Supplementary Information

Visible-Light-Promoted Organic-Dye-Catalyzed Three-Component Coupling of Aldehydes, Hydrazines and Bromodifluorinated Reagents

Jin-Xue Li, Lei Li, Ming-Dong Zhou,* and He Wang*

School of Chemistry and Materials Science, Liaoning Shihua University, Dandong Road 1, Fushun 113001, China.

E-mail: heliwang123@126.com, mingdong.zhou@lnpu.edu.cn.

Contents

I. General Considerations	.2
II. General Procedure and characterization of α, α -difluoroketone hydrazones	.2
III. Large-scale reaction	15
IV. Synthesis and characterization of compound 7 and 9	16
V Mechanism Studies	17
VI. References	25
VII. NMR Spectra	27

I. General Considerations

All chemicals were obtained from commercial sources and were used as received unless otherwise noted. All reactions were carried out under an atmosphere of Ar atmosphere in a sealed tube. NMR Spectra were recorded using CDCl₃ or DMSO as a solvent on a Bruker 500 MHz NMR spectrometer at 298 K. The chemical shift is given in dimensionless δ values and is frequency referenced relative to TMS in ¹H, ¹³C, and ¹⁹F NMR spectroscopy. HRMS data were obtained via ESI mode with a TOF mass analyzer. Column chromatography was performed on silica gel (300-400 mesh) using ethyl acetate (EA)/petroleum ether (PE) or dichloromethane (DCM)/methyl alcohol.

4CzIPN,¹ aldehyde-derived hydrazones **6**,² Estrone aldehyde **1w**,³ and halodifluoromethylated reagents⁴ were prepared according to literature reports and the NMR data agree with those in the literature reports.

II. General Procedure and characterization of α,α-difluoroketone hydrazones

A sealed tube (35 mL) was equipped with a magnetic stir bar, **1e** (0.2 mmol), **2a** (0.24 mmol, 24.5 mg), **3a** (0.4 mmol), Na₂HPO₄ (0.3 mmol, 42.3 mg), MgSO₄ (75.0 mg), and DMF (1 ml). The reaction mixture was stirred under Ar for 12 h at 23°C in the presence of 8 W blue LEDs lamb, and monitored by TLC. After the reaction was finished, the mixture was concentrated under vacuum to remove DMF, and the residue was purified by chromatography on silica gel to afford the **4**.



Following general procedure, the crude product was purified by flash column chromatography (10:1 petroleum ether: ethyl acetate) to afford $4a^{2b}$ (47.4 mg, 76%)

yield) as slight yellow oil with configuration *E*:*Z*=19:1. ¹H NMR (500 MHz, CDCl₃): δ 7.48-7.46 (m, 2H), 7.42-7.38 (m, 3H), 4.38 (q, *J* = 7.0 Hz, 2H), 3.59 (t, *J* = 4.5 Hz, 4H), 2.92 (t, *J* = 5.0 Hz, 4H), 1.38 (t, *J* = 7.0 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃): δ 163.7 (t, *J* = 31.5 Hz), 140.7 (t, *J* = 31.5 Hz), 131.3, 129.7, 128.7, 128.6, 114.3 (t, *J* = 250.0 Hz), 66.0, 62.6, 54.1, 14.1. ¹⁹F NMR (471 MHz, CDCl₃): δ -101.5.



Following general procedure, the crude product was purified by flash column chromatography (10:1 petroleum ether: ethyl acetate) to afford **4b**^{2e} (55.0 mg, 84% yield) as white solid with configuration *E:Z*>20:1. ¹H NMR (500 MHz, CDCl₃): δ 7.39 (d, *J* = 8.0 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 4.40 (q, *J* = 7.0 Hz, 2H), 3.62 (t, *J* = 4.5 Hz, 4H), 2.95 (t, *J* = 4.5 Hz, 4H), 2.40 (s, 3H), 1.40 (t, *J* = 7.0 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃): δ 163.8 (t, *J* = 31.5 Hz), 141.2 (t, *J* = 31.4 Hz), 139.9, 129.3, 128.5, 128.2, 114.4 (t, *J* = 248.0 Hz), 66.0, 62.5, 54.0, 21.5, 14.1; ¹⁹F NMR (471 MHz, CDCl₃): δ -101.5.



Following general procedure, the crude product was purified by flash column chromatography (10:1 petroleum ether: ethyl acetate) to afford $4c^{2e}$ (46.8 mg, 68% yield) as slight yellow oil with configuration *E:Z*>20:1. ¹H NMR (500 MHz, CDCl₃): δ 7.45 (d, *J* = 8.6 Hz, 2H), 6.93 (d, *J* = 8.7 Hz, 2H), 4.37 (q, *J* = 7.1 Hz, 2H), 3.83 (s, 3H), 3.62-3.60 (m, 4H), 2.94-2.92 (m, 4H), 1.37 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃): δ 163.7 (t, *J* = 31.5 Hz), 160.5, 141.5 (t, *J* = 31.2 Hz), 130.0, 123.0, 114.4 (t, *J* = 247.9 Hz), 114.1, 66.0, 62.5, 55.3, 54.1, 14.1; ¹⁹F NMR (471 MHz, CDCl₃): δ -101.5.



