Synthetic Methods Hot Paper

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Direct Catalytic Trifluoromethylthiolation of Boronic Acids and Alkynes Employing Electrophilic Shelf-Stable *N*-(trifluoromethylthio)phthalimide

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Abstract: *A new and safe method for the synthesis of N-(trifluoromethylthio)phthalimide, a convenient and shelf-stable reagent for the direct trifluoromethylthiolation, has been developed. N-(Trifluoromethylthio)phthalimide can be used as an electrophilic source of F_3CS^+ and reacts readily with boronic acids and alkynes under copper catalysis. The utility of CF_3S-containing molecules as biologically active agents, the mild reaction conditions employed, and the high tolerance of functional groups demonstrate the potential of this new methodology to be widely applied in organic synthesis as well as industrial pharmaceutical and agrochemical research and development.*

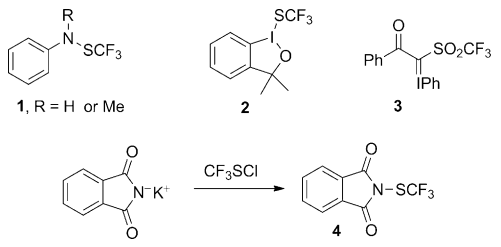
Compounds containing perfluoroalkylated groups have received increased attention because of their widespread biological and therapeutic properties.[1] These substituents have been involved in the manufacturing processes of blockbuster drugs and highly effective agrochemicals. Among the enormous range of fluorinated compounds known to date, those containing perfluorinated alkylthiogroups are valuable for the pharmaceutical and agrochemical industries.[2] Such compounds possess unique and important physical, chemical, and biological properties compared to the parent nonfluorinated ones. The most prominent among them is the trifluoromethylthio group (CF_3S). It plays an important role because of its strong electron-withdrawing effects and high lipophilicity, which increases the ability to cross lipid membranes and create opportunities for the modification of known and new drugs.[3] Additionally, trifluoromethylthioethers (CF_3SR) are also key intermediates in the preparation of trifluoromethylsulfoxides and sulfones.[4] Methodologies to synthesize complex organic molecules containing these functional groups are now vital for both academic and industrial research.[5] Unfortunately, simple approaches for the direct incorporation of a CF_3S group into organic molecules are still limited, and therefore the development of safe and efficient methodologies is highly desirable.

Several methodologies for the direct trifluoromethythiolation have been described. Nucleophilic trifluoromethylthiolation reagents including $AgSCF_3$ and $CuSCF_3$ are known and well studied. They can easily be prepared from silver fluoride[6] and after metal exchange with CuBr.[7] The reaction of aryl halides and alkyl halides with these reagents has been known for a long time.[8] Recent studies described the palladium-catalyzed cross-coupling reaction between aryl halides and $AgSCF_3/R_4NI$.[6] This reaction was also performed with Me_4NSCF_3 in the presence of a nickel catalyst.[9] We recently described a copper-catalyzed trifluormethylthiolation of vinyl halides to yield various vinyl trifluoromethyl thioethers employing Me_4NSCF_3.[10]

Daugulis and co-workers[11] recently reported a protocol for the copper-catalyzed direct sulfenylation of aromatic C–H bonds with auxiliary directing groups using disulfides. In contrast, Zhang and Qing[12] have described the oxidative trifluoromethylthiolation of terminal alkynes and aryl boronic acids starting from elemental sulfur and the Ruppert–Prakash reagent. This methodology does not require the existence of a preformed CF_3S moiety in the reagent. The above-mentioned protocols employ all nucleophilic CF_3S sources, which imply the use of an oxidant or the use of electrophilic substrates, thus making the range of direct trifluoromethylthiolation limited.[6–13]

The simplest electrophilic CF_3S reagent, gaseous CF_3SCl,[14] is toxic and corrosive and thus not safe to use. Shelf-stable, easy-to-handle reagents have been recently developed. One was described by Billard and Langlois[15] (**1**; Scheme 1), the second by Lu and Shen[16] (**2**) and third by Shibata[17] (**3**). These reagents have been employed for the functionalization of alkynes, boronic acids, Grignard reagents, or β-ketoesters and enamines. *N*-(trifluoromethylthio)phthalimide (**4**) is a known compound which acts as an electrophilic source for the trifluoromethylthio group. The synthesis of **4** was initially developed by Munavalli et al.[18] but to date only a very limited use of this reagent has been shown. Moreover, its previously described synthesis requires the use of the unfriendly and difficult-to-work with trifluoromethylsulfenyl chloride.

