Chemistry of Unique Chiral Olefins. 3. Synthesis and Absolute Stereochemistry of *trans*- and *cis*-1,1′,2,2′,3,3′,4,4′-Octahydro-3,3′-dimethyl-4,4′-biphenanthrylidenes

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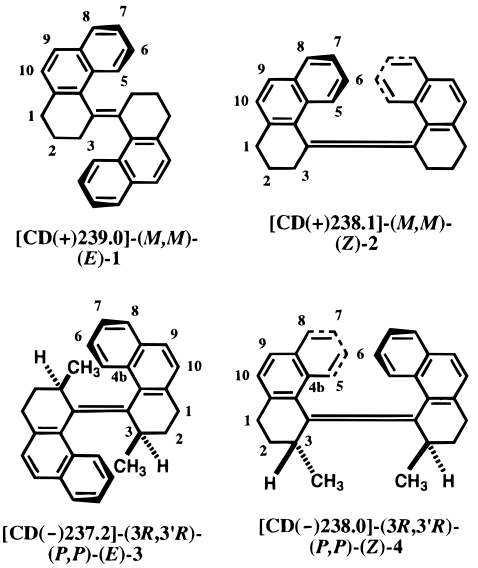
Abstract: Unique chiral olefins with two methyl groups as the internal reference of absolute stereochemistry, (3*R*,3′*R*)-(*P*,*P*)-(*E*)-(−)-1,1′,2,2′,3,3′,4,4′-octahydro-3,3′-dimethyl-4,4′-biphenanthrylidene (**3**) and its (3*R*,3′*R*)-(*P*,*P*)-(*Z*)-isomer (**4**), were synthesized in optically pure form starting from (3*R*,4*R*)-(+)-1,2,3,4-tetrahydro-3-methyl-4-phenanthrenol (**11**), which was obtained by the enantioresolution using a novel chiral auxiliary of dichlorophthalic acid amide (**14**). The absolute stereochemistry of chiral *trans*-dimethyl olefin (−)-**3** was determined by the X-ray crystallographic analyses of ester (−)-**16b** and (−)-**3** itself. Optically pure *cis*-dimethyl olefin **4** was prepared by photochemical reaction of *trans*-olefin (−)-**3**. The CD spectra of these chiral dimethyl olefins exhibit very intense Cotton effects in the ^1B_b transition region reflecting their strongly twisted π-electron systems. The CD spectrum of (3*R*,3′*R*)-(*P*,*P*)-(*E*)-(−)-**3** is almost similar in shape but opposite in sign to that of (*M*,*M*)-(*E*)-1,1′,2,2′,3,3′,4,4′-octahydro-4,4′-biphenanthrylidene (**1**). Therefore, the absolute stereochemistry of (*M*,*M*)-(*E*)-**1** previously theoretically determined was established in an experimental manner. The CD spectrum of (3*R*,3′*R*)-(*P*,*P*)-(*Z*)-**4** is also almost similar in shape but opposite in sign to that of (*M*,*M*)-(*Z*)-1,1′,2,2′,3,3′,4,4′-octahydro-4,4′-biphenanthrylidene (**2**). The absolute stereochemistry of (*M*,*M*)-(*Z*)-**2** theoretically determined was corroborated.

Introduction

In the preceding papers,[2] we have reported the synthesis, enantioresolution, circular dichroism spectra, and theoretical determination of absolute stereochemistry of unique chiral olefins, (*E*)-1,1′,2,2′,3,3′,4,4′-octahydro-4,4′-biphenanthrylidene (**1**) and its (*Z*)-isomer (**2**) (Chart 1).[2a] In addition, we have found a strange phenomenon that sterically hindered *cis*-olefin **2** easily racemizes at room temperature without formation of *trans*-olefin **1** as an intermediate, while *trans*-olefin **1** does not racemize at room temperature.[2b] However, the absolute stereochemistry of the unique chiral olefins **1** and **2** has not been established in an experimental way. In this paper, we report the synthesis, circular dichroism spectra, and X-ray crystallographic structure determination of chiral dimethyl olefins, (3*R*,3′*R*)-(*P*,*P*)-(*E*)-(−)-1,1′,2,2′,3,3′,4,4′-octahydro-3,3′-dimethyl-4,4′-biphenanthrylidene (**3**) and its (3*R*,3′*R*)-(*P*,*P*)-(*Z*)-isomer (**4**) (Chart 1). We also report experimental determination of the absolute configurations of chiral olefins **1** and **2** by comparing their CD spectra with those of chiral dimethyl olefins, (3*R*,3′*R*)-(*P*,*P*)-(*E*)-(−)-**3** and (3*R*,3′*R*)-(*P*,*P*)-(*Z*)-**4**, respectively.

To obtain optically pure both enantiomers in a laboratory scale and to determine their absolute configurations by X-ray crystallographic analysis, the diastereomer method using a chiral auxiliary is the most useful and powerful. For example, we reported that camphorsultam was powerful as a chiral auxiliary for enantioresolution of various carboxylic acids as diastereomers by HPLC.[3,4] The chiral auxiliary of camphorsultam was also useful as an internal reference of absolute configuration for determining the absolute configuration of carboxylic acids by X-ray crystallographic structure analysis. As an extension of this method, we have developed new chiral phthalic and dichlorophthalic acids as chiral auxiliaries useful for enantioresolution of various alcohols as diastereomeric esters by HPLC,

Chart 1



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(1) (a) Tohoku University. (b) University of Groningen.

(2) See papers of this series: (a) (part 1) Harada, N.; Saito, A.; Koumura, N.; Uda, H.; de Lange, B.; Jager, W. F.; Wynberg, H.; Feringa, B. L. *J. Am. Chem. Soc.* **1997**, *119*, 7241. (b) (part 2) Harada, N.; Saito, A.; Koumura, N.; Roe, D. C.; Jager, W. F.; Zijlstra, R. W. J.; de Lange, B.; Feringa, B. L. *J. Am. Chem. Soc.* **1997**, *119*, 7249.

(3) (a) Harada, N.; Soutome, T.; Murai, S.; Uda, H. *Tetrahedron: Asymmetry* **1993**, *4*, 1755. (b) Harada, N.; Soutome, T.; Nehira, T.; Uda, H.; Oi, S.; Okamura, A.; Miyano, S. *J. Am. Chem. Soc.* **1993**, *115*, 7547. (c) Hagiwara, H.; Okamoto, T.; Harada, N.; Uda, H. *Tetrahedron* **1995**, *51*, 9891 and references cited therein.

(4) See also: Toyota, S.; Miyasaka, T.; Matsumoto, Y.; Matsuo, T.; Oki, M. *Bull. Chem. Soc. Jpn.* **1994**, *67*, 1680.

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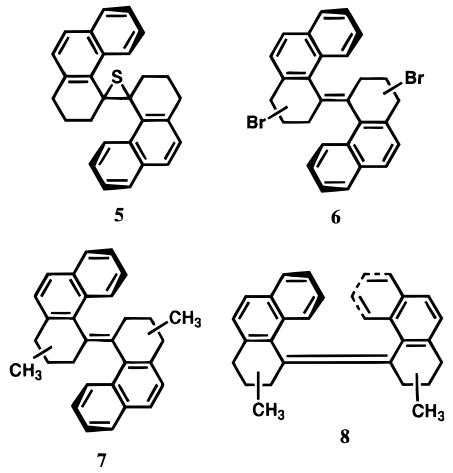
Chart 2



5 6 7 8

and these chiral acids are also useful as internal references of absolute configuration.[5,6] This chiral auxiliary method was applied to the preparation and determination of the absolute stereochemisty of enantiopure *cis*-methyl alcohol **11**, starting from which unique chiral dimethyl olefins **3** and **4** were synthesized, as discussed below.

Results and Discussion

Strategy for Determination of the Absolute Stereochemistry of Chiral Olefins: Introduction of Internal Reference of Absolute Configuration and Control of the Molecular Helicity of Chiral Olefins by Additional Centers of Chirality. To determine the absolute configurations of these chiral olefins by the Bijvoet method[7,8] of X-ray analysis, we tried to synthesize heavy atom derivatives **5** and **6** (Chart 2), but all attempts were unsuccessful. Instead of the Bijvoet method, one can determine absolute configurations of chiral compounds by X-ray crystallography, if the sample compound contains internal reference of absolute configuration. In this case, chiral auxiliaries are usually used as internal references of absolute configuration.[3−6] In our case, however, we adopted the strategy to employ methyl groups as chiral centers, as shown in formulas **7** and **8** of Chart 2, for the following reasons: (i) the methyl group is the minimum substituent and brings little affect to the π-electronic structure of chiral olefins, and therefore we can directly compare the CD spectra of chiral dimethyl olefins **7** and **8** with those of unsubstituted chiral olefins **1** and **2**; (ii) the molecular helicity of chiral olefins may be controlled by the chirality at the methyl group; (iii) if methyl groups are introduced at the 3 and 3′ positions, it may inhibit the racemization of *cis*-olefin because of steric hindrance, and therefore we can expect to synthesize the stable and optically pure chiral *cis*-olefin. From these reasons, among possible 1,1′-, 2,2′-, and 3,3′-dimethyl olefins (Chart 2), we have chosen to synthesize (*E*)-1,1′,2,2′,3,3′,4,4′-octahydro-3,3′-dimethyl-4,4′-biphenanthrylidene (**3**) and its (*Z*)-isomer **4** (Chart 1). If chiral olefins **3** and **4** are synthesized by dimerization of optically active methyl ketone **10**, chiral dimethyl olefins **3** and **4** should have C_2-symmetrical structures.