Following general procedure, the crude product was purified by flash column chromatography (10:1 petroleum ether: ethyl acetate) to afford $4d^{2b}$ (39.0 mg, 59% yield) as slight yellow oil with configuration *E*:*Z*=16:1. ¹H NMR (500 MHz, CDCl₃): δ 7.52-7.50 (m, 2H), 7.14 (t, *J* = 8.6 Hz, 2H), 4.40 (q, *J* = 7.1 Hz, 2H), 3.64-3.62 (m, 4H), 2.95 (t, *J* = 4.8 Hz, 4H), 1.40 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃): δ 163.5 (t, *J* = 31.4 Hz), 163.2 (d, *J* = 249.4 Hz), 139.9 (t, *J* = 31.6 Hz), 130.7 (d, *J* = 8.3 Hz), 127.1 (d, *J* = 3.7 Hz), 116.0 (d, *J* = 21.4 Hz), 114.4 (t, *J* = 248.0 Hz), 65.9, 62.6, 54.1, 14.1; ¹⁹F NMR (471 MHz, CDCl₃): δ -101.5, -109.7.



Following general procedure, the crude product was purified by flash column chromatography (10:1 petroleum ether: ethyl acetate) to afford $4e^{2b}$ (64.4 mg, 93% yield) as slight yellow solid with configuration *E*:*Z*=19:1. ¹H NMR (500 MHz, CDCl₃): δ 7.45 (d, *J* = 8.5 Hz, 2H), 7.41 (d, *J* = 8.6 Hz, 2H), 4.39 (q, *J* = 7.1 Hz, 2H), 3.63-3.61 (m, 4H), 2.96-2.94 (m, 4H), 1.39 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃): δ 163.4 (t, *J* = 31.3 Hz), 139.5 (t, *J* = 31.8 Hz), 135.9, 130.0, 129.5, 129.1, 114.2 (t, *J* = 248.0 Hz), 65.9, 62.7, 54.2, 14.1; ¹⁹F NMR (471 MHz, CDCl₃): δ -101.3.



Following general procedure, the crude product was purified by flash column chromatography (10:1 petroleum ether: ethyl acetate) to afford $4f^{2e}$ (71.8 mg, 92% yield) as slight yellow solid with configuration *E:Z*>20:1. ¹H NMR (500 MHz, CDCl₃): δ 7.57 (d, *J* = 8.5 Hz, 2H), 7.38 (d, *J* = 8.3 Hz, 2H), 4.39 (q, *J* = 7.1 Hz, 2H),

3.62-3.61 (m, 4H), 2.96-2.94 (m, 4H), 1.39 (t, J = 7.2 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃): δ 163.4 (t, J = 31.5 Hz), 139.3 (t, J = 31.7 Hz), 132.0, 130.3, 130.0, 124.2, 114.1 (t, J = 248.2 Hz), 65.9, 62.7, 54.2, 14.1; ¹⁹F NMR (471 MHz, CDCl₃): δ -101.3.



Following general procedure, the crude product was purified by flash column chromatography (10:1 petroleum ether: ethyl acetate) to afford $4g^{2e}$ (52.6 mg, 78% yield) as white solid with configuration *E*:*Z*=20:1. ¹H NMR (500 MHz, CDCl₃): δ 7.74 (d, *J* = 8.3 Hz, 2H), 7.62 (d, *J* = 8.2 Hz, 2H), 4.40 (q, *J* = 7.1 Hz, 2H), 3.62-3.61 (m, 4H), 2.96-2.94 (m, 4H), 1.39 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃): δ 163.1 (t, *J* = 31.2 Hz), 137.7 (t, *J* = 31.9 Hz), 136.0, 132.4, 129.6, 118.0, 114.0 (t, *J* = 248.6 Hz), 113.7, 65.8, 62.8, 54.3, 14.1; ¹⁹F NMR (471 MHz, CDCl₃): δ -100.8.



Following general procedure, the crude product was purified by flash column chromatography (10:1 petroleum ether: ethyl acetate) to afford **4h**^{2b} (47.6 mg, 73% yield) as slight yellow oil with configuration *E*:*Z*=19:1. ¹H NMR (500 MHz, CDCl₃) δ 7.32-7.27 (m, 3H), 7.22 (d, *J* = 7.5 Hz, 1H), 4.39 (q, *J* = 7.0 Hz, 2H), 3.61 (t, *J* = 5 Hz, 4H), 2.95 (t, *J* = 5 Hz, 4H), 2.39 (s, 3H), 1.39 (t, *J* = 7.0 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃): δ 163.7 (t, *J* = 31.5 Hz), 140.7 (t, *J* = 31.6 Hz), 138.4, 131.2, 130.5, 129.0, 128.5, 125.7, 114.3 (t, *J* = 247.8 Hz), 66.0, 62.5, 54.1, 54.1, 21.4, 14.08. ¹⁹F NMR (471 MHz, CDCl₃): δ -101.5.



Following general procedure, the crude product was purified by flash column chromatography (10:1 petroleum ether: ethyl acetate) to afford **4i** (43.0 mg, 65% yield) as slight yellow solid with configuration E:Z>20:1. 1H NMR (500 MHz, CDCl₃): δ 7.40 (td, J = 8.0, 5.8 Hz, 1H), 7.27 (d, J = 7.5 Hz, 1H), 7.22 (dt, J = 9.2, 2.0 Hz, 1H), 7.14-7.09 (m, 1H), 4.38 (q, J = 7.1 Hz, 2H), 3.62-3.60 (m, 4H), 2.96-2.94 (m, J = 5.9, 3.8 Hz, 4H), 1.38 (t, J = 7.1 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃): δ 163.4 (t, J = 31.5 Hz), 162.5 (d, J = 247.3 Hz), 138.7 (t, J = 31.6 Hz), 133.1 (d, J = 7.6 Hz), 130.4 (d, J = 8.2 Hz), 124.6 (d, J = 3.2 Hz), 116.9 (d, J = 21.0 Hz), 115.8 (d, J = 22.2 Hz), 114.1 (t, J = 248.2 Hz), 65.9, 62.7, 54.2, 14.1; 19F NMR (471 MHz, CDCl₃): δ -101.3, -111.4. HRMS (ESI) Calcd for C₁₅H₁₇F₃N₂O₃ [M+H]⁺: 331.1264, found: 331.1265.



