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An entirely new methodology for synthesizing perfluorinated compounds: synthesis of perfluoroalkanesulfonyl fluorides from non-fluorinated compounds

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Abstract

A new synthetic procedure for the preparation of perfluoroalkanesulfonyl fluorides utilizing liquid-phase direct fluorination with elemental fluorine has been developed. Direct fluorination of a partially fluorinated ester, which has alkanesulfonyl fluoride in the end, was synthesized from non-fluorinated counterparts and perfluorinated acid fluoride according to the PERFECT process, gave the desired perfluorinated product in moderate yield as well as by-products arising from C–S bond cleavage. The results of the direct fluorination of some model substrates suggest that the C–S bond cleavage occurred due to radical formation at the α-position rather than the β-position.

Keywords: Alkanesulfonyl fluorides; Acyl fluorides; Direct fluorination; Fluorine; Ion exchange; PERFECT process; Bond cleavage

1. Introduction

Liquid-phase direct fluorination is a powerful tool to make perfluorinated compounds [1–5]. Especially, the Exfluor-Lagow elemental fluorine process is effective under mild conditions [6]. Lagow and co-workers reported direct fluorination of non-fluorinated compounds with relatively simple structure [6]. We have actually examined the reaction with octyl octanoate in order to establish whether it can be applied to the synthesis of useful perfluorinated monomers, and found that it worked well. We have also examined the direct fluorination of small molecules such as monomer precursors. Unfortunately, we found that it was not easy. In some cases, reaction in the vapor phase due to high volatility of the substrate partly took place and led to an explosion. In order to solve this problem, we have developed the PERFECT method (Scheme 1) [7,8]. The name "PERFECT" is the abbreviation of PERFluorination of an Esterified Compound then Thermal elimination.

In the PERFECT method, perfluorination is achieved by direct fluorination of a partially fluorinated compound.

First, we prepare small hydrocarbon component with the backbone structure of the desired compound in the alcohol form **1**, by conventional organic synthesis. Then, it is coupled with a perfluorinated moiety, perfluoroacyl fluoride **2** in a typical case, to form a larger molecule, that is, partially fluorinated ester **3**. Perfluorination is achieved by liquid-phase direct fluorination with elemental fluorine to give the perfluorinated ester **4**. In the direct fluorination process, vapor-phase reaction is avoided since the substrate has low vapor pressure and the solubility of the substrate in the perfluorinated solvent significantly increases. It would be an advantage that we can use various perfluorinated solvents, especially the perfluoroacyl fluoride itself, instead of CFCs. Final thermal elimination gives the starting perfluoroacyl fluoride **2** and the desired perfluoroacyl fluoride **5**. In the situation where the acyl fluoride **2**, which we start with, is

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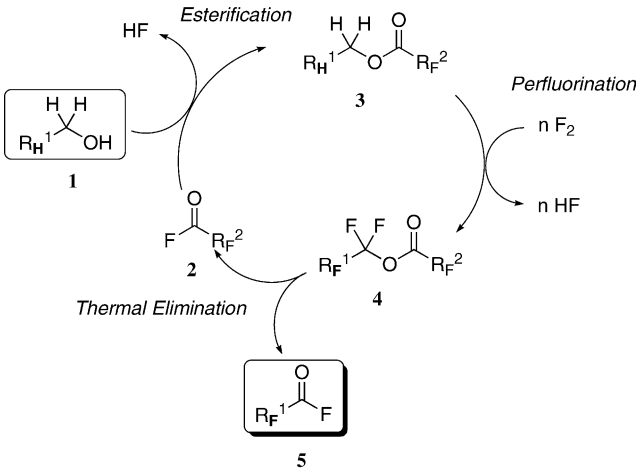


Scheme 1. The PERFECT cycle.

not the same as the desired acyl fluoride **5**, the separation of the mixture of acyl fluorides is achieved by distillation. Then, we can use the desired perfluoroacyl fluoride **5** itself as the starting perfluoroacyl fluoride **2** for the next PERFECT cycle. Thus, the desired perfluoroacyl fluoride can be multiplied by the cycle.

As such an example, we have reported the synthesis of perfluorinated butenyl vinyl ether (BVE) which is the monomer of transparent perfluorinated cyclic polymer, CYTOP [9]. We have also reported the synthesis of the carboxylic acid monomer for ion exchange membrane, Flemion, using a hydrocarbon diol as the starting material [10], and the synthesis of perfluoroketones using a secondary alcohol as the starting material [11].

