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Synthesis of Heteroaromatic Trifluoromethyl Ethers with Trifluoromethyl Triflate as the Source of the Trifluoromethoxy Group

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A series of N-heterocycles have been transformed to the corresponding trifluoromethyl (perfluoroalkyl) ethers by reaction of the corresponding N-oxides with trifluoromethyl triflate. Trifluoromethyl triflate, which has generally been used as a precursor to $[OCF_3]^-$, is used here as a bifunctional reagent to render the heteroarene more electrophilic and to deliver the trifluoromethoxy group. This reagent was easily prepared on large scale (>100 grams) and is stable in either pure form or as a stock solution. Applications and limitations of this method are reported.

Trifluoromethyl aryl ethers ($ArOCF_3$) have unique properties,[1] but are difficult to prepare. Thus, reactions that form these molecules have become targets for the development of synthetic methods. The oxygen lone pairs on $ArOCF_3$ overlap with antibonding orbitals of the C-F bond, leading to a preferential conformation in which the C_{Ar}–O–CF_3 plane is orthogonal to the aromatic plane.[2] Due to the absence of n-π_{Ar}^* conjugation, the OCF_3 group on aromatic rings is considered electron-withdrawing, whereas the similar OMe group is considered electron-donating.[3] In addition, through-space coulombic repulsion between the fluorine electron pairs on the OCF_3 group and the π-electrons of the arene lead to a unique electron distribution of the corresponding aromatic ring, as evidenced by the para-directing effect of the OCF_3 group in aromatic electrophilic substitution.[4] Finally, OCF_3 is among the most lipophilic functional groups.[5] These features have recently been appreciated by researchers in medicinal, agricultural and material sciences.

However, the synthesis of $ArOCF_3$ groups is challenging. Several strategies for the preparation of trifluoromethyl aryl ethers have been published,[6-8] but only a few methods to prepare biologically important *N*-heteroaromatic trifluoromethyl ethers are known.[8g, 9] The challenges facing the preparation of these structures stem from the properties of the $^-OCF_3$ group as reactive unit. Particularly limiting is the decomposition of the trifluoromethoxy anion at elevated temperatures.[10]

Several reagents that generate nucleophilic trifluoromethoxy groups have been reported since 1948. These reagents include trifluoromethyl-hypofluorite FTM,[11] $S(CF_3)_2(OCF_3)_2$,[12] and $SO(CF_3)_2(OCF_3)_2$.[13] Because these reagents are toxic, difficult to produce and labile (Figure 1a-c), few trifluoromethoxylation reactions of these sources of nucleophilic OCF_3 have been reported.[14] In contrast, DNTFB[7e], TFMS[7n], TFMT[15] and TFBz[16] shown in Figure 1 are stable and have been used as precursors to $[OCF_3]^-$ as transient species (figure 1d-g). DNTFB, TFMS and TFBz have been used as a source of nucleophilic OCF_3 by slow release of trifluoromethoxide, but relatively reactive substrates are required.

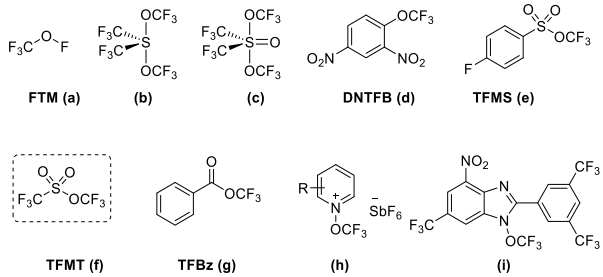

Figure 1: Trifluoromethoxylation reagents.

More recently, reagents that generate electrophilic OCF_3 or a radical of OCF_3 have been reported. A pyridinium *N*-OCF_3 salt has been shown to serve as a source of OCF_3, but the synthesis of this reagent is challenging, and the reactions of electron-rich arenes with this reagent occur in low to moderate yields (figure 1g).[17] An N-OCF_3 reagent was reported by Liu and Ngai as a source of OCF_3 radical for the trifluoromethoxylation of arenes and heteroarenes under photocatalytic conditions (figure 1h). Such radical additions occur to heteroarenes containing electron-withdrawing groups.[9e] Only two recent papers describe the synthesis of $HetArOCF_3$ structures, one by rearrangement of intermediates containing an N-OCF_3 bond and the second by formation of the O-CF_3 bond. [9c-9d] Thus, additional approaches

