JOC The Journal of Organic Chemistry

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Visible-Light-Mediated Additive-Free Decarboxylative Ketonization Reaction of Acrylic Acids: An Access to α-Thiocyanate Ketones

Zhi-Lv Wang, Jie Chen, Yan-Hong He,* and Zhi Guan*

Cite This: J. Org. Chem. 2021, 86, 3741−3749 Read Online

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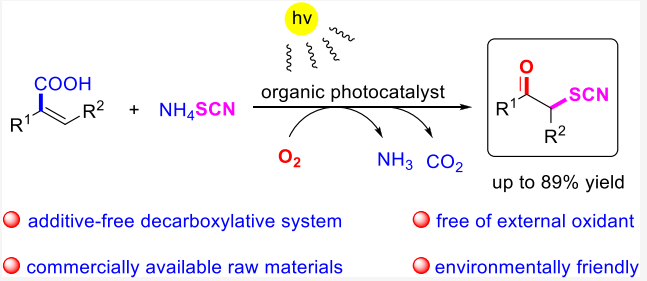
ABSTRACT: Visible-light-mediated additive-free decarboxylative functionalization of acrylic acids has been developed. The reaction uses inexpensive organic dye 9,10-dicyanoanthracene as a photocatalyst and uses the ubiquitous dioxygen as both an oxygen source and an oxidant. Through this mild and environmentally friendly method, a series of important α-thiocyanate ketones can be generated from easily available acrylic acids and ammonium thiocyanate. In addition, the facile transformation of product α-thiocyanate ketones makes this method have great potential for application in organic and pharmaceutical chemistry.



INTRODUCTION

Carboxylic acids are one of the most abundant and inexpensive chemicals, so they are usually used as raw materials for organic synthesis. The decarboxylative functionalization reaction of carboxylic acids has long been regarded as a general platform to access many high-value chemical products.[1] Traditionally, metal catalysis is an effective strategy for decarboxylative functionalization of carboxylic acids.[2] For instance, Wang's group developed a $CuBr_2$-catalyzed decarboxylative acylation of acyl C−H of formamides with α-oxocarboxylic acids, leading to α-ketoamides (Scheme 1A).[2c] Qu's group reported a silver-catalyzed decarboxylative acylarylation of acrylamides with α-oxocarboxylic acids, producing 3-acyl-4-arylquinolin-2(1*H*)-ones (Scheme 1B).[2d] However, metal-catalyzed decarboxylative reactions usually require harsh conditions, such as (over) stoichiometric dangerous oxidants and elevated reaction temperatures. Recently, the visible-light-mediated radical strategy has opened a new window for realizing decarboxylative functionalization reactions, owing to its mild, environmentally friendly, and sustainable conditions.[3] As such, visible-light-mediated decarboxylative functionalization reactions have received extensive attention, and various relevant transformations including the formation of a novel C−C bond and a C−heteroatom bond have been reported.[4]

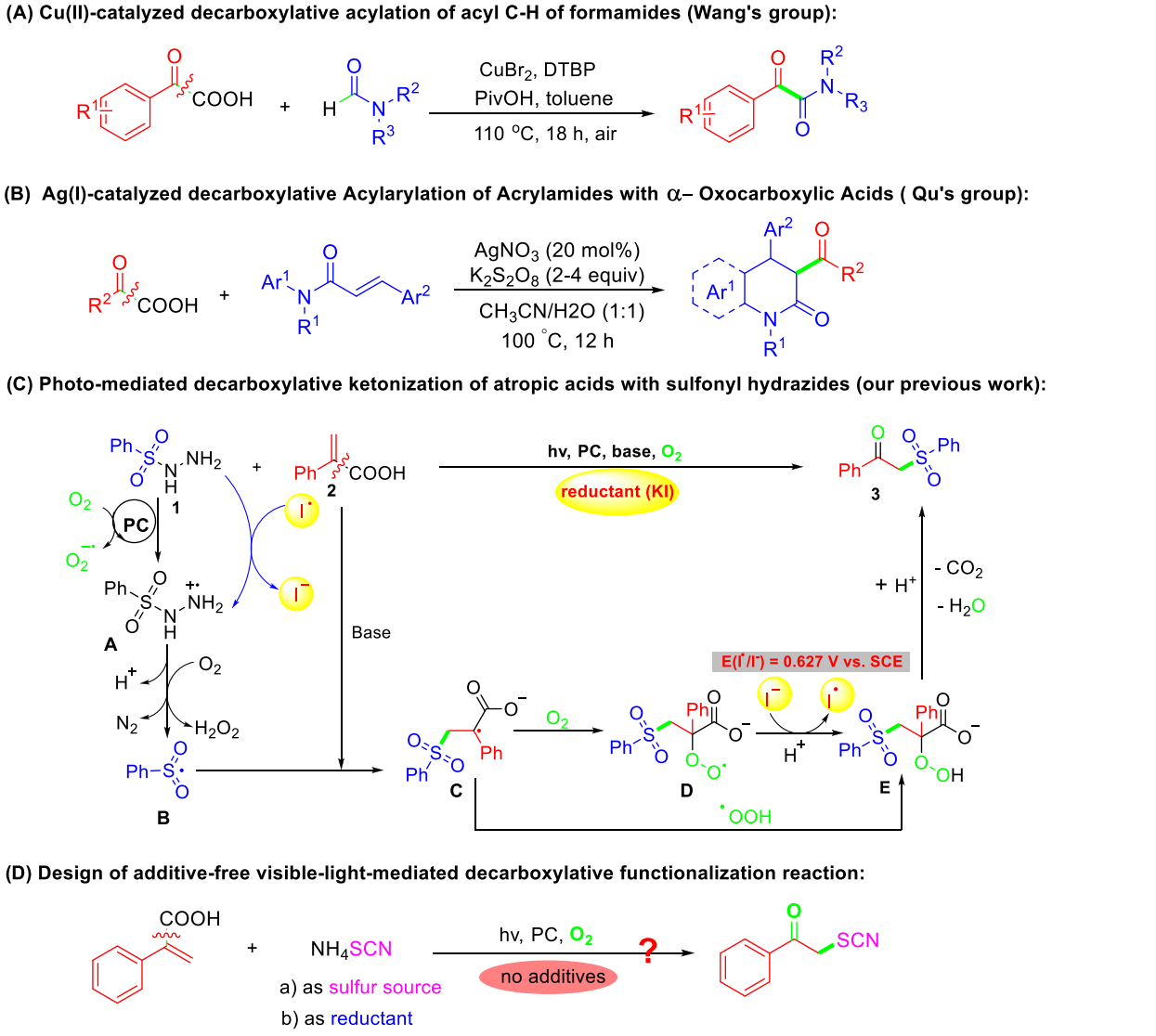
Very recently, our group reported a mild photomediated decarboxylative ketonization reaction of atropic acids with sulfonyl hydrazides for the synthesis of α-ketosulfones (Scheme 1C).[4]The reaction has great advantages of metal-free conditions, readily available materials, and use of dioxygen as both an oxygen source and an oxidant. Nevertheless, this reaction requires a stoichiometric amount of potassium iodide (KI) as an essential additive for reducing the peroxyl radical in intermediate **D** to the peroxy anion (**E**), which generates additional waste and deteriorates the atom efficiency. Since organosulfur compounds are an important class of compounds in biological and pharmaceutical fields, naturally, as a continuation of our work, we wonder whether there exists a more economical and greener approach to simplify the C−S bond-forming conditions and minimize the waste formation, likewise through a visible-light-mediated decarboxylative strategy.

