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Journal of Fluorine Chemistry 110 (2001) 63–73

JOURNAL OF FLUORINE CHEMISTRY

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Reactions of perfluorocycloimines with (polyfluoroalkoxy)trimethylsilanes and polyfluoroalkyltrifluoromethanesulfonates

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Received 20 February 2001; received in revised form 16 April 2001; accepted 17 May 2001

Abstract

The reactions of *F*-(5,6-dihydro-2*H*-1,4-oxazine) and *F*-(3,4-dihydro-2*H*-pyrrole) were investigated using two series of reagents: one is the polyfluoroalkylating agent $RfOSO_2CF_3$ and the other is the (polyfluoroalkoxy)trimethylsilane $RfOSi(CH_3)_3$. Systematic study with polyfluoroalkyl groups such as CF_3CH_2, $C_2F_5CH_2$, CHF_2CH_2, and $(CF_3)_2CH$ revealed that the regio-chemistry, isomer distribution, product distribution between mono-, di-, and tri-substituted products and even the reaction pathways were subtly changed by the structure of these fluoro substituents as well as by the reagent stoichiometry. A notable substitution effect was found in the reaction of *F*-(5,6-dihydro-2*H*-1,4-oxazine): substitution at the 3-position prevented the *N*-polyfluoroalkylation by $CF_3CH_2OSO_2CF_3$. No particular difference was found between the two different heterocyclic systems in contrast with the reaction of these heterocyclic systems with $C_6F_5Si(CH_3)_3$. The discussion about the reaction mechanisms for both reagents are included.

Keywords: *F*-(5,6-dihydro-2*H*-1,4-oxazine); *F*-(3,4-dihydro-2*H*-pyrrole); Polyfluoroalkoxylation; Polyfluoroalkylation; Polysubstituted perfluorocycloimines

1. Introduction

Nitrogen-containing perfluoro compounds are of considerable interest because of their utility as fire extinguishers, surface-active agents, liquid crystals, etc. [1–3]. In the preceding papers, we have reported synthesis and chemistry of perfluoroazaalkenes: perfluorocycloimines and *F*-2-azapropene are easily obtained by pyrolysis of alkali salts of *F*-(cycloamino-substituted acetic) acids [4] and *F*-(dimethylaminoacetic) acid, respectively [5]. About *F*-(5,6-dihydro-2*H*-1,4-oxazine) (**1**), we reported two types of fluoride anion-induced reactions such as carbon–nitrogen bond formation and substitution of an imidoyl fluorine [6]. Thus, in the presence of fluoride anion, perfluorocycloimines act as both nucleophilic and electrophilic reagents: the former case is the reaction of the amide anion intermediate formed by the attack of a fluoride anion on the carbon atom of the carbon–nitrogen double bond, and the latter case is the addition–elimination reactions of nucleophiles, such as polyfluoroalkoxy anions (Scheme 1). Therefore, perfluorocycloimines could be used as useful starting materials in the synthetic chemistry because of their interesting reactivities.

We also reported another fluoride-induced reaction of perfluorocycloimines and trimethyl(pentafluorophenyl)silane shown in Scheme 2: a reaction of **1** with trimethyl(pentafluorophenyl)silane provided not only a mono(pentafluorophenyl) compound but also bis- and tris(pentafluorophenyl) compounds, while a similar reaction of *F*-(3,4-dihydro-2*H*-pyrrole) (**2**) mainly gave a dimer of **2** with a small amount of mono(pentafluorophenyl) compound [7]. In these fluoride-induced reactions of perfluorocycloimines, product distributions, regio-selectivities, and reaction pathways considerably varied by the reagents used. In this paper, based on the above results, we studied the reactions of perfluorocycloimines **1** and **2** with (polyfluoroalkyl)trimethylsilanes and polyfluoroalkyltriflates in the presence of fluoride anion. In the polyfluoroalkylation and the polyfluoroalkoxylation, the effects of the substituent, the hetetocyclic ring, and the stoichiometry on product distributions, regio-selectivites, and reaction pathways were also investigated by the reaction of α-substituted perfluorocycloimines and by the reaction with sodium *F*-(*t*-butoxide).

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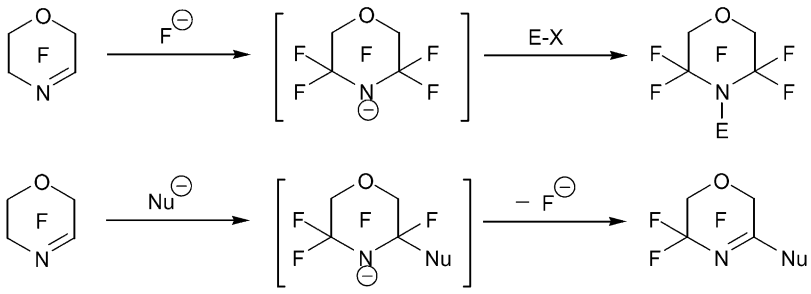
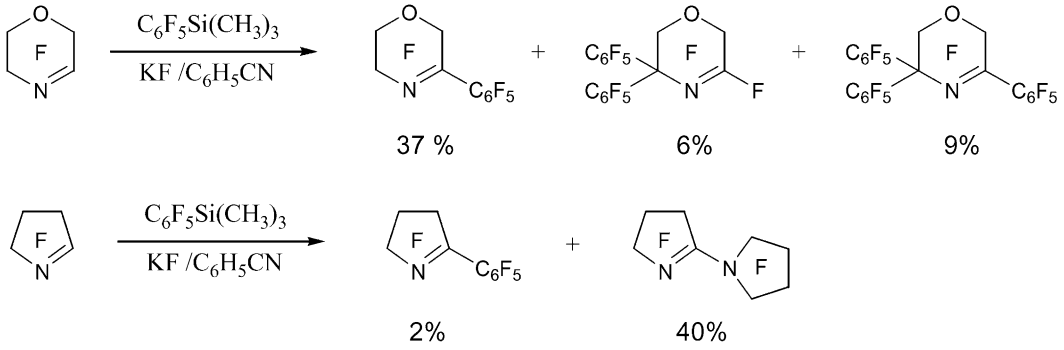
0022-1139/01/$ – see front matter
PII: S0022-1139(01)00411-0



Scheme 1.



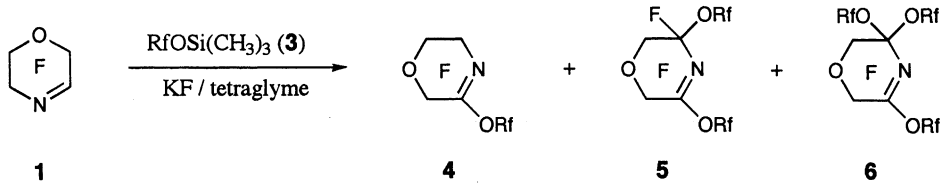
Scheme 2.

2. Results and discussion

We have found that the substituent of reagent significantly changed the reaction pathway in the reaction of *F*-(5,6-dihydro-2*H*-1,4-oxazine) (**1**) with polyfluoroalkyltrifluoromethanesulfonates [6]. In the reaction of **1** with CF_3CH_2O-SO_2CF_3, the morpholide anion formed by the attack of a fluoride anion upon **1** reacted with the methylene carbon of $CF_3CH_2OSO_2CF_3$ to give 4-(2,2,2-trifluoroethyl)-*F*-(5,6-dihydro-2*H*-1,4-oxazine). In the reaction of **1** with $(CF_3)_2$-$CHOSO_2CF_3$, however, $(CF_3)_2CHO$ anion formed by the attack of a fluoride anion upon the sulfur atom of $(CF_3)_2$-$CHOSO_2CF_3$ reacted with the carbon–nitrogen double bond of **1** to provide 3-[2,2,2-trifluoro-1-(trifluoromethyl)-ethoxy]-*F*-(5,6-dihydro-2*H*-1,4-oxazine). Since the pronounced substituent effect was observed in the reaction of **1** with polyfluoroalkyltriflates, several reaction conditions were examined in the reaction of **1** with (polyfluoroalkoxy)-trimethylsilane (**3**), changing substituents of **3** and stoichiometry between **1** and **3**. The reactions of **1** with $RfOSi(CH_3)_3$ (**3**) were carried out in a similar manner reported previously [6]: in tetraglyme in the presence of KF. Structures of products were determined by GC-MS, ^{1}H NMR, ^{19}F NMR, and FT-IR. The results of the reactions of **1** with **3** are summarized in Table 1. In the cases of an equimolar use of **3** for **1**, a catalytic use of KF improved yields of **4** in comparison with the excess use of KF (Table 1, entries 1, 2, 4, and 5). These results may be attributed to the formation of ionic products by reactions of excess KF with the substituted products. With an equimolar use of $CF_3CH_2OSi(CH_3)_3$ (**3a**) and $(CF_3)_3COSi(CH_3)_3$ (**3c**) for **1**, mono-substituted products **4a** and **4c** were selectively formed, respectively (Table 1, entries 2 and 7). In contrast, $(CF_3)_2CHOSi(CH_3)_3$ (**3b**) gave a mono-substituted product **4b** as well as a small amount of di-substituted product **5b** (Table 1, entry 5). An excess use of **3b** provided only the di-substituted product **5b** (Table 1, entry 6), while an excess use of **3a** gave the tri-substituted product **6a** as a main product together with a small amount of di-substituted product **5a** (Table 1, entry 3). The orientation of these di-substituted products **5** was decided by chemical shifts of fluorines in ^{19}F NMR spectra. The 5,5-di-substituted *F*-(5,6-dihydro-2*H*-1,4-oxazine)s had imidonyl fluorines appeared at $\delta = -50$ to 70 ppm and peaks of two equivalent fluorinated substituents at the 5-position in ^{19}F NMR [4,7]. On the other hand, **5** had the fluorine at the 5-position appeared at $\delta = -90$ to 100 ppm and the AB patterns of the fluorine peaks at the 2,6-positions in ^{19}F NMR spectra, therefore, it was decided that polyfluoroalkoxy groups of **5** occupied both 3- and 5-positions of the morpholine ring.

