The Activation of Carbon−Chlorine Bonds in Per- and Polyfluoroalkyl Chlorides: DMSO-Induced Hydroperfluoroalkylation of Alkenes and Alkynes with Sodium Dithionite

Zheng-Yu Long and Qing-Yun Chen*

Laboratory of Fluorine Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 354 Fenglin Lu, 200032 Shanghai, China

Received January 19, 1999 (Revised Manuscript Received April 15, 1999)

In DMSO, the addition reactions of perfluoroalkyl chlorides, R_FCl, to alkenes or alkynes can occur smoothly in the presence of 1.5 equiv of $Na_2S_2O_4$ and $NaHCO_3$ at 75−80 °C for 4−10 h to give the corresponding adducts ($RCH_2CH_2R_F$ or $RCH{=}CHR_F$). Ethyl chlorofluoro- (**1f**), chlorodifluoro- (**1g**) acetates, even nonfluorinated compounds, such as ethyl dichloro- (**1h**), chloro- (**1i**) acetates, and chloroform (**1j**) can undergo the similar reaction. Treatment of ω-iodo (or chloro-) perfluoroalkyl chlorides [$X(CF_2)_nCl$, $n = 2$, 4, X= I or Cl] with >3 equiv of alkenes and $Na_2S_2O_4$ gives directly the symmetrically disubstituted alkanes $(RCH_2CH_2)_2(CF_2)_n$. The symmetrically and unsymmetrically disubstituted adducts $RCH_2CH_2(CF_2)_nCH_2CH_2R'$ from ω- iodoperfluoroalkyl chlorides can be also obtained stepwise, i.e., through the further addition reactions of monoadducts, $RCH_2CH_2(CF_2)_nCl$ to olefins. However, for α,ω-dichloroperfluoroalkanes, the similarly stepwise reactions with an alkene is not clean, both bis-adducts and the corresponding ω-hydrides, $RCH_2CH_2(CF_2)_nH$ as byproducts are also formed. In the absence of alkenes or alkynes, per- and polyfluoroalkyl chlorides can be converted to their sulfinate salts and sulfonyl chlorides.

Introduction

Per- and polyfluoroalkyl halides are useful industrial sources of many fluorine-containing materials.[1] Among them, simple bromides and chlorides are thermally and chemically inert and, thus, used as fire extinguishants (e.g., Halon 1301, CF_3Br; Halon 1211, CF_2BrCl), refrigerants (e.g., CFC-12, CF_2Cl_2; CFC-115, CF_3CF_2Cl), aerosol propellants (e.g., CFC-11, $CFCl_3$) or cleaning solvents (e.g., CFC-113, $ClCF_2CFCl_2$).[2] However, chlorine or bromine atoms, released from long-lived CFCs or Halons by the action of short wavelength solar ultraviolet radiation, causes the depletion of ozone layer. In line with the Montreal Protocol, the production of Halons and CFCs should be stopped since 1994 and 1996, respectively.[3] Along with the appearance of the CFCs and Halons alternatives, there are a quite number of reports on converting CFCs and Halons to useful fluorinated compounds. For example, dibromodifluoromethane was utilized in reductive reactions with olefins to provide 1:1 adducts.[4] Using CF_2Br_2 or CF_2BrCl as the starting materials, Me_3SiCF_2X (X = Cl, Br) compounds were prepared which are useful agents for transferring aldehydes to difluoromethylated alcohols in two steps.[5]

Conversion of chlorofluorocarbons into the corresponding hydropoly-fluorocarbons has attracted much attention because of the latter being the potential CFC replacements. Zinc powder in the presence of catalytic amount of nickel dichloride can reduce perfluoroalkyl chloride to the corresponding hydride in high yields.[6] Reduction of ω-chloroperfluoroalkyl iodides by lithium aluminum hydride in ether at room temperature for several hours not only gives ω-chloroperfluoroalkyl hydrides but also α,ω-dihydroperfluoroalkanes.[7] Palladium-catalytized hydrogenation[8] or electrochemical reduction of CF_2Cl_2[9] results in difluoromethane (HFC-32, CF_2H_2), an excellent new refrigerant.[10] Selective hydrogenolysis of CF_3CCl_3 (CFC-113a) with group VIII transition metal complexes produces CF_3CHCl_2 (HCFC-123)[11] which reacts with zinc and aldehyde to give the corresponding alcohol through organozinc intermediates.[12] Besides the organometallic reductants, such as organotin hydrides,[13] organosilicon-hydrides [e.g., $HSi(C_2H_5)_3$] were reported very recently as selective reductants of halopolyfluorocarbons [e.g.,

(1) (a) Chambers, R. D. *Fluorine in Organic Chemistry*; Wiley-InterScience: New York, 1973. (b) Hudlicky, M. *Chemistry of Organic Fluorine Compounds*; 2nd ed.; Ellis, Horwood: Chichester, England, 1976.

(2) (a) Powell, R. L. Refrigerants, propellants and foam-Blowing Agents. In *Chemistry of Organic Fluorine Compounds II*, Hudlicky, M., Ed.; American Chemical Society, Wishington, DC, 1995. (b) Banks, R. E., Smart, B. E., Tatlow, J. C., Eds.; *Organofluorine Chemistry*: *Principle and Commercial Applications*; Plenum Press: New York, 1994.

(3) (a) Banks, R. E. *J. Fluorine Chem.* **1994**, *67*, 193. (b) Franciso, J. S.; Maricq, M. M. *Acc. Chem. Res.* **1996**, *29*, 391.

(4) (a) Burton, D. J.; Kehoe, L. J. *Tetrahedron Lett.* **1966**, 5163. (b) Maruoka, K.; Sano, H.; Fukutani, Y.; Yamamoto, H. *Chem. Lett.* **1985**, 1689. (c) Hu, C.-M.; Chen, J. *J. Chem. Soc., Chem. Commun.* **1993**, 72.

(5) Yudin, A. K.; Prakash, G. K. S.; Deffieux, D.; Bradley, M.; Bau, R.; Olah, G. A. *J. Am. Chem. Soc.* **1997**, *119*, 1572.

(6) Chen, Q.-Y.; W, J.-P. *Chinese J. Chem.* **1991**, *9*, 181.

(7) Chen, Q.-Y.; Chen, M.-F. *J. Fluorine Chem.* **1990**, *49*, 107.

(8) Cog, B.; Cognion, J. M.; Figneras, D.; Tourigant, D. *J. Catal.* **1993**, *141*, 21.

(9) Delli, E.; Kouloumtzoglou S.; Kyriacou, G.; Lambrou, C. *J. Chem. Soc., Chem. Commun.* **1998**, 1693.

(10) *Chem. Ind.* **1991**, *18*, 31.

(11) Cho, O. J.; Lee, I. M.; Park, K. Y.; Kim, H. S. *J. Fluorine Chem.* **1995**, *71*, 107.

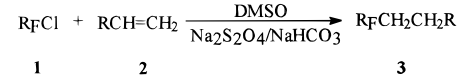
(12) Tamura, M.; Kekiya, A. *J. Fluorine Chem.* **1995**, *71*, 119.

(13) Van, D. P. M.; Belter, R. K.; Borouski, R. J.; Ellis, L. A. S.; Pershichini, P. J., III; Poss, A. J.; Rygas, T. P.; Tung, H. S. *J. Fluorine Chem.* **1995**, 71, *59* and references therein.

10.1021/jo9900937 CCC: $18.00
Published on Web 06/09/1999

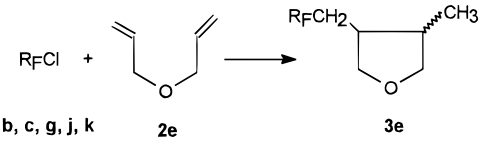
$ClCF_2CFCl_2$, $CF_3CFClCF_2Cl$, and $(CF_3)_2CCl_2$].[14] The order of decreasing activity of different groups in the reduction is $-CCl_2- > -CClF- > -CClH- > -CF_2Cl$. Besides the ability of hydrogenolysis as mentioned above, the carbon−chlorine bond in perfluoroalkyl chloride, R_FCF_2Cl, is hardly functionized by other groups.[15] A special analogue, chlorodifluoromethylbenzene ($C_6H_5CF_2Cl$), was reduced with SmI_2/HMPA to $C_6H_5CF_2H$ (major) through the induction of a simultaneously anionic addition to ketones giving the corresponding alcohols (minor).[16] More importantly, progress in this area was made with the sulfinatodehalogenation of perhalocarbons, which was discovered and developed by Huang and co-workers.[17] Using inexpensive sulfur-containing reductants (e.g., $Na_2S_2O_4$) under mild conditions, per- and polyfluoroalkyl halides (R_FX, X = Br, I; R_FCCl_3) can smoothly give the corresponding sulfinate salts. The sulfinates may be readily converted to perfluoroalkanesulfonyl halides, acids, and their derivatives. More interestingly, this method has been widely applied to perfluoroalkylate alkenes, dienes, allenes, alkynes, and aromatics. However, this system is confined to perhalocarbons and cannot be applied to perfluoroalkyl chlorides, i.e., R_FCF_2Cl.[18] For example, tetrachloromethane afforded the desired product, CCl_3-SO_2Na, with high yield while chloroform was shown to be completely inert.[19] Only recently, it was found that the difluoromethylation of alkenes and alkynes with iododifluoromethane could occur under the standard sulfinatodehalogenation conditions.[20] When we extended this method to 2,2,2-trifluoroethyl halides, the iodide and bromide could be smoothly sulfinatodehalogenated with sodium dithionite in CH_3CN/H_2O at 40−60 °C for 10 h, while the chloride (CF_3CH_2Cl, HCFC-133a) was completely inert.[21] To our surprise, if using dimethyl sulfoxide (DMSO) as a solvent instead of CH_3CN/H_2O, CF_3CH_2Cl could also be converted to the sulfinate and trifluoroethylate alkenes and alkynes.[22] The tremendous role of solvent promoted us to examine the sulfinatodehalogenation possibility of per- and polyfluoroalkyl chlorides. We were fortunate to find the positive results not only for perfluoroalkyl chlorides but also for some nonfluorinated ones.[23] This paper presents our observation.