We have expected that the molecular helicity of chiral olefins **3** and **4** would be controlled by the chirality at the 3 and 3′ positions. To check this possibility, we carried out the calculation of conformational energy of **3** and **4** by the MOPAC 93 AM1 programs.[9] As shown in Figure 1, there are two conformers of *trans*-dimethyl olefin **3**; the most stable conformer has two methyl groups in axial positions to prevent steric hindrance. The other conformer having two methyl groups in equatorial positions is less stable. Since the energy difference ΔE is +10.2 kcal/mol, the population of the less-stable conformer is negligible. From the results, it is now sure that the molecular helicity of chiral olefin is controlled by the chirality of methyl groups at the 3 and 3′ positions; if the chiralities at 3 and 3′ positions are (3*R*,3′*R*), the molecular helicity should be (*P*,*P*). If (3*S*,3′*S*), the helicity is (*M*,*M*).

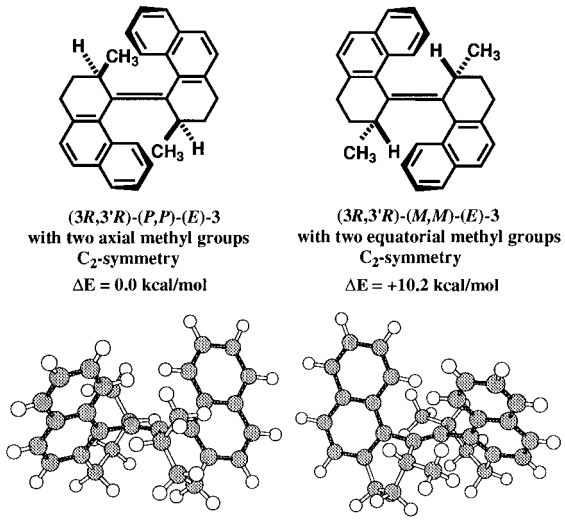


Figure 1. Molecular conformations of (3*R*,3′*R*)-(*E*)-dimethyl olefin **3** calculated by the MOPAC 93 AM1 programs.

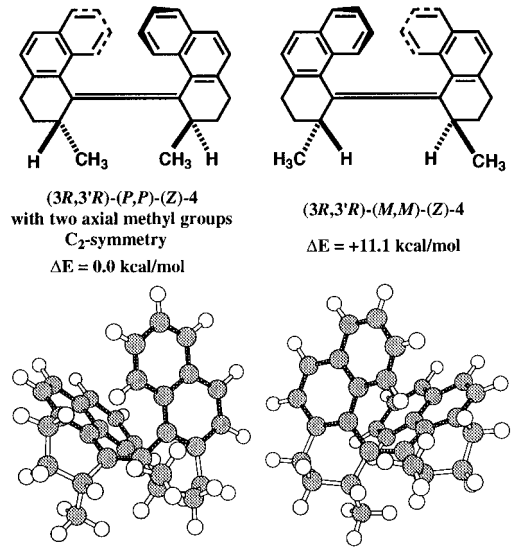


Figure 2. Molecular conformations of (3*R*,3′*R*)-(*Z*)-dimethyl olefin **4** calculated by the MOPAC 93 AM1 programs.

The same is true for *cis*-dimethyl olefin **4** (Figure 2). The most stable conformer of **4** takes a (3*R*,3′*R*)-(*P*,*P*)-(*Z*)- or (3*S*,3′*S*)-(*M*,*M*)-(*Z*)-conformation, where two methyl groups are in axial positions. In the less-stable conformer **4** with (3*R*,3′*R*)-(*M*,*M*)-(*Z*)- or (3*S*,3′*S*)-(*P*,*P*)-(*Z*)-configuration, two methyl groups cannot take equatorial positions at the same time because of severe steric hindrance between two methyl groups, and therefore the conformation deviates from the C_2-symmetrical structure. The less-stable conformer is negligible because of

(5) (a) Harada, N.; Nehira, T.; Soutome, T.; Hiyoshi, N.; Kido, F. *Enantiomer* **1996**, *1*, 35. (b) Harada, N.; Koumura, N.; Robillard, M. *Enantiomer* **1997**, *2*, 303 and references cited therein.

(6) See also: Toyota, S.; Yasutomi, A.; Oki, M. *Tetrahedron Lett.* **1995**, *36*, 6297.

(7) (a) Bijvoet, J. M.; Peerdeman, A. F.; van Bommel, A. J. *Nature* **1951**, *168*, 271. (b) Bijvoet, J. M.; Peerdeman, A. F. *Acta Crystallogr.* **1956**, *9*, 1012 and references cited therein.

(8) See also: Ibers, J.; Hamilton, W. C. *Acta Crystallogr.* **1964**, *17*, 781.

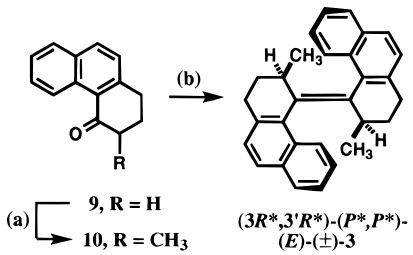
(9) Stewart, J. J. P. MOPAC 93; Fujitsu Limited: Tokyo, Japan, 1993.

Table 1. X-ray Crystallographic Data of Olefin (±)-**3**, Ester (−)-**16b**, Chiral Olefin (−)-**3**, and Olefin (±)-**4**

compound	(±)-**3**	(−)-**16b**	(−)-**3**	(±)-**4**
formula	$C_{30}H_{28}$	$C_{33}H_{33}Cl_2NO_5S$	$C_{30}H_{28}$	$C_{30}H_{28}$
fw (amu)	388.55	626.60	388.55	388.55
mp (°C), solvent	236, hexane	203, EtOAc	240, MeOH	169−170, hexane
cryst. dimens. (mm)	0.32 × 0.23 × 0.19	0.43 × 0.30 × 0.26	0.40 × 0.17 × 0.15	0.46 × 0.37 × 0.35
cryst. syst.	monoclinic	orthorhombic	orthorhombic	monoclinic
space group	*C*2/*c* (No. 15)	$P2_12_12_1$ (No. 19)	$P2_12_12_1$ (No. 19)	$P2_1/a$ (No. 14)
a (Å)	21.563(5)	15.607(2)	10.124(2)	17.815(3)
b (Å)	27.154(6)	15.923(3)	24.330(4)	12.198(2)
c (Å)	7.764(2)	12.249(2)	8.796(1)	10.647(2)
β (deg)	110.56(2)			106.09(1)
V (Å^3)	4257(2)	3044.0(9)	2166.6(6)	2223.0(6)
Z	8	4	4	4
D_x (g/cm^3)	1.213	1.367	1.191	1.161
D_m (g/cm^3)[a]	1.207	1.363	1.194	1.162
μ (cm^{-1})	4.39	27.79	4.31	4.20
no. of independent reflns				
$F_o > 3.0\sigma(F_o)$	4040	2923	2127	3783
absorption corr.	no	statistical[b]	statistical[b]	statistical[b]
absolute config.		3*S*,4*S*	3*R*,3′*R*,*P*,*P*	
final *R* and (R_w)	0.0615 (0.0595)	0.0287 (0.0400)	0.0343 (0.0432)	0.0749 (0.0782)
final *R* and (R_w) for the mirror image		0.0448 (0.0644)		

[a] By flotation using a CCl_4/hexane solution. [b] Katayama, C.; Sakabe, N.; Sakabe, K. *Acta Crystallogr.* **1972**, *A28*, 293.

Scheme 1[a]



[a] Key: (a) LDA, CH_3I/THF; (b) $TiCl_3$, $LiAlH_4$/THF, reflux 20 h.

much difference of conformational energy of $\Delta E = +11.1$ kcal/mol. The molecular helicity of *cis*-olefin **4** is thus controlled by the chirality at the 3 and 3′ positions.

Synthesis of (3*R,3′*R**)-(*P**,*P**)-(*E*)-(±)-Dimethyl Olefin 3 and Its X-ray Crystallographic Analysis.** To confirm the above prediction of the molecular conformation of chiral olefins, we next synthesized *trans*-dimethyl olefin **3** as a racemate (Scheme 1). Ketone **9** was methylated with LDA and CH_3I in THF giving methyl ketone **10** in a good yield. The obtained methyl ketone **10** was subjected to the McMurry reaction affording *trans*-dimethyl olefin **3** in 8% yield. ^{1}H and ^{13}C NMR spectra indicate that olefin **3** has a C_2-symmetrical structure (see the Experimental Section), and its (*E*) geometry was supported by the chemical shift of aromatic protons around δ 7.31−8.44 ppm, because *cis*-olefin shows an upfield shift due to aromatic ring current anisotropy.[2a] The (*E*) geometry of **3** was confirmed by NOE data observed between Me3 and H5′ and between H3 and H5′ (see the Supporting Information).

