Studies on Chiral Organosulfur Compounds. III.[1] Lewis Acid-Catalyzed Intramolecular Asymmetric Pericyclic Reactions of Chiral α-Acetyl and Methoxycarbonylvinylic Sulfoxides

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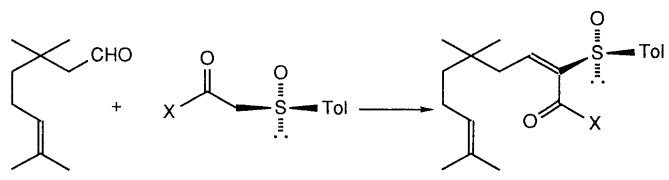
A chiral α-sulfinyl α,β-unsaturated ketone served as a good chiral diene or enophile in intramolecular Lewis acid-catalyzed asymmetric pericyclic reactions, giving hetero-Diels–Alder reaction products, together with ene reaction products in some cases, in high optical yields. The reaction pathways for Diels–Alder or ene reactions were readily controlled depending on the Lewis acids used. A chiral α-sulfinyl α,β-unsaturated ester served as a good enophile to give ene reaction products with high enantioselectivity. The mechanistic pathway for the asymmetric induction is proposed on the basis of the stereochemical results obtained.

Keywords asymmetric Diels–Alder reaction; asymmetric ene reaction; chiral sulfoxide; Lewis acid; diastereoselectivity; enantioselectivity

The Diels–Alder reaction has been widely used for the stereoselective construction of six-membered ring systems.[2] During the past decade much effort has been devoted to the development of new methodologies for asymmetric Diels–Alder reactions using various kinds of chiral auxiliaries,[3] among which chiral organosulfur groups have recently received much attention.[4] However, the known asymmetric Diels–Alder reactions with chiral organosulfur compounds have been limited to intermolecular ones using chiral vinylic sulfoxides[5] and sulfoximines[6] as dienophiles. Few reports have been published on Diels–Alder reactions with dienes having electron-withdrawing groups, such as sulfonyl[7] or achiral sulfinyl groups.[8]

We have successfully executed intramolecular asymmetric pericyclic reactions including Diels–Alder and ene reactions with α,β-unsaturated carbonyl systems bearing optically active sulfinyl group.[9] We wish to report the first example of the asymmetric intramolecular Diels–Alder reaction of a chiral α-sulfinyl α,β-unsaturated ketone, which served as an efficient chiral diene. We also wish to report the Lewis acid-catalyzed intramolecular asymmetric ene reactions[10] of a chiral α-sulfinyl α,β-unsaturated ester.

The model compounds, (*S*)-(+)-3-*p*-toluenesulfinyl-6,6,10-trimethyl-3,9-undecadien-2-one (**3a**) and methyl (*S*)-(+)-2-*p*-toluenesulfinyl-5,5,9-trimethyl-2,8-decadienoate (**3b**), having chiral sulfinyl diene or enophile functions were readily prepared by Knoevenagel condensation of (*R*)-(+)-*p*-toluenesulfinylacetone (**2a**) and methyl (*R*)-(+)-*p*-toluenesulfinylacetate (**2b**) with 3-methylcitronellal (**1**). Compound **1** was obtainable by 1,4-addition of lithium dimethylcuprate to citral.[11] The chiral sulfoxide (*R*)-(+)-**2a** was prepared by acetylation of (*R*)-(+)-methyl *p*-tolyl sulfoxide[12] with ethyl acetate using lithium diisopropylamide (LDA) as a base. The chiral sulfoxide (*R*)-(+)-**2b** was prepared by methanolysis of *tert*-butyl (*R*)-(+)-*p*-toluenesulfinylacetate[13] with sodium methoxide. The Knoevenagel condensations of (*R*)-(+)-**2a** and (*R*)-(+)-**2b** with **1** were carried out in the presence of a catalytic amount of piperidinium acetate in benzene at room temperature for 48 and 72 h to give (*S*)-(+)-**3a** and (*S*)-(+)-**3b** stereoselectively in 63 and 86% yields, respectively.



1 (*R*)-**2a**: X = Me (*R*)-**2b**: X = OMe (*S*)-**3a**: X = Me (*S*)-**3b**: X = OMe

Chart 1

The reactions of (*S*)-(+)-**3a** catalyzed by various Lewis acids were carried out in dichloromethane at 0——78 °C to produce optically active hetero-Diels–Alder reaction products, (4a*S*,8a*S*,*S*s)-(−)-4a,5,6,7,8,8a-hexahydro-1,1,3,6,6-pentamethyl-4-*p*-toluenesulfinyl-1*H*-2-benzopyran (**4a**), (4a*R*,8a*R*,*S*s)-(+)-**4b**, and (4a*S*,8a*R*,*S*s)-(−)-**4c**, and optically active ene reaction products, (1*R*,2*R*,α*R*,*R*s)-(+)-1-(5,5-dimethyl-2-isopropenylcyclohexyl)-1-*p*-toluenesulfinyl-2-propanone (**5a**) and (1*R*,2*R*,α*S*,*R*s)-(−)-**5b**. The results obtained by using various Lewis acids are summarized in Table I. The product ratios were determined by high-performance liquid chromatographic (HPLC) analysis. The ratios of the Diels–Alder adducts to the ene reaction products were dependent on the Lewis acids used. Use of bidentate Lewis acids such as zinc(II) chloride, bromide, and iodide, and tin(IV) chloride provided both of

TABLE I. The Lewis Acid-Catalyzed Asymmetric Hetero-Diels–Alder and Ene Reactions of (*S*)-**3a**

Lewis acid	Reaction conditions[a]		Yield of **4** (%) (**4a**, **b** : **4c**)[b]	de (%) of **4a**, **b**[c]	Yield of **5** (%) (**5a** : **5b**)[b]
	Temp. (°C)	Time (h)			
Et_2AlCl	−78	1	99 (96 : 4)	81.7	—
$EtAlCl_2$	−78	1	96 (84 : 16)	83.8	—
$BF_3 \cdot OEt_2$	0	2	89 (74 : 26)	75.3	—
$FeCl_3$	0	2	45 (89 : 11)	39.4	—
$ZnCl_2$	0	4	38 (83 : 17)	30.5	42 (76 : 24)
$ZnBr_2$	0	2	42 (83 : 17)	33.7	52 (73 : 27)
ZnI_2	0	2	51 (82 : 18)	31.7	38 (76 : 24)
$SnCl_4$	−78	1	66 (88 : 12)	47.8	24 (95 : 5)

a) Each reaction was carried out in dichloromethane in the presence of a Lewis acid (1.5 eq). *b*) The product ratios (%) were determined by HPLC analysis. *c*) The diastereomeric excess (de) was calculated on the basis of HPLC analytic data.

