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Recent advances in the synthesis of trifluoromethyl ethers through the direct *O*-trifluoromethylation of alcohols

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ABSTRACT

In this review, the pivotal achievements and recent advances on direct *O*-trifluoromethylation of alcohols reported up to 2024 are retrospectively considered and their potency for synthesis of useful trifluoromethyl ethers is demonstrated. The reported data are organized according to main types of catalytic systems (*i.e*., metal-catalyzed/mediated, electro-catalyzed, base-mediated, and catalyst-free *O*-trifluoromethylations).

1. Introduction

Organofluorine compounds play a prominent role in various fields, ranging from pharmaceuticals [1-3], agrochemicals [4, 5], to functional materials [6]. Along this line, trifluoromethoxy (OCF_3) group has recently received increasing attention owing to its good metabolic stability and high lipophilic properties [7]. Although, trifluoromethoxy-containing molecules are still underdeveloped, at least five FDA-approved trifluoromethoxy-containing drugs are currently available in the market (Scheme 1) [8], and they are used for the treatment of various types of diseases such as myotrophic sclerosis, tuberculosis, cancer, and high blood pressure. Classically, the synthesis of trifluoromethyl ethers has involved preactivation of hydroxyl group of alcohols through functionalization with carbonyl or thiocarbonyl groups followed by introduction of fluorine [9]. However, many of these approaches have low functional group tolerance due to the use of hydrogen fluoride, Lewis acids, or thermally unstable, reactive trifluoromethylating reagents. In order to over pass these limitations, direct *O*-trifluoromethylation of alcohols has arisen as an efficient synthetic methodology for the preparation of trifluoromethyl ethers (Figure 1), which due to avoiding the needs of pre-functionalization substrates offers an effective approach to minimize the waste generation [10]. Although, several review articles have been appeared related to the synthesis of trifluoromethyl ethers [11-33], to the best of our knowledge, there has not been any no comprehensive overview of the oxidative *O*-trifluoromethylation of alcohols. Therefore, in the present review, we summarize the data available from the literature on the direct *O*-trifluoromethylation of alcohols with special emphasis on the mechanistic aspect of the reactions.

2. Metal-catalyzed/mediated reactions

In 2009, Togni and co-workers informed the first example of metal-mediated direct *O*-

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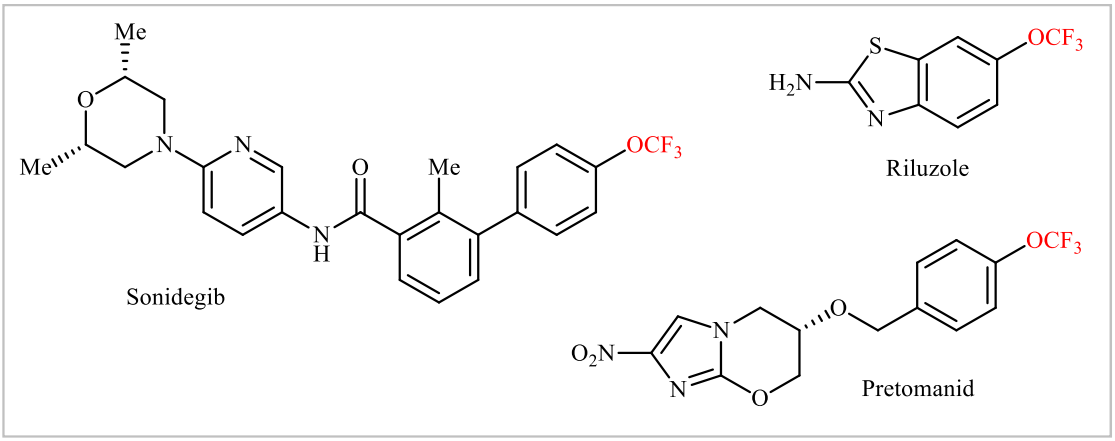
trifluoromethylation of aliphatic alcohols **1** employing Togni reagent II **2** as CF_3 source in the presence of stoichiometric amounts of $Zn(OTf)_2$ as a Lewis acid at room temperature [34].



Scheme 1. Selected examples of OCF_3-containing drugs.

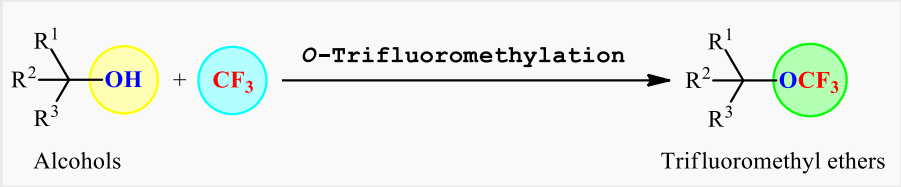
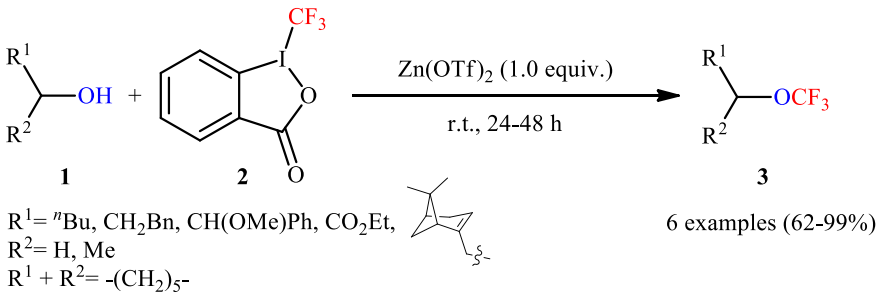


