Synthesis of All the Stereoisomers of 13,17-Dimethyl-1-tritriacontene and 13,17-Dimethyl-1-pentatriacontene, the Contact Sex Pheromone Components of the Female Tsetse Fly, *Glossina austeni*[‡]

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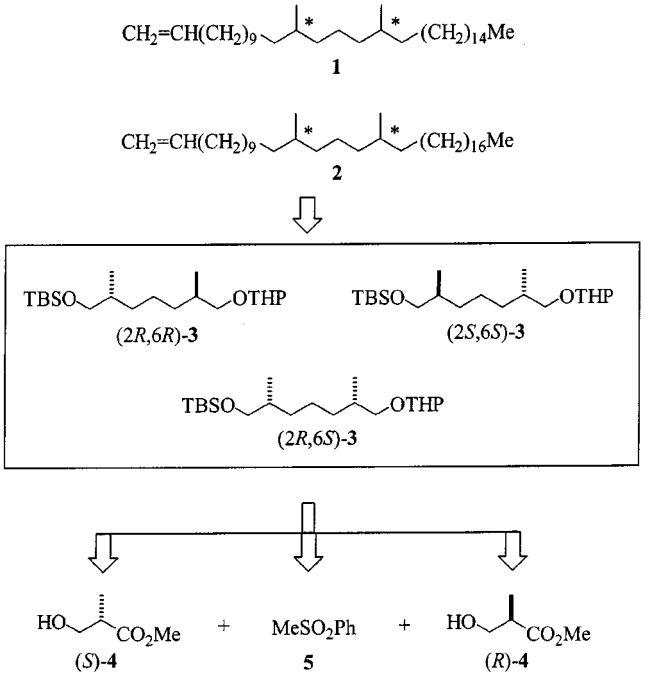
All of the stereoisomers of 13,17-dimethyl-1-tritriacontene (**1**) and 13,17-dimethyl-1-pentatriacontene (**2**), the contact sex pheromone components of the female tsetse fly (*Glossina austeni*), were synthesized starting from the enantiomers of the protected *syn*- and *anti*-2,6-dimethylheptane-1,7-diol (**3**), which were prepared from the enantiomers of methyl 3-hydroxy-2-methylpropanoate (**4**) and methyl phenyl sulfone (**5**).

Introduction

Tsetse flies are a hazard to the health of humans and cattle in Africa because they spread the notorious sleeping sickness. Therefore the elucidation of the pheromone communication system among tsetse flies may help in modern biocontrol efforts against this disease vector by ensuring that the correct strain of fly is used in large-scale sterile male release. The widespread, abundant and economically important species *Glossina austeni* is the tsetse fly that is under consideration for such control schemes.

Recently Carlson and co-workers isolated and identified two alkenes as the components of the female-produced contact sex pheromone in the cuticular wax of *G. austeni*.[1] They are 13,17-dimethyl-1-tritriacontene (**1**, Scheme 1) and 13,17-dimethyl-1-pentatriacontene (**2**), both with two stereogenic centers.

We became interested in synthesizing all the stereoisomers of **1** and **2** for the purpose of establishing the absolute configuration of the natural products. Scheme 1 shows the retrosynthetic analysis of **1** and **2**. It is evident that all the stereoisomers of **1** and **2** can be derived from the three stereoisomers of the building block **3**. The *anti*-stereoisomers (2*R*,6*R*)- and (2*S*,6*S*)-**3** were recently prepared by us employing **4** and **5** as the starting materials, and used for the synthesis of the pheromone components of the apple leafminer.[2] The *syn*-stereoisomer (2*R*,6*S*)-**3** is also a known compound.[3,4]



Scheme 1. Structures and retrosynthetic analysis of the sex pheromone components **1** and **2** of the tsetse fly, *Glossina austeni*

Results and Discussion

We first developed a new synthesis of (2*R*,6*S*)-**3** as shown in Scheme 2. This type of *syn*-1,5-dimethylated chiral building block was previously prepared by the enzymatic desymmetrization of *syn*-2,6-dimethylheptane-1,6-diol (**A**) with isopropenyl acetate in the presence of lipase PS to give the optically active half-acetate **B**.[3,4] This preparative route, however, was rather lengthy and cumbersome due to the difficulty in preparing **A**, and gave **B** in an overall yield of 23% with only about 95% *de* and 95% *ee*.[4] The unsatisfactory *de* of **A** was due to the low diastereoselectivity in the course of its preparation, while the imperfect enantiomeric purity of **B** was caused by the incomplete enantioselectivity of lipase PS to acetylate **A**. Considering the commercial availability of almost pure enantiomers of methyl 3-hydroxy-2-methylpropanoate [(*R*)-**4**, ≈100% *ee*; (*S*)-**4**, 99.8% *ee*], we envisaged that the coupling strategy previously ad-

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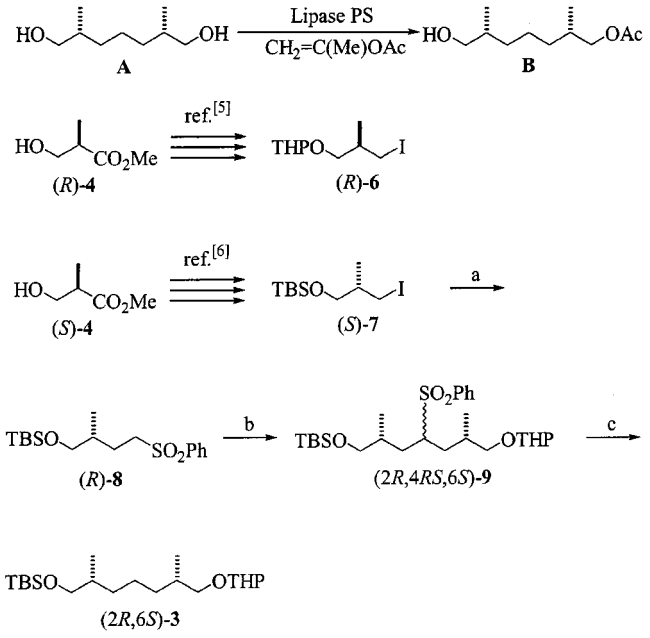
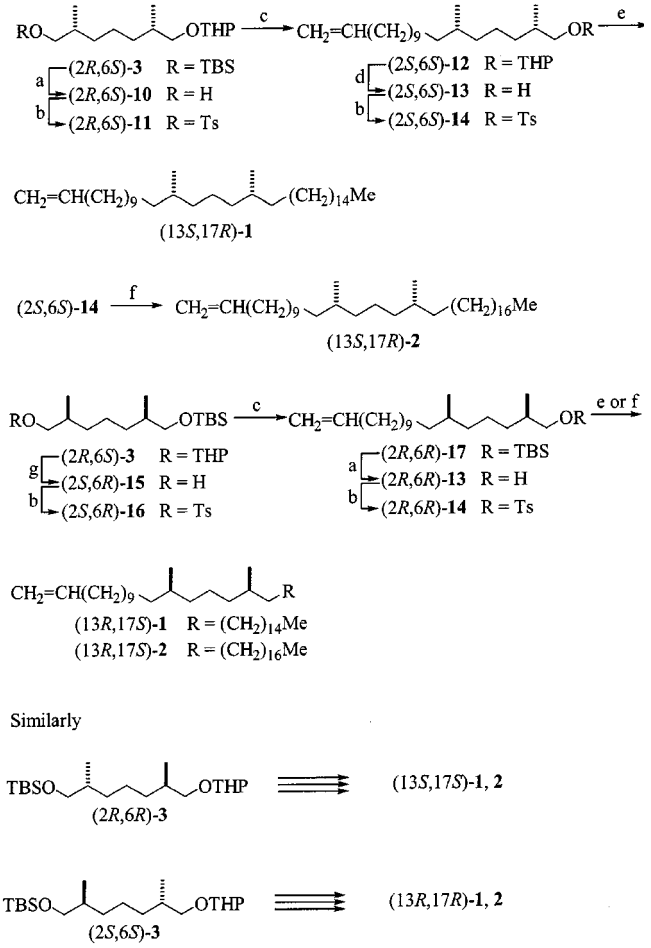
opted by us for the synthesis of (2*R*,6*R*)- and (2*S*,6*S*)-**3**[2] would give better results than the known-enzymatic method of preparation[3] in both chemical and optical yields. The results summarized in Scheme 2 indeed confirmed our premise.



