Synthesis of nitrogen heterocycles via α-aminoalkyl radicals generated from α-silyl secondary-amines under visible light irradiation

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General method.

$^1$H NMR (270 MHz) and $^{13}$C NMR (67.8 MHz) spectra were recorded on a JEOL Excalibur 270 spectrometer in suitable solvents. Elemental analyses were performed at Microanalytical Center of The University of Tokyo. Mass spectra were measured on a JEOL JMS-700 mass spectrometer. Absorption spectra was recorded on Shimadzu MultiSpec-1500 spectrometers. All reactions were carried out under dry nitrogen atmosphere. Solvents were dried by the general methods, and degassed before use. Photoirradiation was carried out with 14 W white LED.

Nitrogen heterocycles 3f$^{S1a}$, 3h$^{S1b}$, 3r$^{S1c}$, 3s$^{S1d}$, 7a$^{S2a}$ and 7b$^{S2b}$ are known compounds. Preparation of $\alpha$-silylamines 1a$^{S3a}$, 1b$^{S3b}$, 1d$^{S3b}$, 1f$^{S3a}$ and 1h$^{S3c}$ were reported elsewhere. $\alpha$,$\beta$-Unsaturated carbonyl compounds 2 and 5 were prepared by Knövenagel condensation.$^{S4}$ Photocatalysts were synthesized according to the literature procedure.$^{S5}$

Preparation of $\alpha$-silylamines 1c, 1e, and 1g.

A typical experimental procedure for the synthesis of N-[(trimethylsilyl)methyl]-4-fluoroaniline 1c is described below. To a flame-dried 100 mL flask were placed THF (40 mL) and 4-fluoroaniline (1.20 mL, 12.7 mmol). $^6$BuLi (1.65 M in hexane, 6.20 mL, 10.2 mmol) was added dropwise at -78 °C, and the resulting mixture was stirred at room temperature for 1 h. Hexamethylenephosphoramide (HMPA, 1.70 mL, 9.77 mmol) and (chloromethyl)trimethylsilane (1.40 mL, 10.0 mmol) were added at -78 °C, then the resulting mixture was stirred at room temperature for 16 h. Water (ca. 50 mL) was added, and the resulting mixture was extracted with Et2O (ca. 30 mL x 3). The combined organic layer was washed with brine and dried over anhydrous MgSO4. After concentration in vacuo, the residue was purified by column chromatography (eluent: hexane) to give N-[(trimethylsilyl)methyl]-4-fluoroaniline 1c (1.45 g, 7.34 mmol).

Isolated yields and spectroscopic data of $\alpha$-silylamines 1c, 1e, and 1g are as follows:

1c: 73% Yield. An orange oil. $^1$H NMR (CDCl3) $\delta$ 6.98-6.89 (m, 2H), 6.66-6.58 (m, 2H), 3.39 (br, 1H), 2.49 (s, 2H), 0.2 (s, 9H). $^{13}$C NMR (CDCl3) $\delta$ 155.6 (d, $^1$J$_{C,F}$ = 233.6 Hz), 146.9 (d, $^4$J$_{C,F}$ = 1.7 Hz), 115.4 (d, $^2$J$_{C,F}$ = 22.3 Hz), 113.0 (d, $^3$J$_{C,F}$ = 7.3 Hz), 34.2, -2.8. $^{19}$F NMR (CDCl3) $\delta$ -128.8. HRMS (EI) Calcd. for C10H16FNSi [M]: 197.1036. Found: 197.1034.
**1e:** 67% Yield. An orange oil. $^1$H NMR (CDCl$_3$) δ 7.10 (t, $J = 7.6$ Hz, 1H), 6.97 (d, $J = 7.6$ Hz, 1H), 6.66 (d, $J = 7.6$ Hz, 1H), 6.59 (t, $J = 7.6$ Hz, 1H), 3.27 (br, 1H), 2.47 (s, 2H), 2.07 (s, 3H), 0.10 (s, 9H). $^{13}$C NMR (CDCl$_3$) δ 148.2, 129.7, 127.1, 121.5, 116.5, 109.3, 33.2, 17.1, -2.7. HRMS (EI) Calcd. for C$_{11}$H$_{19}$NSi [M]: 193.1287. Found: 193.1289.