To determine the configuration at the 3 and 3′ positions, ^{1}H NMR spectra were studied in detail. However, a clearcut information to determine the configuration was not obtained. Racemate **3** crystallized as colorless prisms suitable for X-ray analysis, and those crystals are scarcely soluble in common solvents. A single crystal was selected and subjected to X-ray crystallographic diffraction (Table 1). The crystal was found to be monoclinic: space group *C*2/c (No. 15). The skeletal structure was solved by the 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 $R = 0.0615$ and $R_w = 0.0595$. The

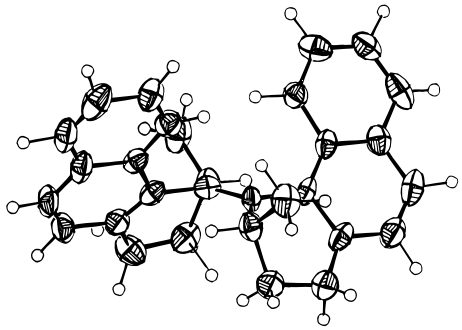


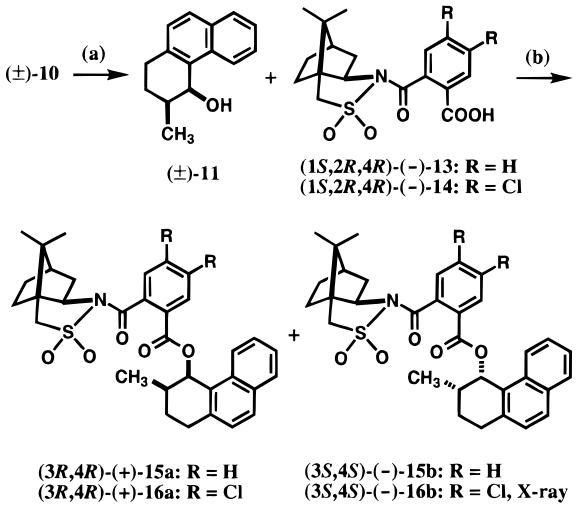
Figure 3. ORTEP drawing of racemic (3*R**,3′*R**)-(*P**,*P**)-(*E*)-(±)-dimethyl olefin **3**. The figure does not express its absolute stereochemistry. The atoms are drawn at 50% probability.

(3*R**,3′*R**)-(*P**,*P**)-(*E*)-configuration of (±)-**3** was determined as shown in Figure 3. Two methyl groups are in axial positions, as predicted by the MOPAC calculation.

The geometry of compound (±)-**3** in the solid state is characterized as follows: central double bond, C4−C4′ = 1.345 Å; average value of the dihedral angle between naphthalene plane and central double bond, C4−C4′−C4′a−C4′b = −61.8°; dihedral angles, C3−C4−C4′−C4′a = −7.9° (average), C3−C4−C4′−C3′ = +158.9°, C4a−C4−C4′−C4′a = −174.2°. The central double bond is thus a little twisted, and the component sp^2 carbon atoms are deviated from a plane structure. These geometrical parameters are almost in agreement with those of *trans*-olefin (±)-**1**.[2a] The proton−proton distance correlating to the ^{1}H NMR NOESY phenomena was calculated from the X-ray data: Me3ax−H5′ (ax = axial) = 3.07 Å, H3eq−H5′ (eq = equatorial) = 2.91 Å. The X−ray analysis thus confirmed the relationship between proton−proton distance and NOESY data.

Enantioresolution of 1,2,3,4-Tetrahydro-3-methyl-4-phenanthrenol (±)-11 as the Chiral Phthalic Acid Ester. To synthesize optically pure (*E*)-1,1′,2,2′,3,3′,4,4′-octahydro-3,3′-dimethyl-4,4′-biphenanthrylidene (**3**), optically pure methyl ketone **10** was needed. To prepare optically pure **10**, we adopted the strategy to make enantioresolution of *cis*-1,2,3,4-tetrahydro-3-methyl-4-phenanthrenol ((±)-**11**) or its *trans*-isomer (±)-**12** with chiral acid (1*S*,2*R*,4*R*)-(−)-**13** (Scheme 2).[5b] Methyl ketone (±)-**10** was reduced with $NaBH_4$ to yield *cis*-alcohol **11** as a major product and *trans*-alcohol **12** as a minor one. The relative

Scheme 2[a]



[a] Key: (a) $NaBH_4$/MeOH; (b) DCC, DMAP/CH_2Cl_2, reflux.

stereochemistry of these alcohols was determined on the basis of ^1H NMR coupling constant data; in both alcohols **11** and **12**, the hydroxyl group at the 4 position takes a quasi-axial conformation. The 3 proton of alcohol **11** was found to be in axial position because of large coupling constant of 12.9 Hz between 3- and 2-axial protons. Therefore, a 3-methyl group is in an equatorial position, indicating the *cis*-configuration. For alcohol **12**, the coupling constant between 3- and 2-axial protons is 3.3 Hz, leading to the *trans*-configuration. These assignments were finally established by the X-ray crystallographic analysis as discussed below.

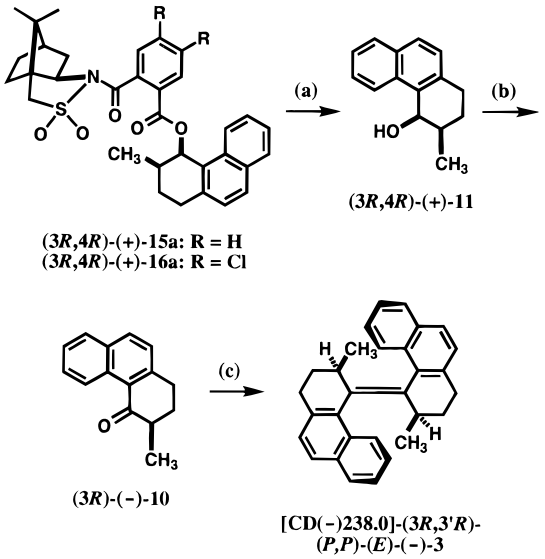
Racemic *cis*-alcohol (±)-**11** was esterified with chiral acid (1*S*,2*R*,4*R*)-(−)-**13** to make enantioresolution (Scheme 2); a mixture of racemic *cis*-alcohol (±)-**11**, chiral acid (−)-**13**, dicyclohexylcarbodiimide (DCC), and 4-(dimethylamino)pyridine (DMAP) in CH_2Cl_2 was refluxed for 9 h, yielding a diastereomeric mixture of esters (+)-**15a** and (−)-**15b**. The mixture was easily separated by HPLC on silica gel (hexane/EtOAc 7:1): separation factor $\alpha = 1.10$; resolution factor $R_s = 1.29$. The first eluted ester (+)-**15a** and the second one (−)-**15b** were obtained.[5b]

To obtain crystals suitable for X-ray crystallographic analysis, we have attempted recrystallization of both esters **15a** and **15b** from various solvents. However, ester **15a** crystallized as fine needles from methanol, while ester **15b** was obtained as an amorphous solid. Therefore, the X-ray crystallographic analysis of esters **15a** and **15b** was unsuccessful.

Ester (+)-**15a** was reduced with $LiAlH_4$ to yield optically pure *cis*-alcohol (+)-**11** as fine needles (Scheme 3). Ester (−)-**15b** similarly gave optically pure *cis*-alcohol (−)-**11** as silky fine needles. Enantioresolution of *cis*-alcohol **11** was thus accomplished by the chiral phthalic acid amide method developed by us.[5b]

Enantioresolution of *cis*-Alcohol (±)-11 as the Chiral Dichlorophthalic Acid Ester. We have recently developed another chiral auxiliary, chiral dichlorophthalic acid amide (1*S*,2*R*,4*R*)-(−)-**14**, useful for enantioresolution and X-ray crystallographic analysis. Racemic *cis*-alcohol (±)-**11** was similarly esterified with chiral acid (1*S*,2*R*,4*R*)-(−)-**14** to achieve enantioresolution (Scheme 2); a mixture of racemic *cis*-alcohol (±)-**11**, chiral acid (−)-**14**, DCC, and DMAP in CH_2Cl_2 was refluxed for 9 h, yielding a diastereomeric mixture of esters (+)-**16a** and (−)-**16b**. We found that the diastereomeric mixture was more easily separable by HPLC on silica gel (hexane/EtOAc 7:1) than the esters **15a** and **15b**: separation factor $\alpha = 1.18$; resolution factor $R_s = 1.31$. The elution times of both esters **16a** and **16b** were almost half those of esters **15a** and **15b**. The first eluted ester (+)-**16a** (47%) and the second one (−)-**16b** (48%) were obtained.

Scheme 3[a]



[a] Key: (a) $LiAlH_4$/THF; (b) PCC, MS-4A/CH_2Cl_2; (c) $TiCl_3$, $LiAlH_4$/THF, reflux 20 h.

The great merit to use chiral dichlorophthalic acid (−)-**14** is the point that the second-eluted ester **16b** crystallized as large prisms suitable for X-ray diffraction. When recrystallized from EtOAc, ester **16b** gave large colorless prisms, while ester **16a** crystallized as fine silky needles from methanol.

Ester (+)-**16a** was reduced with $LiAlH_4$ to yield optically pure *cis*-alcohol (+)-**11**, whose spectral data agreed with those of authentic sample obtained from ester **15a** (Scheme 3). Reduction of ester (−)-**16b** similarly gave optically pure *cis*-alcohol (−)-**11** which was identical with (−)-*cis*-alcohol obtained from ester **15b**.