Following general procedure, the crude product was purified by flash column chromatography (5:1 petroleum ether: ethyl acetate) to afford $4j^{2b}$ (54.4 mg, 79% yield) as slight yellow oil with configuration *E*:*Z*=19:1. ¹H NMR (500 MHz, CDCl₃) δ 7.51 (s, 1H), 7.43-7.37 (m, 3H), 4.40 (q, *J* = 7.2 Hz, 2H), 3.64-3.62 (m, 4H), 2.97 (t, *J* = 4.9 Hz, 4H), 1.40 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 163.4 (t, *J* = 31.4 Hz), 138.5 (t, *J* = 31.9 Hz), 134.8, 132.9, 130.0, 129.9, 128.7, 126.9, 114.1 (t, *J* = 248.2 Hz), 65.9, 62.7, 54.2, 14.1. ¹⁹F NMR (471 MHz, CDCl₃): δ -101.2.



Following general procedure, the crude product was purified by flash column chromatography (5:1 petroleum ether: ethyl acetate) to afford $4k^{2b}$ (66.5 mg, 85% yield) as slight yellow oil with configuration *E*:*Z*=16:1. ¹H NMR (500 MHz, CDCl₃) δ 7.65 (s, 1H), 7.57-7.54 (m, 1H), 7.42 (dt, *J* = 7.8, 1.2 Hz, 1H), 7.30 (t, *J* = 7.9 Hz, 1H), 4.38 (q, *J* = 7.1 Hz, 2H), 3.63-3.61 (m, 4H), 2.95 (t, *J* = 4.9 Hz, 4H), 1.38 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 163.4 (t, *J* = 31.7 Hz), 138.4 (t, *J* = 31.7

Hz), 133.2, 132.9, 131.5, 130.2, 127.3, 122.8, 114.1 (t, *J* = 248.2 Hz), 65.9, 62.7, 54.2, 14.1. ¹⁹F NMR (471 MHz, CDCl₃): δ -101.2.



Following general procedure, the crude product was purified by flash column chromatography (10:1 petroleum ether: ethyl acetate) to afford **4l** (51.3 mg, 67% yield) as slight yellow oil with configuration E:Z=17:1. ¹H NMR (500 MHz, CDCl₃) δ 7.80 (s, 1H), 7.69 (d, J = 7.7 Hz, 2H), 7.57 (t, J = 7.8 Hz, 1H), 4.39 (q, J = 7.2 Hz, 2H), 3.62-3.60 (m, 4H), 2.94-2.92 (m, 4H), 1.39 (t, J = 7.1 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 163.3 (t, J = 31.3 Hz), 138.4 (t, J = 31.8 Hz), 132.0, 131.9, 131.3 (q, J = 32.5 Hz), 129.3, 126.5 (q, J = 3.6 Hz), 125.7 (q, J = 3.7 Hz), 123.6 (q, J = 270.8 Hz), 114.1 (t, J = 248.4 Hz), 65.9, 62.8, 54.2, 14.1. ¹⁹F NMR (471 MHz, CDCl₃): δ -62.9, -101.1. HRMS (ESI) Calcd for C₁₆H₁₇F₅N₂O₃ [M+H]⁺: 381.1232, found: 381.1230.



Following general procedure, the crude product was purified by flash column chromatography (10:1 petroleum ether: ethyl acetate) to afford **4c** (46.5 mg, 69% yield) as slight yellow oil with configuration *E*:*Z*=16:1. ¹H NMR (500 MHz, CDCl₃) δ 7.79 (s, 1H), 7.72 (dt, *J* = 8.0, 1.7 Hz, 2H), 7.57 (t, *J* = 7.8 Hz, 1H), 4.39 (q, *J* = 7.2 Hz, 2H), 3.63-3.61 (m, 4H), 2.95-2.93 (m, 4H), 1.39 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 163.1 (t, *J* = 31.1 Hz), 137.5 (t, *J* = 31.7 Hz), 133.2, 133.0, 132.7, 132.2, 129.7, 117.8, 114.0 (t, *J* = 248.4 Hz), 113.3 65.8, 62.8, 54.3, 14.1. ¹⁹F NMR (471 MHz, CDCl₃): δ -101.0. HRMS (ESI) Calcd for C₁₆H₁₇F₂N₃O₃ [M+H]⁺: 338.1311, found: 338.1314.



Following general procedure, the crude product was purified by flash column chromatography (10:1 petroleum ether: ethyl acetate) to afford $4n^{2e}$ (43.2 mg, 66% yield) as colorless oil with configuration *E:Z*>20:1. ¹H NMR (500 MHz, CDCl₃) δ 7.35-7.32 (m, 2H), 7.25-7.22 (m, 2H), 4.40 (q, *J* = 7.1 Hz, 2H), 3.64-3.56 (m, 4H), 2.93 (m, 4H), 2.31 (s, 3H), 1.40 (t, *J* = 7.2 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 163.9 (t, *J* = 31.9 Hz), 138.7 (dd, *J* = 29.6, 35.2 Hz), 138.1, 131.2, 130.0, 129.7, 128.8, 125.8, 114.5 (t, *J* = 247.6 Hz), 66.3, 62.5, 53.8, 19.7, 14.1.¹⁹F NMR (471 MHz, CDCl₃): δ -101.0 (d, *J* = 269.5 Hz), -103.3 (d, *J* = 269.3 Hz).



