Biosci. Biotechnol. Biochem., **69** (5), 1007–1013, 2005

New Synthesis of the (3*Z*,6*Z*,9*S*,10*R*)-Isomers of 9,10-Epoxy-3,6-henicosadiene and 9,10-Epoxy-1,3,6-henicosatriene, Pheromone Components of the Female Fall Webworm Moth, *Hyphantria cunea**

Akira NAKANISHI[1] and Kenji MORI[2,†]

[1]*Department of Applied Biological Chemistry, The University of Tokyo, Yayoi 1-1-1, Bunkyo-ku, Tokyo 113-8657, Japan*

[2]*Insect Pheromone and Traps Division, Fuji Flavor Co., Ltd., Midorigaoka 3-5-8, Hamura-City, Tokyo 205-8503, Japan*

Received January 18, 2005; Accepted February 14, 2005

(3*Z*,6*Z*,9*S*,10*R*)-9,10-Epoxy-3,6-henicosadiene (1) and (3*Z*,6*Z*,9*S*,10*R*)-9,10-epoxy-1,3,6-henicosatriene (5), pheromone components of the female fall webworm moth (*Hyphantria cunea* Drury), were synthesized by starting from (2*S*,3*R*)-2,3-epoxy-4-*t*-butyldimethylsilyloxy-1-butanol (8). Epoxide 8 was prepared by employing lipase-catalyzed asymmetric acetylation of (±)-8 as the key optical resolution step.

Key words: epoxide; *Hyphantria cunea*; lipase; pheromone; skipped diene

The fall webworm moth (*Hyphantria cunea*) is a troublesome pest in Japan, where its larva attacks fruit trees and ornamental trees such as grape, peach, pear, apple, cherry, poplar and platan. Its female-produced pheromone was first studied by Roelofs and his coworkers, who identified three pheromone components **1**–**3**.[1] A blend of **1**–**3** (Fig. 1), however, was biologically inactive when tested against *H. cunea*. Two additional pheromone components **4** and **5** were subsequently identified by Tóth *et al.*, and a mixture of **1**–**5** attracted *H. cunea* males.[2] Later, Senda *et al.* found that a blend of **1**, **3** and **5** could attract *H. cunea*, and this blend has been developed as a commercial lure for monitoring the population of *H. cunea*.[3]

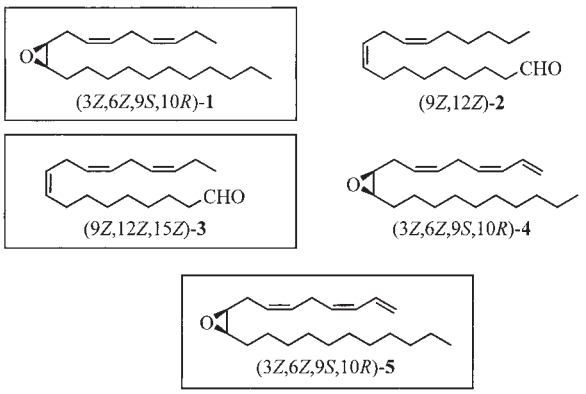


Fig. 1. Structures of Components **1**–**5** of the Female Sex Pheromone of the Fall Webworm Moth, *Hyphantria cunea*.
A mixture of **1**,**3** and **5** attracted the moth.

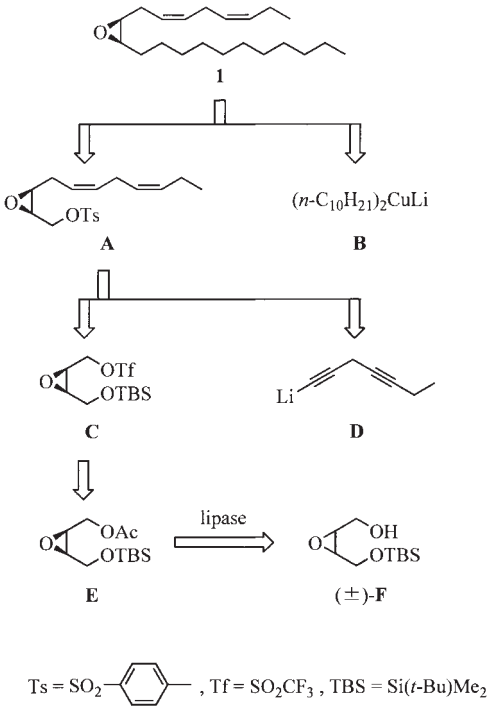
The synthesis of (3*Z*,6*Z*,9*S*,10*R*)-9,10-epoxy-3,6-henicosadiene (**1**) was first reported by Mori and Ebata in 1986 by employing Sharpless asymmetric epoxidation as the key step.[4] Similarly, by employing the same reaction, (3*Z*,6*Z*,9*S*,10*R*)-9,10-epoxy-1,3,6-henicosatriene (**5**) and its lower homolog (**4**) were synthesized in 1989.[5] In these previous syntheses, the overall yield of **1** was 7% (10 steps),[4] and that of **5** was 1.5% (12 steps).[5] Although there have been four additional syntheses of **1** or **5**, none of them was efficient enough to furnish **1** and **5** in suitable quantity.[6–9] We therefore undertook the development of a more efficient route to secure **1** and **5**, this paper describing a new and more practical synthesis of **1** and **5**. It should be added that **3** is readily available from linolenic acid [(9*Z*,12*Z*,15*Z*)-9,12,15-octadecatrienoic acid].

Results and Discussion

Our key idea in exploiting the new synthesis of **1** is to adopt epoxy-containing building block **E** (Scheme 1) as the pivotal intermediate which can be prepared from (±)-**F** by lipase-catalyzed asymmetric acetylation. Such a chiral and non-racemic epoxy building block was first utilized in pheromone synthesis by Brevet and Mori in 1992,[10] and then extensively employed in our subsequent pheromone syntheses.[11] In 2003, Muto and Mori employed a *t*-butyldiphenylsilyl (TBDPS) version [TBDPS instead of *t*-butyldimethylsilyl (TBS)] of **E** in the syntheses of leucomalure[12] and other epoxy pheromones.[13]

* Pheromone Synthesis, Part 230. For Part 229, see Mori, K., *Eur. J. Org. Chem.*, in press.

