A Photo-induced C-O Bond Formation Methodology to Construct Tetrahydroxanthones

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Electronic Supplementary Material (ESI) for Chemical Communications
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### Condition Screening:

![Diagram](image)

<table>
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*Yields were determined by ¹H NMR crude analysis using CH₃Br₂ as an internal standard, unless otherwise noted. ¹Based on conversion.
A Curve of the Progress of the Reaction for the Photolysis:

![Chemical Reaction Diagram]

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\(^a\) Yields were determined by \(^1\)H NMR crude analysis using CH\(_2\)Br\(_2\) as an internal standard, unless otherwise noted. \(^b\) Based on conversion.
General Experimental Procedures:

All reactions were carried out under nitrogen except noted. Anhydrous dichloromethane (CH$_2$Cl$_2$) was distilled from calcium hydride. Tetrahydrofuran (THF) was distilled from sodium-benzophenone ketyl, and anhydrous toluene was prepared from sodium. Flash column chromatography was performed as described by Still (Still, W. C.; Kahn, M.; Mitra, A. J. Org. Chem. 1978, 43, 2923–2925), employing Qingdao Haiyang silica gel 60 (200–300 mesh). TLC analyses were performed on EMD 250 μm Silica Gel HSGF$_{254}$ plates and visualized by quenching of UV fluorescence ($\lambda_{max}$ = 254 nm), or by staining ceric ammonium molybdate, ammonium molybdate, or potassium permanganate. $^1$H and $^{13}$C NMR spectra were recorded on a Bruker-500, 400 spectrometer. Chemical shifts for $^1$H and $^{13}$C NMR spectra are reported in ppm (δ) relative to residue protium in the solvent (CDCl$_3$: δ 7.26, 77.00 ppm;) and the multiplicities are presented as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. High-resolution mass spectra (HRMS) were acquired on a waters GCT premier. The photo reactor used for this photolysis is Rayonet RPR-200 (Southern New England Ultraviolet Company).

General procedure for the preparation of substrates:

S2 and S3 were prepared according to the known procedure.$^{[1,2]}$

To a solution of Brominated (1.0 ~ 1.5 equiv.) in dry THF was added $n$-BuLi (1.0 ~ 1.5 equiv.) at 0 °C ~ -83 °C dropwised. After about 10 min ~ 1 h, aldehyde (1.0 equiv.) in dry THF was added dropwised at the same temperature. TLC monitored the reaction and showed all aldehyde was consumed, the reaction was quenched with water. It was extracted with EtOAc, and the organic layer was washed with water and brine. The combined organic phase was dried over Na$_2$SO$_4$,
filtered, concentrated, and purified by silica gel column chromatography to give the corresponding alcohol.

To a solution of fresh prepared alcohol (1.0 equiv.) in dry CH₂Cl₂ was added DMP (1.5 equiv.) at 25 °C. After stirring for 5 min, water solution (1 μL water / 1 mL CH₂Cl₂) was added. TLC showed all alcohol was consumed, CH₂Cl₂ was evaporated, then EtOAc and an aqueous solution of 1:1 10% Na₂S₂O₃ to saturated NaHCO₃ was then added. After stirring for another 10 min, the biphasic mixture was extracted with EtOAc, the combined organic phase was washed with saturated NaHCO₃ and brine, dried over Na₂SO₄, filtered, concentrated, and purified by silica gel column chromatography to give the precursor of the photolysis.

To a solution of S₄ (1.40 g, 7.5 mmol, 1.5 equiv.) in dry THF (40 mL) was added n-BuLi (3.1 mL, 1.6 M solution in pentane, 5.0 mmol, 1.0 equiv.) dropwise at -20 °C. After 0.5 h, S₂ (0.72 g, 5.0 mmol, 1.0 equiv.) was added dropwise. After about 2 h, TLC showed all S₂ was consumed; the reaction was quenched with water (10 mL). It was extracted with EtOAc (15 mL × 3), and the organic layer was washed with water (25 mL) and brine (25 mL). The organic phase was dried over Na₂SO₄, filtered, concentrated, and purified by silica gel column chromatography (2 % ~ 5 % ethyl acetate–hexanes) to give S₅ as a colorless liquid (0.94 g).

To a solution of the S₅ (0.94 g, 4.2 mmol, 1.0 equiv.) in dry CH₂Cl₂ (30 mL) was added DMP (2.7 g, 6.3 mmol, 1.5 equiv.) at 25 °C. After stirring for 5 min, water solution (1 μL water /1 mL CH₂Cl₂, 30 μL) was added. After about 10 min, TLC showed all S₅ was consumed, CH₂Cl₂ was evaporated, then EtOAc (20 mL) and an aqueous solution of 1:1 10% Na₂S₂O₃ to saturated NaHCO₃ (20 mL) was then added. After stirring for another 10 min, the biphasic mixture was extracted with EtOAc (15 mL × 3), the combined organic phase was washed with saturated NaHCO₃ (20 mL), brine (20 mL), dried over Na₂SO₄, filtered, concentrated, and purified by silica gel column chromatography.
Enone 1d was prepared using the general procedure (using the t-BuLi instead of n-BuLi) in 57% yield over 2 steps, purified by silica gel column chromatography (1% ethyl acetate-petroleum ether) as a colorless liquid. RT = 0.39 (5% ethyl acetate-petroleum ether). 1H NMR (400 MHz, CDCl3) δ 7.71 (dd, J = 7.7, 1.5 Hz, 1H), 7.48 (td, J = 8.1, 1.2 Hz, 1H), 7.02 (t, J = 7.5 Hz, 1H), 6.95 (d, J = 8.4 Hz, 1H), 3.87 (s, 3H), 2.78 – 2.15 (m, 4H), 1.84 – 1.67 (m, 4H) ppm. 13C NMR (100 MHz, CDCl3) δ 196.7, 159.0, 136.8, 133.9, 131.2, 129.1, 127.5, 120.8, 111.8, 56.0, 33.7, 28.0, 23.5, 21.7 ppm. MS (m/z): EI [M] calcd for C130H15O2Cl [M]+: 250, Found 250 (15%), 235 (2%), 215 (40%).

Enone 1b was prepared using the general procedure (using the t-BuLi instead of n-BuLi) in 57% yield over 2 steps, purified by silica gel column chromatography (1% ethyl acetate-petroleum ether) as a colorless liquid. RT = 0.39 (5% ethyl acetate-petroleum ether). 1H NMR (400 MHz, CDCl3) δ 7.48 (dd, J = 7.7, 1.7 Hz, 1H), 7.34 (td, J = 8.2, 1.8 Hz, 1H), 6.98 (t, J = 8.2 Hz, 1H), 6.86 (d, J = 7.7 Hz, 1H), 2.52 – 2.34 (m, 4H), 1.86 – 1.64 (m, 4H), 0.99 (s, 9H), 0.24 (s, 6H) ppm. 13C NMR (100 MHz, CDCl3) δ 196.4, 154.7, 135.4, 133.0, 132.9, 131.1, 130.1, 121.0, 120.5, 34.3, 28.3, 25.8 (3C), 23.3, 21.5, 18.4, -4.1 (2C) ppm. MS (m/z): ESI [M] calcd for C19H22O2ClSi [M]+: 350, Found 351 [M+H]+.

Enone 1e was prepared using the general procedure in 47% yield over 2 steps, purified by silica gel column chromatography (1% ~ 2% ethyl acetate-petroleum ether) as a white solid. RT = 0.22 (5% ethyl acetate-petroleum ether). 1H NMR (400 MHz, CDCl3) δ 7.75 (dd, J = 7.7, 1.7 Hz, 1H), 7.52 – 7.32 (m, 6H), 7.08 – 6.98 (m, 2H), 5.08 (s, 2H), 2.29 – 2.21 (m, 2H), 2.21 – 2.12 (m, 2H), 1.47 – 1.31 (m, 4H) ppm. 13C NMR (100 MHz, CDCl3) δ 196.6, 158.0, 136.8, 136.2, 133.8, 131.2, 129.5, 128.6 (2C), 128.3, 128.0 (3C), 121.0, 112.4, 70.8, 33.6, 27.9, 22.9, 21.1 ppm. HRMS (m/z): EI [M] calcd for C20H15O2Cl [M]+: 326.1074, Found 326.1080.