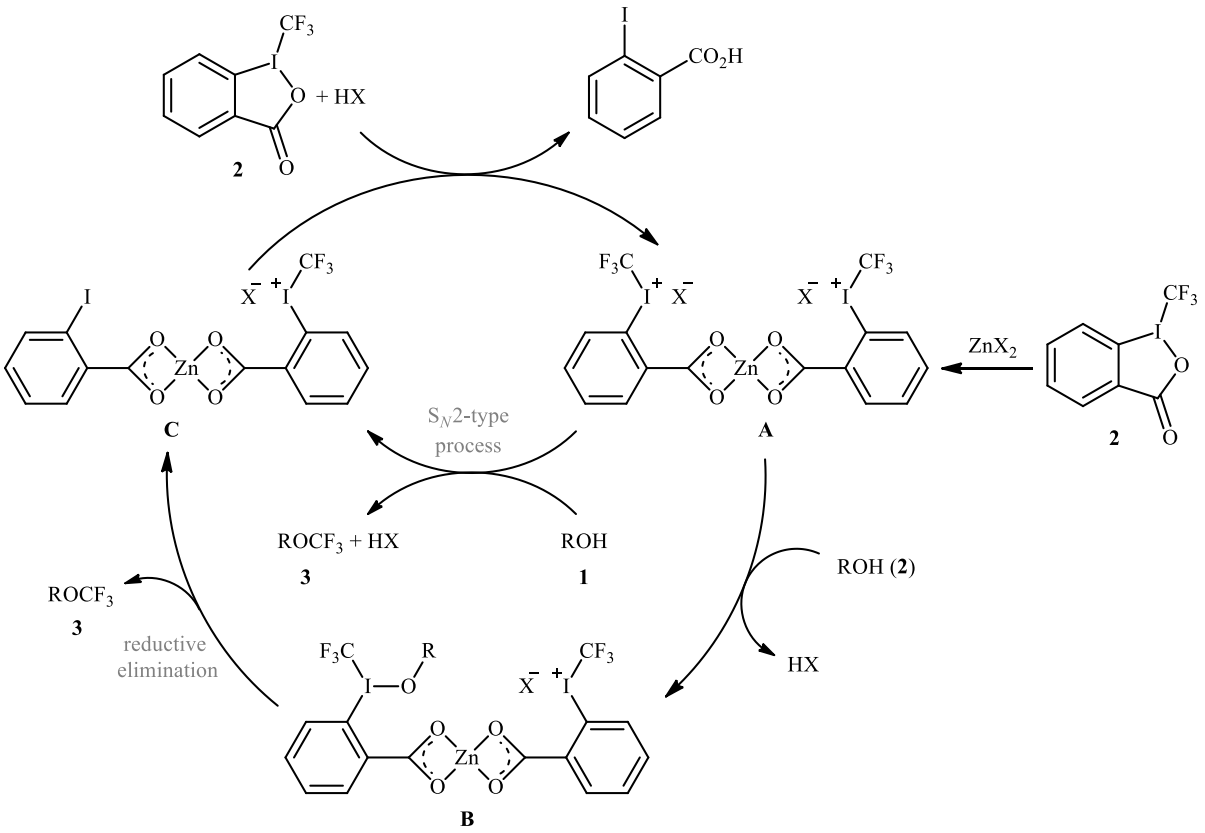
Fig. 1. Direct *O*-trifluoromethylation of alcohols.

In the case of liquid alcohols, no additional reaction solvent was necessary, since the they played a dual role as the solvent and the substrates (Scheme 2). However, for successful *O*- trifluoromethylation of solid alcohols under this condition a proper solvent was required. The results indicated that compared to liquid alcohols, solid alcohols needed longer reaction times and afforded poorer yields. Both primary and secondary alcohols were compatible substrates in this transformation. However, neither tertiary alcohols nor aromatic alcohols could react in this system. The mechanistic cycle proposed by the authors for this transformation is depicted in Scheme 3, and starts with the formation of the zinc dicarboxylato complex **A** by reaction of reagent **2** with the zinc salt. Subsequently, the reaction of this intermediate with alcohol **1** gives the intermediate **B** which undergoes reductive elimination to furnish the observed trifluoromethyl ether product **3** and species **C**. Finally, ligand exchange between species **C** and reagent **2** liberates 2-iodobenzoate and complete the catalytic cycle. In another possibility, trifluoromethyl ether **3** might be formed through the nucleophilic attack of alcohol **1** onto the complex **A** *via* an S_N2-type process.



Scheme 2. Togni's synthesis of trifluoromethyl ethers **3**.

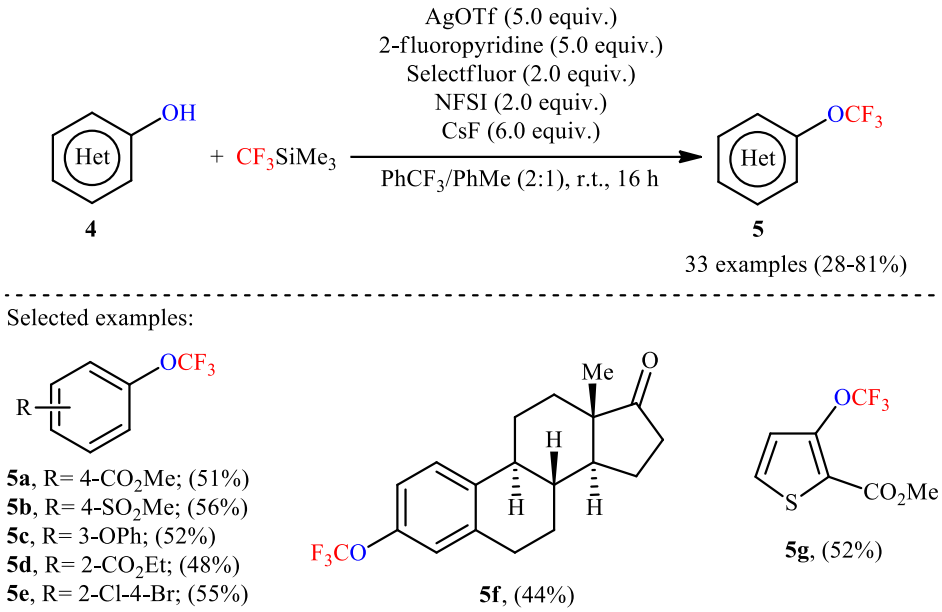
Six years later, Qing and collaborates developed an efficient protocol for the synthesis of OCF_3-substituted (hetero)arenes **5** *via* silver-mediated oxidative trifluoromethylation of corresponding (hetero)aromatic



