Nucleophilic Desulfinylation of α-Fluoro-β-(alkoxy and silyloxy) Sulfoxides. Effects of the β-Oxy Substituents on Protonation, 1,2-Hydrogen Migration, and Nucleophile Addition to the Fluorocarbenoid Centers

Hidemitsu Uno,* Katsuji Sakamoto, and Hitomi Suzuki*,†
Advanced Instrumentation Center for Chemical Analysis, Ehime University, Bunkyo-cho 2-5, Matsuyama 790
† Department of Chemistry, Faculty of Science, Kyoto University, Sakyo-ku, Kyoto 606
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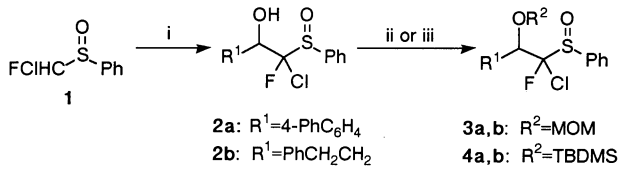
Treatment of 2-(4-biphenylyl)-2-*t*-butyldimethylsilyloxy-1-chloro-1-fluoroethyl phenyl sulfoxide with PhMgBr resulted in the formation of a fluorostilbene derivative, a fluoro enol silyl ether and small amounts of 4-(fluoroacetyl)biphenyl, while a similar reaction of 2-methoxymethoxy analog mainly led to the fluorostilbene derivatives and a simple desulfinylation product. In contrast, both sulfoxides reacted with PhLi to give chlorofluoro compounds and fluoro enol ethers. In these reactions, the stability of carbenoids derived from the nucleophilic removal of the sulfoxide moiety was greatly affected by the β-substituents, thus controlling the product distributions.

The fate of carbenes suffering insertion, cycloaddition or migration largely depends upon substituents not only at the divalent carbon[1] but also at the neighboring carbons.[2] Alkoxy and hydroxy substituents on the β-carbon of carbenes are known to enhance the 1,2-hydrogen transfer to the carbene center giving enol ethers or carbonyl compounds.[3] In the preceding paper,[4] we have described the 1,2-hydrogen shift of α-fluoroalkylcarbenoids generated from the nucleophilic desulfinylation of α-chloro-α-fluoroalkyl sulfoxides occurred mainly to give (*Z*)-fluoroolefin. It is natural consequence to anticipate that α-fluoroalkylcarbenoids bearing a β-alkoxy substituent would be subject to smooth 1,2-hydrogen shift to give synthetically useful fluoro enol ethers or fluoromethyl ketones.[5] In this paper, we describe the behaviors of β-alkoxy- and β-silyloxy-α-chloro-α-fluoroalkyl sulfoxides under the nucleophilic conditions.

Results and Discussion

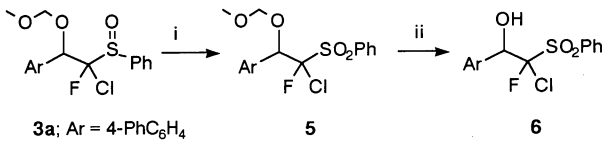
Preparation of Sulfoxides. Treatment of chlorofluoromethyl phenyl sulfoxide (**1**)[4] with MeLi–LiBr at −90 °C for 20 min followed by the addition of 4-biphenylcarbaldehyde gave a diastereomeric mixture (**A**:**B**:**C**:**D**=38:34:21:7, determined by ^{19}F NMR) of α-chloro-α-fluoro-β-hydroxy sulfoxide **2a** in 78% yield (Scheme 1). Different from non-fluorinated α-chloro-β-hydroxy sulfoxides,[6] the sulfoxide **2a** did not undergo the oxirane ring formation under basic conditions. Thus, its hydroxyl group was easily protected by using methoxymethyl chloride (MOMCl) and *N*,*N*-diisopropylethylamine to afford β-methoxymethoxy sulfoxide **3a** (**A**:**B**:**C**:**D**=35:40:10:15) in 89% yield.



Scheme 1. Reagents and conditions: i) MeLi–LiBr, THF, −90 °C; RCHO, −90 °C → r.t. ii) MOMCl, Et(*i*-Pr)$_2$N, CH_2Cl_2, refl. iii) TBDMSCl, imidazole, DMF, 80 °C.

Difficulties are encountered in the determination of relative stereochemistry of these sulfoxides. By careful chromatography on silica gel, the diastereomer mixture of **2a** was separated into two main fractions; the less polar fraction consisted of **A** and **D** (**A**:**D**=66:10) and the other was a mixture of **B** and **C** (**B**:**C**=42:10). Major components **A** and **B** were isolated by recrystallization of each mixture from dichloromethane/hexane. In their IR spectra, the hydroxy stretching band of **A** (ν_{OH}= 3316 cm^{-1}) appeared in the lower region than that of **B** (ν_{OH}=3416 cm^{-1}) due to the intramolecular hydrogen bonding between the hydroxyl and sulfinyl groups, which is also in accord with their chromatographic behaviors described above. From comparison of their IR data with the reported values for β-hydroxy sulfoxides,[7] the relative stereochemistry between sulfur and C-2 in isomer **A** was determined to be (*S**$_S$, 2*R**).

In order to confirm the relative stereochemistry between C-1 and C-2, isomers of the β-hydroxy sulfoxide **2a** were transformed into β-hydroxy sulfone **6** (Scheme 2). Thus, each diastereomer mixture of **2a** (**A**:**D**=15:10 and **B**:**C**=18:5) was refluxed with excess of MOMCl and *N*,*N*-diisopropylethylamine in dichloromethane to afford **3a** (yield, 67%; **A**:**D**=9:5 and yield, 88%;



Scheme 2. Reagents and conditions: i) mCPBA, CH_2Cl_2, r.t. ii) HCl, aq-MeOH.

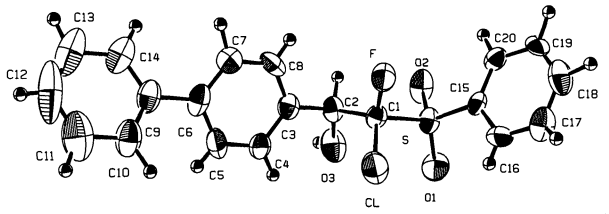


Fig. 1. ORTEP drawing of **6B** showing the atom numbering scheme.

Table 1. Selected Bond Lengths and Angles for **6B**

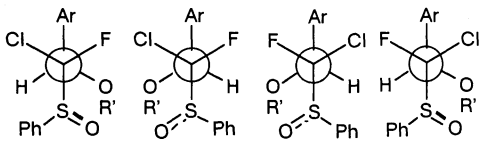
Distance		/Å	Distance		/Å
S	C1	1.86 (1)	O3	C2	1.41 (1)
CL	C1	1.749 (9)	H2	C2	1.06 (7)
F	C1	1.38 (1)	C3	C2	1.51 (1)
C2	C1	1.51 (1)	H(O3)	O3	0.88 (9)

Angle			/°	Angle			/°
S	C1	C2	112.8 (7)	H2	C2	C1	106 (4)
S	C1	CL	108.2 (5)	H2	C2	O3	112 (4)
S	C1	F	105.6 (6)	H2	C2	C3	108 (4)
F	C1	CL	106.6 (6)	O3	C2	C1	104.8 (8)
F	C1	C2	108.7 (8)	O3	C2	C3	113.4 (9)
CL	C1	C2	114.4 (7)	C1	C2	C3	112.7 (8)

B:**C**=18:5, respectively), oxidation of which with *m*-chloroperbenzoic acid (mCPBA) gave diastereomeric sulfones **5** (yield, 90%; **5A**:**5B**=9:5 and yield, 82%; **5A**:**5B**=5:21, respectively). Isomers **2aA** and **2aC** gave the same sulfone **5A** and the other pair afforded **5B**. The MOM group of **5** (**A**:**B**=5:21) was removed by acid treatment to give the β-hydroxy sulfone **6** (**A**:**B**=5:18) in good yield. Fortunately enough, the sulfone **6B** was obtained in a good crystalline state (from hexane–$CHCl_3$). Therefore, it was subjected to X-ray crystallographic analysis, which confirmed the stereochemistry to be (1*S**, 2*S**) (Fig. 1 and Table 1).[8] Isomers **2aA** and **2aB** are thus unambiguously determined to be (*S**$_S$, 1*S**, 2*R**) and (*S**$_S$, 1*S**, 2*S**)-isomers, respectively. The X-ray data show the *gauche* orientation of proton and fluorine atoms of **6B** (the dihedral angle of CH and CF bonds is 53.8°), which makes the $^3J_{HF}$ coupling constant of **6B** small (2.1 Hz; see Table 2, for simplicity, only S_S-isomers are illustrated).

Treatment of the diastereomer mixture of **2a** (**A**:**B**:**C**:**D**=38:34:21:7) with *t*-butyldimethylsilyl chloride (TBDMSCl) and imidazole gave **4a** (**A**:**B**:**C**:**D**= 25:40:25:10) in 72% yield. Relative stereochemistry of these diastereomers was confirmed by the respective transformation of **2aA** and **2aB** into **4aA** and **4aB**, and a mixture of **2aA** and **2aD** into a mixture of **4aA** and **4aD**. Low reactivity toward the silylation observed with the isomer **2aA** may be ascribed to a strong intramolecular chelation of the hydroxyl group toward the sulfinyl moiety.

Table 2. $^3J_{HF}$ Coupling Constants of β-Oxy Sulfoxides and Sulfones



A **B** **C** **D**

Compound			$^3J_{HF}$/Hz[a]			
	R	R'	**A**	**B**	**C**	**D**
2a	4-PhC_6H_4	H	15.3[b]	4.0[b]	24.7[b]	12.2[b]
3a	4-PhC_6H_4	MOM	8.9	4.3	24.1	18.6
4a	4-PhC_6H_4	TBDMS	7.3	3.4	22.9	19.2
2b	$PhCH_2CH_2$	H	13.8[c]	1.8[c]	22.7[c]	7.3[c]
3b	$PhCH_2CH_2$	MOM	6.7	3.7	21.7	13.1
4b	$PhCH_2CH_2$	TBDMS	7.0	2.6	21.4	13.1
5	4-PhC_6H_4	MOM	19.5	4.9		
6	4-PhC_6H_4	H	20.8	2.1		

a) Determined by ^{1}H NMR analysis (in $CDCl_3$) involving homo-decoupling experiments. b) In acetone-d_6. c) Estimated from ^{19}F NMR spectra.

