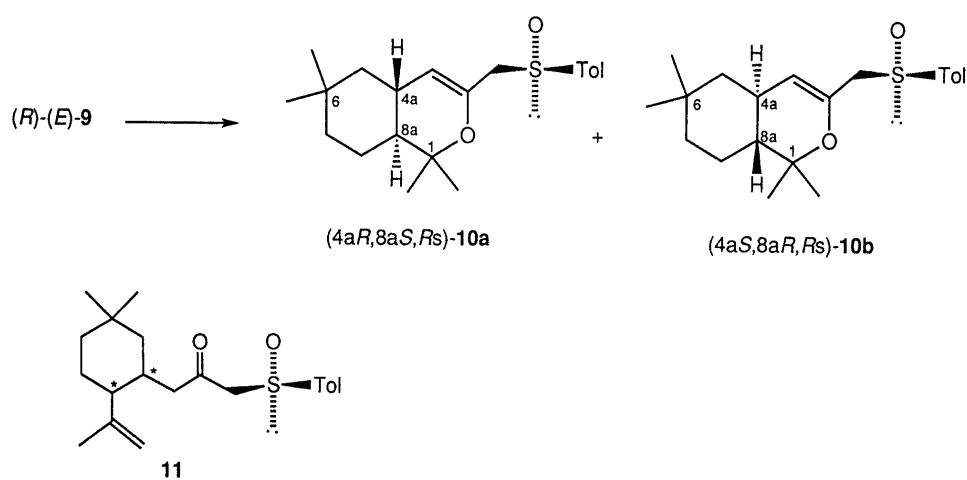
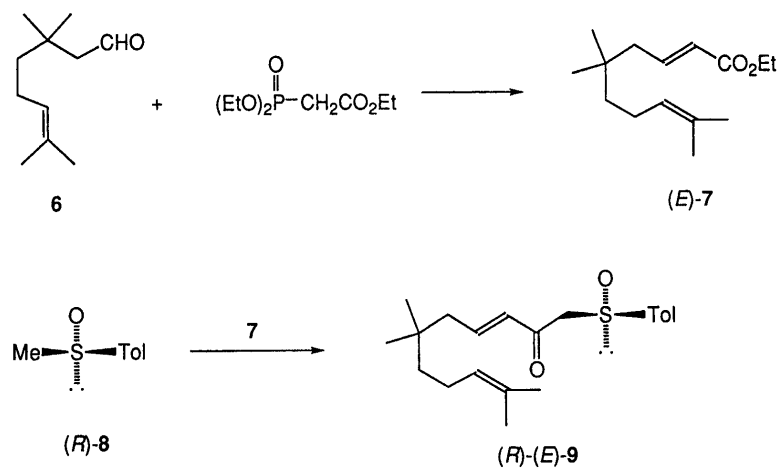


Table 1. Studies on the Lewis Acid-Catalyzed Intramolecular Asymmetric Hetero Diels–Alder Reactions of (*R*)-9

Lewis acid	Solvent	Reaction conditions ^{a)}		Yield of 10 (%)	de (%) of 10 ^{b)}
		Temp. (°C)	Time (h)		
ZnCl ₂	CH ₂ Cl ₂	0	2	94	40.0
ZnCl ₂	Toluene	0	2	63	48.6
ZnBr ₂	CH ₂ Cl ₂	0	3	47	40.2
ZnBr ₂	Toluene	0	3	75	38.3
Zn I ₂	CH ₂ Cl ₂	0	2	82	44.2
Zn I ₂	Toluene	0	2	82	38.6
Et ₂ AlCl	CH ₂ Cl ₂	−78	1	84	42.5
Et ₂ AlCl	Toluene	−78	1	100	28.5
Et ₂ AlCl	Hexane	r.t.	18	48	34.7
EtAlCl ₂	CH ₂ Cl ₂	−78	2	72	38.5
EtAlCl ₂	Toluene	−78	1	82	35.8
AlCl ₃	CH ₂ Cl ₂	−78	2	77	29.0
AlCl ₃	Toluene	−78	2	54	38.0
Me ₃ Al	CH ₂ Cl ₂	−78	1	61	18.5 ^{c)}
FeCl ₃	CH ₂ Cl ₂	0	2	42	44.8
FeCl ₃	Toluene	0	1	68	36.6
TiCl ₄	CH ₂ Cl ₂	−78	1	85	31.7
SnCl ₄	CH ₂ Cl ₂	−78	1	82	45.4
SnCl ₄	Toluene	−78	1	81	60.6
BF ₃ ·OEt ₂	CH ₂ Cl ₂	0	2	74	15.2 ^{c)}
BF ₃ ·OEt ₂	Toluene	0	2	70	3.0 ^{c)}