In order to investigate more details about product distributions and orientations of these reactions, further reactions of isolated mono-substituted compounds **4** with **3** were examined. The results of the reactions of **4a** and **4b** with **3** are also given in Tables 2 and 3, respectively. The reaction of **4a** with **3a** provided **6a** with a small amount of di-substituted compound **5a** in yields similar to the reaction of **1** with excess **3a** (Table 2, entry 1). The reaction of **4b** with **3b** provided only di-substituted compound **5b** (Table 3, entry 2), of which yield was 54%, substantially improved if

Table 1
Reactions of *F*-(5,6-dihydro-2*H*-1,4-oxazine) (**1**) with (polyfluoroalkoxy)trimethylsilanes (**3**)



a: Rf = CH_2CF_3; **b**: Rf = $CH(CF_3)_2$; **c**: Rf = $C(CF_3)_3$

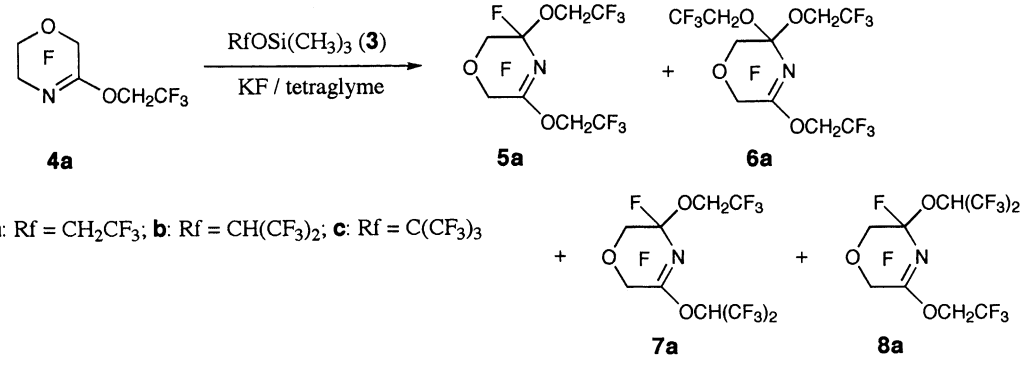
Entry	Siloxane	**1** (mmol)	**3** (mmol)	KF (mmol)	Product (yield[a]) (%)
1	**3a**	2.13	2.13	2.58	**4a** (41)
2	**3a**	3.93	3.87	0.76	**4a** (67)
3	**3a**	2.10	4.56	0.41	**5a** (5[b]), **6a** (46[b])
4	**3b**	2.39	2.50	2.58	**4b** (54), **5b** (3[b])
5	**3b**	3.83	3.66	0.93	**4b** (67), **5b** (6[b])
6	**3b**	1.65	3.66	0.33	**5b** (21)
7	**3c**	2.03	2.13	0.41	**4c** (38)

[a] Isolated yields unless otherwise noted.
[b] Determined by GC.

compared with 21% obtained in the reaction of **1** with excess **3b** (Table 1, entry 6). Both reactions of **4a** with **3b** and of **4b** with **3a** gave a mixture of **8a** (major product) and **7a** (minor product) having the CF_3CH_2O and $(CF_3)_2CHO$ groups at the 3- and 5-positions (Table 2, entry 2 and Table 3, entry 1). In the reactions of **4b** with **3a**, a small amount of **4a** was obtained unexpectedly as a by-product, suggesting the existence of the equilibrium between **4a** and **4b** under the reaction condition. Although a siloxane **3c** only gave a small amount of **5a** in the reaction with **4a** (Table 2, entry 3), **3c** reacted with **4b** to give a mixture of **7c** (major product) and **8c** (minor product) together with **5b** (Table 3, entry 3). Considerable amounts of the starting materials **4** were recovered in both cases.

The results of the reactions of **4** with $RfOSO_2CF_3$ (**9**) are summarized in Table 4. The reaction of **1** with CF_3CH_2O-SO_2CF_3 (**9a**) provided trifluoroethyl tertiary amines, while the reaction of **1** with $(CF_3)CHOSO_2CF_3$ (**9b**) gave **4b** by the substitution with the $(CF_3)_2CHO$ group at the 3-position [5]. The occupation at the 3-position of the morpholine ring, however, inhibited the reaction of **4** with **9a** to provide trifluoroethyl tertiary amines. Thus, the reaction of **4b** with **9a** gave only **5b** having $(CF_3)_2CHO$ groups both at 3- and 5-positions of the morpholine ring (Table 4, entry 3). The

Table 2
Reactions of 3-(2,2,2-trifluoroethoxy)-*F*-(5,6-dihydro-*H*-1,4-oxazine) (**4a**) with (polyfluoroalkoxy)trimethylsilanes (**3**)

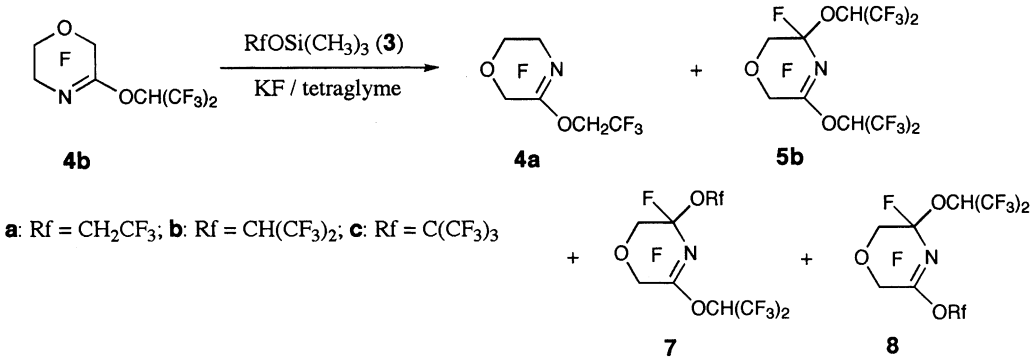


a: Rf = CH_2CF_3; **b**: Rf = $CH(CF_3)_2$; **c**: Rf = $C(CF_3)_3$

Entry	Siloxane	**4a** (mmol)	**3** (mmol)	KF (mmol)	Product (yield[a]) (%)	Recovery of **4a** (%)
1	**3a**	0.73	0.74	0.15	**5a** (9), **6a** (45)	21
2	**3b**	0.76	0.77	0.15	**7a** (7), **8a** (20)	–
3	**3c**	0.47	0.48	0.10	**5a** (5)	55

[a] Determined by GC.

