

"*Syn-Effect*" in the Isomerization of (*E*)-α-Fluorovinylic Sulfones to the Corresponding Allylic Sulfones under Basic Conditions

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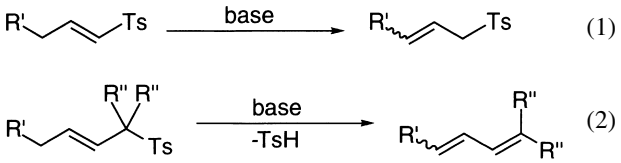
Toward the elucidation of the origin of the "*syn-effect*," the stereochemistry of the isomerization of (*E*)-α-fluorovinylic sulfones to the corresponding allylic sulfones under mild basic conditions was investigated. The ratio of (*Z*)-isomers of the resulting allylic sulfones decreased in the following order for the γ-substituents of the starting vinylic sulfones: F- > EtO- > CH_3- > BnS- > CH_3CH_2- > $(CH_3)_2CH$- > $(CH_3)_3C$-, C_6H_5-. The fluorine atom showed the highest "*syn-effect*," which is herein defined as an effect that stabilizes the *syn*-conformation in the transition state against a steric or nonbonded repulsion; the rest of the series was in accord with previous results found in the conversion of α-unsubstituted (*E*)-vinylic sulfones to the corresponding allylic sulfones under similar conditions. These results were rationalized based on the σ→π* interaction.

There exist many examples in organic chemistry where one cannot invoke the intuitive concept of steric or nonbonded repulsion to predict the relative stabilities of geometrical or conformational isomers of organic molecules. The origin of these puzzling phenomena has remained unclear.[1]

In order to rationalize such a long-standing problem, we have been performing experimental investigations regarding the "*syn-effect*" observed in the isomerization of vinylic sulfones to the corresponding allylic sulfones (Eq. 1)[2] and also in the desulfonylation of α,α-dialkylated allylic sulfones (Eq. 2).[3]



In previous papers,[2] we reported on the stereochemistry of the conversion of vinylic sulfones to the corresponding allylic sulfones by a treatment with a base under mild conditions, that is, (*E*)-vinylic sulfones preferentially afforded (*Z*)-allylic sulfones as kinetically controlled products, while (*Z*)-vinylic sulfones and α-alkylated vinylic sulfones gave (*E*)-allylic sulfones exclusively. The former experimental results were rationalized by the concept of "*conformational acidity*" (a sort of kinetic acidity), which essentially implies the "*syn-effect*." [4]

Several explanations had been proposed for the "*syn-effect*," namely: i) 6π-electron homoaromaticity, ii) a dipole–dipole interaction, iii) a σ-orbital interaction, iv) hydrogen-bonding, and v) chelation.[4] Recently, we have shown that 6π-electron homoaromaticity and/or σ→π* interaction (Fig. 1) is the most probable cause for the "*syn-effect*" found in the desulfonylation reaction of α,α-dialkylated allylic sulfones.[3,5] In order to clarify which is more suitable in the conversion of vinylic sulfones to the corresponding allylic sulfones, we replaced a hydrogen atom at the α-position of (*E*)-vinylic sulfones by a fluorine atom, because its size is not so very different from that of hydrogen and an extra unshared pair of electrons on it avoids 6π-electron homoaromaticity by the formation of an 8π-electron system in the *syn*-transition state. We herein report on the detailed results of an experimental investigation of the stereochemistry for the isomerization reaction of (*E*)-α-fluorovinylic sulfones to the corresponding allylic sulfones, including the

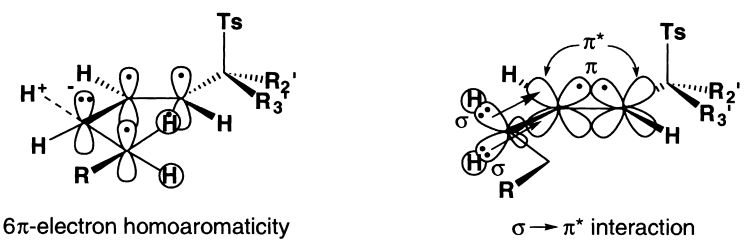
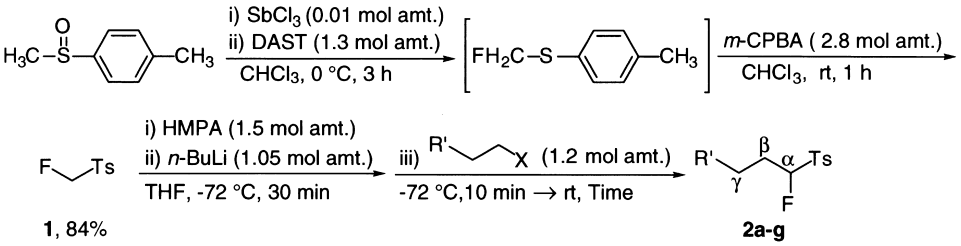
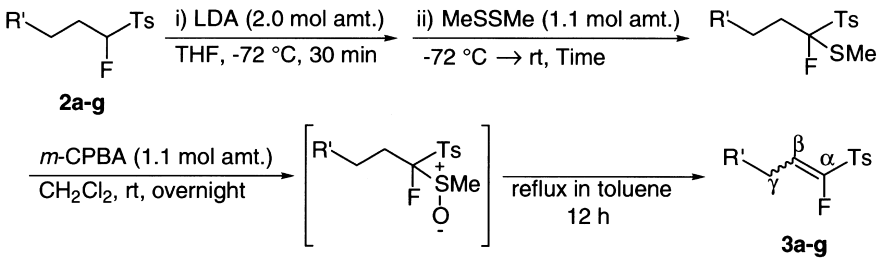


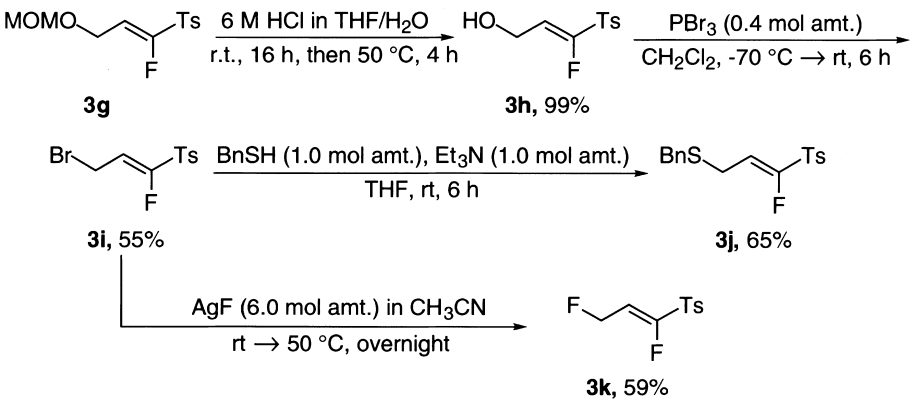
Fig. 1.



Scheme 1.



Scheme 2.



Scheme 3.

Table 1. Preparation of Various γ-Substituted α-Fluorosulfones **2a**–**g**

Entry	R′	X	Time	Yield of **2**/%
1	CH_3	I	1 h	**a**, 76
2	CH_3CH_2	I	overnight	**b**, 85
3	$(CH_3)_2CH$	I	overnight	**c**, 81
4	$(CH_3)_3C$	I	17 h	**d**, 72
5	EtO	Br	4 h	**e**, 81
6	Ph	Br	overnight	**f**, 62
7	MOMO	I	overnight	**g**, 71[a]

a) 27% of the starting material **1** was recovered.

Table 2. Preparation of γ-Substituted α-Fluorovinylic Sulfones **3a**–**g**

Entry	R′	Time	Yield of **3**/%	(*E*/*Z*)[a]
1	CH_3	6 h	**a**, 40	(96/4)
2	CH_3CH_2	16 h	**b**, 46	(96/4)
3	$(CH_3)_2CH$	overnight	**c**, 51	(97/3)
4	$(CH_3)_3C$	2 h	**d**, 56	(99/1)
5	EtO	1 h	**e**, 50[b]	(100/0)
6	Ph	overnight	**f**, 63[b]	(> 98/<2)
7	MOMO	overnight	**g**, 69[b]	(100/0)

a) The ratios were determined by 400 MHz ^{1}H NMR spectra. b) 1.2 mol amt. of LDA was used.

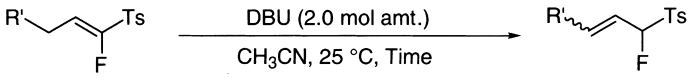
time-course of the reaction in all cases.

Results and Discussion

Preparation of (*E*)-α-Fluorovinylic Sulfones. The (*E*)-α-fluorovinylic sulfones used in the present investigation were prepared according to Schemes 1–3. $TsCH_2F$ (**1**) was readily prepared from *p*-$CH_3C_6H_4SOCH_3$ by treating with $SbCl_3$ and diethylaminosulfur trifluoride (DAST), followed by oxidation with *m*-CPBA.[6] Compound **1** was then alkylated by treating with *n*-BuLi, followed by the addition of various alkyl halides to give γ-substituted α-fluorosulfones **2a**–**g** in good yields (Scheme 1, Table 1).

