

Electronic Supplementary Information

**Mechanochemically-Assisted Solid-State Photocatalysis
(MASSPC)**

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GENERAL COMMENTS

All chemicals were purchased from commercial sources (Sigma Aldrich or Kemika) and were used without further purification. TLC analysis was performed on Merck Silica Gel 60 F₂₅₄ plates. Acetonitrile was dried and distilled before use. Retsch MM200 mixer mill was used for ball milling experiments. Solution ¹H and ¹³C NMR spectra were acquired on Bruker Avance (300 and 600 MHz) spectrometers with tetramethylsilane as an internal standard. FTIR-ATR spectra were recorded using a Fourier Transform- Infrared Attenuated Total Reflection PerkinElmer UATR Two spectrometer in the range 400 cm⁻¹ to 4000 cm⁻¹. Gas chromatography analyses were performed on Varian 3300 gas chromatographer with DB-9 capillary column and FID under the following conditions: $T(\text{column})_{\text{initial}} = 60\text{ }^{\circ}\text{C}$, $T(\text{column})_{\text{final}} = 220\text{ }^{\circ}\text{C}$, $T(\text{injector}) = 250\text{ }^{\circ}\text{C}$, $T(\text{detector}) = 300\text{ }^{\circ}\text{C}$, rate = $40\text{ }^{\circ}\text{C min}^{-1}$, $t_{\text{initial}} = 2\text{ min}$, $t_{\text{hold}} = 10\text{ min}$, $\text{flow}(\text{N}_2)_{\text{column}} = 6.5\text{ mL min}^{-1}$, $\text{flow}(\text{N}_2 + \text{makeup}) = 29.0\text{ mL min}^{-1}$. The quantitative analysis was carried out in the presence of acetophenone as the internal standard. The samples for analysis were prepared by weighing out 15.0–16.0 mg of the solid reaction mixture which was suspended in a mixture of 200 μL of acetonitrile and 50 μL of 0.025 mol dm⁻³ acetophenone solution in acetonitrile. An aliquot of this mixture (0.6–1.0 μL) was injected for the GC analysis. The amount of benzil in the sample was determined from the relative ratio of areas under the corresponding signals in the GC chromatogram.

The LED photoreactors were constructed from a piece of 3 mm thick alumina plate and 20 blue (460–465 nm) or green (520–530 nm) LED bulbs (3 W each), connected into five arrays where four bulbs in each array were connected in series. To prevent the reactor from overheating, three heat sinks were installed. The input power is easily controlled by changing the current/voltage on a standard laboratory current source (Figure S1a and b). Initially, a blue or green LED strip (SMD 5050, 30 cm length, 14 W m^{-1}) was wrapped around the glass jar (Figure S1, c and d). However, after several hours of intensive milling at higher frequencies, the connection between the strip and the power source would brake due to vibration. For that reason, the "shaking reactor" design was replaced with the static one.

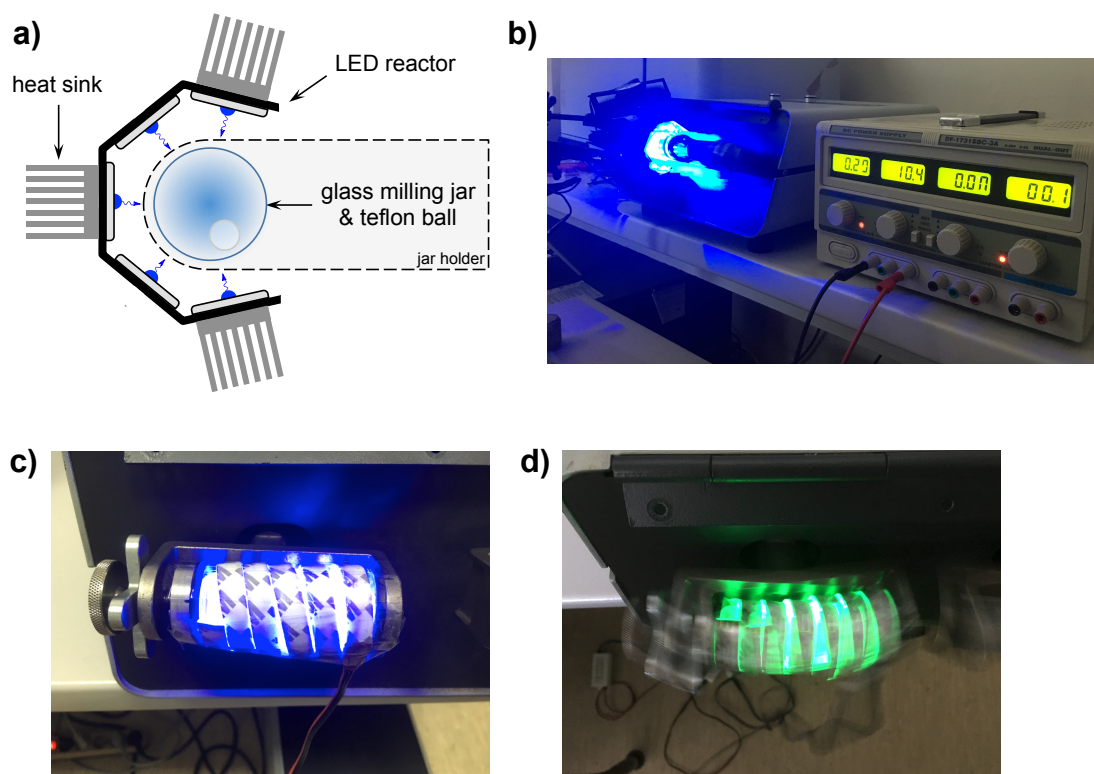


Figure S1. a) Cross-section of the LED reactor used for aging and ball milling experiments under visible light irradiation. b) Setup with the LED reactor connected to a current source. c) and d) Initial design of the setup with an LED strip wrapped around the glass jar.

SOLID-STATE PHOTOCATALYSIS BY AGING

The reaction mixture, previously gently homogenized using a mortar and pestle, was applied in a ca. 1.5 mm thick layer on a glass slide and exposed to blue light of the LED reactor (Figure S2). The yield of benzil in four separate experiments was determined by GC analysis.

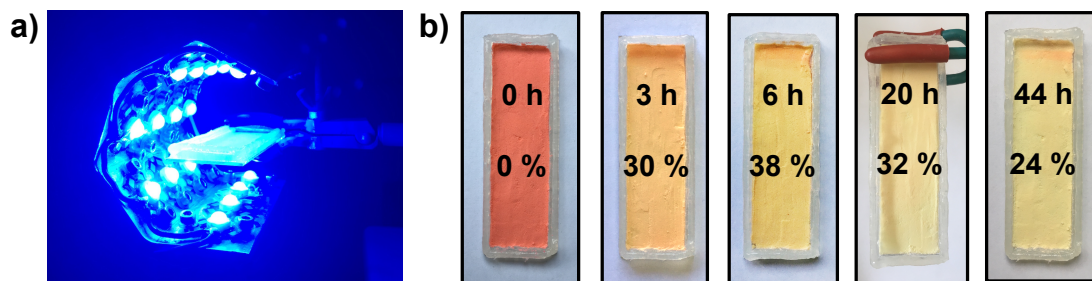


Figure S2. a) The reaction setup for solid-state photocatalysis by aging in air with a glass slide positioned in the centre of the reactor. b) The appearance of the aging mixtures after exposure to blue light. The decrease in benzil (**3**) yield upon prolonged irradiation can be explained by photodegradation of **3** under visible light,¹ but also by its possibility to react further with other radical species (e.g. thiyl radicals) and singlet oxygen present in the mixture.

1. I. Lukáč and C. Kósa, *Macromol. Rapid Commun.*, 1994, **15**, 929.



Figure S3. a) After 3 hours, only the surface layers of solid reaction mixture underwent the reaction (indicated by discolouration) whereas the colour of the inner layers suggested that the reaction was still in progress. b) In the case of 44 h exposure, scratching the surface with a spatula revealed a complete discolouration of the reaction mixture. This observation prompted us to develop a ball milling approach which facilitates mass transfer in the solid-state.

MECHANOCHEMICALLY-ASSISTED SOLID-STATE PHOTOCATALYSIS (MASSPC)

General procedure for mechanochemically-assisted solid-state photocatalysis:

In a typical milling experiment, gently homogenized (using a mortar and pestle) mixture of diphenylacetylene (0.2 mmol), 4-chlorothiophenol (0.4 mmol), eosin Y (2 mol%) and anhydrous sodium sulfate (1.5 g) was milled in a 20 mL glass jar at 27 Hz while simultaneously irradiated under blue light. The input power of the reactor was set to 14.5 W unless otherwise stated. The yield of benzil was determined by GC analysis.

For comparison, the alkyne oxidation was carried out in acetonitrile solution (2.0 mL) by reacting diphenylacetylene (0.2 mmol), 4-chlorothiophenol (0.4 mmol) and eosin Y (2 mol%) under air and blue LED irradiation (14.5 W) for 24 hours. The samples of the reaction mixture were taken for GC analysis after 1.5, 3.0, 4.5, 6.0, 8.0 and 24.0 h.

Table S1. Optimisation of the reaction conditions in MASSPC.^a For details of the GC analysis, see General Comments.

| Entry | Catalyst | Solid support | Yield ^b / % |
|-------|--------------------------------------|---------------------------------|------------------------|
| 1 | Eosin Y | Na ₂ SO ₄ | 43 |
| 2 | Eosin Y (20 mol%) | Na ₂ SO ₄ | 35 |
| 3 | Ru(bpy) ₃ Cl ₂ | Na ₂ SO ₄ | 3.6 ^c |
| 4 | Fluorescein | Na ₂ SO ₄ | 3.9 ^c |
| 5 | Rhodamine B | Na ₂ SO ₄ | 3.4 ^c |
| 6 | Tetraphenylporphirin | Na ₂ SO ₄ | 25 ^d |
| 7 | Eosin Y | NaCl | 35 |
| 8 | Eosin Y | NaNO ₃ | 33 |
| 9 | Eosin Y | Na ₂ CO ₃ | 27 |
| 10 | Eosin Y | silica | 32 |
| 11 | Eosin Y | Na ₂ SO ₄ | 38 ^e |
| 12 | Eosin Y | Na ₂ SO ₄ | 39 ^f |
| 13 | Eosin Y | Na ₂ SO ₄ | 32 ^g |
| 14 | Eosin Y | Na ₂ SO ₄ | 29 ^h |
| 15 | Eosin Y | Na ₂ SO ₄ | 39 ⁱ |
| 16 | Eosin Y | Na ₂ SO ₄ | 33 ^d |
| 17 | - | Na ₂ SO ₄ | 3 ^c |
| 18 | Eosin Y | - | 33 ^j |
| 19 | Eosin Y | Na ₂ SO ₄ | 3 ^k |
| 20 | Eosin Y | Na ₂ SO ₄ | <2 ^{c,l} |

^a Standard conditions were: diphenylacetylene (0.2 mmol), 4-chlorothiophenol (0.4 mmol, 2 eq), photocatalyst (2 mol%) and anhydrous Na₂SO₄ (1.5 g). The input power of the reactor was 14.5 W, milling frequency 27 Hz using one 10 mm teflon ball. ^b GC yield using acetophenone as the internal standard after 6 hours. ^c After 3 hours. ^d Green LED reactor 14.5 W. ^e Aging. ^f 1.5 eq of 4-chlorothiophenol (0.3 mmol). ^g 1.0 eq of 4-chlorothiophenol (0.2 mmol). ^h 5.0 W. ⁱ 32.0 W. ^j In acetonitrile solution (0.1 M). ^k In the dark. ^l Under argon atmosphere.