X-ray Crystallographic Analysis of (3*S*,4*S*)-(−)-1,2,3,4-Tetrahydro-3-methyl-4-phenanthrenol Chiral Dichlorophthalic Acid Ester (16b).[5b] A single crystal of (−)-**16b** was subjected to X-ray analysis (Table 1). The crystal was found to be orthorhombic: space group $P2_12_12_1$ (No. 19). The skeletal structure was solved by direct methods and successive Fourier syntheses, and all hydrogen atoms were found by the difference Fourier syntheses. Absorption correction and full-matrix least-squares refinement of positional and thermal parameters, including anomalous scattering factors of chlorine, sulfur, oxygen, nitrogen, and carbon atoms, led to the final convergence with $R = 0.0287$ and $R_w = 0.0400$, while $R = 0.0448$ and $R_w = 0.0644$ were for the mirror image structure. The absolute stereochemistry of the second-eluted ester (−)-**16b** was thus determined to be (3*S*,4*S*) by the heavy atom effect as shown in Figure 4. The (3*S*,4*S*)-configuration of (−)-**16b** was also determined independently by the internal reference method using the known absolute configuration of the camphor part of auxiliary **14**. The *cis*-configuration of alcohol **11** was corroborated by this X-ray analysis.

Since reduction of ester (3*S*,4*S*)-(−)-**16b** gives (−)-*cis*-alcohol **11**, the absolute configuration of (−)-*cis*-alcohol **11** was determined to be (3*S*,4*S*). According to this determination, the absolute configurations of remaining compounds were unambiguously determined as follows: (3*R*,4*R*)-(+)-*cis*-alcohol **11**, (3*R*,4*R*)-(+)-ester **15a**, (3*R*,4*R*)-(+)-ester **16a**, and (3*S*,4*S*)-(−)-ester **15b** (Schemes 2 and 3).

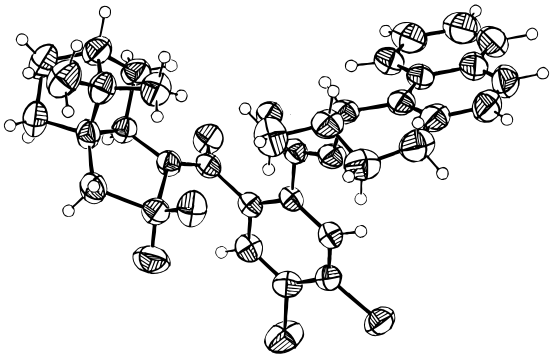


Figure 4. ORTEP drawing of (3*S*,4*S*)-(−)-*cis*-alcohol chiral dichlorophthalic acid ester **16b**. The atoms are drawn at 50% probability.

Synthesis of Optically Pure 1,2,3,4-Tetrahydro-3-methyl-4-phenanthrenone ((3*R*)-(−)-10) and Check of Enantiomeric Purity. To prepare optically pure methyl ketone **10**, optically pure *cis*-alcohol (3*R*,4*R*)-(+)-**11** in CH_2Cl_2 was oxidized with pyridinium chlorochromate (PCC) in the presence of molecular sieves (MS-4A) (Scheme 3). The desired methyl ketone **10** was obtained in a good yield. However, the specific rotation value of the obtained product **10** was remarkably small: $[\alpha]^{20}_D$ −2.9° (*c* 1.27, $CHCl_3$). It may imply that partial racemization occurred during the oxidation reaction, which we had worried about when choosing α-methyl ketone **10** as a chiral starting material. We have checked the enantiomeric purity of (−)-**10** as follows.

Ketone (−)-**10** was reduced with $NaBH_4$ giving *cis*- and *trans*-alcohols, and the fraction of *cis*-alcohol separated by HPLC was next esterified with chiral acid (1*S*,2*R*,4*R*)-(−)-**13** as for racemate (±)-**11** (Scheme 2). The ester product was subjected to HPLC on silica gel under the same condition used for separation of two esters **15a** and **15b**. The HPLC showed only one peak of ester, the retention time of which was the same as that of ester (3*R*,4*R*)-(+)-**15a**. The ^{1}H NMR of the ester product isolated was identical with that of (3*R*,4*R*)-(+)-**15a**. These results clearly indicate that methyl ketone (3*R*)-(−)-**10** with $[\alpha]^{20}_D$ −2.9° is enantiomerically pure.

Synthesis of (3*R*,3′*R*)-(*P*,*P*)-(*E*)-(−)-Dimethyl Olefin 3 and Its X-ray Crystallographic Analysis. Optically pure methyl ketone (3*R*)-(−)-**10** was subjected to the McMurry reaction, affording *trans*-dimethyl olefin (−)-**3** in 5% yield (Scheme 3): $[\alpha]^{20}_D$ −446.2° (*c* 0.22, $CHCl_3$). ^{1}H and ^{13}C NMR spectra of (−)-**3** were identical with those of racemate (±)-**3**. The large negative optical rotation value of (*E*)-dimethyl olefin (−)-**3** indicates that no racemization occurred during the McMurry reaction. At the final stage of HPLC purification of (−)-**3** under the reverse phase condition using ODS as a stationary phase and methanol as solvent, respectively, we were lucky to obtain good results as follows: after the HPLC purification, eluents of methanol solution were allowed to stand at room temperature overnight, and in the next morning, we found the appearance of beautiful prismatic crystals of olefin (−)-**3** suitable for X-ray crystallographic analysis.

A single crystal was selected and subjected to X-ray crystallographic diffraction (Table 1). The crystal was found to be orthorhombic: space group $P2_12_12_1$ (No. 19). The structure was solved by the direct methods and successive Fourier syntheses, and 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 $R = 0.0343$ and $R_w = 0.0432$. The absolute configuration of optically active *trans*-olefin (−)-**3** was determined to be (3*R*,3′*R*)-(*P*,*P*) by the internal reference method using the known absolute configuration of methyl groups at the 3 and 3′ positions, as illustrated in Figure 5.

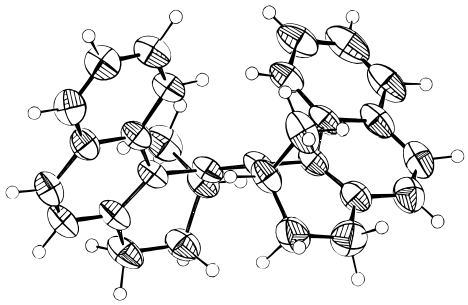


Figure 5. ORTEP drawing of [CD(−)237.2]-(3*R*,3′*R*)-(*P*,*P*)-(*E*)-(−)-dimethyl olefin **3**. The atoms are drawn at 50% probability.

Table 2. Observed UV and CD Spectra of Chiral Olefins

	obsd (MeOH or hexane)	
compound	UV, λ_{max} nm (ϵ)	CD, λ_{ext} nm ($\Delta\epsilon$)
(*M*,*M*)-(*E*)-**1**[a]	329.8 (17 400)	331.8 (+26.0)
	318.8 (17 300)	
		253.4 (−20.9)
	232.2 (61 800)	239.0 (+58.2)
		224.8 (−76.4)
	216.2 (82 800)	214.2 (−153.3)
(3*R*,3′*R*)-(*P*,*P*)-(*E*)-**3**[a]	326.6 (15 300)	
	313.0 (16 600)	313.6 (−18.7)
		254.8 (+33.3)
		237.2 (−92.5)
	218.4 (85 700)	217.8 (+148.5)
(*M*,*M*)-(*Z*)-**2**[b]	301.9 (11 300)	338.0 (−14.0)
		282.5 (+11.9)
		256.8 (−80.1)
		239.6 (+222.2)
	222.8 (71 900)	224.0 (−281.3)
(3*R*,3′*R*)-(*P*,*P*)-(*Z*)-**4**[c]	301.8 (11 800)	300.4 (+13.4)
		279.4 (−10.1)
		254.0 (+86.4)
		238.0 (−226.9)
	222.4 (76 500)	223.4 (+334.0)

[a] Observed in MeOH. [b] Observed in hexane at −50 °C. [c] Observed in hexane.

The molecular geometry of compound (−)-**3** is almost the same as that of racemate (±)-**3**. Two methyl groups at the 3 and 3′ positions are in the axial positions, and the molecular helicity is controlled by the chiralities at the 3 and 3′ positions. It is now established that *trans*-dimethyl olefin (−)-**3** has the (3*R*,3′*R*)-(*P*,*P*) absolute stereochemistry.

CD and UV Spectra of (3*R*,3′*R*)-(*P*,*P*)-(*E*)-(−)-Dimethyl Olefin 3 and Their Comparison with Those of [CD(+)239.0]-(*E*)-Olefin 1. The UV spectrum of *trans*-dimethyl olefin (*E*)-(−)-**3** shows intense absorption bands similar to those of *trans*-olefin (*E*)-**1**: UV (MeOH) λ_{max} 326.6 nm (ϵ 15 300), 313.0 (16 600), 218.4 (85 700) (Table 2 and Figure 6). The shape of UV curve of (*E*)-(−)-**3** closely resembles that of (*E*)-**1** including the small trough around 325 nm and the shoulder around 230 nm.

The CD spectrum of *trans*-dimethyl olefin (*E*)-(−)-**3** exhibits very intense Cotton effects in ^1L_a and ^1B_b transition region of naphthalene chromophore: CD (MeOH) λ_{ext} 313.6 nm ($\Delta\epsilon$ −18.7), 254.8 (+33.3), 237.2 (−92.5), 217.8 (+148.5) (Table 2 and Figure 6). The CD intensities of these Cotton effects never decrease at room temperature, and therefore, it is concluded that *trans*-dimethyl olefin (*E*)-(−)-**3** never racemizes or changes to the other diastereomer ((3*R*,3′*R*)-(*M*,*M*)-**3**). We have expected such stability of (3*R*,3′*R*)-(*P*,*P*)-(*E*)-(−)-**3**, because dimethyl olefin (*E*)-(−)-**3** is sterically more hindered than unsubstituted *trans*-olefin (*E*)-**1** which does not racemize at room temperature.

