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Copper-Catalyzed Direct Trifluoromethylthiolation of Benzylic C−H Bonds via Nondirected Oxidative C(sp^3)−H Activation

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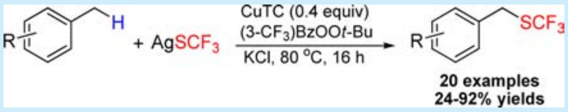
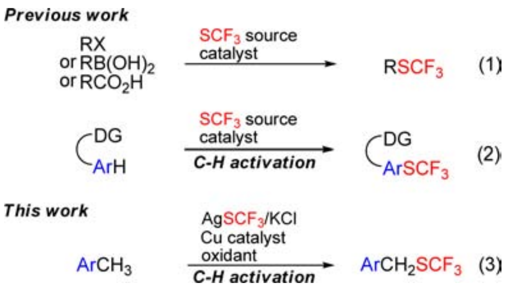
S *Supporting Information*

ABSTRACT: A copper-catalyzed trifluoromethylthiolation of benzylic sp^3 C−H bonds was developed via nondirected oxidative C−H activation using readily prepared and stable $AgSCF_3$. This reaction provides a novel and straightforward method for the preparation of various benzyl trifluoromethyl sulfides.



The incorporation of fluorine-containing groups into an organic molecule can substantially change the chemical, physical, and biological properties of the parent compound.[1] Among various fluorine-containing groups, the trifluoromethylthio group (CF_3S−) has attracted special interest because of its remarkable properties, in particular the strong electron-withdrawing effect and extremely high lipophilicity.[2] Thus, CF_3S-containing compounds have shown unique biological activities.[3] There are mainly two approaches for the formation of trifluoromethylthiolated compounds: trifluoromethylation of sulfur-containing compounds (the formation of the RS−CF_3 bond)[4] and trifluoromethylthiolation of different substrates (the formation of the R−SCF_3 bond).[5,6] Recently, impressive progress has been made in transition-metal-catalyzed trifluoromethylthiolation reactions [Scheme 1, eq 1].[6] These methods mentioned above require prefunctionalizaed starting materials. Consequently, the direct C−H trifluoromethylthiolation represents an attractive alternative on account of its high atom and step economy; however, this approach has been rarely explored. In 2012, Daugulis reported the first example of a copper-catalyzed trifluoromethylthiolation of sp^2 aromatic C−H bonds using CF_3SSCF_3 as the electrophilic reagent [Scheme 1, eq 2].[7a] Very recently, Shen developed a Pd-catalyzed trifluoromethylthiolation of aryl C−H bonds [Scheme 1, eq 2].[7b] In both reaction systems, directing groups (DGs) were needed to assist the transformations and only sp^2 C−H bond activation was accomplished. Thus, it is highly desirable to develop other methods for direct trifluoromethylthiolation of C−H bonds, especially sp^3 C−H bonds.

Scheme 1. Transition-Metal-Catalyzed Trifluoromethylthiolation



Recently, various methods have been developed for direct transformations of benzylic C−H bonds into C−C,[8] C−N,[9] C−O,[10] and C−F bonds.[11] No examples, however, have been reported for the C−S bond formation by direct benzylic C−H activation. Inspired by these intriguing studies and in continuation of our research interest in the development of new methods for trifluoromethylthiolation reaction,[5c,6b,12] we hypothesized that the direct transformation of the benzylic C−H bond into the C−SCF_3 bond would be possible in the presence of a suitable catalyst, oxidant, and trifluoromethylthio (CF_3S−) source. Herein, we describe the Cu-catalyzed trifluoromethylthiolation of benzylic sp^3 C−H bonds from toluene analogues via nondirected oxidative activation with readily prepared and stable $AgSCF_3$ [Scheme 1, eq 3]. This work is the first example of transition-metal-catalyzed direct formation of C(sp^3)−SCF_3 bonds, and it is the most straightforward method for the preparation of benzyl trifluoromethyl sulfides, compared to other methods.[13]

The main challenges in our reaction system are the activation of C(sp^3)−H bonds without using directing groups and using a catalytic amount of metal reagent for the formation of C(sp^3)−SCF_3 bonds. In 2007, Li's group reported $FeCl_2$-catalyzed oxidative activation of benzylic C−H bonds with *tert*-butyl peroxide for the formation of C−C bonds.[14] Inspired by their work, we started optimizing the reaction conditions with excess toluene as the substrate and $AgSCF_3$ as the trifluoromethylthiolation reagent. The desired compound was obtained in only 2% yield detected by ^{19}F NMR (Table 1, entry 1). We surmised

