Electronic Supplementary Material (ESI) for ChemComm.

Online Monitoring of a Photocatalytic Reaction by Real-time High Resolution FlowNMR Spectroscopy

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Supplementary Information

Table of Contents

Experimental

Equipment and reagents

Reactions were carried out in air in an open glass dish (19 cm diameter), with either a double-piston HPLC pump (JASCO PU-2085 Plus) with a semi-micro pump head or peristaltic pump (Vaportech SF-10) used to circulate the mixture around the system to an InsightMR flow tube (Bruker) located within the spectrometer (Bruker Avance II + 500 MHz Ultrashield equipped with a broadband observe probe). In order to minimise the delay time between a change occurring in the reaction vessel and the arrival of the sample to the spectrometer for detection it is desirable to ensure that the volume of the tubing connecting the reaction vessel to the spectrometer is minimised, therefore narrow diameter polyetheretherketone (PEEK) tubing (0.762 mm i.d., Upchurch Scientific) was used. The PEEK tubing offers high chemical and mechanical stability (pH 0 – 14, -50 – 100 °C, >300 bar) along with good flexibility and low gas permeability. All other connections were made using standard HPLC-type PEEK connectors (Upchurch Scientific). All equipment was positioned inside a fume hood, located approximately 1 m from the shielded NMR spectrometer, without experiencing any adverse magnetic effects.

Photochemical reactions were performed using either a 50 W green LED light source (TechBox T50W flood lamp) or a 400 W white halogen light source (Maplin Electronics 400 W halogen flood lamp) positioned 9 cm above the open reaction mixture.

Controlled atmosphere reactions were carried out in a Schlenk flask (100 mL) positioned horizontally 9cm above the lamp, using standard Schlenk technique and dry, degassed solvents. Flasks were kept under a positive pressure of argon or dry air for anaerobic and aerobic reactions respectively. A rubber seal was used to connect the tubing with the reaction solution, and found effective for air-sensitive systems over prolonged times (>10 hours) when sealed off with silicone grease. The sample depth in the Schlenk flask was comparable to that in the open dish reactor.

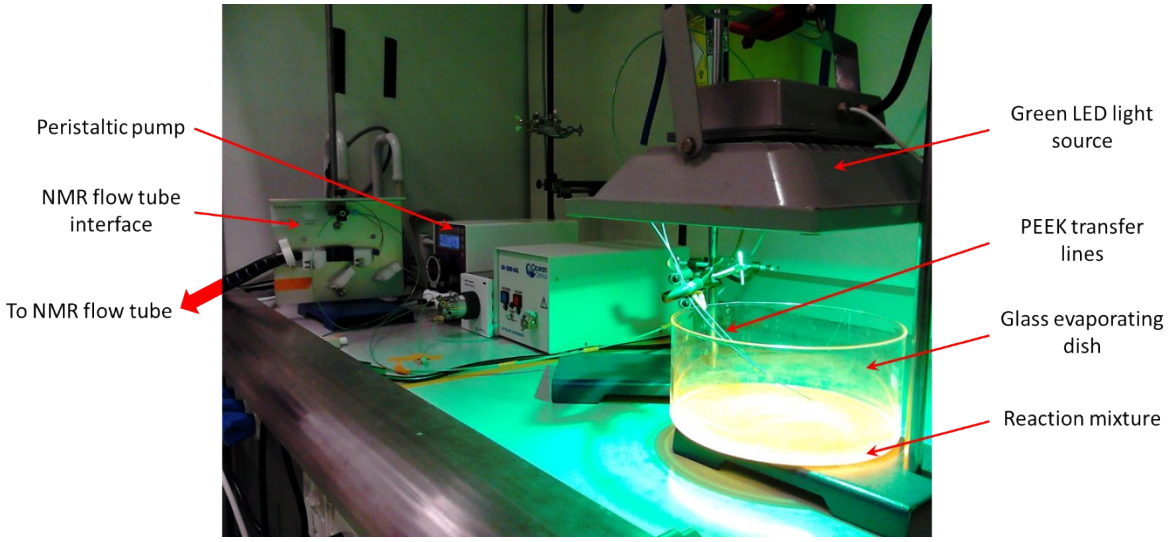


Figure S1: FlowNMR reaction setup inside fume hood.

Data acquisition was performed without lock and with shimming performed using automated ^{1}H shimming routines, followed by manual fine tuning. Data processing was performed using commercially available software. Solvent suppression of the acetonitrile resonance using a WET pulse sequence with a shaped pulse and low power ^{13}C decoupling during acquisition was carried out with the Bruker pulse program "wetdc", using a standard LC-NMR automated acquisition program, "au_lc1d" that first acquires a scout scan to identify and subsequently suppress the desired number of solvent peaks.

All samples were prepared using reagents and catalyst purchased from Sigma Aldrich at reagent grade or higher. All reactions were performed using non-deuterated solvents.

