Synthetic Methods

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Copper-Catalyzed Three-Component Oxytrifluoromethylation of Alkenes with Sodium Trifluoromethanesulfinate and Hydroxamic Acid**

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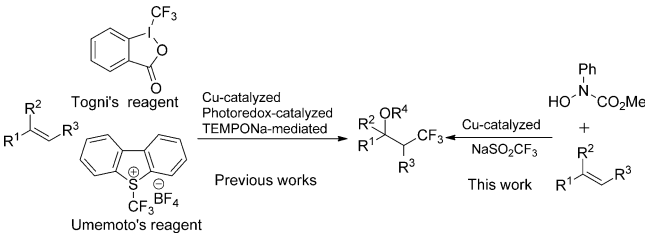
The trifluoromethyl group, having an enhanced electronegativity, lipophilicity, metabolic stability, and bioavailability, is widely prevalent in pharmaceuticals and agrochemicals.[1] Therefore, great efforts have been devoted to the development of new methodologies for efficient and selective incorporation of the trifluoromethyl group into organic compounds. Recently, strategies have been well established for trifluoromethylation of arenes,[2] including transition-metal-catalyzed/mediated trifluoromethylation of aryl halides,[3] aryl boronic acid derivatives,[4] arynes,[5] aromatic amines,[6] and even aromatic C–H bonds.[7] Very recently, the trifluoromethylation of olefins has received considerable attention and tremendous progress has been made in this area. The copper-catalyzed trifluoromethylation of terminal alkenes or allylsilanes with electrophilic trifluoromethylating reagents has been developed, thus providing a series of trifluoromethylated allylic compounds.[8] Our group also developed a complementary route to trifluoromethylated allylic compounds through the copper-catalyzed oxidative trifluoromethylation of terminal alkenes with the Ruppert–Prakash reagent (CF_3SiMe_3).[9] The hydrotrifluoromethylations of unactivated alkenes by using nucleophilic, electrophilic, and radical trifluoromethylating reagents were reported respectively by our group, as well as those of Gouverneur and Nicewicz.[10] Furthermore, the difunctionalization-type trifluoromethylation of alkenes including oxytrifluoromethylation,[11] carbotrifluoromethylation,[12] and aminotrifluoromethylation[13] have been achieved with or without transition-metal catalysis. These difunctionalization reactions allow rapid access to a variety of classes of CF_3-containing building blocks including lactones, cyclic ethers, epoxides, alcohols, ketones, amines, aziridines, and carbocycles. Among these difunctionalization-type trifluoromethylations of alkenes, the electrophilic and radical transformation using Umemoto's reagent [S-(trifluoromethyl)dibenzothiophenium tetrafluoroborate][14] and Togni's reagents (1-trifluoromethyl-1,2-benziodoxol-3-(1*H*)-one and 1-trifluoromethyl-1,3-dihydro-3,3-dimethyl-1,2-benziodoxole)[15] have attracted attention because these reagents are easy to handle; they are solids at room temperture. Especially, only the electrophilic trifluoromethyalting reagents including Togni's reagent and Umemoto's reagent are employed for the oxytrifluoromethylation of alkenes (Scheme 1).[11] However, the high cost and/or lack of ready availability of these electrophilic trifluoromethylating reagents limits their usage on a large scale.



Scheme 1. Copper-catalyzed oxytrifluoromethylation of alkenes.

Since the pioneering work by Langlois and co-workers on the oxidation of $NaSO_2CF_3$ to the trifluoromethyl radical ($CF_3^{\bullet}$) and subsequent addition to electron-rich aromatics,[16] the trifluoromethylation of arenes,[7o] heterocycles,[7g] and aryl boronic acids[4j,m] using $NaSO_2CF_3$ as a stable and inexpensive trifluoromethyl (CF_3-) source has been recently developed. Furthermore, the hydrotrifluoromethylation of alkenes[10c] and decarboxylative trifluoromethylation of α,β-unsaturated carboxylic acids[17] with $NaSO_2CF_3$ have also been reported. In contrast, Alexanian and co-workers have successfully developed the dioxygenation,[18a,b] oxyamination,[18c] and ketooxygenation[18d] of alkenes using hydroxamic acids, which are readily converted into amidoxyl radicals upon exposure to mild oxidants or radical initiators. Inspired by these intriguing studies, we hypothesized that the oxytrifluoromethylation of alkenes would be possible using both $NaSO_2CF_3$ and hydroxamic acid, because copper salts could generate both $BuO^{\bullet}$ and $BuOO^{\bullet}$ from *tert*-butylhydroperoxide (TBHP),[19] and the trifluoromethyl radical ($CF_3^{\bullet}$)[7g] and amidoxyl radical [$ArN(CO_2Me)O^{\bullet}$][18] could be formed from $NaSO_2CF_3$ and hydroxamic acid in the presence of $BuO^{\bullet}$ and $BuOO^{\bullet}$ (Scheme 2). However, the regioselectivity of this process would be a great challenge. When the trifluoromethyl radical first adds to an alkene, the radical intermediate **A** is formed, followed by trapping with an amidoxyl radical to give the product **3** (Scheme 2, Path 1). In the case of the first