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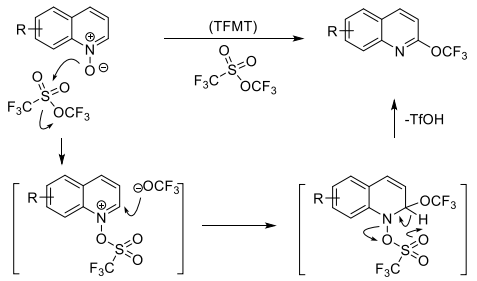
to prepare heteroaryl trifluoromethyl ethers are needed to provide a suite of methods that enable trifluoromethoxylation of a wide range of heteroarene structures.

We envisioned that trifluoromethyl triflate (TFMT) could serve as a source of the OCF_3 anion, while activating the electrophile for attack by this anion. To follow this strategy for the trifluoromethoxylation of basic nitrogen heterocycles, we considered that the *N*-oxide of such a heteroarene (Scheme 1) could react with TFMT to form the anion [$^-OCF_3$] and an *N*-triflate cation, which would be more electrophilic than the starting *N*-oxide. Nucleophilic addition of [$^-OCF_3$] to this cation, followed by elimination of triflic acid would afford the desired trifluoromethyl ether.

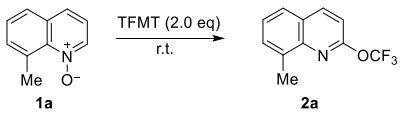


Scheme 1. Trifluoromethoxylation of heterocyclic N-Oxide.

TFMT was initially prepared in 1965 and has generally been used to prepare other trifluoromethoxide reagents. Like $S(CF_3)_2(OCF_3)_2$ and $SO(CF_3)_2(OCF_3)_2$, TFMT is a bifunctional reagent. TFMT can simultaneously generate the OCF_3 nucleophile and transform an oxygen atom into a triflate leaving group. Although the volatility (b.p. 19 °C) has impeded its application to small scale reactions, the stability and accessibility on large scale attracted our attention. It is easily synthesized in over 100 g scale from triflic anhydride,[18] and we found that a stock solution (0.5 M) in DME can be generated easily and handled, even at room temperature, for small scale reactions (e.g. 0.1 mmol). The reactivity of these solutions was maintained over six months when the solution was stored in the freezer.

To test the feasibility of TFMT as a reagent for trifluoromethoxylation of heteroarenes with basic nitrogens, we conducted reactions of 8-methyl quinoline *N*-oxide **1a** with TFMT (Table 1). The reactions were conducted in a series of solvents (entries 1-8). Product **2a** formed only in ethereal solvents, as determined by ^{19}F NMR spectroscopy, giving 36% of the trifluoromethyl heteroaryl ether in DME (entry 8). Because the TfOH byproduct could inhibit the formation of the *N*-OTf species by protonation of the heteroaryl *N*-oxide, we tested reactions with bases, such as proton sponge and DABCO, in DME. However, neither reaction gave any product (entries 9 and 10). To mitigate the decomposition of $^-OCF_3$ to form F^- and carbonyl fluoride and to generate higher concentrations of $^-OCF_3$, we added AgF to favor the $^-OCF_3$ component of such an equilibrium and to increase the concentration of $^-OCF_3$ by reaction of fluoride with TFMT. However, this reaction also gave no ether product (entry 11). Even the reactions with added $AgOCF_3$ gave little product (entry 12).

Table 1. Evaluation of reaction parameters for the trifluoromethyl etherification of 8-methylquinoline N-oxide.[a]



1a 2a

Entry	Solvent	Yield[b]	Entry	Additive	Yield[b]
1	EtOAc	<5%	9[c]	Proton sponge	<5%
2	Acetone	<5%	10[c]	DABCO	<5%
3	NMP	<5%	11[c]	AgF	<5%
4	THF	13%	12[c]	$AgOCF_3$	<5%
5	*t*BuOMe	18%	13[d]	Propylene oxide	40%
6	*i*Pr_2O	15%	14[d]	Tetramethyloxirane	48%
7	Dioxane	29%	15[d]	*t*BuCOMe	47%
8	DME	36%	16[d,e]	*t*BuCOMe	42%[f]

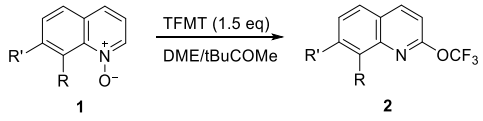
[a] Substrate (0.1 mmol), TFMT (0.5 M, 0.4 mL) in overall 2 mL solvent. [b] yield determined by ^{19}F NMR using $PhCF_3$ as internal standard. [c] DME as solvent, additive (2.0 equiv). [d] DME as solvent, additive (0.1 mL). [e] 1 mmol substrate (0.05 M), TFMT (1.5 equiv). [f] Isolated yield.

