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Cu-Catalyzed Oxidative Thioesterification of Aroylhydrazides with Disulfides

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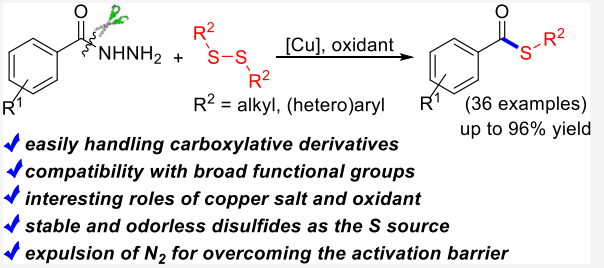
ABSTRACT: An alternative thioesterification reaction via copper-catalyzed oxidative coupling of readily available aroylhydrazides with disulfides is developed, in which oxidative expulsion of N_2 overcomes the activation barrier between the carboxylic acid derivatives and the products. The reaction produces various thioesters in good to excellent yields with good functional group tolerance. In the reaction, stable and easily available aroylhydrazides are used as acyl sources and the relatively odorless disulfides are used as S sources. Mechanistic investigations demonstrate that the reaction of copper salt and oxidant $(NH_4)_2S_2O_8$ allows for achievement of tandem processes, including deprotonation, free-radical-mediated denitrogenation, and C−S bond formation.



INTRODUCTION

Thioesters are important structural units found in a broad range of pharmaceuticals and natural products, and thioesters bearing functional groups with sulfur display unique biological properties (Figure 1).[1,2] This kind of compounds are also frequently used as an acyl transfer reagent in synthetic chemistry and chemical biology.[3]

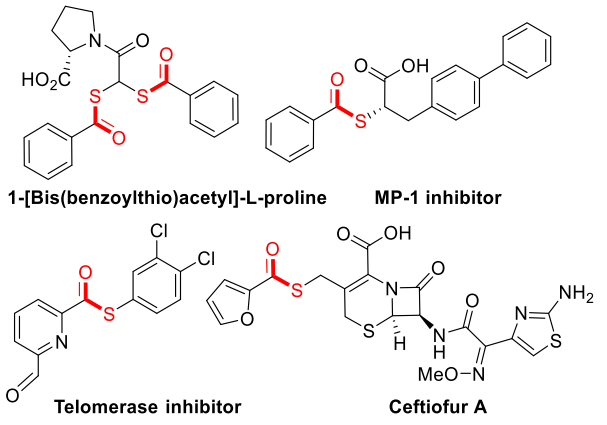


Figure 1. Representative bioactive compounds bearing thioester structures.

Over the past three decades, several strategies[4−12] have been developed, leading to more than 100 methods for the synthesis of thioesters. Among them, nucleophilic substitution of acyl chlorides/anhydrides with thiols/disulfides,[5] direct coupling of aldehydes with thiols/disulfides,[6] thiocarbonylation of aryl halides with CO,[7] and decarboxylation coupling of α-keto acids with thiols/disulfides[8] have been well developed and are frequently used. However, these methods often suffer from some disadvantages, such as the use of toxic, inaccessible, and/or difficult-to-handle substrates and limitations of the substrates. Undoubtedly, use of stable and easily available carboxylic acids and their derivatives as acyl sources is an ideal choice for the direct synthesis of thioesters.

However, there have only been a few reports demonstrating this strategy.[9−12] The underdevelopment of this strategy is due to the thermodynamic disfavor,[9a,13] in which, owing to the strong conjugation effect, the acyl C−O/or C−N bond of the common carboxylic acids and their derivatives is more stable than the acyl C−S bond of thioesters. Indeed, previous studies have employed substrates that have a decreased activation barrier (Scheme 1a−c), which leads to the use of specially structured substrates (or in situ formed).[9b,11,12] For example, Plietker's work limits to the *p*-chloro-substituted aryl esters.[11] Our previous procedure requires the use of specially structured amides, i.e., 1-benzoylpyrrolidine-2,5-dione derivatives, which contain two strong electron-drawing groups (Scheme 1b).[12] Lin's reaction relies on the assistance of hydrosilanes to form reactive species (RCOOSi, Scheme 1c).[9b] Therefore, development of a simple and general approach for the generation of thioesters from carboxylic acid derivatives is still highly attractive and desirable.

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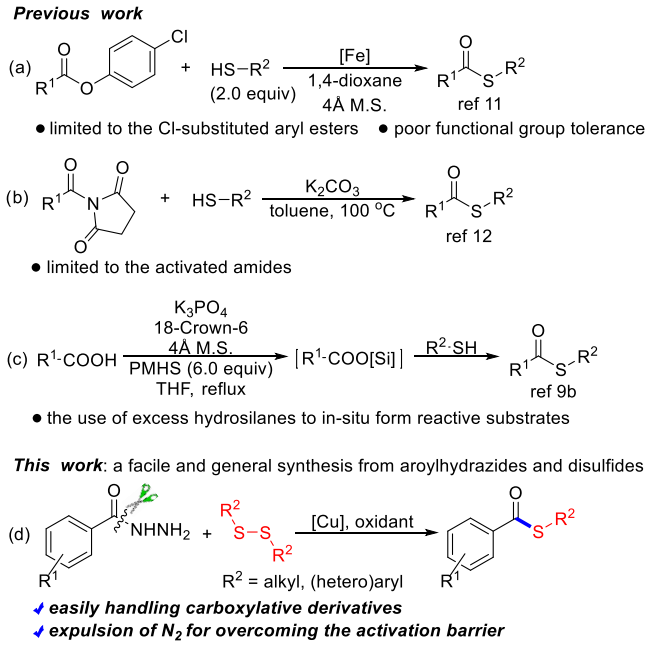
Scheme 1. Synthesis of Thioesters from Carboxylic Acids and Their Derivatives



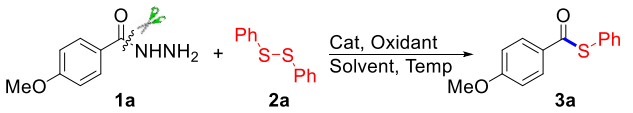
Herein, as a continuation of our interest in copper catalysis,[14] we report a facile and general approach for accessing thioesters via Cu-catalyzed cross-coupling of readily available aroylhydrazides with disulfides (Scheme 1d). This reaction produces a variety of functionalized thioesters in good to excellent yields with broad substrate scope and good functional group tolerance under mild conditions. Different from known methods, this reaction overcomes the activation barrier by the oxidative expulsion of N_2. Subsequent release of acyl radicals allows incorporation of both S atoms of the disulfide into the desired products.

Aroylhydrazides are readily accessible carboxylic acid derivatives. Compared with other types of carboxylic acid derivatives, simple aroylhydrazides are stable solids and compatible with moisture. Due to their easy availability and handling, aroylhydrazides have been proven to be powerful and versatile building blocks in organic synthesis[15−17] by functioning as aryl,[15] acyl,[16] and N sources.[17] In contrast, there have been a few reports on the use of aroylhydrazides as acyl sources.[18] It was noted that the strategy for overcoming the activation barrier by expulsion of CO_2 had been reported.[8a] However, this method employs α-oxocarboxylic acids as substrates, which are not simple and easily available carboxylic acids. Moreover, the known approach involves decarboxylation via C−C bond cleavage, and the acyl radicals in the reaction derive from α-keto of α-oxocarboxylic acids, other than carboxylic groups. Furthermore, it requires 1 equiv of disulfides (2 equiv of S source) and suffers from a limited scope of substrates and functional groups. Therefore, the chemistry of the oxidative thioesterification of aroylhydrazides with disulfides is quite different from the reported reaction.

RESULTS AND DISCUSSION

We commenced our study upon treatment of 4-methoxybenzohydrazide (**1a**) and 1,2-diphenyldisulfane (**2a**) in the presence of CuI (10 mol %) and $(NH_4)_2S_2O_8$ (0.3 mmol, 1.5 equiv) in dimethyl sulfoxide (DMSO) at 100 °C for 6 h. *S*-phenyl 4-methoxybenzothioate (**3a**) was obtained in 70% gas chromatography (GC) yield (Table 1, entry 1, yield based on 0.2 mmol of S). The choice of copper catalysts was critical to this coupling reaction. Cu(I) salts such as CuCl, CuBr, Cu_2O, and CuCN were first investigated, and CuCN gave the highest yield (93%) (Table 1, entries 2−5). Cu(II) catalysts, $CuCl_2$, $CuBr_2$, $Cu(OAc)_2$, and CuO also showed good efficiency for this reaction (Table 1, entries 6−9). In the absence of copper salt, only 16% GC yield of **3a** was obtained, indicating that copper was essential for the reaction (Table 1, entry 10). An assessment of oxidants revealed that $(NH_4)_2S_2O_8$ was optimal for the reaction (Table 1, entry 5), and $K_2S_2O_8$ and $Na_2S_2O_8$ also showed good efficiency, whereas di-*tert*-butyl peroxide (DTBP), *tert*-butyl hydroperoxide (TBHP), molecular oxygen, and Ag_2CO_3 gave very low yields of **3a** (Table 1, entries 11−16). Other solvents such as tetrahydrofuran (THF), CH_3CN, 1,2-dichloroethane (DCE), and *N*,*N*-dimethylformamide (DMF) were inferior to DMSO (Table 1, entries 17−20). The reaction was also sensitive to the reaction temperature (Table 1, entries 21 and 22). A slightly lower yield of **3a** was observed at 120 °C. However, a lower reaction temperature (80 °C) resulted in a lower yield of the product (42%). Under air, a low yield of the coupling product **3a** was observed (Table 1, entry 23). Notably, the reaction did not proceed without $(NH_4)_2S_2O_8$ (Table 1, entry 24).

