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Tf_2O-Promoted Trifluoromethylthiolation of Various Arenes Using $NaSO_2CF_3$

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Abstract: A sulfonic anhydride-promoted direct trifluoromethylthiolation using $NaSO_2CF_3$ has been developed. The simple and practical strategy enabled the direct introduction of SCF_3 moiety into unexplored arene scaffolds under reductant- and metal-free condition at room temperature.

Keywords: trifluoromethylthiolation, sodium trifluoromethanesulfinate, trifluoromethanesulfonic anhydride, arenes

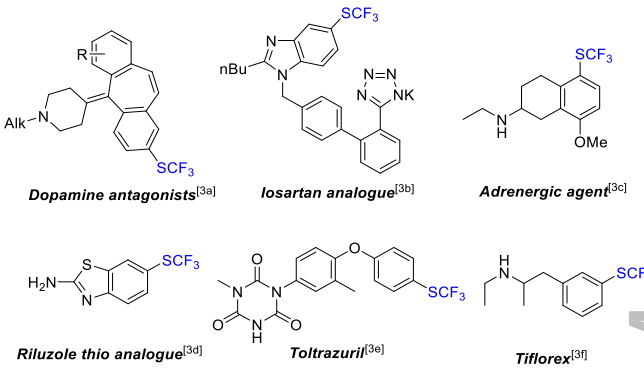

Figure 1. Biologically active compounds containing an arene-SCF_3 group

The growing importance of fluorinated organic compounds in pharmaceuticals, agrochemicals and materials has driven the development of new methods for the introduction of fluorine into small molecules.[1] In the organofluorine family, the trifluoromethylthio group (SCF_3) has attracted special interests in both academia and the pharmaceutical industry due to its high lipophilicity and high electron-withdrawing character.[2] Consequently, compounds bearing this functional group, especially aromatic derivatives, are potentially in the pharmaceutical and agrochemical fields (Figure 1).[3]

In the last few decades, numerous methods for the introduction of SCF_3 group into organic compounds have been developed. The most efficient and elegant strategies are direct methods. Nucleophilic and radical sources of the SCF_3 group are often copper- or silver-based metallic reagents,[4] or $[Me_4N][SCF_3]$.[5] In particular, the popularity of electrophilic trifluoromethylthiolation has grown remarkably with shelf-stable CF_3SN-[6] or CF_3SO-based[7] trifluoromethylthiolating reagents in recent years. In addition, trifluoromethylthiolation *via* C-H activation was explored under the help of directing-groups such as 8-aminoquinoline[8] and pyridine.[9] However, synthesis of these trifluoromethylthiolating reagents also presents a great challenge: the multiple steps needed prior to their use and the possible necessity of expensive reagents. Because of these limitations and negative aspects, it is still necessary to develop an efficient method to introduce the SCF_3 moiety directly.

The development of general and practical methods for the trifluoromethylthiolation of unactivated arenes is highly desirable. In moving towards this goal, Our group,[10] Yang/Vicic,[11] Shibata/Cahard,[12] Lin/Liu[13] and Zhao/Lu[14] disclosed CF_3SO_2Na and CF_3SO_2Cl which could conceivably generate CF_3S^+ for the C(sp^2)-H direct trifluoromethylthiolation in the presence of phosphorus reductant. However, the substrate scope is extremely limited to electron-rich heterocycles such as indoles, pyrroles and some activated arenes. Morever, requirement of sensitive phosphorus reductant decreases the overall synthetic efficiency to some extent.

