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A Sulfoxide Version of the Julia–Lythgoe Olefination: A New Method for the Synthesis of Olefins from Carbonyl Compounds and Sulfoxides with Carbon–Carbon Coupling

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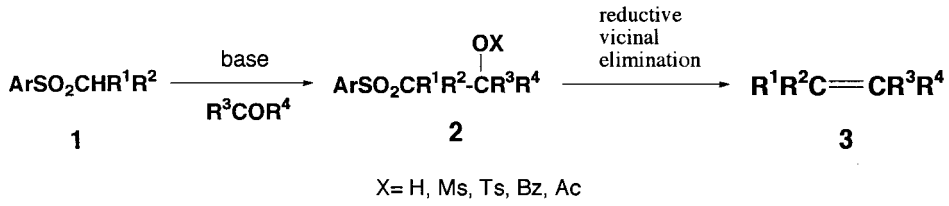
Abstract—Reaction of β-mesyloxy (or acetoxy) sulfoxides, derived from alkyl (or arylmethyl) phenyl sulfoxides and carbonyl compounds in two steps, with alkylmetals (*n*-BuLi, *t*-BuLi, or EtMgBr) at low temperature gave olefins in good to excellent yields. When the β-hydroxy sulfoxides derived from arylaldehydes were treated with mesyl chloride in the presence of triethylamine, the sulfoxides directly gave *E*-olefins in good yields. These reactions offer a sulfoxide version of the Julia–Lythgoe olefination. The reductive vicinal elimination was found to take place through the direct sulfoxide–metal exchange. The stereochemistry of the elimination was investigated and found to be stereospecific; however, the stereospecificity was found to be dependent on the substrates.

Needless to say, the formation of carbon–carbon double bonds is one of the most important reactions in organic synthesis.[1] Especially, the methods including carbon–carbon coupling are of high value. The Wittig and related reactions, Peterson-type reactions, McMurry coupling, Ramberg–Backlund reaction, and Julia–Lythgoe olefination are well-known methods for the formation of olefinic compounds with carbon–carbon coupling.[2]

The Julia–Lythgoe olefination is a method for the formation of olefins **3** from sulfones **1** and carbonyl compounds via β-hydroxy sulfones and their derivatives **2** in two or three steps (Scheme 1).[3] In the original papers[3a,3b] the authors used Na–Hg as a reducing agent in the reductive vicinal elimination. However, because of the high toxicity of Hg, this step was improved by replacing Na–Hg with other reducing agents such as lithium naphthalenide,[4] SmI_2,[5] Mg,[6] and electroreductive reaction.[7] Recently, one-pot synthesis of *trans*-1,2-disubstituted olefins using metallated 1-phenyl-1*H*-tetrazol-5-ylsulfones and aldehydes was reported.[8]

The Julia–Lythgoe olefination entails some drawbacks in the step of formation of the carbon–carbon bond with α-sulfonyl carbanion and carbonyl compounds. Namely, because the hydrogen on the carbon bearing the sulfonyl group is highly acidic, in some cases especially when ketones are used as the carbonyl compounds,[5c] the addition reaction of α-sulfonyl carbanion with carbonyl compounds is reversible with the equilibrium lying towards the starting material.[9] The acidity of the hydrogen is much higher when R^1 is an aromatic group. By this reason, no example of olefination using aryl arylmethyl sulfones (**1:** R^1=Aryl) has appeared so far.

To overcome the problems described above, we planned to use sulfoxides instead of the sulfones as shown in Scheme 2. The advantages in using sulfoxides **4** are as follows. First, as



Scheme 1. Julia–Lythgoe olefination.

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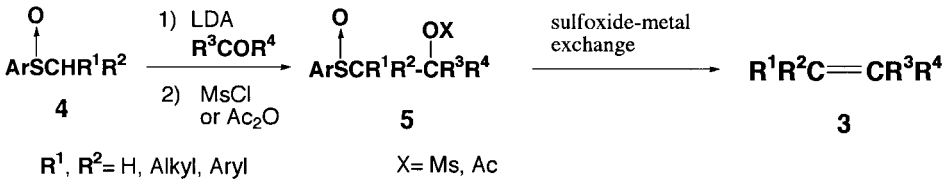


Scheme 2. Sulfoxide version of the Julia–Lythgoe olefination.

the acidity of the hydrogen on the carbon bearing sulfinyl group is much lower than that of the sulfonyl group,[10] the coupling of α-sulfinyl carbanion with carbonyl compounds could be expected to proceed smoothly even with ketones. Second, aryl arylmethyl sulfoxide **4** (R^1 or R^2=Ar) may be used. If this is realized, the Julia–Lythgoe-type olefination could be extended to a synthesis of stylene- and stilbene-type olefins. Third, in the reductive vicinal elimination of **5**, the sulfoxide–metal exchange, which has been extensively studied by our group,[11] would be applied.[12] In this case, no toxic metal or expensive reagent is required.

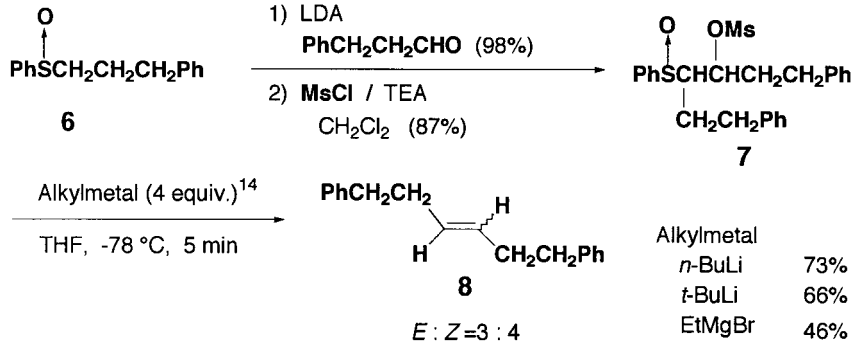
In this paper we report in detail the development of a sulfoxide version of the Julia–Lythgoe olefination based on the concept described above.[13]

Results and Discussion

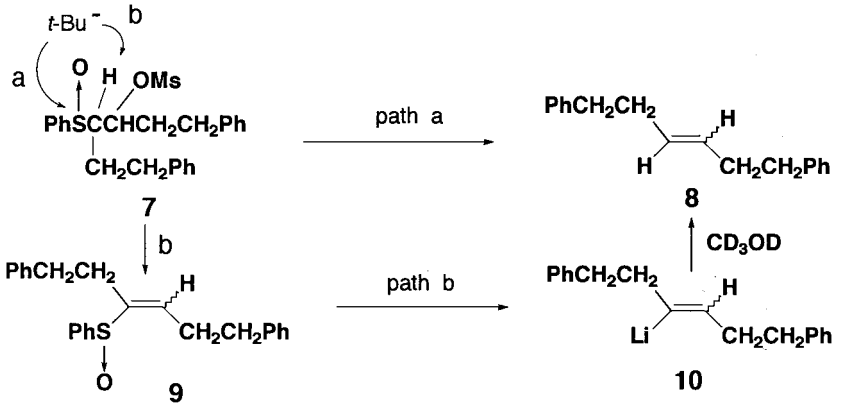
At first, we investigated the feasibility for the vicinal elimination by the sulfoxide–metal exchange using β-mesyloxy sulfoxide **7** as a representative example (Scheme 3). Sulfoxide **7** (a diastereomeric mixture) was synthesized from phenyl 3-phenylpropyl sulfoxide **6** and 3-phenylpropanal in 85% overall yield.

The β-mesyloxy sulfoxide **7** in THF was treated with 4 equiv.[14] of *n*-BuLi at −78°C for 5 min. Fortunately, the reaction gave a clean reaction mixture, from which the desired olefin **8** was obtained as a mixture of geometrical isomers (*E*/*Z*=3:4)[15] in 73% yield. *tert*-Butyllithium (*t*-BuLi) was also found to be effective in this reaction. Even ethylmagnesium bromide (EtMgBr) was effective in this reaction; however, the yield of **8** was moderate.[16] No improvement of the yield of the olefin **8** was obtained by lowering the reaction temperature to −100°C.

In this reaction, two different reaction mechanisms would be expected (Scheme 4). One is the direct β-elimination of the sulfinyl and mesyloxy groups via the sulfoxide–metal exchange (path a). The other is a two-step mechanism (path b). First, the alkyllithium picks up the acidic hydrogen on the carbon bearing the sulfinyl group to give α-sulfinyl carbanion, which gives the vinylsulfoxide **9** by elimination

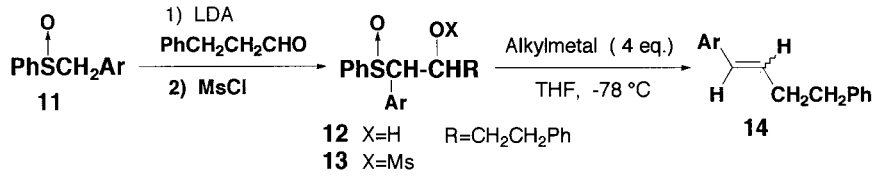


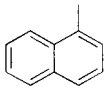
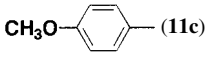
Scheme 3.



Scheme 4.