Thiocyanates are highly versatile building blocks in synthetic chemistry because they can be easily transformed into thiols,[5] disulfides,[6] phosphonothioates,[7] isothicyanats,[8] tri- and difluoromethyl thioethers,[9] and a variety of heterocyclic scaffolds.[10] In addition, thiocyanate can work as a safe cyanide reagent to avoid the toxic cyanide source[11] and be treated as a pseudohalide to function as a leaving group.[12] Consequently, the introduction of a thiocyanate group into organic molecules has very important synthetic significance. Recently, some excellent thiocyanate functionalization reactions have been developed.[13] For instance, *N*-thiocyano-dibenzenesulfonimide (NTSI) was used as a thiocyanation reagent to realize the electrophilic thiocyano semipinacol rearrangement of allylic alcohols[13c] and the electrophilic thiocyano oxyfunctionalization of alkenes,[13d] providing various SCN-containing compounds. In all kinds of thiocyanative reagents, ammonium thiocyanate (NH_4SCN), featuring low cost, commercially availability, good solubility in organic solvents, and traceless byproducts, has attracted considerable attention.[13] In

Received: October 18, 2020
Published: February 17, 2021

https://dx.doi.org/10.1021/acs.joc.0c02471
J. Org. Chem. 2021, 86, 3741−3749

Scheme 1. Decarboxylative Functionalization Reactions



particular, the potential of ammonium thiocyanate [E_{ox}($^{\bullet}$SCN/$^{-}$SCN) = +0.61 V in MeCN vs SCE][14] is close to that of KI [E_{ox}($I^{\bullet}$/I^{-}) = +0.627 V vs SCE],[4g] so we speculate that it may also be a good single-electron reductant. Inspired by these investigations, we envisaged whether NH_4SCN could act as both a sulfur source and a reductant to achieve a visible-light-mediated additive-free decarboxylative functionalization reaction (Scheme 1D), which would be more environmentally friendly and atom-economic.

Herein, we present our work on a visible-light-mediated additive-free decarboxylative ketonization reaction using NH_4SCN as both a sulfur source and a reductant and cheap organic dye 9,10-dicyanoanthracene (DCA) as a green photocatalyst at ambient temperature. In terms of applicability, this reaction is not only feasible for various substituted atropic acids but also can be expanded to alkyl-, heteroaryl-substituted acrylic acids and disubstituted acrylic acids.

RESULTS AND DISCUSSION

Our initial effort to develop a new photomediated decarboxylative C−S bond-forming protocol started with atropic acid (**1a**) and ammonium thiocyanate (**2**) as model substrates. First, in an oxygen atmosphere, using acetonitrile (MeCN) as a solvent and a 23 W compact fluorescent lamp (CFL) as a light source, a series of photocatalysts were screened. It was a delight to find that the proposed reaction was indeed feasible with some photocatalysts (Table 1, entries 1−4). Among the tested photocatalysts, common organic dye 9,10-dicyanoanthracene (DCA) exhibited the best efficiency to afford product **3a** in 71% yield (Table 1, entry 3). Under these conditions, replacing MeCN with other solvents and changes in the molecular ratio of starting materials did not lead to a higher yield of product **3a** (Table 1, entries 5−8). Additionally, it was found that the addition of a small amount of water had no obvious effect on the reaction yield (Table 1, entries 9 and 10). Subsequently, the effects of solvent volume and photocatalyst loading were investigated. Experiments showed that when 1 mL of MeCN was used as a solvent, the reaction yield could be increased to 79% (Table 1, entries 3, and 11−13), and the photocatalyst loading could be decreased to 1.0 mol % without loss in yield (Table 1, entries 12, 14 and 15). Ultimately, control experiments were also conducted (Table 1, entries 16−19). The results demonstrated that the photocatalyst, light

https://dx.doi.org/10.1021/acs.joc.0c02471
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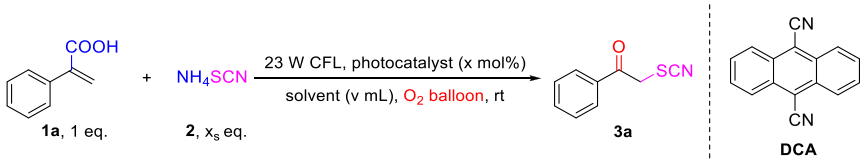
Table 1. Selected Optimization Experiments[a]



entry	photocatalyst (x mol %)	solvent (v mL)	x_s (equiv)	yield (%)[b]
1	rose bengal (2)	MeCN (2)	2	26
2	anthraquinone (2)	MeCN (2)	2	55
3	DCA (2)	MeCN (2)	2	71
4	$Ru(bpy)_3Cl_2$ (2)	MeCN (2)	2	27
5	DCA (2)	EtOH (2)	2	9
6	DCA (2)	THF (2)	2	42
7	DCA (2)	acetone (2)	2	44
8	DCA (2)	MeCN (2)	3	69
9	DCA (2)	MeCN (1.9) + H_2O (0.1)	2	72
10	DCA (2)	MeCN (1.7) + H_2O (0.3)	2	70
11	DCA (2)	MeCN (0.5)	2	32
12	DCA (2)	MeCN (1.0)	2	79
13	DCA (2)	MeCN (3.0)	2	46
14	DCA (1)	MeCN (1.0)	2	79
15	DCA (4)	MeCN (1.0)	2	76
16		MeCN (1.0)	2	<10
17[c]	DCA (1)	MeCN (1.0)	2	trace
18[d]	DCA (1)	MeCN (1.0)	2	42
19[e]	DCA (1)	MeCN (1.0)	2	<10

[a]Reaction conditions: a mixture of **1a** (0.2 mmol), NH_4SCN (x_s equiv), and a photocatalyst (x mol %) in a solvent (v mL) was irradiated by a 23 W CFL under a O_2 balloon at rt for 10 h. [b]Isolated yield after silica gel column chromatography. [c]Without light irradiation. [d]Air balloon instead of an O_2 balloon. [e]Argon balloon instead of an O_2 balloon.

irradiation, and O_2 are all necessary in this reaction (for detailed reaction condition screening, please see SI).

