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Tandem Trifluoromethylthiolation/Aryl Migration of Aryl Alkynoates to Trifluoromethylthiolated Alkenes

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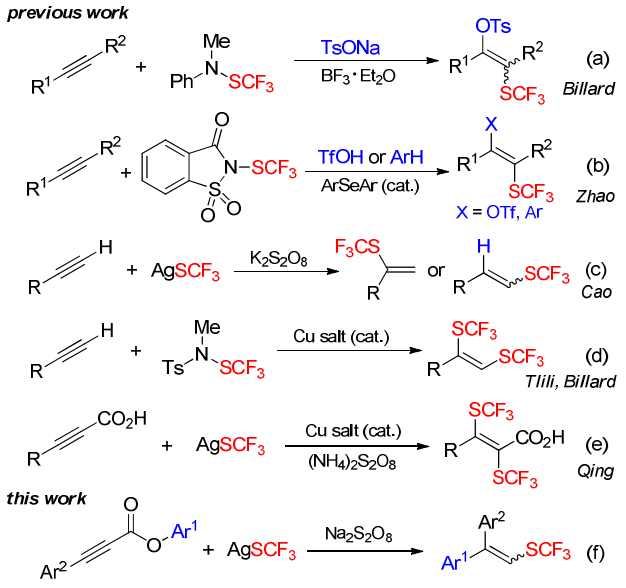
A trifluoromethylthiolation initiated aryl migration of aryl alkynoates was disclosed. This protocol employs $AgSCF_3$ as the SCF_3 source and MeCN as both the solvent and the hydrogen source. It provides a new access to trifluoromethylthiolated alkenes from readily available substrates and reagents.

In the past few years, the trifluoromethylthio group (SCF_3) has experienced a strong acceleration of interest.[1] This renewed interest apparently is stimulated by the strong electron-withdrawing power and extremely high lipophilicity of SCF_3 group.[2] The development of new trifluoromethylthiolating reagents[3] and new (C–H,[4] C–B,[5] C–N,[6] C–O[7] and C–X (X = Cl, Br, I)[8]) trifluoromethylthiolation reactions have provided sought-after strategies for the preparation of SCF_3-containing compounds. However, most of the recent research interests are focused on the preparation of trifluoromethylthiolated arenes, alkynes, and alkanes. Methods for the synthesis of trifluoromethylthiolated alkenes are limited.

Normally, trifluoromethylthiolated alkenes are prepared by transition-metal-mediated/catalyzed trifluoromethylthiolation of vinyl boronic acids, vinyl halides or vinyl triflates.[3b,3e,5b,5f,8f,9] Recently, the C–H trifluoromethylthiolation of alkenes has been reported by Glorius[10] and Shen,[3m] respectively. Very recently, our group disclosed a decarboxylative trifluoromethylthiolation of cinnamic acids for the preparation of trifluoromethylthiolated alkenes.[11] Besides the above trifluoromethylthiolation of vinyl substrates, the addition of SCF_3 group to alkynes has also been explored as alternative approaches to trifluoromethylthiolated alkenes.[12,13] For example, Billard and co-workers disclosed the oxytrifluoromethylthiolation of alkynes with electrophilic



Scheme 1 Methods for the preparation of trifluoromethylthiolated alkenes from alkynes.

trifluoromethylthiolating reagent under $BF_3 \cdot Et_2O$ activation (Scheme 1a).[12a] Recently, Zhao reported a selenide-catalyzed regio- and stereoselective difunctionalization of alkynes to afford trifluoromethylthiolated alkenyl triflates and arenes (Scheme 1b).[12b] The *anti*-Markovnikov- and Markovnikov-selective hydrotrifluoromethylthiolation of terminal alkynes was developed by Cao and co-workers (Scheme 1c).[12c] Very recently, the stereoselective bis-trifluoromethylthiolation of alkynes were respectively reported by Tlili and Billard (Scheme 1d)[12d] as well as our group (Scheme 1e)[12e]. In continuation of our research interest in difunctionalization-type fluoroalkylation reactions,[12e,14] herein we describe a tandem trifluoromethylthiolation/aryl migration of aryl alkynoates with $AgSCF_3$ (Scheme 1f). This protocol provides a new access to trifluoromethylthiolated alkenes.

