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Synthesis of All the Stereoisomers of 6-Methyl-2-octadecanone, 14-Methyl-2-octadecanone, and 6,14-Dimethyl-2-octadecanone, Sex Pheromone Components of the *Lyclene dharma dharma* Moth, from the Enantiomers of Citronellal*

Yasumasa SHIKICHI and Kenji MORI†

Photosensitive Materials Research Center, Toyo Gosei Co., Ltd., 4-2-1 Wakahagi, Inzai, Chiba 270-1609, Japan

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The enantiomers of citronellal were converted to all the stereoisomers of 6-methyl-2-octadecanone, 14-methyl-2-octadecanone, and 6,14-dimethyl-2-octadecanone, the female-produced sex pheromone components of the *Lyclene dharma dharma* moth. Three well-established procedures, the Wittig reaction, alkylation of alkynes, and acetoacetic ester synthesis, were employed for the carbon-carbon bond formation to connect the building blocks.

Key words: citronellal; enantioselective synthesis; *Lyclene dharma dharma*; methyl-branched aliphatic ketone; pheromone

In 2007, Ando and his co-workers identified three antennographically active components of the female-produced sex pheromone of the Lithosiinae moth, *Lyclene dharma dharma*, as 6-methyl-2-octadecanone (**1**), 14-methyl-2-octadecanone (**2**), and 6,14-dimethyl-2-octadecanone (**3**, Fig. 1).[2] They then synthesized mixtures of all the possible stereoisomers of **1**, **2**, and **3**,[2,3] and found that a mixture of **1**, **2** and **3** in a ratio of 2:1:1 as well as a 2:1 mixture of **1** and **2** were pheromonally active, showing that **3** was not indispensable for bioactivity.[3] The absolute configuration of naturally occurring **1**, **2** and **3** was not known at the time when the present work was started.

It is well known that the absolute configuration of a pheromone is often very important for the expression of its pheromone activity.[4] Synthesis and a bioassay of all the possible stereoisomers of a pheromone are the widely accepted paradigm for determining the absolute configuration of a pheromone.[4] In this context, one of the authors has synthesized all the possible stereoisomers of **1**, **2** and **3** by means of olefin cross metathesis.[5] In order to secure additional amounts of the stereoisomers of **1**, **2** and **3**, we planned their alternative synthesis based on classical carbon-carbon bond formation reactions employing the commercially available enantiomers of citronellal, whose use in enantioselective synthesis has recently been reviewed.[6] This paper describes our second synthesis of all the possible stereoisomers of **1**, **2** and **3**.

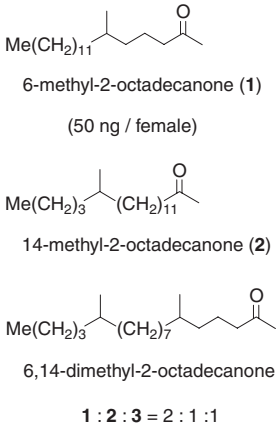


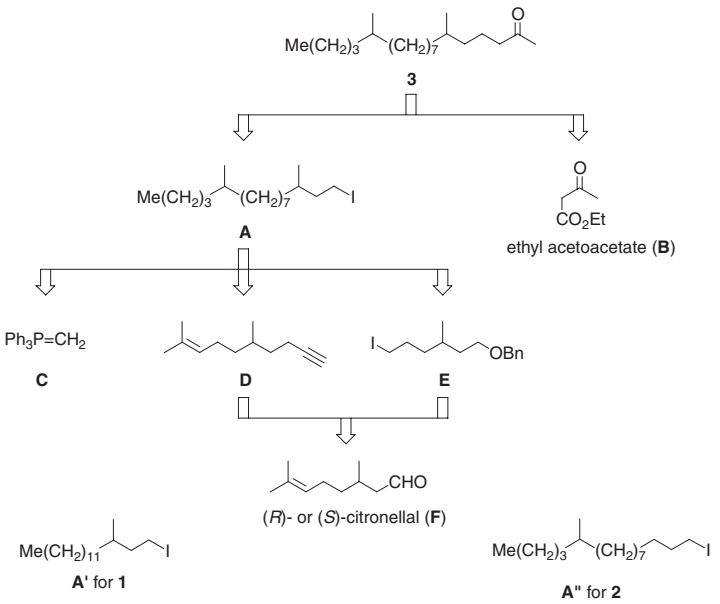
Fig. 1. Structures of the Components of the Female-Produced Sex Pheromone of the *Lyclene dharma dharma* Moth.
A female moth produced about 50 ng of **1**.

Results and Discussion

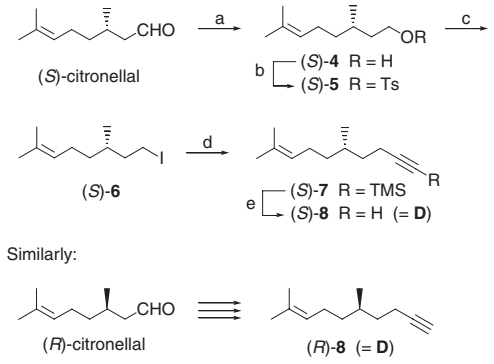
Scheme 1 shows the retrosynthetic analysis of 6,14-dimethyl-2-octadecanone (**3**). Target ketone **3** could be prepared by acetoacetic ester synthesis, using iodide **A** and ethyl acetoacetate (**B**) as the building blocks. Iodide **A** would be synthesized from **C**, **D** and **E**, employing alkylation of the carbanion derived from **D** with **E** as the key reaction. Subsequent replacement of the terminal isopropylidene group with a methylene group could be achieved by cleaving the double bond and subsequent Wittig reaction using **C**. Both **D** and **E** can be readily prepared from citronellal [**F**, Takasago, 97% ee for both (*R*)- and (*S*)-isomers]. The enantiomers of **F** will lead to the four steroisomers of **3** by the appropriate combination of **D** and **E**. Similarly, the two other ketones, **1** and **2**, can be respectively synthesized by employing **A**′ and **A**″, instead of **A** in the case for the preparation of **3**.

The synthesis of (*S*)-5,9-dimethyl-8-decen-1-yne (**8**), the left-hand portion of **3**, is summarized in Scheme 2. We adopted the procedure previously reported for the synthesis of (*R*)-**8**[7,8] with slight modifications to improve the yield in the conversion of **6** to **8**. Accordingly, (*S*)-citronellal was converted to (*S*)-citronellyl iodide (**6**) *via* **4** and **5**. Alkylation of lithium

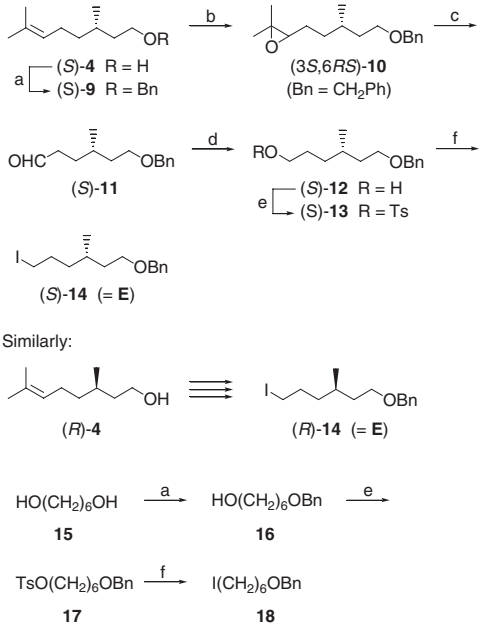
* Pheromone Synthesis, Part 252. See Ref. 1 for Part 251.
† To whom correspondence should be addressed. Fax: +81-3-3813-1516; E-mail: kjk-mori@arion.ocn.ne.jp



Scheme 1. Retrosynthetic Analysis of 6,14-Dimethyl-2-octadecanone (**3**).



Scheme 2. Synthesis of **8**.
Reagents: (a) $LiAlH_4$, Et_2O (94%); (b) TsCl, C_5H_5N (97%); (c) NaI, DMF (83%); (d) HC≡CTMS, *n*-BuLi, THF, HMPA (80%); (e) K_2CO_3, MeOH, H_2O (quant.).



Scheme 3. Synthesis of **14** and **18**.
Reagents: (a) BnCl, *t*-BuOK, DMSO [75% for (*S*)-**9**; 37% for **16**]; (b) MCPBA, CH_2Cl_2 (quant.); (c) $HIO_4 \cdot 2H_2O$, THF, Et_2O (73%); (d) $LiAlH_4$, Et_2O (83%); (e) TsCl, C_5H_5N [91% for (*S*)-**13**; 92% for **17**]; (f) NaI, DMF [75% for (*S*)-**14**; 86% for **18**].

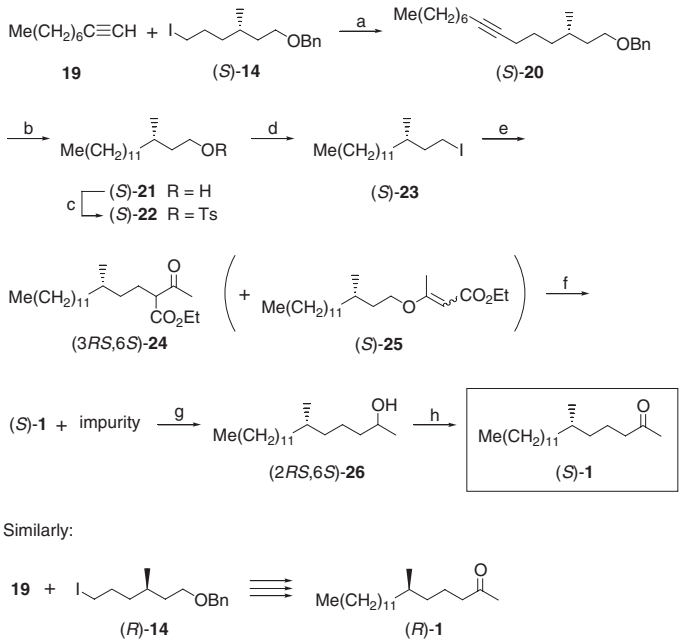
trimethylsilylacetylenide with **6** was best carried out by employing 1.5 eq. of the acetylenide in THF/HMPA (5:1) and then heating the reaction mixture under reflux for 2 h to give (*S*)-**7** in an 80% yield. Treatment of (*S*)-**7** with potassium carbonate in methanol furnished (*S*)-**8** in a quantitative yield. The overall yield of (*S*)-**8** was 61% based on (*S*)-citronellal in 5 steps. (*R*)-citronellal was similarly converted to known (*R*)-**8**.

(*S*)-6-Benzyloxy-4-methylhexyl iodide (**14**), the central part of **3**, was prepared as shown in Scheme 3. Benzylation of (*S*)-citronellol (**4**) afforded (*S*)-**9** which was epoxidized with *m*-chloroperbenzoic acid (MCPBA) to give (3*S*,6*RS*)-**10**. Periodic acid dihydrate cleaved epoxide (3*S*,6*RS*)-**10** to give aldehyde (*S*)-**11**. Reduction of (*S*)-**11** with lithium aluminum hydride furnished alcohol (*S*)-**12** which was converted to iodide (*S*)-**14** *via* (*S*)-**13**. The overall yield of (*S*)-**14** was 29% based on (*S*)-citronellal in 7 steps. (*R*)-**4** was similarly converted to (*R*)-**14**.

It was necessary to provide iodide **18** for the synthesis of 14-methyl-2-octadecanone (**2**). Its synthesis started from hexane-1,6-diol (**15**). Monobenzylation of **15** gave **16** which was tosylated to furnish **17**. Treatment of **17** with sodium iodide in DMF finally afforded **18**. The overall yield of **18** was 29% based on **15**.

With all the required building blocks in hand, we then started the synthesis of the enantiomers of 6-methyl-2-octadecanone (**1**) as shown in Scheme 4. Commercially available 1-nonyne (**19**) was alkylated with (*S*)-**14**, employing *n*-butyllithium in THF/HMPA as the base to give (*S*)-**20**. Hydrogenation of (*S*)-**20** over palladium-charcoal in acetic acid afforded (*S*)-3-methyl-1-pentadecanol (**21**). Corresponding tosylate (*S*)-**22** was treated with sodium iodide to furnish iodide (*S*)-**23**.