Table 1. Synthesis of aryl-substituted olefins from arylmethyl phenyl sulfoxide and 3-phenylpropanal



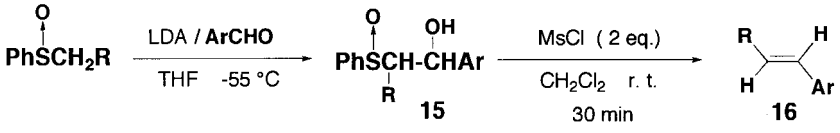
Entry	**11** (Ar)	**12** (yield/%)	**13** (yield/%)	Alkylmetal	**14** yield/% (*E*/*Z*)
1	Ph (**11a**)	**12a** (92)	**13a** (82)	*n*-BuLi	**14a** 89 (10/7)
2				*t*-BuLi	**14a** 92 (10/7)
3				EtMgBr	**14a** 87 (10/7)
4	 (**11b**)	**12b** (98)	**13b** (88)	*n*-BuLi	**14b** 90 (3/1)
5				*t*-BuLi	**14b** 68 (3/1)
6				EtMgBr	**14b** 66 (3/1)
7	 (**11c**)	**12c** (99)	**13c** (93)	*n*-BuLi	**14c** 93 (1/0)[a]
8					**14c** 73 (1/3)
9				*t*-BuLi	**14c** 91 (1/0)[a]
10					**14c** 68 (1/3)
11				EtMgBr	**14c** 75 (1/0)[a]
12					**14c** 98 (1/3)

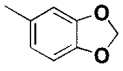
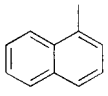
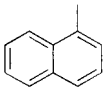
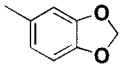
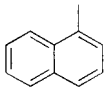
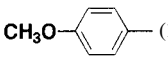
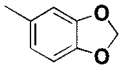
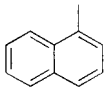
[a] The yield from the crystalline of **13c**. See text.

of the mesyloxy anion. The vinylsulfoxide **9** is again attacked by the alkylmetal[17] to give vinyllithium **10**, which is protonated by quenching with water.

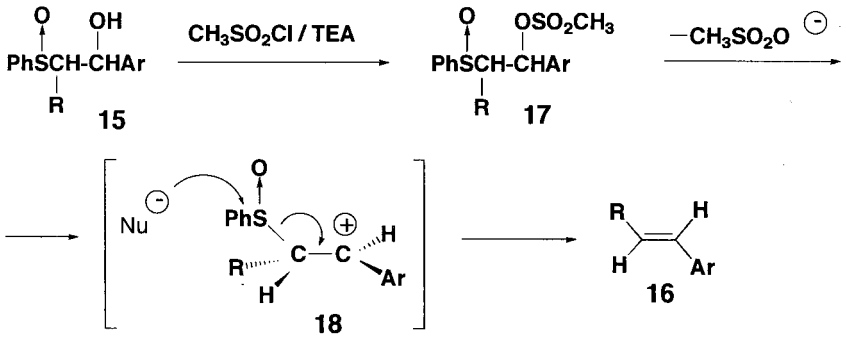
To ascertain which path predominantly takes place, the reaction was conducted with *t*-BuLi at −78°C and after 1 min the reaction was quenched with deuterated methanol. No deuterium incorporation was observed in the produced olefin **8** by ^{1}H NMR. From these results, we concluded that the mechanism of the vicinal elimination is a direct β-elimination via sulfoxide–metal exchange of **7** (path a).

Table 2. Synthesis of aryl-substituted olefins from alkyl phenyl sulfoxide or arylmethyl phenyl sulfoxide and arylaldehydes



Entry	Sulfoxide (R)	ArCHO (Ar)	**15** (yield/%)[a]	**16** (yield/%)[a]
1	$PhCH_2CH_2$ (**6**)		**15a** (92)	**16a** (76)
2			**15b** (98)	**16b** (58)
3	 (**11b**)		**15c** (99)	**16c** (78)
4			**15d** (99)	**16d** (65)
5	 (**11c**)		**15e** (98)	**16e** (90)
6			**15f** (99)	**16f** (84)

[a] Isolated yield after silica gel column chromatography.



Scheme 5. A presumed mechanism for the elimination of **15** with mesyl chloride.

Synthesis of aryl-substituted 1,2-disubstituted olefins from arylmethyl phenyl sulfoxides and 3-phenylpropanal

As described above, the olefination using alkyl phenyl sulfoxide giving 1,2-dialkylated olefin **8** was successful and we next investigated a synthesis of aryl-substituted olefins from arylmethyl phenyl sulfoxides. It is worth noting that, as mentioned in the introduction, the Julia–Lythgoe olefination with aryl arylmethyl sulfones is difficult.

The olefination from arylmethyl phenyl sulfoxide **11** and 3-phenylpropanal was quite successful, and the results are summarized in Table 1. The first step, addition of the carbanion of arylmethyl phenyl sulfoxide **11** to 3-phenylpropanal gave almost quantitative yields (92–99%) of the adduct **12**. Mesylation of **12** with 2 equiv. of mesyl chloride in the presence of triethylamine in dichloromethane gave the mesylate **13** without any problem.

The vicinal elimination of **13** with alkylmetals was investigated under similar conditions as described in Scheme 3. We obtained much better results compared with those from the vicinal elimination of **7** (see Scheme 3). As shown in Table 1, in the step for vicinal elimination with *n*-BuLi, *t*-BuLi, even EtMgBr gave good to excellent yields. It is noted that the mesylates **13a** and **13b** are a mixture of diastereomers with respect to the three chiral centers. The elimination of these mixtures gave predominantly *E*-olefins.

The results in entries 7, 9, and 11 are quite interesting. The adduct of **11c** with 3-phenylpropanal gave a mixture of the diastereomers. In this case one of the isomers could be isolated as a crystal (the relative stereochemistry is not known yet). The crystalline isomer was mesylated and then treated with alkylmetals to give a single geometrical isomer, which was determined to be *E*-configuration. This result implies that the stereochemistry of the elimination must be stereospecific, not stereoselective. The details of the stereochemistry of this elimination are discussed later.

Synthesis of stylene- and stilbene-type olefins from arylaldehydes

We next extended the above-mentioned chemistry to use arylaldehydes. If arylaldehydes can be used in the presented method, we would obtain stylene- and stilbene-type olefins. The results are summarized in Table 2.

Addition of the α-sulfinyl carbanion of **6**, **11b**, and **11c** to piperonal and 1-naphthaldehyde gave the adducts **15a–f** in almost quantitative yields. The adduct **15a** was then mesylated with 2 equiv. of mesyl chloride in CH_2Cl_2 in the presence of triethylamine at room temperature. After 30 min, the starting material disappeared and, to our surprise, the product was found to be not the expected mesylate but olefin **16a**. The geometry of the olefin was determined to be *E* by ^{1}H NMR. As shown in Table 2, all the adducts **15a–f** gave *E*-olefins **16a–f** in one-operation in about 60–90% yields.

The mechanism of this reaction is presumed as follows (Scheme 5). First, the hydroxy group of **15** is mesylated to give the mesylate **17**. As the mesyloxy group is placed on the carbon bearing an aryl group, the mesyloxy group is readily eliminated to give benzyl-type carbocation **18**. A nucleophile in the reaction mixture attacks the sulfinyl group to give the olefin **16**. Because the cation **18** is expected to be the most stable when R and Ar are in *s-trans* conformation, the mixture of the diastereomers **15** stereoselectively affords the single *E*-olefin. As the nucleophile, we are surmising that the chloro anion from triethylamine hydrochloride is the most likely at present.

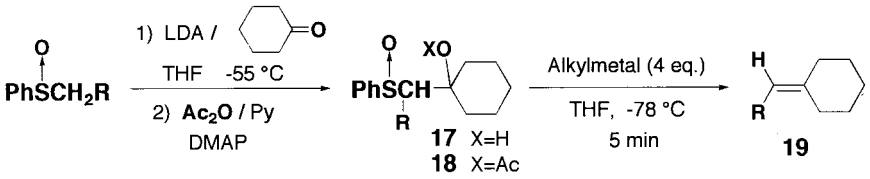
Synthesis of tri-substituted olefins from cyclohexanone

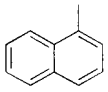
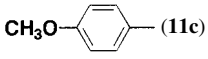
In order to investigate if this method can be extended to a synthesis of tri-substituted olefins, we next examined the reaction using cyclohexanone as a representative example of ketones. The results are summarized in Table 3.

The reaction of the α-sulfinyl carbanion of **6**, **11b**, and **11c** with cyclohexanone again gave the adduct **17** in almost quantitative yields. However, we came across a problem in the next step. Namely, mesylation of the α-hydroxy sulfoxide **17** with mesyl chloride under similar conditions as described above gave only a complex mixture. One cause of this difficulty is the easily eliminative nature of the tertiary mesylate.

We next changed the mesylate to acetate, and this worked well to afford the stable acetate **18** in good yields. The next step was somewhat subtle. If the rate of the reaction of an alkylmetal with the acetoxy group is faster than that with the sulfinyl group, the elimination reaction of **18** would be impossible. At any rate, **18b** was treated with *n*-BuLi in THF at −78°C for 5 min. Fortunately, this reaction also

Table 3. Synthesis of tri-substituted olefins from alkyl phenyl sulfoxide or arylmethyl phenyl sulfoxide and cyclohexanone



Entry	Sulfoxide (R)	**17** (yield/%)	**18** (yield/%)	Alkylmetal	**19** (yield/%)
1	$PhCH_2CH_2$ (**6**)	**17a** (87)	**18a**[a] (84)	*n*-BuLi	**19a** (83)
2				*t*-BuLi	**19a** (93)
3				EtMgBr	**19a** (–)[b]
4	 (**11b**)	**17b** (98)	**18b**[a] (70)	*n*-BuLi	**19b** (78)
5				*t*-BuLi	**19b** (81)
6				EtMgBr	**19b** (41)[c]
7	 (**11c**)	**17c** (95)	**18c** (81)	*n*-BuLi	**19c** (84)
8				*t*-BuLi	**19c** (80)
9				EtMgBr	**19c** (23)[c]

[a] Although the acetates **18a** and **18b** are a mixture of separable diastereomers, the next reaction was carried out without sepatrtion of the diastereomers.
[b] No reaction.
[c] Considerable amount of the starting material **18** remained.

