# The total synthesis of the archaebacterial $C_{40}$-diol and its enantiomer based on (*R*)-5-acetoxy-4-methylpentanoic acid

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Effective convergent syntheses of archaebacterial $C_{40}$-diol [(3*R*,7*R*,11*S*,15*S*,18*S*,22*S*, 26*R*,30*R*)-octamethyldotriacontane-1,32-diol] and its (3*S*,7*S*,11*R*,15*R*,18*R*,22*R*,26*S*,30*S*)-enantiomer have been accomplished using (*R*)-5-acetoxy-4-methylpentanoic acid as the only chiral building block. Both synthetic schemes include consecutive construction of mono- and diterpene fragments of the target molecules followed by dimerization using the Kolbe reaction or the oxidative self-condensation of the corresponding Grignard reagent.

**Key words:** archaebacterial $C_{40}$-diol, (*R*)-5-acetoxy-4-methylpentanoic acid as a chiral building block, convergent synthesis.

The key structural fragment of diglycerol tetraether (**1**), a constituent of thermoacidophilic and methanogenic bacteria,[1] is the title $C_{40}$-diol (**2a**), which has eight chiral centers. The absolute (3*R*,7*R*,11*S*,15*S*,18*S*, 22*S*,26*R*,30*R*)-configuration of the natural product **2a** was established by Heathcock *et al.*[1,2] on the basis of a unique thirty-step synthesis with a 0.4 % overall yield. The construction of the chiral centers was performed using an aldol-Claisen strategy, consisting of Evans variant of aldol condensation of α,β-unsaturated aldehydes with chiral enolates followed by the 1,5-stereoselective Claisen—Ireland rearrangement. The analogous approach was also applied by Heathcock[2] for the synthesis of (15*R*,18*R*)-diastereomer of **2a**. In the present paper syntheses of the natural $C_{40}$-diol **2a** and its (3*S*,7*S*,11*R*, 15*R*,18*R*,22*R*,26*S*,30*S*)-enantiomer (**2b**) based on a single chiral building block, the easily accessible[3] (*R*)-5-acetoxy-4-methylpentanoic acid (**3**), are considered. Previously we used the acid **3** for syntheses of several methyl-branched biologically active compounds.[4,5]

Retrosynthetic analysis of molecule **2a** possessing $C_2$-symmetry (Scheme 1) reveals that it may be con-

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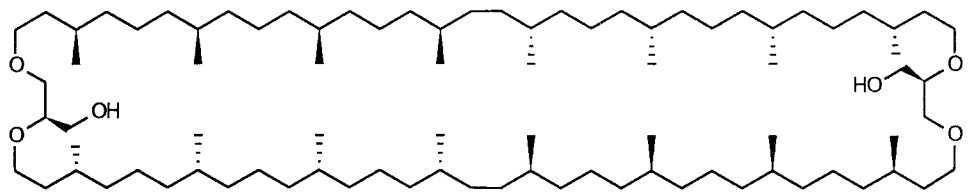
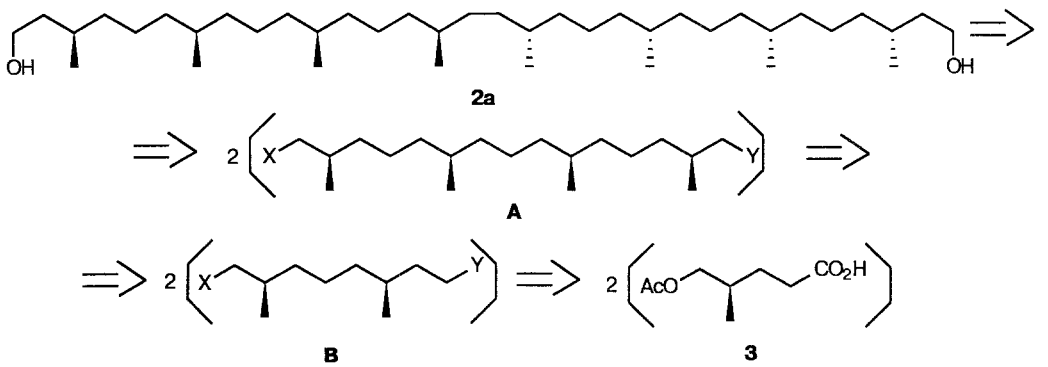



**1**

**Scheme 1**

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structed through the coupling of two norditerpene blocks (**A**), which can be prepared from two norditerpene fragments (**B**). The latter can evidently be presented as a combination of two molecules of the aforementioned synthone block **3**.

The analogous consideration of enantiomer **2b** (Scheme 2) reveals a simpler synthetic route from the same acetoxy acid **3** using stepwise construction of monoterpene (**C**) or diterpene (**D**) fragments of this molecule.

In accordance with the outlined plan for the synthesis of isomer **2a** (Scheme 3), acid **3** was transformed into the known monochiral $C_5$-bromides **4**[4] and **5**,[6] followed by cross-coupling of bromide **5** with the Grignard reagent prepared from **4** in the presence of the Kochi catalyst.[7] The moderate yield of the monoterpene head-to-tail ester (**6**), (*ca.* 60 % taking into account the recovered bromoacetate **5** or 40.5 % neglecting the incompleteness of its conversion) is possibly due to lability of the acetate group under the reaction conditions. This lability could result in the formation of the corresponding α,ω-bromohydrine alcoholate from bromoacetate **5** followed by smooth intramolecular cyclization into volative methyltetrahydrofuran.

The next stage of the synthesis of diol **2a** requires the transformation of acetate **6** into both $C_{10}$-components needed to produce the diterpene intermediate **A** shown in the retrosynthesis Scheme 1. One of the components, **9**, was routinely prepared from **6** *via* the alcohol **7** and the corresponding tosylate **8**, which was introduced into the reaction with NaBr without further purification. The second component, bromoacetate **11**, was prepared through hydroboration-oxidation of olefin **6** into alcohol **10** followed by treatment of the latter with $CBr_4$ and $Ph_3P$.

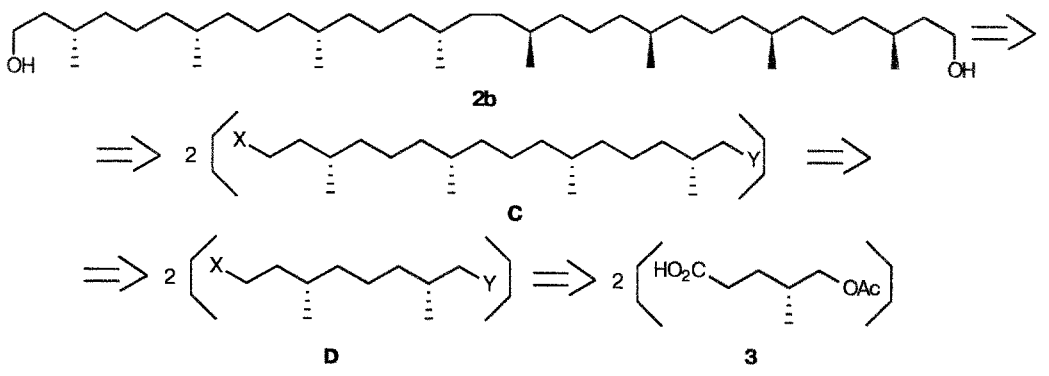
Cross-coupling of the Grignard reagent prepared from bromide **9** with bromoacetate **11** in the presence of the Kochi reagent affords acetate (**12**) in good yield (*ca.* 70%). Acetate **12**, which has four chiral centers, served as a key intermediate for both target products **2a** and **2b**. To obtain **2a**, it was necessary to carry out coupling of **12** from the vinyl group side with simultaneous elimination of two carbon atoms from the same side. To achieve this goal, diolefin **12** was subjected to hydroboration-oxidation and the obtained alcohol (**13**) was oxidized to the corresponding $C_{20}$-acid (**14**) using the Jones procedure. The Kolbe electolysis of acid **14** followed by the saponification of the acetate groups gave the desired diol (**15**). Possible reasons for the somewhat decreased yield of the $C_{38}$-diol **15** at the electrolysis stage are side processes, *e.g.*, decarboxylation-hydroxylation of the acid **14**, giving monomeric $C_{19}$-diol which was identified in the reaction mixture.

