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The main and recent syntheses of the *N*-CF_3 motif

Les principales et plus récentes synthèses du motif N-CF_3

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ABSTRACT

This review provides an overview of the various synthetic pathways of the *N*-CF_3 group. This pattern can be generated either from fluoride ions or from electrophilic, nucleophilic, or radical trifluoromethylation. This article mainly focuses on the most recent and prominent studies.

Mots-clés:
Fluor
Groupe trifluorométhyle
Addition électrophile
Addition nucléophile

RÉSUMÉ

Cette revue montre une vue d'ensemble des différentes voies de synthèse du groupe *N*-CF_3. Ce motif peut être généré, soit à partir d'ions fluorure, soit par trifluorométhylation électrophile, nucléophile ou radicalaire. Nous avons focalisé en particulier la présentation sur les principales et les plus récentes approches.

1. Introduction

The fluorine atom and the fluorine group play a major role in different fields of application, such as the pharmaceutical or material studies [1]. The presence of the fluorine group on the molecule is now widely recognized as fostering particular physicochemical properties [2], which could benefit their use in life sciences [3]. Some publications focused on the presence of the CF_3 group on heteroatoms such as O and S. Because of their high hydrophobic parameters [4], these groups are potentially important targets and are now present in the pharmaceutical and agrochemical fields [1–3]. Thus, we can see in the literature a plethora of articles describing new methodologies or new reagents. In contrast, the physicochemical properties of the *N*-CF_3 group are not known, the synthesis of this motif is relatively rare, and its chemistry has hardly been explored. Thanks to the new reagents and methods, which have been developed, the *N*-CF_3 group is becoming more and more present in the literature. In this review, we report the main and recent syntheses of the *N*-CF_3 group that have appeared in the literature.

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2. Nucleophilic fluorination

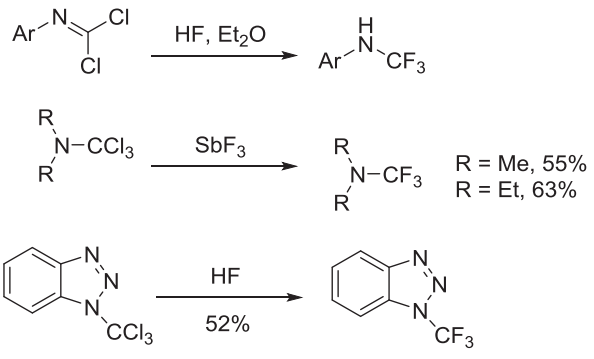
2.1. Fluorine/halogen exchange

One of the first reactions that led to the presence of the CF_3 group on the nitrogen is the fluorine/halogen exchange. The first main building block of the fluorine chemistry was hydrogen fluoride (HF) (or anhydrous hydrofluoric acid). From the dichloroimine in the presence of hydrofluoric acid in ether the *N*-CF_3 aniline was isolated (Scheme 1) [5]. Yagupolskii et al.[6] performed the fluorine/chlorine exchange starting with *N*-trichloromethyl derivatives in the presence of antimony trifluoride or HF.

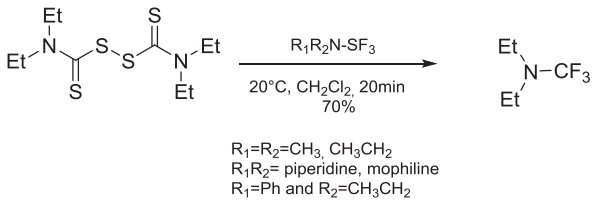
2.2. Oxidative desulfurization–fluorination of dithiocarbamoyl disulfides

Another much more thoroughly studied reaction consists in oxidative desulfurization–fluorination of dithiocarbamoyl disulfides. In organic synthesis, sulfur tetrafluoride (SF_4) was mainly used to convert hydroxyl and carbonyl groups into CF and CF_2 groups, respectively. Harder and Smith [7] similarly reported on the synthesis of the *N*-CF_3 diethyl amine and piperidine in 58% and 70% yield from thiocarbamoyl disulfides in the presence of SF_4 (Scheme 2). Interestingly, Dmowski and Kamiński proposed to use the *N*-dialkyl formamides as precursors to form the *N*-CF_3 derivatives. Using 2.5 equiv of SF_4 and 1.5 equiv of potassium fluoride (KF) for 48 h at 150 °C, the *N*-trifluoromethyl amines were obtained in excellent yields from 89% to 94% [8]. These conditions are applicable to disubstituted, symmetrical, or not amines, as well as cyclic amines. The authors have demonstrated that the R_2N-CF_2H was the intermediate reaction, resulting from the fluorination of the carbonyl and not the formation of the R_2N-COF (Scheme 2).

Other fluorinated agents then appeared, being less constraining to handle, and elaborated from SF_4 and amines [9]. The most popular reagents are the diethylaminosulfur trifluoride (DAST) and the bis-(2-methoxyethyl)aminosulfur trifluoride (Deoxofluor). In 1973, Markovski et al. [10] developed milder conditions using some dialkylaminosulfur trifluoride (R_1R_2N-SF_3) (see Scheme 3).



Scheme 1. Classical exchange reaction chlorine/fluorine by HF or SbF_3.



Scheme 3. Access to *N*-CF_3 derivatives from R_2N-SF_3.

Tyrra [11] studied the transformation of bis(dialkylthiocarbamoyl) disulfides into *N*-CF_3 in the presence of various amounts of silver fluoride. At room temperature in the stoichiometric ratio of 1:1, the corresponding *N,N*-diorganothiocarbamoyl fluorides ($R_2NC(S)_2F$), $AgSC(S)NR_2$, and elemental sulfur were obtained. Under comparable conditions in a ratio >3:1 both reactants selectively yield diorgano(trifluoromethyl)amines, R_2NCF_3, $AgSC(S)NR_2$, Ag_2S, and elemental sulfur. At stoichiometry 6:1, R_2NCF_3, Ag_2S besides elemental sulfur were formed. By analogy, thiocarbamoyl fluorides and silver dithiocarbamates react with AgF yielding selectively the corresponding trifluoromethyl amines (Scheme 4).