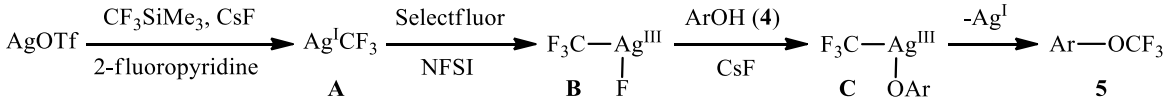
Scheme 3. Mechanistic proposal for the formation of trifluoromethyl ethers **3**.

alcohols **4** by using trifluoromethyltrimethylsilane (CF_3SiMe_3) as a cheap and readily available trifluoromethylating agent [35]. The best conversion efficiency was obtained for the reactions containing a combination of AgOTf, 2-fluoropyridine, Selectfluor, *N*-fluorobenzenesulfonimide (NFSI), and CsF in PhMe/$PhCF_3$ (1:2) at room temperature. In control experiments, no products were detected in the absence of the silver salt, ligand, or oxidant, whereas a significant decrease in yield was observed when either Selectfluor or NFSI was used as the only exogenous oxidant. Replacing AgOTf with other silver salts such as $AgNO_3$, $AgSbF_6$, and Ag_2CO_3 led to much lower yields or even no desired product at all. Under the optimized conditions, various heteroaromatic alcohols and phenol substrates (either electron-rich or electron-poor derivatives) were tolerated well and provided the expected (hetero)aryl trifluoromethyl ethers **5** in fair to high yields (Scheme 4). In accord to the suggested mechanism, this *O*-trifluoromethylation reaction proceeds through the following key steps (Scheme 5): (i) initial formation of $Ag^{I}CF_3$ species **A** *via* the reaction of $Ag^{I}OTf$ with CF_3SiMe_3 in the presence of CsF; (ii) oxidative addition of species **A** with Selectfluor and/or NFSI to give [$Ag^{III}(CF_3)(F)$] complex **B**; (iii) ligand exchange of **B** with phenoxide **4** to afford the key intermediate [$Ag^{III}(CF_3)(OAr)$] **C**; and (iv) reductive elimination of intermediate **C** to produce the desired trifluoromethyl ether **5**. Subsequently, these authors successfully extended their methodology to *O*-trifluoromethylation of aliphatic alcohols (primary, secondary, tertiary) by performing the process in the presence of AgOTf/2-fluoropyridine/KF/selectfluor combination in EtOAc [36].

In a subsequent extension of the substrate scope of the methodology [37], it was shown that α-trifluoromethyl (aryl)methanols **6** could be treated with CF_3SiMe_3 under the abovementioned reaction conditions to give corresponding (2,2,2-trifluoro-1-(trifluoromethoxy)ethyl)arenes **7** in modest to high yields (Scheme 6).

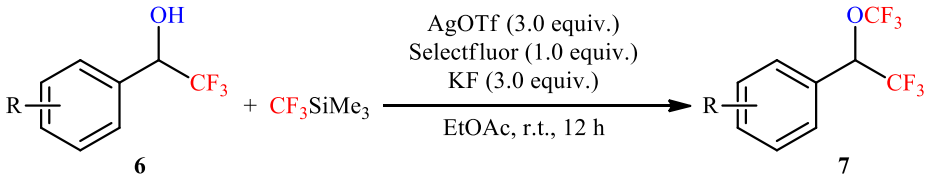


Scheme 4. Qing's synthesis of (hetero)aryl trifluoromethyl ethers **5**.



Scheme 5. Mechanism proposed to explain the formation of(hetero)aryl trifluoromethyl ethers **2**.

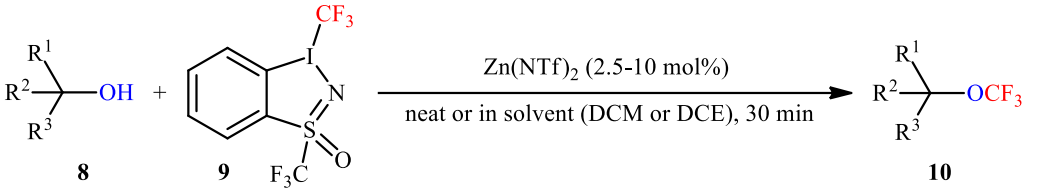
The reaction was also amenable to α-trifluoromethyl allyl alcohols, delivering the $CF_3(OCF_3)CH$-substituted allylic products in moderate yields (6 examples, 35-70%). Moreover, the protocol was extrapolated to other α-fluoroalkyl alcohols such as 2,2-difluoro-1-(naphthalen-2-yl)ethanol, 3,3,3-trifluoro-1-(naphthalen-2-yl)propan-1-ol, and 2,2,3,3,3-pentafluoro-1-(naphthalen-2-yl)propan-1-ol.