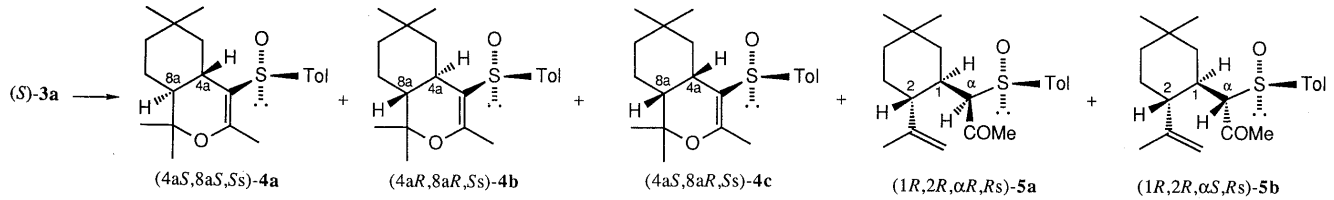


Chart 2

the reaction products, whereas the reactions catalyzed by monodentate Lewis acids, such as diethylaluminum chloride, ethylaluminum dichloride, and boron trifluoride etherate, afforded the Diels–Alder adducts in extremely high yields with high diastereomeric excess (calculated from the ratios of **4a** to **4b**) with no detectable formation of the ene reaction products.

The degree of the diasteromeric excess of **4a**, **b** in the Diels–Alder reactions was dependent on the Lewis acid used. Use of diethylaluminum chloride, ethylaluminum dichloride, and boron trifluoride etherate provided high diastereomeric selectivity. In the ene reaction almost complete asymmetric induction was observed. The products **5a**, **b**, diastereomeric at the α-carbon having a readily epimerizable hydrogen atom, have the same stereochemistry at the C_1 and C_2 positions on the cyclohexane ring.

The stereochemistry of the products was determined as follows. The relative stereochemistry of the substituents at the C_1 and C_2 positions in the ene products **5a**, **b** was assigned as *trans* based on the observation of the nuclear Overhauser effects (NOE) between the hydrogen atoms at C_1 and the methyl groups of the isopropenyl substituents in the NMR spectral analysis. The relative stereochemistry of the C_α carbon center in **5a** was determined on the basis of the formation of (*S*)-(−)-1(*E*)-(5,5-dimethyl-2-isopropenylcyclohexylidene)-2-propanone (**6**) by dehydrosulfenylation (refluxing in CCl_4) of **5a** in a *cis* fashion[14]; the geometry of the resulting olefin was confirmed by the NOE between the olefinic hydrogen next to the acetyl group, and the methyl and the vinyl groups in the isopropenyl substituent in the NMR spectral analysis. The absolute configuration at the C_2 carbon center of the compound (*S*)-(−)-**6** thus obtained was determined as (*S*) by chemical correlation to the related nitrile, (*S*)-(−)-1(*E*)-(5,5-dimethyl-2-isopropenylcyclohexylidene)acetonitrile (**9**), of known absolute configuration,[10] by reductive hydrolysis of the cyano group in (*S*)-(−)-**9** with diisobutylaluminum hydride followed by methylation of (*S*)-(−)-1(*E*)-(5,5-dimethyl-2-isopropenylcyclohexylidene)acetaldehyde (**8**) with methyllithium and oxidation of the alcohol, (*S*)-(−)-1(*E*)-(5,5-dimethyl-2-isopropenylcyclohexylidene)-2-propanol (**7**), with pyridinium chlorochromate.

Treatment of the ene reaction product **5a** with LDA at −78 °C—room temperature gave a 1 : 1 equilibrium mixture of **5a** and **5b**. Furthermore, upon treatment with $TiCl_3$ at room temperature the products **5a**, **b** underwent reduction of the sulfinyl group followed by cyclization to give a single cyclic ethereal compound, (4a*R*,8a*R*)-(+)-4a,5,6,7,8,8a-hexahydro-1,1,3,6,6-pentamethyl-4-*p*-toluenesulfenyl-1*H*-2-benzopyran (**10a**). Therefore the absolute configurations of the ene reaction products **5a**, **b** were determined as (1*R*,2*R*,α*R*,*R*s)-**5a** and (1*R*,2*R*,α*S*,*R*s)-**5b**.

Reduction of the sulfinyl groups in the hetero-Diels–

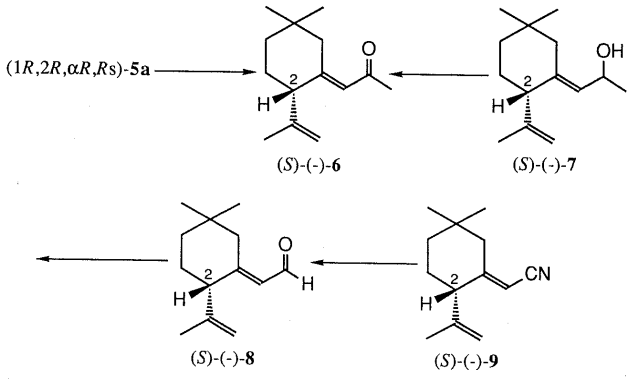


Chart 3

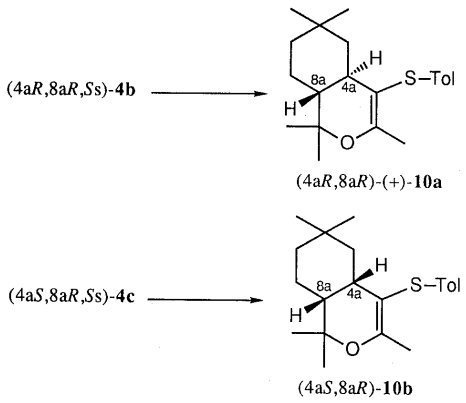


Chart 4

Alder reaction products **4a**, **4b**, and **4c** with $TiCl_3$ gave (4a*S*,8a*S*)-(−)-**10a**, (4a*R*,8a*R*)-(+)-**10a**, and **10b**, respectively. Therefore the absolute configurations of the hetero-Diels–Alder products **4a** and **4b** were determined as (4a*S*,8a*S*,*S*s)-**4a** and (4a*R*,8a*R*,*S*s)-**4b**. Thus, the other minor Diels–Alder product **4c** would have *cis* conjunction, which was confirmed by the observation of the small coupling constant ($J = 6$ Hz) between the hydrogen atoms at the C_{4a} and C_{8a} positions in the NMR spectrum, compared with those ($J = 10$ Hz) of the *trans* isomers **4a**, **b**. The absolute configuration of **4c** was deduced as (4a*S*,8a*R*,*S*s) on the basis of the mechanism of the asymmetric induction and therefore, that of **10b** was deduced as (4a*S*,8a*R*,*S*s).

Treatment of the ene reaction products **5a**,**b** with the Lewis acids employed as described in Table I gave no hetero-Diels–Alder products **4a**, **b**. Therefore it is suggested that the products **4a**, **b** would be formed directly by a [4+2] cycloaddition reaction of (*S*)-(+)-**3a**, not through the ene reaction products.

A chiral α-methoxycarbonylvinylic sulfoxide (*S*)-(+)-**3b** underwent an intramolecular asymmetric ene reaction to

afford a diastereomeric mixture of optically active cyclohexane derivatives, methyl (1*R*,2*R*,α*R*,*R*s)-(+)-(5,5-dimethyl-2-isopropenyl)-α-*p*-toluenesulfinylcyclohexaneacetate (**11a**) and (1*S*,2*S*,α*S*,*R*s)-(+)-(**11b**) with a slightly lower diastereomeric excess, compared to those in the case of the α-cyanovinylic sulfoxide,[10] upon treatment in dichloromethane or toluene at room temperature, 0, −20, or −78 °C with Lewis acids such as zinc(II) bromide and iodide, diethylaluminum chloride, and ethylaluminum dichloride. The diastereomeric excess of the products **11a, b** was determined by HPLC analysis and the results are listed in Table II. Use of diethylaluminum chloride as a catalyst at −78 °C provided the highest diastereomeric excess (86.2%), as shown in Table II.

