76. Synthesis of Monodisperse Macromolecular Bicyclic and Dendritic[1]) Compounds from (*R*)-3-Hydroxybutanoic Acid and Benzene-1,3,5-tricarboxylic Acid and Analysis by Fragmenting MALDI-TOF Mass Spectroscopy

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Dedicated to Professor *Waldemar Adam* on the occasion of his 60th birthday

(11.II.97)

As previously shown, oligo- and poly(β-hydroxyalkanoates) have a high tendency to form lamellar crystallites with *ca.* 50-Å thickness which corresponds to chain lengths of 16 units (*Fig. 1*). To have monodisperse model compounds, we have now prepared bicyclic derivatives with three parallel (**27**–**29**) or two parallel and an antiparallel chain (**68**–**70**) consisting of up to 16 3-hydroxybutanoate (3-HB) units. We also prepared dendritic compounds (**71**–**75**, **82**–**85**) containing oligo(3-HB) chains which cannot possibly be arranged as in the *lamellae*; the branching units were prepared from trimesic acid (= benzene-1,3,5-tricarboxylic acid). So far, none of the prepared samples formed crystals or contained crystalline domains which would have been suitable for single-crystal or powder-diffraction X-ray analysis. The terminally deprotected dendrimers (**74**, **75**, and **85**) are multi-anionic (up to 12 peripheral CO_2H groups) and biodegradable. The macromolecular HB derivatives (molecular weight up to 10150 Da) have been fully characterized by IR, ^{1}H- and ^{13}C-NMR, $[\alpha]_D$, and elemental analysis. Especially important is the analysis by mass spectrometry with the MALDI-TOF technique (*Fig. 2*), proving that the products are monodisperse; application of a new variation of this MS method (*p*ost *s*ource *d*ecay = PSD or *f*ragment *a*nalysis by *s*tructural *t*ime of flight = *FAST*™) allows for the observation of metastable fragment ions and, thus, is a tool for structural oligomer analysis (*Fig. 3*).

1. Introduction. – Poly(β-hydroxyalkanoates) (PHAs), an ubiquitous class of biopolymers [2] have been the subject of research in our group for many years [3]. Besides their occurrence as a high-molecular-weight storage material (sPHA) in microorganisms [4] PHAs have also been found in a low-molecular-weight form (cPHA). *Reusch* and coworkers have shown that low-molecular-weight poly[(*R*)-3-hydroxybutanoic acid] (P(3-HB) = PHB), *ca.* 150 units) and $CaPP_i$ (calcium polyphosphate) form a complex which may function as an ion channel in genetically competent *E. coli* cells [5] [6]. P(3-HB) has also been detected in eucaryotic cells, in human aorta tissue [6], and in blood plasma [5b]. From most of these sources, cPHB and its homolog cPHV (V = valerate = pentanoate) could be extracted with $CHCl_3$ and characterized by NMR spectroscopy [6]. Most recently, however, much larger quantities of PHB and PHV have been detected (by degradation to crotonic acid (= but-2-enoic acid) at higher temperature and/or larger reaction times [7], or by transesterifying conversion to ethyl (*R*)-3-

[1]) Partially published in a preliminary communication [1].

[2]) Postdoctoral fellow of the *Deutsche Forschungsgemeinschaft*, 1995–1996.

[3]) Part of the Ph. D. Thesis of *U. D. L.*, Diss. No. 11405, ETH-Zürich, 1995.

(trifluoroacetoxy)butanoate and -pentanoate [8]) as components of a large number of protein acetone powders.

Along another line of work, we have synthesized linear and cyclic oligomers of alkanoic acids [3] [9]. A linear 128mer and a cylic oligolide consisting of 32 HB units were thus obtained [10]. Furthermore, we have shown that the linear oligomers (OHB), like the high-molecular-weight PHB have a remarkable tendency to form lamellar crystallites of *ca.* 50-Å thickness, in which the chains are arranged as 2_1 helices of 6-Å pitch/strings of 16 HB units [11]. When the OHBs are embedded into phospholipid bilayers, single-channel ion transport can be observed [12], and it was proposed that this is due to bilayer perturbation caused by assemblies of OHBs, a two-dimensional presentation of which is shown in *Fig. 1* for the 32mer.

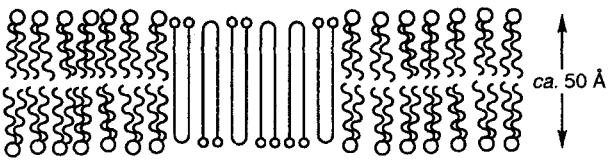


Fig. 1. *Schematic representation of the oligomer* **A** ($n = 32$) *incorporated into a planar phospholipid bilayer, as proposed in* [12]

We now report on the synthesis of HB derivatives with bicyclic and dendritic structures. Both are interesting for membrane permeability and transport experiments. Furthermore, the bicyclic compounds with three parallel or two parallel and an antiparallel PHB chain could serve as models for the arrangement of the chains forming an ion channel, and at the outset of this investigation, we had hoped that they might form crystals suitable for detailed structure determinations, due to their reduced flexibility.

