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Silver-Mediated Radical Aryltrifluoromethylthiolaton of Activated Alkenes

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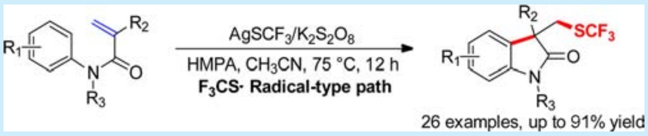
Supporting Information

ABSTRACT: The first example of silver-mediated oxidative aryltrifluoromethylthiolation of activated alkenes to produce valuable trifluoromethylthiole-containing oxindoles was developed. Mechanistic investigations indicated that this novel transformation proceeded through a unique $F_3CS^\bullet$ radical addition path, thus providing a practical and easy-handling method to generate a $F_3CS^\bullet$ radical in the laboratory.



The incorporation of fluorine or fluorine-containing functional groups can effectively improves the physicochemical properties of parent molecules. As a result, fluorinated compounds are widely used in pharmaceuticals, agrochemicals, and materials because of their unique lipophilicity and bioactivities.[1] Among all such intriguing fluorinated moieties, the trifluoromethylthio group (CF_3S) has attracted increasing attention because of its special biological properties, such as enhancement of membrane permeability and absorption rate and improvement of the stability of parent molecules, due to its lipophilicity and high electronegativity.[2]

The classical strategy of choice for the introduction of the trifluoromethylthio group into organic molecules has been limited to indirect methods, such as halogen-fluorine exchange of polyhalogenomethyl thioethers or the trifluoromethylation of sulfur-containing compounds.[3] However, both approaches suffered from harsh reaction conditions and the requirement of prefunctionalization. Thus more general and straightforward methods, in which the C-SCF_3 bond was formed directly, are highly desirable. $MSCF_3$'s, which were previously reported as SCF_3^- sources in S_N2 reactions,[4] have recently been developed as coupling partners in several efficient transition metals, including Pd-,[5] Ni-,[6] and Cu-mediated[7] or -catalyzed trifluoromethylthiolations. Although CF_3SCl has long been used to react directly with some nucleophiles to transfer the CF_3S moiety,[8] its utility was limited as a gaseous and highly toxic reagent. In recent years, several electrophilic trifluoromethylthiolation reagents (SCF_3^+), including trifluoromethanesulfanylamides,[9] trifluoromethylathiolated hypervalent iodine,[10] trifluoromethanesulfonyl hypervalent iodonium ylide,[11] and *N*-trifluoromethylthiophthalimide,[12] have been developed or used for efficient formation of C-SCF_3, especially the C(sp^3)-SCF_3 bond.

Although a diverse array of organic molecules were trifluoromethylthiolated by the nucleophilic and electrophilic CF_3S reagents, the $F_3CS^\bullet$ radical-type pathway remains less explored. The only examples for $F_3CS^\bullet$ radical additions were reported half a century ago, and the CF_3S resources were limited to toxic and gaseous (or volatile) CF_3SH,[8a] CF_3SCl,[8b−d] and CF_3SSCF_3.[13] Inspired by recent advance on silver-mediated or -catalyzed radical additions,[14] we envisioned that the $F_3CS^\bullet$ radical could be triggered by the combination of $AgSCF_3$/oxidant, affording the C(sp^3)-SCF_3 bond after trapping by alkenes. Herein, we report a novel silver-mediated aryltrifluoromethylthiolation of alkenes, to afford bioologically interesting oxindoles.[15] Mechanistic investigations indicate that this transformation proceeds through a radical-type pathway.