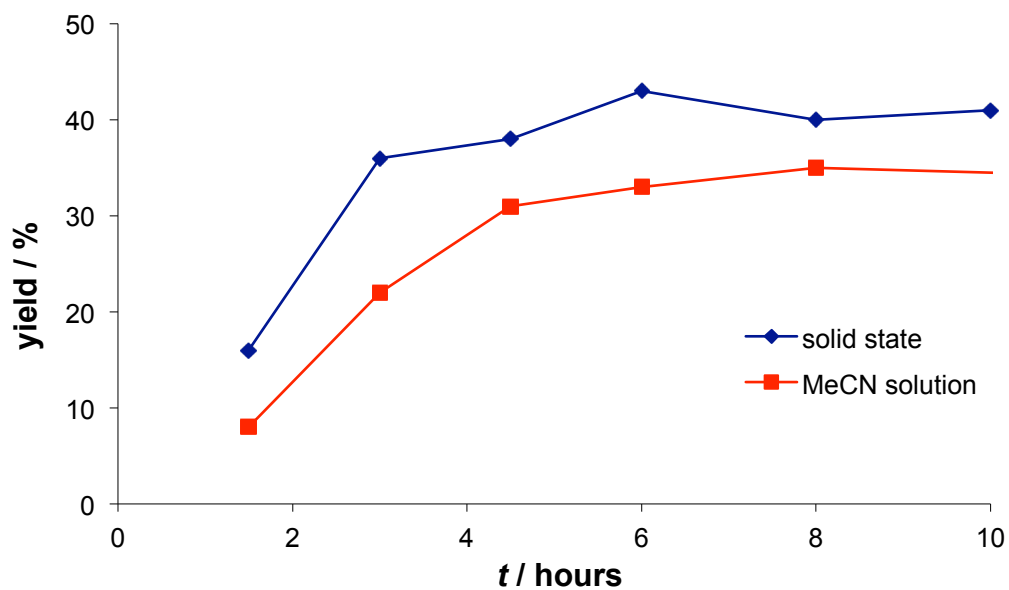


Figure S4. The performance of photocatalytic alkyne oxidation in the solid-state and in acetonitrile solution. Both reactions were performed under blue light irradiation using the LED reactor with 14.5 W input power. Comparable results for the solution reaction over 24 hours were also obtained using the blue 5 W LED strip.

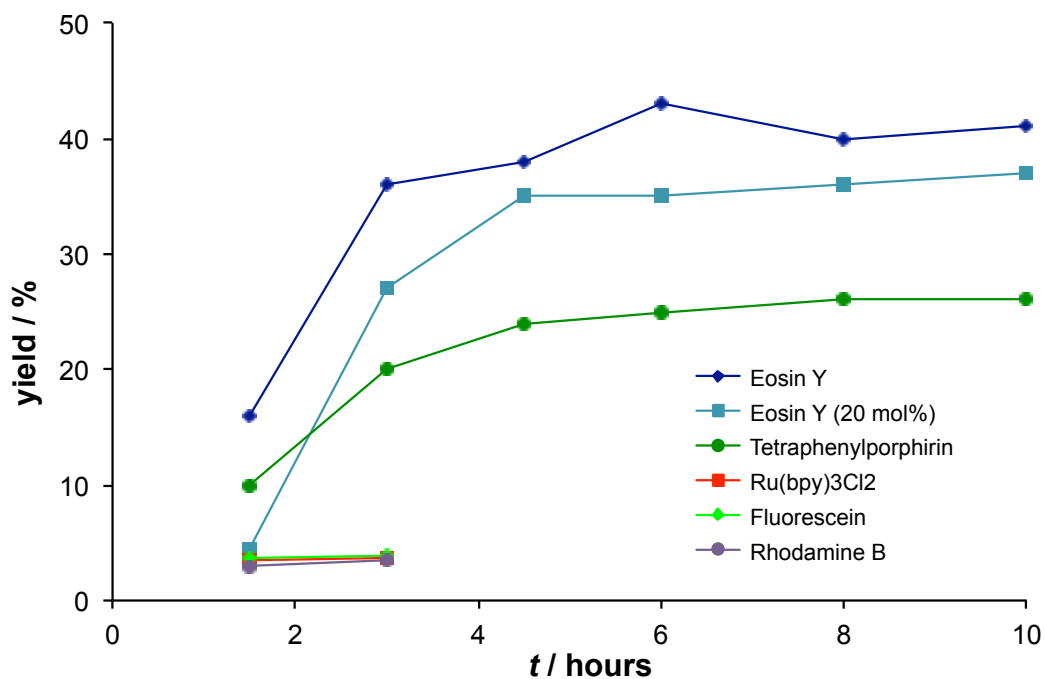


Figure S5. The effect of different photocatalysts on the yield of benzil in MASSPC. The catalyst loading was 2 mol%, unless otherwise stated.

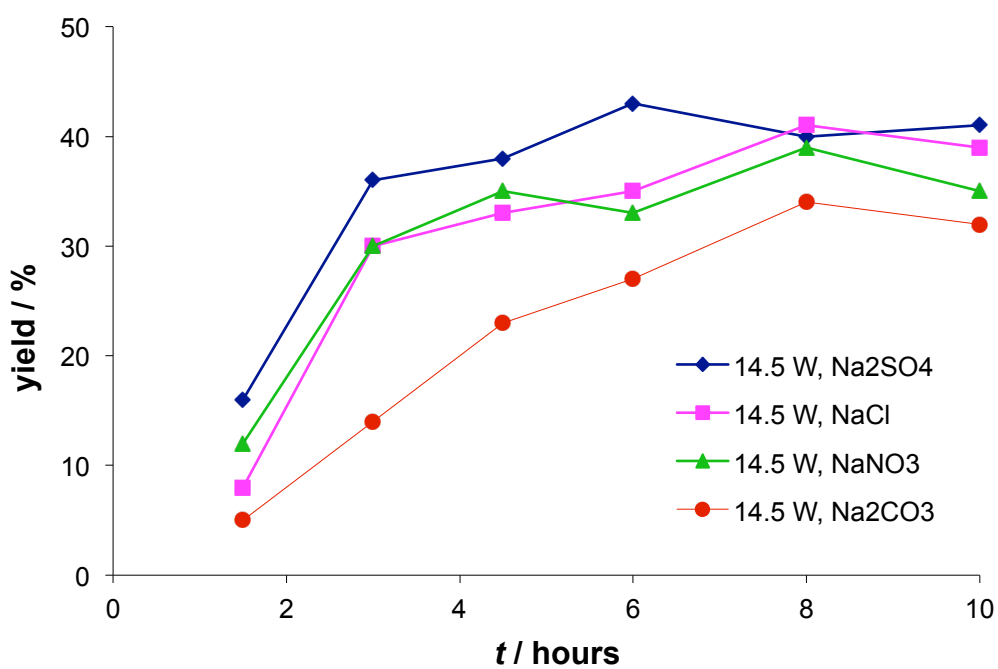


Figure S6. The effect of different solid supports on the yield of benzil in MASSPC. The amount of sodium salts was 1.5 g.

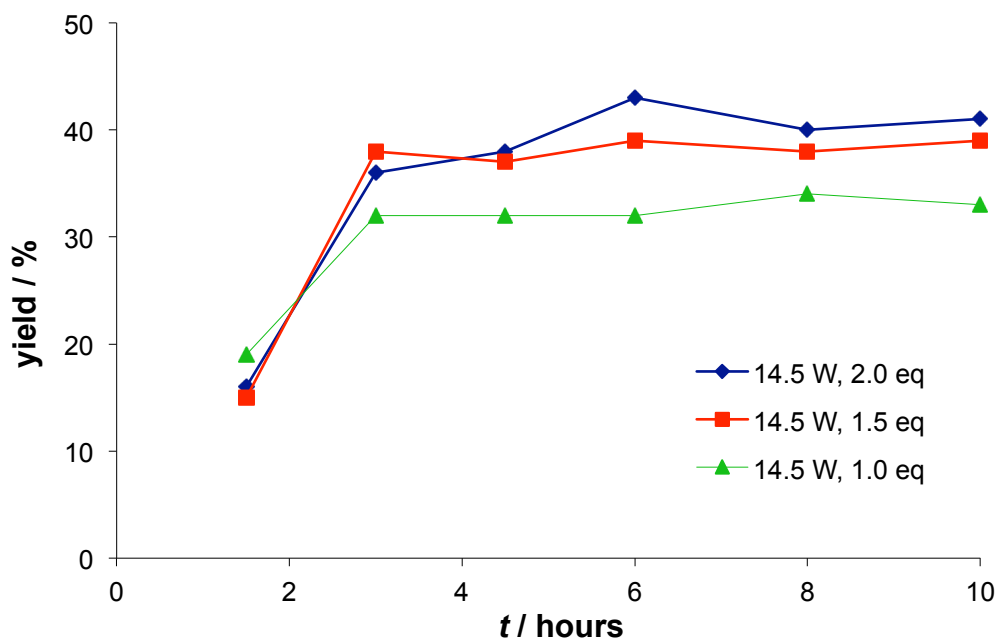


Figure S7. The effect 4-chlorothiophenol loading on the yield of benzil in MASSPC.

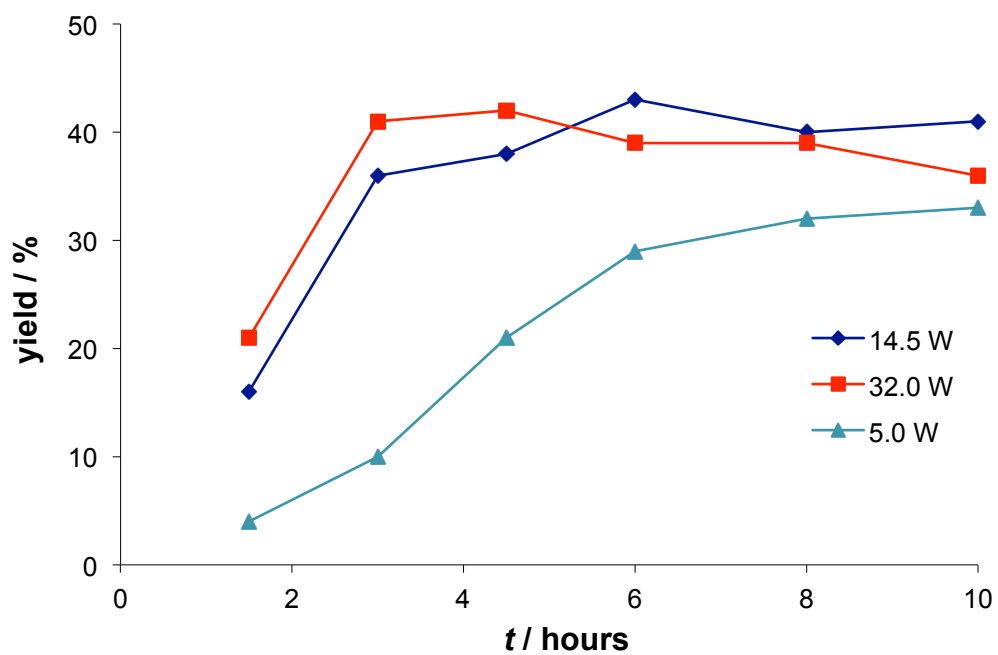


Figure S8. The effect of input power on the yield of benzil in MASSPC. The photodegradation of the product leads to diminished yields in the case of prolonged irradiation with 32.0 W reactor.