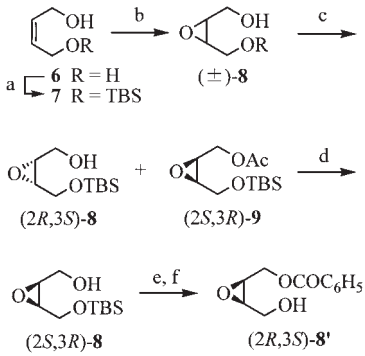
† To whom correspondence should be addressed. Fax: +81-42-555-7920; E-mail: kjk-mori@arion.ocn.ne.jp



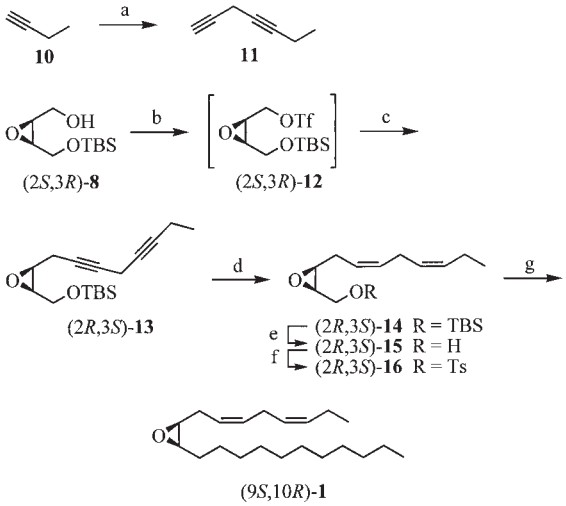
Scheme 1. Retrosynthetic Analysis of **1**.

Scheme 1 shows the retrosynthetic analysis of (9*S*,10*R*)-**1**. Epoxide **1** can be prepared by coupling epoxy tosylate **A** with lithium di(*n*-decyl)cuprate (**B**). The carbon skeleton of **A** is to be constructed by alkylating **D** with triflate **C**,[12] triflate **C** being derived from **E**.

The preparation of epoxy building block (2*S*,3*R*)-**8** is summarized in Scheme 2. Since TBS chloride is much less expensive than TBDPS chloride, (*Z*)-2-butene-1,4-diol (**6**) was converted to mono TBS ether **7**. Epoxidation of **7** with *m*-chloroperbenzoic acid (MCPBA) furnished (±)-**8** in an 82% yield. Lipase PS-C (Amano) was chosen as the catalyst for the asymmetric acetylation of (±)-**8** on the basis of our previous screening experiment.[12] Treatment of (±)-**8** with vinyl acetate in diethyl ether in the presence of lipase PS-C afforded (2*R*,3*S*)-**8** [47% yield based on (±)-**8**] and (2*S*,3*R*)-**9** (49% yield). These stereochemical assignments were made in analogy with those for the corresponding TBDPS-protected compounds,[12] and confirmed by subsequent conversion of **9** to (9*S*,10*R*)-**1** and **5**. Their enantiomeric purity, as determined by an HPLC analysis of the derived 4-benzoyloxy-2,3-epoxy-1-butanol (**8′**), however, was not perfect: 81% e.e. for (2*R*,3*S*)-**8** and 84–87% e.e. for (2*S*,3*R*)-**9**. In contrast, when we employed the TBDPS protective group, each product was almost enantiomerically pure (>99% e.e.).[12,13] The less bulky nature of the TBS group might have resulted in less satisfactory chiral recognition by lipase PS-C. Fortunately, however, final products **1** and **5** with 84–87% e.e. had been found to be as effective attractants as those with >99% e.e. according to the results of field



Scheme 2. Preparation of Epoxy Building Block (2*S*,3*R*)-**8**.
Reagents: (a) 1.0 eq NaH, TBSCl, THF. (b) MCPBA, CH_2Cl_2 (2 steps, 81%). (c) lipase PS-C, CH_2=CHOAc, Et_2O, room temp., 3 h [47% of (2*R*,3*S*)-**8** (81% e.e.) and 49% of (2*S*,3*R*)-**9** (84–87% e.e.)]. (d) K_2CO_3, MeOH (quant.). (e) C_6H_5COCl, C_5H_5N. (f) TBAF, THF (2 steps, 96%).



Scheme 3. Synthesis of (9*S*,10*R*)-**1**.
Reagents: (a) EtMgBr, Cu_2Cl_2, HC≡CCH_2Br, THF (55%). (b) 1.0 eq *n*-BuLi, 1.0 eq Tf_2O, THF/HMPA, −78 °C. (c) 1.2 eq *n*-BuLi, 2.0 eq **11**, THF, −78 °C (2 steps, 67%). (d) H_2, Lindlar Pd-$CaCO_3$-Pb^{2+}, cyclohexane (77%). (e) TBAF, THF (96%). (f) TsCl, C_5H_5N. (g) (*n*-$C_{10}H_{21})_2$CuLi, Et_2O (2 steps, 62%).

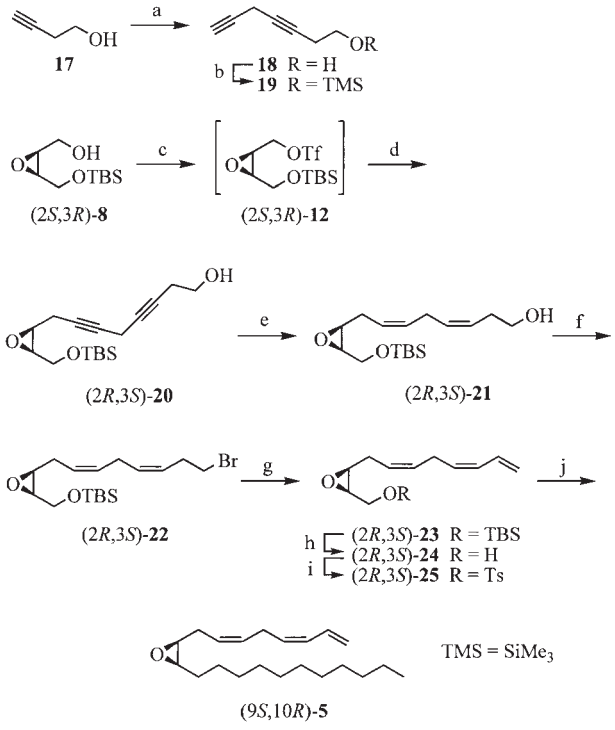
tests by scientists at Nitto Denko Co. (Dr. S. Senda, personal communication to K.M.). Accordingly, we proceeded to the next step, and (2*S*,3*R*)-**9** of 84–87% e.e. was converted to (2*S*,3*R*)-**8** by a treatment with potassium carbonate in methanol. The overall yield of (2*S*,3*R*)-**8** was 40% based on **6** (4 steps).

Scheme 3 summarizes the synthesis of one of the target molecules, (9*S*,10*R*)-**1**. The side-chain diene part of **1** was prepared from 1-butyne (**10**). The Grignard reagent prepared from **10** and ethylmagnesium bromide was alkylated with propargyl bromide in the presence of copper(I) chloride to give 1,4-heptadiyne (**11**). Lithiation of **11** was best carried out in THF at −78 °C by treating an excess (2.0 eq.) of **11** with *n*-butyllithium (1.2 eq.) to give the corresponding lithium alkynide.