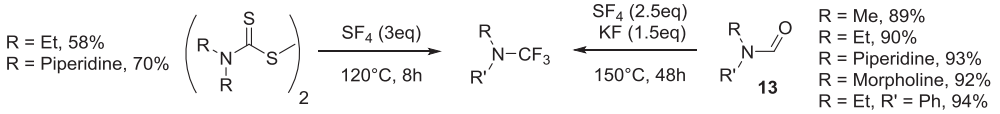
Carbonyl fluoride [12] has also been found to cleave disulfide links and to replace thiono-sulfur by fluorine. Thus, the reaction led to both *N,N*-dimethylthiocarbamoyl fluoride and *N*-trifluorotrimethyl dimethyl amine. In a separate synthesis, *N*-trifluorotrimethyl amine was obtained in 55% conversion from *N,N*-dimethylthiocarbamoyl fluoride and carbonyl fluoride (Scheme 5).

However, given the toxicity of such reagents (SbF_3, SF_4, and so forth) and the need to use specific equipment for HF, such reactions are not widely used in laboratories. In addition, rather stringent conditions (high acidity and high temperatures) make these syntheses not applicable to functionalized molecules.

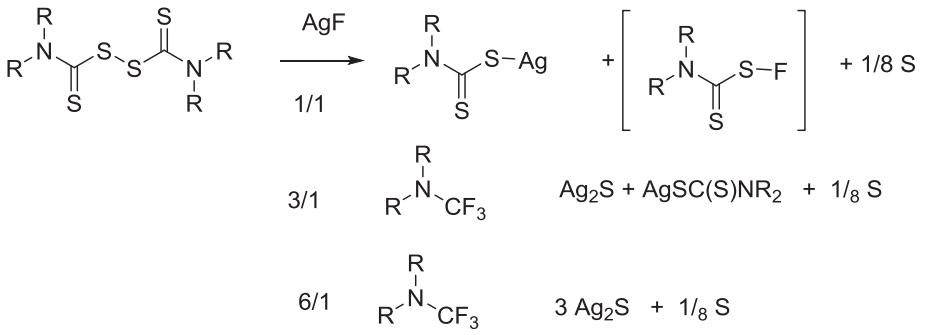
2.3. Oxidative desulfurization–fluorination of dithiocarbamates

After the oxidative desulfurization–fluorination reaction, the transformation of dithiocarbamates has been examined. Previous reagents such as DAST, Deoxofluor, and other derivatives have been used. Here some examples are commented on. The Deoxofluor with $SbCl_3$ as catalyst led to the *N*-CF_3 product (Scheme 6) [13].

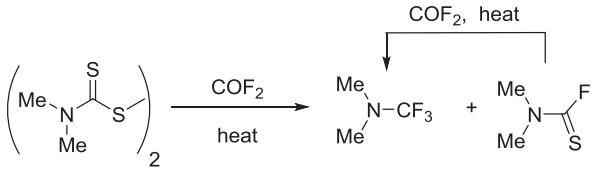
In 2012, Umemoto and Singh [14] described the use of the phenylsulfur chlorotetrafluoride and phenylsulfur trifluoride to synthesize *N*-methyl-*N*-CF_3-aminopyridine from the pyridine-methyl-dithiocarbamate (Scheme 7).



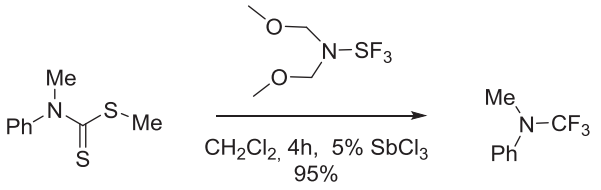
Scheme 2. Access to *N*-CF_3 derivatives with SF_4.



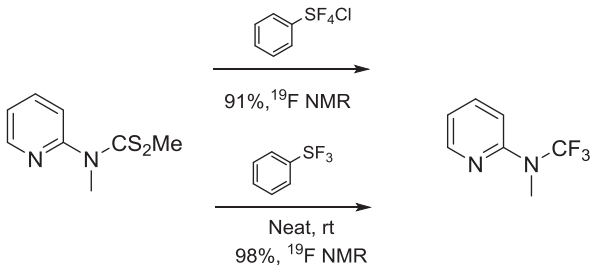
Scheme 4. Access to *N*-CF_3 derivatives with AgF.



Scheme 5. Access to *N*-CF_3 derivatives with COF_2.

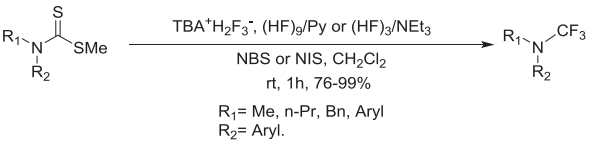


Scheme 6. Access to *N*-CF_3 derivatives with Deoxofluor.



Scheme 7. Access to *N*-CF_3 derivatives with sulfur fluoride reagents.

Milder conditions were developed by Hiyama and colleagues [15], in particular, from dithiocarbamates, *N*-halo amides, and readily available fluoride ions, such as $nBu_4NH_2F_3$, HF_x-pyridine, and HF_x-Et_3N. These are the most common methods for generating trifluoromethyl amines, which allows for the use of very mild conditions. Different conditions have been tested, in particular, by varying the nature of the fluoride ion donor and the halonium ions "X^+". The best results were obtained with *N*-bromosuccinimide (NBS), *N*-iodosuccinimide (NIS), or 1,3-dibromo-5,5-dimethylhydantoin. These conditions are applicable to various types of nitrogen, although it still needs to be disubstituted, and it includes substituted phenyl, heteroaromatics, or alkyl groups (Scheme 8).



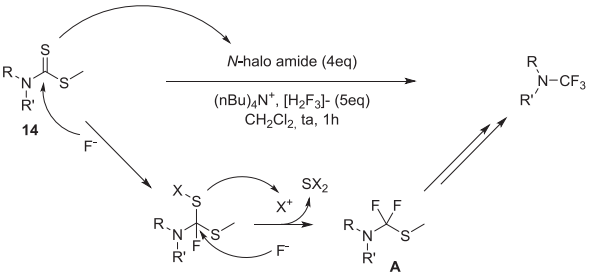
Scheme 8. Access to *N*-CF_3 derivatives with fluoride reagents.