**1g:** 23% Yield. A pale yellow oil. $^1$H NMR (CDCl$_3$) δ 7.93-7.86 (m, 2H), 7.58-7.46 (m, 3H), 7.33 (d, $J = 8.1$ Hz, 1H), 6.82 (d, $J = 7.6$ Hz, 1H), 4.33 (br, 1H), 2.74 (s, 2H), 0.33 (s, 9H). $^{13}$C NMR (CDCl$_3$) δ 145.5, 134.2, 128.7, 126.7, 125.6, 124.5, 123.4, 119.4, 116.9, 104.0, 33.4, -2.5. HRMS (EI) Calcd. for C$_{14}$H$_{19}$NSi [M]: 229.1287. Found: 229.1293.

**Preparation of α-silylamine 1i.**

To a flame-dried 50 mL Schlenk flask were placed DMF (10 mL), aniline (0.910 mL, 9.97 mmol), and NaH (60% dispersion in paraffin liquid, 302.3 mg, 7.56 mmol), and the mixture was stirred at room temperature for 1 h. Then, (1-chloroethyl)trimethylsilane (1.60 mL, 10.3 mmol) was added, and the resulting mixture was stirred at room temperature for 14 h. Water (ca. 50 mL) was added, and the resulting mixture was extracted with Et$_2$O (ca. 30 mL x 3). The combined organic layer was washed with brine and dried over anhydrous Na$_2$SO$_4$. After concentration in vacuo, the residue was purified by column chromatography (eluent: hexane) to give N-(1-(trimethylsilyl)ethyl)aniline 1i (497 mg, 2.43 mmol, 24% yield) as a colorless oil. $^1$H NMR (CD$_6$D$_6$) δ 7.19-7.12 (m, 2H), 6.73 (t, $J = 7.3$ Hz, 1H), 6.50 (d, $J = 7.8$ Hz, 2H), 3.11 (br, 1H), 2.77 (q, $J = 7.0$ Hz, 1H), 0.98 (d, $J = 7.0$ Hz, 3H), -0.9 (s, 9H). $^{13}$C NMR (CD$_6$D$_6$) δ 149.0, 129.5, 117.3, 113.5, 37.5, 15.6, -3.9. HRMS (EI) Calcd. for C$_{11}$H$_{19}$NSi [M]: 193.1287. Found: 193.1290.
Photocatalytic reactions for synthesis of γ-lactams (3).

A typical experimental procedure for the reaction of \(N\)-(trimethylsilylmethyl)aniline (1a) with diethyl benzylidemalonate (2a) is described below. To a flame-dried Schlenk flask (diameter: 2.5 cm) were placed [4a][BF₄] (2.2 mg, 0.0026 mmol) and NMP (2.5 mL). Then, 1a (43.8 mg, 0.244 mmol) and 2a (75.4 mg, 0.303 mmol) were added. The reaction flask was placed in a water bath (25 °C) and illuminated with a 14 W white LED (approximately 2 cm from the light source) for 18 h. The resulting mixture was treated with KOtBu (56.5 mg, 0.503 mmol) at room temperature for 4 h. Then, saturated aqueous NaHCO₃ (ca. 50 mL) was added and the mixture was extracted with Et₂O (ca. 30 mL x 4). The combined organic layer was washed with brine (ca. 50 mL) and dried over anhydrous MgSO₄. After concentration in vacuo, the residue was purified by column chromatography (eluent: hexane/ethyl acetate = 10/1) to give \(N\)-phenyl-3-ethoxycarbonyl-4-phenyl-2-pyrrolidone (3a, 67.2 mg, 0.217 mmol).

