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A new method for synthesis of allenes, including an optically active form, from aldehydes and alkenyl aryl sulfoxides by sulfoxide–metal exchange as the key reaction and an application to a total synthesis of male bean weevil sex attractant

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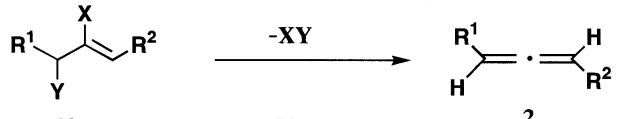
Abstract—The sulfoxide–metal exchange reaction of β-acetoxy sulfoxides or β-mesyloxy sulfoxides, which were derived from alkenyl aryl sulfoxides and aldehydes in two steps, with a Grignard reagent or alkyllithium at low temperature gave allenes in good yields. Optically active allenes were synthesized starting from optically active 2-substituted ethenyl *p*-tolyl sulfoxides. A synthesis of (−)-methyl (*E*)-2,4,5-tetradecatrienoate, a male bean weevil sex attractant, was realized by this method.

Allenes are quite interesting and important compounds in organic and synthetic organic chemistry, and a large number of studies have been reported on their chemistry and synthesis.[1] Some allenes have axial chirality and exist as an optically active form. Many methods for the synthesis of allenes, including an optically active form, have been reported; for example, isomerization of alkynes,[2] reaction of various organometallic reagents with propargyl derivatives,[3] and ring-opening of cyclopropylidenes.[4]

Another interesting method for the formation of allenes is β-elimination of **X** and **Y** in an olefin **1** shown in Scheme 1. Starting from alkenyl stannanes (or alkenyl silanes) **1a**, deoxystannylation reaction gave allenes **2** in good yields.[5] On the other hand, in our previous study, we reported a synthesis of allenes **2** from enol triflate **1b** by sulfoxide–lithium exchange reaction.[6] In continuation of our study on the sulfoxide–metal exchange reaction[7] in organic synthesis, we investigated the sulfoxide–metal exchange reaction with the alkenyl sulfoxides **1c**, and found that the reaction gave good to high yields of the allenes **2**. Herein, we report in detail the above-mentioned method for synthesis of allenes **5**, including an optically active form, from alkenyl aryl sulfoxides **3** and aldehydes through β-acetoxy sulfoxides or β-mesyloxy sulfoxides **4**. The whole sequence is shown in Scheme 2.[8]



1a X=$SnBu_3$ (or $SiEt_3$), Y=OMs or Cl
b X=OTf, Y=S(O)Ar
c X=S(O)Ar, Y=OAc or OMs

Scheme 1. Synthesis of allenes by β-elimination.

1. Results and discussion

1.1. Synthesis of alkenyl sulfoxides and synthesis of allenes from the alkenyl sulfoxides and aldehydes

First of all, we synthesized four alkenyl sulfoxides **8a–d**. The alkenyl sulfoxide **8a** (**3**; R^1=CH_3, R^2=H; about 1:1 mixture of geometrical isomers) was synthesized from thiophenol and allyl bromide.[9] Other alkenyl sulfoxides **8b–d** were synthesized starting from methyl phenyl sulfoxide and carbonyl compounds in three steps in good overall yields as shown in Table 1.[10] In the following investigation, **8a** and **8b** were used as a mixture of two geometrical isomers, and the main *E*-isomer was used as the alkenyl sulfoxide **8c**.

According to the procedure reported by Marino et al.,[11] phenyl propenyl sulfoxide **8a** was treated with LDA followed by 3-phenylpropanal to give the adduct **9a** in almost quantitative yield (Scheme 3). The hydroxyl group of the adduct was mesylated with mesyl chloride in the

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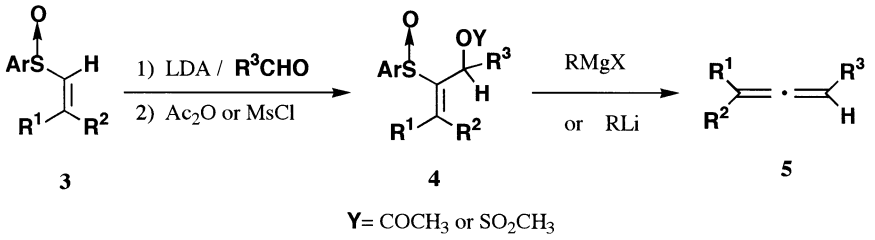
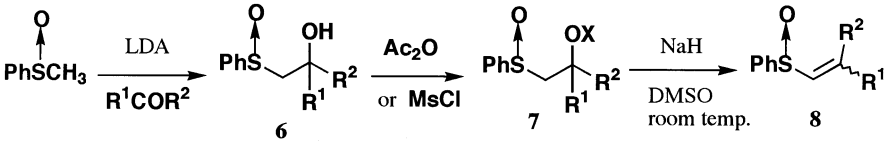
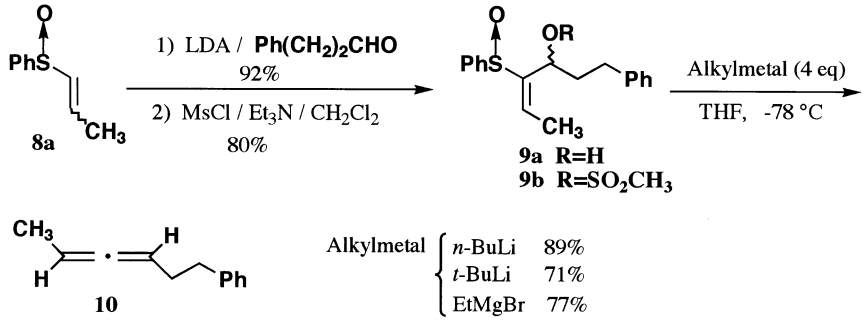


Scheme 2. Synthesis of allenes from alkenyl sulfoxides and aldehydes by sulfoxide–metal exchange.

Table 1. Synthesis of 2-substituted alkenyl sulfoxides **8**



Entry	R^1COR^2		**6**, Yield (%)	**7**, Yield (%)	**8**, Yield (%) (*E*/*Z*)
	R^1	R^2			
1	$CH_2(CH_2)_3$	H	**6a**, 99	**7a** (X=Ms), 92	**8b**, 84 (6/4)
2	Ph	H	**6b**, 91	**7b** (X=Ac), 98	**8c**, 93 (9/1)
3	$(CH_2)_5$		**6c**, 93	**7c** (X=Ac), 99	**8d**, 79



Scheme 3. Synthesis of β-mesyloxy sulfoxide **9b** and treatment with alkylmetals.

presence of triethylamine to afford the mesylate **9b** in good yield.

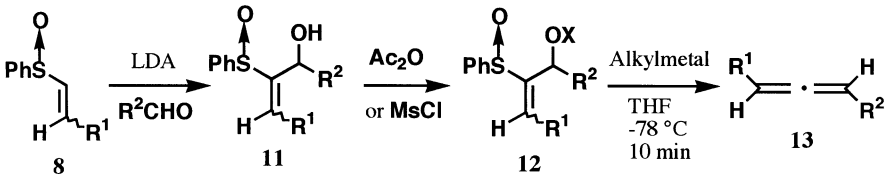
With the desired β-mesyloxy sulfoxide **9b** in hand, we studied the key reaction, sulfoxide–metal exchange, with three alkylmetals. As shown in Scheme 3, *n*-BuLi, *t*-BuLi, and EtMgBr were added to a solution of **9b** in THF at −78°C. Fortunately, these three alkylmetals worked to give the desired allene **10** in up to 89% yield. On detailed investigation of this reaction, it was found that the sulfoxide–metal exchange reaction took place at −78°C within 10 min with both alkyllithium and the Grignard reagent. Four equivalents of the alkylmetals were found to be the amount of choice to give good yield of this reaction. As shown in Scheme 3, *n*-BuLi gave the best yield; however, the Grignard reagent worked similarly in this case.

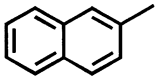
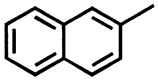
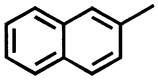
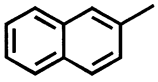
Encouraged by these results, we studied this procedure using the alkenyl sulfoxides **8a–c**, and phenyl vinyl sulfoxide **8e**. As the aldehydes, 3-phenylpropanal and 2-naphthaldehyde were used as the representative examples of *alkyl*-aldehyde and *aryl*-aldehyde, respectively. The results are summarized in Table 2.

Addition of the α-sulfinyl carbanions of **8a–c**, to the aldehydes gave over 80% yields of the adducts **11**. The reaction of phenyl vinyl sulfoxide **8e** and aldehydes gave somewhat lower yields than the other cases (entries 14 and 15). We first investigated the mesylation of the hydroxyl group of **11**; however, only **11b** gave good yield of the mesylate **12b** (entry 4). Other adducts **11** gave complex mixtures. One probable reason for these results is that the mesylate group is eliminated by a base to give a relatively stable allyl cation or benzyl cation. Instead of the mesylation, acetylation of **11a** and **11c–g** was carried out with acetic anhydride and pyridine in the presence of 4-(dimethylamino)pyridine to afford high to quantitative yields of the acetate **12a** and **12c–g**.

Treatment of the mesylate **12b** with alkylmetals (entries 4–6) gave the desired allene **13b** in similar yields as in the case of **9b** (see Scheme 3). We were somewhat nervous about the sulfoxide–metal exchange reaction of the acetates

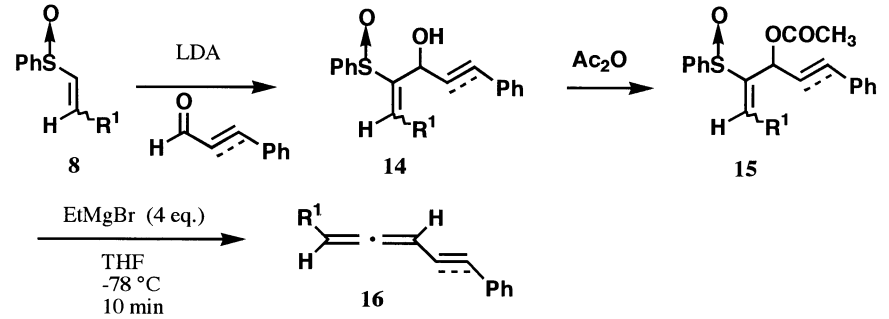
Table 2. Synthesis of allenes **13** from alkenyl sulfoxides **8** and aldehydes by the sulfoxide–metal exchange as a key reaction

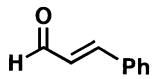
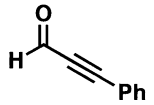
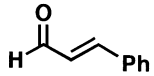
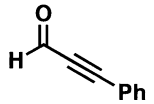


Entry	**8**, R^1	R^2CHO, R^2	**11**, Yield (%)	**12**, X, Yield (%)	Alkylmetal	**13**, Yield (%)
1	CH_3		**11a** (80)	**12a** X=Ac (95)	*n*-BuLi	–[a]
2	**8a**				*t*-BuLi	–[a]
3					EtMgBr	**13a** 77
4	$CH_3(CH_2)_3$	$PhCH_2CH_2$	**11b** (84)	**12b** X=Ms (84)	*n*-BuLi	**13b** 76
5	**8b**				*t*-BuLi	**13b** 45
6					EtMgBr	**13b** 71
7	$CH_3(CH_2)_3$		**11c** (84)	**12c** X=Ac (99)	*n*-BuLi	–[a]
8	**8b**				*t*-BuLi	–[a]
9					EtMgBr	**13c** 75
10	Ph	$PhCH_2CH_2$	**11d** (80)	**12d** X=Ac (99)	EtMgBr	**13d** 88
	8c					
11	Ph		**11e** (95)	**12e** X=Ac (90)	*n*-BuLi	–[a]
12	**8c**				*t*-BuLi	–[a]
13					EtMgBr	**13e** 92
14	H	$PhCH_2CH_2$	**11f** (52)	**12f** X=Ac (85)	EtMgBr	**13f** 91
15	**8e**		**11g** (71)	**12g** X=Ac (95)	EtMgBr	**13g** 99

[a] A complex mixture was obtained.

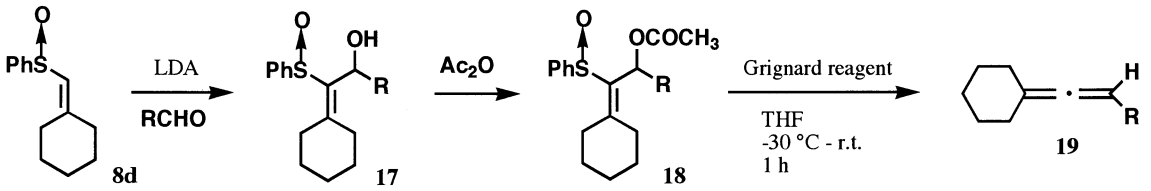
Table 3. Synthesis of conjugated allenes **16** from alkenyl sulfoxides **8** and α,β-unsaturated aldehydes by the sulfoxide–metal exchange as a key reaction

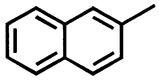
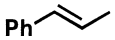
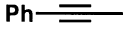


Entry	**8**, R^1	Aldehyde	**14**, Yield (%)	**15**, Yield (%)	**16**, Yield (%)
1	$CH_3(CH_2)_3$		**14a** (81)	**15a** (97)	**16a** (78)
	8b				
2	$CH_3(CH_2)_3$		**14b** (83)	**15b** (99)	**16b** (90)
	8b				
3	Ph		**14c** (84)	**15c-L** (93)[a]	**16c** (84)
	8c		(L/P=33:67)[b]	**15c-P** (97)[c]	**16c** (78)
4	Ph		**14d** (88)	**15d** (98)	**16d** (83)
	8c				

[a] The yield from **14c-L**.
[b] The diastereomers of the adduct could be separated and the less polar product on silica gel TLC is expressed as **L**, and the more polar one expressed as **P**.
[c] The yield from **14c-P**.

Table 4. Synthesis of tri-substituted allenes **19** from alkenyl sulfoxides **8d** and aldehydes by the sulfoxide–magnesium exchange as a key reaction



Entry	RCHO, R	**17**, Yield (%)	**18**, Yield (%)	EtMgBr (4 equiv.), **19**, yield (%)	*i*-PrMgCl (4 equiv.), **19**, yield (%)	*i*-PrMgCl (8 equiv.), **19**, yield (%)
1	$PhCH_2CH_2$	**17a** 77	**18a-L** 99	**19a** 0[a]	8[b]	47[c]
2		(L/P=54:43)	**18a-P** 82	**19a** 0[d]	0[e]	4[f]
3		**17b** 91	**18b-L** 78	**19b** 16[g]	43[h]	81[i]
4		(L/P=40:60)	**18b-P** 94	**19b** 0[j]	32[k]	50[l]
5		**17c** 83	**18c-L** 99	**19c** 22[m]	54[n]	89[o]
6		(L/P=48:52)	**18c-P** 97	**19c** 0[p]	9[q]	36[r]
7		**17d** 80	**18d-L** 94	**19d** 51[s]	66[t]	90[u,v]
8		(L/P=39:61)	**18d-P** 91	**19d** 18[w]	41[x]	56[v,y]

[a] **17a-L** (84%) and **18a-L** (9%).
[b] **17a-L** (5%) and **18a-L** (84%).
[c] **17a-L** (39%) and **18a-L** (10%).
[d] **17a-P** (19%) and **18a-P** (76%).
[e] **17a-P** (3%) and **18a-P** (95%).
[f] **17a-P** (19%) and **18a-P** (68%).
[g] **18a-L** (83%).
[h] **18b-L** (57%).
[i] **17b-L** (15%) and **18b-L** (4%).
[j] **18b-P** (92%).
[k] **18b-P** (66%).
[l] **17b-P** (43%) and **18b-P** (7%).
[m] **17c-L** (45%) and **18c-L** (30%).
[n] **17c-L** (11%) and **18c-L** (35%).
[o] **17c-L** (7%) and **18c-L** (4%).
[p] **17c-P** (87%) and **18c-P** (5%).
[q] **17c-P** (36%) and **18c-P** (55%).
[r] **17c-P** (61%) and **18c-P** (3%).
[s] **18d-L** (47%).
[t] **18d-L** (33%).
[u] **18d-L** (8%).
[v] The reactions were carried out at −78°C for 10 min.
[w] **17d-P** (36%) and **18d-P** (44%).
[x] **17d-L** (8%) and **18d-P** (51%).
[y] **17d-P** (36%) and **18d-P** (6%).

12. Because, the acetate has two positions, sulfoxide and acetyl carbonyl, that could be reacted with alkylmetals. If the alkylmetals react with the acetyl carbonyl carbon faster than with the sulfinyl sulfur, the reaction would not give the desired allene **13** but the alcohol **11**.