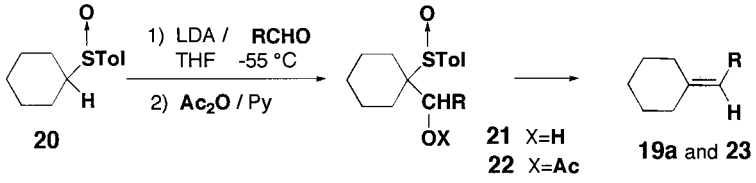
worked to give tri-substituted olefin **19b** in 78% yield. In this reaction a small amount of the starting material was recovered; however, no hydroxy compound **17b** (the product from the reaction of the acetoxy group with *n*-BuLi) was observed. As shown in Table 3, *t*-BuLi was found to be as effective as *n*-BuLi. However, the reaction with EtMgBr was rather slow and after 5 min a considerable amount of the acetate **18** remained in the reaction mixture. Especially, EtMgBr did not work at all with the acetate **18a** (entry 3).

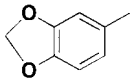
Synthesis of tri-substituted olefins from cyclohexyl *p*-tolyl sulfoxide and aldehydes

Next, we investigated the reaction starting from α-branched sulfoxide, cyclohexyl *p*-tolyl sulfoxide **20**, with 3-phenylpropanal and piperonal. The results are summarized in Table 4.

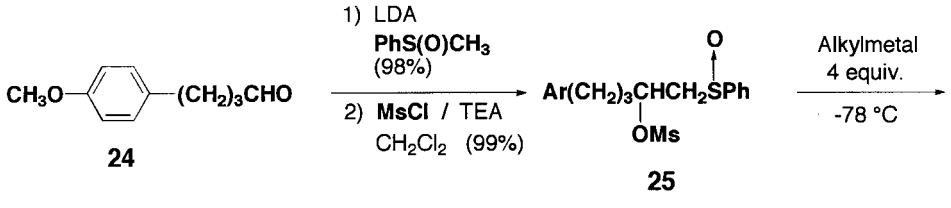
The carbanion of **20** was added to the aldehydes to give the adduct **21**; however, the yields were found to be somewhat lower than the yield of the reaction of the carbanions of sulfoxides **6** and **11** with aldehydes. In these cases, the adducts **21** are mixtures of two diastereomers, which were separated easily by silica gel column chromatography. The next step was conducted with these separated diastereomers (expressed as L and P). The adduct **21a** was acetylated as above to give the acetate **22** in almost quantitative yield. The elimination reaction of **22** was conducted with alkylmetals (entries 1–6). As shown in Table 4, EtMgBr was not a good reagent for this reaction (entries 5 and 6). Both *n*-BuLi and *t*-BuLi worked; however, the yields were

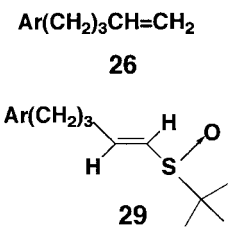
Table 4. Synthesis of tri-substituted olefins from cyclohexyl *p*-tolyl sulfoxide and aldehydes

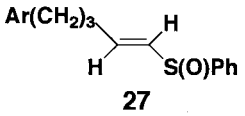


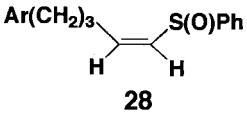
Entry	RCHO (R)	**21** (yield/%)	**22** (yield/%)	Alkylmetal	Olefin (yield/%)
1	$PhCH_2CH_2$	**21a** (78) (L:P=66:34)[a]	**22** (96)	*n*-BuLi (from **22-L**)	**19a** (43)
2				*n*-BuLi (from **22-P**)	**19a** (90)
3				*t*-BuLi (from **22-L**)	**19a** (63)
4				t-BuLi (from **22-P**)	**19a** (79)
5				EtMgBr (from **22-L**)	**19a** (17)
6				EtMgBr (from **22-P**)	**19a** (–)[b]
7		**21b** (64) (L:P=35:65)[a]	–[c]	from **21b-L**	**23** (54)
8				from **21b-P**	**23** (71)

[a] The ratio of the less polar isomer (L) and the more polar isomer (P) on silica gel TLC.
[b] No reaction.
[c] The alcohol **21b** was treated with mesyl chloride in the presence of triethylamine. Refer to the Table 2.









Alkylmetal	26	27	28	29
n-BuLi	33%	42%	---[a]	
t-BuLi	39%	11%	---[a]	50%
EtMgBr	61%	5%	5%	

a) Not observed.

Scheme 6. Treatment of β-mesyloxy sulfoxide **25** with alkylmetals.

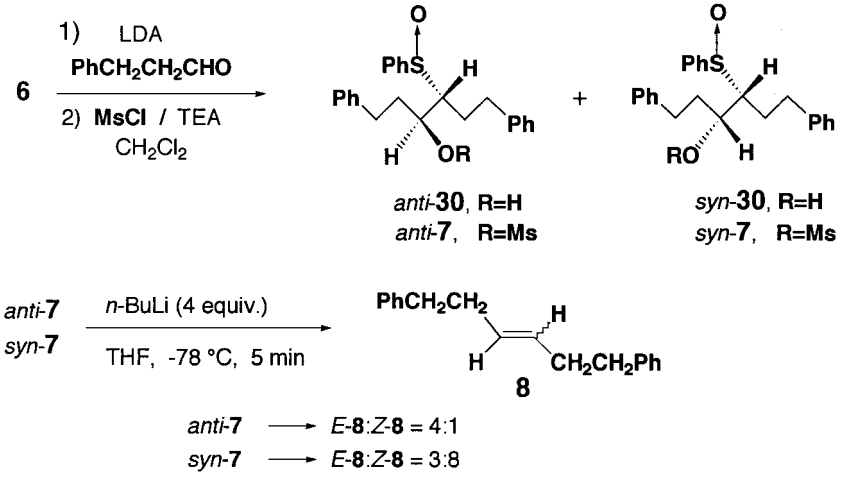
found to be variable with the isomers. Usually, the P-isomer gave better yields than the L-isomer (entries 1–4). Mesylation of the adduct derived from aryl aldehyde **21b** directly gave the olefin **23** in moderate to good yields (entries 7 and 8). Here again, the yields were found to be variable depending on the diastereomers.

An attempt to synthesize tetra-substituted olefins by using cyclohexyl *p*-tolyl sulfoxide **20** with a ketone was examined. However, the reaction of lithium carbanion of **20** with 1,4-cyclohexanedione mono-ethylene ketal gave not the desired adduct but a complex mixture. The synthesis of tetra-substituted olefins by the presented method could not be realized.

Trial to synthesize mono-substituted olefins and stereospecificity of the presented procedure

Methylenation of aldehydes is most conveniently carried out with the Wittig reaction. However, we investigated the feasibility for the methylenation of aldehydes by the presented method starting from methyl phenyl sulfoxide as a one-carbon unit. The results are shown in Scheme 6.

The reaction of the aldehyde **24** with the carbanion of methyl phenyl sulfoxide gave a quantitative yield of the adduct, which was mesylated in the usual way to give the mesylate **25**. The results of the reaction of **25** with alkylmetals are summarized in Scheme 6. The reaction with *n*-BuLi gave the desired olefin **26** in 33% yield; however, the main product was vinylsulfoxide **27**. In this case, *n*-BuLi reacted with both the sulfinyl group and the acidic hydrogen on the carbon bearing the sulfinyl group. The hydrogen on the carbon bearing sulfinyl group of **25** is less sterically hindered compared with other β-mesyloxy (or acetoxy) sulfoxides, for example, **7**, **13**, **18**, and **22**. This is thought to be the reason why the alkylmetals attack the acidic hydrogen to give vinylsulfoxides **27**, **28**, and **29**.



Scheme 7.

EtMgBr was found to be the best reagent of the three. In this case **26** was obtained in 61% yield with a mixture of vinylsulfoxides **27** and **28** (10% yield). The reaction of **25** with *t*-BuLi is very interesting. In this case, the desired **26** was obtained in 39% yield; however, the main product was olefin having *tert*-butylsulfinyl group **29**. The formation of **29** was presumed to take place through the ligand exchange reaction[18] of the produced vinyl sulfoxide **27** with *t*-BuLi.

Finally, we studied the stereochemistry of the elimination. As mentioned above (Table 1; entries 7–12), the elimination of the β-mesyloxy sulfoxides with alkylmetals is thought to proceed in a stereospecific manner. To elucidate the stereochemical correlation between the β-mesyloxy sulfoxide and the product, and ascertain whether the stereospecificity is high or low, we carried out the experiment shown in Scheme 7. First, the two main isomers of the adduct of **6** and 3-phenylpropanal were separated and the relative stereochemistry (*syn* and *anti*) of the hydroxyl and the sulfinyl groups was determined from ^{1}H NMR by comparison of the data with those of Bravo's report.[19]

anti-**30** and *syn*-**30** were mesylated to give *anti*-**7** and *syn*-**7**, respectively. These mesylates were treated with *n*-BuLi at −78°C. From *anti*-**7** the produced olefin **8** was found to be a mixture of *E* and *Z* (*E*/*Z*=4:1). In contrast to this, the elimination of *syn*-**7** gave an *E*/*Z*-mixture of **8**, and the main product was *Z* (*E*/*Z*=3:8). From these results it is concluded that the elimination takes place mainly via *trans*-elimination and that the stereospecificity is dependent on the substrates; the specificity is in some cases high (see Table 1) and in some cases not.