Isolated yields and spectroscopic data of the γ-lactams (3) are as follows:

\(3a\): 89% yield (trans/cis ratio 14/1). A colorless solid. trans-Isomer: \(^1\)H NMR (CDCl₃) δ 7.57-7.52 (m, 2H), 7.32-7.16 (m, 7H), 7.14-7.05 (m, 1H), 4.26-4.11 (m, 3H), 4.01 (dd, \(J = 17.1\) and 8.0 Hz, 1H), 3.84-3.78 (m, 1H), 3.72 (d, \(J = 9.2\) Hz, 1H), 1.21 (t, \(J = 7.3\) Hz, 3H). \(^{13}\)C NMR (CDCl₃) δ 169.0, 167.9, 139.4, 138.6, 129.0, 128.86, 127.7, 126.9, 125.0, 120.0, 61.8, 57.1, 53.6, 41.1, 14.1. cis-Isomer: \(^1\)H NMR (CDCl₃) δ 0.82 (tt, \(J = 7.2\) Hz, 3H). \(^{13}\)C NMR (CDCl₃) δ 128.89, 128.6, 127.5 120.5. HRMS (EI) Calcd. for C₁₉H₁₉NO₃ [M]: 309.1365. Found: 309.1363. The relative configuration of major isomer is determined to be trans-3a (m.p. 64.1-65.8 °C) by X-ray analysis (see below for details).

\(3b\): 95% yield (trans/cis ratio >20/1). A yellow solid. trans-Isomer: \(^1\)H NMR (CDCl₃) δ 7.50 (d, \(J = 8.9\) Hz, 2H), 7.32-7.17 (m, 7H), 4.26-3.97 (m, 4H), 3.81-3.70 (m, 2H), 1.20 (t, \(J = 7.2\) Hz, 3H). \(^{13}\)C NMR (CDCl₃) δ 168.8, 168.0, 139.1, 137.1, 130.2, 129.1, 128.9, 127.8, 126.9, 121.1, 61.9,
cis-Isomer: $^1$H NMR (CDCl$_3$) $\delta$ 0.82 (t, $J = 7.0$ Hz, 3H). HRMS (EI) Calcd. for C$_{19}$H$_{18}$ClNO$_3$ [M]: 343.0975. Found: 343.0964.

trans-Isomer: $^1$H NMR (CDCl$_3$) $\delta$ 7.58-7.48 (m, 2H), 7.32-7.17 (m, 5H), 7.01-6.94 (m, 2H), 4.26-4.09 (m, 3H), 4.02 (dd, $J = 16.3$ and 8.2 Hz, 1H), 3.82-3.70 (m, 2H), 1.21 (t, $J = 7.2$ Hz, 3H). $^{13}$C NMR (CDCl$_3$) $\delta$ 168.9, 167.9, 159.8 ($^1$J$_{C-F}$ = 244.8 Hz), 139.3, 134.7 ($^4$J$_{C-F}$ = 2.8 Hz), 129.1, 127.7, 126.9, 121.8 ($^3$J$_{C-F}$ = 7.8 Hz), 115.6 ($^2$J$_{C-F}$ = 22.3 Hz), 61.9, 56.9, 53.9, 41.1, 14.1. $^{19}$F NMR (CDCl$_3$) $\delta$ -116.6. cis-Isomer: $^1$H NMR (CDCl$_3$) $\delta$ 0.83 (t, $J = 7.0$ Hz, 3H). $^{13}$C NMR (CDCl$_3$) $\delta$ 40.7, 13.6. HRMS (EI) Calcd. for C$_{19}$H$_{18}$FNO$_3$ [M]: 327.1271. Found: 327.1283.

trans-Isomer: $^1$H NMR (CDCl$_3$) $\delta$ 7.43-7.40 (m, 2H), 7.27-7.21 (m, 5H), 7.10-7.07 (m, 2H), 4.22-4.08 (m, 3H), 4.00 (dd, $J = 16.5$ and 8.4 Hz, 1H), 3.82-3.68 (m, 2H), 2.24 (s, 3H), 1.21 (t, $J = 7.2$ Hz, 3H). $^{13}$C NMR (CDCl$_3$) $\delta$ 169.1, 167.7, 139.5, 136.1, 134.8, 129.3, 129.0, 127.6, 126.9, 120.1, 61.8, 57.1, 53.8, 41.2, 20.8, 14.1. cis-Isomer: $^1$H NMR (CDCl$_3$) $\delta$ 0.82 (t, $J = 7.0$ Hz, 3H). $^{13}$C NMR (CDCl$_3$) $\delta$ 128.6, 120.6, 56.1, 52.1. HRMS (EI) Calcd. for C$_{20}$H$_{21}$NO$_3$ [M]: 323.1521. Found: 323.1519.