Alkylation of ethyl acetoacetate with (*S*)-**23** was achieved by using potassium carbonate in DMF as the base to give a mixture of desired *C*-alkylation product



Scheme 4. Synthesis of **1**.
Reagents: (a) *n*-BuLi, THF, HMPA (87%); (b) H_2, Pd–C, AcOH (89%); (c) TsCl, C_5H_5N (94%); (d) NaI, DMF (92%); (e) $MeCOCH_2CO_2Et$, K_2CO_3, DMF; (f) NaOH, MeOH, H_2O (81%, 2 steps); (g) $LiAlH_4$, THF; then SiO_2 chromatography (65%); (h) Jones CrO_3, acetone (82%).

(3*RS*,6*S*)-**24** and unwanted *O*-alkylation product (*S*)-**25** (84:16). The structure of contaminant (*S*)-**25** was supported by its ^{1}H-NMR spectrum to respectively exhibit the presence of C=C*H* and C=CC*H*$_3$ at $\delta = 5.01$ and 2.29. The mixture was treated with sodium hydroxide in aqueous methanol to give (*S*)-**1** contaminated with (*S*)-**25** which resisted hydrolysis under these conditions. Unfortunately, (*S*)-**1** and (*S*)-**25** could not be separated by column chromatography. To remove (*S*)-**25**, the mixture was reduced with lithium aluminum hydride, yielding alcohol (2*RS*,6*S*)-**26**. Curiously, (*S*)-**25** could not be reduced under these conditions. These two compounds, however, could be separated by chromatography to give pure (*S*)-**25** first, and then desired (2*RS*,6*S*)-**26**. Finally, oxidation of (2*RS*,6*S*)-**26** with Jones chromic acid furnished pure (*S*)-**1**, $[\alpha]_D^{25}$ −0.39 (*c* 1.15, hexane). Its IR, ^{1}H- and ^{13}C-NMR, and MS data were identical with those previously reported.[5] The overall yield of (*S*)-**1** based on (*S*)-citronellal was 8.4% in 15 steps. (*R*)-**14** was similarly converted to (*R*)-**1**, $[\alpha]_D^{25}$ +0.39 (*c* 1.13, hexane). The overall yield of (*R*)-**1** was 10% based on (*R*)-citronellal in 15 steps.

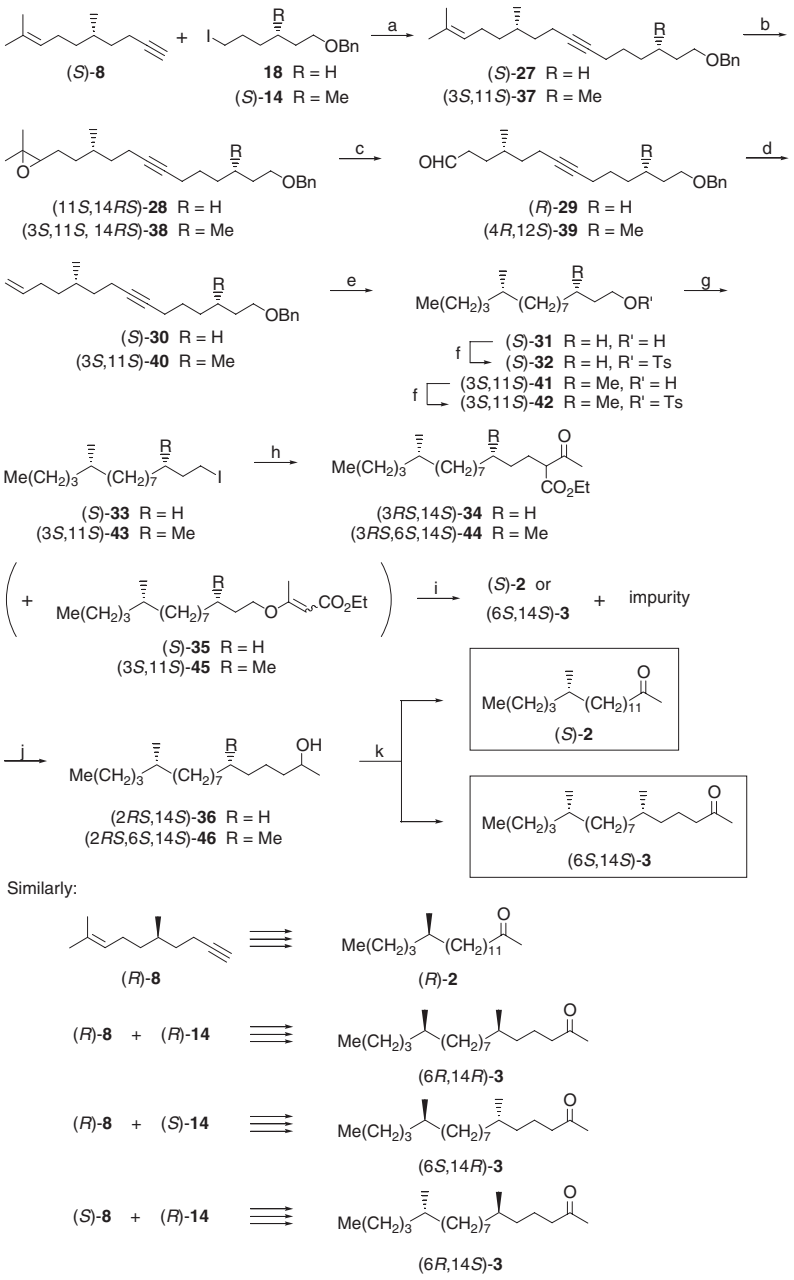
Scheme 5 summarizes the synthesis of the stereoisomers of 14-methyl-2-octadecanone (**2**) and 6,14-dimethyl-2-octadecanone (**3**). Alkylation of (*S*)-**8** with **18** yielded (*S*)-**27** which was epoxidized with MCPBA to give (11*S*,14*RS*)-**28**. Epoxide cleavage of (11*S*,14*RS*)-**28** with periodic acid dihydrate furnished aldehyde (*R*)-**29** which was treated with methylenetriphenylphosphorane to give (*S*)-**30**. Hydrogenation of (*S*)-**30** over palladium-charcoal in acetic acid effected both saturation of the double and triple bonds as well as hydrogenolytic removal of the benzyl protective group to give alcohol (*S*)-**31** in a 69% yield. A small amount of the acetate of (*S*)-**31** was also isolated which, after alkaline hydrolysis, gave an additional amount of (*S*)-**31** [15% based on (*S*)-**30**]. Corresponding tosylate (*S*)-**32** was treated with sodium iodide, yielding (*S*)-**33**.

Acetoacetic ester synthesis employed (*S*)-**33** and ethyl acetoacetate in the presence of potassium carbonate in DMF to give an inseparable mixture of (3*RS*,14*S*)-**34** and (*S*)-**35**. After saponification and decarboxylation, resulting (*S*)-**2** and unchanged (*S*)-**35** (85:15) were reduced with lithium aluminum hydride for the purpose of purification at this stage. Alcohol (2*RS*,14*S*)-**36** could be separated from unreduced by-product (*S*)-**35** by silica gel chromatography. Finally, oxidation of (2*RS*,14*S*)-**36** with Jones chromic acid gave pure (*S*)-**2**, $[\alpha]_D^{25}$ +1.07 (*c* 1.09, hexane). Its IR, ^{1}H- and ^{13}C-NMR, and MS data were identical with those previously reported.[5] The overall yield of (*S*)-**2** based on (*S*)-citronellal was 10% *via* (*S*)-**8** in 16 steps or 4.8% based on hexane-1,6-diol (**15**) in 14 steps.

(*S*)-**8** was alkylated with (*S*)-**14** for the synthesis of (6*S*,14*S*)-**3**. Product (3*S*,11*S*)-**37** was converted to (6*S*,14*S*)-**3** in the same manner as that just described for (*S*)-**2** *via* (3*S*,11*S*)-**38**, **39**, **40**, **41**, **42**, **43**, **44**, and (2*RS*,6*S*,14*S*)-**46**. Final product (6*S*,14*S*)-**3**, $[\alpha]_D^{24}$ +0.59 (*c* 1.01, hexane), showed IR, ^{1}H- and ^{13}C-NMR, and MS data identical with those previously reported.[5] The overall yield of (6*S*,14*S*)-**3** based on (*S*)-citronellal was 7.0% *via* (*S*)-**8** in 16 steps or 3.3% *via* (*S*)-**14** in 18 steps. (6*R*,14*R*)-**3**, $[\alpha]_D^{25}$ −0.42 (*c* 1.03, hexane), was similarly prepared from (*R*)-**8** and (*R*)-**14**; (6*S*,14*R*)-**3**, $[\alpha]_D^{25}$ −1.39 (*c* 1.09, hexane) was prepared from (*R*)-**8** and (*S*)-**14**; and (6*R*,14*S*)-**3**, $[\alpha]_D^{23}$ +1.48 (*c* 1.01, hexane), was synthesized from (*S*)-**8** and (*R*)-**14**.

Conclusion

All of the eight possible stereoisomers of **1**, **2** and **3**, the components of the female sex pheromone of the *Lyclene dharma dharma* moth, were synthesized from the enantiomers of citronellal by using classical reactions. In retrospect, Mori's 2009 synthesis based on olefin cross metathesis was less time-consuming.[5]



Scheme 5. Synthesis of **2** and **3**.

Reagents: (a) *n*-BuLi, THF, HMPA [86% for (*S*)-**27**; 77% for (3*S*,11*S*)-**37**]; (b) MCPBA, CH_2Cl_2 [quant. for (11*S*,14*RS*)-**28**; 99% for (3*S*,11*S*,14*RS*)-**38**]; (c) $HIO_4 \cdot 2H_2O$, THF, Et_2O [65% for (*R*)-**29**; 76% for (4*R*,12*S*)-**39**]; (d) $Ph_3P^+MeBr^-$, *n*-BuLi, THF [83% for (*S*)-**30**; 91% (3*S*,11*S*)-**40**]; (e) H_2/Pd–C, AcOH; then NaOH, MeOH, H_2O [84% for (*S*)-**31**; 82% for (3*S*,11*S*)-**41**]; (f) TsCl, C_5H_5N [87% for (*S*)-**32**; 88% for (3*S*,11*S*)-**42**]; (g) NaI, DMF [84% for (*S*)-**33**; 85% for (3*S*,11*S*)-**43**]; (h) $MeCOCH_2CO_2Et$, K_2CO_3, DMF; (i) NaOH, MeOH, H_2O [84% for (*S*)-**2**; 92% for (6*S*,14*S*)-**3**, 2 steps]; (j) $LiAlH_4$, THF; then SiO_2 chromatography [82% for (2*RS*,14*S*)-**36**; 68% for (2*RS*,6*S*,14*S*)-**46**]; (k) Jones CrO_3, acetone [84% for (*S*)-**2**; 57% for (6*S*,14*S*)-**3**].

A bioassay of these stereoisomers of **1**, **2** and **3** has been carried out by Ando and his co-workers,[9] the results showing that (*S*)-**1** and (*S*)-**2** were bioactive. The absolute configuration and the biological role of natural **3** have remained unknown.[9]

Experimental

Refractive indices (n_D) were measured with an Atago DR-M2 refractometer, and optical rotation values were measured with a Jasco P-1020 polarimeter. IR spectra were measured with a Jasco FT/IR-410 spectrometer, and ^{1}H-NMR spectra (400 MHz, TMS at $\delta = 0.00$ as the internal standard) and ^{13}C-NMR spectra (100 MHz, $CDCl_3$ at $\delta = 77.0$ as the internal standard) were recorded by a Jeol JNM-AL 400 spectrometer. GC-MS data were measured with an Agilent Technologies 5975 Inert XL instrument, and HRMS data were recorded on an Agilent Technologies 6530 Accurate Mass Q-TOF LC/MS instrument. Column chromatography was carried out on Merck Kieselgel 60 Art. 1.07734.