Reaction of **1** with 3-phenylpropionaldehyde was carried out using MeLi–LiBr as a base to afford **2b** (**A**:**B**:**C**:**D**=47:25:9:19) in 88% yield, and further protection of its hydroxyl group with MOM and TBDMS gave **3b** (**A**:**B**:**C**:**D**=42:26:13:19) and **4b** (**A**:**B**:**C**:**D**= 41:33:11:15) in 76% and 89% yields, respectively. Relative stereochemistry of these sulfoxides can be determined by comparing their NMR data with those of **2a**, **3a**, and **4a**. The favored conformation and relative configuration can be readily inferred from the values of $^3J_{HF}$ (*anti* $^3J_{HF}$ > *gauche* $^3J_{HF}$)[9] in Table 2, when comparisons are made with the isomers of the same relative stereochemistry at sulfur and C-1 (**A** vs. **B** and **C** vs. **D**).

Alkylation of α-lithioalkyl sulfoxides with carbonyl compounds is known to occur mainly via the 6-membered cyclic transition state as the electrophiles approach from the sulfur–oxygen bonding side irrespective of substituent group on the sulfur atom.[10] Yamakawa and co-workers reported that the anions derived from diastereomeric (S_S)-α-chloroalkyl phenyl sulfoxides reacted with symmetric ketones below −40 °C to give the (S_S, *S*)-isomers.[11] Their results are in line with the model prediction if the steric bulkiness of alkyl groups and chlorine is taken into consideration.[12] Stereoselectivity observed in the reaction of α-chloro-α-fluoro sulfoxide **1** with aldehydes may be rationalized by assuming that the reaction proceeds via the chair-like 6-membered transition states (Fig. 2).[13] *Trans* orientation of chlorine and phenyl group of lithiated **1** will be favored because of their steric interaction (**A** and **B**) and the large R group will tend to occupy the *pseudo-equatorial* position. Thus, the most favorable transition

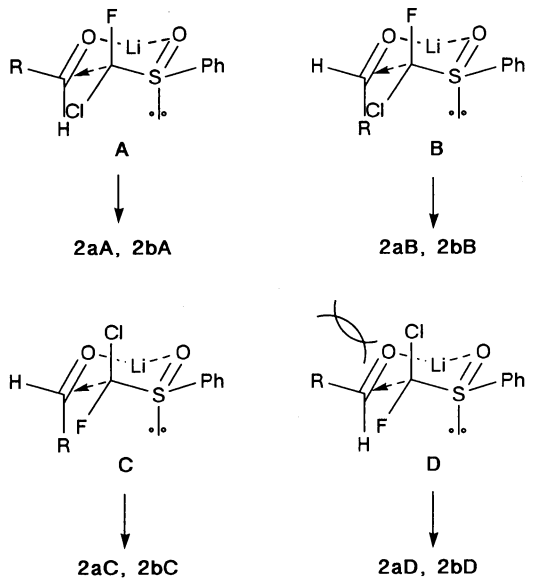
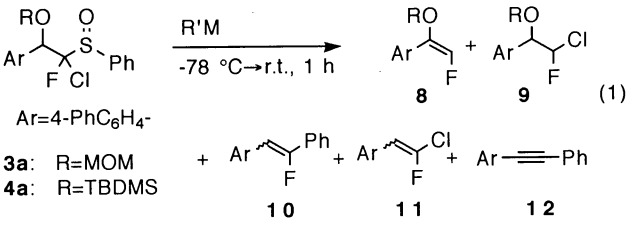


Fig. 2. Possible transition states.

state would be **A** which leads to **2aA** and **2bA**. In the transition state **D** where the R group occupies the *pseudo-equatorial* position, steric repulsion between the R group and chlorine atom would make this transition state least favorable, especially in the reaction with 4-biphenylcarbaldehyde.

Nucleophilic Desulfinylation of β-Oxy Sulfoxides. The nucleophilic desulfinylation of β-oxy sulfoxides with PhMgBr and PhLi was examined under the conditions similar to those described in the preceding paper (Eq. 1 and Table 3).[4] First, the reaction of the β-hydroxy sulfoxide **2a** with PhMgBr was carried out. Treatment of **2a** (**A**:**B**:**C**:**D**=38:34:21:7) with 6 equiv of PhMgBr in the presence of CuI brought about considerable β-fission of **2a** into **1** and 4-biphenylcarbaldehyde, which underwent further reactions with PhMgBr to give a complex mixture. From the mixture, 4-(fluoroacetyl)biphenyl **7** was obtained in only 5% yield in addition to **1**, diphenyl sulfoxide and (4-biphenylyl)phenylmethanol.



(1)

A similar treatment of **3a** (**A**:**B**:**C**:**D**=35:40:10:15) with 3 equiv of PhMgBr in the presence of CuI gave (*E*)-fluoro enol ether **8a** (33%, *E*:*Z*=20:1), chlorofluoro derivative **9a** (31%, 1:1 diastereomer mixture), and fluorostilbene derivative **10** (20%, *E*:*Z*=1:2) (Entry 2). When PhLi (1 equiv) was substituted for the Grignard reagent, the desulfinylation of **3a** occurred predominantly to afford chlorofluoro derivative **9a** as a 1:1 diastereomeric mixture (Entry 3). The use of excess PhLi (3 equiv) brought about the formation of fluoro enol ether **8a** as an isomeric mixture (*E*:*Z*=1:3) in 31% yield. Chlorofluoro derivative **9a** almost consisted of a single isomer (20:1) regardless of the fact that the starting **3a** was an isomeric mixture (**A**:**B**:**C**:**D**=35:40:10:15). This finding suggests that the fate of the intermediates derived from the reaction of **3a** with PhLi may differ among the distereomers. Thus, we examined the desulfinylation of two major isomers **3aA** and **3aB**, the relative stereochemistry of which differs between C-1 and C-2 carbons.

Treatment of the (*S**$_S$, 1*S**, 2*R**)-isomer **3aA** (isomeric purity>95%, contaminated with **3aD**) with 1 equiv of PhLi gave **9a** almost as a single isomer (20:1) and chlorofluoroolefin **11** (*E*:*Z*=20:1) in respective yields of 77 and 9% (Entry 5). The isomer of **9a** obtained was found to be identical with that obtained in the reaction of

Table 3. Nucleophilic Desulfinylation of β-Oxy Sulfoxides **2a**, **3a**, and **4a**

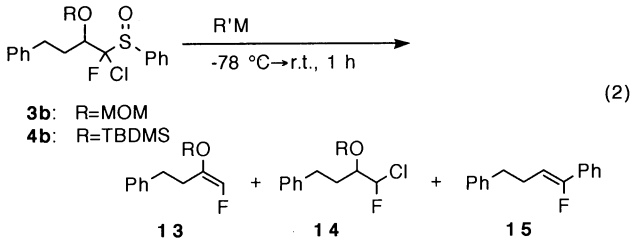
Entry	Sulfoxide	R'M (equiv)	Additive (equiv)	Yield/%[a]				
				8[b]	**9**[c]	**10**[b]	**11**[b]	**12**
1	**2a**[d]	PhMgBr (6)	CuI (0.1)	5[e,f]	—	—	—	—
2	**3a**[g]	PhMgBr (3)	CuI (0.1)	33 (20:1)	31 (1:1)	20 (2:1)	—	—
3	**3a**[g]	PhLi (1)	None	—	75[f] (1:1)	—	10[f] (9:1)	7[f]
4	**3a**[g]	PhLi (3)	None	31 (1:3)	21 (20:1)	—	Trace	16
5	**3aA**	PhLi (1)	None	—	77[f] (20:1)	—	9[f] (20:1)	Trace
6	**3aA**	PhLi (2)	None	6 (1:6)	48 (20:1)	—	16 (20:1)	—
7	**3aB**	PhLi (2)	None	17 (1:20)	25 (1:10)	—	18 (2:3)	20
8	**4a**[h]	PhMgBr (3)	CuI (0.1)	39 (4:5)	9 (1:1)	24 (1:1)	—	Trace
9	**4aA**	PhMgBr (3)	CuI (0.1)	61 (5:6)	13 (20:1)	26 (3:2)	—	—
10	**4aB**	PhMgBr (3)	CuI (0.1)	22 (3:5)	6 (1:5)	63 (6:5)	—	—
11	**4a**[h]	PhLi (1)	None	16 (1:20)	31 (1:1)	—	—	Trace
12	**4a**[h]	PhLi (3)	None	26 (1:20)	52 (1:1)	—	—	Trace

a) Yields were calculated based on the NMR analyses of the chromatographed fractions. b) The *E*:*Z* ratios are given in parentheses. c) Numerals in parentheses refer to the diastereomer ratios (*S***R**:*S***S**). d) **A**:**B**:**C**:**D**=38:34:21:7. e) 4-(Fluoroacetyl)biphenyl. f) Isolated yield. g) **A**:**B**:**C**:**D**=40:35:10:15. h) **A**:**B**:**C**:**D**=25:40:25:10.

diastereomers **3a**. Even when an excess amount of PhLi were employed, the diastereomer ratio of **9a** did not change, although the fluoro enol ether **8a** (*E*:*Z*=1:6) was formed in small amounts (6% yield). It is worthy to note that in the reaction of **3aA** with PhLi, the (*E*)-chlorofluoroolefin **11** was formed in a highly stereoselective manner. On the other hand, the reaction of **3aB** (isomeric purity>90%, contaminated with **3aC**) with 2 equiv of PhLi gave **8a** (*E*:*Z*=1:20), **9a** (diastereomer ratio, 1:10), and **11** (*E*:*Z*=2:3) in 17, 25, and 18% yields, respectively. Although the stereochemical determination of diastereomers **9a** was not successful from their NMR spectra,[14] we may assume that the present nucleophilic desulfinylation also proceeds with the retention of configuration as have been the case with related desulfinylation[15] and coupling reactions.[16] Thus, the major isomer of **9a** obtained in the reaction of **3aA** was assigned to be (*S**, *R**).