Table 1. Optimization of the Reaction Conditions[a]



entry	catalyst	oxidant	solvent	temp (°C)	yield (%)[b]
1	CuI	$(NH_4)_2S_2O_8$	DMSO	100	70
2	CuCl	$(NH_4)_2S_2O_8$	DMSO	100	71
3	CuBr	$(NH_4)_2S_2O_8$	DMSO	100	72
4	Cu_2O	$(NH_4)_2S_2O_8$	DMSO	100	70
5	CuCN	$(NH_4)_2S_2O_8$	DMSO	100	93
6	$CuCl_2$	$(NH_4)_2S_2O_8$	DMSO	100	74
7	$CuBr_2$	$(NH_4)_2S_2O_8$	DMSO	100	69
8	$Cu(OAc)_2$	$(NH_4)_2S_2O_8$	DMSO	100	78
9	CuO	$(NH_4)_2S_2O_8$	DMSO	100	75
10	–	$(NH_4)_2S_2O_8$	DMSO	100	16
11	CuCN	$K_2S_2O_8$	DMSO	100	68
12	CuCN	$Na_2S_2O_8$	DMSO	100	82
13	CuCN	DTBP	DMSO	100	6
14	CuCN	TBHP	DMSO	100	8
15	CuCN	O_2	DMSO	100	25
16	CuCN	Ag_2CO_3	DMSO	100	10
17	CuCN	$(NH_4)_2S_2O_8$	THF	100	20
18	CuCN	$(NH_4)_2S_2O_8$	CH_3CN	100	33
19	CuCN	$(NH_4)_2S_2O_8$	DCE	100	23
20	CuCN	$(NH_4)_2S_2O_8$	DMF	100	trace
21	CuCN	$(NH_4)_2S_2O_8$	DMSO	80	42
22	CuCN	$(NH_4)_2S_2O_8$	DMSO	120	83
23[c]	CuCN	$(NH_4)_2S_2O_8$	DMSO	100	11
24	CuCN	-	DMSO	100	0

[a]Reaction conditions: **1a** (0.4 mmol, 2.0 equiv, 66.5 mg), **2a** (0.1 mmol, 21.8 mg), catalyst (0.02 mmol, 10 mol %, based on 0.2 mmol of S source), oxidant (0.3 mmol, 1.5 equiv), solvent (1.0 mL) at 100 °C for 6 h under N_2. [b]GC yields using *n*-tridecane as an internal standard. [c]Under air.

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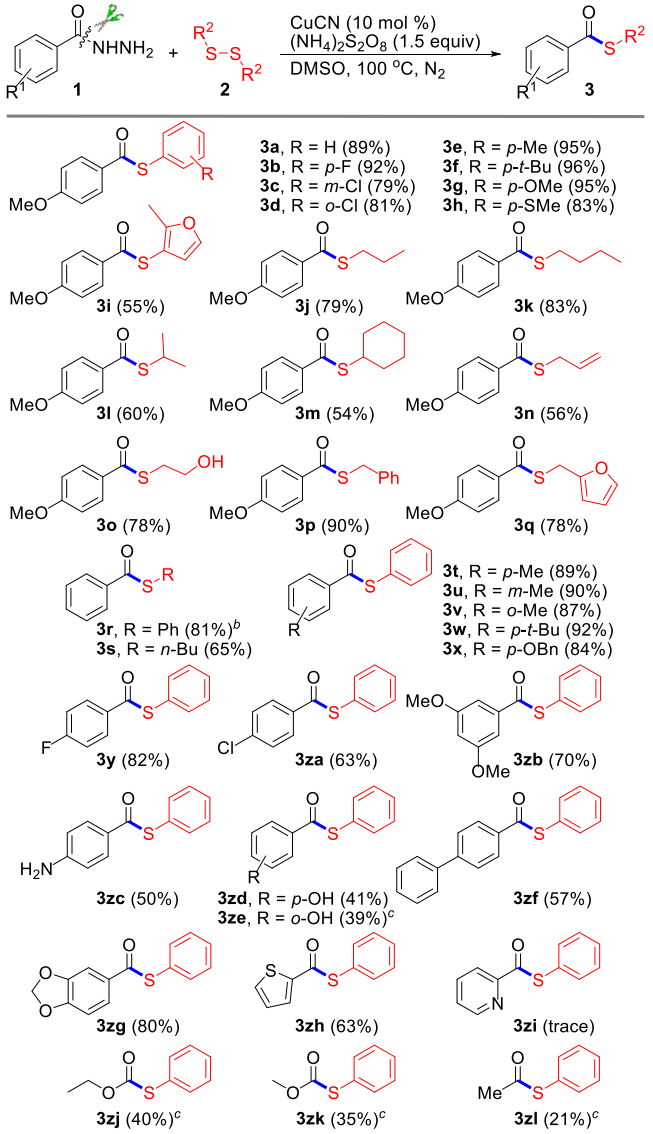
After the optimal conditions were determined, we next investigated the scope of the substrates, and the results are summarized in Table 2. This Cu-catalyzed cross-coupling of aroylhydrazides with disulfides produced a wide scope of substrates and good tolerance toward functional groups, producing various thioesters in good to excellent yields. Aromatic disulfides substituted with fluoro (**3b**), chloro (**3c** and **3d**), alkyl (**3e** and **3f**), methoxy (**3g**), and thiomethyl (**3h**) groups afforded the corresponding thioesters in 79−96% yields. Heteroaromatic disulfides containing a furyl group also reacted efficiently, producing the desired product (**3i**) in 55% yield. Aliphatic disulfides were also good substrates, and the corresponding thioesters were produced in good to excellent yields (54−90%, **3j**−**q**). Functional groups such as alkyl (**3j**−**l**), cycloalkyl (**3m**), vinyl (**3n**), hydroxyl (**3o**), benzyl (**3p**), and furyl (**3q**) were all tolerated.

For aroylhydrazides, benzoyl hydrazide readily underwent cross-coupling with alkyl and aryl disulfides, producing the corresponding thioesters in good yields (**3r**, 81%; **3s**, 65%). Electron-donating groups on the phenyl rings, such as OMe, Me, *t*-Bu, and OBn, significantly facilitated the reaction, and the desired products (**3a** and **3t**−**x**) were obtained in 84−92% yields. In comparison, slightly lower yields were observed when the aromatic ring contained electron-withdrawing substituents (**3y**, 82%; **3za**, 63%). This electronic effect is attributed to electron-donating groups facilitating the formation of the carbonyl radical (*vide infra*), whereas electron-withdrawing groups hindered this process. Furthermore, 3,5-dimethoxy benzohydrazide reacted efficiently with 1,2-diphenyl disulfide, giving the target product (**3zb**) in 70% yield. Notably, NH_2 and phenolic hydroxy groups, which are sensitive to oxidants, were also compatible, and the desired products (**3zc**−**ze**) were isolated in 50, 41, and 39% yields, respectively. 4-Biphenylcarboxylic acid hydrazide also successfully produced the corresponding product (**3zf**) in 57% yield. An *o*-heterocycle-based aroylhydrazide was also very suitable for this transformation (**3zg**, 80% yield). In addition, the arene ring was not limited to benzene, as demonstrated by the isolation of *S*-phenyl thiophene-2-carbothioate **3zh** in good yield (63%). Notably, functional groups such as NH_2, OH, and furyl are very important and are frequently found in functionalized thioester derivatives.[1a] Thus, this method provides a good alternative to previously reported methods.[4−12] Unfortunately, when pyridyl hydrazide was employed as the substrate, only a trace of the desired product, *S*-phenyl pyridine-2-carbothioate (**3zi**), was generated, which was probably due to the strong coordination of the N atom of pyridine with the copper catalyst. In comparison, aliphatic hydrazides showed a lower reactivity. For example, treatment of ethyl carbazate, methyl carbazate, and acethydrazide with **2a** afforded the corresponding products (**3zj**−**zl**) in 40, 35, and 21% yields.

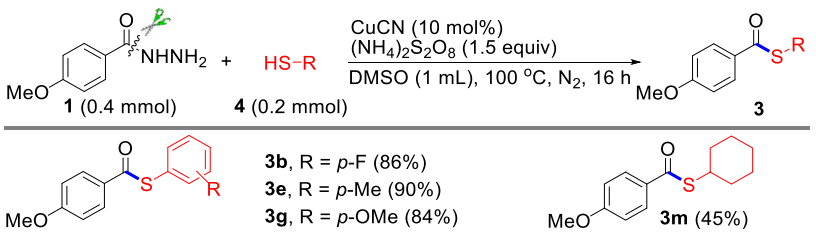
Thiols are malodorous and very toxic. Another problem associated with the use of thiols as coupling partners during C−S bond formation is their propensity to undergo oxidative-

Table 2. Substrate Scope[a]



[a]General reaction conditions: **1** (0.4 mmol, 2.0 equiv), **2** (0.1 mmol), CuCN (0.02 mmol, 10 mol %, 1.79 mg), and $(NH_4)_2S_2O_8$ (0.3 mmol, 1.5 equiv, 68.5 mg) in DMSO (1.0 mL) at 100 °C for 6 h under N_2. Isolated yields based on 0.2 mmol of S. [b]12 h. [c]$(NH_4)_2S_2O_8$ (0.6 mmol, 3.0 equiv).

Scheme 2. Thioesterification of Aroylhydrazides with Thiols



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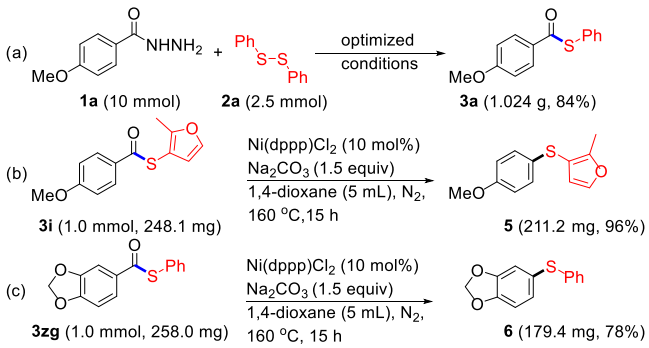
self dimerization, inhibiting the desired C−S bond formation. Thus, replacing thiols with disulfides is a good choice for the synthesis of thioesters.[19] As shown in Scheme 2, an investigation of the efficiency of the reaction of aroylhydrazides with thiols was conducted. 4-Methoxybenzohydrazide coupled with aryl thiols in the presence of 1.5 equiv of the oxidant to produce the corresponding thioesters in high yields (**3b**, **3e**, and **3g**, 86, 90, and 84% yields, respectively). The reaction of the aliphatic thiol cyclohexanethiol with 4-methoxybenzohydrazide produced the desired thioester (**3m**) in 45% yield. In comparison, the reaction efficiency of disulfides was higher than that of thiols, which was another advantage of this reaction.

To further extend the practicability of this new thioesterification reaction, a gram-scale reaction was conducted under standard reaction conditions, and the reaction successfully delivered the desired product (**3a**) in a comparable yield (1.024 g, 84% yield; Scheme 3a).