Following general procedure, the crude product was purified by flash column chromatography (15:1 petroleum ether: ethyl acetate) to afford 40^{2b} (58.8 mg, 86% yield) as slight yellow oil with configuration *E:Z*>20:1. ¹H NMR (500 MHz, CDCl₃) δ 7.39 (td, *J* = 7.9, 1.8 Hz, 1H), 7.27 (d, *J* = 7.8 Hz, 1H), 6.98 (t, *J* = 7.5 Hz, 1H), 6.92 (d, *J* = 8.3 Hz, 1H), 4.37 (q, *J* = 7.1 Hz, 2H), 3.85 (s, 3H), 3.60-3.58 (m, 4H), 2.99 (t, *J* = 4.9 Hz, 4H), 1.38 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 164.1 (t, *J* = 32.1 Hz), 157.6, 134.9 (t, *J* = 35.0 Hz), 131.2, 130.5, 120.9, 120.5, 114.2 (t, *J* = 248.0 Hz), 111.1, 66.2, 62.4, 55.8, 53.4, 14.1. ¹⁹F NMR (471 MHz, CDCl₃): δ -101.5, -103.1.



Following general procedure, the crude product was purified by flash column

chromatography (10:1 petroleum ether: ethyl acetate) to afford $4p^{2b}$ (33.5 mg, 51% yield) as slight yellow oil with configuration *E:Z*>20:1. ¹H NMR (500 MHz, CDCl₃) δ 9.27 (br, 1H), 7.39 (td, *J* = 7.9, 1.8 Hz, 1H), 7.27 (d, *J* = 7.8 Hz, 1H), 6.98 (t, *J* = 7.5 Hz, 1H), 6.92 (d, *J* = 8.3 Hz, 1H), 4.37 (q, *J* = 7.1 Hz, 2H), 3.60-3.58 (m, 4H), 2.99 (t, *J* = 4.9 Hz, 4H), 1.38 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 162.8 (t, *J* = 31.5 Hz), 156.9, 154.6 (t, *J* = 29.3 Hz), 133.2, 128.4 (t, *J* = 3.7 Hz), 120.1, 119.7, 116.7, 113.5 (t, *J* = 253.3 Hz), 65.6, 62.9, 53.9, 13.9. ¹⁹F NMR (471 MHz, CDCl₃): δ -100.4.



Following general procedure, the crude product was purified by flash column chromatography (10:1 petroleum ether: ethyl acetate) to afford $4q^{2b}$ (49.5 mg, 75% yield) as slight yellow oil with configuration *E:Z*>20:1. ¹H NMR (500 MHz, CDCl₃) δ 7.47-7.43 (m, 1H), 7.41-7.38 (m, 1H), 7.22 (td, *J* = 7.6, 1.1 Hz, 1H), 7.17-7.13 (m, 1H), 4.40 (q, *J* = 7.2 Hz, 2H), 3.64-3.62 (m, 4H), 3.03 (t, *J* = 4.9 Hz, 4H), 1.40 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 163.6 (t, *J* = 31.7 Hz), 159.9 (d, *J* = 248.7 Hz), 131.8 (d, *J* = 7.8 Hz), 131.7 (t, *J* = 32.5 Hz), 130.8 (d, *J* = 2.8 Hz), 124.3 (d, *J* = 3.6 Hz), 119.6 (d, *J* = 18.3 Hz), 115.9 (d, *J* = 21.3 Hz), 114.0 (t, *J* = 247.8 Hz), 66.1, 62.6, 53.5, 14.1.¹⁹F NMR (471 MHz, CDCl₃): δ -101.0 (d, *J* = 269.5 Hz), -101.9, -109.8.



Following general procedure, the crude product was purified by flash column chromatography (10:1 petroleum ether: ethyl acetate) to afford $4r^{2b}$ (40.2 mg, 58% yield) as slight yellow oil with configuration *E:Z*>20:1. ¹H NMR (500 MHz, CDCl₃) δ 7.46 (d, *J* = 8.0 Hz, 1H), 7.43-7.37 (m, 2H), 7.33 (td, *J* = 7.5, 1.3 Hz, 1H), 4.41 (q, *J* = 7.1 Hz, 2H), 3.63 (t, *J* = 4.9 Hz, 4H), 3.07 (dt, *J* = 12.2, 5.0 Hz, 2H), 3.00-2.97 (m, 2H), 1.40 (t, *J* = 7.2 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 163.7 (t, *J* = 31.5 Hz),

134.6, 132.6 (dd, J = 30.1, 34.7 Hz), 131.3, 131.1, 131.0, 129.6, 126.7, 114.3 (t, J = 249.1 Hz), 66.3, 62.6, 53.4, 14.1.¹⁹F NMR (471 MHz, CDCl₃): δ -99.9 (d, J = 266.4 Hz), -103.0 (d, J = 266.4 Hz).



Following general procedure, the crude product was purified by flash column chromatography (10:1 petroleum ether: ethyl acetate) to afford $4s^{2e}$ (52.7 mg, 68% yield) as slight yellow liquid with configuration *E:Z*>20:1. ¹H NMR (500 MHz, CDCl₃) δ 7.64 (d, *J* = 7.9 Hz, 1H), 7.42-7.36 (m, 2H), 7.32-7.29 (m, 1H), 4.41 (q, *J* = 7.1 Hz, 2H), 3.64 (t, *J* = 4.9 Hz, 4H), 3.09 (dt, *J* = 10.5, 5.0 Hz, 2H), 3.00 (dt, *J* = 11.7, 5.0 Hz, 2H), 1.41 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 163.7 (t, *J* = 30.1 Hz), 133.5, 133.3 (dd, *J* = 29.7, 35.0 Hz), 132.8, 131.3, 131.0, 127.2, 124.3, 114.3 (dd, *J* = 246.3, 249.1 Hz), 66.3, 62.6, 53.4, 14.1.¹⁹F NMR (471 MHz, CDCl₃): δ -99.6 (d, *J* = 266.4 Hz), -102.7 (d, *J* = 266.4 Hz).