Scheme 2. Synthesis of the building block (2*R*,6*R*)-**3**: reagents: (a) $MeSO_2Ph$, *n*BuLi, THF/HMPA (78%); (b) *n*BuLi, (*R*)-**6**, THF/HMPA (89%); (c) i) Na-Hg, EtOH; ii) MCPBA, CH_2Cl_2, SiO_2 chromatog. (73%)

The starting (*R*)-**4** was converted into the known iodide (*R*)-**6**.[5] (*S*)-**4** was then converted into another known iodide (*S*)-**7**.[6] Alkylation of the anion derived from methyl phenyl sulfone with (*S*)-**7** furnished (*R*)-**8**.[7] The anion subsequently derived from (*R*)-**8** was alkylated with (*R*)-**6** to yield (2*R*,4*RS*,6*S*)-**9**. Finally the phenylsulfonyl group of **9** was removed by treatment with sodium amalgam to give crude (2*R*,6*S*)-**3** contaminated with a small amount (ca. 5%) of alkenes generated by β-elimination of the phenylsulfonyl group. The olefinic impurities were epoxidized with *m*-chloroperbenzoic acid (MCPBA) to give a separable mixture of (2*R*,6*S*)-**3** and the epoxides. Purification of the mixture by silica gel chromatography afforded pure (2*R*,6*S*)-**3** in 29% overall yield based on (*R*)-**4** (7 steps). Reflecting the high enantiomeric purity of (*R*)- and (*S*)-**4**, the product (2*R*,6*S*)-**3** was of high stereochemical purity (>99% *de* and >99% *ee*, see Exp. Sect.). It was therefore proved that the classical iterative connection strategy to provide (2*R*,6*S*)-**3** was better than the aesthetically appealing enzymatic desymmetrization strategy by virtue of the availability of the enantiomerically pure chiral building blocks (*R*)- and (*S*)-**4**.

Scheme 3 summarizes the conversion of (2*R*,6*S*)-**3** to the target alkenes **1** and **2**. Removal of the *tert*-butyldimethylsilyl (TBS) protective group of (2*R*,6*S*)-**3** afforded the alcohol (2*R*,6*S*)-**10**, which was tosylated to give (2*R*,6*S*)-**11**. Chain-elongation of **11** with 10-undecenylmagnesium bromide in the presence of dilithium tetrachlorocuprate[8] gave (2*S*,6*S*)-**12**, whose tetrahydropyranyl (THP) group was removed to give the alkenol (2*S*,6*S*)-**13**. This was tosylated to give the tosylate (2*S*,6*S*)-**14**. Further chain elongation of (2*S*,6*S*)-**14** with pentadecylmagnesium bromide under the Schlosser conditions[9] yielded (13*S*,17*R*)-13,17-dimethyl-1-tritriacontene (**1**). By employing heptadecylmagnesium bromide, (13*S*,17*R*)-13,17-dimethyl-1-pentatriacontene (**2**) was also synthesized. The overall yield of (13*S*,17*R*)-**1** and that of (13*S*,17*R*)-**2** were both 12% based on (*S*)-**4** (13 steps).



Scheme 3. Synthesis of the stereoisomers of **1** and **2**: reagents: (a) $(n\text{Bu})_4NF$, THF (quant.); (b) TsCl, C_5H_5N (quant.); (c) $CH_2=CH(CH_2)_9MgBr$, Li_2CuCl_4, THF [60% for (2*S*,6*S*)-**12**; 67% for (2*R*,6*R*)-**17**]; (d) *p*-TsOH, EtOH (93%); (e) $Me(CH_2)_{14}MgBr$, Li_2CuCl_4, THF [80% for (13*S*,17*R*)-**1**; 70% for (13*R*,17*S*)-**1**]; (f) $Me(CH_2)_{16}MgBr$, Li_2CuCl_4, THF [76% for (13*S*,17*R*)-**2**; 54% for (13*R*,17*S*)-**2**]; (g) Me_2AlCl, CH_2Cl_2 (90%)

For the synthesis of the (13*R*,17*S*)-isomers of **1** and **2**, (2*R*,6*S*)-**3** was converted into (2*S*,6*R*)-**15** by treatment with dimethylaluminum chloride in dichloromethane[9] to remove only the THP group of **3**. The corresponding tosylate (2*S*,6*R*)-**16** gave (2*R*,6*R*)-**17** after chain elongation with 10-undecenylmagnesium bromide. Deprotection of (2*R*,6*R*)-**17** gave the free alcohol (2*R*,6*R*)-**13**, whose tosylate (2*R*,6*R*)-**14** was subjected to a second chain elongation to give (13*R*,17*S*)-**1** and (13*R*,17*S*)-**2**, respectively. The overall yield of (13*R*,17*S*)-**1** and that of (13*R*,17*S*)-**2** were both 9% based on (*S*)-**4** (13 steps). In the same manner, (2*R*,6*R*)-**3**[2] yielded

(13*S*,17*S*)-**1** and (13*S*,17*S*)-**2**, while (2*S*,6*S*)-**3**[2] furnished (13*R*,17*R*)-**1** and (13*R*,17*R*)-**2**. It should be added that the *syn*-13,17-dimethylated **1** and **2** showed $[\alpha]_D$ values (±0.05 and ±0.17 in hexane) rather smaller than those (±0.27 and ±0.52 in hexane) of the *anti*-13,17-dimethylated **1** and **2**.

