

# Copper-Catalyzed Cross-Coupling of Thiols, Alcohols, and Oxygen for the Synthesis of Esters

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**Keywords:** Synthetic methods / Oxidation / Desulfurization / Thiols / Esters / Copper

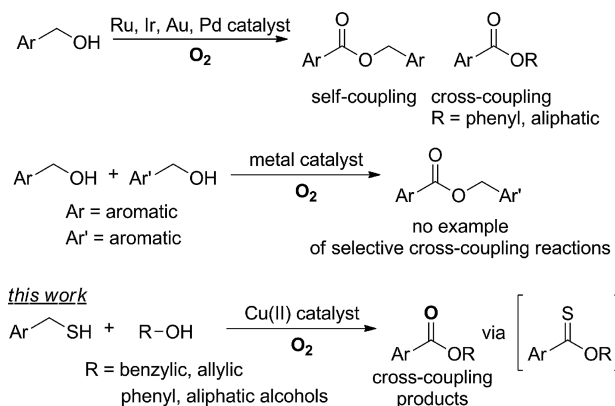
Copper-catalyzed, one-pot, three-component coupling reactions using thiols, alcohols, and oxygen to form a variety of esters in good yields were studied. In the presence of easily oxidized benzylic and allylic alcohols, thiols were selectively

oxidized to form thionoesters, which underwent facile S/O exchange to afford esters. Thiols may be used as an alternative benzoyl source under mild aerobic conditions.

## Introduction

Esters are one of the most important organic functional groups, and there are many synthetic methods to convert carboxylic acids, aldehydes, and alcohols into esters.<sup>[1]</sup> In an effort to synthesize esters efficiently and economically, direct alcohol into ester conversion approaches have been developed by using transition-metal catalysis,<sup>[2,3]</sup> transition-metal-mediated oxidation,<sup>[4]</sup> and transition-metal-free reactions.<sup>[5]</sup> Transition-metal-catalyzed aerobic one-pot esterification of alcohols that use ruthenium, iridium, palladium, and gold complexes have also been studied.<sup>[2]</sup> These reactions only require small amounts of chemicals and are therefore considered green chemical processes. Considering the cost of the currently used catalysts (ruthenium, iridium, palladium, and gold complexes), more economical catalysts should be employed, for example, copper complexes. Although copper catalysts and oxygen have been widely utilized in various oxidative coupling reactions, to our knowledge, they have not been used in the aerobic one-pot oxidation/oxidative esterification of alcohols.<sup>[6,7]</sup>

In addition to examining inexpensive metal sources for these one-pot ester-forming processes, the control of homo-coupling and cross-coupling of alcohols is an important issue in ester synthesis. A synthetically useful cross-esterification of activated alcohols (benzylic and allylic alcohols) and less reactive or nonreactive alcohols (methanol, aliphatic alcohol, and phenol derivatives) under oxidation conditions was carried out successfully;<sup>[2]</sup> however, selective cross-esterification of activated alcohols such as benzylic alcohols or allylic alcohols was not possible (Scheme 1).



Scheme 1. Metal-catalyzed synthesis of esters.

Recently, we have reported a copper-catalyzed oxidative coupling of thiols and amines to produce thioamides.<sup>[8]</sup> Although sulfur and oxygen atoms belong to the same group in the periodic table, the reactivity of thiols is not analogous to that of alcohols.<sup>[9]</sup> This fact can be used to identify the more susceptible species between thiols and alcohols under oxidation conditions. To test this hypothesis, we carried out a cross-coupling of thiols and alcohols. In this study, we developed the first copper-catalyzed, three-component cross-coupling of thiols, alcohols, and oxygen to form a range of esters, whereby benzyl thiols were selectively oxidized in the presence of activated alcohols (Scheme 1). Under copper-catalyzed aerobic oxidation conditions, an oxygen atom from an oxygen gas molecule participated in the ester synthesis.<sup>[10]</sup>

## Results and Discussion

The optimization results are given in Table 1. Benzyl mercaptan **1a** (2 equiv.) and cinnamyl alcohol **1b** (1 equiv.) were subjected to aerobic oxidation conditions. In the pres-

