IF_5-pyridine-HF: air- and moisture-stable fluorination reagent

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ABSTRACT : IF_5-pyridine-HF, an air- and moisture-stable solid, can be used as a fluorination reagent for the introduction of fluorine atoms to the α-position of the sulfur atom in sulfides. The desulfurizing-fluorination reactions of benzylic sulfides, thioacetals, and 2-(methylthio)-1,3-dithiane derivatives were also performed using this reagent.

Keywords:IF_5-pyridine-HF, air- and moisture-stable solid, fluorination reagent, desulfurizing-fluorination

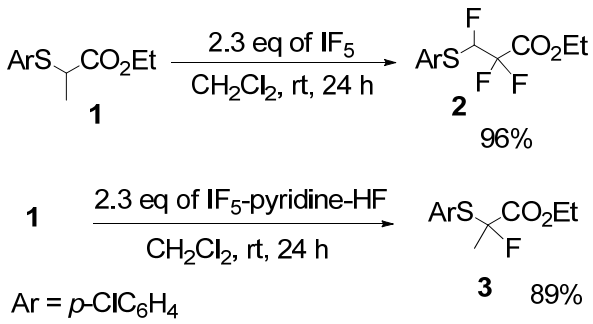
1. Introduction

Organofluorine compounds are widely used, as medicines, pesticides, functional materials, and so on.[1] They are generally prepared artificially by using fluorination reagents because organofluorine compounds are rare in nature. Therefore, the role of the fluorination reagent is important for making the desired organofluorine compounds, and many fluorination reagents have been produced and used.[1b,2] However, most of them are sensitive to air and moisture, and special skills and equipments are required for their use. Therefore, more stable fluorination reagents that can be used without such skills and equipments are desired.[3] We previously reported fluorination reactions using IF_5 for the selective introduction of fluorine atoms to a substrate.[4] However, IF_5 is also unstable in air and decomposes, generating HF. During our continuous study of fluorination reactions using IF_5, we found that upon mixing IF_5 with pyridine-HF (HF 50 mol% pyridine 50 mol%), an air-stable white solid was formed.[5] Herein, we report the fluorination reactions using this stable fluorination reagent, IF_5-pyridine-HF.[6]

2. Results and discussion

Initially, we compared the reactivity of IF_5-pyridine-HF with that of IF_5. In the reaction of IF_5 with ethyl 2-(arylthio)propionate **1**, a *poly*-fluorination reaction took place with the migration of an arylthio group to give ethyl 3-(arylthio)-2,2,3-trifluoropropionate **2** selectively.[4f] On the other hand, when **1** was added to a suspension of IF_5-pyridine-HF in CH_2Cl_2,[8] the color of the mixture changed to dark red, and

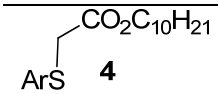
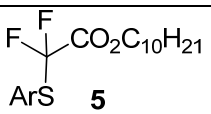
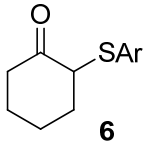
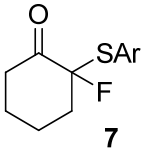
mono-fluorination occurred at the α-position of the sulfur group, giving ethyl 2-(arylthio)-2-fluoropropionate **3**. Under these conditions, **2** was not formed at all (Scheme 1).



Scheme 1. Reactivity of IF_5-pyridine-HF in fluorination of sulfide **1**

In the reaction of decyl 2-arylthioacetate **4** with two equivalents of IF_5-pyridine-HF, the mono-fluorinated product was obtained in 63% yield, with a 17% yield of the difluorinated product **5**; it was difficult to obtain the mono-fluorinated product selectively. On the other hand, when four equivalents of IF_5-pyridine-HF were used, **5** was formed selectively in 54% yield, and the yield of the mono-fluorinated product was only 3%. From 2-(arylthio)cyclohexanone **6**, the mono-fluorinated product **7** was obtained in 76% yield, as shown in Table 1.

Table 1. Fluorination of α-(arylthio)carbonyl compounds using IF_5-pyridine-HF[a]

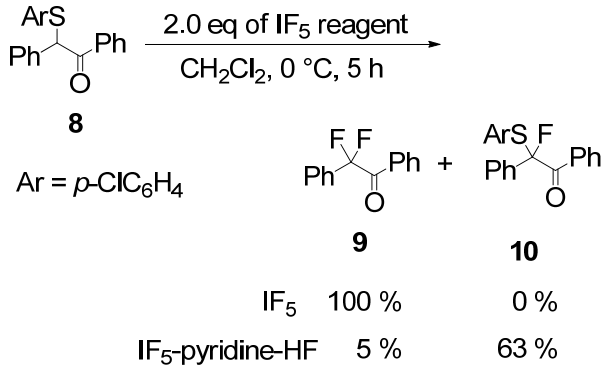
Substrate	IF_5-pyridine-HF/substrate	Product	Yield %[b]
 **4**	4.0	 **5**	54[c]
 **6**	2.0	 **7**	76

[a] The reaction was carried out in CH_2Cl_2 at room temperature for 24 h, Ar = *p*-Cl-C_6H_4.

[b] Isolation yield based on substrate.

[c]Mono-fluorinated product was also formed in 3% yield.

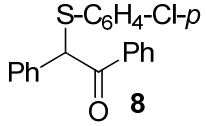
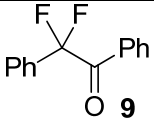
The desulfurizing-difluorination reaction of benzylic sulfide is one of the typical reactions of IF_5.[4e] When 2-(arylthio)-1,2-diphenylethanone **8** was subjected to the reaction with IF_5 at 0 °C for 5 h, the desulfurizing-difluorination reaction took place to give 2,2-difluoro-1,2-diphenylethanone **9** exclusively. On the other hand, in the reaction of IF_5-pyridine-HF with **8** under the same conditions, the yield of **9** was only 5% and formation of a new fluorine compound was observed. From chemical shift in ^{19}F NMR spectra, the new compound was estimated to be mono-fluorinated compound **10**[9] and its yield was 63%. In the desulfurizing-difluorination reaction of **8**, **10** was formed initially as a precursor of **9**.[4e] Therefore, in the reaction of **8** with IF_5-pyridine-HF, the desulfurizing-difluorination was not yet completed under these conditions, and the reactivity of IF_5-pyridine-HF was found to be lower than that of IF_5 (Scheme 2).

