Supplementary Material

Photocatalyst-free Visible Light Promoted $E \rightarrow Z$ Isomerization of Alkenes

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1. General Information

All commercially available chemicals were used as received from Aldrich, TCI, Acros or Strem without further purification. $^1$H NMR and $^{13}$C NMR spectra were recorded on a Bruker Avance 400 Spectrometer ($^1$H 400 MHz and $^{13}$C 100.6 MHz). The blue LED [30.0 W, $\lambda$= 455 nm] was used as a visible light source.

2. The general procedure

In an reaction tube containing a magnetic stirring bar was charged with a mixture solution of (E)-alkene (0.3 mmol) in MeCN (2 ml) and water (0.2 mL), followed by the addition of NaOH (12.0 mg, 0.3 mmol). The reaction mixture was open to air and stirred under the irradiation of 30 W blue LED at room temperature. After reaction 24 hours, the solution was concentrated in vacuum. The residue was purified by column chromatography using a mixture of petroleum ether and ethyl acetate as eluent to give the desired product.

3. screening of reaction conditions

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<th>Entry</th>
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<th>Time</th>
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[^a] Reaction conditions: **E-1a** (0.3 mmol), base (0.3 mmol), solvent (2mL), H₂O (0.2mL), 30W blue LED, air, rt.; [^b] isolated yield; [^c] determined by ¹H NMR of crude product; [^d] No light. [^e] MeCN/H₂O = 1:1; [^f] MeCN/H₂O = 2:1; [^g] MeCN/H₂O = 5:1; [^h] MeCN/H₂O = 20:1;

### 3. Mechanistic Investigation

#### 3.1 Deuteration experiment

In an reaction tube containing a magnetic stirring bar was charged with a mixture solution of (E)-stilbene (54.0 mg, 0.3 mmol) in MeCN (2 ml) and deuterium oxide (0.2 mL), followed by the addition of NaOH (12.0 mg, 0.3 mmol). After being degassed three times of nitrogen, the tube was heated and stirred under the irradiation of 30 W blue LED. After reaction 24 hours, the solution was concentrated in vacuum. The residue was purified by column chromatography using a mixture of petroleum ether and ethyl acetate as eluent to give the product.

#### 3.2 The model reaction was carried under N₂

In an reaction tube containing a magnetic stirring bar was charged with a mixture solution of (E)-stilbene (54.0 mg, 0.3 mmol) in MeCN (2 ml) and water (0.2 mL), followed by the addition of NaOH (12.0 mg, 0.2 mmol). After being degassed three
times of nitrogen, the tube was heated and stirred under the irradiation of 30 W blue LED. After reaction 24 hours, the solution was concentrated in vacuum. The residue was purified by column chromatography using a mixture of petroleum ether and ethyl acetate as eluent to give the product.

3.3 Radical Control Experiment

In an oven-dried reaction tube with a magnetic stirring bar a solution of (E)-stilbene (54.0 mg, 0.3 mmol), MeCN (2 ml), water (0.2 mL), NaOH (12.0 mg, 0.3 mmol) and TEMPO (93.7 mg, 0.6 mmol). The reaction mixture was open to air and stirred under the irradiation of 30 W blue LED at room temperature for 24 h. After completion of the reaction, the solution was concentrated in vacuum. The residue was purified by column chromatography using a mixture of petroleum ether and ethyl acetate as eluent to give the product.

3.4 O$_2^-$ Radical Quenching Experiment

In an oven-dried reaction tube with a magnetic stirring bar a solution of (E)-stilbene (54.0 mg, 0.3 mmol), MeCN (2 ml), water (0.2 mL), NaOH (12.0 mg, 0.3 mmol) and DPPH (236.6 mg, 0.6 mmol). The reaction mixture was open to air and stirred under the irradiation of 30 W blue LED at room temperature for 24 h. After completion of the reaction, the solution was concentrated in vacuum. The residue was purified by column chromatography using a mixture of petroleum ether and ethyl acetate as eluent to give the product.