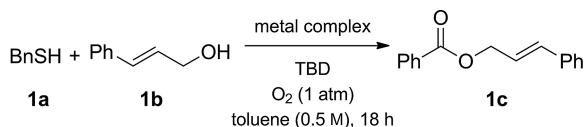
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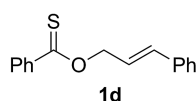
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ence of  $\text{CuCl}_2$  (2 mol-%), a solution of **1a**, **1b**, and 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD, 1 equiv.) in toluene (0.5 M) was stirred at 100 °C under one atmosphere of oxygen, to afford ester **1c** in 32% yield (entry 1). Initially, it was expected to form thionoester **1d**; however, it was found that the sulfur atom was displaced by an oxygen atom (see below). Although both starting materials were consumed in 2 h at 100 °C, the yield of **1c** was not high. At a lower temperature (50 °C), the yield of **1c** increased to 63% (entry 2). When the amount of TBD was increased to 1.5 equiv., a slightly higher yield was obtained (78%, entry 3). We also screened several copper and iron complexes.  $\text{Cu}^{\text{II}}$  complexes,  $\text{CuBr}_2$ ,  $\text{Cu}(\text{OTf})_2$ , and  $\text{Cu}(\text{OAc})_2$  catalyzed the ester formation to afford **1c** in 77, 57, and 79% yield, respectively (entries 4–6).  $\text{Cu}^{\text{I}}$  complexes,  $\text{CuCl}$ ,  $\text{CuI}$ , and  $\text{CuOAc}$  catalyzed the reaction to form **1c** in 79, 78, and 69% yield, respectively (entries 7–9).  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  was also checked for this oxidative coupling reaction; however, a lower yield (41%) compared with those from copper-catalyzed reactions was found (entry 10). In the absence of metal complexes, **1c** was formed in much lower yield (21%; entry 11). Finally, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) was tested instead of TBD, which led to the formation of **1c** in 11% yield (entry 12).

Table 1. Optimization of the formation of ester **1c**.

Entry	Metal complex	TBD (equiv.)	T (°C)	Yield
1	$\text{CuCl}_2$ (2 mol-%)	TBD (1 equiv.)	100	32% <sup>[a]</sup>
2	$\text{CuCl}_2$ (2 mol-%)	TBD (1 equiv.)	50	63%
3	$\text{CuCl}_2$ (2 mol-%)	TBD (1.5 equiv.)	50	78%
4	$\text{CuBr}_2$ (2 mol-%)	TBD (1.5 equiv.)	50	77%
5	$\text{Cu}(\text{OTf})_2$ (2 mol-%)	TBD (1.5 equiv.)	50	57%
6	$\text{Cu}(\text{OAc})_2$ (2 mol-%)	TBD (1.5 equiv.)	50	79%
7	$\text{CuCl}$ (2 mol-%)	TBD (1.5 equiv.)	50	79%
8	$\text{CuI}$ (2 mol-%)	TBD (1.5 equiv.)	50	78%
9	$\text{CuOAc}$ (2 mol-%)	TBD (1.5 equiv.)	50	69%
10	$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (2 mol-%)	TBD (1.5 equiv.)	50	41%
11	–	TBD (1.5 equiv.)	50	21%
12	$\text{CuCl}_2$ (2 mol-%)	DBU (1.5 equiv.)	50	11%

[a] 2 h



To investigate the substrate scope of the reaction, a diverse range of thiols and alcohols were subjected to the aerobic oxidation conditions involving  $\text{CuCl}_2$  (2 mol-%) and TBD (1.5 equiv.) (Tables 2 and 3). In Table 2, the results of the reaction with benzyl mercaptan derivatives and furyl mercaptan with cinnamyl alcohol are shown. Electron-rich *tert*-butyl-substituted benzyl mercaptan was treated with cinnamyl alcohol to form **2c** in 66% yield (entry 1). Electron-deficient fluoro- and chloro-substituted benzyl mer-

captans were treated with cinnamyl alcohol to form the corresponding esters **3c** and **4c** in 69 and 65% yield, respectively (entries 2 and 3). The coupling of furyl mercaptan and cinnamyl alcohol formed the desired ester **5c**, albeit in low yield (entry 4).

Table 2. Examples of esters formed from substituted mercaptans and cinnamyl alcohol.

