Synthesis of Posticlure [(6*Z*,9*Z*,11*S*,12*S*)-11,12-Epoxyhenicosa-6,9-diene], the Female Sex Pheromone of *Orgyia postica*[‡]

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Starting from commercially available (*E*)-2-dodecenoic acid, posticlure [(6*Z*,9*Z*,11*S*,12*S*)-11,12-epoxyhenicosa-6,9-diene (**1**)], the female sex pheromone of the tussock moth (*Orgyia postica*), was synthesized in 25% overall yield (6 steps) by employing Sharpless asymmetric dihydroxylation as the key step. Its (11*R*,12*R*)-isomer as well as its racemate were also synthesized.

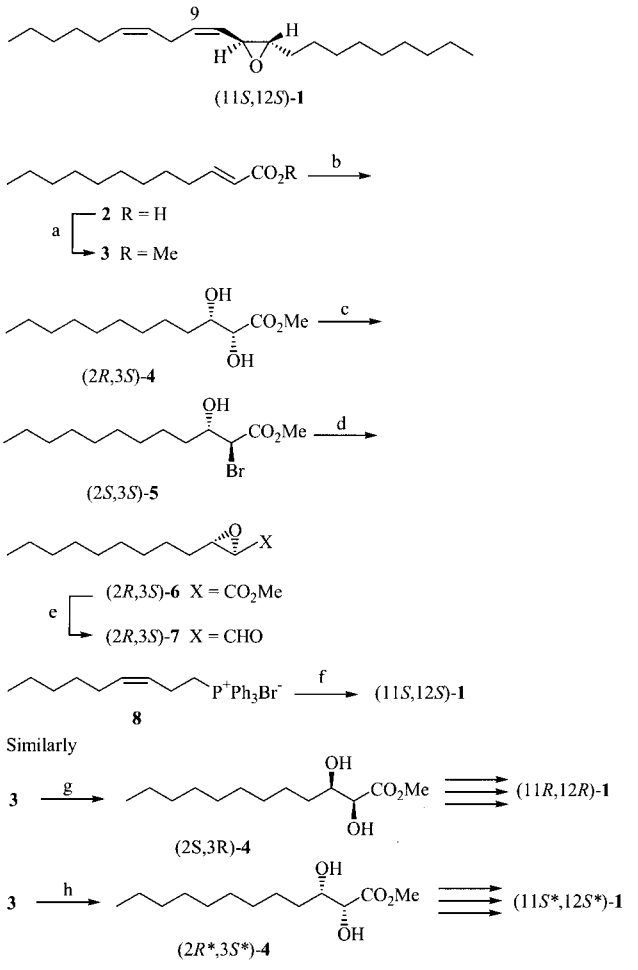
Introduction

In 2001 Wakamura et al. isolated, identified and synthesized (6*Z*,9*Z*,11*S*,12*S*)-11,12-epoxyhenicosa-6,9-diene (posticlure, **1**) as the female sex pheromone of the tussock moth *Orgyia postic*a.[1] This moth is known as a pest on mango and litchi in Okinawa, in the south-western part of Japan. Their synthesis relied upon a Sharpless asymmetric epoxidation, and afforded **1** with an enantiomeric purity of only 59% *ee*. They then purified **1** by preparative HPLC on a chiral stationary phase to give pure **1**.

We envisaged that it might be possible to prepare pure **1** without recourse to HPLC purification by designing a synthetic route in which the intermediate(s) might be purified by simple recrystallization. Adoption of Sharpless asymmetric dihydroxylation[2,3] as the key reaction allowed us to achieve the goal, securing pure **1** (99.5% *ee*) in 25% overall yield (6 steps) based on a commercially available starting material. This paper reports our synthesis of **1**.

Results and Discussion

Our synthetic plan is to dissect **1** at the 9(10)-double bond, which can be reconstructed by the *Z*-selective Bestmann version[4] of the Wittig reaction. The epoxide-containing chiral part of **1** is to be prepared by employing an asymmetric dihydroxylation reaction. Scheme 1 summarizes our synthetic results.