Upon treatment with LDA and MeSSMe, compounds **2a**–**g** gave α-methylthiolated intermediates, which were converted

Table 3. Conversion of the (*E*)-α-Fluorovinylic Sulfones **(*E*)-3** to the Corresponding Allylic Sulfones **4**



(*E*)-3 **4**

(*E*)-3	R′	Time/h	(*E*)-3/4[a]	*Z*/*E* of 4[a]	Isolated total yield (3 + 4)/%
a	CH_3	1	91/9	18/82	—
		2	81/19	16/84	—
		4	51/49	17/83	—
		8	27/73	17/83	—
		12	20/80	16/84	—
		24	4/96	17/83	—
		48	<1/>99	16/84	quant.
		99	0/100	16/84	87
b	CH_3CH_2	1	95/5	13/87	—
		2	89/11	11/89	—
		4	78/22	12/88	—
		8	59/41	13/87	—
		12	41/59	12/88	—
		24	19/81	11/89	—
		48	3/97	13/87	—
		96	0/100	13/87	98
		144	0/100	11/89	quant.
c	$(CH_3)_2CH$	1	94/6	9/91	—
		2	88/12	10/90	—
		4	82/18	10/90	—
		8	60/40	10/90	—
		27	24/76	9/91	—
		48	11/89	10/90	—
		96	2/98	10/90	99
		168	0/100	9/91	74
d	$(CH_3)_3C$	1	>98/<2	0/100	—
		2	98/2	0/100	—
		5	94/6	0/100	—
		8	89/11	0/100	—
		27	72/28	0/100	—
		48	54/46	0/100	—
		122	18/82	0/100	quant.
		197	7/93	0/100	91
e	EtO	1	77/23	37/63	—
		2	58/42	38/62	—
		4	38/62	37/63	—
		7	21/79	37/63	—
		24	< 1/> 99	37/63	—
		48	0/100	36/64	—
		96	0/100	37/63	99
f	Ph	1	0/100	0/100	—
		2	0/100	0/100	—
		4	0/100	0/100	—
		7	0/100	0/100	—
		24	0/100	0/100	—
		48	0/100	0/100	99
j	BnS	1	0/100	13/87	—
		4	0/100	13/87	—
		8	0/100	14/86	—
		24	0/100	14/86	—
		96	0/100	13/87	95
k	F	0.2	76/24	66/34	90[b]
		0.5	59/41	66/34	91[b]
		1	41/59	67/33	91[b]
		2	18/82	73/27	90[b]
		4	8/92	76/24	74[b]
		8	0/100	84/16	57[b]
		25	0/100	100/0	31[b]
		33	0/100	100/0	31[b]
		55	0/100	100/0	26[b]

a) The ratios of **(*E*)-3/4** and *Z*/*E* ratios of **4** were determined by 400 MHz ^{1}H NMR spectra. b) The yield was determined by ^{1}H NMR spectrum (see experimental).

to the corresponding γ-substituted (*E*)-α-fluorovinylic sulfones **3a**–**g** almost exclusively by treating with *m*-CPBA, followed by refluxing in toluene[7] (Scheme 2, Table 2). The phenylselenation or phenylthiolation of **2a**–**g** could not afford satisfactory results.

Vinylic sulfones **3a**–**d**,**f** with an alkyl or aryl group and **3g** with a methoxymethoxy (MOMO) group at the γ-position are sufficiently stable during separation by silica-gel column chromatography or TLC, but the vinylic sulfone **3e** bearing an ethoxy group at the γ-position readily decomposed on weakly acidic silica gel during separation. To prevent decomposition, **3e** was purified by basic alumina column chromatography and immediately applied to the following isomerization reaction.

The γ-benzylthio-substituted (*E*)-α-fluorovinylic sulfone **3j** was prepared from γ-MOMO-substituted vinylic sulfone **3g** via **3h** obtained by acidic hydrolysis, followed by bromination and a reaction with benzenemethanethiol. On the other hand, the γ-fluoro-substituted (*E*)-α-fluorovinylic sulfone **3k** was prepared from the γ-bromo-substituted vinylic sulfone **3i** by treating with silver fluoride in acetonitrile (Scheme 3).

Conversion of (*E*)-α-Fluorovinylic Sulfones to the Corresponding Allylic Sulfones. The (*E*)-α-fluorovinylic sulfones **3** obtained above were converted to the corresponding allylic sulfones **4** under mild basic conditions to investigate the stereochemical relationship. The vinylic sulfones **3a**–**f**,**j**,**k** were treated with two molar amounts of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as a base in acetonitrile at ambient temperature (25 °C). In order to observe the time course of the reaction for every substrate, an aliquot of the reaction mixture was taken out by a syringe at arbitrary time intervals, and immedi-

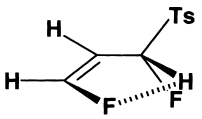


Fig. 2.

ately quenched by introducing into a phosphate buffer solution (pH 7). After extraction with ethyl acetate, the ^{1}H NMR spectra of the resulting residues obtained by the usual manner were taken to determine the ratio of the resulting (*E*)- and (*Z*)-allylic sulfones **4** and the unaffected vinylic sulfones **3**.

The result of the time course of the conversion of (*E*)-α-fluorovinylic sulfones **3** to the corresponding allylic sulfones **4** is shown in Table 3.

Since the isolated total yields of the recovered reactants **3** and products **4** were almost quantitative in every case, except for **3k**, even after a prolonged reaction time, it is obvious that the conversion of **3** to **4** proceeded very cleanly without any other side reactions. From the table, it was found that in the case of γ-alkyl-substituted (*E*)-α-fluorovinylic sulfones **3a**–**d**, the ratio of (*Z*)-isomer of products **4a**–**d** decreased in the order $CH_3 > CH_3CH_2 > (CH_3)_2CH > (CH_3)_3C$, as intuitively predicted from the difference of the steric hindrance. In the case of γ-ethoxy-substituted (*E*)-α-fluorovinylic sulfone **3e**, the reaction was completed within 48 h to afford a *Z*/*E*-mixture of **4e** (*Z*/*E* = 36/64), whereas in the case of γ-fluoro-substituted (*E*)-α-fluorovinylic sulfone **3k**, more than 50% of the reactant was converted into product **4k** within 1 h, affording (*Z*)-isomer as the major product (*Z*/*E* = 67/33). However, only in the case of **3k**, the produced allylic sulfone **4k** was found to be gradually decomposed under the reaction conditions. From a direct observation of the isomerization by ^{1}H NMR, the rate of decomposition of the (*E*)-isomer of **4k** was found to be faster than that of (**Z**)-**4k** to finally afford only (**Z**)-**4k**, which is regarded as a thermodynamically favored product, probably due to a hydrogen bonding interaction between vinylic fluorine and a slightly acidic α-hydrogen, as shown in Fig. 2.[8] In the case of γ-phenyl- and γ-benzylthio-substituted (*E*)-α-fluorovinylic sulfones **3f**,**j**, the reaction completed within 1 h and only (*E*)-allylic sulfones **4f** was obtained from **3f**, while a *Z*/*E* mixture of **4j** from **3j** was obtained in a ratio of around 13/87.

From these results, the relative degree of the "*syn-effect*" for various γ-substituents of (*E*)-α-fluorovinylic sulfones **3** was determined to be as follows:

$$\text{F-} > \text{EtO-} > \text{CH}_3\text{-} > \text{BnS-} > \text{CH}_3\text{CH}_2\text{-} > (\text{CH}_3)_2\text{CH-} > (\text{CH}_3)_3\text{C-}, \text{C}_6\text{H}_5\text{-}$$

The fluorine atom has been found to show the strongest "*syn-effect*" among the substituents we have investigated so far. The relative degree of the "*syn-effect*" for other substituents remains of the same order as found in the conversion of α-unsubstituted vinylic sulfones to the corresponding allylic sulfones.[2]

We previously observed that the *Z*/*E* ratio of the allylic sulfones (R′CH=CHCH$_2$Ts) obtained by the isomerization of (*E*)-1-tosyl-1-alkenes (R′CH$_2$CH=CHTs) with DBU at 25 °C after 12 h was almost constant at around 33/67 regardless of the length of the alkyl substituent, R′ (R′ = –CH$_2$–; Et, *n*-Pr, *n*-Pen, *n*-Oct) except benzyl group (R′ = PhCH$_2$).[2b] This suggests that the steric difference among the linear alkyl substituents R′ in the (*E*)-1-tosyl-1-alkenes is not crucial when we determine the relative degree of the "*syn-effect*" for γ-substituents. Taking into account of this fact, it can be concluded from the results given in Table 3 that the "*syn-effect*" for the methyl group is greater than that for ethyl, namely the methylene group.

On the other hand, only (*E*)-allylic sulfones were obtained from (*E*)-4,4-dimethyl-1-fluoro-1-tosyl-1-pentene (**3d**) and (*E*)-1-fluoro-3-phenyl-1-tosyl-1-propene (**3f**). This is probably due to the bulkiness of the substituents at the γ-position, which precludes the possibility of *syn*-geometry by steric congestion (Figs. 3 and 4).

Except for (*E*)-γ-phenyl- and (*E*)-γ-benzylthio-substituted α-fluorovinylic sulfones **3f**,**j**, the full conversion of the vinylic sulfones **3** to the corresponding allylic sulfones **4** required a rather long time. It is notable that in the case of γ-Me- and *i*-Pr-substituted vinylic sulfones **3a**,**c**, the reactions were completed within 99 and 168 h, respectively, whereas in the case of *t*-Bu-substituted vinylic sulfone **3d**, it required more than 197 h (Table 3). This may be due to not only the bulkiness of the substituent, but also the electron-releasing inductive effect of the alkyl group, which reduces the acidity of the allylic pro-

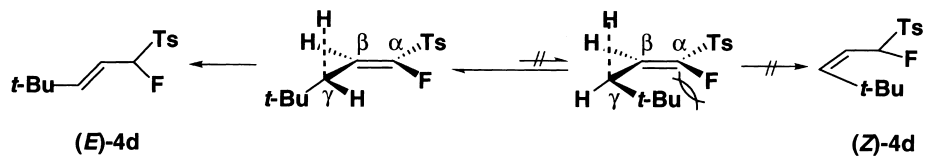


Fig. 3.