As shown in Figure 1, Ar-SCF_3 components occurred widely in a number of pesticides and drugs. In the quest of direct aromatic trifluoromethylthiolation, we envisioned that CF_3SO_2Na could be used as trifluoromethylating sources which applied to more general arenes. In 2006, Magnier and co-workers reported a novel preparation of various aryl trifluoromethyl sulfoxides through aromatic compound mixed with potassium trifluoromethanesulfinate CF_3SO_2K and

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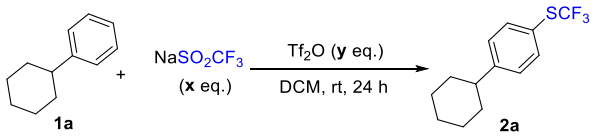
trifluomethanesulfonic acid TfOH.[15a] Then in 2009, the same group found a small amount of trifluoromethylthiolation traces in the process of preparing Yagupol'skii-Umemoto reagent with CF_3SO_2K and trifluoromethanesulfonic anhydride Tf_2O.[15b] Moreover, CF_3SO_2Na was also reported to prepare trifluoromethyl sulfoxide[16] and Yagupol'skii-Umemoto reagent[17] in the presence of TfOH or Tf_2O. However, the method for preparing sulfonium salts required benzene or biphenyl derivatives with special directing substituents as substrates. Therefore, we considered that there should be an efficient and direct approach for the preparation of aromatic trifluoromethyl sulfides under the conditions of CF_3SO_2Na/Tf_2O.

Table 1. Optimization of trifluoromethylthiolation with $NaSO_2CF_3$[a]

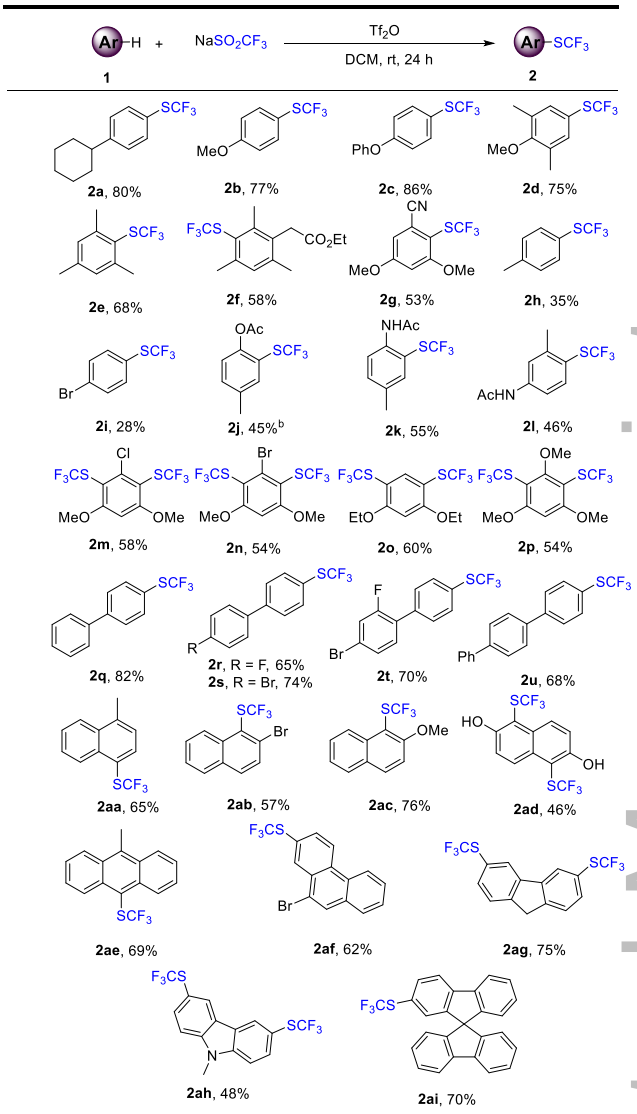


Entry	x	y	Solvent	additive	Yield(%)[b]
1	1	1	DCM	Tf_2O	30
2	1	2	DCM	Tf_2O	48
3	1	3	DCM	Tf_2O	48
4	2	2	DCM	Tf_2O	80
5	3	2	DCM	Tf_2O	78
6	2	2	MeCN	Tf_2O	<5
7	2	2	1,4-dioxane	Tf_2O	19
8	2	2	DMF	Tf_2O	n.r
9	2	2	DMSO	Tf_2O	n.r
10	2	2	DCM	Ac_2O	n.r
11	2	2	DCM	TFAA	n.r
12	2	2	DCM	$(CH_3SO_2)O$	n.r
13	2	2	DCM	Tf_2O	71[c]

[a] Reaction conditions: **1a** (0.2 mmol, 1.0 equiv), solvent (1.0 mL) at room temperature under an atmosphere of argon for 24h.
[b] Yield was determined by ^{19}F NMR, hexafluorobenzene used as internal standard.
[c] Yield was obtained at gram scale (2g).

