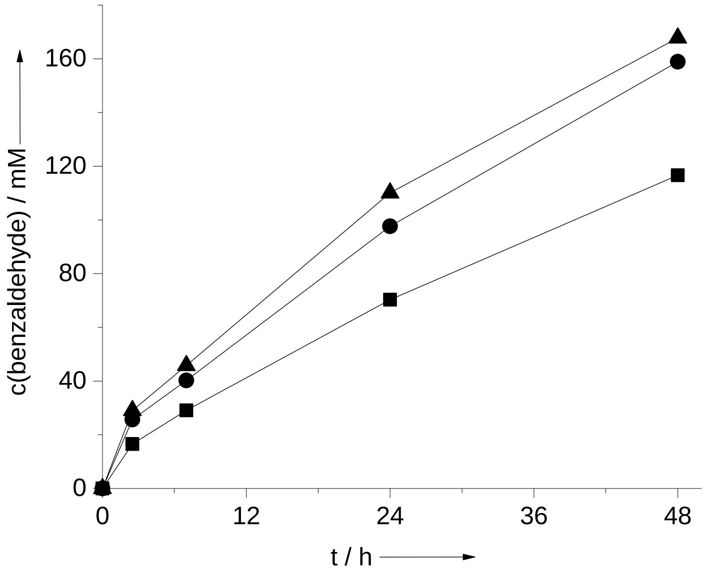


Figure S9. Influence of the light intensity on the rate of the photocatalytic oxidation of toluene. The light **setup 2** was used and light intensity was 118 (■), 341 (●), 613 (▲) W cm^{-2}. Conditions: toluene : water ($c(SAS)_{aq}$ = 1 mM) = 3:7, oxygen atmosphere, T = 30 °C, $\lambda > 400$ nm.

Figure S10. Images of the homemade light setup used in the experiments (**Setup 1**).

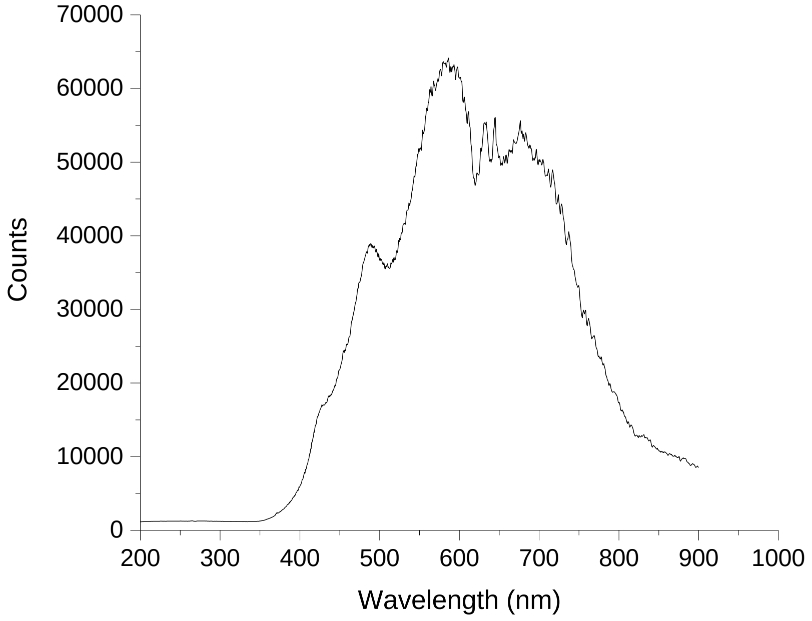


Figure S11. The light spectrum of the homemade light-setup (**Setup 1**) in intensity. The measurement was performed with a distance of 45 cm between the calibrated spectrophotometer and light bulb.

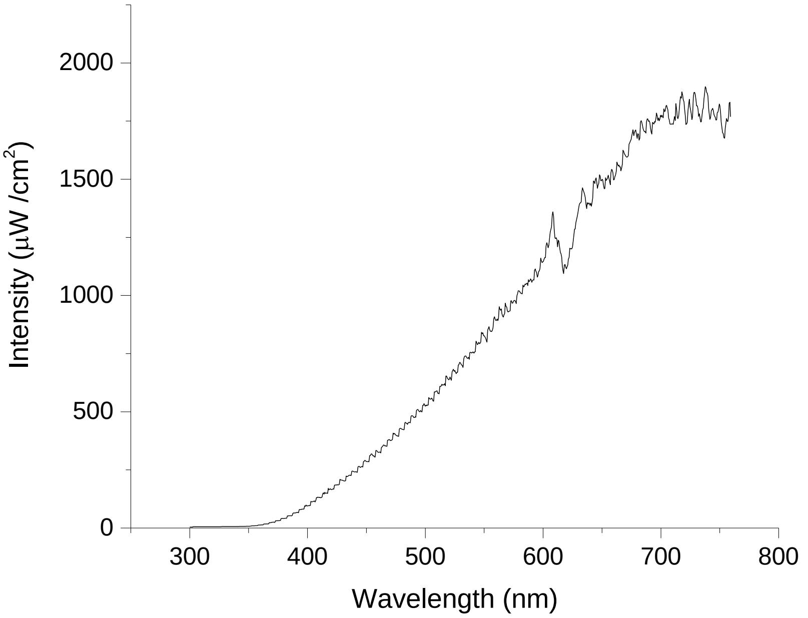


Figure S12. The light spectrum of the homemade light-setup (**Setup 1**) in intensity. The measurement was performed with a distance of 45 cm between the calibrated spectrophotometer and light bulb.