N-allylbenzylamine synthesis

Benzaldehyde (5 mL, 5.2 g, 49 mmol) and allylamine (4 mL, 3.1 g, 53 mmol) were dissolved in dichloromethane (20 mL) and stirred at room temperature for 2 h. Solvent was evaporated under reduced pressure before redissolving in ethanol (20 mL) and cooling in an ice bath. Sodium borohydride (3.250 g, 85.9 mmol) was added slowly and the reaction left to stir for 5 h, before addition of saturated ammonium carbonate solution (10 mL) to quench the reaction. The solvent was evaporated under reduced pressure and the product extracted with ethyl acetate (3 x 25 mL). The crude was purified by column chromatography (eluent: petroleum ether/ethyl acetate 8:2), to produce the final product as a pale-yellow oil (yield = 87%, 36 mmol)

Photochemical reactions

The FlowNMR apparatus was purged with acetone for 5 min at 4 mL/min. The apparatus was filled with a stock solution of 1 mol% Eosin Y in acetonitrile (4 mg/100 mL) (3.7 mL) and connected to the reaction vessel containing 1 mol% Eosin Y in acetonitrile (100 mL), N-allylbenzylamine (100 µL, 0.638 mmol) and N,N-Dimethylsulfoxide (50 µL, 0.704 mmol) as an internal concentration reference.

The flow tube was then inserted into the spectrometer and automated shimming and tuning routines were performed. Best results were obtained if automated shimming and tuning was performed on static samples, however acceptable results were still obtained in flow. Frequency lock was switched off when using non-deuterated solvents, and shimming performed on proton peaks. Manual fine tuning of X and Y shims was often required to get a good peak line width. Spectra of the reagents were recorded without flow and again at the flowrate desired for the reaction. Comparison of the integral area of the peaks in each spectrum was used to calculate a correction factor for each reagent peak. (I = peak integral, CF = correction factor).[1]

$$I_{Corrected} = CF \times I$$

$$CF = \frac{I_{Static}}{I_{Flow}}$$

With the sample flowing, data acquisition was started using an automated kinetic routine or dedicated InsightMR reaction monitoring software, with solvent suppressed ^{1}H spectra recorded at specified time intervals. To start the reaction the light source was switched on.

At the end of the reaction, or if intermediates of interest were observed, additional spectra were recorded with and without flow, and correction factors were calculated for the intermediate or

product peaks, which were applied to each spectrum to give the final peak areas for calculation of species concentration and plotting of kinetic data. Concentrations of species were determined by peak integrals referenced to DMSO internal standard.

Figures

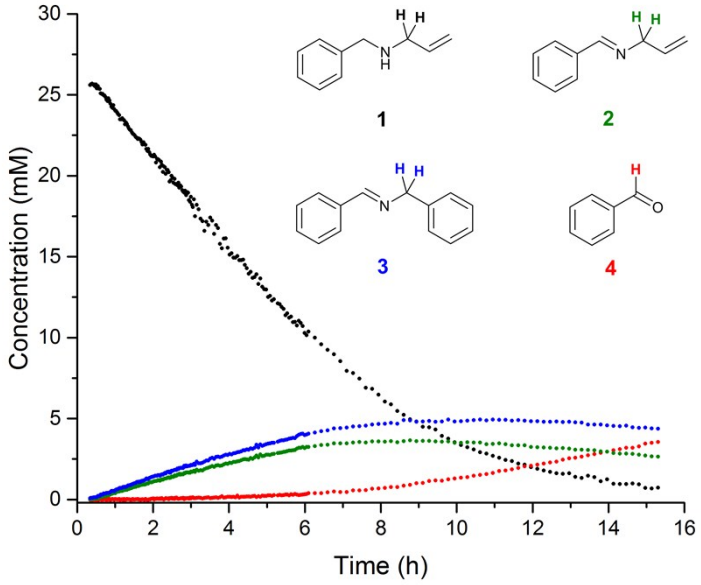


*Figure S2: Kinetic data for the reaction of N-allylbenzylamine **(1)** (25.6 mM) in the presence of green light and Eosin Y catalyst (1 mol% soln. in acetonitrile (100 mL)) to form **2**, **3** and **4**. (20°C, Green LED light source (100 W), WET solvent suppression, 1.64 s acquisition time, 3 s relaxation delay, 12 scans, 4 mLmin^{-1} flowrate).*

