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COMMUNICATION

Fluoride anion-initiated bis-trifluoromethylation of phenyl aromatic carboxylates with (trifluoromethyl)trimethylsilane†

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The fluoride anion-initiated reaction of phenyl aromatic carboxylates with (trifluoromethyl)trimethylsilane (Me_3SiCF_3) with the formation of *O*-silyl-protected 2-aryl-1,1,1,3,3,3-hexafluoroisopropanols is reported. A phenoxide anion, generated during the trifluoromethylation of the phenyl carboxylate, functions to activate the Me_3SiCF_3, which permits a catalytic amount of the fluoride anion source to be used. Various functional groups, which can be used for further elaboration, are tolerated in the reaction.

The intrinsic nature of fluorine atoms enables fluorine-substituted organic compounds to acquire unique properties that differ from their hydrocarbon analogues.[1] Among these, increased attention has been directed to 1,1,1,3,3,3-hexafluoroisopropanol (HFIP) and derivatives thereof.[2] With the aid of two trifluoromethyl groups, the hydroxyhexafluoroisopropyl moiety is sufficiently bulky to confer highly acidic properties on the proton, thus contributing to the formation of strong hydrogen bonding. The introduction of the hydroxyhexafluoroisopropyl group can, therefore be used in the design of catalysts and ligands[3] as well as in chemical sensing materials.[4] Moreover, 2-aryl-1,1,1,3,3,3-hexafluoroisopropanol derivatives are found in pharmaceutically potent products[5] and polymeric materials.[6]

The conventional synthesis of 2-aryl-1,1,1,3,3,3-hexafluoroisopropanols typically involves the electrophilic substitution of arenes or the nucleophilic addition of aryl metal reagents, using hexafluoroacetone as the electrophile.[7] Dehydrogenative coupling of HFIP with electron-rich arenes, including anilines and indoles, has recently been achieved by utilizing Co[8] or Cu[9] catalysis. Alternatively, the introduction of hydroxyhexafluoroisopropyl groups into aromatic compounds has been accomplished by employing a nucleophilic trifluoromethylation protocol.[10] The trifluoromethylation of trifluoroacetophenones is a typical method for the synthesis of 2-aryl-1,1,1,3,3,3-hexafluoroisopropanols, a reaction that usually involves the use of the Ruppert–Prakash reagent, Me_3SiCF_3,[11] or the less reactive Bu_3SnCF_3 in the presence of a catalytic amount of a Lewis base activator.[12] However, the synthesis of trifluoroacetophenone derivatives are not so straightforward compared with carboxylic acid derivatives. The trifluoromethylation of aroyl chlorides is a convenient method for the synthesis of 2-aryl-1,1,1,3,3,3-hexafluoroisopropanols, in which trifluoromethylating reagents derived from a trifluoroacetate salt or a fluoroform are usually employed.[13] Me_3SiCF_3 can also be used for the trifluoromethylation of acid anhydrides as well as acid chlorides.[14] Skrydstrup reported on a practical example that proceeds via the Pd-catalyzed fluorocarbonylation of aryl bromides or fluorosulfates followed by trifluoromethylation using Me_3SiCF_3.[15] In these methods, more than a stoichiometric amount of the fluoride anion (F^-) source is generally required for the efficient activation of Me_3SiCF_3.

To the best of our knowledge, reports on the synthesis of 2-aryl-1,1,1,3,3,3-hexafluoroisopropanols from aromatic esters using Me_3SiCF_3 have been limited despite their availability and synthetic utility. Pentafluorophenyl benzoates can also serve as a substrate for the synthesis of 2-aryl-1,1,1,3,3,3-hexafluoroisopropanols, however the use of a stoichiometric amount of tetramethylammonium fluoride (Me_4NF) is required (Scheme 1a),[14] or alternatively a large excess of Me_3SiCF_3 was used when the amount of Me_4NF was reduced.[16] The trifluoromethylation of methyl benzoates can proceed in the presence of a catalytic amount of the F^- source to give trifluoromethyl ketones (Scheme 1b).[17] However, the synthesis of 2-aryl-1,1,1,3,3,3-hexafluoroisopropanols from methyl benzoates has not been fully explored except for the bis-trifluoromethylation of an electronically deficient methyl benzoate.[5a]

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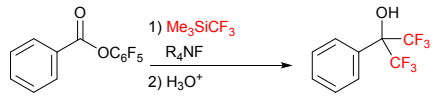
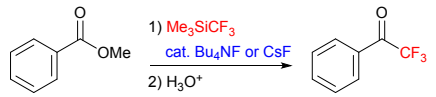
In this report, we disclose that the reaction of phenyl aromatic carboxylates with Me_3SiCF_3 provides *O*-silyl-protected 2-aryl-1,1,1,3,3,3-hexafluoroisopropanols, even in the presence of a catalytic amount of the F^- source (Scheme 1c).

