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Copper and Zinc Copromoted Bromo(chloro)trifluoromethylation of Alkenes and Alkynes with Trifluoromethanesulfonic Anhydride

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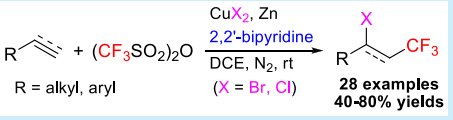
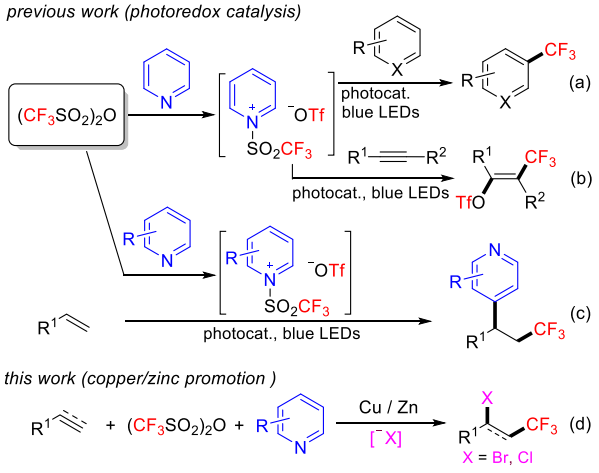
ABSTRACT: The first copper and zinc copromoted trifluoromethylation using trifluoromethanesulfonic anhydride (Tf_2O) as a trifluoromethylating reagent has been developed. The reaction of alkenes or alkynes with Tf_2O in the presence of CuX_2 (X = Br, Cl), Zn powder, and 2,2′-bipyridine affords bromo(chloro)trifluoromethylated products in good yields. CuX_2 plays a dual role as the catalyst and halide source, whereas 2,2′-bipyridine acts as both the activation reagent and ligand.



Trifluoromethanesulfonic anhydride ($(CF_3SO_2)_2O$, Tf_2O) is an inexpensive and abundant chemical. Normally, Tf_2O is used as an electrophilic triflating reagent to transfer the $-SO_2CF_3$ group.[1] We recently reported an unprecedented use of Tf_2O as a radical CF_3 source by merging pyridine activation and photoredox catalysis for C−H trifluoromethylation of (hetero)arenes (Scheme 1a) and trifluoromethyltriflation of alkynes (Scheme 1b).[2] In those reactions, the trifluoromethyl radical was formed by single electron transfer (SET) reduction of the in situ-generated *N*-triflylpyridinium salt[3] with the excited-state photocatalyst.[4] Very recently, Hong and co-workers described the introduction of both CF_3 and pyridyl groups into olefins using *N*-triflylpyridinium salts as modular bifunctional reagents under photocatalysis (Scheme 1c).[5] These works demonstrated that Tf_2O is an attractive alternative trifluoromethyl radical reagent through a combination of pyridine activation and photoredox catalysis.

Scheme 1. Trifluoromethylation with Tf_2O under Pyridine Activation



Over the past decade, the copper-catalyzed radical trifluoromethylation of unsaturated compounds with Togni reagents[6,7] or the Umemoto reagent[8] has been extensively investigated. The SET reduction of Togni reagents or the Umemoto reagent with Cu(I) catalyst gave CF_3 radical. As the reduction potentials of *N*-triflylpyridinium salts[2] are close to those of Togni reagent II[9] (Figure 1), we envisioned that the copper-catalyzed radical trifluoromethylation with *N*-triflylpyridinium salts would be feasible. Herein we disclose the first copper and zinc copromoted trifluoromethylation of alkenes and alkynes with Tf_2O for the preparation of bromo(chloro)-trifluoromethylated products (Scheme 1d).

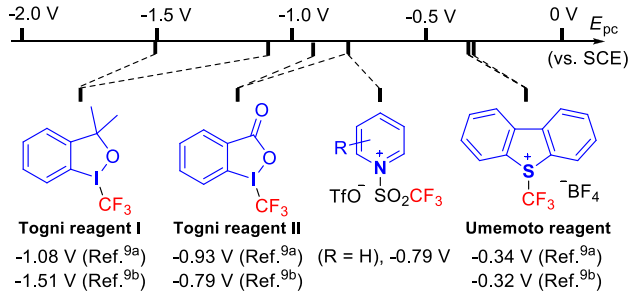


Figure 1. Reduction potentials of trifluoromethylating reagents.