All HRMS data was measured under the following conditions: APCI ionization; positive polarity; 6 μA corona current; N_2 (50 psi) nebulizer; N_2 (5 L/min, 350 °C) drying gas; 350 °C vaporizer; 3000 V capillary current; 0.01 M HCO_2H aq./MeOH (10/90) eluent.

*(3S,6RS)-1-Benzyloxy-6,7-epoxy-3,7-dimethyloctane [(3S,6RS)-**10**].* In the usual manner, (*S*)-**9**[10] {5.01 g, 20.3 mmol, prepared in the same manner as that described in ref. 8, $[\alpha]_D^{19}$ −3.49 (*c* 4.18, hexane)} in CH_2Cl_2 (50 mL) was treated with MCPBA (69% purity, 5.58 g, 22.3 mmol) to give 5.60 g (quant.) of crude (3*S*,6*RS*)-**10** as an oil; IR ν_{max} (film) cm^{-1}: 1250 (m), 1203 (w, C–O–C), 1101 (s, C–O), 872 (w), 737 (s), 698 (s); ^{1}H-NMR δ_H ($CDCl_3$): 0.90 (3H, d, $J = 6.4$ Hz, CH_3),

1.20–1.60 (5H, m), 1.25 (3H, s, CH_3), 1.30 (3H, s, CH_3), 1.60–1.72 (2H, m), 2.68 (1H, t, $J = 6.4$ Hz), 3.46–3.56 (2H, m, CH_2OBn), 4.50 (2H, s, $C_6H_5CH_2$), 7.26–7.34 (5H, m, C_6H_5). This compound was employed for the next step without further purification.

*(*S*)-6-Benzyloxy-4-methylhexanal [(*S*)-**11**].* A solution of crude (3*S*,6*RS*)-**10** (5.60 g, <20.3 mmol) in Et_2O (30 mL) was added to a stirred and ice-cooled solution of $HIO_4 \cdot 2H_2O$ (7.02 g, 30.8 mmol) in THF (30 mL) at 0–10 °C. The mixture was stirred for 1 h at room temperature, before being diluted with water and extracted with Et_2O. The Et_2O solution was successively washed with water, dil. $Na_2S_2O_3$, water, an $NaHCO_3$ solution, and brine, dried ($MgSO_4$), and concentrated *in vacuo*. The residue (4.88 g) was chromatographed over SiO_2 (100 g). Elution with hexane/EtOAc (9:1) gave 3.29 g (73%) of (*S*)-**11** as a colorless oil, n_D^{25} 1.5156; $[\alpha]_D^{25}$ −2.60 (*c* 4.11, hexane); IR ν_{max} (film) cm^{-1}: 1724 (s, C=O), 1203 (w, C–O–C), 1111 (s, C–O), 737 (s), 698 (s); ^{1}H-NMR δ_H ($CDCl_3$): 0.90 (3H, d, $J = 6.4$ Hz, CH_3), 1.40–1.55 (2H, br), 1.58–1.77 (3H, br), 2.38–2.53 (2H, br), 3.46–3.56 (2H, m, CH_2OBn), 4.50 (2H, s, $C_6H_5CH_2$), 7.26–7.34 (5H, m, C_6H_5), 9.76 (1H, CHO); HRMS of (*S*)-**11**: calcd. for $C_{14}H_{21}O_2$ [$(M + H)^+$], 221.1536; found, 221.1542.

*(*S*)-6-Benzyloxy-4-methyl-1-hexanol [(*S*)-**12**].* Reduction of (*S*)-**11** (3.29 g, 14.8 mmol) with $LiAlH_4$ (360 mg, 9.49 mmol) in dry Et_2O (48 mL) gave 3.3 g of crude (*S*)-**12**. This was combined with 11.5 g of crude (*S*)-**12** which had been prepared by extra runs, and the mixture chromatographed over SiO_2 (200 g). Elution with hexane/EtOAc (10:1–3:1) gave 13.5 g (83%) of (*S*)-**13** as an oil, n_D^{23} 1.5013; $[\alpha]_D^{24}$ −2.24 (*c* 4.03, hexane); IR ν_{max} (film) cm^{-1}: 3383 (s, OH), 1205 (w, C–O–C), 1097 (s, C–O), 1057 (m, C–O), 737 (s), 698 (s); ^{1}H-NMR δ_H ($CDCl_3$): 0.90 (3H, d, $J = 6.4$ Hz, CH_3), 1.12–1.70 (8H, m), 3.45–3.55 (2H, m, CH_2OBn), 3.61 (2H, t, $J = 6.4$ Hz, CH_2OH), 4.50 (2H, s, $C_6H_5CH_2$), 7.26–7.34 (5H, m, C_6H_5); HRMS of (*S*)-**12**: calcd. for $C_{14}H_{23}O_2$ [$(M + H)^+$], 223.1693; found, 223.1692.

*(*S*)-6-Benzyloxy-4-methylhexyl tosylate [(*S*)-**13**].* In the same manner as that described previously,[11] (*S*)-**12** (6.88 g, 30.9 mmol) gave 10.6 g (91%) of (*S*)-**13** as an oil; IR ν_{max} (film) cm^{-1}: 1599 (m, arom. C=C), 1358 (s, SO_2), 1176 (s, SO_2), 1097 (s), 964 (s), 916 (s), 816 (s),737 (s), 698 (m), 663 (s), 553 (s); ^{1}H-NMR δ_H ($CDCl_3$): 0.83 (3H, d, $J = 6.4$ Hz, CH_3), 1.08–1.17 (1H, m), 1.26–1.42 (2H, m), 1.50–1.74 (4H, m), 2.44 (3H, s, $C_6H_4CH_3$), 3.41–3.50 (2H, m, CH_2OBn), 4.00 (2H, t, $J = 6.6$ Hz, CH_2OTs), 4.48 (2H, s, $C_6H_5CH_2$), 7.26–7.36 (7H, m), 7.78 (2H, d, $J = 8.0$). This compound was used in the next step without further purification.

*(*S*)-6-Benzyloxy-4-methylhexyl iodide [(*S*)-**14**].* In the same manner as that described previously,[11] (*S*)-**13** (10.2 g, 27.1 mmol) gave 6.71 g (75%) of (*S*)-**14** as a colorless oil, n_D^{25} 1.5373; $[\alpha]_D^{23}$ −7.28 (*c* 4.29, hexane); IR ν_{max} (film) cm^{-1}: 1211 (w, C–O–C), 1174 (w) 1099 (s, C–O), 735 (s), 698 (s), 600 (w); ^{1}H-NMR δ_H ($CDCl_3$): 0.89 (3H, d, $J = 6.4$ Hz, CH_3), 1.18–1.28 (1H, m), 1.36–1.48 (2H, m), 1.59–1.69 (2H, m), 1.73–1.92 (2H, m), 3.11–3.20 (2H, m, CH_2I), 3.46–3.55 (2H, m, CH_2OBn), 4.50 (2H, s, $C_6H_5CH_2$), 7.26–7.35 (5H, m, C_6H_5); HRMS of (*S*)-**14**: calcd. for $C_{14}H_{22}IO$ [$(M + H)^+$], 333.0710; found, 333.0710.

*(*R*)-6-Benzyloxy-4-methylhexyl iodide [(*R*)-**14**].* Similarly, (*R*)-**4** was converted to (*R*)-**14** [45%, 6 steps from (*R*)-**4**]; n_D^{24} 1.5219; $[\alpha]_D^{22}$ +6.39 (*c* 3.58, hexane); its IR and ^{1}H-NMR spectra were identical with those of (*S*)-**14**; HRMS of (*R*)-**14**: calcd. for $C_{14}H_{22}IO$ [$(M + H)^+$], 333.0710; found, 333.0710.

*6-Benzyloxyhexyl tosylate (**17**).* In the same manner as that described for (*S*)-**13**, **16**[12] (12.7 g, 61.0 mmol, which had been prepared in the same manner as that described in ref. 8 gave 20.3 g (92%) of **17** as a colorless oil; IR ν_{max} (film) cm^{-1}: 1599 (m, arom. C=C), 1360 (s, SO_2), 1176 (s, SO_2), 1097 (s), 960 (m), 928 (m), 816 (m), 739 (m), 698 (m), 663 (s), 555 (s); ^{1}H-NMR δ_H ($CDCl_3$): 1.28–1.37 (4H, br), 1.51–1.70 (4H, br), 2.44 (3H, s, $C_6H_4CH_3$), 3.43 (2H, t, $J = 6.6$ Hz, CH_2OBn), 4.02 (2H, t, $J = 6.4$ Hz, CH_2OTs), 4.48 (2H, s, $C_6H_5CH_2$), 7.26–7.40 (7H, m), 7.78 (2H, d, $J = 8.0$ Hz).

*6-Benzyloxyhexyl iodide (**18**).* In the same manner as that described for (*S*)-**14**, **17** (19.7 g, 54.3 mmol) gave 14.8 g (86%) of **18** as an oil, n_D^{23} 1.5434; IR ν_{max} (film) cm^{-1}: 1205 (m, C–O–C), 1169 (w) 1103 (s, C–O), 735 (s), 696 (s), 600 (w); ^{1}H-NMR δ_H ($CDCl_3$): 1.35–1.46 (4H, m), 1.68–1.76 (2H, m), 1.79–1.86 (2H, m), 3.18 (2H, t, $J = 7.2$ Hz, CH_2I), 3.47 (2H, t, $J = 6.6$ Hz, CH_2OBn), 4.50 (2H, s, $C_6H_5CH_2$), 7.26–7.35 (5H, m, C_6H_5); HRMS of **18**: calcd. for $C_{13}H_{20}IO$ [$(M + H)^+$], 319.0553; found, 319.0547.

*1-Benzyloxy-3-methyl-7-pentadecyne (**20**).*

*(i) (*S*)-isomer.* In the same manner as that previously described,[11] (*S*)-**14** (4.00 g, 12.0 mmol) and **19** (2.75 g, 22.1 mmol) gave 3.46 g (87%) of (*S*)-**20** as an oil, n_D^{20} 1.4889; $[\alpha]_D^{24}$ −6.05 (*c* 4.05, hexane); IR ν_{max} (film) cm^{-1}: 1203 (w, C–O–C), 1101 (s, C–O), 735 (s), 696 (s); ^{1}H-NMR δ_H ($CDCl_3$): 0.82–1.02 (6H, m), 1.16–1.77 (17H, m), 2.06–2.28 (4H, br, C≡CCH_2 × 2), 3.46–3.62 (2H, m, CH_2OBn), 4.50 (2H, s, $C_6H_5CH_2$), 7.24–7.50 (5H, m, C_6H_5); HRMS of (*S*)-**20**: calcd. for $C_{23}H_{37}O$ [$(M + H)^+$], 329.2839; found, 329.2843.

*(ii) (*R*)-isomer.* Similarly, (*R*)-**14** (3.00 g, 9.03 mmol) and **19** (2.13 g, 17.1 mmol) gave (*R*)-**20** (2.88 g, 97%) as an oil, n_D^{18} 1.4935; $[\alpha]_D^{20}$ +5.80 (*c* 0.159, hexane). Its IR and ^{1}H-NMR spectra were identical with those of (*S*)-**20**; HRMS of (*R*)-**20**: calcd. for $C_{23}H_{37}O$ [$(M + H)^+$], 329.2839; found, 329.2839.

*3-Methyl-1-pentadecanol (**21**).*

*(i) (*S*)-isomer.* In the usual manner, (*S*)-**20** (3.96 g, 12.1 mmol) in AcOH (35 mL) treated with palladium on charcoal (10%, 880 mg) under H_2 gave 2.59 g (89%) of (*S*)-**21** as an oil, n_D^{21} 1.4510; $[\alpha]_D^{23}$ −3.48 (*c* 3.94, hexane); IR ν_{max} (film) cm^{-1}: 3330 (s, O–H), 1059 (s, C–O); ^{1}H-NMR δ_H ($CDCl_3$): 0.85–0.94 (6H, m), 1.09–1.45 (23H, m), 1.50–1.65 (3H, m), 3.62–3.74 (2H, m, CH_2OH). HRMS data for (*S*)-**21** could not be directly measured, so it was measured after silylation with *N*-methyl-*N*-trimethylsilyltrifluoroacetamide. HRMS of silylated (*S*)-**21**: calcd. for $C_{19}H_{43}OSi$ [$(M + H)^+$], 315.3078; found, 315.3076.

