

Metal-Free Acceptorless Dehydrogenative Cross-Coupling of Aldehydes/Alcohols with Alcohols

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I. General Information

Chemicals and solvents were purchased from commercial suppliers and used as received. ^1H NMR, ^{13}C NMR spectra were recorded on a Bruker AV-III400 (400 MHz) spectrometer. ^1H and ^{13}C NMR spectra were recorded in CDCl_3 (δ 7.26, 77.0 ppm) or benzene- d_6 (δ 7.16, 128.0 ppm) with tetramethylsilane (TMS) as the internal standard. Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublet), br s (broad singlet). All high resolution mass spectra (HRMS) were obtained by either ESI mode with the mass analyzer of TOF used or by MALDI-TOF. The Blue LED strips were used in 2 meter, 18 W (maximum Emission at around 470 nm). Further visualization was achieved by staining with DNP.

II. Survey of Reaction Conditions

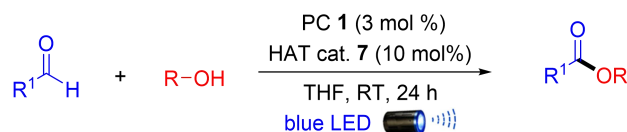
Table S1. Survey of conditions for the acetalization reaction^[a]



Entry	Deviation from the standard conditions	Yield of 74 (%) ^[b]
1	None	93
2	CH_3CN instead of THF	61
3	DCM instead of THF	62
4	DCE instead of THF	82
5	dioxane instead of THF	64
6	PhMe instead of THF	80
7	PC 2 , 3 , 4 instead of PC 1	trace
8	PC 5 instead of PC 1	50
9	HAT cat. 6 instead of 7	46
10	HAT cat. 8 instead of 7	46
11	HAT cat. 10 instead of 7	64
12	HAT cat. 11 or 12 instead of 7	N.D.
13	Without PC, HAT cat. or light	N.D.

[a] Reaction conditions: *para*-methylbenzaldehyde (0.2 mmol), 1-butanol (2 mmol), 4CzIPN (PC **1**, 0.006 mmol), ethyl 2-mercaptopropionate (HAT cat. **7**, 0.02 mmol), THF (2 mL), 18 W blue LED, rt, 24 h. [b] Isolated yield.

III. Typical Procedure for Dehydrogenative Esterification of Aldehydes with Alcohols

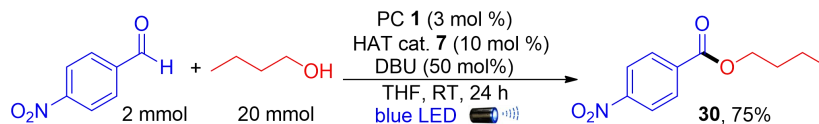


To a 25 mL Schlenk tube equipped with a magnetic stir bar was added the photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol). The Schlenk tube was sealed and degassed via vacuum evacuation and subsequent backfilled with argon for three times. After that anhydrous THF (2 mL), alcohol (2 mmol), aldehyde (0.2 mmol) (for 4-nitrobenzaldehyde, DBU (15 μ L, 0.1 mmol) was added) and ethyl 2-mercaptopropanoate (HAT cat. **7**, 0.02 mmol) were added sequentially by means of syringe. Then the reaction was placed under a blue LED (2 meter strips, 18 W) with an argon balloon and irradiated for 24 h. The solvent was removed on a rotary evaporator under reduced pressure and the crude product was purified by column chromatography isolation on silica gel via gradient elution with hexane / ethyl acetate (40:1-20:1) or by prepared TLC to give the ester product.

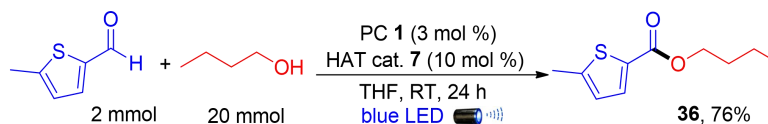
IV. Large Scale Synthesis



To a 50 mL eggplant-shaped reactor equipped with a magnetic stir bar were added the photocatalyst **1** 4CzIPN (47 mg, 0.06 mmol) and 3,4,5-trimethoxybenzaldehyde (392.4 mg, 2 mmol). The reactor was sealed and degassed via vacuum evacuation and subsequent backfilled with argon for three times. After that anhydrous THF (20 mL), 1-butanol (1.83 mL, 20 mmol), and ethyl 2-mercaptopropanoate (HAT cat. **7**, 0.2 mmol) were added sequentially by means of syringe. Then the reaction was placed under a blue LED (2 meter strips, 18 W) with an argon balloon and irradiated for 24 h. The solvent was removed on a rotary evaporator under reduced pressure and the crude product was purified by column chromatography isolation on silica gel via gradient elution with hexane / ethyl acetate (40:1-20:1) or by prepared TLC to give the ester product **21** (386.4 mg) in 72 % yield as a colorless oil.

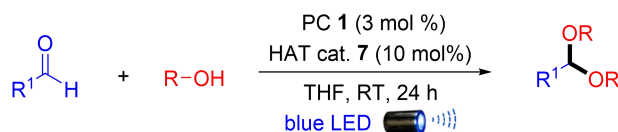


To a 50 mL eggplant-shaped reactor equipped with a magnetic stir bar were added the photocatalyst **1** 4CzIPN (47 mg, 0.06 mmol) and 4-nitrobenzaldehyde (300 mg, 2 mmol). The reactor was sealed and degassed via vacuum evacuation and subsequent backfilled with argon for three times. After that anhydrous THF (20 mL), 1-butanol (1.83 mL, 20 mmol), ethyl 2-mercaptopropanoate (HAT cat. **7**, 0.2 mmol) and DBU (150 μ L, 1 mmol) were added sequentially by means of syringe. Then the reaction was placed under a blue LED (2 meter strips, 18 W) with an argon balloon and irradiated for 24 h. The solvent was removed on a rotary evaporator under reduced pressure and the crude product was purified by column chromatography isolation on silica gel via gradient elution with hexane / ethyl acetate (40:1-20:1) or by prepared TLC to give the ester product **30** (334.8 mg) in 75 % yield as a yellow oil.



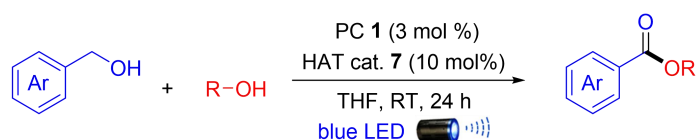
To a 50 mL eggplant-shaped reactor equipped with a magnetic stir bar was added the photocatalyst **1** 4CzIPN (47 mg, 0.06 mmol). The reactor was sealed and degassed via vacuum evacuation and subsequent backfilled with argon for three times. After that anhydrous THF (20 mL), 1-butanol (1.83 mL, 20 mmol), 5-methylthiophene-2-carboxaldehyde (220 μ L, 2 mmol) and ethyl 2-mercaptopropanoate (HAT cat. **7**, 0.2 mmol) were added sequentially by means of syringe. Then the reaction was placed under a blue LED (2 meter strips, 18 W) with an argon balloon and irradiated for 24 h. The solvent was removed on a rotary evaporator under reduced pressure and the crude product was purified by column chromatography isolation on silica gel via gradient elution with hexane / ethyl acetate (40:1-20:1) or by prepared TLC to give the ester product **36** (301.4 mg) in 76 % yield as a colorless oil.

V. Typical Procedure for Acetalization of Aldehydes with Alcohols



To a 25 mL Schlenk tube equipped with a magnetic stir bar was added the photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol). The Schlenk tube was sealed and degassed via vacuum evacuation and subsequent backfilled with argon for three times. After that anhydrous THF (2 mL), alcohol (2 mmol), aldehyde (0.2 mmol) and ethyl 2-mercaptopropanoate (HAT cat. **7**, 0.02 mmol) were added sequentially by means of syringe. Then the reaction was placed under a blue LED (2 meter strips, 18 W) with an argon balloon and irradiated for 24 h. The solvent was removed on a rotary evaporator under reduced pressure and the crude product was purified by column chromatography isolation on silica gel via gradient elution with hexane / ethyl acetate (40:1-20:1) or by prepared TLC to give the acetal product.

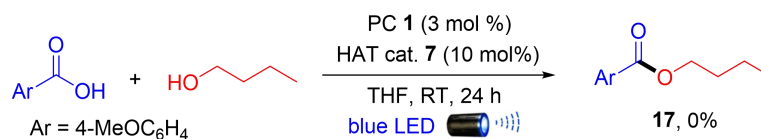
VI. Typical Procedure for Esterification of Two Different Alcohols



To a 25 mL Schlenk tube equipped with a magnetic stir bar was added the photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol). The Schlenk tube was sealed and degassed via vacuum evacuation and subsequent backfilled with argon for three times. After that anhydrous THF (2 mL), alkyl alcohol (2 mmol), benzylic alcohols (0.2 mmol) and ethyl 2-mercaptopropanoate (HAT cat. **7**, 0.02 mmol) were added sequentially by means of syringe. Then the reaction was placed under a blue LED (2 meter strips, 18 W) with an argon balloon and irradiated for 24 h. The solvent was removed on a rotary evaporator under reduced pressure and the crude product was purified by column chromatography isolation on silica gel via gradient elution with hexane/ethyl acetate (40:1-20:1) or by prepared TLC to give the ester product.

VII. Mechanistic Investigations

1) Control experiments



To a 25 mL Schlenk tube equipped with a magnetic stir bar was added the photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol). The Schlenk tube was sealed and degassed via vacuum evacuation and subsequent backfill with argon for three times. After that anhydrous THF (2 mL), 4-methoxybenzoic acid (30 mg, 0.2 mmol), 1-butanol (183 μ L, 2 mmol) and ethyl 2-mercaptopropanoate (HAT cat. **7**, 2.6 μ L, 0.02 mmol) were added sequentially by means of syringe. Then the reaction was placed under a blue LED (2 meter strips, 18 W) with an argon balloon and irradiated for 24 h, and there is no corresponding products were observed according to TLC analysis.



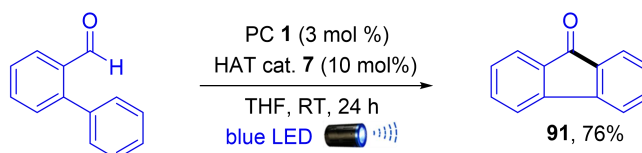
To a 25 mL Schlenk tube equipped with a magnetic stir bar was added the photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol). The Schlenk tube was sealed and degassed via vacuum evacuation and subsequent backfill with argon for three times. After that anhydrous THF (2.0 mL), 4-methoxybenzaldehyde (0.2 mmol), 1-butanol (183 μ L, 2 mmol), TEMPO (0.5 mmol) and ethyl 2-mercaptopropanoate (HAT cat. **7**, 2.6 μ L, 0.02 mmol) were added sequentially by means of syringe. Then the reaction was placed under a blue LED (2 meter strips, 18 W) with an argon balloon and irradiated for 24 h, and there is no corresponding products were observed according to TLC analysis.

2) Trapping the Acyl Radical under the Standard Esterification Conditions with Pyrene-1-carbaldehyde and 1-Butanol

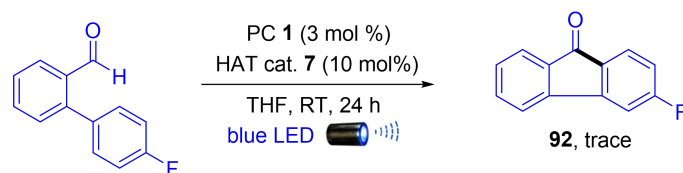


To a 25 mL Schlenk tube equipped with a magnetic stir bar were added the photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol) and pyrene-1-carbaldehyde (46 mg, 0.2 mmol). The Schlenk tube was sealed and degassed via vacuum evacuation and subsequent backfill with argon for three times. After that anhydrous THF (2.0 mL), 1-butanol (183 μ L, 2 mmol) and ethyl 2-mercaptopropanoate (HAT cat. **7**, 2.6 μ L, 0.02 mmol) were added sequentially by means of syringe. Then the reaction was placed under a blue LED (2 meter strips, 18 W) with an argon balloon and irradiated for 24 h. The solvent was removed on a rotary evaporator under reduced pressure and the crude product was purified by column chromatography isolation on silica gel via gradient elution with hexane / ethyl acetate (40:1-20:1) to give the the ester **89** and the dimer **90** in 40% and 33% yields, respectively.

3) Trapping the Acyl Cation with 2-Phenylbenzaldehyde and 2-(4-Fluorophenyl)benzaldehyde



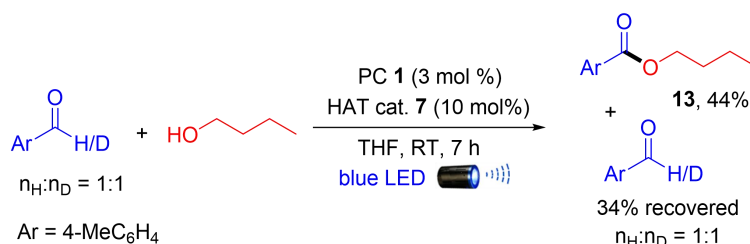
To a 25 mL Schlenk tube equipped with a magnetic stir bar were added the photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol) and 2-phenylbenzaldehyde (36 mg, 0.2 mmol). The Schlenk tube was sealed and degassed via vacuum evacuation and subsequent backfill with argon for three times. After that anhydrous THF (1.5 mL), ethyl 2-mercaptopropanoate (HAT cat. **7**, 2.6 μ L, 0.02 mmol) were added sequentially by means of syringe. Then the reaction was placed under a blue LED (2 meter strips, 18 W) with an argon balloon and irradiated for 24 h. The solvent was removed on a rotary evaporator under reduced pressure and the crude product was purified by column chromatography isolation on silica gel via gradient elution with hexane / ethyl acetate (20:1) to give the 9-fluorenone **91** in 76% yield.



To a 25 mL Schlenk tube equipped with a magnetic stir bar were added the photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol) and 2-(4-fluorophenyl)benzaldehyde (40 mg, 0.2 mmol). The Schlenk tube was sealed and degassed via vacuum evacuation and subsequent backfill with argon for three times. After that anhydrous THF (1.5 mL), ethyl 2-mercaptopropanoate (HAT cat. **7**, 2.6 μ L, 0.02 mmol) were added sequentially by means of syringe. Then the reaction was placed under a blue LED (2 meter strips, 18 W) with an argon balloon and irradiated for 24 h, which led to the formation of 9-fluorenone **92** in only a trace amount.

4) KIE studies

The deuterated *para*-methylbenzaldehyde- d_1 (100%-*D* incorporation) was prepared according to a known method.^[S1]



To a 25 mL Schlenk tube equipped with a magnetic stir bar were added the photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), *para*-methylbenzaldehyde (12 μ L, 0.1 mmol), and *para*-methylbenzaldehyde- d_1 (26 μ L, 0.1 mmol). The Schlenk tube was sealed and degassed via vacuum evacuation and subsequent backfill with argon for three times. After that anhydrous THF (2.0 mL), 1-butanol (2 mmol), and ethyl 2-mercaptopropanoate (HAT cat. **7**, 2.6 μ L, 0.02 mmol) were added sequentially by means of syringe. Then the reaction was placed under a blue LED (2 meter strips, 18 W) with an argon balloon and irradiated for 7 h. The solvent was removed on a rotary evaporator under reduced pressure and the crude product was purified by column chromatography isolation on silica gel via gradient elution with hexane / ethyl acetate (40:1-20:1) to give the recovered *para*-methylbenzaldehyde and the ester product **13** in 34% and 44% yields, respectively. A remained C-H/D ratio was observed in the recovered *para*-methylbenzaldehyde according to ¹H NMR.

