

Supporting Information for:

**Active participation of Amine-Derived Radicals in
Photoredox Catalysis**

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Experimental

Commercial Solvents and Reagents

Deuterated chloroform (CDCl_3), 2-bromoacetophenone, triphenylphosphine, glutaraldehyde (50 %), thioxanthone, 2, 4-diethylthioxanthone, Irgacure 379 (I-379), and N,N-diisopropylethylamine were used as received from the suppliers.

General instrumentation

^1H and ^{13}C NMR spectra were recorded on a Bruker AVANCE 400 spectrometer and chemical shifts are expressed in ppm relative to internal TMS or solvent values (CHCl_3 : δ 7.26 ppm for ^1H NMR, δ 77.0 ppm for ^{13}C NMR). The light source was a Luzchem photoreactor equipped with Luzchem UVA, 420 nm or Visible lamps (typically the unit was operated with 12 lamps, corresponding to 70–80 W/m^2 with \sim 4% spectral contamination in the case of visible lamps). UV-Visible absorption spectra were recorded on a Cary 50 Bio spectrometer.

Synthesis of Enone (1)

Enone (1) was prepared by reaction between corresponding Wittig salt and glutaraldehyde according to the literature procedures¹, and purified by chromatography (ethyl acetate: hexane, 1:5) on silica gel.

^1H NMR (400 MHz, CDCl_3): 1.74 – 1.84 (quintet, $J = 7.5$ Hz, 2H), 2.42 (q, $J = 6.8$ Hz, 4H), 6.91 – 6.96 (m, 2H), 7.04 – 7.11 (m, 2H), 7.46 – 7.50 (m, 4H), 7.55 – 7.60 (m, 2H), 7.93 – 7.96 (m, 4H) ppm.

Cyclization of Enone (1) with I-379 UVA Irradiation

In a 25 mL round bottom flask, enone (1) (61 mg, 0.2 mmol) and I-379 (76 mg, 0.2 mmol) were added. The flask was evacuated and purged with argon. Degassed MeCN (10 mL) was added, and the reaction was irradiated with UVA for 2 hours with stirring. The crude was purified by Prep. TLC (solvent 5:1 hexanes:ethyl acetate), giving compound 2 (73% yield).

¹HNMR (400 MHz, CDCl₃): 1.23 – 1.33 (m, 2H), 1.61 – 1.68 (m, 2H), 1.96 – 2.04 (m, 2H), 2.17 – 2.23 (m, 2H), 2.96 (dd, *J* = 16.5, 8.2 Hz, 2H), 3.21 (dd, *J* = 16.6, 4.6 Hz, 2H), 7.45 – 7.48 (m, 4H), 7.54 – 7.59 (m, 2H), 7.95 – 7.97 (m, 4H) ppm. ²

Cyclization of Enone (1) Using Hydrogen Abstraction Process

Thioxanthone: Into a 50 mL round bottom flask, enone 1 (18 mg, 0.06 mmol) and thioxanthone (13 mg, 0.06 mmol) were added. The flask was then purged to remove O₂. Degassed MeCN (20 mL) and *i*Pr₂NEt (51 uL, 0.3 mmol) was added under argon. The contents of the round bottom flask were then transferred into quartz test tubes (previously purged), and irradiated with visible light for 18 hours. The crude was purified by Prep. TLC (solvent 7:1 hexanes:ethyl acetate), giving compound 2 (83% yield).

Diethylthioxanthone: Into a 50 mL round bottom flask, enone 1 (22 mg, 0.07 mmol) and 2,4-diethylthioxanthone (19 mg, 0.07 mmol) were added. The flask was then purged to remove O₂. Degassed MeCN (20 mL) and *i*Pr₂NEt (62 uL, 0.36 mmol) was added under argon. The contents of the round bottom flask were then transferred into quartz test tubes (previously purged), and irradiated with visible light for 5 hours. The crude was purified by Prep. TLC (solvent 10:1 hexanes:ethyl acetate), giving compound 2 (55% yield).

Diethylthioxanthone (with 420 nm Irradiation): Into a 50 mL round bottom flask, enone 1 (29 mg, 0.095 mmol) and 2,4-diethylthioxanthone (25 mg, 0.095 mmol) were added. The flask was then purged to remove O₂. Degassed MeCN (20 mL) and *i*Pr₂NEt (83 uL, 0.477 mmol) was added under argon. The contents of the round bottom flask were then transferred into quartz test tubes (previously purged), and irradiated with 420 nm light (See Figure S3) for 5 hours. The crude was purified by Prep. TLC (solvent 6:1 hexanes:ethyl acetate), giving compound 2 (52% yield).