Aryl alkynoates are easily available building blocks for the preparation of various 3-functionalized coumarins via cascade

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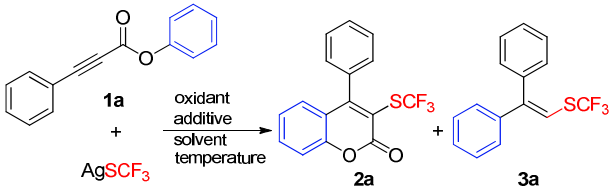
intramolecular cyclization.[15] For example, the trifluoromethylation, carboethoxydifluoromethylation, and trifluoromethylthiolation of aryl alkynoates have been reported by the groups of Lu&Ding,[15b] Fu,[15e] and Wang[13g] for the preparation of the corresponding fluorinated coumarins. During the investigation of the reaction mechanism of bis-trifluoromethylthiolation of alkynes,[12e] it was interesting to find that the reaction of 3-phenylpropiolate (**1a**) and $AgSCF_3$ in the presence of $Na_2S_2O_8$ in MeCN at 80 °C afforded trifluoromethylthiolated coumarin (**2a**) as the minor product and trifluoromethylthiolated alkene (**3a**) as the major product (Table 1, entry 1). This result was in striking contrast to the reported trifluoromethylthiolation/cyclization of **1a** in DMSO,[13g] which gave **2a** as the major product (entry 2).

Intrigued by the above results, we then optimized the reaction conditions to improve the yield of **3a**. To explore the unique effect of solvents to this reaction, other solvents, such as DMF, acetone, $MeNO_2$, and PhCN, were examined, but neither higher yield nor better chemoselectivity was obtained (entries 3-6). Further investigation of the reaction temperature revealed that 100 °C was optimal, giving **3a** in 65% yield (entries 7-9). Subsequently, switching the oxidant from $Na_2S_2O_8$ to $K_2S_2O_8$ or $(NH_4)_2S_2O_8$ could not give better results (entries 10 and 11). Finally, different additives including copper salts ($CuSO_4$ and CuI) and hydrogen sources (1,4-CHD and Et_3SiH) were investigated (entries 12-15). However, the yield of **3a** was not improved.

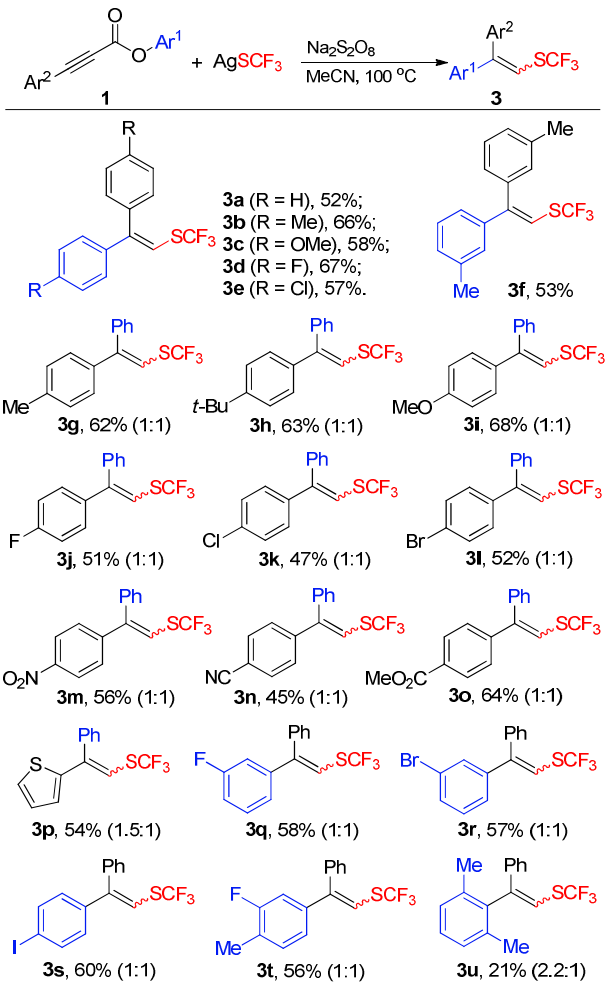
Table 1. Optimization of reaction conditions[a]