These synthetic stereoisomers of **1** and **2** were sent to the U.S.A. to compare them with the natural products. The mass spectra of these synthetic hydrocarbons **1** and **2** show near coincidence with the mass spectra of the natural pheromone molecules. The two natural dimethylalkenes had small amounts of inseparable isomers with their methyl branches in different locations. This is suggested by the mass spectra of the corresponding alkanes isolated at the same time from *Glossina austeni*.[1] Such isomers would contribute fragment ions missing from the mass spectra of the very clean synthetic compounds **1** and **2**. The scrambling of hydrogen ions in the mass spectra of both natural and synthetic alkenes is also curious, an effect not really conspicuous in unbranched alkenes.[1] An additional complication is the comparison of high molecular weight mass spectra recorded on different quadrupole instruments over a period of 20 years, complicated by mass defects caused by so many hydrogens, and the necessity to tune instruments specifically for high mass ranges.

In conclusion we synthesized each of the four stereoisomers of **1** and **2**. These stereoisomers are now being biotested, and the result will hopefully establish the absolute configuration of the pheromone components of *Glossia austeni*. The *syn*-1,5-dimethylated building block (2*R*,6*S*)-**3** will serve as a versatile chiral building block in the synthesis of *syn*-1,5-dimethylated aliphatic compounds.

Experimental Section

General: IR: Jasco A-102. − ^{1}H NMR: Jeol JNM-EX 90A (90 MHz), Jeol JNM-LA400 (400 MHz) and Jeol JNM-LA500 (500 MHz) (TMS at δ = 0.00 or $CHCl_3$ at δ = 7.26 as an internal standard). − ^{13}C NMR: Jeol JNM-LA500 (126 MHz) ($CDCl_3$ at δ = 77.0 as an internal standard). − GC MS: Shimadzu QP5050A with a DB-5® column (15 m × 0.25 mm). − Optical rotation: Jasco DIP-1000. − Column chromatography: Merck Kieselgel 60 Art 1.07734. − TLC: 0.25 mm Merck silica gel plates (60F-254).

(2*R*,4*RS*,6*S*)-1-*tert*-Butyldimethylsilyloxy-2,6-dimethyl-4-phenylsulfonyl-7-tetrahydropyranyloxyheptane [(2*R*,4*RS*,6*S*)-9]: Under argon atmosphere, a solution of *n*-butyllithium in hexane (1.50 M, 12 mL, 18.0 mmol) at −78 °C was added dropwise to a stirred and cooled solution of (*R*)-**8** (5.07 g, 14.8 mmol) in dry THF (50 mL) and dry HMPA (10 mL). After the addition, the mixture was kept at −30 °C for 15 min. and then recooled to −78 °C. A solution of (*R*)-**6** (5.13 g, 18.1 mmol) in dry THF (50 mL) was then added dropwise to the reaction mixture at −78 °C with stirring. The mixture was stirred at ambient temperature for 28 h, then poured into sat. aqueous NH_4Cl and water at 0 °C, and extracted with diethyl ether. The combined organic phases were washed with water and brine, dried with $MgSO_4$, and concentrated in vacuo. The residue was chromatographed on silica gel (200 g, hexane/ethyl acetate, 50:1) to give 6.66 g (89%) of (2*R*,4*RS*,6*S*)-**9** as a yellow oil; n_D^{24} = 1.4961. − $[\alpha]_D^{21}$ = +3.91 (*c* = 1.04, hexane). − IR (film): $\tilde{\nu}_{max}$ = 1590 cm^{-1} (w, aromatic), 1310 (s, SO_2), 1255 (s, Si−CH_3), 1090 (s, Si−O), 1040 (s, C−O). − ^{1}H NMR (90 MHz, $CDCl_3$): δ = 0.00, 0.01 (each s, total 6 H, Si−CH_3), 0.85, 0.87 (each s, total 9 H, *t*Bu), 0.62−1.10 (m, 6 H, 2-, 6-CH_3), 1.10−2.20 (m, 12 H, 2-, 6-H, 3-, 5-, 3′−5′-H_2), 2.91−4.18 (m, 7 H, 4-H, 1-, 7-, 6′-H_2), 4.51 (br. s, 1 H, 2′-H), 7.37−7.70 (m, 3 H, Ar-H), 7.70−7.97 (m, 2 H, Ar-H). − $C_{26}H_{46}O_5SSi$ (498.7): calcd. C 62.61, H 9.31; found C 62.33, H 9.24.

(2*R*,6*S*)-1-*tert*-Butyldimethylsilyloxy-2,6-dimethyl-7-tetrahydropyranyloxyheptane [(2*R*,6*S*)-3]: Under argon atmosphere, a solution of (2*R*,4*RS*,6*S*)-**9** (2.2 g, 4.41 mmol) in dry ethanol (30 mL) was added dropwise to 5% sodium amalgam (19.2 g, sodium 0.96 g, 42 mmol) at 0 °C. The mixture was stirred vigorously at room temperature for 25 h. It was then filtered through Celite, and the filter cake was washed several times with diethyl ether. The combined filtrate and washings were concentrated in vacuo to give crude (2*R*,6*S*)-**3**. This crude material contained ca. 5% of olefinic compounds formed by elimination of the phenylsulfonyl group from (2*R*,4*RS*,6*S*)-**9**. The crude (2*R*,6*S*)-**3** was dissolved in CH_2Cl_2 (20 mL), and *m*-CPBA (0.38 g, 2.2 mmol) was added. The mixture was stirred at room temperature for 18 h, then a sat. aqueous sodium thiosulfate and sat. aqueous $NaHCO_3$ were added, and extracted with CH_2Cl_2. The combined organic phases were washed with water and brine, dried with $MgSO_4$, and concentrated in vacuo. The residue was chromatographed on silica gel (30 g, hexane/ethyl acetate, 25:1) to remove the contaminating epoxide and give 1.16 g (73%) of (2*R*,6*S*)-**3** as a colorless oil; n_D^{23} = 1.4499. − $[\alpha]_D^{21}$ = +2.21 (*c* = 1.09, hexane). − IR (film): $\tilde{\nu}_{max}$ = 1255 cm^{-1} (s, Si−CH_3), 1110 (s, Si−O), 1035 (s, C−O). − ^{1}H NMR (90 MHz, $CDCl_3$): δ = 0.03 (s, 6 H, Si−CH_3), 0.89 (s, 9 H, *t*Bu), 0.48−1.14 (m, 6 H, 2-, 6-CH_3), 1.14−2.02 (m, 14 H, 2-, 6-H, 3-, 5-, 3′−5′-H_2), 3.02−4.05 (m, 6 H, 1-, 7-, 6′-H_2), 4.56 (br. s, 1 H, 2′-H). − $C_{20}H_{42}O_3Si$ (358.6): calcd. C 66.98, H 11.81; found C 66.66, H 11.62.