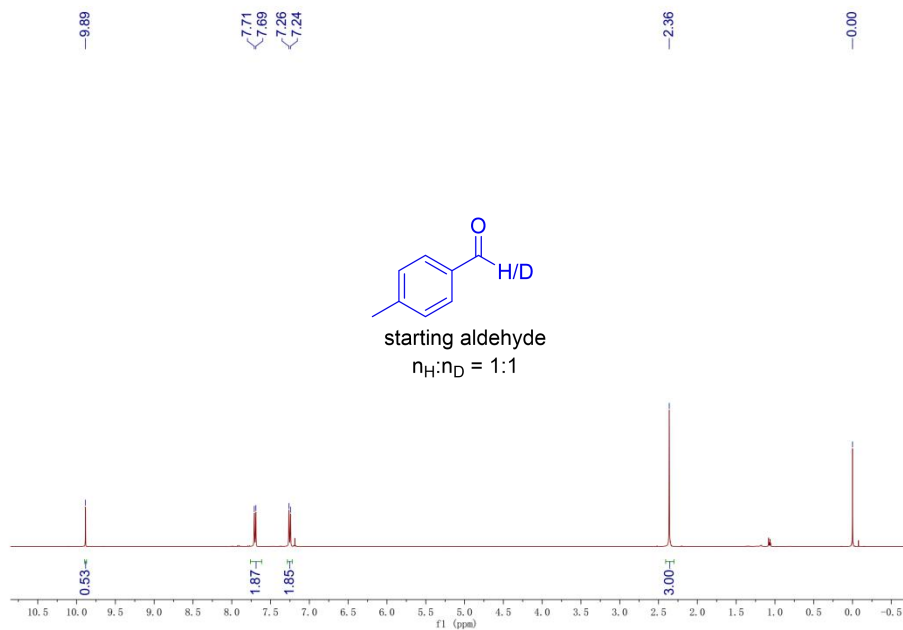


Figure S1. ¹H NMR spectra of the starting aldehyde (n_H:n_D = 1:1)

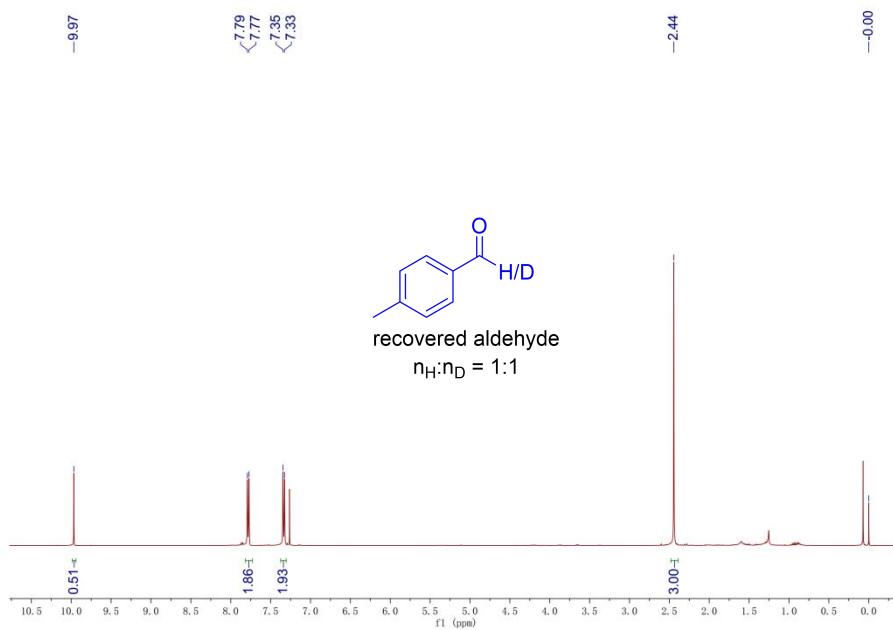
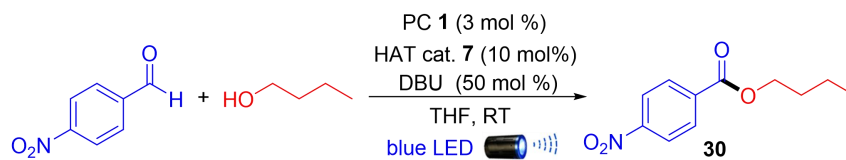


Figure S2. ¹H NMR spectra of the recovered aldehyde (n_H:n_D = 1:1)

5) Light on-off experiments



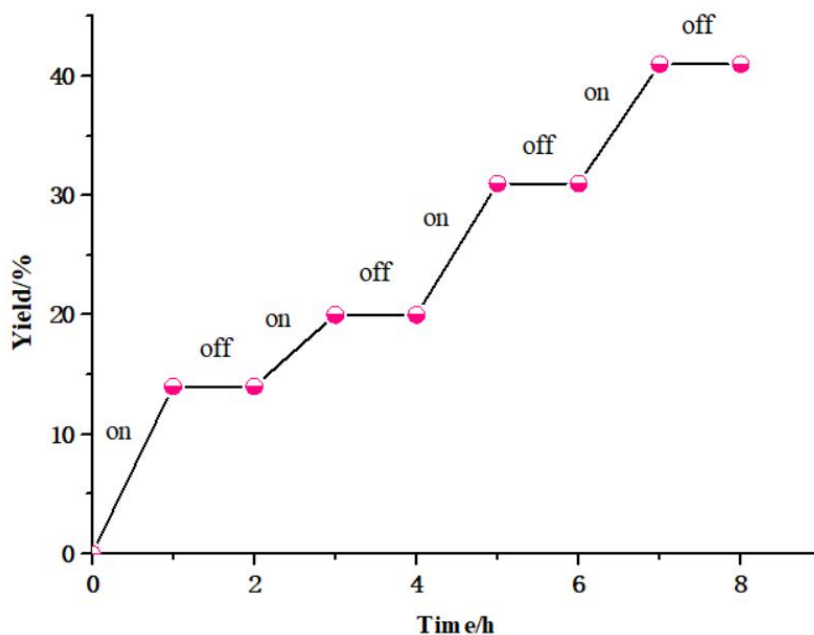


Figure S3. Light on-off experiments for esterification of 4-nitrobenzaldehyde with 1-butanol

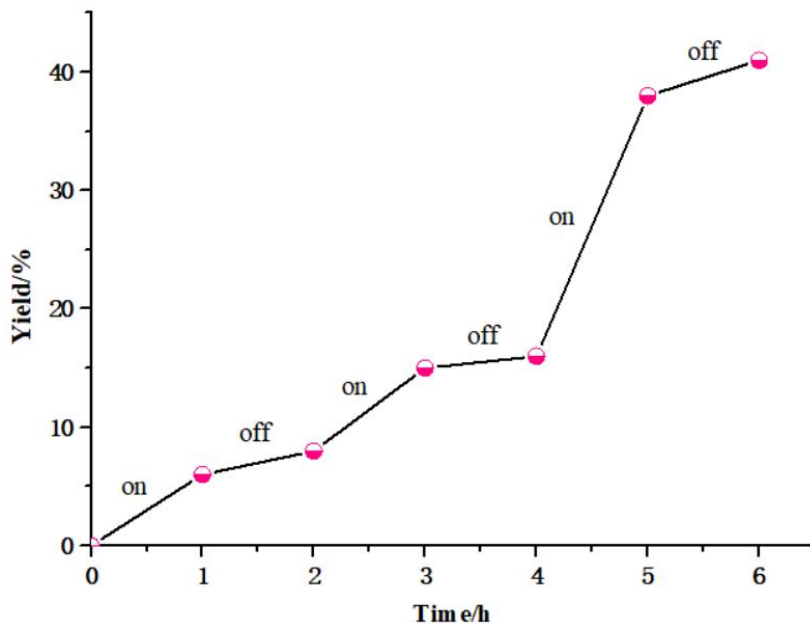


Figure S4. Light on-off experiments for the acetalization of 4-nitrobenzaldehyde with 1-butanol

6) Determination of quantum yields by standard ferrioxalate actinometry

Determination of the light intensity at 470 nm: Following Yoon's procedure,^[S2] the photon flux of the spectrophotometer was determined by standard ferrioxalate actinometry. A 0.15 M solution of ferrioxalate was prepared by dissolving 2.21 g of potassium ferrioxalate hydrate in 30

mL of 0.05 M H₂SO₄. A buffered solution of phenanthroline was prepared by dissolving 50 mg of phenanthroline and 11.25 g of sodium acetate in 50 mL of 0.5 M H₂SO₄. Both solution were stored in the dark. To determine the photon flux of the spectrophotometer, 2.0 mL of the ferrioxalate solution was placed in a cuvette and irradiated for 93.0 second at $\lambda = 470$ nm with an emission slit width at 10.0 nm. After irradiation, 0.35 mL of the phenanthroline solution was added to the cuvette. The solution was then allowed to rest for 1 h to allow the ferrous ions to completely coordinate to the phenanthroline. The absorbance of the solution was measured at 510 nm. A non-irradiated sample was also prepared and the absorbance at 510 nm measured. Conversion was calculated using eq (1).

$$\text{molFe}^{2+} = \frac{V \cdot \Delta A}{l \varepsilon} \quad (1)$$

Where V is the total volume (0.00235 L) of the solution after of phenanthroline, ΔA is the difference in absorbance at 510 nm between the irradiated and non-irradiated solution, l is the path length (1.000 cm), and ε is the molar absorptivity at 510 nm (11,100 L mol⁻¹ cm⁻¹). The photon flux can be calculated using eq (2).

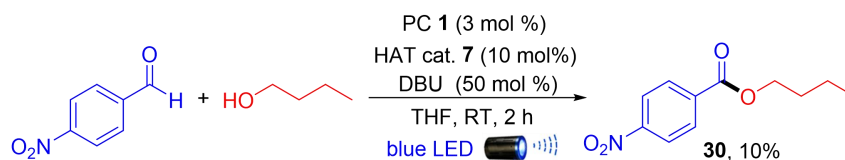
$$\text{Photo flux} = \frac{\text{mol Fe}^{2+}}{\Phi t f} \quad (2)$$

Where Φ is the quantum yield for the ferrioxalate actinometer (0.92 for a 0.15 M solution at $\lambda = 468$ nm), t is the time (93.0 s), and f is the fraction of light absorbed at $\lambda = 470$ nm (0.648, vide infra). The photo flux was calculated (average of three experiments) to be 4.3952×10^{-9} einstein⁻¹.

$$\text{molFe}^{2+} = \frac{0.00235 \text{ L} \cdot 1.151}{1.000 \text{ cm} \cdot 11100 \text{ L mol}^{-1} \text{ cm}^{-1}} = 2.4368 \times 10^{-7} \text{ mol}$$

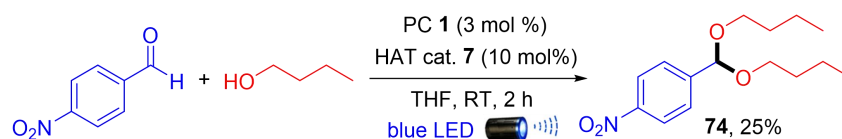
$$\text{Photo flux} = \frac{2.4368 \times 10^{-7}}{0.92 \cdot 93.0 \text{ s} \cdot 0.648} = 4.3952 \times 10^{-9} \text{ mol}$$

Determination of quantum yield:



A cuvette was charged with the photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol) and the 4-nitrobenzaldehyde (30 mg, 0.2mmol). The cuvette was sealed with plastic wrap, a balloon containing argon gas was inserted into the cuvette for about ten minutes to ensure that the cuvette

was filled with argon. After that acetonitrile- d_3 (2.0 mL), 1-butanol (183 μ L, 2 mmol), DBU (15 μ L, 0.1 mmol), and ethyl 2-mercaptopropanoate (HAT cat. **7**, 2.6 μ L, 0.02 mmol) were added sequentially by means of syringe. The cuvette was then capped with a PTFE stopper. Then the reaction was placed under a blue LED (2 meter strips, 18 W) with an argon balloon and irradiated for 7200 s (2 h). After that, and the yield of product **30** was determined as 10% by crude ^1H NMR analysis using 1,3,5-trimethoxybenzene as a internal standard. The quantum yield was determined using eq (3). Essentially all incident light ($f > 0.999$, vide infra) is absorbed by the 4CzIPN at the reaction conditions described above.



A cuvette was charged with the photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol) and the 4-nitrobenzaldehyde (30 mg, 0.2mmol). The cuvette was sealed with plastic wrap, a balloon containing argon gas was inserted into the cuvette for about ten minutes to ensure that the cuvette was filled with argon. After that acetonitrile- d_3 (2.0 mL), 1-butanol (183 μ L, 2 mmol), and ethyl 2-mercaptopropanoate (HAT cat. **7**, 2.6 μ L, 0.02 mmol) were added sequentially by means of syringe. The cuvette was then capped with a PTFE stopper. Then the reaction was placed under a blue LED (2 meter strips, 18 W) with an argon balloon and irradiated for 7200 s (2 h). After that, and the yield of product **74** was determined as 25% by crude ^1H NMR analysis using 1,3,5-trimethoxybenzene as a internal standard. The quantum yield was determined using eq (3). Essentially all incident light ($f > 0.999$, vide infra) is absorbed by the 4CzIPN at the reaction conditions described above.

$$\Phi = \frac{\text{mol product}}{\text{flu } t f} \quad (3)$$

$$\Phi_1 = \frac{2.0 \times 10^{-5} \text{ mol}}{4.3952 \times 10^{-9} \text{ einstein s} \cdot 8280 \text{ s} \cdot 1.00} = 0.63$$

$$\Phi_2 = \frac{5.0 \times 10^{-5} \text{ mol}}{4.3952 \times 10^{-9} \text{ einstein s} \cdot 8280 \text{ s} \cdot 1.00} = 1.58$$

7) Stern-Volmer fluorescence quenching experiments

In a typical experiment, a solution of photocatalyst **1** 4CzIPN in anhydrous THF (1.25×10^{-4} M) was added with an appropriate amount of quencher in a quartz cuvette. Then the

emission of the sample was collected. The emission intensity at 554 nm was collected with excited wavelength of 465 nm.

