  Bull. Chem. Soc. Jpn., 65, 75—96 (1992)

"*Syn-Effect*"[1] in the Conversion of (*E*)-Vinylic Sulfones to the Corresponding Allylic Sulfones

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(Received August 5, 1991)

It was found that (*E*)-vinylic sulfones preferentially afford (*Z*)-allylic sulfones as kinetically-controlled products by treatment with a base under mild conditions, while (*Z*)-vinylic sulfones give (*E*)-allylic sulfones. Such stereochemical relationship was rationalized by "*syn-effect*", and its relative degree for various substituents was determined by observation of *E*/*Z* ratios of the allylic sulfones resulted from the corresponding γ-mono- or γ,γ-disubstituted vinylic sulfones as follows: RO–(R=CH_3, C_2H_5)≅ArO–(Ar=*p*-$CH_3OC_6H_4$, *p*-$CH_3C_6H_4$, C_6H_5, *p*-$NO_2C_6H_4$)≥AcO–>Cl–≥Br–>CH_3–>CH_3S–≥–CH_2– (cyclic and acyclic)>$(CH_3)_2CH$–>>$(CH_3)_3C$–, C_6H_5–. X-Ray crystallography was performed for some vinylic sulfones to reveal the origin of the "*syn-effect*".

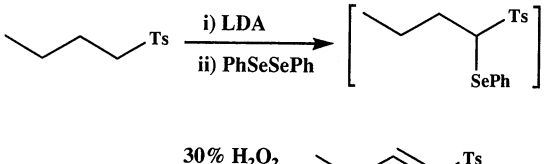
In the previous paper,[2b] we briefly reported regio- and stereoselective syntheses of (*E*)- and (*Z*)-vinylic sulfones from 1-alkenes or 1-alkynes via iodosulfonization, which made it feasible to investigate the stereochemistry of the conversion of vinylic sulfones to the corresponding allylic sulfones by treatment with a base. In the latter investigation, we found that (*E*)-vinylic sulfones preferentially afford (*Z*)-allylic sulfones as kinetically-controlled products, while (*Z*)-vinylic sulfones give (*E*)-allylic sulfones exclusively. The former experimental results were rationalized by the concept "*conformational acidity*" (a sort of kinetic acidity)[2] which essentially depends on a "*syn-effect*".[3]

Several explanations for the "*syn-effect*" have been proposed,[3b] namely (1) 6π-electrons homoaromaticity, (2) σ-orbital interactions, (3) dipole–dipole interactions, (4) chelations, and (5) hydrogen bonding.[3e] In order to make sure which explanation is most suitable in the case of the conversion of vinylic sulfones to allylic sulfones, we determined the relative degree of various substituents by a series of experiments for γ,γ-disubstituted vinylic sulfones.[4a] We describe herein the detail of such experiments including the time-course of the reactions. X-Ray crystallography was performed for some vinylic sulfones to reveal the origin of the "*syn-effect*".

Results and Discussion

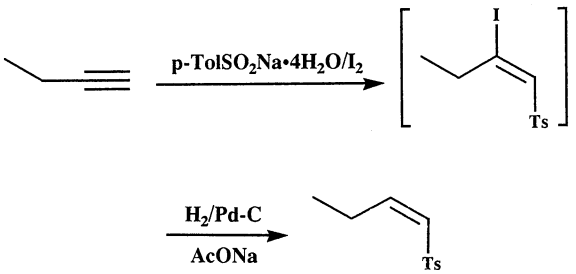
Preparation of Vinylic Sulfones. The stereochemically pure vinylic sulfones used in the present experiments were prepared according to the following Eqs. 1—13. The abbreviation Ts in the Eqs. means *p*-toluenesulfonyl (=tosyl, *p*-$CH_3C_6H_4SO_2$–) group.

(*E*)-1-Tosyl-1-butene [(*E*)-**1**] was prepared from 1-tosylbutane via α-phenylselenation of the sulfone (Eq. 1).[2a] In contrast to the case of the preparation of 1-cyano-1-alkenes,[5] only (*E*)-isomer was obtained. This may be due to the bulkiness of tosyl group.



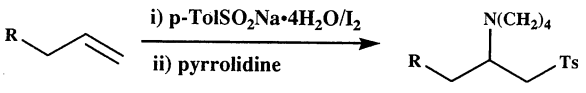
(E)-**1**, 86% (1)

On the other hand, (*Z*)-1-tosyl-1-butene [(*Z*)-**1**] was prepared from 1-butyne via iodosulfonization and the subsequent selective catalytic hydrogenation (Eq. 2).[2b]

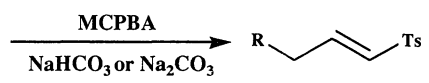


(Z)-**1**, quant. (2)

Other (*E*)-1-tosyl-1-alkenes [(*E*)-**3a**—**f**] were prepared by applying previously reported iodosulfonization of 1-alkenes.[2b] This procedure is superior to the above one described for (*E*)-**1** via α-phenylselenation and is applicable in large scale too (Eq. 3).



2a, R=C_2H_5, not isolated
2b, R=$(CH_3)_2CH$, 99%
2c, R=$(CH_3)_3C$, 98%
2d, R=C_6H_5, not formed
2e, R=p-$CH_3C_6H_4O$, not isolated
2f, R=p-$CH_3OC_6H_4O$, not isolated

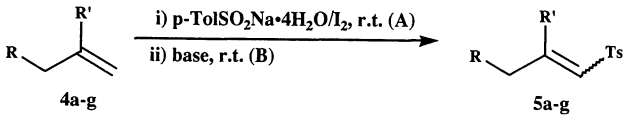


(3)

(E)-3a, quant.
(E)-3b, 94% (from 2b)
(E)-3c, 99% (from 2c)
(E)-3d, 83%
(E)-3e, 73%
(E)-3f, 81%

2-Alkyl-1-tosyl-1-butenes (**5a, b**) and 3-substituted 1-tosyl-1-propenes (**5c—g**) were readily prepared by iodosulfonization of the corresponding 1-alkene derivatives followed by elimination of hydrogen iodide with an amine (Eq. 4 and Table 1).

(*E*)-3-Hydroxy-1-tosyl-1-propene [(*E*)-**5g**] separated by recrystallization from an *E*/*Z* mixture was converted to (*E*)-3-halo-1-tosyl-1-propenes [(*E*)-**6** and **7**] by



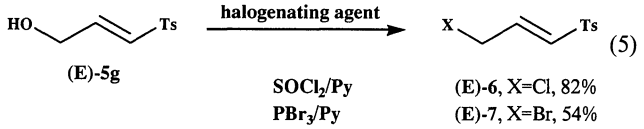
(4)

Table 1.

4a—g	R	R′	(A) Time/h	Base	(B) Time/h	Isolated yield of 5a—g/% (*E*/*Z*)[a]
4a	CH_3	CH_3CH_2	2.5	Et_3N	2.5	**5a** 91 (—)
4b	CH_3	CH_3	3.0	Et_3N	3.0	**5b** 87 (74/26)
4c	C_6H_5O	H	2.0	Py	4.0	**5c** 90 (92/8)
4d	*p*-$NO_2C_6H_4O$	H	24.0	Py	30.0	**5d** 48 (100/0)
4e	C_2H_5O	H	2.5	Py	24.0	**5e** 90 (95/5)
4f	CH_3CO_2	H	2.5	Py	2.0	**5f** 94 (91/9)
4g	HO	H	2.0	Et_3N	2.0	**5g** 90 (83/17)

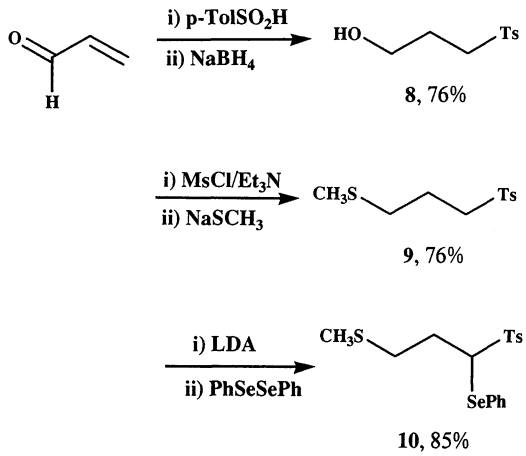
a) Determined by 400 MHz ^{1}H NMR spectra.

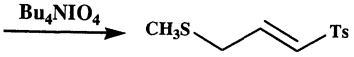
treatment with halogenating agents (Eq. 5).



(5)

Addition of *p*-toluenesulfinic acid toward 2-propenal and the subsequent reduction with sodium borohydride afforded 3-hydroxy-1-tosylpropane (**8**), which was led to (*E*)-3-methythio-1-tosyl-1-propene [(*E*)-**11**] according to Eq. 6. Many attempts to improve the yield of the final step were unsuccessful.

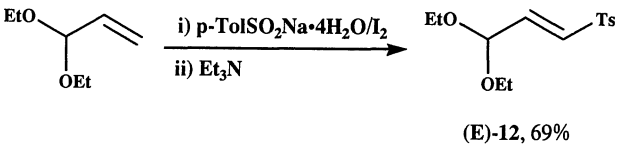




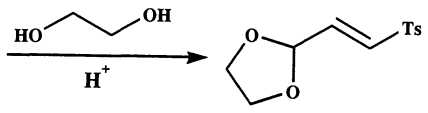
(6)

(E)-11, 16%

(*E*)-3-Tosyl-2-propenal diethyl acetal [(*E*)-**12**] and ethylene acetal [(*E*)-**13**] were prepared from 2-propenal diethyl acetal according to Eq. 7 by applying the iodosulfonization.



(E)-12, 69%

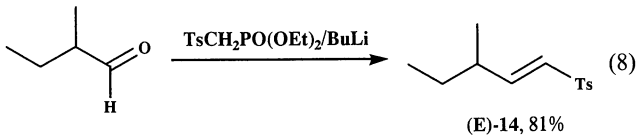


(7)

(E)-13, 97%

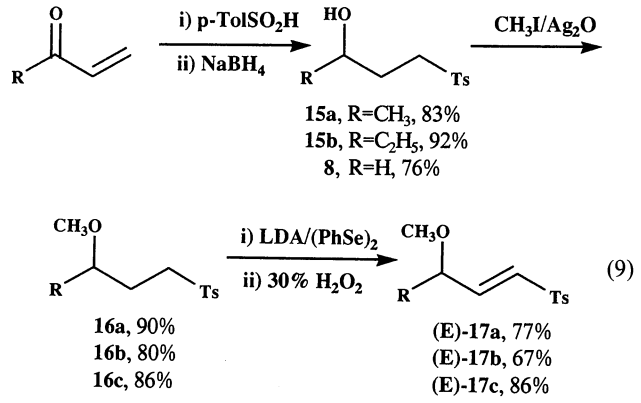
Next, various kinds of γ,γ-disubstituted vinylic sulfones were prepared in order to determine the relative degree of the "*syn-effect*".

Horner–Emmons reaction for 2-methylbutanal with diethyl (tosylmethyl)phosphonate afforded (*E*)-3-methyl-1-tosyl-1-pentene [(*E*)-**14**] without formation of (*Z*)-isomer (Eq. 8).



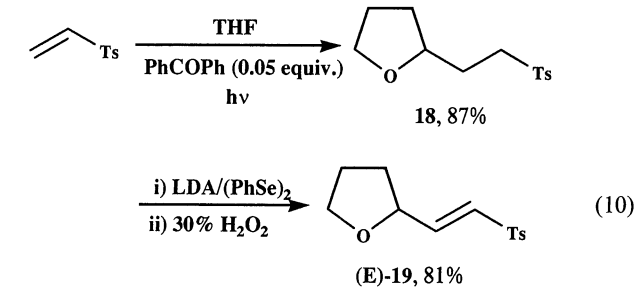
(8)

(*E*)-3-Methoxy-1-tosyl-1-butene and -1-pentene [(*E*)-**17a**, **b**] were prepared starting from methyl vinyl ketone and ethyl vinyl ketone, respectively, according to Eq. 9.



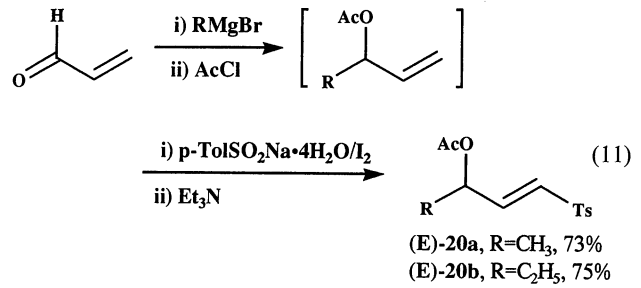
(9)

We previously reported the photoinduced masked-formylation of vinylic sulfones with 1,3-dioxolane, which are useful for the preparation of 3,4-disubstituted pyrroles.[6] A similar photochemical addition reaction of tetrahydrofuran instead of 1,3-dioxolane was successfully employed for the preparation of 2-[(*E*)-2-tosylethenyl]oxolane [(*E*)-**19**] as shown in Eq. 10.



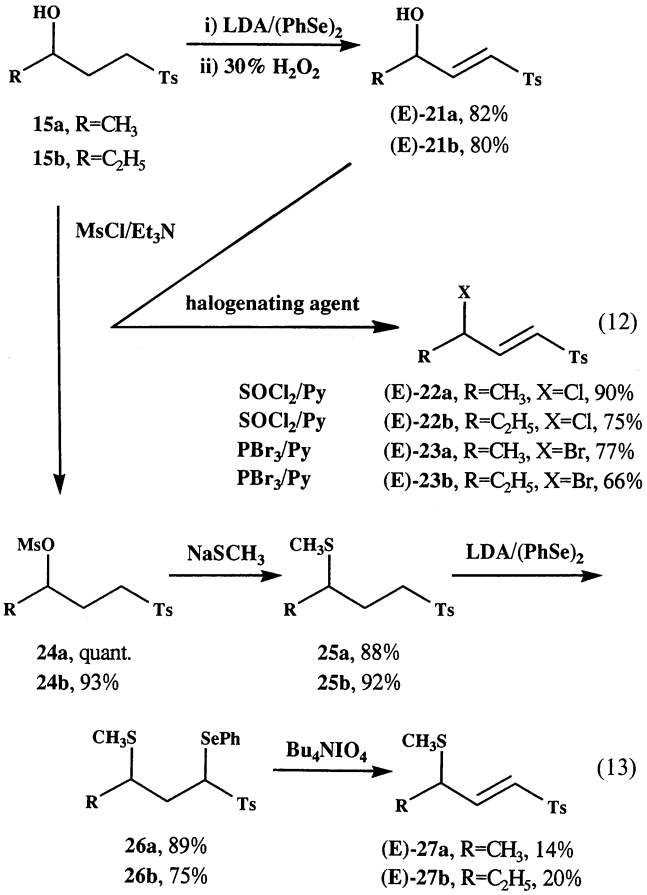
(10)

(*E*)-3-Acetoxy-1-tosyl-1-butene and -1-pentene [(*E*)-**20a**, **b**] were derived from the corresponding 3-acetoxyl-1-alkenes via iodosulfonization and the subsequent treatment with triethylamine to remove hydrogen iodide (Eq. 11). In contrast to the case of the preparation of **5f**, the formation of (*Z*)-isomers was not observed.



(11)

(*E*)-3-Halo- or (*E*)-3-methylthio-1-tosyl-1-butene [(*E*)-**22a**, **23a**, and **27a**] and the corresponding 1-pentene derivatives [(*E*)-**22b**, **23b**, and **27b**] were prepared in the similar manner described for (*E*)-**6**,**7**, and (*E*)-**11**, respectively (Eqs. 12 and 13).



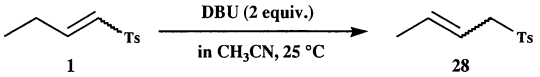
(12)

(13)

Conversion of Vinylic Sulfones to the Corresponding Allylic Sulfones. Conversion of the vinylic sulfones prepared above to the corresponding allylic sulfones under mild basic conditions was investigated to reveal the stereochemical relationship.

