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Studies on Intramolecular Alkylation of an α-Sulfinyl Vinylic Carbanion: a Novel Route to Chiral 1-Cycloalkenyl Sulfoxides

Naoyoshi Maezaki, Mayuko Izumi, Sachiko Yuyama, Hiroaki Sawamoto, Chuzo Iwata and Tetsuaki Tanaka*

Graduate School of Pharmaceutical Sciences, Osaka University, 1-6 Yamadaoka, Suita, Osaka 565-0871, Japan

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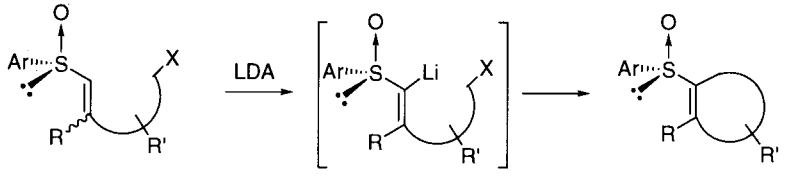
Abstract—Intramolecular alkylation of various β-(ω-haloalkyl) substituted vinylic sulfoxides was investigated. Upon treatment with LDA in THF at −78°C, α-sulfinyl carbanion generated from vinylic sulfoxides cyclized at the α-sulfinyl position to give 1-cycloalkenyl sulfoxides with a five- to seven-membered ring. Although iodide or bromide is normally a good leaving group, chloride affords better results than the corresponding iodide and bromide when the reaction takes place at the benzylic position. The cyclization proceeded even with the secondary iodide in moderate yield. Not only the (*E*)-isomer but also the (*Z*)-isomer cyclized via rapid inversion of the olefin geometry. No loss of optical purity was observed during isomerization. Various 1-cycloalkenyl sulfoxides including a fused ring and a polyoxygenated rings were synthesized in good to moderate yields.

Introduction

In 1978, Posner[1] and Okamura[2] independently reported that the α-proton of vinylic sulfoxides can be abstracted with a base such as MeLi or LDA, and the resulting carbanions are reacted with various electrophiles. The deprotonation at the α-position predominates over that at the γ-position to give the α-substituted vinylic sulfoxides rather than the α-substituted allyl sulfoxides or γ-substituted vinylic sulfoxides. This methodology is very useful for the synthesis of substituted vinylic sulfoxides, which are highly selective in diverse reactions such as Diels–Alder reaction, Michael addition, and vinylogous Pummerer reaction.[3] The stereochemistry of the carbanions is especially noteworthy. α-Sulfinyl carbanions generated from (*Z*)-β-monosubstitued vinylic sulfoxides are configurationally unstable and rapidly isomerize to the thermodynamically more stable (*E*)-isomer even at lower than −78°C.[2] Therefore, vinylic sulfoxides used for intermolecular reactions have been usually non-substituted or β-monosubstitued vinylic sulfoxides, whose (*E*)-isomers are much more stable than the corresponding (*Z*)-isomer not to afford a mixture of geometric isomers.

In contrast to the intermolecular reaction, the intramolecular version has been paid little attention.[4] In our preceding communication,[5] we reported the intramolecular alkylation of α-sulfinyl carbanions generated from the β-(ω-haloalkyl)vinylic sulfoxides, which provides a method for synthesizing five- to seven-membered rings (Scheme 1).[5] In the case of intramolecular reaction, contamination of the geometric isomers by the *E*/*Z*-isomerization is not of consequence, since only one isomer can cyclize to the 1-cycloalkenyl sulfoxide. Neither selective preparation of the geometric isomers nor their separation is required. Furthermore, both geometric isomers of β,β-disubstituted vinylic sulfoxides can also be employed as substrates for the intramolecular alkylation.



Scheme 1.

Keywords: vinylic sulfoxides; cyclization; alkylation; carbanions.

* Corresponding author. Tel.: +81-6-6879-8210; fax: +81-6-6879-8214; e-mail: t-tanaka@phs.osaka-u.ac.jp

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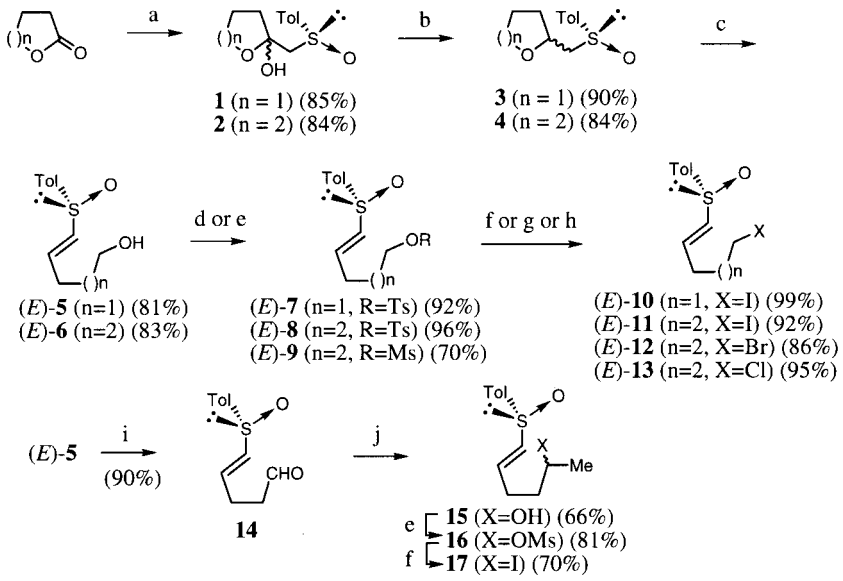
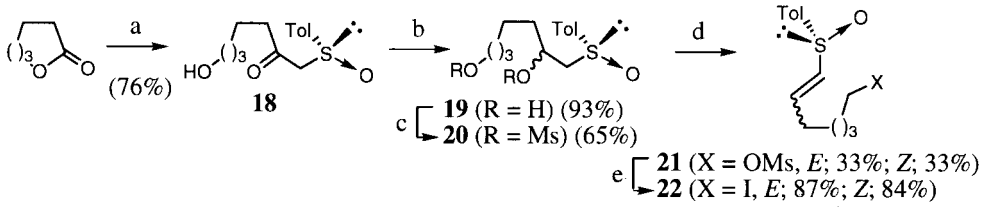
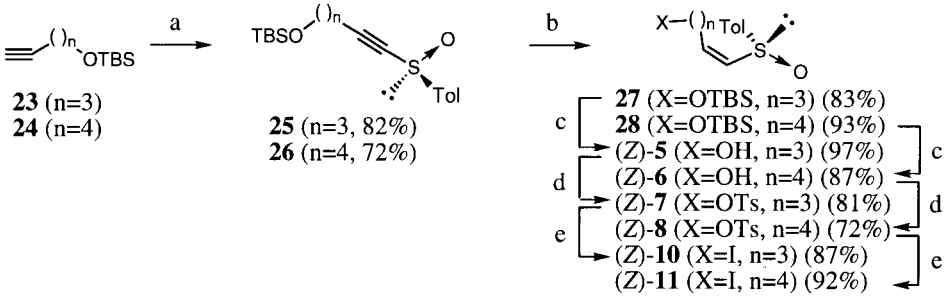


Scheme 2. *Reagents and conditions:* (a) LDA, (*R*)-methyl tolyl sulfoxide, THF, −78°C; (b) Et_3SiH, $BF_3{\cdot}OEt_2$, CH_2Cl_2, 0°C→rt; (c) LDA, THF, −78°C; (d) *p*-TsCl, Et_3N, DMAP, CH_2Cl_2, 0°C→rt; (e) MsCl, Et_3N, CH_2Cl_2, 0°C→rt; (f) NaI, $NaHCO_3$, acetone, reflux; (g) NaBr, $NaHCO_3$, acetone, reflux; (h) LiCl, acetone, reflux; (i) Dess–Martin periodinane, CH_2Cl_2, rt; (j) MeMgBr, THF, 0°C.



Scheme 3. *Reagents and conditions:* (a) LDA, (*R*)-methyl tolyl sulfoxide, THF, −78°C; (b) $NaBH_4$, MeOH, 0°C; (c) MsCl, Et_3N, CH_2Cl_2, 0°C→rt; (d) *t*-BuOK, THF, 0°C→rt; (e) NaI, $NaHCO_3$, acetone, reflux.



Scheme 4. *Reagents and conditions:* (a) EtMgBr, ether, 0°C→reflux then (*S*)-(−)-menthyl *p*-toluenesulfinate, toluene, 0°C; (b) H_2, $RhCl(PPh_3)_3$, benzene, rt; (c) HF·pyridine, THF–pyridine=1:1, rt; (d) *p*-TsCl, Et_3N, DMAP, CH_2Cl_2, 0°C→rt; (e) NaI, $NaHCO_3$, acetone, reflux.

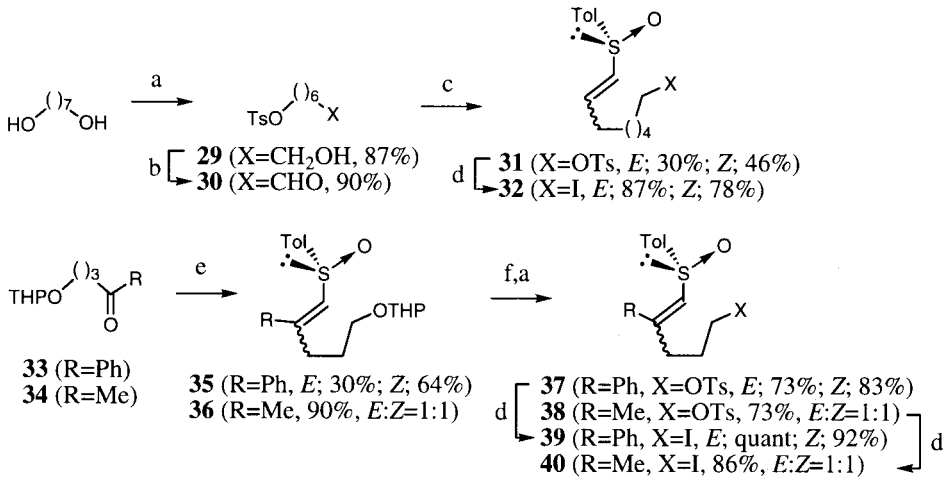
Here, we wish to report full details of the intramolecular alkylation of α-sulfinyl vinylic carbanions and the further application to more functionalized systems.

Results and Discussion

Preparation of β-(ω-haloalkyl)- and β-(ω-sulfonyloxyalkyl) vinylic sulfoxides

The β-(ω-haloalkyl)- and β-(ω-sulfonyloxyalkyl) vinylic sulfoxides were prepared by three methods: (1) base-promoted elimination of β-oxygenated sulfoxides; (2) reduction of alkynyl sulfoxides; and (3) Horner–Wittig reaction of (*R*)-dimethylphosphorylmethyl *p*-tolyl sulfoxide[6] with aldehydes (Schemes 2–5). (*E*)-Vinylic sulfoxides [(*E*)-**7**]–[(*E*)-**13**], the precursors of five- and six-membered ring vinylic sulfoxides, were synthesized by a series of reactions: condensation of lithiated methyl *p*-tolyl sulfoxide with lactones,[†] reduction to the cyclic ethers, and base-promoted β-elimination to give the (*E*)-vinylic sulfoxides exclusively. Then, the hydroxyl group was converted into

[†] Compounds **1** and **2** exist as a mixture of hemiacetal and ketol forms.



Scheme 5. *Reagents and conditions:* (a) *p*-TsCl, Et_3N, DMAP CH_2Cl_2, 0°C→rt; (b) Dess–Martin periodinane, CH_2Cl_2, rt; (c) *n*-BuLi, $(MeO)_2P(O)CH_2S^*(O)Tol$, THF, −78°C; (d) NaI, $NaHCO_3$, acetone, reflux; (e) *n*-BuLi, $(MeO)_2P(O)CH_2S^*(O)Tol$, THF, −78°C→rt; (f) *p*-TsOH·H_2O, MeOH, rt.

the sulfonates (OTs and OMs) or the halides (I, Br and Cl). Synthesis of the secondary iodide **17** was carried out by oxidation of (*E*)-**5** with Dess–Martin periodinane, methylation of the resulting aldehyde with MeMgBr, mesylation, and iodination. The substrate for seven-membered ring formation was prepared via condensation of (*R*)-methyl tolyl sulfoxide with ϵ-caprolactone. In this case, ketol **18** was obtained instead of the lactol, which was converted into bis-mesylate **20** followed by base-promoted β-elimination and iodination to give the vinylic sulfoxide **22** as a 1:1 mixture of the *E*/*Z*-isomers (Scheme 3).

(*Z*)-Vinylic sulfoxides (*Z*)-**10** and (*Z*)-**11** were selectively synthesized according to Kosugi's procedure[7] as shown in Scheme 4. 5-*tert*-Butyldimethylsilyloxy-1-pentynylmagnesium bromide[8] was coupled with (*S*)-(−)-menthyl *p*-toluenesulfinate and the resulting alkynyl sulfoxide **25** was reduced to **27** with Wilkinson's catalyst. Deprotection of TBS protection, tosylation, and iodination led **27** to the iodide (*Z*)-**10**. In a similar manner, **24**[9] was converted into (*Z*)-**11**.

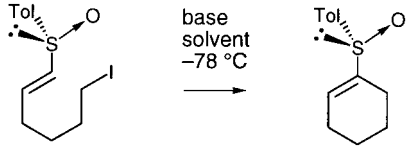
The Horner–Wittig approach affords another convenient method for synthesizing the substrates. Thus, vinylic sulfoxides **32**, **39** and **40** were synthesized from 1,7-heptanediol and known ketones **33** and **34**,[10] respectively, as shown in Scheme 5.

Intramolecular alkylation of β-(ω-haloalkyl)- and β-(ω-sulfonyloxyalkyl) vinylic sulfoxides

Using (*E*)-6-iodo-1-hexenyl *p*-tolyl sulfoxide (*E*)-**11**, we investigated the reaction conditions for cyclization (Table 1). Upon treatment with LDA (1.1–1.5 equiv.) in THF at −78°C, a solution of the vinylic sulfoxide (*E*)-**11** rapidly turned yellow and the reaction completed within 10 min to give 1-cyclohexenyl *p*-tolyl sulfoxide **41** in good yield (entries 1 and 2). Cyclization proceeded selectively at the α-sulfinyl position. On use of two equivalents of LDA, no cyclized product was obtained, and instead, a complex mixture was formed (entry 3). The addition of chelating agents (HMPA and TMEDA) slightly reduced the yields (entries 4 and 5). Other lithium dialkylamides (LICA and LTMP) also afforded the product in acceptable yields (entries 6 and 7). However, hexamethyldisilazides afforded a complex mixture (entries 8–10). Varying the solvent, excluding THF, did not improve the yield (entries 11–13).

Based on the optimized reaction conditions (Table 1, entry 2), the most suitable leaving groups were examined (Table 2, entries 1–5). The iodide and bromide provided the product in good yields. On the other hand, the tosylate, mesylate and chloride were poor leaving groups, causing sluggish reaction. Then, we examined cyclization of β-(ω-iodoalkyl) vinylic sulfoxides (*E*)-**10**, (*E*)-**22**, and (*E*)-**28** with different chain lengths (entries 6–8). Five- to seven-membered rings were formed in 79–82% yields. However, an eight-membered ring was not formed even under highly diluted conditions (0.001 M), yielding instead many unidentified products together with the dimer **49** (22%).[11] We next focused on the intramolecular alkylation of the (*Z*)-isomers.

Table 1. Intramolecular alkylation of vinylic sulfoxide (*E*)-**11** (the substrate was treated with 1.5 equiv. of the base at −78°C under N_2)

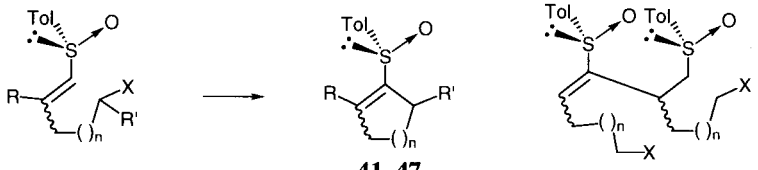


(*E*)-**11** **41**

Entry	Base (equiv.)	Additive	Solvent	Yield (%)[a]
1	LDA (1.1)	–	THF	76
2	LDA (1.5)	–	THF	82
3	LDA (2.0)	–	THF	Complex
4	LDA (1.5)	HMPA	THF	55
5	LDA (1.5)	TMEDA	THF	62
6	LICA (1.5)	–	THF	75
7	LTMP (1.5)	–	THF	65
8	LHMDA (1.5)	–	THF	Complex
9	NHMDS (1.5)	–	THF	Complex
10	KHMDS (1.5)	–	THF	Complex
11	LDA (1.5)	–	DME	39
12	LDA (1.5)	–	Ether	10
13	LDA (1.5)	–	Toluene	21

[a] Isolated yield.

Table 2. Cyclization of vinylic sulfoxides and the optical purities of the products (the substrate was treated with 1.5 equiv. of LDA in THF at −78°C under N_2)



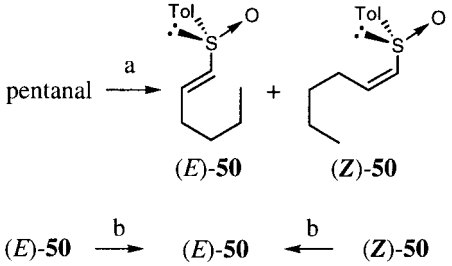
Entry	Substrate	R	R′	*n*	X	Product	Yield[a] (%)	$[\alpha]_D$[b]	ee[c] (%)
1	(*E*)-**9**	H	H	2	OMs	**41**	Complex		
2	(*E*)-**8**	H	H	2	OTs	**41**	24		
3	(*E*)-**11**	H	H	2	I	**41**	82	+9	98
4	(*E*)-**12**	H	H	2	Br	**41**	79		
5	(*E*)-**13**	H	H	2	Cl	**41**	0[d]		
6	(*E*)-**10**	H	H	1	I	**42**	81	+57	98
7	(*E*)-**22**	H	H	3	I	**43**	79	+10	
8	(*E*)-**28**	H	H	4	I	**44**	0[d]		
9	(*Z*)-**10**	H	H	1	I	**42**	66	+57	96
10	(*Z*)-**11**	H	H	2	I	**41**	71	+9	98
11	(*Z*)-**22**	H	H	3	I	**43**	64	+10	
12	(*E*)-**39**	Ph	H	1	I	**45**	44	−421	
13	(*Z*)-**39**	Ph	H	1	I	**45**	43	−411	
14	(*E*/*Z*)-**40**	Me	H	1	I	**46**	34	−155	
15	(*E*)-**17**	H	Me	1	I	**47**	46		

[a] Isolated yield.
[b] Measured in $CHCl_3$.
[c] Determined by chiral HPLC.
[d] (*E*)-**13** and (*E*)-**28** provided their dimers **48** and **49** in 30% and 22% yield, respectively.

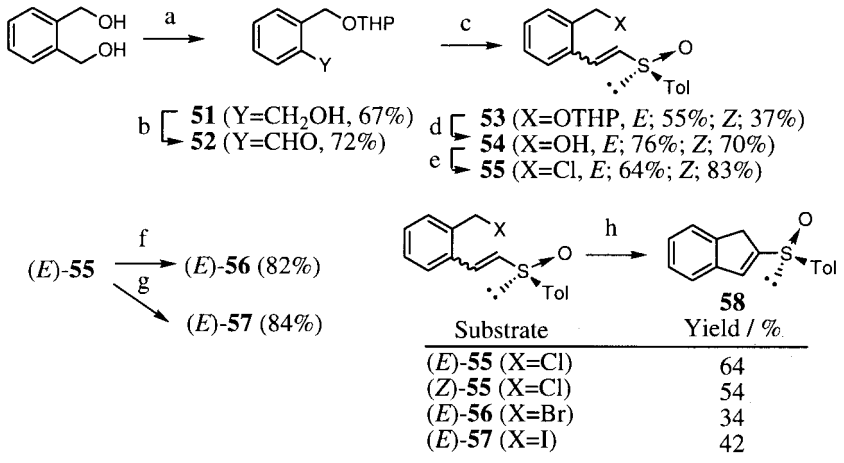
As expected, cyclization of (*Z*)-**10**, (*Z*)-**11**, (*Z*)-**22** provided cyclized products **42**, **41** and **43**, respectively, in moderate yields (64–71%) via isomerization of their olefin geometry (entries 9–11). β,β-Disubstituted vinylic sulfoxides are attractive substrates for the intramolecular alkylation since such substrates are rarely used for the intermolecular version due to the close energy-difference between the geometric isomers, which may afford a mixture of geometric isomers via rapid *E*/*Z*-isomerization in intermolecular alkylation. Both isomers of the β-phenyl vinylic sulfoxides (*E*)- and (*Z*)-**39** underwent α-lithiation and subsequent α-alkylation to give the cyclized product **45** in 44 and 43% yield, respectively (entries 12 and 13). Intramolecular alkylation of the β-methyl vinylic sulfoxide **40** (*E*/*Z*=1:1) provided the 2-methyl-1-cyclopentenyl sulfoxide **46** in 34% yield (entry 14). Alkylation proceeded even with the secondary iodide. Thus, the vinylic sulfoxide (*E*)-**17** cyclized to the product **47** in 46% yield (entry 15).

Posner reported that α-deprotonation of optically pure (*E*)-1-undecenyl *p*-tolyl sulfoxide followed by reprotonation produced no racemization, whereas similar treatment of the corresponding (*Z*)-isomer produced racemization (ca. 30% loss of optical purity).[12] In the intramolecular alkylation, the 1-cycloalkenyl sulfoxides from the (*Z*)-isomers have almost the same specific rotation as those from the corresponding (*E*)-isomers within experimental error (<3%). Furthermore, optical purity of the products **41** and **42** prepared from (*E*)- and (*Z*)-β-(ω-iodoalkyl) vinylic sulfoxides **11** and **10** was confirmed to be high (≥96% ee) by chiral HPLC (Daicel Chiralcel OB). Racemization did not occur during (*Z*)- to (*E*)-isomerization in the intramolecular alkylation of α-lithio vinylic sulfoxides.

In our communication,[5] we assumed that the isomerization and the alkylation would proceed concertedly rather than stepwise in the intramolecular alkylation in order to explain the difference in loss of optical purity between Posner's experiments and ours. An internal C–X bond may assist the isomerization of carbanions and this interaction would prevent racemization. To confirm this speculation, we examined whether racemization would occur by isomerization using the (*Z*)-vinylic sulfoxide [(*Z*)-**50**] having no leaving group on the β-substituent under the same reaction conditions as those of the intramolecular alkylation as shown in Scheme 6. Surprisingly, in both geometric isomers of **50**, no loss of optical purity was observed within experimental error (<3%) even in prolonged reaction time (after 60 min), although the (*Z*)-isomer was completely isomerized to the (*E*)-isomer. Although fears of racemization were dismissed, the previous speculation should be revised as a stepwise mechanism (isomerization followed by alkylation) cannot be ruled out in the intramolecular alkylation. Recemization observed in Posner's experiments may have



Scheme 6. *Reagents and conditions:* (a) *n*-BuLi, $(MeO)_2P(O)CH_2S^*(O)Tol$, THF, −78°C; (b) LDA, THF, −78°C then H_2O.