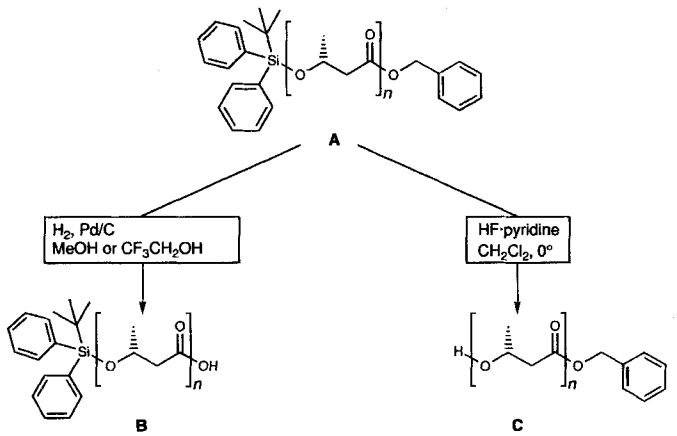
2. Preparative Results. 2.1. *Synthesis of Bicyclic Compounds.* Monodisperse 3-HB oligomers of type **A** with up to 128 3-HB units (*Scheme 1*) have been obtained by *Seebach* and coworkers [10] by a segment-coupling method. Thus, the oligoesters [13] were built up from fragments of type **B** (activated as the acid chlorides with $(COCl)_2$ as the reagent [14]) with the corresponding fragments of type **C** (using pyridine [15] as the catalyst and base). For the synthesis of high-molecular weight bicyclic compounds [16], we had to use more elaborate sequences of steps.

2.1.1. *Synthesis of Bicyclic Compounds with Parallel 3-HB Chains.* This simpler goal was reached by employing trimesic acid (= benzene-1,3,5-tricarboxylic acid) and its reduction product benzene-1,3,5-trimethanol [17].

As outlined in *Scheme 2*, there exist two possible strategies for the construction of the bicyclic compounds[4]): *a*) preassembly of the three 3-HB chains on one bridgehead building block with subsequent ring closure by connection of the three 3-HB chains to the second bridgehead molecule; *b*) preassembly of three 3-HB chains on both bridgehead molecules with subsequent ring closure by connection of the three 3-HB chains.

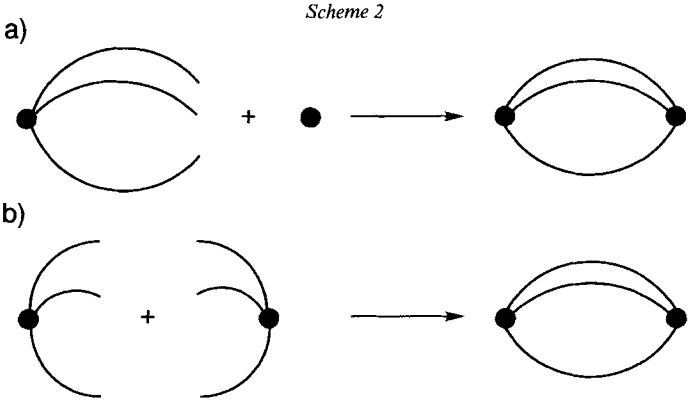
[4]) Since benzene rings are employed as bridgehead molecules, the target molecules are, in a strict sense, *tetra*cyclic.

Scheme 1



n	A	B	C
1	**1**	**5**	**9**
2	**2**	**6**	**10**
3	**3**	**7**	**11**
8	**4**	**8**	**12**