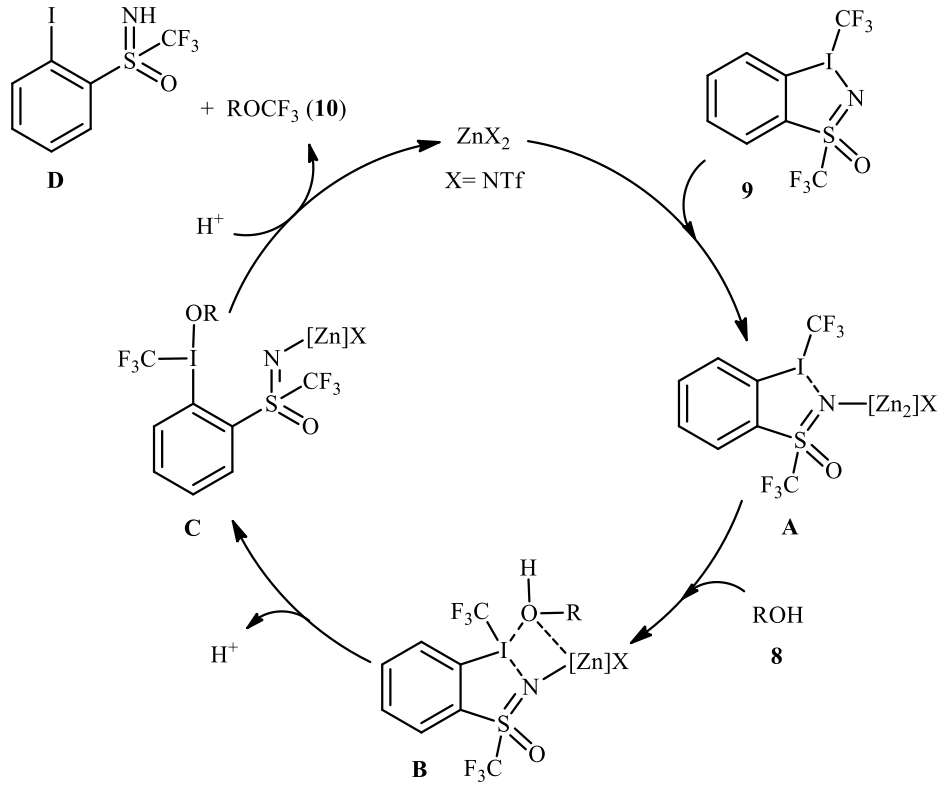
R= H, 4-Ph, 4-OBn, 4-OPh, 4-Cl, 4-Br, 4-CO_2Me, 4-CN, 3-Ph, 2-Ph, 3,4-$(Me)_2$, 3,4-OCH_2CH_2O-, 3,4-(CH=CH-CBr=CH)-, 2,3-$(CH=CH)_2$-, 3,4-$(CH=CH)_2$-

Scheme 6. Qing's synthesis of(2,2,2-trifluoro-1-(trifluoromethoxy)ethyl)arenes **7**.

Shortly afterwards, Magnier and Togni along with their co-workers described a Zn-catalyzed direct O-H oxidative trifluoromethylation of alkanoles **8** (primary, secondary, tertiary) employing hypervalent iodosulfoximine reagent **9** as the trifluoromethyl source [38]. Using only 1.0 equivalent of reagent **9** and 2.5–10 mol % of $Zn(NTf)_2$, a panel of 33 trifluoromethyl ethers **10** were synthesized from the corresponding alkanoles **8** in reasonable yields within minutes (Scheme 7). For all substrates which are oils no solvent was used and the reaction was conducted at room temperature. However, in cases where the alcohol was a solid the reaction was carried out at the melting point of the compound or in solvent (DCM or DCE). According to the authors proposed mechanism (Scheme 8), this C-O bond-forming process occurred *via* the coordination of the alcohol substrate to the hypervalent iodine species and subsequent reductive elimination. Following these works, Qing's research group unraveled the first oxidative chloro- and bromodifluoromethylation of (hetero)aromatic alcohols employing the merge of Me_3SiCF_2X with CuX (X = Cl or Br) in the presence of Selectfluor under mild reaction conditions [39].



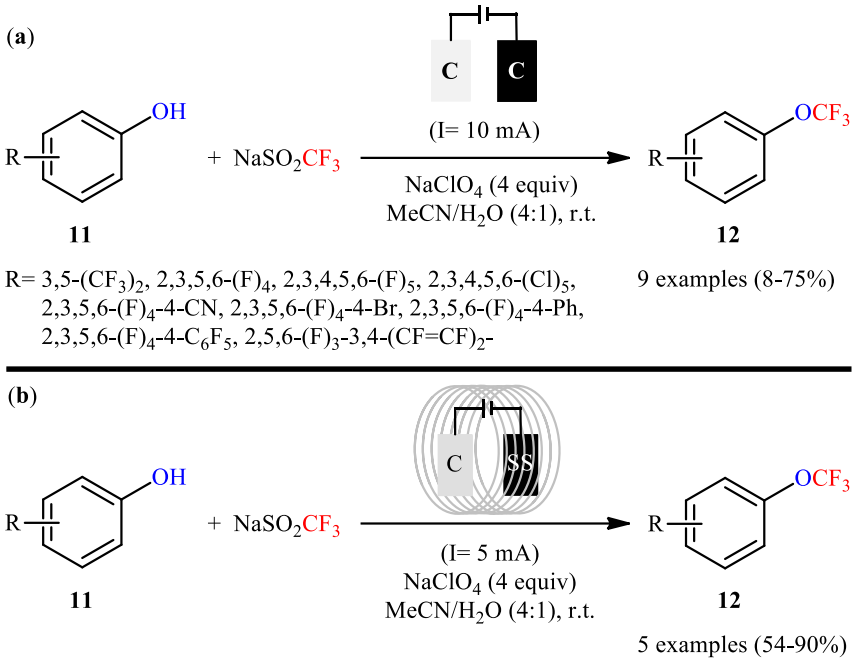
Scheme 7. Magnier-Togni's synthesis of trifluoromethyl ethers **10**.



