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Distal Construction of a Carbon-SCF₂R Bond on Aliphatic Alcohols Enabled by 1,5-Hydrogen-Atom Transfer

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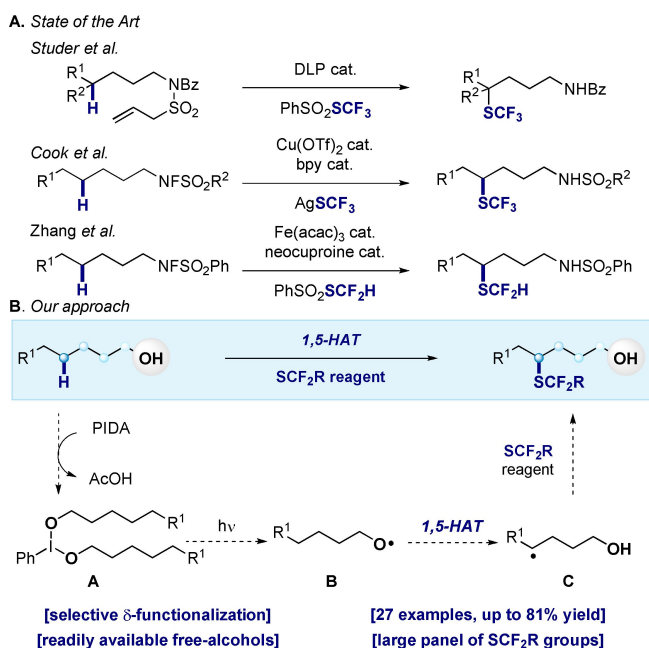
Abstract: An approach for the distal construction of a C(*sp*³)-SCF₂R bond on aliphatic alcohols enabled by 1,5-hydrogen-atom transfer (HAT) was developed. In the presence of a hypervalent iodine (PIDA) and readily available ArSO₂SCF₂R reagents, this transition metal-free approach allowed the remote functionalization of a broad variety of alcohols with emergent and high added-value SCF₂R moieties (R=H, F, CO₂Et and PO(OEt)₂) under blue light irradiation.

Keywords: SCF₂R-containing molecules; Fluorine chemistry; 1,5-HAT; Distal position; C(*sp*³)-H bond functionalization

Because of the remarkable properties of the fluorinated molecules,^[1] interest in the organofluorine chemistry has grown across materials science, pharmaceuticals and agrochemicals as well as modern drug design.^[2] Therefore, given the importance of this class of molecules, a plethora of transformations has been developed and innovative approaches are still needed to push further the boundaries of knowledge in this appealing organofluorine chemistry.^[3]

In particular, the SCF₃ group^[4] is now considered as a key fluorinated moiety thanks to its unique properties such as its high electron-withdrawing character and its Hansch parameter.^[5,6] In addition, this fluorinated moiety can be found in several key compounds such as Fipronil and Toltrazuril. Besides, since 2015, a steadily interest towards the synthesis of SCF₂H and SCF₂FG-containing molecules^[7] (FG=SO₂Ph, CO₂R, PO(OEt)₂)

was observed. The generation of these fluorinated moieties offered novel opportunities to fine-tune the properties of the molecules in which they were incorporated. Although significant advances have been made in the synthesis of trifluoromethylthiolated^[4] and SCF₂R-containing derivatives,^[7] significant synthetic challenges remain when it comes to the remote C–H functionalization of non-activated positions on aliphatic chains. The development of new tools for the direct functionalization of C–H bond offers original synthetic pathways to reach high molecular complexity and challenging compounds in a step economical manner. Among the possible synthetic solutions to carry out the challenging distal C–H functionalization of aliphatic molecules, straightforward and original strategies^[8] based on a 1,5-HAT or the β-fragmentation of constrained rings were designed and applied to access fluorinated molecules.^[9,10] Although the 1,5-HAT strategy has mainly focused on the remote fluorination and trifluoromethylation reactions,^[9,10] only a handful of reports deal with the distal C–H functionalization with a SCF₃ moiety and a unique report regarding the SCF₂H residue has yet been depicted. From the pioneering work from the group of Leonori,^[11] the group of Studer^[12] reported the selective δ-trifluoromethylthiolation of *N*-alkylamide derivatives in the presence of PhSO₂SCF₃ (Scheme 1, A). One year later, Cook and co-workers^[13] developed the copper-catalyzed trifluoromethylthiolation of *N*-fluoro-sulfonamides. In the same vein, in 2021, a significant contribution was depicted by the group of Zhang with the iron-catalyzed δ-difluoromethylthiolation of aliphatic *N*-fluoro-sulfonamides.^[14] In this context, there is a real synthetic challenge to develop innovative tools for the regioselective remote functionalization of non-