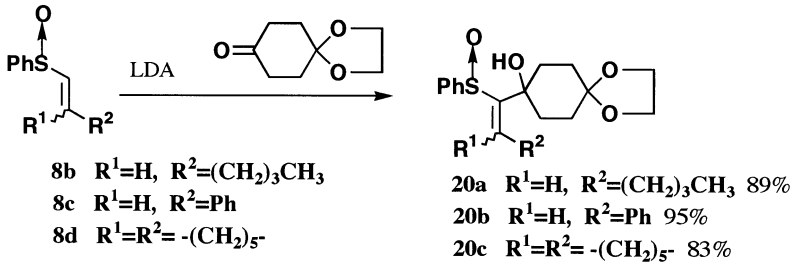
In any event, three acetates **12a**, **12c**, and **12e** were treated with the three alkylmetals (entries 1–3, 7–9, and 11–13). As shown in Table 1, *n*-BuLi and *t*-BuLi gave only a complex mixture; however, fortunately, EtMgBr worked to give good to high yields of the allenes. In the reactions of acetates with EtMgBr, no alcohol compound **11** was observed. It is worthwhile noting that mono-substituted allenes **13f** and **13g** were also synthesized from commercially available phenyl vinyl sulfoxide **8e** and aldehydes in good overall yields (entries 14 and 15). Especially, the key step, the sulfoxide–magnesium exchange reaction, gave almost quantitative yields. Here, we established a new method for the synthesis of allenes with carbon–carbon bond-formation.[12] Based on the results shown in Table 2, we decided to use the acetates and Grignard reagent in this procedure.

Next, we investigated this method with α,β-unsaturated aldehydes. The results are shown in Table 3. *trans*-Cinnamaldehyde and phenylpropargyl aldehyde were used as the α,β-unsaturated aldehyde. The lithium α-sulfinyl carbanion of **8b** and **8c** smoothly reacted with the carbonyl group of the aldehydes to give the alcohol **14** in good yields. No 1,4-addition product was observed in this reaction. Acetylation of the hydroxyl group in **14** gave the acetates **15** without any problem in quantitative yields.

The sulfoxide–magnesium exchange reaction was carried out with 4 equiv. of EtMgBr in THF at −78°C for 10 min. All the acetates **15** in this study smoothly gave the desired allenes conjugated with alkene or acetylene **16** in 78–90% yields. In one case (entry 3), the diastereomers of the adduct **14c** could be separated by column chromatography. The alcohols **14c** were separately acetylated, and then treated with EtMgBr. As shown in entry 3, no difference in reactivity was observed between the diastereomers **15c-L** and **15c-P**.

Next, we studied a synthesis of tri-substituted allenes by the above-mentioned method using the alkenyl sulfoxide **8d** as the 2,2-disubstituted alkenyl sulfoxide, and the results are summarized in Table 4. As shown in Table 4, lithium α-sulfinyl carbanion of **8d** reacted with four aldehydes to give the adducts **17a–d** in good yields. The adducts were obtained as a mixture of two diastereomers, which could be separated by silica gel column chromatography and expressed as **L** and **P** (see the footnote to Table 3). These separated adducts, alcohols, were acetylated to give the acetates **18** in high yields without any problem.

We came across a problem in the next step, the sulfoxide–magnesium exchange reaction. First, the acetates **18a–d** were treated with EtMgBr in THF at −78°C; however, almost no reaction was observed. Next, the reaction was carried out starting from −30°C to room temperature for 1 h. As shown in Table 4, in the first column of the treatment with the Grignard reagent, only **18d-L** gave the allene **19d** in moderate yield (entry 7). These reactions gave a significant



Scheme 4.

amount of the starting acetate and/or the alcohol **17** (see footnotes a, d, g, j, m, p, s, w). From these results it was inferred that the sulfinyl group of **18** is sterically hindered and in some cases EtMgBr attacks the carbonyl carbon of the acetate faster than the sulfinyl group.

We investigated this reaction with *i*-PrMgCl. As shown in the second column in Table 4, the reaction with 4 equiv. of *i*-PrMgCl gave much improved yields of the allenes **19**. As shown in the footnotes b, e, h, k, n, q, t, x the yields of the alcohols **17** were significantly reduced. These results indicated that the isopropyl group of the Grignard reagent selectively attacked not the acetyl carbon but mainly the sulfinyl group. As the yields of the allenes were not satisfactory, we tried this reaction with 8 equiv. of *i*-PrMgCl and the results are summarized in the third column. The yields of the desired allenes were improved; however, the acetate **18a**-**P** still resisted to the reaction (entry 2).

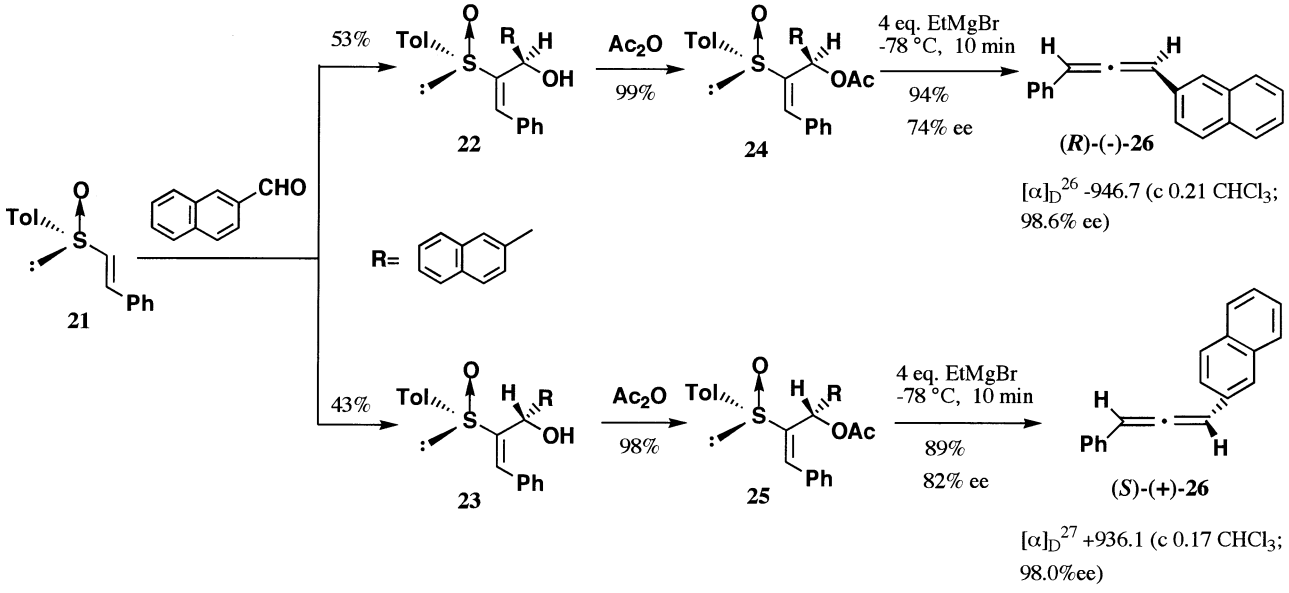
Two remarkable features have been noted in these reactions. First, the elimination reaction of the acetates derived from saturated alkyl aldehydes (**18a**) was quite difficult compared with other cases. Second, although the reason is not clear at present, the reaction always takes place smoothly with the L-isomer and gives better yields.

Finally, we planned to synthesize tri- and tetra-substituted allenes using the sulfoxides **8b**–**d** and a ketone (Scheme 4). Addition of the lithium carbanion of **8b**–**d** to 1,4-cyclohexanedione mono-ethylene ketal gave 83–95% yields of the adducts **20**. The acetylation or mesylation of the hydroxyl group, however, was found to be quite difficult. We tried a variety of known reactions for the acetylation, mesylation and methylation of the hydroxyl group, but no fruitful result was obtained. At present, we have not been able to synthesize allenes from ketones.

1.2. Asymmetric synthesis of optically active allenes from optically active alkenyl sulfoxides

As already mentioned above, some allenes have axial chirality and exist as an optically active form.[1] At present, many natural products having a chiral allenic structure have been isolated. Recently, the asymmetric syntheis of optically active allenes have received considerable attention.[13] In further development of our above-mentioned method, we planned to synthesize optically active allenes starting from optically pure (*E*)-(+)-(*R*)-2-phenyl-1-(*p*-tolylsulfinyl)ethene **21**.[14] The results are summarized in Scheme 5.

Treatment of the lithium carbanion of **21** with 2-naphthaldehyde gave the adducts in quantitative yield. The products were two diastereomers, which were separated by silica gel column chromatography to give less polar adduct **22** and more polar adduct **23** in 53 and 43% yields, respectively. At



Scheme 5. Asymmetric synthesis of both enantiomers of optically active allene **26** from optically active alkenyl sulfoxide **21** and 2-naphthaldehyde.

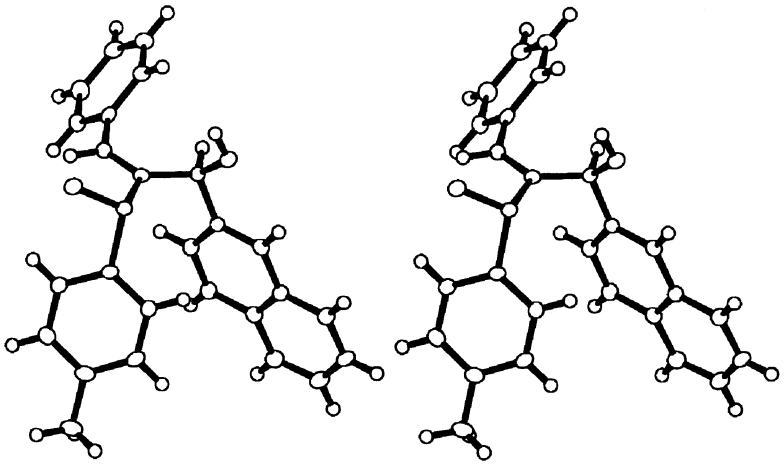


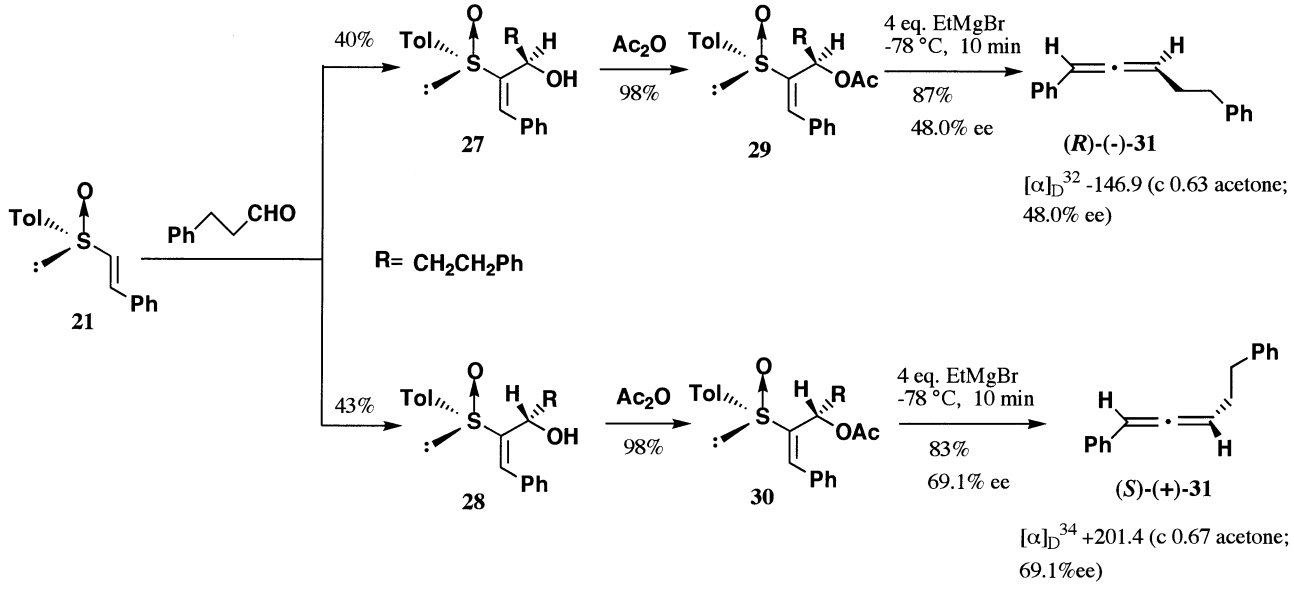
Figure 1. Stereoview of the alcohol **23**.

this stage we were not sure of the exact stereochemistry of the carbon bearing the hydroxy group in these adducts. Later, the stereochemistry of **23** was determined to be as shown in Scheme 5 by X-ray crystallographic analysis (vide infra). Acetylation of the adducts gave the acetates **24** and **25** in quantitative yields, respectively.

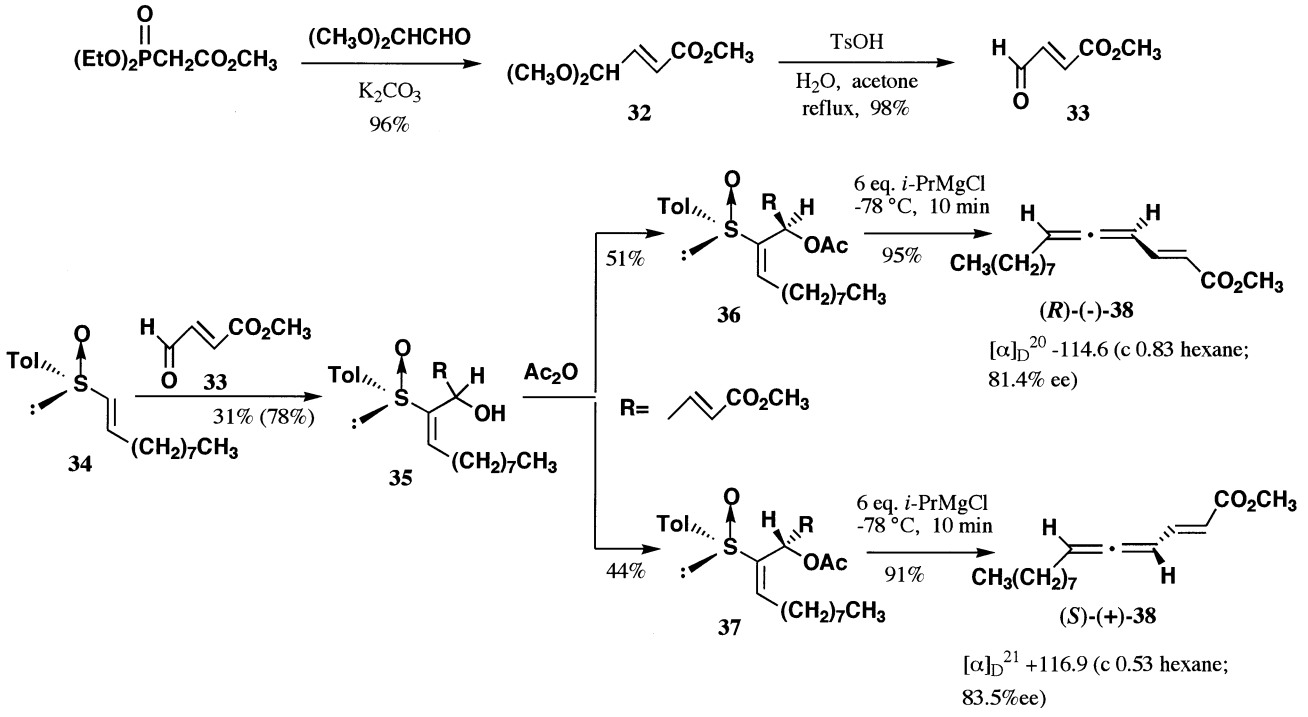
The elimination of the acetates **24** and **25** was carried out in THF with EtMgBr. From the detailed inspection, this reaction was found to be completed with 4 equiv. of EtMgBr at −78°C within 10 min. The acetate **24** gave the desired allene (*R*)-(−)-**26**, as colorless crystals, in 94% yield, which showed a minus sign for the specific rotation. The absolute configuration was determined by the sign of the specific rotation (see lit.1c, pp 31–32). The enantiomeric excess was calculated to be 74% by HPLC using a chiral column (Daicel, Chiralpak AD, hexane/*i*-PrOH=9:1). The optical purity was improved by recrystallization of the product with AcOEt–hexane (mp 85.5–87°C; $[\alpha]_D^{26}=-946.7$ (*c* 0.21, $CHCl_3$), 98.6% ee by HPLC). Quite interestingly, similar treatment of the diastereomer **25** in THF with 4 equiv. of EtMgBr for 10 min gave the enantiomer (*S*)-(+)-**26** as colorless crystals in 89% yield with better optical purity (82% ee).

In order to ascertain the stereochemical course of this elimination, we have to know the accurate structure of the acetates. Fortunately, the alcohol **23** was good for X-ray crystallographic analysis and the result is shown in Fig. 1 as the stereoview.[15] By comparison of the absolute configurations of **23** (and **25**) and the allene (*S*)-(+)-**26**, the elimination reaction of **25** was most likely to proceed via the *anti* conformation where the sulfinyl group and the acetoxy group are antiperiplanar as shown in Scheme 5.

