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Reactions of 1-fluoroalkyl triflates with nucleophiles and bases

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ABSTRACT

A series of 1-fluoroalkyl triflates are prepared, isolated and characterized. Their reactions with a large variety of nucleophiles are described. From these reactions are obtained 1-fluoroalkyl nitriles, azides, formates, acetates, ethers, phenylthio ethers, triphenylphosphonium salts, benztriazoles, benzimidazoles, xanthates, iodides, bromides and chlorides, most in excellent yield.

1. Introduction

1,1-Alkane bistriflates can be readily prepared in high yields from aldehydes by treatment with triflic anhydride in the presence of 2,6-lutidine at 0 °C in methylene chloride [1]. In previous work, Garcia Martinez and coworkers have reported that these highly reactive compounds can be readily converted to 1,1-dihalides [2,3] and 1-fluoro-1-haloalkanes [4], this latter chemistry proceeding through in situ formation of 1-fluoroalkyl triflates (Scheme 1).

Included in such studies of 1,1-bistriflates were reports from Garcia Martinez' group and that of Makosza of their conversion to 1,1-difluorides by use of n-$Bu_4^+(Ph_3SnF_2)^-$ and $KF/Ph_3SnF/n$-$Bu_4N^+HSO_4^-$, respectively as fluoride sources (Scheme 2) [3,5].

Because of our own interest in the development of effective methods for the preparation of *gem*-difluoro compounds, it was decided to take another look at the use of 1,1-bistriflates as precursors of 1,1-difluoroalkanes, and this work resulted in our recent report that triethylamine – 3HF was a good fluoride source for carrying out this conversion (Scheme 3) [6].

During the course of this study, conditions were also found for the preparation *and isolation* of 1-fluoroalkyl triflates in very good yield. For example, when nonane-1,1-bistriflate is allowed to react with 4 equivalents of Et_3N-3HF in dichloromethane at 0 °C for 17 h, the monofluoro product, 1-fluorononyl triflate (**1a**) can be isolated in 91% yield (Scheme 4).

Having demonstrated the ability to prepare and isolate 1-fluoroalkyl triflates such as **1a**, it was decided to carry out a broad study of their use as precursors of monofluoro compounds of broad functionality.

2. Results and discussion

It was our initial thought that 1-fluoroalkyl triflates should be excellent precursors to 1-fluoroalkenes, especially since an α-fluoro substituent on an alkyl halide serves to enhance the E2 elimination reactivity of the compound relative to S_N2 substitution (Scheme 5) [7].

However, when 1-fluorononyl triflate was treated under identical conditions, (CH_3O^-/CH_3OH at 50 °C, *no* elimination product was able to be detected, the only product deriving from double S_N2 substitution (Scheme 6). On the basis of the comparative results shown in these two schemes, we concluded that primary triflates must be very reluctant to undergo E2 eliminations. In order to unambiguously prove this, the reactivity of a simple n-alkyl triflate was examined the under identical conditions, and it was found that again, only substitution was observed (Scheme 7). Even its reaction with triethylamine leads only to substitution product.

To our knowledge, this particular synthetically important reactivity characteristic of n-alkyl triflates has not been specifically mentioned previously in the literature. However, there are a number of published examples where this property has been observed, with the lack of elimination allowing high yield substitutions of n-alkyl triflates in their reactions with nitrogen bases in the formation of ionic liquids and N-alkylpyridinium chromophores and semiconductor materials [8–12], as well as in radiofluorination experiments [13,14].

Interestingly, when DMSO is used as solvent in the reaction of 1-fluorononyl triflate **1a** with methoxide, double substitution to

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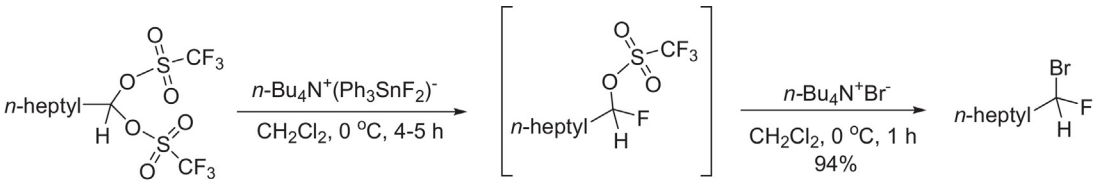
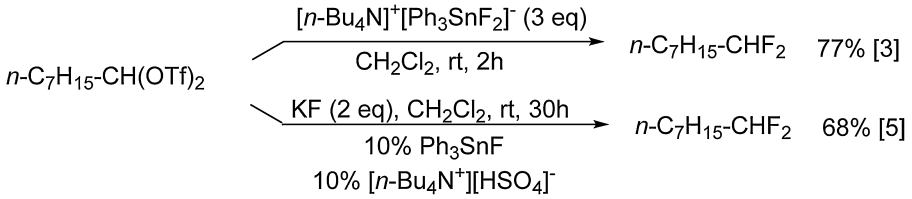
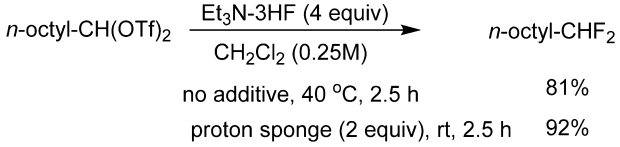


Scheme 1. Garcia Martinez' use of 1-fluoroalkyl triflates to prepare 1-halo-1-fluoroalkanes.



Scheme 2. Conversion of 1,1 bistriflates to 1,1-diflurides via nucleophilic substitution.



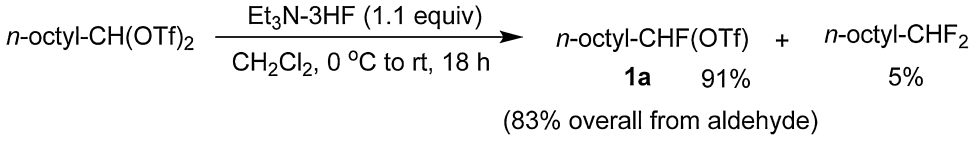
Scheme 3. Conversion of 1,1 bistriflates to 1,1-diflurides using Et_3N-3HF.

form acetal **2** is not observed. Instead an almost quantitative yield of nonaldehyde is observed. Although this reaction is not of interest synthetically, we considered it a mechanistic curiosity. We believe that this reaction must proceed by means of initial nucleophilic attack of **1a** by DMSO, followed by a methoxide-assisted elimination to form the aldehyde, as shown in Scheme 8. The same conversion to aldehyde occurs in the absence of methoxide, under otherwise same conditions to provide 98% of aldehyde.

