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Stereospecific inversion of secondary tosylates to yield chiral methyl-branched building blocks, applied to the asymmetric synthesis of leafminer sex pheromones

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ABSTRACT

All four of the possible stereoisomers of 5,9-dimethylheptadecane, the major sex pheromone component secreted by female moths of the mountain-ash bentwing (*Leucoptera scitella*), were synthesized by the coupling of two chiral blocks with a methyl branch at the 2- or 3-position. The blocks were prepared by applying the stereospecific inversion of secondary tosylates, which were derived from (*R*)- and (*S*)-propylene oxide, and their enantiopurities were confirmed by chiral HPLC analysis.

1. Introduction

Species-specific sex pheromones have been identified from adult females of more than 600 lepidopteran species.[1] While pheromones are mainly composed of fatty alcohols, polyenyl hydrocarbons, and their derivatives with a straight chain, several species utilize methyl-branched compounds for mating communication.[2] In addition to the well-known methyl-branched alkanes, alkenes, and esters of a primary alcohol or acid, we recently found ketones and a secondary alcohol with a branched skeleton in the pheromone glands of female moths,[3] indicating the diverse chemical structures of lepidopteran sex pheromones. With regard to the large number of insect species, however, knowledge of the lepidopteran species secreting branched compounds remains very limited. Almost all methyl-branched compounds are chiral because a tertiary carbon is a stereogenic center, except for that at the 2-position. In order to understand the communication systems of moths, it is important to supply not only a sufficient amount of enantiopure known pheromones but also their analogues, which could possibly be produced by taxonomically related species. We investigated the possibilities of making chiral building blocks with high enantiomeric excess, which could be applied for the systematic synthesis of dimethyl hydrocarbons, such as 5,9-dimethylheptadecane **1** secreted by *Leucoptera scitella* females as a sex pheromone component.[4]

In addition to some unique synthetic routes,[5] the asymmetric synthesis of dimethyl hydrocarbons has reliably been accomplished by the coupling of two chiral methyl-branched building blocks derived from citronellal, 3-hydroxy-2-methylpropanoic acid, and 3-methyl-4-butanolide.[6] The starting materials are commercially available but rather expensive. For another chiral source, we selected (*R*)- and (*S*)-propylene oxide (*R*)-**2** and (*S*)-**2**, which could be converted into the tosylates of 2-alkanols with a different chain length, as shown in Scheme 1. If an alkylating reagent attacks the tosylate via an S_N2 reaction, the desired building block is formed after the inversion of configuration at the reaction site. By selecting an appropriate carbanion, it might be possible to produce chiral blocks **A** and **B** with a methyl group at the 3- and 2-positions, respectively. The two building blocks could be useful for the stereospecific construction of many *n*,(*n*+4)-dimethyl compounds, and so we began applying them to the asymmetric synthesis of all of the stereoisomers of **1**.

2. Results and discussion

First, chiral blocks (*S*)-**A** and (*R*)-**A** [R^1 = *n*-C_4H_9, X = I; (*S*)-**8** and (*R*)-**8**] were synthesized starting from (*R*)-**2** and (*S*)-**2** (>99% ee), respectively, as shown in Scheme 2. The reaction between (*R*)-**2** and *n*-C_3H_7MgBr with Li_2CuCl_4 gave secondary alcohol (*R*)-**3**, which was converted into tosylate (*R*)-**4**. Antipodal tosylate (*S*)-**4** was prepared from (*S*)-**2**. By HPLC equipped with a normal phase chiral column (Daicel Chiralpak AS-H), (*R*)-**4** and (*S*)-**4** could be detected separately. The chiral HPLC analysis confirmed their high enantiomeric excess (>99% ee), as shown in Figure 1A. In order to achieve an S_N2 reaction associated with chain elongation, we attempted to utilize an enolate of *tert*-butyl acetate as the nucleophile because an ester elongated by two carbons would be produced directly. However, the expected product was not obtained. Therefore, we examined a reaction with an enolate of dimethyl malonate. While some studies have reported that the S_N2 reaction of 2-bromo or 2-mesyl compounds with enolates of dialkyl malonate proceed with

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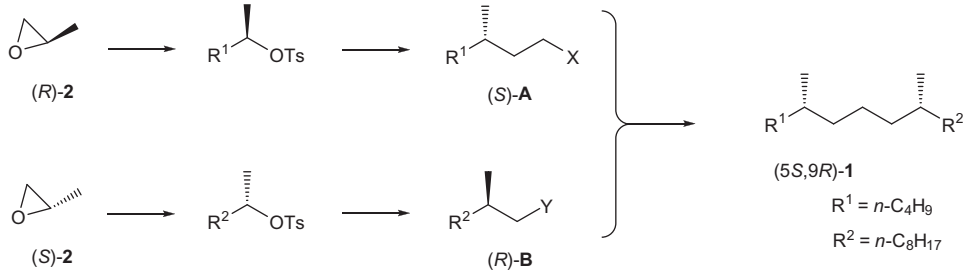
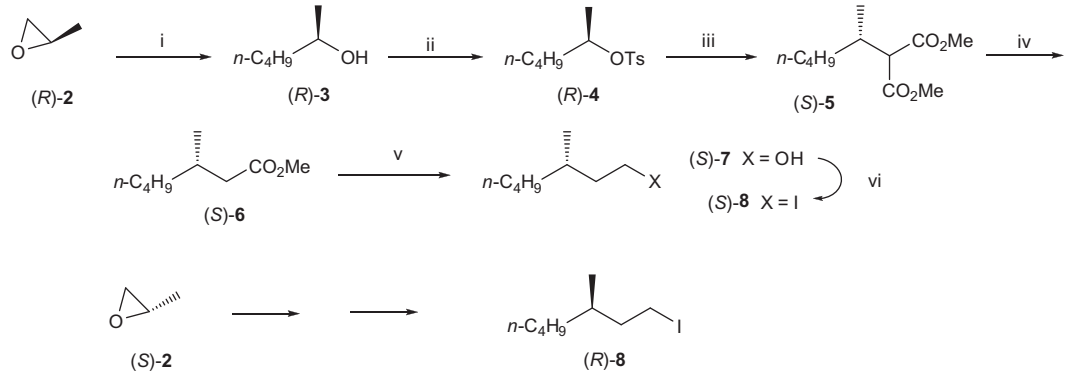


Scheme 1. Synthetic strategy for *n*,(*n*+4)-dimethylalkanes using stereospecific inversion of secondary tosylates.



Scheme 2. Synthetic routes to (*S*)-**8** (chiral building block **A**, $R^1 = n\text{-}C_4H_9$, X = I) and the antipode for the synthesis of 5,9-dimethylheptadecane **1**. Reagents and conditions: (i) $n\text{-}C_3H_7MgBr$, Li_2CuCl_4 (0.1 mol/L, 3 mol %), THF (84%); (ii) TsCl, Et_3N, $Me_3N{\cdot}HCl$ (10 mol %), CH_2Cl_2 (93%); (iii) $NaCH(CO_2Me)_2$, 1,2-dimethoxyethane (94%); (iv) LiCl, DMSO, H_2O, 170–180 °C (82%); (v) $LiAlH_4$, THF (89%); (vi) I_2, PPh_3, imidazole, THF (91%).

