

Direct Trifluoromethylthiolation of Unactivated C(sp³)–H Using Silver(I) Trifluoromethanethiolate and Potassium Persulfate**

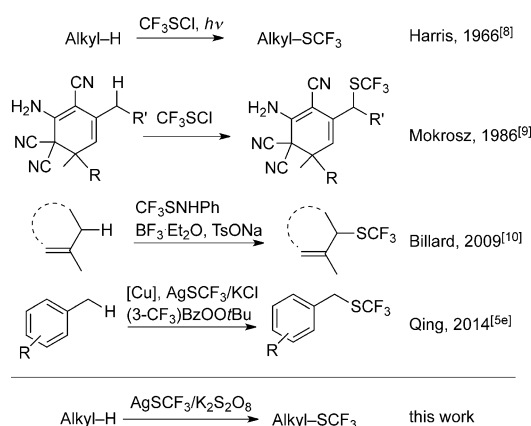
Hao Wu, Zhiwei Xiao, Junhui Wu, Yong Guo, Ji-Chang Xiao, Chao Liu,* and Qing-Yun Chen*

Abstract: A practical and efficient method for the direct trifluoromethylthiolation of unactivated C(sp³)–H bonds by AgSCF₃/K₂S₂O₈ under mild conditions is described. The reaction has a good functional-group tolerance and good selectivity. Initial mechanistic investigations indicate that the reaction may involve a radical process in which K₂S₂O₈ plays key roles in both the activation of the C(sp³)–H bond and the oxidation of AgSCF₃.

A trifluoromethylthio group (CF₃S) can significantly influence the chemical, physical, and biological properties of a parent substrate because of its strong electronegativity and high lipophilicity.^[1] Considerable efforts have thus been devoted to the development of methods to introduce this group into organic molecules. Two major strategies for the chemical introduction of trifluoromethylthio groups were developed: the direct formation of C–S bonds (R–SCF₃) and the trifluoromethylation of thiols and their derivatives (RS–CF₃).^[2] In recent years, several elegant methods have been reported for the electrophilic,^[3] nucleophilic,^[4] and oxidative direct trifluoromethylthiolation.^[5] These methods enable the fast and efficient synthesis of various CF₃S-containing compounds.

In comparison to the recent progress made in the formation of C(sp²)–SCF₃ or C(sp)–SCF₃ bonds, only few methods have been developed for the formation of C(sp³)–SCF₃ bonds. Besides the classical halogen–fluorine exchange of polyhalogenomethyl thioethers or the trifluoromethylation of sulfur-containing compounds,^[2] alkyltrifluoromethyl thioethers are mainly accessed by employing electrophilic^[3a,6] or nucleophilic^[7] trifluoromethylthiolation reagents. Although these methods efficiently lead to the desired alkyltrifluoro-

methylthioethers, they generally require prefunctionalized starting materials. From a preparative and atom-economical point of view, the direct trifluoromethylthiolation of an unactivated C(sp³)–H bond constitutes the most straightforward approach to alkyltrifluoromethylthioethers. However, only few synthetic methods have been reported thus far (Scheme 1). Harris first reported in 1966 the free-radical



Scheme 1. Previous reports on the direct trifluoromethylthiolation of unactivated C(sp³)–H bonds.

chain reaction of alkanes with the highly toxic gas trifluoromethanesulfonyl chloride (CF₃SCl).^[8] Although various trifluoromethylthiolated isomers were successfully obtained, the reaction showed a narrow substrate scope and poor selectivity. In 1986, Mokrosz reported the direct trifluoromethylthiolation of the allylic H atom in alkylidenemalononitrile dimers by reaction with CF₃SCl.^[9] In 2009, Billard and co-workers reported a method for the direct trifluoromethylthiolation of allylic H atoms of hindered olefins with the electrophilic reagent CF₃SNMePh.^[10] Very recently, Qing and co-workers disclosed the Cu-mediated direct trifluoromethylthiolation of a benzylic C–H bond.^[5e] Thus, the development of reagent systems that can efficiently trifluoromethylthiolate the unactivated C(sp³)–H bond under mild conditions is highly desirable.