Table 3
Reactions of 3-[2,2,2-trifluor(1-trifluoromethyl)ethoxy]-*F*-(5,6-dihydro-2*H*-1,4-oxazine) (**4b**) with (polyfluoroalkoxy)trimethylsilanes (**3**)



Entry	Siloxane	**4b** (mmol)	**3** (mmol)	KF (mmol)	Product (yield[a]) (%)	Recovery of **4b** (%)
1	**3a**	1.07	1.08	0.21	**4a** (3), **7a** (11), **8a** (33)	–
2	**3b**	1.26	1.26	0.26	**5b**[b] (54[c])	
3	**3c**	0.50	0.51	0.10	**5b** (12), **7c** (19), **8c** (7.7)	31

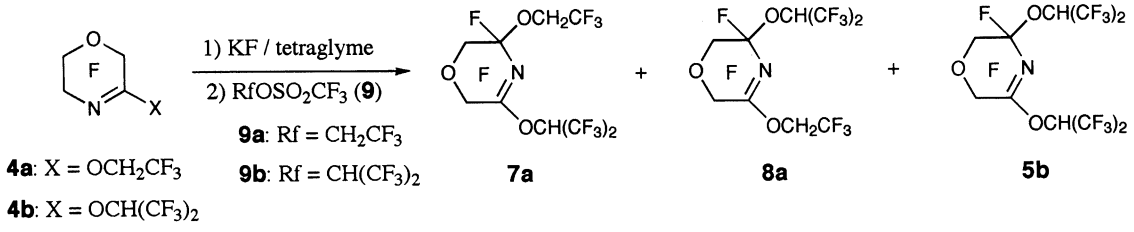
[a] Determined by GC unless otherwise noted.
[b] **5b** = **7b** = **8b**.
[c] Isolated yields.

formation of **5b** is explained by the reaction of **4b** with the $(CF_3)_2CHO$ anion which was catalytically eliminated from **4b** in the presence of KF. In contrast of **9a**, $(CF_3)CHO\text{-}SO_2CF_3$ (**9b**) released $(CF_3)_2CHO$ anion under the reaction condition so that the treatment of either **4a** or **4b** with **9b** gave 3,5-di-substituted compounds (Table 4, entries 2 and 4). The major position isomer was **8a** similarly to the reaction of **4** with **3**.

Next, in order to examine effects of the fluoride anion on the reaction mechanism, the reactions of **1** and **4** with sodium alkoxide $(CF_3)_3CONa$ (**10**) were carried out in the absence of KF. The results are summarized in Table 5. On the reaction of acyclic perfluoroazaalkenes with lithium alkoxides, the formation of a mixture of mono- and di-alkoxy compound was reported by Shreeve and coworkers [8]. However, the reaction of **1** with **10** gave only a mono-substituted compound **4c** (Table 5, entry 1) similarly to the reaction of **1** with **3c** in the presence of KF. The occupation at the 3-position of the morpholine ring inhibited the reaction of **4a** with **10**; the starting material **4a** mostly recovered (Table 5, entry 2). In the reaction of **4b** with **10**, 2-position isomers of 3,5-di-substituted compounds **7c** and **8c** accompanied with a small amount of **5b** (Table 5, entry 3).

With respect to the reaction of perfluorocycloimines with nucleophilic reagents, reactions of *F*-(1-azacyclohexene) with sodium pentachlorophenoxide and sodium bis(trifluoro-

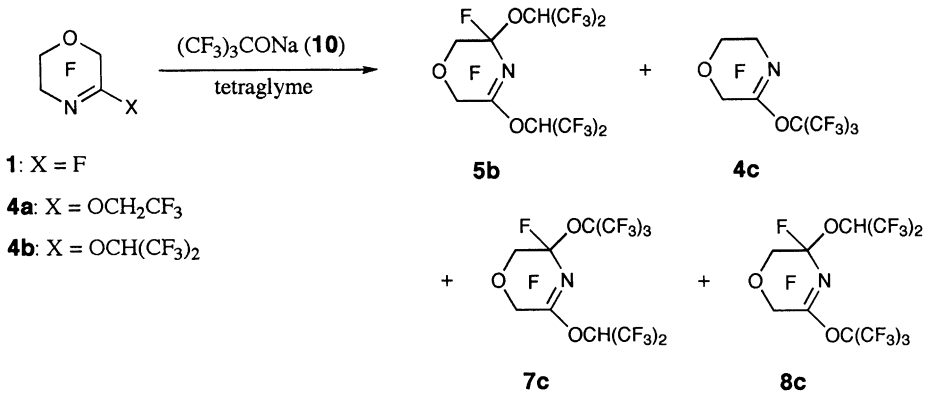
Table 4
Reactions of polyfluoroalkoxylated *F*-(5,6-dihydro-2*H*-1,4-oxazine)s with polyfluoroalkyltriflates (**9**)



Entry	Imine (mmol)	Triflate (mmol)	KF (mmol)	Products (yield[a]) (%)	Recovery of imies (%)
1	**4a** (0.69)	**9a** (0.70)	0.69	–	**4a** (61)
2	**4a** (0.95)	**9b** (0.99)	1.15	**7a** (4), **8a** (11)	**4a** (20)
3	**4b** (0.50)	**9a** (0.50)	0.50	**5b** (27)	**4b** (19)
4	**4b** (1.10)	**9b** (0.75)	1.08	**5b**[b] (58[c])	–

[a] Determined by GC unless otherwise noted.
[b] **5b** = **7b** = **8b**.
[c] Isolated yields.

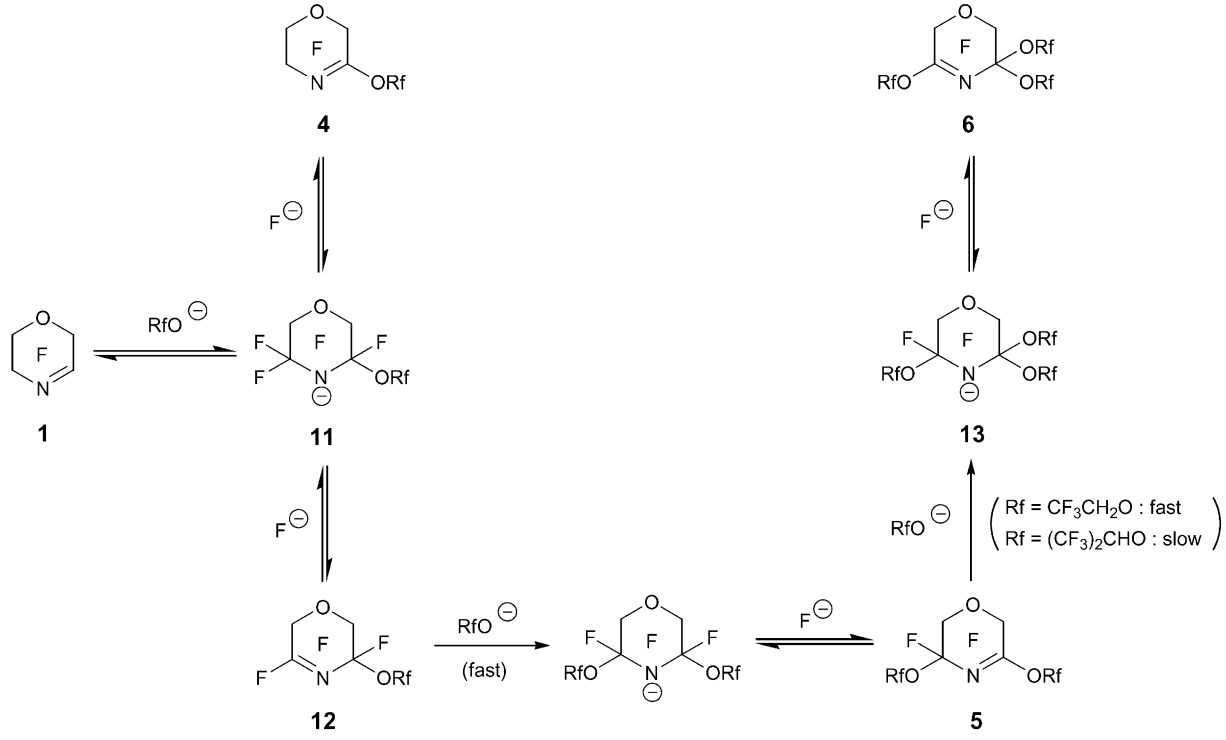
Table 5
Reactions of polyfluoroalkoxylated *F*-(5,6-dihydro-2*H*-1,4-oxazine)s with sodium *F*-(*t*-butoxide) (**10**)



Entry	Imine (mmol)	**10** (mmol)	Product (yield[a])	Recovery of imines (%)
1	**1** (2.32)	2.56	**4c** (36)	**1** (2)
2	**4a** (0.54)	0.54	–	**4a** (42)
3	**4b** (0.54)	0.67	**5b** (2), **7c** (24), **8c** (14)	**4b** (45)

[a] Determined by GC.

methyl)aminoalkoxide were previously reported [9]. These reactions gave only mono-substituted compounds and were explained by the replacement of an imidoyl fluorine via the nucleophilic addition–elimination mechanism (Ad_N–E). In treatment of *F*-(1-azacyclohexene) with *N*,*N*-bis(trifluoromethyl)hydroxyamine, a 2,6-di-substituted compound formed besides the mono-substituted compound; however, the mechanism of this reaction was not described [10]. About the reaction of perfluorocycloimines with polyfluoroalkylsiloxanes, it is considered that the polyfluoroalkoxy (RfO) anion is the active reacting species and polyfluoroalkoxylation also proceeds via the addition–elimination mechanism (Ad_N–E) shown in Scheme 3. The attack of the RfO anion upon the carbon–nitrogen double bond of perfluorocyclo-