Enone 1f was prepared using the general procedure in 72% yield over 2 steps, purified by silica gel column chromatography (2% ~ 3% ethyl acetate-petroleum ether) as a white solid. RT = 0.37 (10% ethyl acetate-petroleum ether). 1H NMR (400 MHz, CDCl3) δ 7.69 (dd, J = 7.7, 1.7 Hz, 1H), 7.47 – 7.41 (m, 1H), 7.15 (d, J = 8.3 Hz, 1H), 7.07 (t, J = 7.5 Hz, 1H), 5.21 (s, 2H), 3.49 (s, 3H), 2.45 – 2.37 (m, 4H), 1.83 – 1.69 (m, 4H) ppm. 13C NMR (100 MHz,
Enone 1a was prepared from enone 1b. **Procedure:** To a solution of enone 1b (250.5 mg, 0.7 mmol) in CH₃CN (5 mL) was added 40 % HF aqueous solution (500 μL) at 45 °C. After 1 h, TLC showed all enone 1b was consumed, it was quenched by TMSOMe (2 mL), and saturated NaHCO₃ was added until no gas generated, then extracted with EtOAc (20 mL), the combined organic phase was washed with saturated NaHCO₃ (10 mL) and brine (10 mL), dried over Na₂SO₄, filtered, concentrated, and purified by silica gel column chromatography (20 % ~ 25 % dichloromethane-petroleum ether) as a white solid (168.7 mg, 100 %). Rf = 0.41 (50 % toluene-petroleum ether). ¹H NMR (400 MHz, CDCl₃) δ 11.90 (s, 1H), 7.60 (dd, J = 8.0, 1.6 Hz, 1H), 7.53 – 7.47 (m, 1H), 7.01 (d, J = 8.4 Hz, 1H), 6.91 (t, J = 7.6 Hz, 1H), 2.53 – 2.45 (m, 2H), 2.40 – 2.32 (m, 2H), 1.92 – 1.82 (m, 2H), 1.82 – 1.74 (m, 2H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 202.9, 163.1, 136.9, 133.2, 132.4, 130.2, 119.2, 118.4, 118.0, 32.9, 28.8, 23.3, 21.3 ppm. MS (M/Z): EI [M] calcd for C₁₃H₁₃O₂Cl [M]+: 236, Found 236 (2 %) 201 (100 %) 121 (21 %).

Enone 1c was prepared from enone 1a. **Procedure:** To a solution of enone 1a (222.3 mg, 0.94 mmol) in CH₂Cl₂ was added NEt₃ (197 μL, 1.4 mmol, 1.5 equiv.) at 0 °C, then added CH₃COCl (80 μL, 1.1 mmol, 1.2 equiv.) dropwise, then warmed to r.t. After TLC showed all enone 1a was consumed, it was quenched by NH₄Cl, then extracted with EtOAc (20 mL), the combined organic phase was washed with saturated NH₄Cl (10 mL) and brine (10 mL),
dried over Na₂SO₄, filtered, concentrated, and purified by silica gel column chromatography (5 % ethyl acetate-petroleum ether) as a white solid (219.4 mg, 84 %). \( R_t = 0.18 \) (10 % ethyl acetate-petroleum ether). \( ^1\)H NMR (400 MHz, CDCl₃) δ 7.73 (dd, \( J = 7.7, 1.6 \) Hz, 1H), 7.56 (td, \( J = 8.0, 1.7 \) Hz, 1H), 7.37 – 7.30 (m, 1H), 7.14 (d, \( J = 7.4 \) Hz, 1H), 2.50 – 2.43 (m, 2H), 2.38 – 2.32 (m, 5H), 1.85 – 1.78 (m, 2H), 1.76 – 1.69 (m, 2H) ppm. \( ^{13}\)C NMR (100 MHz, CDCl₃) δ 195.3, 169.3, 149.7, 135.1, 133.7, 132.1, 131.6, 129.2, 126.1, 123.9, 33.7, 28.4, 23.4, 21.4, 21.0 ppm. HRMS (M/Z): EI [M] calcd for C₁₅H₁₅O₃Cl [M]⁺: 278.0710, Found 278.0712.

Enone S₆ was prepared using the general procedure in 55 % yield over 2 steps, purified by silica gel column chromatography (2 % ~ 3 % ethyl acetate-petroleum ether) as a colorless liquid. \( R_t = 0.27 \) (10 % ethyl acetate-petroleum ether). \( ^1\)H NMR (400 MHz, CDCl₃) δ 7.25 (d, \( J = 3.2 \) Hz, 1H), 7.04 (dd, \( J = 9.0, 3.2 \) Hz, 1H), 6.89 (d, \( J = 9.0 \) Hz, 1H), 3.82 (s, 3H), 3.80 (s, 3H), 2.48 – 2.30 (m, 4H), 1.86 – 1.64 (m, 4H) ppm. \( ^{13}\)C NMR (100 MHz, CDCl₃) δ 196.3, 153.7, 153.6, 137.0, 128.6, 127.9, 120.6, 114.3, 113.7, 56.75, 55.8, 33.6, 28.0, 23.5, 21.7 ppm. HRMS (m/z): EI [M] calcd for C₁₅H₁₇O₃Cl [M]⁺: 280.0866, Found 280.0867.

Enone S₇ was prepared using the general procedure in 25 % yield over 2 steps, purified by silica gel column chromatography (2 % ~ 3 % ethyl acetate-petroleum ether) as a white solid. \( R_t = 0.42 \) (10 % ethyl acetate-petroleum ether). \( ^1\)H NMR (400 MHz, CDCl₃) δ 7.38 (dd, \( J = 8.6, 3.2 \) Hz, 1H), 7.16 (ddd, \( J = 9.0, 7.6, 3.2 \) Hz, 1H), 6.89 (d, \( J = 9.0, 4.0 \) Hz, 1H), 3.84 (s, 3H), 2.54 – 2.21 (m, 4H), 1.90 – 1.62 (m, 4H) ppm. \( ^{13}\)C NMR (100 MHz, CDCl₃) δ 195.4 (d, \( J = 1.4 \) Hz), 156.9 (d, \( J = 240.4 \) Hz), 155.1 (d, \( J = 1.8 \) Hz), 136.3, 130.0, 128.8 (d, \( J = 5.9 \) Hz), 120.1 (d, \( J = 23.4 \) Hz), 116.9 (d, \( J = 24.0 \) Hz), 113.3 (d, \( J = 7.5 \) Hz), 56.6, 33.7, 27.9, 23.4, 21.6 ppm. HRMS (M/Z): EI [M] calcd for C₁₄H₁₄O₂FCl [M]⁺: 268.0666, Found 268.0667.

Enone S₈ was prepared using the general procedure in 42 % yield over 2 steps, purified by silica gel column chromatography (2 % ~ 3 % ethyl acetate-petroleum ether) as a colorless liquid. \( R_t = 0.47 \) (10 % ethyl acetate-petroleum ether). \( ^1\)H NMR (400 MHz, CDCl₃) δ 7.62 (d, \( J = 2.7 \) Hz, 1H), 7.41 (dd, \( J = 8.8, 2.7 \) Hz, 1H), 6.88 (d, \( J = 8.8 \) Hz,
Enone S9 was prepared using the general procedure in 58 % yield over 2 steps, purified by silica gel column chromatography (2 % ~ 3 % ethyl acetate-petroleum ether) as a colorless liquid. $R_f = 0.47$ (10 % ethyl acetate-petroleum ether). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.52 (d, $J = 2.2$ Hz, 1H), 7.27 (dd, $J = 8.4$, 2.2 Hz, 1H), 6.84 (d, $J = 8.4$ Hz, 1H), 3.83 (s, 3H), 2.42 – 2.34 (m, 4H), 2.31 (s, 3H), 1.87 – 1.68 (m, 4H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$) δ 196.7, 157.1, 137.0, 134.6, 131.2, 130.2, 128.6, 127.2, 112.0, 56.1, 33.6, 28.0, 23.5, 21.7, 20.3 ppm. HRMS (m/z): EI [M] calcd for C$_{14}$H$_{14}$O$_2$Cl [M]$^+$: 284.0371, Found 284.0369.