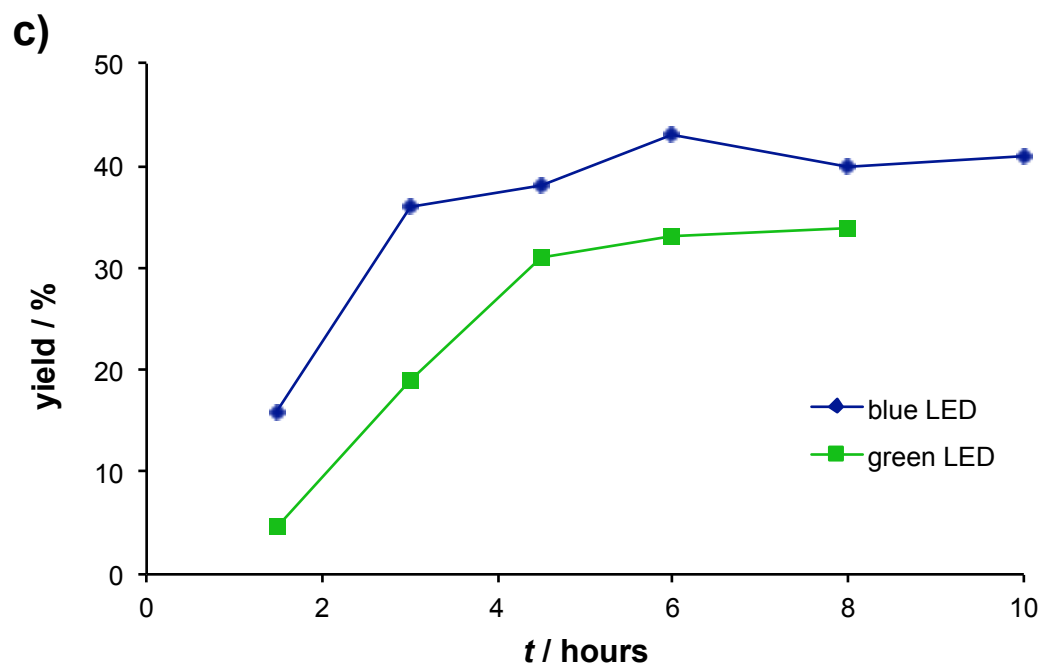
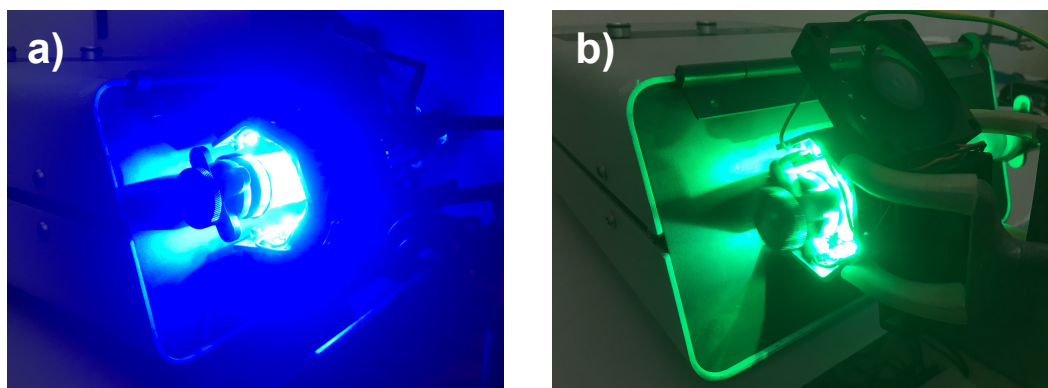


Figure S9. MASSPC reaction setup using a) blue and b) green light reactors. c) The comparison of MASSPC under blue and green light irradiation using 2 mol% of eosin Y as the photocatalyst. The power input was set to 14.5 W.

GC CHROMATOGRAMS

Table S2. Retention times of species detected in solution, aging and milling experiments. For details of the GC analysis, see General Comments.

| Compound | t_R / min |
|---|-------------|
| acetophenone (standard) | 3.4 |
| 4-chlorothiophenol (2) | 3.9 |
| benzoyl peroxide | 4.2 |
| diphenylacetylene (tolane, 1) | 6.0 |
| benzil (3) | 6.5 |
| S-(4-chlorophenyl)benzothioate (8) | 7.6 |
| bis(4-chlorophenyl)disulfide (4) | 8.5 |
| (<i>E</i>)-1-(4-chlorophenylthio)stilbene (<i>E</i> - 5) | 12.4 |
| (<i>Z</i>)-1-(4-chlorophenylthio)stilbene (<i>Z</i> - 5) | 14.0 |

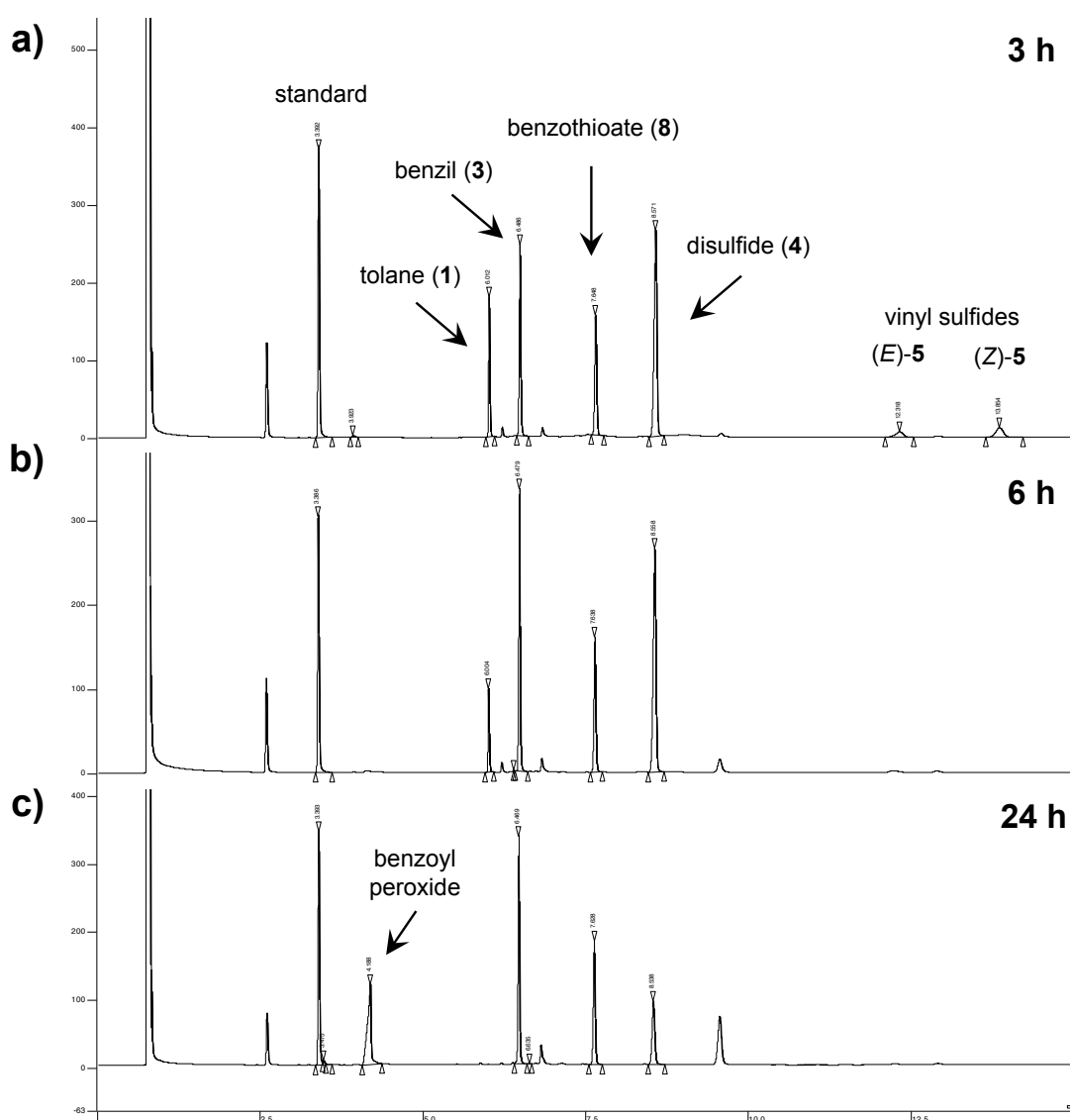


Figure S10. GC chromatograms of the solution reaction in acetonitrile after a) 3 h, b) 6 h and c) 24 h. Besides the desired product benzil (**3**), bis(4-chlorophenyl)disulfide (**4**) and S-(4-chlorophenyl)benzothioate (**8**) are the main byproducts. Prolonged exposure to visible light results in loss of benzil and the formation of benzoyl peroxide.

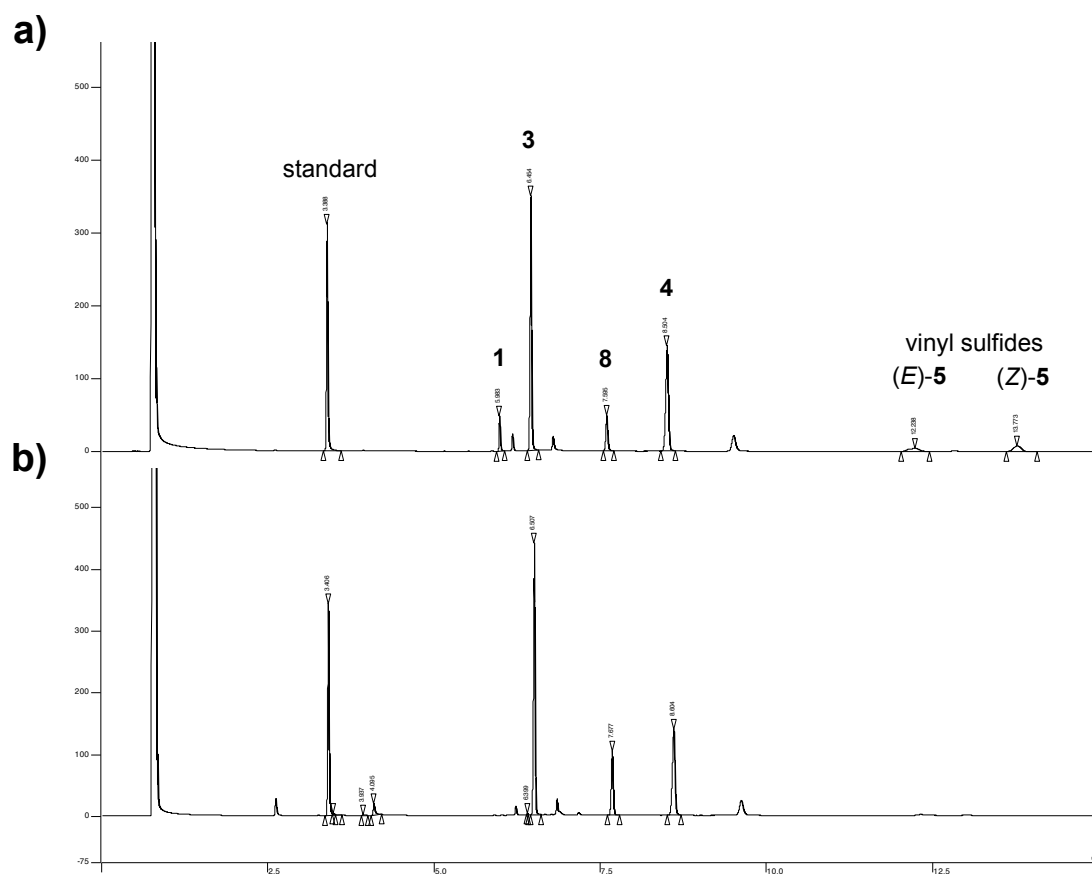


Figure S11. GC chromatograms after 6 hours of a) aging and b) milling (MASSPC) in air under blue light irradiation.

