

Chemistry of Unique Chiral Olefins. 1. Synthesis, Enantioresolution, Circular Dichroism, and Theoretical Determination of the Absolute Stereochemistry of *trans*- and *cis*-1,1',2,2',3,3',4,4'-Octahydro-4,4'-biphenanthrylidenes

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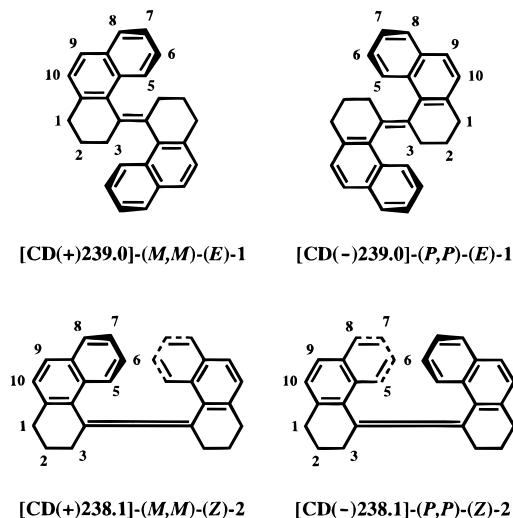
Abstract: Unique chiral olefins, (*E*)-1,1',2,2',3,3',4,4'-octahydro-4,4'-biphenanthrylidene (**1**) and its (*Z*)-isomer **2**, were synthesized. When these compounds are directly enantioresolved by using the HPLC Okamoto column with a chiral stationary phase, optically pure enantiomers were obtained. The CD spectra of these chiral olefins exhibit very intense Cotton effects in the ¹B_b transition region reflecting their strongly twisted π-electron systems. The CD and UV spectra of chiral olefins (*M,M*)-**1** and (*M,M*)-**2** were theoretically calculated by the π-electron self-consistent field/configuration interaction/dipole velocity molecular orbital method. From the calculation results, the absolute stereostructures of these chiral olefins were theoretically determined to be [CD(+)_{239.0}]-(*M,M*)-**1** and [CD(+)_{238.1}]-(*M,M*)-**2**, respectively.

Introduction

There are various kinds of chiral compounds devoid of centers of chirality. Those compounds cannot take a planar structure because of strong steric hindrance. One of these compounds incorporates the class of binaphthyl derivatives with the axis of chirality; some chiral binaphthyl compounds have been used for synthetic reactions as chiral auxiliaries, chiral reagents, chiral catalysts, or chiral hosts of chiral recognition. Another class of chiral compounds without center of chirality is that of helicenes. A hexahelicene composed of six condensed benzene rings is a very interesting compound, whose structure and chemical behavior have been studied well.^{2,3} Investigating a class of such chiral compounds devoid of centers of chirality, one group of the authors reported almost 20 years ago the synthesis and partial enantioresolution of chiral olefins, (*E*)-1,1',2,2',3,3',4,4'-octahydro-4,4'-biphenanthrylidene (**1**) and its (*Z*)-isomer (**2**), in a preliminary form (Chart 1).⁴ These chiral olefins are members of an unique class of helical-shaped sterically overcrowded alkenes, several of which show intriguing photochromic and stereochemical properties⁵ and which form the basis for so-called chiroptical molecular switches.⁶

These chiral olefins (**1** and **2**) cannot take a planar structure because of steric hindrance, and hence, those compounds were

Chart 1



actually resolved into enantiomers by the HPLC method using a chiral stationary phase.^{4,7} The CD spectra of these chiral olefins exhibited intense Cotton effects reflecting their strongly twisted π-electron systems. In spite of their unique structures and behavior, their absolute configuration has remained undetermined. In this paper, we report the theoretical determination of the absolute stereochemistry of these chiral olefins in addition to the details of synthesis, enantioresolution, configuration and conformation, and CD spectra.⁸

To determine the absolute stereochemistry of chiral compounds having a twisted π-electron system, we have used the

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theoretical method to calculate the CD spectra by the π -electron self-consistent field/configuration interaction/dipole velocity molecular orbital method (SCF-CI-DV MO method),^{9–11} For example, by applying this method, we have succeeded in determining the absolute configuration of many natural and unnatural compounds with a twisted π -electron system, *i.e.*, dihydroazulene derivatives isolated from liverworts,¹² marine natural products of halenaquinol family isolated from tropical marine sponges,^{13,14} chiral trononoid spiro compounds,¹⁵ chiral cyanin dyes,¹⁶ biflavone of natural atropisomer isolated from plants,^{17,18} and ternaphthalene compounds.¹⁹ The reliability of this theoretical method has been established by many application examples of synthetic chiral aromatic compounds.¹¹ The chiral olefins **1** and **2** also belong to the class of chiral compounds with twisted π -electron systems, and therefore, the theoretical method would be useful for these compounds. We have succeeded in determining the absolute stereochemistry of these chiral olefins in a nonempirical manner, as described below. The mechanism of the intense CD Cotton effect is also discussed.

Definition of the Absolute Configuration of Chiral Olefins (E)-1 and (Z)-2. Unlike helicenes, these chiral olefins have two moieties of helicity, *i.e.*, helicity between one naphthalene plane and central double bond and another helicity between the other naphthalene plane and central double bond. Therefore, the enantiomer shown in Figure 1a is defined as (*M,M*)-(*E*)-olefin **1**.²⁰ The other enantiomer in Figure 1b is (*P,P*)-(*E*)-olefin **1**. It should be noted that if (*M,P*)-(*E*)-olefin **1** can exist, it is an optically inactive *meso*-olefin. For *cis*-olefin **2**, the absolute configuration was similarly defined (Figure 1). (*M,P*)-(*Z*)-Olefin **2** is a *meso*-compound, although it may be extremely unstable and unfavorable due to steric hindrance.

Computational Section

Computational Methods: Molecular Structure. The molecular geometry of (*M,M*)-(*E*)-**1**, (*P,P*)-(*E*)-**1**, (*M,M*)-(*Z*)-**2**, and (*P,P*)-(*Z*)-**2** was optimized using the MOPAC 93 AM1 programs.²¹ Their

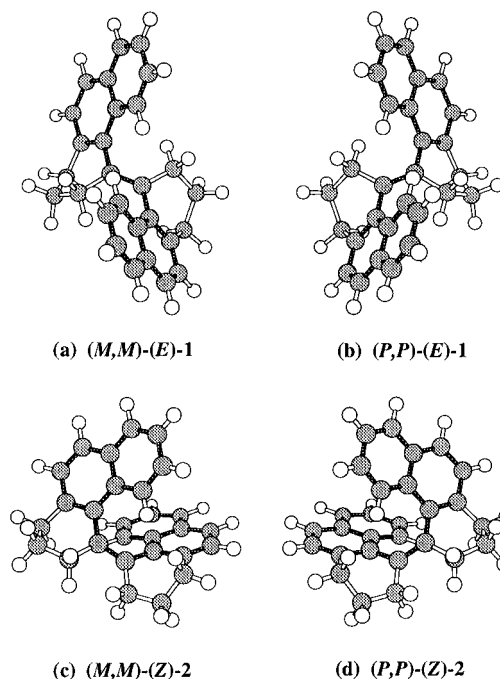


Figure 1. Stereoscopic view of chiral olefins, (*M,M*)-(*E*)-**1**, (*P,P*)-(*E*)-**1**, (*M,M*)-(*Z*)-**2**, and (*P,P*)-(*Z*)-**2**, calculated by the MOPAC 93 AM1 programs.

stereoscopic views are illustrated in Figure 1. The atomic coordinates obtained were used for the following calculation of CD and UV spectra.

