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Copper-Catalyzed, Stereoselective Bis-trifluoromethylthiolation of Propiolic Acid Derivatives with $AgSCF_3$

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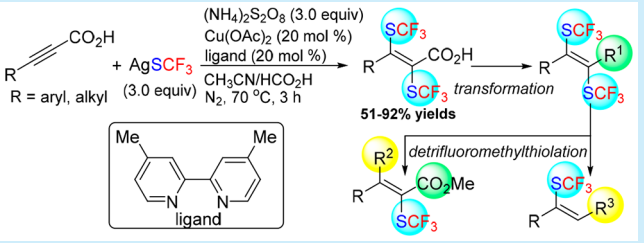
Supporting Information

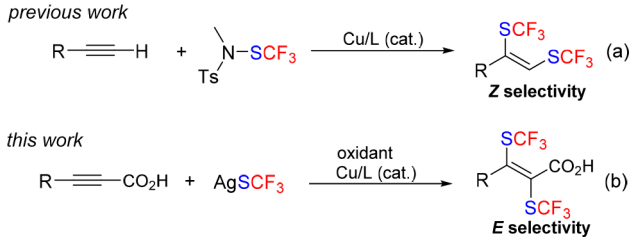
ABSTRACT: A copper-catalyzed chemo- and stereoselective oxidative bis-trifluoromethylthiolation of propiolic acid derivatives was achieved by using carboxylic acid as the activating group and formic acid as a cosolvent. The reaction of propiolic acid derivatives and $AgSCF_3$ in the presence of $(NH_4)_2S_2O_8$ and catalytic $Cu(OAc)_2$ in $MeCN/HCO_2H$ afforded bis-trifluoromethylthiolated acrylic acids in moderate to excellent yields with *E* selectivity. Further derivatization of the resultant products gave a series of polysubstituted SCF_3-containing alkenes.



The vicinal difunctionalization of alkenes and alkynes is a type of fundamentally important transformation and thus has been applied in different research areas.[1] Recently, the difunctionalization strategy has been widely applied in the preparation of fluorinated compounds[2] because of their increasing importance in various fields.[3] Although the simultaneous introduction of a F,[4] CF_3,[5] or SCF_3[6] with another functional group into alkenes and alkynes has made great progress, the vicinal difluorination and bis-trifluoromethyl(thiol)ation are quite limited.

In 2016, Jacobsen and Gilmour reported catalytic difluorination of alkenes with a nucleophilic fluoride source by I(I)/I(III) catalysis, respectively.[7] The bis-trifluoromethylation of alkenes was recently developed by our group using CF_3SO_2Na in the presence of *t*-BuOOH/CuCl.[8] In the case of bis-trifluoromethylthiolation, Tlili and Billard very recently disclosed a novel bis-trifluoromethylthiolation of electron-deficient or heteroatom-containing terminal alkynes with electrophilic $TsNMeSCF_3$ to give the bis-trifluoromethylthiolated alkenes with *Z* selectivity (Scheme 1a).[9] However, this method suffers from the narrow substrate scope and low yields.

Scheme 1. Bis-trifluoromethylthiolation of Alkynes



Herein, we describe an efficient and practical copper-catalyzed stereoselective oxidative bis-trifluoromethylthiolation of internal alkynes with nucleophilic $AgSCF_3$ using carboxylic acid as the activating group to form the bis-trifluoromethylthiolated products in high yields with *E* selectivity (Scheme 1b).

As an extension of our radical bis-trifluoromethylation of alkenes,[8] we became interested in the analogous bis-trifluoromethylthiolation reactions. According to our experiences and other works,[10] the readily available and stable $AgSCF_3$ is an ideal SCF_3 radical source. Thus, we initially investigated the bis-trifluoromethylthiolation of styrene or ethynylbenzene with $AgSCF_3$ in the presence of catalytic $Cu(OAc)_2$ and persulfates. No bis-trifluoromethylthiolated product was detected from the reaction of styrene. The bis-trifluoromethylthiolation of ethynylbenzene (**1a**) took place to give the bis-trifluoromethylthiolated product (**3a**) in 18% yield along with the formation of trifluoromethylthiolated alkyne **2** (Scheme 2) after screening of additives, oxidants, and solvents (see Table S1 in the Supporting Information (SI)), and it was also found that the use of HCO_2H as a cosolvent was crucial for bis-trifluoromethylthiolation reaction.

On the basis of this primary result, we next decided to introduce an activating group to the alkyne to improve the yield and chemoselectivity of bis-trifluoromethylthiolation reaction. We anticipated that the activating group would activate the alkyne to give higher yield and coordinate with the copper salt to form the bis-trifluoromethylthiolated product selectively. A series of activating groups, including ketone, ester, ether, carboxylic acid, and amide, were then investigated (Table 1).

