

Silver-Mediated Radical Aryltrifluoromethylthiolaton of Activated Alkenes

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(5) 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.



T he 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 (CF₃S) 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-SCF₃ bond was formed directly, are highly desirable. MSCF₃'s, which were previously reported as SCF_3^- sources in S_N^2 reactions,⁴ have recently been developed as coupling partners in several efficient transition metals, including Pd-,⁵ Ni-,⁶ and Cu-mediated⁷ or -catalyzed trifluoromethylthiolations. Although CF₃SCl has long been used to react directly with some nucleophiles to transfer the CF₃S moiety,⁸ its utility was limited as a gaseous and highly toxic reagent. In recent years, several electrophilic trifluoromethylthiolation reagents (SCF₃⁺), including trifluoromethanesulfanylamides,⁹ trifluoromethylathiolated hypervalent iodine,¹⁰ trifluor-omethanesulfonyl hypervalent iodonium ylide,¹¹ and Ntrifluoromethylthiophthalimide,¹² have been developed or used for efficient formation of C-SCF₃, especially the $C(sp^3)$ -SCF₃ bond.

Although a diverse array of organic molecules were trifluoromethylthiolated by the nucleophilic and electrophilic CF₃S 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 CF₃S resources were limited to toxic and gaseous (or volatile) CF₃SH,^{8a} CF₃SCl,^{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 AgSCF₃/ oxidant, affording the $C(sp^3)$ -SCF₃ 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, AgSCF₃ has been previously widely used as a CF₃S⁻ source.¹⁶ Our study commenced by examining the aryltrifluoromethylthiolation of N-methyl-N-phenylmethacrylamide (1a) in the presence of AgSCF₃ (1.5 equiv) at 75 °C. A wide range of oxidants, including PhI(OAc)2, TBHP, NFSI, Oxone, $(NH_4)_2S_2O_{84}$ and $K_2S_2O_{84}$ were first investigated to trigger the F_3CS^{\bullet} radical. To our delight, the desired product 2a could be obtained with several oxidants, and K₂S₂O₈ 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), AgSCF₃ (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 AgSCF₃. 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 AgSCF₃ 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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	Me Me	AgSCF ₃ (1.5 equiv)	Me SCF ₃	

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

			O 75 °C, 12 h, CH ₃ CN (0.1	N ₂ M) 2a	,)⊂O N Me		
entry	oxidant (equiv)	base (equiv)	yield ^{b} (%)	entry	oxidant (equiv)	base (equiv)	yield ^{b} (%)
1	$Phl(OAc)_2$ (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
ъ:			1 ()) 1	. (2.0 .) 11 (15 :): CILCN(2 I)	

^{*a*}Reaction conditions: **1a** (0.2 mmol, 1.0 equiv), AgSCF₃ (1.5 equiv), oxidant (2.0 equiv), and base (1.5 equiv) in CH₃CN (2 mL) at 75 °C for 12 h. ^{*b*}Isolated yield. ^{*c*}CH₃CN (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





^{*a*}Reaction conditions: **1** (0.2 mmol, 1.0 equiv), AgSCF₃ (1.5 equiv), $K_2S_2O_8$ (3.0 equiv), and HMPA (0.5 equiv) in CH₃CN (3.0 mL) at 75 °C for 12 h. ^{*b*}AgSCF₃ (2.0 equiv), $K_2S_2O_8$ (4.0 equiv), HMPA (1.0 equiv). ^{*c*}AgSCF₃ (2.0 equiv), $K_2S_2O_8$ (4.0 equiv). ^{*d*}AgSCF₃ (2.5 equiv), $K_2S_2O_8$ (5.0 equiv).

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 (R₁). 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 Nphenylacrylamides 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 K₂S₂O₈ and AgSCF₃. Both electron-donating groups, such as OMe and Me, and electron-withdrawing groups, such as CF₃, F, Cl, Br, I, CO₂Et, Ac, and NO₂, 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 (R₂) 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.

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 ratedetermining. While we failed to capture the coupling product of TEMPO with AgSCF₃, the reaction of AgSCF₃ 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).

To gain insight into the role of silver in this radical reaction, several more experiments were carried out. First, replacement of AgSCF₃ with CuSCF₃ 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's⁵ reports, *n*-Bu₄NI (TBAI) could activate AgSCF₃ in acetonitrile to afford a reactive source of SCF₃⁻ via the formation of [Ag(SCF₃)I]⁻. However, interestingly, the addition of 1.5 equiv of TBAI (TBAI/AgSCF₃ = 1:1) almost quenched the reaction with only 12% yield, while markedly increased yield was obtained with slightly reduced TBAI (64% yield, TBAI/AgSCF₃ = 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, ¹⁹F NMR was next used to track these reactions. It was found that the aryltrifluoromethylation product **2a** increased gradually with the decrease of AgSCF₃ (resonated at $\delta = -22.0$ ppm in ¹⁹F NMR),^{4h} while reaction time was prolonged under the standard conditions. With the addition of 1.5 equiv of TBAI (TBAI/ AgSCF₃ = 1:1), the AgSCF₃ was promptly converted to [IAg(SCF₃)]⁻ species (resonated at $\delta = -16.0$ ppm in ¹⁹F Scheme 4. Role of Silver Experiments



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/ AgSCF₃ = 1:2), an *in situ* generated F_3CS anion species (possibly {I[Ag(SCF₃)]₂}⁻, resonated at $\delta = -19.0$ ppm in ¹⁹F NMR) was formed, which released AgSCF₃ following the capture of I^- anion by the generated Ag(I) as the reaction went on, and then 2a increased until the AgSCF₃ ran out (see Scheme 4, Supporting Information). Since CF₃SSCF₃^{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, ¹⁹F NMR monitoring showed AgSCF₃ was consumed in 1.5 h to give a CF₃SSCF₃containing mixture. It was found the aryltrifluoromethythiolated product 2a was obtained at 30% yield with the subjection of 1a/ AgNO₃ (30 mol %), while no 2a was observed with the subjection of 1a only to this reaction mixture, which indicated CF₃SSCF₃ could regenerate the F₃CS[•] radical with the help of silver in the reaction system (eq 9, Scheme 4).

On the basis of these observations and previous reports,^{14,15} a plausible mechanism is proposed as in Scheme 5. Initially, the





oxidation of AgSCF₃ by $K_2S_2O_8$ affords Ag(II)SCF₃ 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 cyclication 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**.

In summary, we have developed the first example of silvermediated aryltrifluoromethylthiolation of activated alkenes to produce valuable trifluoromethylthiole-containing oxindoles, which had easy handling, was practical and straightforward to construct the $C(sp^3)$ -SCF₃ 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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