Enone S10 was prepared using almost the general procedure (the equiv. of DMP is 4 instead of 1.5) in 18 % yield over 2 steps, purified by silica gel column chromatography (70 % dichloromethane-petroleum ether) as a white solid. $R_f = 0.26$ (pure dichloromethane). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.88 (d, $J = 2.0$ Hz, 1H), 7.72 (dd, $J = 8.7$, 2.0 Hz, 1H), 7.01 (d, $J = 8.7$ Hz, 1H), 3.92 (s, 3H), 2.51 – 2.34 (m, 4H), 1.85 – 1.68 (m, 4H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$) δ 194.5, 161.2, 137.0, 134.6, 131.2, 130.2, 128.6, 127.2, 112.0, 56.1, 33.6, 28.0, 23.5, 21.7, 20.3 ppm. HRMS (m/z): EI [M] calcd for C$_{15}$H$_{17}$O$_2$NCl [M]$^+$: 264, Found 264 (30 %) 249 (28 %) 149 (100 %).

Enone S11 was prepared using the general procedure in 59 % yield over 2 steps, purified by silica gel column chromatography (15 % ~ 20 % ethyl acetate-petroleum ether) as a white solid. $R_f = 0.26$ (20 % ethyl acetate-petroleum ether). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.91 (d, $J = 2.1$ Hz, 2H), 7.69 (dd, $J = 8.6$, 2.1 Hz, 2H), 7.00 (d, $J = 8.6$ Hz, 2H), 3.89 (s, 6H), 2.47 – 2.30 (m, 8H), 1.85 – 1.66 (m, 8H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$) δ 196.4 (2 C), 158.3 (2 C), 136.8 (2 C), 132.5 (2 C), 131.9 (2 C), 129.3 (2 C), 128.9 (2 C), 128.4 (2 C), 127.2 (2 C), 112.0 (2 C), 104.5 (2 C), 56.3, 34.0, 27.8, 23.3, 21.5 ppm. HRMS (M/Z): EI [M] calcd for C$_{15}$H$_{17}$NO$_2$Cl [M]$^+$: 275.0714, Found 275.0713.

S10
Enone S12 was prepared using the general procedure in 49 % yield over 2 steps, purified by silica gel column chromatography (2 % ~ 4 % ethyl acetate-petroleum ether) as a white solid. $R_f = 0.46$ (10 % ethyl acetate-petroleum ether). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.92 (d, $J = 1.8$ Hz, 1H), 7.70 (dd, $J = 8.7$, 1.8 Hz, 1H), 7.02 (d, $J = 8.7$ Hz, 1H), 3.91 (s, 3H), 2.46 - 2.31 (m, 4H), 1.87 - 1.54 (m, 4H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 195.3, 160.8, 136.0, 131.0, 130.5 (q, $J = 3.5$ Hz), 128.3, 128.1 (q, $J = 3.7$ Hz), 123.9 (d, $J = 271.5$ Hz), 123.2 (q, $J = 33.4$ Hz), 111.8, 56.2, 33.9, 27.9, 23.4, 21.6 ppm. HRMS (M/Z): EI [M] calcd for C$_{28}$H$_{28}$O$_4$Cl$_2$ [M$^+$]: 498.1365, Found 498.1368.

Substrate S15 was prepared from S13 in 98 % yield over 2 steps. **Procedure: Step 1:** To a solution of S13 (1.1242 g, 5 mmol, 1 equiv.) in MeOH (25 mL) was added NaBH$_4$ (237 mg, 6 mmol, 1.2 equiv.) at 26 °C, after 15 min, TLC showed S13 was completely consumed, it was quenched by saturated NH$_4$Cl, MeOH was evaporated, extracted with EtOAc (20 mL), washed with brine (20 mL), dried over Na$_2$SO$_4$, filtered, concentrated, and the crude product was used in the next step without purification. **Step 2:** To a solution of S14 in CH$_2$Cl$_2$ (30 mL) was added imidazole (890 mg, 13 mmol, 2.5 equiv.) and TBSCI (946 mg, 6.3 mmol, 1.2 equiv.) at 26 °C, after 15 min, TLC showed All S14 was completely consumed, it was quenched by saturated NH$_4$Cl, extracted with EtOAc (30 mL), washed with brine (20 mL), dried over Na$_2$SO$_4$, filtered, concentrated, and purified by silica gel column chromatography (2 % ethyl acetate-petroleum ether) as a white solid (1.696 g, 98 %). $R_f = 0.67$ (10 % ethyl acetate-petroleum ether). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.50 (d, $J = 1.8$ Hz, 1H), 7.22 (dd, $J = 8.4$, 1.8 Hz, 1H), 6.86 (d, $J = 8.4$ Hz, 1H), 4.65 (s, 2H), 3.88 (s, 3H), 0.93 (s, 9H), 0.09 (s, 6H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 154.8, 135.1, 131.7, 128.9, 128.1 (q, $J = 3.7$ Hz), 123.9 (d, $J = 271.5$ Hz), 123.2 (q, $J = 33.4$ Hz), 111.8, 56.2, 33.9, 27.9, 23.4, 21.6 ppm. HRMS (M/Z): EI [M] calcd for C$_{15}$H$_{14}$O$_2$F$_3$Cl [M$^+$]: 318.0634, Found 318.0635.
Enone S16 was prepared using the general procedure in 70 % yield over 2 steps, purified by silica gel column chromatography (2 % ~ 3 % ethyl acetate-petroleum ether) as a white solid. \( R_t = 0.53 \) (10 % ethyl acetate-petroleum ether). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.64 (d, \( J = 1.9 \) Hz, 1H), 7.46 (dd, \( J = 8.5, 1.9 \) Hz, 1H), 6.93 (d, \( J = 8.5 \) Hz, 1H), 4.70 (s, 2H), 3.86 (s, 3H), 2.52 - 2.26 (m, 4H), 1.91 – 1.65 (m, 4H), 0.93 (s, 9H), 0.08 (s, 6H) ppm. \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 196.5, 158.5, 136.7, 133.4, 132.9, 129.7, 129.3, 127.5, 112.1, 64.4, 56.1, 33.7, 28.0, 23.5, 21.7 ppm. MS (M/Z): ESI [M] calcd for C\(_{14}\)H\(_{23}\)BrO\(_2\)Si [M]+: 330, Found 330 (4 %) 273 (63 %) 199 (100 %).

Enone S16 was prepared using the general procedure in 70 % yield over 2 steps.

