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$AgSCF_3$-Mediated Oxidative Trifluoromethythiolation of Alkynes with Dearomatization to Synthesize SCF_3-Substituted Spiro[4,5]trienones

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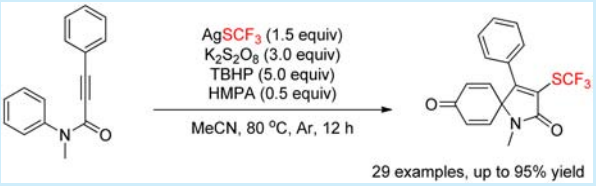
Supporting Information

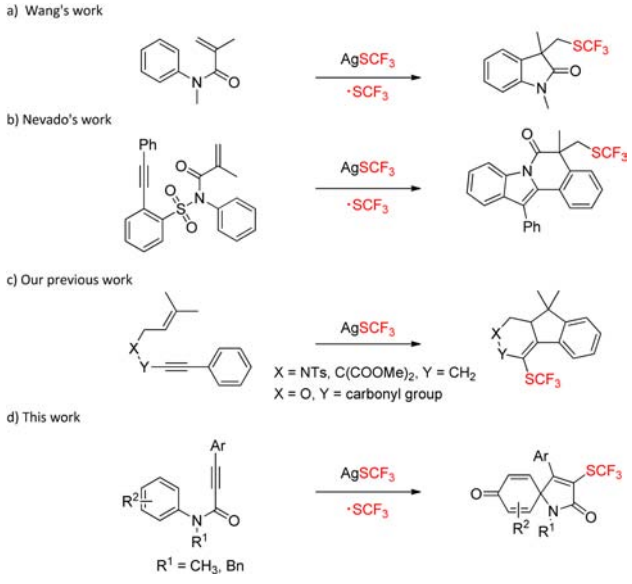
ABSTRACT: A new method for the $AgSCF_3$-mediated radical cascade difunctionalizing trifluoromethythiolation of alkynes with dearomatization is developed. This protocol provides a novel route to SCF_3-substituted spirocyclic compounds via the formation of one C−SCF_3 bond, one C−C bond, and one C−O double bond in a single step.



Organofluorine compounds, owing to their specific physicochemical properties with high electronegativity and low polarizability, have been widely used in the pharmaceutical and agrochemical industries.[1] In recent years, the heteroatom-containing, fluorinated groups have attracted much attention,[2] especially the trifluoromethylthio (SCF_3) moiety, which possesses high lipophilicity, strong electron-withdrawing effects, and metabolic stability. Meanwhile, the incorporation of the trifluoromethylthio group (SCF_3) into drugs or leading compounds may greatly contribute to the promotion of their medicinal properties, such as membrane permeability, absorption rate, and their stability.[3] Classical methods to embed the trifluoromethylthio group (SCF_3) into organic molecules include halogen−fluorine exchange reactions and the trifluoromethylation of sulfur-containing compounds.[4] Continuous efforts have been made for the development of novel, direct trifluoromethylthiolation reagents, and a series of electro- and nucleophilic SCF_3 reagents have been developed.[5] However, the limited scope of substrates and harsh reaction conditions impose restrictions on their application in synthetic chemistry. Recently, $AgSCF_3$, an easily prepared and stable trifluoromethylthiolation reagent,[6] has been widely used in the formation of the C−SCF_3 bond via radical intermediates.[7] In 2014, the Wang group reported the first synthesis of SCF_3-containing oxindoles through a $AgSCF_3$-mediated addition/cyclization (Scheme 1a).[7b] Soon afterward, a trifluoromethylthiolation cascade cyclization involving a 1,4-aryl migration/desulfonylation process was put forward by Nevado (Scheme 1b).[7c] Very recently, our group disclosed a $AgSCF_3$-mediated radical cascade cyclization of 1,6-enynes, leading to a series of novel trifluoromethylthiolated fluorene derivatives (Scheme 1c).[7e]

Azaspirocycles are an important structural feature as they are widely found in many natural products and bioactive compounds. Indeed, they are also pivotal intermediates in organic synthesis.[8] Due to the limited reports for the synthesis of fluorine-containing spirocyclic compounds, especially for multifluoro-substituted spirocyclic compounds,[9] the development of an efficient strategy to access fluorine-containing spirocyclic compounds involving new additional functional groups is still highly desirable.

