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Cascade Reaction of Propargyl Amines with $AgSCF_3$, as Well as One-Pot Reaction of Propargyl Amines, $AgSCF_3$, and Di-*tert*-butyl Peroxide: Access to Allenyl Thiocyanates and Allenyl Trifluoromethylthioethers

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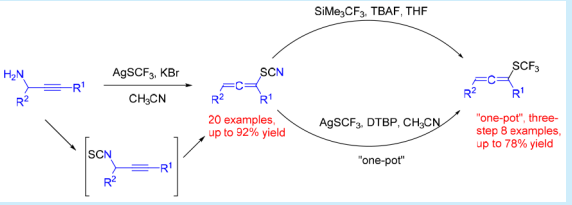
Supporting Information

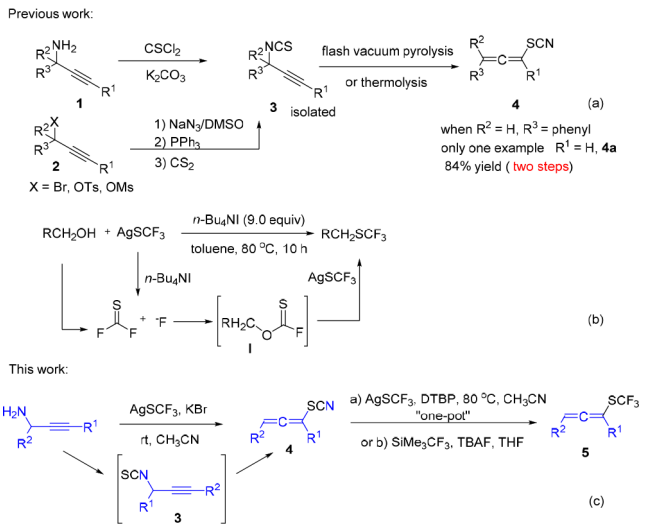
ABSTRACT: An efficient cascade reaction of propargyl amines with $AgSCF_3$ and KBr is developed, affording allenyl thiocyanates at room temperature in high yields. This transformation proceeds via the in situ formation of isothiocyanate intermediates, followed by a [3,3]-sigmatropic rearrangement. The resulting allenyl thiocyanates bearing 3-(electro-donating phenyl) substitutions without isolation can then be reacted with di-*tert*-butyl peroxide and $AgSCF_3$ under reflux to generate novel allenyl trifluoromethylthioether compounds in moderate to good yields via a "one-pot" three-step process.



Allenes have been found in natural products and have been incorporated into drugs and materials.[1,2] The last two decades have witnessed an increasing popularity of allenes as building blocks for a variety of chemical transformations.[2] Organic thiocyanates also exhibit biological and pharmaceutical activities,[3] and they are important precursors for the synthesis of various sulfur-containing compounds, including heterocycles.[4] Many methods have been developed for the construction of organic thiocyanates.[5] However, access to allenyl thiocyanate derivatives is very limited.[6] In 2001, Banert and co-workers reported that propargyl isothiocyanates **3** can be prepared from propargyl amines **1** and thiophosgene or via a multistep sequence from propargylic electrophiles **2** (Scheme 1a).[6a] The equilibration between isolated isothiocyanate **3** and allenyl thiocyanates **4** was established. When R^3 was an aryl, only one example of 3-phenyl allenyl thiocyanate **4a** was reported (Scheme 1a).[6a] However, trisubstituted allenyl thiocyanates (**4**) with R^3 as an aryl have never been synthesized. In addition, thiophosgene is highly toxic, making it challenging to safely handle and store, and its high electrophilic property is also disadvantageous to the functional group tolerance and selectivity. Thus, a safe, convenient, efficient method to access to a variety of allenyl thiocyanates is still in high demand.

