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Deoxytrifluoromethylthiolation and Selenylation of Alcohols using Benzothiazolium Reagents

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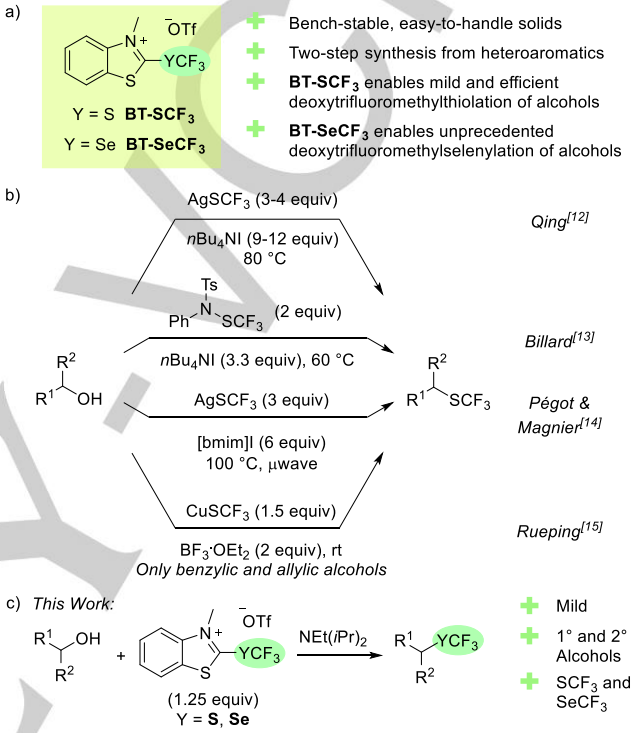
Abstract: Aliphatic compounds substituted with medicinally-important trifluoromethylthio (SCF_3) and trifluoromethylselenyl ($SeCF_3$) groups have been synthesized directly from alcohols using the new benzothiazolium salts **BT-SCF$_3$** and **BT-SeCF$_3$**. These bench-stable fluorine-containing reagents are facile to use and can be prepared in two steps from non-fluorinated heteroaromatic starting materials. The metal-free deoxytrifluoromethylthiolation process using **BT-SCF$_3$** proceeds under mild conditions while the similarly efficient trifluoromethylselenylation reactions using **BT-SeCF$_3$** are, to the best of our knowledge, the first reported examples of this transformation.

Substituting organic molecules with fluorine is a common strategy to improve their biological or physical properties.[1] In addition to single fluorine atoms and established fluorinated moieties such as the trifluoromethyl group (CF_3), alternative fluorine-containing functional groups have been attracting increasing attention. With the highest reported Hansch parameter (π = 1.44) and strong electron-withdrawing properties (Hammett parameters: σ_m = 0.40, σ_p = 0.50), the trifluoromethylthio (SCF_3) group in particular has emerged as a promising substituent in pharmaceuticals that counterintuitively combines significant polarity with high lipophilicity.[2]

The resurgence in interest in the SCF_3 group has been driven in large part by the introduction of new reagents for electrophilic trifluoromethylthiolation. As demonstrated in a number of impressive contributions, reagents such as *N*-(trifluoromethylthio)phthalimide, ((2(2-iodophenyl)propan-2-yl)oxy)(trifluoromethyl)sulfane and Billard's trifluoromethyl sulfenamides have opened up new mild synthetic routes towards SCF_3-substituted molecules that were not accessible using the previously-available toxic gases $F_3CS{-}Cl$ and $F_3CS{-}SCF_3$.[2,3] By contrast, nucleophilic trifluoromethylthiolation reactions are typically performed using only a handful of $^-SCF_3$ sources such as $AgSCF_3$, $CuSCF_3$ and $[Me_4N]SCF_3$.[2] In addition to their high cost, a major challenge associated with these reagents is the relative instability of the free $^-SCF_3$ anion as β-elimination of fluoride can outcompete the desired nucleophilic trifluoromethylthiolation process.[4] An alternative strategy is to instead employ a stable organic reagent which releases $^-SCF_3$ upon *in situ*-activation.[5] Using this approach, free $^-SCF_3$ anions