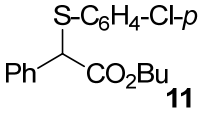
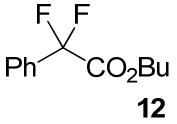
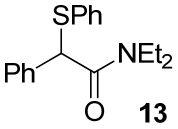
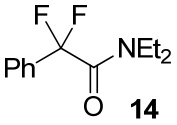
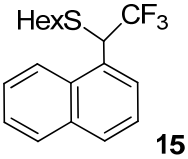
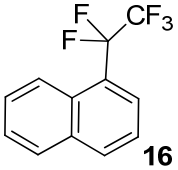
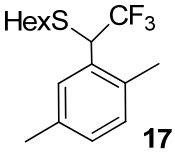
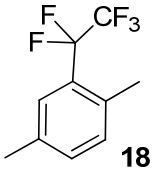


Scheme 2. Reactivity of IF_5-pyridine-HF in desulfurizing-difluorination reaction of **8**

Although the desulfurizing-difluorination reaction of **8** with IF_5-pyridine-HF was slow at 0 °C, the reaction was completed at room temperature in 5 h, and **9** was obtained in 88% yield (Entry 1 in Table 2). Similarly, the reactions of various benzylic sulfides (**11**, **13**, **15**, and **17**) with IF_5-pyridine-HF proceeded at room temperature or at 40 °C to give the corresponding desulfurizing-difluorination products (**12**, **14**, **16**, and **18**) in good yields.

Table 2. Desulfurizing-difluorination of benzylic sulfides using IF_5-pyridine-HF[a]

Entry	Substrate	Reaction conditions	Product	Yield %[b]
1	 **8**	rt, 5 h	 **9**	88

2	 **11**	rt, 24 h	 **12**	89[c]
3	 **13**	rt, 5 h	 **14**	79
4	 **15**	40 °C, 24 h	 **16**	98[d]
5	 **17**	40 °C, 24 h	 **18**	(99)[d]

[a] If otherwise not mentioned, the reaction was carried out in CH_2Cl_2 using 2 eq of IF_5-pyridine-HF.

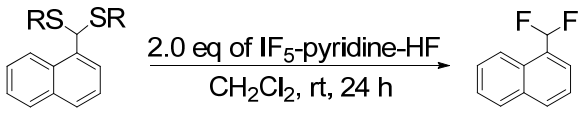
[b] Isolation yield based on substrate, in parenthesis, ^{19}F NMR yield.

[c] 1.5 eq of IF_5-pyridine-HF was used.

[d] 3 eq of IF_5-pyridine-HF was used.

The conversion of carbonyl dithioacetal to *gem*-difluoride is commonly used to introduce fluorine atoms selectively at desired positions in the molecules; many fluorination reagents have been used for this conversion.[10] Therefore, we applied IF_5-pyridine-HF to the reaction with the carbonyl dithioacetal. The reactions of various 1-naphthaldehyde dithioacetals with IF_5-pyridine-HF were examined. When the 1,3-dithiolane derivative was used, the desired *gem*-difluoride was obtained in 57% yield, and 1-naphthaldehyde was also formed in 10% yield (Entry 1 in Table 3). Similar results were obtained with the 1,3-dithiane derivative and bis(hexylthio)methane derivative (Entries 2 and 3). However, when the bis(phenylthio)methane derivative was used, the *gem*-difluoride was obtained in the highest yield of 74% (Entry 4).

Table 3. The Reaction of naphthaldehyde dithioacetals with IF_5-pyridine-HF[a]



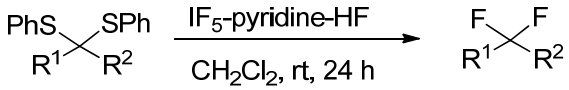
Entry	R	Yield %[b]
1	-$(CH_2)_2$-	57
2	-$(CH_2)_3$-	50
3	C_6H_{13}	59
4	Ph	74

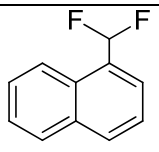
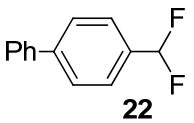
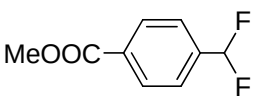
[a] The reaction was carried out in CH_2Cl_2 using 2 eq of IF_5-pyridine-HF.

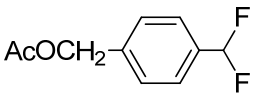
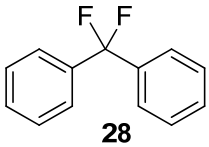
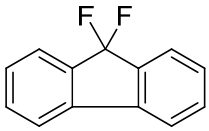
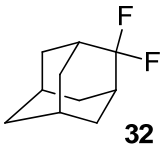
[b] Isolation yield based on dithioacetal used.

From various bis(phenylthio)acetals of aromatic aldehydes and ketones, the corresponding *gem*-difluorides were obtained in good yields. A dithioacetal of an aliphatic ketone, such as adamantanone, is also applicable to this reaction, and 2,2-difluoroadamantane **32** was obtained (Entry 7 in Table 4). However, in the reaction with the bis(phenylthio)acetal of acetophenone, which has protons at the α-position of the carbonyl group, the desired *gem*-difluoride was not obtained, but a complex mixture was formed.