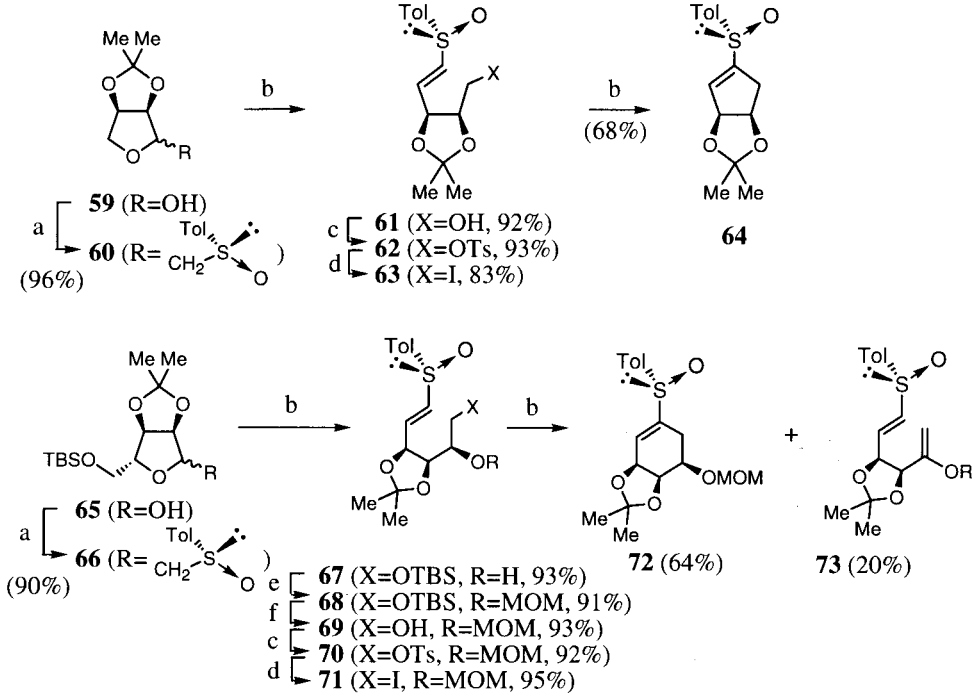


Scheme 7. *Reagents and conditions:* (a) DHP, PPTS, CH_2Cl_2, rt; (b) Dess–Martin periodinane, CH_2Cl_2, rt; (c) *n*-BuLi, $(MeO)_2P(O)CH_2S^*(O)Tol$, THF, −78°C; (d) *p*-TsOH·H_2O, MeOH, rt; (e) *p*-TsCl, Et_3N, DMAP, CH_2Cl_2, 0°C→rt; (f) NaBr, DMF/CH_2Br_2=2:1, 100°C; (g) NaI, $NaHCO_3$, acetone, rt; (h) LDA, THF, −78°C.

occurred under the different reaction conditions, which have not been reported in detail.

The newly developed intramolecular alkylation was applied to the synthesis of fused ring compounds. Ring closure between two substituents on the benzene ring in the chloride (*E*)- and (*Z*)-**55** afforded the indene derivative **58** in 64 and 54% yields, respectively. In the alkylation at the benzylic position, chloride is the better leaving group than iodide and bromide. The corresponding bromide (*E*)-**56** and the iodide (*E*)-**57** afforded **58** in poor yields, presumably due to instability of the substrates under the reaction conditions (Schemes 7 and 8).

Next, we examined the reaction with more functionalized substrates. We investigated the intramolecular alkylation of α-sulfinyl vinylic carbanions having a polyoxygenated β-substituent, which are of interest as a concise access to synthesis of cyclitol derivatives, which are attracting considerable attention by their potent glycosidase inhibitory activity. Vinylic sulfoxide **63** prepared from 2,3-*O*-isopropylidene-D-erythrose **59**[13] was treated with LDA to give the cyclitol derivetives **64** in 68% yield. In a similar manner, vinylic sulfoxide **71** prepared from 2,3-*O*-isopropylidene-D-ribose derivative **65**[14] was led to the cyclitol derivative **72** in 64% yield. In this case, elimination of HI took place to give the vinylic ether **73** in 20% yield.



Scheme 8. *Reagents and conditions:* (a) *n*-BuLi, $(MeO)_2P(O)CH_2S^*(O)Tol$, THF, −78°C→rt; (b) LDA, THF, −78°C; (c) *p*-TsCl, Et_3N, DMAP, CH_2Cl_2, 0°C→rt; (d) NaI, $NaHCO_3$, acetone, reflux; (e) MOMCl, *i*-$PrNEt_2$, CH_2Cl_2, rt; (f) HF·pyridine, THF–pyridine=1:1, rt.

Diastereomeric isomers arising from racemization on the sulfur atom were not detected at all.

Conclusion

In conclusion, we have developed a novel method for the synthesis of 1-cycloalkenyl sulfoxides by intramolecular alkylation of β-(ω-haloalkyl)vinylic sulfoxides. This methodology provides a concise access to the substituted 1-cycloalkenyl sulfoxides having five- to seven-membered ring, including polyoxygenated rings.

Experimental

Melting points are uncorrected. Optical rotations were measured using a JASCO DIP-360 digital polarimeter. IR spectra were measured with a Horiba FT-210 IR spectrometer. ^{1}H NMR spectra were measured with a JEOL JNM-GX500 spectrometer (500 MHz) or a JEOL JNM-LA-500 spectrometer (500 MHz) in $CDCl_3$ solution. ^{13}C NMR spectra were measured with a JEOL JNM-EX270 spectrometer (68 MHz) or a JEOL JNM-AL300 spectrometer (75 MHz) in $CDCl_3$ solution. All signals are expressed as ppm downfield from tetramethylsilane used as an internal standard (δ value). The following abbreviations are used: singlet (s), doublet (d), triplet (t), quartet (q), and multiplet (m). Mass spectra were taken with a Shimadzu QP-1000 mass spectrometer and a JEOL JMS-D300 mass spectrometer. High resolution mass spectra were measured by a JEOL JMS-D300 or a JEOL JMS-600. Merck Kieselgel 60 was used as an adsorbent for column chromatography. For preparative TLC (PTLC), Kieselgel 60 F_{254} (Merck) was used. Unless stated, all solvents were used after dryness and all extracts were dried over $MgSO_4$.

2-[(*R*)-(*p*-Tolylsulfinyl)methyl]tetrahydro-2-furanol (1). A solution of (*R*)-methyl *p*-tolyl sulfoxide (500 mg, 3.24 mmol) in THF (5 ml) was added to a stirred LDA solution [prepared from *n*-BuLi (1.60 M in hexane, 3.0 ml, 4.80 mmol) and *i*-Pr_2NH (0.68 ml, 4.85 mmol) in THF (20 ml)] at −78°C under N_2 and the mixture was stirred at 0°C for 20 min. A solution of γ-butyrolactone (0.27 ml, 3.51 mmol) in THF (5 ml) was added to the stirred mixture at −78°C and stirring was continued at the same temperature for 20 min. The reaction was quenched with saturated NH_4Cl aqueous solution and the whole was extracted with AcOEt. The extract was washed with water and brine prior to drying and solvent evaporation. The residue was chromatographed on silica gel with hexane–AcOEt (1:1) to give **1** (major (a)/minor (b)/ketosulfoxide (c)=ca. 4:1:2, 661 mg, 85%) as a colorless oil along with (*R*)-methyl *p*-tolyl sulfoxide (75 mg, 15%). IR (KBr) cm^{-1}: 3395, 2926, 1713, 1495, 1400, 1086, 1049, 1014. ^{1}H NMR δ: 1.72–1.85 (8/7H, m, 4-Ha), 1.89–2.03 (4/7H, m, 3- and 4-Hb), 2.05–2.25 (12/7H, m, 4-Hc and 3-Ha), 2.42 (3H, s, Ar-CH_3), 2.51–2.71 (4/7H, m, 3-Hc), 2.89 (4/7H, d, *J*=12.8 Hz, S(O)CHa), 3.12 (1/7H, d, *J*=13.4 Hz, S(O)CHb), 3.25 (4/7H, d, *J*=12.8 Hz, S(O)CHa), 3.27 (1/7H, d, *J*=13.4 Hz, S(O)CHb), 3.59 (4/7H, t, *J*=5.5 Hz, 5-Hc), 3.82 (2/7H, d, *J*=14.0 Hz, S(O)CHc), 3.90 (2/7H, d, *J*=14.0 Hz, S(O)CHc), 3.89–4.00 (1/7H, m, 5-Hb), 4.04 (4/7H, td, *J*=8.5, 6.1 Hz, 5-Ha), 4.06–4.14 (1/7H, m, 5-Hb), 4.04 (4/7H, td, *J*=8.5, 6.1 Hz, 5-Ha), 4.36 (1/7H, s, OHb), 5.43 (4/7H, s, OHa), 7.32 (2/7H, d, *J*=8.5 Hz, Ar-Hb), 7.34 (12/7H, d, *J*=8.5 Hz, Ar-Ha and Ar-Hc), 7.53 (4/7H, d, *J*=7.9 Hz, Ar-Hc), 7.56 (2/7H, d, *J*=8.5 Hz, Ar-Hb), 7.57 (8/7H, d, *J*=7.9 Hz, Ar-Ha). ^{13}C NMR (major) δ: 21.3, 24.4, 38.6, 63.8, 67.9, 104.5, 124.0 (2C), 130.0 (2C), 140.3, 142.0. MS (EI) *m/z* (rel. int. %): 240 (M$^+$, 4.1), 139 (100). HRMS (EI) Calcd $C_{12}H_{16}O_3S$: 240.0820. Found: 240.0812.

2-[(*R*)-(*p*-Tolylsulfinyl)methyl]tetrahydro-2*H*-pyran-2-ol (2). Using the procedure for **1**, δ-valerolactone (2.0 ml, 22 mmol) was converted into the hemiacetal **2** (major (a)/minor (b)/ketosulfoxide (c)=ca. 10:3:2, 5.89 g, 84%). A yellow oil: IR (KBr) cm^{-1}: 3350, 2943, 1713, 1597, 1215, 1086, 1043, 1024, 1012. ^{1}H NMR δ: 1.41 (2/3H, ddt, *J*=12.8, 4.3, 2.4 Hz, 4-Ha), 1.50–1.70 (53/15H, m, 3-Ha–b, 4-Ha–c, and 5-Ha–c), 1.77 (2/3H, br d, *J*=12.2 Hz, 5-Ha), 1.91 (1/5H, tt, *J*=12.9, 4.0 Hz, 3-Hb), 1.91–1.96 (2/3H, m, 3-Ha), 2.42 (3H, s, Ar-H), 2.51 (2/15H, dt, *J*=18.3, 6.7 Hz, 3-Hc), 2.60 (2/15H, dt, *J*=18.3, 6.7 Hz, 3-Hc), 2.78 (2/3H, d, *J*=12.8 Hz, S(O)CHa), 3.86 (2/15H, d, *J*=13.4 Hz, S(O)CHc), 2.99 (1/5H, d, *J*=13.4 Hz, S(O)CHb), 3.03 (2/3H, d, *J*=12.8 Hz, S(O)CHa), 3.03 (1/5H, d, *J*=13.4 Hz, S(O)CHb), 3.58–3.68 (1/5H, m, 6-Hb), 3.74 (2/15H, d, *J*=13.4 Hz, S(O)CHc), 3.80–3.84 (2/3H, m, 6-Ha), 4.12 (1/5H, q, 6-Hb), 4.00 (4/15H, td, *J*=11.6, 3.1 Hz, 6-Hc), 4.18 (2/3H, td, *J*=11.6, 3.1 Hz, 6-Ha), 7.32 (2/5H, d, *J*=7.9 Hz, Ar-Hb), 7.34 (8/5H, d, *J*=7.9 Hz, Ar-Ha,c), 7.53 (4/15H, d, *J*=7.9 Hz, Ar-Hc), 7.56 (4/3H, d, *J*=7.9 Hz, Ar-Ha), 7.55 (2/5H, d, *J*=7.9 Hz, Ar-Hb). ^{13}C NMR δ: (major); 17.9, 21.4, 25.1, 35.7, 61.5, 64.5, 95.8, 124.0 (2C), 130.1 (2C), 140.2, 142.0. MS (EI) *m/z* (rel. int. %): 254 (M$^+$, 18.2), 139 (100). HRMS (EI) Calcd $C_{13}H_{18}O_3S$: 254.0976. Found: 254.0976.

2-[(*R*)-(*p*-Tolylsulfinyl)methyl]tetrahydrofuran (3). $BF_3{\cdot}OEt_2$ (0.92 ml, 7.48 mmol) was added to a mixture of **1** (596 mg, 2.48 mmol) and Et_3SiH (0.80 ml, 4.97 mmol) in CH_2Cl_2 (25 ml) with stirring at 0°C. The stirring was continued for 16 h at rt. The reaction was quenched with saturated NH_4Cl aqueous solution and the whole was extracted with AcOEt. The extract was washed with water and brine prior to drying and solvent evaporation. The residue was chromatographed on silica gel with hexane–AcOEt (1:1) to give **3** (503 mg, 90%, 2:1 diastereomeric mixture) as a colorless oil. IR (KBr) cm^{-1}: 2924, 1086, 1045. ^{1}H NMR δ: 1.46–1.54 (2/3H, m, 3-H), 1.63–1.75 (1/3H, m, 3-H), 1.78–1.98 (2H, m, 4-H and 3-H), 1.78–2.43 (1H, m, 4-H and 3-H), 2.33 (3H, s, Ar-CH_3), 2.74 (2/3H, dd, *J*=12.8, 9.2 Hz, S(O)CH), 2.79 (1/3H, dd, *J*=12.8, 5.5 Hz, S(O)CH), 2.88 (2/3H, dd, *J*=12.8, 3.7 Hz, S(O)CH), 3.13 (1/3H, dd, *J*=12.8, 5.5 Hz, S(O)CH), 3.65–3.69 (1/3H, m, 2-H), 3.73–3.84 (2/3H, m, 5-H), 3.84–3.89 (4/3H, m, 5-H), 4.28–4.33 (2/3H, m, 2-H), 7.25 (4/3H, d, *J*=7.9 Hz, Ar-H), 7.26 (2/3H, d, *J*=7.9 Hz, Ar-H), 7.47 (4/3H, d, *J*=7.9 Hz, Ar-H), 7.50 (2/3H, d, *J*=7.9 Hz, Ar-H). ^{13}C NMR (major) δ: 21.3, 25.6, 31.4, 64.3, 68.1, 72.8, 123.7 (2C), 129.8 (2C), 141.3 (2C). (minor) δ: 21.3, 25.5, 31.2, 62.8, 68.2, 73.7, 124.2 (2C), 130.0 (2C), 140.3, 141.5. MS (EI) *m/z* (rel. int. %): 224 (M$^+$, 7.3), 85 (100). HRMS (EI) Calcd $C_{12}H_{16}O_2S$: 224.0871. Found: 224.0864.

2-[(*R*)-(*p*-Tolylsulfinyl)methyl]tetrahydro-2*H*-pyran (4). Using the procedure for **3**, the hemiacetal **2** (3.21 g, 12.6 mmol) was converted into the cyclic ether **4** (2.53 g, 84%). The diastereomeric mixture was used in the next step without further purification. Analytical samples were purified by column chromatography hexane–AcOEt (1:2) to give **4a** (less polar) and **4b** (more polar) each as a colorless oil. **4a**: $[\alpha]_D^{26}=+236$ (*c* 1.23, $CHCl_3$). IR (KBr) cm^{-1}: 2937, 1090, 1045. ^1H NMR δ: 1.31–1.38 (1H, m, 3-H), 1.57–1.61 (4H, m, 3-H, 4-H and, 5-H), 1.85–1.88 (1H, m, 5-H), 2.41 (3H, s, Ar-CH_3), 2.73 (1H, dd, *J*=13.4, 10.4 Hz, S(O)CH_2), 2.79 (1H, dd, *J*=13.4, 2.4 Hz, S(O)CH_2), 3.56–3.61 (1H, m, 6-H), 3.91–3.96 (1H, m, 2-H), 4.06 (1H, ddd, *J*=11.6, 2.4, 1.8 Hz, 6-H), 7.32 (2H, d, *J*=7.9 Hz, Ar-H), 7.54 (2H, d, *J*=7.9 Hz, Ar-H). ^{13}C NMR δ: 21.1, 21.1, 23.0, 31.3, 65.1, 68.3, 71.1, 123.5 (2C), 129.7 (2C), 141.1 (2C). MS (EI) *m/z* (rel. int. %): 238 (M^+, 19.7), 99 (100). HRMS (EI) Calcd $C_{13}H_{18}O_2S$: 238.1027. Found: 238.1029. **4b**: $[\alpha]_D^{26}=+79.0$ (*c* 0.84, $CHCl_3$). IR (KBr) cm^{-1}: 2935, 2850, 1495, 1086, 1043. ^1H NMR δ: 1.41–1.52 (3H, m, 3-H and 4-H), 1.54–1.64 (1H, m, 5-H), 1.66–1.70 (1H, m, 5-H), 1.81–1.85 (1H, m, 3-H), 2.42 (3H, s, Ar-CH_3), 2.71 (1H, dd, *J*=12.8, 4.9 Hz, S(O)CH_2), 3.22 (1H, dd, *J*=12.8, 7.3 Hz, S(O)CH_2), 3.33 (1H, dt, *J*=11.6, 2.4 Hz, 6-H), 3.37–3.42 (1H, m, 2-H), 3.95 (1H, ddt, *J*=11.6, 4.9, 1.8 Hz, 6-H), 7.33 (2H, d, *J*=7.9 Hz, Ar-H), 7.56 (2H, d, *J*=7.9 Hz, Ar-H). ^{13}C NMR δ: 21.1, 22.6, 25.1, 30.8, 63.4, 68.0, 72.5, 124.1 (2C), 129.6 (2C), 140.0, 141.3. MS (EI) *m/z* (rel. int. %): 238 (M^+, 15.7), 99 (100). HRMS (EI) Calcd $C_{13}H_{18}O_2S$: 238.1027. Found: 238.1029.

(*E*)-5-[(*R*)-(*p*-Tolylsulfinyl)]-4-penten-1-ol [(*E*)-5]. A solution of **3** (474 mg, 2.11 mmol) in THF (5 ml) was added to a stirred LDA solution [prepared from *n*-BuLi (1.60 M in hexane, 3.83 ml, 6.13 mmol) and *i*-Pr_2NH (0.89 ml, 6.35 mmol) in THF (25 ml)] at −78°C under N_2 and the mixture was stirred at this temperature for 30 min. The reaction was quenched with saturated NH_4Cl aqueous solution and the whole was extracted with AcOEt. The extract was washed with water and brine prior to drying and solvent evaporation. The residue was chromatographed on silica gel with AcOEt to give (*E*)-**5** (384 mg, 81%) as a colorless oil. $[\alpha]_D^{27}=+114.5$ (*c* 0.11, $CHCl_3$). IR (KBr) cm^{-1}: 3375, 2931, 1038. ^1H NMR δ: 1.67–1.73 (2H, m, 2-H), 2.30–2.34 (2H, m, 3-H), 2.40 (3H, s, Ar-CH_3), 2.87 (1H, br, OH), 3.61 (2H, t, *J*=6.7 Hz, 1-H), 6.24 (1H, d, *J*=15.3 Hz, 5-H), 6.60 (1H, dt, *J*=15.3, 6.7 Hz, 4-H), 7.30 (2H, d, *J*=8.5 Hz, Ar-H), 7.48 (2H, d, *J*=8.5 Hz, Ar-H). ^{13}C NMR δ: 21.4, 28.4, 30.8, 61.5, 124.6 (2C), 130.0 (2C), 135.1, 140.3, 140.5, 141.5. MS (EI) *m/z* (rel. int. %): 224 (M^+, 62.8), 92 (100). HRMS (EI) Calcd $C_{12}H_{16}O_2S$: 224.0871. Found: 224.0882.

(*E*)-6-[(*R*)-(*p*-Tolylsulfinyl)]-5-hexen-1-ol [(*E*)-6]. Using the procedure for (*E*)-**5**, the cyclic ether **4** (3.40 g, 14.3 mmol) was converted into (*E*)-**6** (2.82 g, 83%). A colorless oil: $[\alpha]_D^{28}=+98.2$ (*c* 1.40, $CHCl_3$). IR (KBr) cm^{-1}: 3402, 2866, 1493, 1084, 1041, 1014. ^1H NMR δ: 1.55–1.57 (4H, m, 2-H and 3-H), 2.26 (2H, q, *J*=6.7 Hz, 4-H), 2.41 (3H, s, Ar-CH_3), 3.64 (2H, t, *J*=6.1 Hz, 1-H), 6.22 (1H, d, *J*=15.3 Hz, 6-H), 6.59 (1H, dt, *J*=15.3, 6.7 Hz, 5-H), 7.31 (2H, d, *J*=7.9 Hz, Ar-H), 7.50 (2H, d, *J*=7.9 Hz, Ar-H). ^{13}C NMR δ: 21.2, 24.2, 31.5, 31.8, 61.8, 124.4 (2C), 129.9 (2C), 134.8, 140.5, 140.7, 141.3. MS (EI) *m/z* (rel. int. %): 238 (M^+, 50.6), 131 (100). HRMS (EI) Calcd $C_{13}H_{18}O_2S$: 238.1027. Found: 238.1036.

(*E*)-5-[(*R*)-(*p*-Tolylsulfinyl)]-4-pentenyl *p*-toluenesulfonate [(*E*)-7]. *p*-TsCl (288 mg, 1.51 mmol) was added to a mixture of (*E*)-**5** (282 mg, 1.26 mmol), Et_3N (0.21 ml, 1.51 mmol), and DMAP (31 mg, 0.25 mmol) in CH_2Cl_2 (10 ml) with stirring at 0°C. The stirring was continued at rt for 3.5 h. The reaction was quenched with saturated NH_4Cl aqueous solution and the whole was extracted with AcOEt. The extract was washed with water and brine prior to drying and solvent evaporation. The residue was chromatographed on silica gel with hexane–AcOEt (1:1) to give (*E*)-**7** (438 mg, 92%) as colorless oil. $[\alpha]_D^{28}=+107.7$ (*c* 0.72, $CHCl_3$). IR (KBr) cm^{-1}: 2924, 1597, 1358, 1176, 1045. ^1H NMR δ: 1.78–1.84 (2H, m, 2-H), 2.32 (2H, q, *J*=6.7 Hz, 3-H), 2.41 (3H, s, Ar-CH_3), 2.49 (3H, s, Ar-CH_3), 4.03 (2H, t, *J*=6.1 Hz, 1-H), 6.17 (1H, d, *J*=15.3 Hz, 5-H), 6.47 (1H, dt, *J*=15.3, 6.7 Hz, 4-H), 7.31 (2H, d, *J*=7.9 Hz, Ar-H), 7.34 (2H, d, *J*=7.9 Hz, Ar-H), 7.47 (2H, d, *J*=7.9 Hz, Ar-H), 7.76 (2H, d, *J*=7.9 Hz, Ar-H). ^{13}C NMR δ: 21.3, 21.6, 27.4, 27.7, 69.1, 124.6 (2C), 127.8 (2C), 129.9 (2C), 130.0 (2C), 132.8, 136.2, 137.3, 140.5, 141.6, 144.9. MS (EI) *m/z* (rel. int. %): 378 (M^+, 11.0), 158 (100). HRMS (EI) Calcd $C_{19}H_{22}O_4S_2$: 378.0958. Found: 378.0957.