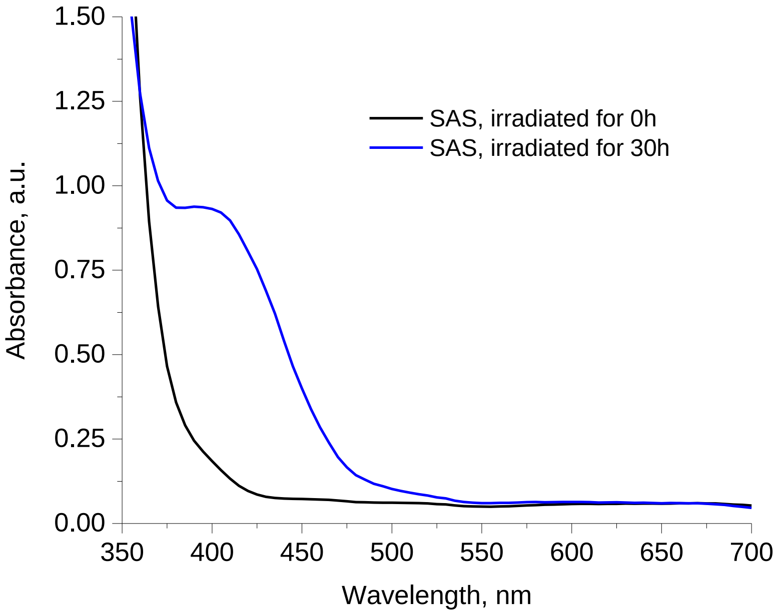


Figure S13. UV-Vis spectra of non-irradiated SAS and irradiated SAS in water for 30 h.

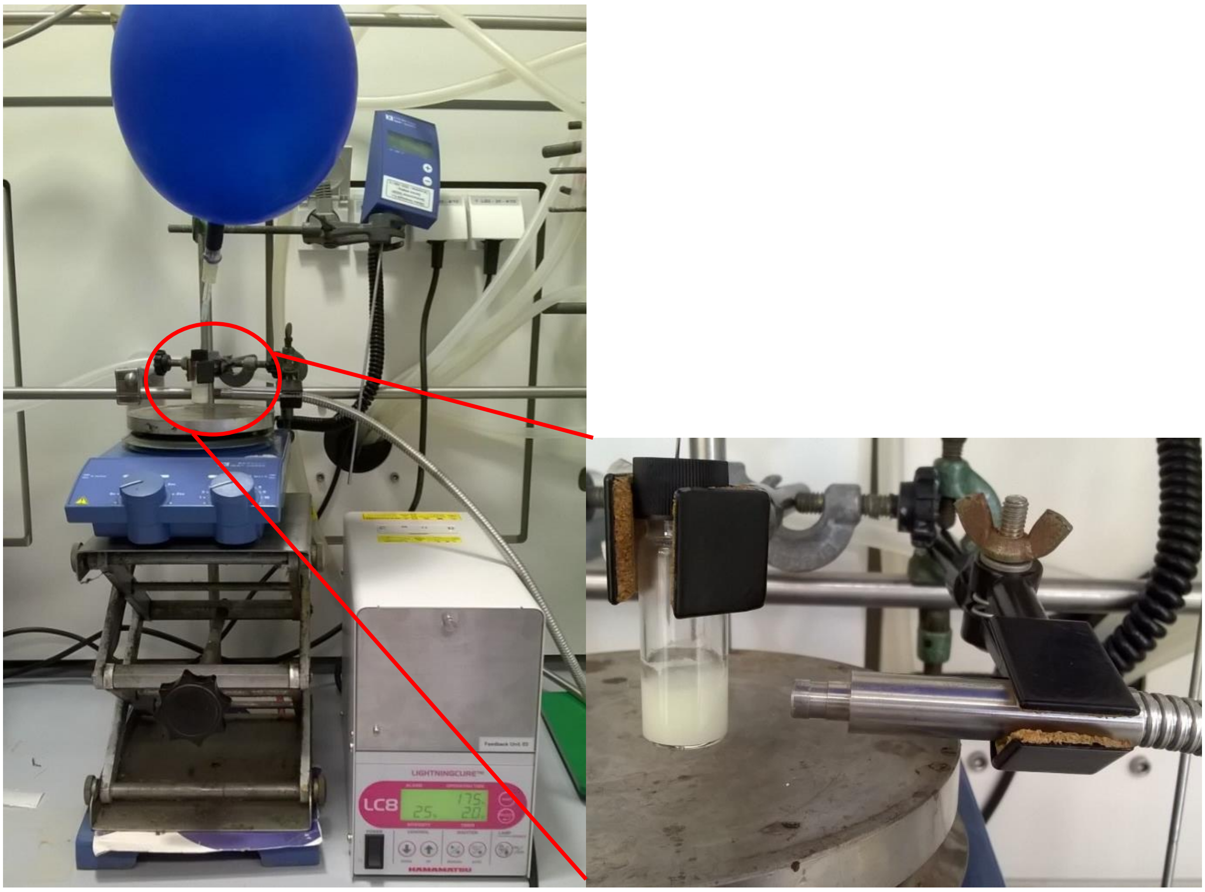


Figure S14. Images of the Hamamatsu light setup used in the experiments (**Setup 2**).

