Synthesis and Structure of Linear and Cyclic Oligomers of 3-Hydroxybutanoic Acid with Specific Sequences of (*R*)- and (*S*)-Configurations

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Dedicated to Professor *Richard A. Lerner*, *The Scripps Research Institute*, La Jolla, California, on the occasion of his 60th birthday

To study the stereoselectivity of enzymatic cleavage of poly(3-hydroxybutyrates) (PHB) in a well-defined system (purified depolymerase and monodisperse substrate of specific relative configuration), linear and cyclic oligomers of HB (OHBs) containing (*R*)- and (*S*)-3-hydroxybutanoate residues were synthesized. The starting material (*R*)-HB was prepared from natural sPHB, and (*S*)-HB by enantioselective reduction of 3-oxobutanoate with yeast or with H_2/*Noyori-Taber* catalyst (*Scheme 2*). The HB building blocks were then protected (*O*-benzyl/*tert*-butyl ester; *Scheme 3*) and coupled to give dimers **3**, **4**, tetramers **5**–**9**, and octamers **10**–**18**; for analytical comparison, a 3mer, 5mer, 6mer, and 7mer (**19**–**22**) were also prepared. Two of the tetramers were subjected to macrolactonization conditions (*Yamaguchi*) to give the cyclic tetramers **23** and **25** and octamers **24** and **26**. All new compounds were fully characterized (m.p., $[\alpha]_D$, CD, IR, ^{1}H- and ^{13}C-NMR, MS, elemental analysis). Single-crystal X-ray structure analyses were performed with oligolides **24** and **25** (*Figs. 2* and *4*), and the structures, as well as the crystal packing, were compared with those of analogs containing only (*R*)-HB units or consisting of 3-amino- instead of 3-hydroxybutanoic-acid moieties.

1. Introduction. – Polymers and oligomers of 3-hydroxybutanoic acid (HB) have been identified as microbial storage materials [1], as components of ubiquitous calcium-polyphosphate complexes [2] which act as ion channels through cell membranes [3], and, most recently, as appendages of proteins [4]. In all those natural sources, the (*R*)-3-hydroxybutanoic acid ((*R*)-HB), and, to a smaller extent, its homolog, the (*R*)-3-hydroxyvaleric acid ((*R*)-HV), have been found to occur[2])[3]). The oligomers (OHB) and polymers (PHB) of (*R*)-3-hydroxybutanoic acid are biocompatible and biodegradable, and numerous enzymes have been identified which are specialized to cleave PHB ester bonds [8]. Using a crude enzyme extract from *A. delafieldii* and cyclic oligomers, so-called oligolactones, of (*R*)-HB, we have shown that enzymatic cleavage does not require the terminal functional groups OH or COOH to be present in the substrate [9a]. To be able to study the stereoselectivity of PHB

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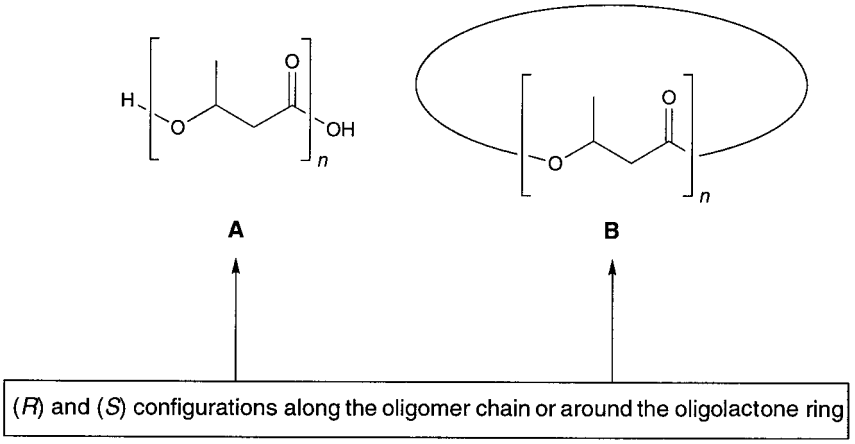
[1]) Part of the Ph.D. thesis of *B.M.B.*, ETH-Zürich, No. 12074, 1997.

[2]) For recent review articles, see [5]. Excellent compilations comprising the state of knowledge about PHB/PHV are the special volumes of ISBP with the papers presented at the symposia on PHB in Sitges (1990), Montpellier (1991), Göttingen (1992), Montreal (1994), and Davos (1996) [6].

[3]) (*R*)-3-Hydroxyalkanoates are the intermediates of fatty-acid synthesis and their (*S*)-enantiomers those of fatty-acid degradation, occurring in multi-enzyme complexes [7].

degradation by enzymes in more detail, we decided to prepare oligomers of HB with specific sequences of (*R*)- and (*S*)-configurations of the stereogenic centers and to examine their degradation by a purified, single enzyme rather than by entire organisms or cell extracts. Results of such an investigation will also be relevant for the biodegradation of HB polymers prepared from racemic monomers[4]).

In this paper, we describe the synthesis of linear OHBs **A** and cyclic OHBs **B**, containing various combinations and sequences of (*R*)- and (*S*)-building blocks, together with some structural investigations. The results of enzymatic-degradation studies with these compounds and the analysis of the cleavage products that led to the formulation of a general model for the enzymatic degradation of OHB and PHB will be published separately, in a more specialized journal [9b].



2. Preparative Results. 2.1. *Preamble.* Derivatives of HB have been studied in the past[5]), and their preparation was published as early as 1965 [12]. With increasing chain length, the preparation of uniform OHBs became more and more difficult: Non-selective coupling of HB units led to a mixture of OHBs, separation of which by chromatography gave pure OHBs with chain lengths of up to five HB units only [13]. Later on, a selective synthesis of longer OHBs was published [14] and claimed to provide up to 16mers [15][6]).

Finally, segment-coupling methods led to pure long-chain OHBs containing up to 128 HB units [16–19][7]). We now slightly modified the method, reducing the coupling temperature to $-78°$, to improve the monodispersity of the oligomeric products

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4) (*S*)-3-Hydroxybutanoic acid and, to a lesser extent, the (*R*)-enantiomer have been shown to exhibit tetratogenic activity in rodents [10].

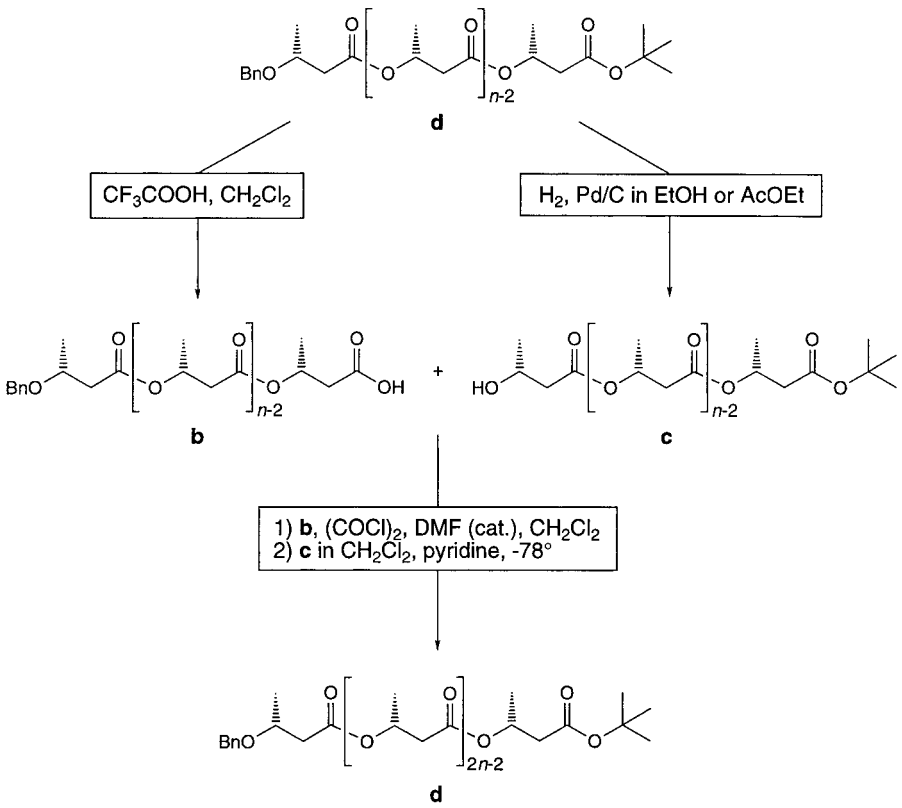
5) The (*R*,*R*)-dimer of HB, for example, was found to be a sex pheromone of spiders [11].

6) Unfortunately, the analytical data of the compounds that have been prepared by this method are limited, and no mass spectrometric evidence of their monodispersity has been provided by the authors.

7) The 128mer was synthesized with (*tert*-butyl)diphenylsilyl protection of the O-terminus and benzyl protection of the C-terminus.

(*Scheme 1*): An *n*-meric acid of type **b**[8]) was coupled with an *n*-meric alcohol of type **c**[8]) (where **b** and **c** were derived from **d**[8]). The resulting 2*n*-meric, fully protected OHB of type **d** could be purified by chromatography. Unfortunately, single HB units may get lost at the stage of the intermediate acid chloride[9]). Thus, only pure OHBs up to a chain length of eight units could be obtained (limit of the preparative chromatographic purification).

Scheme 1[8])



We planned to use the oligomers we were about to synthesize as models for polymers, so that large chain lengths were desirable. For the planned enzymatic degradation studies, we had to restrict the structural variability to a practical degree[10]).

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[8]) Throughout this paper, the following groups R^1 and R^2 at the O- and C-terminus, respectively, of OHBs (R^1O ~~~ $COOR^2$) are used to indicate the type and degree of protection:

	a	**b**	**c**	**d**	**e**	**f**	**g**	**h**
R^1	H	Bn	H	Bn	H	H	Bn	Bn
R^2	H	H	*t*-Bu	*t*-Bu	Me	Et	Me	Et

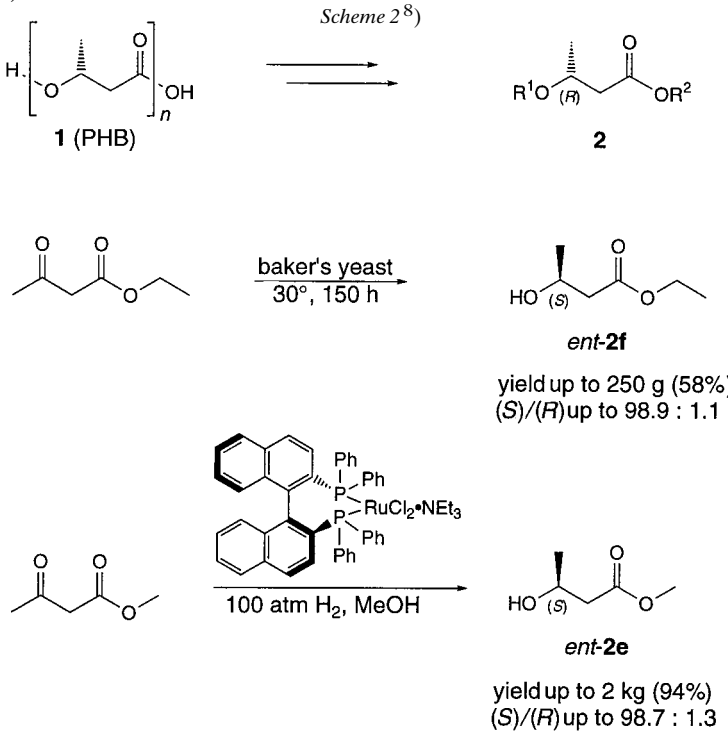
[9]) For a discussion of this phenomenon, see [16][17].

[10]) The complete permutation of (*R*)- and (*S*)-units in an HB octamer results in 256 (2^8) stereoisomeric compounds.

Thus, we decided to synthesize HB octamers that were expected to reveal the most information. One of the most important questions that had to be answered by the planned experiments was whether the degrading enzymes have an *exo*-selectivity (selective cleavage of terminal units). So we decided to synthesize octamers of up to four terminal (*S*)-HB units.

2.2. *Enantiomerically Pure (*R*)- and (*S*)-Building Blocks* **2** *and* ent-**2**, *Respectively, Derived from (*R*)- and (*S*)-3-Hydroxybutanoic Acids* (**2a** *and* ent-**2a**[8]), *resp.*). Following literature procedures [18][20], the (*R*)-HB derivatives **2b**[8]) and **2c**[8]) were prepared from PHB (**1**) as the natural, enantiomerically pure precursor [21] (*Scheme 2*).

Scheme 2[8])



Unfortunately, nature does not provide such a handy access to (*S*)-HB derivatives *ent*-**2**; thus, they had to be prepared by stereoselective syntheses from (preferably cheep) achiral compounds [21], the enantioselective reduction of acetoacetic esters by microorganisms or by H_2 in the presence of chiral transition-metal catalysts being two possibilities[11]). The enzymatic approach using baker's yeast leads to the highest enantiomeric excess when the yeast is 'starved', *i.e.*, when the substrate concentration is kept very low [23][24]. This method was improved by *Leuenberger et al.*, who added the substrate very slowly and so, by continuously starving the yeast, reached enantiomer ratios (e.r.) of up to 98.5 : 1.5 in favor of the (*S*)-isomer *ent*-**2f**[8]) [25]. By

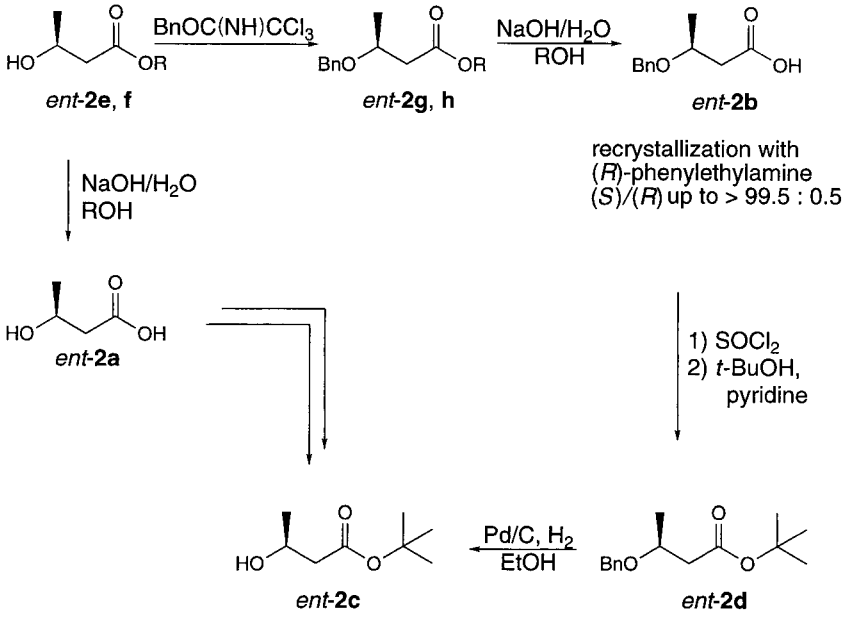
[11]) A configurational inversion *via* the β-lactone [22][23] was considered to be too tedious for the large amounts of enantiomerically pure acid necessary for the present investigation.

futher reducing the substrate concentration, we managed to prepare ethyl (*S*)-3-hydroxybutanoate (*ent*-**2f**) with an e.r. of 98.9:1.1 (*Scheme 2*)[12]). Unfortunately, the large volumes of water used for the fermentation (3% substrate concentration) and the subsequent product extraction make this procedure tedious.

The hydrogenation of β-keto esters with catalytic amounts of a [Ru(binap)] complex (so-called *Noyori* catalyst [27]; binap = 2,2′-bis(diphenylphosphino)-1,1′-binaphthalene = [1,1′-binaphthalene]-2,2′-diylbis[diphenylphosphine]), on the other hand, requires a minimum of catalyst purification, strict exclusion of air, and high H_2 pressures. Following *Taber* and *Silverberg*'s suggestions, we used a modified ruthenium catalyst which does not need to be purified and which allows for lower H_2 pressures in the hydrogenation [28]. Thus, we managed to reduce more than 2 kg of methyl acetoacetate in *one* batch (ratio keto ester/MeOH solvent 1:1). The e.r. of the produced hydroxy ester *ent*-**2e**[8]) was up to 98.7:1.3, with an almost quantitative yield (*Scheme 2*).

For the synthesis of the two (*S*)-HB building blocks *ent*-**2b**[8]) and *ent*-**2c**[8]), the hydroxy esters *ent*-**2e**,**f** were first *O*-benzylated ($\rightarrow$ *ent*-**2g**,**h**[8]); *Scheme 3*), and subsequent saponification yielded *ent*-**2b**, which was recrystallized with (*R*)-1-phenylethylamine, to increase the e.r. to the required value of $>99.5:0.5$[13]). Conversion of the benzyloxy acid to the *t*-Bu ester *ent*-**2d**[8]), and hydrogenolytic debenzylation yielded the second (*S*)-HB building block *ent*-**2c** (*Scheme 3*). An alternative access to this

Scheme 3[8])

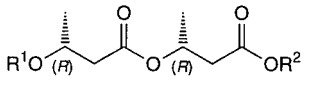


[12]) A further improvement by adding the substrate even more slowly was not possible. With a more complicated procedure ('cell recycling'), the productivity can be improved up to twenty times with no decrease of the e.r. of the product [26].

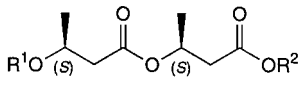
[13]) An octamer that consisted of HB units with an enantiomeric purity of 99.5% had an enantiomeric purity of only 96% (0.995^8).

compound was the saponification of the hydroxy esters *ent*-**2e**,**f** to the hydroxy acid *ent*-**2a**, which was obtained in enantiomerically pure form by crystallization and which was subsequently esterified to give *ent*-**2c** [18][14]).

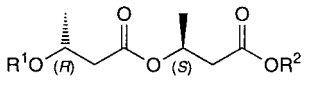
2.3. *Dimers.* Following the procedures of *Müller* [18], the monomeric building blocks **2** and *ent*-**2** were coupled to the dimers, which were then partially or fully deprotected[15]). Of the stereoisomeric dimers **3a**–**d**, *ent*-**3b**–**d**, **4b**–**d**, and *ent*-**4b**–**d**, only the fully protected compounds of type **d**[8]) could be purified by destillation. The other dimers (type **a**–**c**[8])) had to be purified by chromatography[16]).



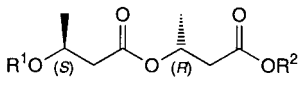
3a-d[8])



ent-**3b-d**[8])



4b-d[8])



ent-**4b-d**[8])

2.4. *Tetramers.* The fully protected tetramers **5d**, **6d**, **7d**, **8d**, and **9d**[8]), and *ent*-**5d**, *ent*-**6d**, *ent*-**7d**, and *ent*-**8d**[8]) were prepared in a similar way as the dimers. In the first step of the coupling procedure, the milder oxalyl chloride instead of thionyl chloride was used to generate the acid chlorides. The pyridine addition during the actual coupling step was then performed at $-78°$ to prevent single HB units to get cleaved off by a base-induced elimination [17][18].

The tetramers were deprotected like the dimers. They were isolated as colorless solids, that could be purified by precipitation from cold hexane (**5a**,**c**,**d**, *ent*-**5c**,**d**,**8a**,**c**,**d**, and *ent*-**8b**,**d**[8])) or as viscous oils that had to be purified by chromatography (**5b**, *ent*-**5b**,**d**, **6c**,**d**, *ent*-**6a**,**b**,**d**, **7c**,**d**, *ent*-**7b**,**d**, and **9d**[8])).

2.5. *Octamers.* The partially deprotected tetramers of type **b** and **c** were again coupled in the same way as the dimers, providing the fully protected type-**d**[8]) octamers **10d** to **18d**, *ent*-**10d**, and *ent*-**14d**. Chromatographic and mass-spectrometric analysis showed that the octamers contained less than 1% of the corresponding heptamers[17]), and these could be removed completely (according to HPLC analysis) by column chromatography on SiO_2. The fully deprotected type-**a**[8]) octamers **10a** to **18a**, *ent*-**10a**, and *ent*-**14a** needed for the enzymatic degradation studies were prepared and purified as described above, and their purity was confirmed by HPLC. All prepared octamers

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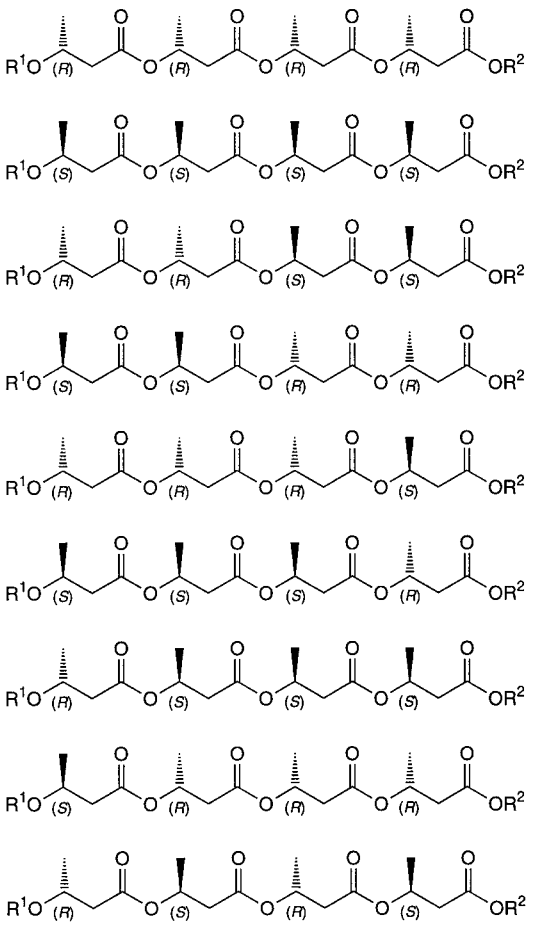
[14]) Problems which may be encountered with this method are discussed in the thesis of *B.M.B.*[1]).

[15]) It turned out to be crucial for the cleavage of the *t*-Bu ester of all OHBs that the reagent CF_3COOH was absolutely dry. Otherwise the reaction time increased from a few minutes to many hours, and single HB units were cleaved off due to the increased duration of OHB exposure to the reagent.

[16]) In their 1965 paper, *Olsen et al.* reported an alternative way to obtain all four stereoisomeric HB dimers: The benzyl rather than the *t*-Bu ester was used to protect the C-terminus [12].

[17]) Another demonstration of the fact that the coupling at very low temperatures allows for a significant reduction of the loss of single HB units.

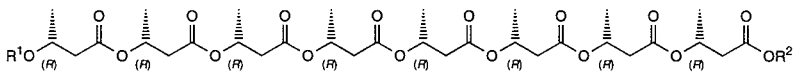


were either colorless solids (**10**, **11**, **14a**, **15a**, and **16**–**18**) or viscous oils (**12**, **13**, **14d**, *ent*-**14**, and **15d**).

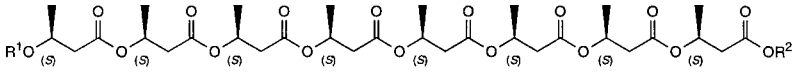
Interestingly, the melting points of the 'mixed' octamers decrease with the number of (*S*)-units they contain. Apparently, the units of 'wrong' configuration disturb the crystal packing and cause melting point decreases from *ca.* 91° for the all-(*R*)-octamer **10d** to *ca.* 38° (**11d**) and *ca.* 83° (**17d**) for the octamers with a C- and O-terminal (*S*)-unit, respectively[18]). At the same time, the melting interval gets broader, the more (*S*)-units the compound contains. In contrast, the syndiotactic octamers **18** have a sharp, considerably higher melting point than the isotactic counterparts **10**; here, the alternating sequence of (*R*)- and (*S*)-units appears to restore order and better packing.

2.6. *Trimers, Pentamers, Hexamers, and Heptamers.* For the enzymatic degradation studies, we needed also small amounts of OHB samples containing 3, 5, 6, and 7 (*R*)-HB units for the identification of octamer fragments [9b]. These were prepared in the

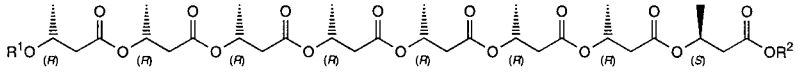
[18]) Obviously, the effect is stronger when the (*S*)-unit lies on the C-terminus of the octamer.



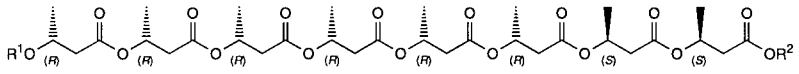
10a,d[8])



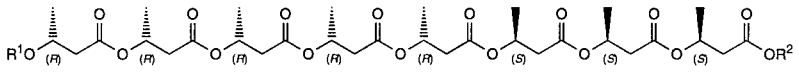
ent-**10a,d**[8])



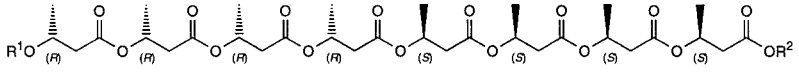
11a,d[8])



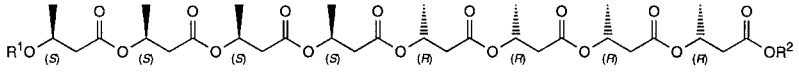
12a,d[8])



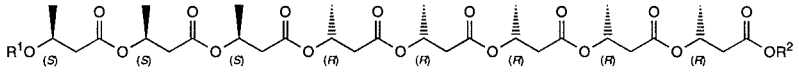
13a,d[8])



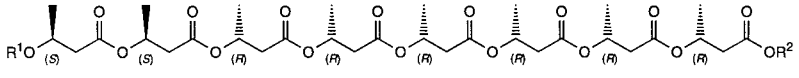
14a,d[8])



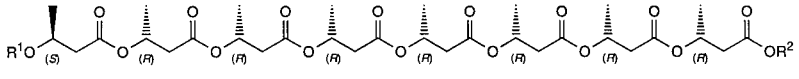
ent-**14a,d**[8])



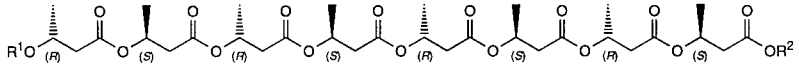
15a,d[8])



16a,d[8])



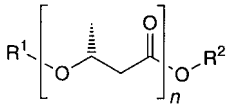
17a,d[8])



18a,d[8])

usual way from the intermediate monomers, dimers, and tetramers of the octamer synthesis, see **19**–**22** and *Exper. Part.*

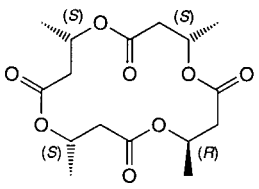
2.7. *Oligolactones.* So far, we have prepared and characterized cyclic oligomers (oligolactones) consisting exclusively of (*R*)-3-hydroxybutanoate or -pentanoate residues [29][30]. We also used PHB/PHV to prepare trilactones containing HB and HV units ('mixolides') [17][29][31], but we have not studied oligolactones built of (*R*)-



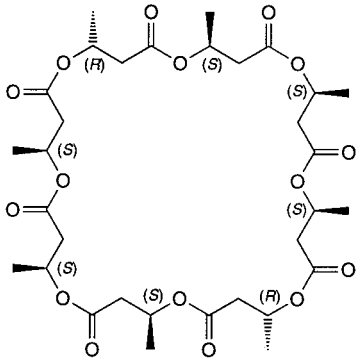
19a,d (n = 3)[8]
20a,d (n = 5)[8]
21a,d (n = 6)[8]
22a,d (n = 7)[8]

and (S)-β-hydroxy-acid moieties. The availability of the corresponding linear oligomers was now exploited for the preparation of such oligolactones.