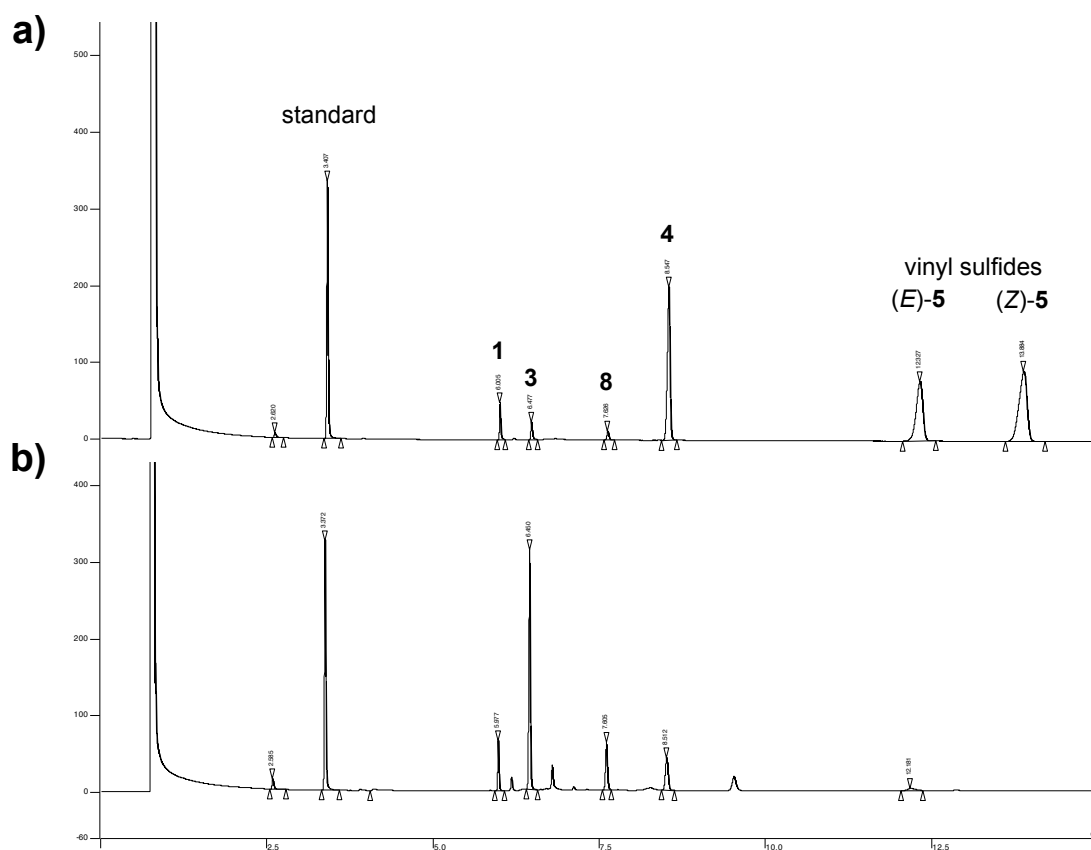


Figure S12. GC chromatograms of MASSPC reactions. a) 3 h with $\text{Ru}(\text{bpy})_3\text{Cl}_2$ catalyst and b) 6 h with eosin y catalyst in the presence of 1.0 eq of 4-chlorothiophenol (**2**). In this case, thiyl radicals recombine to disulfide **4** at a faster rate than they react with the alkyne **1**, resulting in its incomplete consumption.

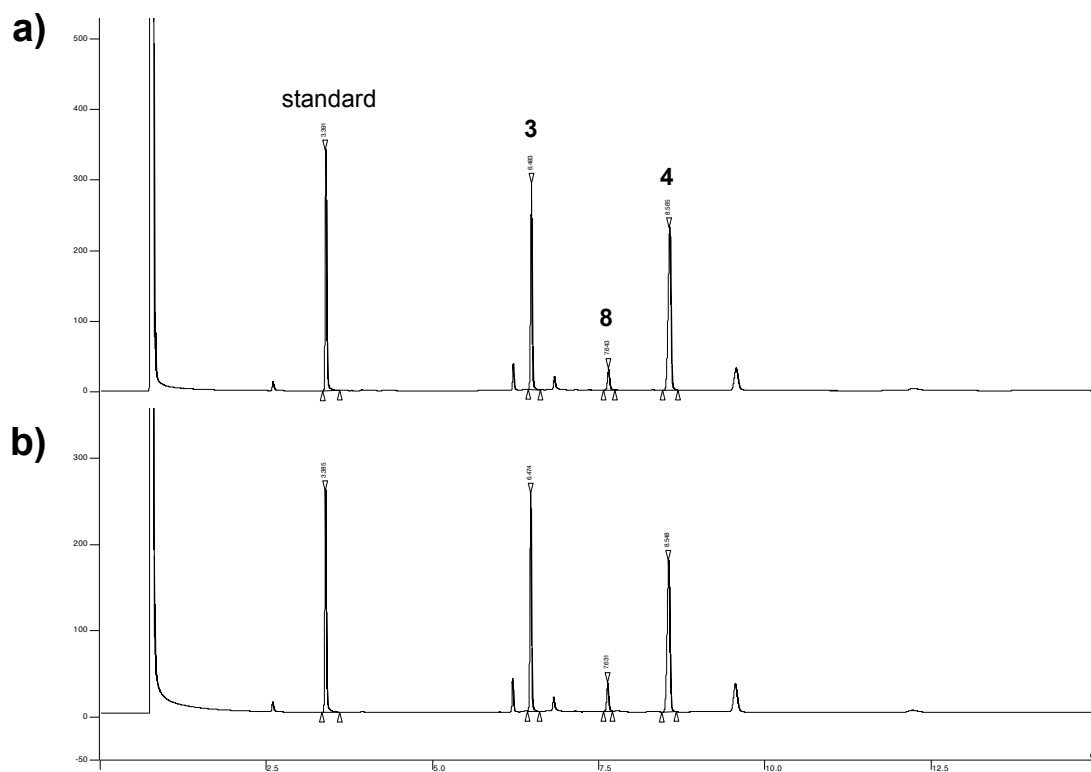


Figure S13. GC chromatograms of MASSPC reactions after 6 hours using a) blue LED reactor at 5.0 W and b) green LED reactor at 14.5 W input power.

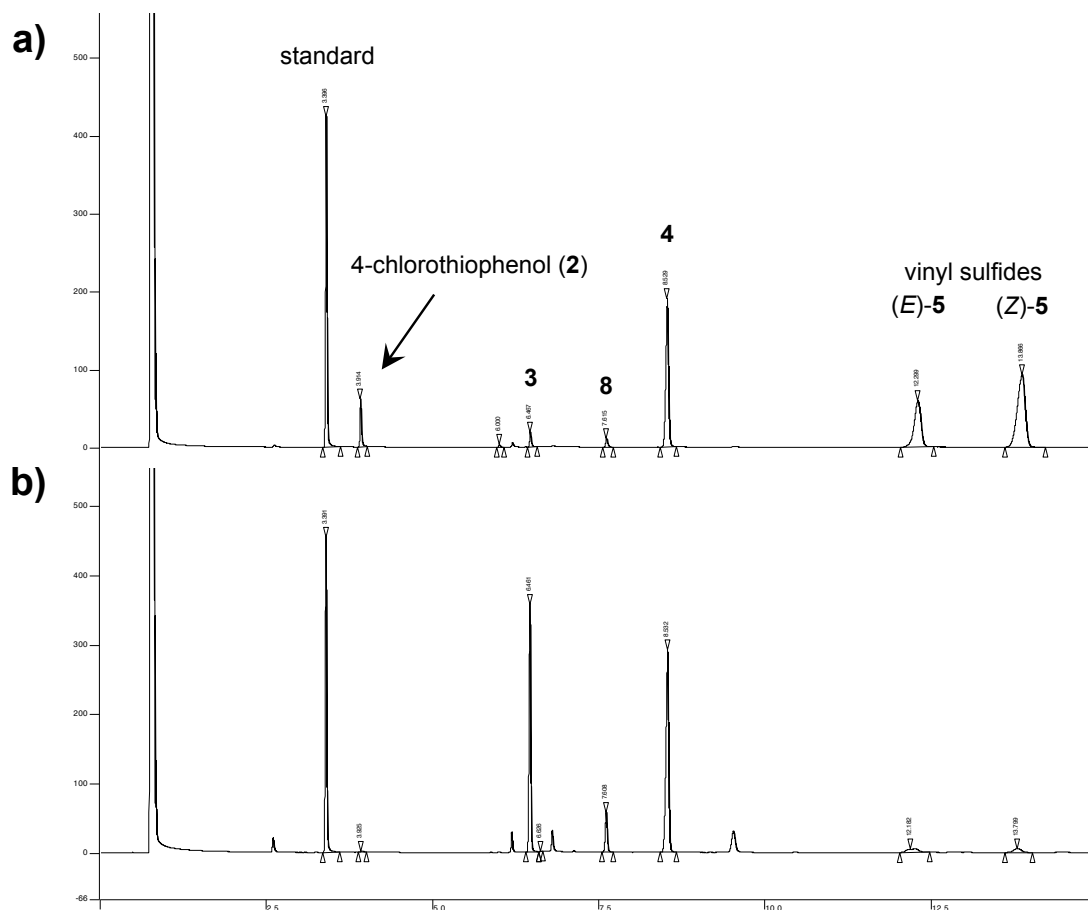


Figure S14. GC chromatograms of MASSPC reaction after a) 6 h in the dark and b) 2 h under blue light irradiation of the mixture (a). The starting materials efficiently reacted even in the absence of light to afford disulfide **4** and a mixture of vinyl sulfides (*E*)-**5** and (*Z*)-**5**. Switching the light on led to almost quantitative conversion of vinyl sulfides to benzil (**3**) and benzothioate **8**. Also, the amount of disulfide **4** in the mixture increased after exposure to blue light.