Scheme 1[a]

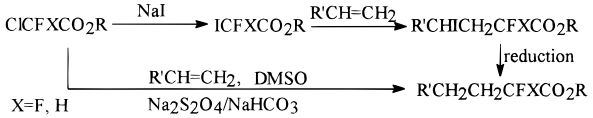


[a] R_F = n-C_4F_9 (**a**), $H(CF_2)_4$ (**b**), $H(CF_2)_6$ (**c**), CF_3CH_2, (**d**), $ClCF_2$ (**e**), $CFHCO_2Et$ (**f**), CF_2CO_2Et (**g**), $ClCHCO_2Et$ (**h**), CH_2CO_2Et (**i**), $HCCl_2$ (**j**), $CF_2ClCFCl$ (**k**). R = n-C_4H_9 (**a**), n-C_5H_{11} (**b**), n-C_6H_{13} (**c**), n-C_7H_{15} (**d**), $CH_2OCH_2CH{=}CH_2$ (**e**), c-C_4H_8 (**f**), CH_2OAc (**g**), $SiMe_3$ (**h**), $CH_2OC_2H_5$ (**i**), CH_2OH (**j**).

Scheme 2



Scheme 3



Results and Discussion

1. Hydroperfluoroalkylation of Alkenes with Per- and Polyfluoroalkyl Chlorides. It was found that per- and polyfluoroalkyl chlorides **1** can smoothly react with alkenes **2** in DMSO in the presence of sodium dithionite and sodium bicarbonate (**1**:**2**:$Na_2S_2O_4$:$NaHCO_3$ = 1:1.5:1.5:1.5) at 75−80 °C for 4−6 h to give the corresponding chlorine-free monoadducts **3** in good yields (see Scheme 1).

The addition products **3be**, **3ce**, **3ge, 3je,** and **3ke** from the chlorides and **2e** are the tetrahydrofuran derivatives, indicative of a free radical intermediate.[24] The cis- and trans- configuration of **3e** can be assigned by comparing the ^1H NMR chemical shift of $-CH_3$ (*cis*- < *trans*-) (see Scheme 2).[24b]

Interestingly, ethyl chlorofluoro- (**1f**), chlorodifluoro- (**1g**), and even nonfluorinated compounds, such as dichloro- (**1h**), chloro-(**1i**) acetates, and chloroform (**1j**) can undergo the similar reaction. Notably, for synthesizing α-fluoro or α,α-difluoroacetates and amides, the starting material chlorocompounds need not be converted first to the corresponding iodides before reduction as previous works did;[25] thus, this method seems to be more straightforward (see Scheme 3).

Both dichlorodifluoromethane (**1e**) and 1,1,2-trifluorotrichloroethane (**1k**) can readily give the monohydroperfluoroalkylated products in the presence of equiva-

(14) Petrov, V. A. *J. Org. Chem.* **1998**, *63*, 7294.

(15) (a) The C−Cl bond in a CF_2Cl group can be weakened by an activating neighboring group, such as chlorodifluoromethylsilanes,[5] chlorodifluoromethyl enol ethers (Rajaonah, M.; Rock, M. H.; Jean-Pierre, Begue; Bonnet-Delpon, D.; Condon, S.; Jean-Yves N. *Tetrahedron Lett.* **1998**, *39*, 3137.), chlorodifluoroesters (Lang, R. W.; Schaub, B. *Tetrahedron Lett.* **1988**, *29*, 2943 and references therein), and chlorodifluoromethylated ketones (Burkholder, C.; Dolbier, W. R. Jr; Medebielle, M.; Ndedi, A. *Tetrahedron Lett.* **1998**, *39*, 8853.). The CF_2^- anion equivalents generated from these compounds by electrochemical metal catalyzed methods or by electron-donor tetrakis(dimethylamino)-ethylene stimulation can be trapped by aldehydes and ketones to give the corresponding alcohols. (b) The attack of sulfur, oxygen and nitrogen nucleophiles on CF_2ClCCl_2F, CF_2ClCCl_3 has been established as a halophilic rather than S_N2 or single electron-transfer mechanism, the products derived are involved in the olefin intermediates (Li, X.-Y.; Jiang, X.-K.; Pan, H.-Q.; Hu, J.-S.; Fu, W.-M. *Pure Appl. Chem.* **1987**, *59*, 1015.).

(16) Yoshida, M.; Suzuki, D.; Tyoda, M. *J. Chem. Soc., Perkin Trans. 1* **1997**, 643.

(17) (a) Huang, W.-Y.; Huang, B.-N.; Wang, W. *Acta Chim. Sin.* (*Chin. Ed.*) **1983**, *41*, 1193. (b) Huang, B.-N.; Wang, B.-H.; Wang, W.; Huang, W.-Y. Acta Chim. Sin. (Engl. Ed.) **1986**, *1*, 68. (c) Huang, W.-Y.; Huang, B.-N.; Wang, W. Acta Chim. Sin. (Engl. Ed.) **1984**, *2*, 188. (d) Huang, W.-Y.; Huang, B.-N.; Wang, W. Acta Chim. Sin. (Engl. Ed.) **1985**, *3*, 253. (e) Huang, W.-Y.; Chen, J.-L. *Acta Chim. Sin.* (Engl. Ed.) **1985**, *4*, 376.

(18) (a) Huang, W.-Y.; Wang, W.; Huang, B.-N. *Acta Chim. Sin.* (Chin. Ed.) **1985**, *43*, 409. (b) Huang, W.-Y.; Lu, L.; Zhang, Y.-F. *Chin. J. Chem.* **1990**, *4*, 350. (c) Huang, W.-Y.; Zhang, H.-Z. *Chin. J. Chem.* **1991**, *1*, 76.

(19) Huang, W.-Y.; Huang, B.-N.; Chen, J.-L. *Acta Chim. Sin.* (*Chin. Ed.*) **1986**, *44*, 45.

(20) Cao, P.; Duan, J.-X.; Chen, Q.-Y. *J. Chem. Soc., Chem. Commun.* **1994**, 737.

(21) Long, Z.-Y.; Chen, Q.-Y. *Tetrahedron Lett.* **1998**, *39*, 8487.

(22) (a) Long, Z.-Y.; Chen, Q.-Y. PRC Patent CN 98110884.9. (b) Long, Z.-Y.; Chen, Q.-Y. PRC Patent CN 98110883.0.

(23) (a) Long, Z.-Y.; Chen, Q.-Y. Patent: CN 98122019.3. (b) Long, Z.-Y.; Chen, Q.-Y. PRC Patent CN 98122021.5.

(24) (a) Chen, Q.-Y. Single electron-transfer reaction of perfluoroalkyl iodides. In *Organofluorine Chemistry in China*; Huang, W. Y., Ed.; Shanghai Science and Technology Press: Shanghai, 1996; Chapter 5, p 112. (b) Chen, Q.-Y. Yang, Z.-Y. *J. Fluorine Chem.* **1985**, *28*, 399.

(25) (a) Zhi, C.-X.; Chen, Q.-Y. *J. Chem. Soc., Perkin Trans. 1* **1996**, 1741. (b) Wang, Y.; Yang, Z.-Y.; Burton, D. J. *Tetrahedron Lett.* **1992**, *33*, 2137. (c)Yang, Z.-Y.; Burton, D. J. *J. Fluorine Chem.* **1989**, *45*, 435. (d) Yang, Z.-Y.; Burton, D. J. *J. Org. Chem.* **1991**, *56*, 5125. (e) Huang, W.-Y.; Lu, L.; Zhang, Y.-F. *Chin. J. Chem.* **1990**, *1*, 68.

Table 1. Reaction of R_FCl with Alkenes in DMSO[a]

entry	R_FCl[b]	alkene	T °C	time (h)	3. yield %[c]
1	**1a**	**2c**	75	6	80
2		**2d**	75	6	81
3		**2f**	70	5	71
4	**1b**	**2a**	70	6	63
5		**2c**	80	4	80
6		**2d**	75	6	88
7		**2e**	70	6	76(cis:trans = 2.3:1)[e]
8		**2f**	70	6	72
9	**1c**	**2a**	75	5	82
10		**2c**	75	6	80
11		**2d**	75	6	82
12		**2e**	75	6	70(cis:trans = 2.3:1)[e]
13		**2f**	75	6	78
14	**1d**	**2a**[d]	90	10	58
15		**2c**[d]	90	10	70
16	**1e**	**2c**[d]	90	10	86
17	**1f**	**2c**	75	6	74
18		**2d**	75	8	71
19		**2f**	75	6	63
20		**2h**	75	6	82
21		**2i**	75	7	75
22	**1g**	**2b**	75	7	80
23		**2c**	75	7	78
24		**2e**	70	6	73(cis:trans = 3:1)[e]
25		**2f**	70	6	88
26		**2g**	75	6	68
27		**2h**	75	6	62
28	**1h**	**2a**	79	6	60
29		**2c**	80	6	71
30		**2f**	75	7	65
31	**1i**	**2g**	75	10	45
32	**1j**	**2a**	80	6	83
33		**2c**	80	5	89
34		**2e**	80	4	73(cis:trans = 4:1)[e]
35		**2g**	80	4	70
36		**2j**	75	6	61
37	**1k**	**2a**	60	6	74
38		**2e**	60	6	48(cis:trans = 1:1)[e]
39		**2f**	60	6	69
40		**2g**	55	6	63

[a] **1**:**2**:$Na_2S_2O_4$:$NaHCO_3$ = 1:1.5:1.5:1.5. [b] The conversion of R_FCl was 100% (determined by ^{19}F NMR). [c] The isolated yields were based on R_FCl and a trace of R_FH was also obtained. [d] In a sealed ampoule. [e] The ratio of cis/trans based on the ^1H NMR.

Scheme 4

$$Y(CF_2)_4Cl + RCH{=}CH_2 \xrightarrow[Na_2S_2O_4/NaHCO_3]{DMSO} RCH_2CH_2(CF_2)_4CH_2CH_2R$$

2 **6**

Y = I (**4**) R = n-C_4H_9 (**a**), n-C_6H_{13} (**c**)
Y = Cl (**5**)

lents of alkene and $Na_2S_2O_4$. For the former, dihydroperfluoroalkylated derivatives $(RCH_2CH_2)_2CF_2$ have never been obtained despite using large excess of alkenes and $Na_2S_2O_4$, while for the latter, one of chlorine at the end group of $-CFCl_2$ was smoothly substituted and the reaction became complicated when employing large excess of $Na_2S_2O_4$. All the results are listed in Table 1.

