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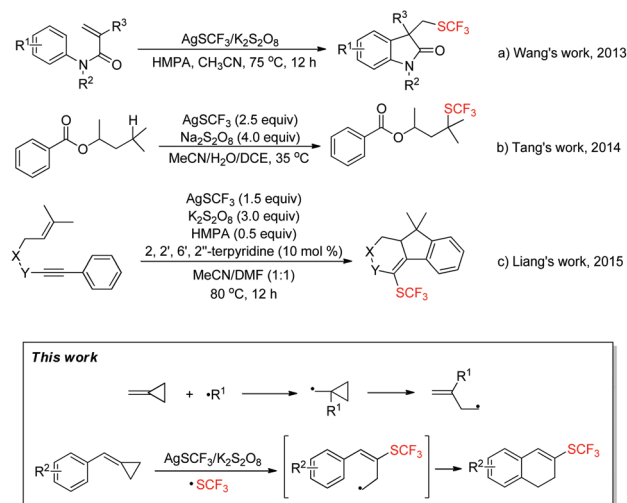
A facile approach for the trifluoromethylthiolation of methylenecyclopropanes†

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A facile approach for the trifluoromethylthiolation of methylenecyclopropanes (MCPs) has been developed by using $\text{AgSCF}_3/\text{Na}_2\text{S}_2\text{O}_8$ as a trifluoromethylthiolation source (SCF_3) to give trifluoromethylthiolated 1,2-dihydro-naphthalene derivatives in moderate to good yields, and the reaction has been proven to go through a radical-type pathway. The products can easily be aromatized upon oxidation, offering a new method for the construction of trifluoromethylthiolated naphthalenes.

Introduction

In recent years, fluorinated organic compounds have gained more and more importance, especially in the fields of pharmaceuticals, agrochemicals and materials¹ due to their unique biological activity and metabolic stability.² Compounds with the trifluoromethylthio (SCF_3) group have drawn great attention from chemists for their high electronegativity and special lipophilicity, and many synthetic methods³ have been developed to introduce the trifluoromethylthio (SCF_3) group into different organic scaffolds. In recent years, a lot of work has been done using AgSCF_3 as a source of the trifluoromethylthio (SCF_3) moiety owing to its stability and easy availability.⁴ The process of trifluoromethylthiolation can go through different pathways in which AgSCF_3 can act as a nucleophile ($^-\text{SCF}_3$),^{4e,5} electrophile ($^+\text{SCF}_3$)^{4f,g,i,6} or radical ($^\bullet\text{SCF}_3$)^{4d,i-k,7,8} precursor, and especially in the radical pathway, trifluoromethylthio (SCF_3) radical can be conveniently accessed by mixing AgSCF_3 and $\text{M}_2\text{S}_2\text{O}_8$ (Na, K, NH_4 , etc.) together in polar solvents such as MeCN, DMSO and DMF. For example, in 2013, Wang's group achieved a radical aryltrifluoromethylthiolation reaction of activated alkenes with $\text{AgSCF}_3/\text{K}_2\text{S}_2\text{O}_8$ (Scheme 1a).^{4d} In 2014, Tang's group succeeded in the radical trifluoromethylthiolation of unactivated aliphatic C–H bonds using $\text{AgSCF}_3/\text{Na}_2\text{S}_2\text{O}_8$ (Scheme 1b).⁸ Moreover, following their work, in 2015, Liang's group successfully achieved a radical trifluoro-



Scheme 1 A general review of recent work on trifluoromethylthiolation using AgSCF_3 as a trifluoromethylthio radical source.

methylthiolation cascade cyclization of 1,6-enynes with $\text{AgSCF}_3/\text{K}_2\text{S}_2\text{O}_8$ (Scheme 1c).⁴ⁱ

On the other hand, methylenecyclopropanes (MCPs) are conveniently available organic building blocks⁹ with special reactivity, which can easily undergo ring-opening or participate in tandem cyclizations when exposed to cationic or radical species. Thus it would be intriguing to bring methylenecyclopropanes (MCPs) and trifluoromethylthio radical ($^\bullet\text{SCF}_3$) together to form some fascinating compounds. Inspired by this idea, a first attempt was made and fortunately it works (Scheme 1, this work). Herein, we wish to report a facile approach for the trifluoromethylthiolation of methylenecyclopropanes along with a mechanistic investigation.

