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Deep Study of Thiocarbamoyl Fluorides: Synthesis and Properties.

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Abstract. Thiocarbamoyl fluoride is an understudied fluorinated group, mainly due to the paucity of data on its properties. Herein, an in-depth study of the stability of thiocarbamoyl fluorides, especially under near-physiological conditions, is described. Since efficient and easy to implement syntheses of these compounds are still under-described, a new method, based on the use of a trifluoromethanesulfenamide, a well-described and versatile reagent, has also been developed.

This trifluoromethanesulfenamide turned out to be able to generate in situ difluorothiophosgene, which was able to react rapidly with amines to efficiently provide various thiocarbamoyl fluorides.

Keywords: Thiocarbamoyl fluorides; Trifluoromethanesulfenamide; Difluorothiophosgene; Fluorine; Sulfur

Introduction

Due to the specific characteristics of the fluorine atom, organofluorinated compounds possess unique properties.^[1] Consequently, they have been found in a wide range of applications in recent decades, from materials to life sciences.^[2]

In order to develop new compounds with selective and specific properties for targeted applications, the development of innovative fluorinated groups appeared these last years as an active research field. In this objective, the merging of fluorine with other heteroatoms has emerged as a fruitful strategy.^[3]

Recently, we have described a detailed study of the properties of carbamoyl fluorides.^[4] In order to continue our investigations on such a family of compounds, we noticed that there was little data available in literature on thiocarbamoyl fluorides. We therefore decided to focus our interest on them.

The synthetic routes to obtain thiocarbamoyl fluorides are still relatively limited and have recently been reviewed.^[5] Although some methods using the explosive CS₂ in combination with toxic and sensitive reagents have recently been described,^[6] the main strategies are essentially based on the use of difluorothiophosgene generated in situ by the degradation of the CF₃S⁻ anion. These methods can then be divided into two approaches. Firstly, the use of the isolated CF₃S⁻ anion, with different counter-cations.^[7] However, due to the high sensitivity of this anion, such methods remain delicate and not so easy to implement. Secondly, the in situ generation of this

anion without isolation.^[7c, 8] Such approaches are more interesting but depend on the availability of fluorinated starting reagents. Most of these methods required the use of metals and/or an excess of phosphines. A strategy using Ruppert-Prakash reagent (CF₃SiMe₃), S₈ and KF could be considered as the most useful.^[7c]

This lack of efficient ways to access to thiocarbamoyl fluorides may explain the under-exploration of their potential use. In this context, we thought that the study of thiocarbamoyl fluorides would be of interest to determine their potential applications.

Results and Discussion

Given the limited number of efficient synthetic routes to obtain thiocarbamoyl fluorides, we decided to develop an “in-house” method. A few years ago, we developed an efficient reagent for carrying out trifluoromethylthiolation reactions, namely the *N*-tosyl, *N*-methyltrifluoromethanesulfenamide **BB23** (Scheme 1).^[9] In particular, we have shown that this reagent was able to generate the CF₃S⁻ anion in presence of Bu₄NI (Scheme 1A).^[10]

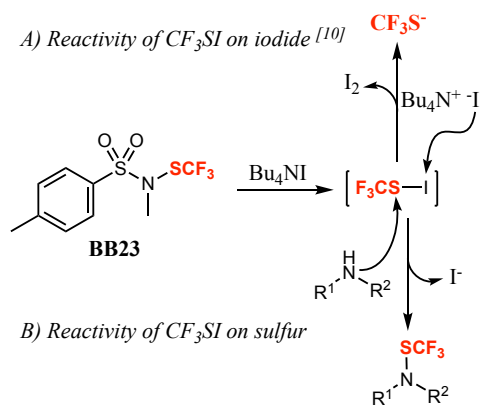
Consequently, in order to pursue the demonstration of the high versatility of the **BB23** reagent, we decided to study its use in the synthesis of thiocarbamoyl fluorides (Table 1).

Table 1. First attempts to obtain thiocarbamoyl fluorides.

Entry	Bu ₄ NI (equiv.)	Additive	2i (%) ^{a)}	Transamination 3i (%) ^{a)}
1	2	-	20	80
2	2	Ca(OTf) ₂	66	-
3	3	Ca(OTf) ₂	85	-
4	4	Ca(OTf) ₂	99	-
5 ^{b)}	4	Ca(OTf) ₂	75	-
6 ^{c)}	4	Ca(OTf) ₂	99	-

^{a)} Yields determined by ¹⁹F NMR spectroscopy with PhCF₃ as internal standard. ^{b)} 40 °C. ^{c)} CH₃CN as solvent.