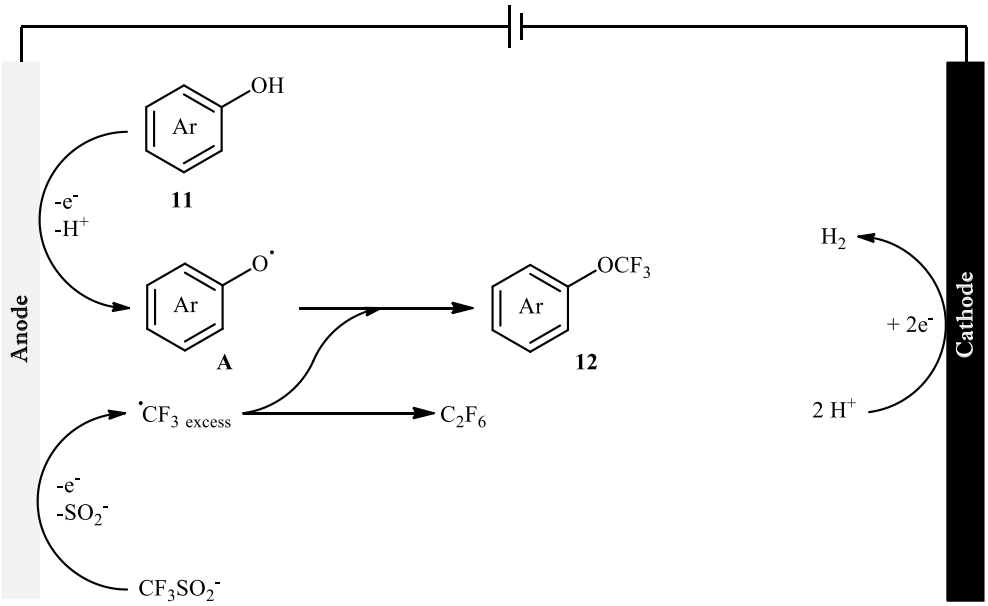
Scheme 8. Mechanistic proposal for the formation of trifluoromethyl ethers **10**.

3. Electro-catalyzed reactions

In 2021, Terfort and co-workers reported an environmentally friendly electrochemical protocol for direct *O*-trifluoromethylation of electron-deficient phenols **11** which offers a simple, mild and efficient way to electron-deficient aryl trifluoromethyl ether derivatives **12** [40]. The optimal system was identified using the Langlois reagent (CF_3SO_2Na) as a stable and inexpensive trifluoromethylating agent and $NaClO_4$ as the electrolyte with an undivided cell equipped with graphite electrodes under constant-current electrolysis at 10 mA in anhydrous MeCN/H_2O (4:1) mixed solvents at room temperature. Under the optimized conditions, nine aryl trifluoromethyl ethers **12** were obtained in low to good yields from the respective halophenols **11** (Scheme 9a). The radical trapping experiments with (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) and 2,6-di-tert-butyl-4-methylphenol (BHT) pointed toward a radical reaction mechanism. Based on the experimental results and the literature, the authors proposed a mechanism for this transformation, where phenoxyl radical **A** and trifluoromethyl radical ($^{\cdot}CF_3$) are first generated simultaneously by anodic oxidation of phenol **11** and Langlois reagent, respectively. These radicals then recombine to yield the observed trifluoromethyl ethers **12** (Scheme 10). Subsequently, the same authors significantly improved the efficiency of this reaction by combining electrochemical synthesis with flow technology (Scheme 9b) [41].



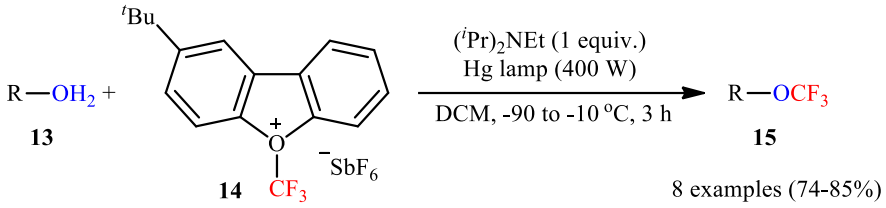
Scheme 9. (a) Electrochemical oxidative *O*-trifluoromethylation **of electron-deficient phenols 11** with Langlois reagent; (b) Electrochemical oxidative *O*-trifluoromethylation **of phenols 11** with Langlois reagent in flow cells.



Scheme 10. Plausible mechanism for reaction in Scheme 9.