The relative stereochemistry of the α-sulfinylacetate at the C_1 and the isopropenyl group at the C_2 position in the ene reaction products **11a, b** was assigned as *trans* based on the observation of NOE between the hydrogen arom at the C_1, and the methyl and the vinyl groups of the isopropenyl substituent at the C_2 position in the NMR spectral analysis. The relative stereochemistry of the C_α carbon center in **11a** was determined on the basis of the formation of methyl (*S*)-(−)-1(*E*)-(5,5-dimethyl-2-isopropenylcyclohexylidene)-acetate (**12**) by thermal *syn*-dehydrosulfenylation of **11a** under reflux in CCl_4.[14] The (*E*)-geometry of the resulting olefin in (*S*)-(−)-**12** was confirmed by the NOE between the olefinic hydrogen next to the methoxycarbonyl group, and the methyl and the vinyl groups of the isopropenyl substituent in the NMR spectral analysis.

Table II. Stereochemical Studies on the Intramolecular Ene Reactions of Chiral Vinyl Sulfoxide (*S*)-**3b**

Lewis acid[a]	Solvent	Reaction temp. (°C)	Reaction time (h)	Yield of **11a, b** (%)[b]	de (%) of **11a, b**[c]
$ZnBr_2$	CH_2Cl_2	r.t.	96	59 (86)	51.9
$ZnBr_2$	Toluene	r.t.	72	25 (97)	46.3
ZnI_2	CH_2Cl_2	r.t.	72	54 (83)	37.2
ZnI_2	Toluene	r.t.	72	42 (79)	32.1
Et_2AlCl	CH_2Cl_2	0	1	73 (95)	65.8
Et_2AlCl	CH_2Cl_2	−20	2	62 (79)	69.4
Et_2AlCl	CH_2Cl_2	−40	4	36 (58)	74.8
Et_2AlCl	CH_2Cl_2	−78	12	30 (62)	86.2
$EtAlCl_2$	CH_2Cl_2	0	1	46 (58)	61.8
$EtAlCl_2$	CH_2Cl_2	−20	1	48 (57)	58.9
$EtAlCl_2$	CH_2Cl_2	−78	2	25 (71)	64.5

a) Each reaction was carried out in the presence of a Lewis acid (1.5 eq). *b*) The yields based on the recovered starting material are listed in parentheses. *c*) The diastereomeric excess (de) was determined by high-performance liquid chromatographic analysis. r.t. = room temperature.

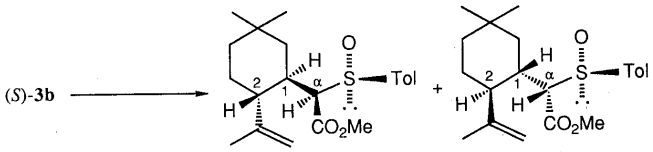


Chart 5

The minor product (+)-**11b** was assumed to be enantiomeric to the main product (+)-**11a** at the C_1 and C_2 positions. This was confirmed by the following transformation. The diethylaluminum chloride-catalyzed ene reaction of (*R*)-(+)-**3b**, derived from **1** and (*S*)-(−)-**2b**, produced a 93.1 : 6.9 mixture of (1*S*,2*S*,α*S*,*S*s)-(−)-**11a** and (1*R*,2*R*,α*R*,*S*s)-**11b**. The sulfinyl group in the major product (1*S*,2*S*,α*S*,*S*s)-(−)-**11a** was reduced by treatment with titanium(III) chloride in tetrahydrofuran (THF) at room temperature for 1 h to provide methyl (1*S*,2*S*,α*S*)-(+)-(5,5-dimethyl-2-isopropenyl)-α-*p*-toluenesulfenylcyclohexaneacetate (**14**). The oxidation of the sulfide (1*S*,2*S*,α*S*)-(+)-**14** with *m*-chloroperbenzoic acid in dichloromethane at −78 °C gave an 83.2 : 16.8 mixture of (1*S*,2*S*,α*S*,*S*s)-(−)-**11a** and (1*S*,2*S*,α*S*,*R*s)-(+)-**11b** in 81% yield. The minor product in this oxidation was identical with the minor product in the ene reaction of (*S*)-(+)-**3b**, in terms of the spectral data.

On the basis of the stereochemical results obtained, the mechanism of the asymmetric induction in this cycloaddition reaction can be rationalized as follows. The most stable conformation in the hetero-Diels–Alder transition state is illustrated in **15a**, in which the largest group (tolyl) on the chiral sulfinyl function is orientated *anti* to the methyl of the acetyl group. The dienophile (isopropylidene group)

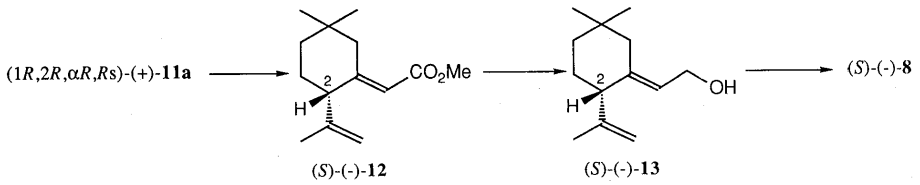


Chart 6

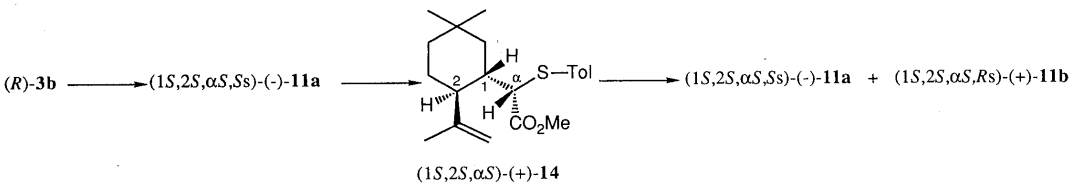


Chart 7

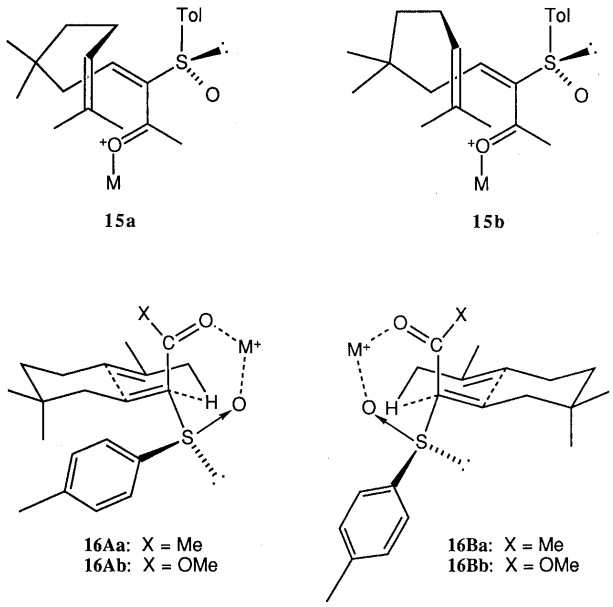


Chart 8

reacts preferentially in the *endo* selective fashion, as shown in **15a**, from the direction of the smallest substituent (lone pair) on the sulfinyl group, giving (4a*S*,8a*S*,*S*s)-(−)-**4a** as a main product, whereas the *endo* selective reaction from the direction of the sulfinyl oxygen atom affords (4a*R*,8a*R*,*S*s)-(+)-**4b** as a minor product. The other minor Diels–Alder adduct **4c** would be formed by the reaction through the *exo* transition state (**15b**) from the direction of the sulfinyl lone pair as mentioned above.