^{a)} The reactions of (*R*)-9 were carried out in the presence of a Lewis acid (1.5 eq). ^{b)} The diastereomeric excess (de) of **10a** over **10b** was determined by HPLC analysis. ^{c)} Compound (4*aS*,8*aR*,*Rs*)-**10b** was obtained as the main product.

(*R*)-(+)-(*E*)-1-(*p*-toluenesulfinyl)-6,6,10-trimethyl-3,9-undecadien-2-one (**9**) in 81% yield. The chirality of the sulfinyl function in (*R*)-**8** was retained in this condensation.

The Lewis acid-catalyzed reactions of (*R*)-(*E*)-**9** were carried out in dichloromethane, toluene, or hexane at -78 – 0 °C to give optically active hetero Diels–Alder reaction products, (4*aR*,8*aS*,*Rs*)- and (4*aS*,8*aR*,*Rs*)-4*a*,5,6,7,8,8*a*,-hexahydro-1,1,6,6-tetramethyl-2-*p*-toluenesulfinylmethyl-1*H*-2-benzopyran (**10a**) and (**10b**), with no ene reaction product **11**. The results obtained by using various Lewis acids are summarized in Table 1. The ratios of the diastereomers **10a** to **10b** obtained under various reaction conditions were determined by high-performance liquid chromatographic (HPLC) analysis and are listed in Table 1.

Upon treatment with zinc(II) halide (chloride, bromide, or iodide) in dichloromethane or toluene at 0 °C for 2–3 h, (*R*)-**9** underwent exclusively an intramolecular hetero Diels–Alder reaction to give **10a, b** with a moderate diastereomeric excess (de) of **10a** over **10b** (38–48%). A slightly increasing de of the product **10a, b** was observed in the reaction of (*R*)-**9** catalyzed with ZnCl_2 in toluene at 0 °C. However, rather a high yield (94 or 82–84%) of **10a, b** was obtained by catalysis with ZnCl_2 in dichloromethane or with ZnI_2 in dichloromethane or toluene, respectively.

The use of aluminum compounds (Et_2AlCl , EtAlCl_2 , AlCl_3 , Me_3Al) as Lewis acids in dichloromethane or toluene at -78 °C led to smooth conversion of (*R*)-**9** into hetero Diels–Alder products **10a, b** with rather lower de in good yield (quantitatively with the use of Et_2AlCl at -78 °C in toluene). However, the opposite distereoselectivity of **10a, b** was observed on the use of trimethylaluminum (18.5% de of **10b** over **10a**).

Further studies on this asymmetric reaction were carried

out using other Lewis acids (e.g. FeCl_3 , TiCl_4 , SnCl_4 , $\text{BF}_3 \cdot \text{OEt}_2$). The highest de (60.6%) of the products **10a, b** was obtained with SnCl_4 under the reaction conditions of -78 °C in toluene for 1 h. Slight preference for **10b** over **10a** was seen with $\text{BF}_3 \cdot \text{OEt}_2$ as a catalyst.

No hetero Diels–Alder reaction occurred under thermal reaction conditions (in toluene under reflux for 48 h) without any catalyst.

The stereochemistry of the products (**10a, b**) was confirmed as *trans* by the observation of nuclear Overhauser effects (NOE) between the C_{4a} hydrogen atom and the methyl groups at the C_1 and C_6 positions in the NMR spectral analysis of the sulfide (4*aR*,8*aS*)- and (4*aS*,8*aR*)-**12** obtained by the TiCl_3 reduction of the sulfinyl function in (4*aR*,8*aS*,*Rs*)-**10a** and (4*aS*,8*aR*,*Rs*)-**10b**, respectively.