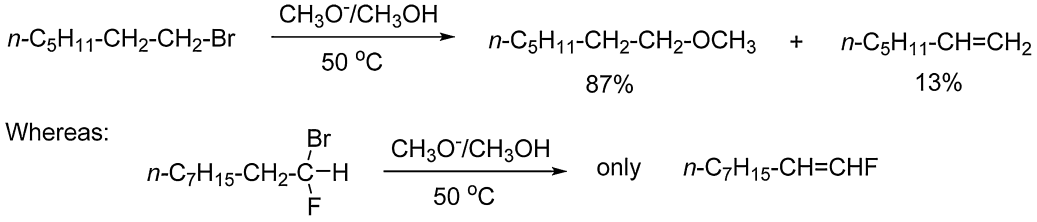
Another curious reaction was observed when 1-fluorononyl triflate (**1a**) was treated with DBU in dichloromethane, again in the hope of observing an elimination process. However, what was observed was a 48–50% yield of 1,1-difluorononane. What we are hypothesizing is happening here is that DBU undergoes a slow reaction that generates fluoride ion, which then reacts rapidly with remaining **1a** to form the difluoro product. Under this scenario, the maximum yield of difluorononane would be 50%, and that is what is observed. Although DBU is considered to be a relatively non-nucleophilic base, it is known to react readily with *n*-alkyl bromides and triflates [8]. Therefore it is proposed that DBU undergoes an S_N2 reaction with **1a**, followed by loss of fluoride, which then allows the reaction of fluoride with another molecule of **1a** (Scheme 9).

Having established that 1-fluoro-*n*-alkyl triflates readily undergo S_N2 nucleophilic substitution reactions, we turned our attention to exploring the diversity of such reactions. Most reactions were carried out in dichloromethane at room temperature, and almost all proceeded with excellent yields. Nucleophiles that were studied included cyanide, azide, acetate, formate, phenoxide, thiophenoxide, hexafluoroisopropoxide, benzimidazole, benztriazole, borohydride, xanthate anion, and the halides: fluoride, chloride, bromide and iodide. The exact conditions along with yields are given in Table 1.

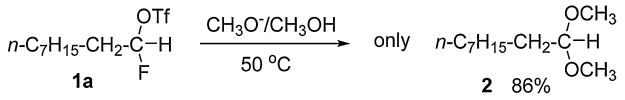
Most of the reactions shown in Table 1 proceeded with excellent yields, with isolation being relatively easy. Many of the types of monofluoro compounds in the table, other than the halo, fluoro compounds, including the α-fluoronitriles [15], 1-fluoroalkyl azides [7], 1-fluoroalkyl acetates [16], and 1-fluoroalkyl benztriazoles [17] have only rarely been seen in the literature; others like the formate, the xanthate ester, the benzimidazole, the phenoxy, and the phosphonium salt derivatives appear to be unknown.



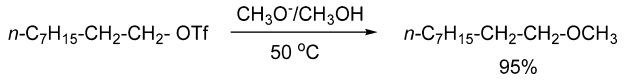
Scheme 4. Preparation of 1-fluorononane triflate.



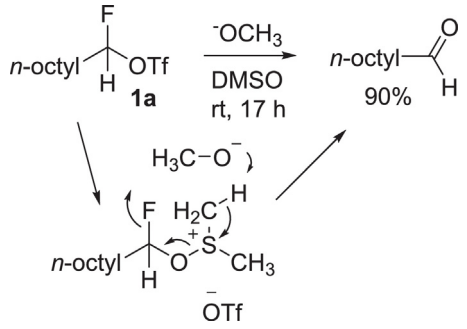
Scheme 5. Impact of α-fluoro substituent on E2 eliminations [7].



Scheme 6. Reaction of 1-fluoroalkyl triflates with methoxide.

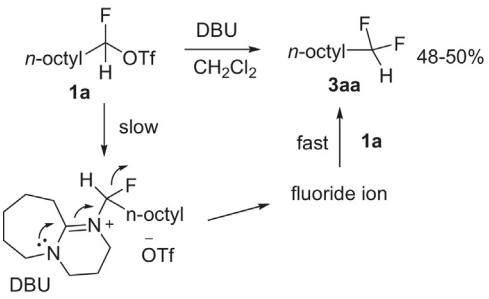


Scheme 7. Reaction of *n*-alkyl triflates with methoxide.



Scheme 8. Reaction of 1-fluoroalkyl triflates with methoxide in DMSO.

1-Fluoroalkyl thiophenoxy compounds have been reported a number of times (prepared by the Pummerer reaction of DAST with phenyl alkyl sulfoxides) [18,19]. In our hands both the 1-fluorononyl phenoxy- and the thiophenoxy-compounds, **3af** and **3ag**, although prepared in high yields, were observed to be unstable, when isolated [20]. The product **3aq** from the reaction of **1a** with *n*-butanol, although also formed in high NMR yield (95%), was even less stable, and was not able to be isolated or fully characterized. Although *fluoromethyl* ethers are sufficiently stable



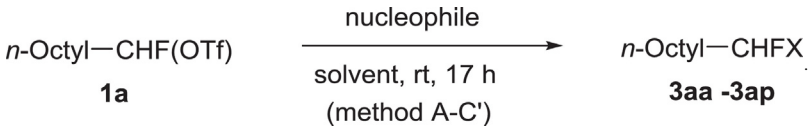
Scheme 9. Reaction of DBU with 1-fluorononyl triflate, **1a**.

to appear frequently in the literature, there do not appear to be any published examples of the preparation of 1-fluoroalkyl ethers, this in spite of the fact that 1-chloroalkyl ethers have been reportedly made for in situ synthetic utilization [21]. In contrast to our observed instability of 1-fluorononyl butyl ether, when fluorinated alcohol, hexafluoro-isopropanol was used as nucleophile, a stable 1-fluorononyl ether, **3ah**, was able to be isolated and fully characterized.

In addition to the application of these reactions to other 1-fluoro-*n*-alkyl triflates, a few examples of reactions 1-fluoroalkyl systems that were branched at the carbon adjacent to the site of reaction were also examined in order to determine steric influences on substrate reactivity. These 1-fluoro-alkyl triflates were prepared in essentially the same manner as was 1-fluorononyl triflate: 1-fluoropentyl triflate **1b** (42%), 2-phenyl-1-fluoroethyl triflate **1c** (70%, overall from aldehyde), 2-ethyl-1-fluorohexyl triflate **1d** (90%), 1-cyclohexyl-1-fluoromethyl triflate **1e** (58%), and 1-fluoro-10-undecenyl triflate **1f** (95%).

For the most part, branching had little effect on the success of the reactions (Table 2). The highly branched 1-fluoroneopentyl triflate was completely unreactive. Because bistriflates are not able to be prepared from benzaldehydes or from ketones [6], it was not possible to prepare α-fluorobenzyl triflates or secondary geminal fluoro, triflates by this methodology.