Scheme 1. a) Benzothiazolium Reagents **BT-SCF$_3$** and **BT-SeCF$_3$**. b) Previously-reported deoxytrifluoromethylthiolation reactions of aliphatic alcohols. c) This work: Deoxytrifluoromethylthiolation and selenylation of alcohols with **BT-SCF$_3$** and **BT-SeCF$_3$**. [bmim] = 1-butyl-3-methylimidazolium.

are generated in a more controlled fashion while reactive electrophiles for nucleophilic substitution reactions can be generated as part of the activation process. Inspired by the success of azolium-based reagents such as 2,2-difluoro-1,3-dimethylimidazolidine (DFI) and Alkylfluor® in nucleophilic fluorination[6] and the use of benzothiazolium salts in coupling reactions,[7] we considered whether the 2-SCF_3-substituted benzothiazolium species **BT-SCF$_3$** (Scheme 1a) could be employed as a new bench-stable metal-free reagent for nucleophilic trifluoromethylthiolation reactions. Herein we report the synthesis of **BT-SCF$_3$** and its successful application in mild deoxytrifluoromethylthiolation reactions of aliphatic alcohols. Moreover, $SeCF_3$-substituted alkyl derivatives could be readily prepared in an unprecedented deoxytrifluoromethylselenylation process using the analogous selenium reagent **BT-SeCF$_3$**.

The synthesis of **BT-SCF$_3$** is shown in Scheme 2a. A two-step approach was investigated starting from inexpensive 2-mercaptobenzothiazole (MBT), which is an industrially-produced bulk material used in the sulfur vulcanization of rubber. In the first step, trifluoromethylation of MBT affords the stable