3.5 EPR experiments

a) standard conditions: A mixture of (E)-stilbene (54.0 mg, 0.3 mmol), MeCN (2 ml), water (0.2 mL), NaOH (12.0 mg, 0.3 mmol) and DMPO (10 μL) was open to air and stirred under the irradiation of 30 W blue LED at room temperature for 2 h. Afterwards, 20 μL of the mixture was quickly taken out into a small tube and analyzed by EPR.

b) without water under the standard conditions: A mixture of (E)-stilbene (54.0 mg, 0.3 mmol), MeCN (2 ml), NaOH (12.0 mg, 0.3 mmol) and DMPO (10 μL) was open to air and stirred under the irradiation of 30 W blue LED at room temperature
for 2 h. Afterwards, 20 uL of the mixture was quickly taken out into a small tube and analyzed by EPR.

c) without NaOH under the standard conditions: A mixture of (E)-stilbene (54.0 mg, 0.3 mmol), MeCN (2 ml), water (0.2 mL) and DMPO (10 uL) was open to air and stirred under the irradiation of 30 W blue LED at room temperature for 2 h. Afterwards, 20 uL of the mixture was quickly taken out into a small tube and analyzed by EPR.

d) without (E)-stilbene under the standard conditions: A mixture of NaOH (12.0 mg, 0.3 mmol), MeCN (2 ml), water (0.2 mL) and DMPO (10 uL) was open to air and stirred under the irradiation of 30 W blue LED at room temperature for 2 h. Afterwards, 20 uL of the mixture was quickly taken out into a small tube and analyzed by EPR.

Figure 1. EPR spectra (X band, 9.4 GHz, rt) of (a) (E)-1a and NaOH in the mixture of CH₃CN and water, under blue LED irritation 2h; (b) (E)-1a and NaOH in CH₃CN, under blue LED irritation 2h; (c) (E)-1a in the mixture of CH₃CN and water, under blue LED irritation 2h; (d) NaOH in the mixture of CH₃CN and water, under blue LED irritation.
4. Characterization Data of Products

(Z)-1,2-phenylethene (Z-1a). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.26-7.18 (m, 10H), 6.60 (s, 2H); $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 137.3, 130.3, 128.9, 128.2, 127.1.

(Z)-1,2-di-p-tolylethene. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.15-7.13 (m, 2H), 7.09-7.05 (m, 2H), 6.94-6.89 (m, 4H), 6.71 (s, 2H), 2.28 (s, 6H); $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 136.5, 136.2, 130.0, 129.5, 129.1, 127.0, 125.4, 19.9.

(Z)-1,2-di-m-tolylethene. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.16 (d, $J = 8.1$ Hz, 4H), 7.02 (d, $J = 7.8$ Hz, 4H), 6.51 (s, 2H), 2.31 (s, 6H); $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 136.8, 134.5, 129.5, 128.9, 128.8, 21.3.

(Z)-1,2-bis(4-fluorophenyl)ethene. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.14-7.12 (m, 4H), 7.09-7.06 (m, 4H), 6.48 (s, 2H); $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 135.2, 133.0, 130.2, 129.6, 128.6.
(Z)-1,2-bis(4-chlorophenyl)ethane.\(^1\) \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta 7.21-7.13\) (m, 6H), 7.09-7.07 (m, 2H), 6.57 (s, 2H); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz): \(\delta 138.5, 134.2, 130.0, 129.6, 128.8, 127.5, 126.9\).

\(\text{Z-1f}\)

(Z)-1,2-bis(3-chlorophenyl)ethene.\(^1\) \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta 7.26-7.15\) (m, 6H), 7.13-7.03 (m, 3H), 6.56 (d, \(J = 1.04\) Hz, 2H); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz): \(\delta 138.5, 134.2, 130.0, 129.9, 129.6, 128.8, 128.6, 127.9, 127.5, 127.0, 126.4, 124.9\).

\(\text{Z-1g}\)

(Z)-1,2-bis(4-bromophenyl)ethane.\(^4\) \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta 7.37-7.34\) (m, 4H), 7.09-7.06 (m, 4H), 6.53 (s, 2H); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz): \(\delta 135.7, 131.5, 130.5, 129.7\).