Following general procedure, the crude product was purified by flash column chromatography (10:1 petroleum ether: ethyl acetate) to afford $4t^{2b}$ (47.6 mg, 70% yield) as slight yellow oil with configuration *E*:*Z*=18:1. ¹H NMR (500 MHz, CDCl₃) δ 7.27 (s, 1H), 7.23 (d, *J* = 7.8 Hz, 1H), 7.18 (d, *J* = 7.8 Hz, 1H), 4.40 (q, *J* = 7.2 Hz, 2H), 3.63-3.61 (m, 4H), 2.96 (t, *J* = 4.8 Hz, 4H), 2.30 (s, 3H), 2.29 (s, 3H), 1.40 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 163.8 (t, *J* = 31.5 Hz), 141.1 (t, *J* = 31.3 Hz), 138.6, 137.1, 129.9, 129.4, 128.5, 126.0, 114.4 (t, *J* = 247.9 Hz), 66.0, 62.5, 54.1, 19.8, 14.1. ¹⁹F NMR (471 MHz, CDCl₃): δ -101.2.



Following general procedure, the crude product was purified by flash column chromatography (10:1 petroleum ether: ethyl acetate) to afford $4v^{2b}$ (29.8 mg, 44% yield) as colorless oil with configuration *E*:*Z*=10:7. ¹H NMR (500 MHz, CDCl₃) δ 7.35-7.30 (m, 2H × 2 + 2H × 0.7), 7.27-7.21 (m, 3H × 1 + 3H × 0.7), 4.38 (q, *J* = 7.2 Hz, 2H), 4.32 (q, *J* = 7.2 Hz, 2H × 0.7), 3.79-3.77 (m, 4H), 3.73-3.71 (m, 4H × 0.7), 3.01-2.97 (m, 2H × 2 + 2H × 0.7), 2.87-2.84 (m, 2H × 2 + 2H × 0.7), 2.80-2.79 (m, 4H), 2.65-2.63 (m, 4H × 0.7), 1.40-1.36 (m, 3H × 1 + 3H × 0.7). ¹³C NMR (125 MHz, CDCl₃) δ 167.9 (t, *J* = 25.1 Hz), 162.9 (t, *J* = 31.2 Hz), 161.8 (t, *J* = 31.1 Hz), 158.1 (t, *J* = 29.8 Hz), 140.5, 140.4, 128.6, 128.5, 128.4, 128.3, 126.5, 126.3, 113.8 (t, *J* = 250.3 Hz), 107.9 (t, *J* = 252.1 Hz), 65.9, 65.4, 62.7, 62.4, 54.9, 54.7, 32.9, 32.1, 31.7, 28.8, 14.1, 14.0. ¹⁹F NMR (471 MHz, CDCl₃): δ -105.1, -105.9.



Following general procedure, the crude product was purified by flash column chromatography (10:1 petroleum ether: ethyl acetate) to afford **4w** (63.5 mg, 65% yield) as slight yellow oil with configuration E:Z=17:1. ¹H NMR (500 MHz, CDCl₃) δ 7.32 (d, J = 8.2 Hz, 1H), 7.27 (d, J = 7.8 Hz, 1H), 7.22 (s, 1H), 4.38 (q, J = 7.1 Hz, 2H), 3.63-3.61 (m, 4H), 2.97-2.92 (m, 6H), 2.52 (dd, J = 18.9, 8.7 Hz, 1H), 2.45-2.41 (m, 1H), 2.33 (td, J = 10.9, 4.2 Hz, 1H), 2.20-2.03 (m, 3H), 1.99 (dt, J = 12.6, 3.0 Hz, 1H), 1.69-1.46 (m, 6H), 1.39 (t, J = 7.1 Hz, 3H), 0.94 (s, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 220.6, 163.8 (t, J = 31.6 Hz), 141.6, 140.9 (t, J = 31.5 Hz), 136.9, 128.8, 128.4, 125.9, 125.5, 114.5 (t, J = 248.1 Hz), 66.0, 62.5, 54.1, 50.5, 47.9, 44.5, 37.8, 35.8, 31.6, 29.3, 26.3, 25.5, 21.6, 14.1, 13.9.

HRMS (ESI) Calcd for C₂₇H₃₄F₂N₂O₄ [M+H]⁺: 489.2559, found: 489.2561.



Following general procedure, the crude product was purified by flash column chromatography (150:1 petroleum ether: ethyl acetate) to afford **4eba** (32.9 mg, 48% yield) as yellow solid with configuration *E:Z*>20:1. ¹H NMR (500 MHz, CDCl₃) δ 7.44 (d, *J* = 8.6 Hz, 2H), 7.40 (d, *J* = 8.6 Hz, 2H), 4.39 (q, *J* = 7.1 Hz, 2H), 2.96 (t, *J* = 5.2 Hz, 4H), 1.48 (m, 6H), 1.40 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 163.9 (t, *J* = 31.4 Hz), 135.5 (t, *J* = 31.8 Hz), 135.4, 130.3, 130.1, 128.8, 114.9 (t, *J* = 247.0 Hz), 62.5, 54.8, 24.7, 23.8, 14.1. ¹⁹F NMR (471 MHz, CDCl₃): δ -100.4. HRMS (ESI) Calcd for C₁₆H₁₉ClF₂N₂O₂ [M+H]⁺: 345.1176, found: 345.1172.