Entry	Oxidant	Additive	Solvent	Temperature	Yield (**2a**/**3a**, %)[b]
1	$Na_2S_2O_8$	—	MeCN	80 °C	8/44
2	$Na_2S_2O_8$	—	DMSO	80 °C	81/5
3	$Na_2S_2O_8$	—	DMF	80 °C	10/8
4	$Na_2S_2O_8$	—	Acetone	80 °C	trace/0
5	$Na_2S_2O_8$	—	$MeNO_2$	80 °C	0/0
6	$Na_2S_2O_8$	—	PhCN	80 °C	0/0
7	$Na_2S_2O_8$	—	MeCN	60 °C	trace/38
8	$Na_2S_2O_8$	—	MeCN	100 °C	6/65
9	$Na_2S_2O_8$	—	MeCN	120 °C	trace/33
10	$K_2S_2O_8$	—	MeCN	100 °C	8/61
11	$(NH_4)_2S_2O_8$	—	MeCN	100 °C	6/53
12	$Na_2S_2O_8$	$CuSO_4$	MeCN	100 °C	trace/49
13	$Na_2S_2O_8$	CuI	MeCN	100 °C	0/0
14	$Na_2S_2O_8$	1,4-CHD	MeCN	100 °C	trace/trace
15	$Na_2S_2O_8$	Et_3SiH	MeCN	100 °C	trace/trace

[a]Reaction conditions: **1a** (0.1 mmol), $AgSCF_3$ (0.25 mmol), oxidant (0.25 mmol), additive (0.1 mmol), solvent (2.0 mL), temperature, under N_2, 2 h. [b]Yields determined by ^{19}F NMR spectroscopy using trifluoromethylbenzene as an internal standard.

Table 2. Substrate scope of trifluoromethylthiolation of aryl alkynoates[a]



[a]Reaction conditions: **1** (0.2 mmol), $AgSCF_3$ (0.5 mmol), $Na_2S_2O_8$ (0.5 mmol), MeCN (4.0 mL), 100 °C, under N_2, 2 h, isolated yields.

With the optimized conditions in hand, we then explored the scope of this tandem trifluoromethylthiolation/aryl migration reaction. As shown in Table 2, various aryl alkynoates **1** underwent this transformation to afford the corresponding trifluoromethylthiolated alkenes **3** in moderate to good yields. Diaryl alkynoates with either electron-donating or electron-withdrawing substituents on both of the benzene rings (**1b**-**f**) reacted smoothly to give the desired products. Substrates with different substituents, such as alkyl (**1g** and **1h**), methoxy (**1i**), halogen (**1j–l**), nitro (**1m**), nitrile (**1n**), and ester (**1o**), on the benzene ring attached onto the triple bond were all compatible under the standard conditions. Noticeably, the reaction was also workable when a thiophenyl group was substituted on the alkyne (**1p**). Finally, different substituents on the phenoxy ring (**1q**-**t**) also showed high tolerance under standard conditions, affording products **3q**-**t** in good yields. It is worth mentioning that substrate **1u** with two methyl groups substituted at the *ortho*-position of the phenoxy ring gave the

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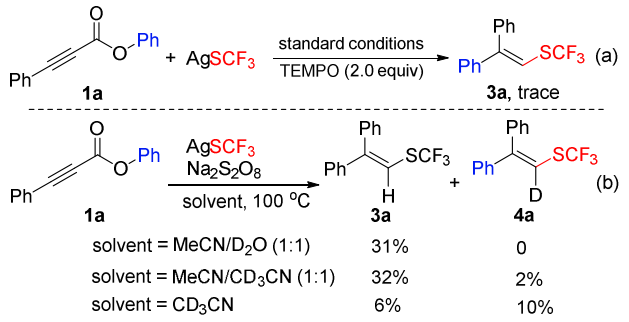
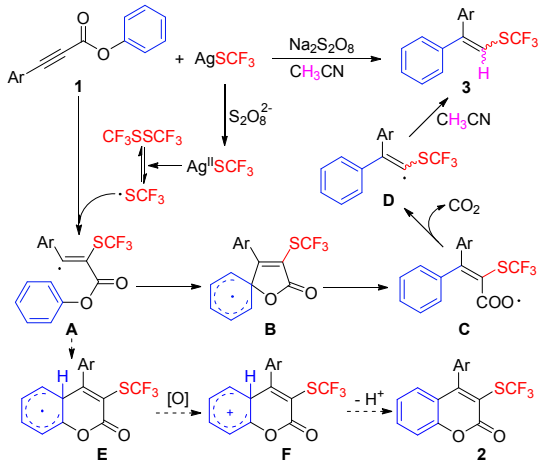
desired product **3u** in 21% yield, probably due to the steric hindrance.