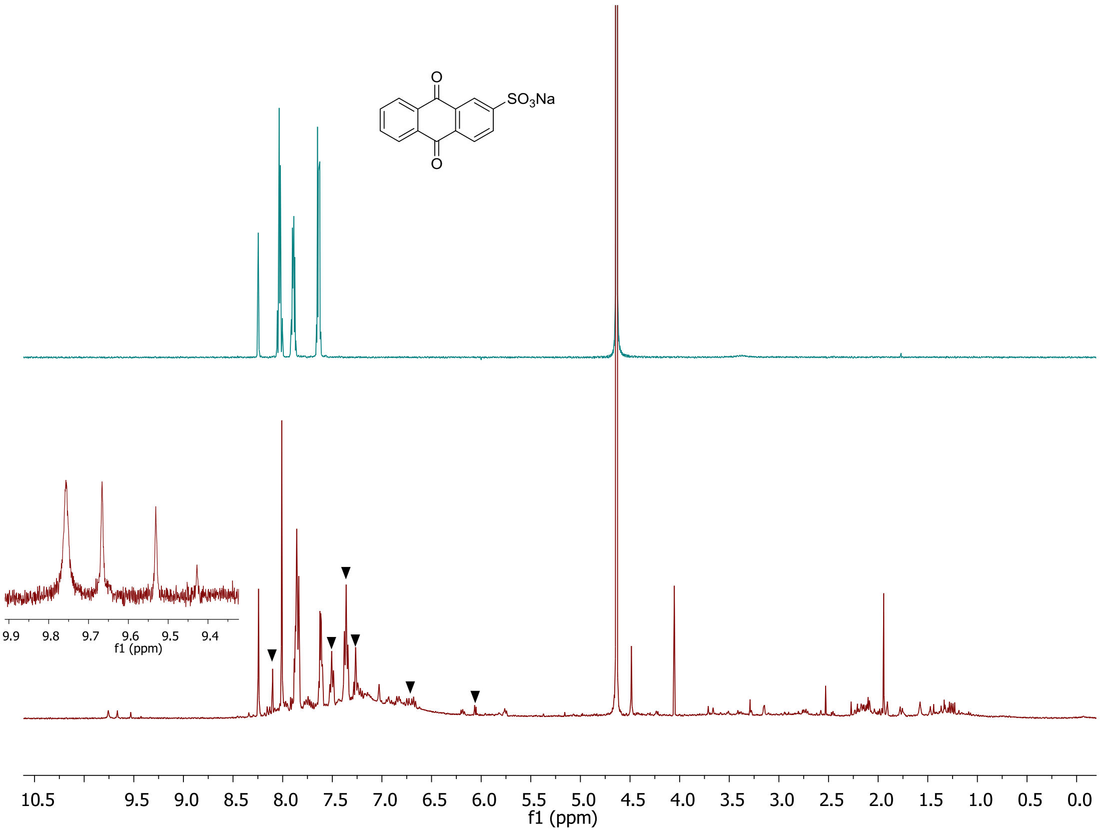


Figure S15. ^{1}H NMR spectra of SAS before (upper) and after irradiation (bottom) for 24h. D_2O was used as solvent. The proton signals marked with triangle are assigned to inactivated and/or reduced SAS. The emerging complicated spectrum of SAS after illumination is a strong indication that SAS was photodegraded, mostly via a complicated pathway.[2] The signals between 9.5-9.8 ppm can be attributed to the degraded products from –OH/–CHO/–COOH in arene.[3]