The reaction was first carried out under the same conditions as previously described to produce the intermediate CF₃S⁻ (Table 1, entry 1).^[10] Under these conditions, only a low yield of the expected thiocarbamoyl fluoride (**2i**) was observed. Surprisingly, however, the product resulting from a transamination reaction (**3i**) was mostly formed. As no significant formation of **3i** was observed by mixing only **BB23** with amine at 60°C, without Bu₄NI, we suggested that the transamination could arise from the reaction of amine with the intermediate CF₃SI (Scheme 1B).

**Scheme 1.** Formation and reactivity of CF₃SI from **BB23**.

This led to suppose that the previously described polarization of the S-I bond in CF₃SI,^[10-11] is ambiguous: the soft iodide anion effectively attacks the iodine atom to release the CF₃S⁻ anion,^[10] whereas the hardest nucleophilic amine reacts on the sulfur atom. In order to avoid this transamination and thus to favor the formation of the CF₃S⁻ anion, a Lewis acid was added in order to chelate the amine and reduce its nucleophilicity. In order to avoid the use of metallic species and to potentially accelerate the

degradation of the CF₃S⁻ anion, calcium triflate was chosen due to the strong Ca-F bond energy (entry 2). In the presence of Ca(OTf)₂, no transamination was observed and a higher yield of thiocarbamoyl fluoride **2i** was obtained. Assuming that a part of the iodide anions can be quenched by Ca(OTf)₂, the amount of Bu₄NI was increased (entries 3-4). A quantitative yield was observed with 4 equivalents of Bu₄NI. A lower yield was obtained by lowering the temperature to 40 °C (entry 5). Finally, a similar result was also obtained in acetonitrile (more polar solvent) instead of THF (entry 6).

Starting from the previously determined best optimal conditions (Table 1, entry 6), further optimizations of the reaction conditions were carried out, in particular in order to reduce the amount of Bu₄NI (Table 2).

Table 2. Optimization of of carbamoyl fluorides formation from **BB23**.

Entry	Bu ₄ NI (equiv.)	CaL ₂ (equiv.)	t	2i (%) ^{a)}
1	4	Ca(OTf) ₂ (1)	1 h	99
2	4	CaCl ₂ (1)	1 h	69
3	2	CaI ₂ (1)	1 h	90
4	1	CaI ₂ (1)	1 h	99
5	1	CaI ₂ (1)	30 min	95
6	1	CaI ₂ (1)	15 min	94
7	0.5	CaI ₂ (1)	1 h	72
8	0.5	CaI ₂ (1)	24 h	90
9	0.1	CaI ₂ (1)	1 h	59
10	0.1	CaI ₂ (1)	24 h	80
11	-	CaI ₂ (1)	1 h	59
12	-	CaI ₂ (1)	24 h	89
13	1	LiI (2)	1 h	68
14	1	NaI (2)	1 h	74
15	1	KI (2)	1 h	10 ^{b)}
16	1	RbI (2)	1 h	7 ^{b)}
17	1	CsI (2)	1 h	8 ^{b)}
18	1	MgI ₂ (1)	1 h	81
19	1	BaI ₂ (1)	1 h	70 ^{c)}
20	1	ClSiMe ₃ (1)	1 h	30 ^{d)}

^{a)} Yields determined by ¹⁹F NMR spectroscopy with PhCF₃ as internal standard. ^{b)} more than 70% of transamination (**3i**). ^{c)} 8 % of transamination. ^{d)} 18 % of transamination.