The mechanism proposed by the authors is the following: the reaction is initiated by an attack of the dithiocarbamate on the halonium ion X^+, followed by a nucleophilic attack of a fluoride ion to give the intermediate **A**. Two successive similar reactions then take place to give the *N*-trifluoromethyl amine (Scheme 9).

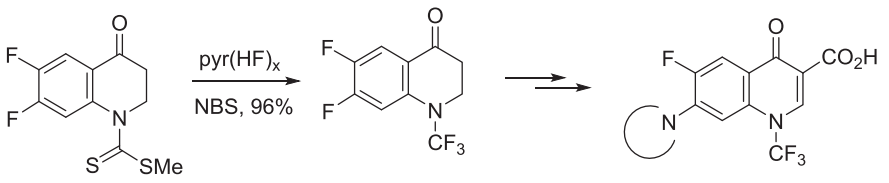
Other reactions have been experimented from dithiocarbamates with different fluoride and halogenated reagents [16]. Furthermore, the conditions involving pyridinium poly(hydrogen fluoride) and NBS have been used to introduce the CF_3 group on 4-quinolone-3-carboxylic acids, which exhibited antibacterial activity (Scheme 10) [17].

2.4. Fluorination by bromine trifluoride

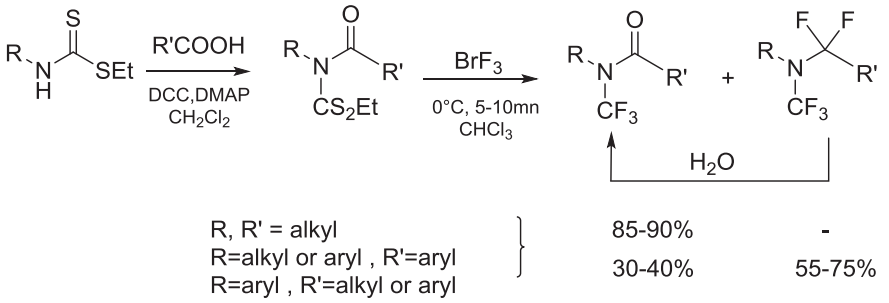
Other fluoride reagents have been used for the oxidative desulfurization–fluorination of dithiocarbamates. Rozen et al. exploited commercially available bromine trifluoride (BrF_3). The reaction proceeded under mild conditions with amides to afford *N*-CF_3 amides. The mechanism of this reaction is the same as the one described in Scheme 9. Excellent yields of *N*-CF_3 amides were obtained from alkyl amides. In the case of aryl/alkyl amides a mixture of *N*-CF_3 and RCF_2-*N*-CF_3 compounds was formed in 30%–40% and



Scheme 9. Mechanism.



Scheme 10. *N*-CF_3 analogue of antibacterial.



Scheme 11. *N*-CF_3 from BrF_3.

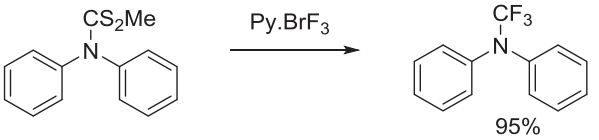
55%–75% yields, respectively. However, the difluoro/*N*-CF_3 products were successfully transformed into the *N*-CF_3 amides after hydrolysis (Scheme 11) [18].

The difference in stability to hydrolysis of the CF_2 group between aliphatic and aromatic series can be explained by fluorine hyperconjugation. In the aliphatic series, this phenomenon is exacerbated by both the lone pair of nitrogen and the donor-inductive effect of alkyl groups, which makes the difluoromethylene group susceptible to nucleophilic attack by the oxygen in the water. The aromatic series, containing ring electron acceptor, decrease the fluorine hyperconjugation required for the hydrolysis of difluoromethylene (Scheme 12).

The same group reported on the use of the Py·BrF_3 complex in the field of aromatic fluorinations. The authors observed that the use of the complex reduced the electrophilic bromination generally observed with most other reagents. In the case of the *N*-diphenyl xanthate, the complex Py·BrF_3 afforded only to the *N*-phenyl *N*-(trifluoromethyl)aniline whereas the BrF_3 led to unidentified brominated and fluorinated compounds (Scheme 13) [19].

2.5. From Me_4NSCF_3

Schoenebeck et al. [20] reported on a simple, fast, and selective one-pot synthesis of *N*-CF_3 compounds. From the stable Me_4NSCF_3 and secondary amines, the thiocarbamoyl fluoride intermediates were obtained in a few minutes at room temperature and then reacted with AgF to be transformed into *N*-CF_3. These mild conditions allowed the introduction of the CF_3 group on the nitrogen of certain pharmaceutical molecules, such as sildenafil or terbinafine (Scheme 14).



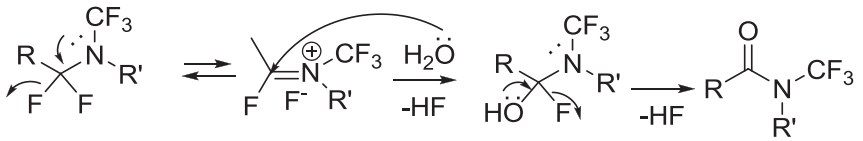
Scheme 13. Use of the pyridine/BrF_3 complex.