The absolute configuration of the two newly created asymmetric carbons in the hetero Diels–Alder products **10a, b** was determined by chemical correlation to the chiral sulfinyl compound **15** of known absolute configuration¹⁰) as follows. The reductive desulfinylation of the chiral sulfoxide **10a** with sodium was carried out in isopropanol–THF¹⁶) at room temperature for 2 h to give (4*aR*,8*aS*)-(+)-4*a*,5,6,7,8,8*a*-hexahydro-1,1,3,6,6-pentamethyl-1*H*-2-benzopyran (**13**) in 90% yield. The same reaction of the chiral sulfoxide **10b** with sodium gave (4*aS*,8*aR*)-(–)-**13**. The bromination of the cyclic enol ether (4*aR*,8*aS*)- or (4*aS*,8*aR*)-**13** with *N*-bromosuccinimide in $\text{THF-H}_2\text{O}$ (4:1) at room temperature for 3 h gave an α -bromo cyclic enol ether (4*aS*,8*aS*)- or (4*aR*,8*aR*)-**14**, respectively. After treatment of the vinylic bromide (4*aS*,8*aS*)- or (4*aR*,8*aR*)-**14** with butyllithium at -78 °C in THF, the sulfonylation reaction of the carbanion generated with methyl (*S*)-*p*-toluenesulfonate at -78 °C for 2 h produced the known chiral sulfinyl compounds, (4*aS*,8*aS*,*Ss*)-**15a**¹⁰) and (4*aR*,8*aR*,*Ss*)-**15b**,¹⁰) respectively. The reduction of the sulfinyl groups in (4*aS*,8*aS*,*Ss*)-**15a**

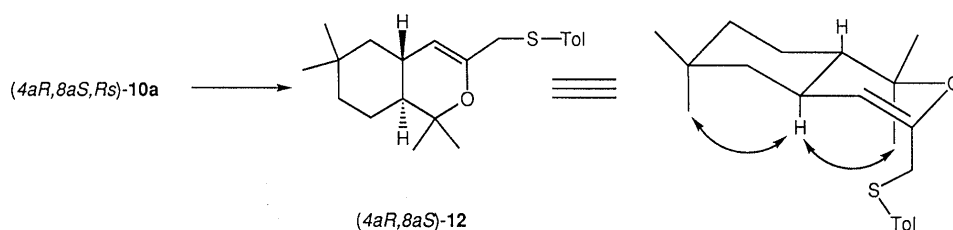


Chart 4

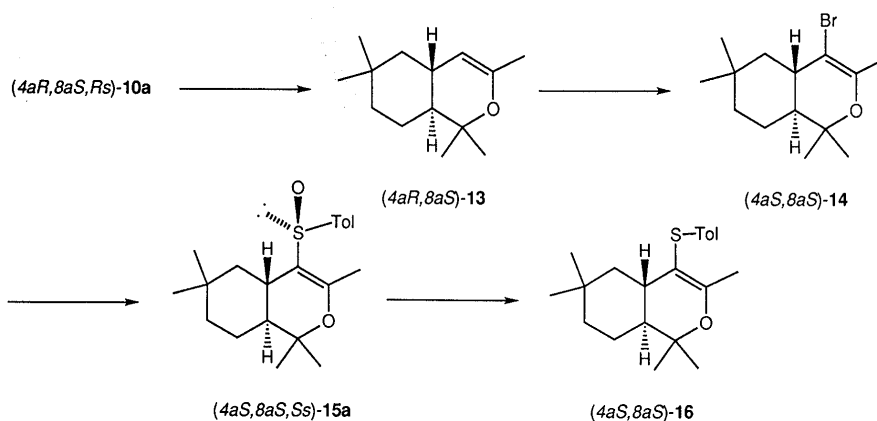


Chart 5

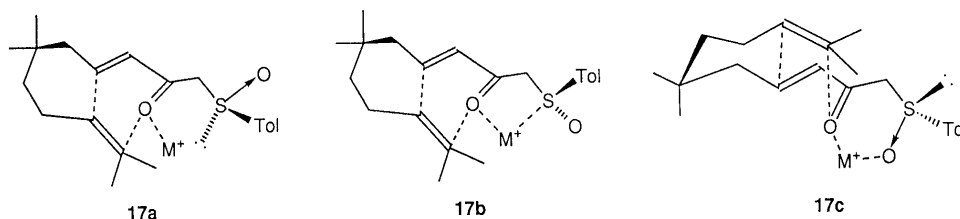


Chart 6

and (4a*R*,8a*R*,*Ss*)-**15b** with TiCl_3 in THF at room temperature furnished the known chiral sulfenyl compound, (4a*S*,8a*S*)-(–)-**16**¹⁰ and (4a*R*,8a*R*)-(+)-**16**,¹⁰ respectively, in 90% yield in both cases. Thus, the absolute configuration of the two newly created asymmetric carbons in **10a** and **10b** formed by this hetero Diels–Alder reaction was determined as (4a*R*,8a*S*) and (4a*S*,8a*R*), respectively.

