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$AgSCF_3$-Mediated Trifluoromethylthiolation/Radical Cascade Cyclization of 1,6-Enynes

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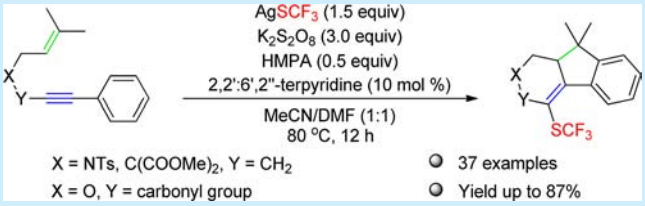
Supporting Information

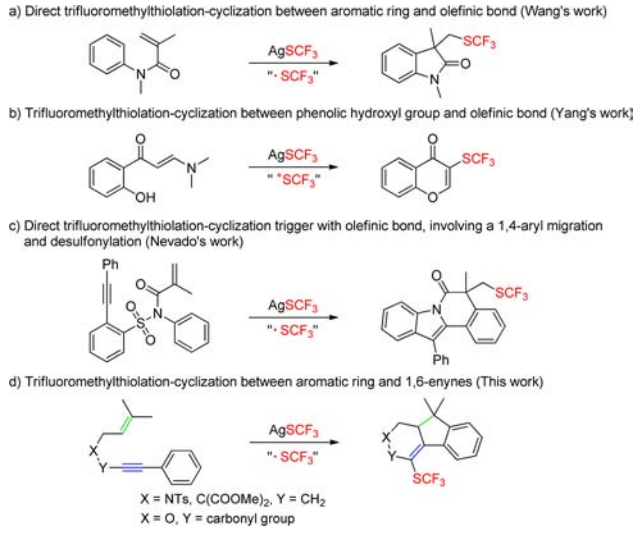
ABSTRACT: A $AgSCF_3$-mediated radical cascade cyclization/trifluoromethylthiolation of 1,6-enynes triggered by a C−C triple bond is developed. This protocol also provides another opportunity to construct a valuable trifluoromethylthio-substituted polycyclic fluorene system through the formations of one C−SCF_3 bond and two C−C bonds in a single step.



Organofluorine compounds have been identified to show wide application and evolution in the pharmaceutical chemistry, pesticide industry, and material science.[1] Among such numerous fascinating fluorine-containing groups, the trifluoromethylthio group (SCF_3) has occupied a significant field due to its desirable bioactivities, such as high electronegativity, lipophilicity, and metabolic stability, which led to a great promotion of membrane permeability and absorption rate in bioavailability.[2] Therefore, advancing aspiration and interest in new routes to introduce the trifluoromethylthio group stimulates further studies in this area.[3] With the persistent efforts of many chemists, adequate evolutions have been achieved on the development of a series of trifluoromethylthiolation reagents.[4] Very recently, various electrophilic trifluoromethylthiolation reagents (SCF_3^+)[5] have been exploited for an efficient trifluoromethylthiolation cyclization reaction.[6] Nevertheless, the incompatibility with a strong acidic system and the sensitivity for electronic effect force reconsideration for some substrates with sensitive functional groups.[6] In subsequent research, $AgSCF_3$, a straightforward and easy-operation reagent,[7] has emerged as a valuable tool in trifluoromethylthiolation/oxidative aromatic cyclization reactions.[8] In 2014, the Wang group reported the first $AgSCF_3$-mediated aryltrifluoromethylthiolation cyclization of activated alkenes in a radical process (Scheme 1a).[8b] Soon afterward, Yang demonstrated a series of trifluoromethylthio-substituted chromones in a "SCF_3^+" course (Scheme 1b).[8d] Very recently, a novel trifluoromethylthiolation oxidative aromatic cyclization involving a 1,4-aryl migration and desulfonylation was presented by Nevado (Scheme 1c).[8f] Still, the development of direct oxidative aromatic radical cascade cyclization with trifluoromethylthiolation on a C−C triple bond is still fueled by the strong and growing aspiration in organofluorine chemistry.