(*E*)-6-[(*R*)-(*p*-Tolylsulfinyl)]-5-hexenyl *p*-toluenesulfonate [(*E*)-8]. Using the procedure for (*E*)-**7**, the alcohol (*E*)-**6** (600 mg, 2.52 mmol) was converted into (*E*)-**8** (0.95 g, 96%). Colorless oil: $[\alpha]_D^{28}=+85.4$ (*c* 1.14, $CHCl_3$). IR (KBr) cm^{-1}: 2926, 1597, 1358, 1176, 1097, 1083, 1043, 1016. ^1H NMR δ: 1.34–1.46 (2H, m, 3-H), 1.56–1.61 (2H, m, 2-H), 2.12 (2H, dq, *J*=6.7, 1.2 Hz, 4-H), 2.33 (3H, s, SO_2CH_3), 2.37 (3H, s, Ar-CH_3), 3.94 (2H, t, *J*=6.1 Hz, 1-H), 6.11 (1H, dt, *J*=15.3, 1.2 Hz, 6-H), 6.43 (1H, dt, *J*=15.3, 6.7 Hz, 5-H), 7.24 (2H, d, *J*=7.9 Hz, Ar-H), 7.26 (2H, d, *J*=7.9 Hz, Ar-H), 7.41 (2H, d, *J*=7.9 Hz, Ar-H), 7.70 (2H, d, *J*=7.9 Hz, Ar-H). ^{13}C NMR δ: 21.4, 21.6, 24.0, 28.1, 31.1, 69.9, 124.5 (2C), 127.8 (2C), 129.8 (2C), 130.0 (2C), 132.9, 135.7, 139.0, 140.7, 141.5, 144.8. MS (EI) *m/z* (rel. int. %): 392 (M^+, 4.8), 91 (100). HRMS (EI) Calcd $C_{20}H_{24}O_4S_2$: 392.1116. Found: 392.1116 (M^+).

(*E*)-6-[(*R*)-(*p*-Tolylsulfinyl)]-5-hexenyl methanesulfonate [(*E*)-9]. MsCl (40 μl, 0.52 mmol) was added to a mixture of (*E*)-**6** (100 mg, 0.42 mmol) and Et_3N (76 μl, 0.51 mmol) in CH_2Cl_2 (3 ml) with stirring at 0°C. The stirring was continued at rt for 20 min. The reaction was quenched with saturated NH_4Cl aqueous solution and the whole was extracted with AcOEt. The extract was washed with water and brine prior to drying and solvent evaporation. The residue was chromatographed on silica gel with hexane–AcOEt (1:1) to give (*E*)-**9** (93.0 mg, 70%) as colorless powder. Mp 52.7–53.4°C (ether). $[\alpha]_D^{28}=+99.8$ (*c* 0.81, $CHCl_3$). IR (KBr) cm^{-1}: 2935, 1493, 1352, 1174. ^1H NMR δ: 1.58–1.64 (2H, m, 3-H), 1.75–1.80 (2H, m, 2-H), 2.29 (2H, q, *J*=7.3 Hz, 4-H), 2.41 (3H, s, Ar-CH_3), 3.00 (3H, s, SO_2CH_3), 4.22 (2H, t, *J*=6.7 Hz, 1-H), 6.24 (1H, dt, *J*=15.3, 1.2 Hz, 6-H), 6.55 (1H, dt, *J*=15.3, 6.7 Hz, 5-H), 7.32 (2H, d, *J*=7.9 Hz, Ar-H), 7.50 (2H, d, *J*=7.9 Hz, Ar-H). ^{13}C NMR δ: 21.5, 24.1, 28.6, 31.2, 37.4, 69.3, 124.5

(2C), 130.0 (2C), 135.7, 138.7, 140.6, 141.4. MS (EI) *m/z* (rel. int. %): 316 (M^+, 8.8), 268 (100). HRMS (EI) Calcd $C_{14}H_{20}O_4S_2$: 316.0803. Found: 316.0829.

(*E*)-(*R*)-5-Iodo-1-pentenyl *p*-tolyl sulfoxide [(*E*)-10]. A mixture of (*E*)-**7** (380 mg, 1.00 mmol), $NaHCO_3$ (480 mg, 5.71 mmol), and NaI (300 mg, 2.00 mmol) in acetone (10 ml) was refluxed for 5 h. The reaction was quenched with water and the whole was extracted with AcOEt. The extract was washed with saturated $Na_2S_2O_3$ aqueous solution, saturated $NaHCO_3$ aqueous solution, and brine prior to drying and solvent evaporation. The residue was chromatographed on silica gel with hexane–AcOEt (2:1) to give (*E*)-**10** (331 mg, 99%) as yellow oil. $[\alpha]_D^{28}=+107.4$ (*c* 0.91, $CHCl_3$). IR (KBr) cm^{-1}: 2931, 1597, 1493, 1084, 1043. ^1H NMR δ: 1.95–2.00 (2H, m, 4-H), 2.36 (2H, dt, *J*=6.7, 1.2 Hz, 3-H), 2.41 (3H, s, Ar-CH_3), 3.18 (2H, t, *J*=6.7 Hz, 5-H), 6.29 (1H, d, *J*=15.3 Hz, 1-H), 6.53 (1H, dt, *J*=15.3, 6.7 Hz, 2-H), 7.32 (2H, d, *J*=7.9 Hz, Ar-H), 7.50 (2H, d, *J*=7.9 Hz, Ar-H). ^{13}C NMR δ: 5.3, 21.3, 31.3, 32.4, 124.5 (2C), 130.0 (2C), 136.2, 137.2, 140.6, 141.5. MS (EI) *m/z* (rel. int. %): 334 (M^+, 15.9), 286 (100), 131 (100). HRMS (EI) Calcd $C_{12}H_{15}IOS$: 333.9886. Found: 333.9901.

(*E*)-(*R*)-6-Iodo-1-hexenyl *p*-tolyl sulfoxide [(*E*)-11]. Using the procedure for (*E*)-**10**, the tosylate (*E*)-**8** (30 mg, 0.076 mmol) was converted into (*E*)-**11** (24 mg, 92%). Pale yellow powder: mp 42.3–43.2°C (ether). $[\alpha]_D^{29}=+81.4$ (*c* 1.07, $CHCl_3$). IR (KBr) cm^{-1}: 2926, 1493, 1217, 1084, 1043. ^1H NMR δ: 1.59 (2H, quint, *J*=7.3 Hz, 3-H), 1.83 (2H, quint, *J*=7.3 Hz, 5-H), 2.26 (2H, q, *J*=6.7 Hz, 3-H), 2.41 (3H, s, Ar-CH_3), 3.17 (2H, t, *J*=7.3 Hz, 6-H), 6.24 (1H, d, *J*=15.3 Hz, 1-H), 6.58 (1H, dt, *J*=6.7, 15.3 Hz, 2-H), 7.32 (2H, d, *J*=7.9 Hz, Ar-H), 7.50 (2H, d, *J*=7.9 Hz, Ar-H). ^{13}C NMR δ: 6.1, 21.3, 28.8, 30.7, 32.5, 124.3 (2C), 129.7 (2C), 135.4, 138.9, 140.5, 141.1. MS (EI) *m/z* (rel. int. %): 348 (M^+, 8.9), 300 (100). HRMS (EI) Calcd $C_{13}H_{17}IOS$: 349.0045. Found: 348.0033.

(*E*)-(*R*)-6-Bromo-1-hexenyl *p*-tolyl sulfoxide [(*E*)-12]. A mixture of (*E*)-**8** (300 mg, 0.76 mmol), $NaHCO_3$ (260 mg, 3.10 mmol), and NaBr (160 mg, 1.56 mmol) in acetone (8 ml) was refluxed for 29 h. The reaction was quenched with water and the whole was extracted with AcOEt. The extract was washed with saturated $Na_2S_2O_3$ aqueous solution, saturated $NaHCO_3$ aqueous solution, and brine prior to drying and solvent evaporation. The residue was chromatographed on silica gel with hexane–AcOEt (2:1) to give (*E*)-**12** (198 mg, 86%) as a colorless oil. $[\alpha]_D^{29}=+103.4$ (*c* 1.07, $CHCl_3$). IR (KBr) cm^{-1}: 2935, 1628, 1597, 1244, 1084, 1045, 1016. ^1H NMR δ: 1.62 (2H, quint, *J*=7.3 Hz, 4-H), 1.88 (2H, m, 5-H), 2.27 (2H, dq, *J*=7.3, 1.2 Hz, 3-H), 2.41 (3H, s, Ar-CH_3), 3.40 (2H, t, *J*=6.7 Hz, 6-H), 6.24 (1H, dt, *J*=15.3, 1.2 Hz, 1-H), 6.56 (1H, dt, *J*=15.3, 6.7 Hz, 2-H), 7.32 (2H, d, *J*=7.9 Hz, Ar-H), 7.50 (2H, d, *J*=7.9 Hz, Ar-H). ^{13}C NMR δ: 21.1, 26.3, 30.7, 31.6, 33.0, 124.3 (2C) 129.8 (2C), 135.4, 139.0, 140.6, 141.1. MS (EI) *m/z* (rel. int. %): 300 (M^+, 9.0), 131 (100). HRMS (EI) Calcd $C_{13}H_{17}BrOS$: 300.0183. Found: 300.0164.

(*E*)-(*R*)-6-Chloro-1-hexenyl *p*-tolyl sulfoxide [(*E*)-13]. A mixture of (*E*)-**8** (99 mg, 0.25 mmol) and LiCl (13 mg, 0.30 mmol) in acetone (2.5 ml) was refluxed for 3 h. The reaction was quenched with water and the whole was extracted with AcOEt. The extract was washed with water and brine prior to drying and solvent evaporation. The residue was chromatographed on silica gel with hexane–AcOEt (1:1) to give (*E*)-**13** (62 mg, 95%) as a colorless oil. $[\alpha]_D^{25}=+104.0$ (*c* 0.77, $CHCl_3$). IR (KBr) cm^{-1}: 2924, 1493, 1084, 1045. ^1H NMR δ: 1.60–1.66 (2H, m, 4-H), 1.76–1.82 (2H, m, 5-H), 2.26 (2H, dq, *J*=6.7, 1.2 Hz, 3-H), 2.41 (3H, s, Ar-CH_3), 3.52 (2H, t, *J*=6.7 Hz, 6-H), 6.24 (1H, dt, *J*=15.3, 1.2 Hz, 1-H), 6.57 (1H, dt, *J*=15.3, 6.7 Hz, 2-H), 7.31 (2H, d, *J*=7.9 Hz, Ar-H), 7.50 (2H, d, *J*=7.9 Hz, Ar-H). ^{13}C NMR δ: 21.4, 25.3, 31.1, 31.7, 44.5, 124.53 (2C) 130.0 (2C), 135.6, 139.3, 140.8, 141.4. MS (EI) *m/z* (rel. int. %): 256 (M^+, 10.8), 131 (100). HRMS (EI) Calcd $C_{13}H_{17}ClOS$: 256.0689. Found: 256.0678.

(*E*)-5-[(*R*)-(*p*-Tolylsulfinyl)]-4-pentenal (14). Dess–Martin periodinane (427 mg, 1.00 mmol) was added to a solution of the alcohol (*E*)-**5** (200 mg, 0.84 mmol) in CH_2Cl_2 (8 ml) with stirring at 0°C and the stirring was continued at rt for 15 min. Then, AcOEt, saturated $Na_2S_2O_3$ aqueous solution, and saturated $NaHCO_3$ aqueous solution were added to the mixture and the whole was stirred for 15 min. The organic layer was separated and washed with water and brine prior to drying and solvent evaporation. The residue was chromatographed on silica gel with hexane–AcOEt (1:2) to give **14** (151 mg, 76%) as a colorless oil. $[\alpha]_D^{27}=+187.8$ (*c* 0.15, $CHCl_3$). IR (KBr) cm^{-1}: 1720, 1600, 1084. ^1H NMR δ: 2.33 (3H, s, Ar-CH_3), 2.45–2.49 (2H, m, 3-H), 2.57 (2H, t, *J*=7.0 Hz, 2-H), 6.18 (1H, dd, *J*=15.3, 1.2 Hz, 5-H), 6.49 (1H, dt, *J*=15.3, 6.7 Hz, 4-H), 7.23 (2H, d, *J*=7.9 Hz, Ar-H), 7.40 (2H, d, *J*=7.9 Hz, Ar-H), 9.69 (1H, s, CHO). ^{13}C NMR δ: 21.4, 24.2, 41.9, 124.4 (2C), 129.9 (2C), 135.9, 137.2, 140.3, 141.4, 199.8. MS (EI) *m/z* (rel. int. %): 222 (M^+, 11.6), 174 (100). HRMS (EI) Calcd $C_{12}H_{14}O_2S$: 222.0714. Found: 222.0715.

(*E*)-6-[(*R*)-(*p*-Tolylsulfinyl)]-5-hexen-2-ol (15). MeMgBr (0.86 M in ether, 0.86 ml, 0.74 mmol) was added to a solution of the aldehyde **14** (150 mg, 0.68 mmol) in THF (6 ml) with stirring at 15 min. The reaction was quenched with saturated NH_4Cl aqueous solution and the whole was extracted with AcOEt. The extract was washed with water and brine prior to drying and solvent evaporation. The residue was chromatographed on silica gel with hexane–AcOEt (1:2) to give **15** (1:1 diastereomeric mixture, 105 mg, 66%) as a pale yellow oil. IR (KBr) cm^{-1}: 3425, 3924, 1084, 1041, 1014. ^1H NMR δ: 1.00–1.12 (3H, m, 1-H), 1.47–1.52 (2H, m, 3-H), 2.07–2.63 (2H, m, 4-H), 2.41 (3H, s, Ar-CH_3), 3.69–3.76 (1H, m, 2-H), 6.13–6.20 (1H, m, 6-H), 6.47–6.56 (1H, m, 5-H), 7.23 (2H, d, *J*=7.9 Hz, Ar-H), 7.41 (2H, d, *J*=7.9 Hz, Ar-H). ^{13}C NMR δ: 21.4, 23.6, 28.3, 37.2, 66.9, 124.5 (2C), 130.0 (2C), 135.0, 140.4, 140.5, 141.4. MS (EI) *m/z* (rel. int. %): 238 (M^+, 60.1), 143 (100). HRMS (EI) Calcd $C_{13}H_{18}O_2S$: 238.1027. Found: 238.1024.

(*E*)-6-[(*R*)-(*p*-Tolylsulfinyl)]-5-hexen-2-yl methanesulfonate (16). Using the procedure for (*E*)-**9**, the alcohol **15** (50 mg, 0.21 mmol) was converted into **16** (1:1 diastereomeric mixture, 54 mg, 81%). A pale yellow oil: IR (KBr) cm^{-1}: 3022, 1599, 1348, 1174, 1045. ^1H NMR δ: 1.35

(3/2H, d, J=1.2 Hz, 1-H), 1.35 (3/2H, d, J=1.2 Hz, 1-H), 1.71–1.87 (2H, m, 3-H), 2.29–2.34 (2H, m, 4-H), 2.34 (3H, s, Ar-CH_3), 2.92 (3/2H, s, SO_2CH_3), 2.93 (3/2H, s, SO_2CH_3), 4.68–4.81 (1H, m, 2-H), 6.21 (1/2H, d, J=15.3 Hz, 6-H), 6.22 (1/2H, d, J=15.3 Hz, 6-H), 6.49 (1H, dt, J=15.3, 6.7 Hz, 5-H), 7.24 (2H, d, J=8.5 Hz, Ar-H), 7.43 (2H, d, J=8.5 Hz, Ar-H). ^{13}C NMR δ: 21.0, 21.3, 27.5, 34.9, 38.6, 78.5, 124.5 (2C), 130.0 (2C), 135.7 (1/2C), 135.8 (1/2C), 137.8 (1/2C), 137.9 (1/2C), 140.4, 141.5. MS (EI) m/z (rel. int. %): 316 (M^+, 12.0), 143 (100). HRMS (EI) Calcd $C_{14}H_{20}O_4S_2$: 316.0803. Found: 316.0818.

(*E*)-(*R*)-5-Iodo-1-hexenyl *p*-tolyl sulfoxide (17). Using the procedure for (*E*)-**10**, the mesylate **16** (561 mg, 1.72 mmol) was converted into **17** (1:1 diastereomeric mixture, 426 mg, 70%). A pale yellow oil: IR (KBr) cm^{-1}: 2920, 1595, 1084, 1043. ^{1}H NMR δ: 1.71–1.73 (1H, m, 3-H), 1.88–1.93 (1H, m, 3-H), 1.88 (3H, d, J=6.5 Hz), 2.28–2.33 (2H, m, 4-H), 2.37 (3H, s, Ar-CH_3), 4.05–4.09 (1H, m, 5-H), 6.24 (1H, d, J=15.3 Hz, 1-H), 6.47–6.51 (1H, dt, J=15.3, 6.7 Hz, 2-H), 7.28 (2H, d, J=8.5 Hz, Ar-H), 7.46 (2H, d, J=8.5 Hz, Ar-H). ^{13}C NMR δ: 21.5, 28.4, 28.9, 32.3, 40.7, 124.5 (2C), 130.0 (2C), 135.8, 137.5, 140.5, 141.4. MS (EI) m/z (rel. int. %): 348 (M^+, 9.2), 300 (100). HRMS (EI) Calcd $C_{13}H_{17}IOS$: 348.0045. Found: 348.0045.

7-Hydroxy-1-[(*R*)-(*p*-tolylsulfinyl)]-2-heptanone (18). Using the procedure for **1**, (*R*)-methyl *p*-tolyl sulfoxide (739 mg, 4.79 mmol) and ϵ-caprolactone (0.40 ml, 5.19 mmol) were converted into **18** (978 mg, 76%). Pale yellow powder: mp 62.0–62.5°C (hexane–AcOEt). $[\alpha]_D^{28}$=+161.1 (c 1.14, $CHCl_3$). IR (KBr) cm^{-1}: 3402, 2935, 1713, 1600, 1086, 1036. ^{1}H NMR δ: 1.31 (2H, quint, J=7.9 Hz, 5-H), 1.49–1.58 (4H, m, 4- and 6-H), 2.42 (3H, s, Ar-CH_3), 2.43–2.55 (2H, m, 3-H), 3.58 (2H, t, J=6.1 Hz, 7-H), 3.76 (1H, d, J=3.8 Hz, 1-H), 3.89 (1H, d, J=3.8 Hz, 1-H), 7.33 (2H, d, J=8.6 Hz, Ar-H), 7.54 (2H, d, J=8.6 Hz, Ar-H). ^{13}C NMR δ: 21.4, 22.7, 25.0, 32.2, 44.6, 62.1, 67.9, 123.8, 129.9, 139.2 (2C), 142.0 (2C), 201.5. MS (EI) m/z (rel. int. %): 268 (M^+, 8.9), 139 (100). HRMS (EI) Calcd $C_{14}H_{20}O_3S$: 268.1133. Found: 268.1133.

7-[(*R*)-(*p*-Tolylsulfinyl)]-1,6-heptanediol (19). $NaBH_4$ (12 mg, 0.45 mmol) was added to a solution of **18** (100 mg, 0.37 mmol) in MeOH (5 ml) with stirring at 0°C. The stirring was continued at rt for 10 min. After the evaporation of MeOH, the residue was partitioned between AcOEt and water. The organic layer was washed with water and brine prior to drying and solvent evaporation. The residue was chromatographed on silica gel with AcOEt to give **19** (2:1 diastereomeric mixture, 93 mg, 93%) as a yellow oil. IR (KBr) cm^{-1}: 3334, 2933, 1600, 1085, 1035. ^{1}H NMR δ: 1.33–1.49 (4H, m, 3- and 4-H), 1.53–2.52 (4H, m, 2- and 5-H), 2.42 (3H, s, Ar-CH_3), 2.54 (1H, br, OH), 2.74 (1/3H, dd, J=13.4, 2.1 Hz, 7-H), 2.79 (2/3H, dd, J=13.4, 3.1 Hz, 7-H), 2.91 (1/3H, dd, J=13.4, 10.4 Hz, 7-H), 3.02 (2/3H, dd, J=13.4, 8.5 Hz, 7-H), 3.59 (2/3H, t, J=6.7 Hz, 1-H), 3.61 (4/3H, t, J=6.7 Hz, 1-H), 4.18–4.24 (1H, m, 6-H), 7.34 (2H, d, J=7.9 Hz, Ar-H), 7.52 (2/3H, d, J=7.9 Hz, Ar-H), 7.55 (4/3H, d, J=7.9 Hz, Ar-H). ^{13}C NMR (major) δ: 21.5, 24.8, 25.5, 32.4, 37.0, 62.3, 63.1, 68.1, 123.9 (2C), 130.0 (2C), 140.1, 141.9. (minor) δ: 21.5, 24.8, 25.4, 32.4, 36.9, 62.3, 63.1, 65.6, 123.8 (2C), 130.0 (2C), 139.5, 141.4. MS (EI) m/z (rel. int. %): 270 (M^+, 1.3), 140 (100). HRMS (EI) Calcd $C_{14}H_{22}O_3S$: 270.1290. Found: 270.1286.

7-[(*R*)-(*p*-Tolylsulfinyl)]-6-[(methylsulfonyl)oxy]heptyl methanesulfonate (20). MsCl (33 μl, 0.42 mmol) was added to a mixture of **19** (52 mg, 0.19 mmol) and Et_3N (59 μl, 0.42 mmol) in CH_2Cl_2 (1.5 ml) with stirring at 0°C. The stirring was continued at rt for 20 min. The reaction was quenched with saturated NH_4Cl aqueous solution and the whole was extracted with AcOEt. The extract was washed with water and brine prior to drying and solvent evaporation. The residue was chromatographed on silica gel with hexane–ether (1:1) to give **20** (2:1 diastereomeric mixture, 53 mg, 65%) as a pale yellow oil. IR (KBr) cm^{-1}: 2935, 1600, 1344, 1172, 1083, 1039. ^{1}H NMR δ: 1.45–1.49 (4H, m, 3- and 4-H), 1.72–1.95 (4H, m, 2-H and 5-H), 2.43 (3H, s, Ar-CH_3), 2.93 (1/3H, dd, J=13.7, 3.4 Hz, 7-H), 2.97–3.05 (1/3H, m, 7-H), 3.00 (1H, s, SO_2CH_3), 3.02 (2H, s, SO_2CH_3), 3.06 (2H, s, SO_2CH_3), 3.07 (2/3H, dd, J=14.0, 6.1 Hz, 7-H), 3.22 (1H, s, SO_2CH_3), 3.25 (2/3H, dd, J=14.0, 5.5 Hz, 7-H), 4.30–4.24 (2H, m, 1-H), 4.98 (2/3H, quint, J=6.1 Hz, 6-H), 5.10–5.20 (1/3H, m, 6-H), 7.36 (2H, d, J=7.9 Hz, Ar-H), 7.54 (2/3H, d, J=8.5 Hz, Ar-H), 7.57 (4/3H, d, J=7.9 Hz, Ar-H). ^{13}C NMR (major) δ: 21.3, 24.1, 24.8, 28.7, 34.3, 37.2, 38.6, 61.7, 70.0, 76.6, 124.0 (2C), 130.1 (2C), 139.7, 142.1. (Minor) δ: 21.3, 23.6, 24.9, 28.7, 34.9, 37.2, 38.3, 61.7, 70.0, 77.2, 123.7 (2C), 130.2 (2C), 139.5, 142.1. MS (EI) m/z (rel. int. %): 426 (M^+, 0.2), 140 (100). HRMS (EI) Calcd $C_{16}H_{26}O_7S_3$: 426.0840. Found: 426.0858.