The mechanism of the asymmetric induction in this hetero Diels–Alder reaction was rationalized on the basis of the following stereochemical considerations. The intramolecular cycloaddition of the olefin to the α,β -unsaturated ketone in (*R*)-**9** would occur preferentially from the side with the less hindered lone pair of the chiral sulfenyl group in the preferred conformation **17a** generated by dipole–dipole repulsion between the carbonyl group of the ketone and the sulfenyl sulfur–oxygen bond, yielding (4a*R*,8a*S*,*Rs*)-**10a** as a main product. The stereochemical results could also be rationalized in terms of cycloaddition from the same side as the oxygen atom of the sulfenyl group in the alternative possible intermediate **17b** formed by the chelation of the carbonyl oxygen and the lone pair of the sulfenyl group to the metal function. On the use of $\text{BF}_3 \cdot \text{Et}_2\text{O}$ or Me_3Al as a catalyst, (4a*S*,8a*R*,*Ss*)-**10b** was formed, with slight de, presumably through the predominant intramolecular cycloaddition of (*R*)-**9** from the side with the less hindered lone pair of the chiral sulfenyl group in the six-membered transition state **17c** formed by the chelation of the carbonyl oxygen and the sulfenyl oxygen to the Lewis acid metals used.

The reaction path in this hetero Diels–Alder reaction depended on the Lewis acids used. The role of Lewis acids in this reaction is unclear. Presumably the acidity of the Lewis acids used would determine the reaction path. It should be noted that rather strong Lewis acids such as AlCl_3 and TiCl_4 provided lower de of **10a** over **10b**, whereas rather weak Lewis acids such as SnCl_4 and ZnCl_2 resulted in higher de. The slightly stronger affinity of the sulfenyl oxygen atom to Me_3Al and BF_3 would favor the intermediate **17c** over **17a,b**, generating the slight diastereoselectivity for **10b** over **10a**.

Thus, the chiral α' -sulfenyl- α,β -unsaturated ketone was demonstrated to serve as a chiral diene in the Lewis acid-catalyzed reaction to provide the asymmetric hetero Diels–Alder adducts with moderate stereoselectivity. This method provided an alternative route to optically active cyclic enol ethers, based on the effect of the chirality of the optically active sulfenyl group.

Experimental

Infrared (IR) spectra were obtained in the indicated state with a JASCO DR-81 Fourier-transform IR spectrometer. NMR spectra were determined in the indicated solvent with JEOL EX-270 (^1H -NMR; 270 MHz, ^{13}C -NMR; 67.5 MHz) and JNM PMX-60si (60 MHz)

high-resolution NMR spectrometers; chemical shifts are given in ppm from tetramethylsilane as an internal standard. Splitting patterns are designated as s, singlet; d, doublet; dd, doublets of 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 at 25 °C with a JASCO DIP-370 polarimeter. HPLC data were obtained with a 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.

Ethyl (E)-5,5,9-Trimethyl-2,8-decadienoate (7) A dry 100 ml two-necked flask equipped with a septum inlet and a magnetic stirring bar, and containing sodium hydride (0.37 g, 7.79 mmol, 50% oil dispersion), was flushed with nitrogen and maintained under a positive pressure of nitrogen. THF (10 ml) was added to the flask and the mixture was cooled to 0 °C. A solution of ethyl diethoxyphosphonyl acetate (1.75 g, 7.79 mmol) in THF (10 ml) was added and the mixture was stirred at 0 °C for 30 min. A solution of 3-methylcitronellal (**6**)¹⁴ (1.00 g, 6.49 mmol) in THF (10 ml) was further added and the reaction mixture was stirred at 0 °C for 30 min. It was diluted with ether and the solution was washed successively with saturated aqueous NH_4Cl and saturated aqueous NaCl, dried over anhydrous Na_2SO_4 , and concentrated *in vacuo*. The crude product was subjected to flash column chromatography (ether–hexane, 1:30) to give (*E*)-**7** (1.25 g, 81% yield).

