

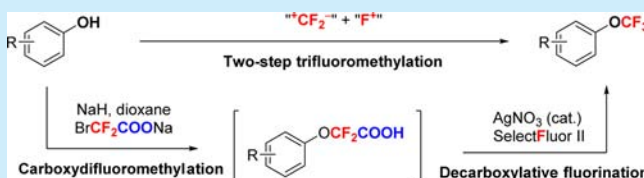
O-Trifluoromethylation of Phenols: Access to Aryl Trifluoromethyl Ethers by O-Carboxydifluoromethylation and Decarboxylative Fluorination

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S Supporting Information

ABSTRACT: A new strategy for the synthesis of aryl trifluoromethyl ethers (ArOCF_3) by combining O-carboxydifluoromethylation of phenols and subsequent decarboxylative fluorination is reported. This protocol allows easy construction of functionalized trifluoromethoxybenzenes and trifluoromethylthiolated arenes (ArSCF_3) in moderate to good yields. Moreover, it utilizes accessible and inexpensive reagents sodium bromodifluoroacetate and SelectFluor II and, thus, is practical for O-trifluoromethylation of phenols. The potential application of this method is demonstrated with the preparation of a plant-growth regulator, Flurprimidol.



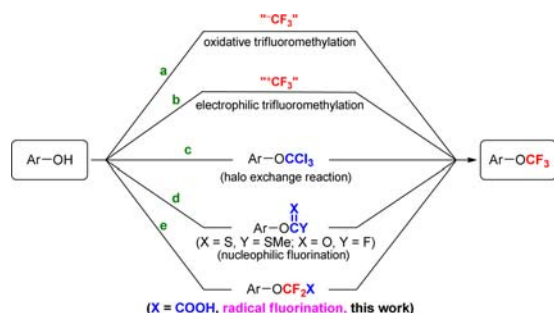
Aryl trifluoromethyl ethers (ArOCF_3) have attracted considerable attention in both academia and industry owing to the unique characteristics of the OCF_3 group.¹ Over the past decades, both trifluoromethoxylation of aromatics and O-trifluoromethylation of phenols have been developed to access ArOCF_3 .^{2–6} The trifluoromethoxylation of aromatics, including radical trifluoromethoxylation of arenes with CF_3OF ,^{2b} nucleophilic trifluoromethoxylation of arynes with trifluoromethoxylate salts (CF_3OM),^{2a} oxidative trifluoromethoxylation of arylstannanes and arylboronic acids with CF_3OM ,^{2c} and intramolecular trifluoromethoxy migration of N-aryl-N-trifluoromethoxylamine derivatives,^{2d–f} suffers from limitations such as requirement of toxic/thermally labile reagents and limited substrate scopes. The O-trifluoromethylation (Scheme 1) becomes a promising strategy owing to the availability of many trifluoromethylation methods.^{3–5} However, unlike the analogous S-trifluoromethylation, the direct O-trifluoromethylation is challenging due to the “hard” nature of the oxygen atom. Only very recently have several examples on direct trifluoromethylation of phenols been reported, either

through Qing’s oxidative trifluoromethylation with Ruppert-Prakash reagent (Me_3SiCF_3) under the promotion of a silver salt (Scheme 1a),³ or through electrophilic trifluoromethylation with Umemoto’s oxonium reagent or Togni’s hypervalent iodine reagents (Scheme 1b).⁴ Conventionally, the synthesis of aryl trifluoromethyl ethers applies two-step procedures: O-carbonfunctionalization followed by tri- or difluorination (Scheme 1c and 1d).⁵ However, these methods usually proceed under harsh conditions with low efficiency because the formation of several C–F bonds is required. Therefore, practical methods for trifluoromethylation of phenols are still desirable.