Even a small excess of *n*-butyllithium abstracted a proton at C-3 of **11**, and gave a less clean product. The alkynide was alkylated with triflate (2*S*,3*R*)-**12** that had been prepared from (2*S*,3*R*)-**8**. As reported previously, this alkylation was successful only when triflate **12** was employed,[12] neither the corresponding tosylate nor iodide giving an acceptable result.[12] Resulting epoxy diyne (2*R*,3*S*)-**13** was obtained in a 67% yield, this being semi-hydrogenated over Lindlar's palladium catalyst to give epoxy diene (2*R*,3*S*)-**14**. The TBS protective group of **14** was then removed by a treatment with tetra(*n*-butyl)ammonium fluoride (TBAF), and resulting alcohol (2*R*,3*S*)-**15** was tosylated to give tosylate (2*R*,3*S*)-**16**. Finally, tosylate **16** was treated with lithium di(*n*-decyl)cuprate to give (3*Z*,6*Z*,9*S*,10*R*)-9,10-epoxy-3,6-henicosadiene (**1**). The overall yield of **1** was 12% based on **6** (10 steps), this being considerably better than the previous result (7%).[4]

The synthesis of (9*S*,10*R*)-**5** is shown in Scheme 4. The side-chain triene part of **5** was prepared from 3-butyn-1-ol (**17**), postponing the introduction of the terminal olefin to a later stage of the synthesis. The Grignard reagent prepared from **17** and 2 eq of ethylmagnesium bromide was alkylated with propargyl bromide in the presence of copper (I) chloride in the same manner as that described for the preparation of **11** to give 3,6-heptadiyn-1-ol (**18**). The hydroxy group of **18** was then protected as a trimethylsilyl (TMS) ether to give **19**, whose lithiate was alkylated with triflate **12** to afford (2*R*,3*S*)-**20**, after removing the TMS group. Semi-hydrogenation of **20** gave epoxy diene alcohol (2*R*,3*S*)-**21** which was treated with carbon tetrabromide and triphenylphosphine to furnish bromide (2*R*,3*S*)-**22**. Dehydrobromination of **22** was accomplished with potassium *t*-butoxide in the presence of 18-crown-6 to give triene (2*R*,3*S*)-**23**.[14] After removing the TBS protective group of **23**, resulting alcohol **24** was converted to corresponding tosylate (2*R*,3*S*)-**25**. Alkylation of **25** with lithium di(*n*-decyl)cuprate provided the desired product, (3*Z*,6*Z*,9*S*,10*R*)-9,10-epoxy-1,3,6-henicosatriene (**5**), in an 8.6% overall yield based on **6** (12 steps). In the case of the previous synthesis, the overall yield was 1.5% (12 steps).

In conclusion, new and more efficient synthetic routes were developed, leading to **1** and **5**. Although the present synthesis involves two low-temperature reactions (**8** → **13** or **20** and **16** → **1** or **25** → **5**) with moderate yields, this new process may be useful in synthesizing practical amounts of **1** and **5**.



Scheme 4. Synthesis of (9*S*,10*R*)-**5**.

Reagents: (a) EtMgBr, Cu_2Cl_2, HC≡CCH_2Br, THF (55%). (b) TMSCl, Et_3N, DMAP, CH_2Cl_2 (93%). (c) 1.0 eq *n*-BuLi, 1.0 eq Tf_2O, THF/HMPA, −78 °C. (d) i) 1.2 eq *n*-BuLi, 3.0 eq **19**, THF, −78 °C. ii) K_2CO_3, MeOH [3 steps, 73% (average 60%)]. (e) H_2, Lindlar Pd-$CaCO_3$-Pb^{2+}, cyclohexane, cyclohexene (83%). (f) CBr_4, PPh_3, CH_2Cl_2 (79%). (g) *t*-BuOK, 18-crown-6, hexane (77%). (h) TBAF, THF (90%). (i) TsCl, C_5H_5N. (j) (*n*-$C_{10}H_{21})_2$-CuLi, Et_2O (2 steps, 65%).

Experimental

IR data were measured with a Jasco FT/IR-410 spectrometer. ^{1}H-NMR data were measured with a Jeol JNM-EX 90A (90 MHz), Jeol JNM-AL300 (300 MHz), Jeol JNM-LA400 (400 MHz) or Jeol JNM-LA500 (500 MHz) spectrometer (TMS at $\delta_H = 0.00$ or $CHCl_3$ at $\delta_H = 7.26$ was used as the internal standard). MS data were measured with a Jeol JMS-SX102 spectrometer, and refractive index (n_D) data were measured with an Atago DMT-1 refractometer.

*(2S,3R)-1-Acetoxy-4-t-butyldimethylsilyloxy-2,3-epoxybutane [(2S,3R)-**9**].* Lipase PS-C (50 mg) was added to a solution of (±)-**8** (2.00 g, 9.23 mmol) in Et_2O (20 ml) and vinyl acetate (1.5 ml) at room temperature (20–24 °C). After stirring for 3 h at room temperature, the enzyme was filtered off, and the resulting filtrate was concentrated *in vacuo*. The residue was purified by chromatography (hexane/EtOAc, 5:1) to give (2*R*,3*S*)-**8** (985 mg, 47%) and (2*S*,3*R*)-**9** (1.22 g, 49%), both as colorless oils. (2*S*,3*R*)-**9**: $n_D^{23} = 1.4414$. $[\alpha]_D^{23} = -9.28$ ($c = 1.04$, CH_2Cl_2). IR ν_{max} (film) cm^{-1}: 1750 (s, C=O), 1470 (m, Si–O), 1370 (m, C–O), 1230 (s, C–O), 1100 (s, Si–O), 1040 (m, C–O). ^{1}H-NMR δ_H (400 MHz, $CDCl_3$): 0.07 (3H, s, Si–Me), 0.08 (3H, s, Si–Me), 0.90 (9H, s, *t*-Bu), 2.10 (3H, s, Ac), 3.19 (1H, ddd, $J = 5.4$, 4.8, 3.6 Hz, 3-H), 3.24 (1H, dt, $J = 7.4$, 3.6 Hz, 2-H), 3.77 (1H, dd, $J = 11.8$, 5.4 Hz, 4-H_a), 3.81 (1H, dd, $J = 11.8$, 4.8 Hz, 4-H_b), 4.05 (1H, dd, $J = 13.1$, 7.4 Hz, 1-H_a), 4.35 (1H, dd, $J = 13.1$, 3.6 Hz, 1-H_b). *Anal.* Found: C, 55.22; H, 9.18%. Calcd. for $C_{12}H_{24}O_4Si$: C, 55.35; H, 9.29%.