The trifluoromethylthio (SCF_3) group possesses remarkable electro-withdrawing character and extremely high lipophilicity.[7] Much effort has been devoted to incorporating the SCF_3 group into organic molecules[8] for the improvement of membrane permeability and absorption rate.[7] However, to the best of our knowledge, the SCF_3 group has never been introduced into allenyl scaffolds. It is well-known that there is an equilibrium between trifluoromethanethiolate with carbonothioic difluoride and fluoride.[9] In 2015, the Qing group successfully applied this reactivity to the direct dehydroxytrifluoromethylthiolation of alcohols with $AgSCF_3$ (see Scheme 1b).[8a] Recently, the same transformation and several other elegant transformations were

Scheme 1. Different Methods for Isothiocyanates and Allenyl Thiocyanates, as Well as for Trifluoromethylthiolation



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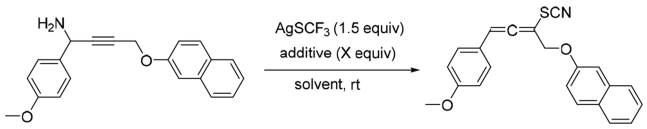
realized using trifluoromethanesulfonamides,[10a] $(Me_4N)SCF_3$,[10b,c] (bpy)$CuSCF_3$,[10d] and sulfuration of difluorocarbene with elemental sulfur.[10e,f] For example, the Schoenebeck group reported the synthesis of isothiocyanates from anilines and aliphatic amines with $(Me_4N)SCF_3$ under Et_3N,[10c] but never reported the reactivity of propargyl amines. Herein, we report that propargyl amines react with carbonothioic difluoride derived from $AgSCF_3$ in the presence of KBr at room temperature to give propargyl isothiocyanate intermediates, which undergo in situ [3,3]-sigmatropic rearrangement to generate allenyl thiocyanates. Allenyl thiocyanates bearing 3-(electron-donating phenyl) substitutions without isolation could then be converted, in the presence of di-*tert*-butyl peroxide (DTBP) and $AgSCF_3$, to the corresponding allenyl trifluoromethylthioethers in moderate to good yields via a "one-pot" three-step process. Other allenyl thiocyanates could be transformed to allenyl trifluoromethylthioethers via treatment with Me_3SiCF_3 and TBAF in THF (see Scheme 1c).

$AgSCF_3$ is a readily prepared,[8i] stable, and easily handled solid. We began our study into the reactivity of propargyl amines with $AgSCF_3$ by evaluating the model reaction between propargyl amine **1b** and 1.5 equiv of $AgSCF_3$ in the presence of an additive (see Table 1). Performing the reaction in acetonitrile with K_2CO_3[6a] as an additive at room temperature for 12 h provided the desired allenyl thiocyanate **4b** in only 12% yield (entry 1). Other bases, including Et_3N,[10c] Cs_2CO_3, and $NaHCO_3$ under otherwise identical conditions, gave uniformly poor results (Table 1, entries 2–4). Next, Lewis acid additives such as $FeCl_3$ were explored, and it was found that the addition of 0.5 equiv of $FeCl_3$ led to 50% yield of the desired allenyl thiocyanate **4b** in 1 h (entry 5). Increasing or decreasing the amount of $FeCl_3$ both led to a decreased yield of **4b** (see the Supporting Information (SI) for details). Replacing $FeCl_3$ with $FeBr_3$ provided similar results (Table 1, entry 6). To our delight, it was observed that the use of 0.75 equiv of $FeBr_2$ led to **4b** in 81% yield (Table 1, entry 7). Hypothesizing that the iron salts simply served as a source of halide to remove the Ag^+ ion of $AgSCF_3$, we next investigated the addition of inexpensive halide salts. The addition of 1.5 equiv of KBr and NaBr afforded the desired allenyl thiocyanate **4b** in 82% and 64% yields, respectively (Table 1, entries 8 and 9). However, *n*-Bu_4NI (Table 1, entry 10),[8a] *n*-Bu_4NBr, NH_4Br, and KI were all less effective than KBr (see the SI). Acetonitrile also proved to be the best solvent for the transformation (Table 1, entries 11 and 12). Thus, our optimized conditions employ 1.0 equiv of propargyl amine **1b**, 1.5 equiv of $AgSCF_3$, and 1.5 equiv of KBr in air at room temperature in acetonitrile over 1 h, affording trisubstituted allene thiocyanate **4b** in 82% yield.