In order to estimate the effect of chelation of the MOM-oxy substituent in **3a**, the reaction of TBDMS-protected compound **4a** with nucleophiles was conducted. A diastereomer mixture of **4a** (**A**:**B**:**C**:**D**=25:40:25:10) was treated with 3 equiv of PhMgBr in the presence of CuI to afford a mixture of fluoro enol silyl ether **8b** (*E*:*Z*=4:5), chlorofluoro derivative **9b** (diastereomer ratio, 1:1), and fluorostilbene **10** (*E*:*Z*=1:1) (Entry 8). Reaction of each diastereomer **4aA** or **4aB** with 3 equiv of PhMgBr gave a mixture of the above three products (Entries 9 and 10). Formation of fluoro enol silyl ether **8b** showed no stereoselectivity, but **9b** was formed stereospecifically in both reactions; **9b** obtained from **4aA** (isomeric purity>95%, contaminated with **4aD**) consisted predominantly of its *S**, *R**-isomer, while **9b** from **4aB** (isomeric purity>90%, contaminated with **4aC**) was opposite in the isomeric composition. Desulfinylation of diastereomeric **4a** with 1 equiv of PhLi gave (*Z*)-fluoro enol silyl ether **8b** (*E*:*Z*=1:20) and a diastereomer mixture of **9b** (1:1) in 16 and 31% yields, respectively. The use of excess PhLi improved the yields of **8b** and **9b** to 26 and 52% respectively but did not affect the stereoselectivity in the formation of the former compound. It should be noted that 1 equiv of nucleophilic reagents was sufficient for the desulfinylation of **3a** but not sufficient for **4a**.

Stereochemistry of **8** was assigned by comparison of their ^{13}C NMR data with those of 2-(4-biphenylyl)-1-fluoroethylene[4] and **11**; larger couplng constants of $^4J_{CF}$ were observed in (*E*)-isomers (7 Hz) than in (*Z*)-isomers (3 Hz). Moreover, in the case of **8b**, large long-range couplings between the fluorine and methyl groups on the silicon atom were observed only with the (*Z*)-isomer, showing the proximity of these groups ($^5J_{CF}$=4 Hz, $^6J_{HF}$=1.8 Hz).[17]



(2)

Next, the aralkyl sulfoxides **3b** and **4b** were subjected to the desulfinylation with PhMgBr and PhLi (Eq. 2 and Table 4). The reaction of **3b** (**A**:**B**:**C**:**D**=47:25:9:19) with 3 equiv of PhMgBr gave a mixture of fluoro enol ether **13a** (isomeric ratio=20:1), dihalogeno derivative **14a** (2:1 diastereomer mixture), and (*Z*)-α-fluorostyrene derivative **15** in respective yields of 36, 50, and 12%, while the treatment of **3b** with 3 equiv of PhLi gave **14a** (3:2 diastereomer mixture) predominantly. High *Z*-stereoselectivity (1:12—1:20) was observed in the formation of **13b**. Stereochemical determination of fluoro enol ether **13b** was based on the long-range couplings. In the case of (*Z*)-**13b**, the "through space" long-range couplings ($^5J_{CF}$=4 Hz and $^6J_{HF}$=1.8 Hz) were also observed.[17] Stereochemistry of **13a** could not be determined, although the major isomer may be anticipated to be an (*E*)-isomer on the analogy of **8**.

Reaction Pathways. Product selectivity in the nucleophilic desulfinylation of β-oxy sulfoxides **3** and **4** could be understood by considering the chelation effects of the β-substituent on the carbanionic or carbenic center which would be formed by an initial attack of nucleophile at the sulfur atom. First, the reaction of the β-MOM-

Table 4. Nucleophilic Desulfinylation of β-Oxy Sulfoxides **3b** and **4b**

Entry	Sulfoxide	R'M (equiv)	Additive (equiv)	Yield/%[a]		
				13[b]	**14**[c]	**15**[b]
13	**3b**[d]	PhMgBr (3)	CuI (0.1)	36 (20:1)[e]	27 (2:1)[f]	12 (1:5)
14	**3b**[d]	PhLi (1)	None	—	89[g] (1:1)	Trace
15	**3b**[d]	PhLi (3)	None	—	82[g] (1:1)	Trace
16	**4b**[h]	PhMgBr (3)	CuI (0.1)	72 (1:20)	Trace	25 (1:5)
17	**4b**[h]	PhLi (3)	None	50 (1:12)	37 (1:1)	5 (1:5)

a) Yields were calculated based on the NMR analyses of the chromatographed fractions. b) The *E*:*Z* ratios are given in parentheses. c) Numerals in parentheses refer to the diastereomer ratios. d) **A**:**B**:**C**:**D**=42:26:13:19. e) The stereochemistry could not be determined. f) A bromofluoro derivative was also obtained in 23% yield (diastereomer ratio, 2:1). g) Isolated yield. h) **A**:**B**:**C**:**D**=41:33:11:15.

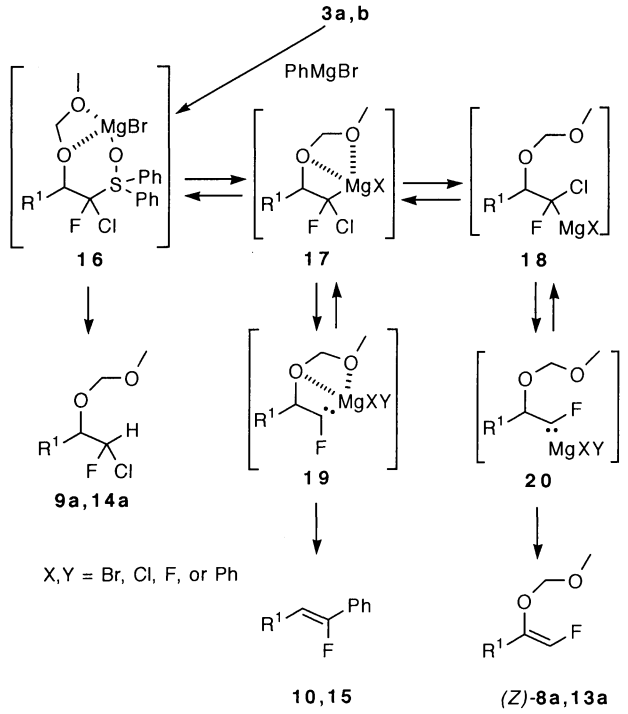


Fig. 3. Proposed reaction pathways (1).

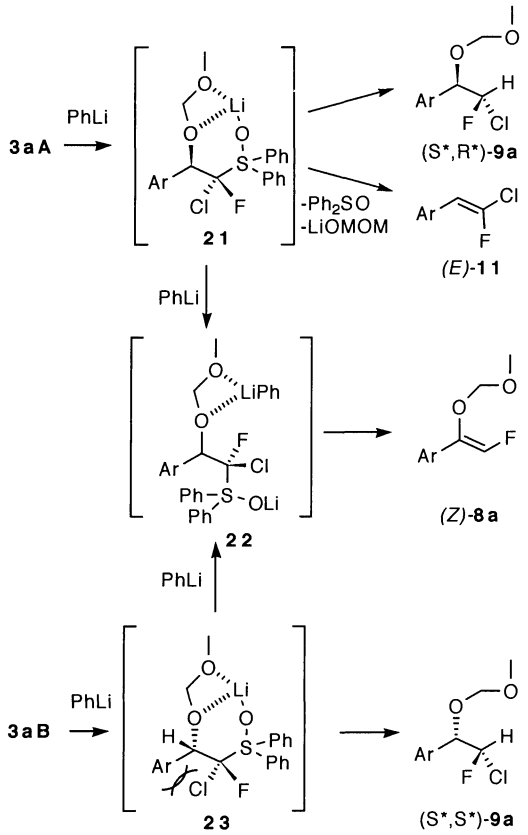


Fig. 4. Proposed reaction pathways (2).

oxy sulfoxides **3a** and **3b** with the Grignard reagent will be discussed (Fig. 3). The initially formed sulfurane **16** would be stabilized by the intramolecular coordination between the MOM oxygen atoms and magnesium. Thus, the chlorofluoro derivatives **9a** and **14a** were favorably formed. Loss of diphenyl sulfoxide from **16** would give the carbanionoid and carbenoid species **17** and **19**. Rotation of the single bond between C-1 and C-2 in **17** and **19** would be interfered by the chelation. Thus, the 1,2-hydrogen migration via carbenoid **20** giving (*Z*)-fluoro enol ethers **8a** and **13a** might be suppressed. Carbenoid **19** would have rather long life-time due to the stabilization of the chelation. Thus, the carbene center would suffer a greater change to the competitive phenylation with PhMgBr giving **10**.

Concerning with the reaction of the β-MOM-oxy sulfoxide **3a** with PhLi, the reaction pathways of each diastereomer should be discussed to understand high stereospecificity observed. As the attack of PhLi on sulfur destroys the chirality of sulfur atom at the initial stage, it would be sufficient to discuss about the major two isomers **3aA** and **3aB** (Fig. 4). Sulfurane **21** from **3aA** would be highly stabilized by the intramolecular chelation and its decomposition to a carbanionoid and diphenyl sulfoxide would not be facilitated. Thus, 1 equiv of PhLi was enough to effect the desulfinylation of **3a** because the competitive consumption of PhLi by diphenyl sulfoxide was excluded. Sulfurane **21** would undergo either hydrolytic loss of diphenyl sulfoxide to give (*S**, *R**)-**9a** or simultaneous loss of diphenyl sulfoxide and lithium methoxymethoxide to give (*E*)-**11**. When an excess amount of PhLi exists, intermolecular chelation between PhLi and the MOM group of sulfurane **21** would occur competitively to give sulfurane **22**. Decomposition of **22** would give (*Z*)-**8a**. In the case of **3aB**, a similar stabilization would be expected in sulfurane **23**, which would decompose to (*S**, *S**)-**9a** or (*Z*)-**11**. The similar rotation of C-1 and C-2 carbon bond of **23** would take place in the presence of excess PhLi. In this case, steric interaction between biphenyl and chlorine would facilitate the rotation better than in the case of **21**.