\(\text{Z-1h}\)

(Z)-1,2-bis(4-(trifluoromethyl)phenyl)ethane.\(^5\) \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta 7.49\) (d, \(J = 8.6\) Hz, 4H), 7.30 (d, \(J = 8.0\) Hz, 4H), 6.72 (s, 2H); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz): \(\delta 140.1, 130.7, 130.0, 129.6, 129.3, 129.1, 126.9, 125.5, 125.4, 125.37, 125.33, 122.7\).

\(\text{Z-1i}\)

(Z)-4-Chloro-4'-methoxystilbene.\(^6\) \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta 7.22-7.11\) (m, 4H), 6.81 (d, \(J = 7.62\) Hz, 1H), 6.78-6.76 (m, 2H), 6.57 (dd, \(J = 37.46, 12.2\) Hz, 2H), 3.67 (s, 3H); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz): \(\delta 159.4, 139.1, 137.9, 134.0, 131.4, 129.5, 129.4, 128.9, 128.8, 127.2, 127.1, 121.5, 113.7, 113.6, 55.1\).
(Z)-1-methoxy-4-styrylbenzene. $^7$ $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.21-7.10 (m, 7H), 6.69-6.66 (m, 2H), 6.41 (s, 2H), 3.70 (s, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 158.7, 137.6, 130.2, 129.8, 128.8, 128.7, 128.3, 126.9, 113.6, 55.2.

(Z)-1-methyl-4-styrylbenzene. $^8$ $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.26-7.15 (m, 5H), 7.10-7.03 (m, 3H), 6.99-6.97 (m, 1H), 6.55 (s, 2H), 2.24 (s, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 137.9, 137.4, 137.3, 130.5, 130.2, 129.7, 128.9, 128.3, 128.2, 127.9, 127.2, 125.9, 21.5.

(Z)-1-methyl-3-styrylbenzene. $^9$ $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.18-7.10 (m, 8H), 7.03-7.01 (m, 1H), 6.64-6.56 (m, 2H), 2.25 (s, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 137.3, 137.2, 136.2, 130.7, 130.2, 129.7, 129.1, 129.0, 128.3, 127.4, 127.2, 125.9, 20.1.

(Z)-1,2,3-Trimethoxy-5-styrylbenzenes. $^{10}$ $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.17-7.10 (m, 4H), 7.06-7.03 (m, 1H), 6.46 (d, $J = 12.16$ Hz, 1H), 6.37-6.34 (m, 3H), 3.70 (s, 3H), 3.49 (s, 6H); $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 152.8, 137.5, 137.1, 132.5, 130.2, 130.0, 128.9, 128.3, 127.2, 106.1, 60.9, 55.8.
(Z)-1-fluoro-4-styrylbenzene.\textsuperscript{12} \( ^1H \) NMR (400 MHz, CDCl\textsubscript{3}): \( \delta \) 7.25-7.18 (m, 7H), 6.93-6.87 (m, 2H), 6.56 (dd, \( J = 22.1, 12.2 \) Hz, 2H); \( ^13C \) NMR (CDCl\textsubscript{3}, 100 MHz): \( \delta \) 163.0, 160.6, 137.0, 133.2, 133.1, 130.6, 130.5, 130.3, 129.1, 128.8, 128.3, 127.3, 115.3, 115.1.

(Z)-1-chloro-4-styrylbenzene.\textsuperscript{1} \( ^1H \) NMR (400 MHz, CDCl\textsubscript{3}): \( \delta \) 7.22-7.15 (m 9H), 6.57 (dd, \( J = 40.4, 21.2 \) Hz, 2H); \( ^13C \) NMR (CDCl\textsubscript{3}, 100 MHz): \( \delta \) 136.9, 135.7, 132.8, 131.0, 130.3, 129.0, 128.9, 128.5, 128.4, 127.4.