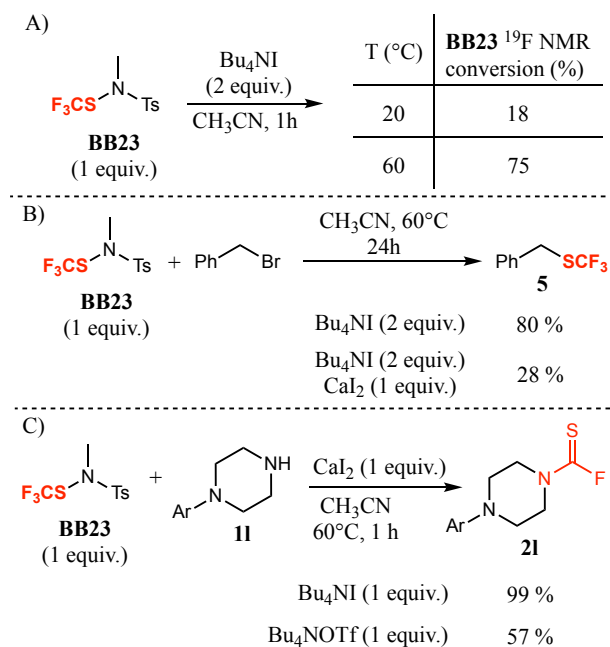
A cheaper source of Ca was tested with CaCl₂, but with a worse result (entry 2), possibly due to a lower solubility. The required 4 equivalents of Bu₄NI can be justified by the probable in situ reaction of Bu₄NI with Ca(OTf)₂ (supported by the difference in chemical shift observed by ⁴³Ca NMR between Ca(OTf)₂ and a mixture Ca(OTf)₂ + Bu₄NI). Consequently, CaI₂ was introduced directly as Ca source in the presence of only 2 equiv. of Bu₄NI, to

respect the 4 equiv. of iodide anion previously used (entry 3). A similar result was observed, confirming the hypothesis of a reaction between $\text{Ca}(\text{OTf})_2$ and a part of the Bu_4NI . The amount of Bu_4NI could be reduced to 1 equiv. without changing of the optimum yield (entry 4). Under these conditions, the reaction time could be reduced to 30 min (entry 5) or 15 min (entry 6) without a significant decrease in yield. Halving the amount of Bu_4NI led to a lower result in 1 h, which could be improved in 24 h (entries 7-8). A similar kinetic effect was observed with only 10% of Bu_4NI , with a slightly lower yield after 24 h (entries 9-10). Finally, the use of CaI_2 alone, without any addition of any Bu_4NI , also required 24 h to obtain a result comparable to that observed with 1 equiv. of Bu_4NI (entries 11-12).

Alkaline iodides were also evaluated. If LiI and NaI gave interesting but lower yields (entries 13-14), KI , RbI , CsI (entries 15-17) gave worse results, where the transamination reaction became predominant. This can be explained by their lower Lewis acidity, which prevents amine chelation.

Other alkaline earth iodides were evaluated. Using MgI_2 gave satisfactory yields, but lower than calcium iodide (entry 18). With BaI_2 a lower yield was obtained and some transamination was observed (entry 19), probably due to the lower Lewis acidity of Ba, compared to Ca. Finally, ClSiMe_3 gave only to a modest result.

To clarify the role of each parameter of the optimal conditions (entry 5), additional experiments were performed (Scheme 2).



Scheme 2. Mechanistic studies.

First, the role of temperature was investigated (Scheme 2A). The main effect of temperature seems to be to favor the attack of **BB23** by iodide anion to release CF_3S^- species. Second, we hypothesized that

calcium would prevent the transamination reaction by chelating amines and also favor the degradation of the CF_3S^- anion to difluorothiophosgene. The formation of a complex between amines and CaI_2 was demonstrated by ^1H NMR, where a signal shift was observed with the addition of calcium salt (Figure 1).

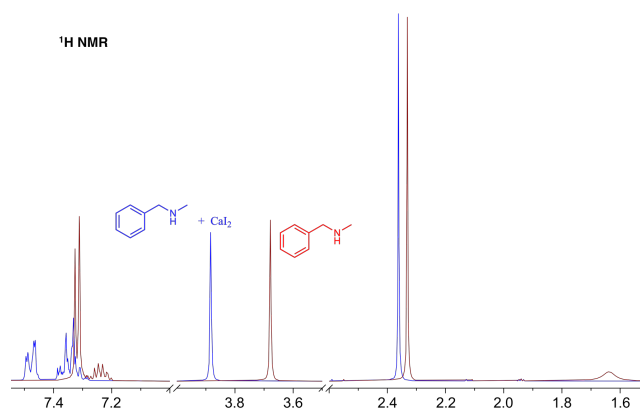
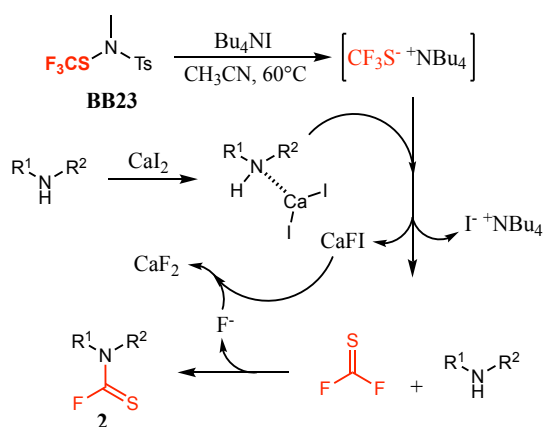