Following general procedure, the crude product was purified by flash column chromatography (100:1 petroleum ether: ethyl acetate) to afford **4eca** (63.6 mg, 70% yield) as slight yellow oil with configuration *E:Z*=13:1. ¹H NMR (500 MHz, CDCl₃) δ 7.34-7.27 (m, 6H), 7.20 (d, *J* = 8.6 Hz, 2H), 7.16 (d, *J* = 8.5 Hz, 2H), 7.07-7.05 (m, 4H), 4.31 (q, *J* = 7.1 Hz, 2H), 4.25 (s, 4H), 1.35 (t, *J* = 7.2 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 164.0 (t, *J* = 31.7 Hz), 136.6, 135.3, 132.7 (t, *J* = 32.5 Hz), 131.0, 128.5, 128.1, 127.7, 127.5, 127.4, 114.9 (t, *J* = 246.3 Hz), 62.6, 59.2, 14.1. ¹⁹F NMR (471 MHz, CDCl₃): δ -99.8. HRMS (ESI) Calcd for C₂₅H₂₃ClF₂N₂O₂ [M+H]⁺: 457.1489, found: 457.1485.



Following general procedure, the crude product was purified by flash column chromatography (10:1 petroleum ether: ethyl acetate) to afford **4eab** (45.4 mg, 61% yield) as slight yellow solid with configuration *E:Z*>20:1. ¹H NMR (500 MHz, CDCl₃) δ 7.48 (d, *J* = 8.2 Hz, 2H), 7.42 (d, *J* = 8.2 Hz, 2H), 3.63-3.61 (m, 4H), 3.46 (q, *J* = 7.1 Hz, 2H), 3.34 (q, *J* = 7.0 Hz, 2H), 2.94 (t, *J* = 4.8 Hz, 4H), 1.20 (td, *J* = 7.0, 4.3 Hz, 6H). ¹³C NMR (125 MHz, CDCl₃) δ 162.4 (t, *J* = 27.3 Hz), 140.8 (t, *J* = 31.3 Hz), 135.9, 129.9, 129.8, 129.1, 115.1 (t, *J* = 246.1 Hz), 66.0, 54.2, 42.3, 40.8, 13.8, 11.7. ¹⁹F NMR (471 MHz, CDCl₃): δ -95.6. HRMS (ESI) Calcd for C₁₇H₂₂ClF₂N₃O₂ [M+H]⁺: 374.1441, found: 374.1440.



Following general procedure, the crude product was purified by flash column chromatography (3:1 petroleum ether: ethyl acetate) to afford **4eac** (69.0 mg, 93% yield) as slight yellow solid with configuration *E:Z*>20:1. ¹H NMR (500 MHz, CDCl₃) δ 7.48 (d, *J* = 8.5 Hz, 2H), 7.42 (d, *J* = 8.5 Hz, 2H), 3.64-3.57 (m, 8H), 2.94-2.92 (m, 4H), 1.97-1.87 (m, 4H). ¹³C NMR (125 MHz, CDCl₃) δ 161.9 (t, *J* = 28.4 Hz), 140.6 (t, *J* = 31.6 Hz), 135.8, 130.0, 129.9, 129.1, 115.2 (t, *J* = 247.1 Hz), 66.0, 54.3, 47.3 (t, *J* = 4.2 Hz), 47.2, 26.4, 23.6. ¹⁹F NMR (471 MHz, CDCl₃): δ -98.1. HRMS (ESI) Calcd for C₁₇H₂₀ClF₂N₃O₂ [M+H]⁺: 372.1285, found: 372.1281.



Following general procedure, the crude product was purified by flash column chromatography (2:1 petroleum ether: ethyl acetate) to afford **4ead**^{2b} (68.5 mg, 88% yield) as slight yellow oil with configuration *E:Z*>20:1. ¹H NMR (500 MHz, CDCl₃) δ 7.45 (d, *J* = 8.6 Hz, 2H), 7.42 (d, *J* = 8.6 Hz, 2H), 3.76-3.74 (m, 2H), 3.71-3.68 (m, 4H), 3.64-3.61 (m, 4H), 3.52 (t, *J* = 4.7 Hz, 2H), 2.97-2.95 (m, 4H). ¹³C NMR (125 MHz, CDCl₃) δ 162.1 (t, *J* = 27.4 Hz), 140.2 (t, *J* = 31.1 Hz), 136.0, 129.8, 129.5, 129.2, 115.2 (t, *J* = 246.0 Hz), 66.7, 66.2, 65.9, 54.4, 47.2 (t, *J* = 4.2 Hz), 43.3. ¹⁹F NMR (471 MHz, CDCl₃): δ -95.0.



Following general procedure, the crude product was purified by flash column chromatography (5:1 petroleum ether: ethyl acetate) to afford **4eae** (56.2 mg, 71% yield) as slight yellow solid with configuration *E:Z*>20:1. ¹H NMR (500 MHz, CDCl₃) δ 8.09 (br, 1H), 7.60 (d, *J* = 7.9 Hz, 2H), 7.46-7.37 (m, 6H), 7.21 (t, *J* = 7.4 Hz, 1H), 3.61-3.59 (m, 4H), 2.95 (t, *J* = 4.8 Hz, 4H). ¹³C NMR (125 MHz, CDCl₃) δ 161.4 (t, *J* = 28.9 Hz), 139.5 (t, *J* = 30.8 Hz), 136.4, 135.9, 130.1, 130.0, 129.2, 129.1, 125.4, 120.3, 114.3 (t, *J* = 251.1 Hz), 66.0, 54.2. ¹⁹F NMR (471 MHz, CDCl₃): δ -101.0. HRMS (ESI) Calcd for C₁₉H₁₈ClF₂N₃O₂ [M+H]⁺: 394.1128, found: 394.1125.



