Materials:

Poly(ethylene glycol) methyl ether (4-cyano-4-pentanoate dodecyl trithiocarbonate) (average Mn 5,400), divinyl benzene (80 %), methane sulfonic acid (> 99 %) and tert-butyl nitrite (90 %) were purchased from Sigma Aldrich. Fumaronitrile (98 %), 1,2-diaminobenzene (> 99 %), benzyl alcohol (99.8 %) and diphenyl sulfide (98 %) were purchased from TCI chemicals. 4,4′-Azobis(4-cyanovaleric acid) (≥ 97 %) was purchased from Santa Cruz Biotech. Methyl phenyl sulfide (≥ 99 %) was purchased form Alfa Aesar. Isobutyl aldehyde (97 %) was purchased from ABCR. Aniline (≥ 99.5 %) was purchased from Riedel-de Haën. Sodium p-toluenesulfinate (95 %) was purchased from Merck chemicals.
All the chemicals and solvents were used without purification. Millipore quality (18.2 MΩ cm) water was used throughout.

Characterization: ^{1}H NMR and ^{13}C NMR spectra were measured by Bruker Avance 300 MHz. Solid State ^{13}C CP MAS NMR measurements were carried out using Bruker Avance II solid state NMR spectrometer operating at 300 MHz Larmor frequency equipped with a standard 4mm magic angle spinning (MAS) double resonance probe head. UV-vis absorption spectra were taken from a Cary 60 UV-vis/NIR spectrometer. UV-vis emission was monitored by J&M TIDAS spectrofluorometer. Photocatalytic porous particle size determination was undertaken using a Zetasizer Nano ZS before and after sonication. Gas chromatograms and corresponding mass-spectra were taken from Shimadzu GC-2010 Plus and GCMS-QP-2010 Ultra. Fourier transform (FTIR) spectroscopy was measured using a Bruker Tensor II FTIR spectrometer. Gas sorption was measured using a Micromeritics Tristar II Plus with samples degassed for 12 h at 120 ^{o}C under vacuum prior to analysis. Samples were prepared by first resuspending them in ethanol (0.1 wt%) and applying to aluminium stub coated with carbon tape and allowing them to dry overnight. Transmission electron microscopy (TEM) was undertaken using a JEM-1400 Transmission Electron Microscope. Samples were prepared by first suspending the particles in ethanol (0.1 wt. %) and applying them to carbon coated copper grids. The samples were negatively stained using a ruthenium stain allowing us to visualise the particles.

Synthesis of photocatalytic divinyl monomer (4,7-bis(4-vinylphenyl)benzo[c][1,2,5]-thiadiazole)

4,7-bis(4-vinylphenyl)benzo[c][1,2,5]thiadiazole: 4-Vinylphenylboronic acid (815 mg, 5.50 mmol, 2.2 eq.), 4,7-Dibromobenzo[c]-1,2,5-thiadiazole (735 mg, 2.50 mmol, 1.0 eq.), K_2CO_3 (2.08 g, 15.0 mmol, 6.00 eq.), H_2O (7.5 mL) and Toluene (22.5 mL) were added to a 200 mL Schlenk flask. The mixture was degassed by Ar bubbling for 30 min. Then $Pd(PPh_3)_4$ (145 mg, 0.125 mmol, 0.05 eq.) was added in an Ar counterstream. The solution was purged with Argon for another 5 min and heated to 90°C for 30h. After cooling to room temperature, the resulting mixture was extracted with dichloromethane (4 x 20 mL). The combined organic phases were washed with brine (50 mL) and dried over anhydrous MgSO4. After filtration and rotary evaporation of solvents the residue was purified by column chromatography on silica gel (petroleum ether / dichloromethane 3:1). The product was obtained as bright yellow powder (605 mg, 1.78 mmol, 71%).

^{1}H NMR (300 MHz, $CDCl_3$) δ = 7,96 (d, 4H), 7,80 (s, 2H), 7,60 (d, 2H), 6,81 (dd, 2H), 5,86 (d, 2H) and 5,33 (d, 2H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 154,24, 137,81, 136,93, 136,55, 133,07, 129,53, 128,02, 126,63 and 114,69 ppm.

Preparation of porous classical polymer photocatalysts

Porous classical polymer catalysts were synthesised by RAFT-mediated polymerisation induced self-assembly. The PEG macro CTA (0.2 g, 0.037 mmol, 1 eq), FN (0.65, 8.33mmol, 225 eq), DVB (1.437 g,11.04 mmol, 298 eq) and 4,7-bis(4-vinylphenyl)benzo[c][1,2,5]thiadiazole (0.0107 g, 0.074 mmol, 2 eq) were dissolved in a mixture of EtOH and H_2O to a concentration of 1 wt.% (60:40, 213 mL) in a round bottomed flask equipped with a magnetic stirrer and septum. To insure homogeneity the sample was sonicated at RT for 30 min, dissolving all components. To this solution the radicle initiator ACVA (0.0021 g, 0.0074 mmol, 0.2 eq) was added. The solution was degassed with N_2 for 30 min and subsequently heated to 70 ^{o}C for 24 h while stirring at 300 rpm. The resulting particles were obtain by precipitation in diethyl ether and dried under vacuum for 24 h resulting in a fluorescent yellow powder.

Photocatalytic benzimidazole synthesis

Porous polymer photocatalytic particles (25 mg particles, 27 µg photocatalyst) were sonicated in the desired solvent (10 mL) in a 20 mL open-top screw cap vial. 1,2 Benzenediamine (54.7 mg, 50mM) and benzyl alcohol (216 mg, 200 mM) were added to the dispersed photocatalyst. The vial was then irradiated with blue LED light (power: 0.16 W cm^{-2}, λ 460 nm) for 16 h. The sample aliquots were mixed with DCM (1.5 mL) to extract reagents and products, conversion and products were determined by GC-MS. The crude product after 16 h was purified by flash chromatography (ethyl acetate 10:1) to yield the final product.

Photocatalytic sulfide oxidation

Porous polymer photocatalytic particles (25 mg particles, 27 µg photocatalyst) were sonicated in the desired solvent (10 mL) in a 20 mL open-top screw cap vial. Methyl pheylsulfide or diphenylsulfide (62 or 92 mg, 50 mM) and isobutyraldehyde (91 mg, 100 mM) were added to the dispersed photocatalyst. The vial was then irradiated with blue LED light (power: 0.16 W cm^{-2}, λ 460 nm) for 18 h. The sample aliquots were mixed with DCM (1.5 mL) to extract reagents and products, conversion and products were determined by GC-MS. The crude product after 18 h was purified by flash chromatography (petroleum ether / ethyl acetate 1:1) to yield the final product.

Photocatalytic sulfoxide formation from aniline and sulfonate salts

Porous polymer photocatalytic particles (50 mg particles, 54 µg photocatalyst) were sonicated in the desired solvent (10 mL) in a 20 mL open-top screw cap vial. Aniline (45 mg, 50 mM) and Sodium p-toluenesulfinate (133 mg, 75 mM) were added to the dispersed photocatalyst in combination with methanesulfonic acid (9.6 mg, 20 mol%) and tert-butyl nitrite (77 mg, 75mM). The vial was then irradiated with blue LED light (power: 0.16 W cm^{-2}, λ 460 nm) for 20 h, with aliquots taken to monitor conversion over time. The sample aliquots were mixed with DCM (1.5 mL) to extract reagents and products, conversion and products were determined by GC-MS. The crude product after 20 h was purified by flash chromatography (petroleum ether / ethyl acetate 10:1) to yield the final product.

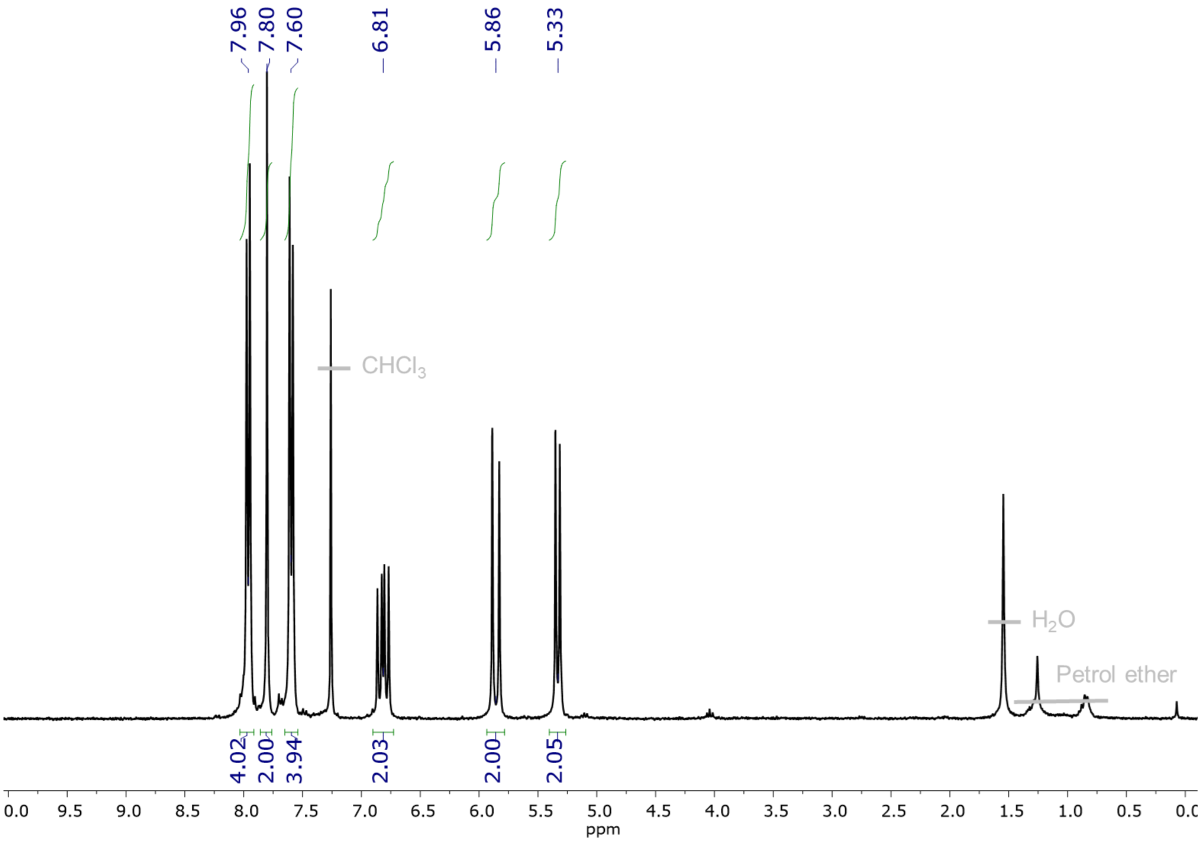

Figure S1. ^{1}H-NMR of photocatalytic 4,7-bis(4-vinylphenyl)benzo[c][1,2,5]thiadiazole monomer