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Scheme 2. Strategy of Introducing an Activating Group

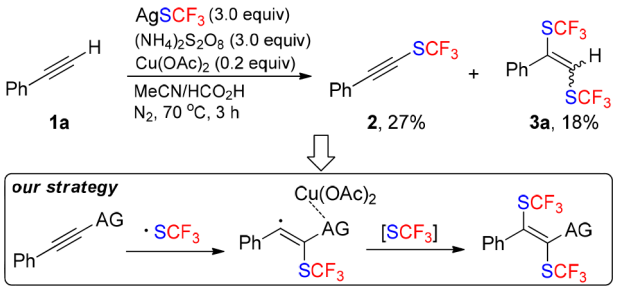
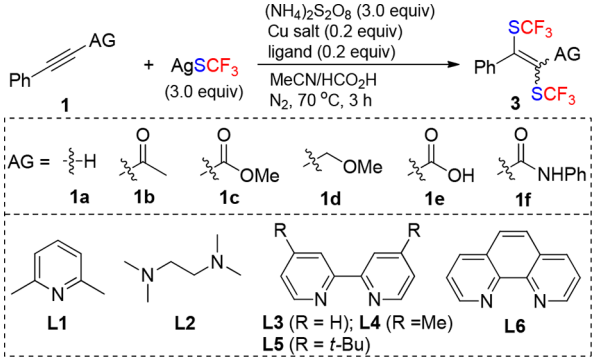


Table 1. Optimization of Reaction Conditions[a]



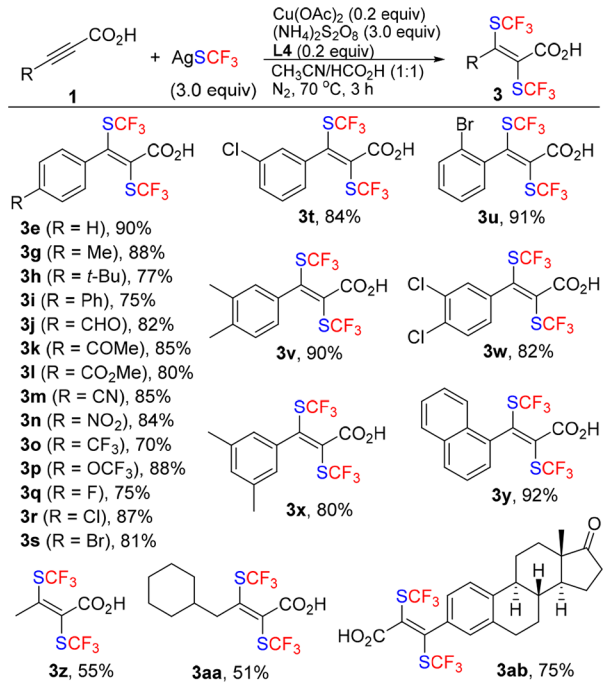
entry	1	Cu salt	ligand	yield[b] (%)	E/Z[b] (%)
1	**1a**	$Cu(OAc)_2$		18	9:1
2	**1b**	$Cu(OAc)_2$		trace	
3	**1c**	$Cu(OAc)_2$		trace	
4	**1d**	$Cu(OAc)_2$		15	9:1
5	**1e**	$Cu(OAc)_2$		63	9:1
6	**1f**	$Cu(OAc)_2$		20	9:1
7	**1e**	$CuCl_2$		54	9:1
8	**1e**	CuI		49	9:1
9	**1e**	CuCN		32	9:1
10	**1e**	$Cu(OAc)_2$	**L1**	85	>99:1
11	**1e**	$Cu(OAc)_2$	**L2**	79	>99:1
12	**1e**	$Cu(OAc)_2$	**L3**	72	>99:1
13	**1e**	$Cu(OAc)_2$	**L4**	96	>99:1
14	**1e**	$Cu(OAc)_2$	**L5**	60	>99:1
15	**1e**	$Cu(OAc)_2$	**L6**	74	>99:1

[a]Reaction conditions: **1** (0.1 mmol), $AgSCF_3$ (0.3 mmol), Cu salt (0.02 mmol), $(NH_4)_2S_2O_8$ (0.3 mmol), ligand (0.02 mmol), MeCN/HCO_2H (1.5 mL/1.5 mL), under air, 70 °C, 3 h. [b]Yields and stereoselectivities determined by ^{19}F NMR spectroscopy using trifluoromethybenzene as an internal standard.

