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Solvolytically DMSO-promoted reactions of 1,1,1-trifluoroethyl chloride (HCFC-133a) or fluoride (HFC-134a) with nucleophiles

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Abstract—Fluorinated gases HCFC-133a (CF_3CH_2Cl, bp=6°C) and HFC-134a (CF_3CH_2F, bp=−27°C) are found highly soluble in DMSO. In their DMSO solutions, oxygen-, nitrogen- and sulfur-nucleophilic reactions may occur in normal glassware rather than in the autoclave.

1. Introduction

The novel fluorous technique discovered and developed by Horvàth, Curran and their co-workers is one of the most important advances in modern organic synthesis.[1] Under fluorous biphase conditions, many catalytic reactions, e.g. Wilkinson's catalytic hydrogenation,[2] Stille transition metal-catalyzed cross-coupling reaction,[3] copper(I)-mediated living radical polymerization,[4] etc. can proceed with the facile separation of products from the catalyst by leaving the catalyst in a reusable state. The key point of designing fluorous catalyst is, as pointed out by Horvàth, 'the catalyst has to be catalyst phase like'.[1a] In other words, fluorous biphase catalysis, either heavy fluorous or light fluorous,[5] is based on its unique solubilities (or temperature-dependent phase miscibilities) in organic solvents.[1,6]

In connection with the solubility of organofluorine compounds, we very recently found that 1,1,1-trifluoroethyl chloride (HCFC-133a, CF_3CH_2Cl, **1a**, bp=6°C), fluoride (HFC-134a, CF_3CH_2F, **1b**, bp=−27°C) are soluble in aprotic solvents, such as DMSO, DMF and NMP. The decision for choosing **1a** and **1b** as the substrates is that they are produced in large scale for chlorofluorocarbon replacements,[7] and considered to be good starting materials for synthesizing many fluorine-containing compounds.[8] Furthermore, our previous report demonstrated that **1a** could react with alcohols (phenols) (**2**) in the presence of aqueous KOH giving the corresponding 2,2,2-trifluoroethyl (2-chloro-1,1-difluoroethyl) ethers in autoclave at 240–280°C.[9] The results were explained in terms of promotion by the near-critical water (SCW) because **1a** was shown to be inert under normal S_N2 conditions.[10] In order to utilize **1** as a fluorine source more effectively, it would be of significance to search for milder reaction conditions. Fortunately, DMSO as the solvent was found to be suitable for this purpose.[11] We, herein, present the results.

2. Results and discussion

First, we examined the solubility of **1a** and **1b** in various solvents and found that DMSO, DMF and NMP are good solvents, DMSO being the best. At room temperature, a saturated solution of **1a** in DMSO, 65.9% ($w_{CF3CH2Cl}/w_{total}$) was obtained from 37.5 g **1a** in 17.7 g DMSO, while of **1b** 19.4% ($w_{CF3CH2F}/w_{total}$) from 3.0 g **1b** in 12.4 g DMSO. Surprisingly, at atmospheric pressure, the weight loss of **1a** and **1b** is less than 3–5% after heating the DMSO solution at 80°C for 6 h if their concentration is kept at 0.43 and 0.56N, respectively. At these concentrations, the DMSO solution of **1a** or **1b** could be stored in normal glassware for months without any loss at room temperature. So it is unnecessary to bubble these gases from the cylinders into DMSO, a solution of the fluorocarbon in DMSO can be readily prepared simply by adding pre-cooled **1a** or **1b** into DMSO.

Using this convenient procedure, some reactions of **1a** and **1b** with oxygen-, nitrogen- and sulfur-nucleophiles were carried out. The nucleophiles were readily prepared from the corresponding alcohols, phenols (**2**), heterocyclic amines (**5**) and thiophenols (**7**) in the presence of KOH.

It was found that **1a** and **1b** could react with phenols or alcohols (**2**) in the presence of KOH in DMSO at 80°C for 6 h to give a mixture of fluorinated ether (**3**) and vinyl ether (*E*/*Z*) (**4**) (Eq. (1)). The results are listed in Table 1.The pure products **3** and **4** derived from alcohols could not be isolated

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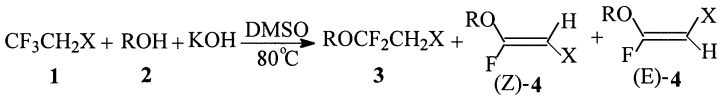
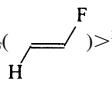
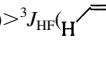


(1)

X=Cl (a), F (b); R=C_6H_5 (a), *o*-$CH_3C_6H_4$ (b), *p*-$CH_3C_6H_4$ (c), *p*-ClC_6H_4 (d), *o*-$CH_3OC_6H_4$ (e),  (f), CH_3CH_2 (g), $(CH_3)_2CH$ (h), $C_6H_5CH_2$ (i), $(CH_3)_3C$ (j)

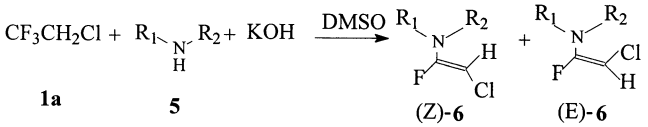
Table 1. Reaction of **1** with phenols and alcohols (**2**) at 80°C for 6 h

Entry	1	2	3 (%)[a]	4 (%)[a]	*E*/*Z* of 4[b]	3+4 (%)
1	**1a**	**2a**	19 (**3aa**)	50 (**4aa**)	2.7	65
2	**1a**	**2b**	31 (**3ab**)	33 (**4ab**)	3.9	64
3	**1a**	**2c**	26 (**3ac**)	42 (**4ac**)	5.6	68
4	**1a**	**2d**	14 (**3ad**)	54 (**4ad**)	6.4	68
5	**1a**	**2e**	31 (**3ae**)	39 (**4ae**)	3.6	70
6	**1a**	**2f**	31 (**3af**)	36 (**4af**)	4.4	67
7[c]	**1a**	**2g**	76[d] (**3ag**)	6[d] (**4ag**)	7.4	80
8[c]	**1a**	**2h**	35[d] (**3ah**)	38[d] (**4ah**)	1.1	73
9[c]	**1a**	**2i**	74 (**3ai**)	0	–	74
10[c]	**1a**	**2j**	0	0	–	0
11	**1b**	**2a**	10 (**3ba**)	47 (**4ba**)	1.0	57
12	**1b**	**2b**	35 (**3bb**)	30 (**4bb**)	1.1	65
13	**1b**	**2c**	23 (**3bc**)	30 (**4bc**)	1.2	53
14	**1b**	**2d**	34 (**3bd**)	38 (**4bd**)	1.3	72
15	**1b**	**2f**	32 (**3bf**)	40 (**4bf**)	2.9	72
16[c]	**1b**	**2g**	64[d] (**3bg**)	2[d] (**4bg**)	7.9	66
17[c]	**1b**	**2h**	21[d] (**3bh**)	53[d] (**4bh**)	3.1	74
18[c]	**1b**	**2i**	72 (**3bi**)	0	–	72
19[c]	**1b**	**2j**	0	0	–	0

1:**2**:KOH=2:1:2.
[a] Isolated yield based on **2**.
[b] *E*/*Z* ratio was determined by ^{1}H NMR ($^3J_{HF}$()>$^3J_{HF}$())[12] and ^{19}F NMR.
[c] **1**:**2**:KOH=1:2:2; 24 h.

because the boiling points of **3** and **4** are very close. Their structures might be identified by GC–MS and their ^{1}H, ^{19}F NMR spectra (as well as compared with the spectra of those known compounds). Benzyl alcohols (**2i**) was shown to afford **3** exclusively, while *t*-butyl alcohol (**2j**) to be inert probably due to steric hindrance.