Another example for the asymmetric synthesis of optically active allene is shown in Scheme 6. The reaction of the alkenyl sulfoxide **21** with 3-phenylpropanal gave the adduct **27** (less polar product) and **28** (more polar product) in almost 1:1 ratio. They were separated and acetylated to give **29** and **30** in quantitative yields. The stereochemistry



Scheme 6. Asymmetric synthesis of both enantiomers of optically active allene **31** from optically active alkenyl sulfoxide **21** and 3-phenylpropanal.



Scheme 7. A short asymmetric synthesis of both enantiomers of optically active methyl 2,4,5-tetradecatrienoate **38**, the male bean weevil sex attractant, from aldehyde **33** and optically active alkenyl sulfoxide **34**.

of these acetates **29** and **30** were assigned as shown in Scheme 6 by the chemical shift of their acetoxy methyl group in ^{1}H NMR. The acetoxy methyl in *R*-isomer (**24**, **29**, **36**) shows about 0.3–0.5 ppm higher than that of *S*-isomer (**25**, **30**, **37**). The acetate **29** was treated with EtMgBr in THF at −78°C to afford the desired allene (*R*)-(−)-**31** as an oil in high yield; however, the enantiomeric excess (analyzed by Daicel Chiralcel OD) was found to be moderate. The same treatment of **30** gave (*S*)-(+)-**31** in 83% yield with 69.1% ee.

1.3. A synthesis of (−)-methyl (*E*)-2,4,5-tetradecatrienoate, a male bean weevil sex attractant

Finally, we applied the above-mentioned method to a short asymmetric synthesis of both enantiomers of methyl 2,4,5-tetradecatrienoate **38**,[16] the male bean weevil sex attractant, starting from α,β-unsaturated aldehyde **33** and optically pure alkenyl sulfoxide **34** (Scheme 7).

The α,β-unsaturated aldehyde **33** was synthesized as follows. The Horner–Wadsworth–Emmons reaction of methyl diethylphosphonoacetate and dimethoxyacetaldehyde[17] gave α,β-unsaturated ester **32** in quantitative yield (*E*/*Z*=96:4). The main *E*-isomer was separated and hydrolyzed in the presence of acid to give the desired aldehyde **33** in quantitative yield. Optically pure alkenyl sulfoxide **34** was synthesized from (*R*)-methyl *p*-tolyl sulfoxide and nonanal by the method mentioned above (see Table 1) via the mesylate.

The alkenyl sulfoxide **34** was treated with LDA followed by the aldehyde **33**. The adduct **35** was obtained in 31% yield; however, the yield based on the consumed **34** was 78%. The adduct **35** was an inseparable mixture of two diastereomers, which was acetylated to give the acetate **36** and **37** in high yields. These two acetates were easily separated by silica gel column chromatography.

The final step, sulfoxide–magnesium exchange reaction, was investigated and 6 equiv. of *i*-PrMgCl at −78°C was found to be the conditions of choice. Both isomers **36** and **37** gave the desired allenes **38** in almost quantitative yields, and it was found that the methyl ester was unreactive to *i*-PrMgCl and remained intact under the conditions. The natural pheromone (*R*)-(−)-**38** was obtained from the main acetate **36** and the enantiomeric excess was determined to be 81.4% by HPLC analysis using a chiral stationary column (CHIRALCEL OD, Daicel). From the minor acetate **37** the enantiomer (*S*)-(+)-**38** was obtained and ee was found to be 83.5%.

2. Experimental

2.1. General

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, pyridine, DMSO, 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.

2.1.1. 1-(Phenylsulfinyl)-2-hexanol (6a). To a THF (200 ml) solution of diisopropylamine (7.42 ml; 53.0 mmol) in a flame-dried flask was added *n*-BuLi (53.0 mmol) at 0°C under argon atmosphere. After 15 min, the solution was cooled to −78°C and a solution of methyl phenyl sulfoxide (5.81 g; 40.8 mmol) in THF was added dropwise with stirring. After 15 min, valeraldehyde (5.64 ml; 53.0 mmol) in THF was added to the reaction mixture at −78°C, and the stirring was continued for 15 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 **6a** (about 2:3 diastereomeric mixture; 8.48 g; 99%) as colorless crystals. IR (neat) 3350, 2958, 2930, 2870, 1444, 1310, 1125, 1085 (SO), 1034 (SO), 1018, 997, 748, 692 cm^{-1}; ^1H NMR δ 0.85 (1.2H, t, J=7.0 Hz), 0.90 (1.8H, t, J=7.0 Hz), 1.23–1.62 (6H, m), 2.70 (0.4H, dd, J=13.6, 1.3 Hz), 2.81 (0.6H, dd, J=13.2, 2.2 Hz), 2.97 (0.6H, dd, J=13.2, 9.3 Hz), 3.05 (0.4H, dd, J=13.6, 9.9 Hz), 3.82 (0.6H, d, J=2.0 Hz, OH), 3.84 (0.4H, bs, OH), 4.15–4.18 (0.4H, m), 4.30–4.35 (0.6H, m), 7.52–7.68 (5H, m). MS *m/z* (%) 210 (M^+, 26), 191 (10), 160 (17), 124 (100), 110 (37), 91 (21), 78 (37). Calcd for $C_{12}H_{18}OS$: M, 210.1077. Found: *m/z* 210.1063.

2.1.2. 2-Mesyloxy-1-(phenylsulfinyl)hexane (7a). To a CH_2Cl_2 (225 ml) solution of **6a** (8.41 g; 40 mmol) in a dried flask was added Et_3N (11.2 ml; 80 mmol) follwed by MsCl (6.2 ml; 80 mmol) at room temperature with stirring, 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 **7a** (11.3 g; 92%) as a colorless oil (about 2:3 diastereomeric mixture). IR (neat) 3019, 2957, 2933, 2871, 1444, 1356, 1174, 1084 (SO), 1045 (SO), 944, 910, 787, 751, 692 cm^{-1}; ^1H NMR δ 0.88 (1.2H, t, J=7.0 Hz), 0.92 (1.8H, t, J=7.4 Hz), 1.33–1.44 (4H, m), 1.84–1.91 (0.8H, m), 1.95 (1.2H, t, J=7.4 Hz), 2.94–3.06 (0.8H, m), 3.05 (1.8H, s), 3.09–3.28 (1.2H, m), 3.22 (1.2H, s), 4.98 (0.6H, quint., J=6.0 Hz), 5.10–5.15 (0.4H, m), 7.53–7.70 (5H, m). MS *m/z* (%) 304 (M^+, 0.4), 287 (61), 125 (100), 97 (20), 83 (69), 77 (33). Calcd for $C_{13}H_{20}O_4S_2$: M, 304.0803. Found: *m/z* 304.0801.

2.1.3. 1-Hexenyl phenyl sulfoxide (8b). Sodium hydride (69 mmol) in a flame-dried flask was added DMSO (172 ml) at room temperature under argon atmosphere. After 2 h, a DMSO solution of **7a** (10.5 g, 34.5 mmol) was added to the reaction mixture dropwise with stirring, and the stirring was continued for 5 h. The reaction was quenched with ether and sat. aq. NH_4Cl, and the mixture was extracted with ether. 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 **8b** (6.0 g; 84%) as a colorless oil (*E*/*Z*=6:4 mixture). IR (neat) 3054, 2957, 2930, 2872, 1617, 1582, 1476, 1465, 1444, 1084 (SO), 1041 (SO), 748, 691 cm^{-1}; ^1H NMR δ 0.90 (1.8H, t, J=7.3 Hz), 0.96 (1.2H, t, J=7.0 Hz), 1.30–1.57 (4H, m), 2.23 (1.2H, dq, J=7.0, 1.2 Hz), 2.51–2.58 (0.4H, m), 2.63–2.70 (0.4H, m), 6.20–6.23 (0.8H, m), 6.23 (0.6H, dt, J=15.3, 1.2 Hz), 6.62 (0.6H, dt, J=15.0, 7.0 Hz), 7.47–7.62 (5H, m). MS *m/z* (%) 208 (M^+, 21), 191 (92), 160 (57), 149 (92), 117 (100), 110 (74), 91 (25), 78 (56). Calcd for $C_{12}H_{16}OS$: M, 208.0921. Found: *m/z* 208.0930.

2.1.4. 1-Phenyl-2-(phenylsulfinyl)-1-ethanol (6b). Colorless oil (about 2:3 diastereomeric mixture); IR (neat) 3259, 3083, 3055, 3024, 1493, 1443, 1088 (SO), 1062 (SO), 1015, 985, 749, 692 cm^{-1}; ^1H NMR δ 2.85 (0.4H, dd, J=13.4, 1.9 Hz), 2.96 (0.6H, dd, J=13.2, 2.6 Hz), 3.21 (0.6H, dd, J=13.2, 10.0 Hz), 3.28 (0.4H, dd, J=13.4, 10.4 Hz), 4.15 (0.4H, d, J=3.0 Hz, OH), 4.30 (0.6H, d, J=1.7 Hz, OH), 5.26 (0.4H, dt, J=10.5, 2.3 Hz), 5.41 (0.6H, dt, J=9.8, 1.7 Hz), 7.25–7.41 (5H, m), 7.51–7.59 (3H, m), 7.65–7.69 (2H, m). MS *m/z* (%) 224 (0.6), 228 (3), 180 (77), 126 (100), 103 (25), 91 (25), 77 (46).

2.1.5. 1-Acetoxy-1-phenyl-2-(phenylsulfinyl)ethane (7b). To a solution of **6b** (8 g; 32.5 mmol) in pyridine (45.8 ml) was added acetic anhydride (38.0 ml) and DMAP (795.0 mg; 6.5 mmol) with stirring at room temperature and the reaction mixture was stirred at room temperature for 30 h. After removal of the excess pyridine and acetic anhydride under vaccum, the product was purified by silica gel column chromatography to give **7b** (9.2 g; 98%) as a colorless oil (about 2:3 diastereomeric mixture). Colorless oil; IR (neat) 3027, 2960, 2921, 1737, 1372, 1250, 1224, 1084 (SO), 1036 (SO), 768, 744, 709, 689 cm^{-1}; ^1H NMR δ 1.93 (1.8H, s), 2.14 (1.2H, s), 3.10 (0.4H, dd, J=13.8, 3.1 Hz), 3.15 (0.6H, dd, J=13.4, 4.6 Hz), 3.25 (0.4H, dd, J=13.8, 10.7 Hz), 3.51 (0.6H, dd, J=13.4, 8.9 Hz), 6.10 (0.6H, dd, J=8.9, 4.6 Hz), 6.21 (0.4H, dd, J=10.7, 3.1 Hz), 7.29–7.37 (5H, m), 7.49–7.56 (3H, m), 7.65–7.68 (2H, m). MS *m/z* (%) 207 (100), 179 (17), 131 (32), 125 (20), 105 (39), 77 (65).

2.1.6. (*E*)-1-Phenyl-2-(phenylsulfinyl)ethene (8c). Colorless oil; IR (neat) 3056, 3023, 1610, 1444, 1084 (SO), 1046 (SO), 740, 689 cm^{-1}; ^1H NMR δ 6.84 (1H, d, J=15.3 Hz), 7.38 (1H, d, J=15.3 Hz), 7.34–7.70 (10H, m). MS *m/z* (%) 228 (M^+, 0.6), 212 (52), 199 (23), 180 (100), 165 (18), 134 (12), 121 (13), 103 (16), 91 (44), 77 (42). Calcd for $C_{14}H_{12}OS$: M, 228.0608. Found: *m/z* 228.0608.

2.1.7. 1-[(Phenylsulfinyl)methyl]cyclohexanol (6c). Colorless oil; IR (neat) 3386, 3065, 2942, 2931, 2860, 2840, 1442, 1388, 1261, 1185, 1133, 1088, 1012, 996, 972, 748, 704 cm^{-1}; ^1H NMR δ 1.33–1.56 (5H, m), 1.66–1.87 (4H, m), 2.04–2.08 (1H, m), 2.79 (1H, d, J=13.4 Hz), 3.00 (1H, d, J=13.4 Hz), 3.86 (1H, s, OH), 7.51–7.57 (3H, m), 7.64–7.67 (2H, m). MS *m/z* (%) 238 (M^+, 0.5), 126 (52), 113 (51), 95 (100), 77 (18). Calcd for $C_{13}H_{18}O_2S$: M, 238.1027. Found: *m/z* 238.1004.

2.1.8. 1-Acetoxy-1-[(phenylsulfinyl)methyl]cyclohexane (7c). Colorless oil; IR (neat) 2967, 2922, 2854, 1734, 1446, 1399, 1367, 1265, 1230, 1166, 1133, 1095, 1083 (SO), 1040 (SO), 1018, 961, 748, 690 cm^{-1}; ^1H NMR δ 1.30–1.34 (1H, m), 1.53–1.66 (7H, m), 2.12 (3H, s), 2.36–2.38 (1H, m), 2.50–2.52 (1H, m), 3.23 (1H, d,

J=13.9 Hz), 3.49 (1H, d, J=14.2 Hz), 7.48–7.54 (3H, m), 7.61–7.64 (2H, m). MS m/z (%) 280 (M^+, 0.3), 263 (0.3), 204 (10), 155 (21), 126 (20), 113 (23), 95 (100), 77 (11). Calcd for $C_{15}H_{20}O_3S$: M, 280.1132. Found: m/z 280.1150.

2.1.9. Cyclohexylidenenyl phenyl sulfoxide (8d). Colorless oil; IR (neat) 3056, 2933, 2855, 1626, 1475, 1443, 1082 (SO), 1037 (SO), 998, 798, 743, 694 cm^{-1}; ^1H NMR δ 1.59–1.81 (6H, m), 2.17–2.45 (2H, m), 2.64–2.69 (1H, m), 2.73–2.78 (1H, m), 5.98 (1H, s), 7.44–7.60 (5H, m). MS m/z (%) 220 (M^+, 4), 203 (100), 147 (6), 123 (7), 110 (11), 93 (27), 77 (17). Calcd for $C_{13}H_{16}OS$: M, 220.0921. Found: m/z 220.0922.

2.1.10. 6-Phenyl-3-(phenylsulfinyl)-2-hexan-4-ol (9a). To a THF (15 ml) solution of diisopropylamine (0.63 ml; 4.5 mmol) in a flame-dried flask was added *n*-BuLi (4.5 mmol) at 0°C under argon atmosphere. After 15 min, the solution was cooled to −78°C and **8a** (500 mg; 3.0 mmol) in THF was added dropwise with stirring. After 15 min, hydrocinnamaldehyde (0.6 ml; 4.5 mmol) in THF was added with stirring to the reaction mixture at −78°C, and the stirring was continued for 15 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 **9a** (about 2:3 diastereomeric mixture; 830.0 mg; 92%) as a colorless oil. Although the alkenyl sulfoxide **8a** was a mixture of *E*, *Z* isomers, the geometry of the olefin in the products **9a** was found to be *E*. Isomerization of the (*Z*)-alkenyl sulfoxide to (*E*)-isomer has been known.[18] IR (neat) 3364, 3060, 3025, 2923, 2859, 1637, 1602, 1496, 1454, 1444, 1081 (SO), 1067, 1029 (SO), 749, 699 cm^{-1}; ^1H NMR δ 1.25–1.32 (1H, m), 1.63–1.70 (1H, m), 1.88 (1.2H, d, J=1.8 Hz), 1.90 (1.8H, d, J=1.9 Hz), 2.37–2.71 (2H, m), 2.86 (0.4H, d, J=4.9 Hz, OH), 2.91 (0.6H, d, J=5.2 Hz, OH), 4.46–4.50 (0.6H, m), 4.59 (0.4H, quint., J=4.9 Hz), 6.45 (0.6H, dd, J=14.6, 7.2 Hz), 6.57 (0.4H, dd, J=14.6, 7.3 Hz), 6.96–7.65 (10H, m). MS m/z (%) 300 (M^+, 0.3), 283 (58), 126 (41), 91 (100). Calcd for $C_{18}H_{20}O_2S$: M, 300.1184. Found: m/z 300.1190.

2.1.11. 4-Mesyloxy-6-phenyl-3-(phenylsulfinyl)-2-hexene (9b). To a CH_2Cl_2 (9 ml) solution of **9a** (555.7 mg; 1.85 mmol) in a dried flask was added Et_3N (0.5 ml; 3.7 mmol) follwed by MsCl (0.28 ml; 3.7 mmol) at room temperature with stirring, 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 **9b** (562.3 mg; 80%) as a colorless oil (about 2:3 diastereomeric mixture). IR (neat) 3026, 2931, 1603, 1444, 1354, 1173, 1083 (SO), 1047 (SO), 905, 751, 699 cm^{-1}; ^1H NMR δ 2.01 (0.4H, d, J=7.3 Hz), 2.04 (0.6H, d, J=7.6 Hz), 2.24–2.34 (1H, m), 2.39 (1.2H, s), 2.57–2.82 (3H, m), 3.05 (1.8H, s), 5.22 (0.6H, dd, J=10.1, 3.4 Hz), 5.30 (0.4H, dd, J=9.1, 5.1 Hz), 6.73–6.87 (1H, m), 7.09–7.68 (10H, m). MS m/z (%) 378 (M^+, 1), 283 (26), 157 (41), 126 (72), 91 (100). Calcd for $C_{19}H_{22}O_4S_2$: M, 378.0960. Found: m/z 378.0967.