Considering that the O-difluoroalkylation of phenols usually proceeds more readily than O-trifluoromethylation, we envisioned that the O-trifluoromethylation of phenols may be achieved through the introduction of a CF_2 moiety followed by monofluorination (Scheme 1e). Indeed, there have been sporadic examples on the displacement of a functional group in ArOCF_2X ($\text{X} = \text{Br}, \text{Cl}, \text{SMe}$) by fluorine to afford ArOCF_3 ; however, the tedious routes to prepare ArOCF_2X and the harsh fluorination conditions impeded their broad applications.^{5f–h,6}

To our knowledge, there has been no report on the fluorodecarboxylation of $\text{ArOCF}_2\text{CO}_2\text{H}$ to construct ArOCF_3 .⁷ Herein, we disclose the development of a new method for O-trifluoromethylation of phenols by combining an effective O-carboxydifluoromethylation reaction and an operationally simple silver-catalyzed decarboxylative fluorination reaction. This two-step O-trifluoromethylation employs the readily available sodium bromodifluoroacetate, SelectFluor II, and a catalytic amount of silver salt, thus providing a practical method to access aryl trifluoromethyl ethers.

Scheme 1. Strategies for O-Trifluoromethylation of Phenols

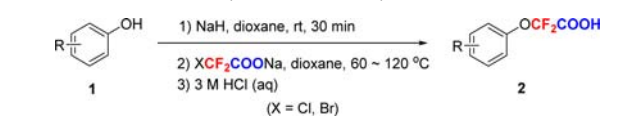


Received: June 19, 2016

Published: July 21, 2016

We began with the preparation of aryloxydifluoroacetic acids ($\text{ArOCF}_2\text{COOH}$) from the sodium salts of phenols (ArONa) via a substitution reaction (Scheme 2). Initially, sodium

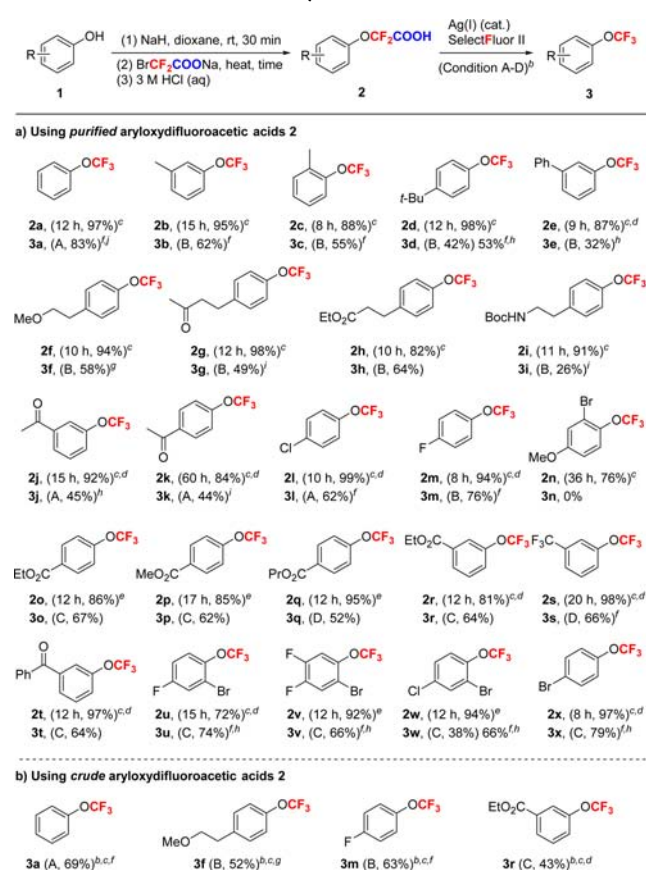
Scheme 2. O-Carboxydifluoromethylation of Phenols



chlorodifluoroacetate ($\text{ClCF}_2\text{COONa}$) was chosen as the source of the difluoroalkyl moiety.⁸ Thus, heating the mixture of ArONa and $\text{ClCF}_2\text{COONa}$ in nonpolar solvent 1,4-dioxane at 120 °C followed by acidification afforded both electron-neutral and -rich aryloxydifluoroacetic acids in high yields. However, we found that this protocol is less efficient for the preparation of electron-deficient aryloxydifluoroacetic acids due to decreased nucleophilicity of the phenolates. To overcome this limitation, the more reactive $\text{BrCF}_2\text{COONa}$ was employed instead of $\text{ClCF}_2\text{COONa}$ as a general carboxydifluoromethylation reagent, and a wide range of aryloxydifluoroacetic acids **2a–x** were prepared in excellent yields from the corresponding phenolates (see Scheme 3a). In the cases of phenolates with electron-donating substituents, the reaction temperature could be decreased to 60 °C (**2b–d**, **2f–i**, **2n**).