(2*R*,6*S*)-2,6-Dimethyl-7-tetrahydropyranyloxy-1-heptanol [(2*R*,6*S*)-10]: (nBu)$_4$NF (1.0 M solution in dry THF, 4.20 mL, 4.20 mmol) at room temperature was added to a solution of (2*R*,6*S*)-**3** (1.16 g, 3.23 mmol) in dry THF (10 mL). After stirring at room temperature for 18 h, the mixture was poured into water and extracted with diethyl ether. The combined organic phases were washed with sat. aqueous $NaHCO_3$ and brine, dried with $MgSO_4$, and concentrated in vacuo. The residue was chromatographed on silica gel (20 g, hexane/ethyl acetate, 5:1) to give 0.79 g (quant.) of (2*R*,6*S*)-**10**; n_D^{23} = 1.4591. − $[\alpha]_D^{21}$ = +9.30 (*c* = 1.32, hexane). − IR (film): $\tilde{\nu}_{max}$ = 3400 cm^{-1} (s, O−H), 1120 (s, C−O), 1035 (s, C−O). − ^{1}H NMR (90 MHz, $CDCl_3$): δ = 0.91 (d, *J* = 6.3 Hz, 6 H, 2-, 6-CH_3), 1.03−1.93 (m, 15 H, 2-, 6-H, 3−5-, 3′−5′-H_2, OH), 2.93−4.02 (m, 6 H, 1-, 7-, 6′-H_b), 4.56 (br. s, 1 H, 2′-H). − $C_{14}H_{28}O_3$ (244.4): calcd. C 68.81, H 11.55; found C 68.76, H 11.76.

(2*R*,6*R*)-2,6-Dimethyl-7-tetrahydropyranyloxy-1-heptanol [(2*R*,6*R*)-10]: In the same manner as described above, (2*R*,6*R*)-**3** (0.99 g, 2.7 mmol) was converted into 0.63 g (95%) of (2*R*,6*R*)-**10** (as a colorless oil); n_D^{23} = 1.4609. − $[\alpha]_D^{23}$ = +2.26 (*c* = 1.29, hexane). Its IR and NMR spectra were almost identical with those of (2*R*,6*S*)-**10**. − $C_{14}H_{28}O_3$ (244.4): calcd. C 68.81, H 11.55; found C 68.96, H 11.78.

(2*S*,6*S*)-2,6-Dimethyl-7-tetrahydropyranyloxy-1-heptanol [(2*S*,6*S*)-10]: In the same manner as described for the preparation of (2*R*,6*S*)-**10**, (2*S*,6*S*)-**3** (2.03 g, 5.66 mmol) was converted into 1.34 g (97%) of (2*S*,6*S*)-**10** (as a colorless oil); n_D^{24} = 1.4590. − $[\alpha]_D^{22}$ = −3.07 (*c* = 1.17, hexane). Its IR and NMR spectra were identical with those of (2*R*,6*R*)-**10**. − $C_{14}H_{28}O_3$ (244.4): calcd. C 68.81, H 11.55; found C 68.90, H 11.59.

(2*R*,6*S*)-2,6-Dimethyl-7-tetrahydropyranyloxyheptyl *p*-Toluenesulfonate [(2*R*,6*S*)-11]: *p*-Toluenesulfonyl chloride (670 mg, 3.51 mmol) was added to a solution of (2*R*,6*S*)-**10** (665 mg, 2.72 mmol) in dry pyridine (7 mL) at 0 °C. After stirring at 4 °C for 12 h, the mixture was poured into water at 0 °C and extracted with diethyl ether. The combined organic phases were washed with sat. aqueous $CuSO_4$, sat. aqueous $NaHCO_3$ and brine, dried with $MgSO_4$, and concentrated in vacuo to give 1.10 g (quant.) of crude (2*R*,6*S*)-**11**. This was employed in the next step without further purification. − IR (film): $\tilde{\nu}_{max}$ = 1360 cm^{-1} (s, SO_2), 1180 (s, SO_2), 1120 (m, SO_2), 1030 (s, C−O). − ^1H NMR (300 MHz, $CDCl_3$): δ = 0.88 (d, *J* = 6.9 Hz, 6 H, 2-, 6-CH_3), 0.97−1.90 (m, 14 H, 2-, 6-H, 3−5-, 3′−5′-H_2), 2.45 (s, 3 H, Ar-CH_3), 3.07−4.16 (m, 6 H, 1-, 7-, 6′-H_a), 4.53 (br, 1 H, 2′-H), 7.34 (d, *J* = 8.1 Hz, 2 H, Ar-H), 7.80 (d, *J* = 8.1 Hz, 2 H, Ar-H).

(2*R*,6*R*)-2,6-Dimethyl-7-tetrahydropyranyloxyheptyl *p*-Toluenesulfonate [(2*R*,6*R*)-11]: In the same manner as described above, (2*R*,6*R*)-**10** (238 mg, 1.15 mmol) was converted into 387 mg (quant.) of (2*R*,6*R*)-**11**. This was employed in the next step without further purification. Its IR and NMR spectra were almost identical with those of (2*R*,6*S*)-**11**.

(2*S*,6*S*)-2,6-Dimethyl-7-tetrahydropyranyloxyheptyl *p*-Toluenesulfonate [(2*S*,6*S*)-11]: In the same manner as described for the preparation of (2*R*,6*S*)-**11**, (2*S*,6*S*)-**10** (1.23 g, 5.03 mmol) was converted into 1.95 g (98%) of (2*S*,6*S*)-**11**. This was employed in the next step without further purification. Its IR and NMR spectra were identical with those of (2*R*,6*R*)-**11**.

(2*S*,6*S*)-2,6-Dimethyl-1-tetrahydropyranyloxy-17-octadecene [(2*S*,6*S*)-12]: Magnesium (410 mg, 16.9 mmol) was added to an argon-purged flask. A solution of 11-bromo-1-undecene (2.62 g, 11.2 mmol) in dry THF (25 mL) was added dropwise to the metal and the mixture was stirred at room temperature for 1 h. The resulting solution was used immediately. Under argon atmosphere, the above Grignard reagent and a solution of Li_2CuCl_4 in dry THF (0.32 M, 0.85 mL, 0.27 mmol) at −78 °C were added to a solution of (2*R*,6*S*)-**11** (1.10 g, 2.72 mmol) in dry THF (10 mL). The mixture was allowed to warm up to 4 °C, and stirred at 4 °C for 12 h. The mixture was quenched with sat. aqueous NH_4Cl and water, and extracted with diethyl ether. The combined organic phases were washed with brine, dried with $MgSO_4$, and concentrated in vacuo. The residue was chromatographed on silica gel (40 g, hexane/ethyl acetate, 75:1) to give 619 mg (60%) of (2*S*,6*S*)-**12** as a colorless oil; n_D^{29} = 1.4554. − $[\alpha]_D^{26}$ = +1.75 (*c* = 1.10, hexane). − IR (film): $\tilde{\nu}_{max}$ = 1640 cm^{-1}(m, C=C), 1120 (s, C−O), 1035 (s, C−O). − ^1H NMR (300 MHz, $CDCl_3$): δ = 0.84 (d, *J* = 6.3 Hz, 3 H, 6-CH_3), 0.98−1.90 (m, 35 H, 2-CH_3, 6-H, 3−5-, 7−15-, 3−5′-H_2, 2-, 6-H), 2.04 (q, *J* = 6.6 Hz, 2 H, 16-H_2), 3.04−3.92 (m, 4 H, 1-, 6′-H_2), 4.50−4.52 (m, 1 H, 2′-H), 4.88−5.04 (m, 2 H, 18-H_2), 5.73−5.90 (m, 1 H, 17-H). − $C_{25}H_{48}O_2$ (380.6): calcd. C 78.88, H 12.71; found C 79.11, H 12.80.