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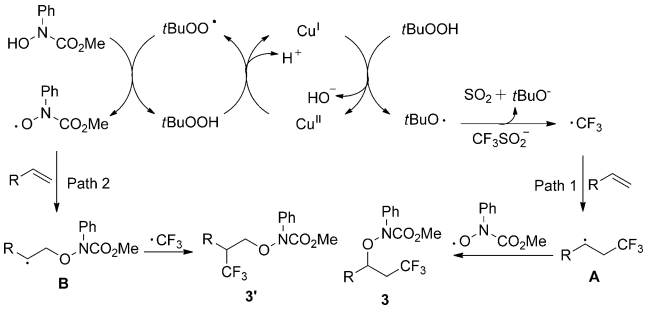


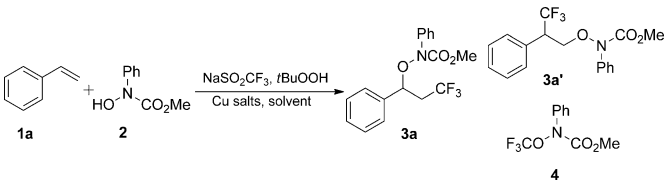
Scheme 2. Proposed mechanism.

addition of an amidoxyl radical to an alkene, the product **3′** would be formed via intermediate **B** (Scheme 2, Path 2). Herein, we describe the copper-catalyzed three-component oxytrifluoromethylation of alkenes by employing sodium trifluoromethanesulfinate ($NaSO_2CF_3$, Langlois reagent) as a trifluoromethyl (CF_3-) source (Scheme 1).[20] This oxytrifluoromethylation proceeds regioselectively to give a single product and is dictated by the initial trifluoromethyl radical.

To test the hypothesis, we began our study by examining the oxytrifluoromethylation of styrene (**1a**) with $NaSO_2CF_3$, *t*BuOOH and *N*-hydroxy-*N*-phenylacetamide (**2**). After examining the effects of solvent and reaction temperature (see Table S1 in the Supporting Information), we found that the oxytrifluoromethylation of **1a** proceeded smoothly at room temperature using CuCl as a catalyst in a mixed solvent (CH_2Cl_2/MeOH/H_2O = 5:5:4), thus giving the desired product **3a** in 61% yield together with the side product *N*-trifluoromethoxy-*N*-phenylacetamide **4** (detected by ^{19}F NMR spectroscopy and GC-MS); the regioisomer **3a′** was not observed (Table 1, entry 1). We speculated that the faster formation of the CF_3 radical or the greater stability of the amidoxyl radical may result in the selective fromation of **3a**. Switching the CuCl catalyst to CuI, CuOAc, CuBr, CuTc, or even to a more Lewis-acidic copper(I) species, such as $(CuOTf)_2Ph$, $Cu(MeCN)_4PF_6$, and $Cu(MeCN)_4BF_4$, the improvement of the yield of **3a** and inhibition of the byproduct **4** (entries 2–8) were not successful. Subsequently, copper(II) catalysts such as $CuSO_4{\cdot}5H_2O$, $Cu(OTf)_2$, $CuCl_2$, and $CuBr_2$ were tested (entries 9–12). Actually, $CuSO_4{\cdot}5H_2O$ was an effective catalyst for oxytrifluoromethylation, thus providing **3a** in 66% yield. Notably, **3a** was not formed in the absence of a copper catalyst (entry 13). As $CuSO_4{\cdot}5H_2O$ is less expensive than other copper catalysts, $CuSO_4{\cdot}5H_2O$ was chosen for the preparative experiments. To reduce the formation of **4** and inhibit polymerization of styrene, the use of 1.0 equivalent of **2** with either 2.0 or 3.0 equivalents of styrene led to improved yields (entries 14 and 15). To our delight, the yield of **3a** was improved to 84% when the amount of $NaSO_2CF_3$ was increased to 4.0 equivalents (entry 16). Additionally, the commercially available aminoxyl radical TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy) was examined as a radical terminator instead of **2** for oxytrifluoromethylation of styrene, however no TEMPO-trapped product was observed (entry 17).

