Electronic Supplementary Information (ESI) for

Photochemical generation of acyl and carbamoyl radicals using a nucleophilic organic catalyst: applications and mechanism thereof

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A. General Information

The NMR spectra were recorded at 400 MHz and 500 MHz for ¹H and 100 or 125 MHz for ¹³C. The chemical shift (δ) for ¹H and ¹³C are given in ppm relative to residual signals of the solvents (CHCl₃ @ 7.26 ppm ¹H NMR and 77.16 ppm ¹³C NMR, and tetramethylsilane @ 0 ppm). Coupling constants are given in Hertz. The following abbreviations are used to indicate the multiplicity: s, singlet; d, doublet; q, quartet; m, multiplet; bs, broad signal; app, apparent.

High resolution mass spectra (HRMS) were obtained from the ICIQ HRMS unit on MicroTOF Focus and Maxis Impact (Bruker Daltonics) with electrospray ionization. (ESI).

UV-vis measurements were carried out on a Shimadzu UV-2401PC spectrophotometer equipped with photomultiplier detector, double beam optics and D_2 and W light sources or an Agilent Cary60 spectrophotometer.

Emission spectra of light sources were recorded on Ocean Optics USB4000 fiber optic spectrometer.

Isolated yields refer to materials of >95% purity as determined by ¹H NMR.

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General Procedures. All reactions were set up under an argon atmosphere in oven-dried glassware. Synthesis grade solvents were used as purchased, anhydrous solvents were taken from a commercial SPS solvent dispenser. Chromatographic purification of products was accomplished using forced-flow chromatography (FC) on silica gel (35-70 mesh). For thin layer chromatography (TLC) analysis throughout this work, Merck pre-coated TLC plates (silica gel 60 GF₂₅₄, 0.25 mm) were employed, using UV light as the visualizing agent and an acidic mixture of vanillin or basic aqueous potassium permanganate (KMnO₄) stain solutions, and heat as developing agents. Organic solutions were concentrated under reduced pressure on a Büchi rotatory evaporator.

Determination of Enantiomeric Purity. UPC² analysis on chiral stationary phase was performed on a Waters Acquity instrument using an ID3 chiral column. The exact conditions for the analyses are specified within the characterization section.

Materials. Most of the starting materials used in this study are commercial and were purchased in the highest purity available from Sigma-Aldrich, Fluka, Alfa Aesar, Fluorochem, and used as received, without further purifications.

The following substrates were synthesized according to reported procedures (Figure S1).¹⁻⁸



Figure S1: Starting materials synthesised according to known procedures.

B. Substrate Synthesis

Synthesis of N-benzylcyclopent-2-en-1-amine:



A 2 M solution of cyclopentene (0.973 mL, 11 mmol) in CCl₄ (5.4 mL) was prepared and then NBS (2.26 g, 10 mmol) and benzoic peroxyanhydride (36 mg, 0.15 mmol) were sequentially added. The solution was stirred at 40 °C for 4 hours, after which the reaction was left at ambient temperature without stirring. After 2 hours, the floating materials were filtered off and washed with CCl₄. The organic phase was then placed in a separatory funnel and washed with distilled water. The organic phase was collected, treated with MgSO₄ and subsequently filtered. At this stage, benzylamine (3.28 mL, 30 mmol) and K_2CO_3 (1.38 g, 10 mmol) were directly added to the solution. The reaction was stirred overnight at r.t and the resulting crude mixture was purified by silica gel chromatography (eluent: 9:1 hexane/AcOEt) to afford 234 mg of *N*-benzylcyclopent-2-en-1-amine (14% yield over 2 steps) as a yellow-orange oil.

 $\frac{^{1}\text{H NMR}}{^{1}\text{2.9 Hz}}$ (400 MHz, CDCl₃) δ 7.39 – 7.24 (m, 5H), 5.89 (m, 2H), 3.93 (m, 1H), 3.84 (dd, *J* = 16.6, 12.9 Hz, 2H), 2.48 (m, 1H), 2.36 – 2.18 (m, 2H), 1.63 (m, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 140.5, 133, 132.8, 128.4, 128.3, 126.9, 63.9, 51.8, 31.3, 30.8

Synthesis of *N*-(4-(trifluoromethyl)benzyl)cyclohex-2-en-1-amine:



N-(4-(trifluoromethyl)benzyl)cyclohex-2-en-1-amine was prepared according to a reported procedure.² A solution of (4-(trifluoromethyl)phenyl)methanamine (1.314 g, 7.5 mmol) in CH₃CN (1.7 mL) was treated with 3-bromocyclohexene (0.288 mL, 2.5 mmol) and K₂CO₃ (346 mg, 2.5 mmol). After 2 hours at ambient temperature, the reaction mixture was quenched with H₂O (20 mL) and extracted with EtOAc (2 x 25 mL). The combined organic extracts were washed with brine (20 mL), dried over MgSO₄, filtered, evaporated under reduced pressure, and purified by column chromatography (eluent: CH₂Cl₂ to CH₂Cl₂/EtOH 9:1) to give the product (607 mg, 95 % yield) as a light-yellow oil.

¹<u>H NMR</u> (400 MHz, CDCl₃) δ 7.57 (d, J = 8.1 Hz, 2H), 7.47 (d, J = 8.0 Hz, 2H) 5.82 – 5.76 (m, 1H), 5.75 – 5.62 (m, 1H) 3.90 (dd, J = 13.6, 3.3 Hz, 2H), 3.23 – 3.16 (m, 1H), 2.10 – 1.97 (m, 2H), 1.93 – 1.85 (m, 1H), 1.80 – 1.70 (m, 1H), 1.61 – 1.42 (m, 2H).

 $\frac{^{13}\text{C NMR}}{^{37}}$ (101 MHz, CDCl₃) δ 145.1, 129.8, 129.4, 129.3 (q, *J* = 32.7 Hz) 128.4, 125.4 (q, *J* = 3.7 Hz), 124.4 (q, *J* = 271.9 Hz), 52.6, 50.6, 29.6, 25.4, 20.3.

¹⁹F NMR (376 MHz, CDCl₃) δ -62.47.

Synthesis of compound 8f:



Compound **8f** was prepared according to a modification of a reported procedure.² To a solution of triphosgene (294 mg, 0.99 mmol) in toluene (15 mL) under N_2 , pyridine (0.290 mL, 3.60 mmol)

and subsequently a solution of thiomorpholine (310 mg, 3 mmol) in toluene (5 mL) were added. The reaction mixture was stirred for 18 hours at ambient temperature, quenched with NH₄Cl (20 mL of a saturated aq. solution) and extracted with Et₂O (2 x 30 mL). The combined organic extracts were washed sequentially with HCl (40 mL of a 0.25 M aq. solution), H₂O (40 mL) and brine (40 mL), dried over MgSO₄, filtered and evaporated under reduced pressure to afford carbamoyl chloride **8f** (310 mg, 75% yield) as a colorless oil.

¹<u>H NMR</u> (400 MHz, CDCl₃) δ 3.94 (dt, J = 38.9, 5.1 Hz, 1H), 2.72 – 2.64 (m, 1H). ¹³<u>C NMR</u> (101 MHz, CDCl₃) δ 148.5, 51.7, 49.3, 27.7, 27.3

Synthesis of 8g:



Compound **8g** was prepared according to a modification of a reported procedure.² To a solution of triphosgene (294 mg, 0.99 mmol) in toluene (15 mL) under N₂, pyridine (0.290 mL, 3.60 mmol) and subsequently a solution of *N*-Boc Piperazine (559 mg, 3 mmol) in toluene (5 mL) were sequentially added. The reaction mixture was stirred for 18 hours at ambient temperature, quenched with NH₄Cl (20 mL of a saturated aq. solution) and extracted with Et₂O (2 x 30 mL). The combined organic extracts were washed sequentially with HCl (40 mL of a 0.25 M aq. solution), H₂O (40 mL) and brine (40 mL), dried over MgSO₄, filtered and evaporated under reduced pressure to give carbamoyl chloride **8g** (597 mg, 82% yield) as a colorless oil.

¹<u>H NMR</u> (300 MHz, CDCl₃) δ 3.64 (m, 4H), 3.48 (d, *J* = 4.8 Hz, 4H), 1.46 (s, 9H). ¹³<u>C NMR</u> (101 MHz, CDCl₃) δ 154.3, 148.5, 80.7, 48.5, 46, 28.3.

HRMS (ESI pos): calculated for C₁₀H₁₇ClNaN₂O₃ (M+Na⁺): 271.0800, found: 271.0818.

Synthesis of compound 8h:



Compound **8h** was prepared according to a modification of a reported procedure.² To a solution of triphosgene (259 mg, 0.872 mmol) in toluene (15 mL) under N₂, pyridine (0.498 mL, 6.15 mmol) and subsequently a solution of 4-chloropiperidine hydrochloride (400 mg, 2.56 mmol) in toluene (5 mL) were sequentially added. The reaction mixture was stirred for 18 hours at ambient temperature, quenched with NH₄Cl (20 mL of a saturated aq. solution) and extracted with Et₂O (2 x 30 mL). The combined organic extracts were washed sequentially with HCl (40 mL of a 0.25 M aq. solution), H₂O (40 mL) and brine (40 mL), dried over MgSO₄, filtered and evaporated under reduced pressure to give carbamoyl chloride **8h** (420 mg, 90% yield) as a colorless oil.

 $\frac{^{1}\text{H NMR}}{^{2}\text{H}}$ (400 MHz, CDCl₃) δ 4.34 (tt, J = 6.5, 3.6 Hz, 1H), 4.01 – 3.64 (m, 4H), 2.18 – 2.03 (m, 2H), 2.00 – 1.86 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 148.4, 55.6, 45.6, 43.1, 34.7, 34.2.

Synthesis of compound 8j:



Compound **8j** was prepared according to a modification of a reported procedure.² To a solution of triphosgene (207 mg, 0.68 mmol) in toluene (15 mL) under N₂, pyridine (0.204 mL, 2.54 mmol) and subsequently a solution of L-methyl prolinate hydrochloride (350 mg, 2.13 mmol). The reaction mixture was stirred for 18 hours at ambient temperature, quenched with NH₄Cl (20 mL of a saturated aq. solution), and extracted with Et₂O (2 x 30 mL). The combined organic extracts were washed sequentially with HCl (40 mL of a 0.25 M aq. solution), H₂O (40 mL) and brine (40 mL), dried over MgSO₄, filtered and evaporated under reduced pressure to give carbamoyl chloride **8j** (275 mg, 68% yield) as a colorless oil.

 $\frac{1}{1}$ H NMR (400 MHz, CDCl₃, 1:1 mixture of rotamers) δ : 4.57 – 4.46 (m, 1H), 3.85 - 3.55 (m, 2H), 3.77 (d, *J* = 12.4 Hz, 3H), 2.35 – 2.25 (m, 1H), 2.17 – 1.93 (m, 3H).

¹³<u>C NMR</u> (124 MHz, CDCl₃, 1:1 mixture of rotamers) δ: 171.8, 171.3, 147.8, 146.9, 62.4, 60.7, 52.9, 50.7, 49.2, 30.4, 30.3, 23.7, 23.6

Synthesis of compound 8k:



Compound **8k** was prepared according to a modification of a reported procedure.² To a solution of triphosgene (89 mg, 0.30 mmol) in toluene (3 mL) under N₂, pyridine (88 μ L, 1 mmol) and subsequently a solution of Paroxetine (300 mg, 0,91 mmol) in toluene (6 mL), were added. The reaction mixture was stirred for 18 hours at ambient temperature, quenched with NH₄Cl (20 mL of a saturated aq. solution) and extracted with Et₂O (2 x 30 mL). The combined organic extracts were washed sequentially with HCl (40 mL of a 0.25 M aq. solution), H₂O (40 mL) and brine (40 mL), dried over MgSO₄, filtered and evaporated under reduced pressure to afford carbamoyl chloride **8k** (130 mg, 36% yield) as a white crystal.

 $\frac{^{1}\text{H NMR}}{^{1}\text{H NMR}} (500 \text{ MHz, CDCl}_{3}) \delta 7.14 \text{ (m, 2H)}, 7.00 \text{ (m, 2H)}, 6.64 \text{ (m, 1H)}, 6.36 \text{ (s, 1H)}, 6.14 \text{ (m, 1H)}, 5.89 \text{ (s, 2H)}, 4.63 \text{ (m, 1H)}, 4.49 \text{ (m, 1H)}, 3.63 \text{ (t, } J = 8.7 \text{ Hz}, 1\text{ H)}, 3.48 \text{ (dd, } J = 9.6, 6.0 \text{ Hz}, 1\text{ H)}, 3.20 \text{ (t, } J = 12.9 \text{ Hz}, 1\text{ H)}, 3.02 \text{ (m, 1H)}, 2.82 \text{ (m, 1H)}, 2.10 \text{ (m, 1H)}, 1.93 \text{ (m, 1H)}, 1.82 \text{ (qd, } J = 12.9, 4.4 \text{ Hz}, 1\text{ H)}$

¹³<u>C NMR</u> (126 MHz, CDCl₃) δ 162.9, 160.9, 154.0, 148.4, 142.0, 128.9, 115.8, 108.0, 105.8, 101.3, 98.1, 68.4, 52.2, 49.6, 47.0, 43.8, 42.3, 33.7

 19 F NMR (376 MHz, CDCl₃, proton decoupled) δ -115.51

HRMS (ESI pos): calculated for C₂₀H₁₉ClFNaNO₄ (M+Na⁺): 414.09, found 414.0884

Synthesis of compound 10b:



Compound **10b** was prepared according to a modification of a reported procedure.² To a solution of triphosgene (252 mg, 0.848 mmol) in toluene (15 mL) under N₂, pyridine (0.242 mL, 2.99 mmol) and subsequently a solution of *N*-(4-(trifluoromethyl)benzyl)cyclohex-2-en-1-amine (637 mg, 2.5 mmol) in toluene (4 mL), were added. The reaction mixture was stirred for 18 hours at ambient temperature, quenched with NH₄Cl (20 mL of a saturated aq. solution) and extracted with Et₂O (2 x 30 mL). The combined organic extracts were washed sequentially with HCl (40 mL of a 0.25 M aq. solution), H₂O (40 mL) and brine (40 mL), dried over MgSO₄, filtered and evaporated under reduced pressure to give carbamoyl chloride **10b** (722 mg, 91% yield) as a yellow oil.

¹<u>H NMR</u> (400 MHz, CDCl₃ mixture of rotamers) δ 7.60 (dd, J = 16.7, 8.1 Hz, 2H), 7.36 (d, J = 7.9 Hz, 2H), 5.85 – 6.00 (m, 1H), 5.55 – 5.41 (m, 1H), 5.10 – 4.90 (m, 1H), 4.82 – 4.49 (m, 2H), 2.08 – 1.94 (m, 3H), 1.85 – 1.40 (m, 3H).

¹³<u>C NMR</u> (101 MHz, CDCl₃ mixture of rotamers) δ 150.4, 150.3, 141.8, 141.4, 133.5, 133.4, 127.3, 126.5, 126.1, 126.1, 125.84 – 125.46 (m), 124.1 (q, J = 271.9 Hz) 58.7, 57.0, 50.4, 49.1, 28.5, 27.6, 24.5, 24.4, 21.2, 21.1.

¹⁹F NMR (376 MHz, CDCl₃ mixture of rotamers) δ -62.59, -62.63.

Synthesis of compound 10e:



Compound **10e** was prepared according to a modification of a reported procedure.² To a solution of triphosgene (134 mg, 0.44 mmol) in toluene (8 mL) under N₂, pyridine (0.129 mL, 1.6 mmol) and subsequently a solution of *N*-benzylcyclopent-2-en-1-amine (231 mg, 1.33 mmol) in toluene (2 mL). The reaction mixture was stirred for 18 hours at ambient temperature, quenched with NH₄Cl (20 mL of a saturated aq. solution) and extracted with Et₂O (2 x 30 mL). The combined organic extracts were washed sequentially with HCl (40 mL of a 0.25 M aq. solution), H₂O (40 mL) and brine (40 mL), dried over MgSO₄, filtered and evaporated under reduced pressure to give carbamoyl chloride **10e** (106 mg, 34% yield) as a yellowish oil.

 $\frac{^{1}\text{H NMR}}{5.58-5.46}$ (400 MHz, CDCl₃, mixture of rotamers) δ . 7.40 – 7.20 (m, 5H), 6.02 - 5.95 (m, 1H), 5.58 – 5.46 (m, 2H), 4.66 – 4.37 (m, 1H), 2.44 – 2.20 (m, 3H), 1.75 – 1.59 (m, 1H).

 $\frac{1^{3}C \text{ NMR}}{128.7, 128.6, 128.5, 127.3, 127.2, 126.2, 67.6, 66, 50.6, 48.9, 31.4, 31.3, 28.9, 28.4, 128.7, 128.6, 128.5, 127.3, 127.2, 126.2, 67.6, 66, 50.6, 48.9, 31.4, 31.3, 28.9, 28.4, 128.9 (ESI pos): calculated for C₁₃H₁₄ClNaNO (M+Na⁺) 258.07, found 258.0653.$

Synthesis of compound 10f:



Compound **10f** was prepared according to a modification of a reported procedure.² To a solution of triphosgene (250 mg, 0.843 mmol) in toluene (15 mL) under N₂, pyridine (0.241 mL, 2.98 mmol) and subsequently a solution of *N*-benzylbut-2-en-1-amine (400 mg, 2.48 mmol) in toluene (4 mL), were added. The reaction mixture was stirred for 18 hours at ambient temperature, quenched with NH₄Cl (20 mL of a saturated aq. solution) and extracted with Et₂O (2 x 30 mL). The combined organic extracts were washed sequentially with HCl (40 mL of a 0.25 M aq. solution), H₂O (40 mL) and brine (40 mL), dried over MgSO₄, filtered and evaporated under reduced pressure to give carbamoyl chloride **10f** (508 mg, 92% yield) as a yellow oil.

¹<u>H NMR</u> (400 MHz, CDCl₃, 1:1 mixture of rotamers) 7.42 - 7.30 (m, 3H), 7.29 - 7.24 (m, 2H), 5.75 - 5.54 (m, 1H), 5.53 - 5.34 (m, 1H), 4.68 (s, 1H), 4.55 (s, 1H), 3.90 (dd, J = 15.6, 6.3 Hz, 2H), 1.78 - 1.66 (m, 3H).

¹³C NMR (101 MHz, CDCl₃, 1:1 mixture of rotamers) δ 150.2, 149.6, 135.8, 135.6, 131.3, 130.7, 129.0, 128.9, 128.4, 128.3, 128.1, 128.1, 127.3, 124.3, 124.0, 53.2, 51.9, 51.5, 50.5, 17.8.

Synthesis of compound 10g:



Compound **10g** was prepared according to a modification of a reported procedure.² To a solution of triphosgene (252 mg, 0.85 mmol) in toluene (15 mL) under N₂, pyridine (0.243 mL, 3.0 mmol) and subsequently a solution of *N*-benzylbut-3-en-1-amine (403 mg, 2.5 mmol) in toluene (4 mL), were added. The reaction mixture was stirred for 18 hours at ambient temperature, quenched with NH₄Cl (20 mL of a saturated aq. solution) and extracted with Et₂O (2 x 30 mL). The combined organic extracts were washed sequentially with HCl (40 mL of a 0.25 M aq. solution), H₂O (40 mL) and brine (40 mL), dried over MgSO₄, filtered and evaporated under reduced pressure to give carbamoyl chloride **10g** (475 mg, 85% yield) as a yellow oil.

 $\frac{^{1}\text{H NMR}}{5.80 - 5.67}$ (m, 1H), 5.16 - 5.04 (m, 2H), 4.72 (s, 1H), 4.59 (s, 1H), 3.53 - 3.35 (m, 2H), 2.42 - 2.30 (m, 2H).

¹³C NMR (101 MHz, CDCl₃, 1:1 mixture of rotamers) δ 150.3, 149.6, 135.8, 135.6, 134.3, 134.0, 129.1, 129.0, 128.3, 128.2, 128.2, 127.2, 118.0, 117.8, 54.7, 52.7, 49.8, 48.9, 32.6, 31.7.