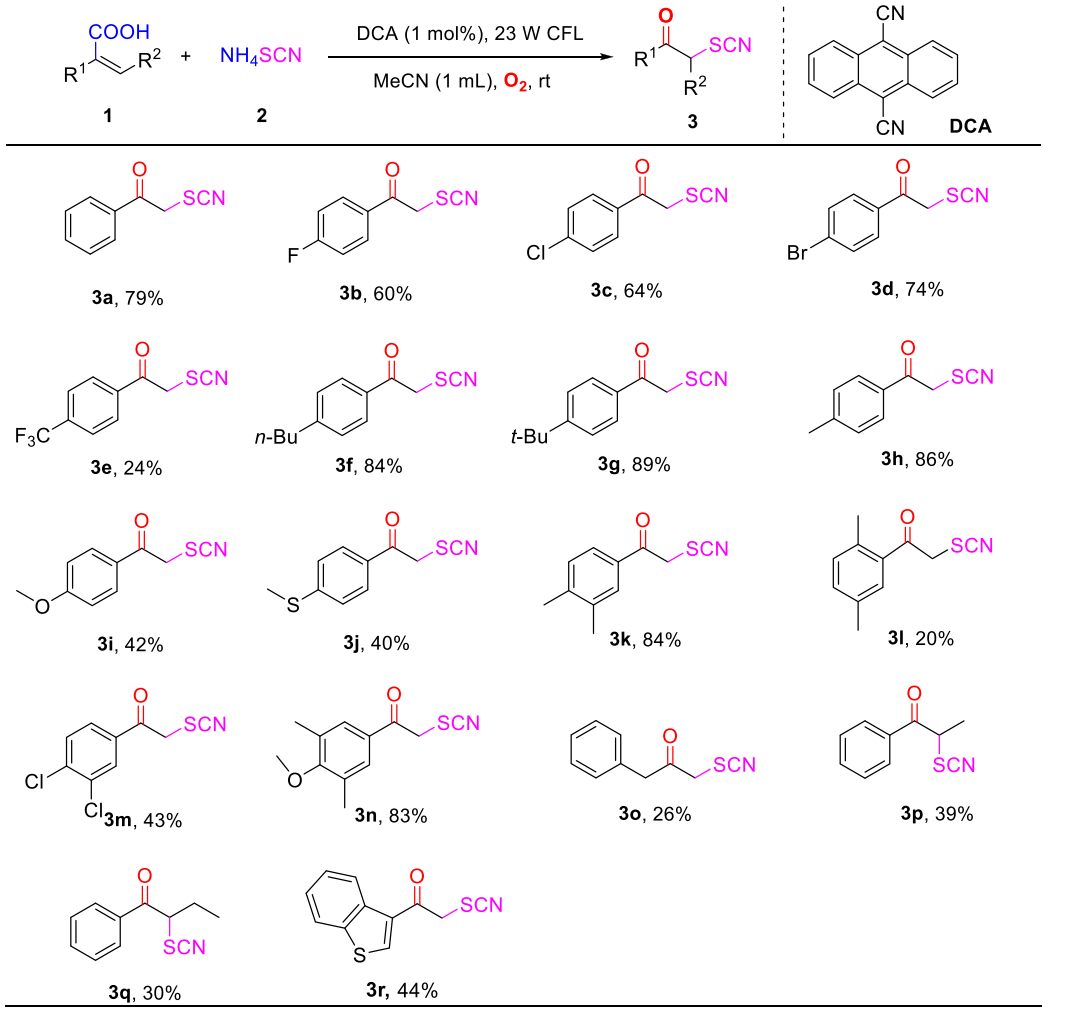
With the optimized conditions in the hand (Table 1, entry 14), we continued our efforts toward exploring the reactivity of various substituted acrylic acids with NH_4SCN (Scheme 2). First, it was found that the electronic nature of the substituents of atropic acid had a great influence on the reaction. Atropic acids with an electron-withdrawing substituent (such as fluoro-, chloro-, bromo-, or trifluoromethyl-) at the para position of the aromatic ring could provide the corresponding products (**3b**−**3e**). However, *para*- cyano-, nitro-, carbonyl-, carboxyl-, and *ortho*-fluoro-substituted atropic acids (**1u** and **1w**−**1z**) could not undergo this transformation. After extending the reaction time to 24 h, no obvious reaction was observed, and a large amount of raw materials still remained, which may be attributed to the strong electron-withdrawing effect of the substituents. The presence of electron-donating groups, such as *para*- *n*-Bu, *t*-Bu, and Me- groups, on the aromatic ring of atropic acid could facilitate the reaction and gave the desired products in good yields (**3f**−**3h**). However, *para*-MeO- and MeS-substituted atropic acids were only converted to the desired products in moderate yields (**3i** and **3j**), and some complicated byproducts were formed. Second, the steric hindrance also exhibited some effect on this reaction. For instance, 2,4,6-trimethyl-substituted atropic acid **1v** could not be decarboxylated in this way, probably because of the high steric hindrance. Pleasingly, some di- and trisubstituted atropic acids with a lower steric hindrance could smoothly react with NH_4SCN under the optimized conditions (**3k**−**3m** and **3n**). Different from a previous visible-light-mediated decarboxylative reaction reported by our group,[4] this reaction is compatible to alkyl-substituted acrylic acids (**3o**). Further investigations demonstrated that some acrylic acids of internal olefins could also successfully participate in this decarboxylative transformation to produce the desired products, albeit in low yields (**3p** and **3q**). However, when using 2,3-diaryl-substituted acrylic acids (**1s** and **1t**), no obvious reaction was observed, possibly due to the high steric hindrance. Finally, 2-heteroaryl-substituted acrylic acid could also participate in the reaction smoothly, giving the desired product in moderate yield (**3r**).

Next, we explored the utility of the products. The carbonyl and thiocyanide in the products are both versatile building blocks. As can be seen in Scheme 3, under simple alkaline conditions, product **3a** could be conveniently converted into disulfide **4** (reaction a) or heteroaromatic compound **5** (reaction b). Under acidic conditions, product **3a** could be easily transformed into heterocyclic compound **6** in a high yield within a short reaction time (reaction c). The facile transformation of α-thiocyanate ketone provides great potential for its application in organic and medicinal chemistry.

