Supplementary Material

High-throughput evaluation of potential commercial photocatalysts: investigation of Sudan Black B

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S1-General information

Materials and equipment

Unless otherwise noted, all reactions were carried out in oven-dried glassware. Commercially available chemicals were purchased from ABCR, Acros Organics, Sigma-Aldrich, Alfa Aesar, Combi-Blocks, Carbolution, Fluorochem, BLD Pharm and TCI Europe and used as received unless otherwise stated. The following solvents were dried by distillation over the drying agents indicated in parentheses: THF (Sodium) and dichloromethane (CaH_2). Additional anhydrous solvents were purchased from Acros Organics, SigmaAldrich, Alfa Aesar and stored over molecular sieves under an argon atmosphere.

LC-MS spectra were recorded on a Waters Acquity UPLC® equipped PDA eλ Detector and SQ Detector 2, mobile phase A: H_2O + 0.1% formic acid, mobile phase B: acetonitrile + 0.1% formic acid.

For HTE plate analysis the following analytical method was used: Run length 8 min; column type: ACQUITY UPLC® CSH™ Phenyl-Hexyl 1.7 µm; gradient (see **Error! Reference source not found.** below).

Table S1. Gradient table for HTE plate analysis

Time (min)	Flow rate (mL/min)	%A	%B
Initial	0.4	95.0	5.0
6.00	0.4	0.0	100.0
6.10	0.6	0.0	100.0
7.00	0.6	0.0	100.0
7.10	0.6	95.0	5.0
7.99	0.6	95.0	5.0
8.00	1.0	95.0	5.0

Photobox set-up

Batch photoredox reactions were run using KESSIL lamps PR160L (420 nm, 660 nm and 740 nm). The photobox set-up is composed of a plexiglass box covered by an inactinic orange lab film. 3 magnetic stirring plates are placed in the photobox, with 3 fans. The top and the back of box were let open for an optimum air circulation. The whole photobox was placed in a fume hood.

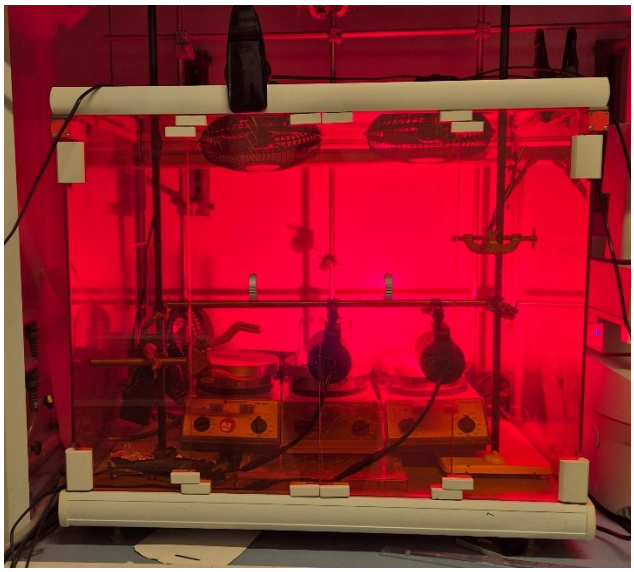


Figure S1. Picture of the photobox set-up used for batch experiments.

Vials/samples are placed at 3 cm from the LEDs (except if a different set-up is specified), to ensure a good reproducibility of all experiments across the project (Figure S2, a.). Up to 3 vials were placed in front of each Kessil LED to afford maximal light intensity based on the intensity map provided by Kessil® (Figure S2, b.)