Figure 1. ^1H NMR of *N*-Me-benzylamine (red) and *N*-Me-benzylamine + CaI_2 (blue)

The potential role of calcium in the degradation of CF_3S^- has been determined by performing the trifluoromethylthiolation of benzyl bromide by a nucleophilic substitution via the in situ generation of CF_3S^- anion (Scheme 2B), as previously described.^[10] The reaction gave a good result under standard conditions, whereas a lower yield was observed in the presence of calcium salt. This suggests that a large amount of CF_3S^- was degraded to difluorothiophosgene. Finally, the role of ammonium was studied. The Bu_4NI seems to accelerate the reaction (Table 2, entries 4 and 11). Phase transfer catalysis with ammonium salt was first considered. However, the same reaction performed with Bu_4NOTf instead of Bu_4NI resulted in a lower yield (Scheme 2C), similar to the reaction with CaI_2 alone (Table 2, entry 11). Consequently, the role of Bu_4NI could be to favor the formation of the CF_3SNBu_4 salt by reacting with **BB23**, which is more dissociated than the corresponding calcium salt. This higher dissociation of the CF_3S^- anion will increase its reactivity and therefore favor its collapse into difluorothiophosgene, mediated by the Ca salt. All these studies led us to propose the mechanism described in Scheme 3.



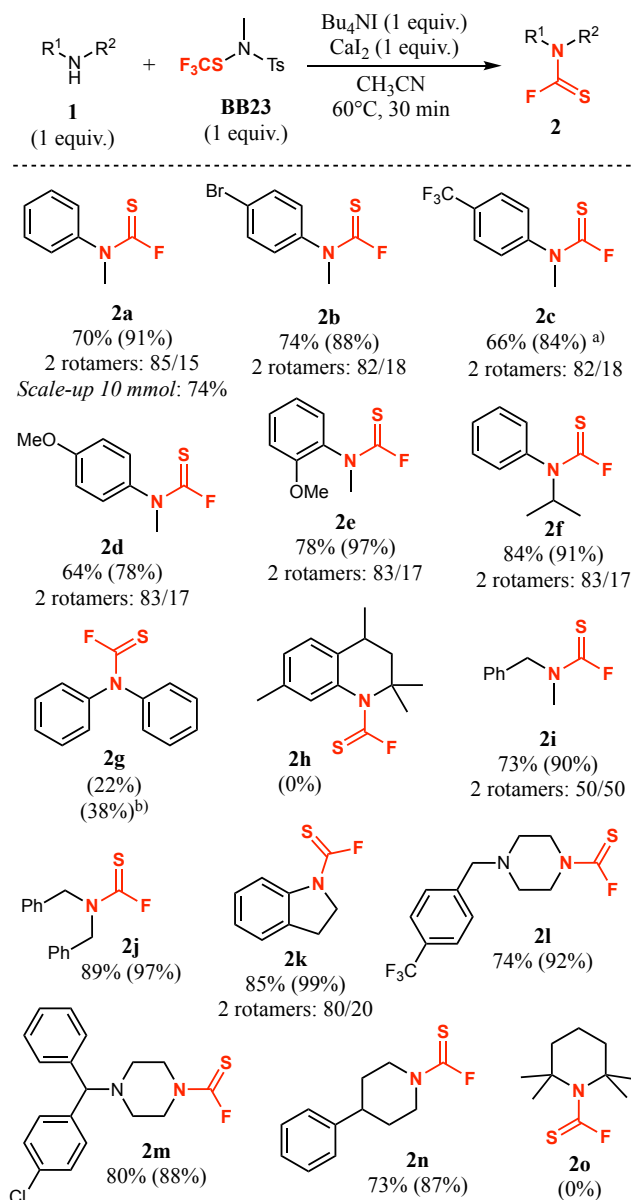
Scheme 3. Proposed mechanism for the formation of thiocarbamoyl fluoride by using **BB23**.