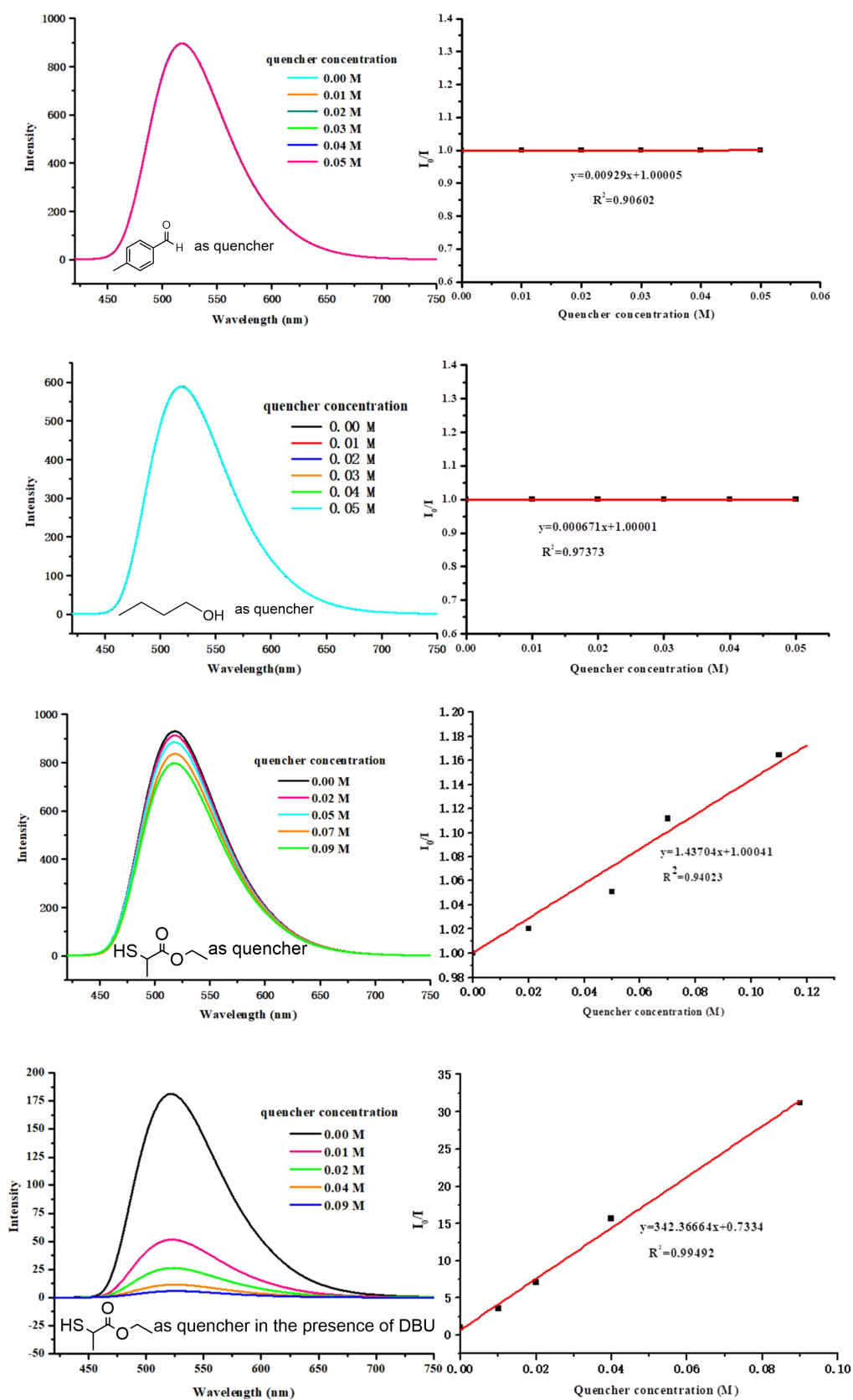
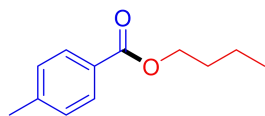


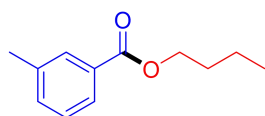
Figure S5. Stern-Volmer fluorescence quenching studies

VIII. Analytical Data of the Products



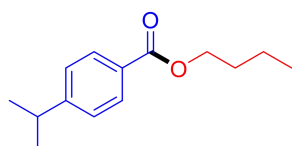
13; A known compound and the characterization data are in accordance with the literature.^[S3]

Following the typical procedure **III**, *p*-tolualdehyde (24 μ L, 0.2 mmol), 1-butanol (183 μ L, 2 mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (2.6 μ L, 0.02 mmol) in THF (2 mL) were employed to give the product **13** (35 mg) in 90 % yield as a colorless oil. ¹H NMR (400 MHz, C₆D₆) δ 7.86 (d, J = 8.2 Hz, 2H), 6.61 (d, J = 7.9 Hz, 2H), 3.90 (t, J = 6.6 Hz, 2H), 1.68 (s, 3H), 1.22 – 1.14 (m, 2H), 0.93 (dq, J = 14.7, 7.4 Hz, 2H), 0.47 (t, J = 7.4 Hz, 3H) ppm; ¹³C NMR (101 MHz, C₆D₆) δ 166.4, 143.23, 130.0, 129.3, 128.7, 64.6, 31.1, 21.3, 19.5, 13.8 ppm.



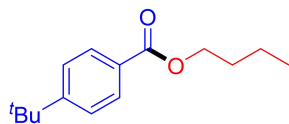
14; A known compound and the characterization data are in accordance with the literature.^[S4]

Following the typical procedure **III**, 3-methylbenzaldehyde (24 μ L, 0.2 mmol), 1-butanol (183 μ L, 2 mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (2.6 μ L, 0.02 mmol) in THF (2 mL) were employed to give the product **14** (32 mg) in 84 % yield as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.84 (d, J = 8.6 Hz, 2H), 7.34 (dt, J = 14.8, 7.5 Hz, 2H), 4.32 (t, J = 6.6 Hz, 2H), 2.40 (s, 3H), 1.76 (dt, J = 14.6, 6.7 Hz, 2H), 1.48 (dq, J = 14.7, 7.4 Hz, 2H), 0.98 (t, J = 7.4 Hz, 3H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 166.9, 138.1, 133.5, 130.4, 130.0, 128.2, 126.6, 64.8, 30.8, 21.3, 19.3, 13.8 ppm.

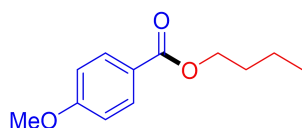


15; Following the typical procedure **III**, 4-isopropylbenzaldehyde (30 μ L, 0.2 mmol), 1-butanol (183 μ L, 2 mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (2.6 μ L, 0.02 mmol) in THF (2 mL) were employed to give the product **15** (27 mg) in 61 % yield as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.97 (d, J = 8.0 Hz, 2H), 7.29 (d, J = 7.9 Hz, 2H), 4.31 (t, J = 6.5 Hz, 2H), 2.96 (dt, J = 13.7, 6.9 Hz, 1H), 1.80 – 1.69 (m, 2H), 1.51 – 1.42 (m, 2H),

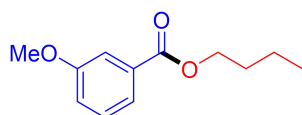
1.27 (d, $J = 6.9$ Hz, 6H), 0.98 (t, $J = 7.4$ Hz, 3H) ppm; ^{13}C NMR (101 MHz, CDCl_3) δ 166.8, 154.2, 129.7, 128.1, 126.4, 64.6, 34.2, 30.8, 23.7, 19.3, 13.8 ppm. HRMS: calcd. for $\text{C}_{14}\text{H}_{20}\text{O}_2$ $[\text{M}+\text{H}]^+$: 221.1536; found: 221.1536.



16; Following the typical procedure **III**, 4-*tert*-butylbenzaldehyde (34 μL , 0.2 mmol), 1-butanol (183 μL , 2 mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (2.6 μL , 0.02 mmol) in THF (2 mL) were employed to give the product **16** (33 mg) in 70 % yield as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.90 (d, $J = 8.4$ Hz, 2H), 7.37 (d, $J = 8.5$ Hz, 2H), 4.23 (t, $J = 6.6$ Hz, 2H), 1.66 (tt, $J = 11.4, 5.8$ Hz, 2H), 1.40 (dd, $J = 15.0, 7.5$ Hz, 2H), 1.26 (s, 9H), 0.90 (t, $J = 7.4$ Hz, 3H) ppm; ^{13}C NMR (101 MHz, CDCl_3) δ 166.7, 156.4, 129.4, 127.7, 125.2, 64.6, 35.0, 31.1, 30.8, 19.3, 13.7 ppm. HRMS: calcd. for $\text{C}_{15}\text{H}_{22}\text{O}_2$ $[\text{M}+\text{H}]^+$: 235.1693; found: 235.1693.

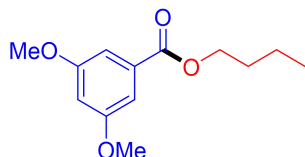


17; A known compound and the characterization data are in accordance with the literature.^[S5] Following the typical procedure **III**, 4-methoxybenzaldehyde (25 μL , 0.2 mmol), 1-butanol (183 μL , 2 mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (2.6 μL , 0.02 mmol) in THF (2 mL) were employed to give the product **17** (35 mg) in 84 % yield as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 8.04 – 7.96 (m, 2H), 6.96 – 6.87 (m, 2H), 4.29 (t, $J = 6.6$ Hz, 2H), 3.86 (s, 3H), 1.74 (dt, $J = 14.5, 6.6$ Hz, 2H), 1.53 – 1.41 (m, 2H), 0.98 (t, $J = 7.4$ Hz, 3H) ppm; ^{13}C NMR (101 MHz, CDCl_3) δ 166.5, 163.2, 131.5, 122.9, 113.5, 64.5, 55.4, 30.8, 19.3, 13.8 ppm.

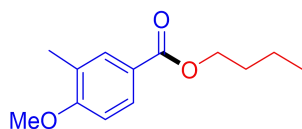


18; A known compound and the characterization data are in accordance with the literature.^[S6] Following the typical procedure **III**, 3-methoxybenzaldehyde (29 μL , 0.2 mmol), 1-butanol (183 μL , 2 mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (2.6 μL , 0.02 mmol) in THF (2 mL) were employed to give the product **18** (37 mg) in 90 % yield as a

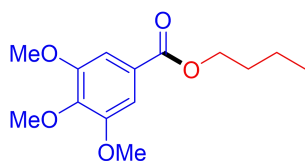
colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.64 (d, $J = 7.7$ Hz, 1H), 7.56 (dd, $J = 7.5, 6.0$ Hz, 1H), 7.34 (dd, $J = 10.2, 5.7$ Hz, 1H), 7.09 (dd, $J = 8.2, 2.6$ Hz, 1H), 4.32 (t, $J = 6.6$ Hz, 2H), 3.85 (s, 3H), 1.80 – 1.68 (m, 2H), 1.48 (dq, $J = 14.7, 7.4$ Hz, 2H), 0.98 (t, $J = 7.4$ Hz, 3H) ppm; ^{13}C NMR (101 MHz, CDCl_3) δ 166.5, 159.5, 131.8, 129.3, 121.9, 119.2, 114.0, 64.9, 55.4, 30.7, 19.2, 13.7 ppm.



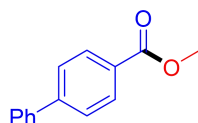
19; A known compound and the characterization data are in accordance with the literature.^[S7] Following the typical procedure **III**, 3, 5-dimethoxybenzaldehyde (30 μL , 0.2 mmol), 1-butanol (183 μL , 2 mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (2.6 μL , 0.02 mmol) in THF (2 mL) were employed to give the product **19** (43 mg) in 90 % yield as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.19 (d, $J = 2.3$ Hz, 2H), 6.64 (t, $J = 2.3$ Hz, 1H), 4.31 (t, $J = 6.6$ Hz, 2H), 3.83 (s, 6H), 1.75 (dt, $J = 14.6, 6.7$ Hz, 2H), 1.47 (dd, $J = 15.2, 7.4$ Hz, 2H), 0.98 (t, $J = 7.4$ Hz, 3H) ppm; ^{13}C NMR (101 MHz, CDCl_3) δ 166.4, 160.6, 132.4, 107.1, 105.4, 65.0, 55.5, 30.7, 19.2, 13.7 ppm.



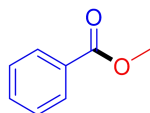
20; Following the typical procedure **III**, 3-methyl-4-anisaldehyde (28 μL , 0.2 mmol), 1-butanol (183 μL , 2 mmol), photocatalyst **1** 4CzIPN (4.7mg, 0.006mmol), and ethyl 2-mercaptopropionate (2.6 μL , 0.02 mmol) in THF (2 mL) were employed to give the product **20** (40 mg) in 89 % yield as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.56 (dd, $J = 7.7, 1.3$ Hz, 1H), 7.48 (s, 1H), 7.17 (d, $J = 7.7$ Hz, 1H), 4.31 (t, $J = 6.6$ Hz, 2H), 3.88 (s, 3H), 2.26 (s, 3H), 1.81 – 1.70 (m, 2H), 1.53 – 1.41 (m, 2H), 1.04 – 0.94 (m, 3H) ppm; ^{13}C NMR (101 MHz, CDCl_3) δ 166.8, 157.5, 132.3, 130.3, 129.2, 121.8, 110.4, 64.7, 55.4, 30.8, 19.3, 16.5, 13.8 ppm. HRMS: calc. for $\text{C}_{13}\text{H}_{18}\text{O}_3$ $[\text{M}+\text{H}]^+$: 223.1329; found: 223.1329.



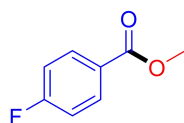
21; Following the typical procedure **III**, 3,4,5-trimethoxybenzaldehyde (40 mg, 0.2 mmol), 1-butanol (183 μ L, 2 mmol), photocatalyst **1** 4CzIPN (4.7mg, 0.006mmol), and ethyl 2-mercaptopropionate (2.6 μ L, 0.02 mmol) in THF (2 mL) were employed to give the product **21** (48 mg) in 90 % yield as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.31 (s, 2H), 4.32 (t, J = 6.7 Hz, 2H), 3.93 (dd, J = 12.5, 2.9 Hz, 9H), 1.76 (dt, J = 14.6, 6.8 Hz, 2H), 1.48 (dt, J = 14.9, 7.4 Hz, 2H), 0.99 (t, J = 7.4 Hz, 3H) ppm; ^{13}C NMR (101 MHz, CDCl_3) δ 166.2, 152.8, 142.0, 125.5, 106.7, 65.0, 60.8, 56.1, 30.7, 19.2, 13.7 ppm. HRMS: calc. for $\text{C}_{14}\text{H}_{20}\text{O}_5$ $[\text{M}+\text{H}]^+$: 269.1384; found: 269.1384.



22; A known compound and the characterization data are in accordance with the literature.^[S8] Following the typical procedure **III**, 4-phenylbenzaldehyde (36 mg, 0.2 mmol), methanol (162 μ L, 4 mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (2.6 μ L, 0.02 mmol) in THF (2 mL) were employed to give the product **22** (32 mg) in 75 % yield as a white powder. ^1H NMR (400 MHz, CDCl_3) δ 8.02 (d, J = 8.4 Hz, 2H), 7.61 – 7.51 (m, 4H), 7.38 (t, J = 7.4 Hz, 2H), 7.30 (t, J = 7.3 Hz, 1H), 3.85 (s, 3H) ppm; ^{13}C NMR (101 MHz, CDCl_3) δ 167.0, 145.6, 139.9, 130.1, 128.9, 128.8, 128.1, 127.2, 127.0, 52.1 ppm.

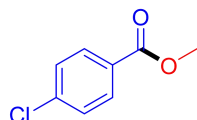


23; A known compound and the characterization data are in accordance with the literature.^[S9] Following the typical procedure **III**, benzaldehyde (20 μ L, 0.2 mmol), methanol (162 μ L, 4 mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (2.6 μ L, 0.02 mmol) in THF (2 mL) were employed to give the product **23** (16 mg) in 60 % yield as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 8.03 (dd, J = 5.2, 3.3 Hz, 2H), 7.52 (ddd, J = 8.6, 2.5, 1.2 Hz, 1H), 7.40 (dd, J = 10.5, 4.7 Hz, 2H), 3.88 (s, 3H) ppm; ^{13}C NMR (101 MHz, CDCl_3) δ 166.8, 132.7, 130.0, 129.3, 128.1, 51.8 ppm.



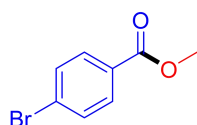
24; A known compound and the characterization data are in accordance with the literature.^[S10] Following the typical procedure **III**, *p*-fluorobenzaldehyde (22 μ L, 0.2 mmol), methanol (162 μ L,

4 mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (2.6 μ L, 0.02 mmol) in THF (2 mL) were employed to give the product **24** (20 mg) in 65 % yield as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 8.09 – 7.94 (m, 2H), 7.16 – 7.00 (m, 2H), 3.89 (s, 3H) ppm; ^{13}C NMR (101 MHz, CDCl_3) δ 165.8, 165.5 (d, $J = 253.7$ Hz), 131.9 (d, $J = 9.3$ Hz), 126.2 (d, $J = 3.0$ Hz), 115.2 (d, $J = 22.0$ Hz), 51.89 ppm.