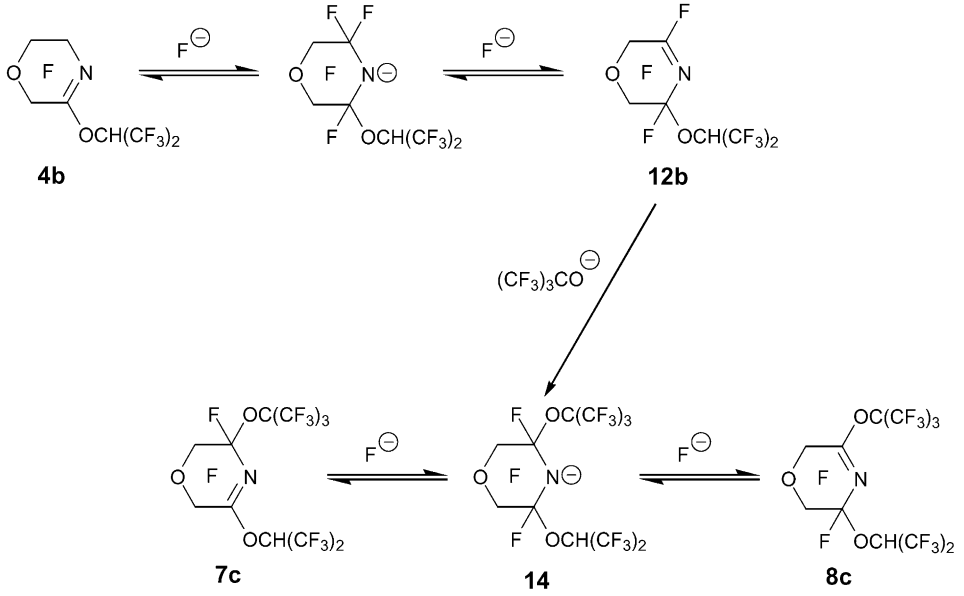


Scheme 3.

imine **1** gives morpholide intermediate **11**, which provides mono-substituted compounds **4** by release of a fluoride anion from the same position as the one where the RfO group is introduced. In the presence of a fluoride anion, the equilibrium between perfluorocycloimine and its amide anion has been known [11]. Through this amide anion **11**, mono-substituted compounds **4** are further equilibrated with their position isomers **12**. Because the addition of the RfO anion to **4** was slow and a dominant isomer was **4** under the equilibrium in the presence of a fluoride anion, the reaction of **1** with an equal mole of polyfluoroalkylsiloxanes gave only mono-substituted compounds **4**. The reaction of the position isomer **12** with the RfO anion gave 3,5-di-substituted compound **5**, which further reacted with the RfO anion to give a 3,3,5-tri-substituted compound **6** via a 3,3,5-tri-substituted anion intermediate **13**. Because the $(CF_3)_2CHO$ anion is more bulky than the CF_3CH_2O anion, the attack of the $(CF_3)_2CHO$ anion upon **5** is more difficult than the one of the CF_3CH_2O anion. By use of excess siloxanes **3**, therefore, $(CF_3)_2CHOSi(CH_3)_3$ (**3b**) provided the di-substituted compound **5b** without formation of the tri-substituted compound **6b**, while $CF_3CH_2OSi(CH_3)_3$ (**3a**) provided the tri-substituted compound **6a**.

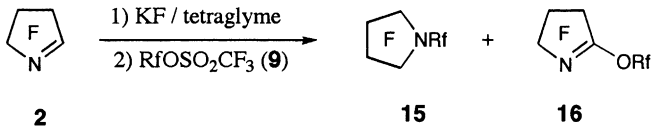
According to the Ad_N–E mechanism, the formation of the position isomer **12b** is prerequisite for the formation of **7c** and **8c** (Scheme 4), which means the requirement of the fluoride anions in the initial stage of the reaction as a trigger. Highly suspected of this trigger is the adventitious water included in the reagent **10** or in the solvent tetraglyme, which reacts with **4** to give a catalytic amount of fluoride anions. If this is the case for **4b**, then, the case for **4a** with no formation of **7a** and **8a** remained as an open question. The product ratios of **7c** to **8c** (**7c** > **8c**), and of **7a** to **8a** (**7a** < **8a**) seem to be ruled by the substituent bonding at the carbon–nitrogen double bond. That is to say, the main isomer is the product formed by the release of a fluoride anion from the position where the substituent having a larger inductive effect (I effect: $–OCH_2CF_3 > –OCH(CF_3)_2 > –OC(CF_3)_3$) is bonded to. The result indicated that the product ratio of the 3,5-di-substituted compounds is not the results of a kinetic control but the results of thermodynamic control.

Hetrocyclic ring effects, which we previously observed in the reactions of **1** and **2** with (pentafluorophenyl)trimethylsilane (Scheme 2), were examined by the reaction of *F*-(3,4-dihydro-2*H*-pyrrole) (**2**) with polyfluoroalkylsiloxanes and polyfluoroalkyltriflates. The reactions of **2** with $RfOSO_2CF_3$ (**9**) showed approximately the same tendency as the reaction of **1** with **9** [6], and the results are given in Table 6. In the cases of primary alkyltriflates (**9a**, **9c**, and **9d**), the methylene carbon of the $Rf'CH_2$ ($Rf'=CF_3$, CF_3CF_2, CHF_2) group of **9** was added to the nitrogen atom (at the 1-position) of the pyrrolidine ring to provide 1-(polyfluoroalkyl)-*F*-pyrrolidine (**15**) (Table 6, entries 1, 3, and 4). The reaction with **9b**, that is secondary alkyltriflates, afforded 5-(polyfluoroalkoxy)-*F*-(3,4-dihydro-2*H*-pyrrole) (**16**) by the attack of the $(CF_3)_2CHO$ anion on the carbon–nitrogen double bond (Table 6, entry 2). Similarly to the reaction of **1** with **9**, the reaction of **2** with **9** is considered to proceed via the different pathway depending on the variety of polyfluoroalkoxy groups (Scheme 5). The fluoride anion could react with two reactants, **2** and **9**; the reaction of the fluoride anion with **2** gave pyrrolidide anion **17** in the cases of the primary alkyltriflates (**9a**, **9c**, and **9d**), and the reaction of the fluoride anion with **9** gave RfO anion in the case of **9b** (Scheme 5, Eq. (1)). The pyrrolidide intermediate **17** attacked the methylene carbon of **9** to provide the *N*-polyfluoroalkyl compound **15** (Scheme 5, Eq. (2)). On the other hand, the RfO anion attacked the carbon–nitrogen double bond of **2** to



Scheme 4.

Table 6
Reactions of *F*-(3,4-dihydro-2*H*-pyrrole) (**2**) with polyfluoroalkyltriflates (**9**)



2 **15** **16**

a: Rf = CH_2CF_3; **b**: Rf = $CH(CF_3)_2$; **c**:Rf = $CH_2C_2F_5$; **d**: Rf = CH_2CHF_2

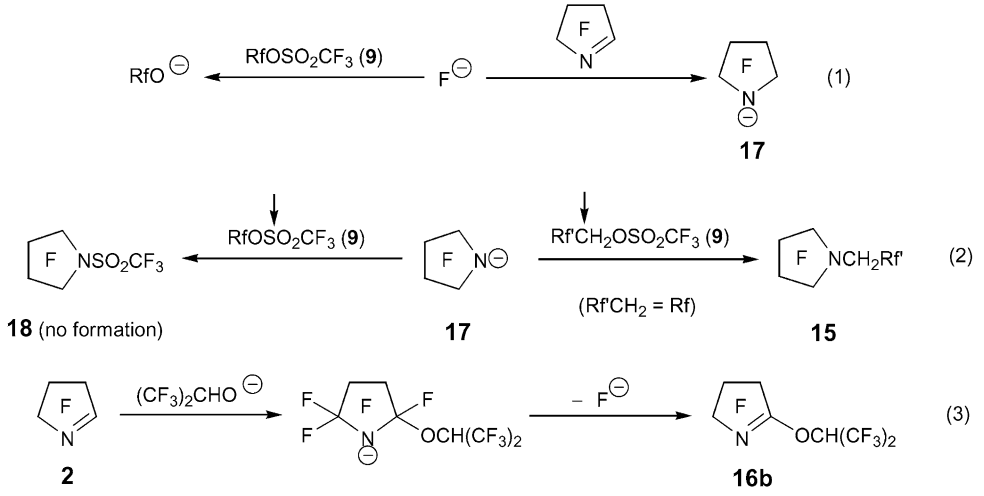
Entry	Triflate	**1** (mmol)	**9** (mmol)	KF (mmol)	Product (yield[a]) (%)
1	**9a**	1.62	1.35	2.07	**15a** (70)
2	**9b**	1.34	1.14	1.72	**16b** (46[b])
3	**9c**	2.46	2.05	2.58	**15c** (71)
4	**9d**	2.34	1.95	2.75	**15d** (70)

[a] Isolated yields based on **9** unless otherwise noted.
[b] Determined by GC.

provide 5-RfO compound **16b** by the successive defluorination (Scheme 5, Eq. (3)). In the case of the reaction of **4a** with **9a**, the reason why no polyfluoroalkylated and polyfluoroalkoxylated compounds was obtained and the starting materials were recovered seems to be low reactivities of both **4a** and **9a** for fluoride anion.