3. Radical trifluoromethylation

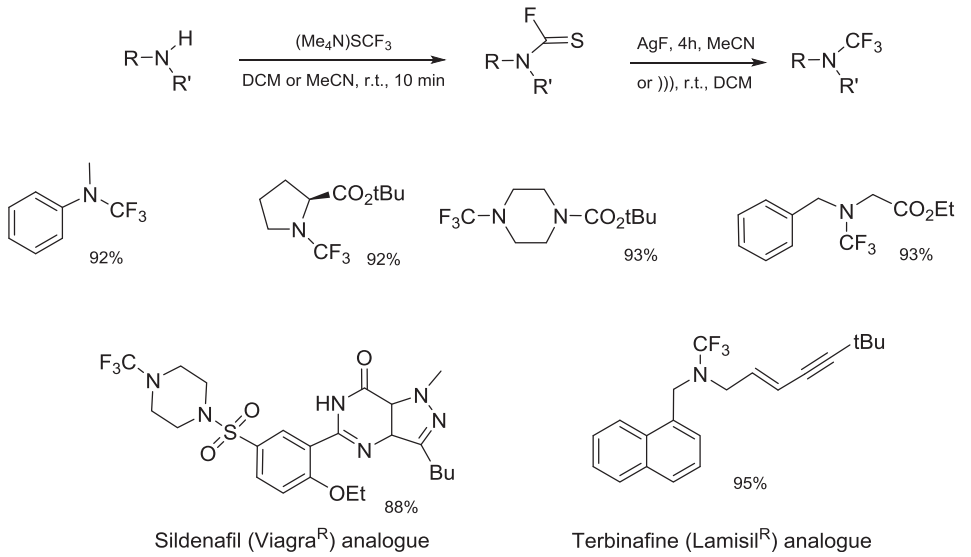
3.1. From Prakash–Ruppert reagent

The first examples of the addition of the CF_3 radical on nitrogen have been described for the detection of radical pathway by electron spin resonance (ESR) studies for the determination of mechanisms. The compound most often detected by ESR is the *tert*-butyl nitroxide trifluoromethyl, which comes from the attack of the radical "CF_3" on the *t*BuNO [21–23]. We will not discuss these articles here and will focus only on the articles that described a pathway to the synthesis of *N*-CF_3 compounds.

In 2015, Bolm et al. [24] released the first trifluoromethylation on sulfoximines in the presence of the Ruppert–Prakash reagent (CF_3TMS) catalyzed by silver carbonate in the presence of 1,10-phenanthroline. After 12 h at 60 °C, symmetrical or unsymmetrical sulfoximines



Scheme 12. Hydrolysis way.



Scheme 14. Synthesis of *N*-CF_3 derivatives from $(Me)_4NSCF_3$.

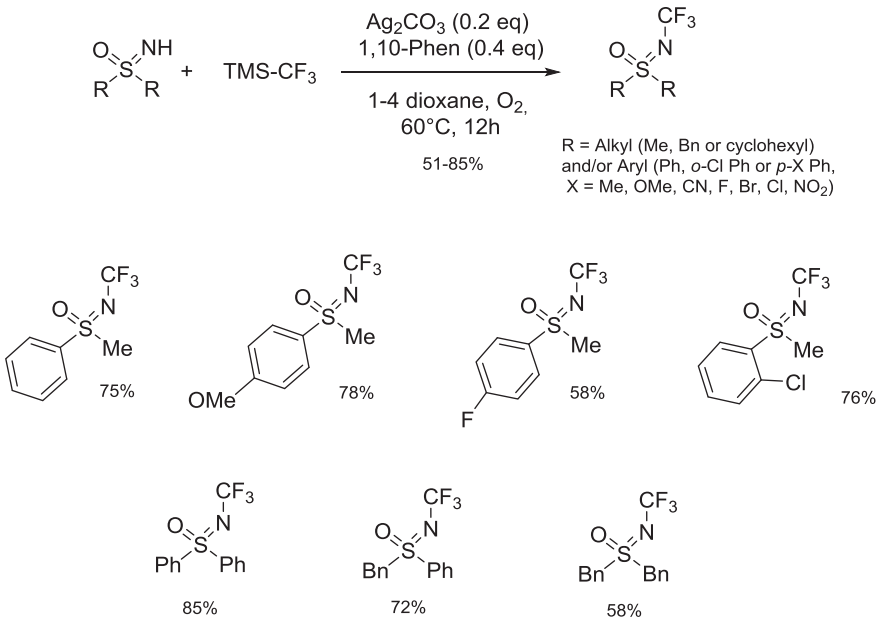
substituted by various aliphatic and/or aromatic series were isolated in moderate to good yields (Scheme 15).

To indicate the pathway to the CF_3 radical, radical traps such as TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxyl) have been added in the media, and the corresponding TEMPO–CF_3 adduct was present. The proposed mechanism is shown in Scheme 16.

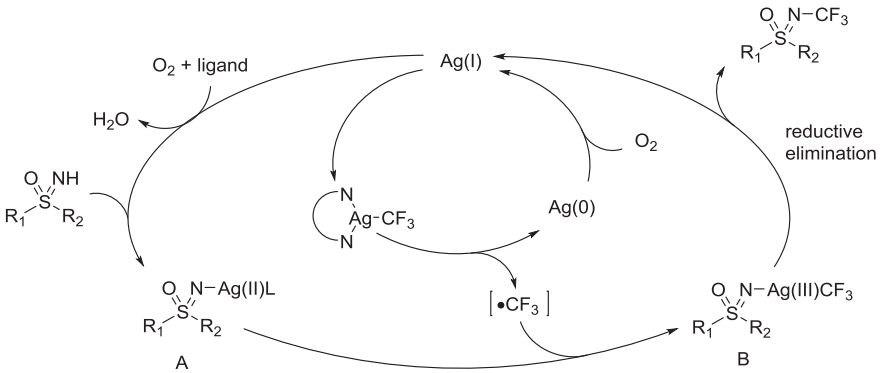
The authors assume the silver(I) cation is oxidized by dioxygen to a silver(II) species (**A**). At the same time, the trifluoromethyl radical is generated in situ from the chelate-stabilized silver $AgCF_3$ complex. Then the Ag(0) species is oxidized to Ag(I) reentering the catalytic cycle. The CF_3 radical reacts with **A** to give Ag(III) intermediate **B**. Reductive elimination of **B** provides the desired product *N*-CF_3 sulfoximine and regenerates the silver(I) cation, which starts the catalytic cycle again.