2. Bishydroperfluoroalkylation of Alkenes with ω-Iodo (or chloro)Perfluoroalkyl Chlorides. When ω-iodo (or chloro) perfluoroalkyl chlorides **4** and **5** were treated with >3 equivalents of alkenes and $Na_2S_2O_4$ in DMSO, the symmetrically disubstituted alkanes **6** were obtained directly (see Scheme 4).

The same disubstituted products from ω-iodoperfluoroalkyl chlorides can be formed stepwise, i.e., monosubstituted perfluoroalkyl chloride, formed in the presence of equivalents of starting materials (ω-iodoperfluoroalkyl chloride:alkene:$Na_2S_2O_4$:$NaHCO_3$ = 1:1.5:1.5:1.5), may react further with the same or different alkene to afford bis-substituted one. For example, treatment of β-iodotetrafluoroethyl chloride (**7**) with 4-acetyl-butene-1 (**2k**) in the presence of 1.5 equiv of $Na_2S_2O_4$ in DMSO at 40 °C for 2 h to give the corresponding monoadduct (**8**). This new adduct can react further with hexene-1 (**2a**) or octene-1 (**2c**) to afford the unsymmetrically bis-adduct (**9**) with a small amount of the hydride as byproduct (see Scheme 5).

Scheme 5

$$I(CF_2)_2Cl + CH_2{=}CH(CH_2)_2COCH_3 \xrightarrow[DMSO,\ 40^\circ C]{Na_2S_2O_4} Cl(CF_2)_2CH_2CH_2(CH_2)_2COCH_3$$

7 **2k** **8**

$$\xrightarrow[Na_2S_2O_4]{RCH{=}CH_2} RCH_2CH_2(CF_2)_2(CH_2)_4COCH_3 + H(CF_2)_2(CH_2)_4COCH_3$$

DMSO, 90°C **9** ~10%

Table 2. Reaction of ω-Iodo (or Chloro) Perfluoroalkyl Chlorides with Alkenes in DMSO (R_FCl:2:$Na_2S_2O_4$:$NaHCO_3$ = 1:3:3:3)

R_FCl	alkene	T °C	time(h)	converted %[a]	product	yield %[b]
4	**2a**	90	10	100	**6a**	73
4	**2c**	85	10	100	**6c**	65
5	**2a**	90	10	90	**6a**	54
5	**2c**	90	12	88	**6c**	50
7	**2k**[c]	40	2	100	**8**	72
8	**2a**[c]	95	10	90	**9a**	52
8	**2c**[c]	90	10	80	**9c**	60

[a] The conversion determined by ^{19}F NMR. [b] The isolated yields based on R_FCl and in addition to 5−10% of R_FH. [c] R_FCl:**2**:Na_2SO_4:$NaHCO_3$ = 1:1.5:1.5:1.5.

Scheme 6

$$Cl(CF_2)_4Cl \xrightarrow[1.5\ eq.\ Na_2S_2O_4,\ DMSO]{C_4H_9CH{=}CH_2}$$

5

$C_4H_9CH_2CH_2(CF_2)_4Cl$ 65%

$C_4H_9CH_2CH_2(CF_2)_4CH_2CH_2C_4H_9$ 10%

$C_4H_9CH_2CH_2(CF_2)_4H$ 25%

However, unlike the ω-iodoperfluoroalkyl chlorides, the α,ω-dichloroperfluoroalkanes (e.g., **5**) are unable to react stepwise cleanly with olefin and both the bis-adduct and the corresponding ω-hydride as byproducts were obtained despite only using 1.5 equiv of starting materials. The results are shown in Table 2. (See also Scheme 6.)

3. Hydroperfluoroalkylation of Alkynes with Per- and Polyfluoroalkyl Chlorides. Similar to alkenes, alkynes reacted with perfluoroalkyl chlorides in the presence of 1.5 equiv. of $Na_2S_2O_4$ in DMSO at 75−80 °C for 7−10 h to give the corresponding *E*/*Z* mixtures of perfluoroalkylated alkene in 45−76% yields and a small amount of R_FH (10−15%). The *E* and *Z* isomers were determined by comparing the chemical shifts of the $-\mathbf{CF_2}CH{=}CHR$ in their respective ^{19}F NMR spectra, the downfield signal being assigned to *Z*-isomer and the upfield being assigned to *E*-isomer.[26] The stereochemistry of **11gd** was designated *E*-isomer on the basis of the coupling constant between the vinyl protons ($^3J_{H,H}$ = 15.8 Hz). The results are shown in Table 3. (See also Scheme 7.)

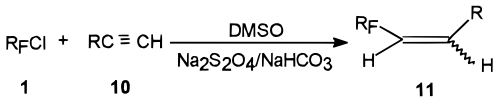
4. The Synthesis of Sodium Perfluoroalkanesulfinates and Their Derivatives from Perfluoroalkyl Chlorides and $Na_2S_2O_4$. Perfluoroalkyl chlorides **1** can be easily converted to the corresponding sulfinate salts **12** with $Na_2S_2O_4$/$NaHCO_3$ in DMSO at 75 °C for 8 h. Both the conversion and yield are high (>80%) as shown by ^{19}F NMR spectroscopy. The isolation of the sulfinate salts

Table 3. Reaction of R_FCl with Alkynes in DMSO[a]

entry	R_FCl[b]	alkyne	*T* °C	time	*Z*/*E*[c]	yield %[d]
1	**1b**	**10a**	75	8	60/40	72
2		**10c**	80	7	92/8	71
3		**10d**	75	8	15/85	65
4	**1c**	**10a**	75	8	53/47	72
5		**10c**	75	8	82/18	69
6		**10d**	75	10	15/85	76
7	**1d**	**10a**	90	10	70/30	47
8		**10b**	90	10	75/25	52
9	**1f**	**10c**	70	10	50/50	58
10	**1g**	**10a**	75	10	55/45	59
11		**10c**	70	10	10/90	64
12		**10d**	75	10	0/100	45
13		**10e**	75	10	38/62	68

[a] **1**:**2**:$Na_2S_2O_4$:$NaHCO_3$ = 1:1.5:1.5:1.5. [b] The conversion of R_FCl was 100% determined by ^{19}F NMR. [c] The ratio of *Z*/*E* was determined by ^{19}F NMR. [d] The isolated yields based on R_FCl.

Scheme 7

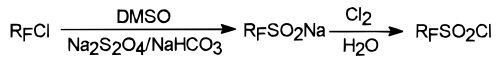


1 10 11

R_F= $H(CF_2)_4$ (b), $H(CF_2)_6$ (c), CF_3CH_2 (d), $CFHCO_2Et$ (f), CF_2CO_2Et (g)

R= C_4H_9 (a), C_6H_{13} (b), Ph (c), CH_2OH (d), CH_2OCH_3 (e)

Scheme 8



1 12 13

R_F= C_4F_9 (a), 40%
$H(CF_2)_4$ (b), 32%
CF_3CH_2 (c), 37%

from inorganic impurities is very difficult because all of them are soluble in water. An usual treatment with chlorine gas in ice-cooled water gives the corresponding sulfonyl chlorides in low yield, sometimes, accompanying the formation of R_FSO_3H (see Scheme 8).

It is known that treatment of the sulfinate salt with an oxidant generates the perfluoroalkyl radical which can add to the olefin producing the corresponding adduct.[27] However, in our case the sodium sulfinate (**12**), obtained without isolation in DMSO, can react with alkene at 80 °C for 8−10 h affording the monoadduct. However, the yield is low because DMSO is a weak oxidant, as demonstrated in Scheme 9.[28]

Scheme 9

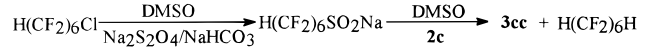


Table 4. Solvents Are Tested in the Reaction of 1a and 1c with 2b at 75 °C for 5 h[a]

R_FCl	alkene	solvent	converted %[b]	**3**%	R_FH%
1a	**2b**	DMSO	100	80	<10
1a	**2b**	HMPA	75	50	50
1c	**2b**	HMPA	60	25	75
1c	**2b**	DMF	10		
1c	**2b**	DMSO/H_2O(5/1)	100	48	35[c]
1a	**2b**	CH_3CN/H_2O(1/1)	0	0	0
1a	**2b**	CH_3OH	0	0	0

[a] **1**:**2**:$Na_2S_2O_4$:$NaHCO_3$ 1:1.5:1.5:1.5. [b] The conversion of R_FCl was determined by ^{19}F NMR. [c] The byproduct is $H(CF_2)_6SO_2Na$.

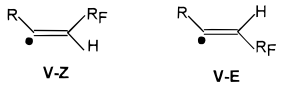
5. Study of Solvent Effect. From the results mentioned above, it is apparent that, dramatically different from CH_3CN/H_2O, DMSO chosen in these reaction seems essential for the activation of carbon−chlorine bonds of perfluoroalkyl chlorides. Because, like DMSO, hexamethylphosphoramide (HMPA) or dimethylforamide (DMF)[29] are usually considered to be good solvents for electron transfer (ET) reaction. Thus, these solvents were employed to study their effect in the course of the reactions (**1a**, **1c**, and **2b** used as an example). The data are listed in Table 4.

The results from Table 4 showed that, as expected, HMPA or DMF can be also used in this reaction. However, the conversion and yield of the adduct were lower as compared with those in DMSO, with the hydride being the major product. When 20% (v/v) of H_2O was used as a cosolvent in DMSO, the yield was greatly decreased accompanying a significant amount of sulfinate salt. Therefore, DMSO seems to be the best solvent for the reaction.

6. Inhibition and Mechanism Consideration. Before the mechanism consideration, some inhibition experiments were carried out. Addition of ET scavenger, i.e., *p*-dinitrobenzene (DNB) (20 mol %) or free radical inhibitor, i.e., hydroquinone (HQ) (20 mol %) to the reaction mixture of **1c** and **2a** decreased the conversion of **1c** significantly (from 100% without DNB and HQ to 50% and 33%, respectively) at the same reaction temperature and time (75 °C for 5 h). UV irradiation accelerated the reaction, e.g., at 75 °C for 1.5 h the conversion of **1c** is 80% under UV while 20% under laboratory illumination.