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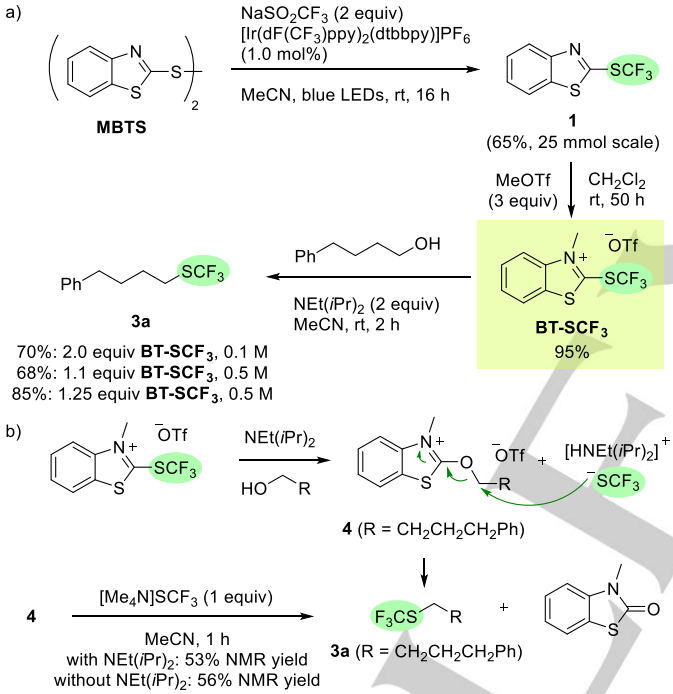
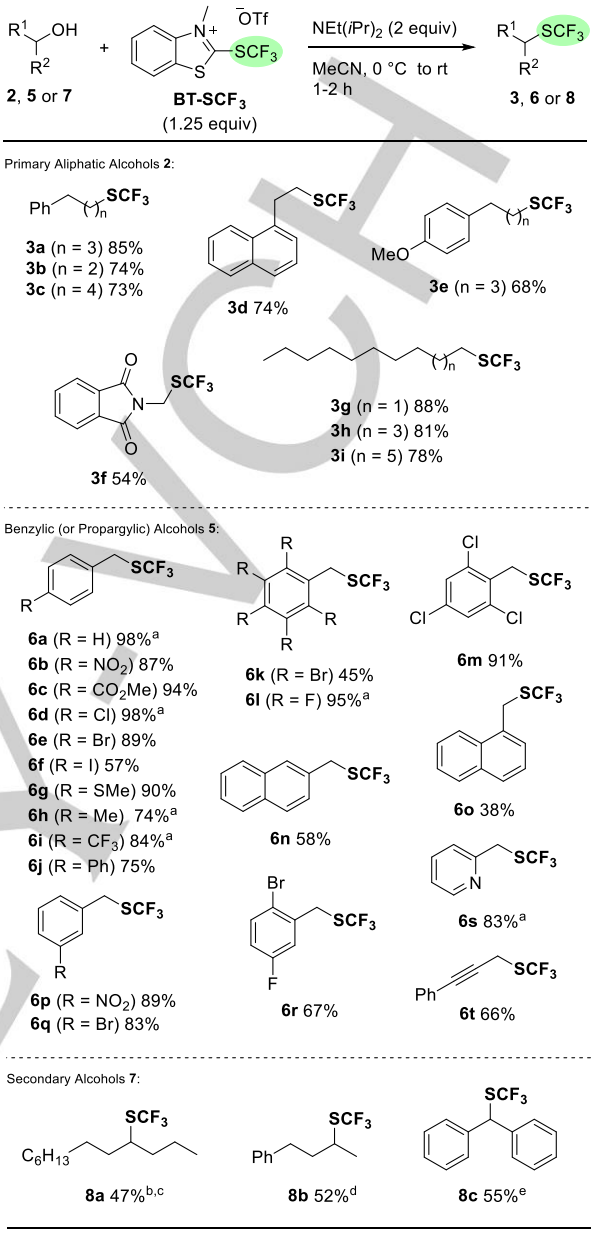
heteroaromatic species **1**, which can be readily purified by column chromatography without decomposition. A reactive reagent is only generated in the second step with simple methylation of the benzothiazole ring nitrogen with MeOTf affording **BT-SCF$_3$**. While there are several literature methods for conducting the *S*-trifluoromethylation of MBT,[8] we found that intermediate compound **1** could be most efficiently generated starting from the disulfide dimer MBTS via an in-house-developed photoredox catalysis method.[8a, 9] Blue light irradiation of inexpensive MBTS with the Langlois reagent ($NaSO_2CF_3$) and the iridium photocatalyst $[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$ (1.0 mol%, $dF(CF_3)ppy$ = 3,5-difluoro-2-(5-trifluoromethyl)-2-pyridine, dtbbpy = 4,4'-di-*tert*-butyl-2,2'-bipyridine) in MeCN cleanly afforded **1** in 65% isolated yield (25 mmol scale).[10] The heteroaromatic intermediate was subsequently stirred with MeOTf (3 equiv) in CH_2Cl_2 and, after 50 h at rt, addition of Et_2O followed by filtration delivered **BT-SCF$_3$** in 95% yield without the need for further purification.



Scheme 2. a) Two-step synthesis of **BT-SCF$_3$** and its application in the deoxytrifluoromethylthiolation of aliphatic alcohol **2a**. b) Likely reaction mechanism via 2-alkoxybenzothiazolium salt **4**.