Experimental

All melting points are uncorrected. ^{1}H NMR spectra were measured in a $CDCl_3$ solution with JEOL JNM-LA 400 and 500 spectrometer. Electron-impact mass spectra (MS) were obtained at 70 eV by direct insertion. Silical gel 60 (MERCK) containing 0.5% fluorescence reagent 254 and quartz column were used for column chromatography and the products having UV absorption were detected by UV irradiation. In experiments requiring a dry reagent and solvent, diisopropylamine and triethylamine were distilled from CaH_2 and THF was distilled from diphenylketyl. Methanol and liquid N_2 were used for the cooling bath at −100°C.

3-Mesyloxy-1,6-diphenyl-4-phenylsulfinylhexane (7). To a THF solution (25 ml) of diisopropylamine (0.9 ml; 6.5 mmol) in a flame-dried flask was added *n*-BuLi (6.5 mmol) at 0°C under argon atmosphere. After 15 min, the solution was cooled to −55°C and 3-phenylpropyl phenyl sulfoxide **6** (1.12 g; 5 mmol) in THF was added dropwise with stirring. After 15 min, 3-phenylpropanal (0.86 ml; 6.5 mmol) in THF was added to the reaction mixture at −55°C, and the stirring was continued for 30 min. The reaction was quenched with sat. aq. NH_4Cl, and the mixture was extracted with AcOEt. The organic layer was washed with sat. aq. NH_4Cl and dried over $MgSO_4$. After removal of the solvent, the product was purified by silica gel column chromatography to give **30** (diastereomeric mixture; 1.85 g; 98%) as colorless crystals. To a CH_2Cl_2 solution of **30** (1.41 g; 3.7 mmol) in a dried flask was added Et_3N (1.0 ml; 7.4 mmol) followed by MsCl (0.6 ml; 7.4 mmol) at room temperature, and the stirring was continued for 30 min. The reaction was quenched with sat. aq. NH_4Cl, and the mixture was extracted with CH_2Cl_2. The organic layer was washed successively with 7% HCl, sat. aq. $NaHCO_3$, and sat. aq. NH_4Cl, and dried over $MgSO_4$. After removal of the solvent, the product was purified by silica gel column chromatography to give **7** (1.5 g; 87%) as a colorless oil (about 4:6:17:13 diastereomeric mixture). IR (neat) 3061, 3026, 2933, 2863, 1603, 1496, 1454, 1354, 1173, 1086 (SO), 1047 (SO), 750, 700 cm^{-1}; ^{1}H NMR δ 1.68–1.94 (1H, m), 2.00–2.40 (4H, m), 2.40–2.73 (2H, m), 2.80–3.02 (2H, m), 2.60 (0.36H, s), 3.00 (1.02H, s), 3.04 (1.38H, s), 3.23 (0.24H, s), 4.65 (0.12H, dt, *J*=11.0, 2.5 Hz), 5.04 (0.46H, dt, *J*=9.75, 3.05 Hz), 5.06 (0.34H, dt, *J*=9.2, 3.5 Hz), 5.12 (0.08H, td, *J*=6.7, 1.5 Hz), 6.81–7.63 (15H, m).

1,6-Diphenyl-3-hexene (8). In a flame-dried flask, to a THF solution of *n*-BuLi (0.72 mmol) at −78°C under argon atmosphere was added a THF solution of **7** (80 mg; 0.18 mmol) dropwise with stirring, and the stirring was continued for 5 min. The reaction was quenched with sat. aq. NH_4Cl, and the mixture was extracted with AcOEt. The organic layer was washed with sat. aq. NH_4Cl, and dried over $MgSO_4$. After removal of the solvent, the product was purified by silica gel column chromatography to give **8** (31 mg; 73%) as a colorless oil (about *E*/*Z*=3:4 mixture). IR (neat) 3026, 2924, 1604, 1496, 1454, 747, 698 cm^{-1}; ^{1}H NMR δ 2.28–2.32 (4H, m), 2.57 (2.3H, t, *J*=7.8 Hz), 2.65 (1.7H, t, *J*=7.8 Hz), 5.42 (1.14H, ddd, *J*=5.5, 5.0, 0.8 Hz), 5.48 (0.86H, ddd, *J*=5.0, 3.5, 1.5 Hz), 7.14–7.28 (10H, m); ^{13}C NMR δ 29.15 (*Z*: vinyl-C), 34.37 (*E*: vinyl-C), 35.82, 35.04, 125.68, 125.74, 128.22, 128.44, 129.43, 130.07, 142.03, 142.06. MS *m*/*z* (%) 236 (M^+, 18), 145 (14), 91 (100). Calcd for $C_{18}H_{20}$: M, 236.1563. Found: *m*/*z* 236.1559.

1,4-Diphenyl-1-phenylsulfinyl-2-butanol (12a). Above-mentioned reaction was carried out with benzyl phenyl sulfoxide to give **12a** as colorless crystals (diastereomeric mixture) in 92% yield. IR (neat) 3384, 3059, 3026, 2911, 2859, 1600, 1493, 1454, 1442, 1085(SO), 1040(SO), 749, 700 cm^{-1}; ^{1}H NMR δ 1.71–2.16 (2H, m), 2.67–2.81 (2H, m), 3.39–3.8 (1H, m), 4.48–4.86 (1H, m), 5.44 (1H, bs, OH), 6.81–7.38 (15H, m).MS *m*/*z* (%) 351 (M^+, 0.7), 225 (10), 207 (30), 126 (13), 91 (100), 77 (10). Calcd for $C_{22}H_{23}O_2S$: M, 351.1419. Found: *m*/*z* 351.1406.

3-Mesyloxy-1,4-diphenyl-4-phenylsulfinylbutane (13a). Colorless oil; IR (neat) 3031, 2934, 2863, 1602, 1496, 1454, 1354, 1173, 1086(SO), 1047(SO), 748, 700 cm^{-1}; ^{1}H NMR δ 1.81–2.17 (2H, m), 2.70–3.01 (2H, m), 3.13, 3.16, 3.37, 3.41 (each s, CH_3), 3.55–3.80 (1H, m), 5.46–5.56 (1H, m), 6.94–7.34 (15H, m).

1,4-Diphenyl-1-butene (14a). Colorless oil (about *E*/*Z*=10:7 mixture); IR (neat) 3060, 3025, 2924, 2853, 1601, 1495, 1453, 741, 698 cm^{-1}; ^{1}H NMR δ 2.50–2.55 (1H, m), 2.63–2.68 (1H, m), 2.74–2.80 (2H, m), 5.75 (0.41H, dt, *J*=11.3, 7.5 Hz), 6.25 (0.59H, dt, *J*=16.0, 6.5 Hz), 6.44 (0.59H, d, *J*=16,0 Hz), 6.46 (0.41H, d, *J*=11.3 Hz), 7.17–

7.33 (10H, m). MS *m/z* (%) 208 (M^+, 26), 117 (100), 91 (24). Calcd for $C_{16}H_{16}$: M, 208.1252. Found: *m/z* 208.1257.

1-(1-Naphthyl)-4-phenyl-1-phenylsulfinyl-2-butanol (12b). Colorless crystals (diastereomeric mixture); IR (KBr) 3366, 3058, 2922, 1596, 1509, 1444, 1086 (SO), 1029 (SO), 802, 780, 746, 699 cm^{-1}; ^1H NMR δ 1.23–2.05 (2H, m), 2.60–3.02 (2H, m), 4.34–4.69 (1H, m), 4.70–4.90 (1H, m), 6.91–8.00 (17H, m).

2-Mesyloxy-1-(1-naphthyl)-4-phenyl-1-phenylsulfinylbutane (13b). Colorless crystals (about 1:3:3:13.5 diastereomeric mixture); IR (KBr) 3024, 2930, 1596, 1496, 1444, 1355, 1173, 1087 (SO), 1046 (SO), 781, 746, 699 cm^{-1}; ^1H NMR δ 1.62–2.47 (2H, m), 2.57–3.10 (2H, m), 3.21 (0.44H, s), 3.32 (0.15H, s), 3.39 (0.44H, s), 3.46 (1.97H, s), 4.30–4.90 (1H, m), 5.56–5.72 (1H, m), 6.77–8.00 (17H, m).

1-(1-Naphthyl)-4-phenyl-1-butene (14b). Colorless oil (about *E*/*Z*=3:1 mixture); IR (neat) 3059, 3026, 2924, 2853, 1646, 1603, 1590, 1496, 1453, 777, 698 cm^{-1}; ^1H NMR δ 2.44–2.51 (0.5H, m), 2.62–2.74 (2H, m), 2.88 (1.5H, t, *J*=15.2 Hz), 5.97 (0.25H, dt, *J*=11.4, 7.3 Hz), 6.24 (0.75H, dt, *J*=15.2, 6.9 Hz), 6.89 (0.25H, d, *J*=11.4 Hz), 7.09 (0.75H, d, *J*=15.5 Hz), 7.09–8.04 (12H, m). MS *m/z* (%) 258 (M^+, 25), 167 (100), 91 (7). Calcd for $C_{20}H_{18}$: M, 258.1408. Found: *m/z* 258.1416.