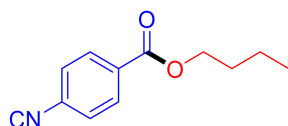
25; A known compound and the characterization data are in accordance with the literature.^[S9]

Following the typical procedure **III**, 4-chlorobenzaldehyde (24 μ L, 0.2 mmol), methanol (162 μ L, 4 mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (2.6 μ L, 0.02 mmol) in THF (2 mL) were employed to give the product **25** (19 mg) in 55 % yield as a white powder. ^1H NMR (400 MHz, CDCl_3) δ 7.97 (d, $J = 8.5$ Hz, 2H), 7.41 (d, $J = 8.5$ Hz, 2H), 3.91 (s, 3H) ppm; ^{13}C NMR (101 MHz, CDCl_3) δ 166.2, 139.3, 130.9, 128.7, 128.5, 52.2 ppm.



26; A known compound and the characterization data are in accordance with the literature.^[S9]

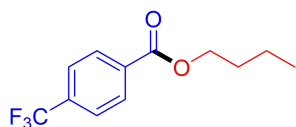
Following the typical procedure **III**, 4-bromobenzaldehyde (37mg, 0.2 mmol), methanol (162 μ L, 4 mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (2.6 μ L, 0.02 mmol) in THF (2 mL) were employed to give the product **26** (30 mg) in 70% yield as a white powder. ^1H NMR (400 MHz, CDCl_3) δ 7.94 – 7.82 (m, 2H), 7.64 – 7.47 (m, 2H), 3.91 (s, 3H) ppm; ^{13}C NMR (101 MHz, CDCl_3) δ 166.3, 131.7, 131.1, 129.0, 128.0, 52.3 ppm.



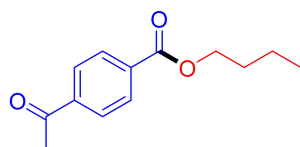
27; A known compound and the characterization data are in accordance with the literature.^[S11]

Following the typical procedure **III**, 4-cyanobenzaldehyde (26 mg, 0.2 mmol), 1-butanol (183 μ L, 2 mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (2.6 μ L, 0.02 mmol) in THF (2 mL) were employed to give the product **27** (30 mg) in 74 % yield as a white powder. ^1H NMR (400 MHz, CDCl_3) δ 8.14 (d, $J = 8.4$ Hz, 2H), 7.75 (d, $J = 8.4$ Hz, 2H), 4.36 (t, $J = 6.6$ Hz, 2H), 1.84 – 1.71 (m, 2H), 1.48 (dq, $J = 14.7, 7.4$ Hz, 2H), 0.99 (t, $J = 7.4$ Hz,

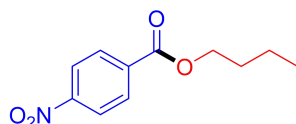
3H) ppm; ^{13}C NMR (101 MHz, CDCl_3) δ 165.0, 134.3, 132.2, 130.0, 118.0, 116.3, 65.7, 30.6, 19.2, 13.7 ppm.



28; A known compound and the characterization data are in accordance with the literature.^[S6] Following the typical procedure **III**, 4-(trifluoromethyl)Benzaldehyde (35 mg, 0.2 mmol), 1-butanol (183 μL , 2 mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (2.6 μL , 0.02 mmol) in THF (2 mL) were employed to give the product **28** (30 mg) in 61 % yield as a white powder. ^1H NMR (400 MHz, CDCl_3) δ 8.14 (dd, $J = 13.5, 8.2$ Hz, 2H), 7.81 (d, $J = 8.2$ Hz, 1H), 7.70 (d, $J = 8.2$ Hz, 1H), 4.36 (t, $J = 6.6$ Hz, 2H), 1.86 – 1.72 (m, 2H), 1.57 – 1.43 (m, 2H), 1.06 – 0.93 (m, 3H) ppm; ^{13}C NMR (101 MHz, CDCl_3) δ 165.4, 134.3 (q, $J = 32.6$ Hz), 130.3, 129.9, 125.3 (q, $J = 3.7$ Hz), 123.6 (d, $J = 272.7$ Hz), 65.4, 30.7, 19.2, 13.7 ppm.

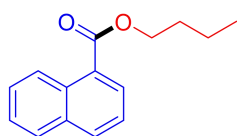


29; A known compound and the characterization data are in accordance with the literature.^[S12] Following the typical procedure **III**, 4-acetylbenzaldehyde (30 mg, 0.2 mmol), 1-butanol (183 μL , 2 mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (2.6 μL , 0.02 mmol) in THF (2 mL) were employed to give the product **29** (29 mg) in 66 % yield as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 8.17 – 8.09 (m, 2H), 8.04 – 7.97 (m, 2H), 4.36 (t, $J = 6.6$ Hz, 2H), 2.65 (s, 3H), 1.78 (dt, $J = 14.5, 6.7$ Hz, 2H), 1.48 (dt, $J = 14.8, 7.4$ Hz, 2H), 0.99 (t, $J = 7.4$ Hz, 3H) ppm; ^{13}C NMR (101 MHz, CDCl_3) δ 197.6, 165.8, 140.1, 134.3, 129.8, 128.2, 65.3, 30.7, 26.9, 19.2, 13.7 ppm.

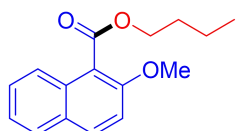


30; A known compound and the characterization data are in accordance with the literature.^[S13] Following the typical procedure **III**, 4-nitrobenzaldehyde (30 mg, 0.2 mmol), 1-butanol (183 μL , 2 mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), ethyl 2-mercaptopropionate (2.6 μL ,

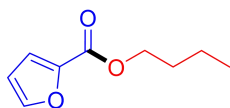
0.02 mmol), and DBU (15 μ L, 0.1 mmol) in THF (2 mL) were employed to give the product **30** (37 mg) in 83 % yield as a yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 8.22 (d, $J = 8.9$ Hz, 2H), 8.14 (d, $J = 8.9$ Hz, 2H), 4.31 (t, $J = 6.6$ Hz, 2H), 1.77 – 1.62 (m, 2H), 1.41 (tt, $J = 12.6, 6.4$ Hz, 2H), 0.92 (t, $J = 7.4$ Hz, 3H) ppm; ^{13}C NMR (101 MHz, CDCl_3) δ 164.7, 150.4, 135.8, 130.6, 123.5, 65.8, 30.6, 19.2, 13.7 ppm.



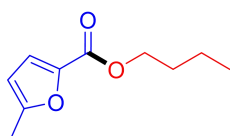
31; A known compound and the characterization data are in accordance with the literature.^[S14] Following the typical procedure **III**, 1-naphthaldehyde (31 mg, 0.2 mmol), 1-butanol (183 μ L, 2 mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (2.6 μ L, 0.02 mmol) in THF (2 mL) were employed to give the product **31** (40 mg) in 88 % yield as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 8.60 (s, 1H), 8.07 (dd, $J = 8.6, 1.7$ Hz, 1H), 7.96 (d, $J = 8.0$ Hz, 1H), 7.88 (d, $J = 8.6$ Hz, 2H), 7.56 (dtd, $J = 14.7, 6.9, 1.3$ Hz, 2H), 4.39 (t, $J = 6.6$ Hz, 2H), 1.81 (dt, $J = 14.6, 6.7$ Hz, 2H), 1.58 – 1.47 (m, 2H), 1.01 (t, $J = 7.4$ Hz, 3H) ppm; ^{13}C NMR (101 MHz, CDCl_3) δ 166.8, 135.5, 132.5, 130.9, 129.3, 128.2, 128.1, 127.7, 126.6, 125.2, 65.0, 30.8, 19.3, 13.8 ppm.



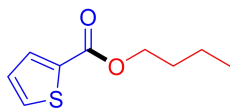
32; Following the typical procedure **III**, 2-methoxy-1-naphthaldehyde (37 mg, 0.2 mmol), 1-butanol (183 μ L, 2mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006mmol), and ethyl 2-mercaptopropionate (2.6 μ L, 0.02 mmol) in THF (2 mL) were employed to give the product **32** (31 mg) in 60 % yield as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.90 (d, $J = 9.1$ Hz, 1H), 7.77 (dd, $J = 18.5, 8.4$ Hz, 2H), 7.49 (t, $J = 7.6$ Hz, 1H), 7.37 (t, $J = 7.5$ Hz, 1H), 7.28 (t, $J = 6.8$ Hz, 1H), 4.47 (t, $J = 6.7$ Hz, 2H), 3.97 (s, 3H), 1.85 – 1.73 (m, 2H), 1.53 – 1.47 (m, 2H), 0.99 (t, $J = 7.4$ Hz, 3H) ppm; ^{13}C NMR (101 MHz, CDCl_3) δ 168.2, 154.3, 131.5, 131.0, 128.5, 128.1, 127.5, 124.1, 123.7, 113.2, 65.3, 56.7, 30.8, 19.2, 13.7 ppm. HRMS calcd for $\text{C}_{16}\text{H}_{18}\text{O}_3$: $[\text{M}+\text{Na}]^+$ 281.1148, found: 281.1148.



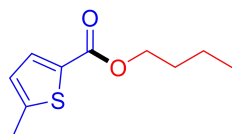
33; A known compound and the characterization data are in accordance with the literature.^[S14] Following the typical procedure **III**, 2-furaldehyde (17 μ L, 0.2 mmol), 1-butanol (183 μ L, 2 mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (2.6 μ L, 0.02 mmol) in THF (2 mL) were employed to give the product **33** (28 mg) in 84% yield as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 6.31 (d, J = 3.2 Hz, 1H), 6.25 (dd, J = 3.0, 1.8 Hz, 1H), 5.44 (s, 1H), 3.49 – 3.41 (m, 2H), 1.53 – 1.47 (m, 2H), 1.35 – 1.29 (m, 2H), 0.85 – 0.81 (m, 3H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 151.8, 142.1, 109.8, 107.8, 96.4, 65.2, 31.6, 19.2, 13.7 ppm.



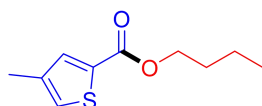
34; Following the typical procedure **III**, 5-methylfurfural (20 μ L, 0.2 mmol), 1-butanol (183 μ L, 2 mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (2.6 μ L, 0.02 mmol) in THF (2 mL) were employed to give the product **34** (29 mg) in 80 % yield as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.07 (d, J = 2.7 Hz, 1H), 6.11 (d, J = 1.4 Hz, 1H), 4.40 – 4.23 (m, 2H), 2.46 – 2.31 (m, 3H), 1.79 – 1.65 (m, 2H), 1.43 (dt, J = 12.1, 6.2 Hz, 2H), 0.96 (dd, J = 8.6, 7.6 Hz, 3H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 159.0, 157.1, 143.2, 119.1, 108.3, 64.5, 30.8, 19.1, 14.0, 13.7 ppm. HRMS calcd for C₁₀H₁₄O₃ [M+H]⁺: 183.1016, found: 183.1016.



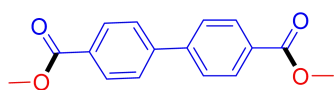
35; A known compound and the characterization data are in accordance with the literature.^[S5] Following the typical procedure **III**, (18 μ L, 0.2 mmol), 1-butanol (183 μ L, 2 mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (2.6 μ L, 0.02 mmol) in THF (2 mL) were employed to give the product **35** (31 mg) in 84 % yield as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.88 – 7.75 (m, 1H), 7.58 – 7.49 (m, 1H), 7.14 – 7.00 (m, 1H), 4.30 (t, J = 6.6 Hz, 2H), 1.72 (dq, J = 13.0, 6.6 Hz, 2H), 1.46 (dq, J = 14.6, 7.4 Hz, 2H), 0.97 (t, J = 7.4 Hz, 3H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 162.3, 134.1, 133.2, 132.1, 127.7, 65.0, 30.7, 19.2, 13.7 ppm.



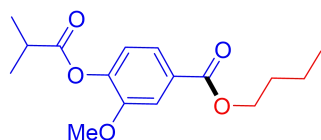
36; Following the typical procedure **III**, 5-methylthiophene-2-carboxaldehyde (22 μ L, 0.2 mmol), 1-butanol (183 μ L, 2 mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (2.6 μ L, 0.02 mmol) in THF (2 mL) were employed to give the product **36** (36 mg) in 90 % yield as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.59 (d, J = 1.2 Hz, 1H), 7.12 (s, 1H), 4.28 (t, J = 6.6 Hz, 2H), 2.27 (s, 3H), 1.72 (dt, J = 14.5, 6.7 Hz, 2H), 1.45 (dt, J = 10.0, 5.1 Hz, 2H), 0.97 (t, J = 7.4 Hz, 3H) ppm; ^{13}C NMR (101 MHz, CDCl_3) δ 182.9, 162.4, 138.3, 135.0, 127.8, 64.8, 30.7, 19.1, 15.5, 13.7 ppm. HRMS: $\text{C}_{10}\text{H}_{14}\text{O}_2\text{S}$ $[\text{M}+\text{H}]^+$, Calc. for: 199.0787; Found: 199.0787.



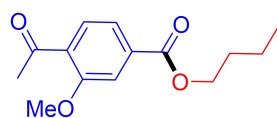
37; A known compound and the characterization data are in accordance with the literature.^[S15] Following the typical procedure **III**, 4-methylthiophene-2-carbaldehyde (25 μ L, 0.2 mmol), 1-butanol (183 μ L, 2 mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (2.6 μ L, 0.02 mmol) in THF (2 mL) were employed to give the product **37** (35 mg) in 89 % yield as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.60 (t, J = 3.8 Hz, 1H), 6.76 (d, J = 3.6 Hz, 1H), 4.27 (t, J = 6.6 Hz, 2H), 2.52 (s, 3H), 1.77 – 1.66 (m, 2H), 1.44 (dt, J = 14.8, 7.6 Hz, 2H), 0.97 (t, J = 7.4 Hz, 3H) ppm; ^{13}C NMR (101 MHz, CDCl_3) δ 182.6, 162.4, 147.7, 133.6, 126.3, 64.7, 30.8, 19.2, 15.7, 13.7 ppm.



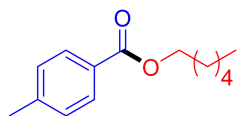
38; A known compound and the characterization data are in accordance with the literature.^[S9] Following the typical procedure **III**, 4,4'-biphenyldicarboxaldehyde (42 mg, 0.2 mmol), 1-butanol (183 μ L, 2 mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (2.6 μ L, 0.02 mmol) in THF (2 mL) were employed to give the product **38** (43 mg) in 80 % yield as a white powder. ^1H NMR (400 MHz, CDCl_3) δ 8.09 – 8.01 (m, 4H), 7.66 – 7.58 (m, 4H), 3.88 (s, 6H) ppm; ^{13}C NMR (101 MHz, CDCl_3) δ 166.8, 144.3, 130.2, 130.0, 127.2, 52.2 ppm.



39; Following the typical procedure **III**, vanillin isobutyrate (39 μL , 0.2 mmol), 1-butanol (183 μL , 2mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (2.6 μL , 0.02 mmol) in THF (2 mL) were employed to give the product **39** (47 mg) in 80 % yield as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.58 (d, $J = 10.2$ Hz, 2H), 7.00 (dd, $J = 7.8, 3.0$ Hz, 1H), 4.35 – 4.16 (m, 2H), 3.79 (d, $J = 2.9$ Hz, 3H), 2.87 – 2.67 (m, 1H), 1.75 – 1.62 (m, 2H), 1.40 (d, $J = 5.7$ Hz, 2H), 1.32 – 1.17 (m, 6H), 0.96 – 0.84 (m, 3H) ppm; ^{13}C NMR (101 MHz, CDCl_3) δ 174.7, 166.0, 151.1, 143.8, 129.0, 122.6, 122.5, 113.4, 65.01, 56.0, 34.0, 30.7, 19.2, 18.9, 13.7 ppm. HRMS: $\text{C}_{16}\text{H}_{22}\text{O}_5$ $[\text{M}+\text{H}]^+$, Calcd for: 295.1540; Found: 295.1540.

