Behaviors of α-Fluorocarbenoids Derived from the Nucleophilic Desulfinylation of α-Chloro-α-fluoroalkyl Sulfoxides

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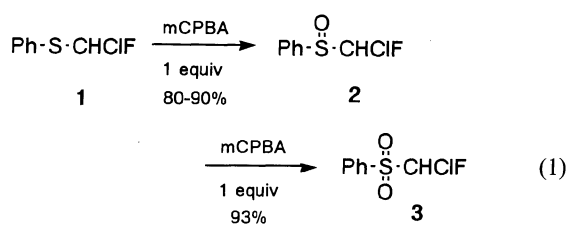
2-Aryl-1-chloro-1-fluoroethyl sulfoxides underwent nucleophilic desulfinylation with PhMgBr to give (*Z*)-fluorostyrene derivatives in a very stereoselective manner (>33:1) via an α-fluorocarbene species. When treated with 3 equiv of PhLi in the presence of *N,N,N',N'*-tetramethylethylenediamine, they similarly formed fluorostyrenes as a stereoisomeric mixture (*E*:*Z*=2:1), but with 1 equiv of PhLi 2-aryl-1-chloro-1-fluoroethanes were the major product. On the other hand, no formation of a fluoroalkene was observed in the desulfinylation of 1-chloro-1-fluoro-4-phenylbutyl sulfoxide with the nucleophiles. In the latter reaction, oxidation and/or phenylation of the intermediate carbene were the main pathways.

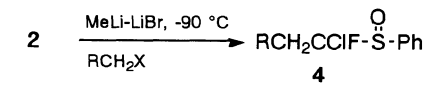
Behaviors of carbenes and carbenoids have been receiving continued attention from both theoretical and practical points of view. Hydrazones, diazirines, diazo compounds, and *gem*-dihalo compounds are commonly-used precursors for such studies.[1] Transformation of carbenoid species into olefins via 1,2-hydrogen migration is one of their important reaction modes.[2] However, molecules of comparatively simple structures have so far been subject to the investigations probably because of the paucity and structural limitations of the available routes to those precursors. We have recently reported that α-chloro-α-fluoroalkyl sulfoxides can serve as a precursor for α-fluoroalkylcarbenoids, which undergo the 1,2-hydrogen shift to form (*Z*)-fluoroolefins.[3] The highly stereoselective formation of (*Z*)-fluoroolefin is quite interesting, because the 1,2-hydrogen migrations of similar halocarbenoids are known to proceed in nonstereoselective manner.[4] From a synthetic point of view for fluoroolefins,[5] that precursor is quite attractive, because numbers of synthetic methods can be available for the preparation of sulfoxides. In this paper, we describe in detail the behaviors of α-fluorocarbenoids generated during the course of desulfinylation of α-chloro-α-fluoroalkyl and α-fluorovinyl sulfoxides with Grignard and organolithium reagents.[6]

Preparation of α-Fluoroalkyl Sulfoxides 4. Our preparation was based on chlorofluoromethyl phenyl sulfide (**1**) readily obtained from thiophenol and dichlorofluoromethane. Oxidation of sulfide **1** with 1 equiv of *m*-chloroperbenzoic acid (mCPBA) gave sulfoxide **2** (diastereomer ratio, 2:1) in good yield, while the use of two equiv of mCPBA led to the formation of sulfone **3** in 93% yield (Eq. 1).[7]



(1)

The sulfoxide **2** was easily lithiated by 1 equiv of MeLi–LiBr at −90 °C in 20 min and treated with reactive alkyl halides (−90 °C, 1 h) to give the corresponding α-chloro-α-fluoroalkyl sulfoxides **4** as a diastereomer mixture (ca. 3:1) in moderate to good yields (Eq. 2 and Table 1). The choice and amount of base employed are critical for this reaction. When MeLi–LiBr was used, only a slight excess amount of the base easily led to the extensive decomposition of the lithiated derivative of **2**, affording methyl phenyl sulfoxide and its further products. Bases such as lithium diisopropylamide (LDA), *n*-BuLi, and PhMgBr were not effective; the first base was too weak to lithiate **2** sufficiently at the low temperatures, while the other two brought about the decomposition of **2**.



(2)

Preparation of α,β-Unsaturated α-Fluoro Sulfoxides 8. Carbenoids are well-known to react with phosphine to form phosphorus ylides. Thus chlorofluoromethyl phenyl sulfide (**1**) was treated with *n*-BuLi in the presence of Ph_3P at −78 °C to give a yellow ylide, which was reacted with 3-phenylpropanal to give α,β-unsaturated α-fluoro sulfide **5d** with low *Z*-selectivity (*E*:*Z*=2:3) in 63% yield (Eq. 3). Use of MeLi–LiBr as a base increased the yield (75%) but decreased the selectivity (*E*:*Z*=1:1). A similar reaction of **1** with 4-biphenylcarbaldehyde gave

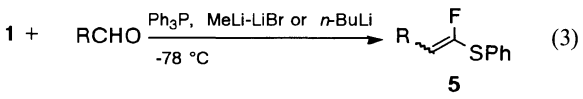
Table 1. Preparation of α-Chloro-α-fluoroalkyl Sulfoxides

	Electrophile	Yield/%[a]
	RCH_2X	**4**
a	4-Ph-$C_6H_4CH_2Br$	57
b	1-$C_{10}H_7CH_2Br$	81
c	$PhCH_2Br$	47
d	$PhCH_2CH_2CH_2I$	73

a) Isolated yield.

α-fluoro sulfide **5a** (*E*:*Z*=1:1) in 80% yield. When Ph_3P was replaced by $(n\text{-Bu})_3P$, the reaction of **1** with 3-phenylpropanal using *n*-BuLi gave a mixture of **5d** (*E*:*Z*=3:2) and α-chloro sulfide **6** (**5d**:**6**=43:10, determined by NMR) in a low yield (28%) (Scheme 1). When MeLi–LiBr was substituted for *n*-BuLi, the reaction afforded predominantly α-bromo sulfide **7** (42%) in addition to the expected **5d** and **6**. This halogen mixing may be ascribed to the increase in basic character of the ylide derived from **1** and $(n\text{-Bu})_3P$. Equilibrium between the α-fluoro ylide leading to **5d** and other halo ylides may be thought to be partially attained via a carbene or bis(tributylphosphonium) ylide.[8]

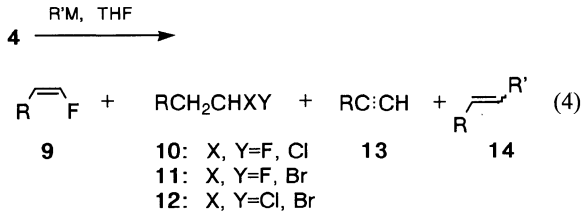
Sulfides **5** were quantitatively oxidized by 1 equiv of mCPBA to give the corresponding sulfoxides **8**.