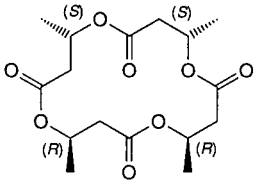
Following the procedure of *Yamaguchi* [32], the tetramers **6a** and **8a** were subjected to macrolactonization conditions which generated not only the tetralactones **23** and **25** but also (to a smaller extent) the octalactones **24** and **26**. Single crystals, suitable for X-



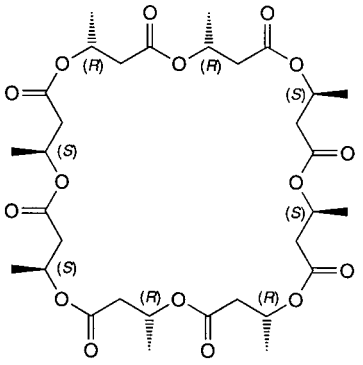
23
symmetry: C_1



24
symmetry: C_2



25
symmetry: C_i



26
symmetry: S_4

ray analysis (see below), of the compounds **24** and **25** were obtained, while the stereoisomer **23** (very fine needles) and **26** (very small quantities formed) could only be investigated by NMR spectroscopy.

3. Structural Investigations. 3.1. *^{1}H-NMR Analysis.* The ^{1}H-NMR spectra of all OHBs that have been prepared show 'three-spin systems' of the *ABX* type. The *AB* parts of the dimer spectra (16 observable transitions) could be resolved[19]). For the higher OHBs, this was no longer possible, even when a high-field spectrometer (500 MHz) was used, but the *AB* part for every compound with its specific chain length and configuration was unique, like a fingerprint. With this *AB* fingerprint, it was, *e.g.*, possible to distinguish the octamers that showed – at a first glance – identical ^{1}H-NMR spectra[20]). The fingerprint regions of the fully deprotected type-**a** octamers **11a** to **17a** and *ent*-**14a** are shown in *Fig. 1*.

3.2. *CD Spectra.* Unlike the linear all-(*R*)-OHBs [34], our 'mixed' OHBs do not show any CD pattern which would indicate the presence of a secondary structure in solution.

3.3. *Fibre Diffraction Data.* The octamer **18a** with a syndiotactic sequence of (*R*)- and (*S*)-HB residues was studied by stretch-fiber and powder X-ray diffraction. Analysis of the powder data gave a new unit cell (with much better resolution, based on the *Rietveld* method), as compared to the one obtained from a sample of largely syndiotactic polymer prepared by *Marchessault et al.*[21]) [35].

3.4. *X-Ray Crystal Structures of the Oligolactones* **24** *and* **25**. The structure of the tetralactone **25** was determined with an *R*-factor of 4% (*Fig. 2*). A comparison with the structures of the corresponding all-(*R*)-tetralactone [18][30][22]) and of the analogous cyclo-*β*-tetrapeptide cyclo[-(*S*)-*β*-homoalanyl-(*S*)-*β*-homoalanyl-(*R*)-*β*-homoalanyl-(*R*)-*β*-homoalanyl-] showed some intriguing differences [37][23]). Each of the three compounds exhibits a very distinct crystal packing (*Fig. 3*): While the all-(*R*)-tetralactone (m.p. 178°) stacks in an orderly manner to form a tubular structure, its (*R*,*R*,*S*,*S*)-isomer **25** (m.p. 210°) is arranged in a stair-like, staggered structure, and its peptide analog (m.p. 300°, dec.) in a fish-bone-type manner (with H-bonding between the rings!).

The cyclic all-(*R*)-HB octamer (corresponding to **24**) crystallized in two different modifications depending on temperature and solvent [18]. Both structures show a typical folding of the ring, one of which can best be described by a comparison with the shape of a tennis-ball seam [18][39]. The structure now determined for the (*R*,*S*,*S*,*S*,*R*,*S*,*S*,*S*)-octalactone **24** (*Fig. 4*) differs significantly from those of the two known octalactone conformations: it is not folded and forms an almost planar 32-membered ring (see the comparison in *Fig. 5*). Actually the octalactone **24** has the shape of a rectangle, with six of the eight carbonyl O-atoms (on the long side) approximately in-plane and two (on the short side) rather perpendicular to the plane of

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19) For the methods of analysis of these spectra, see [33].

20) This, of course, does not hold for enantiomers such as **14a** and *ent*-**14a** (see legend to *Fig. 1*).

21) These experiments were carried out in the laboratories of Prof. *R. Marchessault* of McGill University, Montreal, and we gratefully acknowledge receipt of results prior to publication.

22) See also the thiocarbonyl analogs [36].

23) Derived by the powder X-ray diffracton method [38].

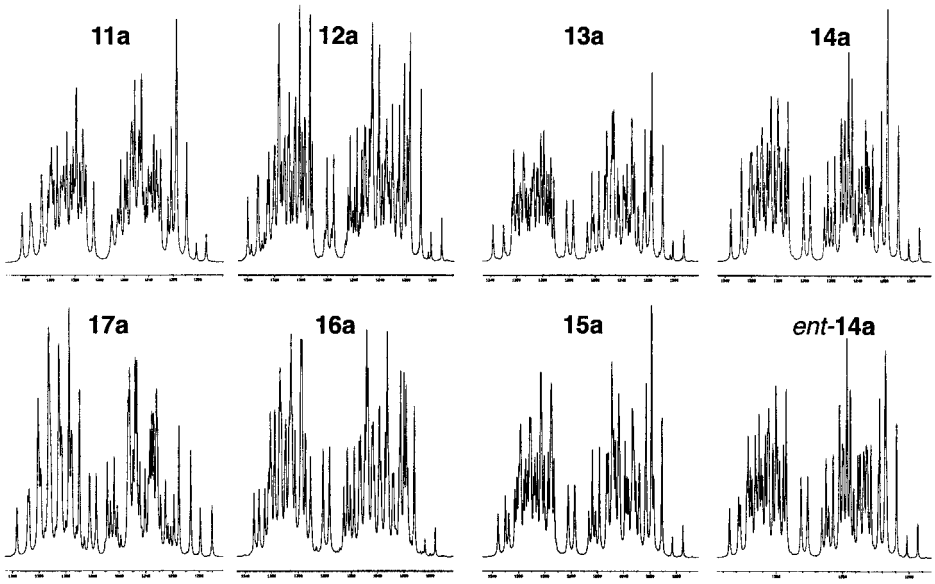

Fig. 1. *Sections of the 500-MHz ^{1}H-NMR spectra* ('fingerprints') *of the type*-**a** *octamers* **11a**–**17a** *and* ent-**14a**. The small differences between the spectra of the enantiomers **14a** and *ent*-**14a** are due to variances in the resolution of the signals.

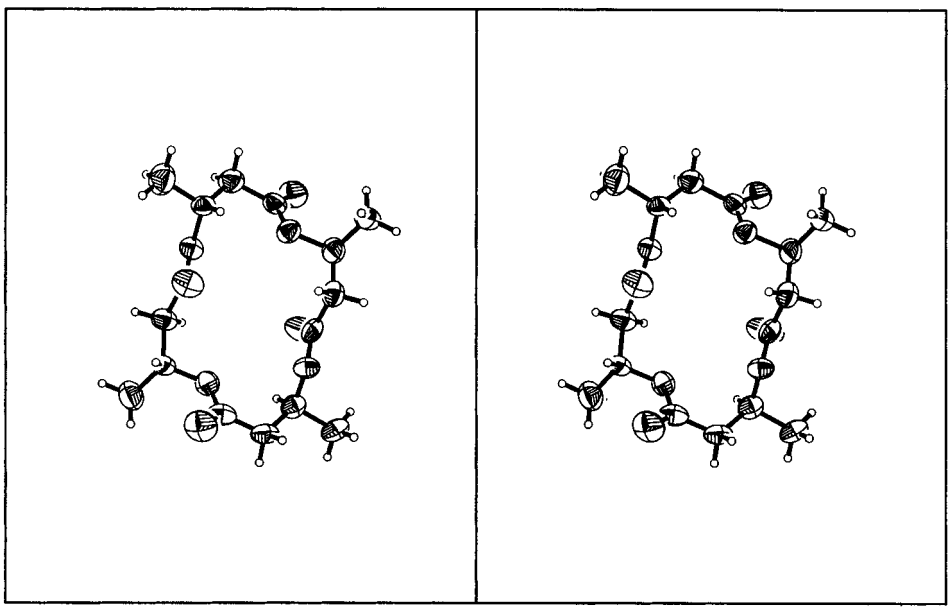

Fig. 2. *Stereo ORTEP plot* (probability 50%) *of the crystal structure of (*R,R,S,S*)-tetralactone* **25** (structure determined by *F.N.M. Kühnle)*

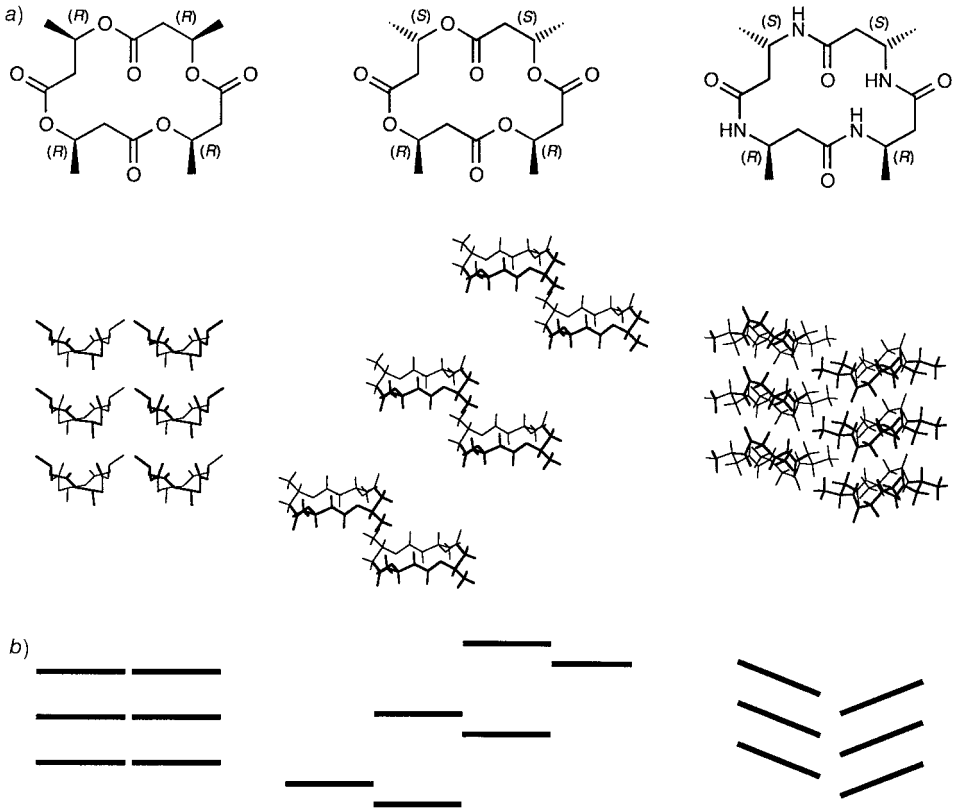

Fig. 3. *Comparison of the crystal packings of two tetralactones and an analogous cyclo-β-tetrapeptide.* a) *Crystal packing of all-(*R*)-HB tetralactone* (left) [30][39], *(*R,R,S,S*)-tetralactone* **25** (center; this paper), *and cyclo-β-tetrapeptide* (right) [37]; b) *schematic representation of the crystal packing*

the ring. As evident from the presentation of the ring packing in *Fig. 4*, the octalactone molecules stack as channels or tubes, with four C=O groups pointing inwards (holding the ring in shape, C=O···CHMe–O dipolar interactions?), with two C=O groups pointing in the direction of the channel axis (intra-staple C=O···C=O interaction holding the rings on top of each other), and with two C=O groups pointing outwards.

We would like to express our gratitude to *Zeneca Bio Products* (Billingham, GB) for supplying us with PHB (**1**). We gratefully acknowledge the assistance of *M. Bollhalder*, *B. Brandenberg*, *M. Hemmi*, and *B. Jaun* (NMR service) and of *R. Häfliger* and *U. Hediger* (MS service). We thank *P. Waser* for supplying compounds **9d**, **18a**, and **18d** (synthesized in the course of his Ph.D. thesis) and *K. Gademann* for the synthesis of the compounds **8a**, **23**, and **24** (as part of the requirements for the advanced organic-chemical laboratory course). We also gratefully acknowledge the help of *S. Sigrist* and *A.K. Beck* in preparing and proof-reading the manuscript. We thank *F.N.M. Kühnle* for determining the X-ray crystal structures of **24** and **25**. The enantioselective Ru-catalyzed hydrogenation (*Scheme 2*) was carried out in the laboratories of *Sandoz AG*, Basel, and we appreciate collaboration with Dr. *H. Mühle* and *K. Killius*. Continuing financial support by *Novartis Pharma AG*, Basel, is acknowledged.

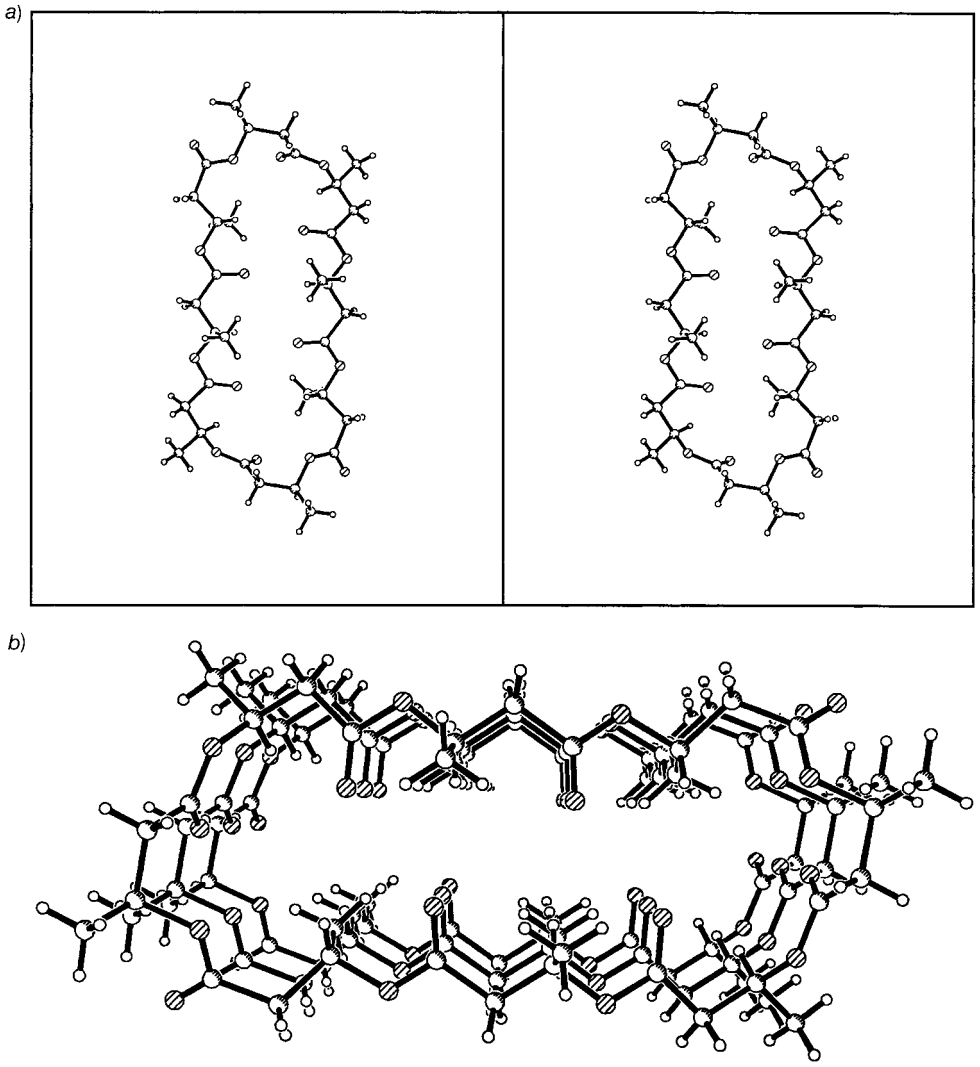

Fig. 4. *Crystal structure of the octalactone* **24**: a) *Stereo PLUTO plot and* b) *crystal packing* (structure determined by *F. N. M. Kühnle*)

Experimental Part

1. *General*. All solvents were either *puriss. p.a.* quality or distilled over P_2O_5. CH_2Cl_2 and pyridine were – as well as CF_3COOH – stored over 4-Å molecular sieves. *t*-BuOH was destilled over CaO and stored at 35° over 4-Å molecular sieves. Benzyl 2,2,2-trichloroacetimidate was prepared according to [40]. *Titristat: Dosimat 665* with exchanging unit 10 ml, *Impulsomat 614*, pH meter *632*, pH electrode *6.0236.100*, *Labograph E 478* (all parts from *Metrohm*). Fermentations: 10-l laboratory fermenter *Basiles* (*Bioengineering*). TLC: *Merck* silica gel *60* F_{254} anal. plates; detection by dipping into a soln. of I_2 (30 g), KI (2 g) in EtOH (200 ml), and H_2O (200 ml) (*A*) or by spraying with a soln. of cerium(IV) sulfate · 4 H_2O (2.5 g), ammonium molybdate · 4 H_2O (75 g), and 10% H_2SO_4 soln. (600 ml) (*B*) or a soln. of 95% EtOH (340 ml), H_2SO_4 (18 ml), anisaldehyde (9 ml), and AcOH

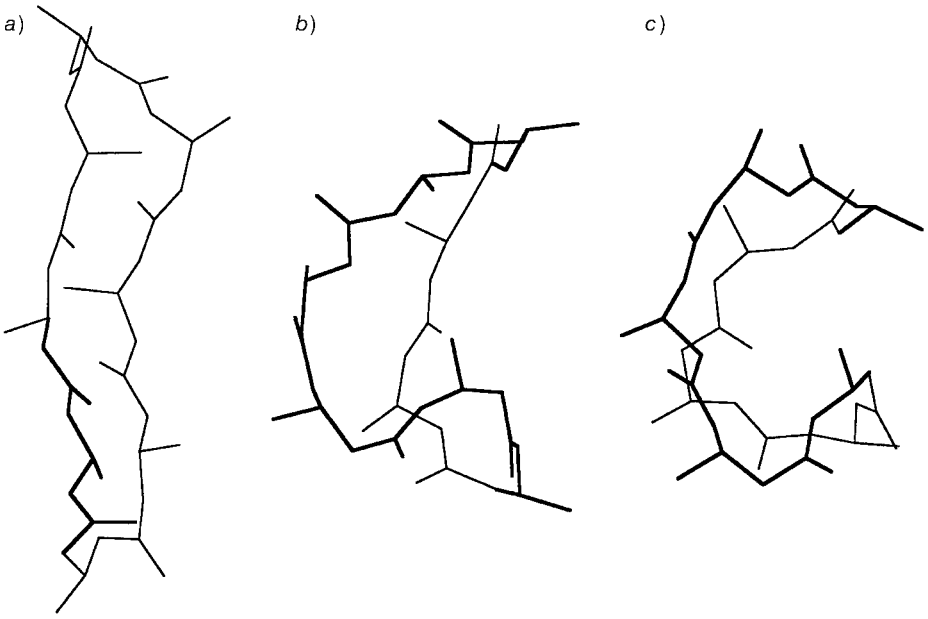

Fig. 5. *Comparison of three octalactone structures:* a) *(*R,S,S,S,R,S,S,S*)-octalactone* **24** (this paper), b) *all-(*R*)-HB octalactone* (modification 1) [39], *and* c) *all-(*R*)-HB octalactone* (modification 2) [39]

(3 ml) (*C*) and heating. FC: *Merck* silica gel *60* (40–60 μm). GC: *Carlo-Erba-HRGC-5160* capillary chromatography with *Carlo-Erba-DP-700-CE* data processor (integrator); column: *FS-Lipodex E* (2,6-*O*-pentyl-3-*O*-butyryl-γ-CD), 50 m. HPLC: *Knauer* system: pump *64*, degasser, variable-wavelength monitor, and HPLC interface; column: *LiChrosorb Si-60* (7 μm, 25 × 0.4 cm); eluent: hexane/i-PrOH 97:3. M.p.: open capillaries, uncorrected. Optical rotations: 10-cm, 1-ml cell; at r.t.; *Perkin-Elmer-241* polarimeter. IR Spectra: *Perkin-Elmer-1600-FTIR* spectrophotometer; neat or in $CHCl_3$; in cm^{-1}. NMR Spectra: *Bruker-AMX-II-500* (500 (^{1}H) and 125 MHz (^{13}C)), *Bruker-AMX-400* (400 (^{1}H) and 100 MHz (^{13}C)), *Varian-Gemini-300* (300 (^{1}H) and 75 MHz (^{13}C)), or *Varian-Gemini-200* (200 (^{1}H) and 50 MHz (^{13}C)) spectrometer; in $CDCl_3$; δ in ppm, J in Hz. MS: *VG (micromass) TRIBRID* for EI (70 eV); *VG (micromass) ZAB2-SEQ* for FAB with 3-nitrobenzyl alcohol as matrix. Elemental analyses were performed in the Microanalytical Laboratory of the Laboratorium für Organische Chemie, ETH-Zürich.

2. *General Procedure I* (*GP I*): *Preparation of Acid Chlorides and Coupling*. The acid (1 equiv.) was dissolved in *x* ml of CH_2Cl_2, and subsequently $(COCl)_2$ or $SOCl_2$ (1.5 equiv.) was added at r.t. (round-bottomed flask with a bubble trap). After 2 h, a few drops of DMF were added, and stirring was continued for an additional 2 h until formation of gas had ceased (2–12 h). The volatile components were then evaporated at r.t., and the obtained greenish or yellowish oil or solid was dried under h.v. for several hours. The crude acid chloride was dissolved in *x* ml of CH_2Cl_2, the soln. cooled in an ice-bath, and 1 equiv. of alcohol in *y* ml of CH_2Cl_2 added. The soln. was cooled to $-78°$ (acetone/dry-ice slush), and pyridine (1.5 equiv.) was added during 20 min by syringe (exothermic reaction, precipitation of a yellowish solid). Depending on the viscosity of the suspension, more CH_2Cl_2 was added. Subsequently, the mixture was allowed to warm up to r.t. during 12–18 h, followed by addition of Et_2O that caused an additional precipitation to appear. The heterogeneous mixture was washed with sat. 1N HCl (which dissolved the precipitation), $NaHCO_3$ soln., and sat. NaCl soln. After drying ($MgSO_4$) and evaporation, the crude product was dried *i.v.*

3. *General Procedure II* (*GP II*): *Cleavage of the* t-*Bu Groups*. The educt was dissolved under Ar in CH_2Cl_2/CF_3COOH 5:1. The cleavage was complete after *ca.* 5 h (^{1}H-NMR monitoring). After evaporation, the yellow soln. was dried at $60°/< 10^{-5}$ mbar for at least 48 h. The resulting yellow or green oil was used for coupling without further purification.

4. *General Procedure III* (*GP III*): *Hydrogenation*. The educt was dissolved in EtOH or AcOEt, then 5–10 weight-% of 10% Pd/C and a few drops of AcOH were added, and hydrogenation was carried out under H_2 (balloon) with vigorous stirring at r.t. The reaction went to completion within 2–5 h (TLC monitoring (Et_2O/pentane 1:1, *B*)). The slightly yellow soln. was filtered through *Celite* and dried *i.v.* The resulting oil or solid was used for coupling without further purification.

5. *General Procedure IV* (*GP IV*): Yamaguchi *Macrolactonization*. The fully deprotected tetramer was dissolved in THF and cooled in an ice-bath. Subsequently, 2,6-dichlorobenzoyl chloride and pyridine were added by syringe. The soln. was first stirred for 30 min in the ice-bath and then for an additional 3 h at r.t. The white precipitate that was formed was filtered off with an Ar funnel. The clear filtrate was diluted with toluene. With a syringe pump (*Infu 362*), the filtrate was added during 3 h to an ice-cooled soln. of 4-(dimethylamino)pyridine in toluene, and subsequently the soln. was stirred for 60 h at the same temp. After extraction with 1N HCl, sat. $NaHCO_3$ soln., and sat. NaCl soln., the soln. was dried ($MgSO_4$) and evaporated. The crude product was purified by chromatography.

6. *General Procedure V* (*GP V*): *Trifluoroacetylation of Hydroxy Esters and Determination of Their Enantiomeric Purity by GC*. In a mini test tube, the hydroxy (1 µl) was dissolved in CH_2Cl_2 (250 µl), and $(CF_3CO)_2O$ (25 µl) was added. After stirring overnight at r.t., the solvents were removed in a stream of N_2, and the resulting oil was dissolved in Et_2O (1 ml). This soln. was injected directly on the GC column.

7. *Monomeric Building Blocks*. 7.1. *(*R*)-Building Blocks* **2**. *(*R*)-3-Hydroxybutanoic Acid* (**2a**) [20]. Poly[(*R*)-3-hydroxybutanoic acid] (**1**) (250 g, 2.91 mol) was suspended in 1,2-dichloroethane (1 l) and heated to reflux (2-l flash). To the yellowish suspension, TsOH (12.5 g) and, after 20 min, MeOH (60 ml) were added. The mixture formed a foam and was further heated to reflux. After *ca*. 15 h, H_2O (300 ml) was added to the yellow-brown emulsion within 15 min. A total of *ca*. 1.1 l (first 1,2-dichloroethane, followed by H_2O) was distilled off within 3 h. During this procedure, H_2O was added 9 × (each time 150 ml); meanwhile the yellow-brown soln. cleared and the bath temp. was increased from 130 to 180°. After cooling to 50°, NaOH (3 g) in H_2O (30 ml) was added, the soln. filtered over *Celite*, and the remaining H_2O distilled off at 30°/19 Torr. After drying *i.v.*, 260 g of a yellow oil resulted. The crude product (170 g) was purified by bulb-to-bulb distillation (in-house model; 90–110°/10^{-5} mbar): 164.8 g (54%) of **2a**. White, very hygroscopic crystals. R_f (Et_2O/pentane 1:1, *B*) <0.1 (smearing). M.p. 44–46° ([20]: 44–46°). $[\alpha]_D^{r.t.} = -24.4$ ($c = 5.05$, H_2O) ([20]: $[\alpha]_D^{r.t.} = -24.7$ ($c = 5.0$, H_2O)). IR ($CHCl_3$): 2979*m* (br.), 1710*vs*, 1412*m*, 1278*w*, 1178*w*, 1084*w*, 1051*w*, 950*w*, 848*w*, 640*w*. ^{1}H-NMR (200 MHz): 4.28–4.18 (*m*, H–C(3)); 2.58, 2.48 (*AB* of *ABX*, $J_{AX} = 7.48$, $J_{BX} = 3.54$, $J_{AB} = 16.05$, CH_2); 1.27 (*d*, $J = 6.4$, Me).

*(*R*)-3-Hydroxybutanoic Acid Methyl Ester* (**2e**) [20]. Poly[(*R*)-3-hydroxybutanoic acid] (**1**) (250 g, 2.91 mol) was suspended in 1,2-dichloroethane (2.5 l) and heated to reflux (4-l flask). To the yellowish suspension, conc. H_2SO_4 (50 ml) in MeOH (1 l) was added. The mixture formed a foam and was further heated to reflux. After 34 h, the mixture was still not clear, and therefore, TosOH (500 mg) was added to the yellow-brown emulsion, and heating was continued for an additional 12 h. After cooling to r.t., half-sat. NaCl soln. (500 ml) was added to the now clear soln., and after vigorous stirring, the org. layer was separated. This procedure was repeated, and the inorg. layer was extracted twice with $CHCl_3$ (700 and 300 ml). After drying ($MgSO_4$) and evaporation of the extract, a yellow liquid was obtained that was purified by distillation at 58–60°/15 Torr: 215 g (57%) of **2e**. Colorless liquid. R_f (Et_2O/pentane 1:1, *B*) 0.63. $[\alpha]_D^{r.t.} = -47.9$ ($c = 1.01$, $CHCl_3$) ([20]: $[\alpha]_D^{r.t.} = -47.6$ ($c = 1.0$, $CHCl_3$)). IR ($CHCl_3$): 3534*w* (br.), 3008*m*, 2976*m*, 2955*m*, 1726*vs*, 1439*s*, 1408*m*, 1378*m*, 1332*m*, 1272*m*, 1177*s*, 1083*w*, 1054*m*, 1005*m*, 938*w*, 848*w*, 841*w*, 653*w*. ^{1}H-NMR (200 MHz): 4.28–4.18 (*m*, H–C(3)); 3.70 (*s*, MeO); 2.95 (*d*, $J = 3.7$, OH); 2.44, 2.33 (*AB* of *ABX*, $J_{AX} = 5.71$, $J_{BX} = 3.80$, $J_{AB} = 19.01$, CH_2); 1.22 (*d*, $J = 6.3$, Me).