Synthesis of compound 10h:



Compound **10h** was prepared according to a modification of a reported procedure.² To a solution of triphosgene (252 mg, 0.85 mmol) in toluene (15 mL) under N₂, pyridine (0.243 mL, 3.0 mmol) and subsequently a solution of *N*-benzylpent-4-en-1-amine (438 mg, 2.5 mmol) in toluene (4 mL), were added. The reaction mixture was stirred for 18 hours at ambient temperature, quenched with NH₄Cl (20 mL of a saturated aq. solution) and extracted with Et₂O (2 x 30 mL). The combined organic extracts were washed sequentially with HCl (40 mL of a 0.25 M aq. solution), H₂O (40

mL) and brine (40 mL), dried over MgSO₄, filtered and evaporated under reduced pressure to give carbamoyl chloride **10h** (553 mg, 93% yield) as a yellow oil.

¹<u>H NMR</u> (400 MHz, CDCl₃, 1:1 mixture of rotamers) δ 7.41 – 7.30 (m, 3H), 7.29 – 7.24 (m, 2H), 5.81 – 5.68 (m, 2H), 5.08 – 4.92 (m, 2H), 4.71 (s, 1H), 4.58 (s, 1H), 3.36 (dt, *J* = 13.6, 7.8 Hz, 2H), 2.05 (q, *J* = 7.5 Hz, 2H), 1.70 (app h, *J* = 7.6 Hz, 2H).

¹³<u>C NMR</u> (101 MHz, CDCl₃, 1:1 mixture of rotamers) δ 150.3, 149.6, 137.3, 137.1, 135.9, 135.7, 129.0, 129.0, 128.2, 127.2, 115.8, 115.6, 54.5, 52.6, 50.0, 49.1, 30.8, 30.8, 27.1, 26.3.

C. Experimental Procedures

C1. Reaction of Aromatic Acyl Chlorides

C1.1 Experimental Setup

Our photoreactor consisted of a 12.5 cm diameter jar, fitted with 4 standard 29 sized ground glass joints arranged in a square and a central 29 sized joint. A commercial 1-meter LED strip was wrapped around the jar, followed by a layer of aluminium foil and cotton for insulation (Figure S2).



Figure S2: Photoreactor used for temperature-controlled reactions - pictures taken at different stages of the set-up assembly.

Each of the joints could be used to fit a standard 16 mm or 25 mm diameter Schlenk tube with a Teflon adaptor (Figure S3).



Figure S3: Teflon adaptors to use Schlenk tubes in the photoreactor.

An inlet and an outlet allow the circulation of liquid from a Huber Minichiller 300 inside the jar. This setup allows to perform reactions at temperatures ranging from -20 °C to 80 °C with accurate control of the reaction temperature (\pm 1°C, Figure S4).



Figure S4: Fully assembled controlled temperature photoreactor in operation.

In order to maintain consistent illumination between different experiments, only the four external positions were used to perform reactions. The central position was used to monitor the

temperature inside a Schlenk tube identical to those used to perform reactions, ensuring that the reaction mixtures are at the desired temperature.

C1.2 Optimization Studies

Table S1. Screening of the catalysts



All reaction performed on 0.5 mmol scale; yield determined by ¹H NMR analysis of the crude reaction mixture using trichloroethylene as the internal standard.

Table S2. Screening of the solvents



All reaction performed on 0.5 mmol scale; yield determined by ¹H NMR analysis of the crude reaction mixture using trichloroethylene as the internal standard.

Table S3. Screening of the bases

Î	+	<i>catalyst</i> B (10 mol%) γ-terpinene (2 equiv.)		S
⊃h ́C∣ 1a	2a	Base (2 equiv.), blue LEDs DCE (0.5 M), 16 h, 27 °C	Ph CN 3a	EtO SK catalyst B
l.5 equiv	. 1 equiv.			
	entry	base	NMR yield (%)	
	1	2,6-lutidine	30	
	2	2,4,6-collidine	16	
	3	N-Methylmorpholine	0	
	4	N-Methylimidazole	0	
	5	K ₂ CO ₃	24	
	6	NaOAc	19	
	7	KH ₂ PO ₄	16	
	8	NaHCO ₃	16	

All reaction performed on 0.5 mmol scale; yield determined by ¹H NMR analysis of the crude reaction mixture using trichloroethylene as the internal standard.

catalyst B (10 mol%) H source (2 equiv.) CN 2,6-lutidine (2 equiv.), blue LEDs EtC DCE (0.5 M), 16 h, 27 °C 2a 1a 3a catalyst **B** 1.5 equiv. 1 equiv. NMR yield (%) H source entry 1 y-terpinene 30 2 Hantzsch ester 25 3 9 1,4-Cyclohexadiene 10 2,5-Dihydrofuran 5

All reaction performed on 0.5 mmol scale; yield determined by ¹H NMR analysis of the crude reaction mixture using trichloroethylene as the internal standard.

Table S5. Screening of the temperature



All reaction performed on 0.5 mmol scale; yield determined by ¹H NMR analysis of the crude reaction mixture using trichloroethylene as the internal standard.

Table S4. Screening of the H-atom source

Table S6. Final cycle of optimization

	0 ∦ +		<i>catalyst</i> B (10 mol% γ-terpinene (X equi	6) V.)	
	Ph Cl	2a ∼CN −	Base , blue LEDs DCE (0.5 M), 16 h, Ter	np. 3a catalyst B	
	1.5 equiv.	1 equiv.			
entry	Base	Base (equiv.)	γ-terpinene (equiv.)	Other variations	yield (%)
1	2,6-lutidine	2	2	-	50
2	2,6-lutidine	1.2	2	-	50
3	Na ₂ CO ₃	1.2	2	-	66
4	Na ₂ HPO ₄	1.2	2	-	20
5	Na ₃ PO ₄	1.2	2	-	66
6	Na ₃ PO ₄	1.2	2	20 mol% catalyst	45
7	Na ₃ PO ₄	1.2	3	-	55
8	Na ₃ PO ₄	2	2	-	84
9	Na ₃ PO ₄	2	2	5 mol% catalyst	62
10	Na ₃ PO ₄	2	2	DCM [0.25 M]	85
11	Na ₃ PO ₄	2	2	Vinyl sulfone as acceptor & DCM [0.25 M]	57
12	Na ₃ PO ₄	2	3	Vinyl sulfone as acceptor & DCM [0.25 M]	85

All reaction performed on 0.5 mmol scale; yield determined by 1H NMR analysis of the crude reaction mixture using trichloroethylene as the internal standard.

Table S7. Anhydride method - optimization



entry	Acid	Chloroformate	Base	Catalyst	Acceptor	NMR yield (%)
1	Benzoic	Ethyl	Na ₃ PO ₄	10 mol% B	Acrylonitrile	50
2	Benzoic	Ethyl	Na ₃ PO ₄	10 mol% C	Acrylonitrile	55
3	Benzoic	Ethyl	Na ₃ PO ₄	20 mol% B	Acrylonitrile	60
4	Benzoic	Ethyl	Na₃PO₄ (1 equiv.)	20 mol% B	Acrylonitrile	69
5	Benzoic	Ethyl	-	20 mol% B	Acrylonitrile	71
6	Benzoic	Methyl	-	20 mol% B	Acrylonitrile	61
7	Benzoic	Isobutyl	-	20 mol% B	Acrylonitrile	15
8	Cyclohexyl	Ethyl	-	20 mol% B	Vinyl sulfone	64
9	Cyclohexyl	Ethyl	-	20 mol% C	Vinyl sulfone	42
10	Cyclohexyl	Ethyl	-	30 mol% B	Vinyl sulfone	83
11	Cyclohexyl	Ethyl	-	50 mol% B	Vinyl sulfone	82

All reaction performed on 0.5 mmol scale; yield determined by 1H NMR analysis of the crude reaction mixture using trichloroethylene as the internal standard.

C1.3 General Procedure A



In an oven dried tube of 15 mL (16 mm × 125 mm) with a Teflon septum screw cap, potassium ethyl xanthogenate **B** (8 mg, 0.05 mmol, 0.1 equiv.), sodium phosphate (164 mg, 1.00 mmol, 2 equiv.), acyl chloride **1** (0.75 mmol, 1.5 equiv.) and the electron-poor olefin **2** (0.5 mmol, 1 equiv., *if solid*), were dissolved in DCM (2 mL, HPLC grade). Then, γ -terpinene (240 µL, 1.5 mmol, 3 equiv.) was added. The resulting yellow mixture was degassed with argon sparging for 60 seconds. When the electron-poor olefin **2** is *liquid*, it was added via syringe after the argon sparging. The reaction vessel was then placed in the temperature-controlled photoreactor (Figures S2-4) set at 60 °C (60-61 °C measured in the central well) and irradiated for 16 hours upon stirring, if not otherwise specified. Then, the solvent was evaporated and the residue purified by column chromatography to afford the corresponding product in the stated yield with >95% purity according to ¹H NMR analysis.

C1.4 Characterization of Products

4-Oxo-4-phenylbutanenitrile (3a): Synthesized according to the general procedure A using benzoyl chloride (87 μ L, 0.75 mmol, 1.5 equiv.) and acrylonitrile (33 μ L, 0.5 mmol, 1 equiv.). The crude mixture was purified by flash column chromatography on silica gel (20% AcOEt in hexanes as eluent) to afford **3a** (65 mg, 82% yield) as a white solid.

 $\frac{^{1}\text{H NMR}}{^{3}\text{H - 3.35}} (500 \text{ MHz}, \text{CDCl}_3) \delta 7.98 - 7.93 \text{ (m, 2H)}, 7.64 - 7.59 \text{ (m, 1H)}, 7.53 - 7.47 \text{ (m, 2H)}, 3.41 - 3.35 \text{ (m, 2H)}, 2.80 - 2.75 \text{ (m, 2H)}.$

¹³C NMR (126 MHz, CDCl₃) δ 195.4, 135.7, 134.0, 129.0, 128.1, 119.3, 34.4, 11.9

Matching reported literature data.9



4-(4-methoxyphenyl)-4-oxobutanenitrile (3b): Synthesized according to the general procedure A using 4-methoxybenzoyl chloride (102 μ L, 0.75 mmol, 1.5 equiv.) and acrylonitrile (33 μ L, 0.5 mmol, 1 equiv.). The crude mixture was purified by flash column chromatography on silica gel (15%

AcOEt in hexanes as eluent) to afford **3b** (80 mg, 84% yield) as a white solid.

¹<u>H NMR</u> (500 MHz, CDCl₃) δ 7.92 (app d, J = 8.9 Hz, 2H), 6.95 (app d, J = 9.0 Hz, 2H), 3.87 (s, 3H), 3.32 (t, J = 7.3 Hz, 2H), 2.75 (t, J = 7.3 Hz, 2H).

¹³C NMR (126 MHz, CDCl₃) δ 193.9, 164.2, 130.4, 128.8, 119.5, 114.1, 55.7, 34.0, 12.0

Matching reported literature data.9



Benzyl 4-(4-methoxyphenyl)-4-oxobutanoate (3c): Synthesized according to the general procedure A using 4-methoxybenzoyl chloride (102 μ L, 0.75 mmol, 1.5 equiv.) and benzyl acrylate (77 μ L, 0.5 mmol, 1 equiv.). The crude mixture was purified by flash column chromatography

on silica gel (15% AcOEt in hexanes as eluent), followed by a second purification (AcOEt/hexanes/toluene 1:6:6 as eluent) to afford 3c (96 mg, 64% yield) as a yellow solid.

 $\frac{^{1}\text{H NMR}}{(s, 2\text{H}), 3.87 (s, 3\text{H}), 3.28 (t, J = 6.7 \text{ Hz}, 2\text{H}), 2.81 (t, J = 6.7 \text{ Hz}, 2\text{H}), 6.96 - 6.91 (m, 2\text{H}), 5.15 (s, 2\text{H}), 3.87 (s, 3\text{H}), 3.28 (t, J = 6.7 \text{ Hz}, 2\text{H}), 2.81 (t, J = 6.7 \text{ Hz}, 2\text{H}).}$

¹³C NMR (126 MHz, CDCl₃) δ 196.6, 173.0, 163.7, 136.1, 130.4, 129.8, 128.6, 128.3 (2C overlapping), 113.9, 66.6, 55.6, 33.1, 28.5.

HRMS (ESI pos): calculated for C₁₈H₁₈NaO₄ (M+Na⁺): 321.1097, found: 321.1091.

Benzyl 4-(4-methoxyphenyl)-4-oxo-2-(trifluoromethyl)butanoate (3d): Synthesized according to the general procedure A using 4methoxybenzoyl chloride (102 μ L, 0.75 mmol, 1.5 equiv.) and benzyl 2-(trifluoromethyl)acrylate (115 mg, 0.5 mmol, 1 equiv.). The crude

mixture was purified by flash column chromatography on silica gel (10% AcOEt in hexanes as eluent). In order to remove traces of *p*-anisaldehyde formed as a byproduct during the reaction, after the chromatographic purification and solvent removal, the mixture was dissolved in 1.5 mL of MeOH, and 7.5 mL of saturated NaHSO₃ (aq) were added. Subsequently, the mixture was stirred for 30 s, diluted with 7.5 mL of H₂O, and extracted with 7.5 mL of 10% AcOEt in hexanes. The organic layer was dried with MgSO₄, filtered, and concentrated in vacuo¹⁰ to afford **3d** (150 mg, 82% yield) as a colorless oil.

¹<u>H NMR</u> (400 MHz, CDCl₃) δ 7.99 – 7.91 (m, 2H), 7.42 – 7.29 (m, 5H), 6.99 – 6.91 (m, 2H), 5.24 (dd, J = 18.3; 12.3 Hz, 2H), 4.01 – 3.89 (m, 1H), 3.87 (s, 3H), 3.78 (dd, J = 17.7, 10.8 Hz, 1H), 3.32 (dd, J = 17.7, 3.1 Hz, 1H).

¹³C NMR (100 MHz, CDCl₃) δ 193.8, 166.9 (q, J = 2.9 Hz), 164.2, 135.2, 130.6 (2CH overlapping), 128.9, 128.7, 128.5, 128.1, 125.0 (q, J = 280.4 Hz), 114.0, 67.9, 55.6, 45.9 (q, J = 27.9 Hz), 34.9 (d, J = 1.4 Hz).

¹⁹F NMR (376 MHz, CDCl₃, proton decoupled) δ -67.51 (s, 3F).

HRMS (ESI pos): calculated for C₁₉H₁₇F₃NaO₄ (M+Na⁺): 389.0971, found: 389.0978.



CF₃

4-(4-Methoxyphenyl)-4-oxobutanal (3e): Synthesized according to the general procedure A using 4-methoxybenzoyl chloride (102 μ L, 0.75 mmol, 1.5 equiv.) and acrolein (33 μ L, 0.5 mmol, 1 equiv.). The crude mixture was purified by flash column chromatography on silica gel (20%

AcOEt in hexanes as eluent), followed by a second purification (5:47:48 of Et_2O/DCM /hexanes as eluent) to afford **3e** (50 mg, 52% yield) as a yellow oil.

¹<u>H NMR</u> (400 MHz, CDCl₃) δ 9.89 (s, 1H), 7.99 – 7.91 (m, 2H), 6.96 – 6.89 (m, 2H), 3.85 (s, 3H), 3.27 (app t, J = 6.4 Hz, 2H), 2.89 (app t, J = 6.5 Hz, 2H).

¹³C NMR (100 MHz, CDCl₃) δ 201.0, 196.4, 163.7, 130.4, 129.6, 113.9, 55.6, 37.8, 30.8

Matching reported literature data.¹¹

1-(4-Methoxyphenyl)pentane-1,4-dione (3f): Synthesized according to the general procedure A using 4-methoxybenzoyl chloride (102 μ L, 0.75 mmol, 1.5 equiv.) and methyl vinyl ketone (41 μ L, 0.5 mmol, 1 equiv.). The crude mixture was purified by flash column chromatography on silica gel

(20% AcOEt in hexanes as eluent), followed by a second one (10:45:45 of $Et_2O/DCM/Hexanes$ as eluent) to afford **3f** (49 mg, 48% yield) white solid.

¹<u>H NMR</u> (400 MHz, CDCl₃) δ 7.98 – 7.91 (m, 2H), 6.95-6.89 (m, 2H), 3.85 (s, 3H), 3.25 – 3.18 (m, 2H), 2.88 – 2.82 (m, 2H), 2.24 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 207.6, 197.1, 164.6, 130.4, 129.9, 113.8, 55.6, 37.2, 32.2, 30.2.

Matching reported literature data.9



Diethyl (3-(4-methoxyphenyl)-3-oxopropyl)phosphonate (3g): Synthesized according to the general procedure A using 4methoxybenzoyl chloride (102 μ L, 0.75 mmol, 1.5 equiv.) and diethyl vinylphosphonate (77 μ L, 0.5 mmol, 1 equiv.). Irradiations time: 24

hours. The crude mixture was purified by flash column chromatography on silica gel (20% AcOEt in hexanes as eluent) to afford **3g** (81 mg, 54% yield) as a white solid.

 $\frac{^{1}\text{H NMR}}{^{3}\text{H NMR}}$ (400 MHz, CDCl₃) δ 7.91 (app d, J = 8.8 Hz, 2H), 6.89 (app d, J = 8.9 Hz, 2H), 4.20 – 3.96 (m, 4H), 3.82 (s, 3H), 3.28 – 3.12 (m, 2H), 2.22 – 2.04 (m, 2H), 1.28 (t, J = 7.0 Hz, 6H).

 $\frac{^{13}\text{C NMR}}{\text{Hz}}$ (100 MHz, CDCl₃) δ 196.0 (d, *J* = 16.2 Hz), 163.7, 130.3, 129.4, 113.8, 61.7 (d, *J* = 6.6 Hz), 55.5, 31.3 (d, *J* = 2.9 Hz), 19.9 (d, *J* = 144.3 Hz), 6.5 (d, *J* = 6.5 Hz).

Matching reported literature data.¹²



1-(4-Methoxyphenyl)-3-(phenylsulfonyl)propan-1-one (3h): Synthesized according to the general procedure A using 4methoxybenzoyl chloride (102 μ L, 0.75 mmol, 1.5 equiv.) and phenyl vinyl sulfone (84 mg, 0.5 mmol, 1 equiv.). Reaction time: 24 hours. The

crude mixture was purified by flash column chromatography on silica gel (25% AcOEt in hexanes as eluent), followed by a second one (20% AcOEt in hexanes as eluent) to afford **3h** (128 mg, 84% yield) as a white solid.

 $\frac{^{1}\text{H NMR}}{7.60-7.54} (500 \text{ MHz}, \text{CDCl}_3) \delta 7.96 - 7.93 (m, 2H), 7.91 - 7.87 (m, 2H), 7.69 - 7.63 (m, 1H), 7.60 - 7.54 (m, 2H), 6.95 - 6.90 (m, 2H), 3.86 (s, 3H), 3.57 - 3.51 (m, 2H), 3.46 - 3.40 (m, 2H).$

¹³C NMR (126 MHz, CDCl₃) δ 193.9, 164.1, 139.3, 134.0, 130.5, 129.5, 129.0, 128.1 114.1, 55.7, 51.3, 31.0.

Matching reported literature data.¹³



N-Isopropyl-3-(4-methoxyphenyl)-3-oxopropane-1-sulfonamide (3i): Synthesized according to the general procedure A using 4-methoxybenzoyl chloride (102 μ L, 0.75 mmol, 1.5 equiv.) and N-isopropylethenesulfonamide (75 mg, 0.5 mmol, 1 equiv.). Reaction

time: 24 hours. The crude mixture was purified by flash column chromatography on silica gel (20% AcOEt in hexanes as eluent) to afford **3i** (98 mg, 69% yield) as a white solid.

 $\frac{^{1}\text{H NMR}}{(s, 3\text{H}), 3.74 - 3.58} (\text{m}, 1\text{H}), 3.54 - 3.38 (\text{m}, 4\text{H}), 1.24 (\text{d}, J = 6.4 \text{ Hz}, 6\text{H}).$

¹³C NMR (100 MHz, CDCl₃) δ 194.7, 164.1, 130.6, 129.2, 114.1, 55.7, 48.7, 46.5, 32.7, 24.4.