Enone S17 was prepared from enone S16. **Procedure:** To a solution of enone S16 (379.2 mg, 0.96 mmol) in C\(_2\)H\(_5\)OH (2 mL) was added 1 % HCl-C\(_2\)H\(_5\)OH (5 mL) at 29 °C. After 15 min, TLC showed all enone S16 was consumed, saturated NaHCO\(_3\) was added until no gas generated, then extracted with EtOAc (30 mL), the combined organic phase was washed with saturated NaHCO\(_3\) (10 mL) and brine (10 mL), dried over Na\(_2\)SO\(_4\), filtered, concentrated, and purified by silica gel column chromatography (30 ~ 35 % ethyl acetate-petroleum ether) as a light yellow liquid (252.4 mg, 94 %). \( R_t = 0.4 \) (40 % ethyl acetate-petroleum ether). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.69 (s, 1H), 7.51 (d, \( J = 8.4 \) Hz, 1H), 6.95 (d, \( J = 8.4 \) Hz, 1H), 4.66 (s, 2H), 3.87 (s, 3H), 2.45 – 2.34 (m, 4H), 1.84 – 1.69 (m, 4H) ppm. \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 196.5, 158.5, 136.7, 133.4, 132.9, 129.7, 129.3, 127.5, 112.1, 64.4, 56.1, 33.7, 28.0, 23.5, 21.7 ppm. HRMS (M/Z): ESI [M] calcd for C\(_{15}\)H\(_{17}\)O\(_3\)Cl [M]+: 280.0866, Found 280.0863.
Enone **S18** was prepared from enone **S17**. **Procedure**: To a solution of enone **S17** (125.2 mg, 0.45 mmol, 1 equiv.) in CH$_2$Cl$_2$ (10 mL) was added MnO$_2$ (390 mg, 4.5 mmol, 10 equiv.) at 30 °C. After 40 h, TLC showed all enone **S17** was consumed, it was filtered through celite, washed with EtOAc, concentrated, and purified by silica gel column chromatography (15 % ethyl acetate-petroleum ether) as a light yellow solid (252.4 mg, 94 %). $R_f = 0.34$ (20 % ethyl acetate-petroleum ether). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.90 (s, 1H), 8.12 (d, $J = 2.0$ Hz, 1H), 7.99 (dd, $J = 8.6$, 2.0 Hz, 1H), 7.06 (d, $J = 8.6$ Hz, 1H), 3.94 (s, 3H), 2.45–2.33 (m, 4H), 1.93–1.57 (m, 4H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 195.4, 190.2, 163.0, 135.9, 134.3, 133.3, 131.5, 129.7, 128.7, 112.0, 56.3, 33.9, 27.9, 23.4, 21.6 ppm. HRMS (M/Z): EI [M] calcd for C$_{13}$H$_{15}$O$_3$Cl [M]$^+$: 278.0710, Found 278.0709.

Enone **S19** was prepared from enone **S18**$^{[3]}$. **Procedure**: To a solution of enone **S18** (76.4 mg, 0.27 mmol, 1 equiv.) in MeOH (2 mL) was added KOH (92.1 mg, 1.64 mmol, 6 equiv.) and I$_2$ (208.7 mg, 0.82 mmol, 3 equiv.) at 0 °C. After 20 min, TLC showed all enone **S18** was consumed, it was quenched by an aqueous solution of 1:1 10% Na$_2$S$_2$O$_3$ to saturated NaHCO$_3$ (5 mL) then extracted with EtOAc (20 mL), washed with brine (10 mL), dried over Na$_2$SO$_4$, filtered, concentrated and purified by silica gel column chromatography (12 % ethyl acetate-petroleum ether) as a white solid (252.4 mg, 94 %). $R_t = 0.36$ (20 % ethyl acetate-petroleum ether). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.30 (d, $J = 2.2$ Hz, 1H), 8.14 (dd, $J = 8.7$, 2.2 Hz, 1H), 6.97 (d, $J = 8.7$ Hz, 1H), 3.91 (s, 3H), 3.89 (s, 3H), 2.60–2.29 (m, 4H), 1.83–1.67 (m, 4H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 195.7, 166.1, 161.9, 136.1, 135.0, 132.5, 131.0, 128.0,
Enone S20 was prepared using the general procedure in 52 % yield over 2 steps, purified by silica gel column chromatography (3 % ethyl acetate-petroleum ether) as a colorless liquid. $R_f = 0.48$ (10 % ethyl acetate-petroleum ether). $^1H$ NMR (400 MHz, CDCl$_3$) $\delta$ 8.25 – 8.21 (m, 1H), 7.88 – 7.83 (m, 1H), 7.74 (d, $J = 8.6$ Hz, 1H), 7.64 (d, $J = 8.6$ Hz, 1H), 7.61 – 7.52 (m, 2H), 4.03 (s, 3H), 2.53 – 2.44 (m, 4H), 1.92 – 1.73 (m, 4H) ppm. $^{13}C$ NMR (100 MHz, CDCl$_3$) $\delta$ 196.4, 157.6, 137.1, 137.0, 130.7, 128.4, 128.1 (2C), 126.5 (2C), 126.1, 124.1, 123.6, 63.8, 28.4, 23.5, 21.8 ppm. MS (M/Z): EI [M] calcd for C$_{16}$H$_{17}$O$_4$Cl [M]$^+$: 308, Found 308 (20 %) 293 (5 %) 249 (87 %).

Enone S21 was prepared using the general procedure in 30 % yield over 2 steps, purified by silica gel column chromatography (40 % ethyl acetate-petroleum ether) as a white solid. $R_f = 0.38$ (2 % methanol-dichloromethane). $^1H$ NMR (400 MHz, CDCl$_3$) $\delta$ 8.70 (s, 1H), 8.55 (d, $J = 5.0$ Hz, 1H), 6.86 (d, $J = 5.8$ Hz, 1H), 3.91 (d, $J = 0.8$ Hz, 3H), 2.39 (d, $J = 5.8$ Hz, 4H), 1.74 (dd, $J = 25.3$, 5.7 Hz, 4H) ppm. $^{13}C$ NMR (100 MHz, CDCl$_3$) $\delta$ 195.0, 164.3, 154.3, 152.1, 135.7, 131.8, 123.8, 107.0, 55.8, 33.9, 27.9, 23.4, 21.6 ppm. MS (M/Z): EI [M] calcd for C$_{13}$H$_{14}$NO$_2$Cl [M]$^+$: 251, Found 251 (34 %) 236 (25 %) 216 (58 %).

Enone S22 was prepared using the general procedure in 43 % yield over 2 steps, purified by silica gel column chromatography (8 % ~ 12 % ethyl acetate-petroleum ether) as a yellow liquid. $R_f = 0.53$ (20 % ethyl acetate-petroleum ether). $^1H$ NMR (400 MHz, CDCl$_3$) $\delta$ 8.25 – 8.21 (m, 1H), 7.88 – 7.84 (m, 1H), 7.65 (s, 2H), 7.63 – 7.54 (m, 2H), 4.51 (t, $J = 2.4$ Hz, 2H), 4.03 (s, 3H), 3.97 (t, $J = 5.6$ Hz, 2H), 2.66 – 2.56 (m, 2H) ppm. $^{13}C$ NMR (100 MHz, CDCl$_3$) $\delta$ 193.8, 157.2, 137.0, 135.8, 130.1, 128.5, 128.1, 127.9, 127.0, 126.6, 125.6, 124.2, 123.5, 67.2, 64.8, 64.0, 33.6 ppm. MS (M/Z): EI [M] calcd for C$_{17}$H$_{15}$O$_3$Cl [M]$^+$: 302, Found 302 (76 %) 267 (24 %) 185 (100 %).
Enone S23 was prepared using the general procedure in 27% yield over 2 steps, purified by silica gel column chromatography (50% ethyl acetate-petroleum ether) as a white solid. $R_f = 0.28$ (50% ethyl acetate-petroleum ether). $^1$H NMR (400 MHz, CDCl$_3$) δ 8.62 (s, 1H), 8.57 (d, $J = 5.9$ Hz, 1H), 6.86 (d, $J = 5.9$ Hz, 1H), 4.43 (t, $J = 2.4$ Hz, 2H), 3.92 (s, 3H), 3.88 (t, $J = 5.6$ Hz, 2H), 2.55 – 2.49 (m, 2H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$) δ 192.2, 164.0, 154.3, 151.2, 134.6, 131.8, 124.8, 106.9, 66.7, 64.7, 55.9, 33.7 ppm. MS (M/Z): EI [M] calcd for C$_{12}$H$_{12}$NO$_3$Cl $[M]^+$: 253, Found 253 (19%) 218 (30%) 136 (100%).

