Studies on Chiral Organosulfur Compounds. V. Palladium-Catalyzed Intramolecular Asymmetric Metallo-Ene Reactions *via* Chiral Allylic Sulfinate–Sulfone Rearrangements

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A palladium-catalyzed intramolecular asymmetric metallo-ene reaction was accomplished using a chiral allylic sulfone (prepared by thermal rearrangement of an optically active allylic sulfinate) as an enophile. The stereoselectivity of the reaction was determined by high-performance liquid chromatography with a chiral column. A plausible mechanistic pathway for this asymmetric cyclization is presented.

Keywords asymmetric cyclization; metallo-ene reaction; palladium catalyst; sulfinate–sulfone rearrangement; chiral allylic sulfinate; chiral allylic sulfone

Intramolecular asymmetric cycloaddition reactions such as Diels–Alder¹⁾ and ene reactions²⁾ can be useful tools for asymmetric synthesis of optically active cyclic compounds. In particular, intramolecular asymmetric ene reactions offer stereoselectivity,³⁾ and our interest has been focussed on asymmetric cyclizations *via* metallo-ene reactions,^{4,5)} since few asymmetric metallo-ene-type cyclizations have been reported quite recently.^{6,7)} A characteristic of our strategy for asymmetric metallo-ene cyclizations is the use of chiral allylic sulfones as chiral enophiles, since they can be derived from readily available optically active sulfinates by thermal rearrangements.⁸⁾ A palladium-catalyzed reaction of a chiral allylic sulfone II, obtained

by thermal rearrangement of a chiral allylic sulfinate I, leads initially to the formation of a π -allylpalladium complex III at the reactive allylic site. The olefin of the allylic sulfone serves as an enophile to undergo a metallo-ene reaction, giving an optically active cyclic compound IV. A new asymmetric carbon center is induced at this cyclization stage owing to the effect of the chirality of the allylic sulfone.

Synthesis of Chiral Allylic Sulfones Regioselective allylic oxidation of nerol tetrahydropyranyl ether (1) with selenium dioxide and *tert*-butyl hydroperoxide⁹⁾ was performed in tetrahydrofuran (THF) at room temperature for 5 h to give 8-hydroxyneryl tetrahydropyranyl ether

Chart 1

Chart 2

Chart 3

(**2**) in 55% yield. Acetylation (90% yield) of **2** with acetic anhydride–triethylamine–4-dimethylaminopyridine followed by deprotection (85% yield) of the tetrahydropyranyl group in **3** with pyridinium *p*-toluenesulfonate in methanol gave 8-acetoxyneryl (**4**). Regioselective allylic oxidation of nerol acetate (**5**) was carried out in the same way to give 8-hydroxyneryl acetate (**6**) in 51% yield.

The chiral sulfonylation of the alcohol **4** was accomplished by the alcoholysis of a chiral sulfinamide, $(S)\text{-(+)-}N,N\text{-diethyl-}p\text{-toluenesulfinamide}$ (**7**), with **4** in toluene at 0°C in the presence of boron trifluoride etherate to give 8-acetoxyneryl $(S)\text{-(}-)\text{-}p\text{-toluenesulfinate}$ (**8**) with 96% stereospecificity in 96% yield. The sulfonylation of **6** was executed in the same way as described above to give $(S)\text{-(}-)\text{-10}$ with 83% stereospecificity in 81% yield. The absolute configuration and the optical purity of the chiral sulfur atoms in the products **8** and **10** were determined by transformation of the compounds into $(R)\text{-(+)-phenyl } p\text{-tolyl sulfoxide}$ of known absolute configuration,¹⁰⁾ by the use of phenylmagnesium bromide. The reaction of a sulfinate with a Grignard reagent proceeds with inversion of configuration and complete stereospecificity.¹⁰⁾ On the basis of this stereochemical characteristic, the absolute configuration and the enantiomeric excess (ee) of the sulfur atoms in the sulfonates were determined as $(S)\text{-(}-)\text{-8}$ (96% ee) and $(S)\text{-(}-)\text{-10}$ (83% ee). Thus, the stereospecificity of the alcoholysis of the chiral sulfinamide **7** with **4** and **6** under the reaction conditions described above was calculated.