*(*R*)-3-(Benzyloxy)butanoic Acid* (**2b**). *Method A:* At r.t. and under vigorous stirring, **2e** (200 g, 1.52 mol) and benzyl 2,2,2-trichloroacetimidate (385 g, 1.52 mol) were dissolved in CH_2Cl_2 (740 ml), and hexane (1.1 l) and CF_3SO_3H (10 ml) were added. After *ca*. 30 min, the temp. rose over 30°, and a white solid precipitated. The suspension was stirred for 4 h at r.t., then the white solid filtered off, and the filtrate evaporated at r.t. Without prior characterization of the oily methyl ester **2g**, 3N NaOH (1.7 l) and MeOH (1 l) were added, and the suspension was stirred vigorously at r.t. overnight (→ emulsion, exothermic reaction). The mixture was first extracted with Et_2O, then the pH of the aq. phase adjusted under ice cooling with conc. soln. HCl to <1, and the so obtained emulsion extracted with Et_2O. The Et_2O phase was subsequently washed with sat. NaCl soln., dried ($MgSO_4$), and evaporated at r.t. Distillation at 115°/0.01 Torr gave 165 g (56%) of **2b**. Colorless oil.

Method B: As described in *Method A*, **2a** (0.5 g, 4.8 mmol) was benzylated with benzyl 2,2,2-trichloroacetimidate (2.66 g, 10.5 mmol, 2.2 equiv.). The resulting (*R*)-3-(benzyloxy)butanoic acid benzyl ester was saponified following *Method A*, and distillation at 118°/0.02 Torr yielded 880 mg (94%) of **2b**. Colorless oil. A sample (50 mg) of this compound was dissolved in Et_2O, diazomethane soln. was added and the mixture then

evaporated. The enantiomeric purity was determined after hydrogenolysis (*GP III*) and trifluoroacetylation (*GP V*) by GC (60° for 5 min, then 2°/min, 120 kPa H_2) e.r. > 99.5 : 0.5. **2b**: R_f (Et_2O/pentane 1 : 1, *B*) < 0.1 (smearing). $[\alpha]_D^{r.t.} = -25.2$ ($c = 0.92$, MeOH) ([18]: $[\alpha]_D^{r.t.} = -25.8$ ($c = 1.20$, $CHCl_3$)). IR ($CHCl_3$): 3008*m*, 2980*m*, 2933*m*, 1713v*s*, 1496*w*, 1453*m*, 1379*m*, 1342*w*, 1178*w*, 1133*m*, 1087*m*, 1045*m*, 1028*w*, 917*w*, 637*w*. ^{1}H-NMR (200 MHz): 7.39–7.27 (*m*, 5 arom. H); 4.62, 4.53 (*AB*, $J_{AB} = 11.5$, PhCH_2O); 4.07–3.97 (*m*, H–C(3)); 2.66, 2.53 (*AB* of *ABX*, $J_{AX} = 7.3$, $J_{BX} = 5.3$, $J_{AB} = 15.5$, CH_2(2)); 1.30 (*d*, $J = 6.2$, Me).

*(*R*)-3-(Benzyloxy)butanoic Acid* tert-*Butyl Ester* (**2d**) [18]. Preparation of the acid chloride (*GP I*) with **2b** (55.0 g) and $SOCl_2$ (100 ml). After drying *i.v.*, the yellow oily acid chloride was dissolved in *t*-BuOH (245 ml), and pyridine (49.0 g, 0.62 mol) was added slowly at r.t. (exothermic reaction). The dark-brown soln. was washed with 1N HCl, sat. $NaHCO_3$ soln., and sat. NaCl soln., dried ($MgSO_4$), and evaporated at r.t. Distillation at 93°/0.05 Torr gave 63.8 g (91%) of **2d**. Faintly yellow oil. R_f (Et_2O/pentane 1 : 1, *B*) 0.91. $[\alpha]_D^{r.t.} = -23.8$ ($c = 1.073$, MeOH); $[\alpha]_D^{r.t.} = -19.4$ ($c = 0.94$, CH_2Cl_2) ([18]: $[\alpha]_D^{r.t.} = -19.5$ ($c = 1.97$, CH_2Cl_2)). IR (neat): 3064*w*, 3031*m*, 2976*s*, 2932*m*, 1730v*s*, 1496*w*, 1454*m*, 1392*m*, 1387*s*, 1344*m*, 1304*m*, 1256*m*, 1205*m*, 1162v*s*, 1090*s*, 1028*m*, 960*w*, 917*w*, 844*w*, 737*m*, 697*m*. ^{1}H-NMR (200 MHz): 7.38–7.24 (*m*, 5 arom. H); 4.56, 4.51 (*AB*, $J_{AB} = 11.5$, PhCH_2O); 4.08–3.89 (*m*, H–C(3)); 2.57, 2.34 (*AB* of *ABX*, $J_{AX} = 7.22$, $J_{BX} = 5.91$, $J_{AB} = 14.85$, CH_2(2)); 1.45 (*s*, *t*-Bu); 1.26 (*d*, $J = 6.2$, Me).

*(*R*)-3-Hydroxybutanoic Acid* tert-*Butyl Ester* (**2c**) [18]. *Method A:* According to *GP III*, **2d** (62.0 g, 248 mmol) in EtOH (540 ml) and AcOH (5.4 ml) was hydrogenated over Pd/C (6.2 g). The obtained oil was dissolved in Et_2O, washed with sat. $NaHCO_3$ and sat. NaCl soln., dried ($MgSO_4$), and evaporated at r.t. 35.56 g (90%) of **2c**. Clear, faintly yellow oil, very pure by ^{1}H-NMR (200 MHz).

Method B: A soln. of **2a** (82.2 g, 790 mmol) and Ac_2O (106 g, 1.04 mol) was stirred overnight at 65°. Then H_2O (10 ml) was added (for the hydrolysis of the remaining anhydride) and the soln. left to cool at r.t. The volatile components were evaporated at 40°. To the obtained colorless oily acid, $SOCl_2$ (200 ml, 3.5 mol) and DMF (2 ml) were added under ice cooling, and the mixture was stirred overnight at r.t. Then the volatile components were evaporated at r.t. Under ice cooling, *t*-BuOH (500 ml) was added within 30 min to the crude acid chloride. Then pyridine (150 ml) was added dropwise under ice cooling keeping the temp. below 35° (exothermic reaction). The mixture (beige colored by a precipitation) was stirred for *ca.* 3 h at 65°. The almost black mixture then was diluted with Et_2O (200 ml), washed with 1N HCl, sat. $NaHCO_3$ soln., and sat. NaCl soln., dried ($MgSO_4$), and evaporated at 40°. To the resulting oil, sat. Na_2CO_3 soln. (300 ml) and MeOH (300 ml) were added (→ white precipitate). After vigorous stirring at r.t. overnight and subsequent workup (evaporation at r.t., washing of the remaining aq. phase with Et_2O, then rewashing of the Et_2O phases with sat. NaCl soln. and drying ($MgSO_4$)), the crude product (45 g of a brown oil) was distilled at 86°/19 Torr: 25.0 g (20%) of **2c**. Colorless, viscous oil. The enantiomeric purity was determined after trifluoracetylation (*GP V*) by GC (60° for 5 min, then 2°/min, 100 kPa H_2): e.r. > 99.5 : 0.5. **2c**: R_f (Et_2O/pentane 1 : 1, *B*) 0.36. $[\alpha]_D^{r.t.} = -16.1$ ($c = 1.01$, MeOH) ([18]: $[\alpha]_D^{r.t.} = -16.0$ ($c = 1.14$, MeOH)). IR (neat): 3434*w* (br.), 2976*s*, 2933*m*, 1729v*s*, 1457*w*, 1393*m*, 1369*s*, 1300*w*, 1257*m*, 1158v*s*, 1087*m*, 945*w*, 864*w*, 839*w*, 800*w*, 762*w*, 699*w*. ^{1}H-NMR (200 MHz): 4.24–4.04 (*m*, H–C(3)); 3.15 (*d*, $J = 3.4$, OH); 2.42, 2.32 (*AB* of *ABX*, $J_{AX} = 8.06$, $J_{BX} = 4.88$, $J_{AB} = 16.82$, CH_2); 1.47 (*s*, *t*-Bu); 1.20 (*d*, $J = 6.3$, Me).

7.2. *(*S*)-Building Blocks* ent-**2**. *(*S*)-3-Hydroxybutanoic Acid Ethyl Ester* (*ent*-**2f**) [25]. In a 10-l fermenter, deionized H_2O (5 l) was autoclaved for 30 min at 124°. After cooling to 30°, sugar (saccharose; 145 g) and baker's yeast (750 g) were added. The suspension was stirred at 600 rpm and aerated with 8 l/h. The excessive formation of foam was suppressed by addition of polypropylene 2000. After 30 min, methyl acetoacetate (= ethyl 3-oxobutanoate; 500 ml) in EtOH (2 l) and sugar (saccharose; 600 g) in H_2O (2 l) were added dropwise by means of a pump (performance: *ca.* 15 ml/h). The pH was maintained at 3–4 by addition of 4N HCl and 4N NaOH, resp. Twice a day, a sample (*ca.* 2 ml) of the fermentation mixture was collected and extracted twice with CH_2Cl_2 (50 ml), the extract filtered over cotton and evaporated, and the residue analyzed by TLC (Et_2O/hexane 2 : 1, *C*). If educt could be identified (R_f (Et_2O/pentane 1 : 1, *B*) 0.44), the addition of the two solns. was reduced. After 138 h, ethyl acetoacetate (421 g, 3.23 mol) was added, and the pump was stopped. The fermentation mixture was centrifuged and the yeast soln. extracted 3 times with AcOEt (6 l). The extract was dried ($MgSO_4$) and evaporated and the residue distilled at 168–170°/13 Torr: 247 g (58%) of *ent*-**2f**. Colorless liquid. The enantiomeric purity was determined after trifluoracetylation (*GP V*) by GC (80°, 2°/min, 200 kPa H_2): e.r. 98.9 : 1.1. *ent*-**2f**: R_f (Et_2O/pentane 1 : 1, *B*) 0.44. $[\alpha]_D^{r.t.} = +41.4$ ($c = 1.01$, $CHCl_3$) ([25]: $[\alpha]_D^{r.t.} = +41.3$ ($c = 1.0$, $CHCl_3$)). IR ($CHCl_3$): 3542*w* (br.), 2983*m*, 2935*m*, 1718v*s*, 1447*w*, 1409*m*, 1378*m*, 1330*m*, 1275*m*, 1178*s*, 1117*w*, 1082*w*, 1054*m*, 1027*m*, 954*w*, 923*w*, 872*w*, 833*w*, 640*w*, 632*w*, 610*w*. ^{1}H-NMR (200 MHz): 4.22–4.10 (*m*, H–C(3), MeCH_2O); 3.14 (br. *s*, OH); 2.53–2.32 (*m*, CH_2(2)); 1.32–1.15 (*m*, Me(4), *Me*CH_2O).

*{(*S*)-[1,1′-Binaphthalene]-2,2′-diylbis[diphenylphosphine-κP]}dichlororuthenium* ([$RuCl_2${(*S*)-binap}] Catalyst) [41]. Under Ar, (*S*)-binap (70 g, 11.24 mmol) was dissolved in degassed toluene (560 ml) and degassed NEt_3 (7.0 ml), and (cycloocta-1,5-diene)dichlororuthenium (2.66 g, 9.50 mmol) was added. The brown soln. was heated to reflux for 8 h. The solvent was distilled off *i.v.* (60°), and after drying for 1 h *i.v.*, 11.73 g of red-brown crystals were obtained which still contained some toluene. The catalyst was used without further purification or characterization.

*(*S*)-3-Hydroxybutanoic Acid Methyl Ester* (*ent*-**2e**) [41]. At 100 atm H_2 and 70°, degassed methyl acetoacetate (= methyl 3-oxobutanoate; 2.06 kg, 17.74 mol) in degassed MeOH (2 l) was hydrogenated for 4 h in the presence of the [$RuCl_2${(*S*)-binap}] catalyst (11.334 g, 1400 mol ratio). After *ca.* 2.5 h, no further H_2 uptake could be detected. From the green soln., MeOH was evaporated at 50–55°/100 mbar, and the liquid was subsequently distilled at 65–71°/30-45 mbar: 1.966 kg (94%) of *ent*-**2e**. Colorless liquid. The enantiomeric purity was determined after trifluoracetylation (*GP V*) by GC (80°, 2°/min, 150 kPa H_2): e.r. 98.7 : 1.3. *ent*-**2e**: R_f (Et_2O/pentane 1 : 1, *B*) 0.63. $[\alpha]_D^{r.t.} = +47.1$ ($c = 1.07$, $CHCl_3$). ^{1}H-NMR (200 MHz): 4.29–4.10 (*m*, H–C(3)); 3.71 (*s*, MeO); 2.97 (br. *s*, OH); 2.51, 2.42 (*AB* of *ABX*, $J_{AX} = 6.28$, $J_{BX} = 6.70$, $J_{AB} = 14.89$, CH_2); 1.23 (*d*, $J = 6.3$, Me). IR ($CHCl_3$): 3675*w*, 3538*w* (br.), 3008*m*, 2975*m*, 2955*w*, 1725v*s*, 1439*s*, 1408*m*, 1377*m*, 1334*m*, 1276*m*, 1177*s*, 1083*w*, 1054*m*, 1005*m*, 938*w*, 886*w*, 841*w*, 846*w*.

*(*S*)-3-(Benzyloxy)butanoic Acid* (*ent*-**2b**). As described for the (*R*)-enantiomer **2b** from *ent*-**2e** (200 g, 1.52 mol) and benzyl 2,2,2-trichloro acetimidate (385 g, 1.52 mol), after saponification and distillation at 109°/0.02 Torr: 160 g (55%) of *ent*-**2b**. Colorless oil. R_f (Et_2O/pentane 1 : 1, *B*) < 0.1 (smearing). $[\alpha]_D^{r.t.} = +25.8$ ($c =$ 1.08, MeOH). IR ($CHCl_3$): 3008*m*, 2980*m*, 2932*m*, 1713v*s*, 1496*w*, 1454*m*, 1379*m*, 1342*w*, 1305*m*, 1133*m*, 1088*m*, 1046*w*, 1028*w*, 939*w*, 628*w*. ^{1}H-NMR (200 MHz): 7.35–7.27 (*m*, 5 arom. H); 4.61, 4.53 (*AB*, $J_{AB} = 11.6$, PhCH_2O); 4.07–3.98 (*m*, H–C(3)); 2.68, 2.52 (*AB* of *ABX*, $J_{AX} = 7.2$, $J_{BX} = 5.4$, $J_{AB} = 15.5$, CH_2(2)); 1.30 (*d*, $J = 6.2$, Me).

Enantiomeric Enrichment of ent-**2b**: *(*R*)-(1-Phenylethyl)ammonium (*S*)-3-(Benzyloxy)butanoate.* (*S*)-Benzyl ester *ent*-**2b** (100.0 g, 0.51 mol) was dissolved in Et_2O, (1 l) and (+)-(*R*)-(1-phenylethyl)amine (62.39 g, 0.51 mol) was added. After a few min, the content of the flask solidified to a white crystal cake from which the solvent was removed *i.v.* The crystals were recrystallized twice from acetone/hexane: 121.4 g (75%) of white salt. M.p. 81.5–82°. $[\alpha]_D^{r.t.} = +19.4$ ($c = 0.99$, $CHCl_3$). IR (KBr): 3500*s*, 3450*m*, 2900*s* (br.), 2230*w*, 1651*m*, 1572v*s*, 1518*s*, 1402*s*, 1337*m*, 1269*w*, 1231*w*, 1144*m*, 1092*s*, 1072*s*, 764*m*, 731*s*, 703*m*, 620*w*. ^{1}H-NMR (300 MHz): 7.34–7.23 (*m*, 5 arom. H); 6.33–6.29 (br. *s*, NH_3^+); 4.48, 4.44 (*AB*, $J_{AB} = 11.8$, PhCH_2O); 4.12 (*q*, $J = 6.8$, PhC*H*(Me)); 3.87–3.81 (*m*, H–C(3)); 2.40, 2.11 (*AB* of *ABX*, $J_{AX} = 6.4$, $J_{BX} = 6.7$, $J_{AB} = 14.8$, CH_2); 1.46 (*d*, $J = 6.6$, PhCH(*Me*)); 1.14 (*d*, $J = 5.9$, Me(4)). ^{13}C-NMR (75 MHz): 177.62; 141.73; 138.92; 128.79; 128.32; 127.96; 127.59; 127.41; 126.27; 73.01; 70.45; 50.92; 44.39; 22.42; 20.02. EI-MS: 194.1 (≪1), 120.1, (≪1), 108.1(11), 107.1(97), 106.1(62), 92.1(12), 91.1(100), 79.1(60), 78.1(11), 77.0(34), 65.0(24), 51.0(26), 50.0(10), 45.0(11), 44.0(209, 43.0(23), 42.0(19), 41.0(15), 39.0(24), 28.0(38), 18.0(21). Anal. calc. for $C_{19}H_{25}NO_3$ (315.41): C 72.35, H 7.99, N 4.44; found: C 72.15, H 8.27, N 4.36.

Of this salt, a batch (115 g, 0.36 mol) was dissolved in 1N HCl (450 ml) and stirred for some minutes. The resulting two-phase mixture was extracted with Et_2O, and the Et_2O phases were washed with $NaHCO_3$ and sat. NaCl soln., dried ($MgSO_4$), and evaporated at r.t.: 65.8 g (94%) of *ent*-**2b**. Yellow oil, very pure by ^{1}H-NMR (200 MHz). A sample (50 mg) was dissolved in EtOH (*ca.* 1 ml), Me_3SiCl (*ca.* 100 mg) added, and the soln. stirred for 1 h and evaporated. After hydrogenation (*GP III*) and subsequent trifluoracetylation (*GP V*) of the hydroxy ester thus obtained GC (80°, 2°/min, 200 kPa H_2) showed an e.r. > 99.5 : 0.5.

*(*S*)-3-Hydroxybutanoic Acid* (*ent*-**2a**) [23]. To a soln. of *ent*-**2e** (307.14 g, 2.6 mol) in H_2O (1.75 l), (2N NaOH 2.65 mol) was added under stirring within 36 h so that the pH of the soln. never exceeded 10.5 (6-l flash). Then the soln. was neutralized with 4N H_2SO_4 (625 ml) and subsequently with citric acid monohydrate (15.83 g). After extraction for 3 d with Et_2O (5 l) in a *Kutscher-Steudel* extractor, the soln. was dried ($MgSO_4$) and partially evaporated. To the remaining *ca.* 3 l, pentane (3.8 l) was added. This mixture was heated for several hours under reflux, and a molecular-sieves insert (molecular sieves 4 Å) [42] was used to further dry the soln. The molecular sieves was replaced twice during this procedure. After cooling, a total of 144.2 g (53%) of *ent*-**2a** precipitated. Big, colorless crystals. R_f (Et_2O/pentane 1 : 1, *B*) < 0.1 (smearing). M.p. 44–46° ([23]: 44–46°). $[\alpha]_D^{r.t.} = +24.4$ ($c = 5.02$, H_2O) ([23]: $[\alpha]_D^{r.t.} = +24.8$ ($c = 4.94$, H_2O)). IR ($CHCl_3$): 2978*s* (br.), 1713v*s*, 1411*m*, 1280*m*, 1178*m*, 1120*w*, 1054*w*, 950*w*, 849*w*. ^{1}H-NMR (200 MHz): 4.31–4.15 (*m*, H–C(3)); 2.55, 2.47 (*AB* of *ABX*, $J_{AX} = 4.90$, $J_{BX} = 2.59$, $J_{AB} = 11.97$, CH_2); 1.27 (*d*, $J = 6.4$, Me).

*(*S*)-3-Hydroxybutanoic Acid* tert-*Butyl Ester* (*ent*-**2c**). As described for the (*R*)-enantiomer **2c** from *ent*-**2a** (100.0 g, 0.69 mol): 56.52 g (37%) of *ent*-**2c**. Colorless, viscous oil. R_f (Et_2O/pentane 1 : 1, *B*) 0.36. $[\alpha]_D^{r.t.} = +16.0$ ($c = 1.17$, MeOH). IR (neat): 3430*m* (br.), 2976*s*, 2933*m*, 1729v*s*, 1456*m*, 1393*m*, 1368*s*, 1301*m*, 1256*m*, 1159v*s*,

1088*m*, 945*w*, 864*w*, 840*w*, 801*w*, 733*w*, 699*w*. ^{1}H-NMR (200 MHz): 4.24–4.04 (*m*, H–C(3)); 3.15 (*d*, *J* = 3.5, OH); 2.41, 2.32 (*AB* of *ABX*, J_{AX} = 6.52, J_{BX} = 5.48, J_{AB} = 15.99, CH_2); 1.46 (*s*, *t*-Bu); 1.20 (*d*, *J* = 6.4, Me).

8. *Dimers* **3**, **4**, ent-**3**, *and* ent-**4**. *(3*R*)-3-{[(3′*R*)-3′-(Benzyloxy)butanoyl]oxy}butanoic Acid* tert-*Butyl Ester* (**3d**) [18]. According to *GP I* with **2b** (27.5 g, 142 mmol) in CH_2Cl_2 (25 ml) and **2c** (20 g, 125 mmol) in CH_2Cl_2 (40 ml). Workup gave a brown-yellow oil (46.65 g) that could be purified by distillation at 128°/0.05 Torr: 42.76 g (> 99%) of **3d**. Faintly yellow oil. R_f (Et_2O/pentane 2:1, *B*) 0.68. $[\alpha]_D^{r.t.} = -20.7$ (*c* = 1.10, MeOH), −12.4 (*c* = 1.13, $CHCl_3$) ([18]: $[\alpha]_D^{r.t.} = -20.2$ (*c* = 1.13, MeOH)). IR (neat): 2978*m*, 2933*w*, 1733v*s*, 1454*w*, 1368*m*, 1301*m*, 1257*w*, 1161*s*, 1101*m*, 1057*m*, 736*w*, 698*w*. ^{1}H-NMR (300 MHz): 7.34–7.28 (*m*, 5 arom. H); 5.31–5.23 (*m*, H–C(3)); 4.56, 4.51 (*AB*, J_{AB} = 11.6, PhCH_2O); 4.03–3.97 (*m*, H–C(3′)); 2.64, 2.41 (*AB* of *ABX*, J_{AX} = 6.9, J_{BX} = 6.2, J_{AB} = 15.1, CH_2(2)); 2.56, 2.40 (*AB* of *ABX*, J_{AX} = 7.4, J_{BX} = 6.1, J_{AB} = 15.32, CH_2(2′)); 1.43 (*s*, *t*-Bu); 1.28 (*d*, *J* = 6.4, Me); 1.26 (*d*, *J* = 6.2, Me). ^{13}C-NMR (75 MHz): 170.52; 169.43; 138.54; 128.31; 127.63; 127.51; 80.85; 71.95; 70.83; 67.71; 42.18; 42.12; 28.04; 19.87; 19.81. EI-MS: 335 (≪1, $[M-H]^+$), 279.2(18), 174.1(32), 173.1(11), 107.1(45), 105.1(15), 91.1(100), 87.1(29), 69.1(30), 57.1(47), 41.1(18).

*(3*S*)-3-{[(3′*S*)-3′-(Benzyloxy)butanoyl]oxy}butanoic Acid* tert-*Butyl Ester* (*ent*-**3d**). According to *GP I*, with *ent*-**2b** (27.5 g, 142 mmol) in CH_2Cl_2 (25 ml) and *ent*-**2c** (20 g, 125 mmol) in CH_2Cl_2 (40 ml). Workup gave a brown oil (43.72 g) that could be purified by distillation at 118–119°/0.01 Torr: 37.85 g (90%) of *ent*-**3d**. Colorless oil. A sample (200 mg) was purified for analyses by FC (CH_2Cl_2). R_f (Et_2O/pentane 2:1, *B*) 0.68. $[\alpha]_D^{r.t.} = +21.2$ (*c* = 1.09, MeOH), +12.8 (*c* = 0.99, $CHCl_3$). IR (neat): 2978*m*, 2933*w*, 1736v*s*, 1454*w*, 1368*m*, 1303*m*, 1258*w*, 1163*s*, 1101*m*, 1056*m*, 737*w*, 698*w*. ^{1}H-NMR (300 MHz): 7.34–7.29 (*m*, 5 arom. H); 5.28–5.25 (*m*, H–C(3)); 4.56, 4.51 (*AB*, J_{AB} = 11.5, PhCH_2O); 4.01–3.97 (*m*, H–C(3′)); 2.64, 2.41 (*AB* of *ABX*, J_{AX} = 6.9, J_{BX} = 6.2, J_{AB} = 15.0, CH_2(2)); 2.56, 2.40 (*AB* of *ABX*, J_{AX} = 7.4, J_{BX} = 6.1, J_{AB} = 15.3, CH_2(2′)); 1.43 (*s*, *t*-Bu); 1.28 (*d*, *J* = 6.3, Me); 1.26 (*d*, *J* = 6.2, Me). ^{13}C-NMR (75 MHz): 170.55; 169.46; 138.51; 128.34; 127.64; 127.63; 80.87; 71.95; 70.83; 67.74; 42.18; 42.12; 28.04; 19.88; 19.81. EI-MS: 335.2 (≪1, $[M-H]^+$), 279.1(11), 174.1(27), 107.1(53), 105.1(21), 92.1(12), 91.1(100), 87.1(38), 69.1(44), 57.1(49), 43.0(14), 41.1(21). Anal. calc. for $C_{19}H_{28}O_5$ (336.43): C 67.83, H 8.39; found: C 67.87, H 8.33.

*(3*S*)-3-{[(3′*R*)-3′-(Benzyloxy)butanoyl]oxy}butanoic Acid* tert-*Butyl-Ester* (**4d**). According to *GP I*, with **2b** (27.5 g, 142 mmol) in CH_2Cl_2 (25 ml) and *ent*-**2c** (20 g, 125 mmol) in CH_2Cl_2 (40 ml). Workup and distillation at 118–124°/0.01 Torr gave 39.21 g (93%) of **4d**. Colorless oil. A sample (200 g) was purified for analyses by FC (CH_2Cl_2). R_f (Et_2O/pentane 2:1, *B*) 0.67. $[\alpha]_D^{r.t.} = -11.6$ (*c* = 0.99, MeOH). IR (neat): 2977*m*, 2933*w*, 1733v*s*, 1454*w*, 1368*m*, 1303*m*, 1258*w*, 1163*s*, 1140*s*, 1101*m*, 1055*m*, 737*w*, 698*w*. ^{1}H-NMR (300 MHz): 7.34–7.28 (*m*, 5 arom. H); 5.29–5.26 (*m*, H–C(3)); 4.57, 4.51 (*AB*, J_{AB} = 11.5, PhCH_2O); 4.03–3.98 (*m*, H–C(3′)); 2.55, (*AB* of *ABX*, J_{AX} = 7.5, J_{BX} = 5.9, J_{AB} = 15.3, CH_2(2)); 2.64, 2.39 (*AB* of *ABX*, J_{AX} = 7.1, J_{BX} = 5.9, J_{AB} = 15.0, CH_2(2′)); 1.44 (*s*, *t*-Bu); 1.28 (*d*, *J* = 6.4, Me); 1.27 (*d*, *J* = 6.2, Me). ^{13}C-NMR (75 MHz): 170.70; 169.47; 138.51; 128.33; 127.67; 127.54; 80.84; 72.15; 70.93; 67.70; 42.17; 42.09; 28.06; 19.91; 19.83. EI-MS: 335.1 (≪1, $[M-H]^+$), 279.1(12), 174.1(42), 173.1(11), 107.1(54), 105.1(22), 92.1(11), 91.1(100), 87.1(33), 69.1(31), 57.1(37), 41.1(13). Anal. calc. for $C_{19}H_{28}O_5$ (336.43): C 67.83, H 8.39; found: C 67.65, H 8.25.

