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Remote trifluoromethylthiolation of alcohols under visible light

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ABSTRACT

An unprecedented remote and regioselective trifluoromethylthiolation reaction of alcohols was developed. Under mild conditions, a panel of free-alcohols was selectively functionalized with $TolSO_2SCF_3$ reagent as the SCF_3 source in the presence of hypervalent iodide (PIDA) under blue light irradiation. This approach offered an operationally simple tool for the construction of a challenging C(sp^3)-SCF_3 bond at the δ-position of an alcohol by C(sp^3)-H bond functionalization. Initial mechanistic studies suggested a radical pathway.

1. Introduction

Organofluorine chemistry is a fascinating research field. Beyond the strong interest that represents fluorinated molecules in several fields such as pharmaceuticals and agrochemicals industries [1], the quest for new tools to overcome difficult-to-achieve synthetic challenges is of prime importance in organic chemistry to extend the portfolio of fluorinated molecules [2]. Indeed, the incorporation of a fluorine atom or a fluorinated group onto a molecule constitutes an efficient way to modulate their physical and chemical properties thanks to the unique properties of the fluorine atom [3]. Any advances will therefore have a strong impact, offering new synthetic pathways to this highly important class of compounds.

Among the fluorinated groups, the SCF_3 residue appeared as a promising motif due to its unique features such as its high electron-withdrawing character and its Hansch parameter [4]. Taking into account these considerations, several research groups dedicated a lot of efforts to offer straightforward and efficient methodologies to introduce such moiety on aromatic, vinylic and aliphatic derivatives [5,6]. Besides, the direct functionalization of a simple C–H bond proved to be very attractive as it affords more step- and atom-economic processes. Although key advances were made for the functionalization of C(sp^3)-H bond with a fluorine atom *via* transition metal catalysis and photocatalysis, the number of reports regarding the introduction of other fluorinated groups is still limited [7–9]. Only a handful of methods allowed the formation of a C(sp^3)-SCF_3 by C(sp^3)-H functionalization [10] and the trifluoromethylthiolation of a C(sp^3)-H bond at a remote position of a functional group remains a challenge, restricted to few examples. Recently, major contributions from the groups of Leonori [11] and Cook [12] described a visible-light-mediated radical cascade process for the synthesis of SCF_3-containing nitrogen heterocycles as well as a copper-catalyzed trifluoromethylthiolation of sulfonamides and amides, respectively. In that context, our purpose was to develop a synthetic tool, which would allow the distal trifluoromethylthiolation of simple and inexpensive alcohols, a ubiquitous functional group. Among others, 1,5-HAT process is one of the strategies used for the remote functionalization of alcohols *via* the *in situ* generation of alkoxy radicals, usually generated from alcohol surrogates or peroxides [13]. In contrast, only few reports depicted the *in situ* generation of an alkoxy radical directly from a free-alcohol [14].

To reach that challenging goal and inspired by the recent work of Zhu, who demonstrated the possibility to employ hypervalent iodine as a radical promotor with alcohols [14d], we envisioned the introduction of a SCF_3 group at a remote position of an alcohol.

Indeed, we hypothesized that in the presence of a proper oxidant and under light irradiation, an alkoxy radical would be generated and would undergo a 1,5-HAT event to afford the

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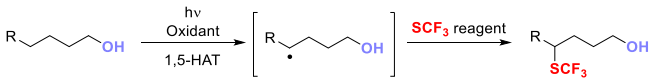


Scheme 1. Working hypothesis for the remote trifluorome-thylthiolation reaction of alcohol derivatives.

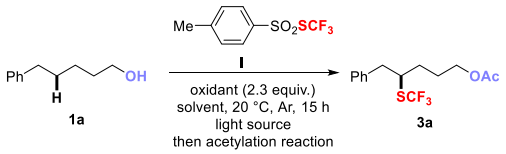
corresponding alkyl radical. This latter would react with a SCF_3 reagent to furnish the corresponding δ-trifluoromethylthiolated alcohol (Scheme 1). With this goal in mind, we selected a new class of SCF_3 sources, namely $ArSO_2SCF_3$ [15]. Herein we report our recent study regarding the first remote trifluoromethylthiolation reaction of free-alcohols under visible light irradiation.

2. Results and discussions

At the outset of the project, a reaction was performed using 5-phenyl-1-pentanol **1a** as model substrate in the presence of $TolSO_2SCF_3$ (reagent **I**) and PIDA under blue light irradiation. Pleasingly, the expected trifluoromethylthiolated product was observed in a 55% NMR yield as a mixture of the corresponding alcohol **2a** and the acetylated one **3a** (Table 1, entry 1). When PIFA was used, a lower yield of the trifluoromethylthiolated products was obtained (Table 1, entry 2). Therefore, we pursue the optimization by a two-steps process (trifluoromethylthiolation/acetylation) to get selectively **3a**. Other solvents such as 1,2-dichloroethane, DMF, acetonitrile and acetone were tested leading in all cases to lower yields (Table 1, entries 3–6). When PIDA was used as the oxidant under more diluted conditions (Table 1, entry 7), **3a** was isolated in an encouraging 49% yield. The reaction is highly selective to the δ position as no other regioisomer was observed [16]. Then, the nature of the oxidant, the reaction concentration as well as the stoichiometry of the oxidant and **1a** were further investigated but no significant improvement was observed (Table 1, entries 8–14). Therefore, PIDA was selected as the oxidant. Indeed, even if the NMR yield obtained with $PhI(OPiv)_2$ was similar to the one obtained with PIDA, the pivaloylation step has been less efficient than the acylation one. Switching from blue LEDs to white bulb (14W or 15.5W, Table 1, entries 15 and 16) led to no conversion. A control experiment carried out in the dark showcased the importance of light in this process (Table 1, entry 17). When the reaction was conducted under air, no significant change was obtained (Table 1, entry 18). Finally, by tuning the irradiation wavelength of the lamp and the reaction time (Table 1, entries 19–22), the best reaction conditions were obtained affording **3a** in 51% yield (Table 1, entry 22).

With the best reaction conditions in hand, we explored the scope of the reaction (Scheme 2). Trifluoromethylthiolation of primary alcohols was first investigated and decent yields were obtained taking into consideration the volatility and the tedious purification of the products. The corresponding acetylated products **3** were obtained with a complete regioselectivity. A panel of alcohols were functionalized with the SCF_3 group such as those having electron rich and electron poor aryl as substituents (**3b** and **3c**) and an alcohol bearing a naphthyl group (**3d**) was isolated in 39% yield. Even alcohols with a simple aliphatic chain (1-pentanol **1e** and 1-octanol **1f**) were trifluoromethylthiolated in moderate yields. Various functional groups such as an ester, an azide and a protected primary amine were tolerated (**3g-i**). In addition, the reaction of alcohols **1j** and **1k** substituted with a cyclohexyl or an adamantanyl group at the C3 position smoothly led to **3j** in 44% yield as a mixture of diastereoisomers (dr = 1.2/1) and **3k** in 42% yield. The reaction was not restricted to the functionalization of secondary $C(sp^3)$ centers as the introduction of the SCF_3 group was also possible on the more sterically hindered methine (**3l**). Finally, when secondary (**1m** and **1n**) and tertiary (**1o**) acyclic alcohols and even the cyclic secondary alcohol **1p** were engaged in the reaction, the corresponding trifluoromethylthiolated compounds **3m-p** were obtained in lower yields.