Following general procedure, the crude product was purified by flash column chromatography (30:1 petroleum ether: ethyl acetate) to afford **4eaf** (47.6 mg, 61% yield) as slight yellow solid with configuration *E:Z*>20:1. ¹H NMR (500 MHz, CDCl₃) δ 7.86 (d, *J* = 6.8 Hz, 1H), 7.64 (d, *J* = 7.5 Hz, 1H), 7.53 (d, *J* = 8.1 Hz, 2H), 7.47-7.41 (m, 4H), 3.55-3.53 (m, 4H), 2.85-2.83 (m, 4H). ¹³C NMR (125 MHz,

CDCl₃) δ 158.1 (t, *J* = 33.5 Hz), 150.7, 140.1, 139.2 (t, *J* = 32.7 Hz), 136.0, 130.3, 130.0, 129.1, 126.3, 125.0, 121.2, 115.2 (t, *J* = 240.9 Hz), 111.2, 65.9, 54.2. ¹⁹F NMR (471 MHz, CDCl₃): δ -94.7. HRMS (ESI) Calcd for C₁₉H₁₆ClF₂N₃O₂ [M+H]⁺: 392.0972, found: 392.0972.



Following general procedure, the crude product was purified by flash column chromatography (7:1 petroleum ether: ethyl acetate) to afford $5u^{2e}$ (65.7 mg, 77% yield) as yellow liquid with configuration *E*:*Z*=13:1. ¹H NMR (500 MHz, CDCl₃) δ 6.86-6.85 (m, 1H), 6.83 (d, *J* = 3.7 Hz, 1H), 4.38 (dq, *J* = 11.8, 7.1 Hz, 4H), 3.75-3.73 (m, 4H), 3.09 (t, *J* = 4.8 Hz, 4H), 1.37 (td, *J* = 7.2, 3.6 Hz, 6H). ¹³C NMR (125 MHz, CDCl₃) δ 163.0 (t, *J* = 31.2 Hz), 161.8 (t, *J* = 33.2 Hz), 145.6 (t, *J* = 33.9 Hz), 144.3, 127.4 (t, *J* = 32.0 Hz), 114.8, 113.9 (t, *J* = 248.4 Hz), 113.0 (t, *J* = 3.5 Hz), 108.3 (t, *J* = 248.0 Hz), 66.1, 63.8, 62.8, 53.8, 14.0, 13.9. ¹⁹F NMR (471 MHz, CDCl₃): δ -102.0, -102.8.

III. Large-scale reaction

A sealed tube (150 mL) was equipped with a magnetic stir bar, **1e** (5 mmol, 702 mg), **2a** (6 mmol, 612.8 mg), **3a** (10 mmol, 2.03 g), Na₂HPO₄ (7.5 mmol, 766.1 mg), MgSO₄ (1.88 g), and DMF (25 ml). The reaction mixture was stirred under Ar for 12 h at 23°C in the presence of 4×8 W blue LEDs lamb, and monitored by TLC. The reaction mixture was poured into water (300 mL) and extracted with CH₂Cl₂ (3×60 mL). The combined organic extracts were dried over anhydrous Na₂SO₄, filtered and concentrated under reduced pressure to yield the corresponding crude product, which was purified by chromatography (silica gel) to give **4e** as a white solid; yield: 1.299 g (75%). Meanwhile, organic photocatalyst 4CzIPN could be recycled in 95% yield.



IV. Synthesis and characterization of compound 7 and 9

A round flask was equipped with a magnetic stir bar, **4b** (0.2 mmol), NaOH (1M, 0.6 ml), and MeOH (0.3M, 0.6 ml). The resulting mixture was stirred overnight at room temperature. The resulting solution was added HCl (2.5M, 0.5ml), and stirred at room temperature for 8 h. The reaction mixture was extracted with CH₂Cl₂ (10 mL \times 3). The combined organic extracts were dried over anhydrous Na₂SO₄, filtered and concentrated under reduced pressure to yield the corresponding crude product, which was purified by chromatography (dichloromethane (DCM)/methyl alcohol = 50:1) to give 7.



7b (23.8 mg, 46% yield) as white solid. ¹H NMR (500 MHz, DMSO- d_6) δ 12.3 (br, 1H), 7.56 (d, J = 8.2 Hz, 2H), 7.20 (d, J = 7.9 Hz, 2H), 4.97 (s, 2H), 4.16 (t, J = 5.1 Hz, 2H), 4.09 (t, J = 5.1 Hz, 2H), 2.34 (s, 3H). ¹³C NMR (125 MHz, DMSO) δ 164.5, 152.0, 142.8, 137.8, 130.3, 129.5, 128.7, 106.7, 64.3, 63.6, 46.9, 21.3. HRMS (ESI) Calcd for C₁₄H₁₄N₂O₃ [M+H]⁺: 259.1077, found: 259.1073.