HRMS (ESI neg): calculated for C₁₃H₁₈NO₄S (M⁻): 284.0962, found 284.0974.



Methyl ((3-(4-methoxyphenyl)-3-oxopropyl)sulfonyl)alaninate (3j): Synthesized according to the general procedure A using 4-methoxybenzoyl chloride (102 μ L, 0.75 mmol, 1.5 equiv.) and methyl (vinylsulfonyl)alaninate (97 mg, 0.5 mmol, 1 equiv.).

Reaction time: 24 hours. The crude mixture was purified by flash column chromatography on silica gel (35% AcOEt in hexanes as eluent), followed by a second one (20:40:40 of AcOEt/DCM/Hexanes as eluent) to afford **3j** (83 mg, 50% yield) as a colorless oil.

 $\frac{^{1}\text{H NMR}}{^{420}\text{ (400 MHz, CDCl_3)}} \delta 7.97 - 7.89 \text{ (m, 2H), } 6.96 - 6.89 \text{ (m, 2H), } 5.29 \text{ (d, } J = 8.4 \text{ Hz, 2H), } 4.25 - 4.14 \text{ (m, 1H), } 3.85 \text{ (s, 3H), } 3.73 \text{ (s, 3H), } 3.53 - 3.40 \text{ (m, 4H), } 1.45 \text{ (d, } J = 7.15 \text{ Hz, 3H). } 1.45 \text$

 $\frac{^{13}\text{C NMR}}{^{32.2}, 19.9} (100 \text{ MHz, CDCl}_3) \delta 194.5, 173.2, 164.0, 130.5, 129.1, 114.0 55.6, 52.9, 51.7, 48.4, 32.2, 19.9. \underline{\text{HRMS (ESI pos)}}: calculated for C_{14}H_{19}NNaO_6S (M+Na^+): 352.0825, found 352.0814.$



3-(4-Methoxyphenyl)-N-methyl-3-oxo-N-(pyridin-2-yl)propane-1-sulfonamide (3k): Synthesized according to the general procedure A using 4-methoxybenzoyl chloride (102 μ L, 0.75 mmol, 1.5 equiv.) and N-methyl-N-(pyridin-2-yl)ethenesulfonamide (99 mg, 0.5 mmol,

1 equiv.). Reaction time: 24 hours. The crude mixture was purified by flash column chromatography on silica gel (20:20:60 of AcOEt/DCM/Hexanes as eluent), followed by a second one (20:20:60 of Et₂O/DCM/Hexanes as eluent) to afford **3k** (75 mg, 45% yield) as a yellowish oil.

¹<u>H NMR</u> (400 MHz, CDCl₃) δ 8.41 – 8.34 (m, 1H), 7.92 – 7.84 (m, 2H), 7.72 – 7.65 (m, 1H), 7.42 (app d, J = 8.3 Hz, 1H), 7.15 – 7.08 (m, 1H), 6.95 – 6.87 (m, 2H), 3.85 (s, 3H), 3.72 – 3.64 (m, 2H), 3.45 (s, 3H), 3.46 – 3.39 (m, 2H).

¹³C NMR (100 MHz, CDCl₃) δ 194.2, 164.0, 154.0, 148.3, 138.2, 130.5, 129.1, 121.0, 118.6, 114.0, 55.6, 46.3, 35.9, 31.8.

HRMS (ESI pos): calculated for C₁₆H₁₉N₂O₄S (M+H⁺): 335.1060, found 335.1043.



Dimethyl 2-(4-methoxybenzoyl)succinate (3l): Synthesized according to the general procedure A using 4-methoxybenzoyl chloride (102 μ L, 0.75 mmol, 1.5 equiv.) and dimethyl fumarate (72 mg, 0.5 mmol, 1 equiv.). The crude mixture was purified by flash column chromatography

on silica gel (20% AcOEt in hexanes as eluent) to afford **31** (122 mg, 87% yield) as a colorless oil.

 $\frac{^{1}\text{H NMR}}{^{3}\text{H NMR}} (500 \text{ MHz, CDCl}_{3}) \delta 8.03 - 7.98 \text{ (m, 2H)}, 6.96 - 6.92 \text{ (m, 2H)}, 4.82 \text{ (t, } J = 7.1 \text{ Hz, 1H)}, 3.85 \text{ (s, 3H)}, 3.66 \text{ (s, 3H)}, 3.65 \text{ (s, 3H)}, 3.09 - 2.97 \text{ (m, 2H)}.$

¹³<u>C NMR</u> (126 MHz, CDCl₃) δ 192.3, 171.9, 169.5, 164.2, 131.4, 128.8, 114.0, 129.0, 128.1, 114.1, 55.6, 52.8, 52.1, 33.2.

Matching reported literature data.¹⁴



3-(4-Methoxybenzoyl)-1-propylpyrrolidine-2,5-dione (3m): Synthesized according to the general procedure A using 4-methoxybenzoyl chloride (102 μ L, 0.75 mmol, 1.5 equiv.) and 1-propyl-1H-pyrrole-2,5-dione (69.6 μ L, 0.5 mmol, 1 equiv.). Chromatography on silica gel (20%

AcOEt in hexanes as eluent) could not remove byproduct completely. Therefore, a further purification by semipreparative HPLC (Column SunFire C18, 60:40 Methanol/Water 6 min, up to 100% Methanol 1 min, 100% Methanol 4 min, 1 mL/min) was performed to obtain an analytical amount of the isolated product as a white solid. NMR yield (Trichloroethylene was used as internal standard): 53%.

¹<u>H NMR</u> (500 MHz, CDCl₃) δ 8.12-8.07 (m, 2H), 7.02 – 6.97 (m, 2H), 4.78 (dd, J = 8.3, 3.9 Hz, 1H), 3.90 (s, 3H), 3.47 (t, J = 7.3 Hz, 2H), 3.37 (dd, J = 18.1, 3.8 Hz, 1H), 2.82 (dd, J = 18.1, 8.8 Hz, 1H), 1.64 – 1.54 (m, 2H, overlapping with water peak), 0.87 (t, J = 7.4 Hz, 3H).

¹³<u>C NMR</u> (126 MHz, CDCl₃) δ 190.9, 176.1, 173.4, 164.7, 132.4, 128.6, 114.2, 55.7, 48.2, 41.0, 31.8, 21.0, 11.3

HRMS (ESI pos): calculated for C₁₅H₁₇NNaO₄ (M+Na⁺): 298.1050, found 298.1056.



Diethyl 2-(1-(4-methoxyphenyl)-1-oxopropan-2-yl)malonate (3n): Synthesized according to the general procedure A using 4methoxybenzoyl chloride (102 μ L, 0.75 mmol, 1.5 equiv.) and diethyl 2ethylidenemalonate (93 μ L, 0.5 mmol, 1 equiv.). The crude mixture was

purified by flash column chromatography on silica gel (10% AcOEt in hexanes as eluent) to afford **3n** (60 mg, 37% yield) as a colorless oil.

 $\frac{^{1}\text{H NMR}}{-4.02}$ (400 MHz, CDCl₃) δ 8.03 – 7.96 (m, 2H), 6.98 – 6.93 (m, 2H), 4.31 – 4.21 (m, 2H) 4.20 – 4.02 (m, 3H), 3.97 (d, *J* = 10.8 Hz, 1H), 3.87 (s, 3H), 1.31 (t, *J* = 7.0 Hz, 3H), 1.19 (d, *J* = 7.0 Hz, 3H), 1.16 (t, *J* = 7.1 Hz, 3H).

 $\frac{13}{100}$ NMR (100 MHz, CDCl₃) δ 200.2, 169.0, 168.5, 163.8, 131.0, 128.6, 114.0, 61.7, 55.6, 55.1, 40.3, 16.25, 14.3, 14.0.

<u>HRMS (ESI pos)</u>: calculated for C₁₇H₂₂NaO₆ (M+Na⁺): 345.1309, found 345.1306.

1-Phenyl-3-(phenylsulfonyl)propan-1-one (4a): Synthesized according to the general procedure A using benzoyl chloride (87 μ L, 0.75 mmol, 1.5 equiv.) and phenyl vinyl sulfone (84 mg, 0.5 mmol, 1 equiv.). The crude mixture was purified by flash column chromatography on silica gel (20% AcOEt in hexanes as eluent) to afford **4a** (112 mg, 82% yield) as a white solid.

 $\underline{^{1}H\ NMR}$ (400 MHz, CDCl₃) δ 7.99 – 7.88 (m, 4H), 7.70 – 7.63 (m, 1H), 7.63 – 7.54 (m, 3H), 7.51 – 7.43 (m, 2H), 3.60 – 3.53 (m, 2H), 3.53 – 3.46 (m, 2H).

¹³<u>C NMR</u> (100 MHz, CDCl₃) δ 195.5, 139.2, 135.9, 134.1, 133.9, 129.6, 128.9, 128.2, 128.1, 51.1, 31.5.

Matching reported literature data.¹³

4-(3-Cyanopropanoyl)benzonitrile (4b): Synthesized according to the general procedure A using using 4-cyanobenzoyl chloride (124 mg, 0.75 mmol, 1.5 equiv.) and acrylonitrile (33 μ L, 0.5 mmol, 1 equiv.). In this case the reaction was irradiated for 60 hours. The crude mixture was purified by flash column chromatography on silica gel (15% AcOEt in hexanes as eluent) to afford **4b** (92 mg, 45% yield) as a white solid.

 $\frac{1}{H}$ NMR (500 MHz, CDCl₃) δ 8.04 (app d, J = 8.2 Hz, 2H), 7.80 (app d, J = 8.2 Hz, 2H), 3.39 (t, J = 6.9 Hz, 2H), 2.79 (t, J = 7.0 Hz, 2H).

¹³C NMR (126 MHz, CDCl₃) δ 194.3, 138.5, 132.8, 128.6, 118.8, 117.7, 117.3, 34.7, 11.8.

Matching reported literature data.9

4-(3-(Phenylsulfonyl)propanoyl)benzonitrile (4c): Synthesized according to the general procedure A using 4-cyanobenzoyl chloride (124 mg, 0.75 mmol, 1.5 equiv.) and phenyl vinyl sulfone (84 mg, 0.5 mmol, 1 equiv.). In

this case the reaction was irradiated for 60 hours. The crude mixture was purified by flash column chromatography on silica gel (25% AcOEt in hexanes as eluent) to afford 4c (79 mg, 53% yield) as a white solid.

¹<u>H NMR</u> (400 MHz, CDCl₃) δ 8.02 (app d, J = 8.5 Hz, 2H), 7.95 (app d, J = 7.3 Hz, 2H), 7.78 (app d, J = 8.4 Hz, 2H), 7.69 (app t, J = 7.4 Hz, 1H), 7.59 (app t, J = 7.7 Hz, 2H), 3.60 – 3.48 (m, 4H).

¹³<u>C NMR</u> (100 MHz, CDCl₃) δ 194.4, 139.1, 138.8, 134.2, 132.8, 129.6, 128.6, 128.1, 117.8, 117.2, 50.9, 31.8.

HRMS (ESI pos): calculated for C₁₆H₁₃NNaO₃S (M+Na⁺): 322.0508, found 322.0505.



1-(4-Iodophenyl)-3-(phenylsulfonyl)propan-1-one (4d): Synthesized according to the general procedure A using 4-iodobenzoyl chloride (200 mg, 0.75 mmol, 1.5 equiv.) and phenyl vinyl sulfone (84 mg, 0.5 mmol, 1 equiv.).

In this case the reaction was irradiated for 60 hours. The crude mixture was purified by flash column chromatography on silica gel (20% AcOEt in hexanes as eluent) to afford **4d** (130 mg, 65% yield) as a white solid.

 $^{1}\underline{H}$ NMR (500 MHz, CDCl₃) δ 7.99 – 7.92 (m, 2H), 7.87 – 7.82 (m, 2H), 7.70 – 7.65 (m, 1H), 7.65 – 7.61 (m, 2H), 7.61 – 7.56 (m, 2H), 3.58 – 3.51 (m, 2H) 3.49 – 3.42 (m, 2H).

¹³<u>C NMR</u> (126 MHz, CDCl₃) δ 194.9, 139.2, 138.3, 135.2, 134.1, 129.6, 129.5, 128.1, 102.1, 51.0, 31.4

HRMS (ESI pos): calculated for C₁₅H₁₃INaO₃S (M+Na⁺): 422.9522, found 422.9519.

3-(Phenylsulfonyl)-1-(2,4,6-trichlorophenyl)propan-1-one (4e): Synthesized according to the general procedure A using 2,4,6-trichlorobenzoyl chloride (183 mg, 0.75 mmol, 1.5 equiv.) and phenyl vinyl sulfone (84 mg, 0.5 mmol, 1 equiv.). In this case the reaction was irradiated for 60 hours. The crude mixture was purified by flash column chromatography on silica gel (25% AcOEt in hexanes as eluent) followed by a second one (5:25:70 of AcOEt/DCM/Hexanes as eluent) to afford **4e** (95 mg, 50% yield) as a withe solid.

 $\frac{^{1}\text{H NMR}}{^{7.36}} (400 \text{ MHz}, \text{CDCl}_3) \ \delta \ 7.98 - 7.92 \ (m, \ 2\text{H}), \ 7.72 - 7.65 \ (m, \ 1\text{H}), \ 7.63 - 7.56 \ (m, \ 2\text{H}), \ 7.36 \ (s, \ 2\text{H}), \ 3.58 - 3.50 \ (m, \ 2\text{H}), \ 3.33 - 3.25 \ (m, \ 2\text{H}).$

¹³<u>C NMR</u> (100 MHz, CDCl₃) δ 197.2, 138.9, 137.0, 136.6, 134.2, 131.2, 129.6, 128.5, 128.1, 50.1, 36.5

<u>HRMS (ESI pos)</u>: calculated for C₁₅H₁₁Cl₃NaO₃S (M+Na⁺): 398.9387, found 398.9390.

SO₂Ph

1-(Benzo[d][1,3]dioxol-5-yl)-3-(phenylsulfonyl)propan-1-one (4f): Synthesized according to the general procedure A using benzo[d][1,3]dioxole-5-carbonyl chloride (138 mg, 0.75 mmol, 1.5 equiv.)

and phenyl vinyl sulfone (84 mg, 0.5 mmol, 1 equiv.). Reaction time: 24 hours. The crude mixture was purified by flash column chromatography on silica gel (25% AcOEt in hexanes as eluent) to afford **4f** (90 mg, 57% yield) as a white solid.

¹<u>H NMR</u> (500 MHz, CDCl₃) δ 7.96 – 7.92 (m, 2H), 7.67 (tt, *J* = 7.3, 1.8 Hz, 1H), 7.60 – 7.55 (m, 2H), 7.52 (dd, *J* = 8.1, 1.8 Hz, 1H), 7.36 (d, *J* = 1.7 Hz, 1H), 6.84 (d, *J* = 8.1 Hz, 1H), 6.04 (s, 2H), 3.57 – 3.50 (m, 2H), 3.44 – 3.37 (m, 2H).

¹³<u>C NMR</u> (126 MHz, CDCl₃) δ 193.5, 152.5, 148.5, 139.2, 134.0, 130.8, 129.5, 128.1, 124.7, 108.2, 107.8, 102.2, 51.3, 31.2.

HRMS (ESI pos): calculated for C₁₆H₁₄NaO₅S (M+Na⁺): 341.0454, found 341.0452.

1-(Benzofuran-2-yl)-3-(phenylsulfonyl)propan-1-one (4g): Synthesized according to the general procedure A using benzofuran-2-carbonyl chloride (135 mg, 0.75 mmol, 1.5 equiv.) and phenyl vinyl sulfone (84 mg, 0.5 mmol,

1 equiv.). Reaction time: 24 hours. The crude mixture was purified by flash column chromatography on silica gel (25% AcOEt in hexanes as eluent) followed by a second one (20% AcOEt in hexanes as eluent) to afford 4g (77 mg, 49% yield) as a yellowish solid.

¹<u>H NMR</u> (500 MHz, CDCl₃) δ 7.99 – 7.94 (m, 2H), 7.71 (app d, *J* = 7.8 Hz, 1H), 7.70 – 7.65 (m, 1H), 7.61 – 7.55 (app t, *J* = 8.0 Hz, 3H), 7.55 (s, 1H), 7.53 – 7.48 (m, 1H), 7.35 – 7.30 (m, 1H), 3.61 – 3.55 (m, 2H), 3.53 – 3.47 (m, 2H).

¹³C NMR (126 MHz, CDCl₃) δ 186.6, 155.9, 151.6, 139.0, 134.2, 129.6, 128.9, 128.2, 126.9, 124.3, 123.6, 113.7, 112.6, 50.6, 31.8

<u>HRMS (ESI pos)</u>: calculated for $C_{17}H_{14}NaO_4S$ (M+Na⁺): 337.0505, found 337.0504.



1-(3-(2,6-Dichlorophenyl)-5-methylisoxazol-4-yl)-3-(**phenylsulfonyl)propan-1-one (4h):** Synthesized according to the general procedure A using 3-(2,6-dichlorophenyl)-5-methylisoxazole-4-carbonyl chloride (218 mg, 0.75 mmol, 1.5 equiv.) and phenyl vinyl sulfone (84 mg,

0.5 mmol, 1 equiv.). Reaction time: 24 hours. The crude mixture was purified by flash column chromatography on silica gel (20% AcOEt in hexanes as eluent) to afford **4h** (75 mg, 35% yield) as a white solid.

 $^{1}\underline{\text{H NMR}}$ (400 MHz, CDCl₃) δ 7.75 – 7.67 (m, 2H), 7.67 – 7.60 (m, 1H), 7.57 – 7.43 (m, 5H), 3.41 – 3.34 (m, 2H), 2.74 (s, 3H), 3.68 – 3.60 (m, 2H).

¹³<u>C NMR</u> (126 MHz, CDCl₃) δ 189.0, 176.5, 157.2, 138.6, 135.6, 134.0, 132.2, 129.5, 128.6, 128.0, 127.9, 116.1, 50.1, 34.3, 14.2.

<u>HRMS (ESI pos)</u>: calculated for C₁₉H₁₅Cl₂NNaO₄S (M+Na⁺): 445.9991, found 445.9992.

^O SO₂Ph **1-Phenyl-5-(phenylsulfonyl)pentan-3-one (5b):** Synthesized according to the general procedure A using hydrocinnamoyl chloride (111 μ L, 0.75 mmol, 1.5 equiv.) and phenyl vinyl sulfone (84 mg, 0.5 mmol, 1 equiv.). In

this case the reaction was irradiated for 60 hours. The crude mixture was purified by two rounds of flash column chromatography on silica gel (25% AcOEt in hexanes as eluent): to afford **5b** (113 mg, 75% yield) as a white solid.

 $\frac{^{1}\text{H NMR}}{^{7}\text{MR}}$ (400 MHz, CDCl₃) δ 7.92 – 7.87 (m, 2H), 7.71 – 7.63 (m, 1H), 7.61 – 7.53 (m, 2H), 7.31 – 7.23 (m, 2H), 7.22 – 7.16 (m, 1H), 7.16 – 7.10 (m, 2H), 3.42 – 3.33 (m, 2H), 2.92 – 2.82 (m, 4H), 2.81 – 2.72 (m, 2H).

¹³C NMR (100MHz, CDCl3) δ 205.3, 140.5, 139.1, 134.1, 129.5, 128.7, 128.4, 128.1, 126.5, 50.6, 44.4, 35.3, 29.7.

Matching reported literature data.¹⁵

EtO₂C SO₂Ph

Ethyl 4-oxo-6-(phenylsulfonyl)hexanoate (5c): Synthesized according to the general procedure A using ethyl 4-chloro-4-oxobutanoate (107 μ L, 0.75 mmol, 1.5 equiv.) and phenyl vinyl sulfone (84 mg, 0.5 mmol, 1

equiv.). Reaction time: 24 hours. The crude mixture was purified by flash column chromatography on silica gel (33% AcOEt in hexanes as eluent). Product was then dissolved in DCM, washed 3 times with a solution of $CuSO_4$ (5% in water), dried with MgSO₄ and evaporated under reduced pressure to afford **5c** (112 mg, 75% yield) as a white solid.