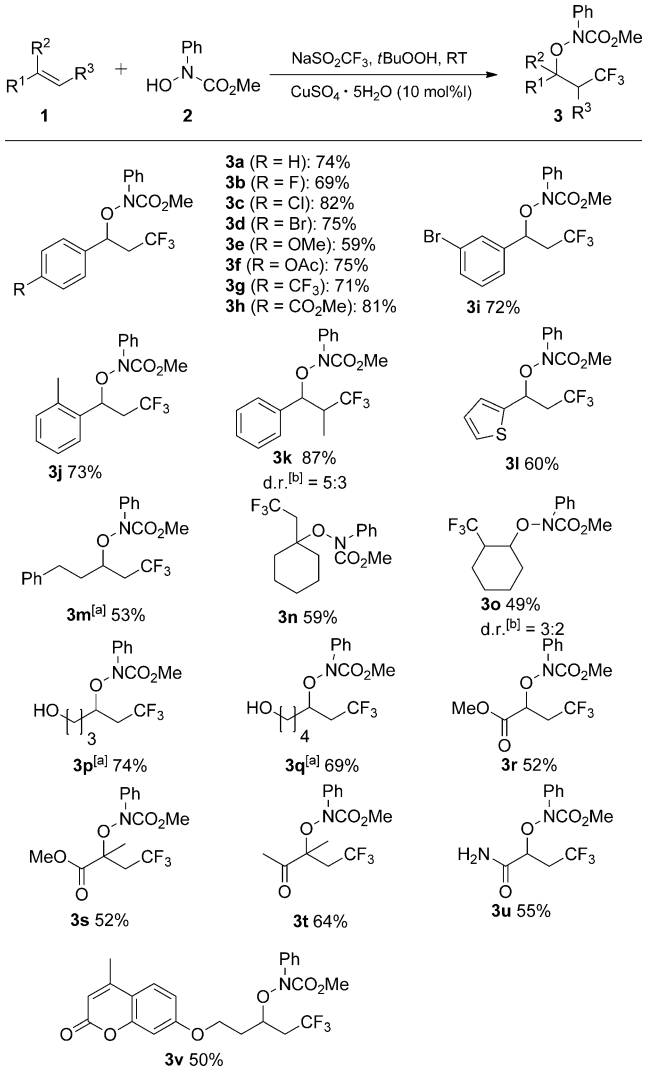
With the optimized reaction conditions in hand, the substrate scope of this copper-catalyzed oxytrifluoromethylation of alkenes was investigated (Scheme 3). Styrenes possessing both electron-donating (**1e**,**f**, **1j**) and electron-withdrawing (**1b–d**, **1g–i**) groups worked well, thus affording the corresponding products in good yield. Functionalities such as chloro, bromo, ether, and ester groups, which serve as useful reaction handles for additional transformations, were tolerated under these mild reaction conditions (**3c–f**, **3h**,**i**). The substituent at the *meta* (**3i**) or *ortho* (**3j**) position of the aromatic ring did not hinder the reaction (72–73% yields). The β-methylstyrene (**1k**) was also a suitable substrate with a moderate level of stereoselection (5:3 d.r.). In addition, the heterocyclic substrate 2-vinylthiophene yielded the desired oxytrifluoromethylated compound **3l** in 60% yield. Importantly, the copper-catalyzed oxytrifluoromethylation presented herein has also been easily extended to unactivated alkenes. A number of unactivated alkenes such as 4-phenyl-1-butene, methylenecyclohexane, and cyclohexene proceeded smoothly to give the corresponding products in moderate yields (**3m–o**). Notably, the oxytrifluoromethylation of 4-pentene-1-ol and 5-hexen-1-ol provided the trifluoromethylated alcohols (**3p**,**q**), rather than the CF_3-containing cyclic ethers that were formed from reactions of 4-pentene-1-ol and 5-hexen-1-ol with Togni's reagent.[11c] To our delight, α,β-unsaturated esters, α,β-unsaturated ketone, and α,β-unsatu-

Table 1: Selected optimization of the copper-catalyzed oxytrifluoromethylation of styrene.[a]



Entry	Cu salts	**3a** Yield [%][b]
1	CuCl	61 (8)
2	CuI	53 (10)
3	CuOAc	61(9)
4	CuBr	63 (12)
5	CuTc	57 (9)
6	$(CuOTf)_2Ph$	62 (12)
7	$[Cu(MeCN)_4PF_6]$	63 (10)
8	$[Cu(MeCN)_4BF_4]$	67 (11)
9	$CuSO_4{\cdot}5H_2O$	66 (9)
10	$Cu(OTf)_2$	65 (11)
11	$CuCl_2$	63 (12)
12	$CuBr_2$	57 (14)
13	–	–
14[c]	$CuSO_4{\cdot}5H_2O$	72 (–)
15[d]	$CuSO_4{\cdot}5H_2O$	77 (–)
16[e]	$CuSO_4{\cdot}5H_2O$	84 (–)
17[f]	$CuSO_4{\cdot}5H_2O$	–[g]

