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Bi-functional fluoroalkylation reagents: an introduction to halo-substituted 3-oxa-perfluoroalkanesulfonyl fluorides

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ABSTRACT

$X(CF_2CF_2)_nOCF_2CF_2SO_2F$ (X=I, Br, Cl; n=1, 2, 3, 4) are widely used fluoroalkylation reagents, which can incorporate ‘heavy’ fluorous tags into organic compounds. $X(CF_2CF_2)_nOCF_2CF_2SO_2F$ have both sulfonyl and halo groups. They behave as bi-functional fluoroalkylation reagents. The cleavage of the C–I bonds of $I(CF_2CF_2)_nOCF_2CF_2SO_2F$ by reductants (such as $Na_2S_2O_4$, Zn), single electron transfer reagents and radical initiator systems (like Bz_2O_2, AIBN, and $(t\text{-BuO})_2$, or under UV and heat) gives, respectively, the sulfinatodehalogenated products, the hydrodehalogenated products, the homo-coupling products and the perfluoroalkylated products (if alkenes, alkynes or arenes were added). The functionalization of the sulfonyl groups (SO_2F) of $X(CF_2CF_2)_nOCF_2CF_2SO_2F$ by esterification, amidation, and fluorination affords the corresponding perfluoroalkanesulfonates, fluoroalkanesulfonamide, and perfluoroalkanes. In many cases, both the halo and sulfonyl groups of $X(CF_2CF_2)_nOCF_2CF_2SO_2F$ are transformed. These transformations finally lead to hundreds of useful highly fluorinated materials, such as supper acids, catalysts, surfactants, ion-exchange resins, electrolytes, polymers, and dense ionic liquids. Furthermore, $X(CF_2CF_2)_nOCF_2CF_2SO_2F$ have commendable advantages, such as the easy preparation, the wide range of substrate tolerance, the mild reaction condition, and the high yields of desired products, which make them very promising. This review briefly summarizes the synthesis, reactivity, and applications of these intriguing reagents.

1. Introduction

Fluorine is the most electronegative element in the world.[1,2] It is a ‘small atom with a big ego’.[1c] The bond formed between fluorine and carbon atoms, being one of the strongest bonds, exhibit extremely good chemical inertness. Fluorine substitution has attracted much attention in discovery of drug candidates and synthesis of functional materials.[2a] The introduction of fluorine atom(s) into organic compounds can modulate their physical and biological properties, and render them valuable effects. These comprise the enhancement of the lipophilic and fluorophilic ability, the thermal and metabolic stability, the water- and oil-resistant ability, membrane permeability, the plasticity, bioavailability, and the ‘like dissolves like’ as well as binding affinity. In general, perfluoroalkylated (or highly fluorinated) compounds are prior employed in material science, whereas the lightly fluorinated compounds are preferably applied in pharmaceutical and agrochemical research.[1,2] Although, elemental F_2 is proved by in situ NMR spectroscopy to occur in nature as an occlusion in ‘antozonite’,[3] the naturally occurring fluorinated organic compounds are still rare (about 13). And almost all of the known fluorine-containing compounds, especially the heavily fluorinated complexes, are synthetic.[1,2]

Over the last few decades, a large number of fluorination reagents and methodologies have been developed to meet the fast growing demands of the synthetic issues in areas of medicinal chemistry and material science. Per- or polyfluoroalkyl halides, such as R_FX and $X(CF_2CF_2)_nOCF_2CF_2SO_2F$ (X=I, Br, Cl; n=1, 2, 3, 4) have been the most prevalent fluoroalkylation reagents, which facilely incorporate ‘heavy’ fluorous pony tails into organic compounds.[1,2h] $X(CF_2CF_2)_nOCF_2CF_2SO_2F$ bearing both sulfonyl and halo groups can behave as bi-functional fluoroalkylation reagents. The reactions of $I(CF_2CF_2)_nOCF_2CF_2SO_2F$ (n=1 (**1a**), 2 (**1b**), 3 (**1c**), 4 (**1d**)) with reductants, such as $Na_2S_2O_4$, Zn, and single electron transfer reagents gives, respectively, the sulfinatodehalogenated products, the hydrodehalogenation products, the homo-coupling products, and the perfluoroalkylated products if alkenes, alkynes or arenes were added. Treatment of $I(CF_2CF_2)_nOCF_2CF_2SO_2F$ with alkenes in the presence of initiators, like Bz_2O_2, AIBN, and $(t\text{-BuO})_2$, or under UV and heat, provides the perfluoroalkylated products as well.

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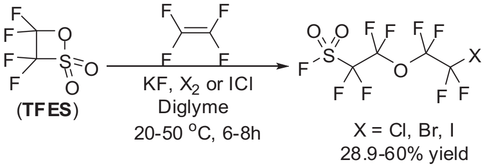
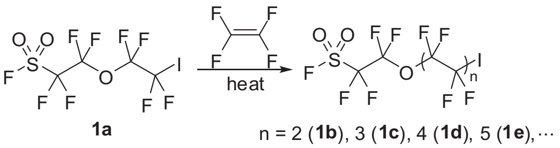
All these transformations are attributed to the cleavage of the C–I bonds of $I(CF_2CF_2)_nOCF_2CF_2SO_2F$. On the other hand, the functionalization of the sulfonyl groups (SO_2F) of $X(CF_2CF_2)_nOCF_2CF_2SO_2F$ is achieved via esterification, amidation, and fluorination, which affords the corresponding perfluoroalkanesulfonates, fluoroalkanesulfonamide, and perfluoroalkanes in good yields. In many cases, it is remarkable that, both the halo and sulfonyl groups of $X(CF_2CF_2)_nOCF_2CF_2SO_2F$ are transformed. These conversions finally constructs hundreds of useful highly fluorinated compounds, such as supper acids, catalysts, surfactants, ion-exchange resins, electrolytes, polymers, and dense ionic liquids.





$XCF_2CF_2OCF_2CF_2SO_2F$ (X=I, Br, Cl) were first synthesized from $CF_2{=}CF_2$ (TFE) and tetrafluoroethane β-sultone (TFES) in 1970s by Chinese chemists.[4a–c] Thermal telomerization of $CF_2{=}CF_2$ with **1a** constructed heavy fluorous $I(CF_2CF_2)_nOCF_2CF_2SO_2F$ (n=2, 3, 4, 5,…). The Cu-mediate reaction of **1a** $CF_2{=}CF_2$ could also provide $I(CF_2CF_2)_nOCF_2CF_2SO_2F$ (Section 2.2.2). Because of the inexpensive industrial production of the starting materials (TFE, TFES), $X(CF_2CF_2)_nOCF_2CF_2SO_2F$ are prepared cheaply.[4] With several decades of development, $X(CF_2CF_2)_nOCF_2CF_2SO_2F$ have been famous reagents in many fields, especially in material science. The rich chemistry of $X(CF_2CF_2)_nOCF_2CF_2SO_2F$ is mainly contributed to the versatility of their sulfonyl and halo groups. To the best of our knowledge, there is no single review to exclusively discuss these bifunctional fluoroalkylation reagents, even though they are extensively studied. In order to give an insight on these reagents, the details of $X(CF_2CF_2)_nOCF_2CF_2SO_2F$ including their synthesis, reactivity and applications are summarized in this review.

2. The chemistry derived from the C–I bond functionalization of $I(CF_2CF_2)_nOCF_2CF_2SO_2F$ (1)

It is well known that perfluoroalkyl iodides (R_FI) are very different from their corresponding alkyl iodides (RI).[1] Due to the inversion of the electrostatic partial charge on iodine caused by the negative inductive effect of the perfluoroalkyl moiety (R_F) and the huge hindrance of fluorine atoms, the R_F group of R_FI is hardly attacked by the nucleophiles via a S_N2 mechanism. In contrast, the iodine atom of R_FI is easily plundered by a certain agent, which generates perfluoroalkyl radical ($R_F^{\bullet}$) with the cleavage of the C–I bond. $R_F^{\bullet}$ is relatively stable and has enough 'shelf-life' for further transformations (due to the steric hindrance and the hyperconjugation effect of α-fluorine atoms). These unique features are also amenable to iodo 3-oxa-perfluoroalkanesulfonyl fluorides ($I(CF_2CF_2)_nOCF_2CF_2SO_2F$). $I(CF_2CF_2)_nOCF_2CF_2SO_2F$ (n=1, 2, 3, 4), initiated by $Na_2S_2O_4$, metals, single electron transfer reagents and radical initiators, generate $[(CF_2CF_2)_nOCF_2CF_2SO_2F]$, which react with alkenes, alkynes and arenes to provide perfluoroalkylated products.

2.1. The transformation of the C–I bonds of $I(CF_2CF_2)_nOCF_2CF_2SO_2F$ by sulfinatodehalogenation systems

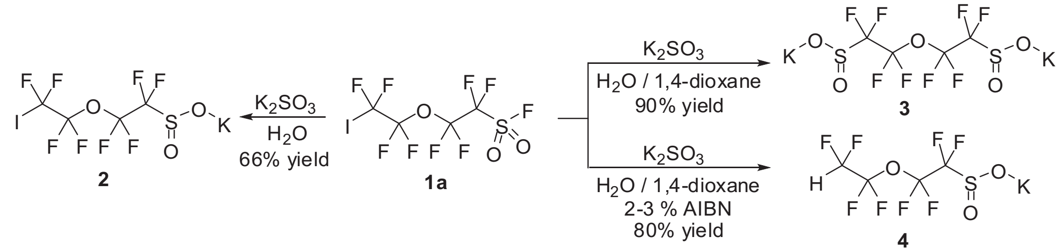
The C–I bonds of $I(CF_2CF_2)_nOCF_2CF_2SO_2F$ (**1a–d**) are cleaved under the standard ($Na_2S_2O_4/NaHCO_3{-}CH_3CN/H_2O$) and modified ($Na_2S_2O_4/NaHCO_3{-}DMSO$) sulfinatodehalogenation reaction conditions.[2h] The resulting intermediates generated from sulfinatodehalogenation reactions reacting with X_2, HX or organic molecules yields a large number of interesting fluorine-containing compounds.[5–15]

2.1.1. Synthesis of perfluoroalkyl halides, perfluorocarboxylic acid, and perfluorosulfonic acid from $ICF_2CF_2OCF_2CF_2SO_2F$. It was reported that $ICF_2CF_2OCF_2CF_2SO_2F$ (**1a**) reacted with K_2SO_3 in H_2O provided $ICF_2CF_2OCF_2CF_2SO_2K$ (**2**) in 66% yield (Scheme 1). When the reaction was carried out in a mixture of 1,4-dioxane and H_2O, however, $KO_2SCF_2CF_2OCF_2CF_2SO_2K$ (**3**) was formed (instead of **2**) in 90% yield. Treatment of $I(CF_2CF_2)_2OCF_2CF_2SO_2F$ (**1b**) with K_2SO_3 under the same conditions afforded $KO_2S(CF_2CF_2)_2OCF_2CF_2SO_2K$ (**5**) in 80% yield. These unexpected findings led to the discovery of sulfinatodehalogenation reaction.[5]

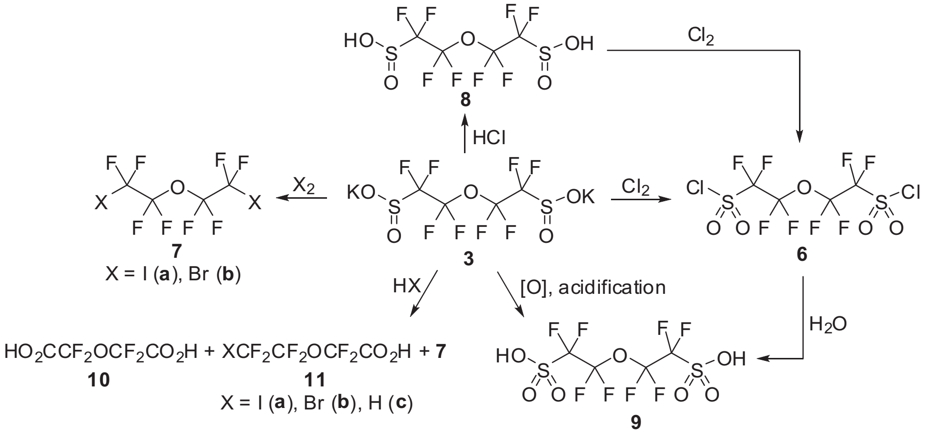
Further investigation indicated that the presence of light benefited the sulfinatodehalogenation reaction.[6] In the darkness, the reaction of **1a** with K_2SO_3 gave only **2** and **4**. Addition of electron scavengers, e.g., *p*-DNB (*p*-dinitrobenzene), into the aqueous 1,4-dioxane system also blocked the sulfinatodehalogenation, but the reduction of CF_2I (**1a**) to CF_2H (**4**) was not inhibited.[6] With a small amount of an inhibitor (1–2% by weight), like hydroquinone, in the same system, the sulfinatodehalogenation was suppressed as well as the hydrodehalogenation of CF_2I. Moreover, the concentration of peroxide in 1,4-dioxane affected the reaction.[6] Using aqueous peroxide-free 1,4-dioxane as solvent, the transformation of CF_2I to CF_2H was suppressed and no **3** was formed. A content of ca. 0.5% of peroxide (by weight) was good enough for the sulfinatodehalogenation of **1a**. Increasing the content of peroxide in aqueous dioxane, e.g., over 10%, however, no **3** was obtained and the conversion of **1a** to **4** became dominant (over 80% yield). Taking azobisisobutyronitrile (AIBN) instead of peroxide in aqueous dioxane, similar results were achieved. These suggested a radical chain process involved in sulfinatodehalogenation reactions.[2h]

Other reductants, such as $Na_2S_2O_4$, $(H_2N)_2C{=}SO_2$, $Na_2S_2O_5/K_3Fe(CN)_6$, $HOCH_2SO_2Na$, Na_2SO_3, were also effective for the sulfinatodehalogenation of **1a**.[10] Solvents like diglyme, THF, CH_3CN, and DMSO were suitable to produce **3**. Using pyridine, triethylamine or *N*-methyl-morpholine instead of 1,4-dioxane, however, the sulfinatodehalogenation of **1a** with K_2SO_3 was completely prohibited.[6] And $HCF_2CF_2OCF_2CF_2SO_3K$ was obtained as the main product (85% yield). The molecular interaction between **1a** and the solvents, determined by ^{19}F NMR (the chemical shifts of CF_2I group of **1a** in nucleophilic solvents shifted remarkably toward the upper field compared to neat **1a**), weakened the C–I bond of **1a**, leading to the hydrodehalogenation of CF_2I.[6] In addition, the SO_2F group of **1a** underwent hydrolysis much faster than reduction under basic circumstances, which finally afforded $HCF_2CF_2OCF_2CF_2SO_3K$.

$KO_2SCF_2CF_2OCF_2CF_2SO_2K$ (**3**) can be converted into many useful chemicals (Scheme 2).[5–10] The reaction of **3** with HI in glacial acetic acid at reflux gave a mixture of 3-oxa-5-iodoperfluoropentanoic acid (**11a**, major product), 3-oxa-1,5-diiodoperfluoropentane (**7a**), 3-oxa-perfluoroglutaric acid (**10**), and trace amount of 3-oxa-5-*H*-perfluoropentanoic acid (**11c**). Addition of a small amount of hydroquinone (e.g., 1.2% by weight) to the reaction mixture of **3**, HI and HOAc improved the yield of **10** (53%). Treatment of **3** with HBr



Scheme 1. The first example of sulfinatodehalogenation reaction.



Scheme 2. Conversion of **3** to useful fluorine-containing building blocks.

similarly provided 3-oxa-5-bromoperfluoropentanoic acid (**11b**, major product), **10** and trace amount of **11c**. Since HCl has poor reducing power, its reaction with **3** gave only 3-oxaoctafluoropentane-1,5-disulfinic acid (**8**). Reactions of **3** with I_2 and Br_2 yielded the corresponding 1,5-dibromo-3-oxaoctafluoropentane (**7a**) and 1,5-diiodo-3-oxaoctafluoropentane (**7b**), respectively, while the reaction of **3** with Cl_2 afforded **6**. Sulfonyl chloride **6** is an important intermediate, which could readily produce perfluorosulfonic acid **9** and its derivatives. The formation of **11a**, **7a** and **11b** with HX was explained by the reaction of **3** with the free halogen (X_2) formed in the production of **10** (Scheme 3, also see Section 3.1). These reactions provided reliable methods for the synthesis of perfluorocarboxylic acids, perfluoroalkyl bromides, and perfluorosulfonic acids from not only **1a** but also other diverse R_FI.[9,10]

$$R_FCF_2SO_2K \xrightarrow{HX} R_FCOOH + KHF_2 + S + X_2 \qquad R_FCF_2SO_2K \xrightarrow[-KX]{X_2} R_FCF_2SO_2X \xrightarrow{-SO_2} R_FCF_2X$$

$$X = I, Br$$

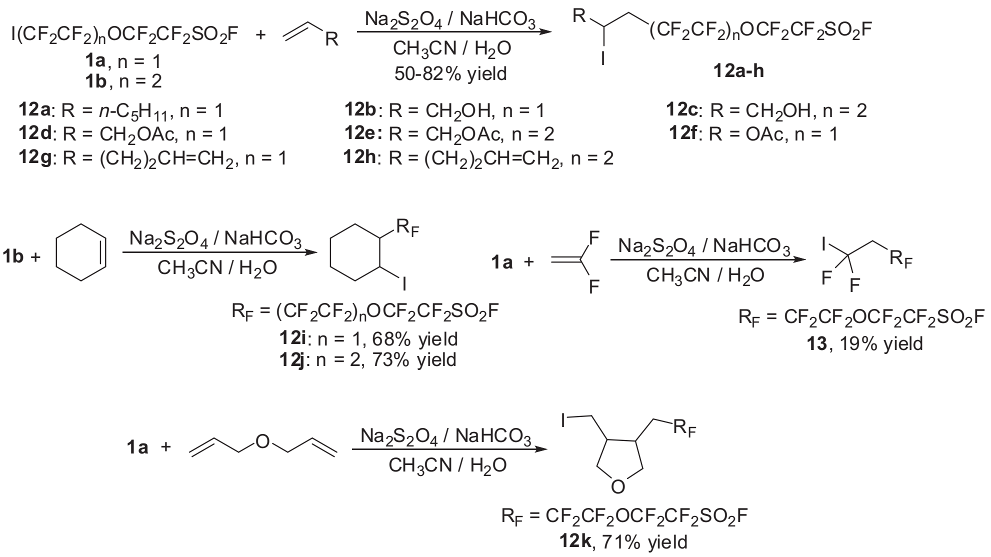
Scheme 3. Mechanism for the generation of **11** and **7** from **3**.

2.1.2. Perfluoroalkylation of alkenes. The sulfinatodehalogenation of **1a** with $Na_2S_2O_4$ has been convinced through a radical mechanism.[2h,11] The reaction of **1a** with $Na_2S_2O_4$ in the presence of 1–1.5 equiv of alkenes at room temperature or higher gave the corresponding adducts **12** in 50–82% yields (Scheme 4).[11b] Vinyl acetate was suitable in this reaction. Disubstituted alkenes, such as cyclohexene reacted with **1a** or **1b** in the presence of $Na_2S_2O_4$ and $NaHCO_3$ to provide **12i** or **12j** with a mixture of *Z*- and *E*-isomers. **1a** treated with diallyl ether, $Na_2S_2O_4$, and $NaHCO_3$ afforded tetrahydrofuran derivative **12k**. The sulfinatodehalogenation of **1a** with vinylidine fluoride ($CH_2{=}CF_2$) yielded **13** regioselectively.

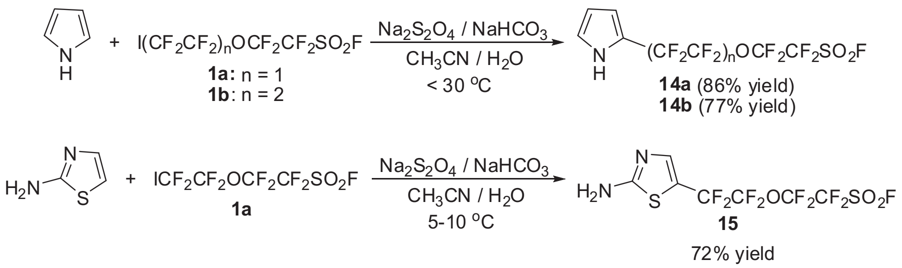
Adduct **13** was an interesting compound, which could be further functionalized. In the presence of large excess of $Na_2S_2O_4$, the reaction of **1a** with $CH_2{=}CF_2$ provided a mixture of **13**, $FO_2SCF_2CF_2OCF_2CF_2CH_2CF_2SO_2Na$ and $NaO_2SCF_2CF_2OCF_2CF_2CH_2CF_2SO_2Na$.

2.1.3. Perfluoroalkylation of arenes. Perfluoroalkyl radical ($R_F^{\bullet}$) generated from R_FI under the standard sulfinatodehalogenation reaction conditions was trapped by a variety of arenes (Scheme 5).[2h] The reaction of **1a** and **1b** with pyrrole in the presence of $Na_2S_2O_4$/$NaHCO_3$ at a temperature lower than 30 °C provided respective α-perfluoroalkyl pyrroles **14a** in 86% yield and **14b** in 77% yield.[12a] Treatment of **1a** with 2-aminothiazole and $Na_2S_2O_4$/$NaHCO_3$ at 5–10 °C in a CH_3CN/H_2O (4:1) mixture gave the coupled product **15** in 72% yield with good selectivity at 5-position of the thiazole ring.[12b] This reaction was not sensitive to the concentration of the reactants, and only the ratio of CH_3CN/H_2O slightly affected the yields of the products.

Further studies showed that porphyrins could also be perfluoroalkylated by **1a**–**c** under the modified sulfinatodehalogenation conditions (Scheme 6).[13] The reactions of tetraphenylporphyrin (H_2TPP), tetra(*p*-trifluoromethylphenyl)porphyrin ($H_2T(p\text{-}CF_3)PP$) and tetra(*p*-chlorophenyl)porphyrin ($H_2T(p\text{-}Cl)PP$) with **1a**, **1b** or **1c** in the presence of $Na_2S_2O_4$ and $NaHCO_3$ in a mixture solvent of $DMSO/CH_2Cl_2$ at room temperature for 8–18 h gave the corresponding β-perfluoroalkyl porphyrins **16** in 20–35% yields



Scheme 4. Perfluoroalkylation of alkenes with **1** under standard sulfinatodehalogenation reaction conditions.



Scheme 5. Perfluoroalkylation of heteroarenes with **1a** or **1b** under standard sulfinatodehalogenation reaction conditions.

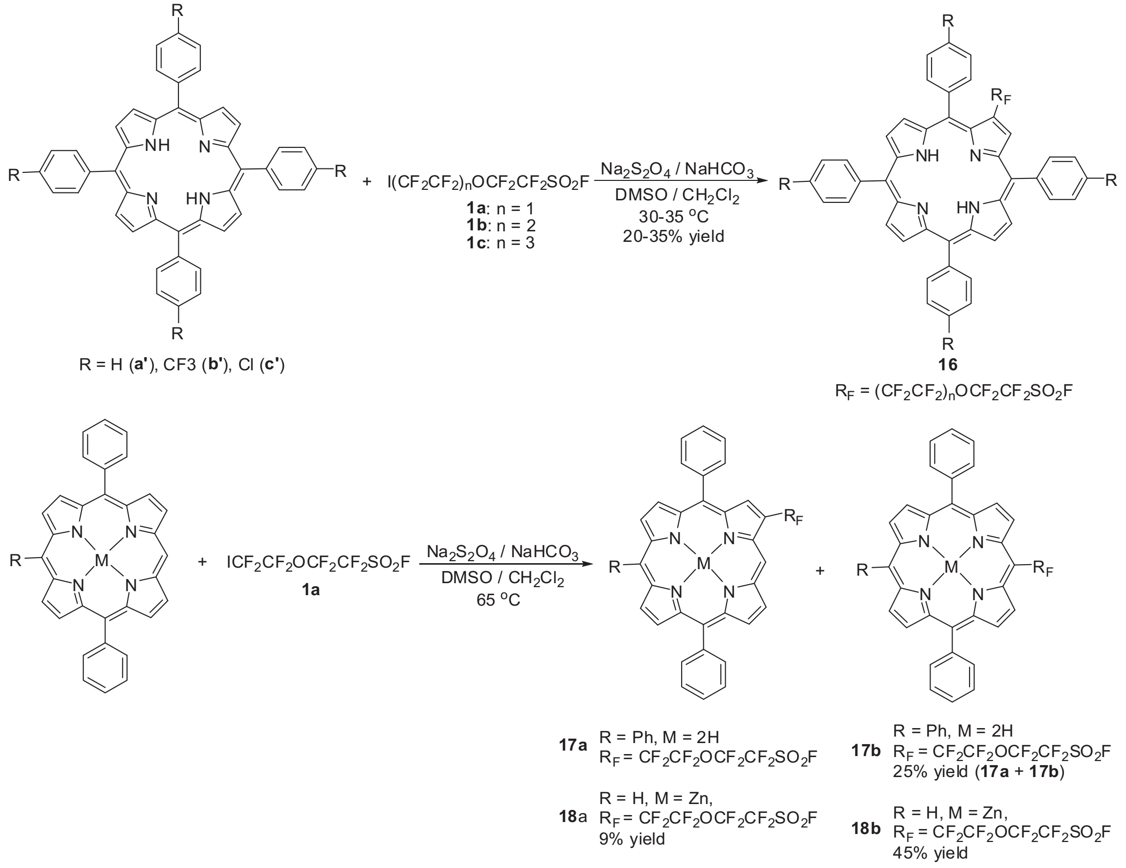
(Scheme 6).[13a] Notably, **16** reacting with 5-(4-hydroxyphenyl)-10,15,20-triphenylporphyrin or BINOL afforded perfluoroetherylsulfonyl ester linked diporphyrins.[13b] These diporphyrins further treated with $Zn(OAc)_2$ in $CHCl_3/CH_3OH$ provided diporphinatozincs, which exhibited particular spectroscopic properties. In addition, the reaction of 5,10,15-triarylporphyrin with **1a** under the modified sulfinatodehalogenation conditions gave a mixture of β (**17a**) and *meso*-(**17b**) perfluoroalkanesulfonyl products with a ratio around 1:3 (**17a**:**17b**).[14a] Treatment of zinc(II) 5,15-diphenylporphyrin with 1.1 equiv of **1a** in the presence of 1.1 equiv of $Na_2S_2O_4$ in DMSO/THF system at 45 °C for 1–2 h produced β-fluoroalkyl-5,15-diphenylporphyrin (**18a**) and *meso*-fluoroalkyl-10,20-diphenylporphyrin (**18b**) in 9% and 45% yield, respectively.[14b] It seems that porphyrins favored the *meso*-perfluoroalkylations with **1** under sulfinatodehalogenation conditions.

p-Perfluoroalkylcalix[4]arenes were readily prepared from the reaction of calix[4]arene with R_FI in the presence of $Na_2S_2O_4$ (Scheme 7).[15] Using cetyltrimethylammonium bromide (CTAB) as phase transfer catalyst, **1a** and **1b** reacted with calix[4]arenes in $CHCl_3$ and H_2O at refluxing to give **19a** (38% yield) and **19b** (35% yield), respectively. Although the yield was slightly low, the sulfonyl fluoride group was not hydrolyzed (The reaction run in a mixture of CH_3CN and H_2O led to the hydrolysis of the sulfonyl fluoride group). Due to the introduction of the fluoroalkyl chains, **19** showed better solubility in common organic solvents compared to the non-fluorinated analogues and could produce inclusion complexes with many neutral molecules as well as fluorocarbons.

