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Trifluoromethylation of Thiophenols and Thiols with Sodium Trifluoromethanesulfinate and Iodine Pentoxide

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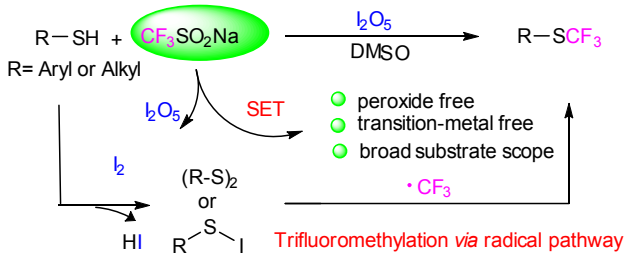

A selective and operationally easy trifluoromethylation of a wide range of thiophenols and thiols under metal free conditions by using two simple and safe solids, sodium trifluoromethanesulfinate and iodine pentoxide, *via* the radical process has been developed.

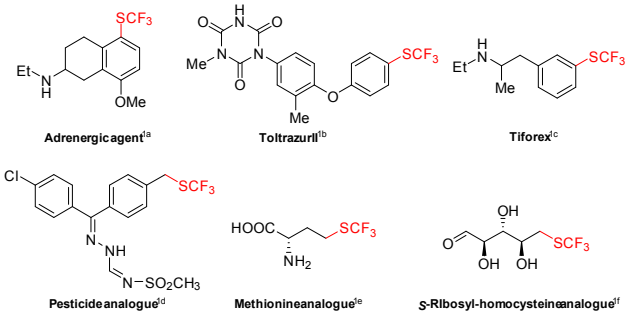

Figure 1. Examples of SCF_3-containing biologically active compounds.

Trifluromethylthio group (SCF_3) has received increasing attention as an enhanced version of CF_3 in bioactive molecules,[1] which is a highly privileged functionality for pharmaceutical and agrochemical agents (Figure 1).[2] SCF_3-containing compounds were generated as the trifluoromethyl group attached to sulfur atoms instead of carbon atoms, which displayed rather different properties, compared to the SCH_3 group.[3] The linkage of a strong electron-withdrawing, and metabolically stable CF_3 group with a highly polarizable and bio-friendly sulfur atom, which makes SCF_3 showed extremely high lipophilicity (Π =1.44)[4] for small molecules to cross lipid membranes and influences intracellular targets.[5] Therefore, numerous efforts have been devoted to the development of new methodologies for the preparation of these SCF_3-containing molecules.

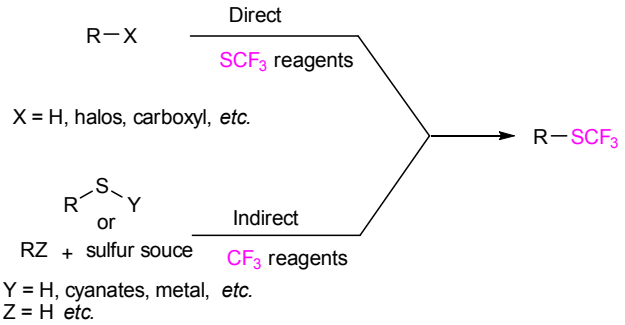

Figure 2. Two major strategies for the preparation of SCF_3-containing compounds.

Accordingly, two major strategies have been developed for the formation of SCF_3 over years (Figure 2). One is the direct trifluoromethylthiolation with SCF_3 reagents.[6] This strategy is a straightforward protocol for the preparation of SCF_3 compounds, which does not require specific skills and use of protective clothing and equipment.[7] Many researches are focused on typical novel trifluoromethylthiolated reagents, such as $MSCF_3$ (M= Cu, Ag, Cs),[8] $(Me_4N)SCF_3$,[9] N-SCF_3 reagents[10], O-SCF_3 reagents[11] and hypervalent iodine SCF_3 reagents,[12] which have replaced the hazardous reagents that were most available in the gaseous form or relatively ineffective reagents.[13] Nevertheless, some of these SCF_3 reagents still existed drawbacks, such as high cost or the pre-preparation process which involved lengthy reactions or harsh conditions.