Upon heating at $100\text{--}105^\circ\text{C}$ in *N,N*-dimethylformamide (DMF) for 8–12 h, the chiral sulfonates $(S)\text{-(}-)\text{-8}$ and $(S)\text{-(}-)\text{-10}$ (96 and 83% ee) underwent chiral allylic sulfinate-sulfone rearrangements to give $(R)\text{-(}-)\text{-8-acetoxy-3,7-dimethyl-3-}p\text{-toluenesulfonyl-1,6(E)-octadiene}$ (**9**) and $(S)\text{-(}-)\text{-8-acetoxy-2,6-dimethyl-3-}p\text{-toluenesulfonyl-1,6(Z)-octadiene}$ (**11**) with 40 and 44% stereospecificity, respectively. The enantiomeric excess of the products was determined on the basis of high-performance liquid chromatography (HPLC) with a chiral column. The

Chart 4

absolute configuration of the products was deduced on the basis of the mechanism of the thermal rearrangements proposed by us previously.^{8a)} Since rather severe steric interaction is observed between the substituents at the β -positions of the allylic parts and the *p*-tolyl group in **12a** and **13a** of the five-membered transition states **12** and **13**, the rearrangements of $(S)\text{-(}-)\text{-8}$ and $(S)\text{-(}-)\text{-10}$ would proceed preferentially *via* the more stable transition states **12b** and **13b**, giving $(R)\text{-(}-)\text{-9}$ and $(S)\text{-(}-)\text{-11}$, respectively.

Palladium-Catalyzed Metallo-Ene Reactions of Chiral Allylic Sulfones We studied intramolecular asymmetric metallo-ene reactions of the chiral allylic sulfones obtained above. Initially, stereochemical studies on the palladium-catalyzed intramolecular ene reaction of $(\pm)\text{-9}$ were performed using tetrakis(triphenylphosphine)palladium

TABLE I. Studies on Palladium-Catalyzed Intramolecular Ene Reactions of ($\pm$)-**9**^{a)}

Catalyst (mol%)	PPh ₃ (mol%)	Reaction temp. (°C)	Reaction time (h)	Yield of 14 (%)	de (%) of 14a, b ^{b)}
Pd(PPh ₃) ₄ (5)	—	80	4	10	99
Pd(PPh ₃) ₄ (10)	—	80	4	20	97
Pd(PPh ₃) ₄ (10)	—	90	1	12	94
Pd(PPh ₃) ₄ (20)	—	80	4	11	76
Pd(dba) ₂ (5)	PPh ₃ (7.5)	80	4	20	95
Pd(dba) ₂ (5)	PPh ₃ (15)	80	4	31	99
Pd(dba) ₂ (5)	PPh ₃ (30)	80	4	27	99
Pd(dba) ₂ (10)	PPh ₃ (30)	80	4	29	99

a) Each reaction was carried out in a 0.07 mol/l AcOH solution of ($\pm$)-**9**. b) The diastereomeric excess (de) was determined by HPLC analysis.

[Pd(PPh₃)₄] or bis(benzylideneacetone)palladium [Pd(dba)₂] as a catalyst with or without triphenylphosphine (PPh₃) to examine the chemical yield and diastereoselectivity. The palladium-catalyzed reaction of ($\pm$)-**9** in hot acetic acid (AcOH) gave 3-isopropenyl-1-methyl-2-methylene-1-*p*-toluenesulfonylcyclopentane (**14a, b**). The stereochemistry of the diastereomeric product **14** was determined by NMR spectral analysis. The nuclear Overhauser effect (NOE) was observed between the methyl group at the C₁ position and the olefinic hydrogen atom of the isopropenyl group in the NMR spectrum of **14a**, whereas no NOE was found in that of **14b**. The diastereomeric excess was determined by HPLC analysis. The results obtained under various reaction conditions (molar amount of catalyst and ligand, concentration of the reaction solution, and reaction temperature and time) are summarized in Table I.