Enone S24 was prepared using the general procedure in 29% yield over 2 steps, purified by silica gel column chromatography (5% ethyl acetate-petroleum ether) as a white solid. $R_f = 0.22$ (50% dichloromethane-petroleum ether). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.29 (dd, $J = 8.4$, 3.1 Hz, 1H), 7.21 – 7.14 (m, 1H), 6.90 (dd, $J = 9.0$, 3.9 Hz, 1H), 4.42 (s, 2H), 3.90 (t, $J = 5.5$ Hz, 2H), 3.85 (s, 3H), 2.57 – 2.48 (m, 2H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$) δ 192.8, 156.9 (d, $J = 240.9$ Hz), 154.7 (d, $J = 1.9$ Hz), 135.2, 129.6, 129.4 (d, $J = 6.2$ Hz), 120.0 (d, $J = 23.4$ Hz), 116.4 (d, $J = 24.2$ Hz), 113.0 (d, $J = 7.5$ Hz), 66.8, 64.7, 56.6, 33.5 ppm. MS (M/Z): EI [M] calcd for C$_{13}$H$_{12}$O$_3$FCl $[M]^+$: 270, Found 270 (16%) 235 (26%) 153 (100%).

Enone S25 was prepared using the general procedure in 34% yield over 2 steps, purified by silica gel column chromatography (6% ~ 8% ethyl acetate-petroleum ether) as a white solid. $R_f = 0.33$ (10% ethyl acetate-petroleum ether). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.52 (d, $J = 2.7$ Hz, 1H), 7.41 (dd, $J = 8.8$, 2.7 Hz, 1H), 6.88 (d, $J = 8.8$ Hz, 1H), 4.42 (t, $J = 2.5$ Hz, 2H), 3.89 (t, $J = 5.6$ Hz, 2H), 3.85 (s, 3H), 2.56 – 2.48 (m, 2H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$) δ 192.6, 157.0, 135.0, 133.2, 130.1, 129.8, 129.7, 126.2, 113.1, 66.8, 64.7, 56.3, 33.6 ppm. MS (M/Z): EI [M] calcd for C$_{13}$H$_{12}$O$_3$Cl $[M]^+$: 286, Found 286 (13%) 251 (27%) 169 (100%).

Enone S26 was prepared using the general procedure in 20% yield over 2 steps, purified by silica gel column chromatography (5% ~ 8% ethyl acetate-petroleum ether) as a white solid. $R_f = 0.41$ (20% ethyl acetate-petroleum ether). $^1$H NMR (400
MHz, CDCl\textsubscript{3} δ 7.41 (d, J = 2.1 Hz, 1H), 7.30 – 7.25 (dd, J = 8.4, 2.1 Hz, 1H), 6.83 (d, J = 8.4 Hz, 1H), 4.40 (t, J = 2.4 Hz, 2H), 3.89 (t, J = 5.5 Hz, 2H), 3.83 (s, 3H), 2.54 – 2.45 (m, 2H), 2.30 (s, 3H) ppm. $^{13}$C NMR (100 MHz, CDCl\textsubscript{3}) δ 194.1, 156.8, 135.9, 134.5, 130.6, 130.3, 127.8 (2C), 111.7, 66.9, 64.7, 56.1, 33.4, 20.2 ppm. MS (M/Z): EI [M] calcd for C\textsubscript{14}H\textsubscript{15}O\textsubscript{2}Cl [M]+: 266, Found 266 (15 %) 231 (29 %) 149 (100 %).

Enone S27 was prepared using the general procedure in 12 % yield over 2 steps, purified by silica gel column chromatography (25 % ~ 35 % ethyl acetate-petroleum ether) as a white solid. $R_f = 0.31$ (30 % ethyl acetate-petroleum ether). $^1$H NMR (400 MHz, CDCl\textsubscript{3}) δ 7.79 (d, J = 2.4 Hz, 2H), 7.69 (dd, J = 8.6, 2.4 Hz, 2H), 7.01 (d, J = 8.6 Hz, 2H), 4.45 (t, J = 2.3 Hz, 4H), 3.95 – 3.88 (m, 10H), 2.59 – 2.48 (m, 4H) ppm. $^{13}$C NMR (100 MHz, CDCl\textsubscript{3}) δ 193.9 (2 C), 158.0 (2 C), 135.6 (2 C), 132.7 (2 C), 131.9 (2 C), 129.0 (2 C), 128.6 (2 C), 128.3 (2 C), 112.2 (2 C), 66.9 (2 C), 64.8 (2 C), 56.2 (2 C), 33.5 (2 C) ppm. HRMS (M/Z): EI [M] calcd for C\textsubscript{26}H\textsubscript{24}O\textsubscript{6}Cl\textsubscript{2} [M]+: 502.0950, Found 502.0953.

**General procedure for the photoysis of substrates:**

To a solution of substrate in a co-solvent of acetonitrile/H\textsubscript{2}O (9:1, v/v) (0.01 M) in quartz tube was added the base TMP (1.0 equiv.). After homogeneous mixing, the solution was photolyzed at r.t. in a Rayonet chamber reactor at 300 nm for 25 min ~ 70 min shown in table 3. TLC showed all substrate consumed, then CH\textsubscript{3}CN was evaporated, an saturated NH\textsubscript{4}Cl solution was added, then extracted with EtOAc, the combined organic phase was washed with brine, dried over Na\textsubscript{2}SO\textsubscript{4}, filtered, concentrated, and purified by silica gel column chromatography to give corresponding products.
To a solution of substrate in a co-solvent of acetonitrile/H$_2$O (9:1, v/v) (0.01 M) in quartz tube was added the base TMP (1.0 equiv.). After all substrate dissolved, the solution was photolyzed at r.t. in a Rayonet chamber reactor at 300 nm for 40 min. TLC showed all 1d consumed, then CH$_3$CN was evaporated, an saturated NH$_4$Cl solution was added, then extracted with EtOAc (10 mL), the combined organic phase was washed with brine (10 mL), dried over Na$_2$SO$_4$, filtered, concentrated, and purified by silica gel column chromatography (1 % acetone-petroleum ether). The product 3 was generated in 78 % yield as a white solid (37.8 mg). $R_f$ = 0.25 (10 % ethyl acetate-petroleum ether).

$^{1}$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.20 (dd, $J$ = 8.0, 1.6 Hz, 1H), 7.61 (ddd, $J$ = 8.6, 7.1, 1.7 Hz, 1H), 7.43 – 7.30 (m, 2H), 2.68 (t, $J$ = 6.4 Hz, 2H), 2.58 (t, $J$ = 6.2 Hz, 2H), 1.88 (m, 2H), 1.82 – 1.72 (m, 2H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 177.6, 163.7, 155.8, 132.8, 125.6, 124.3, 123.0, 118.3, 117.5, 28.1, 21.8, 21.5, 20.9 ppm. The NMR data is same as reported. $^4$ MS (M/Z): EI [M]$^+$ calcd for C$_{13}$H$_{12}$O$_2$ [M]$^+$: 200, Found 200 (86 %) 199 (100 %) 185 (72 %).

Ketone 5 was prepared according to the general procedure in 69 % yield. The reaction time is 40 min under 300 nm light. The product was isolated through silica gel flash chromatography (2 % ~ 4 % ethyl acetate-petroleum ether) as a white solid (47.3 mg): $R_f$ = 0.39 (10 % ethyl acetate-petroleum ether). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.96 (d, $J$ = 2.2 Hz, 1H), 7.40 (dd, $J$ = 8.5, 2.2 Hz, 1H), 7.26 (d, $J$ = 8.5 Hz, 1H), 2.65 (t, $J$ = 6.3 Hz, 2H), 2.57 (t, $J$ = 6.2 Hz, 2H), 2.43 (s, 3H), 1.89 – 1.82 (m, 2H), 1.79 – 1.71 (m, 2H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 177.8, 163.6, 154.2, 134.1, 134.1, 125.0, 122.8, 118.2, 117.3, 28.1, 21.9, 21.7, 21.0, 20.9 ppm. MS (m/z): EI [M]$^+$ calcd for C$_{14}$H$_{14}$O$_2$ [M]$^+$: 214, Found 214 (85 %) 213 (100 %) 199 (57 %).