*(ii) (*R*)-isomer.* Similarly, (*R*)-**20** (2.88 g, 8.77 mmol) gave 1.41 g (66%) of (*R*)-**21** as a colorless oil, n_D^{15} 1.4515; $[\alpha]_D^{25}$ +3.51 (*c* 4.23, hexane). Its IR and ^{1}H-NMR spectra were identical with those reported for (*S*)-**21**. HRMS of silylated (*R*)-**21**: calcd. for $C_{19}H_{43}OSi$ [$(M + H)^+$], 315.3078; found, 315.3078.

*3-Methylpentadecyl tosylate (**22**).*

*(i) (*S*)-isomer.* In the same manner as that described for (*S*)-**13**, (*S*)-**21** (2.59 g, 10.7 mmol) gave 4.00 g (94%) of (*S*)-**22** as an oil, $[\alpha]_D^{23}$ −2.42 (*c* 4.06, hexane); IR ν_{max} (film) cm^{-1}: 1599 (m, arom. C=C), 1365 (s, SO_2), 1178 (s, SO_2), 1097 (m), 945 (s), 889 (m), 814 (m), 663 (s), 553 (s); ^{1}H-NMR δ_H ($CDCl_3$): 0.80 (3H, d, $J = 6.4$ Hz, CH_3), 0.88 (3H, t, $J = 6.8$ Hz, CH_3), 0.99–1.57 (24H, m), 1.60–1.72 (1H, m), 2.45 (3H, s, $C_6H_4CH_3$), 4.00–4.10 (2H, m, CH_2OTs), 7.34 (2H, d, $J = 8.0$ Hz, arom. H), 7.79 (2H, d, $J = 8.0$ Hz, arom. H).

*(ii) (*R*)-isomer.* Similarly, (*R*)-**21** (1.38 g, 5.69 mmol) gave 2.03 g (90%) of (*R*)-**22** as an oil, $[\alpha]_D^{26}$ +2.40 (*c* 4.14, hexane). Its IR and ^{1}H-NMR spectra were identical with those of (*S*)-**22**.

*3-Methylpentadecyl iodide (**23**).*

*(i) (*S*)-isomer.* In the same manner as that described for (*S*)-**14**, crude (*S*)-**22** (4.00 g, 10.1 mmol) gave 3.27 g (92%) of (*S*)-**23** as a colorless oil, n_D^{18} 1.4828; $[\alpha]_D^{25}$ +6.11 (*c* 4.07, hexane); IR ν_{max} (film) cm^{-1}: 1178 (w), 606 (w); ^{1}H-NMR δ_H ($CDCl_3$): 0.84–0.91 (6H, m), 1.08–1.35 (22H, br), 1.48–1.57 (1H, br), 1.60–1.69 (1H, m), 1.83–1.92 (1H, m), 3.14–3.28 (2H, m, CH_2I).

*(ii) (*R*)-isomer.* Similarly, crude (*R*)-**22** (2.00 g, 5.04 mmol) gave 1.46 g (82%) of (*R*)-**23** as a colorless oil, n_D^{18} 1.4833; $[\alpha]_D^{26}$ −6.16 (*c* 4.05, hexane). Its IR and ^{1}H-NMR spectra were identical with those of (*S*)-**23**.

*6-Methyl-2-octadecanone (**1**) as a crude mixture contaminated with **25**.*

*(i) (*S*)-isomer.* Powdered K_2CO_3 (4.10 g, 29.7 mmol) was added portionwise to a solution of (*S*)-**23** (1.20 g, 3.41 mmol) and ethyl acetoacetate (2.00 g, 15.4 mmol) in DMF (50 mL). The mixture was vigorously stirred at room temperature for 3 h, before being diluted with water and extracted with hexane and Et_2O. The organic layer was

successively washed with water and brine, dried ($MgSO_4$), and concentrated *in vacuo* to give 1.40 g (quant.) of crude (3*RS*,6*S*)-**24** as an oil. This oil was dissolved in MeOH (10 mL), and 15% NaOH aq (10 g) was added to the solution. The mixture was stirred at reflux for 2 h and, after cooling, it was diluted with water and extracted with hexane. The hexane solution was successively washed with water and brine, dried ($MgSO_4$), and concentrated *in vacuo*. The residue (1.17 g) was chromatographed over SiO_2 (20 g). Elution with hexane/EtOAc (20:1) gave 780 mg (81%, 2 steps) of crude (*S*)-**1** as an oil contaminated with 16% of (*S*)-**25** which had been generated by *O*-alkylation of ethyl acetoacetate with (*S*)-**23**. Ester (*S*)-**25** could not be separated from (*S*)-**1** by chromatographic purification.

(3*RS*,6*S*)-**24**. IR ν_{max} (film) cm^{-1}: 1743 (s, C=O), 1718 (s, C=O), 1624 (m), 1240 (m), 1144 (m, C–O), 1053 (m, C–O); ^{1}H-NMR δ_H ($CDCl_3$): 0.84–0.92 (6H, m), 1.02–1.45 (28H, m), 1.74–1.94 (2H, m), 2.22 (3H, s, CH_3C=O), 3.35 (1H, t, J = 7.4 Hz, CHC=O), 4.16–4.24 (2H, m, CH_3CH_2O).

*(ii) (*R*)-isomer.* Similarly, (*R*)-**23** (1.42 g, 4.03 mmol) gave 960 mg (84%, 2 steps) of crude (*R*)-**1** contaminated with 18% of (*R*)-**25**.

(3*RS*,6*R*)-**24**. Its IR and ^{1}H-NMR spectra were identical with those of (3*RS*,6*S*)-**24**.

*6-Methyl-2-octadecanol (**26**).*

*(i) (*2RS,6S*)-isomer.* Crude (*S*)-**1** contaminated with 16% of (*S*)-**25** (550 mg, <1.95 mmol) was dissolved in dry THF (2 mL), and added dropwise to a stirred and ice-cooled suspension of $LiAlH_4$ (46 mg, 1.2 mmol) in dry THF (8 mL) at 5–10 °C. The mixture was stirred for 1 h at 5–10 °C, and excess $LiAlH_4$ was destroyed by dropwise addition of water to the stirred and ice-cooled mixture. It was then poured into ice-cooled dil. HCl and extracted with Et_2O. The Et_2O solution was successively washed with water, an $NaHCO_3$ solution, and brine, dried ($MgSO_4$), and concentrated *in vacuo*. The residue (516 mg) was chromatographed over SiO_2 (50 g). Elution with hexane/EtOAc (9:1) gave 68 mg of (*S*)-**25** which could not be reduced under these conditions. Further elution with hexane/EtOAc (5:1) afforded 359 mg (65%) of (2*RS*,6*S*)-**26** as an oil.

(*S*)-**25**. IR ν_{max} (film) cm^{-1}: 1712 (s, C=O), 1626 (s, C=C), 1344 (m), 1275 (s, C–O–C), 1140 (s, C–O), 1055 (s, C–O), 820 (m, C=CH); ^{1}H-NMR δ_H ($CDCl_3$): 0.84–0.92 (6H, m), 1.11–1.35 (24H, br), 1.47–1.59 (3H, m), 1.68–1.78 (1H, m), 2.29 (3H, s, CH_3C=C), 3.73–3.82 (2H, m, CH_2O), 4.13 (2H, q, J = 7.2 Hz, CH_3CH_2O), 5.01 (1H, s, C=CH); HRMS of (*S*)-**25**: calcd. for $C_{22}H_{43}O_3$ [$(M + H)^+$], 355.3207; found, 355.3209.

(2*RS*,6*S*)-**26**. n_D^{18} 1.4528; IR ν_{max} (film) cm^{-1}: 3338 (s, O–H), 1119 (m, C–O), 1077 (w); ^{1}H-NMR δ_H ($CDCl_3$): 0.85 (3H, d, J = 6.8 Hz, CH_3), 0.88 (3H, t, J = 6.8 Hz, CH_3), 1.06–1.50 (30H, br), 1.19 (3H, d, J = 6.0 Hz, CH_3), 3.75–3.85 (1H, br, C*H*OH).

*(ii) (*2RS,6R*)-isomer.* Similarly, crude (*R*)-**1** (960 mg) contaminated with 18% of (*R*)-**25** gave 780 mg (80%) of (2*RS*,6*R*)-**26**.

(2*RS*,6*R*)-**26**. n_D^{18} 1.4522. Its IR and ^{1}H-NMR spectra were identical with those of (2*RS*,6*S*)-**26**.

*6-Methyl-2-octadecanone (**1**).*

*(i) (*S*)-isomer.* Jones chromic acid reagent (8 N, 0.5 mL) was added to a stirred and ice-cooled solution of (2*RS*,6*S*)-**26** (359 mg, 1.26 mmol) in acetone (18 mL). The addition was continued until the green mixture had turned orange in color. After stirring for 20 min at 5–10 °C, 2-propanol was added to the ice-cooled mixture until the excess chromic acid had been destroyed. It was then diluted with water and extracted with Et_2O. The Et_2O solution was successively washed with water, an $NaHCO_3$ solution, and brine, dried ($MgSO_4$), and concentrated *in vacuo*. The residue (378 mg) was chromatographed over SiO_2 (30 g), and elution with hexane/EtOAc (20:1) gave 291 mg (82%) of (*S*)-**1** as an oil. This oil solidified in a refrigerator, n_D^{23} 1.4455; $[\alpha]_D^{25}$ −0.39 (*c* 1.15, hexane) {ref. 5, $[\alpha]_D^{28}$ −0.38 (*c* 3.63, hexane)}; IR ν_{max} (film) cm^{-1}: 2925 (s), 2854 (s), 1720 (s, C=O), 1464 (m), 1360 (m), 1165 (m), 721 (m); ^{1}H-NMR δ_H ($CDCl_3$): 0.85 (3H, d, J = 6.8 Hz, CH_3), 0.88 (3H, t, J = 6.8 Hz, CH_3), 1.04–1.15 (2H, br), 1.18–1.45 (23H, br), 1.48–1.67 (2H, br), 2.13 (3H, s, CH_3C=O), 2.40 (2H, t, J = 7.4 Hz, CH_2C=O); ^{13}C-NMR δ_C ($CDCl_3$): 14.1, 19.5, 21.4, 22.7, 27.0, 29.3, 29.60, 29.67, 29.69, 29.8, 30.0, 31.9, 32.6, 36.5, 36.9, 44.1, 209.1 (C=O); GC-MS [HP-5MS column, 5% phenylmethylsiloxane, 30 m × 0.25 mm i.d.; 60.7 kPa pressure; 70–230 °C temperature (+10 °C/min); He carrier gas] t_R: 17.2 min (3%), 18.3 min [96%, (*S*)-**1**], 18.9 min (1%). MS of (*S*)-**1** (70 eV, EI) *m*/*z*: 282 (4) [M^+, $C_{19}H_{38}O$], 264 (66), 239 (16), 123 (15), 110 (30), 109 (34), 95 (29), 85 (42), 71 (56), 58 (100), 43 (85). HRMS of (*S*)-**1**: calcd. for $C_{19}H_{39}O$ [$(M + H)^+$], 283.2995; found, 283.2994.