Scheme 2



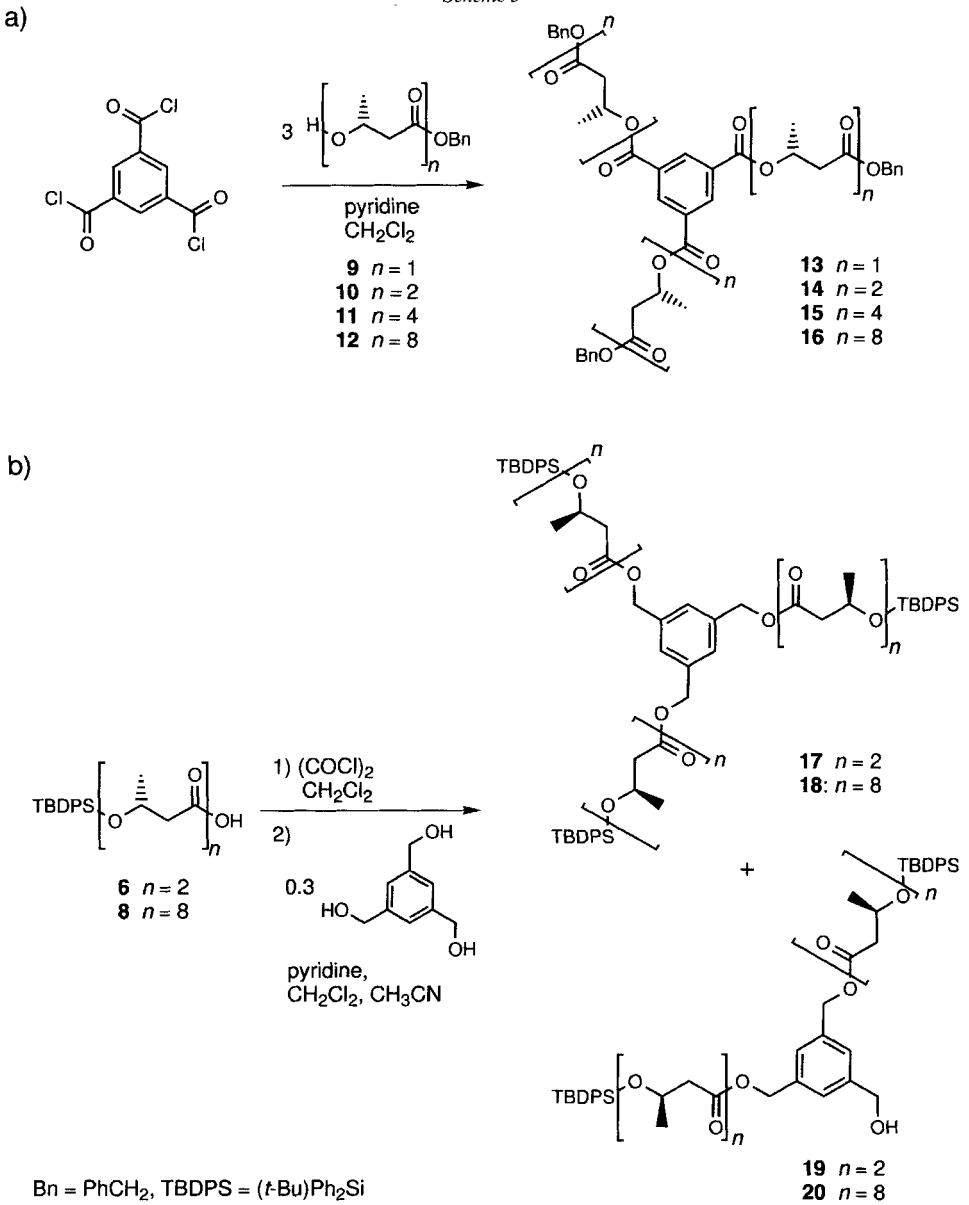
Strategy *a* appeared to us less promising for the following reasons: *i*) benzene-1,3,5-trimethanol is insoluble in CH_2Cl_2 [5]; *ii*) conversion of trimesoyl trichloride by alcoholysis is often incomplete, which is expected to significantly lower the yield of the ring closure step [6]).

[5]) CH_2Cl_2 is the solvent of choice for higher oligomers of 3-HB, especially at low temperatures.

[6]) Cyclizations usually proceed with low yields. Double cyclization reactions are said to yield between 0 and 50% product [16b].

In *Scheme 3*, we show the synthesis of the two types of building blocks, following strategy *b*: Acylation of the benzyl-ester-protected 3-HB oligomers **9** ($n = 1$) – **12** ($n = 8$) with trimesoyl trichloride yielded the protected triacids[7]) **13**–**16** (see *Scheme 3, a*; **9**–**12**