(Z)-1-nitro-4-styrylbenzene.\textsuperscript{13} \( ^1H \) NMR (400 MHz, CDCl\textsubscript{3}): \( \delta \) 8.14 (dd, \( J = 6.96, 1.92 \) Hz, 2H), 7.55 (dd, \( J = 7.04, 1.72 \) Hz, 2H), 7.49-7.47 (m, 2H), 7.35-7.31 (m, 2H), 7.28-7.26 (m, 1H), 7.21-7.17 (m, 1H), 7.06 (d, \( J = 16.32 \) Hz, 1H); \( ^13C \) NMR (CDCl\textsubscript{3}, 100 MHz): \( \delta \) 146.7, 143.9, 136.2, 133.3, 129.0, 127.1, 126.9, 126.3, 124.2.

(Z)-1-styryl-3-(trifluoromethyl)benzene.\textsuperscript{15} \( ^1H \) NMR (400 MHz, CDCl\textsubscript{3}): \( \delta \) 7.44 (d, \( J = 8.20 \) Hz, 2H), 7.31 (d, \( J = 8.56 \) Hz, 2H), 7.22-7.18 (m, 5H), 6.68 (d, \( J = 12.24 \) Hz, 1H), 6.56 (d, \( J = 12.24 \) Hz, 1H); \( ^13C \) NMR (CDCl\textsubscript{3}, 100 MHz): \( \delta \) 141.0, 140.9, 136.6, 132.4, 129.2, 128.9, 128.8, 128.7, 128.5, 127.7, 126.3, 125.3, 125.2.
(Z)-4-styrylaniline.\textsuperscript{11} \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \(\delta\) 7.31-7.28 (m, 2H), 7.25-7.17 (m, 3H), 7.08-7.05 (m, 2H), 6.54-6.51 (m, 2H), 6.45 (dd, \(J = 20.8, 12.24\) Hz, 2H), 3.67 (s, 2H); \textsuperscript{13}C NMR (CDCl\textsubscript{3}, 100 MHz): \(\delta\) 145.5, 138.0, 130.2, 130.1, 128.8, 128.2, 127.6, 127.5, 126.7, 114.7.

(Z)-4-Styrylbenzaldehyde.\textsuperscript{14} \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \(\delta\) 9.95 (s, 1H), 7.73 (d, \(J = 7.48\) Hz, 2H), 7.39 (d, \(J = 7.76\) Hz, 2H), 7.26-7.24 (m, 7H), 6.76 (d, \(J = 12.28\) Hz, 1H), 6.62 (d, \(J = 12.24\) Hz, 1H); \textsuperscript{13}C NMR (CDCl\textsubscript{3}, 100 MHz): \(\delta\) 191.9, 143.8, 136.5, 134.9, 133.0, 129.7, 129.5, 129.0, 128.9, 128.4, 127.7.

(Z)-4-Styrylpyridine.\textsuperscript{15} \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \(\delta\) 8.44 (d, \(J = 5.96\) Hz, 2H), 7.26-7.19 (m, 5H), 7.10 (d, \(J = 5.88\) Hz, 2H), 6.79 (d, \(J = 12.28\) Hz, 1H), 6.50 (d, \(J = 12.28\) Hz, 1H); \textsuperscript{13}C NMR (CDCl\textsubscript{3}, 100 MHz): \(\delta\) 149.8, 145.0, 136.1, 134.1, 128.8, 128.5, 127.9, 127.6, 123.5.

(Z)-3-phenylacrylamide.\textsuperscript{16} \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \(\delta\) 7.49-7.47 (m, 2H), 7.39-7.33 (m, 3H), 6.87 (d, \(J = 12.6\)Hz, 1H), 6.01 (d, \(J = 12.6\) Hz, 1H), 5.43 (s, 2H); \textsuperscript{13}C NMR (CDCl\textsubscript{3}, 100 MHz): \(\delta\) 168.8, 137.6, 134.8, 128.9, 128.8, 128.6, 123.8.