Scheme 3. Synthetic Utility



Because unsymmetrical aryl thioethers are valuable synthetic intermediates and pharmaceutically active molecules, the direct decarbonylative thioetherification of *S*-(2-methylfuran-3-yl) 4-methoxy-benzothioate (**3i**) and *S*-phenyl benzo[*d*][1,3]-dioxole-5-carbothioate (**3zg**) was investigated, and selective C−S cleavage/CO extrusion generated the desired unsymmetrical aryl thioethers **5** and **6** in 96 and 78% yields, respectively (Scheme 3b,c).[20] Therefore, the above results demonstrated the synthetic value of this method in organic synthesis.

To gain insights into the mechanism, Cu-catalyzed coupling of **1a** and **2a** was performed in the presence of the radical scavenger TEMPO (2.0 equiv, based on 0.2 mmol; Scheme 4a). The reaction was thoroughly suppressed, suggesting that the reaction involved a free-radical process. The addition of the radical scavenger 1,1-diphenylethylene could also block this reaction, which further confirmed this suggestion. When **2a** was reacted with benzaldehyde, benzoic acid, or benzoic amide under optimized conditions, no desired product was observed (Scheme 4b). These results demonstrated that the release of N_2 is essential for the reaction to overcome the activation barrier and generate the carbonyl radical (*vide infra*). Copper salt played different roles in this reaction. A low loading of copper(I) promoted the reaction efficiency, and 1, 5, and 10 mol % CuCN resulted in increased yields (respectively, 28, 81, and 93% vs 16%; Scheme 4c). In contrast, higher amounts of CuCN (20 and 100 mol %) produced much lower yields (57 and 45% vs 93%). Although copper(II) salt could also catalyze this coupling reaction (10 mol % $Cu(OAc)_2$, 78% yield), the use of an excess $Cu(OAc)_2$ (2.0 equiv) did not produce the desired product, in spite of the addition of the oxidant (Scheme 4c). This is likely due to the coordination of Cu(II) with the N−N double bond of diazene **C**, which disfavored the formation of the acyl radical **E** (*vide infra*). It has been reported that diazene **C** can be easily transformed into acyl radical **E** via the N−N double-bond radical **D** in the presence of a suitable oxidant.[18] Hence, we propose that the copper(II) salt promoted the oxidation of the aroylhydrazide to diazene **C** in the catalytic cycle, while it disfavored the followed processes (**C** to **E**). Indeed, when a stoichiometric amount of $Cu(OAc)_2$·bipy (**7**) that Cu(II) has been coordinated to the N atom was subjected to the reaction, **3a** was produced in 14% yield. Although low, it was an essential improvement in comparison to $Cu(OAc)_2$. These results further confirmed the suggestion that Cu(II) salts have a detrimental effect on the reaction via coordination with the N−N double bond of diazene **C**, and thus Cu(II) cannot transform **C** to the carbonyl radical **E**.

It was proved that *p*-MePhSCu(I) (**8**) was also a good catalyst for this reaction (90% yield of **3a**, Scheme 4e). But, by the replacement of 1,2-di-*p*-tolyl disulfide (**2e**) with **8**, the thioesterification product **3e** was only isolated in 21% yield (Scheme 4e) in the presence of 1.5 equiv of the oxidant. In addition, the reaction of **1a** and **2a** with a stoichiometric amount of **8** produced **3a** as a major product (56% yield) and concomitant generation of **3e** as a minor product (11% yield, Scheme 4f). These results suggested that *p*-MePhSCu(I) (**8**) was not the major intermediate and that the involvement of the Cu(II) species **G** (*vide infra*) that are probably derived from the combination of sulfur radical **F** and Cu(I) in the reaction was a minor pathway.[23]

Although the specific mechanism remains unclear, tentative pathways have been proposed based on the above results and literature reports (Scheme 5).[18,21−23] Initially, homolytic cleavage of $(NH_4)_2S_2O_8$ produces an ammonium sulfate radical under the reaction conditions. In the presence of copper(I) and $S_2O_8^{2-}$, the cation radical **A** is generated by single electron transfer between aroylhydrazide and a copper(II) species (Scheme 5, major pathway). Then, sequential single electron transfer and deprotonation form diazene **C** via the radical intermediate **B**.[21] Diazene **C** further reacts with an ammonium sulfate radical to generate radical **D**. By the expulsion of molecular nitrogen, the radical **D** quickly turns into acyl radical **E**.[18,21,22] Then, the acyl radical **E** subsequently reacts with disulfide **2** to form thioester **3**, concomitantly generating sulfur radical **F** (**F** can also be produced by homolytic cleavage of disulfide **2**).

The desired products are probably produced by another three pathways: (1) direct combination of acyl radical **E** and sulfur radical **F**; (2) sulfur radical **F** reacts with Cu(I) to form a Cu(II) species **G**,[23] then further reacts with acyl radical **E** to provide Cu(III) species **H**, accompanied by a single electron transfer process. Reductive elimination of Cu(III) species **H** delivers thioesterification product **3** and regenerates Cu(I); (3) ammonium sulfate radical reacts with the aroylhydrazide to form radical **D**, and acyl radical **E** is produced by a release of N_2 by **D**. Finally, **E** is converted into thioester **3** by a free-radical-mediated C−S bond formation (minor pathway, Table 1, entry 10).

CONCLUSIONS

In summary, we have developed a new type of thioesterification reaction via copper-catalyzed oxidative coupling of

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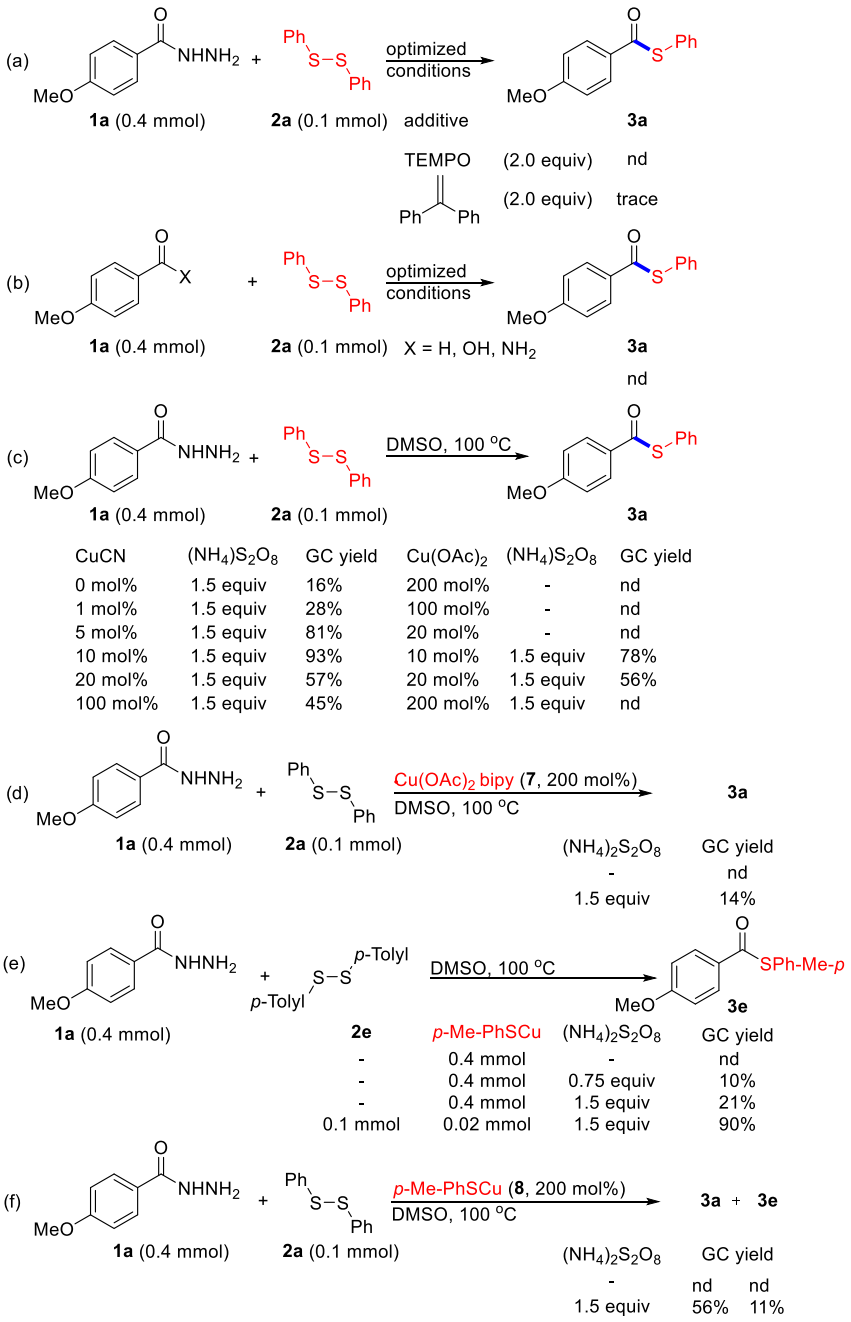
Scheme 4. Control Experiments



readily available aroylhydrazides with disulfides, in which oxidative expulsion of N_2 overcomes the activation barrier between the carboxylic acid derivatives and the products. This procedure is applicable to a wide range of substrates, including aromatic, heteroaromatic, and aliphatic disulfides, and is tolerant to many important functional groups, especially furans, thiophenes, alkenes, SMe, NH_2, and OH. The reaction proceeds via free-radical-mediated acyl C−N bond cleavage and C−S bond formation, allowing the incorporation of both S atoms of disulfides into the desired molecules. Mechanism investigation reveals that some interesting pathways are involved in the reaction, in which the reaction of copper salt and $(NH_4)_2S_2O_8$ allows for achievement tandem processes. This reaction allows for an efficient, practical, and general synthesis of thioesters from readily accessible carboxylic acid derivatives, and the advantages of this reaction, such as the easy availability of the starting materials, use of odorless disulfides, no requirement for exotic additives, and facile operation, make this protocol particularly attractive and represent a good alternative method to synthesize thioesters.