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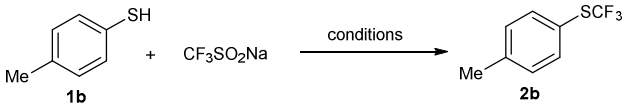
The other was the indirect formation focused on trifluoromethylating of different sulphur sources. Great attention has concentrated on this field since a variety of sulphur sources, such as thiolates,[14] S_8,[15] thiocyanates,[16] $Na_2S_2O_3$,[17] sulfocyanate,[18] disulfides[19] and thiols[20] have been effectively combined with relatively inexpensive trifluoromethylated reagents. For example, pioneering by Umemoto, thiolates were found to be efficient sulphur sources with *Se*-(trifluoromethyl)dibenzoselenophenium for the synthesis of SCF_3.[14a] S_8 was an effective example which could be connected with $FSO_2CF_2CO_2Me$ and CF_3SiMe_3, as well as CF_3SO_2Na to afford SCF_3 moieties.[15a-b,15f] Goossen and co-workers employed thiocyanate to prepare the corresponding aryl trifluoromethyl with arenediazonium salts.[16a] Liu *et al.* reported an effective trifluoromethylthiolation using $Na_2S_2O_3$ as sulphur source.[17] The Langlois group developed a photocatalytic trifluoromethylation method in the presence of disulfides.[19c,19d] Boiko and Yagupolskii demonstrated a series of trifluoromethylation of thiols in liquid ammonia and UV initiation.[20a,20b] Although these approaches provided convenience for the SCF_3-containing compounds, several issues of these approaches should be addressed: (1) the limited starting substrates, such as aryl halogens, aryl boronic acids, terminal alkynes; (2) excess sulphur sources were utilized; (3) high volatile trifluoromethylated reagents were often used under radical process.

In 1989, Langlois and his co-workers described a TBHP-initiated trifluoromethylation of disulfides using CF_3SO_2Na as trifluoromethylated reagent.[21a] Although this method utilized stable and inexpensive trifluoromethylated source, almost half disulfides were oxidized by excess peroxide with low yield.[21b-d] Among these indirect cases, trifluoromethylation of thiols under radical process was an efficient protocol to obtain SCF_3 and several researches have been reported. Hard-handling and poor user-friendliness reagents, such as CF_3Br,[22] CF_3I[23] were used during the original research. Another type of trifluoromethylation reagent used in radical reactions was *N*-trifluoromethyla-*N*-nitrososulfon amide,[24] but difficult preparation process with low yield limited its application. Thus, the radical trifluoromethylation of thiols has not been well-studied.

Very recently, Liu and his co-workers reported a novel method to generate the corresponding CF_3 radical from sodium trifluoromethanesulfinate, using iodine pentoxide as a low-cost, green and stable inorganic oxidant.[25] Inspired by their work, and as part of our efforts in the field of organofluorine chemistry,[26] we herein endeavoured to develop a simple and atom economic trifluoromethylation method of a wide range of thiophenols and thiols in the presence of iodine pentoxide using CF_3SO_2Na as CF_3 source. This method allows for smooth transformation to various SCF_3 without transition metal catalysts and takes advantage of sulphur sources as much as possible.

We initially chose the trifluoromethylation of 4-methylbenzenethiol (**1b**) as the model reaction to optimize reaction conditions (Table 1). After screening several oxidants (entries 1-6), the best result was achieved in the presence of I_2O_5 using DCE/H_2O as solvent, giving *p*- tolyl(trifluoromethyl)-sulfane (**2b**) in 43 % yield (entry 6). Contrasted to aqueous

Table 1. Optimization of the reaction conditions.[a]



1b **2b**

Entry	Oxidant (equiv.)	CF_3SO_2Na (equiv.)	Solvent[b]	T (°C)	Yield (%)[c]
1	I_2 (2.0)	3.0	DCE/H_2O	110	N. D.
2	PhIO (2.0)	3.0	DCE/H_2O	110	N. D.
3	$PhI(OAc)_2$ (2.0)	3.0	DCE/H_2O	110	N. D.
4	$NaIO_3$ (2.0)	3.0	DCE/H_2O	110	N. D.
5	HIO_3 (2.0)	3.0	DCE/H_2O	110	N. D.
6	I_2O_5 (2.0)	3.0	DCE/H_2O	110	43
7[d]	I_2O_5 (2.0)	3.0	DCE/H_2O	110	63
8	I_2O_5 (2.0)	3.0	DMSO	110	92
9	I_2O_5 (2.0)	1.0	DMSO	110	31
10	I_2O_5 (2.0)	2.0	DMSO	110	59
11	I_2O_5 (2.0)	4.0	DMSO	110	88
12	I_2O_5 (1.0)	3.0	DMSO	110	39
13	I_2O_5 (3.0)	3.0	DMSO	110	89
14	I_2O_5 (4.0)	3.0	DMSO	110	81
15	I_2O_5 (2.0)	3.0	DMSO	90	79
16	I_2O_5 (2.0)	3.0	DMSO	70	24
17	I_2O_5 (2.0)	3.0	DMSO	50	trace
18	I_2O_5 (2.0)	3.0	DMSO	R.T.	trace
19[e]	-	3.0	DMSO	110	N. D.
20[f]	I_2O_5 (2.0)	-	DMSO	110	N. D.
21[g]	I_2O_5 (2.0)	3.0	DMSO	110	92