Desulfinylation pathways of the β-silyloxy sulfoxides are in line with those of α-chloro-α-fluoroalkyl sulfoxides,[4] if we consider the steric demand and electron-donating property of the silyloxy group (Fig. 5). Electron-donation from silyloxy group would accelerate both the transformation of carbanionoid **25** into carbenoid **26** and the hydrogen migration to the electron-deficient divalent carbon in **26**. Alkoxyl substituents are reported to occupy the position preferentially *ap* to the lone-pair electrons of carbene center in the 1,2-migration reaction.[3b] Moreover, in the transition state of migration, the bulky TBDMS-oxy group would tend to occupy the position *sc* to the small fluorine atom. Thus, the high *Z*-selectivity is manifested in the

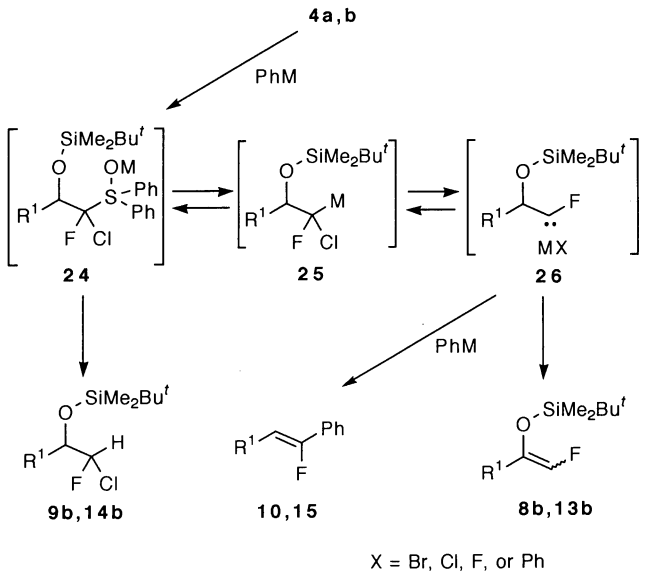


Fig. 5. Proposed reaction pathways (3).

formation of the fluoro enol ethers **8b** and **13b**.

Experimental

Melting points are uncorrected. Unless otherwise noted, all NMR spectra were observed with a GSX-270 spectrometer at ambient temperature by using $CDCl_3$ as the solvent, tetramethylsilane as an internal standard for ^1H and ^{13}C, and $CFCl_3$ as an internal standard for ^{19}F. Mass spectra were measured with a Hitachi M80B-LCAPI spectrometer under the following ionizing conditions: EI (electron impact, 20 eV) and CI (chemical ionization, 70 eV, methane as CI gas). Column chromatography was carried out using Wakogel C-200. Gas liquid chromatography was run using a Shimadzu GC-14A apparatus with a 3% OV-1 packed column (1 m) and/or a CBP10-M25 capillary column (25 m). Preparative GPC was performed using a JAI LC-08 apparatus with JAI-1H (20 mmID×60 cm) and JAI-2H (20 mmID×60 cm) columns. Ether and THF were distilled from sodium benzophenone ketyl. Methyllithium-lithium bromide was prepared from lithium and methyl bromide in ether as usual. Organometallic reagents were titrated prior to use. Other commercially available materials were used without further purification.

Alkylation of 1. Typical Procedure for 2-(4-Biphenylyl)-1-chloro-1-fluoro-2-hydroxyethyl Phenyl Sulfoxide (2a): An ethereal solution of MeLi–LiBr (1.2 M; 0.83 ml, 1 mmol) (1 M=1 mol dm^{-3}) was slowly added to a solution of **1** (193 mg, 1 mmol) in dry THF (10 ml) at −90 °C with stirring under an argon atmosphere over 10 min. After the brownish yellow solution was stirred at that temperature for additional 15 min, a THF (10 ml) solution of 4-biphenylcarbaldehyde (182 mg, 1 mmol) was slowly added. The resulting mixture was stirred at −90 °C for 30 min and then allowed to warm to room temperature. The mixture was diluted with a saturated NH_4Cl solution and extracted with ether. The ethereal extract was washed with brine, dried with Na_2SO_4 and evaporated. The residue was chromatographed on silica gel (hexane–CH_2Cl_2) to give **2a** (diastereomer mixture; **A**:**B**:**C**:**D**=38:34:21:7) as colorless crystals; mp 202—203 °C (hexane–CH_2Cl_2). MS(CI) m/z (rel intensity) 375 (M^++1, 1), 237(7), 232(44), 199(100), and 111(66). Calcd for $C_{20}H_{16}ClFO_2S$: C, 64.08; H, 4.30%. Found: C, 63.80; H, 4.47%.

(*S$_S$, 1*S**, 2*R**)-Isomer 2aA:** Colorless crystals, mp 191—192 °C (hexane–CH_2Cl_2). ^1H NMR (acetone-d_6) δ=5.20 (1H, dd, *J*=15.3 and 5.2 Hz), 5.96 (1H, dd, *J*=5.2 and 0.6 Hz, OH), and 7.3—7.9 (14H, m); ^{13}C NMR (acetone-d_6) δ=76.25 (d, *J*=21 Hz), 124.89 (d, *J*=300 Hz), 127.88, 128.23, 128.67 (d, *J*=1 Hz), 128.93, 130.24 (2C), 130.62 (d, *J*=1 Hz), 134.08, 136.82 (d, *J*=4 Hz), 139.65 (d, *J*=6 Hz), 141.61, and 142.93; ^{19}F NMR (acetone-d_6) δ=−125.37 (d, *J*=16 Hz); IR (KBr) 3316, 1488, 1446, 1084, and 1052 cm^{-1}.

(*S$_S$, 1*S**, 2*S**)-Isomer 2aB:** Colorless crystals, mp 216—217 °C (hexane–CH_2Cl_2). ^1H NMR (acetone-d_6) δ=5.64 (1H, dd, *J*=5.8 and 4.0 Hz), 6.15 (1H, dd, *J*=5.8 and 1.2 Hz, OH), and 7.3—7.9 (14H, m); ^{19}F NMR (acetone-d_6) δ=−124.09 (br s); IR (KBr) 3416, 1488, 1448, 1084, and 1048 cm^{-1}.

(*S$_S$, 1*R**, 2*S**)-Isomer 2aC:** ^1H NMR (acetone-d_6) δ=5.29 (1H, dd, *J*=24.7 and 6.1 Hz), 6.23 (1H, d, *J*=6.1 Hz, OH), and 7.3—7.9 (14H, m); ^{19}F NMR (acetone-d_6) δ=−130.12 (d, *J*=25 Hz).

(*S$_S$, 1*R**, 2*R**)-Isomer 2aD:** ^1H NMR (acetone-d_6) δ=5.15 (1H, dd, *J*=12.2 and 5.5 Hz), 5.84 (1H, dd, *J*=5.5 and 0.6 Hz, OH), and 7.3—7.9 (14H, m); ^{13}C NMR (acetone-d_6) (typical signal) δ=76.24 (d, *J*=23 Hz); ^{19}F NMR (acetone-d_6) δ=−120.23 (d, *J*=12 Hz).

1-Chloro-1-fluoro-2-hydroxy-4-phenylbutyl Phenyl Sulfoxide (2b): IR (neat) 3368, 3060, 3028, 2928, 1498, 1456, 1448, 1086, 1058, and 1000 cm^{-1}; MS(CI) m/z (rel intensity) 329 [$M^+(^{37}Cl)$+1, 9], 327 [$M^+(^{35}Cl)$+1, 23], 119(18), 183(16), 145(37), 126(100), 117(35), 109(48), and 91(99). Calcd for $C_{16}H_{16}ClFO_2S$: C, 58.80; H, 4.93%. Found: C, 58.57; H, 5.01%.

(*S$_S$, 1*S**, 2*R**)-Isomer 2bA:** ^1H NMR δ=2.00—2.37 (2H, m), 2.66—3.03 (2H, m), 4.25 (1H, m), 4.53 (1H, m), and 7.2—7.8 (10H, m); ^{13}C NMR δ=31.2—32.8 (2C), 32.59 (d, *J*=9 Hz), 73.57 (d, *J*=21 Hz), 121.55 (d, *J*=304 Hz), 126.06 (d, *J*=2 Hz), 127.29, 128.43, 128.45, 128.80, 132.81, 136.57 (d, *J*=4 Hz), and 140.75; ^{19}F NMR δ=−127.27 (d, *J*=13.8 Hz).

(*S$_S$, 1*S**, 2*S**)-Isomer 2bB:** ^1H NMR δ=2.00—2.37 (2H, m), 1.6 (1H, br), 4.50 (1H, m), and 7.2—7.8 (10H, m); ^{13}C NMR (typical signals) δ=68.96 (d, *J*=28 Hz), 121.87 (d, *J*=310 Hz), 126.07 (d, *J*=1 Hz), 127.76, 128.70, 132.78, 135.65 (d, *J*=3 Hz), and 141.00; ^{19}F NMR δ=−124.43 (d, *J*=1.8 Hz).

(*S$_S$, 1*R**, 2*S**)-Isomer 2bC:** ^1H NMR δ=2.00—2.37 (2H, m), 2.66—3.03 (2H, m), 1.6 (1H, br), 4.32 (1H, m), and 7.2—7.8 (10H, m); ^{13}C NMR (typical signals) δ=72.58 (d, *J*=20 Hz), 123.67 (d, *J*=297 Hz), 126.70 (d, *J*=2 Hz), 132.49, 136.90, 140.90; ^{19}F NMR δ=−128.48 (d, *J*=22.7 Hz).

(*S$_S$, 1*R**, 2*R**)-Isomer 2bD:** ^1H NMR δ=2.00—2.37 (2H, m), 2.66—3.03 (2H, m), 1.6 (1H, br), 4.30 (1H, m), and 7.2—7.8 (10H, m); ^{13}C NMR (typical signals) δ=73.90 (d, *J*=24 Hz), 122.95 (d, *J*=294 Hz), 126.60 (d, *J*=2 Hz), 132.71, 136.66, and 140.66; ^{19}F NMR δ=−117.08 (d, *J*=7.3 Hz).