(*E*)- and (*Z*)-7-[(*R*)-(*p*-Tolylsulfinyl)]-6-heptenyl methanesulfonate [(*E*)- and (*Z*)-21]. *t*-BuOK (19.9 mg, 0.18 mmol) was added to a solution of **20** (50 mg, 0.12 mmol) in THF (1.5 ml) with stirring at 0°C. The stirring was continued at rt for 1 h. The reaction was quenched with saturated NH_4Cl aqueous solution and the whole was extracted with AcOEt. The extract was washed with water and brine prior to drying and solvent evaporation. The residue was chromatographed on silica gel with hexane–AcOEt (1:3) to give (*E*)-**21** (13 mg, 33%) as colorless powder and (*Z*)-**21** (13 mg, 33%) as a colorless oil. (*E*)-**21**: mp 61.4–62.2°C (hexane–AcOEt). $[\alpha]_D^{27}$=+74.0 (c 0.84, $CHCl_3$). IR (KBr) cm^{-1}: 2931, 1597, 1352, 1174, 1084, 1041. ^{1}H NMR δ: 1.42–1.46 (2H, m, 3-H), 1.49–1.55 (2H, m, 4-H), 1.75 (2H, quint, J=7.0 Hz, 2-H), 2.25 (2H, q, J=6.7 Hz, 5-H), 2.41 (3H, s, Ar-CH_3), 3.00 (3H, s, SO_2CH_3), 4.20 (2H, t, J=6.7 Hz, 1-H), 6.22 (1H, d, J=15.3 Hz, 7-H), 6.57 (1H, dt, J=15.3, 6.7 Hz, 6-H), 7.32 (2H, d, J=7.9 Hz, Ar-H), 7.49 (2H, d, J=8.3 Hz, Ar-H). ^{13}C NMR δ: 21.4, 24.9, 27.5, 28.8, 31.6, 37.3, 69.6, 124.4 (2C), 129.8 (2C), 135.3, 139.5, 140.7, 141.2. MS (EI) m/z (rel. int. %): 330 (M^+, 7.5), 282 (100). HRMS (EI) Calcd $C_{15}H_{22}O_4S_2$: 330.0959. Found: 330.0959. (*Z*)-**21**: $[\alpha]_D^{26}$=+133.1 (c 0.14, $CHCl_3$). IR (KBr) cm^{-1}: 2935, 1597, 1352, 1174, 1038. ^{1}H NMR δ: 1.36–1.55 (4H, m, 3- and 4-H), 1.65–1.78 (2H, m, 2-H), 2.34 (3H, s, Ar-CH_3), 2.37–2.51 (1H, m, 5-H), 2.56–2.67 (1H, m, 5-H), 2.95 (3H, s, SO_2CH_3), 4.18 (2H, t, J=6.5 Hz, 1-H), 6.06–6.47 (2H, m, 6- and 7-H), 7.25 (2H, d, J=8.3 Hz, Ar-H), 7.42 (2H, d, J=8.3 Hz, Ar-H). ^{13}C NMR δ: 21.3, 24.9, 28.3, 28.8, 28.9, 37.3, 69.7, 124.0

(2C), 130.0 (2C), 137.3, 141.0, 141.1, 141.2. MS (EI) *m/z* (rel. int. %): 330 (M^+, 33.3), 313 (100). HRMS (EI) Calcd $C_{15}H_{22}O_4S_2$: 330.0959. Found: 330.0945.

(*E*)-(*R*)-7-Iodo-1-heptenyl *p*-tolyl sulfoxide [(*E*)-22]. Using the procedure for (*E*)-**10**, the mesylate (*E*)-**21** (200 mg, 0.61 mmol) was converted into (*E*)-**22** (191 mg, 87%). A colorless oil: $[\alpha]_D^{24}=+65.4$ (*c* 1.53, $CHCl_3$). IR (KBr) cm^{-1}: 2931, 1597, 1493, 1084, 1043. ^1H NMR δ: 1.38–1.44 (2H, m, 5-H), 1.46–1.52 (2H, m, 4-H), 1.81 (2H, quint, *J*=6.7 Hz, 6-H), 2.24 (2H, dq, *J*=6.7, 1.2 Hz, 3-H), 2.41 (3H, s, Ar-CH_3), 3.17 (2H, t, *J*=6.7 Hz, 7-H), 6.23 (1H, dt, *J*=15.3, 1.2 Hz, 1-H), 6.56 (1H, dt, *J*=15.3, 6.7 Hz, 2-H), 7.31 (2H, d, *J*=7.9 Hz, Ar-H), 7.50 (2H, d, *J*=7.9 Hz, Ar-H). ^{13}C NMR δ: 6.6, 21.3, 26.9, 29.7, 31.6, 32.9, 124.5 (2C), 129.9 (2C), 135.3, 139.8, 140.8, 141.3. MS (FAB) *m/z*: 363 (MH^+). HRMS (FAB) Calcd $C_{14}H_{20}IOS$ (MH^+): 363.0280. Found: 363.0275.

(*Z*)-(*R*)-7-Iodo-1-heptenyl *p*-tolyl sulfoxidfe [(*Z*)-22]. Using the procedure for (*E*)-**10**, the mesylate (*Z*)-**21** (200 mg, 0.61 mmol) was converted into (*Z*)-**22** (184 mg, 84%). A colorless oil: $[\alpha]_D^{24}=-160.4$ (*c* 1.30, $CHCl_3$). IR (KBr) cm^{-1}: 2931, 1597, 1493, 1084, 1041. ^1H NMR δ: 1.46–1.59 (4H, m, 4- and 5-H), 1.86 (2H, quint, *J*=6.7 Hz, 6-H), 2.41 (3H, s, Ar-CH_3), 2.50–2.57 (1H, m, 3-H), 2.62–2.70 (1H, m, 3-H), 3.20 (2H, t, *J*=6.7 Hz, 7-H), 6.17 (1H, dt, *J*=9.8, 7.3 Hz, 2-H), 6.23 (1H, d, *J*=9.8 Hz, 1-H), 7.32 (2H, d, *J*=7.9 Hz, Ar-H), 7.50 (2H, d, *J*=7.9 Hz, Ar-H). ^{13}C NMR δ: 6.6, 21.3, 27.9, 29.0, 29.9, 33.0, 124.0 (2C), 129.9 (2C), 137.3, 141.1 (2C), 141.2. MS (FAB) *m/z*: 363 (MH^+). HRMS (FAB) Calcd $C_{14}H_{20}IOS$ (MH^+): 363.0280. Found: 363.0285.

(*R*)-5-[[*tert*-Butyl(dimethyl)silyl]oxy]-1-pentynyl *p*-tolyl sulfoxide (25). EtMgBr (2.5 M in ether, 3.00 ml, 8.75 mol) was added to a solution of **23** (2.49 g, 12.6 mmol) in ether (5 ml) with stirring at 0°C under N_2 and the whole was refluxed for 1.5 h. Then, a solution of (*S*)-(−)-menthyl *p*-tolylsulfinate (1.85 g, 6.28 mmol) in toluene (20 ml) was added to the mixture with stirring at 0°C and the stirring was continued at the same temperature for 2 h and at rt for 1 h. The reaction was quenched with saturated NH_4Cl aqueous solution and the whole was extracted with AcOEt. The extract was washed with brine prior to drying and solvent evaporation. The residue was chromatographed on silica gel with hexane–AcOEt (10:1) to give **25** (1.75 g, 82%) as a colorless oil. $[\alpha]_D^{27}=+49.86$ (*c* 0.68, $CHCl_3$). IR (KBr) cm^{-1}: 2954, 2856, 1597, 1471, 1105, 1092, 1063. ^1H NMR δ: 0.01 (6H, s, $Si(CH_3)_2$), 0.86 (9H, s, $SiC(CH_3)_3$), 1.75 (2H, quint, *J*=6.7 Hz, 4-H), 2.41 (3H, s, Ar-CH_3), 2.51 (2H, t, *J*=6.7 Hz, 5-H), 3.63 (2H, t, *J*=6.7 Hz, 3-H), 7.33 (2H, d, *J*=7.9 Hz, Ar-H), 7.68 (2H, d, *J*=7.9 Hz, Ar-H). ^{13}C NMR δ: −5.4 (2C), 16.2, 18.2, 21.4, 25.8 (3C), 30.5, 61.0, 78.3, 105.4, 125.0 (2C), 130.1 (2C), 141.3, 142.5. MS (FAB) *m/z*: 337 (MH^+). HRMS (FAB) Calcd $C_{18}H_{29}O_2SiS$ (MH^+): 337.1658. Found: 337.1674.

(*R*)-6-[[*tert*-Butyl(dimethyl)silyl]oxy]-1-hexynyl *p*-tolyl sulfoxide (26). Using the procedure for **25**, the alcohol **24** (5.42 g, 25.5 mmol) and (*S*)-(−)-menthyl *p*-tolylsulfinate (4.00 g, 13.6 mmol) was converted into **26** (3.42 g, 72%). A colorless oil: $[\alpha]_D^{26}=+38.4$ (*c* 0.83, $CHCl_3$). IR (KBr) cm^{-1}: 2950, 2181, 1462, 1255, 1090, 1060. ^1H NMR δ: 0.03 (6H, s, $Si(CH_3)_2$), 0.88 (9H, s, $SiC(CH_3)_3$), 1.57–1.66 (4H, m, 4- and 5-H), 2.42 (3H, s, Ar-CH_3), 2.45 (2H, t, *J*=6.7 Hz, 3-H), 3.60 (2H, t, *J*=6.1 Hz, 6-H), 7.34 (2H, d, *J*=7.9 Hz, Ar-H), 7.75 (2H, d, *J*=7.9 Hz, Ar-H). ^{13}C NMR δ: −5.5 (2C), 18.2, 19.5, 21.4, 24.1, 25.8 (3C), 31.6, 62.2, 78.3, 105.5, 125.0 (2C), 130.1 (2C), 141.2, 142.1. MS (FAB) *m/z*: 351 (MH^+). Anal. Calcd for $C_{19}H_{30}O_2SiS$: C; 65.09, H; 8.62, S; 9.15. Found: C; 65.03, H; 8.51, S; 9.01.

(*Z*)-(*R*)-5-[[*tert*-Butyl(dimethyl)silyl]oxy]-1-pentenyl *p*-tolyl sulfoxide (27). A mixture of **25** (100 mg, 0.30 mmol) and $RhCl(PPh_3)_3$ (10 mg, 0.011 mmol) in degassed benzene (4.5 ml) was stirred under hydrogen (1 atm) at rt for 24 h. The mixture was filtered and the filtrate was concentrated under the reduced pressure to give **27** (83 mg, 83%) as a colorless oil. $[\alpha]_D^{27}=-204.3$ (*c* 1.05, $CHCl_3$). IR (KBr) cm^{-1}: 2929, 2856, 1597, 1471, 1462, 1255, 1105, 1043. ^1H NMR δ: 0.05 (6H, s, $Si(CH_3)_2$), 0.89 (9H, s, $SiC(CH_3)_3$), 1.63–1.75 (2H, m, 4-H), 2.38 (3H, s, Ar-CH_3), 2.61–2.66 (2H, m, 3-H), 3.65 (1H, dt, *J*=12.8, 6.1 Hz, 5-H), 3.67 (1H, dt, *J*=12.8, 6.1 Hz, 5-H), 6.17 (1H, d, *J*=7.9 Hz, 2-H), 6.19 (1H, d, *J*=7.9 Hz, 1-H), 7.28 (2H, d, *J*=7.9 Hz, Ar-H), 7.49 (2H, d, *J*=7.9 Hz, Ar-H). ^{13}C NMR δ: −5.4 (2C), 18.2, 21.3, 25.9 (3C), 26.0, 32.1, 62.0, 124.0 (2C), 129.9 (2C), 137.3, 141.0, 141.3, 131.4. MS (FAB) *m/z*: 339 (MH^+). HRMS (FAB) Calcd $C_{18}H_{31}O_2SSi$ (MH^+): 339.1814. Found: 339.1823.

(*Z*)-(*R*)-6-[[*tert*-Butyl(dimethyl)silyl]oxy]-1-hexenyl *p*-tolyl sulfoxide (28). Using the procedure for **27**, the alcohol **26** (100 mg, 0.29 mmol) was converted into **28** (95 mg, 93%). A colorless oil: $[\alpha]_D^{27}=-183.2$ (*c* 0.94, $CHCl_3$). IR (KBr) cm^{-1}: 2950, 2858, 1462, 1255, 1101, 1045. ^1H NMR δ: 0.03 (6H, s, $Si(CH_3)_2$), 0.87 (9H, s, $SiC(CH_3)_3$), 1.53–1.56 (4H, m, 4-H and 5-H), 2.37 (3H, s, Ar-CH_3), 2.50–2.60 (1H, m, 3-H), 2.58–2.63 (1H, m, 3-H), 3.62 (2H, dt, *J*=5.8, 1.8 Hz, 6-H), 6.12–6.19 (2H, m, 1- and 2-H), 7.27 (2H, d, *J*=7.9 Hz, Ar-H), 7.47 (2H, d, *J*=7.9 Hz, Ar-H). ^{13}C NMR δ: −5.3 (2C), 18.2, 21.3, 25.4, 25.9 (3C), 29.0, 32.1, 62.5, 124.0 (2C), 129.9 (2C), 137.1, 141.0, 141.3, 131.6. MS (FAB) *m/z*: 353 (MH^+). Anal. Calcd for $C_{19}H_{32}O_2SiS$: C; 64.72, H; 9.15, S; 9.09. Found: C; 64.58, H; 8.95, S; 9.03.

(*Z*)-5-[(*R*)-(*p*-Tolylsulfinyl)]-4-penten-1-ol [(*Z*)-5]. HF·pyridine (663 mg, 4.68 mmol) was added to a solution of **27** (1.32 g, 3.90 mmol) in a 1:1 mixture of pyridine and THF (40 ml) with stirring at rt. The stirring was continued for 3 days. The reaction was quenched with water and the whole was extracted with AcOEt. The extract was washed with brine prior to drying and solvent evaporation. The residue was chromatographed on silica gel with hexane–AcOEt (10:1) to give (*Z*)-**5** (851 mg, 97%) as a colorless oil. $[\alpha]_D^{26}=-147.8$ (*c*1.07, $CHCl_3$). IR (KBr) cm^{-1}: 3390, 2937, 1597, 1493, 1084, 1038, 1012. ^1H NMR δ: 1.69–1.77 (2H, m, 2-H), 2.27–2.29 (1H, m, OH), 2.42 (3H, s, Ar-CH_3), 2.53–2.60 (1H, m, 3-H), 2.87–2.95 (1H, m, 3-H), 3.72 (2H, q, *J*=5.5 Hz, 1-H), 6.23 (1H, dt, *J*=9.8, 6.7 Hz, 4-H), 6.28 (1H, dt, *J*=9.8, 1.2 Hz, 5-H), 7.33 (2H, d, *J*=7.9 Hz, Ar-H), 7.52 (2H, d, *J*=7.9 Hz, Ar-H). ^{13}C NMR δ: 21.2, 25.6, 31.4,

60.7, 124.0 (2C), 129.9 (2C), 136.7, 140.5, 141.2, 142.1. MS (EI) *m/z* (rel. int. %): 224 (M^+, 14.1), 207 (100). HRMS (EI) Calcd $C_{12}H_{16}O_2S$: 224.0871. Found: 224.0895.

(*Z*)-6-[(*R*)-(*p*-Tolylsulfinyl)]-5-hexen-1-ol [(*Z*)-6]. Using the procedure for (*Z*)-**5**, the alcohol **28** (58 mg, 0.16 mmol) was converted into (*Z*)-**6** (34 mg, 87%). A colorless oil: $[\alpha]_D^{28}=-236.8$ (*c* 0.58, $CHCl_3$). IR (KBr) cm^{-1}: 3408, 2933, 1493, 1454, 1028. ^1H NMR δ: 1.49–1.60 (4H, m, 2- and 3-H), 2.32 (3H, s, Ar-CH_3), 2.34–2.49 (2H, m, 4-H and OH), 2.57–2.64 (1H, m, 4-H), 3.59 (2H, t, *J*=6.7 Hz, 1-H), 6.12 (2H, m, 5- and 6-H), 7.23 (2H, d, *J*=7.9 Hz, Ar-H), 7.41 (2H, d, *J*=7.9 Hz, Ar-H). ^{13}C NMR δ: 21.3, 25.2, 28.9, 31.8, 61.9, 124.0 (2C), 130.0 (2C), 136.8, 140.9, 141.2, 141.9. MS (FAB) *m/z*: 239 (MH^+). HRMS (FAB) Calcd $C_{13}H_{19}O_2S$ (MH^+): 239.1106. Found: 239.1107.

(*Z*)-5-[(*R*)-(*p*-Tolylsulfinyl)]-4-pentenyl *p*-toluenesulfonate [(*Z*)-7]. Using the procedure for (*E*)-**7**, the alcohol (*Z*)-**5** (433 mg, 1.93 mmol) was converted into (*Z*)-**7** (595 mg, 81%). A colorless oil: $[\alpha]_D^{27}=-175.2$ (*c* 1.15, $CHCl_3$). IR (KBr) cm^{-1}: 2924, 1597, 1493, 1358, 1190, 1176, 1041. ^1H NMR δ: 1.83–1.90 (2H, m, 2-H), 2.41 (3H, s, Ar-CH_3), 2.45 (3H, s, Ar-CH_3), 2.56–2.62 (1H, m, 3-H), 2.64–2.72 (1H, m, 3-H), 4.06–4.14 (2H, m, 1-H), 6.08 (1H, dt, *J*=9.2, 7.3 Hz, 4-H), 6.23 (1H, dt, *J*=9.2, 1.2 Hz, 5-H), 7.32 (2H, d, *J*=8.5 Hz, Ar-H), 7.37 (2H, d, *J*=8.5 Hz, Ar-H), 7.47 (2H, d, *J*=8.5 Hz, Ar-H), 7.81 (2H, d, *J*=8.5 Hz, Ar-H). ^{13}C NMR δ: 21.3, 21.5, 25.3, 28.3, 69.2, 124.0 (2C), 127.8 (2C), 129.9 (2C), 130.0 (2C), 132.8, 138.2, 139.2, 140.9, 141.3, 144.9. MS (FAB) *m/z*: 379 (MH^+). HRMS (FAB) Calcd $C_{19}H_{23}O_4S_2$ (MH^+): 3791034. Found: 379.1040.

(*Z*)-6-[(*R*)-(*p*-Tolylsulfinyl)]-5-hexenyl *p*-toluenesulfonate [(*Z*)-8]. Using the procedure for (*E*)-**7**, the alcohol (*Z*)-**6** (600 mg, 2.52 mmol) was converted into (*Z*)-**8** (708 mg, 72%). A colorless oil: $[\alpha]_D^{28}=-130.0$ (*c* 1.30, $CHCl_3$). IR (KBr) cm^{-1}: 1493, 1356, 1178, 1097, 1038. ^1H NMR δ: 1.48 (2H, quint, *J*=7.9 Hz, 3-H), 1.61–1.68 (2H, m, 2-H), 2.31 (3H, s, Ar-CH_3), 2.35 (3H, s, Ar-CH_3), 2.40 (1H, quint, *J*=7.3 Hz, 4-H), 2.51 (1H, quint, *J*=7.3 Hz, 4-H), 3.98 (2H, dt, *J*=4.3, 1.8 Hz, 1-H), 6.01 (1H, dt, *J*=7.3, 1.2 Hz, 5-H), 6.12 (1H, d, *J*=7.3 Hz, 6-H), 7.22 (2H, d, *J*=8.3 Hz, Ar-H), 7.26 (2H, d, *J*=8.3 Hz, Ar-H), 7.39 (2H, d, *J*=8.3 Hz, Ar-H), 7.70 (2H, d, *J*=8.3 Hz, Ar-H). ^{13}C NMR δ: 21.2, 21.4, 24.7, 28.0, 28.3, 69.7, 123.9 (2C), 127.7 (2C), 129.7 (2C), 129.9 (2C), 132.7, 137.5, 140.5, 140.9, 141.1, 144.7. MS (FAB) *m/z*: 393 (MH^+). HRMS (FAB) Calcd $C_{20}H_{25}O_4S_2$ (MH^+): 393.1195. Found: 393.1185.

(*Z*)-(*R*)-5-Iodo-1-pentenyl *p*-tolyl sulfoxide [(*Z*)-10]. Using the procedure for (*E*)-**10**, the tosylate (*Z*)-**7** (381 mg, 1.01 mmol) was converted into (*Z*)-**10** (294 mg, 87%). A colorless oil: $[\alpha]_D^{24}=-208.4$ (*c* 1.84, $CHCl_3$). IR (KBr) cm^{-1}: 2922, 1595, 1493, 1205, 1082, 1041, 1014. ^1H NMR δ: 1.98–2.09 (2H, m, 4-H), 2.41 (3H, s, Ar-CH_3), 2.62–2.70 (1H, m, 3-H), 2.73–2.80 (1H, m, 3-H), 3.22 (1H, dt, *J*=12.2, 6.7 Hz, 5-H), 3.24 (1H, dt, *J*=12.2, 6.7 Hz, 5-H), 6.13 (1H, dt, *J*=9.8, 7.3 Hz, 2-H), 6.28 (1H, dt, *J*=9.8, 1.2 Hz, 1-H), 7.33 (2H, d, *J*=7.9 Hz, Ar-H), 7.52 (2H, d, *J*=7.9 Hz, Ar-H). ^{13}C NMR δ: 5.0, 21.2, 29.8, 32.2, 123.9 (2C), 129.9 (2C), 138.2, 138.9, 140.9, 141.1. MS (EI) *m/z* (rel. int. %): 334 (M^+, 1.4), 91 (100). MS (EI) *m/z* (rel. int. %): 334 (M^+, 1.4), 91 (100). HRMS (EI) Calcd $C_{12}H_{15}IOS$: 333.9889. Found: 333.9906.