*(3*R*)-3-{[(3′*S*)-3′-(Benzyloxy)butanoyl]oxy}butanoic Acid* tert-*Butyl Ester* (*ent*-**4d**). According to *GP I* with *ent*-**2b** (6.88 g, 35.4 mmol) in CH_2Cl_2 (7 ml) and **2c** (5.0 g, 31.21 mmol) in CH_2Cl_2 (18 ml). Workup gave a yellow-brown oil (11.0 g) that was purified by distillation *ca.* 135°/0.05 Torr. 10.3 g (98%) of *ent*-**4d**. Faintly yellow oil. A sample (200 mg) was purified for analyses by FC (CH_2Cl_2). R_f (Et_2O/pentane 2:1, *B*) 0.68. $[\alpha]_D^{r.t.} = +12.1$ (*c* = 0.99, MeOH). IR (neat): 2978*m*, 2933*w*, 1734v*s*, 1454*w*, 1368*m*, 1304*m*, 1256*w*, 1163*s*, 1099*m*, 1028*w*, 973*w*, 738*w*, 698*w*. ^{1}H-NMR (300 MHz): 7.34–7.28 (*m*, 5 arom. H); 5.29–5.26 (*m*, H–C(3)); 4.57, 4.51 (*AB*, J_{AB} = 11.5, PhCH_2O); 4.05–3.98 (*m*, H–C(3″)); 2.55, 2.40 (*AB* of *ABX*, J_{AX} = 7.5, J_{BX} = 5.9, J_{AB} = 15.3, CH_2(2)); 2.64, 2.39 (*AB* of *ABX*, J_{AX} = 7.1, J_{BX} = 6.0, J_{AB} = 15.0, CH_2(2′)); 1.44 (*s*, *t*-Bu); 1.28 (*d*, *J* = 6.3, Me); 1.26 (*d*, *J* = 6.2, Me). ^{13}C-NMR (75 MHz): 170.70; 169.47; 138.52; 128.53; 127.66; 127.54; 80.84; 72.19; 70.93; 67.71; 42.17; 42.09; 28.06; 19.91; 19.82. EI-MS: 335.1 (≪1, $[M-H]^+$), 174.1(29), 107.1(52), 105.1(23), 92.1(12), 91.1(100), 87.1(43), 69.1(44), 57.1(48), 43.1(12), 41.1(17). Anal. calc. for $C_{19}H_{28}O_5$ (336.43): C 67.83, H 8.39; found: C 67.82, H 8.22.

*(3*R*)-3-{[(3′*R*)-3′-(Benzyloxy)butanoyl]oxy}butanoic Acid* (**3b**) [18]. According to *GP II* with **3d** (15.0 g, 44.59 mmol) in CH_2Cl_2 (38 ml) and CF_3COOH (7.5 ml): 11.86 g (95%) of **3b**. Brown oil, very pure by ^{1}H-NMR (200 MHz). R_f (Et_2O/pentane 1:1, 2% AcOH, *B*) 0.37. $[\alpha]_D^{r.t.} = -27.7$ (*c* = 0.97, MeOH) ([18]: $[\alpha]_D^{r.t.} = -28.1$ (*c* = 1.01, MeOH)). IR ($CHCl_3$): 3672*w*, 2984*m*, 2935*m*, 1731v*s*, 1496*w*, 1454*w*, 1380*m*, 1302*s*, 1178*m*, 1133*m*, 1087*m*, 1056*m*, 1028*w*, 972*w*, 909*w*, 657*w*, 624*w*. ^{1}H-NMR (300 MHz): 7.37–7.25 (*m*, 5 arom. H); 5.32–5.25 (*m*, H–C(3)); 4.56, 4.51 (*AB*, J_{AB} = 11.5, PhCH_2O); 4.03–3.97 (*m*, H–C(3′)); 2.51, 2.43 (*AB* of *ABX*, J_{AX} = 5.9, J_{BX} = 5.9, J_{AB} = 15.5, CH_2(2)); 2.69, 2.64 (*AB* of *ABX*, J_{AX} = 5.0, J_{BX} = 5.1, J_{AB} = 10.5, CH_2(2′)); 1.30 (*d*, *J* = 6.4, Me); 1.26 (*d*, *J* = 6.2, Me). ^{13}C-NMR (75 MHz): 175.96; 170.96 138.39; 128.37; 127.69; 127.60; 72.01; 70.86;

67.12; 42.16; 40.37; 19.81. ES-MS: 281.2 ($\ll$1, $[M+H]^+$), 174.1(29), 107.1(73), 105.1(23), 91.1(100), 87.1(24), 79.1(13), 69.1(11), 43.1(10). Anal. calc. for $C_{15}H_{20}O_5$ (280.32): C 64.27, H 7.19; found: C 64.51, H 7.11.

*(3*S*)-3-{[(3′*S*)-3′-(Benzyloxy)butanoyl]oxy}butanoic Acid* (*ent*-**3b**). According to *GP II* with *ent*-**3d** (15.0 g, 44.59 mmol) in CH_2Cl_2 (38 ml) and CF_3COOH (7.5 ml): 11.89 g (95%) of *ent*-**3b**. Brown oil, very pure by ^{1}H-NMR (200 MHz). R_f (Et_2O/pentane 1:1, 2% AcOH, *B*) 0.37. $[\alpha]_D^{r.t.} = +28.2$ ($c = 1.01$, MeOH). IR ($CHCl_3$): 3684*w*, 2984*w*, 2934*m*, 1731v*s*, 1602*w*, 1496*w*, 1454*w*, 1380*m*, 1302*s*, 1178*m*, 1133*m*, 1085*m*, 1056*m*, 1028*w*, 972*w*, 909*w*. ^{1}H-NMR (300 MHz): 7.35–7.25 (*m*, 5 arom. H); 5.32–5.25 (*m*, H–C(3)); 4.56, 4.50 (*AB*, $J_{AB} = 11.6$, PhCH_2O); 4.03–3.97 (*m*, H–C(3′)); 2.51, 2.43 (*AB* of *ABX*, $J_{AX} = 5.9$, $J_{BX} = 6.0$, $J_{AB} = 15.5$, CH_2(2)); 2.69, 2.64 (*AB* of *ABX*, $J_{AX} = 4.9$, $J_{BX} = 4.9$, $J_{AB} = 10.6$, CH_2(2′)); 1.30 (*d*, $J = 6.4$, Me); 1.26 (*d*, $J = 6.2$, Me). ^{13}C-NMR (75 MHz): 175.96; 170.96; 138.39; 128.37; 127.69; 127.60; 72.01; 70.86; 67.12; 42.16; 40.37; 19.81. EI-MS: 281.1 ($\ll$1, $[M+H]^+$), 174.1(35), 107.1(56), 105.1(28), 91.1(100), 87.1(29), 79.1(11), 69.1(14), 43.1(12). Anal. calc. for $C_{15}H_{20}O_5$ (280.32): C 64.27, H 7.19; found: C 64.03, H 7.05,

*(3*S*)-3-{[(3′*R*)-3′-(Benzyloxy)butanoyl]oxy}butanoic Acid* (**4b**). According to *GP II*, with **4d** (10.0 g, 29.72 mmol) in CH_2Cl_2 (25 ml) and CF_3COOH (5 ml): 8.09 g (97%) **4b**. Brown oil, very pure by ^{1}H-NMR (200 MHz). R_f (Et_2O/pentane 1:1, 2% AcOH, *B*) 0.37. $[\alpha]_D^{r.t.} = -11.0$ ($c = 1.05$, MeOH). IR ($CHCl_3$): 2981*m*, 2933*m*, 1732v*s*, 1496*w*, 1455*w*, 1380*m*, 1302*s*, 1178*m*, 1136*m*, 1082*m*, 1057*m*, 1028*w*, 972*w*, 910*w*. ^{1}H-NMR (300 MHz): 7.34–7.28 (*m*, 5 arom. H); 5.32–5.29 (*m*, H–C(3)); 4.56, 4.50 (*AB*, $J_{AB} = 11.5$, PhCH_2O); 4.05–3.98 (*m*, H–C(3′)); 2.67, 2.51 (*AB* of *ABX*, $J_{AX} = 7.2$, $J_{BX} = 5.8$, $J_{AB} = 16.1$, CH_2(2)); 2.63, 2.41 (*AB* of *ABX*, $J_{AX} = 7.2$, $J_{BX} = 5.9$, $J_{AB} = 15.1$, CH_2(2′)); 1.31 (*d*, $J = 6.3$, Me); 1.26 (*d*, $J = 6.2$, Me). ^{13}C-NMR (75 MHz): 175.70; 170.75; 138.46; 128.33; 127.66; 127.56; 72.14; 70.89; 67.10; 42.16; 40.33; 19.81. EI-MS: 281.1 ($<$1, $[M+H]^+$), 174.1(37), 107.0(5), 105.0(27), 92.1(13), 91.0(100), 87.0(41), 79.0(15), 77.0(11), 69.0(22), 65.0(13), 45.0(12), 43.0(19), 41.0(12). Anal. calc. for $C_{15}H_{20}O_5$ (280.32): C 64.27, H 7.19; found: C 64.21, H 6.99.

*(3*R*)-3-{[(3′*S*)-3′-(Benzyloxy)butanoyl]oxy}butanoic Acid* (*ent*-**4b**). According to *GP II*, with *ent*-**4d** (9.0 g, 26.75 mmol) in CH_2Cl_2 (25 ml), CF_3COOH (5 ml), and benzene (2.5 ml): 7.43 g (99%) of *ent*-**4b**. Colorless oil, very pure by ^{1}H-NMR (200 MHz). R_f (Et_2O/pentane 1:1, 2% AcOH, *B*) 0.37. $[\alpha]_D^{r.t.} = +1.3$ ($c = 0.96$, MeOH). IR ($CHCl_3$): 2983*m*, 2935*w*, 1732v*s*, 1496*w*, 1454*m*, 1380*m*, 1303*m*, 1178*m*, 1135*m*, 1085*m*, 1055*m*, 1028*w*, 972*w*, 910*w*. ^{1}H-NMR (300 MHz): 7.35–7.28 (*m*, 5 arom. H); 5.33–5.26 (*m*, H–C(3)); 4.56, 4.49 (*AB*, $J_{AB} = 11.5$, PhCH_2O); 4.05–3.98 (*m*, H–C(3′)); 2.67, 2.51 (*AB* of *ABX*, $J_{AX} = 7.2$, $J_{BX} = 5.8$, $J_{AB} = 16.1$, CH_2(2)); 2.63, 2.41 (*AB* of *ABX*, $J_{AX} = 7.2$, $J_{BX} = 5.9$, $J_{AB} = 15.1$, CH_2(2′)); 1.31 (*d*, $J = 6.3$, Me); 1.26 (*d*, $J = 6.2$, Me). ^{13}C-NMR (75 MHz): 175.58; 170.75; 138.46; 128.33; 127.66; 127.56; 72.14; 70.89; 67.11; 67.07; 42.16; 40.32; 19.80. EI-MS: 281.1 ($<$1, $[M+H]^+$), 174.1(40), 107.0(62), 105.0(30), 92.0(13), 91.0(100), 88.1(11), 87.0(45), 79.0(15), 77.0(11), 69.0(24), 65.0(14), 45.0812), 43.0(20), 42.0(10), 41.0(13). Anal. calc. for $C_{15}H_{20}O_5$ (280.32): C 64.27, H 7.19; found: C 64.14, H 7.12.

*(3*R*)-3-{[(3′*R*)-3′-Hydroxybutanoyl]oxy}butanoic Acid* tert-*Butyl Ester* (**3c**) [18]. According to *GP III*, with **3d** (12.5 g, 37.15 mmol) in EtOH (30 ml, 5 h): 8.5 g (93%) of **3c**. Faintly yellow oil, very pure by ^{1}H-NMR (200 MHz). A sample (200 g) was purified for analyses by FC (Et_2O/pentane 1:1). R_f (Et_2O/pentane 1:1, *A*) 0.37. $[\alpha]_D^{r.t.} = 13.8$ ($c = 1.06$, MeOH) ([18]: $[\alpha]_D^{r.t.} = -25.9$ ($c = 1.31$, CH_2Cl_2)). IR (neat): 3700–3200*w*, 2929*s*, 2935*m*, 1734v*s*, 1458*m*, 1369*s*, 1307*s*, 1258*s*, 1163v*s*, 1103*m*, 1058*m*, 974*w*, 947*w*, 943*w*. ^{1}H-NMR (300 MHz): 5.34–5.28 (*m*, H–C(3′)); 4.22–4.16 (*m*, H–C(3)); 3.2–3.0 (br. *s*, OH); 2.54, 2.45 (*AB* of *ABX*, $J_{AX} = 8.0$, $J_{BX} = 5.1$, $J_{AB} = 15.4$, CH_2(2)); 2.45, 2.39 (*AB* of *ABX*, $J_{AX} = 2.9$, $J_{BX} = 9.2$, $J_{AB} = 16.0$, CH_2(2′)); 1.44 (*s*, *t*-Bu); 1.30 (*d*, $J = 6.3$, Me); 1.23 (*d*, $J = 6.3$, Me). ^{1}H-NMR (75 MHz): 172.08; 169.62; 81.15; 67.88; 64.42; 43.27; 42.00; 28.03; 22.47; 19.88. EI-MS: 173.1(14), 146.0(14), 105.0(26), 7.0(70), 69.0(53), 57.1(100), 56.0(11), 45.0(24), 43.0(39), 42.0(13), 41.0(28), 29.0(14), 28.0(12). Anal. calc. for $C_{12}H_{22}O_5$ (246.30): C 58.52, H 9.00; found: C 58.30, H 8.99.

*(3*S*)-3-{[(3′*S*)-3′-Hydroxybutanoyl]oxy}butanoic Acid* tert-*Butyl Ester* (*ent*-**3c**). According to *GP III*, with *ent*-**3d** (15.0 g, 44.59 mmol) in EtOH (37 ml; overnight): 10.82 g (99%) of *ent*-**3c**. Faintly yellow oily, very pure by ^{1}H-NMR (200 MHz). A sample (200 mg) was purified for analyses by FC (Et_2O/pentane 1:1). R_f (Et_2O/pentane 1:1, *A*) 0.37. $[\alpha]_D^{r.t.} = +13.8$ ($c = 1.01$, MeOH). IR (neat): 3700–3200*w*, 2980*m*, 2936*w*, 1735v*s*, 1458*w*, 1369*s*, 1306*m*, 1258*m*, 1164*s*, 1103*m*, 1057*m*, 974*w*, 843*w*. ^{1}H-NMR (300 MHz): 5.34–5.27 (*m*, H–C(3′)); 4.21–4.16 (*m*, H–C(3)); 3.2–3.0 (br. *s*, OH); 2.54, 2.45 (*AB* of *ABX*, $J_{AX} = 8.0$, $J_{BX} = 5.1$, $J_{AB} = 15.4$, CH_2(2)); 2.45, 2.38 (*AB* of *ABX*, $J_{AX} = 3.0$, $J_{BX} = 9.2$, $J_{AB} = 16.0$, CH_2(2′)); 1.44 (*s*, *t*-Bu); 1.30 (*d*, $J = 6.4$, Me); 1.23 (*d*, $J = 6.4$, Me). ^{13}C-NMR (75 MHz): 172.12; 169.63; 81.16; 67.89; 64.43; 43.26; 42.00; 28.04; 22.47; 19.89. EI-MS: 173.18(20), 146.1(21), 128.1(11), 105.1(38), 103.1(13), 91.1(11), 87.1(91), 69.1(64), 57.1(100), 56.1(12), 45.1(20), 43.0(309, 42.1(11), 41.1(21). Anal. calc. for $C_{12}H_{22}O_5$ (246.30): C 58.52, H 9.00; found: C 58.77, H 9.03.

(3S)-3-{[(3′R)-3′-Hydroxybutanoyl]oxy}butanoic Acid tert-*Butyl Ester* (**4c**). According to *GP III*, with **4d** (20.0 g, 59.45 mmol) in EtOH (50 ml; overnight): 13.97 g (95%) of **4c**. Faintly yellow oil, very pure by ^{1}H-NMR (200 MHz). A sample (200 mg) was purified for analyses by FC (Et_2O/pentane 1:1). R_f (Et_2O/pentane 1:1, *A*) 0.37. $[\alpha]_D^{r.t.} = -5.8$ (*c* = 1.01, MeOH). IR (neat): 3700–3200*w*, 2977*s*, 2935*m*, 1734v*s*, 1458*w*, 1369*s*, 1308*s*, 1258*s*, 1165v*s*, 1103*m*, 1059*s*, 974*w*, 947*w*, 844*w*. ^{1}H-NMR (300 MHz): 5.33–5.26 (*m*, H–C(3′)); 4.25–4.19 (*m*, H–C(3)); 3.1–3.2 (br. *s*, OH); 2.53, 2.46 (*AB* of *ABX*, J_{AX} = 8.1, J_{BX} = 4.9, J_{AB} = 15.4, CH_2(2)); 2.47, 2.39 (*AB* of *ABX*, J_{AX} = 3.0, J_{BX} = 9.3, J_{AB} = 16.1, CH_2(2′)); 1.44 (*s*, *t*-Bu); 1.30 (*d*, *J* = 6.3, Me); 1.22 (*d*, *J* = 6.3, Me). ^{13}C-NMR (75 MHz): 171.72; 169.76; 81.21, 67.76; 64.18; 43.45; 41.80; 28.03M 22.34; 19.86. EI-MS: 191.1 (18), 175.1 (14), 173.1 (43), 157.1 (14), 155.1 (15), 146.1 (43), 131.1 (13), 128.1 (21), 105.1 (48), 103.1 (19), 87.1 (99), 69.0 (58), 57.1 (100), 45.1 (19), 43.0 (25), 42.1 (12), 41.1 (23). Anal. calc. for $C_{12}H_{22}O_5$ (246.30): C 58.52, H 9.00; found: C 58.68, H 9.02.

(3R)-3-{[(3′S)-3′-Hydroxybutanoyl]oxy}butanoic Acid tert-*Butyl Ester* (*ent*-**4c**). According to *GP III*, with *ent*-**4d** (9.26 g, 27.52 mmol) in EtOH (25 ml; overnight): 6.76 g (99%) of *ent*-**4c**. Faintly yellow oil, very pure by ^{1}H-NMR (200 MHz). A sample (350 mg) was purified for analyses by FC (Et_2O/pentane 1:1). R_f (Et_2O/pentane 1:1, *A*) 0.37. $[\alpha]_D^{r.t.} = +5.4$ (*c* = 1.00, MeOH). IR (neat): 3700–3200*m*, 2979*s*, 2935*m*, 1732v*s*, 1458*m*, 1369v*s*, 1308*s*, 1258*s*, 1163v*s*, 1103*m*, 1059*s*, 974*m*, 947*w*, 844*w*. ^{1}H-NMR (300 MHz): 5.33–5.26 (*m*, H–C(3′)); 4.23–4.17 (*m*, H–C(3)); 3.3–3.1 (br. *s*, OH); 2.53, 2.46 (*AB* of *ABX*, J_{AX} = 8.1, J_{BX} = 5.0, J_{AX} = 15.4, CH_2(2)); 2.47, 2.39 (*AB* of *ABX*, J_{AX} = 3.0, J_{BX} = 9.2, J_{AB} = 16.1, CH_2(2′)); 1.44 (*s*, *t*-Bu); 1.30 (*d*, *J* = 6.4, Me); 1.22 (*d*, *J* = 6.3, Me). ^{13}C-NMR (75 MHz): 171.73; 169.77; 81.21, 67.79; 64.19; 43.45; 41.91; 28.03; 22.33; 19.65. EI-MS: 173.0 (16), 146.0 (18), 128.0 (11), 105.0 (31), 103.0 (11), 87.0 (78), 69.0 (61), 57.0 (100), 56.0 (12), 45.0 (24), 43.0 (37), 42.0 (12), 41.0 (26), 29.0 (12). Anal. calc. for $C_{12}H_{22}O_5$ (246.30): C 58.52, H 9.00; found: C 58.73, H 8.72.

(3R)-3-{[(3′R)-3′-Hydroxybutanoyl]oxy}butanoic Acid (**3a**) [18]. According to *GP III*, **3b** (1.0 g, 3.57 mmol) was hydrogenated in AcOEt (10 ml) over Pd/C (50 mg). FC (Et_2O/pentane 2:1 + 2% AcOH) gave 580 mg (85%) of **3a**. Colorless oil. R_f (Et_2O/pentane 2:1, *A*) 0.16. $[\alpha]_D^{r.t.} = +22.5$ (*c* = 0.95, MeOH) ([18]: $[\alpha]_D^{r.t.} = -20.8$ (*c* = 0.86, MeOH)). IR ($CHCl_3$): 2982*m*, 2936*m*, 1724v*s*, 1406*w*, 1382*m*, 1302*m*, 1178*s*, 1139*m*, 1082*m*, 1054*m*, 974*m*, 931*w*. ^{1}H-NMR (300 MHz): 7.8–6.8 (br. *s*, OH); 5.34–5.23 (*m*, H–C(3)); 4.27–4.16 (*m*, H–C(3′)); 2.63, 2.52 (*AB* of *ABX*, J_{AX} = 8.1, J_{BX} = 6.2, J_{AB} = 20.2, CH_2(2)); 2.49, 2.43 (*AB* of *ABX*, J_{AX} = 5.0, J_{BX} = 3.2, J_{AB} = 6.0, CH_2(2′)); 1.29 (*d*, *J* = 6.4, Me); 1.20 (*d*, *J* = 6,3, Me). ^{13}C-NMR (75 MHz): 174.75; 171.98; 67.69; 64.71; 43.18; 40.36; 22.29; 19.83. EI-MS: 379.4 (63, $[2M - H]^+$), 343.3 (18), 275.3 (14), 189.2 (100, $[M - H]^+$)), 168.1 (16), 153.1 (36), 152.1 (14), 151.1 (33), 103.1 (71). Anal. calc. for $C_8H_{14}O_5$: C 50.52, H 7.42; found: C 50.58, H 7.50.

9. *Tetramers* **5**–**9** *and* ent-**5**–**8**. *(3R)-3-{[(3′R)-3′-{[(3″R)-3″-{[(3‴R)-3‴-(Benzyloxy)butanoyl]oxy}butanoyl]oxy}butanoyl]oxy}butanoic Acid* tert-*Butyl Ester* (**5d**) [18]. According to *GP I*, with **3b** (11.0 g, 39.2 mmol) in CH_2Cl_2 (40 ml) and **3c** (10.73 g, 43.6 mmol) in CH_2Cl_2 (40 ml) 17.64 g of crude brown oil. FC (Et_2O/pentane 1:2.5) yielded 16.39 g (72%) of **5d**. Clear, colorless oil that solidified after 5 days at −18°. R_f (Et_2O/pentane 1:2.5, *B*) 0.13. M.p. 36.0–36.5° ([18]: m.p. 36.0–36.5°). $[\alpha]_D^{r.t.} = -16.4$ (*c* = 1.045, MeOH), −9.0 (*c* = 0.995, $CHCl_3$) ([18]: $[\alpha]_D^{r.t.} = -11.2$ (*c* = 1.01, CH_2Cl_2)). IR ($CHCl_3$): 3009*m*, 2976*s*, 2936*w*, 1735v*s*, 1455*w*, 1382*m*, 1369*s*, 1305*s*, 1179*s*, 1137*s*, 1055*s*, 973*w*, 877*w*. ^{1}H-NMR (500 MHz): 7.33–7.27 (*m*, 5 arom. H); 5.30–5.21 (*m*, 3 H); 4.50 (*AB*, J_{AB} = 11.5, PhCH_2O); 4.02–3.96 (*m*, H–C(3‴)); 2.65–2.35 (*m*, 8 H); 1.43 (*s*, *t*-Bu); 1.28–1.25 (*m*, 12 H). ^{13}C-NMR (125 MHz): 170.51; 169.33; 169.24; 169.15; 138.54; 128.33; 127.63; 127.52; 80.91; 71.94; 70.82; 67.98; 67.60; 67.35; 42.13; 42.01; 40.92; 40.87; 28.05; 19.85; 19.81; 19.75. LSI-MS: 1017.9 (≪1, $[2M + H]^+$), 508.1, (3, M^+), 507.1 (11, $[M - H]^+$), 454.0 (18), 453.0 (55), 259.0 (19), 173.0 (28), 155.0 (44), 154.0 (20), 138.0 (11), 137.0 (20), 136.0 (20), 107.0 (22), 105.0 (12), 91.9 (17), 90.9 (100), 88.9 (12), 86.9 (13), 76.9 (15), 68.9 (66), 56.9 (53).

(3S)-3-{[(3′S)-3′-{[(3″S)-3″-{[(3‴S)-3‴-(Benzyloxy)butanoyl]oxy}butanoyl]oxy}butanoyl]oxy}butanoic Acid tert-*Butyl Ester* (*ent*-**5d**). According to *GP I*, with *ent*-**3b** (4.0 g, 14.3 mmol) in CH_2Cl_2 (14 ml) and *ent*-**3c** (3.91 g, 15.9 mmol) in CH_2Cl_2 (7 ml): 7.28 g of brown-yellow oil. FC (Et_2O/pentane 1:2.5) yielded 3.8 g (52%) of *ent*-**5d**. Clear, colorless oil that solidified after several days at −18°. R_f (Et_2O/pentane 1:2.5, *B*) 0.13. M.p. 36.0–36.5°. $[\alpha]_D^{r.t.} = +9.4$ (*c* = 1.08, $CHCl_3$). IR (neat): 2980*s*, 2935*m*, 1737v*s*, 1497*w*, 1454*m*, 1381*s*, 1369*s*, 1303*s*, 1259*s*, 1183v*s*, 1138*s*, 1055*s*, 1102*s*, 1057*s*, 974*m*, 928*w*, 844*w*, 737*m*, 699*m*. ^{1}H-NMR (400 MHz): 7.34–7.23 (*m*, 5 arom. H); 5.31–5.21 (*m*, 3 H); 4.56, 4.50 (*AB*, J_{AB} = 11.5, PhCH_2O); 4.03–3.95 (*m*, H–C(3‴)); 2.65–2.37 (*m*, 8 H); 1.43 (*s*, *t*-Bu); 1.28–1.24 (*m*, 12 H). ^{13}C-NMR (100 MHz): 170.51; 169.34; 169.25; 169.16; 138.54; 128.33; 127.63; 127.52; 80.91; 71.94; 70.82; 67.98; 67.60; 67.35; 42.12; 42.00; 40.92; 40.87; 28.04; 19.85; 19.81; 19.75. LSI-MS: 1017.6 (≪1, $[2M + H]^+$), 509.3 (11, $[M + H]^+$), 508.3 (4, M^+), 507.3 (12, $[M - H]^+$), 454.2 (19), 453.2 (61), 367.2 (10), 259.1 (229, 173.1 (31), 155.1 (49), 154.1 (23), 138.1 (12), 137.1 (23), 136.0 (219, 107.0 (22),

105.0(13), 92.0(17), 91.0(100), 88.9(13), 86.9(23), 76.9(16), 68.9(64), 56.9(49). Anal. calc. for $C_{27}H_{40}O_9$ (508.61): C 63.76, H 7.93; found: C 63.92, H 8.20.