Both the inhibition experiments and the formation of tetrahydrofuran derivatives from the reaction with diallyl ether indicated that the perfluoroalkyl radical may be involved in the reaction mechanism. The most likely explanation of generation of $R_F^•$ is that R_FCl, quite similar to R_FI,[17] accepts one electron from radical anion of sulfur

(26) Chen, J.; Hu, C.-M. *Chinese J. Chem*. **1994**, *12*, 468. The *Z*/*E* ratios of the addition products in Table 3 are not regular which cannot be completely understood yet. Generally, when the $R_F^•$ adds to alkynes, they will form both *Z*- and *E*- radical intermediate V−*Z* and V−*E*.



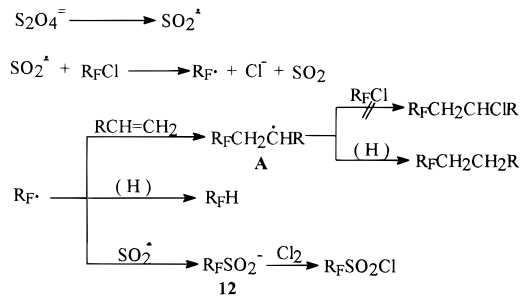
These intermediates can either isomerize or abstract a hydrogen from the solvent. If the lifetimes of the radical intermediates are lengthened by stabilizing (or spin-delocalizing) effects of the substituent R, then these radical intermediates will be able to isomerize and concentration of the more stable isomer will increase greatly, i.e., the amount of radical intermediate V-*E*, hence, **11***E*- isomer will become predominant. On the other hand, if the life-spans of V=-*Z* and V-*E* are very short, then the radical intermediates can abstract hydrogen atom before they have a chance to isomerize, thus leading to a mixture of *Z*/*E* isomers of **11**. (see Li, A.-R.; Chen, Q.-Y. *Synthesis* **1996**, *5*, 606.). This rationalization appears plausible for **11gc** (R=C_6H_5, *Z*/*E* = 10/90, entry 11, Table 3) and **11ba** (*R* = *n*-C_4H_9, *Z*/*E* = 60/40, entry 1, Table 3), because it is known that C_6H_5 substitute is much more effective spin-stabilizer than alkyl substitutes (σ_{ij} of C_6H_5 0.47, σ_{ij} of alkyl = 0.15) (Jiang, X.-K.; Ji, G.-Z. *J. Org. Chem*. **1992**, *57*, 6051.). However, it cannot explain the big difference of the *Z*/*E* ratios between the products **11bc** (*Z*/*E* = 92/8) and **11gc** (*Z*/*E* = 10/90) (entry 2 and 11, Table 3) which were produced from same alkyne (**10**) but different R_FCl (**1b** versus **1g**). Therefore, besides R, the β- substituent R_F in vinyl radicals, V-*Z* and V-*E*, seemingly, has also some influence on the neighboring free radical and, hence, exert the steroselectivity of the addition reaction.

(27) (a) Huang, W.-Y.; Xie, Y. *Chin. J. Chem*. **1990**, *4*, 362. (b) Huang, W.-Y.; Hu, L.-Q.; Xie, Y. *Acta Chim. Sin*. (*Engl. Ed*.) **1989**, *2*, 190.

(28) Huang, S.-L.; Omura, K.; Swern, D. *Synthesis* **1978**, 297.

(29) (a) Meijs, G. F. *J. Org. Chem*. **1986**, *51*, 606. (b) Bunnett, J. F.; Scamehorn, R. G.; Traber, R. P. *J. Org. Chem*. **1976**, *41*, 3677.

Scheme 10



dioxide, produced by decomposition of sodium dithionite, then dissociates to give $R_F^•$ and Cl^-. The $R_F^•$ adds either to alkene to form intermediate A, or to SO_2^{-}. to form sulfinate **12**. The addition reaction of $R_F^•$ to alkene is much faster than that to $SO_2^{-•}$, thus, none of the sulfinate is accompanied. The intermediate, **A**, did not abstract chlorine from R_FCl due to the strong carbon−chlorine bond but easily picked a hydrogen from DMSO to afford the adduct. Chlorination of the sulfinate **12** gives the corresponding sulfonyl chloride. The $R_F^•$ abstracts hydrogen from the solvent producing the byproduct, R_FH (see Scheme 10).

The question arises why the reaction of R_FCl can be induced by DMSO but not by CH_3CN/H_2O, the latter being very suitable for sulfinatodehalogenation of R_FX (X = I, Br) and R_FCCl_3. The reason is not very clear yet now. In fact, although $Na_2S_2O_4$ is sparingly soluble in DMSO at room temperature, the mixture at 75 °C during stirring becomes highly dispersive. However, the solvent polarity, dielectric constant and dipole moment of DMSO and CH_3CN are not different very much [E_TDMSO (30) = 46 kcal/mol, E_T CH_3CN (30) = 45 kcal/mol; ϵ^{DMSO} (25 °C) = 46.7, ϵ^{CH_3CN} (20 °C) = 37.5; μ (DMSO) = 13.0 × 10^{-30} C m, μ (CH_3CN) = 11.5 × 10^{-30} C m.].[30]

In conclusion, we have developed a new practical hydroperfluoroalkylation method of alkenes and alkynes with ever thought inert perfluoroalkyl chlorides in the presence of sodium dithionite. In addition, perfluoroalkanesulfinates and sulfonyl chlorides can be prepared directly from available perfluoroalkyl chlorides. DMSO plays a unique role in these reactions.

Experimental Section

^{1}H NMR and ^{19}F NMR spectra were recorded at 90 or 300 MHz and 282 MHz. Chemical shifts were reported in parts per million relative to TMS as an internal standard for ^{1}H NMR and to CF_3COOH as an external standard (positive for upfield shifts) for ^{19}F NMR. The solvent for NMR measurement was $CDCl_3$ (unless otherwise noted). DMSO were distilled from CaH_2 and other reagents were purified prior to use.

Typical Procedure for the Reaction of 1 with 2. Under a nitrogen atmosphere, **1a** (1.27 g, 5 mmol), **2c** (0.84 g, 7.5 mmol), $Na_2S_2O_4$ (1.38 g, 7.5 mmol), $NaHCO_3$ (0.63 g, 7.5 mmol) and DMSO (25 mL) was added to a 50 mL three-necked round-bottomed flask equipped with stirrer and condenser. The mixture was then heated to 75 °C for 6 h with stirring. The conversion of **1a** was 100%, determined by ^{19}F NMR. After cooling, the mixture was poured into ice water (30 mL). The aqueous layer was extracted three times with ether (3 × 30 mL). The combined extracts were washed with water (3 × 20 mL) and dried over Na_2SO_4. After removing ether, the residue was subjected to column chromatography on silica gel to give **3ac** as a colorless oil (1.33 g, yield 80%).

1,1,1,2,2,3,3,4,4-Nonafluorododecane (3ac): colorless oil; ^{1}H NMR δ 0.88 (t, J = 6.5 Hz, 3H), 1.15−1.50 (m, 12H), 1.80−2.45 (m, 2H); ^{19}F NMR δ 4.2 (s, 3F), 37.7 (t, J = 10.5 Hz, 2F), 47.5 (s, 2F), 49.0 (s, 2F); Ms m/z (relative intensity) 332 (M^+, 1.40), 289 (100), 57 (42.53), 43 (25.41); HRMS calcd for $C_{12}H_{17}F_9$ 332.1187, found 332.1191.

1,1,1,2,2,3,3,4,4-Nonafluorotridecane (3ad): colorless oil; ^{1}H NMR δ 0.90 (t, J = 6.5 Hz, 3H), 1.15−1.55 (m, 14H), 1.80−2.42 (m, 2H); ^{19}F NMR δ 4.2 (s, 3F), 37.6 (t, J = 10.0 Hz, 2F), 47.3 (s, 2F), 49.0 (2F); Ms m/z (relative intensity) 345 (M^+−1, 3.24), 317 (20.12), 303 (43.34), 289 (25.22), 71 (47.85), 43 (100); HRMS calcd for $C_{13}H_{18}F_9$ (M^+ − 1) 345.1264, found 345.1167.

1,1,2,2,3,3,4,4,4-Nonafluorobutylcyclohexane (3af): colorless oil; ^{1}H NMR δ 1.13−2.00 (m, 11H); ^{19}F NMR δ 4.2 (s, 3F), 41.3 (d, J = 12 Hz, 2F), 44.5 (s, 2F), 49.3 (s, 2F); Ms m/z (relative intensity) 302 (M^+, 1.70), 301 (14.39), 263 (20.47), 83 (100); HRMS calcd for $C_{10}H_{10}F_9$ (M^+−1) 301.0638, found 301.0631.

1,1,2,2,3,3,4,4-Octafluorodecane (3ba): colorless oil; ^{1}H NMR δ 0.89 (t, J = 6.5 Hz, 3H), 1.35 (m, 8H), 1.98−2.60 (m, 2H), 6.02 (tt, J = 52, 5.6 Hz, 1H); ^{19}F NMR δ 37.5 (t, J = 10 Hz, 2F), 48.9 (s, 2F), 53.4 (s, 2F), 60.4 (d, J = 49.3 Hz, 2F); Ms m/z (relative intensity) 286 (M^+, 4.05), 285 (34,69), 257 (12.96), 43 (100); HRMS calcd for $C_{10}H_{14}F_8$ 286.0968, found 286.0982.

1,1,2,2,3,3,4,4-Octafluorododecane (3bc): colorless oil; ^{1}H NMR δ 0.89 (t, J = 6.5 Hz, 3H), 1.33 (m, 10H), 1.59 (m, 2H), 2.05 (tt, J = 18.9, 7.9 Hz, 2H), 6.03 (tt, J = 52, 5.6 Hz, 1H); ^{19}F NMR δ 37.5 (t, J = 9.7 Hz, 2F), 48.8 (s, 2F), 53.4 (m, 2F), 60.4 (d, J = 49.3 Hz, 2F); Ms m/z (relative intensity) 314 (M^+, 6.55), 285 (14.58), 57 (81.34), 43 (100); HRMS calcd for $C_{12}H_{18}F_8$ 314.1280, found 314.1277.