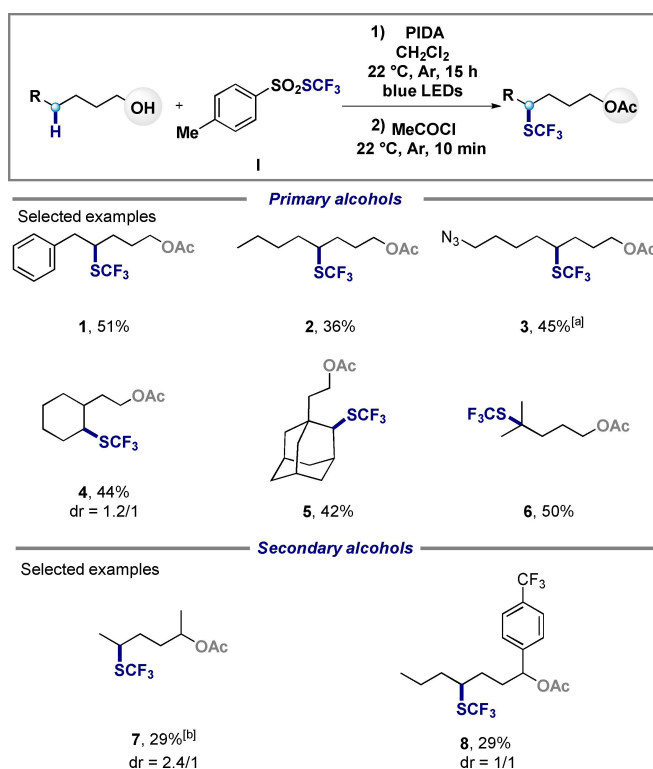


Scheme 1. State of the Art and Our Approach.

activated aliphatic derivatives with SCF₂R residues (R=H, F, CO₂Et and PO(OEt)₂), which will offer an efficient access to unprecedented high value-added compounds. Especially, we focused on the functionalization of the less explored aliphatic free-alcohols with the direct *in situ* generation of an alkoxy radical.^[15] Such approach will constitute a promising alternative to the current manifolds using alcohol surrogates or peroxides for the *in situ* generation of alkoxy radicals.^[4b] Indeed, based on the work of Zhu,^[15e] we suggested that the remote functionalization of alcohols might proceed according to the following synthetic pathway (Scheme 1, B): in the presence of a suitable hypervalent iodine species, a ligand exchange with the alcohol would occur. Upon light irradiation, an alkoxy radical would be generated, affording the corresponding carbon-centered radical by means of a 1,5-HAT process. Then, after reaction with a proper SCF₂R reagent, the corresponding product will be obtained, ArSO₂SCF₂R reagents^[7b,d] being suitable candidates as fluorinated sources.

As part of our ongoing research program dedicated to the introduction of emergent fluorinated building blocks,^[16] we report herein a full report of our contribution to the field related to the distal construction of a C(*sp*³)-SCF₂R bond (R=H, F, CO₂Et, PO(OEt)₂) on aliphatic alcohols by C-H bond functionalization. We aim at developing a regioselective approach towards those difficult-to-synthesize fluorinated compounds, so far inaccessible for most of them, broadening hence the current portfolio of SCF₂R-containing molecules.