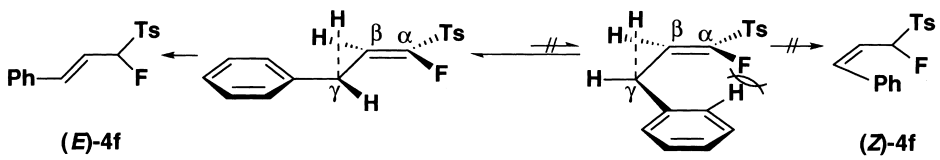


Fig. 4.

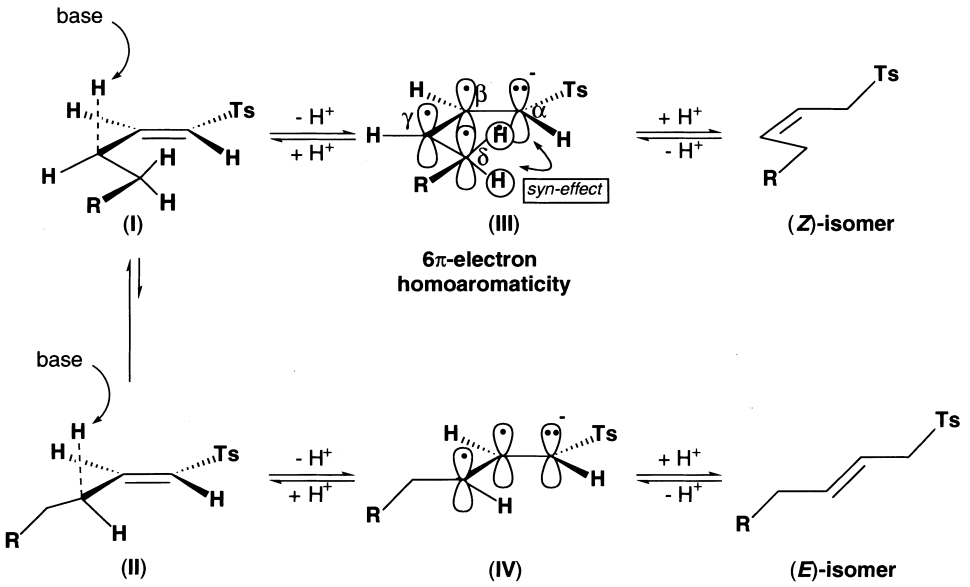


Fig. 5.

ton(s) at the γ-position. In the cases of **3f**,**j**, the conversion was completed within 1 h due to the highly acidic character of the proton(s) neighboring to the phenyl or benzylthio group, which can stabilize the developing anion by conjugation, not only with the neighboring olefinic double bond, but also with a phenyl group or a vacant d-orbital of the sulfur atom.[9] As a result, the activation energy of their reactions would be lowered more than that for vinylic sulfones bearing other γ-substituents, and conversion to the allylic sulfones would have proceeded faster than others. Though the γ-protons of **3e**,**k** were activated by an inductive effect of the highly electronegative oxygen or fluorine atom, the intermediary anions produced by the action of a base were not so effectively stabilized with substituents different from the case of **3f**,**j** being stabilized by conjugation, as mentioned above. Thus, **(*E*)-3e,k** indicated the reactivity between those of **3f**,**j** and **3a**–**d**, as can be seen from Table 3.

We proposed 6π-electron homoaromaticity as one of the most probable origins of the "*syn-effect*."[2,3] Namely, the *syn*-conformation is favored over the *anti*-conformation due to the 6π-electron homoaromaticity to stabilize the developing negative charge at the γ- and/or α-positions [(III) in Fig. 5]. This stabilizing interaction favors the transition state (I) over (II) at the deprotonation stage. As a result, the kinetically controlled (*Z*)-isomer is preferred to the thermodynamically controlled (*E*)-isomer in the conversion of α-unsubstituted vinylic sulfones to the corresponding allylic sulfones.[2]

However, as mentioned above, the 6π-electron homoaromaticity is not applicable in the present reaction in which an α-hydrogen of (*E*)-vinylic sulfones was replaced by a fluorine atom to form an 8π-electron system (Fig. 6a). Nevertheless, we again observed the same tendency of the "*syn-effect*" for the γ-substituents in the conversion of (*E*)-α-fluorovinylic sulfones **3** to the corresponding allylic sulfones **4**, as shown in Table 3. Therefore, another probable cause, namely a $\sigma \rightarrow \pi^*$ interaction (Fig. 6b) between the σ-orbital of the allylic C–H bond(s) and the *anti*-bonding orbital (π^*) of the C=C double bond, which is regarded as a sort of hyperconjugation in the

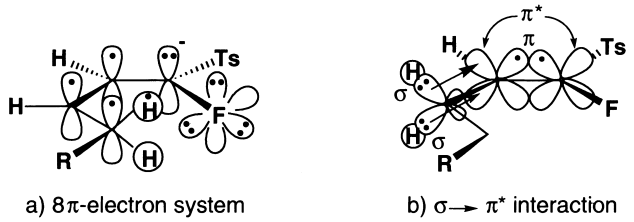


Fig. 6.

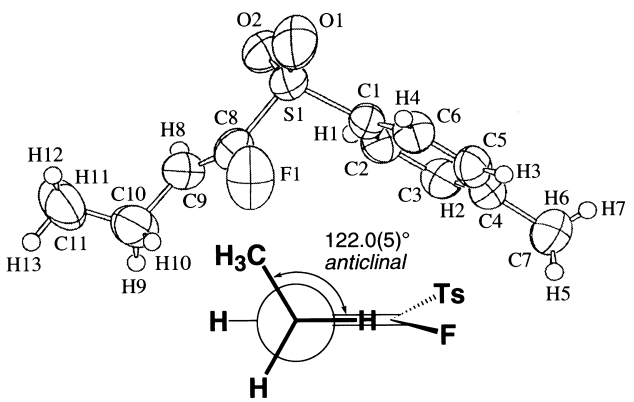


Fig. 7.

transition state, must be responsible for the "*syn-effect*."

We sometimes observed a "*syn-effect*" for the substrate, itself, in the solid state.[2d,e] Thus, the X-ray crystallography of 1-fluoro-1-tosyl-1-butene (**3a**) was performed as shown in Fig. 7.[10] It was found that the γ-methyl group of **3a** has an *anticlinal*-conformation relative to the double-bond axis, suggesting that the "*syn-effect*" does not work in the solid state of **3a**, but at the transition state of the isomerization reaction with a base in the solution phase.

In the case of γ-ethoxy-substituted (*E*)-α-fluorovinylic sulfone **3e**, the ratio of the (*Z*)-allylic sulfone **4e** became higher

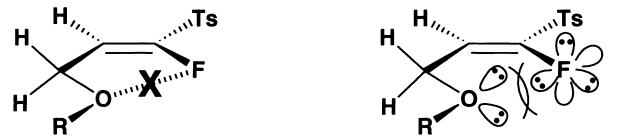


Fig. 8.

than that of γ-alkyl-substituted allylic sulfones **4a**–**d**, even though there is no hydrogen bond that is possible for γ-ethoxy-substituted (*E*)-α-unsubstituted vinylic sulfones[2] to stabilize the *syn*-conformation (Fig. 8a), if anything, an electrostatic repulsion occurs between the lone pairs of the electrons on fluorine and oxygen atoms to destabilize the *syn*-conformation (Fig. 8b).

On the other hand, an ethoxy group can enhance the $\sigma\rightarrow\pi^*$ interaction in the transition state in the presence of a base by increasing the acidity of the allylic proton(s) because of the relatively high electronegativity (3.5) of the oxygen atom (Fig. 9). On the contrary, the electron-releasing effect of the alkyl group reduces the $\sigma\rightarrow\pi^*$ interaction by lowering the acidity of the allylic proton(s) of the vinylic sulfones **3a**–**d**. Thus, due to the strong $\sigma\rightarrow\pi^*$ interaction, the ratio of the *syn*-conformation in the transition state may become higher in the case of an ethoxy group compared with the case of alkyl groups at the γ-position.

In the case of γ-fluorinated (*E*)-α-fluorovinylic sulfone **3k**, this $\sigma\rightarrow\pi^*$ interaction is more enhanced due to the higher electronegativity (4.0) of the fluorine atom compared with that of the oxygen atom (Fig. 9). As a result, the *syn*-conformation is preferred over the *anti*-conformation to afford the (*Z*)-allylic sulfone **(*Z*)-4k** as a major product.

In the present investigation, we found that the proportions of (*Z*)-allylic sulfones are considerably lower in the case of alkyl and ethoxy groups compared with the result observed in similar reaction for α-unsubstituted vinylic sulfones.[2] As shown in Fig. 10, two conformations, **A** and **B**, are possible in the transition state arising from the (*E*)-vinylic sulfones. The *syn*-intermediate **A′** consists of an unfavorable 8π-electron system different from α-unfluorinated (*E*)-vinylic sulfones [see Fig. 5 (III)],[2] whereas the *anti*-intermediate **B′** consists of a 6π-electron system and a sterically favored structure. The stabilization of **B′** by 6π-electron homoaromaticity, however, seems not to be effective because of the long distance between the p-orbitals on the γ-carbon atom and the fluorine atom beyond a hydrogen atom through space.

Furthermore, as shown in Fig. 11, a steric repulsion seems

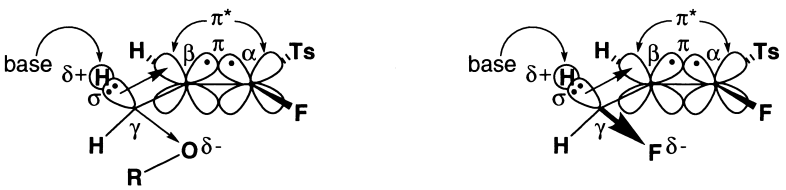


Fig. 9.