*(ii) (*R*)-isomer.* Similarly, (2*RS*,6*R*)-**26** (600 mg, 2.11 mmol) gave 440 mg (74%) of (*R*)-**1** as an oil which solidified in a refrigerator, n_D^{22} 1.4462; $[\alpha]_D^{25}$ +0.39 (*c* 1.13, hexane) {ref. 5, $[\alpha]_D^{26}$ +0.35 (*c* 4.08, hexane)}; GC-MS [same conditions as those for (*S*)-**1**] t_R: 18.3 min [98%, (*R*)-**1**], 18.9 min (2%). Its spectral data (IR, ^{1}H- and ^{13}C-NMR, and MS) were identical with those of (*S*)-**1**. HRMS of (*R*)-**1**: calcd. for $C_{19}H_{39}O$ [$(M + H)^+$], 283.2995; found, 283.2995.

*1-Benzyloxy-11,15-dimethyl-14-hexadecen-7-yne(**27**).*

*(i) (*S*)-isomer.* In the same manner as that described for (*S*)-**20**, (*S*)-**8** (4.17 g, 25.4 mmol) and **18** (6.20 g, 19.5 mmol) gave 5.96 g (86%) of (*S*)-**27** as an oil, n_D^{18} 1.4984; $[\alpha]_D^{26}$ −4.69 (*c* 3.43, hexane); IR ν_{max} (film) cm^{-1}: 2117 (w, C≡C), 1672 (w, C=C), 1203 (w, C–O–C), 1103 (m, C–O), 827 (w), 735 (m), 696 (m); ^{1}H-NMR δ_H ($CDCl_3$): 0.87 (3H, d, J = 6.8 Hz, CH_3), 1.08–1.18 (1H, m), 1.23–1.76 (12H, m), 1.60 (3H, s, CH_3), 1.68 (3H, s, CH_3), 1.91–2.05 (2H, m), 2.05–2.24 (4H, m, $C{\equiv}CCH_2$ × 2), 3.47 (2H, t, J = 6.6 Hz, CH_2OBn), 4.50 (2H, s, $C_6H_5CH_2$), 5.07–5.12 (1H, m, C=CH), 7.26–7.34 (5H, m, C_6H_5). HRMS of (*S*)-**27**: calcd. for $C_{25}H_{39}O$ [$(M + H)^+$], 355.2995; found, 355.2996.

*(ii) (*R*)-isomer.* Similarly, (*R*)-**8** (4.70 g, 28.6 mmol) and **18** (7.00 g, 22.0 mmol) gave 6.76 g (87%) of (*R*)-**27** as an oil, n_D^{18} 1.4991; $[\alpha]_D^{25}$ +3.89 (*c* 4.13, hexane). Its IR and ^{1}H-NMR data were identical with those of (*S*)-**27**. HRMS of (*R*)-**27**: calcd. for $C_{25}H_{39}O$ [$(M + H)^+$], 355.2995; found, 355.2995.

*1-Benzyloxy-14,15-epoxy-11,15-dimethyl-7-hexadecyne (**28**).*

*(i) (11*S,14*RS*)-isomer.* In the same manner as that described for (3*S*,6*RS*)-**10**, (*S*)-**27** (5.84 g, 16.5 mmol) gave 6.24 g (quant.) of crude (11*S*,14*RS*)-**28** as an oil; IR ν_{max} (film) cm^{-1}: 2117 (w, C≡C), 1250 (w), 1205 (w, C–O–C), 1115 (m, C–O), 870 (w), 737 (m), 698 (m); ^{1}H-NMR δ_H ($CDCl_3$): 0.89 (3H, d, J = 6.4 Hz, CH_3), 1.10–1.72 (15H, m), 1.27 (3H, s, CH_3), 1.31 (3H, s, CH_3), 2.05–2.25 (4H, m, $C{\equiv}CCH_2$ × 2), 2.69 (1H, t, J = 6.0 Hz), 3.47 (2H, t, J = 6.6 Hz, CH_2OBn), 4.50 (2H, s, $C_6H_5CH_2$), 7.26–7.40 (5H, m, C_6H_5).

*(ii) (11*R,14*RS*)-isomer.* Similarly, (*R*)-**27** (6.70 g, 18.9 mmol) gave 6.86 g (98%) of crude (11*R*,14*RS*)-**28** as an oil. Its IR and ^{1}H-NMR spectra were identical with those of (11*S*,14*RS*)-**28**.

*14-Benzyloxy-4-methyl-7-tetradecynal (**29**).*

*(i) (*R*)-isomer.* In the same manner as that described for (*S*)-**11**, crude (11*S*,14*RS*)-**28** (6.11 g, 16.5 mmol) gave 3.52 g (65%) of (*R*)-**29** as an oil, n_D^{17} 1.5110; $[\alpha]_D^{23}$ −2.53 (*c* 3.92, hexane); IR ν_{max} (film) cm^{-1}: 2117 (w, C≡C), 1726 (s, C=O), 1203 (w, C–O–C), 1101 (s, C–O), 737 (m), 698 (m); ^{1}H-NMR δ_H ($CDCl_3$): 0.89 (3H, d, J = 6.4 Hz, CH_3), 1.20–1.80 (13H, m), 2.08–2.30 (4H, m, $C{\equiv}CCH_2$ × 2), 2.34–2.50 (2H, m), 3.47 (2H, t, J = 6.6 Hz, CH_2OBn), 4.50 (2H, s, $C_6H_5CH_2$), 7.26–7.45 (5H, m, C_6H_5), 9.77 (1H, t-like, CHO). HRMS of (*R*)-**29**: calcd. for $C_{22}H_{33}O_2$ [$(M + H)^+$], 329.2475; found, 329.2474.

*(ii) (*S*)-isomer.* Similarly, crude (11*R*,14*RS*)-**28** (6.80 g, 18.4 mmol) gave 4.42 g (73%) of (*S*)-**29** as an oil, n_D^{17} 1.5122; $[\alpha]_D^{25}$ +2.42 (*c* 4.14, hexane). Its IR and ^{1}H-NMR spectra were identical with those of (*R*)-**29**. HRMS of (*S*)-**29**: calcd. for $C_{22}H_{33}O_2$ [$(M + H)^+$], 329.2475; found, 329.2479.

*1-Benzyloxy-11-methyl-14-pentadecen-7-yne (**30**).*

*(i) (*S*)-isomer.* A solution of *n*-butyllithium in hexane (1.6 M, 12 mL, 19 mmol) was added dropwise to a stirred and cooled suspension of methyltriphenylphosphonium bromide (7.85 g, 22.0 mmol) in dry THF (70 mL) at between −50 and −40 °C under Ar. The temperature was gradually raised to room temperature. After stirring for 4.5 h, the mixture was cooled to −65 °C. A solution of (*R*)-**29** (3.47 g, 10.6 mmol) in dry THF (15 mL) was added dropwise to the stirred and cooled solution at −65 °C, and the mixture was gradually warmed to room temperature. It was stirred overnight, poured into an ice-cooled NH_4Cl solution and then extracted with hexane. The hexane

solution was successively washed with an MeOH/H_2O mixture (3:2), water and brine, dried ($MgSO_4$), and concentrated *in vacuo*. The residue (4.03 g) was chromatographed over SiO_2 (70 g). Elution with hexane/EtOAc (15:1) gave 2.87 g (83%) of (*S*)-**30** as an oil, n_D^{16} 1.5020; $[\alpha]_D^{26}$ −2.69 (*c* 4.06, hexane); IR ν_{max} (film) cm^{-1}: 1639 (m, C=C), 1203 (w, C–O–C), 1101 (s, C–O), 995 (w), 908 (m), 735 (m), 696 (m); ^{1}H-NMR δ_H ($CDCl_3$): 0.87 (3H, d, $J = 6.4$ Hz, CH_3), 1.15–1.67 (13H, m), 1.96–2.22 (6H, m), 3.47 (2H, t, $J = 6.6$ Hz, CH_2OBn), 4.50 (2H, s, $C_6H_5CH_2$), 4.90–5.03 (2H, m, H_2C=CH), 5.75–5.86 (1H, m, H_2C=C*H*), 7.26–7.40 (5H, m, C_6H_5). HRMS of (*S*)-**30**: calcd. for $C_{23}H_{35}O$ [$(M + H)^+$], 327.2682; found, 327.2684.

(ii) (R)*-isomer.* Similarly, (*S*)-**29** (3.45 g, 10.5 mmol) gave 3.05 g (89%) of (*R*)-**30** as an oil, n_D^{15} 1.5022; $[\alpha]_D^{22}$ +2.51 (*c* 0.108, hexane). Its IR and ^{1}H-NMR spectra were identical with those of (*S*)-**30**. HRMS of (*R*)-**30**: calcd. for $C_{23}H_{35}O$ [$(M + H)^+$], 327.2682; found, 327.2686.

*11-Methyl-1-pentadecanol (**31**).*

(i) (S)*-isomer.* Palladium on charcoal (10%, 710 mg) was added to a solution of (*S*)-**30** (2.87 g, 8.79 mmol) in AcOH (29 mL). The suspension was stirred under H_2 (balloon) at room temperature. After stirring overnight, a GC analysis of the solution showed that the reaction had not been completed. Additional palladium on charcoal (10%, 640 mg) was added to the mixture, and it was stirred overnight under H_2 at room temperature. The mixture was then filtered through Celite, and the catalyst and Celite were washed with Et_2O. The filtrate and washings were diluted with Et_2O and then washed with water. The Et_2O solution was successively washed with water, an $NaHCO_3$ solution (3 times) and brine, dried ($MgSO_4$), and concentrated *in vacuo*. The residue (2.14 g) was chromatographed over SiO_2 (40 g). Elution with hexane/EtOAc (3:1) gave 430 mg of acetylated (*S*)-**31** and 1.48 g (69%) of (*S*)-**31**. This acetate was dissolved in MeOH (1 mL) and treated with a 20% NaOH solution (5.3 g) for 1 h at 65 °C. Subsequent workup and chromatographic purification over SiO_2 [8 g, elution with hexane/EtOAc (3:1)] gave 310 mg [15% from (*S*)-**30**] of (*S*)-**31** as a colorless oil. The total yield of (*S*)-**31** was 84%, n_D^{16} 1.4506; $[\alpha]_D^{25}$ +1.16 (*c* 4.28, hexane); IR ν_{max} (film) cm^{-1}: 3330 (s, O–H), 1057 (m, C–O); ^{1}H-NMR δ_H ($CDCl_3$): 0.84 (3H, d, $J = 6.4$ Hz, CH_3), 0.89 (3H, t, $J = 6.6$ Hz, CH_3), 1.02–1.40 (24H, m), 1.53–1.60 (2H, m), 3.62–3.67 (2H, m, CH_2OH). HRMS of silylated (*S*)-**31**: calcd. for $C_{19}H_{43}OSi$ [$(M + H)^+$], 315.3078; found, 315.3073.

(ii) (R)*-isomer.* Similarly, (*R*)-**30** (3.04 g, 9.31 mmol) gave 1.99 g (88%) of (*R*)-**31** as a colorless oil, n_D^{16} 1.4514; $[\alpha]_D^{25}$ −1.15 (*c* 4.07, hexane). Its IR and ^{1}H-NMR spectra were identical with those of (*S*)-**31**. HRMS of silylated (*R*)-**31**: calcd. for $C_{19}H_{43}OSi$ [$(M + H)^+$], 315.3078; found, 315.3085.

*11-Methylpentadecyl tosylate (**32**).*

(i) (S)*-isomer.* In the same manner as that described for (*S*)-**13**, (*S*)-**31** (1.79 g, 7.38 mmol) gave 2.55 g (87%) of (*S*)-**32** as a colorless oil which solidified in a refrigerator, $[\alpha]_D^{24}$ +0.77 (*c* 4.09, hexane); IR ν_{max} (film) cm^{-1}: 1599 (m, arom. C=C), 1365 (s, SO_2), 1178 (s, SO_2), 1097 (m), 957 (m), 926 (m), 814 (s), 663 (s), 555 (s); ^{1}H-NMR δ_H ($CDCl_3$): 0.84 (3H, d, $J = 6.4$ Hz, CH_3), 0.89 (3H, t, $J = 6.6$ Hz, CH_3), 1.00–1.40 (23H, br), 1.58–1.68 (2H, m), 2.45 (3H, s, $C_6H_4CH_3$), 4.02 (2H, t, $J = 6.6$ Hz, CH_2OTs), 7.34 (2H, d, $J = 8.0$ Hz), 7.79 (2H, d, $J = 8.0$ Hz).