It is known that the status of cascade cyclization as a powerful and ingenious strategy for the synthesis of polycyclic compounds is irreplaceable.[9] Herein, radical cyclization shows undeniable benefits in most cases, including being insensitive to electronic effect, having extensive functional group compatibility, and providing economies of time, labor, and cost.[9b,10] Meanwhile, 1,6-enynes, as interesting and important starting materials with multiple reaction sites, have become star molecules in synthetic methodology.[11] By taking into consideration our current interest in the synthesis of fluorine-containing compounds,[12] as well as the continued anticipation of new approaches to polycyclic skeletons,[13] we designed a silver-mediated trifluoromethylthiolation/radical cascade cyclization of 1,6-enynes. This is the first paper on the trifluoromethylthiolation−cyclization reaction

Scheme 1. $AgSCF_3$ Participating in Oxidative/Aromatic Cyclization Reaction and Our New Anticipation towards Trifluoromethylthiolation/Cascade Cyclization of 1,6-Enynes



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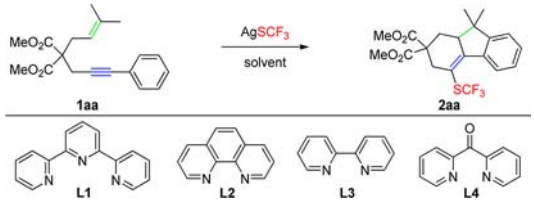
triggered by a C−C triple bond in a radical pathway, with a polycyclic fluorene system constructed in a single step (Scheme 1d).

Our initial attempt was started by employing compound **1aa** (0.2 mmol) as the model substrate with $AgSCF_3$ (1.5 equiv), $K_2S_2O_8$ (3.0 equiv), and HMPA (0.5 equiv) in MeCN at 80 °C under an argon atmosphere for 12 h. To our delight, our anticipated product **2aa** was isolated in 42% yield (Table 1, entry 1). A subsequent brief survey of various representative solvents showed that DMF gave a similar yield of product **2aa** with 18% of substrate **1aa** recovered (entries 2−4). Further study on the effect of solvents revealed that the yield could be increased to 66% in a mixed solvent of MeCN/DMF (1:1) without substrate recovered (entry 5). Simply improving the ratio of DMF in the mixed solvent gave a lower yield with substrate **1aa** recovered (entry 6). We considered that DMF also functioned as a possible ligand to improve the solubility of $AgSCF_3$ and $K_2S_2O_8$. And excess ligand might go against the reaction process as known fact. No better results were obtained after the replacement of oxidant (entries 7−9). And the adjustments on $K_2S_2O_8$ or HMPA failed to give superior yields (entries 10−12). During subsequent attempts, the addition of ligand 2,2′:6′,2″-terpyridine **L1** (10 mol %) proved to be a good option, by which 87% of product **2aa** was isolated (entries 13−17). The role of ligand **L1** was further investigated in MeCN and DMF, respectively (entries 18−19). The coordination between ligand/HMPA and $AgSCF_3$ may reduce the redox potential of the high valent silver species, which hindered the further oxidative decomposition of substrates and products.[8b] Additional control experiments indicated that an argon atmosphere and base were necessary for a high yield (entries 20−21).

A series of substituted 1,6-enynes were prepared to investigate the scope of this trifluoromethylthiolation−cyclization reaction. The corresponding products **2aa**−**2at** were obtained in moderate to excellent yields under the optimal reaction conditions (Scheme 2). The structure of **2at** was also confirmed by X-ray crystal structure analysis (see the Supporting Information (SI)). The electronic effect of substituent groups shows insensitivity in this transformation; in general, both electron-rich (**1aa**−**1ac**) and -deficient (**1ad**−**1ai**) groups on the *para*-position of the substrates could be tolerated. It was noteworthy that substrates with strong electron-withdrawing groups (NO_2 or CN) worked smoothly and gave the corresponding product in 49% and 70% yield, respectively (**2ag** and **2ah**). Furthermore, gratifyingly, substrates bearing electron-deficient groups on the *meta*-position achieved a total regioselective reaction and gave the corresponding products in good yields (**2al** and **2am**), whereas a mixture of the products **2an**′ and **2an**″ was obtained in the ratio 5:2 when *m*-OMe substituted 1,6-enyne was investigated (**1an**). In addition,