Subsequently, with $\text{PhOCF}_2\text{COOH}$ (**2a**) as a model substrate, we set out to explore the optimal fluorodecarboxylation conditions (Table 1). Recently, decarboxylative radical fluorination of carboxylic acids has been well established to be efficient for the synthesis of alkyl fluorides under mild conditions.^{9,10} Li and co-workers have elegantly showed that under the catalysis of AgNO_3 , aliphatic carboxylic acids undergo fluorodecarboxylation with the electrophilic fluorination reagent SelectFluor.^{9a} However, the fluorination of difluoroacetic acids with an aryloxy substituent is still underexplored, and our initial attempts showed that the reported optimized conditions for the fluorination of normal aliphatic carboxylic acids with SelectFluor^{9a–d} are not applicable for the transformation of our difluoroacetic acids such as **2a** (see the Supporting Information (SI), section 7). Thus, an exhaustive screening of fluorination reagents, metal catalysts, and solvents was undertaken (see the SI, section 7). It was shown that, under silver catalysis, SelectFluor II¹¹ was a proper reagent for converting **2a** to trifluoromethyl ether **3a**. The reaction conducted with AgNO_3 (20 mol %) and SelectFluor II (2.0 equiv) in the mixed solvent system $\text{CH}_2\text{Cl}_2/\text{H}_2\text{O}$ (1:1, v/v) afforded the desired product **3a** in 42% yield (Table 1, entry 1). Further optimization of the ratio of $\text{CH}_2\text{Cl}_2/\text{H}_2\text{O}$ to 10:1 was beneficial to this reaction (Table 1, entries 1–5). Screening on silver salts showed that other silver salts, such as AgOTf , AgPF_6 , AgBF_4 , and Ag_2SO_4 , exhibited similar catalytic reactivity as AgNO_3 (see the SI, section 8), and AgI significantly improved the yield (entry 6). However, silver salts AgCl , AgBr , and $\text{Ag}(\text{Phen})_2\text{OTf}$ (Phen = 1,10-phenanthroline) were less efficient than AgNO_3 (see the SI, section 8). Additional screening of additives showed that HBF_4 aq (50% w/w) (3.0 equiv) could improve the AgNO_3 -catalyzed reaction to a yield as high as that with AgI alone (entry 7); nevertheless, the catalysis with AgI was somewhat inhibited by the added HBF_4 (entry 8). The reaction could also be conducted under nonmetal catalysis when xenon difluoride (XeF_2) was used as the fluorination reagent,^{10a–d} but with formation of a significant

Scheme 3. O-Trifluoromethylation of Various Phenols^a

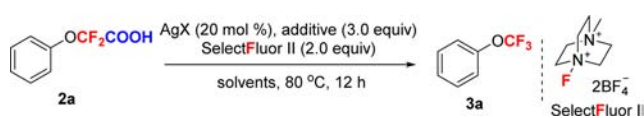


^aUnless otherwise noted, the yield given refers to the isolated yield of the analytically pure compound. ^bCondition A: **2** (0.5 mmol), SelectFluor II (2.0 equiv), AgNO_3 (20 mol %), HBF_4 (aq) (3.0 equiv), $\text{CH}_2\text{Cl}_2/\text{H}_2\text{O}$ (10:1), 80 °C, 12 h; Condition B: **2** (0.5 mmol), SelectFluor II (2.0 equiv), AgI (20 mol %), $\text{CH}_2\text{Cl}_2/\text{H}_2\text{O}$ (10:1), 80 °C, 12 h; Condition C: **2** (0.5 mmol), SelectFluor II (3.5 equiv), AgNO_3 (20 mol %), HOTf (3.0 equiv), $\text{PhCF}_3/\text{H}_2\text{O}$ (10:1), 80 °C, 24 h; Condition D: **2** (0.5 mmol), SelectFluor II (3.5 equiv), AgNO_3 (20 mol %), HOTf (3.0 equiv), $\text{CF}_2\text{ClCF}_2/\text{H}_2\text{O}$ (10:1), 80 °C, 24 h. ^cConditions: **1** (3.0 mmol), NaH (1.1 equiv), $\text{BrCF}_2\text{COONa}$ (1.1 equiv), dioxane (0.2 M), 60 °C. ^d80 °C instead of 60 °C. ^eConditions: **1** (3.0 mmol), NaH (1.2 equiv), $\text{BrCF}_2\text{COONa}$ (1.5 equiv), 100 °C. ^f¹⁹F NMR yield with PhCF_3 , PhSCF_3 or 1,3,5-trifluorobenzene as an internal standard. ^gSelectFluor II (2.5 equiv). ^hSelectFluor II (3.0 equiv). ⁱSelectFluor II (3.5 equiv). ^j AgNO_3 (5 mol %).

amount of difluoromethyl ether as the side product (entry 9; see the SI, section 7).