The final stage of the synthesis of **2a** is $C_1$-homologization of the symmetric molecule **15** from both ends. This was achieved using a routine procedure consisting of the transformation of diol **15** into the ditosylate (**16**) and then to the dinitrile (**17**), followed by two-step hydride reduction into the final product **2a**. The specific rotation of the latter, and the $^1H$ and $^{13}C$ NMR data, are in accordance with those previously published for the natural product.[1,2]

The synthesis of **2b** (Scheme 4) was performed starting from the diterpene acetate **12**, converted into the bromide (**22**) *via* the alcohol (**19**) and the tosylate (**21**) similarly to the transformation of the acetate **6** to the bromide **9**, considered above. The oxidative coupling of the Grignard reagent derived from the bromide **22** gives the $C_{40}$-diolefin **23** in an unexpectedly high yield (74 %, *cf.* Ref. 2); hydroboration-oxidation of the latter completes the synthesis of diol **2b** which was separated from the reaction mixture as the diacetate (**24**). Hydrolysis of **24** gave the final product **2b**, $[\alpha]_D^{31}$ −3.2° (*c* 1.0, $CHCl_3$). Its IR and NMR spectra were identical with those of its enantiomer **2a**.

Because the chiral centers of the intermediates were not affected at any stage of either synthetic scheme the optical purities of the final products **2a** and **2b** correspond to that of the acetoxy acid **3** and, therefore, exceed 98 %. These configurations have been confirmed with $^1H$ and $^{19}F$ NMR spectra of **18**, **20**, and **25**, prepared from the alcohols **2a**, **19**, and **2b**, respectively, and Mosher (*R*)-acid. All of the spectra demonstrate the presence of only one diastereomer, *cf.* Ref. 2. Structures

**Scheme 2**



of the other compounds (Schemes 3 and 4) were established unequivocally on the basis of spectral data and elemental analyses.

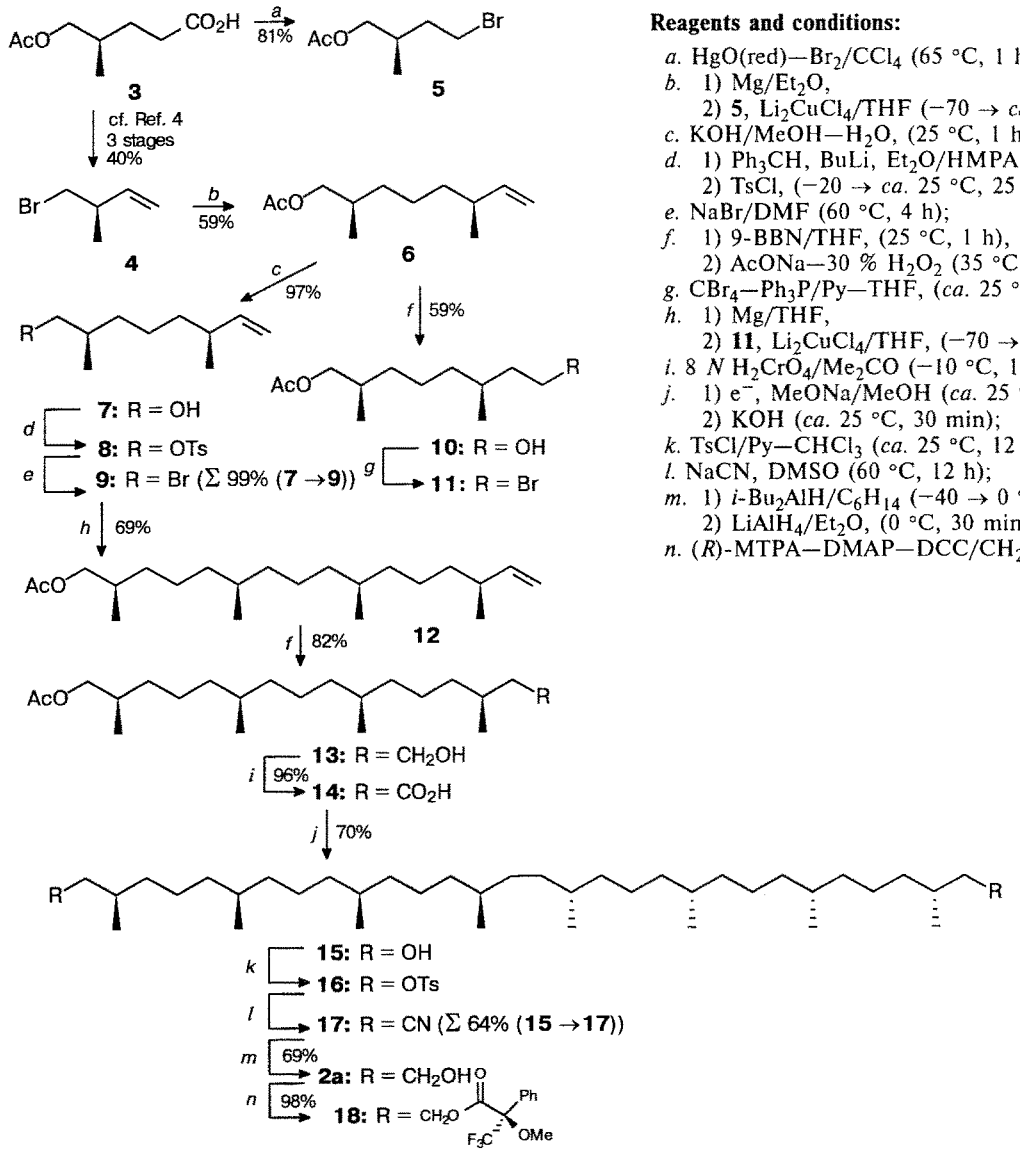
Thus, using the single chiral precursor **3**, convergent 17-step syntheses of the archaebacterial $C_{40}$-diol **2a** and its enantiomer **2b** were perfomed with 1.5 % and 2.5 % overall yields, respectively.

## Experimental

The IR spectra were recorded with an UR-20. spectrometer in $CHCl_3$ solutions. The $^1H$, $^{13}C$ and $^{19}F$ NMR spectra were obtained with Bruker AC-200, Bruker WM-250, Bruker AM-300, and Bruker AMX-400 spectrometers in $CDCl_3$ solutions. The EI mass spectra were measured with Varian MAT CH-6 and Varian MAT 311A instruments at 70 eV. The GLC analyses were made with an LKhM-80 chromatograph (3 m × 3 mm packed column with 15 % Carbowax 20M on Chromaton N-AW-DMCS). The $R_f$ values are given for Silufol plates ($SiO_2$ on aluminium foil). The $[\alpha]_D$ values were measured on a Jasco DIP-360 polarimeter for $CHCl_3$ solutions.

**(*R*)-4-Bromo-2-methylbutyl acetate (5).** A mixture of acetoxy acid **3** (10.9 g, 62.6 mmole) and red HgO (16.97 g, 78.4 mmole) in 170 mL of $CCl_4$ was heated at 50 °C for 30 min, then treated with $Br_2$ (13.5 g, 84.4 mmole) in 20 mL of $CCl_4$ at 65 °C for 40 min. The reaction mixture was stirred at 65 °C for 1 h, then cooled to *ca.* 25 °C, and filtered through a layer of silica gel (*ca.* 5 cm). The filtrate was washed with aqueous saturated solutions of $NaHCO_3$ and NaCl, dried over $Na_2SO_4$, and evaporated. The residue was distilled *in vacuo* giving 10.6 g (81 % yield) of the bromoacetate **5**, b. p. 53 °C (1 Torr), $n_D^{25}$ 1.4567, $[\alpha]_D^{29}$ +7.3° (*c* 3.8). Lit.[6]: b. p. 117—118 °C (25 Torr),