*(2S,3R)-4-t-Butyldimethylsilyloxy-2,3-epoxy-1-butanol [(2S,3R)-**8**].* K_2CO_3 (3.49 g, 25.2 mmol) was added to a solution of (2*S*,3*R*)-**9** (5.52 g, 19.4 mmol) in MeOH (40 ml) at 0 °C. The mixture was stirred for 1 h at 0 °C, quenched with saturated NH_4Cl aq., and then extracted with Et_2O. The extract was successively washed with water and brine, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by chromatography (hexane/Et_2O, 4:1) to give (2*S*,3*R*)-**8** (4.22 g, quant.) as a colorless oil. $n_D^{23} = 1.4481$. $[\alpha]_D^{23} = -11.3$ ($c = 1.01$, CH_2Cl_2) {lit.[15] $[\alpha]_D = -10.5$ ($c = 3$, CH_2Cl_2)}. IR ν_{max} (film) cm^{-1}: 3430 (br s, O–H), 1470 (m, Si–C), 1390 (m, C–O), 1360 (m, C–O), 1100 (s, Si–O), 1045 (m, C–O). ^{1}H-NMR δ_H (90 MHz, $CDCl_3$): 0.09 (6H, s, $SiMe_2$), 0.90 (9H, s, *t*-Bu), 2.13 (1H, t, $J = 6.0$ Hz, O–H), 3.15–3.27 (2H, m, 2-H, 3-H), 3.72–3.91 (4H, m, 1-H, 4-H). The IR and ^{1}H-NMR spectra were identical to those reported.[15]

*Determination of the enantiomeric purity of (2S,3R)-**8**.* Benzoyl chloride (0.083 ml, 0.718 mmol) was added to a stirred solution of (2*S*,3*R*)-**8** (131 mg, 0.598 mmol) in pyridine (0.3 ml) at 0 °C. After stirring for 1 h at 0 °C, the reaction was quenched with water, and the mixture was extracted with EtOAc. The extract was successively washed with saturated $CuSO_4$ aq., water and brine, dried over $MgSO_4$, and concentrated *in vacuo*. The residue (204 mg) was dissolved in THF (5 ml), and then TBAF (1.0 M in THF; 0.657 ml, 0.657 mmol) was added to the solution at 0 °C. After stirring for 30 min at 0 °C, the mixture was diluted with water, and extracted with EtOAc. The resulting extract was successively washed with water and brine, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by chromatography (hexane/EtOAc, 5:1) to give (2*R*,3*S*)-**8′** (120 mg, 96%) as colorless needles. HPLC analysis: column, Chiralcel OD® 25 cm × 4.6 mm; eluent, hexane/2-propanol (9:1); flow rate, 0.5 ml/min; UV detection at 254 nm; t_R 30.8 min [93.4%, (2*R*,3*S*)-**8′**], 34.8 min [6.6%, (2*S*,3*R*)-**8′**]. Enantiomeric purity of (2*S*,3*R*)-**8**: 87% e.e.

*(2R,3S)-1-t-Butyldimethylsilyloxy-2,3-epoxy-5,8-undecadiyne [(2R,3S)-**13**].* A solution of *n*-BuLi (1.59 M in hexane, 12.2 ml, 19.4 mmol) was added dropwise to a solution of (2*S*,3*R*)-**8** (4.21 g, 19.3 mmol) in dry THF (105 ml) at −78 °C under argon. After stirring for 1 h at −78 °C, Tf_2O (3.24 ml, 19.3 mmol) was added dropwise. The mixture was stirred for 80 min at −78 °C, and then a solution of freshly prepared 1,4-heptadiynyllithium [a solution of *n*-BuLi (1.59 M in hexane; 14.6 ml, 23.2 mmol) was added slowly to a solution of freshly distilled 1,4-heptadiyne (**11**; 3.55 g, 38.6 mmol) and dry THF (105 ml) at −78 °C under argon, and then the mixture was stirred for 3 h at −78 °C] and dry HMPA (17.5 ml) was added at −78 °C. The mixture was stirred for 1 h at −78 °C, quenched with water, and then extracted with Et_2O. The extract was washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by chromatography (hexane/AcOEt, 80:1) to give (2*R*,3*S*)-**13** (3.77 g, 67%) as a yellowish oil. IR ν_{max} (film) cm^{-1}: 2215 (w, C≡C), 1470 (m, Si–C), 1390 (w, C–O), 1360 (w, C–O), 1100 (s, Si–O). ^{1}H-NMR δ_H (400 MHz, $CDCl_3$): 0.08 (3H, s, Si–Me), 0.09 (3H, s, Si–Me), 0.90 (9H, s, *t*-Bu), 1.12 (3H, t, $J = 7.5$ Hz, 11-H), 2.17 (2H, tq, $J = 2.4$, 7.5 Hz, 10-H), 2.32 (1H, ddt, $J = 17.5$, 6.6, 2.4 Hz, 4-H_a), 2.57 (1H, ddt, $J = 17.5$, 6.6, 2.4 Hz, 4-H_b), 3.07–3.12 (3H, m, 3-H, 7-H), 3.16 (1H, dt, $J = 4.1$, 5.9 Hz, 2-H), 3.71 (1H, dd, $J = 11.8$, 5.9 Hz, 1-H_a), 3.81 (1H, dd, $J = 11.8$, 5.9 Hz, 1-H_b). This compound was employed in the next step without further purification.

*(2R,3S,5Z,8Z)-1-t-Butyldimethylsilyloxy-2,3-epoxy-5,8-undecadiene [(2R,3S)-**14**].* A solution of (2*R*,3*S*)-**13** (3.43 g, 11.7 mmol) in cyclohexane (50 ml) was added to an ice-cooled suspension of a Lindlar catalyst (5% Pd-$CaCO_3$-Pb^{2+}, 70.2 mg) in cyclohexane (70 ml) under H_2. After stirring for 2 h at room temperature, the mixture was filtered through Celite, and the resulting filtrate was concentrated *in vacuo*. The residue was purified by chromatography (hexane/EtOAc, 100:1) to give (2*R*,3*S*)-**14** (2.69 g, 77%) as a colorless oil. $n_D^{19} = 1.4610$. $[\alpha]_D^{23} = +1.52$ ($c = 1.02$, $CHCl_3$). IR ν_{max} (film) cm^{-1}: 1650 (w, C=C), 1460 (m, Si–O), 1390 (w, C–O), 1360 (w, C–O), 1100 (s, Si–O). ^{1}H-NMR δ_H (400 MHz, $CDCl_3$): 0.09 (3H, s, Si–Me), 0.10 (3H, s, Si–Me), 0.91 (9H, s, *t*-Bu), 0.98 (3H, t, $J = 7.6$ Hz, 11-H), 2.07 (2H, quint, $J = 7.6$ Hz, 10-H), 2.23 (1H, dt, $J = 15.4$, 6.6 Hz, 4-H_a), 2.42 (1H, dt, $J = 15.4$, 6.6 Hz, 4-H_b), 2.80 (2H, t, $J = 7.1$ Hz, 7-H), 3.00 (1H, dt, $J = 4.4$, 6.6 Hz, 3-H), 3.10 (1H, dt, $J = 4.4$, 5.6 Hz, 2-H), 3.76 (1H, dd, $J = 10.7$, 5.6 Hz, 1-H_a), 3.80 (1H, dd, $J = 10.7$, 5.6 Hz, 1-H_b), 5.27–5.55 (4H, m, 5-H, 6-H, 8-H, 9-H). *Anal.* Found: C, 68.67; H, 11.07%. Calcd. for $C_{17}H_{32}O_2Si$: C, 68.86; H, 10.88%.