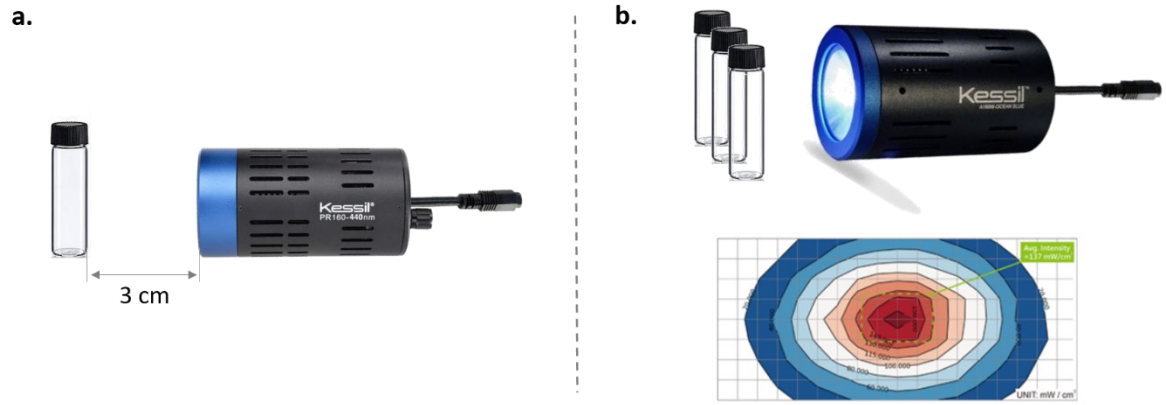


Figure S2. a. Scheme representing the distance between vials and Kessil lamps; b. Scheme of the number of vials placed in front of the lamp and Intensity map provided by Kessil® (pictures from https://www.kessil.com/products/science_PR160L.php).

S2-High-throughput screening of dyes

S2.1- HTE campaign

General procedure of the HTE campaign

Materials description

The screening of reaction conditions was performed in a 96-well plate format using 1 mL vials with 100uL of solvent (8 x 30 mm vials number 884001 from Analytical Sales and Services Figure S3 b.) in a Paradox reactor (96973 from Analytical Sales and Services, Figure S3c). The homogeneous stirring was controlled with a Stainless Steel, Parylene C Coated stirring elements (Analytical Sales and Services, Figure S3 a.) and a tumble stirrer (VP 711D-1 and VP 710 Series from V&P Scientific, Figure S4). The liquid dispensing was performed using calibrated manual pipettes and multipipettes (Fisher/Eppendorf). The Paradox reactor was irradiated with a Lumidox II generation and associated controller (420: LUM296LS420; 660 nm: LUM296LS660 and 730 nm: LUM296LS730 Figure S3d and e). The Paradox system is cooled with 2 fans (see set-up photobox above) and a PR160 Rig With Fan Kit from KESSIL. The HTE experiments were designed using an in-house software called HTDesign® and developed by the GIPSI team at CEA Paris-Saclay (DRF/Joliot).