1,1,2,2,3,3,4,4-Octafluorotridecane (3bd): colorless oil; ^{1}H NMR δ 0.89 (t, J = 6.5 Hz, 3H), 1.20−1.45 (m, 14H), 1.83−2.42 (m, 2H), 6.02 (tt, J = 52, 6 Hz, 1H); ^{19}F NMR δ 37.5 (t, J = 10.0 Hz, 2F), 48.8 (s, 2F), 53.3 (s, 2F), 60.3 (d, J = 51.2 Hz, 2F); Ms m/z (relative intensity) 328 (M^+, 1.69), 299 (10.44), 285 (44.28), 271 (22.86), 257 (14.98), 57 (100); HRMS calcd for $C_{13}H_{20}F_8$ 328.1437, found 328.1428.

3-(2,2,3,3,4,4,5,5-Octafluoropentyl)-4-methyltetrahydrofuran (3be):[24b] colorless oil; ^{1}H NMR δ 1.05 (d, J = 6.5 Hz, 0.7 × 3H, *cis*-CH_3), 1.12 (d, J = 6.1 Hz, 0.3 × 3H, *trans*-CH_3), 1.86−2.66 (m, 4H), 3.30−3.53 (m, 2H), 3.91−4.12 (m, 2H), 6.03 (tt, J = 52, 5.5 Hz, 1H); ^{19}F NMR δ 36.5 (m, 2F), 48.8 (s, 2F), 53.2 (s, 2F), 60.7 (d, J = 51.7 Hz, 2F); Ms m/z (relative intensity) 301 (M^++1, 35.23), 299 (19.61), 270 (71.90), 69 (100); HRMS calcd for $C_{10}H_{12}F_8O$ 300.0760, found 300.0757.

1,1,2,2,3,3,4,4-Octafluorobutylcyclohexane (3bf): colorless oil; ^{1}H NMR δ 1.12−2.20 (m, 11H), 6.03 (tt, J = 52, 6 Hz, 1H); ^{19}F NMR δ 40.7 (d, J = 13 Hz, 2F), 45.8 (s, 2F), 53.5 (s, 2F), 60.2 (d, J = 52 Hz, 2F); Ms m/z (relative intensity) 284 (M^+, 0.43), 283 (2.69), 263 (12.47), 113 (12.43), 83 (100); HRMS calcd for $C_{10}H_{11}F_8$ (M^+−1) 283.0733, found 283.0734.

1,1,2,2,3,3,4,4,5,5,6,6-Dodecafluorododecane (3ca): colorless oil; ^{1}H NMR δ 0.89 (t, J = 6.5 Hz, 3H), 1.32 (m, 6H), 1.56 (m, 2H), 2.05 ((tt, J = 18.5, 8.7 Hz, 2H), 6.03 (tt, J = 52, 5.2 Hz, 1H); ^{19}F NMR δ 37.8 (m, 2F), 45.3 (m, 2F), 47.0 (s, 4F), 53.4 (s, 2F), 60.4 (d, J = 52.6 Hz, 2F); Ms m/z (relative intensity) 386 (M^+, 1.71), 385 (13.14), 367 (14.58), 43 (100). Anal. Calcd for $C_{12}H_{14}F_{12}$: C, 37.32; H, 3.62; F, 59.06. Found C, 37.23; H, 3.56; F, 58.67.

1,1,2,2,3,3,4,4,5,5,6,6-Dodecafluorotetradecane (3cc): colorless oil; ^{1}H NMR δ 0.89 (t, J = 6.5 Hz, 3H), 1.33 (m, 10H), 1.57 (m, 2H), 2.05 (tt, J = 18.6, 8.6 Hz, 2H), 6.03 (tt, J = 52, 6 Hz, 1H); ^{19}F NMR δ 37.7 (t, J = 15.6 Hz, 2F), 45.2 (s, 2F), 46.9 (s, 4F), 53.0 (s, 2F), 60.4 (d, J = 52 Hz, 2F); Ms m/z (relative intensity) 414 (M^+, 1.17), 385 (7.50), 371 (36.99), 57 (93.07), 43 (100); HRMS calcd for $C_{14}H_{18}F_{12}$ 414.1217, found 414.1208. Anal. Calcd for $C_{14}H_{18}F_{12}$: C, 40.58; H, 4.32; F, 55.07. Found: C, 40.29; H, 4.22; F, 55.59.

1,1,2,2,3,3,4,4,5,5,6,6-Dodecafluoropentadecane (3cd): colorless oil; ^{1}H NMR δ 0.89 (t, J = 6.5 Hz, 3H), 1.30 (m, 12H), 1.57 (m, 2H), 2.05 (tt, J = 18.4, 7.8 Hz, 2H), 6.03 (tt, J = 52, 5.2 Hz, 1H); ^{19}F NMR δ 37.8 (t, J = 15.2 Hz, 2F), 45.2 (s, 2F),

(30) Reichardt, C. *Solvent Effects in Organic Chemistry*; Ebel, H. F., Ed.; Monographs—Modern Chemistry; New York: Verlag Chemie, New York, 1979; p 270.

46.9 (s, 4F), 53.1 (s, 2F), 60.1 (d, J = 52.1 Hz, 2F); Ms m/z (relative intensity) 428 (M^+, 4.76), 399 (38.89), 385 (29.84), 43 (100); HRMS calcd for $C_{15}H_{20}F_{12}$ 428.1372, found 428.1370.

3-(2,2,3,3,4,4,5,5,6,6,7,7-Dodecafluoroheptyl)-4-methyltetrahydrofuran(3ce): colorless oil; ^{1}H NMR δ 1.05 (d, J = 6.5 Hz, 0.7 × 3H, cis-CH_3), 1.12 (d, J = 6.1 Hz, 0.3 × 3H, trans-CH_3), 1.80−2.50 (m, 4H), 3.18−3.52 (m, 2H), 3.90−4.10 (m, 2H), 6.03 (tt, J = 52, 5.5 Hz, 1H); ^{19}F NMR δ 36.3 (m, 2F), 45.0 (s, 2F), 46.4 (s, 4F), 52.6 (s, 2F), 60.5 (d, J = 52 Hz, 2F); Ms m/z (relative intensity) 401 (M^++1, 100), 399 (48.28), 383 (44.78), 370 (27.39), 55 (63.37); HRMS calcd for $C_{12}H_{12}F_{12}O$ 400.0707, found 400.0696.

1,1,2,2,3,3,4,4,5,5,6,6-Dodecafluorohexylcyclohexane (3cf): colorless oil; ^{1}H NMR δ 1.15−2.20 (m, 11H), 6.02 (tt, J = 52, 6 Hz, 1H); ^{19}F NMR δ 41.2 (d, J = 13 Hz, 2F), 43.7 (s, 2F), 45.1 (s, 2F), 46.5(s, 2F), 52.8 (s, 2F), 60.2 (d, J = 52 Hz, 2F); Ms m/z (relative intensity) 383 (M^+−1, 1.08), 345 (12.59), 131 (16.56), 83 (100)). Anal. Calcd for $C_{12}H_{12}F_{12}$ C, 37.50; H, 3.15; F, 59.65. Found: C, 37.68; H, 3.11; F, 60.14.

1,1,1-Trifluorooctane (3da):[21] colorless oil; ^{1}H NMR δ 0.90 (t, J = 6.5 Hz, 3H), 1.21−1.50 (m, 10H), 1.90−2.20 (m, 2H); ^{19}F NMR δ −11.2 (t, J = 10 Hz, 3F).

1,1,1-Trifluorodecane (3dc):[21] colorless oil; ^{1}H NMR δ 0.90 (t, J = 6.5 Hz, 3H), 1.28−1.70 (m, 14H), 1.98−2.28 (m, 2H); ^{19}F NMR δ −11.0 (t, J = 10 Hz, 3F).

1-Chloro-1,1-difluorononane (3ec): colorless oil; ^{1}H NMR δ 0.89 (t, J = 6.5 Hz, 3H), 1.08−1.50 (m, 12H), 1.97−2.25 (m, 2H); ^{19}F NMR δ −26.8 (t, J = 13 Hz, 2F); Ms m/z (relative intensity) 198 (M^+, 1.00), 162 (7.56), 105 (15.64), 43 (100); HRMS calcd for $C_9H_{16}F_2Cl$ (M^+−1) 197.0908, found 197.0938.

Ethyl 2-Fluorodecanoate (3fc):[25a] colorless oil;^{1}H NMR δ 0.88 (t, J = 7.0 Hz, 3H), 1.18−1.56 (m, 15H), 1.85 (m, 2H), 4.26 (q, J = 7.2 Hz, 2H), 4.86 (m, 1H); ^{19}F NMR δ 115.4 (dt, J = 49.0, 24.5 Hz, 1F).

Ethyl 2-Fluoroundecanoate (3fd): colorless oil; ^{1}H NMR δ 0.89 (t, J = 6.5 Hz, 3H), 1.01−1.35 (m, 17H), 1.58−1.90 (m, 2H), 4.14 (q, J = 7.2 Hz, 2H), 4.86 (dt, J = 50, 6.5 Hz, 1H); ^{19}F NMR δ 115.4 (dt, J = 49.6, 24 Hz, 1F); Ms m/z (relative intensity) 233 (M^++1, 66.86), 186 (9.16), 171 (29.35), 127 (10.72), 106 (100); HRMS calcd for $C_{13}H_{25}FO_2$ 232.1838, found 232.1840.

Ethyl 2-Cyclohexyl-2-fluoroacetate (3ff):[25a] colorless oil; ^{1}H NMR δ 1.12−2.00 (m, 14H), 4.18 (q, J = 7.1 Hz, 2H), 4.88 (dd, J = 49.3, 4.3 Hz, 1H); ^{19}F NMR δ 121.0 (dd, J = 49.3, 22 Hz, 1F).

Ethyl 2-Fluoro-4-(trimethylsilyl)butanoate (3fh):[25a] colorless oil;^{1}H NMR δ 0.00 (s, 9H), 0.60 (m, 2H), 1.28 (t, J = 7.1 Hz, 3H), 1.87 (m, 2H), 4.25 (q, J = 7.1 Hz, 2H), 4.80 (ddd, J = 49.4, 6.4, 4.9 Hz, 1H); ^{19}F NMR δ 115.5 (dt, J = 49.8, 24 Hz, 1F).