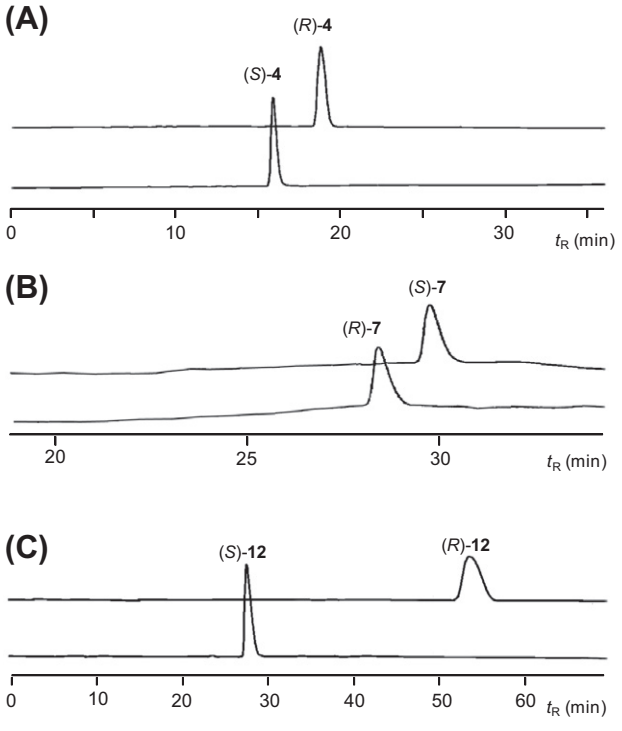
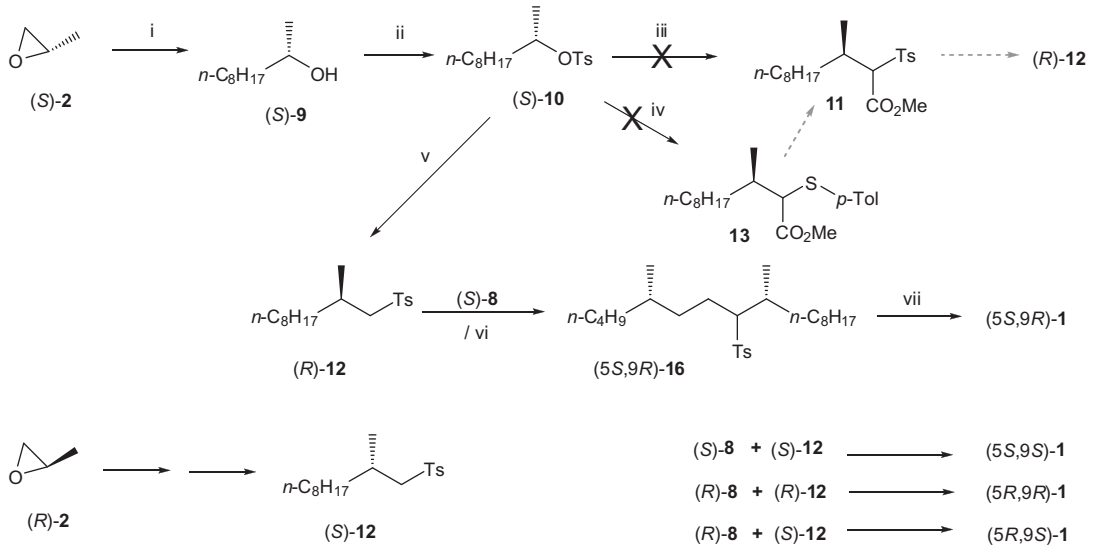


Figure 1. Chiral HPLC analyses of stereoisomers of 2-hexanyl tosylate **4** (A), 3-methylheptan-1-ol **7** (B), and 2-methyl-1-(tolylsulfonyl)decane **12** (C). The HPLC was conducted with a Chiralpack AS-H column (4.6 mm ID × 25 cm) and a UV detector (254 nm) using 10% 2-propanol in hexane as an eluent (flow rate, 0.5 mL/min) for **4** and **12** and with a Chiralpack AY-H column (4.6 mm ID × 25 cm) and an RI detector using 0.4% 2-propanol in hexane as an eluent (flow rate, 0.5 mL/min) for **7**.

considerable racemization,[7] it has also been reported that the reaction of a secondary tosylate with an enolate forms a new C–C-bond along with the complete inversion of stereochemistry.[8] Based on this result, (*R*)-**4** was treated with the enolate of dimethyl malonate to yield geminal ester (*S*)-**5**, which was decarboxylated to ester (*S*)-**6** by the Krapcho's method.[9] The reduction of (*S*)-**6** with $LiAlH_4$ produced primary alcohol (*S*)-**7**, which had been synthesized from (*S*)-β-citronellol in related research.[3b] The antipode (*R*)-**7** was prepared in the same manner. The two chiral alcohols could be separated by another normal phase chiral HPLC column (Daicel Chiralpak AY-H), as shown in Figure 1B, and their high enantiomeric purity (>99% ee) indicated that the nucleophile attacked the tosylates **4** via an S_N2 reaction. By treatment with a mixture of I_2, triphenylphosphine (PPh_3), and imidazole, (*S*)-**7** and (*R*)-**7** were converted into iodides (*S*)-**8** and (*R*)-**8**, respectively. The overall yield of (*S*)-**8** was 49% from (*R*)-**2**, and that of (*R*)-**8** was 53% from (*S*)-**2**.

Next, the chiral building block **B** was synthesized starting from (*S*)-**2** and (*R*)-**2**, respectively, as shown in Scheme 3. The reaction between (*S*)-**2** and $n\text{-}C_7H_{15}MgBr$ with Li_2CuCl_4 gave secondary alcohol (*S*)-**9**, which was converted into tosylate (*S*)-**10**. The antipodal tosylate (*R*)-**10** was prepared from (*R*)-**2**. Chiral HPLC analysis confirmed their high enantiomeric purity (>99% ee). It has been reported that the cyanide ion and the base-generated carbanion of methylthiomethyl *p*-tolyl sulfone can be utilized as a nucleophile in an S_N2 reaction,[10] but information on other reactions for one chain elongation associated with the complete inversion of configuration is to the best of our knowledge very limited. Therefore, we examined other reactions to make an optically active 2-methylundecanyl derivative. One idea was a coupling reaction between the secondary tosylate **10** and a sulfonyl acetate with an active methylene to yield a methyl-branched sulfonyl compound **11**, which might be converted into building block **B** ($R^2 = n\text{-}C_8H_{17}$, X = Ts,



Scheme 3. Synthetic routes to (*R*)-**12** (chiral building block **B**, $R^2 = n\text{-}C_8H_{17}$, X = Ts) and the antipode, which were coupled with block **A** to make all stereoisomers of 5,9-dimethylheptadecane **1**. Reagents and conditions: (i) $n\text{-}C_7H_{15}MgBr$, Li_2CuCl_4 (0.1 mol/L, 3 mol %), THF (92%); (ii) TsCl, Et_3N, $Me_3N{\cdot}HCl$ (10 mol %), CH_2Cl_2 (93%); (iii) $p\text{-}Me(C_6H_4)SO_2CH_2CO_2Me$/base; (iv) $p\text{-}Me(C_6H_4)SCH_2CO_2Me$/base; (v) $p\text{-}Me(C_6H_4)SO_2Me$/BuLi, THF (72%); (vi) BuLi, THF, HMPA (86%); (vii) Mg, MeOH (79%).