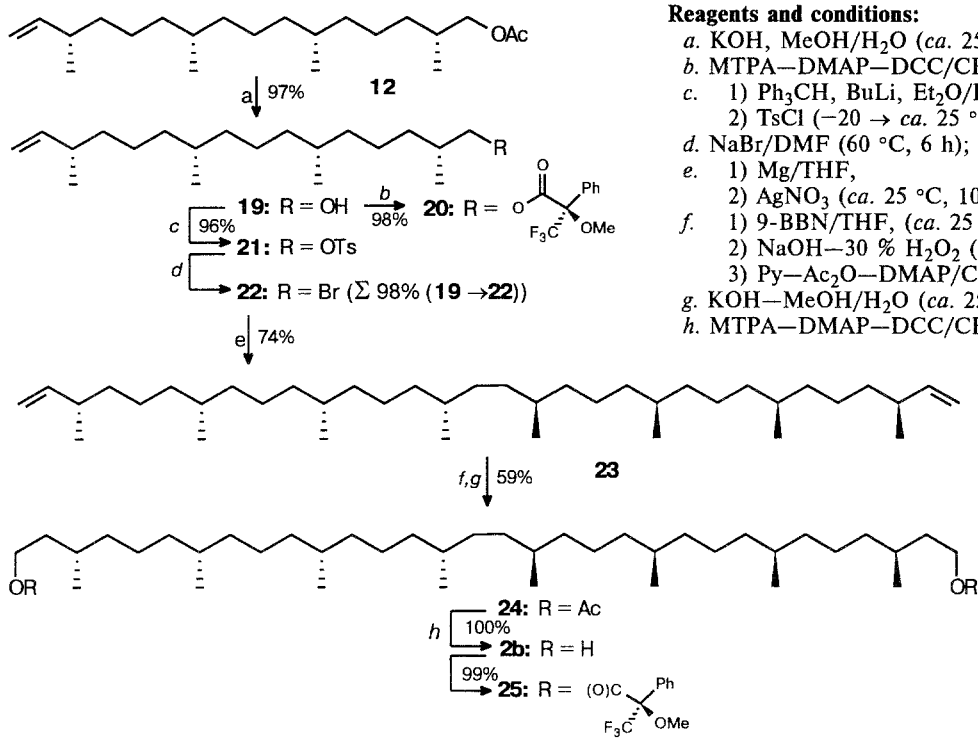
**Scheme 3**




**Reagents and conditions:**

*a.* $HgO(red)—Br_2/CCl_4$ (65 °C, 1 h);
*b.* 1) $Mg/Et_2O$,
2) **5**, $Li_2CuCl_4/THF$ (−70 → *ca.* 25 °C, 3 h);
*c.* $KOH/MeOH—H_2O$, (25 °C, 1 h);
*d.* 1) $Ph_3CH$, BuLi, $Et_2O$/HMPA,
2) TsCl, (−20 → *ca.* 25 °C, 25 min);
*e.* NaBr/DMF (60 °C, 4 h);
*f.* 1) 9-BBN/THF, (25 °C, 1 h),
2) AcONa—30 % $H_2O_2$ (35 °C, 1 h);
*g.* $CBr_4—Ph_3P/Py—THF$, (*ca.* 25 °C, 24 h);
*h.* 1) Mg/THF,
2) **11**, $Li_2CuCl_4$/THF, (−70 → *ca.* 25 °C, 3 h);
*i.* 8 *N* $H_2CrO_4/Me_2CO$ (−10 °C, 1.5 ч);
*j.* 1) $e^-$, MeONa/MeOH (*ca.* 25 °C, *ca.* 2 h),
2) KOH (*ca.* 25 °C, 30 min);
*k.* $TsCl/Py—CHCl_3$ (*ca.* 25 °C, 12 h);
*l.* NaCN, DMSO (60 °C, 12 h);
*m.* 1) *i*-$Bu_2AlH/C_6H_{14}$ (−40 → 0 °C, 30 min),
2) $LiAlH_4/Et_2O$, (0 °C, 30 min);
*n.* (*R*)-MTPA—DMAP—$DCC/CH_2Cl_2$, (25 °C, 12 h).

**Scheme 4**




**Reagents and conditions:**

*a*. KOH, MeOH/$H_2O$ (*ca.* 25 °C, 1 h);
*b*. MTPA—DMAP—DCC/$CH_2Cl_2$ (*ca.* 25 °C, 12 h);
*c*. 1) $Ph_3CH$, BuLi, $Et_2O$/HMPA,
2) TsCl (−20 → *ca.* 25 °C, 25 min);
*d*. NaBr/DMF (60 °C, 6 h);
*e*. 1) Mg/THF,
2) $AgNO_3$ (*ca.* 25 °C, 10 h);
*f*. 1) 9-BBN/THF, (*ca.* 25 °C, 1 h),
2) NaOH—30 % $H_2O_2$ (35 °C, 1 h),
3) Py—$Ac_2O$—DMAP/$CH_2Cl_2$ (*ca.* 25 °C, 2 h);
*g*. KOH—MeOH/$H_2O$ (*ca.* 25 °C, 2 h);
*h*. MTPA—DMAP—DCC/$CH_2Cl_2$ (*ca.* 25 °C, 12 h).

$n_D^{18}$ 1.4659. $^1$H NMR, δ: 0.97 (d, 3 H, $CH_3$, $J$ = 7 Hz); 1.7—2.0 (m, 3 H, HC-2, $H_2C$-3); 2.07 (s, 3 H, $CH_3$); 3.45 (m, 2 H, $H_2C$-4); 3.95 (AB part of ABX spin system) (2 H, $H_2C$-1, $\delta_A$ = 3.92, $\delta_B$ = 3.98, $J_{AB}$ = 10 Hz, $J_{AX}$ = $J_{BX}$ = 4 Hz).

**(2*R*,6*S*)-2,6-Dimethyl-7-octenyl Acetate (6).** At −70 °C under Ar a solution of **5** (2.86 g, 12.8 mmole) in 22 mL of THF was added over 20 min to a stirred solution of Grignard reagent, prepared from the bromide **4**[4] (2.86 g, 19.15 mmole) and Mg (0.51 g, 21.25 mmole) in 15 mL of ether, and then a 0.1 *M* solution of $Li_2CuCl_4$ (1.92 mL, 0.19 mmole) in THF was added in one portion. The reaction mixture was kept at −40 °C for 30 min and at *ca.* 25 °C for 2 h, then treated with AcCl (0.9 mL, 12.7 mmole). After stirring for 30 min it was treated with a saturated solution of $NH_4Cl$, and then extracted with ether. The extract was washed with a saturated solution of NaCl, dried over $MgSO_4$, evaporated *in vacuo,* and the residue (0.25 g) was chromatographed on 100 g of $SiO_2$. The gradient elution (from hexane to hexane—ether, 95:5 v/v) gave 0.85 g of the starting bromoacetate **5** and 1.03 g (59 % yield) of the acetate **6**, b. p. 60 °C (1 Torr), $n_D^{20}$ 1.4345, $[\alpha]_D^{24}$ +11.5° (*c* 2.7). IR, ν/cm$^{-1}$: 640, 670, 685, 704, 714, 920, 1040, 1210, 1370, 1380, 1400, 1430, 1470, 1640, 1730, 3020, 3080. $^1$H NMR, δ: 0.91 (d, 3 H, $CH_3$, $J$ = 7 Hz); 0.98 (d, 3 H, $CH_3$, $J$ = 7 Hz); 1.2—1.4 (m, 6 H, $CH_2$); 1.75 (m, 1 H, HC-2); 2.07 (s, 3 H, $CH_3$); 2.10 (m, 1 H, HC-6); 3.89 (AB part of ABX spin system, 2 H, $H_2C$-1, $\delta_A$ = 3.84, $\delta_B$ = 3.94, $J_{AB}$ = 12 Hz, $J_{AX}$ = $J_{BX}$ = 7 Hz); 4.86—5.00 (m, 2 H, HC-8); 5.67 (ddd, 1 H, HC-7, $J$ = 18, 11 and 7 Hz). Mass spectrum, *m/z* ($I_{rel}$ (%)): $M^+$ 198 (6), 123 (20), 110 (15), 109 (66), 97 (86), 96 (69), 83 (62), 82 (100), 81 (96), 56 (40), 55 (71). Found (%): C, 72.41; H, 11.11. $C_{12}H_{22}O_2$. Calculated (%): C, 72.61; H, 11.17.