In order to get some insight into the reaction mechanism of this visible-light-mediated decarboxylative ketonization reaction, a series of experiments were carried out. The addition of radical scavenger 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) to the reaction system completely inhibited the desired reaction, indicating that a radical pathway may be involved in this transformation. Simultaneously, the detection of TEMPO-adduct **7** by high-resolution mass spectrometry (HRMS) suggested that radical intermediate **II** may be formed during the reaction (Scheme 4a). When 2,6-di-*tert*-butyl-4-methyl-phenol (BHT) and 1,1-diphenylethylene (DE) were,

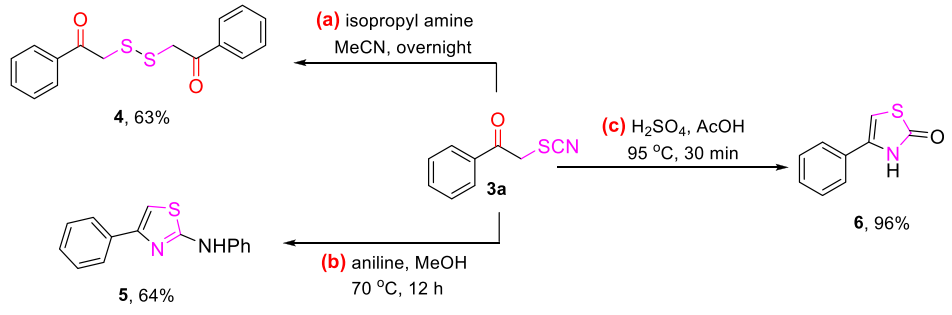
https://dx.doi.org/10.1021/acs.joc.0c02471
J. Org. Chem. 2021, 86, 3741−3749

Scheme 2. Scope of Substrates[a]



[a]Reaction conditions: a mixture of **1** (0.2 mmol), NH_4SCN (0.4 mmol), and DCA (1.0 mol %) in MeCN (1.0 mL) was irradiated by a 23 W CFL under an O_2 balloon at rt for 10 h. [b]Isolated yields were provided.

Scheme 3. Transformation of Products



respectively, added to the model reaction, BHT-adduct **8** and DE-adduct **9** could be detected by HRMS, indicating that both a superoxide radical and a thiocyanate radical may be involved in the reaction (Scheme 4b,c). Subsequently, to find out where the oxygen atom of the carbonyl group in the desired product comes from, we performed an isotope-labeling experiment in

https://dx.doi.org/10.1021/acs.joc.0c02471
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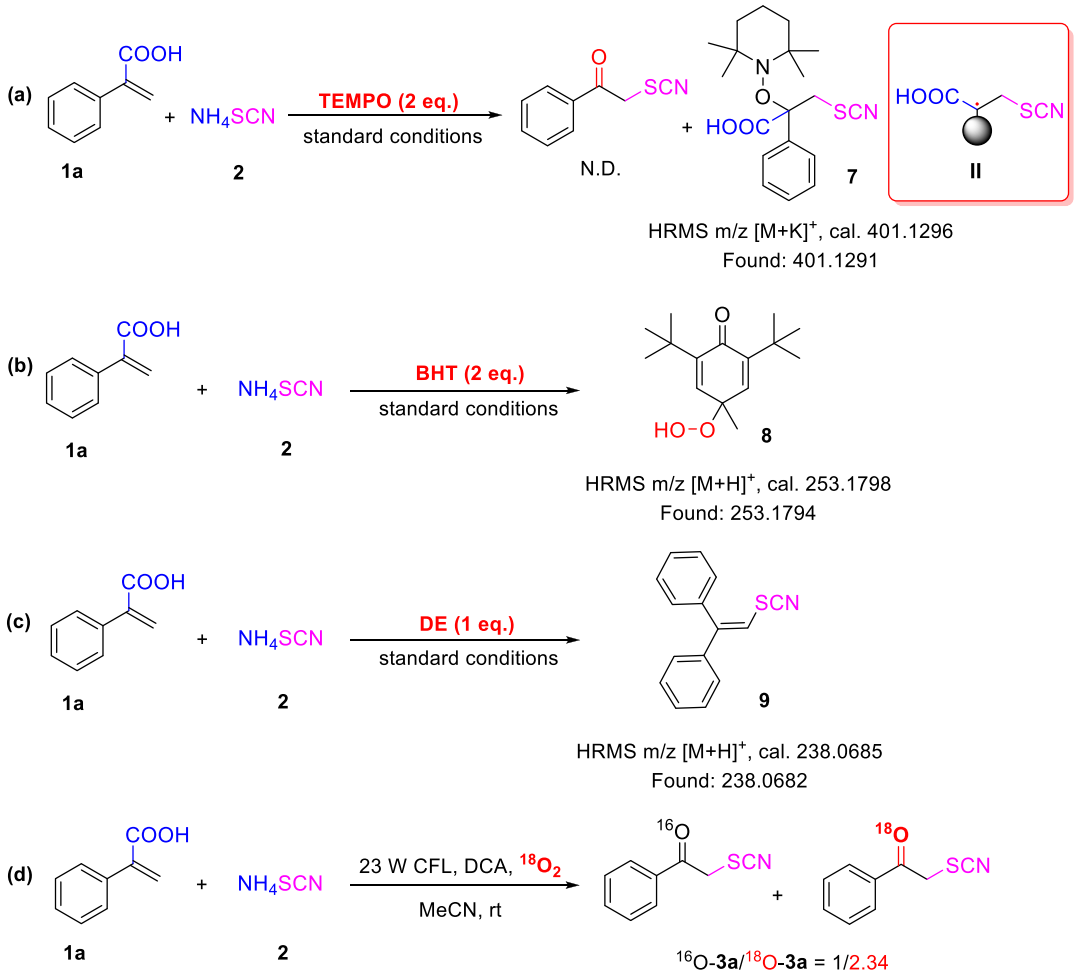
Scheme 4. Mechanistic Studies



the presence of $^{18}O_2$ (Scheme 4d). The result showed that the oxygen atom of the carbonyl group comes from O_2. Besides, on/off visible-light irradiation experiments were carried out to verify whether there is a radical chain propagation process (Figure 1). It was found that in the absence of light, the reaction still continued (the yield was determined by ^1H NMR), so we speculate that there may be a radical chain propagation process. UV−visible absorption spectroscopy demonstrated that except for the photocatalyst, other reactants in this reaction could not absorb the visible light (SI, Figure S2). The fluorescence quenching experiments (Stern−Volmer studies) showed that NH_4SCN could readily quench the luminescence of the excited photocatalyst DCA*, while atropic acid could not (SI, Figures S8−S10). This luminescence quenching is most likely due to the photoinduced electron transfer process, as NH_4SCN [E_{ox}($^{\bullet}$SCN/$^{-}$SCN) = +0.61 V in MeCN vs SCE][14] can be easily oxidized by the excited photocatalyst DCA*, which is reported to have potential among 1.9−2.1 V vs SCE.[15]

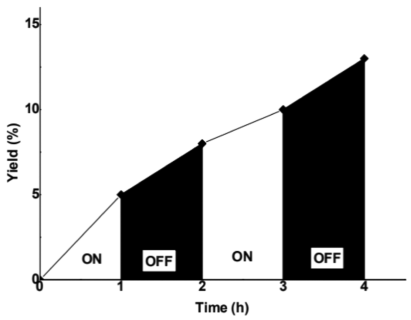


Figure 1. Light on/off experiments.