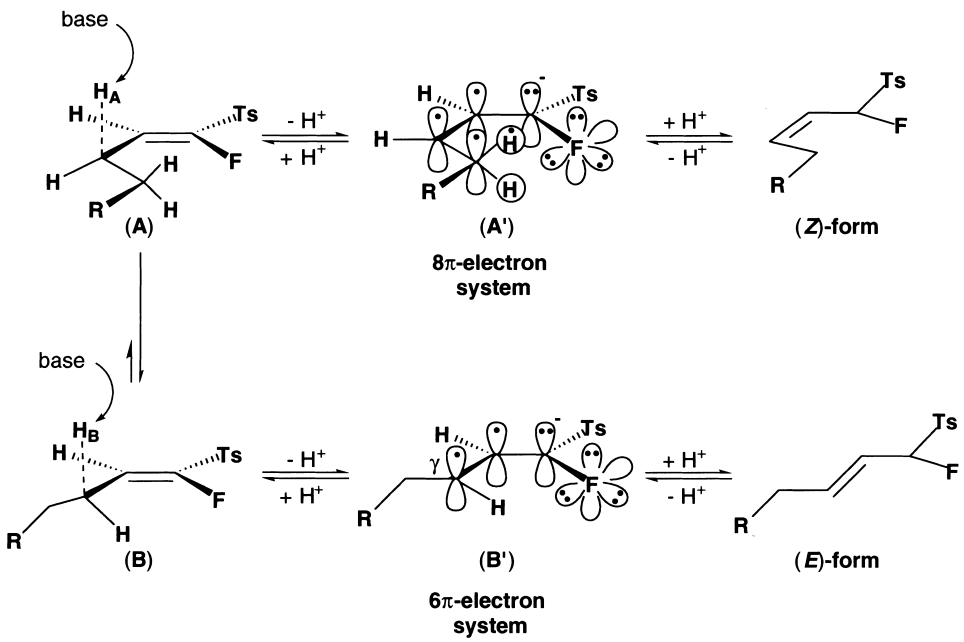


Fig. 10.

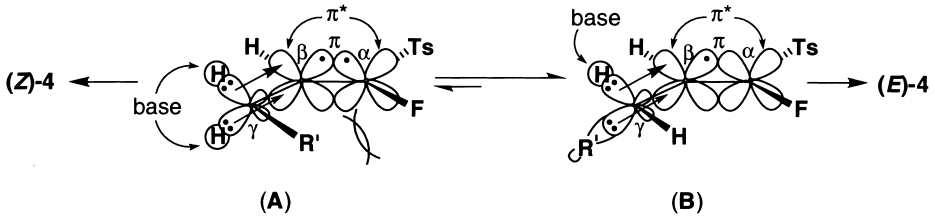


Fig. 11.

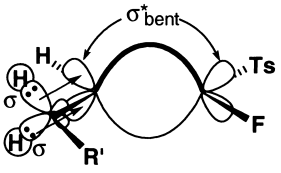


Fig. 12.

to exist between the substituent (R′) at the γ-position and a slightly bigger fluorine atom than hydrogen atom in *syn*-conformation **A**. To avoid this kind of repulsion, conformation **A** tends to change to the sterically more favorable conformation **B**. On account of the electronic (Fig. 10) and steric factors (Fig. 11), conformation **B** is more preferable than conformation **A** in the transition state of the isomerization of γ-substituted (*E*)-α-fluorovinylic sulfones **3a–f,j**, except for γ-fluorinated (*E*)-α-fluorovinylic sulfone **3k**, in which such a steric repulsion is very small.

Although it is not yet clear why the benzylthio group lies between the methyl and methylene groups, the following factors should be involved: (a) the difference in the p- or pseudo p-orbital size and the bond length in connection with the 6π-electron homoaromaticity, (b) the polarizability and electronegativity, and (c) the participation of the 3d-orbital of the sulfur atom to stabilize the developing anion at the neighboring carbon atom, which may reduce the $\sigma\rightarrow\pi^*$ interaction between the allylic C-H σ-orbital and the π^*-orbital of olefin.

The above results are also well explained based on the bent-bond model, namely the τ-bond model of the carbon-carbon double bond using only "single bonds," as proposed by A. Eschenmoser in his report on the stereochemistry of E′- and E″-reactions.[11] Although a conclusive statement cannot be made based on the currently available information, it seems likely that we can continue to consider the σ/π and bent-bond description of the carbon-carbon double bond to be equivalent, as mentioned by Wiberg.[12,13] Based on the bent-bond model, we can assume that in the transition state the $\sigma_{C-H}\rightarrow\sigma^*_{C-C;bent}$ interaction occurs in the *syn*-conformation (Fig. 12). Due to the highly electronegative atoms in the F- and EtO-groups, this $\sigma_{C-H}\rightarrow\sigma^*_{C-C;bent}$ interaction is also enhanced in the presence of a base and, as a result, the *syn*-conformation is preferred over the *anti*-conformation.

Although we could not exclude the influence of 6π-electron homoaromaticity on the relative degree of the "*syn-effect*," the present investigation provided strong evidence to support the $\sigma\rightarrow\pi^*$ interaction as being the most important origin of the "*syn-effect*," in addition to the previous result.[3]

Because of the 8π-electron system and the steric factor of the fluorine atom of (*E*)-α-fluorovinylic sulfone in the transition state, the ratio of the kinetically controlled (*Z*)-products is lowered compared with that of α-unfluorinated (*E*)-vinylic sulfones, but the relative degree of the "*syn-effect*" for various substituents at the γ-position remained the same, as found in the conversion of α-unfluorinated vinylic sulfones to the corresponding allylic sulfones.[2] Thus, in conclusion, we could have shown that the $\sigma\rightarrow\pi^*$ interaction is the most important factor to determine the relative degree of the "*syn-effect*" in the conversion of (*E*)-vinylic sulfones to the corresponding allylic sulfones.

Related work is in progress in our laboratory.

Experimental

The melting point was determined with a micro melting apparatus (Yanagimoto Seisakusho) and was uncorrected. The ^{1}H and ^{19}F NMR spectra were recorded on a JEOL JNM-LA 400FT (400 MHz for ^{1}H and 376 MHz for ^{19}F) and a Varian UNIT plus 750 (only for ^{1}H NMR of **(*E*)-4k** in $CDCl_3$) NMR spectrometers. The chemical shifts of ^{1}H and ^{19}F NMR are reported on the δ-scale relative to $Si(CH_3)_4$ ($\delta = 0.00$ ppm) and C_6F_6 ($\delta = -162.90$ ppm) as internal standards, respectively. IR and MS spectra were measured on a JASCO FT/IR infrared spectrometer and a JEOL SX-102A mass spectrometer, respectively. All of the solvents were distilled and stored over drying agents. Thin-layer chromatography (TLC), flash column chromatography, and HPLC were performed on Merck's silica gel 60 PF_{254} (Art. 7749), Cica-Merck's silica gel 60 (No. 9385-5B), and JAIGL-SIL (s-043-15), respectively.

Preparation of Fluoromethyl *p*-Tolyl Sulfone (1). To a solution of methyl *p*-tolyl sulfoxide (308 mg, 2 mmol) in $CHCl_3$ (18 mL, treated with basic alumina) was added a solution of $SbCl_3$ (5 mg, 0.02 mmol) in $CHCl_3$ (2 mL) dropwise. Then, DAST (0.34 mL, 2.6 mmol) was added very slowly to the mixture at 0 °C. After stirring for 3 h at 0 °C, a solution of NaOH (198 mg) in a saturated $NaHCO_3$ solution (7.5 mL) was added. The crude product obtained by the usual work-up was treated with *m*-chloroperbenzoic acid (*m*-CPBA, ca. 70% pure, 1.381 g, 5.6 mmol) in $CHCl_3$ (35 mL) at room temperature. After stirring for 1 h, a saturated Na_2CO_3 solution (5 mL) was added to the reaction mixture. The organic phase was separated and further extracted with ethyl acetate, and the combined organic extracts were successively washed with a 1 M (= mol dm^{-3}) NaOH solution and brine, and dried over Na_2SO_4. The crude product was purified by column chromatography (hexane/AcOEt = 7/1) to afford **1** in 84% yield (330 mg). Mp 100.5–101.0 °C (from hexane/AcOEt); IR (KBr) 3030, 2970, 1590, 1490, 1450, 1425, 1395, 1380, 1340, 1300, 1290, 1225, 1145, 1085, 1040, 1010, 933, 810, 792, 760, 690 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.48 (3H, s), 5.11 (2H, d, J = 47.13 Hz), 7.41

(2H, d, J = 8.07 Hz), 7.85 (2H, d, J = 8.07 Hz). Found: C, 50.77; H, 4.82%. Calcd for $C_8H_9FO_2S$: C, 51.05; H, 4.82%.

Preparation of 1-Fluoro-1-tosylbutane (2a). To a mixed solution of fluoromethyl *p*-tolyl sulfone (**1**, 376 mg, 2 mmol) and HMPA (0.52 mL, 3.0 mmol) in THF (20 mL) was added a solution of *n*-BuLi in hexane (1.34 mL, 2.1 mmol, 1.57 M) at −72 °C under a nitrogen atmosphere, followed by the addition of 1-iodopropane (0.24 mL, 2.4 mmol) after 30 min. The reaction mixture was stirred for 10 min at −72 °C and for 1 h at room temperature, and then quenched by the addition of a saturated NH_4Cl solution (2 mL). After removing the solvent under reduced pressure, the organic substances were extracted with ethyl acetate, followed by washing with brine and drying over Na_2SO_4. An alkylated product **2a** was isolated by flash column chromatography (SiO_2, hexane/AcOEt = 10/1) in 76% yield (347 mg). Mp 40.8–41.0 °C (from hexane/$CHCl_3$); IR (KBr) 2966, 2878, 1595, 1494, 1466, 1388, 1321, 1292, 1246, 1184, 1154, 1106, 1086, 1036, 1019, 960, 850, 821, 743, 704, 665 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.98 (3H, t, J = 7.32 Hz), 1.45–1.70 (2H, m), 1.78–1.93 (1H, m), 2.00–2.20 (1H, m), 2.47 (3H, s), 5.08 (1H, ddd, J = 2.92, 10.04, 48.56 Hz), 7.39 (2H, d, J = 8.32 Hz), 7.82 (2H, d, J = 8.32 Hz). Found: C, 57.15; H, 6.58%. Calcd for $C_{11}H_{15}FO_2S$: C, 57.37; H, 6.56%.