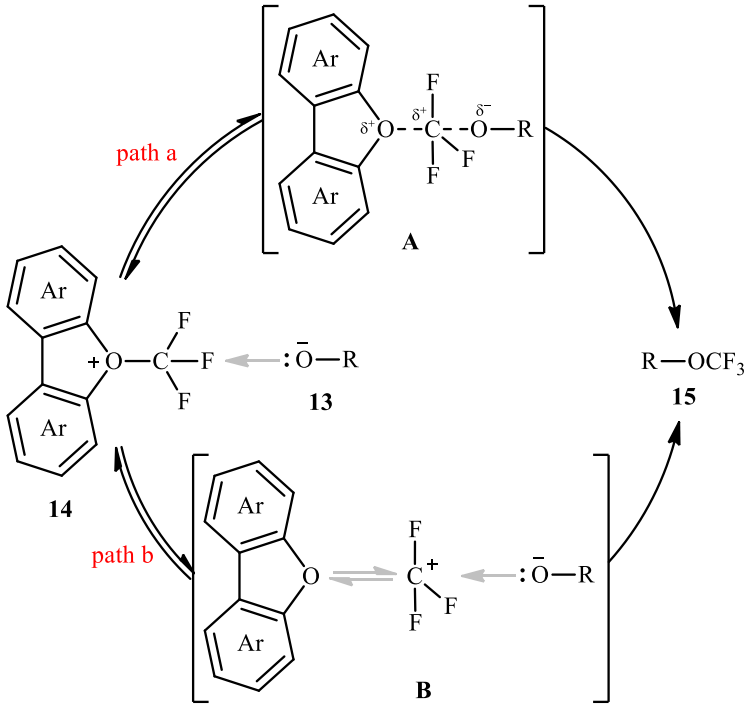
4. Base-mediated reactions

In 2007, Umemoto and co-workers reported that 1-alkanols and phenol derivatives **13** can undergo selective *O*-trifluoromethylation with an electrophilic trifluoromethylating reagent, *O*-(trifluoromethyl)-dibenzofuranium salt **14** in the presence of an alkyl amine base, (^{i}Pr)$_2$NEt, to afford corresponding trifluoromethyl ethers **15** in good yields, ranging from 74% to 85% (Scheme 11) [42]. It should be mentioned that the reagent **14** needs to be activated prior to use by photochemical decomposition at −100 to −90 °C. Notably, a similar reaction conditions were also applied by this innovative research group for *N*-trifluoromethylation of various aromatic and aliphatic amines. According to the authors, this reaction plausibly proceeds through the formation of a five-coordinated carbon transition state **A** (Scheme 12, path a), or by formation of a definite and transient CF_3^+ ion in equilibrium with **14**, as shown in **B** (Scheme 12, path b).



R= $^{n}C_{10}H_{21}$, Ph, 4-Me-C_6H_4, 4-OMe-C_6H_4, 4-Br-C_6H_4, 4-COMe-C_6H_4, 4-CN-C_6H_4, 4-NO_2-C_6H_4

Scheme 11. Umemoto's synthesis of trifluoromethyl ethers **15**.

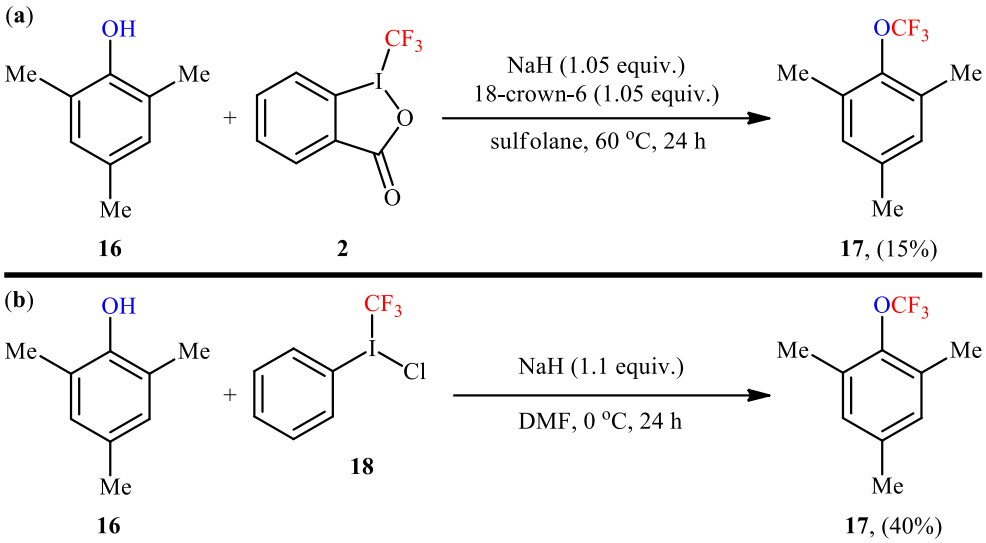


Scheme 12. The possible reaction mechanism for the formation trifluoromethyl ethers **15**.

Shortly afterward, Togni and co-workers investigated the *O*-trifluoromethylation of 2,4,6-trimethylphenol **16** with Togni reagent II **2** under basic conditions [43]. NaH and 18-crown-6 appeared to be the most effective base and additive, respectively. Compared to other solvents (sulfolane, DMSO, DMF, DMF-d_7), sulfolane was the best choice for the conversion. Unfortunately, the expected *O*-trifluoromethylated product **17** was obtained in low yield along with various carbon trifluoromethylation products (Scheme 13a). A decade later, Wang's research group improved the efficiency of this reaction in the terms of the yield and reaction time by replacing Togni reagent II **2** with chloro(phenyl)trifluoromethyliodane **18** [44]. The reaction was performed in DMF at 0 °C under additive-free conditions and provided the expected product **17** in moderate yield of 40% (Scheme 13b).

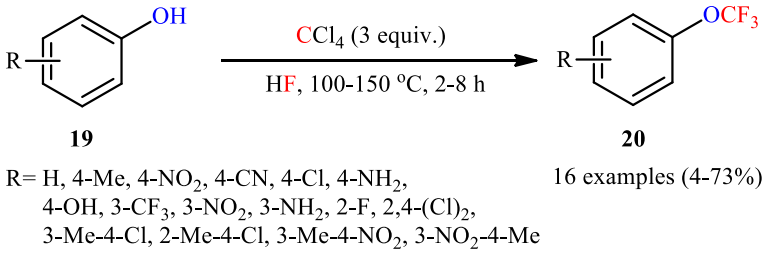
5. Catalyst-free reactions

Drawing inspiration from the pioneering work by Yagupolskii and co-workers on the synthesis of aryl trifluoromethyl ethers through a two-step procedure by PCl_5-catalyzed trichloromethylation of corresponding phenols with Cl_2 followed by $SbCl_5$–catalyzed chlorine-fluorine exchange using SbF_5 under elevated conditions [45], In 1979, Feiring and co-workers disclosed an interesting one-pot catalyst-free protocol for the preparation of trifluoromethyl ethers from the respective alcohols under additive-free conditions [46]. They showed that treatment of phenol derivatives **19** with over-stoichiometric amounts of CCl_4 in HF at 100-150 °C resulted in the corresponding aryl trifluoromethyl ethers **20** within 2-8 h (Scheme 14). The authors speculated that this reaction most likely proceeds *via* a radical pathway as depicted in Scheme 15.