The ketone and ester derivatives (**1b** and **1c**) were transformed into other CF_3S-containing products, but not the desired products (entries 2 and 3). The bis-trifluoromethylthiolation of alkynes **1d** and **1f** afforded the desired products in low yields (entries 4 and 6). Interestingly, the acid derivative (**1e**) gave the bis-trifluoromethylthiolated product **3e** in 63% yield (entry 5). The employment of carboxylic acid as a activating group has been well studied in C−H bond functionalization reactions.[11] Herein, the carboxylic acid was a powerful activating group for difunctionalization reactions. To improve the yield of compound **3e** further, copper salts and ligands were examined. Switching $Cu(OAc)_2$ into other Cu salts including $CuCl_2$, CuI, and CuCN led to lower yields (entries 7−9). In general, the addition of catalytic monodentate or bidentate ligand was beneficial for yield and stereoselectivity (entries 10−15). Among the ligands (**L1**−**L6**) tested, 4,4′-dimethyl-2,2′-bipyridine (**L4**) afforded **3e** in highest yield (96%) with excellent stereoselectivity (E/Z > 99:1) (entry 13). Moreover, when the reaction was carried out in the presence of other oxidants such as $PhI(OAc)_2$ and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), none of the desired product **3e** was detected. It was noteworthy that product **3e** was confirmed as the *trans*-addition product by the X-ray crystallographic analysis (see the SI), which is in contrast to Tlili and Billard's work on the *cis*-bis-trifluoromethylthiolation of alkynes.[9]

The scope of the bis-trifluoromethylthiolation of propiolic acid derivatives is shown in Scheme 3. The aromatic propiolic

Scheme 3. Bis-trifluoromethylthiolation of Propiolic Acid Derivatives[a]



[a]Reaction conditions: **1** (0.2 mmol), $AgSCF_3$ (0.6 mmol), $Cu(OAc)_2$ (0.04 mmol), $(NH_4)_2S_2O_8$ (0.6 mmol), **L4** (0.04 mmol), MeCN/HCO_2H (3.0 mL/3.0 mL), under N_2, 70 °C, 3 h, isolated yields.

acids were transformed into the bis-trifluoromethylthiolated acrylic acids in good to excellent yields. Substrates bearing electron-donating (**1g**−**i**) and electron-withdrawing (**1j**−**p**) groups as well as halides (**1q**−**s**) were all effective. The position and number of substitutions (**1t**−**y**) did not interfere with this transformation. In the cases of aliphatic propiolic acids (**1z** and **1aa**), the desired products (**3z** and **3aa**) were obtained in moderate yields. Notably, this protocol could also be applied for complex molecules such as estrone derivative (**1ab**) to give the bis-trifluoromethylthiolated product (**3ab**) in good yield.

Compounds that contain a bis-SCF_3-substituted acrylic acid moiety are useful precursors for the preparation of SCF_3-containing compounds. As shown in Scheme 4, the decarboxylation of compound **3y** in CH_3CN at 90 °C proceeded smoothly to afford **4y** in high yield. Moreover, **3y** was subjected to several standard transformations to give bis-trifluoromethylthiolated α,β-unsaturated ester (**5**), amide (**6**), aldehyde (**8**), and ketone (**9**) and as well as allylic alcohol (**7**). The trifluoromethylthio group was proven to be a good leaving

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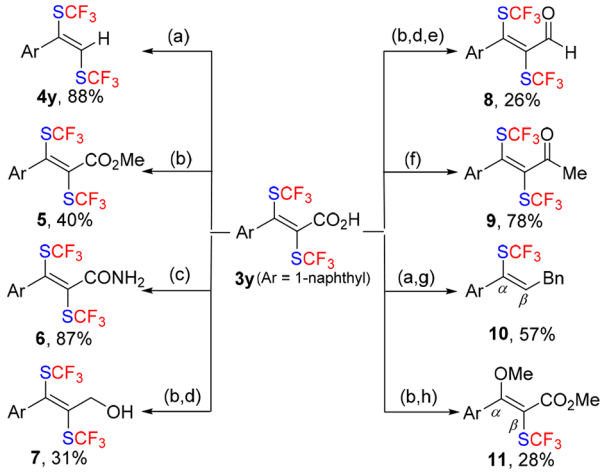
Scheme 4. Transformation of Compound 3y[a]

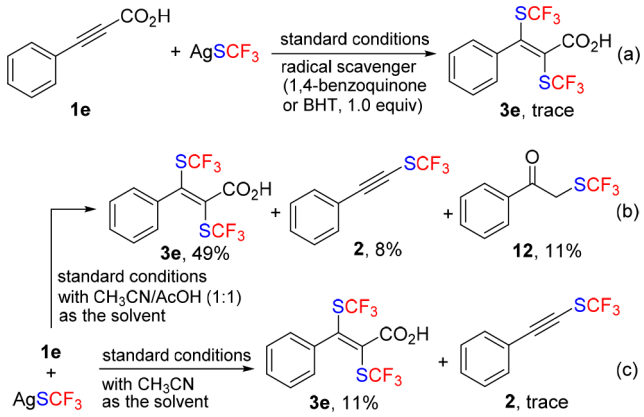


[a]Reaction conditions: (a) CH_3CN, 90 °C, 2 h; (b) H_2SO_4, MeOH, 100 °C, 24 h; (c) $SOCl_2$, rt, 4 h; then NH_3/H_2O, 0 °C to rt, 30 min; (d) DIBAL-H, CH_2Cl_2, −78 °C, 3 h; (e) MnO_2, CH_2Cl_2, reflux, 24 h; (f) $SOCl_2$, rt, 4 h; then $AlMe_3$, CH_2Cl_2; (g) BnMgCl, THF, 0 °C, 2 h; (h) NaOMe, THF, 0 °C, 2 h.