Heterocyclic amines (**5**), such as imidazole (**5a**), 2-methylimidazole (**5b**), indole (**5c**), 3-methylindole (**5d**), 1*H*-benzotriazole (**5e**) and carbazole (**5f**) could also react with **1a** to produce **6** in moderate yields (Eq. (2)). Treatment of pyrrole (**5g**) with **1a** afforded only a non-volatile fluorine-containing compound, which was not identified because of its



(2)

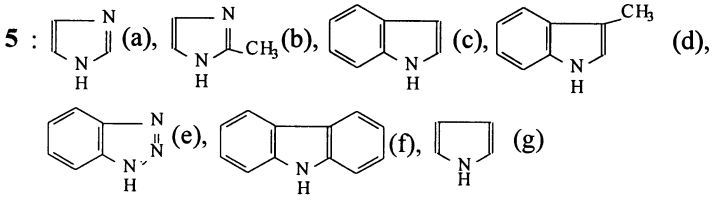
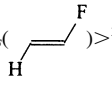
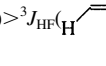
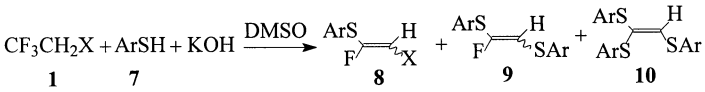


Table 2. Reaction **1a** with **5** in DMSO

Entry	5	*T* (°C)	*t* (h)	6 (%)[a]	*E*/*Z* of 6[b]
1	**5a**	90	8	66 (**6a**)	[c]
2	**5b**	80	9	45 (**6b**)	[c]
3	**5c**	80	10	79 (**6c**)	9.9
4	**5d**	85	7	76 (**6d**)	9.4
5	**5e**	80	9	64 (**6e**)	8.6
6	**5f**	75	9	84 (**6f**)	>10

1a:**5**:KOH=2:1:2.
[a] Isolated yield based on **5**.
[b] *E*/*Z* ratio was determined by ^{1}H NMR ($^3J_{HF}$()>$^3J_{HF}$())[12] and ^{19}F NMR.
[c] Only *E* isomer.



1 7 8 9 10 (3)

X=Cl (a), F (b); Ar=C_6H_5 (a), *p*-$CH_3C_6H_4$ (b), *o*-$CH_3C_6H_4$ (c), *p*-ClC_6H_4 (d)

Table 3. Reaction of **1** with thiophenols (**7**) in DMSO

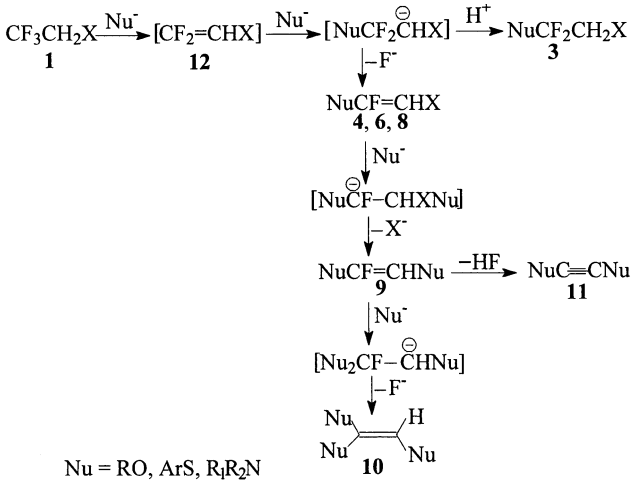
Entry	**1**	**7**	**1**:**7**:KOH	*T* (°C)	*t* (h)	**8** (%)[a]	**9** (%)[a]	**10** (%)[a]
1	**1a**	**7a**	2:1:3	60	11	10 (**8a**)	28 (**9a**)	32 (**10a**)
2	**1a**	**7a**	2:1:3	rt	11	8 (**8a**)	20 (**9a**)	11 (**10a**)
3	**1a**	**7a**	1:2:1	60	12.5	10 (**8a**)	37 (**9a**)	12 (**10a**)
4	**1a**	**7a**	2:1:2	60	22	9 (**8a**)	21 (**9a**)	54 (**10a**)
5	**1a**	**7b**	2:1:2	60	24	8 (**8b**)	54 (**9b**)	26 (**10b**)
6	**1a**	**7c**	2:1:2	60	21	7 (**8a**)	43 (**9c**)	22 (**10c**)
7	**1a**	**7d**	2:1:2	60	22	39 (**8d**)	[b]	56 (**10d**)
8	**1b**	**7a**	2:1:2	60	22	–	–	17 (**10a**)[c]
9	**1b**	**7b**	2:1:2	60	24	–	–	81 (**10b**)
10	**1b**	**7d**	2:1:2	60	32	–	–	39 (**10d**)

[a] Isolated yield based on **7**.
[b] Only trace **9d** was produced.
[c] Besides **10**, bis(phenylthio)acetylene (**11**) 39% was also obtained.

unstability. However, no reaction occurred when **1b** was treated with heterocyclic amines (**5**) under the similar reaction conditions (Eq. (2)). Some other bases, such as *t*-BuOK, K_2CO_3, NaH, DBU and Et_3N were unable to induce the reactions of **1b** with heterocyclic amines (**5**). The results are listed in Table 2.

Treating thiophenols (**7**) with **1a** under similar conditions gave a mixture of ArS-substituted ethylenes **8**, **9** and **10** (Eq. (3)). The regioselectivity among the products could not be improved by changing the reactant ratios and other conditions such as the reaction temperature and time. Thiophenols (**7**) could also react with **1b**, though only to give **10** in low yields. When thiophenol (**7a**) was the reactant, bis(phenylthio)acetylene (**11**) was also obtained besides **10**. The results are listed in Table 3.

Examination of the structures of the products **3**, **4**, **6**, **8**, **9** and **10** unequivocally reveals that, different from the reaction results of **1a** with **2** in high-temperature aqueous medium[9] and CF_3CH_2I with PhO^-,[13] alkoxide ion RO^- does not attack the halogen atom of CF_3CH_2X (**1**), but readily eliminate HF from **1** presumably via the E1cB mechanism to produce difluorohaloethene (**12**)[12] (Scheme 1).



Scheme 1.

Because the ^{19}F NMR signals showed no change before and after a solution of **1a** or **1b** with or without KOH at 80°C for 8 h if none of nucleophiles was added (see Section 3.3), so **12** could not be generated from **1** and KOH alone. Since the electron density of the carbon–carbon double bond of **12** is reduced strongly by the electron-withdrawing fluorine substituent, the nucleophilic addition reactions may occur to give the products in which the nucleophiles attack the difluoromethylene end of **12**. When phenols and alcohols (**2**) are used as the nucleophiles, addition of RO^- to **12** followed by protonation and by loss of fluoride ion gives **3** and **4**, respectively. But the protonation does not take place in case of the reactions of **1a** with **5**, elimination of fluoride ion being the dominant process with **6** as the sole product. However, the mechanism proposed could not explain the big difference of *E*/*Z* ratios of **4** and **6** obtained in the reaction of **1a** and **1b** with either alcohols, phenols (**2**) (see Table 1) or amines (**5**) (see Table 2).