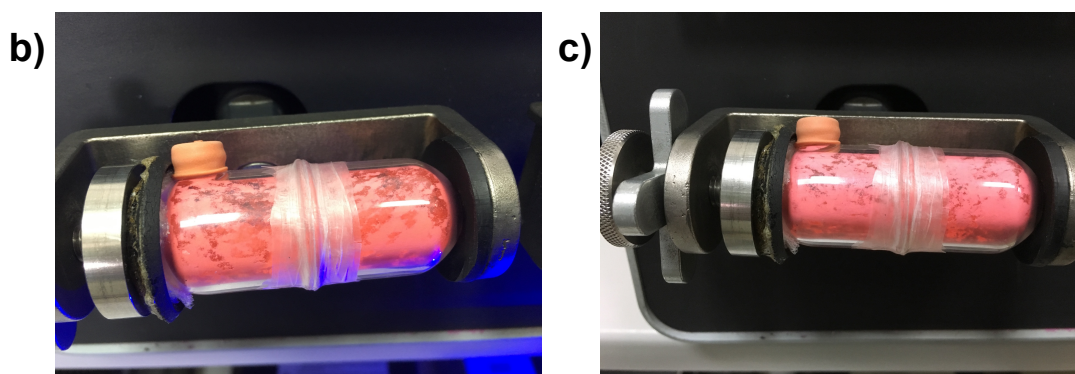
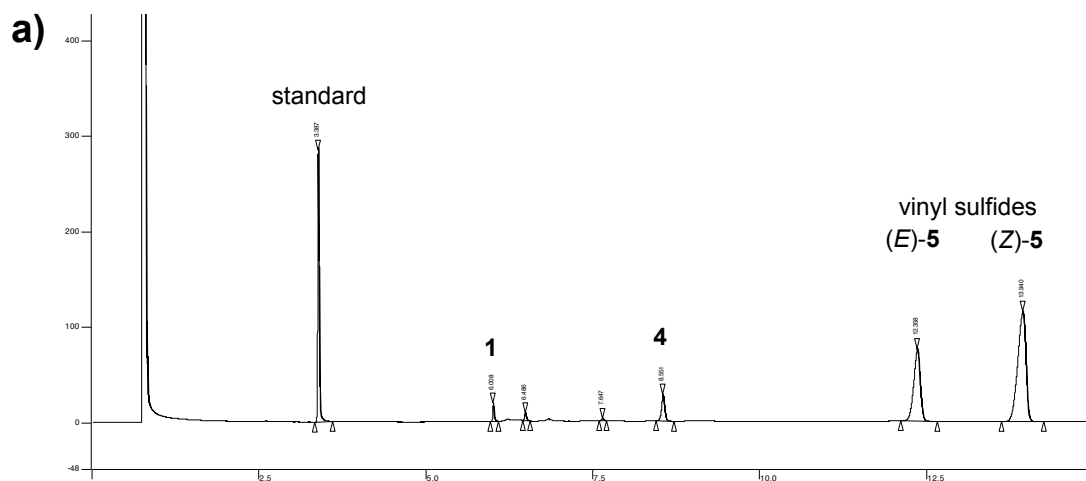
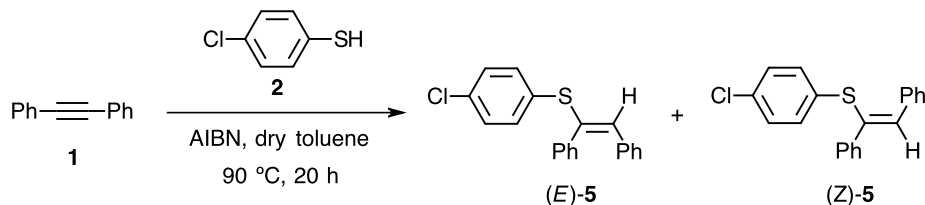


Figure S15. a) GC chromatogram of the reaction carried out in argon atmosphere and irradiated under blue light for 3 hours. Thiophenol and diphenylacetylene (**1**) (traces still present) nearly quantitatively transformed to the isomeric mixture of vinyl sulfides (*E*)-**5** and (*Z*)-**5**. b) and c) The appearance of the reaction mixture after 90 minutes and 3 hours, respectively. Notably, the colour is retained in the absence of oxygen suggesting that the photobleaching observed for aging and milling in air is oxygen-promoted. This experiment also indirectly supports the proposed mechanism where eosin Y as the photocatalyst generates singlet oxygen as the reactive species.

SYNTHESIS AND PHOTOREACTIVITY OF VINYL SULFIDE ISOMERS

Synthesis and characterisation of 1-(4-chlorophenylthio)stilbene (**5**)

In order to confirm the photoreactivity of vinyl sulfide isomers detected by GC, an independent solution synthesis of **5** was carried out.²



Diphenylacetylene (128.2 mg, 0.72 mmol), AIBN (8.2 mg, 0.05 mmol) and 4-chlorothiophenol (173.5 mg, 1.2 mmol) were dissolved in dry toluene (1.0 mL) and the solution was purged with argon for 15 minutes. The reaction mixture was heated at 90 °C for 20 h under argon. The solvent was evaporated and the mixture purified by column chromatography, first using petroleum ether to remove excess thiophenol and disulfide, and then petroleum ether : dichloromethane (1:1) to isolate pure vinyl sulfide isomer mixture as a pale yellow solid (225 mg, 97 %). GC analysis indicated *E* : *Z* = 38 : 62.

δ_{H} (300 MHz; d_6 -DMSO; TMS) 6.97–7.00 (2 H, m, Ar^{E}), 7.01 (1 H, s, H^{E}), 7.12–7.15 (3 H, m, Ar^{Z}), 7.19 (2 H, d, J 8.7 Hz, Ar^{Z}), 7.24 (2 H, d, J 8.7 Hz, Ar^{Z}), 7.25–7.35 (overlapped Ar^{E} + Ph^{Z}), 7.36 (1 H, d, J 8.6 Hz, Ph^{Z}), 7.40 (2 H, t, J 7.7 Hz, Ph^{Z}), 7.43 (1 H, s, H^{Z}), 7.67 (2 H, d, J 7.3 Hz, Ph^{Z}), 7.73 (2 H, d, J 7.5 Hz, Ph^{Z}).

δ_{C} (150 MHz; d_6 -DMSO; TMS) 127.4, 127.7, 128.08, 128.11, 128.17, 128.31, 128.35, 128.5, 128.8, 128.9, 129.0, 129.3, 129.4, 130.1, 130.7, 131.7, 132.14, 132.15, 132.5, 132.9, 133.7, 135.7, 135.8, 136.1, 136.7, 137.0, 139.8.

ν_{max} / cm^{-1} 3017, 1596, 1489, 1474, 1444, 1390, 1092, 1007, 939, 916, 811, 765, 692, 588, 551, 503, 486.

2. R. Pöttsch, H. Komber, B. C. Stahl, C. J. Hawker and B. I. Voit, *Macromol. Rapid Commun.*, 2013, **34**, 1772.

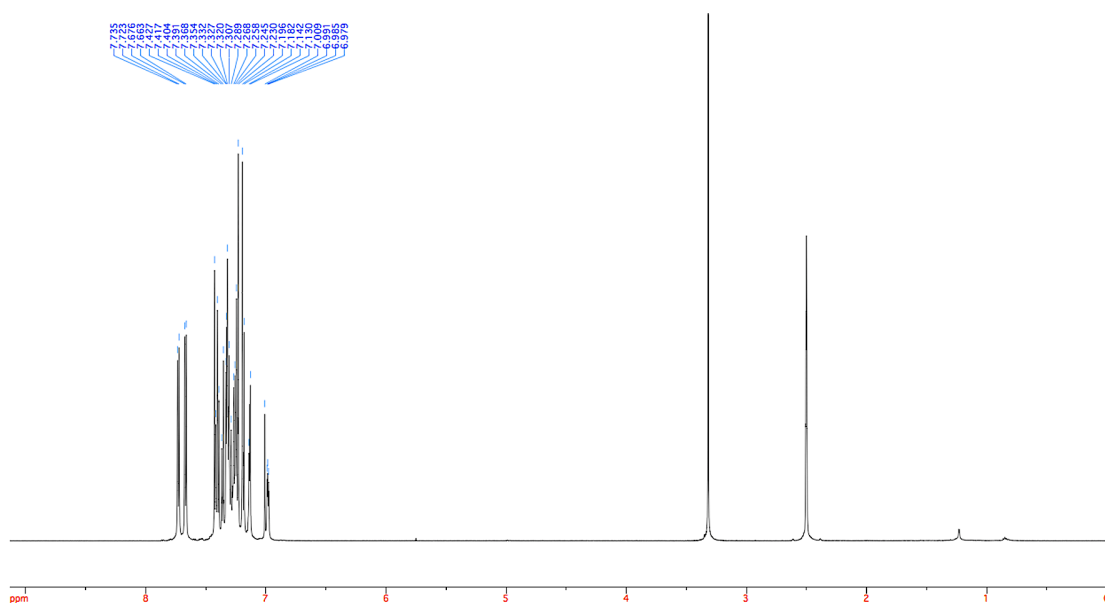


Figure S16. Full ^1H NMR spectrum in d_6 -DMSO of the isomer mixture (*E*)-**5** and (*Z*)-**5** isolated after MASSPC reaction under argon.

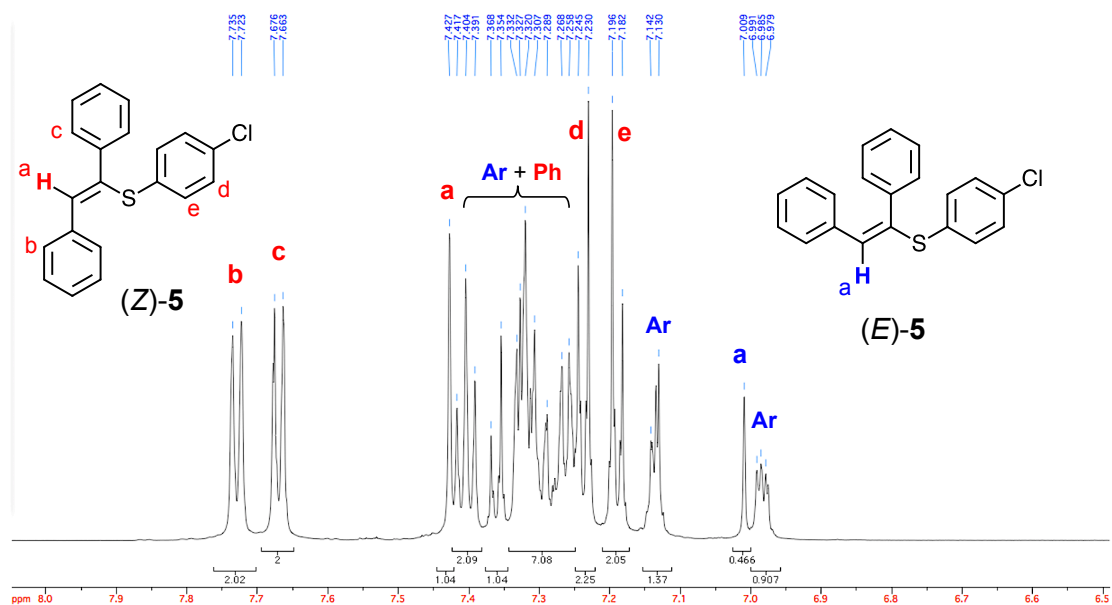


Figure S17. Close-up view of the aromatic region.