3.2. From Langlois reagents

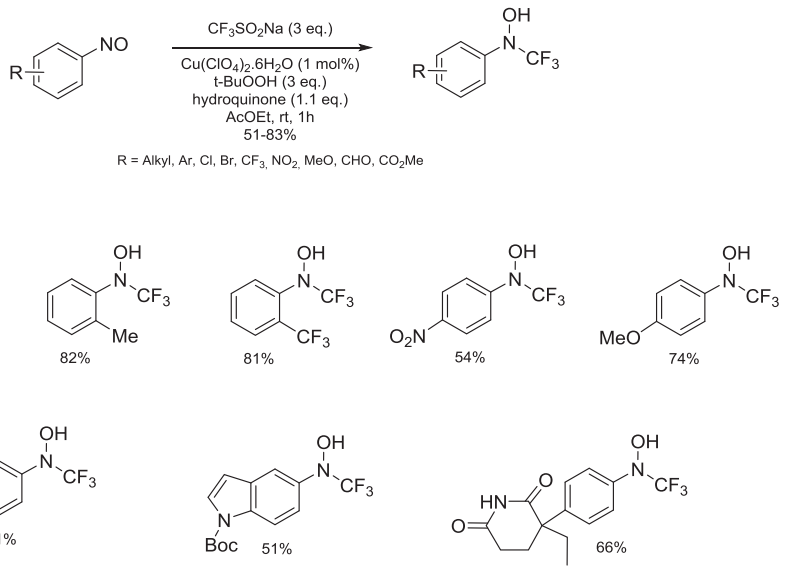
Selander et al. [25], in their 2017 study, reported on the radical addition of the trifluoromethyl group from the reagent of Langlois (CF_3SO_2Na) on aryl nitroso derivatives. The CF_3 radical was generated in combination of copper (II) ($Cu(ClO_4)_2$) and *t*-butyl hydroperoxide. Once the radical was added to the nitrosoarenes, the hydroquinone transferred a proton and released the *N*-CF_3 hydroxylamines.



Scheme 15. Synthesis of *N*-trifluoromethyl sulfoxamines.



Scheme 16. Mechanism of the radical trifluoromethylation of sulfoximines.



Scheme 17. *N*-CF_3 hydroxylamine synthesis.

The reaction that was performed in mild conditions was totally chemoselective (Scheme 17).

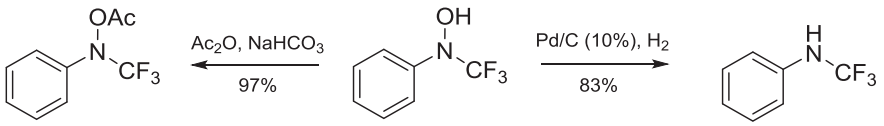
It was possible to convert *N*-trifluoromethylated hydroxylamine into *N*-CF_3 acetylated aniline and into *N*-CF_3 aniline by reduction of the N—O bond (Scheme 18).

4. Electrophilic trifluoromethylation

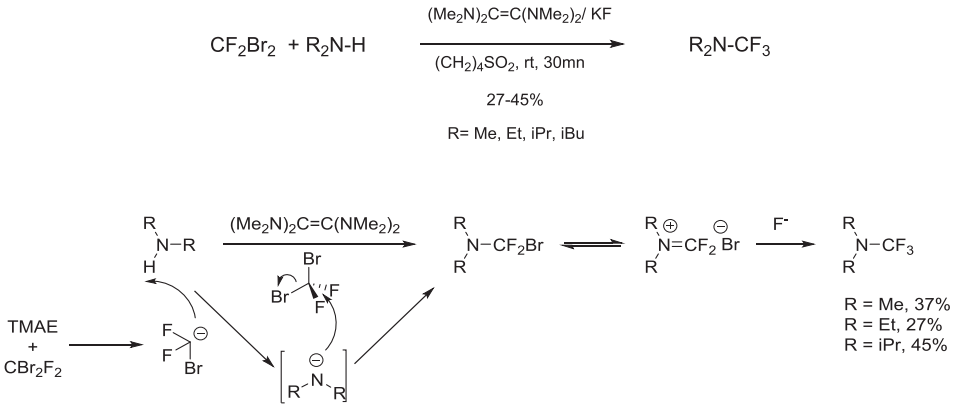
4.1. From CF_2Br_2

The electrophilic trifluoromethylation involves the nucleophilic attack of nitrogen on an electrophilic fluorinated group. Several types of precursors of "CF_3^+" have been developed to achieve these transformations. In 1991, Pawelke [26a] reported on the *N*-trifluoromethylation of secondary amines from the dibromodifluoromethane and the tetrakis(dimethylamino)ethylene (TMAE) in a polar solvent $(CH_2)_4SO_4$. The TMAE reduced the CBr_2F_2 into "F_2BrC^-" that deprotonated the amine. The amide was then combined with the dibromodifluoromethane, resulting in the formation of intermediate *N*-(bromodifluoromethyl) amine. In the polar solvent, this type is in equilibrium with the ionic form that reacts very easily with fluoride to afford the desired *N*-CF_3 products in moderate yields (Scheme 19).

In 2000, Yaguposlkii et al [6b] performed the addition of 2-methyl benzimidazole on CF_2Br_2 by treatment with NaH



Scheme 18. Modification of *N*-CF_3 hydroxylamine.



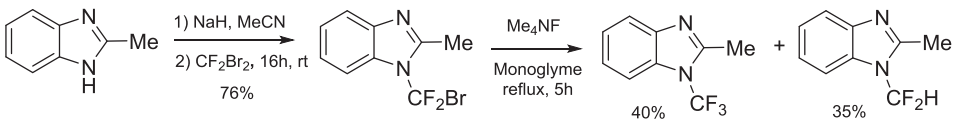
Scheme 19. *N*-CF_3 amine synthesis and mechanism.

in acetonitrile. The 1-bromo-difluoromethyl benzimidazole was converted into the 1-trifluoromethyl benzimidazole by refluxing with tetramethyl ammonium fluoride (Me_4NF) in monoglyme at reflux. The reaction resulted in a mixture of the *N*-CF_3 (40%) and *N*-CF_2H (35%) derivatives, which were separated by fractional distillation (Scheme 20).