As for the reactions of ArS^- with **1a**, **8** is first formed and further attacked by ArS^- with the elimination of a chloride ion to produce **9**. Compound **10** is generated from **9** in a similar way. However, **8** and **9**, which might be produced also in the reaction of **1b**, would be attacked by ArS^- as soon as they were produced, so they were not isolated. When thiophenol (**7a**) was the reactant, **9ba** could also eliminate HF to yield bis(phenylthio)acetylene (**11**). The nucleophiles generated from **5** might be too weak to deprotonate **1b**, so the corresponding addition–elimination products were not formed.

In conclusion, it is found that HCFC-133a (**1a**) and HFC-134a (**1b**) possess very good solubility in DMSO. In their DMSO solutions, oxygen-, nitrogen- and sulfur-nucleophilic reactions may proceed in normal glassware rather than in the autoclave. The investigation on solvent effect of **1** and other HCFCs, HFCs in DMSO or other solvents is in progress.

3. Experimental

3.1. General

Boiling points were uncorrected. ^{1}H NMR spectra were taken on a Brucker AM-300 (300 MHz) NMR spectrometer. ^{19}F NMR spectra were obtained on a Varian EM-360 (56.4 MHz) or a Bruker AM-300 (282 MHz) spectrometer. Chemical shifts were reported in parts per million relative to TMS as an internal standard (δ_{TMS}=0) for ^{1}H NMR spectra and CF_3COOH as an external standard (δCF_3COOH=0) for ^{19}F NMR (downfield shift being designated as negative) spectra. The solvent for NMR measurement was $CDCl_3$ or CD_3COCD_3. IR spectra were recorded on a Perkin–Elmer Jeol 983 spectrometer. MS and HRMS spectra were recorded on a Hewlett-Packard HP-5989A spectrometer and a Finnigan MAT-8483 mass spectrometer. GC and GC–MS data were obtained on a Hewlett-Packard HP-6890 and a Finnigan MD-800 spectrometer. HPIC data were obtained on a Dionex 500 spectrometer.

3.2. General procedure for the reaction of 1 with 2, 5 or 7

CF_3CH_2Cl (**1a**, 0.961 g, 8.11 mmol), which was pre-cooled with dry ice/acetone, was added to 15 ml DMSO, then KOH (0.454 g, 8.11 mmol) and phenol (**2a**, 0.382 g, 4.06 mmol) were added to the solution. After stirring for 8 h at 80°C, water was added to the reaction mixture. The aqueous layer was extracted three times with ether (3×10 ml). The combined extracts were washed with brine (3×10 ml) and dried over Na_2SO_4. After removal of ether, the residue was subjected to column chromatography on silica gel (petroleum ether) to give **3aa** (0.154 g, 19%) and **4aa** (0.349 g, 50%) as colorless oil.

3.2.1. Compound 3aa.[14] Colorless oil; ^{1}H NMR (CD_3COCD_3, 300 MHz) δ: 4.24 (t, J_{HF}=8.8 Hz, 2H), 7.20–7.42 (m, 5H); ^{19}F NMR (CD_3COCD_3, 282 MHz) δ: −2.42 (t, J_{HF}=8.8 Hz, 2F); IR (KBr) ν: 3074, 1591, 1491, 1331, 1193, 859, 799, 747, 619 cm^{-1}; MS *m/z* (%): 192 (M^+, 28), 99 (50), 94 (100), 77 (25), 66 (17), 65 (11).

3.2.2. Compound 4aa.[14] Colorless oil; ^{1}H NMR (CD_3COCD_3, 300 MHz) δ: 5.29 (d, J_{HF}=18.2 Hz, 1H) (*Z*), 5.64 (s, 1H) (*E*), 7.08–7.41 (5H, m); ^{19}F NMR (CD_3COCD_3, 56.4 MHz) δ: 12.1 (m, 1F) (*Z*/*E*); IR (KBr) ν: 3110, 1698, 1591, 1295, 865, 749, 688 cm^{-1}; MS *m/z* (%): 172 (M^+, 38), 137 (11), 96 (19), 77 (100), 51 (24).

3.2.3. Compound 3ab.[14] Colorless oil; ^{1}H NMR (CD_3COCD_3, 300 MHz) δ: 2.31 (s, 3H), 4.17 (t, J_{HF}=8.8 Hz, 2H), 7.18–7.24 (m, 4H); ^{19}F NMR (CD_3COCD_3, 56.4 MHz) δ: −3.0 (t, J_{HF}=8.8 Hz, 2F); IR (KBr) ν: 3100, 1598, 1391, 1328, 772, 618; MS *m/z* (%): 206 (M^+, 17), 157 (9), 108 (100), 91 (21). Anal. calcd for $C_9H_9ClF_2O$: C, 52.32; H, 4.39; F, 18.39; found: C, 52.20; H, 4.46; F, 18.49.

3.2.4. Compound 4ab.[14] Colorless oil; ^{1}H NMR (CD_3COCD_3, 300 MHz) δ: 2.38 (s, 3H) (*Z*), 2.35 (s, 3H) (*E*), 5.23 (d, J_{HF}=18.5 Hz, 1H) (*Z*), 5.61 (s, 1H) (*E*), 6.99–7.04 (m, 2H), 7.16–7.26 (m, 2H); ^{19}F NMR (CD_3COCD_3, 56.4 MHz) δ: 11.9 (m, 1F) (*Z*/*E*); IR (KBr) ν: 3100, 1120, 618 cm^{-1}; MS *m/z* (%): 186 (M^+, 58), 151 (9), 123 (10), 91 (100), 65 (40).

3.2.5. Compound 3ac.[14] Colorless oil; ^{1}H NMR (CD_3COCD_3, 300 MHz) δ: 2.35 (s, 3H), 4.21 (t, J_{HF}=9.0 Hz, 2H), 7.13 (d, J_{HH}=8.4 Hz, 2H), 7.24 (d, J_{HH}=8.4 Hz, 2H); ^{19}F NMR (CD_3COCD_3, 56.4 MHz) δ: −4.8 (t, J_{HF}=9.0 Hz, 2F); IR (KBr) ν: 3150, 1590, 1391, 1254, 772, 618 cm^{-1}; MS *m/z* (%): 206 (M^+, 72), 157 (13), 108 (100), 91 (18), 77 (17). Anal. calcd for $C_9H_9ClF_2O$: C, 52.32; H, 4.39; F, 18.39; found: C, 52.39; H, 4.38; F, 18.56.

3.2.6. Compound 4ac.[14] Colorless oil; ^{1}H NMR (CD_3COCD_3, 300 MHz) δ: 2.28 (s, 3H) (*Z*/*E*), 5.64 (d, J_{HF}=19.1 Hz, 1H) (*Z*), 6.01 (d, J_{HF}=3.8 Hz, 1H) (*E*), 7.02–7.04 (m, 2H), 7.21–7.24 (m, 2H); ^{19}F NMR (CD_3COCD_3, 56.4 MHz) δ: 13.1 (m, 1F) (*Z*/*E*); IR (KBr) ν: 3108, 3059, 1708, 1599, 1257, 960, 880, 794, 770 cm^{-1}; MS *m/z* (%): 186 (M^+, 86), 151 (13), 91 (100), 77 (11), 65 (39).

