COMMUNICATION

# Preparation and Reactivity Study of a Versatile Trifluoromethylthiolating Agent: *S*-Trifluoromethyl Trifluoromethanesulfonothioate (TTST)

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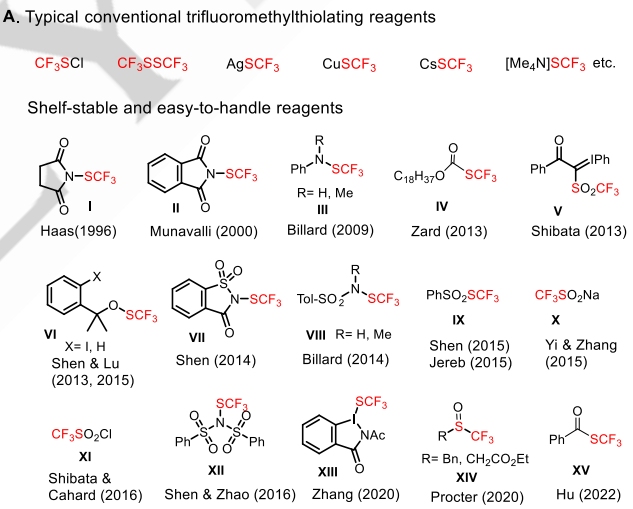
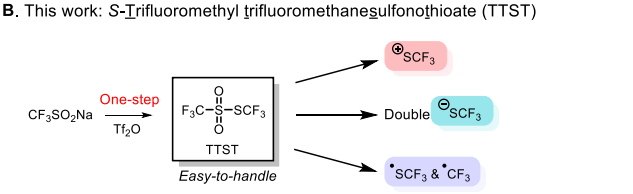
**Abstract:** A novel, air and thermally stable, yet highly reactive trifluoromethylthiolating reagent, $CF_3SO_2SCF_3$ (**1**), was prepared easily in one step from commercially inexpensive $CF_3SO_2Na$ and $Tf_2O$. **1** is a highly versatile and atom-efficient reagent that can generate one equivalent of $CF_3S^+$, two equivalents of $CF_3S^-$, or a combination of $CF_3S^{\cdot}/CF_3^{\cdot}$ species. Many high-yielding $CF_3S$ reactions of *C*, *O*, *S*, and *N*-nucleophiles were achieved, including the simple-step preparations of many reported $CF_3S$ reagents. **1** delivered a hitherto hard-to-synthesize $ArSOCF_3$ that was followed by a novel $CF_3S^{II}$-rearrangement. Through Cu or TDAE/$Ph_3P$ combinations, **1** generated two equivalents of $CF_3S$ anion species, and the photo-catalyzed reactions of alkenes with **1** provided $CF_3$/$CF_3S$-containing products in high atom-efficiency.

The widespread applications of fluorine-containing molecules in drug discovery,[1-3] materials science,[4-5] and agrochemical fields[6-7] are a testament of the unique properties associated with the introduction of fluorine in organic compounds. Among the various fluorine-containing motifs that have become increasingly popular in drug discovery, the trifluoromethylthio ($CF_3S$) group possesses the highest lipophilicity (Hansch's hydrophobic parameter π = 1.44),[8] which greatly enhances the cell membrane permeability of the drug candidates.[9] Thus, the synthesis of $CF_3S$-incorporated molecules is a sought after endeavor, and numerous trifluoromethylthiolation methodologies[10-15] have been reported, with trifluoromethylthiolating reagents playing a pivotal role.[16-19] The first generation of trifluoromethylthiolating ($CF_3S$) reagents included compounds like $CF_3SCl$[20-22] and $CF_3SSCF_3$.[23-25] However, their toxicity and gaseousness made them impractical for general use. On the other hand, nucleophilic $CF_3S$ reagents such as $AgSCF_3$,[26] $CuSCF_3$,[27] $CsSCF_3$,[28] and $[Me_4N]SCF_3$[28-29] are expensive and/or air sensitive. In the past two decades, many shelf-stable and easy-to-handle $CF_3S$ reagents emerged as useful $CF_3S$-transfer tools (Scheme 1A). Haas's *N*-$CF_3S$-succinimide **I**,[30] Munavalli's phthalimide **II**,[31] Billard's amides **III**[32] and sulfonamides **VIII**,[33] Zard's thiocarbonate **IV**,[34] Shibata's ylide **V**,[35-36] Shen and Lu's thioperoxides **VI**,[37-39] Shen's saccharin **VII**,[40] Shen and Jereb's thiosulfate **IX**,[41-42] Shen and Zhao's sulfonimide **XII**,[43-44] Zhang's iodine amide **XIII**,[45] Procter's sulfoxides **XIV**,[46] and Hu's thioate **XV**[47] are among the most cited. The reported $CF_3S$ reagents have significant drawbacks though, namely the use of expensive $AgSCF_3$, or $TMSCF_3$/DAST and/or multi-step synthesis, or narrow applications, as well as low atom-economy. Commercially available $CF_3SO_2Na$ **X**[48-49] and $CF_3SO_2Cl$ **XI**[14, 50] have also been used as electrophilic $CF_3S$ sources but have shown low versatility.