 $\frac{^{1}\text{H NMR}}{^{4.09}}$ (400 MHz, CDCl₃) δ 7.92 – 7.87 (m, 2H), 7.69 – 7.63 (m, 1H), 7.61 – 7.53 (m, 2H), 4.09 (q, *J* = 7.1 Hz, 2H), 3.42 – 3.35 (m, 2H), 2.98 – 2.91 (m, 2H), 2.75 – 2.69 (m, 2H), 2.59 – 2.52 (m, 2H), 1.22 (t, *J* = 7.1 Hz, 3H).

¹³<u>C NMR</u> (126 MHz, CDCl₃) δ 204.5, 172.5, 139.1, 134.1, 129.5, 128.1, 60.9, 50.6, 37.2, 35.3, 28.0, 14.2

<u>HRMS (ESI pos)</u>: calculated for C₁₄H₁₈NaO₅S (M+H⁺): 321.0767, found 321.0765.

C2. Reaction of Aliphatic Acyl Chlorides

C2.1 Experimental Setup

Our 3D printed photoreactor consisted of a 9 cm diameter crystallizing dish with a 3D printed support of 6 positions, and a hole of 22 mm in the middle to allow ventilation. A commercial 1-meter LED strip was wrapped around the crystallizing dish. In order to control the temperature, a fan was used to cool down the reactor. Reaction temperature was measured, through a vial containing a thermometer, and it stayed between 35-40 °C (Figure S5). Each of the positions could be used to fit a standard 16 mm diameter vial with a Teflon screw cap.



Figure S5: Photoreactor used for the reactions of aliphatic acyl chlorides.

Experiments at 465 nm were conducted using a 1m strip, 14.4W "LEDXON MODULAR 9009083 LED, SINGLE 5050" purchased from Farnell, catalog number 9009083. The emission spectrum of these LEDs was recorded (Figure S6).



Figure S6: Emission spectrum of the 465 nm LED strip used in this study.

The emission maximum was determined as 465 nm with a spectral width of 30 nm (450-480 nm) at half peak intensity and a total spectral width of 120 nm (420-540 nm).

C2.2 General Procedure B



In an oven dried tube of 15 mL (16 mm × 125 mm) with a Teflon septum screw cap, potassium ethyl xanthogenate **B** (8 mg, 0.05 mmol, 0.1 equiv.), sodium phosphate (164 mg, 1.00 mmol, 2 equiv.), acyl chloride **1** (0.75 mmol, 1.5 equiv.) and the electron-poor olefin **2** (0.5 mmol, 1 equiv., *if solid*), were dissolved in DCM (2 mL, HPLC grade). Then, γ -terpinene (240 µL, 1.5 mmol, 3 equiv.) was added. The resulting yellow mixture was degassed with argon sparging for 60 seconds. When the electron-poor olefin **2** is *liquid*, it was added via syringe after the argon sparging. The vial was then placed in the 3D printed support photoreactor (Figure S6) and irradiated under stirring for 24 hours, if not otherwise specified. After this, the solvent was evaporated and the residue purified by column chromatography to afford the corresponding product in the stated yield with >95% purity according to ¹H NMR analysis.

C2.3 Characterization of Products

4-(Phenylsulfonyl)butan-2-one (5a): Synthesized according to the general procedure B using acetyl chloride (53 μ L, 0.75 mmol, 1.5 equiv.) and phenyl vinyl sulfone (84 mg, 0.5 mmol, 1 equiv.). The crude mixture was purified by flash column chromatography on silica gel (gradient from 25% to 100% AcOEt in hexanes as eluent): to afford product **5a** (70 mg 66% yield) as a colorless oil.

 $\frac{^{1}\text{H NMR}}{^{3}\text{H O}}$ (400 MHz, CDCl₃) δ 7.94 – 7.86 (m, 2H), 7.70 – 7.62 (m, 1H), 7.61 – 7.53 (m, 2H), 3.40 – 3.33 (m, 2H), 2.96 – 2.88 (m, 2H), 2.17 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 203.8, 139.1, 134.0, 129.6, 128.1, 50.6, 36.0, 30.0

Matching reported literature data.¹⁶

Dimethyl 2-(cyclohexanecarbonyl)succinate (5d): Synthesized according to general procedure B using cyclohexanecarbonyl chloride (100 μ L, 0.75 mmol, 1.5 equiv.) and dimethyl fumarate (72 mg, 0.5 mmol, 1 equiv.). The crude mixture was purified by flash column chromatography on silica gel (10% AcOEt in hexanes as

eluent) to afford **5d** (107 mg, 83% yield) as a white solid.

 $\frac{^{1}\text{H NMR}}{^{3}\text{H NMR}} (500 \text{ MHz, CDCl}_{3}) \delta 4.14 (dd, J = 8.1, 6.2 \text{ Hz}, 1\text{H}), 3.72 (s, 3\text{H}), 3.66 (s, 3\text{H}), 3.82 (s, 3\text{H}), 2.93 (dd, J = 17.5, 8.1 \text{ Hz}, 1\text{H}), 2.81 (dd, J = 17.6, 6.5 \text{ Hz}, 1\text{H}), 2.69 - 2.61 (m, 1\text{H}), 2.00 - 1.93 (m, 1\text{H}), 1.84 - 1.74 (m, 3\text{H}), 1.70 - 1.62 (m, 1\text{H}), 1.46 - 1.36 (m, 1\text{H}), 1.33 - 1.13 (m, 4\text{H}).$

¹³C NMR (126 MHz, CDCl₃) δ 206.7, 171.9, 169.2, 52.8, 52.2, 52.1, 50.72, 32.4, 29.0, 28.1, 25.9, 25.8, 25.5.

Matching reported literature data.¹⁷

4-Cyclohexyl-4-oxobutanenitrile (5e): Synthesized according to the general procedure B using cyclohexanecarbonyl chloride (100 μ L, 0.75 mmol, 1.5 equiv.) and acrylonitrile (33 μ L, 0.5 mmol, 1 equiv.). The crude mixture was purified by flash column chromatography on silica gel (20% Et₂O in pentane as eluent) to afford **5e** (52 mg, 63% yield) as a colorless oil.

(For the gram scale procedure see paragraph C5, general procedure E)

 $\frac{1}{1}$ <u>H NMR</u> (500 MHz, CDCl₃) δ 2.85-2.80 (m, 2H); 2.60-2.54 (m, 2H); 2.36 (tt, *J* = 11.3, 3.5 Hz, 1H); 1.89-1.82 (m, 2H); 1.82-1.75 (m, 2H); 1.71-1.64 (m, 1H); 1.40-1.15 (m, 5H).

¹³C NMR (126 MHz, CDCl₃) δ 209.4, 119.3, 50.6, 35.9, 28.5, 25.8, 25.6, 11.6.

Matching reported literature data.¹⁷



1-Cyclohexyl-3-(phenylsulfonyl)propan-1-one (**5f**): Synthesized according to the general procedure B using cyclohexanecarbonyl chloride (100 μL, 0.75 mmol, 1.5 equiv.) and phenyl vinyl sulfone **2** (84 mg, 0.5 mmol,

1 equiv.). The crude mixture was purified by flash column chromatography on silica gel (20% AcOEt in hexanes as eluent) to afford **5f** (112 mg, 76% yield) as colorless oil.

A purity of 85% weight was determined ¹H NMR analysis (mixture with phenyl vinyl sulfone, see Figure below). Corrected yield: 68%.

 $^{1}\underline{\text{H NMR}}$ (400 MHz, CDCl₃) δ 7.93 – 7.86 (m, 2H), 7.69 – 7.62 (m, 1H), 7.62 – 7.50 (m, 2H), 3.39 – 3.32 (m, 2H), 2.97 – 2.89 (m, 2H), 2.39 – 2.25 (m, 1H), 1.88 – 1.58 (m, 5H), 1.38 – 1.08 (m, 5H).

¹³C NMR (100 MHz, CDCl₃) δ 193.9, 164.2, 130.4, 128.8, 119.5, 114.1, 55.7, 34.0, 12.0.

Matching reported literature data.¹⁸



4-Cyclohexyl-4-oxobutanenitrile (5g): Synthesized according to the general procedure B using isobutanoyl chloride (100 μ L, 0.75 mmol, 1.5 equiv.) and acrylonitrile (33 μ L, 0.5 mmol, 1 equiv.). The crude mixture was purified by flash column chromatography on silica gel (20% Et₂O in pentane as eluent) to afford **5g** (39 mg, 62%

yield) as a colorless oil. <u>¹H NMR</u> (500 MHz, CDCl₃) δ 2.83 (t, *J* = 7.1 Hz, 2H), 2.66 – 2.56 (m, 1H), 2.57 (t, *J* = 7.2 Hz, 2H), 1.12 (d, *J* = 7.0 Hz, 6H).

¹³C NMR (126 MHz, CDCl₃) δ 210.0, 119.2, 40.7, 35.6, 18.2, 11.6

Matching reported literature data.¹⁹

4-Methyl-1-(phenylsulfonyl)pentan-3-one (5h): Synthesized according to the general procedure B using isobutanoyl chloride (100 μ L, 0.75 mmol, 1.5 equiv.) and phenyl vinyl sulfone (84 mg, 0.5 mmol, 1 equiv.). The crude mixture was purified by flash column chromatography on silica gel (20% AcOEt in hexanes as eluent), followed by a second one (15% AcOEt in hexanes as eluent) to afford **5h** (61 mg, 51% yield) as a colorless oil.

 $\frac{1}{11}$ NMR (500 MHz, CDCl₃) δ 7.94 – 7.88 (m, 2H), 7.69 – 7.64 (m, 1H), 7.61 – 7.54 (m, 2H), 3.40 – 3.35 (m, 2H), 3.00 – 2.93 (m, 2H), 2.66 – 2.55 (m, 1H), 1.08 (d, *J* = 7.0 Hz, 6H).

¹³C NMR (126 MHz, CDCl₃) δ 210.0, 139.2, 134.0, 129.5, 128.1, 50.8, 41.1, 32.7, 18.3.

HRMS (ESI pos): calculated for C₁₂H₁₆NaO₃S (M+Na⁺): 263.0712, found 263.0714.

1-Cyclopentyl-3-(phenylsulfonyl)propan-1-one (5i): Synthesized according to the general procedure B using cyclopentanecarbonyl chloride (91 μ L, 0.75 mmol, 1.5 equiv.) and phenyl vinyl sulfone (84 mg, 0.5 mmol, 1 equiv.). The crude mixture was purified by flash column chromatography on silica gel (20% AcOEt in hexanes as eluent) to afford **5i** (102 mg, 77% yield) colorless oil.

 $^{1}\underline{\text{H NMR}}$ (500 MHz, CDCl₃) δ 7.93 – 7.87 (m, 2H), 7.69 – 7.62 (m, 1H), 7.60 – 7.53 (m, 2H), 3.42 – 3.34 (m, 2H), 2.99 – 2.91 (m, 2H), 2.90 – 2.79 (m, 1H), 1.88 – 1.73 (m, 2H), 1.73 – 1.49 (m, 6H).

¹³C NMR (126 MHz, CDCl₃) δ 208.5, 139.2 134.0, 129.5, 128.1, 51.5, 50.8, 34.0, 29.0, 26.0.

HRMS (ESI pos): calculated for C14H18NaO3S (M+Na⁺): 289.0869, found 289.0873.

1-Cyclobutyl-3-(phenylsulfonyl)propan-1-one (5j): Synthesized according to the general procedure B using cyclobutanecarbonyl chloride (86 μ L, 0.75 mmol, 1.5 equiv.) and phenyl vinyl sulfone (84 mg, 0.5 mmol, 1 equiv.). The

crude mixture was purified by flash column chromatography on silica gel (20% AcOEt in hexanes as eluent) to afford **5j** (116 mg, 92% yield) as a colorless oil.

 $^{1}\underline{\text{H NMR}}$ (500 MHz, CDCl₃) δ 7.92 – 7.88 (m, 2H), 7.68 – 7.63 (m, 1H), 7.60 – 7.54 (m, 2H), 3.40 – 3.35 (m, 2H), 3.29 – 3.20 (m, 1H), 2.87 – 2.81 (m, 2H), 2.24 – 2.08 (m, 4H), 2.02 – 1.90 (m, 1H), 1.84 – 1.75 (m, 1H).

¹³C NMR (126 MHz, CDCl₃) δ 207.1, 139.2, 134.1, 129.5, 128.1, 50.6, 45.4, 32.3, 24.5, 17.9

<u>HRMS (ESI pos)</u>: calculated for C₁₃H₁₅NaO₆ (M+Na⁺): 275.0712, found 275.0716.

Dimethyl 2-((3r,5r,7r)-adamantane-1-carbonyl)succinate (5k): Synthesized according to the general procedure B using 1adamantanecarbonyl chloride (149 mg, 0.75 mmol, 1.5 equiv.) and dimethyl fumarate (72 mg, 0.5 mmol, 1 equiv.). The crude mixture was purified by flash column chromatography on silica gel (5% AcOEt in hexanes as eluent) to afford 5k (85 mg, 55% yield) as a colorless oil.

 $\frac{1}{1}$ MMR (500 MHz, CDCl₃) δ 4.37 (app t, *J* = 7.2 Hz, 1H), 3.67 (s, 3H), 3.64 (s, 3H), 2.79 (app d, *J* = 7.2 Hz, 2H), 2.03 (bs, 3H), 1.89 - 1.79 (m, 6H), 1.76 - 1.63 (m, 6H).

¹³C NMR (126 MHz, CDCl₃) δ 208.8, 171.7, 169.5, 52.7, 52.1, 47.7, 47.4, 38.0, 36.4, 33.5, 27.9

HRMS (ESI pos): calculated for C₁₇H₂₄NaO₅ (M+Na⁺): 331.1516, found 331.1523.



1-((3r,5r,7r)-Adamantan-1-yl)-3-(phenylsulfonyl)propan-1-one (51): Synthesized according to the general procedure B using 1adamantanecarbonyl chloride (149 mg, 0.75 mmol, 1.5 equiv.) and phenyl

vinyl sulfone (84 mg, 0.5 mmol, 1 equiv.). The crude mixture was purified by flash column chromatography on silica gel (15% AcOEt in hexanes as eluent) to afford **51** (165 mg, 95% yield) as a colorless oil.

¹<u>H NMR</u> (500 MHz, CDCl₃) δ 7.93 – 7.88 (m, 2H), 7.68 – 7.63 (m, 1H), 7.60 – 7.54 (m, 2H), 3.37 – 3.29 (m, 2H), 3.00-2.93 (m, 2H), 2.03 (bs, 3H), 1.79 - 1.70 (m, 9H), 1.66 (app d, J = 12.2 Hz, 3H).

¹³<u>C NMR</u> (126 MHz, CDCl₃) δ 211.2, 139.3, 133.9, 129.4, 128.0, 50.9, 46.5, 38.3, 36.5, 29.1, 27.9.

HRMS (ESI pos): calculated for C₁₉H₂₅O₃S (M+H⁺): 333.1519, found 333.1519.

C3. Reaction of Carboxylic Acids through Acyl Chloride Formation

C3.1 General Procedure C:



In a round bottom flask, the carboxylic acid (0.75 mmol, 1.5 equiv) was dissolved in DCM (3 mL, HPLC grade). Then, oxalyl chloride (0.79 μ L, 0.90 mmol, 1.8 equiv.) and DMF (17 μ L, 0.22 mmol, 0.45 equiv.) were added at ambient temperature. The reaction was stirred at ambient temperature until complete consumption of the carboxylic acid was observed by TLC. After that, the solvent was evaporated to dryness under vacuum at ambient temperature to obtain the crude acyl chloride, which was used without further purification in the next step.

In an oven dried vial, with a Teflon septum screw cap, potassium ethyl xanthogenate **B** (16 mg, 0.10 mmol, 0.2 equiv.), sodium phosphate (164 mg, 1.00 mmol, 2 equiv.), and the electron-poor olefin **2** (0.5 mmol, 1 equiv.), were added. The crude acyl chloride was dissolved in DCM (2 mL, HPLC grade) and the solution was added to the vial, followed by γ -terpinene (240 μ L, 1.5 mmol, 3 equiv.). The resulting yellow mixture was degassed via argon sparging for 60 seconds. If the electron-poor olefin **2** was *liquid*, it was added via syringe after the argon sparging. The vial was then placed in the correspondent reactor (depending on the temperature used for the reaction) and irradiated for 24 hours. The solvent was evaporated and the residue purified by column chromatography to afford the corresponding product in the stated yield with >95% purity according to ¹H NMR analysis.

C3.2 Characterization of Products



1-(4-Chloro-3-ethyl-1-methyl-1H-pyrazol-5-yl)-3-

(**phenylsulfonyl**)**propan-1-one** (**6a**): Synthesized according to the general procedure C using 4-chloro-3-ethyl-1-methyl-1H-pyrazole-5-carboxylic acid

(141 mg, 0.75 mmol, 1.5 equiv.) and phenyl vinyl sulfone (84 mg, 0.5 mmol, 1 equiv.). Acyl chloride formation was complete after 2 hours. The crude mixture was purified by flash column chromatography on silica gel (20% AcOEt in hexanes as eluent) to afford **6a** (52 mg, 31% yield) as a white solid.

 $\frac{1}{10} \frac{1}{10} \frac$

¹³C NMR (126 MHz, CDCl₃) δ 186.6, 150.4, 139.0, 134.6, 134.1, 129.5, 128.3, 112.7, 50.6, 41.6, 35.5, 19.2, 12.9.

<u>HRMS (ESI pos)</u>: calculated for C₁₅H₁₈ClN₂O₃S (M+H⁺): 341.0721, found 341.0709.



7-chloro-1-(phenylsulfonyl)heptan-3-one (6b): Synthesized according to the general procedure C using 5-chloropentanoic acid (72 μ L, 0.75 mmol, 1.5 equiv.) and dimethyl fumarate (72 mg, 0.5 mmol, 1 equiv.).

Acyl chloride formation was complete after 3 hours. The crude mixture was purified by flash column chromatography on silica gel (20% AcOEt in hexanes as eluent). The product was then dissolved in DCM, washed 3 times with a solution of $CuSO_4$ (5% in water), dried with MgSO₄ and evaporated under reduced pressure to afford **6b** (108 mg, 70% yield) as a white solid.

 $^{1}\underline{\text{H NMR}}$ (400 MHz, CDCl₃) δ 7.92 – 7.87 (m, 2H), 7.69 – 7.63 (m, 1H), 7.60 – 7.54 (m, 2H), 3.53 – 3.47 (m, 2H), 3.41 – 3.35 (m, 2H), 2.92 – 2.86 (m, 2H), 2.50 – 2.44 (m, 2H), 1.78 – 1.64 (m, 4H).

¹³C NMR (100 MHz, CDCl₃) δ 205.5, 139.1, 134.1, 129.5, 128.1, 50.6, 44.6, 41.9 35.0 31.8 20.9.

HRMS (ESI pos): calculated for C₁₃H₁₇ClNaO₃S (M+Na⁺): 311.0479, found 311.0477.

3-(Phenylsulfonyl)-1-(1-tosylpiperidin-4-yl)propan-1-one (6c): Synthesized according to the general procedure C using 1-tosylpiperidine-4-carboxylic acid (213 mg, 0.75 mmol, 1.5 equiv.) and dimethyl fumarate (72 mg, 0.5 mmol, 1 equiv.). Acyl chloride formation was complete after 3 hours. In this case the reaction was irradiated for 36 hours. The crude mixture was purified by flash column chromatography on silica gel (40% AcOEt in hexanes as eluent) to afford **6c** (164 mg, 75% yield) as a white solid.