Scheme 1. Synthesis of the enantiomers and racemate of posticlure: reagents: (a) K_2CO_3, MeI, DMF (92%); (b) AD-mix-α®, $MeSO_2NH_2$, *t*BuOH, H_2O (71%); (c) HBr, AcOH; then MeOH (84%); (d) K_2CO_3, MeOH (71%); (e) DIBAL-H, toluene (85%); (f) NaHMDS, THF, (2*R*,3*S*)-**7** (76%); (g) AD-mix-β®, $MeSO_2NH_2$, *t*BuOH, H_2O (72%); (h) OsO_4, NMO, Me_2CO, H_2O (76%)

Commercially available (*E*)-2-dodecenoic acid (**2**) was esterified with methyl iodide and potassium carbonate to give the corresponding methyl ester **3**. Asymmetric dihy-

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droxylation[2,3] of **3** in the presence of dihydroquinine 1,4-phthalazinediyl diether [$(DHQ)_2PHAL$] was achieved by employing commercially available AD-mix-α® to give the dihydroxy ester, which could be purified by recrystallization to give pure (2*R*,3*S*)-**4**. Its enantiomeric purity was estimated to be 99.5% *ee* by HPLC analysis of the corresponding dibenzoate on Chiralcel® OD.

Conversion of the dihydroxy ester **4** to the glycidic ester **6** was performed via **5** according to Fleming and Sharpless.[5] Namely, the diol **4** was treated with hydrogen bromide in acetic acid to give the bromohydrin (2*S*,3*S*)-**5**, which could also be purified by recrystallization. Potassium carbonate in methanol converted **5** into the oily glycidic ester (2*R*,3*S*)-**6**. Reduction of **6** with diisobutylaluminum hydride (DIBAL-H) gave (2*R*,3*S*)-2,3-epoxydodecanal (**7**), which was recrystallized to give pure **7**. Finally the known phosphonium salt **8**[6] was treated with sodium hexamethyldisilazide (NaHMDS) in THF to give a phosphorane, which reacted with **7** at −100 °C to furnish (11*S*,12*S*)-posticlure (**1**). The isomeric purity at the newly generated double bond at C-9 of **1** was *Z*/*E* = 93:7 as judged by its ^{1}H NMR spectrum. HPLC analysis of **1** revealed its enantiomeric purity as 99.9% *ee*. The ^{1}H NMR and mass spectra of synthetic **1** were in good agreement with the published spectra of the natural pheromone.[1] The overall yield of (11*S*,12*S*)-posticlure (**1**) was 25% based on **2** (6 steps). By employing AD-mix-β®,[2,3] **3** was converted into (2*S*,3*R*)-**4** (99.5% *ee*), which finally yielded the unnatural enantiomer (11*R*,12*R*)-posticlure (99.8% *ee*) in 17% overall yield based on **2** (6 steps). (±)-Posticlure was also synthesized by conventional osmium tetroxide oxidation of **3**.

In conclusion, a short and efficient synthesis of the natural (11*S*,12*S*)-posticlure (**1**) as well as its opposite enantiomer (11*R*,12*R*)-**1** and its racemate (±)-**1** was developed. Purification of the intermediates **4**, **5** and **7** by recrystallization enabled us to obtain the pure enantiomers of **1**. The synthetic sample will be bioassayed in due course.

Experimental Section

Boiling points and melting points: Uncorrected values. IR: Jasco FT/IR-40. ^{1}H NMR: Jeol JNM-LA 500 (500 MHz), with TMS at δ = 0.00 or $CHCl_3$ at δ = 7.26 as an internal standard. ^{13}C NMR: Jeol JNM-LA 500 (126 MHz), with $CDCl_3$ at δ = 77.0 as an internal standard. MS: Jeol JMS-SX 102A and Hitachi M-80B. CC: Merck Kieselgel 60 Art 1.07734. TLC: 0.25 mm Merck silica gel plates (60F-254).