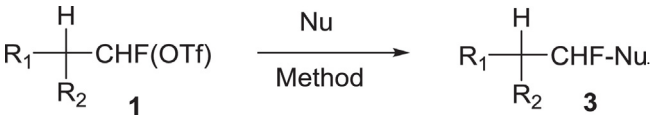
Table 1
Reactions of 1-fluorononyl triflates with nucleophiles.



X	Reagent [nucleophile]	Method	Product (%)[a]
CN	*n*-Bu_4N^+ ^-CN	A	**3ab** (77)
N_3	*n*-Bu_4N^+ $^-N_3$	A	**3ac** (88)
OAc	K^+ ^-OAc	C′	**3ad** (98)
OCOH	HCO_2H/Et_3N [^-OCHO]	C	**3ae** (98)
OPh	K^+ ^-OPh	C′	**3af** (95)[b]
SPh	HSPh/Et_3N [^-SPh]	C	**3ag** (98)[b]
$OCH(CF_3)_2$	$(CF_3)_2CHOH/Et_3N$ [$(CF_3)_2CHO^-$]	C	**3ah** (82)
SCSOEt	K^+ ^-SCSOEt	C′	**3ai** (86)
Ph_3P^+	Ph_3P	B	**3aj** (87)[c]
Benzimidazole-1-yl	Benzimidazole/Et_3N	C	**3ak** (77)
Benztriazole-1-yl	Benztriazole/Et_3N	C	**3al** (87)[d]
H	*n*-Bu_4N^+ $^-BH_4$	A	**3am** (78)
F	*n*-Bu_4N^+ ^-F	A	**3aa** (98)
Cl	*n*-Bu_4N^+ ^-Cl	C	**3an** (99)
Br	*n*-Bu_4N^+ ^-Br	A	**3ao** (98)
I	*n*-Bu_4N^+ ^-I	A	**3ap** (98)

[a] Isolated yields, unless noted otherwise.
[b] NMR yields, products unstable.
[c] Triflate salt.
[d] 10% of the 2-substituted isomer was formed as a co-product.

Table 2
Reactions of 1-fluoro-1-alkyl triflates with selected nucleophiles.



Compound	R_1	R_2	Reagent	Method	Product (%)[a]
1b	*n*-Bu	H	Benztriazole/Et_3N	C	**3ba** (80)
1b	*n*-Bu	H	HOAc/Et_3N [$^-$OAc]	C	**3bb** (35)
1b	*n*-Bu	H	K^+ $^-$SCSOEt	C′	**3bc** (95)
1c	$PhCH_2$	H	Benztriazole/Et_3N	C	**3ca** (66)
1c	$PhCH_2$	H	HOAc/Et_3N [$^-$OAc]	C	**3cb** (66)
1c	$PhCH_2$	H	K^+ $^-$SCSOEt	C′	**3cc** (98)
1d	Et	*n*-Bu	Benztriazole/Et_3N	C	**3da** (95)
1d	Et	*n*-Bu	HOAc/Et_3N [$^-$OAc]	C	**3db** (92)
1d	Et	*n*-Bu	K^+ $^-$SCSOEt	C′	**3dc** (76)
1e	Cyclohexyl		Benztriazole/Et_3N	C	3ea (75)
1e	Cyclohexyl		HOAc/Et_3N [$^-$OAc]	C	3eb (76)
1e	Cyclohexyl		K^+ $^-$SCSOEt	C′	3ec (91)
1f	10-undecenyl	H	Benztriazole/Et_3N	C	**3fa** (72)
1f	10-undecenyl	H	HOAc/Et_3N [$^-$OAc]	C	**3fb** (89)
1f	10-undecenyl	H	K^+ $^-$SCSOEt	C′	**3fc** (97)

[a] All yields are isolated yields.

3. Conclusion

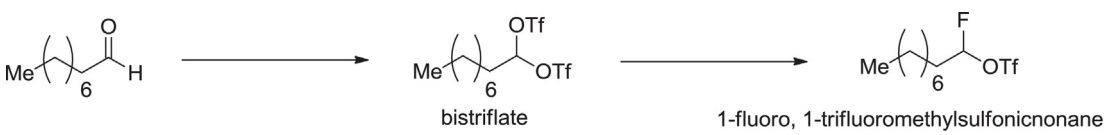
In conclusion, a series of 1-fluoroalkyl triflates have been synthesized, isolated and characterized. These compounds are highly reactive and selective in their reactions with bases/nucleophiles, in all cases undergoing essentially exclusive nucleophilic substitution. A large number of functionalized 1-fluoroalkanes are able to be prepared by these substitution reactions.

4. Experimental

4.1. General experimental details

All reactions were carried out under N_2 or argon atmosphere. All anhydrous solvents were purchased commercially and stored over 4 Å molecular sieves. Reagents were purchased at commercial quality and were used without further purification. All NMR spectra were obtained using $CDCl_3$ as solvent, unless otherwise specified. ^{1}H NMR spectra were recorded at 300 MHz, and chemical shifts are reported in ppm relative to TMS. ^{19}F NMR spectra were recorded at 282 MHz, and chemical shifts are reported in ppm relative to $CFCl_3$ as the external standard. ^{13}C NMR spectra were recorded at 75 MHz with proton decoupling, and chemical shifts are reported in ppm relative to $CDCl_3$ (77.0 ppm).

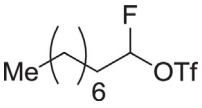
4.2. General method for the preparation of 1-fluoroalkyl triflates



Triflic anhydride (4 g, 14.2 mmol) in 10 mL of dichloromethane was added to a 150 mL triple-necked round bottomed flask containing nonanal (1.0 g, 7 mmol) and 2.6-lutidine (1.3 g, 12 mmol) in 40 mL dichloromethane. After stirring under argon for 5 h at −10 °C, the solution was placed in a refrigerator for 2 days, after which 100 mL of 1N-HCl was added at 0 °C. The lower layer was washed with 100 mL of 1N-HCl and 100 mL saturated $NaHCO_3$ and then dried with $MgSO_4$. The dichloromethane was removed by rotary evaporation, and 2.7 g of the curde bistriflate was obtained as an oil. This bistriflate was used without additional purification.

Et_3N-3HF (1.1 g, 7 mmol) in 20 mL of dichloromethane was added to a 100 mL one-necked HPE bottle containing the crude bistriflate (2.7 g) in 20 mL dichloromethane at 0 °C. The mixture was allowed to reach room temperature and was stirred for 18 h. The reaction was slowly quenched by addition of half saturated $NaHCO_3$ (40 mL) and stirred for 30 min at 0 °C. The lower layer was washed with 50 mL 1N-HCl and 50 mL saturated $NaHCO_3$, after which the organic layer was dried with $MgSO_4$, filtered, and concentrated under reduced pressure to afford a yellow oil. Flash column chromatography (10% diethylether/hexane) gave the known 1-fluoro-nonyl trifluoromethanesulfonate, **1a** as a colorless oil: 1.72 g (5.8 mmol) (83% from nonanal in 2 steps).