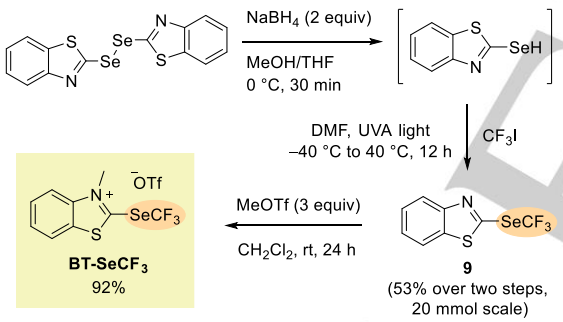


Scheme 3. Deoxytrifluoromethylthiolation of alcohols with **BT-SCF$_3$**. Reaction conditions: alcohol (**2**, **5** or **7**, 0.50 mmol), **BT-SCF$_3$** (1.25 equiv), $NEt(iPr)_2$ (2 equiv), MeCN (0.50 M), 0 °C to rt, 1-2 h. Isolated yields after column chromatography unless otherwise stated. [a] ^{1}H NMR yield stated due to product volatility (internal standard: CH_2Br_2). [b] With **BT-SCF$_3$** (2 equiv), −40 °C. [c] Isolated as an inseparable mixture with alkene side-products. [d] With **BT-SCF$_3$** (2 equiv) added portion-wise. [e] With **BT-SCF$_3$** (3 equiv) added portion-wise, $NEt(iPr)_2$ (3 equiv).

BT-SCF$_3$ is an off-white solid that is stable over at least several months under ambient conditions and hydrolyses only slowly in neutral or acidic MeCN/H_2O solutions.[11] In the presence of Hünig's base ($NEt(iPr)_2$), however, fast hydrolysis to the corresponding benzothiazolone is observed. This result validates the proposed mode of action of **BT-SCF$_3$** and we accordingly turned our attention to the development of a nucleophilic trifluoromethylthiolation process. Addition of an aliphatic alcohol rather than water, for example, would deliver a 2-alkoxybenzothiazolium salt susceptible to subsequent nucleophilic substitution by the released $^-SCF_3$ anion. Deoxytrifluoromethylthiolation reactions are synthetically attractive as they avoid pre-activation steps and provide valuable alkyl-SCF_3 compounds directly from widely-available alcohols. Previously-reported methods by Qing,[12] Billard[13] and Pégot & Magnier[14] have exploited the aforementioned instability of $^-SCF_3$ with substitution occurring on an *in situ*-generated carbonofluoridothioate intermediate (Scheme 1b). This approach, however, requires excess amounts of the expensive trifluoromethylthiolating reagent and high reaction temperatures.

Rueping and co-workers reported a room temperature method using only 1.5 equivalents of $CuSCF_3$ and 2 equivalents of the Lewis acid $BF_3{\cdot}OEt_2$, however, the scope of this process was limited to activated benzylic and allylic alcohols capable of stabilizing the intermediate carbocation.[15,16]

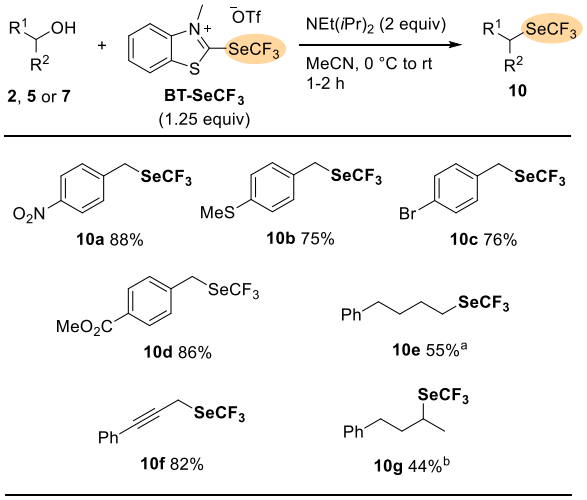
In an initial experiment, the primary aliphatic alcohol **2a** was reacted with 2 equivalents of both **BT-SCF₃** and $NEt(iPr)_2$ in MeCN (0.1 M). After 2 hours at rt, we were delighted to observe clean conversion to the corresponding alkyl-SCF_3 derivative **3a**, which could be isolated in 70% yield after column chromatography. Notably, the reaction proceeded smoothly under ambient conditions and no special precautions to exclude air or moisture were required (Scheme 2a). Optimisation of the reaction conditions confirmed the requirement for a base with $NEt(iPr)_2$ (2 equiv) in MeCN providing **3a** in the highest yields.[11] Moreover, upon increasing the concentration to 0.5 M, efficient deoxytrifluoromethylthiolation could be achieved using only a slight excess of **BT-SCF₃** (68% yield with 1.1 equiv, 85% with 1.25 equiv). Aside from the obvious practical advantages, the low reagent loading indicates that carbonofluoridothioate intermediates generated through *β*-fluoride elimination of $^-SCF_3$ are not the major electrophilic species in this process and that 2-alkoxybenzothiazolium intermediates are likely involved (Scheme 2b).[12-14] This mechanism was further validated by the successful formation of **3a** upon reacting the independently synthesized 2-(4-phenylbutoxy)benzothiazolium salt **4** with $[Me_4N]SCF_3$ (53% and 56% ^1H NMR yield with or without $NEt(iPr)_2$, respectively).