*(3*S*)-3-{{(3′*S*)-3′-{{(3″*R*)-3″-{[(3‴*R*)-3‴-(Benzyloxy)butanoyl]oxy}butanoyl]oxy}butanoyl}oxy}butanoic Acid* tert-*Butyl Ester* (**6d**). According to *GP I*, with **3b** (3.0 g, 10.7 mmol) in CH_2Cl_2 (11 ml) and *ent*-**3c** (2.93 g, 11.9 mmol) in CH_2Cl_2 (5 ml): 6.04 g of crude brown oil. FC (Et_2O/pentane 1:2.5) yielded 3.8 g (33%) of **6d**. Clear, colorless oil. R_f (Et_2O/pentane 1:2.5, *B*) 0.13. $[\alpha]_D^{rt.} = -6.7$ ($c = 0.97$, $CHCl_3$). IR (neat): 2980*s*, 2934*s*, 1732v*s*, 1497*w*, 1455*m*, 1386*s*, 1368*s*, 1306*s*, 1259*s*, 1187v*s*, 1058*s*, 1028*m*, 975*s*, 928*w*, 844*w*, 739*m*, 698*m*. ^{1}H-NMR (400 MHz): 7.35–7.23 (*m*, 5 arom. H); 5.30–5.21 (*m*, 3 H); 4.55, 4.50 (*AB*, $J_{AB} = 11.5$, PhCH_2O); 4.02–3.94 (*m*, H–C(3‴)); 2.65–2.37 (*m*, 8 H); 1.43 (*s*, *t*-Bu); 1.25–1.28 (*m*, 12 H). ^{13}C-NMR (100 MHz): 170.53; 169.35; 169.16; 138.52; 128.34; 127.63; 127.53; 80.91; 71.98; 70.83; 67.96; 67.57; 67.42; 42.15; 42.01; 40.87; 40.81; 28.05; 19.87; 19.79; 19.76. LSI-MS: 508.1 (3, M^+), 454.1(15), 453.1(56), 367.1(10), 259.0(11), 173.0(21), 155.0(35), 154.0(11), 137.0(13), 136.0(11), 106.9(13), 91.9(12), 90.9(100), 86.9(16), 68.8(56), 56.9(41). Anal. calc. for $C_{27}H_{40}O_9$ (508.61): C 63.76, H 7.93; found: C 63.95, H 7.92.

*(3*R*)-3-{{(3′*R*)-3′-{{(3″*S*)-3″-{[(3‴*S*)-3‴-(Benzyloxy)butanoyl]oxy}butanoyl]oxy}butanoyl}oxy}butanoic Acid* tert-*Butyl Ester* (*ent*-**6d**). According to *GP I*, with *ent*-**3b** (3.0 g, 10.7 mmol) in CH_2Cl_2 (11 ml) and **3c** (2.93 g, 11.9 mmol) in CH_2Cl_2 (5 ml): 5.72 g of crude brown oil. FC (Et_2O/pentane 1:2.5) yielded 2.42 g (45%) of *ent*-**6d**. Clear, colorless oil. R_f (Et_2O/pentane 1:2.5, *B*) 0.13. $[\alpha]_D^{rt.} = +7.1$ ($c = 1.05$, $CHCl_3$). IR (neat): 2979*m*, 2935*w*, 1740v*s*, 1497*w*, 1455*m*, 1382*s*, 1369*s*, 1304*s*, 1259*s*, 1184*s*, 1138*s*, 1101*s*, 1058*s*, 1028*w*, 975*w*, 928*w*, 843*w*, 739*w*, 698*w*. ^{1}H-NMR (400 MHz): 7.35–7.23 (*m*, 5 arom. H); 5.30–5.21 (*m*, 3 H); 4.55, 4.50 (*AB*, $J_{AB} = 11.5$, PhCH_2O); 4.02–3.94 (*m*, H–C(3‴)); 2.65–2.36 (*m*, 8 H); 1.43 (*s*, *t*-Bu); 1.29–1.24 (*m*, 12 H). ^{13}C-NMR (100 MHz): 170.52; 169.35; 169.16; 138.53; 128.34; 127.63; 127.53; 80.91; 71.98; 70.83; 67.96; 67.57; 67.42; 42.15; 42.01; 40.87; 40.81; 28.04; 19.86; 19.82; 19.79; 19.76. LSI-MS: 508.1 (2, M^+), 453.1(38), 173.0(20), 155.0(33), 106.9(13), 91.9(12), 90.9(100), 86.9(17), 72.9(13), 68.9(56), 56.9(42). Anal. calc. for $C_{27}H_{40}O_9$ (508.61): C 63.76, H 7.93; found: C 64.02, H 7.93.

*(3*S*)-3-{{(3′*R*)-3′-{{(3″*R*)-3″-{[(3‴*R*)-3‴-(Benzyloxy)butanoyl]oxy}butanoyl]oxy}butanoyl}oxy}butanoic Acid* tert-*Butyl Ester* (**7d**). According to *GP I*, with **3b** (1.1 g, 3.9 mmol) in CH_2Cl_2 (4 ml) and **4c** (1.07 g, 4.4 mmol) in CH_2Cl_2 (4 ml): 2.22 g of crude brown-yellow oil. FC (Et_2O/pentane 1:2.5) yielded 1.24 g (63%) of **7d**. Clear, colorless oil. R_f (Et_2O/pentane 1:2.5, *B*) 0.13. $[\alpha]_D^{rt.} = -9.3$ ($c = 1.12$, $CHCl_3$). IR (neat): 2980*s*, 2934*s*, 1732v*s*, 1496*w*, 1456*s*, 1381*s*, 1369*s*, 1305*s*, 1259*s*, 1184v*s*, 1138*s*, 1101*s*, 1057*s*, 1028*m*, 974*m*, 928*w*, 843*w*, 739*m*, 698*m*. ^{1}H-NMR (200 MHz): 7.34–7.23 (*m*, 5 arom. H); 5.30–5.20 (*m*, 3 H); 4.56, 4.50 (*AB*, $J_{AB} = 11.6$, PhCH_2O); 4.01–3.94 (*m*, H–C(3‴)); 2.69–2.33 (*m*, 8 H); 1.43 (*s*, *t*-Bu); 1.29–1.24 (*m*, 12 H). ^{13}C-NMR (50 MHz): 170.51; 169.32; 169.22; 138.51; 128.33, 127.63; 127.52; 80.90; 71.94; 70.81; 67.95; 67.67; 67.36; 42.13; 42.01; 40.96; 40.71; 28.04; 19.80. LSI-MS: 508.1 (3, M^+), 507.1 (12, $[M-H]^+$), 454.1(22), 453.1(70), 367.0(10), 259.0(19), 173.0(31), 155.0(48), 154.0(11), 137.0(14), 136.0(12), 107.0(19), 105.0(12), 91.9(18), 90.9(100), 86.9(25), 76.9(11), 72.9(12), 68.9(71), 56.9(54). Anal. calc. for $C_{27}H_{40}O_9$ (508.61): C 63.76, H 7.93; found: C 64.03, H 7.78.

*(3*R*)-3-{{(3′*S*)-3′-{{(3″*S*)-3″-{[(3‴*S*)-3‴-(Benzyloxy)butanoyl]oxy}butanoyl]oxy}butanoyl}oxy}butanoic Acid* tert-*Butyl Ester* (*ent*-**7d**). According to *GP I*, with *ent*-**3b** (3.0 g, 10.7 mmol) in CH_2Cl_2 (11 ml) and *ent*-**4c** (2.93 g, 11.9 mmol) in CH_2Cl_2 (5 ml). FC (Et_2O/pentane 1:2.5) yielded 2.55 g (47%) of *ent*-**7d**. Clear, colorless oil. R_f (Et_2O/pentane 1:2.5, *B*) 0.13. $[\alpha]_D^{rt.} = +9.5$ ($c = 1.00$, $CHCl_3$). IR (neat): 2980*m*, 2935*w*, 1738v*s*, 1457*w*, 1383*m*, 1369*m*, 1307*s*, 1258*m*, 1185*s*, 1138*m*, 1101*m*, 1059*m*, 973*w*, 928*w*, 844*w*, 738*w*, 698*w*. ^{1}H-NMR (400 MHz): 7.35–7.23 (*m*, 5 arom. H); 5.31–5.21 (*m*, 3 H); 4.56, 4.50 (*AB*, $J_{AB} = 11.5$, PhCH_2O); 4.03–3.95 (*m*, H–C(3‴)); 2.69–2.36 (*m*, 8 H); 1.43 (*s*, *t*-Bu); 1.30–1.22 (*m*, 12 H). ^{13}C-NMR (100 MHz): 170.52; 169.33; 169.26; 138.54; 128.33; 127.63; 127.52; 80.90; 71.94; 70.82; 67.96; 67.67; 67.37; 42.14; 42.02; 40.97; 40.73; 28.05; 19.85; 19.80, 19.76. LSI-MS: 507.2 (3, $[M-H]^+$), 453.1(24), 281.0(12), 173.0(15), 155.0(26), 147.0(19), 136.0(16), 107.0(12), 91.9(11), 90.9(100), 86.9(17), 72.9(63), 68.9(70), 56.9(50). Anal. calc. for $C_{27}H_{40}O_9$ (508.61): C 63.76, H 7.93; found: C 63.83, H 8.06.

*(3*S*)-3-{{(3′*S*)-3′-{{(3″*S*)-3″-{[(3‴*R*)-3‴-(Benzyloxy)butanoyl]oxy}butanoyl]oxy}butanoyl}oxy}butanoic Acid* tert-*Butyl Ester* (**8d**). According to *GP I*, with **4c** (3.0 g, 10.7 mmol) in CH_2Cl_2 (11 ml) and *ent*-**3c** (2.93 g, 11.9 mmol) in CH_2Cl_2 (5 ml): 6.1 g of crude brown oil. FC (Et_2O/pentane 1:2.5) yielded 3.77 g (69%) of **8d**. Clear, colorless oil that solidified after several days at −18°. R_f (Et_2O/pentane 1:2.5, *B*) 0.13. M.p. 26.0–27.0°. $[\alpha]_D^{rt.} = -6.3$ ($c = 1.03$, $CHCl_3$). IR (neat): 2980*m*, 2935*w*, 1738v*s*, 1497*w*, 1455*m*, 1381*s*, 1369*s*, 1303*s*, 1259*s*, 1185v*s*, 1139*s*, 1101*s*, 1059*s*, 974*w*, 928*w*, 844*w*, 738*w*, 698*w*. ^{1}H-NMR (400 MHz): 7.35–7.23 (*m*, 5 arom. H); 5.32–5.21 (*m*, 3 H); 4.56, 4.50 (*AB*, $J_{AB} = 11.5$, PhCH_2O); 4.04–3.97 (*m*, H–C(3‴)); 2.70–2.36 (*m*, 8 H); 1.44 (*s*,*t*-Bu); 1.29–1.23 (*m*, 12 H). ^{13}C-NMR (100 MHz): 170.67; 169.33; 169.27; 169.14; 138.55; 128.32; 127.65; 127.53; 80.91; 72.12; 70.91; 67.99; 67.58; 67.31; 42.13; 42.01; 40.89; 28.04; 19.87, 1983, 1976. LSI-MS: 1017.5 (≪1,

$[2M+H]^+$), 508.1 (6, M^+), 507.1 (20, $[M-H]^+$), 454.1(26), 453.1(99), 259.0(26), 173.0(43), 156.0(11), 155.0(72), 154.0(16), 137.0(19), 136.0(15), 107.0(25), 105.0(14), 91.9(24), 90.9(100), 88.9(13), 86.9(34), 76.9(16), 68.9(91), 56.9(82). Anal. calc. for $C_{27}H_{40}O_9$ (508.61): C 63.76, H 7.93; found: C 63.49, H 8.17.

*(3*R*)-3-{{(3′*R*)-3′-{{(3″*R*)-3″-{[(3‴*S*)-3‴-(Benzyloxy)butanoyl]oxy}butanoyl}oxy}butanoyl}oxy}butanoic Acid* tert-*Butyl Ester* (*ent*-**8d**). According to *GP I*, with *ent*-**4b** (2.2 g, 7.85 mmol) in CH_2Cl_2 (8 ml) and **3c** (2.14 g, 8.8 mmol) in CH_2Cl_2 (8 ml); 4.0 g of crude yellow oil. FC (Et_2O/pentane 1:2.5) yielded 2.47 g (62%) of *ent*-**8d**. Clear, colorless oil that solidified after several days at −18°. R_f (Et_2O/pentane 1:2.5, *B*) 0.13. M.p. 26.0–27.0°. $[\alpha]_D^{r.t.} = +6.6$ ($c = 0.975$, $CHCl_3$). IR ($CHCl_3$): 3034*w*, 2984*w*, 2933*w*, 1735v*s*, 1455*w*, 1382*m*, 1369*m*, 1306*m*, 1260*m*, 1179*m*, 1137*m*, 1101*m*, 1060*m*, 9784*w*, 841*w*. ^{1}H-NMR (300 MHz): 7.34–7.27 (*m*, 5 arom. H); 5.32–5.23 (*m*, 3 H); 4.57, 4.51 (*AB*, $J_{AB} = 11.5$, PhCH_2O); 4.04–3.97 (*m*, H–C(3‴)); 2.67–2.36 (*m*, 8 H); 1.44 (*s*, *t*-Bu); 1.29–1.23 (*m*, 12 H). ^{13}C-NMR (100 MHz): 170.68; 169.33; 169.27; 169.14; 138.55; 128.33; 127.66; 127.54; 80.92; 72.12; 70.92; 67.98; 67.57; 67.31; 42.13; 42.01; 40.89; 28.05; 19.85, 19.78. LSI-MS: 508.1 (4, M^+), 507.1 (14, $[M-H]^+$), 454.1(22), 453.1(76), 367.1(11), 259.1(22), 173.1(34), 155.1(56), 154.0(13), 137.0(15), 136.0(12), 107.0(20), 105.0(12), 92.0(19), 90.9(100), 86.9(28), 76.9(12), 68.9(80), 56.9(59). Anal. calc. for $C_{27}H_{40}O_9$ (508.61): C 63.76, H 7.93; found: C 63.98, H 7.80.

*(3*R*)-3-{{(3′*R*)-3′-{{(3″*R*)-3″-{[(3‴*R*)-3‴-(Benzyloxy)butanoyl]oxy}butanoyl}oxy}butanoyl}oxy}butanoic Acid* (**5b**) [18]. According to *GP II*, with **5d** (8.0 g, 15.73 mmol) in CH_2Cl_2 (12 ml) and CF_3COOH (12 ml): 6.98 g (98%) of **5b**. Slightly yellow oil, very pure by ^{1}H-NMR (200 MHz). A sample (200 mg) was purified for analyses by FC (Et_2O/pentane 1:1, 1% AcOH). R_f (Et_2O/pentane 1:1, *A*) 0.20. $[\alpha]_D^{r.t.} = -18.0$ ($c = 0.99$, CH_2Cl_2) ([18]: $[\alpha]_D^{r.t.} = -16.6$ ($c = 0.765$, CH_2CH_2)). IR ($CHCl_3$): 2984*m*, 2936*m*, 1732v*s*, 1496*w*, 1455*m*, 1382*s*, 1304*s*, 1263*s*, 1178*s*, 1135*m*, 1100*m*, 1086*m*, 1055*s*, 1028*w*, 976*w*, 928*w*. LSI-MS: 475.2 (32, $[M+Na+H]^+$), 454.2(28), 453.2 (100, $[M+H]^+$), 451.2 (23, $[M-H]^+$), 367.2(18), 173.1(12), 155.1(19), 107.0(12), 91.0(57), 90.0(57), 87.0(14), 68.9(37), 54.9(11). ^{1}H-NMR (400 MHz): 7.35–7.27 (*m*, 5 arom. H); 5.35–5.20 (*m*, 3 H); 4.56, 4.51 (*AB*, $J_{AB} = 11.6$, PhCH_2O); 4.04–3.96 (*m*, H–C(3‴)); 2.67–2.39 (*m*, 8 H); 1.29 (*d*, $J = 6.4$, Me); 1.27 (*d*, $J = 6.5$, Me); 1.26 (*d*, $J = 6.3$, Me); 1.25 (*d*, $J = 6.2$, Me). ^{13}C-NMR (100 MHz): 174.06; 171.03; 169.31; 169.16; 138.34; 128.31; 127.67; 127.54; 71.91; 70.81; 67.73; 67.65; 67.48; 42.11; 40.95; 40.76; 40.39; 19.83; 19.76, 19.72; 19.66. Anal. calc. for $C_{23}H_{32}O_9$ (452.50): C 61.05, H 7.13; found: C 61.15, H 7.20.

*(3*S*)-3-{{(3′*S*)-3′-{{(3″*S*)-3″-{[(3‴*S*)-3‴-(Benzyloxy)butanoyl]oxy}butanoyl}oxy}butanoyl}oxy}butanoic Acid* (*ent*-**5b**). According to *GP II*, with *ent*-**5d** (1.5 g, 2.96 mmol) in CH_2Cl_2 (1.8 ml) and CF_3COOH (1.8 ml) 1.31 g (98%) of *ent*-**5b**. Slightly yellow viscous oil, very pure by ^{1}H-NMR (200 MHz). A sample (200 mg) was purified for analyses by FC (Et_2O/pentane 1:1, 1% AcOH). R_f (Et_2O/pentane 1:1, *A*) 0.20. $[\alpha]_D^{r.t.} = +18.6$ ($c = 1.06$, CH_2Cl_2). IR (neat): 3210*m*, 2982*m*, 2936*m*, 1738v*s*, 1497*w*, 1454*m*, 1382*s*, 1304*s*, 1260*s*, 1186v*s*, 1135*s*, 1101*s*, 1057*s*, 1028*w*, 976*m*, 927*w*, 825*w*, 740*w*, 698*m*. ^{1}H-NMR (400 MHz): 7.35–7.23 (*m*, 5 arom. H); 5.34–5.21 (*m*, 3 H); 4.56, 4.51 (*AB*, $J_{AB} = 11.6$, PhCH_2O); 4.04–3.96 (*m*, H–C(3‴)); 1.29 (*d*, $J = 6.3$, Me); 1.27 (*d*, $J = 6.5$, Me); 1.26 (*d*, $J = 6.2$, Me); 1.25 (*d*, $J = 6.2$, Me). ^{13}C-NMR (100 MHz): 174.58; 170.96; 169.35; 169.25; 138.40; 128.33; 127.70; 127.57; 71.95; 70.83; 67.87; 67.68; 67.51; 42.14; 40.96; 40.81; 40.42; 19.83; 19.80, 19.74; 19.72. LSI-MS: 905.3 ($\ll 1$, $[2M]^+$), 453.1 (33, $[M+H]^+$), 452.1 (2, M^+), 173.1(20), 155.1(32), 137.0(12), 107.0(16), 92.0(15), 91.0(100), 90.0(10), 86.9(22), 76.9(11), 68.9(68). Anal. calc. for $C_{23}H_{32}O_9$ (452.50): C 61.05, H 7.13; found: C 61.25, H 7.18.

*(3*R*)-3-{{(3′*R*)-3′-{{(3″*S*)-3″-{[(3‴*S*)-3‴-(Benzyloxy)butanoyl]oxy}butanoyl}oxy}butanoyl}oxy}butanoic Acid* (*ent*-**6b**). According to *GP II*, with *ent*-**6d** (2.0 g, 3.93 mmol) in CH_2Cl_2 (3 ml) and CF_3COOH (3 ml): 1.74 g (98%) of *ent*-**6b**. Slightly yellow viscous oil, very pure by ^{1}H-NMR (200 MHz). A sample (200 mg) was purified for analyses by FC (Et_2O/pentane 1:1, 1% AcOH). R_f (Et_2O/pentane 1:1, *A*) 0.20. $[\alpha]_D^{r.t.} = +10.2$ ($c = 1.05$, CH_2Cl_2). IR (neat): 3210*m*, 2983*s*, 2035*s*, 1739v*s*, 1497*w*, 1455*m*, 1381*s*, 1302*s*, 1259*s*, 1187v*s*, 1136*s*, 1100*s*, 1057*s*, 1028*w*, 977*m*, 928*w*, 824*w*, 739*m*, 699*m*. ^{1}H-NMR (400 MHz): 7.33–7.24 (*m*, 5 arom. H); 5.33–5.21 (*m*, 3 H); 4.56, 4.50 (*AB*, $J_{AB} = 11.6$, PhCH_2O); 4.03–3.95 (*m*, H–C(3‴)); 1.29 (*d*, $J = 6.4$, Me); 1.27 (*d*, $J = 6.3$, Me); 1.26 (*d*, $J = 6.3$, Me); 1.25 (*d*, $J = 6.2$, Me). ^{13}C-NMR (100 MHz): 174.56; 170.94; 169.32; 169.31; 138.40; 128.35; 127.68; 127.57; 79.98; 70.82; 69.73; 67.61; 67.50; 42.14; 40.87; 40.84; 40.35; 19.80; 19.76. LSI-MS: 905.3 ($\ll 1$, $[2M]^+$), 475.1 (14, $[M+Na+H]^+$), 454.2(10), 453.1 (38, $[M+H]^+$), 452.1 (3, M^+), 173.1(26), 155.1(40), 154.0(11), 137.0(15), 136.0(13), 107.0(21), 105.0(14), 92.0(19), 91.0(100), 88.9(12), 86.9(28), 76.9(15), 68.9(76). Anal. calc. for $C_{23}H_{32}O_9$ (452.50): C 61.05, H 7.13; found: C 60.98, H 7.15.

*(3*R*)-3-{{(3′*S*)-3′-{{(3″*S*)-3″-{[(3‴*S*)-3‴-(Benzyloxy)butanoyl]oxy}butanoyl}oxy}butanoyl}oxy}butanoic Acid* (*ent*-**7b**). According to *GP II*, with *ent*-**7d** (2.0 g, 3.93 mmol) in CH_2Cl_2 (3 ml) and CF_3COOH (3 ml): 1.76 g (99%) of *ent*-**7b**. Slightly yellow viscous oil, very pure by ^{1}H-NMR (200 MHz). A sample (200 mg) was purified for analyses by FC (Et_2O/pentane 1:1, 1% AcOH). R_f (Et_2O/pentane 1:1, *A*) 0.20. $[\alpha]_D^{r.t.} = +12.3$ ($c = 1.07$, CH_2Cl_2). IR (neat): 3210*m*, 2982*m*, 2936*m*, 1732v*s*, 1497*w*, 1455*m*, 1382*s*, 1303*s*, 1259*s*, 1189v*s*, 1134*s*, 1101*s*,

1058*s*, 1028*w*, 976*m*, 929*w*, 822*w*, 739*m*, 699*m*. ^{1}H-NMR (400 MHz): 7.35–7.23 (*m*, 5 arom. H); 5.33–5.21 (*m*, 3 H); 4.56, 4.51 (*AB*, J_{AB} = 11.5, PhCH_2O); 4.04–3.96 (*m*, H–C(3‴)); 1.29 (*d*, *J* = 6.0, Me); 1.28 (*d*, *J* = 6.0, Me); 1.26 (*d*, *J* = 6.3, Me); 1.25 (*d*, *J* = 6.2, Me). ^{13}C-NMR (100 MHz): 173.79; 171.06; 169.47; 169.18; 138.33; 128.34; 127.77; 127.59; 72.02; 70.92; 67.73; 67.56; 67.51; 42.17; 41.08; 40.68; 40.08; 19.80. LSI-MS: 905 (≪1, $[2M]^+$), 453.1 (25, $[M+H]^+$), 452.1 (2, M^+), 173.1(22), 155.1(36), 137.0(11), 136.0(11.3), 107.0(17), 105.0(12), 92.0(17), 91.0(100), 86.9(26), 76.9(11), 72.9(16), 68.9(79), 56.9(11). Anal. calc. for $C_{23}H_{32}O_9$ (452.50): C 61.05, H 7.13; found: C 60.78, H 7.09.

*(3*R*)-3-{[(3′*R*)-3′-{[(3″*R*)-3″-{[(3‴*S*)-3‴-(Benzyloxy)butanoyl]oxy}butanoyl]oxy}butanoyl]oxy}butanoic Acid* (*ent*-**8b**). According to *GP II*, with *ent*-**8d** (2.0 g, 3.93 mmol) in CH_2Cl_2 (3 ml) with CF_3COOH (3 ml): 1.76 g (99%) of *ent*-**8b**. Slightly yellow viscous oil, very pure by ^{1}H-NMR (200 MHz). A sample (200 mg) was purified for analyses by FC (Et_2O/pentane 1:1, 1% AcOH). The obtained colorless oil solidified. R_f (Et_2O/pentane 1:1, *A*) 0.20. M.p. 36.0–37.0°. $[\alpha]_D^{rt.}$ = +4.6 (*c* = 1.12, CH_2Cl_2). IR (neat): 3210*m*, 2981*s*, 2936*s*, 1738v*s*, 1497*w*, 1454*m*, 1382*s*, 1302*s*, 1261*s*, 1187v*s*, 1136*s*, 1101*s*, 1057*s*, 1028*w*, 976*m*, 928*w*, 827*w*, 741*m*, 699*m*. ^{1}H-NMR (400 MHz): 7.34–7.24 (*m*, 5 arom. H); 5.43–5.20 (*m*, 3 H); 4.56, 4.50 (*AB*, J_{AB} = 11.5, PhCH_2O); 4.05–3.97 (*m*, H–C(3‴)); 1.30 (*d*, *J* = 6.4, Me); 1.28 (*d*, *J* = 6.3, Me); 1.26 (*d*, *J* = 6.3, Me); 1.25 (*d*, *J* = 6.2, Me). ^{13}C-NMR (100 MHz): 174.03; 171.21; 169.36; 169.26; 138.39; 128.35; 127.71; 127.60; 80.92; 72.11; 70.90; 67.78; 67.60; 67.57; 42.14; 41.00; 40.82; 40.46; 19.89; 19.79; 1976; 19.73. LSI-MS: 905.3 (≪1, $[2M]^+$), 475.1 (22, $[M+Na+H]^+$), 454.2(19), 453.2 (68, $[M+H]^+$), 452.1 (4, M^+), 451.1(16), 259.1(13), 173.1(32), 155.1(51), 154.0(22), 138.0(11), 137.0(26), 136.0(23), 107.0(26), 105.0(16), 92.0(23), 91.0(100), 89.9(10), 88.9(14), 86.9(33), 76.9(17), 68.9(83), 56.9(19), 54.9(12). Anal. calc. for $C_{23}H_{32}O_9$ (452.50): C 61.05, H 7.13; found: C 61.19, H 6.93.

*(3*R*)-3-{[(3′*R*)-3′-{[(3″*R*)-3″-{[(3‴*R*)-3‴-Hydroxybutanoyl]oxy}butanoyl]oxy}butanoyl]oxy}butanoic Acid* tert-*Butyl Ester* (**5c**) [18]. According to *GP III*, **5d** (7.0 g, 13.76 mmol) was hydrogenated in AcOEt (35 ml) over Pd/C (350 mg): 5.70 g (99%) of **5c**. White solid, very pure by ^{1}H-NMR (200 MHz). A sample (200 mg) was purified for analyses by FC (Et_2O/pentane 1:1). M.p. 29.0–29.5°. $[\alpha]_D^{rt.}$ = –13.7 (*c* = 1.16, $CHCl_3$). IR ($CHCl_3$): 3528*w* (br.), 3008*w*, 2982*m*, 2935*w*, 1734v*s*, 1458*w*, 1383*m*, 1369*m*, 1306*s*, 1260*s*, 1176*s*, 1140*m*, 1102*m*, 1056*s*, 976*w*, 930*w*, 840*w*, 812*w*, 646*w*, 626*w*. ^{1}H-NMR (400 MHz): 5.35–5.21 (*m*, 3 H); 4.22–4.11 (*m*, H–C(3‴)); 3.15–3.00 (br. *s*, OH); 2.63–2.36 (*m*, 8 H); 1.44 (*s*, *t*-Bu); 1.31 (*d*, *J* = 6.4, Me); 1.28 (*d*, *J* = 6.3, Me); 1.27 (*d*, *J* = 6.3, Me); 1.23 (*d*, *J* = 6.3, Me). ^{13}C-NMR (100 MHz): 171.98; 169.37; 169.33; 169.14; 80.89; 67.97; 67.72; 67.50; 64.35; 43.18; 41.96; 40.80; 27.99; 22.47; 19.84; 19.70. LSI-MS: 1255.5 (1, $[3M]^+$), 838.3(12), 837.3 (24, $[2M]^+$), 419.1 (26, M^+), 364.1(16), 363.1(100), 277.1(51), 259.1(35), 191.1(16), 173.1(30), 155.1(36), 154.0(17). Anal. calc. for $C_{20}H_{34}O_9$: C 57.40, H 8.19; found: C 57.28, H 8.00.