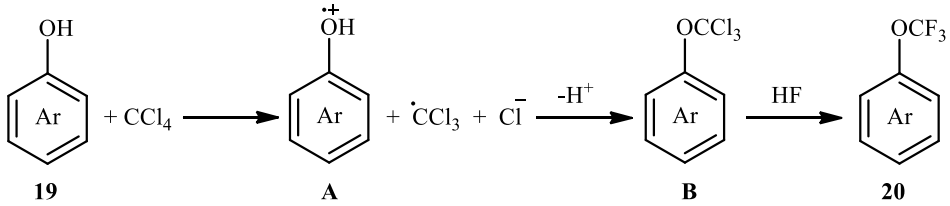


Scheme 13. (a) Togni's synthesis of 1,3,5-trimethyl-2-(trifluoromethoxy)benzene **17**; (b) Wang's synthesis of 1,3,5-trimethyl-2-(trifluoromethoxy)benzene **17**.

Unfortunately, high toxicity of CCl_4, elevated temperature, and low compatibility with electron-rich substrates limited the utility of this method. Although several other chlorine-fluorine exchange methods have been developed for the synthesis of trifluoromethyl ethers from the corresponding alcohols, they all suffer from various inherent drawbacks [47].

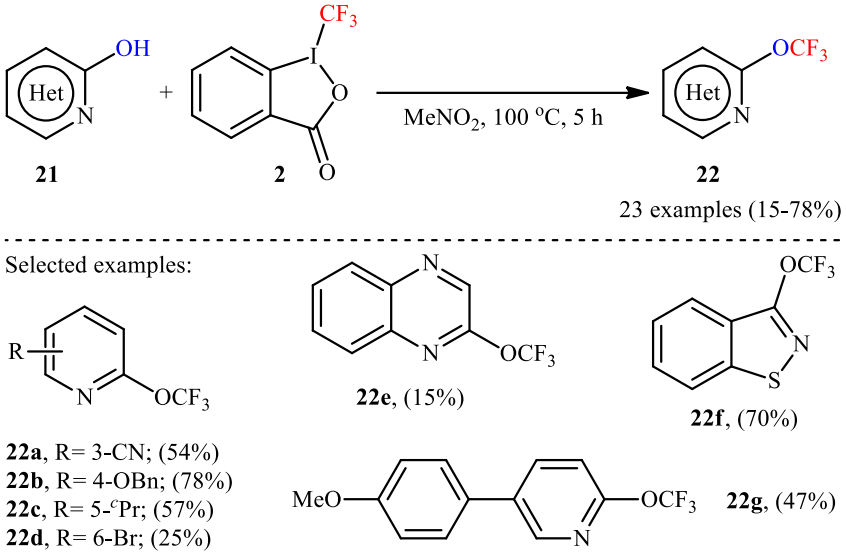


Scheme 14. Feiring's synthesis of aryl trifluoromethyl ethers **20**.



Scheme 15. Proposed pathway of aryl trifluoromethyl ethers **20** formation.

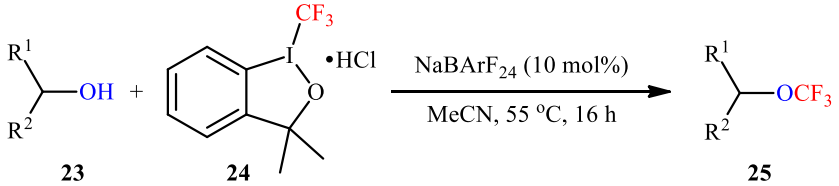
In 2016, Wu's research group synthesized a library of 23 heteroaryl trifluoromethyl ethers **22** in yield ranging from 15% to 78% by simple heating of the respective *N*-heteroaromatic phenols **21** with Togni's reagent II in $MeNO_2$ under air atmosphere and catalyst-/additive-free conditions (Scheme 16) [48]. The reaction could also be easily scaled up to the multigram scale as exemplified by the formation of 5-bromo-2-(trifluoromethoxy)pyridine on a 84-g scale (55%). It was suggested that the acidic phenolic proton is crucial for the activation of the Togni reagent, which reacts further through a single electron transfer (SET) mechanism.



Scheme 16. Wu's synthesis of heteroaryl trifluoromethyl ethers **22**.

6. Miscellaneous reactions

In 2016, the group of Toste accomplished direct *O*-trifluoromethylation of alkanols **23** through the employment of commercially available 3,3-dimethyl-1-(trifluoromethyl)-1,2-benziodoxole **24** as CF_3 source in MeCN as the solvent, with the intervention of sodium tetrakis(3,5-trifluoromethyl)phenylborate ($NaBArF_{24}$) as catalyst in the absence of any additive (Scheme 17) [49]. Notably, various primary and secondary aliphatic alcohols as well as benzyl alcohols and α-hydroxy esters were applicable to this trifluoromethylation reaction. However, aryl and tertiary alcohols were incompatible in this reaction. Notably, a similar principle was also successfully applied to the *N*- and *S*-trifluoromethylation of azoles and thiols, respectively. Furthermore, the reaction was successfully extended to *O*-trifluoromethylation of phosphates and sulfonates.