2.1.12. 6-Phenyl-2,3-hexadiene (10). In a flame-dried flask, to a THF solution of *n*-BuLi (1.48 nnol) at −78°C under argon atmosphere was added a THF solution of **9b** (140.7 mg; 0.37 mmol) dropwise with stirring, and the stirring was continued for 10 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 **10** (52.1 mg; 89%) as a colorless oil. IR (neat) 3084, 3062, 3026, 2923, 2854, 1964 (allene), 1604, 1496, 1454, 869, 744, 698 cm^{-1}; ^1H NMR δ 1.60 (3H, dd, J=7.0, 3.4 Hz), 2.27–2.32 (2H, m), 2.72 (2H, t, J=7.8 Hz), 5.02–5.12 (2H, m), 7.16–7.29 (5H, m). MS m/z (%) 158 (M^+, 19), 143 (42), 129 (100), 91 (91). Calcd for $C_{12}H_{14}$: M, 158.1094. Found: m/z 158.1097.

2.1.13. 1-(2-Naphthyl)-2-(phenylsulfinyl)-2-buten-1-ol (11a). Colorless oil (about 1:2 diastereomeric mixture), the isomers were easily separated by silica gel column chromatography. **11a-L**: colorless oil; IR (neat) 3332, 3056, 2854, 1600, 1443, 1030 (SO), 860, 821, 801, 748, 688 cm^{-1}; ^1H NMR δ 1.89 (3H, d, J=7.0 Hz), 3.28 (1H, d, J=5.5 Hz, OH), 5.92 (1H, d, J=5.5 Hz), 6.74 (1H, q, J=7.2 Hz), 7.22–7.76 (12H, m). MS m/z (%) 322 (M^+, 0.2), 304 (19), 196 (100), 181 (32), 127 (21). Calcd for $C_{20}H_{18}O_2S$: M, 322.1027. Found: m/z 322.1017. **11a-P**: colorless oil; IR (neat) 3382, 3056, 2971, 1443, 1601, 1082 (SO), 1031 (SO), 866, 824, 800, 748, 688 cm^{-1}; ^1H NMR δ 1.67 (3H, d, J=7.3 Hz), 3.63 (1H, bs, OH), 5.77 (1H, s), 6.62 (1H, q, J=7.3 Hz), 7.01 (1H, dd, J=8.6, 1.8 Hz), 7.26–7.82 (11H, m). MS m/z (%) 322 (M^+, 0.1), 304 (16), 195 (100), 181 (33), 127 (21). Calcd for $C_{20}H_{18}O_2S$: M, 322.1027. Found: m/z 322.1042.

2.1.14. 1-Acetoxy-1-(2-naphthyl)-2-(phenylsulfinyl)-2-butene (12a). 12a-L: colorless oil; IR (neat) 3055, 2926, 1746, 1443, 1371, 1225, 1082 (SO), 1045 (SO), 807, 753, 689 cm^{-1}; ^1H NMR δ 1.68 (3H, s), 1.96 (3H, d, J=7.3 Hz), 6.90 (1H, s), 6.96 (1H, q, J=7.3 Hz), 7.33 (1H, dd, J=8.6, 1.9 Hz), 7.46–7.50 (5H, m), 7.64–7.68 (3H, m), 7.78–7.83 (3H, m). MS m/z (%) 364 (M^+, 2), 238 (26), 196 (36), 179 (100), 127 (9). Calcd for $C_{22}H_{20}O_3S$: M, 364.1133. Found: m/z 364.1145. **12a-P**: colorless oil; IR (neat) 3056, 1746, 1444, 1371, 1226, 1083 (SO), 1047 (SO), 819, 753, 688 cm^{-1}; ^1H NMR δ 1.97 (3H, d, J=7.3 Hz), 2.09 (3H, s), 6.87 (1H, q, J=7.3 Hz), 6.91 (1H, s), 7.07 (1H, dd, J=8.6, 1.8 Hz), 7.21–7.77 (11H, m). MS m/z (%) 364 (M^+, 1), 238 (25), 196 (36), 179 (100), 127 (9). Calcd for $C_{22}H_{20}O_3S$: M, 364.1134. Found: m/z 364.1124.

2.1.15. 1-(2-Naphthyl)-1,2-butadiene (13a). Colorless oil; IR (neat) 3052, 1944 (allene), 1569, 1508, 1440, 1366, 1339, 1276, 967, 950, 896, 873, 860, 822 cm^{-1}; ^1H NMR δ 1.83 (3H, dt, J=7.1, 3.2 Hz), 5.61 (1H, quint.d, J=7.1, 1.7 Hz), 6.27 (1H, quint., J=3.2 Hz), 7.36–7.50 (3H, m), 7.57–7.64 (1H, m), 7.74–7.90 (3H, m). MS m/z (%) 180 (M^+, 85), 165 (100), 158 (91), 127 (80). Calcd for $C_{14}H_{12}$: M, 180.0938. Found: m/z 180.0946.

2.1.16. 1-Phenyl-4-(phenylsulfinyl)-4-nonen-3-ol (11b). Colorless oil (about 1:1 diastereomeric mixture); IR (neat) 3366, 3061, 3026, 2956, 2927, 2858, 1636, 1603, 1496,

1455, 1444, 1029 (SO), 749, 698 cm^{-1}; ^1H NMR δ 0.90 (1.5H, t, J=7.2 Hz), 0.91 (1.5H, t, J=7.4 Hz), 1.29–1.48 (4H, m), 1.86–1.93 (2H, m), 2.17–2.34 (2H, m), 2.44–2.50 (1H, m), 2.61–2.67 (1H, m), 2.71 (0.5H, d, J=5.2 Hz, OH), 2.83 (0.5H, d, J=4.9 Hz, OH), 4.47 (0.5H, ddd, J=11.6, 5.2, 3.6 Hz), 4.57 (0.5H, quint., J=4.9 Hz), 6.34 (0.5H, d, J=7.7 Hz), 6.47 (0.5H, t, J=7.7 Hz), 6.97–7.65 (10H, m). MS m/z (%) 342 (M^+, 1), 325 (56), 126 (25), 91 (100). Calcd for $C_{21}H_{26}O_2S$: M, 342.1654. Found: m/z 342.1659.

2.1.17. 3-Mesyloxy-1-phenyl-4-(phenylsulfinyl)-4-nonene (12b). Colorless oil (about 1:1 diastereomeric mixture); IR (neat) 3024, 2957, 2928, 2870, 1644, 1454, 1444, 1360, 1172, 1082 (SO), 1041 (SO), 903, 752, 698 cm^{-1}; ^1H NMR δ 0.93 (3H, t, J=7.1 Hz), 1.33–1.52 (4H, m), 1.90–1.99 (1H, m), 2.23–2.48 (3H, m), 2.36 (1.5H, s), 2.57–2.65 (1H, m), 2.70–2.77 (1H, m), 3.04 (1.5H, s), 5.21 (0.5H, dd, J=10.3, 3.3 Hz), 5.31 (0.5H, dd, J=8.9, 4.9 Hz), 6.68 (0.5H, t, J=7.8 Hz), 6.73 (0.5H, t, J=7.8 Hz), 6.85–7.66 (10H, m). MS m/z (%) 420 (M^+, 0.1), 198 (21), 143 (26), 91 (100). Calcd for $C_{22}H_{28}O_4S_2$: M, 420.1429. Found: m/z 420.1412.

2.1.18. 1-Phenyl-3,4-nonadiene (13b). Colorless oil; IR (neat) 3027, 2956, 2925, 2856, 1963 (allene), 1495, 1454, 868, 744, 698 cm^{-1}; ^1H NMR δ 0.89 (3H, d, J=7.0 Hz), 1.31–1.37 (4H, m), 1.92–1.97 (2H, m), 2.27–2.33 (2H, m), 2.72 (2H, t, J=7.8 Hz), 5.06–5.14 (2H, m), 7.16–7.29 (5H, m). MS m/z (%) 200 (M^+, 10), 157 (33), 144 (52), 129 (66), 91(100). Calcd for $C_{15}H_{20}$: M, 200.1564. Found: m/z 200.1565.

2.1.19. 1-(2-Naphthyl)-2-(phenylsulfinyl)-2-hepten-1-ol (11c). Colorless oil (about 1:1 diastereomeric mixture); the isomers were easily separated by silica gel column chromatography. **11c-L**: colorless oil; IR (neat) 3250, 3052, 2951, 2926, 2868, 1633, 1602, 1444, 1073 (SO), 1046 (SO), 816, 750, 691 cm^{-1}; ^1H NMR δ 0.81 (3H, t, J=7.2 Hz), 1.22–1.45 (4H, m), 2.27 (2H, q, J=7.7 Hz), 3.23 (1H, d, J=6.1 Hz, OH), 5.91 (1H, d, J=5.5 Hz), 6.64 (1H, t, J=7.7 Hz), 7.21–7.75 (12H, m). MS m/z (%) 364 (M^+, 0.1), 346 (16), 239 (13), 195 (100), 127 (14). Calcd for $C_{23}H_{24}O_2S$: M, 364.1497. Found: m/z 364.1489. **11c-P**: colorless oil; IR (neat) 3331, 3056, 2956, 2927, 2870, 1632, 1600, 1444, 1081 (SO), 1019 (SO), 817, 748, 688 cm^{-1}; ^1H NMR δ 0.72 (3H, t, J=7.3 Hz), 1.09–1.34 (4H, m), 1.91–1.99 (1H, m), 2.04–2.12 (1H, m), 3.53 (1H, d, J=3.4 Hz, OH), 5.76 (1H, s), 6.51 (1H, t, J=7.7 Hz), 7.01 (1H, dd, J=8.6, 1.9 Hz), 7.41–7.76 (11H, m). MS m/z (%) 364 (M^+, 0.1), 346 (15), 239 (13), 196 (100), 127 (14). Calcd for $C_{23}H_{24}O_2S$: M, 364.1497. Found: m/z 364.1509.

2.1.20. 1-Acetoxy-1-(2-naphthyl)-2-(phenylsulfinyl)-2-heptene (12c). 12c-L: colorless oil; IR (neat) 2957, 2859, 1748, 1443, 1368, 1224, 1082 (SO), 1043 (SO), 817, 750, 690 cm^{-1}; ^1H NMR δ 0.82 (3H, t, J=7.4 Hz), 1.28 (2H, td, J=14.7, 7.4 Hz), 1.34–1.48 (2H, m), 1.67 (3H, s), 2.35 (2H, q, J=7.6 Hz), 6.87 (1H, t, J=7.6 Hz), 6.89 (1H, s), 7.33 (1H, dd, J=8.6, 1.9 Hz), 7.46–7.50 (5H, m), 7.63–7.67 (3H, m), 7.77–7.82 (3H, m). MS m/z (%) 406 (M^+, 3), 280 (11), 239 (29), 221 (100), 196 (86), 165 (37), 127 (12). Calcd for $C_{25}H_{26}O_3S$: M, 406.1602. Found: m/z 406.1602. **12c-P**: colorless oil; IR (neat) 3057, 2957, 2929, 2871, 1746, 1444, 1370, 1224, 1083 (SO), 1048 (SO), 816, 749, 689 cm^{-1}; ^1H NMR δ 0.85 (3H, t, J=7.3 Hz), 1.30 (2H, td, J=14.7, 7.3 Hz), 1.44 (2H, quint., J=7.3 Hz), 2.08 (3H, s), 2.35 (2H, q, J=7.6 Hz), 6.78 (1H, t, J=7.6 Hz), 6.89 (1H, s), 7.06 (1H, dd, J=8.6, 1.8 Hz), 7.21–7.25 (3H, m), 7.37 (1H, s), 7.42–7.47 (4H, m), 7.59–7.63 (2H, m), 7.72–7.74 (1H, m). MS m/z (%) 406 (M^+, 3), 280 (11), 239 (30), 221 (100), 196 (91), 165 (39), 127 (13). Calcd for $C_{25}H_{26}O_3S$: M, 406.1603. Found: m/z 406.1607.

2.1.21. 1-(2-Naphthyl)-1,2-heptadiene (13c). Colorless oil; IR (neat) 3054, 2956, 2926, 2869, 2856, 1945 (allene), 1630, 1598, 1508, 892, 855, 818, 749 cm^{-1}; ^1H NMR δ 0.92 (3H, t, J=7.2 Hz), 1.37–1.44 (2H, m), 1.46–1.52 (2H, m), 2.17 (2H, dq, J=6.8, 2.9 Hz), 5.63 (1H, q, J=6.8 Hz), 6.30 (1H, quint., J=2.9 Hz), 7.38–7.50 (3H, m), 7.64 (1H, s), 7.75–7.79 (3H, m). MS m/z (%) 222 (M^+, 21), 193 (8), 180 (100), 165 (43), 152 (12), 115 (7). Calcd for $C_{17}H_{18}$: M, 222.1407. Found: m/z 222.1389.

2.1.22. 1,5-Diphenyl-2-(phenylsulfinyl)-1-penten-3-ol (11d). Colorless oil (about 1:1 diastereomeric mixture); IR (neat) 3312, 3057, 3021, 2936, 1443, 1069 (SO), 1044 (SO), 1015, 997, 752, 695 cm^{-1}; ^1H NMR δ 1.57–1.65 (0.5H, m), 1.77–1.86 (1H, m), 2.07–2.17 (0.5H, m), 2.51 (0.5H, d, J=5.8 Hz, OH), 2.54–2.74 (2H, m), 3.04 (0.5H, d, J=6.1 Hz, OH), 4.80–4.89 (1H, m), 6.99–7.76 (16H, m). MS m/z (%) 360 (M^+, 1), 345 (39), 257 (12), 219 (21), 91 (100). Calcd for $C_{23}H_{22}O_2S$: M, 362.1339. Found: m/z 362.1341.

2.1.23. 3-Acetoxy-1,5-diphenyl-2-(phenylsulfinyl)-1-pentene (12d). Colorless oil (about 1:1 diastereomeric mixture); IR (neat) 3058, 3025, 2929, 2861, 1743, 1493, 1444, 1370, 1227, 1081 (SO), 1048 (SO), 1029, 750, 698 cm^{-1}; ^1H NMR δ 1.41 (1.5H, s), 1.70–1.75 (1H, m), 1.81 (1.5H, s), 1.94–2.02 (0.5H, m), 2.24–2.32 (0.5H, m), 2.35–2.41 (0.5H, m), 2.45–2.57 (1.5H, m), 5.91 (0.5H, dd, J=8.3, 6.1 Hz), 5.94 (0.5H, dd, J=9.1, 5.4 Hz), 6.89–7.34 (16H, m). MS m/z (%) 388 (M^+, 4), 279 (14), 237 (27), 219 (81), 91 (100). Calcd for $C_{25}H_{24}O_2S$: M, 388.1497. Found: m/z 388.1490.

2.1.24. 1,5-Diphenyl-1,2-pentadiene (13d). Colorless oil; IR (neat) 3061, 3027, 2917, 2854, 1948 (allene), 1560, 1496, 1454, 911, 875, 778, 745, 698 cm^{-1}; ^1H NMR δ 2.39–2.53 (2H, m), 2.76–2.86 (2H, m), 5.58 (1H, q, J=6.4 Hz), 6.12 (1H, quint., J=3.1 Hz), 7.15–7.30 (10H, m). MS m/z (%) 220 (M^+, 9), 134 (22), 105 (69), 91 (100), 77 (52). Calcd for $C_{17}H_{16}$: M, 220.1251. Found: m/z 220.1249.

2.1.25. 1-(2-Naphthyl)-3-phenyl-2-(phenylsulfinyl)-2-propen-1-ol (11e). Colorless crystals (about 2:3 diastereomeric mixture); IR (KBr) 3317, 3054, 1442, 1027, 818, 747, 686 cm^{-1}; ^1H NMR δ 3.17 (0.4H, d, J=7.1 Hz, OH), 3.86 (0.6H, d, J=6.2 Hz, OH), 6.18 (0.6H, d, J=5.8 Hz), 6.24 (0.4H, d, J=6.8 Hz), 7.17–7.76 (18H, m). MS m/z (%) 304 (0.3), 360 (29), 258 (100), 241 (27), 229 (19), 128 (22), 103 (13), 77 (13).

2.1.26. 1-Acetoxy-1-(2-naphthyl)-3-phenyl-2-(phenylsulfinyl)-2-propene (12e). Colorless oil (about 2:3 diastereomeric mixture); IR (neat) 3056, 1735, 1443,

1363, 1222, 1046 (SO), 1024, 821, 753, 686 cm^{-1}; ^1H NMR δ 1.54 (1.2H, s), 2.06 (1.8H, s), 7.04–7.94 (19H, m). MS *m/z* (%) 426 (M^+, 0.3), 410 (5), 300 (17), 241 (100), 128 (8). Calcd for $C_{27}H_{22}O_3S$: M, 426.1290. Found: *m/z* 426.1272.