Based on the above experiments, we proposed a possible reaction mechanism (Scheme 5), which includes two possible pathways. The photocatalyst DCA is excited by the visible light to the excited state DCA*, which undergoes single-electron transfer with the thiocyanate anion (liberated from ammonium thiocyanate) to afford the thiocyanate radical **I** along with the formation of reduced DCA$^{\bullet-}$. Then, DCA$^{\bullet-}$ is single-electron-oxidized back to DCA by O_2, and at the same time, a superoxide anion radical ($O_2^{\bullet-}$) is formed, thus completing the photoredox catalytic cycle. Subsequently, the radical addition between the thiocyanate radical **I** and the acrylic acid **1** forms the alkyl radical **II**. In path A, intermediate **II** can be added to O_2 to form intermediate **III**. The thiocyanate anion may work as an internal reductant to reduce intermediate **III** to generate intermediate **IV**, while the thiocyanate anion is single-electron-oxidized to the thiocyanate radical **I**, contributing to the radical chain process. Intermediate **IV** undergoes intramolecular proton transfer, protonation, decarboxylation, and dehydration processes, and is finally transformed into the target product **3**. In path B, the alkyl radical **II** is captured by $HO_2^{\bullet}$, which is produced by a combination of $O_2^{\bullet-}$ and the proton from **2**,

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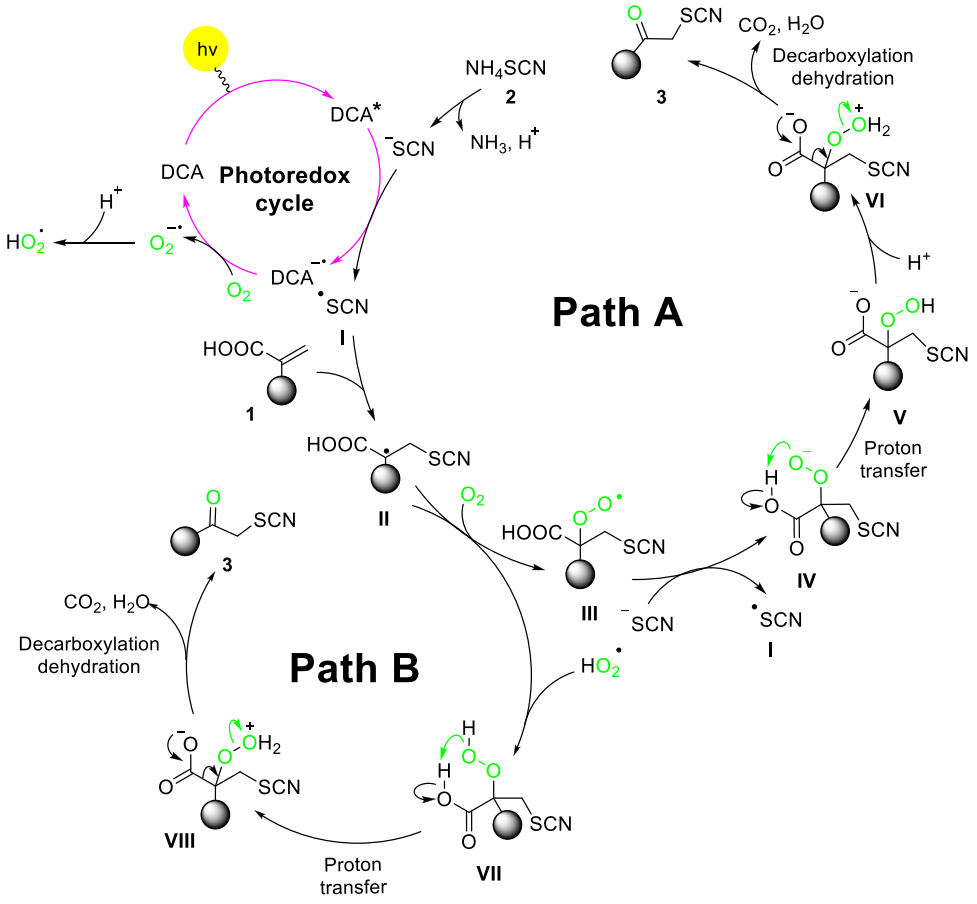
Scheme 5. Possible Mechanism



providing the intermediate **VII**. After successive intramolecular proton transfer, decarboxylation, and dehydration, the intermediate **VII** is finally converted to the desired product **3**.

CONCLUSIONS

In summary, using NH_4SCN as both a sulfur source and a reductant and using inexpensive organic dye DCA as a green photocatalyst, we have successfully developed a visible-light-mediated additive-free decarboxylative reaction for simultaneous construction of C−S and C═O bonds. The reaction has advantages of simple operation and environmental friendliness. Moreover, since the produced α-thiocyanate ketones are important synthons in organic and pharmaceutical fields, this reaction can be used for the further preparation of other important complex molecules, thereby contributing to the progress of organic synthesis.

EXPERIMENTAL SECTION

General Information. All reactions were performed in round bottom flasks made of borosilicate glass. The optimized light source was a 23 W CFL (Philips, 220 V, 50 Hz, 400−780 nm) without any filters, and the spectral distribution and intensity of the lamp are shown in Figure S1. Commercially available reagents were purchased at the highest commercial quality and used without further purifications. Thin-layer chromatography (TLC) plates (Qingdao Haiyang Chemical Industry Co. Ltd., Qingdao, China) were visualized by exposure to UV light and/or staining with the solution of vanillic aldehyde. Flash column chromatography (ethyl acetate/petroleum ether) was carried out using 200−300 mesh silica gel at increased pressure. ^{1}H NMR spectra and ^{13}C{^{1}H} NMR spectra were, respectively, recorded on 600 and 151 MHz NMR spectrometers. Deuterated chloroform with TMS as an internal standard was used as a solvent for NMR analyses. In the evaluation of ^{1}H NMR spectra, chemical shifts (δ) were expressed in parts per million (ppm), wherein "s" stands for singlet, "d" for doublet, "t" for triplet, "q" for quartet, "dd" for doublet of doublets, and "m" for multiplet. The coupling constants (J) were reported in Hz. High-resolution mass spectra were obtained using ESI ionization sources (Varian 7.0 T FTICR-MS) and ESI-TOF. Melting points were taken on a WPX-4 apparatus and were uncorrected (Yice Instrument Equipment Co. Ltd., Shanghai).