Herein, we present a new application of the PERFECT process to the preparation of perfluoroalkanesulfonyl fluoride.

2. Results and discussion

2.1. Synthesis of $FSO_2CF_2CF_2OCF_2COF$ (16)

Flemion, which has developed by Asahi Glass Co., is used as the ion exchange membrane for chlor-alkali production process. Nafion (Dupont) is also used for the same purpose [12,13]. Our aim was the synthesis of a precursor to perfluorinated alkanesulfonic acid for the ion exchange membrane.

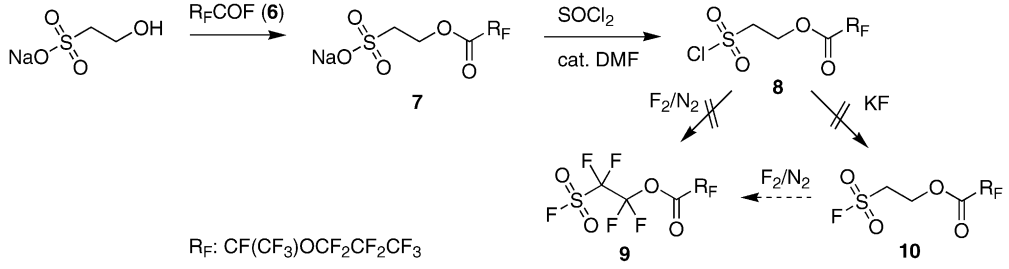
First, direct fluorination of alkanesulfonyl chloride **8** derived from isethionic acid sodium salt and perfluoroacyl fluoride **6** was attempted according to the PERFECT process. The synthetic route of the substrate is shown in Scheme 2.

Liquid-phase direct fluorination of the partially fluorinated alkanesulfonyl chloride **8** did not afford the desired perfluoroalkanesulfonyl fluoride **9** at all. Only compounds with C–S bond cleavage were detected.

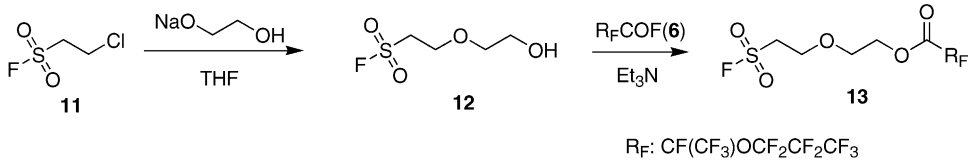
Next, the direct fluorination of the corresponding partially fluorinated alkanesulfonyl fluoride **10**, which could be derived from the chloride **8**, was attempted. However, bond cleavage in the ester bond occurred instead of the substitution of the chlorine atom with potassium fluoride. The desired substrate for the next direct fluorination was not obtained at all.

Then, we decided to adopt another synthetic strategy, which entails formation of the fluorosulfonyl group before the formation of the backbone structure.

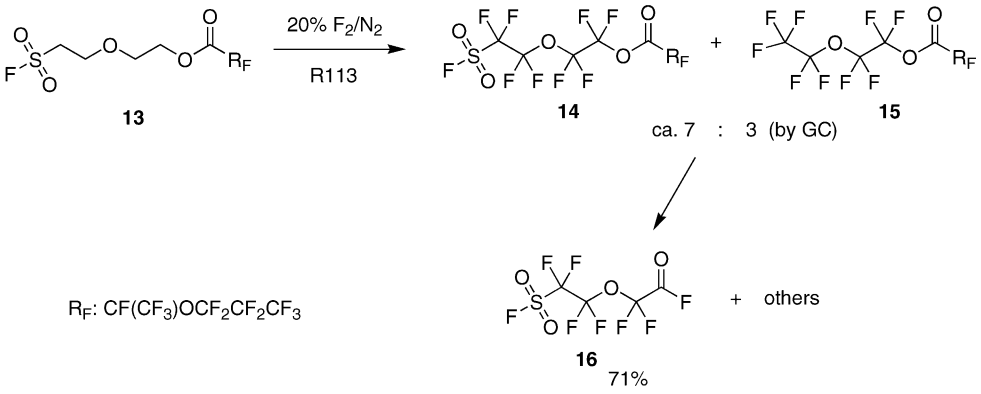
Reaction of 2-chloroethanesulfonyl fluoride **11** [14], which is a derivative of isethionic acid, with the sodium salt of ethylene glycol gave the substrate **12** of the PERFECT process as shown in Scheme 3. Esterification was carried out as in the usual PERFECT methodology to give partially fluorinated ester **13**, although the yield was not satisfactory



Scheme 2.