1-(4-Methoxyphenyl)-4-phenyl-1-phenylsulfinyl-2-butanol (12c). *12c-oil:* Colorless oil (diastereomeric mixture); IR (neat) 3381, 3025, 2933, 2837, 1609, 1513, 1454, 1444, 1609, 1513, 1253, 1086(SO), 1030(SO), 746, 700 cm^{-1}; ^1H NMR δ 1.43–1.97 (2H, m), 2.57–2.87 (2H, m), 3.53–3.65 (1H, m), 3.75, 3.78 (each s, CH_3), 4.56–4.81 (1H, m), 6.62–7.51 (14H, m). *12c-crystal:* Colorless crystals; IR (KBr) 3328, 3057, 3024, 2931, 2837, 1610, 1513, 1458, 1444, 1248, 1088, 1038, 748, 698 cm^{-1}; ^1H NMR δ 1.64–2.12 (2H, m), 2.68–2.94 (2H, m), 3.39 (0.52H, d, *J*=5.9 Hz), 3.65 (0.46H, d, *J*=10.3 Hz), 3.74 (1.63H, s), 3.75 (1.37H, s), 4.50–4.62 (1H, m), 6.70–7.37 (14H, m). Anal. Calcd for $C_{23}H_{24}O_3S$: C, 72.60; H, 6.36; S, 8.43. Found: C, 72.53; H, 6.39; S, 8.51.

2-Mesyloxy-1-(4-methoxyphenyl)-4-phenyl-1-phenylsulfinylbutane (13c). *13c-oil:* Colorless oil (diastereomeric mixture); IR (neat) 3061, 3026, 2931, 2857, 1609, 1514, 1456, 1360, 1253, 1173, 1084(SO), 1040(SO), 749, 700 cm^{-1}; ^1H NMR δ 1.89–2.36 (2H, m), 2.61–2.80 (2H, m), 3.16, 3.38, 3.40 (each s, CH_3), 3.75, 3.77, 3.97 (each s, CH_3), 5.39–5.52 (1H, m), 6.54–7.58 (14H, m). *13c-crystal:* Colorless crystals; IR (KBr) 3058, 3024, 2933, 2840, 1610, 1514, 1355, 1255, 1174, 1085, 1034, 748, 698 cm^{-1}; ^1H NMR δ 2.63–2.69 (1H, m), 2.78–2.91 (2H, m), 2.97–3.03 (3H, m), 3.40 (3H, s), 3.69 (1H, d, *J*=11.0 Hz), 3.75 (3H, s), 5.44 (1H, dt, *J*=11.0, 4.3 Hz), 6.64–7.38 (14H, m). Anal. Calcd for $C_{24}H_{26}O_5S_2$: C, 62.86; H, 5.71; S, 13.98. Found: C, 62.17; H, 5.78; S, 14.02.

1-(4-Methoxyphenyl)-4-phenyl-1-butane (14c) and (*E*)-isomer. 14c: Colorless oil (about *E*/*Z*=1:3 mixture); IR (neat) 3061, 3025, 3004, 2932, 2853, 1607, 1511, 1454, 1248, 1035, 746, 700 cm^{-1};^1H NMR δ 2.36–2.79 (4H, m), 3.79 (0.75H, s), 3.80 (2.25H, s), 5.61 (0.75H, dt, *J*=11.6, 5.8 Hz), 6.11 (0.25H, dt, *J*=15.8, 6.0 Hz), 6.36 (1H, m), 6.82–6.87 (2H, m), 7.17–7.32 (7H, m). MS *m/z* (%) 238 (M^+, 13), 147 (100), 91 (21). Calcd for $C_{17}H_{18}O$: M, 238.1357. Found: *m/z* 238.1363. (E)-*isomer:* Colorless oil; IR (neat) 2999, 2923, 2834, 1605, 1510, 1249, 1029, 718, 695 cm^{-1}; ^1H NMR δ 2.50 (2H, dd, *J*=15.2, 7.2 Hz), 2.78 (2H, t, *J*=7.9 Hz), 3.79 (3H, s), 6.11 (1H, dt, *J*=15.8, 6.8 Hz), 6.36 (1H, d, *J*=15.8 Hz), 6.83 (2H, d, *J*=8.8 Hz), 7.17–7.32 (7H, m). MS *m/z* (%) 238 (M^+, 15), 147 (100), 115 (9), 91 (18). Calcd for $C_{17}H_{18}O$: M, 238.1357. Found: *m/z* 238.1360.

1-(3,4-Methylenedioxyphenyl)-4-phenyl-2-phenysulfinyl-1-butanol (15a). Colorless oil (diastereomeric mixture); IR (neat) 3320, 3061, 3026, 2897, 2779, 1604, 1504, 1486, 1445, 1248, 1085(SO), 1036(SO), 932, 746, 700 cm^{-1}; ^1H NMR δ 1.82–2.04 (4H, m), 2.67–2.70 (1H, m), 3.27 (1H, d, *J*=1.5 Hz), 5.44 (1H, bs), 5.97 (2H, s), 6.57–7.72 (13H, m). MS *m/z* (%) 400 (M^+, 0.5), 256 (98), 183 (99), 165 (100), 91(96). Calcd for $C_{26}H_{24}O_2S$: M, 400.1497. Found: *m/z* 400.1506.

(*E*)-1-(3,4-Methylendioxyphenyl)-4-phenyl-1-butene (16a). Colorless oil; IR (neat) 3062, 3026, 2896, 2778, 1604, 1503, 1489, 1446, 1249, 1040, 964, 929, 749, 700 cm^{-1}; ^1H NMR δ 2.49 (2H, dd, *J*=14.9, 7.3 Hz), 2.77 (2H, t, *J*=7.2 Hz), 5.93 (2H, s), 6.07 (1H, dt, *J*=15.7, 6.8 Hz), 6.32 (1H, d, *J*=15.8 Hz), 6.73 (2H, s), 6.88 (1H, s), 7.17–7.32 (5H, m). MS *m/z* (%) 252 (M^+, 40), 161 (69), 131 (100), 103 (50), 77 (19). Calcd for $C_{17}H_{16}O_2$: M, 252.1149. Found: *m/z* 252.1143.

1-(1-Naphthyl)-4-phenyl-2-phenylsulfinyl-1-butanol (15b). Colorless crystals (diastereomeric mixture); IR (neat) 3284, 1596, 1508, 1444, 1085(SO), 1028(SO), 782, 739, 697 cm^{-1}; ^1H NMR δ 1.69–2.56 (4H, m), 2.77–3.14 (1H, m), 5.70–6.30 (1H, m), 6.28–7.90 (17H, m). MS *m/z* (%) 394 (M^+, 0.1), 268 (48), 208 (44), 151 (100), 93 (69). Calcd for $C_{23}H_{22}O_4S$: M, 394.1239. Found: *m/z* 394.1209.

(*E*)-1-(1-Naphthyl)-4-phenyl-1-butene (16b). Colorless oil; IR (neat) 3060, 3026, 2924, 2853, 1650, 1603, 1590, 1508, 1454, 792, 776, 747, 699 cm^{-1};^1H NMR δ 2.66 (2H, dd, *J*=8.0, 14.9 Hz), 2.88 (2H, t, *J*=8.0 Hz), 6.25 (1H, dt, *J*=15.6, 6.8 Hz), 7.10 (1H, d, *J*=15.6 Hz), 7.20–8.03 (12H, m). MS *m/z* (%) 258 (M^+, 25), 167 (100), 152 (19), 91 (11). Calcd for $C_{20}H_{18}$: M, 258.1407. Found: *m/z* 258.1407.

1-(3,4-Methylenedioxyphenyl)-2-(1-naphthyl)-2-phenylsulfinylethanol (15c). Colorless oil (diastereomeric mixture); IR (neat) 3299, 3061, 2889, 2779, 1595, 1504, 1444, 1245, 1087 (SO), 1036 (SO), 998, 928, 802, 779, 749, 691 cm^{-1}, ^1H NMR δ 4.36 (0.3H, d, *J*=12.7 Hz), 4.72 (0.5H, d, *J*=10.2 Hz), 4.85 (0.1H, d, *J*=9.5 Hz), 4.85 (0.1H, d, *J*=10.3 Hz), 5.67–5.76 (1H, m), 6.01–6.02 (2H, dd, *J*=3.7, 1.5 Hz), 6.35–8.12 (10H, m).

(*E*)-1-(3,4-Methylenedioxyphenyl)-2-(1-naphthyl)ethene (16c). Colorless crystals; mp 105–107°C (AcOEt–hexane); IR (KBr) 3057, 3009, 2891, 2777, 1604, 1589, 1503, 1488, 1446, 1253, 1233, 1040, 958, 932, 803, 790, 773 cm^{-1}; ^1H NMR δ 6.00 (2H, s), 6.84 (1H, d, *J*=7.9 Hz), 7.02 (1H, dd,

J=7.8, 1.5 Hz), 7.07 (1H, d, J=16.0 Hz, vinyl-H), 7.05 (1H, d, J=1.5 Hz), 7.71 (1H, d, J=16.0 Hz, vinyl-H), 7.46–8.21 (7H, m). MS m/z (%) 274 (M^+, 100), 215 (49), 152 (12). Calcd for $C_{19}H_{14}O_2$: M, 274.0993. Found: m/z 274.0995. Anal. Calcd for $C_{19}H_{14}O_2$: C, 83.19; H, 5.14. Found: C, 82.80; H, 5.01.