*(2R,3S,5Z,8Z)-2,3-Epoxy-5,8-undecadien-1-ol [(2R,3S)-**15**].* TBAF (1.0 M in THF; 9.21 ml, 9.21 mmol) was added to a solution of (2*R*,3*S*)-**14** (2.48 g, 8.37 mmol) in THF (70 ml) at 0 °C. After stirring for 1 h at 0 °C, the mixture was diluted with water and extracted with EtOAc. The extract was successively washed with water and brine, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by chromatography (hexane/EtOAc, 5:1) to give (2*R*,3*S*)-**15** (1.46 g, 96%) as a slightly yellowish oil. $n_D^{16} = 1.4821$. $[\alpha]_D^{23} = +8.69$ ($c = 1.07$, $CHCl_3$) {lit.[4] $[\alpha]_D^{22} = +11.6$ ($c = 0.84$, $CHCl_3$)}. IR ν_{max} (film) cm^{-1}: 3400 (br s, O–H), 1650 (w, C=C). ^{1}H-NMR δ_H (400 MHz, $CDCl_3$): 0.97 (3H, t, $J = 7.6$ Hz, 11-H), 1.77 (1H, t, $J = 5.2$ Hz, O–H), 2.07 (2H, quint, $J = 7.6$ Hz, 10-H), 2.27 (1H, dt, $J = 15.2$, 7.6 Hz, 4-H_a), 2.48 (1H, dt, $J = 15.2$, 7.6 Hz, 4-H_b), 2.79 (2H, t, $J = 7.1$ Hz, 7-H), 3.08 (1H, dt, $J = 4.3$, 7.6 Hz, 3-H), 3.17 (1H, dt, $J = 4.3$, 6.6 Hz, 2-H), 3.73 (1H, ddd, $J = 12.0$, 6.6,

5.2 Hz, 1-H_a), 3.87 (1H, ddd, J = 12.0, 6.6, 5.2 Hz, 1-H_b), 5.25–5.55 (4H, m, 5-H, 6-H, 8-H, 9-H). ^{13}C-NMR δ_C (100 MHz, $CDCl_3$): 14.2, 20.6, 25.6, 26.4, 56.4, 56.6, 60.8, 123.6, 126.4, 131.2, 132.4. The IR and ^{1}H-NMR spectra were identical to those published elsewhere.[4)]

*(3Z,6Z,9S,10R)-9,10-Epoxy-3,6-henicosadiene [(9S,10R)-**1**].* *p*-Toluenesulfonyl chloride (1.21 g, 6.39 mmol) was added to a stirred solution of (2*R*,3*S*)-**15** (1.06 g, 5.81 mmol) in pyridine (4.2 ml) at 0 °C. After stirring overnight at 0 °C, the mixture was poured into water, and extracted with CH_2Cl_2. The extract was successively washed with saturated $CuSO_4$ aq., water and brine, dried over $MgSO_4$, and concentrated *in vacuo*. The residue (2.21 g) was dissolved in dry Et_2O (30 ml) and stirred at −40 °C. The solution was added slowly to a stirred suspension of lithium di(*n*-decyl)cuprate in Et_2O [*n*-decyllithium (0.92 M in Et_2O; 24.7 ml, 22.7 mmol) was added to a suspension of CuI (2.16 g, 11.3 mmol) in dry Et_2O (16 ml) at −40 °C under argon, and then the mixture was stirred for 3 h at −40 °C.] at −40 °C. After stirring for 15 min at −40 °C, the suspension was poured into saturated NH_4Cl aq., and extracted with Et_2O. The extract was successively washed with saturated NH_4Cl aq., water and brine, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by chromatography (hexane/EtOAc, 100:1) to give (9*S*,10*R*)-**1** (1.11 g, 62%) as a colorless oil. n_D^{20} = 1.4633. $[\alpha]_D^{22}$ = +3.99 (c = 1.65, CCl_4). IR ν_{max} (film) cm^{-1}: 1650 (w, C=C). ^{1}H-NMR δ_H (500 MHz, $CDCl_3$): 0.90 (3H, t, J = 7.4 Hz, 1-H), 0.92 (3H, t, J = 6.7 Hz, 21-H), 1.28–1.50 (20H, m, 11-H, 12-H, 13-H, 14-H, 15-H, 16-H, 17-H, 18-H, 19-H, 20-H), 1.99 (2H, quint, J = 7.4 Hz, 2-H), 2.16 (1H, dt, J = 14.4, 6.2 Hz, 8-H_a), 2.37 (1H, dt, J = 14.4, 6.2 Hz, 8-H_b), 2.72–2.75 (1H, m, 10-H), 2.77 (2H, t, J = 6.4 Hz, 5-H), 2.81 (1H, dt, J = 4.0, 6.2 Hz, 9-H), 5.35–5.54 (4H, m, 3-H, 4-H, 6-H, 7-H). ^{13}C-NMR δ_C (100 MHz, $CDCl_3$): 14.1, 14.2, 20.6, 22.7, 25.7, 26.2, 26.6, 27.8, 29.3, 29.6, 31.9, 56.4, 57.2, 124.2, 126.7, 130.7, 132.2. *Anal.* Found: C, 78.20; H, 13.12%. Calcd. for $C_{21}H_{38}O$: C, 77.72; H, 13.32%. FAB-HRMS m/z ($[M+H]^+$): calcd. for $C_{21}H_{39}O$, 307.2995; found, 307.2993.

*1-Trimethylsilyloxy-3,6-heptadiyne [**19**].* Triethylamine (9.37 ml, 67.2 mmol), chlorotrimethylsilane (6.80 ml, 32.2 mmol) and DMAP (328 mg, 2.69 mmol) were added to a solution of **18** (2.91 g, 26.9 mmol) in dry CH_2Cl_2 (60 ml) at 0 °C. After stirring for 30 min at 0 °C, the mixture was poured into water and extracted with CH_2Cl_2. The resulting extract was successively washed with water and brine, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by chromatography (pentane/Et_2O, 100:1) to give **19** (4.45 g, 92%) as a yellowish oil. Bp 81 °C at 7.0 Torr. n_D^{25} = 1.4510. IR ν_{max} (film) cm^{-1}: 3300 (s, C≡CH), 2130 (w, C≡C), 1420 (w, Si–C), 1250 (s, Si–C), 1100 (s, Si–O). ^{1}H-NMR δ_H (400 MHz, $CDCl_3$): 0.13 (9H, s, Si–Me_3), 2.06 (1H, t, J = 2.8 Hz, 7-H), 2.40 (2H, tt, J = 6.8, 2.8 Hz, 2-H), 2.53 (2H, q, J = 2.8 Hz, 5-H), 3.68 (2H, t, J = 6.8 Hz, 1-H). This compound was employed in the next step without further purification.