In the case of the ene reactions of (*S*)-**3a**, **b**, the Lewis acids employed activate the reactions by forming six-membered transition states **16A** and **16B**, in which the Lewis acids chelate with the sulfiny oxygen and the carbonyl oxygen of the ketone or ester, in six-membered chair-like form intermediates including the methyl hydrogen atoms of the isopropylidene groups. Rather severe steric repulsion occurs between the tolyl group and the cyclohexane ring in **16A**. Therefore the reactions would proceed selectively *via* **16Ba** or preferentially *via* **16Bb** to give (1*R*,2*R*,α*R*,*R*s)-(+)-**5a** and its α-isomerized product (1*R*,2*R*,α*S*,*R*s)-(−)-**5b** as a sole product, or (1*R*,2*R*,α*R*,*R*s)-(+)-**11a** as a main product, respectively. The other diastereomer (1*S*,2*S*,α*S*,*R*s)-(+)-**11b** would be obtained *via* **16Ab** as a minor product.

No Diels–Alder adduct could be detected when bidentate Lewis acids were used in the Lewis acid-catalyzed reactions of (*S*)-(+)-**3a**, as described earlier. This result can be rationalized in terms of the facile formation of the six-membered transition states by the chelation of the sulfinyl oxygen and the methyl ketone oxygen atom with the bidentate Lewis acids.

Thus, it is concluded that chiral α-sulfinyl α,β-unsaturated ketones and esters served as good chiral dienes or enophiles, depending on the Lewis acid used, to give hetero-Diels–Alder adducts or ene reaction products with high diastereo- and enantioselectivity. This method provides a valuable way for stereo- and enantiocontrolled synthesis of cyclic compounds.

Experimental

Infrared (IR) spectra were obtained in the indicated state with a JASCO DR-81 Fourier-transform infrared spectrometer. NMR spectra were determined in an indicated solvent with a JEOL GSX-400 (^{1}H-NMR, 400 MHz; ^{13}C-NMR, 100 MHz), EX-270 (^{1}H-NMR, 270 MHz; ^{13}C-NMR, 67.5 MHz), or JNM PMX-60SI (60 MHz) high-resolution NMR spectrometer; chemical shifts are given in ppm from tetramethylsilane as an internal standard. Splitting patterns are designated as s, singlet; ss, singlet singlet; d, doublet; dd, double doublet; t, triplet; q, quartet; m, multiplet. Mass spectra (MS) were taken on a JEOL JMS-DX 303/JMA-DA 5000 system. Optical rotations were measured with a JASCO DIP-370 or DIP-360 polarimeter. High-performance liquid chromatographic data (HPLC) were obtained with Tosoh UV-8010, CCPM (column, Tosoh TSK-GEL ODS-80TM). Flash column chromatography was performed with Merck Silica gel 60 (230—400 mesh). Thin layer or thick layer plates (preparative TLC) were made of Merck Silica gel 60PF-254 activated by drying at 140 °C for 3.5 h.

(*R*)-(+)-*p*-Toluenesulfinylacetone (2a) A dry 25 ml two-necked flask equipped with a septum inlet and a magnetic stirring bar was flushed with nitrogen, and maintained under a positive pressure of nitrogen. A solution of diisopropylamine (993 mg, 9.74 mmol) in THF (20 ml) was added to the flask. A 1.5 M butyllithium solution in hexane (6.49 ml, 9.74 mmol) was added to the above solution at 0 °C and the mixture was stirred at 0 °C for 15 min. A solution of optically pure (*R*)-(+)-methyl *p*-tolyl sulfoxide (1.00 g, 6.49 mmol)[12] in THF (10 ml) was added to the above solution. After the mixture had been stirred at 0 °C for 2 h, a solution of ethyl acetate (1.14 g, 12.99 mmol) in THF (10 ml) was added and the reaction mixture was further stirred at 0 °C for 30 min. The reaction solution was diluted with ethyl acetate, quenched with 10% aqueous HCl, and washed with saturated aqueous $NaHCO_3$ and saturated aqueous NaCl. The organic layers were combined, dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The residual oil was subjected to preparative TLC (ether) to give (*R*)-(+)-**2a** (900 mg, 71% yield, $[\alpha]_D^{25}$ +222.5° (*c*=1.07, MeOH)).[15]

Methyl (*R*)-(+)-*p*-Toluenesulfinylacetate (2b) A catalytic amount of sodium methoxide was added to a solution of *tert*-butyl (*R*)-(+)-*p*-toluenesulfinylacetate (1.00 g, 4.13 mmol, $[\alpha]_D^{26}$ +149.8° (*c*=1.66, MeOH))[13] in methanol (10 ml). The reaction mixture was stirred at room temperature for 4 h and then concentrated to dryness under reduced pressure. The residue was diluted with THF. The solution was washed with saturated aqueous NaCl, dried over molecular sieves 4A and concentrated *in vacuo*. The crude product was subjected to preparative TLC (ether–hexane 10:1) to give the methyl ester (*R*)-(+)-**2b** (638 mg, 77%yield, $[\alpha]_D^{27}$ +195.0° (*c*=1.75, MeOH)).[16] The chiral sulfoxide (*S*)-(−)-**2b** was prepared by the alcoholysis of *tert*-butyl (*S*)-(−)-*p*-toluenesulfinylacetate in the same way.

(*S*)-(+)-3-*p*-Toluenesulfinyl-6,6,10-trimethyl-3,9-undecadien-2-one (3a) A catalytic amount of piperidinium acetate was added to a solution of (*R*)-(+)-**2a** (1.00 g, 5.10 mmol, $[\alpha]_D^{25}$ +222.5° (*c*=1.07, MeOH)) and 3-methylcitronellal (**1**)[11] (1.27 g, 7.65 mmol) in benzene (20 ml). The reaction mixture was stirred in the presence of molecular sieves 4A (10 g) at room temperature for 48 h, and then the mixture was diluted with dichloromethane and filtered through Celite. The filtrate was washed with saturated aqueous $NaHCO_3$ and saturated aqueous NaCl, dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The crude product was subjected to preparative TLC (ether–hexane, 1:1) to give (*S*)-(+)-**3a** (1.20 g, 68% yield, $[\alpha]_D^{26}$ +84.4° (*c*=3.35, $CHCl_3$). IR ν_{max}^{film} cm^{-1}: 1690 (C=O), 1660, 1620 (C=C), 1600 (aromatic), 1050 (S=O). ^{1}H-NMR ($CDCl_3$) δ: 1.00 (6H, s, $(CH_3)_2C$), 1.02—2.33 (6H, m, $(CH_2)_2CCH_2$), 1.50, 1.66 (6H, ss, $C=C(CH_3)_2$), 2.15 (3H, s, $COCH_3$), 2.40 (3H, s, $C_6H_4CH_3$), 4.95—5.30 (1H, m, CH=C), 6.80—7.15 (1H, t, CH=CS), 7.37—7.70 (4H, q, C_6H_4). MS *m/z*: 346 (M^+). Exact mass determination: 346.1977 (Calcd for $C_{21}H_{30}O_2S$: 346.1967).