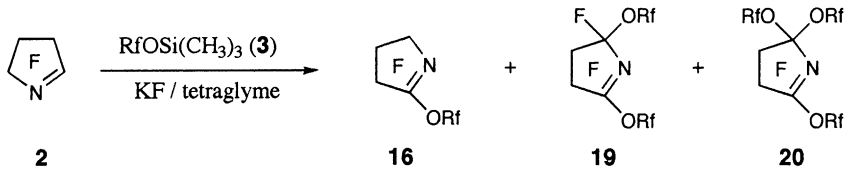
The ambivalent nature of the polyfluoroalkyltriflate on the nucleophilic alkylation was disclosed by Kobayashi et al. [13]. Thus, the enamine, 1-(piperidino)cyclohexene attacks $H(CF_2)_6CH_2OSO_2CF_3$ at the CH_2 carbon [12], while the same nucleophile attacks $CF_3OSO_2CF_3$ at the sulfur atom [13]. In our case, liable nucleophiles are a fluoride anion and a perfluoropyrrolidide anion under the condition of the reaction of **2** with **9**. It was found that **9a**, **9c**, and **9d** followed the same reaction pathway as $H(CF_2)_6CH_2O$-SO_2CF_3, but, interestingly, **9b** followed neither the pathway of $H(CF_2)_6CH_2OSO_2CF_3$ nor the pathway of $CF_3OSO_2CF_3$ (Scheme 5). Thus, both *N*-polyfluoroalkylated product **15** and sulfonamide product **18** were not found even by a rather careful search and the obtained was **16b** only. This product was obviously obtained by the substitution of an imidoyl fluorine with the alkoxide $(CF_3)_2CHO$ anion. The reaction pathways taken by **9a**, **9c**, **9d** and by **9b** were totally different and vigorously exclusive so that no **16** type product was formed in the cases of **9a**, **9c** and **9d** as well as no **15** type product was formed in the case of **9b**. In other words, the acting nuleophile against **9** is exclusively a perfluoropyrrolidide anion in the former and a fluoride anion in the latter. The replacement of a hydrogen of $RfCH_2O$ with CF_3 has two meanings. One is the inhibition of the attack by the perfluoropyrrolidide nuleophile and the other is the endowment of the leaving ability as the alkoxide. This dual effect of the CF_3 substitution seems to be the reason for the switching of the reaction pathways.

The results of the reactions of **2** with $RfOSi(CH_3)_3$ (**3**) also showed similar tendencies to the reactions of **1** with **3** about products and their yields (Table 7) [6]. The substitution of an imidoyl fluorine smoothly proceeded in the cases of the



Scheme 5.

Table 7
Reactions of *F*-(3,4-dihydro-2*H*-pyrrole) (**2**) with (polyfluoroalkoxy)trimethylsilanes (**3**)



a: Rf = CH_2CF_3; **b**: Rf = $CH(CF_3)_2$

Entry	Triflate	**2** (mmol)	**3** (mmol)	KF (mmol)	Product (yield[a]) (%)
1	**3a**	6.10	6.15	1.22	**16a** (56)
2	**3a**	1.95	4.30	0.39	**20a** (24)
3	**3b**	5.98	6.00	1.19	**16b** (68), **19b** (74[b])
4	**3b**	2.00	4.42	0.40	**19b** (18[b,c])

[a] Isolated yields otherwise noted.
[b] Determined by GC, high-boiling decomposed compounds also formed.

reactions of **2** with **3** to give mono-substituted compounds **16** (Table 7, entries 1 and 3). With excess amounts of **3**, a tri-substituted compound **20a** and a di-substituted compound **19b** were obtained depending on the Rf groups (Table 7, entries 2 and 4); however, high-boiling decomposed compounds also formed in the reaction of **2** with **3b**. In every entry, no dimerization of **2** occurred, in contrast with the reaction of **2** with $C_6F_5Si(CH_3)_3$ [7]. Thus, the heterocyclic ring effects between **1** and **2** was not observed in the reactions with **3** and **9**, suggesting the higher reactivities of polyfluoroalkylsiloxanes and polyfluoroalkyltriflates than $C_6F_5Si(CH_3)_3$, surpassing the reactivity of **2** on the dimerization.

In conclusion, the product distributions, regio-selectivites, and reaction pathways depended on the polyfluoroalkoxy group of reagents, for both reactions of perfluorocycloimines with (polyfluoroalkoxy)trimethylsilanes and polyfluoroalkyltrifluoromethanesulfonates. This result was caused by the releasing abilities of polyfluoroalkoxy anions from reagents, that is, the stability of polyfluoroalkoxy anions. The heterocyclic ring effect observed in the reaction of perfluorocycloimines with $C_6F_5Si(CH_3)_3$ was not observed in both reactions of perfluorocycloimines with (polyfluoroalkoxy)-trimethylsilanes and polyfluoroalkyltriflates.

3. Experimental details

3.1. General procedure

Gases and volatile liquids were handled in a conventional Pyrex glass vacuum system equipped with a Heise–Bourdon tube gauge and a Televac thermocouple gauge. Gas chromatography was carried out on a Shimadzu GC-17A instrument (column: 60 m × 0.25 m i.d., 1.5 μm NEUTRA BOND-1, GC Sciences Inc.). GC-MS spectral data were obtained with a Shimadzu QP-5000 quadrupole mass spectrometer by electron-impact ionization at 70 eV (column: 60 m × 0.25 m i.d., 1.5 μm NEUTRA BOND-1, GC Sciences Inc.). FT-IR spectra were obtained with a Shimadzu FT-IR-8600PC spectrometer with KBr windows. ^{19}F NMR spectra were recorded with a Varian INOVA-300 spectrometer at 282.24 MHz with $CDCl_3$ as the solvent; positive δ value downfield from the internal reference, $CFCl_3$.

3.2. Materials

Starting materials, *F*-(5,6-dihydro-2*H*-1,4-oxazine) (**1**) and *F*-(3,4-dihydro-2*H*-pyrrole) (**2**), were prepared by pyrolysis of potassium perfluoromorpholinoacetate and potassium perfluoropyrrolidinoacetate, respectively [4]. These perfluorocycloimines, **1** and **2**, were used as over 95% purities after repeated trap-to-trap distillation. (Polyfluoroalkoxy)trimethylsilanes were prepared by the reactions of the corresponding polyfluoroalcohols with 1,1,1,3,3,3-hexamethyldisilazane in the presence of sodium saccharin [14,15]. Polyfluoroalkyltrifluoromethanesulfonates were prepared by the reactions of trifluoromethanesulfonyl chloride with the corresponding polyfluoroalcohols [16,17]. Sodium 2,2,2-trifluoro-1,1-bis(trifluoromethyl)ethoxide was prepared by the reaction of 2,2,2-trifluoro-1,1-bis(trifluoromethyl)ethanol with sodium hydroxide and dried at 50–60°C under vacuum before using. Spray-dried KF was purchased from Wako Pure Chemical Industries Inc. All solvents were used after drying over Molecular Sieves 4A 1/16 and freeze-degassing.

3.3. Procedure for the reaction of F-(5,6-dihydro-2H-1,4-oxazine) (1) with trimethyl[2,2,2-trifluoro-1,1-bis(trifluoromethyl)ethoxy]silane (3c)

Spray-dried KF (0.024 g, 0.41 mmol) was placed in a 100 ml reaction vessel, and was dried at 80–90°C under

vacuum. Dried tetraglyme (5 ml) was added under an argon atmosphere, and then **1** (0.428 g, 2.03 mmol) and **3c** (0.657 g, 2.13 mmol) were vacuum transferred to the reaction vessel at −196°C. The mixture in the reaction vessel was stirred at 70°C for 48 h. Under reduced pressure from the reaction mixture at 50°C, 3-[2,2,2-trifluoro-1,1-bis(trifluoromethyl)ethoxy]-*F*-(5,6-dihydro-2*H*-1,4-oxazine) (**4c**) was trap-to-trap distilled into a trap cooled at −55°C in 38% isolated yield.