Since the field of direct electrophilic trifluoromethylthiolation reactions and the synthetic utility of such transformations is still limited, we decided to disclose a more efficient pathway toward **4**, examine its properties, and



Scheme 1. Electrophilic trifluoromethylthiolating agents.

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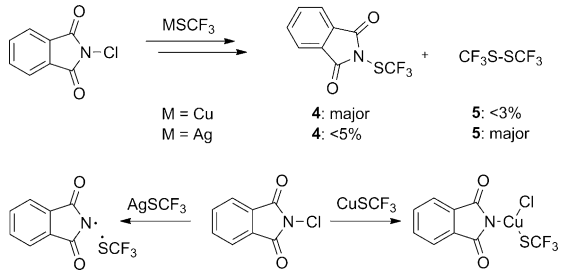


Scheme 2. Electrophilic trifluoromethylthiolating agents.

explore its synthetic utility in direct trifluoromethylthiolations of alkynes and boronic acids.

To develop an efficient synthesis of **4** we decided to perform a series of studies. The cyclic voltammogram of *N*-chlorophthalimide showed a reduction peak at −0.45 V versus SCE in acetonitrile whereas the nucleophilic trifluoromethylthio reagents $AgSCF_3$ and $CuSCF_3$ were oxidized at potentials of +0.37 V and +0.81 V, respectively. This data showed the possibility of a redox transformation of formal F_3CS^- to F_3CS^+ and reduction of formal Cl^+ to Cl^- (see the Supporting Information for spectra). Therefore, we decided to firstly explore the reaction of *N*-chlorophthalimide with $AgSCF_3$ in acetonitrile (Scheme 2).

However, in this case, the expected redox reaction turned out to be quite challenging because of the formation of a substantial amount of F_3CSSCF_3 (**5**) as the main product, thus suggesting a radical mechanism. Evaluation of various reaction conditions such as solvent and temperature did not show any improvement. Interestingly, when $CuSCF_3$ in acetonitrile was used, the desired product was formed in high yield with almost no formation of **5**; approximately 3%, as determined by ^{19}F NMR analysis of the crude reaction mixture. This result might be explained by a nonradical pathway. Insertion of $CuSCF_3$ into the N−Cl bond could form a copper(III) species, which undergoes reductive elimination to provide the desired product (Scheme 2). There is no evidence for the formation of the amino/Cu^{III}/SCF_3 species, but Dobbie and Emeldus reported the preparation of trifluoromethylthio(bistrifluoromethylamino)mercury,[19] thus showing the possibility to form aminometallic SCF_3 species and indicating that such a copper intermediate could be feasible.

Subsequently, the reaction was scaled up to over 5.0 grams and the desired product **4** was isolated as colorless crystals in 90% yield after flash chromatography on silica gel and fully characterized by spectroscopic techniques. The compound **4** melts without decomposition at 115–116 °C (lit. 115–117 °C) and could be easily sublimed at 80 °C/1 mbar. To gain evidence for the potential utility and possible limitations of this reagent, we investigated its stability. Accordingly, **4** is not light sensitive and it is stable in both the solid state and in solution. NMR studies showed no decomposition of the reagent under aerobic conditions in solvents such as [D_6]DMSO, [D_7]DMF, $CDCl_3$, [D_8]toluene, [D_8]THF, [D_6]acetone, CD_3CN, and CD_3OD (Table 1). Standing in solution at room temperature for seven days, or heating of the solutions at 50 °C for 12 hours (DMF and toluene at 100 °C/3 h) showed no signs of decomposition. The presence of transition-metal ions (e.g. Cu^+, Cu^{2+}, Fe^{2+}, Fe^{3+}, Pd^{2+}) also does not decompose **4**.