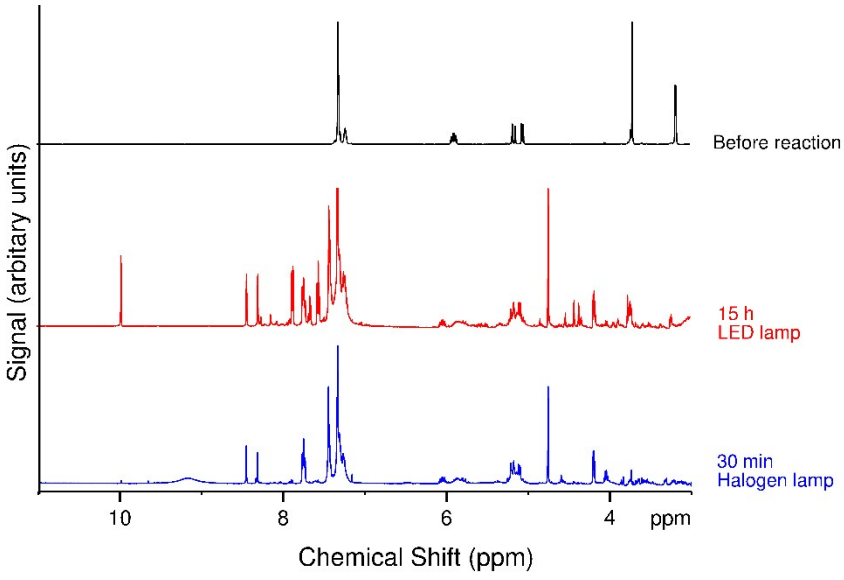


Figure S3: ^{1}H NMR spectra (solvent suppressed) of the reaction mixture a) before irradiation, b) after irradiation for 15 h with a green LED light source (633 µW at 510 nm) and c) after irradiation for 30 min with a white halogen light source (250 mW at 510 nm). (WET solvent suppression, 1.64 s acquisition time, 3 s relaxation delay, 12 scans).

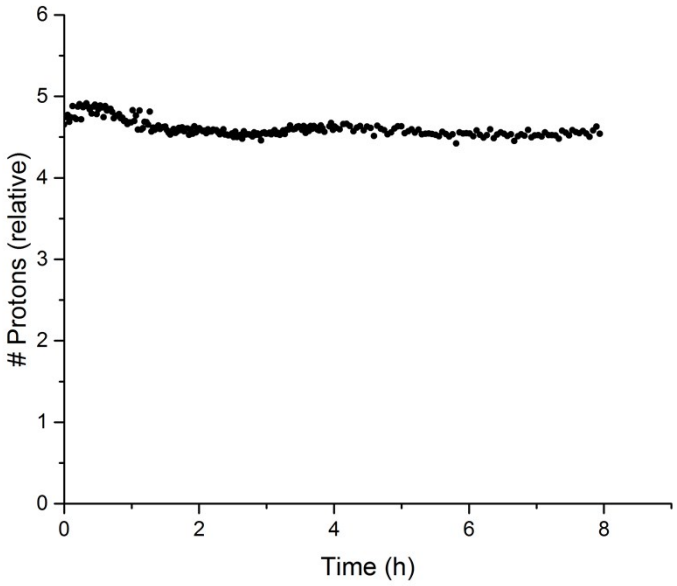


*Figure S4: Sum integration of aromatic region (8.25 – 7 ppm) throughout course of the reaction of N-allylbenzylamine **(1)** (6.4 mM) in the presence of green light and Eosin Y catalyst (1 mol% soln. in acetonitrile (100 mL)) to form **2**, **3** and **4**. (20°C, Green LED light source (633 µW at 510 nm), WET solvent suppression, 1.64 s acquisition time, 3 s relaxation delay, 12 scans, 4 mLmin^{-1} flowrate).*