Scheme 1. Previous Works on Direct Trifluoromethylthiolation−Cyclization via a Radical Pathway and the Current Effort



Based on the development of the trifluoromethylthio group and our ongoing interest in the synthesis of spirocyclic

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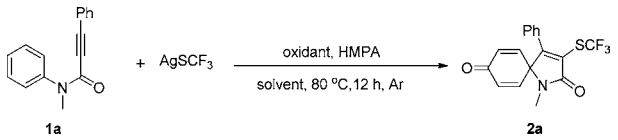
frameworks,[10] we developed a novel oxidative trifluoromethylthiolation of alkynes to create the 3-trifluoromethylthiospiro-[4,5]trienones via a radical pathway. This strategy contains a cascade cyclization process with difunctionalization of alkynes and dearomatization. To the best of our knowledge, it is the first time to construct trifluoromethylthio-substituted spiro-[4,5]trienones through difunctionalization of activated alkynes with $AgSCF_3$.

The initial exploration of this reaction was performed by using *N*-methyl-*N*,3-diphenylpropiolamide **1a** as the model substrate. The desired product **2a** was obtained in 89% yield in the presence of $AgSCF_3$ (1.5 equiv), $K_2S_2O_8$ (3.0 equiv), TBHP (7.0 equiv, 70% aqueous solution), and HMPA (0.5 equiv) in CH_3CN at 80 °C for 12 h (Table 1, entry 1). Encouraged by this preliminary result, various representative solvents were screened to verify CH_3CN as the more efficient solvent for the reaction system (entries 2−4). Other persulphate failed to give a better result, and no desired product was obtained in the absence of $K_2S_2O_8$ (entries 5−7). During subsequent attempts, an argon atmosphere proved to be significant for this reaction (entry 8). In addition, a series of surveys of the TBHP-to-substrate ratio showed that 5.0 equiv of TBHP gave the best yield of 91% (entries 9−10). Unfortunately, other radical initiators, including DTBP (di-*tert*-butyl peroxide) and BPO (benzoyl peroxide), proved to be less effective (entries 11−12). An additional control experiment indicated that HMPA was necessary for a high yield (entry 13). No better result was obtained after the replacement of the SCF_3 source ($CuSCF_3$) (entry 14). Based on the detailed investigations mentioned above, the combination of $AgSCF_3$ (1.5 equiv), $K_2S_2O_8$ (3.0 equiv), TBHP (5.0 equiv, 70% aqueous solution), and HMPA (0.5 equiv) in CH_3CN (2 mL) at 80 °C under an argon atmosphere was defined as the optimal set of conditions for this reaction.

Table 1. Optimization of the Reaction Conditions[a]