(3)

Results and Discussion

Nucleophilic Desulfinylation of α-Fluoro Sulfoxides. The reaction of 1-chlorofluoroalkyl sulfoxides with organometallic reagents was carried out under conditions listed in Table 2 (Eq. 4). Treatment of **4a** (3:1 diastereomer mixture) with 1 equiv of PhMgBr gave (*Z*)-1-(4-biphenylyl)-2-fluoroethylene (**9a**; 12%; *E*:*Z*=1:33, estimated by ^{19}F NMR), dihalo compounds (35%, **10a**:**11a**:**12a**=6:10:1), and the starting sulfoxide **4a** (51%). The low conversion would probably be due to the competitive consumption of the Grignard reagent by diphenyl sulfoxide produced during the course of the reaction, because considerable amounts of biphenyl were isolated from the reaction mixture.[9] When 3 equiv of the Grignard reagent were employed in the presence of CuI, **4a** was consumed completely to give the (*Z*)-fluoroolefin **9a** (54%) at the expense of the dihalo compounds (10%). GC-MS analysis of the reaction mixture showed the presence of biphenylylacetylene **13** and diphenyl sulfide in trace amounts.



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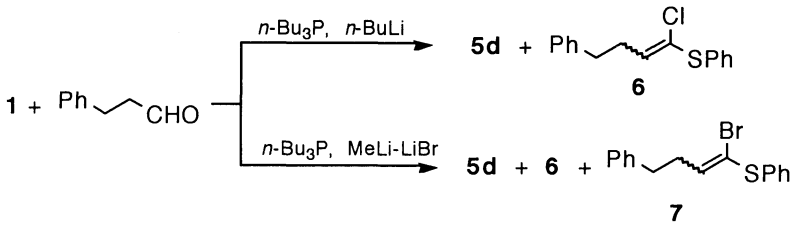
In the reaction of **4a** with PhLi, the product distribution greatly varied according to the conditions employed. Thus, the reaction of **4a** with 1 equiv of PhLi at low temperatures gave predominantly the dihalo



Scheme 1.

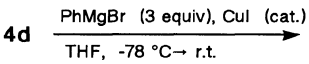
Table 2. Nucleophilic Desulfinylation of α-Chloro-α-fluoroalkyl Sulfoxides **4**

Entry	Substrate	R'M (equiv)	Additive (equiv)	Conditions[a]	Yield/%[b]		
					4	**9**[c]	**10**+**11**+**12**[d]
1	**4a**	PhMgBr (1)	None	A	51	12	35 (6:10:1)
2	**4a**	PhMgBr (1)	CuI (0.1)	A	63	25	10 (6: 9:1)
3	**4a**	PhMgBr (3)	CuI (0.1)	A	—	54 (1:33)	10 (1: 2:1)
4	**4a**	PhLi (1)[e]	None	B	44	Trace	27 (8: 1:0)
5	**4a**	PhLi (1)[e]	None	C	36	Trace	51 (9: 1:0)
6	**4a**	PhLi (3)[e]	None	A	—	16 (1:4)	31 (1: 0:0)
7	**4a**	PhLi (3)[e]	TMEDA (10)	A	—	42 (4:1)	—
8[f]	**4a**	*n*-BuLi (1)	None	C	42	Trace	27 (1: 0:0)
9[g]	**4a**	Ph_2CuLi (3)	None	A	28	—	—
10	**4b**	PhMgBr (3)	CuI (0.1)	A	—	26 (1:50)	—
11	**4c**	PhMgBr (3)	CuI (0.1)	A	—	11 (1:33)	—
12[f]	**4d**	PhMgBr (3)	CuI (0.1)	A	—	Trace	8 (0: 1:0)
13[f]	**4d**	PhLi (3)[e]	None	A	13	—	17 (1: 0:0)

a) A: −78 °C → r.t.; B: −78 °C → −30 °C; C: −78 °C. b) Isolated yield. c) The *E*:*Z* ratio is shown in the parentheses. d) Combined yield. e) The PhLi solution (purchased from Kanto Chem. Co.) contains LiBr. f) See text. g) Sulfoxide **8a** (*E*:*Z*=7:5) was obtained in 55% yield.

derivatives **10a** and **11a**, although considerable amounts of the starting **4a** was recovered intact. On the other hand, the use of 3 equiv PhLi led to entire disappearance of **4a** to give **9a** and **10a** in respective yields of 16 and 31%. When this reaction was carried out in the presence of *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA), fluoroolefin **9a** was the predominant product. It should be noted that the fluoroolefin was obtained as an isomeric mixture under these conditions and the halogen-mixing products **10a** and **11a** were not detected by GC-MS analysis. In the case of *n*-BuLi, a regio- and stereoisomeric mixture of 1-(4-biphenylyl)hexenes **14** was obtained in addition to **10a**. Diethylzinc and lithium diphenylcuprate were not effecive for the desulfinylation of **4a**. No reaction was observed with the former reagent, while the latter led to the elimination of HCl from **4a** to afford α,β-unsaturated α-fluoro sulfoxide **8a** (*E*:*Z*=7:5) in 55% yield.

The reactions of **4d** with PhMgBr and PhLi are worthy to note. When **4d** was treated with 3 equiv of PhMgBr in the presence of CuI, fluoroolefin **9d** was not formed in any appreciable amounts. GC-MS analysis of the crude product mixture revealed the presence of bromofluoro derivative **11d**, 1,4-diphenylbutene (**15**), 1,4-diphenyl-1-butanone (**16**), chlorofluoro derivative **10d**, 1,4-diphenyl-1-butanol (**17**), and ethyl 4-phenylbutanoate (**18**), from which the former three components were isolated in respective yields of 8, 13, and 13%. On the other hand, the reaction of **4d** with PhLi (3 equiv) afforded **10d**, 1-fluoro-1,4-diphenylbutane (**19**), **16**, **18**, and 1,1,4-triphenyl-1-butene (**20**) in respective yields of 17, 10, 4, 12, and 24%. Determination of products **16**, **17**, **18**, **19**, and **20** was made by comparison with authentic samples obtained from 4-phenylbutanoic acid (see Experimental). The formation of **16**, **17**, and **18** is very interesting and will be discussed later.



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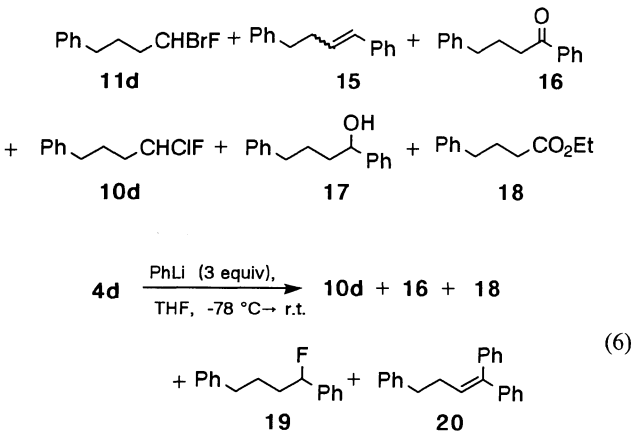
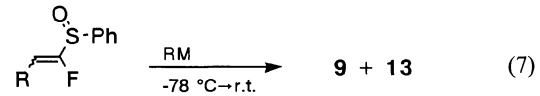


(6)