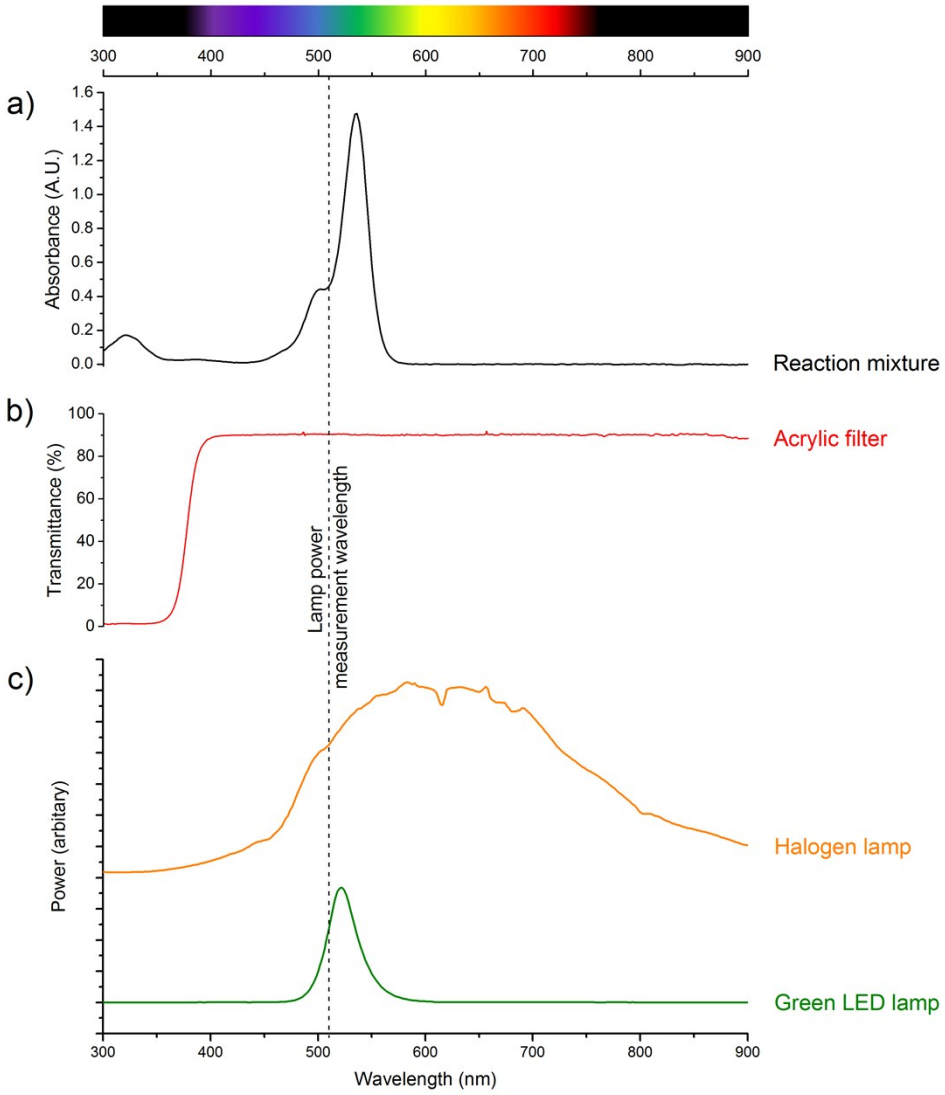


Figure S5: a) UV-vis absorption spectrum for the reaction mixture (6.4 mM N-allylbenzylamine, 7.0 mM DMSO and 1 mol% Eosin Y soln. in acetonitrile); b) UV-vis transmission spectrum for acrylic UV filter used in Figure S7; c) Power spectra for the two lamps used in the study (NB. The power scale is arbitrary and is not comparable for the two lamps due to different slit sizes required when acquiring the data).

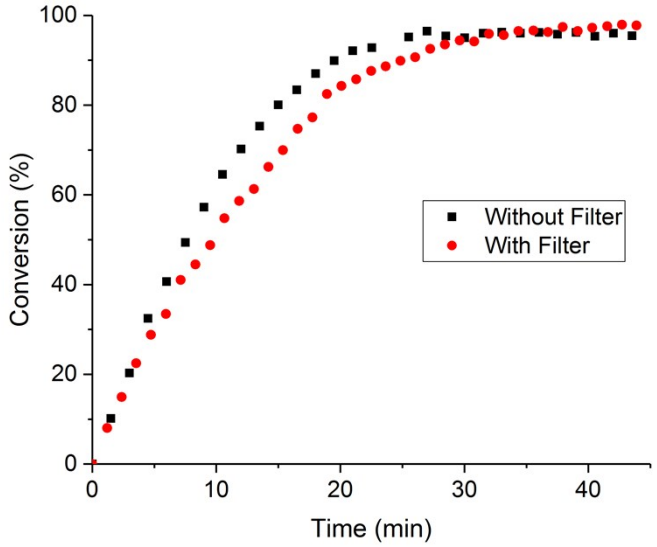


*Figure S6: Conversion profiles for the reaction of N-allylbenzylamine **(1)** (6.4 mM) in the presence of white light and Eosin Y catalyst (1 mol% soln. in acetonitrile (100 mL)) to form **2**, **3** and **4**; a) without filtering of light source, and b) with a colourless acrylic filter to block UV wavelengths (400 nm cut-off). (20°C, White halogen light source (250 mW at 510 nm), WET solvent suppression, 1.64 s acquisition time, 3 s relaxation delay, 16 scans, 4 mLmin^{-1} flowrate).*

Table S1: Measured power outputs of light sources used at 510 nm. Green LED lamp (high setting) measured at 9 cm from reaction surface.

Light source	Nominal power /W	Measured power output at 9 cm /mW
Green LED lamp (mid setting)	50	633×10^{-3}
Green LED lamp (low setting)	50	95×10^{-3}
White Halogen lamp	400	250