Our exploration was initiated with MCP **1a** (0.2 mmol), AgSCF_3 (0.3 mmol), $\text{K}_2\text{S}_2\text{O}_8$ (0.6 mmol), and HMPA (0.1 mmol)

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Table 1 Optimization of the reaction conditions^a


Entry	Solvent (3 mL)	Oxidant (3 eq.)	Additive (0.5 eq.)	Temp./°C	2a : 3a ^b	Yield ^c (%)
1	DMSO	Na ₂ S ₂ O ₈	—	80	— : 46	46
2	CH ₃ CN	Na ₂ S ₂ O ₈	—	80	— : 13	13
3	DMF	Na ₂ S ₂ O ₈	—	80	37 : 2	39
4	Dioxane	Na ₂ S ₂ O ₈	—	80	4 : —	4
5	DMSO	K ₂ S ₂ O ₈	—	80	21 : 22	43
6	DMSO	(NH ₄) ₂ S ₂ O ₈	—	80	— : 44	44
7	DMSO	Na ₂ S ₂ O ₈	K ₂ CO ₃	80	10 : 35	45
8	DMSO	Na ₂ S ₂ O ₈	K ₃ PO ₄	80	15 : 25	40
9	DMSO	Na ₂ S ₂ O ₈	Cs ₂ CO ₃	80	4 : 36	40
10	DMSO	Na ₂ S ₂ O ₈	AgOAc	80	— : 17	17
11	DMSO	Na ₂ S ₂ O ₈	HMPA	80	47 : 5	52
12	DMSO	Na ₂ S ₂ O ₈		80	— : 42	42
13	DMSO	Na ₂ S ₂ O ₈		80	— : 48	48
14 ^d	DMSO	Na ₂ S ₂ O ₈	HMPA	60	44 : 7	51
15 ^d	DMSO	Na ₂ S ₂ O ₈	HMPA	40	31 : 4	35

^a The reaction conditions: **1a** (0.2 mmol), AgSCF₃ (0.3 mmol), oxidant (0.6 mmol), and additive (0.1 mmol) were dissolved in 3 mL DMSO and the reaction mixture was stirred at 80 °C for 6 h. ^b Determined by ¹⁹F NMR with *p*-bromobenzotrifluoride as an internal standard and **1a** was taken as a standard for yield evaluation. ^c The total yield of **2a** and **3a**. ^d The reaction time was prolonged to 12 h.

in MeCN at 80 °C under an argon atmosphere for 6 h. The isolated yield of **2a** was 25%, along with an aromatized product **3a** derived from the further oxidation of **2a** (see ESI†). The yield was not satisfactory but it strengthened our faith that a further optimization of the reaction conditions was worthwhile.

Results and discussion

In order to find out the optimal conditions, various relevant factors have been investigated and the results are summarized in Table 1. Since AgSCF₃ and K₂S₂O₈ are salts, polar solvents such as MeCN, DMSO, and DMF were mainly taken into consideration and DMSO seemed to be the best one, giving **2a** in trace amounts and the aromatized product **3a** in 46% yield (Table 1, entries 1–4). Using DMSO as the solvent, different oxidants were added into the reaction system to examine their efficiency in producing the trifluoromethylthio (SCF₃) radical. We found that Na₂S₂O₈ was more effective than K₂S₂O₈ and (NH₄)₂S₂O₈ (Table 1, entries 5 and 6). Different additives also showed great influence on the reaction outcome. Inorganic bases like K₂CO₃ could partially prevent the oxidation of **2a** to **3a** and further examination revealed that HMPA was the best additive with which the oxidation could be suppressed to the lowest degree and the overall yield was acceptable (52% total yield) (Table 1, entries 7–11). Adding pyridine or bipyridine as a ligand or organic base did not facilitate the formation of **2a** (Table 1, entries 12 and 13). Lowering the reaction temperature and prolonging the reaction time could not improve the yield of **2a** or **3a** (Table 1, entries 14 and 15).

Table 2 Optimization of the reaction conditions^a


Entry	<i>m/n</i> ^b	2a:3a ^c	Yield ^d (%)
1	1 : 1	36 : —	36
2	2 : 2	53 : —	53
3	3 : 3	56 : —	56
4	4 : 4	52 : —	52

^a The reaction conditions: **1a** (*m* equiv.), AgSCF₃ (0.2 mmol), oxidant (*n* equiv.), and additive (0.1 mmol, 0.5 equiv.) were dissolved in 3.0 mL DMSO and the reaction mixture was stirred at 80 °C for 6 h. ^b The ratio of **1a**/Na₂S₂O₈. ^c Determined by ¹⁹F NMR with *p*-bromobenzotrifluoride as an internal standard. ^d The yield of **2a** and AgSCF₃ was taken as a standard for yield evaluation.