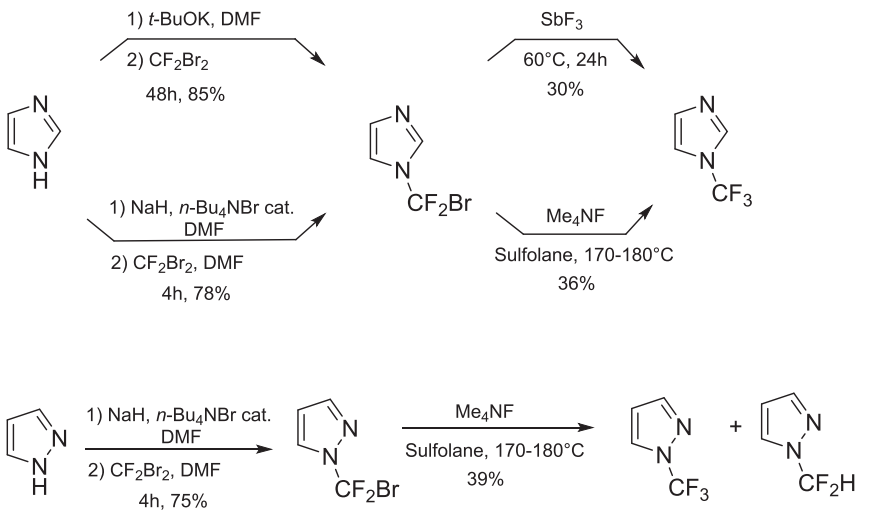
In 2001, Kolomeitsev et al. [26b] reported on the deprotonation of the imidazole with potassium *tert*-butylate (*t*-BuOK) followed by the addition of CF_2Br_2 to afford the *N*-bromodifluoromethyl imidazole. The latter was converted into the *N*-CF_3 imidazole with antimony trifluoride in 30% yield (Scheme 21). In the same way, Sokolenko et al. [26c] in 2009 presented a method for synthesizing the *N*-CF_3 imidazole and *N*-CF_3 pyrazole (Scheme 21). First imidazole and pyrazole were deprotonated with NaH in DMF after the addition of CF_2Br_2 in the presence of tetrabutyl ammonium bromide (*n*-Bu_4NBr) as catalyst to afford in high yield the 1-bromodifluoromethyl imidazole and the 1-bromodifluoromethyl pyrazole. The substitution of the bromide by the fluorine was performed with Me_4NF in sulfolane at 170–180 °C. The 1-trifluoromethyl imidazole was obtained in 36% yield after distillation. In the case of the 1-trifluoromethyl pyrazole, which was obtained in 39% yield, the 1-difluoromethyl pyrazole was additionally formed (20%).

4.2. From trifluoromethyl oxonium

More recently, new reagents have been developed to generate trifluoromethylated carbocations. In 2007,



Scheme 20. *N*-CF_3 benzimidazole synthesis.



Scheme 21. *N*-CF_3 imidazole and pyrazole synthesis.

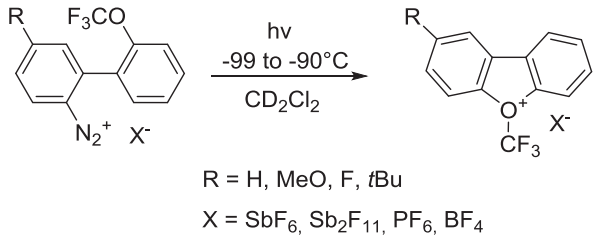


Fig. 1. Umemoto reagents.

Umemoto developed O-(trifluoromethyl)dibenzofuranylium derivatives (Fig. 1).

These CF_3 oxonium were able to generate the CF_3^+ at low temperature and proved to be very good trifluoromethylation agents of primary, secondary, or aromatic amines such as pyridines, anilines, and indolines (Scheme 22) [27].

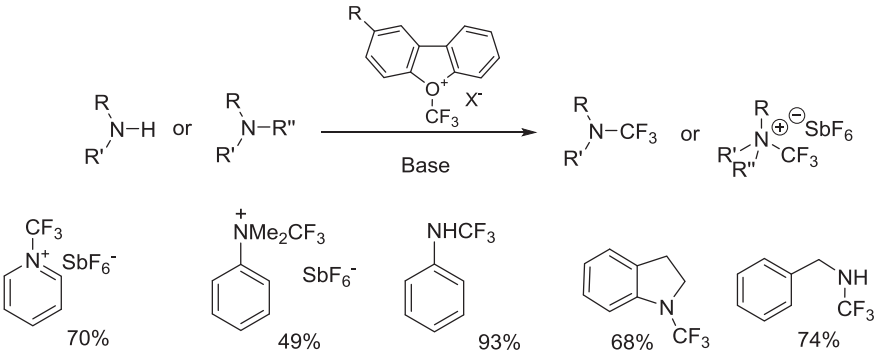
In 2006, Togni et al. [28] developed a new generation of trifluoromethylation reagents based upon hypervalent iodine (Fig. 2), which reacted with a number of C-, S-, P-, and O-centered nucleophiles.

The study of the trifluoromethylation of heteroarenes resulted in the discovery of a Ritter-type reaction of an azole, as corresponding reactions were conducted with a hypervalent iodine trifluoromethylated reagent in acetonitrile. Optimized reaction conditions allowed this first *N*-trifluoromethylation to proceed in up to 63% isolated yield (Scheme 23) [29].

The authors proposed a mechanism that involved the protonated form of the reagent I (**A**) and also the formation of the *N*-trifluoromethyl nitrilium ion (**B**) as intermediates (Scheme 24).

In 2012, the same group [30] developed a selective way to obtain the direct trifluoromethylation of substituted electron-rich heterocycles such as indoles and pyrroles. The heteroarenes were first silylated in situ before being treated with the trifluoromethylated reagent (Scheme 25).

More recently, Wang et al. [31] published a 2015 study on trifluoromethylation of NH-aromatic ketimines by the in situ generation of a hypervalent iodine intermediate as donor of CF_3^+. The intermediate was formed by using the



Scheme 22. *N*-CF_3 amines from CF_3-oxonium derivatives.