Scheme 3.



Scheme 4.

because the reaction of the sulfonyl fluoride group and the hydroxyl group in the structure also took place intramolecularly.

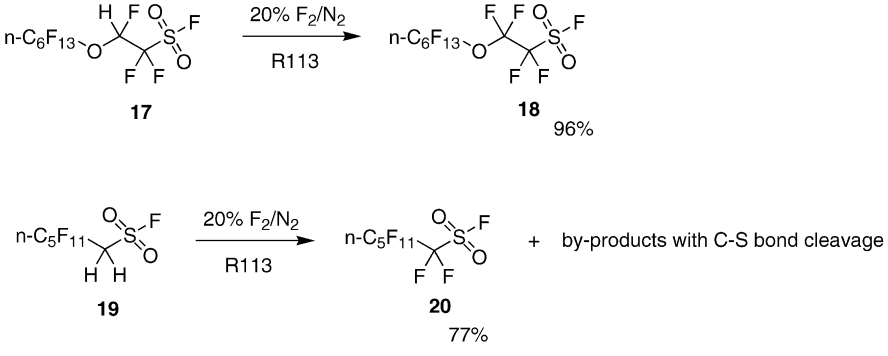
Direct fluorination of this partially fluorinated sulfonyl fluoride **13** was carried out with elemental fluorine as in the usual PERFECT method. The desired perfluorinated ester **14** was obtained in moderate yield, although by-product arising from C–S bond cleavage **15** was still detected even in the PERFECT method. The ratio of the desired product **14** and the by-product **15** was ca. 7:3, as determined by GC area. Thermal elimination led to the desired product **16**, a precursor of a sulfonyl monomer for the ion exchange membrane (Scheme 4).

2.2. Examination of the effect of α- and β-fluorination to a fluorosulfonyl group

The cleavage of C–S bonds during liquid-phase direct fluorination has been reported previously [15,16]. For example, octanesulfonyl fluoride was perfluorinated to give the corresponding perfluorooctanesulfonyl fluoride as well as by-product perfluorooctane arising from C–S bond cleavage, although yields are not described [15]. Kobayashi et al. reported direct fluorination of methanesulfonyl fluoride [17], but also reported that direct fluorination of ethanesulfonyl fluoride led to C–S bond cleavage mainly and gave perfluoroethane and sulfonyl difluoride [16]. This suggests that the C–S bond cleavage may be the result of β-elimination of the intermediate radical species. In our case shown above, the desired perfluorinated alkanesulfonyl fluoride was obtained in moderate yield, however, the C–S bond cleavage was still observed. In order to clarify the cause of the C–S bond cleavage, liquid-phase direct fluorination reactions of the substrates **17** and **19**, respectively, were carried out (Scheme 5).

If a radical at the β-position formed during direct fluorination promotes the C–S bond cleavage, then the direct fluorination of the substrate **17** would give by-products arising from the C–S bond cleavage, because generation of a radical during the direct fluorination takes place only at the β-position. However, no C–S bond cleavage was observed and the desired perfluorinated product **18** was obtained almost quantitatively.

If a radical at the α-position causes the C–S bond cleavage, then direct fluorination of the substrate **19** would give by-products arising from the C–S bond cleavage, because generation of a radical takes place only at the α-position. Actually, the direct fluorination gave the desired perfluorinated product **20** in 77% yield along with the formation of products with the C–S bond cleavage in around 20% yield.



Scheme 5.

From the above results, we concluded that the C–S bond cleavage occurred due to the radical formation at the α-position rather than the β-position, although it cannot explain the case of the direct fluorination of methanesulfonyl fluoride [17].