Scheme 3

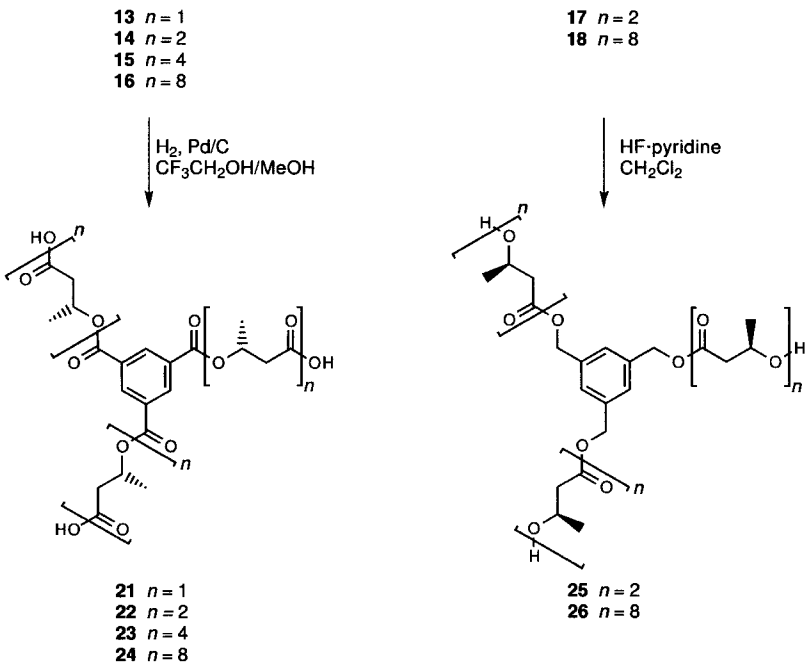


[7]) As a by-product (due to incomplete alcoholysis of the trimesoyl trichloride), the protected mono- and diacids were also formed. However, they were easily separated from the desired product by silica-gel chromatography.

from **1**–**4** according to *Scheme 1*). Benzene-1,3,5-trimethanol was then acylated under *Einhorn* conditions [15] with the acid chlorides of **6** and **8** to yield the protected trihydroxy derivatives **17** and **18**. The diacylated side products **19** and **20** were separated from the desired products by flash chromatography (**17**/**19** = 4:1, **18**/**20** = 2:1; see *Scheme 3,b*; **5**–**8** from **1**–**4** according to *Scheme 1*).

Cleavage of the benzyl-ester groups in **13**–**16** produced the triacids **21** ($n = 1$)–**24** ($n = 8$) (*Scheme 4*), and desilylation of compounds **17** and **18** with HF · pyridine gave the trihydroxy compounds **25** ($n = 2$) and **26** ($n = 8$) in quantitative yield. The stage for the cyclizations was thus set.

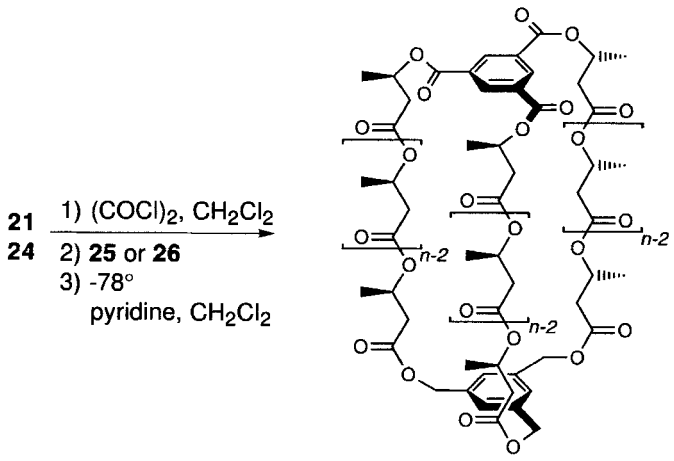
Scheme 4



A solution of the compounds containing three OH groups and of the triacyl trichlorides was added dropwise to a solution of pyridine in CH_2Cl_2 under high dilution conditions [16b]. Bicyclic compound **27** with bridges consisting of three 3-HB units was obtained in 33% yield from **21** and **25** (*Scheme 5*). Activation of the triacid **21** and coupling with the triol **26** gave the bicyclic compound **28** in 9% yield. Compound **29** with 16 3-HB residues bridging the two aromatic rings was obtained from triacid **24** and triol **26** in 5% yield. All bicyclic compounds **27**, **28**, and **29** with parallel 3-HB chains and 15, 39, and 67 atoms between the bridgehead aromatic rings, respectively, were solid materials.