1,2-Di(1-naphthyl)-2-phenylsulfinylethanol (15d). Colorless oil (about 6:8:9:11 diastereomeric mixture); IR (neat) 3357, 3059, 3008, 1596, 1512, 1444, 1084(SO), 1036(SO), 778, 750 cm^{-1}; ^1H NMR δ 5.20 (0.32H, d, J=7.6 Hz), 5.36 (0.18H, d, J=9.0 Hz), 5.54 (0.24H, d, J=9.3 Hz), 6.07 (0.26H, d, J=8.5 Hz), 6.35 (0.32H, d, J=9.3 Hz), 6.46 (0.24H, d, J=9.3 Hz), 6.53 (0.26H, ddd, J=8.6, 6.8, 1.5 Hz), 6.64 (0.18H, d, J=9.3 Hz), 6.86–8.51 (19H, m). MS m/z (%) 422 (M^+, 0.09), 280 (30), 155 (100), 127 (54). Calcd for $C_{28}H_{22}O_2S$: M, 422.1341. Found: m/z 422.1348.

(*E*)-1,2-Di(1-naphthyl)ethene (16d). Colorless crystals; mp 162.5–164.5°C (AcOEt–hexane); IR (neat) 3043, 1648, 1590, 1508, 800, 773 cm^{-1}; ^1H NMR δ 7.91 (2H, s), 7.50–8.26 (14H, m). MS m/z (%) 280 (M^+, 100), 152 (24). Calcd for $C_{22}H_{16}$: M, 280.1252. Found: m/z 280.1253. Anal. Calcd for $C_{22}H_{16}$: C, 94.25; H, 5.75. Found: C, 93.78; H, 5.68.

2-(4-Methoxyphenyl)-1-(3,4-methylendioxyphenyl)-2-phenylsulfinylethanol (15e). Colorless crystals (about 3:3:6:13 diastereomeric mixture); IR (KBr) 3262, 2901, 2836, 1610, 1512, 1488, 1444, 1251, 1085 (SO), 1036 (SO), 747 cm^{-1}; ^1H NMR δ 3.57 (0.52H, d, J=8.6 Hz), 3.64 (0.12H, d, J=2.7 Hz), 3.69 (0.36H, s), 3.73 (0.72H, s), 3.76 (1.56H, s), 3.77(0.36H, s), 3.84 (0.24H, d, J= 9.5 Hz), 3.87 (0.12H, d, J=9.8 Hz), 5.42 (0.24H, d, J= 10.2 Hz), 5.45 (0.52H, d, J=8.5 Hz), 5.55 (0.12H, d, J= 8.6 Hz), 5.65 (0.12H, d, J=2.7 Hz), 5.83 (0.28H, dd, J= 3.3, 1.4 Hz), 5.85 (0.28H, m), 6.00 (0.44H, dd, J=5.1, 1.4 Hz), 6.51–7.43 (12H, m).

(*E*)-1-(4-Methoxyphenyl)-2-(3,4-methylenedioxyphenyl)-ethene (16e). Colorless crystals; mp 141–143°C (AcOEt–hexane); IR (KBr) 2956, 2836, 1602, 1512, 1449, 1255, 1029, 964, 956, 924, 824, 791 cm^{-1}; ^1H NMR δ 6.78 (1H,d, J=8.0 Hz), 6.88 (2H, d, J=8.6 Hz), 6.88 (2H, s), 6.90 (1H,dd, J=8.3, 1.9 Hz), 7.04 (1H, d, J=1.9 Hz), 7.41 (2H, d, J=8.9 Hz). MS m/z (%) 254 (M^+, 100), 239 (12), 181 (15), 153 (20), 127 (7). Calcd for $C_{16}H_{14}O_3$: M, 254.0942. Found: m/z 254.0938. Anal. Calcd for $C_{16}H_{14}O_3$: C, 75.57; H, 5.55. Found: C, 75.17; H, 5.40.

2-(4-Methoxyphenyl)-1-(1-naphthyl)-2-phenylsulfinylethanol (15f). Colorless crystals (diastereomeric mixture); IR (KBr) 3313, 3055, 2930, 2835, 1609, 1509, 1458, 1442, 1252, 1085(SO), 1032(SO), 780, 747, 689 cm^{-1}; ^1H NMR δ 3.60 (0.78H, s), 3.62 (0.86H, s), 3.74 (0.27H, s), 3.75 (1.0H, s), 4.03 (0.34H, d, J=6.8 Hz), 4.21 (0.5H, b), 4.33 (0.32H, d, J=9.3 Hz), 4.40 (0.25H, d, J=9.5 Hz), 6.24 (0.35H, d, J= 9.2 Hz), 6.25 (0.38H, d, J=7.1 Hz), 6.37 (0.27H, d, J= 9.5 Hz), 6.44–8.35 (16H, m). MS m/z (%) 402 (M^+, 0.07), 277 (46), 155 (99), 127 (99), 121 (100). Calcd for $C_{25}H_{22}O_3S$: M, 402.1290. Found: m/z 402.1293.

(*E*)-1-(4-Methoxyphenyl)-1-(1-naphthyl)ethene (16f). Colorless crystal; mp 92–93°C (AcOEt–hexane); IR (KBr) 2956, 1604, 1510, 1255, 1173, 1031, 825, 798, 782, 770 cm^{-1}; ^1H NMR δ 3.85 (3H, s), 6.94 (2H, d, J=8.6 Hz), 7.10 (1H, d, J=15.9 Hz, vinyl-H), 7.49 (1H, d, J=15.9 Hz, vinyl-H), 7.46–8.23 (9H, m). MS m/z (%) 260 (M^+, 100), 229 (18), 215 (24), 152 (14). Calcd for $C_{19}H_{16}O$: M, 260.1201. Found: m/z 260.1205. Anal. Calcd for $C_{19}H_{16}O$: C, 87.66; H, 6.20. Found: C, 87.34; H, 6.11.

1-(3-Phenyl-1-phenylsulfinylpropyl)cyclohexanol (17a). Colorless crystals (about 3:19 diastereomeric mixture); IR (KBr) 3382, 2937, 2855, 1444, 1088 (SO), 1027 (SO), 747, 698 cm^{-1}; ^1H NMR δ 1.24–2.28 (14H, m), 2.47–2.49 (0.85H, m), 2.89–2.90 (0.15H, m), 6.74–7.83 (10H, m). MS m/z (%) 342 (M^+, 0.8), 217 (61), 117 (72), 91 (100). Calcd for $C_{21}H_{26}O_2S$: M, 342.1654. Found: m/z 342.1648.

1-(1-Acetoxycyclohexyl)-3-phenyl-1-phenylsulfinylpropane (18a). To a solution of **17a** (870 mg; 2.54 mmol) in pyridine (3.6 ml) was added acetic anhydride (3.0 ml) and DMAP (62.3 mg; 0.51 mmol) with stirring at room temperature and the reaction mixture was stirred at room temperature for 30 h. After removal of excess pyridine and acetic anhydride under vacuum, the product was purified by silica gel column chromatography to give **18a** (822 mg; 84%) as a colorless oil (about 3:19 diastereomeric mixture). The isomers were easily separated. *18a-L:* Colorless oil; IR (neat) 3060, 3026, 2935, 2862, 1730, 1496, 1478, 1445, 1369, 1284, 1263, 1233, 1131, 1086, 1047 (SO), 1020 (SO), 754, 700 cm^{-1}; ^1H NMR δ 1.19–1.72 (10H, m), 1.77 (1H, ddd, J=12.1, 5.4, 2.9 Hz), 1.97 (1H, ddd, J=12.2, 6.4, 2.9 Hz), 2.13 (3H, s), 2.35–2.47 (2H, m), 3.76 (1H, dd, J=6.4, 3.0 Hz), 6.81–7.62 (10H, m). MS m/z (%) 384 (M^+, 0.3), 199 (29), 167 (53), 125 (100), 91 (71), 78 (33). Calcd for $C_{23}H_{28}O_3S$: M, 384.1759. Found: m/z 384.1751. *18a-P:* Colorless oil; IR (neat) 3026, 2936, 2863, 1731, 1714, 1445, 1359, 1318, 1234, 1154, 1127, 1086 (SO), 1047 (SO), 752, 700 cm^{-1}; ^1H NMR δ 1.18–1.73 (10H, m), 1.78 (1H, ddd, J=12.0, 5.6, 2.9 Hz), 1.98 (1H, ddd, J=11.8, 6.6, 3.2 Hz), 2.31 (3H, s), 2.39–2.52 (2H, m), 3.89 (1H, dd, J=3.4, 3.0 Hz), 6.82–7.64 (10H, m).

1-Cyclohexylidene-3-phenylpropane (19a). This compound was derived from the mixture of **18a-L** and **18a-P**; colorless oil; IR (neat) 3062, 3026, 2926, 2852, 1604, 1495, 1446, 747, 698 cm^{-1}; ^1H NMR δ 1.37–1.54 (6H, m), 2.02–2.07 (4H, m), 2.30 (2H, dd, J=15.4, 7.4 Hz), 2.63 (2H, t, J=7.3 Hz), 5.12 (1H, t, J=7.3 Hz), 7.17–7.29 (5H, m). MS m/z (%) 200 (M^+, 27), 109 (100), 91 (39), 67 (72). Calcd for $C_{15}H_{20}O$: M, 200.1564. Found: m/z 200.1577.

1-[(1-Naphthyl)(phenylsulfinyl)methyl]cyclohexanol (17b). A mixture of colorless crystals and oil (about 4.5:5 diastereomeric mixture); IR (KBr) 3357, 2930, 1509, 1444, 1013 (SO), 781, 750, 688 cm^{-1}; ^1H NMR δ 0.86–2.05 (9H, m), 2.25–2.45 (1H, m), 4.51 (0.53H, s), 4.99 (0.47H, s), 6.89–8.30 (12H, m).