MOM-Protection of 2. Typical Procedure for 2-(4-Biphenylyl)-1-chloro-1-fluoro-2-(methoxymethoxy)ethyl Phenyl Sulfoxide (3a): To a solution of **2a** (**A**:**B**:**C**:**D**=38:34:21:7; 334 mg, 0.89 mmol) in CH_2Cl_2 (10 ml) were added 0.3 ml of MOMCl (3.8 mmol) and 0.7 ml of *N*,*N*-diisopropylethylamine at room temperature. After the mixture was refluxed for 1 d, ether and water were added. The ethereal phase

was separated and the aqueous phase was extracted with ether. The combined organic phase was washed with brine, dried over Na_2SO_4 and concentrated. The residue was chromatographed on silica gel to give 320 mg (89%) of **3a** (**A**:**B**:**C**:**D**=35:40:10:15) as a colorless oil. IR (neat) 2960, 1488, 1448, 1218, 1198, 1154, 1128, 1110, 1088, 1060, 1030, and 1018 cm^{-1}; MS(CI) *m/z* (rel intensity) 419 [$M^+(^{35}Cl)+1$, 3], 387(1), 357(5), 323(1), 303(2), 232(66), 197(20), 170(15), 141(8), and 111(100). Calcd for $C_{22}H_{20}ClFO_3S$: C, 62.97; H, 5.04%. Found: C, 62.97; H, 4.96%.

(*S$_S$, 1*S**, 2*R**)-Isomer 3aA:** Colorless crystals, mp 122—125 °C (hexane–CH_2Cl_2). ^1H NMR δ=3.36 (3H, s), 4.68 (1H, d, *J*=6.4 Hz), 4.75 (1H, d, *J*=6.4 Hz), 5.62 (1H, d, *J*=8.9 Hz), and 7.3—7.8 (14H, m); ^{13}C NMR δ=56.01 (d, *J*=1 Hz), 77.39 (d, *J*=21 Hz), 95.14, 120.40 (d, *J*=313 Hz), 126.89, 127.07 (2C), 127.62, 128.03, 128.57, 128.77, 129.83, 131.82 (d, *J*=6 Hz), 132.74, 136.50 (d, *J*=4 Hz), 140.22, and 142.36; ^{19}F NMR δ=−124.92 (d, *J*=9 Hz).

(*S$_S$, 1*S**, 2*S**)-Isomer 3aB:** ^1H NMR δ=3.57 (3H, s), 4.83 (1H, d, *J*=6.6 Hz), 4.88 (1H, dd, *J*=6.6 and 1.8 Hz), 5.67 (1H, d, *J*=4.3 Hz), and 7.3—7.9 (9H, m); ^{13}C NMR δ=57.05, 73.84 (d, *J*=30 Hz), 95.12, 119.47 (d, *J*=305 Hz), 126.89, 127.08 (2C), 127.53, 127.90, 128.61, 128.76, 129.39 (d, *J*=1 Hz), 131.51, 132.61, 136.76 (d, *J*=4 Hz), 140.36, and 142.12; ^{19}F NMR δ=−124.97 (d, *J*=3 Hz).

(*S$_S$, 1*R**, 2*S**)-Isomer 3aC:** ^1H NMR δ=3.53 (3H, s), 4.70 (1H, d, *J*=6.7 Hz), 4.79 (1H, d, *J*=6.7 Hz), 5.33 (1H, d, *J*=24.1 Hz), and 7.3—7.9 (14H, m); ^{13}C NMR (typical signals) δ=56.74, 79.43 (d, *J*=31 Hz), 94.81, 122.23 (d, *J*=298 Hz), 126.66 (d, *J*=2 Hz), 126.93, 127.00, 127.58, 128.68, 130.15 (d, *J*=1 Hz), 131.68, 132.36, 137.51, 140.28, and 142.19; ^{19}F NMR δ=−128.64 (d, *J*=24 Hz).

(*S$_S$, 1*R**, 2*R**)-Isomer 3aD:** ^1H NMR δ=3.43 (3H, s), 4.70 (2H, m), 5.36 (1H, d, *J*=18.6 Hz), and 7.3—7.9 (14H, m); ^{13}C NMR (typical signals) δ=56.43, 79.37 (d, *J*=20 Hz), 94.85, 122.25 (d, *J*=295 Hz), 126.80 (d, *J*=3 Hz), 127.22, 128.62, 129.74 (d, *J*=1 Hz), 132.09, 132.50, 137.17, 140.19, and 142.41; ^{19}F NMR δ=−121.59 (d, *J*=19 Hz).

1-Chloro-1-fluoro-2-methoxymethoxy-4-phenylbutyl Phenyl Sulfoxide (3b): Colorless oil. IR (neat) 3060, 2952, 1498, 1446, 1152, 1092, 1060, and 1016 cm^{-1}; MS(CI) *m/z* (rel intensity) 371 [$M^+(^{35}Cl)+1$, 6], 341(20), 339(51), 213(12), 183(26), 145(28), 125(100), and 111(50). Calcd for $C_{18}H_{20}ClFO_3S$: C, 58.29; H, 5.44%. Found: C, 58.02; H, 5.50%.

(*S$_S$, 1*S**, 2*R**)-Isomer 3bA:** ^1H NMR δ=2.03—2.34 (2H, m), 2.66—3.07 (2H, m), 3.46 (3H, s), 4.42 (1H, ddd, *J*=9.8, 6.7, 2.4 Hz), 4.89 (1H, dd, *J*=6.7 and 0.6 Hz), 5.05 (1H, dd, *J*=6.7 and 1.2 Hz), and 7.2—7.8 (10H, m); ^{13}C NMR δ=32.37, 33.07 (d, *J*=4 Hz), 56.44 (d, *J*=4 Hz), 78.23 (d, *J*=17 Hz), 98.16 (d, *J*=5 Hz), 120.92 (d, *J*=310 Hz), 126.12 (d, *J*=4 Hz), 127.60, 128.25—128.65 (3C), 132.77, 136.45 (d, *J*=4 Hz), and 140.80; ^{19}F NMR δ=−122.59 (d, *J*=7 Hz).

(*S$_S$, 1*S**, 2*S**)-Isomer 3bB:** ^1H NMR δ=2.03—2.34 (2H, m), 2.66—3.07 (2H, m), 3.54 (3H, s), 4.40 (1H, td, *J*=5.8 and 3.7 Hz), 4.72 (1H, d, *J*=7.2 Hz), 4.82 (1H, d, *J*=7.2 Hz), and 7.1—7.8 (10H, m); ^{13}C NMR (typical signals) δ=31.51 (d, *J*=2 Hz), 31.59, 56.52, 75.90 (d, *J*=28 Hz), 98.12, 121.46 (d, *J*=310 Hz), 132.61, 136.50 (d, *J*=4 Hz), and 141.03; ^{19}F NMR δ=−124.88(m).

(*S$_S$, 1*R**, 2*S**)-Isomer 3bC:** ^1H NMR δ=2.03—2.24 (2H, m), 2.66—3.07 (2H, m), 3.55 (3H, s), 4.23 (1H, ddd, *J*=21.7, 7.5, and 3.2 Hz), 4.90 (1H, d, *J*=6.9 Hz), 4.98 (1H, d, *J*=6.9 Hz), and 7.2—7.8 (10H, m); ^{13}C NMR (typical signals) δ=31.17 (d, *J*=1 Hz), 32.33, 56.62, 79.27 (d, *J*=18 Hz), 98.31, 123.61 (d, *J*=298 Hz), 126.66 (d, *J*=4 Hz), 132.40, 137.17, and 141.03; ^{19}F NMR δ=−124.93 (d, *J*=22 Hz).

(*S$_S$, 1*R**, 2*R**)-Isomer 3bD:** ^1H NMR δ=2.03—2.34 (2H, m), 2.66—3.07 (2H, m), 3.51 (3H, s), 4.17 (1H, ddd, *J*=13.1, 8.0, and 4.0 Hz), 4.78 (1H, d, *J*=7.0 Hz), 4.85 (1H, d, *J*=7.0 Hz), and 7.2—7.8 (10H, m); ^{13}C NMR (typical signals) δ=31.85, 31.97 (d, *J*=2 Hz), 56.55, 81.47 (d, *J*=19 Hz), 98.25 (d, *J*=2 Hz), 122.75 (d, *J*=294 Hz), 126.80 (d, *J*=2 Hz), 132.46, 137.36, and 140.65; ^{19}F NMR δ=−114.39 (d, *J*=14 Hz).

TBDMS-Protection of 2. Typical Procedure for 2-(4-Biphenylyl)-2-(*t*-butyldimethylsilyloxy)-1-chloro-1-fluoroethyl Phenyl Sulfoxide (4a): Imidazole (476 mg, 7 mmol), TBDMSCl (482 mg, 3.2 mmol), and **2a** (**A**:**B**:**C**:**D**=38:34:21:7; 334 mg, 0.89 mmol) were dissolved in DMF (1 ml) and the mixture was heated at 80 °C. After 2 d, the reaction mixture was cooled to room temperature and quenched with water. The mixture was extracted with ether. The ethereal phase was washed with brine, dried over Na_2SO_4, and concentrated. The residue was chromatographed on silica gel to give 303 mg (72%) of **4a** (**A**:**B**:**C**:**D**=25:40:25:10) as a colorless viscous oil. IR (neat) 2956, 2932, 2886, 1488, 1474, 1448, 1256, 1132, 1090, and 1060 cm^{-1}; MS(CI) *m/z* (rel intensity) 489 [$M^+(^{35}Cl)+1$, 0.3], 473(3), 431(3), 357(6), 328(0.4), 260(11), 232(100), 197(13), 167(14), and 125(90). Calcd for $C_{26}H_{30}ClFO_2SSi$: C, 63.85; H, 6.18%. Found: C, 64.21; H, 6.03%.

(*S$_S$, 1*S**, 2*R**)-Isomer 4aA:** Colorless crystals, mp 215—219 °C (hexane–CH_2Cl_2). ^1H NMR δ=−0.02 (3H, s), 0.13 (3H, s), 0.90 (9H, s), 5.65 (1H, d, *J*=7.3 Hz), and 7.3—7.8 (14H, m); ^{13}C NMR (typical signals) δ=75.18 (d, *J*=21 Hz), 120.84 (d, *J*=314 Hz), and 136.69 (d, *J*=4 Hz); ^{19}F NMR δ=−124.58 (d, *J*=7 Hz).