Before discussing the reaction pathways, the desulfinylation of α,β-unsaturated α-fluoro sulfoxide **8** would be better to be described, because **8a** was obtained in a particular case (lithium dimethylcuprate). Treatment of **8a** (*E*:*Z*=10:1) with 1 equiv of PhMgBr gave (*Z*)-fluoroolefin **9a** (8%, *E*:*Z*=1:8) almost stereospecifically[10] and 4-biphenylylacetylene (**13a**; 6%), the starting **8a** being largely recovered (Table 3). However, the use of excess PhMgBr led to a quantitative yield of **13a**. The same tendency was observed in the reactions with organolithiums, although the stereospecificity in the formation of **9a** was lost. When 3 equiv of *t*-BuLi were used, *t*-butylated compound **21** was obtained in 18% yield.[11]



(7)

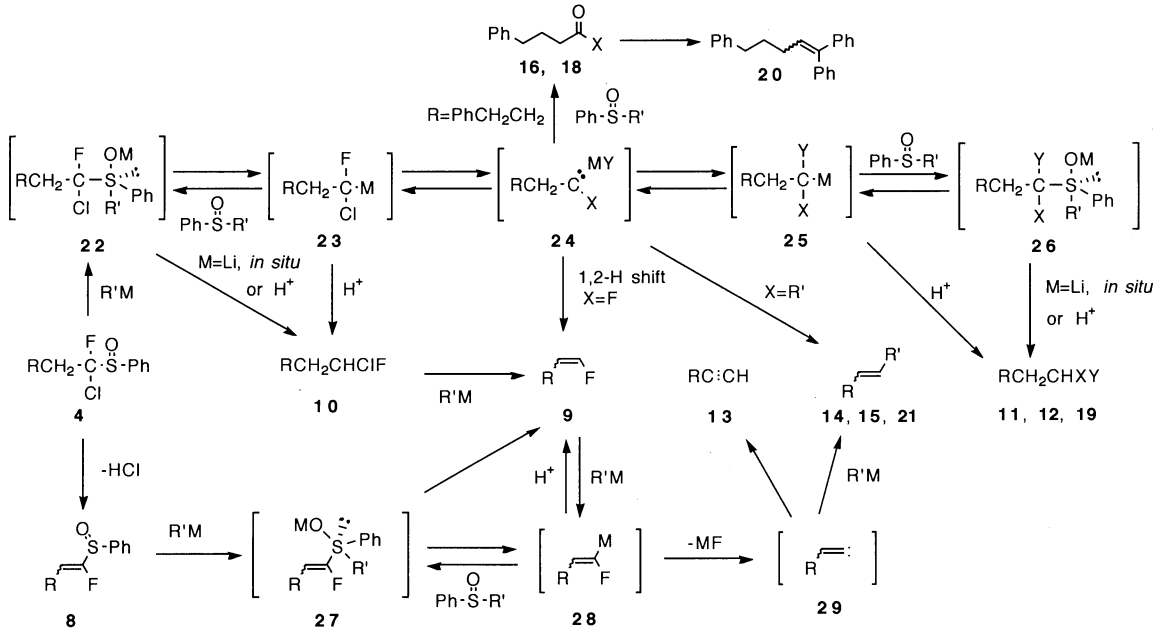
8a: R=4-Ph-C_6H_4-
8d: R=$PhCH_2CH_2$-

Reaction Pathways. Nucleophilic attack on the sulfur atom of **4** is an initial step in the main pathway of desulfinylation. The pathway via elimination of HCl from **4** leading to **8a** is ruled out, because the reaction of

Table 3. Nucleophilic Desulfinylation of α,β-Unsaturated α-Fluoro Sulfoxide **8**

Entry	**8**	R′M (equiv)	Additive (equiv)	Yield/%[a]		
				8	**9**[b]	**13**
1	**a**	PhMgBr (1)	CuI (0.1)	79 (10:1)	8[c] (1:8)	6[c]
2	**a**	PhMgBr (2)	CuI (0.1)	—	—	97
3	**a**	PhMgBr (3)	CuI (0.1)	—	—	98
4	**a**	PhLi (1)	None	43 (6:1)	28[c] (4:5)	28[c]
5	**a**	PhLi (3)	None	—	—	82
6	**a**	*t*-BuLi (1)	None	32 (6:1)	53[c] (5:4)	10[c]
7[d]	**a**	*t*-BuLi (3)	None	—	27[c] (1:1)	51[c]
8	**d**	PhMgBr (2)	CuI (0.1)	—	—	88
9	**d**	PhLi (3)	None	—	31[c] (3:2)	55[c]

a) Isolated yield. b) The *E*:*Z* ratios are given in the parentheses. c) Yields were calculated based on the NMR analyses of the chromatographed fractions. d) 1-(4-Biphenylyl)-3,3-dimethyl-1-butene (**21**) was obtained in 18% yield.



Scheme 2.

α,β-unsaturated α-fluoro sulfoxide **8a** gave the acetylene **13a** predominantly. The observed product variation in the reactions of **4** with PhMgBr or organolithiums can be rationalized well by assuming an equilibrium between the carbenoid and sulfurane formed by an initial attack of nucleophile (Scheme 2).

First, we will discuss about the reaction of **4** with the Grignard reagent. Contribution of carbenoid species **23**, **24**, and **25** should be important, because the mixing of halogens was significantly observed. Presence of CuI favored the formation of carbene species **24**, thus leading to **9** via the 1,2-hydrogen shift. The pathways from dihalo derivatives **10** and **11** to fluoroolefin **9** are thought to be unimportant, since the stereochemistry of **9** was very high. This high *Z*-stereoselectivity could be attributed to a sterically small effect of fluorine atom on the transition state of 1,2-hydrogen migration of a singlet carbene.[12]

In the desulfinylation with organolithiums, chlorofluoro derivative **10** would be formed in situ from sulfurane **22** or carbanionoid **23**, because no deuterium incorporation was observed when the reaction of **4a** with PhLi (1 equiv) was quenched by the addition of deuterium oxide.[10] In that case, the equilibrium worked less and the halogen mixing became insufficient. Treatment of chlorofluoro derivative **10a** with 3 equiv of PhLi in the presence of TMEDA gave a stereoisomeric mixture of **9a** (*E*:*Z*=5:1) and acetylene **13a** in respective yields of 13 and 14%, the starting **10a** being recovered in 69% yield. Therefore, the dihalo compounds in situ generated should be converted only partially into fluoroolefin **9** even in the presence of excess PhLi. Conversion of carbenoid **24** into fluoroolefin **9** might be assisted by excess of PhLi which strips out diphenyl sulfoxide from the carbenoid intermediates.

Incorporation of butyl group giving **14** observed in the reaction of **4a** with *n*-BuLi is thought to occur mainly via the carbenoid **24**. Treatment of chlorofluoro derivative **10a** with 2 equiv of *n*-BuLi under the usual conditions gave a mixture of fluoroolefin **9a** (*E*:*Z*=4:1), 4-biphenylylacetylene (**13a**), 1-(4-biphenylyl)hexenes **14**, and the starting material **1a** in respective yields of 20, 7, 18, and 54%. Marked difference in the fates of carbenoid **24** derived from the reactions with PhLi and *n*-BuLi may be ascribed to the stronger nucleophilicity and higher aggregation state of the latter reagent.[13] The short-lived carbenoid **24** generated by *n*-BuLi would be more easily trapped by aggregated *n*-BuLi than **24** generated by PhLi.