The reaction of **9** with 20 mol% of Pd(PPh₃)₄ in AcOH at 80 °C provided lower diastereoselectivity for **14**, whereas the highest diastereoselectivity was obtained with 5 mol% of the catalyst. The best molar ratio of Pd(dba)₂ to PPh₃ for providing high diastereoselectivity was 1:3. The palladium-catalyzed cyclization of (*S*)-**11** via carbometallation^{2d)} was examined using Pd(PPh₃)₄ or Pd(dba)₂ as a catalyst, but the expected product **15**^{2d)} was not formed.

On the basis of the stereochemical results obtained above, the asymmetric palladium-catalyzed ene reaction of (*R*)-**9** (38% ee) was accomplished under the most favorable reaction conditions found, to give (1*R*,3*S*)-**14a** (19% ee) as a major product with 50% stereospecificity and 99% diastereoselectivity. The diastereomeric excess and the enantiomeric excess of **14** were determined by HPLC analysis with a chiral column. The stereospecificity of this cyclization was calculated on the basis of the enantiomeric excess of the chiral starting allylic sulfone **9** used and the product (1*R*,3*S*)-**14a** obtained. The results obtained under several conditions are summarized in Table II.

Stereochemistry of Palladium-Catalyzed Asymmetric Cyclization of the Chiral Allylic Sulfone A palladium catalyst reacted with the chiral allylic sulfone **9** initially at the reactive allylic site (allylic acetate) to form a chiral π -allylpalladium complex, which underwent an intramolecular metallo-ene reaction via six-membered transition states (**16**–**19**) including the palladium catalyst. Since **17a** and **19a** have extremely severe steric interaction induced by the axially oriented *p*-toluenesulfonyl group, the transition states **16a** and **18a** with the equatorially oriented *p*-toluenesulfonyl group would be preferred. The

Chart 5

TABLE II. Palladium-Catalyzed Metallo-Ene Reactions of (*R*)-(-)-**9**^{a)}

Catalyst (mol%)	PPh ₃ (mol%)	Yield of 14 (%)
Pd(dba) ₂ (5)	15	31
Pd(dba) ₂ (10)	30	29
Pd(PPh ₃) ₄ (5)	—	38
Pd(PPh ₃) ₄ (10)	—	33

a) The palladium-catalyzed reaction of (*R*)-(-)-**9** (38% ee) was carried out in AcOH at 80 °C for 4 h to give (1*R*,3*S*)-**14a** with 19% ee and 99% de

metallo-ene cyclization would proceed preferentially via the transition state **16a**, which has the conformationally more stable five-six-membered *cis* fusion, to give (1*R*,3*S*)-**14a** as a major product through the reductive β -elimination of the palladium catalyst in **16b**. Compound (1*R*,3*R*)-**14b** would be formed as a minor product via the less favorable transition state **18a**, which has the conformationally less stable five-six-membered *trans* fusion, in the same manner. The ratio of the diastereomers **14a** to **14b** would be determined on the basis of the stereochemical environment in the transition states **16a** and **18a**. However, the chirality of the allylic sulfone was slightly lost, not by racemization of the starting allylic sulfone, but presumably by that of the allylic sulfonyl part at the stage of the transition state **16a** for the cyclization, because some of the starting allylic sulfone **9** was recovered without any racemization in this palladium-catalyzed reaction. Thus, a chiral allylic sulfone, prepared by a thermal chiral allylic sulfinat-sulfone rearrangement,

Chart 6

bearing another reactive allylic site at an appropriate position for cyclization underwent an asymmetric metallo-ene reaction, upon treatment with a palladium catalyst in AcOH, to give a chiral cyclopentane derivative with high diastereoselectivity but lower enantiospecificity.