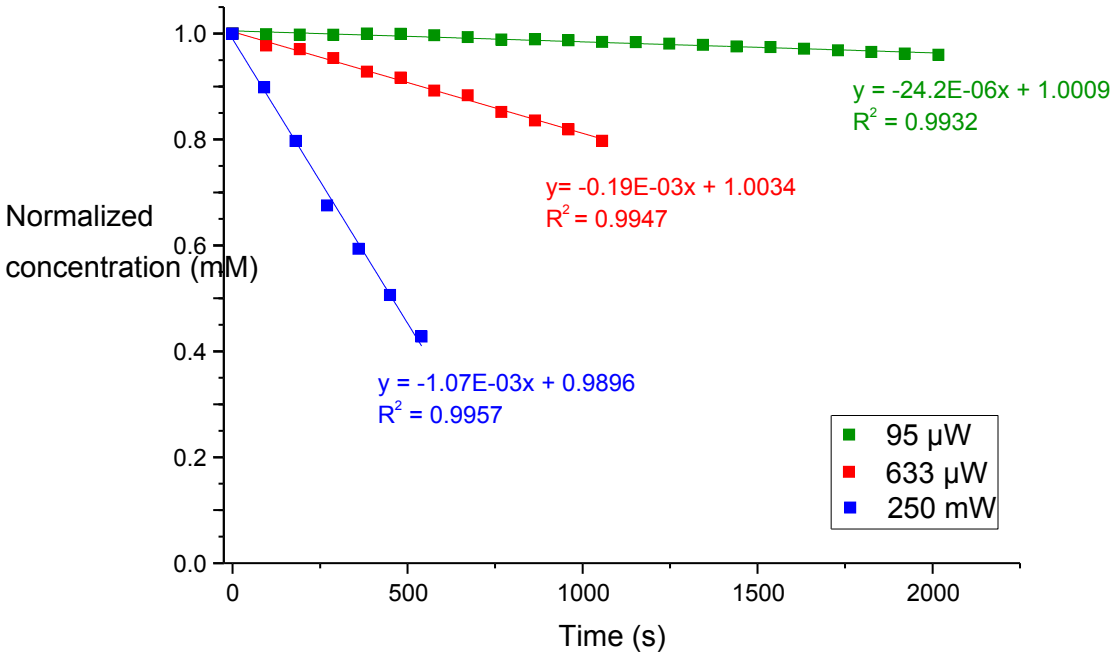


*Figure S7: Initial first order reaction rates on the consumption of N-allylbenzylamine **(1)** (6.4 mM) in the presence of green light and Eosin Y catalyst (1 mol% soln. in acetonitrile (50 mL)) with varying lamp power. All reactions were carried out with same mode of illumination (top) and exposed surface area (19 cm diameter dish).*

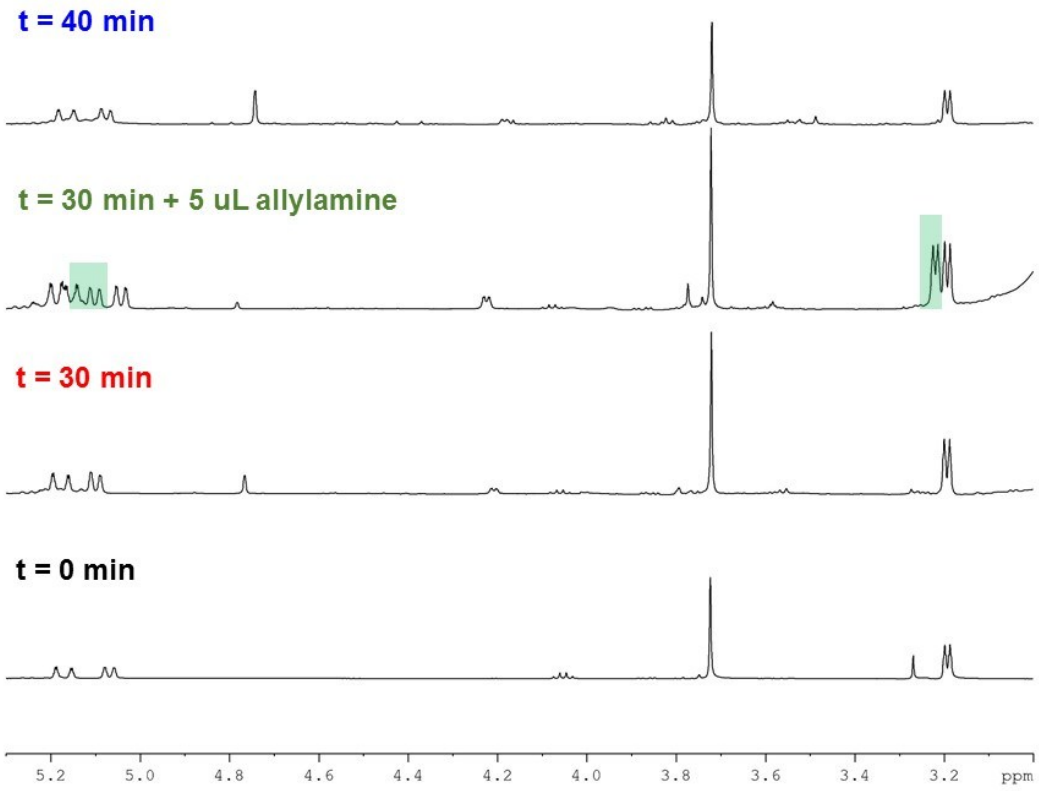


Figure S8: [1]H NMR spectra (solvent suppressed) of the reaction mixture a) before irradiation b) after irradiation for 30 min (633 µW at 510 nm) c) addition of 5 µL allylamine and d) continuation of the reaction for 10 min. (WET solvent suppression, 1.64 s acquisition time, 3 s relaxation decay, 16 scans).