Computational Methods: Numerical Calculation of CD and UV Spectra. The CD and UV spectra of (*M,M*)-(*E*)-**1** and (*M,M*)-(*Z*)-**2** were calculated by the π -electron SCF-CI-DV MO method.^{9–11} In the MO calculation, the configuration interactions between all singly excited states were included, and the following standard values of atomic orbital parameters were used: for aromatic carbon, $W(C) = -11.16$ eV, $(rr)rr(C) = 11.13$ eV, $\beta(C-C, 1.388 \text{ \AA}) = -2.32$ eV, $\langle \nabla \rangle (C-C, 1.388 \text{ \AA}) = 4.70 \times 10^7 \text{ cm}^{-1}$. The electric repulsion integral $(rr)ss$ was estimated by the Nishimoto–Mataga equation. The resonance integral and del values were calculated by employing the following equations, respectively,

$$\beta = [S/S(C-C, 1.388 \text{ \AA})]\beta(C-C, 1.388 \text{ \AA}) \cos \theta \quad (1)$$

$$\langle \nabla \rangle = [\langle \nabla \rangle(\text{empir}, 1.388 \text{ \AA})/\langle \nabla \rangle(\text{theor}, 1.388 \text{ \AA})]\langle \nabla \rangle(\text{theor}) \cos \theta \quad (2)$$

where S is the overlap integral and θ is the dihedral angle.

In the calculation of CD and UV spectra, the component CD and UV bands were approximated by the Gaussian distribution.¹¹

$$\Delta\epsilon(\sigma) = \sum \Delta\epsilon_k \exp[-((\sigma - \sigma_k)/\Delta\sigma)^2] \quad (3)$$

$$\epsilon(\sigma) = \sum \epsilon_k \exp[-((\sigma - \sigma_k)/\Delta\sigma)^2] \quad (4)$$

where $2\Delta\sigma$ is the $1/e$ width of the bands. The $\Delta\sigma$ values were adopted from the observed UV spectra of chiral olefins **1** and **2**. The numerical calculations were carried out on the Sun S-4/10 Work Station in our group and/or the NEC ACOS-3900 computer at the Computer Center of Tohoku University.

Results and Discussion

Synthesis of Chiral Olefins: *trans*- and *cis*-1,1',2,2',3,3',4,4'-Octahydro-4,4'-biphenanthrylidenes. As reported in a preliminary paper,⁴ chiral olefins, *trans*-**1** and *cis*-**2** were first synthesized by one group of the authors. As shown in Scheme 1, 3-(2-naphthoyl)propionic acid (**5a**), which was prepared from naphthalene (**3**) and succinic anhydride (**4**) according to the

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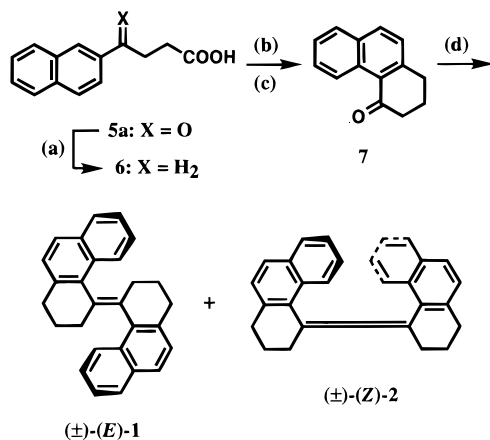
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Scheme 1^a

^a Key: (a) $\text{H}_2\text{NNH}_2 \cdot \text{H}_2\text{O}$, KOH /diethylene glycol; (b) PCl_5 ; (c) SnCl_4 /benzene; (d) TiCl_3 , LiAlH_4 /THF.

procedure of Haworth,²² was reduced by the Huang–Minlon reaction to yield 4-(2-naphthyl)butanoic acid (**6**). Acid **6** was converted to 2,3-dihydro-4(1*H*)-phenanthrenone (**7**) by the Friedel–Crafts reaction (see the Supporting Information).²³ Ketone **7** was then dimerized by the McMurry reaction²⁴ using a low-valent titanium reagent. After separation and purification of the residue by HPLC on silica gel (hexane/benzene 10:1), the desired chiral olefin *trans*-**1** was obtained as a less-polar product in low yield of 8.3–9.4%. *trans*-Olefin **1** was recrystallized from hexane giving colorless crystals: mp 213 °C. *cis*-Olefin **2** was similarly obtained as a more polar product in low yield of 2.5–4.5%: mp 192–195 °C (hexane). We have examined the crude product of the coupling reaction in order to isolate *meso*-olefins. However, all attempts were unsuccessful.

The structure of chiral olefins **1** and **2** were determined mainly by NMR spectra. ¹H and ¹³C NMR spectra of *trans*- and *cis*-olefins indicated their structures to have C_2 -symmetry, and all signals were fully assigned by the analysis of HSQC, HMBC, and NOESY spectra (see the Experimental Section and the Supporting Information). In the ¹H NMR spectrum of *trans*-olefin **1**, all aromatic protons appear in the region of regular aromatic protons, δ 7.3–8.3 ppm. On the other hand, the aromatic protons of *cis*-olefin **2** appear in a higher magnetic field, δ 6.6–7.3 ppm. These upper-field shifts are due to the diamagnetism generated by the aromatic ring current of overlapped two naphthalene rings in *cis*-olefin **2**. The assignment of *trans*- and *cis*-geometry was further confirmed by the analysis of NOESY spectra. The ¹H–¹H NOESY spectrum of *trans*-olefin **1** exhibits a cross peak between H3 and H5'; this phenomenon can be explained only by the *trans*-structure. In the case of *cis*-olefin **2**, a cross peak between H1ax (ax = axial) and H5' was observed in the NOESY spectrum, indicating the *cis*-olefin structure.