Ethyl 5-Ethoxyl-2-fluoropentanoate (3fi):[25a] colorless oil;^{1}H NMR δ 1.20 (t, J = 7.1 Hz, 3H), 1.31 (t, J = 7.1 Hz, 3H), 1.75 (m, 2H), 1.85−2.10 (m, 2H), 3.45 (m, 4H), 4.26 (q, J = 7.1 Hz, 2H), 4.94 (ddd, J = 50.0, 7.6, 4.3 Hz, 1H); ^{19}F NMR δ 115.2 (dt, J = 50.2, 24 Hz, 1F).

Ethyl 2,2-Difluorononanoate (3gb):[25d] colorless oil; ^{1}H NMR δ 0.90 (t, J = 7 Hz, 3H), 1.15−1.48 (m, 13H), 1.90−2.15 (m, 2H), 4.27 (q, J = 7.1 Hz, 2H); ^{19}F NMR δ 28.7 (t, J = 17 Hz, 2F).

Ethyl 2,2-Difluorodecanoate (3gc):[25d] colorless oil; ^{1}H NMR δ 0.90 (t, J = 7 Hz, 3H), 1.12−1.48 (m, 15H), 1.90−2.25 (m, 2H), 4.26 (q, J = 7.1 Hz, 2H); ^{19}F NMR δ 28.7 (t, J = 17 Hz, 2F).

Ethyl 2,2-Difluoro-3-(4-methyltetrhydrofuran-3-yl)-propionate (3ge): colorless oil; ^{1}H NMR δ 0.92 (d, J = 7.0 Hz, 0.75 × 3H, *cis*-CH_3), 1.03 (d, J = 6.2 Hz, 0.25 × 3H, trans-CH_3), 1.34 (t, J = 7.2 Hz, 3H), 1.80−2.05 (m, 2H), 2.10−2.55 (m, 2H), 3.45−3.49 (m, 2H), 3.86−4.06 (m, 2H), 4.31 (q, J = 7.1 Hz, 2H); ^{19}F NMR δ 26.8−30.0 (m, 2F); Ms m/z (relative intensity) 223 (M^++1, 100), 193 (17.16), 177 (11.22), 99 (13.87); HRMS calcd for $C_{10}H_{16}F_2O_3$ 222.1068, found 222.1068.

Ethyl 2,2-Difluoro-2-cyclohexyl acetate (3gf):[25d] colorless oil; ^{1}H NMR δ 1.03−2.05 (m, 14H), 4.33 (q, J = 7 Hz, 2H); ^{19}F NMR δ 36.5 (d, J = 15 Hz, 2F).

$CH_3CO_2CH_2CH_2CH_2CF_2CO_2Et$ (3gg): colorless oil; ^{1}H NMR δ 1.34 (t, J = 7.1 Hz, 3H), 1.80 (m, 2H), 1.99 (s, 3H), 2.10−2.30 (m, 2H), 4.08 (t, J = 6.2 Hz, 2H), 4.32 (q, J = 7.1 Hz, 2H); ^{19}F NMR δ 29.3 (t, J = 17.2 Hz, 2F); Ms m/z (relative intensity) 225 (M^++1, 8.20), 165 (100), 137 (19.67), 116 (8.64); HRMS calcd for $C_9H_{15}O_4F_2$ (M^++1) 225.0938, found 225.0933.

Ethyl 2,2-Difluoro-4-(trimethylsilyl)butanoate (3gh): colorless oil; ^{1}H NMR δ 0.02 (s, 9H), 0.65 (m, 2H), 1.32 (t, J = 7.2 Hz, 3H), 1.80−2.40 (m, 2H), 4.32 (q, J = 7.1 Hz, 2H); ^{19}F NMR δ 29.2 (t, J = 17 Hz, 2F); Ms m/z (relative intensity) 224 (M^+, 0.7), 196 (20.70), 101 (12.64), 73 (100); HRMS calcd for $C_7H_{14}F_2O_2Si$ (M^+−C_2H_4) 196.0732, found 196.0732.

Ethyl 2-Chlorooctanoate (3ha): colorless oil; ^{1}H NMR δ 0.90 (t, J = 7 Hz, 3H), 1.18−1.70 (m, 11H), 2.10−2.35 (m, 2H), 4.18 (q, J = 6.5 Hz, 2H), 4.52 (t, J = 6.5 Hz, 1H); Ms m/z (relative intensity) 207 (M^++1, 7.26), 171 (8.17), 127 (100), 94 (36.56); HRMS calcd for $C_{10}H_{19}O_2$ (M^+−Cl) 171.1385, found 171.1376.

Ethyl 2-Chlorodecanoate (3hc): colorless oil; ^{1}H NMR δ 0.90 (t, J = 7 Hz, 3H), 1.05−1.80 (m, 15H), 2.10−2.30 (m, 2H), 4.18 (q, J = 6.5 Hz, 2H), 4.46 (t, J = 6.5 Hz, 1H); Ms m/z (relative intensity) 237 (M^++1, ^{37}Cl, 5.69), 235 (M^++1, ^{35}Cl, 17.11), 199 (8.60), 191 (18.30), 122 (100); HRMS calcd for $C_{12}H_{23}ClO_2$ (M^+, ^{35}Cl) 234.1387, found 234.1415.

Ethyl 2-Chloro-2-cyclohexyl acetate (3hf): colorless oil; ^{1}H NMR δ 1.20−2.28 (m, 14H), 4.16 (q, J = 6.5 Hz, 2H), 4.45 (d, J = 6.5 Hz, 1H); Ms m/z (relative intensity) 205 (M^++1, 6.72), 169 (22.37), 122 (100); HRMS calcd for $C_{10}H_{17}ClO_2$ (M^+, ^{35}Cl) 204.0917, found 204.0942.

$CH_3COO(CH_2)_4CO_2Et$ (3ig): colorless oil; ^{1}H NMR δ 1.12−1.40 (m, 5H), 1.62 (m, 2H), 1.85−2.50 (m, 5H), 4.08 (m, 4H); Ms m/z (relative intensity) 189 (M^++1, 2.39), 145 (6.98), 128 (38.38), 101 (100); HRMS calcd for $C_9H_{16}O_4$ 188.1049, found 188.1050.

1,1-Dichloroheptane (3ja): colorless oil; ^{1}H NMR δ 0.90 (t, J = 7 Hz, 3H), 1.20−1.65 (m, 8H), 2.14 (m, 2H), 5.72 (t, J = 6.0 Hz, 1H); Ms m/z (relative intensity) 168 (M^+, 0.37), 133 (8.93), 97 (29.60), 83 (10.82), 70 (100); HRMS calcd for $C_7H_{14}Cl_2$ (M^+, ^{35}Cl) 168.0673, found 168.0645.

1,1-Dichlorononane (3jc): colorless oil; ^{1}H NMR δ 0.87 (t, J = 7 Hz, 3H), 1.13−1.64 (m, 12H), 2.10 (m, 2H), 5.68 (t, J = 6.0 Hz, 1H); Ms m/z (relative intensity) 196 (M^+, 2.50), 139 (7.16), 104 (19.77), 83 (41.63), 43 (100); HRMS calcd for $C_9H_{18}Cl_2$ (M^+, ^{35}Cl) 196.0785, found 196.0772.

3-(2,2-Dichloroethyl)-4-methyltetrahydrofuran (3je): colorless oil; ^{1}H NMR δ 0.95 (d, J = 6.3 Hz, 0.8 × 3H, *cis*-CH_3), 1.04 (d, J = 6.6 Hz, 0.2 × 3H, *trans*-CH_3), 1.88−2.21 (m, 2H), 2.30−2.48 (m, 2H), 3.45 (m, 2H), 3.92 (m, 2H), 5.70 (t, J = 6.0 Hz, 1H); Ms m/z (relative intensity) 183 (M^++1, 7.80), 182 (M^+, 6.50), 81 (39.17), 69 (100); HRMS calcd for $C_7H_{12}Cl_2O$ (M^+, ^{35}Cl) 182.0265, found 182.0237. Anal. Calcd for $C_7H_{12}Cl_2O$: C, 45.92; H, 6.61. Found: C, 45.90; H, 6.73.

4,4-Dichlorobutyl acetate (3jg): colorless oil; ^{1}H NMR δ 1.88 (m, 2H), 2.05 (s, 3H), 2.27 (m, 2H), 4.10 (q, J = 6.0 Hz, 2H), 5.77 (t, J = 6.0 Hz, 1H); Ms m/z (relative intensity) 187 (M^++1, ^{37}Cl, 7.24), 185 (M^++1, ^{35}Cl, 11.48), 124 (15.02), 88 (33.43), 43 (100); HRMS calcd for $C_4H_6Cl_2$ (M^+−CH_3CO_2H, ^{35}Cl) 123.9847, found 123.9847.

4,4-Dichloro-1-butanol (3jj): colorless oil; ^{1}H NMR δ 1.76 (m, 2H), 2.28 (m, 2H), 2.84 (s, 1H), 3.66 (t, J = 6.2 Hz, 2H), 5.80 (t, J = 6.0 Hz, 1H); Ms m/z (relative intensity) 143 (M^++1, 0.35), 125 (2.90), 96 (11.50), 76 (100); HRMS calcd for $C_4H_8Cl_2O$ (M^+, ^{35}Cl) 141.9952, found 141.9941. Anal. calcd for $C_4H_8Cl_2O$ C, 33.58; H, 5.60. Found: C, 33.89; H, 5.65.

1,2-Dichloro-1,1,2-trifluorooctane (3ka):[31] colorless oil; ^{1}H NMR δ 0.90 (t, J = 7.1 Hz, 3H), 1.20−1.85 (m, 8H), 2.10−2.59 (m, 2H); ^{19}F NMR δ −10.4 (s, 2F), 43.0 (m, 1F).

3-(2,3-Dichloro-2,3,3-trifluoropropyl)-4-methytetrahydrofuran (3ke):[31] colorless oil; ^{1}H NMR δ 1.02 (d, J = 6.5 Hz, 0.5 × 3H, *cis*-CH_3), 1.13 (d, J = 6.1 Hz, 0.5 × 3H, trans-CH_3), 1.80−2.52 (m, 4H), 3.20−3.55 (m, 2H), 3.75−4.08 (m, 2H); ^{19}F NMR δ −10.0 (s, 2F), 41.5 (m, 0.5F), 43.2 (m, 0.5F).