**(2*R*,6*S*)-2,6-Dimethyl-7-octenol (7).** A solution of acetate **6** (3.0 g, 15.15 mmole) and KOH (1.5 g, 27.1 mmole) in 9 mL of MeOH and 3 mL of water was kept at *ca.* 25 °C for 1 h, then neutralized with 1 *N* HCl and extracted with ether. After the usual workup the extract was dried over $MgSO_4$, and the residue was distilled giving 2.27 g (97 % yield) of **7**, b.p. 65 °C (1 Torr), $n_D^{20}$ 1.4496, $[\alpha]_D^{25}$ +6.79° (*c* 8.3). IR, ν/cm$^{-1}$: 660, 915, 950, 1025, 1200, 1265, 1370, 1410, 1420, 1430, 1465, 1640, 1710, 3080, 3450, 3580, 3630. $^1$H NMR, δ: 0.91 (d, 3 H, $CH_3$, $J$ = 7 Hz); 0.99 (d, 3 H, $CH_3$, $J$ = 7 Hz); 1.2—1.4 (m, 6 H, $CH_2$); 1.60 (m, 1 H, HC-2); 2.10 (m, 1 H, HC-6); 3.46 (AB part of ABX spin system, 2H, $H_2C$-1, $\delta_A$ = 3.42, $\delta_B$ = 3.50, $J_{AB}$ = 10 Hz, $J_{AX}$ = $J_{BX}$ = 7 Hz); 4.86—5.00 (m, 2 H, $H_2C$-8); 5.68 (ddd, 1 H, HC-7, $J$ = 17, 10 and 7 Hz). Mass spectrum, *m/z* ($I_{rel}$ (%)): 138 (3), 136 (8), 123 (10), 109 (20), 96 (16), 95 (17), 83 (28), 82 (26), 81 (37), 69 (32), 67 (31), 55 (100), 43 (28), 41 (44). Found (%): C, 76.90; H, 13.07. $C_{10}H_{20}O$. Calculated (%): C, 76.86; H, 12.90.

**(2*R*,6*S*)-1-Tosyloxy-2,6-dimethyl-7-octene (8).** At −20 °C under Ar a 1.2 *M* solution of BuLi (5.5 mL, 6.6 mmole) was added dropwise to a stirred solution of alcohol **7** (1.0 g, 6.4 mmole) and $Ph_3CH$ (6 mg) in 16 mL of ether and 1.4 mL of HMPA until a stable pink coloration developed. Then the mixture was treated with TsCl (1.39 g 7.29 mmole) for 5 min, heated up to *ca.* 25 °C for 20 min, diluted with water, and extracted with ether. After the usual workup the extract was dried over $MgSO_4$, evaporated *in vacuo,* and 1.9 g of the tosylate **8** was obtained. The latter was introduced into the next reaction without further purification.

**(2*R*,6*S*)-1-Bromo-2,6-dimethyl-7-octene (9).** A mixture of the tostylate **8** prepared as above and NaBr (2.83 g, 27.5 mmole) in 20 mL of DMF was heated at 60 °C for 4 h, then diluted with water and extracted with hexane. The extract was washed with a saturated solution of NaCl, dried over $Na_2SO_4$, evaporated *in vacuo,* and the residue (*ca.* 1.5 g) was chromatographed on 50 g of $SiO_2$. The elution with hexane—ether (98:2 v/v) gave 1.4 g of **9** (99 % on the alcohol **7**), b. p. 56 °C (1 Torr), $n_D^{20}$ 1.4659, $[\alpha]_D^{22}$ +10.1°

(*c* 8.3). IR, ν/cm$^{-1}$: 685, 920, 1000, 1210, 1380, 1420, 1430, 1440, 1460, 1640, 1710, 3010, 3080. $^1$H NMR, δ: 0.99 (d, 3 H, $CH_3$, $J$ = 7 Hz); 1.02 (d, 3 H, $CH_3$, $J$ = 7 Hz); 1.2—1.4 (m, 6 H, $CH_2$); 1.78 (m, 1 H, HC-2); 2.13 (m, 1 H, HC-6); 3.37 (AB part of ABX spin system, 2H, $H_2C$-1, $\delta_A$ = 3.34, $\delta_B$ = 3.40, $J_{AB}$ = 10 Hz, $J_{AX}$ = 7 Hz, $J_{BX}$ = 5 Hz); 4.88—5.01 (m, 2 H, $H_2C$-8); 5.68 (ddd, 1 H, HC-7, $J$ = 17, 10, and 7 Hz). Mass spectrum, *m/z* ($I_{rel}$ (%)): 163 (11), 165 (12), 149 (6), 97 (8), 85 (6), 81 (8), 71 (11), 70 (11), 69 (18), 57 (19), 55 (22), 46 (31), 45 (100), 44 (63), 43 (40), 41 (22). Found (%): C, 55.22; H, 9.06; Br, 36.33. $C_{10}H_{19}Br$. Calculated (%): C, 54.80; H, 8.74; Br, 36.45.

**(2*R*,6*S*)-2,6-Dimethyl-8-hydroxyoctyl acetate (10).** At 0 °C under Ar a solution of acetate **6** (1.1 g, 5.53 mmole) in 5.5 mL of THF was added over 10 min to a stirred suspension of 9-borabicyclo[3.3.1]nonane (9-BBN, 1.05 g, 8.6 mmole) in 10 mL of THF. The reaction mixture was stirred at *ca.* 25 °C for 10 min, then treated first with a solution of AcONa (1.74 g, 21.2 mmole) in 4 mL of water and then with 30 % $H_2O_2$ (6.04 mL, 60.4 mmole). The mixture was kept at 35 °C for 1 h, diluted with ether, washed with a saturated solution of NaCl, dried over $MgSO_4$, evaporated *in vacuo,* and the residue (2.0 g) was chromatographed on 70 g of $SiO_2$. The gradient elution (from hexane to hexane—ethyl acetate 60:40 v/v) gave 0.7 g (59 % yield) of the hydroxyacetate **10** as a colorless oil, $R_f$ 0.44 (ether), $n_D^{19}$ 1.4487, $[\alpha]_D^{27}$ +0.1° (*c* 1.7). IR, ν/cm$^{-1}$: 665, 725, 1035, 1210, 1245, 1370, 1380, 1455, 1465, 1720, 3000, 3610. $^1$H NMR, δ: 0.88 (d, 3 H, $CH_3$, $J$ = 7 Hz); 0.92 (d, 3 H, $CH_3$, $J$ = 7 Hz); 1.1—1.9 (m, 10 H, $CH_2$, CH); 2.07 (s, 3 H, $CH_3$); 3.63—3.75 (m, 2 H, $H_2C$-8); 3.90 (AB part of ABX spin system, 2H, $H_2C$-1, $\delta_A$ = 3.85, $\delta_B$ = 3.95, $J_{AB}$ = 10 Hz, $J_{AX}$ = 7 Hz, $J_{BX}$ = 6 Hz). Mass spectrum, *m/z* ($I_{rel}$ (%)): 202 (10), 200 (7), 126 (12), 123 (9), 111 (9), 110 (14), 109 (13), 96 (18), 95 (15), 85 (23), 83 (43), 82 (33), 81 (50), 69 (57), 68 (30), 56 (40), 55 (57), 43 (100), 41 (43). Found (%): C, 66.37; H, 11.16. $C_{12}H_{24}O_3$. Calculated (%): C, 66.63; H, 11.18.

**(2*R*,6*S*)-2,6-Dimethyl-8-bromooctyl acetate (11).** At 0 °C under Ar $Ph_3P$ (0.73 g, 2.8 mmole) was added in one portion to a stirred solution of hydroxyacetate **10** (0.51 g 2.36 mmole), $CBr_4$ (0.93 g, 2.8 mmole), and Py (0.2 mL, 2.49 mmole) in 15 mL of THF. The reaction mixture was stirred at 5—10 °C for 1 h and at *ca.* 25 °C for 2 h, then diluted with hexane and filtered through a layer of $SiO_2$ (*ca.* 3 cm). The filtrate was evaporated *in vacuo* and the residue (0.65 g) was chromatographed on 50 g of $SiO_2$. The gradient elution (from hexane to hexane—ether 96 : 4 %, v/v) gave 0.54 g (82 % yield) of the bromoacetate **11**, b.p. 78 °C (0.035 Torr), $n_D^{21}$ 1.4625, $[\alpha]_D^{28}$ +4.9° (*c* 2.2). IR, ν/cm$^{-1}$: 640, 730, 990, 1040, 1210, 1250, 1380, 1460, 1725, 3010. $^1$H NMR, δ: 0.90 (d, 3 H, $CH_3$, $J$ = 7 Hz); 0.94 (d, 3 H, $CH_3$, $J$ = 7 Hz); 1.1—1.9 (m, 10 H, $CH_2$, CH); 2.07 (s, 3 H, $CH_3$); 3.35—3.55 (m, 2 H, $H_2C$-8); 3.91 (AB part of ABX spin system, 2 H, $H_2C$-1, $\delta_A$ = 3.86, $\delta_B$ = 3.96, $J_{AB}$ = 10 Hz, $J_{AX}$ = 7 Hz, $J_{BX}$ = 6 Hz). Mass spectrum *m/z* ($I_{rel}$ (%)): 178 (11), 176 (9), 164 (13), 162 (14), 111 (19), 97 (21), 83 (100), 73 (17), 72 (19), 69 (100), 57 (37), 56 (41), 55 (46), 43 (26), 41 (59). Found (%): C, 51.96; H, 8.47; Br, 28.45. $C_{12}H_{23}O_2Br$. Calculated (%): C, 51.62; H, 8.30; Br, 28.62.