3.2.7. Compound 3ad.[14] Colorless oil; ^{1}H NMR (CD_3COCD_3, 300 MHz) δ: 3.90 (t, J_{HF}=8.4 Hz, 2H), 7.01 (d, J_{HH}=7.8 Hz, 2H), 7.18 (d, J_{HH}=7.8 Hz, 2H); ^{19}F NMR (CD_3COCD_3, 56.4 MHz) δ: −2.9 (t, J_{HF}=8.4 Hz, 2F); IR (KBr) ν: 3100, 1484, 1331, 1197, 827, 618 cm^{-1}; MS *m/z* (%): 226 (M^+, 5), 186 (8), 124 (100), 159 (100), 128 (67), 111 (49). Anal. calcd for $C_8H_6Cl_2F_2O$: C, 42.32, H, 2.66; found: C, 42.47, H, 2.64.

3.2.8. Compound 4ad. Colorless oil; ^{1}H NMR (CD_3COCD_3, 300 MHz) δ: 5.35 (d, J_{HF}=18.4 Hz, 1H) (*Z*), 5.64 (s, 1H) (*E*), 7.03–7.08 (m, 2H), 7.26–7.35 (m, 2H); ^{19}F NMR (CD_3COCD_3, 56.4 MHz) δ: 9.8 (m, 1F) (*Z*/*E*); IR (KBr) ν: 3398, 1119, 748, 618 cm^{-1}; MS *m/z* (%): 206 (M^+, 67), 171 (8), 111 (100), 75 (61). Anal. calcd for $C_8H_5Cl_2FO$: C, 44.41, H, 2.43, F, 9.18; found: C, 44.51, H, 2.43, F, 9.38.

3.2.9. Compound 3ae. Colorless oil; ^{1}H NMR (CD_3COCD_3, 300 MHz) δ: 3.86 (s, 3H), 3.97 (t, J_{HF}=9.2 Hz, 2H), 6.90–7.28 (m, 4H); ^{19}F NMR (CD_3COCD_3, 56.4 MHz) δ: 2.65 (t, J_{HF}=9.2 Hz, 2F); IR (KBr) ν: 2974, 1602, 1498, 1331, 1061, 862, 752, 618 cm^{-1}; MS *m/z* (%): 222 (M^+, 43), 186 (16), 124 (100), 109 (58), 99 (24), 77 (35). Anal. calcd for $C_9H_9ClF_2O$: C, 48.56, H, 4.07; found: C, 48.46, H, 4.08.

3.2.10. Compound 4ae. Colorless oil; ^{1}H NMR (CD_3COCD_3, 300 MHz) δ: 3.89 (s, 3H) (*Z*/*E*), 5.09 (d, J_{HF}=18.7 Hz, 1H) (*Z*), 5.51 (s, 1H) (*E*), 6.91–7.27 (m, 4H); ^{19}F NMR (CD_3COCD_3, 56.4 MHz) δ: 14.0 (m, 1F) (*Z*/*E*); IR (KBr) ν: 3103, 1710, 1391, 1299, 1122, 960, 793, 618 cm^{-1}; MS *m/z* (%): 202 (M^+, 91), 124 (43), 92 (50), 77 (100). Anal. calcd for C_9H_8ClFO: C, 53.35, H, 3.98; found: C, 53.11, H, 3.97.

3.2.11. Compound 3af.[14] Colorless oil; ^{1}H NMR (CD_3COCD_3, 300 MHz) δ: 4.45 (t, J_{HF}=8.9 Hz, 2H), 7.47–8.26 (m, 7H); ^{19}F NMR (CD_3COCD_3, 56.4 MHz) δ: −2.5 (t, J_{HF}=8.9 Hz, 2F); IR (KBr) ν: 3100, 1598, 1391, 1105, 772, 618 cm^{-1}; MS *m/z* (%): 242 (M^+, 68), 144 (100), 127 (31), 115 (59).

3.2.12. Compound 4af.[14] Colorless oil; ^{1}H NMR (CD_3COCD_3, 300 MHz) δ: 5.83 (d, J_{HF}=19.1 Hz, 1H) (*Z*), 6.20 (s, 1H) (*E*), 7.27–8.26 (m, 7H); ^{19}F NMR (CD_3COCD_3, 56.4 MHz) δ: 14.2 (m, 1F) (*Z*/*E*); IR (KBr) ν: 3108, 1709, 1596, 1390, 1226, 1051, 960, 880, 793, 618 cm^{-1}; MS *m*/*z* (%): 222 (M^+, 41), 187 (37), 186 (15), 127 (100). Anal. calcd for $C_{12}H_8ClFO$: C, 64.74, H, 3.62, F, 8.53; found: C, 64.74, H, 3.74, F, 8.78.

3.2.13. Compounds 3ag[15] **and 4ag.**[16] Colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz) (mixture of **3ag** and **4ag**) δ: 1.18–1.39 (m, –CH_3), 3.68 (t, J_{HF}=8.2 Hz, CF_2CH_2Cl), 4.10–4.17 (m, –CH_2–), 4.73 (C=CH) (*Z*), 5.18 (C=CH), (*E*); ^{19}F NMR ($CDCl_3$, 56.4 MHz) (mixture of *3ag* and *4ag*) δ: −2.1 (t, J_{HF}=8.2 Hz, CF_2CH_2Cl), 15.5 (m, C=CF) (*Z*/*E*); GC–MS, 144 for **3ag** and 124 for **4ag** (**3ag** require 144 and **4ag** require 124).

3.2.14. Compounds 3ah[15] **and 4ah.**[16] Colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz) (mixture of **3ah** and **4ah**) δ: 1.05–1.35 (m, CH_3), 3.64 (t, J_{HF}=8.6 Hz, CF_2CH_2Cl), 3.99 (m, $(CH_3)_2C$–H), 4.51 (m, $(CH_3)_2C$–H), 4.86 (C=CH) (*Z*), 5.19 (C=CH) (*E*); ^{19}F NMR ($CDCl_3$, 56.4 MHz) (mixture of **3ah** and **4ah**) δ: −2.7 (t, J_{HF}=8.6 Hz, CF_2CH_2Cl), 16.5 (m, C=CF) (*Z*/*E*); GC-MS, 158 for **3ah** and 138 for **4ah** (**3ah** require 158 and **4ah** require 138).

3.2.15. Compound 3ai. Colorless oil; ^{1}H NMR (CD_3COCD_3, 300 MHz) δ: 3.89 (t, J_{HF}=9.0 Hz, 2H), 5.00 (s, 2H), 7.24–7.44 (m, 5H); ^{19}F NMR (CD_3COCD_3, 56.4 MHz) δ: 0.5 (t, J_{HF}=9.0 Hz, 2F); MS *m*/*z* (%): 206 (M^+, 36), 205 (16), 110 (11), 91 (100), 79 (24), 65 (14). HRMS calcd for $C_9H_9F_2ClO$: 206.03100; found: 206.02602.

3.2.16. Compound 3ba.[17] Colorless oil; ^{1}H NMR (CD_3COCD_3, 300 MHz) δ: 4.66 (dt, J_{HF}=8.5, 45.8 Hz, 2H), 7.21–7.41 (m, 5H); ^{19}F NMR (CD_3COCD_3, 282 MHz) δ: 3.81 (dt, J_{HF}=8.5 Hz, J_{FF}=91.0 Hz, 2F), 161.11 (tt, J_{HF}=45.8 Hz, J_{FF}=91.0 Hz, 1F); IR (KBr) ν: 3100, 1591, 1491, 1296, 1108, 935, 750, 619 cm^{-1}; MS *m*/*z* (%): 176 (M^+, 68), 94 (100), 77 (38), 65 (17).