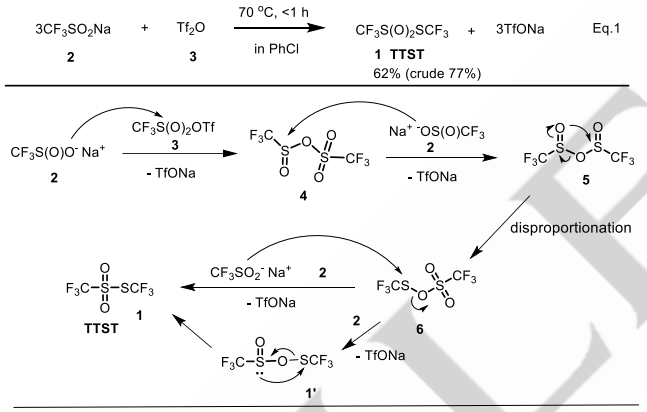




**Scheme 1.** Conventional $CF_3S$ reagents and new TTST.

An easily preparable, atom-economical, bench-stable, yet reactive and versatile $CF_3S$ reagent is highly desirable.[19] Herein, we are pleased to report a trifluoromethylthiolating reagent—*S*-trifluoromethyl trifluoromethanesulfonothioate ($CF_3SO_2SCF_3$: TTST)—that meets all the above requirements. TTST is a thermally stable liquid that is easily and scalable prepared in one-step from commercially inexpensive $CF_3SO_2Na$ (Langlois reagent) and triflic anhydride ($Tf_2O$), and it can generate

electrophilic, nucleophilic, or radical $CF_3S$ species as well as a radical $CF_3$ species (Scheme 1B).

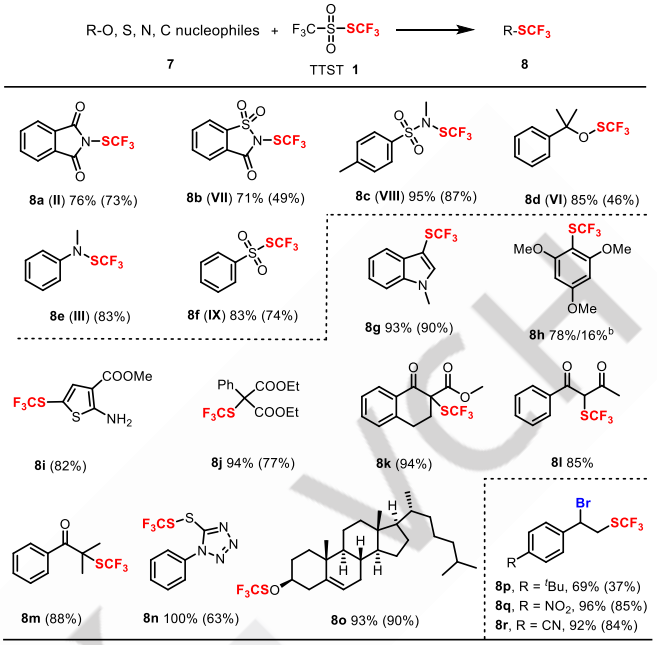
Although TTST (**1**) was first synthesized in 1955,[51-52] it was never used as a $CF_3S$ reagent. The preparative process for **1** involved three steps from $CS_2$ and required the handling of toxic chemicals ($IF_5$, $CF_3SSCF_3$, $CF_3SCl$). Recently, it was reported that **1** was prepared from $CF_3SO_2Cl$ and KXCN (X=S, Se).[53] However, this report was inaccurate because their obtained product's NMR data did not match **1**. From our own studies on reactions of $CF_3SO_2Na$/TfOH/$(CF_3CO)_2O$,[54] we were excited to find that **1** could be obtained in good yield by simply mixing $CF_3SO_2Na$ (**2**) and $Tf_2O$ (**3**) in nonpolar chlorobenzene (Eq.1, Scheme 2). The reaction is fast and its exothermicity can be regulated by a controlled addition of **3**. We proposed a plausible mechanism for this transformation (Scheme 2): trifluoromethanesulfinyl triflate (**4**)[55-56] resulting from the reaction of **2** and **3** reacts with another equivalent of **2** to form trifluoromethanesulfinic anhydride (**5**). Disproportionation of **5** generates trifluoromethanesulfenyl triflate (**6**),[54, 56-57] which then reacts with a third equivalent of **2** to produce **1** directly or through its isomer **1'**; the reaction produces three equivalents of TfONa's as a byproduct. An additional key advantage of the reaction is that it is easily scalable because **1** can be simply isolated from the reaction mixture by direct distillation at atmospheric pressure.