**(2*R*,6*R*,10*S*,14*S*)-2,6,10,14-Tetramethyl-15-hexadecen-1-yl acetate (12).** At −70 °C under Ar a solution of a bromoacetate **11** (0.81 g, 2.91 mmole) in 3 mL of THF was added over 20 min to a stirred solution of Grignard reagent, prepared from the bromide **9** (1.15 g, 5.25 mmole) and Mg (0.15 g, 6.25 mmole) in 5 mL of THF, and then a 0.1 *M* solution of $Li_2CuCl_4$ (0.52 mL, 0.052 mmole) in THF was added in one portion. The reaction mixture was kept at *ca.* 25 °C for 3 h, then treated with AcCl (0.21 mL, 2.91 mmole), and after standing for 30 min was treated with a saturated solution of $NH_4Cl$ and extracted with ether. The extract was washed with a saturated solution of NaCl, dried over $MgSO_4$, evaporated *in vacuo,* and the residue (0.9 g) was chromatographed on 50 g $SiO_2$. The gradient elution (from hexane to hexane—ether, 95:5,v/v) gave 0.07 g of the starting bromoacetate **11** and 0.62 g (69 % yield) of the acetate **12** as a colorless oil, $R_f$ 0.71 (hexane), $n_D^{21}$ 1.4518, $[\alpha]_D^{25}$ +6.1° (*c* 8.3). IR, ν/cm$^{-1}$: 670, 730, 920, 1040, 1210, 1250, 1370, 1380, 1390, 1460, 1640, 1725, 3020. $^1$H NMR, δ: 0.85 (d, 3 H, $CH_3$, $J$ = 7 Hz); 0.86 (d, 3 H, $CH_3$, $J$ = 7 Hz); 0.93 (d, 3 H, $CH_3$, $J$ = 7 Hz); 0.99 (d, 3 H, $CH_3$, $J$ = 7 Hz); 1.1—1.4 (m, 20 H, $CH_2$, $H_2C$-6, $H_2C$-10); 1.78 (m, 1 H, HC-2); 2.08 (s, 3 H, $CH_3$); 2.10 (m, 1 H, HC-14); 3.91 (AB part of ABX spin system, 2 H, $H_2C$-1, $\delta_A$ = 3.86, $\delta_B$ = 3.96, $J_{AB}$ = 10 Hz, $J_{AX}$ = 7 Hz, $J_{BX}$ = 6 Hz); 4.87—5.01 (m, 2 H, $H_2C$-16); 5.70 (ddd, 1 H, HC-15, $J$ = 18, 11 and 7 Hz). Mass spectrum, *m/z* ($I_{rel}$ (%)): $M^+$ 338 (0.4), 278 (14), 138 (12), 137 (12), 125 (17), 124 (19), 123 (35), 111 (33), 110 (23), 97 (43), 96 (30), 95 (42), 83 (58), 82 (54), 81 (39), 71 (29), 70 (37), 69 (95), 57 (57), 56 (41), 55 (94), 45 (48), 43 (100), 41 (42). Found (%): C, 77.99; H, 12.82. $C_{22}H_{42}O_2$. Calculated (%): C, 78.05; H, 12.50.

**(2*R*,6*R*,10*S*,14*S*)-2,6,10,14-Tetramethyl-16-hydroxyhexadecyl acetate (13).** At 0 °C under Ar a solution of acetate **12** (0.75 g, 2.22 mmole) in 3 mL of THF was added over 5 min to a stirred suspension of 9-BBN (0.41 g, 3.36 mmole) in 4 mL of THF. The reaction mixture was stirred at *ca.* 25 °C for 1 h, then treated with aqueous solutions of AcONa (0.71 g, 8.66 mmole) in 2 mL of water and then with a 30% solution of $H_2O_2$ (2.47 mL, 24.4 mmole). The mixture was kept at *ca.* 25 °C for 2 h, and at 35 °C for 1 h, diluted with ether, washed with a saturated solution of NaCl, dried over $MgSO_4$, and evaporated *in vacuo.* The residue (1.7 g) was chromatographed on 50 g of $SiO_2$. The gradient elution (from hexane to hexane—ether, 70:30, v/v) gave 0.65 g (82 % yield) of the hydroxyacetate **13** as a colorless oil, $R_f$ 0.23 (ether—hexane, 1:1), $n_D^{22}$ 1.4596, $[\alpha]_D^{23}$ −1.7° (*c* 6.3). IR, ν/cm$^{-1}$: 670, 730, 990, 1040, 1210, 1250, 1380, 1390, 1460, 1725, 3000, 3610. $^1$H NMR, δ: 0.85 (d, 6 H, $CH_3$, $J$ = 7 Hz); 0.90 (d, 3 H, $CH_3$, $J$ = 7 Hz); 0.93 (d, 3 H, $CH_3$, $J$ = 7 Hz); 1.1—1.9 (m, 24 H, $CH_2$, CH); 2.07 (s, 3H, $CH_3$); 3.65—3.75 (m, 2H, $H_2C$-16); 3.91 (AB part of ABX spin system, 2 H, $H_2C$-1, $\delta_A$ = 3.86, $\delta_B$ = 3.96, $J_{AB}$ = 11 Hz, $J_{AX}$ = 7 Hz, $J_{BX}$ = 6 Hz). Mass spectrum *m/z* ($I_{rel}$ (%)): $M^+$ 356 (1), 296 (3), 277 (27), 266 (33), 265 (30), 127 (90), 126 (90), 125 (90), 124 (80), 111 (87), 110 (93), 109 (90), 97 (97), 96 (90), 95 (77), 85 (43), 83 (100), 82 (97), 81 (83), 71 (90), 70 (83), 69 (97), 57 (97), 56 (93), 55 (90). High resolution Mass spectrum, *m/z*: found for $[M-AcOH]^+$: 296.3097; calculated for $C_{20}H_{40}O$: 296.3079.

**(3*S*,7*S*,11*R*,15*R*)-3,7,11,15-Tetramethyl-16-acetoxyhexadecanoic Acid (14).** An 8 *N* aqueous solution of $H_2CrO_4$ (0.3 mL, 2.34 mmole) was added at −10 °C to a stirred solution of hydroxyacetate **13** (0.1 g, 0.28 mmole) in 2 mL of acetone. The mixture was kept at −10 °C for 1.5 h, then treated with 0.22 mL of 2-propanol, and evaporated *in vacuo.* The residue was dissolved in water and extracted with ether. The extract was washed with a saturated solution of NaCl, dried over $MgSO_4$, and evaporated *in vacuo* giving 0.1 g (96 % yield) of acid **14**, used in the next stage without further purification. $^1$H NMR, δ: 0.85 (d, 6 H, $CH_3$, $J$ = 7 Hz); 0.93 (d, 3 H, $CH_3$, $J$ = 7 Hz); 0.97 (d, 3 H, $CH_3$, $J$ = 7 Hz); 1.1—1.9 (m, 22 H, $CH_2$, CH); 2.07 (s, 3 H, $CH_3$); 2.30—2.46 (m, 2 H, $H_2C$-2); 3.90 (AB part of ABX spin system, 2 H, $H_2C$-16, $\delta_A$ = 3.85, $\delta_B$ = 3.95, $J_{AB}$ = 11 Hz, $J_{AX}$ = 7 Hz, $J_{BX}$ = 5.5 Hz).