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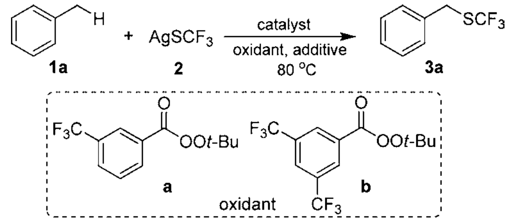
Table 1. Optimization of Reaction Conditions[a]



entry	catalyst	oxidant	additive	yield of 3a[b]
1	$FeCl_2$	t-BuOOt-Bu	–	2%
2	$FeCl_2$	t-BuOOt-Bu	n-Bu_4NI	5%
3	$FeCl_2$	t-BuOOH	n-Bu_4NI	0%
4	$FeCl_2$	PhOOt-Bu	n-Bu_4NI	7%
5	$FeCl_2$	**a**	n-Bu_4NI	11%
6	$FeCl_2$	**b**	n-Bu_4NI	8%
7	$Pd(OAc)_2$	**a**	n-Bu_4NI	0%
8	CuCl	**a**	n-Bu_4NI	41%
9	CuBr	**a**	n-Bu_4NI	36%
10	CuTC	**a**	n-Bu_4NI	45%
11	CuSCN	**a**	n-Bu_4NI	26%
12	$[MeCN]_4CuPF_6$	**a**	n-Bu_4NI	35%
13	$[MeCN]_4CuBF_6$	**a**	n-Bu_4NI	30%
14	$(CuOTf)_2C_6H_6$	**a**	n-Bu_4NI	22%
15	CuTC	**a**	n-Bu_4NBr	49%
16	CuTC	**a**	n-Bu_4NCl	52%
17	CuTC	**a**	Me_4NCl	17%
18	CuTC	**a**	Et_4NCl	18%
19	CuTC	**a**	(n-$C_6H_{14})_4NCl$	65%
20	CuTC	**a**	LiCl	81%
21	CuTC	**a**	NaCl	84%
22	CuTC	**a**	KCl	92%
23[c]	CuTC	**a**	KCl	75%
24	–	**a**	KCl	0%
25[d]	CuTC	**a**	KCl	14%
26[d]	–	**a**	KCl	12%

[a] Reaction conditions: $AgSCF_3$ (0.2 mmol), **1a** (60 equiv, 12.0 mmol), additive (0.2 mmol), catalyst (0.08 mmol), oxidant (0.4 mmol), 80 °C, 16 h, under Ar. [b] Yields determined by ^{19}F NMR spectroscopy using fluorobenzene as an internal standard. [c] Catalyst (0.04 mmol). [d] $CuSCF_3$ (0.2 mmol) instead of $AgSCF_3$ (0.2 mmol).