Table 1
Optimization of the remote trifluoromethylthiolation of the alcohol **1a**.[a]



Entry	Oxidant	Light source	Solvent	Yield 2a+3a (%)[b]
1[c,d]	PIDA	Blue LEDs 34W	CH_2Cl_2	55
2[c,d]	PIFA	Blue LEDs 34W	CH_2Cl_2	33
3[c,d]	PIDA	Blue LEDs 34W	$ClCH_2CH_2Cl$	54
4[c,d]	PIDA	Blue LEDs 34W	DMF	31
5[c,d]	PIDA	Blue LEDs 34W	CH_3CN	39
6[c,d]	PIDA	Blue LEDs 34W	acetone	28
7	PIDA	Blue LEDs 34W	CH_2Cl_2	72 (49)[e]
8	$PhI(OPiv)_2$	Blue LEDs 34W	CH_2Cl_2	73[f] (38)[e]
9	PhIO	Blue LEDs 34W	CH_2Cl_2	52
10[g]	PIDA	Blue LEDs 34W	CH_2Cl_2	47
11[h]	PIDA	Blue LEDs 34W	CH_2Cl_2	67
12[i]	PIDA	Blue LEDs 34W	CH_2Cl_2	53
13[j]	PIDA	Blue LEDs 34W	CH_2Cl_2	55
14[k]	PIDA	Blue LEDs 34W	CH_2Cl_2	43
15	PIDA	White bulb 14W	CH_2Cl_2	NR
16	PIDA	White bulb 15.5W	CH_2Cl_2	NR
17	PIDA	darkness	CH_2Cl_2	NR
18[l]	PIDA	Blue LEDs 34W	CH_2Cl_2	63
19	PIDA	405 nm	CH_2Cl_2	69
20	PIDA	450–455 nm	CH_2Cl_2	73 (50)[e]
21	PIDA	475–480 nm	CH_2Cl_2	27
22[m]	**PIDA**	**450–455 nm**	**CH_2Cl_2**	**76 (51)**[e]

NR = no reaction. PIDA = (Diacetoxyiodo)benzene. PIFA = [Bis(trifluoroacetoxy) iodo]benzene.

[a] Reaction conditions: **1a** (5 equiv.), **I** (0.2 mmol, 1 equiv.), oxidant (2.3 equiv.), solvent (1.5 mL), 20 °C, 15 h, argon.

[b] Yields determined by ^{19}F NMR of the crude reaction mixture after the trifluoromethylthiolation step using α,α,α-trifluoroacetophenone as an internal standard.

[c] 1 mL of CH_2Cl_2 was used.

[d] No acetylation reaction.

[e] Isolated yield of **3a** after acetylation reaction; for detailed reaction conditions, see Supporting Information.

[f] PivCl was used instead of AcCl for the second step.

[g] 0.5 mL of CH_2Cl_2 was used.

[h] 2.5 mL of CH_2Cl_2 was used.

[i] 5 equiv. of PIDA.

[j] 1.5 equiv. of PIDA.

[k] 3 equiv. of **1a**.

[l] Reaction conducted under an air atmosphere.

[m] 16 h.

In order to suggest a plausible mechanism involved in our reaction, the reaction was performed in the presence of a radical inhibitor [17]. The reaction carried out in the presence of BHT did not afford traces of the trifluoromethylthiolated alcohol by ^{19}F NMR, which strongly supported a radical pathway (Scheme 3, a). Based on this result and the literature data [14d], the following mechanism was suggested (Scheme 3, b). The first step might be the formation of the dialkoxyiodo benzene intermediate **A** in the presence of the alcohol **1**. Under irradiation, the homolysis of the intermediate **A** might lead to the formation of the alkoxy radical **B**, which might provide an alkyl radical **C** after a 1,5-HAT event. This alkyl radical could then directly react with the $TolSO_2SCF_3$ (reagent

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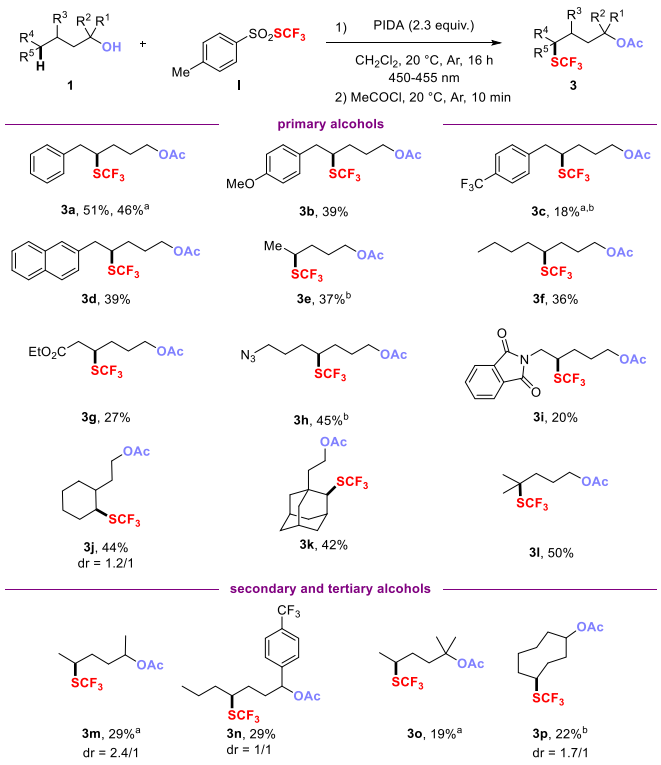
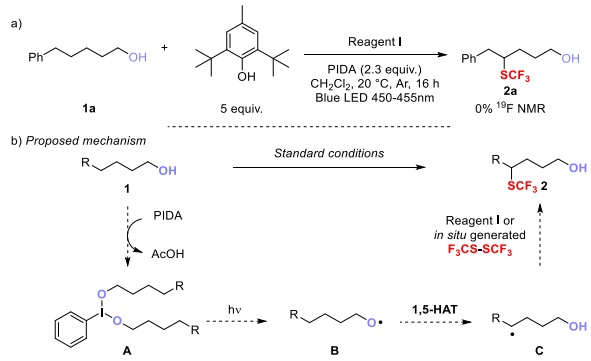


Scheme 2. Remote trifluoromethylthiolation of alcohol derivatives **1**: scope of the reaction. Reaction conditions: 1) **1a** (5 equiv.), **I** (0.4 mmol, 1 equiv.), PIDA (2.3 equiv.), CH_2Cl_2 (3 mL), 20 °C, 16 h, argon then 2) MeCOCl, 20 °C, 10 min under argon. [a] The reaction was carried out using 1.2 mmol of **I**. [b] The product was obtained with an inseparable impurity.



Scheme 3. Control experiment and proposed mechanism.

I) or alternatively, with an *in situ* generated CF_3SSCF_3 dimer, to afford the expected trifluoromethylthiolated product.

3. Conclusion

In conclusion, we developed a straightforward access to δ-trifluoromethylthiolated alcohols under mild and simple reaction conditions. Under blue light irradiation (450–455 nm), this process allows the challenging C(sp^3)-SCF_3 bond formation of a large variety of alcohols with PIDA as a promoter with a complete regioselectivity. Indeed, simple primary, secondary and tertiary unprotected alcohols were functionalized on secondary and tertiary carbon centers and the transformation turned out to be tolerant to various functional groups. Preliminary mechanistic studies suggested a radical pathway for this transformation.