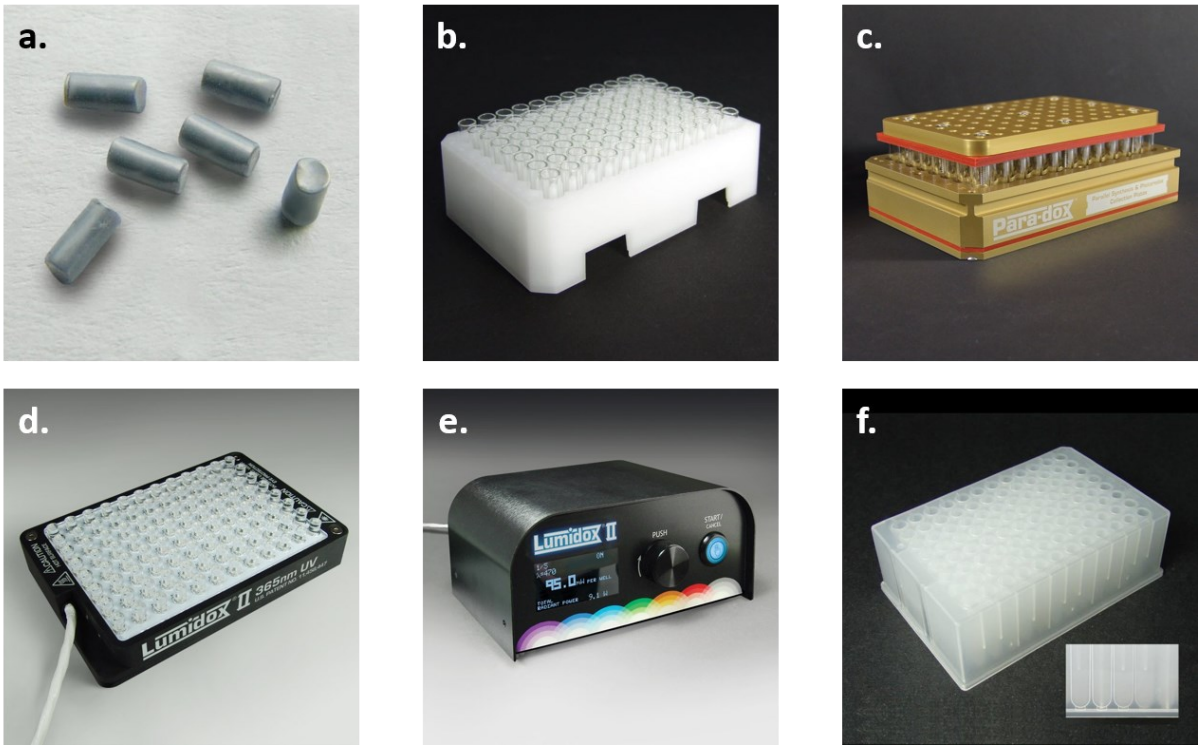


Figure S3. Instrumentation for HTE sept-up. a. stir bar used in HTE; b. 1 mL HTE vials; c. Paradox 96-well plate reactor; d. Lumidox® II LED Arrays; e. Lumidox® II LED Controler; f. analytical 96-well plate.

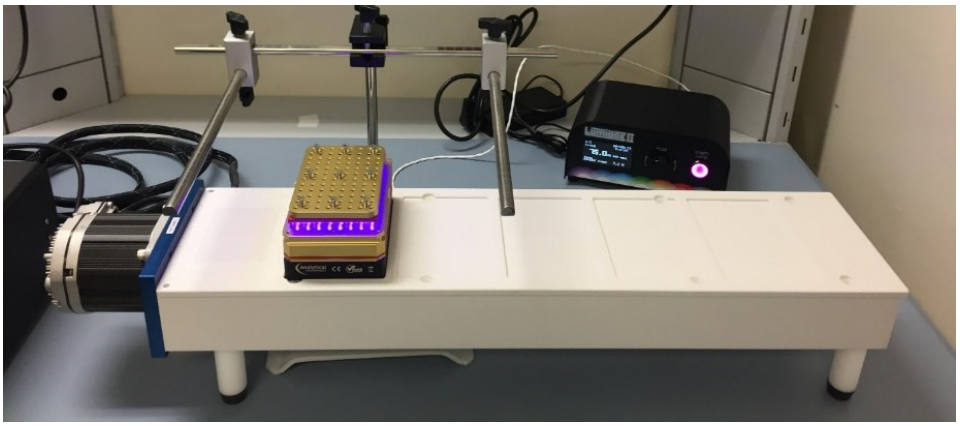


Figure S4. Tumble stirrer from V&P scientific.

Design of the HTE campaign with HTDesign® software

Chemical structures evaluated:

