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## Copper(I)-Promoted Trifluoromethylthiolation of Arenediazonium salts with AgSCF3

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The compound with a aryl trifluoromethyl sulfides (ArSCF<sub>3</sub>) structural motif have recently attracted great attention as pharmaceuticals and agrochemicals.<sup>1</sup> Due to the strong electronwithdrawing effect and high lipophilicity, the trifluoromethylthio group (SCF<sub>3</sub>) could enhance the metabolic stability and bioavailability of the parent molecules. Since natural compounds containing SCF<sub>3</sub> are uncommon, it is urgently needed to develop synthetic methodologies of trifluoromethylthio compound.<sup>2</sup> As the traditional method for introduction of SCF<sub>3</sub> into aromatic backbones, the chlorine-fluorine exchange reactions of trihalogenomethyl thioethers usually suffer from harmful waste and multistep synthesis under harsh reaction conditions (Scheme 1).<sup>3</sup> Through the trifluoromethylations of sulfur-containing substrates precursors, such as thiols,<sup>4</sup> thiocyanates<sup>5</sup> and disulfides,<sup>6</sup> these synthetic methods are limited by substrate availability and/or functional group tolerance. By the transition metal-catalyzed/mediated conversion of halogen7 or boric acid substituents,<sup>8</sup> the one-step trifluoromethylthiolation have been carried out using easily stored, inexpensive and handled reagents as SCF<sub>3</sub> or CF<sub>3</sub> sources. With nucleophilic and electrophilic trifluoromethylthio reagents recently, direct C-H aromatic trifluoromethylthiolation was also developed remarkably.9 The electrophilic trifluoromethylthiolation with aryl-magnesium or lithium reagents have been exemplified employing CF<sub>3</sub>SCl or N-SCF<sub>3</sub> reagents.<sup>10</sup> The straight-forward Sandmeyer-type reaction are potential and easy-to-handle alternatives for the trifluoromethylthiolations, through arenediazonium salts from cheap and broadly available aromatic amines.11

An efficient method for trifluoromethylthiolation of arenediazonium salts has been developed in mild conditions with a stable and convenient AgSCF<sub>3</sub>. It provides a straightforward and convenient way for the synthesis of trifluoromethylthiolated compound from diazonium salts in moderate to good yields.

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Scheme 1. Methods for aryl trifluoromethylthiolation.

Firstly reported by J. H. Clark,<sup>12</sup> the classical Sandmeyer-type reaction system were not suitable for the substrates of electrondonating groups, using the expensive and unstable copper(I) trifluoromethanethiolate (CuSCF<sub>3</sub>) (Scheme 1). Through reaction system of CuSCN and inexpensive Ruppert-Prakash reagent (TMSCF<sub>3</sub>) by Goossen,<sup>13, 14</sup> aryl trifluoromethyl thioethers are exclusively formed using sodium thiocyanate (NaSCN) as a sulfur source. With the unstable Me<sub>4</sub>NSCF<sub>3</sub> as the trifluoromethylthiolation reagent, the Sandmeyer-type reaction could also be carried out in the presence of CuSCN,<sup>15</sup> even under condition of metal-free.<sup>16</sup> Recently, the toxic and hard-to-get bis(trifluoromethyl) disulfide (CF<sub>3</sub>S)<sub>2</sub> can also be employed in the straight-forward Sandmeyer-type trifluoromethylthiolation of readily available arenediazonium salts, in the presence of photocatalyst (eosin Y) by Wangelin.<sup>17</sup> Although some important achievements have been made in Sandmeyer trifluoromethylthiolation, some drawbacks are still found in these reaction systems. For example, the trifluoromethylthiolation reagents employed in these approaches are toxic or unstable to

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storage for extended periods. Recently, Y. Yang and coworker have developed a low-cost method for the preparation of CuSCF<sub>3</sub> via triphenylphospine-mediated deoxygenative reduction of Langlois' reagent (CF<sub>3</sub>SO<sub>2</sub>Na) in the presence of CuCl.<sup>7h</sup> However, the preparation procedure is somewhat complicated which must be carried out in high temperature under nitrogen atmosphere. Moreover, excessive amount of triphenylphosphine is also employed in this procedure, generating a large amount of environmentally harmful Ph<sub>3</sub>P=O as by-product. As the relatively inexpensive, stable and easy-to-handle reagent, AgSCF<sub>3</sub> could form a reactive source of ¬SCF<sub>3</sub> in the presence of n-Bu<sub>4</sub>NI or KI.<sup>18</sup> Intrigued by the Sandmeyer trifluoromethylation of aromatic amines and trifluoromethylthiolation with AgSCF3,19, 20 we have been trying to develop effective approaches for metalmediated trifluoromethylthiolation of arenediazonium salts with AgSCF<sub>3</sub>.