Scheme 4. Synthesis of **BT-SeCF₃**.

With a set of optimized conditions in hand, the scope and limitations of the metal-free deoxytrifluoromethylthiolation process with a range of alcohols was evaluated (Scheme 3). Primary aliphatic alcohols **2** reacted smoothly to afford the corresponding trifluoromethylthiolated products **3a-i** in moderate to excellent yields up to 88%. In each case, complete conversion was observed within 2 hours under ambient conditions and the trifluoromethylthiolated products could be easily isolated by column chromatography. A wide range of diversely-substituted benzylic alcohols **5** could also be smoothly transformed into the corresponding trifluoromethyl thioethers **6a-t** under the same mild conditions. Benzylic alcohols bearing electron-withdrawing groups such as NO_2 and CO_2Me at the *para*-position were particularly effective substrates, delivering the corresponding SCF_3-containing products **6b** and **6c** in 87% and 94% yield, respectively. Comparatively electron-neutral substituents were also successfully deoxytrifluoromethylthiolated, however, strongly electron-donating *para*-substituents such as OMe led to complex reaction mixtures, presumably due to the instability of the 2-alkoxybenzothiazolium intermediates. The halogen-substituents Cl, Br and I were all tolerated under the reaction conditions, opening up the possibility of subsequent elaboration of the products through cross-coupling methodologies. Substitution at the *meta*-position of the aryl rings was well tolerated with the *meta*-NO_2 and *meta*-Br derivatives **6p** and **6q** being afforded in 89% and 83% yields, respectively. Trifluoromethylthioether **6r**, which features an *ortho*-Br and *meta*-F substituent was also isolated in 67% yield, while the propargyl alcohol **5t** was successfully converted to SCF_3-substituted product **6t** in 66% yield. In addition to primary alcohols, a selection of secondary alcohols **7** could also be deoxytrifluoromethylthiolated using **BT-SCF₃**. Two or three equivalents of the reagent were required to effect complete conversion of these more sterically-hindered substrates with the highest yields being obtained upon adding **BT-SCF₃** portion-wise over 2 hours.

The successful synthesis and application of **BT-SCF₃** as a new nucleophilic reagent for installing the trifluoromethylthio group onto organic molecules encouraged us to consider whether the same approach could be adapted to prepare $SeCF_3$-substituted compounds. Selenium derivatives are attracting increasing interest for applications in materials and medicinal chemistry.[17] With a Hansch parameter (π) of 1.29[18] and Hammett constants σ_m and σ_p of 0.44 and 0.45,[19] respectively, the $SeCF_3$ group has lipophilic and electronic properties between those of SCF_3 and OCF_3 and could thus allow for better fine tuning of a molecule's properties. Despite notable recent advances,[17,20] the synthesis of $SeCF_3$-substituted compounds remains dominated by indirect methods and, to the best of our knowledge, there is no previous report of a direct deoxytrifluoromethylselenylation reaction of alcohols.



