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Direct Trifluoromethylthiolation and Perfluoroalkylthiolation of C(sp^2)–H Bonds with CF_3SO_2Na and R_fSO_2Na

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Abstract: *A new method for CF_3SO_2Na-based direct trifluoromethylthiolation of C(sp^2)–H bonds has been developed. CF_3SSCF_3 is generated in situ from cheap and easy-to-handle CF_3SO_2Na, and in the presence of CuCl can be used for electrophilic trifluoromethylthiolation of indoles, pyrroles, and enamines. The method has been extended to perfluoroalkylthiolation reactions using R_fSO_2Na.*

Organofluorination is an area of active research because incorporation of either fluorine or fluorine-containing groups can alter the physical, chemical, and biological properties of the parent molecules.[1] In the organofluorine family, the trifluoromethylthiol (CF_3S) group holds a special position because of its high electron-withdrawing capability, good lipophilicity,[2] and bioavailability.[3] It has a great potential in the development of new pharmaceutical and agrochemical chemicals.[4]

Direct trifluoromethylthiolation using CF_3SH, CF_3SCl, and CF_3SSCF_3 has been reported in the literature.[5] Since they are highly reactive and hard-to-handle gaseous chemicals, a series of CF_3S-based reagents, including quaternary ammonium Me_4NSCF_3,[6] metallic $CuSCF_3$ and $AgSCF_3$,[7] and the shelf-stable chemicals **1a–f**, have been developed for trifluoromethylthiolation (Figure 1).[8–13] However, they have to be prepared by trifluoromethylthiolation or trifluoromethylation reactions, and could be very expansive. In 2009, the group of Magnier reported a CF_3SO_2K-initiated trifluoromethylation reaction. A small amount of trifluoromethylthiolation product was detected in the reaction mixture.[14] The group of Shibata recently used the trifluoromethanesulfonyl hypervalent iodonium ylide **2a** as a CF_3SO_2-based trifluoromethylthiolation agent.[15] It was proposed that CF_3SSCF_3 is generated in the reaction system.[15c] Sodium trifluoromethanesulfinate (CF_3SO_2Na; **2b**), known as the Langlois reagent, is a readily available and is a stable benchtop solid. It is a good source for the generation of CF_3 radical.[16] We envisioned that it could be a CF_3SO_2-based agent for direct electrophilic trifluoromethylthiolation through the in situ generation of CF_3SSCF_3.[5m]

Development of a system for efficient conversion of CF_3SO_2Na into CF_3SSCF_3 was the key for this project. We first examined the CF_3SO_2Na reaction of indole[17] in the presence of hypophosphite,[18] phosphite ester,[19] and iodotrimethylsilane[20] since they are known reducing agents for sulfonate, sulfonate, and sulfoxide (Table 1, entries 1–3). A reaction of 2 equivalents of $(EtO)_2P(O)H$ and CF_3SO_2Na at 110 °C without using any oxidant gave the trifluoromethyl-

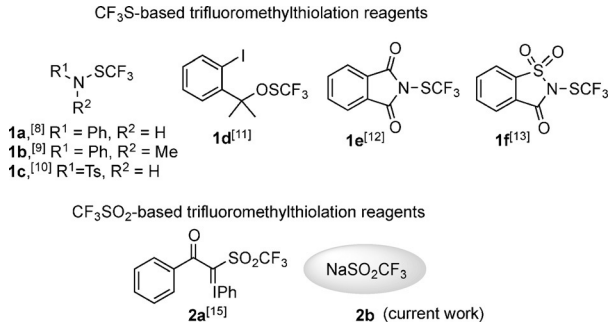
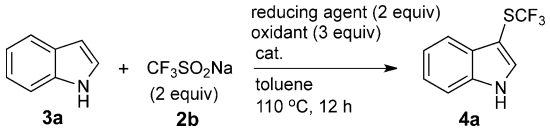


Figure 1. User-friendly trifluoromethylthiolation agents. Ts = 4-toluenesulfonyl.

Table 1: Optimization of trifluoromethylthiolation with $NaSO_2CF_3$.