[a] Unless otherwise stated, all reactions were carried out with **1b** (0.2 mmol), solvent 2.0 mL, 24 h, GC yield. [b] DCE/H_2O (v/v= 3/1, 4.5 mL); DCE = 1,2-dichloroethane. [c] N.D.: not detected by GC-MS. [d] DMSO (1.0 mL) was added; DMSO = (methylsulfonyl)methane. [e] Without I_2O_5. [f] Without CF_3SO_2Na. [g] Under argon atmosphere.

solvents, DMSO was more suitable for this reaction (entry 6 *vs* entry 8). Additionally, 3.0 equiv. CF_3SO_2Na was necessary for the depletion of the thiols after screening (entries 8-11). The content of I_2O_5 was also screening, the result indicated that 2.0 equiv. I_2O_5 was enough for this reaction and the overloading of I_2O_5 might bring the decreasing yield (entries 12-14). Only trace product was found at room temperature, indicating that it is a temperature-dependent reaction (entries 15-18). Both I_2O_5 and CF_3SO_2Na were important for smooth transformation of this reaction (entries 19-20). Almost no difference was found when reacted under the argon atmosphere (entry 21).

Under the optimized reaction conditions, the trifluoromethylation of various thiophenols and thiols were tested to examine the scope of this reaction (Table 2). The reaction proved to be general and amenable to a range of structurally diverse substrates, and the desired products (**2a**-**2w)** were achieved in good yields. In general, both electron-rich and electron-deficient substrates reacted well and a wide variety of functional groups were covered, including methyl (**2b**), *tert*-butyl (**2c**), methoxyl (**2d**), halos (**2e**-**2g**), amino (**2h**, **2i**), nitro (**2k**-**2m**), carboxyl (**2n**). A slight difference in the yield about substituents (such as $-NO_2$) on the aromatic ring at any

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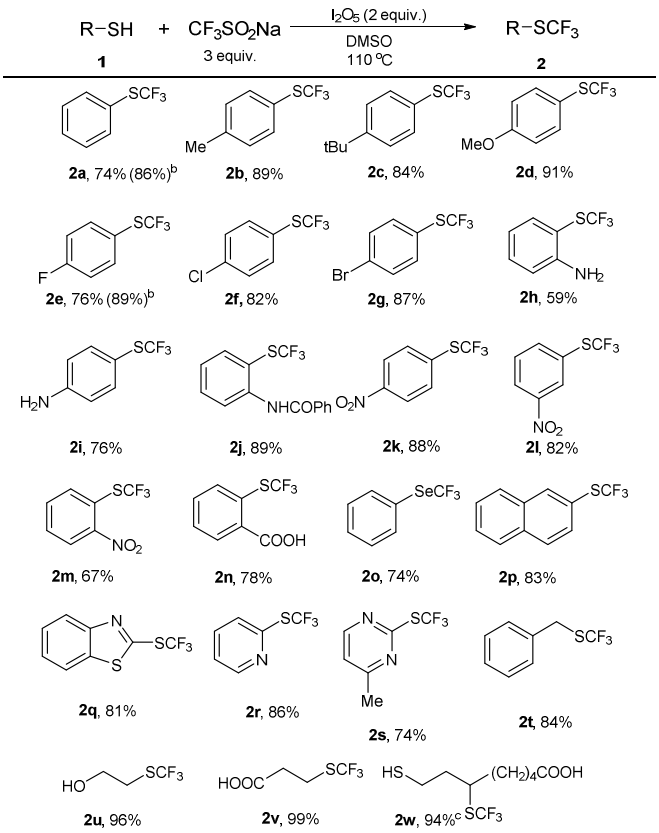
position (*para*-, *meta*-, *ortho*-) was found (**2k**-**2m**). In addition, benzeneselenol was obtained in 74% yield (**2o**). Furthermore, the aromatic rings with nathphyl, thiazole, pyridine, pyrimidine

Table 2. Trifluoromethylation of thiophenols and thiols. [a]