Table 4. The reaction of aldehyde and ketone dithioacetals with IF_5-pyridine-HF[a]



Entry	Product	Yield %[b]
1	 **20**	74
2	 **22**	91
3	 **24**	75

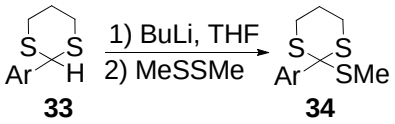
4	 **26**	70
5	 **28**	92
6	 **30**	82
7	 **32**	62

[a] The reaction was carried out in CH_2Cl_2 at room temperature for 24 h using 2 eq of IF_5-pyridine-HF.

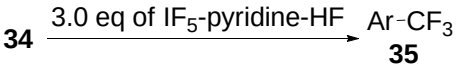
[b] Isolation yield based on dithioacetal used.

The introduction of the trifluoromethyl group to an aromatic ring is an important reaction, and many methods for this have been reported.[11] We planned to make a trifluoromethyl compound by the reaction of the 2-methylthio-1,3-dithiane derivative **34** with IF_5-pyridine-HF. The starting compound **34** was prepared from the 1,3-dithiane derivative **33** of an aromatic aldehyde by metalation with BuLi, followed by reaction with dimethyl disulfide.[12] The reaction of the 2-(methylthio)-1,3-dithiane derivative of 1-naphthaldehyde **34a** with IF_5-pyridine-HF was completed at room temperature in 12 h, and 1-trifluoromethylnaphthalene **35a** was obtained in 78% yield.[13] When an electron-donating group was attached to the aromatic ring (**34e**), the reaction with IF_5-pyridine-HF was fast and the reaction was completed in a shorter time. On the other hand, when an electron-withdrawing group was attached (**34c**), the reaction was slower and a higher temperature (40 °C) was required to obtain the trifluoromethyl product **35c**, as shown in Table 5. The application of the present method to an aliphatic aldehyde was not successful and the corresponding trifluoromethyl derivative was not formed by the reaction of the 2-(methylthio)-1,3-dithiane derivative of the aliphatic aldehyde with IF_5-pyridine-HF.

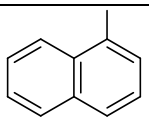
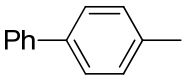
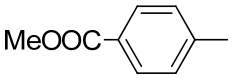
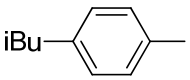
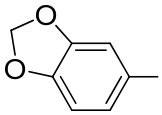
Table 5. Conversion of aldehyde thioacetal to trifluoromethyl group



33 **34**



35

Ar	Yield of **34**, %[a]	Reaction condition s	Yield of **35,** %[b]
 **33a**	87	rt, 12 h	78
 **33b**	92	rt, 24 h	83
 **33c**	61[c]	40 C, 48 h	54
 **33d**	61	rt, 24 h	62
 **33e**	71	rt, 7 h	60

[a] Isolated yield based on thioacetal **33**.

[b] Isolated yield based on thioorthoformate **34**. 3 eq of IF_5-pyridine-HF to **34** was used.

[c] LDA was used as a base instead of BuLi.

3. Conclusion

IF_5-pyridine-HF, prepared by mixing IF_5 with pyridine-HF, is an air- and moisture-stable white solid. Although its reactivity is lower than that of IF_5, it can be used safely for fluorination reactions such as the introduction of one or two fluorine atoms to the α-position of the sulfur atom in sulfides, and the

introduction of two or three fluorine atoms by the desulfurizing-fluorination reaction of benzylic sulfides, thioacetals, and 2-(methylthio)-1,3-dithiane derivatives.

4. Experimental section

General Methods. The melting points were measured with a Yanagimoto micro melting-point apparatus. The IR spectra were recorded using a JASCO FT/IR-410. The ^{1}H NMR (400 MHz) spectra, ^{19}F NMR (376 MHz) spectra, and ^{13}C NMR (100 MHz) were recorded in $CDCl_3$ on a JEOL JNM-A400II FT NMR and the chemical shift, δ, is referred to TMS (^{1}H, ^{13}C) and $CFCl_3$ (^{19}F), respectively. The EI-high-resolution mass spectra were measured on a JEOL JMS-700TZ. IF_5 in a cyclinder was supplied by Asahi Glass Co., Ltd. Although IF_5-pyridine-HF can be handled in air without special care, IF_5 is hygroscopic and decomposes in air. Therefore, when IF_5-pyridine-HF is prepared, IF_5 should be handled in bench hood with rubber gloved hands. The reaction using IF_5-pyridine-HF was perfoemed in a Teflon™ FEP centrifuge tube with a tight screw cap or a reactor made of polyethylene. Silicate glassware is slightly damaged by it.

Preparation of pyridine-HF (HF 50 mol% pyridine 50 mol%). Pyridine-HF was prepared by the addition of freshly distilled pyridine to an equimolar amount of anhydrous HF at 0 °C. As it is highly exothermal, slow and careful additon of pyridine is required. More conveniently, it can be prepared by dilution of commercial pyridine-HF (HF 70w% pyridine 30w%) with calculated amount of pyridine at 0 °C. It is also exothermal but milder.

Preparation of IF_5-pyridine-HF. From a cylinder, IF_5 (30g, 135 mmol) was transferred through a Teflon™ tube into a 500mL round bottomed flask made of Teflon™PFA under an N_2 atmosphere. The flask was cooled with ice bath and CCl_4 (135 mL) was introduced. Then, pyridine-HF (13.38 g, 135 mmol) was dropwisely added at 0 °C. A white solid appeared immediately and the resulting mixture was stirred at 0 °C for 30 min and at room temperature for 2 h. The solid was separated by filtration using filter funnel made of polyethylene and filter paper made of Teflon™, washed with CCl_4 (150 mL X 2). The remained solvent was removed under vacuum to give 41 g of a white solid (95% yield), which can be handled in air and kept in a Teflon™ bottle. IF_5-pyridine-HF decompose gradually above 100 °C, and it is soluble in DMF, slightly soluble in CH_3CN, and insoluble in hexane; ^{1}H NMR (400MHz, CD_3CN) δ 8.75-8.72 (m, 2H), 8.60-8.55 (m, 1H), 8.60-8.55 (m, 2H). ^{19}F NMR (376MHz, CD_3CN) δ -149.17 (s).