3. Conclusions

The synthetic method for perfluoroalkanesulfonyl fluorides utilizing liquid-phase direct fluorination with elemental fluorine was investigated. Direct fluorination of a partially fluorinated ester, which has alkanesulfonyl chloride in the end **8** according to the PERFECT process, did not give the desired perfluorinated alkanesulfonyl fluoride **9**. Direct fluorination of a partially fluorinated ester, which has alkanesulfonyl fluoride, gave the desired perfluorinated products in moderate yield as well as by-products arising from C–S bond cleavage. The results of the direct fluorination of the substrates **17** and **19** suggest that the C–S bond cleavage occurred due to the radical formation at the α- position rather than the β-position.

4. Experimental

4.1. General

NMR spectra were obtained on a JEOL EX-400 (tetramethylsilane as internal standard for ^{1}H, and trichlorofluoromethane for ^{19}F). High-resolution mass spectra were obtained on JEOL SX-102A coupled to HP-5890 with a 60-m capillary column J&W DB-1 or DB-1301 [18]. Elemental fluorine was generated by Fluorodec^{TM} 30, Fluoro Gas (UK) or obtained from Asahi Glass Co. *Elemental fluorine is highly toxic and corrosive gas, and may cause explosion when it meets organics in the vapor phase. Extreme care must be taken when handling it! Both the liquid and vapor of hydrogen fluoride (b.p. 19.5 °C) evolved during the reaction are also highly corrosive and cause severe burns when in contact. Care must be taken! Prior to use, all hydrocarbon greases must be removed and the apparatus must be gradually passivated with elemental fluorine*. Although the use of 1,1,2-trichlorotrifluoroethane (R113) is regulated, we will mention experimental examples with it for convenience, because it is still much more cheaply available (Aldrich) than the target molecule itself for use as solvent. *Care must be taken in order not to emit it to the environment by using, for example, a rotary evaporator with PTFE diaphragm type vacuum pump and cooling trap.* Once enough of the target molecule itself is obtained in the cycle, it should be used instead of R113. Other reagents were obtained from Kanto Chemicals (Japan) and used without purification.

4.2. Typical procedure

4.2.1. Synthesis of $FSO_2CF_2CF_2OCF_2COF$ (*16*)

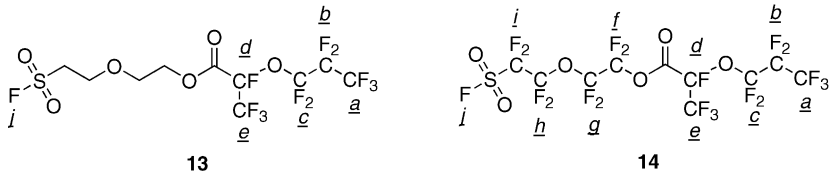
Ethylene glycol (141 g) and a methanol solution of sodium methoxide (28 wt.%, 96.4 g, 0.500 mol) were charged and stirred, and heated under reduced pressure to distill off methanol to afford a solution of sodium salt of ethylene glycol. A solution of **11** [14] (50 g, 0.341 mol) in THF (100 mL) was stirred under cooling with ice bath, and the previously obtained solution of sodium salt of ethyleneglycol was dropwise added thereto over a period of 2.5 h, while maintaining the internal temperature to be at 10 °C. After completion of the dropwise addition, the reaction mixture was stirred at room temperature for 2 h. Then the reaction mixture was added to water (400 mL), extracted with dichloromethane, and the combined organic layer was dried over magnesium sulfate. Filtration and evaporation gave a crude product **12** (47.1 g). The obtained crude liquid was used for the next step without carrying out purification.

^{1}H NMR (300.4 MHz, $CDCl_3$): δ 3.63–3.71 (m, 4H), 3.74–3.79 (m, 2H), 3.99–4.05 (m, 2H) ppm.
^{19}F NMR (282.7 MHz, $CDCl_3$): δ 58.4 (1F) ppm.

The crude liquid **12** (47.1 g) and triethylamine (19.5 g, 0.193 mol) were put into a flask and stirred under cooling with an ice bath. Perfluoro(2-propoxypropanoyl) fluoride **6** (64.1 g, 0.193 mol) was dropwise added over a period of 40 min, while maintaining the internal temperature at or below 10 °C. After being stirred for 2 h at room temperature, the reaction mixture was added to ice water (100 mL). The organic layer was washed twice with water (100 mL) and dried over magnesium sulfate, followed by filtration to obtain a crude liquid. This liquid was purified by silica gel column chromatography (dichloropentafluoropropane (AK-225)) to obtain the product **13** (21.2 g, 43.8 mmol, 13% from **11**).