In a similar manner, **2b**–**g** were prepared in good yields. Their physical and spectral data are given in the following.

1-Fluoro-1-tosylpentane (2b). An oil; IR (neat) 3060, 2960, 2890, 1595, 1495, 1460, 1400, 1380, 1310, 1230, 1150, 1080, 1040, 1015, 970, 895, 810, 775, 715, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.92 (3H, t, J = 7.08 Hz), 1.30–1.62 (4H, m), 1.78–1.93 (1H, m), 2.03–2.24 (1H, m), 2.46 (3H, s), 5.06 (1H, ddd, J = 2.92, 10.04, 48.84 Hz), 7.38 (2H, d, J = 8.04 Hz), 7.81 (2H, d, J = 8.04 Hz) MS m/z 244 (M^+, 4.44%), 157 (55.09), 156 (85.25), 92 (100.00), 91 (90.57), 69 (39.55), 65 (49.32), 43 (44.05), 41 (60.25).

1-Fluoro-4-methyl-1-tosylpentane (2c). An oil; IR (neat) 2975, 2890, 1590, 1465, 1325, 1300, 1150, 1085, 1070, 1025, 895, 805, 715, 695, 655 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.90 (3H, d, J = 6.60 Hz), 0.91 (3H, d, J = 6.60 Hz), 1.31–1.52 (2H, m), 1.54–1.66 (1H, m), 1.79–1.94 (1H, m), 2.06–2.26 (1H, m), 2.47 (3H, s), 5.04 (1H, ddd, J = 2.92, 10.00, 48.84 Hz), 7.39 (2H, d, J = 8.32 Hz), 7.82 (2H, d, J = 8.32 Hz). MS m/z 258 (M^+, 34.44%), 157 (99.61), 156 (100.00), 139 (32.87), 92 (90.47), 91 (47.37), 83 (17.74), 65 (16.94), 61 (25.68), 57 (16.56), 55 (20.33).

1-Fluoro-4,4-dimethyl-1-tosylpentane (2d). An oil; IR (neat) 3065, 2958, 2869, 1597, 1469, 1397, 1367, 1329, 1303, 1249, 1153, 1091, 1070, 1018, 994, 905, 816, 735, 704, 662 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.90 (9H, s), 1.34 (1H, ddd, J = 4.64, 12.14, 13.17 Hz), 1.49 (1H, ddd, J = 4.64, 12.93, 13.17 Hz), 1.80–1.94 (1H, m), 2.03–2.22 (1H, m), 2.47 (3H, s), 5.01 (1H, ddd, J = 2.93, 10.00, 48.79 Hz), 7.39 (2H, d, J = 8.29 Hz), 7.82 (2H, d, J = 8.29 Hz). MS m/z 272 (M^+, 21.75%), 257 (78.08), 157 (100.00), 156 (89.88), 139 (35.02), 92 (21.51), 91 (20.05).

3-Ethoxy-1-fluoro-1-tosylpropane (2e). An oil; IR (neat) 3000, 2890, 1740, 1595, 1490, 1445, 1380, 1330, 1305, 1240, 1215, 1150, 1110, 1080, 1040, 1015, 980, 810, 760, 710, 700, 658 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.17 (3H, t, J = 7.04 Hz), 1.96–2.10 (1H, m), 2.47 (3H, s), 2.15–2.54 (1H, m), 3.41–3.72 (4H, m), 5.33 (1H, ddd, J = 2.68, 10.24, 48.56 Hz), 7.38 (2H, d, J = 8.28 Hz), 7.82 (2H, d, J = 8.28 Hz). MS m/z 261 (M^+ + 1, 0.87%), 231 (5.20), 216 (9.78), 157 (58.46), 139 (25.17), 105 (18.24), 104 (21.70), 92 (30.26), 91 (59.94), 76 (20.33), 65 (33.80), 59 (100.00), 31 (70.54).

1-Fluoro-3-phenyl-1-tosylpropane (2f). Mp 122 °C (from hexane/AcOEt); IR (KBr) 3023, 2962, 2930, 2865, 1594, 1496, 1455, 1321, 1308, 1292, 1152, 1089, 1036, 1018, 923, 821, 801, 757, 704, 663 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.12–2.26 (1H, m), 2.34–2.53 (1H, m), 2.46 (3H, s), 2.77 (1H, ddd, J = 8.18, 8.29, 13.92 Hz), 2.94 (1H, ddd, J = 5.14, 8.76, 13.92 Hz), 5.02 (1H, ddd, J = 2.93, 10.24, 48.32 Hz), 7.17–7.32 (5H, m), 7.38 (2H, d, J = 8.29 Hz), 7.80 (2H, d, J = 8.29 Hz). Found: C, 65.76; H, 5.94%. Calcd for $C_{16}H_{17}FO_2S$: C, 65.73; H, 5.86%.

1-Fluoro-3-(methoxymethoxy)-1-tosylpropane (2g). An oil; IR (neat) 3070, 2932, 2883, 2825, 1596, 1455, 1384, 1329, 1224, 1151, 1110, 1085, 1045, 920, 815, 760, 725, 704, 666 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.98–2.10 (1H, m), 2.37–2.55 (1H, m), 2.45 (3H, s), 3.32 (3H, s), 3.65 (1H, ddd, J = 3.90, 10.00, 10.12 Hz), 3.71–3.76 (1H, m), 4.57 (1H, d, J = 6.59 Hz), 4.60 (1H, d, J = 6.59 Hz), 5.32 (1H, ddd, J = 2.68, 10.00, 48.30 Hz), 7.37 (2H, d, J = 8.29 Hz), 7.81 (2H, d, J = 8.29 Hz). MS m/z 276 (M^+, 0.11%), 245 (3.79), 231 (19.87), 215 (22.93), 157 (23.36), 156 (20.04), 139 (36.05), 121 (19.43), 105 (9.76), 91 (42.75), 75 (9.18), 65 (16.71), 58 (28.11), 45 (100.00), 43 (83.38).

Preparation of 1-Fluoro-1-tosyl-1-butene (3a). In a dry flask, *n*-BuLi in hexane (0.73 mL, 1.13 mmol, 1.55 M) was added to a solution of $[(CH_3)_2CH]_2NH$ (0.148 mL, 1.13 mmol) in THF (4 mL) at −72 °C and the mixture was stirred for 30 min at the temperature, followed by the dropwise addition of a solution of 1-fluoro-1-tosylbutane (**2a**, 130 mg, 0.565 mmol) in THF (2 mL). After stirring for 30 min at −72 °C, MeSSMe (0.055 mL, 0.6215 mmol) was added to the reaction mixture, and the mixture was stirred for 6 h at room temperature. Then, the reaction mixture was quenched with phosphate-buffer (pH 7). After evaporating the organic solvent, the product was extracted with ethyl acetate, followed by washing with brine and drying over Na_2SO_4. After removal of the solvent, the crude product was purified by preparative TLC (hexane/AcOEt = 5/1) to give methylthiolated product (82 mg, 0.297 mmol). The sulfide was then oxidized with *m*-CPBA (ca. 70% pure, 81 mg, 0.326 mmol) in CH_2Cl_2 at room temperature overnight. After the usual work-up, the resulting sulfoxide was refluxed in toluene for 12 h to afford **3a** as a mixture of (*E*)- and (*Z*)-isomers, which were isolated by preparative TLC (hexane/AcOEt = 5/1) in 40% overall yield (51 mg, *E*/*Z* = 96/4) from **2a**. Mp 48.5–49.0 °C [(*E*)-isomer, from hexane/AcOEt]; IR of (*E*)-isomer (KBr) 3059, 2976, 2932, 2872, 1670, 1595, 1495, 1459, 1440, 1345, 1329, 1306, 1172, 1141, 1091, 1043, 1017, 817, 740, 666 cm^{-1}; ^1H NMR ($CDCl_3$) of (*E*)-form δ 1.07 (3H, t, J = 7.56 Hz), 2.23 (2H, dp, J = 2.44, 7.56 Hz), 2.46 (3H, s), 6.22 (1H, dt, J = 32.69, 7.56 Hz), 7.37 (2H, d, J = 8.30 Hz), 7.82 (2H, d, J = 8.30 Hz). ^1H NMR ($CDCl_3$) of (*Z*)-form δ 1.10 (3H, dt, J = 0.73, 7.56 Hz), 2.46 (3H, s), 2.65 (2H, ddq, J =1.71, 8.54, 7.56 Hz), 5.81 (1H, dt, J = 21.96, 8.54 Hz), 7.37 (2H, d, J = 8.30 Hz), 7.84 (2H, d, J = 8.30 Hz). Found: C, 57.75; H, 5.76%. Calcd for $C_{11}H_{13}FO_2S$: C, 57.87; H, 5.74%.

In a similar manner, **3b**–**g** were prepared in good yields. Their physical and spectral data are given in the following.