**Scheme 2.** Proposed mechanism for the preparation of TTST (**1**). *See* SI for detailed procedure of preparation.

TTST (**1**) is a colorless liquid with a b.p. of 66-69 °C. It is bench-stable and easy-to-handle in air. No obvious decomposition was observed (<1%) after heating in toluene-$d_8$ at 130 °C for 15 hours. The high thermal stability of **1** was supported by the fact that **1** was fractionally distilled from the reaction mixture heated to 172 °C (*see* SI).

As an electrophilic trifluoromethylthiolating reagent, **1** reacted with various O, S, N, and C nucleophiles effectively (Scheme 3). It should be noted that **1** provided a simple-step preparation for many of the literature reported $CF_3S$ reagents in high yields, such as **II**[31] (**8a**) and **VII**[40] (**8b**) without using the expensive $AgSCF_3$, and **VIII**[33] (**8c**), **VI**[37-39] (**8d**), **III**[32] (**8e**), **IX**[41-42] (**8f**) without using expensive $CF_3S$ reagents. Consequently, the higher reactivity of **1** compared with these conventional reagents was validated. In addition, **1** reacted with electron rich (hetero)aromatics (**7g-i**). Carbanions generated from malonate (**7j**), β-keto ester (**7k**), β-diketone (**7l**), and ketone (**7m**) were trifluoromethylthiolated with **1** in excellent yields. **1** also reacted with thiol (**7n**) and alcohol (**7o**) to produce the corresponding $CF_3S$ products. In the presence of lithium bromide, **1** gave difunctionalized products (**8p-r**) of alkenes in very good yields.