### Table 1

Optimization of the reaction conditions.<sup>a</sup>

		AgSCF <sub>3</sub> , Cu salt, Base, Additive			SCF <sub>3</sub>	
F		Solvent, air, rt, 12 h			'h	
					2a	
Entry	Cu salt	[Cu] (mmol)	Base	Additive	Solvent	<b>2a</b> Yield (%) <sup>b</sup>
1	CuCl	0.01	K <sub>2</sub> CO <sub>3</sub>	n-Bu <sub>4</sub> NI	CH <sub>3</sub> CN	13
2	CuBr	0.01	K <sub>2</sub> CO <sub>3</sub>	n-Bu <sub>4</sub> NI	CH <sub>3</sub> CN	10
3	CuI	0.01	K <sub>2</sub> CO <sub>3</sub>	n-Bu <sub>4</sub> NI	CH <sub>3</sub> CN	25
4	CuSCN	0.01	$K_2CO_3$	n-Bu <sub>4</sub> NI	CH <sub>3</sub> CN	21
5	CuBr <sub>2</sub>	0.01	$K_2CO_3$	n-Bu <sub>4</sub> NI	CH <sub>3</sub> CN	14
6	Cu(OAc) <sub>2</sub>	0.01	$K_2CO_3$	n-Bu <sub>4</sub> NI	CH <sub>3</sub> CN	20
7	Cu(OTf) <sub>2</sub>	0.01	$K_2CO_3$	n-Bu <sub>4</sub> NI	CH <sub>3</sub> CN	19
8	Cu(MeCN) <sub>4</sub> BF <sub>4</sub>	0.01	$K_2CO_3$	n-Bu <sub>4</sub> NI	CH <sub>3</sub> CN	23
9	CuI	0.02	$K_2CO_3$	n-Bu <sub>4</sub> NI	CH₃CN	32
10	CuI	0.05	K <sub>2</sub> CO <sub>3</sub>	n-Bu <sub>4</sub> NI	CH <sub>3</sub> CN	53
11	CuI	0.1	$K_2CO_3$	n-Bu <sub>4</sub> NI	CH <sub>3</sub> CN	80
12	CuI	0.1	$K_2CO_3$	-	CH <sub>3</sub> CN	82
13	CuI	0.1	Na <sub>2</sub> CO <sub>3</sub>	-	CH <sub>3</sub> CN	46
14	CuI	0.1	NaHCO <sub>3</sub>	-	CH <sub>3</sub> CN	49
15	CuI	0.1	$Cs_2CO_3$		CH <sub>3</sub> CN	52
16	CuI	0.1	K <sub>2</sub> CO <sub>3</sub>	-	DMSO	59
17	CuI	0.1	K <sub>2</sub> CO <sub>3</sub>	-	DMF	63
18	CuI	0.1	K <sub>2</sub> CO <sub>3</sub>	-	NMP	50
19 <sup>c</sup>	CuI	0.1	K <sub>2</sub> CO <sub>3</sub>	-	CH <sub>3</sub> CN	78

<sup>a</sup> Reaction conditions: **1a** (0.1 mmol), AgSCF<sub>3</sub> (0.15 mmol, 1.5 equiv.), copper salt, base (0.2 mmol, 2.0 equiv.), additive (0.2 mmol, 2.0 equiv). solvent (1 mL), <sup>b</sup> Yields were determined by <sup>19</sup>F NMR spectroscopy based on 1a using 4,4'-difluorobiphenyl as an internal standard. <sup>c</sup> under N<sub>2</sub>.