Ketone 6 was prepared according to the general procedure in 72 % yield. The reaction time is 40 min under 300 nm light. The product was isolated through silica gel flash chromatography (1 % acetone-petroleum ether) as a white solid (50.1 mg): $R_f$ = 0.10 (10 % ethyl acetate-petroleum ether). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.54 (d, $J$ = 3.0 Hz, 1H), 7.30...
Ketone 7 was prepared according to the general procedure in 73% yield. The reaction time is 40 min under 300 nm light. The product was isolated through silica gel flash chromatography (2% ~ 4% ethyl acetate-petroleum ether) as a white solid (47.3 mg): $R_f = 0.39$ (10% ethyl acetate-petroleum ether). $^1$H NMR (400 MHz, CDCl$_3$) δ 8.15 (d, $J = 2.3$ Hz, 1H), 7.54 (dd, $J = 8.8$, 2.3 Hz, 1H), 7.34 (d, $J = 8.8$ Hz, 1H), 2.71 – 2.61 (m, 2H), 2.61 – 2.52 (m, 2H), 1.95 – 1.87 (m, 2H), 1.81 – 1.68 (m, 2H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$) δ 176.6, 164.1, 154.2, 133.2, 130.2, 125.1, 124.1, 119.4, 118.6, 28.1, 21.8, 21.5, 21.0 ppm. HRMS (M/Z): EI [M] calcd for C$_{13}$H$_{11}$O[$\text{Cl}$] $^{[M] +}$: 230.0943, Found 230.0945.

Ketone 8 was prepared according to the general procedure in 71% yield. The reaction time is 50 min under 300 nm light. The product was isolated through silica gel flash chromatography (3% ethyl acetate-petroleum ether) as a white solid (30.0 mg): $R_f = 0.34$ (10% ethyl acetate-petroleum ether). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.79 (d, $J = 8.4$, 2.9 Hz, 1H), 7.32 (m, 2H), 2.65 (t, $J = 6.3$ Hz, 2H), 2.55 (t, $J = 6.1$ Hz, 2H), 1.93 – 1.81 (m, 2H), 1.79 – 1.70 (m, 2H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$) δ 176.9 (d, $J = 2.2$ Hz), 164.2, 159.0 (d, $J = 245.2$ Hz), 152.0 (d, $J = 1.4$ Hz), 124.1 (d, $J = 7.2$ Hz), 121.1 (d, $J = 25.5$ Hz), 119.6 (d, $J = 8.0$ Hz), 117.8, 110.3 (d, $J = 23.4$ Hz), 28.1, 21.8, 21.5, 20.9 ppm. HRMS (M/Z): EI [M] calcd for C$_{13}$H$_{11}$O$_2$F $^{[M] +}$: 218.0743, Found 218.0741.

Ketone 9 was prepared according to the general procedure in 67% yield. The reaction time is 50 min under 300 nm light. The product was isolated through silica gel flash chromatography (60% ~ 80% dichloromethane-petroleum ether) as a white solid (36.0 mg): $R_f = 0.24$ (67% dichloromethane-petroleum ether). $^1$H NMR (400 MHz, CDCl$_3$) δ 8.50 (s, 1H), 7.18 (d, $J = 9.1$, 1H), 3.87 (s, 3H), 2.65 (t, $J = 6.1$ Hz, 2H), 2.57 (t, $J = 6.0$ Hz, 2H), 1.91 – 1.81 (m, 2H), 1.78 – 1.69 (m, 2H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$) δ 177.5, 163.6, 156.3, 150.7, 123.6, 123.0, 119.0, 117.6, 104.8, 55.8, 28.1, 21.9, 21.7, 21.0 ppm. The NMR data is same as reported.$^5$ HRMS (M/Z): EI [M] calcd for C$_{14}$H$_{14}$O$_3$ [M]$^+$: 230.0943, Found 230.0945.
Ketone 10 was prepared according to the general procedure in 66 % yield. The reaction time is 40 min under 300 nm light. The product was isolated through silica gel flash chromatography (2 % ~ 5 % dichloromethane-petroleum ether) as a white solid (42.1 mg): $R_f = 0.30$ (10 % ethyl acetate-petroleum ether). $^1$H NMR (400 MHz, CDCl$_3$) δ 8.48 (d, $J = 1.9$ Hz, 1H), 7.81 (dd, $J = 8.8, 1.9$ Hz, 1H), 7.48 (d, $J = 8.8$ Hz, 1H), 2.69 (t, $J = 6.3$ Hz, 2H), 2.57 (t, $J = 6.2$ Hz, 2H), 1.92 – 1.84 (m, 2H), 1.81 – 1.72 (m, 2H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$) δ 176.6, 164.4, 157.3, 129.3 (q, $J = 3.2$ Hz), 126.8 (q, $J = 33.5$ Hz), 123.6 (q, $J = 270.5$ Hz), 123.9 (q, $J = 4.0$ Hz), 122.9, 119.2, 118.7, 28.1, 21.7, 21.4, 20.9 ppm. HRMS (M/Z): EI [M] calcd for C$_{14}$H$_{11}$O$_2$F$_3$: 268.0711, Found 268.0712.

Ketone 11 was prepared according to the general procedure in 75 % yield. The reaction time is 25 min under 300 nm light. The product was isolated through silica gel flash chromatography (30 % ~ 35 % ethyl acetate-petroleum ether) as a white solid (28.2 mg): $R_f = 0.19$ (40 % ethyl acetate-petroleum ether). $^1$H NMR (400 MHz, CDCl$_3$) δ 8.10 (s, 1H), 7.69 – 7.55 (m, 1H), 7.31 (d, $J = 8.5$ Hz, 1H), 4.74 (s, 2H), 2.64 (t, $J = 6.1$ Hz, 2H), 2.54 (t, $J = 5.5$ Hz, 2H), 1.88 – 1.82 (m, 2H), 1.79 – 1.71 (m, 2H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$) δ 177.8, 164.0, 155.2, 137.6, 132.1, 123.6, 122.7, 118.3, 117.8, 64.4, 28.1, 21.8, 21.6, 21.0 ppm. HRMS (M/Z): EI [M] calcd for C$_{14}$H$_{14}$O$_3$: 230.0943, Found 230.0945.

Ketone 12 was prepared according to the general procedure in 64 % yield. The reaction time is 40 min under 300 nm light. The product was isolated through silica gel flash chromatography (2 % ~ 4 % ethyl acetate-petroleum ether) as a white solid (35.9 mg): $R_f = 0.45$ (10 % ethyl acetate-petroleum ether). $^1$H NMR (400 MHz, CDCl$_3$) δ 8.08 (d, $J = 2.0$ Hz, 1H), 7.63 (dd, $J = 8.6, 2.0$ Hz, 1H), 7.35 (d, $J = 8.6$ Hz, 1H), 4.80 (s, 2H), 2.66 (t, $J = 6.3$ Hz, 2H), 2.58 (t,
$J = 6.1$ Hz, 2H), 1.92 – 1.83 (m, 2H), 1.79-1.72 (m, 2H), 0.94 (s, 9H), 0.10 (s, 6H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 177.7, 163.7, 155.0, 137.8, 131.2, 122.7, 122.6, 118.3, 117.6, 64.4, 28.1, 25.9 (3 C), 21.9, 21.7, 21.0, 18.4, -5.3 (2 C) ppm. MS (M/Z): ESI [M] calcd for C$_{20}$H$_{28}$O$_3$Si [M]$^+$: 344, Found 345 [M+H]$^+$.