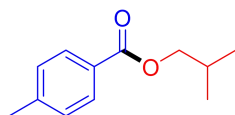


40; Following the typical procedure **III**, vanillin acetate (39 mg, 0.2 mmol), 1-butanol (183 μL , 2mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (2.6 μL , 0.02 mmol) in THF (2 mL) were employed to give the product **40** (45 mg) in 85 % yield as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.64 – 7.54 (m, 2H), 7.07 – 6.96 (m, 1H), 4.31 – 4.17 (m, 2H), 3.89 – 3.70 (m, 3H), 2.33 – 2.16 (m, 3H), 1.73 – 1.61 (m, 2H), 1.46 – 1.31 (m, 2H), 0.96 – 0.81 (m, 3H) ppm; ^{13}C NMR (101 MHz, CDCl_3) δ 168.5, 166.0, 151.0, 143.4, 129.2, 122.7, 122.5, 113.3, 65.0, 56.0, 30.7, 20.6, 19.2, 13.7 ppm. HRMS: $\text{C}_{14}\text{H}_{18}\text{O}_5$ $[\text{M}+\text{H}]^+$, Calcd: 267.1227; Found: 267.1227.

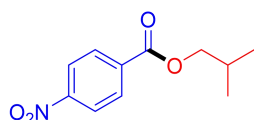


41; A known compound and the characterization data are in accordance with the literature.^[S15] Following the typical procedure **III**, *p*-tolualdehyde (24 μL , 0.2 mmol), 1-hexanol (251 μL , 2 mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (2.6 μL , 0.02 mmol) in THF (2 mL) were employed to give the product **41** (37 mg) in 83% yield as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.93 (d, $J = 8.2$ Hz, 2H), 7.23 (d, $J = 8.0$ Hz, 2H), 4.30 (t, $J = 6.7$ Hz, 2H), 2.41 (s, 3H), 1.80 – 1.70 (m, 2H), 1.48 – 1.41 (m, 2H), 1.34 (td, $J = 7.1, 3.7$ Hz, 4H), 0.94 – 0.88 (m, 3H) ppm; ^{13}C NMR (101 MHz, CDCl_3) δ 166.8, 143.4, 129.5, 129.0,

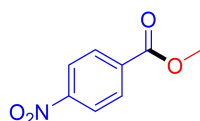
127.8, 64.9, 31.5, 28.7, 25.7, 22.5, 21.6, 14.0 ppm.



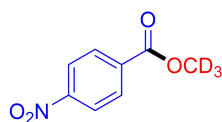
42; A known compound and the characterization data are in accordance with the literature.^[S16] Following the typical procedure **III**, 4-methylbenzaldehyde (24 μ L, 0.2 mmol), isobutanol (185 μ L, 2 mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (2.6 μ L, 0.02 mmol) in THF (2 mL) were employed to give the product **42** (32 mg) in 83 % yield as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.94 (d, J = 8.2 Hz, 2H), 7.23 (d, J = 8.0 Hz, 2H), 4.09 (d, J = 6.6 Hz, 2H), 2.41 (s, 3H), 2.08 (dp, J = 13.4, 6.7 Hz, 1H), 1.02 (d, J = 6.7 Hz, 6H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 166.7, 143.4, 129.5, 129.0, 127.8, 70.8, 27.9, 21.6, 19.2 ppm.



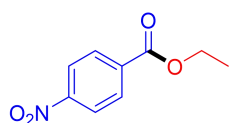
43; A known compound and the characterization data are in accordance with the literature.^[S17] Following the typical procedure **III**, 4-nitrobenzaldehyde (30 mg, 0.2 mmol), isobutyl alcohol (185 μ L, 2 mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), ethyl 2-mercaptopropionate (2.6 μ L, 0.02 mmol), and DBU (15 μ L, 0.1 mmol) in THF (2 mL) were employed to give the product **43** (25 mg) in 56 % yield as a white powder. ¹H NMR (400 MHz, CDCl₃) δ 8.29 (d, J = 8.9 Hz, 2H), 8.22 (d, J = 8.9 Hz, 2H), 4.16 (d, J = 6.6 Hz, 2H), 2.11 (dp, J = 13.4, 6.7 Hz, 1H), 1.04 (d, J = 6.7 Hz, 6H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 164.7, 150.5, 135.9, 130.6, 123.5, 71.9, 27.8, 19.1 ppm.



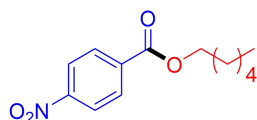
44; A known compound and the characterization data are in accordance with the literature.^[S13] Following the typical procedure **III**, 4-nitrobenzaldehyde (30 mg, 0.2 mmol), methanol (162 μ L, 4 mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), ethyl 2-mercaptopropionate (2.6 μ L, 0.02 mmol), and DBU (15 μ L, 0.1 mmol) in THF (2 mL) were employed to give the product **44** (30 mg) in 83 % yield as a white powder. ¹H NMR (400 MHz, CDCl₃) δ 8.30 (d, J = 8.6 Hz, 2H), 8.22 (d, J = 8.7 Hz, 2H), 3.99 (s, 3H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 165.2, 150.5, 135.5, 130.7, 123.5, 52.8 ppm.



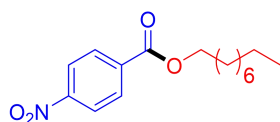
45; Following the typical procedure **III**, 4-nitrobenzaldehyde (30 mg, 0.2 mmol), methanol-*d*₄ (163 μ L, 4 mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), ethyl 2-mercaptopropionate (2.6 μ L, 0.02 mmol), and DBU (15 μ L, 0.1 mmol) in THF (2 mL) were employed to give the product **45** (28 mg) in 76 % yield as a white powder. ¹H NMR (400 MHz, CDCl₃) δ 8.33 – 8.26 (m, 2H), 8.25 – 8.18 (m, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 165.2, 150.5, 135.5, 130.7, 123.5, 29.7. HRMS *m/z*: calcd for C₈H₄D₃NO₄ [M+H]⁺: 185.0636, found: 185.0636.



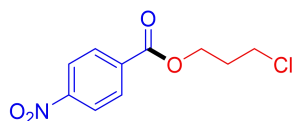
46; A known compound and the characterization data are in accordance with the literature.^[S13] Following the typical procedure **III**, 4-nitrobenzaldehyde (30 mg, 0.2 mmol), ethanol (234 μ L, 4 mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), ethyl 2-mercaptopropionate (2.6 μ L, 0.02 mmol), and DBU (15 μ L, 0.1 mmol) in THF (2 mL) were employed to give the product **46** (25 mg) in 64 % yield as a white powder. ¹H NMR (400 MHz, CDCl₃) δ 8.33 – 8.27 (m, 2H), 8.26 – 8.19 (m, 2H), 4.49 – 4.40 (m, 2H), 1.44 (dd, *J* = 13.0, 7.0 Hz, 3H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 164.7, 150.5, 135.8, 130.7, 123.5, 62.0, 14.2 ppm.



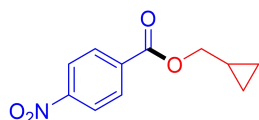
47; A known compound and the characterization data are in accordance with the literature.^[S18] Following the typical procedure **III**, 4-nitrobenzaldehyde (30 mg, 0.2 mmol), 1-hexanol (251 μ L, 2 mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), ethyl 2-mercaptopropionate (2.6 μ L, 0.02 mmol), and DBU (15 μ L, 0.1 mmol) in THF (2 mL) were employed to give the product **47** (25 mg) in 50 % yield as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 8.33 – 8.26 (m, 2H), 8.25 – 8.15 (m, 2H), 4.37 (t, *J* = 6.7 Hz, 2H), 1.86 – 1.73 (m, 2H), 1.50 – 1.41 (m, 2H), 1.39 – 1.31 (m, 4H), 0.97 – 0.88 (m, 3H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 164.8, 150.5, 135.9, 130.7, 123.5, 66.1, 31.4, 28.6, 25.6, 22.5, 14.0 ppm.



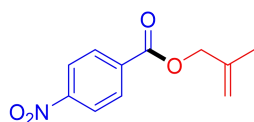
48; Following the typical procedure **III**, 4-nitrobenzaldehyde (30 mg, 0.2 mmol), 1-nonanol (349 μL , 2 mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), ethyl 2-mercaptopropionate (2.6 μL , 0.02 mmol), and DBU (15 μL , 0.1 mmol) in THF (2 mL) were employed to give the product **48** (31 mg) in 53 % yield as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 8.37 – 8.27 (m, 2H), 8.26 – 8.15 (m, 2H), 4.37 (t, J = 6.7 Hz, 2H), 1.86 – 1.74 (m, 2H), 1.45 (dt, J = 15.3, 6.5 Hz, 2H), 1.37 – 1.25 (m, 10H), 0.88 (t, J = 6.8 Hz, 3H) ppm; ^{13}C NMR (101 MHz, CDCl_3) δ 164.8, 150.5, 135.9, 130.6, 123.5, 66.1, 31.8, 29.5, 29.3, 29.2, 28.6, 26.0, 22.7, 14.1 ppm. HRMS m/z : calcd for $\text{C}_{16}\text{H}_{23}\text{NO}_4$: $[\text{M}+\text{H}]^+$: 294.1700, found: 294.1700.



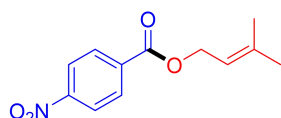
49; A known compound and the characterization data are in accordance with the literature.^[S13] Following the typical procedure **III**, 4-nitrobenzaldehyde (30 mg, 0.2 mmol), 3-chloro-1-propanol (167 μL , 2 mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), ethyl 2-mercaptopropionate (2.6 μL , 0.02 mmol), and DBU (15 μL , 0.1 mmol) in THF (2 mL) were employed to give the product **49** (33 mg) in 68 % yield as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 8.27 – 8.20 (m, 2H), 8.17 – 8.11 (m, 2H), 4.48 (t, J = 6.1 Hz, 2H), 3.64 (dd, J = 10.3, 4.0 Hz, 2H), 2.21 (p, J = 6.2 Hz, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ 164.5, 150.6, 135.3, 130.7, 123.6, 62.7, 41.0, 31.5 ppm.



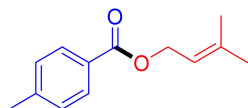
50; A known compound and the characterization data are in accordance with the literature.^[S17] Following the typical procedure **III**, 4-nitrobenzaldehyde (30 mg, 0.2 mmol), cyclopropyl carbinol (162 μL , 2 mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), ethyl 2-mercaptopropionate (2.6 μL , 0.02 mmol), and DBU (15 μL , 0.1 mmol) in THF (2 mL) were employed to give the product **50** (37 mg) in 84 % yield as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 8.32 – 8.27 (m, 2H), 8.26 – 8.22 (m, 2H), 4.21 (d, J = 7.3 Hz, 2H), 1.35 – 1.20 (m, 1H), 0.71 – 0.60 (m, 2H), 0.44 – 0.36 (m, 2H) ppm; ^{13}C NMR (101 MHz, CDCl_3) δ 164.8, 150.5, 135.9, 130.7, 123.5, 70.8, 9.8, 3.4 ppm.



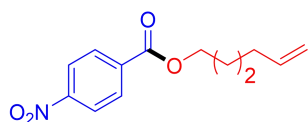
51; Following the typical procedure **III**, 4-nitrobenzaldehyde (30 mg, 0.2 mmol), 2-methyl-2-propen-1-ol (174 μ L, 2 mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), ethyl 2-mercaptopropionate (2.6 μ L, 0.02 mmol), and DBU (15 μ L, 0.1 mmol) in THF (2 mL) were employed to give the product **51** (33 mg) in 75 % yield as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 8.35 – 8.28 (m, 2H), 8.27 – 8.21 (m, 2H), 5.06 (d, J = 24.4 Hz, 2H), 4.80 (s, 2H), 1.86 (s, 3H) ppm; ^{13}C NMR (101 MHz, CDCl_3) δ 164.3, 150.6, 139.3, 135.5, 130.7, 123.6, 113.8, 69.0, 19.6 ppm. HRMS (ESI) m/z $[\text{M}+\text{H}]^+$: calcd for $\text{C}_{11}\text{H}_{11}\text{NO}_4$: 222.0761, found: 222.0761.



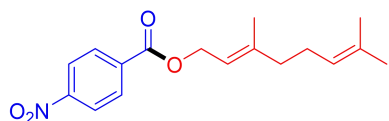
52; A known compound and the characterization data are in accordance with the literature.^[S18] Following the typical procedure **III**, 4-nitrobenzaldehyde (30 mg, 0.2 mmol), 3,3-dimethylallyl alcohol (204 μ L, 2 mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), ethyl 2-mercaptopropionate (2.6 μ L, 0.02 mmol), and DBU (15 μ L, 0.1 mmol) in THF (2 mL) were employed to give the product **52** (42 mg) in 90 % yield as a white powder. ^1H NMR (400 MHz, CDCl_3) δ 8.24 – 8.19 (m, 2H), 8.17 – 8.12 (m, 2H), 5.45 – 5.36 (m, 1H), 4.80 (d, J = 7.3 Hz, 2H), 1.73 (d, J = 7.2 Hz, 6H) ppm; ^{13}C NMR (101 MHz, CDCl_3) δ 164.7, 150.4, 140.2, 135.9, 130.7, 123.5, 117.9, 62.8, 25.8, 18.1 ppm.



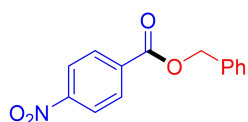
53; A known compound and the characterization data are in accordance with the literature.^[S19] Following the typical procedure **III**, *p*-tolualdehyde (24 μ L, 0.2 mmol), 3,3-dimethylallyl alcohol (204 μ L, 2 mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), ethyl 2-mercaptopropionate (2.6 μ L, 0.02 mmol), and DBU (15 μ L, 0.1 mmol) in THF (2 mL) were employed to give the product **53** (31 mg) in 75 % yield a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.97 – 7.89 (m, 2H), 7.22 (d, J = 7.9 Hz, 2H), 5.50 – 5.42 (m, 1H), 4.80 (d, J = 7.2 Hz, 2H), 2.40 (s, 3H), 1.83 – 1.76 (m, 6H) ppm; ^{13}C NMR (101 MHz, CDCl_3) δ 166.8, 143.4, 139.0, 129.6, 129.0, 127.8, 118.8, 61.7, 25.8, 21.6, 18.1 ppm.



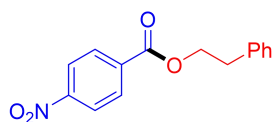
54; Following the typical procedure **III**, 4-nitrobenzaldehyde (30 mg, 0.2 mmol), 5-hexen-1-ol (237 μ L, 2 mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), ethyl 2-mercaptopropionate (2.6 μ L, 0.02 mmol), and DBU (15 μ L, 0.1 mmol) in THF (2 mL) were employed to give the product **54** (40 mg) in 80 % yield a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 8.22 (d, $J = 8.8$ Hz, 2H), 8.14 (d, $J = 8.9$ Hz, 2H), 5.75 (ddt, $J = 16.9, 10.2, 6.7$ Hz, 1H), 4.95 (ddd, $J = 17.8, 9.6, 5.8$ Hz, 2H), 4.31 (t, $J = 6.6$ Hz, 2H), 2.17 – 2.00 (m, 2H), 1.74 (dt, $J = 13.8, 6.8$ Hz, 2H), 1.49 (dt, $J = 15.0, 7.5$ Hz, 2H) ppm; ^{13}C NMR (101 MHz, CDCl_3) δ 164.7, 150.5, 138.1, 135.8, 130.6, 123.5, 115.0, 65.8, 33.2, 28.0, 25.2 ppm.