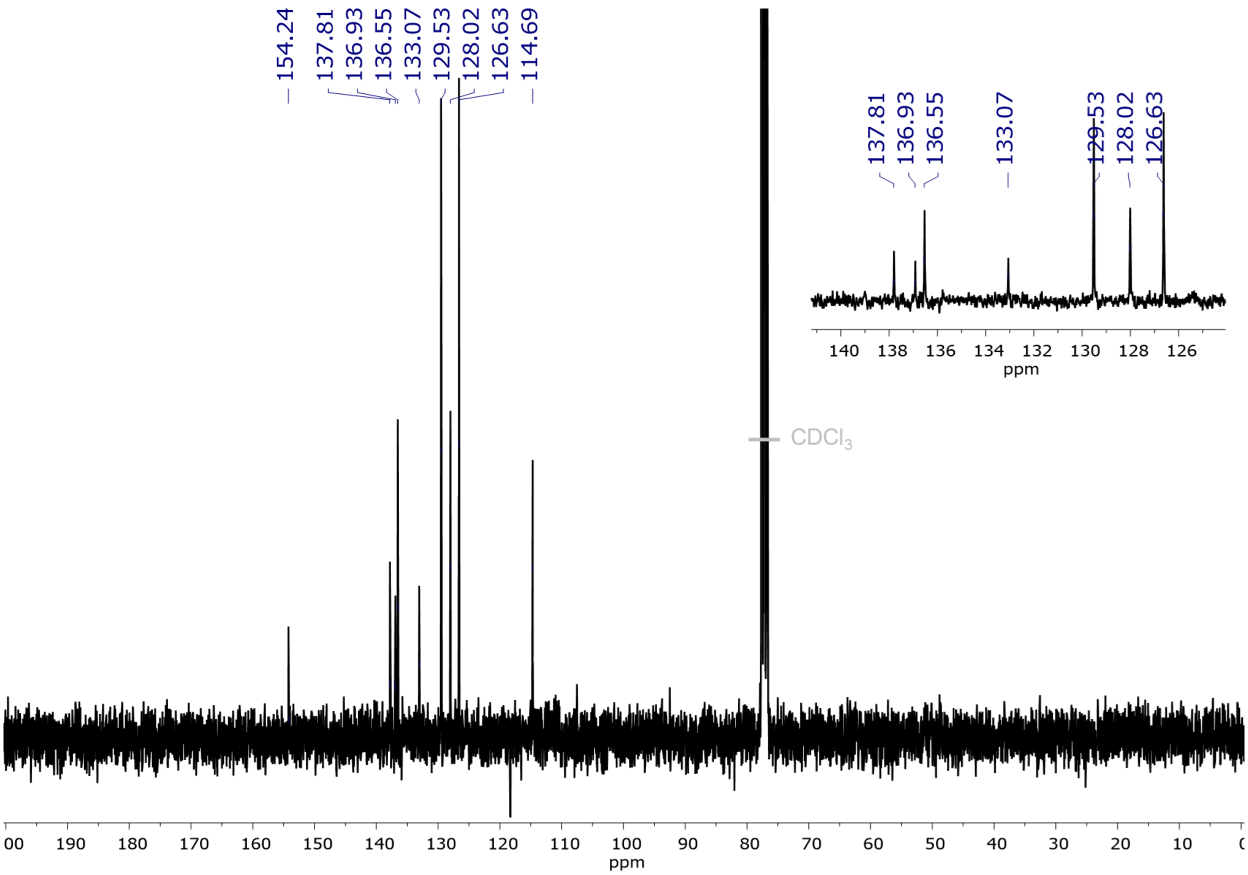

Figure S2. ^{13}**C-NMR of photocatalytic 4,7-bis(4-vinylphenyl)benzo[c][1,2,5]thiadiazole monomer**

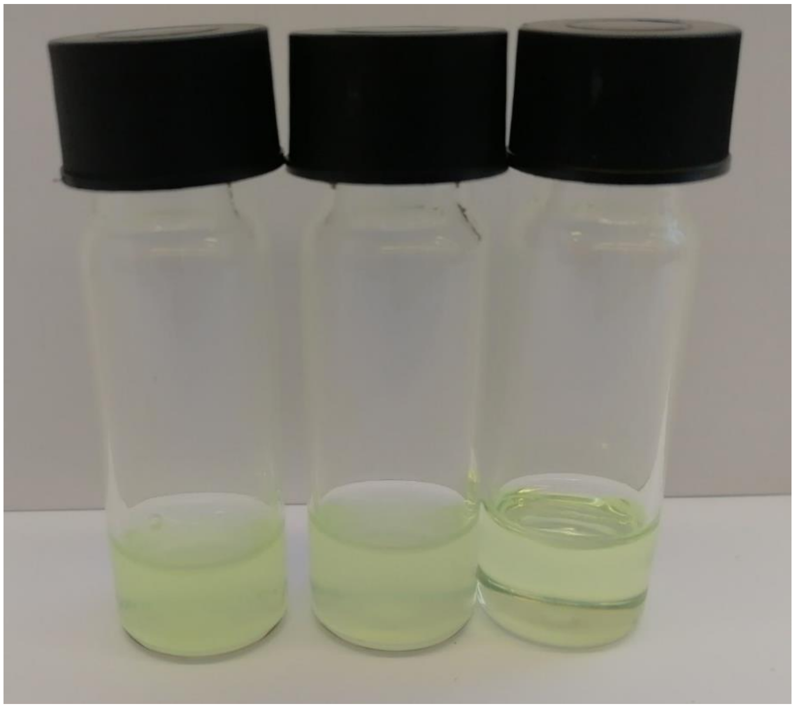

Figure S3. Dispersibility of photocatalytic porous particles in a range of solvents including: water, acetonitrile and toluene (right to left).

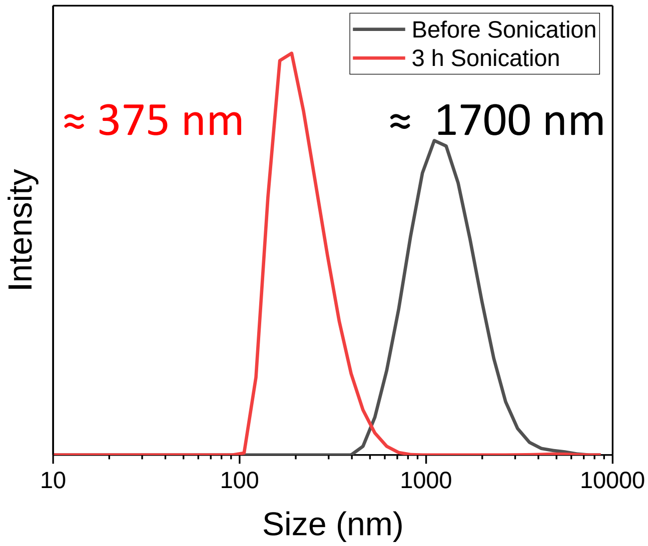

Figure S4. DLS spectra of photocatalytic porous polymers after resuspension in water and subsequent sonication

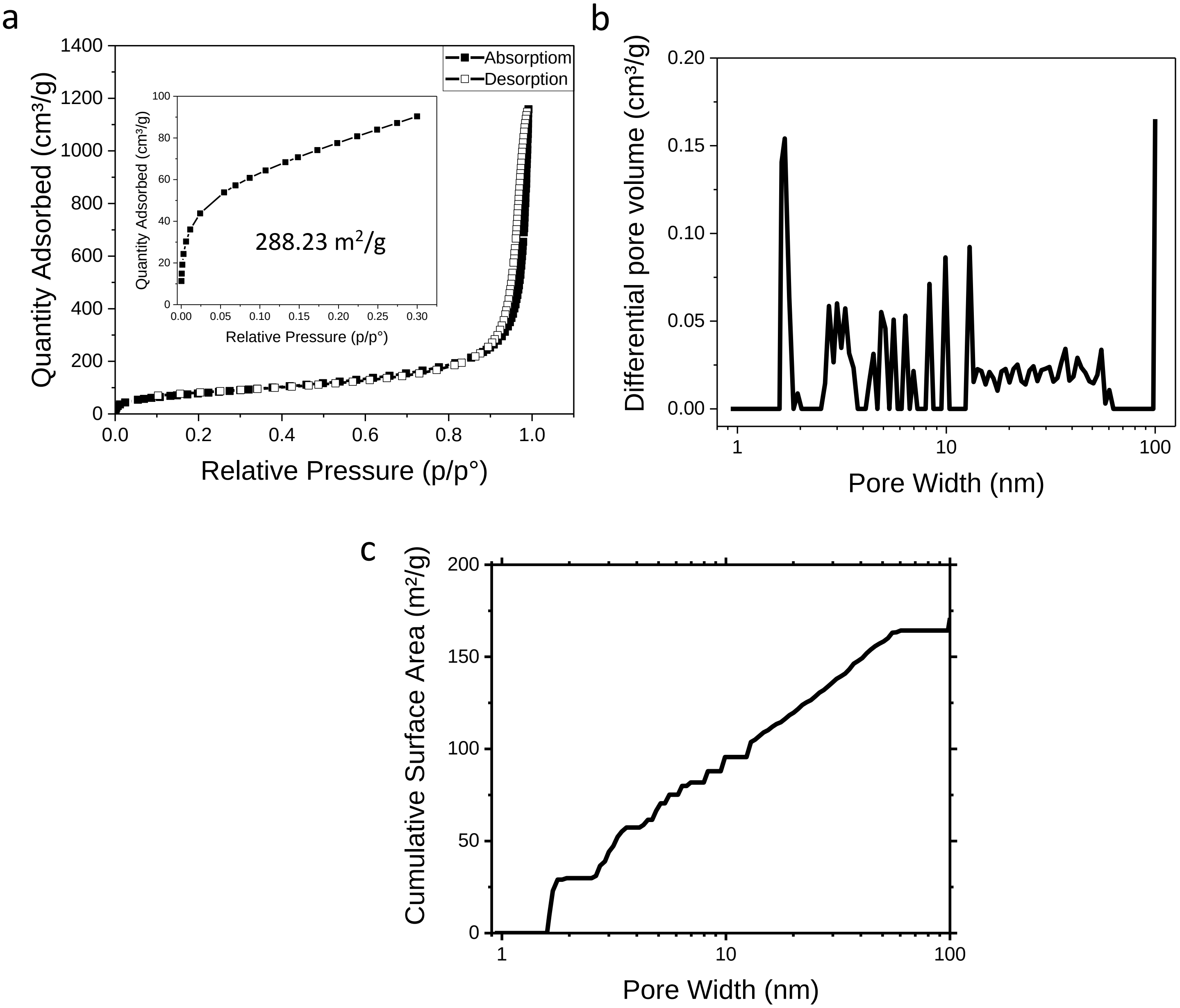

Figure S5. **N_2 absorption and desorption at 77 K (a), insert shows region used to calculate the BET surface area. (b) NLDFT pore size distribution. (c) Cumulative surface area vs. pore width for samples**