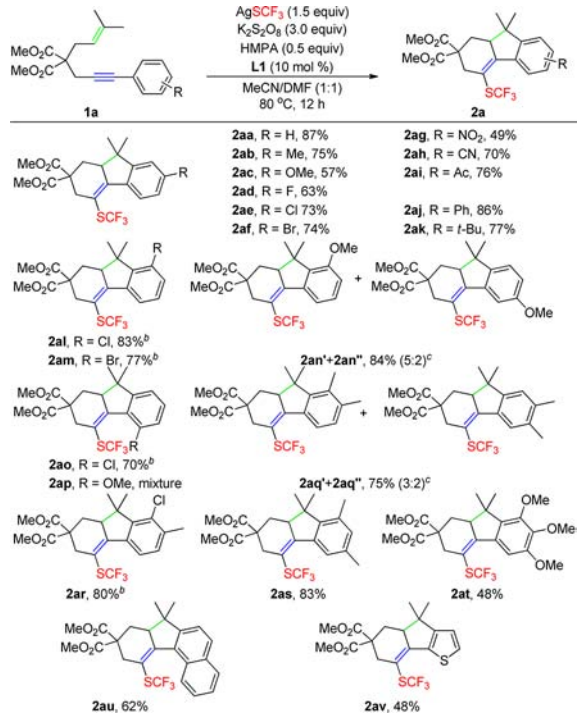
Table 1. Optimization of the Reaction Conditions[a]



entry	solvent	oxidant (equiv)	ligand (mol %)	yield (%)[b]
1	MeCN	$K_2S_2O_8$ (3.0)		42
2	1,2-DCE	$K_2S_2O_8$ (3.0)		0
3	DMSO	$K_2S_2O_8$ (3.0)		36
4	DMF	$K_2S_2O_8$ (3.0)		44[c]
5	MeCN/DMF (1:1)	$K_2S_2O_8$ (3.0)		66
6	MeCN/DMF (1:2)	$K_2S_2O_8$ (3.0)		54[d]
7	MeCN/DMF (1:1)	$Na_2S_2O_8$ (3.0)		34[e]
8	MeCN/DMF (1:1)	$PhI(OAc)_2$ (3.0)		trace
9	MeCN/DMF (1:1)	*m*-CPBA (3.0)		0[f]
10	MeCN/DMF (1:1)	$K_2S_2O_8$ (2.5)		61
11[g]	MeCN/DMF (1:1)	$K_2S_2O_8$ (3.0)		54
12[h]	MeCN/DMF (1:1)	$K_2S_2O_8$ (3.0)		52
13	MeCN/DMF (1:1)	$K_2S_2O_8$ (3.0)	**L1** (20)	84
14	MeCN/DMF (1:1)	$K_2S_2O_8$ (3.0)	**L2** (20)	65
15	MeCN/DMF (1:1)	$K_2S_2O_8$ (3.0)	**L3** (20)	62
16	MeCN/DMF (1:1)	$K_2S_2O_8$ (3.0)	**L4** (20)	66
17	**MeCN/DMF (1:1)**	**$K_2S_2O_8$ (3.0)**	**L1 (10)**	**87**
18	MeCN	$K_2S_2O_8$ (3.0)	**L1** (10)	51
19	DMF	$K_2S_2O_8$ (3.0)	**L1** (10)	59[i]
20[j]	MeCN/DMF (1:1)	$K_2S_2O_8$ (3.0)	**L1** (10)	58
21[k]	MeCN/DMF (1:1)	$K_2S_2O_8$ (3.0)	**L1** (10)	78

[a]Unless otherwise noted, all reactions were performed with **1aa** (0.2 mmol), $AgSCF_3$ (1.5 equiv), oxidant (3.0 equiv), base (0.5 equiv), and ligand (10 mol %) in anhydrous solvent (2 mL) under an argon atmosphere for 12 h. [b]Yields are given for isolated products. [c]18% of **1aa** was recovered. [d]6% of **1aa** was recovered. [e]11% of **1aa** was recovered. [f]Decomposed. [g]HMPA (1.0 equiv) was uesd. [h]NaOAc (0.5 equiv) was used instead of HMPA. [i]21% of **1aa** was recovered. [j]This reaction was performed under an air atmosphere. [k]This reaction was performed in the absence of HMPA.