Spectral data for **4c**: ^{19}F NMR ($CDCl_3$) δ: −68.2 (br s, 9F, 3-OC(CF_3)$_3$), −73.5 (t, J = 5.1 Hz, 2F, 5-F), −89.2 (m, 2F, 2-F), −94.6 (br s, 2F, 6-F); GC-MS (EI, 70 eV, *m/z*): 408 ([M − F]$^+$, 5), 380 ([M − COF]$^+$, 2), 361 ([M − COF_2]$^+$, 12), 142 ($C_3F_4NO^+$, 12), 119 ($C_2F_5^+$, 11), 100 ($C_2F_4^+$, 17), 92 ($C_2F_2NO^+$, 100), 76 ($C_2F_2N^+$, 14), 69 (CF_3^+, 42); IR (cm^{-1}): 1730 ($\nu_{C=N}$).

3.4. General procedure for the reaction of F-(5,6-dihydro-2H-1,4-oxazine) (*1*) with excess (polyfluoroalkoxy)trimethylsilanes (*3*)

Spray-dried KF (0.024 g, 0.41 mmol) was placed in a 100 ml reaction vessel, and was dried at 80–90°C under vacuum. Dried tetraglyme (5 ml) was added under an argon atmosphere, and then **1** (0.436 g, 2.10 mmol) and **3a** (0.786 g, 4.56 mmol) were vacuum transferred to the reaction vessel at −196°C. The mixture in the reaction vessel was stirred at 70°C for 48 h. Under reduced pressure from the reaction mixture at 0°C, a mixture of 3,5-bis(2,2,2-trifluoroethoxy)-*F*-(5,6-dihydro-2*H*-1,4-oxazine) (**5a**) (5% GC yield) and 3,5,5-tris(2,2,2-trifluoroethoxy)-*F*-(5,6-dihydro-2*H*-1,4-oxazine) (**6a**) (2% GC yield) was trap-to-trap distilled into a trap cooled at −78 and −20°C. Then, trap-to-trap distillation (50°C, 1 mmHg) of the residue provided the tris(trifluoroethoxy) product **6a** in 44% isolated yield.

Spectral data for **5a**: ^{1}H NMR ($CDCl_3$) δ: 4.29 (m, 2H, 5-OCH_2CF_3), 4.76 (q, J = 8.4 Hz, 2H, 3-OCH_2CF_3); ^{19}F NMR ($CDCl_3$) δ: −72.5 (AB, J = 181 Hz, 1F, 2-F), −73.9 (m, 3F, 5-OCH_2CF_3), −74.8 (t, J = 8.4 Hz, 3F, 3-OCH_2CF_3), −75.4 (AB, J = 181 Hz, 1F, 2-F), −88.0 (AB, J = 150 Hz, 1F, 6-F), −91.9 (AB, J = 150 Hz, 1F, 6-F), −97.4 (br t, J = 15.5 Hz, 1F, 5-F); GC-MS (EI, 70 eV, *m/z*): 371 ([M − F]$^+$, 9), 305 ([M − COF]$^+$, 37), 272 ([M−OCH_2CF_3]$^+$, 11), 172 ($C_4H_2F_4NO_2^+$, 17), 130 ($C_2F_4NO^+$, 10), 124 ($C_4F_4^+$, 19), 83 (CF_3N^+, 100), 69 (CF_3^+, 13), 64 (CF_2N, 22).

Spectral data for **6a**: ^{1}H NMR ($CDCl_3$) δ: 4.13 (m, 2H, 5-OCH_2CF_3), 4.23 (m, 2H, 5-OCH_2CF_3), 4.72 (q, J = 7.4 Hz, 2H, 3-OCH_2CF_3); ^{19}F NMR ($CDCl_3$) δ: −73.8 (t, J = 5.1 Hz, 2F, 2-F), −73.9 (t, J = 7.4 Hz, 3F, 3-OCH_2CF_3), −74.8 (t, J = 7.8 Hz, 6F, 5-OCH_2CF_3), −86.8 (br s, 2F, 6-F); GC-MS (EI, 70 eV, *m/z*): 432 ([M − F]$^+$, 2), 385 ([M−COF_2]$^+$, 37), 352 ([M − OCH_2CF_3]$^+$, 25), 127 ($C_3HF_4N^+$, 17), 83 (CF_3N^+, 100), 70 (CHF_3^+, 15); IR (cm^{-1}): 1705 ($\nu_{C=N}$).

3.5. General procedure for the reaction of polyfluoroalkoxylated F-(5,6-dihydro-2H-1,4-oxazine) (*4*) with (polyfluoroalkoxy)trimethylsilanes (*3*)

Spray-dried KF (0.015 g, 0.26 mmol) was placed in a 100 ml reaction vessel, and was dried at 80–90°C under vacuum. Dried tetraglyme (5 ml) was added under an argon atmosphere, and then **4b** (0.452 g, 1.26 mmol) and **3a** (0.303 g, 1.26 mmol) were vacuum transferred to the reaction vessel at −196°C. The mixture in the reaction vessel was stirred at 70°C for 20 h. Under reduced pressure from the reaction mixture at 50°C, 3,5-bis[2,2,2-trifluoro-1-(trifluoromethyl)ethoxy]-*F*-(5,6-dihydro-2*H*-1,4-oxazine) (**5b**) was trap-to-trap distilled into a trap cooled at −20°C in 54% isolated yield.

Spectral data for **5b**: ^{1}H NMR ($CDCl_3$) δ: 5.06 (septet, J = 5.1 Hz, 1H, 5-OCH(CF_3)$_2$), 5.87 (septet, J = 5.4 Hz, 1H, 3-OCH(CF_3)$_2$); ^{19}F NMR ($CDCl_3$) δ: −73.6 (m, 3F, 5-OCH(CF_3)$_2$), −73.7 (m, 3F, 5-OCH(CF_3)$_2$), −73.9 (d, J = 5.4 Hz, 6F, 3-OCH(CF_3)$_2$), −74.1 (AB, J = 181 Hz, 1F, 2-F), −75.2 (AB, J = 181 Hz, 1F, 2-F), −89.4 (AB, J = 151 Hz, 1F, 6-F), −91.2 (AB, J = 151 Hz, 1F, 6-F), −96.9 (m, 1F, 5-F); GC-MS (EI, 70 eV, *m/z*): 488 ([M − F]$^+$, 12), 441 ([M − COF_2]$^+$, 39), 340 ([M − OCH(CF_3)$_2$]$^+$, 11), 267 ($C_5HF_{10}O^+$, 9), 240 ($C_5HF_7NO_2^+$, 42), 151 ([CH(CF_3)$_2$]$^+$, 29), 132 ($C_3HF_5^+$, 6), 124 ($C_4F_4^+$, 25), 113 ($C_3HF_4^+$, 8), 92 ($C_2F_2NO^+$, 11), 76 ($C_2F_2N^+$, 6), 70 (CHF_3^+, 8), 69 (CF_3^+, 100); IR (cm^{-1}): 1716 ($\nu_{C=N}$).

3.6. General procedure for the reaction of polyfluoroalkoxylated F-(5,6-dihydro-2H-1,4-oxazine) (*4*) with polyfluoroalkyltrifluoromethanesulfonates (*9*)

Spray-dried KF (0.067 g, 1.15 mmol) was placed in a 100 ml reaction vessel, and was dried at 80–90°C under vacuum. Dried tetraglyme (5 ml) was added under an argon atmosphere, and then **4a** (0.297 g, 0.96 mmol) and **9b** (0.290 g, 0.99 mmol) were vacuum transferred to the reaction vessel at −196°C. The mixture in the reaction vessel was stirred for 0°C for 1 h and then at 50°C for 20 h. Under reduced pressure from the reaction mixture at 50°C, a mixture of 3-[2,2,2-trifluoro-1-(trifluoromethyl)ethoxy]-5-(2,2,2-trifluoroethoxy)-*F*-(5,6-dihydro-2*H*-1,4-oxazine) (**7a**, 4% GC yield) and 3-(2,2,2-trifluoroethoxy)-5-[2,2,2-trifluoro-1-(trifluoromethyl)ethoxy]-*F*-(5,6-dihydro-2*H*-1,4-oxazine) (**8a**, 10% GC yield) was trap-to-trap distilled into a trap cooled at −50 and −20°C.