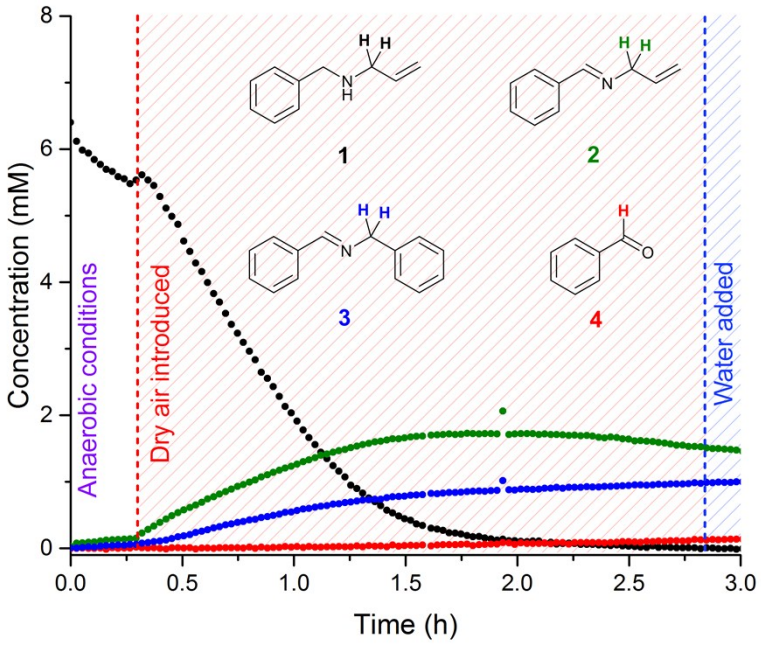
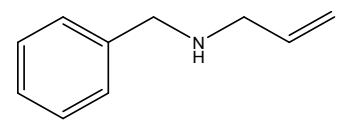


*Figure S9: Kinetic data for the reaction of N-allylbenzylamine **(1)** (6.4 mM) in the presence of green light and Eosin Y catalyst (1 mol% soln. in acetonitrile (50 mL)) to form **2**, **3** and **4**. Reaction performed under anhydrous conditions, with a continuous flow of dry air over the reaction. Reaction spiked with 100 µL distilled water after 170 min. (20°C, Green LED light source (633 µW at 510 nm), WET solvent suppression, 1.64 s acquisition time, 3 s relaxation delay, 16 scans, 4 mLmin^{-1} flowrate)*

N-allylbenzylamine (1)

^{1}H NMR (500 MHz, CH_3CN) δ = 7.38 – 7.33 (m, 4H, Ar), 7.28 – 7.25 (m, 1H, Ar), 5.96 (ddt, *J* = 17.3, 10.5, 5.4 Hz, 1H, $CH_2C\underline{\mathbf{H}}=CH_2$), 5.23 (dq, *J* = 17.2, 1.8 Hz, 1H, $CH_2CH=C\underline{\mathbf{H}}_2$), 5.12 (ddt, *J*=10.3, 2.1, 1.4 Hz 1H, $CH_2CH=C\underline{\mathbf{H}}_2$), 3.77 (s, 2H, benzylic), 3.24 (dt, *J* = 5.8, 1.5 Hz, 2H, $C\underline{\mathbf{H}}_2CH=CH_2$).