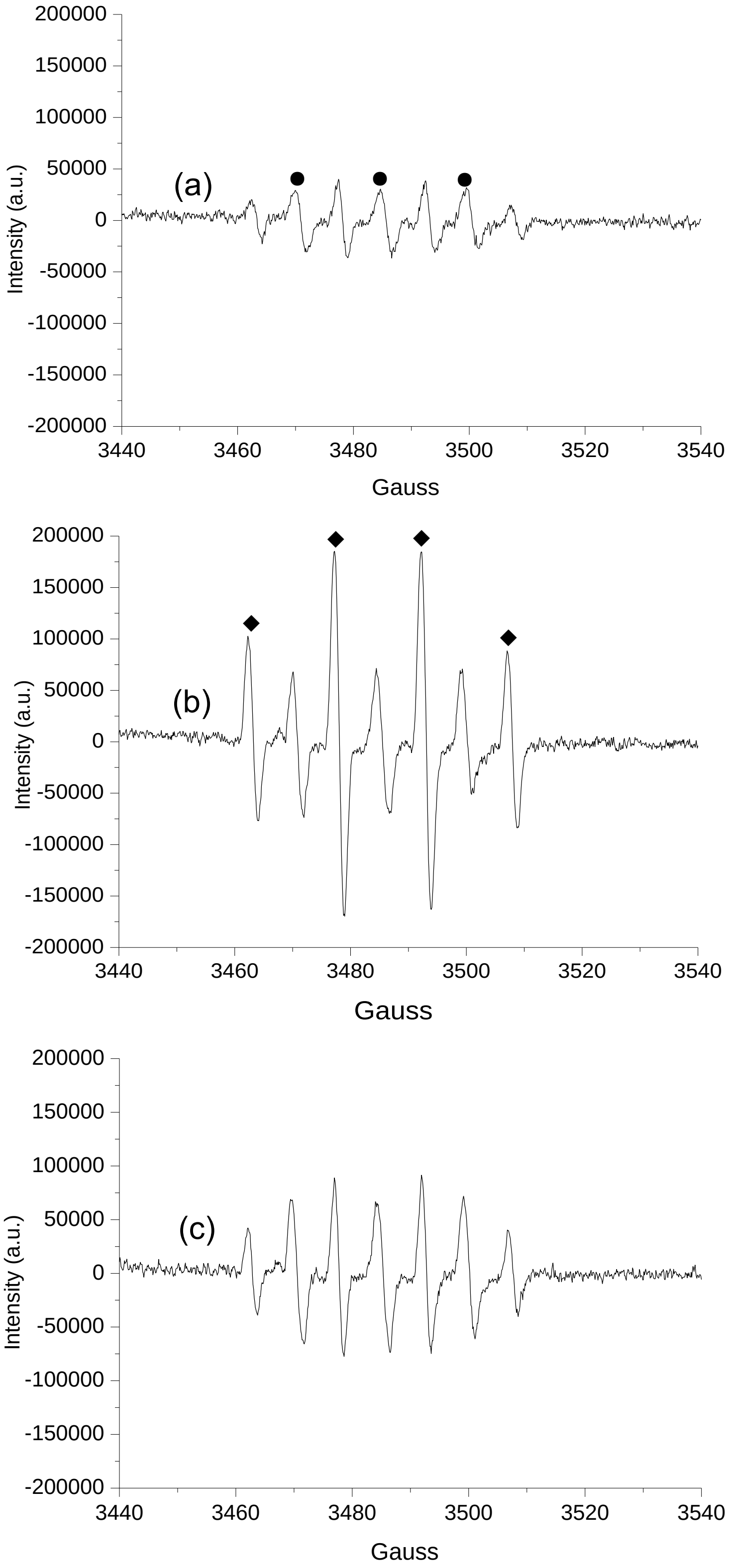


Figure S16. Electron paramagnetic resonance (EPR) spectra recorded during the illumination of SAS and benzyl alcohol for 0 min (a), 10 min (b) and SAS and toluene for 10 min (c). Signals marked with solid circles belong to the oxidation product of DMPO, 5,5-dimethyl-2-oxopyrroline-1-oxyl (DMPOX);[4] Signals marked with solid diamonds belong to the spin-adduct •DMPO-OH (a_H = 1.49, g = 2.0043).[5] Reaction condition: c(SAS) = 0.5 mM, c(DMPO) = 30 mM, c(substrate) = 5 mM, RT, hν > 400 nm. DMPO = 5,5-Dimethyl-1-pyrroline N-oxide.

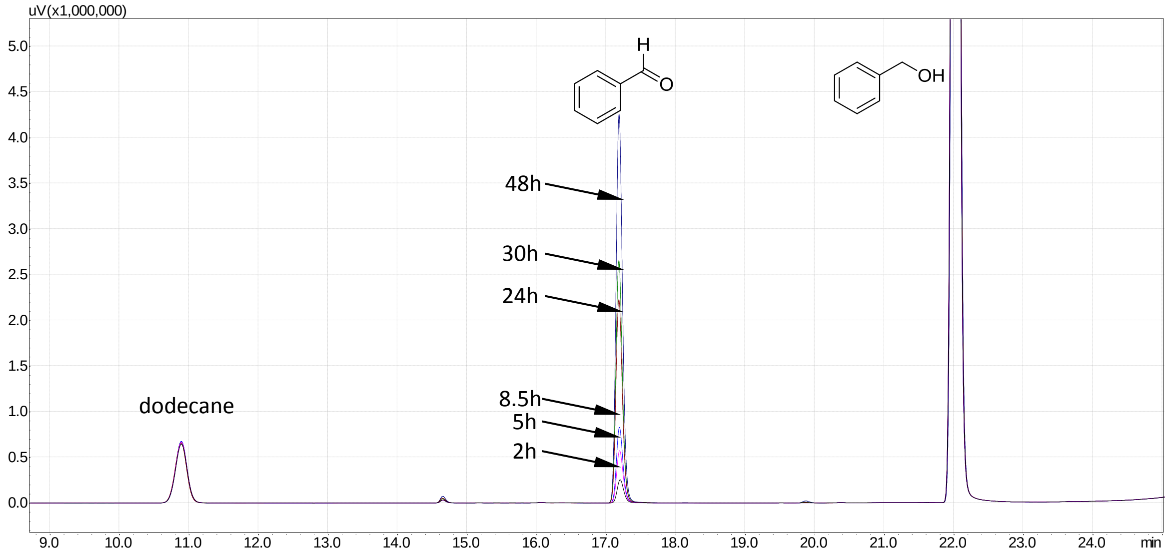


Figure S17. Representative GC chromatogram of the SAS-catalysed oxidation of benzyl alcohol. Samples were diluted by 40 times with ethyl acetate.