*(2R,3S)-1-t-Butyldimethylsilyloxy-2,3-epoxy-5,8-undecadiyn-1-ol [(2R,3S)-**20**].* A solution of *n*-BuLi (1.56 M in hexane; 7.14 ml, 11.1 mmol) was added dropwise to a solution of (2*S*,3*R*)-**8** (2.43 g, 11.1 mmol) in dry THF (60 ml) at −78 °C under argon. After stirring for 40 min at −78 °C, Tf_2O (1.86 ml, 11.1 mmol) was added dropwise. The mixture was stirred for 40 min at −78 °C, and then a solution of freshly prepared 1-trimethylsilyloxy-3,6-heptadiynyllithium [a solution of *n*-BuLi (1.56 M in hexane; 8.53 ml, 13.3 mmol) was added slowly to a solution of freshly distilled **19** (6.02 g, 33.4 mmol) and dry THF (60 ml) at −78 °C under argon, and then the mixture was stirred for 2 h at −78 °C] and dry HMPA (9.96 ml) were added at −78 °C. The mixture was stirred for 1 h at −78 °C and then poured into MeOH (120 ml). K_2CO_3 (3.07 g, 22.2 mmol) was added to the mixture at room temperature. After stirring for 1 h at room temperature, the mixture was concentrated *in vacuo*, diluted with Et_2O, successively washed with water and brine, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by chromatography (hexane/EtOAc, 5:1) to give (2*R*,3*S*)-**20** (2.52 g, 73%) as a yellowish oil. IR ν_{max} (film) cm^{-1}: 3420 (br s, O–H), 2220 (w, C≡C). ^{1}H-NMR δ_H (300 MHz, $CDCl_3$): 0.09 (3H, s, Si–Me), 0.10 (3H, s, Si–Me), 0.91 (9H, s, *t*-Bu), 1.78 (1H, br s, O–H), 2.30–2.37 (1H, m, 4-H_a), 2.45 (2H, tt, J = 6.0, 1.8 Hz, 10-H), 2.53–2.60 (1H, m, 4-H_b), 3.10–3.21 (4H, m, 2-H, 3-H, 7-H), 3.71 (2H, t, J = 6.0 Hz, 11-H), 3.74 (1H, dd, J = 11.7, 9.0 Hz, 1-H_a), 3.83 (1H, dd, J = 11.7, 4.8 Hz, 1-H_b). This compound was employed in the next step without further purification.

*(2R,3S,5Z,8Z)-1-t-Butyldimethylsilyloxy-2,3-epoxy-5,8-undecadien-11-ol [(2R,3S)-**21**].* A solution of (2*R*,3*S*)-**20** (2.52 g, 8.14 mmol) and cyclohexene (4.12 ml, 40.8 mmol) in cyclohexane (24 ml) was added to an ice-cooled suspension of the Lindlar catalyst (5% Pd-$CaCO_3$-Pb^{2+}, 47.0 mg) in cyclohexane (47 ml) under H_2. The addition of cyclohexene prevented over-reduction. After stirring for 4 h at room temperature, the mixture was filtered through Celite, and the resulting filtrate was concentrated *in vacuo*. The residue was purified by chromatography (hexane/EtOAc, 50:1) to give (2*R*,3*S*)-**21** (2.12 g, 83%) as a colorless oil. n_D^{24} = 1.4721, $[\alpha]_D^{24}$ = −5.12 (c = 1.00, $CHCl_3$). IR ν_{max} (film) cm^{-1}: 3420 (br s, O–H), 1650 (w, C=C), 1470 (m, Si–C), 1390 (m, C–O), 1360 (m, C–O), 1100 (s, Si–O). ^{1}H-NMR δ_H (500 MHz, $CDCl_3$): 0.09 (3H, s, Si–Me), 0.08 (3H, s, Si–Me), 0.89 (9H, s, *t*-Bu), 1.74 (1H, br s, O–H), 2.23 (1H, dt, J = 14.7, 6.7 Hz, 4-H_a), 2.28–2.42 (3H, m, 4-H_b, 10-H), 2.83 (2H, m, 7-H), 2.98 (1H, dt, J = 4.9, 6.7 Hz, 3-H), 3.08 (1H, dt, J = 4.9, 5.8 Hz,

2-H), 3.63 (2H, t, $J = 7.0$ Hz, 11-H), 3.75 (1H, dd, $J = 11.6$, 5.8 Hz, 1-H_a), 3.78 (1H, dd, $J = 11.6$, 5.8 Hz, 1-H_b), 5.38–5.53 (4H, m, 5-H, 6-H, 8-H, 9-H). ^{13}C-NMR δ_C (125 Hz, $CDCl_3$): −5.5, −5.4, 18.1, 25.7, 26.2, 30.7, 55.8, 56.8, 61.4, 61.8, 124.2, 126.0, 130.0, 130.4. *Anal.* Found: C, 71.52; H, 11.48%. Calcd. for $C_{17}H_{32}O_3$: C, 71.79; H, 11.34%.

*(2R,3S,5Z,8Z)-11-Bromo-1-t-butyldimethylsilyloxy-2,3-epoxy-5,8-undecadiene [(2R,3S)-**22**].* Carbon tetrabromide (2.22 g, 6.70 mmol) and triphenylphosphine (1.76 g, 6.70 mmol) were added to a solution of (2*R*,3*S*)-**21** (1.91 g, 6.09 mmol) in CH_2Cl_2 (40 ml) at 0 °C. After stirring overnight at 0 °C, the mixture was diluted with pentane. The mixture was filtered through Celite, and the resulting filtrate was concentrated *in vacuo*. The residue was purified by chromatography (hexane/EtOAc, 100:1) to give (2*R*,3*S*)-**22** (1.81 g, 79%) as a yellowish oil. $n_D^{23} = 1.4509$. $[\alpha]_D^{22} = -0.97$ ($c = 1.02$, $CHCl_3$). IR ν_{max} (film) cm^{-1}: 1650 (w, C=C), 1470 (w, Si–C), 1390 (w, C–O), 1360 (w, C–O), 1260 (s, C–Br), 1100 (s, Si–O). ^{1}H-NMR δ_H (500 MHz, $CDCl_3$): 0.07 (3H, s, Si–Me), 0.08 (3H, s, Si–Me), 0.89 (9H, s, *t*-Bu), 2.22 (1H, dt, $J = 14.7$, 6.1 Hz, 4-H_a), 2.37 (1H, dt, $J = 14.7$, 6.1 Hz, 4-H_b), 2.62 (2H, q, $J = 7.0$ Hz, 10-H), 2.80 (2H, t, $J = 6.1$ Hz, 7-H), 2.97 (1H, dt, $J = 4.3$, 6.1 Hz, 3-H), 3.06 (1H, dt, $J = 4.3$, 5.5 Hz, 2-H), 3.35 (2H, t, $J = 7.0$ Hz, 11-H), 3.75 (2H, d, $J = 5.5$ Hz, 1-H), 5.36–5.52 (4H, m, 5-H, 6-H, 8-H, 9-H). ^{13}C-NMR δ_C (125 MHz, $CDCl_3$): −5.4, −5.3, 18.2, 25.8, 26.3, 30.7, 32.1, 55.7, 56.7, 61.4, 124.6, 126.6, 130.0, 130.4. *Anal.* Found: C, 54.68; H, 8.17%. Calcd. for $C_{17}H_{31}O_2BrSi$: C, 54.39; H, 8.32%.