As an easily prepared and stable trifluoromethylthiolation reagent, $AgSCF_3$ has been previously widely used as a CF_3S^- source.[16] Our study commenced by examining the aryltrifluoromethylthiolation of *N*-methyl-*N*-phenylmethacrylamide (**1a**) in the presence of $AgSCF_3$ (1.5 equiv) at 75 °C. A wide range of oxidants, including $PhI(OAc)_2$, TBHP, NFSI, Oxone, $(NH_4)_2S_2O_8$, and $K_2S_2O_8$, were first investigated to trigger the $F_3CS^\bullet$ radical. To our delight, the desired product **2a** could be obtained with several oxidants, and $K_2S_2O_8$ gave the best yield at 47% (Table 1, entries 1−7). A careful survey of solvents and reagents ratio was then performed, which revealed the combination of $K_2S_2O_8$ (3.0 equiv), $AgSCF_3$ (1.5 equiv), and CH_3CN (3.0 mL) was optimal, and the yield was increased to 59% (entry 11). To improve the yield further, a series of inorganic and organic bases were next investigated. While the inorganic bases and most organic bases have almost no effect on this transformation (entries 12−14), HMPA (0.5 equiv) increased the yield notably to 83% (entry 18). It is worth pointing out that HMPA functioned not only as a base but also as a possible ligand to improve the solubility and stability of $AgSCF_3$. Additionally, we found the yield maintained at 50% and almost all of the starting material **1a** consumed after 12 h with no addition of HMPA, which indicated that the coordination between HMPA and $AgSCF_3$ might lower the redox potential of the high valent silver species, thus preventing the oxidative decomposition of starting materials and products. Finally, as a control experiment, no desired product was obtained and an

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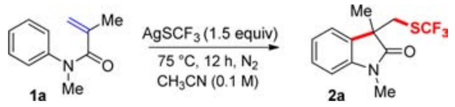
Table 1. Silver-Mediated Aryltrifluoromethylthiolation of Alkenes: Optimization of Reaction Conditions[a]



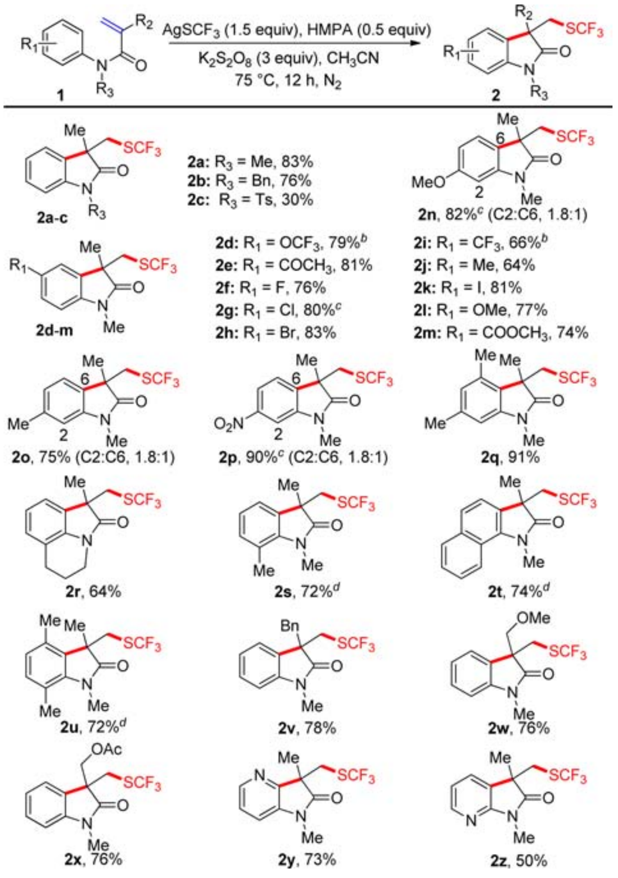
entry	oxidant (equiv)	base (equiv)	yield[b] (%)	entry	oxidant (equiv)	base (equiv)	yield[b] (%)
1	PhI(OAc)$_2$ (2.0)	none	trace	11[c]	$K_2S_2O_8$ (3.0)	none	59
2	TBHP (2.0)	none	trace	12[c]	$K_2S_2O_8$ (3.0)	$NaHCO_3$(1.5)	49
3	NFSI (2.0)	none	trace	13[c]	$K_2S_2O_8$ (3.0)	PhCOONa (2.0)	42
4	Oxone (2.0)	none	0	14[c]	$K_2S_2O_8$ (3.0)	DBU (1.5)	45
5	$Ce(SO_4)_2 \cdot 4H_2O$ (2.0)	none	33	15[c]	$K_2S_2O_8$ (3.0)	HMPA (1.5)	63
6	$K_2S_2O_8$ (2.0)	none	47	16[c]	$K_2S_2O_8$ (3.0)	HMPA (2.0)	50
7	$(NH_4)_2S_2O_8$ (2.0)	none	38	17[c]	$K_2S_2O_8$ (3.0)	HMPA (1.0)	72
8	$K_2S_2O_8$ (1.5)	none	44	18[c]	$K_2S_2O_8$ (3.0)	HMPA (0.5)	83
9	$K_2S_2O_8$ (3.0)	none	54	19[c]	$K_2S_2O_8$ (3.0)	HMPA (0.25)	73
10	$K_2S_2O_8$ (4.0)	none	trace	20[c]	none	HMPA (0.5)	0