The starting materials **1b−m** and **1o−1p** are known compounds, which were all prepared according to the reported procedures.[16,17]

General Procedure for the Preparation of α-Thiocyanate Ketones 3. A round bottom flask (10 mL) equipped with a magnetic stir bar was charged with acrylic acid **1** (0.2 mmol, 1.0 equiv), ammonium thiocyanate **2** (0.4 mmol, 2.0 equiv), 9,10-dicyanoanthracene (DCA, 0.002 mmol, 1 mol %), and MeCN (1.0 mL). The mixture was irradiated by a 23 W CFL (Philips, 220 V, 50 Hz, 400−780 nm, without any filters, placed approximately 2.5 cm from the flask) under an O_2 balloon at room temperature. After completion of the reaction (monitored by TLC), the reaction mixture was concentrated under reduced pressure and the resulting residue was treated with water and extracted with EtOAc. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography using petroleum ether/ethyl acetate as an eluent to give the desired product α-thiocyanate ketones **3** (20−89% yields).

Procedure for the Preparation of 4. A 10 mL vial equipped with a magnetic stir bar was charged with **3a** (0.17 mmol) and MeCN (1 mL) and then isopropylamine (3.6 mmol) was added. The reaction was allowed to proceed overnight. The reaction mixture was concentrated under reduced pressure and the resulting residue was

https://dx.doi.org/10.1021/acs.joc.0c02471
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treated with water and extracted with EtOAc. The organic extracts were combined, dried with sodium sulfate, and the solvent was subsequently removed under reduced pressure to afford the crude product, which then further purified by silica gel column chromatography using 5% EtOAc/hexane as an eluent to give the desired product **4** in 63% yields.

Procedure for the Preparation of 5. To a round bottom flask (10 mL) equipped with a magnetic stir bar, **3a** (0.17 mmol), aniline (0.32 mmol), and methanol (0.30 mL) were added. The mixture was refluxed overnight after which the solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography using petroleum ether/ethyl acetate in a 10:1 ratio to afford the product **5** in 64% yields.

Procedure for the Preparation of 6. **3a** (2.5 mmol) was added to acetic acid (20 mL) in a round bottom flask (50 mL), and the mixture was heated until **3a** completely dissolved. Sulfuric acid (50% v/v, 4 mL) was added and the solution was brought to reflux for 30 min. The reaction mixture was then cooled to ambient temperature and poured into cold water, resulting in precipitation. The precipitate was separated by filtration and washed with hexane to give product **6** in 96% yields.

Enlarged-Scale Synthesis of 3a. A round bottom flask (25 mL) equipped with a magnetic stir bar was charged with 2-phenylacrylic acid **1a** (148.2 mg, 1.0 mmol, 1.0 equiv), ammonium thiocyanate **2** (152.2 mg, 2.0 mmol, 2.0 equiv), 9,10-dicyanoanthracene (DCA, 11.4 mg, 0.01 mmol, 1 mol %), and MeCN (5.0 mL). The mixture was irradiated by a 23 W CFL (Philips, 220 V, 50 Hz, 400−780 nm, without any filters, placed approximately 2.5 cm from the flask) under an O_2 balloon at room temperature. After completion of the reaction (monitored by TLC), the reaction mixture was concentrated under reduced pressure and the resulting residue was treated with water and extracted with EtOAc. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography using petroleum ether/ethyl acetate (10:1 ratio) as an eluent to give the desired product 1-phenyl-2-thiocyanatoethan-1-one **3a** (108 mg, 61%).

Characterization of Products. *1-Phenyl-2-thiocyanatoethan-1-one (3a).*[18] Isolated yield (28.0 mg, 79%), yellow solid, R_f value = 0.2 [EtOAc/petroleum ether = 1:10 (v/v)], melting range: 68−69 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.97−7.93 (m, 2H), 7.67 (t, J = 7.5 Hz, 1H), 7.54 (t, J = 7.8 Hz, 2H), 4.74 (s, 2H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 190.8, 134.8, 134.0, 129.2, 128.5, 111.7, 42.9.

1-(4-Fluorophenyl)-2-thiocyanatoethan-1-one (3b).[19] Isolated yield (23.4 mg, 60%), yellow solid, R_f value = 0.3 [EtOAc/petroleum ether = 1:10 (v/v)], melting range: 95−97 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.99 (dd, J = 8.6, 5.3 Hz, 2H), 7.21 (t, J = 8.4 Hz, 2H), 4.70 (s, 2H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 189.2, 167.5 (C-F, $^1J_{C\text{-}F}$ = 256.5 Hz), 165.8 (C-F, $^1J_{C\text{-}F}$ = 256.5 Hz), 131.3 (C-F, $^3J_{C\text{-}F}$ = 10.5 Hz), 131.2 (C-F, $^3J_{C\text{-}F}$ = 10.5 Hz), 130.6, 116.6 (C-F, $^2J_{C\text{-}F}$ = 22.5 Hz), 116.4 (C-F, $^2J_{C\text{-}F}$ = 22.5 Hz), 111.5, 42.6; ^{19}F NMR (565 MHz, $CDCl_3$): δ −101.3.

1-(4-Chlorophenyl)-2-thiocyanatoethan-1-one (3c).[19] Isolated yield (27.1 mg, 64%), yellow solid, R_f value = 0.3 [EtOAc/petroleum ether = 1:10 (v/v)], melting range: 122−124 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.89 (d, J = 8.2 Hz, 2H), 7.52 (d, J = 8.2 Hz, 2H), 4.69 (s, 2H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 189.7, 141.6, 132.4, 129.9, 129.6, 111.5, 42.6.

1-(4-Bromophenyl)-2-thiocyanatoethan-1-one (3d).[19] Isolated yield (37.7 mg, 74%), yellow solid, R_f value = 0.3 [EtOAc/petroleum ether = 1:10 (v/v)], melting range: 114−116 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.81 (d, J = 8.6 Hz, 2H), 7.69 (d, J = 8.6 Hz, 2H), 4.68 (s, 2H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 189.8, 132.7, 132.6, 130.3, 129.8, 111.4, 42.5.