On the other hand, unactivated C(sp³)–H bonds, especially those that are not adjacent to an sp²-hybridized C atom or a functional group that favors the formation of radicals or anions, exhibit the least reactivity, as they are less acidic and have no empty low-energy or filled high-energy orbitals that easily interact with orbitals of a metal center. Their selective functionalization under mild conditions represents a significant challenge and goal in modern synthetic chemistry.^[11] Recently, the direct fluorination of unactivated C(sp³)–H

[*] H. Wu, Z. Xiao, Prof. Dr. Y. Guo, Prof. Dr. J.-C. Xiao, Prof. Dr. C. Liu, Prof. Dr. Q.-Y. Chen
Key Laboratory of Organofluorine Chemistry
Shanghai Institute of Organic Chemistry
Chinese Academy of Sciences
345 Lingling Road, 200032, Shanghai (China)
E-mail: chaoliu@sioc.ac.cn
chenqy@sioc.ac.cn

J. Wu
School of Chemical and Environmental Engineering
Shanghai Institute of Technology
100 Haiquan Road, Shanghai 201418 (China)

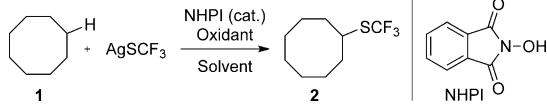
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bonds has received great interest and impressive progress has been made.^[12] Various C(sp³)-F bond-containing compounds were efficiently and readily produced, typically through a radical pathway involving the generation and trapping of alkyl radicals with fluorine-transfer reagents. These important advances inspired us to investigate the formation of C(sp³)-SCF₃ bonds through radical C(sp³)-H activation and functionalization.

In order to test our hypothesis, we chose cyclooctane **1** as the model substrate for the direct trifluoromethylthiolation of C(sp³)-H bonds. As radical initiator we used *N*-hydroxyphthalimide (NHPI), a precursor of the phthalimido-*N*-oxyl (PINO) radical and a well-known organocatalyst for the effective C(sp³)-H activation by hydrogen abstraction.^[13] For a CF₃S-transfer reagent system, we used AgSCF₃^[14] as the convenient CF₃S resource and K₂S₂O₈ as the oxidant.^[5 g] When a mixture of **1** (1 equiv), NHPI (0.1 equiv), AgSCF₃ (1.5 equiv), and K₂S₂O₈ (2 equiv) in CH₃CN was stirred at 60 °C under Ar atmosphere for 12 h, the desired mono-trifluoromethylthiolated product **2** was formed in 43 % yield along with some poly-trifluoromethylthiolated products, which were identified by their characteristic signals in ¹⁹F NMR spectroscopy and GC-MS mass spectrometry. Encouraged by this preliminary result, we optimized the reaction conditions (Table 1). When AgSCF₃ was used as the limiting reagent with 10 equiv of **1** under similar conditions, the desired mono-trifluoromethylthiolated product **2** was obtained in 82 % yield without the formation of any poly-trifluoromethylthiolated products (Table 1, entry 1). Later, we found that only a little excess of substrate (2 equiv) was required for the selective formation of the mono-trifluoromethylthiolated product, thus demonstrating the high efficiency of the reaction (Table 1, entry 2). The oxidant K₂S₂O₈ played an important role in the reaction, as no desired product was obtained in its absence or in the presence of other oxidants, such as NaIO₄, PhI(OAc)₂, Pb(OAc)₄ (Table 1, entries 3–5). A survey of the oxidant-to-substrate ratio showed that 2 equiv of K₂S₂O₈ gave the best yield (Table 1, entries 6 and 7). Among several common solvents that we screened, CH₃CN stood out as the best one and water was harmful for the reaction (Table 1, entries 8–13). A reaction temperature higher than 50 °C was required for an effective transformation, as no obvious conversion of AgSCF₃ was observed at lower temperatures (Table 1, entries 14–18). Interestingly, when the reaction was conducted at 50 °C, a longer reaction time (12 h) was required, as no reaction occurred within 4 h (Table 1, entry 16). Finally, the presence of the free silver cation was crucial for the reaction, because both the replacement of AgSCF₃ with CuSCF₃ and the addition of KCl (KCl/AgSCF₃ = 1:1) to the reaction mixture prevented the formation of the desired trifluoromethylthiolated product (Table 1, entries 19 and 20). To our surprise, the reaction proceeded smoothly in the absence of NHPI, which we originally considered as the key alkyl radical initiator (Table 1, entry 21). Based on these test reactions, the combination of AgSCF₃, K₂S₂O₈, and CH₃CN at 60 °C was established as the optimal conditions for the simple, mild, and efficient direct trifluoromethylthiolation of unactivated C(sp³)-H bonds.