3.2.17. Compound 4ba.[17] Colorless oil; ^{1}H NMR (CD_3COCD_3, 300 MHz) δ: 6.61 (dd, J_{HF}=72.5, 13.2 Hz, 1H) (*Z*), 6.81 (d, J_{HH}=73.3 Hz, 1H) (*E*), 7.05–7.40 (m, 5H); ^{19}F NMR (CD_3COCD_3, 58.4 MHz) δ: 24.4 (t, J_{HF}=J_{FF}=13.2 Hz, 1F) (*Z*), 50.2 (d, J_{HF}=0 Hz, J_{FF}=122.0 Hz, 1F) (*E*), 109.2 (dd, J_{HF}=72.5 Hz, J_{FF}=13.2 Hz, 1F) (*Z*), 115.4 (dd, J_{HF}=73.3 Hz, J_{FF}=122.0 Hz, 1F) (*E*); IR (KBr) ν: 3105, 1503, 1334, 1251, 619, 1123 cm^{-1}; MS *m*/*z* (%): 156 (M^+, 47), 109 (9), 77 (100), 51 (38).

3.2.18. Compound 3bb. Colorless oil; ^{1}H NMR (CD_3COCD_3, 300 MHz) δ: 2.06 (s, 3H), 4.92 (dt, J_{HF}=8.7, 45.8 Hz, 2H), 7.02–7.33 (m, 4H); ^{19}F NMR (CD_3COCD_3, 282 MHz) δ: −1.72 (dt, J_{HF}=8.7 Hz, J_{FF}=9.5 Hz, 2F), 166.13 (tt, J_{HF}=45.8 Hz, J_{FF}=9.5 Hz, 1F); IR (KBr) ν: 3197, 1666, 1491, 1291, 1164, 975, 750, 618 cm^{-1}; MS *m*/*z* (%): 190 (M^+, 69), 108 (100), 91 (29), 77 (34). HRMS calcd for $C_9H_9F_3O$: 190.06055; found: 190.05991.

3.2.19. Compound 4bb. Colorless oil; ^{1}H NMR (CD_3COCD_3, 300 MHz) δ: 2.30 (s, 3H), 5.94 (dd, J_{HF}=8.7, 44.6 Hz, 1H) (*Z*), 6.19 (d, J_{HF}=72.2 Hz, 1H) (*E*), 7.36–7.22 (m, 4H); ^{19}F NMR (CD_3COCD_3, 56.4 MHz) δ: 38.2 (m, 1F) (*Z*), 52.4 (m, 1F) (*E*), 112.1 (m, 1F) (*Z*), 108.7 (m, 1F) (*E*); IR (KBr) ν: 3100, 1747, 1491, 1247, 1113, 919, 750, 618 cm^{-1}; MS *m*/*z* (%): 170 (M^+, 55), 137 (14), 123 (6), 91 (100), 65 (44). HRMS calcd for $C_9H_8F_2O$: 170.05432; found: 170.05240.

3.2.20. Compound 3bc. Colorless oil; ^{1}H NMR (CD_3COCD_3, 300 MHz) δ: 2.33 (s, 3H), 4.90 (dt, J_{HF}=8.8, 47.8 Hz, 2H), 7.13 (d, J_{HH}=8.5 Hz, 2H), 7.25 (d, J_{HH}=8.5 Hz, 2H); ^{19}F NMR (CD_3COCD_3, 56.4 MHz) δ: 16.1 (m, 2F), 157.7 (m, 1F); IR (KBr) ν: 3100, 1491, 1122, 619 cm^{-1}; MS *m*/*z* (%): 190 (M^+, 82), 108 (100), 107 (69), 91 (35), 77 (50), 51 (22). HRMS calcd for $C_9H_9F_3O$: 190.06055; found: 190.06017.

3.2.21. Compound 4bc. Colorless oil; ^{1}H NMR (CD_3COCD_3, 300 MHz) δ: 2.30 (s, 3H) (*Z*), 2.32 (s, 3H) (*E*), 6.93 (dd, J_{HF}=13.1, 73.0 Hz, 1H) (*Z*), 7.09 (dd, J_{HF}=73.0, 3.6 Hz, 1H) (*E*), 6.99–7.26 (m, 4H); ^{19}F NMR (CD_3COCD_3, 282 MHz) δ: 21.63 (t, J_{FF}=J_{HF}=13.1 Hz, 1F) (*Z*), 47.28 (dd, J_{HF}=3.6 Hz, J_{FF}=121.9 Hz, 1F) (*E*), 105.45 (dd, J_{HF}=73.0 Hz, J_{FF}=13.1 Hz, 1F) (*Z*), 112.14 (dd, J_{FF}=121.9 Hz, J_{HF}=73.0 Hz, 1F) (*E*); MS *m*/*z* (%): 170 (M^+, 58), 127 (14), 91 (100), 65 (44). HRMS calcd for $C_9H_8F_2O$: 170.05432; found: 170.05356.

3.2.22. Compound 3bd. Colorless oil; ^{1}H NMR (CD_3COCD_3, 300 MHz) δ: 4.54 (dt, J_{HF}=8.3, 45.8 Hz, 2H), 6.91 (d, J_{HH}=8.2 Hz, 2H), 7.21 (d, J_{HH}=8.2 Hz, 2H); ^{19}F NMR (CD_3COCD_3, 282 MHz) δ: −1.82 (dt, J_{HF}=19.2 Hz, J_{FF}=8.2 Hz, 2F), 155.43 (tt, J_{HF}=45.8 Hz, J_{FF}=19.2 Hz, 1F); MS *m*/*z* (%): 210 (67), 190 (26), 128 (100), 111 (65), 75 (35). HRMS calcd for $C_8H_6F_3ClO$: 210.00593; found: 210.00476.

3.2.23. Compound 4bd. Colorless oil; ^{1}H NMR (CD_3COCD_3, 300 MHz) δ: 6.99 (dd, J_{HF}=13.4, 71.9 Hz, 1H) (*Z*), 7.29 (dd, J_{HF}=74.1, 121.2 Hz, 1H) (*E*), 7.22–7.25 (m, 2H), 7.46–7.51 (m, 2H); ^{19}F NMR (CD_3COCD_3, 282 MHz) δ: 22.42 (t, J_{HF}=J_{FF}=13.4 Hz, 1F) (*Z*), 47.82 (dd, J_{HF}=41.2 Hz, J_{FF}=121.2 Hz, 1F) (*E*), 104.11 (dd, J_{HF}=71.9 Hz, J_{FF}=72.9 Hz, 1F) (*Z*), 110.67 (dd, J_{HF}=41.2 Hz, J_{FF}=121.2 Hz, 1F) (*E*); MS *m*/*z* (%): 190 (M^+, 62), 155 (15), 143 (29), 111 (100), 75 (82). HRMS calcd for $C_8H_5F_2ClO$: 189.99970; found: 190.00069.