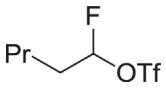
1-Fluorononyl trifluoromethanesulfonate (**1a**)



^{1}H NMR, δ 0.88 (t, 3H, J = 7.2 Hz), 1.28–1.54(m, 12 H), 1.92–2.02 (m, 2H), 6.13 (dt, 1H, J = 54.6 Hz and 5.1 Hz); ^{19}F NMR, δ −75.6 (d, 3F, J = 4.2), −119.4 to −119.0 (m, 1F); ^{13}C NMR, δ 14.0, 22.30, 22.36, 22.60, 28.76, 29.95 (d, J = 11.5), 31.74, 33.65 (d, J = 19.5), 112.69 (d,

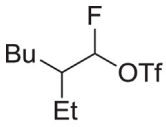
J = 244.7), 118.33 (q, J = 318.0 Hz); HRMS (ESI) $[M-H]^+$; calc for 293.0835, found 293.0829, mass error 1.88 ppm.

1-Fluoropentyl trifluoromethanesulfonate (**1b**)



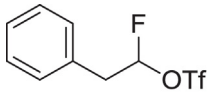
^{1}H NMR, δ 0.95 (t, 3H, J = 7.2 Hz), 1.28–1.54(m, 4H), 1.92–2.02 (m, 2H), 6.13 (dt, 1H, J = 54.3 Hz and 5.1 Hz); ^{19}F NMR, δ −75.51 (d, 3F, J = 6.3), −119.37 to −119.03 (m, 1F); ^{13}C NMR, δ 13.6, 21.92, 24.36 (d, J = 4.6 Hz), 33.35 (d, J = 19.4 Hz), 112.72 (d, J = 244), 118.34 (q, J = 318 Hz).

1-Fluoro-2-ethyl-hexyltrifluoromethanesulfonate (**1d**)



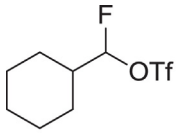
^{1}H NMR, δ 0.89 (m, 6H), 1.32–1.53 (m, 8 H), 1.75–1.92 (m, 1H), 6.07 (dt, 1H, J = 54.3 Hz and 4.1 Hz); ^{19}F NMR, δ −75.4 (d, 3F, J = 7.1), −126.4 to −126.1 (m, 1F). ^{13}C NMR, δ 10.95, 13.79, 20.63, 22.74, 26.88, 28.74, 43.29 (d, J = 17.2 Hz), 114.24 (d, J = 247 Hz), 118.34 (q, J = 318 Hz).

1-Fluoro-2-phenyl-ethyltrifluoromethanesulfonate (**1c**)



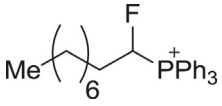
^{1}H NMR, δ 3.17–3.39 (m, 2H), 6.23 (dt, 1H, J = 54 Hz and 5.4 Hz), 7.23–7.37 (m, 5H). ^{19}F NMR, δ −75.6 (d, 3F, J = 5.6 Hz), −118.08 to −117.78 (m, 1F); ^{13}C NMR, δ 40.25 (d, J = 20.6 Hz), 111.84 (d, 246 Hz), 118.22 (q, J = 318 Hz), 128.08, 128.94 (2C), 129.75 (2C), 141.8.

Cyclohexylfluoromethyl trifluoromethanesulfonate (**1e**)



^{1}H NMR, δ 1.13–1.38 (m, 6H),1.55–1.88 (m, 5H), 5.87 (dd, 1H, J = 55 Hz and 5.1 Hz). ^{19}F NMR, δ-75.4 (d, 3F, J = 7.3), −126.1 to −125.8 (m, 1F); ^{13}C NMR, δ 24.90 (2 C), 25.58, 25.64 (2 C), 25.74, 41.244 (d, J = 18.4) 114.61 (d, J = 247) 118.35 (q, J = 318 Hz).

1-Fluoro-10-undecenyl trifluoromethanesulfonate (**1f**)

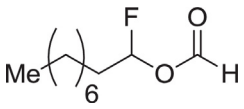


^{1}H NMR, δ 1.31–1.55 (m, 12H), 1.93–2.06 (m, 4H), 4.94 (d, 1H, J = 11.0 Hz), 4.98 (d, 1H, J = 17.7 Hz), 5.76–5.85 (m, 1H), 6.13 (dt, 1H, J = 54.6 Hz and 5.4 Hz); ^{19}F NMR, δ −75.6 (d, 3F, J = 7.3), −119.4 to −119.1 (m, 1F); ^{13}C NMR, δ 14.3 (d, J = 4.6 Hz), 22.35, 22.5 (d, J = 27.5 Hz), 28.9 (d, J = 18.3 Hz), 28.9, 33.5, 33.8, 112.6 (d, J = 243 Hz), 114.2, 118.3 (q, J = 317 Hz), 139.0.

HRMS (ESI) $[M+H]^+$; calc for 321.1136, found 321.1136, mass error 0.190 ppm.

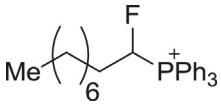
4.3. General methods for reactions of 1-fluoroalkyl triflates with nucleophiles

4.3.1. Method A: preparation of 1-chloro-1-fluorononane, **3an**



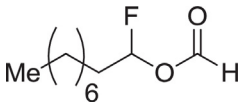
Tetra-*n*-butyl ammonium chloride (3.3 g, 12 mmol) in 20 mL of dichloromethane was added to a 250 mL triple-necked round bottomed flask containing 1-fluorononyl trifluoromethanesulfonate, **1a** (3.0 g, 10 mmol) in 50 mL dichloromethane. After stirring under argon for 17 h at room temperature, 20 mL of 1N-HCl was added. The lower layer was washed with saturated $NaHCO_3$ and dried with $MgSO_4$. Dichloromethane was removed by rotary evaporation, and the crude product was purified by column chromatography (hexane/Et_2O = 8/1) to obtain 1-chloro-1-fluorononane, **3an**, 1.8 g (99%) as a colorless oil.

4.3.2. Method B: preparation of 1-fluorononyl triphenylphosphonium triflate, **3aj**



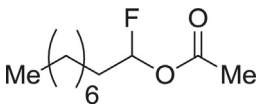
1-Fluorononyl trifluoromethanesulfonate (300 mg, 1.0 mmol) was added to a 5 mL PFA vial containing triphenylphosphine (180 mg, 1.0 mmol) in 2 mL MeCN, and after stirring under argon for 20 h at room temperature, the MeCN was carefully removed by rotary evaporation. The collected, moisture-sensitive crude product, **3aj**, was obtained as a white solid: 331 mg (86%).