4.1. Fluorination of sulfide with IF_5-pyridine-HF

*4.1.1. Ethyl 2-[(4-chlorophenyl)thio]-2-fluoropropanoate (**3**)*

To a CH_2Cl_2 solution (2 mL) of ethyl 2-[(4-chlorophenyl)thio]propanoate (**1**) (122 mg, 0.5 mmol) was added at room temperature IF_5-pyridine-HF (370 mg, 1.15 mmol), and the

mixture was stirred at room temperature for 24 h. The resulting dark red solution was poured into water (20 mL) and extracted with CH_2Cl_2 (20 mL X 3). The combined organic layer was washed with aq $NaHCO_3$ and aq $Na_2S_2O_3$, and dried over $MgSO_4$. After concentration under reduced pressure, **3** was isolated in 89% yield by column chromatography (silica gel/hexane-ether); IR (neat) 2985, 1754 (C=O), 1476, 1279, 1127 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.3 Hz, 2H), 4.10-3.98 (m, 2H), 1.90 (d, *J* = 18.3 Hz, 3H), 1.11 (t, *J* = 7.2 Hz, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ –127.1 (q, *J* = 18.5 Hz, 1F); ^{13}C NMR (100 MHz) δ 167.7 (d, $^2J_{F-C}$ = 30.6 Hz), 136.9 (2C), 136.3, 129.1 (2C), 127.5, 101.6 (d, $^1J_{F-C}$ =233.7 Hz), 62.2, 24.2 (d, $^2J_{F-C}$ = 24.8 Hz), 13.8; HRMS (EI) calcd for $C_{11}H_{12}ClFO_2S$ 262.02306, found 262.02227.

*4.1.2. Decyl 2-[(4-chlorophenyl)thio]-2,2-difluoroacetate (**5**)*

IR (neat) 2926, 2855, 1767, 1293, 1113 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.4 Hz, 2H), 7.38 (d, *J* = 8.4 Hz, 2H), 4.21 (t, *J* = 6.7 Hz, 2H), 1.65-1.62 (m, 2H), 1.29-1.27 (m, 14H), 0.89 (t, *J* = 6.7 Hz, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ –82.57 (s, 2F); ^{13}C NMR (100 MHz) δ 161.5 (t, $^2J_{F-C}$ = 32.2 Hz), 137.8 (2C), 137.3, 129.5 (2C), 123.2 (t, $^3J_{F-C}$ = 2.8 Hz), 119.7 (t, $^1J_{F-C}$ =288.0 Hz), 67.8, 31.9, 29.5, 29.4, 29.3, 29.1, 28.1, 25.5, 22.7, 14.1; HRMS (EI) calcd for $C_{18}H_{25}ClF_2O_2S$ 378.1232, found 378.1230.

*4.1.3. 2-[(4-Chlorophenyl)thio]-2-fluorocyclohexanone (**7**)*

White solid; mp 54.5–55.5 °C. IR (KBr) 2950, 1729, 1477 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.45-7.42 (m, 2H), 7.33-7.29 (m, 2H), 2.91-2.82 (m, 1H), 2.50-2.34 (m, 2H), 2.25-1.90 (m, 4H), 1.77-1.65 (m, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ –128.13 (d, *J* = 12.4 Hz, 1F). ^{13}C NMR (100 MHz) δ 200.3 (d, $^2J_{F-C}$ = 20.0 Hz), 136.1 (2C), 129.4 (3C), 126.4 (d, $^3J_{F-C}$ = 1.9 Hz), 105.2 (d, $^1J_{F-C}$ = 238.6 Hz), 38.9, 38.7 (d, $^2J_{F-C}$ = 20.1 Hz), 26.7, 23.1 (d, $^3J_{F-C}$ = 6.7 Hz); HRMS (EI) calcd for $C_{12}H_{12}ClFOS$ 258.0281, found 258.0281.

4.2. Desulfurizing difluorination of a benzylic sulfide with IF_5-pyridine-HF

*4.2.1. 2,2-Difluoro-1,2-diphenylethanone (**9**)*

To a CH_2Cl_2 solution (2 mL) of the 2-[(4-chlorophenyl)thio]-1,2-diphenylethanone (**8**) (169 mg, 0.5 mmol) was added at room temperature IF_5-pyridine-HF (322 mg, 1 mmol). The mixture was stirred at room temperature for 5 h. The resulting dark red solution was poured into water (20 mL) and extracted with CH_2Cl_2 (20 mL X 3). The combined organic layer was washed with aq $NaHCO_3$ and aq $Na_2S_2O_3$, and dried over $MgSO_4$. After concentration under reduced pressure, **9** was isolated in 88% yield by column chromatography (silica gel/hexane-CH_2Cl_2); IR (neat) 1703 (C=O), 1450, 1256, 1135 cm^{-1}; ^1H NMR (400MHz, $CDCl_3$) δ 7.43–7.61 (m, 8H), 8.02–8.04 (m, 2H); ^{19}F NMR (376MHz, $CDCl_3$) δ –98.12 (s, 2F) {lit[14] –98.44 (s, 2F)}; ^{13}C NMR (100MHz, $CDCl_3$) δ 116.88 (t, $^1J_{c-F}$ = 253.9 Hz), 125.59 (t, $^3J_{c-F}$ = 5.8 Hz,

2C), 128.62 (2C), 128.81 (2C), 130.25 (t, $^{4}J_{c\text{-}F}$ = 2.9 Hz, 2C), 130.91, 132.10, 133.08 (t, $^{2}J_{c\text{-}F}$ = 24.9 Hz), 134.20, 188.94 (t, $^{2}J_{c\text{-}F}$ = 30.7 Hz); HRMS (EI) calcd for $C_{14}H_{10}F_2O$: (M^+) 232.0700. Found: 232.0683.