¹<u>H NMR</u> (500 MHz, CDCl₃) δ 7.90 – 7.85 (m, 2H), 7.69 – 7.64 (m, 1H), 7.64 – 7.60 (m, 2H), 7.60 – 7.54 (m, 2H), 7.32 (app d, *J*= 7.9 Hz, 2H), 3.71 (dt, *J*= 12.2, 3.5 Hz, 2H), 3.35 (app t, *J*= 7.4 Hz, 2H), 2.91 (app t, *J*= 7.4 Hz, 2H), 2.43 (s, 3H), 2.38 (td, *J*= 11.7, 2.5 Hz, 2H), 2.33 – 2.24 (m, 1H), 1.93 – 1.84 (m, 2H), 1.75 – 1.63 (m, 2H).

¹³C NMR (126 MHz, CDCl₃) δ 206.9, 143.8, 139.1, 134.2, 133.2, 129.9, 129.6, 128.0, 127.8, 50.6, 47.6, 45.5, 33.0, 27.0, 21.7.

HRMS (ESI pos): calculated for C₂₁H₂₆NO₅S₂ (M+H⁺): 436.1247, found 436.1251.



dimethyl 2-(4,4-difluorocyclohexane-1-carbonyl)succinate (6d): Synthesized according to the general procedure C using 4,4difluorocyclohexane-1-carboxylic acid (123 mg, 0.75 mmol, 1.5 equiv.) and dimethyl fumarate (72 mg, 0.5 mmol, 1 equiv.). Acyl chloride formation was complete after 1 hour. The crude mixture was purified by flash column chromatography on silica gel (20% Et₂O in hexanes as eluent) to afford **6d** (128 mg, 88% yield) as a white solid.

¹H NMR (400 MHz, CDCl₃) δ 4.16 (dd, J = 9.1, 5.3 Hz, 1H), 3.73 (s, 3H), 3.67 (s, 3H), 3.03 (dd, J = 17.6, 9.3 Hz, 1H), 2.82 (dd, J = 17.5, 5.3 Hz, 1H), 2.83 – 2.74 (m, 1H), 2.22 – 2.02 (m, 3H), 1.98 – 1.65 (m, 5H).

 13 C NMR (100 MHz, CDCl₃) δ 205.6, 171.9, 168.8, 122.7 (dd, J = 241.6, 240.9 Hz), 53.0, 52.2, 52.1, 48.0, 32.7 (dd, J = 25.0 Hz), 25.2 (d, J = 9.0 Hz) 24.4 (d, J = 8.6 Hz)

¹⁹F NMR (376 MHz, CDCl₃, proton decoupled) δ -93.75 (d, J = 237.2 Hz, 1F); -100.48 (d, J =238.2 Hz, 1F).

HRMS (ESI pos): calculated for $C_{13}H_{18}F_2NaO_5$ (M+Na⁺): 315.1015, found 315.1017.



SO₂Ph

1-(4,4-Difluorocyclohexyl)-3-(phenylsulfonyl)propan-1-one (6e): Synthesized according to the general procedure C using 4,4difluorocyclohexane-1-carboxylic acid (123 mg, 0.75 mmol, 1.5 equiv.) and dimethyl fumarate (72 mg, 0.5 mmol, 1 equiv.). Acyl chloride

formation was complete after 1 hour. The crude mixture was purified by flash column chromatography on silica gel (30% AcOEt in hexanes as eluent) to afford **6e** (112 mg, 71% yield) as a white solid.

¹H NMR (400 MHz, CDCl₃) δ 7.93 – 7.88 (m, 2H), 7.70 – 7.64 (m, 1H), 7.61 – 7.55 (m, 2H), 3.41 - 3.35 (m, 2H), 3.01 - 2.94 (m, 2H), 2.52 - 2.39 (m, 1H), 2.18 - 2.04 (m, 2H), 1.99 - 1.86 (m, 2H), 1.85 - 1.64 (m, 4H).

¹³C NMR (100 MHz, CDCl₃) δ 207.4, 139.2, 134.1, 129.6, 128.0, 122.5 (dd, J = 241.6, 240.7 Hz) 50.6, 48.1, 33.2, 32.7 (dd, *J* = 24.4, 24.2 Hz), 24.7 (d, *J* = 9.5 Hz).

 19 F NMR (376 MHz, CDCl₃, proton decoupled) δ -93.72 (dd, J = 237.6 Hz); -100.82 (d, J = 237.7Hz).

<u>HRMS (ESI pos)</u>: calculated for $C_{15}H_{18}F_2NaO_3S$ (M+Na⁺): 339.0837, found 339.0840.

3-(Phenylsulfonyl)-1-(tetrahydrofuran-3-yl)propan-1-one (**6f**): Synthesized according to the general procedure C using tetrahydrofuran-3-

carboxylic acid (72 µL, 0.75 mmol, 1.5 equiv.) and dimethyl fumarate (72 mg, 0.5 mmol, 1 equiv.). Acyl chloride formation was complete after 1 hour. The crude mixture was purified by flash column chromatography on silica gel (50% AcOEt in hexanes as eluent). The product was then dissolved in DCM, washed 3 times with a solution of CuSO₄ (5% in water), dried with MgSO₄ and evaporated under reduced pressure to afford **6f** (78 mg, 58% yield) as a colorless oil.

¹H NMR (500 MHz, CDCl₃) δ 7.94 – 7.87 (m, 2H), 7.71 – 7.64 (m, 1H), 7.62 – 7.54 (m, 2H), 3.94 - 3.73 (m, 4H), 3.47 - 3.34 (m, 2H), 3.26 - 3.17 (m, 1H), 3.07 - 2.89 (m, 2H), 3.16 - 2.01 (m, 2H).

¹³C NMR (126 MHz, CDCl₃) δ 205.6, 139.1, 134.1, 129.6, 128.1, 69.3, 68.4, 51.1, 50.6, 34.4, 29.1.

HRMS (ESI pos): calculated for C₁₃H₁₆NaO₄S (M+Na⁺): 291.0662, found 291.0665.



3-(Phenylsulfonyl)-1-(1-tosylazetidin-3-yl)propan-1-one

(6g): Synthesized according to the general procedure C using 1-tosylazetidine-3-

carboxylic acid (191 mg, 0.75 mmol, 1.5 equiv.) and dimethyl fumarate (72 mg, 0.5 mmol, 1 equiv.). Acyl chloride formation was complete after 2 hours. In this case the reaction was irradiated for 36 hours. The crude mixture was purified by flash column chromatography on silica gel (40% AcOEt in hexanes as eluent) to afford **6g** (63 mg, 31% yield) as a white solid.

¹<u>H NMR</u> (400 MHz, CDCl₃) δ 7.88 – 7.82 (m, 2H), 7.74 – 7.63 (m, 3H), 7.60 – 7.53 (m, 2H), 7.40 – 7.33 (m, 2H), 3.92 - 3.88 (m, 2H), 3.88 - 3.81 (m, 2H), 3.41 - 3.28 (m, 3H), 2.79 (app t, *J*= 7.3 Hz, 2H), 2.44 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 202.1, 144.6, 138.9, 134.2, 131.3, 130.0, 129.6, 128.5, 128.0, 51.8, 50.3, 38.1, 33.1, 21.7.

HRMS (ESI pos): calculated for C₁₉H₂₁NNaO₅S₂ (M+Na⁺): 430.0753, found 430.0748.



1-(4-Pentylbicyclo[2.2.2]octan-1-yl)-3-(phenylsulfonyl)propan-1one (6h): Synthesized according to the general procedure C using 4pentylbicyclo[2.2.2]octane-1-carboxylic acid (168 mg, 0.75 mmol, 1.5 equiv.) and phenyl vinyl sulfone (84 mg, 0.5 mmol, 1 equiv.). Acyl

chloride formation was complete after 2 hours. Chromatography on silica gel (10% AcOEt in hexanes as eluent) could not remove byproducts completely. Purification by semipreparative HPLC (IC column, 60:40 Hexane/Ethanol, 1 mL/min) was performed to obtain an analytical amount of product **6h** as a white solid. NMR yield (Trichloroethylene was used as internal standard): 80%.

 $\frac{^{1}\text{H NMR}}{^{3}\text{C500 MHz}, \text{CDCl}_{3}} \delta 7.93 - 7.87 \text{ (m, 2H)}, 7.69 - 7.63 \text{ (m, 1H)}, 7.61 - 7.54 \text{ (m, 2H)}, 3.36 - 3.29 \text{ (m, 2H)}, 2.97 - 2.90 \text{ (m, 2H)}, 1.69 - 1.61 \text{ (m, 6H)}, 1.43 - 1.34 \text{ (m, 6H)}, 1.31 - 1.24 \text{ (m, 2H)}, 1.24 - 1.12 \text{ (m, 4H)}, 1.11 - 1.04 \text{ (m, 2H)}, 0.87 \text{ (t, } J = 7.3 \text{ Hz}, 3\text{H}).$

¹³<u>C NMR</u> (126 MHz, CDCl₃) δ 211.6, 139.4, 134.0, 129.5, 128.1, 51.0, 45.3, 41.3, 32.9, 30.8, 30.5, 30.1, 28.2, 23.5, 22.8, 14.2.

HRMS (ESI pos): calculated for C₂₂H₃₂NaO₃S (M+Na⁺): 399.1964, found 399.1951.

C4. Reaction of Carboxylic Acids through Anhydride Formation

C4.1 General Procedure D1



In a round bottom flask or vial, the carboxylic acid (0.75 mmol, 1.5 equiv) was dissolved in THF (2.5 mL, HPLC grade). Then, triethylamine (TEA, 105 μ L, 0.75 mmol, 1.5 equiv.) and ethyl chloroformate (72 μ L, 0.75 mmol, 1.5 equiv.) were added at ambient temperature. The reaction was stirred at ambient temperature for 1 hour. After that, it was filtered and the remaining solid was washed with diethyl ether. The organic layers were concentrated to dryness under reduced pressure to obtain the crude anhydride, which was used without further purification in the next step. (When the carboxylic acid is not completely soluble in 2.5 mL of THF, follow the general procedure D2 detailed below).

In an oven dried tube or a vial, with a Teflon septum screw cap, potassium ethyl xanthogenate **B** (16 mg, 0.10 mmol, 0.2 equiv.) and the electron-poor olefin **2** (0.5 mmol, 1 equiv., *if solid*), were added. The crude anhydride was dissolved in DCM (2 mL, HPLC grade) and the solution was added to the vial, followed by γ -terpinene (240 μ L, 1.5 mmol, 3 equiv.). The resulting yellow mixture was degassed with argon sparging for 60 seconds. If the electron-poor olefin **2** was *liquid*, it was added via syringe after the argon sparging. The vial was then placed in the correspondent photoreactor (Figure S4 or S5, depending on the temperature used for the reaction) and irradiated for 24 hours. The solvent was evaporated and the residue purified by column chromatography to

afford the corresponding product in the stated yield with >95% purity, according to 1 H NMR analysis.

This procedure was employed for the optimization of the catalytic reaction with anhydride as radical precursor and for the scale-up process, as indicated below.

Note: Filtration of the triethylamonium salt is crucial for the reaction to work. Therefore, attempts to perform the reaction one-pot without removal of the ammonium salt were unsuccessful.

C4.2 General Procedure D2

In a round bottom flask or vial, the carboxylic acid (0.75 mmol, 1.5 equiv.) was dissolved in THF (10 mL, HPLC grade). Then, triethylamine (105 μ L, 0.75 mmol, 1.5 equiv.) and ethyl chloroformate (72 μ L, 0.75 mmol, 1.5 equiv.) were added at ambient temperature. The reaction was stirred for 1 hour. The reaction crude was washed with water and NaHCO₃ saturated solution, dried over MgSO₄, filtered and the organic layers concentrated to dryness under vacuum. The crude carbonate was used without further purification in the next step.

In an oven dried tube of 15 mL (16 mm \times 12.5 mm) or a vial, with a Teflon septum screw cap, potassium ethyl xanthogenate (16.02 mg, 0.10 mmol, 0.2 equiv.) and the electron-poor olefin **2** (0.5 mmol, 1 equiv. *if solid*), were added. The crude carbonate was dissolved in DCM (2 mL, HPLC grade) and the solution was added to the vial, followed by γ -terpinene (240 μ L, 1.5 mmol, 3 equiv.). The resulting yellow mixture was degassed with argon sparging for 60 seconds. If the electron-poor olefin **2** was *liquid*, it was added via syringe after the argon sparging. The vial was then placed in the correspondent photoreactor (Figure S4 or S5, depending on the temperature used for the reaction) and irradiated for 24 hours. After cooling to ambient temperature, the solvent was evaporated and the residue purified by column chromatography to afford the corresponding product in the stated yield with >95% purity according to ¹H NMR analysis.

C4.3 Characterization of Products



 $(8R,9S,10S,13R,14S,17R)-10,13-dimethyl-17-((R)-5-oxo-7-(phenylsulfonyl)heptan-2-yl)dodecahydro-3H-cyclopenta[a]phenanthrene-3,7,12(2H,4H)-trione (7): Synthesized according to the general procedure D2 using dehydrocholic acid (302 <math display="inline">\mu$ L, 0.75 mmol, 1.5 equiv.) and phenyl vinyl sulfone (84 mg, 0.5 mmol, 1 equiv.). The crude mixture

was purified by flash column chromatography on silica gel (33% acetone in hexanes as eluent), followed by a second purification (20% AcOEt in DCM as eluent) to afford **7** (145 mg, 52% yield) as a colorless oil.

 $\frac{^{1}\text{H NMR}}{^{3}\text{MR}} (500 \text{ MHz, CDCl}_{3}) \delta 7.93 - 7.88 \text{ (m, 2H)}, 7.70 - 7.64 \text{ (m, 1H)}, 7.61 - 7.55 \text{ (m, 2H)}, 3.44 - 3.32 \text{ (m, 2H)}, 2.95 - 2.79 \text{ (m, 5H)}, 2.54 - 2.44 \text{ (m, 1H)}, 2.44 - 2.10 \text{ (m, 9H)}, 2.07 - 1.90 \text{ (m, 4H)}, 1.89 - 1.80 \text{ (m, 1H)}, 1.80 - 1.70 \text{ (m, 1H)}, 1.67 - 1.56 \text{ (m, 1H)}, 1.39 \text{ (s, 3H)}, 1.36 - 1.20 \text{ (m, 4H)}, 1.05 \text{ (s, 3H)}, 0.81 \text{ (d, } J = 6.5 \text{ Hz}, 3\text{H)}.$

¹³C NMR (126 MHz, CDCl₃) δ 212.0, 209.1, 208.8, 206.5, 139.2, 134.1, 129.6, 128.1, 57.0, 51.9, 50.6, 49.1, 47.0, 45.7, 45.7, 45.1, 42.9, 40.0, 38.8, 36.6, 36.1, 35.4, 35.4, 35.1, 29.1, 27.8, 25.2, 22.0, 18.9, 12.0.

HRMS (ESI pos): calculated for C₃₂H₄₂NaO₆S (M+Na⁺): 577.2594, found 577.2607.

C5 Scaled-Up Reaction

C5.1 Experimental Setup and Procedure



In a 100 mL round bottom flask, cyclohexanecarboxylic acid (2.34 mL, 18.75 mmol, 1.5 equiv.) was dissolved in THF (60 mL, HPLC grade). Then, triethylamine (2.61 mL, 18.75 mmol, 1.5 equiv.) and ethyl chloroformate (1.80 mL, 18.75 mmol, 1.5 equiv.) were added at ambient temperature. The reaction was stirred at ambient temperature for 1 hour. Then, it was filtered into a 100 mL reaction flask that will be used as reaction vessel for the next step (the remaining solid was carefully washed with diethyl ether). The organic phase was concentrated to dryness under vacuum to obtain the crude carbonate, which was used without further purification in the next step.

In the same 100 mL round bottom flask with a Teflon septum, the crude carbonate was dissolved in DCM (50 mL, HPLC grade). Potassium ethyl xanthogenate **B** (601 mg, 3.75 mmol, 0.3 equiv.) and γ -terpinene (6.01 mL, 37.5 mmol, 3 equiv.) were added to the solution. The resulting yellow mixture was degassed with Nitrogen sparging for 2 minutes. Finally, acrylonitrile (0.819 mL, 12.5 mmol, 1 equiv.) was added via syringe. The round bottom flask was then irradiated for 20 hours with a one meter 14W blue LED strip and cooled with a fan to keep the temperature between 30 and 35 °C (see Figure S7). After 24 hours, complete conversion of acrylonitrile was inferred by ¹H NMR analysis. The mixture was transferred to an extraction funnel, water was added and the organic layer was extracted with DCM. The organic layer was dried (MgSO₄) and concentrated to dryness. The product was then purified by chromatography on silica gel (10% AcOEt in hexanes) to afford 1.130 g of product **5e** (6.87 mmol, 55% yield) as a yellowish oil. NMR analysis was consistent with product synthesized in the small scale process.



Figure S7: Experimental setup used for the large scale set up. (Left) Before irradiation. (Middle) Reaction set up from above. (Right) Reaction set up from the front.

C6. Reaction of Carbamoyl Chlorides

C6.1 Experimental Setup

For the generation of carbamoyl radicals, we used the Hepatochem PhotoRedOx Box equipped with an EvoluChem LED 18 W light source at 405 nm, supplied by Hepatochem. The reactor was connected to a Huber Minichiller 300 in order to perform reactions at 50 °C with accurate control of the reaction temperature (\pm 1°C, Figure S8).



Figure S8: Photoreactor used for the reaction with the carbamoyl chlorides

C6.2 Optimization Studies

Table S8. Screening of the Catalysts

0 L		catalyst (20 mol%) γ-terpinene (2 equiv.)		Š x 3H₂O	
Me ₂ N CI + 8a	SO ₂ Ph -	Base (2 equiv.), LEDs solvent (0.25 M), 18 h, 50 °C	9a	Et ₂ N ^r `SNa Catalyst C ·3H ₂ O	

entry	catalyst	wavelenght (nm)	Base	Solvent	NMR yield (%)
1	В	460	Na ₃ PO ₄	DCM	<5
2	В	405	Na ₃ PO ₄	DCM	10%
3	C ⋅3H ₂ O	405	Na ₃ PO ₄	DCM	11%
4	C ⋅3H ₂ O	405	Na ₃ PO ₄	MeCN	20%
5	C ⋅3H ₂ O	405	K ₃ PO ₄	MeCN	60%

All reaction performed on 0.2 mmol scale, yield determined by ¹H NMR analysis of the crude reaction mixture by comparison with trichloroethylene as internal standard.

C6.3 General Procedure for the intermolecular Giese addition (General Procedure E)



An oven-dried 15 mL Schlenk tube was charged with a mixture of carbamoyl chloride **8** (0.4 mmol, 2 equiv.), catalyst **C** trihydrate (9 mg, 0.04 mmol, 0.2 equiv.), alkene **2** (0.2 mmol, 1 equiv.), γ -terpinene (64 µL, 0.4 mmol, 2 equiv.) and K₃PO₄ (85 mg, 0.4 mmol, 2 equiv.) in acetonitrile (0.8 mL, 0.25 M). The reaction mixture was placed under an atmosphere of argon, cooled to -78 °C, degassed *via* vacuum evacuation (5 minutes), backfilled with argon and, ultimately, warmed to ambient temperature. This freeze-pump-thaw cycle was repeated four times, and then the Schlenk tube was sealed with Parafilm and put into the Hepatochem PhotoRedOx Box equipped with a 405 nm EvoluChem LED 18 W light source at 50 °C (Figure S8). After 18 hours stirring, the reaction was cooled down to ambient temperature, water was added and the mixture was extracted with ethyl acetate (2x15 mL). The combined layers were dried over magnesium sulfate, filtered, and concentrated. The resulting crude mixture was purified by column chromatography on silica gel to give the corresponding product **9** in the stated yield.

C6.4 Characterization of Products



N,N-Dimethyl-3-(phenylsulfonyl)propanamide (9a): Synthesized according to general procedure E using dimethylcarbamic chloride (37 μ L, 0.4 mmol, 2.0 equiv.) and phenyl vinyl sulfone (34 mg, 0.2 mmol). The crude mixture was

purified by flash column chromatography on silica gel (gradient from hexane 100% to ethyl acetate 100%) to afford product 9a (29 mg, 60% yield) as a pale-yellow oil.