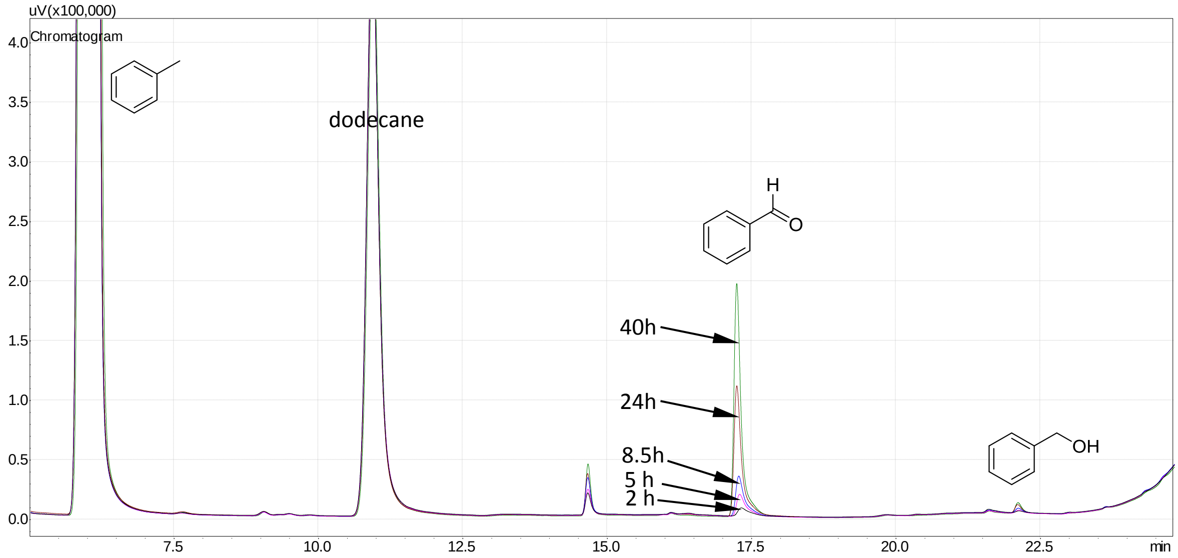


Figure S18. Representative GC chromatogram of the SAS-catalysed oxidation of toluene. Samples were diluted by 40 times with ethyl acetate.

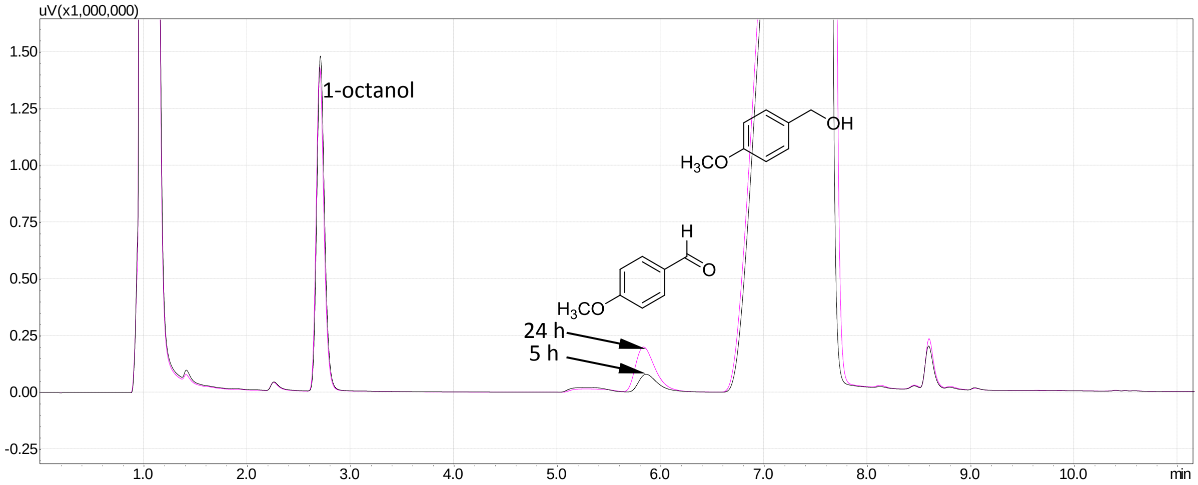


Figure S19. Representative GC chromatogram of the SAS-catalysed oxidation of *p*-Anisyl alcohol. Samples were diluted by 40 times with ethyl acetate.

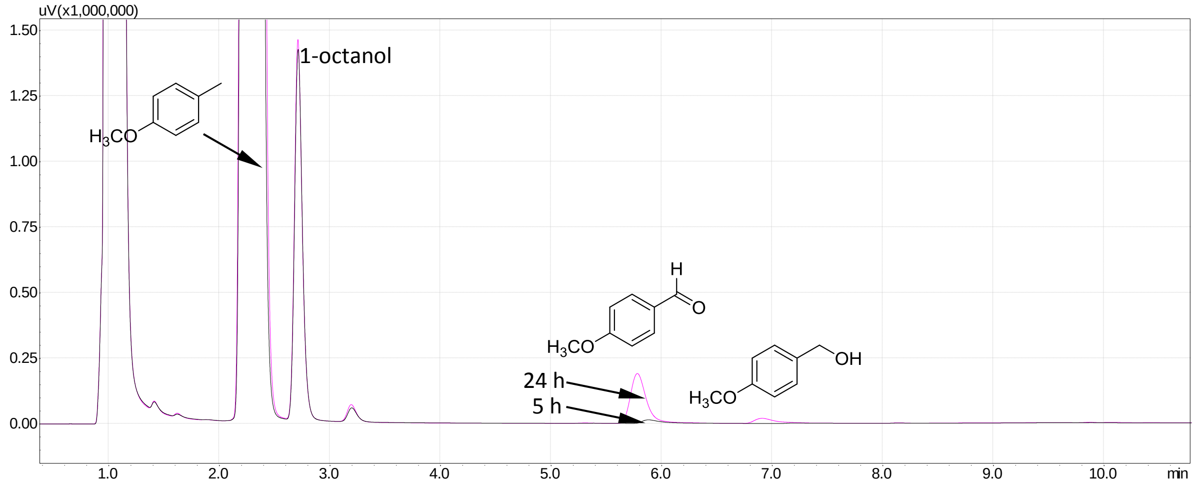


Figure S20. Representative GC chromatogram of the SAS-catalysed oxidation of *1-methoxy-4-methylbenzene*. Samples were diluted by 40 times with ethyl acetate.