[a] Reaction conditions: **1a** (0.2 mmol, 1.0 equiv), $AgSCF_3$ (1.5 equiv), oxidant (2.0 equiv), and base (1.5 equiv) in CH_3CN (2 mL) at 75 °C for 12 h. [b] Isolated yield. [c] CH_3CN (3 mL).

almost quantitive amount of **1a** was recovered when $K_2S_2O_8$ was removed from the reaction system (entry 20).

With the optimized conditions in hand, we then investigated the substrate scope of silver-mediated aryltrifluoromethylthiolation of alkenes (Scheme 1). Unsurprisingly, a benzyl group protecting substrate afforded the oxindole at only slightly reduced yield (**2b**, R$_3$), while an electon-withdrawing protecting group like tosyl inhibited the reacion with only 30% yield (**2c**, R$_3$). We then investigated the substitute effect of the aryl ring (R$_1$). A variety of *N*-methyl-*N*-phenylmethacryl amides **1** with substituents at *para*, *meta*, as well as *ortho* positions in the aniline ring were aryltrifluoromethylthiolated smoothly to give the corresponding oxindoles in moderate to good yields. *meta*-Substituted *N*-phenylacrylamides could also be cyclized successfully in good yields although with inevitable regioisomers (**2n**−**p**, C2:C6 = 1.8:1). To our satisfaction, the less reactive *N*-phenylacrylamides substrates with *ortho* substituents, presumably due to steric effect, afforded the corresponding oxindoles still with good yields, albeit requiring further increase of the amount of $K_2S_2O_8$ and $AgSCF_3$. Both electron-donating groups, such as OMe and Me, and electron-withdrawing groups, such as CF_3, F, Cl, Br, I, CO_2Et, Ac, and NO_2, were well-tolerated on the aryl rings. The presence of halogen atoms (F, Cl, Br, I) in the oxindoles offers the potential for further synthetic elaboration by transition-metal-catalyzed cross-coupling reactions. The substitute effect at the α-position (R$_2$) of the acrylamides was next explored, and it was found that several α-sustitutents, including benzyl, methoxyl, and ester, were compatible with this transformation to furnish the desired products in good yields (**2v**−**x**). Notably, heterocyclic substrates **1y** and **1z** could also be cyclized smoothly to afford **2y** and **2z** with acceptable yields.

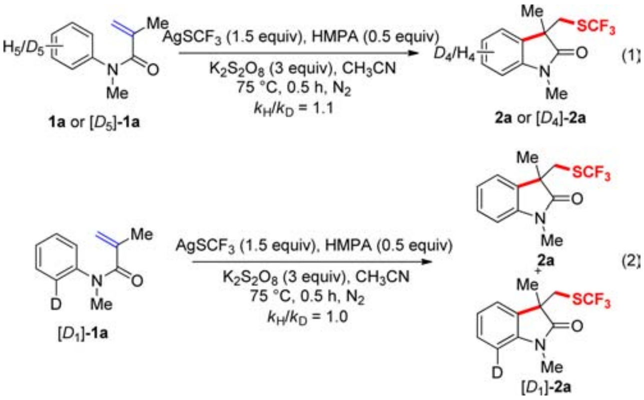
Scheme 1. Scope of Activated Alkenes[a]



[a] Reaction conditions: **1** (0.2 mmol, 1.0 equiv), $AgSCF_3$ (1.5 equiv), $K_2S_2O_8$ (3.0 equiv), and HMPA (0.5 equiv) in CH_3CN (3.0 mL) at 75 °C for 12 h. [b] $AgSCF_3$ (2.0 equiv), $K_2S_2O_8$ (4.0 equiv), HMPA (1.0 equiv). [c] $AgSCF_3$ (2.0 equiv), $K_2S_2O_8$ (4.0 equiv). [d] $AgSCF_3$ (2.5 equiv), $K_2S_2O_8$ (5.0 equiv).