1-Fluoro-1-tosyl-1-pentene (3b). Mp 31.5 °C [(*E*)-isomer, from hexane]; IR of (*E*)-isomer (KBr) 3059, 2955, 2921, 2865, 1664, 1595, 1460, 1439, 1334, 1306, 1164, 1130, 1092, 1043, 980, 882, 817, 799, 731, 665 cm^{-1}; ^1H NMR ($CDCl_3$) of (*E*)-form δ 0.92 (3H, t, J = 7.34 Hz), 1.49 (2H, sx, J = 7.34 Hz), 2.19 (2H, ddt, J = 2.20, 7.89, 7.34 Hz), 2.45 (3H, s), 6.23 (1H, dt, J = 32.65, 7.89 Hz), 7.37 (2H, d, J = 8.25 Hz), 7.83 (2H, d, J = 8.25 Hz). ^1H NMR ($CDCl_3$) of (*Z*)-form δ 0.97 (3H, t, J = 7.34 Hz), 1.50 (2H, sx, J = 7.34 Hz), 2.46 (3H, s), 2.62 (2H, m), 5.81 (1H, dt, J = 22.19, 8.44 Hz), 7.37 (2H, d, J = 8.25 Hz), 7.83 (2H, d, J

= 8.25 Hz). HRMS (FAB) ($M^+ + 1$), Found: *m/z* 243.0854. Calcd for $C_{12}H_{16}FO_2S$: 243.0855.

1-Fluoro-4-methyl-1-tosyl-1-pentene (3c). Mp 34.0 °C [(*E*)-isomer, from hexane]; IR of (*E*)-isomer (KBr) 3071, 2959, 2865, 1671, 1594, 1465, 1440, 1330, 1294, 1173, 1147, 1091, 1045, 909, 888, 810, 754, 665 cm^{-1}; ^1H NMR ($CDCl_3$) of (*E*)-form δ 0.89 (6H, d, J = 6.83 Hz), 1.76 (1H, th, J = 6.59, 6.83 Hz), 2.07 (2H, ddd, J = 2.20, 6.59, 8.05 Hz), 2.44 (3H, s), 6.22 (1H, dt, J = 32.44, 8.05 Hz), 7.34 (2H, d, J = 8.29 Hz), 7.81 (2H, d, J = 8.29 Hz). ^1H NMR ($CDCl_3$) of (*Z*)-form δ 0.94 (6H, d, J = 6.83 Hz), 1.67–1.81 (1H, m), 2.46 (3H, s), 2.55 (2H, m), 5.80 (1H, dt, J = 22.69, 8.54 Hz), 7.34 (2H, d, J = 8.29 Hz), 7.80 (2H, d, J = 8.29 Hz). Found: C, 60.75; H, 6.69%. Calcd for $C_{13}H_{17}FO_2S$: C, 60.91; H, 6.68%.

(*E*)-1-Fluoro-4,4-dimethyl-1-tosyl-1-pentene (3d). An oil; IR (neat) 3065, 2959, 2870, 1670, 1597, 1475, 1367, 1343, 1157, 1103, 1042, 814, 734, 665 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.93 (9H, s), 2.08 (2H, dd, J = 2.20, 8.29 Hz), 2.45 (3H, s), 6.29 (1H, dt, J = 32.20, 8.29 Hz), 7.37 (2H, d, J = 8.29 Hz), 7.83 (2H, d, J = 8.29 Hz). MS *m/z* 270 (M^+, 4.45%), 255 (2.57), 214 (100.00), 139 (78.43), 91 (29.20), 65 (13.56), 57 (38.08).

(*E*)-3-Ethoxy-1-fluoro-1-tosyl-1-propene (3e). An oil [separated by column chromatography with aluminium oxide 90 active basic (Merck, 101076, Activity I, hexane/AcOEt = 8/1)]; IR (neat) 3068, 2979, 2929, 2344, 1735, 1676, 1597, 1448, 1377, 1338, 1306, 1166, 1122, 1035, 1011, 816, 705, 667 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.20 (3H, t, J = 7.07 Hz), 2.46 (3H, s), 3.48 (2H, q, J = 7.07 Hz), 4.17 (2H, dd, J = 2.93, 6.59 Hz), 6.36 (1H, dt, J = 32.69, 6.59 Hz), 7.38 (2H, d, J = 8.05 Hz), 7.84 (2H, d, J = 8.05 Hz). MS *m/z* 258 (M^+, 0.05%), 201 (31.46), 140 (23.98), 139 (42.98), 103.15 (84.15), 92 (60.01), 91 (52.41), 75 (100.00), 65 (35.06).

(*E*)-1-Fluoro-3-phenyl-1-tosyl-1-propene (3f). Mp 101.0–101.5 °C (from hexane/AcOEt); IR (KBr) 3073, 3029, 2929, 1668, 1596, 1494, 1456, 1401, 1385, 1334, 1305, 1202, 1155, 1104, 1082, 1064, 1014, 936, 895, 876, 819, 759, 702, 667 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.46 (3H, s), 3.53 (2H, dd, J = 2.32, 7.93 Hz), 6.41 (1H, dt, J = 31.71, 7.93 Hz), 7.14–7.33 (5H, m), 7.38 (2H, d, J = 8.29 Hz), 7.83 (2H, d, J = 8.29 Hz). Found: C, 66.01; H, 5.33%. Calcd for $C_{16}H_{15}FO_2S$: C, 66.19; H, 5.21%.

(*E*)-1-Fluoro-3-(methoxymethoxy)-1-tosyl-1-propene (3g). An oil; IR (neat) 3067, 2949, 2889, 2826, 1676, 1596, 1493, 1450, 1383, 1338, 1306, 1213, 1166, 1155, 1126, 1086, 1051, 923, 815, 705, 666 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.46 (3H, s), 3.35 (3H, s), 4.25 (2H, dd, J = 2.93, 6.60 Hz), 4.61 (2H, s), 6.37 (1H, dt, J = 32.46, 6.60 Hz), 7.38 (2H, d, J = 8.25 Hz), 7.84 (2H, d, J = 8.25 Hz). MS *m/z* 274 (M^+, 0.12%), 214 (9.11), 155 (5.86), 139 (69.08), 119 (22.77), 99 (5.91), 91 (39.27), 65 (17.76), 58 (38.17), 45 (100.00), 43 (98.43).

(*E*)-3-Fluoro-3-tosyl-2-propen-1-ol (3h). After (*E*)-1-fluoro-3-(methoxymethoxy)-1-tosyl-1-propene (**3g**, 252 mg, 0.919 mmol) was dissolved in THF (10 mL), 6 M HCl (5 mL) and H_2O (5 mL) were added to it. After stirring for 16 h at room temperature, the reaction mixture was stirred at 50 °C for 4 h. Then a saturated NH_4Cl solution was added to the reaction mixture and the solvent was evaporated. The organic substances were extracted with ethyl acetate, followed by washing with H_2O and brine, and dried over Na_2SO_4. After evaporating the solvent, the product **3h** was isolated by preparative TLC (hexane/AcOEt = 2/1) in 99% yield (210 mg). An oil; IR (neat) 3384, 3065, 2950, 2920, 2850, 1676, 1596, 1450, 1340, 1186, 1165, 1127, 1085, 1058, 811, 780, 705 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.65 (1H, brs), 2.47 (3H, s), 4.74 (2H, dd, J = 2.68, 6.59 Hz), 6.34 (1H, dt, J = 31.47, 6.59 Hz), 7.39 (2H, d, J = 8.29 Hz), 7.84 (2H, d, J = 8.29 Hz). MS *m/z* 230 (M^+, 8.84%), 201 (100.00), 156 (24.34), 139 (48.17), 91 (68.97), 65 (28.76), 43 (24.23).

(*E*)-3-Bromo-1-fluoro-1-tosyl-1-propene (3i). To a solution of (*E*)-3-fluoro-3-tosyl-2-propen-1-ol (**3h**, 73 mg, 0.317 mmol) in CH_2Cl_2 (1.5 mL) was added a solution of PBr_3 (34 mg, 0.127 mmol) in CH_2Cl_2 (1.5 mL) at −70 °C under a nitrogen atmosphere. After stirring for 6 h at room temperature, the reaction mixture was quenched with H_2O. The solvent was evaporated and the organic substances were extracted with ethyl acetate, followed by washing with brine and dried over Na_2SO_4. After evaporating the solvent, the product **3i** was isolated by preparative TLC (hexane/AcOEt = 3/1) in 55% yield (55 mg). An oil; IR (neat) 3076, 2925, 1668, 1596, 1492, 1442, 1402, 1341, 1305, 1213, 1191, 1154, 1097, 1076, 1032, 1016, 912, 866, 815, 747, 704, 668 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.47 (3H, s), 3.97 (2H, dd, J = 1.96, 8.52 Hz), 6.48 (1H, dt, J = 29.04, 8.52 Hz), 7.40 (2H, d, J = 8.04 Hz), 7.84 (2H, d, J = 8.04 Hz). MS *m/z* 294 [$M^+(^{81}Br)$, 10.38%], 292 [$M^+(^{79}Br)$, 10.54], 155 (9.35), 139 (100.00), 91 (58.54), 65 (25.91), 43 (71.19).

(*E*)-3-(Benzylthio)-1-fluoro-1-tosyl-1-propene (3j). To a solution of benzenemethanethiol (12 mg, 0.096 mmol) in THF (1.5 mL), Et_3N (0.013 mL, 0.096 mmol) was added under a nitrogen atmosphere. After 30 min, this solution was transferred to a solution of (*E*)-3-bromo-1-fluoro-1-tosyl-1-propene (**3i**, 28 mg, 0.096 mmol) in THF (2.5 mL) very slowly. After stirring for 6 h at room temperature, the reaction mixture was quenched with a phosphate buffer solution (pH = 7). The solvent was evaporated and the organic substances were extracted with ethyl acetate, followed by washing with brine and dried over Na_2SO_4. After removal of the solvent, the product **3j** was isolated by preparative TLC (hexane/AcOEt = 15/1) in 65% yield (21 mg). An oil; IR (neat) 3060, 3030, 2921, 2850, 1655, 1596, 1493, 1452, 1339, 1305, 1155, 1099, 1070, 1015, 814, 699, 661 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.46 (3H, s), 3.12 (2H, dd, J = 1.95, 8.05 Hz), 3.62 (2H, s), 6.27 (1H, dt, J = 30.74, 8.05 Hz), 7.19–7.30 (5H, m), 7.38 (2H, d, J = 8.05 Hz), 7.84 (2H, d, J = 8.05 Hz). MS *m/z* 336 (M^+, 0.88%), 181 (5.28), 165 (1.88), 155 (0.26), 139 (14.31), 123 (37.26), 92 (12.85), 91 (100.00), 79 (1.58), 77 (5.09), 65 (17.05), 39 (7.86).