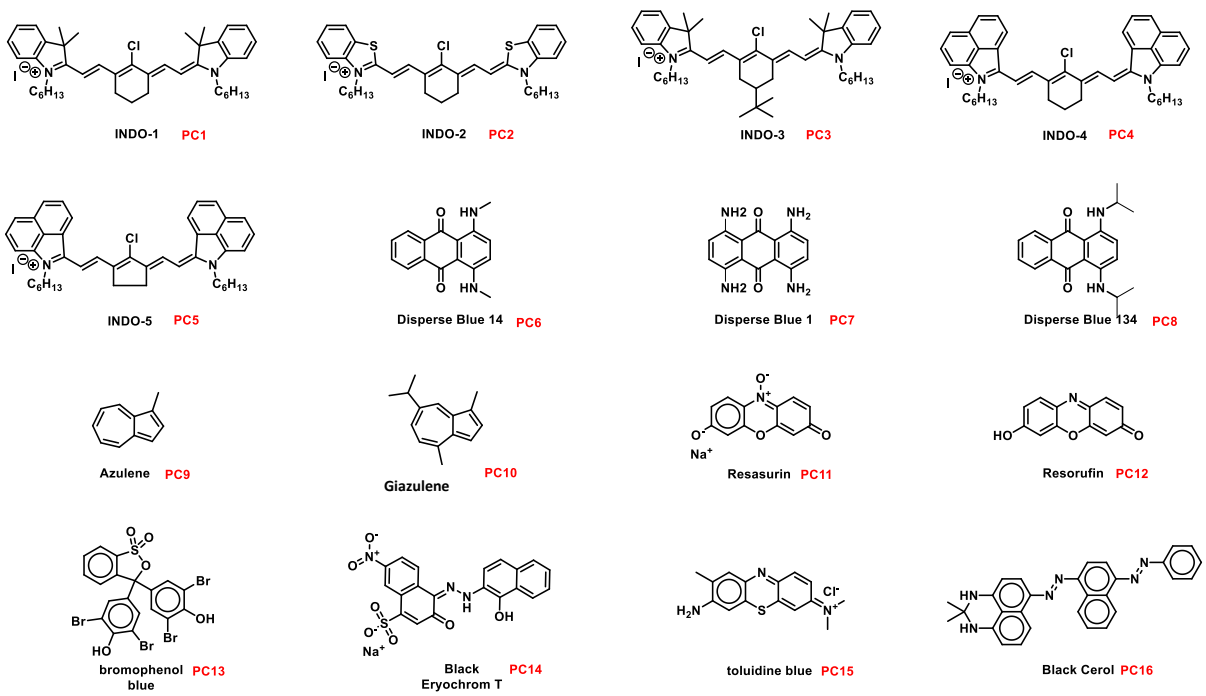


Figure S4. Chemical structures of dyes screened.

Design of the 96 well plate:

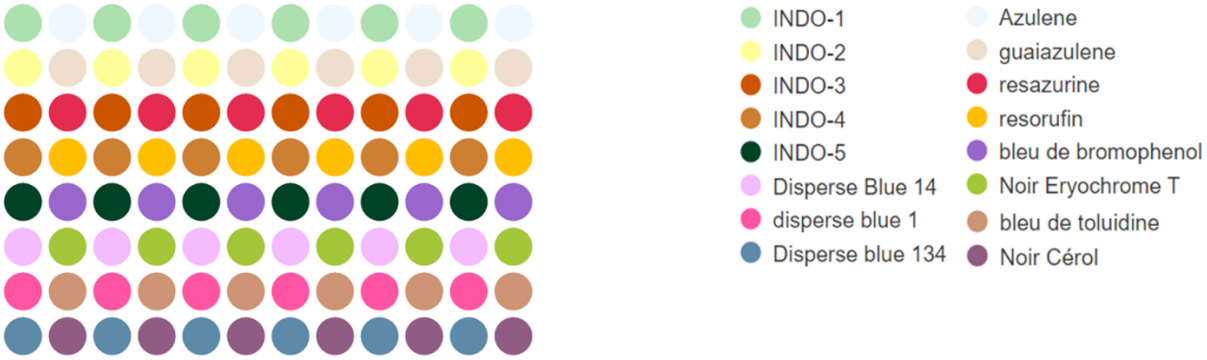


Figure S5: Design of the plate.

Reactions evaluated in duplicate:

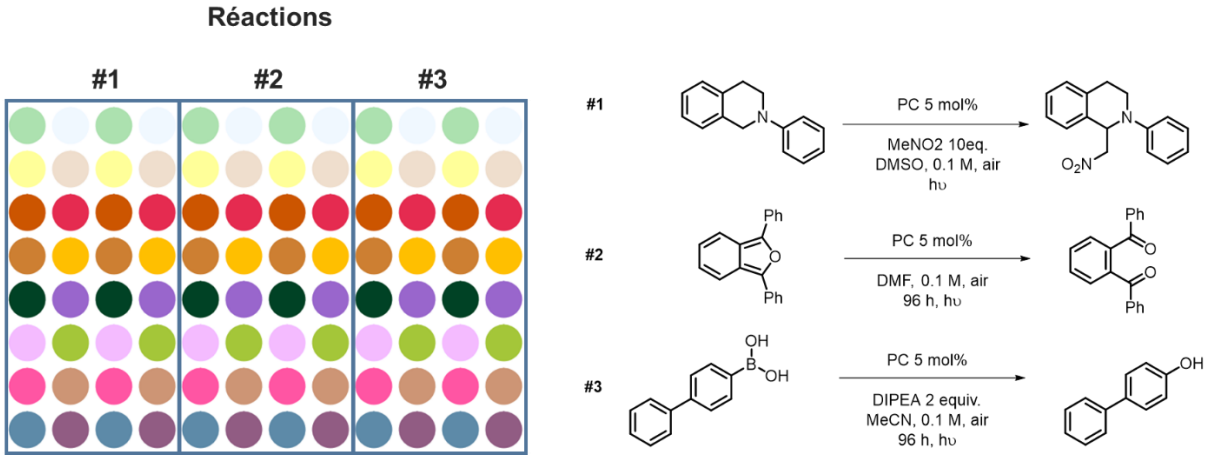


Figure S6. Evaluated transformations in the HTE screening.

