Supplementary Information

Visible-light-promoted Difunctionalization of Olefins Leading to α-Thiocyanato ketones

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1. General information

All commercially available reagent grade chemicals were purchased from Aldrich, Acros, Alfa Aesar and Beijing Ouhe Chemical Company and used as received without further purification unless otherwise stated. All solvents were dried according to standard procedures. $^1$H NMR and $^{13}$C NMR were recorded in CDCl$_3$ on a Bruker Avance III 400 spectrometer with TMS as internal standard (500 MHz $^1$H, 125 MHz $^{13}$C) at room temperature, the chemical shifts ($\delta$) were expressed in ppm and $J$ values were given in Hz. The following abbreviations are used to indicate the multiplicity: singlet (s), doublet (d), triplet (t), quartet (q), doublet of doublets (dd), doublet of triplets (dt), and multiplet (m). All first order splitting patterns were assigned on the basis of the appearance of the multiplet. Splitting patterns that could not be easily interpreted were designated as multiplet (m). Mass analyses and HRMS were obtained on a Finnigan-LCQDECA mass spectrometer and a Bruker Daltonics Bio-TOF-Q mass spectrometer by the ESI method, respectively. Column chromatography was performed on silica gel (200-300 mesh). There is 3.0 cm distance between the reactor and LEDs.

2. General procedure for visible-light-induced difunctionalization of olefins leading to $\alpha$-thiocyanato ketones.

\[
\begin{align*}
R^1\rightleftharpoons R^2 + NH_4SCN + O_2 &\xrightarrow{\text{Na}_2\text{-Eosin Y (2 mol%)} \atop \text{3w blue LED} } CH_3CN, \text{rt, 5h}} \rightarrow R^1\overset{\text{SCN}}{\rightleftharpoons} R^2
\end{align*}
\]

To a solution of NH$_4$SCN 2 (0.4 mmol) and Na$_2$-EosinY (0.004 mmol, 2 mol %) in CH$_3$CN 5 mL was added alkene 1 (0.2 mmol). The reaction mixture was stirred under the irradiation of 3w blue LEDs in oxygen atmosphere at room temperature for 5h. After completion of the reaction, the solution was concentrated in vacuum. The residue was purified using a mixture of ethyl acetate as eluent to give the desired product 4.

3. Preliminary mechanistic studies

3.1 The addition of TEMPO in the model reaction system.
To a solution of NH₄SCN 2 (0.4 mmol), TEMPO (0.4 mmol), and Na₂-EosinY (0.004 mmol, 2 mol %) in CH₃CN 5 mL was added styrene 1a (0.2 mmol). The reaction mixture was stirred under the irradiation of 3W blue LEDs in oxygen atmosphere at room temperature for 5h. After completion of the reaction, the solution was concentrated in vacuum, no desired product 4a was detected.

3.1.1 The addition of BHT in the model reaction system.

To a solution of NH₄SCN 2 (0.4 mmol), BHT (0.4 mmol), and Na₂-EosinY (0.004 mmol, 2 mol %) in CH₃CN 5 mL was added styrene 1a (0.2 mmol). The reaction mixture was stirred under the irradiation of 3W blue LEDs in oxygen atmosphere at room temperature for 5h. After completion of the reaction, the solution was concentrated in vacuum, only a trace amount of desired product 4a was detected.

3.2. The UV-visible spectroscopy and Fluorescence quenching studies (Stern – Volmer Studies)

UV-visible spectroscopy of reaction solution was recorded on a SHIMADZU UV-3600 UV-visible spectrophotometer. The sample was prepared by mixing Na₂-EosinY, NH₄SCN and styrene with solvent CH₃CN (M[Na₂-EosinY] = 4.0×10⁻⁵mol/L, M[styrene] = 2.0×10⁻³mol/L, M[NH₄SCN] = 4.0×10⁻³mol/L in a light path quartz UV cuvette. The UV-visible spectroscopy indicated that the maximum absorption wavelength of reaction solution was found to be 535 nm. The absorption was collected and the result was listed in Figure S1.
Figure S1. UV–vis spectra of the reaction mixture.

The fluorescence emission intensity of reaction solution was recorded on a Fluoromax-4600 spectrofluorimeter. The excitation wavelength was fixed at 537nm, and the emission wavelength was measured at 555 nm. The sample was prepared by mixing Na2-EosinY, styrene, NH4SCN with solvent CH3CN (M[Na2-EosinY] = 4.0×10^{-6}mol/L, M[styrene] = 2.0×10^{-4}mol/L, M[NH4SCN] = 4.0×10^{-4}mol/L) in a light path quartz fluorescence cuvette. The emission intensity was collected and the result was listed in Figure S2.