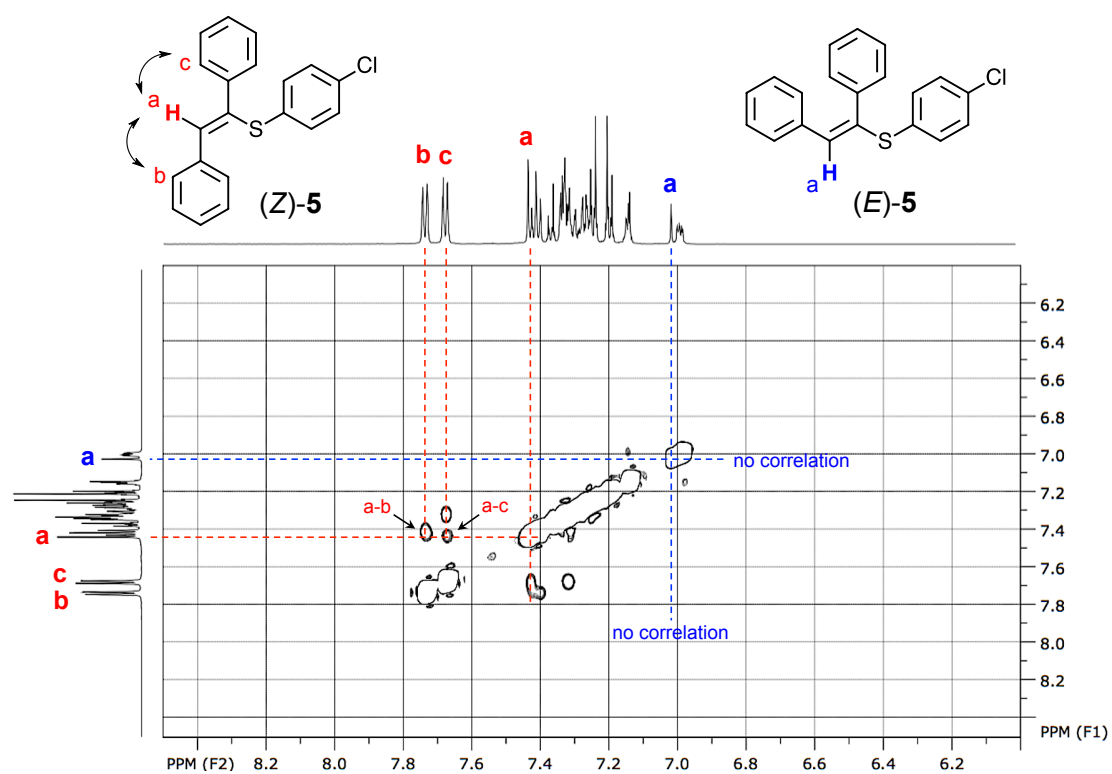


Figure S18. NOESY spectrum of (E,Z) -5.

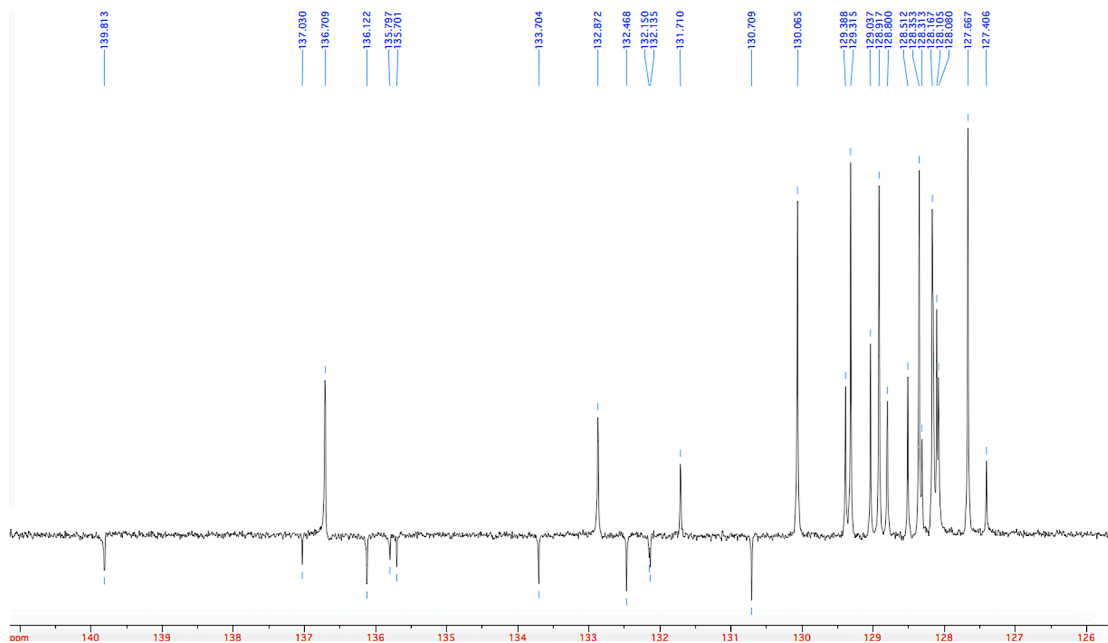


Figure S19. ^{13}C NMR spectrum in d_6 -DMSO of the isomer mixture (*E*)-5 and (*Z*)-5.

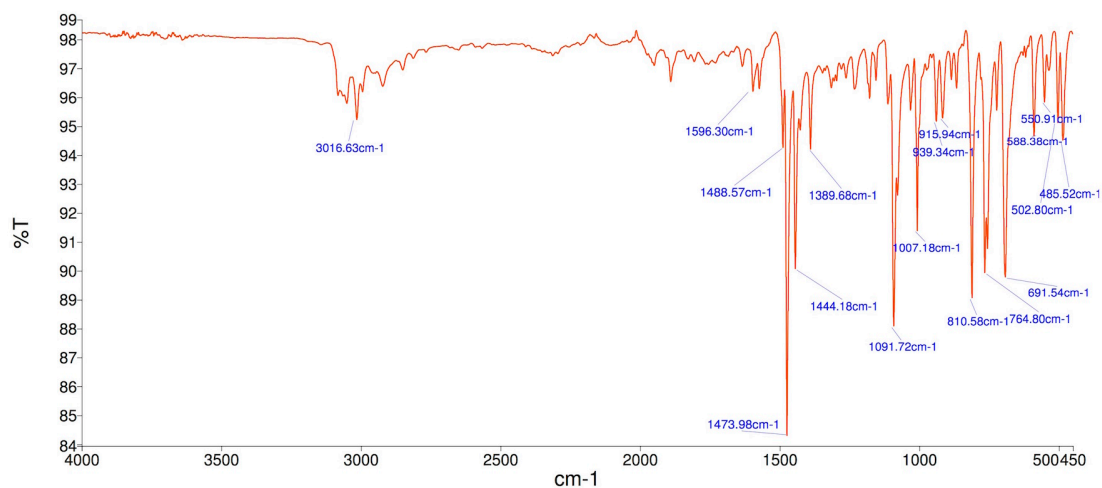


Figure S20. FTIR-ATR spectrum of the isomer mixture (*E*)-5 and (*Z*)-5.

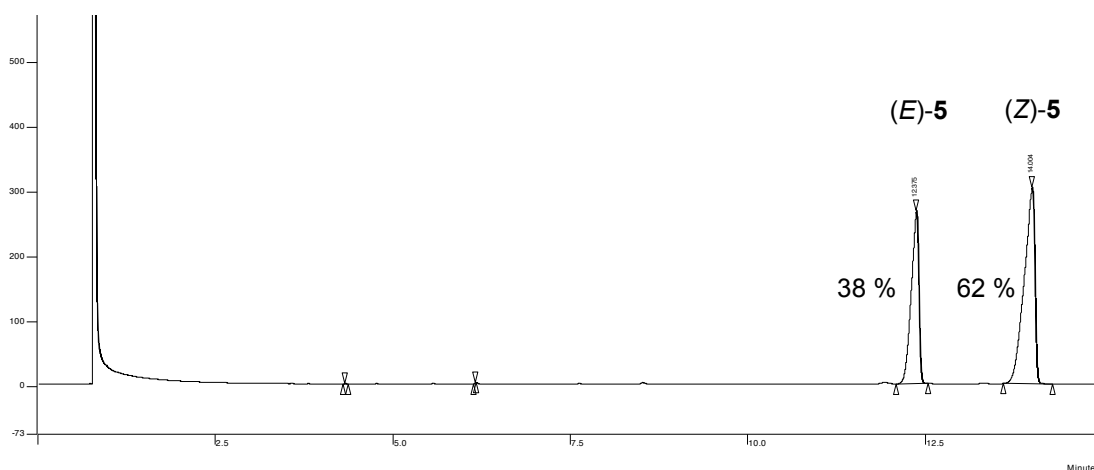


Figure S21. GC chromatogram of the mixture obtained by solution synthesis.

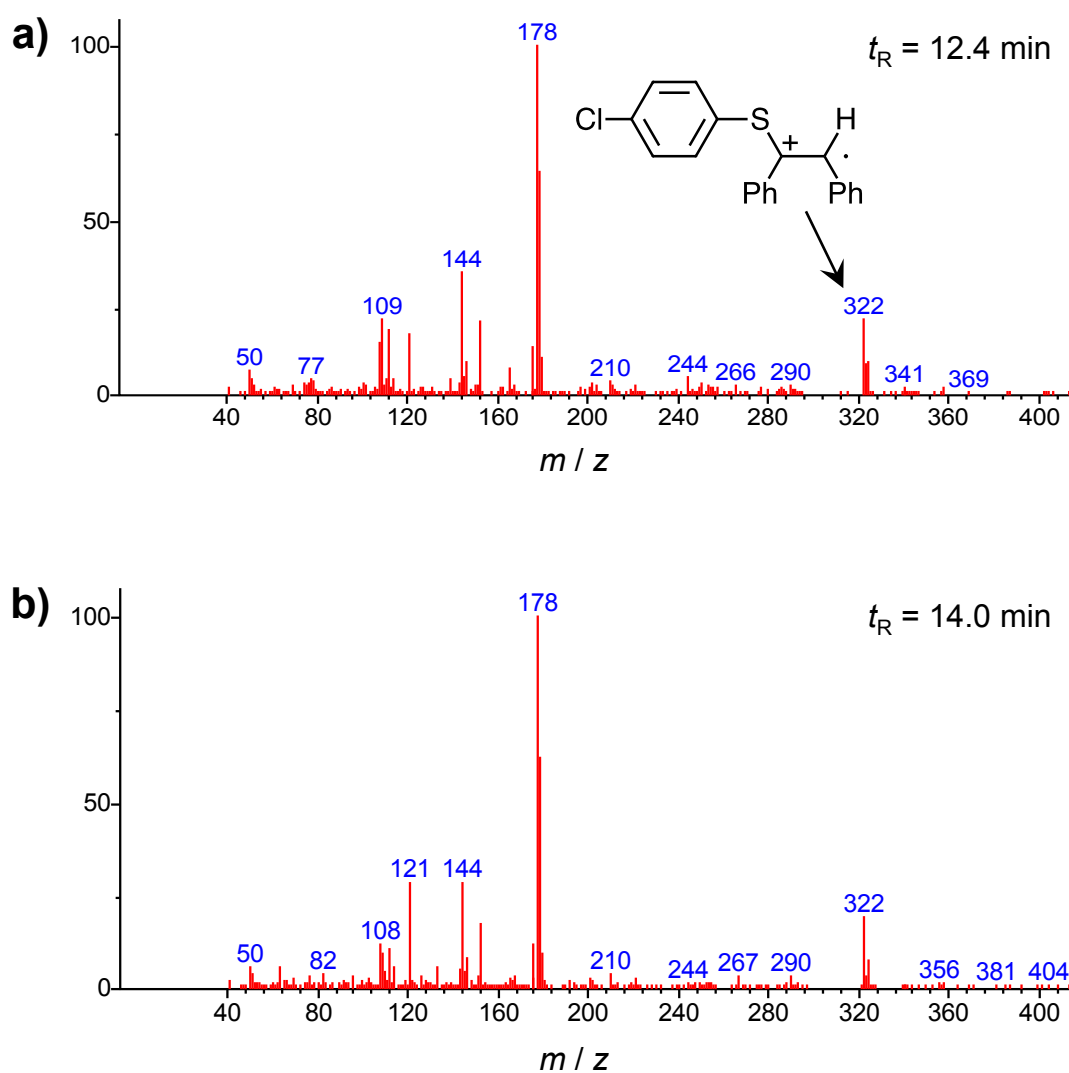


Figure S22. GC-MS analysis of vinyl sulfide isomers, $t_R(E-5) = 12.4$ min and $t_R(Z-5) = 14.0$ min. The MS spectra are almost identical with the molecular ion peak at m/z 322 and consistent with the proposed structure.