To gain insights into the reaction mechanism, preliminary mechanistic experiments were carried out (Scheme 2). Addition of 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO), a well-known free radical scavenger, to the standard reaction conditions of **1a** could significantly inhibit the formation of desired product **3a** (Scheme 2a), which indicated that a radical pathway was probably involved in this reaction. Furthermore, several deuterium-labeling experiments were performed to elucidate the hydrogen source of trifluoromethylthiolated alkenes (Scheme 2b). The reaction in MeCN/D_2O gave **3a** in 35% yield. No deuterated product **4a** was detected by ^{19}F NMR or GC-MS. **4a** was formed in MeCN/CD_3CN or CD_3CN (see the supporting information), These results showed that MeCN served as the hydrogen atom source in this reaction. As silver (I) trifluoromethanethiolate was prepared from the reaction of AgF and CS_2 in CH_3CN, the exact molecular formula of silver (I) trifluoromethanethiolate is $3AgSCF_3{\cdot}CH_3CN$.[4i] This resulted in the formation of compound **3a** when CD_3CN was used as the solvent.

On the basis of the results above and previous reports,[16] a plausible reaction mechanism is depicted in Scheme 3. Initially, $AgSCF_3$ is oxidized by $Na_2S_2O_8$ to furnish the SCF_3 radical via $Ag^{II}SCF_3$.[4h,4i,17] Then, the addition of SCF_3 radical to aryl alkynoates **1** generates intermediate **A**, which could undergo ipsocyclization to give the spiro intermediate **B**.[16] Subsequently,



Scheme 2 Mechanistic investigation.



Scheme 3 Proposed reaction mechanism.

1,4-aryl migration on an ester moiety, followed by decarboxylation of carboxyl radical **C** yields the vinyl radical **D**. Finally, the radical **D** abstracts hydrogen from MeCN to afford the desired products **3**. Alternatively, vinyl radical **A** might undergo 6-*endo* cyclization/oxidation/deprotonation processes to give trifluoromethylthiolated coumarins **2** as the major product in DMSO.[13g] The better solubility of $Na_2S_2O_8$ in DMSO than that in MeCN might accelerate the oxidation of radical intermediate **E** to cation intermediate **F**, thus providing **2** as the major product. However, it is not clear how exactly the solvents affect the chemoselectivity in this reaction at the moment.

In conclusion, we have developed a new approach to trifluoromethylthiolated alkenes by oxidative trifluoromethylthiolation of aryl alkynoates with $AgSCF_3$. Primary mechanistic investigations revealed that this reaction proceeds through a radical trifluoromethylthiolation-initiated aryl migration process. Further explorations of the reaction mechanism and other tandem fluoroalkylation/migration reactions are in progress in our laboratory.

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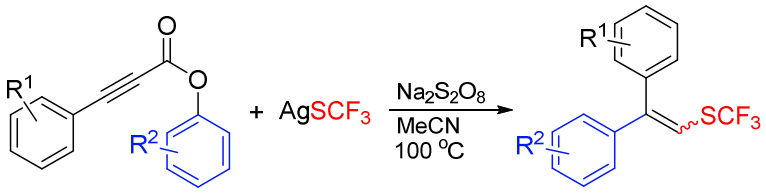

The oxidative trifluoromethylthiolation of aryl alkynoates with $AgSCF_3$ provided a new access to trifluoromethylthiolated alkenes.