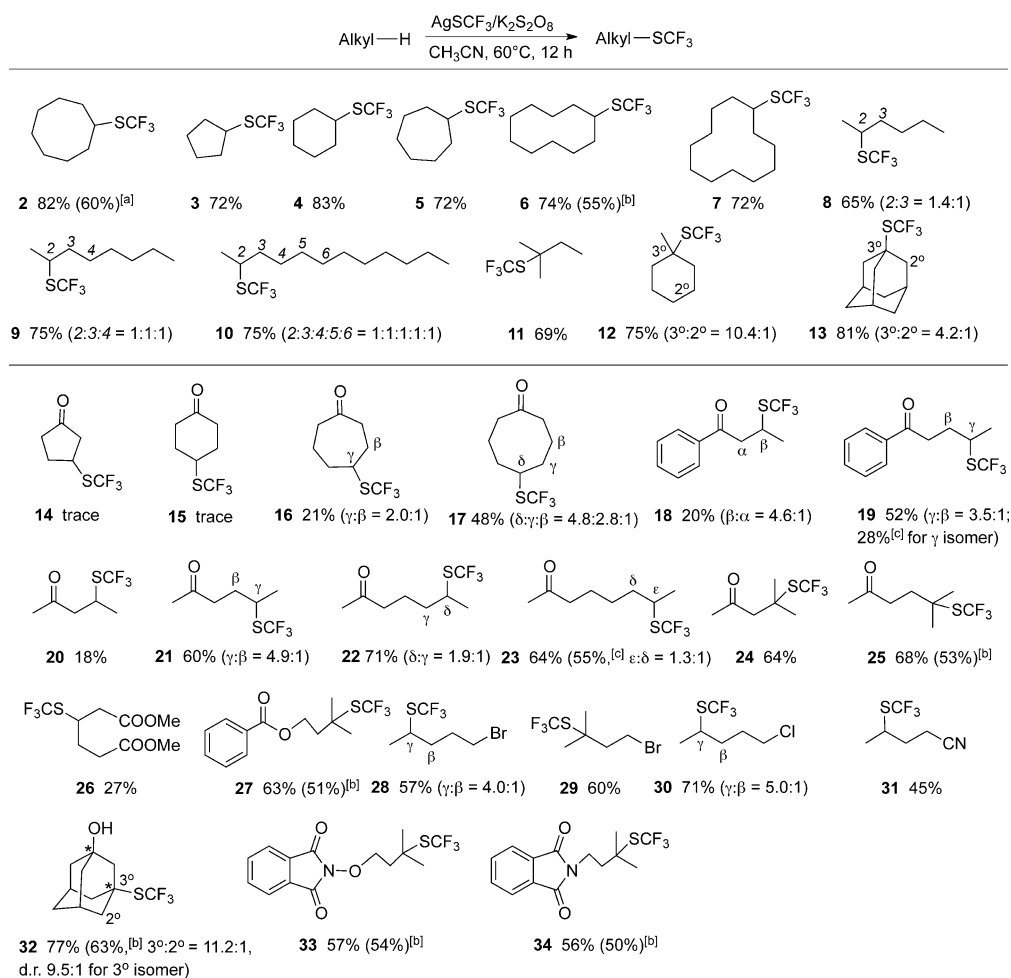
Table 1: Optimization of reaction conditions for trifluoromethylthiolation of cyclooctane.^[a]



Entry	Oxidant	Solvent	T [°C]	Yield [%] ^[b]
1 ^[c]	K ₂ S ₂ O ₈	CH ₃ CN	60	82
2	K ₂ S ₂ O ₈	CH ₃ CN	60	82
3	NaIO ₄	CH ₃ CN	60	0
4	PhI(OAc) ₂	CH ₃ CN	60	< 5
5	Pb(OAc) ₄	CH ₃ CN	60	0
6	K ₂ S ₂ O ₈ ^[d]	CH ₃ CN	60	74
7	K ₂ S ₂ O ₈ ^[e]	CH ₃ CN	60	48
8	K ₂ S ₂ O ₈	DMF	60	trace
9	K ₂ S ₂ O ₈	DMSO	60	8
10	K ₂ S ₂ O ₈	acetone	60	10
11	K ₂ S ₂ O ₈	ClCH ₂ CH ₂ Cl	60	0
12	K ₂ S ₂ O ₈	MeOH	60	0
13	K ₂ S ₂ O ₈	CH ₃ CN/H ₂ O ^[f]	60	< 5
14	K ₂ S ₂ O ₈	CH ₃ CN	40	0
15	K ₂ S ₂ O ₈	CH ₃ CN	50	80
16 ^[g]	K ₂ S ₂ O ₈	CH ₃ CN	50	0
17	K ₂ S ₂ O ₈	CH ₃ CN	70	81
18	K ₂ S ₂ O ₈	CH ₃ CN	80	79
19 ^[h]	K ₂ S ₂ O ₈	CH ₃ CN	60	0
20 ^[i]	K ₂ S ₂ O ₈	CH ₃ CN	60	0
21 ^[j]	K₂S₂O₈	CH₃CN	60	82