We chose cyclohexylbenzene (**1a**) as a model substrate to search for the optimal reaction conditions. A reaction of 1.0 equiv of $NaSO_2CF_3$ in the presence of 1.0 equiv of Tf_2O in dichloromethane without any catalyst delivered trifluoromethylthiolation product **2a** in 30% yield at room temperature for 24 h (Table 1, entry 1), which was similar to the result of Magnier's work.[15b] It was found that when increasing the amount of trifluoromethanesulfonic anhydride and sodium trifluoromethanesulfinate to 2.0 equiv respectively, the yield significantly increased to 80% (entries 2-5). Further studies indicated that DCM was the best choice of solvents, consequently providing a homogeneous reaction mixture (entries 6-9). Finally, switching Tf_2O to other additives including Ac_2O, TFAA, $(CH_3SO_2)O$ did not give any desired products

Table 2. Scope of Trifluoromethylthiolation of arene derivatives[a]



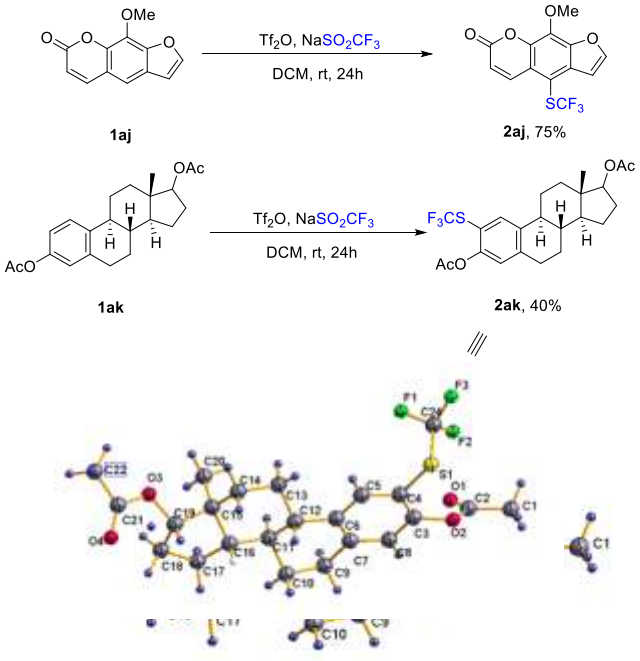
[a] Reaction conditions: **1** (0.5 mmol), $NaSO_2CF_3$ (1.0 mmol), and Tf_2O (1.0 mmol) in DCM at room temperature under an atmosphere of argon for 24h.
[b] Yield was determined by ^{19}F NMR, hexafluorobenzene used as internal standard.

(entries 10-12). The method is effective on the gram scale, which highlights the inherent practicality of this synthetic transformation (entry 13).

Having established the optimized reaction conditions, we examined the scope of substrates with structurally diverse arenes (Table 2). A broad range of functional groups, such as alkyl, alkoxy, halides, ester, hydroxyl and amino were tolerated under the standard reaction conditions. Alkoxy (**2b**), phenoxy (**2c**), methyl (**2h**), bromo (**2i**) and polysubstituted benzenes (**2d-g**) provided the expected products in moderate to good yields. Trifluoromethylthiolation occurred at the position para to the substituent due to the electronic effects. Additionally, potentially bioactive compounds[18] with acetoxy (**2j**) and acetamido (**2k**) were obtained in moderate yields.