Table 1: Stability of **3**[a] in different solvents and in the presence of additives.

Entry	Solvent	$\delta(^{19}F)$ [ppm]	**3d** (RT)	(RT)	**7d** (12 h, 50 °C)
1	[D_6]DMSO	−48.6	n.c.	n.c.	n.c.
2[b]	[D_6]DMSO	−48.6	n.c.	n.c.	–
3[c]	[D_6]DMSO	−48.6	n.c.	n.c.	–
4[d]	[D_7]DMF	−49.7	n.c.	n.c.	n.c.
5[d]	$CDCl_3$	−49.0	n.c.	n.c.	n.c.
6	$CDCl_3$/DBU	−49.0	dec.: 40%[e]	dec.[f]	–
7	$CDCl_3$/lutidine	−49.0	n.c.	–	n.c.
8	$CDCl_3$/Et_3N	−49.0	n.c.	–	dec.: <5%
9	$CDCl_3$/D_2O	−49.0	n.c.	–	n.c.
10[d]	[D_8]toluene	−44.5	n.c.	n.c.	n.c.
11[d]	[D_8]THF	−50.6	n.c.	n.c.	n.c.
12[d]	[D_6]acetone	−50.4	n.c.	n.c.	n.c.
13[d]	CD_3CN	−50.1	n.c.	n.c.	n.c.
14	CD_3OD	−51.3	n.c.	–	n.c.

[a] NMR experiment conditions: **4** (9.25 mg, 0.037 mmol) and ethyl trifluoroacetate (internal standard, 5.3 mg, 0.037 mmol) in 0.75 mL of appropriate solvent. Final concentration of reagent was 50 mM. Decomposition as detected by signals with respect to the internal standard. [b] 21.09 mg (5 equiv) of TFA was added. [c] 11.1 mg (15 equiv) of D_2O was added. [d] (Trifluoromethyl)benzene (5.5 mg, 0.037 mmol) was used as an internal standard. [e] 40% decomposition after 15 min. [f] Complete decomposition after 24 h. DBU = 1,8-diazabicyclo[5.4.0] undec-7-ene, DMF = *N*,*N*-dimethylformamide, DMSO = dimethylsulfoxide, n.c. = no change, dec. = decomposition, THF = tetrahydrofuran.

To our delight, **4** was totally inactive toward acidic conditions (e.g. AcOH, MsOH, TsOH, TfOH) and the presence of water. In contrast, **4** can be sensitive to strong bases. In the presence of weak bases such as lutidine there was no decomposition, and Et_3N as a moderate base gave less than 5% decomposition after 12 hours at 50 °C. In the presence of a strong base such as DBU, **4** decomposed in short time. Noteworthy, by ^{19}F NMR spectroscopy we realized that during this process new species were formed: F_3CSSCF_3 ($\delta = -45.6$ ppm), F_3CSOH ($\delta = -5.2$ ppm), F_3CSO_2H ($\delta = -81.8$ ppm), and the corresponding anion $F_3CSO_2^-$ ($\delta = -86.1$ ppm).[20]

With this shelf-stable electrophilic trifluoromethylthiolating reagent **4** in hand, we started to test its usefulness in reaction with representative C nucleophiles such as boronic acids and terminal acetylenes. Initial attempts showed that there was no product formation when heating in diglyme or DCE (see the Supporting Information, and Tables 2 and 3) Hence, we turned our attention to copper catalysis which is widely applied in transformations involving boronic acids and alkynes. We observed that the reactions proceeded only in the presence of copper(I) salts whereas copper(II) salts showed no activity. Further examination of various commercially available copper sources revealed that CuCl and CuI were the most appropriate for the reaction with boronic acids and only CuI showed good catalytic activity for the functionalization of alkynes. Interestingly, the ligand had a strong influence on the

reactivity of the copper catalyst. The unsubstituted bipyridine was effective, and the trifluoromethylthiolated products were obtained in high yields. However, when different substituted bipyridines and phenantrolines were applied, yields dramatically dropped. Other factors such as solvent, base and temperature also had an influence on the reaction outcome and were successfully optimized (see the Supporting Information). With the optimized reaction conditions in hand, **4** was used with a broad range of boronic acids as well as alkynes (Tables 2 and 3).