^{1}H NMR (300.4 MHz, $CDCl_3$): δ 3.57–3.63 (m, 2H), 3.81 (t, ^{3}J = 4.5 Hz, 2H), 3.95–4.00 (m, 2H), 4.48–4.60 (m, 2H) ppm.
^{19}F NMR (282.7 MHz, $CDCl_3$): δ 58.2 (1F, *j*), −79.8 (1F of *c*), −81.3 (3F, *a*), −82.1 (3F, *e*), −86.6 (1F of *c*), −129.4 (2F, *b*), −131.5 (1F, *d*) ppm (Fig. 1).

Into a 500-mL autoclave made of nickel, R113 (313 g) was charged, stirred and maintained at 25 °C. At the gas outlet of the autoclave, a cooler maintained at 20 °C, a packed layer of NaF pellets and a cooler maintained at −10 °C were installed in series. Further, a liquid-returning line was installed to return any condensed liquid from the cooler maintained at −10 °C to the autoclave. After supplying nitrogen gas for 1 h, 20% F_2/N_2 was supplied for 1 h at a flow rate of 7.78 L/h. Then, while supplying 20% F_2/N_2 at the same flow rate, a solution of **13** (7.01 g,



13 14

Fig. 1. Structural formulae for NMR peak assignment.

14.5 mmol) in R113 (140 g) was supplied over a period of 5.5 h. Then, a solution of benzene in R113 (0.01 g/mL, 6 mL) was supplied at 0.15 MPa intermittently, and this operation was repeated four times. Nitrogen gas was supplied to remove solvent and volatile materials to give the crude perfluorinated product. The ratio of the desired perfluorinated ester **14** and by-products arising from the C–S bond cleavage was ca. 7:3, as determined by GC area. The structure of the desired perfluorinated ester **14** was confirmed by ^{19}F NMR (376.0 MHz, $CDCl_3$): δ 45.2 (1F, *j*), −79.9 (1F of *c*), −82.0 (3F, *a*), −82.2 (3F, *e*), −82.6 (2F, *h*), −87.0 (1F of *c*), −88.5 (2F, *g*), −92.3 (2F, *f*), −112.9 (2F, *i*), −130.2 (2F, *b*), −132.1 (1F, *d*) ppm (Fig. 1).

Crude perfluorinated ester **14** (3.1 g) obtained, as described above, was charged into a flask together with NaF powder (0.02 g) and heated at 140 °C for 10 h in an oil bath with vigorous stirring. At the upper portion of the flask, a reflux condenser having the temperature adjusted at 20 °C was installed. After cooling, the liquid sample (3.0 g) was recovered. As a result of the analysis by GC–MS, starting perfluoroacyl fluoride **6** and the desired product **16** were confirmed to be the main products. The structure of the desired product **16** was confirmed by ^{19}F NMR [19] and the yield determined by the ^{19}F NMR was 71%.

4.2.2. Synthesis of n-$C_6F_{13}OCF_2CF_2SO_2F$ (18)

Addition of benzyl mercaptan to perfluorovinyl ether was carried out in a manner similar to the procedure described in literature [20].

Into a solution of 48% aqueous potassium hydroxide (3.1 g, 26 mmol) and dioxane (8.0 g), *n*-$C_6F_{13}OCF{=}CF_2$ (7.1 g, 17 mmol) was added, then benzyl mercaptan (2.4 g, 19 mmol) was added dropwise at 10 °C, and the mixture was stirred at room temperature for 4 h. The reaction mixture was diluted with AK-225, washed three times with water, and dried over $MgSO_4$. Evaporation gave the crude thioether (7.1 g, 13 mmol, 77%), which structure was confirmed and quantitatively analyzed by ^{19}F NMR. The purity was 99%.

^{1}H NMR (300.4 MHz, $CDCl_3$): δ 4.1 (s, 2H, SCH_2), 5.78–5.99 (dt, $^2J_{HF}$ = 54.4 Hz, $^3J_{HF}$ = 3.9 Hz, 1H, CHF), 7.27 (m, 5H, C_6H_5) ppm.
^{19}F NMR (282.7 MHz, $CDCl_3$): δ −81.2 (3F, *a*), −83.6 to −86.2 (2F, *f*), −89.6 to −91.5 (2F, *h*), −122.7 to −126.7 (8F, *b*, *c*, *d*, *e*), −139.6 (1F, *g*) ppm (Fig. 2).