Methyl (*E*)-2-Dodecanoate (3): K_2CO_3 (10.5 g, 76.0 mmol) and MeI (10.7 g, 75.4 mmol) were added to a solution of (*E*)-2-dodecenoic acid (10.1 g, 50.4 mmol) in DMF (100 mL) at room temperature. The reaction mixture was stirred overnight at room temperature, then diluted with water, and extracted with Et_2O. The extract was washed with saturated aqueous Na_2SO_3, saturated aqueous $NaHCO_3$ and brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by distillation to give **3** (9.90 g, 92%) as a colorless oil, b.p. 105 °C/3 Torr. n_D^{24} = 1.4482. IR (film): $\tilde{\nu}_{max}$ = 1730 (s, C=O), 1655 cm^{-1} (m, C=C). ^{1}H NMR ($CDCl_3$): δ = 0.88 (t, *J* = 6.9 Hz, 3 H, 12-H), 1.26 (br. s, 12 H, 6-, 7-, 8-, 9-, 10-, 11-H), 1.45 (m, 2 H, 5-H), 2.19 (dt, *J* = 7.5, 7.0 Hz, 2 H, 4-H), 3.72 (s, 3 H, OMe), 5.81 (d, *J* = 15.6 Hz, 1 H, 2-H), 6.97 (dt, *J* = 15.6, 7.0 Hz, 1 H, 3-H). ^{13}C NMR (126 MHz, $CHCl_3$): δ = 14.1, 22.6, 28.0, 29.1, 29.3, 29.4, 29.5, 31.9, 32.2, 51.3, 120.8, 149.8, 167.2. $C_{13}H_{24}O_2$ (212.3): calcd. C 73.54, H 11.39; found C 73.31, H 11.27.

Methyl (2*R*,3*S*)-2,3-Dihydroxydodecanoate [(2*R*,3*S*)-4]: AD-mix-α® (26.4 g) and $MeSO_2NH_2$ (1.80 g, 18.9 mmol) were added to a solution of **3** (4.00 g, 18.9 mmol) in *tert*-butyl alcohol (30 mL) and water (30 mL) at 0 °C. The mixture was stirred overnight at 0 °C, then quenched with Na_2SO_3, diluted with water, and extracted with EtOAc. The extract was washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by chromatography (hexane/EtOAc = 3:1) to give crude (2*R*,3*S*)-**4** (4.42 g) as a colorless solid. The solid was recrystallized from hexane to yield (2*R*,3*S*)-**4** (3.31 g, 71%) as colorless needles, m.p. 43.5−44.5 °C. $[\alpha]_D^{23}$ = −15.6 (*c* = 1.02, $CHCl_3$). IR (KBr): $\tilde{\nu}_{max}$ = 3465 (s, O−H), 1730 cm^{-1} (s, C=O). ^{1}H NMR ($CDCl_3$): δ = 0.88 (t, *J* = 7.0 Hz, 3 H, 12-H), 1.26 (br. s, 14 H, 5-, 6-, 7-, 8-, 9-, 10-, 11-H), 1.60 (m, 2 H, 4-H), 1.85 (d, *J* = 9.0 Hz, 1 H, OH), 3.00 (d, *J* = 5.2 Hz, 1 H, OH), 3.83 (s, 3 H, OMe), 3.99 (ddt, *J* = 2.0, 7.2, 9.0 Hz, 1 H, 3-H), 4.11 (dd, *J* = 2.0, 5.2 Hz, 1 H, 2-H). ^{13}C NMR (126 MHz, $CHCl_3$): δ = 14.1, 22.7, 25.7, 29.3, 29.4, 29.51, 29.53, 31.9, 33.8, 52.9, 72.5, 73.0, 174.1. $C_{13}H_{26}O_4$ (246.2): calcd. C 63.38, H 10.64; found C 63.12, H 10.55.