3a 2b 4a

Entry	Reductant	Oxidant	Cat. (equiv)	Yield [%][a]
1	$EtOP(O)H_2$	–	–	–
2	$(EtO)_2P(O)H$	–	–	32
3	Me_3SiI	–		–
4	$(EtO)_2P(O)H$	DMSO	–	trace
5	$(EtO)_2P(O)H$	TMSO	–	–
6	$(EtO)_2P(O)H$	I_2	–	–
7	$(EtO)_2P(O)H$	–	CuCl (0.5)	31
8	$(EtO)_2P(O)H$	DMSO	CuI (0.5)	13
9	$(EtO)_2P(O)H$	DMSO	CuOAc (0.5)	20
10	$(EtO)_2P(O)H$	DMSO	$CuCl_2$ (0.5)	14
11	$(EtO)_2P(O)H$	DMSO	$AgNO_3$ (0.5)	–
12	$(EtO)_2P(O)H$	DMSO	I_2 (0.2)	trace
13	$(EtO)_2P(O)H$	DMSO	CuCl (0.5)	55
14	$(EtO)_2P(O)H$	DMSO	CuCl (0.8)	77
15	$(EtO)_2P(O)H$	DMSO	CuCl (1.0)	94
16[b]	$(EtO)_2P(O)H$	DMSO	CuCl (1.0)	52
17[c]	$(EtO)_2P(O)H$	DMSO	CuCl (1.0)	74

Reaction conditions: **3a** (0.2 mmol), PhMe (1 mL), 110 °C, under N_2. [a] Determined by GC analysis. [b] **2b** (1 equiv). [c] **2b** (1.5 equiv). DMSO = dimethylsulfoxide, TMSO = tetramethylene sulfoxide.

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thiolation product **4a** in 32% yield (entry 2). Electrophilic trifluoromethylthiolation of CF_3SSCF_3 generates 1 equivalent of CF_3S^-, which could be oxidized back to CF_3SSCF_3 with agents such DMSO.[21]

We then performed reactions by adding either DMSO, TMSO, or I_2 to the reaction system (Table 1, entries 4–6). The reaction with DMSO afforded a trace amount of **4a**. Metal salts are able to catalyze trifluoromethylthiolation with **2b**,[15] while I_2 is able to promote sulfenylation of sodium sulfinates.[19] After testing copper and silver salts, as well as I_2 for the CF_3SO_2Na reactions (entries 7–13), we found that the reaction with CuCl (0.5 equiv) together with DMSO afforded a good amount of **4a** (55%; entry 13). Optimization of the reaction conditions (entries 10–17) revealed that using $(EtO)_2P(O)H$ (2.0 equiv), DMSO (3.0 equiv), and CuCl (1.0 equiv) in toluene at 110°C for 12 hours could increase the product yield to 94% (entry 14).

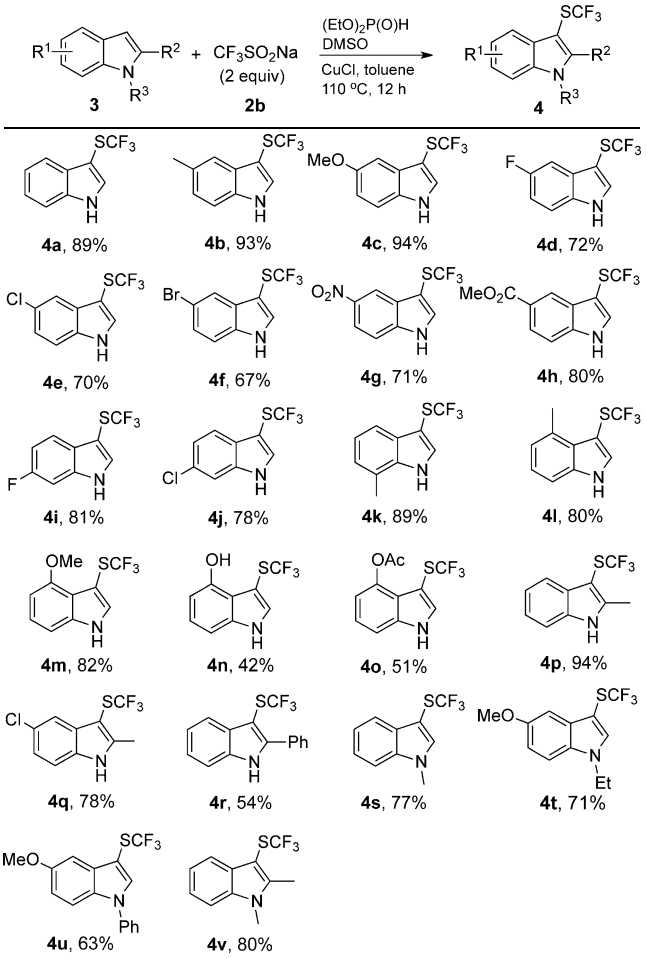
Reactions of a series of substituted indoles under the optimized reaction conditions were conducted. Trifluoromethylthiolation took place selectively at the 3-position of indoles to form products bearing methyl (**4b**), methoxy (**4c**), halogens (**4d–f**), nitro (**4g**), esters (**4h**, **4o**), and hydroxy (**4n**) groups at the 4-, 5-, 6-, and 7-positions in 42–93% yields (Table 2). It was found that indoles with an electron-donating group gave better results than those with an electron-withdrawing group, for example, **4n** and **4o**. The bulky substituent in **4o** and **4r** affected the yields. N-substituted indoles with either Me, Et, or Ph groups afforded the products **4s–v** in 77, 71, and 63% yield, respectively. The structure of **4h** was confirmed by single-crystal X-ray analysis (see the Supporting Information).