4.3.3. Method C: preparation of 1-fluorononyl formate, **3ae**



Formic acid (64 mg, 1.4 mmol), 1-fluorononyl trifluoromethanesulfonate (200 mg, 0.67 mmol) and triethylamine (100 mg, 1 mmol) in dichloromethane were added to 5 mL vial, and after stirring under argon for 17 h at room temperature, 1 mL 1N-HCl was added to the solution The lower layer was washed with saturated $NaHCO_3$ and dried with $MgSO_4$, and the dichloromethane was removed by rotary evaporation. The collected crude product was purified by column chromatography (hexane/Et_2O = 8/1) to give 124 mg (98%) of 1-fluorononyl formate (**3ae**) as a colorless oil.

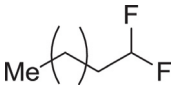
4.3.4. Method C′ (used potassium acetate instead of acetic acid; otherwise the same as method C): preparation of 1-fluorononyl acetate, **3ad**



Potassium acetate (136 mg, 1.4 mmol), 1-fluorononyl trifluoromethanesulfonate (200 mg, 0.67 mmol) and triethylamine (100 mg, 1 mmol) in dichloromethane were added to a 5 mL vial, and after stirring under argon for 17 h at room temperature, 1 mL

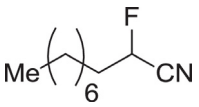
1N-HCl was added to the solution, and the lower layer was washed with saturated $NaHCO_3$ and dried with $MgSO_4$. The dichloromethane was removed by rotary evaporation, and the crude product was purified by column chromatography (hexane/Et_2O = 8/1) to give 136 mg (99%) of 1-fluorononyl acetate (**3ad**) as colorless oil.

1,1-Difluorononane **(3aa)**



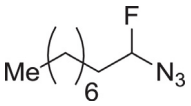
^{1}H NMR, δ 0.88 (t, 3H, J = 7.2 Hz), 1.15–1.47 (m, 12 H), 1.70–1.90 (m, 2H), 5.79 (tt, 1H, J = 57.0 Hz and 4.5 Hz); ^{19}F NMR, δ −116.2 (dt, 1F, J = 57 Hz and 17.5 Hz); ^{13}C NMR, δ 14.0, 22.2 (t, J = 5.7 Hz), 22.7, 29.1, 29.1, 29.4, 31.8, 34.1 (t, J = 21 Hz), 117.5 (t, J = 238 Hz).

2-Fluorodecanenitrile (**3ab**)



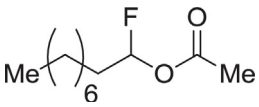
^{1}H NMR, δ 0.89 (t, 3H, J = 6.2 Hz), 1.27–1.56 (m, 12 H), 1.90–2.04 (m, 2H), 5.10 (dt, 1H, J = 46.8 Hz and 6.3 Hz); ^{19}F NMR, δ −178.9 (dt, 1F, J = 47 Hz and 21.3 Hz); ^{13}C NMR, δ 14.0, 22.6, 23.8 (d, J = 3.5 Hz), 28.7, 29.0, 29.2, 31.7, 33.5 (d, J = 22 Hz), 79.6 (d, J = 181 Hz, 116.1 (d, J = 30 Hz).

1-Azide-1-fluorononane (**3ac**)



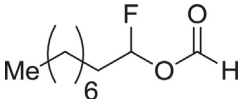
^{1}H NMR, δ 0.88 (t, 3H, J = 6.8 Hz), 1.15–1.42 (m, 12 H), 1.60–1.80 (m, 2H), 5.47 (dt, 1H, J = 57.0 Hz and 5.6 Hz); ^{19}F NMR, δ −137.8 (dt, 1F, J = 57 Hz and 17.5 Hz); **3ac** was very sensitive toward moisture and heat and easily decomposed with HF gas evolution. Therefore, the yields of these products were determined by ^{19}F NMR using PhF as an internal standard.

1-Fluorononyl acetate (**3ad**)



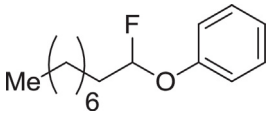
^{1}H NMR, δ 0.88 (t, 3H, J = 6.5 Hz), 1.27–1.42 (m, 12 H), 1.72–1.84 (m, 2H), 2.13 (s, 3H), 6.31 (dt, 1H, J = 55.8 Hz and 5.3 Hz); ^{19}F NMR, δ −129.3 (dt, 1F, J = 57.0 Hz and 16.1 Hz); ^{13}C NMR, δ 14.1, 20.8, 22.6, 22.9, 23.0, 29.0, 29.3, 31.8, 33.2 (d, J = 21.8 Hz), 103.2 (d, J = 220 Hz), 169.2.

1-Fluorononyl formate (**3ae**)



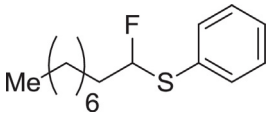
^{1}H NMR, δ 0.89 (t, 3H, J = 5.4 Hz), 1.28–1.44 (m, 12 H), 1.79–1.89 (m, 2H), 6.40 (dt, 1H, J = 54.6 Hz and 4.8 Hz), 8.08 (s, 1H); ^{19}F NMR, δ −129.5 (dt, 1F, J = 56 Hz and 17.5 Hz); ^{13}C NMR, δ 14.0, 22.6, 22.7, 22.8, 29.0 (d, J = 3.5 Hz), 29.3, 31.8, 33.1 (d, J = 20.6 Hz), 103.0 (d, J = 222 Hz), 158.9.

1-Fluoro-1-phenoxynonane (**3af**)



^{1}H NMR, δ 0.89 (t, 3H, J = 6.8 Hz), 1.20–1.60 (m, 12 H), 1.88–1.98 (m, 2H), 5.76 (dt, 1H, J = 63 Hz and 5.1 Hz), 7.06–7.34 (m, 5H); ^{19}F NMR, δ −121.4 (dt, 1F, J = 62 Hz and 15.37 Hz). ^{13}C NMR, δ 14.1, 22.7, 23.3, 23.4, 29.2 (d, J = 3.38 Hz), 29.4, 31.9, 34.7 (d, J = 23 Hz), 110.5 (d, J = 218 Hz), 117.0, 123.1, 129.6, 156.7.

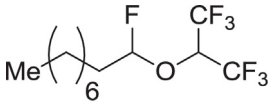
1-Fluorononylthiobenzene (**3ag**)



^{1}H NMR, δ 0.88 (t, 3H, J = 6.6 Hz), 1.20–1.60 (m, 12 H), 1.80–2.10 (m, 2H), 5.78 (dt, 1H, J = 55.5 Hz and 6.0 Hz), 7.06–7.50 (m, 6H); ^{19}F NMR, δ −145.3 (dt, 1F, J = 55.5 Hz and 17.6 Hz).