cis-Isomer: $^1$H NMR (CDCl$_3$) $\delta$ 3.81 (dd, $J = 15.7$ and 8.4 Hz), 0.86 (t, $J = 7.3$ Hz, 3H). $^{13}$C NMR (CDCl$_3$) $\delta$ 61.1, 13.7 HRMS (EI) Calcd. for C$_{20}$H$_{21}$NO$_3$ [M]: 323.1521. Found: 323.1525.
3g: 75% yield (trans/cis ratio 9/1). A pale yellow oil. trans-Isomer: $^1$H NMR (CDCl$_3$) $\delta$ 7.83-7.75 (m, 3H), 7.49-7.20 (m, 9H), 4.30-4.14 (m, 4H), 3.91-3.79 (m, 2H), 1.25 (t, $J = 7.2$ Hz, 3H). $^{13}$C NMR (CDCl$_3$) $\delta$ 169.5, 169.1, 140.2, 134.6, 134.5, 129.5, 129.1, 128.7, 128.51, 127.7, 126.97, 126.9, 126.4, 125.5, 124.6, 122.5, 61.9, 56.8, 56.2, 42.3, 14.1. cis-Isomer: $^1$H NMR (CDCl$_3$) $\delta$ 7.78-7.75 (m, 3H). 13C NMR (CDCl$_3$) $\delta$ 169.5, 169.1, 140.2, 134.6, 134.5, 129.5, 129.1, 128.7, 128.51, 127.7, 126.97, 126.9, 126.4, 125.5, 124.6, 122.5, 61.9, 56.8, 56.2, 42.3, 14.1. HRMS (EI) Calcd. for C$_{23}$H$_{21}$NO$_3$ [M]: 359.1521. Found: 359.1508.

3i: 62% yield (isomeric ratio 6/1). A pale yellow solid. Major isomer: $^1$H NMR (CDCl$_3$) $\delta$ 7.36-7.21 (m, 9H), 7.20-7.15 (m, 1H), 4.27-4.05 (m, 3H), 3.72 (d, $J = 10.4$ Hz, 1H), 3.50 (dd, $J = 10.4$ and 7.7 Hz, 1H), 1.20 (t, $J = 7.3$ Hz, 3H), 1.16 (d, $J = 6.2$ Hz, 3H). $^{13}$C NMR (CDCl$_3$) $\delta$ 169.2, 167.9, 138.9, 136.7, 129.0, 128.9, 127.8, 127.7, 126.4, 124.7, 61.7, 60.6, 56.7, 50.6, 18.5, 14.1. Minor isomer: $^1$H NMR (CDCl$_3$) $\delta$ 7.54-7.46 (m, 2H), 4.69-4.58 (m, 1H), 1.29 (t, $J = 7.2$ Hz, 3H), 0.84 (d, $J = 6.8$ Hz, 3H). HRMS (EI) Calcd. for C$_{20}$H$_{21}$NO$_3$ [M]: 323.1521. Found: 323.1511. The stereochemistry of major- and minor-3i was confirmed by the NOE measurements:

3j: 79% yield (trans/cis ratio >20/1). A pale yellow solid. trans-Isomer: $^1$H NMR (CDCl$_3$) $\delta$ 7.56-7.51 (m, 2H), 7.33-7.26 (m, 4H), 7.18-7.08 (m, 3H), 4.28-3.96 (m, 3H), 4.00 (dd, $J = 17.1$ and 8.2 Hz, 1H), 3.82-3.75 (m, 1H), 3.67 (d, $J = 9.2$ Hz, 1H), 1.22 (t, $J = 7.2$ Hz, 3H). $^{13}$C NMR (CDCl$_3$)
δ 168.7, 167.6, 138.5, 137.8, 133.6, 129.2, 128.9, 128.4, 125.2, 120.0, 61.9, 57.1, 53.4, 40.6, 14.1.
cis-Isomer: ¹H NMR (CDCl₃) δ 0.76 (t, J = 7.0 Hz, 3H). HRMS (EI) Calcd. for C₁₉H₁₈ClNO₃ [M]: 343.0975. Found: 343.0964.