Photoreactivity of 1-(4-chlorophenylthio)stilbene (**5**)

A sample of (*E,Z*)-1-(4-chlorophenylthio)stilbene (64.6 mg, 0.2 mmol) (**5**) was dissolved in 600 μ L of dichloromethane and applied on sodium sulfate support (1.5 g) in a mortar. The mixture was homogenized by gentle manual grinding. Then eosin Y (2.6 mg, 2 mol%) was added, again briefly ground and milled in a 20 mL glass jar at 27 Hz while simultaneously irradiated under blue light. The input power of the reactor was set to 14.5 W. In the experiment with 4-chlorothiophenol additive, 1.0 eq was added (28.9 mg, 0.2 mmol). The yield of benzil was determined by GC analysis.

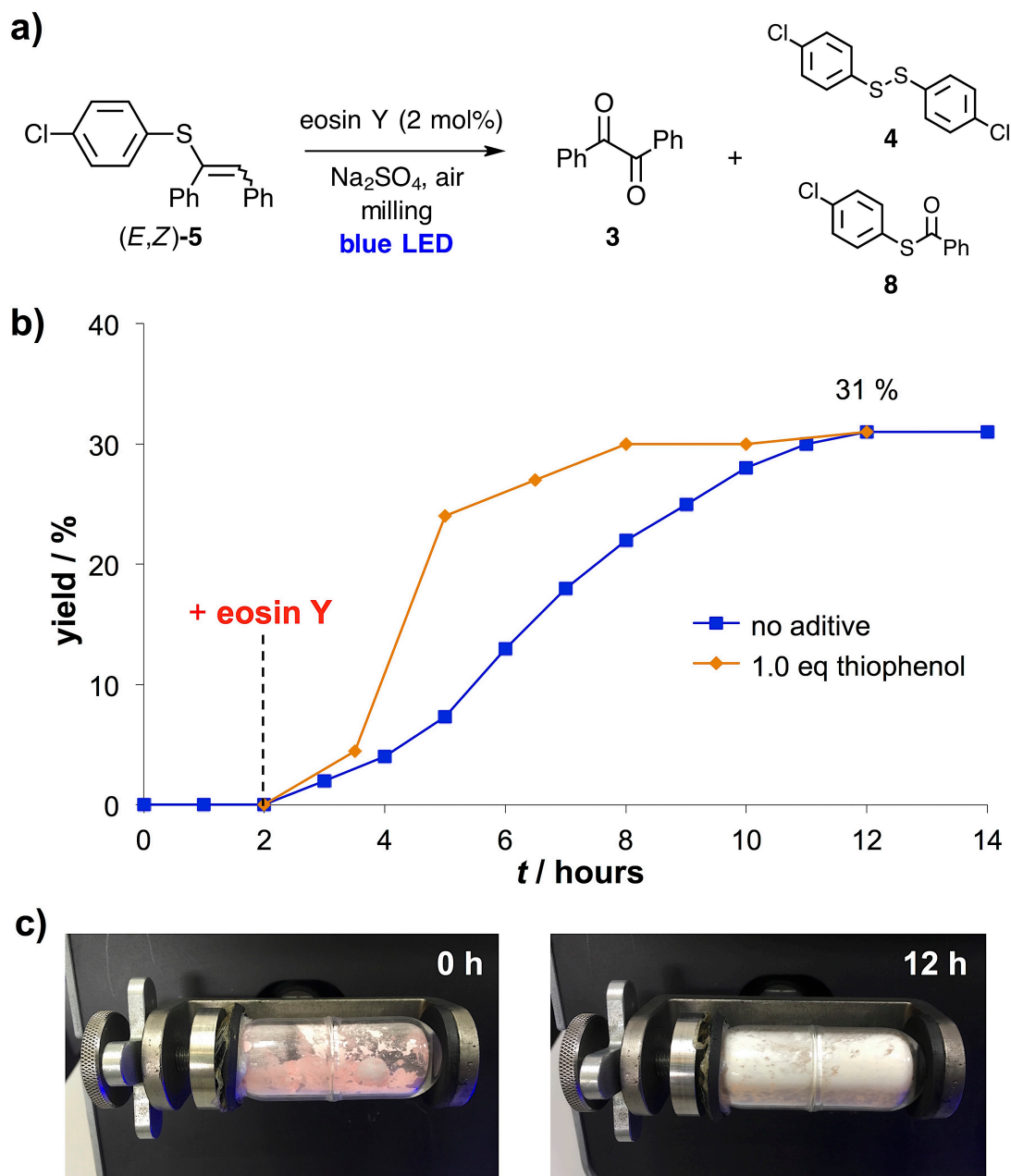


Figure S23. a) The reactivity of **5** in MASSPC reaction with eosin Y as the photocatalyst. b) Monitoring of benzil (**3**) formation from the mixture of (*E*)- and (*Z*)-**5** by simultaneous ball milling and blue light irradiation. After 2 hours, 2 mol% of eosin Y was added resulting in the photocatalytic conversion of (*E,Z*)-**5** to **3**. c) Colour change before (0 h; $t_{\text{tot}} = 2$ h) and after the reaction (12 h; $t_{\text{tot}} = 14$ h) in the presence of eosin Y. Presumably, the generation of singlet oxygen led to photobleaching of the photocatalyst and its discoloration.

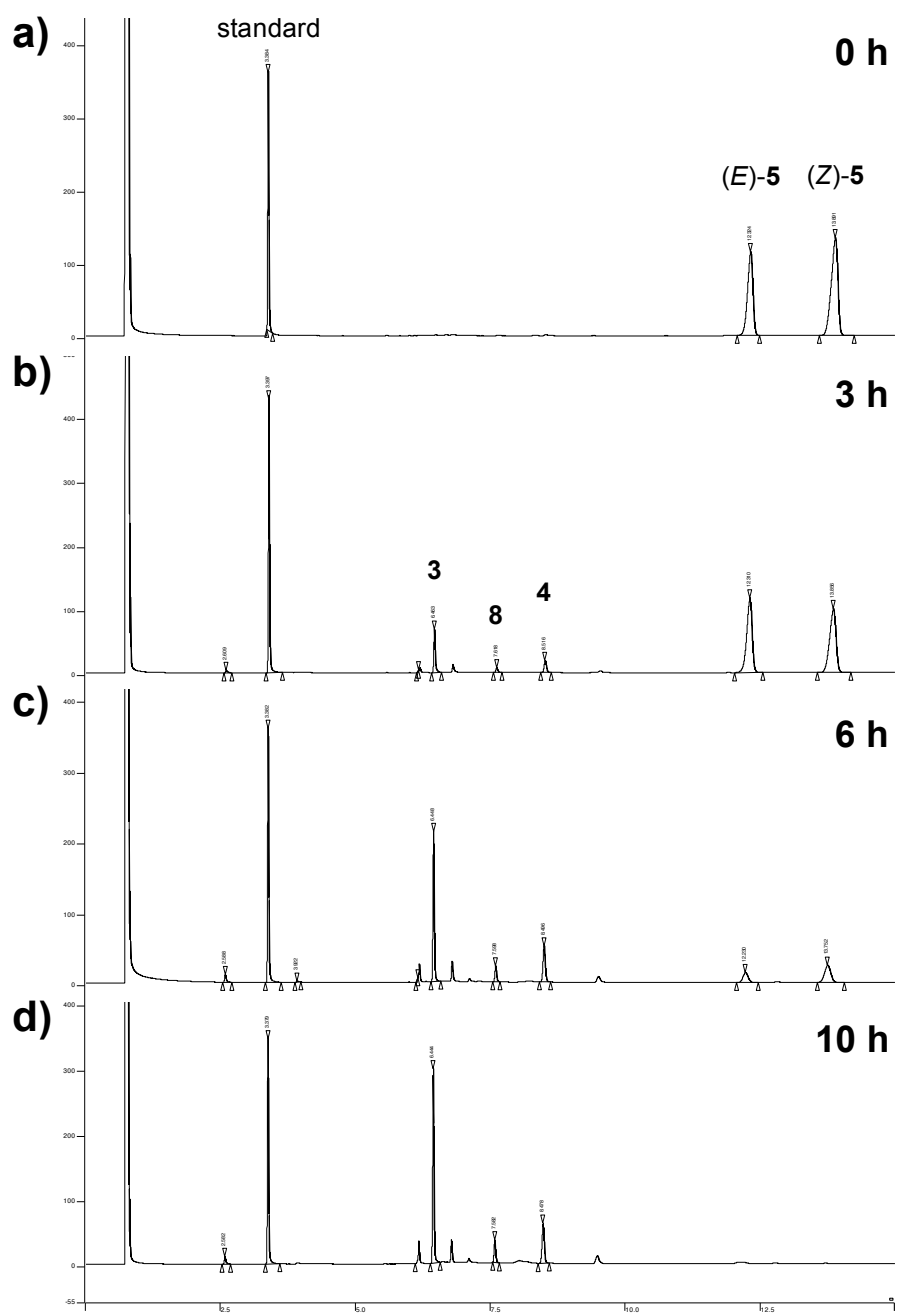


Figure S24. Monitoring of the photocatalytic conversion of (E,Z)-5 to 3 by GC. The reaction time refers to the eosin Y-catalysed reaction.