55; A known compound and the characterization data are in accordance with the literature.^[S20] Following the typical procedure **III**, 4-nitrobenzaldehyde (30 mg, 0.2 mmol), 3,7-dimethyl-2,6-Octadien-1-ol (347 μ L, 2 mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), ethyl 2-mercaptopropionate (2.6 μ L, 0.02 mmol), and DBU (15 μ L, 0.1 mmol) in THF (2 mL) were employed to give the product **55** (45 mg) in 75 % yield as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 8.32 – 8.25 (m, 2H), 8.22 (dd, $J = 8.9, 1.8$ Hz, 2H), 5.48 (t, $J = 6.9$ Hz, 1H), 5.09 (s, 1H), 4.90 (d, $J = 7.1$ Hz, 2H), 2.17 – 2.06 (m, 4H), 1.79 (s, 3H), 1.68 (s, 3H), 1.61 (s, 3H) ppm; ^{13}C NMR (101 MHz, CDCl_3) δ 164.7, 150.4, 143.4, 135.9, 131.9, 130.7, 123.6, 123.5, 117.6, 62.7, 39.5, 26.2, 25.7, 17.7, 16.6 ppm.

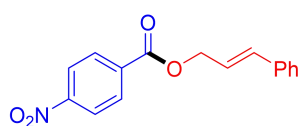


56; A known compound and the characterization data are in accordance with the literature.^[S13] Following the typical procedure **III**, 4-nitrobenzaldehyde (30 mg, 0.2 mmol), benzyl alcohol (207 μ L, 2 mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), ethyl 2-mercaptopropionate (2.6 μ L, 0.02 mmol), and DBU (15 μ L, 0.1 mmol) in THF (2 mL) were employed to give the product **56** (30 mg) in 58 % yield as a white powder. ^1H NMR (400 MHz, CDCl_3) δ 8.26 (q, $J = 8.9$ Hz, 4H), 7.49 – 7.35 (m, 5H), 5.41 (s, 2H) ppm; ^{13}C NMR (101 MHz, CDCl_3) δ 164.5, 150.6, 135.5, 135.2, 130.8, 128.7, 128.6, 128.4, 123.5, 67.7 ppm.



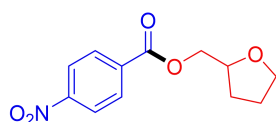
57; A known compound and the characterization data are in accordance with the literature.^[S21]

Following the typical procedure **III**, 4-nitrobenzaldehyde (30 mg, 0.2 mmol), phenethyl alcohol (239 μ L, 2 mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (2.6 μ L, 0.02 mmol) in THF (2 mL) were employed to give the product **57** (25 mg) in 46 % yield as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 8.28 (d, J = 8.6 Hz, 2H), 8.16 (d, J = 8.6 Hz, 2H), 7.37 – 7.26 (m, 5H), 4.59 (t, J = 6.9 Hz, 2H), 3.11 (t, J = 6.9 Hz, 2H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 164.6, 150.5, 137.4, 135.6, 130.7, 128.9, 128.6, 126.8, 123.5, 66.3, 35.1 ppm.



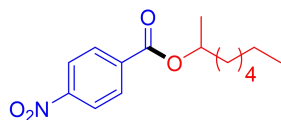
58; A known compound and the characterization data are in accordance with the literature.^[S13]

Following the typical procedure **III**, 4-nitrobenzaldehyde (30 mg, 0.2 mmol), cinnamic alcohol (257 μ L, 2 mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), ethyl 2-mercaptopropionate (2.6 μ L, 0.02 mmol), and DBU (15 μ L, 0.1 mmol) in THF (2 mL) were employed to give the product **58** (33 mg) in 58 % yield as a white powder. ¹H NMR (400 MHz, CDCl₃) δ 8.19 (dt, J = 13.7, 6.8 Hz, 4H), 7.39 – 7.21 (m, 5H), 6.70 (d, J = 15.9 Hz, 1H), 6.34 (dt, J = 15.8, 6.6 Hz, 1H), 4.96 (d, J = 6.6 Hz, 2H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 164.5, 150.6, 135.9, 135.6, 135.3, 130.8, 128.7, 128.4, 126.7, 123.6, 122.3, 66.5 ppm.

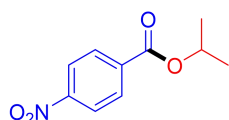


59; A known compound and the characterization data are in accordance with the literature.^[S13]

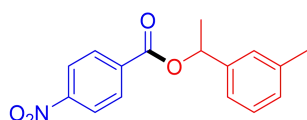
Following the typical procedure **III**, 4-nitrobenzaldehyde (30 mg, 0.2 mmol), tetrahydrofurfuryl alcohol (194 μ L, 2 mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), ethyl 2-mercaptopropionate (2.6 μ L, 0.02 mmol), and DBU (15 μ L, 0.1 mmol) in THF (2 mL) were employed to give the product **59** (25 mg) in 50 % yield as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 8.32 – 8.27 (m, 2H), 8.26 – 8.21 (m, 2H), 4.44 (m, J = 10.5, 2.6 Hz, 1H), 4.36 – 4.25 (m, 2H), 3.98 – 3.82 (m, 2H), 2.17 – 2.06 (m, 1H), 2.02 – 1.90 (m, 2H), 1.79 – 1.65 (m, 1H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 164.6, 150.6, 135.4, 130.8, 123.5, 76.4, 68.6, 67.8, 28.0, 25.7 ppm.



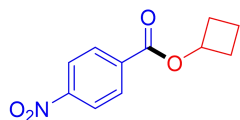
60; A known compound and the characterization data are in accordance with the literature.^[S22] Following the typical procedure **III**, 4-nitrobenzaldehyde (30 mg, 0.2 mmol), 2-octanol (318 μ L, 2 mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), ethyl 2-mercaptopropionate (2.6 μ L, 0.02 mmol), and DBU (15 μ L, 0.1 mmol) in THF (2 mL) were employed to give the product **60** (52 mg) in 93 % yield as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 8.32 – 8.25 (m, 2H), 8.24 – 8.17 (m, 2H), 5.25 – 5.14 (m, 1H), 1.82 – 1.71 (m, 1H), 1.64 (ddd, J = 14.2, 10.0, 4.5 Hz, 1H), 1.38 – 1.26 (m, 11H), 0.88 (t, J = 6.8 Hz, 3H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 164.3, 150.4, 136.3, 130.6, 123.5, 73.1, 35.9, 31.7, 29.1, 25.4, 22.6, 20.0, 14.0 ppm.



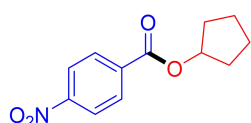
61; A known compound and the characterization data are in accordance with the literature.^[S13] Following the typical procedure **III**, 4-nitrobenzaldehyde (30 mg, 0.2 mmol), isopropyl alcohol (153 μ L, 2 mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), ethyl 2-mercaptopropionate (2.6 μ L, 0.02 mmol), and DBU (15 μ L, 0.1 mmol) in THF (2 mL) were employed to give the product **61** (25 mg) in 60 % yield as a white powder. ¹H NMR (400 MHz, CDCl₃) δ 8.23 – 8.19 (m, 2H), 8.16 – 8.11 (m, 2H), 5.28 – 5.16 (m, 1H), 1.33 (d, J = 6.3 Hz, 6H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 164.2, 150.4, 136.3, 130.6, 123.4, 69.7, 21.8 ppm.



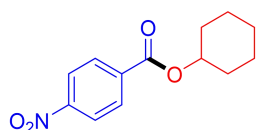
62; Following the typical procedure **III**, 4-nitrobenzaldehyde (30 mg, 0.2 mmol), 1-(2-methylphenyl)ethanol (41 mg, 0.3 mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), ethyl 2-mercaptopropionate (2.6 μ L, 0.02 mmol), and DBU (15 μ L, 0.1 mmol) in THF (2 mL) were employed to give the product **62** (29 mg) in 50 % yield as a white powder. Mp: 100 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.34 – 8.20 (m, 4H), 7.51 – 7.45 (m, 1H), 7.28 – 7.16 (m, 3H), 6.35 (q, J = 6.6 Hz, 1H), 2.45 (s, 3H), 1.68 (d, J = 6.6 Hz, 3H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 163.9, 150.5, 139.4, 135.9, 134.8, 130.7, 130.6, 128.0, 126.5, 125.2, 123.5, 71.2, 21.4, 19.1 ppm. HRMS m/z : calcd for C₁₆H₁₅NO₄ [M+Na]⁺: 308.0893, found: 308.0893.



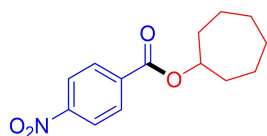
63; Following the typical procedure **III**, 4-nitrobenzaldehyde (30 mg, 0.2 mmol), cyclobutanol (157 μ L, 2 mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), ethyl 2-mercaptopropionate (2.6 μ L, 0.02 mmol), and DBU (15 μ L, 0.1 mmol) in THF (2 mL) were employed to give the product **63** (33 mg) in 75 % yield as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 8.31 – 8.26 (m, 2H), 8.24 – 8.18 (m, 2H), 5.31 – 5.20 (m, 1H), 2.49 (m, $J = 12.4, 9.8, 5.6, 2.6$ Hz, 2H), 2.31 – 2.18 (m, 2H), 1.98 – 1.84 (m, 1H), 1.80 – 1.65 (m, 1H) ppm; ^{13}C NMR (101 MHz, CDCl_3) δ 164.0, 150.5, 135.8, 130.7, 123.5, 70.2, 30.3, 13.5 ppm.



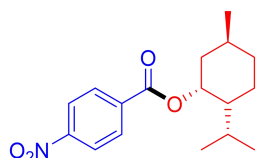
64; A known compound and the characterization data are in accordance with the literature.^[S23] Following the typical procedure **III**, 4-nitrobenzaldehyde (30 mg, 0.2 mmol), cyclopentanol (182 μ L, 2 mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), ethyl 2-mercaptopropionate (2.6 μ L, 0.02 mmol), and DBU (15 μ L, 0.1 mmol) in THF (2 mL) were employed to give the product **64** (37 mg) in 79 % yield as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 8.28 (d, $J = 8.8$ Hz, 2H), 8.18 (d, $J = 8.8$ Hz, 2H), 5.48 – 5.42 (m, 1H), 2.05 – 1.95 (m, 2H), 1.88 (d, $J = 1.9$ Hz, 1H), 1.86 – 1.77 (m, 3H), 1.70 (dt, $J = 8.8, 6.2$ Hz, 2H) ppm; ^{13}C NMR (101 MHz, CDCl_3) δ 164.4, 150.4, 136.2, 130.6, 123.5, 78.9, 32.8, 23.8 ppm.



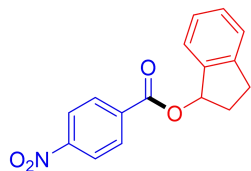
65; A known compound and the characterization data are in accordance with the literature.^[S15] Following the typical procedure **III**, 4-nitrobenzaldehyde (30 mg, 0.2 mmol), cyclohexanol (211 μ L, 2 mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), ethyl 2-mercaptopropionate (2.6 μ L, 0.02 mmol), and DBU (15 μ L, 0.1 mmol) in THF (2 mL) were employed to give the product **65** (25 mg) in 50 % yield as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 8.25 – 8.18 (m, 2H), 8.17 – 8.10 (m, 2H), 5.00 (ddd, $J = 12.8, 8.7, 3.8$ Hz, 1H), 1.91 (dd, $J = 12.2, 5.1$ Hz, 2H), 1.74 (dd, $J = 9.5, 3.5$ Hz, 2H), 1.59 – 1.52 (m, 2H), 1.39 (tdd, $J = 10.2, 8.3, 3.4$ Hz, 2H), 1.31 – 1.14 (m, 2H) ppm; ^{13}C NMR (101 MHz, CDCl_3) δ 164.1, 150.4, 136.4, 130.6, 123.5, 74.4, 31.5, 25.3, 23.6 ppm.



66; Following the typical procedure **III**, 4-nitrobenzaldehyde (30 mg, 0.2 mmol), cycloheptanol (242 μ L, 2 mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), ethyl 2-mercaptopropionate (2.6 μ L, 0.02 mmol), and DBU (15 μ L, 0.1 mmol) in THF (2 mL) were employed to give the product **66** (30 mg) in 57 % yield as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 8.28 (d, $J = 8.8$ Hz, 2H), 8.20 (d, $J = 8.8$ Hz, 2H), 5.23 (ddd, $J = 12.5, 8.3, 4.4$ Hz, 1H), 2.04 (ddd, $J = 13.0, 7.7, 3.4$ Hz, 2H), 1.91 – 1.79 (m, 2H), 1.79 – 1.69 (m, 2H), 1.68 – 1.59 (m, 4H), 1.25 (s, 2H) ppm; ^{13}C NMR (101 MHz, CDCl_3) δ 164.0, 150.4, 136.4, 130.6, 123.5, 33.8, 28.3, 22.8 ppm.

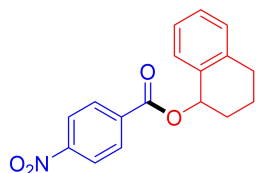


67; A known compound and the characterization data are in accordance with the literature.^[S24] Following the typical procedure **III**, 4-nitrobenzaldehyde (30 mg, 0.2 mmol), L-menthol (47 mg, 0.3 mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), ethyl 2-mercaptopropionate (2.6 μ L, 0.02 mmol), and DBU (15 μ L, 0.1 mmol) in THF (2 mL) were employed to give the product **67** (26 mg) in 43 % yield as a white powder. ^1H NMR (400 MHz, CDCl_3) δ 8.10 – 8.04 (m, 2H), 8.03 – 7.94 (m, 2H), 4.76 (td, $J = 10.9, 4.4$ Hz, 1H), 1.97 – 1.87 (m, 1H), 1.71 (dtd, $J = 13.9, 7.0, 2.7$ Hz, 1H), 1.59 – 1.46 (m, 2H), 1.36 (ddd, $J = 12.5, 6.3, 3.2$ Hz, 4H), 0.74 – 0.70 (m, 6H), 0.58 (d, $J = 7.0$ Hz, 3H) ppm; ^{13}C NMR (101 MHz, CDCl_3) δ 164.2, 150.4, 136.2, 130.7, 123.5, 76.1, 47.2, 40.8, 34.2, 31.5, 26.6, 23.6, 22.0, 20.7, 16.5 ppm.

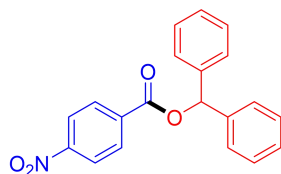


68; Following the typical procedure **III**, 4-nitrobenzaldehyde (30 mg, 0.2 mmol), 1-indanol (40 mg, 0.3 mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), ethyl 2-mercaptopropionate (2.6 μ L, 0.02 mmol), and DBU (15 μ L, 0.1 mmol) in THF (2 mL) were employed to give the product **68** (23 mg) in 41 % yield as a white powder. ^1H NMR (400 MHz, CDCl_3) δ 8.04 (d, $J = 8.9$ Hz, 2H), 7.98 (d, $J = 8.7$ Hz, 2H), 7.28 (d, $J = 7.5$ Hz, 1H), 7.13 (d, $J = 4.2$ Hz, 2H), 7.08 – 7.04 (m,

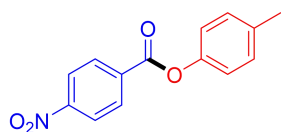
1H), 6.26 (dd, $J = 7.0, 3.6$ Hz, 1H), 3.08 – 2.94 (m, 1H), 2.76 (ddd, $J = 16.1, 8.6, 4.7$ Hz, 1H), 2.43 (dd, $J = 14.7, 7.9$ Hz, 1H), 2.06 (ddd, $J = 13.8, 8.4, 4.2$ Hz, 1H) ppm; ^{13}C NMR (101 MHz, CDCl_3) δ 164.7, 144.6, 140.4, 135.9, 130.8, 129.3, 128.1, 126.9, 125.7, 125.0, 123.5, 80.1, 32.4, 30.3 ppm. HRMS m/z : calcd for $\text{C}_{16}\text{H}_{13}\text{NO}_4$ $[\text{M}+\text{H}]^+$: 284.0917, found: 284.0917.