Methyl (*S*)-(+)-2-*p*-Toluenesulfinyl-5,5,9-trimethyl-2,8-decadienoate (3b) A catalytic amount of piperidinium acetate was added to a solution of (*R*)-(+)-**2b** (400 mg, 2.00 mmol, $[\alpha]_D^{27}$ +195.0° (*c*=1.75, MeOH)) and 3-methylcitronellal (**1**) (498 mg, 3.00 mmol) in benzene (10 ml). The reaction mixture was stirred in the presence of molecular sieves 4A (4.0 g) at room temperature for 72 h, and then the mixture was diluted with dichloromethane and filtered through Celite. The filtrate was washed with saturated aqueous $NaHCO_3$ and saturated aqueous NaCl, dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The crude product was subjected to preparative TLC (ether–hexane, 1:1) to give (*S*)-(+)-**3b** (623 mg, 86% yield). The reaction of (*S*)-(−)-**2b** (77% ee) with **1** was carried out in the same way to produce (*R*)-(−)-**3b** ($[\alpha]_D^{27}$ −139.1° (*c*=3.51, $CHCl_3$)).

(*S*)-(+)-**3b**: $[\alpha]_D^{25}$ +164.5° (*c*=1.10, $CHCl_3$). IR ν_{max}^{film} cm^{-1}: 1720 (ester),

1620 (C=C), 1600 (aromatic), 1050 (S=O). ^{1}H-NMR ($CDCl_3$) δ: 1.00 (6H, s, $(CH_3)_2C$), 1.00—2.75 (6H, m, $(CH_2)_2CCH_2$), 1.55—1.66 (6H, d, $(CH_3)_2C=C$), 2.40 (3H, s, $C_6H_4C\underline{H}_3$), 3.66 (3H, s, CO_2CH_3), 4.90—5.15 (1H, t, C=CH), 7.00—7.25 (1H, t, CH=CS), 7.33—7.60 (4H, q, C_6H_4). MS *m/z*: 362 (M^+). Exact mass determination: 362.1949 (Calcd for $C_{21}H_{30}O_3S$: 362.1916).

The Lewis Acid-Catalyzed Cycloaddition Reaction of (*S*)-(+)-3a A dry 25 ml two-necked flask equipped with a septum inlet and a magnetic stirring bar was flushed with nitrogen, and maintained under a positive pressure of nitrogen. A solution of Lewis acid (0.43 mmol) in dichloromethane (2 ml) was added to the flask. A solution of (*S*)-(+)-**3a** (100 mg, 0.29 mmol, $[\alpha]_D^{26}$ +84.4° (*c*=3.35, $CHCl_3$)) in dichloromethane (2 ml) was added to the above solution. The reaction mixture was stirred at the reaction temperature for the reaction time listed in Table I. The reaction mixture was diluted with dichloromethane and the solution was washed with saturated aqueous $NaHCO_3$ and saturated aqueous NaCl, dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The crude product was subjected to preparative TLC (ether–hexane, 1:2) to give (4a*S*,8a*S*,*Ss*)-(−)-4a,5,6,7,8,8a-hexahydro-1,1,3,6,6-pentamethyl-4-*p*-toluenesulfinyl-1*H*-2-benzopyran (**4a**), (4a*R*,8a*R*,*Ss*)-(+)-**4b**, (4a*S*,8a*R*,*Ss*)-(−)-**4c**, (1*R*,2*R*,α*R*,*Rs*)-(+)-1-(5,5-dimethyl-2-isopropenylcyclohexyl)-1-*p*-toluenesulfinyl-2-propanone (**5a**), and (1*R*,2*R*,α*S*,*Rs*)-(−)-**5b**. The yields and the diastereomeric excess of the products are summarized in Table I.

(4s*S*,8a*S*,*Ss*)-(−)-**4a**: $[\alpha]_D^{24}$ −102.8° (*c*=0.87, $CHCl_3$). IR ν_{max}^{film} cm^{-1}: 1640 (C=C), 1600 (aromatic), 1050 (S=O). ^{1}H-NMR ($CDCl_3$) δ: 0.62, 0.88 (6H, ss, $(CH_3)_2C$), 1.05—2.56 (7H, m, $CH(CH_2)_2CCH_2$), 1.18, 1.30 (6H, ss, $OC(CH_3)_2$), 1.74—1.82 (1H, t, *J*=10 Hz, CHC=C), 2.10 (3H, d, $C=CCH_3$), 2.39 (3H, s, $C_6H_4C\underline{H}_3$), 7.22—7.40 (4H, q, C_6H_4). MS *m/z*: 346 (M^+). Exact mass determination: 346.1944 (Calcd for $C_{21}H_{30}O_2S$: 346.1967).

(4a*R*,8a*R*,*Ss*)-(+)-**4b**: $[\alpha]_D^{26}$ +81.3° (*c*=1.67, $CHCl_3$). IR ν_{max}^{film} cm^{-1}: 1640 (C=C), 1600 (aromatic), 1050 (S=O). ^{1}H-NMR ($CDCl_3$) δ: 0.35, 0.83 (6H, ss, $(CH_3)_2C$), 0.91—1.79 (7H, m, $CH(CH_2)_2CCH_2$), 0.98, 1.27 (6H, ss, OC $(CH_3)_2$), 2.28 (3H, d, $C=CCH_3$), 2.40 (3H, s, $C_6H_4C\underline{H}_3$), 2.90—3.05 (1H, t, *J*=10 Hz, CHC=C), 7.26—7.43 (4H, q, C_6H_4). MS *m/z*: 346 (M^+). Exact mass determination: 346.1943 (Calcd for $C_{21}H_{30}O_2S$: 346.1967).

(4a*S*,8a*R*,*Ss*)-(−)-**4c**: $[\alpha]_D^{25}$ −46.7° (*c*=0.30, $CHCl_3$). IR ν_{max}^{film} cm^{-1}: 1640 (C=C), 1600 (aromatic), 1050 (S=O). ^{1}H-NMR ($CDCl_3$) δ: 0.62, 0.83 (6H, ss, $(CH_3)_2C$), 1.00—1.80 (7H, m, $CH(CH_2)_2CCH_2$), 1.28 (6H, s, $OC(CH_3)_2$), 2.15 (3H, d, $C=CCH_3$), 2.39 (3H, s, $C_6H_4C\underline{H}_3$), 2.61—2.53 (1H, t, *J*=6 Hz, CHC=C), 7.24—7.44 (4H, q, C_6H_4). MS *m/z*: 346 (M^+). Exact mass determination: 346.1944 (Calcd for $C_{21}H_{30}O_2S$: 346.1967).