(2*R*,6*S*)-2,6-Dimethyl-1-tetrahydropyranyloxy-17-octadecene [(2*R*,6*S*)-12]: In the same manner as described above, (2*R*,6*R*)-**11** (396 mg, 0.993 mmol) was converted into 321 mg (85%) of (2*R*,6*S*)-**12** (as a colorless oil); n_D^{23} = 1.4601. − $[\alpha]_D^{22}$ = − 3.64 (*c* = 1.01, hexane). Its IR and NMR spectra were almost identical with those of (2*S*,6*S*)-**12**. − $C_{25}H_{48}O_2$ (380.6): calcd. C 78.88, H 12.71; found C 78.77, H 13.04.

(2*S*,6*R*)-2,6-Dimethyl-1-tetrahydropyranyloxy-17-octadecene [(2*S*,6*R*)-12]: In the same manner as described for the preparation of (2*S*,6*S*)-**12**, (2*S*,6*S*)-**11** (1.95 g, 4.89 mmol) was converted into 1.19 g (62%) of (2*S*,6*R*)-**12** (as a colorless oil); n_D^{20} = 1.4602. − $[\alpha]_D^{22}$ = +2.08 (*c* = 1.06, hexane). Its IR and NMR spectra were identical with those of (2*R*,6*S*)-**12**. − $C_{25}H_{48}O_2$ (380.6): calcd. C 78.88, H 12.71; found C 78.72, H 12.48.

(2*S*,6*S*)-2,6-Dimethyl-17-octadecen-1-ol [(2*S*,6*S*)-13]: *p*-Toluenesulfonic acid monohydrate (10.0 mg, 0.06 mmol) was added to a solution of (2*S*,6*S*)-**12** (519 mg, 1.36 mmol) in 95% EtOH (5 mL) and the mixture was warmed up to 50 °C. The mixture was stirred for 5 h at 50 °C and then cooled to room temperature. After neutralization with K_2CO_3, the mixture was extracted with diethyl ether. The combined organic phases were washed with sat. aqueous $NaHCO_3$ and brine, dried with $MgSO_4$ and concentrated in vacuo. The residue was chromatographed on silica gel (10 g, hexane/ethyl acetate, 30:1) to give 377 mg (93%) of (2*S*,6*S*)-**13** as a colorless oil; n_D^{26} = 1.4529. − $[\alpha]_D^{26}$ = −6.56 (*c* = 1.01, hexane). − IR (film): $\tilde{\nu}_{max}$ = 3330 cm^{-1} (s, O−H), 1640 (m, C=C). − ^1H NMR (300 MHz, $CDCl_3$): δ = 0.84 (d, *J* = 6.3 Hz, 3 H, 6-CH_3), 0.92 (d, *J* = 6.9 Hz, 3 H, 2-CH_3), 0.98−1.69 (m, 27 H, 2-, 6-H, 3-, 5-, 7-, 15-H_2, OH), 2.04 (q, *J* = 6.6 Hz, 2 H, 16-H_2), 3.37−3.57 (m, 2 H, 1-H_a), 4.86−5.03 (m, 2 H, 18-H_a), 5.74−5.90 (m, 1 H, 17-H). − $C_{20}H_{40}O$ (296.5): calcd. C 81.01, H 13.59; found C 81.21, H 13.78.

(2*R*,6*S*)-2,6-Dimethyl-17-octadecen-1-ol [(2*R*,6*S*)-13]: In the same manner as described above, (2*R*,6*S*)-**12** (318 mg, 0.835 mmol) was converted into 165 mg (88%) of (2*R*,6*S*)-**13** (as a colorless oil); n_D^{24} = 1.4496. − $[\alpha]_D^{26}$ = +6.35(*c* = 0.95, hexane). Its IR and NMR spectra were almost identical with those of (2*S*,6*S*)-**13**. − $C_{25}H_{48}O_2$ (296.5): calcd. C 81.01, H 13.59; found C 80.93, H 13.70.

(2*S*,6*R*)-2,6-Dimethyl-17-octadecene-1-ol [(2*S*,6*R*)-13]: In the same manner as described for the preparation of (2*S*,6*S*)-**13**, (2*S*,6*R*)-**12** (1.08 g, 28.4 mmol) was converted into 0.71 g (84%) of (2*S*,6*R*)-**12** (as a colorless oil); n_D^{22} = 1.4600. − $[\alpha]_D^{28}$ = −6.62 (*c* = 1.05, hexane). Its IR and NMR spectra were identical with those of (2*R*,6*S*)-**13**. − $C_{25}H_{48}O_2$ (296.5): calcd. C 81.01, H 13.59; found C 80.81, H 13.87.

(2*S*,6*S*)-2,6-Dimethyl-17-octadecenyl *p*-Toluenesulfonate [(2*S*,6*S*)-14]: *p*-Toluenesulfonyl chloride (264 mg, 1.38 mmol) was added to a solution of (2*S*,6*S*)-**13** (316 mg, 1.06 mmol) in dry pyridine (3 mL) at 0 °C. After stirring at 4 °C for 15 h, the mixture was poured into water at 0 °C and extracted with diethyl ether. The combined organic phases were washed with sat. aqueous $CuSO_4$, sat. aqueous $NaHCO_3$ and brine, dried with $MgSO_4$, and concentrated in vacuo to give 463 mg (97%) of crude (2*S*,6*S*)-**14**. This was employed in the next step without further purification. − IR (film): $\tilde{\nu}_{max}$ = 1640 cm^{-1} (m, C=C), 1600 (m, aromatic), 1365 (s, SO_2), 1180 (s, SO_2). − ^1H NMR (90 MHz, $CDCl_3$): δ = 0.64−0.94 (m, 2-, 6-CH_3), 0.94−2.13 (m, 28 H, 2-, 6-H, 3−5-, 7−16-H_2), 2.45 (s, 3 H, Ar-CH_3), 3.84 (dd, *J* = 3.0, 5.7 Hz, 2 H, 1-H_a), 4.82−5.10 (m, 2 H, 18-H_2), 5.55−6.01 (m, 1 H, 17-H), 7.34 (d, *J* = 8.2 Hz, 2 H, Ar-H), 7.78 (d, *J* = 8.2 Hz, 2 H, Ar-H).