Figure S2. Fluorescence spectra of the photooxysulfonation reaction mixture

Fluorescence quenching experiments
The fluorescence emission intensities were recorded on a Fluormax-4600 spectrofluorimeter. The excitation wavelength was fixed at 537 nm, and the emission wavelength was measured at 555 nm (emission maximum). The samples were prepared by mixing Na\textsubscript{2}-EosinY (4.0×10\textsuperscript{-6} mol/L) and different amounts of NH\textsubscript{4}SCN in CH\textsubscript{3}CN (total volume = 0.1 mL) in a light path quartz fluorescence cuvette. The concentration of NH\textsubscript{4}SCN stock solution is 4.0×10\textsuperscript{-8} mol/L in CH\textsubscript{3}CN. For each quenching experiment, 0.1 mL of NH\textsubscript{4}SCN stock solution was titrated to a mixed solution of Na\textsubscript{2}-EosinY (0.1 mL, in a total volume = 1.0 mL). Then the emission intensity was collected and the results were presented in Figure S3.

![Figure S3](image.png)

**Figure S3.** Quenching of Na\textsubscript{2}-EosinY fluorescence emission in the presence of NH\textsubscript{4}SCN

An indeed fluorescence quenching phenomenon of Na\textsubscript{2}-EosinY under various concentrations of NH\textsubscript{4}SCN was demonstrated in a curve of \( [I_0/I] \) vs C [NH\textsubscript{4}SCN], as shown in Figure S4 (Stern-Volmer plots).
Figure S4. Stern-volmer plots

The fluorescence emission intensities were recorded on a Fluormax-4600 spectrophotometer. The excitation wavelength was fixed at 537 nm, and the emission wavelength was measured at 555 nm (emission maximum). The samples were prepared by mixing Na2-EosinY (4.0×10^{-6} mol/L) and different amounts of styrene in CH3CN (total volume = 0.1 mL) in a light path quartz fluorescence cuvette. The concentration of styrene stock solution is 2.0×10^{-8} mol/L in CH3CN. For each quenching experiment, 0.1 mL of styrene stock solution was titrated to a mixed solution of Na2-EosinY (0.1 mL, in a total volume = 1.0 mL). Then the emission intensity was collected and the results were presented in Figure S5. An fluorescence quenching phenomenon of Na2-EosinY under various concentrations of alkynes was shown in Figure S6 (Stern-Volmer plots).

Figure S5. Quenching of Na2-EosinY fluorescence emission in the presence of styrene

Figure S6. Stern-volmer plots
4. Characterization data of products 4a-4p

**1-phenyl-2-thiocyanatoethanone.** Compound 4a was obtained in 79% yield according to the general procedure. $^1$H NMR (CDCl$_3$, 500 MHz, ppm): $\delta$ 7.95 (d, $J = 8.0$ Hz, 2H), 7.68 (t, $J = 7.3$ Hz), 7.54 (t, $J = 7.7$ Hz, 2H), 4.75 (s, 2H); $^{13}$C NMR (CDCl$_3$, 125MHz, ppm): $\delta$ 190.8, 134.8, 134.0, 129.2, 128.5, 111.9, 43.0; HRMS calc. for C$_9$H$_7$NOSNa (M+Na)$^+$, 200.0146; found, 200.0149.

**2-thiocyanato-1-p-tolylethanone,** Compound 4b was obtained in 70% yield according to the general procedure. $^1$H NMR (CDCl$_3$, 500 MHz, ppm): $\delta$ 7.84 (d, $J = 8.2$ Hz, 2H), 7.32 (d, $J = 8.0$ Hz, 2H), 4.72 (s, 2H), 2.45 (s, 3H); $^{13}$C NMR (CDCl$_3$, 125MHz, ppm): $\delta$ 190.4, 146.1, 131.5, 129.9, 128.6, 112.0, 43.1, 21.9; HRMS calc. for C$_{10}$H$_9$NOSNa (M+Na)$^+$, 214.0303; found, 214.0308.

**2-thiocyanato-1-m-tolylethanone,** Compound 4c was obtained in 78% yield according to the general procedure. $^1$H NMR (CDCl$_3$, 500 MHz, ppm): $\delta$ 7.74 (t, $J = 6.7$ Hz, 2H), 7.48 (d, $J = 7.6$ Hz, 1H), 7.41 (t, $J = 7.6$ Hz, 1H), 4.74 (s, 2H), 2.44 (s, 3H); $^{13}$C NMR (CDCl$_3$, 125 MHz, ppm): $\delta$ 191.0, 139.2, 135.6, 134.0, 129.0, 129.0, 125.7, 111.9, 43.1, 21.3; HRMS calc. for C$_{10}$H$_9$NOSNa (M+Na)$^+$, 214.0303; found, 214.0305.