2.1.27. 1-(2-Naphthyl)-3-phenyl-1,2-propadiene (13e). Colorless crystals; mp 85–87°C (hexane); IR (KBr) 3049, 3026, 2982, 1936 (allene), 1594, 903, 862, 825, 750, 690 cm^{-1}; ^1H NMR δ 6.67 (1H, d, *J*=6.6 Hz), 6.77 (1H, d, *J*=6.6 Hz), 7.22–7.53 (8H, m), 7.74–7.80 (4H, m). MS *m/z* (%) 242 (M^+, 100), 215 (19), 165 (12), 119 (9). Calcd for $C_{19}H_{14}$: M, 242.1095. Found: *m/z* 242.1103.

2.1.28. 5-Phenyl-2-(phenylsulfinyl)-1-penten-3-ol (11f). Colorless oil (about 1:1 diastereomeric mixture); IR (neat) 3369, 3026, 2929, 1603, 1496, 1444, 1082 (SO), 1030 (SO), 935, 751, 689 cm^{-1}; ^1H NMR δ 1.85–1.95 (1.6H, m), 2.05 (0.5H, d, *J*=5.2 Hz, OH), 2.50–2.73 (2.4H, m), 2.92 (0.5H, s, OH), 4.19–4.21 (1H, m), 5.89 (1H, s), 6.09 (1H, s), 7.01–7.24 (4H, m), 7.48–7.64 (6H, m). MS *m/z* (%) 287 ($[M+H]^+$, 0.1), 269 (42), 166 (41), 126 (57), 91 (100), 77 (23). Calcd for $C_{17}H_{19}O_2S$ (M+H): M, 287.1105. Found: *m/z* 287.1133.

2.1.29. 3-Acetoxy-5-phenyl-2-(phenylsulfinyl)-1-pentene (12f). Colorless oil (about 1:1 diastereomeric mixture); IR (neat) 3061, 3027, 2933, 2863, 1743, 1603, 1497, 1455, 1444, 1372, 1229, 1083 (SO), 1050 (SO), 957, 753, 700 cm^{-1}; ^1H NMR δ 1.78 (1.5H, s), 1.79–2.07 (2H, m), 1.88 (1.5H, s), 2.44–2.61 (2H, m), 5.18 (1H, quint., *J*=4.3 Hz), 5.89 (0.5H, s), 5.96 (0.5H, s), 6.25 (0.5H, s), 6.32 (0.5H, s), 7.01–7.06 (2H, m), 7.16–7.29 (3H, m), 7.44–7.64 (5H, m). MS *m/z* (%) 329 ($[M+H]^+$, 0.1), 311 (9), 220 (25), 143 (59), 120 (57), 91 (100), 77 (27). Calcd for $C_{19}H_{21}O_3S$ (M+H): M, 329.1220. Found: *m/z* 329.1221.

2.1.30. 5-Phenyl-1,2-pentadiene (13f). Colorless oil. IR (neat) 3085, 3063, 3028, 2984, 2923, 2856, 1956 (allene), 1604, 1496, 1454, 1440, 845, 698 cm^{-1}; ^1H NMR δ 2.29–2.35 (2H, m), 2.73 (2H, t, *J*=7.8 Hz), 4.67 (2H, quint., *J*=3.4 Hz), 5.15 (1H, quint., *J*=6.7 Hz), 7.17–7.30 (5H, m). MS *m/z* (%) 144 (M^+, 32), 129 (89), 115 (12), 91 (100), 65 (23). Calcd for $C_{11}H_{12}$: M, 144.0939. Found: *m/z* 144.0935.

2.1.31. 1-(2-Naphthyl)-2-(phenylsulfinyl)-2-propen-1-ol (11g). Colorless oil (about 2:3 diastereomeric mixture); Colorless oil; IR (neat) 3339, 3057, 1602, 1509, 1444, 1367, 1033 (SO), 821, 750, 688 cm^{-1}; ^1H NMR δ 2.80 (0.4H, d, *J*=4.9 Hz, OH), 3.90 (0.6H, d, *J*=2.5 Hz, OH), 5.45 (0.4H, d, *J*=4.9 Hz), 5.49 (1H, s), 5.50 (0.4H, s), 5.52 (0.6H, d, *J*=4.9 Hz), 6.11 (1H, s), 7.07 (0.6H, dd, *J*=8.6, 1.9 Hz), 7.26 (0.4H, dd, *J*=8.6, 1.9 Hz), 7.43–7.56 (5H, m), 7.63–7.81 (6H, m). MS *m/z* (%) 308 (M^+, 1), 290 (7), 182 (100), 165 (25), 153 (20), 127 (19), 77 (9). Calcd for $C_{19}H_{16}O_2S$: M, 308.0871. Found: *m/z* 308.0867.

2.1.32. 1-Acetoxy-1-(2-naphthyl)-2-(phenylsulfinyl)-2-propene (12g). Colorless oil (about 2:3 diastereomeric mixture); Colorless oil; IR (neat) 3057, 1747, 1444, 1372, 1224, 1082 (SO), 1051 (SO), 751 cm^{-1}; ^1H NMR δ 1.94 (1.2H, s), 1.99 (1.8H, s), 5.71 (0.4H, t, *J*=1.1 Hz), 6.05 (0.6H, t, *J*=0.8 Hz), 6.31 (0.4H, s), 6.39 (0.6H, s), 6.40 (1H, s), 7.40–7.81 (12H, m). MS *m/z* (%) 350 (M^+, 2), 224 (32), 165 (100), 153 (9), 127 (8), 77 (6). Calcd for $C_{21}H_{18}O_3S$: M, 350.0977. Found: *m/z* 350.0976.

2.1.33. 1-(2-Naphthyl)-1,2-pentadiene (13g). Colorless oil; IR (neat) 1939 (allene), 1596, 897, 844, 822, 742 cm^{-1}; ^1H NMR δ 5.22 (2H, d, *J*=6.7 Hz), 6.34 (1H, t, *J*=6.7 Hz), 7.40–8.01 (7H, m). MS *m/z* (%) 166 (M^+, 85), 165 (100), 156 (27), 127 (29), 115 (6), 83 (8). Calcd for $C_{13}H_{10}$: M, 166.0773. Found: *m/z* 166.0772.

2.1.34. (1*E*)-1-Phenyl-4-(phenylsulfinyl)-1,4-nonadien-3-ol (14a). Colorless oil (about 1:1 diastereomeric mixture); IR (neat) 3330, 3059, 3026, 2956, 2928, 2858, 1444, 1082 (SO), 1030 (SO), 750, 693 cm^{-1}; ^1H NMR δ 0.89 (1.5H, t, *J*=7.3 Hz), 0.92 (1.5H, t, *J*=7.3 Hz), 1.32–1.51 (4H, m), 2.35–2.44 (2H, m), 2.90 (0.5H, d, *J*=4.3 Hz, OH), 3.43 (0.5H, d, *J*=5.5 Hz, OH), 5.12 (0.5H, dd, *J*=5.8, 1.6 Hz), 5.32 (0.5H, dd, *J*=5.5, 1.6 Hz), 5.74 (0.5H, dd, *J*=15.9, 6.1 Hz), 5.84 (0.5H, dd, *J*=15.9, 5.8 Hz), 6.20 (0.5H, dd, *J*=15.9, 1.2 Hz), 6.44 (0.5H, dd, *J*=15.9, 1.2 Hz), 6.50 (0.5H, t, *J*=7.6 Hz), 6.56 (0.5H, t, *J*=7.6 Hz), 7.09–7.65 (10H, m). MS *m/z* (%) 340 (M^+, 3), 322 (14), 172 (100), 91 (41). Calcd for $C_{21}H_{24}O_2S$: M, 340.1497. Found: *m/z* 340.1501.

2.1.35. (1*E*)-3-Acetoxy1-1-phenyl-4-(phenylsulfinyl)-1,4-nonadiene (15a). Colorless oil (about 1:1 diastereomeric mixture); IR (neat) 3057, 2957, 2929, 2871, 1743, 1444, 1371, 1226, 1082 (SO), 1050 (SO), 1020, 964, 750, 692 cm^{-1}; ^1H NMR δ 0.93 (3H, t, *J*=7.3 Hz), 1.40 (2H, quint., *J*=7.3 Hz), 1.50–1.56 (2H, m), 1.67 (1.5H, s), 1.95 (1.5H, s), 2.41 (1H, q, *J*=7.3 Hz), 2.47 (1H, q, *J*=7.6 Hz), 5.67 (0.5H, dd, *J*=15.9, 7.4 Hz), 6.09 (0.5H, dd, *J*=15.9, 6.1 Hz), 6.16 (0.5H, d, *J*=6.1 Hz), 6.22 (0.5H, d, *J*=15.9 Hz), 6.27 (0.5H, d, *J*=7.4 Hz), 6.36 (0.5H, d, *J*=15.9 Hz), 6.65 (0.5H, t, *J*=7.6 Hz), 6.77 (0.5H, t, *J*=7.6 Hz), 7.07–7.09 (1H, m), 7.19–7.32 (4H, m), 7.40–7.49 (3H, m), 7.65–7.68 (2H, m). MS *m/z* (%) 382 (M^+, 3), 256 (21), 220 (43), 197 (67), 172 (100), 141 (50), 91 (51). Calcd for $C_{23}H_{26}O_3S$: M, 382.1603. Found: *m/z* 382.1608.

2.1.36. (*E*)-1-Phenyl-1,3,4-nonatriene (16a).[19] Colorless oil; IR (neat) 3081, 3061, 3027, 2958, 2928, 2858, 1941 (allene), 1596, 1496, 1451, 962, 755, 690 cm^{-1}; ^1H NMR δ 0.91 (3H, t, *J*=7.0 Hz), 1.34–1.48 (4H, m), 2.07 (2H, dq, *J*=6.7, 2.8 Hz), 5.40 (1H, q, *J*=6.7 Hz), 5.94–5.99 (1H, m), 6.47 (1H, d, *J*=15.9 Hz), 6.59 (1H, ddd, *J*=15.9, 10.4, 0.9 Hz), 7.18–7.21 (1H, m), 7.28–7.31 (2H, m), 7.37–7.38 (2H, m).

2.1.37. 1-Phenyl-4-(phenylsulfinyl)-4-nonen-1-yn-3-ol (14b). Colorless oil (about 3:7 diastereomeric mixture); IR (neat) 3295, 3060, 2957, 2929, 2859, 1634, 1489, 1443, 1304, 1081 (SO), 1032 (SO), 997, 756, 691 cm^{-1}; ^1H NMR δ 0.91 (2.1H, t, *J*=7.4 Hz), 0.93 (0.9H, t, *J*=7.4 Hz), 1.37–1.43 (2H, m), 1.51–1.58 (2H, m), 2.43–2.49 (0.3H, m), 2.50–2.55 (0.3H, m), 2.58–2.63 (1.4H, m), 3.29 (0.7H, d, *J*=3.4 Hz, OH), 3.33 (0.3H, d, *J*=6.7 Hz, OH), 5.42 (0.7H, d, *J*=2.1 Hz), 5.56 (0.3H, d, *J*=6.1 Hz), 6.56 (0.7H, t, *J*=7.7 Hz), 6.63 (0.3H, t, *J*=7.8 Hz),

7.17–7.74 (10H, m). MS *m/z* (%) 338 (M^+, 6), 281 (49), 229 (85), 169 (92), 105 (100), 77 (86). Calcd for $C_{21}H_{22}O_2S$: M, 338.1340. Found: *m/z* 338.1340.

2.1.38. 3-Acetoxy-1-phenyl-4-(phenylsulfinyl)-4-nonen-1-yne (15b). Colorless oil (about 3:7 diastereomeric mixture); IR (neat) 3058, 2958, 2929, 2871, 1750, 1490, 1443, 1370, 1220, 1083 (SO), 1050 (SO), 1020, 997, 970, 757, 691 cm^{-1}; ^1H NMR δ 0.93 (3H, t, *J*=7.2 Hz), 1.39–1.45 (2H, m), 1.53–1.61 (2H, m), 1.64 (0.9H, s), 2.03 (2.1H, s), 2.52–2.64 (2H, m), 6.34 (0.7H, m), 6.36 (0.3H, m), 6.73 (0.7H, t, *J*=7.8 Hz), 6.81 (0.3H, t, *J*=7.7 Hz), 7.13–7.15 (1H, m), 7.22–7.49 (7H, m), 7.68–7.71 (2H, m). MS *m/z* (%) 380 (M^+, 3), 338 (51), 281 (59), 229 (100), 165 (34), 105 (76), 91 (23), 77 (34). Calcd for $C_{23}H_{24}O_3S$: M, 380.1444. Found: *m/z* 380.1455.

2.1.39. 1-Phenyl-3,4-nonadien-1-yne (16b). Colorless oil; IR (neat) 3055, 2956, 2927, 2871, 2858, 1948 (allene), 1597, 1491, 1276, 863, 754, 690 cm^{-1}; ^1H NMR δ 0.92 (3H, t, *J*=7.0 Hz), 1.39 (2H, q, *J*=7.7 Hz), 1.46 (2H, q, *J*=7.0 Hz), 3.16 (2H, ddd, *J*=13.8, 6.7, 3.1 Hz), 5.47 (1H, dd, *J*=13.8, 6.7 Hz), 5.57 (1H, q, *J*=3.1 Hz), 7.25–7.31 (3H, m), 7.42–7.44 (2H, m). MS *m/z* (%) 196 (M^+, 3), 165 (18), 154 (100), 139 (12), 115 (8). Calcd for $C_{15}H_{16}$: M, 196.1251. Found: *m/z* 196.1253.

2.1.40. (1*E*,4*E*)-1,5-Diphenyl-2-(phenylsulfinyl)-1,4-pentadien-3-ol (14c). Colorless oil (about 3:7 diastereomeric mixture); the isomers were easily separated by silica gel column chromatography. **14c-L**: colorless oil; IR (neat) 3321, 3058, 3025, 1493, 1444, 1078 (SO), 1028 (SO), 998, 967, 750, 694 cm^{-1}; ^1H NMR δ 3.15 (1H, d, *J*=6.7 Hz, OH), 5.57 (1H, dd, *J*=6.7, 4.9 Hz), 6.09 (1H, dd, *J*=15.9, 4.9 Hz), 6.50 (1H, dd, *J*=15.9, 1.2 Hz), 7.11–7.22 (16H, m). MS *m/z* (%) 360 (M^+, 0.8), 342 (42), 234 (100), 115 (26), 91 (59), 77 (34). Calcd for $C_{23}H_{20}O_2S$: M, 360.1184. Found: *m/z* 360.1181. **14c-P**: colorless crystals; mp 115–118°C (AcOEt–hexane); IR (KBr) 3237, 3057, 3025, 1442, 1078 (SO), 1013, 748, 694 cm^{-1}; ^1H NMR δ 3.19 (1H, d, *J*=4.9 Hz, OH), 5.52 (1H, dd, *J*=5.5, 4.9 Hz), 5.80 (1H, dd, *J*=15.9, 5.5 Hz), 6.30 (1H, dd, *J*=15.9, 1.2 Hz), 7.01–7.75 (16H, m). MS *m/z* (%) 360 (M^+, 1), 342 (39), 234 (100), 115 (27), 91 (62), 77 (34). Calcd for $C_{23}H_{20}O_2S$: M, 360.1184. Found: *m/z* 360.1190. Anal. Calcd for $C_{23}H_{20}O_2S$: C, 76.64; H, 5.59; S, 8.89. Found: C, 76.31; H, 5.62; S, 8.95.

2.1.41. (1*E*,4*E*)-3-Acetoxy-1,5-diphenyl-2-(phenylsulfinyl)-1,4-pentadiene (15c). 15c-L: colorless oil; IR (neat) 3057, 3026, 1742, 1444, 1370, 1224, 1081 (SO), 1050 (SO), 1020, 964, 751, 693 cm^{-1}; ^1H NMR δ 1.55 (3H, s), 6.19 (1H, dd, *J*=16.2, 6.1 Hz), 6.45 (1H, d, *J*=16.2 Hz), 6.53 (1H, dd, *J*=6.1, 1.2 Hz), 7.23–7.56 (13H, m), 7.76–7.79 (3H, m). MS *m/z* (%) 402 (M^+, 4), 235 (50), 217 (100), 115 (24), 91 (30). Calcd for $C_{25}H_{22}O_3S$: M, 402.1289. Found: *m/z* 402.1296. **15c-P**: colorless oil; IR (neat) 3057, 3025, 1745, 1493, 1444, 1370, 1223, 1081 (SO), 1052 (SO), 1020, 964, 751, 693 cm^{-1}; ^1H NMR δ 1.96 (3H, s), 5.66 (1H, dd, *J*=15.9, 6.4 Hz), 6.22 (1H, d, *J*=15.9 Hz), 6.53 (1H, d, *J*=6.4 Hz), 6.98–7.00 (2H, m), 7.20–7.23 (3H, m), 7.34–7.50 (8H, m), 7.64 (1H, s), 7.75–7.77 (1H, m). MS *m/z* (%) 402 (M^+, 3), 276 (10), 235 (58), 217 (100), 115 (27), 91 (37). Calcd for $C_{25}H_{22}O_3S$: M, 402.1290. Found: *m/z* 402.1285.