At the outset of these investigations, we first studied, in 2020, the distal trifluoromethylthiolation of unprotected alcohols under visible light irradiation with the TolSO₂SCF₃ **I** reagent by a two-steps process (trifluoromethylthiolation/acetylation).^[17] Several primary alcohols were selectively trifluoromethylthiolated at the δ -position (16 examples, up to 51% yield).^[17] Worth to mention that despite tedious purifications along with volatility issues, the expected products were obtained in decent yields. 5-Phenyl-1-pentanol and octanol turned out to be suitable substrates in this transformation and the selective acetylated products **1** and **2** were isolated in 51% and 36% yield, respectively (Scheme 2). The transformation was tolerant to functional groups such as an azide, offering possibilities for post-functionalization. Interestingly, the incorporation of the SCF₃ moiety on alcohols substituted with a cyclohexyl or an adamantyl group at the γ -position was possible leading to the corresponding products **4** in 44% yield as a mixture of diastereoisomers (dr=1.2/1) and **5** in 42% yield, respectively. The function-



Scheme 2. Remote trifluoromethylthiolation of alcohols. Selected examples from the reference 17. Reaction conditions: 1) alcohol (1 mmol, 5 equiv.), **I** (0.2 mmol, 1 equiv.), PIDA (0.46 mmol, 2.3 equiv.), CH₂Cl₂ (0.13 M), 22 °C, 15 h, Argon, blue LEDs 450 nm 30 W. 2) MeCOCl (27 mmol, 135 equiv.), 22 °C, 10 min, Argon. The diastereomeric ratios were determined by ¹⁹F NMR spectroscopy of the crude reaction mixture. ^[a] The product contains an inseparable impurity. ^[b] The reaction was carried out using 1.2 mmol of **I**.

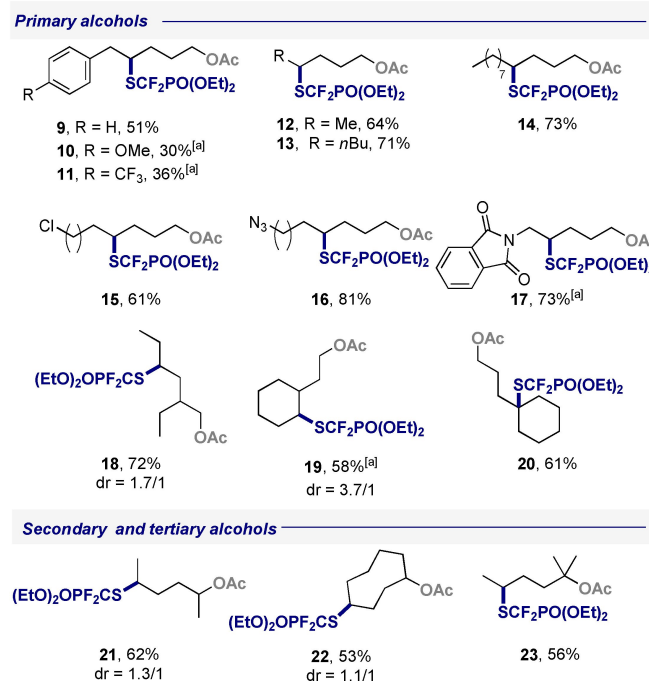
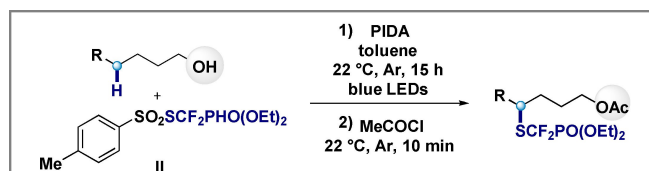
alization of a tertiary C(sp³) center was also possible affording the compound **6**. When secondary alcohols were used as the substrates, the corresponding products **7** and **8** were obtained, albeit with lower yields.

Inspired by these initial results^[17] and taking into consideration the interest of SCF₂R-containing molecules, we investigated the possibility to have a general approach towards these fluorinated compounds.

We first studied the (diethyl phosphono)difluoromethylthiolation reaction of the 5-phenyl-1-pentanol as a model substrate. After a short optimization, the optimal reaction conditions turned out to be when the transformation was carried out in toluene, in the presence of PIDA and the reagent **II** under blue light irradiation (Table 1, entry 1). Any changes from these reaction conditions such as the nature of the solvent (Table 1, entries 2–4) and the concentration (Table 1, entry 5) led to a significant drop of the reaction efficiency. Replacement of the hypervalent iodine source from PIDA to PIFA afforded the expected product in only 35% ¹⁹F NMR yield (Table 1, entry 6). A control experiment was conducted in the absence of light irradiation, leading to a total shutdown of the reactivity (Table 1, entry 7).