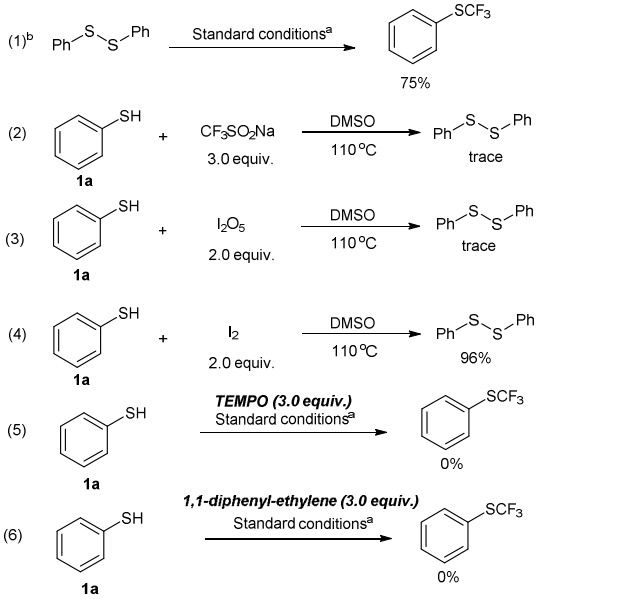


[a] Reaction condition: 1 (0.2 mmol), CF_3SO_2Na (3.0 equiv.), I_2O_5 (2.0 equiv.) and DMSO 2.0 mL, 110 ℃ for 24 h, isolated yield. [b] GC yield (due to high volatility). [c] Used DL-thioctic acid as **1w**.

were viable substrates under the current reaction, giving the corresponding products (**2p**-**2s**) in satisfactory yields. Thiols, such as benzylthiol, 2-mercaptoethanol and 3-mercapto-propanoic acid, were also smooth transformation for the products (**2t**-**2v**). Selective trifluoromethylation with branched sulfur (**2w**) was found when DL-thioctic acid used as substrate.[27]

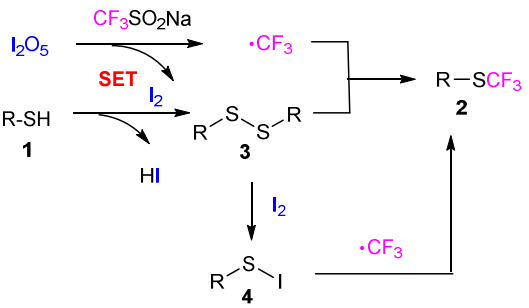
In the initial stage of the reaction, disulfides **3** was found and gradually reduced as the extension of the reaction time. This might indicated that **3** was an intermediate. Using disulfide to replace thiol and afforded almost the same result (Scheme 1, equ. 1). According to the contrast experiments, CF_3SO_2Na, as well as I_2O_5 was failed to promote the formation of disulfides **3**, Iodine, which was the residue of CF_3SO_2Na and I_2O_5, could be achieved (equ. 2-4). DMSO was also tested but failed, which were not shown in Scheme 1. To better understand the mechanism of this transformation, radical trapping experiments were carried out. No desired product was detected in the reaction in the presence of TEMPO (2,2,6, 6-tetramethyl-1-piperidinyloxy) (3.0 equiv.) and 1,1-diphenylethylene (3.0 equiv.) as radical scavengers (equ. 5 and 6), which points toward a radical mechanism.

Although the precise reaction mechanism remains to be clarified, we prefer a plausible mechanism in Scheme 2.[25,28]



Scheme 1. Control experiments. [a] CF_3SO_2Na (3.0 equiv.), I_2O_5 (2.0 equiv.) and DMSO 2.0 mL, 110 ℃ for 24 h. [b] 0.1 mmol disulphide

High temperature leaded to rapid reacting of iodine pentoxide and CF_3SO_2Na. As a result, I_2 was released and generated the CF_3 radical *via* single electron transfer. I_2 then reacted with thiols or thiophenols to form **3** and further reacted to form **4**.[28c,28d] Finally, the CF_3 radical coordinated to **3** or **4**, giving the desired products.



Scheme 2. Proposed reaction mechanisms.

In conclusion, we developed a convenient trifluoromethylation reaction of various thiophenols and thiols by using sodium trifluoromethanesulfinate and iodine pentoxide. The advantages such as good yields, excellent functional group tolerance made this transition-metal-free trifluoromethylation strategy for useful and practical formation of SCF_3-containing compounds. Mechanistic investigation revealed that this reaction proceeded via a radical pathway.

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