(*Z*)-(*R*)-6-Iodo-1-hexenyl *p*-tolyl sulfoxide [(*Z*)-11]. Using the procedure for (*E*)-**10**, the tosylate (*Z*)-**8** (100 mg, 0.26 mmol) was converted into (*Z*)-**11** (82 mg, 92%). A yellow oil: $[\alpha]_D^{28}=-177.4$ (*c* 1.05, $CHCl_3$). IR (KBr) cm^{-1}: 2933, 1492, 1450, 1081, 1041. ^1H NMR δ: 1.64 (2H, quint, *J*=7.3 Hz, 4-H), 1.88–1.92 (2H, m, 5-H), 2.41 (3H, s, Ar-CH_3), 2.57 (1H, quint, *J*=7.3 Hz, 3-H), 2.66 (1H, quint, *J*=7.3 Hz, 3-H), 3.27 (2H, t, *J*=7.3 Hz, 6-H), 6.14–6.19 (1H, m, 2-H), 6.25 (1H, d, *J*=9.2 Hz, 1-H), 7.32 (2H, d, *J*=7.9 Hz, Ar-H), 7.51 (2H, d, *J*=7.9 Hz, Ar-H). ^{13}C NMR δ: 6.1, 21.4, 28.1, 29.7, 32.6, 124.1 (2C), 130.0 (2C), 137.7, 140.7, 141.1, 141.2. MS (FAB) *m/z*: 349 (MH^+). Anal. Calcd for $C_{13}H_{17}IOS$: C; 44.84, H; 4.92. Found: C; 44.52, H; 4.89.

7-Hydroxyheptyl *p*-toluenesulfonate (29). Using the procedure for (*E*)-**7**, 1,7-heptanediol (3.00 g, 22.7 mmol) was converted into **29** (5.66 g, 87%). A colorless oil: IR (KBr) cm^{-1}: 3350, 2929, 1356, 1176. ^1H NMR δ: 1.24–1.34 (6H, m, 3-, 4-, and 5-H), 1.52 (2H, quint, *J*=7.3 Hz, 6-H), 1.64 (2H, quint, *J*=6.7 Hz, 2-H), 1.78 (1H, s, OH), 2.45 (3H, s, Ar-CH_3), 3.61 (2H, t, *J*=6.7 Hz, 7-H), 4.02 (2H, t, *J*=6.7 Hz, 1-H), 7.35 (2H, d, *J*=8.5 Hz, Ar-H), 7.87 (2H, d, *J*=8.5 Hz, Ar-H). ^{13}C NMR δ: 21.7, 25.3, 25.5, 28.7, 28.7, 32.5, 62.8, 70.6, 127.7 (2C), 129.7 (2C), 133.0, 144.5. MS (EI) *m/z* (rel. int. %): 286 (M^+, 16.7), 91 (100). HRMS (EI) Calcd $C_{14}H_{22}O_4S$: 286.1239. Found: 286.1226.

7-Oxoheptyl *p*-toluenesulfonate (30). Using the procedure for **14**, the alcohol **29** (289 mg, 1.01 mmol) was converted into **30** (256 mg, 90%). A colorless oil: IR (KBr) cm^{-1}: 2941, 1724, 1599, 1356, 1188. ^1H NMR δ: 1.24–1.36 (4H, m, 3- and 4-H), 1.58 (2H, quint, *J*=7.3 Hz, 5-H), 1.64 (2H, quint, *J*=6.7 Hz, 2-H), 2.41 (2H, dt, *J*=7.3, 1.8 Hz, 6-H), 2.45 (3H, s, Ar-CH_3), 4.02 (2H, t, *J*=6.7 Hz, 1-H), 7.36 (2H, d, *J*=7.9 Hz, Ar-H), 7.78 (2H, d, *J*=7.9 Hz, Ar-H), 9.74 (1H, t, *J*=1.8 Hz, CHO). ^{13}C NMR δ: 21.6, 21.7, 25.1, 28.4, 28.6, 43.6, 70.3, 127.6 (2C), 129.6 (2C), 132.9, 144.5, 202.2. MS (EI) *m/z* (rel. int. %): 284 (M^+, 1.7), 173 (100). HRMS (EI) Calcd $C_{14}H_{20}O_4S$: 284.1082. Found: 284.1054.

(*E*)- and (*Z*)-8-[(*R*)-(*p*-Tolylsulfinyl)]-7-octenyl *p*-toluenesulfonate [(*E*)- and (*Z*)-31]. *n*-BuLi (1.54 M in hexane, 0.45 ml, 0.69 mmol) was added to a solution of (*R*)-dimethylphosphorylmethyl *p*-tolyl sulfoxide (180 mg, 0.69 mmol) in THF (5 ml) with stirring at −78°C and the stirring was continued at the same temperature for 30 min. Then, a solution of the aldehyde **30** (150 mg, 0.53 mmol) in THF (3 ml) was added to the mixture and the stirring was continued at −78°C for 30 min. The reaction was quenched with water and the whole was extracted with AcOEt. The extract was washed with water and brine prior to drying and solvent evaporation. The residue was chromatographed on silica gel with hexane–AcOEt (1:1) to give (*E*)-**31** (67 mg, 30%) as colorless powder and (*Z*)-**31** (102 mg, 46%) as a yellow oil. (*E*)-**31**: mp 49.7–50.7°C (hexane–AcOEt). $[\alpha]_D^{28}=+51.5$ (*c* 0.48, acetone). IR (KBr) cm^{-1}: 2927, 1597, 1358, 1188, 1176, 1097, 1084, 1043. ^1H NMR δ:

1.24–1.33 (4H, m, 3- and 4-H), 1.41 (2H, quint, J=7.3 Hz, 5-H), 1.62 (2H, quint, J=6.2 Hz, 2-H), 2.18 (2H, q, J=6.7 Hz, 6-H), 2.41 (3H, s, Ar-CH_3), 2.45 (3H, s, Ar-CH_3), 4.00 (2H, t, J=7.3 Hz, 1-H), 6.19 (1H, d, J=15.2 Hz, 8-H), 6.55 (1H, dt, J=15.2, 6.7 Hz, 7-H), 7.31 (2H, d, J=8.2 Hz, Ar-H), 7.35 (2H, d, J=8.2 Hz, Ar-H), 7.49 (2H, d, J=8.5 Hz, Ar-H), 7.78 (2H, d, J=8.5 Hz, Ar-H). ^{13}C NMR δ: 21.4, 21.7, 25.1, 27.8, 28.3, 28.7, 31.8, 70.3, 124.4 (2C), 127.7 (2C), 129.7 (2C), 129.8 (2C), 133.0, 135.1, 140.1, 140.1, 141.2, 144.5. MS (EI) m/z (rel. int. %): 420 (M^+, 11.5), 124 (100). HRMS (EI) Calcd $C_{22}H_{28}O_4S_2$: 420.1429. Found: 420.1434. (*Z*)-**31**: $[\alpha]_D^{28}$=−149.3 (c 0.29, acetone). IR (KBr) cm^{-1}: 2929, 1597, 1358, 1176, 1041. ^{1}H NMR δ: 1.32–1.37 (4H, m, 3- and 4-H), 1.46 (2H, quint, J=6.7 Hz, 5-H), 1.66 (2H, quint, J=6.7 Hz, 2-H), 2.41 (3H, s, Ar-CH_3), 2.45 (3H, s, Ar-CH_3), 2.46–2.55 (1H, m, 6-H), 2.55–2.63 (1H, m, 6-H), 4.03 (2H, t, J=6.7 Hz, 1-H), 6.12–6.17 (1H, dt, J=9.7, 7.9 Hz, 7-H), 6.21 (1H, d, J=9.7 Hz, 8-H), 7.31 (2H, d, J=8.5 Hz, Ar-H), 7.35 (2H, d, J=8.5 Hz, Ar-H), 7.49 (2H, d, J=7.9 Hz, Ar-H), 7.79 (2H, d, J=7.9 Hz, Ar-H). ^{13}C NMR δ: 21.3, 21.6, 25.1, 28.4, 28.6, 28.7, 29.1, 70.4, 124.0 (2C), 127.8 (2C), 129.8 (2C), 130.0 (2C), 137.0, 141.1, 133.0, 141.1, 141.6, 144.7. MS (EI) m/z (rel. int. %): 420 (M^+, 40.8), 140 (100). HRMS (EI) Calcd $C_{22}H_{28}O_4S_2$: 420.1429. Found: 420.1420.

(*E*)-(*R*)-8-Iodo-1-octenyl *p*-tolyl sulfoxide [(*E*)-32]. Using the procedure for (*E*)-**10**, the tosylate (*E*)-**31** (735 mg, 1.75 mmol) was converted into (*E*)-**32** (564 mg, 87%). Colorless powder: mp 60.8–61.5°C (hexane–AcOEt). $[\alpha]_D^{28}$=+78.3 (c 0.69, acetone). IR (KBr) cm^{-1}: 2929, 1625 1082, 1045. ^{1}H NMR δ: 1.29–1.42 (4H, m, 5- and 6-H), 1.47 (2H, quint, J=7.3 Hz, 4-H), 1.79 (2H, quint, J=7.3 Hz, 7-H), 2.23 (2H, q, J=6.7 Hz, 3-H), 2.41 (3H, s, Ar-CH_3), 3.16 (2H, t, J=6.7 Hz, 8-H), 6.21 (1H, d, J=15.3 Hz, 1-H), 6.58 (1H, dt, J=15.3, 6.7 Hz, 2-H), 7.31 (2H, d, J=7.9 Hz, Ar-H), 7.50 (2H, d, J=7.9 Hz, Ar-H). ^{13}C NMR δ: 7.0, 21.4, 27.8, 27.9, 30.1, 31.8, 33.2, 124.4, 129.8 (2C), 135.1 (2C), 140.1, 140.8, 141.2. MS (EI) m/z (rel. int. %): 376 (M^+, 15.1), 359 (100). Anal. Calcd for $C_{15}H_{21}IOS$: C, 47.88; H, 5.63. Found: C, 48.04; H, 5.54.

(*Z*)-(*R*)-8-Iodo-1-octenyl *p*-tolyl sulfoxide [(*Z*)-32]. Using the procedure for (*E*)-**10**, the tosylate (*Z*)-**31** (1.20 g, 2.86 mmol) was converted into (*Z*)-**32** (842 mg, 78%). A pale yellow oil: $[\alpha]_D^{28}$=−183.1 (c 0.31, acetone). IR (KBr) cm^{-1}: 2927, 1618, 1493, 1084, 1039. ^{1}H NMR δ: 1.38–1.57 (6H, m, 4-, 5-, and 6-H), 1.84 (2H, quint, J=7.3 Hz, 7-H), 2.41 (3H, s, Ar-CH_3), 2.48–2.55 (1H, m, 3-H), 2.61–2.69 (1H, m, 3-H), 3.20 (2H, t, J=7.3 Hz, 8-H), 6.14–6.19 (1H, m, 2-H), 6.21–6.23 (1H, d, J=9.8 Hz, 1-H), 7.32 (2H, d, J=8.5 Hz, Ar-H), 7.50 (2H, d, J=8.5 Hz, Ar-H). ^{13}C NMR δ: 7.0, 21.4, 28.1, 28.9, 29.2, 30.2, 33.3, 124.0 (2C), 129.9 (2C), 137.1, 141.0, 141.2, 141.4. MS (EI) m/z (rel. int. %): 376 (M^+, 23.7), 328 (100). Anal. Calcd for $C_{15}H_{21}IOS$: C, 47.88; H, 5.63. Found: C, 47.66; H, 5.57.

(*E*)-(*R*)- and (*Z*)-(*R*)-2-Phenyl-5-(tetrahydro-2*H*-pyran-2-yloxy)-1-pentenyl *p*-tolyl sulfoxide [(*E*)- and (*Z*)-35]. Using the procedure for **31**, the ketone **33** (500 mg, 2.02 mmol) was converted into (*E*)-**35** (234 mg, 30%) and (*Z*)-**35** (496 mg, 64%). (*E*)-**35** (a colorless oil): $[\alpha]_D^{24}$=−60.4 (c 1.25, $CHCl_3$). IR (KBr) cm^{-1}: 2941, 1597, 1120, 1038. ^{1}H NMR δ: 1.50–1.59 (4H, m, THP), 1.68–1.80 (2H, m, 4-H), 1.83–1.88 (2H, m, THP), 2.41 (3H, s, Ar-CH_3), 3.08–3.23 (2H, m, 3-H), 3.40–3.46 (1H, m, 5-H), 3.48–3.53 (2H, m, OCH_2), 3.77–3.79 (1/2H, t, J=6.1 Hz, 5-H), 3.79–3.81 (1/2H, t, J=6.1 Hz, 5-H), 4.55–4.56 (1/2H, dd, J=4.9, 3.1 Hz, O–CH–O), 4.58–4.59 (1/2H, dd, J=4.9, 3.1 Hz, O–CH–O), 6.33 (1H, s, 1-H), 7.31–7.34 (5H, m, Ar-H), 7.38–7.40 (2H, m, Ar-H), 7.56–7.58 (1H, d, J=7.9 Hz, Ar-H), 7.57–7.58 (1H, d, J=7.9 Hz, Ar-H). ^{13}C NMR δ: 19.5 (1/2C), 19.7 (1/2C), 21.3, 25.4, 28.1 (1/2C), 28.3 (1/2C), 28.7 (1/2C), 29.1 (1/2C), 30.6, 62.2 (1/2C), 62.5 (1/2C), 66.1 (1/2C), 66.4 (1/2C), 98.7 (1/2C), 99.0 (1/2C), 124.1 (2C), 126.6 (2C), 128.6 (2C), 129.2, 130.0 (2C), 133.9 (1/2C), 134.2 (1/2C), 138.3 (1/2C), 138.4 (1/2C), 141.0, 141.6, 152.0 (1/2C), 152.4 (1/2C). MS (FAB) m/z: 385 (MH^+). HRMS (FAB) Calcd $C_{23}H_{29}O_3S$ (MH^+): 385.1837. Found: 385.1836. (*Z*)-**35** (a colorless oil): $[\alpha]_D^{24}$=−216.7 (c 1.05, $CHCl_3$). IR (KBr) cm^{-1}: 2943, 1595, 1078, 1036. ^{1}H NMR δ: 1.49–1.51 (4H, m, THP), 1.66–1.70 (3H, m, 4-H and THP), 1.71–1.78 (1H, m, 4-H), 2.41 (3H, s, Ar-CH_3), 2.57–2.64 (2H, m, 3-H), 3.30–3.33 (1H, m, 5-H), 3.34–3.47 (1H, m, THP), 3.66–3.74 (1H, m, 5-H), 3.75–3.82 (1H, m, THP), 4.43–4.44 (1/2H, m, O–CH–O), 4.45–4.51 (1/2H, m, O–CH–O), 6.33–6.34 (1H, m, 1-H), 7.29–7.48 (9H, m, Ar-H). ^{13}C NMR δ: 19.5, 21.3, 25.3, 27.4, 30.5, 35.7, 62.2 (1/2C), 62.3 (1/2C), 66.1 (1/2C), 66.2 (1/2C), 98.7 (1/2C), 98.8 (1/2C), 124.3 (2C), 128.2 (2C), 128.4 (2C), 128.6, 129.9 (2C), 133.8, 137.6, 140.9, 141.9, 154.2 (1/2C), 154.3 (1/2C). MS (FAB) m/z: 385 (MH^+). HRMS (FAB) Calcd $C_{23}H_{29}O_3S$ (MH^+): 385.1837. Found: 385.1839.

(*R*)-2-Methyl-5-(tetrahydro-2*H*-pyran-2-yloxy)-1-pentenyl *p*-tolyl sulfoxide (36). Using the procedure for **31**, the ketone **34** (352 mg, 1.89 mmol) was converted into **36** (1:1 *E*/*Z* mixture, 550 mg, 90%). A colorless oil: IR (KBr) cm^{-1}: 2941, 2868, 1597, 1493, 1440, 1379, 1352, 1120, 1080, 1036. ^{1}H NMR δ: 1.50–1.65 (6H, m, THP), 1.67–1.80 (2H, m, 4-H), 1.89 (3/2H, s, 2-CH_3), 2.17 (3/2H, s, 2-CH_3), 2.21–2.27 (1H, m, 3-H), 2.40 (3H, s, Ar-CH_3), 2.53–2.70 (1H, m, 3-H), 3.29–3.38 (1H, m, 5-H), 3.43–3.55 (1H, m, THP), 3.67–3.72 (1H, m, 5-H), 3.72–3.90 (1H, m, THP), 4.44–4.62 (1H, m, O–CH–O), 6.03–6.05 (1H, m, 1-H), 7.30 (2H, d, J=7.9 Hz, Ar-H), 7.50 (2H, m, Ar-H). ^{13}C NMR δ: 18.6 (1/4C), 18.7 (1/4C), 19.6 (1/4C), 19.7 (1/4C), 21.3, 23.1 (1/4C), 23.2 (1/4C), 25.4, 27.1 (1/2C), 27.2 (1/2C), 28.2 (1/2C), 28.4 (1/2C), 30.5 (1/4C), 30.6 (1/4C), 30.7 (1/2C), 35.8 (1/2C), 62.3 (1/4C), 62.4 (1/2C), 62.5 (1/4C), 66.4 (1/2C), 66.5 (1/4C), 66.7 (1/4C), 98.9 (1/2C), 99.0 (1/2C), 124.0, 124.1, 129.9 (2C), 132.1 (1/4C), 132.2 (1/4C), 132.8 (1/4C), 133.0 (1/4C), 140.7 (1/2C), 140.8 (1/2C), 141.9 (1/2C), 141.9 (1/2C), 151.5 (1/4C), 151.6 (1/4C), 151.9 (1/2C). MS (FAB) m/z: 323 (MH^+). HRMS (FAB) Calcd $C_{18}H_{27}O_3S$ (MH^+): 323.1681. Found: 323.1681.

(*E*)-5-[(*R*)-(*p*-Tolylsulfinyl)]-4-phenyl-4-pentenyl *p*-toluenesulfonate [(*E*)-37]. *p*-TsOH·H_2O (375 mg, 1.97 mmol) was added to a solution of (*E*)-**35** (379 mg, 0.99 mmol) in MeOH (10 ml) with stirring at rt. The stirring was continued at rt for 1 h. The reaction was quenched with saturated $NaHCO_3$ aqueous solution and the whole was extracted with

AcOEt. The extract was washed with water and brine prior to drying and solvent evaporation. The residue was chromatographed on silica gel with hexane–AcOEt (1:5) to give the alcohol (239 mg, 81%) as a colorless oil. $[\alpha]_D^{26}=-39.0$ (*c* 0.75, $CHCl_3$). IR (KBr) cm^{-1}: 3396, 2951, 1597, 1493, 1038, 1011. ^1H NMR δ: 1.60–1.68 (1H, m, 2-H), 1.77–1.86 (1H, m, 2-H), 2.41 (3H, s, Ar-CH_3), 2.75 (1H, t, *J*=6.1 Hz, OH), 3.04 (1H, quint, *J*=6.7 Hz, 3-H), 3.44 (1H, quint, *J*=6.7 Hz, 3-H), 3.61–3.67 (2H, m, 1-H), 6.50 (1H, s, 5-H), 7.33 (2H, d, *J*=7.9 Hz, Ar-H), 7.35–7.36 (3H, m, Ar-H), 7.39–7.41 (2H, m, Ar-H), 7.57 (2H, d, *J*=7.9 Hz, Ar-H). ^{13}C NMR δ: 21.3, 27.4, 30.9, 60.4, 124.2 (2C), 126.6 (2C), 128.7 (2C), 129.3, 130.0 (2C), 133.8, 138.2, 140.7, 141.3, 153.9. MS (FAB) *m/z*: 301 (MH^+). HRMS (FAB) Calcd $C_{18}H_{21}O_2S$ (MH^+): 301.1262. Found: 301.1263. Using the procedure for (*E*)-**7**, the alcohol (82 mg, 0.27 mmol) was converted into (*E*)-**37** (111 mg, 90%). A colorless oil: $[\alpha]_D^{27}=-31.0$ (*c* 1.09, $CHCl_3$). IR (KBr) cm^{-1}: 1597, 1360, 1176, 1039. ^1H NMR δ: 1.71–1.87 (2H, m, 2-H), 2.38 (3H, s, Ar-CH_3), 2.41 (3H, s, Ar-CH_3), 3.06 (2H, t, *J*=7.3 Hz, 3-H), 4.05 (2H, t, *J*=6.1 Hz, 1-H), 6.39 (1H, s, 5-H), 7.27–7.32 (9H, m, Ar-H), 7.51 (2H, d, *J*=8.5 Hz, Ar-H), 7.76 (2H, d, *J*=8.5 Hz, Ar-H). ^{13}C NMR δ: 21.3, 21.6, 27.6, 28.2, 69.4, 124.2 (2C), 126.6 (2C), 127.8 (2C), 128.8 (2C), 129.4, 129.8 (2C), 130.1 (2C), 132.9, 134.8, 137.9, 141.3 (2C), 144.8, 150.9. MS (EI) *m/z* (rel. int. %): 454 (M^+, 1.8), 91 (100). HRMS (EI) Calcd $C_{25}H_{26}O_4S_2$: 454.1272. *F*ound: 454.1263.

(*Z*)-5-[(*R*)-(*p*-Tolylsulfinyl)]-4-phenyl-4-pentenyl *p*-toluenesulfonate [(*Z*)-37]. Using the procedure for (*E*)-**37**, (*Z*)-**35** (179 mg, 0.47 mmol) was converted into the alcohol (132 mg, 94%). A colorless oil: $[\alpha]_D^{26}=-298.4$ (*c* 0.71, $CHCl_3$). IR (KBr) cm^{-1}: 3386, 2947, 1595, 1493, 1442, 1082, 1024. ^1H NMR δ: 1.63–1.67 (2H, m, 2-H), 2.41 (3H, s, Ar-CH_3), 2.56–2.66 (2H, m, 3-H), 3.61 (2H, br s, 5-H), 6.34 (2H, t, *J*=1.2 Hz, 1-H), 7.30 (2H, d, *J*=8.5 Hz, Ar-H), 7.35–7.37 (2H, m, Ar-H), 7.40–7.44 (3H, m, Ar-H), 7.46 (2H, d, *J*=8.5 Hz, Ar-H). ^{13}C NMR δ: 21.3, 29.9, 35.4, 61.2, 124.3 (2C), 128.1 (2C), 128.4 (2C), 128.7, 129.9 (2C), 133.6, 137.5, 141.1, 141.4, 154.7. MS (FAB) *m/z*: 301 (MH^+). HRMS (FAB) Calcd $C_{18}H_{21}O_2S$ (MH^+): 301.1262. Found: 301.1263. Using the procedure for (*E*)-**37**, the alcohol (179 mg, 0.60 mmol) was converted into (*Z*)-**37** (238 mg, 88%). A colorless oil: $[\alpha]_D^{27}=-174.2$ (*c* 0.35, $CHCl_3$). IR (KBr) cm^{-1}: 1358, 1597, 1176, 1036. ^1H NMR δ: 1.69–1.74 (2H, m, 2-H), 2.41 (3H, s, Ar-CH_3), 2.44 (3H, s, Ar-CH_3), 2.52 (2H, t, *J*=6.7 Hz, 3-H), 3.97 (2H, t, *J*=6.1 Hz, 1-H), 6.26 (1H, s, 5-H), 7.28–7.32 (6H, m, Ar-H), 7.41–7.45 (5H, m, Ar-H), 7.72 (2H, d, *J*=8.5 Hz, Ar-H). ^{13}C NMR δ: 21.3, 21.6, 26.5, 34.8, 69.2, 124.2 (2C), 127.7 (2C), 128.1 (2C), 128.5, 128.9 (2C), 129.8 (2C), 129.9 (2C), 132.6, 134.4, 136.9, 141.1, 141.5, 144.8, 152.6. MS (FAB) *m/z*: 455 (MH^+). HRMS (FAB) Calcd $C_{25}H_{27}O_4S_2$ (MH^+): 455.1351. Found: 455.1348.