Chlorination of benzyl thioether was carried out in a manner similar to the procedure in literature [21].

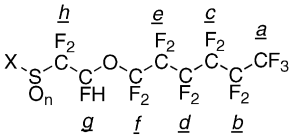


Fig. 2. Structural formula for NMR peak assignment.

Into a mixture of the crude thioether (7.1 g, 13 mmol), acetic acid (20 g), and water (1.6 g), nitrogen gas was passed through and then chlorine gas (2.7 g, 38 mmol) was gradually supplied with maintaining the internal temperature at around 10 °C. Nitrogen gas was supplied in order to remove chlorine, and the reaction mixture was diluted by AK-225, washed three times with water, washed with brine, and dried over $MgSO_4$. Evaporation gave the crude sulfonyl chloride (6.3 g). The product was quantitatively analyzed by ^{19}F NMR, and the yield was 60%.

^{1}H NMR (300.4 MHz, $CDCl_3$): δ 6.45 (dt, $^2J_{HF}$ = 52.7 Hz, $^3J_{HF}$ = 5.0 Hz, 1H, CHF) ppm.
^{19}F NMR (282.7 MHz, $CDCl_3$): δ −81.0 (3F, *a*), −83.5 to −86.2 (2F, *f*), −109.6 to −110.1 (2F, *h*), −122.5 to −126.4 (8F, *b*, *c*, *d*, *e*), −140.8 (1F, *g*) ppm (Fig. 2).

The crude sulfonyl chloride (6.3 g, 7.3 mmol) was added dropwise to a mixture of KHF_2 (2 g, 26 mmol), acetonitrile (10 g), and water (8.5 g) at room temperature. After the mixture was stirred for 2 days, diluted with AK-225, and washed three times with water, sat. $NaHCO_3$, and brine, respectively, the organic layer was dried over $MgSO_4$ and evaporated to give the crude product (5.0 g). The residue was distilled (b.p. 83 °C/3.2 kPa) to give the desired product **17** (2.5 g, 5.0 mmol, 68%).

^{1}H NMR (300.4 MHz, $CDCl_3$): δ 6.38 (dt, $^2J_{HF}$ = 52.9 Hz, $^3J_{HF}$ = 5.1 Hz, 1H, CHF) ppm.
^{19}F NMR (282.7 MHz, $CDCl_3$): δ 44.4 (1F, SO_2F), −81.2 (3F, *a*), −83.7 to −86.7 (2F, *f*), −113.0 (2F, *h*), −122.7 to −126.7 (8F, *b*, *c*, *d*, *e*), −142.5 (1F, *g*) ppm (Fig. 2).

High-resolution mass spectrum (CI^+) 500.9444 ($[M + H]^+$, calculated for $C_8H_2F_{17}O_3S$: 500.9453).

The direct fluorination was carried out in a manner similar to the procedure for the direct fluorination of **13**, where the flow rate of 20% F_2/N_2 was 2.97 L/h, and a solution of **17** (2.5 g) in R113 (15.4 g) was supplied over a period of 0.65 h. The structure of the desired product **18** was

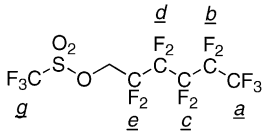


Fig. 3. Structural formula for NMR peak assignment.

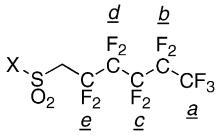


Fig. 5. Structural formula for NMR peak assignment.

confirmed by ^{19}F NMR [22] and the yield determined by the ^{19}F NMR was 96%.

*4.2.3. Synthesis of n-$C_6F_{13}SO_2F$ (**20**)*

Conversion from polyfluorinated alcohol to its triflate was carried out in a manner similar to the procedure described in literature [23].

To a solution of $C_5F_{11}CH_2OH$ (13 g, 43 mmol) in AK-225 (12 g), trifluoromethanesulfonic anhydride (13 g, 46 mmol) was added, and the mixture was stirred at 60 °C for 1 day and further stirred at 80 °C for 1 day. The reaction mixture was poured into water, and extracted with AK-225. The organic layer was washed with water, saturated aqueous $NaHCO_3$, and brine, respectively. Evaporation gave the crude triflate (15 g, purity = 96%, 35 mmol, 78% yield).