Determination of the Enantiomeric Purity of (2*R*,3*S*)-4:The corresponding dibenzoate of (2*R*,3*S*)-**4** was analyzed by HPLC (Chiralcel OD®, 25 cm × 4.6 mm; eluent: hexane/2-propanol = 500:1; flow rate: 1.0 mL/min]: t_R = 40.7 (99.75%), 51.9 (0.25%). The enantiomeric purity of (2*R*,3*S*)-**4** was determined to be 99.5% *ee*.

Methyl (2*S*,3*R*)-2,3-Dihydroxydodecanoate [(2*S*,3*R*)-4]: To a solution of **3** (2.00 g, 9.43 mmol) in *tert*-butyl alcohol (15 mL) and water (15 mL) at 0 °C were added AD-mix-β® (13.2 g) and $MeSO_2NH_2$ (900 mg, 9.45 mmol), and the mixture was stirred overnight at 0 °C. The same workup procedure as described for the preparation of (2*R*,3*S*)-**4** gave crude (2*S*,3*R*)-**4** (2.17 g) as a colorless solid. The solid was recrystallized from hexane to yield (2*S*,3*R*)-**4** (1.67 g, 72%) as colorless needles, m.p. 43.5−44.5 °C. $[\alpha]_D^{24}$ = +15.4 (*c* = 1.07, $CHCl_3$). $C_{13}H_{26}O_4$ (246.2): calcd. C 63.38, H 10.64; found C 63.47, H 10.72. Its IR, ^{1}H NMR and ^{13}C NMR spectra were identical with those of (2*R*,3*S*)-**4.**

Determination of the Enantiomeric Purity of (2*S*,3*R*)-4:The corresponding dibenzoate of (2*S*,3*R*)-**4** was analyzed by HPLC (Chiralcel OD®, 25 cm × 4.6 mm; eluent: hexane/2-propanol = 500:1; flow rate: 1.0 mL/min]: t_R = 49.3 (0.25%), 56.0 (99.75%). The enantiomeric purity of (2*S*,3*R*)-**4** was determined to be 99.5% *ee*.

Methyl (2*S*,3*S*)-2-Bromo-3-hydroxydodecanoate [(2*S*,3*S*)-5]: Hydrogen bromide (33% in AcOH, 15 mL, 44.3 mmol) was added to (2*R*,3*S*)-**4** (3.00 g, 12.2 mmol) at room temperature, and the reaction mixture was heated at 45 °C. After 1 h of stirring, MeOH (30 mL) was added dropwise. The mixture was stirred overnight at 45 °C, and then allowed to cool to room temperature over 1 h. The mixture was quenched by slowly pouring it into ice-water, diluted with Et_2O and neutralized by addition of $NaHCO_3$. The precipitated NaOAc was filtered off and the filtrate was extracted with Et_2O. The extract was washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by chromatography (hexane/EtOAc = 10:1) to give (2*S*,3*S*)-**5** (3.18 g, 84%) as a colorless solid. A portion of it was further purified by recrystallization from hexane to afford an analytical sample as needles, m.p. 44.0−44.5 °C. $[\alpha]_D^{23}$ = −30.4 (*c* = 1.03, $CHCl_3$). IR

(KBr): $\tilde{\nu}_{max}$ = 3325 (s, O−H), 1735 cm^{-1} (s, C=O). ^1H NMR ($CDCl_3$): δ = 0.88 (t, *J* = 6.9 Hz, 3 H, 12-H), 1.22−1.42 (m, 13 H, 5-H_a, 6-, 7-, 8-, 9-, 10-, 11-H), 1.51 (m, 2 H, 4-H_a, 5-H_b), 1.81 (m, 1 H, 4-H_b), 2.58 (d, *J* = 6.4 Hz, 1 H, OH), 3.80 (s, 3 H, OMe), 4.00 (dddd, *J* = 3.0, 6.4, 7.6, 9.1 Hz, 1 H, 3-H), 4.15 (d, *J* = 7.6 Hz, 1 H, 2-H). ^{13}C NMR (126 MHz, $CHCl_3$): δ = 14.1, 22.7, 25.3, 29.28, 29.33, 29.48, 29.51, 31.9, 33.4, 47.9, 53.1, 72.5, 169.8. $C_{13}H_{25}BrO_3$ (309.2): calcd. C 50.49, H 8.15; found C 50.86, H 8.01.