Analysis protocol

At the end of the reaction each sample was diluted with a solution containing 1 µmol of biphenyl as internal standard (500 µL, 0.002 M) in MeCN. 50 µL aliquots were sampled into a 1 mL deep 96-well plate (Figure S3f) containing 600 µL MeCN. Ratios of Area Under Curve (AUC) of starting material, products and side products were tabulated as well as areas for peaks of interest. The analytical method was described in materials and equipment.

S3-Optical studies

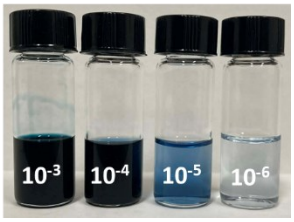
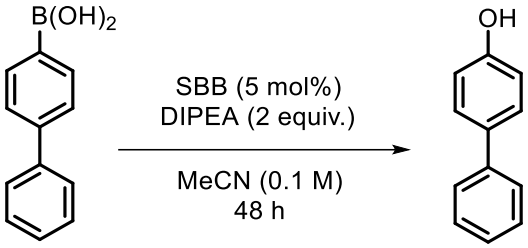


Figure S7. Pictures of SBB solutions at different concentrations.

S4-Investigated transformations

S4.1- Experimental procedures

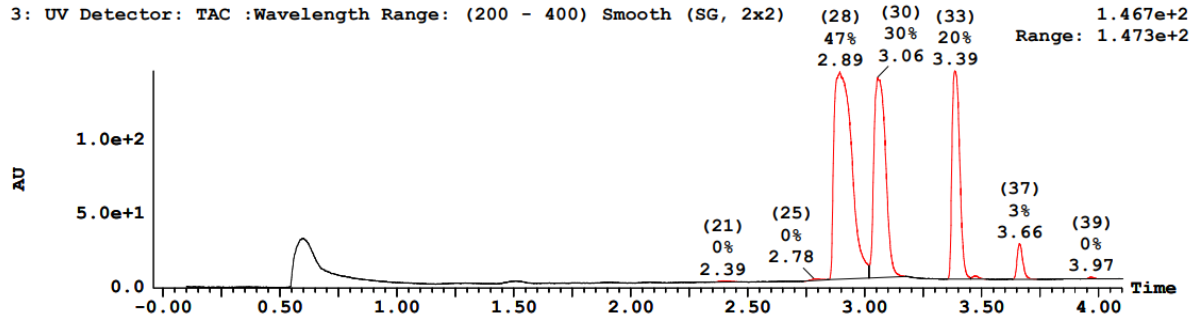
General procedure for photocatalyzed hydroxylation of boronic acid



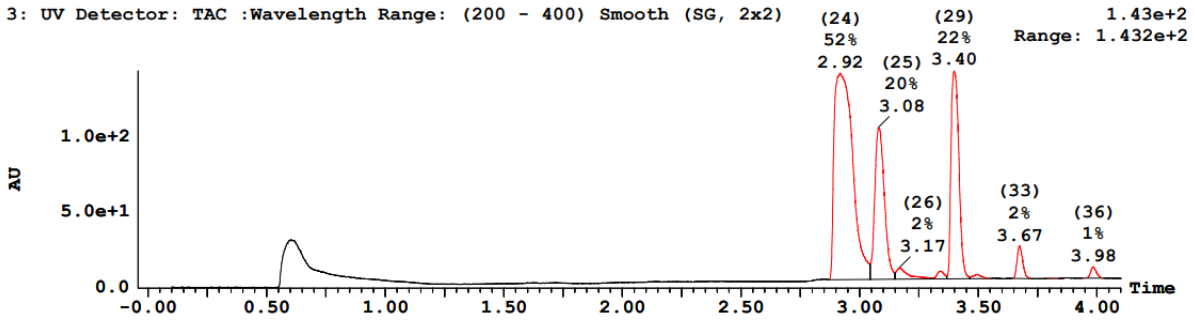
Scheme S8. Scheme for the photocatalyzed hydroxylation of boronic acid reaction.