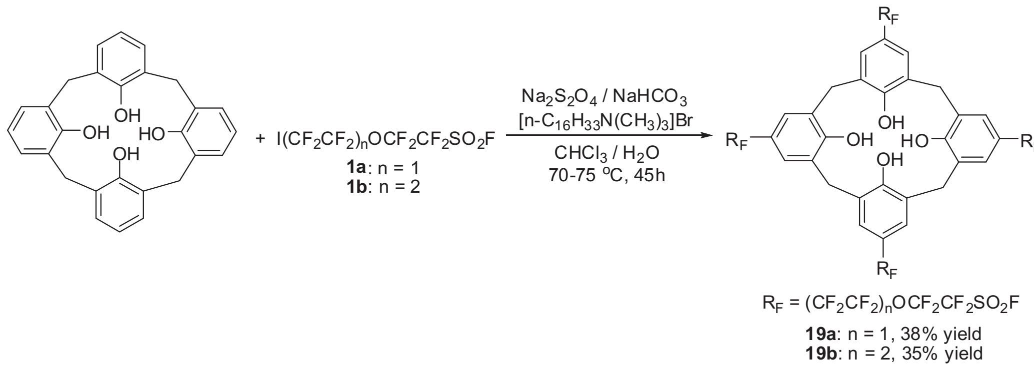
2.2. Metal-initiated conversion of the C–I bonds in $I(CF_2CF_2)_nOCF_2CF_2SO_2F$

Reductive metals can behave in a similar manner with the sulfinatodehalogenation reagents to activate the C–I bond of R_FI.[16] The reactions of **1** with alkenes and arenes in the presence of metals, such as Cu and Mg also provides the perfluoroalkylated products. When R_FI is initiated by Mg and Zn, however, the products are not always the same with those observed in the sulfinatodehalogenation reactions. For example, treatment of R_FI with Mg in an ether-type solvent probably gave a perfluoroalkyl Grignard reagent. The reaction of **1** with Zn in the absence of organic substrates provided the homo-coupling product or the hydrodehalogenation product rather than perfluoroalkyl sulfites, which was exceedingly dependent upon the type of the solvents.

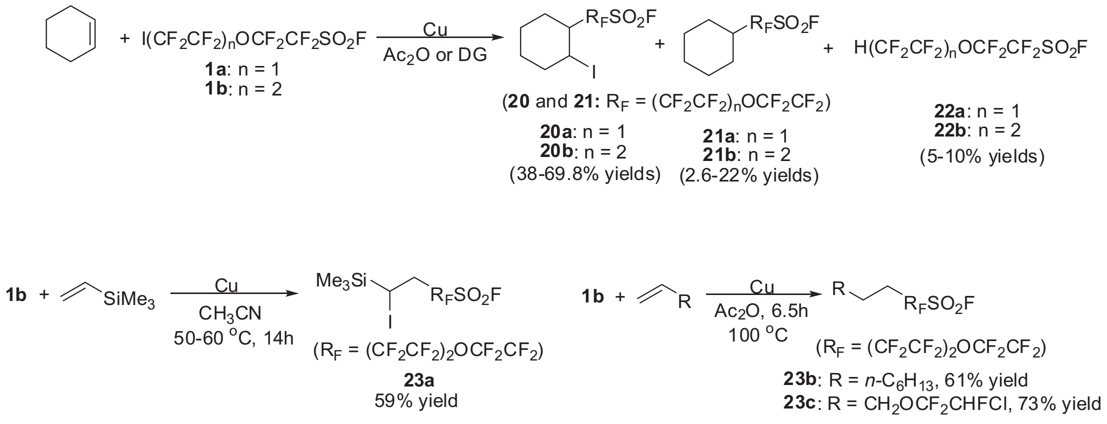
2.2.1. Perfluoroalkylation of alkenes, carbonyl compounds, arenes, and aryl, allyl and alkyl halides. Copper-initiated perfluoroalkylation of alkenes with **1** was performed. The reaction of **1a**–**b** with cyclohexene in the presence of catalytic amount of copper (e.g., 24 mol %) in Ac_2O or DG (diglyme) at 100 °C or 50 °C for 6.5 h or 13 h provided **20** in 38–69.8% yields (Scheme 8).[17a] Cu-catalyzed reaction of **1b** with vinyltrimethylsilane afforded 1:1 adduct (**23a**) in good yield.[17b] Reactions of **1b** with olefins, such as *n*-octene and chlorotrifluoroethoxylpropene also gave the 1:1 adducts (**23b**,**c**) in good yields. The amount of Cu had little influence on the reaction of **1a**–**b** with cyclohexene. Nevertheless, the temperature affected the reaction greatly. Reactions with cyclohexene



Scheme 6. Perfluoroalkylation of porphyrins with **1a**–**c** under modified sulfinatodehalogenation reaction conditions.

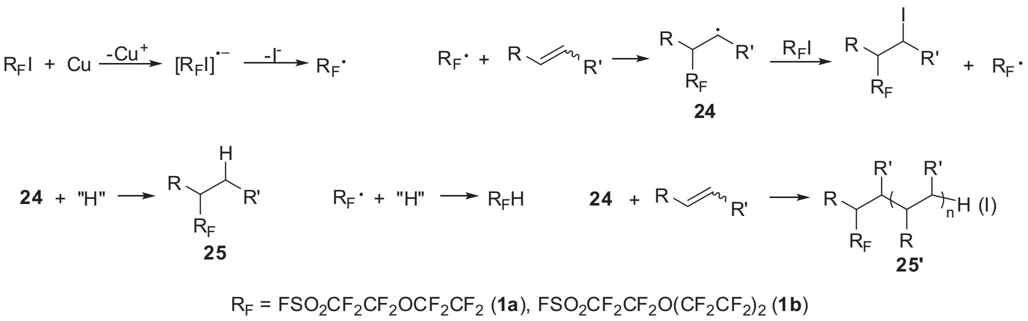


Scheme 7. Synthesis of *p*-perfluoroalkylcalix[4]arenes from calix[4]arene and **1a**–**b** under standard sulfinatodehalogenation reaction conditions.



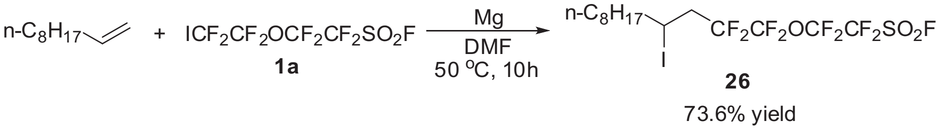
Scheme 8. Cu(0)-mediated perfluoroalkylation of alkenes with **1a**,**b**.

did not occur at 15–20 °C and proceeded very slowly at 50 °C. In the presence of *p*-DNB or hydroquinone, the reaction was partly or completely inhibited. When highly reactive olefins, such as styrene and acrylates were employed in this reaction, the fluorinated nonvolatile amorphous solids (**25′**) were formed. These results suggested a single electron transfer-radical chain mechanism (Scheme 9). Firstly, **1a** (or **1b**) obtained an electron from copper to form radical anion, which was decomposed to $R_F^{\bullet}$. Radicals $R_F^{\bullet}$ then trapped by alkenes produced **24**. **24** abstracted iodine atoms from **1a** (or **1b**) to afford the final products, or hydrogen atoms from solvents to provide **25**. For highly active olefins, the reaction of **24** with olefin was much faster than that of **24** with **1a** (or **1b**) and solvents, thus leading to fluorine-containing polymers (**25′**).[17]



Scheme 9. Proposed mechanism for Cu(0)-mediated perfluoroalkylation with **1a**,**b**.

Transition metals and their complexes, e.g., Cu, Pd(0), Pt(0), Rh(I), Ni, Fe, Zn, Ir, Ag, etc., have been confirmed effective to catalyze the radical addition of R_FI to carbon–carbon multiple compounds.[16] Magnesium (Mg), one of the most important main group metals, which has been widely used with RX to prepare Grignard reagents, is also amenable to initiate the reaction of R_FI with alkenes and alkynes.[18,19] It was reported that **1a** reacting with alkenes at 50 °C in the presence of 40 mol % of Mg gave the corresponding adducts (**26**) in 73.6% yield (Scheme 10).[18]



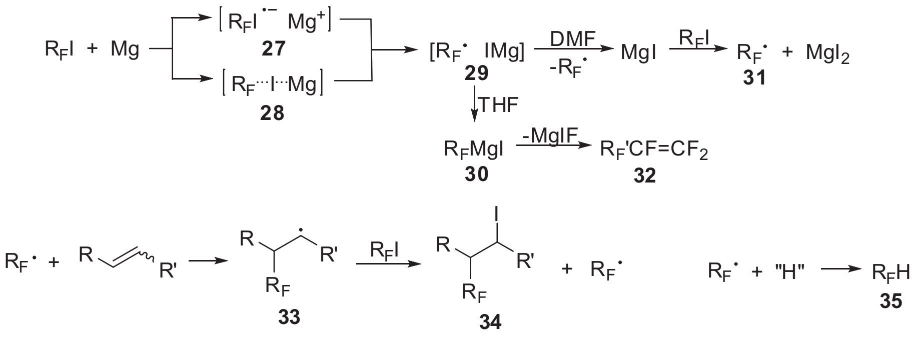
Scheme 10. Mg-initiated perfluoroalkylation of alkenes with **1a**.

Further investigation showed that Mg-initiated reactions of R_FI with alkenes and alkynes were influenced by the state of the metal and the solvents.[18] Magnesium powder seemed more efficient in the reaction than the turnings. The possibility of magnesium oxide and magnesium iodide catalyzing the reaction, which might exist during the course of the reaction, was excluded by the control experiments.[18] The reactions of R_FI with alkenes (or alkynes) and Mg occurred successfully in DMF, acetonitrile and acetone. Without solvents, no desired products were obtained. The use of *p*-DNB and oxygen did not affect the reaction in DMF, but the reaction was partially suppressed with hydroquinone and completely inhibited by 2-nitroso-2-nitropropane.

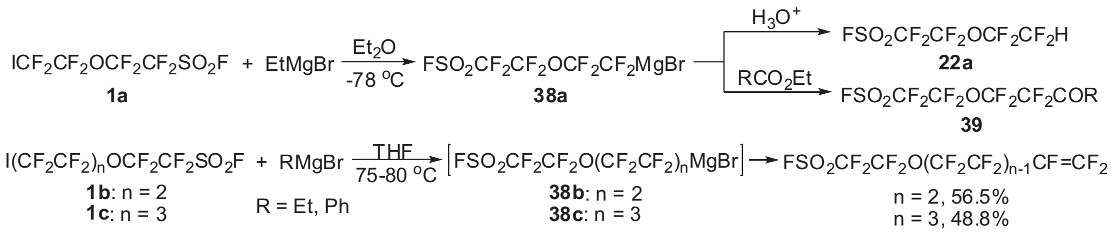
Using THF as solvent, perfluoroalkenes ($R_F'CF{=}CF_2$, **32**) were formed in addition to **34** and **35** (Scheme 11). The generation of **32** in THF was difficult to explain by a single electron transfer-radical chain mechanism. **32** might arise from the β-elimination of the perfluoroalkyl Grignard reagent (R_FMgI, **30**) as reported by Tamborski and others (Scheme 11).[19] On the other hand, taking non-ether type solvents instead of THF, no **32** was formed, even though the reaction was conducted at 80 °C. These results indicated that a single electron transfer initiated radical addition might be involved in non-ethereal solvents, and that both radical addition and perfluoroalkyl Grignard reagent reactions were probably included in THF.

The utility of main group metals to prepare $R_FM(X)$ encountered strict limitation because of the poor thermal stability of the R_F-M type intermediates, especially R_F bearing reactive functional groups.[19] $R_FM(X)$ are powerful nucleophilic fluoroalkylation reagents. Although some perfluoroalkyl ketones and aldehydes were synthesized by the reaction of $R_FM(X)$ with carbonyl compounds,[20] this method was not very suitable for functionalized R_FI since the corresponding $R_FM(X)$ intermediates were hard to prepare. The only successful example before the present report was perfluoroalkylether magnesium bromide $[ROCOCF_2CF_2CF_2CF_2OCF_2CF_2MgBr(I)]$ (**36**), which was prepared from the metal–halogen exchange reaction between a perfluoroalkylether iodide ester $[ROCOCF_2CF_2CF_2CF_2OCF_2CF_2I]$ (**37**) and EtMgBr, and then treated with $R^1CO_2R^2$ to provide the desired ketones.[20f] Considering the relatively stable fluorosulfonyl group of **1**, $FSO_2CF_2CF_2O(CF_2CF_2)_nMgBr$ (**38**) were possibly synthesize from **1**.[20a] Indeed, the metal–halogen exchange of **1a** with EtMgBr in Et_2O at −78 °C for 2 h afforded **38a** successfully (Scheme 12). If the reaction mixture was quenched by 2 M HCl, only **22a** was obtained. Treatment of **1b**,**c** with EtMgBr or PhMgBr in THF at 75–80 °C for 1.5 h gave $CF_2{=}CF(CF_2CF_2)_{n-1}OCF_2CF_2SO_2F$ in good yields.[25] **38b**–**c** were assumed to be the reasonable intermediates. These meant that the fluorosulfonyl group (SO_2F) of **1** was not vulnerable enough to be attacked by EtMgBr under the transmetallation reaction conditions.

Perfluoroalkylether Grignard reagent **38a** did not undergo cyclization but reacted with carboxylic esters to give ω-fluorosulfonylperfluoroalkyl ketones **39a**–**f** (Table 1).[20a] Treatment of **38a** with α,β-unsaturated esters afforded only 1,2-addition product **39g**. In the case of α,β-unsaturated aldehyde, similar result was obtained. **38a** reacting with HCO_2Et provided ω-fluorosulfonylperfluoroalkyl acetal



Scheme 11. Proposed mechanism for Mg-initiated perfluoroalkylation.



Scheme 12. The synthesis and reactivity of R_FMgX compounds.

Table 1
The reactions of **38a** with carbonyl compounds[a]

Entry	RCO_2Et	$FSO_2CF_2CF_2OCF_2CF_2COR$	Yield (%)[b]
1	CH_3CO_2Et	$FSO_2CF_2CF_2OCF_2CF_2COCH_3$ (**39a**)	81.3
2	$C_2H_5CO_2Et$	$FSO_2CF_2CF_2OCF_2CF_2COC_2H_5$ (**39b**)	76.0
3	n-$C_3H_7CO_2Et$	$FSO_2CF_2CF_2OCF_2CF_2CO(n\text{-}C_3H_7)$ (**39c**)	82.7
4	i-$C_3H_7CO_2Et$	$FSO_2CF_2CF_2OCF_2CF_2CO(i\text{-}C_3H_7)$ (**39d**)	76.9
5	$PhCH_2CO_2Et$	$FSO_2CF_2CF_2OCF_2CF_2COCH_2Ph$ (**39e**)	76.9
6	n-$C_5H_{11}CO_2Et$	$FSO_2CF_2CF_2OCF_2CF_2CO(n\text{-}C_5H_{11})$ (**39f**)	77.2
7	$CH_2{=}C(CH_3)CO_2Et$	$FSO_2CF_2CF_2OCF_2CF_2COC(CH_3){=}CH_2$ (**39g**)	73.8
8	$CH_3CH{=}CHCHO$	$FSO_2CF_2CF_2OCF_2CF_2CH(OH)CH{=}CHCH_3$ (**39h**)	75.3
9	HCO_2Et	$FSO_2CF_2CF_2OCF_2CF_2CHO\cdot H_2O$ (**39i**)	74.2

[a] All the reactions were run at −78 °C in Et_2O under N_2 atmosphere.
[b] Isolated yields.

39i, which could be dehydrated by concentrated H_2SO_4 to give the corresponding aldehyde.

Recently, **38** was 'immobilized' by Me_3SiCl.[21] The reaction of **1a** and **1d** with MeMgBr in the presence of Me_3SiCl in a mixture solvent of THF and Et_2O at −78 °C gave stable derivatives $Me_3Si(CF_2CF_2)_nOCF_2CF_2SO_2F$ (**40**) in good yields (Scheme 13). **40** could be initiated by $[(Me_2N)_3S]^+[Me_3SiF_2]^-$ (TASF), $[Bu_4N]^+[Me_3SiF_2]^-$ (TBAT) and $[(Pip_2N)_3S]^+[Me_3SnF_2]^-$ (TPSF) to generate the perfluoroalkylether nucleophiles $[FO_2SCF_2CF_2O(CF_2CF_2)_n]^-$ (**41**), which reacted with hexafluorobenzene, monosubstituted pentafluorobenzenes, and pentafluoropyridine over a range of temperatures between −78 and 25 °C to provide $ArCF_2CF_2OCF_2CF_2SO_2F$ (**42**) in 24–73% yields. The fluorides had influence on the reaction. When either catalytic or stoichiometric quantities of CsF or $Bu_4N^+F^-$ was employed instead of TASF, TBAT or TPSF, the substitution didn't occur, even varying the thermal conditions and reaction times. However, it was surprising that CsF and $Bu_4N^+F^-$ could catalyze the reaction of **40a**,**b** with cyanuric fluoride to afford **43a**,**b**, which were characterized by their molecular ions at m/z 975 and 1875, respectively, in the mass spectra.

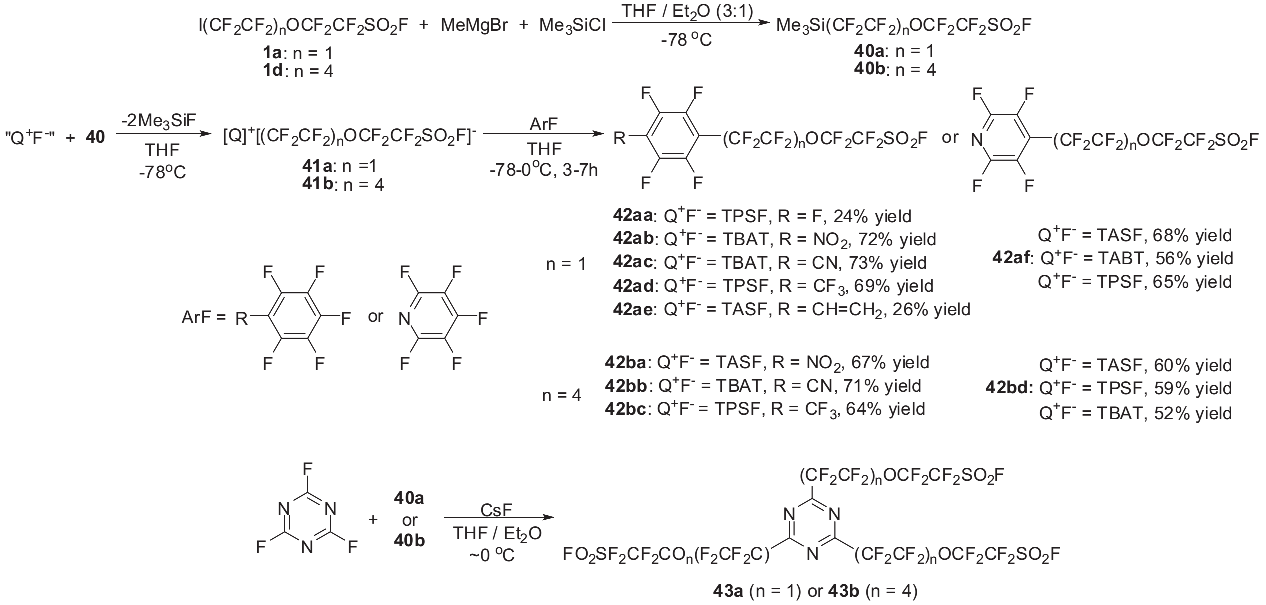
Copper-mediated perfluoroalkylation of aryl, allyl, and alkyl halides (ArX) with R_FI have drawn great attentions because this method can selectively introduce the perfluoroalkyl group into organic molecules. Studies showed that **1a** and **1b** were also suitable perfluoroalkyl iodides in this reaction.[22] The reactions of **1a** and **1b** with iodobenzene in DMF provided **44a** in 44% yield and **44b** in 51% yield, respectively (Scheme 14).[22a] The solvents had great influence on these reactions.[22a] Taking DMSO instead of DMF as solvent, no desired products were formed. When the reaction was carried out in Ac_2O, **1a** gave both mono- and bis-perfluoroalkylated benzenes (**45a** and **46a**) and **1b** yielded **44b** and **45b** (Scheme 14). It seemed that the reaction run in diverse solvents proceeded through different mechanisms.

Further investigation showed that **1a** reacting with **47** in the presence of copper in Ac_2O provided a mixture of *o*-, *m*- and *p*-perfluoroalkylated products **48** (Scheme 15).[22b] Arenes **47** with electron donating groups favored the perfluoroalkylation and gave high yield of **48**, whereas arenes with electron-withdrawing groups suppressed the reaction and afforded low yield of **48**. Addition of cyclohexene into the reaction mixture, the reaction of R_FI, toluene and Cu was inhibited, leading to **49** and **50** rather than perfluoroalkylated arenes (Scheme 16). Toluene was recovered quantitatively. This indicated that Cu-mediated reaction of R_FI with cyclohexene was much faster than that of R_FI with toluene. This was also evidence that Cu-mediated perfluoroalkylation of arenes (via C–H activation) in Ac_2O might involve a single electron transfer-radical mechanism.

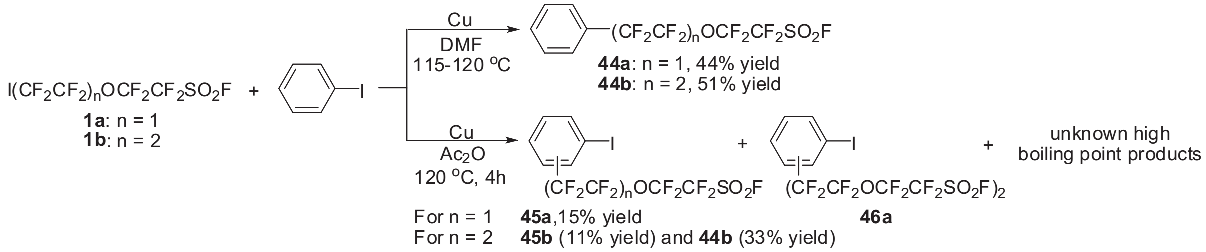
Moreover, Cu-mediated perfluoroalkylation of vinyl, allylic and styryl bromides with **1b** was investigated in DMF (Scheme 17).[23a] The reactions of **1b** with $PhCH_2Br$, $CH_2{=}CHCH_2Br$ and $PhCH{=}CHBr$ in the presence of excess of Cu in DMF gave the corresponding cross-coupling products in moderate yield. **22b** was obtained as the byproduct. In the case of $CH_2{=}CHCH_2Br$, the cross-coupling product was converted to **53** by treatment with Br_2 for the purpose of isolation. Perfluoroalkyl copper complex (**51**), generated from **1b** and Cu, was assumed as the key intermediate for these couplings.

2.2.2. Telomerization of tetrafluoroethylene with $ICF_2CF_2OCF_2CF_2SO_2F$.

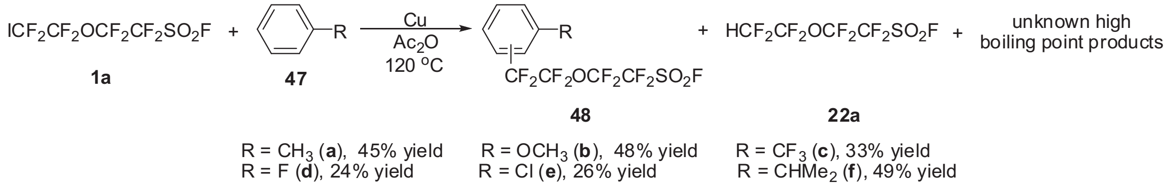
The reaction of **1a** with tetrafluoroethylene ($CF_2{=}CF_2$) were initiated by copper (Table 2).[24] Compared to thermal initiation



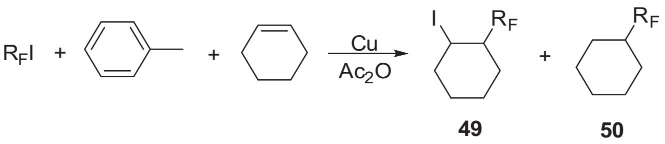
Scheme 13. The synthesis of TMSR$_F$ (**40**) and their reactions with per(poly)fluoroarenes.



Scheme 14. Cu(0)-mediated perfluoroalkylation of aryl iodides with **1**.

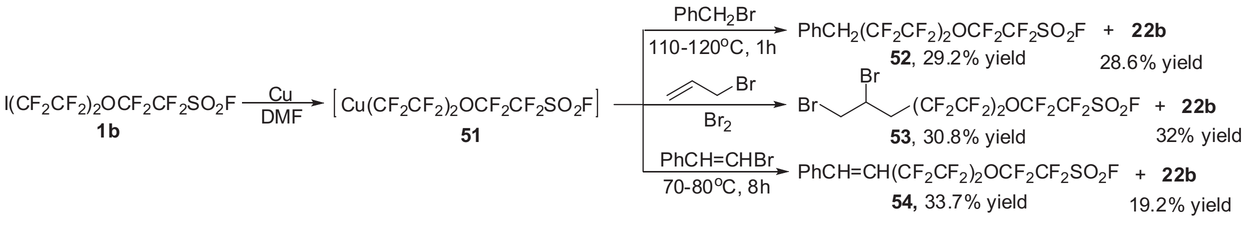


Scheme 15. Cu(0)-mediated perfluoroalkylation of substituted arenes with **1a**.



Scheme 16. Mechanism study of Cu(0)-mediated perfluoroalkylation in Ac$_2$O.

(180–190 °C), copper-mediated telomerization occurred very smoothly. **1a** reacted with $CF_2{=}CF_2$ in the presence of catalytic amounts of copper at 90–100 °C for 3 or 3.5 h under decreased pressure to give a mixture of telomers **1b**–**e** in comparable yields. Copper initiation also prevented the side reaction. When **1a** and $CF_2{=}CF_2$ were heated at 180–190 °C in the absence of copper, **1b**–**e**



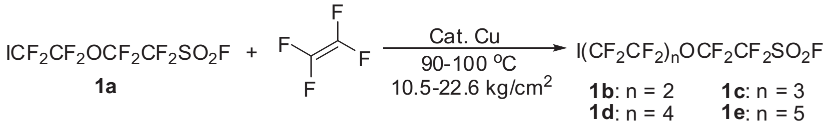
Scheme 17. Cu(0)-mediated perfluoroalkylation of vinyl, allylic and styryl bromides with **1b**.

Table 2
Cu-mediated telomerization of tetrafluoroethylene with **1a**

Entry	**1a**:$CF_2{=}CF_2$		Temperature (°C)	Pressure (max, kg/cm^2)	Time (min)	$I(CF_2CF_2)_nOCF_2CF_2SO_2F$ (g)[a]					
	(g:g)[a]	(mol:mol)[b]				n=1	n=2	n=3	n=4	n=5	n>5
1	63.9:3.75	4:1	90	10.5	180	52.8	2.0	1.7	1.2	0.3	0.4
2	60.0:7.0	2:1	90	14.6	180	37.9	6.5	3.8	1.9	0.4	8.8
3	60.0:10.5	2:1.5	90	23.3	210	25.4	13.0	6.8	3.1	0.7	15
4	60.0:14.0	1:1	90–100	22.6	180	29.2	11.4	5.0	1.4	0.1	21.3
5[c]	42.6:7.5	2:1.5	180–190	26.0	480	17.1	12.0	3.4	0.6	3.1	1.7

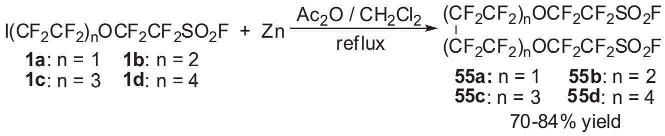
[a] The amounts were described in grams.
[b] The molar ratio of the reactants.
[c] The reaction was conducted in the absence of Cu and perfluorocyclobutane was obtained.

as well as perfluorocyclobutane were obtained. The reaction with Cu at a lower temperature, however, didn't form this byproduct. Therefore, copper-mediated telomerization provided a safe and reliable method for the preparation of $I(CF_2CF_2)_nOCF_2CF_2SO_2F$ from **1a**.



In addition, the reactant ratio had influence on the copper-mediated telomerization. Decreasing the ratio of **1a** to $CF_2{=}CF_2$, the undesired solid products (e.g., n>4) were increased. To maintain a relatively stable distribution of the products, a stepwise addition of $CF_2{=}CF_2$ to excess **1a** was suggested. Besides, palladium catalysis ($Pd(PPh_3)_4$) could induce the telomerization of **1a** with $CF_2{=}CF_2$.

2.2.3. Metal-mediated homo-coupling and hydrodehalogenation of $I(CF_2CF_2)_nOCF_2CF_2SO_2F$. Zinc-initiated conversion of **1** was investigated. The reaction of **1a**–**d** with Zn in Ac_2O/CH_2Cl_2 provided the homo-coupling products **55a**–**d** in 70–84% yield (Scheme 18).[4c] Replacement of Ac_2O/CH_2Cl_2 by solvents, such as AcOH, THF, and 1,4-dioxane, however, almost only $H(CF_2CF_2)_nOCF_2CF_2SO_2F$ (**22**) were obtained. This indicates again that Ac_2O is a good solvent for generation and maintenance of perfluoroalkyl radicals ($R_F^{\bullet}$). In Ac_2O, the hydrogenation of $R_F^{\bullet}$ is suppressed, which gives them sufficient 'shelf-life' for further transformation.