Instead, experiments to trap the triflic acid with an epoxide led to conditions that gave higher yields of the trifluoromethyl heteroaryl ether. Reactions with propylene oxide and tetramethyloxirane gave the trifluoromethoxy heteroarene **2a** in 40% and 48% yield, respectively (entries 13 and 14). Because rearrangement of tetramethyloxirane in the presence of strong acid gives *t*BuC(O)Me, we also ran reactions with added *t*BuC(O)Me; the yield of the reaction with added *t*BuC(O)Me was similar to that of reactions with added epoxide (47%, entry 15). After some additional experimentation, we found that the reaction of quinoline oxide on a 1 mmol scale with *t*Bu(O)Me as additive with just 1.5 equiv of TFMT gave ether **2a** in 42% isolated yield (Entry 16). Although the yield is modest, these reactions enable the isolation of a class of substituted heterocycle that has been reported to be prepared in only a few methods.

Under these conditions for the preparation of 8-methyl 2-quinolyl trifluoromethyl ether, a series of heteroaryl *N*-oxides (0.05 M) in DME:*t*BuC(O)Me (20:1) were treated with TFMT (1.5 equiv) at room temperature (Table 2). Our results showed that a substituent at the 8-position is needed for the reaction to occur. Quinoline *N*-oxide, a close analogue of our model substrate **1a**, gave byproducts and less than 5% yield of the ether. The substrate with a more sterically demanding isopropyl group formed the ether product **2b** in 57% isolated yield, that containing a more electron-donating methoxy group gave ether **2c** in 52% isolated yield, and those containing more electron-withdrawing halides gave **2d**-**2g** in yields ranging from 31% to 66%. The disubstituted substrates **1h** and **1i** also reacted to give ethers **2h** and **2i** in 49% and 53% isolated yields, respectively. The origin of the effect of the 8-substituent is not clear, but the

halide in product **2d** can be removed to give the unsubstituted product 2-(trifluoromethoxyl)quinoline. For example, treatment of **2d** with BuLi and then quenched water gave the unsubstituted trifluoromethyl quinolinyl ether **2d'** in 86% yield.

Table 2. Scope of the reaction of quinoline *N*-oxides.[a]



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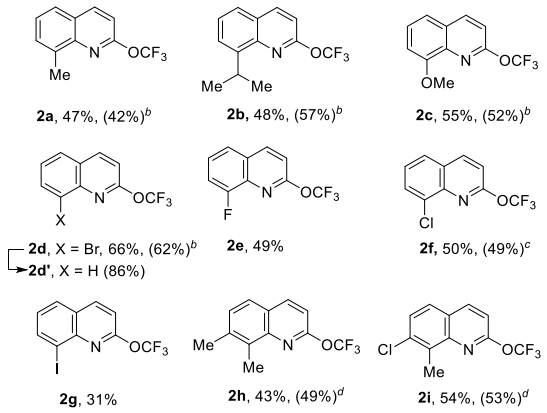
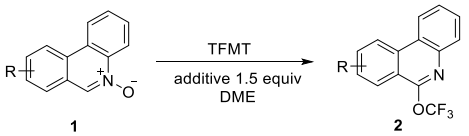


[a]Substrate (0.05 M), and TFMT (1.5 equiv) in DME and *t*BuCOMe (20:1). ^{19}F NMR yield using $PhCF_3$ as internal standard. Isolated yield of 1 mmol scale was shown in the parenthesis. [b]1.0 mmol substrates was used. [c]0.46 mmol substrates was used. [d]0.5 mmol substrates was used.