EXPERIMENTAL SECTION

General Information. All reactions were carried out in 25 mL Schlenk tubes under N_2 atmosphere. The heat source is an IKA magnetic stirrer with RCT Basic. Reagents and solvents were obtained from commercial sources (Energy Chemical, Alfa Aesar, Aladdin, Sigma-Aldrich, and J&K Scientific) and used without further purification. Column chromatography was performed using Silica Gel 60 (300−400 mesh). The reactions were monitored by GC and gas chromatography−mass spectrometry (GC−MS). The GC−MS results were recorded on a GC−MS QP2010, and the GC analysis

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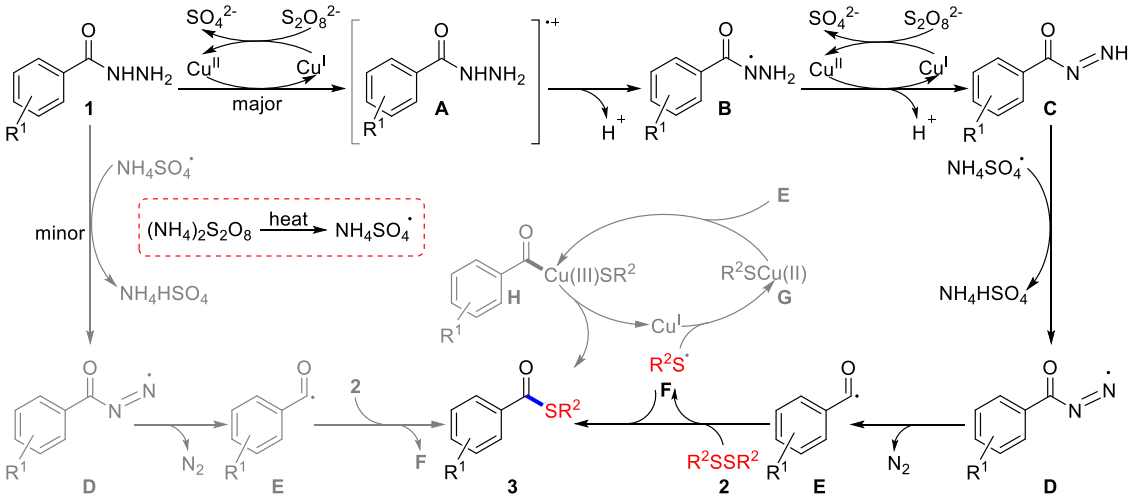
Scheme 5. Possible Reaction Mechanism



was performed on a GC 2014 Plus. The ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded on Bruker 400 and 500 MHz spectrometers at 20 °C, and chemical shifts were reported in parts per million (ppm). Electron ionization (EI) method was used for HRMS measurement, and a time-of-flight (TOF) mass analyzer was used for EI.

General Experimental Procedure for the Synthesis of Thioesters. An oven-dried 25 mL Schlenk tube equipped with a magnetic stir bar was charged with CuCN (0.02 mmol, 1.79 mg, 10 mol %, based on 0.2 mmol of S source), to which $(NH_4)_2S_2O_8$ (0.3 mmol, 1.5 equiv, 68.5 mg), aryl hydrazide **1** (0.40 mmol, 2.0 equiv), disulfide **2** (0.1 mmol), and DMSO (0.2 M, 1.0 mL) were added. The reaction mixture was heated at 100 °C for 6 h under N_2. After completion of the reaction, the reaction mixture was cooled to room temperature, then washed with saturated NH_4Cl aqueous solution (5.0 mL), and extracted with ethyl acetate (3 × 5 mL). The organic layer was dried over anhydrous Na_2SO_4 and concentrated under vacuum. The desired product **3** was isolated by column chromatography (eluent: ethyl acetate/petroleum ether = 1/40−1/20) over silica gel (300−400 mesh) using petroleum ether−ethyl acetate as an eluent.

General Experimental Procedure for the Thioesterification of Aroylhydrazides with Thiols. An oven-dried 25 mL Schlenk tube equipped with a magnetic stir bar was charged with CuCN (0.02 mmol, 1.79 mg), to which $(NH_4)_2S_2O_8$ (0.3 mmol, 1.5 equiv, 68.5 mg), aryl hydrazide **1** (0.40 mmol, 2.0 equiv), thiol **4** (0.2 mmol), and DMSO (0.2 M, 1.0 mL) were added. The reaction mixture was heated at 100 °C for 16 h under N_2. After completion of the reaction, the reaction mixture was cooled to room temperature, then washed with saturated NH_4Cl aqueous solution (5.0 mL), and extracted with ethyl acetate (3 × 5 mL). The organic layer was dried over anhydrous Na_2SO_4 and concentrated under vacuum. The desired product **3** was isolated by column chromatography (eluent: ethyl acetate/petroleum ether = 1/40−1/20) over silica gel (300−400 mesh) using petroleum ether−ethyl acetate as an eluent.

General Procedure for the Synthesis of 5 and 6.[20] An oven-dried 25 mL Schlenk tube equipped with a magnetic stir bar was charged with a thioester substrate (0.1 mmol), to which Ni(dppp)Cl_2 (0.01 mmol, 5.42 mg), Na_2CO_3 (0.15 mmol, 15.9 mg), and anhydrous 1,4-dioxane (0.5 mL, 0.2 M) were added. The reaction mixture was heated at 160 °C for 15 h under N_2. After the indicated time, the reaction mixture was diluted with CH_2Cl_2 (2 mL), filtered, and concentrated. The desired product was isolated by column chromatography (eluent: ethyl acetate/petroleum ether = 1/80) over silica gel (300−400 mesh) using petroleum ether−ethyl acetate as an eluent.

^{1}H, ^{13}C, and ^{19}F NMR Spectral Data of the Products. *S-Phenyl 4-Methoxybenzothioate (**3a**).*[7b] The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (40:1) to afford a colorless solid in 89% yield (43.4 mg); mp 92−93 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02 (d, J = 8.4 Hz, 2H), 7.54−7.45 (m, 5H), 6.96 (d, J = 8.4 Hz, 2H), 3.87 (s, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 188.5, 163.9, 135.1, 129.6, 129.3, 129.3, 129.1, 127.6, 113.9, 55.5.

*S-(4-Fluorophenyl) 4-Methoxybenzothioate (**3b**).*[7b] The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (20:1) to afford a colorless solid in 92% yield (48.2 mg); mp 86−87 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 (d, J = 9.2 Hz, 2H), 7.48 (dd, J = 8.8 Hz, J = 5.6 Hz, 2H), 7.14 (t, J = 8.8 Hz, 2H), 6.95 (d, J = 8.8 Hz, 2H), 3.86 (s, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 188.3, 164.0, 163.4 (d, $J_{C\text{-}F}$ = 248 Hz), 137.1 (d, $J_{C\text{-}F}$ = 8.6 Hz), 129.6, 129.0, 122.9 (d, $J_{C\text{-}F}$ = 3.5 Hz), 116.3 (d, $J_{C\text{-}F}$ = 21.9 Hz), 113.9, 55.4. ^{19}F NMR (376 MHz, $CDCl_3$): δ −111.3 (s, 1F).

*S-(3-Chlorophenyl) 4-Methoxybenzothioate (**3c**).* The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (40:1) to afford a yellow oil in 79% yield (43.9 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (d, J = 8.4 Hz, 2H), 7.43 (s, 1H), 7.32−7.24 (m, 3H), 6.85 (d, J = 8.8 Hz, 2H), 3.76 (s, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 187.5, 164.1, 134.7, 134.5, 133.2, 130.0, 129.7, 129.4, 129.4, 128.9, 113.9, 55.5. HRMS (EI) m/z: [M + H^+] calcd for $C_{14}H_{12}ClO_2S^+$: 279.0241, found: 279.0246.

*S-(2-Chlorophenyl) 4-Methoxybenzothioate (**3d**).* The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (20:1) to afford a yellow oil in 81% yield (45.0 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 (d, J = 8.4 Hz, 2H), 7.61 (d, J = 7.6 Hz, 1H), 7.55 (d, J = 8.0 Hz, 1H), 7.41−7.31 (m, 2H), 6.96 (d, J = 8.4 Hz, 2H), 3.86 (s, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 186.6, 164.0, 139.0, 137.6, 131.0, 130.1, 129.8, 128.9, 127.2, 113.9, 55.5. HRMS (EI) m/z: [M + H^+] calcd for $C_{14}H_{12}ClO_2S^+$: 279.0241, found: 279.0248.

*S-(p-Tolyl) 4-Methoxybenzothioate (**3e**).*[5e] The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (40:1) to afford a yellow solid in 95% yield (49.2 mg); mp 65−66 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 (d, J = 8.8 Hz, 2H), 7.39 (d, J = 7.6 Hz, 2H), 7.25 (d, J = 8.0 Hz, 2H), 6.93 (d, J = 8.4 Hz, 2H), 3.84 (s, 3H), 2.39 (s, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 188.9, 163.8, 139.5, 135.0, 129.9, 129.6, 129.4, 123.9, 113.8, 55.4, 21.3.

*S-(4-(tert-Butyl) Phenyl) 4-Methoxybenzothioate (**3f**).* The title compound was prepared according to the general procedure and

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purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (40:1) to afford a colorless oil in 96% yield (57.6 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02 (d, J = 8.0 Hz, 2H), 7.49−7.43 (m, 4H), 6.96 (d, J = 8.0 Hz, 2H), 3.87 (s, 3H), 1.36 (s, 9H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 188.9, 163.9, 152.5, 134.8, 129.6, 129.5, 126.3, 124.1, 113.8, 55.5, 34.7, 31.2. HRMS (EI) m/z: [M + H$^+$] calcd for $C_{18}H_{21}O_2S^+$: 301.1257, found: 301.1259.

*S-(3-Methoxyphenyl) 4-Methoxybenzothioate (**3g**).*[7b] The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (5:1) to afford a colorless solid in 95% yield (52.1 mg); mp 138−139 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 (d, J = 8.0 Hz, 2H), 7.42 (d, J = 8.0 Hz, 2H), 6.98 (d, J = 8.0 Hz, 2H), 6.95 (d, J = 8.4 Hz, 2H), 3.86 (s, 3H), 3.84 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 189.4, 163.8, 160.6, 136.6, 129.6, 129.4, 118.1, 114.8, 113.8, 55.4, 55.3.

*S-(4-(Methylthio)phenyl) 4-Methoxybenzothioate (**3h**).* The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (20:1) to afford a yellow oil in 83% yield (48.1 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (d, J = 8.4 Hz, 2H), 7.39 (d, J = 7.6 Hz, 2H), 7.29 (d, J = 8.0 Hz, 2H), 6.95 (d, J = 8.4 Hz, 2H), 3.86 (s, 3H), 2.50 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 188.7, 163.9, 140.9, 135.4, 129.6, 129.2, 126.5, 123.3, 113.8, 55.5, 15.3. HRMS (EI) m/z: [M + H$^+$] calcd for $C_{15}H_{15}O_2S_2^+$: 291.0508, found: 291.0512.