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 a JEOL GSX-400 (^1H -NMR, 400 MHz), EX-270 (^1H -NMR, 270 MHz), or JNM-PMX 60 si (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, doublet doublet; 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-360 or 370 polarimeter. HPLC data were obtained with a Tosoh UV-8010, CCPM (column, Tosoh TSK-gel ODS-80TM, Daicel Chiralpak AS). Flash column chromatography was performed with Merck Silica gel 60 (230–400 mesh). Thin layer or thick layer plates having been dried at 140°C for 3.5 h were used.

2,6-Dimethyl-8-[(tetrahydro-2H-pyran-2-yl)oxy]-2(E),6(Z)-octadien-1-ol (2) Selenium dioxide (93 mg, 0.84 mmol) was added to a solution of 3,7-dimethyl-1-[(tetrahydro-2H-pyran-2-yl)oxy]-2(Z),6-octadiene (1) (1000 mg, 4.20 mmol) in dichloromethane (15 ml) and 70% aqueous *tert*-butyl hydroperoxide (7.3 ml, 4.62 mmol). The reaction mixture was stirred at room temperature for 3 h and then concentrated to dryness. The residue was diluted with ether. The organic layer was washed with saturated aqueous NaCl, dried over anhydrous Na_2SO_4 , and concentrated *in vacuo*. The residual colorless oil was subjected to column chromatography (ether–hexane, 1:3) to give 2 (587 mg, 55% yield). IR

$\nu_{\text{max}}^{\text{film}} \text{ cm}^{-1}$: 3420 (OH), 1650 (C=C). ^1H -NMR (CDCl_3) δ : 1.16–2.06 (6H, m, $(\text{CH}_2)_3$), 1.70 (3H, s, $\text{CH}_3\text{C}=\text{C}$), 1.80 (3H, s, $=\text{C}(\text{CH}_3)\text{CH}_2\text{OH}$), 1.50–2.25 (4H, m, $(\text{CH}_2)_2$), 3.30–3.90 (2H, m, CHOCH_2), 3.90–4.21 (3H, m, HO, THPOCH_2), 4.21–4.40 (1H, m, OCHO), 4.40–4.60 (2H, m, HOCH_2), 4.90–5.30 (2H, m, $2\text{C}=\text{CH}$). MS m/z : 254 (M^+). Exact mass determination: 254.1846 (Calcd for $\text{C}_{15}\text{H}_{26}\text{O}_3$: 254.1882).

1-Acetoxy-2,6-dimethyl-8-[(tetrahydro-2H-pyran-2-yl)oxy]-2(E),6(Z)-octadiene (3) A catalytic amount of 4-dimethylaminopyridine was added to a solution of 2 (250 mg, 0.98 mmol) and triethylamine (0.2 ml, 1.47 mmol) in anhydrous dichloromethane (8 ml). A solution of acetic anhydride (150 mg, 1.47 mmol) in anhydrous dichloromethane (3 ml) was added to the above solution. The reaction mixture was stirred at room temperature for 1 h. The reaction solution was diluted with dichloromethane, and washed with 10% aqueous HCl, 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 colorless oil was subjected to column chromatography (ether–hexane, 1:2) to give 3 (261 mg, 90% yield). IR $\nu_{\text{max}}^{\text{film}} \text{ cm}^{-1}$: 1750 (C=O), 1650 (C=C). ^1H -NMR (CDCl_3) δ : 1.16–2.06 (6H, m, $(\text{CH}_2)_3$), 1.70 (3H, s, $\text{CH}_3\text{C}=\text{C}$), 1.80 (3H, s, $=\text{C}(\text{CH}_3)\text{CH}_2\text{OH}$), 1.50–2.25 (4H, m, $(\text{CH}_2)_2$), 2.10 (3H, s, CH_3CO_2), 3.30–3.90 (2H, m, CHOCH_2), 3.90–4.21 (2H, m, THPOCH_2), 4.21–4.40 (1H, m, OCHO), 4.50 (2H, s, AcOCH_2), 4.90–5.40 (2H, m, $2\text{C}=\text{CH}$). MS m/z : 296 (M^+). Exact mass determination: 296.1717 (Calcd for $\text{C}_{17}\text{H}_{28}\text{O}_5$: 296.1988).