Initially, the model substrate **1a** of trifluoromethylthiolation reaction was screened to investigate the effects of different copper salts, bases, solvents, and additives (Table 1). There is only 13% yield of trifluoromethylthiolated product to be obtained, using 0.01 mmol CuCl as the catalyst. Investigating copper catalyst such as CuCl, CuBr, CuI, CuSCN, CuBr<sub>2</sub>, Cu(OAc)<sub>2</sub>, Cu(OTf)<sub>2</sub> and Cu(MeCN)<sub>4</sub>BF<sub>4</sub> (entries 1–8), CuI was suggested to be best choice for the reaction with the highest yield. With increasement of the amount of CuCl, the improved significantly yield of 2a show that catalytic amounts of copper salt were insufficient to achieve high yields. Surprisingly, a slightly higher yield of 82% was achieved in the absence of n-Bu<sub>4</sub>NI (entry 12). Several bases such as Na<sub>2</sub>CO<sub>3</sub>, NaHCO<sub>3</sub>, Cs<sub>2</sub>CO<sub>3</sub> and K<sub>2</sub>CO<sub>3</sub> were also examined to further optimize the reaction conditions. Obviously, K<sub>2</sub>CO<sub>3</sub> is most suitable for achievement of corresponding product 2a in the highest yield (entries 12-15). The influence of solvents was also investigated in such solvents as DMSO, DMF and NMP (entries 16-18)

besides CH<sub>3</sub>CN. Furthermore, the reaction was carried out under nitrogen to gain the expected product. A slightly higher yield in air shows that the reaction proceeds can be carried through in an easy-to-handle approach. (entry 19).

Based on the optimized reaction conditions (Table 1, Entry 12), the substrate scope of oxidative trifluoromethylthiolation for arenediazonium salts was investigated as summarized in Table 2. With the electron-donating substituent in aromatic ring as aryl, alkyl, alkoxy and methylthio, the arenediazonium salt derivatives reacted smoothly to give the corresponding trifluoromethylthiolated products (2a-2i) in reasonable yields of 58-72%. The 2-naphthyl diazonium salt was also suitable for the reaction system to give product 2j in 60% yield. Examined the substrate with electron-withdrawing substituent in aromatic ring, such as halogen (1k and 1l), acetyl (1m and 1n), carbomethoxy (10 and 1p) and cyano (1q and 1r), the arenediazonium salt derivatives can tolerate this reaction system more efficiently with slightly higher yields (2k-2u, 73-92%, Table 2) than the electrondonating substituent. Comparing with aromatic substrates with in nitro substituent in ortho (2t, 89%) and meta- (2u, 90%) position, the pretty higher yield of the electron-withdrawing nitro in para (2s, 92%) position indicated that electronic effect rather than steric effects remains to be the most important influence to the reaction system. Contrary to other SCF<sub>3</sub> or CF<sub>3</sub> sources, the trifluoromethylthiolated vield of electron-deficient substrates is overall higher than the electron-rich substrates using AgSCF<sub>3</sub>. In addition, some arenediazonium salt derivatives, bearing pyridine moiety (1v) and electron-withdrawing substituent, can be converted to the corresponding trifluoromethylthiolated products in higher yields to the reported.11-16

#### Table 2.

Trifluoromethylthiolation of Arenediazonium salts under the optimized reaction conditions.<sup>*a,b*</sup>



<sup>&</sup>lt;sup>a</sup> Reaction conditions: 1a-1w (0.5 mmol), AgSCF<sub>3</sub> (0.75 mmol, 1.5 equiv.), CuI (0.5 mmol, 1.0 equiv.), K<sub>2</sub>CO<sub>3</sub> (1.0 mmol, 2.0 equiv.), CH<sub>3</sub>CN (5 mL), air, rt, 12 h. b Isolated yields.

Secondarily, this reaction system is feasible particularly for large-scale applications due to its irreplaceable advantages as easily available raw material, air insensitivity and mild reaction conditions. To illustrate the practical application of this transformation, the reaction was scaled up using 5 mmol of the substrate 1s. The corresponding trifluoromethylthiolated product

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**2s** was also obtained in isolated yield of 85% through this reaction proceeds under the optimal conditions.