At first, (*E*)- and (*Z*)-**1** and their 1/1 mixture were treated with two equivalents of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as a base in acetonitrile at ambient temperature (25 °C). An aliquot of the reaction mixture was taken out at arbitrary time intervals and was immediately quenched by introducing into a phosphate buffer solution (pH 7). The extract with ethyl acetate was worked up in the usual manner. ^{1}H NMR spectrum of the resulting residue was taken to determine the ratio of the (*E*)- and (*Z*)-allylic sulfones (**28**) and the unaffected **1**. Table 2 shows the results of the time-course of the reaction. Since total yields of **1** and **28** after 3 h were over 95%, it is obvious that the conversion reaction proceeded very cleanly without any side reactions. From the Table, it was found that (*E*)-**1** was initially converted to (*Z*)-**28** in preference to the more stable (*E*)-**28**, whereas (*Z*)-**1** to (*E*)-**28**. The final value of *E*/*Z*-

Table 2. Conversion of 1-Tosyl-1-butene (**1**) to 1-Tosyl-2-butene (**28**)



1 28

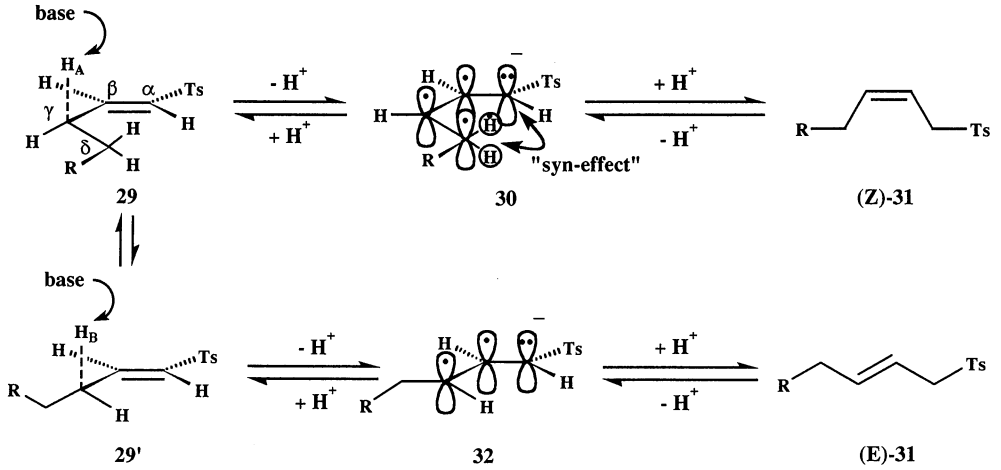
E/*Z* Ratio of **1**	Time	Products ratio[a]				*E*/*Z* of **28**
		(*E*)-**1**	(*Z*)-**1**	(*E*)-**28**	(*Z*)-**28**	
	0 min	100	0	0	0	—
	10 min	65	0	5	30	14/86
	30 min	22	0	9	69	12/88
	1 h	8	0	14	78	15/85
	2 h	5	0	16	79	17/83
100/0	3 h[b]	4	0	17	79	18/82
	6 h	3	0	23	74	24/76
	12 h	2	0	27	71	28/72
	24 h	2	0	40	58	41/59
	48 h	1	0	56	43	57/43
	105 h	1	0	70	29	71/29
	0 min	0	100	0	0	—
	10 min	0	83	17	0	100/0
	30 min	2	34	61	3	95/5
	1 h	1	16	75	8	90/10
	2 h	0	3	86	11	89/11
0/100	3 h[c]	0	0	90	10	90/10
	6 h	0	0	86	14	86/14
	12 h	0	0	88	12	88/12
	24 h	0	0	84	16	84/16
	48 h	0	0	81	19	81/19
	105 h	0	0	79	21	79/21
	0 min	51	49	0	0	—
	10 min	30	37	15	18	45/55
	30 min	11	19	33	37	47/53
	1 h	5	10	42	43	49/51
	2 h	2	3	49	46	52/48
51/49	3 h[d]	2	0	53	45	54/46
	6 h	2	0	54	44	55/45
	12 h	1	0	57	42	58/42
	24 h	1	0	62	37	63/37
	48 h	1	0	66	33	67/33
	105 h	1	0	71	28	72/28

a) Determined by 400 MHz ^{1}H NMR spectra. b) Isolated total yield of products was quantitative. c) Total yield was 95%. d) Total yield was 95%.

ratio of **28** converged to about 70/30 in the equilibrium state as can be seen also in the case starting from the 1/1 mixture of (*E*)- and (*Z*)-**1**.

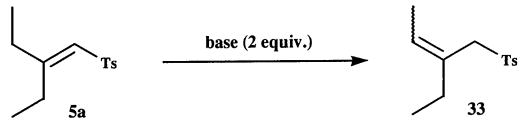
These results, coinciding with the previous ones,[2a] suggest that (*Z*)-**28** is kinetically-controlled product from (*E*)-**1** and the more stable (*E*)-**28** is the thermodynamically-controlled one. The kinetic stereoselectivity of the former reaction has been rationalized by a "*syn-effect*", namely, a stabilizing interaction (**30**) between the developing charge at the α-position and the CH_2-group at the δ-position favoring transition state (**29**) over **29′** for deprotonation (Scheme 1).

In other words, this means that H_A on the γ-carbon of (*E*)-**1** in the conformation **29** is more acidic than H_B in the conformation **29′**. Thus, a new concept "*conformational acidity*" proposed by us[4] is quite important as a factor to determine the stereochemistry of the allylic sulfones kinetically produced. In addition, it should be realized that (*E*)-**1** was a little more reactive than (*Z*)-**1** at the initial step of the reaction, namely the protons on γ-carbon of (*E*)-**1** are a little more acidic than those of (*Z*)-isomer. This agrees with the result observed in the reaction using 2-ethyl-1-tosyl-1-butene (**5a**).[2b] The time-course of the latter reaction is shown in Table 3. To our surprise, (*Z*)-**33** was exclusively obtained using DBU as a base at 25 °C, in contrast to the case where a stronger base, potassium *t*-butoxide, was used in *t*-butyl alcohol at 30 °C or under reflux to attain equilibrium more quickly. The formation of (*E*)-**33** was not observed at the initial stage of the reaction. These facts strongly suggested that the substrate **5a** has the conformation ready to afford the (*Z*)-allylic sulfone [(*Z*)-**33**] before it interacts with DBU. This speculation that "*syn-effect*" works not only in the transition state of the



Scheme 1. A probable course of the conversion of (*E*)-vinylic sulfone to the corresponding allylic sulfone.

Table 3. Conversion of 2-Ethyl-1-tosyl-1-butene (**5a**) to 2-Ethyl-1-tosyl-2-butene (**33**)



Base/Solvent/ Temperature	Time	Products ratio[a]			*E*/*Z* of **33**	Isolated total yield/%
		5a	(*E*)-**33**	(*Z*)-**33**		
	0 min	100	0	0	—	—
	20 min	90	0	10	0/100	—
DBU	40 min	83	0	17	0/100	—
CH_3CN	1 h	69	3	28	10/90	—
25°C	2 h	50	5	45	10/90	—
	3 h	35	6	59	9/91	—
	20 h	0	8	92	8/92	Quant.
	0 min	100	0	0	—	—
t-BuOK	30 min	0	38	62	38/62	Quant.
t-BuOH	1 h	0	39	61	39/61	96
30°C	2 h	0	39	61	39/61	Quant.
	3 h	0	39	61	39/61	96
t-BuOK	0 min	100	0	0	—	—
t-BuOH	5 h	0	46	54	46/54	85
Reflux	10 h	0	46	54	46/54	81

a) Determined by 400 MHz ^{1}H NMR spectra.

conversion of **5a** to **33**, but also in the substrate (**5a**) itself, has been confirmed by the X-ray crystallography as shown in Fig. 1.[4a] H9, C8, C9, C10, and C11 exist on a plane, and H4 and H5 are placed parallel to the axis of p-orbital on C8. Such a structure makes the γ-protons H10 and H11 trans to the sulfonyl group more reactive than H14 and H15 cis to the sulfonyl group toward a base, due to the formation of the anionic intermediate stabilized by 6π-electrons homoaromaticity proposed as an explanation for the "*syn-effect*".[3b] This will be the first structural evidence to support the explanation, if the long distances between C8 and the protons H4 and H5 are reasonable (C8–H4, 2.86 Å; C8–H5, 2.84 Å; C8–C11, 2.89(5) Å) for the through-space interaction.

Such result prompted us to examine the similar reaction using DBU as a base for (*E*)-2-methyl-1-tosyl-1-butene [(*E*)-**5b**] under mild conditions (Table 4). The "*syn-effect*" was again confirmed by the experimental fact that (*Z*)-**34** was initially formed in preference to the thermodynamically more stable (*E*)-**34** which was produced predominantly in equilibrium with potassium *t*-butoxide.

Interestingly, the "*syn-effect*" was also observed for (*E*)-4-methyl-1-tosyl-1-pentene [(*E*)-**3b**] (Table 5). This result shows that the "*syn-effect*" is an important factor to control the stereochemistry even for isopropyl

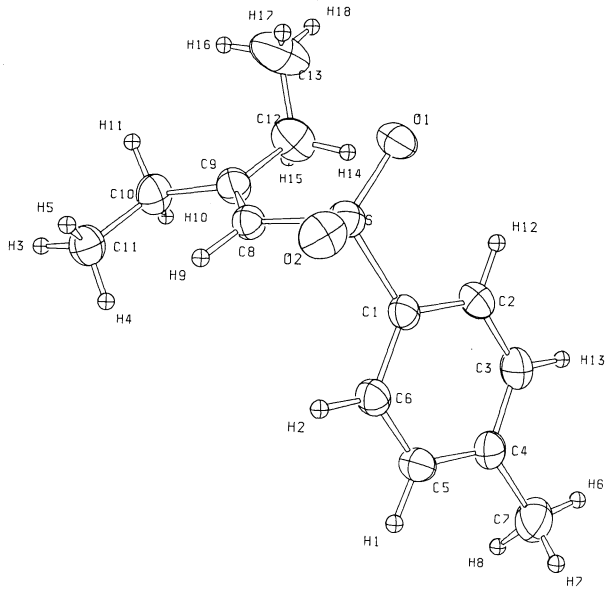


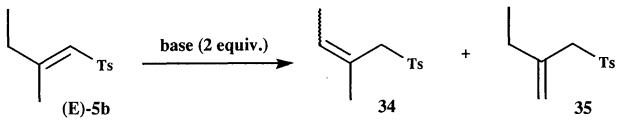
Fig. 1. ORTEP diagram of **5a**.

substituent on γ-position of the vinylic sulfone. On the other hand, it should be noted that only (*E*)-allylic sulfones were obtained from (*E*)-4,4-dimethyl-1-tosyl-1-pentene [(*E*)-**3c**] (Table 5) and 3-phenyl-1-tosyl-1-propenes [(*E*)-**3d**] (Table 6) having the bulky group which precludes the possibility of *syn*-geometry by steric congestion.

The conversion of vinylic sulfone to allylic sulfone was further examined for 3-heteroatom-substituted 1-tosyl-1-propenes (**3**, **5**, **6**, **7**, **11**) as shown in Table 6. (*E*)-Vinylic sulfones are preferentially converted to the corresponding (*Z*)-allylic sulfones, especially when *N*,*N*-diisopropylethylamine was used for (*E*)-3-methylthio-1-tosyl-1-propene [(*E*)-**11**] and (*E*)-3-halo-1-tosyl-1-propenes [(*E*)-**6** and (*E*)-**7**]. On the other hand, (*Z*)-**5c** was predominantly converted to (*E*)-**39** in accord with the tendency observed above for (*Z*)-3-alkylated 1-tosyl-1-propenes.

It is noteworthy that the selectivity of (*Z*)-allylic sulfones from (*E*)-3-heteroatom-substituted vinylic sulfones [(*E*)-**5c**,**d** and (*E*)-**3e**,**f** (Table 7), (*E*)-**5e** (Table 8), and (*E*)-**6**,**7** (Table 10)] is rather higher except **11** (Table 9) compared with the case of (*E*)-3-alkyl-substituted vinylic sulfones. In order to reveal the origin of such high (*Z*)-selectivity, X-ray crystallography of (*E*)-3-phenoxy-1-tosyl-1-propene [(*E*)-**5c**] was performed (Fig. 2). It was found that H1, C1, C2, C3, O3, and H5, C17, C18, C19, O6 exist on a plane, respectively, showing that "*syn-effect*" works in the solid state of (*E*)-**5c**. The *syn*-conformation seems to arise from the intramolecular hydrogen bonding between the acidic α-hydrogen (H1 and H5), neighboring to the electron-withdrawing tosyl group, and oxygens (O3 and O6) using the electron pairs of their sp^2 orbitals (O3–H1 2.36 Å, O6–H5 2.39 Å) and/or dipole–dipole interaction between C_{sp^2}←H and C→OR. However, 6π-electrons homoaromaticity could not be excluded in spite of the long distance of O3–C1 (2.72(2) Å) and O6–C17 (2.78(2) Å), because there are p-orbitals on oxygen atoms (O3 and O6) conjugating with a phenyl group, which appear to correspond to the pseudo-p-orbital of the methyl group useful to stabilize *syn*-conformation of **5a** in which the intramolecular hydrogen bonding is impossible. Crystallographic analysis was therefore performed for (*E*)-3-tosyl-2-propenal ethylene acetal [(*E*)-**13**] which gave single

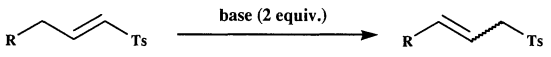
Table 4. Conversion of (*E*)-2-Methyl-1-tosyl-1-butene [(*E*)-**5b**] to 2-Methyl-1-tosyl-2-butene (**34**) or 2-Tosylmethyl-1-butene (**35**)



Base/Solvent/ Temperature	Time	Products ratio[a]				*E*/*Z* of **34**	Isolated total yield/%
		(*E*)-**5b**	(*E*)-**34**	(*Z*)-**34**	**35**		
DBU	0 min	100	0	0	0	—	—
CH_3CN/25°C	19 h	0	6	84	10	7/93	Quant.
	0 min	100	0	0	0	—	—
t-BuOK	30 min	0	29	69	2	30/70	Quant.
t-BuOH	1 h	0	35	64	1	35/65	92
30°C	3 h	0	48	51	1	48/52	96
	23 h	0	62	37	1	63/37	96
	0 min	100	0	0	0	—	—
t-BuOK	30 min	0	63	36	1	64/36	93
t-BuOH	2 h	0	64	35	1	65/35	81
Reflux[b]	5 h	0	63	36	1	64/36	69

a) Determined by 400 MHz ^1H NMR spectra. b) Products gradually decomposed under reflux. Total yield was only 3% after refluxing for 2 d.

Table 5. Conversion of (*E*)-4-Methyl- and (*E*)-4,4-Dimethyl-1-tosyl-1-pentene [(*E*)-**3b,c**] to the Corresponding 1-Tosyl-2-pentene Derivatives (**36** and **37**)



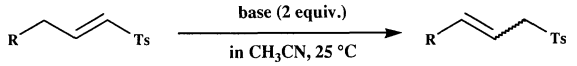
R=i-Pr, (E)-3b
R=t-Bu, (E)-3c

36
37

R	Base/Solvent/ Temperature	Time	Products ratio[a]			*E*/*Z* of **36**	Isolated total yield/%
			(*E*)-**3b**	(*E*)-**36**	(*Z*)-**36**		
		0 min	100	0	0	—	—
		30 min	73	11	16	41/59	—
		1 h	59	16	25	40/60	—
	DBU	2 h	38	25	37	40/60	—
	CH_3CN	4 h	16	36	48	42/58	—
	25°C	6 h	9	41	50	45/55	—
		12 h	8	49	43	53/47	97
i-Pr		25 h	6	66	28	70/30	—
		48 h	4	76	20	79/21	—
		0 min	100	0	0	—	—
	t-BuOK	1 h	0	87	13	87/13	86
	t-BuOH	6 h	0	87	13	87/13	—
	30°C	12 h	0	88	12	88/12	—
		24 h	0	87	13	87/13	—
			(*E*)-**3c**	(*E*)-**37**	(*Z*)-**37**	*E*/*Z* of **37**	
		0 min	100	0	0	—	—
		30 min	91	9	0	100/0	—
		1 h	88	12	0	100/0	—
	DBU	2 h	78	22	0	100/0	—
t-Bu	CH_3CN	4 h	65	35	0	100/0	—
	25°C	6 h	54	46	0	100/0	—
		12 h	31	69	0	100/0	—
		24 h	13	87	0	100/0	98
		48 h	2	98	0	100/0	—

a) Determined by 400 MHz ^{1}H NMR spectra.

Table 6. Conversion of 3-Substituted 1-Tosyl-1-propenes to 3-Substituted 1-Tosyl-2-propenes



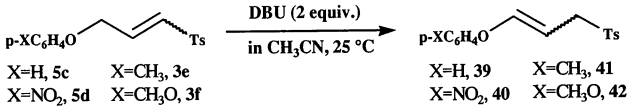
3, 5, 6, 7, 11

38-47

Substrate	R	Base	Time/h	Isolated yield of **38**—**47**/% (*E*/*Z*)[a]		
(*E*)-**3d**	C_6H_5	DBU	1	**38**	Quant.	(100/0)
(*E*)-**5c**	C_6H_5O	DBU	0.5	**39**	100	(3/97)[b]
(*Z*)-**5c**	C_6H_5O	DBU	0.5	**39**	95	(85/15)[b]
(*E*)-**5d**	*p*-$NO_2C_6H_4O$	DBU	0.5	**40**	Quant.	(3/97)[b]
(*E*)-**3e**	*p*-$CH_3C_6H_4O$	DBU	0.5	**41**	Quant.	(1/99)[b]
(*E*)-**3f**	*p*-$CH_3OC_6H_4O$	DBU	0.5	**42**	Quant.	(3/97)[b]
(*E*)-**5e**	C_2H_5O	DBU	3	**43**	97	(5/95)[c]
(*Z*)-**5e**	C_2H_5O	DBU	3	**43**	92	(41/59)[c]
(*E*)-**5f**	OAc	DBU	3	**44**	—	(Messy)
(*Z*)-**5f**	OAc	DBU	3	**44**	—	(Messy)
(*E*)-**11**	SCH_3	DBU	24	**45**	Quant.	(80/20)[d]
(*E*)-**11**	SCH_3	*i*-Pr_2NEt	24	**45**	98	(21/79)[d,f]
(*E*)-**6**	Cl	*i*-Pr_2NEt	24	**46**	90	(4/96)[e]
(*E*)-**7**	Br	*i*-Pr_2NEt	24	**47**	68	(21/79)[e,g]

a) *E*/*Z* ratios were determined by 400 MHz ^{1}H NMR spectra. b—e) The time-courses are shown in Tables 7—10, respectively. f) Contaminated with a small amount of starting materials which were reduced from the yields shown here (see Table 9). g) 19% of (*E*)-**7** was recovered.