When the reaction was carried out at 0 °C for 5 h, two singlet peaks appeared at -98 ppm for **9** and at -128 ppm for **10**[9] in ^{19}F NMR. Their yields were determined to be 5% (**9**) and 63% (**10**) by using fluorobenzene as a internal standard. During the isolation by silica gel column chromatography, **10** was decomposed and its isolation was failed.

*4.2.2. Butyl 2,2-difluoro-2-phenylacetate (**12**)*

IR (neat) 2963, 1764 (C=O), 1265, 1105 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62-7.60 (m, 2H), 7.49-7.45 (m, 3H), 4.24 (t, *J* = 6.6 Hz, 2H), 1.68-1.60 (m, 2H), 1.37-1.28 (m, 2H), 0.90 (t, *J* = 7.4 Hz, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ –104.65 (s, 2F); ^{13}C NMR (100 MHz) δ 164.3 (t, $^{2}J_{F\text{-}C}$ = 35.7 Hz), 132.8 (t, $^{2}J_{F\text{-}C}$ = 25.8 Hz), 130.9, 128.6 (2C), 125.4 (t, $^{3}J_{F\text{-}C}$ = 6.2 Hz, 2C), 113.4 (t, $^{1}J_{F\text{-}C}$ =251.9 Hz), 66.8, 30.2, 18.9, 13.5; HRMS (EI) calcd for $C_{12}H_{14}F_2O_2$ 228.09619, found 228.09563.

*4.2.3. N,N-Diethyl-2,2-difluoro-2-phenylacetamide (**14**)*

IR (neat) 2979, 1669(C=O), 1452, 1364, 1260, 1178, 1093, 858, 775, 700, 642 cm^{-1}; ^{1}H NMR (400MHz, $CDCl_3$) δ 7.56 (d, *J* = 7.0 Hz, 2H), 7.44-7.49 (m, 3H), 3.42 (q, *J* = 7.2 Hz, 2H), 3.25 (q, *J* = 7.2 Hz, 2H), 1.17 (t, *J* = 7.2Hz, 3H), 1.03 (t, *J* = 7.0 Hz, 3H); ^{19}F NMR (376MHz, $CDCl_3$) δ -95.41 (s, 2F); ^{13}C NMR (100MHz, $CDCl_3$) δ 162.7 (t, $^{2}J_{C\text{-}F}$ = 29.7 Hz), 133.9 (t, $^{2}J_{C\text{-}F}$ = 23.6 Hz), 130.7 (t, $^{4}J_{C\text{-}F}$ = 1.9 Hz, 2C), 128.7, 125.1 (t, $^{3}J_{C\text{-}F}$ = 5.8 Hz, 2C), 115.5 (t, $^{1}J_{C\text{-}F}$ = 251.5 Hz), 42.0 (t, $^{4}J_{C\text{-}F}$ = 3.8 Hz), 41.4, 13.7, 12.2; HRMS(EI) calcd for $C_{12}H_{15}F_2NO$ 227.1122, found 227.1128.

*4.2.4. 1-(Perfluoroethyl)naphthalene (**16**)*

IR (neat) 3059, 1133 cm^{-1}; ^{1}H NMR δ 7.52-7.62 (m, 3H), 7.83 (d, *J* = 7.3 Hz, 1H), 7.92 (d, *J* = 8.3 Hz, 1H), 8.04 (*J* = 8.2 Hz, 1H), 8.24 (d, *J* = 8.3 Hz, 1H); ^{19}F NMR δ -83.97 (s, 3F), -108.90 (s, 2F) (lit.[15] -83.8 (3F, s), -108.9 (2F, s)); ^{13}C NMR δ 134.1, 133.3, 129.9, 129.0, 127.6, 127.4 (t, $^{3}J_{C\text{-}F}$ = 9.5 Hz), 126.4, 124.7-124.8 (m), 124.3, 124.2 (t, $^{2}J_{C\text{-}F}$ = 21.7 Hz), 119.7 (tq, $^{2}J_{C\text{-}F}$ = 39.3 Hz, $^{1}J_{C\text{-}F}$ = 287.0 Hz), 115.3 (tq, $^{1}J_{C\text{-}F}$ = 255.3 Hz, $^{2}J_{C\text{-}F}$ = 39.4 Hz).

*4.2.5. 1,4-Dimethyl-2-(perfluoroethyl)benzene (**18**)*

IR (neat) 2931, 1207, 1187 cm^{-1}; ^{1}H NMR δ 7.14-7.31 (m, 3H), 2.43 (t, *J* = 3.0 Hz, 3H), 2.36 (s, 3H); ^{19}F NMR δ -85.24 (s, 3F), -111.07 (s, 2F), (lit.[4g] -84.86 (s, 3F), -110.94 (s, 2F)); ^{13}C NMR δ 135.8, 134.7 (t, $^{3}J_{C\text{-}F}$ = 2.2 Hz), 132.5, 132.4, 128.5 (t, $^{3}J_{C\text{-}F}$ = 8.6 Hz), 126.6 (t, $^{2}J_{C\text{-}F}$ = 21.7 Hz), 119.7 (tq, $^{2}J_{C\text{-}F}$ = 40.1 Hz, $^{1}J_{C\text{-}F}$ = 286.1), 115.0 (tq, $^{1}J_{C\text{-}F}$ = 254.2 Hz, $^{2}J_{C\text{-}F}$ = 38.2 Hz), 20.7, 19.7-19.8 (m).