(*E*)-**7**: IR $\nu_{\text{max}}^{\text{film}}$ cm^{-1} : 1700 (ester), 1640 ($\text{C}=\text{C}$). ^1H -NMR (60 MHz) (CCl_4) δ : 0.92 (6H, s, $(\text{CH}_3)_2\text{C}$), 1.00–2.05 (6H, m, $\text{CH}_2\text{C}(\text{CH}_3)_2$), 1.25 (3H, t, $J=7\text{ Hz}$, CH_2CH_3), 1.58, 1.65 (6H, s, s, $(\text{CH}_3)_2=\text{C}$), 4.10 (2H, q, $J=7\text{ Hz}$, CH_2CH_3), 4.96 (1H, t, $J=6\text{ Hz}$, $\text{CH}=\text{C}$), 5.68 (1H, d, $J=16\text{ Hz}$, $\text{CH}=\text{CHCO}$), 6.67 (1H, dd, $J=8, 16\text{ Hz}$, $\text{CH}=\text{CHCO}$). MS m/z : 238 (M^+). Exact mass determination: 238.1931 (Calcd for $\text{C}_{15}\text{H}_{26}\text{O}_2$: 238.1933).

(R)-(+)-(E)-1-(p-Toluenesulfinyl)-6,6,10-trimethyl-3,9-undecadien-2-one (9) A dry 50 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 (0.68 ml, 4.87 mmol) in THF (10 ml) was added to the flask and a 1.17 M ether solution of methylolithium (4.16 ml, 4.87 mmol) was further added at 0 °C. The mixture was stirred for 15 min. A solution of optically pure (*R*)-(+)-methyl *p*-tolyl sulfoxide (**8**)¹⁵ (500 mg, 3.24 mmol, $[\alpha]_{\text{D}} +158.3^\circ$ ($c=1.03$, acetone)) in THF (10 ml) was added. The whole was stirred for 1 h, then a solution of (*E*)-**7** (855 mg, 3.89 mmol) in THF (10 ml) was added and stirring was continued at 0 °C for 30 min. The reaction 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) to give (*R*)-(*E*)-**9** (448 mg, 85% yield).

(*R*)-(+)-(*E*)-**9**: $[\alpha]_{\text{D}} +132.5^\circ$ ($c=1.61$, CHCl_3) IR $\nu_{\text{max}}^{\text{film}}$ cm^{-1} : 1660 ($\text{C}=\text{O}$), 1680, 1620 ($\text{C}=\text{C}$), 1600 (aromatic), 1050 ($\text{S}=\text{O}$). ^1H -NMR (60 MHz) (CCl_4) δ : 0.98, (6H, s, $(\text{CH}_3)_2\text{C}$), 1.00–2.33 (6H, m, $\text{CH}_2\text{C}(\text{CH}_3)_2$), 1.60, 1.66 (6H, ss, $(\text{CH}_3)_2=\text{C}$), 2.45 (3H, s, $\text{C}_6\text{H}_4\text{CH}_3$), 3.85–4.00 (2H, m, SCH_2), 4.95 (1H, t, $J=6\text{ Hz}$, $\text{CH}=\text{C}$), 5.95 (1H, d, $J=16\text{ Hz}$, $\text{CH}=\text{CHCO}$), 6.67 (1H, dd, $J=8, 16\text{ Hz}$, $\text{CH}=\text{CHCO}$), 7.20–7.66 (4H, m, C_6H_4). MS m/z : 346 (M^+). Exact mass determination: 346.1987 (Calcd for $\text{C}_{21}\text{H}_{30}\text{O}_2\text{S}$: 346.1967).