4. Experimental section

4.1. Material and instrumentation

All reactions were carried out using oven-dried glassware and magnetic stirring under argon unless otherwise stated. Analytical thin layer chromatography was performed on silica gel aluminum plates with F-254 indicator and visualized by UV light (254 nm) and/or chemical staining with a $KMnO_4$ solution, *p*-anisaldehyde or a phosphomolybdic acid solution. Flash column chromatography was performed using 0.040–0.063 nm silica gel. Reverse-phase chromatography was performed with a Puriflash® interchim 4250 using a Thermoscientific® hypersil gold 5 μm. ^{1}H NMR spectra were recorded on a Bruker DXP 300 MHz spectrometer at 300.1 MHz, ^{13}C NMR spectra at 75.5 MHz and ^{19}F NMR spectra at 282.4 MHz. Chemical shifts (δ) are quoted in ppm relative to $CDCl_3$ (^{1}H, ^{13}C) and $CFCl_3$ (^{19}F). Coupling constants (J) are reported in Hz. The following abbreviations were used to show the multiplicities: s: singlet, d: doublet, t: triplet, q: quadruplet, dd: doublet of doublet, m: multiplet. The residual solvent signals were used as references ($CDCl_3$: δ_H = 7.26 ppm, δ_C = 77.00 ppm) or relative to internal standard ($CFCl_3$: δ_F = 0 ppm). High-resolution mass spectrometry (HRMS) was recorded with a Waters LCT Premier mass spectrometer with a micro-TOF analyzer. IR spectra were recorded on a PerkinElmer Spectrum 100, the wave numbers (ν) of recorded IR-signals (ATR) are quoted in cm^{-1}. Melting points were reported for new compounds, recorded on a Heizbank system Kofler WME and were uncorrected.

Tetrahydrofuran (THF) and toluene were distilled over sodium/benzophenone and dichloromethane (CH_2Cl_2) was distilled over CaH_2 prior use. HPLC grade methanol (MeOH) was used for hydrogenation. Dry *N*,*N*-dimethylformamide (DMF) over molecular sieve from Acros Organic was used. *n*-Butylamine purchased from Merck was used without purification. Unless otherwise stated, the reaction optimization was performed using a PhotoRedOx Box supplied by HepatoChem® using a 34W blue kessil LED. An Evoluchem® P201-18-2 450–455 nm 18W was used for the photochemical reactions. All commercially available alcohols were used without prior purification. Alcohols **1b**, **1c**, **1d, 1h**, **1i** and **1n** were prepared as described below.

4.2. General procedures

4.2.1. Procedure for the synthesis of S-(Trifluoromethyl)-4-methylbenzenesulfonothioate *I*

The procedure was adapted from a previously reported procedure [18]. Sodium 4-methylbenzenesulfinate (4.0 g, 23 mmol, 1.5 equiv.) and *N*-trifluoromethylthiophthalimide [19] (3.7 g, 15 mmol, 1 equiv.) were placed into an over-dried flask equipped with a stirring bar under Ar, then glacial acetic acid (75 mL) was added. The reaction was stirred 2 h at 25 °C, protected from light. After full conversion observed by ^{19}F NMR, 60 mL of brine and 300 mL of Et_2O were added, and the organic layer was separated. The aqueous layer was extracted with Et_2O (3 × 100 mL) and the combined organic layers were washed with a saturated aqueous solution of $NaHCO_3$ (3 × 200 mL). The combined organic layers were dried over Na_2SO_4 and concentrated under vacuum. The residue was purified by flash column chromatography on silica gel (height: 17 cm, width: 4 cm, Petroleum ether/EtOAc = 90/10) to afford **I** as a pale-yellow oil (3.3 g, 12.9 mmol, **86%**).

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*4.2.2. General procedure for the synthesis of the alcohols **1b-d** with a representative example for the synthesis of 5-(naphthalen-2-yl) pentan-1-ol **1d***

5-(Naphthalen-2-yl)pentan-1-ol **1d** was synthesized following the literature [20]. An oven-dried Schlenk tube equipped with a Rotaflo® tap, under nitrogen, was charged with $PdCl_2(PPh_3)_2$ (168 mg, 0.24 mmol, 0.05 equiv.) and degassed n-$BuNH_2$ (10 mL). Then, CuI (91 mg, 0.48 mmol, 0.1 equiv.) was added along with 2-bromonaphthalene (1.0 g, 4.8 mmol, 1 equiv.) and 4-pentyn-1-ol (493 μL, 5.3 mmol, 1.1 equiv.). The tube was sealed and the mixture stirred at 80 °C for 17 h. After cooling down, the reaction was quenched with a saturated aqueous solution of NH_4Cl (30 mL) and the aqueous layer was extracted with ethyl acetate (3 × 30 mL). The combined organic layers were washed with water (3 × 100 mL), brine (100 mL), dried over Na_2SO_4 and concentrated under vacuum. The crude material was purified by flash chromatography (height: 17 cm, width: 4 cm, Petroleum ether/EtOAc = 70/30) to afford **1d-*int*** as a beige solid (0.930 g, **87%**). An oven-dried 100 mL round-bottomed flask, under nitrogen, was charged with Pd/C (93 mg, 10% w/w) followed by **1d-*int*** (0.9 g, 4.4 mmol, 1 equiv.) dissolved in MeOH (44 mL). The flask was evacuated then backfilled with hydrogen three times. The mixture was stirred at 25 °C for 17 h. Then, the crude mixture was filtered over celite, concentrated under vacuum and purified by flash chromatography (height: 17 cm, width: 4 cm; Petroleum ether/EtOAc = 70/30) to afford **1d** as a colorless oil (0.834 g, 3.9 mmol, **89%**).

*4.2.3. Procedure for the synthesis of 8-azidooctan-1-ol **1h***

An oven dried 3-neck round bottom flask equipped with a reflux condenser was charged with sodium azide (2.4 g, 32.4 mmol, 2 equiv.). The flask was evacuated under high vacuum and backfilled with argon three times. Dry DMF (26 mL) was added followed by 8-chlorooctanol (2.8 mL, 16.2 mmol, 1 equiv.). The reaction mixture was stirred at 60 °C for 16 h. The reaction mixture was diluted with diethyl ether (100 mL) and the organic layer was washed with water (5 × 150 mL). The combined organic layers were dried over Na_2SO_4 and concentrated under vacuum. The crude mixture was purified by flash column chromatography (height: 15 cm, width: 4 cm, Cyclohexane/EtOAc = 70/30) to afford **1h** as a colorless oil (2.1 g, 12.2 mmol, **75%**).

*4.2.4. Procedure for the synthesis of 5-phthalimido-1-pentanol **1i***

5-Phthalimido-1-pentanol **1i** was synthesized following the literature [21]. A round-bottom flask, equipped with a condenser, under argon, was charged with 5-aminopentanol (1 mL, 9 mmol, 1 equiv.), phthalimide (2.2 g, 15.3 mmol, 1.7 equiv.) and toluene (9 mL). Iron-(III) nitrate nonahydrate (181.8 mg, 0.45 mmol, 0.05 equiv.) was added and the reaction mixture was stirred at 110 °C for 24 h. The reaction mixture was filtered over celite® and the solvent was evaporated under vacuum. The crude mixture was purified by flash column chromatography (height: 20 cm, width: 4 cm, CH_2Cl_2/EtOAc = 90/10) to afford **1i** as a colorless oil (1.3 g, 5.4 mmol, **60%**).