Scheme 18. Zn-initiated homo-coupling of $I(CF_2CF_2)_nOCF_2CF_2SO_2F$.

Compounds **22** were often observed in the reactions of **1** with reductants. Although they were usually thought as common byproducts under reductive conditions, they were indeed a useful material to prepare functionalized sulfonic acid and its derivatives (see Section 3.3). The hydrodehalogenation of R_FX with $LiAlH_4$ was also reported in literature.[23]

To the best of our knowledge, Zn-mediated homo-coupling of **1** was the first example of the metal-mediated perfluoroalkyl-perfluoroalkyl cross-coupling reaction. Besides **1**, other R_FI were also suitable in this reaction.

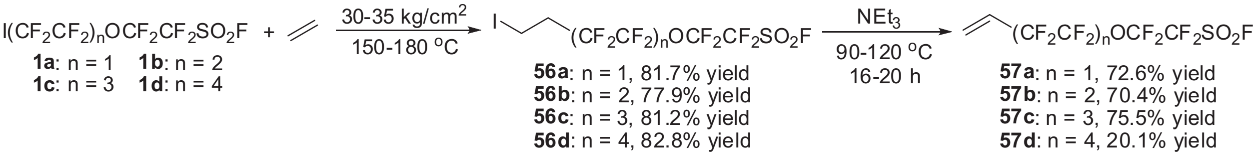
2.3. The cleavage of the C–I bonds of $I(CF_2CF_2)_nOCF_2CF_2SO_2F$ by radical initiation systems

Radical initiation systems can rupture the C–I bonds of **1**. The reactions of **1** with alkenes, alkynes, and arenes under heat and UV, or in the presence of 2-(*tert*-butylperoxy)-2-methylpropane ((*t*-BuO)$_2$), benzoic peroxyanhydride (Bz_2O_2, BPO) and AIBN, give the corresponding perfluoroalkylated products in good yields. The reactions with radical initiators are faster and the yields of the products are higher compared to those with only heat or light. These reactions proceed through a radical chain mechanism, thereby only catalytic amounts of initiators are employed.

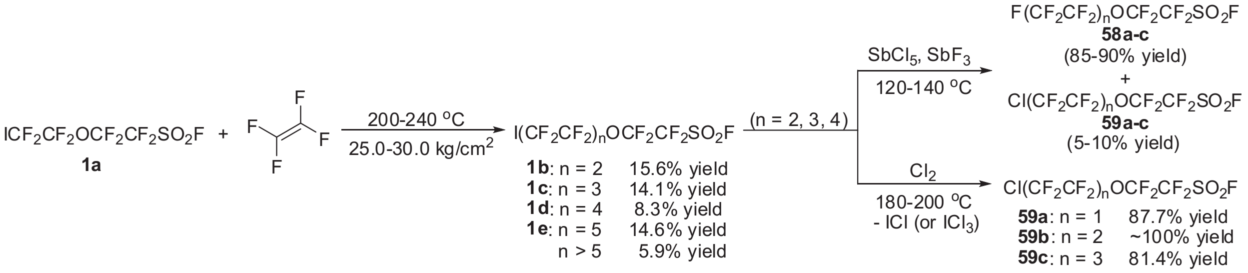
2.3.1. The radical addition of $I(CF_2CF_2)_nOCF_2CF_2SO_2F$ to alkenes and fluoroalkenes under heat. Fluorocarbon sulfonyl fluorides have been widely used to synthesize functionalized materials; e.g., a sulfonyl fluoride group (SO_2F) incorporated into molecular systems can make compounds useful as ion-exchange resins, surface-active agents and strong sulfonic acids (see Section 3.2). To prepare these important compounds, the key is to gain the feedstocks containing not only the SO_2F groups but also C=C bonds, alcohol groups or C–I bonds. There have been methods to prepare these bifunctional compounds.[2h] Except these approaches, thermally initiated radical addition of **1** to alkenes can provide adducts with both SO_2F groups and C–I or C=C bonds (Scheme 19).[25] The reaction of **1a**–**d** with ethylene at 150–180 °C provided **56a**–**d** (77.9–82.8% yields), which were further treated with NEt_3 to give **57a**–**d** in 20.1–75.5% yields. Compounds **56** and **57** are useful building blocks, which can be incorporated into bioactive molecules and polymers.

In addition, the reaction of **1a** with fluoroalkenes is induced by heat (Scheme 20). **1a** reacted with tetrafluoroethylene at 200–240 °C under a pressure of 25.5–30.0 kg/cm^2 to give a mixture of telomerized products **1b**–**e**, which were readily isolated by fractional distillation.[4a–d] Moreover, **1b**–**d** could be fluorinated by SbF_5 to provide **58**.[4a–c] The chlorination of **1b**–**d** with Cl_2 at 180–200 °C under atmospheric or autogenous pressure afforded **59a**–**c** in high yield.[4c] Using $SbCl_5$ as reagent instead of Cl_2, all of **1a**–**d** were successfully chlorinated (Scheme 57).

Compounds **58** and **59** are applied to prepare potassium oxaperfluoroalkanesulfonates, e.g., $F(CF_2CF_2)_3OCF_2CF_2SO_3K$, which is an excellent surfactant and has been widely used as powerful suppression agent of chromic acid mist in China.[4a–c]

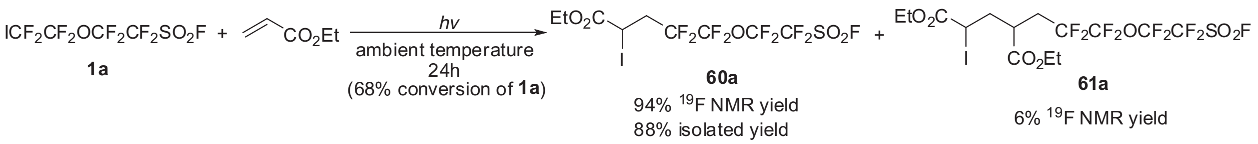


Scheme 19. Thermally initiated radical addition of **1** to ethylene.



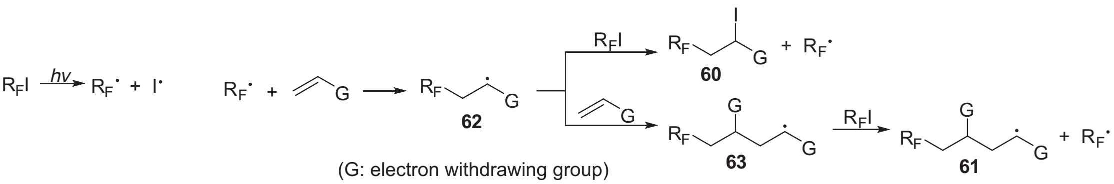
Scheme 20. Thermally initiated radical addition of **1a** to tetrafluoroethylene.

2.3.2. The homolysis of the C—I bonds of I(CF_2CF_2)$_n$$OCF_2CF_2SO_2F$ by UV irradiation. The C—I bonds of I(CF_2CF_2)$_n$$OCF_2CF_2SO_2F$ can be cleaved by UV irradiation.[1,26–29] Burton et al. reported that the reaction of **1a** with ethyl acrylate under irradiation with 254 nm W light at ambient temperature gave the 1:l addition product **60a** in 94% yield (88% isolated yield) and 1:2 adduct **61a** in 6% yield (Scheme 21).[27]



Scheme 21. UV-initiated radical addition of **1a** to ethyl acrylate.

According to the proposals reported before,[1] a similar photoirradiation-radical chain mechanism was proposed for the reaction of **1a** with ethyl acrylate, in which the C—I bond of **1a** was homolytically cleaved by UV generating $R_F^•$ (Scheme 22). UV-initiated reaction of electron-deficient alkenes with R_FI has shortages. Even the reaction conducted with large excessive alkenes for a long time, R_FI was not completely converted. This led to inefficient synthesis of **60**. Attempts were made to assist the cleavage the C—I bond of R_FI by addition of copper. However, the addition of copper neither facilitated the formation of the 1:l adduct nor the conversion of R_FI.

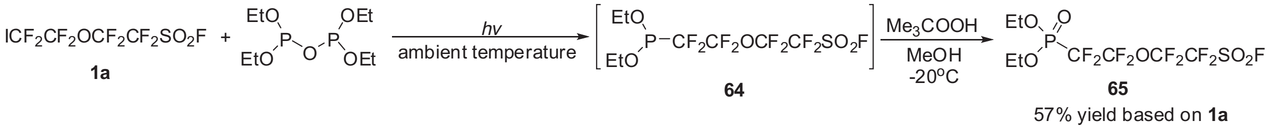


Scheme 22. Proposed mechanism for UV-initiated radical reaction with **1a**.

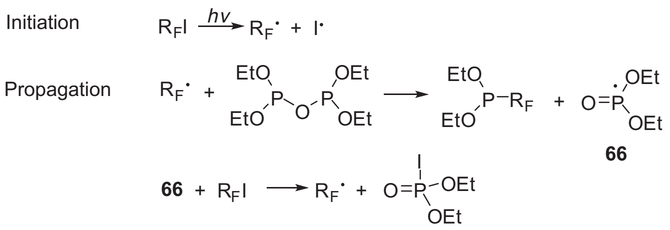
Moreover, UV-induced perfluoroalkylation was used to prepare fluorinated phosphonates.[28a] Fluorinated phosphonates have been investigated as phosphonate analogues, enzyme inhibitors, fuel cell electrolytes, and chelating agents. Nevertheless, only few fluorinated phosphonates were reported. This scarcity was attributed to the lack of synthetic procedures, since methods commonly used for the preparation of phosphonates cannot usually be applied to fluorinated analogues.[28a] Kato et al. prepared $R_FP(O)(OEt)_2$ (R_F=*n*-C_6F_{13}, *n*-C_4F_9, and $CF(CF_3)_2$) in 41–71% yield via thermally-induced radical reaction by heating a mixture of $(EtO)_2POP(OEt)_2$ and R_FI in the presence of (*t*-BuO)$_2$ in an autoclave.[28b] However, the preparation of a functionalized phosphonate, e.g., a dialkyl (β-halo or ω-halofluoroalkyl)phosphonate or **65**, has not been demonstrated by this procedure. In general, reactions favorable to cleavage of C—I bond of **1** are often suitable for those of R_FI. But the conditions feasible for R_FI are not always suitable for **1** due to the presence of the reactive sulfonyl group. Hence, a milder procedure was developed to synthesize fluoroalkyl as well as functionalized fluoroalkyl phosphonates, which avoided heating the reaction mixture with a peroxide at high temperature.[28a] A degassed mixture of $(EtO)_2POP(OEt)_2$ and **1a** reacting under UV irradiation (254 nm) at ambient temperature afforded fluorinated phosphonite **64**, which was oxidized in situ by Me_3COOH to give the corresponding fluorinated phosphonates **65** in 57% yield (Scheme 23).

A possible mechanism for this photochemical transformation was illustrated in Scheme 24, which was applicable to not only **1a**, but also other types of R_FI. Firstly, the photolytic cleavage of R_FI afforded $R_F^•$ and $I^•$ in the initiation step. Then $R_F^•$ reacted with $(EtO)_2POP(OEt)_2$ to provide $(EtO)_2PR_F$ and $(EtO)_2P(O)^•$; $(EtO)_2P(O)^•$ abstracted iodine atom from R_FI generating $R_F^•$, which continued the chain process.

UV-induced hydrolysis of R_FCF_2I was studied.[29] Irradiation of I(CF_2CF_2)$_3$$OCF_2CF_2SO_2F$ (**1c**) with UV (500 W) in the presence of Et_3N (4 equiv) and O_2 in MeOH for 24 h gave $FSO_2CF_2CF_2O(CF_2CF_2)_2CF_2CO_2H$ in 90% yields. No hydrodehalogenation

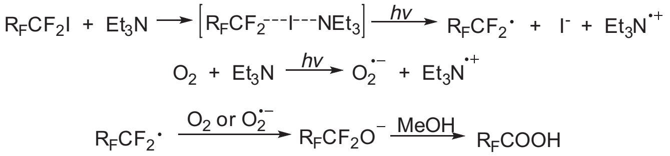


Scheme 23. Synthesis of fluorinated phosphonates from $(EtO)_2POP(OEt)_2$ and **1a** under UV irradiation.



Scheme 24. Proposed mechanism for the photochemical reaction of **1a** with $(EtO)_2POP(OEt)_2$.

product (R_FCF_2H) was formed. Other perfluoroalkyl iodides (R_FCF_2I) were also amenable to this reaction. NEt_3 was essential for the hydrolysis of R_FCF_2I, since without NEt_3 or taking Na_2CO_3 instead of NEt_3 no reaction happened. Addition of *p*-DNB in a mixture of **1c**, Et_3N, O_2, and MeOH, the UV-initiated reaction was seriously inhibited. MeOH appeared to be the best solvent (MeOH>MeCN≈DMF>DG). Based on these, a photo-oxidation mechanism was suggested in Scheme 25. This reaction provides a mild method for the synthesis of R_FCO_2H from R_FCF_2I.



Scheme 25. Proposed mechanism for the photohydrolysis of R_FCF_2I with Et_3N and O_2 in MeOH.

2.3.3. (t-BuO)$_2$, Bz$_2$O$_2$ or AIBN induced perfluoroalkylation of alkenes, alkynes, and arenes with I(CF$_2$CF$_2$)$_n$OCF$_2$CF$_2$SO$_2$F. The reactions of **1** with alkenes, alkynes, and arenes are much milder and faster, compared to the corresponding thermal and photochemical reactions, when $(t\text{-BuO})_2$, Bz_2O_2, and AIBN are employed.[30,31] **1a** reacted with ethylene at 100–120 °C in the presence of Bz_2O_2 to give **56a** in comparable yield.[30] Treatment of **1a**–**c** with allyl alcohol, allyl acetate and oct-1-ene in the presence of Bz_2O_2 or AIBN at 125–136 °C or 70–84 °C for only several hours afforded the desired products **74** in good yields.[31]

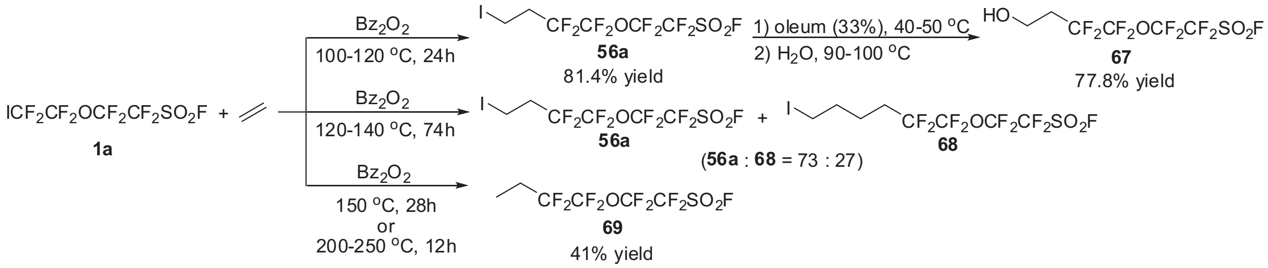
Further investigation showed that when the reaction temperature was increased to 120–140 °C, the reaction of **1a** with excess ethylene in the presence of Bz_2O_2 provided a mixture of **56a** and **68** (Scheme 26).[30] Continuously increasing the reaction temperature to 200–250 °C, the reaction gave **69** in 41% yield, which was attributed to the reaction of HI with **56a**. HI was produced from the dehydroiodination of **56a**. In addition, treatment of **1a** with ally1 chloride in the presence of Bz_2O_2 at 140–160 °C, no iodoadduct (**71**) was formed.[30] When the reaction was heated at 190 °C, both **70** and **71** were produced (Scheme 27). The lack of reactivity of ally1 chloride might be caused by the electron-withdrawing effect of the chloro group, which reduced the electron density at the olefinic site and lowered the rate of addition of the electrophilic free radical ($[FSO_2CF_2CF_2OCF_2CF_2]^\bullet$). At higher temperatures (>190 °C), the allyl free radical, generated from the cleavage of C–Cl bond, reacted and coupled with two equivalence of $[FSO_2CF_2CF_2OCF_2CF_2]^\bullet$ followed by abstraction of hydrogen atom to form compound **70**.

The reaction of **1a** with acetylene in the presence of Bz_2O_2 at 128–130 °C was also effective, which produced a mixture of the *cis*- and *trans*-iodofluoroolefinic sulfonyl fluorides, **72** and **73**, in 78% yield (Scheme 28).[30] Similarly, **1a** reacted with prop-2-yn-1-ol and Bz_2O_2 to provide a mixture of *cis* and *trans* isomers of **76** in 67% yield (Scheme 29).[31] Treatment of **1a** (or **1b**) with Bz_2O_2 in benzene, **44a** (or **44b**) was formed in 20% (or 24.2%) yield.

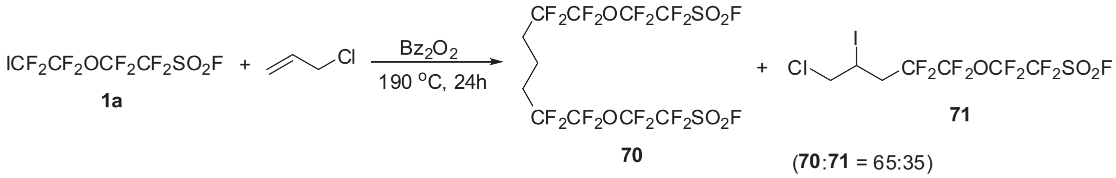
The 1:1 adducts of **1** with alkenes are very useful. The reaction of **56a** with oleum (33%) followed by hydrolysis at 90–100 °C afforded the alcoholic sulfonyl fluoride **67** in 77.8% yield, while the previous reduction of the corresponding ester could not produce such type of alcohols (Scheme 26).[30] Treatment of **74a**–**f** with zinc in isopropanol gave **75a**–**c** in 52–72% yields (Scheme 29).[31] **75a**–**c** are important monomers in polymer chemistry. This reaction provides an environment friendly method to prepare allyl perfluoroalkanesulfonyl fluorides.

2.3.4. Pb(OAc)$_4$-initiated perfluoroalkylation of alkenes and arenes with I(CF$_2$CF$_2$)$_n$OCF$_2$CF$_2$SO$_2$F. Oxidants, such as $Pb(OAc)_4$ and PbO_2 can also cleave the C–I bond of R_FI, which generates $R_F^\bullet$ to be trapped by alkenes and arenes to provide the corresponding perfluoroalkylated product (Scheme 30).[32] Details showed that **1a**,**b** reacting with cyclohexene in the presence of catalytic amount of $Pb(OAc)_4$ at 95 °C for 6 h gave the 1:1 adducts (**20a**,**b**) in 77.6–81.8% yield.[32a] Pb-promoted reaction of **1b** with oct-1-ene afforded **23b** in 86.2% yield. Treatment of **1a** with anisole in similar condition provided a mixture of *o*-, *m*-, *p*-isomer of **48b** in 55.5% yield.

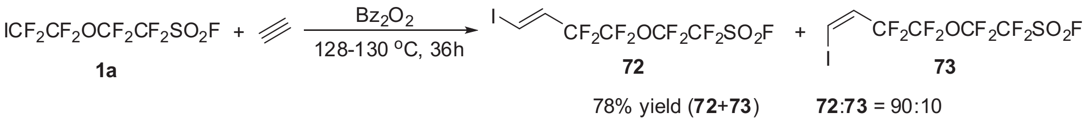
$Pb(OAc)_4$-initiated reactions were suppressed by excessive *p*-DNB.[32] When R_FI reacted with $Pb(OAc)_4$ or PbO_2 in the presence of diallyl ether, perfluoroalkylated tetrahydrofuran derivative was formed. These suggested a free radical chain mechanism involved in this reaction.



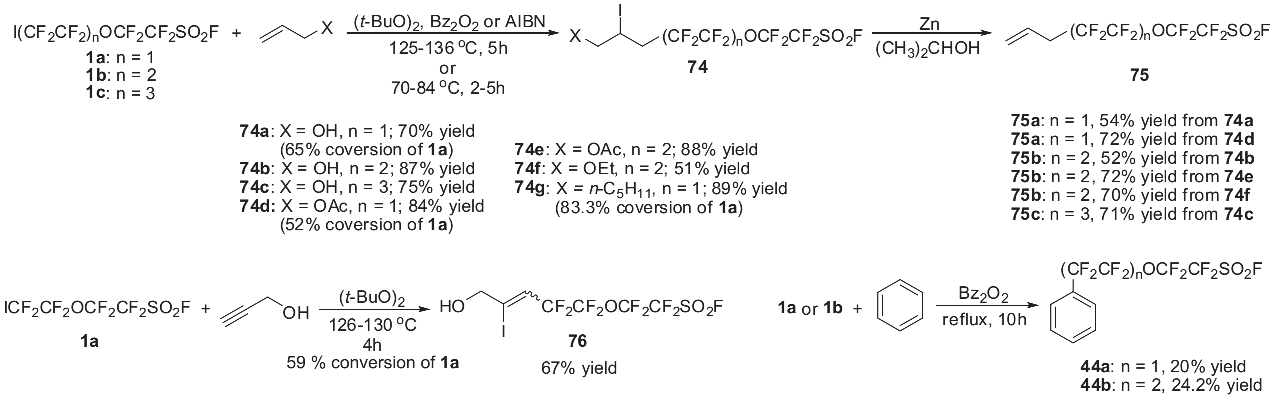
Scheme 26. Bz_2O_2-promoted radical addition of **1a** to ethylene at different temperature.



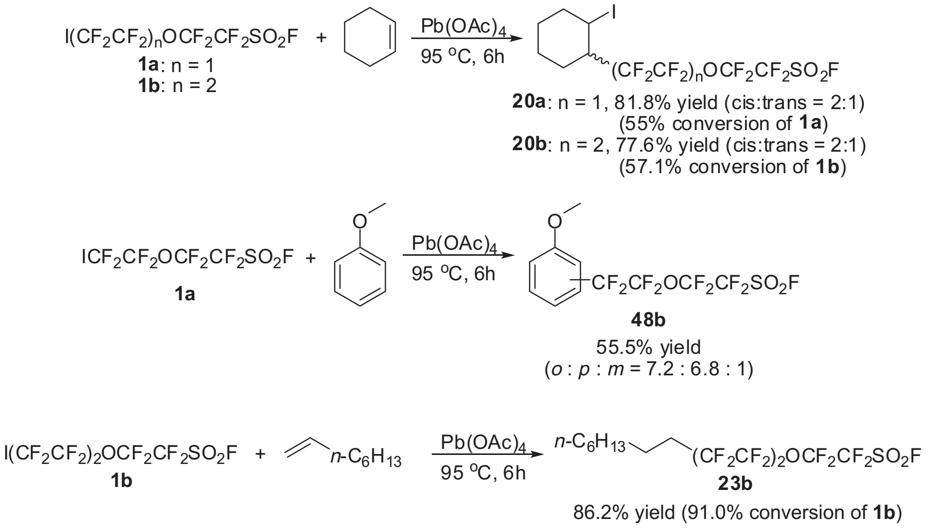
Scheme 27. Bz_2O_2-initiated radical addition of **1a** to allyl chloride.



Scheme 28. Bz_2O_2-promoted radical addition of **1a** to acetylene.



Scheme 29. Bz_2O_2-initiated reaction of **1** with allyl alcohol, allyl acetate, oct-2-en-1-ol, prop-2-yn-1-ol and benzene.

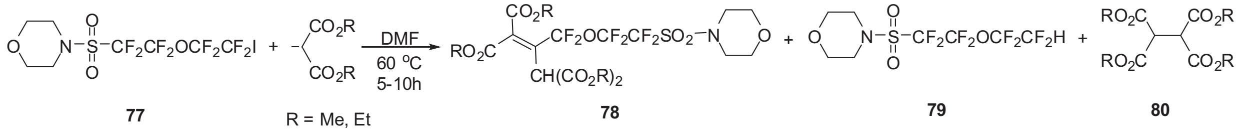


Scheme 30. Pb(IV)-mediated perfluoroalkylation of alkenes and arenes with **1a**,**b**.

2.4. Nucleophiles as SET agents to initiate the cleavage of the C–I bonds of $I(CF_2CF_2)_nOCF_2CF_2SO_2F$ and its derivatives

Poly- or per-fluoroalkyl iodides R_FX (including **1** and their derivatives) are initiated by C-, N-, P- or S-nucleophiles. The reaction of C-, N-, P- or S-nucleophiles with R_FX in the presence of alkenes provide the poly- or per-fluoroalkylated products through a single electron transfer mechanism. Treatment of R_FX with MNO_2, $NaCH_2NO_2$, $MeCHNaNO_2$, Me_2CNaNO_2 or $Na_2S_2O_4$ in the presence of 2-methyl-2-nitrosoptopane affords *t*-butyl nitroxides *t*-BuN(O$^{\bullet}$)R_F, which is readily determined by EPR.[33] In these reactions, nucleophiles are used as electron transfer agents to convert R_FX to $R_F^{\bullet}$ for further transformations.

2.4.1. C-nucleophiles as SET agents. The iodide atoms of R_FI cannot be displaced through a S_N1 or S_N2 mechanism due to the shielding of the carbon center by the surrounding lone pair electrons of fluorine. However, they are able to undergo nucleophilic substitutions via $S_{RN}1$ radical-chain processes.[34] These are ascribed to the good electron accepting ability of R_FI on the one hand, and suitable electron donors on the other hand. Malonate ester anion is a good $S_{RN}1$ donor for various *p*-nitrobenzyl derivatives and α-haloketones.[35] Inspired by these, the reactions between R_FI and malonate were investigated.[36] The reaction of R_FI with diethyl or dimethyl methylmalonate anion gave the substitution-elimination products (**81**), 1-*H*-perfluoroalkanes (**82**) and dimers of the anion (**80**), rather than the desired perfluoroalkylated products (Scheme 31).[36] Similarly, a sulfonamide derivative of **1a** (**77**) reacting with sodium malonates in DMF at 60 °C for 10 h provided **78** and **79** accompanied by a small amount of **80**.



Scheme 31. The reaction of malonate ester anion with a sulfonyl group-protected derivative of **1a**.

The conversion of R_FI was strongly dependent upon the ratio of reactants.[36] The yields, however, changed only slightly, being 45–60% for substitution-elimination products, 30–45% for 1-*H*-perfluoroalkanes. The dimers of the anion (~4%) were observed only when the ratio of R_FI to malonates was low. The reaction occurred under ambient laboratory light, and was accelerated by irradiation. The presence of the single electron transfer (SET) scavenger, *p*-DNB, partly suppressed the reaction. All these results indicated that the reaction of R_FI with malonate included but was not limited to a $S_{RN}1$ mechanism.

At the beginning, a normal radical-chain process, initiated by SET from malonate anion to R_FI, was involved, leading to the desired perfluoroalkylated product (**83**) (Scheme 32).[36] However, **83** could not be isolated because under the reaction conditions it readily eliminated F^- to give olefin (**84**). Intermediate **84** was then attacked by another molecule of malonate to provide **81**. Due to the higher acidity, dialkyl malonate **81** was always formed. The formation of **80**, was undoubtedly, a good indication for the intermediacy of malonate radical. In order to further elucidate the initial $S_{RN}1$ mechanism, diallyl ether (DAE) was employed as a radical trap in this reaction (Scheme 33).[36] Results showed that the reaction of R_FI with malonate in the presence of DAE gave cyclic products **85** and **86** instead of **81** and **82**.