Similar to indoles, pyrroles are important nitrogen-containing heterocyclic rings existing in many natural products, biologically active molecules, and dyes for solar cells.[22] We were able to do direct trifluoromethylthiolation reaction of pyrroles (Scheme 1). Under the same reaction conditions for indoles, the reaction of pyrroles afforded **5a–c** in good yields. Enamines, an important building block for a variety of biologically and synthetically interested nitrogen-containing heterocycles,[23] were also used for the synthesis of **6a–b**.

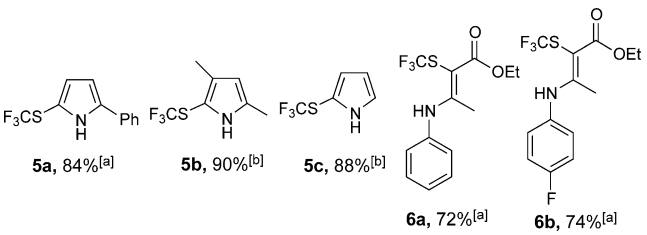
It was found in the study of glycosidase inhibitors that the introduction of CF_3S and R_fS with a fluorous chain could stabilize the parent molecules and change their amphiphilic properties.[24] The R_fS groups were introduced by the reaction of a thiophenol or sulfide with perfluoroalkyl iodides.[25] We have successfully extended the direct trifluoromethylthiolation for perfluoroalkylthiolation. Sodium perfluoroalkanesulfinates (R_fSO_2Na), with a different R_f group, were prepared following the procedure reported by Hu and DesMarteau.[26] These compounds were used for the perfluoroalkylthiolation reactions with indole. The products **7a–d**, bearing C_2F_5S, C_4F_9S, $C_6F_{13}S$, and $C_8F_{17}S$ groups, respectiey, were obtained in good yields (Scheme 2).

To understand the mechanism of CF_3SO_2Na-based direct trifluoromethylthiolation, a reaction of indole under the optimized reaction conditions was closely monitored by ^{19}F NMR spectroscopy using $PhCF_3$ as an internal standard. During the 12 hour reaction process, five fluorine peaks, including those for the reagent **2b** ($\delta = -84.46$ ppm), three

Table 2: Copper-catalyzed trifluoromethylthiolation of indoles.

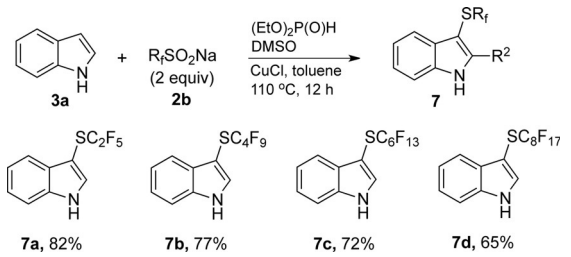


Reaction conditions: **3** (0.2 mmol), **2b** (0.4 mmol), $(EtO)_2P(O)H$ (0.4 mmol), DMSO (0.6 mmol), CuCl (0.2 mmol) in PhMe (1 mL) under N_2 at 110°C for 12 h. Yields are those for the isolated products.