Spectral data for **7a**: ^{1}H NMR ($CDCl_3$) δ: 4.16 (m, 2H, 5-OCH_2CF_3), 5.92 (m, 1H, 3-OCH(CF_3)$_2$); ^{19}F NMR ($CDCl_3$) δ: −72.9 (AB, J = 181 Hz, 1F, 2-F), −73.8 (m, 6F, 3-OCH(CF_3)$_2$), −73.9 (t, J = 7.8 Hz, 3F, 5-OCH_2CF_3), −75.1 (AB, J = 181 Hz, 1F, 2-F), −88.3 (AB, J = 152 Hz, 1F, 6-F), −91.7 (AB, J = 152 Hz, 1F, 6-F), −94.4 (m, 1F, 5-F); GC-MS (EI, 70 eV, *m/z*): 420 ([M − F]$^+$, 16), 373 ([M − COF_2]$^+$, 64), 272 ([M−OCH(CF_3)$_2$]$^+$, 18), 240 ($C_5HF_7NO_2^+$, 23), 199 ($C_4H_2F_7O^+$,

8), 151 ($[CH(CF_3)_2]^+$, 18), 132 ($C_3HF_5^+$, 8), 124 ($C_4F_4^+$, 51), 97 ($C_2H_2F_3N^+$, 10), 92 ($C_2F_2NO^+$, 10), 83 ($CF_3CH_2^+$, 100), 76 ($C_2F_2N^+$, 9), 70 (CHF_3^+, 10), 69 (CF_3^+, 89); IR (cm^{-1}): 1700 ($\nu_{C=N}$).

Spectral data for **8a**: ^1H NMR ($CDCl_3$) δ: 4.46 (q, $J = 7.8$ Hz, 2H, 3-OCH_2CF_3), 5.92 (septet, $J = 5.4$ Hz, 1H, 5-$OCH(CF_3)_2$); ^{19}F NMR ($CDCl_3$) δ: −73.4 (m, 6F, 5-$OCH(CF_3)_2$), −73.5 (AB, $J = 181$ Hz, 1F, 2-F), −74.9 (t, $J = 8.1$ Hz, 3F, 3-OCH_2CF_3), −75.2 (AB, $J = 181$ Hz, 1F, 2-F), −89.1 (AB, $J = 150$ Hz, 1F, 6-F), −91.1 (AB, $J = 150$ Hz, 1F, 6-F), −99.7 (m, 1F, 5-F); GC-MS (EI, 70 eV, *m/z*): 420 ($[M - F]^+$, 10), 373 ($[M - COF_2]^+$, 49), 340 ($[M - OCH_2CF_3]^+$, 9), 267 ($C_5HF_{10}O^+$, 9), 172 ($C_4H_2F_4NO_2^+$, 57), 151 ($[CH(CF_3)_2]^+$, 11), 124 ($C_4F_4^+$, 18), 83 ($CF_3CH_2^+$, 100), 76 ($C_2F_2N^+$, 8), 70 (CHF_3^+, 9), 69 (CF_3^+, 71); IR (cm^{-1}): 1734 ($\nu_{C=N}$).

*3.7. General procedure for the reaction of F-(5,6-dihydro-2H-1,4-oxazine)s (**4**) with sodium 2,2,2-trifluoro-1,1-bis(trifluoromethyl)ethoxide (**10**)*

A 0.173 g (0.67 mmol) of **10** was placed in a 100 ml reaction vessel, and was dried at 80–90°C under vacuum. Dried tetraglyme (5 ml) was added under an argon atmosphere, and then **4b** (0.193 g, 0.54 mmol) were vacuum transferred to the reaction vessel at −196°C. The mixture in the reaction vessel was stirred for 70°C for 20 h. Under reduced pressure from the reaction mixture at 50°C, a mixture of three 3,5-di-substituted compounds, 3-[2,2,2-trifluoro-1-(trifluoromethyl)ethoxy]-5-[2,2,2-trifluoro-1,1-bis(trifluoromethyl)ethoxy]-*F*-(5,6-dihydro-2*H*-1,4-oxazine) (**7c**, 24% GC yield), 3-[2,2,2-trifluoro-1,1-bis(trifluoromethyl)ethoxy]-5-[2,2,2-trifluoro-1-(trifluoromethyl)ethoxy]-*F*-(5,6-dihydro-2*H*-1,4-oxazine) (**8c**, 14% GC yield), and **5b** (2% GC yield), were trap-to-trap distilled into a trap cooled at −55 and −20°C. A 45% of **4b** was also recovered.

Spectral data for **7c**: ^1H NMR ($CDCl_3$) δ: 5.83 (septet, $J = 5.4$ Hz); ^{19}F NMR ($CDCl_3$) δ: −70.1 (br s, 9F, 5-$OC(CF_3)_3$), −73.0 (AB, $J = 181$ Hz, 1F, 2-F), −73.5 (m, 6F, 3-$OCH(CF_3)_2$), −75.8 (AB, $J = 181$ Hz, 1F, 2-F), −88.9 (AB, $J = 146$ Hz, 1F, 6-F), −92.7 (m, 1F, 5-F), −93.0 (AB, $J = 146$ Hz, 1F, 6-F); GC-MS (EI, 70 eV, *m/z*): 556 ($[M - F]^+$, 9), 509 ($[M - COF_2]^+$, 20), 340 ($[M - OC(CF_3)_3]^+$, 14), 308 ($C_7HF_{11}N^+$, 17), 151 ($[CH(CF_3)_2]^+$, 18), 124 ($C_4F_4^+$, 14), 92 ($C_2F_2NO^+$, 12), 69 (CF_3^+, 100).

Spectral data for **8c**: ^1H NMR ($CDCl_3$) δ: 5.01 (septet, $J = 5.7$ Hz); ^{19}F NMR ($CDCl_3$) δ: −69.3 (br s, 9F, 3-$OC(CF_3)_3$), −72.7 (AB, $J = 180$ Hz, 1F, 2-F), −73.6 (m, 6F, 5-$OCH(CF_3)_2$), −76.1 (AB, $J = 180$ Hz, 1F, 2-F), −87.5 (AB, $J = 152$ Hz, 1F, 6-F), −92.0 (m, 1F, 5-F), −93.1 (AB, $J = 152$ Hz, 1F, 6-F); GC-MS (EI, 70 eV, *m/z*): 556 ($[M - F]^+$, 9), 509 ($[M - COF_2]^+$, 14), 408 ($[M - OCH(CF_3)_2]^+$, 6), 240 ($C_5HF_7NO_2^+$, 71), 151 ($[CH(CF_3)_2]^+$, 18), 92 ($C_2F_2NO^+$, 12), 69 (CF_3^+, 100).

*3.8. General procedure for the reaction of F-(3,4-dihydro-2H-pyrrole) (**2**) with polyfluoroalkyltrifluoromethanesulfonates (**9**)*

In a 100 ml reaction vessel, 0.120 g (2.07 mmol) of spray-dried KF was placed using a glove box vessel then dried with a hot heat gun using a vacuum line. A 5 ml portion of dried tetraglyme was added under an argon atmosphere, and 0.316 g (1.62 mmol) of **2** was vacuum transferred to the reaction vessel at −196°C. The mixture in the reaction vessel was stirred at room temperature for 5 h, the vessel was cooled to −196°C, and 0.313 g (1.35 mmol) of 2,2,2-trifluoroethyltrifluoromethanesulfonate (**9a**) was vacuum transferred to it. This reaction mixture was heated at 50°C for 20 h. Under reduced pressure from the reaction mixture at 50°C, 1-(2,2,2-trifluoroethyl)-*F*-pyrrolidine (**15a**, 70% yield) was collected in traps cooled at −78 and −55°C.

Spectral data for **15a**: bp 83.5–84.5°C; ^1H NMR ($CDCl_3$) δ: 3.84 (br q, $J = 8.4$ Hz); ^{19}F NMR ($CDCl_3$) δ: −71.4 (m, 3F, CF_3), −93.5 (br s, 4F, 2,5-F), −131.9 (m, 4F, 3,4-F); GC-MS (EI, 70 eV, *m/z*): 278 ($[M - F]^+$, 32), 228 ($[M - CF_3]^+$, 100), 178 ($C_4H_2F_6N^+$, 28), 131 ($C_3F_5^+$, 8), 114 ($C_2F_4N^+$, 6), 100 ($C_2F_4^+$, 31), 83 (CF_3N^+, 19), 78 ($C_2F_2O^+$, 17), 69 (CF_3^+, 32).

Similarly the reaction of **2** with **9c** and **9d** gave 1-(2,2,3,3,3-pentafluoropropyl)-*F*-pyrrolidine (**15c**) and 1-(2,2-difluoroethyl)-*F*-pyrrolidine (**15d**), respectively.