(Z)-3-(p-tolyl) acrylamide. Yellow Solid, mp. 119-121\degree C. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \(\delta\) 7.38 (d, \(J = 8.08\) Hz, 2H), 7.17 (d, \(J = 8.0\) Hz, 2H), 6.83 (d, \(J = 12.56\) Hz, 1H), 5.94 (d, \(J = 12.52\) Hz, 1H), 5.44 (d, \(J = 22.12\) Hz, 2H), 2.36 (s, 3H); \textsuperscript{13}C NMR
(CDCl₃, 100 MHz): δ 169.0, 139.0, 137.7, 131.9, 129.3, 128.9, 123.0, 21.3. HRMS (ESI) calcd. for C₁₀H₁₂NO [M+H]^+: 162.0913, found: 162.0915.

(Z)-3-(4-methoxyphenyl) acrylamide. White Solid, mp. 146-147 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.51-7.49 (m, 2H), 6.89-6.87 (m, 2H), 6.77 (d, J = 12.56 Hz, 1H), 5.87 (d, J = 12.56 Hz, 1H), 5.66 (d, J = 18.84 Hz, 2H), 3.82 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz): δ 169.3, 137.8, 130.9, 130.2, 127.2, 121.4, 113.8, 55.3. HRMS (ESI) calcd. for C₁₀H₁₂NO [M+H]^+: 178.0863, found: 178.0864.

(Z)-3-(2-methoxyphenyl) acrylamide. Yellow oil, mp. 132-133 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.44 (d, J = 7.52 Hz, 1H), 7.32-7.28 (m, 1H), 7.00-6.97 (m, 1H), 6.94-6.88 (m, 2H), 6.20 (s, 1H), 5.97 (d, J = 12.56 Hz, 1H), 5.68 (s, 1H), 3.84 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz): δ 169.5, 157.0, 133.6, 130.4, 130.2, 124.1, 123.7, 120.5, 110.6, 55.4. HRMS (ESI) calcd. for C₁₀H₁₂NO₂ [M+H]^+: 178.0863, found: 178.0862.

(Z)-3-(m-tolyl) acrylamide. White Solid, mp. 123-124 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.28-7.21 (m, 3H), 7.12 (d, J = 7.32 Hz, 1H), 6.78 (d, J = 12.6 Hz, 1H), 6.17 (s, 1H), 5.94 (d, J = 12.6 Hz, 1H), 5.74 (s, 1H), 2.34 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz): δ 169.5, 138.2, 137.7, 134.8, 129.5, 128.5, 125.9, 123.7, 21.4. HRMS (ESI) calcd. for C₁₀H₁₂NO [M+H]^+: 162.0913, found: 162.0914.

(Z)-3-(4-fluorophenyl) acrylamide. Colorless Oil. ¹H NMR (400 MHz, CDCl₃): δ 7.55-7.52 (m, 2H), 7.07-7.03 (m, 2H), 6.79 (d, J = 12.56 Hz, 1H), 5.97 (d, J = 12.6 Hz,
$^1$H, 5.42 (s, 2H); $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 168.9, 136.9, 131.2, 131.1, 122.9, 115.6, 115.4. HRMS (ESI) calcd. for C$_9$H$_9$FNO [$M+H]^+$: 166.0663, found: 166.0666.

(Z)-3-(4-chlorophenyl) acrylamide. Yellow Oil. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.48-7.46 (m, 2H), 7.34-7.32 (m, 2H), 6.77 (d, $J = 12.6$ Hz, 1H), 6.01 (d, $J = 12.6$ Hz, 1H), 5.45 (s, 2H); $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 168.4, 136.7, 133.1, 130.5, 128.7, 123.7. HRMS (ESI) calcd. for C$_9$H$_9$ClNO [$M+H]^+$: 182.0367, found: 182.0368.

(Z)-3-(4-bromophenyl) acrylamide. Yellow Solid, mp. 156-158 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.50-7.48 (m, 2H), 7.41-7.39 (m, 2H), 6.75 (d, $J = 12.6$ Hz, 1H), 6.02 (d, $J = 12.56$ Hz, 1H), 5.45 (s, 2H); $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 169.1, 136.7, 133.6, 131.6, 130.7, 123.9, 123.1. HRMS (ESI) calcd. for C$_9$H$_9$BrNO [$M+H]^+$: 225.9862, found: 225.9866.
5. References


6. NMR spectra of products