Table 1. Optimization of Reaction Conditions of Propargyl Amine 1b and $AgSCF_3$ for Allenyl Thiocyanate 4b[a]

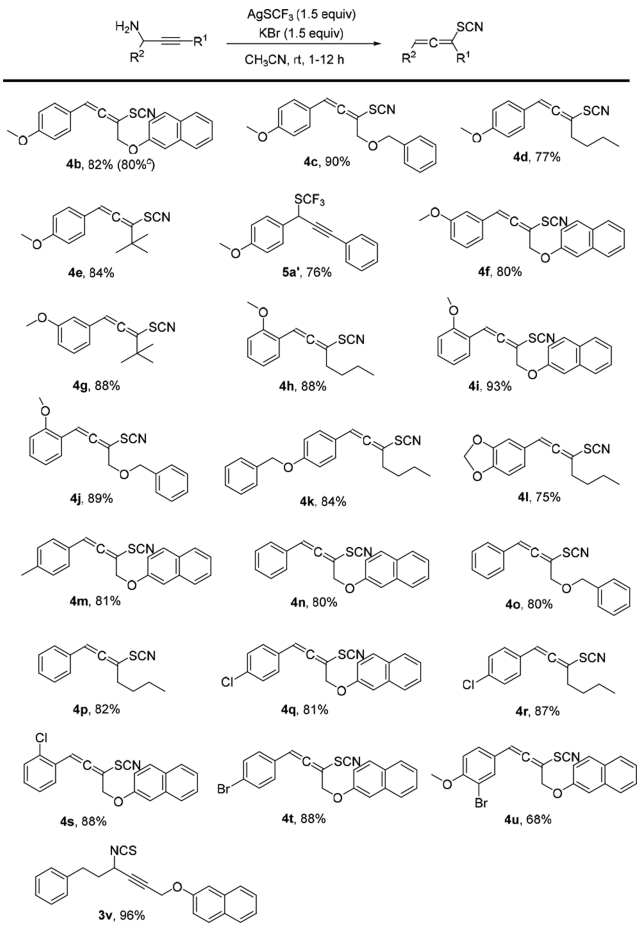


entry	additive	additive, *X* (equiv)	solvent	yield[b] (%)
1	K_2CO_3	1.5	CH_3CN	12
2	Et_3N	2.5	CH_3CN	<3
3	Cs_2CO_3	1.5	CH_3CN	0
4	$NaHCO_3$	2.5	CH_3CN	8
5	$FeCl_3$	0.5	CH_3CN	50
6	$FeBr_3$	0.5	CH_3CN	49
7	$FeBr_2$	0.75	CH_3CN	81
8	KBr	1.5	CH_3CN	82
9	NaBr	1.5	CH_3CN	64
10	*n*-Bu_4NI	1.5	CH_3CN	45
11	KBr	1.5	CH_2Cl_2	29
12	KBr	1.5	toluene	30

[a]Conditions: 0.1 mmol of **1b**, 0.15 mmol of $AgSCF_3$, and *X* equiv of additive react at air for 12 h (entries 1–4) or for 1 h (entries 5–12). [b]Isolated yield.