12) after decarboxylation. Methyl (toluene-4-sulfonyl)acetate, which was prepared with sodium *p*-toluenesulfinate and methyl 2-chloroacetate, was treated with NaH, but the base-generated carbanion did not couple to **10** even when heating at 85 °C for 24 h. Another reaction of **10** with the dianion of sulfonylacetate, which was prepared by treatment with NaH and butyllithium (BuLi), produced a complicated mixture. Next, we attempted the reaction with a carbanion of methyl *p*-tolylsulfanylacetate, which was synthesized by the reaction with 4-methylbenzenethiol and methyl 2-chloroacetate. When lithium diisopropylamide (LDA), sodium hexamethyldisilazide (NaHMDS), or potassium hexamethyldisilazide (KHMDS) were used as a base, the desired sulfanyl product **13** was not obtained.

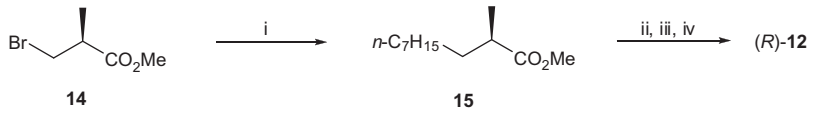
However, the carbanion of 1-methanesulfonyl-4-methylbenzene (methyl *p*-tolyl sulfone), which was generated by treatment with BuLi, successfully attacked (*S*)-**10**, and (*R*)-**12** was produced. We examined the best reaction conditions by changing the type of base, solvent, temperature, and substrate concentration, as shown in Table 1. The highest yield (72%) was achieved with BuLi in THF at 55 °C and a low concentration of methyl *p*-tolyl sulfone. When a THF solution of the carbanion was stirred without (*S*)-**10** for several minutes, the yield of (*R*)-**12** decreased. The coupling reaction between an anion of the sulfone and an alkyl halide usually required the addition of a very polar solvent, such as hexamethylphosphoric triamide (HMPA),[11] but the co-solvent had a negative effect on the synthesis of (*R*)-**12**. The S_N2 reaction of a primary alkyl halide by the anion of methyl sulfone has been more often reported than that of an alkyl tosylate.[6a,d] To the best of our knowledge, the S_N2 reaction of **10** is the first successful example of an intermolecular coupling between an optically active secondary tosylate and an anion of a sulfonyl compound, although an intramolecular S_N2 reaction compound with a secondary tosyl and methanesulfonyl groups has been reported.[11] The desired intermolecular S_N2 reaction produced successfully the methyl-branched sulfone **12** without racemization and E2 elimination of the secondary tosylate. The absolute configuration was confirmed by comparison with (*R*)-**12**, which was synthesized starting from methyl (*S*)-3-bromoisobutylate **14** by the route shown in Scheme 4. By using *N*-methylpyrrolidinone (NMP) as the co-solvent,[12] bromide **14** was treated with $n\text{-}C_7H_{15}MgBr$ and Li_2CuCl_4 to yield methyl 2-methyloctadecanoate **15**. Reduction of **15** with $LiAlH_4$, iodination of the produced alcohol, and the substitution of the iodine with a sulfonyl group yielded (*R*)-**12**. The sulfones synthesized by two different routes showed almost the same specific rotation values. Compound (*S*)-**12** was prepared from (*R*)-**10**, and the high enantiomeric purity of (*R*)-**12** and (*S*)-**12** (>99% ee) was confirmed by chiral HPLC analyses using an AS-H column (Fig. 1C). The total yield of (*R*)-**12** was 62% from (*S*)-**2**, while that of (*S*)-**12** was 63% from (*R*)-**2**.

Sulfone (*R*)-**12** was alkylated with (*S*)-**8** to give (5*S*,9*R*)-**16** with a 5,9-dimethyl skeleton by using a known procedure.[6a,d] Reductive removal of the sulfonyl moiety of (5*S*,9*R*)-**16** was achieved smoothly by using magnesium turnings in methanol,[13] and the desired final product (5*S*,9*R*)-**1** was obtained in 68% yield from (*R*)-**12**. Before the reaction, magnesium was activated with a catalytic amount of methylmagnesium bromide (MeMgBr) in THF. No olefinic by-products were formed, as reported by Kuwahara et al. using a method involving lithium in liquid ethylamine.[6d] In the same manner, three other stereoisomers were synthesized by the following combination of two synthetic building blocks; (5*S*,9*S*)-**1** from (*S*)-**8** and (*S*)-**12**, (5*R*,9*R*)-**1** from (*R*)-**8** and (*R*)-**12**, and (5*R*,9*S*)-**1** from (*R*)-**8** and (*S*)-**12**. The chemical data for each isomer were almost identical to those published with regard to previous syntheses,[6] indicating that racemization did not occur after the alkylation. While the ^{13}C NMR spectra of the enantiomers were identical, the diastereomers showed small but discernible differ-

Table 1
Synthesis of methyl (*R*)-2-methyl-1-(4-methylphenylsulfonyl)decane (**12**) by coupling of a tosylate [(*S*)-**10**] and a carbanion of methyl *p*-tolyl sulfone

$p\text{-}Me(C_6H_4)SO_2Me$ + base $\xrightarrow{(S)\text{-}\mathbf{10}}$ (*R*)-**12**·

Entry	Base	Solvent	Temp (°C)	Concentration (M)	Yield (ee)
1	BuLi	THF	55	0.5	41% (>99%)
2	BuLi	THF	55	0.07	72% (>99%)
3	BuLi	THF	20	0.07	None
4	BuLi	THF–HMPA	55	0.07	None
5	BuLi	THF–HMPA	20	0.07	23% (>99%)
6	BuLi	THF–NMP	20	0.07	None
7	LDA	THF	55	0.07	18%
8	NaHMDS	THF	55	0.07	30%
9	KHMDS	THF	55	0.07	None



Scheme 4. Synthetic route to (*R*)-**12** starting from methyl (*S*)-3-bromoisobutyrate **14**. Reagents and conditions: (i) *n*-$C_7H_{15}MgBr$, Li_2CuCl_4, NMP–THF (91%); (ii) $LiAlH_4$, THF; (iii) I_2, PPh_3, imidazole, THF; (iv) *p*-Me(C_6H_4)SO_2Na, PEG400, MeOH (44% from **15**).

ences of chemical shifts for some ^{13}C signals as indicated for 5,9-dimethylpentadecane.[6d] We tentatively assigned each ^{13}C signal, and the assignments indicated the differences for carbons of the two branched-methyl groups and carbons around the branches, reflecting the conformational differences of the diastereomers (see Section 4).