*(3*S*)-3-{[(3′*S*)-3′-{[(3″*S*)-3″-{[(3‴*S*)-3‴-Hydroxybutanoyl]oxy}butanoyl]oxy}butanoyl]oxy}butanoic Acid* tert-*Butyl Ester* (*ent*-**5c**). According to *GP III*, *ent*-**5d** (1.5 g, 2.96 mmol) was hydrogenated in AcOEt (8 ml) over Pd/C (80 mg): 1.23 g (99%) of *ent*-**5c**. Colorless oil that solidified after several days and was very pure by ^{1}H-NMR (200 MHz). A sample (200 mg) was purified for analyses by FC (Et_2O/pentane 1:1). R_f (Et_2O/pentane 1:1, *A*) 0.14. M.p. 29.0–29.5°. $[\alpha]_D^{rt.}$ = +14.6 (*c* = 1.00, $CHCl_3$). IR (neat): 3533*m*, 2979*s*, 2936*w*, 1737v*s*, 1458*w*, 1383*s*, 1369*s*, 1306*s*, 1259*s*, 1184v*s*, 1141*s*, 1102*m*, 1058*s*, 976*w*, 844*w*, 759*w*. ^{1}H-NMR (400 MHz): 5.35–5.21 (*m*, 3 H); 4.22–4.13 (*m*, H–C(3‴)); 3.15–3.00 (br. *s*, OH); 2.66–2.36 (*m*, 8 H); 1.44 (*s*, *t*-Bu); 1.31 (*d*, *J* = 6.4, Me); 1.28 (*d*, *J* = 6.3, Me); 1.27 (*d*, *J* = 6.3, Me); 1.23 (*d*, *J* = 6.3, Me). ^{13}C-NMR (100 MHz): 172.02; 169.42; 169.38; 169.19; 80.94; 68.03; 67.77; 67.55; 64.40; 43.25; 42.01; 40.85; 28.04; 22.52; 19.89; 19.75. LSI-MS: 837.3 (1, $[2M]^+$), 441.1(4), 419.1 (20, M^+), 364.1(20), 363.1(100), 277.1(23), 259.1(18), 191.1(17), 173.0(50), 155.0(47), 154.0(17), 137.0(26), 136.0(15), 107.0(10), 105.0(17), 86.9(42), 72.9(13), 68.9(86), 56.9(62), 54.9(15). Anal. calc. for $C_{20}H_{34}O_9$ (418.48): C 57.40, H 8.19; found: C 57.53, H 8.31.

*(3*S*)-3-{[(3′*S*)-3′-{[(3″*R*)-3″-{[(3‴*R*)-3‴-Hydroxybutanoyl]oxy}butanoyl]oxy}butanoyl]oxy}butanoic Acid* tert-*Butyl Ester* (**6c**). According to *GP III*, *ent*-**6d** (1.6 g, 3.16 mmol) was hydrogenated in AcOEt (8 ml) over Pd/C (80 mg): 1.31 g (99%) of **6c**. Colorless oil, very pure by ^{1}H-NMR (200 MHz). A sample (200 mg) was purified for analyses by FC (Et_2O/pentane 1:1). R_f (Et_2O/pentane 1:1, *A*) 0.14. $[\alpha]_D^{rt.}$ = +14.4 (*c* = 1.075, $CHCl_3$). IR (neat): 3532*w*, 2980*s*, 2935*m*, 1739v*s*, 1457*m*, 1383*s*, 1369*s*, 1306*s*, 1258*s*, 1185v*s*, 1142*s*, 1103*s*, 1058*s*, 977*m*, 843*w*, 759*w*. ^{1}H-NMR (400 MHz): 5.34–5.21 (*m*, 3 H); 4.23–4.13 (*m*, H–C(3‴)); 3.20–2.95 (br. *s*, OH); 2.66–2.36 (*m*, 8 H); 1.44 (*s*, *t*-Bu); 1.31 (*d*, *J* = 6.4, Me); 1.29 (*d*, *J* = 6.5, Me); 1.27 (*d*, *J* = 6.3, Me); 1.22 (*d*, *J* = 6.3, Me). ^{13}C-NMR (100 MHz): 171.99; 169.48; 169.39; 169.21; 80.94; 68.03; 67.76; 67.62; 64.41; 43.29; 42.02; 40.83; 40.79; 28.05; 22.52; 19.89; 19.81; 19.76. LSI-MS: 837.3 (4, $[2M]^+$), 419.1 (27, M^+), 364.1(21), 363.1(100), 277.0(23), 259.0(15), 191.0(17), 173.0(46), 155.0(43), 154.0(23), 138.0(12), 137.0(31), 136.0(19), 107.0(11), 105.0(15), 86.9(37), 68.9(69), 56.9(51). Anal. calc. for $C_{20}H_{34}O_9$ (418.48): C 57.40, H 8.19; found: C 57.32, H 8.00.

(3S)-3-{{(3′R)-3′-{{(3″R)-3″-{[(3‴R)-3‴-Hydroxybutanoyl]oxy}butanoyl}oxy}butanoyl}oxy}butanoic Acid tert-*Butyl Ester* (**7c**). According to *GP III*, **7d** (7.0 g, 13.76 mmol) was hydrogenated in AcOEt (35 ml) over Pd/C (350 mg): 5.70 g (99%) of **7c**. Colorless oil, very pure by ^{1}H-NMR (200 MHz). A sample (200 mg) was purified for analyses by FC (Et_2O/pentane 1:1). R_f (Et_2O/pentane 1:1, *A*) 0.14. $[\alpha]_D^{r.t.} = -14.9$ ($c = 1.02$, $CHCl_3$). IR (neat): 3529*m*, 2980*s*, 2936*m*, 1737v*s*, 1458*m*, 1382*s*, 1369*s*, 1304*s*, 1259*s*, 1184v*s*, 1136*s*, 1103*s*, 1060*s*, 976*m*, 842*w*, 759*w*. ^{1}H-NMR (400 MHz): 5.35–5.21 (*m*, 3 H); 4.22–4.13 (*m*, H–C(3‴)); 3.20–2.95 (br. *s*, OH); 2.67–2.35 (*m*, 8 H); 1.44 (*s*, *t*-Bu); 1.31 (*d*, $J = 6.3$, Me); 1.29 (*d*, $J = 6.3$, Me); 1.28 (*d*, $J = 6.3$, Me); 1.23 (*d*, $J = 6.3$, Me). ^{13}C-NMR (100 MHz): 172.03; 169.41; 169.37; 169.28; 80.95; 68.02; 67.58; 67.57; 64.41; 43.25; 42.03; 40.90; 40.74; 28.05; 22.53; 19.89; 19.81; 19.76. LSI-MS: 837.3 (3, $[2M]^+$), 441.1 (12), 419.1 (33, M^+), 364.1 (21), 363.1 (100), 277.0 (18), 259.0 (17), 191.0 (15), 173.0 (42), 155.0 (43), 154.0 (21), 138.0 (10), 137.0 (30), 136.0 (18), 107.0 (11), 105.0 (15), 86.9 (36), 68.9 (72), 56.9 (52). Anal. calc. for $C_{20}H_{34}O_9$ (418.48): C 57.40, H 8.19; found: C 57.42, H 7.89.

(3S)-3-{{(3′S)-3′-{{(3″S)-3″-{[(3‴R)-3‴-Hydroxybutanoyl]oxy}butanoyl}oxy}butanoyl}oxy}butanoic Acid tert-*Butyl Ester* (**8c**). According to *GP III*, **8d** (2.0 g, 3.93 mmol) was hydrogenated in AcOEt (10 ml) over Pd/C (100 mg): 1.63 g (99%) of **8c**. Colorless oil, very pure by ^{1}H-NMR (200 MHz). A sample (200 mg) was purified for analyses by FC (Et_2O/pentane 1:1). R_f (Et_2O/pentane 1:1, *A*) 0.14. $[\alpha]_D^{r.t.} = -11.9$ ($c = 1.05$, $CHCl_3$). IR (neat): 3535*w*, 2980*m*, 2935*w*, 1737v*s*, 1458*w*, 1384*m*, 1369*m*, 1306*s*, 1259*s*, 1184*s*, 1142*s*, 1102*s*, 1057*s*, 977*w*, 842*w*. ^{1}H-NMR (400 MHz): 5.35–5.21 (*m*, 3 H); 4.24–4.13 (*m*, H–C(3‴)); 3.25–3.00 (br. *s*, OH); 2.66–2.35 (*m*, 8 H); 1.44 (*s*, *t*-Bu); 1.30 (*d*, $J = 6.3$, Me); 1.28 (*d*, $J = 6.3$, Me); 1.27 (*d*, $J = 6.3$, Me); 1.22 (*d*, $J = 6.3$, Me). ^{13}C-NMR (100 MHz): 171.78; 169.56; 169.36; 169.18; 80.95; 68.03; 67.79; 67.45; 64.19; 43.37; 42.02; 40.85; 40.77; 28.05; 22.39; 19.87; 19.75. LSI-MS: 837.2 ($\ll 1$, $[2M]^+$), 419.1 (15, M^+), 364.0 (15), 363.0 (86), 277.0 (41), 259.0 (38), 191.0 (40), 174.0 (12), 173.0 (100), 156.0 (10), 155.0 (83), 154.0 (32), 137.0 (41), 136.0 (22), 131.0 (18), 106.9 (12), 104.9 (10), 90.9 (13), 88.9 (15), 86.9 (71), 76.9 (13), 68.9 (79), 56.9 (81), 54.8 (14). Anal. calc. for $C_{20}H_{34}O_9$ (418.48): C 57.40, H 8.19; found: C 57.33, H 8.05.

(3R)-3-{{(3′R)-3′-{{(3″R)-3″-{[(3‴R)-3‴-Hydroxybutanoyl]oxy}butanoyl}oxy}butanoyl}oxy}butanoic Acid (**5a**) [18]. According to *GP III*, **5b** (1.0 g, 2.2 mmol) was hydrogenated in AcOEt (10 ml) over Pd/C (50 mg). FC (Et_2O/pentane 5:1 + 2% AcOH) gave 630 mg (79%) of **5a**. Colorless oil that solidified after several days at $< -18°$. R_f (Et_2O/pentane 5:1, *A*) 0.32. M.p. 48.5–49.5° ([18]: m.p. 48.5–49.5°). $[\alpha]_D^{r.t.} = -22.2$ ($c = 1.01$, $CHCl_3$), -20.3 ($c = 0.99$, CH_2CH_2) ([18]: $[\alpha]_D^{r.t.} = -20.3$ ($c = 1.28$, CH_2CH_2)). IR ($CHCl_3$): 2986*m*, 2936*m*, 1735v*s*, 1458*w*, 1448*w*, 1383*m*, 1304*m*, 1264*m*, 1178*s*, 1137*m*, 1102*m*, 1056*m*, 975*w*, 929*w*. ^{1}H-NMR (400 MHz): 7.1–6.3 (br. *s*, OH); 5.34–5.23 (*m*, 3 H); 4.27–4.19 (*m*, H–C(3‴)); 2.68–2.38 (*m*, 8 H); 1.31 (*d*, $J = 6.3$, Me); 1.31 (*d*, $J = 6.4$, Me); 1.28 (*d*, $J = 6.3$, Me); 1.24 (*d*, $J = 6.3$, Me). ^{13}C-NMR (100 MHz): 173.93; 172.10; 169.49; 169.37; 67.84; 67.71; 67.63; 64.62; 43.27; 40.82; 40.71; 40.42; 22.33; 19.79; 19.75; 19.73. LSI-MS: 723.8 (19, $[2M - H]^+$), 362.1 (11, M^+), 181.2 (26), 171.2 (13), 168.1 (18), 153.1 (32), 152.1 (18), 151.1 (36), 103.1 (100). Anal. calc. for $C_{16}H_{26}O_9$: C 53.03, H 7.23; found: C 52.92, H 7.00.

(3R)-3-{{(3′R)-3′-{{(3″S)-3″-{[(3‴S)-3‴-Hydroxybutanoyl]oxy}butanoyl}oxy}butanoyl}oxy}butanoic Acid (*ent*-**6a**). According to *GP II*, with *ent*-**6b** (2.5 g, 4.9 mmol) in CH_2Cl_2 (10 ml) and CF_3COOH (5 ml): 1.78 g (80%) of a slightly yellow viscous oil, very pure by ^{1}H-NMR (200 MHz). According to *GP III*, the crude product was hydrogenated in EtOH (7.5 ml) over Pd/C (100 mg). FC (Et_2O/pentane 5:1 + 2% AcOH) gave 650 mg (46%) of *ent*-**6a**. Colorless oil. R_f (Et_2O/pentane 5:1, *A*) 0.33. $[\alpha]_D^{r.t.} = +13.1$ ($c = 1.00$, $CHCl_3$). IR ($CHCl_3$): 2987*m*, 2935*w*, 1736v*s*, 1449*w*, 1383*m*, 1304*m*, 1264*m*, 1178*s*, 1136*m*, 1102*m*, 1056*m*, 976*w*, 930*w*, 626*w*. ^{1}H-NMR (400 MHz): 6.5–5.6 (br. *s*, OH); 5.34–5.24 (*m*, 3 H); 4.27–4.19 (*m*, H–C(3‴)); 2.70–2.41 (*m*, 8 H); 1.32 (*d*, $J = 6.3$, 2 Me); 1.30 (*d*, $J = 6.4$, Me); 1.25 (*d*, $J = 6.3$, Me). ^{13}C-NMR (100 MHz): 174.04; 172.17; 169.41; 67.83; 67.79; 67.65; 64.57; 43.18; 40.87; 40.76; 40.41; 22.38; 19.81; 19.78. LSI-MS: 723.8 (44, $[2M - H]^+$), 515.6 (14), 514.6 (13), 362.4 (18), 361.4 (85), 306.3 (34), 305.3 (27), 275.3 (12), 256.2 (11), 199.2 (54), 189.2 (35), 171.2 (19), 168.1 (100), 167.1 (15), 166.1 (39), 164.1 (11). Anal. calc. for $C_{16}H_{26}O_9$: C 53.03, H 7.23; found: C 53.07, H 7.09.

(3S)-3-{{(3′S)-3′-{{(3″S)-3″-{[(3‴R)-3‴-Hydroxybutanoyl]oxy}butanoyl}oxy}butanoyl}oxy}butanoic Acid (**8a**). According to *GP II*, with **8b** (1.3 g, 2.57 mmol) in CH_2Cl_2 (1.5 ml) and CF_3COOH (1.5 ml): 1.15 g (99%) of a slightly yellow viscous oil, very pure by ^{1}H-NMR (200 MHz). According to *GP III*, the crude product was hydrogenated in AcOEt (7.5 ml) over Pd/C (75 mg). Precipitation from Et_2O/pentane at 8° gave 800 mg (86%) of **8a**. White powder. R_f (Et_2O/pentane 5:1, *A*) 0.32. $[\alpha]_D^{r.t.} = -5.1$ ($c = 1.00$, $CHCl_3$). M.p. 35–36°. IR ($CHCl_3$): 3512*w*, 3009*m*, 2982*m*, 2937*m*, 1734v*s*, 1449*w*, 1383*s*, 1303*s*, 1262*m*, 1179*s*, 1137*m*, 1103*m*, 1056*s*, 976*w*, 928*w*. ^{1}H-NMR (400 MHz): 6.5–5.5 (br. *s*, OH); 5.34–5.23 (*m*, 3 H); 4.26–4.19 (*m*, H–C(3‴)); 2.68–2.38 (*m*, 8 H), 1.31 (*d*, $J = 6.3$, Me); 1.31 (*d*, $J = 6.3$, Me); 1.28 (*d*, $J = 6.3$, Me); 1.23 (*d*, $J = 6.3$, Me). ^{13}C-NMR (100 MHz): 174.05; 171.83; 169.67; 169.42; 67.92; 67.74; 67.68; 64.44; 43.37; 40.87; 40.76; 40.44; 22.33; 19.85; 19.82; 19.78.

LSI-MS: 725.2 (7, $[2M+H]^+$), 386.1 (10), 385.1 (57, $[M+Na]^+$), 364.1 (17), 363.1 (91), 277.1 (21), 259.1 (14), 191.1 (19), 173.1 (52), 155.1 (50), 154.0 (36), 138.0 (18), 137.0 (46), 136.0 (32), 131.0 (11), 107.0 (19), 105.0 (23), 95.0 (11), 91.0 (17), 87.9 (16), 86.9 (53), 80.9 (11), 76.9 (19), 68.9 (100), 56.9 (17), 54.9 (21). Anal. calc. for $C_{16}H_{26}O_9$: C 53.03, H 7.23; found: C 53.02, H 7.06.

10. *Octamers* **10**–**18** *and* ent-**14**. *(*R,R,R,R,R,R,R,R*)-α-Benzyl-ω-(*tert-*butoxy)octakis[oxy(1-methyl-3-oxopropane-1,3-diyl)]* (**10d**) [18]. According to *GP I*, with **5b** (1.85 mg, 4.09 mmol) in CH_2Cl_2 (5 ml) and **5c** (1.75 g, 4.18 mmol) in CH_2Cl_2 (5 ml): 3.72 g of crude, almost white solid, very pure by ^{1}H-NMR (200 MHz). FC (Et_2O/pentane 1:1) gave 3.27 g (74%) of **10d**. White solid. R_f (Et_2O/pentane 1:1, *B*) 0.14. M.p. 89.5–90.5° ([18]: m.p. 91–92°). $[\alpha]_D^{r.t.} = -12.4$ ($c = 1.04$, MeOH), $[\alpha]_{365}^{r.t.} = -28.2$ ($c = 1.04$, MeOH), $[\alpha]_D^{r.t.} = -6.0$ ($c = 1.05$, $CHCl_3$) ([18]: $[\alpha]_D^{r.t.} = -6.7$ ($c = 1.18$, CH_2Cl_2), $[\alpha]_{365}^{r.t.} = -13.8$ ($c = 0.83$, MeOH)). IR ($CHCl_3$): 2984*m*, 2936*w*, 1737v*s*, 1457*w*, 1382*s*, 1371*m*, 1307*s*, 1260*m*, 1178*s*, 1135*s*, 1101*s*, 1058*s*, 977*w*, 841*w*. ^{1}H-NMR (400 MHz): 7.34–7.23 (*m*, 5 arom. H); 5.30–5.20 (*m*, 7 H); 4.53, 4.48 (*AB*, $J_{AB} = 11.6$, PhCH_2O); 4.02–3.94 (*m*, 1 H); 2.67–2.37 (*m*, 16 H); 1.44 (*s*, *t*-Bu); 1.28–1.23 (*m*, 24 H). ^{13}C-NMR (100 MHz): 170.40; 169.37; 169.23; 169.11; 138.53; 128.34; 127.60; 127.51; 80.87; 71.98; 70.81; 67.96; 67.66; 67.60; 67.40; 42.17; 42.03; 40.85; 40.78; 28.01; 19.85; 19.80; 19.76. LSI-MS: 851.7 (13, $[M-1]^+$), 799.2 (15), 798.7 (26), 797.6 (100), 711.6 (11), 259.2 (10), 241.2 (12), 173.1 (18), 156.1 (10), 155.1 (72), 154.0 (19), 137.1 (18), 136.1 (15), 107.0 (13).

*(*R,R,R,R,R,R,R,S*)-α-Benzyl-ω-(*tert-*butoxy)octakis[oxy(1-methyl-3-oxopropane-1,3-diyl)]* (**11d**). According to *GP I*, with **5b** (700 mg, 1.67 mmol) in CH_2Cl_2 (1 ml) and **7c** (800 mg, 1.77 mmol) in CH_2Cl_2 (3 ml): 1.39 g of yellow oil. FC (Et_2O/pentane 1:1) gave 883 mg (62%) of **11d**. White solid. R_f (Et_2O/pentane 1:1, *B*) 0.14. M.p. 37.5–39.5°. $[\alpha]_D^{r.t.} = -11.6$ ($c = 1.01$, MeOH). IR ($CHCl_3$): 2983*w*, 2937*w*, 1736v*s*, 1457*w*, 1383*m*, 1370*m*, 1306*s*, 1262*m*, 1179*s*, 1136*m*, 1101*m*, 1059*s*, 977*w*. ^{1}H-NMR (500 MHz): 7.34–7.24 (*m*, 5 arom. H); 5.30–5.22 (*m*, 7 H); 4.56, 4.50 (*AB*, $J_{AB} = 11.5$, PhCH_2O); 4.01–3.96 (*m*, 1 H); 2.65–2.38 (*m*, 16 H); 1.43 (*s*, *t*-Bu); 1.30–1.21 (*m*, 24 H). ^{13}C-NMR (125 MHz): 170.56; 169.32; 169.24; 169.15; 169.14; 138.54; 128.33; 127.63; 127.52; 80.91; 71.94; 70.81; 67.96; 67.71; 67.63; 67.62; 67.60; 67.57; 67.35; 42.12; 42.02; 40.90; 40.86; 40.81; 40.72; 28.05; 19.85; 19.81; 19.77. LSI-MS: 852.5 (3, M^+), 798.4 (30), 797.4 (75), 431.2 (12), 345.1 (16), 259.1 (14), 241.1 (18), 173.1 (20), 156.1 (10), 155.1 (87), 154.1 (20), 137.1 (16), 136.0 (17), 107.0 (20), 105.0 (13), 92.0 (12), 91.0 (100), 90.0 (11), 89.0 (20), 86.9 (17), 78.9 (13), 77.9 (13), 76.9 (30), 68.9 (94), 64.9 (13), 62.9 (13), 56.9 (92), 54.9 (12). Anal. calc. for $C_{43}H_{64}O_{17}$ (852.97): C 60.55, H 7.56; found: C 60.58, H 7.40.

*(*R,R,R,R,R,R,S,S*)-α-Benzyl-ω-(*tert-*butoxy)octakis[oxy(1-methyl-3-oxopropane-1,3-diyl)]* (**12d**). According to *GP I*, with **5b** (1.1 g, 2.43 mmol) in CH_2Cl_2 (2 ml) and **6c** (1.0 g, 1.77 mmol) in CH_2Cl_2 (9 ml): 2.23 g of a yellow-brown oil. FC (Et_2O/pentane 1:1) gave 1.69 g (83%) of **12d**. Colorless viscous oil. R_f (Et_2O/pentane 1:1, *B*) 0.14. $[\alpha]_D^{r.t.} = -10.0$ ($c = 0.98$, MeOH). IR (neat): 2981*m*, 2936*w*, 1738v*s*, 1455*w*, 1382*s*, 1370*m*, 1304*s*, 1260*s*, 1186v*s*, 1136*s*, 1102*s*, 1059*s*, 977*w*, 738*w*, 699*w*. ^{1}H-NMR (400 MHz): 7.35–7.24 (*m*, 5 arom. H); 5.31–5.21 (*m*, 7 H); 4.56, 4.50 (*AB*, $J_{AB} = 11.5$, PhCH_2O); 4.01–3.95 (*m*, 1 H); 2.65–2.37 (*m*, 16 H); 1.44 (*s*, *t*-Bu); 1.30–1.22 (*m*, 24 H). ^{13}C-NMR (100 MHz): 170.55; 169.35; 169.26; 169.156; 138.33; 127.63; 127.53; 80.93; 71.94; 70.81; 67.99; 67.70; 67.62; 67.58; 67.36; 42.12; 42.01; 40.90; 40.86; 40.82; 40.69; 28.05; 19.85; 19.81; 19.76. LSI-MS: 851.3 (2, $[M-1]^+$), 797.3 (15), 173.1 (17), 155.1 (70), 107.0 (11), 91.0 (79), 86.9 (19), 68.9 (100), 56.9 (53). Anal. calc. for $C_{43}H_{64}O_{17}$ (852.97): C 60.55, H 7.56; found: C 60.48, H 7.83.

*(*R,R,R,R,R,S,S,S*)-α-Benzyl-ω-(*tert-*butoxy)octakis[oxy(1-methyl-3-oxopropane-1,3-diyl)]* (**13d**). According to *GP I*, with **5b** (1.1 g, 2.43 mmol) CH_2Cl_2 (2 ml) and **8c** (1.0 g, 2.39 mmol) in CH_2Cl_2 (9 ml): 2.16 g of brown-yellow oil. FC (Et_2O/pentane 1:1) gave 1.73 g (85%) of **13d**. Colorless viscous oil. R_f (Et_2O/pentane 1:1, *B*) 0.14. $[\alpha]_D^{r.t.} = -8.6$ ($c = 0.97$, MeOH). IR (neat): 3453*w*, 2982*s*, 2935*m*, 2878*w*, 1736v*s*, 1497*w*, 1455*m*, 1382*s*, 1370*s*, 1306*s*, 1262*s*, 1184v*s*, 1136*s*, 1100*s*, 1058*s*, 976*s*, 928*m*, 844*w*, 740*w*, 699*w*. ^{1}H-NMR (400 MHz): 7.35–7.23 (*m*, 5 arom. H); 5.31–5.21 (*m*, 7 H); 4.56, 4.50 (*AB*, $J_{AB} = 11.5$, PhCH_2O); 4.03–3.95 (*m*, 1 H); 2.65–2.37 (*m*, 16 H); 1.44 (*s*, *t*-Bu); 1.29–1.24 (*m*, 24 H). ^{13}C-NMR (100 MHz): 170.50; 169.33; 169.25; 169.15; 138.55; 128.33; 127.62; 127.51; 80.90; 71.94; 70.81; 67.98; 67.68; 67.62; 67.58; 67.34; 42.12; 42.00; 40.90; 40.87; 40.82; 40.67; 28.04; 19.85; 19.83; 19.81; 19.76. LSI-MS: 851.0 (2, $[M-1]^+$), 173.1 (14), 155.1 (56), 90.9 (73), 86.9 (17), 68.9 (100), 56.9 (41). Anal. calc. for $C_{43}H_{64}O_{17}$ (852.97): C 60.55, H 7.28; found: C 60.59, H 7.86.

*(*R,R,R,R,S,S,S,S*)-α-Benzyl-ω-(*tert-*butoxy)octakis[oxy(1-methyl-3-oxopropane-1,3-diyl)]* (**14d**). According to *GP I*, with **5b** (1.1 g, 2.43 mmol) in CH_2Cl_2 (2 ml) and **7c** (1.0 g, 2.39 mmol) in CH_2Cl_2 (9 ml): 2.15 g of brown-yellow oil. FC (Et_2O/pentane 1:1) gave 1.64 g (80%) of **14d**. Colorless viscous oil. R_f (Et_2O/pentane 1:1, *B*) 0.14. $[\alpha]_D^{r.t.} = -7.0$ ($c = 1.04$, MeOH). IR (neat): 3449*w*, 2980*s*, 2935*s*, 2878*m*, 1734v*s*, 1497*w*, 1454*s*, 1381*s*, 1370*s*, 1302*s*, 1258*s*, 1182v*s*, 1136*s*, 1100*s*, 1057*s*, 976*s*, 928*m*, 843*w*, 737*m*, 699*w*. ^{1}H-NMR (400 MHz): 7.35–7.23 (*m*, 5 arom. H); 5.30–5.20 (*m*, 7 H); 4.56, 4.50 (*AB*, $J_{AB} = 11.5$, PhCH_2O); 4.03–3.95 (*m*, 1 H); 2.65–2.37 (*m*, 16 H); 1.44 (*s*, *t*-Bu); 1.28–1.25 (*m*, 24 H). ^{13}C-NMR (100 MHz): 170.52; 169.35; 169.28; 169.24; 169.17; 138.54; 128.33; 127.63; 127.53; 80.92; 71.95; 70.81; 67.99; 67.65; 67.62; 67.59; 67.38; 42.14; 42.00; 40.96; 40.86;

40.81; 40.67; 28.05; 19.84; 19.82; 19.76. LSI-MS: 851.0 (2, $[M-1]^+$), 797.0(13), 240.1(12), 172.9(18), 154.9(64), 153.9(12), 136.9(12), 135.9(11), 106.9(13), 90.9(71), 86.8(23), 68.8(100), 56.8(34). Anal. calc. for $C_{43}H_{64}O_{17}$ (852.97): C 60.55, H 7.56; found: C 60.25, H 7.75.