8-Acetoxy-3,7-dimethyl-2(Z),6(E)-octadien-1-ol (4) Pyridinium *p*-toluenesulfonate (8.5 mg, 0.034 mmol) was added to a solution of 3 (200 mg, 0.68 mmol) in methanol (2 ml). The reaction mixture was stirred at room temperature for 12 h and then concentrated to dryness. The residue was diluted with ether. The solution was washed with saturated aqueous NaCl. The organic layers were combined, dried over anhydrous Na_2SO_4 , and concentrated *in vacuo*. The residual colorless oil was subjected to column chromatography (ether–hexane, 1:1) to give 4 (123 mg, 85% yield). IR $\nu_{\text{max}}^{\text{film}} \text{ cm}^{-1}$: 3400 (OH), 1750 (C=O), 1650

(C=C). ¹H-NMR (CDCl₃) δ: 1.70 (3H, s, CH₃C=), 1.80 (3H, s, CH₃C(CH₂)=CHOH), 1.50–2.25 (4H, m, (CH₂)₂), 2.10 (3H, s, CH₃CO₂), 3.45–4.20 (3H, m, HOCH₂), 4.45 (2H, s, AcOCH₂), 5.15–5.50 (2H, m, 2C=CH). MS *m/z*: 212 (M⁺). Exact mass determination: 212.1507 (Calcd for C₁₂H₂₀O₃: 212.1012).

8-Acetoxy-2,6-dimethyl-2(E),6(Z)-octadien-1-ol (6) Selenium dioxide (57 mg, 0.51 mmol) was added to a solution of 1-acetoxy-3,7-dimethyl-2(Z),6-octadiene (**5**) (1000 mg, 5.10 mmol) in dichloromethane (18 ml) and 70% aqueous *tert*-butyl hydroperoxide (8.9 ml, 5.61 mmol). The reaction mixture was stirred at room temperature for 3 h and then concentrated to dryness. The residue was diluted with ether. The organic layer was washed with saturated aqueous NaCl, dried over anhydrous Na₂SO₄, and concentrated *in vacuo*. The residual colorless oil was subjected to column chromatography (ether–hexane, 1:3) to give **6** (554 mg, 51% yield). **6**: IR $\nu_{\text{max}}^{\text{film}}$ cm⁻¹: 3420 (OH), 1740 (C=O), 1670 (C=C). ¹H-NMR (CDCl₃) δ: 1.50–1.85 (6H, m, 2CH₃C=), 2.00 (3H, s, CH₃CO₂), 2.05–2.35 (4H, m, (CH₂)₂), 3.85 (2H, s, HOCH₂), 4.95 (2H, d, *J* = 7 Hz, CH₂OAc), 5.05–5.50 (2H, m, 2C=CH). MS *m/z*: 212 (M⁺). Exact mass determination: 212.1295 (Calcd for C₁₂H₂₀O₃: 212.1412).