**1-(4-tert-butylphenyl)-2-thiocyanatoethanone,** Compound 4d was obtained in 74% yield according to the general procedure. $^1$H NMR (CDCl$_3$, 500 MHz, ppm): $\delta$ 7.70 (d, $J = 7.9$ Hz, 1H), 7.50-7.48 (m, 1H), 7.34 (t, $J = 7.9$ Hz, 2H), 4.71 (s, 2H), 2.57 (s, 3H); $^{13}$C
NMR (CDCl₃, 125 MHz, ppm): δ 193.1, 140.5, 133.5, 133.4, 132.8, 130.0, 126.2, 112.0, 45.0, 21.9; HRMS calc. for C₁₀H₉NOSNa (M+Na)⁺, 214.0303; found, 214.0301.

**1-(4-tert-butylphenyl)-2-thiocyanatoethanone**, Compound 4e was obtained in 69% yield according to the general procedure. ¹H NMR (CDCl₃, 500 MHz, ppm): δ 7.88 (d, J = 8.5 Hz, 2H), 7.54 (d, J = 8.5 Hz, 2H), 4.73 (s, 2H), 1.35 (s, 9H); ¹³C NMR (CDCl₃, 125 MHz, ppm): δ 190.4, 159.0, 131.4, 128.5, 126.2, 112.1, 43.1, 35.4, 31.0; HRMS calc. for C₁₃H₁₅NOSNa (M+Na)⁺, 256.0772; found, 256.0777.

![Image](https://via.placeholder.com/150)

1-(4-methoxyphenyl)-2-thiocyanatoethanone, Compound 4f was obtained in 51% yield according to the general procedure; ¹H NMR (CDCl₃, 500 MHz, ppm): δ 7.92 (d, J = 8.9 Hz, 2H), 6.99 (d, J = 9.0 Hz, 2H), 4.71 (s, 2H), 3.90 (s, 3H); ¹³C NMR (CDCl₃, 125 MHz, ppm): δ 189.2, 164.8, 130.9, 127.0, 114.4, 112.2, 55.7, 43.0; HRMS calc. for C₁₀H₉NO₂SNa (M+Na)⁺, 230.0252; found, 230.0249.

![Image](https://via.placeholder.com/150)

**1-(4-(chloromethyl)phenyl)-2-thiocyanatoethanone**, Compound 4g was obtained in 72% yield according to the general procedure; ¹H NMR (CDCl₃, 500 MHz, ppm): δ 7.94 (d, J = 8.2 Hz, 2H), 7.56 (d, J = 8.2 Hz, 2H), 4.73 (s, 2H), 4.63 (s, 2H); ¹³C NMR (CDCl₃, 125 MHz, ppm): δ 190.2, 144.3, 133.7, 129.2, 128.9, 111.7, 45.0, 42.9; HRMS calc. for C₁₀H₉ClNOSNa (M+Na)⁺, 247.9913; found, 247.9916.

![Image](https://via.placeholder.com/150)

**4-(2-thiocyanatoacetyl)phenyl acetate**, Compound 4h was obtained in 49% yield according to the general. ¹H NMR (CDCl₃, 500 MHz, ppm): δ 7.97 (d, J = 8.6 Hz, 2H), 7.27 (d, J = 8.7 Hz, 2H), 4.72 (s, 2H), 2.34 (s, 3H); ¹³C NMR (CDCl₃, 125 MHz, ppm): δ
1-(4-fluorophenyl)-2-thiocyanatoethanone, Compound 4i was obtained in 79% yield according to the general procedure. $^1$H NMR (CDCl$_3$, 500 MHz, ppm): $\delta$ 8.00-7.98 (m, 2H), 7.23-7.20 (m, 2H), 4.71 (s, 2H); $^{13}$C NMR (CDCl$_3$, 125 MHz, ppm): $\delta$ 189.3, 166.6 (d, $J$ = 256.7 Hz), 131.3 (d, $J$ = 9.7 Hz), 130.5 (d, $J$ = 3.0 Hz), 116.5 (d, $J$ = 22.1 Hz), 42.7; HRMS calc. for C$_{11}$H$_8$FNOSNa (M+Na)$^+$, 258.0205; found, 258.0205.

1-(3-fluorophenyl)-2-thiocyanatoethanone, Compound 4j was obtained in 71% yield according to the general procedure. $^1$H NMR (CDCl$_3$, 500 MHz, ppm): $\delta$ 7.72 (d, $J$ = 7.8 Hz, 1H), 7.65 (d, $J$ = 9.0 Hz, 1H), 7.56-7.51 (m, 1H), 7.40-7.37 (m, 1H), 4.70 (s, 2H); $^{13}$C NMR (CDCl$_3$, 125 MHz, ppm): $\delta$ 189.7, 162.7 (d, $J$ = 248.5 Hz), 135.9 (d, $J$ = 6.4 Hz), 131.0 (d, $J$ = 7.7 Hz), 124.3 (d, $J$ = 3.1 Hz), 122.0 (d, $J$ = 21.3 Hz), 115.2 (d, $J$ = 22.6 Hz), 111.5, 42.7; HRMS calc. for C$_{10}$H$_6$FNOSNa (M+Na)$^+$, 218.0059; found, 218.0053.