3. Conclusion

In many syntheses of chiral methyl-branched insect pheromones, the original configuration at a stereogenic center in the starting material was retained in the final product.[14] Stereospecific conversion has been rarely used in pheromone syntheses because of the risk of racemization. Our synthetic strategy, however, utilized the S_N2 reaction of a tosylate of a 2-alkanol. The reason was that we expected the possibility of enantiomeric separation of methyl-branched synthetic intermediates by a chiral HPLC column.[3] In fact, we could confirm, by chiral HPLC analyses, the stereospecific conversion of a chiral secondary tosylate after an S_N2 reaction with an alkylating reagent, such as the enolate of dimethyl malonate and the anion of methyl sulfone. In the reaction, elongation by two or one carbon(s) was accomplished, in association with complete inversion of the original stereochemistry, which successfully produced two chiral methyl-branched building blocks, **A** and **B**, with high enantiomeric purity (>99% ee). In addition to 5,9-dimethylheptadecane **1**, these building blocks can be utilized for the synthesis of other 5,9-dimethylalkanes with a different carbon chain identified from Lyonetiidae species as well as 7,11-dimethylalkanes identified from Geometridae species. The synthetic pheromones will be utilized as a monitoring tool for pest control and an authentic standard for the identification of new pheromones.[2]

4. Experimental

4.1. General

The specific rotation of each $CHCl_3$ solution was measured on a JASCO DIP-4 polarimeter. IR spectra were recorded as a thin film (neat liquid) with a Jasco FT/IR-350 (JASCO, Tokyo, Japan). ^1H and ^{13}C NMR spectra were recorded by a JNM-ECA 500 FT-NMR spectrometer (JEOL, Tokyo, Japan) at 500.16 and 125.77 MHz, respectively, for $CDCl_3$ solutions containing TMS as the internal standard. GC–MS was conducted in EI mode (70 eV) with an HP5973 mass spectrometer system (Hewlett–Packard) equipped with a split/splitless injector and a DB-23 column (0.25 mm ID × 30 m, 0.25 μm film, J & W Scientific, Folsom, CA, USA). The column temperature program was 50 °C for 2 min, 4 °C/min to 150 °C, 10 °C/min to 220 °C, and 220 °C for 10 min. The carrier gas was He. High-resolution MS (HR-MS) analysis was performed with a JMS-MS700V mass spectrometer (JEOL). Enantiomeric excess (ee) was determined by a Chiral HPLC analysis, which employed a system composed of a pump (PU-980, JASCO), an RI detector (RI-98SCOPE, Labo System, Tokyo, Japan) or a UV detector (UV-970, JASCO), an integrator (807-IT, JASCO), and a normal phase chiral column, Chiralpak AS-H or AY-H (4.6 mm ID × 25 cm, Daicel Chemical Industry, Osaka, Japan). The resolution of tosylates **4** and **10** and sulfone **12** was achieved with the AS-H column using 10% 2-propanol in hexane as an eluent, and each enantiomer was detected by UV 254 nm. The resolution of alcohol **7** was achieved with the AY-H column using 0.4% 2-propanol in hexane, and each enantiomer was detected by RI. The flow rate of the eluents was 0.5 mL/min.

4.2. 2-Hexanols (*R*)- and (*S*)-3

To an ice-cooled and stirred mixture of *n*-C_3H_7Br (7.38 g, 60 mmol) and magnesium turnings (2.92 g, 120 mmol) in dry THF (60 mL), a catalytic amount of MeMgBr (3.0 M, two drops) was added as an initiator for making a Grignard reagent under an argon atmosphere. After stirring for 1 h at 0 °C, Li_2CuCl_4 in THF (0.1 M, 18 mL, 1.8 mmol) was added to a solution with a cloudy gray color at −78 °C. Then, (*R*)-(+)-propylene oxide (*R*)-**2** (2.90 g, 50 mmol) dissolved in dry THF (5 mL) was added dropwise through a syringe, and stirring of the mixture was continued for 30 min at −78 °C and an additional 1 h at room temperature. The reaction mixture was then poured into an ice-cooled aqueous solution of NH_4Cl (300 mL), and the crude products were extracted with Et_2O. The extract was washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The residue was chromatographed over SiO_2 (50 g). Elution with hexane/EtOAc (4:1) afforded 4.28 g (42 mmol, 84%) of (*R*)-**3** as an oil, $[\alpha]_D^{23} = -8.1$ (*c* 1.5, $CHCl_3$); ν_{max} (cm^{-1}): 3354 (s, O-H), 2925 (s), 2854 (s), 1458 (m), 1377 (m), 1115 (m); δ_H: 0.91 (3H, t, CH_3CH_2, *J* = 7.0 Hz), 1.19 (3H, d, CH_3CHOH *J* = 6.2 Hz), ~1.3 (4H, m), ~1.4 (2H, m), 3.80 (1H, m, CH_3CHOH); δ_C: 14.0, 22.7, 23.4, 28.0, 39.0, 68.1. In the same manner, (*S*)-(−)-propylene oxide (*S*)-**2** (2.90 g, 50 mmol) was reacted with *n*-C_3H_7MgBr to yield 4.59 g (45 mmol, 90%) of (*S*)-**3** as an oil, $[\alpha]_D^{23} = +7.9$ (*c* 1.2, $CHCl_3$).