1-Acetoxy-1[(1-naphthyl)(phenylsulfinyl)methyl]cyclohexane (18b). Colorless oil (about 1:2 diastereomeric mixture), the isomers were easily separated by silica gel column chromatography. *18b-L:* Colorless oil; IR (neat)

3060, 2935, 2861, 1729, 1714, 1569, 1512, 1445, 1368, 1258, 1232, 1088, 1052 (SO), 1020 (SO), 803, 784, 751, 691 cm^{-1}; ^1H NMR d 0.96–1.04 (2H, m), 1.38–1.45 (2H, m), 1.59–1.68 (2H, m), 1.77 (1H, ddt, *J*=26.0, 12.9, 3.4 Hz), 1.95 (1H, dt, *J*=12.9, 4.1 Hz), 2.31 (3H, s), 3.72 (1H, dd, *J*=13.9, 1.9 Hz), 2.80 (1H, d, *J*=13.4 Hz), 5.84 (1H, s), 6.91–8.14 (12H, m). *18b-P:* Colorless oil; IR (neat) 3053, 2935, 2864, 1732, 1714, 1596, 1512, 1445, 1359, 1323, 1241, 1129, 1082 (SO), 1049 (SO), 807, 786, 756, 690 cm^{-1}; ^1H NMR d 1.03–1.07 (2H, m), 1.52–1.74 (7H, m), 2.12 (1H, dt, *J*=12.4, 4.9 Hz), 2.35 (3H, s), 2.77 (1H, dd, *J*=13.9, 2.2 Hz), 2.83 (1H, dd, *J*=13.0, 2.9 Hz), 6.33 (1H, s), 6.87–7.91 (12H, m).

Cyclohexylidene(1-naphthyl)methane (19b). Colorless oil; IR (neat) 3042, 2926, 2852, 1655, 1590, 1446, 801, 781 cm^{-1}; ^1H NMR δ 1.51 (2H, m), 1.61 (2H, m), 1.73 (2H, m), 2.18 (2H, t, *J*=6.1 Hz), 2.42 (2H, t, *J*=5.9 Hz), 6.58 (1H, s), 7.25–8.04 (7H, m). MS *m/z* (%) 222 (M^+, 100), 179 (44), 165 (80), 141 (35), 128 (12). Calcd for $C_{17}H_{18}$: M, 222.1407. Found: *m/z* 222.1397.

1-[(4-Methoxyphenyl)(phenylsulfinyl)methyl]cyclohexanol (17c). Colorless crystals (about 1:2 diastereomeric mixture); IR (KBr) 3366, 3051, 2931, 2846, 1610, 1511, 1458, 1444, 1253, 1180, 1083 (SO), 1032 (SO), 1012, 746, 693 cm^{-1}; ^1H NMR δ 0.94–2.38 (10H, m), 3.57 (0.67H, s), 3.73 (2H, s), 3.79 (1H, s), 3.90 (0.33H, s), 7.07–7.26 (9H, m). MS *m/z* (%) 344 (M^+, 0.02), 219 (100), 137 (41), 121 (56), 77 (11). Calcd for $C_{20}H_{24}O_3S$: M, 344.1446. Found: *m/z* 344.1452.

1-Acetoxy-1-[(4-methoxyphenyl)(phenylsulfinyl)methyl]-cyclohexane (18c). Colorless crystals (diastereomeric mixture); IR (KBr) 2936, 2862, 1732, 1714, 1609, 1512, 1444, 1253, 1181, 1128, 1086 (SO), 1047 (SO), 753 cm^{-1}; ^1H NMR δ 1.11–1.63 (8H, m), 2.13, 2.26 (each s, CH_3), 2.51–2.91 (2H, m), 3.74, 3.75 (each s, CH_3), 4.45, 4.52 (each s), 6.67–7.53 (9H, m).

Cyclohexylidene(4-methoxyphenyl)methane (19c). Colorless oil; IR (neat) 3032, 2998, 2927, 2852, 2834, 1608, 1509, 1464, 1446, 1295, 1247, 1175, 1038, 864, 849, 821 cm^{-1}; ^1H NMR δ 1.52–1.65 (6H, m), 2.23 (2H, t, *J*=5.6 Hz), 2.35 (2H, t, *J*=5.5 Hz), 3.80 (3H, s), 6.16 (1H, s), 6.85 (2H, dd, *J*=6.6, 1.9 Hz), 7.13 (2H, dd, *J*=6.6, 1.9 Hz). MS *m/z* (%) 202 (M^+, 100), 173 (15), 159 (24), 134 (30), 121 (65), 108 (9), 91 (15). Calcd for $C_{14}H_{18}O$: M, 202.1357. Found: *m/z* 202.1358.

3-Phenyl-1-(1-*p*-tolylsulfinylcyclohexyl)-1-propanol (21a). *21a-L:* Colorless oil; IR (neat) 3357, 3025, 2934, 2861, 1598, 1494, 1454, 1079 (SO), 1045 (SO), 999, 811, 752, 701 cm^{-1}; ^1H NMR δ 1.23–1.30 (1H, m), 1.38–1.43 (1H, m), 1.55–1.81 (8H, m), 1.88–1.95 (2H, m), 2.45 (3H, s), 2.54 (1H, ddd, *J*=16.5, 9.5, 7.0 Hz), 2.94 (1H, ddd, *J*=14.0, 9.8, 4.5 Hz), 3.92 (1H, m), 7.13–7.25 (5H, m), 7.34 (2H, d, *J*=8.3 Hz), 7.50 (2H, d, *J*=8.2 Hz). MS *m/z* (%) 357 (M^+, 2), 216 (67), 111 (99), 91 (100). Calcd for $C_{22}H_{24}O_2S$: M, 357.1888. Found: *m/z* 357.1902. *21a-P:* Colorless crystals; IR (KBr) 3320, 2927, 2854, 1492, 1449, 1076 (SO), 1054 (SO), 1019 (SO), 812, 750, 702 cm^{-1}; ^1H NMR δ 1.15–1.94 (12H, m), 2.41 (3H, s), 2.55 (1H, m), 2.86 (1H, ddd, *J*=14.1, 9.8, 5.2 Hz), 3.92 (1H, dd, *J*=11.0, 2.1 Hz), 7.14–7.54 (9H, m). Anal. Calcd for $C_{22}H_{28}O_2S$: C, 74.12; H, 7.92; S, 8.99. Found: C, 74.02; H, 7.93; S, 8.91.

1-Acetoxy-3-phenyl-1-(1-*p*-tolylsulfinylcyclohexyl)propane (22). *22-L:* Colorless oil; IR (neat) 3026, 2932, 2862, 1738, 1494, 1454, 1372, 1231, 1081 (SO), 1043 (SO), 812, 753, 700 cm^{-1}; ^1H NMR δ 1.26–1.31 (2H, m), 1.51–1.77 (10H, m), 1.86–1.98 (1H, m), 1.98 (3H, s), 2.42 (3H, s), 2.55 (1H, ddd, *J*=14.4, 9.8, 5.1 Hz), 5.48 (1H, dd, *J*=11.2, 2.2 Hz), 7.07–7.27 (5H, m), 7.29 (2H, d, *J*=8.3 Hz), 7.48 (2H, d, *J*=8.04 Hz). MS *m/z* (%) 399 (M^+, 0.2), 216 (39), 198 (98), 91 (100), 77(20). Calcd for $C_{24}H_{31}O_3S$: M, 399.1994. Found: *m/z* 399.2001. **22-P:** Colorless oil; IR (neat) 3026, 2934, 2964, 1738, 1494, 1454, 1372, 1232, 1079 (SO), 1031 (SO), 812, 753, 700 cm^{-1}; ^1H NMR δ 1.32–1.49 (4H, m), 1.62–1.80 (6H, m), 1.86 (3H, s), 2.14–2.34 (2H, m), 2.42 (3H, s), 2.44–2.50 (1H, m), 2.54–2.62 (1H, m), 5.32 (1H, dd, *J*=10.5, 2.2 Hz), 7.18–7.31 (7H, m), 7.48 (2H, d, *J*=8.0 Hz).

[(3,4-Methylenedioxyphenyl)(1-*p*-tolylsulfinylcyclohexyl)]-methanol (21b). *21b-L:* Colorless oil; IR (neat) 3319, 2934, 2863, 1597, 1504, 1488, 1452, 1240, 1093 (SO), 1040 (SO), 998, 932, 812, 733 cm^{-1}; ^1H NMR δ 1.09–1.82 (8H, m), 1.83–2.06 (1H, m), 2.48 (3H, s), 2.67–2.72 (1H, m), 4.83 (1H, s), 5.92 (2H, q), 6.12 (1H, s), 6.54 (1H, dd, *J*=8.1, 1.5 Hz), 6.68, (1H, d, *J*=8.0 Hz), 6.75 (1H, d, *J*=1.7 Hz), 7.41 (2H, d, *J*=7.8 Hz), 7.64 (2H, d, *J*=7.8 Hz). MS *m/z* (%) 372 (M^+, 0.5), 232 (94), 149 (100). Calcd for $C_{21}H_{24}O_4S$: M, 372.1392. Found: *m/z* 372.1396. *21b-P:* Colorless crystals; IR (KBr) 3310, 2938, 2862, 1500, 1485, 1449, 1242, 1041 (SO), 1021 (SO), 935, 815, 743 cm^{-1}; ^1H NMR δ 0.97 (1H, ddd, *J*=14.4, 10.8, 4.2 Hz), 1.17–1.21 (1H, m), 1.36–1.41 (1H, m), 1.61 (2H, m), 1.74–2.01 (5H, m), 2.41 (3H, s), 5.94 (2H, s), 6.73 (2H, s), 6.81 (1H, s), 7.33 (2H, d, *J*=8.3 Hz), 7.62 (2H,d, *J*=8.3 Hz). Anal. Calcd for $C_{21}H_{24}O_4S$: C, 67.12; H, 6.49; S, 8.61. Found: C, 67.18; H, 6.50; S, 8.56.