We began our investigation of bromotrifluoromethylation with the model substrate but-3-enylbenzene (**1a**).[8b,10] The reaction of **1a** with Tf_2O in the presence of different copper catalysts, pyridine derivatives, and bromide sources was examined (Table 1). To our disappointment, none of the

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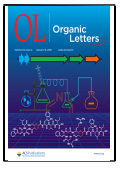

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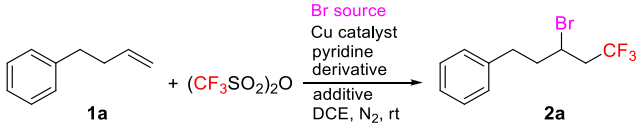
Table 1. Optimization of the Reaction Conditions[a]



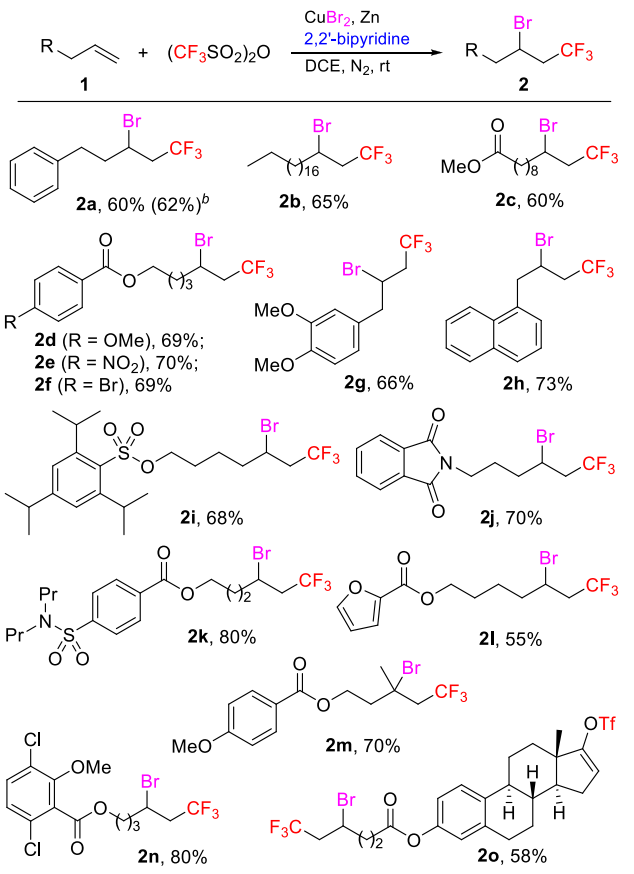
entry	Cu catalyst	pyridine derivative	Br source	additive	yield (%)[b]
1	CuI	pyridine	NaBr	–	0
2	CuBr	pyridine	NaBr	–	0
3	CuOTf	pyridine	NaBr	–	0
4	$CuBr_2$	pyridine	NaBr	–	5
5	$CuBr_2$	2-fluoropyridine	NaBr	–	trace
6	$CuBr_2$	4-phenylpyridine	NaBr	–	trace
7	$CuBr_2$	2,2′-bipyridine	NaBr	–	16
8	$CuBr_2$	phen[f]	NaBr	–	0
9	$CuBr_2$	2,2′-bipyridine	n-Bu_4NBr	–	6
10	$CuBr_2$	2,2′-bipyridine	NaBr	Zn	34
11	$CuBr_2$	2,2′-bipyridine	NaBr	Fe	18
12[c]	$CuBr_2$	2,2′-bipyridine	NaBr	Zn	60
13[d]	$CuBr_2$	2,2′-bipyridine	NaBr	Zn	62
14[c]	$CuBr_2$	2,2′-bipyridine	——	Zn	55
15[c,e]	$CuBr_2$	2,2′-bipyridine	——	Zn	78