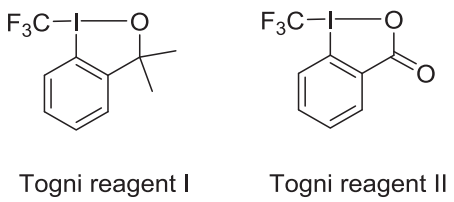
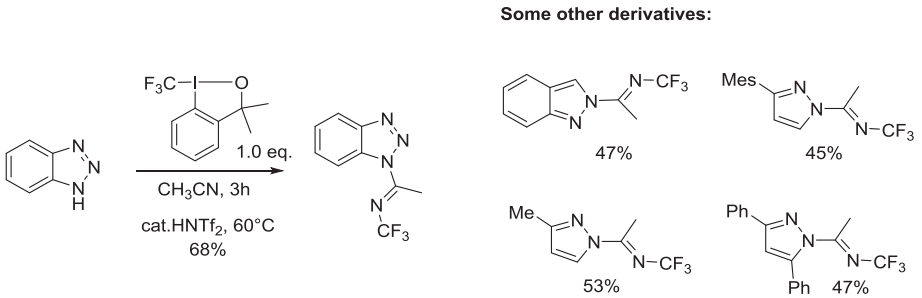
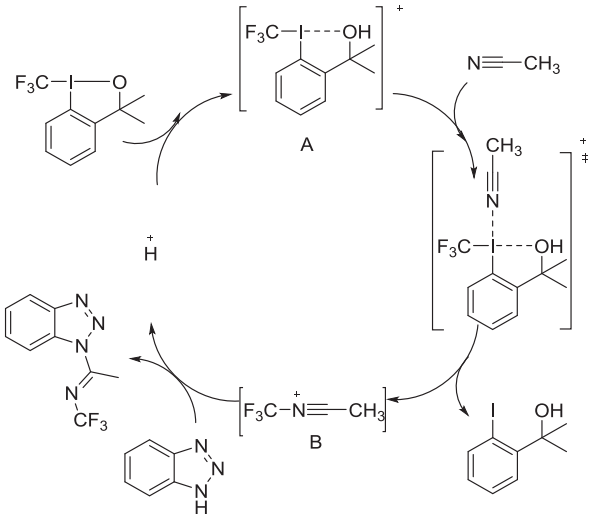


Fig. 2. Togni's reagents I and II.

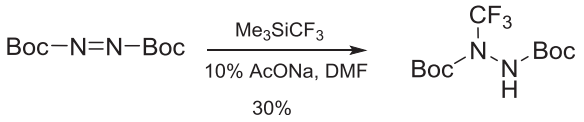
Ruppert–Prakash reagent and the iodosobenzene diacetate in the presence of a fluoride ion donor (KF) or by using Togni's reagent II with copper salt as catalyst in acetonitrile. The trifluoromethylation of primary ketimines occurs with yields ranging from 40% to 88% (Scheme 26). They proposed the following mechanism: the trifluoromethyl anion "CF_3^-", generated in situ by the attack of KF on the Ruppert–Prakash reagent, reacted with the iodosobenzene diacetate to form the active species $[PhICF_3]^+[OAc]^-$. The ketimine was



Scheme 23. *N*-CF_3 imines from Togni reagent I.



Scheme 24. Mechanism.



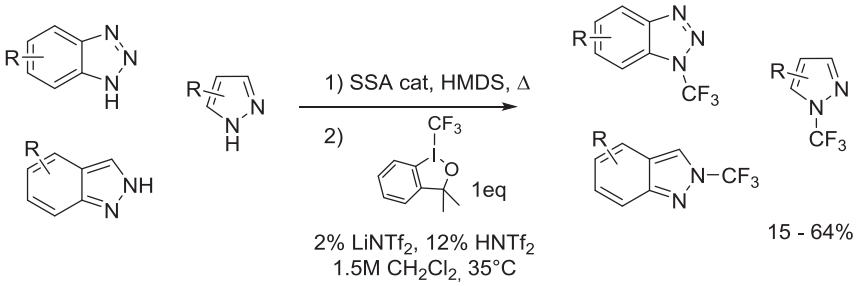
Scheme 28. Nucleophilic trifluoromethylation of di-*t*Bu azodicarboxylate.

added onto this derivative resulting in the *N*-CF_3 ketimine after deprotonation and reductive elimination. In the case of Togni's reagent, the copper catalyst increased the electrophilic character of the hypervalent iodine reagent by chelation on the oxygen of the carbonyl [28].

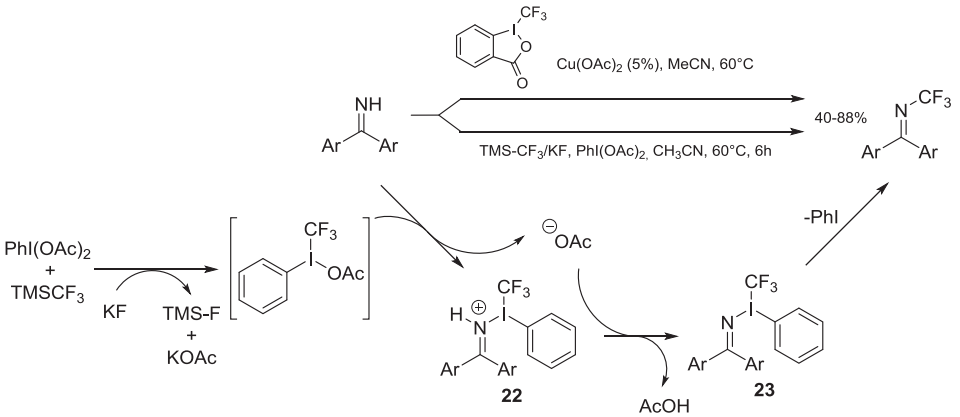
4.3. Nucleophilic trifluoromethylation

In this section, the principal investigation was carried out with the addition of the Ruppert–Prakash reagent on various electrophilic nitrogen derivatives.

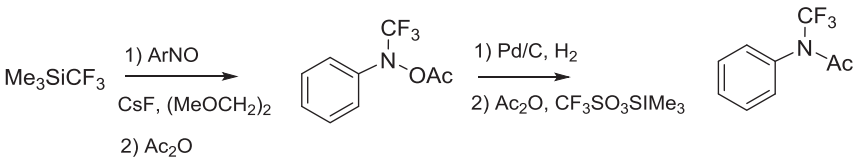
In 2012, the nucleophilic trifluoromethylation of nitrosoarenes using $TMSCF_3$ and CsF in 1.2-dimethoxyethane has been disclosed by Inoue and Handa [32]. After



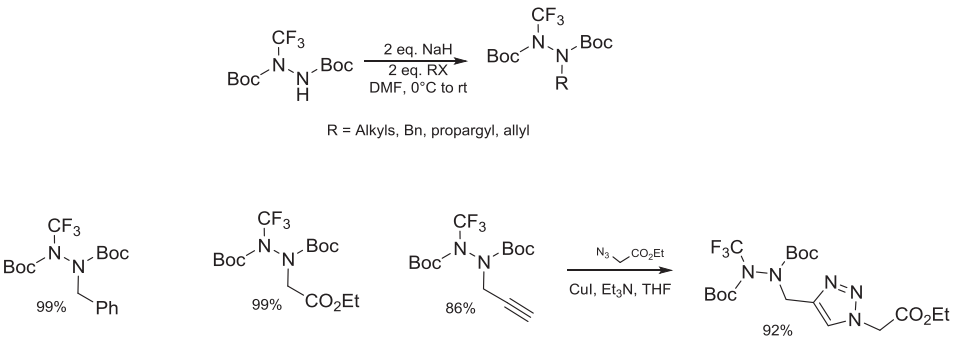
Scheme 25. Direct synthesis of *N*-CF_3 heteroarenes from Togni reagent I.