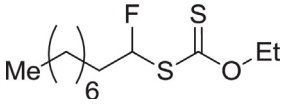
3ag was very sensitive toward moisture, and decomposed rapidly when stored at rt with HF gas evolution. Therefore, the yields of these products were determined by ^{19}F NMR using PhF as an internal standard.

1-Hexafluoropropyl 1-fluorononane (**3ah**)



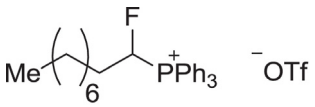
^{1}H NMR, δ 0.88 (t, 3H, J = 6.5 Hz), 1.27–1.44(m, 12 H), 1.77–1.89 (m, 2H), 4.45 (m, 1H), 5.40 (dt, 1H, J = 65.1 Hz and 5.0 Hz); ^{19}F NMR, δ-74.48, (s, 3F), −128.523 (dt, 1F, J = 65.7 Hz and 16.1 Hz); ^{13}C NMR, δ 14.0, 22.65, 22.7, 22.8, 29.1 (d, J = 6.8 Hz), 29.3, 31.8, 34.0 (d, J = 19.5 Hz), 72.4–74.1 (m, 2C), 113.0 (d, J = 226 Hz), 118.7–123.3 (m).

1-Fluorononyl *O*-ethyl dithiocarbonate (**3ai**)



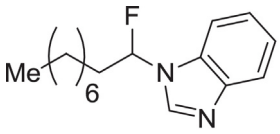
^{1}H NMR, δ 0.88 (t, 3H, J = 6.5 Hz), 1.20–1.60 (m, 15 H), 1.92–2.01 (m, 2H), 4.69 (q, 1H, J = 6.9 Hz), 6.45 (dt, 1H, J = 52.2 Hz and 6.5 Hz); ^{19}F NMR, δ −154.0 (dt, 1F, J = 52.4 Hz and 18.3 Hz); ^{13}C NMR, δ 13.6, 14.0, 22.6, 25.1 (d, J = 2.3 Hz), 29.0, 29.0, 29.2, 31.7, 33.8 (d, J = 20.6 Hz), 70.2, 100.2 (d, J = 217 Hz), 210.2.

1-Fluorononyl triphenylphosphonium triflate salt (**3aj**)



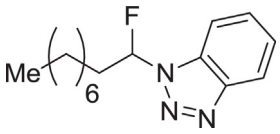
^{19}F NMR, δ-78.8, −146.2 (dt, 1F, J = 57.4 Hz and 21.9 Hz); **3aj** was moisture sensitive.

1-Benzimidazole-1-yl 1-fluorononane (**3ak**)



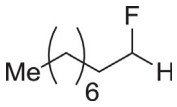
^{1}H NMR, δ 0.88 (t, 3H, J = 6.6 Hz), 1.20–1.60 (m, 12 H), 2.15–2.46 (m, 2H), 6.31 (dt, 1H, J = 51.7 Hz and 6.6 Hz), 7.34–8.12 (m, 5H); ^{19}F NMR, δ −136.2 (ddd, 1F, J = 51.4 Hz, 22.0 Hz and 10.2 Hz); ^{13}C NMR, 13.9, 22.5, 24.4 (d, J = 4.6 Hz), 28.8, 28.9, 29.1, 31.6, 33.2 (d, J = 25.2 Hz), 94.0 (d, J = 200 Hz), 110.3, 120.4, 123.2, 123.8, 132.65, 140.3, 143.7.

1-Benztriazole-1-yl 1-fluorononane (**3al**)



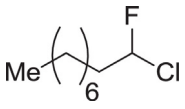
^{1}H NMR, δ 0.88 (t, 3H, J = 6.6 Hz), 1.20–1.60 (m, 12 H), 2.40–2.70 (m, 2H), 6.74 (dt, 1H, J = 50.4 Hz and 6.8 Hz), 7.41–8.13 (m, 4H); ^{19}F NMR, δ −139.45 (ddd, 1F, J = 50.2 Hz, 21.8 Hz and 10.9 Hz); ^{13}C NMR, δ 14.0, 22.55, 24.2, 28.65, 28.8, 29.1 (d, J = 12.5 Hz), 31.7, 32.7 (d, J = 24.0 Hz), 96.5 (d, J = 204 Hz), 109.9, 120.3, 124.6, 128.2, 132.05, 146.5.

1-Fluorononane (**3am**)



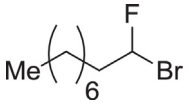
^{1}H NMR, δ 0.88 (t, 3H, J = 7.2 Hz), 1.15–1.40 (m, 12 H), 1.68 (dt, 2H, J = 24.0 Hz and 6.6 Hz), 4.44 (dt, 1H, J = 47.4 Hz and 6.2 Hz); ^{19}F NMR, δ −218.5 (tt, 1F, J = 47.9 Hz and 24.1 Hz); ^{13}C NMR, δ 14.1, 22.7, 25.1, 25.2, 29.3, 29.5, 30.4 (d, J = 19.4 Hz), 31.9, 84.2 (d, J = 163 Hz).

1-Chloro-1-fluorononane (**3an**)



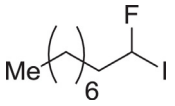
^{1}H NMR, δ 0.89 (t, 3H, J = 7.2 Hz), 1.20–1.53(m, 12 H), 2.10–2.25 (m, 2H), 6.15 (dt, 1H, J = 51.0 Hz and 5.3 Hz); ^{19}F NMR, δ −130.7 (dt, 1F, J = 50.5 Hz and 17.5 Hz); ^{13}C NMR, δ 14.1, 22.6, 24.2 (d, J = 3.2 Hz), 28.8, 29.1, 29.3, 31.8, 39.3 (d, J = 19.4 Hz), 102.95 (d, J = 240 Hz).

1-Bromo-1-fluorononane (**3ao**)



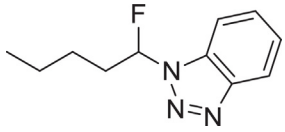
^{1}H NMR, δ 0.89 (t, 3H, J = 7.2 Hz), 1.20–1.53(m, 12 H), 2.10–2.25 (m, 2H), 6.45 (dt, 1H, J = 51.0 Hz and 5.3 Hz); ^{19}F NMR, δ −131.0 (dt, 1F, J = 51.0 Hz and 20.3 Hz); ^{13}C NMR, δ 14.1, 22.6, 25.05 (d, J = 3.5 Hz), 28.7, 29.1, 29.3, 31.8, 40.7 (d, J = 18.4 Hz), 95.7 (d, J = 251 Hz).