Formation of oxygen-containing compounds in the reactions of **4d** is quite interesting and it may be informative of the intermediate species involved in the desulfinylation. In this case, the 1,2-hydrogen shift of the carbene species is thought to be slower than in the cases of **4a**—**c**, because hydrogen atoms are not activated by hyperconjugation in the former case. Thus, the carbene species would become more susceptible to the attack by nucleophile such as bromide, phenyl anion or sulfoxide present in the reaction mixture. Compounds **16** and **18** are thought to be derived from the oxidation of carbene species with diphenyl sulfoxide, because considerable amounts of diphenyl sulfide were formed in these reactions.[14] Incorporation of the ethoxy group giving **18** is difficult to understand. It may arise from esterification of the corresponding acyl halide during the work-up. The high *Z*-stereoselectivity of fluoroolefin **9**

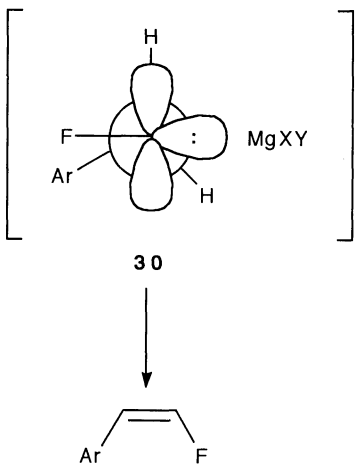


Fig. 1. Z-Preference in the formation of fluoroolefins.

would be understood by taking the metal coordination into account. In the reactions with the Grignard reagent, steric bulkiness around the sp^2-hydridized orbital in carbenoid **30** would be greatly enhanced by the coordination of magnesium halide (Fig. 1).[15]

Experimental

Melting points are uncorrected. Distillation was carried out by using a Kugelrohr apparatus. 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 $CFCl_3$ 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. Dichloromethane, pentane and toluene were distilled from CaH_2 and stored over 4 Å molecular sieves. 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.

Chlorofluoromethyl Phenyl Sulfide (1): Thiophenol (2.0 ml, 20 mmol), benzyltrimethylammonium chloride (0.2 g), NaOH (5 g), benzene (20 ml), and water (10 ml) were placed in a 100 ml stainless steel autoclave. Dichlorofluoromethane was introduced into the vessel with vigorous stirring for 10 min. During that period, the temperature rose to about 50 °C and the pressure became 3—5 kg cm^{-2}. After stirring for 4 h, the vessel was opened and the contents were poured into water. The mixture was extracted with ether and the ethereal extract was washed five times with a cold 5% NaOH solution, dried over Na_2SO_4 and concentrated in vacuo. Distillation of the residue gave 2.47 g (70%) of **1** as a pale yellow oil. Oven temp 37—38 °C/0.2 mmHg#; ^1H NMR δ=7.03 (1H, d, J=55.8 Hz), 7.38 (3H, m), and 7.58 (2H, m); IR (neat) 3030, 1456, 1435, 1290, and 1185 cm^{-1}. Calcd for C_7H_6ClFS: C, 47.60; H, 3.42%. Found: C, 47.77; H, 3.31%.

Chlorofluoromethyl Phenyl Sulfoxide (2): mCPBA (3.61 g; 70% purity; 14.6 mmol) was added to a stirred solution of **1** (2.030 g, 13 mmol) in CH_2Cl_2 (50 ml) at 0 °C. After the disappearance of **1** (overnight), the reaction was quenched by adding several drops of 1 M aq solution of $Na_2S_2O_3$ (1 M=1 mol dm^{-3}). The solvent was evaporated and 50 ml of benzene was added to a white residual solid. The suspension was filtered and the white solid was washed twice with 30 ml of bnzene. The combined benzene solution was washed with 0.5 M NaOH solution (5 times) and brine, dried over Na_2SO_4, and evaporated. The residue was chromatographed on silica gel (hexane–CH_2Cl_2) to give 2.453 g (12.7 mmol, 98%) of crude **2** as a pale yellow oil. Distillation of the oil through a Kugelrohr apparatus gave 2.15 g (86%) of pure **2** (2:1 diastereomer mixture), which solidified below 0 °C. Colorless oil, oven temp 65—68 °C/0.2 mmHg. ^1H NMR δ=6.62 (1H of minor isomer, d, J=50.4 Hz), 6.65 (1H of major isomer, d, J=50.0 Hz), 7.57 (3H, m), and 7.74 (2H, m); ^{13}C NMR major isomer: δ=110.44 (d, J=288 Hz), 125.67(d, J=1 Hz), 129.33, 132.79, and 137.27 (d, J=5 Hz); minor isomer: δ=108.91 (d, J=287 Hz), 126.15(d, J=1 Hz), 129.29, 132.95, and 137.33 (d, J=3 Hz); IR (neat) 3030, 1470, 1440, 1080, and 1055 cm^{-1}.

Chlorofluoromethyl Phenyl Sulfone (3): Colorless oil, oven temp 85—87 °C/0.2 mmHg. ^1H NMR δ=6.61 (1H, d, J=48.8 Hz), 7.65 (2H, m), 7.80 (1H, m), and 8.01 (2H, m); ^{13}C NMR δ=104.46 (d, J=284 Hz), 129.54, 130.72 (d, J=1 Hz), 132.02, and 135.77; IR (neat) 3040, 1575, 1440, 1340, 1250, 1240, 1080, and 1060 cm^{-1}. Calcd for $C_7H_6ClFO_2S$: C, 40.30; H, 2.90%. Found: C, 40.49; H, 2.76%.

Alkylation of 2. Typical Procedure for 2-(4-Biphenylyl)-1-chloro-1-fluoroethyl Phenyl Sulfoxide (4a): An ethereal solution of MeLi–LiBr (1.2 M; 0.83 ml, 1 mmol) was slowly added to a solution of **2** (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-(bromomethyl)biphenyl (248 mg, 1 mmol) was slowly added. The resulting mixture was stirred at −90 °C for 30 min, allowed to warm to room temperature, quenched 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 **4a** (diastereomer mixture 3:1) as colorless crystals; mp 86—88 °C (hexane–CH_2Cl_2). ^1H NMR δ=3.43 (1H of minor isomer, dd, J=26.6 and 14.8 Hz), 3.66 (2H of major isomer, m), 3.91 (1H of minor isomer, J=18.0 and 14.8 Hz), and 7.3—7.9 (14H, m); ^{13}C NMR major isomer: δ=41.39 (d, J=21 Hz), 120.20 (d, J=305 Hz), 127.06, 127.19, 127.40 (d, J=1 Hz), 127.45, 127.78, 128.84, 130.00, 131.57, 132.73, 136.90 (d, J=3 Hz), 140.46, and 140.92; minor isomer: (typical signals) δ=42.49 (d, J=19 Hz), 131.45, 132.57, 137.45, 140.07, and 140.56; ^{19}F NMR δ=−112.63 (minor isomer, dd, J=27 and 18 Hz) and −114.69 (major isomer, dd, J=23 and 11 Hz); IR (KBr) 1488, 1450, 1316, 1090, and 1060 cm^{-1}; MS

1 mmHg≅133.322 Pa.