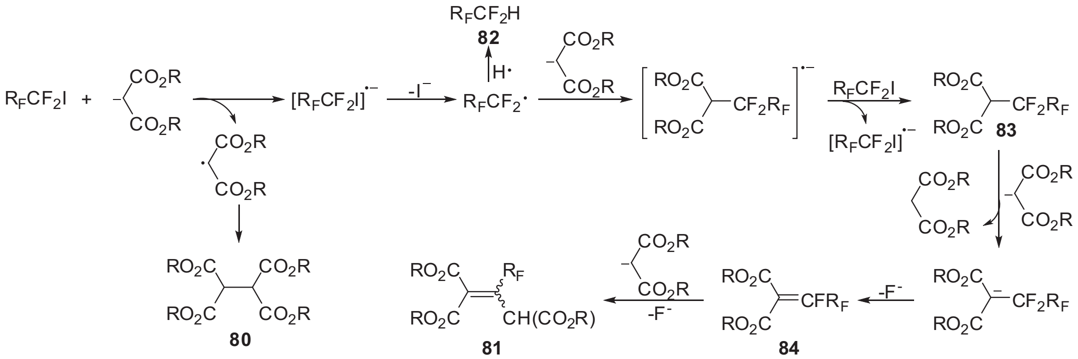
Except malonate, fluoroalkyl captodative compounds can induce the reaction of R_FI (beyond derivatives of **1**) with alkenes, which affords the corresponding perfluoroalkylated products in good yields.[37]

2.4.2. The interaction between R_FI and N- or O-nucleophiles. Per(poly)fluoroalkyl halides (R_FX), unlike the alkyl halides, reacting with tertiary amines does not form quaternary ammonium salts. Instead, the reaction provides 1:l acceptor/donor adducts (**87**) via halogen bonding.[38] Halogen bonding describes the tendency of halogen atoms of R_FX to interact with lone pair possessing atoms, which drives the intermolecular self-assembly of hydrocarbons and perfluorocarbons and weakens the C–X bond of R_FX. The fluorine resonances of the CF_2I groups in acceptor/donor adducts provide evidence for this interaction, wherein the signals of CF_2I are markedly shifted upfield compared to those in net R_FI.[38i]

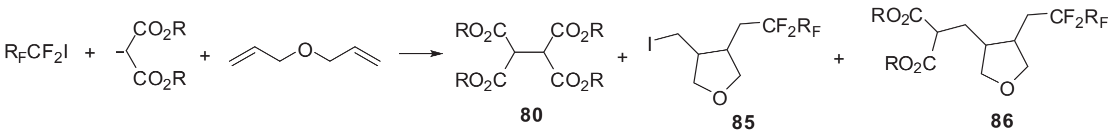
With this special interaction, nickel-, palladium-, and platinum-catalyzed reactions of R_FX with tertiary amines were studied.[39] UV-initiated reactions of R_FCF_2I with Et_3N and O_2 in methanol was investigated (see Section 2.3.2).[29]

Oxygen is a weaker electron donor in halogen bond than nitrogen. Even so, two different types of interactions between α,ω-diiodoperfluoroalkane and oxygen were observed.[40] The oxygen of hexamethylphosphoramide (HMPA) was a good electron donor, which formed two electron donor–acceptor bonds to halogens.

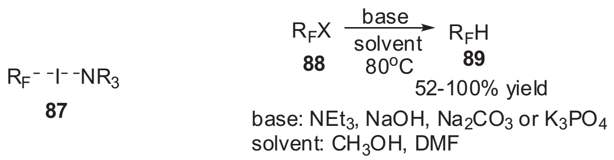
The hydrodehalogenation of per(poly)fluoroalkyl halides (R_FX, X=Br, I) with N- and O-nucleophiles was developed, which gave the corresponding hydrogenolysis products in moderate to high yields (Scheme 34).[41] In this reaction, the halogen bond formed between X and N or O plays the key role to cleave the C–X bond of R_FX, including the C–I bond of $ICF_2CF_2OCF_2CF_2SO_2NH_2$ (**88a**).



Scheme 32. Proposed mechanism for the reaction of malonate ester anion with perfluoroalkyl iodides.



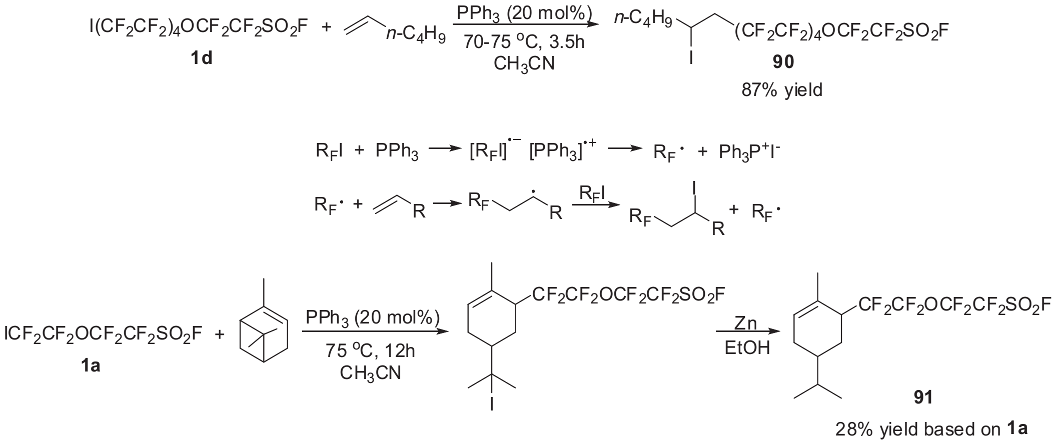
Scheme 33. The reaction of R_FCF_2I with diallyl ether in the presence of malonate ester anion.



Scheme 34. Hydrodehalogenation of per(poly)fluoroalkyl halides (R_FX, X=Br, I) with N- and O-nucleophiles.

Moreover, some of the *N*-nucleophiles, e.g., NH_2OH, initiated the addition of R_FI to alkenes.[42] Using $HNEt_2$ or NEt_3 as initiator, the reaction became complicated and R_FH was formed.

2.4.3. P-nucleophiles as SET agents. The addition reaction of **1** to alkenes can be initiated by thermolysis, photolysis, radical initiators, metals and metal complexes, sodium dithionate, and related reagents, C-nucleophiles, and triethyl borane. Further investigations shows that organophosphines (PR_3) can also induce the addition of **1** to alkenes.[42] The reaction of **1d** with hex-1-ene in the presence of catalytic amounts of PPh_3 provided 1:1 adduct **90** in 87% yield (Scheme 35). By prolonging the reaction time, this reaction was applied to nonterminal alkenes. **1a** reacting with α-pinene gave rearrangement product, which was further reduced by Zn/EtOH to afford **91**.



Scheme 35. Organophosphine-initiated reaction of **1** with alkenes.

Moreover, the reaction of R_FI with diallyl ether and PPh_3 (20 mol %) provided tetrahydrofuran derivatives. In the presence of 0.1 equiv of hydroquinone, the reaction of R_FI with pinene was completely suppressed. These results indicate a PPh_3-initiated free radical chain mechanism (Scheme 35).

The solvents have influence on the reaction. CH_3CN seems to be the most suitable solvent, since in DMF and THF, the reaction was very slow and R_FH was inevitably formed. Other trivalent phosphines, such as $P(OEt)_3$ and PBu_3 were successfully used to induce the addition of R_FI to alkenes. When $P(NEt_2)_3$ was employed, however, the reaction gave mainly the hydrodehalogenation product (R_FH). This might be caused by the highly reductive ability of $P(NEt_2)_3$. By the way, $AsPh_3$ also initiated the addition reaction, but the reaction proceeded very slowly.

2.4.4. S-nucleophiles as SET agents. Perfluoroalkyl iodides (R_FI) react with aromatic and aliphatic thiols in liquid ammonia or DMF with or without UV irradiation via a $S_{RN}1$ process.[34a–c] This is appropriate for the sulfonic acid derivatives of **1a**. The reaction of **92a** with sodium benzenethiolate (PhSNa) provided the $S_{RN}1$-type perfluoroalkylated product **93** in 76.9% yield (Scheme 36).[43] This reaction was partly suppressed by *p*-DNB. $BrCF_2CF_2OCF_2CF_2SO_2NEt_2$ (**92b**) reacting with PhSNa at 80 °C for 4 h gave lower yield of **93** (46.9% yield). Replacement of **92a** or **92b** with $HCF_2CF_2OCF_2CF_2SO_2NEt_2$ (**92c**) and $ClCF_2CF_2OCF_2CF_2SO_2NEt_2$ (**92d**), no reaction happened, even with highly excessive PhSNa.

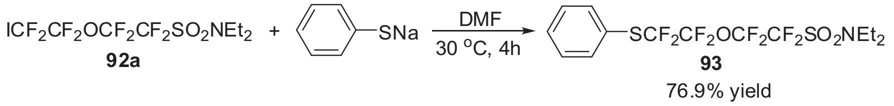
In addition, the analogues of **1a**, $Cl_2CYCF_2OCF_2CF_2SO_2NEt_2$ (Y=Cl, F), reacting with PhSNa afforded a mixture of $PhSCF_2CYClH$, $PhSCF_2CYCl_2$, $(PhS)_2C{=}C(SPh)_2$ and $PhSCOCF_2SO_2NEt_2$, which indicated an anionic chain process accompanied by the cleavage of the C–O bond (Scheme 37).[43]

2.5. The cleavage of the C–I bond of $ICF_2CF_2OCF_2CF_2SO_2F$ by oleum

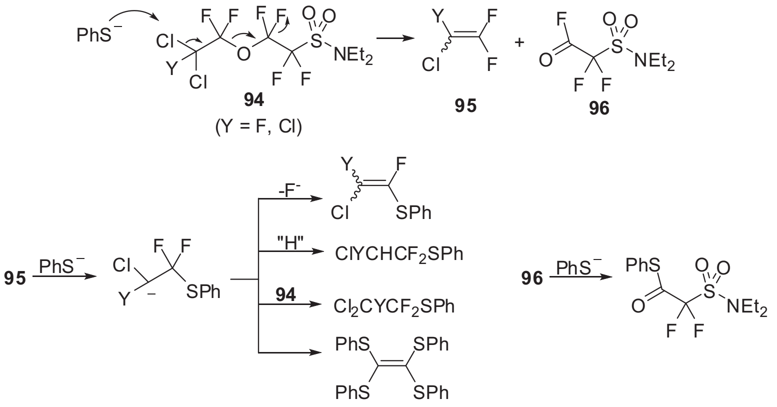
Oleum can initiate the cleavage of the C–I bond of **1a**. The reaction of **1a** with 50% oleum at 100 °C for 25 h gave perfluoroalkyl acyl fluoride **97** in 51.8% yield (Scheme 38).[44] Compound **97** is a useful building block, which has derived many interesting products. Hydrolysis of **97** at 0 °C for 4 h provided fluorosulfonylperfluoroalkanoic acid **98** (in 79.7% yield). Treatment of **97** with alcohols at reflux for 3 h afforded carboxylic esters **100** in 55–82% yields. When R^1ONa was employed instead of alcohols, both acyl and sulfonyl groups of **97** were transformed, leading to **101**. The reaction of **97** with KF gave $[FSO_2CF_2CF_2OCF_2CF_2O]^-$, which was further treated with alkyl halides to yield ethers **102**. Moreover, the reactions between **97** and arenes in the presence of anhydrous $AlCl_3$ provided Friedel–Crafts acylation products (**103**) in good yields.

The concentration of oleum affected the formation of **97**. Results showed that when **1a** reacted with 26% oleum at 70 °C for 7 days, the carboxylic acid (**104**) was formed instead of the desired **97**.[45a] In order to obtain **97** in this case, **104** was converted to **105** by $SOCl_2$ with DMF as a catalyst. The resulting mixture, after distillation, was then treated with SbF_3 in the presence of Cl_2 to give **97** in 95% yield (based on **104**).

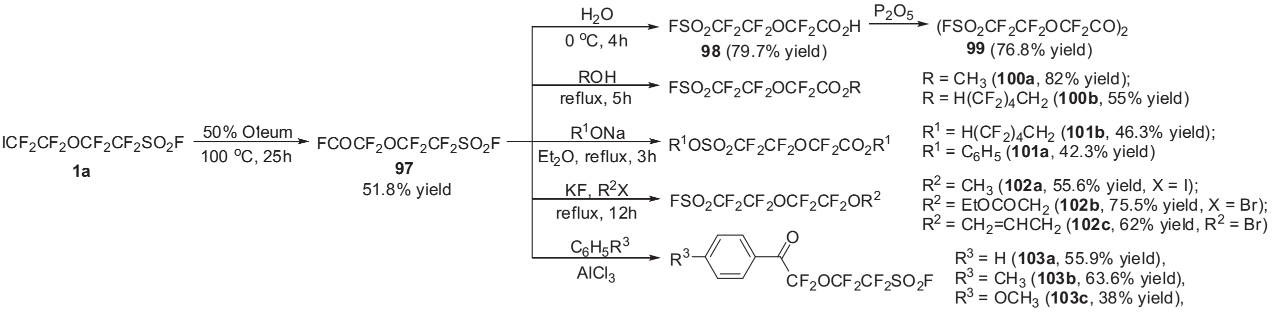
Significantly, the important monomer, perfluoroethanesulfonyl fluoride vinyl ether (**108**), was derived from **97** (Scheme 39).[45a] As part of a program for the development of new fuel cell membranes, the synthesis of **108** was of great interest.[45] There were routes to prepare **108**.[45a] In the first approach, acyl fluoride **97** was transformed to hypofluorite **106** by direct fluorination with F_2 in the presence of CsF. Hypofluorite **106** was then treated with 1,2-dichlorodifluoroethylene at −60 °C to form the ether intermediate



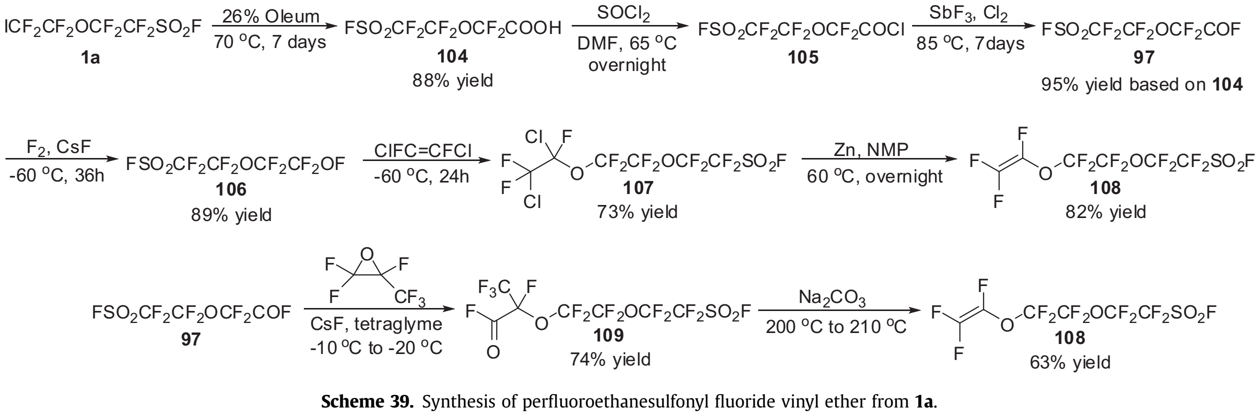
Scheme 36. The $S_{RN}1$ reaction of the sulfonamide derivative of **1a** with aromatic thiols.



Scheme 37. Proposed mechanism for the reaction of **94** with aromatic thiols.



Scheme 38. Synthesis of **97** from **1a** and its useful transformations.



Scheme 39. Synthesis of perfluoroethanesulfonyl fluoride vinyl ether from **1a**.

107, which was dechlorinated with zinc in NMP to finally afford **108** in 82% yield. In the second synthetic route, **97** was mixed with hexafluoropropylene oxide (HFPO) in a solvent with CsF as a catalyst to form **109**. Compound **109** reacted with Na_2CO_3, followed by pyrolysis, to afford the desired **108**. It should be mentioned that compound **106** would undergo explosive decomposition at 22 °C. Special attentions must be made when working on it.

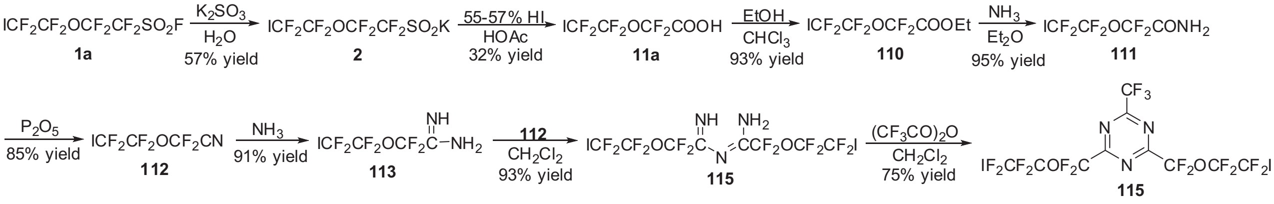
3. Transformation of the sulfonyl group of $X(CF_2CF_2)_nOCF_2CF_2SO_2F$ and its applications in ranging from drug design to material synthesis

$I(CF_2CF_2)_nOCF_2CF_2SO_2F$ have showed rich chemistry in the transformation of their C–I bonds. With the presence of sulfonyl group, $I(CF_2CF_2)_nOCF_2CF_2SO_2F$ are further functionalized by K_2SO_3, KOH (or NaOH), alcohols, and amines to provide the respective perfluoroalkanesulfite, perfluoroalkanesulfonic acid salts, perfluoroalkanesulfonic acid esters, and fluoroalkanesulfonamides. Other $X(CF_2CF_2)_nOCF_2CF_2SO_2F$ (X=Br, Cl) are also active in these transformations. It is remarkable that the conversion of the C–X bonds and the functionalization of the SO_2F groups can be carried out in tandem for the purpose of preparing highly fluorinated compounds with intriguing properties. In this section, we will summarize these 'joint transformations' and highlight their contributions in modern synthesis.

Moreover, per(poly)fluoroalkanesulfonyl fluorides ($R_FCF_2SO_2F$, e.g., **22b**, **55a**, **59a**,**b**, **185b**) reacting with CoF_3 affords perfluoroalkanes (R_FCF_3) by releasing equal equivalent of SO_2, which deactivates the molecule.[4e] This is the first report for the fluorination of the SO_2F groups in $R_FCF_2SO_2F$.

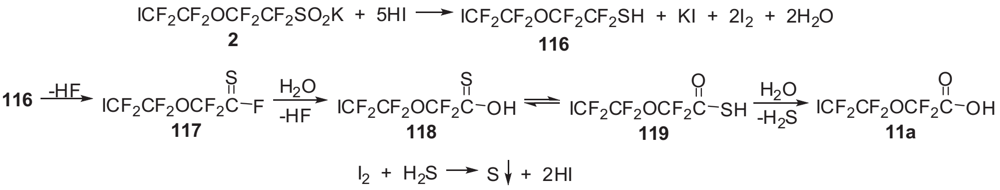
3.1. Reduction of the sulfonyl group of $ICF_2CF_2OCF_2CF_2SO_2F$ under sulfinatodehalogenation conditions and its application in triazine derivative synthesis

The sulfonyl group of **1a** can be reduced under sulfinatodehalogenation conditions (see Section 2.1.1).[5a,46] The reaction of **1a** with K_2SO_3 in aqueous solution selectively gave **2**. Using **2** as starting material, a novel triazine monomer, 2-trifluoromethyl-4,6-bis(4′-iodo-2′-oxa-hexafluorobutyl)-1,3,5-triazine (**115**), was synthesized (Scheme 40).[46]



Scheme 40. Synthesis of novel fluorine-containing triazine monomer from **1a**.

A possible redox-hydrolysis mechanism for the transformation of **2** to its corresponding acid (**11a**) by HI was described in Scheme 41. Byproducts, like HF, H_2S, I_2, and sulfur formed in the reaction, were thought to be the strong evidence for this process.



Scheme 41. A possible mechanism for the transformation of **2** to **11a**.

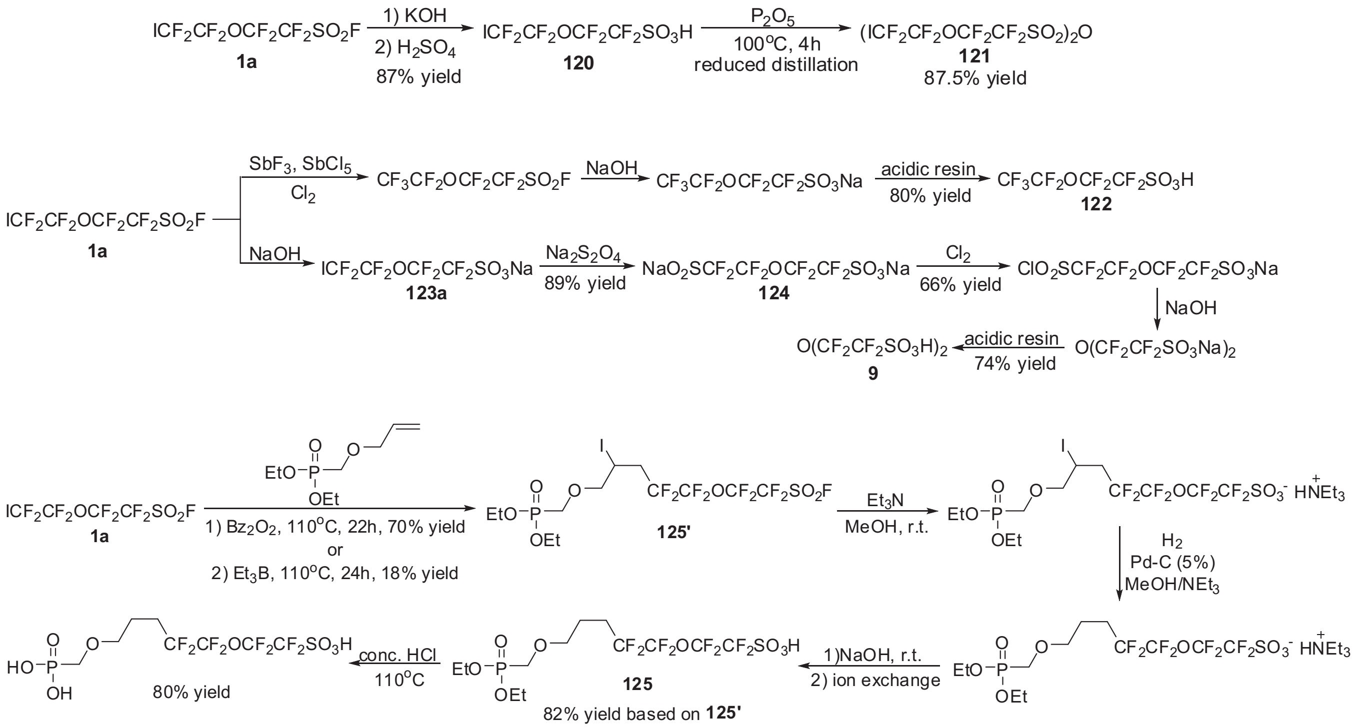
3.2. Synthesis of functional sulfonic acids and their salts from $I(CF_2CF_2)_nOCF_2CF_2SO_2F$ by conversion of both of the sulfonyl and iodo group

3.2.1. Synthesis and application of 5-iodo-3-oxa-perfluoropentanesulfonic acid and its derivatives. 5-Iodo-3-oxa-perfluoropentanesulfonic acid (**120**) was prepared in the reaction of **1a** with KOH followed by acidification with concentrated H_2SO_4 (Scheme 42).[44] Dehydration of **120** by P_2O_5 provided the corresponding anhydride **121**. $CF_3CF_2OCF_2CF_2SO_3H$ (**122**) was synthesized similarly, wherein **1a** was first fluorinated by Swarts reaction, then subjected to basic hydrolysis and distilled from H_2SO_4 (Scheme 42).[47a] Disulfonic acid $HO_3SCF_2CF_2OCF_2CF_2SO_3H$ (**9**) was derived from **1a** as well (Scheme 42). The most crucial step for **9** was the conversion of $ICF_2CF_2OCF_2CF_2SO_3Na$ (**123a**) to $NaO_2SCF_2CF_2OCF_2CF_2SO_3Na$ (**124**). This step was finally accomplished by classical sulfinatodehalogenation reaction, which gave **124** in 89% yield. Basic hydrolysis of other 1,1,2,2-tetrafluoro-2-(polyfluoroalkoxy)ethanesulfonyl fluorides (e.g., **125′**) also gave the corresponding polyfluoroalkylsulfonic acids (e.g., **125**) by passing the aqueous solution through a strongly acidic resin.[47a–b] **120**, **122**, and **9** as well as the polyfluoroalkylsulfonic acids are classified as a kind of very useful 'supper acids'.

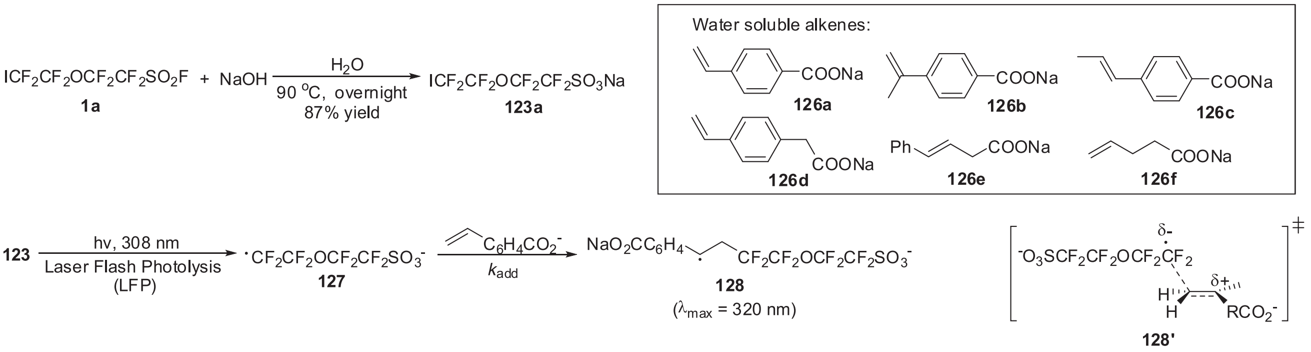
Sodium 5-iodo-3-oxa-perfluoropentanesulfonate (**123a**), generated from the alkaline hydrolysis of **1a**, was initiated by *hν* to form $[^{\bullet}CF_2CF_2OCF_2CF_2SO_3]^-$ (**127**) (Scheme 43). Absolute rate constants of $[^{\bullet}CF_2CF_2OCF_2CF_2SO_3]^-$ radical addition to a series of water-soluble alkenes bearing carboxylate ion functionality in aqueous solution were measured by laser flash photolysis (LFP) experiments (Table 3).[48] Thermodynamic, polar, and steric effects were all observed to be important factors in determining the dynamics of these addition reactions. With comparison of the relative rates for the series with a similar series in F113, it was apparent that steric and thermodynamic factors were similar and essentially independent on the nature of the solvents (Table 4). The rate constants for the series in water were all considerably larger than those of their counterparts in F113, with rate factors of 3–9 fold being observed, despite the expected retardation of the additions by Coulombic repulsion. These rate enhancements most probably derived from more effective stabilization of the polar transition state (**128′**) for addition of the electrophilic perfluoroalkyl radical to alkenes by the polar solvent, water, than by the nonpolar organic solvent, F113.

3.2.2. Polyfluoroalkanesulfonic acids and their derivatives from $I(CF_2CF_2)_nOCF_2CF_2SO_2F$ utilized as Bronsted or Lewis acid catalysts. Polyfluoroalkanesulfonic acids and their derivatives are used as Bronsted or Lewis acid catalysts.[49–53] 5-*H*-3-Oxa-perfluoropentanesulfonic acid (**130**), prepared from **1a** by hydrodehalogenation of the C–I bond and subsequent hydrolysis of the sulfonyl group, effectively catalyzed the reaction of citric acid with *n*-butanol or with *n*-butanol and acetic anhydride, which provided the environmental friendly plasticizer TBC (**131**) or ATBC (**132**) in high yield (Scheme 44).[49] The catalyst loading was very low in this process, and **130** could be recycled.

A versatile reagent, $(HO)_3Si(CH_2)_3(CF_2)_2O(CF_2)_2SO_3K$ (**134**), derived from **1a**, was surface attached to produce a series of strong



Scheme 42. Synthesis of 3-oxa-per(poly)fluoropentanesulfonic acids from **1a**.



Scheme 43. The radical reaction of **123a** with water-soluble alkenes under UV.