(4'-methoxy-[1,1'-biphenyl]-4-yl)boronic acid (1 equiv.) and SBB (5 mol%) were added to an 8 mL vial equipped with a stir bar. DMF (0.1 M) and DIPEA (2 equiv.) were added. The reaction mixture (open to air) was stirred for 48 h under 660 nm irradiation.

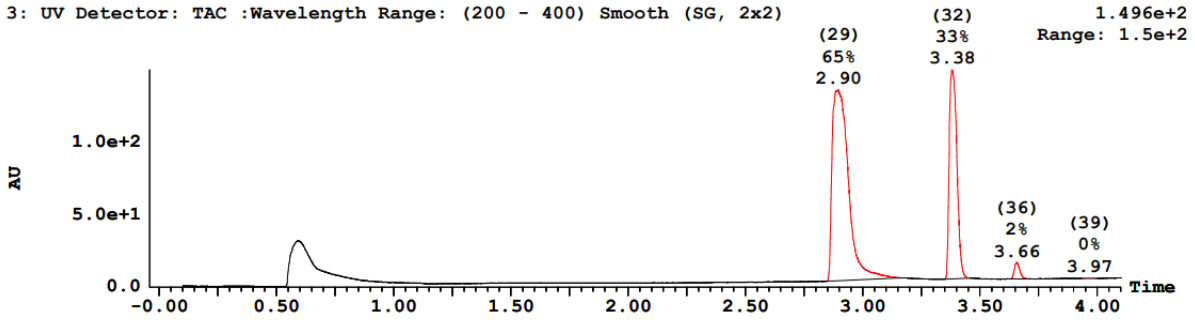
UV Chromatogram after 48 h of irradiation under UV light:



UV Chromatogram after 48 h of irradiation under blue light:



UV Chromatogram after 48 h of irradiation under red light:



Retention times:

2.90 min = Starting Material

3.08 min = Final product

3.38 min = internal standard (diOMe-biphenyl)

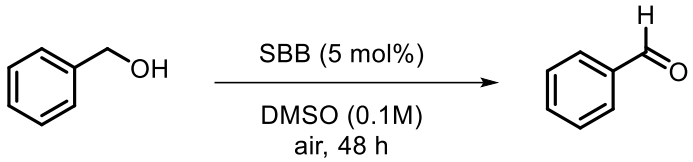
Estimated conversion = [$AUC_{product}$ / ($AUC_{product}$+$AUC_{starting\ material}$)]x100

Under UV light: [3.81e+004/(3.81e+004+4.00e+004)]x100 = 48.78%

Under blue light: [4.75e+006/(4.75e+006+1.24e+007)]x100 = 27.70%

Under red light: 0% (or traces in the tail of the SM peak)

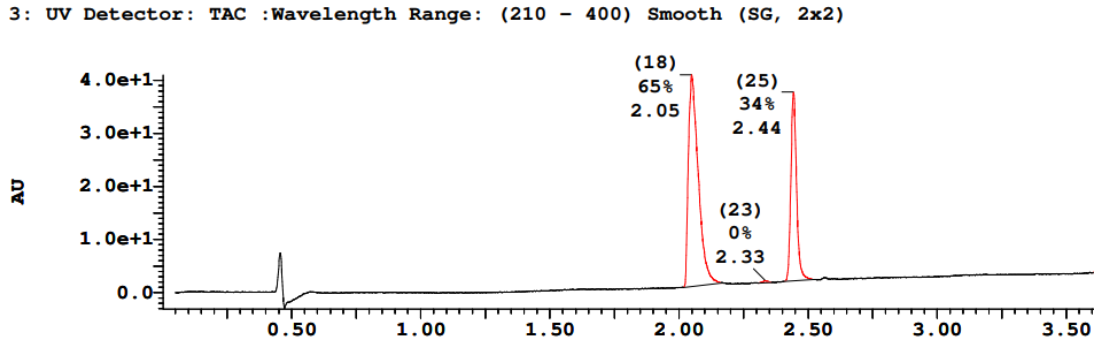
General procedure for the photocatalyzed oxidation of benzyl alcohol