Conformation of Chiral Olefins: *trans*-1 and *cis*-2. The chiral olefins **1** and **2** cannot take planar structures because of steric hindrance and hence are strongly twisted. Their preferred conformations were calculated by using the MOPAC 93 AM1 programs (Figure 1). The conformations of **1** and **2** calculated are of C_2 -symmetry in agreement with the NMR results described above. For *trans*-olefin **1**, the cyclohexylidene ring

adopts a boat conformation, giving rise to a large helicity between naphthalene ring and central double bond, while the central double bond is little deviated from a flat structure. The characteristic geometrical values are as follows: central double bond, C4–C4' = 1.350 Å; average value of the dihedral angle between naphthalene plane and central double bond, C4'–C4–C4a–C4b = –56.9°; dihedral angles, C3'–C4'–C4–C4a = –4.5° (average), C3'–C4'–C4–C3 = +169.9°, C4'a–C4'–C4–C4a = –178.9°; distance, H1eq–H10 (eq = equatorial) = 2.39 Å, H3ax–H5' = 2.34 Å, H3eq–H5' = 2.72 Å. Those values are almost in agreement with the experimental values obtained by the X-ray analysis of **1** as shown below.

The stable conformation of *cis*-olefin **2** is also of C_2 -symmetry and strongly twisted, two naphthalene rings closely overlapping to each other: C4b–C4'b = 3.507 Å. The cyclohexylidene ring takes a boat conformation, and the torsional angle between naphthalene ring and central double bond is also very large: central double bond, C4–C4' = 1.356 Å; average value of the dihedral angle between naphthalene plane and central double bond, C4'–C4–C4a–C4b = –51.0°; dihedral angles, C4'a–C4'–C4–C4a = –7.2°, C3'–C4'–C4–C3 = –12.2°, C4'a–C4'–C4–C3 = +170.3° (average); distance, H1eq–H10 = 2.38 Å, H1ax–H5' = 2.27 Å. The NOESY relation of H1eq–H10 and H1ax–H5' is thus supported by the calculation.

X-ray Crystallographic Analysis of (±)-*trans*-Olefin 1. The structure of *trans*-olefin **1** was established by the X-ray crystallographic analysis of its racemate. Although authors in the Netherlands already reported the X-ray crystallographic analysis and crystal structure of **1**,²⁵ authors in Japan also performed the X-ray analysis to confirm its structure, because the melting point (234–235 °C) of the sample prepared in the Netherlands is much different from that (mp 213 °C) of the sample in Japan.

Single crystals of colorless prisms suitable for X-ray analysis were obtained by recrystallization from hexane: mp 213 °C. The crystal was found to be monoclinic: space group $C2/c$ (No. 15). One asymmetrical unit contained a half molecule of **1**. The skeletal structure was solved by direct methods and successive Fourier syntheses. All hydrogen atoms were found by the difference Fourier syntheses. Full-matrix least-squares refinement of positional and thermal parameters led to the final convergence with $R = 0.0688$ and $R_w = 0.0577$. The *trans*-geometry of **1** was thus established as shown in Figure 2.

The geometry of compound **1** in the solid state is characterized as follows: central double bond, C4–C4' = 1.318 Å; average value of the dihedral angle between naphthalene plane and central double bond, C4–C4'–C4'a–C4'b = –60.6°; dihedral angles, C3–C4–C4'–C4'a = –8.3° (average), C3–C4–C4'–C3' = +163.2°, C4a–C4–C4'–C4'a = –179.8°; dihedral angle between planes C3–C4–C4' and C4a–C4–C4' = –171.5°. The central double bond is thus a little twisted, and the sp^2 carbon atoms are deviated from a plane structure. These geometrical parameters are almost in agreement with the previous X-ray results.²⁵ The previous X-ray analysis revealed that the crystal used was tetragonal, taking space group $I\bar{4}$, and its melting point was different from that of the sample used here. Therefore, this compound may undergo polymorphism.

The proton–proton distance correlating to the ¹H NMR NOESY phenomena was calculated from the X-ray data: H1eq–H10 = 2.36 Å, H3ax–H5' = 2.57 Å, H3eq–H5' = 2.79 Å. The X-ray analysis thus confirmed the relationship between proton–proton distance and NOESY data.

Enantioresolution of (±)-(E)-Olefin 1 by HPLC. In the previous preliminary paper,⁴ the HPLC alumina column im-

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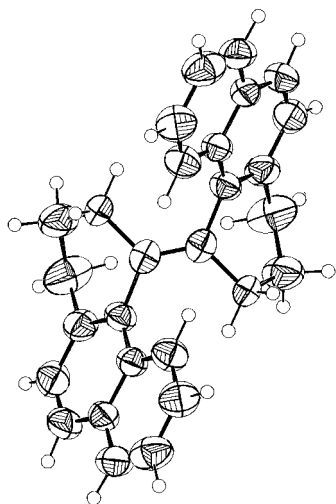


Figure 2. ORTEP drawing of racemic *trans*-olefin (\pm)-(*E*)-**1**. The figure does not express its absolute stereochemistry. The atoms are drawn at 50% probability.

pregnated with (+)-2-(((2,4,5,7-tetranitro-9-fluorenylidene)-amino)oxy)propionic acid (TAPA) was used for enantioresolution. Since the resolutions on the chiral TAPA column were however difficult, we explored other chiral HPLC columns.

The HPLC column with a chiral stationary phase of (+)-poly(triphenylmethyl methacrylate) developed by Okamoto and co-workers has been extensively employed for enantioresolution of various racemates.²⁶ The Okamoto column (commercially available as Chiralpak OT(+) from Daicel Co. Ltd) was used for direct enantioresolution of *trans*-olefin **1**. After several trials, we found that hydrocarbon **1** could be completely resolved into enantiomers under the reverse phase condition using methanol as eluent and a column temperature of 3 °C. The sample of (\pm)-*trans*-**1** was injected as a methanol solution, and separation of enantiomers was monitored by a UV detector. Both enantiomers were completely resolved by this method: $\alpha = 2.01$, $R_s = 1.51$ (see the Supporting Information). On the other hand, *cis*-olefin **2** was not separated. Since a small amount of the polymer of the chiral stationary phase was present as a contaminant, the fraction of each enantiomer resolved was purified by HPLC (ODS-C₁₈, MeOH). From the first eluted fraction, chiral olefin [CD(+)-239.0]-(*E*)-**1** was obtained;²⁷ the ¹H NMR data of optically active **1** were identical with those of (\pm)-**1**. From the second-eluted fraction, chiral olefin [CD(-)-239.0]-(*E*)-**1** was obtained, and its CD Cotton effects were opposite in sign but almost equal in intensity to those of [CD(+)-239.0]-(*E*)-**1**.