(CI) m/z (rel intensity) 359 [$M^+(^{35}Cl)+1,4$], 323 (3), 306 (4), 275 (9), 250 (9), 233 (100), 210 (10), 197 (33), and 167 (22). Calcd for $C_{20}H_{16}ClFOS$: C, 61.85; H, 5.15%. Found: C, 61.93; H, 5.14%.

1-Chloro-1-fluoro-2-(1-naphthyl)ethyl Phenyl Sulfoxide (4b): Colorless crystals, mp 70—72 °C (hexane–CH_2Cl_2). ^1H NMR δ=3.80 (1H of minor isomer, dd, J=25.3 and 15.5 Hz), 3.91 (1H of major isomer, dd, J=29.9 and 15.0 Hz), 4.08 (1H of major isomer, dd, J=15.0 and 7.8 Hz), 4.35 (1H of minor isomer, dd, J=16.8 and 15.3 Hz), and 7.3—7.9 (12H, m); ^{19}F NMR δ=−110.03 (minor isomer, dd, J=25 and 17 Hz) and −113.17 (major isomer, dd, J=30 and 8 Hz); IR (KBr) 1512, 1446, 1398, 1318, 1206, 1118, 1092, 1060, 1044, and 1018 cm^{-1}; MS (EI) m/z (rel intensity) 332 [$M^+(^{35}Cl)$, 2], 206 (34), 172 (18), 171 (100), 170 (21), and 126 (23). Calcd for $C_{18}H_{14}ClFS$: C, 64.96; H, 4.24%. Found: C, 65.13; H, 4.41%.

1-Chloro-1-fluoro-2-phenylethyl Phenyl Sulfoxide (4c): Colorless solid, mp 53—55 °C. ^1H NMR δ=3.38 (1H of minor isomer, dd, J=26.5 and 15.0 Hz), 3.62 (2H of major isomer, m), 3.86 (1H of minor isomer, dd, J=18.0 and 15.0 Hz), and 7.3—7.9(10H, m); ^{19}F NMR δ=−126.64 (minor isomer, dd, J=27 and 18 Hz) and −114.73 (major isomer, dd, J=22 and 12 Hz); IR (neat) 3064, 3036, 2244, 1498, 1448, 1090, and 1032 cm^{-1}; MS (CI) m/z (rel intensity) 283 [$M^+(^{35}Cl)+1,3$], 265 (2), 231 (1), 229 (3), 199 (17), 157 (38), 126 (100), and 109 (36). Found: m/z 283.0348. Calcd for $C_{14}H_{12}{}^{35}ClFOS+H$: M+H, 283.0360.

1-Chloro-1-fluoro-4-phenylbutyl Phenyl Sulfoxide (4d): Colorless crystals, mp 41—43 °C (hexane–CH_2Cl_2). ^1H NMR δ=2.03 (2H, m), 2.25 (2H, m), 2.68 (2H, t, J=7.5 Hz), and 7.2—7.8(10H, m); ^{13}C NMR major isomer: δ=24.59 (d, J=4 Hz), 34.80, 35.40 (d, J=19 Hz), 121.45 (d, J=303 Hz), 126.04, 127.06 (d, J=1 Hz), 128.20, 128.35, 128.61, 132.49, 136.92 (d, J=3.2 Hz), and 140.61; minor isomer: (typical signals) δ=24.54 (d, J=3 Hz), 34.85, 36.00 (d, J=19 Hz), 122.95 (d, J=286 Hz), 126.46 (d, J=2 Hz), 132.38, and 137.41 (d, J=2 Hz); ^{19}F NMR δ=−111.63 (minor isomer, dd, J=27 and 12 Hz) and −114.11 (major isomer, dd, J=18 and 17 Hz); IR (KBr) 3056, 3024, 1480, 1086, 1058, and 1042 cm^{-1}; MS (CI) m/z (rel intensity) 313 [$M^+(^{37}Cl)+1$, 10], 311 [$M^+(^{35}Cl)+1$, 28], 255 (37), 225 (15), 207 (17), 185 (27), 177 (55), 165 (100), and 155 (74). Calcd for $C_{16}H_{16}ClFOS$: C, 61.85; H, 5.15%. Found: C, 61.93; H, 5.14%.

1-Fluoro-2-(4-biphenylyl)-1-(phenylthio)ethylene (5a): To a solution of **1** (1.767 g, 10 mmol) and Ph_3P (3.147 g, 12 mmol) in THF (40 ml) was added an ethereal solution of MeLi–LiBr (0.5 M; 19 ml, 10 mmol) at −78 °C over 10 min. After 1 h a solution of 4-biphenylcarbaldehyde (2.184 g, 12 mmol) in THF (20 ml) was slowly added at the same temperature and the mixture was stirred for additional 30 min. The reaction mixture was then allowed to warm to room temperature and quenched with a saturated NH_4Cl solution. The 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) to give 2.456 g (8.0 mmol, 80%) of **5a** (E:Z=1:1) as a pale yellow solid. Mp 60 °C (hexane–CH_2Cl_2, (E)-isomer). ^1H NMR δ=6.29 (1H of (E)-isomer, d, J=32.7 Hz), 6.75 (1H of (Z)-isomer, d, J=16.5 Hz), and 7.2—7.6 (14H, m); IR (neat) 1630, 1580, 1480, 1442, 1408, 1304, 1046, and 1030 cm^{-1}; MS (EI) m/z (rel intensity) 307 (M^++1, 27), 306 (M^+, 100), 284 (8), 261 (24), 228 (7), 196 (24), 165 (25), and 121 (6).

1-Fluoro-4-phenyl-1-phenylthio-1-butene (5d): Pale yellow oil (E:Z=1:1). ^1H NMR δ=2.55 (2H, m), 2.71 (2H, m), 5.44 (1H of (E)-isomer, dt, J=30.2 and 7.6 Hz), 5.74 (1H of (Z)-isomer, dt, J=14.3 and 7.6 Hz), and 7.2—7.4 (10H, m); IR (neat) 3060, 2924, 1648, 1584, 1480, 1438, 1090, 1072, 1026, and 1000 cm^{-1}; MS (EI) m/z (rel intensity) 258 (M^+, 25), 238 (4), 167 (100), 147 (21), 134 (13), and 109 (16).

1-Chloro-4-phenyl-1-phenylthio-1-butene (6): ^1H NMR δ=2.49—2.80 (4H, m), 6.27 (1H, t, J=7.0 Hz), and 7.2—7.3 (10H, m); MS (EI) m/z (rel intensity) 276 [$M^+(^{37}Cl)$, 10], 274 [$M^+(^{35}Cl)$, 27], 262 (4), 238 (49), 183 (100), 167 (12), 147 (46), 125 (9), and 109 (7).