 $\frac{^{1}\text{H NMR}}{^{3}\text{CDCl}_{3}} (400 \text{ MHz, CDCl}_{3}) \delta 7.95 - 7.88 \text{ (m, 2H)}, 7.69 - 7.62 \text{ (m, 1H)}, 7.61 - 7.52 \text{ (m, 2H)}, 3.53 - 3.33 \text{ (m, 2H)}, 2.99 \text{ (s, 3H)}, 2.89 \text{ (s, 3H)}, 2.85 - 2.73 \text{ (m, 2H)}.$

¹³C NMR (100 MHz, CDCl₃) δ 168.8, 139.2, 134.0, 129.5, 128.1, 52.2, 37.2, 35.7, 26.2.

HRMS (ESI pos): calculated for C₁₁H₁₅NnaO₃S (M+Na⁺): 264.0665, found 264.0653.

3-Cyano-*N*,*N***-dimethylpropanamide (9b):** Synthesized according to general procedure E using dimethylcarbamic chloride (37 μ L, 0.4 mmol, 2.0 equiv.) and acrylonitrile (13 μ L, 0.2 mmol). The crude mixture was purified by flash column

chromatography on silica gel (gradient from hexane 100% to ethyl acetate 100%) to afford product 9b (16 mg, 63% yield) as a pale-yellow oil.

¹<u>H NMR</u> (400 MHz, CDCl₃) δ 3.01 (s, 3H), 2.97 (s, 3H), 2.68 (s, 4H).

¹³C NMR (100 MHz, CDCl₃) δ168.8, 119.6, 37.0, 35.7, 29.5, 13.1.

<u>HRMS (ESI pos)</u>: calculated for $C_6H_{11}N_2O$ (M+H⁺): 127.0866, found: 127.0869.

dimethyl 2-(dimethylcarbamoyl)succinate (9c): Synthesized according to general procedure E using dimethylcarbamic chloride (37 μ L, 0.4 mmol, 2.0 equiv.) and dimethyl fumarate (29 mg, 0.2 mmol). The crude mixture was

purified by flash column chromatography on silica gel (gradient from hexane 100% to ethyl acetate 100%) to afford product 9c (27 mg, 62% yield) as a pale-yellow oil.

¹<u>H NMR</u> (400 MHz, CDCl₃) δ 4.14 (dd, J = 8.3, 6.0 Hz, 1H), 3.72 (s, 3H), 3.67 (s, 3H), 3.16 (s, 3H), 3.11 – 2.80 (m, 6H).

¹³C NMR (100 MHz, CDCl₃) δ 172.4, 169.5, 167.9, 53.0, 52.2, 44.6, 38.0, 36.4, 33.6.

<u>HRMS (ESI pos)</u>: calculated for C₉H₁₅NNaO₅ (M+Na⁺): 240.0842, found: 240.0844.

MeO N SO₂Ph

N-Methoxy-*N*-methyl-3-(phenylsulfonyl)propanamide (9d): Synthesized according to general procedure E using methoxy(methyl)carbamic chloride (41 μ L, 0.4 mmol, 2.0 equiv.) and phenyl vinyl sulfone (34 mg, 0.2 mmol).

The crude mixture was purified by flash column chromatography on silica gel (gradient from hexane 100% to hexane 50% : 50% ethyl acetate) to afford product **9d** (16 mg, 30% yield) as a pale yellow oil.

 $\frac{^{1}\text{H NMR}}{^{3.69}}$ (400 MHz, CDCl₃) δ 7.97 – 7.90 (m, 2H), 7.75 – 7.63 (m, 1H), 7.63 – 7.54 (m, 2H), 3.69 (s, 3H), 3.52 – 3.37 (m, 2H), 3.14 (s, 3H), 2.97 – 2.92 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) 170.4, 139.2, 134.0, 129.5, 128.2, 61.6, 51.5, 32.3, 25.4.

HRMS (ESI pos): calculated for C₉H₁₅NNaO₅ (M+Na⁺): 240.0842, found: 240.0844.

1-Morpholino-3-(phenylsulfonyl)propan-1-one (9e): Synthesized according to general procedure E using morpholine-4-carbonyl chloride (47 μ L, 0.4 mmol, 2.0 equiv.) and phenyl vinyl sulfone (34 mg, 0.2 mmol). The crude mixture was purified by flash column chromatography on silica gel (gradient from hexane

100% to ethyl acetate 100%) to afford product **9e** (42 mg, 74% yield) as a pale-yellow oil.

 $\frac{^{1}\text{H NMR}}{^{3}\text{CDCl}_{3}} (400 \text{ MHz}, \text{CDCl}_{3}) \delta 8.00 - 7.85 \text{ (m, 2H)}, 7.71 - 7.62 \text{ (m, 1H)}, 7.62 - 7.51 \text{ (m, 1H)}, 3.76 - 3.58 \text{ (m, 5H)}, 3.55 - 3.49 \text{ (m, 2H)}, 3.47 - 3.42 \text{ (m, 3H)}, 2.94 - 2.74 \text{ (m, 2H)}.$

 $\frac{^{13}\text{C NMR}}{25.9. \text{ HRMS (ESI pos)}}$: calculated for C₁₃H₁₇NNaO₄S (M+Na⁺): 306.0770, found: 306.0762.



3-(Phenylsulfonyl)-1-thiomorpholinopropan-1-one (9f): synthesized according the general procedure E using thiomorpholine-4-carbonyl chloride **8f** (99 mg, 0.4 mmol, 2 eq.) and phenyl vinyl sulfone (34 mg, 0.2 mmol, 1 eq.). The crude mixture was purified by flash column chromatography on

silica gel (5% AcOEt in hexane), followed by a second one (50% AcOEt in Hexane as eluent) to afford **9f** (37.8 mg, 63% yield) as a colorless oil.

¹<u>H NMR</u> (400 MHz, CDCl₃) δ 7.96 (m, 2H) 7.70 (m, 1H) 7.61 (m, 2H) 3.85 (m, 2H), 3.76 (m, 1H), 3.65 (m, 1H), 3.50 (m, 1H), 2.86, (m, 2H), 2.64 (m, 6H).

¹³<u>C NMR</u> (126 MHz, CDCl₃) δ 167.3, 139.3, 134.1, 129.5, 128.1, 52.2, 48.3, 44.8, 27.9, 27.4, 26.2

<u>HRMS (ESI pos)</u>: calculated for C₁₃H₁₇NaNO₃S₂ (M+Na⁺): 322.05, found: 322.0533.

tert-Butyl 4-(3-(phenylsulfonyl)propanoyl)piperazine-1-carboxylate (9g): synthesized according general procedure E using tert-butyl 4-(chlorocarbonyl)piperazine-1-carboxylate 8g (99 mg, 0.4 mmol, 2 eq.) and phenyl vinyl sulfone (34 mg, 0.2 mmol, 1 eq.). The crude mixture was

purified by flash column chromatography on silica gel (5% AcOEt in hexane), followed by a second purification (50% AcOEt in hexane as eluent) to afford 9g (55 mg, 73% yield) as a white solid.

 $\frac{^{1}\text{H NMR}}{^{6}\text{H}}$ (400 MHz, CDCl₃) δ 7.91 (m, 2H), 7.66 (m, 1H), 7.57 (m, 2H), 3.42 (m, 4H) 3.21 (m, 6H), 2.83 (t, *J* = 7.8 Hz, 2H), 1.45 (s, 9H)

¹³<u>C NMR</u> (126 MHz, CDCl₃) δ 167.6, 154.6, 139.3, 134.1, 129.6, 128.1, 80.7, 52.1, 45.4, 41.9, 28.5, 26.1

<u>HRMS (ESI pos)</u>: calculated for C₁₈H₂₆NaN₂O₅S (M+Na⁺): 405.15, found 405.1455.



1-(4-Chloropiperidin-1-yl)-3-(phenylsulfonyl)propan-1-one (9h): Synthesized according to general procedure E using 4-chloropiperidine-1-carbonyl chloride (73 mg, 0.4 mmol, 2 equiv.) and phenyl vinyl sulfone (34 mg, 0.2 mmol). The crude mixture was purified by flash column

chromatography on silica gel (gradient from hexane 100% to ethyl acetate 100%) to afford product **9h** (41 mg, 65% yield) as a pale-yellow oil.

¹H NMR (400 MHz, CDCl₃) δ 7.96 – 7.87 (m, 2H), 7.72 – 7.62 (m, 1H), 7.60 – 7.53 (m, 2H), 4.27 (tt, J = 7.0, 3.6 Hz, 1H), 3.68 (tdt, J = 11.7, 8.2, 3.5 Hz, 2H), 3.58 (ddd, J = 13.6, 6.9, 4.0 Hz, 1H), 3.49 - 3.42 (m, 2H), 3.38 (ddd, J = 13.9, 7.0, 3.7 Hz, 1H), 2.83 (td, J = 7.1, 1.9 Hz, 2H), 2.16 – 1.93 (m, 2H), 1.90 – 1.72 (m, 2H).

¹³C NMR (100 MHz, CDCl₃) δ 167.2, 139.2, 134.0, 129.5, 128.0, 56.1, 52.1, 42.5, 39.1, 35.1, 34.4, 25.9.

HRMS (ESI pos): calculated for C₁₄H₁₉ClNO₃S (M+H⁺): 316.0769, found: 316.0773.



1-(4,4-Difluoropiperidin-1-yl)-3-(phenylsulfonyl)propan-1-one (9i): Synthesized according to general procedure E using 4,4-difluoropiperidine-1-carbonyl chloride (73 mg, 0.4 mmol, 2 equiv.) and phenyl vinyl sulfone (34 mg, 0.2 mmol). The crude mixture was purified by flash column

chromatography on silica gel (gradient from hexane 100% to 1:1 hexane/ethyl acetate) to afford product 9i (43 mg, 68% yield) as an off-white solid.

¹<u>H NMR</u> (400 MHz, CDCl₃) δ 7.96 – 7.88 (m, 2H), 7.71 – 7.63 (m, 1H), 7.61 – 7.54 (m, 2H), 3.61 (dt, J = 43.9, 6.0 Hz, 4H), 3.51 - 3.43 (m, 2H), 2.92 - 2.83 (m, 2H), 2.13 - 1.84 (m, 4H).

 13 C NMR (100 MHz, CDCl₃) δ 167.4, 139.2, 134.1, 129.5, 128.0, 121.3 (t, *J* = 242.4 Hz), 52.1, 40.7 (dt, *J* = 330.8, 5.4 Hz), 34.1 (dt, *J* = 78.0, 23.6 Hz), 25.9.

¹⁹F NMR (376 MHz, CDCl₃) δ -98.22 (p, J = 13.5 Hz).

HRMS (ESI pos): calculated for C₁₈H₁₈NaO₄ (M+Na⁺): 340.0789, found: 340.0785.



Methyl (3-(phenylsulfonyl)propanoyl)-L-prolinate (9j): synthesized according the general procedure E using methyl (chlorocarbonyl)-Lprolinate (77 mg, 0.4 mmol, 2 eq.) and phenyl vinyl sulfone (34 mg, 0.2 mmol, 1 eq.). The crude mixture was purified by flash column chromatography on silica gel (5%

AcOEt in hexane) to afford 9j (46 mg, 58% yield) as a yellowish oil. ¹H NMR (400 MHz, CDCl₃) δ 7.95 – 7.89 (m, 2H), 7.69 – 7.64 (m, 1H), 7.61 – 7.53 (m, 2H), 4.42 (dd, J = 8.4, 3.5 Hz, 1H), 3.70 (s, 3H), 3.68 - 3.59 (m, 1H), 3.56 - 3.38 (m, 3H), 2.83 (dt, J)

= 9.7, 5.6 Hz, 2H), 2.11 – 1.94 (m, 4H).

¹³C NMR (126 MHz, CDCl₃) δ 172.6, 167.8, 139.2, 134, 129.5, 128.1, 58.9, 52.4, 51.7, 47.1, 29.3, 27.4, 24.8.

HRMS (ESI pos): calculated for $C_{15}H_{19}NaNO_5S$ (M+Na⁺): 326.10, found: 326.1063.



1-(3-((Benzo[d][1,3]dioxol-5-vloxy)methyl)-4-(4fluorophenyl)piperidin-1-yl)-3-(phenylsulfonyl)propan-1-one (9k): synthesized according the general procedure E using 3-((benzo[d][1,3]dioxol-5-yloxy)methyl)-4-(4fluorophenyl)piperidine-1-carbonyl chloride 8k (157 mg, 0.4 mmol, 2 eq.) and phenyl vinyl sulfone (34 mg, 0.2 mmol, 1 eq.). The crude

mixture was purified by flash column chromatography on silica gel (gradient from hexane 100% to hexane 50% : 50% ethyl acetate) to afford product 9k (46 mg, 29% yield) as a yellowish oil.

<u>¹H NMR</u> (400 MHz, CDCl₃) δ 7.98 (m, 2H), 7.71 (m, 1H), 7.65 – 7.58 (m, 2H), 7.17 – 7.11 (m, 2H), 7.01 (m, 2H), 6.66 (dd, J = 17.8, 8.4 Hz, 1H), 6.38 (dd, J = 11.9, 2.5 Hz, 1H), 6.17 (ddd, J = 15.1, 8.5, 2.5 Hz, 1H), 5.92 (d, J = 13.5 Hz, 2H), 4.79 (dd, J = 55.2, 13.1 Hz, 1H), 4.07 (dd, J = 69.6, 13.5 Hz, 1H), 3.68 – 3.60 (m, 1H), 3.59 – 3.45 (m, 3H), 3.17 (m, 1H), 3.03 – 2.80 (m, 2H), 2.80 – 2.62 (m, 1H), 1.92 (m, 1H), 1.81 – 1.53 (m, 3H).

¹³<u>C NMR</u> (126 MHz, CDCl₃) δ 167.5, 154.5, 148.7, 142.3, 139.6, 138.4, 134.3, 129.7, 129.1, 128.3, 115.7, 115.8, 108.2, 106.0, 101.5, 98.4, 68.9, 52.5, 49.2, 46.4, 44.5, 42.2, 34.6, 33.8, 30.1, 26.3.

¹⁹F NMR (376 MHz, CDCl₃, proton decoupled) δ – 115.58

HRMS (ESI pos): calculated for C₂₈H₂₉FNO₆S (M+H⁺): 526.16, found: 526.1702.

C6.5 General Procedure for the intramolecular Giese type addition (General Procedure F)



An oven-dried 15 mL Schlenk tube was charged with a mixture of carbamoyl chloride **10** (0.2 mmol, 1 equiv.), catalyst **C** trihydrate (9 mg, 0.04 mmol, 0.2 equiv.), γ -terpinene (48 µL, 0.3 mmol, 1.5 equiv.) and K₃PO₄ (85 mg, 0.4 mmol, 2 equiv.) in acetonitrile (0.8 mL, 0.25 M). The reaction mixture was placed under an atmosphere of argon, cooled to -78 °C, degassed *via* vacuum evacuation (5 minutes), backfilled with argon and, ultimately, warmed to ambient temperature. This freeze-pump-thaw cycle was repeated four times, and then the Schlenk tube was sealed with Parafilm and put into the Hepatochem PhotoRedOx Box equipped with a 405 nm EvoluChem LED 18 W light source at 50 °C (Figure S8). After 18 hours, the reaction vessel was cooled down to ambient temperature, water was added and the mixture was extracted with ethyl acetate (2x15 mL). The combined layers were dried over magnesium sulfate, filtered, and concentrated. The resulting crude mixture was purified by column chromatography on silica gel to give the corresponding product **3** in the stated yield.

C6.6 Characterization of Products



7-Benzyl-7-azabicyclo[4.2.0]octan-8-one (**11a**): Synthesized according to the general procedure F using benzyl(cyclohex-2-en-1-yl)carbamic chloride (50 mg, 0.2 mmol). The crude mixture was purified by flash column chromatography on silica gel (10% AcOEt in hexanes as eluent) to afford product **11a** (26 mg, 60% yield) as a pale-

yellow oil.

¹<u>H NMR</u> (500 MHz, CDCl₃) δ 7.35 – 7.29 (m, 2H), 7.29 – 7.22 (m, 3H), 4.57 (d, *J* = 15.1 Hz, 1H), 4.08 (d, *J* = 15.1 Hz, 1H), 3.62 (ddd, *J* = 5.4, 4.2, 3.1 Hz, 1H), 3.20 – 3.15 (m, 1H), 1.89 – 1.80 (m, 1H), 1.74 – 1.49 (m, 5H), 1.49 – 1.33 (m, 2H).

¹³<u>C NMR</u> (126 MHz, CDCl₃) δ 171.1, 136.4, 128.9, 128.5, 127.8, 50.3, 47.1, 44.6, 23.0, 19.8, 19.1, 17.0.

HRMS (ESI pos): calculated for C₁₈H₁₈NaO₄ (M+H⁺): 216.1383, found: 216.1374.


7-(4-(Trifluoromethyl)benzyl)-7-azabicyclo[4.2.0]octan-8-one (11b): Synthesized according to general procedure F using cyclohex-2-en-1-yl(4-(trifluoromethyl)benzyl)carbamic chloride (64 mg, 0.2 mmol). The crude mixture was purified by flash column chromatography on silica gel (5% AcOEt in hexanes as eluent) to afford product 11b (31 mg, 55% yield) as a yellow oil.

¹H NMR (400 MHz, CDCl₃) δ 7.59 (d, J = 8.0 Hz, 2H), 7.39 (d, J = 8.0 Hz, 2H), 4.62 (d, J = 15.4 Hz, 1H), 4.16 (d, J = 15.4 Hz, 1H), 3.66 (dt, J = 5.1, 3.6 Hz, 1H), 3.23 (dt, J = 6.8),4.6 Hz, 1H), 1.92 – 1.83 (m, 1H), 1.77 – 1.55 (m, 5H), 1.50 – 1.34 (m, 2H.

 13 C NMR (126 MHz, CDCl₃) δ 171.1, 140.5, 130.1 (q, *J* = 32.6 Hz), 128.6, 125.9 (q, *J* = 3.8 Hz), 124.2 (q, J = 272.1 Hz), 50.5, 47.3, 44.1, 23.0, 19.7, 19.0, 16.9.

<u>HRMS (ESI pos)</u>: calculated for C₁₅H₁₇F₃NO (M+H⁺): 284.1257, found: 284.1258.

7-(4-Methoxybenzyl)-7-azabicyclo[4.2.0]octan-8-one (11c): Synthesized general according to procedure F using cyclohex-2-en-1-yl(4methoxybenzyl)carbamic chloride (56 mg, 0.2 mmol). The crude mixture was purified by flash column chromatography on silica gel (15% AcOEt in hexanes as eluent) to afford product 11c (30 mg, 61% yield) as a yellow oil.

¹H NMR (400 MHz, CDCl₃) δ 7.23 – 7.14 (m, 2H), 6.91 – 6.80 (m, 2H), 4.51 (d, J = 14.9 Hz, 1H), 4.04 (d, J = 14.9 Hz, 1H), 3.80 (s, 3H), 3.61 (ddd, J = 5.4, 4.1, 3.2 Hz, 1H), 3.17 (dt, J = 6.9, 4.6 Hz, 1H), 1.93 - 1.79 (m, 1H), 1.74 - 1.50 (m, 4H), 1.49 - 1.31 (m, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 170.9, 159.2, 129.7, 128.4, 114.2, 55.4, 50.0, 46.9, 43.9, 23.0, 19.7, 19.0, 16.9.

HRMS (ESI pos): calculated for $C_{15}H_{19}NnaO_2$ (M+Na⁺): 268.1308, found: 268.1304.



7-Octyl-7-azabicyclo[4.2.0]octan-8-one (11d): synthesized according the general procedure F using cyclohex-1-en-1-yl(octyl)carbamic chloride 10d (54 mg, 0.2 mmol, 1 eq.). The crude mixture was purified by flash column chromatography on silica gel (5% AcOEt in Hexane) to afford 11d (13 mg, 28% yield) as a colorless oil.