(1*R*,2*R*,α*R*,*Rs*)-(+)-**5a**: $[\alpha]_D^{26}$ +141.7 (*c*=1.01, $CHCl_3$). IR ν_{max}^{film} cm^{-1}: 1710 (C=O), 1640 (C=C), 1600 (aromatic), 1050 (S=O). ^{1}H-NMR ($CDCl_3$) δ: 0.97, 0.99 (6H, ss, $(CH_3)_2C$), 1.00—2.33 (8H, m, $(CH)_2(CH_2)_2CCH_2$), 1.33 (3H, s, $CH_3C=C$), 2.33 (3H, s, $COCH_3$), 2.50 (3H, s, $C_6H_4C\underline{H}_3$), 3.80 (1H, s, CHS), 4.66, 4.80 (2H, s, $CH_2=C$), 7.33—7.70 (4H, q, C_6H_4). MS *m/z*: 346 (M^+). Exact mass determination: 346.1993 (Calcd for $C_{21}H_{30}O_2S$: 346.1967).

(1*R*,2*R*,α*S*,*Rs*)-(−)-**5b**: $[\alpha]_D^{24}$ −25.7° (*c*=1.01, $CHCl_3$). IR ν_{max}^{film} cm^{-1}: 1710 (C=O), 1640 (C=C), 1600 (aromatic), 1050 (S=O). ^{1}H-NMR ($CDCl_3$) δ: 1.00, 1.02 (6H, ss, $(CH_3)_2C$), 1.05—2.33 (8H, m, $(CH)_2(CH_2)_2CCH_2$), 1.66 (3H, s, $CH_3C=C$), 2.33 (3H, s, $COCH_3$), 2.40 (3H, s, $C_6H_4C\underline{H}_3$), 4.15 (1H, d, CHS), 5.00 (2H, s, $CH_2=C$), 7.15—7.66 (4H, q, C_6H_4). MS *m/z*: 346 (M^+). Exact mass determination: 346.1993 (Calcd for $C_{21}H_{30}O_2S$: 346.1967).

(*S*)-(−)-1-(*E*)-(5,5-Dimethyl-2-isopropenylcyclohexylidene)-2-propanone (6) A solution of (1*R*,2*R*,α*R*,*Rs*)-(+)-**5a** (50 mg, 0.14 mmol) in carbon tetrachloride (10 ml) was refluxed for 12 h. After being cooled, the solution was concentrated *in vacuo*. The crude product was subjected to preparative TLC (benzene–hexane, 4:1) to give (*S*)-(−)-(**6**) (18 mg, 63% yield), $[\alpha]_D^{25}$ −18.2° (*c*=0.39, $CHCl_3$). IR ν_{max}^{film} cm^{-1}: 1690 (C=O), 1650, 1620 (C=C). ^{1}H-NMR ($CDCl_3$) δ: 0.98, 1.00 (6H, ss, $(CH_3)_2C$), 1.15—3.30 (7H, m, $CH(CH_2)_2CCH_2$), 4.90—5.00 (2H, d, $CH_2=C$), 6.00 (1H, s, C=CH). MS *m/z*: 206 (M^+). Exact mass determination: 206.1640 (Calcd for $C_{14}H_{22}O$: 206.1671).

(*S*)-(−)-1(*E*)-(5,5-Dimethyl-2-isopropenylcyclohexylidene)acetaldehyde (8) A 0.98 M diisobutylaluminum hydride solution in hexane (0.81 ml, 0.79 mmol) was added to a solution of (*S*)-(−)-1(*E*)-(5,5-dimethyl-2-isopropenylcyclohexylidene)acetonitrile (**9**)[10] (66 mg, 0.35 mmol, $[\alpha]_D^{21}$ −12.4° (*c*=3.07, $CHCl_3$)) in ether (2 ml) and the mixture was stirred at 0 °C for 1 h. The reaction mixture was diluted with ether, quenched with 10% aqueous HCl, and warmed to room temperature during 30 min. The organic layer was washed with saturated aqueous $NaHCO_3$ and saturated aqueous NaCl, dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The crude product was subjected to preparative TLC (ether–hexane, 1:5) to give (*S*)-(−)-(**8**) (64 mg, 96% yield, $[\alpha]_D^{28}$ −76.1° (*c*=3.05, $CHCl_3$). IR ν_{max}^{film} cm^{-1}: 1670 (C=O), 1620 (C=C). ^{1}H-NMR ($CDCl_3$) δ: 0.87, 1.05 (6H, ss, $(CH_3)_2C$), 1.46—1.85 (4H, m, $C(CH_2)_2$), 1.72 (3H, s, CH_3C), 2.14—2.91 (2H, dd, $C=CCH_2$), 2.70—2.74 (1H, t, CH), 4.81—5.02 (2H, ss, $CH_2=C$), 5.89—5.90 (1H, d, C=CH), 10.00—10.03 (1H, d, CHO). MS *m/z*: 192 (M^+). Exact mass determination: 192.1553 (Calcd for $C_{13}H_{20}O$: 192.1514).

(*S*)-(−)-1(*E*)-(5,5-Dimethyl-2-isopropenylcyclohexylidene)-2-propanol (7) A 0.98 M methyllithium solution in ether (0.31 ml, 0.30 mmol) was added to a solution of (*S*)-(−)-**8** (38 mg, 0.20 mmol, $[\alpha]_D^{28}$ −69.3° (*c*=2.44, $CHCl_3$)) at −78 °C and the reaction mixture was stirred for 2 h. The mixture was diluted with ether and washed with saturated aqueous NaCl. The organic layer was dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The residual oil was subjected to flash column chromatography (ether–hexane, 1:5) to give (*S*)-(−)-**7** (34 mg, 83% yield, $[\alpha]_D^{28}$ −66.6° (*c*=1.11, $CHCl_3$)). IR ν_{max}^{film} cm^{-1}: 3350 (OH), 1660, 1640 (C=C). ^{1}H-NMR ($CDCl_3$) δ: 0.95—1.15 (6H, ss, $(CH_3)_2C$), 1.15, 1.33 (3H, d, $OCCH_3$), 1.33—2.66 (8H, m, $CH(CH_2)_2CCH_2$, OCH), 4.33—5.00 (2H, d, $CH_2=C$), 5.15, 5.33 (1H, d, C=CH). MS *m/z*: 208 (M^+). Exact mass determination: 208.1890 (Calcd for $C_{14}H_{24}O$: 208.1827).

Synthesis of (*S*)-(−)-6 by Oxidation of (*S*)-(−)-7 A mixture of (*S*)-(−)-**7** (33 mg, 0.16 mmol, $[\alpha]_D^{28}$ −66.6° (*c*=1.11, $CHCl_3$)) and pyridinium chlorochromate (51 mg, 0.24 mmol) in dichloromethane (3 ml) was stirred vigorously at room temperature for 4 h. The reaction mixture was diluted with ether and filtered through Celite. The filtrate was concentrated *in vacuo* and the residual oil was subjected to flash column chromatography (ether–hexane, 1:10) to give (*S*)-(−)-**6** (25 mg, 77% yield, $[\alpha]_D^{27}$ −16.5° (*c*=1.03, $CHCl_3$)). The spectral data were identical with those of the sample obtained from (1*R*,2*R*,α*R*,*Rs*)-(+)-**5a**, as described above.

