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# Electrophilic *N*-trifluoromethylthiophthalimide as a fluorinated reagent in the synthesis of acyl fluorides†

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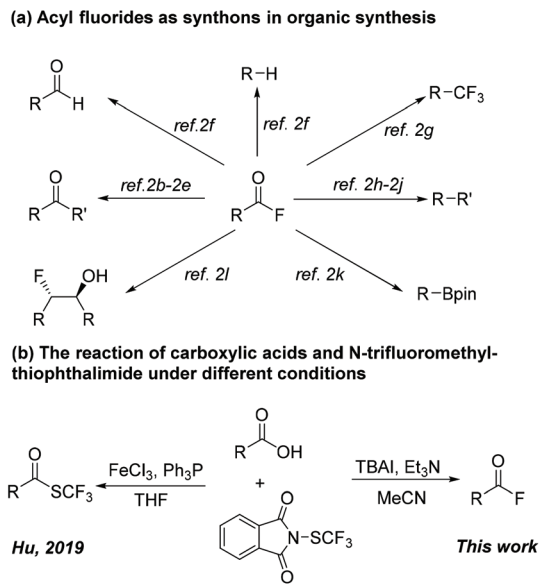
Herein we report the deoxygenated fluorination of readily available carboxylic acids. A series of acyl fluorides have been synthesized using shelf-stable *N*-trifluoromethylthiophthalimide as a fluorinated reagent for the first time. Scale-up reactions and sequential cross-couplings were performed successfully to demonstrate the practicability of this fluorination protocol.



Fluorine-containing molecules are one class of the most important organic compounds due to the unique character of the fluorine atom in modulating the chemical and biological properties such as metabolic stability, lipophilicity, and bioavailability.[1] Therefore, the development of methods to access such compounds is always a research focus for organic chemists. In this context, acyl fluorides represent intriguing targets that play an important role in organic synthesis. Due to the outstanding balance between stability and reactivity, acyl fluorides were widely employed as versatile synthons in different types of organic transformations (Scheme 1a).[2] Also, acyl fluorides could be used for the activation of silyl enol ethers or other silicon species in the presence of a Lewis base.[3] Conventional methods to access acyl fluorides depend on the halogen exchange reaction of acyl chlorides with "$F^-$" sources.[4] Recent advances were mainly focused on the deoxyfluorination of readily available carboxylic acids with various fluorinated reagents (*e.g.*, $CF_3SO_2OCF_3$,[5] $PPh_3$/Selectfluor,[6] $Me_4NSCF_3$,[7] cyanuric fluoride,[8] HF-Pyridine/DCC,[9] sulphur tetrafluoride derivatives,[10] and Carpino'salt TFFH[11]). Notably, Shibata and coworkers developed a general and practical method to prepare acyl fluorides, in which acids, aldehydes, and alcohols all could be transformed into acyl fluorides by using inexpensive reagents, TCCA and CsF.[12] In addition, acyl fluorides were skillfully accessed *via* selective C–C bond cleavage using DAST or its derivatives as fluorination reagents.[13] Although these achievements provide good alternatives, most of them suffered from some drawbacks, mainly including high reaction temperature or the use of fluorinated reagents that are toxic, unstable, or expensive. Thus, the development of new approaches for the preparation of acyl fluorides is still highly desirable.

Shelf-stable *N*-trifluoromethylthiophthalimide has been developed as an easily synthesized and efficient trifluoromethylthiolation reagent, and an array of valuable compounds were obtained employing this versatile $SCF_3$-reagent.[14] In 2000, Munavalli and coworkers reported the reaction of $SCF_3$-phthalimide with enamines, affording the α-trifluoromethylthiolated ketones.[14a] Our group realized the enantioselective trifluoromethylthiolation of β-ketoester[14b] and oxindoles,[14c] Cu-catalyzed cross-coupling of boronic acids and alkynes,[14d] as




**Scheme 1** Acyl fluorides as synthons in organic synthesis and the reaction of *N*-trifluoromethylthiophthalimide and carboxylic acids.

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well as the metal-free ring-opening/trifluoromethylthiolation of cycloalkanols[15] with this $SCF_3$-reagent.