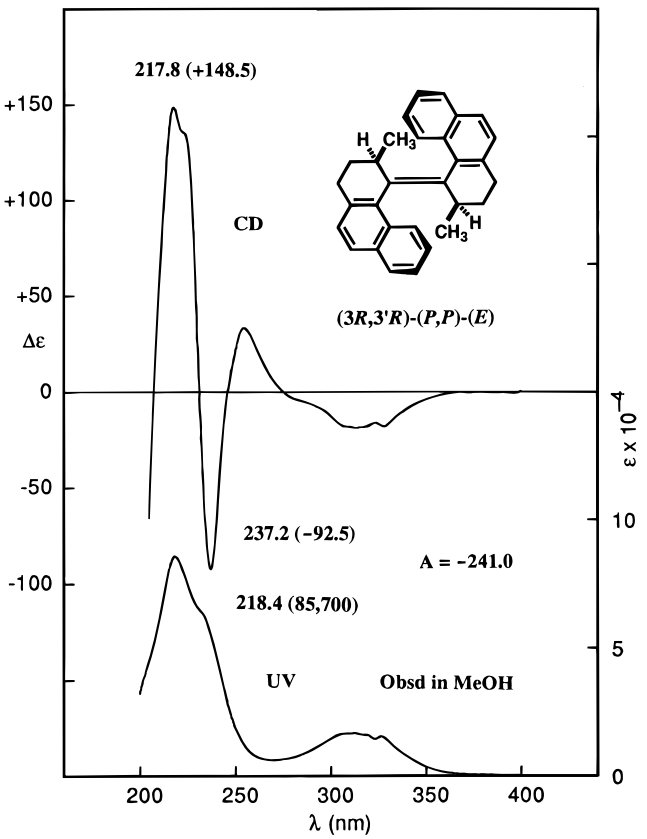


Figure 6. CD and UV spectra of (3*R*,3′*R*)-(*P*,*P*)-(*E*)-(−)-dimethyl olefin **3** in methanol.

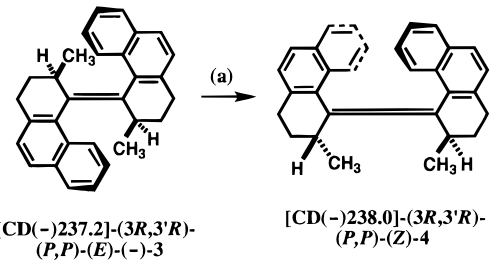
The CD curve of (3*R*,3′*R*)-(*P*,*P*)-(*E*)-(−)-**3** is very similar in shape to that of unsubstituted *trans*-olefin [CD(+)239.0]-(*E*)-**1**,[10] except for the position of shoulder around 225 nm (compare Figure 6 with Figure 3 of the first paper of this series).[2a] The similarity of CD and UV spectra of *trans*-dimethyl olefin (−)-**3** to those of (*E*)-**1** indicates that two methyl groups at the 3 and 3′ positions little affect the twisted π-electron structure of these chiral olefins. Since the CD Cotton effects of (3*R*,3′*R*)-(*P*,*P*)-(*E*)-(−)-**3** are opposite in sign to those of [CD(+)239.0]-(*E*)-**1**, the absolute stereochemistry of [CD(+)239.0]-(*E*)-**1** is now determined to be (*M*,*M*). We have thus succeeded in determining the absolute stereochemistry of these chiral olefins in experimental manner. These results of stereochemical assignment are consistent with the absolute stereochemistry of [CD-(+)239.0]-(*E*)-**1** theoretically determined.[2a]

Photochemical Conversion of *trans*-Dimethyl Olefin (3*R,3′*R**)-(*P**,*P**)-(*E*)-(±)-3 to *cis*-Dimethyl Olefin (3*R**,3′*R**)-(*P**,*P**)-(*Z*)-(±)-4 and X-ray Crystallographic Analysis of the Product.** To obtain *cis*-dimethyl olefin **4**, we checked the crude product of the McMurry reaction of methyl ketone **10**. However, we were unsuccessful in isolating the *cis*-dimethyl olefin **4** in both cases using racemic and optically pure methyl ketone **10**. This may imply the severe steric hindrance in the dimerization reaction.

Instead, we adopted the strategy of photochemical conversion of *trans*-dimethyl olefin **3** to *cis*-dimethyl olefin **4** (Scheme 4). A solution of racemate (±)-**3** in acetone-d_6 was irradiated by a high-pressure mercury lamp using a Pyrex glass filter for 5 h, during which time the photoreaction was monitored by ^{1}H NMR. *cis*-Dimethyl olefin (±)-**4** was obtained as crystals in 43% yield,

(10) For definition of enantiomer by using CD data, see: Harada, N.; Iwabuchi, J.; Yokota, Y.; Uda, H.; Okamoto, Y.; Yuki, H.; Kawada, Y. *J. Chem. Soc., Perkin. Trans. 1* **1985**, 1845. Harada, N. *Enantiomer* **1996**, *1*, 81.

Scheme 4[a]



[a] Key: (a) hν, Hg lamp, Pyrex/acetone.

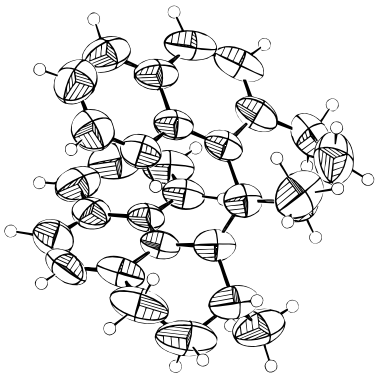


Figure 7. ORTEP drawing of racemic (3*R**,3′*R**)-(*P**,*P**)-(*Z*)-(±)-dimethyl olefin **4**. The figure does not express its absolute stereochemistry. The atoms are drawn at 50% probability.

which were recrystallized from hexane giving colorless prisms: mp 169−170 °C. ^{1}H and ^{13}C NMR spectra indicated the C_2-symmetric structure of *cis*-dimethyl olefin **4**, the (*Z*)-geometry of which was corroborated by the chemical shift data of aromatic protons appearing at 6.6−7.2 ppm as for (*Z*)-**2** and also by the NOE between 1-H and 5′-H (see the Experimental Section and the Supporting Information). The configuration of two methyl groups at the 3 and 3′ positions was estimated to be axial, because of steric hindrance as discussed above (Figure 2). These stereochemical remarks were confirmed by the X-ray crystallographic analysis of racemate (±)-**4** as follows.

Single crystals suitable for X-ray analysis were obtained as colorless prisms by recrystallization from hexane (Table 1). The crystal was found to be monoclinic: space group $P2_1/a$ (No. 14). The skeletal structure was solved by the direct methods and successive Fourier syntheses, and all hydrogen atoms were found by the difference Fourier syntheses. Absorption correction and full-matrix least-squares refinement of positional and thermal parameters led to the final convergence with $R = 0.0749$ and $R_w = 0.0782$. The relative stereochemistry of *cis*-dimethyl olefin (±)-**4** was determined to be (3*R**,3′*R**)-(*P**,*P**), as shown in Figure 7. Two methyl groups are in axial positions as discussed above. The molecular helicity of *cis*-dimethyl olefin **4** is thus controlled by the chiralities at the 3 and 3′ positions.

The molecular geometry of *cis*-dimethyl olefin (±)-**4** is characterized as follows: central double bond, C4−C4′ = 1.347 Å; dihedral angle between naphthalene plane and central double bond, C4−C4′−C4′a−C4′b = +54.4° (average); dihedral angles, C3−C4−C4′−C4′a = −178.7° (average), C3−C4−C4′−C3′ = +5.9°, C4a−C4−C4′−C4′a = −3.2°. The bond length of the central double bond is thus similar to that of *trans*-dimethyl olefin **3** (1.345 Å), and therefore, the bond length of the central double bond is little affected by the (*Z*)- and (*E*)-geometrical isomerism. As seen from the dihedral angle data, the central double bond is a little twisted and the component sp^2 carbon atoms are a little deviated from a planar structure.