Ketone 13 was prepared according to the general procedure in 48 % yield. The reaction time is 50 min under 300 nm light. The product was isolated through silica gel flash chromatography (50 % ~ 70 % dichloromethane-petroleum ether) as a white solid (26.4 mg): $R_f = 0.32$ (pure dichloromethane). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 10.08 (s, 1H), 8.68 (d, $J = 1.7$ Hz, 1H), 8.15 (dd, $J = 8.6$, 1.7 Hz, 1H), 7.50 (d, $J = 8.6$ Hz, 1H), 2.70 (t, $J = 6.2$ Hz, 2H), 2.60 (t, $J = 5.9$ Hz, 2H), 1.97 – 1.85 (m, 2H), 1.81-1.75 (m, 2H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 190.7, 176.9, 164.4, 159.3, 132.8, 131.1, 131.0, 123.2, 119.4, 119.1, 28.1, 21.8, 21.4, 20.9 ppm. HRMS (M/Z): ESI [M] calcd for C$_{14}$H$_{12}$O$_3$ [M]$^+$: 228.0786, Found 228.0787.

Ketone 14 was prepared according to the general procedure in 67 % yield. The reaction time is 45 min under 300 nm light. The product was isolated through silica gel flash chromatography (70 % ~ 80 % dichloromethane-petroleum ether) as a white solid (41.5 mg): $R_f = 0.29$ (pure dichloromethane). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.83 (d, $J = 2.0$ Hz, 1H), 8.22 (dd, $J = 8.8$, 2.0 Hz, 1H), 7.38 (d, $J = 8.8$ Hz, 1H), 3.92 (s, 3H), 2.65 (t, $J = 6.3$ Hz, 2H), 2.55 (t, $J = 6.2$ Hz, 2H), 1.91 – 1.82 (m, 2H), 1.81 – 1.68 (m, 2H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 175.7, 165.9, 164.0, 158.3, 133.5, 128.3, 126.4, 122.7, 119.0, 118.0, 52.3, 28.0, 21.7, 21.4, 20.9 ppm. MS (m/z): EI [M] calcd for C$_{15}$H$_{14}$O$_2$ [M]$^+$: 258, Found 258 (100 %) 257 (85 %) 243 (48 %).

Ketone 15 was prepared according to the general procedure in 75 % yield. The reaction time is 45 min under 300 nm light. The product was isolated through silica gel flash chromatography (8 % ~ 10 % ethyl acetate-petroleum ether) as a white solid (33.4 mg): $R_f = 0.31$ (20 % ethyl acetate-petroleum ether). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.95 (s, 1H), 7.44 (d, $J = 8.5$ Hz, 1H), 7.30 (d, $J = 8.5$ Hz, 1H), 4.65 (s, 2H), 4.00 (t, $J = 5.5$ Hz, 2H), 2.81 – 2.71 (m, 2H), 2.43 (s, 3H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 175.7, 160.5, 154.3, 134.8, 134.6, 124.8,
Ketone 16 was prepared according to the general procedure in 74 % yield. The reaction time is 35 min under 300 nm light. The product was isolated through silica gel flash chromatography (8 % ~ 12 % ethyl acetate-petroleum ether) as a white solid (42.4mg): $R_f = 0.17$ (10 % ethyl acetate-petroleum ether). $^1$H NMR (400 MHz, CDCl$_3$) δ 8.11 (s, 1H), 7.57 (d, $J = 8.8$ Hz, 1H), 7.36 (d, $J = 8.8$ Hz, 1H), 4.63 (s, 2H), 4.01 (t, $J = 5.3$ Hz, 2H), 2.82 – 2.72 (m, 2H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$) δ 174.3, 161.1, 154.3, 133.6, 130.8, 125.0, 124.4, 119.5, 117.2, 63.7, 62.5, 27.6 ppm. MS (m/z): EI [M] calcd for C$_{13}$H$_{12}$O$_3$ [M]$^+$: 216, Found 216 (30 %) 188 (58 %) 187 (100 %).

Ketone 17 was prepared according to the general procedure in 77 % yield. The reaction time is 30 min under 300 nm light. The product was isolated through silica gel flash chromatography (9 % ~ 15 % ethyl acetate-petroleum ether) as a white solid (33.4 mg): $R_f = 0.32$ (20 % ethyl acetate-petroleum ether). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.79 (dd, $J = 8.2$, 3.0 Hz, 1H), 7.42 (dd, $J = 9.1$, 4.3 Hz, 1H), 7.39 – 7.32 (m, 1H), 4.64 (s, 2H), 4.01 (t, $J = 5.6$ Hz, 2H), 2.81 – 2.74 (m, 2H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$) δ 174.8 (d, $J = 2.4$ Hz), 161.1, 159.3 (d, $J = 246.4$ Hz), 152.2 (d, $J = 1.6$ Hz), 124.6 (d, $J = 7.3$ Hz), 121.6 (d, $J = 25.5$ Hz), 119.8 (d, $J = 8.0$ Hz), 116.5, 110.4 (d, $J = 23.6$ Hz), 63.7, 62.5, 27.6 ppm. MS (m/z): EI [M] calcd for C$_{12}$H$_9$FO$_3$ [M]$^+$: 220, Found 220 (29 %) 192 (66 %) 191 (100 %).

Ketone 18 was prepared according to the general procedure in 52 % yield. The reaction time is 70 min under 300 nm light. The product was isolated through silica gel flash chromatography (0.5 % ~ 2 % methanol-dichloromethane) as a white solid (25.2 mg): $R_f = 0.53$ (2 % methanol-dichloromethane). $^1$H NMR (400 MHz, CDCl$_3$) δ 9.37 (s, 1H), 8.69 (d, $J = 5.9$ Hz, 1H), 7.25 (d, $J = 5.6$ Hz, 1H), 2.67 (t, $J = 6.3$ Hz, 2H), 2.56 (t, $J = 6.2$ Hz, 2H), 1.94 – 1.83 (m, 2H), 1.80 – 1.71 (m, 2H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$) δ 176.6, 164.3, 160.6, 152.4, 150.0, 124.6, 121.6 (d, $J = 25.5$ Hz), 119.8 (d, $J = 8.0$ Hz), 116.5, 110.4 (d, $J = 23.6$ Hz), 63.7, 62.5, 27.6 ppm. MS (m/z): EI [M] calcd for C$_{12}$H$_9$FO$_3$ [M]$^+$: 220, Found 220 (29 %) 192 (66 %) 191 (100 %).
Ketone 19 was prepared according to the general procedure in 45 % yield. The reaction time is 70 min under 300 nm light. The product was isolated through silica gel flash chromatography (0.5 % ~ 2 % methanol-dichloromethane) as a white solid (21.2 mg): $R_f = 0.44$ (2 % methanol-dichloromethane). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.36 (s, 1H), 8.74 (d, $J = 5.9$ Hz, 1H), 7.30 (d, $J = 5.9$ Hz, 1H), 4.62 (t, $J = 1.6$ Hz, 2H), 4.01 (t, $J = 5.6$ Hz, 2H), 2.81 – 2.74 (m, 2H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 174.5, 161.3, 160.7, 152.9, 149.8, 119.5, 119.0, 112.2, 63.6, 62.2, 27.5 ppm. MS (m/z): EI [M] calcd for C$_{12}$H$_{11}$NO$_2$ [M]$^+$: 201, Found 201 (100 %) 200 (84 %) 186 (63 %).