[a]Reaction conditions: **1a** (0.2 mmol), Tf_2O (0.6 mmol), Br source (0.4 mmol), Cu catalyst (0.02 mmol), pyridine derivative (0.6 mmol), additive (0.2 mmol), DCE (2.0 mL), N_2, rt, overnight. [b]Yields were determined by ^{19}F NMR spectroscopy using trifluoromethylbenzene as an internal standard. [c]$CuBr_2$ (0.1 mmol). [d]$CuBr_2$ (0.16 mmol). [e]Tf_2O (0.8 mmol), 2,2′-bipyridine (0.8 mmol). [f]phen = 1,10-phenanthroline.

desired product **2a** was detected in the presence of Cu(I) catalysts, including CuI, CuBr, and CuOTf (entries 1−3). **2a** was formed in 5% yield when $CuBr_2$ was used as the catalyst (entry 4). The screening of a variety of pyridine derivatives indicated that 2,2′-bipyridine was optimal, giving **2a** in 16% yield (entries 5−8). We reasoned that 2,2′-bipyridine probably was used as both the activating reagent of Tf_2O and the ligand to coordinate to $CuBr_2$. The reaction efficiency was not improved when n-Bu_4NBr instead of NaBr was used as bromide source (entry 9). Subsequently, the yield of **2a** was increased in the presence of Zn or Fe powder as a reductant (entries 10 and 11), with Zn leading to a higher yield. The yield was improved to 60% by increasing the amount of $CuBr_2$ to 0.5 equiv (entry 12). However, a further increase in equivalents of $CuBr_2$ had little effect on the yield (entry 13). Notably, even without NaBr, **2a** was formed in 55% yield (entry 14). This result showed that $CuBr_2$ played a dual role as the catalyst and bromide source. Lastly, the yield of **2a** was improved to 78% when larger amounts of Tf_2O and 2,2′-bipyridine were employed (entry 15).

Having optimized the reaction conditions, we then explored the substrate scope of this copper and zinc copromoted bromotrifluoromethylation reaction (Scheme 2). A variety of unactivated alkenes (**1a−o**) underwent this reaction smoothly to give the bromotrifluoromethylated products (**2a−o**) in moderate to excellent yields. The reaction of **1a** was easily scaled up to 1.0 mmol. The mild conditions tolerated a range of functional groups, including ether, ester, amide, sulfonate, sulfamide, chloro, bromo, and nitro. 1,1-Disubstituted alkene **1m** was efficiently converted to the desired product **2m** in good yield. However, internal alkenes were not suitable substrates. Alkenes derived from biologically relevant compounds including, dicamba (**1n**) and estrone (**1o**), were also compatible with the reaction conditions. In the case of substrate **1o** containing a cyclic ketone, electrophilic triflation also took place to form enol triflate **2o**.

Scheme 2. Substrate Scope of Bromotrifluoromethylation of Unactivated Alkenes[a]



[a]Reaction conditions: **1** (0.4 mmol), Tf_2O (1.6 mmol), 2,2′-bipyridine (1.6 mmol), $CuBr_2$ (0.2 mmol), Zn (0.4 mmol), DCE (4.0 mL), N_2, rt, overnight. Isolated yields are shown. [b]The reaction was performed on a 1.0 mmol scale.

To expand the scope of the method, styrenes and alkynes were tested under the standard reaction conditions (Table 1, entry 15). Styrenes **1p−t** bearing different substituents on the benzene ring furnished the corresponding products **2p−t** in moderate yields (Scheme 3). Bromotrifluoromethylation of heterocyclic substrates such as 2-vinylthiophene and 2-vinylpyridine failed to provide any of the desired products. Furthermore, terminal and internal alkynes **3a−d** were smoothly converted to substituted CF_3-containing alkenes **4a−d** with excellent regio- and stereoselectivities (Scheme 4).

Subsequently, this copper and zinc copromoted protocol was successfully extended to chlorotrifluoromethylation reactions[11] by replacing $CuBr_2$ with $CuCl_2$ and n-Bu_4NCl (for details, see the Supporting Information). As shown in Scheme 5, alkenes **1a−o** underwent this reaction smoothly to give the chlorotrifluoromethylated products **5a−o** in good yields. Unfortunately, the analogous fluoro- and iodotrifluoromethylation reactions were unsuccessful.