(ii) (R)*-isomer.* Similarly, (*R*)-**31** (1.94 g, 8.00 mmol) gave 2.44 g (77%) of (*R*)-**32** as a colorless oil which solidified in a refrigerator, $[\alpha]_D^{26}$ −0.79 (*c* 4.31, hexane). Its IR and ^{1}H-NMR spectra were identical with those of (*S*)-**32**.

*11-Methylpentadecyl iodide (**33**).*

(i) (S)*-isomer.* In the same manner as that described for (*S*)-**14**, (*S*)-**32** (800 mg, 2.02 mmol) gave 600 mg (84%) of (*S*)-**33** as a colorless oil, n_D^{19} 1.4831; $[\alpha]_D^{25}$ +1.00 (*c* 4.01, hexane); IR ν_{max} (film) cm^{-1}: 1180 (m), 600 (w); ^{1}H-NMR δ_H ($CDCl_3$): 0.84 (3H, d, $J = 6.4$ Hz, CH_3), 0.89 (3H, t, $J = 6.8$ Hz, CH_3), 1.01–1.45 (23H, br), 1.78–1.86 (2H, m), 3.19 (2H, t, $J = 7.1$ Hz, CH_2I).

(ii) (R)*-isomer.* Similarly, (*R*)-**32** (2.42 g, 6.10 mmol) gave 1.81 g (84%) of (*R*)-**33** as a colorless oil, n_D^{18} 1.4831; $[\alpha]_D^{25}$ −0.87 (*c* 4.03, hexane). Its IR and ^{1}H-NMR spectra were identical with those of (*S*)-**33**.

*14-Methyl-2-octadecanone (**2**) as a crude mixture contaminated with **35**.*

(i) (S)*-isomer.* In the same manner as that described for crude (*S*)-**1**, (*S*)-**33** (680 mg, 1.93 mmol) and ethyl acetoacetate (1.14 g, 8.76 mmol) gave 740 mg (quant.) of crude (3*RS*,14*S*)-**34** as an oil which contained 15% of (*S*)-**35**. This was treated with 15% NaOH to give 460 mg (84%, 2 steps) of crude (*S*)-**2** contaminated with 15% of (*S*)-**35**.

(3*RS*,14*S*)-**34**. IR ν_{max} (film) cm^{-1}: 1743 (s, C=O), 1718 (s, C=O), 1626 (m), 1240 (m), 1147 (m, C–O), 1043 (m, C–O); ^{1}H-NMR δ_H ($CDCl_3$): 0.84 (3H, d, $J = 6.4$ Hz, CH_3), 0.89 (3H, t, $J = 6.8$ Hz, CH_3), 1.01–1.42 (28H, br), 1.75–1.92 (2H, m), 2.22 (3H, s, CH_3C=O), 3.39 (1H, t, $J = 7.4$ Hz, CHC=O), 4.16–4.24 (2H, m, CH_3CH_2O).

(ii) (R)*-isomer.* Similarly, (*R*)-**33** (1.77 g, 5.02 mmol) and ethyl acetoacetate (3.0 g, 22.7 mmol) gave 1.23 g (87%, 2 steps) of crude (*R*)-**2** contaminated with 18% of (*R*)-**35**. The IR and ^{1}H-NMR spectra of (3*RS*,14*R*)-**34** were identical with those for (3*RS*,14*S*)-**34**.

*14-Methyl-2-octadecanol (**36**).*

(i) (2RS,*14*S)*-isomer.* In the same manner as that described for (2*RS*,6*S*)-**26**, crude (*S*)-**2** (460 mg, <1.63 mmol) contaminated with 18% of (*S*)-**35** gave 380 mg (82%) of (2*RS*,14*S*)-**36** as an oil, n_D^{19} 1.4525; IR ν_{max} (film) cm^{-1}: 3343 (s, O–H), 1120 (m, C–O), 1077 (w); ^{1}H-NMR δ_H (400 MHz, $CDCl_3$): 0.84 (3H, d, $J = 6.4$ Hz, CH_3), 0.89 (3H, t, $J = 6.8$ Hz, CH_3), 1.02–1.52 (30H, br), 1.19 (3H, d, $J = 6.1$ Hz, CH_3), 3.74–3.84 (1H, m).

(ii) (2RS,*14*R)*-isomer.* Similarly, crude (*R*)-**2** (1.23 g, <4.35 mmol) contaminated with 18% of (*R*)-**35** gave (2*RS*,14*R*)-**36** (970 mg, 78%) as an oil, n_D^{18} 1.4522. Its IR and ^{1}H-NMR spectra were identical with those of (2*RS*,14*S*)-**36**.

*14-Methyl-2-octadecanone (**2**).*

(i) (S)*-isomer.* In the same manner as that described for (*S*)-**1**, (2*RS*,14*S*)-**36** (310 mg, 1.09 mmol) gave 260 mg (84%) of (*S*)-**2** as an oil which solidified in a refrigerator, n_D^{22} 1.4472; $[\alpha]_D^{25}$ +1.07 (*c* 1.09, hexane), {ref. 5, $[\alpha]_D^{24}$ +1.05 (*c* 3.13, hexane)}; IR ν_{max} (film) cm^{-1}: 2925 (s), 2854 (s), 1720 (s, C=O), 1466 (m), 1358 (m), 1163 (m), 717 (w); ^{1}H-NMR δ_H ($CDCl_3$): 0.84 (3H, d, $J = 6.8$ Hz, CH_3), 0.89 (3H, t, $J = 6.8$ Hz, CH_3), 1.02–1.16 (2H, br), 1.18–1.46 (23H, br), 1.52–1.62 (2H, br), 2.13 (3H, s, CH_3C=O), 2.41 (2H, t, $J = 7.6$ Hz, CH_2C=O); ^{13}C-NMR δ_C ($CDCl_3$): 14.2, 19.7, 23.0, 23.9, 27.1, 29.2, 29.31, 29.38, 29.44, 29.58, 29.62, 29.7, 29.8, 30.0, 32.7, 36.7, 37.1, 43.8, 209.2 (C=O); GC-MS [same conditions as those for (*S*)-**1**] t_R: 17.4 min (3%), 18.3 min [95%, (*S*)-**2**], 19.0 min (1%), 20.1 min (1%). MS of (*S*)-**2** (70 eV, EI): *m/z*: 282 (23) [M^+, $C_{19}H_{38}O$], 264 (16), 222 (11), 127 (8), 109 (12), 96 (22), 85 (28), 71 (63), 59 (72), 58 (100), 43 (91). HRMS of (*S*)-**2**: calcd. for $C_{19}H_{39}O$ [$(M + H)^+$], 283.2995; found, 283.2993.

(ii) (R)*-isomer.* Similarly, (2*RS*,14*R*)-**36** (690 mg, 2.43 mmol) gave 630 mg (92%) of (*R*)-**2** as an oil which solidified in a refrigerator, n_D^{21} 1.4470; $[\alpha]_D^{25}$ −1.07 (*c* 1.04, hexane) {ref. 5, $[\alpha]_D^{25}$ −0.60 (*c* 3.07, hexane)}; GC-MS [same conditions as those for (*S*)-**1**] t_R: 17.4 (2%), 18.3 [95%, (*R*)-**2**], 19.1 (3%). Its spectral data (IR, ^{1}H and ^{13}C-NMR, and MS) were identical with those of (*S*)-**2**. HRMS of (*R*)-**2**: calcd. for $C_{19}H_{39}O$ [$(M + H)^+$], 283.2995; found, 283.2995.

*1-Benzyloxy-3,11,15-trimethyl-14-hexadecen-7-yne (**37**).*

(i) (3S,*11*S)*-isomer.* In the same manner as that described for (*S*)-**20**, (*S*)-**8** (2.12 g, 12.9 mmol) and (*S*)-**14** (3.30 g, 9.93 mmol) gave 2.82 g (77%) of (3*S*,11*S*)-**37** as a colorless oil, n_D^{21} 1.4989; $[\alpha]_D^{25}$ −9.46 (*c* 3.93, hexane); IR ν_{max} (film) cm^{-1}: 2117 (w, C≡C), 1672 (w, C=C), 1203 (w, C–O–C), 1101 (s, C–O), 825 (w), 735 (s), 696 (s); ^{1}H-NMR δ_H ($CDCl_3$): 0.84–0.92 (6H, m), 1.04–1.88 (12H, m), 1.60 (3H, s, CH_3), 1.68 (3H, s, CH_3), 1.89–2.05 (2H, m), 2.05–2.30 (4H, m, $C{\equiv}CCH_2 \times 2$), 3.46–3.55 (2H, m, CH_2OBn), 4.50 (2H, s, $C_6H_5CH_2$), 5.06–5.13 (1H, br, C=CH), 7.26–7.36 (5H, m, C_6H_5). HRMS of (3*S*,11*S*)-**37**: calcd. for $C_{26}H_{41}O$ [$(M + H)^+$], 369.3152; found, 369.3153.

(ii) (3R,*11*R)*-isomer.* Similarly, (*R*)-**8** (3.82 g, 23.3 mmol) and (*R*)-**14** (5.61 g, 16.9 mmol) gave 5.85 g (94%) of (3*R*,11*R*)-**37** as an oil, n_D^{20} 1.4989; $[\alpha]_D^{25}$ +8.27 (*c* 4.18, hexane). Its IR and ^{1}H-NMR spectra were identical with those of (3*S*,11*S*)-**37**. HRMS of (3*R*,11*R*)-**37**: calcd. for $C_{26}H_{41}O$ [$(M + H)^+$], 369.3152; found, 369.3152.

(iii) (3S,11R)-isomer. Similarly, (*R*)-**8** (2.11 g, 12.8 mmol) and (*S*)-**14** (3.28 g, 9.87 mmol) gave 2.94 g (81%) of (3*S*,11*R*)-**37** as an oil, n_D^{19} 1.4975; $[\alpha]_D^{25}$ −1.12 (*c* 4.10, hexane). Its IR and ^{1}H-NMR spectra were indistinguishable from those of (3*S*,11*S*)-**37**. HRMS of (3*S*,11*R*)-**37**: calcd. for $C_{26}H_{41}O$ $[(M+H)^+]$, 369.3152; found, 369.3151.

(iv) (3R,11S)-isomer. Similarly, (*S*)-**8** (4.00 g, 24.3 mmol) and (*R*)-**14** (6.22 g, 18.7 mmol) gave 5.09 g (74%) of (3*R*,11*S*)-**37** as an oil, n_D^{19} 1.4992; $[\alpha]_D^{26}$ +1.43 (*c* 4.07, hexane). Its IR and ^{1}H-NMR spectra were identical with those of (3*S*,11*R*)-**37**. HRMS of (3*R*,11*S*)-**37**: calcd. for $C_{26}H_{41}O$ $[(M+H)^+]$, 369.3152; found, 369.3152.

*1-Benzyloxy-14,15-epoxy-3,11,15-trimethyl-7-hexadecyne (**38**).*

(i) (3S,11S,14RS)-isomer. In the same manner as that described for (3*S*,6*RS*)-**10**, (3*S*,11*S*)-**37** (2.80 g, 7.60 mmol) gave 2.88 g (99%) of (3*S*,11*S*,14*RS*)-**38** as an oil; IR ν_{max} (film) cm^{-1}: 2116 (w, C≡C), 1250 (w), 1205 (w, C–O–C), 1101 (s, C–O), 870 (w), 737 (m), 698 (m); ^{1}H-NMR δ_H (400 MHz, $CDCl_3$): 0.87–0.90 (6H, m), 1.14–1.74 (14H, m), 1.27 (3H, s, CH_3), 1.31 (3H, s, CH_3), 2.08–2.25 (4H, m, C≡CCH_2 × 2), 2.69 (1H, t-like), 3.44–3.57 (2H, m, CH_2OBn), 4.50 (2H, s, $C_6H_5CH_2$), 7.26–7.40 (5H, m, C_6H_5).