Impurities: Ethyl acetate, N-Allyl-1-phenylmethanimine **(2)**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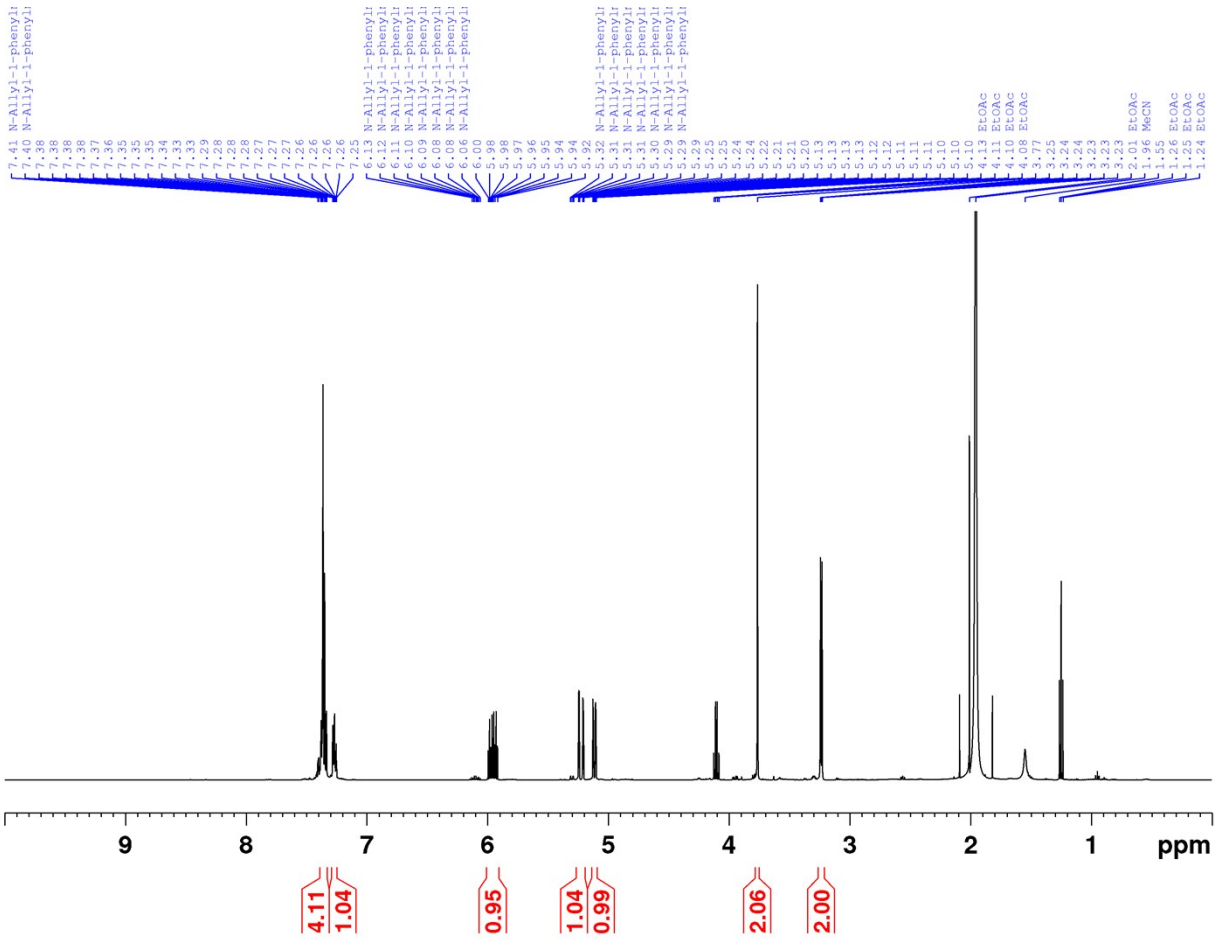
9
8
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5
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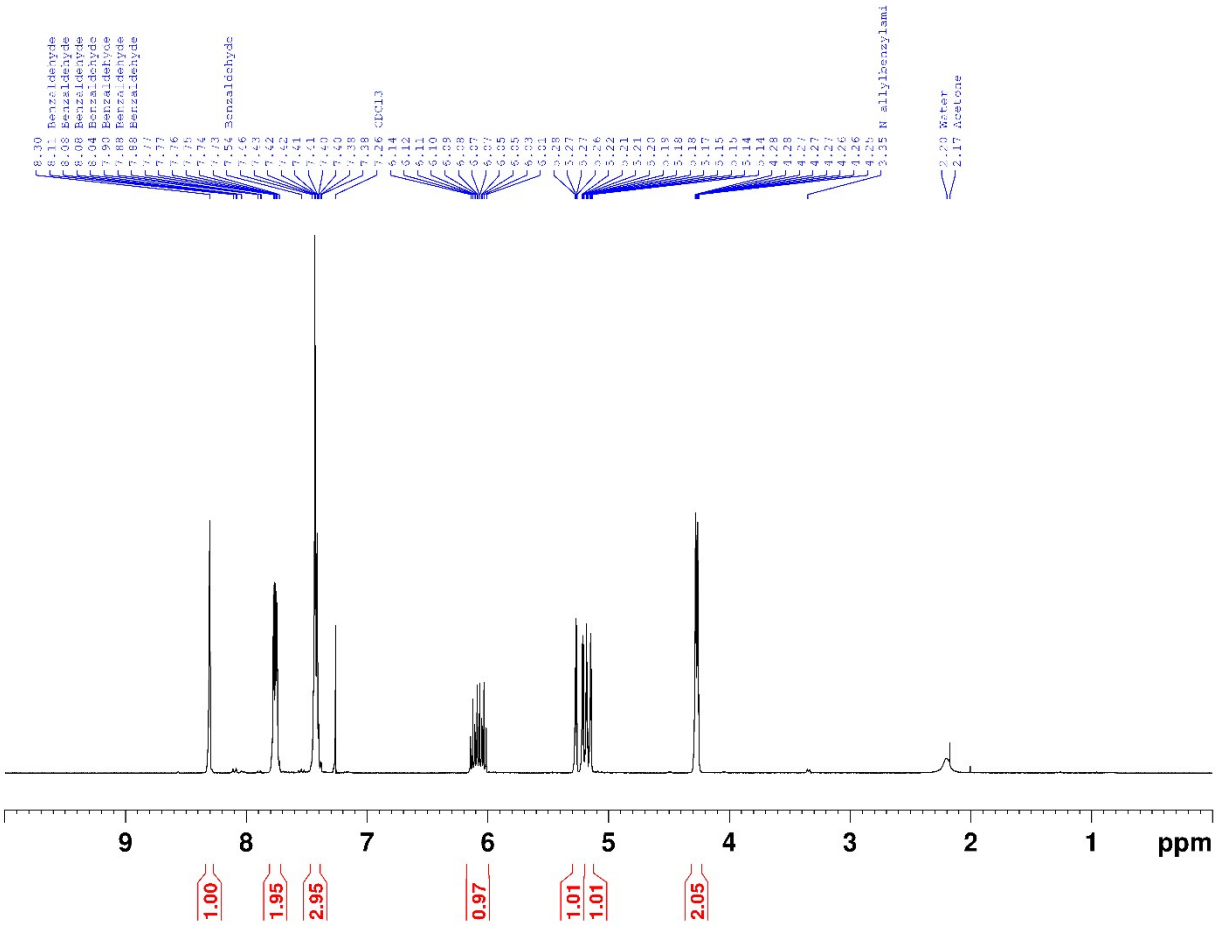
2.00

N-Allyl-1-phenylmethanimine (2)

^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.30 (s, 1H ArC**H**=N), 7.80 – 7.72 (m, 2H, Ar), 7.46 – 7.38 (m, 3H, Ar), 6.07 (ddt, 1H, J = 17.1, 10.3, 5.7 Hz, CH_2C**H**=CH_2), 5.24 (dq, 1H, J = 17.2, 1.7 Hz, CH_2CH=C**H**$_2$), 5.17 (dq, 1H, J = 10.3, 1.7 Hz, CH_2CH=C**H**$_2$), 4.27 (dq, 2H, J = 5.7, 1.5 Hz, C**H**$_2CH$=CH_2).