Mechanistic experiments were then performed to gain insight into the reaction mechanism. The reaction of **1a** was completely blocked when 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO) was added to the standard conditions, whereas the

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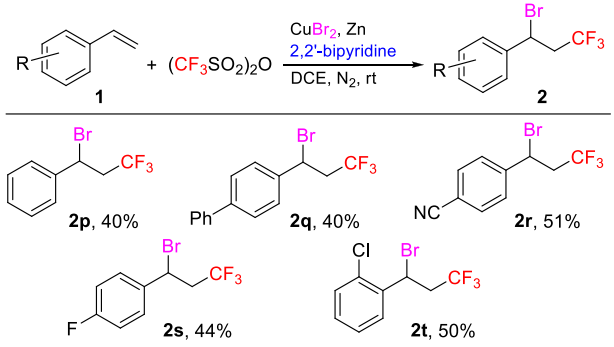
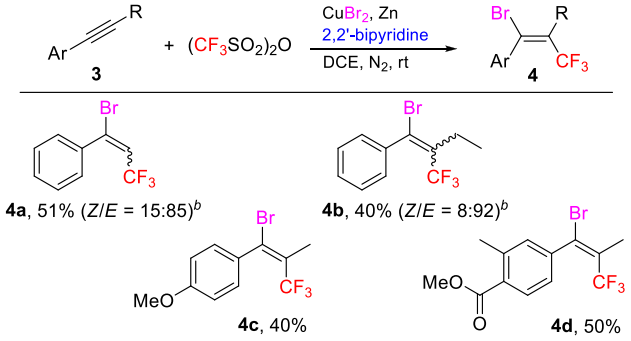
Scheme 3. Substrate Scope of Bromotrifluoromethylation of Styrenes[a]



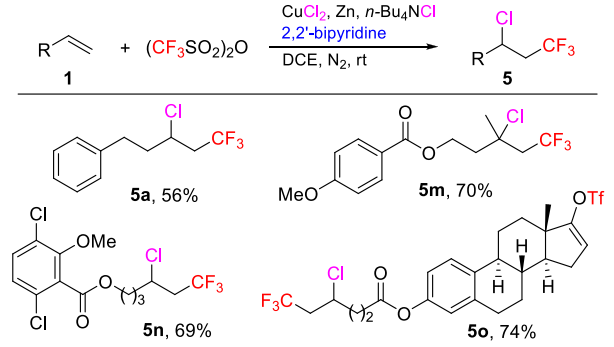
[a]Reaction conditions: **1** (0.4 mmol), Tf_2O (1.6 mmol), 2,2′-bipyridine (1.6 mmol), $CuBr_2$ (0.2 mmol), Zn (0.4 mmol), DCE (4.0 mL), N_2, rt, overnight. Isolated yields are shown.

Scheme 4. Substrate Scope of Bromotrifluoromethylation of Alkynes[a]



[a]Reaction conditions: **3** (0.4 mmol), Tf_2O (1.6 mmol), 2,2′-bipyridine (1.6 mmol), $CuBr_2$ (0.2 mmol), Zn (0.4 mmol), DCE (4.0 mL), N_2, rt, overnight. Isolated yields are shown. [b]The *Z*/*E* ratio was determined by ^{19}F NMR spectroscopy of the crude reaction mixture.

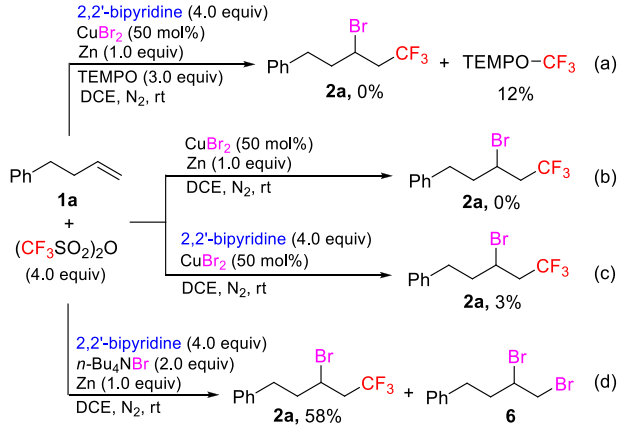
Scheme 5. Substrate Scope of Chlorotrifluoromethylation of Alkenes[a]



[a]Reaction conditions: **1** (0.4 mmol), Tf_2O (1.6 mmol), 2,2′-bipyridine (1.6 mmol), $CuCl_2$ (0.2 mmol), Zn (0.4 mmol), *n*-Bu_4NCl (0.8 mmol), DCE (4.0 mL), N_2, rt, overnight. Isolated yields are shown.