Enantioresolution of (\pm)-(Z)-Olefin **2 by HPLC.** *Cis*-Olefin **2** could not be resolved under the reverse phase condition using methanol as eluent. When the solvent was changed from methanol to hexane, we found that *cis*-olefin **2** was partially separated into enantiomers at 3 °C: $\alpha = 1.09$ (see the Supporting Information). On the other hand, *trans*-olefin **1** could not be resolved under this normal phase condition. Since the separation of two enantiomers of **2** was not perfect, the first-eluted fraction was recycled five times, where in each time the band of the second-eluted enantiomer was shaved from the recycle path. After recycling the fraction five times, *cis*-olefin

2 of the first-eluted fraction was obtained in an almost enantiopure form. As reported in the second paper of this series, we found the unexpected thermal racemization of *cis*-olefin **2** at room temperature,²⁸ and therefore, the CD and UV spectra were immediately measured after enantioresolution. From the CD data, the first-eluted enantiomer was designated as [CD(+)-238.1]-(*Z*)-**2**. The CD spectrum of the second-eluted fraction was similarly measured, and its CD Cotton effects observed were opposite in sign to those of the first-eluted enantiomer, although its CD Cotton effects were considerably weak. The second-eluted enantiomer was thus designated as [CD(-)-238.1]-(*Z*)-**2**.

CD and UV Spectra of the First-Eluted Enantiomers [CD(+)-239.0]-(*E*)-Olefin **1** and [CD(+)-238.1]-(*Z*)-Olefin **2**.

Both chiral olefins **1** and **2** are composed of two naphthalene chromophores connected with the central double bond, and therefore, the π -electron conjugation is widespread almost over the molecular system. The UV spectrum of (*E*)-**1**, however, shows intense absorption bands similar to those of naphthalene, maintaining the nature of naphthalene chromophore: UV (MeOH) λ_{\max} 329.8 nm (ϵ 17 400), 318.8 (17 300), 232.2 (61 800), 216.2 (82 800) (Table 1 and Figure 3). Therefore, the absorption band of medium intensity at 329.8 nm may be assigned to the ¹L_a transition of naphthalene, although it shows a red shift of ca. 55 nm when compared with the ¹L_a band of naphthalene at 275 nm. The remaining two intense bands at 232.2 and 216.2 nm may be due to the ¹B_b transition of naphthalene. Those phenomena can be interpreted as follows: since the dihedral angle between the naphthalene chromophore and the central double bond in *trans*-olefin **1** is as large as 60°, the π -electron conjugation between naphthalene and double-bond chromophores are strongly inhibited. Therefore, the π -electron system of *trans*-olefin **1** retains the nature of the naphthalene chromophore.

The CD spectrum of the first-eluted enantiomer [CD-(+)-239.0]-(*E*)-**1** exhibits very intense Cotton effects of a complex pattern: CD (MeOH) λ_{ext} 331.8 nm ($\Delta\epsilon$ +26.0), 253.4 (-20.9), 239.0 (+58.2), 224.8 (-76.4), 214.2 (-153.3) (Table 1 and Figure 3). A positive Cotton effect of medium intensity at 331.8 nm is assigned to the ¹L_a transition, but the origin of the negative Cotton effect at 253.4 nm is unknown, since its wavelength position is deviated from the UV absorption maximum. In the ¹B_b transition region, a strong positive Cotton effect at 239.0 nm and two very intense negative Cotton effects at 224.8 and 214.2 nm are observed. The CD amplitude, A ($=\Delta\epsilon_{\text{peak}} - \Delta\epsilon_{\text{trough}}$), in this region is +211.5. These strong CD Cotton effects reflect the fact that the π -electron system of *trans*-**1** is strongly twisted.

The UV spectrum of (*Z*)-**2** also resemble those of naphthalene: UV (MeOH) λ_{\max} 329.3 nm (ϵ 7 800)sh, 301.9 (11 300), 222.8 (71 900) (Table 1 and Figure 4). The absorption band of medium intensity at 301.9 nm is assigned to the ¹L_a transition of naphthalene and the intense band at 223.0 nm to the ¹B_b transition. The π -electron system of *cis*-olefin **2** also retains the characteristics of naphthalene chromophore.

The CD spectrum of the first-eluted enantiomer [CD-(+)-238.1]-(*Z*)-**2** also shows very intense Cotton effects of complex pattern: CD (MeOH) λ_{ext} 339.0 nm ($\Delta\epsilon$ -12.3), 303.8 (-8.4), 281.5 (+8.5), 256.0 (-63.2), 238.1 (+189.7), 223.5 (-239.3) (Table 1 and Figure 4). A negative weak Cotton effect at 339.0 nm is assigned to the ¹L_a transition, but the origin of the weak positive Cotton effect at 281.5 nm and the negative

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Table 1. Observed and Calculated UV and CD Spectra of Chiral Olefins and Related Compounds

compound	obsd (MeOH or hexane)		calcd (π -SCF-CI-DV MO)	
	UV, λ_{\max} nm (ϵ)	CD, λ_{ext} nm ($\Delta\epsilon$)	UV, λ_{\max} nm (ϵ)	CD, λ_{ext} nm ($\Delta\epsilon$)
<i>(M,M)</i> -(<i>E</i>)- 1 ^a	329.8 (17 400)	331.8 (+26.0)	295.9 (18 700)	295.9 (+7.9)
	318.8 (17 300)	253.4 (-20.9)		
	232.2 (61 800)	239.0 (+58.2)		240.4 (+87.9)
	216.2 (82 800)	224.8 (-76.4)	223.2 (94 400)	219.3 (-256.0)
<i>(M,M)</i> -(<i>E</i>)- 8		214.2 (-153.3)	274.7 (7 000)	273.2 (+4.2)
				230.4 (+248.0)
			219.3 (119 100)	211.9 (-244.2)
<i>(M,M)</i> -(<i>Z</i>)- 2 ^{b,c}	329.3 (7 800)sh	339.0 (-12.3)	329.0 (6 400)	331.1 (-48.8)
	301.9 (11 300)	303.8 (-8.4)		
		281.5 (+8.5)		
		256.0 (-63.2)		260.4 (-12.8)
	223.0 (73 700)	238.1 (+189.7)	211.9 (57 600)	232.6 (+76.7)
<i>(M,M)</i> -(<i>Z</i>)- 9		223.5 (-239.3)	271.7 (2 200)	270.2 (-9.5)
				234.7 (+215.9)
			208.3 (79 300)	215.5 (-372.8)

^a Observed in MeOH. ^b Observed in hexane. ^c sh: shoulder.

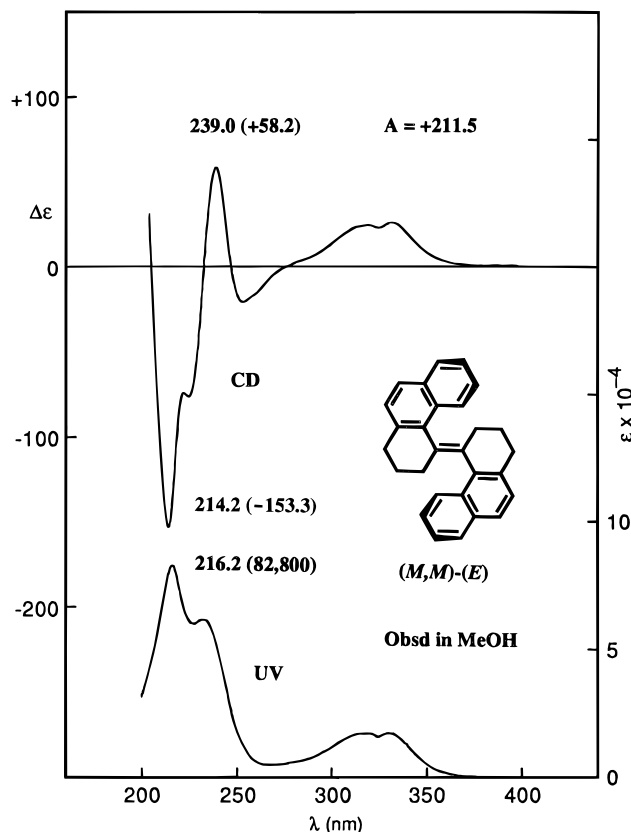


Figure 3. Observed CD and UV spectra of the first-eluted *trans*-olefin [CD(+239.0)]-(*M,M*)-(*E*)-**1** in methanol.