(*S$_S$, 1*S**, 2*S**)-Isomer 4aB:** Viscous oil. ^1H NMR δ=−0.08 (3H, s), 0.30 (3H, s), 1.03 (9H, s), 5.65 (1H, d, *J*=3.4 Hz), and 7.3—7.9 (14H, m); ^{13}C NMR δ=−5.31, −4.04, 18.15, 25.72, 71.57 (d, *J*=30 Hz), 120.74 (d, *J*=307 Hz), 126.48, 127.06, 127.10, 127.45, 127.88, 128.53, 128.74, 129.05 (d, *J*=1 Hz), 132.42, 134.70 (d, *J*=1 Hz), 137.04 (d, *J*=4 Hz), 140.47, and 141.72; ^{19}F NMR δ=−125.64 (br s).

(*S$_S$, 1*R**, 2*S**)-Isomer 4aC:** ^1H NMR δ=−0.14 (3H, s), 0.24 (3H, s), 0.97 (9H, s), 5.30 (1H, d, *J*=22.9 Hz), and 7.3—7.9 (14H, m); ^{13}C NMR (typical signals) δ=76.23 (d, *J*=17 Hz), 123.09 (d, *J*=300 Hz), and 137.83; ^{19}F NMR δ=−130.98 (d, *J*=23 Hz).

(*S$_S$, 1*R**, 2*R**)-Isomer 4aD:** ^1H NMR δ=−0.08 (3H, s), 0.15 (3H, s), 0.91 (9H, s), 5.31 (1H, d, *J*=19.2 Hz), and 7.3—7.9 (14H, m); ^{13}C NMR (typical signals) δ=25.59, 78.37 (d, *J*=18 Hz), 132.33, 137.50, and 141.97; ^{19}F NMR δ=−122.84 (d, *J*=19 Hz).

2-(*t*-Butyldimethylsilyloxy)-1-chloro-1-fluoro-4-phenylbutyl Phenyl Sulfoxide (4b): Colorless viscous oil. IR (neat) 2952, 2928, 2888, 2856, 1498, 1474, 1130, 1094, and 1060 cm^{-1}; MS(CI) *m/z* (rel intensity) 443 [$M^+(^{37}Cl)+1$, 9], 441 [$M^+(^{35}Cl)+1$, 20], 383 (23), 279 (6), 211 (6), 183 (29), 145 (100), 117 (73), 91 (89), and 57 (25). Calcd for $C_{22}H_{30}ClFO_2SSi$: C, 59.91; H, 6.86%. Found: C, 59.96; H, 6.68%.

(*S$_S$, 1*S**, 2*R**)-Isomer 4bA:** ^1H NMR δ=0.08 (3H, d, *J*=2.8 Hz), 0.14 (3H, s), 0.93 (9H, s), 1.9—2.2 (2H, m), 2.5—2.8 (2H, m), 4.53 (1H, ddd, *J*=9.5, 7.0, and 2.3 Hz), 7.1—7.8 (10H, m); ^{13}C NMR δ=−4.61 (d, *J*=5 Hz), −3.78, 18.34, 25.80, 32.10,

34.79 (d, J=4 Hz), 73.57 (d, J=19 Hz), 120.99 (d, J=310 Hz), 126.11 (d, J=1 Hz), 127.8—128.8 (4C), 132.82, 136.78 (d, J=4 Hz), and 141.16 (d, J=1 Hz); ^{19}F NMR δ=−121.10 (m).

(*S$_S$, 1*S**, 2*S**)-Isomer 4bB:** ^{1}H NMR δ=0.20 (3H, s), 0.29 (3H, s), 0.98 (9H, s), 1.9—2.2 (2H, m), 2.5—2.8 (2H, m), 4.65 (1H, td, J=5.6 and 2.6 Hz), 7.1—7.8 (10H, m); ^{13}C NMR (typical signals) δ=−4.80, −4.40 (d, J=1 Hz), 18.20, 25.81, 31.77 (d, J=3 Hz), 34.86, 69.66 (d, J=28 Hz), 122.53 (d, J=308 Hz), 126.07 (d, J=5 Hz), 132.44, 136.90 (d, J=4 Hz), and 141.27; ^{19}F NMR δ=−126.04 (m).

(*S$_S$, 1*R**, 2*S**)-Isomer 4bC:** ^{1}H NMR δ=0.15 (3H, s), 0.25 (3H, s), 1.01 (9H, s), 1.9—2.2 (2H, m), 2.5—2.8 (2H, m), 4.40 (1H, dt, J=21.7 and 4.5 Hz), 7.1—7.8 (10H, m); ^{13}C NMR (typical signals) δ=−4.88 (d, J=1 Hz), −4.04, 18.34, 25.86, 30.82 (d, J=3 Hz), 34.86, 73.10 (d, J=18 Hz), 124.18 (d, J=300 Hz), 126.74 (d, J=3 Hz), 132.29, 137.55, and 141.56; ^{19}F NMR δ=−124.37 (d, J=21 Hz).

(*S$_S$, 1*R**, 2*R**)-Isomer 4bD:** ^{1}H NMR δ=0.16 (3H, s), 0.19 (3H, d, J=2 Hz), 1.01 (9H, s), 1.9—2.2 (2H, m), 2.5—2.8 (2H, m), 4.30 (1H, ddd, J=13.1, 8.4, and 4.0 Hz), 7.1—7.8 (10H, m); ^{13}C NMR (typical signals) δ=−4.36 (d, J=5 Hz), −4.31, 18.40, 25.90, 32.66, 34.04 (d, J=3 Hz), 77.90 (d, J=19 Hz), 122.70 (d, J=293 Hz), 126.92 (d, J=3 Hz), 132.32, 137.75, and 140.85; ^{19}F NMR δ=−110.20 (d, J=12 Hz).

2-(4-Biphenylyl)-1-chloro-1-fluoro-2-(methoxymethoxy)-ethyl Phenyl Sulfone (5): To a stirred solution of **4a** (**A**:**D**=18:10; 93 mg, 0.22 mmol) in CH_2Cl_2 (5 ml) was added mCPBA (116 mg; 70% purity; 0.45 mmol) at room temperature. After being stirred overnight, the reaction was quenched by adding a few drops of 1M *aq*-$Na_2S_2O_3$ solution. The solvent was removed and then 20 ml of benzene was added. The suspension was filtered and the precipitate was washed with benzene. The filtrate was washed with sat. aq-$NaHCO_3$ and brine, dried over Na_2SO_4, and concentrated. The residue was chromatographed on silica gel (hexane–CH_2Cl_2) to give 87 mg (90%) of **5** (**A**:**B**=9:5) as colorless crystals, mp 107—110 °C. IR (KBr) 2956, 1488, 1450, 1340, 1316, 1166, 1152, 1108, 1086, 1068, 1030, and 1018 cm^{-1}; MS (EI) m/z (rel intensity) 436 [M$^+$(^{37}Cl), 1], 434 [M$^+$(^{35}Cl), 2], 373(1), 338(1), 232(15), 227(100), 181(18), and 149(5). Calcd for $C_{22}H_{20}ClFO_4S$: C, 60.76; H, 4.64%. Found: C, 60.38; H, 4.89%.

(1*S, 2*R**)-Isomer 5A:** ^{1}H NMR δ=3.39 (3H, s), 4.60 (1H, d, J=7.3 Hz), 4.74 (1H, d, J=7.3 Hz), 5.57 (1H, d, J=19.5 Hz), and 7.3—8.1 (14H, m); ^{13}C NMR δ=56.96, 75.34 (d, J=28 Hz), 94.89, 117.05 (d, J=280 Hz), 126.84, 126.98, 127.53, 128.78, 128.86, 129.49 (d, J=1 Hz), 131.24 (d, J=1 Hz), 131.60, 135.00, 140.15, and 142.22; ^{19}F NMR δ=−122.21 (d, J=19 Hz).

(1*S, 2*S**)-Isomer 5B:** ^{1}H NMR δ=3.52 (3H, s), 4.74 (1H, d, J=6.7 Hz), 4.86 (1H, dd, J=6.7 and 1.8 Hz), 5.82 (1H, d, J=4.9 Hz), and 7.3—8.1 (14H, m); ^{13}C NMR δ=56.54, 78.24 (d, J=18 Hz), 95.00, 117.44 (d, J=297 Hz), 126.84, 126.98, 127.53, 128.69, 128.79, 130.00 (d, J=1 Hz), 130.74, 131.88 (d, J=1 Hz), 134.47, 134.84, 140.12, and 142.18; ^{19}F NMR δ=−109.67 (d, J=4 Hz).

2-(4-Biphenylyl)-1-chloro-1-fluoro-2-hydroxyethyl Phenyl Sulfone (6): Sulfone **5** (**A**:**B**=5:21; 51 mg, 0.12 mmol) was dissolved in MeOH (20 ml). To the solution were added 5 ml of water and 0.1 ml of conc HCl. After the mixture was refluxed for 3 d, ether and sat. aq-$NaHCO_3$ were added. The organic phase was separated and the aqueous phase was extracted with ether. The organic phase was washed with brine, dried over Na_2SO_4, and concentrated. The residue was chromatographed on silica gel (hexane–CH_2Cl_2) to give 37 mg (81%) of **6** (**A**:**B**=5:18) as a colorless solid. IR (KBr) 3054, 1488, 1450, 1332, 1316, 1186, 1162, 1120, 1084, and 1020 cm^{-1}; MS (EI) m/z (rel intensity) 390 [M$^+$(^{35}Cl), 2], 338(1), 184(17), 183(100), 182(17), 181(17), 155(21), and 141(10). Calcd for $C_{20}H_{16}ClFO_3S$: C, 61.46; H, 4.13%. Found: C, 61.31; H, 4.12%.

(1*S, 2*R**)-Isomer 6A:** ^{1}H NMR δ=3.73 (1H, d, J=3.4 Hz, OH), 5.64 (1H, dd, J=20.8 and 3.4 Hz), and 7.2—8.1 (14H, m); ^{13}C NMR (typical signals) δ=75.52 (d, J=19 Hz), 116.77 (d, J=297 Hz), 126.98, 127.59, 128.61 (d, J=2 Hz), 132.18, 132.90, 135.50, 140.33, and 142.31; ^{19}F NMR δ=−128.31 (d, J=20 Hz).