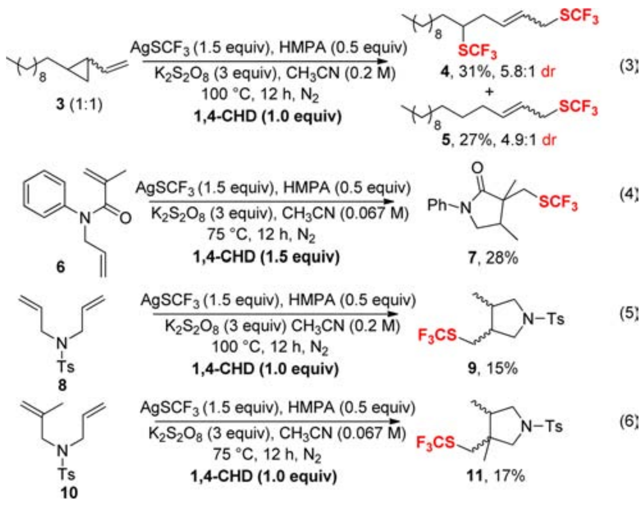
To understand the mechanism of this transformation, a series of experiments were carried out. First, we performed the reaction in the presence of 1.0 equiv of TEMPO as a radical scavenger, and only a trace of desired product was obtained with 85% of **1a** recovered. This observation was consistent with the hypothesis that the reaction proceeds via a radical pathway. Kinetic isotope experiments, including intermolecular and intramolecular experiments, were next undertaken, and low kinetic isotope effects (Scheme 2) were observed for both cases, which indicated the C−H cleavage step was not rate-determining. While we failed to capture the coupling product of TEMPO with $AgSCF_3$, the reaction of $AgSCF_3$ with a normal radical probe vinyl cyclopropane **3**,[17] in the presence of H-donor 1,4-CHD to facilitate quenching of the cyclic carbon radical intermediates, afforded the ring-opened products **4** (5.8:1, dr) and **5** (4.9:1, dr), which were detected by GC−MS and HRMS, as an inseparable mixture in 58% combined yield (eq 3, Scheme

Scheme 2. Kinetic Isotope Effect (KIE) Studies



3). Furthermore, additional direct evidence for the radical mechanism was obtained by trapping the $F_3CS^\bullet$ radical with radical clocks **6**, **8**, and **10**, where the desired cyclization products were isolated in 28%, 15%, and 17%, respectivly (eqs 4−6, Scheme 3).

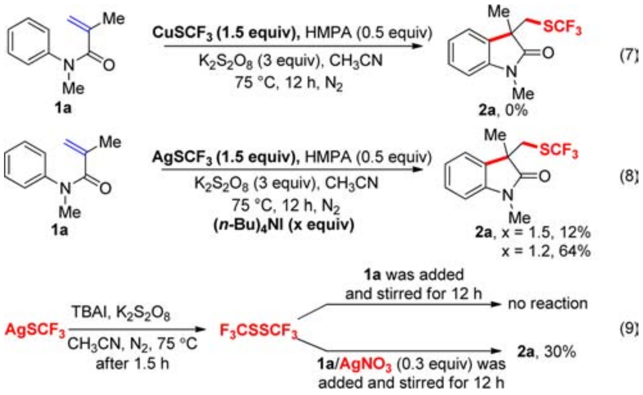
Scheme 3. Radical Trapping Experiments



To gain insight into the role of silver in this radical reaction, several more experiments were carried out. First, replacement of $AgSCF_3$ with $CuSCF_3$ in the standard reaction conditions gave no **2a**, which indicated silver was crucial to this transformation (eq 7, Scheme 4). According to Clark's[4g] and Buchwald's[5] reports, *n*-Bu_4NI (TBAI) could activate $AgSCF_3$ in acetonitrile to afford a reactive source of SCF_3^- via the formation of $[Ag(SCF_3)I]^-$. However, interestingly, the addition of 1.5 equiv of TBAI (TBAI/$AgSCF_3$ = 1:1) almost quenched the reaction with only 12% yield, while markedly increased yield was obtained with slightly reduced TBAI (64% yield, TBAI/$AgSCF_3$ = 0.8:1), which confirmed the key role of the free silver in our reaction system (eq 8, Scheme 4).