(4a*R*,8a*R*)-(+)-4a,5,6,7,8,8a-Hexahydro-1,1,3,6,6-pentamethyl-4-*p*-toluenesulfenyl-1*H*-2-benzopyran (10a) A mixture of (1*R*,2*R*,α*R*,*Rs*)-(+)-**5a** (30 mg, 0.09 mmol) and 1.1 M aqueous titanium(III) chloride (1.64 ml, 1.80 mmol) in THF (1 ml) was stirred at room temperature for 8 h. The reaction mixture was diluted with ether. The solution was washed with saturated aqueous $NaHCO_3$ and saturated aqueous NaCl, dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The residual oil was subjected to flash column chromatography (ether–hexane, 1:10) to give (4a*R*,8a*R*)-(+)-**10a** (2 mg, 7% yield, $[\alpha]_D^{28}$ +37.0° (*c*=0.16, $CHCl_3$)). Upon treatment with titanium(III) chloride under the same reaction conditions, (1*R*,2*R*,α*S*,*Rs*)-(−)-**5b** produced (4a*R*,8a*R*)-(+)-**10a** $[\alpha]_D^{25}$ +55.5° (*c*=0.05, $CHCl_3$). IR ν_{max}^{film} cm^{-1}: 1640 (C=C), 1600 (aromatic) ^{1}H-NMR ($CDCl_3$) δ: 0.76, 0.86 (6H, ss, $(CH_3)_2C$), 0.79—1.99 (8H, m, $CH(CH_2)_2CCH_2CH$), 1.16, 1.30 (6H, ss, $OC(CH_3)_2$), 2.03, 2.04 (3H, d, $C=CCH_3$), 2.29 (3H, s, $C_6H_4C\underline{H}_3$), 7.05—7.09 (4H, q, C_6H_4). ^{13}C-NMR ($CDCl_3$) δ: 19.5, 20.2, 20.9, 23.9, 24.8, 27.5, 30.9, 33.1, 33.6, 39.4, 43.5, 49.4, 77.6, 101.3, 126.4, 129.4, 134.3, 135.2, 157.5. MS *m/z*: 330 (M^+). Exact mass determination: 330.2022 (Calcd for $C_{21}H_{30}OS$: 330.2018).

Reduction of 4a—c A mixture of (4a*S*,8a*S*,*Ss*)-(−)-**4a** (35 mg, 0.10 mmol) and 1.1 M aqueous titanium(III) chloride (0.28 ml, 0.30 mmol) in THF (1 ml) was stirred at room temperature for 1 h. The reaction mixture was diluted with ether. The solution was washed with saturated aqueous $NaHCO_3$ and saturated aqueous NaCl, dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The residual oil was subjected to flash column chromatography (ether–hexane, 1:10) to give (4a*S*,8a*S*)-(−)-**10a** (30 mg, 91% yield, $[\alpha]_D^{28}$ −29.1° (*c*=1.93, $CHCl_3$)). The reductions of (4a*R*,8a*R*,*Ss*)-(+)-**4b** and (4a*S*,8a*R*,*Ss*)-(−)-**4c** were carried out in the same way to give (4a*R*,8a*R*)-(+)-**10a** ($[\alpha]_D^{29}$ +26.2° (*c*=1.56, $CHCl_3$)) and (4a*S*,8a*R*)-**10b**, respectively. The spectral data of (4a*S*,8a*S*)-(−)-**10a** were identical with those of the product (4a*R*,8a*R*)-(+)-**10a** obtained from (1*R*,2*R*,α*R*,*Rs*)-(+)-**5a** as described above, except for the optical rotation.

(4a*S*,8a*R*)-**10b**: IR ν_{max}^{film} cm^{-1}: 1640 (C=C), 1600 (aromatic). ^{1}H-NMR ($CDCl_3$) δ: 0.86, 0.94 (6H, ss, $(CH_3)_2C$), 1.09—2.51 (8H, m, $CH(CH_2)_2CCH_2CH$), 1.27, 1.29 (6H, ss, $OC(CH_3)_2$), 2.08, 2.09 (3H, d, $C=CCH_3$), 2.29 (3H, s, $C_6H_4C\underline{H}_3$), 7.03—7.13 (4H, q, C_6H_4). ^{13}C-NMR ($CDCl_3$) δ: 19.5, 19.8, 20.9, 25.3, 26.1, 26.2, 29.6, 29.7, 32.3, 33.2, 39.2, 39.4, 42.2, 96.1, 102.7, 127.2, 129.5, 134.7, 156.6. MS *m/z*: 330 (M^+). Exact mass determination: 330.2022 (Calcd for $C_{21}H_{30}OS$: 330.2018).

The Lewis Acid-Catalyzed Ene Reaction of (*S*)-(+)-3b A dry 25 ml two-necked flask equipped with a septum inlet and a magnetic stirring bar was flushed with nitrogen, and maintaind under a positive pressure of nitrogen. A solution of a Lewis acid (0.41 mmol) in dichloromethane (2 ml)

was added to the flask. A solution of (*S*)-(+)-**3b** (100 mg, 0.28 mmol, $[\alpha]_D^{25}$ +164.5° (*c*=1.10, $CHCl_3$)) in dichloromethane (2 ml) was added to the above solution. The reaction mixture was stirred at the reaction temperature for the reaction time listed in Table I. It was then diluted with dichloromethane and the solution was washed with saturated aqueous $NaHCO_3$ and saturated aqueous NaCl, dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The crude product was subjected to preparative TLC (ether–hexane, 1:2) to give methyl (1*R*,2*R*,α*R*,*Rs*)-(+)-(5,5-dimethyl-2-isopropenyl)-α-*p*-toluenesulfinylcyclohexaneacetate (**11a**) and (1*S*,2*S*,α*S*,*Rs*)-(+)-(**11b**). The yields and the diastereomeric excess of the products are summarized in Table II.

(1*R*,2*R*,α*R*,*Rs*)-(+)-**11a**: $[\alpha]_D^{27}$ +41.2° (*c*=1.24, $CHCl_3$). IR ν_{max}^{film} cm^{-1}: 1735 (ester), 1640 (C=C), 1600 (aromatic), 1050 (S=O). ^{1}H-NMR ($CDCl_3$) δ: 0.80, 0.93 (6H, ss, $(CH_3)_2C$), 1.11—1.76 (7H, m, $(CH_2)_2CCH_2CH$), 1.24 (3H, s, CH_3C=C), 1.77—1.85 (1H, t, CHCS), 2.43 (3H, s, $C_6H_4C\underline{H}_3$), 3.76—3.77 (1H, d, CHS), 3.81 (3H, s, CO_2CH_3), 4.40—4.69 (2H, d, CH_2=C), 7.32—7.61 (4H, q, C_6H_4). ^{13}C-NMR ($CDCl_3$) δ: 19.1, 21.6, 24.1, 28.4, 30.8, 33.0, 34.8, 38.4, 41.1, 48.2, 52.3, 74.4, 112.6, 126.0, 129.8, 138.9, 142.9, 146.4, 168.4. MS *m/z*: 362 (M^+). Exact mass determination; 362.1913 (Calcd for $C_{21}H_{30}O_3S$: 362.1916).