With two sets of optimized decarboxylative fluorination conditions in hand (condition A: Table 1, entry 7; condition B: entry 6), we explored the scope of this trifluoromethylation method with respect to the phenols. As shown in Scheme 3a, with the exception of methoxy-substituted phenols (**3n**), both moderately electron-rich substrates with alkyl/aryl substituents (**3b–3i**, condition B) and moderately electron-deficient substrates with acetyl/halogen substituents (**3j–3m**, condition A or B) smoothly underwent the sequence of O-carboxydifluoromethylation and fluorodecarboxylation to give the O-trifluoromethylation products in moderate yields. In the cases of alkyl-substituted phenols, functional groups such as ether, ketone, ester, and amide were tolerated under the acid-free, fluorodecarboxylation conditions (**3f–3i**). As for the methoxy-substituted phenol, the fluorodecarboxylation failed to give the

Table 1. Optimization on the Reaction Conditions for Fluorodecarboxylation of PhOCF₂COOH^a



entry	AgX	solvent (v/v)	additive	yield (%) ^b
1 ^c	AgNO ₃	CH ₂ Cl ₂ /H ₂ O (1:1)	—	42
2	AgNO ₃	CH ₂ Cl ₂ /H ₂ O (4:1)	—	57
3	AgNO ₃	CH ₂ Cl ₂ /H ₂ O (10:1)	—	66
4	AgNO ₃	CH ₂ Cl ₂	—	0
5	AgNO ₃	H ₂ O	—	0
6	AgI	CH ₂ Cl ₂ /H ₂ O (10:1)	—	79
7	AgNO ₃	CH ₂ Cl ₂ /H ₂ O (10:1)	HBF ₄	78
8 ^d	AgI	CH ₂ Cl ₂ /H ₂ O (10:1)	HBF ₄	50
9 ^d	—	CH ₂ Cl ₂	—	33(21)

^aReaction conditions: **2a** (0.1 mmol), SelectFluor II (0.2 mmol), AgX (0.02 mmol), solvent (1.0 mL), 80 °C, 12 h. ^bYields were determined by ¹⁹F NMR spectroscopy using PhCF₃ as an internal standard. ^c55 °C. ^dXeF₂ was used as the fluorination reagent. Reaction conditions: **2a** (0.1 mmol), XeF₂ (0.1 mmol), CH₂Cl₂ (2.0 mL), rt, 15 h. The yield of PhOCF₂H was given in the parentheses.

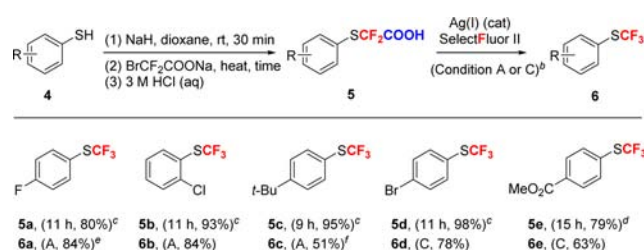
trifluoromethyl ether due to the ready fluorination on the electron-rich aromatic ring (**3n**).⁹ⁱ However, the aforementioned optimized conditions (conditions A and B) are not applicable to the transformation of substrates with ester, trifluoromethyl, benzoyl, and polyhalogen substituents on the aromatic ring due to the rather sluggish fluorodecarboxylation (**3o–3w**). A further screening of the reaction conditions showed that a switch of the organic solvent could significantly accelerate the fluorination. Thus, performing the AgNO₃-catalyzed fluorodecarboxylation in PhCF₃/H₂O (10:1, v/v) (condition C) or CF₂ClCFCl₂/H₂O (10:1, v/v) (condition D) as the solvent with triflic acid (3.0 equiv) as the additive provided the desired trifluoromethyl ethers (**3o–3w**) in 52–74% yields. Trifluoromethyl ethers of monohalogenated phenols were also successfully prepared by using PhCF₃/H₂O (10:1, v/v) as the solvent (**3x**).