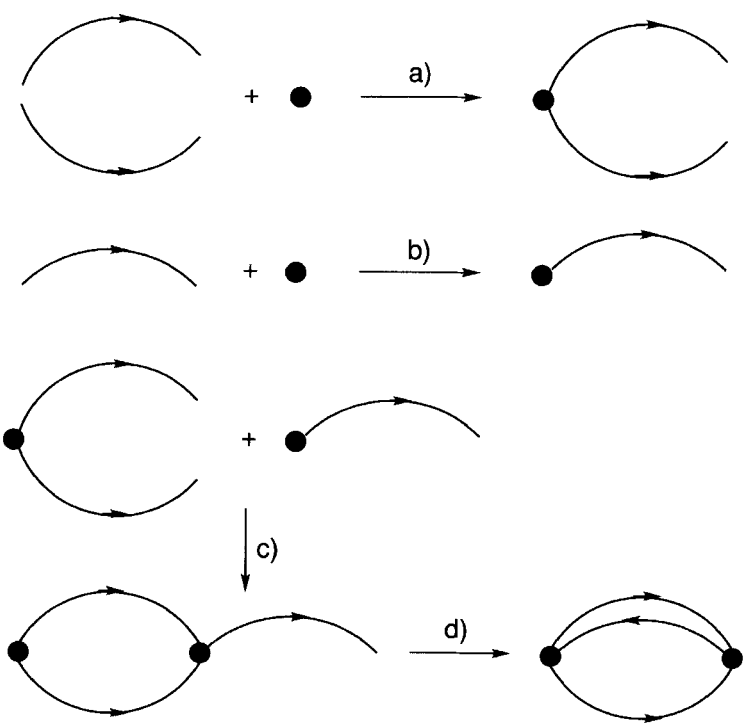
2.1.2. *Synthesis of Bicyclic Compounds with Antiparallel 3-HB Chains.* In lamellar crystallites of PHB and of linear 3-HB oligomers each chain is surrounded by two parallel and four antiparallel chains [3b]. Thus, bicyclic model compounds should ideally contain two parallel and one antiparallel 3-HB chain, thereby mimicking the arrangement of

Scheme 5



27 n = 3 (33 %)
28 n = 9 (9 %)
29 n = 16 (5 %)

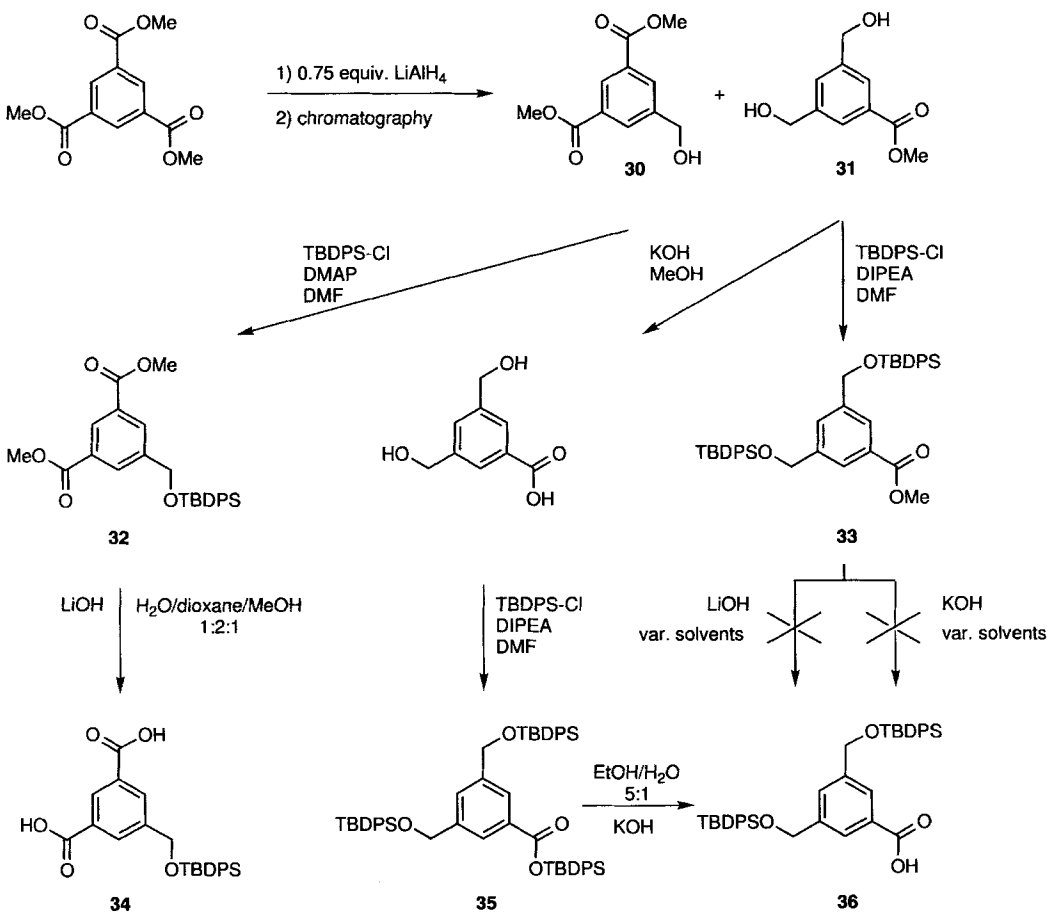
Scheme 6



chains in the solid state of the polymer. *Scheme 6* outlines the strategy for the synthesis of bicyclic compounds with antiparallel 3-HB chains in four steps: *a*) joining two 3-HB oligomers with their OH groups to a matching functionalized bridgehead molecule, which bears one protected hydroxy and two free CO_2H groups; *b*) attaching a third 3-HB oligomer unit with its OH group to the second bridgehead molecule, which bears one free CO_2H and two protected hydroxy groups; *c*) a first ring closure to give the monocyclic product, and *d*) a second ring closure to yield the bicyclic final product.