Table 7. Conversion of 3-Phenoxy- and 3-(*p*-Substituted Phenoxyl)-1-tosyl-1-propenes to the Corresponding 1-Tosyl-2-propene Derivatives (**39**—**42**)



X=H, 5c X=CH_3, 3e
X=NO_2, 5d X=CH_3O, 3f

X=H, 39 X=CH_3, 41
X=NO_2, 40 X=CH_3O, 42

Substrate	Time	Products ratio[a]				*E*/*Z* of **39**
		(*E*)-5c	(*Z*)-5c	(*E*)-39	(*Z*)-39	
	0 min	100	0	0	0	—
	30 min	0	0	3	97	3/97
(*E*)-5c	2 h	0	0	3	97	3/97
	12 h	0	0	4	96	4/96
	96 h	0	0	8	92	8/92
	0 min	0	100	0	0	—
	30 min	0	0	89	11	89/11
(*Z*)-5c	2 h	0	0	89	11	89/11
	12 h	0	0	88	12	88/12
	96 h	0	0	79	21	79/21
		(*E*)-5d	(*Z*)-5d	(*E*)-40	(*Z*)-40	*E*/*Z* of **40**
	0 min	100	0	0	0	—
	30 min	0	0	3	97	3/97
(*E*)-5d	2 h	0	0	4	96	4/96
	12 h	0	0	14	86	14/86
	24 h	0	0	18	82	18/82
		(*E*)-3e	(*Z*)-3e	(*E*)-41	(*Z*)-41	*E*/*Z* of **41**
	0 min	100	0	0	0	—
	30 min	0	0	1	99	1/99
(*E*)-3e	2 h	0	0	2	98	2/98
	12 h	0	0	3	97	3/97
	24 h	0	0	3	97	3/97
		(*E*)-3f	(*Z*)-3f	(*E*)-42	(*Z*)-42	*E*/*Z* of **42**
	0 min	100	0	0	0	—
	30 min	0	0	3	97	3/97
(*E*)-3f	2 h	0	0	2	98	2/98
	12 h	0	0	3	97	3/97
	24 h	0	0	3	97	3/97

a) Determined by 400 MHz ^{1}H NMR spectra.

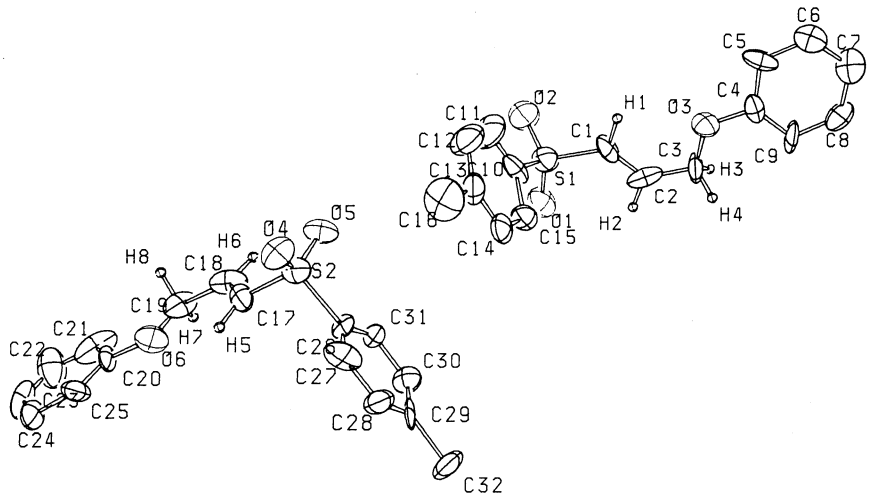
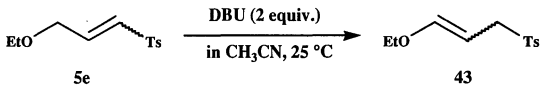


Fig. 2. ORTEP diagram of the crystallographycally independent units of (*E*)-**5c**.

Table 8. Conversion of 3-Ethoxy-1-tosyl-1-propene (**5e**) to 3-Ethoxy-1-tosyl-2-propene (**43**)

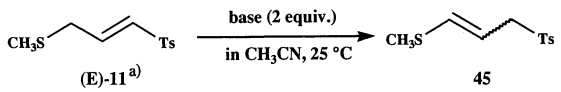


5e 43

E/*Z* Ratio of **5e**	Time	Products Ratio[a]				*E*/*Z* of **43**
		(*E*)-**5e**	(*Z*)-**5e**	(*E*)-**43**	(*Z*)-**43**	
100/0	0 min	100	0	0	0	—
	30 min	27	0	2	71	3/97
	1 h	6	0	4	90	4/96
	2 h	0	0	5	95	5/95
	6 h	0	0	4	96	4/96
	24 h	0	0	4	96	4/96
	72 h	0	0	4	96	4/96
0/100[b]	0 min	0	100	0	0	—
	10 min	10	53	23	14	62/38
	30 min	16	24	30	30	50/50
	1 h	4	6	38	52	42/58
	2 h	0	0	42	58	42/58
	6 h	0	0	41	59	41/59
	24 h	0	0	42	58	42/58
	72 h	0	0	43	57	43/57

a) Determined by 400 MHz ^{1}H NMR spectra. b) Contaminated by a small amount (ca. 6%) of $H_2C{=}C(Ts)CH_2OEt$. It was confirmed by 400 MHz ^{1}H NMR spectra that the contamination did not affect the conversion.

Table 9. Conversion of (*E*)-3-Methylthio-1-tosyl-1-propene [(*E*)-**11**] to 3-Methylthio-1-tosyl-2-propene (**45**)



(E)-11[a] 45

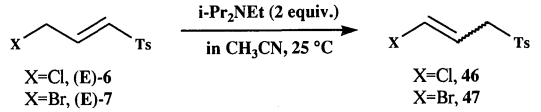
Base	Time	Products ratio[b]			*E*/*Z* of **45**	Isolated total yield/%
		(*E*)-**11**	(*E*)-**45**	(*Z*)-**45**		
DBU	0 min	98	0	2	0/100	—
	10 min	0	63	37	63/37	—
	30 min	0	76	24	76/24	—
	1 h	0	76	24	76/24	—
	6 h	0	77	23	77/23	—
	12 h	0	78	22	78/22	—
	24 h	0	80	20	80/20	Quant.
	72 h	0	79	21	79/21	88
i-Pr$_2$NEt	0 min	98	0	2	0/100	—
	10 min	85	4	11	28/72	—
	30 min	81	5	14	25/75	—
	1 h	77	6	17	25/75	—
	2 h	63	9	28	23/77	—
	6 h	31	16	53	23/77	—
	12 h	13	18	69	21/79	—
	24 h	2	21	77	21/79	Quant.

a) Contaminated with 2% of (*Z*)-**45**. b) Determined by 400 MHz ^{1}H NMR spectra.

crystal suitable for the X-ray analysis (Fig. 3). As shown in Fig. 3, H8, C8, C9, C10, and O4 exist on a plane with *syn*-conformation (O4–C8 2.788(5) Å, O4–H8 2.56(4) Å) in spite of the lack of p-orbital on the oxygen atom (O4). Therefore, the *syn*-conformation of (*E*)-**5c** and (*E*)-**13**, as the origin of "*syn-effect*" observed in the conversion of the (*E*)-vinylic sulfones to the corresponding allylic sulfones with DBU, should be ascribed to intramolecular hydrogen bonding and/or dipole–dipole interaction, but not to 6π-electrons homoaromaticity.

However, (*E*)-**13** could not be converted to the corresponding allylic sulfone by treatment with DBU. It may be due to the unstable ketene acetal structure of

Table 10. Conversion of (*E*)-3-Halo-1-tosyl-1-propenes [(*E*)-**6**,**7**] to 3-Halo-1-tosyl-2-propenes (**46**, **47**)



	Time	Products ratio[a]			*E*/*Z* of **46**	Isolated total yield/%
		(*E*)-**6**	(*E*)-**46**	(*Z*)-**46**		
X=Cl	0 min	100	0	0	—	—
	30 min	30	1	69	1/99	—
	1 h	12	1	87	1/99	—
	2 h	4	2	94	2/98	—
	4 h	3	2	95	2/98	—
	6 h	3	2	95	2/98	—
	12 h	3	3	94	3/97	—
	24 h	3	4	93	4/96	93
	48 h	3	7	90	7/93	93
	72 h	3	9	88	9/91	Quant.
		(*E*)-**7**	(*E*)-**47**	(*Z*)-**47**	*E*/*Z* of **47**	
X=Br	0 min	100	0	0	—	—
	10 min	75	Trace	25	0/100	—
	30 min	51	1	48	3/97	—
	1 h	38	2	60	3/97	—
	2 h	29	3	68	4/96	—
	4 h	27	4	69	6/94	—
	6 h	26	5	69	7/93	—
	12 h	24	10	66	13/87	—
	24 h	22	16	62	21/79	87
	48 h	21	24	55	31/69	70
	74 h	16	32	52	38/62	68

a) Determined by 400 MHz ^{1}H NMR spectra.

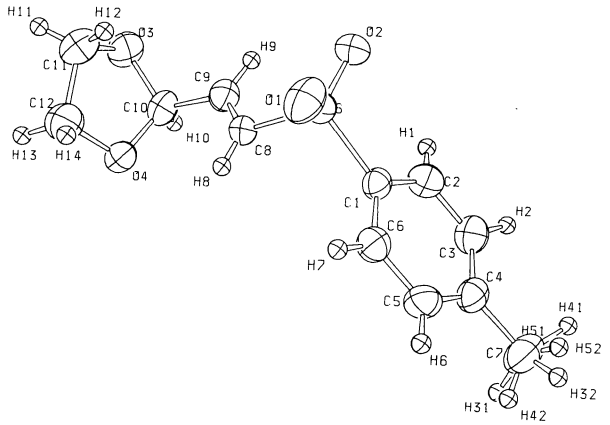


Fig. 3. ORTEP diagram of (*E*)-**13**.

the expected allylic sulfone, since (*E*)-**12** could not be converted to the corresponding allylic sulfone, either.

(*Z*)-**5c** and (*Z*)-**5e** tend to prefer (*Z*)-allylic sulfones thermodynamically (Tables 7 and 8), compared with (*Z*)-1-tosyl-1-alkenes[2] which afforded (*E*)-allylic sulfones exclusively due to the steric congestion of their *syn*-conformation in transition state.[2]

Crystallographic analysis of (*Z*)-**42** revealed that such results arise from the attractive interaction between oxygen atom (or electron-rich phenyl group) and electron-deficient tosyl group (Fig. 4). It is also consistent with the fact that when (*E*)-3-(*p*-nitrophenoxy)-1-tosyl-1-propene [(*E*)-**5d**] was treated with DBU, (*E*)-allylic sulfone [(*E*)-**40**] gradually increased due to the electron-withdrawing nitro group which diminishes the above interaction (see Table 7).

The highly selective formation of (*Z*)-allylic sulfones from 3-halo-substituted (*E*)-vinylic sulfones [(*E*)-**6** and **7**] can be explained in a similar way discussed for (*E*)-3-aryloxy (or alkoxy)-1-tosyl-1-propene, namely on the basis of the hydrogen bonding between halogen atom on γ-carbon and olefinic α-hydrogen and/or dipole–dipole interactions between C_{sp^2}←H and C→X. The relatively low selectivity for (*E*)-**11** may be due to the poor ability of soft sulfur atom to form hydrogen bonding and/or its low electronegativity.

In order to determine the relative degree of the "*syn-effect*" for various substituents, similar experiments were further performed for γ,γ-disubstituted vinylic sulfones (Scheme 2). The relative degree of the "*syn-effect*" for the substituents R′X and RY was justified by observing the *E*/*Z* ratios of the resulting allylic sulfones (V and VI in Scheme 2). The structures of (*E*)- and (*Z*)-isomers of the resulting allylic sulfones were confirmed by NOE measurement or the empirical rule that the protons of alkyl group syn to the tosylmethyl group in an allylic sulfone appear at higher field in NMR spectrum than those of alkyl group anti to the tosylmethyl group.[7]

Conversion of (*E*)-3-methyl-1-tosyl-1-pentene [(*E*)-**14**]

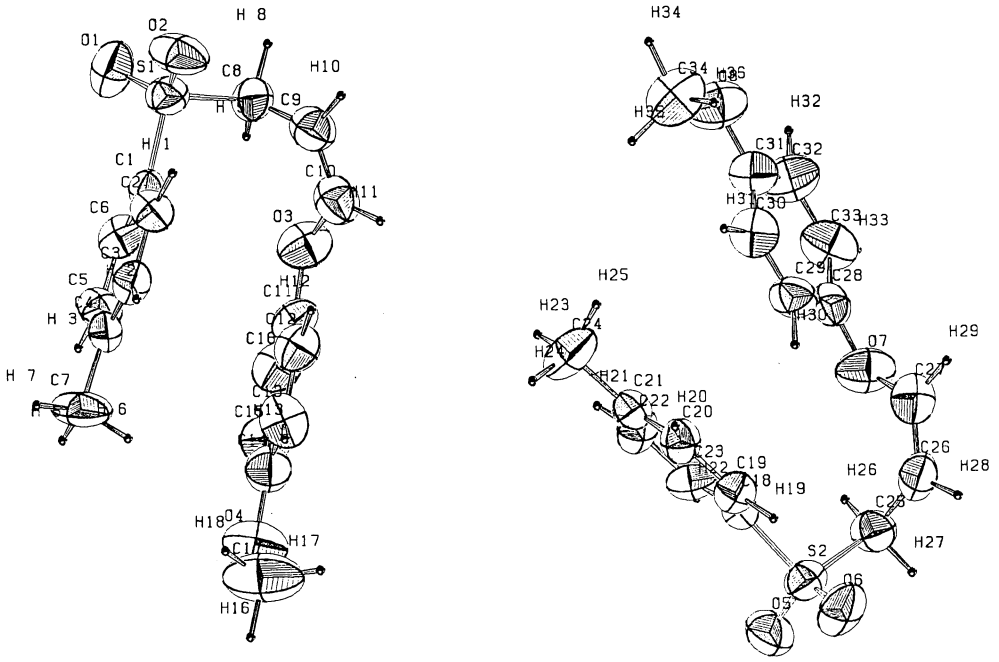
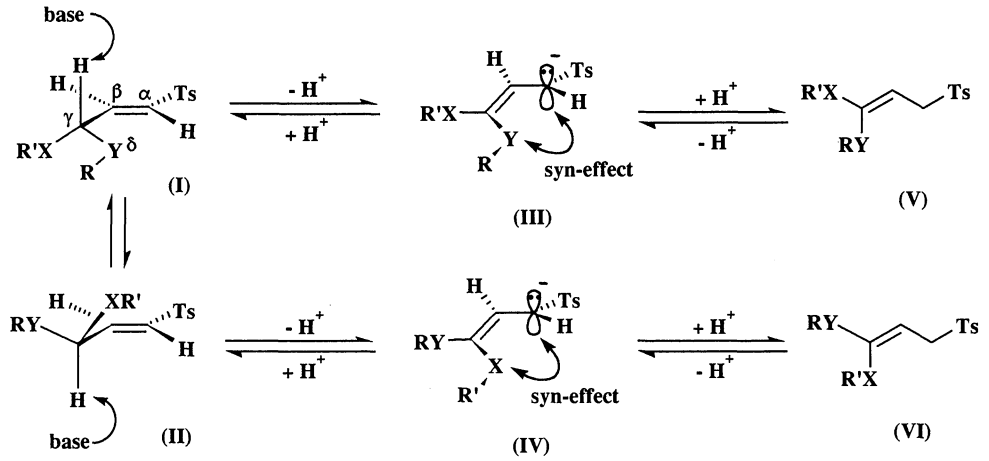


Fig. 4. ORTEP diagram of the crystallographycally independent units of (*Z*)-**42**.



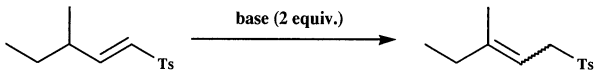
Scheme 2. The relative degree of "*syn-effect*" for various γ,γ-disubstituted vinylic sulfones.

to the corresponding allylic isomer (**48**) was performed to determine the difference of "*syn-effect*" between methyl and ethyl groups under basic conditions as shown in Table 11. We previously observed that the proportion of (*Z*)- and (*E*)-allylic sulfones ($RCH{=}CHCH_2Ts$) obtained from (*E*)-1-tosyl-1-alkene ($RCH_2CH{=}CHTs$) with DBU was almost constant around 70/30 at 25 °C after 12 h regardless of the length of alkyl substituents R (R=Et, *n*-Pr, *n*-C_5H_{11}, *n*-C_8H_{17}) except benzyl group.[2b] This suggests that the steric difference among the linear alkyl substituents R in $RCH_2CH{=}CHTs$ is not so important when we determine the relative degree of "*syn-effect*" for γ-substituents. Taking into account of this fact, it can be concluded from the results shown in Table 11 that "*syn-effect*" for methyl group is greater than that for ethyl, namely methylene group.

The relative degree of the "*syn-effect*" for methyl, ethyl, acetoxyl, alkoxyl, chloro, bromo, and methylthio groups was similarly examined as shown in Tables 12—16. From these results and the facts described above or in the previous paper,[2b] the following relative degree of "*syn-effect*" for various γ-substituents could be elucidated.

$RO{-}$ ($R{=}CH_3$, C_2H_5)≅$ArO{-}$(Ar=*p*-$CH_3OC_6H_4$, *p*-$CH_3C_6H_4$, C_6H_5, *p*-$NO_2C_6H_4$)≥$AcO{-}$>$Cl{-}$≥$Br{-}$>$CH_3{-}$>$CH_3S{-}$≥$-CH_2-$ (cyclic and acylic)>$(CH_3)_2CH{-}$>>$(CH_3)_3C{-}$, $C_6H_5{-}$

Table 11. Conversion of (*E*)-3-Methyl-1-tosyl-1-pentene [(*E*)-**14**] to 3-Methyl-1-tosyl-2-pentene (**48**)

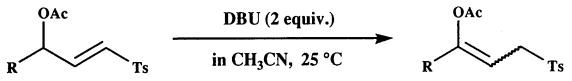


(E)-14 48

Base/Solvent/ Temperature	Time	Products ratio[a]			*E*/*Z* of **48**	Isolated total yield/%
		(*E*)-**14**	(*E*)-**48**	(*Z*)-**48**		
	0 min	100	0	0	—	—
	30 min	87	10	3	77/23	—
DBU	1 h	79	15	6	72/28	—
CH_3CN	2 h	68	23	9	72/28	—
25°C	4 h	37	44	19	70/30	—
	6 h	28	51	21	70/30	Quant.
	11 h	10	60	30	67/33	—
	18 h	0	70	30	70/30	—
	0 min	100	0	0	—	—
t-BuOK	1 h	0	69	31	69/31	90
t-BuOH	6 h	0	69	31	69/31	—
30°C	12 h	0	70	30	70/30	—
	24 h	0	73	27	73/27	—

a) Determined by 400 MHz ^{1}H NMR spectra.