*S-(2-Methylfuran-3-yl) 4-Methoxybenzothioate (**3i**).* The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (40:1) to afford a white solid in 55% yield (27.3 mg). mp 89−90 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.00 (d, J = 8.5 Hz, 2H), 7.41−7.40 (m, 1H), 6.95 (d, J = 9.0 Hz, 2H), 6.40−6.39 (m, 1H), 3.87 (s, 3H), 2.30 (s, 3H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 188.0, 163.9, 156.6, 141.1, 129.7, 129.1, 115.2, 113.8, 103.5, 55.5, 11.9. HRMS (EI) m/z: [M + H$^+$] calcd for $C_{13}H_{13}O_3S^+$: 249.0580, found: 249.0585.

*S-Propyl 4-Methoxybenzothioate (**3j**).*[25] The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (80:1) to afford a colorless oil in 79% yield (33.2 mg); mp 89−90 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (d, J = 8.8 Hz, 2H), 6.90 (d, J = 9.2 Hz, 2H), 3.84 (s, 3H), 3.02 (t, J = 7.2 Hz, 2H), 1.71−1.66 (m, 2H), 1.02 (t, J = 7.2 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 190.5, 163.6, 130.1, 129.3, 113.6, 55.4, 30.7, 23.1, 13.4.

*S-(n-Butyl) 4-Methoxybenzothioate (**3k**).*[6g] The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (40:1) to afford a colorless oil in 83% yield (37.2 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 (d, J = 8.8 Hz, 2H), 6.90 (d, J = 9.2 Hz, 2H), 3.84 (s, 3H), 3.04 (t, J = 7.2 Hz, 2H), 1.67−1.60 (m, 2H), 1.49−1.39 (m, 2H), 0.93 (t, J = 7.6 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 190.6, 163.6, 130.1, 129.2, 113.6, 55.4, 31.7, 28.54, 22.0, 13.6.

*S-Isopropyl 4-Methoxybenzothioate (**3l**).* The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (40:1) to afford a yellow oil in 60% yield (25.2 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 (d, J = 9.2 Hz, 2H), 6.90 (d, J = 8.8 Hz, 2H), 3.85 (s, 3H), 3.83−3.77 (m, 1H), 1.39 (d, J = 7.2 Hz, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 190.7, 163.6, 130.3, 129.2, 113.7, 55.5, 34.7, 23.2. HRMS (EI) m/z: [M + H$^+$] calcd for $C_{11}H_{15}O_2S^+$: 211.0750, found: 211.0756.

*S-Cyclohexyl 4-Methoxybenzothioate (**3m**).*[5e] The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (40:1) to afford a yellow oil in 54% yield (27 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 (d, J = 9.2 Hz, 2H), 6.90 (d, J = 8.8 Hz, 2H), 3.85 (s, 3H), 3.72−3.65 (m, 1H), 2.03−1.99 (m, 2H), 1.77−1.72 (m, 2H), 1.63−1.38 (m, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 190.4, 163.5, 130.4, 129.2, 113.6, 55.4, 42.4, 33.3, 26.0, 25.6.

*S-Allyl 4-Methoxybenzothioate (**3n**).*[26] The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (40:1) to afford a colorless oil in 56% yield (23.3 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (d, J = 8.8 Hz, 2H), 6.91 (d, J = 8.8 Hz, 2H), 5.94−5.84 (m, 1H), 5.33−5.28 (m, 1H), 5.14−5.12 (m, 1H), 3.85 (s, 3H), 3.71 (d, J = 6.8 Hz, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 189.7, 163.8, 133.4, 129.8, 129.4, 117.8, 113.8, 55.5, 31.7.

*S-(2-Hydroxyethyl) 4-Methoxybenzothioate (**3o**).*[5e] The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (2:1) to afford a colorless oil in 78% yield (33.1 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (d, J = 8.8 Hz, 2H), 6.91 (d, J = 9.2 Hz, 2H), 3.86−3.83 (m, 5H), 3.26 (t, J = 6.0 Hz, 2H), 2.26 (br s, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 190.6, 163.9, 129.6, 129.5, 113.8, 62.0, 55.5, 31.8.

*S-Benzyl 4-Methoxybenzothioate (**3p**).*[26] The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (40:1) to afford a white solid in 90% yield (46.4 mg); mp 50−51 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.94 (d, J = 9.0 Hz, 2H), 7.37 (d, J = 7.5 Hz, 2H), 7.31 (t, J = 7.5 Hz, 2H), 7.26−7.23 (m, 1H), 6.90 (d, J = 9.0 Hz, 2H), 4.30 (s, 2H), 3.84 (s, 3H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 189.7, 163.7, 137.7, 129.5, 129.4, 128.9, 128.6, 127.2, 113.7, 55.4, 33.1.

*S-(Furan-2-ylmethyl) 4-Methoxybenzothioate (**3q**).* The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (40:1) to afford a colorless oil in 78% yield (38.7 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (d, J = 9.2 Hz, 2H), 7.34−7.33 (m, 1H), 6.91 (d, J = 9.2 Hz, 2H), 6.31−6.28 (m, 2H), 4.33 (s, 2H), 3.84 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 189.1, 163.9, 150.7, 142.1, 129.5, 113.8, 110.6, 107.9, 55.4, 25.6. HRMS (EI) m/z: [M + H$^+$] calcd for $C_{13}H_{13}O_3S^+$: 249.0580, found: 249.0582.

*S-Phenyl Benzothioate (**3r**).*[7b] The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (40:1) to afford a colorless solid in 81% yield (34.7 mg); mp 56−57 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 (d, J = 8.0 Hz, 2H), 7.63−7.59 (m, 1H), 7.54−7.45 (m, 7H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 190.1, 136.6, 135.1, 133.6, 129.5, 129.2, 129.0, 128.7, 127.5.

*S-(n-Butyl)benzothioate (**3s**).*[6g] The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (100:1) to afford a white solid in 65% yield (25.2 mg); mp 119−120 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (d, J = 8.4 Hz, 2H), 7.55 (t, J = 7.6 Hz, 1H), 7.44 (t, J = 8.0 Hz, 2H), 3.08 (t, J = 7.6 Hz, 2H), 1.70−1.62 (m, 2H), 1.50−1.41 (m, 2H), 0.95 (t, J = 7.2 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 192.1, 137.3, 133.1, 128.5, 127.1, 31.61, 28.7, 22.0, 13.6.

*S-Phenyl 4-Methylbenzothioate (**3t**).*[7b] The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (40:1) to afford a colorless solid in 89% yield (40.6 mg); mp 94−95 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 (d, J = 8.0 Hz, 2H), 7.51−7.42 (m, 5H), 7.25 (d, J = 7.6 Hz, 2H), 2.39 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 189.6, 144.5, 135.1, 134.0, 129.3, 129.1, 127.5, 21.6.

*S-Phenyl 3-Methylbenzothioate (**3u**).*[7b] The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (40:1) to afford a colorless oil in 90% yield (41.0 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87−7.85 (m, 2H), 7.55−7.36 (m, 7H), 2.44 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 190.2, 138.6, 136.6, 135.0, 134.4, 129.4, 129.2, 128.6, 127.9, 127.4, 124.6, 21.3.

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*S-Phenyl 2-Methylbenzothioate (**3v**).*[7b] The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (40:1) to afford a colorless solid in 87% yield (39.7 mg); mp 45−46 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (dd, J = 7.6, 0.8 Hz, 1H), 7.55−7.41 (m, 6H), 7.33−7.26 (m, 2H), 2.51 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 192.1, 137.4, 136.7, 134.9, 131.9, 131.7, 129.4, 129.2, 128.6, 128.2, 125.8, 20.7.

*S-Phenyl 4-(tert-Butyl) Benzothioate (**3w**).*[6g] The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (40:1) to afford a colorless oil in 92% yield (49.7 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 (d, J = 8.8 Hz, 2H), 7.56−7.43 (m, 7H), 1.38 (s, 9H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 189.6, 157.5, 135.1, 133.9, 129.3, 129.1, 127.6, 127.4, 125.6, 35.2, 31.0.

*S-Phenyl 4-(Benzyloxy) Benzothioate (**3x**).*[27] The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (20:1) to afford a colorless solid in 84% yield (53.8 mg); mp 160−161 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02 (d, J = 8.8 Hz, 2H), 7.53−7.34 (m, 10H), 7.04 (d, J = 8.8 Hz, 2H), 5.15 (s, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 188.5, 163.1, 136.0, 135.2, 129.7, 129.6, 129.3, 129.1, 128.7, 128.3, 127.6, 127.5, 114.8, 70.2.

*S-Phenyl 4-Fluorobenzothioate (**3y**).*[7a] The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (40:1) to afford a colorless solid in 82% yield (38.1 mg); mp 59−60 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07−8.04 (m, 2H), 7.50−7.46 (m, 5H), 7.16 (t, J = 8.0 Hz, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 188.6, 166.0 (d, $J_{C\text{-}F}$ = 255.4 Hz), 135.1, 132.9 (d, $J_{C\text{-}F}$ = 3.2 Hz), 130.0 (d, $J_{C\text{-}F}$ = 9.4 Hz), 129.6, 129.3, 127.0, 115.9 (d, $J_{C\text{-}F}$ = 22.2 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): δ −104.2 (s, 1F).

*S-Phenyl 4-Chlorobenzothioate (**3za**).*[7b] The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (40:1) to afford a colorless solid in 63% yield (31.2 mg); mp 81−82 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (d, J = 8.4 Hz, 2H), 7.52−7.45 (m, 7H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 189.0, 140.0, 135.0, 134.9, 129.7, 129.3, 129.0, 128.8, 126.9.

*S-Phenyl 3,5-Dimethoxybenzothioate (**3zb**).* The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (20:1) to afford a colorless oil in 70% yield (38.4 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53−7.45 (m, 5H), 7.17−7.15 (m, 2H), 6.70−6.68 (m, 1H), 3.84 (s, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 189.9, 160.9, 138.5, 134.9, 129.5, 129.2, 127.4, 105.9, 105.1, 55.6. HRMS (EI) m/z: [M + H$^+$] calcd for $C_{15}H_{15}O_3S^+$: 275.0736, found: 275.0739.

*S-Phenyl 4-Aminobenzothioate (**3zc**).*[7a] The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (5:1) to afford a colorless solid in 50% yield (22.9 mg); mp 157−158 °C;. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (d, J = 8.0 Hz, 2H), 7.51−7.42 (m, 5H), 6.64 (d, J = 8.0 Hz, 2H), 4.16 (br s, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 188.0, 151.7, 135.2, 129.9, 129.1, 129.0, 128.0, 126.6, 113.8.