3k: 79% yield (trans/cis ratio 20/1). A yellow oil. trans-Isomer: ¹H NMR (CDCl₃) δ 7.56-7.52 (m, 2H), 7.32-7.26 (m, 2H), 7.16-7.06 (m, 5H), 4.24-4.07 (m, 3H), 3.98 (dd, J = 17.4 and 8.2 Hz, 1H), 3.82-3.75 (m, 1H), 3.70 (d, J = 9.5 Hz, 1H), 2.26 (s, 3H), 1.21 (t, J = 7.2 Hz, 3H). ¹³C NMR (CDCl₃) δ 169.0, 168.0, 138.7, 137.4, 136.3, 129.7, 128.9, 126.8, 125.0, 120.0, 61.8, 57.3, 53.7, 40.8, 21.0, 14.1. cis-Isomer: ¹H NMR (CDCl₃) δ 0.86 (t, J = 7.2 Hz, 3H). ¹³C NMR (CDCl₃) δ 137.3, 129.2, 127.4, 120.5. HRMS (EI) Calcd. for C₂₀H₂₁NO₃ [M]: 323.1521. Found: 323.1506.

3l: 62% yield (trans/cis ratio >20/1). A pale yellow oil. trans-Isomer: ¹H NMR (CDCl₃) δ 7.57-7.52 (m, 2H), 7.33-7.26 (m, 2H), 7.21-7.01 (m, 5H), 4.24-4.09 (m, 3H), 3.99 (dd, J = 17.0 and 8.1 Hz, 1H), 3.84-3.78 (m, 1H), 3.72 (d, J = 9.2 Hz, 1H), 2.28 (s, 3H), 1.22 (t, J = 7.0 Hz, 3H). ¹³C NMR (CDCl₃) δ 169.0, 168.0, 139.4, 138.8, 138.7, 129.0, 128.9, 128.4, 127.7, 125.0, 123.9, 120.1, 62.0, 57.2, 53.7, 41.1, 21.4, 14.1. cis-Isomer: ¹H NMR (CDCl₃) δ 0.85 (t, J = 7.5 Hz, 3H). HRMS (EI) Calcd. for C₂₀H₂₁NO₃ [M]: 323.1521. Found: 323.1535.

3m: 81% yield (trans/cis ratio 20/1). A yellow oil. trans-Isomer: ¹H NMR (CDCl₃) δ 7.64-7.59 (m, 2H), 7.40-7.33 (m, 2H), 7.25-7.14 (m, 3H), 6.92-6.87 (m, 2H), 4.32-4.15 (m, 3H), 4.04 (dd, J = 17.3 and 8.4 Hz, 1H), 3.88-3.74 (m, 5H), 1.29 (t, J = 7.0 Hz, 3H). ¹³C NMR (CDCl₃) δ 169.0, 168.0, 159.0, 138.6, 131.2, 128.9, 128.0, 125.0, 120.0, 114.4, 61.7, 57.4, 55.2, 53.8, 40.6, 14.1. cis-Isomer: ¹H NMR (CDCl₃) δ 0.96 (t, J = 7.0 Hz, 3H). ¹³C NMR (CDCl₃) δ 128.7, 125.1, 120.5, 114.0. HRMS (EI) Calcd. for C₂₀H₂₁NO₄ [M]: 339.1471. Found: 339.1480.
3n: 61% yield (trans/cis ratio 14/1). A colorless solid. *trans*-Isomer: $^1$H NMR (CDCl$_3$) $\delta$ 7.59-7.49 (m, 6H), 7.40-7.25 (m, 7H), 7.15-7.08 (m, 1H), 4.27-4.03 (m, 4H), 3.90-3.84 (m, 1H), 3.77 (d, $J = 9.2$ Hz, 1H), 1.24 (t, $J = 7.2$ Hz, 3H). $^{13}$C NMR (CDCl$_3$) $\delta$ 169.0, 167.9, 140.7, 140.4, 138.6, 138.4, 128.9, 128.8, 127.8, 127.5, 127.4, 126.99, 125.1, 120.1, 61.9, 57.2, 53.7, 40.9, 14.1. *cis*-Isomer: $^1$H NMR (CDCl$_3$) $\delta$ 0.86 (t, $J = 7.2$ Hz, 3H). $^{13}$C NMR (CDCl$_3$) $\delta$ 128.0, 126.95, 126.9. HRMS (EI) Calcd. for C$_{25}$H$_{23}$NO$_3$ [M]: 385.1678. Found: 385.1672.