The trifluoromethylation of phenols can be performed by using the crude aryloxydifluoroacetic acids (Scheme 3b). Thus, a liquid–liquid extraction of the aryloxydifluoroacetic acids with CH₂Cl₂/H₂O to remove the bromide ion followed by silver-catalyzed decarboxylative fluorination afforded the trifluoromethyl ethers in overall yields similar to those performed with purified aryloxydifluoroacetic acids.

This two-step trifluoromethylation method is also applicable to the transformation of thiophenols. As shown in Scheme 4, the arylthiodifluoroacetic acids derived from the corresponding thiophenols were readily converted to the trifluoromethyl sulfides (**5a–5e**). The influence of the electronic nature of the substituents on the aromatic ring is in line with the reaction of aryloxydifluoroacetic acids.

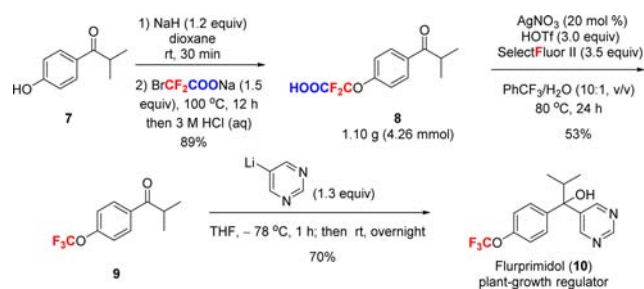
To demonstrate the synthetic value of our method, we synthesized Flurprimidol **10** (Scheme 5), a plant-growth regulator,¹² which exhibits activity in a wide range of mono- and dicotyledonous species. After difluoroacetic acid **8** was prepared in excellent yield, its decarboxylative fluorination was carried out on a gram scale under the optimized conditions (condition C) to give trifluoromethyl ether **9** in moderate yield. Subsequent nucleophilic carbonyl addition of **9** with 5-pyrimidyllithium gave **10** in good yield. It is worth noting

Scheme 4. S-Trifluoromethylation of Aryl Thiophenol^a



^aUnless otherwise noted, the yield given refers to the isolated yield of the analytically pure compound. ^bCondition A: **2** (0.5 mmol), SelectFluor II (2.0 equiv), AgNO₃ (20 mol %), HBF₄ (aq) (3.0 equiv), CH₂Cl₂/H₂O (10:1), 80 °C, 12 h; Condition C: **2** (0.5 mmol), SelectFluor II (3.5 equiv), AgNO₃ (20 mol %), HOTf (3.0 equiv), PhCF₃/H₂O (10:1), 80 °C, 24 h. ^cConditions: **1** (3.0 mmol), NaH (1.1 equiv), BrCF₂COONa (1.1 equiv), dioxane (0.2 M), 80 °C. ^dNaH (1.2 equiv), BrCF₂COONa (1.5 equiv), 100 °C. ^e¹⁹F NMR yield with PhCF₃ as an internal standard. ^fSelectFluor II (3.0 equiv).

Scheme 5. Synthesis of Flurprimidol (10)



that the whole process employs inexpensive reagents, which serves as a promising alternative synthetic route to Flurprimidol.

In summary, we have developed an expedient synthesis of aryl trifluoromethyl ethers (ArOCF₃) from phenols by combining *O*-carboxydifluoromethylation and silver-catalyzed decarboxylative fluorination. This two-step method utilizes readily accessible reagents sodium bromodifluoroacetate and SelectFluor II and is operationally simple and, thus, is practical for the synthesis of various aryl trifluoromethyl ethers. We also demonstrated the potential application of this method in the synthesis of a plant-growth regulator, Flurprimidol.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.6b01779.

Experimental procedures and characterization data for products (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the National Basic Research Program of China (2015CB931900, 2012CB215500), the National Natural Science Foundation of China (21372246, 21421002, 21472221, 21402227), the Chinese Academy of Sciences, Shanghai Academic Research Leader Program (15XD1504400), Shanghai Rising-Star Program (16QA1404600), and the Youth Innovation Promotion Association CAS (2014231) for financial support.

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