Table 3
Absolute rate constants for the addition of **127** to six alkene substrate at 295 K in H_2O, Measured by LFP

Entry	Alkenes	$k_{add}/10^7$ M^{-1} s^{-1}	Rel k_{add}
1	**126a**	23.2±0.16	1
2	**126b**	55.3±0.25	2.38
3	**126c**	3.31±0.28	0.143
4	**126d**	20.2±0.13	0.871
5	**126e**	1.88±0.11	0.081
6	**126f**	2.08±0.26	0.090

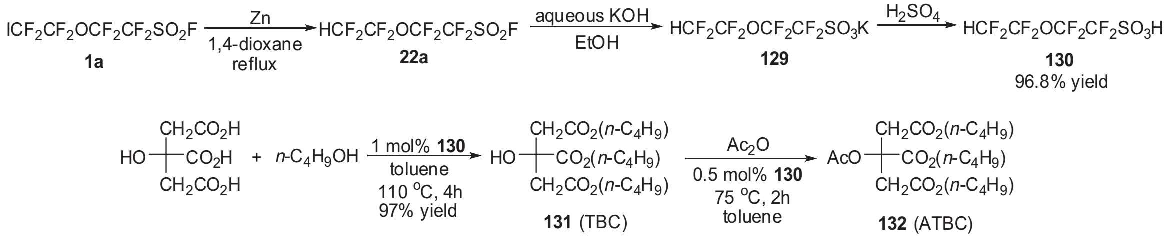
Table 4
Comparison of the rate constants for fluorinated radicals to alkenes in F113 versus H_2O

Similar group of olefins to **126**	k_{rel} (F113)[a]	Alkenes	k_{rel} (H_2O)[a]	$k(H_2O)/k(F113)$[b]
$CH_2{=}CHC_6H_5$	(1)	**126a**	(1)	5.4
$CH_2{=}C(CH_3)C_6H_5$	1.9	**126b**	2.4	7.1
$CH_3CH{=}CHC_6H_5$	0.088	**126c**	0.14	8.7
		126e	0.081	5.0
$CH_2{=}CHC_6H_4(p\text{-}CH_3)$	1.3	**126d**	0.87	4.7
$CH_2{=}CHCH_2CH_2CH_3$	0.14	**126f**	0.090	3.4

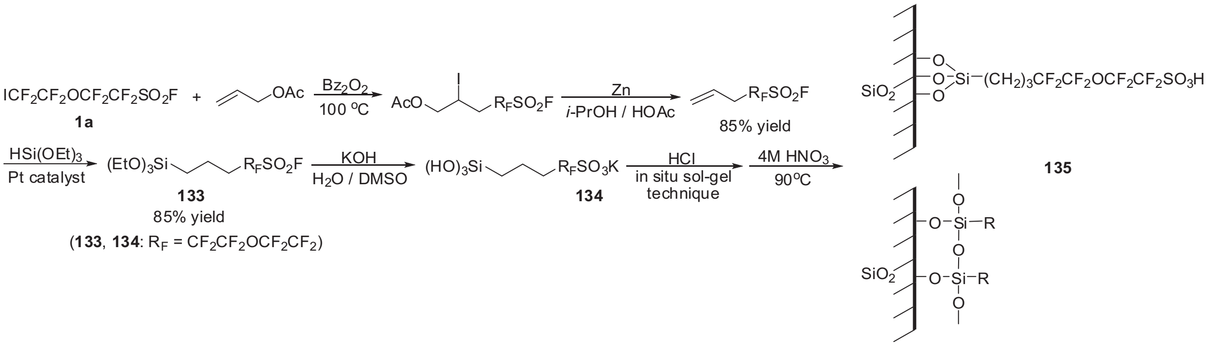
[a] Relative rate constants. The observed trend [$k_{rel}(H_2O)$] in reactivities for the series **126a–f** in water bore a marked similarity to the trend [k_{rel}(F113)] of reactivities of the n-$C_3F_7^{\bullet}$ radical in its additions to a similar group of olefins in F113.
[b] Absolute rate constants. The rate constants of **126a–f** in water were all significantly larger than the rate constants of the most closely analogous alkenes in F113.

solid acid catalyst (Scheme 45).[50] The synthesis of **134** has been achieved via the hydrosilylation of $CH_2{=}CHCH_2(CF_2)_2O(CF_2)_2SO_2F$ with $HSi(OEt)_3$ and hydrolysis of **133** with KOH in aqueous DMSO.[50] Solid acid catalysts (**135**) from **134** were made by the surface modification and attachment to an existing support, or, alternatively, were synthesized using an in situ sol–gel technique. These acid functionalities were stable on the surface and showed good activities for a range of acid catalyzed reactions, for example, electrophilic aromatic alkylations, alkene isomerizations and Friedel–Crafts acylations. In many cases, the activity of these materials (based upon acid equivalents), compared to Amberlyst resins, were orders of magnitude higher, which reflected the increased acid strength due to the perfluoroalkyl group.

Perfluoroalkanesulfonic acid functionalized periodic mesostructured organosilica (**137**) with surface areas up to 500 m^2/g and

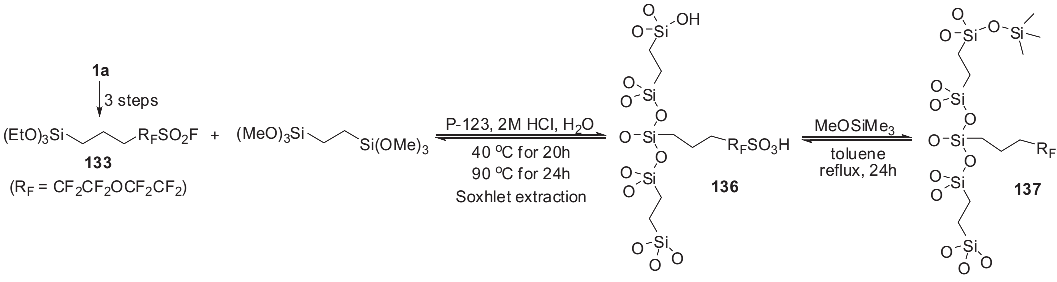


Scheme 44. Synthesis of environmental friendly plasticizers catalyzed by **130**.



Scheme 45. Surface attached perfluoroalkanesulfonic acid derived from **1a**.

pore size distribution around 4.1 nm was synthesized in one-pot by using 1,2-bis(trimethoxysilyl)ethane (BTME) as framework precursor, perfluorinated sulfonic acid silane (PTSE, **133**) as acidic function source and Pluronic P-123 as surfactant under acidic conditions (Scheme 46).[51] In this case, the key starting material **133** was prepared from **1a** in the same route with Scheme 45. These solid acid catalysts (**137**) showed high thermal stability (up to 350 °C), acid site density (up to 0.40 mmol H^+/g) and RT proton conductivity (up to 1.3×10^{-2} S/cm), which exhibited a high catalytic activity in self-condensation of heptanal.



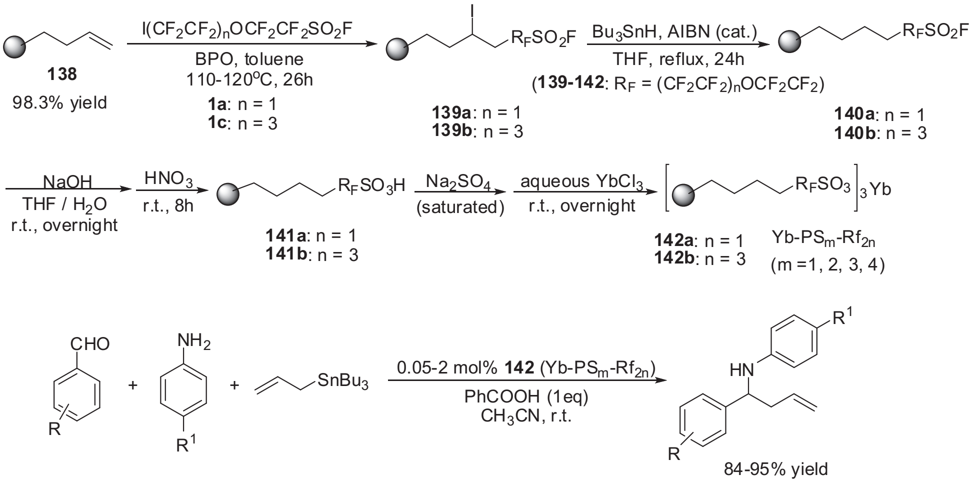
Scheme 46. Synthesis of PMO acid catalyst from **1a**.

Polymer-bound polyfluoroalkyl super Brönsted acids and their ytterbium salts were synthesized from **1a** and **1c** (Scheme 47).[52] Initially, the addition reaction of **1a** or **1c** with Merrifield resin allyl-PS_m **138** under classical sulfinatodehalogenation conditions failed even with longer reaction time. Poor swelling of the Merrifield resin in the aqueous solvent might account for this result. Then Bz_2O_2-initiated radical addition was employed. Bz_2O_2 dissolved in CH_2Cl_2, THF and toluene, which swelled the Merrifield resin well, and successfully provided **139**. Reduction of **139** by Bu_3SnH in the presence of catalytic amount of AIBN in THF under reflux gave **140** with comparable loading of F and S. Alkaline hydrolysis of **140** with aqueous NaOH solution in THF followed by acidification with HNO_3 afforded **141**. Subsequently, **141** was dispersed in saturated Na_2SO_4 solution with several drops of THF to exchange all of the H^+ in **141**. The filtrate was washed till neutral, then re-dispersed in $YbCl_3$ solution and stirred overnight, leading to **142**. The polymer-bound-Yb salts **142**, behaving as Lewis acids, could catalyze the three-component coupling reaction of benzaldehyde, aniline, and tributylallylstannane in the presence of 1 equiv of benzoic acid at room temperature. These heterogeneous catalysts were highly efficient, recyclable, and reusable.

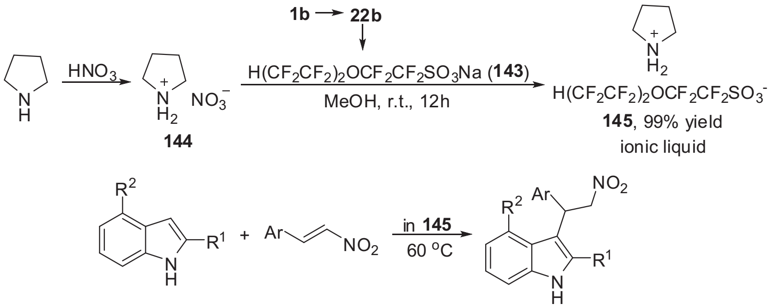
Moreover, ionic liquid **145** with a 1,1,2,2-tetrafluoro-2-(1,1,2,2,3,3,4,4-octafluorobutoxy)ethanesulfonate anion was synthesized from **143**.[53] The key **143** was prepared by hydrolysis of **22b** with aqueous NaOH. **145** was a highly fluid at room temperature. It was used both as a recyclable solvent and as an efficient catalyst for Friedel–Crafts alkylations of indoles with nitroalkenes (Scheme 48).

3.2.3. Per(poly)fluoroalkanesulfonic acid salts from $I(CF_2CF_2)_nOCF_2CF_2SO_2F$ as photoacid generators.

Photoacid generators (PAGs) are photosensitive molecules, which release protons upon exposure to irradiation.[54a] Due to the fast and well-controlled in situ generation of acid catalysts, PAGs have been widely used in the fields of coatings, adhesives, and photoresists.[54b–d] They are also of great interest for applications including photo-directed oligonucleotide synthesis, two-photon three-dimensional microfabrication, organic electronics patterning, and mesoporous silica film patterning.[54e–h] Till now, there have been several classes of PAGs including onium salts, sulfonate esters, and organohalides developed.[54] Onium salts



Scheme 47. Synthesis of polystyrene-bound perfluoroalkyl sulfonic acids and their ytterbium salts from **1** and their applications in three-component coupling reactions.



Scheme 48. A novel ionic liquid (**145**) derived from **22b** as a recyclable medium and efficient catalyst.

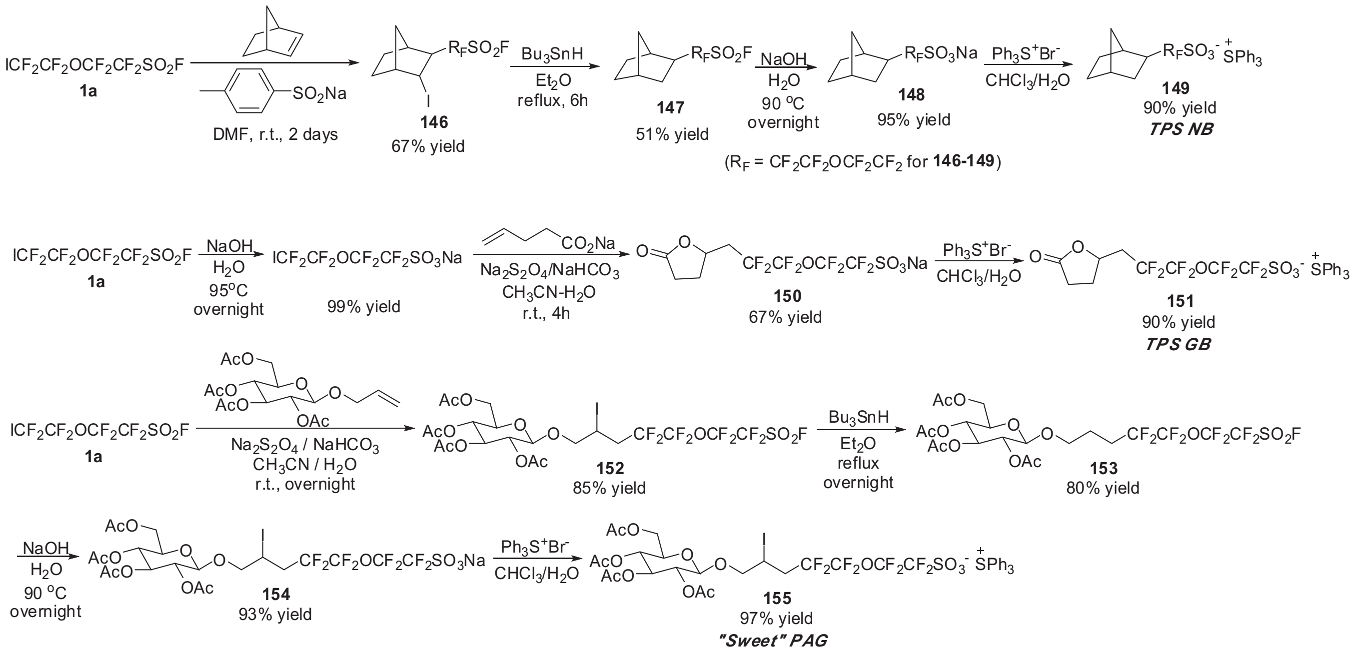
containing perfluoroalkyl sulfonate (PFAS) as anions are particularly attractive due to their high acid-generation efficiency and excellent thermal stability.[55] Among these salts, perfluorooctyl sulfonates (PFOS) were the most commonly used because the generated PFOS acid was strong, stable, and nonvolatile. However, many recent studies revealed that perfluorooctyl sulfonate and its PFOS-related materials were potentially environmentally hazardous. Their worldwide distribution, environmental persistence, and bio-accumulation potential have been concerned, which regulated and restricted their use in many applications. PFOS-based PAGs also had undesirable properties, for example, inhomogeneous distribution in polymer films due to self-aggregation of PFOS units, which resulted in nonuniform acid distribution after exposure and poor patterning performance. Therefore, it was necessary to look for alternatives with environmental compatibility and excellent performance.

Sulfonium salts derived from $ICF_2CF_2OCF_2CF_2SO_2F$ (**1a**) are promising alternatives for perfluorooctyl sulfonate (PFOS), which would probably solve the environmental problems (Scheme 49).[55] By utilizing simple and unique chemistries of **1a** mentioned above, alicyclic-group functionalized octafluoro-3-oxapentanesulfonate anions (**148**, **150**, and **154**) were prepared in high yield.[55] Triphenylsulfonium (TPS) salts of norbornyl and γ-butyrolactone groups functionalized octafluoro-3-oxapentanesulfonates (**149** and **151**) showed excellent thermal stability and good solubility in various polar solvents. Angle resolved X-ray photoelectron spectroscopy (XPS) analysis confirmed that these new TPS salts were uniformly distributed in polymer films, whereas triphenylsulfonium perfluorooctyl sulfonate (TPS-PFOS) was heavily segregated to a polymer film surface. Lithographic performance study showed that resist compositions containing **149** and **151** were capable of resolving sub-100 nm dense lines and spaces at both tested wavelengths. A specific TPS salt of monosaccharide-functionalized octafluoro-3-oxapentanesulfonate, a 'sweet' PAG (**155**), was also synthesized.[55] This PAG was capable of resolving 90 nm lines in 193 nm lithography. PAGs **149**, **151**, and **155** showed comparable performance with triphenylsulfonium perfluorobutyl sulfonate (TPS-PFBS) and better performance than TPS-PFOS, which made them very environmentally friendly candidates for high resolution lithography applications.[55]

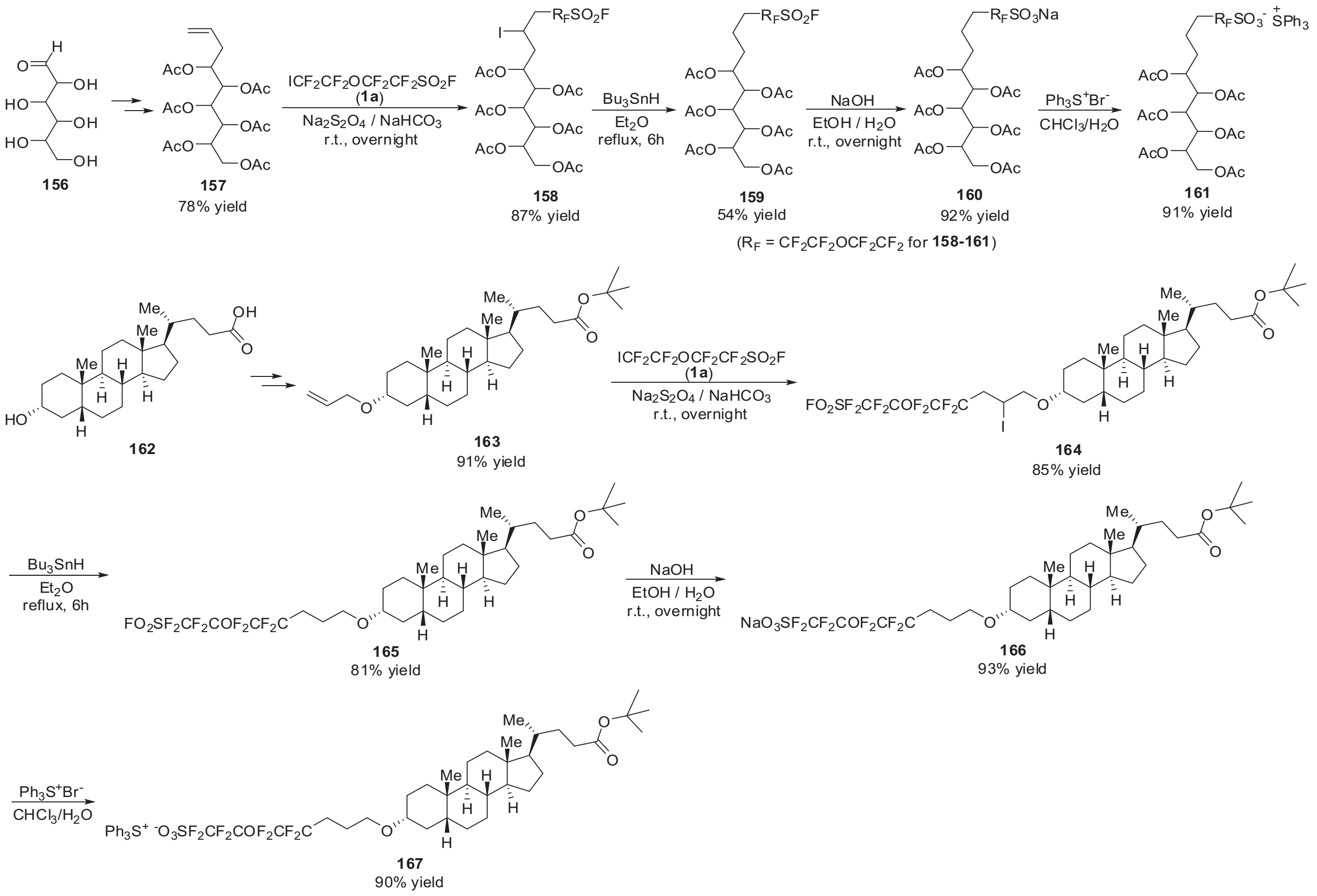
Triphenylsulfonium photoacid generators (TPS-PAGs, **161** and **167**) with fluorinated sulfonate anions containing glucose and other natural product groups were developed again from **1a** (Scheme 50).[56] Similar to **149**, **151**, and **155**, these TPS-PAGs were synthesized efficiently in high yield by transformation of both of the sulfonyl and iodo groups in **1a**. PAGs **161** and **167** were applied to pattern sub-100 nm features by using 254 nm and e-beam lithography. They are non-toxic and show susceptibility to chemical degradation and to microbial attack under aerobic/anaerobic conditions. Therefore, they are very attractive materials for high resolution photoresist applications and particularly useful in addressing the environmental concerns caused by PFOS and other perfluoroalkyl surfactants.

3.2.4. Synthesis of fluorinated surfactant, tetrapus molecule, and polymer electrolyte membranes from $I(CF_2CF_2)_nOCF_2CF_2SO_2F$ by transformation of both of the sulfonyl and iodo group.-

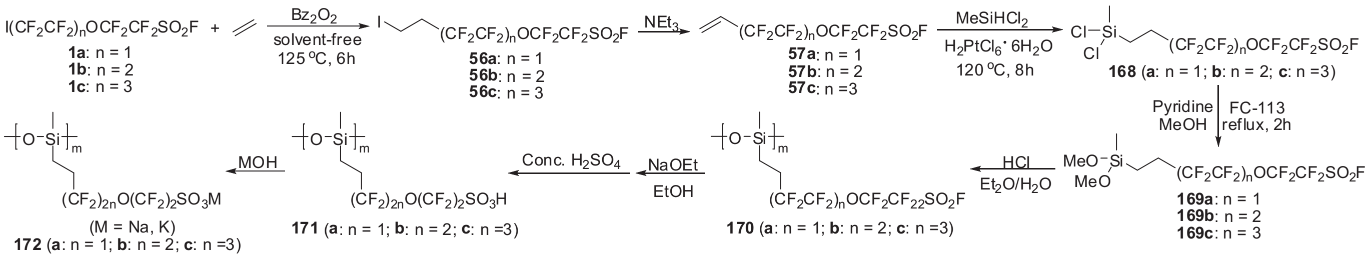
Polyfluoroalkanesulfonyl fluorides (**57a**–**c**), derived from the reaction of **1a**–**c** with ethylene followed by the elimination of HI, reacted with methyldichlorosilane in the presence of $H_2PtCl_6 \cdot 6H_2O$ providing **168a**–**c**, which underwent methanolysis to give the monomer **169a**–**c** (Scheme 51).[57] Treatment of **169** with hydrochloric acid in Et_2O/H_2O system afforded a self-polymerized



Scheme 49. Synthesis of photoacid generators from **1a** as environmentally friendly alternative candidates.



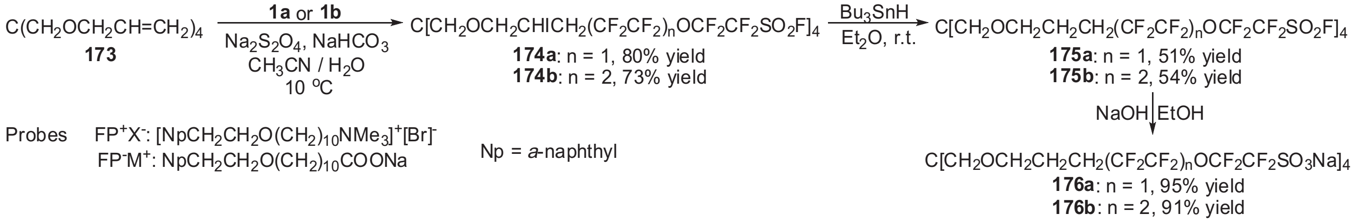
Scheme 50. Synthesis of the linear type ‘sweet’ PAG and biocompatible PAG based on **1a** and natural compounds.



Scheme 51. Preparation of polymerized surfactants (**172**) from **1**.

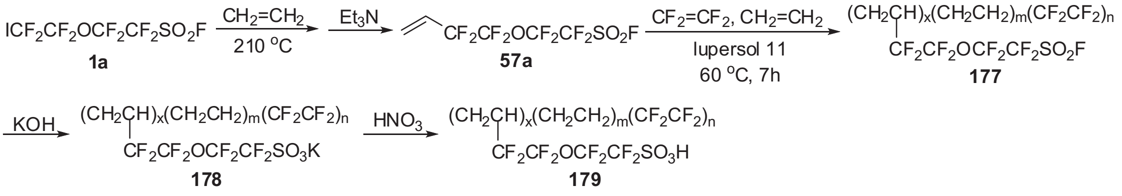
product (**170**). Upon hydrolysis, **170** could be converted to **172**. Polymer **172** is an excellent surfactant, which exhibits good surface activity in water.

An interesting tetrapus molecule (**176**) was synthesized from **1a** by $Na_2S_2O_4$-initiated radical addition of **1a** to **173**, hydrodehalogenation of **174** with Bu_3SnH and basic hydrolysis of **175** (Scheme 52).[58] Compound **176** possessed four fluorinated tentacles with anionic terminals. Cationic and anionic naphthalene fluorescence probes (FP^+ and FP^-) containing $-[CH_2CH_2O(CH_2)_{10}]-$ chain were used to study the host–guest interactions between the partners of the following pairs: FP^+X^- and **176**, FP^-M^+ and **176**. The results demonstrated that electrostatic attraction was a powerful factor in facilitating the host–guest interactions among them.



Scheme 52. Synthesis of fluorinated tetrapus molecules from **1**.

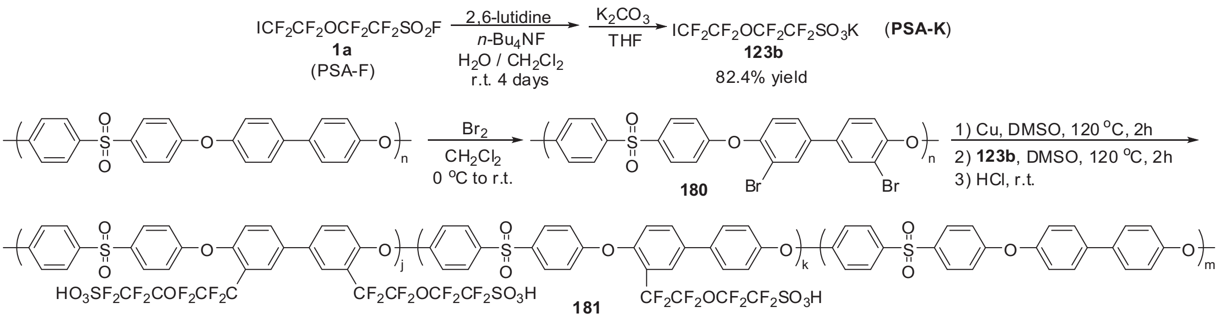
Copolymerization of tetrafluoroethylene and ethylene with **57a** in the presence of lupersol 11 at 60 °C for 7 h provided melt-processable terpolymers **177**, which could be readily hydrolyzed and acidified to afford membranes **179** (Scheme 53).[59] The key starting material (**57a**) was synthesized by the reaction of **1a** with ethylene under heat. Because of the simple polymerization process and the low monomer cost, **179** were produced cheaply. Membranes **179** exhibited excellent conductivity and stability. Their fuel-cell performance was comparable to, or slightly better than, that of Nafion, although it was still to be optimized.[59] The polymeric lithium salts of **179** also showed excellent lithium-ion conductivity. They are attractive candidates for lithium-battery applications.



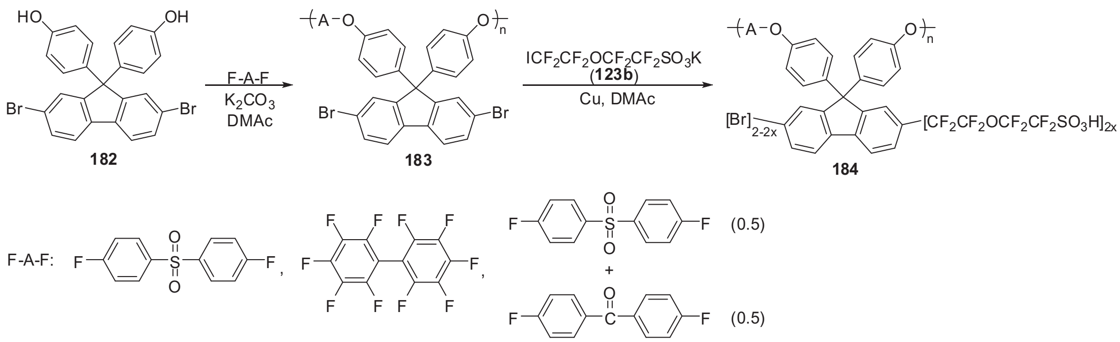
Scheme 53. Preparation of high-proton-conductive membranes from **1a** for fuel-cell applications.