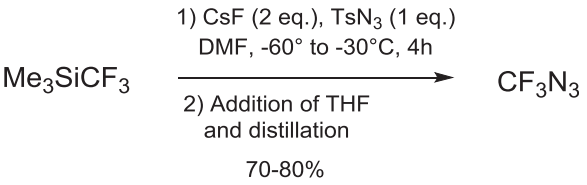
Scheme 26. Electrophilic trifluoromethylation of ketimines.



Scheme 27. Nucleophilic trifluoromethylation of nitrosoarenes.



Scheme 29. Reactivity of the *N*-CF_3 hydrazides.



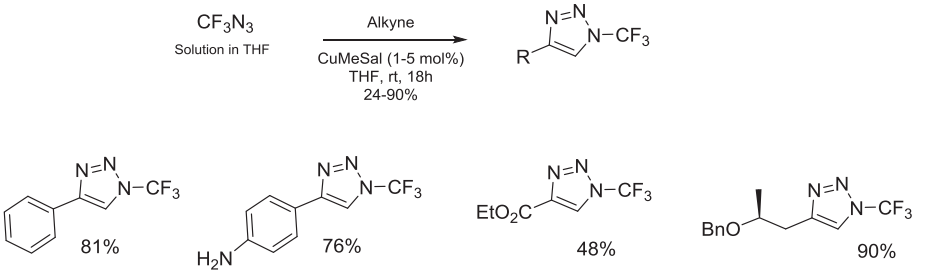
Scheme 30. Synthesis of the CF_3N_3.

treatment with Ac_2O, the O-acetylated, *N*-trifluoromethylated hydroxylamines were obtained and were hydrogenated using Pd/C in THF to afford the $PhNHCF_3$. The *N*-CF_3 aniline was also treated with Ac_2O and $CF_3SO_3SiMe_3$ at 40° for 6 h to lead $PhNAcCF_3$ in 78% yield (Scheme 27).

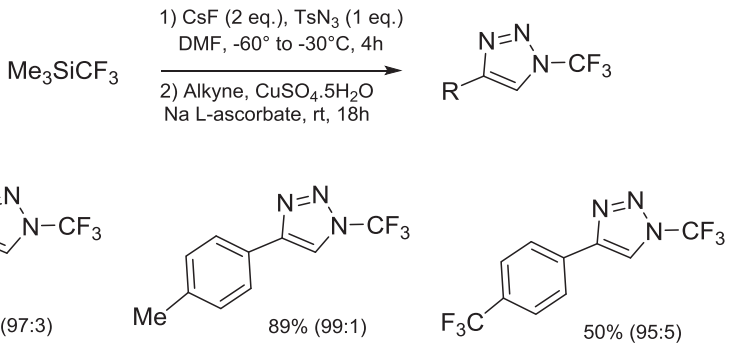
Our group performed the nucleophilic addition of another electrophilic nitrogen, the azodicarboxylate derivatives. After exploring various conditions, it was determined that the best one consisted in the use of CF_3TMS and the *t*-butyl azodicarboxylate in the presence of AcONa as catalyst in DMF at 0 °C. The corresponding *N*-CF_3 hydrazide was isolated in 30% yield. From other azodicarboxylate derivatives such as Cbz, Et, and *i*Pr, the trifluoromethylation addition occurred exclusively on the carbonyl of the ester group (Scheme 28) [33].

Under basic conditions, the *N*-CF_3 hydrazide was very stable and reacted with different nucleophiles such as allyl bromide, propargyl bromide, and ethyl iodoacetate, without decomposition and loss of fluorine. Furthermore, the azide methylester reacted easily with propargyl derivative, resulting in triazole in excellent yield (Scheme 29).

More recently, the addition of the Ruppert–Prakash reagent has been investigated on the *p*-toluenesulfonyl



Scheme 31. CuAAC of CF_3N_3 with alkynes.



Scheme 32. One-pot synthesis of *N*-CF_3 triazoles.

azide (TsN_3) to afford azidotrifluoromethane (CF_3N_3) for the first time. The reaction was performed at −60 °C in DMF with cesium fluoride (CsF, eq 1.2). The CF_3N_3 was isolated by distillation with THF in 70%–80% (Scheme 30) [34].

The reactivity of the solution of trifluoromethyl azide in THF has then been tested in CuAAC with alkynes and a catalytic amount of copper (I) 3-methylsalicylate in THF at room temperature for 18 h. The corresponding *N*-CF_3 triazoles were isolated in good yields with exclusive formation of 1,4-disubstituted triazoles (Scheme 31) [31].

Because of the high volatility of the CF_3N_3 (bp −28.5 °C), the authors attempted the direct one-pot, two-step synthesis of *N*-CF_3 triazoles. After the reaction of CF_3TMS with CsF and TsN_3 at −60 °C in DMF, alkyne, an aqueous solution of $CuSO_4$, and sodium ascorbate were added. These conditions allowed for the access of *N*-CF_3 triazoles in reasonable yields comparable with the two-step procedure, although with a slightly lower regioselectivity (Scheme 32).

5. Conclusion

Over the last decades, the chemistry of the *N*-CF_3 group has been weakly explored and considered. This can be explained by a small number of pathways to these motifs and an incompatibility with functionalized molecules. In the past few years, the setup of the new recent reagents and methodologies has led to simple, safe, and powerful processes for the synthesis of *N*-CF_3 compounds. Furthermore, despite the absence of significant data on the *N*-CF_3 motif, its incorporation in bioactive molecules constitutes a very attractive way in chemical and biomedical research. We strongly believe that fluorine chemistry of the *N*-CF_3 is only at its infancy and will be increasingly explored and used by chemists to foster novel properties, thereby extending their fields of application.

Acknowledgments

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