(*E*)-1,3-Difluoro-1-tosyl-1-propene (3k). To a suspension of AgF (539 mg, 4.248 mmol, 3 mol amt.) in CH_3CN (35 mL) was added slowly a solution of (*E*)-3-bromo-1-fluoro-1-tosyl-1-propene (**3i**, 415 mg, 1.416 mmol) in CH_3CN (15 mL) in the dark under a nitrogen atmosphere. Even after stirring for 18 h, no reaction occurred (monitored by TLC). The reaction mixture was then stirred at 50 °C for 3 h; still, the reaction did not occur. Then, another 3 mol amt. of AgF was added to the reaction mixture and stirred overnight at room temperature. The reaction mixture was filtered, and the solvent was evaporated. The residue was separated by column chromatography (hexane/AcOEt = 5/1) to afford **3k** in 59% yield (193 mg). An oil; IR (neat) 3082, 2960, 2926, 1680, 1596, 1494, 1458, 1387, 1340, 1306, 1168, 1131, 1086, 1041, 1017, 991, 815, 734, 705, 667 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.48 (3H, s), 5.08 (2H, ddd, J = 2.93, 6.36, 46.12 Hz), 6.44 (1H, ddt, J = 31.48, 12.20, 6.36 Hz), 7.40 (2H, d, J = 8.29 Hz), 7.85 (2H, d, J = 8.29 Hz). ^1H NMR (CD_3CN) δ 2.46 (3H, s), 5.10 (2H, ddd, J = 2.75, 6.24, 46.03 Hz), 6.46 (1H, ddt, J = 32.92, 13.21, 6.24 Hz), 7.49 (2H, d, J = 8.25 Hz), 7.84 (2H, d, J = 8.25 Hz). MS *m/z* 232 (M^+, 30.37%), 155 (12.80), 139 (100.00), 91 (69.57), 65 (21.02).

Conversion of (*E*)-α-Fluorovinylic Sulfones 3a–f,j to the Corresponding Allylic Sulfones. To a solution of (*E*)-α-fluorovinylic sulfone **3** (0.72 mmol) in dry acetonitrile (8 mL) was added DBU (0.22 mL, 1.44 mmol) at 25 °C. An aliquot (1 mL) of the reaction mixture was taken out with a syringe at arbitrary time intervals and immediately quenched by introducing into a phosphate buffer solution (pH 7). After concentration under reduced pressure to remove the acetonitrile, the organic substances were extracted with ethyl acetate, followed by washing with brine and drying over Na_2SO_4. The ^{1}H NMR spectrum of the residue obtained by evaporation of the solvent was taken to determine the ratio of the (*E*)- and (*Z*)-allylic sulfones **4** and the unaffected vinylic sulfone (**3**). Some of the residues were separated by TLC to determine the isolated total yield.

Direct Observation of the Isomerization of 3k to 4k by ^{1}H NMR: To a solution of (*E*)-1,3-difluoro-1-tosyl-1-propene (**3k**) (47 mg, 0.202 mmol) in CD_3CN (3 mL) was added a solution of trimethylphenylsilane (10.28 mg, 0.0683 mmol) in CD_3CN (0.5 mL) and a solution of DBU (61 mg, 0.4 mmol) in CD_3CN (0.5 mL) at 25 °C under a nitrogen atmosphere. After adding DBU, ca. 0.5 mL of the reaction mixture was taken out into a NMR tube under a nitrogen atmosphere to take 400 MHz ^{1}H NMR spectrum. The amounts of the **(*E*)-3k**, **(*E*)-4k**, and **(*Z*)-4k** were determined based on a CH_3 signal in trimethylphenylsilane as an internal standard. After 55 h, the reaction mixture in the NMR tube was combined with that in the reaction flask and quenched with a phosphate-buffer solution (pH = 7). After evaporating the solvent, the organic substances were extracted with ethyl acetate, washed with H_2O and brine, and dried over Na_2SO_4. The crude product was separated by TLC (hexane/AcOEt = 5/1) to obtain the product **4k** in the same yield (26%, 12 mg) as determined by the NMR spectrum.

As unambiguous assignment of the stereochemistry of **(*E*)-** and **(*Z*)-4k** by measuring ^{1}H NMR of the mixture of them, each isomer was carefully separated by HPLC from the sample obtained at the initial stage of the isomerization and subjected to NMR analysis.

The physical and spectral data of the resulting allylic sulfones **4** are given in the following.

1-Fluoro-1-tosyl-2-butene (4a). (*E*/*Z* = 84/16). Mp 47.0–48.0 °C (from hexane, *E*/*Z* mixture); IR (KBr) 3038, 2955, 1666, 1595, 1450, 1324, 1294, 1150, 1088, 1006, 962, 830, 813, 748, 718, 661 cm^{-1}; ^{1}H NMR ($CDCl_3$) of (*E*)-form δ 1.83 (3H, m), 2.47 (3H, s), 5.42 (1H, dd, J = 7.07, 47.08 Hz), 5.61 (1H, dddq, J = 7.07, 13.42, 15.37, 1.71 Hz), 6.07–6.22 (1H, m), 7.38 (2H, d, J = 8.29 Hz), 7.80 (2H, d, J = 8.29 Hz). Decoupled ^{1}H NMR ($CDCl_3$) by irradiation of the terminal methyl protons of (*E*)-form δ 2.47 (3H, s), 5.43 (1H, ddd, J = 0.98, 7.08, 47.08 Hz), 5.61 (1H, ddd, J = 7.08, 13.42, 15.37 Hz), 6.12 (1H, ddd, J = 0.98, 3.78, 15.37 Hz), 7.38 (2H, d, J = 8.29 Hz), 7.80 (2H, d, J = 8.29 Hz). ^{1}H NMR ($CDCl_3$) of (*Z*)-form δ 1.83 (3H, m), 2.47 (3H, s), 5.35–5.46 (1H, m), 5.80 (1H, dd, J = 8.54, 47.33 Hz), 6.07–6.22 (1H, m), 7.38 (2H, d, J = 8.29 Hz), 7.80 (2H, d, J = 8.29 Hz). Decoupled ^{1}H NMR ($CDCl_3$) by irradiation of the terminal methyl protons of (*Z*)-form δ 2.47 (3H, s), 5.41 (1H, ddd, J = 8.54, 11.47, 12.93 Hz), 5.80 (1H, ddd, J = 0.98, 8.54, 47.33 Hz), 6.17 (1H, dd, J = 3.90, 11.47 Hz), 7.38 (2H, d, J = 8.29 Hz), 7.80 (2H, d, J = 8.29 Hz). HRMS (FAB) (M^+ + 1), Found: *m*/*z* 229.0692. Calcd for $C_{11}H_{14}FO_2S$: 229.0699.

1-Fluoro-1-tosyl-2-pentene (4b). (*E*/*Z* = 87/13). An oil; IR (neat) 3032, 2967, 2933, 2876, 1663, 1597, 1459, 1328, 1305, 1220, 1153, 1107, 1088, 1018, 970, 817, 661 cm^{-1}; ^{1}H NMR ($CDCl_3$) of (*E*)-form δ 1.02 (3H, t, J = 7.56 Hz), 2.12–2.28 (2H, m), 2.47 (3H, s), 5.44 (1H, dd, J = 6.84, 46.84 Hz), 5.50–5.62 (1H, m), 6.08–6.18 (1H, m), 7.38 (2H, d, J = 8.28 Hz), 7.80 (2H, d, J = 8.28 Hz). Decoupled ^{1}H NMR ($CDCl_3$) by irradiation of the methylene protons of (*E*)-form δ 1.01 (3H, s), 2.52 (3H, s), 5.45 (1H, dd, J = 6.83, 47.08 Hz), 5.57 (1H, ddd, J = 6.83, 13.91, 15.61 Hz), 6.14 (1H, dd, J = 2.44, 15.61 Hz), 7.39 (2H, d, J = 8.29 Hz), 7.81 (2H, d, J = 8.29 Hz). ^{1}H NMR ($CDCl_3$) of (*Z*)-form δ 1.05 (3H, t, J = 7.56 Hz), 2.12–2.28 (2H, m), 2.47 (3H, s), 5.30–5.40 (1H, m), 5.77 (1H, dd, J = 7.80, 46.12 Hz), 6.02–6.22 (1H, m), 7.38 (2H, d, J = 8.28 Hz), 7.82 (2H, d, J = 8.28 Hz). Decoupled ^{1}H NMR ($CDCl_3$) by irradiation of the methylene protons of (*Z*)-form δ 1.04 (3H, s), 2.53 (3H, s), 5.36 (1H, ddd, J = 8.54, 11.24, 12.93 Hz), 5.78 (1H, ddd, J = 1.20, 8.54, 47.12 Hz), 6.07 (1H, dd, J = 1.20, 11.24 Hz), 7.39 (2H, d, J = 8.05 Hz), 7.83 (2H, d, J = 8.05 Hz). HRMS (FAB) (M^+ + 1), Found: *m*/*z* 243.0858. Calcd for $C_{12}H_{16}FO_2S$: 243.0855.