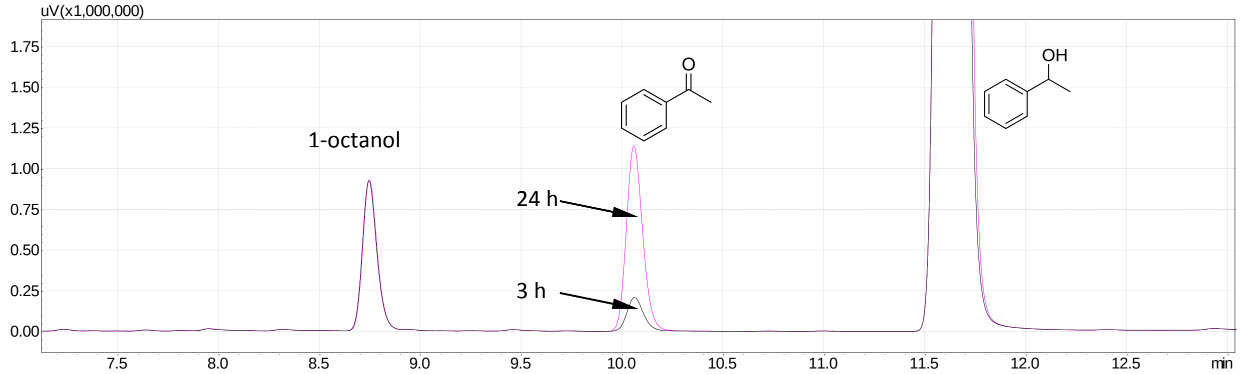


Figure S21. Representative GC chromatogram of the SAS-catalysed oxidation of 1-phenyl ethanol. Samples were diluted by 40 times with ethyl acetate.

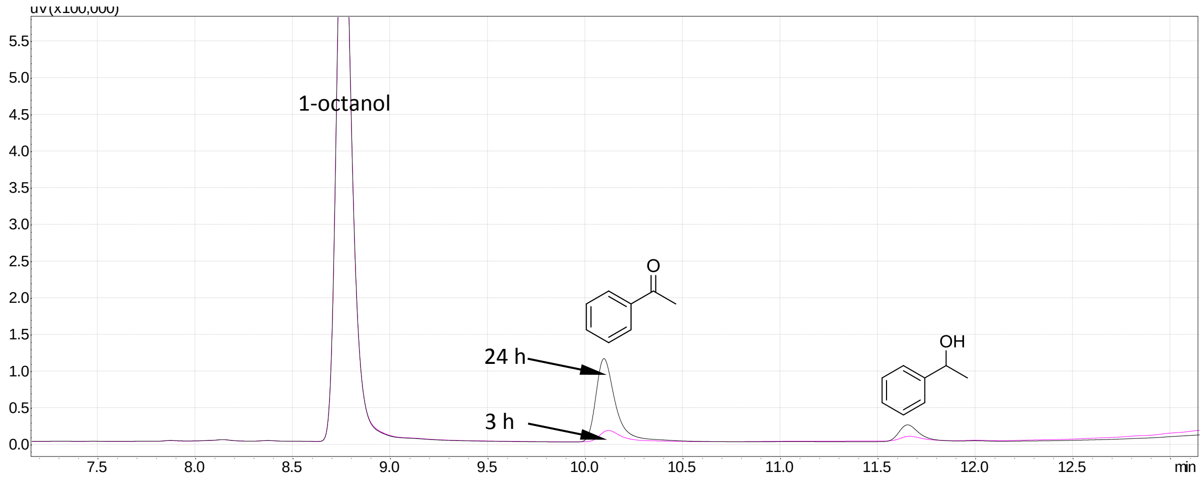


Figure S22. Representative GC chromatogram of the SAS-catalysed oxidation of ethyl benzene. Samples were diluted by 40 times with ethyl acetate.

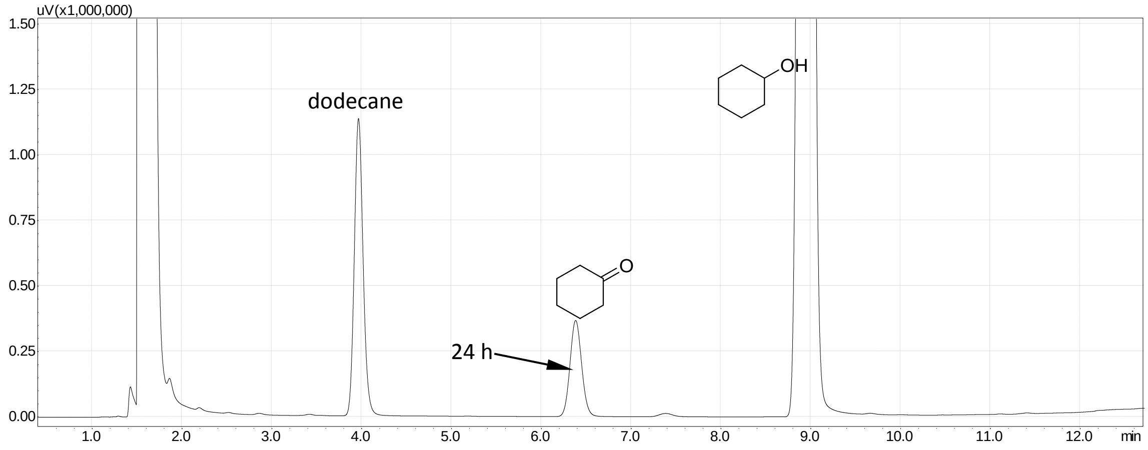


Figure S23. Representative GC chromatogram of the SAS-catalysed oxidation of cyclohexanol. Samples were diluted by 40 times with ethyl acetate.