4.3. Desulfurizing-fluorination of dithioacetal with IF_5-pyridine-HF

*4.3.1. 1-(Difluoromethyl)naphthalene (**20**)*

To a CH_2Cl_2 solution (1.0 mL) of naphthaldehyde diphenyl dithioacetal (**19**) (179 mg, 0.5 mmol) was added at room temperature IF_5-pyridine-HF (321 mg, 1 mmol) and the mixture was stirred at room temperature for 24h. The resulting dark red solution was poured into water (20 mL) and extracted with ether (20 mL X 3). The combined organic layer was washed with aq $NaHCO_3$ and aq $Na_2S_2O_3$, and dried over $MgSO_4$. After concentration under reduced pressure, **20** was isolated by column chromatography (silica gel/hexane-CH_2Cl_2) in 74% yield; IR (neat) 1514, 1349, 1242 cm^{-1}; ^1H NMR δ 8.19-7.49 (m, 7H), 7.14 (t, J = 55.8 Hz, 1H); ^{19}F NMR δ -111.48 (d, J = 56.0 Hz, 2F) (lit.[16] -111.1); ^{13}C NMR δ 133.7, 131.5, 129.7, 129.5 (t, $^2J_{C-F}$ = 21.1 Hz), 128.7, 127.1, 126.4, 124.8 (t, $^3J_{C-F}$ = 8.6 Hz), 124.6, 123.5, 115.4 (t, $^1J_{C-F}$ = 239.5 Hz).

*4.3.2. 4-(Difluoromethyl)-1,1'-biphenyl (**22**)*

White solid. mp 71-72 °C (lit.[17] 77.0-77.5 °C); IR (KBr) 1414, 1380, 1226, 1077, 1024, 767 cm^{-1}; ^1H NMR δ 7.69-7.39 (m, 9H), 6.70 (t, J = 56.5 Hz, 1H); ^{19}F NMR δ -110.98 (d, J = 57.3 Hz, 2F); ^{13}C NMR δ 143.7 (t, $^5J_{C-F}$ = 1.9 Hz), 140.2, 133.2 (t, $^2J_{C-F}$ = 22.1 Hz), 128.9 (2C), 127.9, 127.4 (2C), 127.2 (2C), 126.0 (t, $^3J_{C-F}$ = 6.2 Hz, 2C), 114.7 (t, $^1J_{C-F}$ = 238.5 Hz).

*4.3.3. Methyl 4-(difluoromethyl)benzoate (**24**)*

White solid. mp 38 °C (lit.[18] 36.5-37.0 °C); IR (KBr) 1724 (C=O), 1442, 1281 cm^{-1}; ^1H NMR δ 8.13 (d, J = 8.0 Hz, 2H), 7.59 (d, J = 8.1 Hz, 2H), 6.70 (t, J = 56.7 Hz, 1H), 3.95 (s, 3H); ^{19}F NMR δ -112.86 (d, J = 57.9 Hz, 2F); ^{13}C NMR δ 166.2, 138.4 (t, $^2J_{C-F}$ = 22.5 Hz), 132.3 (t, $^4J_{C-F}$ = 1.9 Hz), 129.9 (2C), 125.6 (t, $^3J_{C-F}$ = 6.3 Hz, 2C), 114.0 (t, $^1J_{C-F}$ = 240.9 Hz), 52.3.

*4.3.4. 4-(Difluoromethyl)benzyl acetate (**26**)*

IR (neat) 2961, 1743 (C=O), 1380, 1227 cm^{-1}; ^1H NMR δ 7.51 (d, J = 8.2 Hz, 2H), 7.44 (d, J = 8.1 Hz, 2H), 6.65 (t, J = 57.0 Hz, 1H), 5.14 (s, 2H), 2.12 (s, 3H); ^{19}F NMR δ -111.35 (d, J = 56.0 Hz, 2F); ^{13}C NMR δ 170.7, 138.7 (t, $^5J_{C-F}$ = 1.9 Hz), 134.2 (t, $^2J_{C-F}$ = 22.8 Hz), 128.2 (2C), 125.8 (t, $^3J_{C-F}$ = 6.2 Hz, 2C), 114.4 (t, $^1J_{C-F}$ = 240.0 Hz), 65.5, 20.8; HRMS (EI) calcd for $C_{10}H_{10}F_2O_2$ 200.06489, found 200.06395.

*4.3.5. Difluorodiphenylmethane (**28**)*

IR (neat) 1453, 1274, 1223 cm^{-1}; ^1H NMR δ 7.51-7.41 (m, 10H); ^{19}F NMR δ -89.43 (s, 2F) (lit.[10f] -89); ^{13}C NMR δ 137.6 (t, $^2J_{C-F}$ = 28.3 Hz, 2C), 129.8 (t, $^3J_{C-F}$ = 1.9 Hz, 4C), 128.4 (2C), 125.8 (4C), 120.7 (t, $^1J_{C-F}$ = 243.0 Hz).

*4.3.6. 9,9-Difluoro-9H-fluorene (**30**)*

White solid. mp 46-48 °C (lit.[19] 47-48 °C). IR (KBr) 1918, 1454, 1261 cm^{-1}; ^1H NMR δ 7.62 (d, *J* = 7.0 Hz, 2H), 7.56 (d, *J* = 7.3 Hz, 2H), 7.45 (dd, *J* = 7.5, 7.5 Hz, 2H), 7.33 (dd, *J* = 7.6, 7.6 Hz, 2H); ^{19} F NMR δ -112.12 (s, 2F); ^{13}C NMR δ 139.4 (t, $^3J_{C\text{-}F}$ = 5.3 Hz, 2C), 137.9 (t, $^2J_{C\text{-}F}$ = 25.1 Hz, 2C), 132.0 (2C), 128.7 (2C), 123.7 (2C), 123.2 (t, $^1J_{C\text{-}F}$ = 244.0 Hz), 120.3 (2C).