Scheme 2. Synthesis of Products 2a from 1,6-Enynes 1a[a]



[a]Unless otherwise noted, all reactions were performed with **1a** (0.2 mmol), $AgSCF_3$ (1.5 equiv), $K_2S_2O_8$ (3.0 equiv), HMPA (0.5 equiv), and ligand **L1** (10 mol %) in anhydrous MeCN/DMF (2 mL, 1:1) under an argon atmosphere for 12 h. Yields are given for isolated products. [b]The configuration was determined by ^1H NMR spectrum. [c]The configuration and the ratio were determined by ^1H NMR and NOE spectra.

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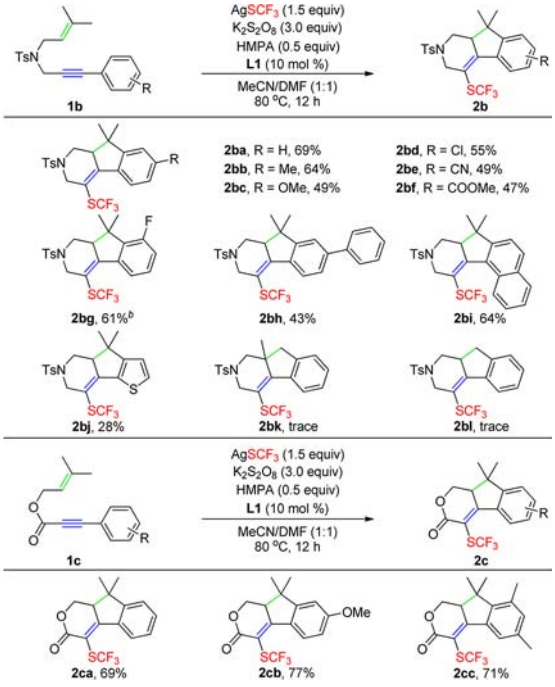
these halogenated products may provide other potential applications for further transformations through orthogonal cross-couplings. The steric effect for *ortho*-position substituent groups was then explored. When substrate **1ao** (*o*-chlorophenly) was utilized under the optimal conditions, 70% yield of product **2ao** was isolated. Compared with **2ao**, product **2ap** could not be isolated from a mixture product. Several multisubstituted substrates were also applied, which all showed excellent tolerance (**2aq**−**2at**). Similarly, a mixture of product **2aq**′ with **2aq**″ and a single configuration of product **2ar** was isolated. Notably, the transformation proceeded smoothly for the substrates with a multiple-ring group (1-naphthyl group, **1au**) or a heterocyclic group (2-thienyl, **1av**).

Encouraged by the above results, the reactions of *N*-tethered 1,6-enynes were further examined under the optimal conditions. Generally, as described in Scheme 3, the reactions showed steric

Scheme 3. Synthesis of Products 2b (2c) from 1,6-Enynes 1b (1c)[a]

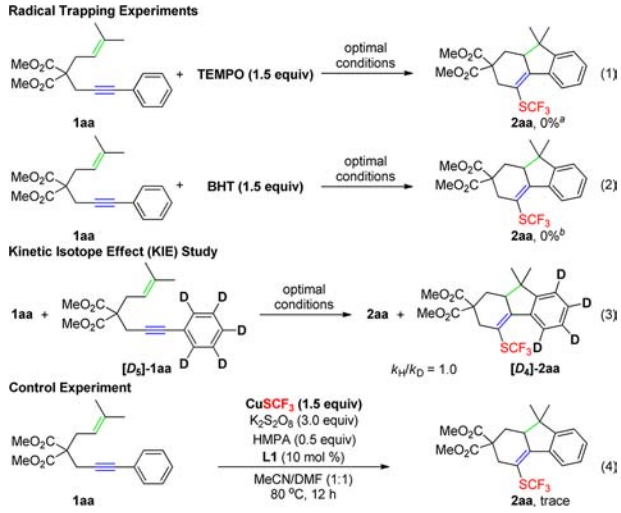


[a]Unless otherwise noted, all reactions were performed with **1b** (0.2 mmol), $AgSCF_3$ (1.5 equiv), $K_2S_2O_8$ (3.0 equiv), HMPA (0.5 equiv), and ligand **L1** (10 mol %) in anhydrous MeCN/DMF (2 mL, 1:1) under an argon atmosphere for 12 h. Yields are given for isolated products.