[a] Reaction conditions: **1a** (0.2 mmol), **2** (0.24 mmol), $NaSO_2CF_3$ (0.6 mmol), Cu salts (0.02 mmol). *t*BuOOH (1.2 mmol), CH_2Cl_2/MeOH/H_2O (1 mL:1 mL:0.8 mL), 12 h, N_2, RT. [b] Determined by ^{19}F NMR spectroscopy using fluorobenzene as an internal standard. The value within parentheses is the yield of **4**. [c] **1a** (0.4 mmol), **2** (0.2 mmol). [d] **1a** (0.6 mmol), **2** (0.2 mmol). [e] **1a** (0.6 mmol), **2** (0.2 mmol), $NaSO_2CF_3$ (0.8 mmol). [f] TEMPO (0.2 mmol) was used instead of **2** (0.2 mmol). [g] No TEMPO adduct was detected. Tc = thiophene-2-carboxylate, Tf = trifluoromethanesulfonyl.

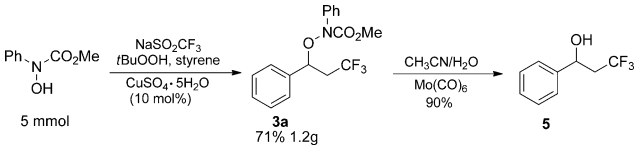


Scheme 3. Scope of the copper-catalyzed oxytrifluoromethylation of alkenes. Reaction conditons: **1a** (0.6 mmol), **2** (0.2 mmol), $NaSO_2CF_3$ (0.8 mmol), $CuSO_4{\cdot}5H_2O$ (0.02 mmol), *t*BuOOH (1.2 mmol), CH_2Cl_2/MeOH/H_2O (1 mL:1 mL:0.8 mL), 12 h, N_2, RT. Yields shown are those of the isolated products. [a] Used $CuBr_2$ (0.02 mmol) as a catalyst. [b] Obtained as a mixture of diastereoisomers. The diastereomeric ratio determined by ^{19}F NMR spectroscopy.

rated amide were smoothly converted into the corresponding compounds (**3r–u**) in moderate yields. These results demonstrated the scope of our system to electron-poor conjugated olefins. Finally, the substrate **1v**, derived from 4-methylumbelliferone, was also examined and the corresponding trifluoromethylated compound **3v** was obtained in 50% yield.

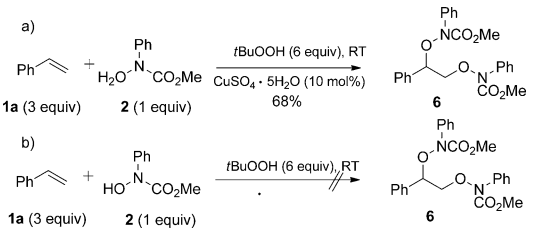
To demonstrate the application of this method on a larger scale, we undertook the oxytrifluoromethylation of **1a** using 5 mmol of **2** to afford 1.2 grams of **3a** in 71% yield (Scheme 4). Then the reduction of the N–O bond of compound **3a** was accomplished using $[Mo(CO)_6]$ as the reductant to give the trifluoromethylated alcohol **5**.

As shown in Scheme 2, an amidoxyl radical [ArN-$(CO_2Me)O^{\bullet}$] could be formed from hydroxamic acid in the presence of *tert*-butylhydroperoxide and a catalytic amount of a copper salt. To figure out whether the amidoxyl radical



Scheme 4. Synthesis of ß-trifluoromethyl-substituted alcohol.

intermediate was formed in this reaction, **1a** was subjected to our standard reaction conditions in the absence of $NaSO_2CF_3$, and the dioxygenation product **6** was obtained in 68% yield (Scheme 5a). However, **6** was not formed without $CuSO_4{\cdot}5H_2O$ (Scheme 5b). These results (Scheme 5 and entry 13 of Table 1) suggested that the catalytic copper salt played a key role in the formation of both the trifluoromethyl radical ($CF_3^{\bullet}$) and amidoxyl radical [$ArN(CO_2Me)O^{\bullet}$].



Scheme 5. Mechanistic experiments.

In conclusion, we have developed a copper-catalyzed regioselective oxytrifluoromethylation of alkenes. This reaction employs the stable and inexpensive $NaSO_2CF_3$ as the CF_3 source and $CuSO_4{\cdot}5H_2O$ as the catalyst. More importantly, this system is tolerant of a wide range of functional groups. The cheapness of reactants and the mild reaction conditions make this reaction a practical method for oxytrifluoromethylation of alkenes.

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