[a] Reaction conditions: cyclooctane (2.0 equiv), AgSCF₃ (0.2 mmol, 1.0 equiv), oxidant (2.0 equiv) and NHPI (0.1 equiv) in solvent (2 mL) under Ar atmosphere for 12 h. [b] Yields were determined by ¹⁹F NMR spectroscopy with trifluorotoluene as an internal standard. [c] Cyclooctane (10 equiv) was used. [d] K₂S₂O₈ (3.0 equiv) was used. [e] K₂S₂O₈ (1.0 equiv) was used. [f] The reaction was conducted in CH₃CN/H₂O (1:0.1 v/v). [g] Reaction time: 4 h. [h] CuSCF₃ (1.0 equiv) was used instead of AgSCF₃. [i] KCl (1.0 equiv) was added to the reaction. [j] No NHPI was used. The entry in bold marks optimized reaction conditions.

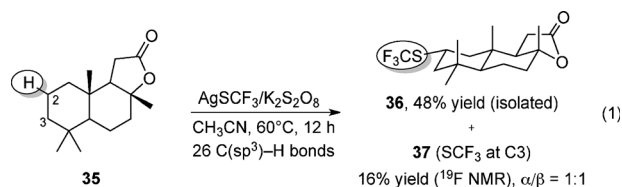
Various unactivated saturated hydrocarbons were then subjected to the optimized reaction conditions. All examined substrates were effectively transformed to the desired products in good yields (Scheme 2, **2–13**). The reaction also showed good site selectivity with preference for tertiary C–H bonds over secondary ones (**11–13**). The substrate scope of the reaction was investigated next. A variety of functional groups, such as ketones, esters, bromides, chlorides, alcohols, cyanates, and phthalimides, were well tolerated under the reaction conditions (**14–34**). Similarly, the direct C(sp³)-H trifluoromethylthiolation occurred predominantly at tertiary C–H bonds. Cyclopentanone and cyclohexanone were not suitable substrates for the reaction, as only trace amounts of the desired products were observed, however, the reaction of cycloheptanone and cyclooctanone successfully resulted in the desired products (**14–17**). Various acyclic ketones underwent the trifluoromethylthiolation to give the desired products in acceptable yields (**18–25**). Notably, although the α position of the carbonyl group is generally the most reactive site in ketones, α-CF₃S products were not the major products and were commonly formed in negligible yields, which might be ascribed to the strong polar effect exerted by the carbonyl group in the C(sp³)-H bond cleavage step in this reac-



Scheme 2. Scope of the direct trifluoromethylthiolation of various unactivated C(sp³)-H bonds. Reaction conditions: substrate (2.0 equiv), AgSCF₃ (0.2 mmol, 1.0 equiv), oxidant (2.0 equiv) in acetonitrile (2 mL) under Ar atmosphere for 12 h. Yields were determined by ¹⁹F NMR spectroscopy with trifluorotoluene as internal standard. The ratio of isomers was determined by ¹⁹F NMR spectroscopy or GC-MS. Yields of isolated products are given in parentheses. [a] 5.0 mmol scale. [b] 1.0 mmol scale. 2° = secondary carbon center, 3° = tertiary carbon center.

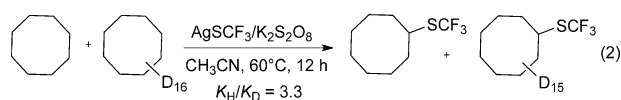
tion.^[13b,15] It should be mentioned that primary and secondary aliphatic alcohols could not be transformed in the reaction and no desired trifluoromethylthiolated products were observed, which might be due to the thermodynamically weaker C-H bond adjacent to the OH group. Indeed, when 1-adamantanol was used as the substrate, the trifluoromethylthiolation reaction proceeded smoothly to produce the desired trifluoromethylthiolated product in good yield (**32**). However, the reaction was not compatible with alkene and alkyne groups and a complicated reaction mixture was formed.