4-Methyl-5-[(*R*)-(*p*-tolylsulfinyl)]-4-pentenyl *p*-toluenesulfonate (38). Using the procedure for **37**, **36** (630 mg, 1.95 mmol) was converted into **38** (1:1 *E*/*Z* mixture, 559 mg, 73%). A colorless oil: IR (KBr) cm^{-1}: 2924, 1597, 1358, 1176, 1038. ^1H NMR δ: 1.78–1.83 (1H, m, 2-H), 1.85 (3/2H, d, *J*=1.2 Hz, 4-CH_3), 1.86–1.97 (1H, m, 2-H), 2.12 (3/2H, d, *J*=1.2 Hz, 4-CH_3), 2.17–2.20 (1H, m, 3-H), 2.41 (3H, s, Ar-CH_3), 2.45 (3H, s, Ar-CH_3), 2.55–2.71 (1H, m, 3-H), 4.00 (1H, t, *J*=6.1 Hz, 1-H), 4.11 (1H, t, *J*=6.1 Hz, 1-H), 5.97 (1/2H, d, *J*=1.2 Hz, 5-H), 6.05 (1/2H, d, *J*=1.2 Hz, 5-H), 7.31 (2H, d, *J*=7.9 Hz, Ar-H), 7.33 (1H, d, *J*=7.9 Hz, Ar-H), 7.35 (1H, d, *J*=7.9 Hz, Ar-H), 7.45 (1H, d, *J*=7.9 Hz, Ar-H), 7.46 (1H, d, *J*=8.5 Hz, Ar-H), 7.75 (1H, d, *J*=7.9 Hz, Ar-H), 7.81 (1H, d, *J*=8.5 Hz, Ar-H). ^{13}C NMR δ: 18.7 (1/2C), 21.3, 21.6, 23.1 (1/2C), 26.4 (1/2C), 27.6 (1/2C), 29.8 (1/2C), 34.8 (1/2C), 69.2 (1/2C), 69.5 (1/2C), 124.0, 124.1, 127.7, 127.8, 129.9, 129.9, 129.9 (2C), 132.5 (1/2C), 132.9, 133.3 (1/2C), 141.0, 141.1 (1/2C), 141.2 (1/2C), 144.9 (1/2C), 144.9 (1/2C), 150.1 (1/2C), 150.5 (1/2C). MS (FAB) *m/z*: 411 (MH^+). HRMS (FAB) Calcd $C_{20}H_{25}O_4S_2$ (MH^+): 393.1194. Found: 393.1207.

(*E*)-(*R*)-5-Iodo-2-phenyl-1-pentenyl *p*-tolyl sulfoxide [(*E*)-39]. Using the procedure for (*E*)-**10**, the tosylate (*E*)-**37** (50 mg, 0.11 mmol) was converted into (*E*)-**39** (45 mg, quant). A yellow oil: $[\alpha]_D^{27}=-65.8$ (*c* 0.89, $CHCl_3$). IR (KBr): 2954, 1597, 1211, 1082, 1039. ^1H NMR δ: 1.87–2.06 (2H, m, 4-H), 2.38 (3H, s, Ar-CH_3), 3.09–3.20 (4H, m, 3-H and 5-H), 6.44 (1H, s, 1-H), 7.30–7.36 (7H, m, Ar-H), 7.55 (2H, d, *J*=7.9 Hz, Ar-H). ^{13}C NMR δ: 5.4, 21.5, 32.4 (2C), 124.2 (2C), 126.6 (2C), 128.7 (2C), 129.4, 130.0 (2C), 134.8, 138.0, 141.2, 141.3, 150.8. MS (EI) *m/z* (rel. int. %): 410 (M^+, 9.4), 362 (100). HRMS (EI) Calcd $C_{18}H_{19}IOS$: 410.0202. Found: 410.0186.

(*Z*)-(*R*)-5-Iodo-2-phenyl-1-pentenyl *p*-tolyl sulfoxide [(*Z*)-39]. Using the procedure for (*E*)-**10**, the tosylate (*Z*)-**37** (73 mg, 0.16 mmol) was converted into (*Z*)-**39** (60 mg, 92%). A colorless oil: $[\alpha]_D^{26}=-210.9$ (*c* 1.11, $CHCl_3$). IR (KBr) cm^{-1}: 2951, 1595, 1217, 1036. ^1H NMR δ: 1.87 (2H, quint, *J*=7.3 Hz, 4-H), 2.41 (3H, s, Ar-CH_3), 2.60 (1H, dd, *J*=14.6, 7.5 Hz, 3-H), 2.66 (1H, dd, *J*=14.6, 7.0 Hz, 3-H), 3.10 (1H, dt, *J*=11.6, 6.7 Hz, 5-H), 3.12 (1H, dt, *J*=11.6, 6.7 Hz, 5-H), 6.37 (1H, s, 1-H), 7.31 (2H, d, *J*=7.9 Hz, Ar-H), 7.34–7.45 (5H, m, Ar-H), 7.47 (2H, d, *J*=7.9 Hz, Ar-H). ^{13}C NMR δ: 5.3, 21.5, 30.7, 39.6, 124.3 (2C), 128.1 (2C), 128.5 (2C), 128.9, 129.9 (2C), 134.7, 137.0, 141.1, 141.7, 152.4. MS (FAB) *m/z*: 411 (MH^+). HRMS (FAB) Calcd $C_{18}H_{19}IOS$ (MH^+): 411.0284. Found: 411.0277.

(*R*)-5-Iodo-2-methyl-1-pentenyl *p*-tolyl sulfoxide (40). Using the procedure for (*E*)-**10**, the tosylate **38** (483 mg, 1.23 mmol) was converted into **40** (1:1 *E*/*Z* mixture, 370 mg, 86%). A colorless oil: IR ($CHCl_3$): 2918, 1597, 1302, 1082, 1038. ^1H NMR δ: 1.87 (3/2H, d, *J*=1.2 Hz, 2-CH_3), 1.91–1.96 (1H, m, 4-H), 1.99–2.05 (1/2H, m, 4-H), 2.07–2.12 (1/2H, m, 4-H), 2.14 (3/2H, d, *J*=1.2 Hz, 2-CH_3), 2.22–2.25 (1H, t, *J*=7.3 Hz, 3-H), 2.39 (3H, s, Ar-CH_3), 2.64–2.73 (1H, m, 3-H), 3.06–3.14 (1H, m, 5-H), 3.18–3.26 (1H, m, 5-H), 6.04–6.05 (1/2H, br s, 1-H), 6.06 (1/2H, br s, 1-H), 7.29 (1H, d, *J*=7.9 Hz, Ar-H), 7.30 (1H, d, *J*=7.9 Hz, Ar-H), 7.46 (1H, d, *J*=7.9 Hz, Ar-H), 7.49 (1H, d, *J*=7.9 Hz, Ar-H). ^{13}C NMR δ: 5.0 (1/2C), 5.1 (1/2C), 18.8 (1/2C), 21.5, 23.4 (1/2C), 30.2 (1/2C), 31.6 (1/2C), 34.3 (1/2C), 39.2 (1/2C), 123.7, 123.9, 129.7 (2C), 132.7 (1/2C), 133.4 (1/2C), 140.7 (1/2C), 140.8 (1/2C), 141.2, 149.4 (1/2C), 149.9 (1/2C). MS (EI) *m/z* (rel. int. %): 348 (M^+, 46.5), 300 (100). HRMS (EI) Calcd $C_{13}H_{17}IOS$: 348.0045. Found: 348.0064.

Typical procedure for intramolecular alkylation of iodides

(*R*)-1-Cyclohexenyl *p*-tolyl sulfoxide (41). A solution of the iodide (*E*)-**11** (43 mg, 0.12 mmol) in dry THF (2.3 ml) was added to a solution of LDA (1.5 equiv.) (prepared from *i*-Pr_2NH (25 μl, 0.18 mmol) and 1.58 M *n*-BuLi in hexane (115 μl, 0.18 mmol) in THF (2.3 ml)]. The solution was stirred at −78°C under N_2. After 30 min, the reaction was quenched with saturated aqueous NH_4Cl solution and the whole was extracted with AcOEt. The extract was washed with brine prior to drying and solvent evaporation. The crude product was purified by preparative TLC on silica gel with hexane–AcOEt (2:1) to give the 1-cycloalkenyl sulfoxide **41** (22 mg, 82%). Colorless powder: mp 59.8–60.2°C (ether). $[\alpha]_D^{25}$=+8.60 (*c* 0.48, $CHCl_3$). IR (KBr) cm^{-1}: 2933, 1493, 1084, 1049, 1014. ^1H NMR δ: 1.48–1.56 (1H, m, 4-H), 1.58–1.67 (4H, m, 3-, 4-, and 5-H), 2.13–2.16 (1H, m, 3-H), 2.24–2.25 (2H, m, 6-H), 2.40 (3H, s, Ar-CH_3), 6.67–6.68 (1H, m, 2-H), 7.28–7.29 (2H, d, *J*=7.9 Hz, Ar-H), 7.28–7.29 (2H, d, *J*=7.9 Hz, Ar-H). ^{13}C NMR δ: 19.5, 21.3, 21.7, 22.0, 25.7, 124.8 (2C), 129.7 (2C), 133.7, 139.5, 140.9, 143.7. MS (EI) *m/z* (rel. int. %): 220 (M^+, 100). HRMS (EI) Calcd $C_{13}H_{16}OS$: 220.0922. Found: 220.0941.

(*R*)-1-Cyclopentenyl *p*-tolyl sulfoxide (42). Colorless powder: mp 64.9–65.7°C (ether). $[\alpha]_D^{28}$=+56.9 (*c* 0.65, $CHCl_3$). IR (KBr) cm^{-1}: 2926, 1597, 1039. ^1H NMR δ: 1.86–1.98 (2H, m, 4-H), 2.07–2.13 (1H, m, 3-H), 2.38 (3H, s, Ar-CH_3), 2.40–2.56 (3H, m, 3-H and 5-H), 6.52 (1H, t, *J*=1.8 Hz, 2-H), 7.28 (2H, d, *J*=7.9 Hz, Ar-H), 7.47 (2H, d, *J*=7.9 Hz, Ar-H). ^{13}C NMR δ: 21.4, 23.0, 28.0, 32.9, 124.6 (2C), 129.8 (2C), 137.9, 139.4, 140.1, 147.8. MS (EI) *m/z* (rel. int. %): 206 (M^+, 72.9), 158 (100), 143 (100). HRMS (EI) Calcd $C_{12}H_{14}OS$: 206.0765. Found: 206.0773.

(*R*)-1-Cycloheptenyl *p*-tolyl sulfoxide (43). Colorless oil: $[\alpha]_D^{24}$=+10.4 (*c* 0.52, $CHCl_3$). IR (KBr) cm^{-1}: 2922, 1597, 1446, 1082, 1047. ^1H NMR δ: 1.26–1.38 (2H, m, 5-H), 1.52–1.58 (2H, m, 4-H), 1.63–1.66 (1H, m, 6-H), 1.68–1.72 (1H, m, 6-H), 2.01 (1H, ddd, *J*=15.9, 6.7, 2.4 Hz, 3-H), 2.19 (1H, ddd, *J*=15.9, 6.7, 2.4 Hz, 3-H), 2.30–2.38 (2H, m, 7-H), 2.40 (3H, s, Ar-CH_3), 6.80 (1H, t, *J*=6.7 Hz, 2-H), 7.28 (2H, d, *J*=7.9 Hz, Ar-H), 7.47 (2H, d, *J*=7.9 Hz, Ar-H). ^{13}C NMR δ: 21.3, 24.9, 26.2, 26.6, 29.0, 31.3, 125.1 (2C), 130.0 (2C), 137.2, 139.7, 140.9, 148.0. MS (EI) *m/z* (rel. int. %): 234 (M^+, 70.1), 124 (100). HRMS (EI) Calcd $C_{14}H_{18}OS$: 234.1078. Found: 234.1075.

(*R*)-2-Phenyl-1-cyclopentenyl *p*-tolyl sulfoxide (45). Colorless powder: mp 96.3–97.1°C (ether). $[\alpha]_D^{26}$=−420.6 (*c* 0.53, $CHCl_3$). IR (KBr) cm^{-1}: 1597, 1491, 1080, 1041, 1014. ^1H NMR δ: 1.79–1.88 (1H, m, 4-H), 1.92–2.00 (1H, m, 4-H), 2.06–2.11 (1H, m, 3-H), 2.33 (3H, s, Ar-CH_3), 2.85–2.93 (3H, m, 3-H and 5-H), 7.22 (2H, d, *J*=7.9 Hz, Ar-H), 7.29–7.38 (5H, m, Ar-H), 7.43 (2H, d, *J*=7.9 Hz, Ar-H). ^{13}C NMR δ: 21.3, 21.6, 28.8, 38.8, 124.4 (2C), 127.6, 128.0, 128.3 (2C), 128.5 (2C), 128.9, 129.6, 129.8 (2C), 131.7, 140.7. MS (EI) *m/z* (rel. int. %): 282 (M^+, 4.3), 234 (100). HRMS (FAB) Calcd $C_{18}H_{19}OS$ (MH^+): 283.1157. Found: 283.1169.

(*R*)-2-Methyl-1-cyclopentenyl *p*-tolyl sulfoxide (46). Colorless powder: mp 104.0–104.6°C (ether). $[\alpha]_D^{24}$=−155.0 (*c* 0.21, $CHCl_3$). IR (KBr) cm^{-1}: 2858, 1597, 1083, 1043, 1026, 1014. ^1H NMR δ: 1.69–1.84 (1H, m, 4-H), 1.82–1.91 (1H, m, 4-H), 1.92–1.95 (1H, m, 3-H), 2.10 (3H, s, 2-CH_3), 2.37 (3H, s, Ar-CH_3), 2.43–2.48 (2H, m, 5-H), 2.70–2.75 (1H, m, 3-H), 7.26 (2H, d, *J*=7.9 Hz, Ar-H), 7.40 (2H, d, *J*=7.9 Hz, Ar-H). ^{13}C NMR δ: 15.0, 21.3 (2C), 27.5, 39.4, 124.0 (2C), 129.6 (2C), 138.6, 139.7, 140.4, 150.9. MS (EI) *m/z* (rel. int. %): 220 (M^+, 76.6), 124 (100). HRMS (EI) Calcd $C_{13}H_{16}OS$: 220.0922. Found: 220.0926.

(*Rs*)-5-Methyl-1-cyclopentenyl *p*-tolyl sulfoxide (47). A colorless oil: IR (KBr) cm^{-1}: 2956, 1598, 1082, 1014. ^1H NMR δ: 0.89 (3/2H, d, *J*=6.7 Hz, 5-CH_3), 1.04 (3/2H, d, *J*=6.7 Hz, 5-CH_3), 1.51–1.53 (1H, m, 4-H), 2.04–2.16 (1H, m, 4-H), 2.29–2.40 (1H, m, 3-H), 2.42–2.60 (3/2H, m, 3- and 5-H), 2.34 (3H, s, Ar-CH_3), 2.72 (1/2H, m, 5-H), 6.33 (1/2H, s, 2-H), 6.44 (1/2H, s, 2-H), 7.22 (1H, d, *J*=7.9 Hz, Ar-H), 7.23 (1H, d, *J*=7.9 Hz, Ar-H), 7.43 (1H, d, *J*=7.9 Hz, Ar-H), 7.46 43 (1H, d, *J*=7.9 Hz, Ar-H). ^{13}C NMR δ: 19.6 (1/2C), 20.2 (1/2C), 21.4 (1/2C), 21.5 (1/2C), 31.1, 33.5 (1/2C), 33.6 (1/2C), 38.8 (1/2C), 39.0 (1/2C), 124.9, 125.5, 129.7, 129.9, 135.0, 139.8, 141.0, 141.8. MS (EI) *m/z* (rel. int. %): 220 (M^+, 100), 172 (89). HRMS (EI) Calcd $C_{13}H_{16}OS$: 220.0922. Found: 220.0925.

6-Chloro-1-hexenyl *p*-tolyl sulfoxide dimer (48). A colorless oil: IR (KBr) cm^{-1}: 2937, 2929, 1493, 1084, 1043. ^1H NMR (major) δ: 1.04–1.27 (2H, m), 1.38–1.86 (8H, m), 2.29 (2H, td, *J*=7.9, 7.3 Hz, CH_2CH═), 2.41 (3H, s, Ar-CH_3), 2.42 (3H, s, Ar-CH_3), 2.29 (1H, dd, *J*=12.8, 4.3 Hz, CH_2S(O)Tol), 2.72 (1H, dd, *J*=12.8, 10.4 Hz, CH_2S(O)Tol), 2.81–2.92 (1H, m, C*H*C═), 3.30–3.43 (2H, m, CH_2Cl), 3.55 (2H, t, *J*=6.4 Hz, CH_2Cl), 6.47 (1H, t, *J*=7.6 Hz, CH_2CH═), 7.27 (2H, d, *J*=8.5 Hz, Ar-H), 7.28 (2H, d, *J*=8.5 Hz, Ar-H), 7.36 (2H, d, *J*=8.5 Hz, Ar-H), 7.48 (2H, d, *J*=8.5 Hz, Ar-H). ^{13}C NMR δ: 21.4 (2C), 24.6, 26.2, 28.0, 31.5, 32.0, 32.1, 33.1, 44.5, 44.8, 61.8, 124.1 (2C), 125.8 (2C), 129.9 (2C), 130.0 (2C), 135.3, 139.6, 140.6, 141.7, 142.0, 144.9. MS (FAB) *m/z*: 513 (MH^+). HRMS (FAB) Calcd $C_{26}H_{35}Cl_2O_2S_2$ (MH^+): 513.1456. Found: 513.1449.

8-Iodo-1-octenyl *p*-tolyl sulfoxide dimer (49). A colorless oil: IR (KBr) cm^{-1}: 2927, 1597, 1493, 1460, 1081, 1047. ^1H NMR δ: 0.95–1.44 (14H, m), 1.62–1.77 (4H, m), 2.15–2.19 (2H, m, CH_2CH═), 2.30–2.45 (1H, m, C*H*C═), 2.35 (6H, s, Ar-CH_3), 2.59–2.75 (2H, m, CH_2S(O)Tol), 3.07–3.11 (4H, m, CH_2I), 6.39 (1H, t, *J*=7.3 Hz, CH_2CH═), 7.20–7.22 (4H, m, Ar-H), 7.29 (2H, d, *J*=7.9 Hz, Ar-H), 7.42 (2H, d, *J*=7.9 Hz, Ar-H). ^{13}C NMR δ: 7.1, 7.0, 21.5 (2C), 27.1, 28.3 (2C), 28.8 (2C), 30.3 (2C), 32.3, 33.2, 33.3 (2C), 62.0, 124.0 (2C), 125.8 (2C), 129.8 (4C), 135.4, 139.7, 140.7, 141.5, 141.6, 144.4. MS (EI) *m/z* (rel. int. %): 234 (M^+, 70.1), 124 (100). MS (FAB) *m/z*: 753 (MH^+). HRMS (FAB) Calcd $C_{30}H_{43}I_2O_2S_2$ (MH^+): 753.0776. Found: 753.0793.

(*E*)-(*R*)- and (*Z*)-(*R*)-1-Hexenyl *p*-tolyl sulfoxide [(*E*)- and (*Z*)-50]. Using the procedure for **31**, *n*-pentanal (1.99 g, 23.1 mmol) was converted into (*E*)-**50** (1.85 g, 36%) and (*Z*)-**50** (2.48 g, 48%). (*E*)-**50** (a colorless oil):

$[\alpha]_D^{27}$=+109.3 (*c* 1.19, $CHCl_3$). IR (KBr) cm^{-1}: 2926, 1084, 1047. ^1H NMR δ: 0.84 (3H, t, *J*=7.3 Hz, 6-H), 1.28 (2H, dt, *J*=14.6, 7.3 Hz, 5-H), 1.38 (2H, quint, *J*=7.3 Hz, 4-H), 2.16 (2H, dd, *J*=14.6, 6.7 Hz, 3-H), 2.41 (3H, s, Ar-CH_3), 6.15 (1H, dd, *J*=15.3, 1.2 Hz, 1-H), 6.54 (1H, dt, *J*=15.3, 7.9 Hz, 2-H), 7.25 (2H, d, *J*=7.9 Hz, Ar-H), 7.44 (2H, d, *J*=7.9 Hz, Ar-H). ^{13}C NMR δ: 13.7, 21.3, 21.4, 22.1, 30.1, 31.6, 124.5, 129.9 (2C), 135.0 (2C), 141.0, 141.2. MS (FAB) *m/z*: 223 (MH^+). HRMS (FAB) Calcd $C_{13}H_{19}OS$ (MH^+): 223.1157. Found: 223.1149. (*Z*)-**50** (a colorless oil): $[\alpha]_D^{25}$=−307.2 (*c* 0.45, $CHCl_3$). IR (KBr) cm^{-1}: 2954, 1082, 1041. ^1H NMR δ: 0.88 (3H, t, *J*=6.7 Hz, 6-H), 1.33 (2H, dt, *J*=6.7, 15.3 Hz, 5-H), 1.41 (2H, quint, *J*=6.7 Hz, 4-H), 2.33 (3H, s, Ar-CH_3), 2.45 (1H, dt, *J*=14.0, 6.7 Hz, 3-H), 2.56 (1H, dt, *J*=14.0, 6.7 Hz, 3-H), 6.08–6.14 (2H, m, 1-H, 2-H), 7.24 (2H, d, *J*=7.9 Hz, Ar-H), 7.42 (2H, d, *J*=7.3 Hz, Ar-H). ^{13}C NMR δ: 13.7, 21.3, 22.1, 29.0, 31.1, 124.0 (2C), 129.9 (2C), 136.8, 141.0, 141.2, 141.9. MS (FAB) *m/z*: 223 (MH^+). HRMS (FAB) Calcd $C_{13}H_{19}OS$ (MH^+): 223.1157. Found: 223.1146.

Deprotonation and reprotonation of (*E*)- and (*Z*)-50

A solution of the vinylic sulfoxide (*Z*)-**50** (114 mg, 0.51 mmol) in THF (2 ml) was added to a stirred LDA solution [prepared from *n*-BuLi (1.50 M in hexane, 0.51 ml, 0.77 mmol) and *i*-Pr_2NH (0.12 ml, 0.82 mmol) in THF (5 ml)] at −78°C under N_2 and the mixture was stirred at −78°C. The reaction was quenched with water, and the whole was extracted with AcOEt. The extract was washed with water and brine prior to drying and solvent evaporation. The residue was chromatographed on silica gel with hexane–acetone (5:2) to give (*E*)-**50** (94 mg, 83%).