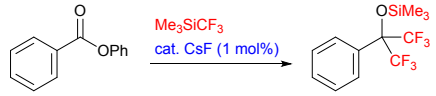
(a) Bis-trifluoromethylation of pentafluorophenyl benzoates using a stoichiometric amount of R_4NF or a large excess amount of Me_3SiCF_3 in the presence of a catalytic amount of R_4NF.



(b) Trifluoromethylation of methyl benzoates using a catalytic amount of F^- sources.



(c) **This work**: Bis-trifluoromethylation of phenyl benzoates using a catalytic amount of CsF.



Scheme 1 Trifluoromethylation of aromatic esters with Me_3SiCF_3.

We began our studies by conducting the reaction of phenyl 2-naphthoate (**1a**, 0.3 mmol) with Me_3SiCF_3 (3 equiv) in the presence of 10 mol% of CsF in 1,4-dioxane at room temperature, giving the 1,1,1,3,3,3-hexafluoro-2-naphthylisopropyl silyl ether (**2a**) in 81% isolated yield (Table 1, entry 1). $PhOSiMe_3$ was also present in the crude reaction mixture, as evidenced by ^1H NMR and GC analysis. Reducing the amount of CsF to 1 mol% improved the yield of **2a** to 98% (entry 2). When 1 mol% of KF was used in place of CsF as an additive, the yield of **2a** was significantly decreased (entry 3), due, in part, to the low solubility of KF in 1,4-dioxane. In fact, the addition of KF with 18-crown-6 provided the desired trifluoromethylation product without loss of the yield of **2a** (entry 4). It should be noted that this reaction also proceeded when 1 mol% of CsOPh was added, leading to the formation of **2a** in 70% yield (entry 5). However, other additives including NaOPh/15-crown-5, PPh_3, and Et_3N were ineffective (entries 6-8), and no reaction occurred in the absence of an additive (entry 9). Lowering the amount of Me_3SiCF_3 (2.2 equiv) decreased the yield of **2a**. (entry 10). After the screening of solvents and leaving groups, 1,4-dioxane and a phenoxy group, respectively, were suitable for achieving an efficient transformation.[18]

Table 1 Optimization of reaction conditions.

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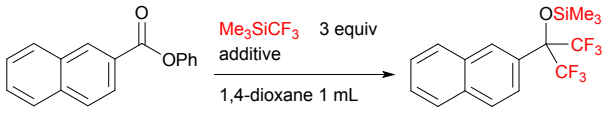
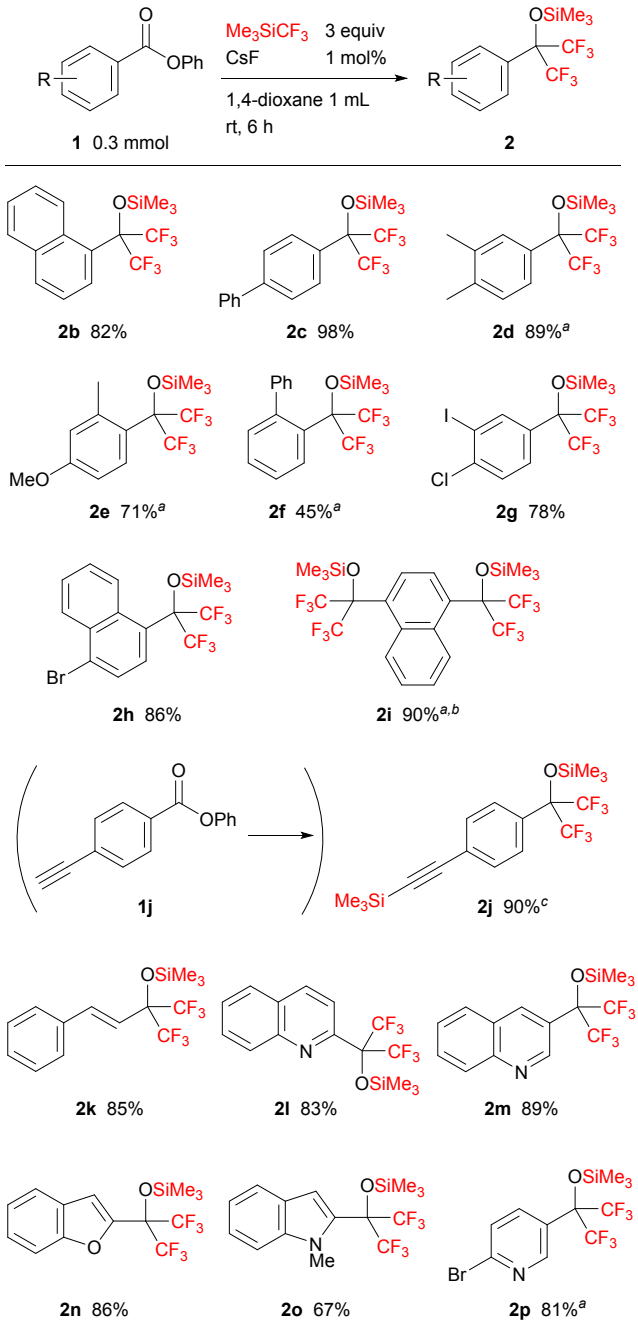