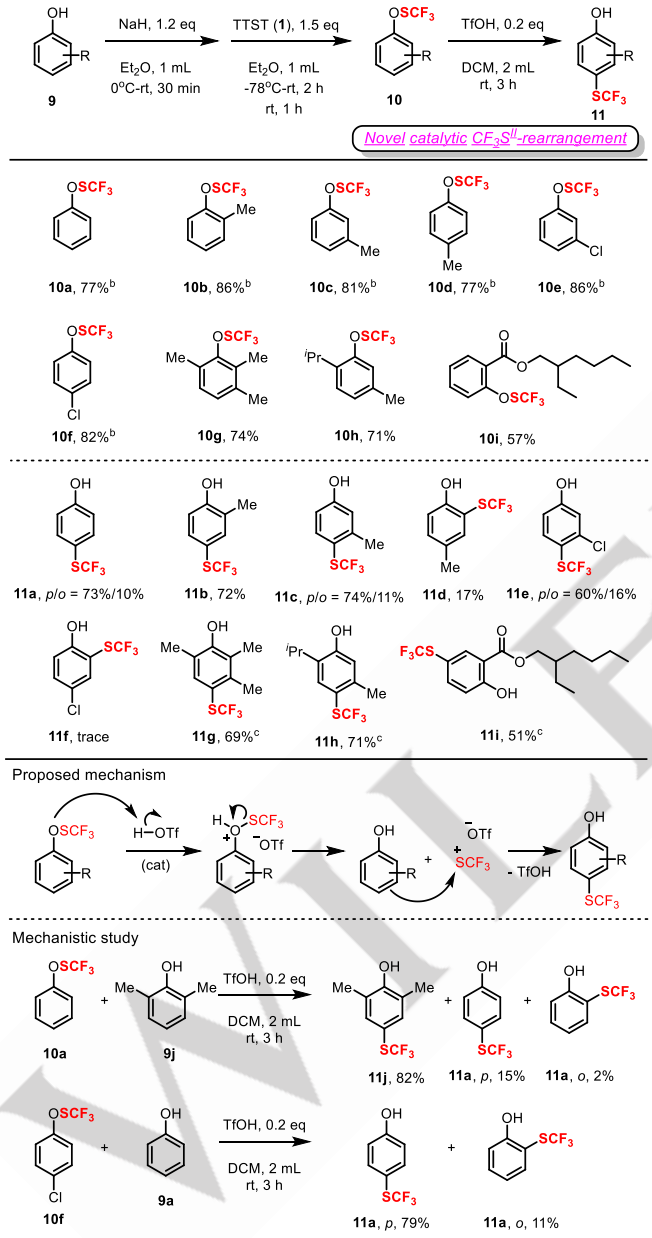



**Scheme 3.** Electrophilic reactions with TTST (**1**)[a]. For **8a-f**: **7a-f** (2~10 mmol), NaH or $Et_3N$ (1~2 eq), **1** (1.2~1.5 eq), $CH_3CN$, DCM or AcOH, 0 °C~rt, 0.5~1 h. For **8g-o**: **7g-o** (0.5 mmol), no base or NaH, KH or $Et_3N$ (1.1~2.3 eq), **1** (1.2 eq), $CHCl_3$, HFIP, DCM or THF, -78 °C~rt, 45 min~o.n. (overnight). For **8p-r**: **7p-r** (0.5 mmol), LiBr (2 eq), **1** (1.2~1.5 eq), DCM or HFIP, rt, o.n. (*see* SI for details). [a]Yields are $^{19}F$-NMR yields using $PhCF_3$, $CF_3COOEt$ or 4-Cl-$PhCF_3$ as an internal standard. Yields in parentheses are isolated yields. [b]Di-$SCF_3$ product (*see* SI).

To our knowledge, aryl trifluoromethanesulfenates ($ArOSCF_3$) have never been characterized or studied except for a short preparative description of $PhOSCF_3$ that appeared in 1986, but without its spectral data.[58] We were pleased to find that $ArOSCF_3$ can be easily obtained by reacting **1** with the corresponding phenoxides in high yields, and that $ArOSCF_3$ underwent a novel triflic acid-catalyzed $CF_3S^{II}$-rearrangement to produce *p*/*o*-$CF_3S$-substituted phenols in which the *p*-isomer predominated (Scheme 4).

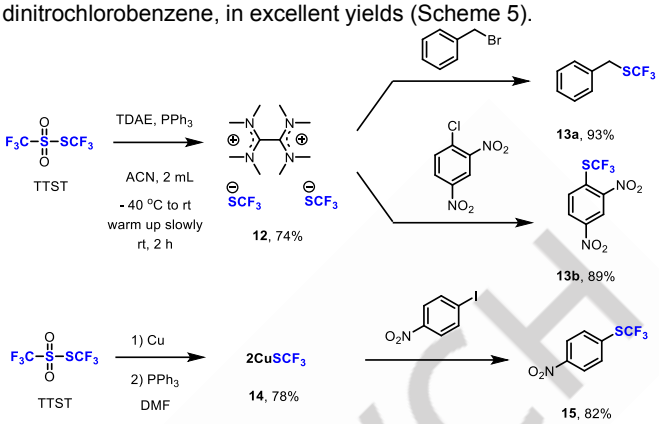
$ArOSCF_3$ is thermally stable and its derivatives with lower boiling point were isolated by distillation (**10a-f**). Although they could not be isolated and purified by $SiO_2$ column chromatography because of their decomposition on silica gel, we found that by simply filtrating the reaction mixture, followed by the evaporation of solvent, led to products with >95% purity in most cases. Although this rearrangement may seem formally like the Fries rearrangement,[59] the mechanism ought to be different because, in our rearrangement, the reaction starts by protonation of the oxygen atom of the phenol moiety (*see* proposed mechanism in Scheme 4). Instead, the traditional Fries rearrangement of $PhOC(O)R$[59] starts with the activation of the functional group (-C(O)-) connected to the oxygen of the phenol moiety with an acid, such as a Lewis acid. A similar $CF_3S^{IV}(O)$-rearrangement of $ArOS^{IV}(O)CF_3$ has been reported.[60] Our favorable rearrangement to the *para* position (**10a-c**,**e**,**g-i**) is similar to the Fries rearrangement. However, low yields were