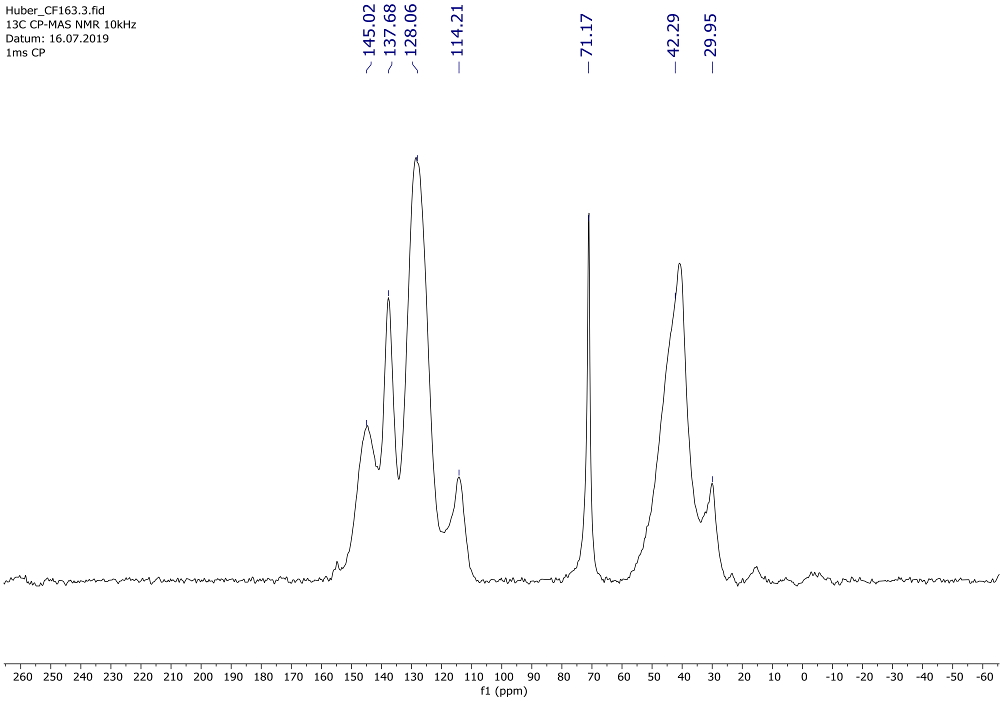

Figure S6. ssNMR of porous classical photocatalytic particles

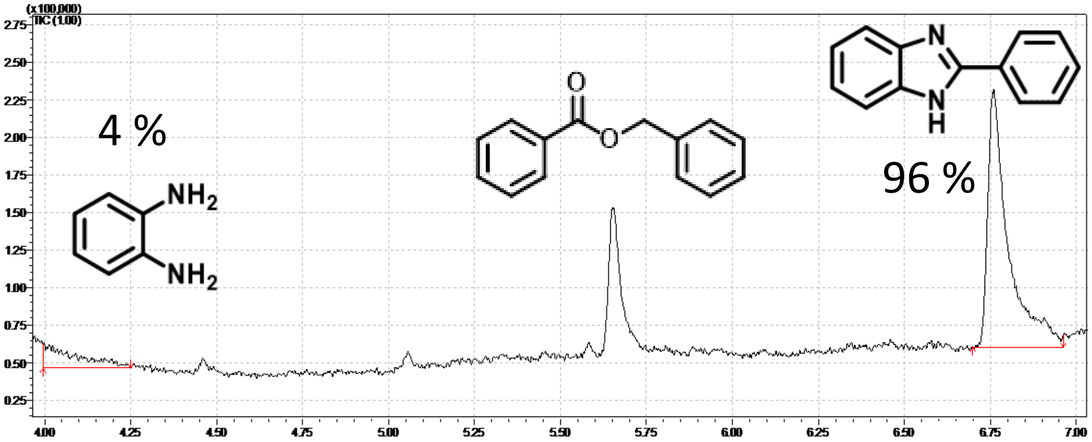

Figure S7. GCMS trace of benzimidazole formation in water

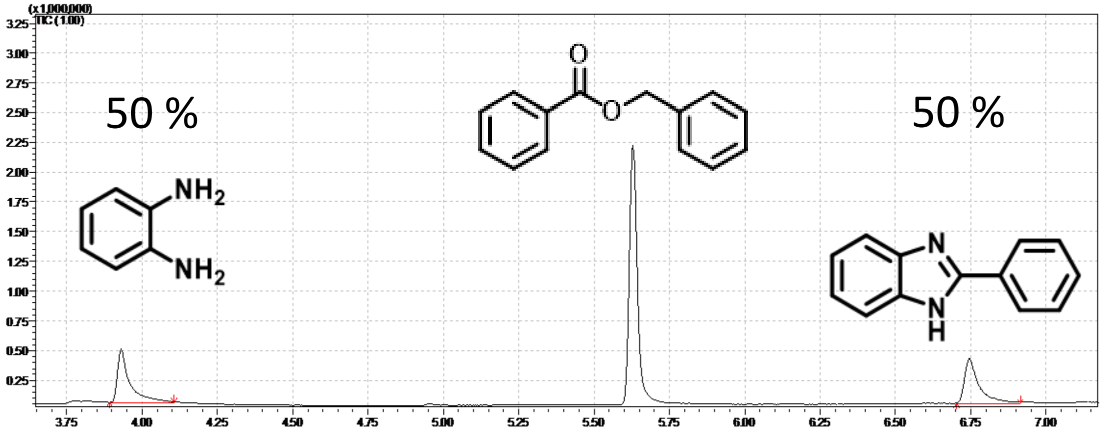

Figure S8. GCMS trace of benzimidazole formation in acetonitrile

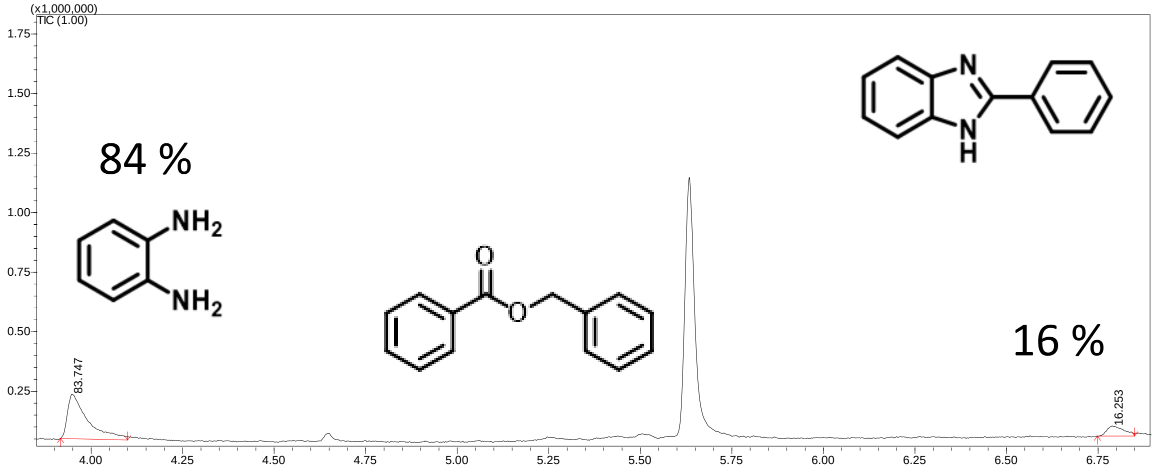

Figure S9. GCMS trace of benzimidazole formation in toluene

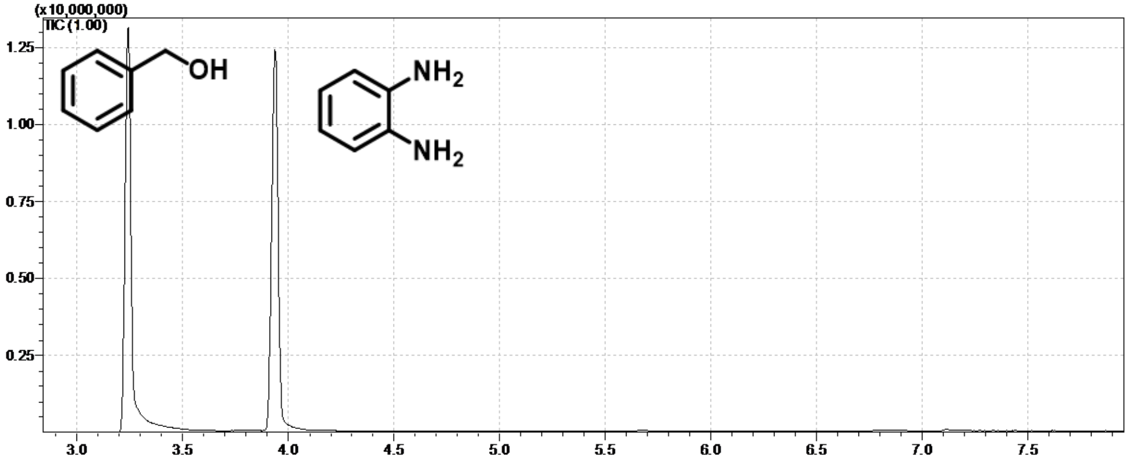

Figure S10. GCMS trace of benzimidazole formation in water with no light

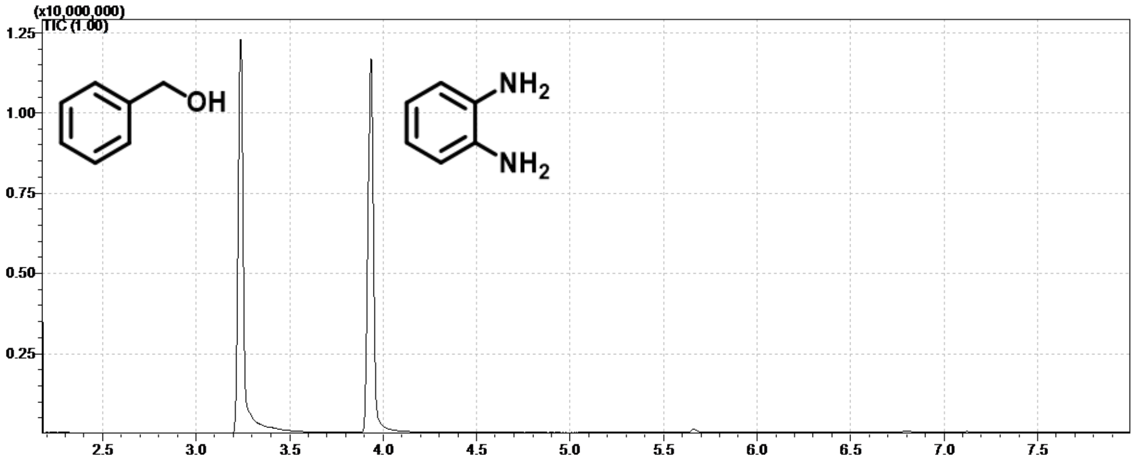

Figure S11. GCMS trace of benzimidazole formation in water with no photocatalyst