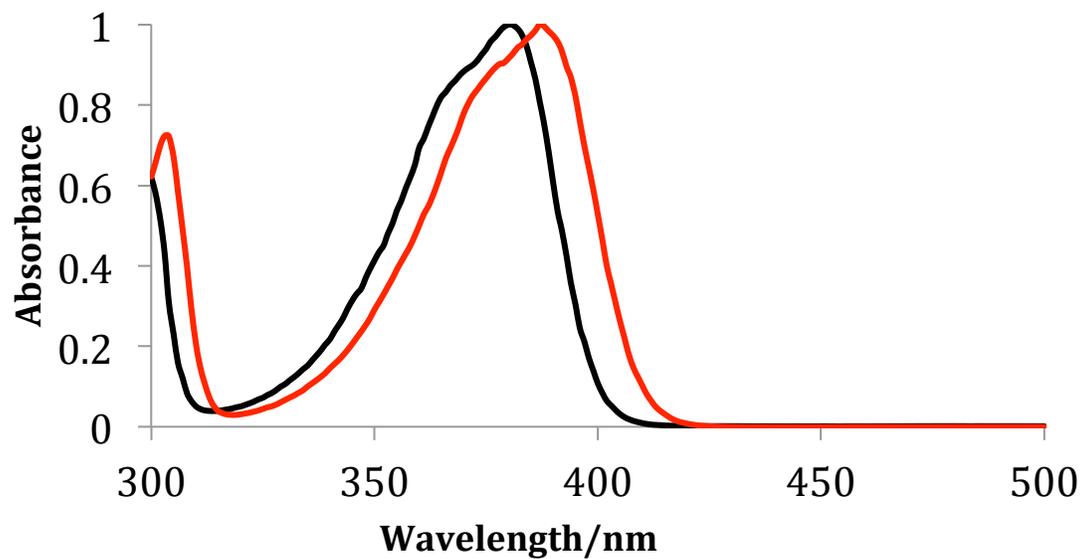


Figure S1. Normalized UV-Vis absorption spectra of thioxanthone (black) and 2,4-diethylthioxanthone (red) in MeCN