2-Thiocyanato-1-(4-(trifluoromethyl)phenyl)ethan-1-one (3e). Isolated yield (11.7 mg, 24%), yellow solid, R_f value = 0.3 [EtOAc/petroleum ether = 1:10 (v/v)], FTIR ν_{max} (neat): 3416, 2156, 1675, 1261, 1100, 1068, 1019, 801 cm^{-1}, melting range: 110−111 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.07 (d, J = 8.1 Hz, 2H), 7.81 (d, J = 8.0 Hz, 2H), 4.72 (s, 2H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 189.9, 136.7, 136.3 (C-F, $^2J_{C\text{-}F}$ = 30.0 Hz), 136.1(C-F, $^2J_{C\text{-}F}$ = 30.0 Hz), 135.9 (C-F, $^2J_{C\text{-}F}$ = 30.0 Hz), 135.7 (C-F, $^2J_{C\text{-}F}$ = 30.0 Hz), 128.9, 126.3, 125.9 (C-F, $^1J_{C\text{-}F}$ = 270.0 Hz), 124.1 (C-F, $^1J_{C\text{-}F}$ = 270.0 Hz), 122.3 (C-F, $^1J_{C\text{-}F}$ = 270.0 Hz), 120.5 (C-F, $^1J_{C\text{-}F}$ = 270.0 Hz), 111.2, 42.5; ^{19}F NMR (565 MHz, $CDCl_3$): δ −63.4; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{10}H_7F_3NOS$ 246.0195; found: 246.0192.

1-(4-Butylphenyl)-2-thiocyanatoethan-1-one (3f). Isolated yield (39.2 mg, 84%), yellow solid, R_f value = 0.2 [EtOAc/petroleum ether = 1:10 (v/v)], FTIR ν_{max} (neat): 3414, 2928, 2152, 1673, 1601, 1381, 1296, 1179, 996, 821, 610, 564 cm^{-1}, melting: 83 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.85 (d, J = 8.1 Hz, 2H), 7.33 (d, J = 8.1 Hz, 2H), 4.72 (s, 2H), 2.70 (t, J = 7.7 Hz, 2H), 1.64−1.61 (m, 2H), 1.38−1.34 (m, 2H), 0.94 (t, J = 7.4 Hz, 3H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 190.4, 151.0, 129.2, 128.6, 126.2, 111.9, 43.0, 35.8, 33.1. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{13}H_{16}NOS$ 234.0947; found: 234.0944.

1-(4-(tert-Butyl)phenyl)-2-thiocyanatoethan-1-one (3g).[18] Isolated yield (41.5 mg, 89%), yellow solid, R_f value = 0.2 [EtOAc/petroleum ether = 1:10 (v/v)], melting range: 79−81 °C; ^{1}H NMR (600 MHz, $CDCl_3$): 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); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 190.4, 159.0, 131.5, 128.5, 126.2, 111.9, 43.0, 35.4, 31.0.

2-Thiocyanato-1-(p-tolyl)ethan-1-one (3h).[19] Isolated yield (32.9 mg, 86%), yellow solid, R_f value = 0.2 [EtOAc/petroleum ether = 1:10 (v/v)], melting range: 99−101 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.83 (d, J = 8.2 Hz, 2H), 7.32 (d, J = 8.1 Hz, 2H), 4.72 (s, 2H), 2.45 (s, 3H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 190.4, 146.1, 131.6, 129.9, 128.6, 111.9, 43.0, 21.8.

1-(4-Methoxyphenyl)-2-thiocyanatoethan-1-one (3i). Isolated yield (17.4 mg, 42%), yellow solid, R_f value = 0.1 [EtOAc/petroleum ether = 1:10 (v/v)]; ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.99 (d, J = 8.8 Hz, 2H), 7.09 (d, J = 8.8 Hz, 2H), 5.05 (s, 2H), 3.86 (s, 3H); $^{13}C\{^1H\}$ NMR (151 MHz, DMSO-d_6) δ 191.0, 164.5, 131.5, 127.6, 114.7, 113.4, 56.2, 42.0.

1-(4-(Methylthio)phenyl)-2-thiocyanatoethan-1-one (3j). Isolated yield (17.9 mg, 40%), yellow solid, R_f value = 0.1 [EtOAc/petroleum ether = 1:10 (v/v)]; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.83 (d, J = 8.2 Hz, 1H), 7.30 (d, J = 8.2 Hz, 1H), 4.69 (s, 1H), 2.54 (s, 2H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 189.8, 148.9, 130.2, 128.9, 125.3, 112.0, 42.9, 14.8.

1-(3,4-Dimethylphenyl)-2-thiocyanatoethan-1-one (3k). Isolated yield (34.5 mg, 84%), yellow solid, R_f value = 0.2 [EtOAc/petroleum ether = 1:10 (v/v)], FTIR ν_{max} (neat): 3422, 2974, 2151, 1672, 1601, 1304, 1228, 1129, 828, 600 cm^{-1}, melting range: 87−88 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.70 (s, 1H), 7.66 (d, J = 7.9 Hz, 1H), 7.28 (s, 1H), 4.72 (s, 2H), 2.35 (s, 3H), 2.34 (s, 3H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 190.6, 144.8, 137.7, 131.9, 130.3, 129.5, 126.2, 112.0, 43.1, 20.2, 19.8; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{11}H_{12}NOS$ 206.0634; found: 206.0633.

1-(2,5-Dimethylphenyl)-2-thiocyanatoethan-1-one (3l). Isolated yield (8.1 mg, 20%), yellow solid, R_f value = 0.2 [EtOAc/petroleum ether = 1:10 (v/v)], FTIR ν_{max} (neat): 3432, 2941, 2151, 1667, 1387, 1274, 1135, 818, 651 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.49 (s, 1H), 7.30 (d, J = 7.7 Hz, 1H), 7.20 (d, J = 7.7 Hz, 1H), 4.71 (s, 2H), 2.51 (s, 3H), 2.39 (s, 3H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 193.2, 137.3, 135.9, 134.2, 133.4, 132.7, 130.1, 112.0, 45.0, 21.3, 20.9; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{11}H_{12}NOS$ 206.0634; found: 206.0635.

1-(3,4-Dichlorophenyl)-2-thiocyanatoethan-1-one (3m). Isolated yield (20.9 mg, 43%), yellow solid, R_f value = 0.3 [EtOAc/petroleum ether = 1:10 (v/v)], FTIR ν_{max} (neat): 3428, 2926, 2159, 1670. 1465, 1383, 1202, 1008, 799 cm^{-1}, melting range: 95−97 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.03 (d, J = 1.9 Hz, 1H), 7.77 (dd, J = 8.4, 1.9 Hz, 1H), 7.63 (d, J = 8.4 Hz, 1H), 4.65 (s, 2H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 188.8, 139.7, 134.2, 133.5, 131.4, 130.4, 127.3, 111.1, 42.2; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_9H_6Cl_2NOS$ 245.9542; found: 245.9538.

1-(4-Methoxy-3,5-dimethylphenyl)-2-thiocyanatoethan-1-one (3n). Isolated yield (39.1 mg, 83%), pale yellow solid, R_f value = 0.1 [EtOAc/petroleum ether = 1:10 (v/v)], FTIR ν_{max} (neat): 3419,

https://dx.doi.org/10.1021/acs.joc.0c02471
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2933, 2157, 1672, 1596, 1328, 1152, 1006, 866, 654 cm^{-1}, melting range: 111−113 °C; ^1H NMR (600 MHz, $CDCl_3$): δ 7.61 (s, 2H), 4.70 (s, 2H), 3.78 (s, 3H), 2.34 (s, 6H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 190.1, 162.8, 132.1, 129.6, 112.0, 59.8, 43.0, 16.3; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{12}H_{14}NO_2S$ 236.0740; found: 236.0739.