Now, we were still faced with two problems: the yield was still not satisfactory and the oxidation of **2a** to **3a** was not under control. Further control experiments demonstrated that substrate **1a** was not stable and could be easily oxidized by Na₂S₂O₈ in the reaction system, which might limit the yield of **2a** or **3a** (see ESI†). To overcome these problems, we decided to change the ratio of **1a** and oxidant with regard to AgSCF₃ to improve the yield of **2a** and the results are shown in Table 2. To our delight, we found that when the employed amounts of substrate **1a** and Na₂S₂O₈ (oxidant) were raised to 3.0 equiv. (*m/n* = 3/3) and AgSCF₃ was taken as 1.0 equiv., **2a** was obtained in a yield of 56% as a single product (Table 2, entry 3).

With the optimized conditions in hand, we then examined the substrate scope of this trifluoromethylthiolation of methyl-



Scheme 2 Substrate scope of 1. The reaction conditions: 1 (0.6 mmol), AgSCF_3 (0.2 mmol), $\text{Na}_2\text{S}_2\text{O}_8$ (0.6 mmol), and HMPA (0.1 mmol) were dissolved in 3 mL DMSO and the reaction mixture was stirred at 80 °C for 6 h. All the yields are isolated yields and AgSCF_3 was taken as a standard for yield evaluation. ^a The two isomers can be separated. ^b The two isomers cannot be isolated.

enecyclopropanes as summarized in Scheme 2. Substrates 1 with a variety of substituents at the aromatic ring were successfully converted into the desired products in yields ranging from 25% to 65%.

In general, substrates 1b–1f bearing electron-withdrawing substituents gave the desired products in relatively low yields. For example, substrate 1b having a strongly electron-withdrawing nitro group afforded the corresponding product 2b in 25% yield. As for substrates bearing electron-donating groups, the transformations of 1 to 2 are generally favored. For instance, the conversion efficiency of 1j to 2j with three electron-donating methoxy groups was much higher than others. However, in the case of 1i, the desired product 2i was formed in 40% yield, presumably due to its instability in the presence of a large amount of oxidant. It should be also noted that in the cases of 1c and 1e, two trifluoromethylthiolated regioisomers were formed at the same time. The *p*-toluenesulfonylamino group-containing substrates 1m and 1n can be well tolerated under the reaction conditions, affording the desired products 2m and 2n in good yields. The X-ray crystal structure of 2n has been obtained (Fig. 1) and the CIF data are given in the ESI.† Diphenylmethylenecyclopropane 1p was also compatible in this transformation, but naphthylmethylenecyclopropane only resulted in a complex product mixture under the standard conditions.

Product 2 could undergo dehydrogenation to a great tendency in the presence of oxidants and the formation of the aromatized product 3 provided a new synthetic protocol to prepare trifluoromethylthiolated naphthalene derivatives.

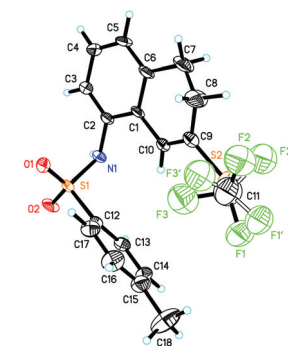
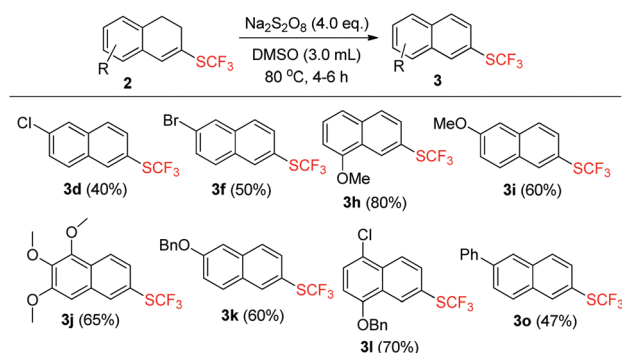


Fig. 1 X-ray crystal structure of product 2n.



Scheme 3 Substrate scope of 2. The reaction conditions: 2 (0.2 mmol), $\text{Na}_2\text{S}_2\text{O}_8$ (0.8 mmol) in 3.0 mL DMSO. All the yields are isolated yields.

Inspired by the result that the aromatized compound was obtained while screening the reaction conditions (Table 1, entry 1), we attempted to use the same oxidant $\text{Na}_2\text{S}_2\text{O}_8$ to achieve the dehydrogenation. After a brief investigation, using 4.0 equiv. of $\text{Na}_2\text{S}_2\text{O}_8$ alone and stirring the reaction mixture for 4–6 h at 80 °C could produce the aromatized products 3 in moderate to good yields ranging from 40% to 80% and the results are summarized in Scheme 3.

In order to directly obtain 3a, we just needed to mix 1a (1.0 eq.), AgSCF_3 (1.5 eq.), and $\text{Na}_2\text{S}_2\text{O}_8$ (3 eq.) together in DMSO upon heating at 80 °C for about 6 h, directly giving 3a in 46% yield in a one pot manner (Table 1, entry 1 or Scheme 4).