(1*S, 2*S**)-Isomer 6B:** Colorless crystals, mp 176—177 °C (hexane–$CHCl_3$). ^{1}H NMR δ=3.62 (1H, d, J=3.1 Hz), 5.76 (d, J=2.1 Hz), and 7.2—8.1 (14H, m); ^{13}C NMR δ=71.53 (d, J=25 Hz), 117.42 (d, J=286 Hz), 126.83, 127.12, 127.56, 128.78, 129.11, 129.24, 131.22 (d, J=1 Hz), 133.07, 134.07, 135.61, 140.38, and 142.19; ^{19}F NMR δ=−111.80 (br s).

Nucleophilic Desulfinylation. General Procedure: A stirred solution of sulfoxide **3** or **4** (0.3 mmol) and an additive in THF (10 ml) was cooled to −78 °C by a Dry Ice–acetone bath and then a solution of an organometallic reagent was slowly added to the mixture over 5 min. The reaction mixture was stirred for 2 h and then the cooling bath was removed. After the temperature of the reaction mixture reached up to 10 °C, a saturated solution of NH_4Cl was added. The reaction mixture was extracted with ether and the ethereal extract was washed with brine, dried over Na_2SO_4, and evaporated. The residue was chromatographed on silica gel (hexane–CH_2Cl_2). Yields of the producuts were calculated at this stage by ^{1}H and ^{19}F NMR analyses. Further separation of the products was performed by preparative GPC.

4-(Fluoroacetyl)biphenyl (7): Colorless crystals, mp 134—135 °C (hexane–CH_2Cl_2). ^{1}H NMR δ=5.53 (2H, d, J=47.0 Hz) and 7.6—8.0 (9H, m); ^{13}C NMR δ=83.59 (d, J=182.5 Hz), 127.25, 127.49, 128.45, 128.49, 128.82 (d, J=2 Hz), 129.00, 139.51, 146.81, and 193.02 (d, J=16 Hz); ^{19}F NMR δ=−230.88 (t, J=47 Hz); IR (KBr) 2936, 1700, 1606, 1410, 1244, and 1094 cm^{-1}; MS (EI) m/z (rel intensity) 215 (M$^+$+1, 6), 214 (M$^+$, 38), 181(100), 153 (26), and 152 (31). Calcd for $C_{14}H_{11}FO$: C, 78.49; H, 5.18%. Found: C, 78.30; H, 5.08%.

1-(4-Biphenylyl)-2-fluoro-1-(methoxymethoxy)ethylene (8a). (*Z*)-Isomer: Colorless crystals, mp 75—77 °C (hexane–CH_2Cl_2). ^{1}H NMR δ=3.57 (3H, s), 5.01 (2H, s), 6.68 (1H, d, J=77.2 Hz), and 7.3—7.7 (9H, m); ^{13}C NMR δ=56.98 (d, J=2 Hz, CH_3), 96.07 (d, J=5 Hz, CH_2), 126.34 (d, J=3 Hz, C_2 and C_6), 127.00, 127.35, 127.57, 128.84, 130.81 (d, J=4 Hz, C_1), 138.02 (d, J=259 Hz, C_β), 139.91 (d, J=7 Hz, Cα), 140.36 (C_1'), and 141.61 (d, J=1 Hz, C_4); ^{19}F NMR δ=−154.03 (d, J=77 Hz); IR (KBr) 2960, 2900, 1664, 1488, 1400, 1330, 1278, 1214, 1160, 1132, 1092, 1038, and 1016 cm^{-1}; MS(EI) m/z (rel intensity) 259 (M$^+$+1,7), 258 (M$^+$, 42), 226(11), 185(11), 181(100), 153(14), and 152(13). Calcd for $C_{16}H_{15}FO_2$: C, 74.40; H, 5.85%. Found: C, 74.57; H, 5.77%.

(*E*)-Isomer: ^{1}H NMR δ=2.50 (3H, s), 4.91 (2H, s), and 7.3—7.7 (10H, m); ^{13}C NMR (typical signals) δ=56.19 (CH_3), 96.30 (d, J=2 Hz, CH_2), and 141.37 (d, J=254 Hz, C_β); ^{19}F NMR δ=−162.95 (d, J=79 Hz).

1-(4-Biphenylyl)-1-(*t*-butyldimethylsilyloxy)-2-fluoroethylene (8b). (*Z*)-Isomer: Colorless crystals, mp 51—54 °C (hexane–CH_2Cl_2). ^{1}H NMR δ=0.17 (6H, d, J=1.8 Hz), 1.00

(9H, s), 6.95 (1H, d, J=77.8 Hz), and 7.4—7.6 (9H, m); ^{13}C NMR δ=−4.55 (d, J=4 Hz), 18.47, 25.78, 125.22 (d, J=3 Hz, C_2 and C_6), 126.95, 127.02, 127.25 (d, J=22 Hz, C_α), 127.41, 128.80, 133.85, 135.69 (d, J=250 Hz, C_β), 137.53, and 140.48; ^{19}F NMR δ=−157.20 (d-septet, J=78 and 2 Hz); IR (KBr) 2932, 2896, 2860, 1662, 1348, 1254, 1132, and 1074 cm^{-1}; MS (EI) m/z (rel intensity) 329 (M^++1, 3), 328 (M^+, 10), 271(7), 243(27), 215(10), 193(53), and 77(100). Calcd for $C_{20}H_{25}FOSi$: C, 73.13; H, 7.67%. Found: C, 73.47; H, 7.68%.

(*E*)-Isomer: ^{1}H NMR δ=0.02 (6H, s), 1.00 (9H, s), 7.19 (1H, d, J=82.4 Hz), and 7.4—7.6 (9H, m); ^{19}F NMR δ=−164.74 (d, J=80 Hz).

1-(4-Biphenylyl)-2-chloro-2-fluoro-1-(methoxymethoxy)-ethane (9a): IR (KBr) 1490, 1412, 1212, 1154, 1108, 1050, 1030, and 1018 cm^{-1}; MS(EI) m/z (rel intensity) 296 [M^+(^{37}Cl), 9], 294 [M^+(^{35}Cl), 17], 233(17), 227(100), 198(20), 167(19), and 58(7). Calcd for $C_{16}H_{16}ClFO_2$: C, 65.20; H, 5.47%. Found: C, 65.57; H, 5.39%.

(1*S, 2*R**)-Isomer:** Colorless crystals, mp 58 °C (hexane–CH_2Cl_2). ^{1}H NMR δ=3.41 (3H, s), 4.67 (1H, d, J=6.7 Hz), 4.73 (1H, d, J=6.7 Hz), 4.95 (1H, dd, J=12.4 and 5.2 Hz), 6.26 (1H, dd, J=50.0 and 5.2 Hz), and 7.3—7.6 (9H, m); ^{13}C NMR δ=55.94, 79.36 (d, J=21 Hz), 94.87, 101.82 (d, J=249 Hz), 127.12, 127.23, 127.57, 128.67, 128.81, 134.02 (d, J=3 Hz), 140.43, and 141.98; ^{19}F NMR δ=−142.90 (dd, J=50 and 12 Hz).

(1*S, 2*S**)-Isomer:** ^{1}H NMR δ=3.42 (3H, s), 4.66 (1H, d, J=6.7 Hz), 4.71 (1H, d, J=6.7 Hz), 4.94 (1H, dd, J=11.6 and 4.8 Hz), 6.23 (1H, dd, J=49.6 and 4.8 Hz), and 7.3—7.6 (9H, m); ^{13}C NMR δ=55.99, 79.22 (d, J=23 Hz), 94.62, 102.08 (d, J=246 Hz), 127.12, 127.24, 127.56, 128.66, 128.80, 133.70 (d, J=2 Hz), 140.45, and 141.96; ^{19}F NMR δ=−142.14 (dd, J=50 and 11.0 Hz).

1-(4-Biphenylyl)-1-(*t*-butyldimethylsiloxy)-2-chloro-2-fluoroethane (9b): Colorless oil. IR (neat) 2956, 2932, 2888, 2860, 1488, 1256, 1108, 1080, and 1040 cm^{-1}; MS (CI) m/z (rel intensity) 367 [M^+(^{37}Cl)+1, 2], 365 [M^+(^{35}Cl)+1, 5], 345(1), 307(5), 233(9), 195(16), 166(100), 155(12), and 115(10). Calcd for $C_{20}H_{26}ClFOSi$: C, 65.82; H, 7.18%. Found: C, 66.20; H, 7.23%.

(1*S, 2*R**)-Isomer:** ^{1}H NMR δ=0.12 (3H, s), 0.14 (3H, s), 0.92 (9H, s), 4.90 (1H, dd, J=11.0 and 5.5 Hz), 6.04 (1H, dd, J=50.8 and 5.5 Hz), and 7.3—7.6 (9H, m); ^{19}F NMR δ=−141.11 (dd, J=51 and 11 Hz).

(1*S, 2*S**)-Isomer:** ^{1}H NMR δ=−0.03 (3H, s), −0.02 (3H, s), 0.90 (9H, s), 4.90 (1H, dd, J=8.6 and 5.2 Hz), 6.04 (1H, dd, J=49.6 and 5.2 Hz), and 7.3—7.6 (9H, m); ^{19}F NMR δ=−140.21 (dd, J=50 and 8 Hz).

2-(4-Biphenylyl)-1-fluoro-1-phenylethylene (10): Colorless crystals, mp 189—191 °C (hexane–CH_2Cl_2). IR (KBr) 1702, 1668, 1496, 1448, 1410, 1182, 1096, 1054, and 1024 cm^{-1}; MS(EI) m/z (rel intensity) 274 (M^+, 100), 254(9), 253(11), 252(7), and 202(10). Found: m/z 274.1150. Calcd for $C_{20}H_{15}F$: M, 274.1158.

(*E*)-Isomer: ^{1}H NMR δ=6.47 (1H, d, J=22.6 Hz) and 7.3—7.7 (14H, m); ^{13}C NMR (typical signals) δ=105.47 (d, J=11 Hz) and 157.33 (d, J=258 Hz); ^{19}F NMR δ=−95.47 (d, J=22 Hz).