With the best reaction conditions in hand, the remote (diethyl phosphono)difluoromethylthiolation of primary, secondary and tertiary alcohols was studied (Scheme 3).

The selective functionalization of a panel of primary alcohols was achieved (12 examples). 5-Aryl-1-pentanol derivatives were suitable in this transformation and the corresponding products **9–11** were isolated in up to 51% yield. Moreover, pentanol, octanol and 1-dodecanol were efficiently functionalized. Pleasingly, the transformation turned out to be tolerant to various functional groups such as a chlorine atom, an azide or a protected primary amine, and the desired products **15–17** were smoothly obtained in up to 81% yield. With a substrate bearing two potential



Scheme 3. Distal Construction of a Carbon–SCF₂PO(OEt)₂ Bond on Aliphatic Alcohols. Reaction conditions: 1) alcohol (1 mmol, 5 equiv.), **I** (0.2 mmol, 1 equiv.), PIDA (0.46 mmol, 2.3 equiv.), toluene (0.13 M), 22 °C, 15 h, Argon, blue LEDs 450 nm 30 W. 2) MeCOCl (27 mmol, 135 equiv.), 22 °C, 10 min, Argon. The diastereomeric ratios were determined by ¹⁹F NMR spectroscopy of the crude reaction mixture. ^[a] The product contains an inseparable impurity.

sites to be functionalized, the (diethyl phosphono)difluoromethylthiolation was selective to the secondary position and the product **18** was selectively obtained in 72% yield as a mixture of diastereoisomers. When the reaction was carried out with alcohols substituted with a cyclohexyl at the γ or δ positions, products **19** and **20**, bearing a quaternary center, were isolated in 58% and 61% yields, respectively. Functionalization of acyclic and cyclic secondary alcohols went smoothly, affording compounds **21** and **22** as a mixture of diastereoisomers in 62% and 53% yields, respectively. Finally, when a tertiary alcohol was used in this reaction, **23** was isolated in 56% yield.

To further demonstrate the synthetic utility of the methodology, the remote incorporation of the interesting SCF₂CO₂Et^[18,19] and SCF₂H moieties^[7c,e,20] was studied (Scheme 4). Using our in-home reagent **III**,^[19] the desired acyclic and cyclic acetylated alcohols **24**

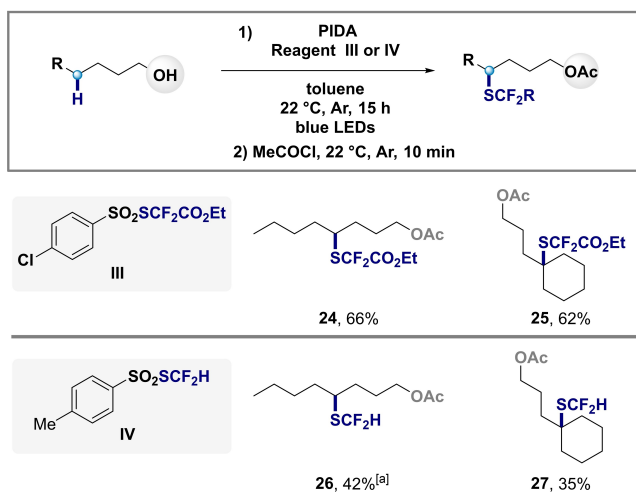
Table 1. Optimization of the remote (diethyl phosphono)difluoromethylthiolation reaction with the reagent **II**.

| Entry | Variation from standard reaction conditions | Yield (%) ^[a] |
|-------|--|--------------------------|
| 1 | None | (51) ^[b] |
| 2 | CH ₂ Cl ₂ instead of toluene | 36 |
| 3 | THF instead of toluene | 12 |
| 4 | MeCN instead of toluene | 20 |
| 5 | Toluene 0.3 M instead of 0.13 M | 38 |
| 6 | PIFA instead of PIDA | 35 |
| 7 | No light | NR |

^[a] Yields were determined by ¹⁹F NMR spectroscopy using the α,α,α-trifluoroacetophenone as an internal standard.

^[b] Isolated yields were given in parentheses.

NR = No Reaction.