observed with the *para*-blocked compounds (**10d**, **f**). We propose that the reaction mechanism involves intra- and inter-molecular reactions of the resulting reactive $CF_3S$ cationic species on the basis that when a more electron rich phenol (**9j** or **9a**) co-participated, the $CF_3S$ product (**11j** or **11a**) from the electron-rich phenol was formed by the intermolecular reaction (*see* Mechanistic study in Scheme 4). TTST did not react with phenol under the acid conditions employed by Billard's[61] in which **III** (R=H) reacted with phenol in the presence of triflic acid (1.2 eq) to produce *p*-$CF_3S$-phenol.



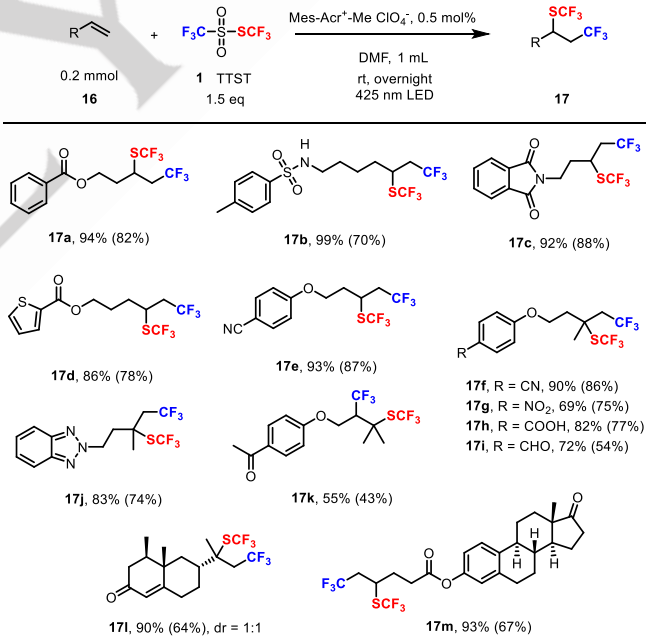

**Scheme 4.** Preparation of $ArOSCF_3$ and the novel catalytic $CF_3S^{II}$-rearrangement.[a] For **10a-h**: **9a-h** (0.5~10 mmol), NaH (1.2~1.5 eq), $Et_2O$, 0 °C~rt, 1 h; then **1** (1.5 eq), $Et_2O$, -78 °C~rt, 3~4 h. For **11a-i**: **10a-i** (0.5 mmol), TfOH (0.2 eq), DCM, rt, 3 h (*see* SI for details). [a]Yields are $^{19}F$-NMR yields using 4-Cl or Br-$PhCF_3$ as an internal standard. [b]Isolated yields after distillation. [c]Crude **10** was used and $^{19}F$-NMR yields are based on **9**.

We have also showed that TTST (**1**) can be a nucleophilic $CF_3S$ source. **1** reacted with tetrakis(dimethylamino)ethylene (TDAE), a two-electron donor, in the presence of $Ph_3P$ (2 eq) to produce $TDAE^{2+}$ $2SCF_3^-$ (**12**),[62] leading to the substitution of bromine in benzyl bromide, and chlorine in 2,4-dinitrochlorobenzene, in excellent yields (Scheme 5).




**Scheme 5.** Nucleophilic reactions using TTST as $SCF_3$ source. Yields are $^{19}F$-NMR yields using 4-Cl-$PhCF_3$ as an internal standard.

We showed another example in which **1** reacted with copper powder and $Ph_3P$ to provide 2 equivalents of $CuSCF_3$ (**14**), which we then treated with *p*-iodonitrobenzene to produce $CF_3S$ product **15**.[63-64] (Scheme 5, bottom). It should be noted that **1** exhibited a high atom economy performance because two $CF_3S^-$ equivalents were generated from one equivalent of **1**.