TEMPO−CF_3 adduct was formed in low yield (Scheme 6a). These results indicated that CF_3 radical is involved in this reaction. Furthermore, the control experiments indicated that both of activator (2,2′-bipyridine) and reductant (Zn powder) are crucial for the bromotrifluoromethylation reaction

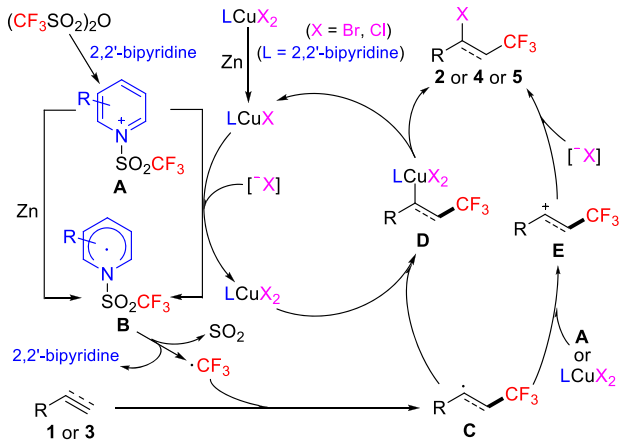
Scheme 6. Mechanistic Experiments



(Scheme 6b,c). The reaction proceeded when *n*-Bu_4NBr was used instead of $CuBr_2$ in the absence of Cu salt, affording **2a** in 58% yield along with the formation of dibrominated byproduct **6** (Scheme 6d). This result revealed that the Zn promoted bromotrifluoromethylation reaction was feasible but less efficient than the copper and zinc copromoted bromotrifluoromethylation reaction (Table 1, entry 15).

On the basis of the above results and previous reports,[2,5−8,10,11] a plausible mechanism for this reaction is proposed in Scheme 7. Initially, the reaction of Tf_2O and 2,2′-

Scheme 7. Proposed Reaction Mechanism



bipyridine generates the corresponding *N*-triflylpyridinium salt **A**. Then SET reduction of **A** with Zn powder affords radical species **B**, which rapidly collapses to release 2,2′-bipyridine, SO_2, and CF_3 radical. On the other hand, $LCuX_2$ (L = 2,2′-bipyridine, X = Br or Cl) is reduced by Zn powder or other factors[12] to deliver LCuX, which might also act as a reductant and then enable the conversion of *N*-triflylpyridinium salt **A** to radical species **B**. Subsequently, the addition of CF_3 radical to the unsaturated substrate (**1** or **3**) gives *β*-trifluoromethyl carbon radical **C**. There might be two possible pathways for the conversion of **C** to the final bromo(chloro)-trifluoromethylated products (**2** or **4** or **5**). First, reaction of $LCuX_2$ and intermediate **C** could furnish Cu(III) intermediate **D**, which would undergo reductive elimination to afford the desired products and regenerate LCuX. The alternative way would involve oxidation of intermediate **C** by *N*-triflylpyr-

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idinium salt **A**[13] or $LCuX_2$ to give carbocation intermediate **E** followed by nucleophilic attack by bromide or chloride anion.

In conclusion, we have developed a unique reaction system to realize the copper and zinc copromoted trifluoromethylation using low-cost and abundant Tf_2O as the trifluoromethylating reagent. The combination of CuX_2 (X = Br, Cl), Zn powder, and 2,2′-bipyridine enables various unactivated alkenes, styrenes, and alkynes to be transformed to the halotrifluoromethylated products.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.0c03855.

Experimental procedures, characterization data, and copies of ^1H, ^{19}F, and ^{13}C NMR spectra (PDF)

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Notes

The authors declare no competing financial interest.

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