1-(4-chlorophenyl)-2-thiocyanatoethanone, Compound 4k was obtained in 68% yield according to the general procedure. $^1$H NMR (CDCl$_3$, 500 MHz, ppm): $\delta$ 7.89 (d, $J$ = 9.1 Hz, 2H), 7.51 (d, $J$ = 8.7 Hz, 2H), 4.70 (s, 2H); $^{13}$C NMR (CDCl$_3$, 125 MHz, ppm): $\delta$ 189.7, 141.6, 132.3, 129.8, 129.6, 111.6, 42.7; HRMS calc. for C$_{10}$H$_6$ClNOSNa (M+Na)$^+$, 233.9755; found, 233.9755.

1-(3-chlorophenyl)-2-thiocyanatoethanone, Compound 4l was obtained in 72% yield according to the general procedure. $^1$H NMR (CDCl$_3$, 500 MHz, ppm): $\delta$ 7.93 (t, $J$ = 1.9 Hz, 1H), 7.82 (d, $J$ = 7.8 Hz, 1H), 7.66-7.64 (m, 1H), 7.49 (t, $J$ = 7.9 Hz, 1H), 4.70 (s,
2H); $^{13}$C NMR (CDCl$_3$, 125 MHz, ppm): $\delta$ 189.7, 135.7, 135.4, 134.8, 130.5, 128.5, 126.5, 111.4, 42.6; HRMS calc. for C$_9$H$_6$ClNOSNa (M+Na)$^+$, 233.9756; found, 233.9751.

1-(4-bromophenyl)-2-thiocyanatoethanone, Compound 4m was obtained in 64% yield according to the general procedure. $^1$H NMR (CDCl$_3$, 500 MHz, ppm): $\delta$ 7.81 (d, $J$ = 8.6 Hz, 2H), 7.69 (d, $J$ = 8.7 Hz, 2H), 4.69 (s, 2H); $^{13}$C NMR (CDCl$_3$, 125 MHz, ppm): $\delta$ 189.9, 132.7, 132.6, 130.4, 129.9, 111.5, 42.6; HRMS calc. for C$_9$H$_6$BrNOSNa (M+Na)$^+$, 277.9251; found, 277.9257.

1-(2-bromophenyl)-2-thiocyanatoethanone, Compound 4n was obtained in 62% yield according to the general procedure. $^1$H NMR (CDCl$_3$, 500 MHz, ppm): $\delta$ 7.69-7.67 (m, 1H), 7.59-7.57 (m, 1H), 7.48-7.57 (m, 2H), 4.63 (s, 2H); $^{13}$C NMR (CDCl$_3$, 125 MHz, ppm): $\delta$ 193.9, 137.7, 134.2, 133.5, 130.2, 128.0, 119.7, 111.2, 44.0; HRMS calc. for C$_9$H$_6$BrNOSNa (M+Na)$^+$, 277.9251; found, 277.9253.

1-(naphthalen-2-yl)-2-thiocyanatoethanone, Compound 4o was obtained in 82% yield according to the general procedure. $^1$H NMR (CDCl$_3$, 500 MHz, ppm): $\delta$ 8.43 (s, 1H), 7.98-7.89 (m, 4H), 7.68-7.59 (m, 2H), 4.86 (s, 2H); $^{13}$C NMR (CDCl$_3$, 125 MHz, ppm): $\delta$ 190.8, 136.2, 132.3, 131.3, 130.8, 129.8, 129.6, 129.2, 128.0, 127.5, 123.3, 112.0, 43.1; HRMS calc. for C$_{13}$H$_9$NOSNa (M+Na)$^+$, 250.0303; found, 250.0307.
1-phenyl-2-thiocyanatopropan-1-one, Compound 4p was obtained in 51% yield according to the general procedure. $^1$H NMR (CDCl₃, 500 MHz, ppm): $\delta$ 7.93 (d, $J = 7.2$ Hz, 2H), 7.67 (t, $J = 7.5$ Hz, 1H), 7.54 (t, $J = 7.9$ Hz, 2H), 5.10-5.06 (m, 1H), 1.87 (d, $J = 7.2$ Hz, 3H); $^{13}$C NMR (CDCl₃, 125 MHz, ppm): $\delta$ 194.8, 134.6, 133.2, 129.2, 128.8, 111.5, 50.0, 19.9; HRMS calc. for C₁₀H₉NOSNa (M+Na)$^+$, 214.0303; found, 214.0305.
5. Copies of NMR spectra for 4a–4p