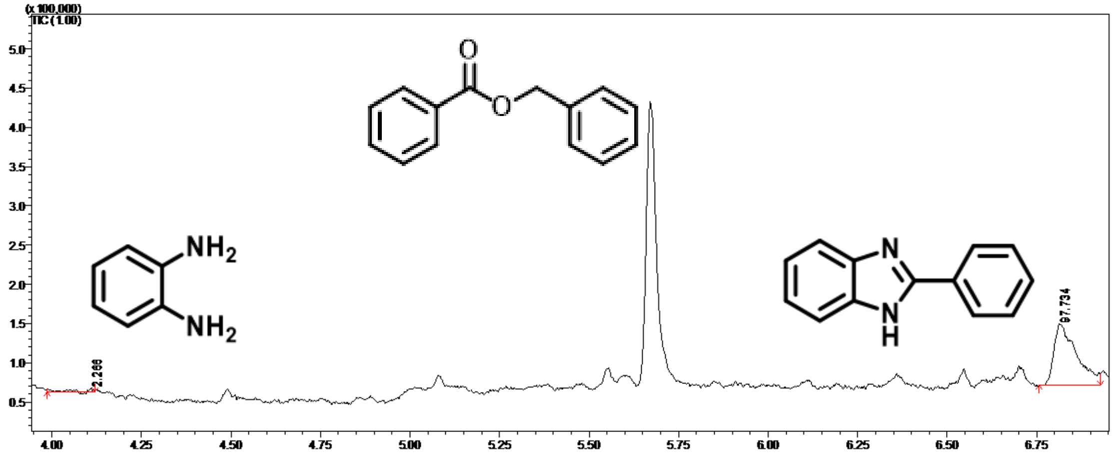

Figure S12. GCMS trace of benzimidazole formation in water using photocatalytic monomer

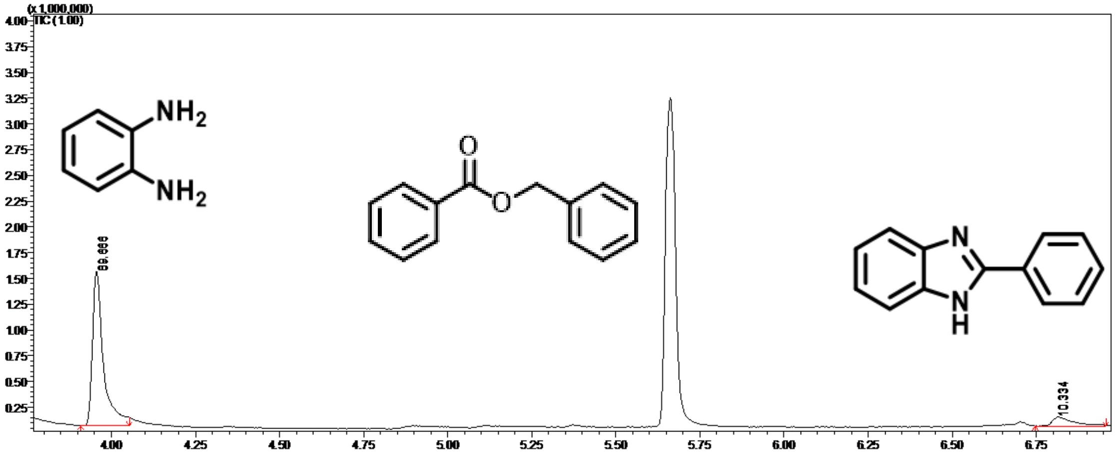

Figure S13. GCMS trace of benzimidazole formation in acetonitrile using photocatalytic monomer

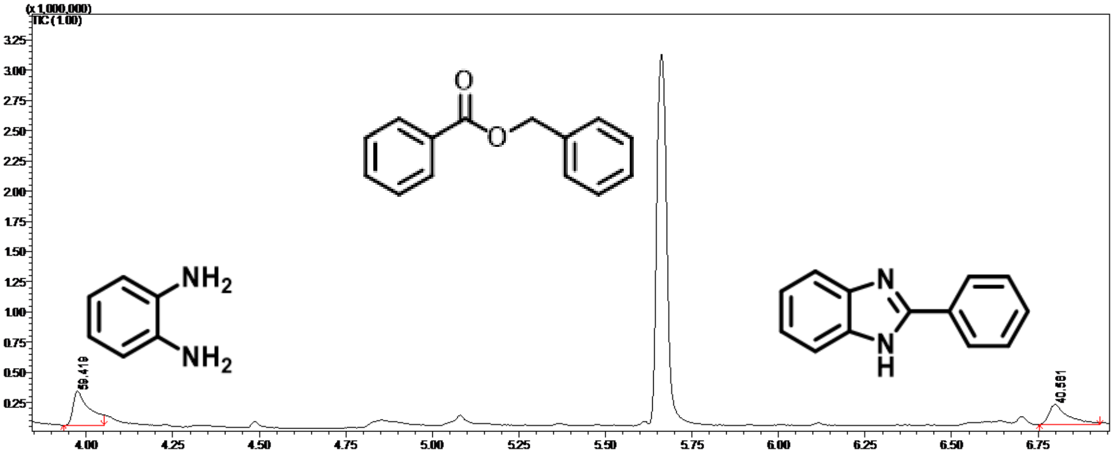

Figure S14. GCMS trace of benzimidazole formation in toluene using photocatalytic monomer

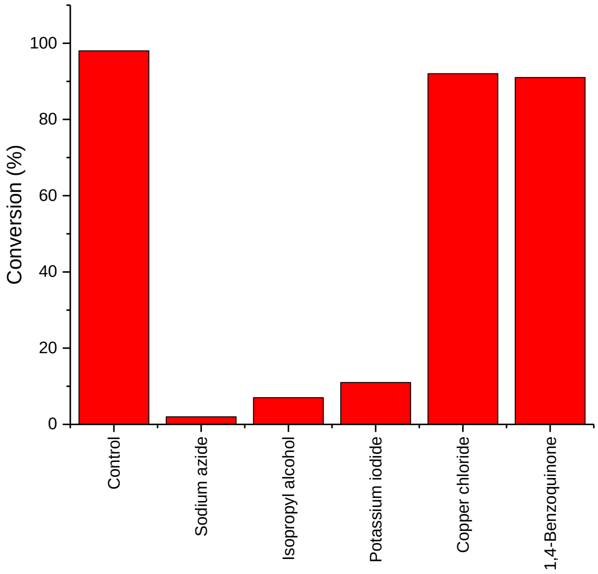

Figure S15. Benzimidazole formation in presence of scavengers. Sodium azide (NaN_3), isopropanol (IPA), potassium iodide (KI), copper (II) chloride ($CuCl_2$), 1,4-benzoquinone (BQ) and were introduced as $^1O_2$, •OH, h^+, e^- and $•O_2^-$ scavengers