*4.3.7. 2,2-Difluoroadamantane (**32**)*

White solid. mp 102-103 °C (lit.[4d] 104-105 °C); IR (KBr).2938, 2917, 1389, 1121 cm^{-1}; ^1H NMR δ 2.18 (brs, 2H), 1.97 (brs, 2H), 1.94 (brs, 2H), 1.86 (brs, 2H), 1.78-1.72 (m, 6H); ^{19}F NMR δ -100.41 (s, 2F); ^{13}C NMR δ 125.5 (t, $^1J_{C\text{-}F}$ = 248.2 Hz), 36.6 (2C), 35.8 (t, $^2J_{C\text{-}F}$ = 4.0 Hz, 2C), 34.0 (t, $^3J_{C\text{-}F}$ = 4.0 Hz, 4C), 26.4.

4.4. Methylthiolation of 1,3-dithiane derivatives

*4.4.1. 2-(Methylthio)-2-(naphthalen-1-yl)-1,3-dithiane (**34a**)*

To a THF solution (6 mL) of 2-(naphthalene-1-yl)-1,3-dithiane (**33a**) (246 mg, 1 mmol) was added at -30 °C a 1.6 M hexane solution of BuLi (0.63 mL, 1 mmol), and the mixture was stirred at 0 °C for 1.5h. Then, dimethyl disulfide (188 mg, 2 mmol) was added and the mixture was stirred at 0 °C for 2 h and at room temperature over night. The reaction mixture was poured into water (20 mL) and extracted with ether (20 mL X 3). The combined organic layer was dried over $MgSO_4$, and concentrated under reduced pressure. Purification by column chromatography (silica gel/ hexane-ether) gave **34a** in 87% yield; White solid, mp 104-105 °C; IR (KBr) 2912, 783 cm^{-1}; ^1H NMR δ 9.49 (d, *J* = 8.6 Hz, 1H), 8.16 (d, *J* = 7.3 Hz, 1H), 7.84 (dd, *J* = 7.5, 7.4 Hz, 2 H), 7.54-7.42 (m, 3H), 3.58 (ddd, *J* = 11.7, 11.6, 2.6 Hz, 2H), 2.81 (ddd, *J* =14.4, 5.1, 3.2 Hz, 2H), 2.25-2.17 (m, 1H), 2.11-2.00 (m, 1H), 1.94 (s, 3H); ^{13}C NMR δ 135.1, 134.4, 130.4, 130.3,128.8, 128.4, 127.4, 125.5, 124.4, 124.1, 64.4, 29.0 (2C), 24.5, 16.2; HRMS (EI) calcd for $C_{15}H_{16}S_3$, 292.0414, found 292.0408.

*4.4.2. 2-[(1,1'-Biphenyl)-4-yl]-2-(methylthio)-1,3-dithiane (**34b**)*

White solid. mp 93-94 °C; IR (KBr) 2903, 1481, 1401, 1272 cm^{-1}; ^1H NMR δ 8.00 (d, *J* = 7.7 Hz, 2H), 7.61 (d, *J* = 13.9 Hz, 4H), 7.46-7.34 (m, 3 H), 3.44-3.37 (m, 2H), 2.80-2.74 (m 2H), 2.17-2.13 (m, 1H), 2.03-1.92 (m, 1H), 2.02 (s, 3H); ^{13}C NMR δ 141.0, 140.3, 139.8, 128.7(2C), 128.2(2C), 127.4, 127.1(2C), 127.0(2C), 63.7, 28.8(2C), 24.3, 16.3; HRMS (EI) calcd for $C_{17}H_{18}S_3$, 318.0571, found 318.0570.

*4.4.3. Methyl 4-[2-(methylthio)-1,3-dithian-2-yl]benzoate (**34c**)*

White solid. mp 51-52 °C; IR (KBr) 2910, 1719 (C=O), 1283, 1114 cm^{-1}; ^1H NMR δ 8.05-7.99 (m, 4H), 3.92 (s, 3H), 3.41-3.34 (m, 2H), 2.77-2.72 (m, 2H), 2.17-2.10 (m, 1H), 1.97 (s, 3H), 1.94-1.87 (m, 1H); ^{13}C NMR δ 166.4, 145.8, 129.8, 129.6 (2C), 127.8 (2C), 63.4, 52.1, 28.7 (2C), 24.1, 16.1; HRMS (EI) (M^+-SMe) calcd for $C_{12}H_{13}O_2S_2$, 253.03570, found 253.03503.

*4.4.4. 2-(4-Isobutylphenyl)-2-(methylthio)-1,3-dithiane (**34d**)*

IR (neat) 2952, 2912, 1410 cm^{-1}; ^{1}H NMR δ 7.81(d, *J* = 8.3 Hz, 2H), 7.15 (d, *J* = 8.3 Hz, 2H), 3.43-3.36 (m, 2H), 2.77-2.71 (m, 2H), 2.47 (d, *J* = 7.1 Hz, 2H), 2.17-2.11 (m, 1H), 1.96 (s, 3H), 1.94-1.83 (m, 2H), 0.90 (d, *J* = 6.7 Hz, 6H); ^{13}C NMR 141.9, 138.0, 129.1 (2C), 127.3 (2C), 63.7, 44.9, 30.0, 28.7 (2C), 24.4, 22.3 (2C), 16.2: HRMS (EI) (M^{+}-SMe) calcd for $C_{14}H_{19}O_2S_2$, 251.09282, found 251.09223.

*4.4.5. 5-[2-(Methylthio)-1,3-dithian-2-yl]benzo[d][1,3]dioxole (**34e**)*

White solid. mp 73-74 °C; IR (KBr) 2899, 1484, 1254, 1034 cm^{-1}; ^{1}H NMR δ 7.49 (d, *J* = 1.7 Hz, 1H), 7.45 (dd, *J* = 1.8, 8.2 Hz, 1H), 6.78 (d, *J* = 8.3 Hz, 1 H), 5.98 (s, 2H), 3.36 (dd, *J* = 11.4, 11.6 Hz, 2H), 2.77-2.71 (m, 2H), 2.16-2.10 (m, 1H), 1.99 (s, 3H), 1.95-1.86 (m, 1H); ^{13}C NMR δ 147.7, 147.4, 134.6, 121.6, 108.5, 107.3, 101.3, 63.6, 28.9 (2C), 24.2, 16.2; HRMS (EI) (M^{+}-Me) calcd for $C_{11}H_{11}O_2S_3$, 270.9911, found 270.9917.