**(2*R*,6*R*,10*S*,14*S*,17*S*,21*S*,25*R*,29*R*)-2,6,10,14,17,21,25,29-Octamethyltriacontane-1,30-diol (15).** A mixture of the acid **14** (37.4 mg, 0.101 mmole) and 0.3 *M* solution of MeONa

in MeOH (0.15 mL) was subjected to electrolysis in an electrolyzer equipped with platinum electrodes at 10 mA for *ca.* 2 h until the pH of the medium became basic, then diluted with 1 mL of MeOH and treated with KOH (0.3 g, 5.31 mmole). After standing for 30 min the reaction mixture was diluted with water and extracted with ether. The extract was neutralized with 1 *N* HCl, washed with a saturated solution of NaCl, dried over $MgSO_4$, evaporated *in vacuo*, and the residue (33 mg) was chromatographed on 10 g of $SiO_2$. Elution with ether gave 20 mg (70 % yield) of the diol **15** as a colorless oil, $R_f$ 0.49 (ether), $n_D^{23}$ 1.4925, $[\alpha]_D^{24}$ +3.4° (*c* 1.0). IR, $\nu/cm^{-1}$: 670, 930, 1025, 1065, 1110, 1140, 1210, 1320, 1380, 1400, 1460, 1520, 3010, 3630. $^1H$ NMR, δ: 0.85 (d, 18 H, $CH_3$, $J$ = 7 Hz); 0.93 (d, 6 H, $CH_3$, $J$ = 7 Hz); 1.05—1.45 (m, 46 H, $CH_2$, CH); 1.62 (m, 2 H, HC-2, HC-29); 3.48 (AB part of ABX spin system, 4 H, $H_2C$-1, $H_2C$-30, $\delta_A$ = 3.44, $\delta_B$ = 3.52, $J_{AB}$ = 10 Hz, $J_{AX}$ = $J_{BX}$ = 7 Hz). Mass spectrum, *m/z* ($I_{rel}$ (%)): $M^+$ 566 (3), 266 (7), 196 (8), 139 (9), 126 (16), 125 (18), 123 (19), 111 (72), 110 (39), 109 (23), 97 (56), 83 (72), 81 (39), 71 (56), 69 (100), 63 (44), 57 (83), 55 (61), 43 (56). High resolution. Mass spectrum, *m/z*: for $M^+$ found 566.6023; calculated for $C_{38}H_{78}O_2$: 566.6001.

**(2*R*,6*R*,10*S*,14*S*,17*S*,21*S*,25*R*,29*R*)-1,30-Ditosyloxy-2,6,10,14,17,21,25,29-octamethyltriacontane (16).** TsCl (0.1 g, 0.525 mmole) was added in one portion to a stirred solution of diol **15** (0.1 g, 0.177 mmole) and Py (0.07 mL, 0.87 mmole) in 2 mL of $CHCl_3$ at *ca.* 25 °C. After standing for 12 h the mixture was diluted with ether, washed with 5 % HCl, then with a saturated solution of NaCl, dried over $MgSO_4$, and evaporated *in vacuo* giving 0.12 g of tosylate **16**. The latter was introduced into the next stage without further purification. $^1H$ NMR, δ: 0.82 (d, 6 H, $CH_3$, $J$ = 7 Hz); 0.84 (d, 12 H, $CH_3$, $J$ = 7 Hz); 0.89 (d, 6 H, $CH_3$, $J$ = 7 Hz); 1.1—1.4 (m, 46 H, $CH_2$, CH); 1.77 (m, 2 H, HC-2, HC-29); 2.47 (c, 6 H, $CH_3$ of Ts); 3.85 (AB part of ABX spin system, 4 H, $H_2C$-1, $H_2C$-30, $\delta_A$ = 3.80, $\delta_B$ = 3.90, $J_{AB}$ = 12 Hz, $J_{AX}$ = 7 Hz, $J_{BX}$ = 6 Hz); 7.34 (д, 4 H, CH of Ts, $J$ = 8 Hz); 7.80 (d, 4 H, CH of Ts, $J$ = 8 Hz).

**(2*R*,6*R*,10*S*,14*S*,17*S*,21*S*,25*R*,29*R*)-1,30-Dicyano-2,6,10,14,17,21,25,29-octamethyltriacontane (17).** A solution of tosylate **16** prepared in the experiment described above and NaCN (70 mg, 1.43 mmole) in 2 mL of DMSO was heated at 55—60 °C for 12 h, then diluted with water and extracted with an ether—hexane mixture (3:1, v/v). The extract was washed with a saturated solution of NaCl, dried over $MgSO_4$, and evaporated *in vacuo*. The residue (*ca.* 0.1 g) was chromatographed on 15 g of $SiO_2$. The gradient elution (from hexane to hexane—ether, 80:20, v/v) gave 66 mg (64 % yield calculated on the diol **15**) of the dinitrile **17** as a colorless oil, $R_f$ 0.46 (hexane—ether, 2:3), $[\alpha]_D^{25}$ +4.3° (*c* 2.7). IR, $\nu/cm^{-1}$: 560, 700, 930, 1100, 1130, 1180, 1185, 1200, 1300, 1380, 1410, 1490, 1520, 2330, 2360, 2400, 3030. $^1H$ NMR, δ: 0.83—0.88 (m, 18 H, $CH_3$); 1.07 (d, 6 H, $CH_3$, $J$ = 7 Hz); 1.15—1.45 (m, 46 H, $CH_2$, CH); 1.85 (m, 2 H, HC-2, HC-29); 2.28 (AB part of ABX spin system, 4 H, $H_2C$-1, $H_2C$-30, $\delta_A$ = 2.24, $\delta_B$ = 2.32, $J_{AB}$ = 17 Hz, $J_{AX}$ = 7 Hz, $J_{BX}$ = 6 Hz). $^{13}C$ NMR, δ: 19.51, 19.66, 19.72 and 19.77 ($CH_3$); 24.29, 24.43, 24.45 and 24.48 ($CH_2$); 30.49, 32.69, 32.79 and 33.05 (CH); 34.31, 36.22, 36.89, 37.34, 37.38, 37.39 и 37.55 ($CH_2$); 118.91 (CN). Mass spectrum, *m/z* ($I_{rel}$ (%)): $M^+$ 584 (13), 335 (40), 279 (38), 250 (30), 222 (30), 208 (50), 194 (30), 180 (40), 167 (58), 151 (60), 139 (100), 138 (70), 109 (40), 97 (58), 85 (80), 84 (58), 83 (70), 71 (58), 70 (70), 57 (90), 56 (83), 55 (80), 43 (58). High resolution. Mass spectrum, *m/z*: for $M^+$ found 584.5978; calculated for $C_{40}H_{76}N_2$: 584.6004.

**(3*R*,7*R*,11*S*,15*S*,18*S*,22*S*,26*R*,30*R*)-3,7,11,15,18,22,26,30-Octamethyldotriacontane-1,32-diol (2a).** A 20 % solution of *i*-$Bu_2AlH$ (0.080 mL, 0.1 mmole) was added to a stirred solution of dinitrile **17** (20 mg, 0.034 mmole) in 0.5 mL of hexane under Ar at −40 °C. The mixture was heated to 0 °C for 30 min, diluted with ether, washed with saturated solutions of $NaHSO_4$ and NaCl, dried over $Na_2SO_4$, and evaporated *in vacuo*. The residue (*ca.* 20 mg) was dissolved in 0.5 mL of ether at 0 °C, and $LiAlH_4$ (3 mg, 0.08 mmole) was added. After standing for 30 min the mixture was treated with water and extracted with ether. The extract was dried over $MgSO_4$, evaporated *in vacuo*, and the residue (*ca.* 20 mg) was chromatographed on 10 g of $SiO_2$. The gradient elution (from hexane to hexane—ether, 20:80 v/v) gave 14 mg (69 % yield) of the diol **2a** as a colorless oil, $R_f$ 0.38 (ether—hexane, 3:1), $[\alpha]_D^{26}$ +3.6° (*c* 1.5). Lit.[1,2]: $[\alpha]_D$ +1.9° (*c* 0.97, $CHCl_3$); for natural product: $[\alpha]_D$ +4.8° ±0.63° (*c* 0.3, $CHCl_3$). $^1H$ NMR, δ: 0.85 (d, 18 H, $CH_3$, $J$ = 7 Hz); 0.90 (d, 6 H, $CH_3$, $J$ = 7 Hz); 1.05—1.45 (m, 48 H, $CH_2$, CH); 1.5—1.7 (m, 4 H, $H_2C$-2, $H_2C$-31); 3.70 (m, 4 H, $H_2C$-1, $H_2C$-32). $^{13}C$ NMR, δ: 19.69 (3-$CH_3$ and 30-$CH_3$), 19.74 (15-$CH_3$ and 18-$CH_3$), 19.77 (7-$CH_3$ and 26-$CH_3$), 19.79 (11-$CH_3$ and 22-$CH_3$); 24.37 (C-5 and C-28), 24.47 (C-9 and C-24), 24.49 (C-13 and C-20); 29.55 (C-3 and C-30), 32.81 (C-7 and C-26, C-11 and C-22), 33.07 (C-15 and C-18), 34.32 (C-16 and C-17), 37.33 (C-10 and C-23), 37.40 (C-6 and C-27), 37.42 (C-4 and C-29, C-8 and C-25), 37.50 (C-12 and C-21), 37.56 (C-14 and C-19), 39.99 (C-2 and C-31), 61.27 (C-1 and C-32).