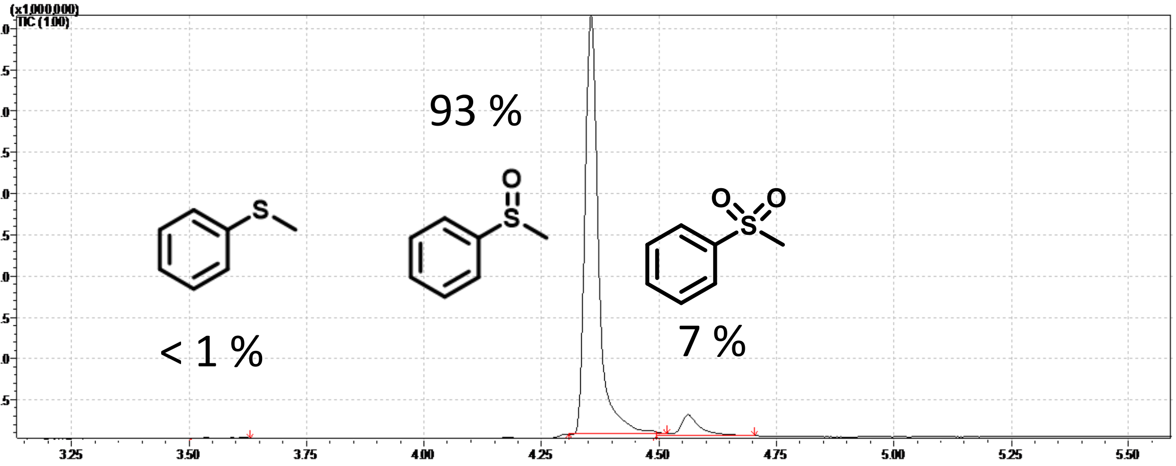

Figure S16. GCMS trace of (methylsulfonyl)benzene formation water GCMS

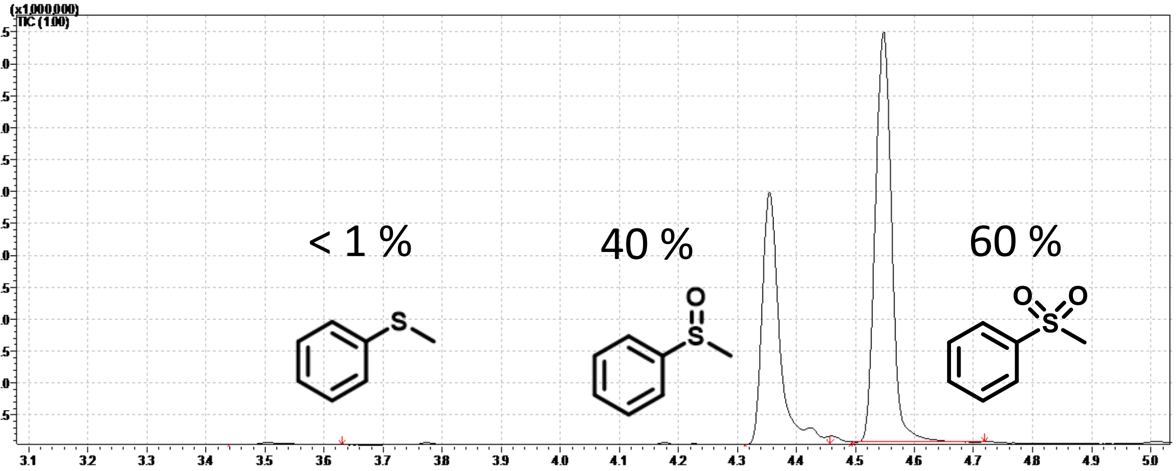

Figure S17. GCMS trace of (methylsulfonyl)benzene formation in acetonitrile

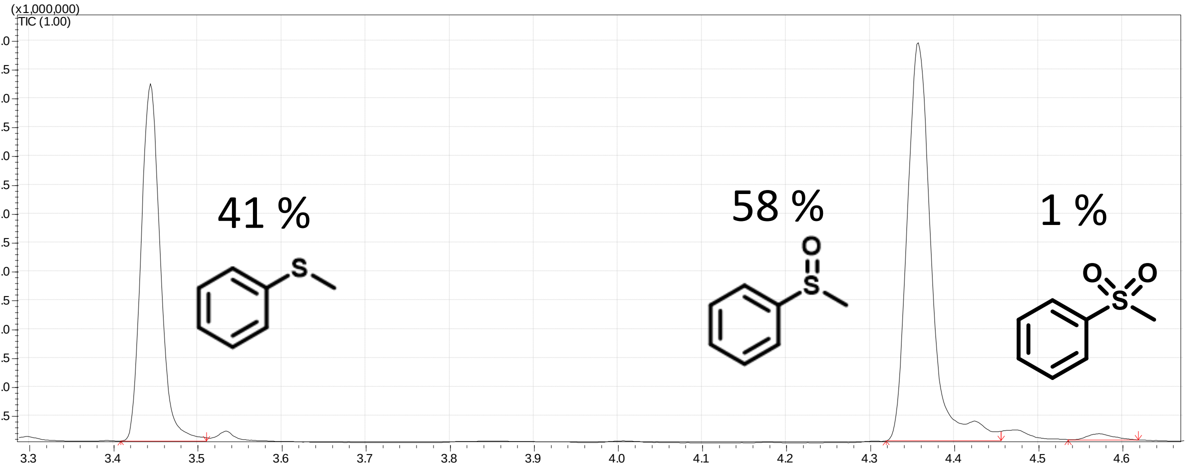

Figure S18. GCMS trace of (methylsulfonyl)benzene formation in toluene

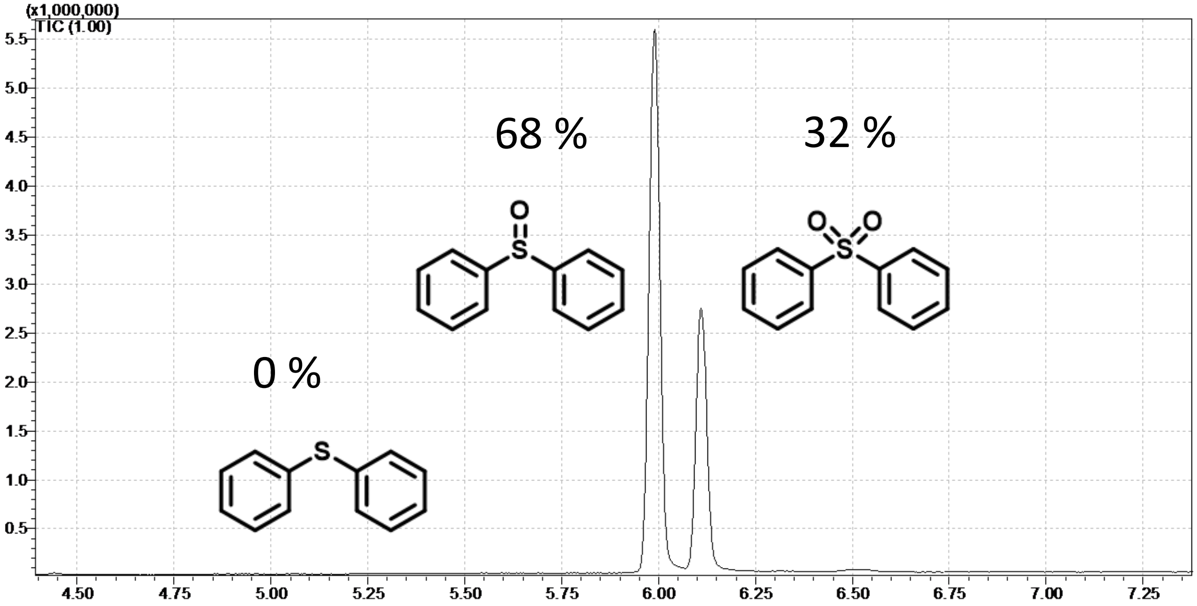

Figure S19. GCMS trace of sulfonyldibenzene formation in water

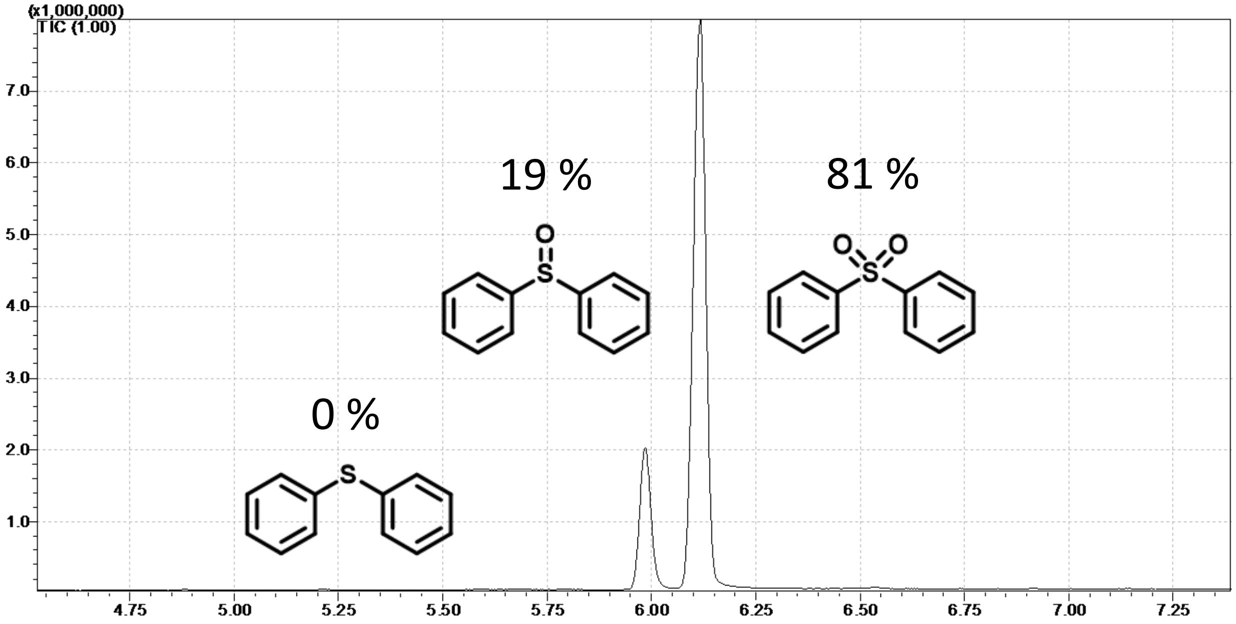

Figure S20. GCMS trace of sulfonyldibenzene formation acetonitrile GCMS

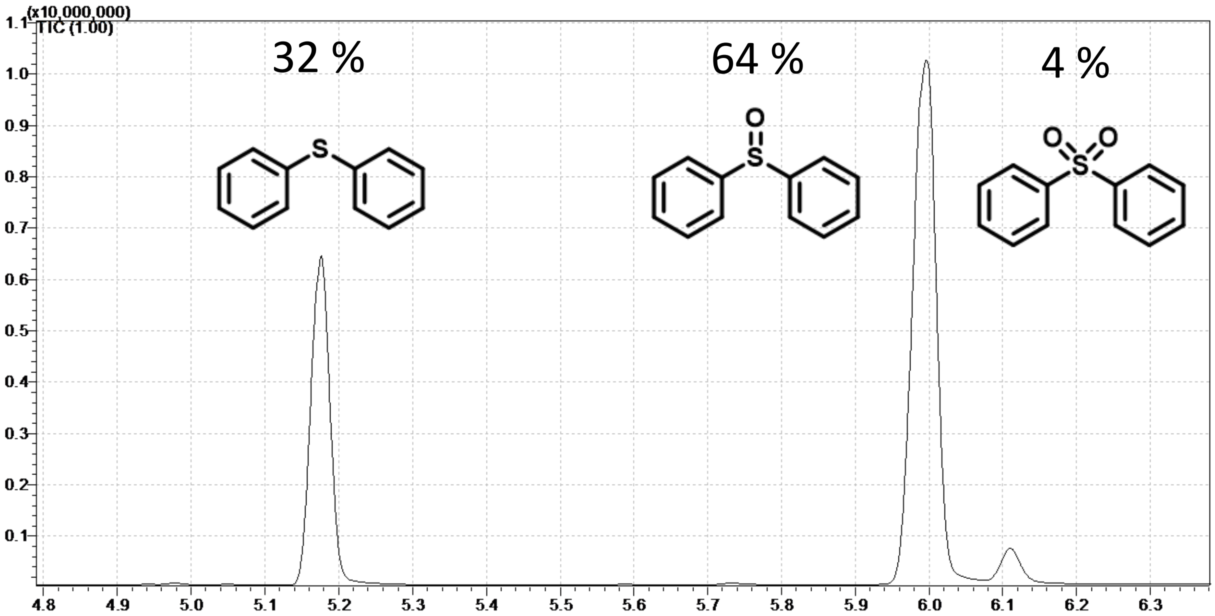

Figure S21. GCMS trace of Sulfonyldibenzene formation in toluene