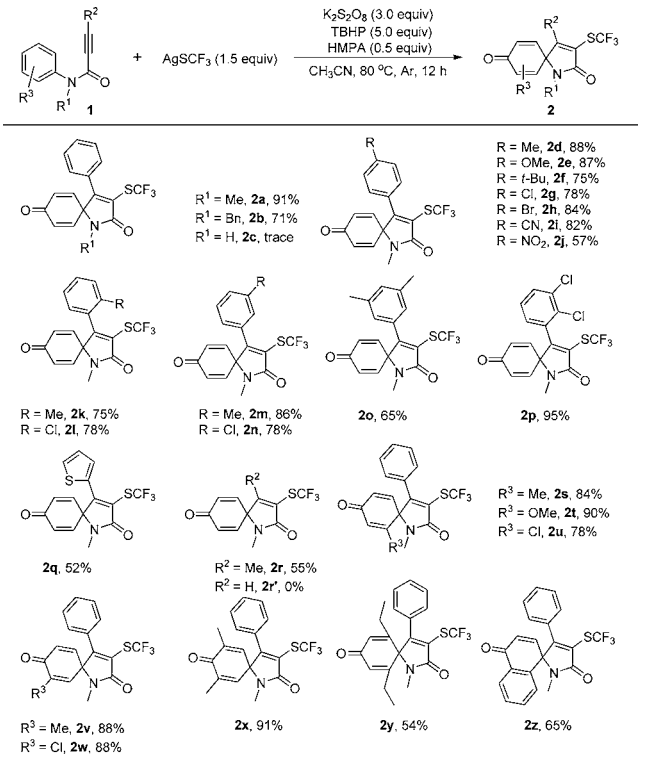


entry	solvent	oxidant (equiv)	yield (%)[b]
1	CH_3CN	$K_2S_2O_8$/TBHP (3.0/7.0)	89
2	toluene	$K_2S_2O_8$/TBHP (3.0/7.0)	0
3	DMF	$K_2S_2O_8$/TBHP (3.0/7.0)	0
4	DCE	$K_2S_2O_8$/TBHP (3.0/7.0)	trace
5	CH_3CN	$Na_2S_2O_8$/TBHP (3.0/7.0)	15
6	CH_3CN	$(NH_4)_2S_2O_8$/TBHP (3.0/7.0)	20
7	CH_3CN	TBHP (7.0)	0
8	CH_3CN	$K_2S_2O_8$/TBHP (3.0/7.0)	60[c]
9	**CH_3CN**	**$K_2S_2O_8$/TBHP (3.0/5.0)**	**91**
10	CH_3CN	$K_2S_2O_8$/TBHP (3.0/4.0)	80
11	CH_3CN	$K_2S_2O_8$/DTBP (3.0/5.0)	0[d]
12	CH_3CN	$K_2S_2O_8$/BPO (3.0/5.0)	0
13	CH_3CN	$K_2S_2O_8$/TBHP (3.0/5.0)	0[e]
14	CH_3CN	$K_2S_2O_8$/TBHP (3.0/5.0)	trace[f]

[a]Reaction conditions: **1a** (0.2 mmol), $AgSCF_3$ (1.5 equiv), $K_2S_2O_8$ (3.0 equiv), TBHP (7.0 equiv, 70% aqueous solution), and HMPA (0.5 equiv) in CH_3CN (2 mL) at 80 °C under an argon atmosphere for 12 h. [b]Yields are given for isolated products. [c]This reaction was performed under an air atmosphere. [d]The substrate was decomposed. [e]This reaction was performed without HMPA. [f]$CuSCF_3$ was used instead of $AgSCF_3$.

With the optimized reaction conditions in hand, a series of substituted *N*-arylpropiolamides were subjected to this $AgSCF_3$-mediated dearomatization reaction system (Scheme 2). Initially, the substituent groups at the nitrogen atom were investigated (R^1). The substrate **1b** (R^1 = Bn) was successfully converted to the corresponding SCF_3-substituted spirocycle product **2b** in 71% yield, whereas substrate **1c** (R^1 = H) only gave a trace amount of the desired product. A survey was conducted on the electronic effect of the aromatic ring at the terminal alkyne, including electron-donating (**1d−1f**) and electron-withdrawing (**1g−1h**) groups on the *para*-position. The optimized conditions were compatible with most of the substrates and gave the corresponding products in moderate to excellent yields (**2d−2h**). Notably, substrate **1f** with a bulky *t*-Bu group also afforded the corresponding product **2f** in 75% yield. It was noteworthy that the substrate with strong electron-withdrawing groups (CN and NO_2) could be tolerated and gave the corresponding products in 82% and 57% yield (**2i**, **2j**). Analogous to the situation of the *para*-substituent groups, substrates containing *ortho*- (**1k−1l**) or *meta*- (**1m−1n**) substituent groups also showed good compatibility with similar rules. It is noteworthy that *halo*-substituted alkynes worked smoothly and furnished the corresponding SCF_3-substituted spirocycle products, which might be readily applied in various cross-coupling reactions. The substrates with two substituents were also applied (**2o**, **2p**), and substrate **1o** gave the highest yield of 95%. The substrate with heteroarylalkynes **1q** and a

Scheme 2. Substrate Scope for the Reaction[a]



[a]Reaction conditions: **1** (0.2 mmol), $AgSCF_3$ (1.5 equiv), $K_2S_2O_8$ (3.0 equiv), TBHP (5.0 equiv, 70% aqueous solution), and HMPA (0.5 equiv) in CH_3CN (2 mL) at 80 °C under an argon atmosphere for 12 h. Yields are given for isolated products.

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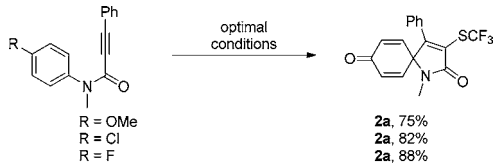
methyl group on the terminal alkyne **1r** were also viable for the reaction, affording the product **2q** in 52% yield and **2r** in 55% yield. A substrate with a terminal alkyne (R^2 = H) failed to give the corresponding product. Soon after, the investigation on the *N*-aryl moiety (R^3 group) was carried out. Either the *ortho*- (**1s**−**1u**) or *meta*- (**1v**−**1w**) substituent groups were efficiently transformed into the desired products (**2s**−**2w**) in excellent yields. However, the multisubstituted substrates **1x** and **1y** provided yields of 91% and 54%, respectively, which might be due to the steric effect of the bulky group. Substrate **1z** with a naphthyl group replacing the phenyl group gave the desired product **2z** in 65% yield.