(ii) (3R,11R,14RS)-isomer. Similarly, (3*R*,11*R*)-**37** (5.78 g, 15.7 mmol) gave 4.69 g (78%) of (3*R*,11*R*,14*RS*)-**38** as an oil. Its IR and ^{1}H-NMR spectra were identical with those of (3*S*,11*S*,14*RS*)-**38**.

(iii) (3S,11R,14RS)-isomer. Similarly, (3*S*,11*R*)-**37** (2.92 g, 7.92 mmol) gave 2.80 g (92%) of (3*S*,11*R*,14*RS*)-**38** as an oil. Its IR and ^{1}H-NMR were indistinguishable from those of (3*S*,11*S*,14*RS*)-**38**.

(iv) (3R,11S,14RS)-isomer. Similarly, (3*R*,11*S*)-**37** (5.00 g, 13.6 mmol) gave 4.23 g (81%) of (3*R*,11*S*,14*RS*)-**38** as an oil. Its IR and ^{1}H-NMR spectra were identical with those of (3*S*,11*R*,14*RS*)-**38**.

*14-Benzyloxy-4,12-dimethyl-7-tetradecynal (**39**).*

(i) (4R,12S)-isomer. In the same manner as that described for (*S*)-**11**, crude (3*S*,11*S*,14*RS*)-**38** (2.88 g, 7.49 mmol) gave 1.94 g (76%) of (4*R*,12*S*)-**39** as a colorless oil, n_D^{19} 1.5096; $[\alpha]_D^{26}$ −8.75 (*c* 3.96, hexane); IR ν_{max} (film) cm^{-1}: 2116 (w, C≡C), 1726 (s, C=O), 1203 (w, C–O–C), 1101 (s, C–O), 737 (s), 698 (s); ^{1}H-NMR δ_H ($CDCl_3$): 0.85–0.91 (6H, m), 1.15–1.76 (12H, m), 2.06–2.26 (4H, m, C≡CCH_2 × 2), 2.39–2.48 (2H, m), 3.45–3.55 (2H, m, CH_2OBn), 4.50 (2H, s, $C_6H_5CH_2$), 7.26–7.40 (5H, m, C_6H_5), 9.77 (1H, t-like, CHO). HRMS of (4*R*,12*S*)-**39**: calcd. for $C_{23}H_{35}O_2$ $[(M+H)^+]$, 343.2632; found, 343.2635.

(ii) (4S,12R)-isomer. Similarly, (3*R*,11*R*,14*RS*)-**38** (4.67 g, 12.1 mmol) gave 2.71 g (65%) of (4*S*,12*R*)-**39** as a colorless oil, n_D^{18} 1.5109; $[\alpha]_D^{25}$ +8.09 (*c* 4.15, hexane). Its IR and ^{1}H-NMR spectra were identical with those of (4*R*,12*S*)-**39**. HRMS of (4*S*,12*R*)-**39**: calcd. for $C_{23}H_{35}O_2$ $[(M+H)^+]$, 343.2632; found, 343.2633.

(iii) (4S,12S)-isomer. Similarly, (3*S*,11*R*,14*RS*)-**38** (2.78 g, 7.23 mmol) gave 1.67 g (67%) of (4*S*,12*S*)-**39** as a colorless oil, n_D^{18} 1.5007; $[\alpha]_D^{24}$ −2.56 (*c* 4.00, hexane). Its IR and ^{1}H-NMR spectra were indistinguishable from those of (4*R*,12*S*)-**39**. HRMS of (4*S*,12*S*)-**39**: calcd. for $C_{23}H_{35}O_2$ $[(M+H)^+]$, 343.2632; found, 343.2635.

(iv) (4R,12R)-isomer. Similarly, (3*R*,11*S*,14*RS*)-**38** (4.20 g, 10.9 mmol) gave 2.24 g (60%) of (4*R*,12*R*)-**39** as a colorless oil, n_D^{17} 1.5098; $[\alpha]_D^{24}$ +2.33 (*c* 4.08, hexane). Its IR and ^{1}H-NMR spectra were idetical with those of (4*S*,12*S*)-**39**. HRMS of (4*R*,12*R*)-**39**: calcd. for $C_{23}H_{35}O_2$ $[(M+H)^+]$, 343.2632; found, 343.2623.

*1-Benzyloxy-3,11-dimethyl-14-pentadecen-7-yne (**40**).*

(i) (3S,11S)-isomer. In the same manner as that described for (*S*)-**30**, (4*R*,12*S*)-**39** (1.90 g, 5.55 mmol) gave 1.72 g (91%) of (3*S*,11*S*)-**40** as an oil, n_D^{20} 1.5005; $[\alpha]_D^{25}$ −9.29 (*c* 4.04, hexane); IR ν_{max} (film) cm^{-1}: 1639 (m, C=C), 1203 (w, C–O–C), 1099 (s, C–O), 995 (m), 910 (m), 735 (s), 696 (s); ^{1}H-NMR δ_H ($CDCl_3$): 0.86–0.89 (6H, m), 1.15–1.70 (12H, m), 1.98–2.22 (6H, m), 3.47–3.54 (2H, m, CH_2OBn), 4.50 (2H, s, $C_6H_5CH_2$), 4.91–5.02 (2H, m, H_2C=CH), 5.76–5.86 (1H, m, H_2C=C*H*), 7.26–7.37 (5H, m, C_6H_5). HRMS of (3*S*,11*S*)-**40**: calcd. for $C_{24}H_{37}O$ $[(M+H)^+]$, 341.2839; found, 341.2839.

(ii) (3R,11R)-isomer. Similarly, (4*S*,12*R*)-**39** (2.69 g, 7.85 mmol) gave 2.35 g (88%) of (3*R*,11*R*)-**40** as an oil, n_D^{19} 1.4990; $[\alpha]_D^{25}$ +8.91 (*c* 4.04, hexane). Its IR and ^{1}H-NMR spectra were identical with those of (3*S*,11*S*)-**40**. HRMS of (3*R*,11*R*)-**40**: calcd. for $C_{24}H_{37}O$ $[(M+H)^+]$, 341.2839; found, 341.2838.

(iii) (3S,11R)-isomer. Similarly, (4*S*,12*S*)-**39** (1.64 g, 4.79 mmol) gave 1.48 g (91%) of (3*S*,11*R*)-**40** as an oil, n_D^{18} 1.5009; $[\alpha]_D^{24}$ −2.51 (*c* 4.09, hexane). Its IR and ^{1}H-NMR spectra were indistinguishable from those of (3*S*,11*S*)-**40**. HRMS of (3*S*,11*R*)-**40**: calcd. for $C_{24}H_{37}O$ $[(M+H)^+]$, 341.2839; found, 341.2837.

(iv) (3R,11S)-isomer. Similarly, (4*R*,12*R*)-**39** (2.19 g, 6.39 mmol) gave 1.81 g (83%) of (3*R*,11*S*)-**40** as an oil, n_D^{17} 1.5002; $[\alpha]_D^{25}$ +2.39 (*c* 4.03, hexane). Its IR and ^{1}H-NMR spectra were identical with those of (3*S*,11*R*)-**40**. HRMS of (3*R*,11*S*)-**40**: calcd. for $C_{24}H_{37}O$ $[(M+H)^+]$, 341.2839; found, 341.2837.

*3,11-Dimethyl-1-pentadecanol (**41**).*

(i) (3S,11S)-isomer. In the same manner as that described for (*S*)-**31**, (3*S*,11*S*)-**40** (1.70 g, 4.99 mmol) gave 1.05 g (82%) of (3*S*,11*S*)-**41** as an oil, n_D^{18} 1.4520; $[\alpha]_D^{22}$ −2.39 (*c* 4.00, hexane); IR ν_{max} (film) cm^{-1}: 3325 (s, O–H), 1057 (m, C–O); ^{1}H-NMR δ_H ($CDCl_3$): 0.82–0.94 (9H, m), 1.02–1.45 (23H, m), 1.50–1.67 (2H, m), 3.62–3.75 (2H, br, CH_2OH). HRMS of silylated (3*S*,11*S*)-**41**: calcd. for $C_{20}H_{45}OSi$ $[(M+H)^+]$, 329.3234; found, 329.3237.

(ii) (3R,11R)-isomer. Similarly, (3*R*,11*R*)-**40** (2.30 g, 6.75 mmol) gave 1.60 g (92%) of (3*R*,11*R*)-**41** as an oil, n_D^{17} 1.4523; $[\alpha]_D^{26}$ +2.44 (*c* 4.03, hexane). Its IR and ^{1}H-NMR spectra were identical with those of (3*S*,11*S*)-**41**. HRMS of silylated (3*R*,11*R*)-**41**: calcd. for $C_{20}H_{45}OSi$ $[(M+H)^+]$, 329.3234; found, 329.3235.

(iii) (3S,11R)-isomer. Similarly, (3*S*,11*R*)-**40** (1.44 g, 4.23 mmol) gave 910 mg (84%) of (3*S*,11*R*)-**41** as an oil, n_D^{16} 1.4521; $[\alpha]_D^{24}$ −4.54 (*c* 4.01, hexane). Its IR and ^{1}H-NMR spectra were indistinguishable from those of (3*S*,11*S*)-**41**. HRMS of silylated (3*S*,11*R*)-**41**: calcd. for $C_{20}H_{45}OSi$ $[(M+H)^+]$, 329.3234; found, 329.3235.

(iv) (3R,11S)-isomer. Similarly, (3*R*,11*S*)-**40** (1.80 g, 5.29 mmol) gave 1.12 g (82%) of (3*R*,11*S*)-**41** as an oil, n_D^{16} 1.4523; $[\alpha]_D^{25}$ +4.64 (*c* 4.36, hexane). Its IR and ^{1}H-NMR spectra were identical with those of (3*S*,11*R*)-**41**. HRMS of silylated (3*R*,11*S*)-**41**: calcd. for $C_{20}H_{45}OSi$ $[(M+H)^+]$, 329.3234; found, 329.3237.

*3,11-Dimethylpentadecyl tosylate (**42**).*

(i) (3S,11S)-isomer. In the same manner as that described for (*S*)-**13**, (3*S*,11*S*)-**41** (1.03 g, 4.02 mmol) gave 1.45 g (88%) of (3*S*,11*S*)-**42** as an oil, $[\alpha]_D^{23}$ −2.11 (*c* 0.132, hexane); IR ν_{max} (film) cm^{-1}: 1599 (w, arom. C=C), 1365 (s, SO_2), 1178 (s, SO_2), 1097 (m), 947 (s), 889 (m), 814 (m), 665 (m), 555 (m); ^{1}H-NMR δ_H ($CDCl_3$): 0.80 (3H, d, J = 6.4 Hz, CH_3), 0.84 (3H, d, J = 6.4 Hz, CH_3), 0.89 (3H, t, J = 6.8 Hz, CH_3), 1.02–1.57 (23H, m), 1.61–1.70 (1H, m), 2.45 (3H, s, $C_6H_4CH_3$), 4.02–4.10 (2H, m, CH_2OTs), 7.34 (2H, d, J = 8.0 Hz), 7.79 (2H, d, J = 8.0 Hz).

(ii) (3R,11R)-isomer. Similarly, (3*R*,11*R*)-**41** (1.57 g, 6.12 mmol) gave 1.92 g (76%) of (3*R*,11*R*)-**42** as an oil, $[\alpha]_D^{27}$ +1.76 (*c* 4.04, hexane). Its IR and ^{1}H-NMR spectra were identical with those of (3*S*,11*S*)-**42**.

(iii) (3S,11R)-isomer. Similarly, (3*S*,11*R*)-**41** (910 mg, 3.55 mmol) gave 1.33 g (91%) of (3*S*,11*R*)-**42** as an oil, $[\alpha]_D^{25}$ −3.19 (*c* 4.10, hexane). Its IR and ^{1}H-NMR spectra were indistinguishable from those of (3*S*,11*S*)-**42**.