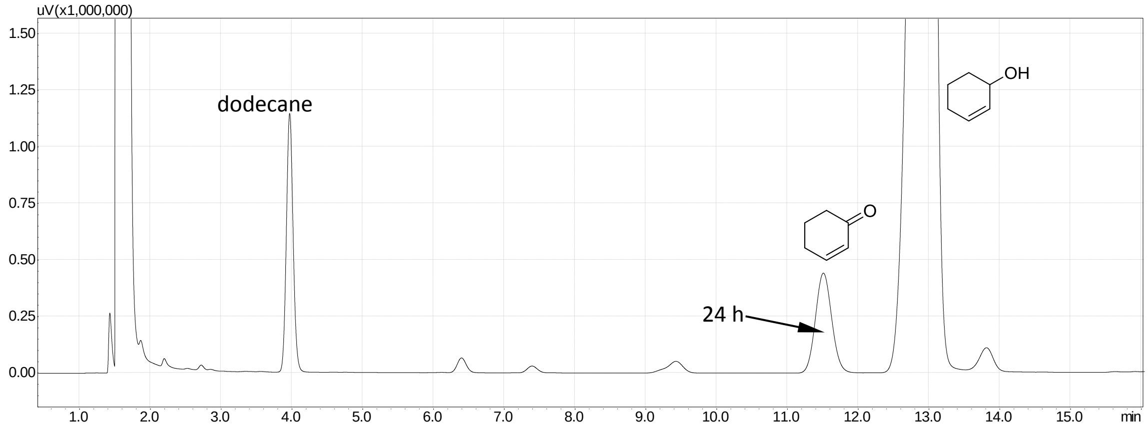


Figure S24. Representative GC chromatogram of the SAS-catalysed oxidation of 2-Cyclohexen-1-ol. Samples were diluted by 40 times with ethyl acetate.

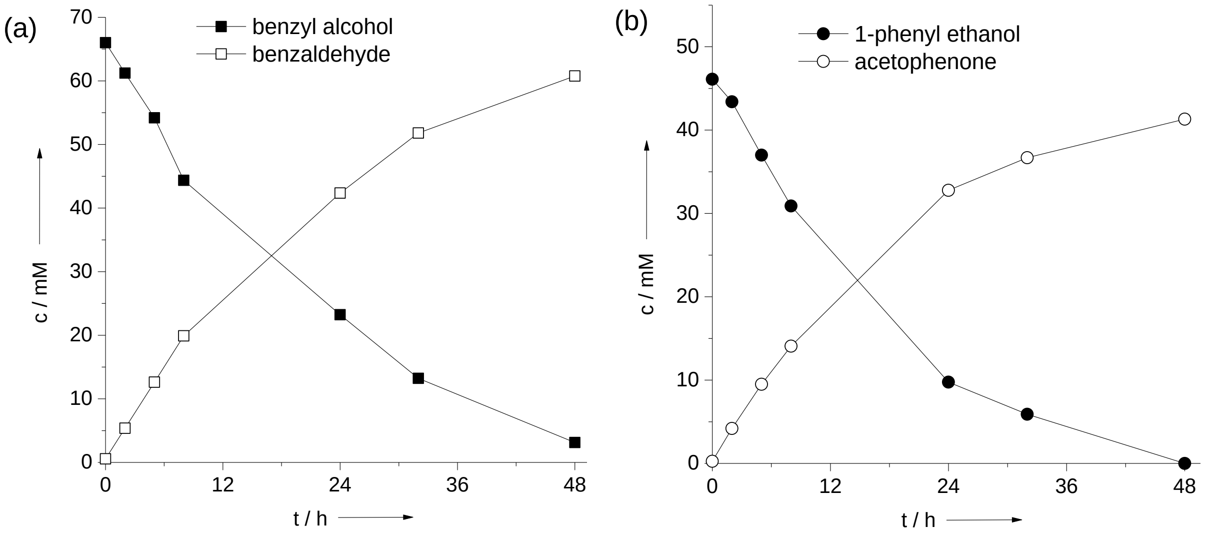
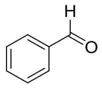
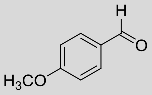
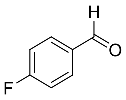
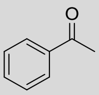
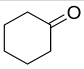
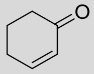
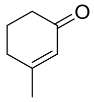
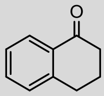
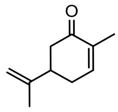
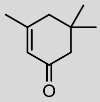
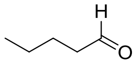
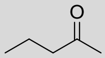
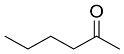


Figure S25. monophasic photooxidation of benzyl alcohol (a) and 1-phenyl ethanol (b). Reaction conditions: 1mM of SAS, T = 30 °C, λ > 400 nm, ambient atmosphere.