*(*S,R,R,R,R,R,R,R*)-α-Benzyl-ω-(*tert-*butoxy)octakis[oxy(1-methyl-3-oxopropane-1,3-diyl)]* (**17d**). According to *GP I*, with *ent*-**8b** (1.1 g, 2.43 mmol) in CH_2Cl_2 (3 ml) and **5c** (1.0 g, 2.39 mmol) in CH_2Cl_2 (5.5 ml): FC (Et_2O/pentane 1:1) gave 1.43 g (70%) of **17d**. White solid. R_f (Et_2O/pentane 1:1, *B*) 0.14. M.p. 82–84°. $[\alpha]_D^{rt.} = -0.4$ ($c = 1.01$, MeOH). IR ($CHCl_3$): 3010*w*, 2984*m*, 2936*w*, 1738v*s*, 1458*w*, 1382*s*, 1369*m*, 1305*s*, 1261*m*, 1179*s*, 1136*s*, 1101*s*, 1059*s*, 978*w*. ^{1}H-NMR (400 MHz): 7.34–7.23 (*m*, 5 arom. H); 5.35–5.21 (*m*, 7 H); 4.56, 4.50 (*AB*, $J_{AB} = 11.5$, PhCH_2O); 4.01–3.97 (*m*, 1 H); 2.64–2.36 (*m*, 16 H); 1.44 (*s*, *t*-Bu); 1.32–1.22 (*m*, 24 H). ^{13}C-NMR (100 MHz): 170.66; 169.33; 169.26; 169.14; 138.55; 128.32; 127.65; 127.52; 80.90; 72.12; 70.91; 67.98; 67.61; 67.56; 67.31; 42.13; 42.00; 40.86; 40.82; 28.04; 19.87; 19.83; 19.77. LSI-MS: 852.4 (2, M^+), 798.3(10), 797.3(24), 173.1(17), 155.1(65), 154.1(17), 137.0(17), 136.0(15), 107.0(13), 91.0(76), 86.9(21), 68.9(100), 56.9(38), 54.9(10). Anal. calc. for $C_{43}H_{64}O_{17}$ (852.97): C 60.55, H 7.56; found: C 60.75, H 7.69.

*(*S,S,R,R,R,R,R,R*)-α-Benzyl-ω-(*tert-*butoxy)octakis[oxy(1-methyl-3-oxopropane-1,3-diyl)]* (**16d**). According to *GP I*, with *ent*-**6b** (1.1 g, 2.43 mmol) in CH_2Cl_2 (2 ml) and **5c** (1.0 g, 2.39 mmol) in CH_2Cl_2 (9 ml): 2.05 g of brown-yellow oil. FC (Et_2O/pentane 1:1) gave 550 mg (27%) of **16d**. White solid. R_f (Et_2O/pentane 1:1, *B*) 0.14. M.p. 56–62°. $[\alpha]_D^{rt.} = +2.7$ ($c = 1.02$, MeOH). IR ($CHCl_3$): 2982*m*, 2936*w*, 1734v*s*, 1457*w*, 1382*s*, 1370*m*, 1305*s*, 1261*m*, 1179*s*, 1135*s*, 1101*s*, 1057*s*, 978*w*, 909*w*. ^{1}H-NMR (400 MHz): 7.35–7.23 (*m*, 5 arom. H); 5.30–5.21 (*m*, 7 H); 4.55, 4.50 (*AB*, $J_{AB} = 11.6$, PhCH_2O); 4.01–3.94 (*m*, 1 H); 2.66–2.37 (*m*, 16 H); 1.44 (*s*, *t*-Bu); 1.28–1.25 (*m*, 24 H). ^{13}C-NMR (100 MHz): 170.52; 169.35; 169.33; 169.15; 138.53; 128.33; 127.63; 127.52; 80.91; 71.98; 70.82; 67.98; 67.61; 67.55; 67.42; 42.15; 42.00; 40.86; 40.81; 28.04; 19.86; 19.81; 19.77. LSI-MS: 851.3 (< 1, $[M-1]^+$), 281.0(12), 259.1(11), 241.1(15), 207.0(14), 173.1(25), 156.1(14), 155.1(73), 154.0(30), 147.1(32), 138.0(14), 137.0(28), 136.0(48), 133.0(12), 131.0(11), 120.0(14), 119.0(11), 107.0(29), 106.0(12), 105.0(20), 95.0(15), 92.0(17), 91.0(83), 89.9(24), 89.9(19), 86.9(31), 85.0(11), 83.0(12), 80,9(15), 78.9(15), 77.9(12), 76.9(25), 74.9(11), 72.9(74), 69.9(11), 68.9(100), 66.9(15), 64.9(11), 62.9(13), 56.9(68), 54.9(28). Anal. calc. for $C_{43}H_{64}O_{17}$ (852.97): C 60.55, H 7.56; found: C 60.34, H 7.49.

*(*S,S,S,R,R,R,R,R*)-α-Benzyl-ω-(*tert-*butoxy)octakis[oxy(1-methyl-3-oxopropane-1,3-diyl)]* (**15d**). According to *GP I*, with *ent*-**7b** (1.1 g, 2.43 mmol) in CH_2Cl_2 (2 ml) and **5c** (1.0 g, 2.39 mmol) in CH_2Cl_2 (9 ml): 2.17 g of brown-yellow oil that solidified at −18°. FC (Et_2O/pentane 1:1) gave 1.88 g (92%) of **15d**. Colorless oil that solidified at −18°. R_f (Et_2O/pentane 1:1, *B*) 0.14. $[\alpha]_D^{rt.} = +5.7$ ($c = 0.99$, MeOH). IR (neat): 2982*s*, 2935*m*, 1738v*s*, 1455*m*, 1383*s*, 1369*s*, 1305*s*, 1260*s*, 1186v*s*, 1137*s*, 1101*s*, 1059*s*, 978*m*, 928*w*, 845*w*, 738*w*, 699*w*. ^{1}H-NMR (400 MHz): 7.35–7.23 (*m*, 5 arom. H); 5.30–5.20 (*m*, 7 H); 4.56, 4.50 (*AB*, $J_{AB} = 11.5$, PhCH_2O); 4.01–3.95 (*m*, 1 H); 2.65–2.37 (*m*, 16 H); 1.44 (*s*, *t*-Bu); 1.28–1.25 (*m*, 24 H). ^{13}C-NMR (100 MHz): 170.52; 169.34; 169.28; 169.24; 169.17; 138.54; 128.33; 127.63; 127.53; 80.92; 71.95; 70.81; 67.99; 67.65; 67.62; 67.59; 67.38; 42.14; 42.00; 40.96; 40.86; 40.81; 40.67; 28.05; 19.84; 19.82; 19.76. LSI-MS: 851.3 (2, $[M-1]^+$), 797.3(15), 259.1(12), 241.1(15), 173.1(24), 156.0(12), 155.0(81), 154.0(12), 137.0(13), 136.0(10), 107.0(15), 91.9(13), 90.9(86), 86.9(30), 76.9(11), 68.8(100), 56.9(44). Anal. calc. for $C_{43}H_{64}O_{17}$ (852.97): C 60.55, H 7.56; found: C 60.35, H 7.86.

*(*S,S,S,S,R,R,R,R*)-α-Benzyl-ω-(*tert-*butoxy)octakis[oxy(1-methyl-3-oxopropane-1,3-diyl)]* (*ent*-**14d**). According to *GP I*, with *ent*-**5b** (1.0 g, 2.21 mmol) in CH_2Cl_2 (2 ml) and **5c** (900 mg, 2.15 mmol) in CH_2Cl_2 (9 ml): 1.92 g of brown-yellow oil. FC (Et_2O/pentane 1:1) gave 1.47 g (80%) of *ent*-**14d**. Colorless viscous oil. R_f (Et_2O/pentane 1:1, *B*) 0.14. $[\alpha]_D^{rt.} = +6.0$ ($c = 1.04$, MeOH). IR (neat): 2980*m*, 2935*w*, 1740v*s*, 1454*w*, 1383*m*, 1370*m*, 1305*s*, 1261*s*, 1186v*s*, 1136*s*, 1101*s*, 1058*s*, 976*w*, 929*w*, 844*w*, 737*w*, 698*w*. ^{1}H-NMR (400 MHz): 7.35–7.23 (*m*, 5 arom. H); 5.30–5.20 (*m*, 7 H); 4.56, 4.50 (*AB*, $J_{AB} = 11.5$, PhCH_2O); 4.03–3.95 (*m*, 1 H); 2.65–2.37 (*m*, 16 H); 1.44 (*s*, *t*-Bu); 1.28–1.25 (*m*, 24 H). ^{13}C-NMR (100 MHz): 170.52; 169.35; 169.28; 169.24; 169.17; 138.54; 128.33; 127.63; 127.53; 80.92; 71.95; 70.81; 67.99; 67.65; 67.62; 67.59; 67.38; 42.14; 42.00; 40.96; 40.86; 40.81; 40.67; 28.05; 19.84; 19.82; 19.76. LSI-MS: 851.3 (1, $[M-1]^+$), 259.1(10), 242.1(13), 173.1(21), 155.1(76), 107.0(14), 92.0(11), 91.0(83), 86.9(28), 68.9(100), 56.9(47). Anal. calc. for $C_{43}H_{64}O_{17}$ (852.97): C 60.55, H 7.56; found: C 60.35, H 7.66.

*(*R,R,R,R,R,R,R,R*)-α-Hydro-ω-hydroxyoctakis[oxy(1-methyl-3-oxopropane-1,3-diyl)]* (**10a**). According to *GP II*, with **10d** (250 mg, 0.29 mmol) in CF_3COOH (700 µl) and CH_2Cl_2 (2 ml). According to *GP III*, the crude product was hydrogenated in AcOEt (2 ml) over Pd/C (20 mg). Precipitation from CH_2Cl_2/hexane at −18° yielded 160 mg (77%) of **10a**. White powder. R_f (Et_2O/pentane 5:1, *A*) 0.17. M.p. 100–101° ([18]: m.p. 100–101°). $[\alpha]_D^{rt.} = -10.8$ ($c = 1.04$, $CHCl_3$) ([18]: $[\alpha]_D^{rt.} = -11.7$ ($c = 1.14$, CH_2Cl_2)). IR ($CHCl_3$): 2984*m*, 2936*w*, 1737v*s*, 1458*w*, 1448*w*, 1383*m*, 1305*m*, 1263*m*, 1178*s*, 1136*m*, 1102*m*, 1057*s*, 978*w*, 930*w*. ^{1}H-NMR (500 MHz): 5.34–5.20 (*m*, 7 H); 4.24–4.17 (*m*, 1 H); 2.66–2.39 (*m*, 16 H); 1.31–1.22 (*m*, 24 H). ^{13}C-NMR

(125 MHz): 173.01; 172.04; 169.63; 169.55; 169.40; 169.39; 169.38; 169.19; 68.00; 67.81; 67.76; 67.73; 67.62; 64.52; 43.21; 40.88; 40.82; 40.81; 40.46; 40.29; 22.47; 19.90; 19.88; 19.77; 19.69; 19.39. LSI-MS: 1414.0 (3, $[2M]^+$), 729.3 (48, $[M+Na]^+$), 707.4 (100, $[M+H]^+$), 345.2(11), 307.1(15), 259.2(14), 241.2(13), 173.1(24), 155.1(71), 154.1(55), 139.1(20), 138.1(32), 137.1(52), 136.1(45), 107.0(24).

*(*R,R,R,R,R,R,R,S*)-α-Hydro-ω-hydroxyoctakis[oxy(1-methyl-3-oxopropane-1,3-diyl)]* (**11a**). According to *GP II*, with **11d** (320 mg, 0.38 mmol) in CF_3COOH (1 ml) and CH_2Cl_2 (3 ml). According to *GP III*, the crude product was hydrogenated in EtOH (2 ml) over Pd/C (30 mg). FC (Et_2O/pentane 5:1 + 2% AcOH) gave 200 mg (75%) of **11a**. White solid. R_f (Et_2O/pentane 5:1, *A*) 0.17. $[\alpha]_D^{rt.} = -5.4$ ($c = 1.07$, $CHCl_3$). IR ($CHCl_3$): 3632*w* (br.), 3032*w*, 2986*m*, 2937*w*, 1737v*s*, 1458*w*, 1448*w*, 1383*m*, 1305*s*, 1265*m*, 1178*s*, 1135*m*, 1102*m*, 1058*s*, 977*w*, 642*w*. ^{1}H-NMR (500 MHz): 5.34–5.23 (*m*, 7 H); 4.23–4.17 (*m*, 1 H); 2.69–2.40 (*m*, 16 H); 1.31–1.22 (*m*, 24 H). ^{13}C-NMR (125 MHz): 173.15; 172.03; 169.65; 169.53; 169.43; 169.35; 169.34; 169.21; 67.86; 67.81; 67.76; 67.71; 67.68; 67.62; 64.51; 43.21; 41.08; 40.86; 40.82; 40.80; 40.69; 40.21; 22.47; 19.88; 19.83; 19.81; 19.77. LSI-MS: 745.3(13), 729.3(40), 708.6 (16, M^+), 707.3(100), 431.2(13), 345.1(23), 307.1(21), 289.1(13), 259.1(26), 241.1(24), 173.1(50). Anal. calc. for $C_{32}H_{50}O_{17}$ (706.74): C 54.38, H 7.13; found: C 54.30, H 7.10.

*(*R,R,R,R,R,R,S,S*)-α-Hydro-ω-hydroxyoctakis[oxy(1-methyl-3-oxopropane-1,3-diyl)]* (**12a**). According to *GP II*, with **12d** (1.33 g, 1.85 mmol) in CF_3COOH (5 ml) and CH_2Cl_2 (10 ml). According to *GP III*, the crude product was hydrogenated in EtOH (8 ml) over Pd/C (100 mg). FC (Et_2O/pentane 5:1 + 2% AcOH) gave 760 mg (69%) of **12a**. Colorless oil. R_f (Et_2O/pentane 5:1, *A*) 0.17. $[\alpha]_D^{rt.} = -6.9$ ($c = 1.01$, $CHCl_3$). IR ($CHCl_3$): 3688*w* (br.), 3032*w*, 2986*m*, 2936*w*, 1737v*s*, 1458*w*, 1448*w*, 1383*m*, 1305*s*, 1266*m*, 1178*s*, 1136*m*, 1102*m*, 1058*s*, 978*w*, 929*w*. ^{1}H-NMR (500 MHz): 5.34–5.20 (*m*, 7 H); 4.23–4.17 (*m*, 1 H); 2.67–2.40 (*m*, 16 H); 1.31–1.22 (*m*, 24 H). ^{13}C-NMR (125 MHz): 173.25; 172.03; 169.57; 169.54; 169.45; 169.39; 169.36; 169.23; 67.89; 67.81; 67.79; 67.72; 67.66; 67.62; 64.52; 43.24; 43.21; 40.93; 40.91; 40.85; 40.82; 40.80; 40.34; 22.46; 19.88; 19.85; 19.84; 19.79; 19.77; 19.74. LSI-MS: 730.5(13), 729.3(60), 708.5 (23, M^+), 707.3(100), 431.2(15), 363.1(13), 345.1(28), 307.1(17), 289.1(12), 277.1(10), 259.1(34), 241.1(33), 191.1(13), 173.1(65), 171.1(10), 166.1(10). Anal. calc. for $C_{32}H_{50}O_{17}$ (706.74): C 54.38, H 7.13; found: C 54.10, H 6.92.

*(*R,R,R,R,R,S,S,S*)-α-Hydro-ω-hydroxyoctakis[oxy(1-methyl-3-oxopropane-1,3-diyl)]* (**13a**). According to *GP II*, with **13d** (1.58 g, 1.85 mmol) in CF_3COOH (5 ml) and CH_2Cl_2 (10 ml). According to *GP III*, the crude product was hydrogenated in EtOH (10 ml) over Pd/C (120 mg). FC (Et_2O/pentane 5:1 + 2% AcOH) gave 1.01 g (77%) of **13a**. Faintly yellow viscous oil. R_f (Et_2O/pentane 5:1, *A*) 0.17. $[\alpha]_D^{rt.} = -5.3$ ($c = 1.02$, $CHCl_3$). IR ($CHCl_3$): 3520*w* (br.), 2985*m*, 2936*w*, 1737v*s*, 1458*w*, 1448*w*, 1383*m*, 1305*s*, 1264*m*, 1178*s*, 1136*m*, 1102*m*, 1057*s*, 978*w*, 928*w*, 909*w*, 824*w*. ^{1}H-NMR (500 MHz): 5.34–5.20 (*m*, 7 H); 4.23–4.17 (*m*, 1 H); 2.67–2.40 (*m*, 16 H); 1.31–1.22 (*m*, 24 H). ^{13}C-NMR (125 MHz): 173.12; 172.03; 169.65; 169.53; 169.42; 169.38; 169.35; 169.17; 67.94; 67.80; 67.77; 67.76; 67.72; 67.65; 67.61; 64.52; 43.19; 40.86; 40.84; 40.82; 40.81; 40.74; 40.40; 22.45; 19.88; 19.78; 19.76; 19.74. LSI-MS: 729.2(24), 707.2(41), 345.1(11), 307.0(23), 259.0(15), 241.0(14), 173.0(24), 165.1(11), 156.0(17), 155.0(100), 154.0(95), 153.0(11), 152.0(13), 149.1(10), 139.0(28), 138.0(46), 137.0(87), 136.0(70), 135.0(19), 131.0(11), 124.0(17), 123.1(29), 121.0(23), 120.0(17), 119.0(18), 111.1(21), 109.0(36), 107.0(40), 105.0(25). Anal. calc. for $C_{32}H_{50}O_{17}$ (706.74): C 54.38, H 7.13; found: C 54.24, H 6.88.

*(*R,R,R,R,S,S,S,S*)-α-Hydro-ω-hydroxyoctakis[oxy(1-methyl-3-oxopropane-1,3-diyl)]* (**14a**). According to *GP II*, with **14d** (1.57 g, 1.84 mmol) in CF_3COOH (5 ml) and CH_2Cl_2 (10 ml). According to *GP III*, the crude product was hydrogenated in EtOH (10 ml) over Pd/C (120 mg). FC (Et_2O/pentane 5:1 + 2% AcOH) gave 1.01 g (78%) of **14a**. Faintly yellow and excessively viscous oil that eventually solidified after months at −18°. R_f (Et_2O/pentane 5:1, *A*) 0.17. M.p. 48–51°. $[\alpha]_D^{rt.} = -5.6$ ($c = 1.00$, $CHCl_3$). IR ($CHCl_3$): 3528*w* (br.), 3032*w*, 2986*m*, 2936*w*, 1737v*s*, 1458*w*, 1448*w*, 1383*m*, 1305*s*, 1265*m*, 1178*s*, 1136*m*, 1102*m*, 1057*s*, 978*w*, 909*w*. ^{1}H-NMR (500 MHz): 5.34–5.20 (*m*, 7 H); 4.23–4.17 (*m*, 1 H); 2.67–2.39 (*m*, 16 H); 1.31–1.22 (*m*, 24 H). ^{13}C-NMR (125 MHz): 173.16; 172.03; 169.58; 169.54; 169.46; 169.36; 169.35; 169.18; 67.95; 67.82; 67.78; 67.74; 67.67; 67.61; 64.52; 43.20; 40.86; 40.82; 40.71; 40.42; 22.45; 19.88; 19.83; 19.76; 19.70. LSI-MS: 730.6(20), 729.3(100), 708.6 (23, M^+), 707.4(91), 621.3(11), 431.2(11), 345.1(12), 307.1(13), 259.1(13), 241.1(13), 173.1(22), 156.1(15), 155.1(86), 154.1(68), 147.1(16), 139.1(22), 138.1(34), 137.1(66), 136.0(61), 135.1(18), 123.1(31), 121.1(23), 120.0(18), 119.0(21), 111.1(23), 109.1(40), 107.0(38), 105.0(30). Anal. calc. for $C_{32}H_{50}O_{17}$ (706.74): C 54.38, H 7.13; found: C 54.24, H 7.04.

*(*S,R,R,R,R,R,R,R*)-α-Hydro-ω-hydroxyoctakis[oxy(1-methyl-3-oxopropane-1,3-diyl)]* (**17a**). According to *GP II*, with **17d** (1.21 g, 1.42 mmol) in CF_3COOH (5 ml) and CH_2Cl_2 (10 ml). According to *GP III*, the crude product was hydrogenated in EtOH (8 ml) over Pd/C (100 mg). FC (Et_2O/pentane 5:1 + 2% AcOH) gave 720 mg (72%) of **17a**. White solid. R_f (Et_2O/pentane 5:1, *A*) 0.17. M.p. 89–92°. $[\alpha]_D^{rt.} = +1.6$ ($c = 1.03$, $CHCl_3$). IR ($CHCl_3$): 2986*m*, 2936*w*, 1737v*s*, 1458*w*, 1448*w*, 1383*m*, 1305*m*, 1264*m*, 1178*s*, 1135*m*, 1102*m*, 1058*s*,

978*w*, 930*w*, 830*w*, 626*w*. ^{1}H-NMR (500 MHz): 5.45–5.21 (*m*, 7 H); 4.26–4.18 (*m*, 1 H); 2.67–2.38 (*m*, 16 H); 1.32–1.21 (*m*, 24 H). ^{13}C-NMR (125 MHz): 173.27; 171.75; 169.65; 169.56; 169.35; 169.33; 169.18; 67.95; 67.82; 67.75; 67.72; 67.66; 67.53; 64.33; 43.32; 40.87; 40.82; 40.79; 40.76; 40.40; 22.33; 19.88; 19.86; 19.81; 19.78; 19.76; 19.70. LSI-MS: 1413.8 (3, $[2M]^+$), 729.3 (38), 708.6 (18, M^+), 707.3 (100), 431.2 (14), 363.1 (11), 345.1 (26), 307.1 (24), 289.1 (15), 259.1 (30), 241.1 (26), 191.1 (11), 173.1 (60), 166.1 (12). Anal. calc. for $C_{32}H_{50}O_{17}$ (706.74): C 54.38, H 7.13; found: C 54.37, H 7.03.

*(*S,S,R,R,R,R,R,R*)-α-Hydro-ω-hydroxyoctakis[oxy(1-methyl-3-oxopropane-1,3-diyl)]* (**16a**). According to *GP II*, with **16d** (500 mg, 0.59 mmol) in CF_3COOH (1.5 ml) and CH_2Cl_2 (3.5 ml). According to *GP III*, the crude product was hydrogenated in EtOH (4 ml) over Pd/C (60 mg). FC (Et_2O/pentane 5 : 1 + 2% AcOH) gave 290 mg (70%) of **16a**. White solid. R_f (Et_2O/pentane 5 : 1, *A*) 0.17. M.p. 63–70°. $[\alpha]_D^{r.t.} = +5.1$ ($c = 1.04$, $CHCl_3$). IR ($CHCl_3$): 2984*m*, 2936*w*, 1737v*s*, 1459*w*, 1449*w*, 1383*m*, 1305*s*, 1263*m*, 1178*s*, 1136*m*, 1102*m*, 1057*s*, 977*w*, 928*w*, 823*w*. ^{1}H-NMR (500 MHz): 5.34–5.20 (*m*, 7 H); 4.26–4.18 (*m*, 1 H); 2.67–2.38 (*m*, 16 H); 1.31–1.22 (*m*, 24 H). ^{13}C-NMR (125 MHz): 172.94; 172.03; 169,62; 169,57; 169,41; 169,37; 169,17; 67.99; 67.78; 67.76; 67.73; 67.68; 64.54; 43.24; 40.88; 40.81; 40.75; 40.41; 22.45; 19.90; 19.88; 19.82; 19.77; 19.69. LSI-MS: 1413.9 (2, $[2M]^+$), 730.5 (10), 729.3 (48), 708.5 (24, M^+), 707.3 (100), 431.2 (14), 345.1 (28), 307.1 (29), 289.1 (18), 259.1 (30), 241.1 (29), 191.1 (12), 176.1 (10), 173.1 (57), 166.1 (13), 165.1 (11). Anal. calc. for $C_{32}H_{50}O_{17}$ (706.74): C 54.38, H 7.13; found: C 54.38, H 6.96.

*(*S,S,S,R,R,R,R,R*)-α-Hydro-ω-hydroxyoctakis[oxy(1-methyl-3-oxopropane-1,3-diyl)]* (**15a**). According to *GP II*, with **15d** (1.66 g, 1.95 mmol) in CF_3COOH (5 ml) and CH_2Cl_2 (10 ml). According to *GP III*, the crude product was hydrogenated in EtOH (10 ml) over Pd/C (120 mg). FC (Et_2O/pentane 5 : 1 + 2% AcOH) gave 970 mg (70%) of **15a**. White solid. R_f (Et_2O/pentane 5 : 1, *A*) 0.17. M.p. 62–68°. $[\alpha]_D^{r.t.} = +5.3$ ($c = 1.05$, $CHCl_3$). IR ($CHCl_3$): 2984*m*, 2936*w*, 1737v*s*, 1459*w*, 1449*w*, 1383*m*, 1305*s*, 1264*m*, 1178*s*, 1135*m*, 1103*m*, 1057*s*, 978*w*, 931*w*, 828*w*. ^{1}H-NMR (500 MHz): 5.34–5.20 (*m*, 7 H); 4.26–4.18 (*m*, 1 H); 2.67–2.38 (*m*, 16 H); 1.31–1.22 (*m*, 24 H). ^{13}C-NMR (125 MHz): 172.94; 172.03; 169.62; 169.57; 169.41; 169.37; 169.17; 67.99; 67.78; 67.76; 67.73; 67.68; 64.54; 43.24; 40.88; 40.81; 40.75; 40.41; 22.45; 19.90; 19.88; 19.82; 19.77; 19.69. LSI-MS: 730.0 (26), 729.1 (37), 707.7 (24), 707.0 (34), 345.1 (20), 329.1 (16), 307.1 (100), 291.1 (17), 290.1 (21), 289.1 (51), 277.1 (16), 273.1 (20), 260.1 (17), 259.1 (34), 242.1 (18), 241.1 (28), 207.1 (18). Anal. calc. for $C_{32}H_{50}O_{17}$ (706.74): C 54.38, H 7.13; found: C 54.36, H 6.90.