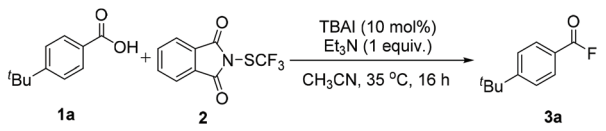
More recently, Hu and coworkers developed a protocol on deoxygenated trifluoromethylthiolation of carboxylic acids in the presence of $FeCl_3$ and $PPh_3$, wherein $SCF_3$-phthalimide acted as a nucleophilic "$SCF_3$" source.[14e] In contrast, we herein report that electrophilic *N*-trifluoromethylthiophthalimide acts as a fluorinated reagent in the reaction of carboxylic acids (Scheme 1b).

We started our investigation by evaluating the reaction of 4-(*tert*-butyl)benzoic acid **1a** and *N*-trifluoromethylthiophthalimide **2a** (Table 1). After a series of screening, the optimal reaction conditions were assigned as follows: 10 mol% TBAI as catalyst, 1 equiv. of $Et_3N$ as reductant in 2 mL $CH_3CN$ at 35 °C. The use of DIPEA as base gave lower yield, while the application of other bases including 2,6-lutidine, pyridine, and $^nBnN$ led to no formation of the desired product. Other solvents such as DMF, DMA, DMSO, THF, acetone were also suitable for this transformation, albeit delivering the acyl fluoride product in low to moderate yields. Using NaI or KI instead of TBAI decreased the yields dramatically. Reversing the ratio of **1a** and **2** from 1 : 1 to 1 : 2 also damaged the yield. Control experiments showed that both TBAI and $Et_3N$ are essential for the high efficiency of this transformation.

With the optimized reaction conditions in hand, the generality of the fluorination reaction was first examined. As shown in Table 2, a variety of aryl carboxylic acids could undergo this efficient fluorination transformation smoothly, affording the corresponding products in good to excellent yields. In addition to alkyl (**3a** and **3b**), methoxyl (**3c**), methylthio (**3d**), and phenoxyl (**3e**) functional groups, reactive chloride (**3f**), bromide (**3g**), iodide (**3h**) were also tolerated in this fluorination protocol, allowing the further sequential functionalization of the generated acyl fluoride products. Aryl carboxylic acid bearing *N*-Boc protected amine was fluorinated in 99% yield (**3i**). Also, biphenyl carboxylic acids could undergo this transformation with good to high efficiency (**3j** and **3k**). In addition, bicyclic carboxylic acid bearing acetal group (**3l**), as well as naphthyl carboxylic acid (3 m and 3n), could all give the corresponding product in high yield. Notably, steric hindrance seems to have no significant influence on the reactivity of the substrates (**3b**, **3c**, **3k**, and **3n**).

Gratefully, our fluorination protocol could be readily extended to vinyl carboxylic acids. As shown in Table 3, the reaction of cinnamic acid proceeded in good yield (**5a**). Vinyl carboxylic acids bearing methoxyl (**5b** and **5c**) and fluoride (**5d**) on the aromatic ring underwent the protocol in good to excellent yields. The reactions of vinyl carboxyl acids containing benzodioxole and naphthyl groups (**5e** and **5f**) with *N*-trifluoromethylthiophthalimide took place in good to high yields. Importantly, heterocycles such as furan and thiophene (**5e–5i**) were also tolerated in this protocol, providing the possi-