3.2.24. Compound 3bf. Colorless oil; ^{1}H NMR (CD_3COCD_3, 300 MHz) δ: 5.07 (dt, J_{HF}=8.8, 45.7 Hz, 2H), 7.48–8.18 (m, 7H); ^{19}F NMR (CD_3COCD_3, 282 MHz) δ: 1.31 (dt, J_{HF}=8.8 Hz, J_{FF}=17.3 Hz, 2F), 154.44 (tt, J_{HF}=45.7 Hz, J_{FF}=17.3 Hz, 1F); MS *m*/*z* (%): 226 (M^+, 97), 144 (79), 127 (16), 115 (100), 89 (12), 63 (15). HRMS calcd for $C_{12}H_9F_3O$: 226.06055; found: 226.05822.

3.2.25. Compound 4bf. Colorless oil; ^{1}H NMR (CD_3COCD_3, 300 MHz) δ: 5.84 (dd, J_{HF}=12.7, 71.2 Hz, 1H) (*Z*), 6.02 (d, J_{HF}=71.2 Hz, 1H) (*E*), 7.28–8.23 (m, 7H); ^{19}F NMR (CD_3COCD_3, 56.4 MHz) δ: 23.4 (m, 1F)

(*Z*), 46.8 (m, 1F) (*E*), 106.1 (m, 1F) (*Z*), 113.7 (m, 1F) (*E*); MS *m/z* (%): 206 (M^+, 54), 186 (16), 159 (13), 127 (100), 77 (13). HRMS calcd for $C_{12}H_8F_2O$: 206.05432; found: 206.05100.

3.2.26. Compounds 3bg[18] and 4bg.[19] Colorless oil; ^1H NMR ($CDCl_3$, 300 MHz) (mixture of *3bg* and *4bg*) δ: 1.18–1.26 (m, CH_3), 2.12–2.35 (m, $MeCH_2$), 4.43 (dt, J_{HF}=46.2, 8.5 Hz, CF_2CH_2F), 4.91 (m, C=CH) (*Z*), 4.96 (m, C=CH) (*E*); ^{19}F NMR ($CDCl_3$, 56.4 MHz) (mixture of **3bg** and **4bg**) δ: 5.2 (m, $-CF_2$), 27.1 (m, C=F) (*Z*), 51.2 (m, C=CF) (*E*), 117.4 (m, C=CF) (*Z*), 121 (m, C=CF) (*E*), 158.0 (m, CH_2F); GC-MS, 128 for **3bg** and 108 for **4bg** (**3bg** require 128 and **4bg** require 108).

3.2.27. Compounds 3bh[18] and 4bh.[19] Colorless oil; ^1H NMR ($CDCl_3$, 300 MHz) (mixture of **3bh** and **4bh**) δ: 1.17–1.34 (m, CH_3), 4.01 (m, $(CH_3)_2C-H$), 4.39 (dt, J_{HF}=45.0, 9.0 Hz, CF_2CH_2F), 4.61 (m, $(CH_3)_2C-H$), 6.51 (m, C=CH) (*Z*), 6.69 (m, C=CH) (*E*); ^{19}F NMR ($CDCl_3$, 56.4 MHz) (mixture of **3bh** and **4bh**) δ: 5.7 (m, CF_2), 27.9 (m, C=F) (*Z*), 54.2 (m, C=CF) (*E*), 119.8 (m, C=CF) (*Z*), 122.3 (m, C=CF) (*E*), 156.5 (m, CH_2F); GC-MS, 142 for **3bh** and 122 for **4bh** (**3bh** require 142 and **4bh** require 122).

3.2.28. Compound 3bi. Colorless oil; ^1H NMR (CD_3COCD_3, 300 MHz) δ: 5.21 (dt, J_{HF}=8.8, 45.8 Hz, 2H), 5.56 (s, 2H), 7.83–7.95 (m, 5H); ^{19}F NMR (CD_3COCD_3, 282 MHz) δ: −2.08 (dt, J_{HF}=8.8 Hz, J_{FF}=15.3 Hz, 2F), 155.12 (tt, J_{HF}=45.8 Hz, J_{FF}=15.3 Hz, 1F); MS *m/z* (%): 190 (M^+, 59), 107 (17), 91 (100), 79 (44), 77 (27), 65 (21). HRMS calcd for $C_9H_9F_3O$: 190.06055; found: 190.06040.

3.2.29. Compound 6a. Colorless oil; ^1H NMR ($CDCl_3$, 300 MHz) δ: 6.06 (d, J_{HF}=3.7 Hz, 1H), 7.18 (d, J_{HH}=3.1 Hz, 1H), 7.93 (d, J_{HH}=3.1 Hz, 1H), 7.94 (s, 1H); ^{19}F NMR ($CDCCl_3$, 56.4 MHz) δ: 20.0 (d, J_{HF}=3.7 Hz, 1F); MS *m/z* (%): 146 (M^+, 95), 111 (100), 84 (26), 79 (21), 57 (22). HRMS calcd for $C_5H_4N_2FCl$: 146.00470; found: 146.00711.

3.2.30. Compound 6b. Colorless oil; ^1H NMR (CD_3COCD_3, 300 MHz) δ: 2.39 (s, 3H), 6.83 (d, J_{HH}=1.5 Hz, 1H), 6.98 (s, 1H), 7.29 (d, J_{HH}=1.5 Hz, 1H); ^{19}F NMR (CD_3COCD_3, 58.4 MHz) δ: 10.8 (s, 1F); MS *m/z* (%): 160 (M^+, 99), 125 (100), 84 (22), 79 (23), 74 (18), 42 (23). HRMS calcd for $C_6H_6N_2FCl$: 160.02035; found: 160.01744.

3.2.31. Compound 6c. Colorless oil; ^1H NMR (CD_3COCD_3, 300 MHz) δ: 6.31 (d, J_{HF}=19.8 Hz, 1H) (*Z*), 6.70 (s, 1H) (*E*), 7.22–7.66 (m, 6H); ^{19}F NMR (CD_3COCD_3, 58.4 MHz) δ: 11.6 (m, 1F) (*Z*/*E*); MS *m/z* (%): 195 (M^+, 100), 160 (89), 133 (69), 117 (40), 77 (28). HRMS calcd for $C_{10}H_7NFCl$: 195.02511; found: 195.02626.

3.2.32. Compound 6d. Colorless oil; ^1H NMR (CD_3COCD_3, 300 MHz) δ: 2.30–2.31 (s, 3H) (*Z*/*E*), 6.15 (d, J_{HF}=21.0 Hz, 1H) (*Z*), 6.59 (s, 1H) (*E*), 7.18–7.61 (m, 5H); ^{19}F NMR (CD_3COCD_3, 58.4 MHz) δ: 17.3 (m, 1F) (*Z*/*E*); MS *m/z* (%): 209 (M^+, 100), 174 (11), 154 (10), 128 (43). Anal. calcd for $C_{11}H_9NFCl$: C, 63.32, H, 3.86, N, 6.71, F, 9.11; found: C, 63.37, H, 4.08, N, 6.90, F, 9.19.

3.2.33. Compound 6e. Colorless oil; ^1H NMR (CD_3COCD_3, 300 MHz) δ: 6.88 (d, J_{HF}=19.6 Hz, 1H) (*Z*), 7.20 (s, 1H) (*E*), 7.59–8.23 (m, 4H); ^{19}F NMR (CD_3COCD_3, 58.4 MHz) δ: 16.1 (m, 1F) (*Z*/*E*); MS *m/z* (%): 197 (M^+, 28), 171 (33), 169 (100), 136 (38), 107 (83). HRMS calcd for $C_8H_5N_3FCl$: 197.01560; found: 197.01433.