With the optimized conditions in hand, the substrate scope of the cascade reaction was investigated (see Scheme 2). First, we investigated the effect of substituent R^1 on the terminal alkyne of the propargyl amine **1**. The propargyl amine bearing a benzyloxymethyl group (R^1 = benzyloxymethyl, R^2 = *p*-methoxyphenyl) afforded the corresponding allenyl thiocyanate product **4c** in 90% yield. Simple alkyl groups are also tolerated (R^1 = *n*-butyl, R^2 = *p*-methoxyphenyl), and the corresponding allenyl thiocyanate **4d** was obtained in 77% yield. The substrate bearing a bulky *tert*-butyl group on the triple bond also proceeded smoothly to furnish **4e** in 84% yield. However, the propargyl amine bearing a phenyl group on the terminal alkyne (R^1 = phenyl, R^2 = *p*-methoxyphenyl) gave no desired allenyl thiocyanate product product, and the use of 3 equiv of $AgSCF_3$

Scheme 2. Scope of the Cascade Reaction of Propargyl Amine 1 with $AgSCF_3$ under KBr for Allenyl Cyanate 4[a,b]



[a]Conditions: 0.1 mmol of **1**, 0.15 mmol of $AgSCF_3$, and 0.15 mmol of KBr react at air for 1–12 h. [b]Isolated yield. [c]Scale = 1 mmol.

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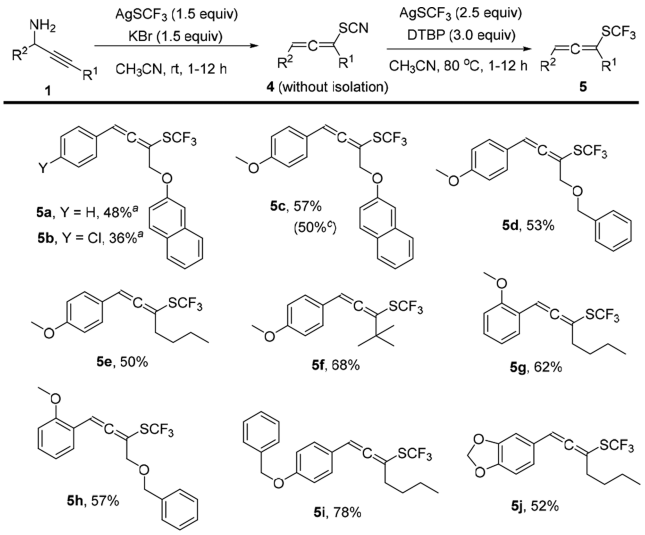
afforded 76% of propargyl trifluoromethylthioether **5a′**. Next, we turned our attention to the substituent R^2 at the 1-position of propargyl amine **1**. It was found that various aryls bearing electron-donating (**1b−1l**), neutral (**1m−1p**), or electron-withdrawing (**1q−1t**) substituents at the *para*-, *meta*-, or *ortho*-positions served as R^2, consistently furnishing the allenyl thiocyanate products (**4b−4t**) in high yields. A variety of functional groups including methoxy (**4b−4j**), benzyloxy (**4k**), [1,3]dioxolyl (**4l**), methyl (**4m**), chloro (**4q−4s**), and bromo (**4t**) were well-tolerated. Chlorine and bromine groups could serve as highly valuable synthetic handles for further functionalization. In the case of **4u**, which bears both electron-donating and electron-withdrawing substituents on the phenyl ring, a slightly decreased yield of 68% was observed. When R^2 was alkyl, such as 2-phenyl substituted ethyl (**1v**), the propargyl isothiocyanate **3v** was obtained in 96% yield.

We then sought to develop conditions to convert our allenyl thiocyanate products into trifluoromethylthioethers (**5**). The use of Prakash's reagent (Me_3SiCF_3) and Cs_2CO_3 in acetonitrile[11a] failed to convert allenyl thiocyanates **4** to allenyl trifluoromethylthioethers **5**. However, we found that subjecting the isolated allenyl thiocyanates **4n** and **4q**, which bear neutral or electron-deficient aryl substituents, to the conditions reported by Langlois (2.0 equiv of Me_3SiCF_3 and 0.2 equiv of TBAF in THF at 0 °C to room temperature (rt)),[11b] the corresponding allenyl trifluoromethylthioethers **5a** and **5b** could be obtained in moderate yields (Scheme 3, condition a). However, these reported conditions failed to deliver the allenyl trifluoromethylthioether **5c** from the corresponding allenyl thiocyanates **4b**, which bears a strong electron-donating group on the 3-aryl substituent.