1a 0.3 mmol **2a**

Entry	Additive (mol%)	Yield of **2a** (%)[a]
1	CsF (10)	81
2	**CsF (1)**	**98**
3	KF (1)	4
4	KF (1) + 18-crown-6 (2)	98
5	CsOPh (1)	70
6	NaOPh (1) + 15-crown-5 (5)	11
7	PPh_3 (1)	0
8	Et_3N (3)	trace
9	none	0
10[b]	CsF (1)	69

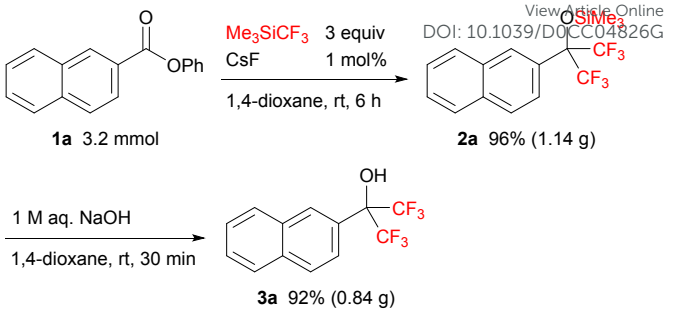
[a] Isolated yield. [b] Me_3SiCF_3 (2.2 equiv) was used.

With the optimized conditions in hand, we investigated the scope of the reaction with respect to phenyl aromatic carboxylates (Scheme 2). Phenyl 1-naphthoate (**1b**), 4-phenylbenzoate (**1c**), and 3,4-dimethylbenzoate (**1d**) could be converted into the corresponding silyl ethers in good yields (**2b–d**). Steric hindrance of *ortho*-substituents affected the progress of the reaction, resulting in only modest yields of **2e** and **2f** even when the reaction run for 24 h. The trifluoromethylation of halogenated aryl esters (**1g** and **1h**) proceeded smoothly to give **2g** and **2h**, which would serve as valuable intermediates in cross-coupling reactions. Both of the ester groups in the diphenyl naphthalene-1,4-dicarboxylate (**1i**) could be converted into siloxyhexafluoroisopropyl groups. When **1j**, bearing a terminal alkyne functionality, was reacted with 5 equivalents of Me_3SiCF_3, the silylation of the terminal alkyne took place along with the formation of the desired trifluoromethylation of ester, affording **2j** in 90% yield.[19] Phenyl cinnamate (**1k**) as well as phenyl heteroaromatic carboxylates, including quinoline (**1l**, **1m**), benzofuran (**1n**), indole (**1o**), and pyridine (**1p**), were also applicable for use in this protocol, giving the corresponding trifluoromethylation products **2k–p** in good yields. Unfortunately, the reaction of phenyl aromatic carboxylates with other (perfluoroalkyl)trialkylsilanes, such as Et_3SiCF_3, $Me_3SiC_2F_5$, and Me_3SiCF_2H, was unsuccessful under the optimized conditions.[20]