*(*S,S,S,S,R,R,R,R*)-α-Hydro-ω-hydroxyoctakis[oxy(1-methyl-3-oxopropane-1,3-diyl)]* (*ent*-**14a**). According to *GP II*, with *ent*-**14d** (1.29 g, 1.51 mmol) in CF_3COOH (5 ml) and CH_2Cl_2 (10 ml). According to *GP III*, the crude product was hydrogenated in EtOH (8 ml) over Pd/C (100 mg). FC (Et_2O/pentane 5 : 1 + 2% AcOH) gave 750 mg (70%) of *ent*-**14a**. Faintly yellow and very viscous oil. R_f (Et_2O/pentane 5 : 1, *A*) 0.17. $[\alpha]_D^{r.t.} = +6.0$ ($c = 1.07$, $CHCl_3$). IR ($CHCl_3$): 2985*m*, 2936*w*, 1737v*s*, 1460*w*, 1450*w*, 1383*m*, 1305*s*, 1260*m*, 1178*s*, 1136*m*, 1102*m*, 1057*s*, 979*w*, 929*w*, 822*w*. ^{1}H-NMR (500 MHz): 5.34–5.20 (*m*, 7 H); 4.25–4.17 (*m*, 1 H); 2.67–2.39 (*m*, 16 H); 1.31–1.22 (*m*, 24 H). ^{13}C-NMR (125 MHz): 173.08; 172.03; 169.59; 169.54; 169.46; 169.36; 169.35; 169.17; 67.96; 67.82; 67.78; 67.74; 67.67; 67.66; 67.61; 64.52; 43.20; 40.88; 40.86; 40.82; 40.71; 40.41; 22.44; 19.88; 19.83; 19.76; 19.69. LSI-MS: 729.3 (20), 707.3 (34), 345.2 (12), 307.1 (10), 259.1 (16), 241.1 (15), 191.1 (11), 173.1 (29), 165.1 (14), 163.1 (11), 156.1 (18), 155.1 (100), 154.1 (74), 138.1 (37), 137.1 (77), 136.1 (55), 123.1 (44), 121.1 (30), 111.1 (36), 109.1 (65), 107.0 (48), 105.0 (38). Anal. calc. for $C_{32}H_{50}O_{17}$ (706.74): C 54.38, H 7.13; found: C 54.31, H 6.92.

11. *Trimers* **19**. *(3*R*)-3-{[(3′*R*)-3′-{[(3″*R*)-3″-(Benzyloxy)butanoyl]oxy}butanoyl]oxy}butanoic Acid* tert-*Butyl Ester* (**19d**). According to *GP I*, with crude **3b** (2.5 g, 8.92 mmol) in CH_2Cl_2 (10 ml) and **2c** (1.6 g, 9.99 mmol) in CH_2Cl_2 (5 ml): 3.74 g of brown oil. FC (Et_2O/pentane 1 : 3) yielded 1.63 g (43%) of **19d** (yield not optimized). Clear, colorless oil. R_f (Et_2O/pentane 1 : 3, *B*) 0.17. $[\alpha]_D^{r.t.} = -19.5$ ($c = 1.128$, MeOH). IR (neat): 3339*w*, 3064*w*, 2979v*s*, 2934*m*, 1738v*s*, 1497*w*, 1455*m*, 1382*s*, 1369*s*, 1302*s*, 1258*s*, 1184*s*, 1057*s*, 1028*m*, 974*m*, 843*w*, 738*m*, 698*w*. ^{1}H-NMR (400 MHz): 7.32–7.23 (*m*, 5 arom. H); 5.30–5.22 (*m*, 2 H); 4.55, 4.50 (*AB*, $J_{AB} = 11.6$, PhCH_2O); 4.01–3.96 (*m*, H–C(3″)); 2.65–2.36 (*m*, 6 H); 1.43 (*s*, *t*-Bu); 1.29–1.23 (*m*, 9 H). ^{13}C-NMR (100 MHz): 170.43; 169.26; 169.15; 138.45; 128.25; 127.54; 127.44; 80.79; 71.86; 70.74; 67.85; 67.28; 42.06; 41.91; 40.87; 27.96; 19.76; 19.71; 19.67. LSI-MS: 423.3 (14, $[M+H]^+$), 422.2 (7, M^+), 421.2 (23, $[M-H]^+$), 368.2 (23), 367.2 (80), 281.1 (13), 259.1 (12), 173.1 (28), 155.1 (25), 154.1 (12), 137.1 (15), 136.0 (10), 107.0 (16), 105.0 (11), 92.0 (16), 91.0 (100), 87.0 (20), 68.9 (43), 56.9 (42). Anal. calc. for $C_{23}H_{34}O_7$ (422.36): C 65.38, H 8.11; found: C 65.42, H 7.91.

*(3*R*)-3-{[(3′*R*)-3′-{[(3″*R*)-3″-Hydroxybutanoyl]oxy}butanoyl]oxy]butanoic Acid* (**19a**). According to *GP II*, with **19a** (1.3 g, 3.08 mmol) in CH_2Cl_2 (12 ml) and CF_3COOH (6 ml). According to *GP III*, the crude product was hydrogenated in AcOEt (15 ml) over Pd/C (100 mg). FC (Et_2O/pentane 2 : 1 + 2% AcOH) gave 650 mg (76%) of **19a**. Colorless oil. R_f (Et_2O/pentane 2 : 1, *A*) 0.13. $[\alpha]_D^{r.t.} = -26.0$ ($c = 1.07$, $CHCl_3$). IR

($CHCl_3$): 3032*m*, 2981*m*, 2936*m*, 1734v*s*, 1458*w*, 1448*w*, 1383*m*, 1303*m*, 1263*m*, 1178*s*, 1137*m*, 1104*m*, 1055*m*, 975*w*, 968*w*, 930*w*. ^{1}H-NMR (400 MHz): 7.20–6.85 (br. *s*, OH); 5.37–5.22 (*m*, 2 H); 4.29–4.19 (*m*, H–C(3″)); 2.67–2.40 (*m*, 6 H); 1.31 (*d*, J = 6.4, Me); 1.30 (*d*, J = 6.4, Me); 1.24 (*d*, J = 6.3, Me). ^{13}C-NMR (100 MHz): 174.14; 171.76; 169.71; 67.78; 67.68; 64.62; 43.00; 40.93; 40.51; 22.34; 19.92; 19.80. LSI-MS: 553.4 (17, $[2M+H]^+$), 299.2 (60, $[M+Na]^+$), 277.2 (100, $[M+H]^+$), 259.2(12), 191.1(50), 173.1(66), 155.1(33), 154.1(19), 137.1(30), 136.1(20), 131.1(14), 105.0(30). Anal. calc. for $C_{23}H_{32}O_9$ (470.31): C 61.05, H 7.13; found: C 60.95, H 7.10.

12. *Pentamers* **20**. *(*R,R,R,R,R*)-α-Benzyl-ω-(*tert*-butoxy)pentakis[oxy(1-methyl-3-oxopropane-1,3-diyl)]* (**20d**). According to *GP I*, with crude **5b** (1.3 g, 2.87 mmol) in CH_2Cl_2 (5 ml) and **2c** (480 mg, 3.00 mmol) in CH_2Cl_2 (3 ml): 1.73 g of brown oil that solidified at 8° after several days. FC (Et_2O/pentane 1:2) yielded 1.24 g (73%) of **20d** (yield not optimized). Colorless oil which crystallized *i.v.* after several hours. R_f (Et_2O/pentane 2:3, *B*) 0.17. M.p. 44–45°. $[\alpha]_D^{r.t.} = -15.3$ (c = 1.025, MeOH). IR ($CHCl_3$): 2982*m*, 2937*w*, 2878*w*, 1735v*s*, 1455*w*, 1382*m*, 1370*m*, 1305*s*, 1260*m*, 1178*s*, 1100*m*, 1058*s*, 976*m*, 927*w*, 844*w*, 621*w*. ^{1}H-NMR (400 MHz): 7.33–7.23 (*m*, 5 arom. H); 5.31–5.21 (*m*, 4 H); 4.56, 4.50 (*AB*, J_{AB} = 11.6, PhCH_2O); 4.03–3.95 (*m*, 1 H); 2.67–2.37 (*m*, 10 H); 1.44 (*s*, *t*-Bu); 1.28–1.23 (*m*, 15 H). ^{13}C-NMR (100 MHz): 170.46; 169.29; 169.19; 169.11; 169.10; 138.50; 128.29; 127.58; 127.47; 80.86; 71.90; 70.77; 67.94; 67.58; 67.53; 67.30; 42.08; 41.96; 40.86; 40.82; 40.78; 28.00; 19.81; 19.76; 19.71. LSI-MS: 1189.6 (≪1, $[2M]^+$), 595.3 (13, $[M+H]^+$), 594.3 (9, M^+), 593.3 (4, $[M-H]^+$), 541.2(11), 540.2(42), 539.3(100), 345.1(18), 263.1(12), 259.1(26), 241.1(15), 177.1(12), 173.1(43), 156.1(18), 155.1(86), 154.1(38), 139.1(12), 138.0(20), 137.0(38), 136.0(34), 131.1(12), 107.0(29), 105.0(18). Anal. calc. for $C_{31}H_{46}O_{11}$ (594.08): C 62.61, H 7.80; found: C 62.77, H 7.55.

*(*R,R,R,R,R*)-α-Hydro-ω-hydroxypentakis[oxy(1-methyl-3-oxopropane-1,3-diyl)]* (**20a**). According to *GP II*, with **20d** (900 mg, 151 mmol) in CH_2Cl_2 (10 ml) and CF_3COOH (5 ml). According to *GP III*, the crude product was hydrogenated in AcOEt (12 ml) over Pd/C (80 mg). FC (Et_2O/pentane 3:1 + 2% AcOH) gave 520 mg (77%) of **20a**. White solid. R_f (Et_2O/pentane 3:1, *A*) 0.14. M.p. 58–59°. $[\alpha]_D^{r.t.} = -15.8$ (c = 1.053, $CHCl_3$). IR ($CHCl_3$): 3519*w* (br.), 3033*m*, 2984*m*, 2936*m*, 1735v*s*, 1458*w*, 1448*w*, 1383*m*, 1304*m*, 1264*m*, 1178*s*, 1136*m*, 1103*m*, 1056*s*, 976*w*, 928*w*. ^{1}H-NMR (400 MHz): 5.36–5.20 (*m*, 4 H); 4.27–4.19 (*m*, 1 H); 2.66–2.39 (*m*, 10 H); 1.31–1-23 (*m*, 15 H). ^{13}C-NMR (100 MHz): 173.23; 172.00; 169.83; 169.37; 169.16; 68.09; 67.72; 67.64; 67.60; 64.62; 43.17; 40.85; 40.79; 40.76; 40.41; 22.34; 19.86; 19.85; 19.70; 19.64. LSI-MS: 897.5 (26, $[2M]^+$), 471.2 (33, $[M+Na]^+$), 449.2 (100, $[M+H]^+$), 363.2(16), 307.1(21), 289.1(13), 277.2(11), 259.2(20), 191.2(10), 173.1(31). Anal. calc. for $C_{20}H_{32}O_{11}$ (448.46): C 53.57, H 7.19; found: C 53.54, H 7.19.

13. *Hexamers* **21**. *(*R,R,R,R,R,R*)-α-Benzyl-ω-(*tert*-butoxy)hexakis[oxy(1-methyl-3-oxopropane-1,3-diyl)]* (**21d**). According to *GP I*, with crude **5b** (1.3 g, 2.87 mmol) in CH_2Cl_2 (5 ml) and **3c** (740 mg, 3.00 mmol) in CH_2Cl_2 (3 ml): 1.90 g of brown oil that solidified at 8°. FC (Et_2O/pentane 1:1) yielded 900 mg (46%) of **21d** (yield not optimized). Colorless oil which crystallized *i.v.* R_f (Et_2O/pentane 1:1, *B*) 0.26. M.p. 62.5–63.5°. $[\alpha]_D^{r.t.} = -15.2$ (c = 0.995, MeOH). IR ($CHCl_3$): 2983*m*, 2937*w*, 1736v*s*, 1457*w*, 1382*m*, 1370*m*, 1305*s*, 1264*m*, 1177*s*, 1136*m*, 1101*m*, 1058*m*, 1027*w*, 976*w*, 916*w*, 844*w*, 636*w*, 622*w*. ^{1}H-NMR (400 MHz): 7.35–7.23 (*m*, 5 arom. H); 5.31–5.21 (*m*, 5 H); 4.56, 4.50 (*AB*, J_{AB} = 11.5, PhCH_2O); 4.03–3.95 (*m*, 1 H); 2.65–2.37 (*m*, 12 H); 1.44 (*s*, *t*-Bu); 1.29–1.22 (*m*, 18 H). ^{13}C-NMR (100 MHz): 170.50; 169.33; 169.23; 169.14; 138.54; 128.33; 127.62; 127.51; 80.90; 71.94; 70.81; 67.98; 67.62; 67.60; 67.56; 67.34; 42.12; 41.99; 40.89; 40.86; 40.81; 28.04; 19.85; 19.80; 19.76. LSI-MS: 1361.7 (≪1, $[2M]^+$), 681.3 (10, $[M+H]^+$), 680.3 (7, M^+), 679.3 (19, $[M-H]^+$), 627.3(12), 625.3(86), 431.2(12), 345.1(20), 263.1(11), 259.1(27), 242.1(10), 241.1(22), 177.1(12), 173.1(43), 156.1(23), 155.1(100), 154.1(51), 152.0(11), 139.1(19), 138.0(30), 137.0(50), 136.0(46), 135.0(11), 131.1(14), 124.0(12), 123.0(13), 121.0(12), 120.0(13), 119.0(11), 108.0(11), 107.0(34), 105.0(21). Anal. calc. for $C_{35}H_{52}O_{13}$ (680.12): C 61.75, H 7.70; found: C 61.65, H 7.53.

*(*R,R,R,R,R,R*)-α-Hydro-ω-hydroxyhexakis[oxy(1-methyl-3-oxopropane-1,3-diyl)]* (**21a**). According to *GP II*, with **21d** (570 mg, 1.10 mmol) in CH_2Cl_2 (5 ml) and CF_3COOH (2.5 ml). According to *GP III*, the crude product was hydrogenated in AcOEt (6 ml) over Pd/C (40 mg). FC (Et_2O/pentane 4:1 + 2% AcOH) gave 440 mg (75%) of **21a**. White solid. R_f (Et_2O/pentane 4:1, *A*) 0.22. M.p. 75–76.5°. $[\alpha]_D^{r.t.} = 13.6$ (c = 1.01, $CHCl_3$). IR ($CHCl_3$): 3519*w* (br.), 2985*m*, 2936*m*, 1737v*s*, 1459*w*, 1449*w*, 1383*m*, 1304*m*, 1261*m*, 1178*s*, 1137*m*, 1102*m*, 1056*s*, 978*w*, 930*w*. ^{1}H-NMR (400 MHz): 5.35–5.20 (*m*, 5 H); 4.26–4.18 (*m*, 1 H); 2.67–2.38 (*m*, 12 H); 1.31–1.23 (*m*, 15 H). ^{13}C-NMR (100 MHz): 173.13; 172.00; 169.62; 169.58; 169.35; 169.17; 68.00; 67.80; 67.72; 67.63; 67.59; 64.54; 43.18; 40.84; 40.81; 40.76; 40.40; 22.37; 19.84; 19.73; 19.71; 19.64. LSI-MS: 1091.5 (12, $[2M+Na]^+$), 1069.5 (22, $[2M]^+$), 557.3 (62, $[M+Na]^+$), 535.3 (100, $[M+H]^+$), 449.2(17), 345.2(16), 307.1(10), 259.1(24), 241.2(14), 191.1(12), 173.1(40), 156.1(17), 155.1(88), 154.1(54), 139.1(19), 138.1(30), 137.1(59), 136.1(46), 107.0(24). Anal. calc. for $C_{24}H_{38}O_{13}$ (534.56): C 53.93, H 7.16; found: C 54.18, H 7.13.

14. *Heptamers* **22**. *(*R,R,R,R,R,R,R*)-α-Benzyl-ω-(*tert-*butoxy)heptakis[oxy(1-methyl-3-oxopropane-1,3-diyl)]* (**22d**). When the coupling to octamer **10d** was carried out at r.t., heptamer **22d** was obtained as a by-product in quantities of up to 30%. Heptamer **22d** could be separated from octamer **10d** by FC: white solid. R_f (Et_2O/pentane 1:1, *B*) 0.18. M.p. 74–75°. $[\alpha]_D^{r.t.} = -12.5$ ($c = 1.06$, MeOH). IR ($CHCl_3$): 2984*m*, 2936*w*, 1736v*s*, 1457*w*, 1382*m*, 1369*m*, 1305*s*, 1264*m*, 1178*s*, 1136*m*, 1101*m*, 1058*s*, 977*w*, 841*w*. ^{1}H-NMR (400 MHz): 7.34–7.24 (*m*, 5 arom. H); 5.32–5.22 (*m*, 6 H); 4.57, 4.51 (*AB*, $J_{AB} = 11.5$, PhCH_2O); 4.04–3.96 (*m*, 1 H); 2.66–2.38 (*m*, 14 H); 1.45 (*s*, *t*-Bu); 1.36–1.21 (*m*, 21 H). ^{13}C-NMR (100 MHz): 170.44; 169.27; 169.17; 169.09; 138.48; 128.27; 127.56; 127.46; 80.84; 71.87; 70.74; 67.92; 67.54; 67.51; 67.28; 42.06; 41.93; 40.83; 40.79; 40.74; 27.98; 19.79; 19.74; 19.70. LSI-MS: 767.2 (6, $[M+H]^+$), 766.2 (5, M^+), 765.2 (11, $[M-H]^+$), 713.2 (10), 712.1 (37), 711.1 (100), 173.0 (10), 155.0 (37), 154.0 (16), 137.0 (15), 136.0 (13). Anal. calc. for $C_{39}H_{58}O_{15}$ (766.17): C 61.08, H 7.62; found: C 60.99, H 7.57.

*(*R,R,R,R,R,R,R*)-α-Hydro-ω-hydroxyheptakis[oxy(1-methyl-3-oxopropane-1,3-diyl)]* (**22a**). According to *GP II*, with **22d** (80 mg, 0.129 mmol) in CH_2Cl_2 (600 µl) and CF_3OOH (300 µl). According to *GP III*, the crude product was hydrogenated in AcOEt (2 ml) with Pd/C (10 mg). FC (Et_2O/pentane 4:1 + 2% AcOH) gave 70 mg (87%) of **22a**. White solid. R_f (Et_2O/pentane 4:1, *A*) 0.15. M.p. 89.5–91°. $[\alpha]_D^{r.t.} = -13.6$ ($c = 1.01$, $CHCl_3$). IR ($CHCl_3$): 3523*w* (br.), 2987*m*, 2936*m*, 1737v*s*, 1458*w*, 1448*w*, 1383*m*, 1305*m*, 1258*m*, 1178*s*, 1137*m*, 1102*m*, 1058*s*, 978*w*. ^{1}H-NMR (400 MHz): 5.36–5.19 (*m*, 6 H); 4.25–4.17 (*m*, 1 H); 2.67–2.38 (*m*, 14 H); 1.31–1.19 (*m*, 21 H). ^{13}C-NMR (100 MHz): 172.51; 172.01; 169.68; 169.59; 169.40; 169.36; 169.13; 68.03; 67.81; 67.73; 67.70; 67.69; 67.59; 64.53; 43.16; 40.86; 40.77; 40.42; 22.38; 19.89; 19.86; 19.74; 19.64. LSI-MS: 1241.6 (3, $[2M]^+$), 643.3 (15, $[M+Na]^+$), 621.3 (100, $[M+H]^+$), 307.1 (10), 173.1 (9). Anal. calc. for $C_{28}H_{44}O_{15}$ (620.65): C 54.19, H 7.15; found: C 53.25, H 7.05.

15. *Cyclic Oligomers* (*Oligolactones*). *Cyclization of Tetramer* **8a** *to Oligolactones* **23** *and* **24**. With a syringe and under Ar, 2,6-dichlorobenzoyl chloride (445 mg, 2.12 mmol) followed by pyridine (168 mg, 2.12 mmol) were added to a soln. of **8a** (700 mg, 1.93 mmol) in THF (10 ml) (heat-dried flask). The soln. was first stirred for 30 min in an ice-bath and then another 3 h at r.t. The resulting white precipitation was filtered off with an Ar funnel, and the clear filtrate was diluted to 20 ml with toluene. With a syringe pump, the soln. was added within 3 h to a soln. of 4-(dimethylamino)pyridine (943 mg, 7.72 mmol) in toluene (50 ml), that was cooled in an ice-bath. The soln. was stirred at the same temp. for 60 h. Workup with 1N HCl, sat. $NaHCO_3$ soln., and sat. NaCl soln., drying ($MgSO_4$), and evaporation gave 350 mg of a yellow, oily, partly crystalline mixture that was separated and purified by FC (Et_2O/pentane 2:1): **23** and **24**.

*(4*R,*8*S,*12*S,*16*S*)-4,8,12,16-Tetramethyl-1,5,9,13-tetraoxacyclohexadecane-2,6,10,14-tetrone* (**23**): 130 mg (20%) of white crystals. R_f (Et_2O/pentane 2:1, *A*) 0.30. M.p. 119–119.5°. $[\alpha]_D^{r.t.} = +15.1$ ($c = 1.04$, $CHCl_3$). IR ($CHCl_3$): 3010*w*, 2986*w*, 2937*w*, 1739v*s*, 1458*w*, 1447*w*, 1383*s*, 1304*s*, 1266*m*, 1179*s*, 1135*s*, 1102*s*, 1057*s*, 974*s*. ^{1}H-NMR (400 MHz): 5.33–5.21 (*m*, 4 H); 2.64–2.42 (*m*, 8 H); 1.34 (*d*, $J = 6.5$, 3 H); 1.34 (*d*, $J = 6.4$, 3 H); 1.30 (*d*, $J = 6.4$, 3 H); 1.29 (*d*, $J = 6.5$, 3 H). ^{13}C-NMR (100 MHz): 170.04; 169.70; 169.60; 168.96; 68.25; 68.03; 67.57; 67.39; 41.72; 41.29; 40.82; 40.64; 20.49; 20.15; 20.02; 19.47. LSI-MS: 346.0 (20), 345.0 (100, $[M+H]^+$), 173.0 (11), 155.0 (49), 154.0 (32), 138.0 (13), 137.0 (30), 135.9 (25), 106.9 (13), 90.9 (10), 88.9 (10), 86.9 (11), 76.9 (14), 68.8 (67), 56.8 (10), 54.8 (15). Anal. calc. for $C_{16}H_{24}O_8$ (344.36): C 55.81, H 7.02; found: C 55.82, H 6.80.

*(4*R,*8*S,*12*S,*16*S,*20*R,*24*S,*28*S,*32*S*)-4,8,12,16,20,24,28,32-Octamethyl-1,5,9,13,17,21,25,29-octaoxacyclodotriacontane-2,6,10,14,18,22,26,30-octone* (**24**): 100 mg (30%) of colorless, rhombic crystals. R_f (Et_2O/pentane 2:1, *A*) 0.21. M.p. 93.5–94°. $[\alpha]_D^{r.t.} = -4.1$ ($c = 0.96$, $CHCl_3$). IR ($CHCl_3$): 2984*w*, 2936*w*, 1740v*s*, 1458*w*, 1447*w*, 1383*m*, 1305*s*, 1264*m*, 1178*s*, 1135*m*, 1102*m*, 1058*s*, 978*w*. ^{1}H-NMR (500 MHz): 5.30–5.21 (*m*, 8 H); 2.64–2.42 (*m*, 16 H); 1.30–1.27 (*m*, 24 H). ^{13}C-NMR (125 MHz): 169.34; 169.26; 169.23; 169.18; 67.78; 67.71; 67.64; 67.60; 40.97; 40.85; 40.80; 40.71; 19.83; 19.80. LSI-MS: 690.2 (26), 689.2 (70, $[M+H]^+$), 345.1 (13), 259.1 (14), 241.1 (28), 173.1 (22), 156.1 (19), 155.0 (100), 154.0 (28), 138.0 (16), 137.0 (37), 136.0 (26), 107.0 (12). Anal. calc. for $C_{32}H_{48}O_{16}$ (688.70): C 55.81, H 7.02; found: C 55.69, H 6.96.

Crystal-Structure Analysis of **24**: The determination of the cell parameters and collection of the reflection intensities were performed at r.t. on an *Enraf-Nonius-CAD-4* four-circle diffractometer (graphite monochromatized MoK_α radiation, λ 0.7107 Å). Monoclinic, space group *C*2, $a = 19.461(4)$, $b = 5.424(3)$, $c = 17.338(4)$ Å, $\beta = 90.5°$ (2); $V = 1830(10)$ Å^3, $Z = 2$, $\rho_{calc.} = 1.250$ gcm^{-3}, $\mu = 0.100$ mm^{-1}, $F(000) = 736$; $\omega/2\theta$ scan, $2.5 < 2\theta < 50°$; 2004 unique reflections with $I > 3\sigma(I)$ were used for the solution (direct methods, SHELXS86 [43]) and the refinement of the structure (SHELXL92 [44]). The non-H-atoms were refined anisotropically (unit weights), the H-atoms were added to this structure model with constant isotropic temp. factors on calculated positions and included in the structure-factor calculation using the riding model. The refinement converged finally at *R* 0.038 (number of variables 217).

Cyclization of Tetramer ent-**6a** *to the Oligolactones* **25** *and* **26**. As described for the cyclization of **8a**, with 2,6-dichlorobenzoyl chloride (244 µl, 1.71 mmol), pyridine (140 µl, 1.71 mmol), *ent*-**6a** (565 mg, 1.56 mmol), and then 4-(dimethylamino)pyridine (761 mg, 6.28 mmol) in toluene (50 ml): 86 mg of a yellow, oily, partly crystalline mixture that was separated and purified by FC (Et_2O/pentane 2:1): **25** and **26**.

*(4*R,*8*R,*12*S,*16*S*)-4,8,12,16-Tetramethyl-1,5,9,13-tetraoxacyclohexadecane-2,6,10,14-tetrone* (**25**): 67 mg (12%) of colorless crystals. R_f (Et_2O/pentane 2:1, *A*) 0.30. M.p. 209.5–210°. IR ($CHCl_3$): 3032*w*, 2986*w*, 2935*w*, 1742v*s*, 1460*w*, 1450*w*, 1353*w*, 1303*s*, 1265*s*, 1178*s*, 1141*m*, 1102*s*, 1056*s*, 974*s*, 924*w*, 904*w*, 834*w*. ^{1}H-NMR (400 MHz): 5.54–5.43 (*m*, 4 H); 2.70–2.34 (*m*, 8 H); 1.24 (*d*, *J* = 6.6, 3 H); 1.22 (*d*, *J* = 6.6, 3 H); 1.22 (*d*, *J* = 6.6, 3 H); 1.29 (*d*, *J* = 6.6, 3 H). ^{13}C-NMR (100 MHz): 169.57; 168.56; 66.71; 66.57; 41.72; 39.97; 20.10. LSI-MS: 346.1(30), 345.1 (100, $[M+H]^+$), 307.1(20), 289.1(12), 173.1(15), 156.1(14), 155.1(57), 154.1(58), 139.1(20), 138.1(31), 137.1(55), 136.0(47), 135.0(11), 124.0(12), 123.1(12), 121.0(11), 120.0(13), 107.0(22), 105.0(11). Anal. calc. for $C_{16}H_{24}O_8$ (344.36): C 55.81, H 7.02; found: C 55.73, H 6.90.

Crystal-Structure Analysis of **25**. As described for **24**. Monoclinic, space group *P*2(1), *a* = 8.3297(13), *b* = 9.003(5), *c* = 12.148(7) Å, *β* = 92.26°(3); *V* = 910.3(8) Å^3, *Z* = 2, $\rho_{calc.}$ = 1.256 gcm^{-3}, *µ* = 0.101 mm^{-1}, *F*(000) = 368; *ω*/2*θ* scan, 2.5 < 2*θ* < 50°; 1708 unique reflections with *I* > 3*σ*(*I*) were used for the solution (direct methods, SHELXS86 [43]) and the refinement of the structure (SHELXL92 [44]). The non-H-atoms were refined anisotropically (unit weights), the H-atoms were added to this structure model with constant isotropic temp. factors on calculated positions and included in the structure-factor calculation using the riding model. The refinement converged finally at *R* 0.0395 (number of variables 218).

*(4*R,*8*R,*12*S,*16*S,*20*R,*24*R,*28*S,*32*S*)-4,8,12,16,20,24,28,32-Octamethyl-1,5,9,13,17,21,25,29-octaoxacyclodotriacontane-2,6,10,14,18,22,26,30-octone* (**26**): 5 mg (2%) of white solid. R_f (Et_2O/pentane 2:1, *A*) of 0.20. ^{1}H-NMR (300 MHz): 5.31–5.20 (*m*, 8 H); 2.66–2.42 (*m*, 16 H); 1.31–1.25 (*m*, 24 H).

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