Table 12. Conversion of (*E*)-3-Acetoxy-1-tosyl-1-alkenes [(*E*)-**20a,b**] to the Corresponding 3-Acetoxy-1-tosyl-2-alkenes (**49a,b**)



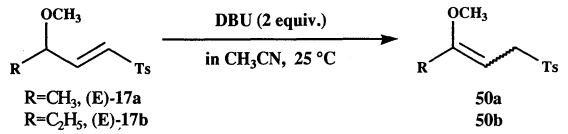
R=CH_3, (E)-20a
R=C_2H_5, (E)-20b

49a
49b

Substrate	Time	Products ratio[a]			*E*/*Z* of **49a**	Isolated total yield/%
		(*E*)-**20a**	(*E*)-**49a**	(*Z*)-**49a**		
	0 min	100	0	0	—	—
	30 min	51	13	36	27/73	—
	1 h	27	21	52	29/71	—
	2 h	7	27	66	29/71	—
	4 h	0	29	71	29/71	52
(*E*)-**20a**	6 h	0	30	70	30/70	—
	12 h	0	30	70	30/70	—
	24 h	0	31	69	31/69	—
	48 h	0	33	67	33/67	—
	96 h	0	36	64	36/64	—
		(*E*)-**20b**	(*E*)-**49b**	(*Z*)-**49b**	*E*/*Z* of **49b**	
	0 min	100	0	0	—	—
	30 min	74	5	21	19/81	—
	1 h	52	9	39	19/81	—
	2 h	28	14	58	19/81	—
(*E*)-**20b**	4 h	8	19	73	20/80	—
	6 h	1	19	80	19/81	—
	12 h	0	21	79	21/79	—
	24 h	0	20	80	20/80	60
	48 h	0	19	81	19/81	—

a) Determined by 400 MHz ^{1}H NMR spectra.

Table 13. Conversion of (*E*)-3-Methoxy-1-tosyl-1-alkenes [(*E*)-**17a,b**] to the Corresponding 3-Methoxy-1-tosyl-2-alkenes (**50a,b**)



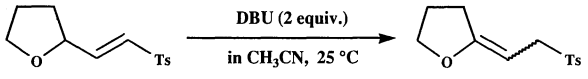
R=CH_3, (E)-17a
R=C_2H_5, (E)-17b

50a
50b

Substrate	Time	Products ratio[a]			*E*/*Z* of **50a**	Isolated total yield/%
		(*E*)-**17a**	(*E*)-**50a**	(*Z*)-**50a**		
(*E*)-**17a**	0 min	100	0	0	—	—
	30 min	95	1	4	22/78	—
	1 h	90	2	8	20/80	—
	2 h	80	4	16	20/80	—
	4 h	43	11	46	20/80	—
	6 h	27	14	59	19/81	—
	12 h	9	20	71	21/79	Quant.
	24 h	0	20	80	20/80	—
	48 h	0	20	80	20/80	—
		(*E*)-**17b**	(*E*)-**50b**	(*Z*)-**50b**	*E*/*Z* of **50b**	
(*E*)-**17b**	0 min	100	0	0	—	—
	30 min	99	Trace	1	0/100	—
	1 h	96	Trace	4	0/100	—
	2 h	92	Trace	8	4/96	—
	4 h	84	1	15	5/95	—
	6 h	74	2	24	8/92	—
	12 h	52	4	44	9/91	—
	24 h	24	8	68	10/90	97
	48 h	5	9	86	9/91	—

a) Determined by 400 MHz ^{1}H NMR spectra.

Table 14. Conversion of 2-[(*E*)-2-tosylethenyl]oxolane [(*E*)-**19**] to 2-(2-Tosylethylidene)oxolane (**51**)



(E)-19

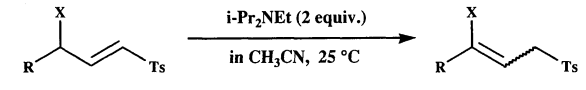
51

Time	Products ratio[a]			*E*/*Z* of **51**	Isolated total yield/%
	(*E*)-**19**	(*E*)-**51**	(*Z*)-**51**		
0 h	100	0	0	—	—
1 h	87	3	10	23/77	—
2 h	76	5	19	19/81	—
4 h	55	7	38	16/84	—
6 h	37	10	53	16/84	—
12 h	13	15	72	17/83	—
24 h	0	16	84	16/84	88

a) Determined by 400 MHz ^{1}H NMR spectra.

For the conversion of (*E*)-3-halo-1-tosyl-1-alkenes [(*E*)-**22a,b** and (*E*)-**23a,b**] to the corresponding 3-halo-1-tosyl-2-alkenes (**52a,b** and **53a,b**), *N*,*N*-diisopropylethylamine was used as a base to avoid the formation of the quaternary ammonium salts (Table 15). The difference of the degree of "*syn-effect*" between chloro and bromo groups was not clear from the results shown in the Table, but chloro group [(*E*)-**6**] seems to be a little more effective than bromo group [(*E*)-**7**] from the results shown in Table 10.

Table 15. Conversion of (*E*)-3-Halo-1-tosyl-1-alkenes [(*E*)-**22a,b** and (*E*)-**23a,b**] to the Corresponding 3-Halo-1-tosyl-2-alkenes (**52a,b** and **53a,b**)



R=CH_3, X=Cl, (E)-**22a** — **52a**
R=C_2H_5, X=Cl, (E)-**22b** — **52b**
R=CH_3, X=Br, (E)-**23a** — **53a**
R=C_2H_5, X=Br, (E)-**23b** — **53b**

Substrate	Time	Products ratio[a]			*E*/*Z* of **52a**	Isolated total yield/%
		(*E*)-**22a**	(*E*)-**52a**	(*Z*)-**52a**		
	0 h	100	0	0	—	—
	2 h	89	Trace	11	0/100	—
	6 h	80	3	17	14/86	—
(*E*)-**22a**	12 h	64	4	32	12/88	—
	24 h	41	8	51	13/87	94
	48 h	18	11	71	13/87	—
	100 h	2	12	86	12/88	95
		(*E*)-**22b**	(*E*)-**52b**	(*Z*)-**52b**	*E*/*Z* of **52b**	
	0 h	100	0	0	—	—
	2 h	97	Trace	3	0/100	—
	6 h	92	Trace	8	0/100	—
(*E*)-**22b**	12 h	82	1	17	7/93	—
	24 h	66	3	31	8/92	94
	48 h	44	4	52	7/93	—
	100 h	12	7	81	8/92	98
		(*E*)-**23a**	(*E*)-**53a**	(*Z*)-**53a**	*E*/*Z* of **53a**	
	0 h	100	0	0	—	—
	2 h	96	Trace	4	0/100	—
	6 h	88	2	10	14/86	—
(*E*)-**23a**	12 h	78	3	19	15/85	83
	24 h	61	5	34	14/86	83
	48 h	37	9	54	14/86	95
	120 h	7	12	81	13/87	83
		(*E*)-**23b**	(*E*)-**53b**	(*Z*)-**53b**	*E*/*Z* of **53b**	
	0 h	100	0	0	—	—
	2 h	97	Trace	3	0/100	—
	6 h	93	Trace	7	0/100	—
(*E*)-**23b**	12 h	84	1	15	8/92	—
	24 h	74	2	24	8/92	Quant.
	48 h	60	4	36	9/91	Quant.
	96 h	33	6	61	9/91	89

a) Determined by 400 MHz ^{1}H NMR spectra.

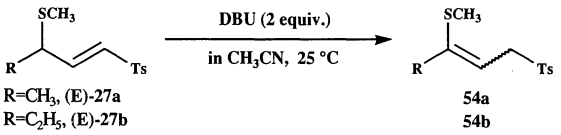
In order to compare the "*syn-effect*" for alkoxyl group with chloro group, *N*,*N*-diisopropylethylamine was used as a base for (*E*)-3-methoxy-1-tosyl-1-propene [(*E*)-**17c**]. The reaction did not proceed so rapidly as the case with DBU, however, the geometry of 3-methoxy-1-tosyl-2-propene resulted in 14% was only *Z*-form even after 144 h. Thus, the "*syn-effect*" of them was proven to decrease in the order of RO>Cl.

The order of $-CH_2->(CH_3)_2CH-$ was determined from the results in Table 5 taking into account of the fact that the *Z*/*E*-ratio of allylic sulfones ($RCH=CHCH_2Ts$) obtained from (*E*)-1-tosyl-1-alkenes ($RCH_2CH=CHTs$) with DBU was almost constant around 70/30 at 25 °C after 12 h regardless of the substituents R (R=Et, *n*-Pr, *n*-C_5H_{11}, *n*-C_8H_{17}).[2]

From the results mentioned above, the origin of "*syn-effect*" is now likely to be intramolecular hydrogen bonding and/or dipole–dipole interaction in the case of (*E*)-3-heteroatom-substituted vinylic sulfones. On the other hand, the origin of "*syn-effect*" observed for simple (*E*)-1-tosyl-1-alkenes seems to be due to the 6π-electrons homoaromaticity involving the hyperconjugation of methyl or methylene group.

Related works are further in progress in our laboratory.

Table 16. Conversion of (*E*)-3-Methylthio-1-tosyl-1-alkenes [(*E*)-**27a,b**] to the Corresponding 3-Methylthio-1-tosyl-2-alkenes (**54a,b**)



R=CH_3, (E)-27a
R=C_2H_5, (E)-27b

54a
54b

Substrate	Time	Products ratio[a]			*E*/*Z* of **54a**	Isolated total yield/%
		(*E*)-**27a**	(*E*)-**54a**	(*Z*)-**54a**		
	0 min	100	0	0	—	—
	10 min	0	65	35	65/35	—
	30 min	0	66	34	66/34	—
(*E*)-**27a**	1 h	0	66	34	66/34	—
	6 h	0	70	30	70/30	—
	12 h	0	70	30	70/30	84
	24 h	0	68	32	68/32	Quant.
		(*E*)-**27b**	(*E*)-**54b**	(*Z*)-**54b**	*E*/*Z* of **54b**	
	0 min	100	0	0	—	—
	10 min	0	46	54	46/54	—
	30 min	0	46	54	46/54	—
(*E*)-**27b**	1 h	0	49	51	49/51	—
	6 h	0	51	49	51/49	—
	12 h	0	57	43	57/43	—
	24 h	0	60	40	60/40	90

a) Determined by 400 MHz ^{1}H NMR spectra.

Experimental

All the melting points were determined with a micro melting apparatus (Yanagimoto-Seisakusho) and were uncorrected. The ^{1}H NMR and IR spectra were recorded on JEOL JNM-GX400 (400 MHz) FT-NMR spectrometer and JASCO IRA-1 diffraction grating infrared spectrometer, respectively. The chemical shifts of NMR are reported in the δ-scale relative to TMS as an internal standard.

Materials. All the solvents were distilled and stored over a drying agent. Thin-layer chromatography (TLC) was performed on Merck's silica gel 60 PF_{254} (Art. 7749).

Preparation of (*E*)-1-Tosyl-1-butene [(*E*)-1]. (*E*)-1-Tosyl-1-butene [(*E*)-**1**] was prepared according to the Eq. 1, the experimental detail of which has been described in the previous paper.[2a] It is also available from 1-butene in the similar manner described for the preparation of (*E*)-1-tosyl-1-pentene [(*E*)-**3a**] below.

Preparation of (*Z*)-1-Tosyl-1-butene [(*Z*)-1]. An aqueous solution (1 ml) of sodium *p*-toluenesulfinate (*p*-$CH_3C_6H_4$-$SOONa{\cdot}4H_2O$, 375 mg, 1.5 mmol) was vigorously stirred with a solution of iodine (254 mg, 1 mmol) in ethyl acetate (2 ml) at room temperature for 3 h in a flask equipped with a balloon containing 1-butyne. The product was extracted with ethyl acetate and washed successively with aq $NaHCO_3$ containing a small amount of $NaHSO_3$, brine, and dried over Na_2SO_4. After evaporation of the solvent, the resulting residue was subjected to preparative TLC (solvent; hexane:AcOEt=5:1, v/v) to afford 336 mg of (*E*)-2-iodo-1-tosyl-1-butene. The addition product was treated with 5% Pd–C (25 mg) deactivated with a small amount of quinoline in methanol in the presence of sodium acetate (2 equiv) under hydrogen atmosphere. After the usual work-up, (*Z*)-**1** was isolated by preparative TLC (solvent; hexane:AcOEt=5:1, v/v) as an oil in quantitative yield based on the used iodine. MS *m*/*z* 210 (M^+); IR (neat) 2960, 1610, 1590, 1440, 1300, 1130, 1070, 800 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.03 (3H, t, *J*=7.3 Hz), 2.43 (3H, s), 2.66 (2H, p, *J*=7.3 Hz), 6.20 (1H, dt, *J*=10.9, 7.3 Hz), 6.25 (1H, d, *J*=10.9 Hz), 7.33 (2H, d, *J*=8.0 Hz), 7.79 (2H, d, *J*=8.0 Hz).

Preparation of (*E*)-1-Tosyl-1-pentene [(*E*)-3a].[8] To a heterogeneous mixture of *p*-$CH_3C_6H_4SOONa{\cdot}4H_2O$ (375 mg, 1.5 mmol) in water (1 ml) and ethyl acetate (2 ml) were added 1-pentene (105 mg, 1.5 mmol) and iodine (254 mg, 1 mmol) at room temperature. After stirring for 2 h, 20 ml of ethyl acetate was added. The organic phase was separated and washed successively with aqueous $NaHCO_3$ containing a small amount of $NaHSO_3$, brine, and dried over Na_2SO_4. The residue obtained by evaporation of the solvent was treated with pyrrolidine (285 mg, 4 mmol) in dry acetonitrile at room temperature overnight. After removal of the solvent, the resulting residue was taken up in ethyl acetate, washed with brine, and dried over Na_2SO_4. The crude **2a** obtained by evaporation of the solvent was then treated with *m*-chloroperbenzoic acid (*m*-CPBA, 345 mg, 1.4 mmol) in the presence of Na_2CO_3 (212 mg, 2 mmol) in CH_2Cl_2 at room temperature overnight. After the usual work-up, (*E*)-**3a** was isolated by preparative TLC (solvent; hexane:AcOEt=5:1, v/v) as an oil in quantitative yield (243 mg) based on the used iodine. MS *m*/*z* 224 (M^+); IR (neat) 3032, 2948, 2856, 1619, 1584, 1446, 1310, 1138, 1079, 959, 802 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.92 (3H, t, *J*=7 Hz), 1.43—1.56 (2H, m), 2.16—2.24 (2H, m), 2.44 (3H, s), 6.30 (1H, d, *J*=15 Hz), 6.96 (1H, dt, *J*=7, 15 Hz), 7.33 (2H, d, *J*=8 Hz), 7.76 (2H, d, *J*=8 Hz).

Other (*E*)-vinylic sulfones [(*E*)-**3b**—**f**] were prepared in a similar manner. The intermediates **2b** and **2c** were isolated

prior to oxidation with *m*-CPBA.

2b: Prepared from equimolar amounts of 4-methyl-1-pentene and iodine with 3 equiv of pyrrolidine. Isolated by preparative TLC (solvent; hexane:AcOEt:Et_3N=50:20:1, v/v/v). Mp 72—74 °C (not recrystallized); MS *m/z* 309 (M^+); IR (KBr) 2960, 2860, 2800, 1590, 1460, 1380, 1320, 1300, 1260, 1140, 1080, 1040, 910, 800, 760 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.87 (6H, m), 1.29 (1H, m), 1.43 (1H, m), 1.55 (4H, m), 1.69 (1H, m), 2.31 (2H, m), 2.45 (2H, m), 2.45 (3H, s), 2.95 (1H, dd, *J*=14, 6 Hz), 3.27 (1H, dd, *J*=14, 5 Hz), 3.37 (1H, m), 7.33 (2H, d, *J*=8.5 Hz), 7.78 (2H, d, *J*=8.5 Hz).

(*E*)-3b: $NaHCO_3$ (2 equiv) was used instead of Na_2CO_3 for oxidation. An oil; MS *m/z* 238 (M^+); IR (neat) 3050, 2940, 1630, 1590, 1490, 1460, 1320, 1300, 1150, 1090, 970 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.91 (6H, d, *J*=7 Hz), 1.79 (1H, m), 2.11 (2H, m), 2.43 (3H, s), 6.29 (1H, d, *J*=15 Hz), 6.92 (1H, dt, *J*=15, 8 Hz), 7.33 (2H, d, *J*=8 Hz), 7.75 (2H, d, *J*=8 Hz).

2c: Prepared by the use of 1.06 equiv of 4,4-dimethyl-1-pentene and 3 equiv of pyrrolidine. Separated in a similar manner described for **2b**. Mp 67—69 °C (from hexane); MS *m/z* 323 (M^+); IR (KBr) 2950, 1590, 1460, 1400, 1360, 1300, 1140, 1080, 900 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.92 (9H, s), 1.24 (1H, m), 1.42 (1H, m), 1.49 (4H, m), 2.24 (2H, m), 2.40 (2H, m), 2.44 (3H, s), 2.97 (1H, dd, *J*=14.3, 6.1 Hz), 3.27 (1H, dd, *J*=14.3, 5.8 Hz), 3.44 (1H, m), 7.32 (2H, d, *J*=8.5 Hz), 7.78 (2H, d, *J*=8.5 Hz).