Scheme 1. Trifluoromethylthiolation of pyrroles and enamines. Reaction conditions: pyrroles or enamines (0.2 mmol), **2b** (0.4 mmol), $(EtO)_2P(O)H$ (0.4 mmol), DMSO (0.6 mmol), CuCl (0.2 mmol) in PhMe (1 mL) under N_2 at 110°C for 12 h. [a] Yield of isolated product. [b] Yield determined by GC-MS.

intermediates (**8** at $\delta = -78.58$ ppm, **9** at $\delta = -62.14$ ppm, and **10** at $\delta = -45.48$ ppm), and product **4a** ($\delta = -44.50$ ppm) were observed (Figure 2). The CF_3SO_2Na peak disappeared after 2 hours. The amount of **4a** increased steadily during the reaction process. The structure of **10** was confirmed to be CF_3SSCF_3 by its ^{19}F NMR data.[15b,c] To gain more information for the intermediates, we performed four control reactions in



Scheme 2. Perfluoroalkylthiolation of indole. Reaction conditions: **3a** (0.2 mmol), R_fSO_2Na (0.4 mmol), $(EtO)_2P(O)H$ (0.4 mmol), DMSO (0.6 mmol), CuCl (0.2 mmol) in PhMe (1 mL) under N_2 at 110 °C for 12 h. Yields are those of the isolated products.

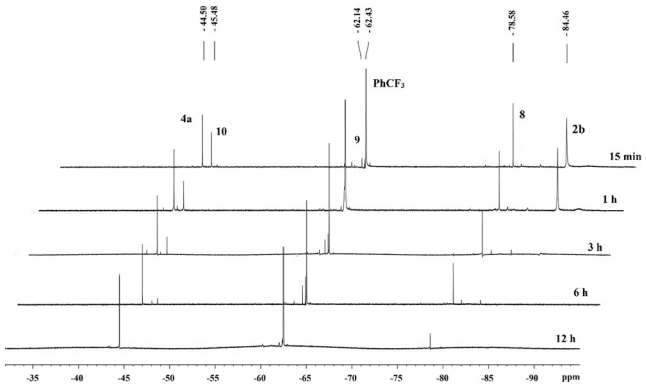


Figure 2. Progress of the reaction of **3a**, for up to 12 h, by ^{19}F NMR spectroscopy. The peaks (in $CDCl_3$) represent CF_3SO_2Na (**2b**, $\delta = -84.46$ ppm), $CF_3S(O)H$ (**8**, $\delta = -78.58$), the internal standard ($PhCF_3$, $\delta = -62.43$ ppm), CF_3S-OH (**9**, $\delta = -62.14$ ppm), CF_3SSCF_3 (**10**, $\delta = -45.48$ ppm), and **4a** ($\delta = -44.50$ ppm).

the absence of indole. From the reaction of CF_3SO_2Na and $(EtO)_2P(O)H$, a small peak for CF_3SO_2Na and a big peak for **8** were detected (Figure 3, I). Similar peaks were detected for the reaction with either CuCl (Figure 3, II) or DMSO (Figure 3, III). When both CuCl and DMSO were added, all fluorine peaks, including those of the intermediates **8**, **9**, **10**, were detected (Figure 3, IV). We inferred that **8** is $CF_3S(O)H$, a reduction product of **2b**, and that **9** is CF_3SOH,[27] which was