Cotton effect at 256.0 nm is again unknown. In the 1B_u transition region, very intense positive and negative Cotton effects are observed at 238.1 and 223.5 nm, respectively. The CD amplitude, A ($=+429.0$), is much larger than that of *trans*-olefin **1**. These intense CD Cotton effects indicate that the π -electron system of *cis*-**2** is also strongly twisted.

Theoretical Determination of the Absolute Stereochemistry of *trans*-Olefin [CD(+239.0)]-(*E*)-1**.** To determine the absolute stereochemistry of these chiral olefins in a nonempirical manner, their CD and UV spectra were calculated by the π -electron SCF-CI-DV MO method.⁹⁻¹¹ As the model system used for the theoretical calculation of CD spectra, the (*M,M*)-

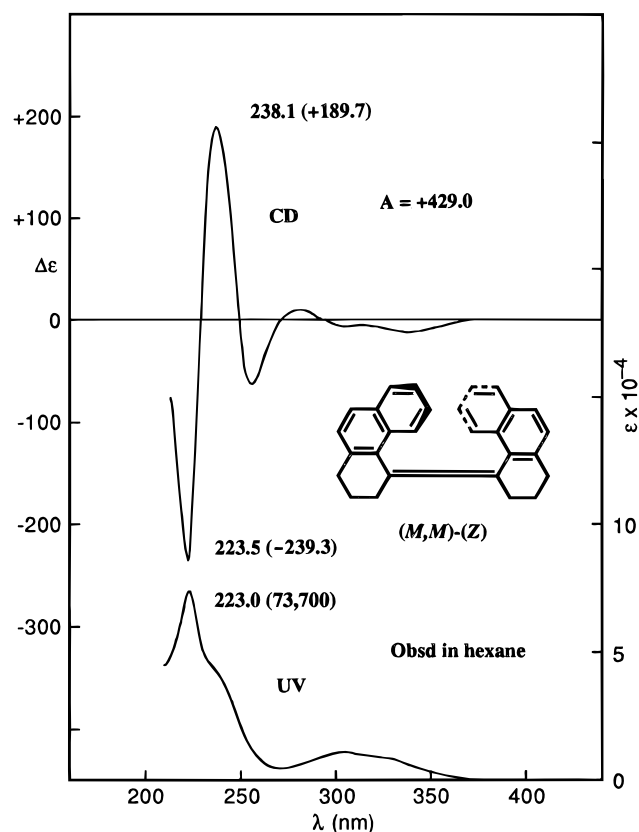


Figure 4. Observed CD and UV spectra of the first-eluted *cis*-olefin [CD(+238.1)]-(*M,M*)-(*Z*)-**2** in hexane.

(*E*)-enantiomer **1** was arbitrarily chosen. The atomic coordinates of π -electron carbon atoms were obtained from the MOPAC 93 AM1 calculation results. The angular dependence of the resonance integral was calculated by eq 1, where angle θ was estimated from the dihedral angle between naphthalene plane and central double bond. The shape of component CD and UV bands was approximated by the Gaussian distribution as shown in eqs 3 and 4. The $2\Delta\sigma$ values, $1/e$ bandwidth, were adopted from the observed UV spectra of chiral olefin **1**.

The UV spectrum of (*M,M*)-(*E*)-enantiomer **1** was well reproduced by the calculation, λ_{\max} 295.9 nm (ϵ 18 700) and 223.2 (94 400); observed, λ_{\max} 329.8 nm (ϵ 17 400),

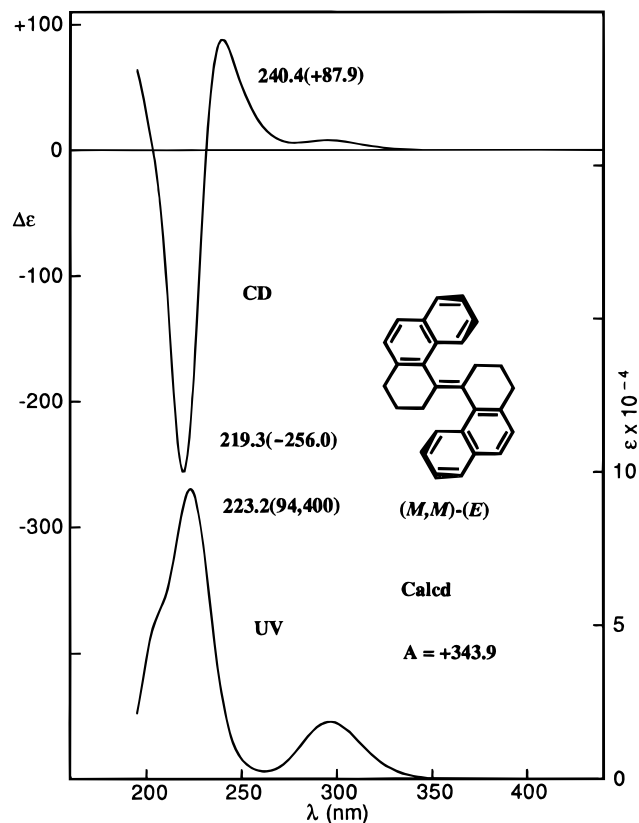


Figure 5. CD and UV spectral curves of *trans*-olefin (*M,M*)-(E)-1 calculated by the π -electron SCF-CI-DV MO method.

318.8 (17 300), 232.2 (61 800), and 216.2 (82 800) (Figure 5 and Table 1). The calculated 1L_a band appeared in much shorter wavelength region than the observed one. The CD spectrum of (*M,M*)-(E)-enantiomer **1** was also calculated by the π -electron SCF-CI-DV MO method: calculated, λ_{ext} 295.9 nm ($\Delta\epsilon$ +7.9), 240.4 (+87.9), and 219.3 (−256.0); observed, λ_{ext} 331.8 nm ($\Delta\epsilon$ +26.0), 253.4 (−20.9), 239.0 (+58.2), 224.8 (−76.4), and 214.2 (−153.3) (Figure 5 and Table 1). Although the location and intensity of the calculated CD Cotton effect of 1L_a transition are much different from the observed ones, its positive sign agrees with that of observed one. In the 1B_b transition region, the intense positive and negative Cotton effects around 240 and 220 nm, respectively, were well reproduced by the π -electron SCF-CI-DV MO calculations. The basic pattern of the calculated and observed CD spectra thus agree with each other, and therefore, the absolute stereochemistry of the first-eluted *trans*-olefin [CD(+) λ_{ext} 239.0]-(E)-(**1**) was nonempirically determined to be (*M,M*) by the theoretical calculation of its CD spectrum.