(*E*)-3c: An oil; MS *m/z* 253 (M^++1); IR (neat) 3040, 2950, 2850, 1620, 1580, 1480, 1460, 1360, 1310, 1130, 1080, 960 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.93 (9H, s), 2.10 (2H, d, *J*=7.5 Hz), 2.44 (3H, s), 6.23 (1H, d, *J*=15 Hz), 6.97 (1H, dt, *J*=15, 7.5 Hz), 7.33 (2H, d, *J*=8 Hz), 7.76 (2H, d, *J*=8 Hz).

(*E*)-3d: Iodosulfonization was carried out by employing equimolar amounts of 3-phenyl-1-propene and iodine. Intermediary 3-phenyl-2-(1-pyrrolidinyl)-1-tosylpropane (**2d**) was not formed by the reaction with pyrrolidine, but directly afforded (*E*)-**3d**. Mp 120 °C (from *i*-PrOH); IR (KBr) 3020, 1620, 1590, 1490, 1440, 1300, 1130, 1080, 970, 920, 810, 780, 750, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.43 (3H, s), 3.54 (2H, d, *J*=6 Hz), 6.24 (1H, d, *J*=15 Hz), 7.11 (1H, dt, *J*=15, 6 Hz), 7.12—7.30 (5H, m), 7.32 (2H, d, *J*=8.5 Hz), 7.74 (2H, d, *J*=8.5 Hz). Found: C, 70.40; H, 5.94%. Calcd for $C_{16}H_{16}O_2S$: C, 70.56; H, 5.92%.

(*E*)-3e: Prepared by the use of 1 equiv of 3-(*p*-methylphenoxyl)-1-propene, 2 equiv of *p*-$CH_3C_6H_4SOONa\cdot 4H_2O$, and 1.2 equiv of iodine. Mp 110.2—111.5 °C (from MeOH); IR (KBr) 3020, 2880, 2840, 1580, 1500, 1480. 1360, 1300, 1235, 1120, 1070, 940 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.27 (3H, s), 2.43 (3H, s), 4.68 (2H, d, *J*=3.4 Hz), 6.74 (1H, d, *J*=15 Hz), 6.76 (2H, d, *J*=8.9 Hz), 7.05 (1H, dt, *J*=15, 3.4 Hz), 7.05 (2H, d, *J*=8.9 Hz), 7.32 (2H, d, *J*=8.6 Hz), 7.77 (2H, d, *J*=8.6 Hz). Found: C, 67.38; H, 6.08%. Calcd for $C_{17}H_{18}O_3S$: C, 67.52; H, 6.00%.

(*E*)-3f: Prepared in a similar manner as above. Mp 87.0—87.8 °C (from MeOH); IR (KBr) 3040, 2940, 2890, 1630, 1585, 1510, 1480, 1450, 1380, 1310, 1240, 1135, 1075, 966 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.43 (3H, s), 3.75 (3H, s), 4.66 (2H, d, *J*=3.4 Hz), 6.74 (1H, d, *J*=15 Hz), 6.80 (4H, s), 7.07 (1H, dt, *J*=15, 3.4 Hz), 7.33 (2H, d, *J*=8 Hz), 7.78 (2H, d, *J*=8 Hz). Found: C, 64.01; H, 5.78%. Calcd for $C_{17}H_{18}O_4S$: C, 64.13; H, 5.70%.

Preparation of 2-Ethyl-1-tosyl-1-butene (5a). A heterogeneous mixture of 2-ethyl-1-butene (1.67 g, 20 mmol), *p*-$CH_3C_6H_4SOONa\cdot 4H_2O$ (7.5 g, 30 mmol), and iodine (5.08 g, 20 mmol) in water (40 ml) and ethyl acetate (40 ml) was vigorously stirred at room temperature for 2.5 h, and worked up in a similar manner described above for (*E*)-**3a**. Intermediary iodosulfonization product was treated with 2 equiv of triethylamine (5.6 ml, 40 mmol) in dry acetonitrile (40 ml) at room temperature for 2.5 h. After addition of phosphate buffer (pH 7) and the usual work-up, **5a** was isolated by a flash column chromatography (SiO_2; eluent, hexane: AcOEt=5:2, v/v) in 91% yield (4.35 g). Mp 62 °C (from *i*-PrOH); IR (KBr) 2970, 2870, 1610, 1590, 1450, 1300, 1140, 1080, 940 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.03 (6H, t, *J*=7.5 Hz), 2.18 (2H, q, *J*=7.5 Hz), 2.43 (3H, s), 2.60 (2H, q, *J*=7.5 Hz), 6.09 (1H, s), 7.32 (2H, d, *J*=8 Hz), 7.79 (2H, d, *J*=8 Hz). Found: C, 65.33; H, 7.62%. Calcd for $C_{13}H_{18}O_2S$: C, 65.51; H, 7.61%.

Other vinylic sulfones (**5b—g**) were prepared in a similar manner.

5b: (*E*)-**5b** was isolated from the *E*/*Z*-mixture by recrystallization. Mp 56—57 °C (from EtOH); IR (KBr) 3060, 2960, 1610, 1590, 1410, 1370, 1280, 1130, 1070, 800 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.04 (3H, t, *J*=7.33 Hz), 2.13 (3H, s), 2.15 (2H, q, *J*=7.33 Hz), 2.44 (3H, s), 6.16 (1H, s), 7.32 (2H, d, *J*=8.2 Hz), 7.79 (2H, d, *J*=8.2 Hz). Found: C, 64.22; H, 7.11%. Calcd for $C_{12}H_{16}O_2S$: C, 64.25; H, 7.19%. ^1H NMR of (*Z*)-**5b** ($CDCl_3$) δ=1.04 (3H, t, *J*=7.33 Hz), 1.64 (3H, s), 2.44 (3H, s), 2.60 (2H, q, *J*=7.33 Hz), 6.14 (1H, s), 7.32 (2H, d, *J*=8.2 Hz), 7.79 (2H, d, *J*=8.2 Hz).

(*E*)-5c: Mp 70 °C (from *i*-PrOH); IR (KBr) 3050, 2880, 1630, 1590, 1490, 1430, 1380, 1300, 1250, 1200, 1140, 1080, 1010, 960, 940 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.44 (3H, s), 4.71 (2H, d, *J*=3.4 Hz), 6.75 (1H, d, *J*=15 Hz), 6.86—7.27 (5H, m), 7.09 (1H, dt, *J*=15, 3.4 Hz), 7.34 (2H, d, *J*=8.3 Hz), 7.78 (2H, d, *J*=8.3 Hz). Found: C, 66.87; H, 5.64%. Calcd for $C_{16}H_{16}O_3S$: C, 66.64; H, 5.59%.

(*Z*)-5c: Mp 103 °C (from *i*-PrOH); IR (KBr) 3040, 2900, 1630, 1590, 1490, 1440, 1370, 1310, 1240, 1140, 1080, 1030 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.46 (3H, s), 5.24 (2H, d, *J*=4.9 Hz), 6.33 (1H, d, *J*=11.6 Hz), 6.48 (1H, dt, *J*=11.6, 4.9 Hz), 6.87—7.31 (5H, m), 7.37 (2H, d, *J*=8 Hz), 7.87 (2H, d, *J*=8 Hz). Found: C, 66.54; H, 5.51%. Calcd for $C_{16}H_{16}O_3S$: C, 66.64; H, 5.59%.

(*E*)-5d: Mp 134.0—134.3 °C (from MeOH); IR (KBr) 3040, 1635, 1600, 1580, 1500, 1450, 1375, 1340, 1250, 1140, 1075, 950, 875 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.44 (3H, s), 4.84 (2H, d, *J*=3.5 Hz), 6.95 (1H, d, *J*=15 Hz), 6.96 (2H, d, *J*=9.3 Hz), 7.09 (1H, dt, *J*=15, 3.5 Hz), 7.35 (2H, d, *J*=8 Hz), 7.78 (2H, d, *J*=8 Hz), 8.18 (2H, d, *J*=9.3 Hz). Found: C, 57.55; H, 4.57; N, 4.23%. Calcd for $C_{16}H_{15}NO_5S$: C, 57.65; H, 4.54; N, 4.20%.

(*E*)-5e: An oil; MS *m/z* 241 (M^++1); IR (neat) 3040, 2860, 2850, 1620, 1580, 1480, 1440, 1310, 1140, 1080, 1010, 940 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.19 (3H, t, *J*=7 Hz), 2.44 (3H, s), 3.51 (2H, q, *J*=7 Hz), 4.51 (2H, d, *J*=3.5 Hz), 6.60 (1H, d, *J*=15 Hz), 6.95 (1H, dt, *J*=15, 3.5 Hz), 7.33 (2H, d, *J*=8.2 Hz), 7.77 (2H, d, *J*=8.2 Hz).

(*Z*)-5e: An oil; MS *m/z* 240 (M^+); IR (neat) 3040, 2960, 2850, 1620, 1580, 1480, 1440, 1360, 1300, 1140, 1100, 1080, 1000 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.22 (3H, t, *J*=7 Hz), 2.45 (3H, s), 3.53 (2H, q, *J*=7 Hz), 4.64 (2H, d, *J*=5.2 Hz), 6.24 (1H, d, *J*=11.6 Hz), 6.36 (1H, dt, *J*=11.6, 5.2 Hz), 7.35 (2H, d, *J*=8.2 Hz), 7.78 (2H, d, *J*=8.2 Hz).

(*E*)-5f: An oil; (lit,[9]) mp 23—24 °C); MS *m/z* 254 (M^+); IR

(neat) 3040, 2940, 1740, 1630, 1580, 1480, 1430, 1370, 1310, 1220, 1140, 1080, 1020, 940 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.09 (3H, s), 2.45 (3H, s), 4.77 (2H, d, J=4 Hz), 6.55 (1H, d, J=15.4 Hz), 6.95 (1H, dt, J=15.4, 4 Hz), 7.35 (2H, d, J=8 Hz), 7.77 (2H, d, J=8 Hz).

(*Z*)-5f: An oil; MS m/z 254 (M^+); IR (neat) 3040, 2920, 1730, 1620, 1590, 1480, 1420, 1360, 1310, 1220, 1140, 1080, 1030 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.09 (3H, s), 2.45 (3H, s), 5.28 (2H, d, J=4.9 Hz), 6.23 (1H, dt, J=11.3, 4.9 Hz), 6.29 (1H, d, J=11.3 Hz), 7.36 (2H, d, J=8 Hz), 7.82 (2H, d, J=8 Hz).

(*E*)-5g: (*E*)-**5g** was isolated from the *E*/*Z*-mixture of **5g** by recrystallization. Mp 123 °C [from H_2O, lit,[10] 122 °C (from benzene)]; IR (KBr) 3520, 3050, 2880, 1620, 1590, 1480, 1430, 1270, 1130, 1080, 1010, 940 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.08 (1H, br), 2.44 (3H, s), 4.39 (2H, m), 6.64 (1H, d, J=15 Hz), 7.01 (1H, dt, J=15, 3.4 Hz), 7.33 (2H, d, J=8 Hz), 7.76 (2H, d, J=8 Hz). Found: C, 56.44; H, 5.74%. Calcd for $C_{10}H_{12}O_3S$: C, 56.59; H, 5.70%.

Preparation of (*E*)-3-Chloro-1-tosyl-1-propene [(*E*)-6]. To a solution of (*E*)-3-tosyl-2-propen-1-ol [(*E*)-**5g**, 212 mg, 1.0 mmol] in dry dichloromethane (5 ml) were added thionyl chloride (0.09 ml, 1.0 mmol) and pyridine (0.1 ml, 1.0 mmol) at room temperature. After stirring overnight, the reaction mixture was treated with 1M (1M=1 mol dm^{-3}) HCl, followed by the usual work-up. (*E*)-**6** was isolated by preparative TLC (solvent; hexane: AcOEt=5:2, v/v) in 82% yield. Mp 57 °C [from *i*-PrOH, lit, 58 °C (from light petroleum and a little benzene),[10] 57.2—58.3 °C (from pentane)[11]]; IR (KBr) 3040, 2960, 1620, 1580, 1410, 1290, 1270, 1130, 1070, 960, 910, 840, 800, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.45 (3H, s), 4.19 (2H, d, J=5.2 Hz), 6.65 (1H, d, J=15 Hz), 7.00 (1H, dt, J=15, 5.2 Hz), 7.36 (2H, d, J=8 Hz), 7.77 (2H, d, J=8 Hz). Found: C, 52.10; H, 4.78%. Calcd for $C_{10}H_{11}O_2SCl$: C, 52.06; H, 4.81%.

In a similar manner, (*E*)-**7** was prepared by the use of equimolar amount of phosphorus tribromide instead of thionyl chloride.

(*E*)-7: Mp 55 °C [from *i*-PrOH, lit, 65—66 °C (from light petroleum and a little benzene)[10]]; IR (KBr) 3040, 1620, 1580, 1420, 1310, 1280, 1140, 1080, 950, 900, 800, 780 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.45 (3H, s), 4.00 (2H, d, J=6.7 Hz), 6.56 (1H, d, J=15 Hz), 7.00 (1H, dt, J=15, 6.7 Hz), 7.36 (2H, d, J=8.2 Hz), 7.77 (2H, d, J=8.2 Hz). Found: C, 43.78; H, 3.99%. Calcd for $C_{10}H_{11}O_2SBr$: C, 43.65; H, 4.03%.

Preparation of 3-Methylthio-1-tosyl-1-propene [(*E*)-11]. To a solution of 2-propenal (280 mg, 5.0 mmol) in THF/H_2O (8 ml, 3/1, v/v) was added *p*-toluenesulfinic acid (*p*-$CH_3C_6H_4SOOH$, 781 mg, 5.0 mmol) at room temperature. After stirring for 2 h, the solvent was removed under reduced pressure. The resulting residue was dissolved in ethanol and reduced with $NaBH_4$, followed by the usual work-up. 3-Tosyl-1-propanol (**8**) was isolated by preparatice TLC (solvent; hexane:AcOEt:EtOH=5:4:1, v/v/v) in 76% yield. An oil; MS m/z 214 (M^+); IR (neat) 3500, 2920, 1590, 1430, 1300, 1140, 1080, 1050, 900 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.82 (1H, s), 1.97 (2H, m), 2.46 (3H, s), 3.22 (2H, m), 3.73 (2H, t, J=6.1 Hz), 7.37 (2H, d, J=8 Hz), 7.79 (2H, d, J=8 Hz).

3-Tosyl-1-propanol (**8**, 800 mg, 3.7 mmol) prepared above was treated with methanesulfonyl chloride (0.58 ml, 7.5 mmol) and triethylamine (1.1 ml, 7.5 mmol) in CH_2Cl_2 at room temperature for 10 min, followed by the usual work-up to afford the crude mesylated compound. It was further reacted with 15% aqueous sodium methanethiolate (1.9 ml, 4.0 mmol) in DMF (3 ml) at room temperature overnight. After the usual work-up, 3-methylthio-1-tosylpropane (**9**) was isolated by preparative TLC (solvent; hexane:AcOEt=5:2, v/v) in 76% yield. An oil; MS m/z 244 (M^+); IR (neat) 2920, 1590, 1440, 1400, 1300, 1210, 1140, 1110, 1080, 1020, 810, 740 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.01 (2H, m), 2.03 (3H, s), 2.46 (3H, s), 2.56 (2H, t, J=7 Hz), 3.21 (2H, m), 7.37 (2H, d, J=8.2 Hz), 7.79 (2H, d, J=8.2 Hz).

Phenylseleno group was introduced on α-position of the sulfone **9** according to the procedure reported previously.[2a] The resulting product **10** was isolated by preparative TLC (solvent; hexane:AcOEt=5:2, v/v). An oil; MS m/z 400 (M^++1); IR (neat) 3050, 2930, 1590, 1570, 1480, 1470, 1430, 1300, 1130, 1080, 1010, 990, 950, 800 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.93 (3H, s), 1.99 (1H, m), 2.43 (3H, s), 2.45 (1H, m), 2.70—2.87 (2H, m), 4.43 (1H, dd, J=11, 3.1 Hz), 7.18—7.30 (5H, m), 7.46 (2H, d, J=8.2 Hz), 7.78 (2H, d, J=8.2 Hz).

To a solution of 1-phenylseleno-3-methylthio-1-tosylpropane (**10**, 693 mg, 1.7 mmol) in dry methanol (7 ml) containing molecular sieves 3A was added tetrabutylammonium periodate (750 mg, 1.7 mmol) at room temperature. After stirring for 4 h, the solvent was replaced by ethyl acetate. The resulting solution was washed with brine and dried over Na_2SO_4. The residue obtained by evaporation of the solvent was separated by preparative TLC (solvent; hexane:AcOEt=5:2, v/v) to afford **11** as a mixture of (*E*)- and (*Z*)-isomers (94/6). (*E*)-**11** was obtained by recrystallization of the mixture from *i*-PrOH. Mp 63—64 °C (contaminated with a small amount of (*Z*)-**45**); MS m/z 242 (M^+); IR (KBr) 3020, 2880, 1680, 1610, 1580, 1480, 1300, 1280, 1140, 1080, 960 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.89 (3H, s), 2.44 (3H, s), 3.20 (2H, d, J=7 Hz), 6.41 (1H, d, J=15 Hz), 6.88 (1H, dt, J=15, 7 Hz), 7.34 (2H, d, J=8 Hz), 7.78 (2H, d, J=8 Hz). Found: C, 54.28; H, 5.80%. Calcd for $C_{11}H_{14}O_2S_2$: C, 54.51; H, 5.82%.

Preparation of (*E*)-3-Tosyl-2-propenal Diethyl Acetal [(*E*)-12]. Prepared from 2-propenal diethyl acetal in a similar manner described for **4a**. An oil; MS m/z 285 (M^++1); IR (neat) 3050, 2970, 2880, 1730, 1590, 1440, 1310, 1140, 1080, 1050, 1000, 950, 810 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.19 (6H, t, J=7 Hz), 2.44 (3H, s), 3.49 (2H, m), 3.60 (2H, m), 5.10 (1H, d, J=3.2 Hz), 6.67 (1H, d, J=15.3 Hz), 6.79 (1H, dd, J=15.3, 3.2 Hz), 7.34 (2H, d, J=8.2 Hz), 7.77 (2H, d, J=8.2 Hz).