2.1.42. (4*E*)-1,5-Diphenyl-1,2,4-pentatriene (16c).[20] Colorless oil; IR (neat) 3081, 3059, 3026, 2963, 2925, 1928 (allene), 1597, 1494, 1449, 963, 788, 751, 729, 691 cm^{-1}; ^1H NMR δ 6.42 (1H, d, *J*=15.9 Hz), 6.42–6.44 (1H, m), 6.61 (1H, d, *J*=15.9 Hz), 6.63–6.68 (1H, m), 7.29–7.41 (10H, m).

2.1.43. 1,5-Diphenyl-4-(phenylsulfinyl)-1-penten-4-yn-3-ol (14d). Colorless oil (about 2:3 diastereomeric mixture); IR (neat) 3276, 1653, 1490, 1443, 1027 (SO), 752, 690 cm^{-1}; ^1H NMR δ 3.24 (0.4H, d, *J*=7.7 Hz, OH), 3.29 (0.6H, d, *J*=5.2 Hz, OH), 5.75 (0.4H, d, *J*=7.7 Hz), 5.77 (0.6H, d, *J*=4.9 Hz), 7.07–7.86 (16H, m). MS *m/z* (%) 358 (M^+, 2), 312 (28), 249 (90), 215 (100), 203 (70), 131 (65), 105 (65), 77 (65). Calcd for $C_{23}H_{18}O_2S$: M, 358.1028. Found: *m/z* 358.1036.

2.1.44. 3-Acetoxy-1,5-diphenyl-4-(phenylsulfinyl)-1-penten-4-yne (15d). Colorless oil (about 2:3 diastereomeric mixture); IR (neat) 3058, 3025, 1748, 1489, 1443, 1370, 1219, 1082 (SO), 1051 (SO), 1019, 996, 951, 756, 690, 608 cm^{-1}; ^1H NMR δ 1.61 (1.2H, s), 2.05 (1.8H, s), 6.61 (0.4H, s), 6.62 (0.6H, s), 7.01–7.03 (1H, m), 7.19–7.64 (12H, m), 7.76–7.84 (2H, m). MS *m/z* (%) 358 (M^+, 11), 291 (23), 249 (53), 215 (100), 105 (39), 77 (14). Calcd for $C_{23}H_{18}O_2S$: M, 358.1026. Found: *m/z* 358.1024.

2.1.45. 1,5-Diphenyl-1,2-pentadien-4-yne (16d). Colorless oil; IR (neat) 3060, 3028, 2923, 1940 (allene), 1599, 1489, 755, 689 cm^{-1}; ^1H NMR δ 6.76–7.69 (12H, m). MS *m/z* (%) 216 (M^+, 63), 215 (100), 189 (8), 83 (8). Calcd for $C_{17}H_{12}$: M, 216.0937. Found: *m/z* 216.0937.

2.1.46. 1-Cyclohexylidene-4-phenyl-1-(phenylsulfinyl)-2-butanol (17a). Colorless crystals and oil (about 6:4 diastereomeric mixture), the isomers were easily separated by silica gel column chromatography. **17a-L**: colorless crystals; mp 130–133°C (AcOEt–hexane); IR (KBr) 3384, 3057, 3024, 2934, 2851, 1624, 1440, 1079 (SO), 1062 (SO), 1024 (SO), 996, 747, 695 cm^{-1}; ^1H NMR δ 1.59–1.93 (8H, m), 2.36–2.48 (3H, m), 2.61–2.82 (3H, m), 3.25 (1H, d, *J*=4.9 Hz, OH), 4.70 (1H, quint., *J*=4.9 Hz), 7.01–7.59 (10H, m). MS *m/z* (%) 354 (M^+, 3), 337 (16), 210 (40), 91 (100). Calcd for $C_{22}H_{26}O_2S$: M, 354.1651. Found: *m/z* 354.1637. Anal. Calcd for $C_{22}H_{26}O_2S$: C, 74.54; H, 7.39; S, 9.04. Found: C, 74.39; H, 7.38; S, 9.04. **17a-P**: colorless oil; IR (neat) 3395, 3059, 3024, 2929, 2855, 1624, 1444, 1081 (SO), 1038 (SO), 996, 749, 698 cm^{-1}; ^1H NMR δ 1.12–1.20 (1H, m), 1.25–1.30 (2H, m), 1.62–1.79 (4H, m), 2.04–2.14 (1H, m), 2.37–3.42 (3H, m), 2.56–2.78 (3H, m), 3.38 (1H, d, *J*=6.3 Hz, OH), 4.56 (1H, ddd, *J*=10.5, 6.4, 2.7 Hz), 6.95–7.52 (10H, m). MS *m/z* (%) 354 (M^+, 1), 337 (8), 203 (29), 91 (100). Calcd for $C_{22}H_{26}O_2S$: M, 354.1652. Found: *m/z* 354.1656.

2.1.47. 2-Acetoxy-1-cyclohexylidene-4-phenyl-1-(phenylsulfinyl)butane (18a). 18a-L: colorless oil; IR (neat) 3060, 3024, 2931, 2855, 1742, 1627, 1724, 1443, 1370, 1232, 1080 (SO), 1042 (SO), 750, 698 cm^{-1}; ^1H NMR δ 1.64–1.67 (4H, m), 1.70 (3H, s), 1.72–1.83 (2H, m), 2.05–2.18

(2H, m), 2.45–2.50 (1H, m), 2.53–2.58 (1H, m), 2.64 (1H, ddd, *J*=9.8, 6.9, 3.1 Hz), 2.76–2.87 (2H, m), 5.63 (1H, dd, *J*=8.2, 6.4 Hz), 7.15–7.17 (3H, m), 7.24–7.27 (2H, m), 7.40–7.53 (5H, m). MS *m/z* (%) 396 (M^+, 3), 336 (23), 221 (73), 143 (51), 91 (100). Calcd for $C_{24}H_{28}O_3S$: M, 396.1759. Found: *m/z* 396.1761. **18a-P**: colorless oil; IR (neat) 3059, 2931, 2856, 1742, 1628, 1443, 1367, 1234, 1081 (SO), 1046 (SO), 751, 699 cm^{-1}; ^1H NMR δ 1.64 (3H, s), 1.66–1.79 (7H, m), 2.21–2.32 (2H, m), 2.38–2.49 (3H, m), 2.68 (1H, ddd, *J*=12.8, 9.0, 3.9 Hz), 2.86–2.91 (1H, m), 5.91 (1H, dd, *J*=9.7, 3.9 Hz), 6.95 (2H, d, *J*=7.0 Hz), 7.12–7.15 (1H, m), 7.19–7.22 (2H, m), 7.40–7.44 (1H, m), 7.47–7.50 (2H, m), 7.53–7.55 (2H, m). MS *m/z* (%) 396 (M^+, 5), 336 (22), 211 (71), 143 (50), 91 (100). Calcd for $C_{24}H_{28}O_3S$: M, 396.1759. Found: *m/z* 396.1771.

2.1.48. 1-Cyclohexylidene-4-phenyl-1-butene (19a). Colorless oil; IR (neat) 3085, 3063, 3027, 2926, 2853, 1965 (allene), 1604, 1496, 1447, 1264, 1239, 745, 698 cm^{-1}; ^1H NMR δ 1.45–1.60 (6H, m), 2.03–2.05 (4H, m), 2.26–2.31 (2H, m), 2.71 (2H, t, *J*=7.7 Hz), 4.98–5.03 (1H, m), 7.15–7.29 (5H, m). MS *m/z* (%) 212 (M^+, 52), 184 (25), 169 (39), 144 (50), 129 (93), 91 (100), 79 (69). Calcd for $C_{16}H_{20}$: M, 212.1563. Found: *m/z* 212.1560.

2.1.49. 1-Cyclohexylidene-2-(2-naphthyl)-1-(phenylsulfinyl)-2-ethanol (17b). Colorless crystals and oil (about 2:3 diastereomeric mixture), the isomers were easily separated by silica gel column chromatography. **17b-L**: colorless crystals; mp 166–168°C (AcOEt–hexane); IR (KBr) 3481, 3054, 2932, 2851, 1624, 1439, 1078 (SO), 1031 (SO), 1016, 814, 750, 732 cm^{-1}; ^1H NMR δ 1.35–1.47 (2H, m), 1.55–1.63 (2H, m), 1.70–1.75 (1H, m), 1.80–1.86 (1H, m), 2.23–2.28 (1H, m), 2.34–2.39 (1H, m), 2.79–2.85 (1H, m), 2.87–2.92 (1H, m), 2.90 (1H, d, *J*=5.5 Hz, OH), 5.93 (1H, d, *J*=5.5 Hz), 7.26–7.85 (12H, m). MS *m/z* (%) 376 (M^+, 0.1), 358 (12), 250 (100), 207 (17), 127 (14). Calcd for $C_{24}H_{24}O_2S$: M, 376.1497. Found: *m/z* 376.1499. Anal. Calcd for $C_{24}H_{24}O_2S$: C, 76.56; H, 6.42; S, 8.51. Found: C, 76.59; H, 6.48; S, 8.51. **17b-P**: colorless oil; IR (neat) 3377, 3056, 3004, 1622, 1600, 1506, 1444, 1354, 1270, 1159, 1121, 1080 (SO), 1020 (SO), 854, 813, 742, 696 cm^{-1}; ^1H NMR δ 1.21–1.24 (1H, m), 1.34–1.36 (1H, m), 1.48–1.50 (1H, m), 1.54–1.56 (1H, m), 1.66–1.71 (1H, m), 1.82–1.85 (1H, m), 1.97–2.01 (1H, m), 2.13–2.17 (1H, m), 2.73–2.78 (1H, m), 2.88–2.90 (1H, m), 3.52 (1H, bs, OH), 5.86 (1H, s), 6.90 (1H, dd, *J*=8.6, 1.6 Hz), 7.26–7.73 (11H, m). MS *m/z* (%) 376 (M^+, 0.1), 358 (12), 250 (100), 207 (18), 127 (13). Calcd for $C_{24}H_{24}O_2S$: M, 376.1497. Found: *m/z* 376.1508.

2.1.50. 2-Acetoxy-1-cyclohexylidene-2-(2-naphthyl)-1-(phenylsulfinyl)ethane (18b). 18b-L: colorless oil; IR (neat) 3056, 2932, 2854, 1745, 1632, 1444, 1370, 1225, 1080 (SO), 1039 (SO), 854, 813, 752, 691 cm^{-1}; ^1H NMR δ 1.11–1.20 (1H, m), 1.24–1.36 (1H, m), 1.44–1.58 (2H, m), 1.66–1.75 (1H, m), 1.77–1.86 (1H, m), 1.79 (3H, s), 2.05 (1H, ddd, *J*=12.9, 8.5, 4.0 Hz), 2.26 (1H, ddd, *J*=13.0, 8.3, 4.3 Hz), 2.87–2.90 (2H, m), 6.86 (1H, s), 7.40–7.46 (4H, m), 7.48–7.52 (2H, m), 7.58–7.62 (3H, m), 7.60–7.80 (3H, m). MS *m/z* (%) 418 (M^+, 1), 292 (48), 233 (100), 191 (21), 127 (12). Calcd for $C_{26}H_{26}O_3S$: M, 418.1603. Found: *m/z* 418.1620. **18b-P**: colorless oil; IR (neat) 3057, 2930, 2855, 1746, 1632, 1443, 1371, 1225, 1082 (SO), 1045 (SO), 856, 812, 754, 697 cm^{-1}; ^1H NMR δ 1.37–1.66 (4H, m), 1.70–1.86 (2H, m), 2.11 (3H, s), 2.17 (1H, ddd, *J*=13.1, 8.6, 4.3 Hz), 2.39 (1H, ddd, *J*=12.6, 7.7, 4.0 Hz), 2.80 (1H, ddd, *J*=13.3, 8.8, 4.3 Hz), 3.02 (1H, ddd, *J*=12.5, 7.5, 4.0 Hz), 6.90 (1H, dd, *J*=8.9, 1.9 Hz), 7.03 (1H, s), 7.16 (1H, s), 7.31–7.34 (1H, m), 7.37–7.41 (4H, m), 7.50–7.52 (1H, m), 7.55–7.59 (3H, m), 7.69–7.71 (1H, m). MS *m/z* (%) 418 (M^+, 0.6), 292 (48), 250 (32), 233 (100), 191 (25), 127 (11). Calcd for $C_{26}H_{26}O_3S$: M, 418.1602. Found: *m/z* 418.1599.

2.1.51. 1-Cyclohexylidene-2-(2-naphthyl)ethene (19b). Colorless crystals; mp 81–84°C (AcOEt–hexane); IR (KBr) 2921, 1945 (allene), 1232, 950, 901, 865, 829 cm^{-1}; ^1H NMR δ 1.56–1.75 (6H, m), 2.20–2.35 (4H, m), 6.18 (1H, t, *J*=2.0 Hz), 7.37–7.78 (7H, m). MS *m/z* (%) 234 (M^+, 100), 219 (8), 205 (28), 191 (74), 178 (32), 165 (22), 152 (23). Calcd for $C_{18}H_{18}$: M, 234.1407. Found: *m/z* 234.1399.

2.1.52. 1-Cyclohexylidene-4-phenyl-1-(phenylsulfinyl)-3-buten-2-ol (17c). Colorless crystals and oil (about 1:1 diastereomeric mixture), the isomers were easily separated by silica gel column chromatography. **17c-L**: colorless crystals; mp 156–159°C (AcOEt–hexane); IR (KBr) 3392, 3050, 2836, 2911, 2851, 1654, 1438, 1077 (SO), 1024 (SO), 1016, 749, 692 cm^{-1}; ^1H NMR δ 1.60–1.76 (5H, m), 1.86–1.90 (1H, m), 2.47–2.56 (2H, m), 2.74–2.79 (1H, m), 2.84–2.89 (1H, m), 3.34 (1H, d, *J*=5.5 Hz, OH), 5.93 (1H, ddd, *J*=5.5, 4.9, 1.6 Hz), 6.01 (1H, dd, *J*=15.9, 4.9 Hz), 6.50 (1H, dd, *J*=15.9, 1.6 Hz), 7.11–7.59 (10H, m). MS *m/z* (%) 352 (M^+, 2), 334 (17), 226 (100), 183 (17), 141 (27), 91 (46), 77 (28). Calcd for $C_{22}H_{24}O_2S$: M, 352.1494. Found: *m/z* 352.1489. Anal. Calcd for $C_{22}H_{24}O_2S$: C, 74.96; H, 6.86; S,9.10. Found: C, 74.90; H, 6.86; S, 9.13. **17c-P**: colorless oil; IR (neat) 3340, 3025, 2928, 2860, 1621, 1444, 1081 (SO), 1046 (SO), 1028, 1007, 967, 758, 744, 693 cm^{-1}; ^1H NMR δ 1.59–1.68 (5H, m), 1.82–1.87 (1H, m), 2.49–2.59 (2H, m), 2.71–2.75 (1H, m), 2.80–2.85 (1H, m), 3.28 (1H, d, *J*=3.7 Hz, OH), 5.23 (1H, ddd, *J*=4.9, 3.7, 1.6 Hz), 5.86 (1H, dd, *J*=15.9, 4.9 Hz), 6.01 (1H, dd, *J*=15.9, 1.6 Hz), 7.09–7.58 (10H, m). MS *m/z* (%) 352 (M^+, 1), 334 (14), 226 (100), 189 (27), 141 (31), 91 (50), 77 (31). Calcd for $C_{22}H_{24}O_2S$: M, 352.1496. Found: *m/z* 352.1502.

2.1.53. 2-Acetoxy-1-cyclohexylidene-4-phenyl-1-(phenylsulfinyl)-3-butene (18c). 18c-L: colorless oil; IR (neat) 3058, 2931, 2856, 1742, 1629, 1444, 1370, 1227, 1080 (SO), 1043 (SO), 962, 753, 693 cm^{-1}; ^1H NMR δ 1.63–1.75 (5H, m), 1.70 (3H, s), 1.83–1.92 (1H, m), 2.44–2.55 (2H, m), 2.88 (2H, ddd, *J*=7.0, 4.9, 2.2 Hz), 6.24 (1H, dd, *J*=15.9, 4.6 Hz), 6.31 (1H, dd, *J*=4.6, 1.8 Hz), 6.50 (1H, dd, *J*=15.9, 1.6 Hz), 7.20–7.33 (5H, m), 7.40–7.49 (3H, m), 7.56–7.57 (2H, m). MS *m/z* (%) 394 (M^+, 7), 268 (58), 227 (83), 209 (100), 141 (83), 91 (56). Calcd for $C_{24}H_{26}O_3S$: M, 394.1603. Found: *m/z* 394.1607. **18c-P**: colorless oil; IR (neat) 2930, 2855, 1742, 1626, 1444, 1371, 1231, 1081 (SO), 1045 (SO), 960, 753, 693 cm^{-1}; ^1H NMR δ 1.68–1.75 (5H, m), 1.85–1.90 (1H, m), 1.93 (3H, s), 2.47–2.52 (1H, m), 2.57–2.62 (1H, m), 2.78–2.83 (1H, m), 2.93–2.98 (1H, m), 5.80 (1H, d, *J*=15.9 Hz), 5.89 (1H, dd, *J*=15.9, 6.4 Hz), 6.36 (1H, d, *J*=6.4 Hz),

7.03–7.04 (2H, m), 7.15–7.22 (3H, m), 7.33–7.36 (1H, m), 7.43–7.47 (2H, m), 7.57–7.60 (2H, m). MS *m/z* (%) 394 (M^+, 6), 334 (14), 268 (54), 227 (85), 209 (100), 141 (84), 91 (55). Calcd for $C_{24}H_{26}O_3S$: M, 394.1603. Found: *m/z* 394.1607.