and electronic effects similar to those of carbon-tethered substrates. The structure of **2bd** was also confirmed by X-ray crystal structure analysis (see the SI). Substrate **1bg** (*m*-fluorophenyl) still gave the single configuration. Substrates **1bk** and **1bl** bearing a terminal olefinic bond failed to give the corresponding product due to an unstable radical intermediate **B** (see Scheme 5). Several *O*-tethered 1,6-enyne substrates were studied next under the optimal conditions (Scheme 3). Gratifyingly, the corresponding trifluoromethylthio-substituted 2-pyrone derivatives were obtained. 2-Pyrones have been identified to be significant intermediates and vitally important flavonoid skeletal structures, which are found in a wide variety of natural products and pharmaceutically active molecules. Meanwhile, the structure of **2cb** was confirmed by X-ray crystal structure analysis (see the SI).

To gain further understanding of the reaction mechanism, some necessary inhibition experiments were performed (Scheme 4). When 1.5 equiv of TEMPO (2,2,6,6-tetramethylpiperidine-1-

Scheme 4. Verification Experiments for the Mechanism

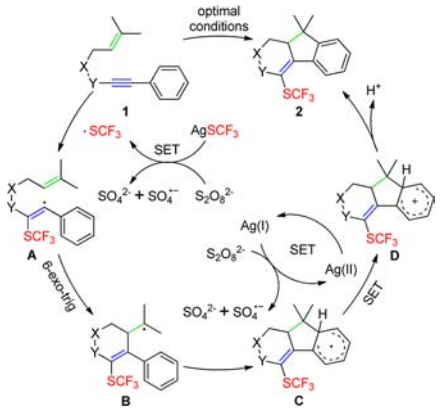


[a]97% of **1aa** was recovered. [b]93% of **1aa** was recovered.

oxyl) or BHT (2,6-di-*tert*-butyl-4-methylphenol) were added into the reaction system, the desired transformation was found to be completely inhibited with over 90% of **1aa** recovered, respectively. This observation was consistent with the hypothesis that the reaction proceeds via a radical pathway, which indicated an SET (single electron transfer) process triggered by a free radical. Then, a kinetic isotope experiment was carried out with low kinetic isotope effects detected, which pointed out the C−H cleavage step was not a rate-limiting step. And the replacement of a SCF_3 source ($CuSCF_3$) led to no product, which indicated that silver had a vital impact on this transformation.

A plausible mechanism that is consistent with the experimental results mentioned above and the precedent literature[8b,e,f] is proposed in Scheme 5. In fact, $AgSCF_3$ is initially oxidized by $K_2S_2O_8$ and generates the SCF_3· radical. The intermolecular regioselective addition of the SCF_3· radical onto the triple bond of substrate **1** affords alkenyl radical intermediate **A**,[13b,c] which undergoes a subsequent 6-exo-trig process to give alkyl radical

Scheme 5. Proposed Reaction Mechanism



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intermediate **B**. The intramolecular addition of intermediate **B** onto the aromatic ring generates aryl radical intermediate **C**. Ultimately, the desired product **2** is obtained with another SET from intermediate **C** to Ag(II) species as an oxidant,[8b,f] followed by releasing a proton.

In summary, we have disclosed a $AgSCF_3$-mediated oxidative aromatic radical cyclization of 1,6-enynes to synthesize various trifluoromethylthio-substituted fluorene derivatives. The reaction occurred smoothly with one C−SCF_3 bond and two C−C bonds constructed concurrently in good to excellent yields. This transformation proved to proceed through a radical process triggered by a C−C triple bond, which avoids the direct influence of the electronic effect and enhances the application scope of some particular functional groups (cyan and nitro groups). In addition, during the substrate expansion, several trifluoromethylthio-substituted fluorenes containing a 2-pyrone moiety were obtained in good yields, which may show huge potential in vital applications in pharmacy research.

■ ASSOCIATED CONTENT

Supporting Information

Detailed experimental procedures, spectral data, and CIF for all new compounds are provided. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.5b01657.

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Notes

The authors declare no competing financial interest.

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