*4.2.5. Procedure for the synthesis of 1-[(4-trifluoromethyl)phenyl]-1-heptanol **1o***

1-[(4-Trifluoromethyl)phenyl]-1-heptanol **1o** was synthesized following the literature [22]. An oven-dried round-bottom flask, under argon, was charged with 4-(trifluoromethyl)benzaldehyde (780 μL, 5.7 mmol, 1 equiv.), then evacuated under high vacuum and backfilled with argon three times. Freshly distilled THF (10 mL) was added. A solution of hexyllithium in hexanes (2.2 M, 5.2 mL, 11.5 mmol, 2 equiv.) was diluted in freshly distilled THF (10 mL) and added dropwise at −78 °C to the reaction mixture. The reaction mixture was then allowed to warm up to room temperature and stirred for 2 h at 25 °C. Then, water (10 mL) was added, and the aqueous layer was extracted with Et_2O (3 × 15 mL). The combined organic layers were dried over Na_2SO_4 and concentrated under vacuum. The crude mixture was purified by flash column chromatography (height: 20 cm, width: 3 cm, Cyclohexane/EtOAc = 90/10) to afford **1o** as a yellow oil (1.11 g, 4.05 mmol, **71%**).

*4.2.6. General procedure for the synthesis of the derivatives **3***

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 CH_2Cl_2 (3 mL), **I** (102 mg, 0.4 mmol, 1 equiv.) followed by **1** (2 mmol, 5 equiv.). The mixture was stirred at 20 °C for 16 h under irradiation with a blue LED (450–455 nm) placed 5 cm away. α,α,α-Trifluoroacetophenone (56 μL, 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 $NaHCO_3$ (100 mL). The aqueous layer was extracted with CH_2Cl_2 (3 × 30 mL). The combined organic layers were washed with brine (70 mL), dried over Na_2SO_4, concentrated under vacuum and purified by flash column chromatography to afford the desired product **3**.

4.3. Physical and spectral data

*4.3.1. S-(Trifluoromethyl)-4-methylbenzenesulfonothioate **I***

$\mathbf{R_f}$ (Petroleum ether/EtOAc = 90/10): 0.3. **^{1}H NMR** (300.1 MHz, $CDCl_3$) δ 7.88 (d, *J* = 7.8 Hz, 2H), 7.40 (d, *J* = 7.9 Hz, 2H), 2.49 (s, 3H). **^{19}F NMR** (282.4 MHz, $CDCl_3$) δ −39.0 (s, 3F), *NMR data are in accordance with the literature data.* [23].

*4.3.2. 5-(4-Methoxyphenyl)pentan-1-ol **1b***

Purification by flash column chromatography (height: 15 cm, width: 3 cm, Petroleum ether/EtOAc = 80/20 to 70/30) afforded **1b** as a colorless oil (0.797 g, 0.21 mmol, **52%**) from 4-bromoanisole (1.0 mL, 8 mmol), according to the procedure described above. $\mathbf{R_f}$ (petroleum ether/EtOAc = 80/20): 0.3. **^{1}H NMR** (300.1 MHz, $CDCl_3$) δ 7.09 (d, *J* = 8.6 Hz, 2H), 6.82 (d, *J* = 8.6 Hz, 2H), 3.79 (s, 3H), 3.70–3.56 (m, 2H), 2.64–2.49 (m, 2H), 1.72–1.51 (m, 4H), 1.46–1.32 (m, 2H). *The −OH proton was not observed in ^{1}H NMR. NMR data are in accordance with the literature data.* [24].

*4.3.3. 5-(4-(Trifluoromethyl)phenyl)pentan-1-ol **1c***

Purification by flash column chromatography (height: 15 cm, width: 3 cm, Petroleum ether/EtOAc = 80/20) afforded **1c** as a colorless oil (0.66 g, 0.13 mmol, **33%**) from 1-bromo-4-(trifluoromethyl)benzene (1.61 mL, 8 mmol) according to the procedure described above. $\mathbf{R_f}$ (petroleum ether/EtOAc = 80/20): 0.3. **^{1}H NMR** (300.1 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.1 Hz, 2H), 7.28 (d, *J* = 8.1 Hz, 2H), 3.76–3.56 (m, 2H), 2.75–2.60 (m, 2H), 1.73–1.54 (m, 4H), 1.49–1.33 (m, 2H). **^{19}F NMR** (282.4 MHz, $CDCl_3$) δ −62.8 (s, 3F). *The −OH proton was not observed in ^{1}H NMR. NMR data are in accordance with the literature data.* [25].

*4.3.4. 5-(Naphthalen-2-yl)pentan-1-ol **1d***

$\mathbf{R_f}$ (Petroleum ether/EtOAc = 70/30): 0.5. **^{1}H NMR** (300.1 MHz, $CDCl_3$) δ 7.84–7.73 (m, 3H), 7.61 (s, 1H), 7.49–7.37 (m, 2H), 7.34 (dd, *J* = 8.2, 0.8 Hz, 1H), 3.71–3.59 (m, 2H), 2.80 (dd, *J* = 7.8, 7.8 Hz, 2H), 1.83–1.70 (m, 2H), 1.69–1.56 (m, 2H), 1.52–1.39 (m, 2H). *The −OH proton was not observed in ^{1}H NMR. NMR data are in accordance with the literature data* [26].

*4.3.5. 8-Azidooctan-1-ol **1h***

$\mathbf{R_f}$ (Cyclohexane/EtOAc = 70/30): 0.5. **^{1}H NMR** (300.1 MHz, $CDCl_3$) δ 3.60 (t, *J* = 6.6 Hz, 2H), 3.23 (t, *J* = 6.9 Hz, 2H), 1.96–1.88 (m,

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1H), 1.61–1.24 (m, 12H). **^{13}C NMR** (75.5 MHz, $CDCl_3$) δ 62.7, 51.3, 32.6, 29.1, 29.0, 28.7, 26.5, 25.5. **IR** (neat, cm^{-1}) ν: 3336, 2929, 2857, 2090, 1463, 1349, 1251, 1055, 892, 724, 636, 556. **HRMS** (EI^+) calcd for $C_8H_{17}NO$ *m/z* 143.1310 $[M-N_2]^+$, found 143.1304 (Δ = −4.55 ppm).

*4.3.6. 5-Phthalimido-1-pentanol **1i***

R_f (CH_2Cl_2/EtOAc = 90/10): 0.51. **^{1}H NMR** (300.1 MHz, $CDCl_3$) δ 7.85–7.73 (m, 2H), 7.73–7.60 (m, 2H), 3.74–3.52 (m, 4H), 2.09 (s, 1H), 1.75–1.51 (m, 4H), 1.45–1.30 (m, 2H). **^{13}C NMR** (75.5 MHz, $CDCl_3$) δ 168.4, 133.8, 131.9, 123.0, 62.3, 37.7, 32.0, 28.2, 22.9. *NMR data are in accordance with the literature data* [27].

*4.3.7. 1-[(4-Trifluoromethyl)phenyl]-1-heptanol **1n***

R_f (Cyclohexane/EtOAc = 90/10): 0.1. **^{1}H NMR** (300.1 MHz, $CDCl_3$) δ 7.58 (d, J = 7.8 Hz, 2H), 7.42 (d, J = 7.8 Hz, 2H), 4.77–4.63 (m, 1H), 2.45 (br s, 1H), 1.82–1.60 (m, 2H), 1.46–1.15 (m, 8H), 0.96–0.81 (m, 3H). **^{19}F NMR** (282.4 MHz, $CDCl_3$) δ −62.5 (s). **^{13}C NMR** (75.5 MHz, $CDCl_3$) δ 148.8, 129.6 (q, J = 32.4 Hz), 126.1, 125.3 (q, J = 3.8 Hz), 124.2 (q, J = 271.8 Hz), 74.0, 39.2, 31.7, 29.1, 25.6, 22.5, 14.0. **IR** (neat, cm^{-1}) ν: 3344, 2931, 2859, 1621, 1467, 1418, 1323, 1163, 1122, 1067, 1017, 842, 763, 732, 658, 543. **HRMS** (EI^+) calcd for $C_{14}H_{19}F_3O$ *m/z* 260.1388 $[M]^+$, found 260.1379 (Δ = −3.32 ppm).