4.5. The desulfurizing-fluorination reaction of 2-(methylthio)-1,3-dithiane derivatives with IF_5-pyridine-HF

*4.5.1. 1-(Trifluoromethyl)naphthalene (**35a**)*

To a CH_2Cl_2 solution (2 mL) of **34a** (146 mg, 0.5 mmol) was added at room temperature IF_5-pyridine-HF (482 mg, 1.5 mmol), and the mixture was stirred at room temperature for 12h. The mixture was poured into water (20 mL) and extracted with CH_2Cl_2 (20 mL X 3). The combined organic layer was washed with aq $NaHCO_3$ and aq $Na_2S_2O_3$, and dried over $MgSO_4$. After concentration under reduced pressure, **35a** was isolated by column chromatography (silica gel, Hexane-CH_2Cl_2) in 78% yield; IR (neat) 3060, 1515, 1316, 1119 cm^{-1}; ^{1}H NMR δ 8.19 (d, *J* = 8.5 Hz, 1H), 8.03 (d, *J* = 8.3 Hz, 1H), 7.93 (d, *J* = 8.0 Hz, 1H), 7.87 (d, *J* = 7.3 Hz, 1H), 7.65-7.49 (m, 3H); ^{19}F NMR δ -60.39 (s, 3F) (lit.[20] -59.72 (s, 3F); ^{13}C NMR δ 133.8, 132.7, 128.9, 128.7, 127.6, 126.6, 126.0 (q, $^{2}J_{C-F}$ = 30.5 Hz), 124.7 (q, $^{3}J_{C-F}$ = 5.7 Hz), 124.6 (q, $^{1}J_{C-F}$ = 273.4 Hz), 124.2 (q, $^{3}J_{C-F}$ = 2.6 Hz), 124.1.

*4.5.2. 4-(Trifluoromethyl)-1,1'-biphenyl (**35b**)*

White solid. mp 68-69 °C (lit.[21] 69-70 °C); IR (KBr) 1614, 1334, 1116 cm^{-1}; ^{1}H NMR δ 7.68 (s, 5H), 7.58-7.38 (m, 4H) ; ^{19}F NMR δ -63.83 (s, 3F); ^{13}C NMR δ 144.7, 139.7, 129.3 (q, $^{2}J_{C-F}$ = 32.6 Hz), 129.0 (2C), 128.2, 127.4 (2C), 127.2 (2C), 125.7 (q, $^{3}J_{C-F}$ = 3.8 Hz, 2C), 124.3(q, $^{1}J_{C-F}$ = 271.8 Hz).

*4.5.3. Methyl 4-(trifluoromethyl)benzoate (**35c**)*

IR (neat) 2957, 1731 (C=O), 1328, 1282, 1131 cm^{-1}; ^{1}H NMR δ 8.16 (d, *J* = 8.0 Hz, 2H), 7.71 (d, *J* = 8.1 Hz, 2H), 3.96 (s, 3H); ^{19}F NMR δ -63.73 (s, 3F) (lit.[22] -62.9 (s, 3F)); ^{13}C NMR δ 165.8, 134.4 (q, $^{2}J_{C-F}$ = 32.9 Hz), 133.3, 129.9 (2C), 125.4 (q, $^{3}J_{C-F}$ = 3.6 Hz, 2C), 123.6 (q, $^{1}J_{C-F}$ = 272.8 Hz), 52.5.

*4.5.4. 1-Isobutyl-4-(trifluoromethyl)benzene (**35d**)*

IR (neat) 2960, 1327, 1124 cm^{-1}; ^{1}H NMR δ 7.52 (d, *J* = 8.9 Hz, 2H), 7.25 (d, *J* = 8.9 Hz, 2H), 2.53 (d, *J* = 7.2 Hz, 2H), 1.92-1.85 (m, 1H), 0.91 (d, *J* = 6.5 Hz, 6H); ^{19}F NMR δ -62.87 (s, 3F); ^{13}C NMR δ 145.8, 129.3 (2C), 128.0 (q, $^{2}J_{C\text{-}F}$ = 32.2 Hz), 125.0 (q, $^{3}J_{C\text{-}F}$ =3.7 Hz, 2C), 124.4 (q, $^{1}J_{C\text{-}F}$ = 271.8 Hz), 45.2, 30.1, 22.2 (2C); HRMS (EI) calcd for $C_{11}H_{13}F_3$ 202.09693, found 202.09653.

*4.5.5. 5-(Trifluoromethyl)benzo[d][1,3]dioxole (**35e**)*

IR (neat) 2911, 1449, 1317, 1265, 1119 cm^{-1}; ^{1}H NMR δ 7.14 (d, *J* = 8.2 Hz, 1H), 7.03 (d, *J* = 1.6 Hz, 1H), 6.86 (d, *J* = 8.2 Hz, 1H) 6.04 (s, 2H); ^{19}F NMR δ -62.03 (s, 3F) (lit.[22] -61.3 (s, 3F)); ^{13}C NMR δ 150.3, 147.9, 124.2 (q, $^{2}J_{C\text{-}F}$ = 33.2 Hz), 124.1 (q, $^{1}J_{C\text{-}F}$ = 270.9 Hz), 119.8 (q, $^{3}J_{C\text{-}F}$ = 4.1 Hz), 108.2, 105.8 (q, $^{3}J_{C\text{-}F}$ = 2.8 Hz), 101.9.

Acknowledgments

We are grateful to Asahi Glass Co., Ltd. for their donation of IF_5.

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