(iv) (3R,11S)-isomer. Similarly, (3*R*,11*S*)-**41** (1.10 g, 4.29 mmol) gave 1.48 g (84%) of (3*R*,11*S*)-**42** as an oil, $[\alpha]_D^{25}$ +3.28 (*c* 4.15, hexane). Its IR and ^{1}H-NMR spectra were identical with those of (3*S*,11*R*)-**42**.

*3,11-Dimethylpentadecyl iodide (**43**).*

(i) (3S,11S)-isomer. In the same manner as that described for (*S*)-**14**, (3*S*,11*S*)-**42** (700 mg, 1.70 mmol) gave 530 mg (85%) of (3*S*,11*S*)-**43** as an oil, n_D^{17} 1.4827; $[\alpha]_D^{26}$ +6.87 (*c* 4.07, hexane); IR ν_{max} (film) cm^{-1}: 1178 (m), 604 (w); ^{1}H-NMR δ_H ($CDCl_3$): 0.82–0.97 (9H, m), 1.00–1.59 (22H, br), 1.60–1.69 (1H, m), 1.83–1.92 (1H, m), 3.12–3.28 (2H, m, CH_2I).

(ii) (3R,11R)-isomer. Similarly, (3*R*,11*R*)-**42** (1.90 g, 4.63 mmol) gave 1.44 g (85%) of (3*R*,11*R*)-**43** as an oil, n_D^{17} 1.4832; $[\alpha]_D^{25}$ −6.96 (*c* 4.01, hexane). Its IR and ^{1}H-NMR spectra were identical with those of (3*S*,11*S*)-**43**.

(iii) (3S,11R)-isomer. Similarly, (3*S*,11*R*)-**42** (1.30 g, 3.17 mmol) gave 940 mg (81%) of (3*S*,11*R*)-**43** as an oil, n_D^{17} 1.4822; $[\alpha]_D^{25}$ +5.33 (*c* 4.01, hexane). Its IR and ^{1}H-NMR spectra were indistinguishable from those of (3*S*,11*S*)-**43**.

*(iv) (3*R*,11*S*)-isomer.* Similarly, (3*R*,11*S*)-**42** (680 mg, 1.66 mmol) gave 530 mg (87%) of (3*R*,11*S*)-**43** as an oil, n_D^{17} 1.4834; $[\alpha]_D^{25}$ −5.30 (*c* 4.05, hexane). Its IR and ^{1}H-NMR spectra were identical with those of (3*S*,11*R*)-**43**.

*6,14-Dimethyl-2-octadecanone (**3**) as a crude mixture contaminated with **45**.*

*(i) (6*S*,14*S*)-isomer.* In the same manner as that described for crude (*S*)-**1**, (3*S*,11*S*)-**43** (470 mg, 1.28 mmol) and ethyl acetoacetate (750 mg, 5.76 mmol) gave 530 mg (quant.) of crude (3*RS*,6*S*,14*S*)-**44** as an oil. This oil was treated with 15% NaOH to give 350 mg (92%, 2 steps) of (6*S*,14*S*)-**3** contaminated with 20% of (3*S*,11*S*)-**45**.

(3*RS*,6*S*,14*S*)-**44**. IR ν_{max} (film) cm^{-1}: 1743 (s, C=O), 1718 (s, C=O), 1624 (m), 1242 (m), 1142 (m, C–O), 1055 (m, C–O); ^{1}H-NMR δ_H (400 MHz, $CDCl_3$): 0.82–0.93 (9H, m), 1.02–1.45 (27H, br), 1.70–1.94 (2H, m), 2.22 (3H, s, CH_3C=O), 3.35 (1H, t, J = 7.4 Hz, CHC=O), 4.16–4.24 (2H, m, CH_3CH_2O).

*(ii) (6*R*,14*R*)-isomer.* Similarly, (3*R*,11*R*)-**43** (1.41 g, 3.85 mmol) gave 1.51 g (quant.) of crude (3*RS*,6*R*,14*R*)-**44** as an oil. This oil yielded 1.04 g (91%, 2 steps) of crude (6*R*,14*R*)-**3** contaminated with 18% of (3*R*,11*S*)-**45**. The IR and ^{1}H-NMR spectra of (3*RS*,6*R*,14*R*)-**44** were identical with those of (3*RS*,6*S*,14*S*)-**44**.

*(iii) (6*S*,14*R*)-isomer.* Similarly, (3*S*,11*R*)-**43** (940 mg, 2.57 mmol) gave 1.03 g (quant.) of crude (3*RS*,6*S*,14*R*)-**44** as an oil. This oil yielded 700 mg (92%, 2 steps) of crude (6*S*,14*R*)-**3** contaminated with 22% of (3*S*,11*R*)-**45**. The IR and ^{1}H-NMR spectra of (3*RS*,6*S*,14*R*)-**44** were indistinguishable from those of (3*RS*,6*S*,14*S*)-**44**.

*(iv) (6*R*,14*S*)-isomer.* Similarly, (3*R*,11*S*)-**43** (510 mg, 1.39 mmol) gave 550 mg (quant.) of crude (3*RS*,6*R*,14*S*)-**44** as an oil. This oil yielded 380 mg (92%, 2 steps) of crude (6*R*,14*S*)-**3** contaminated with 23% of (3*R*,11*S*)-**45**. The IR and ^{1}H-NMR spectra of (3*RS*,6*R*,14*S*)-**44** were identical with those of (3*RS*,6*S*,14*R*)-**44**.

*6,14-Dimethyl-2-octadecanol (**46**).*

*(i) (2*RS*,6*S*,14*S*)-isomer.* In the same manner as that described for (*S*)-**26**, crude (6*S*,14*S*)-**3** (350 mg, <1.18 mmol) gave 240 mg (68%) of (2*RS*,6*S*,14*S*)-**46** as an oil, n_D^{20} 1.4534; IR ν_{max} (film) cm^{-1}: 3338 (s, O–H), 1120 (m, C–O), 1077 (w); ^{1}H-NMR δ_H ($CDCl_3$): 0.82–0.92 (9H, m), 0.98–1.49 (29H, br), 1.19 (3H, d, J = 6.1 Hz, CH_3), 3.74–3.86 (1H, br).

*(ii) (2*RS*,6*R*,14*R*)-isomer.* Similarly, crude (6*R*,14*R*)-**3** (1.04 g, <3.51 mmol) gave 830 mg (79%) of (2*RS*,6*R*,14*R*)-**46**, n_D^{19} 1.4528. Its IR and ^{1}H-NMR spectra were identical with those of (2*RS*,6*S*,14*S*)-**46**.

*(iii) (2*RS*,6*S*,14*R*)-isomer.* Similarly, crude (6*S*,14*R*)-**3** (700 mg, <2.36 mmol) gave 490 mg (70%) of (2*RS*,6*S*,14*R*)-**46**, n_D^{21} 1.4529. Its IR and ^{1}H-NMR spectra were indistinguishable from those of (2*RS*,6*S*,14*S*)-**46**.

*(iv) (2*RS*,6*R*,14*S*)-isomer.* Similarly, crude (6*R*,14*S*)-**3** (380 mg, <1.28 mmol) gave 260 mg (68%) of (2*RS*,6*R*,14*S*)-**46**, n_D^{20} 1.4532. Its IR and ^{1}H-NMR spectra were identical with those of (2*RS*,6*S*,14*R*)-**46**.

*6,14-Dimethyl-2-octadecanone (**3**).*

*(i) (6*S*,14*S*)-isomer.* In the same manner as that described for (*S*)-**1**, (2*RS*,6*S*,14*S*)-**46** (210 mg, 0.703 mmol) gave 120 mg (57%) of (6*S*,14*S*)-**3** as an oil, n_D^{21} 1.4471; $[\alpha]_D^{24}$ +0.59 (*c* 1.01, hexane) {ref. 5, $[\alpha]_D^{26}$ +0.65 (*c* 3.81, hexane)}; IR ν_{max} (film) cm^{-1}: 2954 (m), 2925 (s), 2854 (s), 1720 (s, C=O), 1462 (m), 1377 (m), 1360 (m), 1163 (m), 725 (w); ^{1}H-NMR δ_H ($CDCl_3$): 0.82–0.92 (9H, m), 1.02–1.15 (4H, br), 1.15–1.44 (20H, br), 1.48–1.66 (2H, m), 2.13 (3H, s, CH_3C=O), 2.40 (2H, t, J = 7.6 Hz, CH_2C=O); ^{13}C-NMR δ_C ($CDCl_3$): 14.2, 19.6, 19.8, 21.5, 23.1, 27.09, 27.15, 29.4, 29.8, 30.05, 30.09, 32.7, 32.8, 36.6, 36.8, 36.9, 37.1, 44.2, 209.2 (C=O); GC-MS [same conditions as those for (*S*)-**1**] t_R: 17.8 min (3%), 18.8 min [89%, (6*S*,14*S*)-**3**], 19.5 min (2%), 20.6 min (1%), 22.1 min (5%). MS of (6*S*,14*S*)-**3** (70 eV, EI) *m*/*z*: 296 (4) [M^+, $C_{20}H_{40}O$], 278 (62), 253 (16), 236 (12), 123 (19), 110 (34), 109 (41), 95 (32), 85 (45), 71 (55), 58 (93), 43 (100). HRMS of (6*S*,14*S*)-**3**: calcd. for $C_{20}H_{41}O$ [$(M + H)^+$], 297.3152; found, 297.3152.

*(ii) (6*R*,14*R*)-isomer.* Similarly, (2*RS*,6*R*,14*R*)-**46** (580 mg, 1.9 mmol) gave 520 mg (90%) of (6*R*,14*R*)-**3** as an oil, n_D^{23} 1.4476; $[\alpha]_D^{25}$ −0.42 (*c* 1.03, hexane) {ref. 5, $[\alpha]_D^{27}$ −0.50 (*c* 2.65, hexane)}; GC-MS [same conditions as those for (*S*)-**1**] t_R: 17.8 min (4%), 18.8 min [94%, (6*R*,14*R*)-**3**], 19.5 min (2%). Its spectral data (IR, ^{1}H- and ^{13}C-NMR, and MS) were identical with those of (6*S*,14*S*)-**3**. HRMS of (6*R*,14*R*)-**3**: calcd. for $C_{20}H_{41}O$ [$(M + H)^+$], 297.3152; found, 297.3153.

*(iii) (6*S*,14*R*)-isomer.* Similarly, (2*RS*,6*S*,14*R*)-**46** (490 mg, 1.64 mmol) gave 330 mg (68%) of (6*S*,14*R*)-**3** as an oil, n_D^{21} 1.4486; $[\alpha]_D^{25}$ −1.39 (*c* 1.09, hexane) {ref. 5, $[\alpha]_D^{27}$ −1.16 (*c* 3.07, hexane)}; GC-MS [same conditions as those for (*S*)-**1**] t_R: 17.8 min (3%), 18.8 min [93%, (6*S*,14*R*)-**3**], 19.5 min (2%), 22.1 min (2%). Its spectral data (IR, ^{1}H- and ^{13}C-NMR, and MS) were indistinguishable from those of (6*S*,14*S*)-**3**. HRMS of (6*S*,14*R*)-**3**: calcd. for $C_{20}H_{41}O$ [$(M + H)^+$], 297.3152; found, 297.3152.

*(iv) (6*R*,14*S*)-isomer.* Similarly, (2*RS*,6*R*,14*S*)-**46** (260 mg, 0.871 mmol) gave 230 mg (89%) of (6*R*,14*S*)-**3** as an oil, n_D^{22} 1.4463; $[\alpha]_D^{23}$ +1.48 (*c* 1.01, hexane) {ref. 5, $[\alpha]_D^{24}$ +1.54 (*c* 3.07, hexane)}; GC-MS [same conditions as those for (*S*)-**1**] t_R: 17.8 min (4%), 18.8 min [93%, (6*R*,14*S*)-**3**], 19.5 min (1%), 20.6 min (2%). Its spectral data (IR, ^{1}H- and ^{13}C-NMR, and MS) were identical with those of (6*S*,14*R*)-**3**. HRMS of (6*R*,14*S*)-**3**: calcd. for $C_{20}H_{41}O$ [$(M + H)^+$], 297.3152; found, 297.3154.

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