*S-Phenyl 4-Hydroxybenzothioate (**3zd**).*[7a] The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (2:1) to afford colorless crystals in 41% yield (18.9 mg); mp 173−174 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (d, J = 8.8 Hz, 2H), 7.53−7.43 (m, 5H), 6.84 (d, J = 8.4 Hz, 2H), 6.27 (br s, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 189.6, 160.8, 135.2, 131.9, 130.0, 129.5, 129.2, 127.4, 115.5.

*S-Phenyl 2-Hydroxybenzothioate (**3ze**).*[28] The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (40:1) to afford a yellow oil in 39% yield (17.9 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.76 (s, 1H), 8.00 (dd, J = 8.0, 1.2 Hz, 1H), 7.55−7.49 (m, 6H), 7.01−6.95 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.8, 159.7, 136.3, 135.5, 130.0, 129.4, 128.9, 125.9, 119.5, 119.4, 118.3.

*S-Phenyl [1,1′-Biphenyl]-4-carbothioate (**3zf**).*[29] The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (40:1) to afford a colorless oil in 57% yield (33.1 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11 (d, J = 8.0 Hz, 2H), 7.72−7.64 (m, 4H), 7.55−7.40 (m, 8H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 189.7, 146.4, 139.7, 135.3, 135.1, 129.5, 129.2, 128.9, 128.3, 128.0, 127.4, 127.3.

*S-Phenyl Benzo[d][1,3]dioxole-5-carbothioate (**3zg**).* The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (20:1) to afford a white solid in 80% yield (41.3 mg); mp 84−85 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70−7.68 (m, 1H), 7.52−7.43 (m, 6H), 6.88 (d, J = 8.4 Hz, 1H), 6.05 (s, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 188.3, 152.2, 148.1, 135.1, 131.0, 129.4, 129.1, 127.5, 123.6, 108.1, 107.4, 101.9. HRMS (EI) m/z: [M + H$^+$] calcd for $C_{14}H_{11}O_3S^+$: 259.0423, found: 259.0428.

*S-Phenyl Thiophene-2-carbothioate (**3zh**).*[7b] The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (40:1) to afford a yellow solid in 63% yield (27.7 mg); mp 59−60 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92−7.90 (m, 1H), 7.67−7.65 (m, 1H), 7.54−7.44 (m, 5H), 7.17−7.14 (m, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 182.0, 141.4, 135.0, 133.2, 131.6, 129.6, 129.2, 127.9, 126.9.

*O-Ethyl-S-phenyl Carbonothioate (**3zj**).*[30] The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (40:1) to afford a yellow oil in 40% yield (14.6 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56−7.52 (m, 2H), 7.45−7.37 (m, 3H), 4.30 (q, J = 7.2 Hz, 2H), 1.33 (t, J = 6.8 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 169.5, 134.8, 129.4, 129.1, 127.8, 63.9, 14.2.

*O-Methyl-S-phenyl Carbonothioate (**3zk**).*[30] The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (40:1) to afford a colorless oil in 35% yield (11.8 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56−7.51 (m, 2H), 7.44−7.39 (m, 3H), 3.84 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 170.2, 134.8, 129.6, 129.2, 127.6, 54.5.

*S-Phenyl Ethanethioate (**3zl**).*[31] The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (40:1) to afford a yellow oil in 21% yield (6.4 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44−7.41 (m, 5H), 2.42 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 193.9, 134.4, 129.4, 129.2, 127.9, 30.2.

*3-((4-Methoxyphenyl)thio)-2-methylfuran (**5**).* The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether to afford a yellow oil in 96% yield (211.2 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32−7.30 (m, 1H), 7.13 (d, J = 8.8 Hz, 2H), 6.80 (d, J = 9.2 Hz, 2H), 6.34−6.32 (m, 1H), 3.76 (s, 3H), 2.36 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 158.2, 155.6, 140.9, 129.3, 128.2, 115.1, 114.6, 109.7, 55.3, 11.8. HRMS (EI) m/z: [M + H$^+$] calcd for $C_{12}H_{13}O_2S^+$: 221.0631, found: 221.0636.

*5-(Phenylthio)benzo[d][1,3]dioxole (**6**).*[32] The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether to afford a colorless oil in 78% yield (179.4 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30−7.17 (m, 5H), 7.03−7.01 (m, 1H), 6.94−6.92 (m, 1H), 6.81 (d, J = 8.0 Hz, 1H), 6.00 (s, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 148.3, 147.9, 137.9, 128.9, 128.9, 127.3, 126.3, 126.2, 113.5, 108.9, 101.4.

*Cu(OAc)$_2$·bipy (**7**).* The title compound was prepared according to the known methods.[24] 2,2′-Bipyridine (5.44 mmol, 849.6 mg), DMF

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(20 mL), $Cu(OAc)_2·H_2O$ (8.16 mmol, 1.63 g), DMF (40 mL), blue powder. Anal. calcd for $C_{14}H_{14}N_2O_4Cu$: C, 48.48; H, 4.36; N, 8.08. Found: C, 48.58; H, 4.42; N, 8.17. IR (neat, cm^{-1}): 2924, 1580, 1400, 1330,1248, 1169, 1023, 919, 769, 673.

p-Me-PhSCu (8).[23] The title compound was prepared according to the known methods.[23] Conc. aq. NH_3 (6.25 mL), H_2O (25 mL), $CuSO_4·5H_2O$ (6.25 mmol, 1.56 g), $NH_2OH·HCl$ (14 mmol, 0.97 g), *p*-TolylSH (6.45 mmol, 0.8 g), EtOH (40 mL). Yellow solid (1.10 g, 80%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.37 (d, J = 7.6 Hz, 2H), 7.09 (d, J = 8.0 Hz, 2H), 2.31 (s, 3H).

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.0c02328.

GC−MS analysis of the control experiments and copies of ^{1}H, ^{19}F, and ^{13}C NMR spectra for all products (PDF)

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) (a) Dawson, P. E.; Muir, T. W.; Clark-Lewis, I.; Kent, S. B. Synthesis of proteins by native chemical ligation. *Science.* **1994**, *266*, 776. (b) Keating, T. A.; Walsh, C. T. Initiation, elongation, and termination strategies in polyketide and polypeptide antibiotic biosynthesis. *Curr. Opin. Chem. Biol.* **1999**, *3*, 598. (c) Dawson, P. E.; Kent, S. B. H. Synthesis of Native Proteins by Chemical Ligation. *Annu. Rev. Biochem.* **2000**, *69*, 923. (d) Khosla, C.; Tang, Y.; Chen, A. Y.; Schnarr, N. A.; Cane, D. E. Structure and Mechanism of the 6-Deoxyerythronolide B Synthase. *Annu. Rev. Biochem.* **2007**, *76*, 195. (e) Wang, M.; Dai, Z.; Jiang, X. Design and application of α-ketothioesters as 1,2-dicarbonyl-forming reagents. *Nat. Commun.* **2019**, *10*, No. 2661.

(2) (a) Fontecave, M.; Ollagnier-de-Choudens, S.; Mulliez, E. Biological Radical Sulfur Insertion Reactions. *Chem. Rev.* **2003**, *103*, 2149. (b) Greenlee, M. L.; Laub, J. B.; Balkovec, J. M.; Hammond, M. L.; Hammond, G. G.; Pompliano, D. L.; Epstein-Toney, J. H. Synthesis and SAR of thioester and thiol inhibitors of IMP-1 Metallo-β-Lactamase. *Bioorg. Med. Chem. Lett.* **1999**, *9*, 2549. (c) Feng, M.; Tang, B.; Liang, S.; Jiang, X. *Curr. Top. Med. Chem.* **2016**, *16*, 1200. (d) Wang, N.; Saidhareddy, P.; Jiang, X. Construction of sulfur-containing moieties in the total synthesis of natural products. *Nat. Prod. Rep.* **2020**, *37*, 246. (e) Liu, H.; Jiang, X. Transfer of Sulfur: From Simple to Diverse. *Chem. Asian J.* **2013**, *8*, 2546. (f) Lee, C.-F.; Basha, R. S.; Badsara, S. S. Engineered C−S Bond Construction. *Top. Curr. Chem.* **2018**, *376*, No. 25.

(3) (a) Alonso, D. A.; Kitagaki, S.; Utsumi, N.; Barbas, C. F., III Towards Organocatalytic Polyketide Synthases with Diverse Electrophile Scope: Trifluoroethyl Thioesters as Nucleophiles in Organocatalytic Michael Reactions and Beyond. *Angew. Chem., Int. Ed.* **2008**, *47*, 4588. (b) Crich, D.; Sasaki, K. Reaction of Thioacids with Isocyanates and Isothiocyanates: A Convenient Amide Ligation Process. *Org. Lett.* **2009**, *11*, 3514. (c) Crich, D.; Sharma, I. Epimerization-Free Block Synthesis of Peptides from Thioacids and Amines with the Sanger and Mukaiyama Reagents. *Angew. Chem., Int. Ed.* **2009**, *48*, 2355. (d) Kunchithapatham, K.; Eichman, C. C.; Stambuli, J. P. Synthesis of diaryl ketonesvia a phosphine-free Fukuyama reaction. *Chem. Commun.* **2011**, *47*, 12679. (e) Li, H.; Yang, H.; Liebeskind, L. S. Synthesis of High Enantiopurity N-Protected α-Amino Ketones by Thiol Ester−Organostannane Cross-Coupling Using pH-Neutral Conditions. *Org. Lett.* **2008**, *10*, 4375. (f) Lutter, F. H.; Grokenberger, L.; Hofmayer, M. S.; Knochel, P. Cobalt-catalyzed acylation-reactions of (hetero)arylzinc pivalates with thiopyridyl ester derivatives. *Chem. Sci.* **2019**, *10*, 8241. (g) Matsuo, K.; Shindo, M. Cu(II)-Catalyzed Acylation by Thiol Esters Under Neutral Conditions: Tandem Acylation-Wittig Reaction Leading to a One-Pot Synthesis of Butenolides. *Org. Lett.* **2010**, *12*, 5346. (h) Wang, J.; Cary, B. P.; Beyer, P. D.; Gellman, S. H.; Weix, D. J. Ketones from Nickel-Catalyzed Decarboxylative, Non-Symmetric Cross-Electrophile Coupling of Carboxylic Acid Esters. *Angew. Chem., Int. Ed.* **2019**, *58*, 12081. (i) Yang, H.; Li, H.; Wittenberg, R.; Egi, M.; Huang, W.; Liebeskind, L. S. Ambient Temperature Synthesis of High Enantiopurity N-Protected Peptidyl Ketones by Peptidyl Thiol Ester−Boronic Acid Cross-Coupling. *J. Am. Chem. Soc.* **2007**, *129*, 1132.