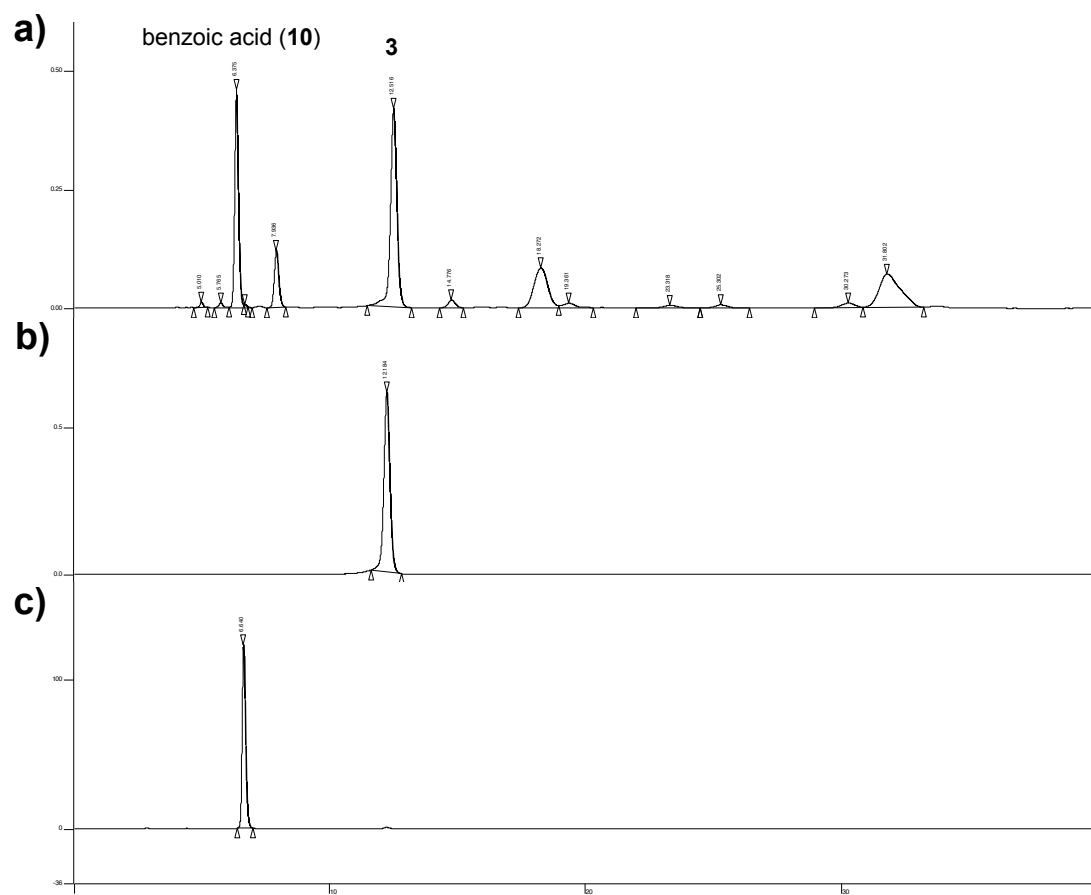


Figure S25. HPLC analysis of a) the crude reaction mixture after photocatalytic conversion of (*E,Z*)-**5** to **3**, b) benzil (**3**) sample and c) benzoic acid (**10**) sample. HPLC analysis was done using Restek Ultra IBD column (25 x 4.6 mm) with 2% acetic acid : methanol = 50 : 50, 254 nm, and a flow rate 1.0 mL min⁻¹.

GENERATION OF SINGLET OXYGEN BY MASSPC

A mixture of eosin Y (2.6 mg,) anthracene (17.8 mg, 0.1 mmol) and anhydrous sodium sulfate (750 mg) was ball milled for 3 hours at 27 Hz under blue light irradiation (14.5 W) using a 10 mm teflon ball. TLC analysis of the reaction mixture in chloroform : hexane (3:1) (Figure S25) revealed the presence of unreacted anthracene (left) and anthracene-9,10-endoperoxide (right) with a characteristic R_f value 0.33 (middle).

The peroxide sample for TLC analysis was synthesised independently according to literature procedure.³

3. M. Klaper, P. Wessig and T. Linker, *Chem. Commun.*, 2016, **52**, 1210.

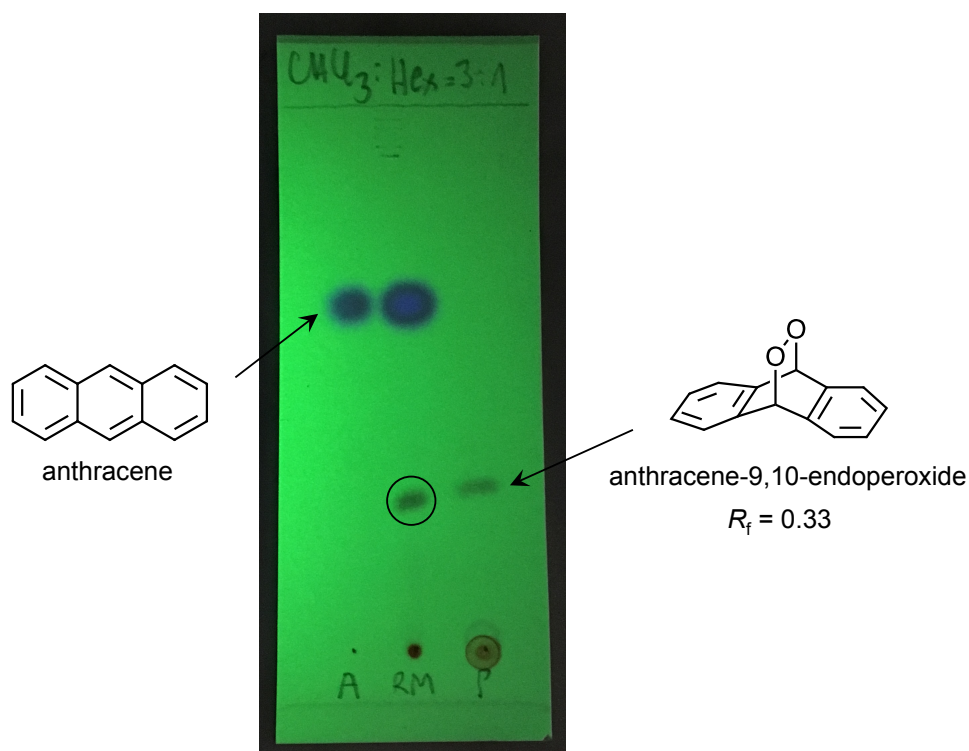


Figure S26. Quenching of singlet oxygen using anthracene during MASSPC reaction.

MONITORING OF DISULFIDE 4 FORMATION BY MASSPC

The formation of disulfide **4** during photocatalytic oxidation of vinyl sulfide **5** was established by GC analysis using acetophenone as the internal standard. The yield of **4** is also given for the standard reaction performed in the dark for 6 hours followed by blue light irradiation for 4 hours. In this case, the formation of disulfide **4** took place even in the absence of light due to the residual mechanochemical reaction between diphenylacetylene and 4-chlorothiophenol (in excess). When the mixture was exposed to blue light, the yield of disulfide **4** again increased as a result of the photocatalytic oxidation of vinyl sulfide **5** (Figure S27a).

To test if disulfide **4** underwent a reaction with singlet oxygen, a mixture of **4** (28.7 mg, 0.1 mmol), eosin Y (2.6 mg) and anhydrous sodium sulfate (1.5 g) was ball milled for 2 hours in the dark, followed by 3 hours under blue light irradiation. The yield did not change significantly indicating the absence of reactivity with singlet oxygen (Figure S27b).

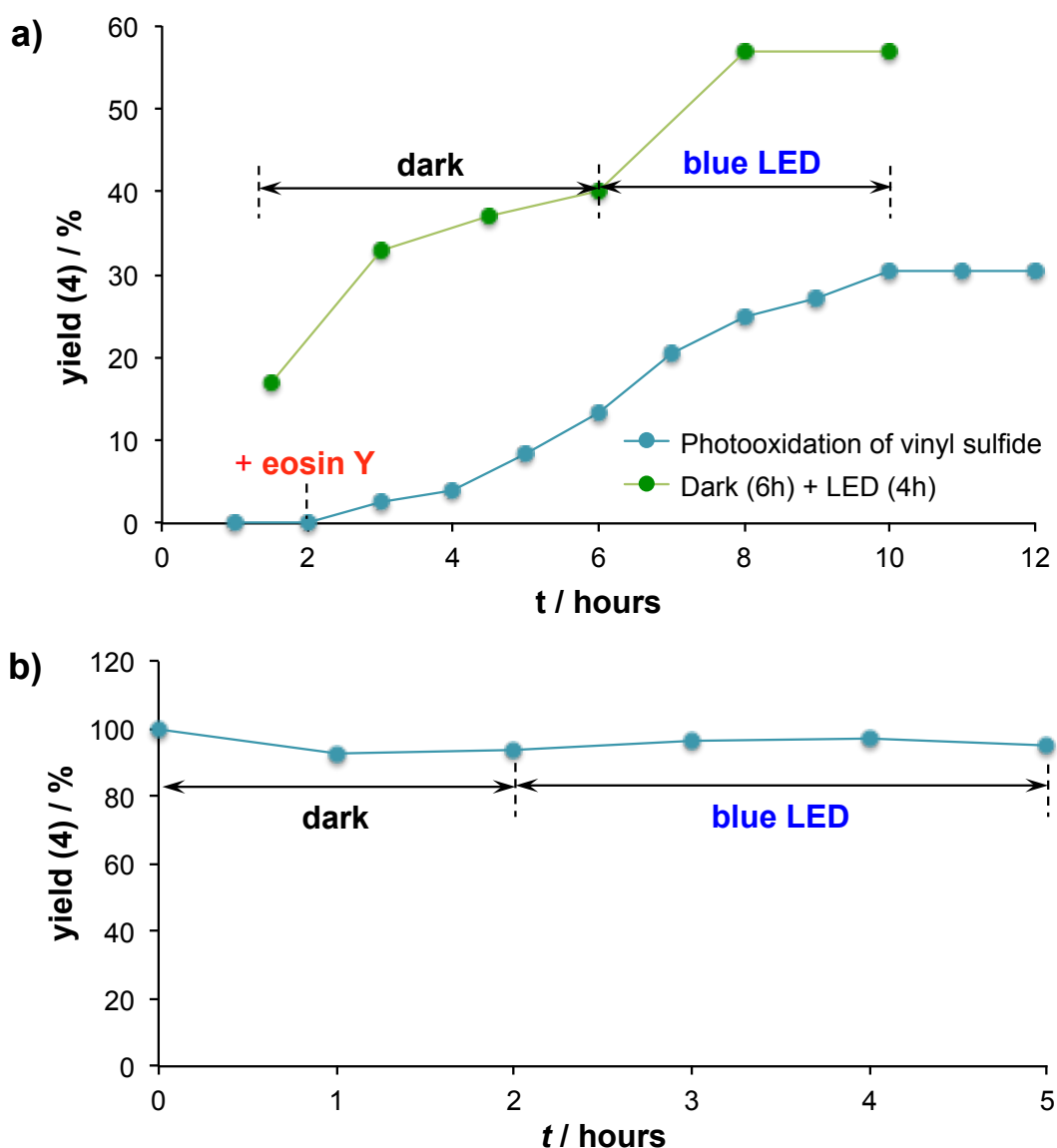


Figure S27. a) The change in disulfide **4** yield for the photocatalytic oxidation of vinyl sulfide **5** (turquoise curve) and for the standard reaction (starting from diphenylacetylene and thiophenol) in the dark and under blue light (green curve). b) The absence of reactivity between **4** and singlet oxygen under MASSPC reaction conditions.