(2*R*,6*S*)-2,6-Dimethyl-17-octadecenyl *p*-Toluenesufonate [(2*R*,6*S*)-14]: In the same manner as described above, (2*R*,6*S*)-**13** (165 mg, 0.55 mmol) was converted into 231 mg (95%) of (2*R*,6*S*)-**14**. This was employed in the next step without further purification. Its IR and NMR spectra were almost identical with those of (2*S*,6*S*)-**14**.

(2*S*,6*R*)-2,6-Dimethyl-17-octadecenyl *p*-Toluenesufonate [(2*S*,6*R*)-14]: In the same manner as described for the preparation of (2*S*,6*S*)-**14**, (2*S*,6*R*)-**13** (192 mg,0.64 mmol) was converted into 289 mg (quant.) of (2*S*,6*R*)-**14**. This was employed in the next step without further purification. Its IR and NMR spectra were identical with those of (2*R*,6*S*)-**14**.

(13*S*,17*R*)-13,17-Dimethyl-1-tritriacontene [(13*S*,17*R*)-1]: Magnesium (83 mg, 3.41 mmol) was added to an argon-purged flask. A solution of 1-bromopentadecane(710 mg, 2.44 mmol) in dry THF (7 mL) was added dropwise to the metal, and the mixture was stirred at room temperature for 1 h. The resulting solution was used immediately. Under argon atmosphere, the above Grignard reagent and a solution of Li_2CuCl_4 in dry THF (0.32 M, 0.20 mL, 0.10 mmol) were added to a solution of (2*S*,6*S*)-**14** (246 mg, 0.56 mmol) in dry THF (3 mL) at −78 °C. The mixture was allowed to warm to 4 °C, and stirred at this temperature for 24 h. The mixture was quenched with sat. aqueous NH_4Cl and water, and extracted with distilled hexane. The combined organic phases were washed with brine, dried with $MgSO_4$, and concentrated in vacuo. The residue was chromatographed on silica gel (20 g, hexane) and silver nitrate-impregnated silica gel (20%, 25 g) to give 222 mg (80%) of (13*S*,17*R*)-**1** as a colorless oil; n_D^{24} = 1.4580. − $[\alpha]_D^{25}$ = +0.17 (*c* = 1.40, $CHCl_3$). − IR (film): $\tilde{\nu}_{max}$ = 3080 cm^{-1} (w, C=C−H), 2930 (s, C−H), 2850 (s, C−H), 1640 (m, C=C), 1460 (s, C−H), 1380 (m, C−H), 990 (w), 910 (s), 720 (w). − ^1H NMR (500 MHz, $CDCl_3$): δ = 0.84 (d, *J* = 8.0 Hz, 6 H, 13-, 17-CH_3), 0.88 (t, *J* = 8.5 Hz, 3 H, 33-H_3), 0.99−1.45 (m, 56 H, 13-, 17-H, 4−12-, 14−16-, 18−32-H_2), 2.04 (q, *J* = 9.5 Hz, 2 H, 3-H_2), 4.86−5.05 (m, 2 H, 1-H_2), 5.73−5.87 (m,1 H, 2-H). − ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.1, 19.8, 22.7, 24.5, 27.1, 29.0, 29.2, 29.4, 29.6, 29.70, 29.72, 29.75, 29.79, 30.1, 32.0, 32.8, 33.9, 37.1, 37.2, 37.5, 114.1, 139.2. − EI MS (70 eV): *m*/*z* (%) = 491 (1.6) [M^+ +1], 336 (0.8), 321(0.9), 280 (2.4), 266 (6.2), 251 (9.5), 250 (10.4), 210 (12.1), 192 (20.8), 182 (9.0), 167 (9.9), 153 (13.0), 139 (22.3), 125 (45.4), 111 (100.0). − $C_{35}H_{70}$ (490.9): calcd. C 85.63, H 14.37; found C 85.88, H 14.63. − GC [column: DB-5® (0.25 mm × 30 m), 200 to 320 °C/min., +4.0 °C/min.; carrier gas: He, pressure: 100 kPa]: t_R = 32.4 min. (97.8% chemical purity).

(13*S*,17*S*)-13,17-Dimethyl-1-tritriacontene [(13*S*,17*S*)-1]: In the same manner as described above, (2*R*,6*S*)-**14** (220 mg, 0.506 mmol) was converted into 127 mg (45%) of (13*S*,17*S*)-**1** (as a colorless oil); n_D^{22} = 1.4574. $[\alpha]_D^{22}$ = +0.49 (*c* = 2.20, hexane). Its IR, NMR and MS spectra were almost identical with those of (13*S*,17*R*)-**1**. − $C_{35}H_{70}$ (490.9): calcd. C 85.63, H 14.37; found C 85.53, H 14.66. − GC [column: DB-5®(0.25 mm × 30 m), 200 to 320 °C/min., +4.0 °C/min.; carrier gas: He, pressure: 100 kPa]: t_R = 32.9 min. (98.0% chemical purity).

(13*R*,17*R*)-13,17-Dimethyl-1-tritriacontene [(13*R*,17*R*)-1]: In the same manner as described above for the preparation of (13*S*,17*R*)-**1**, (2*S*,6*R*)-**14** (275 mg, 0.633 mmol) was converted into 218 mg (70%) of (13*R*,17*R*)-**1** (as a colorless oil); n_D^{24} = 1.4563. − $[\alpha]_D^{24}$ = −0.40 (*c* = 3.35, hexane). Its IR, NMR and MS spectra were identical with those of (13*S*,17*S*)-**1**. − $C_{35}H_{70}$ (490.9): calcd. C 85.63, H 14.37; found C 85.38, H 14.60. − GC [column: DB-5® (0.25 mm × 30 m), 200 to 320 °C/min., +4.0 °C/min.; carrier gas: He, pressure: 100 kPa]: t_R = 32.9 min. (97.9% chemical purity).