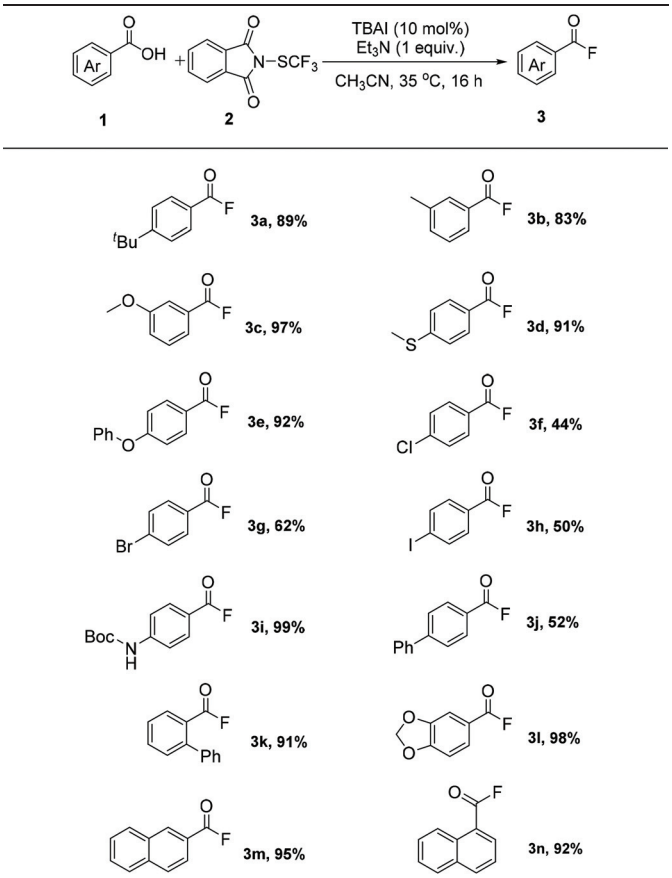
**Table 1** Optimization of the reaction of carboxylic acid and *N*-trifluoromethylthiophthalimide to form acyl fluoride[a]




| Entry | Variables | Yield[b] (%) |
|---|---|---|
| **1** | **None** | **91** |
| 2 | DIPEA as base | 57 |
| 3 | 2,6-Lutidine as base | 0 |
| 4 | Pyridine as base | 0 |
| 5 | $^nBn_3N$ as base | 0 |
| 6 | DMF as solvent | 55 |
| 7 | DMA as solvent | 60 |
| 8 | DMSO as solvent | 35 |
| 9 | THF as solvent | 42 |
| 10 | Acetone as solvent | 33 |
| 11 | 10 mol% NaI as additive | 60 |
| 12 | 10 mol% KI as additive | 42 |
| 13 | 0.5 mL $CH_3CN$ | 46 |
| 14 | **1a : 2** = 1 : 2 | 42 |
| 15 | No TBAI | 50 |
| 16 | NO $Et_3N$ | 0 |

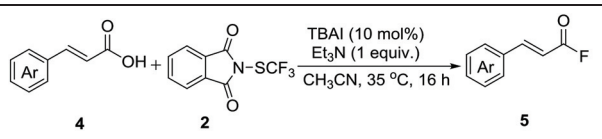
[a] Reaction conditions: **1a** (0.40 mmol), **2** (0.20 mmol), TBAI (10 mol%), $Et_3N$ (1 equiv.) in $CH_3CN$ (2 mL) at 35 °C for 16 h. [b] GC Yields using dodecane as internal standard.

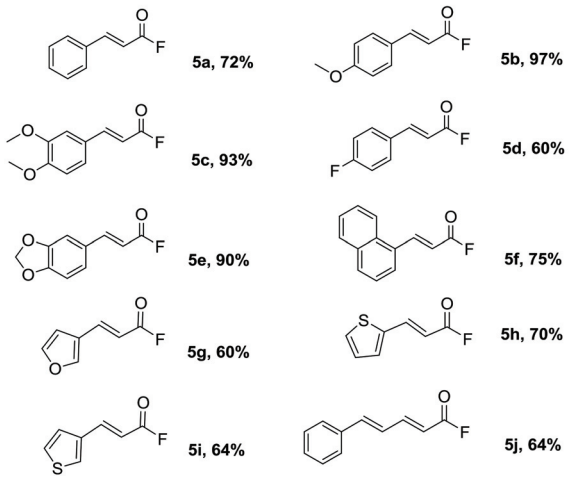
**Table 2** Substrate scope of the fluorination reaction of aryl carboxylic acids[a,b]




[a] Reaction conditions: Reaction conditions: **1** (0.40 mmol), **2** (0.20 mmol), TBAI (10 mol%), $Et_3N$ (1 equiv.) in $CH_3CN$ (2 mL) at 35 °C for 16 h. [b] Isolated yield.