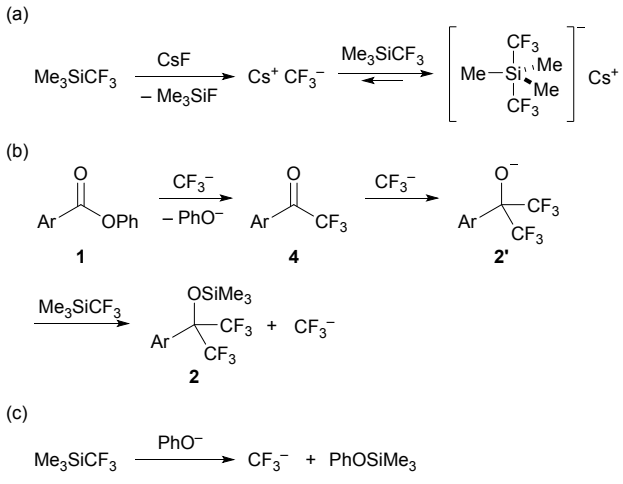
Scheme 2 Scope of phenyl carboxylates. Reaction conditions: phenyl carboxylate (0.3 mmol), Me_3SiCF_3 (0.9 mmol), CsF (0.003 mmol), 1,4-dioxane (1 mL), rt, 6 h unless otherwise noted. [a] Run for 24 h. [b] Me_3SiCF_3 (6 equiv) was used. [c] Me_3SiCF_3 (5 equiv) was used.

We next examined a large-scale trifluoromethylation of **1a**, which successfully afforded **2a** without any loss of yield (Scheme 3). The subsequent deprotection of **2a** by treatment with a base led to the formation of 2-naphthylhexafluoroisopropanol (**3a**) in 88% yield in 2 steps.



Scheme 3 Large-scale synthesis of 2-naphthylhexafluoroisopropanol **3a**.

Recently, Lloyd-Jones reported on a detailed mechanistic investigation of anion-initiated trifluoromethylation using Me_3SiCF_3.[21] They concluded that the pentacoordinate silicon intermediates such as $Me_3SiF(CF_3)^-$ or $Me_3Si(CF_3)_2^-$ are unable to transfer a CF_3 group directly, while CF_3^- can serve as an active nucleophile. It should also be noted that metal phenoxides such as CsOPh and KOPh are effective initiators for the anion-initiated trifluoromethylations using Me_3SiCF_3. On the basis of this report and our results, a proposed reaction mechanism for this transformation is illustrated in Scheme 4. The reaction of Me_3SiCF_3 with CsF initially gives $CsCF_3$, which then reacts with Me_3SiCF_3 to produce an equilibrium mixture of a pentacoordinate silicon intermediate (Scheme 4a). The nucleophilic attack of CF_3^- to the carbonyl group in **1** then gives the trifluoroacetophenone **4** along with the elimination of PhO^-. The subsequent addition of CF_3^- to **4** results in the deprotonation of the 2-aryl-1,1,1,3,3,3-hexafluoroisopropanol (**2'**), which then reacts with Me_3SiCF_3 to afford CF_3^- and **2** (Scheme 4b). The reaction of PhO^- with Me_3SiCF_3 can also provide CF_3^- along with the formation of $PhOSiMe_3$ (Scheme 4c). Owing to this process, the use of a catalytic amount of CsF initiator is sufficient to allow the transformation of **1** into **2**.



Scheme 4 A proposed mechanism.

In conclusion, we report on the development of an efficient method for the synthesis of 2-(hetero)aryl-1,1,1,3,3,3-hexafluoroisopropanol derivatives from phenyl (hetero)aromatic carboxylates by using Me_3SiCF_3 in

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combination with a catalytic amount of CsF. Various functionalities including metal-malleable halogen groups are compatible to this protocol. A key to the successful reaction is the sufficient leaving ability and basicity of the phenoxide anion that can activate Me_3SiCF_3 to promote the following trifluoromethylation.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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20 In the reaction using a stoichiometric amount of CsF, the bis-perfluoroalkylation of **1a** with Et_3SiCF_3 or $Me_3SiC_2F_5$ took place. However, a mixture of the expected *O*-silyl-protected alcohols and the free alcohols was formed. See the Electronic Supplementary Information (ESI) for details.

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Fluoride anion-initiated trifluoromethylation of phenyl aromatic carboxylates with (trifluoromethyl)trimethylsilane leading to the formation of 2-aryl-1,1,1,3,3,3-hexafluoroisopropanols†

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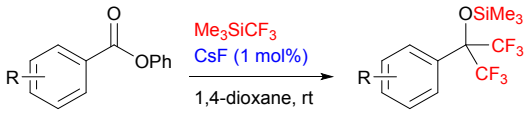

activation of Me_3SiCF_3 by F^- and leaving PhO^-

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