1-Phenyl-3-thiocyanatopropan-2-one ***(3o)***. Isolated yield (9.9 mg, 26%), yellow solid, R_f value = 0.2 [EtOAc/petroleum ether = 1:10 (v/v)]; ^1H NMR (600 MHz, $CDCl_3$): δ 7.40−7.36 (m, 2H), 7.33 (t, J = 7.1 Hz, 1H), 7.22 (t, J = 7.6 Hz, 2H), 4.02 (s, 2H), 3.86 (s, 2H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 198.8, 132.2, 129.3, 128.0, 126.2, 111.0, 48.8, 43.3; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{10}H_{10}NOS$ 192.0478; found: 192.0477.

1-Phenyl-2-thiocyanatopropan-1-one ***(3p)***.[19] Isolated yield (14.9 mg, 39%), yellow solid, R_f value = 0.2 [EtOAc/petroleum ether = 1:10 (v/v)], melting range: 76−77 °C; ^1H NMR (600 MHz, $CDCl_3$): δ 7.96−7.91 (m, 2H), 7.67 (t, J = 7.4 Hz, 1H), 7.54 (t, J = 7.8 Hz, 2H), 5.08 (q, J = 7.1 Hz, 1H), 1.87 (d, J = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 194.8, 134.6, 133.3, 129.2, 128.8, 111.4, 49.9, 19.8.

1-Phenyl-2-thiocyanatobutan-1-one ***(3q)***. Isolated yield (12.5 mg, 30%), yellow solid, R_f value = 0.2 [EtOAc/petroleum ether = 1:10 (v/v)]; ^1H NMR (600 MHz, $CDCl_3$): δ 7.98−7.88 (m, 2H), 7.67 (t, J = 7.4 Hz, 1H), 7.54 (t, J = 7.7 Hz, 2H), 5.00 (t, J = 5.9 Hz, 1H), 2.30 (m, 1H), 2.19 (m, 1H), 1.06 (t, J = 7.3 Hz, 3H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 194.7, 134.6, 134.1, 129.3, 128.8, 111.5, 55.9, 26.2, 10.2; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{11}H_{12}NOS$ 206.0634; found: 206.0634.

1-(Benzo[b]thiophen-3-yl)-2-thiocyanatoethan-1-one ***(3r)***. Isolated yield (20.5 mg, 44%), yellow solid, R_f value = 0.2 [EtOAc/petroleum ether = 1:10 (v/v)]; ^1H NMR (600 MHz, DMSO-d_6) δ 9.14 (s, 1H), 8.58 (d, J = 8.0 Hz, 1H), 8.14 (d, J = 7.5 Hz, 1H), 7.56 (t, J = 6.9 Hz, 1H), 7.51 (t, J = 6.9 Hz, 1H), 5.09 (s, 2H); $^{13}C\{^1H\}$ NMR (151 MHz, DMSO-d_6) δ 187.4, 142.4, 139.7, 136.3, 132.1, 126.6, 126.2, 124.8, 123.6, 113.4, 42.3.

2,2′-Disulfanediylbis(1-phenylethan-1-one) ***(4)***.[20] Isolated yield (32.4 mg, 63%), white solid, R_f value = 0.2 [EtOAc/petroleum ether = 1:10 (v/v)], ^1H NMR (600 MHz, $CDCl_3$): δ 7.97 (t, J = 7.0 Hz, 4H), 7.58 (t, J = 7.4 Hz, 2H), 7.47 (t, J = 7.8 Hz, 4H), 3.99 (s, 4H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 194.2, 135.5, 133.5, 128.7, 128.6, 37.6.

N,4-Diphenylthiazol-2-amine ***(5)***.[21] Isolated yield (27.5 mg, 64%), yellow solid, R_f value = 0.2 [EtOAc/petroleum ether = 1:10 (v/v)]; ^1H NMR (600 MHz, DMSO-d_6): δ 10.27 (s, 1H), 7.94 (d, J = 7.6 Hz, 2H), 7.75 (d, J = 8.0 Hz, 2H), 7.45 (t, J = 7.5 Hz, 2H), 7.39−7.30 (m, 4H), 6.98 (t, J = 7.3 Hz, 1H); $^{13}C\{^1H\}$ NMR (151 MHz, DMSO-d_6): δ 163.5, 150.5, 141.6, 134.9, 129.4, 129.0, 127.9, 126.0, 121.6, 117.2, 103.3.

4-Phenylthiazol-2(3H)-one ***(6)***.[22] Isolated yield (425.3 mg, 96%), white solid, R_f value = 0.2 [EtOAc/petroleum ether = 1:10 (v/v)]; ^1H NMR (600 MHz, DMSO-d_6): δ 11.77 (s, 1H), 7.68−7.62 (m, 2H), 7.43 (t, J = 7.6 Hz, 2H), 7.36 (t, J = 7.4 Hz, 1H), 6.81 (s, 1H); $^{13}C\{^1H\}$ NMR (151 MHz, DMSO-d_6): δ 172.9, 133.8, 129.6, 128.7, 128.4, 124.8, 98.0.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.0c02471.

Additional screening data; mechanistic investigation; and copies of ^1H, $^{13}C\{1\ H\}$, ^{19}F NMR, and IR spectra of all new products (ZIP)

■ AUTHOR INFORMATION

Corresponding Authors

Yan-Hong He − *Key Laboratory of Applied Chemistry of Chongqing Municipality, School of Chemistry and Chemical Engineering, Southwest University, Chongqing 400715, China;* orcid.org/0000-0002-6405-285X; Email: heyh@swu.edu.cn

Zhi Guan − *Key Laboratory of Applied Chemistry of Chongqing Municipality, School of Chemistry and Chemical Engineering, Southwest University, Chongqing 400715, China;* orcid.org/0000-0002-0369-6141; Email: guanzhi@swu.edu.cn

Authors

Zhi-Lv Wang − *Key Laboratory of Applied Chemistry of Chongqing Municipality, School of Chemistry and Chemical Engineering, Southwest University, Chongqing 400715, China*

Jie Chen − *Key Laboratory of Applied Chemistry of Chongqing Municipality, School of Chemistry and Chemical Engineering, Southwest University, Chongqing 400715, China*

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.joc.0c02471

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was financially supported by the National Natural Science Foundation of China (Nos. 21977084 and 22078268).

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https://dx.doi.org/10.1021/acs.joc.0c02471
J. Org. Chem. 2021, 86, 3741−3749