Lewis Acid-Catalyzed Intramolecular Asymmetric Hetero Diels–Alder Reaction of (R)-(*E*)-9 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 a Lewis acid (0.22 mmol) in dichloromethane (2 ml) was added to the flask. A solution of (*R*)-(*E*)-**9** (50 mg, 0.14 mmol, $[\alpha]_{\text{D}} +132.5^\circ$ ($c=1.61$, CHCl_3)) in dichloromethane (2 ml) was further added. The reaction mixture was stirred under the conditions listed in Table 1, then diluted with dichloromethane and the solution was washed with saturated aqueous

NaHCO₃ and saturated aqueous NaCl, dried over anhydrous Na₂SO₄, and concentrated *in vacuo*. The crude product was subjected to preparative TLC (ether–hexane, 1:2) to give (4*R*,8*a*,*S*,*Rs*)- and (4*S*,8*a*,*R*,*Ss*)-4*a*,5,6,7,8,8*a*-hexahydro-1,1,6,6-tetramethyl-2-(*p*-toluenesulfinylmethyl)-1*H*-2-benzopyran (**10a**, **10b**). The yields and the diastereomeric excess of the products are summarized in Table 1.

(4*R*,8*a*,*S*,*Rs*)-**10a**: [α]_D +137.1° (*c*=2.50, CHCl₃). IR $\nu_{\text{max}}^{\text{film}}$ cm⁻¹: 1640 (C=C), 1600 (aromatic), 1050 (S=O). ¹H-NMR (270 MHz) (CDCl₃) δ : 0.90, (6H, s, (CH₃)₂C), 1.12 (3H, s, CH₃CO), 1.26 (3H, s, CH₃CO), 1.30–2.05 (8H, m, CHCH₂C(CH₃)CH), 2.41 (3H, s, C₆H₄CH₃), 3.21–3.50 (2H, m, CH₂SO), 4.40 (1H, s, CH=C), 7.26–7.54 (4H, m, C₆H₄). ¹³C-NMR (CDCl₃) δ : 21.4, 22.4, 25.3, 26.1, 27.1, 30.3, 33.1, 39.7, 41.2, 47.2, 64.0, 106.6, 124.6, 129.8. MS *m/z*: 346 (M⁺). Exact mass determination: 346.2048 (Calcd for C₂₁H₃₀O₂S: 346.1967).

(4*S*,8*a*,*R*,*Ss*)-**10b**: [α]_D +122.0° (*c*=2.50, CHCl₃). IR $\nu_{\text{max}}^{\text{film}}$ cm⁻¹: 1640 (C=C), 1600 (aromatic), 1050 (S=O). ¹H-NMR (270 MHz) (CDCl₃) δ : 0.90, (6H, s, (CH₃)₂C), 1.03 (3H, s, CH₃CO), 1.19 (3H, s, CH₃CO), 1.30–2.05 (8H, m, CHCH₂C(CH₃)CH), 2.41 (3H, s, C₆H₄CH₃), 3.21–3.81 (2H, m, CH₂SO), 4.33 (1H, s, CH=C), 7.27–7.54 (4H, m, C₆H₄). ¹³C-NMR (CDCl₃) δ : 19.7, 21.4, 23.4, 24.9, 27.3, 30.1, 33.0, 39.8, 45.4, 48.1, 64.2, 107.3, 124.4, 129.6. MS *m/z*: 346 (M⁺). Exact mass determination: 346.1957 (Calcd for C₂₁H₃₀O₂S: 346.1967).

(4*R*,8*a*,*S*)-(+)-4*a*,5,6,7,8,8*a*-Hexahydro-1,1,6,6-tetramethyl-2-(*p*-toluenesulfinylmethyl)-1*H*-2-benzopyran (**12**) A 1.1 M aqueous solution of TiCl₃ (0.95 ml, 1.04 mmol) was added to a solution of (4*R*,8*a*,*Ss*)-**10a** (120 mg, 0.35 mmol) in THF (3 ml) at 0°C. The reaction mixture was stirred at room temperature for 2 h. The reaction solution was quenched with saturated aqueous NaHCO₃ and the mixture was diluted with dichloromethane. The organic layer was washed with saturated aqueous NaCl, dried over anhydrous Na₂SO₄, and concentrated *in vacuo*. The crude product was subjected to flash column chromatography (ether–hexane, 1:10) to give (4*R*,8*a*,*S*)-(+)-**12** (98 mg, 86% yield). The reaction of (4*S*,8*a*,*R*,*Ss*)-**10b** (100 mg, 0.29 mmol) with TiCl₃ (0.79 ml, 0.87 mmol), was carried out in the same way to afford (4*S*,8*a*,*R*)-(–)-**12** (82 mg, 86% yield, [α]_D –38.0° (*c*=1.53, CHCl₃)).