In *Scheme 7*, the synthesis of the two bridgehead molecules **34** and **36,** starting from trimesic acid triester [18] is outlined. Reduction of trimesic acid triester with 0.5 equiv. of $LiAlH_4$ yielded the singly and doubly reduced compounds **30** and **31** (ratio 1:1.2),

Scheme 7

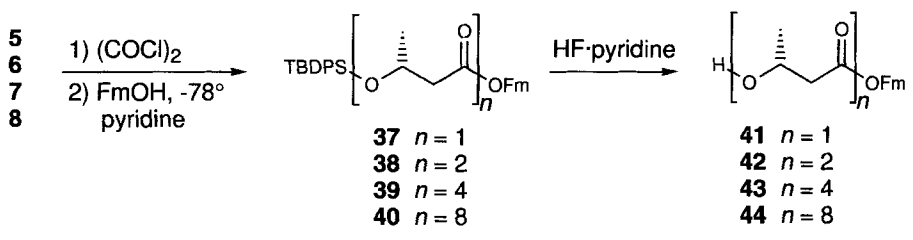


TBDPS = (*t*-Bu)Ph_2Si, DIPEA = (*i*-Pr)$_2$EtN, DMAP = 4-(dimethylamino)pyridine

respectively, which were separated from the starting material by flash chromatography[8]). Silylation of the OH groups gave the silylated diester **32** and the disilylated ester **33**, respectively. Saponification of the ester groups in **32** was effected with LiOH in H_2O/dioxane/MeOH[9]) and yielded the bridgehead molecule **34**; saponification of the monoester **33** succeeded neither with LiOH nor with KOH in various solvents. We, therefore, had to reverse the sequence of steps leading from the dihydroxy ester **31** to the second bridge-building block, the bis(silyloxy) acid **36**: the methyl-ester group was first hydrolyzed, then three (*t*-Bu)Ph_2Si groups were introduced (→ **35**), and finally the labile silyl ester was saponified with KOH in EtOH/H_2O.

Realization of the transformation *d* in *Scheme 6* required removal of the (*t*-Bu)Ph_2Si groups at the bridgehead unit (**34** joined with two 3-HB oligomers) and deprotection of the carboxy terminus of the third 3-HB oligomer chain, before ring closure to the bicyclic compound could be accomplished. Due to the fact that the bridgehead molecules **34** and **36** contain benzylic CH_2–O bonds, which are susceptible to hydrogenolysis, the **C** terminus of this third 3-HB oligomer could not be protected as a benzyl ester. We, therefore, employed the (9*H*-fluoren-9-yl)methyl group (Fm) which is labile under basic conditions [19]. The preparation of the Fm-protected 3-HB oligomers **41**–**44** from the (*t*-Bu)Ph_2Si-protected 3-HB oligomers **5**–**8** is outlined in *Scheme 8*. The Fm-protected oligomers **37**–**40** were obtained in high yields and the cleavage of the (*t*-Bu)Ph_2Si groups proceeded quantitatively. The excellent stability of the Fm group towards HF · pyridine, observed here, will be important at a later stage of the synthesis of the bicyclic compounds (see the second step in *Scheme 10*).

Scheme 8



Fm = (9*H*-Fluoren-9-yl)methyl, TBDPS = (*t*-Bu)Ph_2Si

In *Schemes 9* and *10*, we show the execution of the general transformations *a* and *b* pictured in *Scheme 6*, *i. e.*, the preparation of specifically protected oligo(3-HB) derivatives with two free CO_2H and one CH_2OSi (**49**–**52**), with two benzyl ester and one CH_2OH (**53**–**55**), and with one CO_2Fm and two CH_2OH (**59**–**61**) moieties from the corresponding fully protected compounds **45**–**48** and **56**–**58**. Bridgehead molecule **34** was converted to the diacid chloride[10]) by adding a catalytic amount of DMF [20] to a