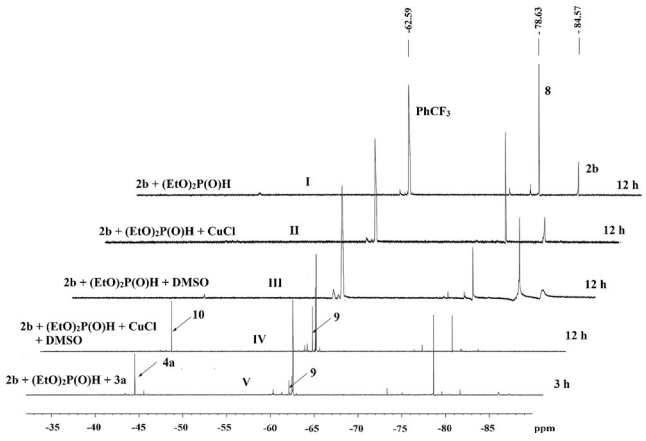


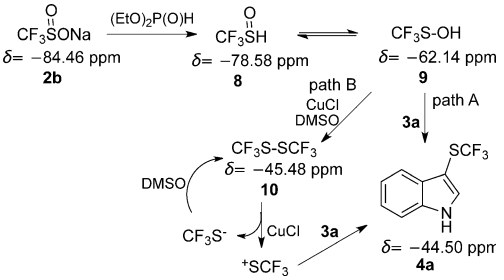
Figure 3. Progress of reactions without indole, at 110 °C, using ^{19}F NMR (in $CDCl_3$) spectroscopy.

generated through intramolecular nucleophilic collapse of $CF_3S(O)H$.[15c] The compound **9** is less stable than **8** and **10** and difficult for ^{19}F NMR detection. Analysis of a reaction mixture of **2b** and $(EtO)_2P(O)H$ showed a strong MS peak at m/z 119 ($M+1$), which matches the molecular weight of **8** and **9**, both of which have a molecular weight of 118 (see the Supporting Information). We also monitored the reaction of **3a** with **2b** and $(EtO)_2P(O)H$ (Figure 3, V), and were able to detect **4a** after 3 hours, along with a small amount of CF_3SSCF_3. This result suggests path A (see Scheme 3) is possible, but not as efficient as path B. Only ^{19}F NMR data for RSO_nCF_3 compounds were found in the literature,[11,28] and no information for $CF_3S(O)H$ and CF_3SOH is available. The ^{19}F NMR data of related compounds are listed in Table 3 for comparison.

Table 3: ^{19}F NMR data for CF_3SO_nR and CF_3SO_nNa/H.

CF_3SO_nR (literature) ^{19}F NMR (δ in ppm)	CF_3SO_nNa/H (this work) ^{19}F NMR (δ in ppm, in $CDCl_3$)
$CF_3SO_2CH_3$: −79.95[28a]	CF_3SO_2Na (**2b**): −84.46
$CF_3S(O)CH_3$: −76.6[28b]	$CF_3S(O)H$ (**8**): −78.58
CF_3SOR (**1d**): −51.91[11]	CF_3SOH (**9**): −62.15

On the bases of the experimental results shown in Table 1 as well as Figures 2 and 3, we proposed a possible mechanism for trifluoromethylthiolation with CF_3SO_2Na. By using 2 equivalents each of CF_3SO_2Na and $(EtO)_2P(O)H$, 3 equivalents of DMSO, and 1 equivalent of CuCl (Scheme 3), the



Scheme 3. Proposed mechanism for CF_3SO_2Na trifluoromethylthiolation.

reduction of CF_3SO_2Na with $(EtO)_2P(O)H$ leads to the formation of $CF_3S(O)H$, which is then converted into CF_3SOH though intramolecular nucleophilic collapse.[15c] CF_3SOH is unstable and able to produce CF_3S^+[27] for the formation of a small amount of **4a** (Table 1, entry 2) through path A (Scheme 3). Path B is more efficient for trifluoromethylthiolation since CuCl reduces CF_3SOH to CF_3SSCF_3 (Figure 3, IV). In this reaction DMSO assists the CuCl reduction of CF_3SOH and also serves as an oxidizing agent for the conversion of CF_3S^- back into CF_3SSCF_3.[21] CuCl serves as both a reducing agent for CF_3SO_2Na and also a catalyst for CF_3SSCF_3.

In summary, we have developed a new method using the cheap and stable sulfinate CF_3SO_2Na for direct trifluoromethylthiolation of $C(sp^2)$–H bonds. The reaction system consists of a reducing agent, $(EtO)_2P(O)H$ and CuCl, and an oxidizing agent, DMSO. CuCl is as a catalyst for the electrophilic trifluoromethylthiolation of CF_3SSCF_3 with indoles, pyrroles, and enamines. The method has been successfully extended for perfluoroalkylthiolation using R_fSO_2Na. This economically favorable and easy-to-handle reaction could be suitable for large-scale trifluoromethylthiolation reaction.

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