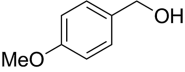
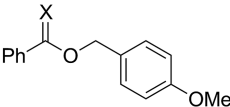
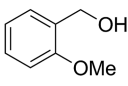
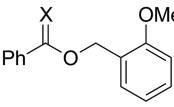
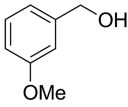
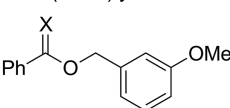
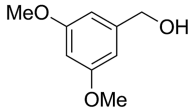
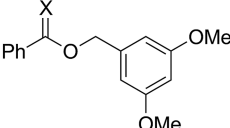
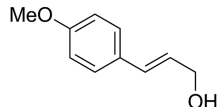
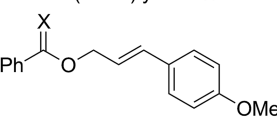
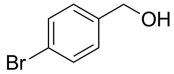
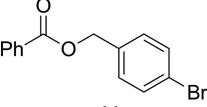
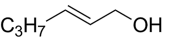
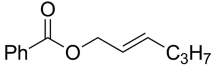
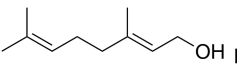
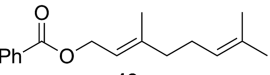
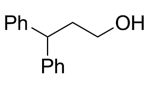
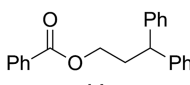
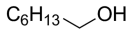
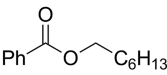
Entry	Reactants	Products
1		 yield 66% <sup>[a]</sup>
2		 yield 69% <sup>[a]</sup>
3		 yield 65% <sup>[b]</sup>
4		 yield 37% <sup>[b]</sup>

[a] Reaction performed at 50 °C. [b] Reaction performed at room temp.

A variety of alcohols were then treated with benzyl mercaptan (Table 3). Interestingly, electron-rich methoxy-substituted benzyl and cinnamyl alcohols reacted with benzyl mercaptan to form esters in better yields at room temperature than at 50 °C, along with the isolation of thionoesters (entries 1–5). Benzyl alcohols substituted with *p*-, *o*-, and *m*-methoxy groups underwent esterification with benzyl mercaptan to form the desired esters/thionoesters in 68/7% (**6c/6d**), 61/9% (**7c/7d**), and 62/11% (**8c/8d**) yield, respectively (entries 1–3). The position of the methoxy substituent did not affect the yield or the ratio of esters and thionoesters. Benzyl alcohol possessing two methoxy groups was also used to form **9c** (60% yield) and **9d** (7% yield) (entry 4). In addition to benzyl alcohol derivatives, methoxy-substituted cinnamyl alcohol was submitted to the reaction conditions, to afford **10c** (65%) and **10d** (5%) (entry 5). In the case of the reaction of cinnamyl alcohols, thionoester **1d** was not formed even at room temperature. The reaction of electron-rich alcohols led to the formation of a small amount of thionoesters **6d**–**10d**, which presumably served as the intermediates for conversion into the major product, esters. Electron-deficient benzyl alcohols were tested. *p*-Bromobenzyl alcohol was subjected to the reaction conditions to provide **11c** in 58% yield (entry 6). *p*-Nitrobenzyl

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Table 3. Examples of esters formed from benzyl mercaptan and various alcohols.

Entry	Reactants	Products
1	BnSH 	 <b>6c</b> (X = O) yield 68% <sup>[b]</sup> <b>6d</b> (X = S) yield 7% <sup>[b]</sup>
2	BnSH 	 <b>7c</b> (X = O) yield 61% <sup>[b]</sup> <b>7d</b> (X = S) yield 9% <sup>[b]</sup>
3	BnSH 	 <b>8c</b> (X = O) yield 62% <sup>[b]</sup> <b>8d</b> (X = S) yield 11% <sup>[b]</sup>
4	BnSH 	 <b>9c</b> (X = O) yield 60% <sup>[b]</sup> <b>9d</b> (X = S) yield 7% <sup>[b]</sup>
5	BnSH 	 <b>10c</b> (X = O) yield 65% <sup>[b]</sup> <b>10d</b> (X = S) yield 5% <sup>[b]</sup>
6	BnSH 	 <b>11c</b> yield 58% <sup>[a]</sup>
7	BnSH 	 <b>12c</b> yield 70% <sup>[a]</sup>
8	BnSH 	 <b>13c</b> yield 66% <sup>[a]</sup>
9	BnSH 	 <b>14c</b> yield 74% <sup>[a]</sup>
10	BnSH 	 <b>15c</b> yield 56% <sup>[c]</sup>