*4.3.8. 5-Phenyl-4-((trifluoromethyl)thio)pentyl acetate **3a***

Purification by flash column chromatography (height: 15 cm, width: 3 cm, Petroleum ether/EtOAc = 98/2) afforded **3a** as a colorless oil (62 mg, 0.20 mmol, **51%**) from 5-phenyl-1-pentanol (336 μL, 2 mmol, 5 equiv.). A scale-up with **I** (307 mg, 1.2 mmol, 1 equiv.) and 5-phenyl-1-pentanol (1.0 mL, 6 mmol, 5 equiv.) led to **3a** (168 mg, 0.55 mmol **46%**). **R_f** (Petroleum ether/EtOAc = 98/2): 0.29. **^{1}H NMR** (300.1 MHz, $CDCl_3$) δ 7.38–7.14 (m, 5H), 4.03 (t, J = 6.0 Hz, 2H), 3.49–3.35 (m, 1H), 3.12 (dd, J = 13.9, 5.6 Hz, 1H), 2.90 (dd, J = 13.9, 8.5 Hz, 1H), 2.00 (s, 3H), 1.96–1.47 (m, 4H). **^{19}F NMR** (282.4 MHz, $CDCl_3$) δ −39.6 (s, 3F). **^{13}C NMR** (75.5 MHz, $CDCl_3$) δ 171.0, 137.6, 130.9 (q, J = 306.8 Hz), 129.3, 128.5, 126.9, 63.5, 47.0, 42.1, 29.9, 25.4, 20.8. **IR** (neat, cm^{-1}) ν: 3030, 2932, 2853, 1737, 1603, 1496, 1454, 1365, 1237, 1144, 1103, 1041, 743, 699, 634, 605, 555, 480, 451. **HRMS** (CI^+) calcd for $C_{12}H_{14}F_3S$ *m/z* 247.0768 $[M-OAc]^+$, found 247.0779 (Δ = 4.40 ppm).

*4.3.9. 5-(4-Methoxyphenyl)-4-((trifluoromethyl)thio)pentyl acetate **3b***

Purification by flash column chromatography (height: 15 cm, width: 3 cm, Petroleum ether/EtOAc = 95/5) afforded **3b** as a colorless oil (52 mg, 0.16 mmol, **39%**) from 5-(4-methoxyphenyl) pentan-1-ol (388 mg, 2 mmol, 5 equiv.). **R_f** (Petroleum ether/EtOAc = 95/5): 0.29. **^{1}H NMR** (300.1 MHz, $CDCl_3$) δ 7.10 (d, J = 8.5 Hz, 2H), 6.85 (d, J = 8.5 Hz, 2H), 4.03 (t, J = 6.0 Hz, 2H), 3.80 (s, 3H), 3.44–3.30 (m, 1H), 3.05 (dd, J = 14.3, 5.7 Hz, 1H), 2.84 (dd, J = 14.3, 8.3 Hz, 1H), 2.01 (s, 3H), 1.93–1.55 (m, 4H). **^{19}F NMR** (282.4 MHz, $CDCl_3$) δ −39.5 (s, 3F). **^{13}C NMR** (75.5 MHz, $CDCl_3$) δ 171.0, 158.5, 131.1 (q, J = 305.7 Hz), 130.3, 129.6, 113.9, 63.6, 55.2, 47.3, 41.2, 29.8, 25.4, 20.8. **IR** (neat, cm^{-1}) ν: 2956, 2839, 1737, 1612, 1584, 1512, 1465, 1365, 1301, 1243, 1178, 1145, 1104, 1035, 910, 832, 811, 755, 732, 648, 605, 522, 490. **HRMS** (API^+) calcd for $C_{15}H_{20}F_3O_3S$ *m/z* 337.1085 $[M+H]^+$, found 337.1087 (Δ = −0.90 ppm).

*4.3.10. 5-(4-(Trifluoromethyl)phenyl)-4-((trifluorome-thyl)thio) pentyl acetate **3c***

Purification by flash column chromatography (height: 15 cm, width: 3 cm, Petroleum ether/EtOAc = 98/2) afforded **3c** as a colorless oil (79 mg, 0.22 mmol, **18%**, *with an inseparable impurity*) from **I** (307 mg, 1.2 mmol, 1 equiv.) and 5-(4-(trifluoromethyl) phenyl)pentan-1-ol (1.39 g, 6 mmol, 5 equiv.). **R_f** (Petroleum ether/EtOAc = 98/2): 0.29. **^{1}H NMR** (300.1 MHz, $CDCl_3$) δ 7.58 (d, J = 8.0 Hz, 2H), 7.31 (d, J = 8.0 Hz, 2H), 4.05 (t, J = 5.9 Hz, 2H), 3.48–3.33 (m, 1H), 3.15 (dd, J = 14.2, 6.4 Hz, 1H), 2.99 (dd, J = 14.2, 8.3 Hz, 1H), 1.99 (s, 3H), 1.92–1.57 (m, 4H). **^{19}F NMR** (282.4 MHz, $CDCl_3$) δ −39.6 (s, 3F), −63.0 (s, 3F). **^{13}C NMR** (75.5 MHz, $CDCl_3$) δ 171.0, 141.7, 131.0 (q, J = 305.8 Hz), 129.7, 129.3 (q, J = 32.3 Hz), 125.5 (q, J = 3.7 Hz), 124.0 (q, J = 272.6 Hz), 63.4, 46.7, 41.9, 30.2, 25.5, 20.8. **IR** (neat, cm^{-1}) ν: 2940, 2866, 1735, 1620, 1420, 1366, 1323, 1241, 1161, 1107, 1066, 1018, 952, 909, 843, 817, 756, 732, 664, 634, 596, 507, 489. **HRMS** (CI^+) calcd for $C_{13}H_{13}F_6S$ *m/z* 315.0642 $[M-OAc]^+$, found 315.0643 (Δ = 0.28 ppm).