2.1.54. 1-Cyclohexylidene-4-phenyl-1,3-butadiene (19c). Colorless oil; IR (neat) 3080, 3059, 3026, 2929, 2885, 2853, 1944 (allene), 1596, 1497, 1447, 1272, 961, 746, 691 cm^{-1}; ^1H NMR δ 1.53–1.58 (2H, m), 1.61–1.65 (4H, m), 2.13–2.21 (4H, m), 5.86 (1H, dt, *J*=10.4, 1.9 Hz), 6.45 (1H, d, *J*=15.9 Hz), 6.59 (1H, dd, *J*=15.9, 10.4 Hz), 7.16–7.38 (5H, m). MS *m/z* (%) 210 (M^+, 100), 167 (98), 128 (59), 91 (41), 77 (47). Calcd for $C_{16}H_{18}$: M, 210.1408. Found: *m/z* 210.1414.

2.1.55. 1-Cyclohexylidene-4-phenyl-1-(phenylsulfinyl)-3-butyn-2-ol (17d). Colorless oil (about 2:3 diastereomeric mixture), the isomers were easily separated by silica gel column chromatography. **17d-L**: colorless oil; IR (neat) 3335, 3060, 2931, 2857, 1628, 1599, 1490, 1444, 1081 (SO), 1018 (SO), 997, 754, 691 cm^{-1}; ^1H NMR δ 1.67–1.74 (4H, m), 1.84–1.88 (2H, m), 2.60 (1H, ddd, *J*=13.5, 9.2, 4.0 Hz), 2.70 (1H, ddd, *J*=13.5, 9.2, 4.0 Hz), 2.76–2.80 (1H, m), 2.88–2.95 (1H, m), 3.31 (1H, d, *J*=5.5 Hz, OH), 5.70 (1H, d, *J*=5.5 Hz), 7.20–7.65 (10H, m). MS *m/z* (%) 350 (M^+, 0.7), 334 (2), 286 (7), 233 (15), 187 (38), 131 (100), 103 (35), 77 (46). Calcd for $C_{22}H_{22}O_2S$: M, 350.1340. Found: *m/z* 350.1343. **17d-P**: colorless oil; IR (neat) 3324, 3060, 3008, 2932, 2857, 1627, 1599, 1490, 1444, 1080 (SO), 1027 (SO), 997, 755, 691 cm^{-1}; ^1H NMR δ 1.69–1.90 (6H, m), 2.68–2.77 (2H, m), 2.83–2.88 (1H, m), 2.89–2.94 (1H, m), 3.14 (1H, d, *J*=4.6 Hz, OH), 5.44 (1H, d, *J*=4.3 Hz), 7.17–7.27 (5H, m), 7.42–7.51 (3H, m), 7.57–7.59 (2H, m). MS *m/z* (%) 350 (M^+, 6), 332 (21), 304 (37), 233 (65), 207 (56), 167 (70), 129 (84), 105 (100), 77 (92). Calcd for $C_{22}H_{22}O_2S$: M, 350.1339. Found: *m/z* 350.1344.

2.1.56. 2-Acetoxy-1-cyclohexylidene-4-phenyl-1-(phenylsulfinyl)-3-butyne (18d). 18d-L: colorless oil; IR (neat) 3058, 2998, 2932, 2857, 1747, 1628, 1598, 1491, 1444, 1369, 1219, 1081 (SO), 1043 (SO), 976, 946, 755, 691 cm^{-1}; ^1H NMR δ 1.58 (3H, s), 1.69–1.91 (6H, m), 2.68 (1H, ddd, *J*=13.1, 8.9, 3.9 Hz), 2.78 (1H, ddd, *J*=13.4, 9.2, 4.3 Hz), 2.93–2.97 (1H, m), 3.01–3.06 (1H, m), 7.26–7.55 (10H, m). MS *m/z* (%) 392 (M^+, 1), 350 (41), 283 (40), 241 (77), 207 (82), 165 (66), 105 (100), 77 (48). Calcd for $C_{24}H_{24}O_3S$: M, 392.1445. Found: *m/z* 392.1471. **18d-P**: colorless oil; IR (neat) 3058, 2999, 2932, 2857, 1748, 1628, 1598, 1490, 1444, 1371, 1225, 1081 (SO), 1045 (SO), 1017, 986, 949, 755, 692 cm^{-1}; ^1H NMR δ 1.70–1.95 (6H, m), 2.07 (3H, s), 2.67 (1H, ddd, *J*=13.1, 8.6, 4.3 Hz), 2.78–2.86 (2H, m), 2.89–2.94 (1H, m), 6.32 (1H, s), 7.10–7.12 (2H, m), 7.20–7.27 (3H, m), 7.40–7.49 (3H, m), 7.60–7.62 (2H, m). MS *m/z* (%) 392 (M^+, 2), 350 (50), 283 (49), 241 (83), 207 (98), 165 (71), 105 (100), 91 (55), 77 (47). Calcd for $C_{24}H_{24}O_3S$: M, 392.1444. Found: *m/z* 392.1434.

2.1.57. 1-Cyclohexylidene-4-phenyl-1-buten-3-yne (19d). Colorless oil; IR (neat) 3053, 3019, 2931, 2853, 1948 (allene), 1596, 1489, 1441, 1266, 1238, 754, 690 cm^{-1}; ^1H NMR δ 1.50–1.71 (6H, m), 2.19 (4H, dt, *J*=6.1, 2.2 Hz), 5.46 (1H, t, *J*=2.2 Hz), 7.26–7.29 (3H, m), 7.42–7.44 (2H, m). MS *m/z* (%) 208 (M^+, 100), 180 (65), 165 (57), 152 (24), 139 (14), 126 (32), 91 (14), 77 (11). Calcd for $C_{16}H_{16}$: M, 208.1251. Found: *m/z* 208.1257.

2.1.58. 1-[Hexylidene(phenylsulfinyl)methyl]-4,4-ethylenedioxycyclohexanol (20a). Colorless oil; IR (neat) 3305, 2958, 2931, 2873, 1470, 1443, 1367, 1252, 1158, 1104, 1080 (SO), 1032 (SO), 989, 965, 748, 696 cm^{-1}; ^1H NMR δ 0.97 (3H, t, *J*=7.4 Hz), 1.41–1.61 (8H, m), 1.84 (2H, dt, *J*=12.8, 4.0 Hz), 2.06–2.14 (2H, m), 2.44 (1H, ddd, *J*=15.2, 8.0, 3.7 Hz), 3.30 (1H, s, OH), 3.91 (4H, dd, *J*=5.8, 3.7 Hz), 6.36 (1H, t, *J*=8.0 Hz), 7.42–7.49 (3H, m), 7.62–7.64 (2H, m). MS *m/z* (%) 364 (M^+, 5), 347 (18), 221 (100), 177 (42), 135 (33), 101 (81). Calcd for $C_{20}H_{28}O_4S$: M, 364.1708. Found: *m/z* 364.1705.

2.1.59. 1-[Benzylidene(phenylsulfinyl)methyl]-4,4-ethylenedioxycyclohexanol (20b). Colorless crystals; mp 183.5–185.0°C (AcOEt–hexane); IR (KBr) 3332, 2931, 1443, 1369, 1254, 1154, 1103, 1030 (SO), 986, 746, 697, 689 cm^{-1}; ^1H NMR δ 1.33–1.38 (2H, m), 1.39–1.43 (1H, m), 1.65–1.69 (1H, m), 1.72–1.85 (2H, m), 2.01–2.13 (2H, m), 2.40 (1H, s, OH), 3.81–3.86 (4H, m), 7.31–7.52 (8H, m), 7.54 (1H, s), 7.76–7.79 (2H, m). MS *m/z* (%) 384 (M^+, 0.7), 312 (29), 241 (38), 156 (32), 99 (100), 86 (62). Calcd for $C_{22}H_{24}O_4S$: M, 384.1395. Found: *m/z* 384.1405. Anal. Calcd for $C_{22}H_{24}O_4S$: C, 68.77; H, 6.18; S, 8.34. Found: C, 68.72; H, 6.29; S, 8.34.

2.1.60. 1-[Cyclohexylidene(phenylsulfinyl)methyl]-4,4-ethylenedioxycyclohexanol (20c). Colorless crystals; mp 130–133°C (AcOEt–hexane); IR (KBr) 3336, 2932, 2878, 1473, 1432, 1100, 1089 (SO), 1016 (SO), 986, 750 cm^{-1}; ^1H NMR δ 1.30–1.34 (1H, m), 1.36–1.40 (1H, m), 1.46–1.50 (1H, m), 1.63–1.71 (4H, m), 1.82–2.01 (5H, m), 2.04–2.10 (1H, m), 2.27–2.33 (1H, m), 2.46–2.51 (1H, m), 2.64–2.80 (3H, m), 3.90 (4H, t, *J*=3.1 Hz), 5.64 (1H, d, *J*=3.1 Hz, OH), 7.39–7.51 (5H, m). MS *m/z* (%) 376 (M^+, 3), 341 (9), 233 (100), 189 (21), 99 (26). Calcd for $C_{21}H_{28}O_4S$: M, 376.1709. Found: *m/z* 376.1714. Anal. Calcd for $C_{21}H_{28}O_4S$: C, 67.36; H, 7.36; S, 8.12. Found: C, 66.99; H, 7.50; S, 8.51.

2.1.61. (*E*)-(*R*)-(+)-1-(*p*-Tolylsulfinyl)-2-phenylethene (21). Colorless crystals; mp 77.5–79.5°C (AcOEt–hexane); IR (KBr) 3019, 1492, 1444, 1083 (SO), 1045 (SO), 1014, 971, 806, 762, 740, 692, 527 cm^{-1}; ^1H NMR δ 2.41 (3H, s), 6.81 (1H, d, *J*=15.3 Hz), 7.31–7.38 (6H, m), 7.44–7.46 (2H, m), 7.56–7.58 (2H, m). MS *m/z* (%) 242 (M^+, 0.4), 226 (12), 213 (13), 194 (100), 179 (48), 91 (35), 77 (20). Calcd for $C_{15}H_{14}OS$: M, 242.0765. Found: *m/z* 242.0768. Anal. Calcd for $C_{15}H_{14}OS$: C, 74.34; H, 5.82; S, 13.23. Found: C, 74.19; H, 5.55; S, 13.43. $[\alpha]_D^{23}$=+198.8° (*c* 0.42, acetone).

2.1.62. (*E*)-(*Ss*,1*R*)-(+)-1-(2-Naphthyl)-3-phenyl-2-(*p*-tolylsulfinyl)-2-propen-1-ol (22). Colorless crystals; mp 157–159°C (AcOEt–hexane); IR (KBr) 3192 (OH), 1624, 1494, 1063 (SO), 1019 (SO), 986, 814, 695 cm^{-1}; ^1H NMR δ 2.26 (3H, s), 3.16 (1H, d, *J*=7.0 Hz, OH), 6.23 (1H, d, *J*=7.1 Hz), 7.06 (2H, d, *J*=8.0 Hz), 7.33–7.78 (15H, H). Anal. Calcd for $C_{26}H_{22}O_2S$: C, 78.36; H, 5.56; S, 8.04.

Found: C, 78.11; H, 5.39; S, 8.09. $[\alpha]_D^{28}=+219.7°$ (*c* 0.46, $CHCl_3$).

2.1.63. (*E*)-(*S*s,1*S*)-(−)-1-(2-Naphthyl)-3-phenyl-2-(*p*-tolylsulfinyl)-2-propen-1-ol (23). Colorless crystals; mp 157–159°C (AcOEt–hexane); IR (KBr) 3370 (OH), 1491, 1074 (SO), 1039 (SO), 806, 759, 702 cm^{-1}; ^1H NMR δ 2.17 (3H, s), 4.06 (1H, d, *J*=5.8 Hz, OH), 6.19 (1H, d, *J*=5.8 Hz), 6.99 (2H, d, *J*=7.9 Hz), 7.21–7.73 (15H, H). Anal. Calcd for $C_{26}H_{22}O_2S$: C, 78.36; H, 5.56; S, 8.04. Found: C, 77.81; H, 5.22; S, 8.13. $[\alpha]_D^{28}=-228.0°$ (*c* 0.41, $CHCl_3$).

2.1.64. (*E*)-(*S*s,1*R*)-(+)-1-Acetoxy-1-(2-naphthyl)-3-phenyl-2-(*p*-tolylsulfinyl)-2-propene (24). Colorless oil; IR (neat) 3050, 3014, 1736, 1594, 1363, 1228, 1051 (SO), 1024 (SO), 822, 807, 755, 703 cm^{-1}; ^1H NMR δ 1.55 (3 H, s), 2.39 (3H, s), 7.28–7.38 (7H, m), 7.46–7.52 (4H, m), 7.63–7.65 (3H, m), 7.75–7.81 (3H, m), 7.92 (1H, s). MS *m*/*z* (%) 440 (M^+, 0.14), 300 (9), 259 (29), 241 (100), 91 (9), 77 (5). Calcd for $C_{28}H_{24}O_3S$: M, 440.1446. Found: *m*/*z* 440.1452. $[\alpha]_D^{28}=+302.7°$ (*c* 0.12, $CHCl_3$).

2.1.65. (*E*)-(*S*s,1*S*)-(−)-1-Acetoxy-1-(2-naphthyl)-3-phenyl-2-(*p*-tolylsulfinyl)-2-propene (25). Colorless oil; IR (neat) 3056, 1747, 1634, 1597, 1493, 1369, 1224, 1084 (SO), 1030 (SO), 813, 756, 696 cm^{-1}; ^1H NMR δ 2.06 (3H, s), 2.09 (3H, s), 6.88 (2H, d, *J*=8.3 Hz), 7.06 (1H, dd, *J*=8.6, 1.6 Hz), 7.17–7.20 (2H, m), 7.27–7.34 (5H, m), 7.39–7.50 (5H, m), 7.56 (1H, d, *J*=8.6 Hz), 7.71–7.73 (1H, m), 7.79 (1H, s). MS *m*/*z* (%) 440 (M^+, 0.1), 300 (9), 259 (31), 241 (100), 91 (8), 77 (5). Calcd for $C_{28}H_{24}O_3S$: M, 440.1446. Found: *m*/*z* 440.1446. $[\alpha]_D^{28}=-3.5°$ (*c* 0.46, $CHCl_3$).

2.1.66. (*R*)-(−)-1-(2-Naphthyl)-3-phenyl-1,2-propadiene (*R*)-(−)-(26). Colorless crystals; mp 85–87°C (AcOEt–hexane); IR (KBr) 3053, 2960, 2923, 1933 (allene), 1654, 1560, 904, 860, 820, 750, 732, 691 m^{-1}; ^1H NMR δ 6.66 (1H, d, *J*=6.7 Hz), 6.77 (1H, d, *J*=6.7 Hz), 7.22–7.53 (8H, m), 7.74–7.79 (4H, m). MS *m*/*z* (%) 242 (M^+, 100), 215 (10), 165 (14), 120 (8). Calcd for $C_{19}H_{14}$: M, 242.1094. Found: *m*/*z* 242.1091. $[\alpha]_D^{26}=-946.7°$ (*c* 0.21, $CHCl_3$).

2.1.67. (*S*)-(+)-1-(2-Naphthyl)-3-phenyl-1,2-propadiene (*S*)-(+)-(26). Colorless crystals; mp 85–87°C (AcOEt–hexane); $[\alpha]_D^{27}=+936.1°$ (*c* 0.17, $CHCl_3$).

2.1.68. (*E*)-(*S*s,3*R*)-(+)-1,5-Diphenyl-2-(*p*-tolylsulfinyl)-1-penten-3-ol (27). Colorless oil; IR (neat) 3368, 3019, 2926, 1598, 1494, 1455, 1082 (SO), 1029 (SO), 1014, 809, 756 cm^{-1}; ^1H NMR δ 1.79–1.86 (1H, m), 2.07–2.14 (1H, m), 2.34 (1H, d, *J*=6.1 Hz, OH), 2.41 (3H, s), 2.58–2.64 (1H, m), 2.67–2.73 (1H, m), 4.85 (1H, ddd, *J*=10.1, 5.8, 4.6 Hz), 7.03–7.04 (2H, m), 7.20–7.31 (10H, m), 7.44–7.46 (1H, m), 7.62–7.63 (2H, m). MS *m*/*z* (%) 376 (M^+, 1), 359 (19), 219 (15), 140 (22), 91 (100), 77 (15). Calcd for $C_{24}H_{24}O_2S$: M, 376.1496. Found: *m*/*z* 376.1513. $[\alpha]_D^{30}=+181.2°$ (*c* 0.46, acetone).