**Table 3** Substrate scope of the fluorination reaction of vinyl carboxylic acids[a,b]



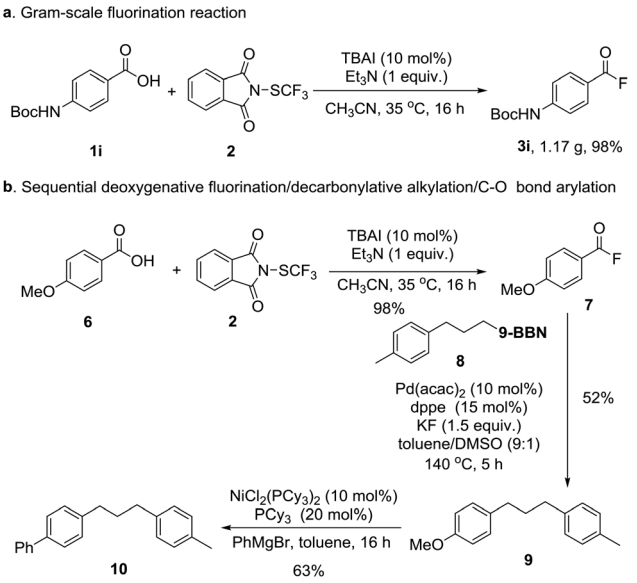

[a] Reaction conditions: Reaction conditions: **4** (0.40 mmol), **2** (0.20 mmol), TBAI (10 mol%), $Et_3N$ (1 equiv.) in $CH_3CN$ (2 mL) at 35 °C for 16 h. [b] Isolated yield.

bility for the synthesis of pharmaceutical-related molecules. Moreover, larger π-extended vinyl acid could also be converted to the corresponding acyl fluoride in good yield (**5j**).

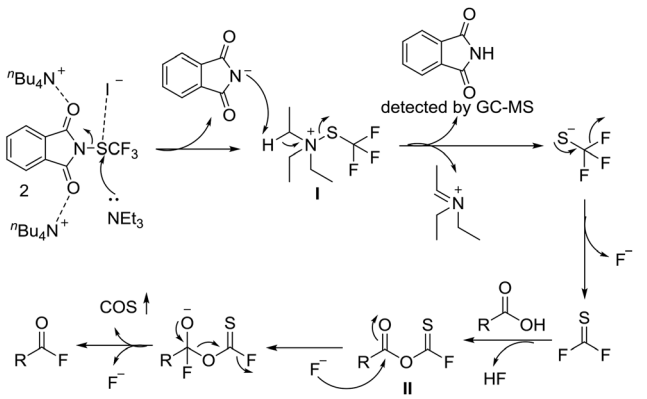
In order to demonstrate the practicality of this newly developed fluorination methodology from carboxylic acids, the gram-scale experiment of phenyl naphthalene-2-carboxylate **1i** was conducted, and 98% yield of the desired product **3i** was obtained (Scheme 2a). Furthermore, we also achieved the sequential deoxygenated fluorination/decarbonylative alkylation/C–O bond arylation, showing great advantages of this protocol (Scheme 2b).

Based on our results and previous studies,[13,16] a mechanism for this fluorination protocol is proposed (Scheme 3). First, $Et_3N$ attacks the electrophilic sulfur center with the aid of TBAI, affording the phthalimide anion and intermediate **I**. Next, the phthalimide anion attacks one of the protons of the ethyl group at $Et_3N$ to generate the nucleophilic trifluoromethylthio group along with phthalimide and the aminium. Then the $^{-}SCF_3$ anion degrades to $CSF_2$ with the release of one fluoride ion. The rapid reaction of $CSF_2$ with carboxylic acid delivers the intermediate **II** that was attacked by a fluoride ion to afford the acyl fluoride product.

In summary, we have developed an efficient deoxygenated fluorination of readily available carboxylic acids. In contrast to previous reports wherein bench-stable *N*-trifluoromethylthiophthalimide was always used as a trifluoromethylthiolation reagent, this newly developed protocol employed it as a fluorinated reagent for the first time. A series of aryl and vinyl carboxylic acid could be converted to acyl fluorides with good to high efficiency. Gram-scale reaction and sequential synthesis, including deoxygenated fluorination/decarbonyl-ative alkylation/C–O bond arylation, were realized in good yield. This protocol provides a good alternative for the fluorination of carboxylic acids.




**Scheme 2** Gram-scale reaction and synthetic application.




**Scheme 3** Proposed mechanism for the reaction of carboxylic acids and *N*-trifluoromethylthiophthalimide.

## Conflicts of interest

There are no conflicts to declare.

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