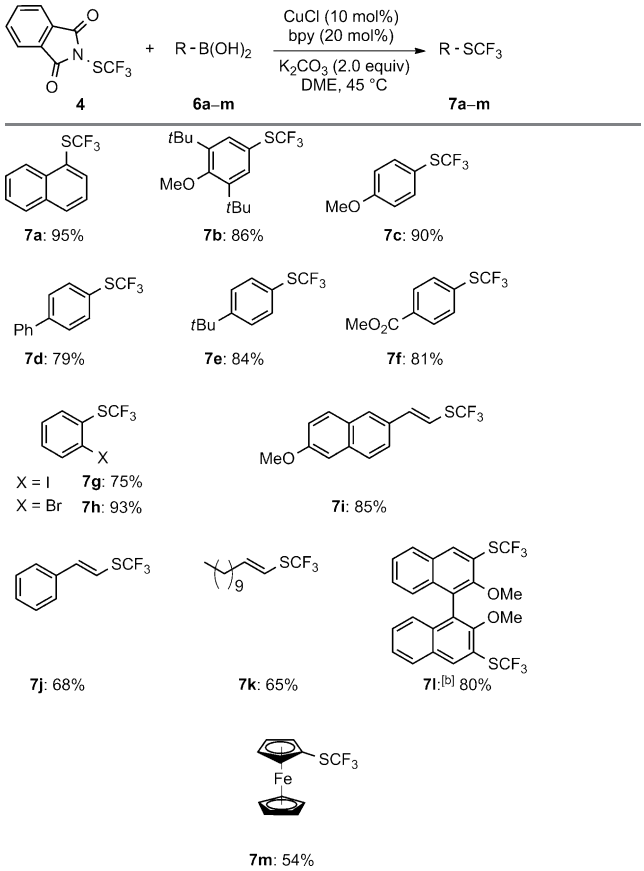
All tested arylboronic acids (**6a–h** and **6l,m**) reacted with **4** and the corresponding trifluoromethylthiolated arenes **7a–h** and **7l,m** were obtained in good to very high yields (54–95%, Table 2). Of note, the reaction conditions were tolerant to different substituents. When *o*-substituted boronic acids were used, no significant steric hindrance effect was found and the products were isolated in good yield. A slight decrease in the yield was observed when *o*-iodoboronic acid was used as compared to the *o*-bromo derivative. Also, the vinyl boronic acids **6i–k** could be used and the corresponding trifluoromethylthioethers **7i–k** were obtained in good yield.[10]

The terminal alkynes **8** also reacted with **4**, but to achieve good conversion, the reaction mixture needs to be heated up to 80°C for 15 hours (see Table 3 and the Supporting Information). Under the optimized reaction conditions we examined the substrate scope of this transformation (Table 3). Both electron-rich and electron-deficient terminal alkynes could be converted into their corresponding alkynyl trifluoromethyl sulfides **9** in good yields. The optimized reaction conditions allowed the transformation of various terminal alkynes containing a wide range of functional groups, including amino, ester, keto, nitro, ethers, heterocyclic, and aliphatic compounds. Additionally, a bromide substituent was compatible with the reaction conditions, which offers the opportunity for further modifications.

Finally, to demonstrate the synthetic utility of our methodology we prepared the protected bis(trifluoromethylthiolate)d binol **7l**, which can be oxidized to the corresponding disulfone **10** in high yield (Scheme 3). The latter product could be used as an intermediate for catalyst preparation.[21] Additionally, oxidation of the alkyne derivative **9b** gave the trifluoromethylsulfoxide **11**, a useful building block for organic synthesis.