2.1.69. (*E*)-(*S*s,3*S*)-(+)-1,5-Diphenyl-2-(*p*-tolylsulfinyl)-1-penten-3-ol (28). Colorless oil; IR (neat) 3339, 3024, 2923, 1596, 1493, 1447, 1082 (SO), 1027 (SO), 1011, 928, 809, 751, 698 cm^{-1}; ^1H NMR δ 1.60–1.67 (1H, m), 1.79–1.87 (1H, m), 2.41 (3H, s), 2.53–2.59 (1H, m), 2.62–2.67 (1H, m), 3.01 (1H, d, *J*=6.1 Hz, OH), 4.81 (1H, ddd, *J*=10.1, 6.1, 3.7 Hz), 7.00–7.02 (2H, m), 7.16–7.30 (11H, m), 7.58–7.60 (2H, m). MS *m*/*z* (%) 376 (M^+, 2), 359 (24), 271 (8), 237 (8), 219 (14), 140 (28), 91 (100), 77 (20). Calcd for $C_{24}H_{24}O_2S$: M, 376.1494. Found: *m*/*z* 376.1489. $[\alpha]_D^{32}=+16.5°$ (*c* 0.46, acetone).

2.1.70. (*E*)-(*S*s,3*R*)-(+)-3-Acetoxy-1,5-diphenyl-2-(*p*-tolylsulfinyl)-1-pentene (29). Colorless oil; IR (neat) 3026, 2927, 1743, 1596, 1494, 1455, 1371, 1227, 1083 (SO), 1029 (SO), 811, 752, 699 cm^{-1}; ^1H NMR δ 1.42 (3H, s), 1.92–1.99 (1H, m), 2.31–2.34 (1H, m), 2.40 (3H, s), 2.45–2.57 (2H, m), 5.92 (1H, dd, *J*=8.9, 5.2 Hz), 6.97 (2H, d, *J*=7.7 Hz), 7.15–7.22 (3H, m), 7.28–7.36 (5H, m), 7.43–7.44 (2H, m), 7.61 (2H, d, *J*=8.3 Hz), 7.66 (1H, s). MS *m*/*z* (%) 417 (M^+, 0.1), 402 (8), 279 (18), 219 (79), 140 (15), 117 (16), 91 (100), 77 (77). Calcd for $C_{26}H_{25}O_3S$: M, 417.525. Found: *m*/*z* 417.1522. $[\alpha]_D^{32}=+113.7°$ (*c* 0.46, acetone).

2.1.71. (*E*)-(*S*s,3*S*)-(+)-3-Acetoxy-1,5-diphenyl-2-(*p*-tolylsulfinyl)-1-pentene (30). Colorless oil; IR (neat) 3058, 3026, 2927, 2864, 1747, 1596, 1494, 1455, 1371, 1227, 1083 (SO), 1056 (SO), 811, 754, 699 cm^{-1}; ^1H NMR δ 1.63–1.68 (2H, m), 1.86 (3H, s), 2.33–2.39 (1H, m), 2.41 (3H, s), 2.43–2.49 (1H, m), 5.90 (1H, dd, *J*=8.3, 6.4 Hz), 6.88–6.90 (2H, m), 7.15–7.23 (3H, m), 7.30–7.31 (7H, m), 7.46 (1H, s), 7.59 (2H, d, *J*=8.3 Hz). MS *m*/*z* (%) 417 (M^+, 0.1), 402 (6), 219 (55), 140 (12), 115 (16), 91 (100), 77 (9). Calcd for $C_{26}H_{25}O_3S$: M, 417.1525. Found: *m*/*z* 417.1513. $[\alpha]_D^{31}=+44.8°$ (*c* 0.42, acetone).

2.1.72. (*R*)-(−)-1,5-Diphenyl-1,2-pentadiene (*R*)-(−)-(31). Colorless oil; IR (neat) 3083, 3062, 3028, 2921, 2855, 1949 (allene), 1602, 1496, 1454, 875, 779, 698 cm^{-1}; ^1H NMR δ 2.39–2.53 (2H, m), 2.76–2.85 (2H, m), 5.59 (1H, q, *J*=6.7 Hz), 6.12 (1H, quint., *J*=3.1 Hz), 7.15–7.30 (10H, m). MS *m*/*z* (%) 220 (M^+, 2), 162 (8), 149 (20), 134 (18), 117 (15), 105 (74), 91 (100), 77 (43). Calcd for $C_{17}H_{16}$: M, 200.1251. Found: *m*/*z* 220.1247. $[\alpha]_D^{32}=-149.6°$ (*c* 0.63, acetone).

2.1.73. (*S*)-(+)-1,5-Diphenyl-1,2-pentadiene (*S*)-(+)-(31). Colorless oil; $[\alpha]_D^{34}=+201.4°$ (*c* 0.67, acetone).

2.1.74. (*E*)-Methyl 4,4-dimethoxy-2-butenoate (32). To a solution of methyl dimethylphosphonoacetate (10 g; 47.6 mmol) in 120 ml of cyclohexane in a flask was added K_2CO_3 (9.87 g, 71.4 mmol) and finally dimethoxyactaldehyde (14.3 ml; 95.2 mmol) at 60°C under argon atmosphere, and the solution was stirred for 1 h. The reaction was quenched with sat. aq. NH_4Cl, and the mixture was extracted with ether. 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 **32** (*E*/*Z*=96:4 mixture; 7.33 g; 96%) as a colorless oil. IR (neat) 2954, 2834, 1723, 1670, 1438, 1366, 1307, 1276, 1170, 1130, 1059 cm^{-1}; ^1H NMR δ 3.34 (6H, s), 3.76 (3H, s), 4.95 (1H, dd, *J*=4.0, 1.6 Hz), 6.15 (1H, dd, *J*=15.9, 1.3 Hz), 6.77 (1H, dd, *J*=15.9, 4.0 Hz). MS *m*/*z* (%) 159 ($[M-H]^+$, 3), 145, (13), 129 (100), 113

(13), 101 (87), 75 (33), 69 (24). Calcd for $C_7H_{11}O_4$: [M−H], 159.0656. Found: *m/z* 159.0659.

2.1.75. (*E*)-Methyl 3-formyl-2-propenoate (33). A solution of 345 mg of *p*-toluensulfonic acid in a 1:1 mixture of water and acetone (96 ml) was added to a solution of **32** (4.15 g; 25.9 mmol) in acetone and the reaction mixture was heated under reflux for 1.5 h. The reaction was quenched with sat. aq. $NaHCO_3$, and the mixture was extracted with ether. 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 **33** (2.89 g; 98%) as colorless oil. IR (neat) 3056, 2962, 2873, 1727, 1683, 1643, 1435, 1309, 1257, 1200, 1177, 1116, 997 cm^{-1}; ^1H NMR δ 3.86 (3H, s), 6.74 (1H, d, *J*=15.9 Hz), 6.99 (1H, dd, *J*=15.9, 7.6 Hz), 9.78 (1H, d, *J*=7.6 Hz). MS *m/z* (%) 114 (M^+, 10), 99, (100), 85 (54), 59 (13), 55 (24). Calcd for $C_5H_6O_3$: M, 114.0315. Found: *m/z* 114.0297.

2.1.76. (*E*)-(*R*)-(+)-1-(*p*-Tolylsulfinyl)-1-decene (34). Colorless oil; IR (neat) 2926, 2855, 1628, 1597, 1493, 1465, 1084 (SO), 1048 (SO), 1016, 964, 810 cm^{-1}; ^1H NMR δ 0.88 (3H, t, *J*=7.1 Hz), 1.25–1.31 (10H, m), 1.45 (2H, quint., *J*=7.3 Hz), 2.21 (2H, ddd, *J*=14.9, 6.8, 1.5 Hz), 2.41 (3H, s), 6.20 (1H, dt, *J*=15.1, 1.5 Hz), 6.59 (1H, dt, *J*=15.1, 6.8 Hz), 7.30–7.32 (2H, m), 7.48–7.51 (2H, m). MS *m/z* (%) 278 (M^+, 14), 261 (25), 230 (70), 131 (100), 181 (59), 91 (23). Calcd for $C_{17}H_{26}O_5S$: M, 278.1703. Found: *m/z* 278.1706. $[\alpha]_D^{22}$=+92.7° (*c* 0.62, acetone).

2.1.77. (2*E*,5*E*)-(*S*s)-Methyl 4-hydroxy-5-(*p*-tolylsulfinyl)-2,5-tetradecadienoate (35). Colorless oil (46:54 diastereomeric mixture); IR (neat) 3339, 2926, 2855, 1728, 1657, 1493, 1436, 1271, 1167, 1113, 1083 (SO), 809 cm^{-1}; ^1H NMR δ 0.88 (0.54H, t, *J*=7.0 Hz), 0.89 (0.46H, t, *J*=7.0 Hz), 1.25–1.62 (12H, m), 2.22–2.37 (2H, m), 2.39 (1.38H, s), 2.40 (1.62H, s), 3.12 (0.46H, d, *J*=4.6 Hz, OH), 3.66 (1.38H, s), 3.67 (1.62H, s), 3.79 (0.54H, d, *J*=5.5 Hz, OH), 5.10–5.12 (0.54H, m), 5.30–5.32 (0.46H, m), 5.80 (0.54H, dd, *J*=15.6, 1.9 Hz), 5.83 (0.46H, dd, *J*=15.6, 2.2 Hz), 6.39 (0.54H, dd, *J*=15.6, 4.0 Hz), 6.48 (0.46H, t, *J*=7.6 Hz), 6.49 (0.54H, dd, *J*=15.6, 3.7 Hz), 6.56 (0.46H, t, *J*=7.6 Hz), 7.28 (0.92H, d, *J*=8.3 Hz), 7.32 (1.08H, d, *J*=8.3 Hz), 7.45 (0.92H, d, *J*=8.3 Hz), 7.46 1(1.08H, d, *J*=8.3 Hz). MS *m/z* (%) 392 (M^+, 2), 253 (38), 140 (100), 91 (53). Calcd for $C_{22}H_{32}O_4S$: M, 392.2019. Found: *m/z* 392.2015.

2.1.78. (2*E*,5*E*)-(*S*s,4*R*)-(+)-Methyl 4-acetoxy-5-(*p*-tolylsulfinyl)-2,5-tetradecadienoate (36). Colorless oil; IR (neat) 2928, 2857, 1749, 1729, 1661, 1494, 1436, 1371, 1309, 1273, 1223, 1083 (SO), 1051 (SO), 978, 811 cm^{-1}; ^1H NMR δ 0.88 (3H, t, *J*=7.1 Hz), 1.28–1.32 (10H, m), 1.51 (2H, quint., *J*=7.7 Hz), 1.70 (3H, s), 2.38 (2H, q, *J*=7.7 Hz), 2.39 (3H, s), 3.73 (3H, s), 5.76 (1H, dd, *J*=15.6, 1.9 Hz), 6.08 (1H, dd, *J*=4.3, 1.9 Hz), 6.68 (1H, dd, *J*=15.6, 4.3 Hz), 6.76 (1H, t, *J*=7.6 Hz), 7.28 (2H, d, *J*=8.0 Hz), 7.50 (2H, d, *J*=8.3 Hz). MS *m/z* (%) 434 (M^+, 10), 375 (10), 295 (43), 271 (100), 253 (82), 235 (35), 140 (51), 91 (32). Calcd for $C_{24}H_{34}O_5S$: M, 434.2127. Found: *m/z* 434.2130. $[\alpha]_D^{20}$=+59.9° (*c* 0.33, acetone).

2.1.79. (2*E*,5*E*)-(*S*s,4*S*)-(+)-Methyl 4-acetoxy-5-(*p*-tolylsulfinyl)-2,5-tetradecadienoate (37). Colorless oil; IR (neat) 2927, 2856, 1749, 1729, 1661, 1493, 1436, 1372, 1309, 1275, 1222, 1172, 1084 (SO), 1054 (SO), 978, 810 cm^{-1}; ^1H NMR δ 0.89 (3H, t, *J*=6.9 Hz), 1.28–1.37 (10H, m), 1.52 (2H, quint., *J*=7.3 Hz), 2.01 (3H, s), 2.34 (2H, dq, *J*=7.5, 2.5 Hz), 2.37 (3H, s), 3.65 (3H, s), 5.43 (1H, dd, *J*=15.6, 1.9 Hz), 6.20 (1H, dd, *J*=4.6, 1.9 Hz), 6.28 (1H, dd, *J*=15.6, 4.6 Hz), 6.66 (1H, t, *J*=7.6 Hz), 7.26 (2H, d, *J*=7.7 Hz), 7.48 (2H, d, *J*=8.0 Hz). MS *m/z* (%) 434 (M^+, 9), 375 (34), 295 (73), 271 (100), 253 (90), 221 (38), 140 (61), 91 (38). Calcd for $C_{24}H_{34}O_5S$: M, 434.2127. Found: *m/z* 434.2129. $[\alpha]_D^{21}$=+6.4° (*c* 0.34, acetone).

2.1.80. (*E*)-(*R*)-(−)-Methyl 2,4,5-tetradecatrienoate (*R*)-(−)-(38).[16b] Colorless oil; IR (neat) 2927, 2856, 1943 (allene), 1722, 1630, 1436, 1306, 1264, 1241, 1177, 1139, 983 cm^{-1}; ^1H NMR δ 0.88 (3H, t, *J*=7.1 Hz), 1.27–1.34 (10H, m), 1.42 (2H, quint., *J*=7.1 Hz), 2.06 (2H, qd, *J*=7.1, 2.8 Hz), 3.74 (3H, s), 5.44 (1H, q, *J*=6.7 Hz), 5.86 (1H, dt, *J*=15.3, 0.9 Hz), 5.87–5.92 (1H, m), 7.18 (1H, ddd, *J*=15.3, 11.0, 0.9 Hz). $[\alpha]_D^{20}$=−114.6° (*c* 0.83, hexane).

2.1.81. (*E*)-(*S*)-(+)-Methyl 2,4,5-tetradecatrienoate (*S*)-(+)-(38).[16b] Colorless oil; $[\alpha]_D^{21}$=+116.9° (*c* 0.53, hexane).

2.2. X-Ray crystallography

Quality single crystals were mounted on glass fibers. Diffraction data were collected on a Bruker Smart APEX CCD X-ray diffractometer with graphite-monochromated Mo Kα radiation (λ=0.71073 Å). The data were corrected for Lorentz and polarization effects, and for absorption using the SADABS program.[21] Structures were solved by the direct method.[22] All non-hydrogen atoms were refined anisotropically on F^2 by full-matrix least-squares using the SHELXL-97 program.[23] The KenX program[24] was used to visualize the molecules and to locate new atoms during the refinement procedures. In each case, a hydrogen atom on a hydroxy unit was clearly visible in the difference Fourier map, was located, and was refined isotropically. All the remaining hydrogen atoms were located in their idealized positions and refined as riding atoms with isotropic thermal parameters. The teXsan program[25] was also used to generate ORTEP diagrams. The absolute configuration of **23** (in the (*S*)-(−) form) was unambiguously determined by comparing the reliability factors (*R*1=0.0548 for the reported structure and *R*1=0.0556 for the other) as well as the Flack parameters (−0.02(8) for the reported one and 1.03(8) for the other) obtained in the refinements conducted for two possibilities. A racimic from of **23** was similarly prepared as **23**, and was also structurally analyzed by X-ray diffraction.

2.3. Crystallographic data for 23

$C_{26}H_{22}O_2S$, *M*=398.50, *Orthorhombic*, space group $P2_12_12_1$ (#19), *a*=6.3835(4), *b*=11.5925(7), *c*=26.6603(16) Å, *V*=1972.9(2) $Å^3$, *Z*=4, *F*(000)=840. D_{calc}=1.342 g cm^{-3}, μ (Mo Kα)=1.84 cm^{-1}, *T*=100(2) K, radiation=0.71073 Å, *R*1=0.0548 for $I>2.0\sigma(I)$. *wR*2=0.1263 for all data (5615 reflections), GOF=1.071 (267 parameters),

crystal dimensions 0.48×0.06×0.04 mm^3. Data deposited at the Cambridge Crystallographic Data Centre; deposition number CCDC 176502.

2.4. Crystallographic data for racemic form of 23

$C_{26}H_{22}O_2S$, M=398.50, *Triclinic*, space group $P\bar{1}$ (#2), a=6.3462(5), b=11.9476(9), c=13.9832(11) Å, α=67.5420(10)°, β=88.776(2)°, γ=89.570(2)°, V=979.60(13) $Å^3$, Z=2, $F(000)$=420. D_{calc}=1.351 g cm^{-3}, μ(Mo Kα)=1.86 cm^{-1}, T=100(2) K, radiation=0.71073 Å, $R1$=0.0617 for $I>2.0\sigma(I)$. $wR2$=0.1537 for all data (5404 reflections), GOF=1.102 (267 parameters), crystal dimensions 0.26×0.09×0.06 mm^3. Data deposited at the Cambridge Crystallographic Data Centre; deposition number CCDC 176503.

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