$ICF_2CF_2OCF_2CF_2SO_2F$ (**1a**) was employed to prepare proton exchange membranes, which were investigated as polymer electrolyte membranes (PEMs) for polymer electrolyte membrane fuel cells (PEMFCs) (Scheme 54).[60,61] Polymers (**181**) with poly(arylene ether sulfone) in the main chain and $-CF_2CF_2OCF_2CF_2SO_3H$ in the side chain (PES–PSA) were synthesized by Cu-mediated cross-coupling of poly{oxy-4,40-(3,30-dibromobiphenylene)oxy-4,40-diphenylsulfone} (PES–Br, **180**) with **123b** (PSA–K), followed by treatment with aqueous HCl.[60] Potassium 1,1,2,2-tetrafluoro-2-(1,1,2,2-tetrafluoro-2-iodoethoxy)ethanesulfonate (**123b**) was readily derived from **1a**. The proton conductivity of membranes **181** with an ion-exchange capacity (IEC) of 1.58 mmol/g was 0.12 S/cm at 80 °C under 90% relative humidity. When **181** with an IEC of 1.34 mmol/g was used as the membrane for PEMFC, the maximum power output at 80 °C was 805 mW/cm^2 if fully humidified hydrogen and air were provided. Moreover, the dynamic mechanical analysis measurement and the tensile test revealed that **181** had a higher α-relaxation temperature than Nafion and higher flexibility than sulfonated polyethersulfone (SPES).

Poly(arylene ether)s (**184**) containing ‘super acid’ groups (FSPEs) were synthesized from **1a** via Cu-mediated perfluoroalkylation of brominated poly(arylene ether)s (**183**) with **123b** (Scheme 55).[61] The key reagent (**123b**) was also prepared from **1a**. **184** are good proton conducting membranes for fuel cells. By solution casting, tough, flexible and transparent membranes with the ion-exchange capacity (IEC) ranging from 0.34 to 1.29 mequiv g^{-1} were formed. These FSPE membranes did not show obvious glass transition behavior up to the decomposition temperature (180 °C). Microscopic analyses revealed homogeneous and well-connected ionic clusters for the high IEC membrane. Compared to conventional sulfonated poly(arylene ether) membranes, the FSPE membranes exhibited much higher proton conductivity. The highest proton conductivity of 0.07 S/cm was achieved at 80 °C and 86% relative humidity (RH)



Scheme 54. Synthesis of aromatic polymers with pendant perfluoroalkyl sulfonic acids for fuel cell applications from **1a**.

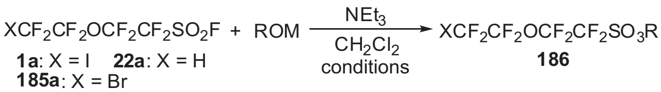


Scheme 55. Synthesis of perfluorosulfonated poly(arylene ether)s from **1a**.

with the IEC=1.29 mequiv g^{-1} membrane. A fuel cell using the FSPE membrane showed comparable performance to that of a Nafion cell at 78% RH and 80 °C.

3.3. Synthesis and applications of perfluoroalkanesulfonic acid esters generated from $X(CF_2CF_2)_nOCF_2CF_2SO_2F$

3.3.1. Synthesis of perfluoroalkanesulfonic acid esters from $ICF_2CF_2OCF_2CF_2SO_2F$ and its analogues. Perfluoroalkanesulfonic acid esters ($ICF_2CF_2OCF_2CF_2SO_3R$, **186a**–**c**) were synthesized from the reaction of **1a** with 2,2,3,3-tetrafluoropropan-1-ol, 2,2,3,3,4,4,5,5-octafluoropentan-1-ol and phenol in the presence of NEt_3 or aqueous KOH solution at ≤0 °C for several hours (Table 5).[62,63] The temperature and the nature of the nucleophiles have great influence on the reaction. When **1a** reacting with $H(CF_2)_2CH_2OH$ at reflux, no desired **186b** was obtained.[62] Treatment of **1a** with sodium pentafluorophenoxide and sodium 4′-clorotetrafluorophenoxide, the corresponding 5-iodo-3-oxaperfluoroalkanesulfonates (**186d**–**e**) were obtained (at 60–80 °C for 6 h) in the absence of NEt_3.[64] In addition, the reactions of **22a** and **185a** with more nucleophilic phenols, compared to fluorophenols, provided **186f**–**i** smoothly in NEt_3 at room temperature.[65]

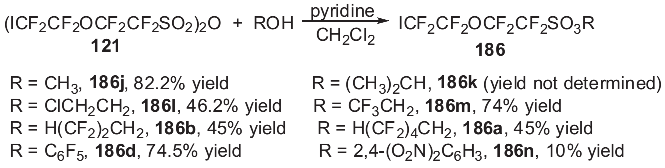


Anhydrides **121** derived from **1a** (Scheme 42) were used to prepare 5-iodo-3-oxaperfluoroalkanesulfonic acid esters. **121** reacted with alcohols in the presence of pyridine giving the corresponding esters **186a**–**b**, **186d**, and **186j**–**n** in moderate to good yield (Scheme 56).[44] Treatment of $XCF_2CF_2OCF_2CF_2SO_3H$ with P_2O_5 at 200 °C for 10 h, perfluoroalkyl 5-substituted-3-oxaperfluoroalkanesulfonic acid esters (**186o**–**q**) were synthesized (Scheme 57).[66] These esters are interesting starting materials for the extensive investigation of the nucleophilic reactions of perfluoroalkanesulfonates.[62–66]

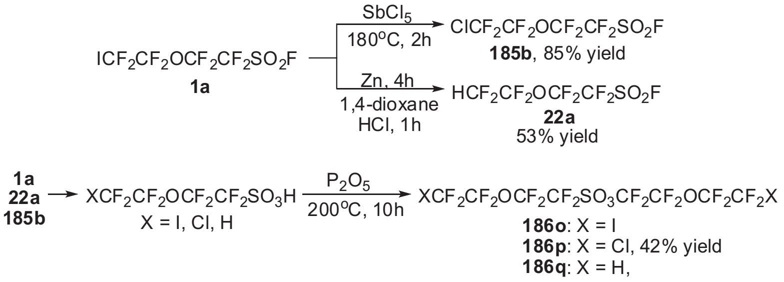
Table 5
Synthesis of perfluoroalkanesulfonic acid esters from **1a**, **22a**, and **185a**

Entry	R_FSO_2F	ROM	Conditions	R_FSO_3R (yield, %)[a]
1	**1a**	$H(CF_2)_4CH_2OH$	−10 to 0 °C, 4 h	$ICF_2CF_2OCF_2CF_2SO_3CH_2(CF_2)_4H$ (**186a**, 84.3)
2[b]	**1a**	$H(CF_2)_4CH_2OH$	−10 to 0 °C	$ICF_2CF_2OCF_2CF_2SO_3CH_2(CF_2)_4H$ (**186a**, 51.1)
3	**1a**	$H(CF_2)_2CH_2OH$	0 °C, 3.5 h	$ICF_2CF_2OCF_2CF_2SO_3CH_2(CF_2)_2H$ (**186b**, 86)
4	**1a**	C_6H_5OH	−20 °C, 3.0 h	$ICF_2CF_2OCF_2CF_2SO_3C_6H_5$ (**186c**, 63)
5[c]	**1a**	C_6F_5ONa	60–80 °C, 6 h	$ICF_2CF_2OCF_2CF_2SO_3C_6F_5$ (**186d**, 82)
6[c]	**1a**	$4\text{-}ClC_6F_4ONa$	60–80 °C, 6 h	$ICF_2CF_2OCF_2CF_2SO_3C_6F_4(4\text{-}Cl)$ (**186e**, >80)
8[d]	**22a**	C_6H_5OH	rt, 4 h	$HCF_2CF_2OCF_2CF_2SO_3C_6H_5$ (**186f**, 87)
9[d]	**22a**	$2\text{-}ClC_6H_4OH$	rt, 4 h	$HCF_2CF_2OCF_2CF_2SO_3C_6H_4(2\text{-}Cl)$ (**186g**, 81)
10[d]	**22a**	$3\text{-}MeOC_6H_4OH$	rt, 6 h	$HCF_2CF_2OCF_2CF_2SO_3C_6H_4(3\text{-}Ome)$ (**186h**, 89)
11[d]	**22a**	$2,6\text{-}MeC_6H_3OH$	rt, overnight	$HCF_2CF_2OCF_2CF_2SO_3C_6H_3(2,6\text{-}Me)$ (**186i**, 59)
12[d]	**185a**	C_6H_5OH	rt, 5 h	$BrCF_2CF_2OCF_2CF_2SO_3C_6H_5$ (**186u**, 83)

[a] Isolated yield.
[b] Aqueous KOH (7%) solution was employed instead of NEt_3.
[c] DG (diglyme) was used as solvent without Et_3N.
[d] Et_3N was used both as base and solvent.



Scheme 56. Synthesis of 5-iodo-3-oxaperfluoroalkanesulfonic acid esters from **121**.



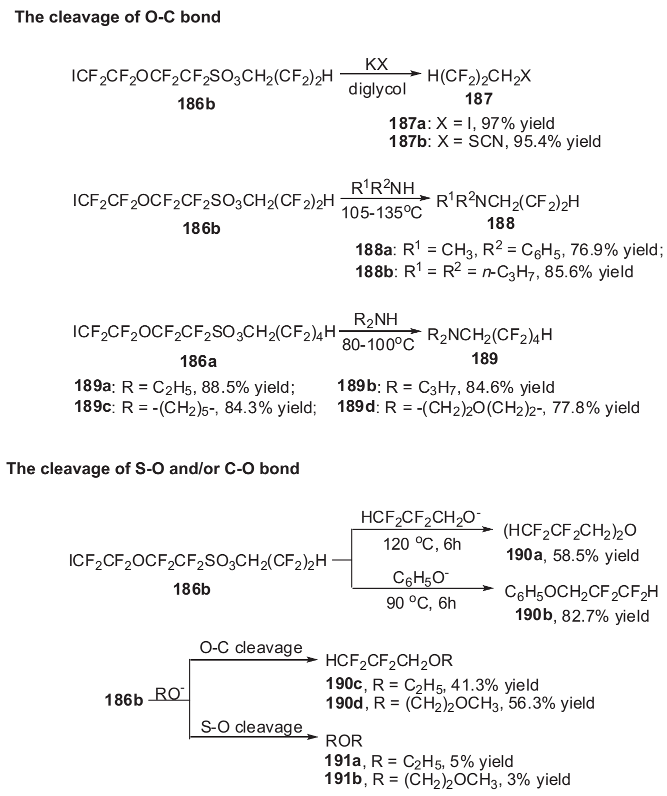
Scheme 57. Synthesis of perfluoroalkyl 5-substituted-3-oxaperfluoroalkanesulfonic acid esters from $XCF_2CF_2OCF_2CF_2SO_3H$ (X=I, Cl, H).

3.3.2. The cleavage of S—O and/or O—C bonds of perfluoroalkanesulfonic acid esters in nucleophilic substitutions (S_N2). Perfluoroalkanesulfonic acid esters (R_FSO_3R) have two reactive sites in nucleophilic substitutions (S_N2): the sulfur atom in SO_2 groups and the carbon atom (combined to oxygen) in R groups (Scheme 58). The reaction of **186b** with KX (X=F, SCN), amines and $NaOC_6H_5$ occurred at alkyl carbon atom by the cleavage of O—C bond to give **187a**—**b**, **188a**—**b**, and **190b**, respectively.[62] However, when **186b** was treated with $NaOC_2H_5$ and $NaOCH_2CH_2OCH_3$, both the sulfur and carbon atoms of sulfonate were attacked, leading to the O—C bond fragment and the S—O bond breakage, which afforded **190c**,**d** as well as **191a**,**b**. Treatment of **186b** with $NaOCH_2CF_2CF_2H$ gave symmetrical ether **190a**, which might be through either S—O bond or O—C bond cleavage.

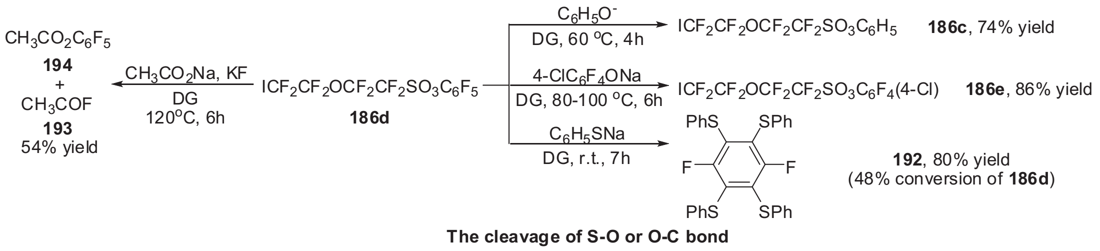
In contrast to alkyl and polyfluoroalkyl perfluoroalkanesulfonates, phenyl and per(poly)fluorophenyl perfluoroalkanesulfonates reacted with NaOR providing only S—O bond cleavage products (Scheme 59).[64] Per(poly)fluorophenyl perfluoroalkanesulfonates (e.g., **186d**,**e**) were more reactive than phenyl perfluoroalkanesulfonates (e.g., **186c**) in these substitutions. Nucleophiles (Nu^-), like KF, Et_2NH and KOH, reacted with $XCF_2CF_2OCF_2CF_2SO_3C_6F_4Y$ (e.g., **186d**—**e**) also on the sulfur atom, which produced $XCF_2CF_2OCF_2CF_2SO_2Nu$ (X=I or Cl) in good yields. When $NaSC_6H_5$ was treated with **186d**, however, **192** was formed as the sole product. The destruction of O—C bond and the substitution of the fluorine atoms on phenyl ring of **186d** by $C_6H_5S^-$ were involved in this reaction. Moreover, the reaction of per(poly) fluorophenyl perfluoroalkanesulfonates with CH_3CO_2Na afforded per(poly)fluorophenyl acetates ($CH_3CO_2C_6F_4Y$) and sodium perfluoroalkanesulfonates $XCF_2CF_2OCF_2CF_2SO_3Na$. By addition of equal equivalent of KF into the same reaction, the yield of $CH_3CO_2C_6F_4X$ was decreased and the major product was CH_3COF (**193**). This indicated that the intermediary mixed anhydride ($ICF_2CF_2OCF_2CF_2SO_2OCOCH_3$) might be initially formed via S—O bond cleavage, which was then attacked by $XC_6F_4O^-$ or F^- to provide the final **194** and **193**.

Perfluoroalkoxide ions generated from TFES or FO_2SCF_2COF, perfluoroalkyl ketone and perfluoroacyl fluorides (R_FCOF), were also suitable for the nucleophilic substitution of alkyl and polyfluoroalkyl perfluoroalkanesulfonates (Scheme 60).[62] The products were particularly dependent upon the concentration of $R_FCF_2O^-$, which was formed from R_FCOF and F^- in a reversible equilibrium. Therefore, the choice of solvent has great influence on the reaction. When the reaction of **186b**, KF and R_FCOF was carried out in HMPA and diglyme, the ethers **198** were obtained as major products. Using DMSO instead of HMPA or DG, the esters **199** were formed predominantly. Running the reaction in DMF, both ethers and esters were observed. In the absence of KF, **186b** could also react with R_FCOF to give **198** and/or **199** in HMPA, DMSO and DMF. However, no reaction occurred when the mixture was stirred in DG. It seems that aprotic solvents with high dielectric constant assisted the S—O bond of **186b** and afforded $H(CF_2)_2CH_2O^-$, which further reacted with R_FCOF to give **199** and F^-. The resulting F^- was then combined with R_FCOF, followed by treatment with **186b** via C—O bond cleavage, to produce **198**. Finally, a mixture of **198** and **199** was obtained.

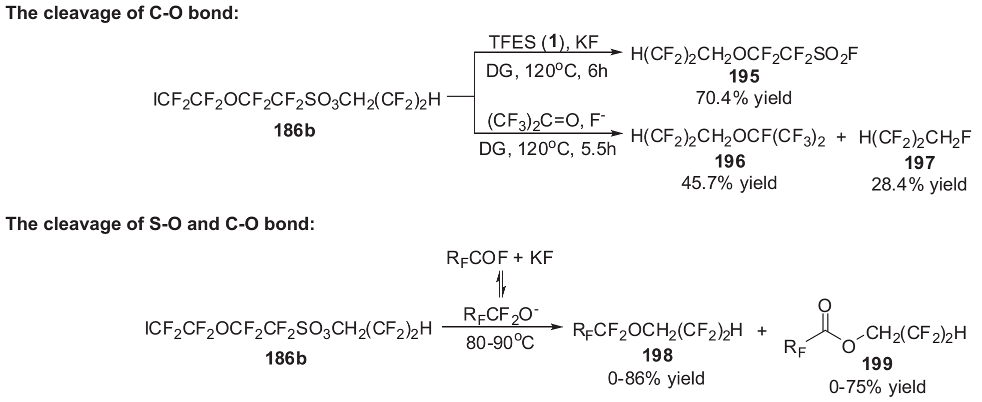
The reaction of phenyl and per(poly)fluorophenyl perfluoroalkanesulfonates with $R_FCF_2O^-$ was complicated but still provided the S—O bond cleavage products (Scheme 61).[64] **186d** reacting with FO_2SCF_2COF in the presence of KF yielded **1a**, **202** and **203** in 76%, 60% and 7% yield, respectively. Compound **201** generated from the substitution of the perfluorophenoxyl



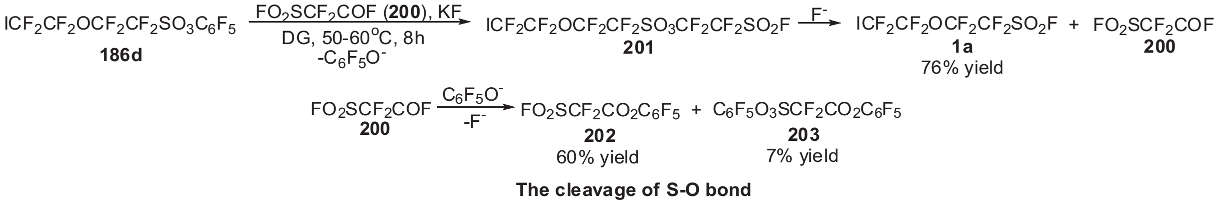
Scheme 58. The reactions between alkyl perfluoroalkanesulfonates and nucleophiles.



Scheme 59. The reactions of pentafluorophenyl perfluoroalkanesulfonate with nucleophiles.



Scheme 60. The reactions of alkyl perfluoroalkanesulfonate with perfluoroalkoxide ions.

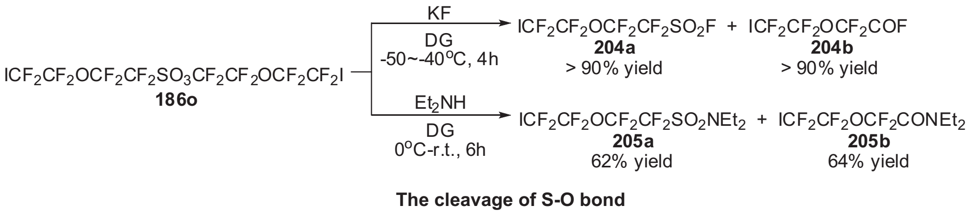


Scheme 61. The reaction of pentafluorophenyl perfluoroalkanesulfonate with FO_2SCF_2COF and KF.

group of **186d** by $FO_2SCF_2CF_2O^-$ was assumed as the intermediate. Acyl fluoride **200** reacted with $C_6F_5O^-$ readily affording **202** and **203**.

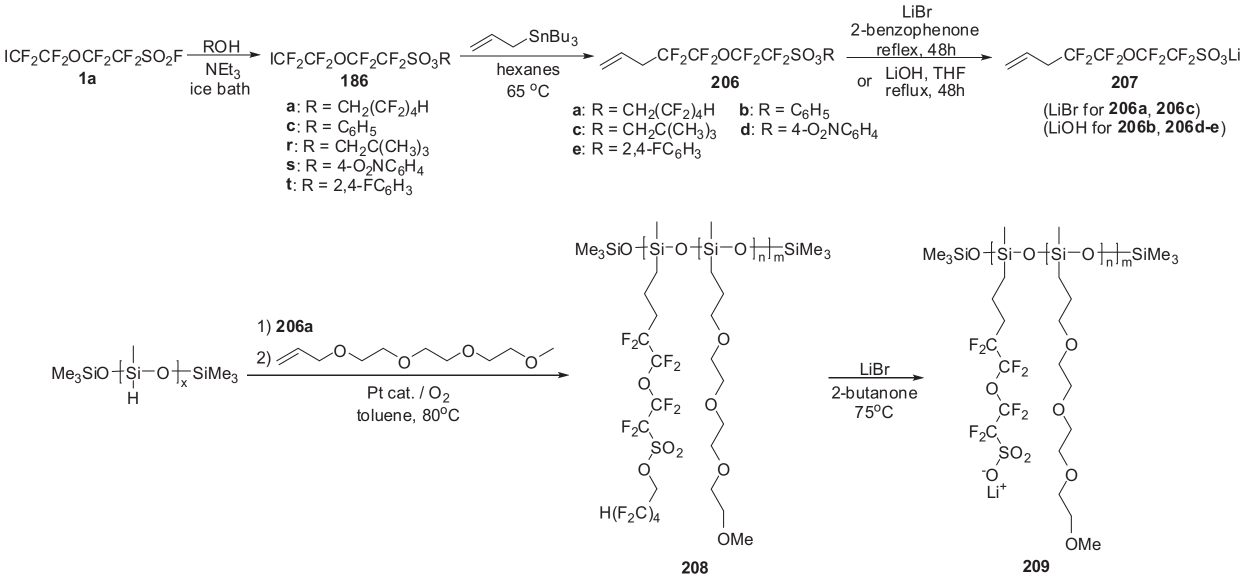
Furthermore, perfluoroalkyl 5-substituted-3-oxaperfluoroalkanesulfonic acid esters reacted with various nucleophiles via S–O bond breakage (Scheme 62).[66] In the presence of catalytic amount of X^- (X=F, Cl, Br, I) and $[SCN]^-$, perfluoroalkyl esters were decomposed to form the corresponding sulfonyl fluorides (e.g., **204a**) and acyl fluorides (e.g., **204b**). The reaction of **186p** with EtOH didn't happen at room temperature, but at refluxing for 12.5 h, the reaction gave both **185b** (61% yield) and $ClCF_2CF_2OCF_2CO_2Et$ (67% yield). More powerful nucleophiles, NaOR ($R=C_2H_5$, $CH_2(CF_2)_2H$), reacted with **186p** at −60 to −50 °C yielding Et_2O and $ClCF_2CF_2OCF_2CO_2R$, whereas $NaOC_6X_5$ (X=H, F) provided $ClCF_2CF_2OCF_2CF_2SO_3C_6X_5$ and $ClCF_2CF_2OCF_2CO_2C_6X_5$. Carboxylates, like CF_3CO_2Na and CH_3CO_2Na, could also cause the S–O bond cleavage of perfluoroalkyl sulfonic acid esters, which produced the intermediary asymmetric anhydrides and $R_FCF_2O^-$. The resulting anhydrides were then attacked by F^- (generated from the decomposition of $R_FCF_2O^-$) to provide the corresponding sulfonyl fluorides and acyl fluorides again. The reaction of **186o** with $HNEt_2$ afforded amides **205a** and **205b** in good yield.

In contrast to the nucleophilic substitutions of **186a** and **186b** mainly via a C–O bond fragment, the S_N2 transformations of **186o** and **186p** proceeded through a S–O bond cleavage.[66] This might be caused by the huge steric hindrance of the fluorine atoms located on the α-carbon atom, which made the S_N2 attack of the nucleophiles at the carbon atom highly difficult.[66,67]



Scheme 62. The reaction of perfluoroalkyl 5-substituted-3-oxaperfluoroalkanesulfonate with nucleophiles.

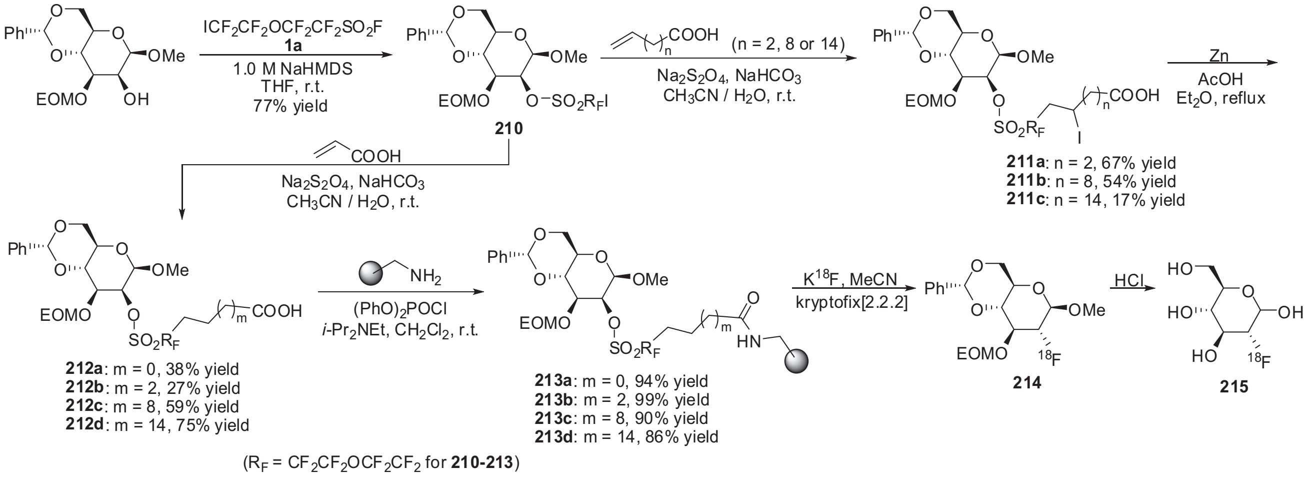
3.3.3. Synthesis of lithium sulfonate salts and [^{18}F]2-fluoro-glucose from the corresponding alkyl perfluoroalkanesulfonates via nucleophilic substitutions (S_N2). Recently, S_N2 induced O–C bond fragment of perfluoroalkanesulfonic acid esters (**186a**, **186c**, and **186r**–**t**) was employed to prepare lithium perfluoroalkanesulfonate **207** (Scheme 63).[68] Methods for the direct deprotection of perfluorosulfonate groups to yield the corresponding lithium salts were developed by using LiBr and LiOH as reagents. LiBr was an effective nucleophile to displace the alkyl and polyfluoroalkyl groups of **186c** and **186a**, whereas LiOH was viable to prepare the lithium salt from the aryl-protected sulfonates **186r**–**t**. Consequently, sulfonate **206a** was introduced into the polyelectrolytes (**208**) (the $H(CF_2)_2CH_2$ group of **206a** was responded in ^{19}F NMR experiments and could be used as a quantifiable probe to monitor the reaction). By the nucleophilic subsitution of the polyfluoroalkyl group of **208** with LiBr in 2-butanone, comb polyelectrolytes (**209**) consisting of a polysiloxane backbone with tetraglyme and lithium sulfonate terminated perfluoroether side chains were successfully obtained (Scheme 63).



Scheme 63. Synthesis of polyelectrolytes from alkyl fluoroalkanesulfonates via nucleophilic substitutions.

Moreover, a method for the facile synthesis of [^{18}F]-2-fluoro-2-deoxy-D-glucose ([^{18}F]FDG, [^{18}F]-**215**) was developed based on **1a** (Scheme 64).[69] Polystyrene resin-supported perfluoroalkylsulfonates **213a**–**d** were the key precursors in this approach. Initially, to achieve **213**, linker-sugar conjugates **212a**–**d** were prepared from the esterification of D-mannose derivative with **1a** followed by radical-mediated couplings of the resulting iodide **210** with a series of enoic acids of various chain lengths.[69] Reaction of acrylic acid with **210** provided the reduced product **212a** directly, whilst radical coupling products **211a**–**c** required deiodination with zinc powder in refluxing Et_2O/AcOH yielding **212b**–**d**. The resulting acids **212a**–**d** then reacted with aminomethyl-functionalized polystyrene to give **213a**–**d** in high yields. Using resin **213c** as substrate, the labeling reaction with [^{18}F]KF (185–350 MBq) and kryptofix[2.2.2] in CH_3CN in a carbon glass vessel at 86 °C for 3–4 min led to 70–91% incorporation of ^{18}F into [^{18}F]-**214** via nucleophilic substitution (S_N2). Five labeling experiments re-using the same sample of resin **213c** all led to the formation of the protected [^{18}F]-**214** with consistently high radiochemical yields. These demonstrated that the majority of the protected D-mannose derivative remained attached to the resin through the fluoroalkylsulfonyl linker during the ^{18}F-labeling reactions.