3.2.34. Compound 6f. Mp=79–80°C; ^1H NMR (CD_3COCD_3, 300 MHz) δ: 7.03 (s, 1H) (*E*), 7.36–7.61 (m, 8H); ^{19}F NMR (CD_3COCD_3, 58.4 MHz) δ: 13.4 (s, 1F) (*E*); MS *m/z* (%): 245 (M^+, 100), 210 (81), 209 (52), 190 (12). HRMS calcd for $C_{14}H_9NFCl$: 245.04076; found: 245.03621.

3.2.35. Compound 8a.[20] Colorless oil; ^1H NMR ($CDCl_3$, 300 MHz) δ: 5.32 (d, J_{HF}=22.7 Hz, 1H) (*Z*), 5.95 (d, J_{HF}=8.9 Hz, 1H) (*E*), 7.21–7.48 (m, 5H); ^{19}F NMR ($CDCl_3$, 282 MHz) δ: 12.77 (d, J_{HF}=22.7 Hz, 1H) (*Z*), 22.09 (d, J_{HF}=8.9 Hz, 1H) (*E*); MS *m/z* (%): 188 (M^+, 86), 153 (100), 109 (86), 77 (35), 51 (36).

3.2.36. Compound 9a. Colorless oil; ^1H NMR ($CDCl_3$, 300 MHz) δ: 6.34 (d, J_{HF}=28.2 Hz, 1H) (*E*), 6.48 (d, J_{HF}=9.9 Hz, 1H) (*Z*), 7.29–7.53 (m, 10H); ^{19}F NMR ($CDCl_3$, 282 MHz) δ: 4.11 (d, J_{HF}=28.2 Hz, 1F) (*E*), 8.91 (d, J_{HF}=9.9 Hz, 1F) (*Z*); MS *m/z* (%): 262 (M^+, 98), 153 (100), 152 (91), 109 (86), 77 (19). HRMS calcd for $C_{14}H_{11}FS_2$ 262.02862; found: 262.02754.

3.2.37. Compound 10a.[21] Mp=53–54°C; ^1H NMR ($CDCl_3$, 300 MHz) δ: 5.74 (s, 1H), 7.18–7.44 (m, 15H); MS *m/z* (%): 352 (M^+, 70), 243 (14), 165 (57), 134 (100), 109 (39), 77 (22); IR (KBr) ν: 3102, 1576, 1475, 1021, 902, 800, 744, 735, 688.

3.2.38. Compound 8b.[20] Colorless oil; ^1H NMR ($CDCl_3$, 300 MHz) δ: 2.31–2.32 (m, 3H) (*Z*/*E*), 5.40 (d, J_{HF}=23.1 Hz, 1H) (*E*), 5.95 (d, J_{HF}=11.3 Hz, 1H) (*Z*), 7.18–7.37 (m, 6H); ^{19}F NMR ($CDCl_3$, 282 MHz) δ: 13.67 (d, J_{HF}=11.3 Hz, 1H) (*Z*), 26.78 (d, J_{HF}=23.1 Hz, 1H) (*E*); MS *m/z* (%): 202 (M^+, 71), 167 (78), 152 (33), 133 (21), 91 (28).

3.2.39. Compound 9b.[20b] Colorless oil; ^1H NMR ($CDCl_3$, 300 MHz) δ: 2.33–2.34 (m, 6H) (*Z*/*E*), 6.21 (d, J_{HF}=26.8 Hz, 1H) (*E*), 6.28 (d, J_{HF}=11.9 Hz, 1H) (*Z*), 7.11–7.39 (m, 8H); ^{19}F NMR ($CDCl_3$, 282 MHz) δ: 3.81 (d, J_{HF}=11.9 Hz, 1F) (*Z*), 7.45 (d, J_{HF}=26.8 Hz, 1F) (*E*); MS *m/z* (%): 290 (M^+, 31), 167 (100), 152 (75), 123 (61), 91 (32), 77 (23). Anal. calcd for $C_{16}H_{15}FS_2$: C, 66.17, H, 5.21; found: C, 66.27, H, 5.31.

3.2.40. Compound 10b.[21] Mp=58–59°C; ^1H NMR ($CDCl_3$, 300 MHz) δ: 2.39–2.41 (m, 9H), 6.38 (3, 1H), 7.11–7.40 (m, 12H); MS *m/z* (%): 394 (M^+, 77), 271 (18), 148 (100), 147 (90), 123 (55), 91 (35).

3.2.41. Compound 8c. Colorless oil; ^1H NMR ($CDCl_3$, 300 MHz) δ: 2.14–2.16 (m, 3H) (*Z*/*E*), 5.94 (d, J_{HF}=22.8 Hz, 1H) (*E*), 6.15 (d, J_{HF}=9.3 Hz, 1H) (*Z*),

Table 4. ^{19}F NMR signals of **1** in DMSO in the absence or in the presence of KOH before and after heating at 80°C for 8 h

	At 25°C (ppm)		After heating (ppm)	
	Absence of KOH	KOH	Absence of KOH	KOH
1a	−7.37	−7.95	−7.37	−7.96
1b	−2.09 (CF_3) 161.85 (CH_2F)	−2.09 (CF_3) 161.92 (CH_2F)	−2.09 (CF_3) 161.86 (CH_2F)	2.27 (CF_3) 161.68 (CH_2F)

7.18–7.38 (m, 4H); ^{19}F NMR ($CDCl_3$, 282 MHz) δ: 13.56 (d, J_{HF}=9.3 Hz, 1F) (*Z*), 17.98 (d, J_{HF}=22.8 Hz, 1F) (*E*); MS *m/z* (%): 202 (M^+, 50), 167 (81), 152 (39), 133 (11), 91 (28). HRMS calcd for C_9H_8ClFS: 202.00193; found: 202.02361.

3.2.42. Compound 9c. Colorless oil; ^1H NMR ($CDCl_3$, 300 MHz) δ: 2.35–2.41 (m, 6H) (*Z*/*E*), 6.21 (d, J_{HF}=29.1 Hz, 1H) (*E*), 6.35 (d, J_{HF}=10.2 Hz, 1H) (*Z*), 7.13–7.40 (m, 8H); ^{19}F NMR ($CDCl_3$, 282 MHz) δ: 3.66 (d, J_{HF}=10.2 Hz, 1F) (*Z*), 7.58 (d, J_{HF}=29.1 Hz, 1F) (*E*); MS *m/z* (%): 290 (M^+, 100), 167 (83), 152 (41), 123 (29), 91 (22). Anal. calcd for $C_{16}H_{15}FS_2$: C, 66.17, H, 5.21; found: C, 66.11, H, 5.23.

3.2.43. Compound 10c.[21] Mp=62–63°C; ^1H NMR ($CDCl_3$, 300 MHz) δ: 2.29–2.30 (m, 9H), 6.45 (s, 1H), 7.16–7.77 (m, 12H); MS *m/z* (%): 394 (M^+, 65), 271 (12), 239 (10), 179 (81), 148 (100), 123 (49).