With the optimal conditions in hand (Table 2, entry 5), the scope of the reaction was evaluated (Scheme 4).

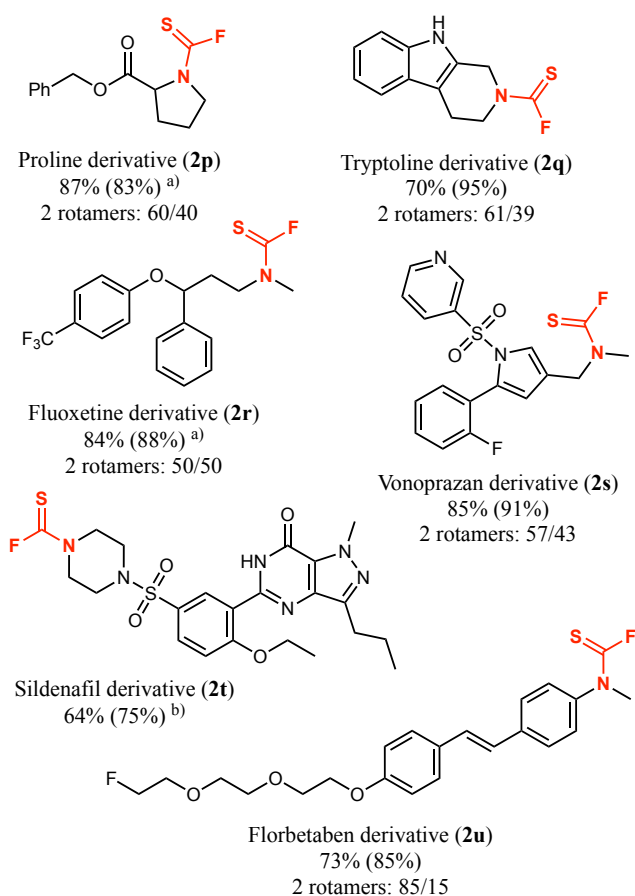
Good to excellent yields were observed with anilines, regardless of the electronic character of the substituents (**2a-f**). In the case of highly deactivated aniline, a reaction time of 1 h is required instead of 30 min (**2c**). No specific steric hindrance effect was observed with an ortho substituent (**2e**). Benzylamines also gave rise to excellent results (**2i-j**). Cyclic amines such as indoline (**2k**), piperazines (**2l-m**) or piperidine (**2n**) also gave very good yields. While no detrimental effect of moderate steric hindrance of the amine was observed (**2f**), highly hindered amines could not be functionalized (**2h, o**). The poorly nucleophilic diphenylamine resulted in a low yield even after 24 h (**2g**). The method was scaled up to the 10 mmol scale with no detrimental effect on yield (**2a**).

These results demonstrate the efficiency of the method over a wide range of substrates. To validate the synthetic potential of the method, some bioactive and more complex compounds were also functionalized (Scheme 5).

The good to excellent results obtained confirm the robustness of the method. The reaction seems to be compatible with free NH moieties (**2q, 2t**). Compatibility with various functional groups such as ester, sulfonamide, amide and double bond has also been demonstrated. Starting amines in the hydrochloride form can also be involved in the reaction. In this case, however, the addition of one equivalent of DIPEA is recommended to improve the yield (**2p, 2r**). In the case of the sildenafil derivative (**2t**), in order to avoid some purification problems, the reaction was carried out without Bu₄NI and only in the presence of CaI₂, but for 24 h.



Scheme 4. Synthesis of thiocarbamoyl fluorides with isolated yields. Yields determined by ¹⁹F NMR spectroscopy with PhCF₃ as internal standard are given in parentheses. ^{a)} 1 h instead of 30 min. ^{b)} 24 h instead of 30 min.



Scheme 5. Synthesis of thiocarbamoyl fluorides from bioactive compounds with isolated yields. Yields determined by ¹⁹F NMR spectroscopy with PhCF₃ as internal standard are given in parentheses. ^a) from hydrochloride, with 1 equiv. of DIPEA. ^b) without Bu₄NI, 24h.