To elucidate a plausible reaction mechanism, some control experiments were carried as shown in Table 3. Without copper salt in the reaction system, only 10% desired product 2a was detected. Obviously, the reactivity of metallic silver is low without copper salt. Using 1.0 equivalents of Cu(MeCN)<sub>4</sub>BF<sub>4</sub> as catalyst instead of CuI, the yield of 2a was apparently declined to 40%. Added 1.0 equivalents of KI to the above reaction system, the improved yield 78% of 2a indicated that iodine anion (I-) play a significant role in this reaction system. As the previous reported,<sup>21</sup> the active species [Ag(SCF<sub>3</sub>)I]<sup>-</sup> can generate through this reaction system with the stronger nucleophilicity than AgSCF<sub>3</sub>. The result of the above investigation show further that CuSCF<sub>3</sub> species will generate on site in the presence of AgSCF<sub>3</sub> or [Ag(SCF<sub>3</sub>)I]<sup>-</sup> with copper salt.<sup>22</sup> Added 4.0 equivalents of the radical-trapping reagent TEMPO (2,2,6,6-tetramethyl-1oxylpiperidine), the reaction was obviously suppressed to give only 8% products under the optimal conditions. It indicates that the reaction may proceed via a radical pathway. The investigations of reaction temperature suggest that the yield of product 2a decreases significantly by increase of the reaction temperature, along with the augment of the iodobenzene as main by-product (See the Supporting Information).

### Table 3

Control experiments

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$\begin{array}{c} \begin{array}{c} & & \\ & & \\ & & \\ & & \\ \end{array} \end{array} \xrightarrow{\begin{array}{c} \\ \\ \\ \end{array} } \begin{array}{c} \\ \\ \\ \\ \\ \\ \\ \\ \\ \end{array} \end{array} \xrightarrow{\begin{array}{c} \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\$								
	1a		2	a				
Entry	Cu salt	KI	TEMPO	<b>2a</b> Yield (%) <sup>c</sup>				
$1^a$	-	-	-	10%				
$2^a$	Cu(MeCN) <sub>4</sub> BF <sub>4</sub> (1.0)	-	-	40%				
3 <i>a</i>	Cu(MeCN) <sub>4</sub> BF <sub>4</sub> (1.0)	1.0	-	78%				
$4^b$	CuI (1.0)	-	2.0	21%				
$5^b$	CuI (1.0)	-	4.0	8%				

Reaction conditions: **1a** ( $^a$  0.1 mmol, 1 equiv;  $^b$  0.5 mmol, 1 equiv.), AgSCF<sub>3</sub> (1.5 equiv.), K<sub>2</sub>CO<sub>3</sub> (2.0 equiv.), CH<sub>3</sub>CN (5 mL), air, rt, 12 h, Cu salt, KI, and TEMPO (equiv.). <sup>c</sup>Yield was determined by <sup>19</sup>F NMRspectroscopy using 4,4'- diffuorobiphenyl as an internal standard.

Based on the above experimental results, a plausible mechanism was proposed about the copper(I)-promoted trifluoromethylthiolation process *via*  $[Ag(SCF_3)I]^{-}$  as shown in Scheme 2. Firstly transferred a single electron (SET) to arenediazonium salts 1, Cu(I) afford aryl radicals and Cu(II) species. Then, Cu(II)SCF<sub>3</sub> species will generate on-site quickly through combination of Cu(II) and active species  $[Ag(SCF_3)I]^{-}$  from the reaction of  $AgSCF_3$  and iodine anion. The desired product **2a** can achieve by aryl radicals with Cu(II)SCF<sub>3</sub>.



Scheme 2. Plausible mechanism.

In summary, we have developed an efficient preparation method through copper(I)-promoted trifluoromethylthiolation for the various arenediazonium salts, using a stable and inexpensive AgSCF<sub>3</sub> in moderate to good yields and mild reaction conditions. A preliminary mechanistic investigation suggests that this reaction process *via* a radical pathway. With the extensive reaction tolerance, mild reaction condition and the easy-to-get raw material, this method achieve a useful and practical strategy in the synthesis of aryl trifluoromethyl sulfides, for great

potential application of synthetic, medicinal, and agrochemical research.

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### **Graphical Abstract**

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### **Supplementary Material**

Supplementary material for this article is available online at http://dx.doi.org/10.1016/j.tetlet.

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An efficient method with a stable and convenient AgSCF<sub>3</sub> provides an additional way for the synthesis of trifluoromethylthiolated compound with arenediazonium salts, in very mild conditions and good yield.

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Highlights

The first example of the stable AgSCF<sub>3</sub> for trifluoromethylthiolation of arenediazonium salts.

An efficient method for trifluoromethylthiolation of arenediazonium salts was developed.

The mild reaction condition.

The trifluoromethylthiolated products with electron-withdrawing substituent were obtained in higher yields.