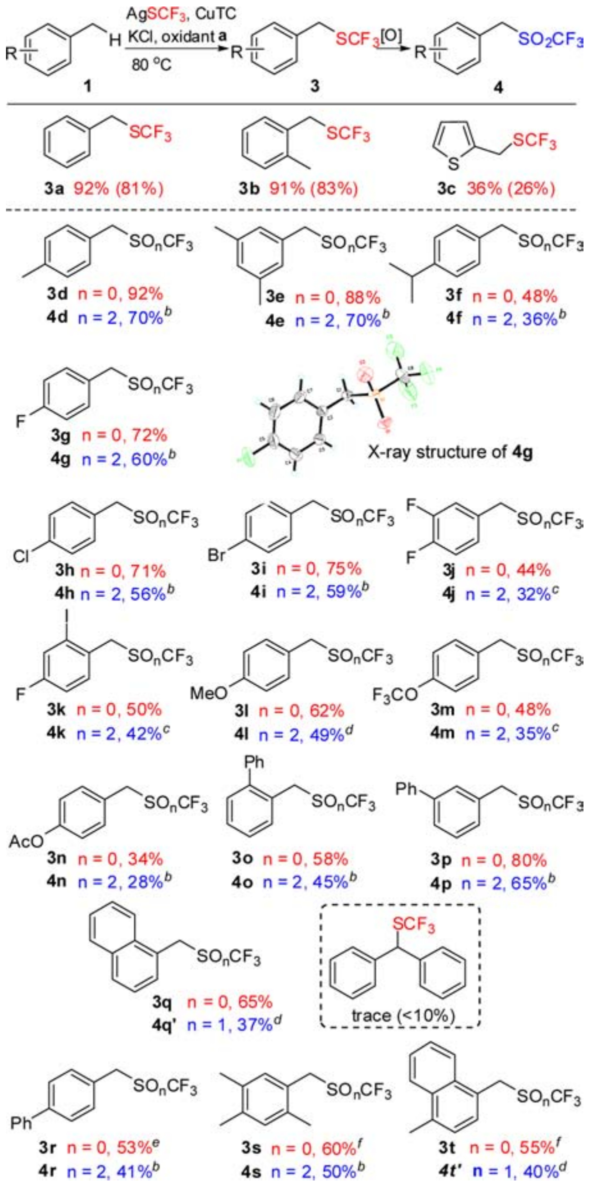
that $AgSCF_3$ was not active enough for this reaction. In 2000, Clark reported that the addition of n-Bu_4NI to $AgSCF_3$ in acetonitrile resulted in the formation of a reactive source of $[SCF_3]^-$.[15] Based on this work, n-Bu_4NI was added to the reaction system, and the yield was slightly improved to 5% (Table 1, entry 2). Having seen these initial results in hand, the optimization of reaction conditions was continued from screening the oxidants, which should lead to the generation of a benzyl radical. Among several oxidants, (3-CF_3)BzOOt-Bu (**a**) was proven to be optimal, increasing the yield to 11% (Table 1, entries 2–6). This unique oxidant **a** was developed by Powell and Fan and used in their reaction system for the amination of benzylic C–H bonds in 2010.[16] Then, we focused on the metal catalyst, which was vital to the catalytic cycle. Two of the other metals $Pd(OAc)_2$ and CuCl gave totally different results (Table 1, entries 7 and 8). No desired product was obtained when $Pd(OAc)_2$ was used, and the yield was sharply increased to 41% with CuCl as the catalyst. Encouraged by the result caused by CuCl, different Cu salts were then screened (Table 1, entries 9–14), and CuTC was selected. To further improve the yield, different additives were investigated. This was carried out from two aspects. In the case of anions, n-Bu_4NCl showed higher activity than n-Bu_4NI and n-Bu_4NBr (Table 1, entries 15 and 16). In the case of cations, the yields were found to increase when the alkyl chain became longer (Table 1, entries 17–19). To our delight, all the alkali metal chlorides gave good yields (Table 1, entries 20–22). Particularly, the yield reached as high as 92% when KCl was added. It was noteworthy that the yield dropped to 75% when the amount of CuTC decreased to 0.2 equiv and no desired product was obtained in the absence of CuTC (Table 1, entries 23 and 24). These results showed the important role of a metal catalyst in our reaction system. When $CuSCF_3$ was used as the trifluoromethylthio source, low yields were obtained whether CuTC was added or not (Table 1, entries 25 and 26).

Under the optimized reaction conditions, various toluene analogues were tested as the substrates for the direct benzylic C–H trifluoromethylthiolation reaction. As shown in Scheme 2, different electron-donating or -withdrawing substituents, such as alkyl, alkoxyl, halogen, and aryl groups, at different positions of the aromatic ring were all well tolerated and the desired products were obtained in moderate to excellent yields. It was noteworthy that halogens, such as F, Cl, and Br, were stable in our reaction system. No C–X (F, Cl, and Br) functionalized product was obtained. For the heteroaromatic compound **1c**, the yield of product **3c** was lower than that of the aromatic analogue, probably because the coordination of the heteroatom to copper affected the catalytic cycle. In the case of substrate **1f** bearing two different benzylic H-atoms, a trace of byproduct was detected in the crude reaction mixture. Unfortunately, the activation of secondary benzylic C–H bonds was not successful, giving the desired products in low yields (<10%). To our delight, moderate yields of products **3r–t** were obtained when the amount of substrates was decreased to 6 or 10 equiv. Moreover, this method can also be applied in the synthesis of benzyl trifluoromethyl sulfide derivatives. Benzyl trifluoromethanesulfones **4** and trifluoromethanesulfoxides **4′** were prepared from compounds **1** in two steps by trifluoromethylthiolation and subsequent oxidation, without purification of intermediates **3**.