The distance between two overlapped naphthalene planes is

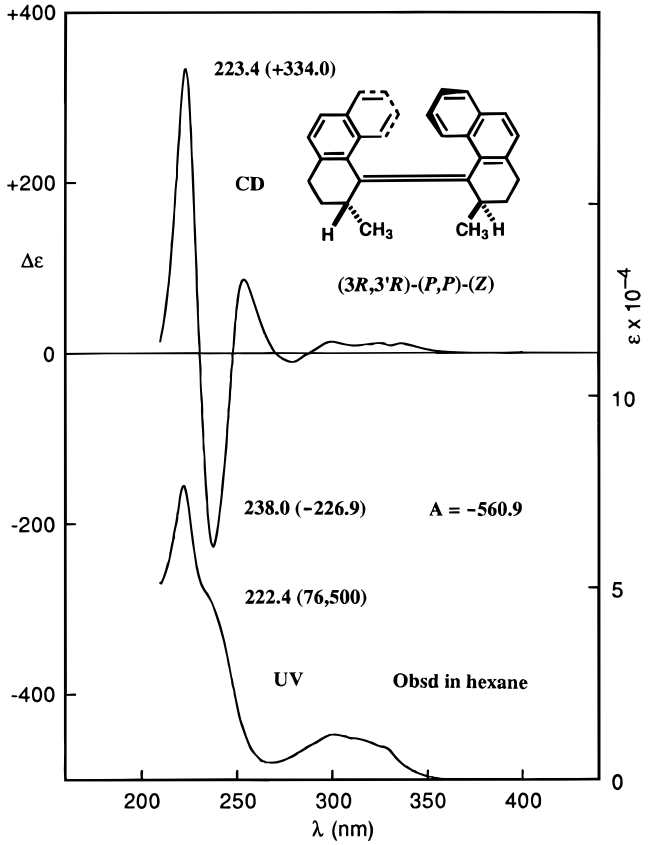


Figure 8. CD and UV spectra of (3*R*,3′*R*)-(*P*,*P*)-(*Z*)-dimethyl olefin **4** in hexane.

represented by the interatomic distance (3.253 Å) between C4b and C4′b. Two naphthalene groups in *cis*-dimethyl olefin **4** are thus in contact with each other within twice of the van der Waals' radius (1.70 Å) of aromatic planes. The H1−H5′ distance correlating to the observed ^{1}H NMR NOE was calculated from the X-ray data: H1ax−H5′ = 2.32 Å. The X-ray analysis thus confirmed the relationship between proton−proton distance and NOESY data.

Synthesis of *cis*-Dimethyl Olefin [CD(−)238.0]-(3*R*,3′*R*)-(*P*,*P*)-(*Z*)-4, Its CD and UV Spectra, and Determination of the Absolute Stereochemistry of *cis*-Olefins. A solution of optically pure *trans*-dimethyl olefin [CD(−)237.2]-(3*R*,3′*R*)-(*P*,*P*)-(*E*)-(−)-**3** was subjected to the photochemical reaction as for racemate (±)-**3**, giving the desired optically active *cis*-dimethyl olefin **4** in 55% yield (Scheme 4). Since the CD spectrum of the optically active *cis*-dimethyl olefin **4** obtained exhibited a negative Cotton effect at 238.0 nm, the *cis*-olefin product is designated as [CD(−)238.0]-(*Z*)-**4**. ^{1}H and ^{13}C NMR spectra of [CD(−)238.0]-(*Z*)-**4** are identical with those of racemate (±)-**4**, the relative stereochemistry of which was determined to be (3*R*,3′*R*)-(*P*,*P*)-(*Z*) or (3*S*,3′*S*)-(*M*,*M*)-(*Z*) by X-ray analysis discussed above. Since the absolute configuration of methyl groups is retained during the photochemical (*E*) and (*Z*) interconversion, it is evident that *cis*-dimethyl olefin [CD(−)238.0]-(*Z*)-**4** has the (3*R*,3′*R*)-(*P*,*P*)-(*Z*) absolute stereochemistry.

The CD spectrum of [CD(−)238.0]-(3*R*,3′*R*)-(*P*,*P*)-(*Z*)-**4** shows very intense Cotton effects in ^1L_a and ^1B_b transition region of naphthalene chromophore: CD (hexane) λ_{ext} 300.4 nm ($\Delta\epsilon$ +13.4), 279.4 (−10.1), 254.0 (+86.4), 238.0 (−226.9), 223.4 (+334.0) (Table 2 and Figure 8). The CD amplitude A ($=\Delta\epsilon_{peak} - \Delta\epsilon_{trough}$) in the ^1B_b transition region is −560.9, which is comparable to that of unsubstituted *cis*-olefin [CD(+)239.6]-(*M*,*M*)-(*Z*)-**2** (A = +503.5). The CD intensities of these Cotton effects do not change at room temperature, and therefore, it is obvious that *cis*-dimethyl olefin (3*R*,3′*R*)-(*P*,*P*)-(*Z*)-**4** does not change or racemize at room temperature, in contrast to the unsubstituted *cis*-olefin **2** which undergoes easy racemization at room temperature. This is what we expected to occur in our strategy. This stability of *cis*-dimethyl olefin [CD(−)238.0]-(3*R*,3′*R*)-(*P*,*P*)-(*Z*)-**4**, of course, is due to the steric hindrance between two methyl groups at the 3 and 3′ positions, which blocks racemization and/or conversion to other diastereomers.

The CD curve of [CD(−)238.0]-(3*R*,3′*R*)-(*P*,*P*)-(*Z*)-**4** is very similar in shape to that of unsubstituted *cis*-olefin [CD(+)239.6]-(*Z*)-**2** (see Table 2 and also compare Figure 8 with Figure 2 of the second paper of this series).[2b] This similarity of CD and UV spectra of [CD(−)238.0]-(3*R*,3′*R*)-(*P*,*P*)-(*Z*)-**4** to those of [CD(+)239.6]-(*Z*)-**2** indicates that two methyl groups little affect the twisted π-electron structure of these chiral olefins as for the *trans*-olefins discussed above. Those aspects allow us to determine the absolute stereochemistry of *cis*-olefin **2** by direct comparison of CD spectra of olefins **2** and **4**. Since the CD Cotton effects of [CD(−)238.0]-(3*R*,3′*R*)-(*P*,*P*)-(*Z*)-**4** are opposite in sign to those of [CD(+)239.6]-(*Z*)-**2**, the absolute stereochemistry of [CD(+)239.6]-(*Z*)-**2** was determined to be (*M*,*M*). This absolute stereochemistry of *cis*-olefin [CD(+)-239.6]-(*Z*)-**2** agrees with that obtained by the theoretical calculation of CD spectra.[11] Our strategy and execution to determine the absolute stereochemistry of these unique chiral olefins thus brought fruitful results as described here.

Experimental Section

General Procedures. Melting points are uncorrected. IR spectra were obtained as KBr disks on a Jasco FT/IR-8300 spectrophotometer. ^{1}H NMR spectra were recorded on a Jeol JNM-LA400 (400 MHz), a Jeol GSX-500 (500.0 MHz), or a Jeol JNM-LA600 (600 MHz) spectrometer. ^{13}C NMR spectra were obtained on a Jeol JNM-LA400 (100 MHz), a Jeol GSX-500 (125 MHz), or a Jeol JNM-LA600 (150 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-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 Mac Science MXC18 automated four-circle diffractometer. The purities of the title compounds were shown to be ≥95% by ^{1}H NMR, TLC, HPLC, and/or elemental analysis.

X-ray Crystallography. A single crystal was selected for data collection and mounted on a Mac Science MXC18 automated four-circle diffractometer: radiation, Cu Kα (1.541 78 Å); monochromator, graphite crystal. The crystal system, space group, unit cell parameters, and orientation matrix were determined. Data collection was carried out by using a $2\theta-\theta$ scan: temperature, 20 °C; scan speed, 14°/min; scan range, $1.75-1.87° + 0.2° \tan\theta$; 2θ scan limits, 2−130°; standard reflections, 3 per 100 reflections; crystal stability, no indication of standard reflection decay during data collection. The density of crystals were measured by flotation using a CCl_4/hexane solution.

(3*R,3′*R**)-(*P**,*P**)-(*E*)-(±)-1,1′,2,2′,3,3′,4,4′-Octahydro-3,3′-dimethyl-4,4′-biphenanthrylidene (3).** To a mixture of $TiCl_3$ (523 mg, 3.39 mmol) and dry THF (4 mL) cooled at 0 °C was added dropwise a mixture of $LiAlH_4$ (64 mg, 1.69 mmol) and dry THF (3 mL). The reaction mixture was stirred at 0 °C for 30 min and then refluxed for 1 h. After a solution of methyl ketone (±)-**10** (237 mg, 1.13 mmol) in dry THF (5 mL) was added, the reaction mixture was gently refluxed for 20 h. The reaction mixture was treated with dilute aqueous HCl and extracted with chloroform three times. The combined organic

(11) Harada, N.; Nakanishi, K. *Circular Dichroic Spectroscopy - Exciton Coupling in Organic Stereochemistry*; University Science Books: Mill Valley, CA, and Oxford University Press: Oxford, 1983.

layers were washed with brine, dried with anhydrous $MgSO_4$, and evaporated to dryness. The crude product was purified by a short column chromatography and successive HPLC on silica gel (hexane) to yield (±)-*trans*-dimethyl olefin **3** (17 mg, 8%) as colorless prisms: mp 236 °C (hexane); TLC (silica gel, hexane) R_f 0.33; IR (KBr) ν_{max} 3050, 2972, 2929, 2869, 1506, 1455, 1426, 1373, 1212, 1032, 952, 869, 812, 759, 720 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 0.78 (3 H, d, J = 6.8 Hz, Me3ax), 1.26 (1 H, dddd, J = 13.0, 7.1, 7.1, 6.6 Hz, H2ax), 1.88 (1 H, dddd, J = 13.0, 7.1, 7.1, 3.3 Hz, H2eq), 2.67 (1 H, ddq, J = 7.1, 6.8, 3.3 Hz, H3eq), 2.73 (1 H, ddd, J = 15.8, 7.1, 6.6 Hz, H1ax), 2.75 (1 H, ddd, J = 15.8, 7.1, 7.1 Hz, H1eq), 7.31 (1 H, d, J = 8.2 Hz, H10), 7.47 (1 H, ddd, J = 8.2, 7.0, 1.2 Hz, H7), 7.55 (1 H, ddd, J = 8.4, 7.0, 1.3 Hz, H6), 7.74 (1 H, d, J = 8.2 Hz, H9), 7.88 (1 H, dd, J = 8.2, 1.3 Hz, H8), 8.44 (1 H, dd, J = 8.4, 1.2 Hz, H5); ^{13}C NMR (125 MHz, $CDCl_3$) δ 18.6 (Me3ax), 27.5 (C1), 31.2 (C2), 33.8 (C3), 124.7 (C7), 125.6 (C6), 125.9 (C5), 126.4 (C9), 126.6 (C10), 128.2 (C8), 132.3 (C4b), 132.3 (C8a), 134.8 (C4a), 136.3 (C4), 136.5 (C10a); $^1H-^1H$ NOESY and HMBC (600 MHz, $CDCl_3$), see tables in Supporting Information; HSQC (500 MHz, $CDCl_3$) H3Me−C3Me, H1ax−C1, H1eq−C1, H2ax−C2, H2eq−C2, H3−C3, H5−C5, H6−C6, H7−C7, H8−C8, H9−C9, H10−C10. Anal. Calcd for $C_{30}H_{28}$: C, 92.74; H, 7.26. Found: C, 92.67; H, 7.26.