1-Bromo-4-phenyl-1-phenylthio-1-butene (7): ^1H NMR =2.22—2.96 (2H, m), 6.45 (1H of (Z)-isomer, t, J=7.0 Hz), 6.55 (1H of (E)-isomer, t, J=7.3 Hz), and 7.1—7.5 (10H, m); MS (EI) m/z (rel intensity) 320 [$M^+(^{81}Br)$, 30], 318 [$M^+(^{79}Br)$, 26], 238 (2), 227 (96), 205 (12), 147 (100), 129 (55), and 103 (32).

1-Fluoro-2-(4-biphenylyl)vinyl Phenyl Sulfoxide (8a): Colorless crystals, 143—146 °C (hexane–CH_2Cl_2, (E)-isomer). ^1H NMR δ=6.69 (1H of (E)-isomer, d, J=37.2 Hz), 6.86 (1H of (Z)-isomer, d, J=17.4 Hz), and 7.3—8.0 (14H, m); ^{13}C NMR (E)-isomer: δ=111.66, 125.36, 127.02, 127.46, 127.80, 128.88, 129.51, 129.90, 130.00, 132.08, 140.10, 140.36 (d, J=35 Hz), 142.06 (d, J=3 Hz), and 158.64 (d, J=319 Hz); ^{19}F NMR δ=−122.77((E)-isomer, d, J=38 Hz); IR (KBr) 1490, 1446, 1410, 1312, 1102, 1088, 1042, and 1008 cm^{-1}; MS (CI) m/z (rel intensity) 323 (M^++1, 90), 322 (M^+, 2), 275 (10), 229 (16), 199 (17), 179 (20), 153 (7), and 111 (100). Calcd for $C_{20}H_{15}FOS$: C, 74.51; H, 4.69%. Found: C, 74.34; H, 4.80%.

1-Fluoro-4-phenyl-1-butenyl Phenyl Sulfoxide (8d): Colorless crystals, mp 39—42 °C (hexane–CH_2Cl_2, E:Z=1:1). ^1H NMR δ=2.55 (2H of (E)-isomer, m), 2.71—2.95 (2H of (E)-isomer and 4H of (Z)-isomer, m), 5.18 (1H of (E)-isomer, dt, J=34.5 and 7.6 Hz), 5.74 (1H of (Z)-isomer, dt, J=17.1 and 7.0 Hz), and 7.1—7.6 (10H, m); ^{19}F NMR δ=−126.03 ((Z)-isomer, d, J=17 Hz) and −127.92 ((E)-isomer, d, J=34.4 Hz); IR (KBr) 1664, 1496, 1478, 1446, 1304, 1198, 1112, 1102, 1086, 1070, 1048, and 1022 cm^{-1}; MS (EI) m/z (rel intensity) 274 (M^+, 2), 257 (10), 226 (8), 206 (9), 179 (5), 167 (61), 147 (100), 135 (70), and 109 (45). Calcd for $C_{16}H_{15}FOS$: C, 70.05; H, 5.51%. Found: C, 69.82; H, 5.63%.

Nucleophilic Desulfinylation. General Procedure: To a stirred solution of sulfoxide **4** or **8** (0.3 mmol) and an appropriate additive in THF (10 ml) cooled to −78 °C by a Dry Ice–acetone bath was added slowly a solution of an organometallic reagent over 5 min. The mixture was stirred for 2 h and then the cooling bath was removed. After the temperature of the mixture reached up to 10 °C, a saturated NH_4Cl solution was added. The 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).

4-(2-Fluorovinyl)biphenyl (9a): Colorless crystals, mp 66—67 °C (hexane–CH_2Cl_2, (Z)-isomer). ^1H NMR δ=5.65 (1H of (Z)-isomer, dd, J=44.7 and 5.3 Hz), 6.43 (1H of (E)-isomer, dd, J=19.2 and 11.3 Hz), 6.88 (1H of (Z)-isomer, dd, J=82.6 and 5.3 Hz), 7.22 (1H of (E)-isomer, dd, J=83.3 and 11.3 Hz), and 7.3—7.6 (9H, m); ^{13}C NMR (E)-isomer: δ=113.50 (d, J=17 Hz, Cα), 126.52 (d, J=3 Hz, C3 and C5), 126.88, 127.37, 127.42, 128.80, 131.64 (d, J=12 Hz, C4), 140.31 (d, J=2 Hz, C1), 140.50 (C1′), and 150.19 (d, J=259 Hz, Cβ); (Z)-isomer: δ=110.44 (d, J=1 Hz), 126.96, 127.14, 127.37, 128.78, 129.23 (d, J=7 Hz, C3

and C5), 131.62 (d, J=1 Hz, C4), 140.20 (d, J=3 Hz, C1), 140.60 (C1′), and 148.35 (d, J=271 Hz, Cα); ^{19}F NMR δ=−122.23 ((*Z*)-isomer, dd, J=83 and 45 Hz) and −130.03 ((*E*)-isomer, dd, J=83 and 19 Hz); IR (KBr) 3050, 1664, 1488, 1410, 1234, 1026, and 1014 cm^{-1}; MS (EI) m/z (rel intensity) 199 (M^++1, 16), 198 (M^+, 100), 197 (7), 196 (9), 183 (3), and 178 (3). Calcd for $C_{14}H_{11}F$:C, 84.82; H, 5.59%. Found: C, 84.45; H, 5.67%.

1-(2-Fluorovinyl)naphthalene (9b): Yellow oil. ^{1}H NMR δ=6.31 (1H of (*Z*)-isomer, dd, J=42.4 and 5.5 Hz), 6.89 (1H of (*Z*)-isomer, dd, J=83.3 and 5.5 Hz), 7.15 (2H of (*E*)-isomer, m), and 7.4—8.0 (12H, m); ^{19}F NMR δ=−123.62 ((*Z*)-isomer, dd, J=83 and 43 Hz) and −124.20 ((*E*)-isomer, dd, J=86 and 16 Hz); IR (neat) 3056, 1656, 1592, 1510, 1230, 1168, 1102, 1084, and 1034 cm^{-1}; MS (EI) m/z (rel intensity) 173 (M^++1, 13), 172 (100), 171 (95), 170 (40), and 152 (29). Found: m/z 172.0693. Calcd for $C_{12}H_9F$: M, 172.0688.

(2-Fluorovinyl)benzene (9c): ^{19}F NMR δ=−122.74 ((*Z*)-isomer, dd, J=84 and 42 Hz) and δ=−130.51 ((*E*)-isomer, dd, J=83 and 19 Hz); Lit,[16] (*Z*)-isomer: −123.0 (J=79.5 and 44 Hz); (*Z*)-isomer: −130.5 (J=79.8 and 17.9 Hz).