4.3. 2-Hexanyl tosylates (*R*)- and (*S*)-4

Triethylamine (8.10 g, 80 mmol) was added dropwise to a stirred solution of tosyl chloride (TsCl, 11.4 g, 60 mmol) and $Me_3N{\cdot}HCl$ (0.38 g, 4 mmol) in CH_2Cl_2 (70 mL) at 0 °C under an argon atmosphere. Then (*R*)-**3** (4.08 g, 40 mmol) dissolved in CH_2Cl_2 (8 mL) was added to the solution through a syringe. After stirring at 0 °C for 1.5 h, 1,3-diaminopropane (1.48 g, 20 mmol) dissolved in CH_2Cl_2 (2 mL) was added to decompose the excess TsCl. The mixture was stirred for 10 min and poured into water, after which the crude product was extracted with CH_2Cl_2. The extract was washed with dil HCl, saturated $NaHCO_3$ solution, and brine, dried over Na_2SO_4, and concentrated in vacuo. The residue was chromatographed over SiO_2 (50 g). Elution with hexane/EtOAc (9:1) afforded 9.49 g (37 mmol, 93%) of (*R*)-**4** as an oil, $[\alpha]_D^{23} = -3.7$ (*c* 2.0, $CHCl_3$); ν_{max} (cm^{-1}): 2931 (s), 2856 (s), 1599 (m, benzene ring), 1363 (s, S=O), 1176 (s, S=O); δ_H: 0.81 (3H, t, CH_3CH_2, *J* = 6.9 Hz), ~1.2 (4H, m), 1.25 (3H, d, CH_3CHOTs, *J* = 6.3 Hz), 1.50 and 1.59 (2H, m), 2.45 (3H, s, CH_3Ph), 4.60 (1H, tq, *J* = 6.3, 6.3 Hz, CH_3CHOTs), 7.33 (2H, d, CH=CH, *J* = 8.2 Hz), 7.80 (2H, d, CH=CH, *J* = 8.2 Hz); δ_C: 13.8, 20.8, 21.6, 22.2, 27.0, 36.2, 80.7, 127.7 (×2), 129.7 (×2), 134.6, 144.4; GC-MS: t_R 20.32 min, *m/z* 256 (M^+, 1%), 199 (18%), 155 (100%). In the same manner, (*S*)-**3** (4.08 g, 40 mmol) was treated with tosyl chloride to yield 10.0 g (39 mmol, 98%) of (*S*)-**4** as an oil, $[\alpha]_D^{23} = +3.8$ (*c* 2.1, $CHCl_3$). The two enantiomers were analyzed by chiral HPLC equipped with a Chiralpak AS-H column and a UV

detector (254 nm). Peaks of the two enantiomers were detected at different t_R values [(*R*)-**4**, 18.8 min and (*S*)-**4**, 16.0 min] by elution with hexane/2-propanol (9:1) at a flow rate (0.5 mL/min), and chromatograms showed their enantiomeric purity (>99% ee).

4.4. 2-(1-Methylpentyl)malonic acid dimethyl esters (*S*)- and (*R*)-5

Dimethyl malonate (7.13 g, 54 mmol) was added dropwise to a suspension of sodium hydride (60%, 2.16 g, 54 mmol) in 1,2-dimethoxyethane at 0 °C and stirred for 15 min. Then (*R*)-**4** (9.23 g, 36 mmol) was added to the mixture, which produced sodium *p*-toluenesulfonate as a white solid after stirring at 80–85 °C for 12 h. The suspension was concentrated in vacuo and a saturated NH_4Cl solution was poured into the residue. The product was extracted with EtOAc, and the extract was washed with brine, dried over Na_2SO_4, concentrated in vacuo, and chromatographed over SiO_2 (50 g). Elution with hexane/EtOAc (9:1) afforded 7.35 g (34 mmol, 94%) of (*S*)-**5** as an oil, $[\alpha]_D^{23} = -2.9$ (*c* 1.2, $CHCl_3$); ν_{max} (cm^{-1}): 2956 (s), 1737 (s, C=O), 1435 (s), 1151 (s), 1022 (m); δ_H: 0.89 (3H, t, C*H*$_3$CH$_2$, *J* = 6.8 Hz), 0.97 (3H, d, C*H*$_3$CH, *J* = 6.8 Hz), ~1.3 (6H, m), 2.25 (1H, m, CH$_3$C*H*), 3.27 (1H, d, C*H*CO$_2$CH$_3$, *J* = 8.2 Hz), 3.73 (6H, s, CO$_2$C*H*$_3$); δ_C: 14.0, 17.0, 22.7, 29.0, 33.5, 34.0, 52.2, 52.3, 57.6, 169.3, 169.5; GC-MS: t_R 12.04 min, *m/z* 185 ($[M-32]^+$, 10%), 132 (100%). In the same manner, (*S*)-**4** (9.74 g, 38 mmol) was treated with sodium malonic ester to yield 7.35 g (34 mmol, 89%) of (*R*)-**5** as an oil, $[\alpha]_D^{23} = +3.0$ (*c* 0.74, $CHCl_3$).

4.5. Methyl 3-methylheptanoates (*S*)- and (*R*)-6

Water (2.34 g, 130 mmol) was added to a solution of (*S*)-**5** (7.14 g, 33 mmol) and lithium chloride (2.80 g, 66 mmol) in DMSO (170 mL), and the mixture was stirred at 170–180 °C for 3.5 h. After cooling, the mixture was poured into NaCl solution (12%, 500 mL) and the product was extracted with EtOAc. The extract was washed with water and brine, dried over Na_2SO_4, concentrated in vacuo, and chromatographed over SiO_2 (50 g). Elution with hexane/EtOAc (9:1) afforded 4.27 g (27 mmol, 82%) of (*S*)-**6** as an oil, $[\alpha]_D^{23} = -3.1$ (*c* 0.82, $CHCl_3$); ν_{max} (cm^{-1}): 2956 (s), 2858 (s), 1741 (s, C=O), 1437 (s), 1173 (s), 1009 (m); δ_H: 0.89 (3H, t, C*H*$_3$CH$_2$, *J* = 6.8 Hz), 0.93 (3H, d, C*H*$_3$CH, *J* = 6.6 Hz), ~1.3 (6H, m), 1.95 (1H, m, CH$_3$C*H*), 2.11 (1H, dd, C*H*HCO$_2$CH$_3$, *J* = 14.5, 8.1 Hz), 2.31 (1H, dd, CH*H*CO$_2$CH$_3$, *J* = 14.5, 6.1 Hz), 3.67 (3H, s, CO$_2$C*H*$_3$); δ_C: 14.1, 19.8, 22.8, 29.1, 30.3, 36.4, 41.7, 51.4, 173.9; GC-MS: t_R 6.53 min, *m/z* 158 (M^+, 1%), 127 (11%), 74 (100%). In the same manner, decarboxylation of (*R*)-**5** (7.57 g, 35 mmol) produced 4.59 g (29 mmol, 83%) of (*R*)-**6** as an oil, $[\alpha]_D^{23} = +2.9$ (*c* 0.63, $CHCl_3$).