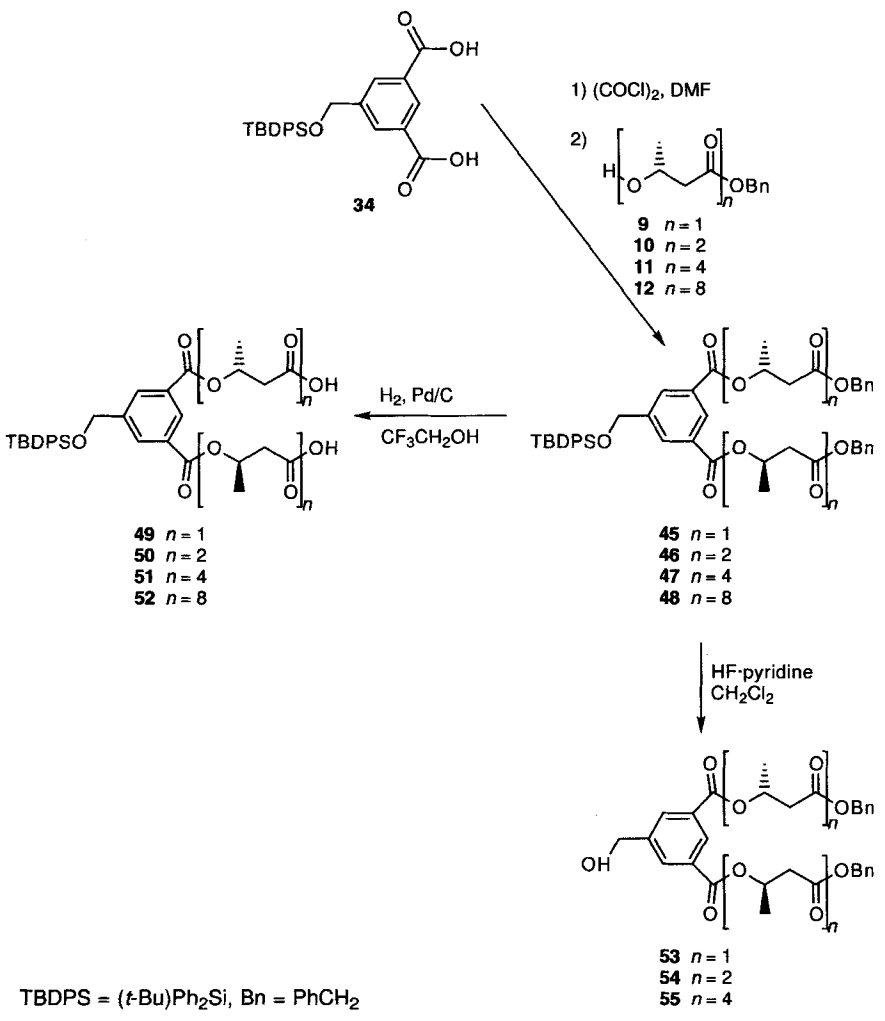
[8]) The triply reduced product benzene-1,3,5-trimethanol was easily removed during the aqueous workup.

[9]) Saponification with KOH in H_2O/EtOH or EtOH also caused cleavage of (*t*-Bu)Ph_2Si groups.

[10]) Generation of the acid chloride was not performed in CH_2Cl_2, because **34** is not soluble in this solvent. $SOCl_2$ could also not be employed as a reagent, because of the expected low stability of the silyl-protecting groups towards $SOCl_2$. Attempted esterification using DCC/DMAP (dicyclohexyldicarbodiimide/4-(dimethylamino)pyridine) was also unsuccessful.

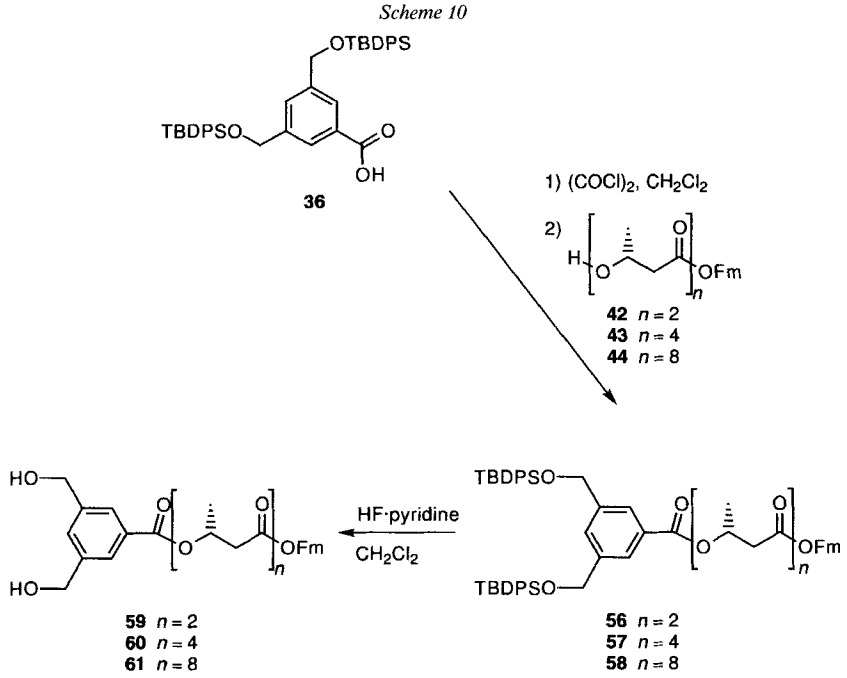
suspension of **34** in oxalyl chloride: After *ca.* 1 h, a clear solution had been formed, and 2 equiv. of the 3-HB oligomer hydroxy esters **9**–**12** were added, to give the silyl diesters **45**–**48**. The benzyl-ester groups were cleaved with H_2/Pd-C in quantitative yield without affecting the benzylic $SiO-CH_2$ group. On the other hand, the CO_2H group of the bridgehead molecule **36** was activated ($(COCl)_2$, cat. DMF in CH_2Cl_2) and coupled with the Fm-protected 3-HB oligomers **42**–**44** to the disilyl esters **56**–**58** which, in turn, were desilylated quantitatively with HF · pyridine (→ **59**–**61**).