1-Fluoro-4-phenyl-1-butene (9d): ^{1}H NMR (*E*)-isomer: δ=2.22 (2H, qt, J=7.4 and 1.8 Hz), 2.67 (2H, t, J=7.4 Hz), 5.37 (1H, ddt, J=18.9, 11.0, and 7.6 Hz), 6.48 (1H, ddt, J=85.8, 11.0, and 1.8 Hz), and 7.15—7.40 (5H, m); (*Z*)-isomer: δ=2.44 (2H, m), 2.70 (2H, t, J=7.6 Hz), 4.75 (1H, dtd, J=43.2, 7.6, and 4.9 Hz), 6.43 (1H, ddt, J=85.8, 4.9, and ca. 1 Hz), and 7.15—7.40 (5H, m); ^{19}F NMR δ=−130.33 ((*E*)-isomer, dd, J=85 and 19 Hz) and δ=−130.63 ((*Z*)-isomer, dd, J=86 and 43 Hz)

2-(4-Biphenylyl)-1-chloro-1-fluoroethane (10a): Colorless crystals, mp 72—73 °C (hexane–CH_2Cl_2). ^{1}H NMR δ=3.41 (2H, m), 6.30 (1H, ddd, J=50.7, 6.1, and 4.9 Hz), and 7.3—7.6 (9H, m); ^{13}C NMR δ=45.45 (d, J=21 Hz), 102.02 (d, J=244 Hz), 127.06, 127.37, 127.39, 128.78, 130.18, 132.79 (d, J=4 Hz), 140.57, and 140.59; ^{19}F NMR δ=−130.52 (ddd, J=51, 22, and 17 Hz); IR (KBr) 2920, 1490, 1410, 1292, 1066, and 1016 cm^{-1}; MS (EI) m/z (rel intensity) 236 [M^+(^{37}Cl), 19], 234 [M^+(^{35}Cl), 53], 198 (6), 178 (4), 167 (100), and 152 (7). Calcd for $C_{14}H_{12}ClF$: C, 71.67; H, 5.12%. Found: C, 72.00, H, 5.36%.

1-Chloro-1-fluoro-2-(1-naphthyl)ethane (10b): Pale yellow oil. ^{1}H NMR δ=3.7—4.2 (2H, m), 6.43 (1H, ddd, J=50.4, 7.0, and 4.0 Hz) and 7.2—8.0 (7H, m); ^{19}F NMR δ=−128.87 (ddd, J=51, 23, and 15 Hz); IR (neat) 3064, 1580, 1478, 1442, 1082, and 1024 cm^{-1}; MS (EI) m/z (rel intensity) 210 [M^+(^{37}Cl), 8], 208 [M^+(^{35}Cl), 32], 186 (3), 171 (2), 153 (15), 141 (100), and 115 (11). Found: m/z 208.0477. Calcd for $C_{12}H_{10}{}^{35}ClF$: M, 208.0455.

1-Chloro-1-fluoro-4-phenylbutane (10d): Colorless oil. ^{1}H NMR δ=1.85 (2H, m), 2.11 (2H, m), 2.68 (2H, t, J=7.5 Hz), 6.16 (1H, dt, J=50.7 and 5.3 Hz), and 7.2—7.6 (4H, m); ^{13}C NMR δ=25.65 (d, J=4 Hz), 34.89, 38.64 (d, J=20 Hz), 102.64 (d, J=242 Hz), 126.10, 128.35, 128.47, and 141.16; ^{19}F NMR δ=−130.34 (dt, J=51 and 17 Hz); IR (neat) 2932, 1498, 1456, 1304, 1096, and 1032 cm^{-1}; MS (EI) m/z (rel intensity) 188 [M^+(^{37}Cl), 2], 186 [M^+(^{35}Cl), 5], 131 (2), 104 (8), 92 (12), 91 (100), and 65 (4). Found: m/z 186.0609. Calcd for $C_{10}H_{12}{}^{35}ClF$: M, 186.0612.

2-(4-Biphenylyl)-1-bromo-1-fluoroethane (11a): ^{1}H NMR δ=3.33—3.76 (2H, m), 6.59 (1H, ddd, J=50.4, 6.6, and 4.8 Hz), and 7.2—7.6 (9H, m); MS (EI) m/z (rel intensity) 280 [M^+(^{81}Br), 59], 278 [M^+(^{79}Br), 58], 234 (3), 199 (30), 179 (17), 167 (100), and 152 (13).

1-Bromo-1-fluoro-2-(1-naphthyl)ethane (11b): ^{1}H NMR δ=3.7—4.2 (2H, m), 6.70 (1H, ddd, J=50.4, 7.0, and 4.6 Hz), and 7.2—8.0 (7H, m); ^{19}F NMR δ=−130.24 (ddd, J=51, 25, and 16 Hz). MS (EI) m/z (rel intensity) 254 [M^+(^{81}Br), 19], 252 [M^+(^{79}Br), 26], 173 (14), 153 (20), 141 (100), 127 (10), and 115 (9). Found: m/z 251.9951. Calcd for $C_{12}H_{10}{}^{79}BrF$: M, 251.9950.

1-Bromo-1-fluoro-4-phenylbutane (11d): ^{1}H NMR δ=1.88 (2H, m), 2.22 (2H, m), 6.47 (1H, dt, J=50.4 and 5.3 Hz), and 7.1—7.4 (5H, m); ^{19}F NMR δ=−131.07 (ddd, J=50, 20, and 18 Hz); MS (EI) m/z (rel intensity) 232 [M^+(^{81}Br), 11], 230 [M^+(^{79}Br), 11], 131 (35), 109 (3), 91 (100), and 73 (6).

2-(4-Biphenylyl)-1-bromo-1-chloroethane (12a): ^{1}H NMR δ=3.33—3.76 (2H, m), 5.88 (1H, t, J=6.5 Hz), and 7.2—7.6 (9H, m); MS (EI) m/z (rel intensity) 296 [M^+(^{81}Br), 16], 294 [M^+(^{79}Br), 10], 252 (4), 214 (1), 198 (4), and 167 (100).

(4-Biphenylyl)acetylene (13a): Colorless crystals, mp 85—87 °C (hexane–$CHCl_3$). ^{1}H NMR δ=3.13 (1H, s) and 7.4—7.6 (9H, m); IR (KBr) 3272, 3056, 1482, 1448, 1252, and 1006 cm^{-1}; MS (EI) m/z (rel intensity) 179 (M^++1, 25), 178 (M^+, 100), 177 (14), 176 (22), 152 (13), and 151 (8). Found: m/z 178.0765. Calcd for $C_{14}H_{10}$: M, 178.073.

4-Phenyl-1-butyne (13b): ^{1}H NMR δ=1.97(1H, t, J=2.6 Hz), 2.48 (2H, td, J=7.4 and 2.6 Hz), 2.85 (2H, t, J=7.4 Hz), and 7.15—7.45 (5H, m).

1-(4-Biphenylyl)hexenes (14): Cololess oil. ^{1}H NMR δ=0.91 (3H, m), 1.3—1.6 (2H and 2H of $^1\Delta$-isomer, m), 2.0—2.4 (2H, m), 3.37 (2H of $^2\Delta E$-isomer, d, J=5.2 Hz), 3.44 (2H of $^2\Delta Z$-isomer, d, J=6.1 Hz), 5.57 (2H of $^2\Delta$-isomers), 6.28 (1H of $^1\Delta E$-isomer, dt, J=15.6 and 6.6 Hz), 6.41 (1H of $^1\Delta E$-isomer, d, J=15.6 Hz), and 7.2—7.65 (9H, m); MS (EI) m/z (rel intensity) 237 (M^++1, 54), 236 (M^+, 100), 207 (8), 193 (76), 178 (30), 167 (93), and 115 (10).