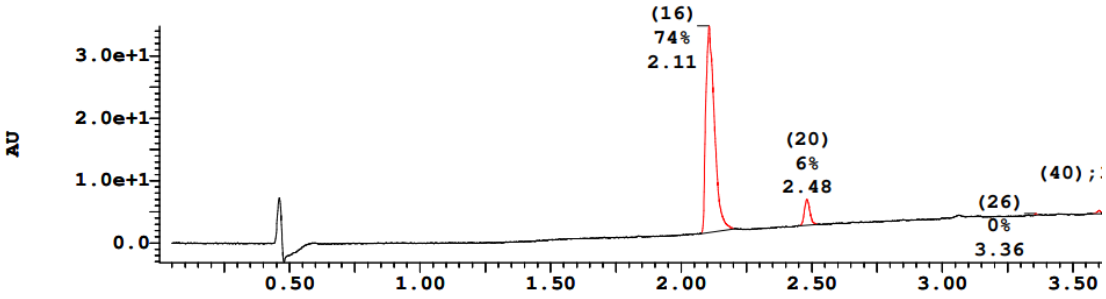
Scheme S9. Scheme of oxidation of benzyl alcohol.

Benzyl alcohol (1 equiv.) and SBB (5 mol%) were added in an 8 mL vial equipped with a stir bar. Then DMSO (0.1M) was added, the reaction was kept under air and the vial was closed with a cap. The reaction mixture was stirred for 48 h under irradiation.

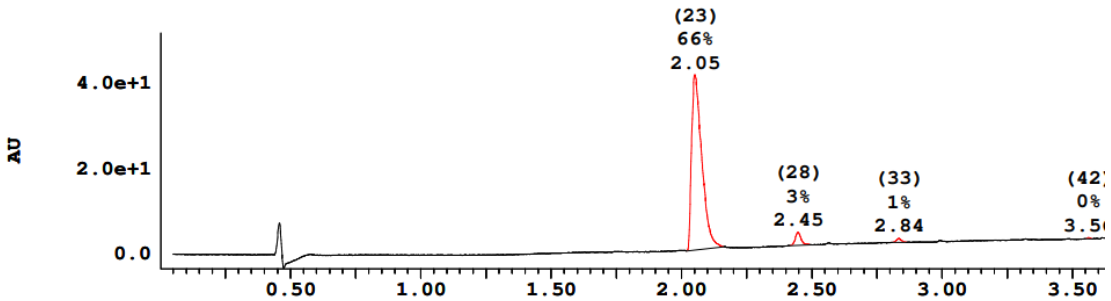
UV Chromatogram after 48 h of irradiation under UV light:



UV Chromatogram after 48 h of irradiation under blue light:



UV Chromatogram after 48 h of irradiation under red light:



Retention times:

2.05 min = Starting Material

2.45 min = Final product

Estimated conversion = [$AUC_{product}$ / ($AUC_{product}$+$AUC_{starting\ material}$)]x100

Under UV light: [9.88e+005/(9.88e+005+1.47e+006)]x100 = 40.20%

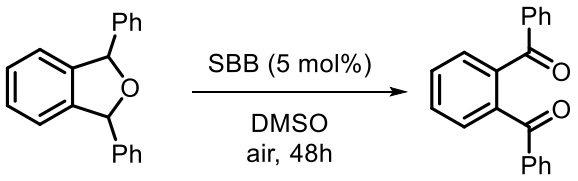
Under blue light: [1.68e+005/(1.68e+005+1.27e+006)]x100 = 11.68%

Under red light: [7.71e+004/(1.87e+006+7.71e+004)]x100 = 3.96%

S4.2- Unsuccessful transformations performed

Additional reactions, listed below, have been attempted in the context of the study, but were unsuccessful. Reactions 1-10 have been reproduced according to reported procedures. [14-19]

reaction #1: oxidation of DPBF



reaction #2: oxidation of 1,5-DHN

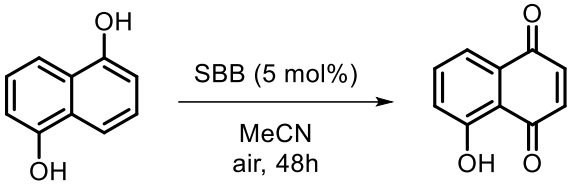


Figure S10. reactions evaluated but unsuccessful.