(13*S*,17*R*)-13,17-Dimethyl-1-pentatriacontene [(13*S*,17*R*)-2]: Magnesium (82 mg, 3.4 mmol) was added to an argon-purged flask. A solution of 1-bromoheptadecane (670 mg, 2.10 mmol) in dry THF (7 mL) was added dropwise to the metal, and the mixture was stirred at room temperature for 1 h. The resulting solution was used immediately. Under argon atmosphere, the above Grignard reagent and a solution of Li_2CuCl_4 in dry THF (0.32 M, 0.16 mL, 0.051 mmol) were added to a solution of (2*S*,6*S*)-**14** (230 mg, 0.53 mmol) in dry THF (3 mL) at −78 °C. The mixture was allowed to warm to 4 °C, and stirred at this temperature for 36 h. The mixture was quenched with sat. aqueous NH_4Cl and water, and then extracted with distilled hexane. The combined organic phases were washed with brine, dried with $MgSO_4$, and concentrated in vacuo. The residue was chromatographed on silica gel (20 g, hexane) and silver nitrate-impregnated silica gel (20%, 25 g) to give 207 mg (76%) of (13*S*,17*R*)-**2** as a colorless oil; n_D^{28} = 1.4591. − $[\alpha]_D^{28}$ = +0.055 (*c* = 1.90, hexane). − IR (film): $\tilde{\nu}_{max}$ = 3100 cm^{-1} (w, C=C−H), 2940 (s, C−H), 2860 (s, C−H), 1640 (m, C=C), 1460 (s, C−H), 1380 (m, C−H), 990 (w), 910 (m), 720 (w). − ^1H NMR (500 MHz, $CDCl_3$): δ = 0.84 (d, *J* = 8.2 Hz, 6 H, 13-, 17-CH_3), 0.88 (t, *J* = 8.8 Hz, 3 H, 35-H_3), 1.00−1.45 (m, 60 H, 13-, 17-H, 4−12-, 14−16-, 18−34-H_2), 2.04 (q, *J* = 9.4 Hz, 2 H, 3-H_2), 4.87−5.05 (m, 2 H, 1-H_2), 5.72−5.87 (m, 1 H, 2-H). − ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.1, 19.8, 22.7, 24.5, 27.1, 29.0, 29.2, 29.4, 29.5, 29.6, 29.74, 29.77, 30.1, 32.0, 32.8, 33.8, 37.1, 37.5, 114.1, 139.2. − EI MS (70 eV): *m*/*z* (%) = 519 (0.6) [M^+ +1], 365 (0.4), 349 (0.5), 321 (0.6), 308 (0.6), 278 (8.1), 210 (9.0), 195 (20.4), 139 (22.0), 125 (45.6), 111 (100.0). − $C_{37}H_{74}$ (519.0): calcd. C 85.63, H 14.37; found C 85.69, H 14.39. − GC [column: DB-5® (0.25 mm × 30 m), 200 to 320 °C/min., +4.0 °C/min.; carrier gas: He, pressure: 100 kPa]: t_R = 36.7 min. (98.5% chemical purity).

(13*S*,17*S*)-13,17-Dimethyl-1-pentatriacontene [(13*S*,17*S*)-2]: In the same manner as described above, (2*R*,6*S*)-**14** (97 mg, 0.22 mmol) was converted into 72 mg (65%) of (13*S*,17*S*)-**2** (as a colorless oil); n_D^{24} = 1.4496. − $[\alpha]_D^{26}$ = +0.52 (*c* = 3.01, hexane). Its IR, NMR and MS spectra were almost identical with those of (13*S*,17*R*)-**2**. − $C_{37}H_{74}$ (519.0): calcd. C 85.63, H 14.37; found C 85.81, H 14.56. − GC [column: DB-5® (0.25 mm × 30 m), 200 to 320 °C/min., +4.0 °C/min.; carrier gas: He, pressure: 100 kPa]: t_R = 36.4 min. (96.5% chemical purity).

(13*R*,17*R*)-13,17-Dimethyl-1-pentatriacontene [(13*R*,17*R*)-2]: In the same manner as described for the preparation of (13*S*,17*R*)-**2**, (2*S*,6*R*)-**14** (271 mg, 0.623 mmol) was converted into 234 mg (70%) of (13*R*,17*R*)-**2** (as a colorless oil); n_D^{24} = 1.4600. − $[\alpha]_D^{23}$ = −0.27 (*c* = 2.84, hexane). Its IR, NMR and MS spectra were identical with those of (13*S*,17*S*)-**2**. − $C_{37}H_{74}$ (519.0): calcd. C 85.63, H 14.37; found C 85.35, H 14.55. − GC [column: DB-5® (0.25 mm × 30 m), 200 to 320 °C/min., +4.0 °C/min.; carrier gas: He, pressure: 100 kPa]: t_R = 36.5 min. (98.2% chemical purity).

(2*S*,6*R*)-7-*tert*-Butyldimethylsilyloxy-2,6-dimethyl-1-heptanol [(2*S*,6*R*)-15]: Under argon atmosphere, a solution of dimethylaluminum chloride in hexane (1.01 M, 8.3 mL, 8.38 mmol) was added dropwise to a stirred and cooled solution of (2*R*,6*S*)-**3** (1.50 g, 4.18 mmol) in dry CH_2Cl_2 (15 mL) at −30 °C. After the addition, the mixture was stirred at ambient temperature for 44 h, then poured into sat. aqueous $NaHCO_3$ and extracted with diethyl ether. The combined organic phases were washed with sat. aqueous $NaHCO_3$ and brine, dried with $MgSO_4$, and concentrated in vacuo. The residue was chromatographed on silica gel (30 g, hexane/ethyl acetate, 30:1) to give 1.03 g (90%) of (2*S*,6*R*)-**15** as a colorless oil; n_D^{22} = 1.4449. − $[\alpha]_D^{27}$ = −3.49 (*c* = 1.10, $CHCl_3$). − IR (film): $\tilde{\nu}_{max}$ = 3340 cm^{-1} (s, O−H), 1250 (s, Si−CH_3), 1095 (s, Si−O). − ^1H NMR (90 MHz, $CDCl_3$): δ = 0.03 (s, 6 H, Si−CH_3), 0.89 (s, 9 H, *t*Bu), 0.58−1.82 (m, 15 H, 2-, 6-H, 3-, 5-H_2, 2-, 6-CH_3, OH), 3.10−3.67 (m, 4 H, 1-, 7-H_2). − $C_{15}H_{34}O_2Si$ (274.2): calcd. C 65.63, H 12.48; found C 65.47, H 12.71.

(2*S*,6*R*)-2,6-Dimethyl-7-(*tert*-butyldimethylsilyloxyheptyl) *p*-Toluenesulfonate [(2*S*,6*R*)-16]: *p*-Toluenesulfonyl chloride (0.82 g, 4.3 mmol) was added to a solution of (2*S*,6*R*)-**15** (0.91 g, 3.3 mmol) in dry pyridine (10 mL) at 0 °C. After stirring at 4 °C for 24 h, the mixture was poured into water at 0 °C and extracted with diethyl ether. The combined organic phases were washed with sat. aqueous $CuSO_4$, sat. aqueous $NaHCO_3$ and brine, dried with $MgSO_4$, and

concentrated in vacuo to give 1.33 g (98%) of crude (2*S*,6*R*)-**16**. This was employed in the next step without further purification. − IR (film): $\tilde{\nu}_{max}$ = 1600 cm^{-1} (w, aromatic), 1365 (s, SO_2), 1250 (s, Si−CH_3), 1175 (s, SO_2), 1100 (s, Si−O), 1020 (w, C−O). − ^1H NMR (90 MHz, $CDCl_3$): δ = 0.03 (s, 6 H, Si-CH_3), 0.89 (s, 9 H, *t*Bu) 0.58−2.00 (m, 14 H, 2-, 6-H, 3−5-H_2, 2-,6-CH_3), 2.45 (s, 3 H, Ar-CH_3), 3.37 (dd, *J* = 1.8, 4.5 Hz, 2 H, 7-H_2), 3.85 (dd, *J* = 2.7, 4.5 Hz, 2 H, 1-H_2), 7.34 (d, *J* = 8.1 Hz, 2 H, Ar-H), 7.78 (d, *J* = 8.1 Hz, 2 H, Ar-H).