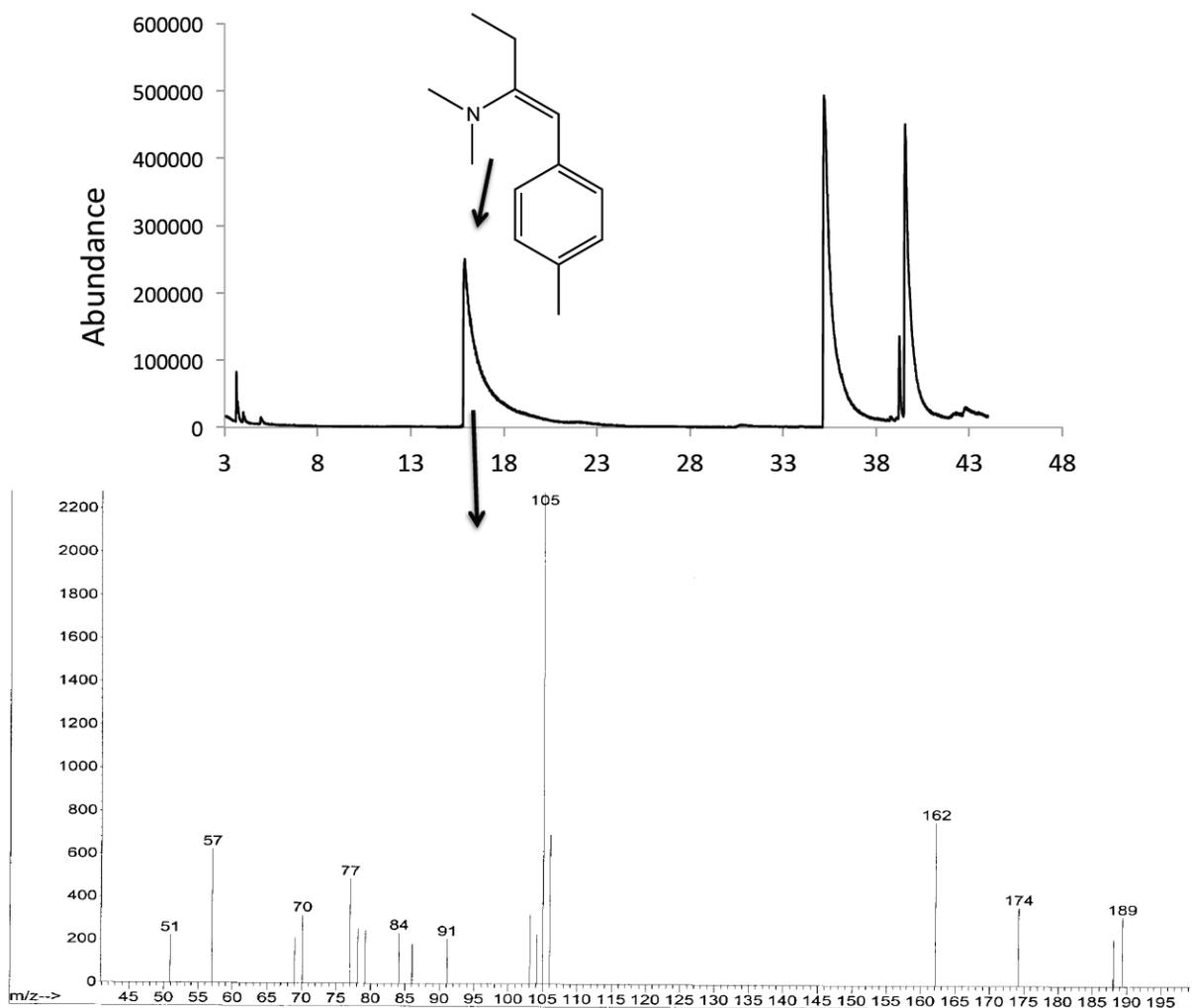


Figure S2. GC-MS spectrum of reaction mixture after 2h UVA Irradiation of Enone (1) and I-379.

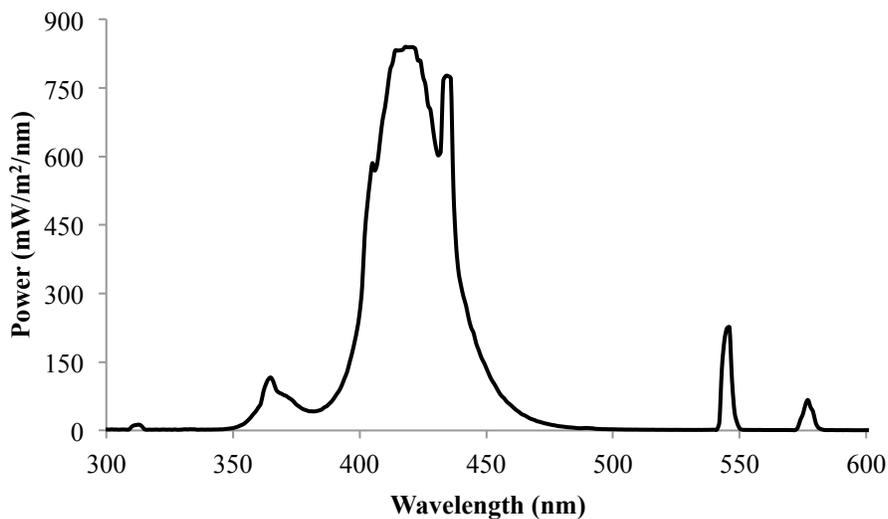


Figure S3. Emission spectrum corresponding to six Luzchem 420 nm bulbs.

For emission spectra of the visible and UV-A bulbs from Luzchem used in the experimental procedures, see links below:

<http://www.luzchem.com/handbook/LESVis011.pdf>

<http://www.luzchem.com/handbook/LESUVA011.pdf>

- 1) Yang, J.; Felton, G. A. N.; Bauld, N. L.; Krische, M. J., *J. Am. Chem. Soc.* **2004**, 126, 1634-1635.
- 2) Du, J.; Espelt, L. R.; Guzei, I. A.; Yoon, T. P., *Chem. Sci.* **2011**, 2, 2115-2119.