Scheme 3. Scope of the "One-Pot" Reaction for Trifluoromethylthioethers 5[b]



[b]Conditions: 0.1 mmol of isolated **4n** or **4q**, 0.2 mmol of Me_3SiCF_3, and 0.02 equiv of TBAF in THF reacted at 0 °C for 5 min, then at rt for 3 h; isolated yield. [a]Conditions: 0.1 mmol of **1**, 0.15 mmol of $AgSCF_3$, and 0.15 mmol of KBr reacted at air for 1−12 h, 0.25 mmol of $AgSCF_3$ and 0.3 mmol of DTBP were added and refluxed for 1−12 h; isolated yield. [c]Scale = 1 mmol.

Our next goal was to develop a method for preparing allenyl trifluoromethylthioethers bearing electron-rich aryl substituents at the 3-position. After **4b** was formed under the above optimized conditions, 1.5 equiv of $AgSCF_3$, and 2.0 equiv of oxidant was added to the crude reaction solution and the mixture was refluxed in the presence of an oxidant. We found that the addition of $Na_2S_2O_8$, $K_2S_2O_8$, $PhI(OAc)_2$, or TBHP as oxidant gave none of the desired allenyl trifluoromethylthioether **5c**. To our delight, however, when di-*tert*-butyl peroxide (DTBP) was used as an oxidant, **5c** was obtained in 50% yield. After further optimization of the amounts of DTBP and $AgSCF_3$, as well as temperature (details in the SI), we found that 2.5 equiv of $AgSCF_3$ and 3.0 equiv of DTBP were optimal, and that 57% yield of **5c** could be obtained after 12 h at 80 °C through this "one-pot" three-step process (Scheme 3, condition b).

Under the optimized conditions, the substrate scope of this "one-pot" three-step process was investigated, as shown in Scheme 3. Other 1-(*p*-methoxy phenyl)-substituted propargyl amines also afforded the corresponding allenyl trifluoromethylthioethers **5d−5f** in moderate to good yields. The 1-(*o*-methoxy phenyl) substituted substrates containing either alkyl or ether groups on the terminal alkyne gave the desired products **5g** and **5h** in 62% and 57% yields, respectively. The 1-(*p*-benzyloxy phenyl) substituted propargyl amine furnished the desired allenyl trifluoromethylthioether **5i** in 78% yield. Product **5j** containing a dioxolane functional group also obtained in 52% yield. The structure of **5c** was unambiguously confirmed by single-crystal X-ray analysis (shown in the SI).

To gain insight into the mechanism for formation of trifluoromethylthioethers **5**, the control reaction without DTBP was performed, affording the mixture of **5c** and **5b′** in a ratio of 2:1 in 48% yield (Figure 1). We rationalized that,

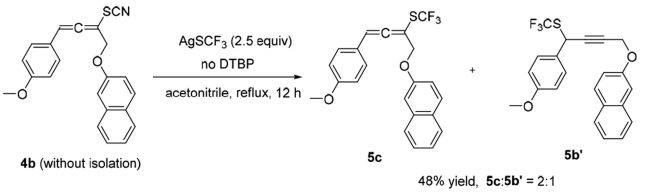


Figure 1. Control reaction without DTBP.

without DTBP, the attack of $^-SCF_3$ at the C1 position of the allene in **4b** was sterically hindered through the SN2 mechanism, thus leading to attack at the C3 position to form **5b′**. We believe that the addition of DTBP with $AgSCF_3$ to the allene **4b** leads to the formation of an allenyl carbocation after loss of the thiocyanate group. Therefore, ESI-MS analysis of the "one-pot" model reaction mixture was performed and a peak corresponding to this proposed carbocation intermediate was observed in the mass spectrum (see the SI). In addition, the "one-pot" reaction performed in the presence of 3.0 equiv of TEMPO gave **5c** in 37% yield. Isothiocyanate intermediate **3q** could also be isolated and characterized (see the SI).