¹H NMR (400 MHz, CDCl₃) δ : 3.72 (ddd, J = 5.3, 4.2, 3.2 Hz, 1H), 3.33 (dt, J = 13.9, 7.6 Hz, 1H), 3.20 – 3.11 (m, 1H), 2.94 (ddd, J = 14.0, 7.9, 6.2 Hz, 1H), 1.94 – 1.39 (m, 10H), 1.35 – 1.20 (m, 9H), 1.00 - 0.81 (m, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 171, 50.2, 46.6, 40.3, 31.9, 29.4, 29.3, 28.2, 27.3, 23.3, 22.8, 19.7. 19. 17.1. 14.2.

HRMS (ESI pos): calculated for C₁₅H₂₇NO (M+H⁺): 238,21 found: 238,2157



6-Benzyl-6-azabicyclo[3.2.0]heptan-7-one (11e): synthesized according the general procedure F using benzyl(cyclopent-2-en-1-yl)carbamic chloride 10e (47 mg, 0.2 mmol, 1 eq.). The crude mixture was purified by flash column chromatography on silica gel (5% AcOEt in hexane) to afford 11e (11 mg, 30% yield) as a yellowish oil.

¹<u>H NMR</u> (400 MHz, CDCl₃) δ 7.54 – 7.08 (m, 5H), 4.50 (d, *J* = 15.1 Hz, 1H), 4.08 (d, *J* = 15.1 Hz, 1H), 3.91 (t, J = 4.1 Hz, 1H), 3.47 (dd, J = 8.0, 3.6 Hz, 1H), 2.05 (dd, J = 13.2, 6.3 Hz, 1H), 1.83 – 1.70 (m, 2H), 1.58 (m, 1H), 1.47 – 1.30 (m, 1H), 1.18 (m, 1H).

¹³C NMR (126 MHz, CDCl₃) δ 169.6, 136.3, 128.8, 128.4, 127.8, 57.6, 55.1, 44.2, 27, 25.1, 22.8. HRMS (ESI pos): calculated for C₁₃H₁₅NaNO (M+Na⁺): 224.11 found: 224.1041



1-Benzyl-3-ethylazetidin-2-one (**11f**): synthesized according the general procedure F using benzyl(but-2-en-1-yl)carbamic chloride **10f** (47 mg, 0.2 mmol, 1 eq.). The crude mixture was purified by flash column chromatography on silica gel (5% AcOEt in hexane) to afford **11d** (11 mg, 29% yield) as a yellowish oil.

 $\frac{^{1}\text{H NMR}}{(m, 1H)} (500 \text{ MHz, CDCl}_{3}) \delta 7.37 - 7.26 (m, 5H), 4.46 (s, 2H), 3.60 - 3.52 (m, 2H), 3.18 - 3.10 (m, 1H), 1.72 - 1.65 (m, 2H), 0.93 (t, <math>J = 7.3 \text{ Hz}, 3H)$

¹³C NMR (126 MHz, CDCl₃) δ: 171.9 (C), 136.3 (C), 128.9 (CH), 128.3 (CH), 127.9 (CH), 53.6 (CH₂), 48.7 (CH₂), 44 (CH), 29 (CH₂), 11.9 (CH₃).

Matching reported literature data. ²⁰

1-Benzyl-3-methylpyrrolidin-2-one (11g): Synthesized according to the general procedure F using benzyl(but-3-en-1-yl)carbamic chloride **10g** (48 mg, 0.2 mmol). The crude mixture was purified by flash column chromatography on silica gel (10% AcOEt in hexanes as eluent) to afford product **11g** (23 mg, 60% yield) as a yellow oil.

¹<u>H NMR</u> (500 MHz, CDCl₃) δ 7.37 – 7.30 (m, 2H), 7.29 – 7.24 (m, 1H), 7.24 – 7.20 (m, 2H), 4.49 – 4.40 (m, 2H), 3.22 – 3.09 (m, 2H), 2.51 (ddt, *J* = 15.8, 8.7, 7.2 Hz, 1H), 2.21 (dddd, *J* = 12.9, 8.7, 6.5, 4.4 Hz, 1H), 1.59 (dq, *J* = 12.6, 8.5 Hz, 1H), 1.24 (d, *J* = 7.1 Hz, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 177.5, 136.8, 128.8, 128.2, 127.6, 46.9, 44.8, 36.9, 27.2, 16.5.

HRMS (ESI pos): calculated for C₁₂H₁₆NO (M+H⁺): 190.1226, found: 190.1228.

1-Benzyl-3-methylpiperidin-2-one (11h): Synthesized according to the general procedure F using benzyl(pent-4-en-1-yl)carbamic chloride 10h (48 mg, 0.2 mmol). The crude mixture was purified by flash column chromatography on silica gel (10% AcOEt in hexanes as eluent) to afford product 11h (21 mg, 52% yield) as a yellow oil.

 $\frac{1 \text{H NMR}}{1 \text{H NMR}} (400 \text{ MHz, CDCl}_3) \delta 7.36 - 7.28 \text{ (m, 2H)}, 7.28 - 7.21 \text{ (m, 3H)}, 4.66 \text{ (d, } J = 14.6 \text{ Hz}, 1\text{H}), 4.50 \text{ (d, } J = 14.6 \text{ Hz}, 1\text{H}), 3.20 \text{ (dd, } J = 7.2, 5.1 \text{ Hz}, 2\text{H}), 2.56 - 2.42 \text{ (m, 1H)}, 1.96 \text{ (dtd, } J = 12.8, 6.2, 3.4 \text{ Hz}, 1\text{H}), 1.84 \text{ (ddtd, } J = 13.5, 6.6, 5.0, 3.4 \text{ Hz}, 1\text{H}), 1.78 - 1.66 \text{ (m, 1H)}, 1.53 \text{ (dddd, } J = 12.8, 10.4, 9.1, 3.4 \text{ Hz}, 1\text{H}), 1.30 \text{ (d, } J = 7.2 \text{ Hz}, 3\text{H}).$

¹³<u>C NMR</u> (101 MHz, CDCl₃) δ 173.5, 137.7, 128.7, 128.1, 127.4, 50.4, 47.7, 36.8, 29.7, 21.8, 18.2.

HRMS (ESI pos): calculated for C₁₃H₁₈NO (M+H⁺): 204.1383, found: 204.1376.

C7. Unsuccessful Substrates



Figure S9: Unsuccessful substrates: (a) Intermolecular reaction using acrylonitrile as the electron-poor olefin. (b) Intramolecular reaction.

D. Mechanistic Studies

D1. Characterisation of Acylxanthate and Carbamoyldithiocarbamate Intermediates:

D1.1 General procedure for the synthesis of acyl xanthate intermediates (general procedure G)



In a round bottom flask, acyl chloride (1.1 equiv.) was dissolved in acetone (0.1 M) and cooled to 0 °C. The dithiocarbamate anion or the xanthate salt **1a-c** (1 equiv.) was then added and the resulting reaction mixture was stirred for 1 hour at 0 °C. The solvent was removed under reduced pressure at ambient temperature. The residue was then dissolved in DCM and washed with distilled water, NaHCO₃ solution and brine. The combined organic fractions were dried over MgSO₄ and concentrated to dryness to obtain the desired product.

D1.2 Characterization of the Intermediates

Benzoic (O-ethyl carbonothioic) thioanhydride (Ia).

Eto $\overset{\bullet}{}_{s} \overset{\bullet}{}_{Ph}$ Prepared according to the general procedure G using potassium ethyl xanthogenate **B** (1 mmol, 160 mg) and benzoyl chloride (1.1 mmol, 128 µL) in 10 mL of acetone. After work-up, the product **Ia** (226 mg, 99% yield) was obtained as a yellow oil.

 $\frac{1}{11}$ NMR (300 MHz, CDCl₃) δ 7.87 (app d, J = 7.7 Hz, 2 H); 7.64-7.54 (m, 1H); 7.49-7.39 (m, 2H); 4.69 (q, J = 7.1 Hz, 2H); 1.45 (t, J = 7.1 Hz, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 203.4, 185.0, 135.7, 134.4, 129.0, 127.9, 71.1, 13.5.

Matching reported literature data.²¹

Benzoic diethylcarbamothioic thioanhydride (Ib).

 Et_2N S Ph Prepared according to the general procedure G using sodium diethylcarbamodithioate trihydrate C (1.05 mmol, 237 mg) and benzoyl chloride (1 mmol, 116 μ L) in 10 mL of acetone. After work-up, the product **Ib** was obtained as a yellow oil (220 mg, 87% yield).

¹<u>H NMR</u> (300 MHz, CDCl₃) δ 7.95-7.88 (m, 2 H); 7.64-7.56 (m, 1H); 7.52-7.42 (m, 2H); 4.07-3.86 (m, 2H); 1.36 (t, *J* = 7.1 Hz, 3H).

Matching reported literature data.²²

cyclohexanecarboxylic (O-ethyl carbonothioic) thioanhydride (Ic).

Prepared according to the general procedure G using potassium ethyl xanthogenate **B** (1 mmol, 160 mg) and cyclohexanecarbonyl chloride (1.1

mmol, 128 $\mu L)$ in 10 mL of acetone. After work-up, the product Ic was obtained as a yellow oil (207 mg, 89% yield).

¹<u>H NMR</u> (300 MHz, CDCl₃) δ 4.65 (q, J = 7.1 Hz, 2H); 2.53-2.39 (m, 1H); 1.98-1.85 (m, 2H); 1.83-1.70 (m, 2H); 1.68-1.53 (m, 1H); 1.55-1.35 (m, 5H); 1.34-1.10 (m, 3 H).

¹³C NMR (75 MHz, CDCl₃) δ 204.6 (C); 194.9 (C); 70.8 (CH₂); 52.8 (CH); 29.1 (CH₂); 25.5 (CH₂); 25.32 (CH₂); 13.6 (CH₃).

HRMS (ESI pos): calculated for C₁₀H₁₆NaO₂S₂ (M+Na⁺): 255.0484, found: 255.0482.

S O N-Diethyl, N'-Dimethyl-Thiodicarbonic diamide (Id).

 Et_2N S NMe_2 Prepared according to the general procedure G using potassium diethylcarbamodithioate trihydrate C (3 mmol, 724 mg) and dimethylcarbamyl chloride (1.1 mmol, 128 μ L) in 10 mL of acetone. After work-up and chromatography on silica gel (8:2 hexane/AcOEt), the product **Id** was obtained as a yellow oil (177 mg, 80% yield).

 $\frac{1}{11}$ NMR (400 MHz, CDCl₃) δ 4.02 (q, *J* = 7.1 Hz, 1H), 3.79 (q, *J* = 7.2 Hz, 1H), 3.06 (s, 3H), 1.32 (dt, *J* = 9.7, 7.1 Hz, 3H)

¹³C NMR (126 MHz, CDCl₃) δ 185.2 (C), 162 (C), 50.1 (CH₃), 49 (CH₃), 38.5 (CH₂), 37.3 (CH₂), 13.5 (CH₃), 11.3 (CH₃).

D1.3 UV-Vis Characterization of the Intermediates.

Et	S O S Ph Et ₂ N S la lb	Ph Eto S	Et ₂ N Id
	Intermediate	λmax	tail of absorption
	la	397 nm	490 nm
	lb	400 nm	490 nm
	lc	400 nm	490 nm
	ld	343 nm	500 nm

Table S9. Spectroscopic characteristics of la-d



Figure S10: UV-Vis absorption spectrum of la recorded at 1.10⁻²M concentration in acetonitrile



Figure S11: UV-Vis absorption spectrum of **Ib** recorded at 1.10⁻² M concentration in acetonitrile.



Figure S12: UV-Vis absorption spectrum of Ic recorded at 2.10⁻² M concentration in acetonitrile.



Figure S13: Superposition of the absorption spectra of the different acyl xanthates and acyl dithiocarbamate intermediates at the same concentration (2·10⁻² M in acetonitrile).



Figure S14: UV-Vis absorption spectrum of intermediate Id recorded at 2.10⁻³ M concentration in acetonitrile.



Figure S15: UV-Vis absorption spectrum of IXa recorded at 1.10⁻² M in acetonitrile

D1.4 TEMPO Trapping Experiments.

Stoichiometric reaction between TEMPO and in-situ acyl xanthate intermediate



In an oven dried tube of 15 mL (16 mm \times 125 mm) with a Teflon septum screw cap, potassium ethyl xanthogenate **B** (80.1 mg, 0.5 mmol, 1 equiv.) was suspended in DCM (2 mL, HPLC grade). Then, benzoyl chloride **1** (69.6 µL, 0.6 mmol, 1.2 equiv.) was added and the mixture was stirred at ambient temperature for 30 minutes. Then, TEMPO (234.4 mg, 1.5 mmol, 3 equiv.) was added and the resulting yellow solution was degassed with argon sparging for 60 seconds. The tube was then placed in the temperature controlled photoreactor (Figure S4) set at a temperature of 60 °C (60-61°C measured in the central well) and irradiated for 16 hours. Chromatography on silica gel (5% AcOEt in hexanes as eluent) afforded adduct **12** (66 mg, yellow oil, 51% yield).

 $\frac{1}{1}$ H NMR (500 MHz, CDCl₃) δ 8.35 (d, *J* = 6.9 Hz, 2H), 7.83 (m, 1H), 7.74 (m, 2H), 2.12 - 1.70 (m, 6H), 1.55 (s, 6H), 1.40 (s, 6H).

¹³<u>C NMR</u> (126 MHz, CDCl₃) δ 161.45, 128.17, 124.89, 124.74, 123.78, 55.52, 34.28, 27.19, 16.09, 12.26.

Matching reported literature data.²³

Stoichiometric reaction between TEMPO and dithiocarbamate intermediate Id



In an oven-dried 15 mL Schlenk tube was added a 0.25 M solution of the dithiocarbamate intermediate **Id** (28 mg, 127 mmol, 1 equiv.) and TEMPO (60 mg, 0.38 mmol, 3 equiv.) in acetonitrile (0.5 mL). The reaction mixture was placed under an atmosphere of argon, cooled to -78 °C, degassed *via* vacuum evacuation (5 minutes), backfilled with argon and, ultimately, warmed to ambient temperature. This freeze-pump-thaw cycle was repeated four times, and then the Schlenk tube was sealed with Parafilm and put into the Hepatochem PhotoRedOx Box (Figure S8) equipped with a 405 nm EvoluChem LED 18 W light source at 50 °C. After 18 hours, the reaction vessel was cooled down to ambient temperature, water was added and the mixture was extracted with ethyl acetate (2x15 mL). The combined layers were dried over MgSO₄, filtered, and concentrated. The resulting crude mixture was purified by column chromatography on silica gel (5% to 30% AcOEt in hexane) to give the corresponding product **11** (21 mg, 75% yield).

 $\frac{1}{H}$ NMR (400 MHz, CDCl₃) δ 2.96 (s, 6H), 1.73 – 1.48 (m, 6H), 3.06 (s, 3H), 1.13 (d, *J* = 17.6 Hz, 1H)

¹³C NMR (101 MHz, CDCl₃) δ 157.8, 60.2, 50.1, 39.1, 31.9, 21.1, 17.2.

TEMPO inhibition of the model reactions



Reaction performed according to the general procedure A using benzoyl chloride (87 μ L, 0.75 mmol, 1.5 equiv.) and acrylonitrile (33 μ L, 0.5 mmol, 1 equiv.) and adding TEMPO (156.3 mg, 1 mmol, 2 equiv.) before the degassing step. The crude mixture was analyzed by ¹H NMR analysis after 16 hours using trichloroethylene (45 μ L, 0.5 mmol, 1 equiv.) as internal standard, and by GC-MS. NMR yield: 5%. Traces of the TEMPO adduct **12** were detected by GC-MS analysis.



Reaction performed according to the general procedure E using dimethylcarbamyl chloride (37 μ L, 0.4 mmol, 2 equiv.) and phenyl vinyl sulfone (34 mg, 0.2 mmol, 1 equiv.) and adding TEMPO (62 mg, 0.4 mmol, 2 equiv.) before the degassing step.

D1.5 Experiments with the Dimeric Catalysts.

Model reaction with catalyst dimer VIIa - Acylation



Reaction performed according to the general procedure A using benzoyl chloride (87 μ L, 0.75 mmol, 1.5 equiv.) and acrylonitrile (33 μ L, 0.5 mmol, 1 equiv.) while replacing *catalyst* **B** with dimer **VIIa** (6 mg, 0.025 mmol, 0.05 equiv.). The crude reaction mixture was analyzed by ¹H NMR analysis using trichloroethylene as internal standard. NMR yield: 64%.

Model reaction with dimer catalyst C - Carbamoylation



Reaction performed according to general procedure E using dimethylcarbamic chloride (37 μ L, 0.4 mmol, 2.0 equiv.) and phenyl vinyl sulfone (34 mg, 0.2 mmol, 1 equiv.) while replacing *catalyst* **C** with *dimer catalyst* **C** (6 mg, 0.02 mmol, 0.1 equiv.). The crude reaction mixture was analyzed by ¹H NMR analysis using trichloroethylene as internal standard. NMR yield: 53%.

Turn-over experiment with dimer catalyst B and terpinene



In an oven dried vial (16 mm \times 50 mm) with a Teflon septum screw cap, *dimer catalyst* **B** (60.6 mg, 0.25 mmol, 1 equiv.) and sodium phosphate (82 mg, 0.5 mmol, 2 equiv) were dissolved in DCM (2 mL, HPLC grade). Then, γ -terpinene (40 μ L, 0.25 mmol, 1 equiv.) was added. The resulting yellow mixture was degassed with argon, sparging for 60 seconds. The vial was then placed in the 3D-printed support photoreactor (Figure S6) and irradiated for 24 hours. Trichloroethylene was added as internal standard and a sample of the crude mixture was diluted in d₆-DMSO to record the NMR yield.

D1.6 Group Transfer Experiments. Stoichiometric group transfer reaction with in-situ acyl xanthate intermediate



In an oven dried tube of 15 mL (16 mm \times 125 mm) with a Teflon septum screw cap, potassium ethyl xanthogenate **B** (112 mg, 0.7 mmol, 1.4 equiv.) was suspended in DCM (2 mL, HPLC

grade). Then, benzoyl chloride (87 μ L, 0.75 mmol, 1.5 equiv.) was added and the mixture was stirred at ambient temperature for 30 min. The reaction mixture was then degassed with argon, sparging for 60 seconds. Finally, acrylonitrile (33 μ L, 0.5 mmol, 1 equiv.) was added via syringe. The tube was then placed in the temperature controlled photoreactor (Figure S4) set at a temperature of 60 °C (60-61°C measured in the central well) and irradiated for 16 hours. The crude mixture was purified by flash column chromatography on silica gel (5% to 10% AcOEt in hexanes as eluent) to afford **IXa** (50 mg, 35% yield) as a yellow oil.

¹<u>H NMR</u> (400 MHz, CDCl₃) δ 7.97 – 7.89 (m, 2H), 7.69 – 7.58 (m, 1H), 7.50 (app t, *J* = 7.5 Hz, 2H), 5.08 (t, *J* = 6.2 Hz, 1H), 4.72 (q, *J* = 7.1 Hz, 2H), 3.70 (d, *J* = 6.3 Hz, 2H), 1.47 (t, *J* = 7.1 Hz, 3H).

¹³<u>C NMR</u> (101 MHz, CDCl₃) δ 209.05, 193.54, 135.35, 134.39, 129.09, 128.30, 117.96, 71.54, 40.67, 32.49, 13.84.

Stoichiometric group transfer reaction with in-situ acyl xanthate intermediate in the presence of γ -terpinene



In an oven dried tube of 15 mL (16 mm \times 125 mm) with a Teflon septum screw cap, potassium ethyl xanthogenate (112 mg, 0.7 mmol, 1.4 equiv.) and sodium phosphate (164 mg, 1.0 mmol, 2 equiv) were dissolved in DCM (2 mL, HPLC grade). Benzoyl chloride (87 µL, 0.75 mmol, 1.5 equiv.) was added and the mixture was stirred at ambient temperature for 30 min. Then, γ -terpinene (240 µL, 1.5 mmol, 3 equiv.) was added. The mixture was degassed via argon sparging for 60 seconds. Finally, acrylonitrile (33 µL, 0.5 mmol, 1 equiv.) was added via syringe. The tube was then placed in the temperature controlled photoreactor (Figure S4) set at a temperature of 60 °C (60-61 °C measured in the central well) and irradiated for 16 hours. Trichloroethylene was added as internal standard, and a sample of the crude mixture was diluted in CDCl₃ to record the NMR yield. *No group transfer product* **12** *was observed*.