*4.3.11. **5**-(Naphthalen-2-yl)-4-((trifluoromethyl)thio)pentyl acetate **3d***

Purification by flash column chromatography (height: 15 cm, width: 3 cm, Pentane/EtOAc = 98/2 to 96/4) afforded **3d** as a colorless oil (56 mg, 0.16 mmol, **39%**) from 5-(naphthalen-2-yl) pentan-1-ol (373 mg, 2 mmol, 5 equiv.). **R_f** (Petroleum ether/EtOAc = 98/2): 0.2. **^{1}H NMR** (300.1 MHz, $CDCl_3$) δ 7.89–7.78 (m, 3H), 7.65 (s, 1H), 7.55–7.43 (m, 2H), 7.33 (dd, J = 8.2, 1.1 Hz, 1H), 4.03 (t, J = 6.0 Hz, 2H), 3.62–3.46 (m, 1H), 3.30 (dd, J = 14.0, 5.9 Hz, 1H), 3.07 (dd, J = 13.9, 8.7 Hz, 1H), 2.01–1.54 (m, 7H). **^{19}F NMR** (282.4 MHz, $CDCl_3$) δ −39.5 (s, 3F). **^{13}C NMR** (75.5 MHz, $CDCl_3$) δ 170.9, 135.1, 133.4, 132.4, 131.1 (q, J = 305.5 Hz), 128.2, 128.0, 127.6, 127.6, 127.3, 126.2, 125.7, 63.5, 46.9, 42.3, 29.9, 25.4, 20.7. **IR** (neat, cm^{-1}) ν: 3053, 2953, 2860, 1735, 1606, 1508, 1448, 1365, 1236, 1105, 1040, 957, 908, 856, 816, 748, 731, 634, 620, 605, 584, 557, 475. **HRMS** (API^+) calcd for $C_{16}H_{16}F_3S$ *m/z* 297.0925 $[M-OAc]^+$, found 297.0916 (Δ = −3.00 ppm).

*4.3.12. 4-((Trifluoromethyl)thio)pentyl acetate **3e***

Purification by flash column chromatography (height: 15 cm, width: 3 cm, Pentane/EtOAc = 98/2) afforded **3e** as a colorless oil (34 mg, 0.15 mmol, **37%**, *with an inseparable impurity*) from pentanol (217 μL, 2 mmol, 5 equiv.). **R_f** (Petroleum ether/EtOAc = 98/2): 0.3. **^{1}H NMR** (300.1 MHz, $CDCl_3$) δ 4.15–4.02 (m, 2H), 3.40–3.26 (m, 1H), 2.05 (s, 3H), 1.85–1.59 (m, 4H), 1.43 (d, J = 6.8 Hz, 3H). **^{19}F NMR** (282.4 MHz, $CDCl_3$) δ −39.7 (s, 3F). **^{13}C NMR** (75.5 MHz, $CDCl_3$) δ 171.1, 131.0 (q, J = 305.6 Hz), 63.8, 40.8, 33.3, 25.8, 22.3, 20.9. **IR** (neat, cm^{-1}) ν: 2966, 1739, 1454, 1385, 1365, 1234, 1189, 1178, 1149, 1101, 1051, 962, 913, 815, 755, 663, 634, 606, 555. **HRMS** (CI^+) calcd for $C_6H_{10}F_3S$ *m/z* 171.0455 $[M-OAc]^+$, found 171.0454 (Δ = −0.88 ppm).

*4.3.13. 4-((Trifluoromethyl)thio)octyl acetate **3f***

Purification by flash column chromatography (height: 15 cm, width: 3 cm, Pentane/EtOAc = 98/2) afforded **3f** as a colorless oil (39 mg, 0.14 mmol, **36%**) from octanol (314 μL, 2 mmol, 5 equiv.). **R_f** (Petroleum ether/EtOAc = 98/2): 0.3. **^{1}H NMR** (300.1 MHz, $CDCl_3$) δ 4.16–4.01 (m, 2H), 3.24–3.07 (m, 1H), 2.05 (s, 3H), 1.90–1.55 (m, 6H), 1.54–1.23 (m, 4H), 0.91 (t, J = 6.9 Hz, 3H). **^{19}F NMR** (282.4 MHz, $CDCl_3$) δ −39.6 (s, 3F). **^{13}C NMR** (75.5 MHz, $CDCl_3$) δ 171.0, 131.0 (q, J = 306.0 Hz), 63.8, 46.2, 34.8, 31.5, 28.5, 25.5, 22.3, 20.8, 13.8. **IR** (neat, cm^{-1}) ν: 2935, 2862, 1739, 1458, 1365, 1234, 1177, 1148, 1108, 1038, 953, 878, 807, 755, 733, 663, 634, 606, 555. **HRMS** (CI^+) calcd for $C_9H_{16}F_3S$ *m/z* 213.0925 $[M-OAc]^+$, found 213.0925 (Δ = 0.17 ppm).

*4.3.14. Ethyl 6-acetoxy-3-((trifluoromethyl)thio)hexanoate **3g***

Purification by flash column chromatography (height: 15 cm, width: 3 cm, Pentane/CH_2Cl_2 = 60/40 to 50/50 then Pentane/EtOAc = 95/5) afforded **3g** as a colorless oil (33 mg, 0.11 mmol, **27%**) from ethyl 6-hydroxyhexanoate (320 μL, 2 mmol, 5 equiv.). **R_f** (Petroleum ether/EtOAc = 98/2): 0.2. **^{1}H NMR** (300.1 MHz, $CDCl_3$)

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δ 4.18 (q, *J* = 7.2 Hz, 2H), 4.13–4.02 (m, 2H), 3.62–3.45 (m, 1H), 2.86–2.63 (m, 2H), 2.05 (s, 3H), 1.95–1.66 (m, 4H), 1.28 (t, *J* = 7.2 Hz, 3H). **^{19}F NMR** (282.4 MHz, $CDCl_3$) δ −39.9 (s, 3F). **^{13}C NMR** (75.5 MHz, $CDCl_3$) δ 171.0, 170.2, 130.7 (q, *J* = 306.7 Hz), 63.5, 61.0, 41.6, 40.8, 31.4, 25.9, 20.8, 14.1. **IR** (neat, cm^{-1}) *ν*: 2984, 2879, 1730, 1375, 1351, 1234, 1149, 1099, 1031, 945, 756, 634, 606, 474. **HRMS** (CI^+) calcd for $C_{11}H_{18}F_3O_4S$ *m/z* 303.0878 $[M+H]^+$, found 303.0882 (Δ = 1.33 ppm).

4.3.15. 8-Azide-4-((trifluoromethyl)thio)octyl acetate **3h**

Purification by flash column chromatography (height: 15 cm, width: 3 cm, Pentane/EtOAc = 80/20) afforded **3h** as a colorless oil (56 mg, 0.18 mmol, **45%**, *with an inseparable impurity*), from 8-azidooctan-1-ol (0.34 g, 2 mmol, 5 equiv.). R_f (Petroleum ether/EtOAc = 80/20): 0.4. **^{1}H NMR** (300.1 MHz, $CDCl_3$) δ 4.14–4.02 (m, 2H), 3.36–3.24 (m, 2H), 3.19–3.09 (m, 1H), 2.04 (s, 3H), 1.87–1.48 (m, 10H). **^{19}F NMR** (282.4 MHz, $CDCl_3$) δ −39.5 (s, 3F). **^{13}C NMR** (75.5 MHz, $CDCl_3$) δ 171.0, 131.0 (q, *J* = 306.5 Hz), 63.7, 51.1, 46.0, 34.7, 31.6, 28.5, 25.5, 23.6, 20.8. **IR** (neat, cm^{-1}) *ν*: 2959, 2932, 2862, 1741, 1457, 1365, 1236, 1106, 755. **HRMS** (AP^+) calcd for $C_{11}H_{19}F_3N_3O_2S$ *m/z* 314.1150 $[M+H]^+$, found 314.1145 (Δ = −1.6 ppm).