3o: 61% yield (trans/cis ratio 19/1). A pale yellow oil. *trans*-Isomer: $^1$H NMR (CDCl$_3$) $\delta$ 7.88-7.80 (m, 3H), 7.76 (br, 1H), 7.67-7.63 (m, 2H), 7.54-7.45 (m, 2H), 7.42-7.15 (m, 1H), 4.33-4.17 (m, 4H), 4.05-3.90 (m, 2H), 1.29 (t, $J = 7.2$ Hz, 3H). $^{13}$C NMR (CDCl$_3$) $\delta$ 169.0, 167.9, 138.7, 136.7, 133.4, 132.7, 129.1, 128.9, 127.73, 127.66, 126.6, 126.2, 126.0, 125.1, 124.6, 120.1, 61.9, 57.2, 53.6, 41.4, 14.1. *cis*-Isomer: $^1$H NMR (CDCl$_3$) $\delta$ 0.79 (t, $J = 7.0$ Hz, 3H). $^{13}$C NMR (CDCl$_3$) $\delta$ 0.79 (t, $J = 7.0$ Hz, 3H). HRMS (EI) Calcd. for C$_{23}$H$_{23}$NO$_3$ [M]: 359.1521. Found: 323.1507.

3p: 79% yield (trans/cis ratio 11/1). A yellow oil. *trans*-Isomer: $^1$H NMR (CDCl$_3$) $\delta$ 7.60 (d, $J = 7.7$ Hz, 2H), 7.36 (t, $J = 7.7$ Hz, 2H), 7.15 (t, $J = 7.7$ Hz, 1H), 4.27 (q, $J = 7.0$ Hz, 2H), 3.99 (dd, $J = 9.2$ and 8.1 Hz, 1H), 3.48 (dd, $J = 9.2$ and 7.7 Hz, 1H), 3.32 (d, $J = 8.6$ Hz, 1H), 2.93-2.78 (m, 1H), 1.62-1.50 (m, 2H), 1.47-1.30 (m, 5H), 0.96 (t, $J = 7.2$ Hz, 3H). $^{13}$C NMR (CDCl$_3$) $\delta$ 169.7, 168.7, 138.9, 128.8, 124.8, 120.0, 61.6, 56.6, 52.7, 35.8, 35.7, 20.2, 14.1, 13.89. *cis*-Isomer: $^1$H NMR (CDCl$_3$) $\delta$ 3.81 (dd, $J = 8.8$ and 5.5 Hz, 1H), 3.58 (d, $J = 8.6$ Hz, 1H), 2.76-2.66 (m, 1H). $^{13}$C NMR (CDCl$_3$) $\delta$ 124.9, 120.4, 61.2, 54.6, 53.4, 31.2, 20.7, 14.2, 13.94. HRMS (EI) Calcd. for C$_{16}$H$_{21}$NO$_3$ [M]: 275.1521. Found: 275.1526.
3q: 81% yield (trans/cis ratio 8/1). A pale yellow oil. trans-Isomer: $^1$H NMR (CD$_2$Cl$_2$) δ 7.67-7.60 (m, 2H), 7.50-7.37 (m, 7H), 7.27-7.22 (m, 1H), 4.24-4.08 (m, 1H), 4.05-3.89 (m, 3H). $^{13}$C NMR (CD$_2$Cl$_2$) δ 164.5, 138.6, 136.8, 129.8, 129.46, 129.0, 127.4, 126.1, 120.67, 116.6, 53.6, 43.5, 43.2. cis-Isomer: $^1$H NMR (CDCl$_3$) δ 7.35-7.29 (m, 2H), 4.31 (dd, $J$ = 10.4 and 6.9 Hz, 1H). $^{13}$C NMR (CDCl$_3$) δ 138.1, 129.6, 128.9, 127.7, 126.2, 120.71, 53.6, 43.0, 40.1. HRMS (EI) Calcd. for C$_{17}$H$_{14}$N$_2$O [M]: 262.1106. Found: 262.1106.