(*Z*)-Isomer: ^{1}H NMR δ=6.36 (1H, d, J=39.4 Hz) and 7.3—7.8 (14H, m); ^{13}C NMR (typical signal) δ=108.96 (d, J=31 Hz); ^{19}F NMR δ=−114.33 (d, J=40 Hz).

2-(4-Biphenylyl)-1-chloro-1-fluoroethylene (11): Colorless crystals, mp 82—84 °C (hexane–CH_2Cl_2). IR (KBr) 1658, 1488, 1480, 1332, 1316, and 1068 cm^{-1}; MS(EI) m/z (rel intensity) 234 [M^+(^{37}Cl), 60], 232 [M^+(^{35}Cl), 100], 197(11), 196(40), 177(6), and 176(8). Calcd for $C_{14}H_{10}ClF$: C, 72.27; H, 4.33%. Found: C, 71.92; H, 4.30%.

(*E*)-Isomer: ^{1}H NMR δ=5.86 (1H, d, J=30.5 Hz) and 7.3—7.6 (9H, m); ^{13}C NMR δ=107.32 (d, J=10 Hz, Cα), 126.96, 127.31, 127.52, 128.44 (d, J=7 Hz, C_2 and C_6), 128.84, 130.97 (d, J=6 Hz, C_1), 140.38 (C_1'), 140.49 (d, J=2 Hz, C_4), and 144.66 (d, J=313 Hz, C_β); ^{19}F NMR δ=−73.97 (d, J=31 Hz).

(*Z*)-Isomer: ^{1}H NMR δ=6.43 (1H, d, J=12.8 Hz) and 7.3—7.6 (9H, m); ^{13}C NMR (typical signals) δ=106.88 (d, J=28 Hz), 127.16, 127.31, 128.70, and 128.74; ^{19}F NMR δ=−71.32 (d, J=13 Hz).

1-(4-Biphenylyl)-2-phenylacetylene (12): Colorless crystals, mp 165—167 °C (hexane–CH_2Cl_2). ^{1}H NMR δ=7.3—7.6 (14H, m); IR (KBr) 3056, 3032, 1492, 1444, 1406, 1168, 1072, and 1006 cm^{-1}; MS(EI) m/z (rel intensity) 255 (M^++1, 23), 254(M^+, 100), and 252(10). Found: m/z 254.1068. Calcd for $C_{20}H_{14}$: M, 254.1096.

1-Fluoro-2-(methoxymethoxy)-4-phenyl-1-butene (13a): Colorless oil. ^{1}H NMR δ=2.57 (2H, m), 2.82 (2H, m), 3.38 (3H, s), 4.78 (2H, s), 6.83 (1H, d, J=81.2 Hz), and 7.15—7.35 (5H, m); ^{13}C NMR δ=28.84, 32.69 (d, J=2 Hz), 55.75, 95.12 (d, J=1 Hz), 125.98, 128.30, 128.38, 137.06 (d, J=235 Hz), 141.23, and 145.96 (d, J=28 Hz); ^{19}F NMR δ=−175.03 (dt, J=81 and 5 Hz); IR (neat) 2932, 1456, 1232, 1150, 1114, 1086, and 1028 cm^{-1}; MS(EI) m/z (rel intensity) 210 (M^+, 0.2), 178(62), 150(11), 136(16), 117(11), 105(37), and 91(100). Found: m/z 210.1058. Calcd for $C_{12}H_{15}FO_2$: M, 210.1056.

2-(*t*-Butyldimethylsilyloxy)-1-fluoro-4-phenyl-1-butene (13b): Colorless oil. IR (neat) 2932, 1692, 1474, 1348, 1256, 1208, 1100, and 1012 cm^{-1}; MS(CI) m/z (rel intensity) 281 (M^+1, 1), 280 (M^+, 0.3), 265(8), 223(61), 155(14), 129(100), and 107(15). Found: m/z 280.1369. Calcd for $C_{16}H_{25}FOSi$: M, 280.1659.

(*E*)-Isomer: ^{1}H NMR (typical signals) δ=0.14 (6H, s), 0.95 (9H, s), and 6.61 (1H, d, J=82.6 Hz); ^{19}F NMR δ=−173.23 (dt, J=82 and 5 Hz).

(*Z*)-Isomer: ^{1}H NMR δ=0.18 (6H, d, J=1.8 Hz), 0.98 (9H, s), 2.14 (2H, m), 2.78 (2H, m), 6.18 (1H, d, J=79.0 Hz), and 7.15—7.35 (5H, m); ^{13}C NMR δ=−4.71 (d, J=4 Hz), 18.26, 25.70, 32.99 (d, J=3 Hz), 33.15 (d, J=2 Hz), 125.98, 128.36, 128.37, 133.23 (d, J=244 Hz), 137.28 (d, J=5 Hz), and 141.32; ^{19}F NMR δ=−160.79 (dm, J=79 Hz).

1-Chloro-1-fluoro-2-(methoxymethoxy)-4-phenylbutane (14a): Colorless oil. IR (neat) 3060, 3028, 2952, 2824, 1498, 1456, 1214, 1150, 1106, and 1032 cm^{-1}; MS(CI) m/z (rel intensity) 246 [M^+(^{35}Cl), 0.2], 215(20), 201(29), 185(13), 179(13), 149(52), 147(66), 129(28), and 105(100). Found: m/z 246.0794. Calcd for $C_{12}H_{16}{}^{35}ClFO_2$: M, 246.0823.

Major Isomer: ^{1}H NMR δ=2.02 (2H, m), 2.67—2.87 (2H, m), 3.44 (3H, s), 3.66—3.82 (1H, m), 4.71 (1H, d, J=7.0 Hz), 4.81 (1H, d, J=7.0 Hz), 6.21 (1H, dd, J=50.3 and 2.4 Hz), 7.1—7.4 (5H, m); ^{13}C NMR δ=31.01, 31.05 (d, J=2 Hz), 56.20, 79.14 (d, J=22 Hz), 97.77 (d, J=1 Hz), 102.10 (d, J=248 Hz), 126.13, 128.37, 128.53, and 141.06; ^{19}F NMR δ=−146.88 (dd, J=50.3 and 16.2 Hz).

Minor Isomer: ^{1}H NMR δ=2.02 (2H, m), 2.67—2.87 (2H, m), 3.45 (3H, s), 3.66—3.82 (1H, m), 4.71 (1H, d, J=7.0 Hz), 4.78 (1H, d, J=7.0 Hz), 6.20 (1H, dd, J=49.7 and 4.8 Hz), and 7.1—7.4 (5H, m); ^{13}C NMR δ=30.44 (d, J=4 Hz), 31.24, 56.00, 79.92 (d, J=21 Hz), 97.53 (d, J=1 Hz), 102.69 (d, J=246 Hz),

126.15, 128.37, 128.53, and 141.13; ^{19}F NMR δ=−142.08 (dd, *J*=49.5 and 8.1 Hz).

2-(*t*-Butyldimethylsilyloxy)-1-chloro-1-fluoro-4-phenylbutane (14b): (1:1 Diastereomer mixture) Colorless oil. ^{1}H NMR δ=0.10 (3H of one isomer, d, *J*=1.2 Hz), 0.12 (3H of one isomer and 6H of another, s), 0.93 (9H of one isomer, s), 0.94 (9H of another, s), 1.92 (2H, m), 2.70 (2H, m), 3.96 (1H, m), 5.93 (1H of one isomer, dd, *J*=50.7 and 6.1 Hz), 6.00 (1H of another, dd, *J*=50.0 and 3.4 Hz), and 7.15—7.35 (5H, m); ^{13}C NMR δ=−4.74 (d, *J*=1 Hz), −4.62 (d, *J*=5 Hz), −4.57 (d, *J*=2 Hz), −4.45 (d, *J*=2 Hz), 18.18 (both), 25.76, 25.78, 30.18, 31.06, 33.82 (d, *J*=21 Hz), 34.20 (d, *J*=3 Hz), 74.29 (d, *J*=22 Hz), 74.38 (d, *J*=21 Hz), 103.00 (d, *J*=247 Hz), 103.39(d, *J*=247 Hz), 126.02, 126.06, 128.31 (both), 128.48, 128.49, 141.46, and 141.54; ^{19}F NMR δ=−142.38 (dd, *J*=50 and 12 Hz) and −140.21 (dd, *J*=50 and 10 Hz); IR (neat) 3060, 3028, 2924, 2856, 1678, 1602, 1496, 1454, 1282, and 1074 cm^{-1}; MS(CI) *m*/*z* (rel intensity) 317 [M$^+$(^{35}Cl)+1, 2], 281(5), 261(7), 233(40), 165(23), 149(70), and 129(100). Found: *m*/*z* 317.1537. Calcd for $C_{16}H_{27}{}^{35}ClFOSi$: M+H, 317.1504.

1,4-Diphenyl-1-fluoro-1-butene (15): Colorless oil. IR (neat) 3060, 3028, 2928, 1678, 1496, and 1284 cm^{-1}; MS(EI) *m*/*z* (rel intensity) 227 (M$^+$+1, 7), 226 (M$^+$, 43), 135(100), 115(60), and 91(40). Found: *m*/*z* 226.1166. Calcd for $C_{16}H_{15}F$: M, 226.1158.

(*Z*)-Isomer: ^{1}H NMR δ=2.62 (2H, m), 2.77 (2H, m), 5.39 (1H, dt, *J*=37.2 and 7.6 Hz), and 7.2—7.5 (10H, m); ^{13}C NMR δ=25.90 (d, *J*=5 Hz), 35.60 (d, *J*=2 Hz), 105.16 (d, *J*=17 Hz), 123.90 (d, *J*=7 Hz), 125.97, 128—129 (4C), 132.64 (d, *J*=29 Hz), 141.52, and 156.94 (d, *J*=247 Hz); ^{19}F NMR δ=−120.57 (d, *J*=37 Hz).

(*E*)-Isomer: ^{1}H NMR δ=2.56 (2H, m), 2.70 (2H, m), 5.36 (1H, dt, *J*=24.1 and 6.9 Hz), and 7.2—7.5 (10H, m); ^{13}C NMR (typical signals) δ=27.98 (d, *J*=8 Hz), 36.26 (d, *J*=2 Hz), and 107.53 (d, *J*=26 Hz); ^{19}F NMR δ=−101.74 (d, *J*=23 Hz).

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