group when bis-trifluoromethylthiolated alkene was subjected to nucleophiles. For example, treatment of compound **4y** with BnMgCl gave α-CF_3S-substituted naphthyl alkene (**10**). On the other hand, the substitution of compound **5** by NaOMe afforded β-CF_3S-substituted naphthyl alkene (**11**). These unique detrifluoromethylthiolation reactions probably proceed through a nucleophilic addition followed by the elimination of trifluoromethanethiolate.

To gain mechanistic insights into this reaction process, some preliminary studies were conducted. Only a trace of the desired product was detected when a radical scavenger, 1,4-benzoquinone or 2,6-di-*tert*-butyl-4-methylphenol (BHT), was added to the reaction mixture (Scheme 5a), which indicated

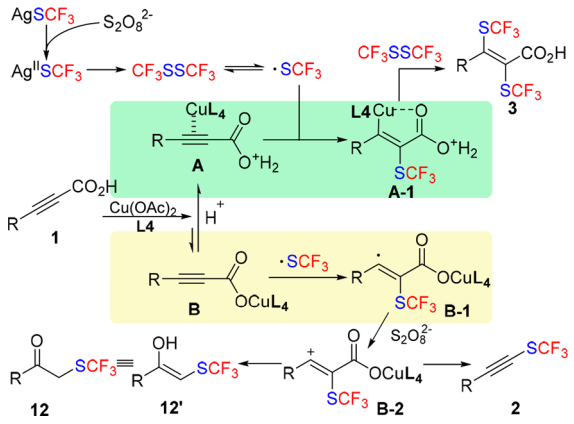
Scheme 5. Preliminary Mechanistic Studies



this transformation probably proceeded through a radical pathway. Moreover, the reaction in MeCN/AcOH gave **3e** in 49% yield along with the decarboxylation products, trifluoromethylthiolated alkyne (**2**) and α-trifluoromethylthiolated ketone (**12**), in low yields (Scheme 5b).[12] Compound **3e** was formed in only 11% yield when the reaction was performed in MeCN (Scheme 5c). These results revealed the importance of HCO_2H in this reaction.

On the basis of the above results, a plausible reaction mechanism was proposed (Scheme 6). First, oxidation of

Scheme 6. Proposed Reaction Mechanism



$AgSCF_3$ by $(NH_4)_2S_2O_8$ generates $Ag^{II}SCF_3$, which could be further transformed to CF_3S radical or CF_3SSCF_3.[10] In fact, we could detect the formation of CF_3SSCF_3 in the reaction mixture by ^{19}F NMR spectroscopy. On the other hand, substrate **1** is transformed into copper complexes **A**[9] and **B**.[12a,d] There is an equilibrium between **A** and **B**, which is affected by the acidity of the reaction mixture. In formic acid, complex **A** is primary and reacts with CF_3S radical to generate possible intermediates **A-1**. Finally, the copper-assisted trifluoromethylthiolation with CF_3SSCF_3 affords products **3**. In less acidic solution, the addition of CF_3S radical to complex **B** produces the radical intermediate **B-1**, which is further oxidized to cationic intermediate **B-2**. Compound **B-2** may undergo decarboxylation or nucleophilic attack/decarboxylation to give the byproducts **2** and **12**. However, the exact mechanism of this transformation remains unclear at the present stage.

In conclusion, we have disclosed an unprecedented copper-catalyzed, oxidative bis-trifluoromethylthiolation of propiolic acid derivatives with $AgSCF_3$. The use of HCO_2H as the cosolvent was crucial for this reaction. The resulting bis-trifluoromethylthiolated acrylic acids and their derivatives are previously unknown, difficult to obtain by other methods, and potentially useful in drug discovery and material science. Further investigation of the reaction mechanism and the applications of bis-trifluoromethylthiolated products are currently in progress in our laboratory.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.7b01366.

Table S1, experimental procedures, characterization data, mechanistic study data, ^1H, ^{19}F, and ^{13}C NMR spectra, and X-ray crystal structure of **3-e** (PDF)

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Notes

The authors declare no competing financial interest.

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