(4*R*,8*a*,*S*)-(+)-**12**: [α]_D +38.4° (*c*=1.60, CHCl₃). IR $\nu_{\text{max}}^{\text{film}}$ cm⁻¹: 1670 (C=C), 1600 (aromatic). ¹H-NMR (270 MHz) (CDCl₃) δ : 0.90, (6H, s, (CH₃)₂C), 0.90–1.93 (8H, m, CHCH₂C(CH₃)₂CH), 1.21, 1.24 (6H, s, s, (CH₃)₂CO), 2.40 (3H, s, C₆H₄CH₃), 2.30 (2H, d, *J*=3 Hz, CH₂S), 3.37 (1H, d, *J*=3 Hz, CH=C), 7.05–7.34 (4H, m, C₆H₄). ¹³C-NMR (CDCl₃) δ : 19.6, 21.0, 23.5, 25.1, 27.4, 30.0, 30.9, 33.1, 38.7, 39.9, 45.7, 48.4, 77.7, 96.1, 102.7, 129.4, 130.9, 136.2, 147.4. MS *m/z*: 330 (M⁺). Exact mass determination: 330.1968 (Calcd for C₂₁H₃₀O₂S: 330.2017).

(4*R*,8*a*,*S*)-(+)-4*a*,5,6,7,8,8*a*-Hexahydro-1,1,3,6,6-pentamethyl-1*H*-2-benzopyran (**13**) A solution of (4*R*,8*a*,*Ss*)-**10a** (100 mg, 0.29 mmol) in THF–isopropanol (1:1) (4 ml) was added to a mixture of sodium (1.00 g, 43.48 mmol) in THF (2 ml) and the reaction mixture was stirred at room temperature for 2 h. A small amount of methanol was added to decompose excess sodium and the mixture was concentrated *in vacuo*. The residue was dissolved in ether and the ethereal solution was washed with saturated aqueous NH₄Cl and saturated aqueous NaCl, dried over anhydrous Na₂SO₄, and concentrated *in vacuo*. The crude product was subjected to flash column chromatography (ether–hexane, 1:30) to give (4*R*,8*a*,*S*)-(+)-**13** (53 mg, 90% yield). The reductive desulfinylation of (4*S*,8*a*,*R*,*Ss*)-**10b** (90 mg, 0.26 mmol) with sodium was carried out in the same way to give (4*S*,8*a*,*R*)-(–)-**13** (49 mg, 90% yield, [α]_D –56.0° (*c*=3.50, CHCl₃)).

(4*R*,8*a*,*S*)-(+)-**13**: [α]_D +56.4° (*c*=3.60, CHCl₃). IR $\nu_{\text{max}}^{\text{film}}$ cm⁻¹: 1680 (C=C). ¹H-NMR (CCl₄) δ : 0.95, (6H, s, (CH₃)₂C), 0.95–2.15 (8H, m, CHCH₂C(CH₃)₂CH), 1.04, 1.08 (6H, s, s, (CH₃)₂CO), 1.60 (3H, s, CH₃C=C), 4.01 (1H, s, CH=C). MS *m/z*: 208 (M⁺). Exact mass determination: 208.1825 (Calcd for C₁₄H₂₄O: 208.1827).

(4*S*,8*a*,*R*)-(–)-4-Bromo-4*a*,5,6,7,8,8*a*-hexahydro-1,1,3,6,6-pentamethyl-1*H*-2-benzopyran (**14**) *N*-Bromosuccinimide (94 mg, 0.48 mmol) was added to a solution of (4*R*,8*a*,*S*)-(+)-**13** (90 mg, 0.43 mmol, [α]_D +56.4° (*c*=3.60, CHCl₃)) in aqueous THF (THF–H₂O, 10:1) (4 ml) and the reaction mixture was stirred at room temperature for 2 h. The reaction was quenched with saturated aqueous NaHCO₃ and the mixture was diluted with dichloromethane. The organic layer was washed with saturated aqueous NaCl, dried over anhydrous Na₂SO₄, and concentrated *in vacuo*. The crude product was subjected to flash column chromatography (ether–hexane, 1:10) to give (4*S*,8*a*,*R*)-(–)-**14** (43 mg, 35% yield). The reaction of (4*S*,8*a*,*R*)-(–)-**13** (80 mg, 0.38 mmol, [α]_D –56.0° (*c*=3.50, CHCl₃)) with *N*-bromosuccinimide (84 mg, 0.43 mmol)

was carried out in the same way to afford (4*R*,8*a*,*R*)-(+)-**14** (37 mg, 34% yield, [α]_D +36.0° (*c*=1.65, CHCl₃)).