(31) Hu, C.-M.; Qing, F.-L. *Tetrahydron Lett.* **1990**, *31*, 1307.

1,2-Dichloro-1,2,2-trifluoroethylcyclohexane (3kf):[31] colorless oil; ^{1}H NMR δ 1.00−2.52 (m, 11H); ^{19}F NMR δ −15.8 (s, 2F), 39.5 (m, 1F).

4,5-Dichloro-4,5,5-trifluoropentyl acetate (3kg):[31] colorless oil; ^{1}H NMR δ 2.00 (s, 3H), 2.15−2.60 (m, 4H), 4.10 (t, J = 6.0 Hz, 2H); ^{19}F NMR δ −10.3 (s, 2F), 42.8 (m, 1F).

7,7,8,8,9,9,10,10-Octafluorohexadecane (6a): colorless oil; ^{1}H NMR δ 0.89 (m, 6H), 1.17−1.50 (m, 16H), 1.75−2.20 (m, 4H); ^{19}F NMR δ 37.5 (m, 4F), 46.7 (s, 4F); Ms *m*/*z* (relative intensity) 370 (M^+, 1.55), 369 (9.09), 135 (25.24), 57 (72.20), 43 (100); HRMS calcd for $C_{16}H_{26}F_8$ 370.1970, found 370.1968.

7,7,8,8,9,9,10,10-Octafluoroeicosane (6c): colorless oil; ^{1}H NMR δ 0.89 (m, 6H), 1.20−1.52 (m, 24H), 1.78−2.23 (m, 4H); ^{19}F NMR δ 37.3 (m, 4F), 46.4 (s, 4F); Ms *m*/*z* (relative intensity) 426 (M^+, 0.87), 383 (2.58), 85 (35.93), 71 (56.06), 57 (100); HRMS calcd for $C_{20}H_{34}F_8$ 426.2533, found 426.2536.

7,7,8,8-Tetrafluoro-8-chloro-2-octanone (8): colorless oil; ^{1}H NMR δ 1.55−1.80 (m, 4H), 2.15 (s, 3H), 2.30−2.65 (m, 4H); ^{19}F NMR δ −6.6 (s, 2F), 36.8 (m, 2F); Ms *m*/*z* (relative intensity) 237 (M^++1, ^{37}Cl, 15.64), 235 (M^++1, ^{35}Cl, 46.25), 135 (25.24), 43 (100). Anal. Calcd for $C_8H_{11}F_4ClO$: C, 40.95; H, 4.73; F, 32.39. Found: C, 40.74; H, 4.71; F, 32.28.

7,7,8,8-Tetrafluoro-2-tetradecanone (9a): colorless oil; ^{1}H NMR δ 0.89 (t, J = 7 Hz, 3H), 1.25−1.58 (m, 12H), 1.85−2.40 (m, 7H), 2.68 (t, J = 7 Hz, 2H); ^{19}F NMR δ 38.2 (m, 4F); Ms *m*/*z* (relative intensity) 285 (M^++1, 100), 264 (2.64), 58 (79.80), 43 (69.22); HRMS calcd for $C_{14}H_{24}F_4O$ 284.1763, found 284.1769.

7,7,8,8-Tetrafluoro-2-hexadecanone (9c): colorless oil; ^{1}H NMR δ 0.89 (t, J = 7 Hz, 3H), 1.22−1.57 (m, 16H), 1.86−2.41 (m, 7H), 2.74 (t, J = 7 Hz, 2H); ^{19}F NMR δ 38.3 (m, 4F); Ms *m*/*z* (relative intensity) 313 (M^++1, 64.03), 311 (6.31), 58 (77.24), 43 (100); HRMS calcd for $C_{16}H_{28}F_4O$: 312.2076, found: 312.2065.

Typical Procedure for the Reaction of 1 with 10. Under a nitrogen atmosphere, into a 50 mL three-necked round-bottomed flask, equipped with magnetic stirrer, thermometer, and condenser, was added the mixture of **1b** (1.18 g, 5 mmol), **10a** (0.63 g, 7.5 mmol), $Na_2S_2O_4$ (1.38 g, 7.5 mmol), $NaHCO_3$ (0.63 g, 7.5 mmol), and DMSO (25 mL). The mixture was then heated to 75 °C for 8 h with stirring. The conversion of **1a** was 100%, determined by ^{19}F NMR. After cooling, the mixture was poured into ice water (30 mL). The aqueous layer was extracted three times with ether (3 × 30 mL). The combined extracts were washed with water (3 × 20 mL) and dried over Na_2SO_4. After removing ether, the residue was subjected to column chromatography on silica gel to afford **11ba** as a colorless oil (1.02 g, yield 72%).

H(CF$_2$)$_4$CH=CHC$_4$H$_9$ (11ba): colorless oil; ^{1}H NMR δ 0.92 (t, J = 7.0 Hz, 3H), 1.22−1.60 (m, 4H), 2.30−2.33 (m, 2H), 5.37−6.55 (m, 2H), 6.02 (tt, J = 52, 5.2 Hz, 1H); ^{19}F NMR δ 29.7 (d, J = 9.6 Hz, 0.6 × 2F, Z-), 34.2 (d, J = 10.5 Hz, 0.4 × 2F, *E*-), 48.6 (s, 2F), 53.0 (s, 2F), 60.5 (d, J = 52 Hz, 2F); Ms *m*/*z* (relative intensity) 284 (M^+, 8.96), 264 (12.20), 222 (12.75), 68 (100); HRMS calcd for $C_{10}H_{12}F_8$ 284.0811, found 284.0805.

H(CF$_2$)$_4$CH=CHC$_6$H$_5$ (11bc): colorless oil; ^{1}H NMR δ 5.52−6.96 (m, 3H), 7.20 (m, 5H); ^{19}F NMR δ 28.3 (d, J = 10.0 Hz, 0.92 × 2F, *Z*-), 33.9 (d, J = 11 Hz, 0.08 × 2F, E-), 48.3 (s, 2F), 53.0 (s, 2F), 60.3 (d, J = 51.0 Hz, 2F); Ms *m*/*z* (relative intensity) 304 (M^+, 36.87), 153 (100), 133 (62.84); HRMS calcd for $C_{12}H_8F_8$ 304.0498, found 304.0493.

H(CF$_2$)$_4$CH=CHCH$_2$OH (11bd): colorless oil; ^{1}H NMR δ 2.50 (s, 1H), 4.32 (dd, J = 6.1, 3.6 Hz, 0.85 × 2H, E-CH$_2$O), 4.44 (dt, J = 7.9, 3.5 Hz, 0.15 × 2H, Z-CH$_2$O), 5.47−6.58 (m, 2H), 6.05 (tt, J = 52, 5.6 Hz, 1H); ^{19}F NMR δ 30.9 (s, 0.15 × 2F, Z-CF$_2$CH), 34.9 (d, J = 8.1 Hz, 0.85 × 2F, E-CF$_2$CH), 48.7 (t, J = 7.8 Hz, 0.85 × 2F), 49.0 (t, J = 7.0 Hz, 0.15 × 2F), 53.0 (d, J = 4.3 Hz, 2F), 60.5 (d, J = 51.8 Hz, 2F); Ms *m*/*z* (relative intensity) 258 (M^+, 0.30), 241 (8.71), 221 (3.64), 57 (100); HRMS calcd for $C_7H_5F_8O$ (M^+−1) 257.0213, found 257.0192.

H(CF$_2$)$_6$CH=CHC$_4$H$_9$ (11ca): colorless oil; ^{1}H NMR δ 0.92 (t, J = 7.0 Hz, 3H), 1.24−1.60 (m, 4H), 2.30−2.33 (m, 2H), 5.43−6.39 (m, 2H), 6.04 (tt, J = 52, 6 Hz, 1H); ^{19}F NMR δ 30.0 (d, J = 11.9 Hz, 0.53 × 2F, Z-CF$_2$CH), 34.6 (d, J = 11.9 Hz, 0.47 × 2F, E-CF$_2$CH), 45.1 (s, 2F), 47.0 (m, 4F), 53.2 (s, 2F), 60.5 (d, J = 51.9 Hz, 2F); Ms *m*/*z* (relative intensity) 384 (M^+, 0.89), 344 (9.71), 322 (7.18), 121 (38.05), 68 (100); HRMS calcd for $C_{12}H_{12}F_{12}$ 384.0747, found 384.0748.

H(CF$_2$)$_6$CH=CHC$_6$H$_5$ (11cc): colorless oil; ^{1}H NMR δ 5.35−6.95 (m, 3H), 7.27 (m, 5H); ^{19}F NMR δ 29.3 (d, J = 13 Hz, 0.82 × 2F, Z-CF$_2$CH), 34.0 (d, J = 12 Hz, 0.18 × 2F, E-CF$_2$-CH), 44.8 (s, 2F), 46.9 (s, 4F), 53.2 (s, 2F), 60.4 (d, J = 51.0 Hz, 2F); Ms *m*/*z* (relative intensity) 404 (M^+, 14.32), 403 (100), 384 (12.38), 153 (11.96); HRMS calcd for $C_{14}H_8F_{12}$ 404.0434, found 404.0438. Anal. Calcd for $C_{14}H_8F_{12}$: C, 41.60; H, 2.00; F, 56.40. Found: C, 41.47; H, 1.96; F, 56.52.

H(CF$_2$)$_6$CH=CHCH$_2$OH (11cd): colorless oil; ^{1}H NMR δ (CD_3COCD_3) 3.45 (s, 1H), 4.40−4.30 (m, 2H), 5.70−6.72 (m, 2H), 6.82 (tt, J = 50.9, 5.3 Hz, 1H); ^{19}F NMR δ (CD_3COCD_3) 25.7 (d, J = 12.6 Hz, 0.15 × 2F, Z-CF$_2$CH), 29.4 (d, J = 11.9 Hz, 0.85 × 2F, E-CF$_2$CH), 40.2 (s, 2F), 42.1 (s, 4F), 48.3 (s, 2F), 57.2 (d, J = 50.7 Hz, 2F); Ms *m*/*z* (relative intensity) 357 (M^+−1, 2.12), 340 (15.56), 290 (18.86), 139 (40.63), 57 (100). Anal. Calcd for $C_9H_6F_{12}O$: C, 30.18; H, 1.68; F, 63.65. Found: C, 30.24; H, 1.87; F, 63.22.