Table 3. Scope of the reaction of phenanthridine *N*-oxides.[a]



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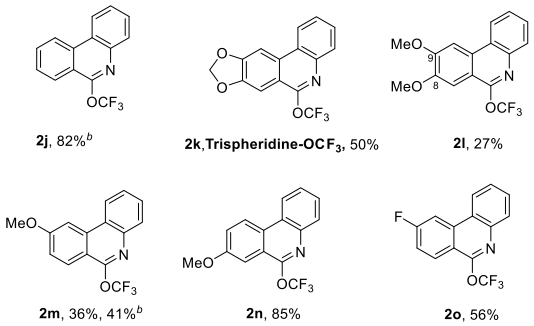

[a]Substrate (0.01 M), 2,6-dichloropyridine (1.5 equiv) and TFMT (1.5 equiv) in DME. Isolated yields were shown. [b]1 mmol scale.

The reaction also occurred between TFMT and phenanthridine *N*-oxides under slightly modified conditions (see SI for details) to form a class of trifluoromethyl ether not reported previously. As shown in table 3, phenanthridine *N*-oxide could gave 82% yield ether product **2j**. The *N*-oxide of the natural product trispheridine (**1k**) was transformed to the corresponding trifluomethyl ether in 50% yield.[19] The methoxy and dimethoxy phenanthridine *N*-oxides **1l-1n** gave the trifluoromethyl ether products **2l**-**2n** in 27%, 41%, and 85% yields respectively. Finally, the 8-fluorophenanthridine gave **2o** in 56% yield.

Considering that the 8-substituent dramatically influenced the outcome of the reactions of quinoline *N*-oxides, we tested if a similar effect of groups in the analogous position of tricyclic systems would be observed (Figure 2). Indeed, the reaction of phenanthridine *N*-oxides, benzo[h]quinoline *N*-oxide gave trifluoromethyl ether product **2p** in 21% NMR yield. In addition, the reaction of benzo[f]quinoline *N*-oxides (**1q**) with an iodine substituent at the 5-position, which is analogous to the 8-position of the quinoline *N*-oxide, gave the trifluoromethyl ether product, albeit in a modest 19% yield by NMR spectroscopy, but compound **1o** lacking the iodide gave no product (<5% NMR). Similar phenomena were observed from reactions of quinolone-type substrates. 6-Methoxy quinoline N-oxide lacking an 8-substituent **1s** did not afford the trifluoromethyl ether product, while the analogue **1t** containing an 8-bromo substituent formed trifluoromethyl **2t** in 21% yield. Although the yields of **2r** and **2t** were modest, the reactions gave sufficient material to isolate the unusual heteroaryl trifluoromethyl ether in pure form and provide a method to access new structures for discovery applications.

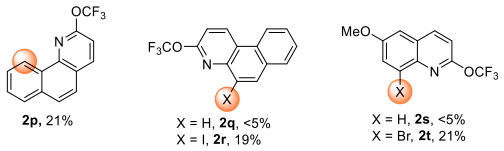

Figure 2. Influence of peri substituents on the reactions of N-oxides.

To assess the scope of our method for the introduction of homologs of the OCF_3 group, we prepared the two analogues of TFMT, $C_2F_5SO_3C_2F_5$ and $C_4F_9SO_3C_4F_9$, and tested their ability to form heteroaryl trifluoromethyl ethers by the developed process. Both reagents were synthesized and applied to the reaction of 8-methyl-quinoline and penanthridine *N*-oxides (Figure 3).[20] Indeed, the corresponding perfluoroalkyl ethers were isolated in yields that were comparable to those obtained with TFMT.

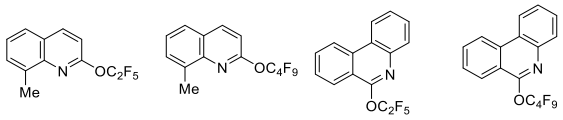

Figure 3. Synthesis of perfluoroalkyl ethers, isolated yields were shown.

In summary, we developed a new synthesis of unusual *N*-heterocyclic trifluoromethyl ethers by exploiting the dual ability of the fluorine-containing reagent TFMT. It has been known for many years but has been used only as a source of $[OCF_3]^-$. This reagent is commercially available and stable, was synthesized in our lab on over 100 g scale. A series of *N*-oxides of 8-substituted quinolines, benzoquinolines and penanthridines gave the corresponding trifluoromethyl ethers under mild conditions. Four additional perfluoroalkyl ethers were synthesized using higher homologs of TFMT, providing a valuable tool for preparing heteroaryl perfluoroalkyl ethers with varying steric properties and

lipophilicity. This bifunctional reagent should find applications in additional dehydrative trifluoromethoxylation reactions, and such processes will be the subject of future studies.

Conflicts of interest

There are no conflicts to declare

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