**Di-1,32-[(*R*)-2-methoxy-2-phenyl-3,3,3-trifluoropropionyloxy]-(3*R*,7*R*,11*S*,15*S*,18*S*,22*S*,26*R*,30*R*)-3,7,11,15,18,22,26,30-octamethyldotriacontane (18).** *N,N*-Dimethylaminopyridine (DMAP) (1 mg, 0.008 mmole) and *N,N*-dicyclohexylcarbodiimide (DCC) (10 mg, 0.048 mmole) were added to a solution of diol **2a** (10 mg, 0.0168 mmole) in 0.5 mL of $CH_2Cl_2$ (*R*)-2-methoxy-2-phenyl-3,3,3-trifluoropropionic acid (MTPA, 10 mg, 0.043 mmole) stirred at 0 °C. The reaction mixture was kept at *ca.* 25 °C for 12 h, then chromatographed on 3 g of $SiO_2$. The gradient elution (from hexane to hexane—ether, 90:10,v/v) gave 17 mg (98 % yield) of diester **18** as a colorless oil, $R_f$ 0.71 (hexane—ether, 1:1). $^1H$ NMR, δ: 0.85 (d, 18 H, $CH_3$, $J$ = 7 Hz); 0.90 (d, 6 H, $CH_3$, $J$ = 7 Hz); 1.05—1.55 (m, 48 H, $CH_2$, CH); 1.65—1.80 (m, 4H, $H_2C$-2, $H_2C$-31); 3.58 (s, 6 H, $CH_3$); 4.36 (m, 4 H, $H_2C$-1, $H_2C$-32); 7.36—7.60 (m, 10 H, Ph). $^{19}F$ NMR, δ: −71.31 (s).

**(2*R*,6*R*,10*S*,14*S*)-2,6,10,14-Tetramethyl-15-hexadecene-1-ol (19).** A solution of acetate **12** (1.03 g, 3.05 mmole) and KOH (0.44 g, 7.86 mmole) in 2 mL of MeOH and 0.9 mL of water was kept at *ca.* 25 °C for 1 h, then neutralized with 1 *N* HCl and extracted with ether. After the usual workup the extract was dried over $MgSO_4$, evaporated *in vacuo*, and the residue (0.9 g) was chromatographed on 50 g of $SiO_2$. The gradient elution (from hexane to hexane—ether, 75:25, v/v) gave 0.88 g (97 % yield) of alcohol **19** as a colorless oil, $R_f$ 0.38 (hexane—ether, 1 : 1), $n_D^{21}$ 1.4650, $[\alpha]_D^{25}$ +4.8° (*c* 8.3). IR, $\nu/cm^{-1}$: 660, 915, 950, 1025, 1240, 1270, 1380, 1420, 1465, 1640, 3080, 3130, 3560, 3630. $^1H$ NMR, δ: 0.85 (d, 3 H, $CH_3$, $J$ = 7 Hz); 0.86 (d, 3 H, $CH_3$, $J$ = 7 Hz); 0.93 (d, 3 H, $CH_3$, $J$ = 7 Hz); 0.99 (d, 3 H, $CH_3$, $J$ = 7 Hz); 1.1—1.4 (m, 20 H, $CH_2$, HC-6, HC-10); 1.62 (m, 1 H, HC-2); 2.10 (m, 1 H, HC-14); 3.35—3.58 (m, 2 H, $H_2C$-1); 4.87—5.01 (m, 2 H, $H_2C$-16); 5.70 (ddd, 1 H, HC-15, $J$ = 17, 10, and 7 Hz). Mass spectrum, *m/z* ($I_{rel}$ (%)): $M^+$ 296 (16), 277 (11), 241 (7), 179 (9), 140 (16), 137 (13), 125 (22), 123 (41), 111 (53), 110 (41), 109 (53), 97 (65), 95 (63), 83 (88), 82 (53), 81 (59), 70 (76), 69 (100), 57 (71), 56 (53), 55 (100), 43 (59), 41 (76). High

resolution. Mass spectrum, *m/z*: for $M^+$ found: 296.3077; calculated for $C_{20}H_{40}O$: 296.3078.

**1-[(*R*)-2-Methoxy-2-phenyl-3,3,3-trifluoropropionyloxy]-(2*R*,6*R*,10*S*,14*S*)-2,6,10,14-tetramethyl-15-hexadecene (20).** Starting from alcohol **19** (19.85 mg, 0.067 mmole), (*R*)-MPTA (15.7 mg, 0.067 mmole), DMAP (0.8 mg, 0.0065 mmole), and DCC (15.2 mg, 0.0737 mmole) dissolved in 1.6 mL of $CH_2Cl_2$, **20** (33.6 mg, 98 % yield) was obtained as a colorless oil using a procedure similar to that presented for **18** (see above). $R_f$ 0.65 (hexane—ether, 1:1). $^1H$ NMR, δ: 0.85 (d, 3 H, $CH_3$, $J$ = 7 Hz); 0.86 (d, 3 H, $CH_3$, $J$ = 7 Hz); 0.93 (d, 3 H, $CH_3$, $J$ = 7 Hz); 1.00 (d, 3 H, $CH_3$, $J$ = 7 Hz); 1.05—1.45 (m, 20 H, $CH_2$, HC-6, HC-10); 1.65—2.15 (m, 2 H, HC-2, HC-14); 3.57 (s, 3 H, $CH_3$); 4.17 (d, 2 H, $H_2C$-1, $J$ = 7 Hz); 4.87—5.01 (m, 2 H, $H_2C$-16); 5.70 (ddd, 1 H, HC-15, $J$ = 18, 11 and 7 Hz); 7.35—7.60 (m, 5 H, Ph). $^{19}F$ NMR, δ: −71.29 (s).

**(2*R*,6*R*,10*S*,14*S*)-1-Tosyloxy-2,6,10,14-tetramethyl-15-hexadecene (21).** At −20 °C under Ar a 1.24 *M* solution of BuLi in hexane (*ca.* 2.3 mL; 2.85 mmole) was added dropwise to a stirred solution of alcohol **19** (0.82 g, 2.77 mmole) and $Ph_3CH$ (5 mg) in 15 mL of ether and 1.3 mL of HMPA until a stable pink coloration developed, then the mixture was treated with TsCl (0.71 g, 3.7 mmole) for 5 min. The reaction mixture was heated to *ca.* 25 °C for 20 min, diluted with water, and extracted with ether. After the usual workup the extract was dried over $MgSO_4$, evaporated *in vacuo*, and 1.45 g of tosylate **21** was obtained. The product was used for the next stage without further purification.

**(2*R*,6*R*,10*S*,14*S*)-1-Bromo-2,6,10,14-tetramethyl-15-hexadecene (22).** A mixture of tosylate **21** prepared by procedure described above and NaBr (1.73 g, 16.68 mmole) in 11 mL of DMF was heated at 60 °C for 6 h, then diluted with water and extracted with hexane. The extract was washed with a saturated solution of NaCl, dried over $MgSO_4$, evaporated *in vacuo*, and the residue (*ca.* 1.1 g) was chromatographed on 30 g of $SiO_2$. Elution with hexane gave 0.97 g of bromide **22** (98 % yield calculated on alcohol **19**) as a colorless oil, $R_f$ 0.46 (hexane), $n_D^{20}$ 1.4693, $[\alpha]_D^{22}$ +5.5° (*c* 8.3). IR, ν/cm$^{-1}$: 655, 670, 725, 920, 1000, 1205, 1380, 1420, 1465, 1640, 3080. $^1H$ NMR, δ: 0.85 (d, 3 H, $CH_3$, $J$ = 7 Hz); 0.86 (d, 3 H, $CH_3$, $J$ = 7 Hz); 0.99 (d, 3 H, $CH_3$, $J$ = 7 Hz); 1.03 (d, 3 H, $CH_3$, $J$ = 7 Hz); 1.1—1.5 (m, 20 H, $CH_2$, HC-6, HC-10); 1.79 (m, 1 H, HC-2); 2.10 (m, 1 H, HC-14); 3.38 (AB part of ABX spin system, 2 H, $H_2C$-1, $\delta_A$ = 3.34, $\delta_B$ = 3.42, $J_{AB}$ = 10 Hz, $J_{AX}$ = 6 Hz, $J_{BX}$ = 5 Hz); 4.87—5.01 (m, 2 H, $H_2C$-16); 5.70 (ddd, 1 H, HC-15, $J$ = 17, 10, and 7 Hz). Mass spectrum, *m/z* ($I_{rel}$ (%)): $M^+$ 360 (35), 358 (30), 261 (10), 259 (9), 210 (12), 195 (14), 167 (13), 163 (15), 153 (18), 141 (38), 140 (80), 139 (55), 127 (30), 126 (77), 125 (90), 124 (43),111 (53), 110 (38), 109 (35), 99 (38), 95 (33), 85 (100), 84 (75), 83 (85), 81 (63), 71 (60), 70 (75), 69 (68), 57 (48), 55 (55), 43 (68), 41 (50). Found (%): C, 67.13; H, 10.86; Br, 21.75. $C_{20}H_{39}Br$. Calculated (%): C, 66.83; H, 10.94; Br 22.23.