To clarify the mechanism of the intense CD Cotton effects in the 1B_b transition region, the following computational experiments were performed. We supposed a hypothetical compound (*M,M*)-(E)-**8** where the central double bond was blocked by an appropriate substituent, e.g., epoxide or cyclopropane moiety, but the coordinates of the remaining atoms were kept as the same as those of the original *trans*-olefin (*M,M*)-(E)-**1** (Chart 2). In this compound, the π -electron system is composed of two isolated naphthalene chromophores, and therefore, intense bisignate split Cotton effects due to the exciton coupling between two naphthalene chromophores are expected. In fact, the calculation of CD and UV spectra of this hypothetical model compound gave intense positive first and negative second Cotton effects in the 1B_b transition region as shown in Table 1 (see the Supporting Information). In Table 2, the calculated dipole and rotational strengths of the transitions of chiral olefin (*M,M*)-(E)-**1** and model compound (*M,M*)-(E)-**8** are listed. The

Chart 2. Hypothetical Model Compounds **8** and **9**

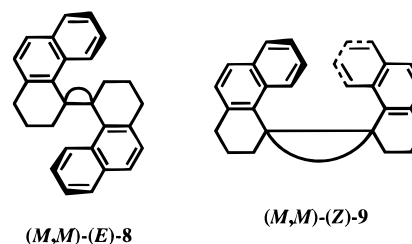


Table 2. Calculated Dipole and Rotational Strengths of the Transitions of Chiral Olefins and Their Hypothetical Model Compounds

compound/ transition no.	wavelength (λ), nm	dipole strength ($10^{36}D$), cgs unit	rotational strength ($10^{40}R$), cgs unit
<i>(M,M)</i> -(E)- 1			
1	296.7	22.6	+22.6
2	248.9	2.9	+74.5
3	227.3	20.6	+1467.8
4	223.9	58.1	−1907.4
5	219.2	1.5	+24.9
6	216.2	7.6	+83.3
<i>(M,M)</i> -(E)- 8			
1	274.6	7.8	+9.4
2	271.0	0.1	+2.4
3	222.9	32.9	+2281.2
4	219.5	71.0	−2200.0
<i>(M,M)</i> -(Z)- 2			
1	330.2	8.5	−163.7
2	281.5	3.7	−31.7
3	260.8	0.2	−9.3
4	243.4	6.2	−400.9
5	242.6	6.2	+384.7
6	235.4	5.7	+1.6
7	226.7	5.2	+334.0
8	219.3	0.3	−13.7
9	215.6	36.0	−615.0
<i>(M,M)</i> -(Z)- 9			
1	277.2	0.9	+12.6
2	270.5	1.7	−38.3
3	231.0	9.8	+691.9
4	216.2	48.0	−1062.0

transitions of numbers 3 and 4 of (*M,M*)-(E)-**8** have the character of exciton coupling, where intense rotational strengths but of opposite sign are accompanied. The dipole strength of transition number 3 at longer wavelength side is weaker than that of transition number 4 in (*M,M*)-(E)-**8**. These characteristic patterns are also observed in the transitions numbers 3 and 4 of olefin (*M,M*)-(E)-**1**. Therefore, it is interpreted that the observed Cotton effects of [CD(+) λ_{ext} 238.5]-(E)-**1** in the 1B_b transition region are keeping the nature of the exciton coupling between the long axis polarized transition moments of two naphthalene chromophores.

Theoretical Determination of the Absolute Stereochemistry of *cis*-Olefin [CD(+) λ_{ext} 238.1]-(Z)-2**.** The UV spectrum of (*M,M*)-(Z)-enantiomer **2** was also reproduced by the calculation: calculated, λ_{max} 329.0 nm (ϵ 6 400) and 211.9 (57 600); observed, λ_{max} 329.3 nm (ϵ 7 800)sh, 301.9 (11 300), and 223.0 (73 700) (Figure 6 and Table 1). Unlike *trans*-olefin **1**, the calculated 1L_a band appeared in a longer wavelength region than the observed one. The CD spectrum of (*M,M*)-(Z)-enantiomer **2** was also calculated by the π -electron SCF-CI-DV MO method: calculated, λ_{ext} 331.1 nm ($\Delta\epsilon$ −48.8), 260.4 (−12.8), 232.6 (+76.7), and 215.5 (−158.8); observed, λ_{ext} 339.0 nm ($\Delta\epsilon$ −12.3), 303.8 (−8.4), 281.5 (+8.5), 256.0 (−63.2), 238.1 (+189.7), and 223.5 (−239.3) (Table 1). Although the shape of the calculated CD curve in the 1L_a transition region is much

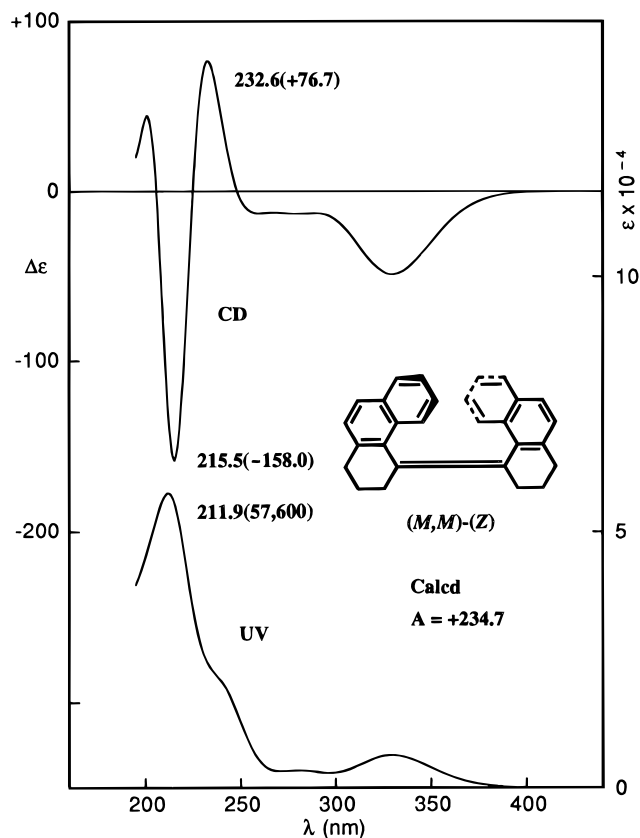


Figure 6. CD and UV spectral curves of *cis*-olefin (*M,M*)-(Z)-2 calculated by the π -electron SCF-CI-DV MO method.

different from the observed one, the negative sign of the Cotton effect around 330 nm agrees with that of observed one. The intense positive and negative Cotton effects in the 1B_b transition region were also reproduced by the π -electron SCF-CI-DV MO calculations, although the CD $\Delta\epsilon$ values are still much different from those of observed ones. Since the principal Cotton effects of the calculated and observed CD spectra thus agree with each other, the absolute stereochemistry of the first-eluted *cis*-olefin [CD(+238.1)]-(Z)-2 was also nonempirically determined to be (*M,M*) by the theoretical calculation of its CD spectrum.