*(2R,3S,5Z,8Z)-1-t-Butyldimethylsilyloxy-2,3-epoxy-5,8,10-undecatriene [(2R,3S)-**23**].* Potassium *t*-butoxide (44.9 mg, 0.400 mmol) and 18-crown-6 (7.0 mg, 0.027 mmol) were added to a solution of (2*R*,3*S*)-**22** (100 mg, 0.267 mmol) in hexane (2.6 ml) at −40 °C. After stirring for 3 h at −20 °C, the mixture was poured into saturated NH_4Cl aq. and extracted with Et_2O. The extract was washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by chromatography (hexane/EtOAc, 200:1) to give (2*R*,3*S*)-**23** (61.0 mg, 77%) as a yellowish oil. $n_D^{22} = 1.4781$. $[\alpha]_D^{23} = -2.05$ ($c = 1.10$, $CHCl_3$). IR ν_{max} (film) cm^{-1}: 1640 (w, C=C), 1470 (w, Si–C), 1390 (w, C–O), 1100 (s, Si–O), 1000 (m, C=C), 910 (m, C=C). ^{1}H-NMR δ_H (300 MHz, $CDCl_3$): 0.06 (3H, s, Si–Me), 0.08 (3H, s, Si–Me), 0.89 (9H, s, *t*-Bu), 2.24 (1H, dt, $J = 14.4$, 6.4 Hz, 4-H_a), 2.41 (1H, dt, $J = 14.4$, 6.4 Hz, 4-H_b), 2.95 (2H, t, $J = 6.5$ Hz, 7-H), 3.00 (1H, dt, $J = 4.5$, 6.4 Hz, 3-H), 3.10 (1H, dt, $J = 4.5$, 6.4 Hz, 2-H), 3.77 (2H, d, $J = 6.4$ Hz, 1-H), 5.13 (1H, d, $J = 10.2$ Hz, 11-H_a), 5.21 (1H, d, $J = 16.8$ Hz, 11-H_b), 5.35–5.58 (3H, m, 5-H, 6-H, 8-H), 6.02 (1H, t, $J = 11.1$ Hz, 9-H), 6.64 (1H, dddd, $J = 16.8$, 11.1, 10.2, 1.2 Hz, 10-H). ^{13}C-NMR δ_C (75 MHz, $CDCl_3$): −5.4, −5.3, 18.2, 25.8, 26.2, 26.4, 55.9, 56.9, 61.5, 117.7, 124.7, 129.5, 129.8, 130.0, 131.7. *Anal.* Found: C, 69.42; H, 10.20%. Calcd. for $C_{17}H_{30}O_2Si$: C, 69.33; H, 10.27%.

*(2R,3S,5Z,8Z)-2,3-Epoxy-5,8,10-undecatrien-1-ol [(2R,3S)-**24**].* TBAF (1.0 M in THF; 0.241 ml, 0.241 mmol) was added to a solution of (2*R*,3*S*)-**23** (59.4 mg, 0.201 mmol) in THF (2.0 ml) at 0 °C. After stirring for 2 h at 0 °C, the mixture was diluted with water and extracted with EtOAc. The extract was successively washed with water and brine, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by chromatography (hexane/EtOAc, 5:1) to give (2*R*,3*S*)-**24** (32.5 mg, 90%) as a colorless oil. $n_D^{24} = 1.4981$. $[\alpha]_D^{24} = +5.09$ ($c = 0.93$, $CHCl_3$) {lit.[5] $[\alpha]_D^{18} = +6.20$ ($c = 1.66$, $CHCl_3$)}. IR ν_{max}(film) cm^{-1}: 3410 (br s, O–H), 1640 (w, C=C). ^{1}H-NMR δ_H (500 MHz, $CDCl_3$): 1.81 (1H, br s, O–H), 2.28 (1H, dt, $J = 15.0$, 6.7 Hz, 4-H_a), 2.47 (1H, dt, $J = 15.0$, 6.7 Hz, 4-H_b), 2.95 (2H, t, $J = 7.5$ Hz, 7-H), 3.07 (1H, dt, $J = 4.3$, 6.7 Hz, 3-H), 3.17 (1H, dt, $J = 4.3$, 6.7 Hz, 2-H), 3.73 (1H, dd, $J = 12.2$, 6.7 Hz, 1-H_a), 3.86 (1H, dd, $J = 12.2$, 6.7 Hz, 1-H_b), 5.14 (1H, d, $J = 10.1$ Hz, 11-H_a), 5.22 (1H, d, $J = 16.8$ Hz, 11-H_b), 5.39 (1H, dt, $J = 11.0$, 7.5 Hz, 8-H), 5.45–5.56 (2H, m, 5-H, 6-H), 6.03 (1H, t, $J = 11.0$ Hz, 9-H), 6.64 (1H, dddd, $J = 16.8$, 11.0, 10.1, 0.9 Hz, 10-H). ^{13}C-NMR δ_C (125 MHz, $CDCl_3$): 26.2, 26.4, 56.3, 56.6, 60.7, 117.8, 124.4, 129.59, 129.64, 130.3, 131.8. The IR and ^{1}H-NMR spectra were identical to those published.[5]