Direct photolysis of the group transfer product under reaction conditions



In an oven dried tube of 15 mL (16 mm \times 125 mm) with a Teflon septum screw cap, the group transfer product **12** (28.01 mg, 0.1 mmol, 1 equiv.) and sodium phosphate (33 mg, 0.2 mmol, 2 equiv) were dissolved in DCM (2 mL, HPLC grade). Then, γ -terpinene (33 μ L, 0.2 mmol, 2 equiv.) was added. The reaction mixture was degassed with Argon sparging for 60 seconds. The tube was then placed in the temperature controlled photoreactor (Figure S4) set at a temperature of 60 °C (60-61 °C measured in the central well) and irradiated for 16 hours.

Trichloroethylene was added as internal standard and a sample of the crude mixture was diluted in $CDCl_3$ to record the NMR yield – product **3a** was formed in 35%.

Direct photolysis of the group transfer product for the intramolecular reaction



An oven-dried 15 mL Schlenk tube was charged with an authentic sample of the group transfer adduct **A**, prepared according to Ref. 2, γ -terpinene (48 µL, 0.3 mmol, 1.5 equiv.) and K₃PO₄ (85 mg, 0.4 mmol, 2 equiv.) in acetonitrile (0.8 mL, 0.25 M). The reaction mixture was placed under an atmosphere of argon, cooled to -78 °C, degassed *via* vacuum evacuation (5 minutes), backfilled with argon and, ultimately, warmed to ambient temperature. This freeze-pump-thaw cycle was repeated four times, and then the Schlenk tube was sealed with Parafilm and put into the Hepatochem PhotoRedOx Box equipped with a 405 nm EvoluChem LED 18 W light source at 50 °C (Figure S8). After 18 hours stirring, the reaction was cooled down to ambient temperature, trichloroethylene was added as internal standard and a sample of the crude mixture was diluted in CDCl₃ to record the NMR of the crude - product **11a** was formed in 48%.

D2. Cyclic Voltammetry Measurements

For the cyclic voltammetry (CV) measurements, a glassy carbon disk electrode (diameter: 3 mm) was used as a working electrode. A silver wire coated with AgCl immersed in a 3.5 M aqueous solution of KCl and separated from the analyte by a fritted glass disk was employed as the reference electrode. A Pt wire counter-electrode completed the electrochemical setup. The scan rate of used in each CV experiment is indicated case by case.

Potentials are quoted with the following notation: E_p^C refers to the cathodic peak potential, E_p^A refers to the anodic peak potential, while the E^{red} value describes the electrochemical properties of the referred compound.



Figure S16: Cyclic voltammogram of benzoyl chloride **1a** [0.02 M] in [0.1 M] TBAPF₆ in CH₃CN. Sweep rate: 100 mV/s. Glassy carbon electrode working electrode, Ag/AgCl (KCl 3.5 M) reference electrode, Pt wire auxiliary electrode. Irreversible reduction, $E_p^{C} = E^{red} (1a/1a^{-1}) = -1.57 \text{ V}.$



Figure S17: Cyclic voltammogram of cyclohexanecarbonyl chloride [0.02 M] in [0.1 M] TBAPF₆ in CH₃CN. Sweep rate: 100 mV/s. Glassy carbon electrode working electrode, Ag/AgCl (KCl 3.5 M) reference electrode, Pt wire auxiliary electrode. Reduction of cyclohexanecarbonyl chloride was not observed in the registered potential window (from 0 to -2.50 V).



Figure S18: Cyclic voltammogram for **8a** [0.02M] in [0.1 M] TBAPF₆ in CH₃CN. Sweep rate: 50 mV/s. Glassy carbon electrode working electrode, Ag/AgCl (KCl 3.5 M) reference electrode, Pt wire auxiliary electrode. Reduction of **8a** was not observed in the registered potential window (from 0 to -2.50 V).



Figure S19: Cyclic voltammogram for **8e** [0.02M] in [0.1 M] TBAPF₆ in CH₃CN. Sweep rate: 100 mV/s. Glassy carbon electrode working electrode, Ag/AgCl (KCl 3.5 M) reference electrode, Pt wire auxiliary electrode. Reduction of **8e** was not observed in the registered potential window (from 0 to -2.50 V).



Figure S20: Cyclic voltammogram for catalyst **B** [0.02 M] in [0.1 M] TBAPF₆ in CH₃CN. Measurement started by oxidation from 0 to +1.5 V, followed by reduction from +1.5 V to -2.0 V, and finishing at 0 V. Glassy carbon electrode working electrode, Ag/AgCI (KCI 3.5 M) reference electrode, Pt wire auxiliary electrode. Two irreversible peaks observed increasing with sweep rate.



Figure S21: Cyclic voltammogram for catalyst **B** [0.02M] in [0.1 M] TBAPF₆ in CH₃CN. Measurement started by reduction from 0 to -2.0 V, followed by oxidation from -2.0 V to +1.5 V, and finishing at 0 V. Glassy carbon electrode working electrode, Ag/AgCI (KCI 3.5 M) reference electrode, Pt wire auxiliary electrode. Only one irreversible peak observed. Sweep rate: 500 mV/s.



Figure S22: Cyclic voltammogram for dimer **VIIa** [0.02 M] in [0.1 M] TBAPF₆ in CH₃CN. Measurement started by reduction from 0 to -2.0 V, followed by oxidation from -2.0 V to +1.5 V, and finishing at 0 V. Glassy carbon electrode working electrode, Ag/AgCI (KCI 3.5 M) reference electrode, Pt wire auxiliary electrode. Two irreversible peaks observed increasing with sweep rate.



Figure S23: Cyclic voltammogram for dimer **VIIa** [0.02M] in [0.1 M] TBAPF₆ in CH₃CN. Measurement started by oxidation from 0 to +1.5 V, followed by reduction from +1.5 V to -2.0 V, and finishing at 0 V. Glassy carbon electrode working electrode, Ag/AgCI (KCI 3.5 M) reference electrode, Pt wire auxiliary electrode. Two irreversible peaks observed increasing with sweep rate.

D3. Transient Absorption Spectroscopy (TAS).

Studies with microsecond transient absorption spectroscopy (TAS) were performed using an excitation source of NdYAG (neodymium-doped yttrium aluminium garnet) Opolette laser with an optical parametric oscillator (OPO) system that allows variable wavelength excitation from 400 -1800 nm, pulse width of 6 ns, up to 2 mJ of energy from OPO output with fiber optic coupled, and high energy output from direct NdYAG harmonics 355 (20 mJ, 5 ns) and 532 (45mJ, 6 ns). The system is completed with 150 W tungsten lamp as probe; 2 monochromators Minuteman MM151; Si amplified photodetector module for VIS; DSPDAU high speed data rate recorder and interface software from RAMDSP. Laser intensities for each wavelength were the following: 355 nm - 1.30 mJ; 420 nm- 1.20 mJ; 460 nm - 1.95 mJ.

Several studies with different wavelengths and laser intensities were carried out, each of the conditions are indicated in a case by case bases. We selected a logarithmic time scale suitable for clearly showing the decay of the transient species in the samples. The characteristics of the detected transient species match literature data.²⁴

In a typical transient absorption spectroscopy experiment, solutions in acetonitrile of each of the substrates were prepared under an argon atmosphere and transferred into a screw-top 3.0 mL quartz cuvette for measurement. Upon irradiation with the appropriated wavelength, the decay of absorption at 620 nm of the transient xanthyl radical **IIIa** was recorded.

Acylxanthate Ia



Figure S24: Absorption at 620 nm of the transient xanthyl radical **IIIa** (blue line) generated upon 355 nm laser excitation of Acylxanthate **Ia** ([**Ia**]₀ = 3.00 mM in acetonitrile). Note logarithmic scale for time. Absorption decay (black line) processed through Savinsky Golay filter to facilitate lifetime measurement. \triangle OD: optical density variation.

Compound **Ia** was also measured upon 460 nm excitation in order to mimic the conditions of photolysis under catalytic conditions. Since photolysis of **Ia** is less efficient at longer wavelengths, a higher concentration of **Ia** was needed to obtain a comparable scale signal. Note that changes in concentration of both **Ia** and transient **IIIa** generated upon photolytic cleavage directly affects the lifetime of the detected species.



Figure S25: Absorption at 620 nm of the transient xanthyl radical **IIIa** (blue line) generated upon 460 nm laser excitation of acylxanthate **Ia** ([**Ia**]₀ = 300 mM in acetonitrile). Note logarithmic scale for time. Absorption decay (black line) processed through Savinsky Golay filter to facilitate lifetime measurement. \triangle OD: optical density variation.

Dimer VIIa



Figure S26: Absorption at 620 nm of the transient xanthyl radical **IIIa** (black line) generated upon 355 nm laser excitation of dimer **VIIa** ([**VIIa**]₀ = 3.00 mM in acetonitrile). Note logarithmic scale for time. $\triangle OD$: optical density variation.

Dimer **VIIa** was also measured upon 420 nm and 460 nm irradiation in order to support photolysis under the reaction conditions. A higher concentration of **VIIa** was used to ensure comparable scale signal.



Figure S27: Absorption at 620 nm of the transient xanthyl radical **IIIa** (black line) generated upon 420 nm laser excitation of dimer **VIIa** ([**VIIa**]₀ = 300 mM in acetonitrile). Note logarithmic scale for time. $\triangle OD$: optical density variation.



Figure S28: Absorption at 620 nm of the transient xanthyl radical **IIIa** (blue line) generated upon 460 nm laser excitation of dimer **VIIa** ([**VIIa**]₀ = 300 mM in acetonitrile). Note logarithmic scale for time. Absorption decay (black line) processed through Savinsky Golay filter to facilitate lifetime measurement. $\triangle OD$: optical density variation.

In order to perform the quenching experiment, increasing amounts of pure γ -terpinene was added while observing the effect on the absorption at 620 nm of the transient **IIIa**, which was recorded after every addition. Increasing amounts of pure γ -terpinene (up to 60 equivalents, 60 µL) were added sequentially to a 2 mL solution of **VIIa** (3 mM in acetonitrile) in a screw-top quartz cuvette, providing a final concentration of 2.91 mM. A decay of absorption of the transient xanthyl radical,

and therefore a shorter lifetime, was observed upon addition of γ -terpinene (Figure S29), which is consonant with a reaction between the two species. Turquoise line: ratio **VIIa**/ γ -terpinene mimics the reaction conditions.

Note that precipitation of a solid, associated to ethyl xanthogenate, was observed upon addition and irradiation of the sample.



Figure S29: Absorption at 620 nm of the transient xanthyl radical **IIIa** (black line) generated upon 355 nm laser excitation of dimer **VIIa** ([**VIIa**]₀ = 3 mM in acetonitrile) and subsequent decay of the absorption upon addition of 10 (orange line), 30 (green line, mimics proportions under reaction conditions) and 60 (blue line) equivalents of γ -terpinene, respectively. Note logarithmic scale for time. Absorption decay was normalized to 1. Δ OD: normalized optical density variation.



Figure S30: Absorption at 620 nm of the transient xanthyl radical **IIIa** (blue line) generated upon 355 nm laser excitation of **IXa** ([**IXa**]₀ = 3 mM in acetonitrile). Note logarithmic scale for time. Absorption decay (black line) processed through Savinsky Golay filter to facilitate lifetime measurement. $\triangle OD$: optical density variation.



Figure S31: Absorption spectra of the transient xanthyl radical **IIIa** generated upon 355 nm laser excitation of Dimer **VIIa** ([**VIIa**]₀ = 3 mM in acetonitrile) at 1 μ S time of irradiation. Maximum characteristic from xanthyl raical can be observed around 625 nm.

D4. Electron paramagnetic resonance (EPR)

EPR spectra were acquired on a Bruker EMX X-band EPR spectrometer with an ER 4116 HS cavity (9.86 GHz at room temperature) using 100 kHz field modulation (modulation amplitude: 1 G). Individual EPR tubes were filled with ~0.7 mL of the solution and were placed at the same position of the resonant cavity for EPR spectral acquisition. The spectral data were collected at 298 K with the following spectrometer settings: microwave power = 2.020 mW; center field = 3518 G, sweep width = 200 G, sweep time = 30 s, modulation frequency = 100 KHz, modulation amplitude = 1 G, power attenuation = 20 dB, time constant = 0.01 ms.

A fresh solution of acylxanthate **Ia** 0.10 M in Toluene was prepared under air and measured without further precautions to remove oxygen from the solution. As expected, no signal was observed before of irradiation (note that **Ia** decomposes rapidly, and a sample older than one day did show signals appearing before irradiation, due to decomposition); on the other hand, upon irradiation of the sample, appearance of a triplet at 3505 G was observed with a g-value of 2.00272 and a hyperfine splitting value $\alpha_{\rm H}$ (2.6, 2H, γ -H). This signal reaches a maximum of intensity after 12.5 minutes of irradiation. The calculated EPR spectrum for the carbon radical of type **VI**, which lies in proximity of two sulfur atoms and an ethoxy moiety, is shown in the right panel of Figure S32.



Figure S32: Comparison between (left) EPR spectra of acylxanthate **Ia** (0.1 M in toluene) before irradiation (blue line) and after irradiation with a LSB610 100W mercury lamp during 12.5 min (black line). Open-shell specie was detected by appearance of a new signal centered at 3505 G (triplet); and (right) calculated EPR spectrum for intermediate **VI** for a hyperfine coupling with two equivalent nuclei of spin ½.

D5. Quantum Yield Determination

A ferrioxalate actinometer solution was prepared by following the Hammond variation of the Hatchard and Parker procedure outlined in the Handbook of Photochemistry.²⁵ The ferrioxalate actinometer solution measures the decomposition of ferric ions to ferrous ions, which are complexed by 1,10-phenanthroline and monitored by UV/Vis absorbance at 510 nm. The moles of iron-phenanthroline complex formed are related to moles of photons absorbed. The following solutions were prepared and stored in a dark laboratory (red light):

1. Potassium ferrioxalate solution: 294.8 mg of potassium ferrioxalate (commercially available from Alfa Aesar) and 139 μ L of sulfuric acid (96%) were added to a 50 mL volumetric flask, and filled to the mark with water (HPLC grade).

2. Phenanthroline solution: 0.2% by weight of 1,10-phenanthroline in water (100 mg in 50 mL volumetric flask).

3. Buffer solution: 2.47 g of NaOAc and 0.5 mL of sulfuric acid (96%) were added to a 50 mL volumetric flask, and filled to the mark with water (HPLC grade).

The actinometry measurements were done as follows:

1. 1 mL of the actinometer solution was added to a screw-cap vial and placed om a single HP LED 1.5 cm away from the light source. The solution was irradiated at 460 nm (irradiance 40 mW/cm²). This procedure was repeated 4 times, quenching the solutions after different time intervals: 10 sec, 15 sec, 20 sec, and 25 sec.

2. After irradiation, the actinometer solutions were removed and placed in a 10 mL volumetric flask containing 0.5 mL of 1,10-phenanthroline solution and 2 mL of buffer solution. These flasks were filled to the mark with water (HPLC grade).

3. The UV-Vis spectra of the complexed actinometer samples were recorded for each time interval. The absorbance of the complexed actinometer solution was monitored at 510 nm.



Figure S33: Absorbance of the complexed actinometer solutions.

The moles of Fe²⁺ formed for each sample is determined using Beers' Law (Eq. 1) :

Mols of
$$Fe(II) = V_1 \times V_3 \times \Delta A(510 \text{ nm})/10^3 \times V_2 \times l \times \varepsilon(510 \text{ nm})$$
 (Eq. 1)

where V₁ is the irradiated volume (1 mL), V₂ is the aliquot of the irradiated solution taken for the determination of the ferrous ions (1 mL), V₃ is the final volume after complexation with phenanthroline (10 mL), *l* is the optical path-length of the irradiation cell (1 cm), $\Delta A(510 \text{ nm})$ is the optical difference in absorbance between the irradiated solution and the one stored in the dark, $\epsilon(510 \text{ nm})$ is the extinction coefficient the complex Fe(phen)₃²⁺ at 510 nm (11100 L mol⁻¹ cm⁻¹). The moles of Fe²⁺ formed (x) are plotted as a function of time (t). The slope of this line was correlated to the moles of incident photons by unit of time (*q*_n, ⁰) by the use of the following Equation 2:

$$\Phi(\lambda) = dx/dt q_{n,p} \left[1 - 10^{-A(\lambda)} \right]$$
 (Eq. 2)

where dx/dt is the rate of change of a measurable quantity (spectral or any other property), the quantum yield (Φ) for Fe²⁺ at 458 nm is 1.1⁴⁵, [1-10^{-A(λ)}] is the ratio of absorbed photons by the

solution, and $A(\lambda)$ is the absorbance of the actinometer at the wavelength used to carry out the experiments (460 nm). The absorbance at 460 nm A(460) was measured using a Shimadzu 2401PC UV-Vis spectrophotometer in a 1 cm path quartz cuvette, obtaining an absorbance of 0.158.



 $q_{n,0}^{0}$, which is the photon flux, was determined to be 1.048x10⁻⁷ einstein s⁻¹.

Consequently, the model reactions were performed.

The reactions were prepared on a screw-cap vial with stir bar. Cyclohexanecarbonyl chloride (50 μL, 0.375 mmol, 1.5 equiv.), γ-terpinene (120 μL, 0.75 mmol, 3 equiv.), and lutidine (58 μL, 0.5 mmol, 2 equiv.), were added to a solution of catalyst **B** (4 mg, 0.1 equiv.) in acetonitrile (1 mL). After degassing by bubbling Argon for 30 s, acrylonitrile 2a (16 µL, 0.25 mmol) was added and the tube was sealed with parafilm and put in the HP-LED 460 nm at 1 cm distance at ambient temperature (reaction reaches around 35 °C) with irradiance of 40 mW/cm². Four different reactions were setup and irradiated for different times: 60 min, 80 min, 100 min and 120 min. The moles of product **5e** formed for the model reaction were determined by GC measurement (FID detector) using 1,3,5-trimethoxybenzene as internal standard. The moles of product per unit of time are related to the number of photons absorbed. The photons absorbed are correlated to the number of incident photons by the use of Equation 1. According to this, plotting the moles of product (x) versus the moles of incident photons $(q_n, 0, dt)$, the slope is equal to: $\Phi \cdot (1-10^{-A(\lambda)/460})$ ^{nm)}), where Φ is the quantum yield to be determined and A(460 nm) is the absorption of the reaction under study. A(460 nm) was measured using a Shimadzu 2401PC UV-Vis spectrophotometer in 10 mm path quartz. An absorbance of 0.103 was determined for the model reaction mixture. The quantum yield (Φ) of the photochemical transformation was measured to be 0.0338. The procedure was repeated a second time to provide a similar value: quantum yield (Φ) at 460 nm of 0.0332.



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F. NMR Spectra

F1. Starting Materials

















S67











S72






















S82























S93















S100


































































-60

-70

-80

-90

-100

-110

-120

-130

-140

ppm





























F3. Acyl Intermediates, TEMPO Trapping and Group Transfer Products












S146



G. UPC² Traces

Conditions: UPC2 (Daicel Chiralpak ID-3 column, 20 °C, gradient CO₂/EtOH from 100% CO₂ to 60:40 over 4 minutes, curve 6, flow rate 3 mL/min, $\lambda = 220$ nm).



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Conditions: UPC2 (Daicel Chiralpak ID-3 column, 20 °C, gradient CO₂/EtOH from 100% CO₂ to 60:40 over 4 minutes, curve 6, flow rate 3 mL/min, $\lambda = 268$ nm).

Conditions: UPC2 (Daicel Chiralpak ID-3 column, 20 °C, gradient CO₂/EtOH from 100% CO₂ to 60:40 over 4 minutes, curve 6, flow rate 3 mL/min, $\lambda = 268$ nm).