**(3*S*,7*S*,11*R*,15*R*,18*R*,22*R*,26*S*,30*S*)-3,7,11,15,18,22,26,30-Octamethyl-1,31-dotriacontadiene (23).** At *ca.* 25 °C under Ar in darkness $AgNO_3$ (0.38 g, 2.235 mmole) was added in one portion to a stirred solution of Grignard reagent, freshly prepared from bromide **22** (0.4 g, 1.114 mmole) and Mg (40 mg, 1.667 mmole) in 1.2 mL of THF. The reaction mixture was stirred at *ca.* 25 °C for 10 h, then diluted with ether, filtered, and the filtrate was washed with saturated solutions of $NH_4Cl$ and NaCl, dried over $MgSO_4$, evaporated *in vacuo*, and the residue (0.3 g) was chromatographed on 20 g of $SiO_2$. Elution with hexane gave 0.23 g (74 % yield) of diene **23** as a colorless oil, $R_f$ 0.53 (hexane), $n_D^{22}$ 1.4578, $[\alpha]_D^{28}$ +3.1° (*c* 7.9). IR, ν/cm$^{-1}$: 730, 920, 1000, 1210, 1380, 1420, 1460, 1635, 3070. $^1H$ NMR, δ: 0.85 (d, 12 H, $CH_3$, $J$ = 7 Hz); 0.88 (d, 6 H, $CH_3$, $J$ = 7 Hz); 0.98 (d, 6 H, $CH_3$, $J$ = 7 Hz); 1.05—1.40 (m, 46 H, $CH_2$, CH); 2.10 (m, 2 H, HC-3, HC-30); 4.87—5.01 (m, 4 H, $H_2C$-1, $H_2C$-32); 5.71 (ddd, 2 H, HC-2, HC-31, $J$ = 17, 10, and 7 Hz). Mass spectrum, *m/z* ($I_{rel}$ (%)): $M^+$ 558 (34), 278 (14), 153 (11), 151 (13), 139 (18), 138 (21), 137 (19), 125 (56), 124 (35), 123 (42), 111 (80), 110 (31), 109 (42), 97 (70), 96 (34), 95 (38), 85 (43), 83 (70), 82 (36), 81 (35), 71 (74), 70 (44), 69 (99), 57 (100), 55 (94). Found (%): C, 85.80; H, 14.26. $C_{40}H_{78}$. Calculated (%): C, 85.54; H, 14.06.

**1,32-Diacetoxy-(3*S*,7*S*,11*R*,15*R*,18*R*,22*R*,26*S*,30*S*)-3,7,11,15,18,22,26,30-octamethyldotriacontane (24).** At 0 °C under Ar diene **23** (0.42 g, 0.75 mmole) in 3 mL of THF was added over 5 min to a stirred suspension of 9-BBN (0.27 g, 2.21 mmole) in 5 mL of THF. The reaction mixture was stirred at *ca.* 25 °C for 1 h, treated with a NaOH solution (0.21 g, 5.25 mmole in 2 mL of water), then treated with 30 % $H_2O_2$ (2 mL, 15.78 mmole ). The mixture was kept at *ca.* 25 °C for 2 h, then at 35 °C for 1 h, diluted with ether, washed with a saturated solution of NaCl, dried over $MgSO_4$, and evaporated *in vacuo*. The residue (0.8 g) was dissolved in 10 mL of $CH_2Cl_2$, and then Py (1.85 mL, 23 mmole), $Ac_2O$ (1.41 mL, 15 mmole) and DMAP (10 mg, 0.08 mmole) were added at *ca.* 25 °C. After standing for 2 h the reaction mixture was washed with saturated solutions of $CuSO_4$, $NaHCO_3$, and NaCl, dried over $MgSO_4$, evaporated *in vacuo*, and the residue (0.9 g) was chromatographed on 50 g of $SiO_2$. The gradient elution (from hexane to hexane—ether, 80:20, v/v) gave 0.3 g (59 % yield) of diacetate **24** as a colorless oil, $R_f$ 0.51 (hexane—ether, 1:1), $n_D^{22}$ 1.4613, $[\alpha]_D^{25}$ −0.1° (*c* 14.1). IR, ν/cm$^{-1}$: 610, 670, 730, 960, 970, 1040, 1050, 1150, 1210, 1255, 1360, 1370, 1460, 1730, 2340, 2360. $^1H$ NMR, δ: 0.84 (d, 18 H, $CH_3$, $J$ = 7 Hz); 0.90 (d, 6 H, $CH_3$, $J$ = 7 Hz); 1.05—1.45 (m, 48 H, $CH_2$, CH); 1.5—1.7 (m, 4 H, $H_2C$-2, $H_2C$-31); 2.06 (s, 6 H, $CH_3$); 4.08 (m, 4 H, $H_2C$-1, $H_2C$-32). Mass spectrum, *m/z* ($I_{rel}$ (%)): $M^+$ 678 (17), 618 (6), 558 (8), 280 (7), 165 (7), 151 (7), 139 (9), 125 (14), 123 (19), 111 (23), 81 (23), 71 (50), 69 (50), 57 (38), 55 (36), 44 (100), 43 (32). Found (%): C, 77.51; H, 12.67. $C_{44}H_{86}O_4$. Calculated (%): C, 77.81; H, 12.76.

**(3*S*,7*S*,11*R*,15*R*,18*R*,22*R*,26*S*,30*S*)-3,7,11,15,18,22,26,30-Octamethyldotriacontane-1,32-diol (2b).** A solution of diacetate **24** (0.28 g, 0.41 mmole) and KOH (0.12 g, 2.14 mmole) in 2 mL of MeOH and 1 mL of water was kept at *ca.* 25 °C for 2 h, then neutralized with 1 *N* HCl and extracted with ether. After the usual workup the extract was dried over $MgSO_4$, evaporated *in vacuo* and the residue (0.26 g) was chromatographed on 6 g of $SiO_2$. The gradient elution (from hexane to hexane—ether, 20:80, v/v) gave 0.25 g (100 % yield) of diene **2b** as a colorless oil, $[\alpha]_D^{28}$ −3.2° (*c* 3.4). The $R_f$ value and $^1H$ and $^{13}C$ NMR data are identical with those for **2a** presented above.

**Di-1,32-[(*R*)-2-methoxy-2-phenyl-3,3,3-trifluoropropionyloxy]-(3*S*,7*S*,11*R*,15*R*,18*R*,22*R*,26*S*,30*S*)-3,7,11,15,18,22,26,30-octamethyldotriacontane (25).** Starting from alcohol **2b** (0.11 g, 0.19 mmole), (*R*)-MPTA (98 mg, 0.42 mmole), DMAP (4 mg, 0.033 mmole), and DCC (86 mg, 0.42 mmole) dissolved in 8 mL of $CH_2Cl_2$, diester **25** (0.19 g, 99 % yield) was obtained as a colorless oil, $R_f$ 0.70 (hexane—ether, 1:1). $^1H$ NMR, δ: 0.85 (d, 18 H, $CH_3$, $J$ = 7 Hz); 0.90 (d, 6 H, $CH_3$, $J$ =7 Hz); 1.05—1.55 (m, 48 H, $CH_2$, CH); 1.65—1.80 (m, 4 H, $H_2C$-2, $H_2C$-31); 3.58 (s, 6 H, $CH_3$); 4.38 (t, 4 H, $H_2C$-1, $H_2C$-32, $J$ = 7 Hz); 7.37—7.60 (m, 10 H, Ph). $^{19}F$ NMR, δ: −71.31 (s).

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