(1*S*,2*S*,α*S*,*Rs*)-(+)-**11b**: $[\alpha]_D^{27}$ +30.6° (*c*=1.11, $CHCl_3$). IR ν_{max}^{film} cm^{-1}: 1740 (ester), 1640 (C=C), 1600 (aromatic), 1050 (S=O). ^{1}H-NMR ($CDCl_3$) δ: 1.10 1.15 (6H, ss, $(CH_3)_2C$), 1.12—2.33 (8H, m, $(CH_2)_2CCH_2(CH_2)_2$), 1.70 (3H, s, CH_3C=C), 2.43 (3H, s, $C_6H_4C\underline{H}_3$), 3.66 (3H, s, CO_2CH_3), 3.76—3.77 (1H, d, CHS), 4.90—5.00 (2H, d, CH_2=C), 7.33—7.70 (4H, q, C_6H_4). MS *m/z*: 362 (M^+). Exact mass determination: 362.1913 (Calcd for $C_{21}H_{30}O_3S$: 362.1916).

Methyl (*S*)-(−)-1(*E*)-(5,5-Dimethyl-2-isopropenylcyclohexylidene)-acetate (12) A solution of (1*R*,2*R*,α*R*,*Rs*)-(+)-**11a** (110 mg, 0.30 mmol) in carbon tetrachloride (10 ml) was refluxed for 4 h. After being cooled, the solution was concentrated *in vacuo*. The crude product was subjected to preparative TLC (benzene–hexane, 4:1) to give (*S*)-(−)-**12** (49 mg, 73% yield), $[\alpha]_D^{25}$ −34.9° (*c*=2.29, $CHCl_3$)). IR ν_{max}^{film} cm^{-1}: 1720 (ester), 1640 (C=C). ^{1}H-NMR ($CDCl_3$) δ: 0.90, 1.10 (6H, ss, $(CH_3)_2C$), 1.33—2.70 (4H, m, $(CH_2)_2$), 1.75 (3H, s, CH_3C=C), 2.00—3.40 (2H, m, CCH_2), 2.50—2.60 (1H, t, CH), 3.66 (3H, s, CO_2CH_3), 4.70—5.00 (2H, d, CH_2=C), 5.66 (1H, s, C=CH). MS *m/z*: 222 (M^+). Exact mass determination: 222.1597 (Calcd for $C_{14}H_{22}O_2$: 222.1619).

(*S*)-(−)-1(*E*)-(5,5-Dimethyl-2-isopropenylcyclohexylidene)ethanol (13) A 0.98 M diisobutylaluminum hydride solution in hexane (0.44 ml, 0.40 mmol) was added to a solution of (*S*)-(−)-**12** (40 mg, 0.18 mmol, $[\alpha]_D^{25}$ −34.9° (*c*=2.29, $CHCl_3$)) in ether (4 ml) and the reaction mixture was stirred at 0 °C for 1 h. The reaction mixture was diluted with ether, then quenched with saturated aqueous NaCl, and extracted with ether. The extracts were combined, dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The crude product was subjected to flash column chromatography (ether–hexane, 1:5) to give (*S*)-(−)-**13** (34 mg, 97% yield, $[\alpha]_D^{25}$ −62.6° (*c*=0.66, $CHCl_3$)). IR ν_{max}^{film} cm^{-1}: 3350 (OH), 1640 (C=C). ^{1}H-NMR ($CDCl_3$) δ: 0.95, 1.10 (6H, ss, $(CH_3)_2C$), 1.33—2.50 (6H, m, $(CH_2)_2CCH_2$), 1.72 (3H, s, CH_3C), 2.55—2.75 (1H, t, CH), 4.15—4.33 (2H, d, C=CCH_2), 4.80—5.10 (2H, d, CH_2=C), 5.33—5.66 (1H, m, C=CH). MS *m/z*: 194 (M^+). Exact mass determination: 194.1673 (Calcd for $C_{13}H_{22}O$: 194.1671).

Conversion of (*S*)-(−)-13 into (*S*)-(−)-8 A mixture of (*S*)-(−)-**13** (34 mg, 0.18 mmol, $[\alpha]_D^{25}$ −62.6° (*c*=0.66, $CHCl_3$)) and pyridinium chlorochromate (57 mg, 0.26 mmol) in dichloromethane (4 ml) was stirred at room temperature for 4 h. The mixture was diluted with ether and filtered through Celite. The filtrate was concentrated *in vacuo*. The crude product was subjected to flash column chromatography (ether–hexane, 1:5) to give (*S*)-(−)-**8** (33 mg, 97% yield, $[\alpha]_D^{23}$ −70.5° (*c*=1.23, $CHCl_3$)). The spectral data were identical with those of (*S*)-(−)-**8** obtained from (*S*)-(−)-**9**, as described earlier.

Methyl (1*S*,2*S*,α*S*)-(+)-(5,5-Dimethyl-2-isopropenyl)-α-*p*-toluenesulfenylcyclohexaneacetate (14) A 1.1 M aqueous solution of titanium(III) chloride (0.60 ml, 0.66 mmol) was added to a solution of (1*S*,2*S*,α*S*,*Ss*)-(−)-**11a** (80 mg, 0.22 mmol) in THF (5 ml) at 0 °C. The reaction mixture was warmed to room temperature and stirred for 1 h. The reaction was quenched with saturated aqueous $NaHCO_3$, and the mixture was extracted with ether. The extracts were combined, washed with saturated aqueous NaCl, dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The crude product was subjected to preparative TLC (ether–hexane, 1:10) to give (1*S*,2*S*,α*S*)-(+)-**14** (42 mg, 55% yield), $[\alpha]_D^{25}$ +17.5° (*c*=4.23, $CHCl_3$). IR ν_{max}^{film} cm^{-1}: 1740 (C=O), 1640 (C=C), 1600 (aromatic). ^{1}H-NMR ($CDCl_3$) δ: 0.90, 0.95 (6H, ss, $(CH_3)_2C$), 1.20—2.20 (8H, m, $(CH)_2CH_2C(CH_2)_2$), 1.65 (3H, s, CH_3C=C), 2.33 (3H, s, $C_6H_4C\underline{H}_3$), 3.66 (3H, s, CO_2CH_3), 4.85—4.90 (1H, d, CHS), 4.50—4.70 (2H, d, CH_2=C), 6.95—7.45 (4H, q, C_6H_4). MS *m/z*: 346 (M^+). Exact mass determination: 346.1970 (Calcd for $C_{21}H_{30}O_2S$: 346.1967).

Preparation of (1*S*,2*S*,α*S*,*Ss*)-(−)-11a and (1*S*,2*S*,α*S*,*Rs*)-(+)-11b by Oxidation of (1*S*,2*S*,α*S*)-(+)-14 *m*-Chloroperbenzoic acid (25 mg, 0.15 mmol) was added to a solution of (1*S*,2*S*,α*S*)-(+)-**14** (40 mg, 0.12 mmol) in dichloromethane (5 ml) at −78 °C, and the mixture was stirred at −78 °C for 4 h. The reaction was quenched with saturated aqueous $NaHCO_3$, and the mixture was diluted with dichloromethane. The solution was washed with saturated aqueous NaCl, dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The crude product was subjected to preparative TLC (ether–hexane, 1:1) to give a 83.2:16.8 mixture of (1*S*,2*S*,α*S*,*Ss*)-(−)-**11a** ($[\alpha]_D^{25}$ −40.4° (*c*=1.04, $CHCl_3$)) and (1*S*,2*S*,α*S*,*Rs*)-(+)-**11b** ($[\alpha]_D^{27}$ +56.3° (*c*=0.32, $CHCl_3$)) (35 mg, 81% yield). The spectral data of these products were identical with those of the ene reaction products of (*S*)-(+)-**3b**.

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