Preparation of (*E*)-3-Tosyl-2-propenal Ethylene Acetal [(*E*)-13]. (*E*)-3-Tosylpropenal diethyl acetal [(*E*)-**12**, 284 mg, 1.0 mmol] was converted to (*E*)-**13** by employing 1,2-ethanediol (0.06 ml, 1.0 mmol) and *p*-TsOH (19 mg, 0.1 mmol) in refluxing benzene (2 ml) by the use of an azeotropic distillation apparatus. Mp 107 °C (from *i*-PrOH); IR (KBr) 3040, 2960, 2900, 1920, 1580, 1470, 1440, 1340, 1290, 1180, 1130, 1070, 1020, 970, 930, 910, 800 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.45 (3H, s), 3.42 (4H, m), 5.49 (1H, d, J=3.4 Hz), 6.66 (1H, d, J=15 Hz), 6.76 (1H, dd, J=15, 3.4 Hz), 7.34 (2H, d, J=8 Hz), 7.77 (2H, d, J=8 Hz). Found: C, 56.53; H, 5.60%. Calcd for $C_{12}H_{14}O_4S$: C, 56.68; H, 5.55%.

Preparation of (*E*)-3-Methyl-1-tosyl-1-pentene [(*E*)-14]. Prepared from equimolar amounts of diethyl (*p*-tolylsulfonylmethyl)phosphonate and 2-methylbutanal according to the procedure reported previously[2a] and separated by preparative TLC (solvent; hexane:AcOEt=5:1, v/v). Only *E*-isomer was obtained. An oil; MS m/z 238 (M^+); IR (neat) 3040, 2960, 2920, 2870, 1610, 1590, 1450, 1310, 1140, 1080, 970 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.86 (3H, t, J=7 Hz), 1.04 (3H,

d, J=7 Hz), 1.43 (2H, m), 2.26 (1H, m), 2.44 (3H, s), 6.25 (1H, d, J=15 Hz), 6.88 (1H, dd, J=15, 7.7 Hz), 7.32 (2H, d, J=8 Hz), 7.75 (2H, d, J=8 Hz).

Preparation of (*E*)-3-Methoxy-1-tosyl-1-butene [(*E*)-17a]. 4-Tosyl-2-butanol (**15a**) was prepared from equimolar amounts of 3-buten-2-one and *p*-toluenesulfinic acid in a similar manner described for **8**, and isolated by a flash column chromatography (SiO_2; eluent, hexane: AcOEt=1:1, v/v). An oil; MS m/z 228 (M^+); IR (neat) 3500, 2960, 1590, 1440, 1400, 1300, 1140, 1080, 930 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.19 (3H, d, J=6.1 Hz), 1.76 (1H, m), 1.90 (1H, m), 2.02 (1H, br), 2.45 (3H, s), 3.17 (1H, m), 3.27 (1H, m), 3.89 (1H, m), 7.36 (2H, d, J=8 Hz), 7.78 (2H, d, J=8 Hz).

To a solution of **15a** (520 mg, 2.3 mmol) in dry DMF (5 ml) were added iodomethane (1.4 ml, 23 mmol) and silver(I) oxide (2.65 g, 11.5 mmol) with stirring in the dark. After stirring for 2 d, insoluble material was filtered off and washed with ethyl acetate. The filtrate was successively washed with 1 M HCl and brine and dried over Na_2SO_4. The residue obtained by evaporation of the solvent in vacuo was subjected to preparative TLC (solvent; hexane:AcOEt=5:4, v/v) to afford 3-methoxy-1-tosylbutane (**16a**) in 90% yield (500 mg). An oil; MS m/z 241 (M^+-1); IR (neat) 2970, 2930, 1600, 1460, 1380, 1320, 1140, 1080, 1020 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.11 (3H, d, J=6.1 Hz), 1.78 (1H, m), 1.93 (1H, m), 2.45 (3H, s), 3.03—3.27 (2H, m), 3.23 (3H, s), 3.39 (1H, m), 7.36 (2H, d, J=8 Hz), 7.79 (2H, d, J=8 Hz).

α-Phenylselenation of **16a** and the subsequent oxidative elimination to introduce the double bond were carried out in a similar manner described in the the previous paper.[2a] The resulting 3-methoxy-1-tosyl-1-butene [(*E*)-**17a**] was isolated by preparative TLC (solvent; hexane:AcOEt=5:1, v/v). An oil; MS m/z 240 (M^+); IR (neat) 3030, 2960, 2900, 2800, 1610, 1580, 1430, 1300, 1130, 1090, 1070, 1000, 950 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.27 (3H, d, J=6.4 Hz), 2.44 (3H, s), 3.29 (3H, s), 3.96 (1H, m), 6.51 (1H, d, J=15 Hz), 6.85 (1H, dd, J=15, 4.9 Hz), 7.34 (2H, d, J=8 Hz), 7.77 (2H, d, J=8 Hz).

In a similar manner, **15b**, **16b**, **c**, and (*E*)-**17b**, **c** were prepared.

15b: An oil; MS m/z 242 (M^+); IR (neat) 3500, 3040, 2960, 2920, 1590, 1440, 1400, 1300, 1130, 1080, 1020, 980, 920 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.93 (3H, t, J=7.3 Hz), 1.47 (2H, m), 1.56 (1H, s), 1.74 (1H, m), 1.96 (1H, m), 2.46 (1H, m), 3.18 (1H, m), 3.29 (1H, m), 3.62 (1H, m), 7.36 (2H, d, J=8 Hz), 7.79 (2H, d, J=8 Hz).

16b: An oil; Ms m/z 241 (M^+-15); IR (neat) 2970, 2930, 1590, 1450, 1310, 1270, 1140, 1080, 810 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.85 (3H, t, J=7.3 Hz), 1.39 (1H, m), 1.51 (1H, m), 1.78 (1H, m), 1.95 (1H, m), 2.45 (3H, s), 3.06—3.22 (2H, m), 3.17 (1H, m), 3.25 (3H, s), 7.36 (2H, d, J=8 Hz), 7.79 (2H, d, J=8 Hz).

16c: An oil; MS m/z 228 (M^+); IR (neat) 2920, 1750, 1590, 1440, 1400, 1320, 1140, 1110, 1080, 1040, 1010, 870, 810, 720 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.97 (2H, m), 2.45 (3H, s), 3.17 (2H, m), 3.27 (3H, s), 3.41 (2H, t, J=6.1 Hz), 7.36 (2H, d, J=8.4 Hz), 7.79 (2H, d, J=8.4 Hz).

(*E*)-17b: An oil; MS m/z 240 (M^+); IR (neat) 3030, 2960, 2900, 2800, 1610, 1580, 1430, 1300, 1130, 1090, 1070, 1000, 950 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.27 (3H, d, J=6.4 Hz), 2.44 (3H, s), 3.29 (3H, s), 3.96 (1H, m), 6.51 (1H, d, J=15 Hz), 6.85 (1H, dd, J=15, 4.9 Hz), 7.34 (2H, d, J=8 Hz), 7.77 (2H, d, J=8 Hz).

(*E*)-17c: Mp 87 °C (from *i*-PrOH); IR (KBr) 3050, 3000, 2960, 2830, 1640, 1590, 1440, 1390, 1300, 1280, 1180, 1140, 1110, 1080, 1020, 960, 920, 820, 800 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.43 (3H, s), 3.37 (3H, s), 4.11 (2H, dd, J=2.1, 3.7 Hz), 6.59 (1H, dt, J=15, 2.1 Hz), 6.94 (1H, dt, J=15, 3.7 Hz), 7.33 (2H, d, J=8 Hz), 7.77 (2H, d, J=8 Hz). Found: C, 58.20; H, 6.28%. Calcd for $C_{11}H_{14}O_3S$: C, 58.38; H, 6.24%.

Preparation of (*E*)-2-(2-Tosylethenyl)oxolane [(*E*)-19]. A THF solution (3 ml) of *p*-tolyl vinyl sulfone (55 mg, 0.3 mmol) was irradiated in a Pyrex tube by 300 W high-pressure mercury lamp (Eiko-sha) for 1 h at room temperature in the presence of benzophenone (3 mg, 0.05 mmol) as a photosensitizer. 2-(2-Tosylethyl)oxolane (**18**) was isolated by preparative TLC (solvent; hexane:AcOEt=5:3, v/v) in 87% yield (66 mg) from the residue obtained by evaporation of the solvent. Mp 34 °C (from EtOH); IR (KBr) 2940, 2850, 1585, 1440, 1295, 1135, 1080, 805 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.42—1.50 (1H, m), 1.78—2.03 (5H, m), 2.45 (3H, s), 3.07—3.15 (1H, m), 3.23—3.31 (1H, m), 3.65—3.70 (1H, m), 3.76—3.87 (2H, m), 7.35 (2H, d, J=8.2 Hz), 7.78 (2H, d, J=8.2 Hz).

The introduction of a double bond to **18** was performed via α-phenylselenation according to the procedure reported previously.[2a] The product (*E*)-**19** was isolated by preparative TLC (solvent; hexane:AcOEt=5:2, v/v) in 81% yield. An oil; MS m/z 252 (M^+); IR (neat) 3060, 2970, 2860, 1590, 1440, 1310, 1300, 1140, 1080, 1060, 1010, 960, 800 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.71 (1H, m), 1.91 (2H, m), 2.16 (1H, m), 2.43 (3H, s), 3.81 (1H, m), 3.90 (1H, m), 4.55 (1H, m), 6.54 (1H, d, J=15 Hz), 6.93 (1H, dd, J=15, 4 Hz), 7.32 (2H, d, J=8 Hz), 7.76 (2H, d, J=8 Hz).

(*E*)-3-Acetoxy-1-tosyl-1-butene [(*E*)-20a].[9] To a solution of 2-propenal (31 mg, 0.5 mmol) in THF (1 ml) was added a THF solution of methylmagnesium bromide (0.6 mmol) at room temperature under nitrogen, followed by addition of acetyl chloride (47 mg, 0.6 mmol) after 30 min. After stirring for 2 h at room temperature, ethyl acetate (2 ml), *p*-$CH_3C_6H_4SOONa \cdot 4H_2O$ (188 mg, 0.75 mmol) in water (2 ml), and iodine (127 mg, 0.5 mmol) were added with vigorous stirring. The subsequent procedure was carried out in a similar manner described for **5a**. The final product (*E*)-**20a** was isolated by preparative TLC (solvent; hexane:AcOEt=5:2, v/v) in 73% yield. Formation of *Z*-isomer was not observed. An oil; MS m/z 268 (M^+); IR (neat) 3040, 2970, 2920, 1730, 1620, 1580, 1480, 1440, 1360, 1300, 1240, 1130, 1080, 1030, 950 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.37 (3H, d, J=6.7 Hz), 2.06 (3H, s), 2.45 (3H, s), 5.50 (1H, dq, J=4.3, 6.7 Hz), 6.46 (1H, d, J=15.3 Hz), 6.88 (1H, dd, J=15.3, 4.3 Hz), 7.35 (2H, d, J=8 Hz), 7.76 (2H, d, J=8 Hz).

Similarly, (*E*)-**20b** was prepared.

(*E*)-20b: An oil; MS m/z 282 (M^+); IR (neat) 3050, 2950, 1740, 1590, 1320, 1230, 1140, 1080, 1020, 960, 810 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.91 (3H, t, J=7.6 Hz), 1.72 (2H, m), 2.07 (3H, s), 2.44 (3H, s), 5.40 (1H, m), 6.45 (1H, d, J=15.3 Hz), 6.87 (1H, dd, J=15.3, 4.6 Hz), 7.34 (2H, d, J=8.2 Hz), 7.75 (2H, d, 8.2 Hz).

(*E*)-**21a,b**, (*E*)-**22a,b**, and (*E*)-**23a,b** were prepared in similar manners described for **5g**, (*E*)-**6**, and (*E*)-**7**, respectively, without formation of the corresponding (*Z*)-isomers.

(*E*)-21a: An oil; MS m/z 226 (M^+); IR (neat) 3480, 3040, 2960, 1610, 1580, 1440, 1300, 1140, 1080, 960, 830, 800 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.35 (3H, d, J=6.7 Hz), 1.63 (1H, s), 2.44 (3H, s), 4.54 (1H, m), 6.58 (1H, d, J=15 Hz), 6.95 (1H, dd, J=15, 3.7 Hz), 7.34 (2H, d, J=8 Hz), 7.77 (2H, d, J=8 Hz).

(*E*)-21b: An oil; MS *m/z* 240 (M^+); IR (neat) 3500, 3060, 2980, 2880, 1620, 1600, 1460, 1400, 1320, 1300, 1150, 1090, 970, 810 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.94 (3H, t, *J*=7.6 Hz), 1.61 (2H, m), 2.32 (1H, br), 2.43 (3H, s), 4.29 (1H, m), 6.58 (1H, d, *J*=15 Hz), 6.94 (1H, dd, *J*=15, 3.7 Hz), 7.33 (2H, d, *J*=8 Hz), 7.75 (2H, d, *J*=8 Hz).

(*E*)-22a: An oil; MS *m/z* 244 (M^+); IR (neat) 3040, 2960, 2920, 1620, 1590, 1440, 1310, 1140, 1080, 1010, 960, 830, 800, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.64 (3H, d, *J*=6.7 Hz), 2.45 (3H, s), 4.61 (1H, m), 6.55 (1H, d, *J*=14.7 Hz), 6.95 (1H, dd, *J*=14.7, 6.1 Hz), 7.36 (2H, d, *J*=8.2 Hz), 7.77 (2H, d, *J*=8.2 Hz).

(*E*)-22b: An oil; MS *m/z* 258 (M^+); IR (neat) 3040, 2960, 1620, 1590, 1450, 1310, 1300, 1140, 1080, 960, 830, 800, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.03 (3H, t, *J*=7.3 Hz), 1.90 (2H, m), 2.45 (3H, s), 4.42 (1H, m), 6.57 (1H, d, *J*=15 Hz), 6.92 (1H, dd, *J*=15, 6.7 Hz), 7.35 (2H, d, *J*=8 Hz), 7.77 (2H, d, *J*=8 Hz).

(*E*)-23a: An oil; MS *m/z* 288 (M^+, ^{79}Br) and 290 (M^+, ^{81}Br); IR (neat) 3060, 2980, 2930, 1620, 1600, 1450, 1320, 1150, 1090, 1010, 970, 840, 800 cm^1; ^1H NMR ($CDCl_3$) δ=1.81 (3H, d, *J*=6.7 Hz), 2.45 (3H, s), 4.66 (1H, dq, *J*=7.6, 6.7 Hz), 6.44 (1H, d, *J*=15 Hz), 7.01 (1H, dd, *J*=15, 7.6 Hz), 7.36 (2H, d, *J*=8.2 Hz), 7.77 (2H, d, *J*=8.2 Hz).

(*E*)-23b: An oil; MS *m/z* 302 (M^+, ^{79}Br) and 304 (M^+, ^{81}Br); IR (neat) 3040, 2910, 1580, 1430, 1310, 1140, 1080, 960, 830, 790 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.02 (3H, t, *J*=7.3 Hz), 1.96 (2H, m), 2.45 (3H, s), 4.44 (1H, m), 6.46 (1H, d, *J*=15 Hz), 6.96 (1H, dd, *J*=15, 8.5 Hz), 7.35 (2H, d, *J*=8.5 Hz), 7.76 (2H, d, *J*=8.5 Hz).

24a,b—(*E*)-**27a,b** were prepared in similar manners described for **9**—(*E*)-**11**, respectively.

24a: An oil; MS *m/z* 306 (M^+); IR (neat) 3030, 2980, 2930, 1730, 1590, 1490, 1450, 1360, 1280, 1240, 1170, 1150, 1080, 970, 930 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.44 (3H, d, *J*=6.4 Hz), 2.11 (2H, m), 2.47 (3H, s), 3.01 (3H, s), 3.20 (2H, m), 4.90 (1H, m), 7.38 (2H, d, *J*=8 Hz), 7.79 (2H, d, *J*=8 Hz).

24b: An oil; MS *m/z* 320 (M^+); IR (neat) 3030, 2970, 2930, 1590, 1450, 1400, 1350, 1280, 1170, 1140, 1080, 960, 920 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.97 (3H, t, *J*=7.3 Hz), 1.74 (2H, m), 2.11 (2H, m), 2.46 (3H, s), 3.01 (3H, s), 3.21 (2H, m), 4.73 (1H, m), 7.38 (2H, d, *J*=8 Hz), 7.79 (2H, d, *J*=8 Hz).

25a: An oil; MS *m/z* 258 (M^+); IR (neat) 3040, 2960, 1920, 1590, 1490, 1450, 1310, 1280, 1150, 1080, 1010, 950, 810 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.25 (3H, d, *J*=7 Hz), 1.87 (1H, m), 1.96 (1H, m), 1.97 (3H, s), 2.46 (3H, s), 2.73 (1H, m), 3.24 (2H, m), 7.37 (2H, d, *J*=8 Hz), 7.79 (2H, d, *J*=8 Hz).

25b: An oil; MS *m/z* 272 (M^+); IR (neat) 2960, 2920, 1590, 1450, 1300, 1150, 1080, 960, 810 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.96 (3H, t, *J*=7.3 Hz), 1.53 (2H, m), 1.82 (1H, m), 1.90 (3H, s), 2.03 (1H, m), 2.46 (3H, s), 2.48 (1H, m), 3.22 (1H, m), 3.33 (1H, m), 7.37 (2H, d, *J*=8 Hz), 7.80 (2H, d, *J*=8 Hz).

26a: An oil; MS *m/z* 414 (M^++1); IR (neat) 3050, 2960, 2920, 1590, 1570, 1480, 1470, 1430, 1300, 1140, 1080, 1010, 990, 950, 800, 730 cm^{-1}; ^1H NMR spectrum shows the resulting **26a** consists of ca. 61/39 mixture of diastereoisomers.