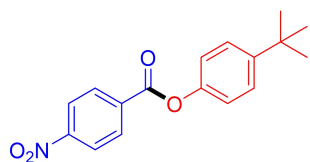
69; A known compound and the characterization data are in accordance with the literature.^[S25] Following the typical procedure **III**, 4-nitrobenzaldehyde (30 mg, 0.2 mmol), tetrahydro-1-naphthol (44 mg, 0.3 mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), ethyl 2-mercaptopropionate (2.6 μL , 0.02 mmol), and DBU (15 μL , 0.1 mmol) in THF (2 mL) were employed to give the product **69** (20 mg) in 34 % yield as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 8.07 – 8.02 (m, 2H), 8.02 – 7.96 (m, 2H), 7.13 (d, $J = 7.6$ Hz, 1H), 7.08 – 7.04 (m, 1H), 6.98 (t, $J = 7.5$ Hz, 2H), 6.07 (t, $J = 4.4$ Hz, 1H), 2.81 – 2.53 (m, 2H), 1.98 – 1.89 (m, 2H), 1.89 – 1.78 (m, 1H), 1.70 (ddd, $J = 9.6, 7.7, 4.8$ Hz, 1H) ppm; ^{13}C NMR (101 MHz, CDCl_3) δ 164.3, 150.5, 138.1, 136.1, 133.9, 130.8, 129.6, 129.2, 128.5, 126.2, 123.5, 71.9, 30.3, 29.1, 18.9 ppm.



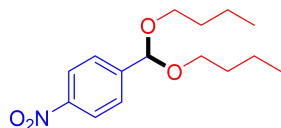
70; A known compound and the characterization data are in accordance with the literature.^[S26] Following the typical procedure **III**, 4-nitrobenzaldehyde (30 mg, 0.2 mmol), benzhydrol (55 mg, 0.3 mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), ethyl 2-mercaptopropionate (2.6 μL , 0.02 mmol), and DBU (15 μL , 0.1 mmol) in THF (2 mL) were employed to give the product **70** (38 mg) in 57 % yield as a white powder. ^1H NMR (400 MHz, CDCl_3) δ 8.30 (s, 4H), 7.36 (ddt, $J = 19.2, 13.5, 8.3$ Hz, 10H), 7.14 (s, 1H) ppm; ^{13}C NMR (101 MHz, CDCl_3) δ 163.7, 150.6, 139.5, 135.6, 130.9, 128.7, 128.3, 127.1, 123.6, 78.5 ppm.



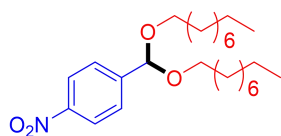
72; Following the typical procedure **III**, 4-nitrobenzaldehyde (30 mg, 0.2 mmol), *p*-methylphenol (32 mg, 0.3 mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), ethyl 2-mercaptopropionate (2.6 μ L, 0.02 mmol), and DBU (15 μ L, 0.1 mmol) in THF (2 mL) were employed to give the product **72** (12 mg) in 24 % yield as a white powder. Mp: 104 $^{\circ}$ C. 1 H NMR (400 MHz, CDCl_3) δ 8.29 (t, J = 5.6 Hz, 4H), 7.18 (d, J = 7.9 Hz, 2H), 7.04 (d, J = 8.2 Hz, 2H), 2.32 (s, 3H) ppm; 13 C NMR (101 MHz, CDCl_3) δ 163.5, 150.8, 148.3, 136.1, 135.1, 131.3, 130.2, 123.7, 121.0, 20.9 ppm. HRMS m/z : calcd for $\text{C}_{14}\text{H}_{11}\text{NO}_4$ $[\text{M}+\text{H}]^+$: 258.0761, found: 258.0761.



73; Following the typical procedure **III**, 4-nitrobenzaldehyde (30 mg, 0.2 mmol), 4-*tert*-butylphenol (45 mg, 0.3 mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), ethyl 2-mercaptopropionate (2.6 μ L, 0.02 mmol), and DBU (15 μ L, 0.1 mmol) in THF (2 mL) were employed to give the product **73** (13 mg) in 22 % yield as a yellow oil. 1 H NMR (400 MHz, CDCl_3) δ 8.41 – 8.34 (m, 4H), 7.49 – 7.43 (m, 2H), 7.18 – 7.12 (m, 2H), 1.35 (s, 9H) ppm; 13 C NMR (101 MHz, CDCl_3) δ 163.5, 150.8, 149.3, 148.1, 135.1, 131.3, 126.6, 123.7, 120.7, 34.6, 31.4 ppm. HRMS m/z : calcd for $\text{C}_{17}\text{H}_{17}\text{NO}_4$ $[\text{M}+\text{Na}]^+$: 322.1050, found: 322.1050.

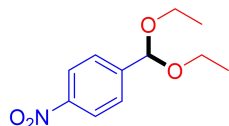


74; Following the typical procedure **IV**, 4-nitrobenzaldehyde (30 mg, 0.2 mmol), 1-butanol (183 μ L, 2 mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (2.6 μ L, 0.02 mmol) in THF (2 mL) were employed to give the product **74** (52 mg) in 93 % yield as a colorless oil. 1 H NMR (400 MHz, CDCl_3) δ 8.26 – 8.18 (m, 2H), 7.65 (d, J = 8.4 Hz, 2H), 5.57 (s, 1H), 3.62 – 3.38 (m, 4H), 1.64 – 1.57 (m, 4H), 1.46 – 1.35 (m, 4H), 0.93 (t, J = 7.4 Hz, 6H) ppm; 13 C NMR (101 MHz, CDCl_3) δ 147.8, 146.2, 127.7, 123.4, 100.1, 65.3, 31.7, 19.4, 13.9 ppm. HRMS calc. for $\text{C}_{15}\text{H}_{23}\text{NO}_4$ $[\text{M}+\text{Na}]^+$: 304.1519, found: 304.1519.

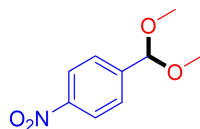


75; Following the typical procedure **IV**, 4-nitrobenzaldehyde (30 mg, 0.2 mmol), 1-nonanol (349

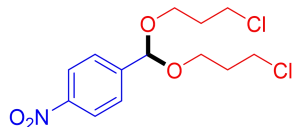
μL , 2 mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (2.6 μL , 0.02 mmol) in THF (2 mL) were employed to give the product **75** (65 mg) in 77 % yield as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 8.22 – 8.07 (m, 2H), 7.57 (d, $J = 8.5$ Hz, 2H), 5.49 (s, 1H), 3.49 – 3.34 (m, 4H), 1.61 – 1.49 (m, 4H), 1.32 – 1.16 (m, 24H), 0.86 – 0.76 (m, 6H) ppm; ^{13}C NMR (101 MHz, CDCl_3) δ 147.8, 146.2, 127.7, 123.3, 100.1, 65.7, 31.9, 29.7, 29.5, 29.4, 29.3, 26.2, 22.6, 14.1 ppm. HRMS calc. for $\text{C}_{25}\text{H}_{43}\text{NO}_4$ $[\text{M}+\text{Na}]^+$: 444.3084, found: 444.3084.



76; Following the typical procedure **IV**, 4-nitrobenzaldehyde (30 mg, 0.2 mmol), ethanol (234 μL , 4 mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), ethyl 2-mercaptopropionate (2.6 μL , 0.02 mmol) in THF (2 mL) were employed to give the product **76** (37 mg) in 82 % yield as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 8.22 (d, $J = 8.8$ Hz, 2H), 7.66 (d, $J = 8.7$ Hz, 2H), 5.58 (s, 1H), 3.66 – 3.52 (m, 4H), 1.26 (t, $J = 7.1$ Hz, 6H) ppm; ^{13}C NMR (101 MHz, CDCl_3) δ 147.9, 146.1, 127.7, 123.4, 100.1, 61.3, 15.1 ppm. HRMS calc. for $\text{C}_{11}\text{H}_{15}\text{NO}_4$ $[\text{M}+\text{Na}]^+$: 248.0893, found: 248.0893.

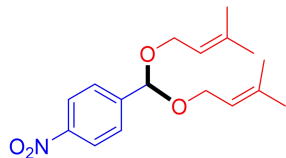


77; Following the typical procedure **IV**, 4-nitrobenzaldehyde (30 mg, 0.2 mmol), methanol (162 μL , 4 mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), ethyl 2-mercaptopropionate (2.6 μL , 0.02 mmol) in THF (2 mL) were employed to give the product **77** (35 mg) in 89 % yield as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 8.23 (d, $J = 8.4$ Hz, 2H), 7.65 (d, $J = 8.4$ Hz, 2H), 5.48 (s, 1H), 3.34 (s, 6H) ppm; ^{13}C NMR (101 MHz, CDCl_3) δ 148.0, 145.0, 127.8, 123.4, 101.5, 52.7 ppm. HRMS calc. for $\text{C}_9\text{H}_{11}\text{NO}_4$ $[\text{M}-\text{CH}_3\text{O}]^+$: 166.0499, found: 166.0463.

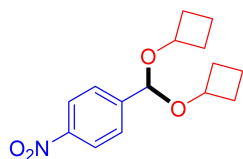


78; Following the typical procedure **IV**, 4-nitrobenzaldehyde (30 mg, 0.2 mmol), 3-chloro-1-propanol (167 μL , 2 mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (2.6 μL , 0.02 mmol) in THF (2 mL) were employed to give the product **78**

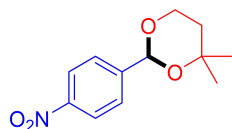
(44 mg) in 68% yield as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 8.34 – 8.17 (m, 2H), 7.64 (d, $J = 8.1$ Hz, 2H), 5.62 (s, 1H), 3.76 – 3.61 (m, 8H), 2.08 (p, $J = 5.9$ Hz, 4H) ppm; ^{13}C NMR (101 MHz, CDCl_3) δ 148.0, 145.1, 127.7, 123.5, 100.3, 61.9, 41.7, 32.4 ppm. HRMS calc. for $\text{C}_{13}\text{H}_{16}\text{NO}_4\text{Cl}_2$ $[\text{M}+\text{H}]^+$: 323.0291, found: 323.0289.



79; Following the typical procedure **IV**, 4-nitrobenzaldehyde (30 mg, 0.2 mmol), 3,3-dimethylallyl alcohol (204 μL , 2 mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (2.6 μL , 0.02 mmol) in THF (2 mL) were employed to give the product **79** (54 mg) in 88 % yield as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 8.15 (d, $J = 8.4$ Hz, 2H), 7.61 (d, $J = 8.5$ Hz, 2H), 5.57 (s, 1H), 5.30 (t, $J = 6.6$ Hz, 2H), 4.08 – 3.91 (m, 4H), 1.69 (s, 6H), 1.59 (s, 6H) ppm; ^{13}C NMR (101 MHz, CDCl_3) δ 147.9, 146.1, 137.8, 127.8, 123.4, 120.2, 98.8, 62.0, 25.8, 18.0 ppm. HRMS calc. for $\text{C}_{17}\text{H}_{23}\text{NO}_4$ $[\text{M}+\text{Na}]^+$: 328.1519, found: 328.1519.

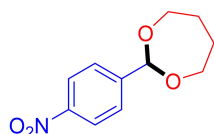


80; Following the typical procedure **IV**, 4-nitrobenzaldehyde (30 mg, 0.2 mmol), cyclobutanol (157 μL , 2 mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), ethyl 2-mercaptopropionate (2.6 μL , 0.02 mmol) in THF (2 mL) were employed to give the product **80** (40 mg) in 72 % yield as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 8.21 (d, $J = 8.7$ Hz, 2H), 7.64 (d, $J = 8.7$ Hz, 2H), 5.47 (s, 1H), 4.22 – 4.11 (m, 2H), 2.26 – 2.15 (m, 2H), 2.13 – 1.91 (m, 6H), 1.75 – 1.62 (m, 2H), 1.47 (qt, $J = 10.6, 8.1$ Hz, 2H) ppm; ^{13}C NMR (101 MHz, CDCl_3) δ 147.9, 146.6, 127.7, 123.4, 97.6, 69.7, 31.3, 31.0, 12.8 ppm. HRMS calc. for $\text{C}_{15}\text{H}_{19}\text{NO}_4$ $[\text{M}+\text{Na}]^+$: 300.1260, found: 300.1260.

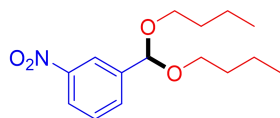


81; Following the typical procedure **IV**, 4-nitro-benzaldehyd (30mg, 0.2 mmol), 3-methyl-1,3-butanediol (213 μL , 2 mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (2.6 μL , 0.02 mmol) in THF (2 mL) were employed to give the

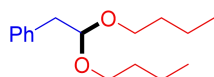
product **81** (31 mg) in 65 % yield as a white powder. Mp: 70 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.21 (d, *J* = 8.8 Hz, 2H), 7.67 (d, *J* = 8.7 Hz, 2H), 5.79 (s, 1H), 4.21 (q, *J* = 7.1 Hz, 1H), 4.15 – 4.08 (m, 2H), 2.02 (ddd, *J* = 13.1, 11.7, 7.2 Hz, 1H), 1.46 (s, 3H), 1.36 (s, 3H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 148.0, 145.9, 127.3, 123.4, 93.7, 72.7, 63.6, 35.7, 31.6, 21.5 ppm. HRMS calc. for C₁₂H₁₅NO₄ [M+Na]⁺: 260.0893, found: 260.0893.



82; Following the typical procedure **IV**, 4-nitro-benzaldehyde (30mg, 0.2 mmol), 1,4-butanediol (177 μL, 2 mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (2.6 μL, 0.02 mmol) in THF (2 mL) were employed to give the product **82** (34 mg) in 76 % yield as a white powder. Mp: 80 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.21 (d, *J* = 8.7 Hz, 2H), 7.68 (d, *J* = 8.7 Hz, 2H), 5.75 (s, 1H), 3.94 – 3.87 (m, 2H), 3.79 (dt, *J* = 11.6, 3.5 Hz, 2H), 1.88 – 1.71 (m, 4H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 147.8, 147.0, 127.5, 123.3, 99.6, 65.8, 29.2 ppm. HRMS calc. for C₁₁H₁₃NO₄ [M+H]⁺: 224.0917, found: 224.0917.

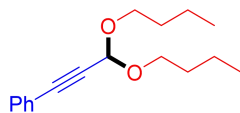


83; Following the typical procedure **IV**, 3-nitrobenzaldehyde (30 mg, 0.2 mmol), 1-butanol (183 μL, 2 mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), ethyl 2-mercaptopropionate (2.6 μL, 0.02 mmol) in THF (2 mL) were employed to give the product **83** (39 mg) in 70 % yield as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 8.35 (s, 1H), 8.24 – 8.12 (m, 1H), 7.81 (t, *J* = 8.9 Hz, 1H), 7.55 (t, *J* = 7.9 Hz, 1H), 5.58 (s, 1H), 3.59 – 3.44 (m, 4H), 1.62 (dt, *J* = 14.5, 6.7 Hz, 4H), 1.42 (dq, *J* = 14.4, 7.3 Hz, 4H), 0.93 (t, *J* = 7.4 Hz, 6H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 148.2, 141.4, 132.8, 129.1, 123.1, 121.9, 100.0, 65.3, 31.7, 19.4, 13.8 ppm. HRMS calc. for C₁₅H₂₃NO₄ [M+Na]⁺: 304.1519, found: 304.1519.