Based on the well-established Kharasch–Sosnovsky reaction,[17] a plausible mechanism for the Cu-catalyzed oxidative trifluoromethylthiolation of benzylic C–H bonds is proposed in Scheme 3. First, in the presence of a Cu(I) catalyst, the homolytic cleavage of oxidant **a** gives Cu(II) carboxylate **A** and *tert*-butoxy radical **B**. Sequentially the intermediate **B** abstracts a benzylic H-atom from the substrate to afford the benzyl radical **C**, which then reacted with intermediate **A** giving the Cu(III) complex **D**.[18] Complex **D** was converted to Cu(III) complex **E** by reacting with trifluoromethanethiolate, prepared from the reaction of $AgSCF_3$ and KCl,[15] through an anion-exchange process. The last step is reductive elimination of complex **E** to afford the final product along with regeneration of the active Cu(I) species for the next catalytic cycle. Alternatively, complex **D** undergoes reductive elimination to give intermediate **F**.[19] However, when **F** reacted with $AgSCF_3$/KCl, no desired product was obtained (see the Supporting Information); thus, **F** was the byproduct of this reaction system.

The influence of the catalyst, oxidant, and additive to the yield (Table 1) can be well explained according to the above mechanism. First, it is very clear that the Cu catalyst is crucial in the catalytic cycle. Second, the oxidant plays an important role in this reaction system. Its oxidative ability affects the formation of intermediate **A**, and its coordination property to copper is

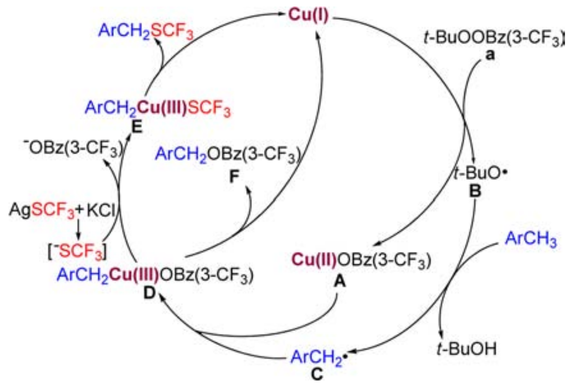
Scheme 2. Screening Scope of Substrates[a]



[a] Reaction conditions: $AgSCF_3$ (0.2 mmol), KCl (0.2 mmol), **1** (12.0 mmol), CuTC (0.08 mmol), Oxidant **a** (0.4 mmol), 80 °C, 16 h, under Ar, yields determined by ^{19}F NMR using fluorobenzene as an internal standard (isolated yields in parentheses). [b] 30 wt % H_2O_2 (1.6 mmol), AcOH (3.0 mL), 90 °C, under Ar, isolated yields for two steps. [c] CrO_3 (0.01 mmol), H_5IO_6 (0.8 mmol), MeCN (4.0 mL), rt, isolated yields for two steps. [d] Condition a, temperature = 40 °C. [e] **1** (2.0 mmol, 10 equiv), DCE (1.6 mL) was used as the solvent. [f] **1** (1.2 mmol, 6 equiv), DCE (1.6 mL) was used as the solvent.

necessary to stabilize Cu(II) complex **A** and Cu(III) complex **D**. Moreover, as mentioned above, there are two competing reactions from intermediate **D**: anion exchange to intermediate **E** and reductive elimination to compound **F**. The good leaving ability of the OBz(3-CF_3) group makes the anion-exchange step much easier, which probably is the major reason for choosing oxidant **a**. Last, the combination of the additive and $AgSCF_3$ produces a new source of $[SCF_3]^-$, whose nucleophilic ability is also important in the anion-exchange step, thus affecting the yield of the desired compound.

Scheme 3. Proposed Mechanism for Benzylic C−H Trifluoromethylthiolation



In conclusion, the first Cu-catalyzed direct trifluoromethylthiolation of benzylic sp^3 C−H bonds has been developed. In this reaction system, *t*-BuOOBz(3-CF_3) was used as the oxidant and $AgSCF_3$/KCl was used as the active trifluoromethylthio source. Various benzyl trifluoromethyl sulfides were conveniently prepared in moderate to excellent yields. Further studies to probe the mechanism of this current reaction and to evaluate the direct trifluoromethylthiolation of other types of sp^3 C−H bonds are in progress.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Detailed experimental procedures and spectral data for all compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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