4.6. 3-Methylheptan-1-ols (*S*)- and (*R*)-7

A solution of (*S*)-**6** (4.27 g, 27 mmol) in dry THF (10 mL) was added dropwise through a syringe to an ice-cooled and stirred suspension of $LiAlH_4$ (1.02 g, 27 mmol) in dry THF (50 mL) under an argon atmosphere. The mixture was stirred for 30 min at 0 °C, after which water (50 mL) was added slowly to the mixture. After acidification with dilute HCl solution, the product was extracted with Et_2O. The extract was washed with saturated $NaHCO_3$ solution and brine, dried over Na_2SO_4, and concentrated in vacuo. The residue was chromatographed over SiO_2 (50 g), and elution with hexane/EtOAc (4:1) to afford 3.13 g (24 mmol, 89%) of (*S*)-**7** as an oil, $[\alpha]_D^{23} = -2.6$ (*c* 1.4, $CHCl_3$); ν_{max} (cm^{-1}): 3336 (s, O-H), 2925 (s), 1460 (s), 1379 (m), 1057 (s); δ_H: 0.89 (3H, t, C*H*$_3$CH$_2$, *J* = 6.8 Hz), 0.89 (3H, d, C*H*$_3$CH, *J* = 6.6 Hz), ~1.3 (7H, m), ~1.6 (2H, m), 3.68 (2H, m, C*H*$_2$OH); δ_C: 14.2, 19.7, 23.0, 29.2, 29.5, 36.8, 40.0, 61.3; GC-MS: t_R 8.00 min, *m/z* 112 ($[M-18]^+$, 2%), 84 (72%), 55 (100%). In the same manner, $LiAlH_4$ reduction of (*R*)-**6** (4.43 g, 28 mmol) produced 3.26 g (25 mmol, 89%) of (*R*)-**7** as an oil, $[\alpha]_D^{23} = +2.7$ (*c* 1.2, $CHCl_3$). The two enantiomers were analyzed by chiral HPLC equipped with a Chiralpak AY-H column and a RI detector. The peaks of the two enantiomers were detected at different t_R values [(*S*)-**7**, 29.6 min and (*R*)-**7**, 28.4 min] by elution with hexane/2-propanol (99.6:0.4) at a flow rate (0.5 mL/min), and chromatograms showed their enantiomeric purity (>99% ee).

4.7. 1-Iodo-3-methylheptanes (*S*)- and (*R*)-8

Iodine (7.11 g, 28 mmol) was added to a solution of triphenylphosphine (6.56 g, 25 mmol) and imidazole (3.74 g, 55 mmol) in dry THF (150 mL) at 0 °C under an argon atmosphere. After stirring for 15 min, (*S*)-**7** (3.00 g, 23 mmol) dissolved in THF (5 mL) was added through a syringe. The mixture was stirred at 0 °C for 1 h, and then poured into saturated $Na_2S_2O_3$ solution and the product was extracted with EtOAc. The extract was washed with water and brine, dried over Na_2SO_4, and concentrated in vacuo. The residue was chromatographed over SiO_2 (50 g), and elution with hexane/EtOAc (9:1) to afford 5.04 g (21 mmol, 91%) of (*S*)-**8** as an oil, $[\alpha]_D^{23} = -12.6$ (*c* 1.4, $CHCl_3$); ν_{max} (cm^{-1}): 2956 (s), 2925 (s), 2856 (s), 1464 (s), 1379 (m), 1178 (s), 602 (w); δ_H: 0.87 (3H, d, C*H*$_3$CH, *J* = 6.5 Hz), 0.89 (3H, t, C*H*$_3$CH$_2$, *J* = 6.5 Hz), 1.14 (1H, m) ~1.3 (5H, m), 1.54 (1H, m, C*H*CH$_2$), 1.64 (1H, ddd, C*H*HCH$_2$I, *J* = 21.3, 8.1, 5.8 Hz), 1.87 (1H, ddd, CH*H*CH$_2$I, *J* = 21.3, 8.1, 5.8 Hz), 3.17 (1H, ddd, C*H*HI, *J* = 9.0, 8.0, 8.0 Hz), 3.25 (1H, ddd, CH*H*I, *J* = 9.0, 9.0, 5.8 Hz); δ_C: 5.3, 14.1, 18.8, 22.9, 29.0, 33.9, 35.9, 41.0; GC-MS: t_R 9.72 min, *m/z* 240 (M^+, 3%), 113 (23%), 57 (100%). In the same manner, iodization of (*R*)-**7** (3.26 g, 25 mmol) produced 5.52 g (23 mmol, 92%) of (*R*)-**8** as an oil, $[\alpha]_D^{23} = +12.5$ (*c* 0.60, $CHCl_3$).

4.8. 2-Decanols (*S*)- and (*R*)-9

In the same manner as that described for the preparation of (*S*)-**3**, (*S*)-**2** (3.48 g, 60 mmol) was reacted with *n*-C_7H_{15}MgBr, which was prepared from *n*-C_7H_{15}Br (16.1 g, 90 mmol), to produce 8.71 g (55 mmol, 92%) of (*S*)-**9** as an oil, $[\alpha]_D^{23} = +8.1$ (*c* 1.1, $CHCl_3$); ν_{max} (cm^{-1}): 3354 (s, O-H), 2925 (s), 2854 (s), 1458 (m), 1377 (m), 1115 (m); δ_H: 0.88 (3H, t, C*H*$_3$CH$_2$, *J* = 6.7 Hz), 1.19 (3H, d, C*H*$_3$CHOH *J* = 6.2 Hz), ~1.3 (12H, m), ~1.4 (2H, m), 3.79 (1H, m, CH$_3$C*H*OH); δ_C: 14.1, 22.7, 23.5, 25.8, 29.3, 29.6, 29.7, 31.9, 39.4, 68.2; GC-MS: t_R 9.90 min, *m/z* 140 (M-18, 3%), 112 (7%), 45 (100%). In the same manner, (*R*)-**2** (4.07 g, 70 mmol) was reacted with *n*-C_7H_{15}MgBr to yield 10.9 g (69 mmol, 99%) of (*R*)-**9** as an oil, $[\alpha]_D^{23} = -8.0$ (*c* 0.61, $CHCl_3$).

4.9. 2-Decanyl tosylates (*S*)- and (*R*)-10

In the same manner as that described for the preparation of (*S*)-**4**, (*S*)-**9** (7.28 g, 46 mmol) was treated with tosyl chloride (13.2 g, 69 mmol) to produce 13.4 g (43 mmol, 93%) of (*S*)-**10** as an oil, $[\alpha]_D^{23} = +3.5$ (*c* 2.0, $CHCl_3$); ν_{max} (cm^{-1}): 2927 (s), 2856 (s), 1599 (m, benzene ring), 1363 (s, S=O), 1176 (s, S=O); δ_H: 0.87 (3H, t, C*H*$_3$CH$_2$, *J* = 6.9 Hz), ~1.2 (12H, m), 1.26 (3H, d, C*H*$_3$CHOTs, *J* = 6.2 Hz), 1.50 and 1.59 (2H, m), 2.44 (3H, s, C*H*$_3$Ph), 4.59 (1H, tq, *J* = 6.3, 6.3 Hz, CH$_3$C*H*OTs), 7.33 (2H, d, C*H*=CH, *J* = 8.2 Hz), 7.80 (2H, d, CH=C*H*, *J* = 8.2 Hz); δ_C: 14.1, 20.9, 21.6, 22.6, 24.9, 29.07, 29.09 (×2), 31.7, 36.5, 80.7, 127.7 (×2), 129.7 (×2), 134.6, 144.4. In the same manner, (*R*)-**9** (8.86 g, 56 mmol) was treated with tosyl chloride to yield 15.9 g (51 mmol, 91%) of (*R*)-**10** as an oil, $[\alpha]_D^{23} = -3.5$ (*c* 2.0, $CHCl_3$). The two enantiomers were analyzed by chiral HPLC equipped with a Chiralpak AS-H column and a UV detector (254 nm). The peaks of the two enantiomers were detected at different t_R values [(*S*)-**10**, 11.5 min and (*R*)-**10**, 14.5 min] and the chromatograms showed their enantiomeric purity (>99% ee).