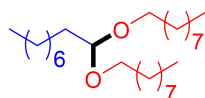


84; Following the typical procedure **IV**, phenylacetaldehyde (24 μL, 0.2 mmol), 1-butanol (183 μL, 2 mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (2.6 μL, 0.02 mmol) in THF (2 mL) were employed to give the product **84** (43 mg) in 85 % yield as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.29 (d, *J* = 7.3 Hz, 1H), 7.26 – 7.22 (m, 4H), 4.61 (t,

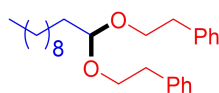
$J = 5.7$ Hz, 1H), 3.61 (dt, $J = 9.2$, 6.5 Hz, 2H), 3.38 (dt, $J = 9.3$, 6.6 Hz, 2H), 2.92 (d, $J = 5.7$ Hz, 2H), 1.52 (tt, $J = 13.6$, 6.6 Hz, 4H), 1.33 (dq, $J = 14.3$, 7.2 Hz, 4H), 0.88 (t, $J = 7.4$ Hz, 6H) ppm; ^{13}C NMR (101 MHz, CDCl_3) δ 137.4, 129.6, 128.1, 126.2, 104.0, 66.0, 40.7, 31.9, 19.3, 13.9 ppm. HRMS calc. for $\text{C}_{16}\text{H}_{26}\text{O}_2$ $[\text{M}+\text{Na}]^+$: 273.1825, found: 273.1825.



85; Following the typical procedure **IV**, phenylpropionaldehyde (24 μL , 0.2 mmol), 1-butanol (183 μL , 2 mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (2.6 μL , 0.02 mmol) in THF (2 mL) were employed to give the product **85** (34 mg) in 66 % yield as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.50 – 7.46 (m, 2H), 7.35 – 7.28 (m, 3H), 5.48 (s, 1H), 3.77 (dt, $J = 9.4$, 6.7 Hz, 2H), 3.59 (dt, $J = 9.4$, 6.6 Hz, 2H), 1.67 – 1.59 (m, 4H), 1.43 (dq, $J = 14.6$, 7.3 Hz, 4H), 0.94 (t, $J = 7.4$ Hz, 6H) ppm; ^{13}C NMR (101 MHz, CDCl_3) δ 131.9, 128.7, 128.2, 121.9, 92.0, 85.2, 84.5, 65.2, 31.6, 19.4, 13.9 ppm. HRMS calc. for $\text{C}_{17}\text{H}_{24}\text{O}_2$ $[\text{M}+\text{Na}]^+$: 283.1669, found: 283.1669.

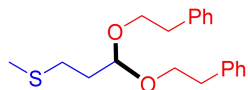


86; Following the typical procedure **IV**, 1-nonanal (34 μL , 0.2 mmol), 1-nonanol (349 μL , 2 mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (2.6 μL , 0.02 mmol) in THF (2 mL) were employed to give the product **86** (33 mg) in 40 % yield as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 4.46 (t, $J = 5.8$ Hz, 1H), 3.56 (dt, $J = 9.3$, 6.6 Hz, 2H), 3.40 (dt, $J = 9.3$, 6.7 Hz, 2H), 1.64 – 1.51 (m, 6H), 1.28 (d, $J = 11.1$ Hz, 36H), 0.88 (t, $J = 6.8$ Hz, 9H) ppm; ^{13}C NMR (101 MHz, CDCl_3) δ 103.1, 65.4, 33.4, 31.9, 29.9, 29.6, 29.5, 29.4, 29.3, 29.2, 26.3, 24.8, 22.7, 14.1 ppm. HRMS calc. for $\text{C}_{27}\text{H}_{56}\text{O}_2$ $[\text{M}+\text{Na}]^+$: 435.4173, found: 435.4173.

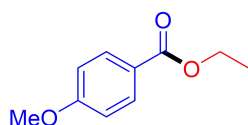


87; Following the typical procedure **IV**, undecanaldehyde (41 μL , 0.2 mmol), phenethyl alcohol (240 μL , 2 mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (2.6 μL , 0.02 mmol) in THF (2 mL) were employed to give the product **87** (46 mg) in 58 % yield as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.19 – 7.06 (m, 10H), 4.37 (t, $J = 5.8$ Hz, 1H), 3.65 – 3.54 (m, 2H), 3.47 (dt, $J = 9.4$, 7.2 Hz, 2H), 2.73 (t, $J = 7.1$ Hz, 4H), 1.52 – 1.44 (m, 2H),

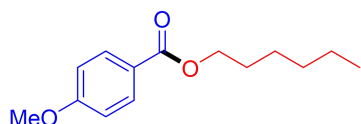
1.17 (d, $J = 7.9$ Hz, 16H), 0.80 (t, $J = 6.8$ Hz, 3H) ppm; ^{13}C NMR (101 MHz, CDCl_3) δ 139.0, 128.9, 128.2, 126.1, 103.2, 66.2, 36.4, 33.3, 31.9, 29.7, 29.6, 29.5, 29.4, 29.3, 24.6, 22.7, 14.1 ppm. HRMS calc. for $\text{C}_{27}\text{H}_{40}\text{O}_2$ $[\text{M}+\text{Na}]^+$: 419.2921, found: 419.2921.



88; Following the typical procedure **IV**, 3-(methylthio)propionaldehyde (20 μL , 0.2 mmol), phenethyl alcohol (240 μL , 2 mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (2.6 μL , 0.02 mmol) in THF (2 mL) were employed to give the product **88** (36 mg) in 55 % yield as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.29 – 7.24 (m, 4H), 7.21 – 7.16 (m, 6H), 4.57 (t, $J = 5.7$ Hz, 1H), 3.72 (dt, $J = 9.3, 6.9$ Hz, 2H), 3.58 (dt, $J = 9.4, 7.1$ Hz, 2H), 2.83 (t, $J = 7.0$ Hz, 4H), 2.43 – 2.35 (m, 2H), 2.03 (s, 3H), 1.89 – 1.79 (m, 2H) ppm; ^{13}C NMR (101 MHz, CDCl_3) δ 138.9, 128.9, 128.3, 126.2, 101.9, 66.8, 36.4, 33.0, 29.2, 15.5 ppm. HRMS calc. for $\text{C}_{20}\text{H}_{26}\text{O}_2\text{S}$ $[\text{M}+\text{Na}]^+$: 353.1546, found: 353.1546.

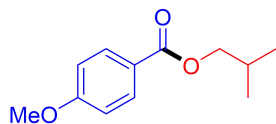


89; A known compound and the characterization data are in accordance with the literature.^[7] Following the typical procedure **V**, 4-methoxybenzyl alcohol (24 μL , 0.2 mmol), ethanol (234 μL , 2 mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (2.6 μL , 0.02 mmol) in THF (2 mL) were employed to give the product **89** (24 mg) in 67% yield as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 8.13 – 7.85 (m, 2H), 7.02 – 6.75 (m, 2H), 4.34 (q, $J = 7.1$ Hz, 2H), 3.85 (s, 3H), 1.38 (t, $J = 7.1$ Hz, 3H) ppm; ^{13}C NMR (101 MHz, CDCl_3) δ 166.3, 163.2, 131.5, 122.9, 113.5, 60.6, 55.3, 14.3 ppm.

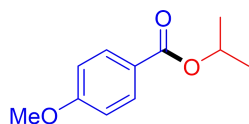


90; A known compound and the characterization data are in accordance with the literature.^[S28] Following the typical procedure **V**, 4-methoxybenzyl alcohol (24 μL , 0.2 mmol), 1-hexanol (251 μL , 2 mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (2.6 μL , 0.02 mmol) in THF (2 mL) were employed to give the product **90** (30 mg) in 63% yield as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 8.00 (d, $J = 8.9$ Hz, 2H), 6.92 (d, $J = 8.9$ Hz, 2H),

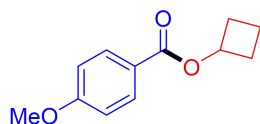
4.28 (t, $J = 6.7$ Hz, 2H), 3.85 (s, 3H), 1.80 – 1.69 (m, 2H), 1.47 – 1.40 (m, 2H), 1.33 (ddd, $J = 10.1$, 6.9, 3.4 Hz, 4H), 0.95 – 0.85 (m, 3H) ppm; ^{13}C NMR (101 MHz, CDCl_3) δ 166.4, 163.2, 131.5, 123.0, 113.5, 64.8, 55.4, 31.5, 28.7, 25.7, 22.5, 14.0 ppm.



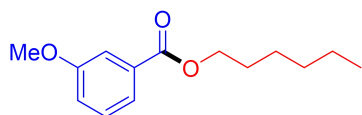
91; A known compound and the characterization data are in accordance with the literature.^[S29] Following the typical procedure **V**, 4-methoxybenzyl alcohol (24 μL , 0.2 mmol), isobutanol (185 μL , 2 mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (2.6 μL , 0.02 mmol) in THF (2 mL) were employed to give the product **91** (29 mg) in 70% yield as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.97 – 7.83 (m, 2H), 6.90 – 6.71 (m, 2H), 4.00 (d, $J = 6.6$ Hz, 2H), 3.77 (s, 3H), 1.99 (dp, $J = 13.4$, 6.7 Hz, 1H), 0.94 (d, $J = 6.7$ Hz, 6H) ppm; ^{13}C NMR (101 MHz, CDCl_3) δ 166.3, 163.2, 131.5, 122.9, 113.5, 77.3, 55.4, 27.9, 19.2 ppm.



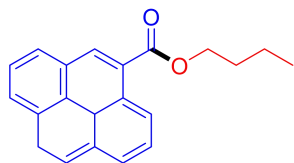
92; A known compound and the characterization data are in accordance with the literature.^[S14] Following the typical procedure **V**, 4-methoxybenzyl alcohol (24 μL , 0.2 mmol), isopropyl alcohol (153 μL , 2 mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (2.6 μL , 0.02 mmol) in THF (2 mL) were employed to give the product **92** (29 mg) in 77% yield as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 8.02 – 7.71 (m, 2H), 6.94 – 6.60 (m, 2H), 5.22 – 4.92 (m, 1H), 3.91 – 3.52 (m, 3H), 1.29 – 1.19 (m, 6H) ppm; ^{13}C NMR (101 MHz, CDCl_3) δ 165.8, 163.1, 131.4, 123.3, 113.4, 67.9, 55.3, 21.9 ppm.



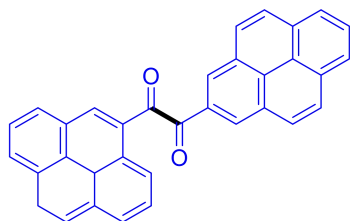
93; Following the typical procedure **V**, 4-methoxybenzyl alcohol (24 μL , 0.2 mmol), cyclobutanol (157 μL , 2 mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (2.6 μL , 0.02 mmol) in THF (2 mL) were employed to give the product **93** (33 mg) in 80% yield as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.99 (d, $J = 8.4$ Hz, 2H), 6.91 (d, $J = 8.5$ Hz, 2H), 5.33 – 5.04 (m, 1H), 3.85 (s, 3H), 2.51 – 2.39 (m, 2H), 2.24 – 2.13 (m, 2H), 1.89 – 1.81 (m, 1H), 1.72 – 1.65 (m, 1H) ppm; ^{13}C NMR (101 MHz, CDCl_3) δ 165.7, 163.3, 131.5, 122.8, 113.5, 69.0, 55.4, 30.4, 13.6 ppm. HRMS (ESI+, m/z) calc. for $\text{C}_{12}\text{H}_{14}\text{O}_3$ $[\text{M}+\text{H}]^+$: 207.1016, found: 207.1016.



94; A known compound and the characterization data are in accordance with the literature.^[S4] Following the typical procedure **V**, (3-methoxyphenyl)methanol (25 μ L, 0.2 mmol), 1-hexanol (251 μ L, 2 mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (2.6 μ L, 0.02 mmol) in THF (2 mL) were employed to give the product **94** (23 mg) in 48% yield as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.63 (t, J = 9.7 Hz, 1H), 7.57 (d, J = 1.1 Hz, 1H), 7.33 (t, J = 7.9 Hz, 1H), 7.12 – 7.05 (m, 1H), 4.31 (t, J = 6.7 Hz, 2H), 3.84 (d, J = 1.1 Hz, 3H), 1.81 – 1.68 (m, 2H), 1.43 (dd, J = 13.9, 6.5 Hz, 2H), 1.39 – 1.28 (m, 4H), 0.90 (dd, J = 6.9, 6.1 Hz, 3H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 166.4, 159.4, 131.8, 129.2, 121.8, 119.1, 114.0, 65.1, 55.3, 31.4, 28.6, 25.6, 22.5, 13.9 ppm.

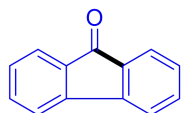


95; Following the typical procedure **III**, 1-pyrenecarboxaldehyde (46 mg, 0.2 mmol), 1-butanol (183 μ L, 2 mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (2.6 μ L, 0.02 mmol) in THF (2 mL) were employed to give the product **95** (24 mg) in 40 % yield as a yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 9.15 (dd, J = 9.4, 1.6 Hz, 1H), 8.51 (dd, J = 8.1, 1.9 Hz, 1H), 8.12 (t, J = 8.6 Hz, 3H), 8.05 – 8.00 (m, 2H), 7.96 – 7.89 (m, 2H), 4.42 (td, J = 6.6, 1.3 Hz, 2H), 1.86 – 1.73 (m, 2H), 1.55 – 1.45 (m, 2H), 0.95 (td, J = 7.3, 1.3 Hz, 3H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 168.1, 134.1, 131.0, 130.9, 130.3, 129.4, 129.3, 128.3, 127.1, 126.2, 126.1, 126.0, 124.9, 124.1, 124.0, 123.8, 99.9, 65.1, 30.9, 19.4, 13.8 ppm. HRMS calc. for C₂₁H₁₈O₂ [M+H]⁺: 303.1380, found: 303.1380.



96; Following the typical procedure **III**, the product **96** (33 mg) in 33 % yield as a yellow powder. ¹H NMR (400 MHz, CDCl₃) δ 10.80 (s, 2H), 9.45 (d, J = 9.3 Hz, 2H), 8.47 (d, J = 7.9 Hz, 2H), 8.34 (dd, J = 8.3, 4.2 Hz, 4H), 8.30 (d, J = 5.4 Hz, 2H), 8.27 (d, J = 4.2 Hz, 1H), 8.24 (s, 1H), 8.11

(dd, $J = 12.3, 4.7$ Hz, 4H) ppm; ^{13}C NMR (101 MHz, CDCl_3) δ 193.1, 135.5, 131.4, 131.0, 130.9, 130.8, 130.7, 130.4, 127.3, 127.2, 127.0, 126.8, 126.5, 124.6, 124.5, 124.0, 123.0 ppm. HRMS calc. for $\text{C}_{34}\text{H}_{18}\text{O}_2$ [$\text{M}-\text{C}_{17}\text{H}_9\text{O}+\text{H}$] $^+$: 230.0726, found: 230.0726.



97; A known compound and the characterization data are in accordance with the literature.^[S27] 2-biphenylcarboxaldehyde (36 mg, 0.2 mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (2.6 μL , 0.02 mmol) in THF (1.5 mL) were employed to give the product **91** (28 mg) in 76 % yield as a yellow powder. ^1H NMR (400 MHz, CDCl_3) δ 7.66 (d, $J = 7.3$ Hz, 2H), 7.50 (dt, $J = 15.0, 7.4$ Hz, 4H), 7.30 (t, $J = 7.3$ Hz, 2H) ppm; ^{13}C NMR (101 MHz, CDCl_3) δ 193.9, 144.4, 134.7, 134.1, 129.1, 124.3, 120.1 ppm.

IX. References

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X. ^1H , ^{13}C NMR Spectra of Products