Enantioresolution of (±)-*cis*-1,2,3,4-Tetrahydro-3-methyl-4-phenanthrenol (11) as the Chiral Phthalic Acid Ester. A mixture of racemic *cis*-alcohol (±)-**11** (205 mg, 0.97 mmol), chiral phthalic acid amide (−)-**13** (526 mg, 1.46 mmol), 1,3-dicyclohexylcarbodiimide (DCC, 299 mg, 1.46 mmol), and 4-(dimethylamino)pyridine (DMAP, 18 mg, 0.15 mmol) in CH_2Cl_2 (10 mL) was refluxed for 9 h. After insoluble material was removed by short column chromatography on silica gel (hexane/EtOAc 1:1), the crude product was subjected to column chromatography on silica gel (hexane/EtOAc 3:1). The diastereomeric mixture obtained was separated by HPLC on silica gel (hexane/EtOAc 7:1): separation factor α = 1.10; resolution factor R_s = 1.29. The first-eluted ester **15a** was recrystallized from MeOH to give colorless needles (238 mg, 44%): mp 176−179 °C; $[\alpha]_D$ +67.0° (*c* 0.49, $CHCl_3$); TLC (silica gel, hexane/EtOAc 3:1) R_f 0.35; IR (KBr) ν_{max} 2957, 2878, 1720, 1684, 1601, 1579, 1514, 1462, 1317, 1304, 1259, 1168, 1137, 894, 772 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.92 (3 H, s), 1.14 (3 H, d, J = 6.1 Hz), 1.22−1.30 (2 H, m), 1.26 (3 H, s), 1.70−1.90 (4 H, m), 1.95−2.20 (2 H, m), 2.48 (1 H, m), 2.65 (1 H, m), 3.01−3.20 (4 H, m), 3.41 (1 H, br s), 6.98 (1 H, br s), 7.29 (1 H, d, J = 8.4 Hz), 7.35 (1 H, d, J = 7.4 Hz), 7.39−7.55 (4 H, m), 7.75 (2 H, d, J = 8.2 Hz), 8.08 (1 H, d, J = 7.7 Hz), 8.13 (1 H, d, J = 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.0, 20.0, 21.2, 25.2, 26.3, 30.6, 32.6, 34.8, 38.0, 44.9, 47.5, 48.0, 52.4, 65.2, 70.3, 123.9, 125.2, 126.9, 127.5, 127.9, 128.2, 128.7, 129.0, 129.3, 129.9, 130.5, 131.8, 132.1, 132.5, 135.5, 136.5, 164.6, 167.2. Anal. Calcd for $C_{33}H_{35}NO_5S$: C, 71.07; H, 6.33; N, 2.51; S, 5.75. Found. C, 71.31; H, 6.34; N, 2.73; S, 5.75.

The second-eluted ester **15b** was obtained as amorphous solid (263 mg, 49%): $[\alpha]_D$ −188.3° (*c* 0.99, $CHCl_3$); TLC (silica gel, hexane/EtOAc 3:1) R_f 0.34; IR (KBr) ν_{max} 2962, 2880, 1718, 1683, 1600, 1579, 1512, 1455, 1373, 1300, 1263, 1169, 1138, 891, 751 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.93 (3 H, s), 1.17 (3 H, d, J = 6.8 Hz), 1.22 (3 H, s), 1.23−1.35 (2 H, m), 1.70−1.85 (4 H, m), 2.02−2.15 (2 H, m), 2.33 (1 H, br s), 2.98−3.14 (3 H, m), 3.15−3.40 (2 H, m), 3.57 (1 H, br s), 6.93 (1 H, br s), 7.28 (1 H, d, J = 8.3 Hz), 7.37−7.53 (5 H, m), 7.75−7.79 (2 H, m), 7.89 (1 H, br s), 8.08 (1 H, d, J = 8.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.8, 19.8, 21.0, 25.1, 26.3, 30.6, 32.7, 34.6, 37.7, 44.7, 47.5, 48.1, 52.8, 65.2, 70.4, 123.2, 125.1, 127.0, 127.6, 128.1, 128.77, 128.82, 130.0, 131.6, 132.0, 132.5, 135.6, 136.5, 164.8, 167.4. Anal. Calcd for $C_{33}H_{35}NO_5S$: C, 71.07; H, 6.33; N, 2.51; S, 5.75. Found. C, 71.02; H, 6.50; N, 2.67; S, 5.46.

(3*R*,4*R*)-(+)-1,2,3,4-Tetrahydro-3-methyl-4-phenanthrenol (11). To a mixture of $LiAlH_4$ (50 mg, 1.35 mmol) and dry tetrahydrofuran (THF, 2 mL) cooled at 0 °C was added dropwise a solution of chiral phthalic acid amide ester **15a** (150 mg, 0.27 mmol) in THF (5 mL), and the reaction mixture was stirred at room temperature for 1 h. The reaction was quenched with a minimum amount of aqueous NH_4Cl, and the supernatant organic layer was filtered and evaporated to dryness. The crude product was purified by HPLC on silica gel (hexane/EtOAc 10:1) to yield optically pure *cis*-alcohol (+)-**11** (52 mg, 91%) as colorless silky needles: mp 119−120 °C (MeOH); $[\alpha]_D$ +26.2° (*c* 1.09, $CHCl_3$). Anal. Calcd for $C_{15}H_{16}O$: C, 84.87; H, 7.60. Found. C, 85.09; H, 7.66.

(3*S*,4*S*)-(−)-*cis*-Alcohol 11. Chiral phthalic acid amide ester **15b** (70 mg, 0.13 mmol) in THF (3 mL) was reduced with $LiAlH_4$ (24 mg, 0.63 mmol) to yield optically pure *cis*-alcohol (−)-**11** (24 mg, 90%) as colorless silky needles: mp 120 °C (MeOH); $[\alpha]_D$ −26.5° (*c* 1.01, $CHCl_3$). Anal. Calcd for $C_{15}H_{16}O$: C, 84.87; H, 7.60. Found. C, 84.77; H, 7.59.

Enantioresolution of (±)-*cis*-Alcohol 11 as the Chiral Dichlorophthalic Acid Ester. A mixture of racemic *cis*-alcohol (±)-**11** (101 mg, 0.47 mmol), chiral dichlorophthalic acid amide **14** (510 mg, 1.18 mmol), DCC (243 mg, 1.18 mmol), and DMAP (14 mg, 0.12 mmol) in CH_2Cl_2 (5 mL) was refluxed for 9 h. After insoluble material was removed by short column chromatography on silica gel (hexane/EtOAc 1:1), the crude product was subjected to column chromatography on silica gel (hexane/EtOAc 5:1). The diastereomeric mixture obtained was separated by HPLC on silica gel (hexane/EtOAc 7:1): separation factor α = 1.18; resolution factor R_s = 1.31. The first-eluted ester **16a** was recrystallized from MeOH to give colorless silky needles (139 mg, 47%): mp 204 °C; $[\alpha]_D$ +55.1° (*c* 0.18, $CHCl_3$); TLC (silica gel, hexane/EtOAc 4:1) R_f 0.39; IR (KBr) ν_{max} 2960, 2880, 1721, 1690, 1590, 1558, 1456, 1340, 1300, 1239, 1142, 1062, 879, 761 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.93 (3 H, s), 1.12 (3 H, d, J = 6.6 Hz), 1.22−1.30 (2 H, m), 1.26 (3 H, s), 1.70−1.78 (2 H, m), 1.81−1.90 (2 H, m), 1.99−2.17 (3 H, m), 2.48 (1 H, br d, J = 12.6 Hz), 2.62 (1 H, br s), 3.01−3.22 (4 H, m), 3.35 (1 H, br s), 6.95 (1 H, br d, J = 2.2 Hz), 7.30 (1 H, d, J = 8.6 Hz), 7.40 (1 H, s), 7.42 (1 H, br t, J = 7.1 Hz), 7.50 (1 H, ddd, J = 8.4, 7.1, 1.3 Hz), 7.77 (2 H, d, J = 8.4 Hz), 8.04 (1 H, br d, J = 8.4 Hz), 8.12 (1 H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.0, 20.0, 21.2, 25.2, 26.3, 30.6, 32.7, 34.8, 37.8, 44.9, 47.5, 48.2, 52.4, 65.3, 71.2, 123.7, 125.4, 127.0, 127.5, 127.97, 128.04, 128.8, 129.3, 130.6, 132.1, 132.3, 132.4, 134.5, 134.7, 136.6, 136.7, 163.0, 164.7. Anal. Calcd for $C_{33}H_{33}Cl_2NO_5S$: C, 63.26; H, 5.31; Cl, 11.32; N, 2.24; S, 5.12. Found. C, 63.07; H, 5.35; Cl, 11.49; N, 2.15; S, 5.37.