Ketone 20 was prepared according to the general procedure in 71 % yield. The reaction time is 40 min under 300 nm light. The product was isolated through silica gel flash chromatography (4 % ~ 8 % ethyl acetate-petroleum ether) as a white solid (42.6 mg): $R_f = 0.30$ (10 % ethyl acetate-petroleum ether). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.45 (d, $J = 7.6$ Hz, 1H), 8.14 (d, $J = 8.7$ Hz, 1H), 7.89 (d, $J = 7.9$ Hz, 1H), 7.72 – 7.58 (m, 3H), 2.81 (t, $J = 6.0$ Hz, 2H), 2.64 (t, $J = 6.0$ Hz, 2H), 1.97 – 1.89 (m, 2H), 1.84 – 1.77 (m, 2H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 177.5, 163.0, 153.1, 135.5, 128.8, 128.0, 126.7, 124.4, 124.0, 122.1, 121.1, 119.8, 119.2, 28.0, 21.9, 21.6, 21.1 ppm. MS (m/z): EI [M] calcd for C$_{17}$H$_{14}$O$_2$ [M]$^+$: 250, Found 250 (100 %) 249 (98 %) 235 (32 %).

Ketone 21 was prepared according to the general procedure in 93 % yield. The reaction time is 40 min under 300 nm light. The product was isolated through silica gel flash chromatography (10 % ~ 12 % ethyl acetate-petroleum ether) as a white solid (56 mg): $R_f = 0.29$ (20 % ethyl acetate-petroleum ether). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.45 (d, $J = 7.9$ Hz, 1H), 8.11 (d, $J = 8.7$ Hz, 1H), 7.90 (d, $J = 7.9$ Hz, 1H), 7.76 – 7.60 (m, 3H), 4.72 (s, 2H), 4.07 (t, $J = 5.5$ Hz, 2H), 2.97 – 2.88 (m, 2H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 175.4, 159.8,
Ketone 22 was prepared according to the general procedure in 56 % yield. The reaction time is 60 min under 300 nm light. The product was isolated through silica gel flash chromatography (30 % ~ 40 % dichloromethane-petroleum ether) as a white solid (33.6 mg): \( R_f = 0.14 \) (20 % ethyl acetate-petroleum ether). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 8.44 (d, \( J = 2.2 \) Hz, 2H), 7.95 (dd, \( J = 8.7, 2.2 \) Hz, 2H), 7.48 (d, \( J = 8.7 \) Hz, 2H), 2.70 (t, \( J = 6.1 \) Hz, 4H), 2.61 (t, \( J = 5.9 \) Hz, 4H), 1.94 – 1.83 (m, 4H), 1.82 – 1.74 (m, 4H) ppm. \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 177.6 (2 C), 164.0 (2 C), 155.5 (2 C), 136.0 (2 C), 131.9 (2 C), 123.7 (2 C), 123.3 (2 C), 118.6 (2 C), 118.4 (2 C), 28.2 (2 C), 21.9 (2 C), 21.6 (2 C), 21.1 (2 C) ppm. HRMS (m/z): EI [M] calcd for C\(_{26}\)H\(_{22}\)O\(_4\) [M]\(^+\): 398.1518, Found 398.1514.

Ketone 23 was prepared according to the general procedure in 73 % yield. The reaction time is 60 min under 300 nm light. The product was isolated through silica gel flash chromatography (10 % ~ 20 % ethyl acetate-dichloromethane) as a white solid (33.4 mg): \( R_f = 0.36 \) (20 % ethyl acetate-dichloromethane). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 8.40 (d, \( J = 2.3 \) Hz, 2H), 7.95 (dd, \( J = 8.7, 2.3 \) Hz, 2H), 7.51 (d, \( J = 8.7 \) Hz, 2H), 4.67 (s, 4H), 4.03 (t, \( J = 5.6 \) Hz, 4H), 2.80 (t, \( J = 5.5 \) Hz, 4H) ppm. \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 175.4 (2 C), 160.9 (2 C), 155.6 (2 C), 136.2 (2 C), 132.2 (2 C), 123.7 (2 C), 123.5 (2 C), 118.6 (2 C), 117.2 (2 C), 63.7 (2 C), 62.6 (2 C), 27.6 (2 C) ppm. HRMS (m/z): EI [M] calcd for C\(_{24}\)H\(_{18}\)O\(_6\) [M]\(^+\): 402.1103, Found 402.1102.

Large Scale experiments:

To a solution of substrate 1d (502.0 mg, 2 mmol) in a co-solvent of acetonitrile/H\(_2\)O (9:1, v/v) (0.2 M) 10 mL in quartz tube was added TMP (338 \( \mu \)L, 2 mmol, 1.0 equiv.). After all substrate dissolved, the solution was photolyzed at r.t. in a Rayonet chamber reactor at 300 nm for 5 h 20 min, then CH\(_3\)CN was evaporated, an saturated NH\(_4\)Cl solution was added, then extracted with EtOAc.
(20 mL), the combined organic phase was washed with brine (15 mL), dried over Na₂SO₄, filtered, concentrated, and purified by silica gel column chromatography (1 % ~ 2 % acetone-petroleum ether). The product 3 were generated as a white solid in 81 % yield (325.2 mg).

Repeat the reaction of 1d at a scale of 507.6 mg in a co-solvent of acetonitrile/H₂O (9:1, v/v) (0.2 M) 10 mL, after irradiation at 300 nm for 5 h 30 min, we isolated product 3 in 79 % yield (318.1 mg).

We then scaled up the reaction to a gram scale (1.29 g, 5.2 mmol) in a co-solvent of acetonitrile/H₂O (9:1, v/v) (0.5 M) 10 mL, after irradiation at 300 nm for 13 h 10 min, we isolated product 3 in 80 % yield (828.0 mg).

To a solution of substrate S7 (330.4 mg, 1.2 mmol) in a co-solvent of acetonitrile/H₂O (9:1, v/v) (0.15 M) 8 mL in quartz tube was added TMP (208 µL, 1.2 mmol, 1.0 equiv.). After all substrate dissolved, the solution was photolyzed at r.t. in a Rayonet chamber reactor at 300 nm for 3 h 20 min, then CH₃CN was evaporated, an saturated NH₄Cl solution was added, then extracted with EtOAc (20 mL), the combined organic phase was washed with brine (15 mL), dried over Na₂SO₄, filtered, concentrated, and purified by silica gel column chromatography (3 % ~ 4 % ethyl acetate-petroleum ether). The product 8 were generated as a white solid in 90 % yield (241.2 mg).

Repeat the reaction of S7 at a scale of 322.5 mg in a co-solvent of acetonitrile/H₂O (9:1, v/v) (0.15 M) 8 mL, after irradiation at 300 nm for 3 h 30 min, we isolated product 8 in 86 % yield (225.5 mg).

Reference:
$^1$H and $^{13}$C NMR Spectra of the Synthetic Intermediates and Products:

**Chemical Formula: C$_{19}$H$_{13}$ClO$_2$**

400 MHz, CDCl$_3$

Chemical Formula: C$_{19}$H$_{13}$ClO$_2$

100 MHz, CDCl$_3$

S25
Electronic Supplementary Material (ESI) for Chemical Communications

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Chemical Formula: C₉H₇ClO₂
400 MHz, CDCl₃

Chemical Formula: C₉H₇ClO₂
100 MHz, CDCl₃
Chemical Formula: C13H14CINO2
400 MHz, CDCl3

Chemical Formula: C13H14CINO2
129 MHz, CDCl3
Chemical Formula: C_{12}H_{15}ClO_3
400 MHz, CDCl_3

Chemical Formula: C_{12}H_{15}ClO_3
100 MHz, CDCl_3
Electronic Supplementary Material (ESI) for Chemical Communications

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Chemical Formula: C_{12}H_{15}ClFO_{3}
400 MHz, CDCl₃

Chemical Formula: C_{12}H_{15}ClFO_{3}
100 MHz, CDCl₃
Electronic Supplementary Material (ESI) for Chemical Communications

Chemical Formula: C_{11}H_{14}NO_{3}
400 MHz, CDCl_{3}

Chemical Formula: C_{11}H_{14}NO_{3}
100 MHz, CDCl_{3}

S66
Chemical Formula: C_{16}H_{12}O_3
400 MHz, CDCl_3

Chemical Formula: C_{13}H_{12}O_3
100 MHz, CDCl_3