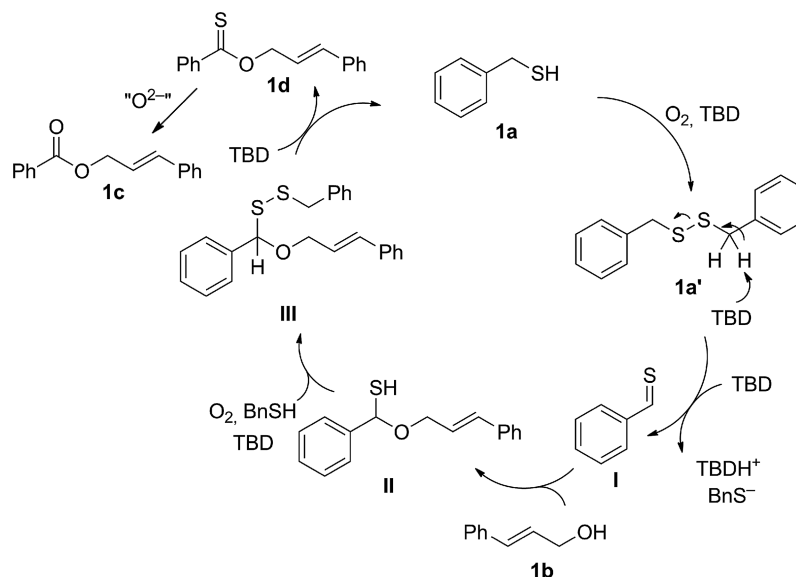
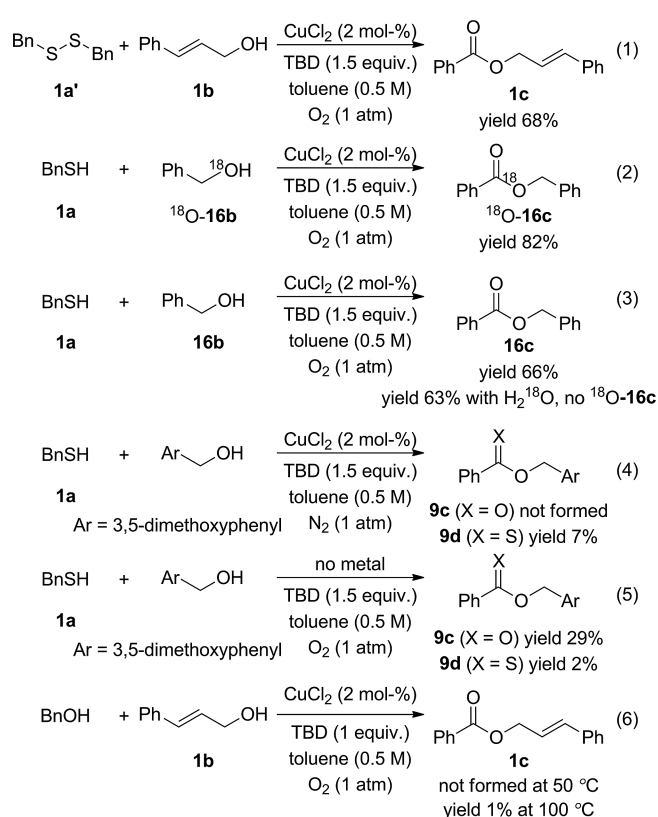
[a] Reaction performed at 50 °C. [b] Reaction performed at room temp. [c] Reaction performed at 100 °C.

alcohol did not form the oxidative coupling product under our reaction conditions. Hexenol and geraniol were converted into the corresponding products **12c** and **13c** in 70 and 66% yield, respectively (entries 7 and 8). Additionally, aliphatic alcohols reacted to form esters **14c** (74% yield) and **15c** (56% yield) (entries 9 and 10).

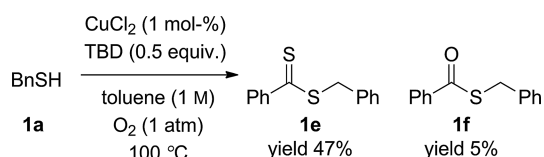
We propose a possible reaction mechanism, which is shown in Scheme 2. Thiol **1a** is converted into disulfide **1a'** under oxidation conditions.<sup>[11]</sup> In Scheme 3, Equation (1), the reaction of **1a'** with **1b** to provide **1c** in 68% yield is shown; this is comparable to the yield obtained from **1a**. This result confirms that disulfide can be a key intermediate of this transformation. Thiobenzaldehyde **I** is assumed to be formed through the reaction of disulfide **1a'** with TBD.<sup>[8,12]</sup> Thiobenzaldehyde **I** reacts with cinnamyl alcohol **1b** to afford thioacetal **II**. Similar to the formation of **I**, thioacetal **II** undergoes disulfide formation and deprotonation to generate thionoesters, which were isolated in the reactions of methoxy-substituted benzyl alcohols. To account for the formation of an ester as the major product, we conducted a number of control experiments, see Scheme 3 and Equations (2)–(5). To determine the oxygen source in the S/O exchange, independently prepared <sup>18</sup>O-labeled benzyl alcohol **16b** was submitted to the reaction conditions to form ester **16c** having a single <sup>18</sup>O atom, see Equation (2). Upon the addition of <sup>18</sup>O-labeled water, no <sup>18</sup>O-incorporated **16c** was observed by mass spectrometry, see Equation (3), implying that the formation of **1c** is not induced by simple water hydrolysis of **1d**. The reactions of benzyl mercaptan **1a** and dimethoxy substituted benzyl alcohol were then performed independently in the absence of either O<sub>2</sub> or copper catalysts, see Equations (4) and (5). In the absence of O<sub>2</sub>, ester **9c** was not formed and thionoester **9d** was formed in 7% yield, see Equation (4). In the absence of copper catalysts, both ester **9c** and thionoester **9d** were formed, albeit in low yields, see Equation (5). Because esters were formed in the absence of copper catalysts with low yields, the copper complex is presumed to accelerate the oxidation of **1a** and **II**.