(4) (a) Ali, W.; Guin, S.; Rout, S. K.; Gogoi, A.; Patel, B. K. Thioesterification of Alkylbenzenes with Thiols via Copper- Catalyzed Cross-Dehydrogenative Coupling without a Directing Group. *Adv. Synth. Catal.* **2014**, *356*, 3099. (b) Bao, W.-H.; Wu, C.; Wang, J.-T.; Xia, W.; Chen, P.; Tang, Z.; Xu, X.; He, W.-M. Molecular iodine-mediated synthesis of thiocarbamates from thiols, isocyanides and water under metal-free conditions. *Org. Biomol. Chem.* **2018**, *16*, 8403. (c) Hirschbeck, V.; Gehrtz, P. H.; Fleischer, I. Regioselective Thiocarbonylation of Vinyl Arenes. *J. Am. Chem. Soc.* **2016**, *138*, 16794. (d) Hirschbeck, V.; Gehrtz, P. H.; Fleischer, I. Metal-Catalyzed Synthesis and Use of Thioesters: Recent Developments. *Chem. − Eur. J.* **2018**, *24*, 7092. (e) Kazemi, M.; Shiri, L. Thioesters synthesis: recent adventures in the esterification of thiols. *J. Sulfur Chem.* **2015**, *36*, 613. (f) Ranu, B. C.; Jana, R. Ionic Liquid as Catalyst and Reaction Medium: A Simple, Convenient and Green Procedure for the Synthesis of Thioethers, Thioesters and Dithianes using an

Inexpensive Ionic Liquid, [pmIm]Br. *Adv. Synth. Catal.* **2005**, *347*, 1811.
(5) (a) Azeredo, J. B.; Godoi, M.; Schwab, R. S.; Botteselle, G. V.; Braga, A. L. Synthesis of Thiol Esters Using Nano CuO/Ionic Liquid as an Eco-Friendly Reductive System Under Microwave Irradiation. *Eur. J. Org. Chem.* **2013**, *2013*, 5188. (b) Basu, B.; Paul, S.; Nanda, A. K. Silica-promoted facile synthesis of thioesters and thioethers: a highly efficient, reusable and environmentally safe solid support. *Green Chem.* **2010**, *12*, 767. (c) Dan, W.; Deng, H.; Chen, J.; Liu, M.; Ding, J.; Wu, H. A new odorless one-pot synthesis of thioesters and selenoesters promoted by Rongalite. *Tetrahedron* **2010**, *66*, 7384. (d) Meshram, H.; Reddy, G. S.; Bindu, K. H.; Yadav, J. Zinc promoted convenient and general synthesis of thiol esters. *Synlett* **1998**, *1998*, 877. (e) Singh, P.; Peddinti, R. K. Harnessing the catalytic behaviour of 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP): An expeditious synthesis of thioesters. *Tetrahedron Lett.* **2017**, *58*, 1875. (f) Temperini, A.; Annesi, D.; Testaferri, L.; Tiecco, M. A simple acylation of thiols with anhydrides. *Tetrahedron Lett.* **2010**, *51*, 5368.
(6) (a) Chung, J.; Seo, U. R.; Chun, S.; Chung, Y. K. Poly(3,4-dimethyl-5-vinylthiazolium)/DBU-Catalyzed Thioesterification of Aldehydes with Thiols. *ChemCatChem* **2016**, *8*, 318. (b) Huang, Y.-T.; Lu, S.-Y.; Yi, C.-L.; Lee, C.-F. Iron-Catalyzed Synthesis of Thioesters from Thiols and Aldehydes in Water. *J. Org. Chem.* **2014**, *79*, 4561. (c) Nambu, H.; Hata, K.; Matsugi, M.; Kita, Y. The direct synthesis of thioesters using an intermolecular radical reaction of aldehydes with dipentafluorophenyl disulfide in water. *Chem. Commun.* **2002**, *38*, 1082. (d) Ogawa, K. A.; Boydston, A. J. Organocatalyzed Anodic Oxidation of Aldehydes to Thioesters. *Org. Lett.* **2014**, *16*, 1928. (e) Uno, T.; Inokuma, T.; Takemoto, Y. NHC-catalyzed thioesterification of aldehydes by external redox activation. *Chem. Commun.* **2012**, *48*, 1901. (f) Yi, C.-L.; Huang, Y.-T.; Lee, C.-F. Synthesis of thioesters through copper-catalyzed coupling of aldehydes with thiols in water. *Green Chem.* **2013**, *15*, 2476. (g) Zeng, J.-W.; Liu, Y.-C.; Hsieh, P.-A.; Huang, Y.-T.; Yi, C.-L.; Badsara, S. S.; Lee, C.-F. Metal-free cross-coupling reaction of aldehydes with disulfides by using DTBP as an oxidant under solvent-free conditions. *Green Chem.* **2014**, *16*, 2644. (h) Zhu, X.; Shi, Y.; Mao, H.; Cheng, Y.; Zhu, C. Tetraethylammonium Bromide-Catalyzed Oxidative Thioesterification of Aldehydes and Alcohols. *Adv. Synth. Catal.* **2013**, *355*, 3558.
(7) (a) Burhardt, M. N.; Ahlburg, A.; Skrydstrup, T. Palladium-Catalyzed Thiocarbonylation of Aryl, Vinyl, and Benzyl Bromides. *J. Org. Chem.* **2014**, *79*, 11830. (b) Burhardt, M. N.; Taaning, R. H.; Skrydstrup, T. Pd-Catalyzed Thiocarbonylation with Stoichiometric Carbon Monoxide: Scope and Applications. *Org. Lett.* **2013**, *15*, 948. (c) Cao, H.; McNamee, L.; Alper, H. Palladium-Catalyzed Thiocarbonylation of Iodoarenes with Thiols in Phosphonium Salt Ionic Liquids. *J. Org. Chem.* **2008**, *73*, 3530. (d) Hu, Y.; Liu, J.; Lü, Z.; Luo, X.; Zhang, H.; Lan, Y.; Lei, A. Base-Induced Mechanistic Variation in Palladium-Catalyzed Carbonylation of Aryl Iodides. *J. Am. Chem. Soc.* **2010**, *132*, 3153.
(8) (a) Rong, G.; Mao, J.; Liu, D.; Yan, H.; Zheng, Y.; Chen, J. Formation of C(sp^2)−S bonds through decarboxylation of α-oxocarboxylic acids with disulfides or thiophenols. *RSC Adv.* **2015**, *5*, 26461. (b) Yan, K.; Yang, D.; Wei, W.; Zhao, J.; Shuai, Y.; Tian, L.; Wang, H. Catalyst-free direct decarboxylative coupling of α-keto acids with thiols: a facile access to thioesters. *Org. Biomol. Chem.* **2015**, *13*, 7323.
(9) (a) Iimura, S.; Manabe, K.; Kobayashi, S. Direct thioesterification from carboxylic acids and thiols catalyzed by a Brønsted acid. *Chem. Commun.* **2002**, *38*, 94. (b) Xuan, M.; Lu, C.; Liu, M.; Lin, B.-L. Air-Tolerant Direct Thiol Esterification with Carboxylic Acids Using Hydrosilane via Simple Inorganic Base Catalysis. *J. Org. Chem.* **2019**, *84*, 7694.
(10) (a) El-Azab, A. S.; Abdel-Aziz, A. A. M. An Efficient Synthesis of Thioesters Via TFA-Catalyzed Reaction of Carboxylic Acid and Thiols: Remarkably Facile C−S Bond Formation. *Phosphorus, Sulfur Silicon Relat. Elem* **2012**, *187*, 1046. (b) Imamoto, T.; Kodera, M.; Yokoyama, M. A convenient method for the preparation of thiol esters. *Synthesis* **1982**, *1982*, 134. (c) Iranpoor, N.; Firouzabadi, H.; Khalili, D.; Motevalli, S. Easily Prepared Azopyridines As Potent and Recyclable Reagents for Facile Esterification Reactions. An Efficient Modified Mitsunobu Reaction. *J. Org. Chem.* **2008**, *73*, 4882. (d) Lara, R. G.; Rodrigues, D. C.; Mendes, S. R.; Panatieri, R. B.; Jacob, R. G.; Alves, D.; Lenardão, E. J.; Perin, G. Synthesis of Thiol Esters by the Reaction of Ricinoleic Acid with Thiols Under Solvent-Free Conditions. *Synth. Commun.* **2011**, *41*, 2974. (e) Liu, H.-J.; Sabesan, S. I. Direct transformation of carboxylic acids to thiol esters induced by phenyl dichlorophosphate. *Can. J. Chem.* **1980**, *58*, 2645. (f) Yamada, S.; Yokoyama, Y.; Shioiri, T. New synthesis of thiol esters. *J. Org. Chem.* **1974**, *39*, 3302.
(11) Magens, S.; Plietker, B. Fe-Catalyzed Thioesterification of Carboxylic Esters. *Chem. − Eur. J.* **2011**, *17*, 8807.
(12) Wang, Q.; Liu, L.; Dong, J.; Tian, Z.; Chen, T. Metal-free thioesterification of amides generating acyl thioesters. *New J. Chem.* **2019**, *43*, 9384.
(13) Bruice, T. C. *Organic Sulphur Compounds*; Kharasch, N., Ed.; Pergamon: London, 1961; Vol. *1*, p 421.
(14) (a) Liu, L.; Qian, L.-W.; Wu, S.; Dong, J.; Xu, Q.; Zhou, Y.; Yin, S.-F. Selective Aerobic C−H Amination of Phenols with Primary Amines over Copper toward Benzoxazoles. *Org. Lett.* **2017**, *19*, 2849. (b) Su, L.; Dong, J.; Liu, L.; Sun, M.; Qiu, R.; Zhou, Y.; Yin, S.-F. Copper Catalysis for Selective Heterocoupling of Terminal Alkynes. *J. Am. Chem. Soc.* **2016**, *138*, 12348. (c) Su, L.; Ren, T.; Dong, J.; Liu, L.; Xie, S.; Yuan, L.; Zhou, Y.; Yin, S.-F. Cu(I)-Catalyzed 6-endo-dig Cyclization of Terminal Alkynes, 2-Bromoaryl Ketones, and Amides toward 1-Naphthylamines: Applications and Photophysical Properties. *J. Am. Chem. Soc.* **2019**, *141*, 2535. (d) Su, L.; Sun, K.; Pan, N.; Liu, L.; Sun, M.; Dong, J.; Zhou, Y.; Yin, S.-F. Cyclization of Ketones with Nitriles under Base: A General and Economical Synthesis of Pyrimidines. *Org. Lett.* **2018**, *20*, 3399.
(15) (a) Dong, J.; Liu, L.; Ji, X.; Shang, Q.; Liu, L.; Su, L.; Chen, B.; Kan, R.; Zhou, Y.; Yin, S.-F.; Han, L.-B. General Oxidative Aryl C−P Bond Formation through Palladium-Catalyzed Decarbonylative Coupling of Aroylhydrazides with P(O)H Compounds. *Org. Lett.* **2019**, *21*, 3198. (b) Liu, C.; Yang, F. Palladium/Copper Cocatalyzed Coupling Reaction of Aroyl Hydrazides with Indoles. *Chin. J. Chem.* **2016**, *34*, 1213. (c) Zhang, Y.-G.; Liu, X.-L.; He, Z.-Y.; Li, X.-M.; Kang, H.-J.; Tian, S.-K. Palladium/Copper-Catalyzed Oxidative Arylation of Terminal Alkenes with Aroyl Hydrazides. *Chem. − Eur. J.* **2014**, *20*, 2765.
(16) (a) Amos, R. I. J.; Gourlay, B. S.; Yates, B. F.; Schiesser, C. H.; Lewis, T. W.; Smith, J. A. Mechanistic investigation of the oxidation of hydrazides: implications for the activation of the TB drug isoniazid. *Org. Biomol. Chem.* **2013**, *11*, 170. (b) Braslau, R.; Anderson, M. O.; Rivera, F.; Jimenez, A.; Haddad, T.; Axon, J. R. Acyl hydrazines as precursors to acyl radicals. *Tetrahedron* **2002**, *58*, 5513. (c) Liu, G.; Jin, C.; Wu, G. Cu (II)/TBAI-Catalyzed Esterification of Acid Hydrazides via C (sp^3)−H Oxidative Coupling. *Synlett* **2014**, *25*, 2908. (d) Su, Y.-H.; Wu, Z.; Tian, S.-K. Oxidative alkoxycarbonylation of terminal alkenes with carbazates. *Chem. Commun.* **2013**, *49*, 6528.
(17) (a) Gholivand, K.; Mahzouni, H. R.; Molaei, F.; Kalateh, A. A. A phosphoryl to spiro-bicyclophosphorane transformation via β-amidic proton elimination in phosphorylated hydrazides. *Tetrahedron Lett.* **2012**, *53*, 5944. (b) Periakaruppan, P.; Abraham, R.; Mahendran, K.; Ramanathan, M. Simple synthesis of hydrazones with quorum quenching activity at room temperature in water. *Environ. Chem. Lett.* **2018**, *16*, 1063. (c) Yang, P.; Zhang, C.; Ma, Y.; Zhang, C.; Li, A.; Tang, B.; Zhou, J. S. Nickel-Catalyzed N-Alkylation of Acylhydrazines and Arylamines Using Alcohols and Enantioselective Examples. *Angew. Chem., Int. Ed.* **2017**, *56*, 14702. (d) Zimin, D. P.; Dar'in, D. V.; Rassadin, V. A.; Kukushkin, V. Y. Gold-Catalyzed Hydrohydrazidation of Terminal Alkynes. *Org. Lett.* **2018**, *20*, 4880.
(18) Ma, H.-Y.; Zha, Z.-G.; Zhang, Z.-L.; Meng, L.; Wang, Z.-Y. Electrosynthesis of oxadiazoles from benzoylhydrazines. *Chin. Chem. Lett.* **2013**, *24*, 780.