CF$_3$CH$_2$CH=CHC$_4$H$_9$ (11da):[22] colorless oil; ^{1}H NMR δ 0.89 (t, J = 7.1 Hz, 3H), 1.24 (m, 4H), 1.94 (m, 2H), 2.65 (m, 2H), 5.40−6.30 (m, 2H); ^{19}F NMR δ −11.6 (t, J = 11.0 Hz, 0.7 × 3F, Z-), −10.6 (t, J = 10.9 Hz, 0.3 × 3F, E-); Ms *m*/*z* (relative intensity) 166 (M^+, 28.03), 119 (100), 117 (85.75), 69 (18.95); HRMS calcd for $C_8H_{13}F_3$ 166.0969, found 166.0965.

CF$_3$CH$_2$CH=CHC$_6$H$_{13}$ (11db):[22] colorless oil;^{1}H NMR δ 0.88 (t, J = 7.1 Hz, 3H), 1.27 (m, 8H), 1.98 (m, 2H), 2.67 (m, 2H), 5.45−6.43 (m, 2H); ^{19}F NMR δ −11.4 (t, J = 11.0 Hz, 0.75 × 3F, Z-), −10.2 (t, J = 10 Hz, 0.25 × 3F, E-); Ms *m*/*z* (relative intensity) 194 (M^+, 40.70), 151 (28.88), 69 (72.98), 43 (100); HRMS calcd for $C_{10}H_{17}F_{12}$: 194.1283, found: 194.1291.

C$_6$H$_5$CH=CHCFHCO$_2$Et (11fc): colorless oil; ^{1}H NMR δ 1.32 (t, J = 7.2 Hz, 3H), 4.30 (q, J = 7.2 Hz, 2H), 5.40−6.35 (m, 2H), 6.85−7.05 (m, 1H), 7.40 (m, 5H); ^{19}F NMR δ 97.8 (ddd, J = 48.0, 10.9, 4.0 Hz, 0.5F, Z-), 106.7 (dd, J = 48.0, 11.0 Hz, 0.5F, *E*-); Ms *m*/*z* (relative intensity) 209 (M^++1, 2.21), 208 (M^+, 16.49), 135 (100), 115 (73.29); HRMS calcd for $C_{12}H_{13}FO_2$ 208.0899, found 208.0889.

C$_4$H$_9$CH=CHCF$_2$CO$_2$Et (11ga): colorless oil; ^{1}H NMR δ 0.90 (t, J = 7.2 Hz, 3H), 1.27−1.47 (m, 7H), 2.20−2.32 (m, 2H), 4.30 (q, J = 7.2 Hz, 2H), 5.51−6.30 (m, 2H); ^{19}F NMR δ 21.8 (d, J = 13.7 Hz, 0.55 × 2F, Z-), 26.0 (dd, J = 10.8, 4.5 Hz, 0.45 × 2F, *E*-); Ms *m*/*z* (relative intensity) 207 (M^++1, 2.02), 206 M^+, 2.73), 186 (5.20), 113 (100), 77 (99.99); HRMS calcd for $C_{10}H_{16}F_2O_2$: 206.1118, found: 206.1116. Anal. Calcd for $C_{10}H_{16}F_2O_2$: C, 58.24; H, 7.82; F, 18.42. Found: C, 58.17; H, 7.70; F, 17.97.

***E*−C$_6$H$_5$CH=CHCF$_2$CO$_2$Et (11gc)**: colorless oil; ^{1}H NMR δ (CD_3COCD_3): 1.08 (t, J = 7.2 Hz, 3H), 4.06 (q, J = 7.2 Hz, 2H), 5.92 (dt, J = 14.6, 12.7 Hz, 1H), 7.04 (dt, J = 14.6, 1.8 Hz, 1H), 7.36 (m, 5H); ^{19}F NMR δ (CD_3COCD_3): 11.5 (d, J = 13 Hz, 2F); Ms *m*/*z* (relative intensity) 227 (M^++1, 1.34), 226 (M^+, 9.14), 153 (100), 133 (67.75); HRMS calcd for $C_{12}H_{12}F_2O_2$ 226.0805, found 226.0807.

***E*-HOCH$_2$CH=CHCF$_2$CO$_2$Et (11gd)**: colorless oil; ^{1}H NMR δ 1.30 (t, J = 7.2 Hz, 3H), 3.23 (s, 1H), 4.21 (dd, J = 4.2, 2.0 Hz, 2H), 4.29 (q, J = 7.2 Hz, 2H), 5.95 (dtt, J = 15.8, 11.3, 2.0 Hz, 1H), 6.42 (dtt, J = 15.8, 4.1, 2.5 Hz, 1H); ^{19}F NMR δ 26.4 (dd, J = 10.6, 3.9 Hz, 2F); Ms *m*/*z* (relative intensity) 181-(M^++1, 14.04), 163 (84.06), 135 (100), 107 (53.34), 90 (74.74); HRMS calcd for $C_7H_{10}F_2O_3$ 180.0598, found 180.0581.

CH$_3$OCH$_2$CH=CHCF$_2$CO$_2$Et (11ge): colorless oil; ^{1}H NMR δ 1.35 (t, J = 7.2 Hz, 3H), 3.30 (s, 0.38 × 3H, *Z*-CH$_3$O), 3.37(s, 0.62 × 3H, E-CH$_3$O), 4.05 (dq, J = 7.7, 2.0 Hz, 0.62 × 2H, *E*-**CH$_2$**CH=CH), 4.20 (dq, J = 7.6, 2.2 Hz, 0.38 × 2H, Z-**CH$_2$**-CH=CH), 4.35 (q, J = 7.2 Hz, 2H), 5.56−6.36 (m, 2H); ^{19}F NMR δ 22.8 (d, J = 15.9 Hz, 0.38 × 2F, *Z*-), 27.0 (dd, J = 11.0, 4.1 Hz, 0.62 × 2F, *E*-); Ms *m*/*z* (relative intensity) 195-(M^++1, 1.86), 174 (91.06), 163 (10.60), 121 (100), 90 (69.49). Anal. Calcd for $C_8H_{12}F_2O_3$: C, 49.48; H, 6.23; F, 19.57. Found: C, 49.74; H, 6.40; F, 19.63.

Typical Procedure for Preparation of 12 and 13. An amount of **1a** (2.55 g, 10 mmol), $Na_2S_2O_4$ (2.61 g, 15 mmol), $NaHCO_3$ (1.26 g, 15 mmol) and DMSO (30 mL) was stirred at

75 °C for 10 h. After removal of solvent under reduced pressure, the residure was extracted with hot ethanol. Evaporation of the ethanol gave the sodium salt **12a**. Chlorine gas was bubbled into a solution of **12a** in H_2O (10 mL) at 0 °C for 4 h. The mixture was extracted three times with CH_2Cl_2 (3 × 10 mL). The oil layer separated was dried over anhydrous MgS_2O_4. After removing the solvent, **13a** (1.27 g, 40%) was obtained.

$CF_3(CF_2)_3SO_2Na$ (12a):[17d] white solid; ^{19}F NMR δ (D_2O) 4.3 (s, 3F), 46.5 (s, 2F), 48.5 (s, F), 53.1 (s, 2F, CF_2SO_2Na).

$H(CF_2)_4SO_2Na$ (12b):[17e] white solid; ^{19}F NMR δ (D_2O) 47.2 (s, 2F), 52.6 (s, 2F), 53.3 (s, 2F, CF_2SO_2Na), 61.6 (d, J = 51 Hz, 2F).

$CF_3CH_2SO_2Na$ (12d):[21] white solid, ^{19}F NMR δ (D_2O) −17.6 (t, J = 12 Hz, 3F), ^{1}H NMR δ (D_2O) 3.23 (q, J = 12 Hz, 2H).

$CF_3(CF_2)_3SO_2Cl$ (13a):[17d] colorless oil;^{19}F NMR δ (neat) 4.3 (s, 3F), 27.7 (s, 2F, CF_2SO_2Cl), 43.1 (s, 2F), 49.0 (s, 2F).

$H(CF_2)_4SO_2Cl$ (13b):[17e] colorless oil; ^{19}F NMR δ (neat) 27.7 (s, 2F, CF_2SO_2Cl), 43.6 (s, 2F), 51.3 (s, 2F), 60.8 (d, J = 51 Hz, 2F).

$CF_3CH_2SO_2Cl$ (13d):[21] colorless oil;^{19}F NMR δ (neat) −15.0 (t, J = 10 Hz, 3F); ^{1}H NMR δ (neat) 4.37 (q, J = 9 Hz, 2H).

Typical Inhibition Experiment: Under N_2 atmosphere, **1c** (1.68 g, 5 mmol), **2a** (0.63 g, 7.5 mmol), $Na_2S_2O_4$ (1.38 g, 7.5 mmol), $NaHCO_3$ (0.63 g, 7.5 mmol), and DMSO (25 mL) was added to a three-necked round-bottomed flask. After the mixture was stirred for 5 h at 75 °C under the laboratory light, ^{19}F NMR analysis, i.e., intergration ratio of peaks at −8.0 ppm ($R_F\mathbf{CF_2}Cl$) and 37.7 ppm ($R_F\mathbf{CF_2}CH_2CH_2R$), indicated that the conversion of **1c** was 100%. When *p*-DNB (0.17 g, 1 mmol) was present, after the mixture was stirred for 5 h at 75 °C, ^{19}F NMR analysis showed 50% conversion of **1c**.

Similarly, when HQ (0.11 g, 1 mmol) was present instead of *p*-DNB and the reaction conducted for 5 h at 75 °C, ^{19}F NMR analysis showed 33% conversion of **1c**.

Acknowledgment. We thank Professor Huang, W.-Y. for his encouragement and the Natural Science Foundation of China for support of this work.

Supporting Information Available: ^{1}H NMR spectra of **3bc**, **3be**, **3ca**, **3cc**, **3cd**, **3fh**, **3fi**, **3ge**, **3gg**, **3jj**, **11bd**, **11ca**, **11cd**, **11ga**, **11gd**, and **11ge**. ^{19}F NMR spectra of **3bc**, **3be**, **3ca**, **3cc**, **3cd**, **3fh**, **3fi**, **3gg**, **11bd**, **11ca**, **11cd**, **11ga**, **11gd**, and **11ge**.

JO9900937