The mechanism of the intense CD Cotton effects of *cis*-olefin [CD(+238.1)]-(Z)-2 in the 1B_b transition region was also clarified by the calculation of the hypothetical model compound (*M,M*)-(Z)-9 as for [CD(+239.0)]-(E)-1 (Chart 2). The calculation gave intense positive first and negative second Cotton effects due to the exciton coupling between two naphthalene chromophores in the 1B_b transition region (Table 1). The nature of the exciton coupling seen in the transitions of numbers 3 and 4 of model compound (*M,M*)-(Z)-9 is retained in the transitions of numbers 7 and 9 of *cis*-olefin (*M,M*)-(Z)-2 (Table 2). Therefore, the observed Cotton effects of [CD(+238.1)]-(Z)-2 in the 1B_b transition region are considered to be mainly arising from the exciton coupling between two naphthalene chromophores.

The theoretical CD method is thus powerful for determination of the absolute stereochemistry of chiral compounds with a twisted π -electron system. The absolute stereochemistry of chiral olefins **1** and **2** theoretically determined was later experimentally proved by the X-ray crystallographic analysis of their derivatives as described in the third paper of this series.²⁸

Experimental Section

General Procedures. Melting points are uncorrected. IR spectra were obtained as KBr disks on a Jasco FT/IR-8300 spectrophotometer. 1H NMR spectra were recorded on a Jeol JNM-LA400 (400 MHz) or

a Jeol JNM-LA600 (600 MHz) spectrometer. ^{13}C NMR spectra were obtained on a Jeol JNM-LA400 (100 MHz) spectrometer. All NMR data are reported in ppm (δ) downfield from tetramethylsilane, and the NMR data of C_2 -symmetrical compounds are listed for a half molecule. Optical rotations $[\alpha]_D$ were measured on a Jasco DIP-1000 spectropolarimeter. UV and CD spectra were recorded on Jasco Ubest-50 and Jasco J-400X or J-720WI spectrometers, respectively. MS spectra were obtained with a Jeol JMS DX-300/JMA-3100/3500 spectrometer by the electron ionization (EI) procedure (70 eV), unless otherwise noted. X-ray single-crystal diffraction measurement was performed on a Rigaku AFC-6B automated four-circle diffractometer. The purities of the title compounds were shown to be $\geq 95\%$ by 1H NMR, TLC, HPLC, and/or elemental analysis.

(\pm)-(E)-1,1',2,2',3,3',4,4'-Octahydro-4,4'-biphenanthrylidene (**1**) and its *cis*-isomer (\pm)-(Z)-2. To a mixture of $TiCl_3$ (7.15 g, 45.9 mmol) and dry tetrahydrofuran (THF, 15 mL) cooled at 0 °C was added dropwise a mixture of $LiAlH_4$ (0.87 g, 23.0 mmol) and dry THF (10 mL) under a stream of argon gas, and the reaction mixture was stirred for 10 min. To the reaction mixture was added a solution of ketone **7** (3.0 g, 15.3 mmol) in dry THF (20 mL), and the reaction mixture was gently refluxed overnight. THF was removed under a reduced pressure, and the residue was extracted with ethyl acetate three times. The organic layer was washed with brine, dried with anhydrous $MgSO_4$, and evaporated to dryness. After the crude product obtained was purified by a short column chromatography on silica gel (benzene), the hydrocarbon fractions were further purified by repeating HPLC on silica gel (hexane/benzene 10:1) several times. From the less-polar fraction, *trans*-olefin (\pm)-**1** was obtained as a crystalline material, which was recrystallized from hexane giving colorless crystals (0.228 g, 8.3%): mp 213 °C; TLC (silica gel, hexane/benzene 10:1) R_f 0.61; IR (KBr) ν_{max} 3054, 2958, 2848, 1591, 1509, 1441, 1384, 1297, 1210, 1026, 958, 867, 815, 751 cm^{-1} ; 1H NMR (600 MHz, $CDCl_3$) δ 1.50 (1 H, dddt, $J = 12.7, 10.1, 7.1, 5.1$ Hz, H2ax), 1.74 (1 H, dddt, $J = 12.7, 7.1, 5.8, 4.0$ Hz, H2eq), 2.23 (2 H, t, $J = 7.1$ Hz, H3), 2.59 (1 H, ddd, $J = 14.7, 10.1, 5.8$ Hz, H1ax), 2.75 (1 H, ddd, $J = 14.7, 5.1, 4.0$ Hz, H1eq), 7.36 (1 H, d, $J = 8.2$ Hz, H10), 7.46 (1 H, ddd, $J = 8.2, 6.7, 1.3$ Hz, H7), 7.52 (1 H, ddd, $J = 8.4, 6.7, 1.1$ Hz, H6), 7.77 (1 H, d, $J = 8.2$ Hz, H9), 7.89 (1 H, dd, $J = 8.2, 1.3$ Hz, H8), 8.28 (1 H, dd, $J = 8.4, 1.1$ Hz, H5); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.8 (C2), 29.8 (C1), 30.2 (C3), 124.5 (C7), 125.9 (C6), 126.0 (C5), 126.3 (C10), 126.9 (C9), 128.5 (C8), 131.0 (C4b), 132.0 (C4), 132.4 (C8a), 135.6 (C4a), 138.8 (C10a); 1H - 1H NOESY and HMBC (600 MHz, $CDCl_3$), see tables in Supporting Information; HSQC (600 MHz, $CDCl_3$) H1ax-C1, H1eq-C1, H2ax-C2, H2eq-C2, H3-C3, H5-C5, H6-C6, H7-C7, H8-C8, H9-C9, H10-C10; UV (MeOH) λ_{max} 316.0 nm (ϵ 16 900), 231.5 (62 500), 215.7 (84 300); MS m/z 360 (parent). Anal. Calcd for $C_{28}H_{24}$: C, 93.29; H, 6.71. Found: C, 93.22; H, 6.76.