1-Fluoro-4-methyl-1-tosyl-2-pentene (4c). (*E*/*Z* = 91/9). An oil; IR (neat) 3031, 2963, 2930, 2872, 1662, 1597, 1467, 1330, 1305, 1293, 1220, 1154, 1088, 1018, 975, 841, 816, 758, 704, 665 cm^{-1}; ^{1}H NMR ($CDCl_3$) of (*E*)-form δ 0.99 (3H, d, J = 6.84 Hz), 1.00 (3H, d, J = 6.84 Hz), 2.32–2.45 (1H, m), 2.47 (3H, s), 5.45 (1H, dd, J = 6.83, 46.11 Hz), 5.51 (1H, dddd, J = 1.46, 6.83, 14.52, 15.86 Hz), 6.02 (1H, dd, J = 7.08, 15.86 Hz), 7.37 (2H, d, J = 8.29 Hz), 7.80 (2H, d, J = 8.29 Hz). ^{1}H NMR ($CDCl_3$) of (*Z*)-form δ 1.07 (6H, d, J = 6.60 Hz), 2.32–2.45 (1H, m), 2.47 (3H, s), 5.25 (1H, dt, J = 11.22, 8.78 Hz), 5.79 (1H, dd, J = 8.78, 47.33 Hz), 5.88 (1H, t, J = 11.22 Hz), 7.37 (2H, d, J = 8.05 Hz), 7.82 (2H, d, J = 8.05 Hz). HRMS (FAB) (M^+ + 1), Found: *m*/*z* 257.1049. Calcd for $C_{13}H_{18}FO_2S$: 257.1012.

(*E*)-1-Fluoro-4,4-dimethyl-1-tosyl-2-pentene (4d). An oil; IR (neat) 2962, 2869, 1655, 1597, 1460, 1365, 1329, 1305, 1227, 1153, 1112, 1087, 1038, 1013, 976, 922, 816, 742, 704, 665 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.00 (9H, s), 2.46 (3H, s), 5.45 (1H, ddd, J = 6.59, 13.17, 15.61 Hz), 5.46 (1H, dd, J = 6.59, 48.79 Hz), 6.00 (1H, dd, J = 2.80, 15.61 Hz), 7.37 (2H, d, J = 8.28 Hz), 7.78 (2H, d, J = 8.28 Hz). MS *m*/*z* 270 (M^+, 0.15%), 155 (9.30), 139 (5.49), 115 (100.00), 91 (42.26), 73 (52.25), 65 (20.74).

1-Ethoxy-3-fluoro-3-tosyl-1-propene (4e). (*E*/*Z* = 63/37). An oil [separated by column chromatography with aluminium oxide 90 active basic (Merck, 101076, Activity I, hexane/AcOEt = 10/1); gradually decomposed at room temperature]; IR (neat) 3067, 2978, 2929, 1732, 1674, 1596, 1495, 1446, 1400, 1377, 1337, 1305, 1214, 1165, 1119, 1012, 920, 815, 704, 666 cm^{-1}; ^{1}H NMR ($CDCl_3$) of (*E*)-form δ 1.32 (3H, t, J = 7.08 Hz), 2.47 (3H, s), 3.89 (1H, dq, J = 15.84, 7.08 Hz), 3.90 (1H, dq, J = 15.84, 7.08 Hz), 4.85 (1H, ddd, J = 8.28, 9.28, 12.72 Hz), 5.36 (1H, dd, J = 9.28, 47.08 Hz), 6.79 (1H, dd, J = 4.64, 12.72 Hz), 7.38 (2H, d, J = 8.28 Hz), 7.82 (2H, d, J = 8.28 Hz). ^{1}H NMR ($CDCl_3$) of (*Z*)-form δ 1.27 (3H, t, J = 7.08 Hz), 2.46 (3H, s), 3.87 (1H, dq, J = 9.44, 7.08 Hz), 3.97 (1H, dq, J = 9.44, 7.08 Hz), 4.56 (1H, ddd, J = 6.12, 7.80, 9.76 Hz), 6.03 (1H, dd, J = 9.76, 47.60 Hz), 6.52 (1H, dd, J = 2.44, 6.12 Hz), 7.37 (2H, d, J = 8.08 Hz), 7.84 (2H, d, J = 8.08 Hz). MS *m*/*z* 258 (M^+, 22.97%), 165 (4.35), 139 (100.00), 123 (9.93), 92 (22.71), 91 (48.15), 77 (13.73), 75 (10.37), 65 (31.90), 57 (13.97), 43 (7.34), 39 (18.15), 29 (69.69).

(*E*)-3-Fluoro-1-phenyl-3-tosyl-1-propene (4f). Mp 151 °C (from hexane/AcOEt); IR (KBr) 3059, 3024, 2948, 2920, 2844, 1648, 1593, 1490, 1450, 1322, 1150, 1085, 1017, 973, 817, 767, 734, 695 cm^{-1}; ^{1}H NMR ($CDCl_3$) of (*E*)-form δ 2.47 (3H, s), 5.68 (1H, ddd, J = 1.22, 6.59, 47.08 Hz), 6.21 (1H, ddd, J = 6.59, 15.66, 16.10 Hz), 6.84 (1H, dd, J = 1.71, 16.10 Hz), 7.31–7.38 (7H, m), 7.82 (2H, d, J = 8.05 Hz). HRMS (FAB) (M^+ + 1),

Found: *m/z* 291.0873. Calcd for $C_{16}H_{16}FO_2S$: 291.0856. Found: C, 66.15; H, 5.25%. Calcd for $C_{16}H_{15}FO_2S$: C, 66.19; H, 5.21%.

1-(Benzylthio)-3-fluoro-3-tosyl-1-propene (4j). (*E*/*Z* = 87/13). Gummy substance; IR (neat) 3022, 2969, 1591, 1494, 1454, 1395, 1321, 1293, 1148, 1118, 1086, 1018, 939, 847, 817, 712, 661 cm^{-1}; ^1H NMR ($CDCl_3$) of (*E*)-form δ 2.46 (3H, s), 3.97 (2H, s), 5.45 (1H, dd, J = 7.08, 39.32 Hz), 5.54 (1H, ddd, J = 7.08, 15.12, 15.37 Hz), 6.67 (1H, dd, J = 2.93, 15.12 Hz), 7.25–7.36 (7H, m), 7.72 (2H, d, J = 8.29 Hz). ^1H NMR ($CDCl_3$) of (*Z*)-form δ 2.46 (3H, s), 3.93 (2H, s), 5.42-5.48 (1H, m), 5.87 (1H, dd, J = 8.54, 46.59 Hz), 6.72 (1H, ddd, J = 0.92, 2.14, 9.77 Hz), 7.25–7.36 (7H, m), 7.80 (2H, d, J = 8.08 Hz). MS *m/z* 336 (M^+, 0.41%), 181 (98.54), 163 (10.45), 155 (8.52), 123 (5.27), 91 (100.00), 65 (52.54), 43 (25.03).

1,3-Difluoro-3-tosyl-1-propene (4k). (*E*)-form: Mp 57–58 °C (from hexane/AcOEt), IR (KBr) 2931, 2364, 1673, 1595, 1322, 1299, 1267, 1218, 1153, 1119, 1084, 1021, 927, 853, 811, 776 cm^{-1}; ^1H NMR ($CDCl_3$, 750 MHz) δ 2.48 (3H, s), 5.46 (1H, dd, J = 8.06, 46.84 Hz), 5.56 (1H, dddd, J = 8.06, 11.08, 13.47, 14.67 Hz), 6.87 (1H, ddd, J = 3.53, 11.08, 78.57 Hz), 7.41 (2H, d, J = 8.25 Hz), 7.81 (2H, d, J = 8.25 Hz). ^1H NMR (CD_3CN) δ 2.47 (3H, s), 5.60 (1H, dddd, J = 8.78, 11.10, 11.22, 15.36 Hz), 5.76 (1H, dd, J = 8.78, 46.11 Hz), 7.07 (1H, dddd, J = 0.76, 4.64, 11.22, 79.77 Hz), 7.49 (2H, d, J = 8.29 Hz), 7.80 (2H, d, J = 8.29 Hz). ^{19}F NMR ($CDCl_3$) δ −173.69 (1F, m), −112.33 (1F, ddd, J = 0.67, 14.67, 78.57 Hz). HRMS (FAB) (M^+ + 1), Found: *m/z* 233.0454. Calcd for $C_{10}H_{11}F_2O_2S$: 233.0448.

(*Z*)-form: Mp 66.5–67.5 °C (from hexane/AcOEt), IR (KBr) 3112, 1669, 1597, 1387, 1324, 1309, 1294, 1252, 1210, 1155, 1120, 1088, 1032, 984, 829, 802, 783, 706, 676 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.48 (3H, s), 5.13 (1H, dtd, J = 4.88, 9.27, 36.59 Hz), 5.95 (1H, dd, J = 9.27, 47.33 Hz), 6.87 (1H, ddd, J = 0.98, 4.88, 80.26 Hz), 7.41 (2H, d, J = 8.27 Hz), 7.84 (2H, d, J = 8.27 Hz). ^1H NMR (CD_3CN) δ 2.47 (3H, s), 5.15 (1H, dddd, J = 4.88, 9.27, 10.25, 38.06 Hz), 6.14 (1H, dd, J = 9.27, 46.59 Hz), 6.99 (1H, dddd, J = 0.73, 1.95, 4.88, 80.99 Hz), 7.49 (2H, d, J = 8.27 Hz), 7.82 (2H, d, J = 8.27 Hz). ^{19}F NMR ($CDCl_3$) δ −173.46 (1F, m), −114.12 (1F, ddd, J = 7.60, 36.59, 80.26 Hz). Found: C, 51.78; H, 4.40%. Calcd for $C_{10}H_{10}F_2O_2S$: C, 51.72; H, 4.34%.

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