Based on the above experimental results, a plausible mechanism is proposed in Scheme 4. $AgSCF_3$ and KBr react to give $KSCF_3$ and AgBr as a precipitate, and the coordination of Ag^+ with the amine of the propargyl amine **1** is avoided (eq 1 in Scheme 4). An equilibrium between potassium trifluoromethanethiolate with carbonothioic difluoride and potassium fluoride is established (eq 2 in Scheme 4). The propargyl amine **1** reacts with the in-situ-generated carbonothioic difluoride to form the propargyl isothiocyanate **3**, which is subsequently transformed to the corresponding allenyl thiocyanate **4** through [3,3] sigmatropic rearrangement (eq 3 in Scheme 4). After

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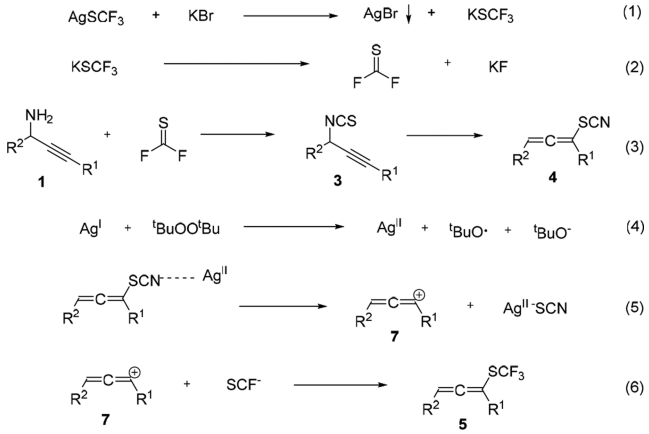
Scheme 4. Proposed Mechanisms for Formation of Allenyl Thiocyanate 4 and Allenyl Trifluoromethylthioether 5



adding $AgSCF_3$ and DTBP, the Ag^+ ion is oxidized to Ag^{2+} ion with DTBP (eq 4 in Scheme 4). Ag^{II} facilitates abstraction of the ^-SCN anion, resulting in the formation of allenyl carbocation **7** (eq 5 in Scheme 4). The $^-SCF_3$ then reacts with allenyl carbocation **7** to afford the desired allenyl trifluorothioether **5** (eq 6 in Scheme 4). We could not rule out that $Ag^{II}{}^-SCN$ might transform to Ag^+ and SCN radical, which might terminate the radical translation with another SCN radical or O^{t}Bu radical.

In conclusion, a safe, convenient, and highly efficient cascade reaction of propargyl amines, $AgSCF_3$, and KBr was developed, affording a series of trisubstituted allenes bearing a thiocyanate functional group. This transformation proceeds at room temperature and gives the allene products in high yields. The reaction proceeds through in situ formation of isothiocyanate intermediates, followed by a [3,3] sigmatropic rearrangement. In addition, a "one-pot" reaction of propargyl amines bearing electro-rich aryl substituents at 1-position with $AgSCF_3$, KBr, and di-*tert*-butyl peroxide afforded trisubstituted allenes bearing a trifluoromethylthio group in moderate to good yields. The proposed allenyl carbocation intermediate was detected by ESI-MS to rationalize the high regioselectivity. Allenyl thiocyanates bearing electron-neutral and electron-poor phenyl substituents at the 3-position could also be transformed to the corresponding allenyl trifluoromethylthioethers through treatment with Me_3SiCF_3 and TBAF in THF. This report represents the first synthesis of allenyl trifluoromethylthioether compounds.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.8b01181.

Experimental procedures and spectroscopic characterization data, ^1H and ^{13}C NMR spectra of the new compounds (PDF)

Accession Codes

CCDC 1588662 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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