^{1}H NMR (300.4 MHz, $CDCl_3$): δ 4.8 (t, $^3J_{HF}$ = 12.3 Hz, 2H) ppm.
^{19}F NMR (282.7 MHz, $CDCl_3$): δ −74.4 (3F, *g*), −81.3 (3F, *a*), −120.2 (2F, *e*), −122.5 to −124.2 (4F, *c*, *d*), −126.7 (2F, *b*) ppm (Fig. 3).

The crude triflate (15 g, 35 mmol) was added dropwise to a mixture of ethylxanthic acid potassium salt (6.1 g, 38 - mmol) in acetone (30 g) at 0 °C with stirring. After the mixture was stirred at room temperature for 12 h, AK-225 was added. The reaction mixture was washed five times with water. The organic layer was dried over $MgSO_4$ and evaporated to give the crude xanthate (10 g). The crude product was used without further purification for the next reaction.

^{1}H NMR (300.4 MHz, $CDCl_3$): δ 1.4 (t, $^3J_{HH}$ = 7.2 Hz, CH_3), 4.0 (t, $^3J_{HF}$ = 17.4 Hz, 2H, SCH_2), 4.7 (d, $^3J_{HH}$ = 7.2 Hz, 2H, OCH_2) ppm.
^{19}F NMR (282.7 MHz, $CDCl_3$): δ −81.3 (3F, *a*), −112.5 (2F, *e*), −122.9 to −123.5 (4F, *c*, *d*), −126.9 (2F, *b*) ppm (Fig. 4).

Into a mixture of the crude xanthate (10 g), acetic acid (20 g), and water (1.5 g), nitrogen gas was passed through and then chlorine gas (4.2 g, 59 mmol) was gradually supplied with maintaining the internal temperature at around 10 °C. Nitrogen gas was supplied in order to remove chlorine, and the reaction mixture was diluted by AK-225, washed three times with water, washed with brine, and dried over $MgSO_4$. Evaporation gave the crude sulfonyl chloride (9.3 g, purity = 96%, 23 mmol, 67% yield for two steps).

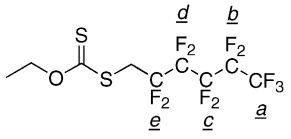


Fig. 4.

^{1}H NMR (300.4 MHz, $CDCl_3$): δ 4.4 (t, $^3J_{HF}$ = 15.0 Hz, 2H) ppm.
^{19}F NMR (282.7 MHz, $CDCl_3$): δ −81.1 (3F, *a*), −113.1 (2F, *e*), −122.8 to −123.2 (4F, *c*, *d*), −126.6 (2F, *b*) ppm (Fig. 5).

The crude sulfonyl chloride (9.3 g, 23 mmol) was added dropwise to a mixture of KHF_2 (5.0 g, 64 mmol) and DMF (8 g) at 0 °C. After the mixture was stirred for 2 h, diluted with AK-225, and washed three times with water, sat. $NaHCO_3$, and brine, respectively, the organic layer was dried over $MgSO_4$ and evaporated. The residue was distilled (b.p. 41–46 °C/2.4 kPa) to give a mixture of DMF and the desired product. DMF was removed by washing three times with water to give **19** with purity of 90% (0.91 g, 2.5 mmol, 10% yield). This crude product was used without further purification for the next reaction.

^{1}H NMR (300.4 MHz, $CDCl_3$): δ 4.2 (t, $^3J_{HF}$ = 15.1 Hz, 2H) ppm.
^{19}F NMR (282.7 MHz, $CDCl_3$): δ 66.7 (1F, SO_2F), −81.2 (3F, *a*), −113.0 (2F, *e*), −122.8 (4F, *c*, *d*), −126.6 (2F, *b*) ppm (Fig. 5).

The direct fluorination was carried out in a manner similar to the procedure for the direct fluorination of **13**, where the flow rate of 20% F_2/N_2 was 3.04 L/h, and a solution of **19** (0.91 g, 2.5 mmol) in R113 (13.7 g) was supplied over a period of 0.6 h. Perfluorohexanesulfonyl fluoride was obtained, and the yield was 77%, which was determined by ^{19}F NMR.

Acknowledgement

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