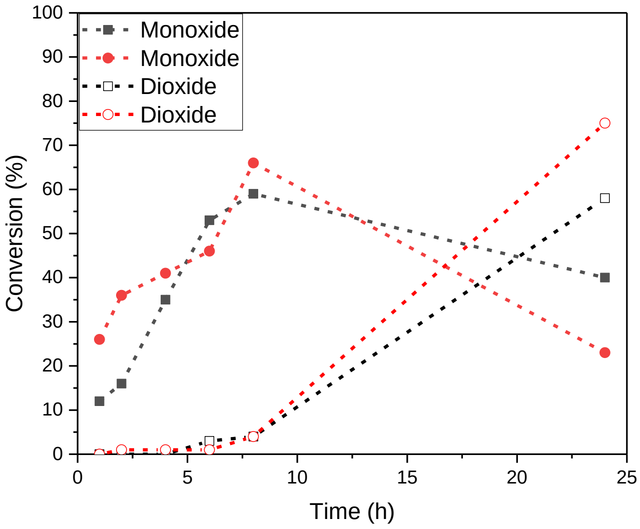

Figure S22. Sulfonyldibenzene kinetic testing in water (black) and acetonitrile (red).

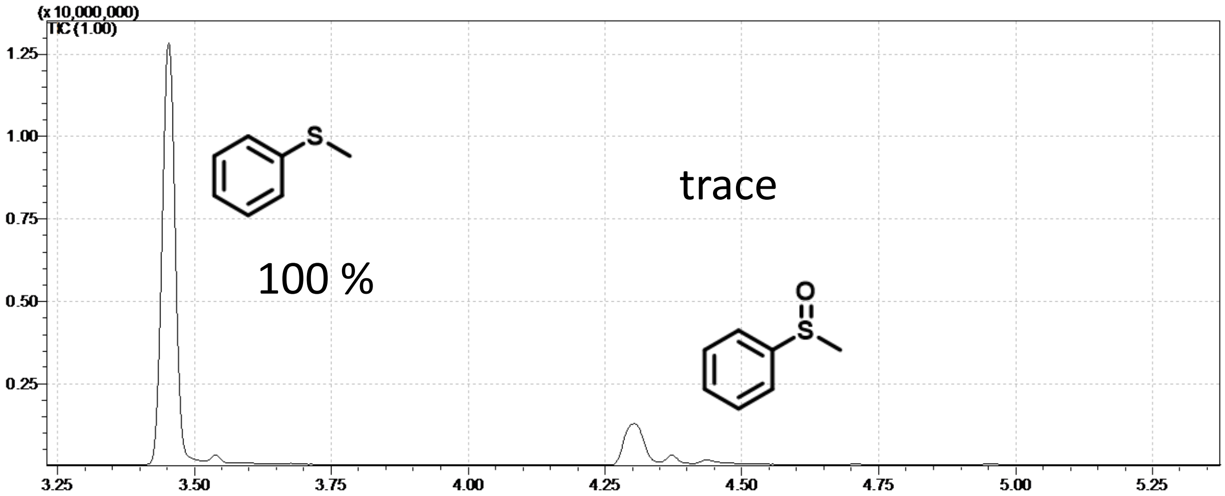

Figure S23. GCMS trace of (Methylsulfonyl)benzene formation in acetonitrile with no light

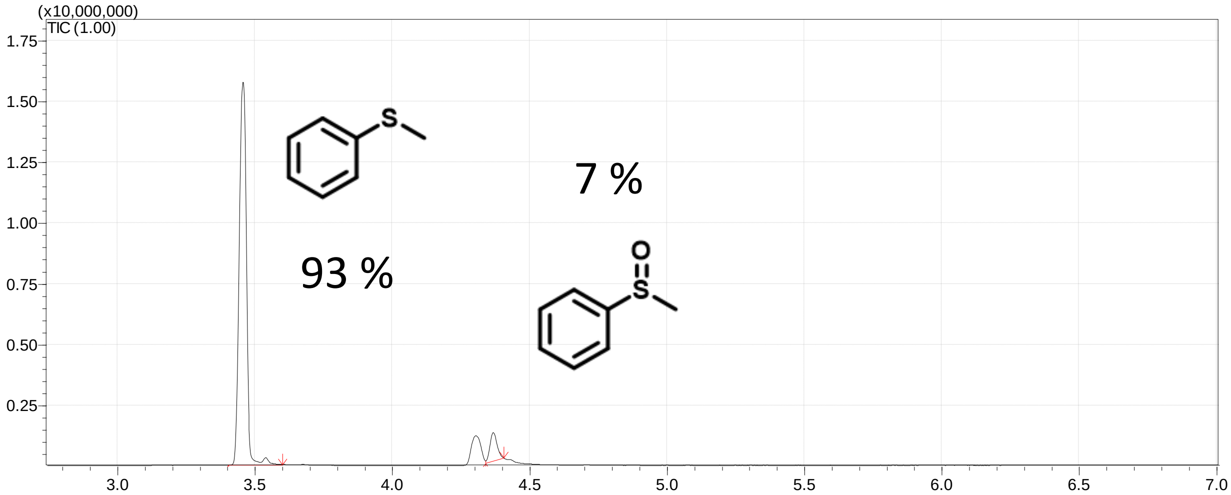

Figure S24. (Methylsulfonyl)benzene formation acetonitrile GCMS no photocatalyst

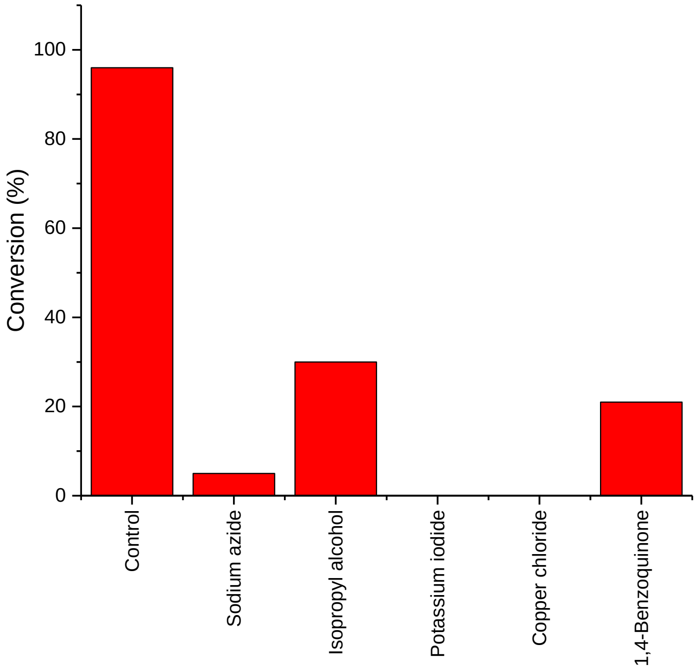

Figure S25. (Methylsulfonyl)benzene formation in acetonitrile in the presence of scavengers. Sodium azide (NaN_3), isopropanol (IPA), potassium iodide (KI), copper (II) chloride ($CuCl_2$), 1,4-benzoquinone (BQ) and were introduced as $^1O_2$, •OH, h^+, e^- and $•O_2^-$ scavengers