Scheme 4. Extension to the formation of a C–SCF₂CO₂Et and C–SCF₂H bonds at the δ -position. Reaction conditions: 1) alcohol (1 mmol, 5 equiv.), **III** or **IV** (0.2 mmol, 1 equiv.), PIDA (0.46 mmol, 2.3 equiv.), toluene (0.13 M), 22 °C, 15 h, Argon, blue LEDs 450 nm 30 W. 2) MeCOCl (27 mmol, 135 equiv.), 22 °C, 10 min, Argon. ^[a] The product contains an inseparable impurity.

and **25** were isolated in 66% and 62% yields, respectively. Pleasingly the methodology was also applied to the synthesis of the high-value added difluoromethylthiolated compounds **26** and **27**, albeit in lower yields.

In order to get more information about the transformation, radical trapping experiments were conducted. When the reaction was carried out in the presence of the 3,5-di-*tert*-4-butylhydroxytoluene (BHT, 2–4 equiv.) or 2,2,6,6-tetramethylpiperidine-*N*-oxyl (TEMPO, 2–4 equiv.), no product was observed by ¹⁹F NMR.^[21] These results suggested that a free radical pathway might be involved and reinforced our working hypothesis shown in Scheme 1, B.

In summary, we developed a methodology allowing the remote and direct construction of a C(*sp*³)–SCF₂R bond on aliphatic alcohols by 1,5-Hydrogen Atom Transfer. This transition metal-free approach provided an access to otherwise difficult-to-synthesize fluorinated molecules. A panel of fluorinated moieties was incorporated with a complete regioselectivity at a distal position on primary, secondary and even tertiary alcohols (27 examples, up to 81% yield). The salient features of this transformation are the use of free-alcohols, the absence of photocatalysts or transition metal catalysts, the versatility and applicability of the method to various SCF₂R groups and the total control of the regioselectivity for the δ -position. By tackling an unmet synthetic goal, this approach paves the way towards synthetic routes to fluorinated scaffolds and considerably extends the portfolio of aliphatic SCF₂R-containing molecules.

Experimental Section

General procedure for the preparation of trifluoromethylthiolated products 1–8. An oven-dried microwave tube equipped with a stirring bar under argon was charged with PIDA (296 mg, 0.9 mmol, 2.3 equiv.), freshly distilled degassed CH₂Cl₂ (3 mL), **I** (102 mg, 0.4 mmol, 1 equiv.), followed by the suitable alcohol (2 mmol, 5 equiv.). The mixture was stirred at 20 °C for 16 h under irradiation with a blue LEDs (450–455 nm) placed 5 cm away. α,α,α -Trifluoroacetophenone (56 μ L, 0.4 mmol, 1 equiv.) was added as an internal standard. The reaction volume was halved *via* argon bubbling and acetyl chloride (3.9 mL, 56 mmol, 135 equiv.) was added. The mixture was stirred at 20 °C for 10 min. Upon full conversion by TLC, the crude mixture was poured onto an ice-cold saturated solution of NaHCO₃ (100 mL). The aqueous layer was extracted with CH₂Cl₂ (3 \times 30 mL). The combined organic layers were washed with brine (70 mL), dried over Na₂SO₄, concentrated under vacuum, and purified by flash column chromatography to afford the desired products **1–8**.

General procedure for the preparation of SCF₂R-containing products 9–27. The reagent **II**, **III** or **IV** (0.2 mmol, 1 equiv.) was charged in an oven-dried 10 mL tube equipped with a stirring bar and filled under argon followed by PIDA (148 mg, 0.46 mmol, 2.3 equiv.) and 1.5 mL of toluene. Then, the alcohol **1** (1 mmol, 5 equiv.) was finally introduced and the tube was put in a home-made box and the resulting mixture was placed 5 cm away from the blue LEDs (450 nm, 30 W) and stirred at 22 °C for 15 h. Acetyl chloride (2 mL, 23 mmol, 135 equiv.) was added and the mixture was stirred at 22 °C during 10 min under Argon. The resulting crude mixture was poured into 100 mL of a saturated solution of NaHCO₃ at 0 °C and the aqueous layer was extracted with 3 \times 50 mL of CH₂Cl₂. Then, the combined organic layers were dried under Na₂SO₄, filtered and concentrated under vacuum. The crude was purified by flash column chromatography on silica to afford the desired product.

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- [21] For more details, see the Supporting Information.