**Scheme 6.** Photocatalytic radical trifluoromethyl-trifluoromethylthiolation of alkenes using TTST (**1**). For **17a-m: 16a-m** (0.2 mmol), **1** (1.5 eq), Mes-$Acr^+$-Me $ClO_4^-$ (0.5 mol%), DMF, 425 nm LED, rt, o.n. Yields are $^{19}F$-NMR yields using 4-Cl-$PhCF_3$ as an internal standard. Yields in parentheses are isolated yields.

The high atom economy and wide applicability of TTST (**1**) were further demonstrated by the radical trifluoromethyl-trifluoromethylthiolation of alkenes using a photo organo catalyst, 9-mesityl-10-methylacridinium perchlorate[65] (Mes-$Acr^+$-Me $ClO_4^-$) (Scheme 6). The reported methods for this transformation required both $CF_3S$ and $CF_3$ reagents,[66-67] or multiple transition metal catalysts with an equimolar oxidizer ($K_2S_2O_8$) and a ligand

($Ph_3P$).[68] Instead, under our new metal-free photocatalytic conditions, **1** produced simultaneously both $CF_3S$ and $CF_3$ radicals, which were then trapped by the double bond in excellent yields and without using extra additives. Mono-, di-, and tri-substituted alkenes possessing a variety of functional groups such as ester (**16a**), sulfonamide (**16b**), imide (**16c**), nitriles (**16e**,**f**), nitro (**16g**), ethers (**16e-i,k**), carboxylic acid (**16h**), aldehyde (**16i**), and ketone (**16k**) were tolerated. Heterocycles like thiophene (**16d**) and benzotriazole (**16j**) as well as bioactive molecules (**16l,m**) produced the corresponding products in excellent yields. Regarding a possible mechanism, there are two possibilities at present; (1) a SET mechanism from the photo excited catalyst to **1**, as reported by Zhang,[69] or (2) a novel energy transfer mechanism of the photo excited catalyst to **1**, as recently reported by Maes.[70] In the first case, the single-electron received ~~by~~ **1** could generate a reactive $CF_3S$ radical and $CF_3SO_2$ anion. Assuming the $CF_3S$ radical reacts first with alkene **16**, it would result in the formation of $RR'(CF_3)CH_2SCF_3$ but not the product **17**, $RR'(SCF_3)CH_2CF_3$, which would be expected by the reaction of $CF_3$ radical to the double bond of **16** followed by a $CF_3S$ species. In the second case scenario, the resulting activated **1** could simultaneously generate a $CF_3$ radical, a $CF_3S$ radical, and $SO_2$ by homolitic cleavage but only if the $CF_3$ radical reacts first with **16**, it would form product **17**. Thus, in depth studies are needed to study the mechanism. Radical inhibition and cyclization experiments supported a radical pathway in this reaction (*see* SI).

In conclusion, we have developed a new, practical, and atom-efficient trifluoromethylthiolating reagent, $CF_3SO_2SCF_3$ (TTST, **1**), which is simply prepared in one step using inexpensive $CF_3SO_2Na$ and $Tf_2O$. **1** is an easy-to-handle, thermally stable, yet highly reactive and versatile reagent that can be used for both electrophilic and nucleophilic $CF_3S$ transfer reactions, as well as radical $CF_3S$ and $CF_3$ incorporation to alkenes. TTST is expected to be an attractive alternative to the current $CF_3S$ reagents in terms of preparation, application, and practicability.

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**Keywords:** trifluoromethylthiolation • $CF_3S$ reagents • rearrangement • photocatalysis • atom-economy

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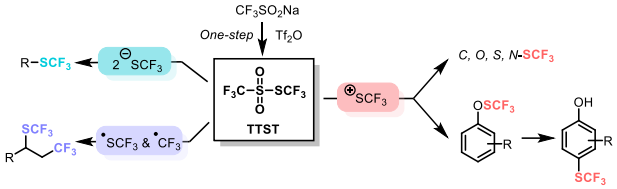
## Entry for the Table of Contents




A novel $CF_3S$ reagent, TTST, has been prepared in one step using commercially inexpensive materials. TTST is easy-to-handle and highly reactive, and can be used to prepare many existing $CF_3S$ reagents. TTST can generate one $CF_3S^+$, two $CF_3S^-$, or both $CF_3S^{\bullet}/CF_3^{\bullet}$ species. TTST has high atom economy—all atoms except oxygen can be used. TTST enabled a new type of molecule, $ArOSCF_3$, and revealed a novel catalytic $CF_3S^{II}$-rearrangement.