Methyl (2*R*,3*R*)-2-Bromo-3-hydroxydodecanoate [(2*R*,3*R*)-5]: In the same manner as described for the preparation of (2*S*,3*S*)-**5**, (2*R*,3*S*)-**4** (3.00 g, 12.2 mmol) gave (2*R*,3*R*)-**5** (3.05 g, 81%) as a colorless solid. A portion of it was further purified by recrystallization from hexane to afford an analytical sample as needles, m.p. 44.0−44.5 °C. $[\alpha]_D^{24}$ = +30.5 (*c* = 1.23, $CHCl_3$). $C_{13}H_{25}BrO_3$ (309.2): calcd. C 50.49, H 8.15; found C 50.61, H 8.16. Its IR, ^1H NMR and ^{13}C NMR spectra were identical with those of (2*S*,3*S*)-**5**.

Methyl (2*R*,3*S*)-2,3-Epoxydodecanoate [(2*R*,3*S*)-6]: K_2CO_3 (3.00 g, 21.7 mmol) was added to a solution of (2*S*,3*S*)-**5** (3.04 g, 9.83 mmol) in MeOH (10 mL) at room temperature. After stirring for 2 h, the reaction mixture was diluted with water and extracted with Et_2O. The extract was washed with water and brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by chromatography (hexane/EtOAc = 30:1) to give (2*R*,3*S*)-**6** (1.60 g, 71%) as a colorless oil, n_D^{24} = 1.4722. $[\alpha]_D^{24}$ = −23.0 (*c* = 1.03, $CHCl_3$). IR (film): $\tilde{\nu}_{max}$ = 1760 cm^{-1} (s, C=O). ^1H NMR ($CDCl_3$): δ = 0.88 (t, *J* = 7.0 Hz, 3 H, 12-H), 1.26 (br. s, 12 H, 6-, 7-, 8-, 9-, 10-, 11-H), 1.45 (m, 2 H, 5-H), 1.60 (m, 2 H, 4-H), 3.16 (ddd, *J* = 1.8, 5.2, 6.4 Hz, 1 H, 3-H), 3.22 (d, *J* = 1.8 Hz, 1 H, 2-H), 3.78 (s, 3 H, OMe). ^{13}C NMR (126 MHz, $CHCl_3$): δ = 14.1, 22.6, 25.7, 29.21, 29.24, 29.42, 31.4, 31.8, 52.4, 52.9, 58.6, 169.8. $C_{13}H_{24}O_3$ (228.3): calcd. C 68.38, H 10.59; found C 68.17, H 10.53.

Methyl (2*S*,3*R*)-2,3-Epoxydodecanoate [(2*S*,3*R*)-6]: In the same manner as described for the preparation of (2*R*,3*S*)-**6**, (2*R*,3*R*)-**5** (2.62 g, 8.48 mmol) gave (2*S*,3*R*)-**6** (1.39 g, 72%) as a colorless oil, n_D^{24} = 1.4721. $[\alpha]_D^{24}$ = +23.0 (*c* = 1.07, $CHCl_3$). $C_{13}H_{24}O_3$ (228.3): calcd. C 68.38, H 10.59; found C 68.10, H 10.69. Its IR, ^1H NMR and ^{13}C NMR spectra were identical with those of (2*R*,3*S*)-**6**.