Recent reports on copper-catalyzed aerobic desulfurization involving the conversion of thiocarbonyl into carbonyl compounds have proposed that the reduced oxygen species O<sub>2</sub><sup>•−</sup> was an active species.<sup>[13]</sup> Similarly, reduced oxygen species generated during the formation of disulfides **1a'** or **III**, might induce the desulfurization of **1d** to afford **1c**. Finally, to compare the reactivity of alcohols with thiols under our reaction conditions, we tested ester formation by using benzyl alcohol instead of thiols; unfortunately, the ester was formed in very low yield at 100 °C and was not formed at all at 50 °C, see Equation (6).

During the reaction, the oxidative dimerization of benzyl mercaptan occurred as a side reaction to form dithioester **1e** and thioester **1f**. In the absence of alcohols, **1a** was converted into dithioester **1e** in 47% yield and **1f** in 5% yield (Scheme 4). Dithioester **1e** was formed from the reaction of thioaldehyde **I** with **1a**, and thioester **1f** was transformed from **1e** by the same mechanism forming ester **1c** from **1d** (Scheme 2). Compared with thionoesters, dithioesters ap-

Scheme 2. Plausible reaction mechanism for the formation of ester **1c**.

Scheme 3. Control experiments.



Scheme 4. Oxidative dimerization of benzyl mercaptan.

pear to be less susceptible to aerobic desulfurization and they form thioester **1f** as the minor product.

## Conclusions

We have reported an efficient copper-catalyzed oxidation for the one-pot cross-coupling of thiols, alcohols, and oxygen. Under our reaction conditions, the reactivity of benzyl thiols was significantly higher than that of allylic and benzylic alcohols, which allowed the selective oxidation of benzyl thiols in the presence of alcohols. In this reaction, the oxygen molecule functions as both a mild oxidant and a reactant to form esters. A possible mechanism for the formation of esters was investigated by conducting several control experiments including  $^{18}\text{O}$ -labeling studies. The cross-coupling of thiols and alcohols first provides thionoester intermediates, which undergo the S-to-O exchange by oxygen to form various esters.

## Experimental Section

**General Procedure for the Reaction:** Copper(II) chloride (1.3 mg, 0.01 mmol) and 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD, 105 mg, 0.75 mmol) were added to a solution of benzyl mercaptan (124.2 mg, 1.0 mmol) and cinnamyl alcohol (67 mg, 0.5 mmol) in toluene (0.5 M, 1 mL). A slow stream of  $\text{O}_2$  was passed through this solution for 10 min. The reaction mixture was then stirred at 50 °C for 18 h under an  $\text{O}_2$  atmosphere. The solvent was removed under vacuum, and the residue was purified by flash silica gel column chromatography (ether/hexane, 1%) to obtain cinnamyl benzoate **1c** (92.4 mg, 78%). In a larger scale reaction, the yield of **1c** was 63, 63, and 46%, respectively, using 1.0, 1.5, and 2.0 mmol of cinnamyl alcohol.

## Acknowledgments

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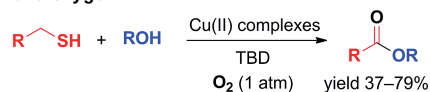
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## Synthetic Methods

Copper-catalyzed coupling of thiols, alcohols, and oxygen provided a variety of esters through S/O exchange of thionoester intermediates

**Copper-catalyzed coupling of thiols, alcohols, and oxygen**



S. Lim, M. Ji, X. Wang, C. Lee,  
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Copper-Catalyzed Cross-Coupling of Thiols, Alcohols, and Oxygen for the Synthesis of Esters 

**Keywords:** Synthetic methods / Oxidation / Desulfurization / Thiols / Esters / Copper