*(3Z,6Z,9S,10R)-9,10-Epoxy-1,3,6-henicosatriene [(9S,10R)-**5**].* *p*-Toluenesulfonyl chloride (51.2 mg, 0.269 mmol) was added to a solution of (2*R*,3*S*)-**24** (36.2 mg, 0.201 mmol) in pyridine (1.0 ml) and CH_2Cl_2 (1.0 ml) at 0 °C. After stirring overnight at 0 °C, the mixture was poured into water and extracted with CH_2Cl_2. The extract was successively washed with saturated $CuSO_4$ aq., water and brine, dried over $MgSO_4$, and concentrated *in vacuo*. The residue (70.3 mg) was dissolved in dry Et_2O (1.0 ml) and stirred at −40 °C. This solution was added slowly to a suspension of lithium di(*n*-decyl)cuprate in Et_2O [*n*-decyllithium (1.07 M in Et_2O; 0.632 ml, 0.676 mmol) was added to a suspension of CuI (65.3 mg, 0.342 mmol) in dry Et_2O (1.0 ml) at −45 °C under argon, and then the mixture was stirred for 3 h at −45 °C] at −45 °C. After stirring for 15 min at −45 °C, the suspension was poured into saturated NH_4Cl aq. and extracted with Et_2O. The extract was successively washed with saturated NH_4Cl aq., water and brine, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by chromatography (hexane/EtOAc, 100:1) to give (9*S*,10*R*)-**5** (40.0 mg, 65%) as a colorless oil. $n_D^{15} = 1.4841$. $[\alpha]_D^{21} = -0.38$ ($c = 1.04$, $CHCl_3$). IR ν_{max} (film) cm^{-1}: 1630 (w, C=C). ^{1}H-NMR δ_H (500 MHz, $CDCl_3$): 0.88 (3H, t, $J = 7.3$ Hz, 21-H), 1.26–1.54 (20H, m, 11-H, 12-H, 13-H, 14-H, 15-H, 16-H, 17-H, 18-H, 19-H, 20-H), 2.24

(1H, dt, $J = 14.4$, 6.1 Hz, 8-H_a), 2.40 (1H, dt, $J = 14.4$, 6.1 Hz, 8-H_b), 2.91–2.98 (4H, m, 5-H, 9-H, 10-H), 5.13 (1H, d, $J = 10.7$ Hz, 1-H_a), 5.22 (1H, d, $J = 16.8$ Hz, 1-H_b), 5.41 (1H, dt, $J = 10.5$, 8.0 Hz, 4-H), 5.46–5.55 (2H, m, 6-H, 7-H), 6.03 (1H, t, $J = 10.5$ Hz, 3-H), 6.65 (1H, ddd, $J = 16.8$, 10.7, 10.5 Hz, 2-H). ^{13}C-NMR δ_C (100 MHz, $CDCl_3$): 14.1, 22.7, 26.2, 26.6, 27.8, 29.3, 29.6, 31.9, 56.3, 57.2, 117.7, 124.8, 129.7, 129.8, 130.0, 131.8. *Anal.* Found: C, 82.71; H, 12.04%. Calcd. for $C_{21}H_{36}O$: C, 82.83; H, 11.92%. FAB-HRMS m/z ($[M + H]^+$): calcd. for $C_{21}H_{37}O$, 305.2844; found, 305.2849.

Acknowledgments

We thank Dr. S. Senda (Nitto Denko Co., Tokyo) for his support. Our thanks are due to Dr. Y. Hirose (Amano Enzyme Co.) for supplying lipase. We are grateful to Miss Tomoko Nomura for her help in the early phase of this work.

References

1) Hill, A. S., Kovalev, B. G., Nikolaeva, L. N., and Roelofs, W. L., Sex pheromone of the fall webworm moth, *Hyphantria cunea*. *J. Chem. Ecol.*, **8**, 383–396 (1982).
2) Tóth, M., Buser, H. R., Peña, A., Arn, H., Mori, K., Takeuchi, T., Nicolaeva, L. N., and Kovalev, B. G., Identification of (3*Z*,6*Z*)-1,3,6-9,10-epoxyheneicosatriene and (3*Z*,6*Z*)-1,3,6-9,10-epoxyeicosatriene in the sex pheromone of *Hyphantria cunea*. *Tetrahedron Lett.*, **30**, 3405–3408 (1989).
3) Senda, S., Saika, T., and Furumori, K., Pheromone control of fall webworm, *Hyphantria cunea* Drury (*Lepidoptera*:*Arctiidae*). *Nitto Giho*, **31**, 97–102 (1993).
4) Mori, K., and Ebata, T., Synthesis of optically active pheromones with an epoxy ring, (+)-disparlure and both the enantiomers of (3*Z*,6*Z*)-*cis*-9,10-epoxy-3,6-henicosadiene. *Tetrahedron*, **42**, 3471–3478 (1986).
5) Mori, K., and Takeuchi, T., Synthesis of the enantiomers of (3*Z*,6*Z*)-*cis*-9,10-epoxy-1,3,6-henicosatriene and (3*Z*,6*Z*)-*cis*-9,10-epoxy-1,3,6-icosatriene, the new pheromone components of *Hyphantria cunea*. *Liebigs Ann. Chem.*, 453–457 (1989).
6) Bell, T. W., and Ciaccio, J. A., Alkylative epoxide rearrangement. A stereospecific approach to chiral epoxide pheromone. *J. Org. Chem.*, **58**, 5153–5162 (1993).
7) Yadav, J. S., Valli, M. Y., and Prasad, A. R., Total synthesis of enantiomers of (3*Z*,6*Z*)-*cis*-9,10-epoxy-1,3,6-henicosatriene—the pheromonal component of *Diacrisia obliqua*. *Tetrahedron*, **54**, 7551–7562 (1998).
8) Zhang, Z.-B., Wang, Z.-M., Wang, Y.-X., Liu, H.-Q., Lei, G.-X., and Shi, M., A facile synthetic method for chiral 1,2-epoxides and the total synthesis of chiral pheromone epoxides. *Tetrahedron: Asymmetry*, **10**, 837–840 (1999).
9) Yadav, J. S., Valli, M. Y., and Prasad, A. R., Isolation, identification, synthesis, and bioefficacy of female *Diacrisia obliqua* (Arctiidae) sex pheromone blend. An Indian agricultural pest. *Pure Appl. Chem.*, **73**, 1157–1162 (2001).
10) Brevet, J.-L., and Mori, K., Enzymatic preparation of (2*S*,3*R*)-4-acetoxy-2,3-epoxybutan-1-ol and its conversion to the epoxy pheromones of the gypsy moth and the ruby tiger moth. *Synthesis*, 1007–1012 (1992).
11) Mori, K., Enantioselective synthesis in natural product chemistry—a personal account—. *J. Synth. Org. Chem. Jpn.*, **53**, 952–962 (1995).
12) Muto, S., and Mori, K., Synthesis of all four stereoisomers of Leucomalure, components of the female sex pheromone of the satin moth, *Leucoma salicis*. *Eur. J. Org. Chem.*, 1300–1307 (2003).
13) Muto, S., and Mori, K., Synthesis of the four components of the female sex pheromone of the painted apple moth, *Teia anartoides*. *Biosci. Biotechnol. Biochem.*, **67**, 1559–1567 (2003).
14) Millar, J. G., and Underhill, E. W., Short synthesis of 1,3*Z*,6*Z*,9*Z*-triene hydrocarbons. Lepidopteran sex attractants. *Can. J. Chem.*, **64**, 2427–2430 (1986).
15) Soulié, J., Ta, C., and Lallemand, J.-Y., Access to unsaturated chiral epoxides. I: Bisallylic chiral epoxide. Application to the synthesis of Lepidopteran pheromones. *Tetrahedron*, **48**, 443–452 (1992).