(2*R*,3*S*)-2,3-Epoxydodecanal [(2*R*,3*S*)-7]: To a stirred and cooled solution of (2*R*,3*S*)-**6** (1.15 g, 5.04 mmol) in dry toluene (10 mL), DIBAL-H (1.01 M in toluene; 5.50 mL, 5.45 mmol) was added dropwise at −78 °C under argon. After stirring for 2 h at −78 °C, the mixture was quenched with saturated aqueous Rochelle's salt and then diethyl ether was added. The resulting slurry was stirred at room temperature until two clear layers separated. The layers were separated, and the aqueous layer was extracted with Et_2O. The combined organic layer was washed with water and brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by chromatography (hexane/EtOAc = 30:1) to give (2*R*,3*S*)-**7** (850 mg, 85%) as a colorless solid. A portion of it was further purified by recrystallization from hexane to afford an analytical sample as needles, m.p. 34.0−35.0 °C. $[\alpha]_D^{24}$ = +90.0 (*c* = 1.01, $CHCl_3$). IR (KBr): $\tilde{\nu}_{max}$ = 1738 cm^{-1} (s, C=O). ^1H NMR ($CDCl_3$): δ = 0.88 (t, *J* = 7.0 Hz, 3 H, 12-H), 1.27 (br. s, 12 H, 6-, 7-, 8-, 9-, 10-, 11-H), 1.47 (m, 2 H, 5-H), 1.65 (m, 2 H, 4-H), 3.14 (dd, *J* = 1.6, 6.1 Hz, 1 H, 2-H), 3.23 (ddd, *J* = 1.6, 5.2, 6.0 Hz, 1 H, 3-H), 9.01 (d, *J* = 6.1 Hz, 1 H, CHO). ^{13}C NMR (126 MHz, $CHCl_3$): δ = 14.1, 22.6, 25.8, 29.21, 29.24, 29.4, 31.2, 31.8, 56.8, 59.2, 198.5. HRMS (EI) $[M^+]$ ($C_{12}H_{22}O_2$): calcd. 198.1620; found 198.1619

(2*S*,3*R*)-2,3-Epoxydodecanal [(2*S*,3*R*)-7]: In the same manner as described for the preparation of (2*R*,3*S*)-**7**, (2*S*,3*R*)-**6** (1.08 g, 4.74 mmol) gave (2*S*,3*R*)-**7** (645 mg, 69%) as a colorless solid. A portion of it was further purified by recrystallization from hexane to afford an analytical sample as needles, m.p. 34.0−35.0 °C. $[\alpha]_D^{24}$ = −89.3 (*c* = 1.03, $CHCl_3$). $C_{12}H_{22}O_2$ (198.2): calcd. C 72.68, H 11.18; found C 72.65, H 11.33. Its IR, ^1H NMR and ^{13}C NMR spectra were identical with those of (2*R*,3*S*)-**7**.