The possible scalability of the direct trifluoromethylthiolation of unactivated C(sp³)-H bonds was demonstrated by the reaction of cyclooctane on a 5 mmol scale. The reaction proceeded smoothly and led to the isolated product in 60% yield (Scheme 2, **2**). Furthermore, to show the potential of the reaction in late-stage synthetic planning, (+)-sclareolide (**35**), a terpenoid natural product with antifungal and cytotoxic properties, was subjected to the direct C(sp³)-H trifluoromethylthiolation [Eq. (1)]. Although **35** contains 26 aliphatic C(sp³)-H bonds, the C2-equatorial trifluoromethylthiolated

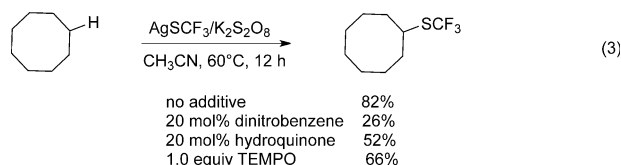


product **36** was isolated as the major product in 48% yield with minor amounts of product **37** (SCF₃ at C3). The structure of **36** was unambiguously determined by various analytical techniques, including X-ray single-crystal analysis (see the Supporting Information for details).

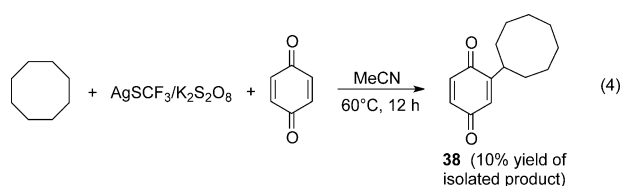
Some preliminary mechanistic studies on the direct trifluoromethylthiolation of C(sp³)-H bonds were conducted in order to gain some insights into the reaction pathway. First, kinetic isotope effects (KIE) were measured by using cyclooctane and [D₁₆]cyclooctane (1:1) as the substrates under the standard reaction conditions [Eq. (2)], affording an intermolecular competitive KIE of 3.3. This large KIE suggested that



the cleavage of the C–H bond is the rate-limiting step. Second, an electron-transfer scavenger (1,4-dinitrobenzene), a radical inhibitor (hydroquinone), or a radical scavenger (2,2,6,6-tetramethyl-1-piperidinyloxy, TEMPO) were added to the reaction of cyclooctane [Eq. (3)]. The addition of 1,4-

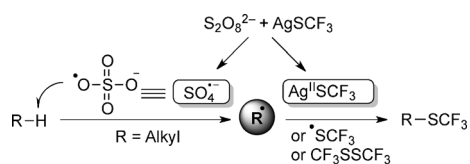


dinitrobenzene resulted in a sharp decrease in the yield, while the addition of hydroquinone and TEMPO did not have a significant impact on the reaction. These results might be due to the consumption of hydroquinone and TEMPO under the strongly oxidizing reaction conditions.^[16] Moreover, the addition of benzoquinone to the reaction system resulted in the formation of product **38** [Eq. (4)].^[7m] All these exper-



imental results indicate that the direct trifluoromethylthiolation of C(sp³)–H bonds might proceed through a radical pathway. In addition, the reactivity of the C(sp³)–H bonds increases in the order of primary < secondary < tertiary (see Scheme 2) and the main side product in most cases is CF₃SSCF₃ (¹⁹F NMR signal at –46.65 ppm), thus demonstrating a radical reaction pathway as well.

Based on these preliminary results and previous reports on the C(sp³)–H activation,^[11–13] we propose a radical mechanism for the direct trifluoromethylthiolation of C(sp³)–H bonds (Scheme 3). K₂S₂O₈ decomposes into a sulfate radical anion with the help of the silver cation present in the reaction system, which (as PINO) abstracts the hydrogen atom from a C(sp³)–H bond in the substrate to generate the corresponding alkyl radical.^[17] At the same time, the oxidation of



Scheme 3. Proposed mechanism for the direct trifluoromethylthiolation of unactivated C(sp³)–H bond.

AgSCF₃ by K₂S₂O₈ affords the Ag^{II}SCF₃ species,^[18] a CF₃S radical, or CF₃SSCF₃. The produced alkyl radical abstracts the CF₃S ligand of Ag(II)SCF₃ or couples with a CF₃S radical or CF₃SSCF₃ to afford the corresponding trifluoromethylthiolated product.

In conclusion, a direct trifluoromethylthiolation of unactivated C(sp³)–H bond proceeds with AgSCF₃ and K₂S₂O₈. The reaction is mild, efficient, and practical and produced C(sp³)–SCF₃ bonds with good functional-group tolerance and selectivity. Preliminary investigations show a radical reaction pathway with K₂S₂O₈ not only as an oxidant, but also as a good H atom abstractor. Further studies on the exploration of K₂S₂O₈ as an efficient radical initiator for other radical reactions are in progress.

Keywords: C–H activation · fluorine · radical reactions · synthetic methods · trifluoromethylthiolation

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