The second-eluted ester **16b** was recrystallized from EtOAc giving colorless prisms (142 mg, 48%): mp 203 °C; $[\alpha]_D$ −96.4° (*c* 1.76, $CHCl_3$); TLC (silica gel, hexane/EtOAc 4:1) R_f 0.37; IR (KBr) ν_{max} 2959, 2888, 1717, 1694, 1587, 1554, 1453, 1346, 1290, 1251, 1142, 1079, 868, 757 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.96 (3 H, s), 1.14 (3 H, d, J = 7.0 Hz), 1.22 (3 H, s), 1.23−1.40 (2 H, m), 1.75 (1 H, m), 1.90−2.05 (4 H, m), 2.13 (1 H, m), 2.40 (1 H, br s), 3.00−3.13 (3 H, m), 3.30−3.49 (2 H, m), 3.66 (1 H, br s), 6.90 (1 H, br s), 7.29 (1 H, d, J = 8.4 Hz), 7.42 (1 H, br t, J = 7.1 Hz), 7.47 (1 H, br s), 7.49 (1 H, br t, J = 7.1 Hz), 7.77−7.81 (2 H, m), 7.90 (1 H, br s), 7.99 (1 H, d, J = 8.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.9, 19.9, 21.1, 25.1, 26.4, 30.6, 32.9, 34.6, 37.7, 44.7, 47.7, 48.3, 53.0, 65.4, 71.2, 122.9, 125.3, 127.2, 127.6, 128.3, 128.6, 129.1, 130.9, 131.9, 132.2, 132.4, 134.6, 134.9, 163.1, 165.0. Anal. Calcd for $C_{33}H_{33}Cl_2NO_5S$: C, 63.26; H, 5.31; Cl, 11.32; N, 2.24; S, 5.12. Found. C, 63.48; H, 5.27; Cl, 11.38; N, 2.18; S, 4.98.

(3*R*,4*R*)-(+)-*cis*-Alcohol 11 Derived from Ester 16a. Chiral dichlorophthalic acid amide ester **16a** (2.1 g, 3.35 mmol) in THF (70 mL) was reduced with $LiAlH_4$ (382 mg, 10.1 mmol) to yield optically pure *cis*-alcohol (+)-**11** (640 mg, 90%) as colorless silky needles, which were identical with (+)-*cis*-alcohol obtained from ester **15a**.

(3*S*,4*S*)-(−)-*cis*-Alcohol 11 Derived from Ester 16b. Chiral dichlorophthalic acid amide ester **16b** was similarly reduced with $LiAlH_4$ to yield optically pure *cis*-alcohol (−)-**11**, which was identical with *cis*-alcohol (−)-**11** obtained from ester **15b**.

(3*R*)-(−)-2,3-Dihydro-3-methyl-4(1*H*)-phenanthrenone (10). To a solution of *cis*-alcohol (3*R*,4*R*)-(+)-**11** (80 mg, 0.38 mmol) in CH_2Cl_2 (3 mL) was added 4A molecular sieves (200 mg) and pyridinium chlorochromate (PCC, 244 mg, 1.13 mmol), and the reaction mixture was stirred at room temperature for 40 min. After the dichloromethane was removed under reduced pressure, the residue was subjected to a short column chromatography on silica gel (diethyl ether). The crude product was purified by HPLC on silica gel (hexane/EtOAc 20:1) to yield optically pure methyl ketone **10** (76 mg, 95%) as colorless oil: $[\alpha]_D$ −2.9° (*c* 1.27, $CHCl_3$).

[CD(−)237.2]-(3*R*,3′*R*)-(*P*,*P*)-(*E*)-(−)-Dimethyl Olefin 3. Optically pure methyl ketone (3*R*)-(−)-**10** (600 mg, 2.85 mmol) was subjected to the McMurry reaction with low-valent titanium made from $TiCl_3$ (1.32 mg, 8.56 mmol) and $LiAlH_4$ (160 mg, 4.22 mmol) as for the racemic methyl ketone (±)-**10**. The crude product was purified by HPLC on silica gel (hexane) and further purified by HPLC (ODS, MeOH) to afford chiral *trans*-dimethyl olefin **3** (28 mg, 5%), which was recrystallized from MeOH giving colorless prisms: mp 240 °C (sublimed); IR (KBr) ν_{max} 3050, 2972, 2929, 2869, 1506, 1455, 1426, 1373, 1212, 1032, 952, 869, 812, 759, 720 cm^{-1}; ^1H and ^{13}C NMR spectra were identical with those of racemate (±)-**3**; $[\alpha]_D$ −446.2° (*c* 0.22, $CHCl_3$); CD and UV spectra, see Table 3 and Figure 6; high-resolution mass spectrum (HRMS), calcd for $C_{30}H_{28}$ 388.2190, found: 388.2188.

(3*R,3′*R**)-(*P**,*P**)-(*Z*)-(±)-1,1′,2,2′,3,3′,4,4′-Octahydro-3,3′-dimethyl-4,4′-biphenanthrylidene (4).** A solution of *trans*-dimethyl olefin (±)-(3*R**,3′*R**)-(*P**,*P**)-(*E*)-**3** (38.0 mg, 0.098 mmol) in acetone-d_6 (10 mL) was irradiated by a high-pressure mercury lamp using a Pyrex glass filter for 5 h, during which time the photoreaction was monitored by ^1H NMR. After the solvent was removed, the products were separated by HPLC on silica gel (hexane). *cis*-Dimethyl olefin **4** was obtained as crystals (16.3 mg, 43%), which were recrystallized from hexane affording colorless prisms: mp 169−170 °C; TLC (silica gel, hexane) R_f 0.20; IR (KBr) ν_{max} 3045, 2955, 2933, 2857, 1510, 1451, 1371, 1126, 1008, 955, 859, 805, 750 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 1.13 (3 H, d, J = 6.8 Hz, Me3ax), 1.26 (1 H, ddt, J = 12.6, 7.3, 8.3 Hz, H2ax), 2.52 (1 H, ddt, J = 12.6, 8.3, 4.2 Hz, H2eq), 2.85 (2 H, dd, J = 8.3, 4.2 Hz, H1), 3.63 (1 H, ddq, J = 8.3, 7.3, 6.8 Hz, H3eq), 6.66 (1 H, ddd, J = 8.4, 6.8, 1.4 Hz, H6), 6.84 (1 H, ddd, J = 8.1, 6.8, 1.3 Hz, H7), 6.93 (1 H, dd, J = 8.4, 1.3 Hz, H5), 7.15 (1 H, d, J = 8.2 Hz, H10), 7.20 (1 H, dd, J = 8.1, 1.4 Hz, H8), 7.22 (1 H, d, J = 8.2 Hz, H9); ^{13}C NMR (150 MHz, $CDCl_3$) δ 22.5 (Me3ax), 30.4 (C1), 31.8 (C2), 32.1 (C3), 123.3 (C7), 124.0 (C6), 124.6 (C5), 125.6 (C10), 126.3 (C9), 126.7 (C8), 130.2 (C4b), 131.7 (C8a), 134.9 (C4a), 135.7 (C4), 139.0 (C10a); $^1H-^1H$ NOESY and HMBC (600 MHz, $CDCl_3$), see tables in the Supporting Information. Anal. Calcd for $C_{30}H_{28}$: C 92.74; H 7.26. Found. C 92.47; H 7.34.

[CD(−)238.0]-(3*R*,3′*R*)-(*P*,*P*)-(*Z*)-Dimethyl Olefin (4). A solution of *trans*-dimethyl olefin [CD(−)238.0]-(3*R*,3′*R*)-(*P*,*P*)-(*E*)-(−)-**3** (1.8 mg, 0.0046 mmol) in acetone-d_6 (2 mL) was irradiated by a high-pressure mercury lamp using a Pyrex glass filter for 6 h, during which time the photoreaction was monitored by ^1H NMR. After the solvent was removed, the products were separated by HPLC on silica gel (hexane). *cis*-Dimethyl olefin [CD(−)238.0]-(3*R*,3′*R*)-(*P*,*P*)-(*Z*)-**4** was obtained as crystals (1.0 mg, 55%), which were recrystallized from hexane affording colorless prisms: mp 154−156 °C; TLC (silica gel, hexane) R_f 0.20; IR (KBr) ν_{max} 3045, 2955, 2933, 2857, 1510, 1451, 1371, 1126, 1008, 955, 859, 805, 750 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (150 MHz, $CDCl_3$) were identical with those of racemate (3*R**,3′*R**)-(*P**,*P**)-(*Z*)-(±)-**4**. CD and UV spectra (see Table 3 and Figure 8).

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Supporting Information Available: Experimental procedures for the synthesis of **10**, **11**, and **12**, as well as their spectroscopic and physical data, and NOESY and HMBC data of (*E*)-**3** and (*Z*)-**4** (4 pages). See any current masthead page for ordering and Internet access instructions.

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