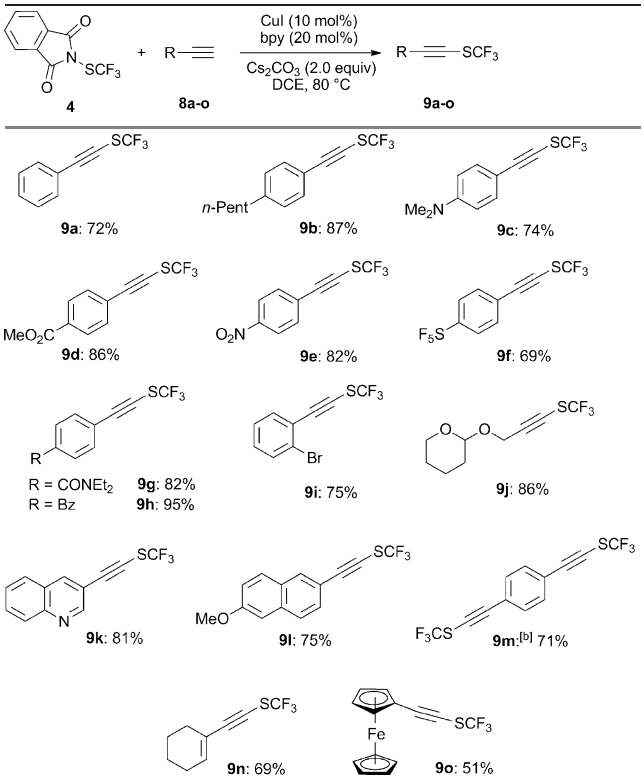
In summary, we have developed for the first time a new and safe method for the synthesis of *N*-(trifluoromethylthio)-phthalimide (**4**), a convenient and shelf-stable reagent for the direct trifluoromethylthiolation of readily available boronic acids and alkynes. Because of the utility of the CF_3S group in biologically active agents, the mild reaction conditions

Table 2: Reaction scope of the copper-catalyzed trifluoromethylthiolation of boronic acids.[a]

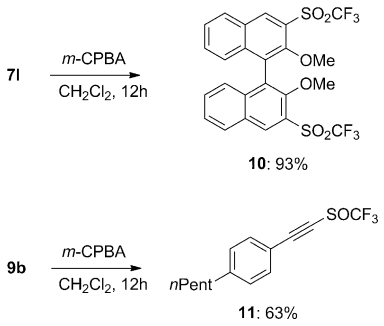


[a] Reaction conditions: **6** (1.0 equiv), **4** (1.15 equiv), CuCl (10 mol%), bpy (20 mol%), and K_2CO_3 (2.0 equiv), in DME at 45°C for 18 h. Yield of the isolated product after column chromatography. [b] Used 0.5 equiv of **6l**. bpy = 4,4′-bipyridine, DME = dimethoxyethane.

Table 3: Reaction scope of the copper-catalyzed trifluoromethylthiolation of alkynes.[a]



[a] Reaction conditions: **8** (1.0 equiv), **4** (1.2 equiv), CuI (10 mol%), bpy (20 mol%), and Cs_2CO_3 (2.0 equiv), in DCE at 80°C for 15 h. Yield of the isolated product after column chromatography. [b] **8m** (0.5 equiv) was used. DCE = 1,2-dichloroethane, *m*-CPBA = *meta*-chloroperbenzoic acid.



Scheme 3. Oxidation of the trifluoromethylthioether products.

employed, and high tolerance of functional groups, the method developed has the potential of being widely applied in organic synthesis as well as industrial pharmaceutical and agrochemical research and development. Further research toward trifluoromethylthiolations under mild reaction conditions as well as asymmetric reactions is ongoing in our laboratories. Results will be reported in due course.

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