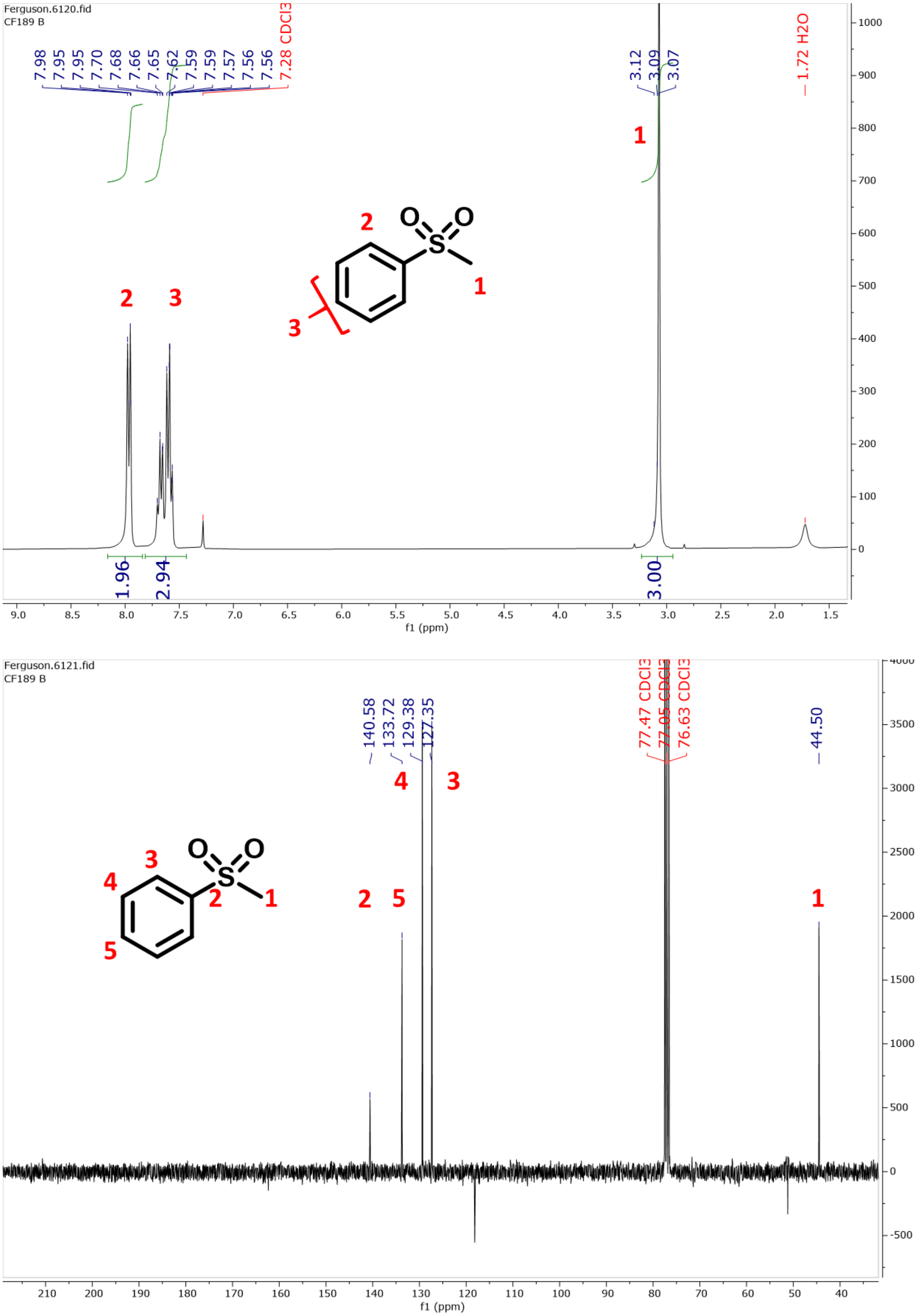

Figure S26. (Methylsulfonyl)benzene 1H and 13C NMR

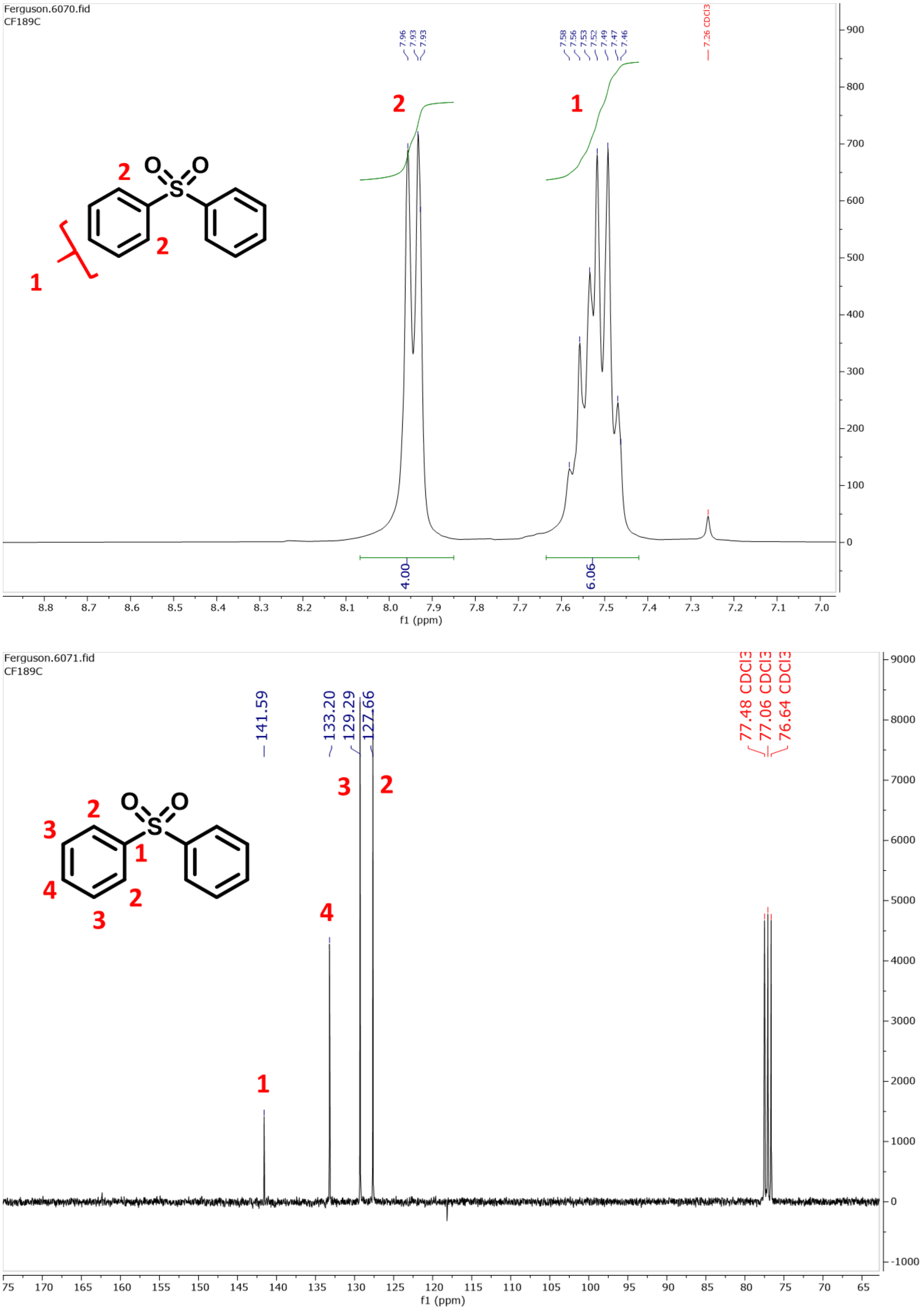

Figure S27. Sulfonyldibenzene 1H and 13C NMR

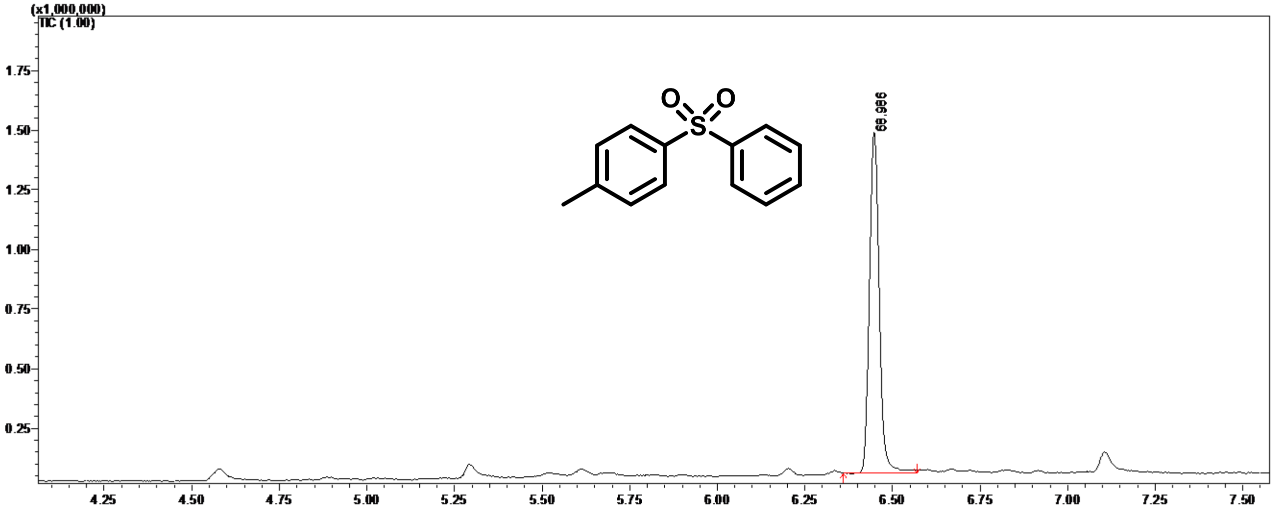

Figure S28. 1-methyl-4-(phenylsulfonyl)benzene formation in water GCMS without photocatalyst using the sulfinate and diazonium salt using white light in a nitrogen atmosphere for 20 h.