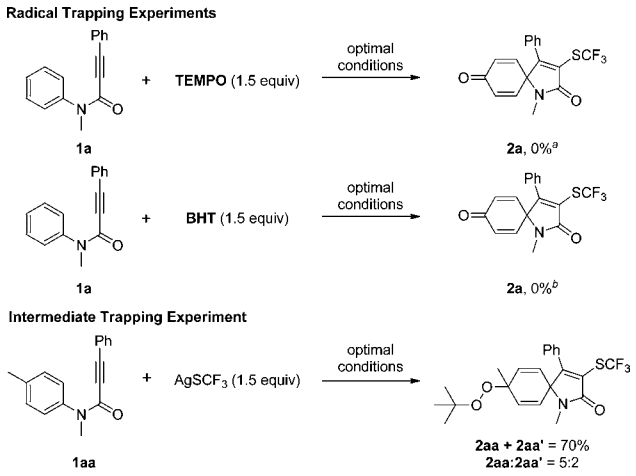
Interestingly, when the R group was at the *para*-position, such as *p*-OMe, *p*-Cl, and *p*-F, the product **2a** was obtained in good to excellent yields, which indicated the formation of a C−O double bond along with the cleavage of a C−Cl or C−F bond, respectively (Scheme 3).

Scheme 3. Trifluoromethylation of Substrates with *para* Substituents on the *N*-Aryl Moiety



To gain further understanding of the reaction mechanism, some control experiments were carried out (Scheme 4). When

Scheme 4. Verification Experiments for the Mechanism

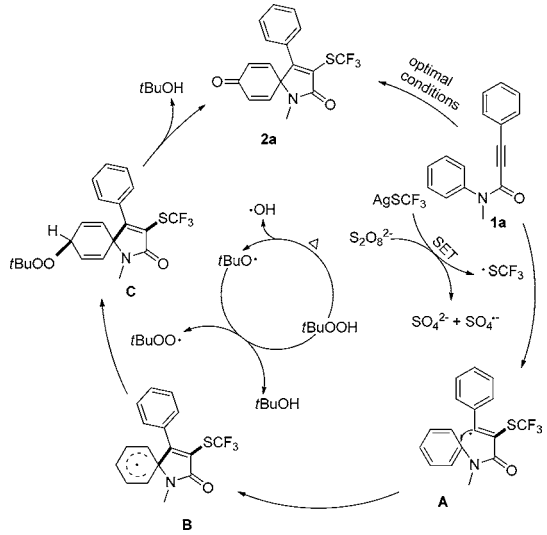


[a]90% of **1a** was recovered. [b]95% of **1a** was recovered.

1.5 equiv of radical inhibitors were added into the reaction system, TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl) or BHT (2,6-di-*tert*-butyl-4-methylphenol), the reactions were found to be inhibited, with over 90% of **1a** was recovered, which implied that the reaction may proceed by a radical pathway. It is worth pointing out that HMPA functioned not only as a base but also as a potential ligand to improve the solubility and stability of $AgSCF_3$.[7b,e] In addition, an intermediate trapping experiment was conducted. The substrate with a methyl group at the *para*-positon of the *N*-phenyl moiety (**1aa**) was used and afforded the product **2aa**. According to this result, we could confirm that the *tert*-butylperoxy radical (from TBHP) added to the *para*-position of the phenyl group. The structure of **2aa** was also confirmed by X-ray crystal structure analysis (see the Supporting Information).

On the basis of these results mentioned above and the precedent literature,[7b,c,e] a plausible mechanism is proposed in Scheme 5. Initially, the addition of the trifluoromethythio

Scheme 5. Proposed Reaction Mechanism



radical, which was generated from $AgSCF_3$ and $K_2S_2O_8$, onto the alkynyl bond of **1a** affords vinyl radical **A**.[8k,10d] Then, the intermediate **A** undergoes an intramolecular radical cyclization to give radical intermediate **B**, which can be easily trapped by the *tert*-butylperoxy radical to generate intermediate **C** (the *tert*-butylperoxy radical comes from the interaction of TBHP with the *tert*-butyloxy radical).[10d] Finally, the desired product **2a** is generated by the elimination of ^{t}BuOH from intermediate **C**.[10d]

In conclusion, we have reported an efficient synthesis of 3-trifluoromethylthiospiro[4,5]trienones through a radical oxidative dearomatization process with $AgSCF_3$. This reaction was smoothly promoted by the combination of $K_2S_2O_8$ and TBHP. Moreover, the oxygen atom in the product comes from the TBHP. Due to the broad functional group tolerance and the potential utility of fluorine-substituted spirocyclic compounds, wide application of this method in the pharmaceutical and agrochemical fields is expected.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.6b01702.

Detailed experimental procedures, spectral data, and crystallographic data (PDF)
Crystallographic data for **2a** (CIF)
Crystallographic data for **2aa** (CIF)

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Notes

The authors declare no competing financial interest.

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