26b: An oil; MS *m/z* 428 (M^++1); IR (neat) 3050, 2960, 2920, 1590, 1570, 1470, 1430, 1310, 1290, 1140, 1080, 1010, 990, 950, 900, 800, 730 cm^{-1}; ^1H NMR spectrum shows the resulting **26b** consists of ca. 60/40 mixture of diastereoisomers.

(*E*)-27a: An oil; MS *m/z* 256 (M^+); IR (neat) 3040, 2960, 2900, 1600, 1580, 1430, 1310, 1140, 1080, 1010, 960 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.37 (3H, d, *J*=6.7 Hz), 1.91 (3H, s), 2.44 (3H, s), 3.32 (1H, m), 6.29 (1H, d, *J*=15 Hz), 6.79 (1H, dd, *J*=15, 8.2 Hz), 7.34 (2H, d, *J*=8 Hz), 7.77 (2H, d, *J*=8 Hz).

(*E*)-27b: An oil; MS *m/z* 270 (M^+); IR (neat) 3040, 2970, 2920, 2880, 1610, 1590, 1450, 1310, 1150, 1080, 970, 810 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.97 (3H, t, *J*=7.3 Hz), 1.61 (2H, m), 1.87 (3H, s), 2.44 (3H, s), 3.07 (1H, dt, *J*=9.3, 7.0 Hz), 6.29 (1H, d, *J*=15 Hz), 6.73 (1H, dd, *J*=15, 9.3 Hz), 7.33 (2H, d, *J*=8.2 Hz), 7.77 (2H, d, *J*=8.2 Hz).

Conversion of Vinylic Sulfones to the Corresponding Allylic Sulfones. To a solution of a vinylic sulfone (1.0 mmol) in dry acetonitrile (8 ml) [or in dry *t*-butyl alcohol (10 ml)] was added DBU (0.3 ml, 2.0 mmol) or *N*,*N*-diisopropylethylamine (0.35 ml, 2.0 mmol) [or *t*-BuOK (224 mg, 2.0 mmol)] at room temperature (25 °C) [at 30 °C or under reflux]. An aliquot (0.5 ml) of the reaction mixture was taken out with a syringe at arbitrary time intervals and immediately quenched by introducing into 2 ml of phosphate buffer solution (pH 7). After concentration under reduced pressure to remove acetonitrile [or *t*-butyl alcohol], the organic substances were extracted with ethyl acetate or ether, followed by washing with brine and drying over Na_2SO_4. ^1H NMR spectrum of the residue obtained by evaporation of the solvent was taken to determine the ratio of the (*E*)- and (*Z*)-allylic sulfones and the unaffected vinylic sulfone. In order to determine the yield, the residue obtained from a larger portion of the reaction mixture was separated by preparative TLC. Physical data of the resulting allylic sulfones were given in the following.

28: An oil; MS *m/z* 210 (M^+); IR (neat) 3020, 2910, 1590, 1310, 1140, 1080, 960, 810, 720 cm^{-1}; ^1H NMR ($CDCl_3$) of (*E*)-**28** δ=1.68 (3H, d, *J*=6.4 Hz), 2.45 (3H, s), 3.71 (2H, d, *J*=7.3 Hz), 5.41 (1H, dt, *J*=15.3, 7.3 Hz), 5.56 (1H, dq, *J*=15.3, 6.4 Hz), 7.33 (2H, d, *J*=8 Hz), 7.73 (2H, d, *J*=8 Hz); ^1H NMR ($CDCl_3$) of (*Z*)-**28** δ=1.37 (3H, d, *J*=7.0 Hz), 2.45 (3H, s), 3.84 (2H, d, *J*=7.9 Hz), 5.42 (1H, dt, *J*=10.7, 7.9 Hz), 5.82 (1H, dq, *J*=10.7, 7.0 Hz), 7.34 (2H, d, *J*=8 Hz), 7.76 (2H, d, *J*=8 Hz).

33: An oil; MS *m/z* 238 (M^+); IR (neat) 2960, 1590, 1450, 1400, 1310, 1150, 1120, 1080, 810 cm^{-1}; ^1H NMR ($CDCl_3$) of (*E*)-**33** δ=0.95 (3H, t, *J*=7.6 Hz), 1.57 (3H, d, *J*=6.7 Hz), 2.17 (2H, m), 2.44 (3H, s), 3.70 (2H, s), 5.19 (1H, q, *J*=6.7 Hz), 7.32 (2H, d, *J*=8.5 Hz), 7.71 (2H, d, *J*=8.5 Hz); ^1H NMR ($CDCl_3$) of (*Z*)-**33** δ=0.98 (3H, t, *J*=7.3 Hz), 1.24 (3H, d, *J*=7.1 Hz), 2.17 (2H, m), 2.44 (3H, s), 3.84 (2H, s), 5.54 (1H, q, *J*=7.1 Hz), 7.32 (2H, d, *J*=8.2 Hz), 7.75 (2H, d, *J*=8.2 Hz).

34/35: Solidified (not recrystallized); MS *m/z* 224 (M^+); IR (KBr) 2940, 1590, 1440, 1390, 1310, 1130, 1090, 810 cm^{-1}; ^1H NMR ($CDCl_3$) of (*E*)-**34** δ=1.55 (3H, d, *J*=7.7 Hz), 1.74 (3H, s), 2.44 (3H, s), 3.69 (2H, s), 5.19 (1H, q, *J*=7.7 Hz), 7.32 (2H, d, *J*=8.2 Hz), 7.71 (2H, d, *J*=8.2 Hz); ^1H NMR ($CDCl_3$) of (*Z*)-**34** δ=1.20 (3H, d, *J*=6.7 Hz), 1.83 (3H, s), 2.44 (3H, s), 3.82 (2H, s), 5.54 (1H, q, *J*=6.7 Hz), 7.33 (2H, d, *J*=8 Hz), 7.76 (2H, d, *J*=8 Hz); ^1H NMR ($CDCl_3$) of **35** δ=1.01 (3H, t, *J*=7.3 Hz), 2.17 (2H, q, *J*=7.3 Hz), 2.44 (3H, s), 3.76 (2H, s), 4.76 (1H, s), 5.03 (1H, s), 7.33 (2H, d, *J*=8.2 Hz), 7.74 (2H, d, *J*=8.2 Hz).

36: An oil; MS *m/z* 238 (M^+); IR (neat) 2950, 1580, 1450, 1390, 1300, 1290, 1220, 1140, 1080, 960, 800 cm^{-1}; ^1H NMR ($CDCl_3$) of (*E*)-**36** δ=0.89 (6H, d, *J*=6.7 Hz), 2.25 (1H, m), 2.44 (3H, s), 3.70 (2H, d, *J*=7.0 Hz), 5.35 (1H, m), 5.42 (1H, dd, *J*=6.1, 15.6 Hz), 7.33 (2H, d, *J*=8.2 Hz), 7.22 (2H, d, *J*=8.2 Hz); ^1H NMR ($CDCl_3$) of (*Z*)-**36** δ=0.74 (6H, d, *J*=6.4 Hz), 2.25 (1H, m), 2.44 (3H, s), 3.83 (2H, d, *J*=8.0 Hz), 5.27 (1H, m), 5.51 (1H, t, *J*=10.1 Hz), 7.33 (2H, d, *J*=8.3 Hz), 7.76 (2H, d, *J*=8.3 Hz).

(*E*)-37: An oil; MS *m/z* 253 (M^++1); IR (neat) 2950, 1580,

1450, 1310, 1290, 1140, 1120, 1080, 960 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.90 (9H, s), 2.43 (3H, s), 3.71 (2H, d, J=7.0 Hz), 5.31 (1H, dt, J=15.7, 7.0 Hz), 5.43 (1H, d, J=15.7 Hz), 7.32 (2H, d, J=8 Hz), 7.71 (2H, d, J=8 Hz).

(*E*)-38: Mp 125 °C (from *i*-PrOH); IR (KBr) 3000, 2900, 1580, 1480, 1440, 1400, 1300, 1280, 1140, 1130, 1080, 960, 800 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.44 (3H, s), 3.93 (2H, d, J=7.6 Hz), 6.10 (1H, dt, J=15.9, 7.6 Hz), 6.39 (1H, d, J=15.9 Hz), 7.24—7.74 (5H, m), 7.32 (2H, d, J=8.3 Hz), 7.75 (2H, d, J=8.3 Hz). Found: C, 70.47; H, 5.91%. Calcd for $C_{16}H_{16}O_2S$: C, 70.56; H, 5.92%.

39: (*Z*)-Form could be isolated from *E*/*Z*-mixture by recrystallization. Mp 89 °C (from AcOEt–hexane); IR (KBr) 1580, 1480, 1300, 1250, 1200, 1130, 1070, 980 cm^{-1}; ^{1}H NMR ($CDCl_3$) of (*Z*)-**39** δ=2.34 (3H, s), 4.04 (2H, d, J=7.9 Hz), 4.89 (1H, dt, J=6.1, 7.9 Hz), 6.48 (1H, d, J=6.1 Hz), 6.63—7.23 (5H, m), 7.24 (2H, d, J=8 Hz), 7.78 (2H, d, J=8 Hz). Found: C, 66.50; H, 5.61%. Calcd for $C_{16}H_{16}O_3S$: C, 66.64; H, 5.59%. ^{1}H NMR ($CDCl_3$) of (*E*)-**39** δ=2.46 (3H, s), 3.73 (2H, d, J=8.2 Hz), 5.19 (1H, dt, J=12.2, 8.2 Hz), 6.45 (1H, d, J=12.2 Hz), 6.83—7.27 (5H, m), 7.37 (2H, d, J=8 Hz), 7.78 (2H, d, J=8 Hz).

40: Mp 146.8—147.0 °C (from AcOEt, *E*/*Z*-mixture); IR (KBr) 2900, 2180, 1900, 1640, 1590, 1580, 1500, 1480, 1400, 1370, 1330, 1250, 1120, 1070, 850, 725 cm^{-1}; ^{1}H NMR ($CDCl_3$) of (*E*)-**40** δ=2.43 (3H, s), 3.79 (2H, d, J=8.2 Hz), 5.44 (1H, dt, J=12.2, 8.2 Hz), 6.56 (1H, d, J=12.2 Hz), 6.95 (2H, d, J=9.3 Hz), 7.39 (2H, d, J=7.9 Hz), 7.79 (2H, m), 8.20 (2H, d, J=9.3 Hz); ^{1}H NMR ($CDCl_3$) of (*Z*)-**40** δ=2.33 (3H, s), 4.06 (2H, d, J=8.2 Hz), 5.14 (1H, dt, J=8.2, 5.9 Hz), 6.58 (1H, d, J=5.9 Hz), 6.79 (2H, d, J=9.2 Hz), 7.24 (2H, d, J=8 Hz), 7.76 (2H, d, J=8 Hz), 8.15 (2H, d, J=9.2 Hz). Found: C, 57.74; H, 4.54; N, 4.50%. Calcd for $C_{16}H_{15}NO_5S$: C, 57.65; H, 4.54; N, 4.20%.

41: Mp 71.5—73.7 °C (from MeOH, *E*/*Z*-mixture); MS *m*/*z* 302 (M$^+$); IR (KBr) 2900, 2840, 1645, 1590, 1500, 1400, 1300, 1270, 1245, 1130, 725, 690 cm^{-1}; ^{1}H NMR ($CDCl_3$) of (*E*)-**41** δ=2.30 (3H, s), 2.46 (3H, s), 3.71 (2H, d, J=7.9 Hz), 5.11—5.16 (1H, m), 6.41 (1H, d, J=12.2 Hz), 6.72 (2H, d, J=8.7 Hz), 7.07 (2H, d, J=8.7 Hz), 7.37 (2H, d, J=8.2 Hz), 7.78 (2H, d, J=8.2 Hz); ^{1}H NMR ($CDCl_3$) of (*Z*)-**41** δ=2.27 (3H, s), 2.36 (3H, s), 4.03 (2H, d, J=7.9 Hz), 4.84 (1H, dt, J=6.1, 7.9 Hz), 6.44 (1H, d, J=6.1 Hz), 6.52 (2H, d, J=8.3 Hz), 7.22 (2H, d, J=8.3 Hz), 7.25 (2H, d, J=8 Hz), 7.78 (2H, d, J=8 Hz).

42: (*Z*)-Form could be isolated from *E*/*Z*-mixture by recrystallization. Mp 89.2—89.8 °C (from MeOH); IR (KBr) 3060, 3020, 2940, 2920, 2820, 1645, 1585, 1500, 1450, 1400, 1370, 1300, 1230, 1130, 1075, 730 cm^{-1}; ^{1}H NMR ($CDCl_3$) of (*Z*)-**42** δ=2.38 (3H, s), 3.75 (3H, s), 4.02 (2H, d, J=7.9 Hz), 4.82 (1H, dt, J=6.1, 7.9 Hz), 6.40 (1H, d, J=6.1 Hz), 6.56 (2H, d, J=9.2 Hz), 6.74 (2H, d, J=9.2 Hz), 7.27 (2H, d, J=8.2 Hz), 7.79 (2H, d, J=8.2 Hz). Found: C, 64.13; H, 5.70%. Calcd for $C_{17}H_{18}O_4S$: C, 64.01; H, 5.63%. ^{1}H NMR ($CDCl_3$) of (*E*)-**42** δ=2.47 (3H, s), 3.70 (2H, d, J=8.2 Hz), 3.78 (3H, s), 5.07 (1H, dt, J=12.2, 8.2 Hz), 6.93 (1H, d, J=12.2 Hz), 6.56 (2H, d, J=9 Hz), 6.79 (2H, d, J=9 Hz), 7.36 (2H, d, J=8 Hz), 7.77 (2H, d, J=8 Hz).

43: An oil; MS *m*/*z* 241 (M$^+$+1); IR (neat) 2960, 1640, 1580, 1480, 1430, 1370, 1300, 1250, 1130, 1100, 1080, 1040 cm^{-1}; ^{1}H NMR ($CDCl_3$) of (*E*)-**43** δ=1.25 (3H, t, J=7 Hz), 2.45 (3H, s), 3.63 (2H, d, J=7.9 Hz), 3.74 (2H, q, J=7 Hz), 4.65 (1H, dt, J=12.8, 7.9 Hz), 6.23 (1H, d, J=12.8 Hz), 7.34 (2H, d, J=8 Hz), 7.74 (2H, d, J=8 Hz); ^{1}H NMR ($CDCl_3$) of (*Z*)-**43** δ=1.01 (3H, t, J=7 Hz), 2.43 (3H, s), 3.58 (2H, q, J=7 Hz), 3.88 (2H, d, J=7.7 Hz), 4.42 (1H, dt, J=6.1, 7.7 Hz), 6.10 (1H, d, J=6.1 Hz), 7.31 (2H, d, J=8 Hz), 7.78 (2H, d, J=8 Hz).

45:[13] An oil; MS *m*/*z* 242 (M$^+$); IR (neat) 1590, 1430, 1390, 1300, 1260, 1150, 1120, 1080, 940, 900, 810, 720 cm^{-1}; ^{1}H NMR ($CDCl_3$) of (*E*)-**45** δ=2.23 (3H, s), 2.45 (3H, s), 3.80 (2H, d, J=7.6 Hz), 5.22 (1H, dt, J=15, 7.6 Hz), 6.16 (1H, d, J=15 Hz), 7.35 (2H, d, J=8 Hz), 7.73 (2H, d, J=8 Hz); ^{1}H NMR ($CDCl_3$) of (*Z*)-**45** δ=2.14 (3H, s), 2.45 (3H, s), 3.95 (2H, d, J=7.9 Hz), 5.55 (1H, dt, J=9.5, 7.9 Hz), 6.29 (1H, d, J=9.5 Hz), 7.35 (2H, d, J=8 Hz), 7.78 (2H, d, J=8 Hz).

46: (*Z*)-Form could be isolated from *E*/*Z*-mixture by recrystallization. Mp 72 °C (from *i*-PrOH, lit,[10,14] 73 °C); IR (KBr) 2980, 2920, 1620, 1590, 1490, 1440, 1390, 1290, 1240, 1160, 1130, 1080, 1020, 890, 810, 750, 710 cm^{-1}; ^{1}H NMR ($CDCl_3$) of (*Z*)-**46** δ=2.45 (3H, s), 4.04 (2H, d, J=7.6 Hz), 5.90 (1H, dt, J=7.3, 7.6 Hz), 6.29 (1H, d, J=7.3 Hz), 7.34 (2H, d, J=8 Hz), 7.77 (2H, d, J=8 Hz). Found: C, 51.95; H, 4.77%. Calcd for $C_{10}H_{11}O_2SCl$: C, 52.06; H, 4.81%. ^{1}H NMR ($CDCl_3$) of (*E*)-**46** δ=2.45 (3H, s), 3.75 (2H, d, J=8.3 Hz), 5.87 (1H, m), 6.08 (1H, d, J=13.4 Hz), 7.34 (2H, d, J=8 Hz), 7.77 (2H, d, J=8 Hz).

47: An oil; MS *m*/*z* 274 (M$^+$, ^{79}Br) and 276 (M$^+$, ^{81}Br); IR (neat) 3040, 2970, 2920, 1610, 1590, 1490, 1440, 1400, 1300, 1140, 1080, 1010, 960, 890, 800, 710 cm^{-1}; ^{1}H NMR ($CDCl_3$) of (*E*)-**47** δ=2.46 (3H, s), 3.75 (2H, d, J=7.6 Hz), 6.16 (1H, dd, J=7.6, 14.5 Hz), 6.23 (1H, d, J=14.5 Hz), 7.35 (2H, d, J=8 Hz), 7.74 (2H, d, J=8 Hz); ^{1}H NMR ($CDCl_3$) of (*Z*)-**47** δ=2.45 (3H, s), 4.03 (2H, d, J=7.6 Hz), 6.23 (1H, dd, J=7.3, 7.6 Hz), 6.49 (1H, d, J=7.3 Hz), 7.35 (2H, d, J=8 Hz), 7.77 (2H, d, J=8 Hz).