In the case of unsymmetric amines ($R^1 \neq R^2$), 2 rotamers were observed (ratio 50/50 to 85/15), as previously observed with carbamoyl fluorides.^[4] To compare both functional groups, and the effect of the $O \leftrightarrow S$ substitution, coalescence temperatures were determined by variable temperature ¹⁹F NMR spectroscopy with aromatic and aliphatic substrates (**2a** and **2i**). The free energies of activation at the coalescence were also estimated by using equations from the literature (Figure 2).^[12]

From this study, it appears first that the coalescence temperatures and the rotational barrier of the aliphatic compounds (**2i**, **4i**) are superior to those of the aromatic compounds (**2a**, **4a**). Regarding the influence of sulfur or oxygen atoms, the coalescence temperatures of thiocarbamoyl fluorides (**2**) are systematically superior to those of carbamoyl fluorides (**4**). Consequently, the free energies of activation during coalescence are also higher for thiocarbamoyl fluorides than for carbamoyl fluorides. This higher rotational barrier for thiocarbamoyl fluorides is in agreement with the observation made in the literature for thioformamides compared to formamides.^[13]

	2a	4a
Rotamers	85 / 15	70 / 30
T_{coalescence}	120 °C	70 °C
ΔG[#]	23.73 ± 0.99 kJ.mol ⁻¹	14.63 ± 0.35 kJ.mol ⁻¹

	2i	4i
Rotamers	50 / 50	60 / 40
T_{coalescence}	> 150 °C ^a	140 °C
ΔG[#]	> 30.79 ± 0.04 kJ.mol ⁻¹	28.59 ± 0.13 kJ.mol ⁻¹

Figure 2. Coalescence temperatures and activation free energies for the coalescence of thiocarbamoyl and carbamoyl fluorides. ΔG[#] is given as the mean ± standard deviation between ΔG_A[#] and ΔG_B[#] (see SI and ref. [12]). ^a) Coalescence was not achieved.

To complete our study of the properties of thiocarbamoyl fluorides, we next turned our attention to their stability. The stability in organic solvents and various aqueous media was investigated using compound **2a** as model substrate (Figure 3).

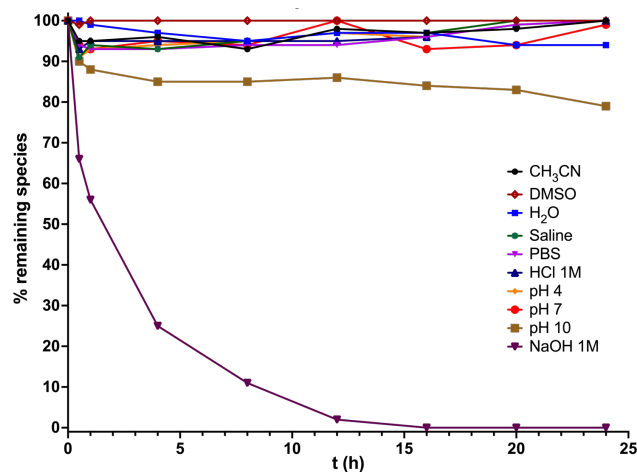


Figure 3. Stability of thiocarbamoyl fluoride **2a** in various media (T = 22 °C). PBS: phosphate buffered saline (pH 7.4).

Thiocarbamoyl fluorides are stable not only in organic solvents (CH₃CN, DMSO) but also in water. Similar stability has also been observed in more physiological media such as saline or phosphate buffered saline (PBS). As carbamoyl fluorides,^[4] thiocarbamoyl fluorides tolerate a wide range of pH range from concentrated acid (HCl 1M) to pH = 7.4. In contrast, thiocarbamoyl fluorides have a higher stability in basic solutions compared to carbamoyl

fluorides (Figure 4). In particular, a slower hydrolysis of thiocarbamoyl fluorides was observed in NaOH 1M, whereas carbamoyl fluorides were degraded quite instantly.

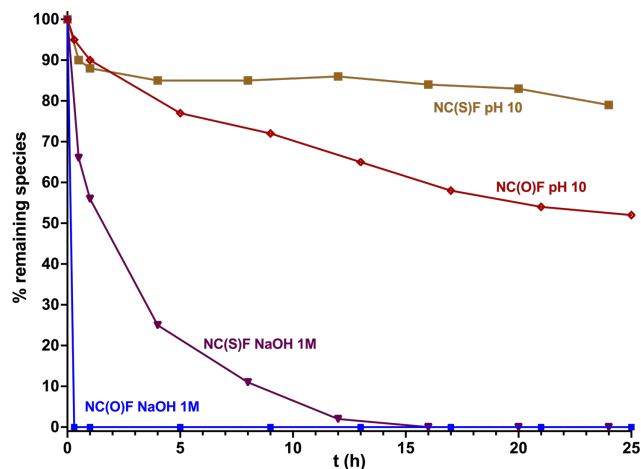


Figure 4. Comparison of the stability of carbamoyl and thiocarbamoyl fluorides under basic conditions.