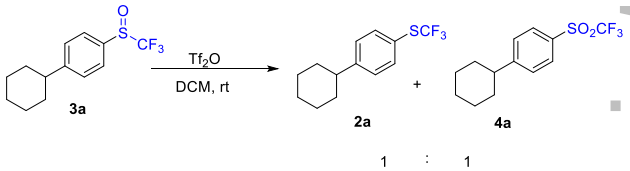
The acetanilide led to the selective formation of the product **2l** (46%), thus confirming that under superacid conditions the amide function is protonated and that the methyl group directs the electrophilic substitution.[18] Notably, reactions of electron-rich benzenes afforded the products with two SCF_3 moieties in good yields at room temperature for a short time (**2m-p**) as main products. This demonstrated the potentiality of this strategy for multiple trifluoromethylthiolation of aromatic derivatives. Unfortunately, arenes bearing electron-withdrawing groups such as nitro and cyano groups only gave trace of SCF_3 products.

Other than single benzene structure, biphenyls (**2q-u**) proceeded smoothly to give trifluoromethylthiolation products in moderate to good yields. Since the steric hindrance and the electronic effects, 4-SCF_3-substituted products were formed. It was worth noting that sulfonium salts were also observed in <10% yield determined by ^{19}F NMR as side products. Different from Magnier's observasion,[15b] the biphenyls selected in this work mainly led to SCF_3 products, the formation of sulfonium salts depend on the directing influence of the substituents located on the phenyl groups. The standard conditions were compatible with the active *α*-position of the naphthalenes bearing methyl (**2aa**), bromo (**2ab**), methoxy (**2ac**), hydroxyl (**2ad**), and delivered the products in good yields. Importantly, multi-ring aromatic compounds including 9-methylanthracene and 9-bromophenanthrene were good substrates to give corresponding products **2ae** and **2af** in 69% and 62% yields respectively. Fluorene, *N*-methylcarbazole and 9,9'-spirobi[9H-fluorene] were also successfully subjected to this simple protocol to access their trifluoromethylated derivatives with 48%-75% yields (**2ag-2aj**).



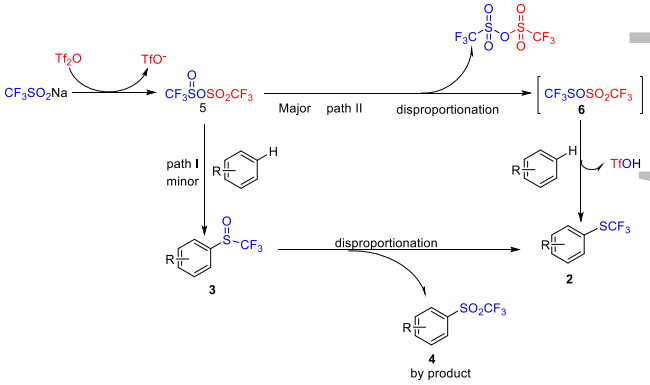
Scheme 1. TfO_2-promoted trifluoromethylthiolation of drug-like molecules and X-ray structure of **2ak**

In a context where direct late-stage functionalization of bioactive molecules is being fully embraced as an innovative approach in medicinal chemistry, we decided to investigate the possibility of late-stage trifluoromethylthiolation using our method (Scheme 1).[18] The direct trifluoromethythiolation of xanthotoxin, which was the intermediate of "Methoxsalen"[19], was selectively achieved (**2aj**). To evaluate the ability to extend our strategy to aromatic steroids, our method was therefore extended to the protected 17β-estradiol to generate its SCF_3 analogue (**2ak**) in 40% yield. The selectivity of the substrate was unambiguously confirmed by single crystal X-ray analysis.



Scheme 2. Reaction of cyclohexylbenzene CF_3-sulfoxide with triflic anhydride.

To gain some insights into the formation of the SCF_3 products, we turned our attention to the transformation of Ar-$SOCF_3$ to Ar-SCF_3. Aryl trifluoromethyl sulfoxide (**3a**)[15a] was prepared for the reaction with TfOH or $NaSO_2CF_3$. It was found that trifluoromethyl sulfoxide **3a** was converted to the target product and side-product sulfinate at a ratio of 1 : 1 (Scheme 2). This indicated that Tf_2O could promote disproportionation of trifluoromethyl sulfoxide to the SCF_3 product.