Synthesis of 3a'.

To a flame-dried Schlenk flask (diameter: 2.5 cm) were placed [4a][BF$_4$] (2.2 mg, 0.0026 mmol) and NMP (2.5 mL). Then, 1a (43.9 mg, 0.245 mmol) and 2a (74.1 mg, 0.298 mmol) were added. The reaction flask was placed in a water bath (25 °C) and illuminated with a 14 W white LED (approximately 2 cm from the light source) for 18 h. The resulting mixture was purified by column chromatography (eluent: hexane/ethyl acetate = 10/1) to give 3a' (51.0 mg, 0.143 mmol, 58% yield) as a yellow oil. $^1$H NMR (CDCl$_3$) δ 7.42-7.15 (m, 7H), 6.73 (t, $J$ = 7.3 Hz, 1H), 6.60 (d, $J$ = 7.6 Hz, 2H), 4.27 (q, $J$ = 7.2 Hz, 2H), 3.98-3.86 (m, 2H), 3.84-3.76 (m, 2H), 3.70-3.63 (brm, 2H), 3.42-3.31 (m, 1H), 1.30 (t, $J$ = 7.2 Hz, 3H), 0.97 (t, $J$ = 7.2 Hz, 3H). $^{13}$C NMR (CDCl$_3$) δ 168.3, 167.6, 147.5, 139.2, 129.2, 128.6, 128.4, 127.4, 117.6, 113.0, 61.7, 61.3, 56.2, 47.5, 44.5, 14.0, 13.6. HRMS (EI) Calcd. for C$_{21}$H$_{25}$NO$_4$ [M]: 355.1784. Found: 355.1777.

Photocatalytic reactions for synthesis of dihydropyrrole 6.

To a flame-dried Schlenk flask (diameter: 2.5 cm) were placed [4a][BF$_4$] (2.1 mg, 0.0025 mmol) and NMP (2.5 mL). Then, 1a (44.8 mg, 0.250 mmol) and 5 (65.4 mg, 0.300 mmol) were added. The reaction flask was placed in a water bath (25 °C) and illuminated with a 14 W white LED (approximately 2 cm from the light source) for 18 h. Then, saturated aqueous NaHCO$_3$ (ca. 50 mL) was added and the mixture was extracted with Et$_2$O (ca. 30 mL x 3). The combined organic layer was washed with brine (ca. 50 mL) and dried over anhydrous MgSO$_4$. After concentration in vacuo, the residue was purified by column chromatography (eluent: hexane/ethyl acetate = 10/1) to give dihydropyrrole 6 (49.3 mg, 0.160 mmol, 64% yield) as a pale yellow oil. $^1$H NMR (CDCl$_3$)
δ 7.31-7.17 (m, 6H), 7.14-7.07 (m, 2H), 7.04-6.98 (m, 2H), 4.31 (dd, J = 11.1 and 9.9 Hz, 1H), 4.17 (ddd, J = 11.1, 3.9 and 0.9 Hz, 1H), 4.02-3.84 (m, 2H), 3.70 (dd, J = 9.9 and 3.9 Hz, 1H), 2.30 (s, 3H), 0.98 (t, J = 7.0 Hz, 3H). 13C NMR (CDCl3) δ 166.9, 158.2, 146.0, 141.7, 129.2, 128.2, 127.0, 126.4, 124.7, 123.6, 106.1, 62.2, 58.5, 45.1, 14.3, 14.1. HRMS (EI) Calcd. for C20H21NO2 [M]: 307.1572. Found: 307.1583.

Photocatalytic reactions for synthesis of pyrroles 7a and 7b.

A typical experimental procedure for the reaction of 1a with 5 is described below. To a flame-dried Schlenk flask (diameter: 2.5 cm) were placed [4a][BF4] (2.1 mg, 0.0025 mmol) and NMP (2.5 mL). Then, 1a (44.8 mg, 0.250 mmol) and 5 (66.4 mg, 0.304 mmol) were added. The reaction flask was placed in a water bath (25 °C) and illuminated with a 14 W white LED (approximately 2 cm from the light source) for 18 h. The resulting mixture was treated with DDQ (114.3 mg, 0.503 mmol) at room temperature for 30 min. Then, water (ca. 50 mL) was added and the mixture was extracted with Et2O (ca. 30 mL x 4). The combined organic layer was washed with brine (ca. 50 mL) and dried over anhydrous MgSO4. After concentration in vacuo, the residue was purified by column chromatography (eluent: hexane/ethyl acetate = 10/1) to give 7a (55.1 mg, 0.180 mmol, 72% yield). Spectroscopic characterization of 7aS2a and 7bS2b were reported elsewhere.