To determine the compatibility of thiocarbamoyl fluorides with environments closer to the physiological environment, the stabilities in the presence of various nucleophilic amino acids were then investigated (Figure 5).

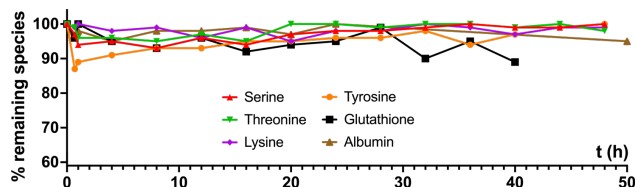


Figure 5. Stability of thiocarbamoyl fluoride **2a** in the presence of different nucleophilic amino acids ($T = 22^\circ\text{C}$).

Good stability was observed, even in the presence of glutathione. To confirm this “physiological” stability, further studies were performed in the presence of albumin, human serum or by incubation in PBS at 37°C (Figure 6).

Good stability was obtained with albumin. Incubation in PBS at 37°C for a long time did not alter the thiocarbamoyl fluoride. Finally, good persistence was observed in the presence of human serum, with a half-life $T_{1/2} = 7.5\text{ h}$ ($k_{el} = 0.09\text{ h}^{-1}$).

These good results demonstrate the excellent stability of thiocarbamoyl fluorides in conditions mimicking a physiological environment and open the way to potential applications in life sciences.

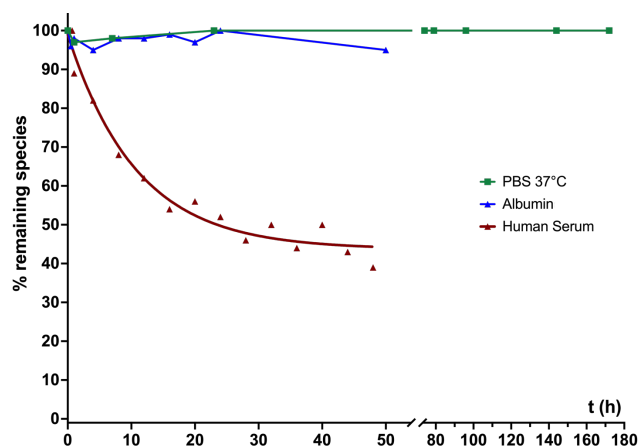


Figure 6. Stability of thiocarbamoyl fluoride **2a** in the presence of albumin, human serum ($T = 22^\circ\text{C}$) and by incubation in PBS at 37°C

Conclusion

In this work, the versatility of trifluoromethanesulfenamide **BB23** as a fluorinating reagent has been confirmed by extending its range of applications to the in situ generation of difluorothiophosgene. This metal-free method, based on the dual role of the calcium salt (intermediate amine protecting group and activation of the CF_3S^- anion), provides an efficient method for the easy preparation of thiocarbamoyl fluorides.

The study of the stability of the little studied thiocarbamoyl fluorides has highlighted their high stability under different conditions, especially those close to physiological conditions.

These studies will contribute to a better knowledge of thiocarbamoyl fluorides and should encourage to consider this fluorinated group for further applications.

Experimental Section

Typical procedure for the synthesis of thiocarbamoyl fluorides: In a 10 mL vial, **BB23** (145 mg, 0.5 mmol, 1 equiv.) is dissolved in anhydrous acetonitrile (1 mL) and the amine (0.5 mmol, 1 equiv.) is added. Tetrabutylammonium iodide (188 mg, 0.5 mmol, 1 equiv.) and calcium iodide (149 mg, 0.5 mmol, 1 equiv.) are added together to the reaction mixture. The reaction is stirred at 60°C for 30 minutes. The reaction mixture is then transferred to a separatory funnel and water (10 mL) and dichloromethane (10 mL) are added (if traces of **BB23** remain, 2 or 3 small spatulas of tetrabutylammonium iodide can be added to the mixture of DCM/water and stirred to quench it). The aqueous layer is extracted with dichloromethane ($3 \times 10\text{ mL}$). The organic layers are combined and dried with MgSO_4 , filtered and concentrated under vacuum. The crude obtained is purified by flash chromatography to give the desired compound.

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