Impurities: Acetone, Water, N-allylbenzylamine **(1)**, Benzaldehyde.



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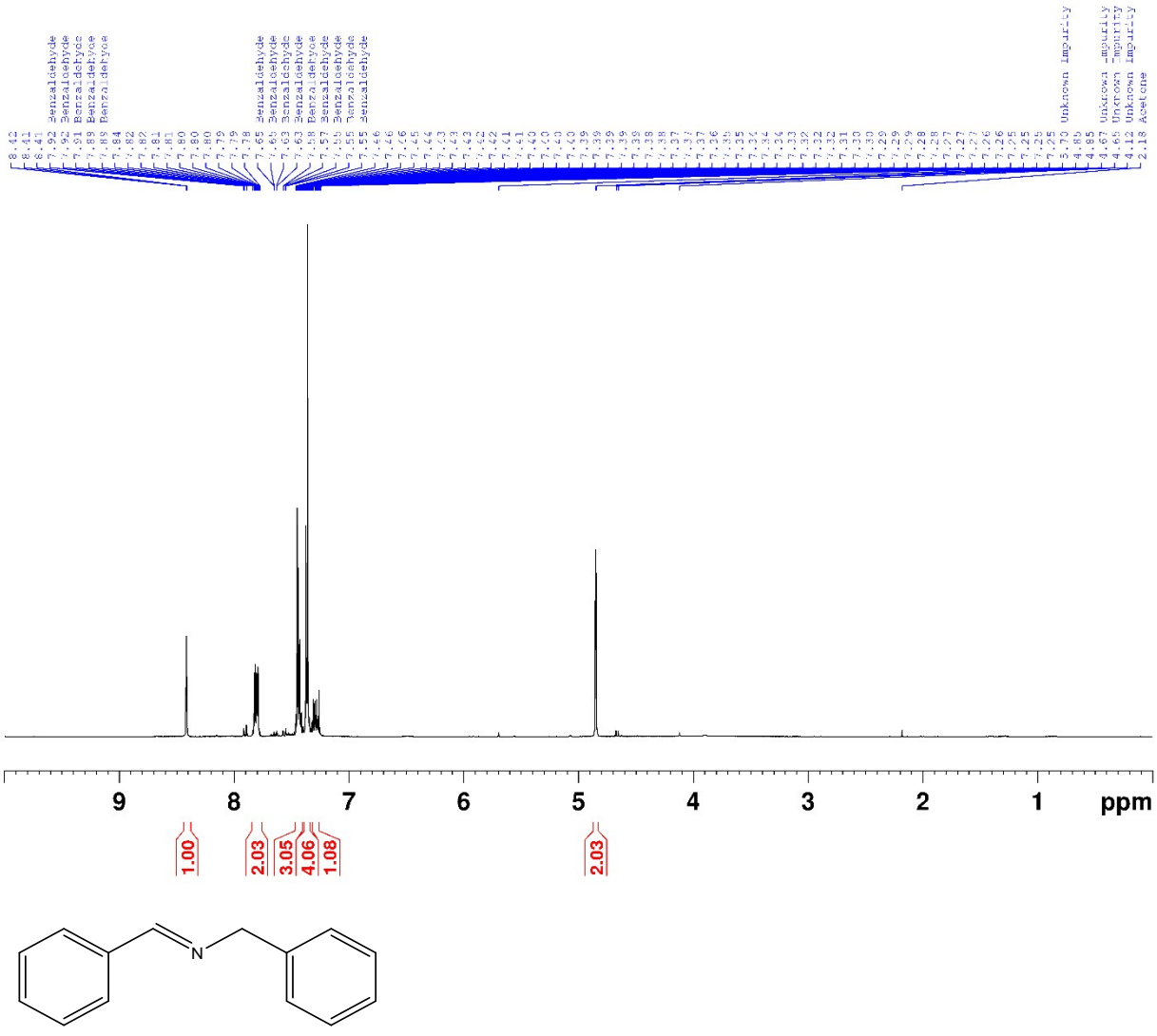
N-Benzyl-1-phenylmethanimine (3)

^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.41 (t, 1H, 1.5 Hz, ArC**H**=N), 7.84 – 7.77 (m, 2H, Ar), 7.46 – 7.41 (m, 3H, Ar), 7.38 – 7.34 (m, 4H, Ar), 7.32 – 7.27 (m, 1H, Ar), 4.85 (d, 2H, J = 1.5 Hz, NC**H**$_2$Ar).

Impurities: Acetone, Benzaldehyde



References

1. A. M. R. Hall, J. C. Chouler, A. Codina, P. T. Gierth, J. P. Lowe and U. Hintermair, *Catalysis Science & Technology*, 2016, **6**, 8406-8417.