Determination of the quantum yield.

When the quantum yield of the photochemical reaction of 1a with 2a was determined, the reaction mixture was irradiated with an Ushio high pressure mercury lamp USH-250SC (250 W) with a 440 nm band-pass filter Kenko B-440 filter. The irradiated light intensity was estimated to be 1.41 x 10⁻⁷ einstein s⁻¹ by using K3[Fe(C₂O₄)₃] as an actinometer.6 The quantum yield of the reaction of 1a with 1.2 equiv. of 2a in the presence of 1 mol% of [4a][BF4] in 2.5 mL of NMP was determined to be Φ = 0.13 by the initial reaction rate (1.83 x 10⁻⁸ mol s⁻¹).

Effect of visible light irradiation on the initial stage of the reaction.

To obtain information on the reaction pathway, we investigated the effect of visible light irradiation at the initial stage of the reaction. When the reaction of 1a with 2a was carried out under
visible light illumination for 1 h, the addition product 3a’ was observed in 27% yield along with a trace amount of 3a. Then, the reaction mixture was stirred under dark for 17 h, and the same amount of the addition products were obtained. This result indicates that no further increase of the product yield was observed under dark. Considering this result, the contribution of radical chain mechanism initiated by visible light is negligible.

X-ray diffraction study of trans-3a.

After repeated recrystallization of 3a from ethanol, the pure major isomer trans-3a was obtained as colorless crystals. Colorless block crystals suitable for an X-ray analysis were obtained by recrystallization of trans-3a from ethanol. Diffraction data were collected on a Rigaku R-AXIS RAPID imaging plate diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.71075 Å) with Varimax optics. Reflections were collected for the 2θ range of 6° to 55°. Intensity data were corrected for empirical absorptions and Lorentz and polarization effects. Structure solutions and refinements were carried out by using CrystalStructure package. The positions of non-hydrogen atoms were determined by direct methods (SIR-97) and subsequent Fourier synthesis, and were refined on F₀² using all the unique reflections by full-matrix least squares with anisotropic thermal parameters. All the hydrogen atoms were placed at the calculated positions with fixed isotropic parameters. Anomalous dispersion effects were included in Fc, and atom scattering factors and the value for Δf’ and Δf’’ were taken from ref. S9. Details of the crystal and data collection parameters are summarized in Table S1. An ORTEP drawing of trans-3a is shown in Fig. S1.

CCDC 992086 (trans-3a) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
### Table S1  Crystallographic data for trans-3a

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<tr>
<th>Property</th>
<th>Value</th>
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<tr>
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<tr>
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<tr>
<td>α (deg)</td>
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<tr>
<td>β (deg)</td>
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<td>μ_calcd (cm⁻¹)</td>
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<td>GOF</td>
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<td>Max/min residual peaks (e⁻/Å³)</td>
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</table>

\[ R1 = \Sigma |F_0| - |F_c|/\Sigma |F_0|. \]

\[ wR2 = [\Sigma w(F_0^2 - F_c^2)^2]/\Sigma w(F_0^2)^2]^{1/2}; \quad w = 4F_0^2/(0.0023F_0^2 + 2\sigma(F_0^2)). \]

\[ \text{GOF} = [\Sigma w(F_0^2 - F_c^2)^2/\text{N}_{\text{obs}} - \text{N}_{\text{params}}]^{1/2}. \]
Fig. S1  ORTEP drawing of trans-3a.

References.


$^1$H, $^{13}$C, and $^{19}$F NMR spectra.
GCMS spectra.
Hexamethyldisiloxane (C₅H₁₅OSi₂ [M-CH₃]: m/z = 147):

3a' (C₂₁H₂₅NO₄ [M]: m/z = 355)