48: An oil; MS *m*/*z* 238 (M$^+$); IR (neat) 2910, 1640, 1580, 1440, 1300, 1230, 1140, 1080, 880, 800, 730 cm^{-1}; ^{1}H NMR ($CDCl_3$) of (*E*)-**48** δ=0.95 (3H, t, J=7.3 Hz), 1.32 (3H, s), 2.00 (2H, q, J=7.3 Hz), 2.44 (3H, s), 3.78 (2H, d, J=7.9 Hz), 5.17 (1H, m), 7.32 (2H, d, J=8 Hz), 7.73 (2H, d, J=8 Hz). 5.1% of NOE was observed on tosylmethyl protons when 3-methyl protons were irradiated.[4a] ^{1}H NMR ($CDCl_3$) of (*Z*)-**48** δ=0.76 (3H, t, J=7.4 Hz), 1.71 (3H, s), 1.79 (2H, q, J=7.4 Hz), 2.44 (3H, s), 3.78 (2H, d, J=7.9 Hz), 5.17 (1H, m), 7.32 (2H, d, J=8 Hz), 7.73 (2H, d, J=8 Hz).

49a: An oil; MS *m*/*z* 268 (M$^+$); IR (neat) 3040, 1730, 1620, 1590, 1440, 1370, 1310, 1230, 1140, 1080, 1040, 950, 800 cm^{-1}; ^{1}H NMR ($CDCl_3$) of (*E*)-**49a** δ=1.56 (3H, s), 2.11 (3H, s), 2.46 (3H, s), 3.76 (2H, d, J=8.5 Hz), 5.18 (1H, t, J=8.5 Hz), 7.36 (2H, d, J=8 Hz), 7.79 (2H, d, J=8 Hz); ^{1}H NMR ($CDCl_3$) of (*Z*)-**49a** δ=1.92 (3H, s), 2.02 (3H, s), 2.46 (3H, s), 3.74 (2H, d, J=7.9 Hz), 5.03 (1H, t, J=7.6 Hz), 7.34 (2H, d, J=8.2 Hz), 7.75 (2H, d, J=8.2 Hz). 4.3% of NOE was observed on methyl protons attached to olefin when olefinic proton was irradiated.[4a]

49b: An oil; MS *m*/*z* 241 (M$^+$−41); IR (neat) 2970, 2920, 1710, 1590, 1480, 1450, 1400, 1360, 1300, 1220, 1140, 1100, 1080, 1010, 970, 930 cm^{-1}; ^{1}H NMR ($CDCl_3$) of (*E*)-**49b** δ=0.78 (3H, t, J=7.6 Hz), 2.00 (2H, q, J=7.6 Hz), 2.13 (3H, s), 2.45 (3H, s), 3.79 (2H, d, J=8.2 Hz), 5.14 (1H, t, J=8.2 Hz), 7.34 (2H, d, J=7.9 Hz), 7.80 (2H, d, J=7.9 Hz); ^{1}H NMR ($CDCl_3$) of (*Z*)-**49b** δ=0.97 (3H, t, J=7.6 Hz), 2.03 (3H, s), 2.22 (2H, q, J=7.6 Hz), 2.46 (3H, s), 3.73 (2H, d, J=7.9 Hz), 5.06 (1H, t, J=7.9 Hz), 7.34 (2H, d, J=7.9 Hz), 7.75 (2H, d, J=7.9 Hz).

50a: An oil; MS *m*/*z* 240 (M$^+$); IR (neat) 3040, 2980, 2920, 1730, 1650, 1590, 1440, 1400, 1370, 1320, 1290, 1240, 1180,

1140, 1080, 1040, 810, 740 cm^{-1}; ^1H NMR ($CDCl_3$) of (*E*)-**50a** δ=1.48 (3H, s), 2.45 (3H, s), 3.51 (3H, s), 3.74 (2H, d, *J*=8.2 Hz), 4.37 (1H, t, *J*=8.2 Hz), 7.32 (2H, d, *J*=8.3 Hz), 7.77 (2H, d, *J*=8.3 Hz); ^1H NMR ($CDCl_3$) of (*Z*)-**50a** δ=1.80 (3H, s), 2.44 (3H, s), 3.26 (3H, s), 3.85 (2H, d, *J*=6.8 Hz), 4.43 (1H, t, *J*=6.8 Hz), 7.32 (2H, d, *J*=8.3 Hz), 7.77 (2H, d, *J*=8.3 Hz).

50b: An oil; MS *m*/*z* 241 (M^+-13); IR (neat) 2970, 2930, 1660, 1590, 1450, 1400, 1360, 1310, 1290, 1220, 1140, 1120, 1080, 1060, 1040, 880, 810, 740 cm^{-1}; ^1H NMR ($CDCl_3$) of (*E*)-**50b** δ=0.82 (3H, t, *J*=7.6 Hz), 1.87 (2H, q, *J*=7.6 Hz), 2.43 (3H, s), 3.51 (3H, s), 3.76 (2H, d, *J*=8.2 Hz), 4.32 (1H, t, *J*=8.2 Hz), 7.31 (2H, d, *J*=8 Hz), 7.76 (2H, d, *J*=8 Hz); ^1H NMR ($CDCl_3$) of (*Z*)-**50b** δ=0.99 (3H, t, *J*=7.3 Hz), 2.10 (2H, q, *J*=7.3 Hz), 2.43 (3H, s), 3.23 (3H, s), 3.88 (2H, d, *J*=7.6 Hz), 4.50 (1H, t, *J*=7.6 Hz), 7.31 (2H, d, *J*=8 Hz), 7.76 (2H, d, *J*=8 Hz).

51: An oil; MS *m*/*z* 252 (M^+); IR (neat) 2960, 2900, 1680, 1590, 1440, 1400, 1370, 1300, 1230, 1200, 1180, 1140, 1080, 1020, 980, 920, 900, 810 cm^{-1}; ^1H NMR ($CDCl_3$) of (*E*)-**51** δ=1.87 (2H, m), 2.42 (3H, s), 2.29 (2H, m), 3.67 (2H, d, *J*=8.6 Hz), 4.05 (2H, t, *J*=6.7 Hz), 4.60 (1H, t, *J*=8.6 Hz), 7.33 (2H, d, *J*=8 Hz), 7.77 (2H, d, *J*=8 Hz); ^1H NMR ($CDCl_3$) of (*Z*)-**51** δ=1.82 (2H, m), 2.43 (3H, s), 2.43 (2H, m), 3.82 (2H, t, *J*=6.7 Hz), 3.86 (2H, d, *J*=7.9 Hz), 4.26 (1H, t, *J*=7.9 Hz), 7.30 (2H, d, *J*=8.3 Hz), 7.77 (2H, d, *J*=8.3 Hz). 3.6% of NOE was observed on methylene protons of oxolane ring attached to olefin when olefinic proton was irradiated.[4a]

52a: An oil; MS *m*/*z* 244 (M^+); IR (neat) 3050, 2980, 2920, 1730, 1650, 1590, 1440, 1400, 1380, 1310, 1290, 1140, 1080, 1010, 960, 810, 740 cm^{-1}; ^1H NMR ($CDCl_3$) of (*E*)-**52a** δ=1.78 (3H, s), 2.46 (3H, s), 3.77 (2H, d, *J*=8.6 Hz), 5.60 (1H, t, *J*=8.6 Hz), 7.37 (2H, d, *J*=8.2 Hz), 7.76 (2H, d, *J*=8.2 Hz); ^1H NMR ($CDCl_3$) of (*Z*)-**52a** δ=2.09 (3H, s), 2.45 (3H, s), 3.97 (2H, d, *J*=7.6 Hz), 5.60 (1H, t, *J*=7.6 Hz), 7.34 (2H, d, *J*=8.5 Hz), 7.76 (2H, d, *J*=8.5 Hz).

52b: An oil; MS *m*/*z* 258 (M^+); IR (neat) 3050, 2970, 1620, 1590, 1450, 1400, 1320, 1300, 1140, 1080, 960, 800 cm^{-1}; ^1H NMR ($CDCl_3$) of (*E*)-**52b** δ=0.91 (3H, t, *J*=7.3 Hz), 2.11 (2H, q, *J*=7.3 Hz), 2.45 (3H, s), 3.79 (2H, d, *J*=8.2 Hz), 5.56 (1H, t, *J*=8.2 Hz), 7.33 (2H, d, *J*=8 Hz), 7.75 (2H, d, *J*=8 Hz); ^1H NMR ($CDCl_3$) of (*Z*)-**52b** δ=1.04 (3H, t, *J*=7.3 Hz), 2.32 (2H, q, *J*=7.3 Hz), 2.45 (3H, s), 3.99 (2H, d, *J*=7.6 Hz), 5.60 (1H, t, *J*=7.6 Hz), 7.33 (2H, d, *J*=8 Hz), 7.75 (2H, d, *J*=8 Hz).

53a: An oil; MS *m*/*z* 288 (M^+, ^{79}Br) and 290 (M^+, ^{81}Br); IR (neat) 3040, 2970, 2920, 1590, 1430, 1320, 1140, 1080, 1010, 960, 820 cm^{-1}; ^1H NMR ($CDCl_3$) of (*E*)-**53a** δ=1.96 (3H, s), 2.45 (3H, s), 3.73 (2H, d, *J*=8.2 Hz), 5.86 (1H, t, *J*=8.2 Hz), 7.34 (2H, d, *J*=8 Hz), 7.76 (2H, d, *J*=8 Hz); ^1H NMR ($CDCl_3$) of (*Z*)-**53a** δ=2.28 (3H, s), 2.45 (3H, s), 3.96 (2H, d, *J*=7.6 Hz), 5.78 (1H, t, *J*=7.6 Hz), 7.34 (2H, d, *J*=8 Hz), 7.76 (2H, d, *J*=8 Hz).

53b: An oil; MS *m*/*z* 302 (M^+, ^{79}Br) and 304 (M^+, ^{81}Br); IR (neat) 3040, 2970, 1640, 1590, 1450, 1320, 1280, 1140, 1080, 1010, 960, 830, 800 cm^{-1}; ^1H NMR ($CDCl_3$) of (*E*)-**53b** δ=0.89 (3H, t, *J*=7.6 Hz), 2.32 (2H, q, *J*=7.6 Hz), 2.45 (3H, s), 3.75 (2H, d, *J*=8.2 Hz), 5.50 (1H, t, *J*=8.2 Hz), 7.33 (2H, d, *J*=7.9 Hz), 7.75 (2H, d, *J*=7.9 Hz); ^1H NMR ($CDCl_3$) of (*Z*)-**53b** δ=1.04 (3H, t, *J*=7.3 Hz), 2.45 (2H, q, *J*=7.3 Hz), 2.45 (3H, s), 3.98 (2H, d, *J*=7.3 Hz), 5.79 (1H, t, *J*=7.3 Hz), 7.33 (2H, d, *J*=7.9 Hz), 7.75 (2H, d, *J*=7.9 Hz).

54a:[15] An oil; MS *m*/*z* 256 (M^+); IR (neat) 2920, 1740, 1610, 1590, 1430, 1300, 1140, 1080, 1010, 960, 800, 740 cm^{-1}; ^1H NMR ($CDCl_3$) of (*E*)-**54a** δ=1.57 (3H, s), 2.22 (3H, s), 2.45 (3H, s), 3.87 (2H, d, *J*=8.2 Hz), 4.95 (1H, t, *J*=8.2 Hz), 7.34 (2H, d, *J*=8 Hz), 7.74 (2H, d, *J*=8 Hz); ^1H NMR ($CDCl_3$) of (*Z*)-**54a** δ=2.01 (3H, s), 2.02 (3H, s), 2.44 (3H, s), 4.05 (2H, d, *J*=7.6 Hz), 5.50 (1H, t, *J*=7.6 Hz), 7.34 (2H, d, *J*=8 Hz), 7.76 (2H, d, *J*=8 Hz).

54b: An oil; MS *m*/*z* 270 (M^+); IR (neat) 3040, 2960, 2920, 1740, 1700, 1590, 1430, 1310, 1140, 1080, 910, 810, 730 cm^{-1}; ^1H NMR ($CDCl_3$) of (*E*)-**54b** δ=0.89 (3H, t, *J*=7.6 Hz), 1.98 (2H, q, *J*=7.6 Hz), 2.20 (3H, s), 2.45 (3H, s), 3.88 (2H, d, *J*=8 Hz), 4.89 (1H, t, *J*=8 Hz), 7.34 (2H, d, *J*=8.2 Hz), 7.74 (2H, d, *J*=8.2 Hz); ^1H NMR ($CDCl_3$) of (*Z*)-**54b** δ=1.05 (3H, t, *J*=7.3 Hz), 1.95 (3H, s), 2.26 (2H, q, *J*=7.3 Hz), 2.44 (3H, s), 4.11 (2H, d, *J*=7.6 Hz), 5.57 (1H, t, *J*=7.6 Hz), 7.34 (2H, d, *J*=8.3 Hz), 7.75 (2H, d, *J*=8.3 Hz).

X-Ray Crystallography of 5a.[16] $C_{13}H_{18}O_2S$, FW=238.3, monoclinic, space group $P2_1/n$, a=7.9603(9), b=10.001(1), c=16.662(2) Å, β=102.361(8)°, V=1295.8(3) Å^3, Mo $K\alpha$ radiation (graphite-monochromated, λ=0.71069 Å), Z=4, D_c=1.22 g cm^{-3}, $F(000)$=512, μ(Mo $K\alpha$)=2.32 cm^{-1}. Intensities were measured on a Rigaku AFC-5R diffractometer using Mo $K\alpha$ radiation within $2\theta \leq 55.1°$ and θ–2θ scan method at 23 °C. Observed independent reflections of 1675 with $I>3\sigma(I)$ were used in the structure analysis and refinement applying TEXSAN program system. Number of variables was 145. The final R and R_w were 0.052 and 0.069, respectively. Selected bond distances (l/Å) and dihedral angles (ϕ/°): C8–H9 0.981, C8–C9 1.328(4), C9–C10 1.506(5), C10–C11 1.492(5), C11–H4 0.957, C11–H5 0.946; C8–C9–C10–C11 −1.142, C9–C10–C11–H3 −179.453.

(*E*)-5c:[16] $C_{16}H_{16}O_3S$, FW=288.4, monoclinic, space group $P2_1/n$, a=16.630(4), b=7.669(2) c=24.046(7) Å, β=92.88(2)°, V=3063(2) Å^3, Mo $K\alpha$ radiation (graphite-monochromated, λ=0.71069 Å), Z=8, D_c=1.25 g cm^{-3}, $F(000)$=1216, μ(Mo $K\alpha$)=2.15 cm^{-1}, Rigaku AFC-5R, $2\theta \leq 45.0°$, θ–2θ scan method, temperature 23 °C, number of observation=982 [$I>3\sigma(I)$], number of variables 361, TEXSAN program system. The final R and R_w were 0.070 and 0.085, respectively. Selected bond distances (l/Å) and dihedral angles (ϕ/°): Cl–Hl 0.991, Cl–C2 1.35 (3), C2–C3 1.39 (3), C3–O3 1.38(2), C17–H5 1.007, C17–C18 1.37(3), C18–C19 1.51(3), C19–O6 1.32(3); C1–C2–C3–O3 6(4), C2–C3–O3–C4 −173(2), C17–C18–C19–O6 −1(3), C18–C19–O6–C20 178 (2).

(*E*)-13:[16] $C_{12}H_{14}O_4S$, FW=254.3, monoclinic, space group $P2_1$, a=5.489 (1), b=7.824(2) c=13.877(2) Å, β=90.95(1)°, V=595.8(2) Å^3, Mo $K\alpha$ radiation (graphite-monochromated, λ=0.71069 Å), Z=2, D_c=1.42 g cm^{-3}, $F(000)$=268, μ(Mo $K\alpha$)=2.71 cm^{-1}, Rigaku AFC-5R, $2\theta \leq 55.1°$, θ–2θ scan method, temperature 23 °C, number of observation=1077 [$I>3\sigma(I)$], number of variables 221, TEXSAN program system. The final R and R_w were 0.034 and 0.040, respectively. Selected bond distances (l/Å) and dihedral angles (ϕ/°): C8–H8 0.85(4), C8–C9 1.302(6), C9–C10 1.500(6), C10–O3 1.405(5), C10–O4 1.406(5); C8–C9–C10–O4 5.1(6), C9–C10–O4–C12 97.9(4). The methyl group centered at C7 suffered from twofold disorder with half occupancy for two sets of hydrogen atoms.

(*Z*)-42:[16] $C_{17}H_{18}O_4S$, FW=318.39, monoclinic, space group $P2_1/a$, a=19.892(5), b=7.511(2) c=23.228(8) Å, β=112.10(2)°, V=3215(2) Å^3, Mo $K\alpha$ radiation (graphite-monochromated, λ=0.71069 Å), Z=8, D_c=1.32 g cm^{-3}, $F(000)$=1344, μ(Mo $K\alpha$)=2.06 cm^{-1}, Rigaku AFC-5R, $2\theta \leq 55.1°$, θ–2θ scan method, temperature 23 °C, number of

observation=2552 [$I>3\sigma(I)$], number of variables 542, TEXSAN program system. The final R and R_w were 0.078 and 0.054, respectively.

Authors express their sincere thanks to Dr. S. Hosoi of Faculty of Pharmaceutical Sciences, Kanazawa University, for his kind help for X-ray analyses. This work is partly supported by the Research Grant-in-Aid from the Ministry of Education, Science and Culture.

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16) Tables (15 pages) containing X-ray crystallographic data consisting of all atomic and hydrogen coordinates (with estimated standard deviations and temperature coefficients), bond lengths and angles (with estimated standard deviations) are deposited as Document No. 8974 at the Office of the Editor of Bull. Chem. Soc. Jpn.