1-Fluoro-1-iodononane, (**3ap**)



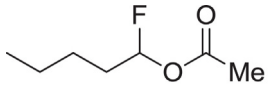
^{1}H NMR, δ 0.89 (t, 3H, J = 7.2 Hz), 1.28–1.52 (m, 12 H), 2.10–2.25 (m, 2H), 6.82 (dt, 1H, J = 49.8 Hz and 5.5 Hz); ^{19}F NMR, δ −136.1 (dt, 1F, J = 50.2 Hz and 19.7 Hz); ^{13}C NMR, δ 14.0, 22.6, 26.7, 28.45, 29.1, 29.3, 31.8, 43.2 (d, J = 18.4 Hz), 75.6 (d, J = 253 Hz).

1-Benztriazole-1-yl 1-fluoropentane (**3ba**)



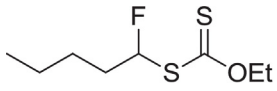
^{1}H NMR, δ 0.93 (t, 3H, J = 7.1 Hz), 1.20–1.48 (m, 4H), 2.40–2.70 (m, 2H), 6.74 (dt, 1H, J = 50.8 Hz and 6.8 Hz), 7.35–8.12 (m, 4H); ^{19}F NMR, δ −139.3 (ddd, 1F, J = 50.0 Hz, 21.6 Hz and 10.5 Hz); ^{13}C NMR, δ 13.6, 21.9, 26.3, 26.2, 32.3 (d, J = 24.1 Hz), 96.3 (d, J = 204 Hz), 109.8, 120.1, 124.5, 128.2, 132.0, 146.3.

1-Fluoropentyl acetate (**3bb**)



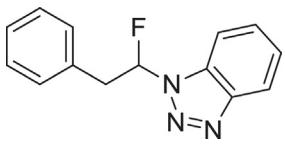
^{1}H NMR, δ 0.92 (t, 3H, J = 7.1 Hz), 1.30–1.43 (m, 4H), 1.75–1.82 (m, 2H), 2.13 (s, 3H), 6.31 (dt, 1H, J = 55.6 Hz and 5.3 Hz); ^{19}F NMR, δ −129.3 (ddd, 1F, J = 56.3 Hz, 19.6 Hz and 16.0 Hz); ^{13}C NMR, δ 13.8, 20.8, 22.2, 25.0 (d, J = 4.6 Hz), 33.85 (d, J = 21.6 Hz), 103.2 (d, J = 220 Hz), 169.2.

S-1-fluoropentyl *O*-ethyl dithiocarbonate (**3bc**)



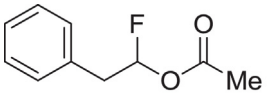
^{1}H NMR, δ 0.93 (t, 3H, J = 7.4 Hz), 1.30–1.55 (m, 8 H), 1.80–2.10 (m, 2H), 4.68 (q, 2H, J = 6.8 Hz), 6.45 (dt, 1H, J = 51.9 Hz and 6.5 Hz); ^{19}F NMR, δ −154.0 (dt, 1F, J = 52.0 Hz and 18.7 Hz); ^{13}C NMR, δ 13.6, 13.7, 22.1, 27.15 (d, J = 3.5 Hz), 33.45 (d, J = 21.6 Hz), 70.2, 100.1 (d, J = 217 Hz), 210.1.

2-Phenyl 1-benztriazole-1-yl 1-fluoroethane (**3ca**)



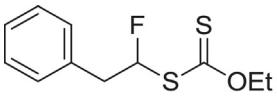
^{1}H NMR, δ 3.84–3.95 (m, 2H), 6.87 (dt, 1H, J = 51.2 Hz and 6.5 Hz), 7.20–8.10 (m, 9 H); ^{19}F NMR (282 MHz, $CDCl_3$); δ −137.6 (ddd, 1F, J = 50.3 Hz, 21.2 Hz and 13.1 Hz); C NMR, δ 39.15 (d, J = 25.2 Hz), 96.1 (d, J = 206 Hz), 109.65, 120.2, 124.6, 127.5, 128.3, 128.7, 129.4, 132.3, 133.5 (d, J = 5.7 Hz), 146.3.

1-Fluoro-2-phenylethy acetate (**3cb**)



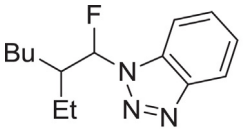
^{1}H NMR, δ 2.10 (s, 3H), 3.05–3.16 (m, 2H), 6.46 (dt, 1H, J = 55.6 Hz and 5.5 Hz), 7.23–7.35 (m, 5 H); ^{19}F NMR, δ −128.1 (dt, 1F, J = 55.5 Hz and 16.6 Hz); ^{13}C NMR, δ 20.7, 39.8 (d, J = 22.9 Hz), 102.8 (d, J = 222 Hz), 127.2, 128.5, 129.6, 133.5 (d, J = 5.7 Hz), 168.85.

S-1-fluoro-2-phenylethyl *O*-ethyl dithiocarbonate (**3cc**)



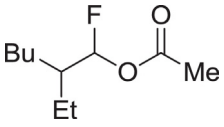
^{1}H NMR, δ 1.43 (t, 3H, J = 7.1 Hz), 3.24–3.33 (m, 2H), 4.62–4.69 (q, 2H, J = 7.1 Hz), 6.63 (dt, 1H, J = 51.4 Hz and 6.3 Hz), 7.25–7.36 (m, 5 H); ^{19}F NMR, δ −153.0 (dt, 1F, J = 51.0 Hz and 18.9 Hz); ^{13}C NMR, δ 13.5, 40.1 (d, J = 21.8 Hz), 70.3, 100.0 (d, J = 221 Hz), 127.3, 128.5, 129.5, 134.7 (d, J = 3.5 Hz), 209.5.

1-Benztriazole-1-yl 2-ethyl 1-fluorohexane (**3da**)



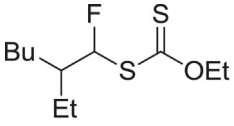
^{1}H NMR, δ 0.70–1.95 (m, 14H), 2.75–2.80 (m, 1H), 6.56 (dt, 1H, J = 48.0 Hz and 9.6 Hz), 7.20–8.10 (m, 9 H); ^{19}F NMR, δ −147.4 and −148.0 (dt, 1F, J = 48.2 Hz and 8.7 Hz); ^{13}C NMR, δ 9.7 and 9.9, 13.5 and 13.9, 20.85 and 21.2, 22.5 and 22.9, 27.1 and 27.8, 27.6 and 28.1, 41.5 and 41.6 (d, J = 21.2 Hz), 99.2 and 99.35 (d, J = 207 Hz), 110.1, 120.25, 124.5, 128.1, 132.0, 146.4. **3da** was a mixture of diastereomers.