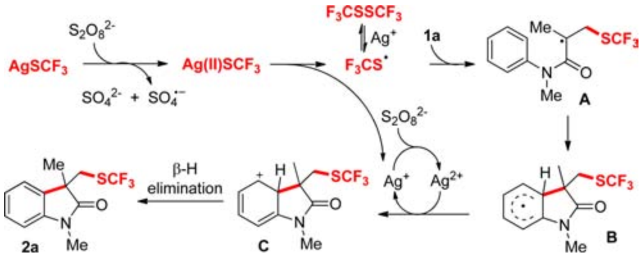
To obtain more details in the reaction process, ^{19}F NMR was next used to track these reactions. It was found that the aryltrifluoromethylation product **2a** increased gradually with the decrease of $AgSCF_3$ (resonated at $\delta = -22.0$ ppm in ^{19}F NMR),[4h] while reaction time was prolonged under the standard conditions. With the addition of 1.5 equiv of TBAI (TBAI/$AgSCF_3$ = 1:1), the $AgSCF_3$ was promptly converted to $[IAg(SCF_3)]^-$ species (resonated at $\delta = -16.0$ ppm in ^{19}F NMR),[4h] which ws consumed rapidly in 1 h, and no additional gain of the product **2a** was observed after that. When the amount of added TBAI was decreased to 0.75 equiv (TBAI/$AgSCF_3$ = 1:2), an *in situ* generated F_3CS anion species (possibly $\{I[Ag(SCF_3)]_2\}^-$, resonated at $\delta = -19.0$ ppm in ^{19}F NMR) was formed, which released $AgSCF_3$ following the capture of I^- anion by the generated Ag(I) as the reaction went on, and then **2a** increased until the $AgSCF_3$ ran out (see Scheme 4, Supporting Information). Since CF_3SSCF_3[13a] was found in all above cases, we further set out to investigate the role of this species. With the addition of TBAI (1.5 equiv, TBAI/$AgSCF_3$ = 1:1) under the standard conditions, ^{19}F NMR monitoring showed $AgSCF_3$ was consumed in 1.5 h to give a CF_3SSCF_3-containing mixture. It was found the aryltrifluoromethythiolated product **2a** was obtained at 30% yield with the subjection of **1a**/$AgNO_3$ (30 mol %), while no **2a** was observed with the subjection of **1a** only to this reaction mixture, which indicated CF_3SSCF_3 could regeneratethe $F_3CS^\bullet$ radical with the help of silver in the reaction system (eq 9, Scheme 4).

Scheme 4. Role of Silver Experiments



On the basis of these observations and previous reports,[14,15] a plausible mechanism is proposed as in Scheme 5. Initially, the oxidation of $AgSCF_3$ by $K_2S_2O_8$ affords $Ag(II)SCF_3$ species, which triggers the $F_3CS^\bullet$ radical after the following single electron transfer course. The addition of $F_3CS^\bullet$ radical to **1a** generates the corresponding alkyl radical intermediate **A**, followed by cyclization to give the aryl radical **B**. Single electron transfer from **B** to an additional 1 equiv of Ag(II), followed by *β*-H elimination, yields the desired product **2a**.

Scheme 5. Proposed Mechanism



In summary, we have developed the first example of silver-mediated aryltrifluoromethylthiolation of activated alkenes to produce valuable trifluoromethylthiole-containing oxindoles, which had easy handling, was practical and straightforward to construct the C(sp^3)-SCF_3 bond, and was of broad functional group compatibility. Mechanistic investigations indicated that this novel transformation proceeded through an unreported $F_3CS^\bullet$ radical addition path.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedure and characterization of all new 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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