4.3.16. 5-Phthalimido-4-((trifluoromethyl)thio)pentyl acetate **3i**

Purification by reverse phase chromatography (height: 25 cm, width: 2 cm, H_2O/acetonitrile = 100/0 to 10/90) afforded **3i** as a white solid (30 mg, 0.08 mmol, **20%**) from 5-phthalimido-1-pentanol (0.47 g, 2 mmol, 5 equiv.). **mp** = 59–60 °C. R_f (Petroleum ether/EtOAc = 80/20): 0.1. **^{1}H NMR** (300.1 MHz, $CDCl_3$) δ 7.92–7.83 (m, 2H), 7.80–7.69 (m, 2H), 4.08 (t, *J* = 6.0 Hz, 2H), 4.00–3.81 (m, 2H), 3.70–3.56 (m, 1H), 2.01 (s, 3H) 1.91–1.60 (m, 4H). **^{19}F NMR** (282.4 MHz, $CDCl_3$) δ −39.7 (s, 3F). **^{13}C NMR** (75.5 MHz, $CDCl_3$) δ 170.9, 168.0, 134.2, 131.7, 130.6 (q, *J* = 307.3 Hz), 123.5, 63.5, 44.2, 42.1, 29.3, 25.5, 20.8. **IR** (neat, cm^{-1}) *ν*: 2924, 2854, 1773, 1740, 1713, 1469, 1429, 1397, 1366, 1247, 1149, 1028, 1108, 722. **HRMS** (CI^+) calcd for $C_{16}H_{17}F_3NO_4S$ *m/z* 376.0830 $[M+H]^+$, found 376.0838 (Δ = 1.97 ppm).

4.3.17. 2-(2-((Trifluoromethyl)thio)cyclohexyl)ethyl acetate **3j**

Purification by flash column chromatography (height: 15 cm, width: 3 cm, Pentane/CH_2Cl_2 = 30/70 to 50/50 then Pentane/EtOAc = 98/2) afforded **3j** as a colorless oil (47 mg, 0.18 mmol, **44%**, *d.r.* 1.2/1) from 2-cyclohexylethanol (279 μL, 2 mmol, 5 equiv.). R_f (Petroleum ether/EtOAc = 98/2): 0.3. **^{1}H NMR** (300.1 MHz, $CDCl_3$) δ 4.20–4.39 (m, 4H, *maj* + *min*), 3.59–3.50 (m, 1H, *min*), 2.89 (td, *J* = 10.1, 4.1 Hz, 1H, *maj*), 2.32–2.16 (m, 2H, *maj* + *min*), 2.08–1.90 (m, 8H, *maj* + *min*), 1.88–1.44 (m, 14H, *maj* + *min*), 1.38–1.23 (m, 3H, *maj* + *min*), 1.19–1.00 (m, 2H, *maj* + *min*). **^{19}F NMR** (282.4 MHz, $CDCl_3$) δ −39.3 (s, 3F, *min*), −40.1 (s, 3F, *maj*). **^{13}C NMR** (75.5 MHz, $CDCl_3$) δ 171.1 (*maj* + *min*), 131.5 (q, *J* = 305.6 Hz, *min*), 131.3 (q, *J* = 305.6 Hz, *maj*), 62.1 (*maj*), 62.0 (*min*), 49.8 (*maj*), 48.6 (*min*), 38.6 (*maj*), 37.6 (*min*), 35.3 (*maj*), 33.0 (*maj*), 32.6 (*min*), 32.1 (*min*), 31.6 (*min*), 28.6 (*maj*), 25.9 (*min*), 24.6 (*maj*), 24.5 (*maj*), 21.7 (*min*), 20.9 (*maj* + *min*). **IR** (neat, cm^{-1}) *ν*: 2933, 2859, 1738, 1449, 1388, 1367, 1233, 1144, 1100, 1043, 968, 757, 733, 697, 635, 606. **HRMS** (CI^+) calcd for $C_9H_{14}F_3S$ *m/z* 211.0768 $[M-OAc]^+$, found 211.0760 (Δ = −4.05 ppm).

4.3.18. 2-((1r,3s,5R,7S)-2-((Trifluoromethyl)thio)adamantan-1-yl) ethyl acetate **3k**

Purification by flash column chromatography (height: 15 cm, width: 3 cm, Pentane/CH_2Cl_2 = 30/70 to 50/50 then Pentane/EtOAc = 95/5) afforded **3k** as a colorless oil (54 mg, 0.17 mmol, **42%**) from 2-(adamantan-1-yl)ethan-1-ol (360 mg, 2 mmol, 5 equiv.). R_f (Petroleum ether/EtOAc = 98/2): 0.3. **^{1}H NMR** (300.1 MHz, $CDCl_3$) δ 4.24–4.05 (m, 2H), 3.37 (s, 1H), 2.27–2.16 (m, 1H), 2.09–1.57 (m, 15H), 1.54–1.37 (m, 2H). **^{19}F NMR** (282.4 MHz, $CDCl_3$) δ −40.0 (s, 3F). **^{13}C NMR** (75.5 MHz, $CDCl_3$) δ 171.1, 131.4 (q, *J* = 305.6 Hz), 60.0, 56.9, 42.3, 39.1, 38.6, 37.7, 36.4, 35.7, 35.4, 31.5, 27.6, 27.4, 21.0. **IR** (neat, cm^{-1}) *ν*: 2910, 2850, 1723, 1451, 1367, 1253, 1139, 1097, 1037, 979, 967, 951, 896, 826, 768, 754, 644, 609, 480. **HRMS** (CI^+) calcd for $C_{13}H_{18}F_3S$ *m/z* 263.1081 $[M-OAc]^+$, found 263.1091 (Δ = 3.63 ppm).

4.3.19. 4-Methyl-4-((trifluoromethyl)thio)pentyl acetate **3l**

Purification by flash column chromatography (height: 15 cm, width: 3 cm, Pentane/CH_2Cl_2 = 70/30 to 50/50 then Pentane/EtOAc = 98/2) afforded **3l** as a colorless oil (49 mg, 0.20 mmol, **50%**) from 4-methyl-1-pentanol (248 μL, 2 mmol, 5 equiv.). R_f (Petroleum ether/EtOAc = 98/2): 0.3. **^{1}H NMR** (300.1 MHz, $CDCl_3$) δ 4.06 (t, *J* = 5.5 Hz, 2H), 2.04 (s, 3H), 1.85–1.65 (m, 4H), 1.44 (s, 6H). **^{19}F NMR** (282.4 MHz, $CDCl_3$) δ −36.3 (s, 3F). **^{13}C NMR** (75.5 MHz, $CDCl_3$) δ 171.1, 130.7 (q, *J* = 308.0 Hz), 64.1, 51.5, 39.3 (d, *J* = 1.1 Hz), 29.4 (d, *J* = 1.8 Hz), 24.1, 20.9. **IR** (neat, cm^{-1}) *ν*: 2966, 1740, 1599, 1505, 1469, 1389, 1370, 1238, 1098, 1041, 877, 839, 755, 699, 635, 606, 556, 419. **HRMS** (CI^+) calcd for $C_7H_{12}F_3S$ *m/z* 185.0612 $[M-OAc]^+$, found 185.0603 (Δ = −4.83 ppm).