https://dx.doi.org/10.1021/acs.joc.0c02328
J. Org. Chem. XXXX, XXX, XXX−XXX

(19) (a) He, C.; Qian, X.; Sun, P. Syntheses of thiol and selenol esters by oxidative coupling reaction of aldehydes with RYYR (Y = S, Se) under metal-free conditions. *Org. Biomol. Chem.* **2014**, *12*, 6072. (b) Movassagh, B.; Lakouraj, M. M.; Fadaei, Z. A convenient one-pot synthesis of thiol esters from disulfides using a $Zn/AlCl_3$ system. *J. Chem. Res.* **2001**, *2001*, 22. (c) Singh, S.; Yadav, L. D. S. The direct thioesterification of aldehydes with disulfides via NHC-catalyzed carbonyl umpolung strategy. *Tetrahedron Lett.* **2012**, *53*, 5136. (d) Singh, S.; Yadav, L. D. S. Unprecedented dithiolation of enals via their NHC-catalysed umpolung reaction with organic disulfides. *Org. Biomol. Chem.* **2012**, *10*, 3932. (e) Zhang, S.; Qian, P.; Zhang, M.; Hu, M.; Cheng, J. Copper-Catalyzed Thiolation of the Di- or Trimethoxybenzene Arene C−H Bond with Disulfides. *J. Org. Chem.* **2010**, *75*, 6732.

(20) Liu, C.; Szostak, M. Decarbonylative thioetherification by nickel catalysis using air- and moisture-stable nickel precatalysts. *Chem. Commun.* **2018**, *54*, 2130.

(21) (a) Gao, Y.; Lu, W.; Liu, P.; Sun, P. Iron-Catalyzed Regioselective Alkoxycarbonylation of Imidazoheterocycles with Carbazates. *J. Org. Chem.* **2016**, *81*, 2482. (b) Taniguchi, T.; Sugiura, Y.; Zaimoku, H.; Ishibashi, H. Iron-Catalyzed Oxidative Addition of Alkoxycarbonyl Radicals to Alkenes with Carbazates and Air. *Angew. Chem., Int. Ed.* **2010**, *49*, 10154. (c) Wang, G.; Chen, S.-Y.; Yu, X.-Q. Synthesis of 6-carboxylated phenanthridines by oxidative alkoxycarbonylation−cyclization of 2-isocyanobiphenyls with carbazates. *Tetrahedron Lett.* **2014**, *55*, 5338.

(22) (a) Li, X.; Fang, M.; Hu, P.; Hong, G.; Tang, Y.; Xu, X. Tetrabutylammonium Iodide-Catalyzed Radical Alkoxycarbonylation of 2-Isocyanobiphenyls with Carbazates: Synthesis of Phenanthridine-6-carboxylates. *Adv. Synth. Catal.* **2014**, *356*, 2103. (b) Xu, X.; Tang, Y.; Li, X.; Hong, G.; Fang, M.; Du, X. Iron-Catalyzed Arylalkoxycarbonylation of N-Aryl Acrylamides with Carbazates. *J. Org. Chem.* **2014**, *79*, 446.

(23) (a) Teng, F.; Yu, J.-T.; Yang, H.; Jiang, Y.; Cheng, J. Copper-catalyzed cyanation of disulfides by azobisisobutyronitrile leading to thiocyanates. *Chem. Commun.* **2014**, *50*, 12139. (b) Xiao, F.; Chen, S.; Li, C.; Huang, H.; Deng, G.-J. Copper-Catalyzed Three-Component One-Pot Synthesis of Aryl Sulfides with Sulfur Powder under Aqueous Conditions. *Adv. Synth. Catal.* **2016**, *358*, 3881.

(24) (a) Tahir, N.; Wang, G.; Onyshchenko, I.; De Geyter, N.; Leus, K.; Morent, R.; Van Der Voort, P. High-nitrogen containing covalent triazine frameworks as basic catalytic support for the Cu-catalyzed Henry reaction. *J. Catal.* **2019**, *375*, 242. (b) Koo, B. K. Synthesis, Crystal Structure, and Characterization of Copper(II) Acetate Complex. *Bull. Korean Chem. Soc.* **2001**, *22*, 113.

(25) Gopinath, P.; Vidyarini, R. S.; Chandrasekaran, S. Synthesis of Thioesters by Simultaneous Activation of Carboxylic Acids and Alcohols Using PPh_3/NBS with Benzyltriethylammonium Tetrathiomolybdate as the Sulfur Transfer Reagent. *Eur. J. Org. Chem.* **2009**, *2009*, 6043.

(26) Liao, Y. S.; Liang, C. F. One-pot synthesis of thioesters with sodium thiosulfate as a sulfur surrogate under transition metal-free conditions. *Org. Biomol. Chem.* **2018**, *16*, 1871.

(27) Zheng, X.; Fu, W.-Q.; Xiong, J.; Xi, J.-C.; Ni, X.-J.; Tang, T.-D. Zeolite Beta nanoparticles assembled Cu catalysts with superior catalytic performances in the synthesis of thioesters by cross-coupling of aldehydes and disulfides. *Catal. Today* **2016**, *264*, 152.

(28) Roy, H. N.; Sarker, A. K.; Al Mamun, A. H. Rapid and Regiospecific Phenylthiolation of Some Organic Acids Catalyzed by $AlCl_3$ in the Presence of Excess Anhydrous $ZnCl_2$. *Synth. Commun.* **2010**, *40*, 2158.

(29) Ochiai, H.; Uetake, Y.; Niwa, T.; Hosoya, T. Rhodium-Catalyzed Decarbonylative Borylation of Aromatic Thioesters for Facile Diversification of Aromatic Carboxylic Acids. *Angew. Chem., Int. Ed.* **2017**, *56*, 2482.

(30) Movassagh, B.; Soleiman-Beigi, M. Convenient route to thiocarbonates from alcohols, thiols, and triphosgene. *Synth. Commun.* **2010**, *40*, 3467.

(31) Barbero, M.; Cadamuro, S.; Dughera, S.; Venturello, P. o-Benzenedisulfonimide as a Soft, Efficient, and Recyclable Catalyst for the Acylation of Alcohols, Phenols, and Thiols under Solvent-Free Conditions: Advantages and Limitations. *Synthesis* **2008**, *2008*, 3625.

(32) Scattolin, T.; Senol, E.; Yin, G.; Guo, Q.; Schoenebeck, F. Site-Selective C-S Bond Formation at C-Br over C-OTf and C-Cl Enabled by an Air-Stable, Easily Recoverable, and Recyclable Palladium (I) Catalyst. *Angew. Chem., Int. Ed.* **2018**, *57*, 12425.

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