[^{18}F]-**215**, a distinguished radiochemical tracer in PET applications, which possesses the positron-emitting radionuclide ^{18}F with half-life of 110 min, has been widely applied to measure glucose uptake by tissue, produce real-time images for diagnosis and

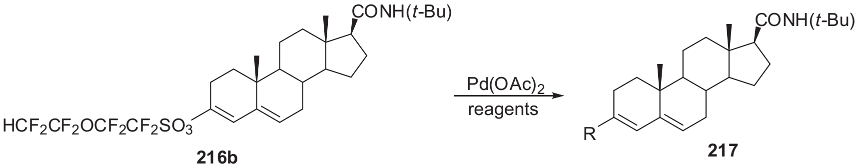


Scheme 64. Synthesis of [^{18}F]-2-fluoro-2-deoxy-D-glucose from polystyrene resin-supported perfluoroalkylsulfonates via nucleophilic substitutions.

management, and study the diseases, such as cancer.[69,70a] The first radiosynthesis of [^{18}F]-**215** was achieved by the electrophilic fluorination of D-glucal with [^{18}F]F_2, which endured relatively low yields and limited stereoselectivity.[70b] In the following years, methods of [^{18}F]FDG preparation still had the disadvantage that the FDG was produced as a mixture with a large stoichiometric excess of D-glucose and other degradation products that arose from side reactions of the starting material during the fluoridation and deprotection steps.[70c] Significantly, the nucleophilic substitution of the solid-bound **213a-d** by [^{18}F]F^- affords [^{18}F]-**215** in high radiochemical yield, and most of the unreacted precursor remains on the resin thereby avoiding the presence of excess sulfonates in subsequent deprotection steps.

3.3.4. Application of vinyl and phenyl perfluoroalkanesulfonates in cross-coupling reactions with the fragment of the O–C bond. Vinyl and phenyl 5-substituted-3-oxaperfluoroalkanesulfonic acid esters were successfully transformed in metal catalyzed cross-coupling reactions via the O–C bond cleavage.[71–73] Similar to enol triflates, Pd-catalyzed carbonylation of 5-*H*-3-oxa-octafluoropentanosulfonate **216b** with CO and MeOH produced 3-carboxyl steroid **217a** in 90% yield, which was readily converted to a new type of steroidal 5α-reductase inhibitor Epristeride (**217b**) by hydrolysis (Table 6).[71] Without MeOH, the reaction between **216b** and CO in the presence of $Pd(OAc)_2$ gave **217b** directly.[72] Other Pd-catalyzed cross-couplings of **216b** with HCOOH, CO and Et_2NH, $EtOCH{=}CH_2$, $HPO(OEt)_2$, and $HC{\equiv}CC_6H_5$ also proceeded very well, which ultimately provided a series of novel 3-substituted steroids (**217**) with significant pharmacological importance. The resulting 3-substituted steroids **217f** and **217g**, for example, showed inhibitory activity against steroidal 5α-reductase in preliminary bioactivity assay.

Table 6
Pd-catalyzed cross-coupling reactions of **216b**



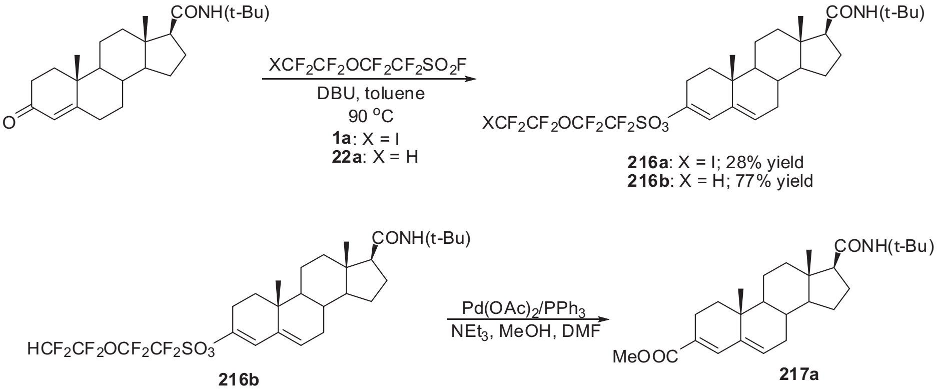
Entry	Condition	Products	Yield (%)
1	CO, MeOH, DMF	R=COOMe (**217a**)	90
2	CO, DMF	R=COOH (**217b**)	70
3	HCOOH, DMF	R=H (**217c**)	85
4	CO, DMF, Et_2NH	R=$CONEt_2$ (**217d**)	82
5	$EtOCH{=}CH_2$	R=$COCH_3$ (**217e**)	74
6	$HPO(OEt)_2$	R=$PO(OEt)_2$ (**217f**)	92
7	$HC{\equiv}CC_6H_5$	R=$C{\equiv}CC_6H_5$ (**217g**)	85

Enol triflates are important intermediates for C–C bond formation and they have been widely applied to the synthesis of natural products and bioactive molecules.[72] However, the preparation of enol triflates has disadvantages because it uses expensive and moisture-sensitive triflating agents. Enol 5-substituted-3-oxaperfluoroalkanesulfonates, generated from **22a** (or **1a**) and 3-ketosteroids, provide good alternatives, which have overcome these shortages. Meantime, the reactivity of these enol poly(per)fluoroalkanesulfonates is comparable to that of enol triflates.

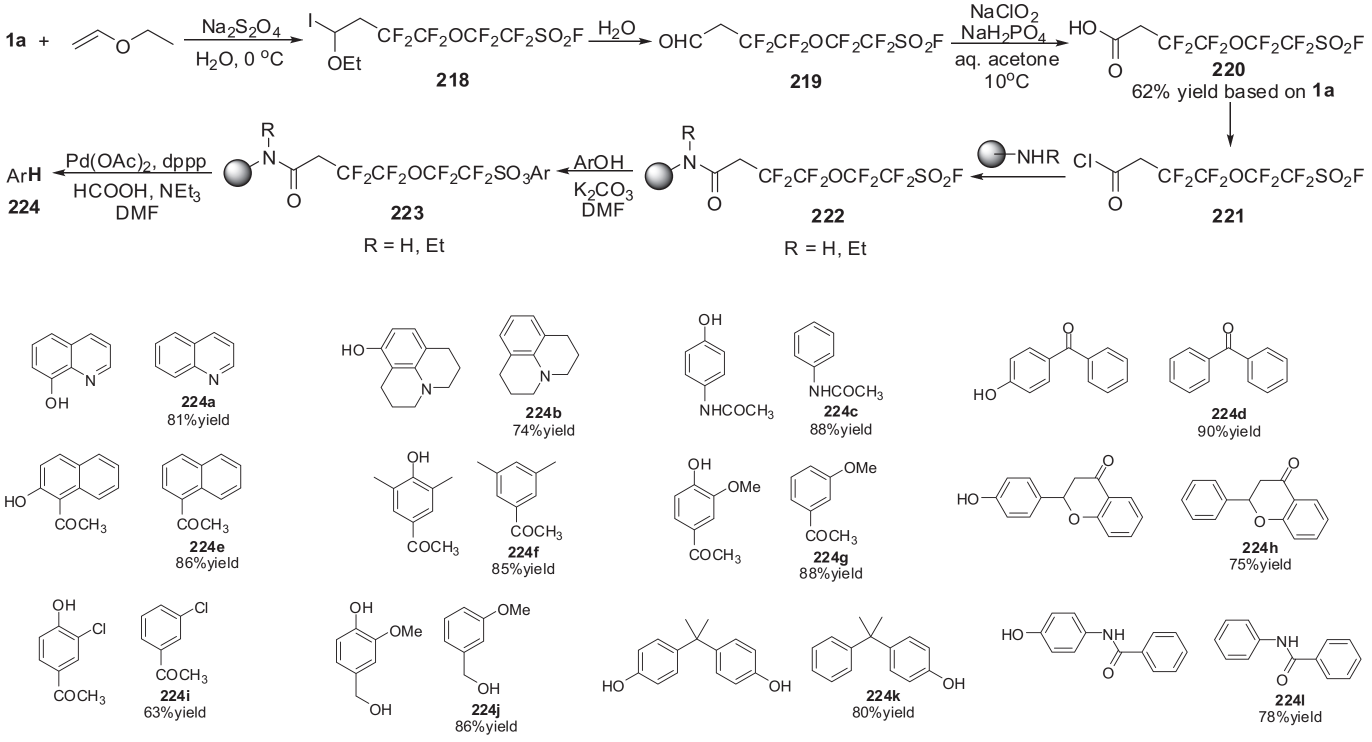
Enol poly(per)fluoroalkanesulfonates were conveniently prepared (Scheme 65). When steroidal ketone was treated with **22a** in the presence of DBU (1, 8-diazabicyclo-[5,4,0]undec-7-ene) at 90 °C, the steroid 3-enol 5-H-3-oxaoctafluoropentano sulfonate **216b** was produced as the sole product.[71,72] The most satisfactory solvent for this reaction seems to be the anhydrous toluene, since in other solvents, such as CH_2Cl_2, $CHCl_3$, CCl_4, and THF, no reaction was observed. DBU was found to be the best base. In addition, the 5-*H*-3-oxa-octafluoropentanosulfonylation reactions of steroid-3-one occurred only at the C-3 position, other functional groups, such as amide and ketal were not affected. When steroidal diketones were subjected to this reaction, no reactions occurred to the C-6, the C-17 and the C-20 carbonyls while the C-3 ones were selectively transformed to the corresponding enol sulfonate. Such high chemo- and regioselectivity is obviously of great value in steroid chemistry. By the way, the yields of the enol 5-substituted-3-oxaperfluoroalkanesulfonates were dependent upon not only the poly(per)fluoroalkanesulfonyl fluorides, bases as well as solvents, but also the ability of enolization of the carbonyl groups. Generally, in the presence of 3 equiv of **22a** and 3 equiv of DBU in toluene at 90 °C for 6–12 h, the corresponding 3-enol sulfonates were formed in 56–91% yields.

Pd-mediated reductive cleavage of aryl perfluoroalkylsulfonates to generate the parent arenes was investigated.[73a–b] Polymer-bound aryl 5-substituted-3-oxaperfluoroalkanesulfonates (**223**) were efficiently transformed with $Et_3N{-}HCO_2H$ in the presence of a catalytic amount of $Pd(OAc)_2$ and 1,3-bis(diphenylphosphino) propane (dppp) to afford high yields of reduced arenes (**224**) under mild conditions (Scheme 66).[73a] A broad range of function group compatibility offered proof of the advantages inherent in this perfluoroalkyl sulfonate strategy. The cleavage did not suffer from steric nor electronic effects. The formation of **224j** illustrated the chemoselectivity obtainable when one has both a phenolic and an aliphatic alcohol available for coupling. The use of symmetric bisphenols with resin **222** could afford monophenols (**224k**) after cleavage. **224a–l** were easily isolated by two phase extraction, and the residual metal catalyst was removed by eluting the organic solution through a thin pad of silica gel, which gave **224a–l** with purity suitable for high throughput screening (~90%). This solid-phase approach provided an operationally simple, inexpensive, and general protocol for the activation/reductive cleavage of the aryl-oxygen bond.

In addition, Pd-mediated reduction of vinyl sulfonates generated from resin **222** and ketones are envisaged.[73a] As is the case for aryl triflates, the polymer-bound aryl perfluoroalkylsulfonates are also amenable to other cross-coupling reactions, such as Suzuki, Heck, and organozinc couplings.[73c] **222**-based aryl sulfonates appears to be stable to a variety of reaction conditions, like acidic (20% TFA in CH_2Cl_2) conditions, reductive amination conditions and



Scheme 65. Synthesis of steroidal per(poly)fluoroalkanesulfonates and their applications in Pd-catalyzed cross-coupling reactions.



Scheme 66. A traceless perfluoroalkylsulfonyl linker for the deoxygenation of phenols.

acylation conditions.[73a,73c] The ease of preparation, excellent stability, and synthetic versatility of **222** will find broad application in solid-phase synthesis and combinatorial chemistry via metal catalyzed cross-couplings.

The polymer supported perfluoroalkylsulfonyl linker (**222**) was derived from **1a**, which allowed the attachment of phenols to the solid-phase and subsequent reductive transformations.[73a] In the beginning, **1a** was treated with ethyl vinyl ether through a radical mechanism to provide **218**. **218** was hydrolyzed to aldehyde **219** and then oxidized to afford carboxyl acid **220**, which was converted to acyl chloride **221**. Either treatment of **221** with amine resins or direct coupling of **220** with amine resins by using *O*-(7-azabenzotriazol-1-yl)-*N*,*N*,*N*′,*N*′-tetramethyluronium hexafluorophosphate (HATU) as activating reagent, the sulfonyl fluoride resin **222** was favorably prepared. Phenols with disparate steric and electronic environments were attached to resin **222** via sulfonate formation by using K_2CO_3 or Et_3N as base in DMF at room temperature. The actual loading of the phenols on resin **222** was in the range of 0.31–0.36 mmol/g resin as determined by elemental analysis.

3.4. Synthesis and applications of fluoroalkanesulfonamides generated from $X(CF_2CF_2)_nOCF_2CF_2SO_2F$

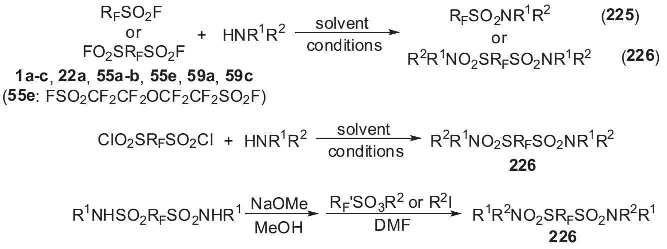
Per(ploy)fluoroalkanesulfonamides and bis(fluoroalkanesulfon) amides are important derivatives of $X(CF_2CF_2)_nOCF_2CF_2SO_2F$, which have been widely used to prepare functional molecules. The reactions of $X(CF_2CF_2)_nOCF_2CF_2SO_2F$ with amines or sodium azide with subsequent transformation have readily provided sulfonamides in good yields. The anions of per(ploy)fluoroalkanesulfonamides possess gentle nucleophilic ability to electrophiles. Bis(-fluoroalkanesulfon)amides, a kind of ‘supper acids’ derived from fluoroalkanesulfonamides or directly from $X(CF_2CF_2)_nOCF_2CF_2SO_2F$, have been favorably employed to prepare amine-based functionalized ionic liquids.

3.4.1. Synthesis and reactivity of fluoroalkanesulfonamides from $X(CF_2CF_2)_nOCF_2CF_2SO_2F$. There are several methods to the synthesis of fluoroalkanesulfonamides (Table 7): (1) The reactions of R_FSO_2F or $FO_2SR_FSO_2F$ with amines either with or without solvent; (2) Reactions of R_FSO_2Cl or $ClO_2SR_FSO_2Cl$ with amines in ether or under solvent-free conditions; (3) $R_FSO_2NHR^1$ or $R^1NHSO_2R_FSO_2NHR^1$ reacting with NaOMe followed by treatment with $R_F'SO_3R^2$ or R^2I.[74–79] By these approaches, numerous sulfonamides (e.g., **225a–o**, **226a–i**) were prepared. The starting sulfonyl fluorides, such as $X(CF_2)_2O(CF_2)_2SO_2F$ (X=F, Cl, H), $FO_2S(CF_2)_2O(CF_2)_2SO_2F$, and $FO_2S(CF_2)_2O(CF_2)_4O(CF_2)_2SO_2F$ were readily derived from **1a**. Treatment of $R_FSO_2NH_2$ with NaOMe followed by MeI, both *N*-methyl and *N*,*N*-dimethyl amines were formed.[74a] *N*-mono substituted amine **226e** reacted with NaOMe and CH_2I_2 or **228** providing polymer **227a** or **227b**, respectively (Scheme 67).

Table 7
The synthesis of fluoroalkanesulfonamides from **1** and their derivatives

Entry	HNR^1R^2	Solvent	Conditions	Products (**225** or **226**)	Yield (%)[a]
1	n-$C_3H_7NH_2$	Et_2O	30 °C, 5 h	$I(CF_2)_4O(CF_2)_2SO_2NH(n\text{-}C_3H_7)$ (**225a**)	93
2	i-$C_4H_9NH_2$	Et_2O	35 °C, 7 h	$I(CF_2)_4O(CF_2)_2SO_2NH(i\text{-}C_4H_9)$ (**225b**)	90
3[b]	$Et_2N(CH_2)_3NH_2$	Et_2O	35 °C, 10 h	$I(CF_2)_4O(CF_2)_2SO_2NH(CH_2)_3NEt_2$ (**225c**)	84
4	NH_3	Et_2O	−20 °C, 7 h	$I(CF_2)_4O(CF_2)_2SO_2NH_2$ (**225d**)	90
5	$(n\text{-}C_3H_7)_2NH$	Et_2O	35 °C, 13 h	$I(CF_2)_4O(CF_2)_2SO_2N(n\text{-}C_3H_7)_2$ (**225e**)	63
6	$(EtO)_3Si(CH_2)_3NH_2$	Et_2O	35 °C, 9 h	$I(CF_2)_4O(CF_2)_2SO_2NH(CH_2)_3Si(OEt)_3$ (**225f**)	60
7[b,c]	$C_6H_5CH_2NH_2$	Dioxane	80 °C, 2 h	$C_6H_5CH_2NHSO_2(CF_2)_2O(CF_2)_8O(CF_2)_2SO_2NHCH_2C_6H_5$ (**226a**)	93
8[b,c]	$C_6H_5NH_2$	—	90 °C, 65 h	$C_6H_5NHSO_2(CF_2)_2O(CF_2)_8O(CF_2)_2SO_2NHC_6H_5$ (**226b**)	70
9[b]	p-$CH_3OC_6H_4NH_2$	Dioxane	85 °C, 33 h	$p\text{-}CH_3OC_6H_4NHSO_2(CF_2)_2O(CF_2)_8O(CF_2)_2SO_2NHC_6H_4(p\text{-}OCH_3)$ (**226c**)	75
10	NH_3	Et_2O	−20 °C, 7 h	$H_2NSO_2(CF_2)_2O(CF_2)_4O(CF_2)_2SO_2NH_2$ (**226d**)	90
11	CH_3NH_2	Et_2O	0 °C, 4 h	$CH_3NHSO_2(CF_2)_2O(CF_2)_4O(CF_2)_2SO_2NHCH_3$ (**226e**)	87
12[c]	CH_3NH_2	Et_2O	−80 °C, 4 h	$CH_3NHSO_2(CF_2)_2O(CF_2)_2SO_2NHCH_3$ (**226f**)	
13[d]	—	(1) MeOH (2) DMF	rt, 2 h 80 °C, 3.5 h	$H(CF_2)_6CH_2NHSO_2(CF_2)_2O(CF_2)_4O(CF_2)_2SO_2NHCH_2(CF_2)_6H$ (**226g**)	98
14	CH_3NH_2	—	−78 °C	$H(CF_2)_2O(CF_2)_2SO_2NHCH_3$ (**225g**)	70
15	$C_2H_5NH_2$	—	−78 °C	$H(CF_2)_2O(CF_2)_2SO_2NHC_2H_5$ (**225h**)	68
16	CH_3NH_2	—	−78 °C	$I(CF_2)_2O(CF_2)_2SO_2NHCH_3$ (**225i**)	74
17	$C_2H_5NH_2$	—	−78 °C	$I(CF_2)_2O(CF_2)_2SO_2NH\ C_2H_5$ (**225j**)	75
18	CH_3NH_2	—	−78 °C	$Cl(CF_2)_2O(CF_2)_2SO_2NHCH_3$ (**225k**)	72
19	NH_3	—	<−60 °C	$I(CF_2)_2O(CF_2)_2SO_2NH_2$ (**225l**, **88a**)	92
20	NH_3	—	<−60 °C	$H(CF_2)_2O(CF_2)_2SO_2NH_2$ (**225m**)	87
21	NH_3	—	<−60 °C	$I(CF_2)_4O(CF_2)_2SO_2NH_2$ (**225d**)	94
22	NH_3	—	<−60 °C	$I(CF_2)_6O(CF_2)_2SO_2NH_2$ (**225n**)	93
23	NH_3	—	<−60 °C	$Cl(CF_2)_6O(CF_2)_2SO_2NH_2$ (**225o**)	98
24	NH_3	—	<−60 °C	$H_2NSO_2(CF_2)_2O(CF_2)_2SO_2NH_2$ (**226h**)	97
25	NH_3	—	<−60 °C	$H_2NSO_2(CF_2)_2O(CF_2)_4O(CF_2)_2SO_2NH_2$ (**226d**)	94

[a] Isolated yields. Entries 1–13 were from Ref. 74a, entries 14–18 were from Ref. 77 and entries 19–25 were from Ref. 79. The starting material for the preparation of **226f** could be found in Ref. 74b.
[b] NEt_3 was added as the base. In other entries, HNR^1R^2 were used as both the reagent and base.
[c] The products could also be prepared by the reaction of $ClSO_2R_FSO_2Cl$ with HNR^1R^2.
[d] **226g** was obtained from the reaction of **226d** with NaOMe followed by treatment with $Cl(CF_2)_4O(CF_2)_2SO_3CH_2(CF_2)_6H$.

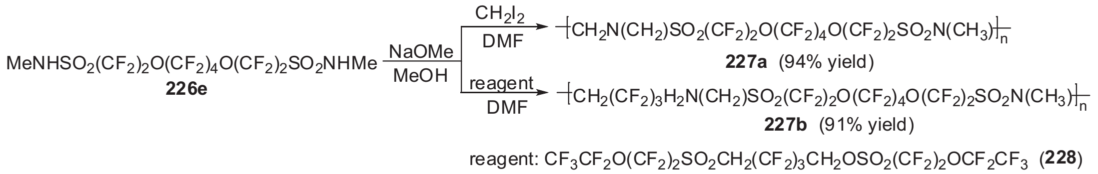


3-Oxaperfluoroalkanesulfonyl fluorides **58**, derived from **1**, reacting with allylamine afforded *N*-allylsulfonamide **229** in good yield, which was treated with NaOMe and MeI to give the corresponding *N*-methyl-*N*-allyl-3-oxaperfluoroalkanesulfonamides **231** favorably (Scheme 68).[75] **229** and **231** were further converted to the respective trichlorosilyl substituted amine **230** and **232**. Subsequent treatment of **232** with CH_3OH and pyridine in FC-113 ($ClCF_2CFCl_2$) provided trimethoxysilane **233** in high yield. Compounds **230** and **232** were good surface treating agents, which could be used to treat glass surfaces and endow them water and oil resisting properties.

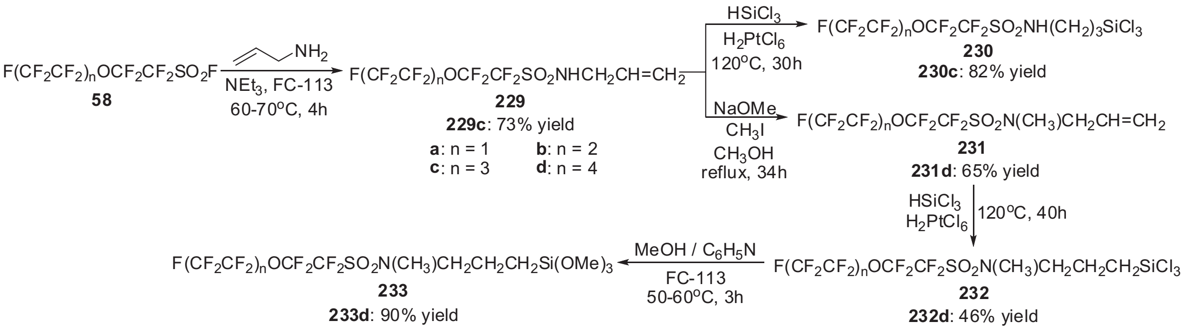
3,8-Dioxaperfluorodecyldisulfonyl fluoride (**55a**), formed from **1a**, reacted with $EtNH_2$ to give *N*,*N*′-diethyl-3,8-dioxaperfluorodecyldisulfonylamide (**226i**), which was treated with $Cl(CH_2)_2OH$ to provide 2,2′-(*N*,*N*′-diethyl-3,8-dioxaperfluorodecyldisulfonylamido) diethanol (**234**) (Scheme 69).[76a] Compound **234** could be polymerized with TDI (tolylene-2,4-diisocyanate) to afford polyurethane that showed good resistances to water and chemicals, consequently being used as coatings for leather and textiles.[76]

A unique, polyfluorinated, 32-membered multifunctional heterocycle (**235**) with two α,β-diketone and four ether functional groups was synthesized from *N*-methyl sulfonamide **226e** (Scheme 70).[78] Initially, **1a** refluxed with Zn in CH_2C1_2/Ac_2O (1:1) for 8 h gave **55a** in 85% yield. Subsequently, treatment of **55a** with CH_3NH_2 at −40 °C over a period of 4 h provided **226e** in 90% yield. Compound **226e** was then quantitatively converted to the bis(*N*-methyl sodium sulfonamide) by reaction at 25 °C with sodium in anhydrous ethanol. When the sodium sulfonamide was added dropwise to a solution of oxalyl chloride with vigorous stirring at 0 °C followed by the addition of water and filtration, **235** was ultimately isolated in 60% yield.

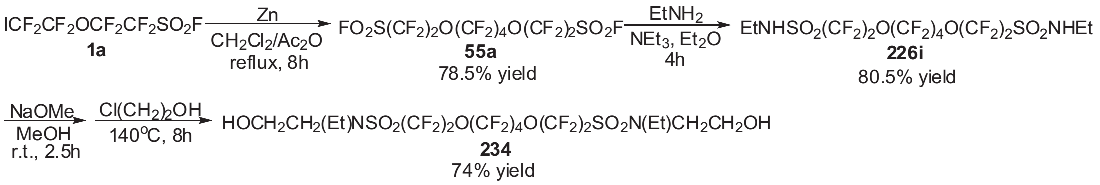
Recently, the pK_a1 and pK_a2 values of a series of fluoroalkanesulfonylamides were measured by potentiometric titration.[79] Details showed that the sulfonylamides with longer fluoroalkyl chain had stronger acidity. The terminal substituents of the fluoroalkyl chain also had influences on their pK_a values. Different alkyl halides and tosylates were employed to investigate the nucleophilicity of fluoroalkanesulfonylamides directly using K_2CO_3 as base (Scheme 71). As a result, numerous *N*-substituted and/or



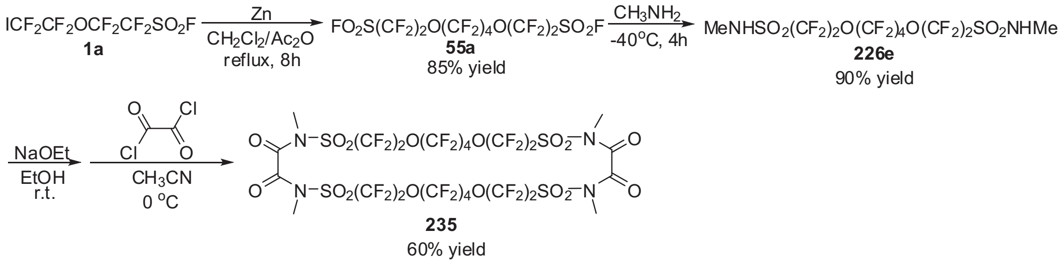
Scheme 67. Synthesis of amine-based polymers from the reactions of sodium salt of fluoroalkanesulfonamides with alkyl iodide or alkyl perfluoroalkanesulfonates.



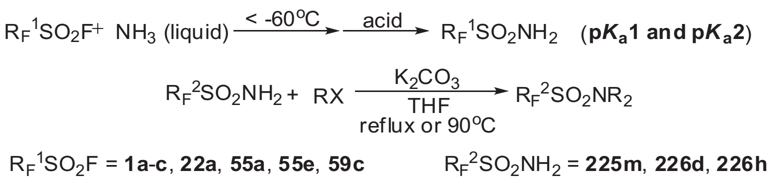
Scheme 68. Preparation of surface treating agents from **58** and allylamine.



Scheme 69. Synthesis of sulfonamide-based surface coating agents from **1a**.



Scheme 70. Synthesis of a 32-membered fluorinated multifunctional heterocycle from **1a**.



Scheme 71. Synthesis of *N*-substituted and/or *N*,*N*-disubstituted fluoroalkanesulfonylamides by treatment of $R_FSO_2NH_2$ with K_2CO_3 and electrophiles in one-pot.