3.2.44. Compound 8d. Colorless oil; ^1H NMR ($CDCl_3$, 300 MHz) δ: 6.15 (d, J_{HF}=18.6 Hz, 1H) (*E*), 6.41 (d, J_{HF}=6.0 Hz, 1H) (*Z*), 7.25–7.41 (m, 4H); ^{19}F NMR ($CDCl_3$, 282 MHz) δ: 13.91 (d, J_{HF}=18.6 Hz, 1H) (*E*), 19.09 (d, J_{HF}=6.0 Hz, 1H) (*Z*); MS *m/z* (%): 222 (M^+, 50), 187 (40), 159 (15), 143 (15), 108 (20), 75 (18). HRMS calcd for $C_8H_5ClFS_2$: 221.94731; found: 222.02156.

3.2.45. Compound 10d. Bp=83–85°C; ^1H NMR ($CDCl_3$, 300 MHz) δ: 6.58 (m, 1H), 7.10–7.36 (m, 12H); MS *m/z* (%): 456 (M^+, 24), 313 (4), 267 (12), 235 (26), 199 (57), 168 (100), 143 (45); IR (KBr) ν: 3011, 475, 1388, 1089, 1011, 817, 799, 741. Anal. calcd for $C_{20}H_{13}Cl_3S_2$: C, 52.70, H, 2.87, S, 21.10; found: C, 52.82, H, 2.92, S, 20.69.

3.2.46. Compound 11.[22] Mp=40–41°C; ^1H NMR ($CDCl_3$, 300 MHz) δ: 7.30–7.55 (m, 10H); MS *m/z* (%): 242 (M^+, 100), 165 (31), 133 (6), 109 (5), 77 (35).

3.3. An attempt to obtain 12 from 1

A solution of CF_3CH_2X (**1a**, 1.113 g, 0.00939 mol; **1b**, 1.048 g, 0.0103 mol) in 12 ml DMSO was obtained as described as above. Their ^{19}F NMR spectra were measured at 25°C or after heating at 80°C for 8 h. After adding KOH (0.789 g, 0.0141 mol) to the solution of **1a**, and KOH (0.863 g, 0.0154 mol) to the solution of **1b**, the corresponding ^{19}F NMR spectra were also measured (see Table 4).

All the data showed that **12** could not be obtained from **1**. At the same time, a part of **1a** could be recovered from the mixture of **1a**/KOH/DMSO by distillation. The ^{19}F NMR signal of **1a** was disappeared after treating **1a**/KOH/DMSO with H_2O, and the fluoride ion was observed by ^{19}F NMR (40.11 ppm) and HPIC. Therefore, the following reaction seems to occur.

$$CF_3CH_2Cl + KOH \xrightarrow[DMSO]{H_2O} [CF_2{=}CHCl]$$

1a

$$\longrightarrow [CF_2CH_2Cl \xrightarrow[-F^-]{H_2O} ClCH_2COOH]$$

$$\longrightarrow ClCH_2COOK \text{ (decomposed)}$$

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References

1. (a) Horvàth, I. T. *Acc. Chem. Res.* **1998**, *31*, 641–650. (b) Dewolf, E.; Vankoten, G.; Deelman, B. J. *Chem. Soc. Rev.* **1999**, *28*, 37–41.
2. Richter, B.; Spek, A. L.; Koten, G. V.; Deelman, B. J. *J. Am. Chem. Soc.* **2000**, *122*, 3945–3951.
3. (a) Schneider, S.; Bannwarth, W. *Angew. Chem., Int. Ed. Engl.* **2000**, *39*, 4142–4145. (b) Curran, D. P.; Hoshino, M. *J. Org. Chem.* **1996**, *61*, 6480–6481.
4. Haddletan, D.; Jackson, S. G.; Bon, S. A. F. *J. Am. Chem. Soc.* **2000**, *122*, 1542–1543.
5. Curran, D. P.; Luo, Z. *J. Am. Chem. Soc.* **1999**, *121*, 9049–9072.
6. (a) Rocaboy, C.; Rutherford, D.; Bennett, B. L.; Gladysz, J. A. *J. Phys. Org. Chem.* **2000**, *13*, 596–603. (b) Wende, M.; Meier, R.; Gladysz, J. A. *J. Am. Chem. Soc.* **2001**, *123*, 11490–11491.
7. Powell, R. L. Refrigerants, Propellants and Foaming-blowing Agents. In *Chemistry of Organic Fluorine Compounds II*; Hudlicky, M., Pavlath, A. E., Eds.; *ACS Monograph 187*; American Chemical Society, Washington, DC, 1995; pp 1087–1098.
8. (a) Drakesmith, F. G.; Richardson, R. D.; Stewart, O. J.; Tarrant, P. *J. Org. Chem.* **1968**, *33*, 286–291. (b) Burdon, J.; Coe, P. L.; Haslock, I. B.; Powell, R. L. *J. Chem. Soc., Chem. Comm.* **1996**, 49–50. (c) Burdon, J.; Coe, P. L.; Haslock, I. B.; Powell, R. L. *J. Fluorine Chem.* **1997**, *85*, 151–153. (d) Coe, P. L. *J. Fluorine Chem.* **1999**, *100*, 45–52.
9. Wu, K.; Chen, Q. Y. *J. Fluorine Chem.* **2002**, *113*, 79–83.
10. Fuchigami, T.; Yamamoto, K.; Nakagaw, Y. *J. Org. Chem.* **1991**, *56*, 137–142 and references cited therein.
11. A preliminary note see: Wu, K.; Chen, Q. Y. *Chin. J. Chem.* **2001**, *19*, 1273–1279.
12. Nakai, T.; Tanaka, K.; Ishikawa, N. *J. Fluorine Chem.* **1977**, *9*, 89–93.

13. Cushman, M.; He, H. M.; Katezenllenbogen, J. A.; Varma, R. K.; Harnal, E.; Lin, C. M.; Ram, S.; Sachdeva, Y. P. *J. Med. Chem.* **1997**, *40*, 2323–2334.
14. McBee, E. T.; Bolt, R. O. *Ind. Eng. Chem.* **1947**, *39*, 412–415.
15. Tarrant, P.; Brown, H. C. *J. Am. Chem. Soc.* **1951**, *73*, 1781–1783.
16. (a) Shainyan, B. A.; Danilevich, Y. S. *Russ. J. Org. Chem.* **1996**, *32*, 188. (b) Air Reduktion, US Patent 2799712, 1954.
17. Barbara, Z.; Marko, Z. *J. Org. Chem.* **1990**, *55*, 1099–1102.
18. Park, J. D.; Cummings, H. L.; Lacher, J. R. *J. Org. Chem.* **1958**, *23*, 1785–1786.
19. Makin, S. V.; Kruglikova, R. I.; Kharitonova, O. V.; Alshava, B. M.; Yaguplskii, L. M.; Bogolyubskii, A. V. *J. Org. Chem. USSR* **1990**, *26*, 637–639.
20. (a) Pelavarenne, S. Y.; Viehe, H. G. *Chem. Ber.* **1970**, *103*, 1198–1208. (b) Shainyan, B. A.; Vereshchagin, A. L. *Russ. J. Org. Chem.* **1993**, *29*, 1981–1988.
21. (a) Prilezhaeva, E. N.; Donzova, N. E.; Petvkchova, N. P.; Bogdanov, V. S. *Gazz. Chim. Ital.* **1990**, *120*, 235–240. (b) Riera, A.; Cabre, F.; Moyano, A.; Pericas, M. A.; Santamaria, J. *Tetrahedron* **1990**, 2169–2172.
22. Stang, P. J.; Zhdankin, V. V. *J. Am. Chem. Soc.* **1991**, *113*, 4571–4576.