It was believed that the reaction proceeded *via* a radical-type pathway on the basis of previously reported literature.^{4d,i,8} Therefore, control experiments with radical inhibitors TEMPO and BHT were performed as shown in Scheme 5. The formation of the corresponding trifluoromethylthiolated product was significantly suppressed (for more details, see ESI†), rendering a radical process reasonable. However, it is true that



Scheme 4 Direct conversion of 1a to 3a.



Scheme 5 Radical inhibition experiments.



Scheme 6 Proposed reaction mechanism.

AgSCF_3 decomposed partially in the presence of a large amount of BHT and even completely decomposed in the presence of a large amount of TEMPO, thus such control experiments can only give mechanistic support to some degree. Moreover, F_3CSSCF_3 ¹⁰ can be detected in the reaction system by ^{19}F NMR spectroscopy resulting from coupling of two SCF_3 radicals. Overall, we believe that this reaction goes through a radical process.

Taking all the above information into consideration, a plausible mechanism of this trifluoromethylthiolation has been proposed in Scheme 6. AgSCF_3 can release SCF_3 radical upon oxidation with $\text{Na}_2\text{S}_2\text{O}_8$ and the SCF_3 radical can be transformed into its dimer F_3CSSCF_3 , which can also be converted into SCF_3 radical with the help of Ag^+ .^{4d,i} Then, the SCF_3 radical adds to the double bond of substrate **1** to form a ring-opening radical intermediate **A**, followed by a cyclization to give intermediate **B**. The intermediate **B** is oxidized by $\text{SO}_4^{\cdot-}$ to afford product **2**, which can be easily dehydrogenated and aromatized by $\text{Na}_2\text{S}_2\text{O}_8$ to afford product **3**.

In summary, we have developed a practical method for the facile trifluoromethylthiolation of methylenecyclopropanes (MCPs) in the presence of $\text{AgSCF}_3/\text{Na}_2\text{S}_2\text{O}_8$, and a variety of substrates can tolerate the oxidative conditions to give trifluoromethylthiolated 1,2-dihydronaphthalene derivatives in moderate to good yields. The products can conveniently be further aromatized upon oxidation with $\text{Na}_2\text{S}_2\text{O}_8$, offering a new synthetic method for the preparation of trifluoromethylthiolated naphthalenes. Efforts are in progress for the appli-

cation of this new methodology to synthesizing interesting biologically active trifluoromethylthiolated compounds in our laboratory.

Experimental section

General remarks

^1H NMR spectra were recorded on a Varian Mercury-300 and 400 spectrometer for solutions in CDCl_3 with tetramethylsilane (TMS) as an internal standard; coupling constants J are given in Hz. ^{13}C NMR spectra were recorded on Varian Mercury-300 and 400 spectrophotometers (75 or 100 MHz) with complete proton decoupling (CDCl_3 : 77.0 ppm). Mass and HRMS spectra were recorded by EI method. Organic solvents used were dried by standard methods where necessary. Infrared spectra were recorded on a Perkin-Elmer PE-983 spectrometer with absorption in cm^{-1} . Melting points were determined on a digital melting point apparatus and temperatures were uncorrected. Commercially obtained reagents were used without further purification. All these reactions were monitored by TLC with silica gel coated plates or ^{19}F NMR. Flash column chromatography was carried out using silica gel at increased pressure.

General procedure for the trifluoromethylthiolation of MCPs

Compound **1** (0.6 mmol), AgSCF_3 (42 mg, 0.2 mmol), and $\text{Na}_2\text{S}_2\text{O}_8$ (142 mg, 0.6 mmol) were placed in a Schlenk tube. The tube was evacuated and backfilled with Ar three times and then DMSO (3 mL) and HMPA (0.1 mmol) were injected. Afterwards, the reaction mixture was stirred at 80 °C in an oil bath for 6 h. When the reaction was complete, the product was extracted with EtOAc and washed with water. The organic layer was dried over Na_2SO_4 and concentrated on a rotary evaporator. The residue was roughly purified by silica gel flash chromatography and further purified by gel permeation chromatography (GPC) to give a pure product.

General procedure for the dehydrogenation of **2**

The product **2** (0.2 mmol) and $\text{Na}_2\text{S}_2\text{O}_8$ (191 mg, 0.8 mmol) were placed in a flask and DMSO (3 mL) was added. Then, the reaction mixture was stirred at 80 °C in an oil bath for about 4–6 h. When the reaction was complete, the aromatized product was extracted with EtOAc and washed with water. The organic layer was dried over Na_2SO_4 and concentrated on a rotary evaporator. The residue was purified by silica gel flash chromatography and if necessary, it was further purified by gel permeation chromatography (GPC) to give a pure product.

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