7e (23.4 mg, 42% yield) as white solid. ¹H NMR (500 MHz, DMSO-*d*₆) 12.51 (br, 1H), 7.73-7.70 (m, 2H), 7.548-7.45 (m, 2H), 4.98 (s, 2H), 4.18 (t, J = 5.1 Hz, 2H), 4.10 (t, J = 5.1 Hz, 2H). ¹³C NMR (125 MHz, DMSO) δ 164.3, 150.8, 143.0, 133.3, 132.0, 131.3, 128.2, 107.0, 64.2, 63.6, 47.0. HRMS (ESI) Calcd for C₁₃H₁₁ClN₂O₃ [M+H]⁺: 279.0531, found: 279.0528.

A round flask was equipped with a magnetic stir bar, **8b** (0.2 mmol), K_2CO_3 (1M, 0.6 ml), and MeOH (0.3M, 0.6 ml). The resulting mixture was stirred overnight at 55 °C. After the reaction was finished, the mixture was poured into 0.5M HCl to acidify to PH 1. The reaction mixture was extracted with CH₂Cl₂ (10 mL × 3). The combined organic extracts were dried over anhydrous Na₂SO₄, filtered and concentrated under reduced pressure to yield the corresponding crude product, which was purified by chromatography (dichloromethane (DCM)/methyl alcohol = 5:1) to give **9b**.



9b (36.9 mg, 86% yield) as white solid. ¹H NMR (500 MHz, DMSO-*d*₆) δ 8.02 (d, *J* = 8.0 Hz, 2H), 7.34-7.33 (m, 3H), 2.47 (s, 3H). ¹³C NMR (125 MHz, DMSO) δ 185.1 (t, *J* = 27.4 Hz), 164.9 (t, *J* = 30.5 Hz), 146.9, 130.2 (t, *J* = 2.7 Hz), 129.8, 128.2, 110.0 (t, *J* = 264.0 Hz), 21.9. HRMS (ESI) Calcd for C₁₄H₁₄N₂O₃ [M+H]⁺: 215.0514, found: 215.0515.

V Mechanism Studies

1. Fluorescence Quenching Experiment

Fluorescence spectra were collected on Cary Eclipse Fluorescence Spectrophotometer. All 4CzIPN solutions were excited at 435 nm and emission intensity at 545 nm was observed.¹ In a typical experiment, a 5×10^{-5} M solution of 4CzIPN in DMF was added to the appropriate amount of quencher in a quartz cuvette. After degassing with a stream of N_2 for 15 min, the emission spectrum of the sample was collected. I_0 and I represent the intensities of the emission in the absence and presence of the quencher at 545 nm. It might support our hypothesis on the initiation of this reaction through reductive quenching of the excited state of the photocatalyst by **2a** and **6e**.



Figure S1. Emission spectra of 5×10^{-5} M 4CzIPN at $\lambda_{ex} = 435$ nm showing the quenching effect of increasing concentrations of 4-chlorobenzaldehyde (1e).



Figure S2. The liner relationship over the increasing concentrations of 4-chlorobenzaldehyde (1e).



Figure S3. Emission spectra of 5×10^{-5} M 4CzIPN at $\lambda_{ex} = 435$ nm showing the quenching effect of increasing concentrations of morpholin-4-amine (2a).



Figure S4. The liner relationship over the increasing concentrations of morpholin-4-amine (2a).



Figure S5. Emission spectra of 5×10^{-5} M 4CzIPN at $\lambda_{ex} = 435$ nm showing the quenching effect of increasing concentrations of ethyl 2-bromo-2,2-difluoroacetate (3a).



Figure S6. The liner relationship over the increasing concentrations of ethyl 2-bromo-2,2-difluoroacetate (3a).



Figure S7. Emission spectra of 5×10^{-5} M 4CzIPN at $\lambda_{ex} = 435$ nm showing the quenching effect of increasing concentrations of 1-(4-chlorophenyl)-N-morpholinomethanimine (**6e**).



Figure S8. The liner relationship over the increasing concentrations of 1-(4-chlorophenyl)-N-morpholinomethanimine (**6e**).

2. Cyclic voltammetry experiments

Cyclic voltammetry (CV) was performed using a CHI660D potentiostat. Measurement was carried out in 0.1 M of Bu₄NPF₆/acetonitrile at a scan rate of 100 mV/s (in the range -2.0 to 2.0 V). The working electrode is a glassy carbon, the counter electrode is a Pt wire, and the reference electrode is Ag/AgCl (KCl, 3 M) with ferrocene as an external reference ($E^{0}_{1/2} = +$ 0.40 V vs SCE).



Figure S9. Blank experiment



Figure S10. CV of ferrocenium-ferrocene (Fc+/Fc) (pre-experiment)



Figure S11. CV of ferrocenium-ferrocene (Fc+/Fc) (post-experiment)



Figure S12. CV of ferrocenium-ferrocene (Fc+/Fc), (blue, pre-experiment) and (green post-experiment)



Figure S13. CV of ferrocenium-ferrocene (Fc+/Fc), (blue, pre-experiment and green post-experiment) and Blank (black)



Figure *S14*. CV of compound **2a** (red) and Blank (black); potential sweep rate was 100 mV/s. E_{ox} = 0.39 V *vs*. SCE



Figure *S15.* CV of compound **3a** (red) and Blank (black); potential sweep rate was 100 mV/s. $\text{E}_{\text{red}} = -1.08 \text{ V} vs$. SCE



Figure *S16.* CV of compound **6e** (red) and Blank (black); potential sweep rate was 100 mV/s. $\text{E}_{ox} = 1.02 \text{ V} vs$. SCE

3. Alternative Catalytic Cycle



Scheme S1. Proposed Mechanism

VI. References

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210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 f1 (ppm)



4f












4i













20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -2: f1 (ppm)

41











4n















4r























4eba



20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -2: f1 (ppm)









4eab











4eae













7b


S73



210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 f1 (ppm)