2-[(Tetrahydro-2*H*-pyran-2-yloxy)methyl]phenylmethanol (51). A mixture of *o*-xyleneglycol (5.00 g, 36.2 mmol) and dihydropyran (3.27 ml, 36.2 mmol) in the presence of PPTS (909 mg, 3.62 mmol) in CH_2Cl_2 (200 ml) was stirred at rt for 1 h. The reaction was quenched with saturated $NaHCO_3$ aqueous solution and the whole was extracted with AcOEt. The extract was washed with water and brine prior to drying and solvent evaporation. The residue was chromatographed on silica gel with hexane–AcOEt (1:2) to give **51** (5.39 g, 67%) as a colorless oil. IR (KBr) cm^{-1}: 3415, 2947, 1454, 1122, 1024. ^1H NMR δ: 1.50–1.60 (4H, m, THP), 1.68–1.81 (2H, m, THP), 3.53–3.57 (1H, m, THP), 3.85–3.90 (1H, m, THP), 4.56 (1H, d, *J*=11.6 Hz, THPOCH_2), 4.66 (1H, dd, *J*=11.6, 6.1 Hz, CH_2OH), 4.68 (1H, dd, *J*=11.6, 6.1 Hz, CH_2OH), 4.71 (1H, t, *J*=3.7 Hz, O–CH–O), 4.88 (1H, d, *J*=11.6 Hz, THPOCH_2), 7.26–7.39 (4H, m, Ar-H). ^{13}C NMR δ: 19.0, 25.1, 30.3, 62.1, 63.2, 67.6, 97.7, 127.7, 128.4, 129.1, 129.7, 135.6, 140.1. MS (FAB) *m/z*: 223 (MH^+). HRMS (FAB) Calcd $C_{13}H_{19}O_3$ (MH^+): 223.1334. Found: 223.1318.

2-[(Tetrahydro-2*H*-pyran-2-yloxy)methyl]benzaldehyde (52). Using the procedure for **14**, the alcohol **51** (3.00 g, 13.5 mmol) was converted into **52** (2.15 g, 72%). A colorless oil: IR (KBr) cm^{-1}: 2941, 1697, 1201, 1034. ^1H NMR δ: 1.54–1.89 (6H, m, THP), 3.53–3.57 (1H, m, THP), 3.87–3.91 (1H, m, THP), 4.77 (1H, t, *J*=3.7 Hz, O–CH–O), 4.94 (1H, d, *J*=14.0 Hz, THPOCH_2), 5.18 (1H, d, *J*=14.0 Hz, THPOCH_2), 7.46 (1H, t, *J*=7.3 Hz, Ar-H), 7.59 (1H, dt, *J*=7.3, 1.2 Hz, Ar-H), 7.64 (1H, t, *J*=7.9 Hz, Ar-H), 7.86 (1H, dd, *J*=7.3, 1.2 Hz, Ar-H), 10.26 (1H, s, CHO). ^{13}C NMR δ: 19.3, 25.3, 30.5, 62.3, 66.3, 98.3, 127.5, 128.3, 131.9, 133.4, 133.7, 140.8, 192.6. MS (EI) *m/z*(%): 220 (M^+, 2.5), 213 (100). HRMS (EI) Calcd $C_{13}H_{16}O_3$: 220.1099. Found: 220.1090.

(*E*)-(*R*)- and (*Z*)-(*R*)-2-[2-[(Tetrahydro-2*H*-pyran-2-yloxy)-methyl]phenyl]ethenyl *p*-tolyl sulfoxide [(*E*)-53 and (*Z*)-53]. Using the procedure for **31**, the aldehyde **52** (5.77 g, 26.1 mmol) was converted into (*E*)-**53** (5.15 g, 55%) and (*Z*)-**53** (3.41 g, 37%). (*E*)-**53** (a colorless oil): $[\alpha]_D^{26}$=+98.4 (*c* 0.43, $CHCl_3$). IR (KBr) cm^{-1}: 3022, 3959, 1120, 1038. ^1H NMR δ: 1.54–1.87 (6H, m, THP), 2.41 (3H, s, Ar-CH_3), 3.56–3.59 (1H, m, THP), 3.90–3.95 (1H, m, THP), 4.59 (2/3H, d, *J*=12.2 Hz, THPOCH_2), 4.61 (1/3H, d, *J*=12.2 Hz, THPOCH_2), 4.62–4.74 (1H, m, O–CH–O), 4.90 (2/3H, d, *J*=12.2 Hz, THPOCH_2), 4.92 (1/H, d, *J*=12.2 Hz, THPOCH_2), 6.80 (1H, d, *J*=15.9 Hz, 1-H), 7.28–7.34 (4H, m, Ar-H), 7.42 (1H, d, *J*=7.3 Hz, Ar-H), 7.46 (1H, d, *J*=7.3 Hz, Ar-H), 7.57 (2H, d, *J*=8.5 Hz, Ar-H), 7.72 (1H, dd, *J*=15.9, 2.4 Hz, 2-H). ^{13}C NMR δ: 19.3 (1/3C), 19.4 (2/3C), 21.4, 25.4, 30.5, 62.2 (1/3C), 62.3 (2/3C), 66.9 (1/3C), 67.0 (2/3C), 98.0 (1/3C), 98.1 (2/3C), 124.8 (2C), 126.9, 128.2, 129.5, 129.7, 130.1 (2C), 133.2, 133.6, 135.1, 136.5, 140.7, 141.6. MS (FAB) *m/z*: 379 (MNa^+). HRMS (FAB) Calcd $C_{21}H_{24}NaO_3S$ (MNa^+): 379.1344. Found: 379.1329. (*Z*)-**53** (a colorless oil): $[\alpha]_D^{26}$=−313.7 (*c* 0.37, $CHCl_3$). IR (KBr) cm^{-1}: 2943, 2870, 1080, 1036. ^1H NMR δ: 1.52–1.84 (6H, m, THP), 2.41 (3H, s, Ar-CH_3), 3.51–3.56 (1H, m, THP), 3.84–3.88 (1H, m, THP), 4.47 (2/3H, d, *J*=12.2 Hz, THPOCH_2), 4.49 (1/3H, d, *J*=12.2 Hz, THPOCH_2), 4.66–4.67 (1H, m, O–CH–O), 4.76 (1/3H, dd, *J*=12.2 Hz, THPOCH_2), 4.79 (2/3H, dd, *J*=12.2 Hz, THPOCH_2), 6.53 (1H, dd, *J*=10.1, 6.7 Hz, 2-H), 7.35 (2H, d, *J*=7.9 Hz, Ar-H), 7.37–7.42 (3H, m, Ar-H), 7.46–7.52 (3H, m, Ar-H), 7.56 (1H, dd, *J*=6.7 Hz, 2-H). ^{13}C NMR δ: 19.3, 21.4, 25.4, 30.5, 62.3, 66.9, 97.9 (1/3C), 98.0 (2/3C), 124.4 (2C), 127.8 (1/3C), 127.8 (2/3C), 129.0, 129.4, 130.0 (2C), 130.2, 133.1, 136.5, 137.2, 138.4, 141.4, 141.5. MS (FAB) *m/z*: 357 (MH^+). HRMS (FAB) Calcd $C_{21}H_{25}O_3S$ (MH^+): 357.1525. Found: 357.1549.

[2-[(*E*)-2-[(*R*)-(*p*-Tolylsulfinyl)]ethenyl]phenyl]methanol [(*E*)-54]. Using the procedure for (*E*)-**37**, the THP ether (*E*)-**53** (1.92 g, 5.38 mmol) was converted into (*E*)-**54** (1.11 g, 76%). Colorless prisms: mp 233.0–133.0°C ($CHCl_3$). $[\alpha]_D^{26}$=+189.7 (*c* 0.47, $CHCl_3$). IR (KBr) cm^{-1}: 3354, 3030, 1084, 1039. ^1H NMR δ: 2.40 (3H, s, Ar-CH_3), 4.81 (2H, d, *J*=5.5 Hz, CH_2OH), 6.77 (1H, d, *J*=15.3 Hz, 1-H), 7.25–7.28 (1H, m, Ar-H), 7.30 (2H, d, *J*=7.9 Hz, Ar-H), 7.33 (1H, dd, *J*=7.3, 1.2 Hz, Ar-H), 7.43 (2H, d, *J*=7.3 Hz, Ar-H), 7.56 (2H, d, *J*=7.9 Hz, Ar-H), 7.70 (1H, d, *J*=15.3 Hz, 2-H). ^{13}C NMR δ: 21.4, 62.7, 125.0 (2C), 126.9 (2C), 128.0, 128.8, 129.6, 130.1, 132.5, 133.4, 135.0, 139.3, 149.2, 141.8. MS (FAB) *m/z*: 273 (MH^+). HRMS (FAB) Calcd $C_{16}H_{17}O_2S$ (MH^+): 273.0949. Found: 273.0940.

[2-[(*Z*)-2-[(*R*)-(*p*-Tolylsulfinyl)]ethenyl]phenyl]methanol [(*Z*)-54]. Using the procedure for (*E*)-**37**, the THP ether (*Z*)-**53** (1.24 g, 3.47 mmol) was converted into (*Z*)-**54** (663 mg,

70%). A colorless oil: $[\alpha]_D^{28}=-384.1$ (*c* 0.77, $CHCl_3$). IR (KBr) cm^{-1}: 3332, 2922, 1082, 1022. ^1H NMR δ: 2.39 (3H, s, Ar-CH_3), 4.62 (2H, d, *J*=5.5 Hz, CH_2OH), 6.49 (1H, d, *J*=10.4 Hz, 1-H), 7.28 (2H, d, *J*=8.5 Hz, Ar-H), 7.35 (1H, dd, *J*=7.3, 1.2 Hz, Ar-H), 7.37 (1H, dd, *J*=7.3, 1.2 Hz, Ar-H), 7.39 (1H, d, *J*=10.4 Hz, 2-H), 7.39–7.44 (2H, m, Ar-H), 7.47 (2H, d, *J*=7.9 Hz, Ar-H). ^{13}C NMR δ: 21.4, 62.8, 124.4 (2C), 127.5 (2C), 128.3, 129.4, 129.9, 130.0, 132.5, 137.8, 138.1, 139.3, 140.8, 141.5. MS (FAB) *m/z*: 273 (MH^+). HRMS (FAB) Calcd $C_{16}H_{17}O_2S$ (MH^+): 273.0949. Found: 273.0947.

(*E*)-(*R*)-2-[2-(Chloromethyl)phenyl]ethenyl *p*-tolyl sulfoxide [(*E*)-55]. Using the procedure for (*E*)-**7**, the alcohol (*E*)-**54** (1.05 g, 3.86 mmol) was converted into (*E*)-**55** (711 mg, 64%). Colorless needles: mp 205.0–106.0°C ($CHCl_3$). $[\alpha]_D^{27}=+167.1$ (*c* 0.47, $CHCl_3$). IR (KBr) cm^{-1}: 3022, 2922, 1263, 1084. ^1H NMR δ: 2.40 (3H, s, Ar-CH_3), 4.68 (1H, d, *J*=11.6 Hz, CH_2Cl), 4.71 (1H, d, *J*=11.6 Hz, CH_2Cl), 6.83 (1H, d, *J*=15.3 Hz, 1-H), 7.28–7.38 (5H, m, Ar-H), 7.43–7.46 (1H, m, Ar-H), 7.59 (2H, d, *J*=7.9 Hz, Ar-H), 7.73 (1H, d, *J*=15.3 Hz, 2-H). ^{13}C NMR δ: 21.1, 43.7, 124.6 (2C), 127.1, 128.9, 129.4, 129.9 (2C), 130.2, 131.4, 133.0, 135.3, 136.0, 140.1, 141.5. MS (FAB) *m/z*: 291 (MH^+). HRMS (FAB) Calcd $C_{16}H_{16}ClOS$ (MH^+): 291.0611. Found: 291.0605.

(*Z*)-(*R*)-2-[2-(Chloromethyl)phenyl]ethenyl *p*-tolyl sulfoxide [(*Z*)-55]. Using the procedure for (*E*)-**7**, the alcohol (*Z*)-**54** (600 mg, 2.20 mmol) was converted into (*Z*)-**55** (532 mg, 83%). A colorless oil: $[\alpha]_D^{26}=-352.8$ (*c* 0.90, $CHCl_3$). IR (KBr) cm^{-1}: 3022, 1493, 1082, 1038. ^1H NMR δ: 2.41 (3H, s, Ar-CH_3), 4.51 (1H, d, *J*=11.6 Hz, CH_2Cl), 4.62 (1H, d, *J*=11.6 Hz, CH_2Cl), 6.62 (1H, d, *J*=10.4 Hz, 1-H), 7.32 (2H, d, *J*=7.9 Hz, Ar-H), 7.41–7.44 (4H, m, Ar-H), 7.50 (2H, d, *J*=7.9 Hz, Ar-H), 7.56–7.57 (1H, m, 2-H). ^{13}C NMR δ: 21.3, 44.0, 124.3 (2C), 128.8, 129.6, 130.0 (2C), 130.0, 130.5, 133.5, 135.4, 136.0, 139.6, 140.9, 141.5. MS (FAB) *m/z*: 383 (MH^+). HRMS (FAB) Calcd $C_{16}H_{16}ClOS$ (MH^+): 382.9966. Found: 382.9983.

(*E*)-(*R*)-2-[2-(Bromomethyl)phenyl]ethenyl *p*-tolyl sulfoxide [(*E*)-56]. A mixture of (*E*)-**55** (50 mg, 0.17 mmol) and NaBr (89 mg, 0.86 mmol) in DMF–CH_2Br_2 (1.5 ml) was refluxed at 100°C for 2 h. After cooling, the reaction was quenched with brine and the whole was extracted with ether. The extract was washed with brine prior to drying and solvent evaporation. The residue was chromatographed on silica gel with hexane–AcOEt (3:1) to give (*E*)-**56** (46 mg, 82%) as colorless needles. Mp 121.5–122.5°C (hexane–AcOEt). $[\alpha]_D^{26}=+151.5$ (*c* 0.51, $CHCl_3$). IR (KBr) cm^{-1}: 3018, 1493, 1032. ^1H NMR δ: 2.41 (3H, s, Ar-CH_3), 4.59 (1H, d, *J*=11.0 Hz, CH_2Br), 4.62 (1H, d, *J*=11.0 Hz, CH_2Br), 6.84 (1H, d, *J*=15.3 Hz, 1-H), 7.29 (1H, m, Ar-H), 7.30 (1H, m, Ar-H), 7.33 (2H, d, *J*=7.9 Hz, Ar-H), 7.37 (1H, m, Ar-H), 7.44 (1H, m, Ar-H), 7.60 (2H, d, *J*=7.9 Hz, Ar-H), 7.70 (1H, d, *J*=15.3 Hz, 2-H). ^{13}C NMR δ: 21.4, 30.7, 124.9 (2C), 127.5, 129.2, 129.8, 130.2 (2C), 130.6, 132.0, 133.3, 135.9, 136.2, 140.3, 141.9. MS (FAB) *m/z*: 335 (MH^+). HRMS (FAB) Calcd $C_{16}H_{16}BrOS$ (MH^+): 335.0105. Found: 335.0103.

(*E*)-(*R*)-2-[2-(Iodomethyl)phenyl]ethenyl *p*-tolyl sulfoxide [(*E*)-57]. A mixture of (*E*)-**55** (342 mg, 1.18 mmol), $NaHCO_3$ (424 mg, 5.04 mmol), and NaI (941 mg, 6.28 mmol) in acetone (12 ml) was stirred at rt for 4 h. The reaction was quenched with water and the whole was extracted with AcOEt. The extract was washed with saturated $Na_2S_2O_3$ aqueous solution, saturated $NaHCO_3$ aqueous solution, and brine prior to drying and solvent evaporation. The residue was chromatographed on silica gel with hexane–AcOEt (2:1) to give (*E*)-**57** (374 mg, 84%) as colorless needles. Mp 216.5–219.0°C ($CHCl_3$). $[\alpha]_D^{30}=+160.8$ (*c* 0.32, $CHCl_3$). IR (KBr) cm^{-1}: 3024, 2974, 115, 1045. ^1H NMR δ: 2.41 (3H, s, Ar-CH_3), 4.55 (2H, s, CH_2I), 6.85 (1H, d, *J*=15.3 Hz, 1-H), 7.24–7.28 (2H, m, Ar-H), 7.34 (2H, d, *J*=7.9 Hz, Ar-H), 7.36–7.40 (2H, m, Ar-H), 7.63 (2H, d, *J*=7.9 Hz, Ar-H), 7.69 (2H, d, *J*=15.3 Hz, 2-H). ^{13}C NMR δ: 2.8, 21.4, 124.9, 125.0, 127.5 (2C), 128.6, 129.8, 129.9, 130.1, 132.1, 132.6, 135.7, 137.7, 140.2, 141.8. MS (FAB) *m/z*: 383 (MH^+). HRMS (FAB) Calcd $C_{16}H_{16}IOS$ (MH^+): 382.9966. Found: 382.9983.

(*R*)-2-Indenyl *p*-tolyl sulfoxide (58). Using the procedure for (*E*)-**41**, the chloride (*E*)-**55** (50 mg, 0.17 mmol) was converted into **58** (28 mg, 64%). Colorless needles: mp 148.5–149.5°C (hexane–AcOEt). $[\alpha]_D^{26}=+66.8$ (*c* 0.61, $CHCl_3$). IR (KBr) cm^{-1}: 2923, 1080, 1045. ^1H NMR δ: 2.40 (3H, s, Ar-CH_3), 3.26 (1H, d, *J*=22.9 Hz, 1-H), 3.56 (1H, d, *J*=22.9 Hz, 1-H), 7.25–7.27 (1H, m, 5-H, Ar-H), 7.29–7.32 (3H, m, 6-H, Ar-H), 7.38 (1H, d, *J*=7.3 Hz, 7-H), 7.47 (1H, d, *J*=7.3 Hz, 4-H), 7.48 (1H, s, 3-H), 7.56 (2H, d, *J*=7.9 Hz, Ar-H). ^{13}C NMR δ: 21.4, 35.2, 122.8, 124.2, 124.5 (2C), 127.0 (2C), 130.0 (2C), 136.5, 140.6, 141.5, 141.9, 143.9, 150.4. MS (FAB) *m/z*: 225 (MH^+). HRMS (FAB) Calcd $C_{16}H_{15}OS$ (MH^+): 255.0844. Found: 255.0840.

(*R*)-[(3*S*,4*R*)-3,4-(Isopropylidenedioxy)-2,5-epoxy-1-pentenyl] *p*-tolyl sulfoxide (60). Using the procedure for **31**, 2-*O*-isopropylidene-D-erythrose **59** (760 mg, 4.75 mmol) was converted into **60** (6:1 diastereomeric mixture, 1.35 g, 96%). Colorless powder: mp 122.0–123.0°C (hexane–AcOEt). IR (KBr) cm^{-1}: 2931, 1597, 1381, 1209, 1090, 1045. ^1H NMR δ: (major): 1.29 (5/2H, s, $C(CH_3)_2$), 1.44 (5/2H, s, $C(CH_3)_2$), 2.42 (5/2H, s, Ar-CH_3), 3.01 (5/6H, dd, *J*=13.4, 9.8 Hz, 1-H), 3.06 (5/6H, dd, *J*=13.4, 3.1 Hz, 1-H), 3.60 (5/6H, dd, *J*=11.0, 3.67 Hz, 5-H), 4.01–4.04 (5/6H, m, 2-H), 4.10 (5/6H, d, *J*=11.0 Hz, 5-H), 4.59 (5/6H, dd, *J*=6.1, 3.7 Hz, 3-H), 4.83 (5/6H, dd, *J*=6.1, 3.7 Hz, 4-H), 7.34 (10/6H, d, *J*=7.9 Hz, Ar-H), 7.57 (10/6H, d, *J*=7.9 Hz, Ar-H) (minor): 1.31 (3/6H, s, $C(CH_3)_2$), 1.47 (3/6H, s, $C(CH_3)_2$), 2.42 (3/6H, s, Ar-CH_3), 2.86 (1/6H, dd, *J*=13.4, 5.5 Hz, 1-H), 3.12 (1/6H, dd, *J*=13.4, 7.3 Hz, 1-H), 4.01–4.04 (1/6H, m, 5-H), 4.10 (1/6H, d, *J*=11.0 Hz, 5-H), 4.14–4.16 (1/6H, m, 2-H), 4.73 (1/6H, dd, *J*=6.1, 1.8 Hz, 3-H), 4.88 (1/6H, dt, *J*=6.1, 3.1 Hz, 4-H), 7.34 (2/6H, d, *J*=7.9 Hz, Ar-H). 7.57 (2/6H, d, *J*=7.9 Hz, Ar-H). ^{13}C NMR (major): δ: 21.4, 24.6, 24.9, 25.9, 58.2, 73.1, 75.9, 80.9, 112.4, 123.9 (2C), 130.0 (2C), 141.1, 141.6. MS (EI) *m/z* (rel. int. %): 296 (M^+, 8.7), 157 (100). HRMS (EI) Calcd $C_{15}H_{20}O_4S$: 296.1075. Found: 296.1082.

(*E*)-(2*R*,3*S*)-2,3-(Isopropylidenedioxy)-5-[(*R*)-(*p*-tolylsulfinyl)]-4-penten-1-ol (61). Using the procedure for (*E*)-**5**, **60** (600 mg, 2.02 mmol) was converted into **61**

(550 mg, 92%). Colorless powder: mp 66.0–67.0°C (hexane–AcOEt). $[\alpha]_D^{29}=+206.0$ (*c* 0.90, $CHCl_3$). IR (KBr) cm^{-1}: 3388, 1049. ^1H NMR δ: 1.30 (3H, s, $C(CH_3)_2$), 1.42 (3H, s, $C(CH_3)_2$), 2.34 (3H, s, Ar-CH_3), 2.98 (1H, s, OH), 3.55 (2H, d, *J*=6.1 Hz, 1-H), 4.31 (1H, dt, *J*=6.1 Hz, 2-H), 4.78 (1H, dd, *J*=6.1, 4.9 Hz, 3-H), 6.48 (1H, d, *J*=15.3 Hz, 5-H), 6.56 (1H, dd, *J*=15.3, 4.9 Hz, 4-H), 7.25 (2H, d, *J*=7.9 Hz, Ar-H), 7.45 (2H, d, *J*=7.9 Hz, Ar-H). ^{13}C NMR δ: 21.5, 25.2, 27.6, 61.4, 76.0, 78.1, 109.2, 124.8 (2C), 130.0 (2C), 132.6, 136.3, 139.7, 141.8. MS (EI) *m/z* (rel. int. %): 296 (M^+, 31.0), 279 (100). HRMS (EI) Calcd $C_{15}H_{20}O_4S$: 296.1082. Found: 296.1079. Anal. Calcd $C_{15}H_{20}O_4S$: C, 60.79; H, 6.80; S, 10.82. Found: C, 61.05; H, 6.70; S, 10.63.

(*E*)-(2*R*,3*S*)-2,3-(Isopropylidenedioxy)-5-[(*R*)-(*p*-tolylsulfinyl)]-4-pentenyl *p*-toluenesulfonate (62). Using the procedure for (*E*)-**7**, **61** (414 mg, 1.40 mmol) was converted into **62** (585 mg, 93%). A colorless oil: $[\alpha]_D^{27}=+159.3$ (*c* 0.89, $CHCl_3$). IR (KBr) cm^{-1}: 1597, 1365, 1176. ^1H NMR δ: 1.32 (3H, s, $C(CH_3)_2$), 1.39 (3H, s, $C(CH_3)_2$), 2.41 (3H, s, Ar-CH_3), 2.46 (3H, s, Ar-CH_3), 3.90–3.96 (2H, m, 1-H), 4.42 (1H, dt, *J*=6.7, 6.1 Hz, 2-H), 4.42 (1H, ddd, *J*=6.7, 4.9, 1.2 Hz, 3-H), 6.47 (1H, dd, *J*=4.9, 14.6 Hz, 4-H), 6.57 (1H, dd, *J*=14.6, 1.2 Hz, 5-H), 7.32 (2H, d, *J*=7.9 Hz, Ar-H), 7.37 (2H, d, *J*=7.9 Hz, Ar-H), 7.51 (2H, d, *J*=7.9 Hz, Ar-H), 7.83 (2H, d, *J*=7.9 Hz, Ar-H). ^{13}C NMR δ: 21.5, 21.8, 25.2, 27.5, 67.6, 75.1, 75.7, 109.9, 124.8 (2C), 127.9 (2C), 129.7, 129.8 (2C), 130.1 (2C), 132.5, 138.0, 139.8, 141.9, 145.0. MS (EI) *m/z* (rel. int. %): 450 (M^+, 8.3), 91 (100). HRMS (EI) Calcd $C_{22}H_{26}O_6S_2$: 450.1171. Found: 450.1180.