(2*R*,6*R*)-2,6-Dimethyl-1-*tert*-butyldimethylsilyloxy-17-octadecene [(2*R*,6*R*)-17]: Magnesium (0.48 g, 20 mmol) was added to an argon-purged flask. A solution of 11-bromo-1-undecene (3.09 g, 13.3 mmol) in dry THF (30 mL) was added dropwise to the metal, and the mixture was stirred at room temperature for 1 h. The resulting solution was used immediately. Under argon atmosphere, the above Grignard reagent and a solution of Li_2CuCl_4 in dry THF (0.32 M, 1.0 mL, 0.27 mmol) were added to a solution of (2*S*,6*R*)-**16** (1.33 g, 3.22 mmol) in dry THF (13 mL) at −78 °C. The mixture was allowed to warm up to 4 °C, and stirred at this temperature for 33 h. The mixture was quenched with sat. aqueous NH_4Cl and water, and extracted with diethyl ether. The combined organic phases were washed with brine, dried with $MgSO_4$, and concentrated in vacuo. The residue was chromatographed on silica gel (50 g, hexane/ethyl acetate, 100:1) to give 0.89 g (67%) of (2*R*,6*R*)-**17** as a colorless oil; n_D^{28} = 1.4468. − $[\alpha]_D^{26}$ = +1.36 (*c* = 1.25, hexane). − IR (film): $\tilde{\nu}_{max}$ = 1640 cm^{-1} (m, C=C), 1255 (s, Si−CH_3), 1095 (s, Si−O). − ^1H NMR (300 MHz, $CDCl_3$): δ = 0.04 (s, 6 H, Si-CH_3), 0.89 (s, 9 H, *t*Bu) 0.80−0.97 (m, 6 H, 2-,6-CH_3), 0.97−1.63 (m, 26 H, 3−5-, 7−15-, 2-, 6-H), 2.04 (q, *J* = 6.6 Hz, 2 H, 16-H_2), 3.34 (dd, *J* = 6.6, 9.9 Hz, 1 H 1-H_a), 3.44 (dd, *J* = 5.7, 9.9 Hz, 1 H 1-H_b), 4.89−5.03 (m, 2 H, 18-H_2), 5.74−5.88 (m, 1 H, 17-H). − $C_{26}H_{54}OSi$ (410.8): calcd. C 76.34, H 13.29; found C 76.10, H 13.21.

(2*R*,6*R*)-2,6-Dimethyl-17-octadecen-1-ol [(2*R*,6*R*)-13]: *p*-Toluenesulfonic acid monohydrate (15.0 mg, 0.09 mmol) was added to a solution of (2*R*,6*R*)-**17** (738 mg, 1.80 mmol) in 95% EtOH (4 mL) and THF (4 mL) and the mixture was warmed up to 50 °C. The mixture was stirred for 5 h at 70 °C, and cooled to room temperature. After neutralization with K_2CO_3, the mixture was extracted with diethyl ether. The combined organic phases were washed with sat. aqueous $NaHCO_3$ and brine, dried with $MgSO_4$ and concentrated in vacuo. The residue was chromatographed on silica gel (20 g, hexane/ethyl acetate, 30:1) to give 455 mg (86%) of (2*R*,6*R*)-**13** as a colorless oil; n_D^{24} = 1.4595. − $[\alpha]_D^{27}$ = +6.40 (*c* = 1.05, hexane). − IR (film): $\tilde{\nu}_{max}$ = 3350 cm^{-1} (s, O−H), 1640 (m, C=C). − ^1H NMR (90 MHz, $CDCl_3$): δ = 0.60−1.00 (m, 6 H, 2-, 6-CH_3), 0.98−2.10 (m, 29 H, 2-, 6-H, 3−5-, 7−16-H_2, OH), 3.47 (dd, *J* = 2.6, 5.8 Hz, 2 H, 1-H_2), 4.91−5.12 (m, 2 H, 18-H_a), 5.58−6.09 (m, 1 H, 17-H). − $C_{20}H_{40}O$ (296.5): calcd. C 81.01, H 13.59; found C 80.65, H 13.85.

(2*R*,6*R*)-2,6-Dimethyl-17-octadecenyl *p*-Toluenesufonate [(2*R*,6*R*)-14]: In the same manner as described above, (2*R*,6*R*)-**13** (165 mg, 0.55 mmol) was converted into 231 mg (95%) of (2*R*,6*R*)-**14**. This was employed in the next step without further purification. Its IR and NMR spectra were identical with those of (2*S*,6*S*)-**14**.

(13*R*,17*S*)-13,17-Dimethyl-1-tritriacontene [(13*R*,17*S*)-1]: In the same manner as described for the preparation of (13*S*,17*R*)-**1**, (2*R*,6*R*)-**14** (275 mg, 0.633 mmol) was converted into 218 mg (70%) of (13*R*,17*S*)-**1** (as a colorless oil); n_D^{24} = 1.4572. − $[\alpha]_D^{24}$ = − 0.08 (*c* = 1.29, hexane). Its IR, NMR and MS spectra were identical with those of (13*S*,17*R*)-**1**. − $C_{35}H_{70}$ (490.9): calcd. C 85.63, H 14.37; found C 85.83, H 14.43. − GC [column: DB-5® (0.25 mm × 30 m), 200 to 320 °C/min., +4.0 °C/min.; carrier gas: He, pressure: 100 kPa]: t_R = 32.5 min. (97.7% chemical purity).

(13*R*,17*S*)-13,17-Dimethyl-1-pentatriacontene [(13*R*,17*S*)-2]: In the same manner as described for the preparation of (13*S*,17*R*)-**2**, (2*R*,6*R*)-**14** (199 mg, 0.458 mmol) was converted into 129 mg (54%) of (13*R*,17*S*)-**2** (as a colorless oil); n_D^{22} = 1.4600. − $[\alpha]_D^{26}$ = −0.07 (*c* = 1.30, hexane). Its IR, NMR and MS spectra were identical with those of (13*S*,17*R*)-**2**. − $C_{37}H_{74}$ (519.0): calcd. C 85.63, H 14.37; found C 85.41, H 14.64. − GC [column: DB-5® (0.25 mm × 30 m), 200 to 320 °C/min., +4.0 °C/min.; carrier gas: He, pressure: 100 kPa]: t_R = 36.8 min. (96.9% chemical purity).

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