(*E*)-1-(4-Biphenylyl)-3,3-dimethyl-1-butene (21): Colorless oil. ^{1}H NMR δ=1.14 (9H, s), 6.31 (1H, d, J=16.2 Hz), 6.33 (1H, d, J=16.2 Hz), and 7.0—7.6 (9H, m); IR (neat) 3056, 3028, 2956, 2864, 1488, and 1448 cm^{-1}; MS (EI) m/z (rel intensity) 237 (M^++1, 16), 236(M^+, 77), 221 (100), 206 (7), 193 (9), 179 (25), and 165 (23). Calcd for $C_{16}H_{20}$: C, 91.47; H, 8.53%. Found: C, 91.27; H, 8.55%.

Preparation of Authentic Samples: To a stirred solution of 4-phenylbutanoic acid (1.65 g, 10 mmol) in 50 ml of dry ether was added a solution of PhLi (1.8 M; 11.1 ml, 20 mmol) at room temperature. The mixture was refluxed overnight, and then quenched with a saturated NH_4Cl solution. The organic phase was separated and the aqueous phase was extracted with ether. The combined ethereal phase was washed with brine, dried over Na_2SO_4, and evaporated. The residue was chromatographed on silica gel (hexane–CH_2Cl_2) to give 0.27 g of 1,1,4-triphenyl-1-butanol and 1.58 g of 1,4-diphenyl-1-butanone (**16**) as a colorless oil; oven temp 123—125 °C/0.1 mmHg. ^{1}H NMR δ=2.10 (2H, quintet, J=7.6 Hz), 2.74 (2H, t, J=7.9 Hz), 3.00 (2H, t, J=7.6 Hz), and 7.2—8.0 (10H, m); IR (neat) 1684, 1598, 1453, 1368, 1264, 1228, and 1200 cm^{-1}; MS (EI) m/z (rel intensity) 224 (M^+, 10), 147 (43), 120 (100), 105 (43), 91 (34), 77 (15), and 55 (7). Calcd for $C_{16}H_{16}O$: C, 85.68; H, 7.19%. Found: C, 85.51; H, 7.21%.

To a solution of $NaBH_4$ (38 mg, 1 mmol) in EtOH (10 ml) was added a solution of **16** (224 mg, 1 mmol) in EtOH (1 ml) at room temperature. After being stirred overnight, the reaction 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 concentrated. The residue was

chromatographed on silica gel (hexane–CH_2Cl_2) to give 152 mg of 1,4-diphenyl-1-butanol (**17**) as a colorless oil; oven temp 123—125 °C/0.1 mmHg. ^1H NMR δ=1.83 (4H, m), 2.22 (1H, br s), 2.69 (2H, t, J=7.3 Hz), 4.71 (1H, t, J=6.3 Hz), and 7.2—7.4 (10H, m); IR (neat) 3396, 3064, 3028, 2936, 2860, 1496, and 1454 cm^{-1}; MS (EI) m/z (rel intensity) 227 (M^++1, 2), 226 (M^+, 14), 135 (100), 115 (27), and 91 (16). Calcd for $C_{16}H_{18}O$: C, 85.68; H, 7.19%. Found: C, 85.51; H, 7.21%.

To a solution of **17** (179 mg, 0.8 mmol) in CH_2Cl_2 (10 ml) were added 0.08 ml of methanesulfonyl chloride followed by 0.32 ml of triethylamine at room temperature. After being refluxed overnight, the reaction mixture was quenched with a saturated NH_4Cl solution. The 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) to give 110 mg of (*E*)-1,4-diphenyl-1-butene (**15**) as colorless crystals; mp 34—36 °C. ^1H NMR δ=2.55 (2H, q, J=7.3 Hz), 2.82 (2H, t, J=7.3 Hz), 6.29 (1H, dt, J=16.8 and 7.3 Hz), 6.43 (1H, d, J=16.8 Hz), and 7.2—7.4 (10H, m); IR (KBr) 3024, 2932, 1598, 1494, 1452, and 1072 cm^{-1}; MS (EI) m/z (rel intensity) 209 (M^++1, 4), 208 (M^+, 27), 180 (16), 179 (12), 130 (17), 117 (100), and 91 (28).

To a solution of **17** (81 mg, 0.36 mmol) in dry CH_2Cl_2 was added 0.03 ml of diethylaminosulfur trifluoride (DAST) at −78 °C. After 15 min the reaction mixture was allowed to warm up to room temperature and then quenched with water. The mixture was extracted with ether. The ethereal extract was washed with brine, dried over Na_2SO_4, and concentrated. The residue was chromatographed on silica gel (hexane) to give 46 mg of 1-fluoro-1,4-diphenylbutane (**19**) as a pale yellow oil; ^1H NMR δ=1.6—2.0 (4H, m), 2.66 (2H, t, J=7.3 Hz), 5.43 (1H, ddd, J=47.6, 7.9, and 4.3 Hz), 7.1—7.4 (10H, m); ^{13}C NMR δ=26.78 (d, J=4 Hz), 35.50, 36.66 (d, J=24 Hz), 94.46 (d, J=170 Hz), 125.49 (d, J=7 Hz), 125.38, 128.17 (d, J=2 Hz), 128.32, 128.38, 128.40, 140.35 (d, J=20 Hz), and 141.88; IR (neat) 2948, 1604, 1496, 1456, and 1032 cm^{-1}; MS (EI) m/z (rel intensity) 228 (M^+, 6), 208 (13), 117 (92), 109 (24), 104 (100), and 91 (56). Calcd for $C_{16}H_{17}F$: C, 84.17; H, 7.51%. Found: C, 84.38; H, 7.46%.

To a solution of 1,1,4-triphenyl-1-butanol (825 mg, 2.7 mmol) were added 0.23 ml of methanesulfonyl chloride followed by 0.95 ml of triethylamine at room temperature. After being refluxed overnight, the reaction mixture was quenched with a saturated NH_4Cl solution. The 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) to give 178 mg of 1,1,4-triphenyl-1-butene (**20**) as a colorless oil; oven temp 133—135 °C/0.1 mmHg. ^1H NMR δ=2.53 (2H, q, J=7.5 Hz), 2.85 (2H, t, J=7.5 Hz), 6.21 (1H, t, J=7.5 Hz), and 7.2—7.5 (15H, m); IR (neat) 3080, 3056, 3028, 1600, 1496, 1456, 1446, 1076, and 1032 cm^{-1}; MS (EI) m/z (rel intensity) 284 (M^+, 3), 193 (9), 183 (100), 105 (75), and 77 (8).

Ethyl 4-Phenylbutanoate (18): ^1H NMR δ=1.25 (3H, t, J=7.0 Hz), 1.97 (2H, quintet, J=7.3 Hz), 2.32 (2H, t, J=7.3 Hz), 2.65 (2H, t, J=7.3 Hz), 4.12 (2H, q, J=7.0 Hz), and 7.15—7.35 (5H, m); IR (neat) 2932, 1736, 1456, 1374, 1246, 1200, 1144, and 1032 cm^{-1}; MS (EI) m/z (rel intensity) 192 (M^+, 20), 147 (42), 117 (13), 88 (100), and 66 (74).

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