(4*S*,8*a*,*R*)-(–)-**14**: [α]_D –36.4° (*c*=1.70, CHCl₃). IR $\nu_{\text{max}}^{\text{film}}$ cm⁻¹: 1660 (C=C). ¹H-NMR (CCl₄) δ : 0.99, 1.00 (6H, s, s, (CH₃)₂C), 1.00–2.33 (8H, m, CHCH₂C(CH₃)₂CH), 1.10, 1.30 (6H, s, s, (CH₃)₂CO), 1.95 (3H, s, CH₃C=C). MS *m/z*: 286 (M⁺). Exact mass determination: 286.0941 (Calcd for C₁₄H₂₃OBr: 286.0950).

Sulfinylation of (4*S*,8*a*,*S*)-14**** 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 (4*S*,8*a*,*S*)-(–)-**14** (38 mg, 0.13 mmol, [α]_D –36.4° (*c*=1.70, CHCl₃)) in THF (2 ml) was added to the flask. A 1.5 M hexane solution of butyllithium (0.13 ml, 0.20 mmol) was further added at –78°C and the mixture was stirred at –78°C for 1 h. A solution of methyl (*S*)-(–)-*p*-toluenesulfinate (34 mg, 0.20 mmol, 87% ee) in THF (1 ml) was next added and the reaction solution was stirred at –78°C for 1 h. It was then diluted with dichloromethane and the solution was washed with saturated aqueous NaCl, dried over anhydrous Na₂SO₄, and concentrated *in vacuo*. The crude product was subjected to preparative TLC (ether–hexane, 1:2) to give (4*S*,8*a*,*S*,*Ss*)-4*a*,5,6,7,8,8*a*-hexahydro-1,1,3,6,6-pentamethyl-4-(*p*-toluenesulfinyl)-1*H*-2-benzopyran (**15a**) (17 mg, 37% yield, [α]_D –106.2° (*c*=0.87, CHCl₃)). The reaction of (4*R*,8*a*,*R*)-(+)-**14** (35 mg, 0.12 mmol, [α]_D +36.0° (*c*=1.65, CHCl₃)) with methyl (*S*)-(–)-*p*-toluenesulfinate (31 mg, 0.18 mmol, 87% ee) was carried out in the same way to give (4*R*,8*a*,*R*,*Ss*)-**15b** (16 mg, 38% yield, [α]_D –83.1° (*c*=0.67, CHCl₃)).

The spectral data of the diastereomer isolated above were superimposable on those of the products obtained by us previously.¹⁰

(4*S*,8*a*,*S*)-(+)-4*a*,5,6,7,8,8*a*-Hexahydro-1,1,3,6,6-pentamethyl-4-(*p*-toluenesulfinyl)-1*H*-2-benzopyran (**16**) A 1.1 M aqueous solution of TiCl₃ (0.13 ml, 0.14 mmol) was added to a solution of (4*S*,8*a*,*Ss*)-**15a** (22 mg, 0.06 mmol, [α]_D –106.2° (*c*=0.87, CHCl₃)) in THF (1 ml) and the reaction solution was stirred at room temperature for 1 h. The reaction was quenched with saturated aqueous NaCl and the mixture was diluted with dichloromethane. The organic layer was washed with saturated aqueous NaCl, dried over Na₂SO₄, and concentrated *in vacuo*. The crude product was subjected to flash column chromatography (ether–hexane, 1:10) to give (4*S*,8*a*,*S*)-(–)-**16** (19 mg, 90% yield, [α]_D –30.6° (*c*=1.03, CHCl₃)). The reduction of (4*R*,8*a*,*R*,*Ss*)-**15b** (20 mg, 0.06 mmol, [α]_D –83.1° (*c*=0.67, CHCl₃)) was carried out in the same manner to give (4*R*,8*a*,*R*)-(+)-**16** (17 mg, 90% yield, [α]_D +27.5° (*c*=1.06, CHCl₃)). The spectral data of **16** obtained above were superimposable on those of the product obtained by us previously.¹⁰

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