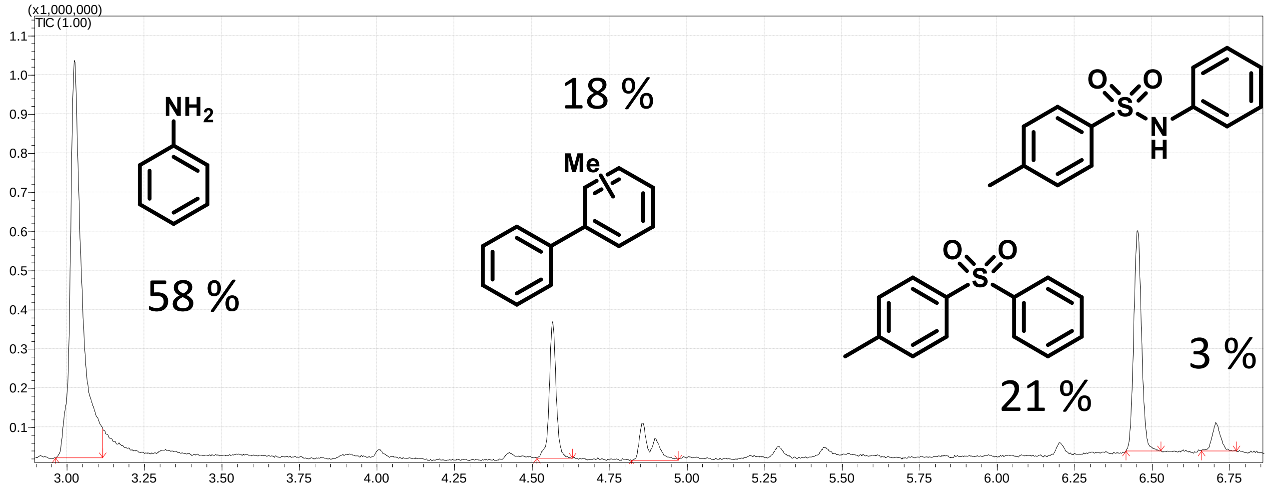

Figure S29. 1-methyl-4-(phenylsulfonyl)benzene formation in water GCMS

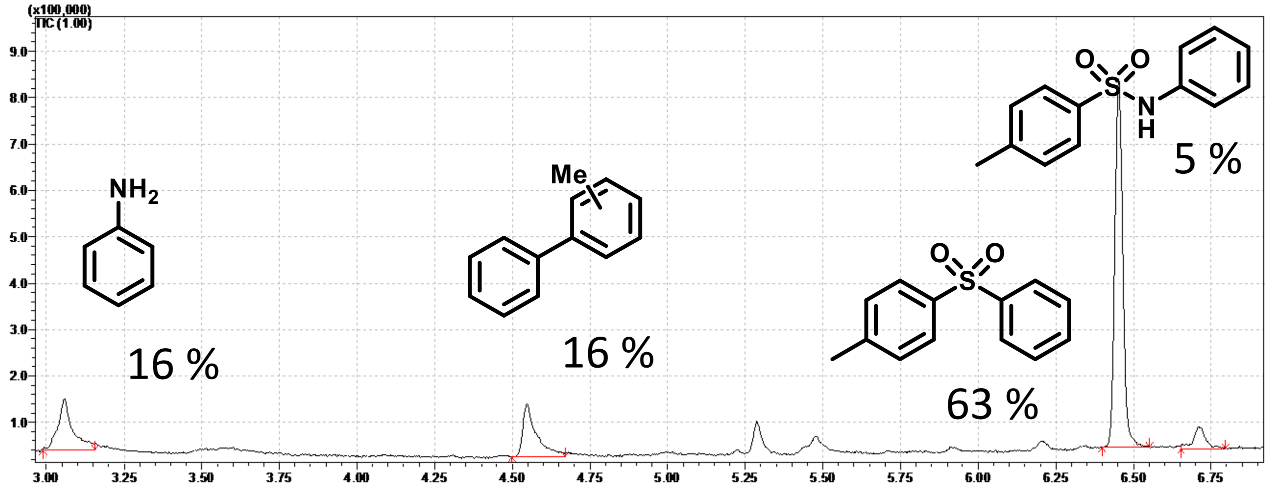

Figure S30. 1-methyl-4-(phenylsulfonyl)benzene formation in acetonitrile GCMS

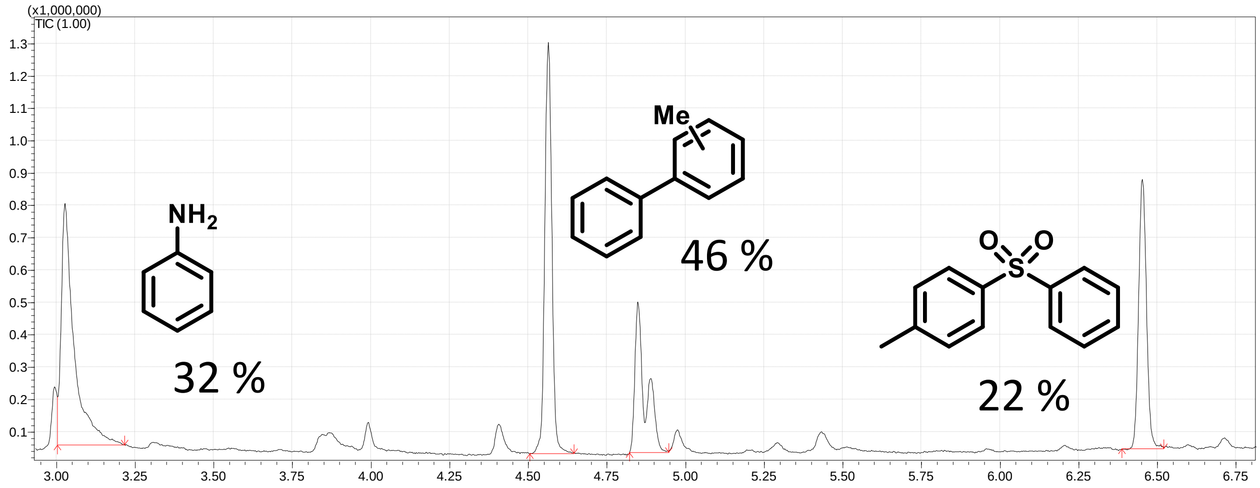

Figure S31. 1-methyl-4-(phenylsulfonyl)benzene formation in toluene GCMS

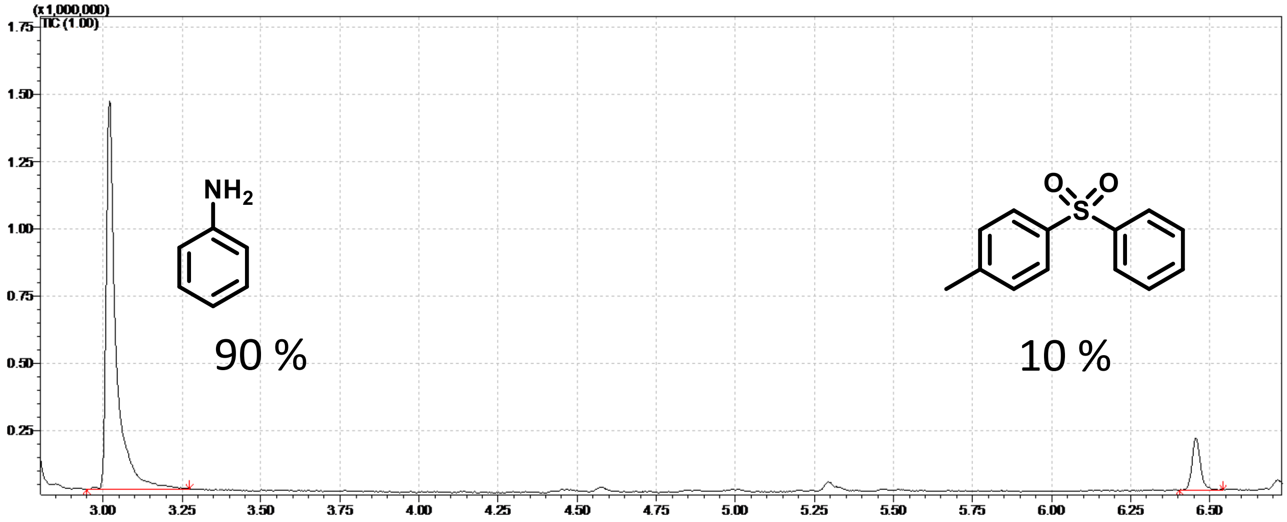

Figure S32. 1-methyl-4-(phenylsulfonyl)benzene formation in acetonitrile GCMS without photocata;yst

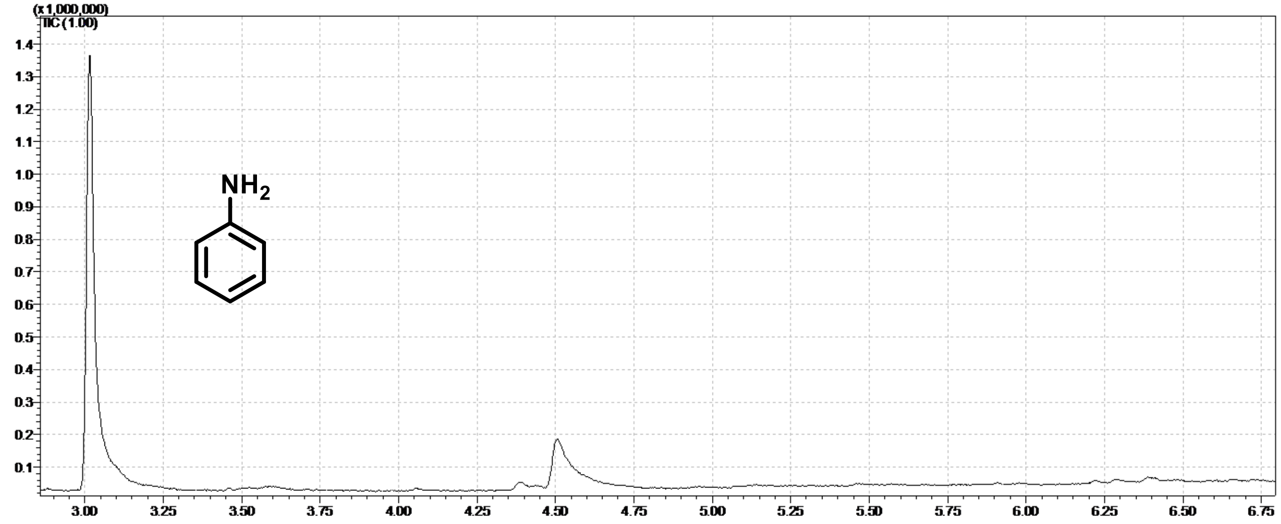

Figure S33. 1-methyl-4-(phenylsulfonyl)benzene formation in acetonitrile GCMS in dark conditions

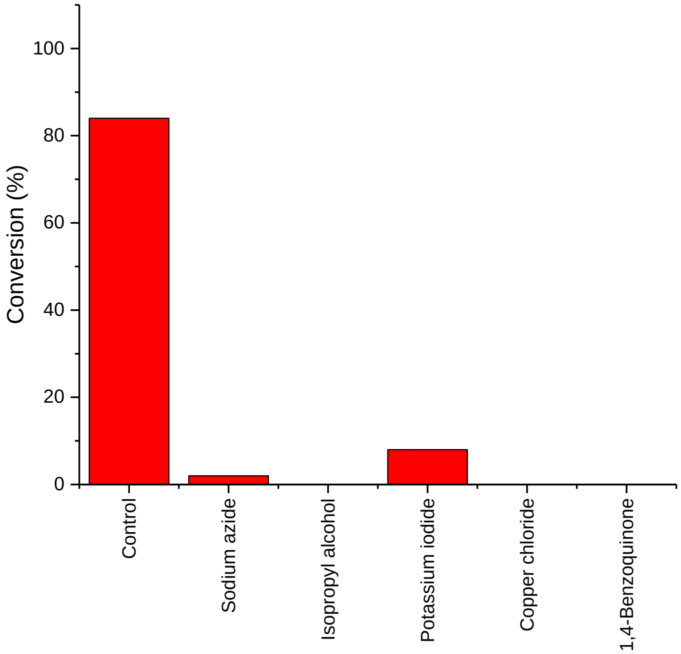

Figure S34. 1-Methyl-4-(phenylsulfonyl)benzene formation in acetonitrile in the presence of scavengers. Sodium azide (NaN_3), isopropanol (IPA), potassium iodide (KI), copper (II) chloride ($CuCl_2$), 1,4-benzoquinone (BQ) and were introduced as $^1O_2$, •OH, h^+, e^- and $•O_2^-$ scavengers