4.3.20. 5-((Trifluoromethyl)thio)hexan-2-yl acetate **3m**

Purification by flash column chromatography (height: 15 cm, width: 3 cm, Pentane/CH_2Cl_2 = 70/30 to 50/50 then Pentane/EtOAc = 98/2) afforded **3m** as a colorless oil (84 mg, 0.12 mmol, **29%**, *d.r.* 2.4/1) from **I** (307 mg, 1.2 mmol, 1 equiv.) and 2-hexanol (756 μL, 6 mmol, 5 equiv.). R_f (Petroleum ether/EtOAc = 98/2): 0.3. **^{1}H NMR** (300.1 MHz, $CDCl_3$) δ 4.99–4.81 (m, 1H, *maj* + *min*), 3.39–3.21 (m, 1H, *maj* + *min*), 2.03 (s, 3H, *maj* + *min*), 1.79–1.54 (m, 4H, *maj* + *min*), 1.41 (d, *J* = 6.9 Hz, 3H, *maj* + *min*), 1.22 (d, *J* = 6.4 Hz, 3H, *maj* + *min*). **^{19}F NMR** (282.4 MHz, $CDCl_3$) δ −39.7 (s, 3F). **^{13}C NMR** (75.5 MHz, $CDCl_3$) δ 170.7 (*maj* + *min*), 131.3 (q, *J* = 307.3 Hz, *maj* + *min*), 70.3 (*min*), 70.2 (*maj*), 41.0 (*min*), 40.9 (*maj*), 32.9 (*min*), 32.7 (*maj*), 32.6 (*min*), 32.5 (*maj*), 22.3 (*maj*), 22.2 (*min*), 21.2 (*maj* + *min*), 19.9 (*maj* + *min*). **IR** (neat, cm^{-1}) *ν*: 2979, 2938, 1873, 1736, 1454, 1373, 1239, 1101, 1049, 1020, 952, 837, 756, 631, 609, 492. **HRMS** (CI^+) calcd for $C_7H_{12}F_3S$ *m/z* 185.0612 $[M-OAc]^+$, found 185.0606 (Δ = −3.14 ppm).

4.3.21. 1-[(4-Trifluoromethyl)phenyl]-4-((trifluoromethyl)-thio)-heptyl acetate **3n**

Purification by flash column chromatography (height 15 cm, width 3 cm, Pentane/Et_2O = 95/5) afforded **3n** as a colorless oil (46 mg, 0.12 mmol, **29%**, *d.r.* 1/1) from 1-[(4-trifluoromethyl) phenyl]-1-heptanol (0.52 g, 2 mmol, 5 equiv.). R_f (Petroleum ether/EtOAc = 95/5): 0.4. **^{1}H NMR** (300.1 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.1 Hz, 2H), 7.44 (d, *J* = 8.1 Hz, 2H), 5.85–5.71 (m 1H), 3.23–3.08 (m, 1H), 2.14–2.06 (m, 3H), 2.06–1.86 (m, 2H), 1.79–1.53 (m, 4H), 1.51–1.34 (m, 2H), 0.91 (t, *J* = 7.2 Hz, 3H). **^{19}F NMR** (282.4 MHz, $CDCl_3$) δ −39.6 (s, 3F), −39.6 (s, 3F), −63.2 (s, 6F). **^{13}C NMR** (75.5 MHz, $CDCl_3$) δ 170.1 (*maj* + *min*), 144.2 (*maj* + *min*), 131.1 (q, *J* = 306 Hz, *maj* + *min*), 130.3 (q, *J* = 32.3 Hz, *maj* + *min*), 126.7 (*min*), 126.6 (*maj*), 125.6 (q, *J* = 3.6 Hz, *maj* + *min*), 123.9 (q, *J* = 272.7 Hz, *maj* + *min*), 74.9 (*maj*), 74.6 (*min*), 46.0 (*min*), 45.8 (*maj*), 37.2 (*min*), 37.1 (*maj*), 32.9 (*maj* + *min*), 31.0 (*min*), 30.8 (*maj*), 21.0 (*maj* + *min*), 19.7 (*maj* + *min*), 13.6 (*maj* + *min*). **IR** (neat, cm^{-1}) *ν*: 2963, 2877, 1739, 1623, 1421, 1374, 1325, 1231, 1104, 1067, 1017, 954, 898, 840, 756, 665, 633, 605. **HRMS** (API^-) calcd for $C_{17}H_{20}F_6O_2S$ *m/z* 402.1088 $[M]^-$, found 402.1095 (Δ = 1.70 ppm).

4.3.22. 2-Methyl-5-((trifluoromethyl)thio)hexan-2-yl acetate **3o**

Purification by flash column chromatography (height: 15 cm, width: 3 cm, Pentane/CH_2Cl_2 = 70/30 to 50/50 then Pentane/EtOAc = 98/2) afforded **3o** as a colorless oil (60 mg, 0.08 mmol, **19%**)

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from **I** (307 mg, 1.2 mmol, 1 equiv.) and 2-methyl-2-hexanol (857 μL, 6 mmol, 5 equiv.). $\mathbf{R_f}$ (Petroleum ether/EtOAc = 98/2): 0.3. **^{1}H NMR** (300.1 MHz, $CDCl_3$) δ 3.38–3.21 (m, 1H), 1.96 (s, 3H), 1.92–1.80 (m, 2H), 1.72–1.57 (m, 2H), 1.43 (s, 6H), 1.40 (s, 3H). **^{19}F NMR** (282.4 MHz, $CDCl_3$) δ −39.7 (s, 3F). **^{13}C NMR** (75.5 MHz, $CDCl_3$) δ 170.4, 130.9 (q, J = 305.9 Hz), 81.5, 41.3, 37.6, 31.1, 26.0, 25.9, 22.3, 22.1. **IR** (neat, cm^{-1}) ν: 2979, 2936, 1732, 1454, 1385, 1367, 1252, 1212, 1100, 1047, 1017, 943, 856, 756, 635, 610, 491. **HRMS** (CI^+) calcd for $C_8H_{14}F_3S$ m/z 199.0768 $[M-OAc]^+$, found 199.0762 (Δ = −3.3 ppm).

*4.3.23. 4-((Trifluoromethyl)thio)cyclooctyl acetate **3p***

Purification by flash column chromatography (height: 15 cm, width: 3 cm, Pentane/CH_2Cl_2 = 80/20 to 50/50 then Pentane/EtOAc = 98/2) afforded **3p** as a colorless oil (24 mg, 0.09 mmol, **22%,** *d.r.* 1.7/1, *with an inseparable impurity*) from cyclooctanol (264 μL, 2 mmol, 5 equiv.). $\mathbf{R_f}$ (Petroleum ether/EtOAc = 98/2): 0.32. **^{1}H NMR** (300.1 MHz, $CDCl_3$) δ 5.02–4.81 (m, 1H, *maj* + *min*), 3.60–3.34 (m, 1H, *maj* + *min*), 2.33–1.37 (m, 15H, *maj* + *min*). **^{19}F NMR** (282.4 MHz, $CDCl_3$) δ −39.4 (s, 3F, *min*), −39.6 (s, 3F, *maj*). **^{13}C NMR** (75.5 MHz, $CDCl_3$) δ 170.3 (*maj* + *min*), 130.9 (q, J = 306.2 Hz, *maj* + *min*), 73.8 (*maj*), 73.4 (*min*), 45.4 (*min*), 45.1 (*maj*), 32.7 (*min*), 31.4 (*maj*), 31.1 (*min*), 30.8 (*maj*), 30.2 (*min*), 29.1 (*maj*), 29.0 (*maj*), 28.6 (*min*), 24.5 (*maj*), 24.4 (*min*), 23.1 (*maj*), 22.1 (*min*), 21.4 (*min*), 21.4 (*maj*). **IR** (neat, cm^{-1}) ν: 2939, 2862, 1731, 1470, 1448, 1367, 1239, 1100, 1037, 1018, 960, 871, 786, 756, 649, 609, 542. **HRMS** (CI^+) calcd for $C_9H_{14}F_3S$ m/z 211.0768 $[M-OAc]^+$, found 211.0766 (Δ = −1.16 ppm).

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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