(6*Z*,9*Z*,11*S*,12*S*)-11,12-Epoxyhenicosa-6,9-diene (posticlure) [(11*S*,12*S*)-1]: NaHMDS (1 M in THF, 0.75 mL, 0.75 mmol) was added to a suspension of **8** (370 mg, 0.792 mmol) in dry THF (5 mL) and dry toluene (5 mL) at −30 °C under argon. After stirring for 2 h at room temperature, the orange solution was cooled to −100 °C and a solution of (2*R*,3*S*)-**7** (100 mg, 0.505 mmol) in dry THF (3 mL) was added dropwise. The mixture was allowed to warm to room temperature overnight, and the reaction was quenched with saturated aqueous NH_4Cl. The aqueous layer was extracted with Et_2O, and the combined organic layer was washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by chromatography (hexane/EtOAc = 100:1) to give (11*S*,12*S*)-**1** (118 mg, 76%) as a colorless oil, n_D^{24} = 1.4638. $[\alpha]_D^{24}$ = −10.8 (*c* = 1.07, $CHCl_3$). IR (film): $\tilde{\nu}_{max}$ = 3010 (m, C−O−C), 1720 cm^{-1} (w, C=C). ^1H NMR ($CDCl_3$): δ = 0.88 and 0.89 (each t, *J* = 7.0 Hz, 3 H, 1, 21-H), 1.27 (m, 20 H, 2-, 3-, 4-, 14-, 15-, 16-, 17-, 18-, 19-, 20-H), 1.46 (m, 2 H, 4-H), 1.46 (m, 2 H, 13-H), 2.06 (dt, *J* = 7.2, 7.2 Hz, 2 H, 5-H), 2.82 (dt, *J* = 2.2, 6.8 Hz, 1 H, 12-H), 2.96 (br. dd, *J* = 7.3, 7.3 Hz, 2 H, 8-H), 3.36 (dd, *J* = 2.2, 8.9 Hz, 1 H, 11-H), 5.07 (ddt, *J* = 1.5, 8.9, 10.9 Hz, 1 H, 10-H), 5.36 (dtt, *J* = 1.5, 7.2, 10.7 Hz, 1 H, 7-H), 5.44 (dtt, *J* = 1.5, 7.2, 10.7 Hz, 1 H, 6-H), 5.66 (dt, *J* = 7.3, 10.9 Hz, 1 H, 9-H). ^{13}C NMR (126 MHz, $CHCl_3$): δ = 14.04, 14.09, 22.5, 22.7, 25.9, 26.1, 27.2, 29.23, 29.28, 29.45, 29.51, 29.55, 31.5, 31.9, 32.1, 54.3, 60.2, 126.8, 127.3, 131.1, 134.3. EI MS (70 eV): *m*/*z* (%) = 306 (8) $[M^+]$, 288 (2), 277 (3), 249 (2), 235 (5), 209 (6), 195 (35), 179 (10), 155 (97), 136 (20), 109 (17), 95 (44), 85 (47), 79 (57), 71 (69), 57 (70), 43 (100), 29 (45). HRMS (EI) $[M^+]$ ($C_{21}H_{38}O$): calcd. 306.2923; found 306.2909.[7]

Determination of the Enantiomeric Purity of (11*S*,12*S*)-1: This was analyzed by HPLC [Chiralcel OD® (25 cm × 4.6 mm) × 2; eluent: hexane/2-propanol = 1000:1; flow rate: 0.5 mL/min]: t_R = 26.4 (99.94%), 29.5 (0.06%). The enantiomeric purity of (11*S*,12*S*)-**1** was determined to be 99.9% *ee*.

(6*Z*,9*Z*,11*R*,12*R*)-11,12-Epoxyhenicosa-6,9-diene [(11*R*,12*R*)-1]: In the same manner as described for the preparation of (11*S*,12*S*)-**1**, (2*S*,3*R*)-**7** (100 mg, 0.505 mmol) gave (11*R*,12*R*)-**1** (101 mg, 65%) as a colorless oil, n_D^{24} = 1.4639. $[\alpha]_D^{24}$ = +10.9 (*c* = 1.09, $CHCl_3$). HRMS (EI) $[M^+]$ ($C_{21}H_{38}O$): calcd. 306.2923; found 306.2915. Its IR, ^1H NMR and ^{13}C NMR spectra were identical with those of (11*S*,12*S*)-**1**.

Determination of the Enantiomeric Purity of (11*R*,12*R*)-1: This was analyzed by HPLC [Chiralcel OD® (25 cm × 4.6 mm) × 2; eluent: hexane/2-propanol = 1000:1; flow rate: 0.5 mL/min]: t_R = 26.2 (0.09%), 28.4 (99.91%). The enantiomeric purity of (11*R*,12*R*)-**1** was determined to be 99.8% *ee*.

(6*Z*,9*Z*,11*R*,12*R*)-(±)-11,12-Epoxyhenicosa-6,9-diene [(±)-1]: In the same manner as above, (±)-**1** (92 mg) was prepared by employing OsO_4 and NMO for the dihydroxylation,. n_D^{24} = 1.4639. HRMS (EI) $[M^+]$ ($C_{21}H_{38}O$): calcd. 306.2923; found 306.2916. Its IR, ^1H NMR and ^{13}C NMR spectra were identical with those of (11*S*,12*S*)-**1**.

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[7] Supporting information for this article (IR, ^{1}H NMR, ^{13}C NMR, and MS of **1**) is available (see footnote on page one).

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