(*R*)-[(*E*)-(3*S*,4*R*)-5-Iodo-3,4-(isopropylidenedioxy)-1-pentenyl] *p*-tolyl sulfoxide (63). Using the procedure for (*E*)-**10**, **62** (250 mg, 0.55 mmol) was converted into **63** (186 mg, 83%). A colorless oil: $[\alpha]_D^{27}=+164.8$ (*c* 1.22, $CHCl_3$). IR (KBr) cm^{-1}: 2987, 1597, 1219, 1083, 1043. ^1H NMR δ: 1.37 (3H, s, $C(CH_3)_2$), 1.50 (3H, s, $C(CH_3)_2$), 2.41(3H, s, Ar-CH_3), 3.00 (1H, dd, *J*=10.4, 6.7 Hz, 5-H), 3.15 (1H, dd, *J*=10.4, 6.7 Hz, 5-H), 4.52 (1H, td, *J*=6.7, 6.1 Hz, 4-H), 4.84 (1H, dt, *J*=6.1, 1.8 Hz, 3-H), 6.60 (2H, d, *J*=1.8 Hz, 1-H and 2-H), 7.32 (2H, d, *J*=7.9 Hz, Ar-H), 7.53 (2H, d, *J*=7.9 Hz, Ar-H). ^{13}C NMR δ: 2.6, 21.4, 25.4, 28.0, 76.9, 78.4, 109.7, 124.9 (2C), 130.2 (2C), 130.6, 138.2, 140.0, 142.0. MS (EI) *m/z* (rel. int. %): 406 (M^+, 6.3), 85 (100). HRMS (EI) Calcd $C_{15}H_{19}IO_3S$: 406.0100. Found: 406.0098. Anal. Calcd $C_{15}H_{19}IO_3S$: C, 44.35; H, 4.71. Found: C, 44.30; H, 4.67.

(*R*)-[(*E*)-(3*S*,4*R*)-3,4-(Isopropylidenedioxy)-1-cyclopentenyl] *p*-tolyl sulfoxide (64). Using the procedure for **41**, **63** (30 mg, 0.074 mmol) was converted into **64** (14 mg, 68%). Yellow powder: mp 80.4–81.3°C (hexane–AcOEt). $[\alpha]_D^{29}=+145.2$ (*c* 1.13, $CHCl_3$). IR (KBr) cm^{-1}: 2929, 1597, 1379, 1371, 1228, 1209, 1084, 1053, 1014. ^1H NMR δ: 1.31 (3H, s, $C(CH_3)_2$), 1.35 (3H, s, $C(CH_3)_2$), 2.41 (3H, s, Ar-CH_3), 2.47–2.48 (2H, m, 5-H), 4.78–4.81 (1H, m, 4-H), 5.16–5.18 (1H, d, *J*=5.5 Hz, 3-H), 6.44 (1H, d, *J*=1.2 Hz, 2-H), 7.39 (2H, d, *J*=7.9 Hz, Ar-H), 7.51 (2H, d, *J*=7.9 Hz, Ar-H). ^{13}C NMR δ: 21.4, 25.8, 27.5, 34.9, 78.0, 84.3, 110.7, 125.1 (2C), 130.0 (2C), 132.9, 138.5, 142.1, 150.0. MS (EI) *m/z* (rel. int. %): 278 (M^+, 16.2), 155 (100). HRMS (EI) Calcd $C_{15}H_{18}O_3S$: 278.0977. Found: 278.0977.

(*R*)-[(3*S*,4*R*,5*R*)-6-[[*tert*-Butyl(dimethyl)silyl]oxy]-3,4-(isopropylidenedioxy)-2,5-epoxyhexyl] *p*-tolyl sulfoxide (66). Using the procedure for **31**, the lactol **65** (1.76 g, 5.78 mmol) was converted into **66a** (less polar: 1.95 g, 77%) and **66b** (more polar: 0.32 g, 13%). **66a** (a colorless oil): $[\alpha]_D^{27}=+69.0$ (*c* 0.81, $CHCl_3$). IR (KBr) cm^{-1}: 2929, 1257, 1209, 1163, 1099, 1049. ^1H NMR δ: 0.09 (3H, s, $SiCH_3$), 0.10 (3H, s, $SiCH_3$), 0.91 (9H, s, $SiC(CH_3)_3$), 1.31 (3H, s, $C(CH_3)_2$), 1.44 (3H, s, $C(CH_3)_2$), 2.41 (3H, s, Ar-CH_3), 2.93 (1H, dd, *J*=13.4, 9.8 Hz, 1-H), 3.03 (1H, dd, *J*=13.4, 3.1 Hz, 1-H), 3.72–3.78 (2H, m, 6-H), 4.18 (1H, t, *J*=3.7 Hz, 5-H), 4.59–4.62 (1H, m, 2-H), 4.62–4.65 (1H, m, 3-H), 4.87 (1H, d, *J*=6.1 Hz, 4-H), 7.32 (2H, d, *J*=7.9 Hz, Ar-H), 7.57 (2H, d, *J*=7.9 Hz, Ar-H). ^{13}C NMR δ: −5.7, −5.5, 18.2, 21.4, 24.7, 25.9 (3C), 26.2, 59.6, 64.5, 76.1, 82.4, 83.3, 84.8, 112.4, 124.0 (2C), 129.9 (2C), 141.4 (2C). MS (FAB) *m/z*: 441 (MH^+). HRMS (FAB) Calcd $C_{22}H_{37}O_5SiS$ (MH^+): 441.2151. Found: 441.2153. **66b** (a colorless oil): $[\alpha]_D^{27}=+26.4$ (*c* 0.55, $CHCl_3$). IR (KBr) cm^{-1}: 2929, 1084. ^1H NMR δ: 0.08 (3H, s, $SiCH_3$), 0.09 (3H, s, $SiCH_3$), 0.91 (9H, s, $SiC(CH_3)_3$), 1.32 (3H, s, $C(CH_3)_2$), 1.45 (3H, s, $C(CH_3)_2$), 2.42 (3H, s, Ar-CH_3), 2.98 (1H, dd, *J*=12.8, 4.9 Hz, 1-H), 3.27 (1H, dd, *J*=12.8, 6.7 Hz, 1-H), 3.75 (2H, d, *J*=2.4 Hz, 6-H), 4.00–4.03 (1H, m, 2-H), 4.07 (1H, q, *J*=3.1 Hz, 5-H), 4.64 (1H, dd, *J*=6.1, 4.3 Hz, 3-H), 4.68 (1H, dd, *J*=6.1, 3.1 Hz, 4-H), 7.33 (2H, d, *J*=7.9 Hz, Ar-H), 7.58 (2H, d, *J*=7.9 Hz, Ar-H). ^{13}C NMR δ: −5.4, −5.3, 18.4, 21.5, 25.5, 26.0 (3C), 27.3, 60.9, 63.8, 80.0, 81.8, 84.3, 85.4, 113.9, 124.4 (2C), 129.9 (2C), 140.2, 141.7. MS (FAB) *m/z*: 441 (MH^+). HRMS (FAB) Calcd $C_{22}H_{37}O_5SiS$ (MH^+): 441.2147. Found: 441.2149.

(*E*)-(2*R*,3*R*,4*S*)-1-[*tert*-Butyl(dimethyl)silyl]oxy-3,4-(isopropylidenedioxy)-6-[(*R*)-(*p*-tolylsulfinyl)]-5-hexen-2-ol (67). Using the procedure for (*E*)-**5**, the lactol **66** (6:1 diastereomeric mixture, 2.13 g, 4.84 mmol) was converted into **67** (1.98 g, 93%). A colorless oil: $[\alpha]_D^{28}=+102.2$ (*c* 0.91, $CHCl_3$). IR (KBr) cm^{-1}: 2931, 1597, 1255, 1059. ^1H NMR δ: 0.09 (6H, s, $Si(CH_3)_2$), 0.92 (9H, s, $SiC(CH_3)_3$), 1.34 (3H, s, $C(CH_3)_2$), 1.43 (3H, s, $C(CH_3)_2$), 2.40 (3H, s, Ar-CH_3), 2.63 (1H, d, *J*=5.5 Hz, OH), 3.56 (1H, m, 2-H), 3.65 (1H, dd, *J*=10.4, 5.5 Hz, 1-H), 3.80 (1H, dd, *J*=10.4, 3.1 Hz, 1-H), 4.12 (1H, dd, *J*=9.8, 6.7 Hz, 3-H), 4.89 (1H, ddd, *J*=6.7, 4.9, 1.8 Hz, 4-H), 6.54 (1H, dd, *J*=14.6, 1.8 Hz, 6-H), 6.82 (1H, dd, *J*=14.6, 4.9 Hz, 5-H), 7.30 (2H, d, *J*=7.9 Hz, Ar-H), 7.54 (2H, d, *J*=7.9 Hz, Ar-H). ^{13}C NMR δ: −5.6, −5.4, 18.2 (3C), 21.3, 25.1, 25.8, 27.5, 64.4, 69.5, 76.7, 77.3, 109.3, 124.9 (2C), 129.9 (2C), 134.5, 135.9, 140.4, 141.5. MS (EI) *m/z* (rel. int. %): 440 (M^+, 4.2), 383 (100). HRMS (EI) Calcd $C_{22}H_{36}O_5SiS$: 440.2053. Found: 440.2044.

(*R*)-[(*E*)-(3*S*,4*R*,5*R*)-6-[*tert*-Butyl(dimethyl)silyl]oxy-3,4-(isopropylidenedioxy)-5-(methoxymethoxy)-1-hexenyl] *p*-tolyl sulfoxide (68). Chloromethyl methyl ether (0.12 ml, 1.58 mmol) was added to a mixture of **67** (602 mg, 1.37 mmol) and *i*-Pr_2NEt (0.29 ml, 1.67 mmol) in CH_2Cl_2 (10 ml) with stirring at 0°C. The stirring was continued at rt for 3 days. The reaction was quenched with saturated NH_4Cl aqueous solution, and the whole was extracted with AcOEt.

The extract was washed with water and brine prior to drying and solvent evaporation. The residue was chromatographed on silica gel with hexane–AcOEt (3:1) to give **68** (605 mg, 91%) as a colorless oil. $[\alpha]_D^{27}$=+95.5 (*c* 1.04, $CHCl_3$). IR (KBr) cm^{-1}: 2929, 1597, 1255, 1215, 1051. ^1H NMR δ: 0.06 (6H, s, $Si(CH_3)_2$), 0.92 (9H, s, $SiC(CH_3)_3$), 1.33 (3H, s, $C(CH_3)_2$), 1.42 (3H, s, $C(CH_3)_2$), 2.39 (3H, s, Ar-CH_3), 3.39 (3H, s, OCH_3), 3.50 (1H, dt, *J*=7.9, 3.1 Hz, 5-H), 3.75 (1H, dd, *J*=11.0, 3.1 Hz, 6-H), 3.95 (1H, dd, *J*=11.0, 2.4 Hz, 6-H), 4.40 (1H, dd, *J*=7.9, 6.1 Hz, 4-H), 4.62 (1H, d, *J*=6.7 Hz, OCH_2O), 4.68 (1H, d, *J*=6.7 Hz, OCH_2O), 4.82 (1H, ddd, *J*=6.1, 4.9, 1.2 Hz, 3-H), 6.50 (1H, dd, *J*=14.6, 1.2 Hz, 1-H), 6.72 (1H, dd, *J*=14.6, 4.9 Hz, 2-H), 7.29 (2H, d, *J*=7.9 Hz, Ar-H), 7.50 (2H, d, *J*=7.9 Hz, Ar-H). ^{13}C NMR δ: −5.6, −5.5, 18.3, 21.4, 25.2, 25.8 (3C), 27.6, 55.9, 62.8, 76.0, 76.6, 77.4, 96.7, 108.9, 124.7 (2C), 130.0 (2C), 134.4, 136.3, 140.5, 141.6. MS (FAB) *m/z*: 485 (MH^+). Anal. Calcd $C_{24}H_{40}O_6SiS$: C, 59.42; H, 8.32; S, 6.61. Found: C, 59.29; H, 8.14; S, 6.57.

(*E*)-(2*S*,3*R*,4*S*)-3,4-(Isopropylidenedioxy)-2-(methoxymethoxy)-6-[(*R*)-(*p*-tolylsulfinyl)]-5-hexen-1-ol (69). Using the procedure for (*Z*)-**5**, the TBS ether **68** (558 mg, 1.15 mmol) was converted into **69** (398 mg, 93%). Colorless powder: mp 47.9–48.6°C (hexane–AcOEt). $[\alpha]_D^{27}$=+212.1 (*c* 0.94, $CHCl_3$). IR (KBr) cm^{-1}: 3404, 2935, 1246, 1217, 1039. ^1H NMR δ: 1.35 (3H, s, $C(CH_3)_2$), 1.46 (3H, s, $C(CH_3)_2$), 1.78 (1H, br, OH), 2.41 (3H, s, Ar-CH_3), 3.42 (3H, s, OCH_3), 3.43 (1H, ddd, *J*=9.2, 6.7, 2.4 Hz, 5-H), 3.62 (1H, dd, *J*=12.2, 6.7 Hz, 6-H), 3.87 (1H, dd, *J*=12.2, 2.4 Hz, 6-H), 4.20 (1H, dd, *J*=9.2, 6.1 Hz, 4-H), 4.54 (1H, d, *J*=6.7 Hz, OCH_2O), 4.64 (1H, d, *J*=6.7 Hz, OCH_2O), 4.87 (1H, ddd, *J*=6.1, 4.9, 1.2 Hz, 3-H), 6.54 (1H, dd, *J*=14.6, 1.2 Hz, 1-H), 6.64 (1H, dd, *J*=14.6, 4.9 Hz, 2-H), 7.32 (2H, d, *J*=7.9 Hz, Ar-H), 7.51 (2H, d, *J*=7.9 Hz, Ar-H). ^{13}C NMR δ: 21.3, 25.1, 27.5, 55.9, 63.9, 76.6, 77.2, 81.4, 97.6, 109.2, 124.7 (2C), 130.1 (2C), 132.3, 135.6, 140.2, 141.8. MS (FAB) *m/z*: 371 (MH^+). HRMS (FAB) Calcd $C_{18}H_{27}O_6S$ (MH^+): 371.1501. Found: 371.1503.

[(*E*)-(2*R*,3*R*,4*S*)-3,4-(Isopropylidenedioxy)-2-(methoxymethoxy)-6-[(*R*)-(*p*-tolylsulfinyl)]-5-hexenyl] *p*-toluenesulfonate (70). Using the procedure for (*E*)-**7**, the alcohol **69** (320 mg, 0.86 mmol) was converted into **70** (417 mg, 92%). A colorless oil: $[\alpha]_D^{27}$=+139.2 (*c* 0.78, $CHCl_3$). IR (KBr) cm^{-1}: 2987, 1362, 1215, 1176, 1084, 1055, 1005. ^1H NMR δ: 1.19 (3H, s, $C(CH_3)_2$), 1.26 (3H, s, $C(CH_3)_2$), 2.32 (3H, s, Ar-CH_3), 2.37 (3H, s, Ar-CH_3), 3.20 (3H, s, OCH_3), 3.46 (1H, ddd, *J*=8.5, 3.1, 1.8 Hz, 2-H), 4.09 (1H, dd, *J*=10.4, 3.1 Hz, 1-H), 4.21 (1H, dd, *J*=8.5, 6.1 Hz, 3-H), 4.30 (1H, dd, *J*=10.4, 1.8 Hz, 1-H), 4.44–4.49 (2H, m, OCH_2O), 4.76 (1H, dd, *J*=6.1, 4.9 Hz, 4-H), 6.44 (1H, d, *J*=15.3 Hz, 6-H), 6.53 (1H, dd, *J*=15.3, 4.9 Hz, 5-H), 7.23 (2H, d, *J*=7.9 Hz, Ar-H), 7.27 (2H, d, *J*=7.9 Hz, Ar-H), 7.42 (2H, d, *J*=7.9 Hz, Ar-H), 7.73 (2H, d, *J*=7.9 Hz, Ar-H). ^{13}C NMR δ: 21.4, 21.6, 25.0, 27.4, 56.1, 69.6, 75.2, 75.7, 76.2, 97.4, 109.1, 124.7 (2C), 128.1 (2C), 129.7 (2C), 130.1 (2C), 131.7, 132.8, 136.3, 140.1, 141.8, 144.7. MS (FAB) *m/z*: 525 (MH^+). HRMS (FAB) Calcd $C_{25}H_{33}O_8S_2$ (MH^+): 525.1614. Found: 525.1614.

(*R*)-[(*E*)-(3*S*,4*R*,5*S*)-6-Iodo-3,4-(isopropylidenedioxy)-5-(methoxymethoxy)-1-hexenyl] *p*-tolyl sulfoxide (71). Using the procedure for (*E*)-**10**, the alcohol **70** (264 mg, 0.50 mmol) was converted into **71** (229 mg, 95%). A colorless oil: $[\alpha]_D^{27}$=+155.7 (*c* 1.34, $CHCl_3$). IR (KBr) cm^{-1}: 2931, 1597, 1373, 1151, 1086, 1039. ^1H NMR δ: 1.37 (3H, s, $C(CH_3)_2$), 1.44 (3H, s, $C(CH_3)_2$), 2.40 (3H, s, Ar-CH_3), 2.94 (1H, dt, *J*=2.4, 8.5 Hz, 5-H), 3.47 (3H, s, OCH_3), 3.54 (1H, dd, *J*=11.0, 2.4 Hz, 6-H), 3.64 (1H, dd, *J*=2.4, 11.0 Hz, 6-H), 4.27 (1H, dd, *J*=6.7, 8.5 Hz, 4-H), 4.59 (1H, d, *J*=7.3 Hz, OCH_2O), 4.62 (1H, d, *J*=7.3 Hz, OCH_2O), 4.87 (1H, ddd, *J*=6.7, 4.3, 1.2 Hz, 3-H), 6.53 (1H, dd, *J*=14.6, 1.2 Hz, 1-H), 6.65 (1H, dd, *J*=14.6, 4.3 Hz, 2-H), 7.31 (2H, d, *J*=7.9 Hz, Ar-H), 7.51 (2H, d, *J*=7.9 Hz, Ar-H). ^{13}C NMR δ: 12.1, 21.8, 25.5, 28.0, 57.8, 75.1, 76.6, 79.5, 97.9, 109.6, 125.2 (2C), 130.5 (2C), 132.7, 136.3, 140.6, 142.2. MS (FAB) *m/z*: 481 (MH^+). HRMS (FAB) Calcd $C_{18}H_{26}IO_5S$ (MH^+): 481.0546. Found: 481.0052. Anal. Calcd $C_{18}H_{25}IO_5S$: C, 45.01; H, 5.25. Found: C, 45.06; H, 5.22.

(*R*)-[(3*S*,4*R*,5*R*)-3,4-(Isopropylidenedioxy)-5-(methoxymethoxy)-1-cyclohexenyl] *p*-tolyl sulfoxide (72) and (*R*)-[(3*S*,4*R*,*E*)-3,4-(isopropylidenedioxy)-5-(methoxymethoxy)-1,5-hexadienyl] *p*-tolyl sulfoxide (73). Using the procedure for **41**, **71** (200 mg, 0.42 mmol) was converted into **72** (94 mg, 64%) along with **73** (29 mg, 20%). **72** (a yellow oil): $[\alpha]_D^{26}$=+42.9 (*c* 0.97, $CHCl_3$). IR (KBr) cm^{-1}: 2931, 1597, 1381, 1371, 1221, 1111, 1086, 1061, 1038. ^1H NMR δ: 1.28 (3H, s, $C(CH_3)_2$), 1.38 (3H, s, $C(CH_3)_2$), 2.01–2.07 (1H, m, 6-H), 2.16 (1H, dd, *J*=15.9, 5.5 Hz, 6-H), 2.40 (3H, s, Ar-CH_3), 3.31 (3H, s, OCH_3), 3.89 (1H, ddd, *J*=10.4, 5.5, 1.8 Hz, 5-H), 4.48 (1H, dd, *J*=5.5, 1.8 Hz, 4-H), 4.68 (2H, s, OCH_2O), 4.78–4.83 (1H, m, 3-H), 6.47 (1H, t, *J*=3.1 Hz, 2-H), 7.28 (2H, d, *J*=7.9 Hz, Ar-H), 7.50 (2H, d, *J*=7.9 Hz, Ar-H). ^{13}C NMR δ: 21.3, 23.6, 26.5, 27.8, 55.5, 72.8, 73.3, 75.0, 95.4, 114.3, 125.3 (3C), 129.9 (2C), 138.7, 142.2, 142.8. MS (EI) *m/z* (rel. int. %): 352 (M^+, 5.2), 123 (100). HRMS (EI) Calcd $C_{18}H_{24}O_5S$: 352.1344. Found: 352.1342. **73** (a yellow oil): $[\alpha]_D^{26}$=+142.6 (*c* 0.21, $CHCl_3$). IR (KBr) cm^{-1}: 1215, 1155, 1084, 1055, 1016. ^1H NMR δ: 1.39 (3H, s, $C(CH_3)_2$), 1.53 (3H, s, $C(CH_3)_2$), 2.40 (3H, s, Ar-CH_3), 3.43 (3H, s, OCH_3), 4.39 (1H, d, *J*=2.4 Hz, 6-H), 4.42 (1H, d, *J*=2.4 Hz, 6-H), 4.65 (1H, d, *J*=7.3 Hz, 4-H), 4.88 (1H, d, *J*=6.1 Hz, OCH_2O), 4.88 (1H, dd, *J*=7.3, 4.8 Hz, 3-H), 4.94 (1H, d, *J*=6.1 Hz, OCH_2O), 6.48 (1H, d, *J*=14.7 Hz, 1-H), 6.53 (1H, dd, *J*=14.7, 4.8 Hz, 2-H), 7.30 (2H, d, *J*=7.9 Hz, Ar-H), 7.49 (2H, d, *J*=7.9 Hz, Ar-H). ^{13}C NMR δ: 21.4, 25.1, 27.1, 56.6, 77.8, 76.9, 86.6, 94.2, 109.8, 124.8 (2C), 130.0 (2C), 133.7, 136.6, 140.4, 141.6, 155.8. MS (FAB) *m/z*: 353 (MH^+). HRMS (FAB) Calcd $C_{18}H_{25}O_5S$ (MH^+): 353.1422. Found: 353.1456.

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