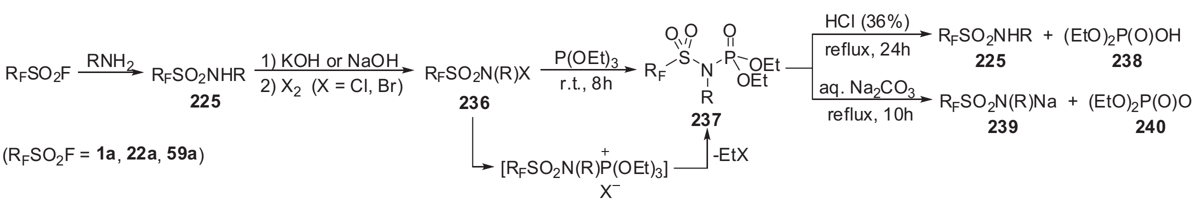
N,*N*-disubstituted fluoroalkanesulfonylamides were formed in a one-pot procedure under mild conditions. It was demonstrated that elongation of the fluoroalkyl chain reduced the nucleophilicity of the sulfonamides, which is, to some extent, in accordance with the decrease of their pK_a values.

Moreover, *N*-halogenperfluoroalkanesulfonylamines **236** were obtained from the reaction of the sodium or potassium salt of *N*-alkylfluoroalkanesulfonylamines ($R_FSO_2N(R)M$) with Br_2 or Cl_2 (Table 8).[77] Treatment of **236** with $P(OEt)_3$, *N*-alkyl-*N*-perfluoroalkanesulfonylphosphoramides **237** were readily formed. Similar to the reactions of $P(OEt)_3$ with alkyl halides, this reaction proceeded through an ionic Arbouzov-type reaction mechanism rather than a radical process. Compounds **236** are unstable. When stored in a flask at room temperature, they decomposed slowly to

Table 8
Preparation of *N*-halogenperfluoroalkanesulfonylamines and *N*-alkyl-*N*-perfluoroalkanesulfonylphosphoramides from **1a** and its derivatives

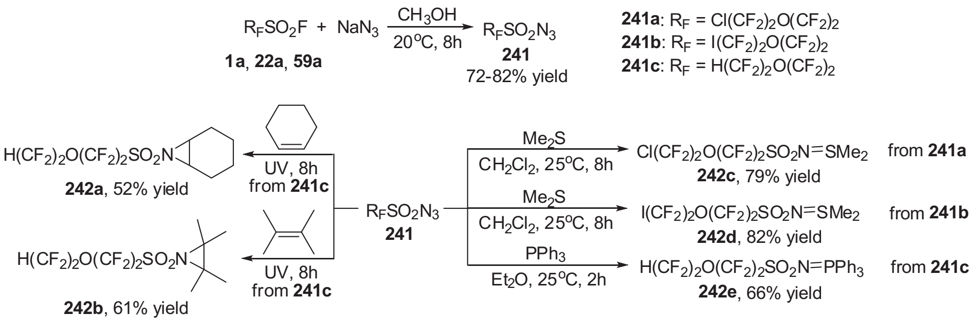
$R_FSO_2N(R)X$ (**236**)	Yield (%)	$R_FSO_2N(R)P(O)(OEt)_2$ (**237**)	Yield (%)
$H(CF_2)_2O(CF_2)_2N(CH_3)Cl$ (**236a**)	75	$H(CF_2)_2O(CF_2)_2N(CH_3)P(O)(OEt)_2$ (**237a**)	81
$H(CF_2)_2O(CF_2)_2N(C_2H_5)Cl$ (**236b**)	78	$H(CF_2)_2O(CF_2)_2N(C_2H_5)P(O)(OEt)_2$ (**237b**)	78
$I(CF_2)_2O(CF_2)_2N(CH_3)Br$ (**236c**)	73	$I(CF_2)_2O(CF_2)_2N(CH_3)P(O)(OEt)_2$ (**237c**)	85
$I(CF_2)_2O(CF_2)_2N(C_2H_5)Br$ (**236d**)	80	$I(CF_2)_2O(CF_2)_2N(C_2H_5)P(O)(OEt)_2$ (**237d**)	68
$Cl(CF_2)_2O(CF_2)_2N(CH_3)Cl$ (**236e**)	70	—	—

the corresponding R_FSO_2NHR. **237** have nitrogen atoms, which are attached by strong electron-withdrawing groups (R_FSO_2) and bond directly to the phosphorous atom of $P(O)(OEt)_2$ moiety. Hydrolysis of **237** in acidic and basic conditions, both gave the N–P bond cleavage product.



3.4.2. *Synthesis and properties of fluoroalkanesulfonyl azides and N,N-dichlorofluoroalkanesulfonamides from $X(CF_2CF_2)_nOCF_2CF_2SO_2F$.*

Azides, such as phenyl azide, azidoformate, alkane or aryl sulfonylazide etc., when decomposed thermally or under UV, can form nitrene intermediates (R–N:).[80] Perfluoroalkanesulfonyl azides (**241**), initiated under similar conditions, also generate perfluoroalkanesulfonyl nitrenes (**244**) (Scheme 72).[81–83] Perfluoroalkanesulfonyl nitrenes, trapped by alkenes, dimethyl sulfide or triphenylphosphine, afforded the insertion or addition products (**242**) in good yields.[81,82] Perfluoroalkanesulfonyl azides **241** were readily prepared from the reaction of R_FSO_2F (**1a**, **22a** or **59a**) with NaN_3 in methanol at room temperature.[81] Azides **241** are colorless liquids with a characteristic pungent odor. They are stable (decomposition temperature is around 120 °C) and can be stored at room temperature without changes.



Scheme 72. Synthesis of fluoroalkanesulfonyl azides and their applications as fluoroalkanesulfonyl nitrene precursors.

Zn-mediated reduction of *N*,*N*-dichlorofluoroalkanesulfonamides (**243**) provides the nitrene intermediates **244** as well (Scheme 73).[82] Reactions of **243** with alkanes, alkenes, benzene, dimethyl sulfide, dimethyl sulfoxide, pyridine and triphenylphosphine in the presence of zinc gave the corresponding insertion or addition products (**242**) in good yields. Treatment of **243a** with alkene in the absence of zinc, however, afforded only a 1:1 adduct (**245**) (via a free radical intermediate [$R_FSO_2N(Cl)^\bullet$]). Reduction of **245** by $NaHSO_3$, followed by elimination of HCl with alcoholic NaOEt, ultimately produced *N*-fluoroalkylsulfonylaziridine **242h**.

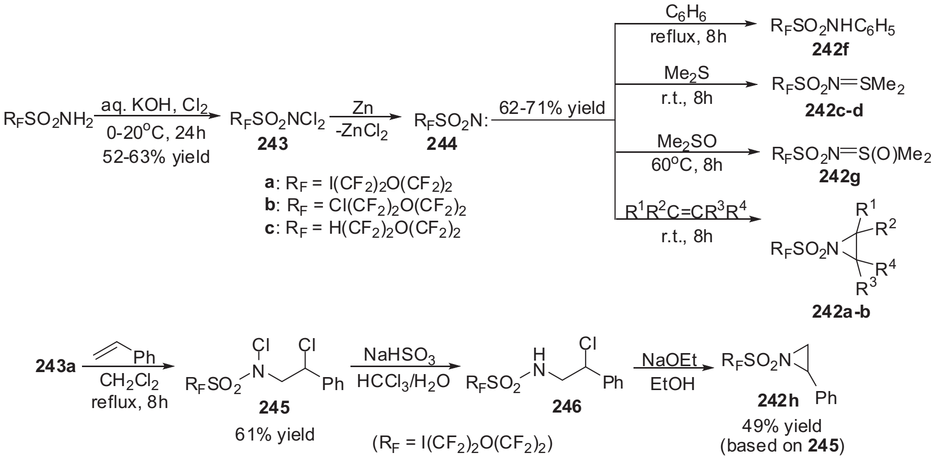
N,*N*-Dichlorofluoroalkanesulfonamides (**243**) were conveniently synthesized from the one-pot reaction of fluoroalkanesulfonamides with aq KOH and chlorine gas.[82] **241** and **243** are reactive compounds, which react with organic reagents under conditions to give a variety of fluoroalkanesulfonamide derivatives. The easy preparation of these compounds together with their unique reactivity makes them attractive and useful reagents for the introduction of the R_FSO_2N functionality into organic molecules.

The reaction of *N*,*N*-dichloro-5-iodo-3-oxa-octafluoropentane sulfonyl amide (**243a**) with 2-methyl-2-nitrosopropane (*t*-BuNO) was studied (Scheme 74).[83] According to EPR spectroscopy, this reaction was suggested to be initiated by an electron transfer (ET) between *N*,*N*-dichlorofluoroalkanesulfonamides and *t*-BuNO. Finally, this reaction produced either the unsymmetrical nitroxide **250** or the symmetrical nitroxide **252**, which was dependent upon the nature of the solvent and the amount of **243a** used. Possible mechanistic paths are discussed in Scheme 74.

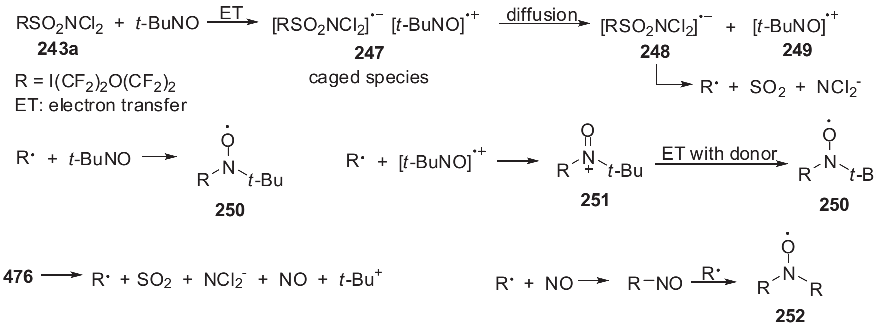
3.4.3. *Synthesis of fluorinated bis(sulfonyl)imides from $X(CF_2CF_2)_nOCF_2CF_2SO_2F$ and their applications in ionic liquids.*

Numerous symmetrical bis(perfluoroalkanesulfonyl)imides ($(R_FSO_2)_2NH$) and unsymmetrical perfluoroalkanesulfonylimides ($R_FSO_2NHSO_2R_F'$) were prepared by the reaction of the sodium salts of the silylated sulfonylamides with the corresponding sulfonyl fluorides.[84] In this approach, the sodium salts of the silylated sulfonylamides (e.g., **253**) were synthesized from sulfonylamides by alkanization and then silylation. Thanks to the strong electron-withdrawing effect of the perfluoroalkanesulfonyl groups, these imides are conceptually defined as 'supper acids'. With $(R_FSO_2)_2NH$ or $R_FSO_2NHSO_2R_F'$ in hand, the versatile derivatives, such as $(R_FSO_2)_2NX$ or $R_FSO_2NXSO_2R_F'$ (X=Cl, NO, NO_2, and $SiMe_3$) and $(R_FSO_2)_2NM$ or $R_FSO_2NMSO_2R_F'$ (M=Cs and Ag) were synthesized.[84]

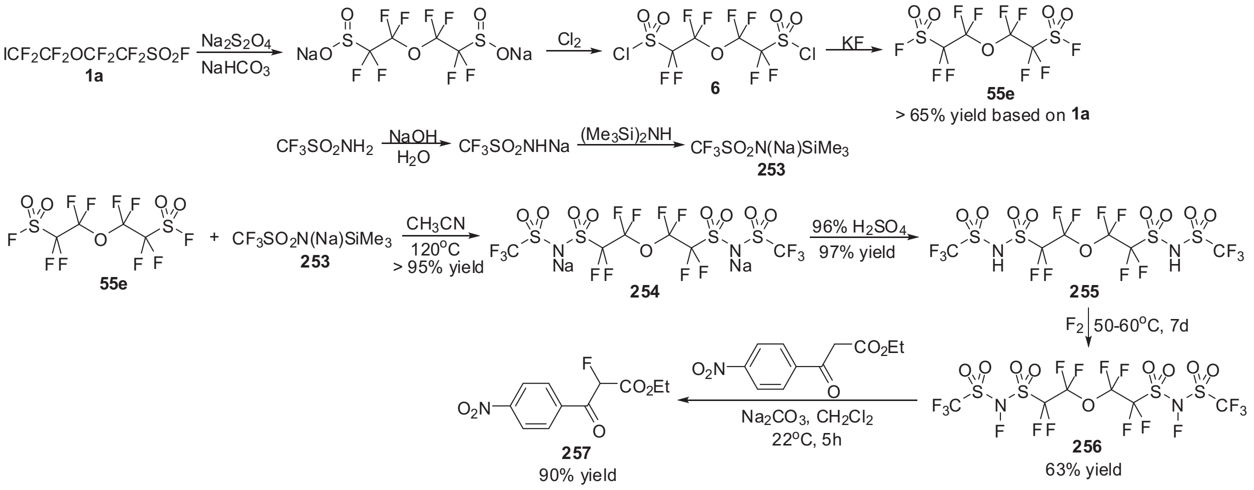
Recently, difunctional *N*,*N*′-difluoroperfluoroalkanesulfonylimide (**256**) possessing an oxygen linkage was prepared in a similar manner (Scheme 75).[85] Initially, α,ω-disulfonyl fluoride **55e** was formed



Scheme 73. Synthesis and reactions of *N*,*N*-dichlorofluoroalkanesulfonamides.



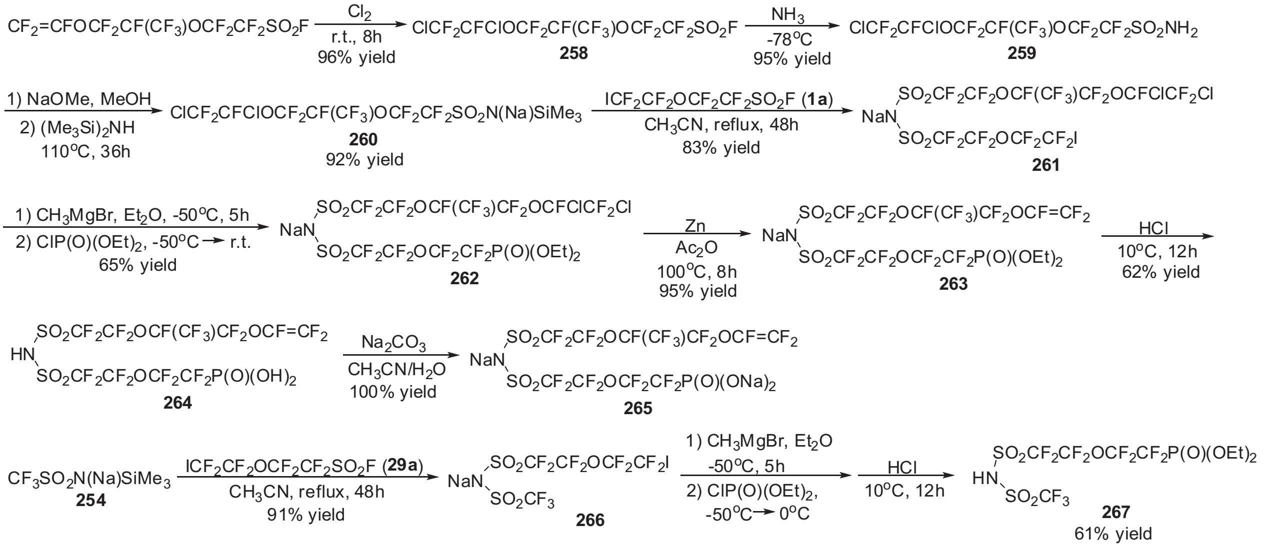
Scheme 74. The electron transfer initiated reaction of *N*,*N*-dichloro-5-iodo-3-oxa-octafluoropentane sulfonyl amide (**243a**) with *t*-BuNO.



Scheme 75. Synthesis and application of the difunctional *N*-fluoro perfluoroalkylsulfonlimide.

from **1a** via sulfinatodehalogenation, chlorination and halogen exchange. Then **55e** reacted with **253** in CH_3CN in a stainless steel bomb at 120 °C for 6 h to afford **254**. Diimide **255** was readily obtained by sublimation from a mixture of **254** and concentrated H_2SO_4 at 70 °C under high vacuum. Fluorination of **255** with F_2 at 50–60 °C for 7 days provided the desired **256** in good yield. Compound **256** is a high boiling colorless liquid with an onset decomposition temperature of 225 °C. It shows good electrophilic fluorination activity similar to $(CF_3SO_2)_2NF$.[84,85] When reacted with 1,3-dicarbonyl compound, only 0.5 equiv of **256** could give a very clean monofluorination.

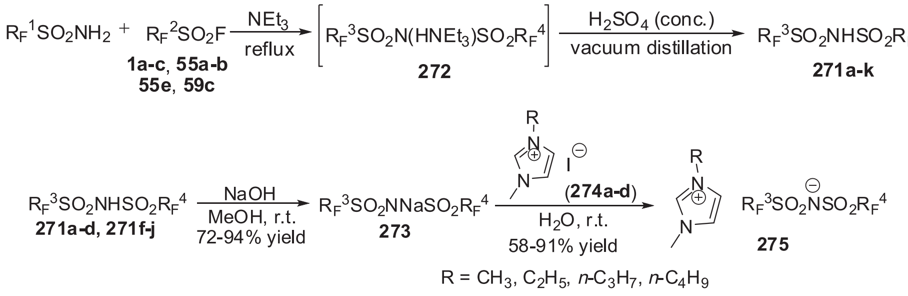
Ethyl 3-oxa-5-(trifluoromethylsulfonimido sulfonyl)octafluoropentyl phosphonate (**267**) and perfluorinated vinyl ethers (**264**), containing both sulfonylimide and phosphonic acid functionalities, were synthesized from **1a** by multiple steps in a similar strategy (Scheme 76).[86a] The key step for the synthesis of **264** was



Scheme 76. Synthesis of novel perfluorinated sulfonimides containing phosphonates from **1a** and its analogues.

the introduction of phosphonate group into the fluoroalkyl chain.[86] The reaction of the silylated sulfonamide **260** with **1a** first gave the intermediate **261**, which was treated with CH_3MgBr followed by coupling with $ClP(O)(OEt)_2$ to provide **262**. This avoided the use of the expensive phosphonation reagent $[(EtO)_2POP(OEt)_2]$ (Scheme 23). Elimination of chlorine from **262** with subsequent acidification and hydrolysis yielded the ultimate product (**264**). Imide **264** is a very strong bi-functional acid, which exhibited a high degree of stability in aqueous solution at an elevated temperature. These properties make it an attractive monomer for the preparation of the copolymer with TFE to obtain the high quality ionomer membrane and proton conductor.

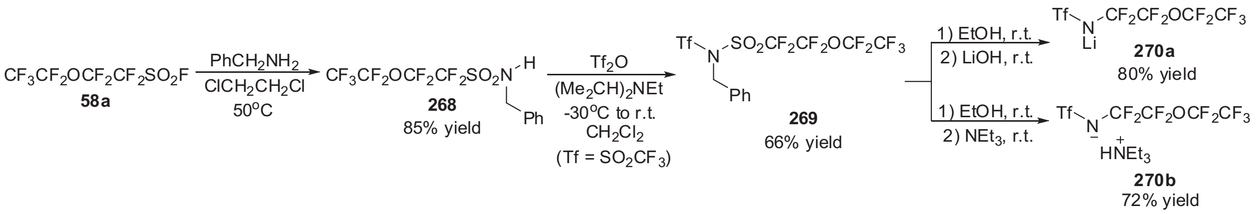
Interestingly, the salts of perfluoroalkanesulfonylimides (e.g., **270a**,**b**) were produced from *N*-benzyl or *N*-allyl perfluoroal-kanesulfonylimides according to an original one-pot procedure (Scheme 77).[87] At first, *N*-benzyl perfluoroalkanesulfonylamides (e.g., **268**) were synthesized from $(R_FSO_2)_2O$ or R_FSO_2F (e.g., **58a**). Second, *N*-benzyl perfluoroalkanesulfonylimides (e.g., **269**) were obtained in one-pot by treatment of *N*-benzyl perfluoroalkanesulfonylamides with Tf_2O in the presence of tertiary amines. *N*-substituted perfluoroalkanesulfonylimides (e.g., **269**) were then treated with ethanol to form oxonium intermediates, which were easily neutralized by various bases to provide metallic or trialkylammonium perfluoralkyl sulfonylimide salts. Such salts can find applications as electrolytes for batteries and fuel cells, ionic liquids or Lewis acids.



A series of bis(fluoroalkanesulfon)amides and unsymmetrical fluoroalkanesulfonylimides were prepared in good yields from the reaction of fluoroalkanesulfonamides and fluoroalkylsulfonyl fluorides (e.g., **1a**–**c**) instead of the reactions between the sodium salts of the silylated sulfonylamides and the corresponding sulfonyl fluorides (Table 9).[88] NEt_3 was used as the solvent as well as the catalyst and reagent for the reaction. Hydrodeiodination of CF_2I group inevitably happened under the basic conditions, thus affording the corresponding hydrogenolysis amides (**271b**–**d**). Similarly, diamides **271i**–**k** were obtained from the reaction of the disulfonyl fluorides with trifluoromethanesulfonamide in NEt_3.

Ionic liquids have attracted significant attention in recent years. Due to their favorable properties, such as high ionic mobility, negligible vapor pressure, wide electrochemical window, good thermal stability, and high conductivity, numerous ionic liquids have been synthesized and used as solvents for electrochemistry, biochemistry, polymer chemistry, organic synthesis, and catalytic process as well as separation science.[89] It has been inferred that using bis(fluoroalkanesulfonyl)imides as the anion, ionic liquids would obtain useful and unique properties. Indeed, ionic liquids consist of the above amide anions and an imidazolium cation demonstrated high densities ranging from 1.66 to 1.95 g/cm^3.[88] Different from the bis(trifluoromethylsulfonyl)imide-based ionic liquids, these fluoroalkanesulfonylimide-based species (**275**) were all liquid at room temperature, showing a rather low glass transition temperature below −80 °C. Moreover, ionic liquids **275** were thermally stable to>390 °C, as determined by thermogravimetric analysis (TGA), demonstrating a wide temperature range for the liquid state.

Later, a series of heavily fluorinated imide-based ionic liquids were synthesized in a one-pot procedure (Scheme 78).[90] The sodium salts of fluoroalkanesulfonylimides and the imidazolium methyl sulfate (**277**) prepared for the ion-exchange reaction were used without any purification. By introduction of fluoroalkyl chain into the imidazolium cation, ionic liquids possessed higher density (>1.98 g/cm^3) with low glass transition temperature (<−45.2 °C), high decomposing temperature (>326.0 °C) and tunable viscosity.

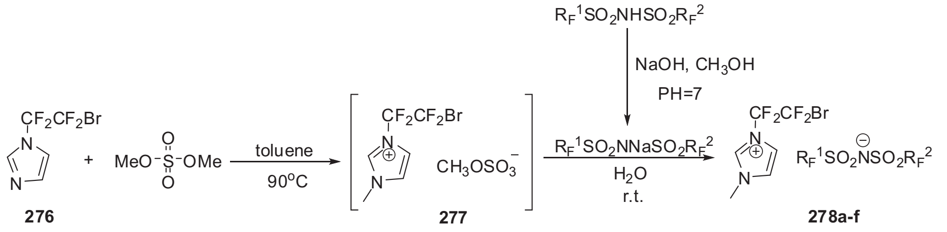


Scheme 77. A simple access to metallic or onium perfluorinated sulfonylimide salts.

Table 9
Preparation of symmetric and asymmetric imides

Entry	R_F^1[a]	$R_F^2SO_2F$	Time (h)	$R_F^3SO_2NHSO_2R_F^4$	Yield (%)[b]
1	$Cl(CF_2)_2$	$Cl(CF_2)_2SO_2F$	12	$[Cl(CF_2)_2SO_2]_2NH$ (**271a**)	81
2	$I(CF_2)_2O(CF_2)_2$	$I(CF_2)_2O(CF_2)_2SO_2F$	29	$[H(CF_2)_2O(CF_2)_2SO_2]_2NH$ (**271b**)	86
3	$I(CF_2)_4O(CF_2)_2$	$I(CF_2)_4O(CF_2)_2SO_2F$	36	$[H(CF_2)_4O(CF_2)_2SO_2]_2NH$ (**271c**)	82
4[c]	$I(CF_2)_6O(CF_2)_2$	$I(CF_2)_6O(CF_2)_2SO_2F$	60	$[H(CF_2)_6O(CF_2)_2SO_2]_2NH$ (**271d**)	41
5[c]	$Cl(CF_2)_6O(CF_2)_2$	$Cl(CF_2)_6O(CF_2)_2SO_2F$	50	$[Cl(CF_2)_6O(CF_2)_2SO_2]_2NH$ (**271e**)	46
6	$CF_3(CF_2)_3$	$I(CF_2)_2O(CF_2)_2SO_2F$	42	$CF_3(CF_2)_3SO_2NHSO_2(CF_2)_2O(CF_2)_2H$ (**271f**)	88
7	$Cl(CF_2)_2$	$I(CF_2)_2O(CF_2)_2SO_2F$	29	$Cl(CF_2)_2SO_2NHSO_2(CF_2)_2O(CF_2)_2H$ (**271g**)	70
8	CF_3	$I(CF_2)_2O(CF_2)_2SO_2F$	37	$CF_3SO_2NHSO_2(CF_2)_2O(CF_2)_2H$ (**271h**)	69
9	CF_3	$FSO_2(CF_2)_2O(CF_2)_2SO_2F$	27	$CF_3SO_2NHSO_2(CF_2)_2O(CF_2)_2SO_2NHSO_2CF_3$ (**271i**)	64
10	CF_3	$FSO_2(CF_2)_2O(CF_2)_4O(CF_2)_2SO_2F$	43	$CF_3SO_2NHSO_2(CF_2)_2O(CF_2)_4O(CF_2)_2SO_2NHSO_2CF_3$ (**271j**)	94
11[c]	CF_3	$FSO_2(CF_2)_2O(CF_2)_8O(CF_2)_2\ SO_2F$	48	$CF_3SO_2NHSO_2(CF_2)_2O(CF_2)_8O(CF_2)_2SO_2NHSO_2CF_3$ (**271k**)	66

[a] $R_F^1SO_2NH_2$ were synthesized according to our previous work.[79]
[b] Isolated yield.
[c] Purified by column chromatography.



278a: $R_F^1 = R_F^2 = CF_3$, 85% yield,
278b: $R_F^1 = R_F^2 = (CF_2)_2Cl$, 71% yield,
278c: $R_F^1 = R_F^2 = (CF_2)_2O(CF_2)_2H$, 81% yield,
278d: $R_F^1 = R_F^2 = (CF_2)_2O(CF_2)_4H$, 85% yield,
278e: $R_F^1 = R_F^2 = (CF_2)_2O(CF_2)_6H$, 72% yield,
278f: $R_F^1 = (CF_2)_2O(CF_2)_2H$, $R_F^2 = (CF_2)_2Cl$, 88% yield

ρ = 1.98 to 2.16 g/cm^3
T_g = -115.9 to -45.2 °C
T_d = 326.0 to 358.4 °C
η = 953.4 to 2960.3 cP (30 °C)
46.4 to 282.4 cP (60 °C)

Scheme 78. Synthesis and properties of room temperature ionic liquids with high density.

4. Summary

This review has summarized the synthesis, reactivity and applications of halo-3-oxa-perfluoroalkanesulfonyl fluorides. Compared to $ICF_2CF_2OCF_2CF_2SO_2F$ as a trifluoromethylation reagent,[4h] $X(CF_2CF_2)_nOCF_2CF_2SO_2F$ (X=H, F, Cl, Br, I; n=1–4) are more concerned as versatile fluoroalkylation reagents. $X(CF_2CF_2)_nOCF_2CF_2SO_2F$ have both reactive sulfonyl and halo groups, which are easily functionalized. The reactions of $I(CF_2CF_2)_nOCF_2CF_2SO_2F$ with reductants (such as $Na_2S_2O_4$, Zn), single electron transfer reagents and radical initiator systems (like Bz_2O_2, AIBN and $(t\text{-}BuO)_2$, or under UV and heat) gave, respectively, the sulfinatodehalogenated products, the hydrodehalogenated products, the homo-coupling products and the perfluoroalkylated products (if alkenes, alkynes or arenes were added). Hydrolysis, esterification, amidation or fluorination of $X(CF_2CF_2)_nOCF_2CF_2SO_2F$ provided perfluoroalkanesulfonic acids, perfluoroalkanesulfonates, fluoroalkanesulfonamide or perfluoroalkanes, which finally yielded thousands of useful highly fluorinated compounds. $X(CF_2CF_2)_nOCF_2CF_2SO_2F$ and their derivatives have promising advantages: the easy and cheap preparation, the wide range of substrate tolerance, the mild reaction conditions and the high yields of desired products make them very attractive. To feed the increasing requirement of utilizing the unique properties of fluorine and fluorinated functional groups in areas of medicinal chemistry and material science, $X(CF_2CF_2)_nOCF_2CF_2SO_2F$ will be more thoroughly studied in the near future.

Acknowledgements

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