8-Acetoxy-3,7-dimethyl-2(Z),6(E)-octadienyl (S)-(-)-*p*-Toluenesulfinate (8) A mixture of (S)-(+)-*N,N*-diethyl-*p*-toluenesulfonamide (**7**) (99.6 mg, 0.47 mmol, 100% ee) and **4** (200 mg, 0.94 mmol) in anhydrous toluene (10 ml) was stirred at 0 °C for 3 h in the presence of boron trifluoride etherate (67 mg, 0.47 mmol) under a nitrogen atmosphere. The reaction solution was diluted with ether, and washed with 10% aqueous HCl, saturated aqueous NaHCO₃ and saturated aqueous NaCl. The organic layers were combined, then dried over anhydrous Na₂SO₄ and concentrated *in vacuo*. The crude product was subjected to preparative TLC (ether–hexane, 1:1) to give (S)-(-)-**8** (158 mg, 96% yield, $[\alpha]_{\text{D}}^{20}$ –103.6° (*c* = 2.7, acetone), 96% ee). IR $\nu_{\text{max}}^{\text{film}}$ cm⁻¹: 1740 (C=O), 1680 (C=C), 1600 (aromatic), 1140 (sulfinate). ¹H-NMR (CDCl₃) δ: 1.70 (3H, s, CH₃C=), 1.80 (3H, s, CH₃C(CH₂)=CHOH), 1.50–2.40 (4H, m, (CH₂)₂), 2.10 (3H, s, CH₃CO₂), 2.40 (3H, s, CH₃C₆H₄), 3.70–4.20 (2H, m, TolS(O)OCH₂), 4.30 (2H, s, AcOCH₂), 5.00–5.60 (2H, m, 2C=CH), 7.10–7.70 (4H, m, C₆H₄). MS *m/z*: 350 (M⁺). Exact mass determination: 350.1632 (Calcd for C₁₉H₂₆O₄S: 350.1552).

8-Acetoxy-2,6-dimethyl-2(E),6(Z)-octadienyl (S)-(-)-*p*-Toluenesulfinate (10) The reaction of (S)-(+)-**7** (100 mg, 0.47 mmol) with **6** (200 mg, 0.94 mmol) was carried out in the same way as described above to give **10** (134 mg, 81% yield, $[\alpha]_{\text{D}}^{20}$ –89.1° (*c* = 2.7, acetone), 83% ee). IR $\nu_{\text{max}}^{\text{film}}$ cm⁻¹: 1740 (C=O), 1690 (C=C), 1600 (aromatic), 1140 (sulfinate). ¹H-NMR (CDCl₃) δ: 1.55–1.85 (6H, m, 2CH₃C=), 2.00 (3H, s, CH₃CO₂), 2.05–2.25 (4H, m, (CH₂)₂), 2.40 (3H, s, CH₃C₆H₄), 3.75–4.70 (4H, m, TolS(O)OCH₂, AcOCH₂), 5.10–5.65 (2H, m, 2C=CH), 7.10–7.75 (4H, m, C₆H₄). MS *m/z*: 350 (M⁺). Exact mass determination: 350.1544 (Calcd for C₁₉H₂₆O₄S: 350.1552).

(R)-(-)-8-Acetoxy-3,7-dimethyl-3-*p*-toluenesulfonyl-1,6(Z)-octadiene (9) A solution of (S)-(-)-**8** (100 mg, 0.29 mmol, $[\alpha]_{\text{D}}^{20}$ –103.6° (*c* = 2.7, acetone), 96% ee) in anhydrous DMF (2 ml) was stirred at 105 °C for 8 h and then concentrated *in vacuo*. The crude product was subjected to preparative TLC (ether–hexane, 1:1) to give (R)-(-)-**9** (95 mg, 95% yield, $[\alpha]_{\text{D}}^{20}$ –5.8° (*c* = 1.2, acetone), 38% ee). IR $\nu_{\text{max}}^{\text{film}}$ cm⁻¹: 1740 (C=O), 1640 (C=C), 1600 (aromatic), 1300, 1140 (sulfone). ¹H-NMR (CDCl₃) δ: 1.70 (3H, s, CH₃C=), 1.80 (3H, s, =C(CH₃)CH₂OH), 2.00 (3H, s, CH₃CO₂), 2.10–2.50 (4H, m, (CH₂)₂), 2.40 (3H, s, CH₃C₆H₄), 4.40–4.70 (2H, m, AcOCH₂), 4.80–5.95 (5H, m, CH=CH, CH₂=CH), 7.30–8.00 (4H, m, C₆H₄). MS *m/z*: 350 (M⁺). Exact mass determination: 350.1874 (Calcd for C₁₉H₂₆O₄S: 350.1552).