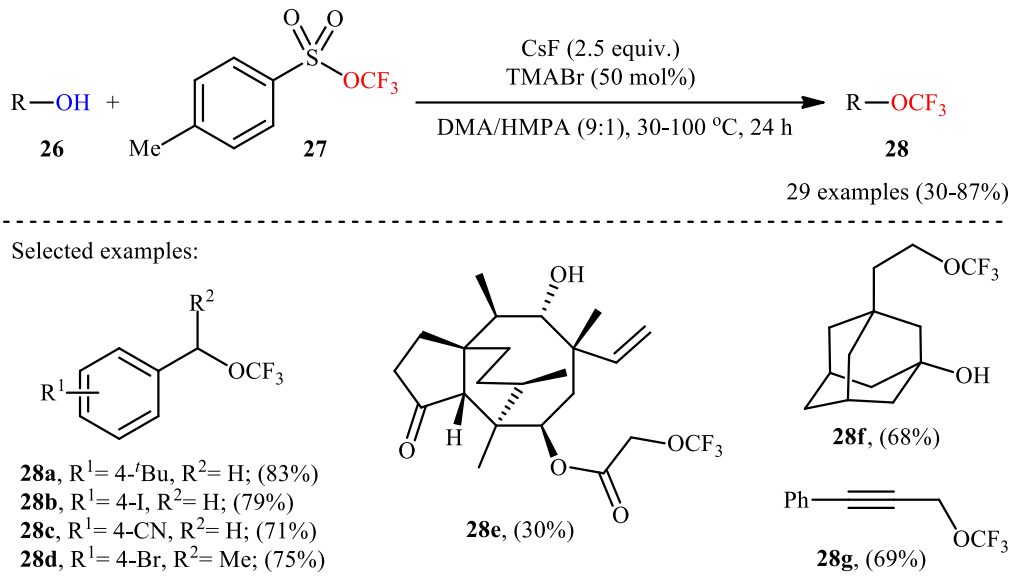


R^1= CO_2Et, 4-I-C_6H_4, 4-NO_2-C_6H_4, CH_2Bn, 4-NO_2-Bn, CH_2-N-phth, 2-naphthyl, 1-adamantyl
R^2= H, Me
$R^1 + R^2$= -$(CH_2)_5$-

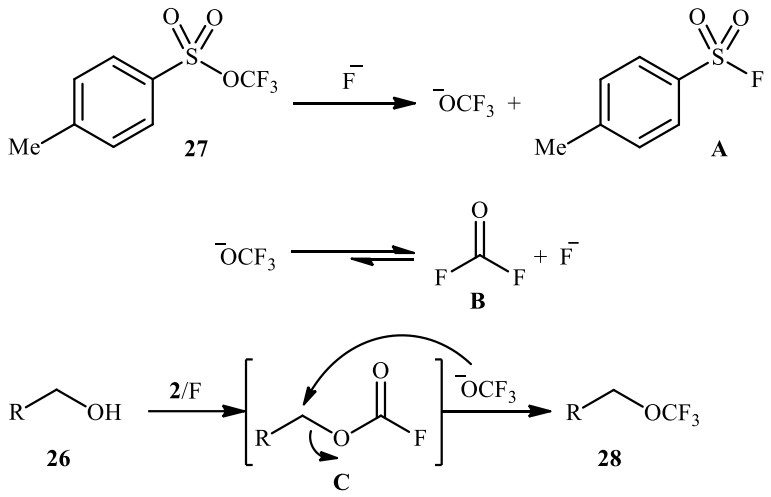
6 examples (18-58%)

Scheme 17. Toste's synthesis of trifluoromethyl ethers **25**.

Two years later, Tang and co-workers developed an interesting dehydroxytrifluoromethoxylation of alcohols **26** using trifluoromethyl 4-methylbenzenesulfonate **27** as OCF_3 source employing a combination of CsF and tetramethylammonium bromide (TMABr) as the mix activator [50]. Among several solvents tested, the binary solvent DMA/HMPA (9:1) was found to be the best medium for the reaction. In this reaction, TMABr presumably plays a dual role: (i) stabilizing the trifluoromethoxide anion ($^-OCF_3$); and (ii) improving the solubility of CsF. Under the optimized conditions, various primary, secondary, and tertiary alkanols **26** were tolerated well and provided the expected trifluoromethyl ethers **28** in modest to high yields (Scheme 18). Noteworthy, this procedure was applied to the C–OH trifluoromethylation of complex small molecules such as pleuromutilin **28e**. The mechanism depicted in Scheme 19 was proposed by the authors for thistrifluoromethoxylation reaction. Later, several research groups investigated the scope and limitation of this transformation [11]. Since these reactions are beyond the scope of the current review, we will limit ourselves to the example presented above.



Scheme 18. Tang's synthesis of trifluoromethyl ethers **28**.



Scheme 19. Presumable pathway of trifluoromethyl ethers **28** formation.

7. Conclusion

In summary, significant advances have been achieved in the field of oxidative *O*-trifluoromethylation reactions. As shown by the examples in this review, this page of trifluoromethyl ether synthesis exhibits a number of advantages over the traditional protocols including the avoidance of pre-activation/pre-functionalization of starting materials and using toxic reagents. Thanks to the mild conditions employed, majority of reactions covered in this review tolerated a wide range of sensitive functional groups. It is believed that this synthetic strategy will play an important role in synthesis of pharmaceutically important trifluoromethyl ether derivatives. Although great progress has been achieved, this field is still in its infancy, so a continuous investment on the development of more efficient trifluoromethylating agents and catalytic systems is needed to reach maturity.

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