4.10. 2-Methyl-1-(4-methylphenylsulfonyl)decanes (*R*)- and (*S*)-12 from 10

In a two necked flask, methyl *p*-tolyl sulfone (2.04 g, 12 mmol) was dissolved in dry THF (180 mL). A hexane solution of BuLi (2.69 M, 4.7 mL, 12 mmol) and (*S*)-**10** (2.50 g, 8.0 mmol) dissolved in THF (4 mL) were added successively into the flask through a syringe at 0 °C under an argon atmosphere. The reaction mixture was stirred at 55 °C for 4 h and then poured into an aqueous solution of NH_4Cl (100 mL). The crude product was extracted with EtOAc and the extract was washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The residue was chromatographed over SiO_2 (40 g). Elution with hexane/EtOAc (14:1) afforded 1.79 g (5.8 mmol, 72%) of (*R*)-**12** as an oil, $[\alpha]_D^{23} = -1.1$ (*c* 2.5, $CHCl_3$); ν_{max} (cm^{-1}): 2925 (s), 2854 (s), 1599 (m, benzene ring), 1313 (s, S=O), 1147 (s, S=O), 1088 (s); δ_H: 0.88 (3H, t, C*H*$_3$CH$_2$, *J* = 6.9 Hz), 1.05 (3H, d, C*H*$_3$CH, *J* = 6.2 Hz), ~1.2 (12H, m), 2.04 (3H, m, CH$_3$C*H*), 2.45 (3H, s, C*H*$_3$Ph), 2.90 (1H, dd, *J* = 14.2, 7.9 Hz, C*H*HTs), 3.06 (1H, dd, *J* = 14.2, 4.6 Hz, CH*H*Ts), 7.35 (2H, d, C*H*=CH, *J* = 8.2 Hz), 7.79 (2H, d, CH=C*H*, *J* = 8.2 Hz); δ_C: 14.1, 19.9, 21.6, 22.7, 26.3, 28.6, 29.2, 29.5 (×2), 31.8, 36.7, 62.7, 127.9 (×2), 129.9 (×2), 137.3, 144.4. In the same manner, (*R*)-**10** (2.50 g, 8.0 mmol) was treated with the carbanion of methyl *p*-tolyl sulfone to yield 1.74 g (5.6 mmol, 70%) of (*S*)-**12** as an oil, $[\alpha]_D^{23} = +1.1$ (*c* 2.5, $CHCl_3$). The two enantiomers were analyzed by chiral HPLC (AS-H column) and detected at different t_R values [(*R*)-**12**, 53.4 min and (*S*)-**12**, 28.2 min] by elution with hexane/2-propanol (9:1). The chromatograms showed their enantiomeric purity (>99% ee).

4.11. Methyl (*R*)-2-methylundecanoate (*R*)-15

In the same manner as that described for the preparation of (*S*)-**3**, methyl (*S*)-3-bromoisobutylate (*S*)-**14** (1.99 g, 11 mmol) was reacted with *n*-$C_7H_{15}MgBr$, which was prepared from *n*-$C_7H_{15}Br$ (4.48 g, 25 mmol), to produce 2.00 g (10 mmol, 91%) of (*R*)-**15** as an oil, $[\alpha]_D^{23} = -16.0$ (*c* 1.0, $CHCl_3$); ν_{max} (cm^{-1}): 2925 (s), 2856 (s), 1739 (s, C=O), 1464 (s), 1196 (s), 1167 (s); δ_H: 0.88 (3H, t, C*H*$_3$CH$_2$, *J* = 6.7 Hz), 1.14 (3H, d, C*H*$_3$CH, *J* = 6.9 Hz), ~1.3 (12H, m), 1.64 (1H, m, C*H*HCH), 2.43 (1H, tq, *J* = 6.9, 6.9 Hz, CH$_3$C*H*), 3.67 (3H, s, OCH$_3$); δ_C: 14.1, 17.1, 22.7, 27.3, 29.3, 29.46, 29.54, 31.9, 33.8, 39.5, 51.5, 177.5.

4.12. (*R*)-2-Methyl-1-(4-methylphenylsulfonyl)decane (*R*)-12 from (*R*)-15

In the same manner as that described for the preparation of (*S*)-**7**, (*R*)-**15** (2.00 g, 10 mmol) was treated with $LiAlH_4$ (0.38 g, 10 mmol) to produce 1.38 g (8.0 mmol, 80%) of (*R*)-2-methyl-1-decanol as an oil; δ_H: 0.88 (3H, t, C*H*$_3$CH$_2$, *J* = 6.9 Hz), 0.91 (3H, d, C*H*$_3$CH, *J* = 6.7 Hz), ~1.3 (14H, m), 1.61 (1H, m, CH$_3$C*H*), 3.41 (1H, dd, C*H*HOH, *J* = 10.5, 6.6 Hz), 3.51 (1H, dd, CH*H*OH, *J* = 10.5, 5.7 Hz); δ_C: 14.1, 16.6, 22.7, 27.0, 29.4, 29.6, 30.0, 31.9, 33.2, 35.8. Next, in the same manner as that described for the preparation of (*S*)-**8**, the alcohol was treated with a mixture of iodine (2.28 g, 9.0 mmol), triphenylphosphine (2.62 g, 10 mmol), and imidazole (1.36 g, 20 mmol) to produce 2.05 g (7.3 mmol, 91%) of (*R*)-1-iodo-2-methyldecane as an oil; δ_H: 0.88 (3H, t, C*H*$_3$CH$_2$, *J* = 6.6 Hz), 0.97 (3H, d, C*H*$_3$CH, *J* = 6.4 Hz), ~1.3 (14H, m), 1.45 (1H, m, CH$_3$C*H*), 3.15 (1H, dd, C*H*HI, *J* = 9.5, 5.9 Hz), 3.23 (1H, dd, CH*H*I, *J* = 9.5, 4.6 Hz); δ_C: 14.1, 18.1, 20.6, 22.7, 26.9, 29.3, 29.6, 29.7, 31.9, 34.7, 36.5. The iodo compound was added into a stirred mixture of sodium *p*-toluenesulfinate (1.78 g, 10 mmol), PEG-400 (10 mL), and DMSO (5 mL) at 80 °C. The reaction mixture was stirred for 2 h at 80 °C and then poured into a 10% NaCl solution (75 mL) after cooling to room temperature. The crude product was extracted with EtOAc and the extract was washed with water and brine, dried over Na_2SO_4, and concentrated in vacuo. The residue was chromatographed over SiO_2 (50 g). Elution with hexane/EtOAc (14:1) afforded 1.37 g (4.4 mmol, 60%) of (*R*)-**12** as an oil, which was analyzed by chiral HPLC.