From the more polar fraction, *cis*-olefin (\pm)-**2** was obtained as a crystalline material, which was recrystallized from hexane giving colorless crystals (0.069 g, 2.5%): mp 192–195 °C; TLC (silica gel, hexane/benzene 10:1) R_f 0.56; IR (KBr) ν_{max} 3049, 2949, 2887, 1595, 1509, 1430, 1377, 1235, 1025, 845, 813, 749 cm^{-1} ; 1H NMR (600 MHz, $CDCl_3$) δ 1.67 (1 H, ddddd, $J = 15.4, 11.4, 8.6, 8.4, 4.3$ Hz, H2ax), 2.31 (1 H, ddddd, $J = 15.4, 8.4, 5.0, 4.3, 3.5$ Hz, H2eq), 2.65 (1 H, ddd, $J = 14.7, 8.6, 3.5$ Hz, H3ax), 2.90 (1 H, ddd, $J = 14.7, 11.4, 5.0$ Hz, H1ax), 2.96 (1 H, ddd, $J = 14.7, 4.3, 4.3$ Hz, H1eq), 3.18 (1 H, ddd, $J = 14.7, 8.4, 8.4$ Hz, H3eq), 6.65 (1 H, ddd, $J = 8.4, 6.8, 1.3$ Hz, H6), 6.83 (1 H, ddd, $J = 8.1, 6.8, 1.3$ Hz, H7), 7.00 (1 H, dd, $J = 8.4, 1.3$ Hz, H5), 7.19 (1 H, d, $J = 8.3$ Hz, H10), 7.21 (1 H, dd, $J = 8.1, 1.3$ Hz, H8), 7.26 (1 H, d, $J = 8.3$ Hz, H9); ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.0 (C2), 28.9 (C3), 31.2 (C1), 123.4 (C7), 123.9 (C6), 124.6 (C5), 126.1 (C10), 126.4 (C9), 126.7 (C8), 129.2 (C4b), 131.4 (C4), 131.9 (C8a), 135.8 (C4a), 138.8 (C10a); 1H - 1H NOESY and HMBC (600 MHz, $CDCl_3$), see tables in Supporting Information; HSQC (600 MHz, $CDCl_3$) H1ax-C1, H1eq-C1, H2ax-C2, H2eq-C2, H3ax-C3, H3eq-C3, H5-C5, H6-C6, H7-C7, H8-C8, H9-C9, H10-C10; UV (hexane) λ_{max} 301.9 nm (ϵ 11 300), 222.8 (71 900); MS m/z 360 (parent). Anal. Calcd for $C_{28}H_{24}$: C, 93.24; H, 6.86.

X-ray Crystallography of (\pm)-(E)-Olefin (1**).** Crystals were obtained as colorless prisms by crystallization from hexane: mp 213 °C. A single crystal (dimensions of 0.36 \times 0.23 \times 0.22 mm) was

selected for data collection and mounted on a Rigaku AFC-6B automated four-circle diffractometer. The crystal was found to be monoclinic, and the unit cell parameters and orientation matrix were obtained. Data collection was carried out by using a $2\theta - \theta$ scan: formula, $C_{28}H_{24}$; $M_r = 360.50$; space group $C2/c$ (No. 15); $a = 19.188(2)$, $b = 6.6750(4)$, and $c = 15.337(2)$ Å, $\beta = 90.35(1)^\circ$; $V = 1964.4(3)$ Å³; $Z = 4$; $D_x = 1.219$ g cm⁻³; $D_m = 1.211$ g cm⁻³ by flotation using a CCl_4 /hexane solution; radiation, Cu K α (1.541 78 Å); monochromator, graphite crystal; linear absorption coefficient, 4.43 cm⁻¹; temperature, 20 °C; scan speed, 2.0°/min; scan range, 1.3° + 0.3° tan θ ; 2θ scan limits, 2° – 130°; standard reflections, 3 per 50 reflections; indices, (1,1,3), (1,1,0), (3,1,1); crystal stability, no indication of standard reflection decay during data collection; total reflections scanned, 3780; unique data $F_o > 3\sigma(F_o)$, 1544. One asymmetrical unit contained a half molecule of **1**. The skeletal structure was solved by direct methods and successive Fourier syntheses. All hydrogen atoms were found by the difference Fourier syntheses. Full-matrix least-squares refinement of positional and thermal parameters led to the final convergence with $R = 0.0688$ and $R_w = 0.0577$.

Enantioresolution of (\pm)-(*E*)-Olefin **1 by HPLC.** The HPLC column with a chiral stationary phase of (+)-poly(triphenylmethyl methacrylate) (Chiralpak OT(+)) from Daicel Co. Ltd.) was installed in a HPLC system, cooled at 3 °C by circulating cold methanol in a column jacket, and equilibrated with methanol as eluent. The sample of (\pm)-*trans*-**1** was injected as a methanol solution, and the separation of enantiomers was monitored by a UV detector. Since a small amount of the polymer of the chiral stationary phase was present as a contaminant, the fraction of each enantiomer resolved was purified by HPLC (ODS-C₁₈, MeOH). From the first eluted fraction, chiral olefin [CD(+)_{239.0}]-(*E*)-**1** was obtained; the ¹H NMR data of optically active **1** were identical with those of (\pm)-**1**: CD (MeOH), see Table 1, where the concentration of the sample was determined from the UV absorption intensity. From the second-eluted fraction, chiral olefin [CD(-)_{239.0}]-(*E*)-**1** was obtained, and its CD Cotton effects were opposite in sign but almost equal in intensity to those of [CD(+)_{239.0}]-(*E*)-**1**.

Enantioresolution of (\pm)-(*Z*)-Olefin **2 by HPLC.** The HPLC column with a chiral stationary phase of (+)-poly(triphenylmethyl

methacrylate) connected in series with a short HPLC column of silica gel was installed in a HPLC system, cooled at 3 °C by circulating cold methanol, and equilibrated with hexane as eluent. The sample of (\pm)-*cis*-**2** was injected as a hexane solution, and the separation of enantiomers was monitored by a UV detector. The first-eluted fraction was collected and recycled five times. After separation, the CD spectrum of the first-eluted fraction was immediately measured: CD (MeOH), see Table 1, where the concentration of the sample was determined from the UV absorption intensity. Since the ¹H NMR data of optically active **2** thus separated were identical with those of (\pm)-**2**, the enantiomer of the first-eluted fraction was defined as [CD(+)_{238.1}]-(*Z*)-**2**. The CD spectrum of the second-eluted fraction was measured, and its CD Cotton effects observed were opposite in sign to those of the first-eluted enantiomer, although its CD Cotton effects were considerably weak. The second-eluted enantiomer was thus designated as [CD(-)_{238.1}]-(*Z*)-**2**.

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Supporting Information Available: Experimental procedures for the synthesis of **5a**, **6**, and **7**, as well as their spectroscopic and physical data, NOESY and HMBC data of (*E*)-**1** and (*Z*)-**2**, HPLC figure for enantioresolution of (*E*)-**1** and (*Z*)-**2**, and calculated CD and UV spectral curves of (*M,M*)-(*E*)-**8** and (*M,M*)-(*Z*)-**9** (7 pages). See any current masthead page for ordering and Internet access instructions.

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