Scheme 5. Deoxytrifluoromethylselenylation of alcohols with **BT-SeCF₃**. Reaction conditions: alcohol (**2**, **5** or **7**, 0.20 mmol), **BT-SeCF₃** (1.25 equiv), $NEt(iPr)_2$ (2 equiv), MeCN (0.50 M), 0 °C to rt, 1-2 h. Isolated yields after column chromatography. [a] Reaction performed at −40 °C. [b] Reaction performed at −40 °C, **BT-SeCF₃** (2 equiv).

BT-SeCF$_3$ was synthesized via the same general strategy used to prepare **BT-SCF$_3$**. In the first stage, the known trifluoromethylselenylated benzothiazole **9**[21] was prepared in 53% yield from bis(2-benzothiazolyl)diselenide upon sequential reduction with $NaBH_4$ and UVA light-facilitated radical trifluoromethylation with CF_3I and NaH.[9b, 22] Subsequent methylation with MeOTf (3 equiv) in CH_2Cl_2 at rt for 24 h provided pure **BT-SeCF$_3$** in 92% yield upon precipitation with Et_2O and filtration (Scheme 4). As for **BT-SCF$_3$**, the selenium derivative was obtained as an off-white solid that is remarkably stable towards hydrolysis in the absence of a base. With **BT-SeCF$_3$** in hand, its potential as a reagent for deoxytrifluoromethylselenylation reactions was tested with a selection of aliphatic alcohols (Scheme 5). Upon treating the benzylic alcohol **5b** with **BT-SeCF$_3$** (1.25 equiv) under the same mild reaction conditions used with **BT-SCF$_3$**, a clean deoxytrifluoromethylselenylation process was observed leading to the $SeCF_3$-substituted product **10a** in 88% yield. Moreover, several other benzylic and propargylic alcohols reacted with similarly high yields while, upon decreasing the reaction temperature to −40 °C, the primary aliphatic alcohol **2a** and even the secondary alcohol **7b** could be successfully transformed into the corresponding selenoethers **10e** and **10g** in 55% and 44% yield, respectively.

In conclusion, we have introduced two new reagents for installing valuable fluorine-containing functional groups onto organic compounds. Based on the benzothiazolium motif, **BT-SCF$_3$** and **BT-SeCF$_3$** are bench stable and easy to handle solids that release $^-SCF_3$ or $^-SeCF_3$ anions in a controlled fashion upon activation *in situ*. Using only a slight excess of **BT-SCF$_3$**, a wide-range of aliphatic alcohols can be successfully converted into the corresponding trifluoromethylthioethers at room temperature while **BT-SeCF$_3$** enables hitherto unprecedented deoxytrifluoromethylselenylation reactions. We believe that benzothiazolium salts could open up new routes towards important organofluorine compounds and further studies are underway in our laboratory.

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Keywords: fluorine • reagent development • trifluoromethylthio (SCF_3) group • trifluoromethylselenyl ($SeCF_3$) group • alcohols

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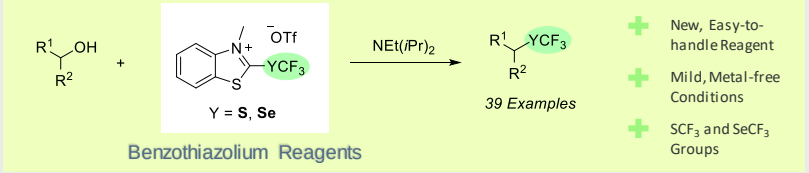

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Deoxytrifluoromethylthiolation and Selenylation of Alcohols using Benzothiazolium Reagents

Benzothiazolium salts have been developed as new reagents for installing valuable fluorine-containing functional groups onto organic molecules. The bench stable and easy-to-handle solid **BT-SCF$_3$** delivers a wide range of alkyl-SCF$_3$ compounds directly from alcohols under mild conditions, while the related selenium derivative **BT-SeCF$_3$** can be employed in unprecedented deoxytrifluoromethylselenylation reactions.