(S)-(-)-8-Acetoxy-2,6-dimethyl-3-*p*-toluenesulfonyl-1,6(Z)-octadiene (11) The thermal rearrangement of (S)-(-)-**10** ($[\alpha]_{\text{D}}^{20}$ –89.1° (*c* = 2.7, acetone), 83% ee) was carried out in DMF at 100 °C for 8 h and the same work-up as described above gave (S)-(-)-**11** (95% yield, $[\alpha]_{\text{D}}^{20}$ –6.1° (*c* = 2.2, acetone), 37% ee). IR $\nu_{\text{max}}^{\text{film}}$ cm⁻¹: 1740 (C=O), 1640 (C=C), 1600 (aromatic), 1300, 1140 (sulfone). ¹H-NMR (CDCl₃) δ: 1.50–2.25 (4H, m, (CH₂)₂), 1.70 (3H, s, CH₃C=), 1.80 (3H, s,

=C(CH₃)CH₂OH), 2.00 (3H, s, CH₃CO₂), 2.40 (3H, s, CH₃C₆H₄), 4.35 (2H, d, *J* = 7 Hz, AcOCH₂), 5.10–5.95 (5H, m, CH=CH, CH₂=CH), 7.05–7.80 (4H, m, C₆H₄). MS *m/z*: 350 (M⁺). Exact mass determination: 350.1371 (Calcd for C₁₉H₂₆O₄S: 350.1552).

(1R,3S)-3-Isopropenyl-1-methyl-2-methylene-1-*p*-toluenesulfonyl-cyclopentane (14a) A mixture of bis(dibenzylideneacetone)palladium [Pd(dba)₂] (4.1 mg, 0.007 mmol) and PPh₃ (5.6 mg, 0.021 mmol) in anhydrous AcOH (1 ml) was stirred at room temperature for 5 min under a nitrogen atmosphere. A solution of (R)-(-)-**9** (50 mg, 0.14 mmol) in anhydrous AcOH (1 ml) was added and the reaction mixture was stirred at 80 °C for 4 h. The mixture was filtered through Celite and the filtrate was concentrated to dryness under reduced pressure. The residue was diluted with dichloromethane, and the solution was washed with saturated aqueous NaHCO₃ and saturated aqueous NaCl. The organic layers were combined, dried over anhydrous Na₂SO₄, and concentrated *in vacuo*. The crude product was subjected to preparative TLC (ether–hexane, 1:2) to give (1R,3S)-**14a** (13 mg, 31% yield). The results with (±)-**9** and (R)-(-)-**9** obtained under other reaction conditions are listed in Tables I and II. IR $\nu_{\text{max}}^{\text{film}}$ cm⁻¹: 1660 (C=C), 1600 (aromatic), 1300, 1140 (sulfone). ¹H-NMR (CDCl₃) δ: 1.55 (3H, s, CH₃CSO₂Tol), 1.70 (3H, s, CH₃C=), 2.40 (3H, s, CH₃C₆H₄), 1.60–2.70 (5H, m, CH₂=C(CH₃)CH, (CH₂)₂), 4.80, 4.90 (2H, ss, CH₂=C), 5.10–5.30 (2H, dd, CH₂=C), 7.25–7.80 (4H, dd, C₆H₄). MS *m/z*: 290 (M⁺). Exact mass determination: 290.1339 (Calcd for C₁₇H₂₂O₂S: 290.1028).

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