Table S1. Details for GC analysis

Product	**Analysis, column** [a]	**T_R [min]** [b]	**Temperature profile**
	Column A	Benzyl alcohol 22.04 Benzaldehyde 17.2 Dodecane 10.85	55 °C hold 7 min, 10 °C /min to 80 °C hold 2 min, 15 °C /min to 145 °C hold 3 min, 20 °C /min to 185 °C hold 2 min. 30 °C /min to 250 °C hold 3 min.
	Column B	*p*-Anisaldehyde 5.76 *p*-Anisyl alcohol 6.84 1-Octanol 2.69	100 °C hold 7 min, 30 °C /min to 290 °C hold 1.5 min.
	Column A	4-Fluoro benzyl alcohol 10.71 4-Fluoro benzaldehyde 7.43 Dodecane 3.66	90 °C hold 2 min, 15 °C /min to 105 °C hold 1.5 min, 30 °C /min to 160 °C hold 1.5 min, 20 °C /min to 205 °C hold 2.5 min, 30 °C /min to 250 °C hold 1 min.
	Column E	1-Phenylethanol 11.62 Acetophenone 10.07 1-Octanol 8.75	80 °C hold 3 min, 20 °C /min to 90 °C hold 1 min, 20 °C /min to 160 °C hold 1 min, 20 °C /min to 168 °C hold 1 min, 20 °C /min to 180 °C hold 1 min, 30 °C /min to 250 °C hold 1 min.
	Column A	Cyclohexanone 6.41 Cyclohexanol 8.92	90 °C hold 3 min, 20 °C /min to 100 °C hold 4.5 min, 30 °C /min to

		Dodecane 3.98	200 °C hold 3 min, 30 °C /min to 230 °C hold 1 min.
	Column A	Cyclohexen-1-one 11.52 Cyclohexen-1-ol 12.82 Dodecane 3.98	90 °C hold 3 min, 20 °C /min to 100 °C hold 10 min, 30 °C /min to 240 °C hold 2 min.
	Column C	3-Methyl-2-cyclohexen-1-ol 7.81 3-Methyl-2-cyclohexenone 12.65 Dodecane 8.53	100 °C hold 3.5 min, 5 °C /min to 135 °C hold 0 min, 25 °C /min to 210 °C hold 2 min.
	Column D	1,2,3,4-Tetranaphthalene 7.14 (*S*)-1,2,3,4-Tetrahydro-1-naphthol 10.98 (*R*)-1,2,3,4-Tetrahydro-1-naphthol 11.11 α-Tetralone 9.36 Dodecane 4.46	130 °C hold 2 min, 10 °C /min to 150 °C hold 4 min, 10 °C /min to 165°C hold 3.5 min, 25 °C /min to 2255°C hold 1.5 min. .
	Column E	*p*-Mentha-6,8-dien-2-ol, 10.86 *p*-Mentha-6,8-dien-2-one, 10.12 &11.32, two enantiomers Dodecane 3.78	130 °C hold 3.5 min, 20 °C /min to 210 °C hold 4.1 min, 25 °C /min to 240 °C hold 2 min.
	Column C	3,5,5-Trimethyl-2-cyclohexen-1-ol, 10.50 3,5,5-Trimethyl-2-cyclohexen-1-one, 17.1 Dodecane 8.72	100 °C hold 3.5 min, 5 °C /min to 125 °C hold 12.2 min, 25 °C /min to 210 °C hold 2 min.
	Column E	Pentanal, 3.23 n-Pentanol, 6.40 Dodecane, 5.62	100 °C hold 4 min, 25 °C /min to 135 °C hold 1.5 min, 30 °C /min to 245 °C hold 2 min.
	Column E	2-Pentanone, 3.20 2-Pentanol, 6.21 Dodecane, 4.67	100 °C hold 5 min, 25 °C /min to 110 °C hold 1.5 min, 30 °C /min to 245 °C hold 2 min.
	Column E	2-Hexanone, 3.88 2-Hexanol, 5.27 1-Octanol, 9.34	110 °C hold 3 min, 20 °C /min to 125 °C hold 2 min, 30 °C /min to 220 °C hold 1 min 30 °C /min to 255 °C hold 2 min.

[a] Column A: cp wax 52 CB, (50 m × 0.53 mm × 2.0 µm), FID, N_2 is the carrier gas; Column B: cp sil 5 CB, (50 m × 0.53 mm × 1.0 µm), FID, N_2 is the carrier gas; Column C: LIPODEX E (50 m × 0.25 mm × 0.25 µm);), FID, He is the carrier gas; Column D: Chiralsil Dex CB column (25 m × 0.32 mm × 0.25 µm), FID, He is the carrier gas. Column E: CP Wax 52CB column (25 m × 0.25 mm × 1.2 µm), FID, N_2 is the carrier gas.

References:

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[2] R. Kosydar, A. Drelinkiewicz, J. P. Ganhy, *Catal. Lett.* **2010**, *139*, 105-113.

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[4] P. Bilski, K. Reszka, M. Bilska, C. F. Chignell, *Journal of the American Chemical Society* **1996**, *118*, 1330-1338.

[5] D. Dvoranova, Z. Barbierikova, V. Brezova, *Molecules* **2014**, *19*, 17279-17304.