4.13. 5,9-Dimethyl-8-(4-methylphenylsulfonyl)heptadecanes (5*S*,8*SR*,9*R*)-, (5*S*,8*SR*,9*S*)-, (5*R*,8*SR*,9*S*)-, and (5*R*,8*SR*,9*R*)-16

A hexane solution of BuLi (1.63 M, 3.7 mL, 6.0 mmol) was added through a syringe to a stirred solution of (*R*)-**12** (1.55 g, 5.0 mmol) in THF (10 mL) at −78 °C under an argon atmosphere. The mixture was stirred at −78 °C for 10 min and then at −35 °C for 30 min. After cooling to −78 °C, (*S*)-**8** (1.44 g, 6.0 mmol) dissolved in HMPA (3.5 mL) was added dropwise. The mixture was then allowed to warm gradually to room temperature and stirred for 8 h. The resulting mixture was poured into 1 M HCl (50 mL) and the crude products were extracted with EtOAc, washed with a saturated $NaHCO_3$ solution and brine, dried over Na_2SO_4, and concentrated in vacuo. The residue was chromatographed over SiO_2 (50 g). Elution with hexane/EtOAc (19:1) afforded 1.82 g (4.3 mmol, 86%) of (5*S*,8*SR*,9*R*)-**16** as an oil, ν_{max} (cm^{-1}): 2925 (s), 2854 (s), 1597 (m, benzene ring), 1464 (s), 1300 (s, S=O), 1146 (s, S=O), 1086 (s); δ_H: 0.77 and 0.78 (3H, d, C*H*$_3$CH, *J* = 6.1 Hz), 0.87 (3H, t, C*H*$_3$CH$_2$, *J* = 6.3 Hz), 0.88 (3H, t, C*H*$_3$CH$_2$, *J* = 6.3 Hz), 1.00 and 1.03 (3H, d, C*H*$_3$CH, *J* = 7.1 Hz), ~1.2 (22H, m), 1.67 (2H, m), 1.82 (1H, m), 2.19 (1H, m), 2.44 (3H, s, C*H*$_3$Ph), 2.85 (1H, m, C*H*Ts), 7.33 (2H, d, C*H*=CH, *J* = 8.0 Hz), 7.76 (2H, d, CH=C*H*, *J* = 8.0 Hz). In the same manner, the syntheses of (5*S*,8*SR*,9*S*)-**16** from (*S*)-**8** and (*S*)-**12**, (5*R*,8*SR*,9*S*)-**16** from (*R*)-**8** and (*S*)-**12**, and (5*R*,8*SR*,9*R*)-**16** from (*R*)-**8** and (*R*)-**12** were accomplished in similar yields (80–85%).

4.14. 5,9-Dimethylheptadecanes (5*S*,9*R*)-, (5*S*,9*S*)-, (5*R*,9*S*)-, and (5*R*,9*R*)-1

To magnesium turnings (1.46 g, 60 mmol) stirred in dry THF (2.5 mL), a catalytic amount of MeMgBr (3.0 M, two drops) was added to activate the metal under an argon atmosphere. After stirring for 15 min at room temperature, a solution of (5*S*,8*SR*,9*R*)-**16** (1.65 g, 3.9 mmol) in dry MeOH (60 mL) was added through a syringe, and the mixture was stirred at 50 °C for 4 h. Next, the mixture was evaporated to remove MeOH and an ice-cooled 1 M HCl solution (20 mL) was added to dissolve the white residues. The crude products were extracted with Et_2O, washed with saturated $NaHCO_3$ solution and brine, dried over Na_2SO_4, and concentrated in vacuo. The residue was chromatographed over SiO_2 (20 g). Elution with hexane afforded 0.84 g (3.1 mmol, 79%) of (5*S*,9*R*)-**1** as an oil, $[\alpha]_D^{23} = +1.1$ (*c* 0.63, $CHCl_3$); ν_{max} (cm^{-1}): 2924 (s), 2854 (s), 1464 (m), 1377 (m), 723 (w); δ_H: 0.841 and 0.843 (6H, d, C*H*$_3$CH, *J* = 6.7 Hz), 0.88 (3H, t, C*H*$_3$CH$_2$, *J* = 7.2 Hz), 0.89 (3H, t, C*H*$_3$CH$_2$, *J* = 7.2 Hz), 1.0-1.4 (28H, m); δ_C: 14.14 and 14.19 (C-1, 17), 19.78 (×2, $CHCH_3$), 22.73 (C-16), 23.09 (C-2), 24.50 (C-7), 27.12 (C-11), 29.38 and 29.41 (C-13, 14), 29.73 (C-12), 30.08 (C-3), 31.98 (C-15), 32.80 (×2, C-5, 9), 36.79 (C-10), 37.10 (C-4), 37.47 (×2, C-6, 8); GC-MS: t_R 18.95 min, *m/z* 268 (M^+, 1%), 211 (9%), 155 (15%), 140 (13%), 85 (83%), 57 (100%); HR-MS calcd for $C_{19}H_{40}$ 268.3130; found 268.3126. In the same manner, the syntheses of (5*S*,9*S*)-**1** from (5*S*,8*SR*,9*S*)-**16**, (5*R*,9*S*)-**1** from (5*R*,8*SR*,9*S*)-**16**, and (5*R*,9*R*)-**1** from (5*R*,8*SR*,9*R*)-**16** were accomplished in similar yields (75–80%). (5*S*,9*S*)-**1**, $[\alpha]_D^{23} = +2.2$ (*c* 1.3, $CHCl_3$); ν_{max} (cm^{-1}): 2924 (s), 2854 (s), 1464 (m), 1377 (m), 723 (w); δ_H: 0.839 and 0.841 (6H, d, C*H*$_3$CH, *J* = 6.3 Hz), 0.88 (3H, t, C*H*$_3$CH$_2$, *J* = 7.0 Hz), 0.89 (3H, t, C*H*$_3$CH$_2$, *J* = 7.0 Hz), 1.0–1.4 (28H, m); δ_C: 14.14 and 14.19 (C-1, 17), 19.72 (×2, $CHCH_3$), 22.73 (C-16), 23.09 (C-2), 24.50 (C-7), 27.13 (C-11), 29.39 and 29.41 (C-13, 14), 29.73 (C-12), 30.08 (C-3), 31.98 (C-15), 32.77 (×2, C-5, 9), 36.89 (C-10), 37.19 (C-4),

37.41 (×2, C-6, 8) GC-MS: t_R 18.93 min, *m/z* 268 (M^+, 1%), 211 (8%), 155 (13%), 140 (13%), 85 (83%), 57 (100%); HR-MS calcd for $C_{19}H_{40}$ 268.3130; found 268.3125. (5*R*,9*S*)-**1**, $[\alpha]_D^{23} = -1.1$ (*c* 1.2, $CHCl_3$); HR-MS calcd for $C_{19}H_{40}$ 268.3130; found 268.3125. (5*R*,9*R*)-**1**, $[\alpha]_D^{23} = -2.1$ (*c* 1.3, $CHCl_3$); HR-MS calcd for $C_{19}H_{40}$ 268.3130; found 268.3126.

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