2-Ethyl-1-fluorohexyl acetate (**3db**)

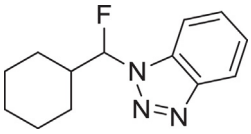


^{1}H NMR, δ 0.85–0.98 (m, 6H), 1.20–1.70 (m, 9 H), 2.13 (s, 3H), 6.26 (dt, 1H, J = 55.7 Hz and 4.4 Hz); ^{19}F NMR, δ −137.0 and −136.5 (dd, 1F, J = 55.4 Hz and 13.8 Hz); ^{13}C NMR, δ 11.1, 11.2, 13.9, 20.8, 21.0 and 21.0, 22.9, 27.3 and 27.3, 29.0 and 29.0, 42.5 (d, J = 20.6 Hz), 104.5 (d, J = 222 Hz), 169.2. **3db** was a mixture of diastereomers.

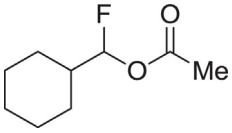
S-1-fluoro-2-ethylhexyl *O*-ethyl dithiocarbonate (**3dc**)



^{1}H NMR, δ 0.91–0.99 (m, 6H), 1.20–1.80 (m, 12 H), 18.5–1.95 (m, 1H), 4.69 (q, 2H, J = 7.3 Hz), 6.54 (dt, 1H, J = 51.3 Hz and 4.2 Hz); ^{19}F NMR, δ −136.5 (dt, 1F, J = 55.4 Hz and 13.9 Hz); ^{13}C NMR, δ 11.5, 13.6, 13.9, 22.8, 23.3, 29.2, 29.7, 44.15 (d, J = 19.5 Hz), 103.7 (d, J = 221 Hz), 210.8. **3dc** was mixed diastereomer.Benztriazole-1-yl fluoromethylcyclohexane (**3ea**)

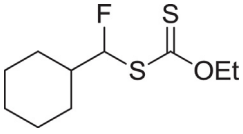


^{1}H NMR, δ 0.95–2.29 (m, 10H), 2.65–2.75 (m, 1H), 6.43 (dt, 1H, J = 48.0 Hz and 9.6 Hz), 7.40–8.12 (m, 4H H); ^{19}F NMR, δ −147.7 (dd, 1F, J = 47.9 Hz and 8.7 Hz); ^{13}C NMR, δ 24.7 (s, 2 C), 25.55, 26.85 (d, J = 5.7 Hz), 28.25 (d, J = 2.3 Hz), 40.2 (d, 21.8 Hz), 100.0 (d, J = 207 Hz), 110.0, 120.0, 124.4, 128.1, 131.9, 146.2.Cyclohexyl-fluoromethyl acetate (**3eb**)



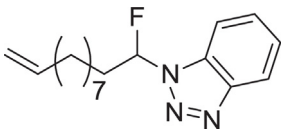
^{1}H NMR, δ 1.10–1.35 (m, 5H), 1.65–1.95 (m, 6H), 2.13 (s, 3H), 6.05 (dd, 1H, J = 56.1 Hz and 5.1 Hz); ^{19}F NMR, δ −136.5 (dd, 1F, J = 55.4 Hz and 13.1 Hz); ^{13}C NMR, δ 20.6, 25.2, 25.2, 25.95, 26.1 (d, J = 3.5 Hz), 26.2 (d, J = 4.6 Hz), 40.7 (d, 19.5 Hz), 105.1 (d, J = 223 Hz), 169.2.

S-cyclohexylfluoromehyl *O*-ethyl dithiocarbonate (**3ec**)



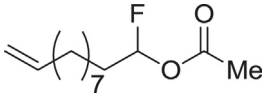
^{1}H NMR, δ 1.20–1.87 (m, 14H), 4.69 (q, 2H, J = 7.2 Hz), 6.30 (dd, 1H, J = 51.6 Hz and 5.4 Hz); ^{19}F NMR (282 MHz, $CDCl_3$); δ −159.99 (dd, 1F, J = 51.0 Hz and 14.4 Hz); ^{13}C NMR, δ 13.5, 25.4, 25.5, 25.8, 27.95 (d, J = 4.6 Hz), 28.7, 41.9 (d, 20.6 Hz), 70.2, 104.1 (d, J = 220 Hz), 210.5.

1-Fluoro-1-benztriazole-1-yl-undecan-10-en (**3fa**)



^{1}H NMR, δ 1.20–1.80 (m, 12 H), 2.02–2.10 (m, 2H), 2.50–2.63 (m, 2H), 4.91–5.02 (m, 2H), 5.73–5.85 (m, 1H), 6.74 (dt, 1H, J = 50.4 Hz and 7.1 Hz) 7.41–8.13 (m, 4H); ^{19}F NMR, δ −139.3 (dd, 1F, J = 50.7 Hz and 11.0 Hz); ^{13}C NMR, δ 24.1, 24.2, 28.7, 28.9, 29.1, 32.5, 32.85, 33.6, 96.5 (d, J = 204 Hz), 109.9, 114.1, 120.25, 124.5, 128.2, 132.1, 138.9, 146.5.

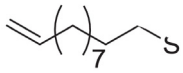
1-Fluoro-10-undecenyl acetate (**3fb**)



^{1}H NMR, δ 1.30–1.42 (m, 12 H), 1.65–1.85 (m, 2H), 2.01–2.07 (m, 2H), 2.13 (s, 3H), 4.91–5.02 (m, 2H), 5.76–5.88 (m, 1H), 6.31 (dt,

1H, J = 55.8 Hz and 5.3 Hz); ^{19}F NMR, δ −129.3 (dd, 1F, J = 55.0 Hz and 15.7 Hz); ^{13}C NMR, δ 20.7, 22.9 (d, J = 4.6 Hz), 28.9 (d, J = 9.2 Hz), 29.0, 29.2, 29.3, 33.2 (d, J = 14.3 Hz), 103.2 (d, J = 220 Hz), 114.1, 139.0, 169.0.

S-1-fluoro-10-undecenyl *O*-ethyl dithiocarbonate (**3fc**)



^{1}H NMR, δ 1.20–1.58 (m, 15 H), 1.85–2.05 (m, 4H), 4.69 (q, 2H, J = 6.5 Hz), 4.91–5.02 (m, 2H), 5.76–5.86 (m, 1H), 6.45 (dt, 1H, J = 51.9 Hz and 5.9 Hz); ^{19}F NMR, δ −154.0 (dd, 1F, J = 52.6 Hz and 17.5 Hz); ^{13}C NMR, δ 13.6, 13.7, 25.1 (d, J = 2.3 Hz), 28.8, 28.9, 33.7 (d, J = 11.0 Hz), 34.0, 70.2, 100.2 (d, J = 218.6 Hz), 114.1, 139.0, 210.2.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jfluchem.2015.01.013.

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