Scheme 3. Proposed reaction mechanism

Although the details of the reaction process are not clear, the mechanism was hypothesized as shown in Scheme 3 on the basis of the control experimental results and literature information. A close examination of the literature shows that the cornerstone of the previously described synthesis is the formation of an intermediate sulfonate sulfinate anhydride **5**.[15a] Two potential paths may achieve final result. As shown in path I, trifluoromethyl sulfoxide **3**, which was detected by GC-MS, partly contributed to the formation of SCF_3 product *via* disproportionation. From path I, the sulfoxide **3** can disproportionate itself under the anhydride system to affort the product **2**. Therefore, we suspect that the

intermediate **5** also undergoes self-disproportionation. Half of intermediate **5** was oxidized to form $TfO-SO_2CF_3$, and another part was reduced to form the true reactive species, the intermediate **6**. To gain more insights into the intermediates **5** and **6**, we performed a control experiment only in the presence of $NaSO_2CF_3$ and Tf_2O. ^{19}F analysis of the reaction mixture after 1 h gave four new signals (δ= -37.00, -77.67, -79.51 and -80.23ppm). Based on their peak integrations and comparison of the ^{19}F NMR of reported similar compounds,[17c, 20] the four signals were suggested to be the intermediates **5** (δ= -77.67 and -80.23ppm) and **6** (δ= -37.00 and -79.51 ppm). The two intermediates were also confirmed by MS study.[21] Finally, the transfer trifluoromethylthiolation from **6** to the nucleophile *via* an electrophilic path which mainly contributed to the formation of product **2**.

In summary, we have developed a direct Tf_2O-promoted trifluoromethylthiolation using CF_3SO_2Na. This system has been successfully applied to a wide range of benzenes by a one-pot strategy for conventional laboratory applications. This use-friendly reagent $NaSO_2CF_3$ has a great potential for the preparation of more complicated, densely functionalized drug molecules with SCF_3 moiety.

Experimental Section

General Procedure for the Formation of Product 2a-2aj

A 25mL oven-dried reaction vessel was charged with aromatic compounds (0.5mmol), sodium trifluoromethanesulfinate (156.0 mg, 1.0 mmol), trifluoromethanesulfonic anhydride (162 μL, 1.0 mmol) under an atmosphere of argon. Dichloromethane (1.0 mL) was added to the sealed reaction vessel by syringe. The mixture was stirred vigorously at room temperature for 24 h. After consumption of the starting material, it was quenched with brine. The aqueous layer was extracted with dichloromethane (3×50 mL), then organic layers was neutralized with $NaHCO_3$ and dried with Na_2SO_4. The residue was purified by column chromatography to give the corresponding SCF_3 substituted products.

Synthesis of 3a

Under argon, a 25mL oven-dried reaction vessel was charged with sodium trifluoromethanesulfinate (1.2 g, 7.6 mmol) and trifluoromethanesulfonic acid (4.10 mL, 0.046 mol, 6 equiv). Then, cyclohexylbenzene (1.94 mL, 11.5 mmol, 1.5 equiv) was added. Dichloromethane (8 mL) was added to the sealed reaction vessel by syringe. After 24 h stirring at room temperature, the resulting mixture was hydrolyzed with ice-water, neutralized with $NaHCO_3$, extracted with dichloromethane (3 x 50 mL). The organic phases were mixed, dried over Na_2SO_4 and concentrated under reduced pressure. Distillation of the crude mixture afforded 1.59 g (50%) of the desired compound.

Synthesis of 1ak

To a ice cold solution of 17β-estradiol (3.0g, 11.1mmol) in pyridine (15 mL) added acetic anhydride (7.36 g, 72.1mmol) and stirred at room temperature 16 h. Reaction mixture poured on ice water mixture (300 mL) and resulting solid filtered, washed with water and dried to give pure product (**1ak**) (3.8g, 98%).

CCDC 1856060 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

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[21] For details of ^{19}F NMR and mass study of intermediates **5** and 6, see supporting information.

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