Cyclohexylidene(3,4-methylenedioxyphenyl)methane (23). Colorless oil; IR (neat) 2927, 2853, 2775, 1649, 1605, 1503, 1487, 1434, 1240, 1192, 1103, 1041, 934, 874, 808, 764 cm^{-1}; ^1H NMR δ 1.56–1.61 (6H, m), 2.22 (2H, t, *J*=5.9 Hz), 2.34 (2H, t, *J*=5.9 Hz), 5.93 (2H, s), 6.13 (1H, s), 6.65 (1H, dd, *J*=8.1, 1.5 Hz), 6.69 (1H, s), 6.75 (1H, dd, *J*=7.8, 1.7 Hz). MS *m/z* (%) 216 (M^+, 100), 135 (45), 115 (17). Calcd for $C_{14}H_{16}O_2$: M, 216.1150. Found: *m/z* 216.1147.

2-Mesyloxy-5-(4-methoxyphenyl)-1-phenylsulfinylpentane (25). Colorless oil (about 1:2 diastereomeric mixture); IR (neat) 3007, 2935, 1612, 1514, 1355, 1246, 1174, 1087 (SO), 1038 (SO), 908, 751, 692 cm^{-1}; ^1H NMR δ 1.59–1.80 (2H, m), 1.85–1.98 (2H, m), 2.54–2.63 (2H, m), 3.03 (1.88H, s), 3.20 (1.12H, s), 2.89–3.27 (2H, m), 3.78 (1.12H, s), 3.79 (1.88H, s), 5.01 (0.63H, quint, *J*=5.6 Hz), 5.11–5.17 (0.37H, m), 6.79–6.84 (2H, m), 7.03–7.09 (2H, m), 7.03–7.09 (2H, m), 7.51–7.68 (5H, m). MS *m/z* (%) 396 (M^+, 2), 175 (25), 121 (100). Calcd for $C_{19}H_{24}O_5S_2$: M, 396.1052. Found: *m/z* 396.1052.

5-(4-Methoxyphenyl)-1-pentene (26). Colorless oil; IR (neat) 3074, 2975, 2932, 2855, 1640, 1613, 1513, 1464,

1441, 1246, 1177, 1039, 911, 831, 808 cm^{-1}; ^1H NMR δ 1.68 (2H, quint, J=7.8 Hz), 2.08 (2H, q, J=6.6 Hz), 2.56 (2H, t, J=7.8 Hz), 3.79 (3H, s), 4.97 (1H, dd, J=10.0, 1.9 Hz), 5.02 (1H, dq, J=17.1, 1.9 Hz), 5.83 (1H, ddt, J=10.2, 17.1, 6.6 Hz), 7.10 (2H, dd, J=6.6, 2.0 Hz). MS m/z (%) 176 (M^+, 19), 134 (57), 121 (100), 91 (10). Calcd for $C_{12}H_{16}O$: M, 176.1178. Found: m/z 176.1189.

(*E*)-5-(4-Methoxyphenyl)-1-phenylsulfinyl-1-pentene (27). Colorless oil; IR (neat) 3056, 2997, 2932, 2834, 1612, 1513, 1443, 1246, 1178, 1085 (SO), 1040 (SO), 883, 816, 748, 691 cm^{-1}; ^1H NMR δ 1.76 (2H, quint, J=7.8 Hz), 2.24 (2H, ddd, J=15.1, 7.1, 1.2 Hz), 2.57 (2H, t, J=7.6 Hz), 3.78 (3H, s), 6.23 (1H, dt, J=15.1, 1.5 Hz), 6.62 (1H, dt, J=15.1, 6.8 Hz), 6.81 (2H, d, 8.6 Hz), 7.04 (2H, d, J=8.8 Hz), 7.47–7.62 (5H, m). MS m/z (%) 300 (M^+, 4.6), 283 (7), 166 (69), 149(80), 121(100). Calcd for $C_{18}H_{20}O_2S$: M, 300.1182. Found: m/z 300.1180.

(*Z*)-5-(4-Methoxyphenyl)-1-phenylsulfinyl-1-pentene (28). Colorless oil; IR (neat) 3057, 2998, 2933, 2856, 1612, 1513, 1246, 1178, 1084 (SO), 1037 (SO), 833, 815, 746, 690 cm^{-1}; ^1H NMR δ 1.74–1.89 (2H, m), 2.51–2.74 (4H, m), 3.79 (3H, s), 6.22 (1H, dd, J=10.2, 7.0 Hz), 6.23 (1H, d, J=10.2 Hz), 6.85 (2H, dd, J=6.5, 2.1 Hz), 7.12 (2H, dd, J=6.7, 2.0 Hz), 7.44–7.60 (5H, m). MS m/z (%) 300 ($[M-C_{18}H_{20}O_2S]^+$, 4), 149 ($[M-C_{10}H_{13}O]^+$, 100), 121 ($[M-C_8H_9O]^+$, 86).

(*E*)-5-(4-Methoxyphenyl)-1-*tert*-butylsulfinyl-1-pentene (29). Colorless oil; IR (neat) 2931, 2860, 1612, 1513, 1458, 1246, 1178, 1037 (SO), 816, 752 cm^{-1}; ^1H NMR δ 1.22 (9H, s), 1.76 (2H, quint, J=7.8 Hz), 2.29 (2H, ddd, J= 15.2, 7.1, 1.5 Hz), 2.59 (2H, t, J=7.8 Hz), 3.79 (3H, s), 6.12 (1H, dt, J=15.1, 1.5 Hz), 4.56 (1H, dt, J=15.1, 6.8 Hz), 6.83 (2H, dd, J=6.6, 2.2 Hz), 7.08 (2H, dd, J=6.6, 2.2 Hz); ^{13}C NMR (DEPT) δ 23.25 (CH_3), 30.67 (CH_2), 32.12 (CH_2), 34.72 (CH_2), 54.73 (C), 55.64 (CH_3), 114.19 (CH), 128.57 (CH), 129.69 (CH), 134.06 (C), 142.70 (CH), 158.23 (C). MS m/z (%) 224 (54), 207 (44), 121 ($[M-C_8H_9O]^+$, 100), 57 ($[M-C_4H_9O]^+$, 86).

The structure of this compound was further confirmed by oxidation of **29** with *m*-CPBA to give a sulfone ((*E*)-5-(4-Methoxyphenyl)-1-*tert*-butylsulfonyl-1-pentene) colorless oil; IR (neat) 3014, 2971, 2935, 2859, 1613, 1513, 1301, 1285, 1247 (SO_2), 1130, 816, 754 cm^{-1}; ^1H NMR δ 1.35 (9H, s), 1.80 (2H, quint, J=7.8 Hz), 2.32 (2H, ddd, J= 15.1, 7.1, 1.2 Hz), 2.61 (2H, t, J=7.6 Hz), 3.79 (3H, s), 6.25 (1H, dt, J=15.1, 1.5 Hz), 6.84 (2H, d, J=8.6 Hz), 6.94 (1H, dt, J=15.1, 6.8 Hz), 7.08 (2H, d, J=8.6 Hz); MS m/z (%) 296 (M^+, 35), 240 (14), 175 (20), 121 (60), 57 (100). Calcd for $C_{16}H_{24}O_3S$: M, 296.1446. Found: m/z 296.1438.

4-Phenyl-1-(2-phenylethyl)-1-phenylsulfinyl-2-butanol (30). *anti-30:* Colorless oil; IR (neat) 3357, 3083, 3060, 3025, 2930, 2860, 1496, 1454, 1444, 1084 (SO), 1030 (SO), 748, 699 cm^{-1}; ^1H NMR δ 1.67–2.13 (5H, m), 2.51–2.90 (4H, m), 4.35 (1H, m, half high width=18.9 Hz), 6.80–7.64 (15H, m). Anal. Calcd for $C_{24}H_{26}O_2S$: C, 76.29; H, 7.06; S, 8.47. Found: C, 76.15; H, 6.92; S, 8.47. *syn-30:* Colorless crystals; IR (KBr) 3414, 3081, 3056, 3026, 2944, 2874, 1495, 1454, 1443, 1086 (SO), 1073 (SO), 1038(SO), 747, 698 cm^{-1}; ^1H NMR δ 1.74–1.78 (1H, m), 1.92–1.99 (2H, m), 2.13–2.17 (1H, m), 2.31 (1H, dt, J=7.7, 3.7 Hz), 2.49–2.56 (2H, m), 2.71 (1H, ddd, J=16.2, 9.2, 7.0 Hz), 2.92 (1H, ddd, J=14.4, 9.5, 5.2 Hz), 4.02 (1H, dddd, J=9.2, 6.1, 5.5, 3.7), 6.83–7.60 (15H, m). MS m/z (%) 378 (M^+, 0.7), 161 (25), 91 (100). Calcd for $C_{24}H_{26}O_2S$: M, 378.1654. Found: m/z 378.1657.

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15. Geometry of the produced olefins **8** was determined by their chemical shift of allylic carbon. The ^{13}C NMR of the allylic carbon of the main isomer and minor isomer showed δ 29.15 and 34.37, respectively, from which the geometry can be determined to be *Z*

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