Spectral data for **15c**: bp 97.0–98.0°C; ^1H NMR ($CDCl_3$) δ: 3.85 (br q, $J = 14.4$ Hz); ^{19}F NMR ($CDCl_3$) δ: −84.8 (m, 3F, CF_3), −93.6 (br s, 4F, 2,5-F), −120.5 (m, 2F, CF_2), −132.0 (m, 4F, 3,4-F); GC-MS (EI, 70 eV, *m/z*): 328 ($[M - F]^+$, 25), 228 ($[M - C_2F_5]^+$, 100), 178 ($C_4H_2F_6N^+$, 22), 131 ($C_3F_5^+$, 6), 109 ($C_3H_2F_3N^+$, 5), 100 ($C_2F_4^+$, 20), 83 (CF_3N^+, 15), 69 (CF_3^+, 40).

Spectral data for **15d**: bp 94.0–95.0°C; ^1H NMR ($CDCl_3$) δ: 3.63 (dt, $J = 15.1$, 4.5 Hz, 2H, CH_2), 5.93 (dd, $J = 54.9$, 4.5 Hz, 1H, CHF_2); ^{19}F NMR ($CDCl_3$) δ: −92.9 (s, 4F, 2,5-F), −121.7 (m, 2F, CHF_2), −131.6 (m, 4F, 3,4-F); GC-MS (EI, 70 eV, *m/z*): 279 ($[M - H]^+$, 2), 260 ($[M - F]^+$, 21), 228 ($[M - CHF_2]^+$, 100), 178 ($C_4H_2F_6N^+$, 25), 131 ($C_3F_5^+$, 7), 109 ($C_3H_2F_4N^+$, 7), 100 ($C_2F_4^+$, 15), 78 ($C_2F_2O^+$, 20), 69 (CF_3^+, 17); 66 ($CH_2CHF_2^+$, 55), 51 (CHF_2^+, 10).

*3.9. General procedure for the reaction of F-(3,4-dihydro-2H-pyrrole) (**2**) with (polyfluoroalkoxy)-trimethylsilanes (**3**)*

Spray-dried KF (0.071 g, 1.22 mmol) was placed in a 100 ml reaction vessel, and was dried at 80–90°C under vacuum. Dried tetraglyme (5 ml) was added under an argon atmosphere, and then **2** (1.19 g, 6.10 mmol) and **3a** (1.06 g, 6.15 mmol) were vacuum transferred to the reaction vessel at −196°C. The mixture in the reaction vessel was stirred at 70°C for 20 h. Under reduced pressure from the reaction mixture at 50°C, 5-(2,2,2-trifluoroethoxy)-*F*-(3,4-dihydro-

2*H*-pyrrole) (**16a**) was trap-to-trap distilled into a trap cooled at −55°C in 56% isolated yield.

Spectral data for **16a**: ^{1}H NMR ($CDCl_3$) δ: 4.83 (q, $J = 7.4$ Hz); ^{19}F NMR ($CDCl_3$) δ: −74.1 (t, $J = 7.4$ Hz, 3F, OCH_2CF_3), −92.0 (br s, 2F, 5-F), −123.2 (br s, 2F, 3-F), −131.0 (br s, 2F, 4-F); GC-MS (EI, 70 eV, *m/z*): 275 (M^+, 28), 256 ($[M - F]^+$, 22), 225 ($[M - CF_2]^+$, 17), 177 ($C_4HF_6N^+$, 14), 100 ($C_2F_4^+$, 19), 92 ($C_2F_2NO^+$, 100), 83 (CF_3N^+, 63), 69 (CF_3^+, 37); IR (cm^{-1}): 1668 ($\nu_{C=N}$).

Similarly the reaction of **2** with **3b** gave 5-[2,2,2-trifluoro-1-(trifluoromethyl)ethoxy]-*F*-(3,4-dihydro-2*H*-pyrrole) (**18b**), accompanied with a small amount of 2,5-bis[2,2,2-trifluoro-1-(trifluoromethyl)ethoxy]-*F*-(3,4-dihydro-2*H*-pyrrole) (**19b**).

Spectral data for **16b**: ^{1}H NMR ($CDCl_3$) δ: 5.89 (sept, $J = 5.2$ Hz); ^{19}F NMR ($CDCl_3$) δ: −73.5 (d, $J = 5.2$ Hz, 6F, $OCH(CF_3)_2$), −92.7 (br s, 2F, 5-F), −123.2 (br s, 2F, 3-F), −130.4 (br s, 2F, 4-F); GC-MS (EI, 70 eV, *m/z*): 343 (M^+, 30), 324 ($[M - F]^+$, 23), 304 ($[M - H - 2F]^+$, 22), 293 ($[M - CF_2]^+$, 11), 177 ($C_4HF_6N^+$, 10), 164 ($C_3F_6N^+$, 23), 114 ($C_2F_4N^+$, 13), 100 ($C_2F_4^+$, 17), 92 ($C_2F_2NO^+$, 100), 76 ($C_2F_2N^+$, 10), 69 (CF_3^+, 67); IR (cm^{-1}): 1676 ($\nu_{C=N}$).

Spectral data for **19b**: ^{1}H NMR ($CDCl_3$) δ: 5.04 (sept, $J = 5.4$ Hz, 1H, 5-$OCH(CF_3)_2$), 5.79 (sept, $J = 5.79$ Hz, 1H, 2-$OCH(CF_3)_2$); ^{19}F NMR ($CDCl_3$) δ: −73.5 (m, 3F, 2-$OCH(CF_3)_2$), −73.6 (m, 3F, 2-$OCH(CF_3)_2$), −73.8 (m, 3F, 5-$OCH(CF_3)_2$), −74.0 (m, 3F, 5-$OCH(CF_3)_2$), −93.2 (br s, 2F, 5-F), −122.7 (AB, $J = 277$ Hz, 1F, 3-F), −123.6 (AB, $J = 277$ Hz, 1F, 3-F), −129.4 (AB, $J = 241$ Hz, 1F, 4-F), −130.5 (AB, $J = 241$ Hz, 1F, 4-F); GC-MS (EI, 70 eV, *m/z*): 491 (M^+, 5), 472 ($[M - F]^+$, 12), 340 ($[M - CH(CF_3)_2]^+$, 14), 324 ($[M - OCH(CF_3)_2]^+$, 14), 312 ($C_6HF_{11}NO^+$, 22), 240 ($C_5HF_7NO^+$, 22), 174 ($C_5F_6^+$, 14), 151 ($C_3HF_6^+$, 31), 69 (CF_3^+, 73); IR (cm^{-1}): 1676 ($\nu_{C=N}$).

3.10. General procedure for the reaction of F-(3,4-dihydro-2H-pyrrole) (2) with excess (polyfluoroalkoxy)trimethylsilanes (3)

Spray-dried KF (0.036 g, 0.39 mmol) was placed in a 100 ml reaction vessel, and was dried at 80–90°C under vacuum. Dried tetraglyme (5 ml) was added under an argon atmosphere, and then **2** (0.381, 1.95 mmol) and **3a** (0.741 g, 4.30 mmol) were vacuum transferred to the reaction vessel at −196°C. The mixture in the reaction vessel was stirred at 70°C for 48 h. Under reduced pressure from the reaction mixture at 50°C, 2,2,5-tris(2,2,2-trifluoroethoxy)-*F*-(3,4-dihydro-2*H*-pyrrole) (**20a**) was trap-to-trap distilled into a trap cooled at −30°C in 24% isolated yield.

Spectral data for **20a**: ^{1}H NMR ($CDCl_3$) δ: 4.18 (m, 4H, 5-OCH_2CF_3), 4.77 (q, $J = 7.8$ Hz, 2H, 2-OCH_2CF_3); ^{19}F NMR ($CDCl_3$) δ: −74.1 (t, $J = 7.8$ Hz, 3F, 2-OCH_2CF_3), −74.8 (t, $J = 7.8$ Hz, 6F, 5-OCH_2CF_3), −123.6 (t, $J = 6.1$ Hz, 2F, 3-F), −128.7 (t, $J = 6.1$ Hz, 2F, 4-F); GC-MS (EI, 70 eV, *m/z*): 435 (M^+, 3), 416 ($[M - F]^+$, 5), 336 ($[M - OCH_2CF_3]^+$, 36), 254 ($C_9F_6O_2^+$, 11), 252 ($C_9F_6NO^+$, 13), 127 ($C_3H_2F_3O_2^+$, 15), 83 (CF_3N^+, 100), 70 (CHF_3^+, 11); IR (cm^{-1}): 1670 ($\nu_{C=N}$).

Similarly the reaction of **2** with excess **3b** gave 2,5-[2,2,2-trifluoro-1-(trifluoromethyl)ethoxy]-*F*-(3,4-dihydro-2*H*-pyrrole) (**19b**), accompanied with a fairly large amount of high-boiling point decomposed materials.

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