Scheme 9



With the complementary building blocks **50**–**52** and **59**–**61** in hand, we proceeded to the final steps of synthesis of the bicyclic compounds with one antiparallel oligo(3-HB) chain (*cf.* operations *c* and *d* of *Scheme 6*). For the two-component cyclization

Scheme 10

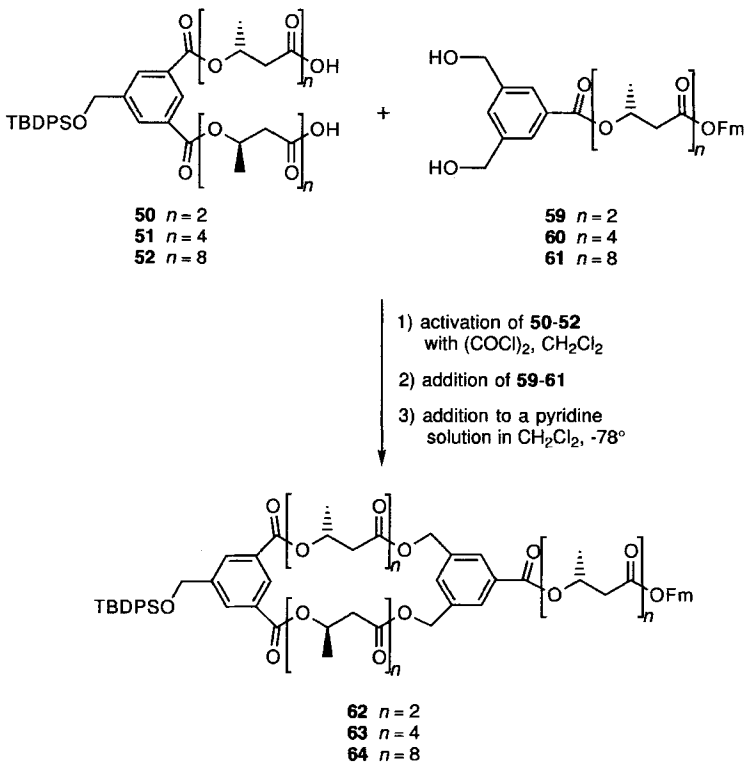


TBDPS = (*t*-Bu)Ph_2Si, Fm = (9*H*-fluoren-9-yl)methyl

(*Scheme 11*), a solution containing the corresponding diol and diacid chloride was added dropwise to a solution of pyridine in CH_2Cl_2 under high dilution conditions [16b]. The cyclic compound **62** was thus obtained in 50%, **63** in 19%, and **64** (n = 8) in 35% yield. For the subsequent third (intramolecular) esterification step, the protecting groups were removed (first the (*t*-Bu)Ph_2Si group with HF · pyridine, then the Fm group with piperidine; *Scheme 12*), to produce the unprotected hydroxy acids[11]) **65**–**67**. In contrast to the first cyclization, in which the CO_2H and the CH_2OH groups were in different molecules, the carboxylic acid could not be activated *via* the acid chloride in the macrolactonization to be carried out now, due to the presence of an unprotected OH group in the same molecule. Cyclization did not take place with the thioester method ([21]: after 72 h, no conversion of the hydroxy acid **65** could be detected by ^{1}H-NMR analysis). We then tried our favorite cyclization method [22], which uses 2,6-dichlorobenzoyl chloride as reagent for activation of the CO_2H group and pyridine as base for the cyclization step [10] (modified *Yamaguchi* method). By employing these cyclization conditions, the macrobicyclic product **68** was obtained in 33% yield after flash chromatography. The same procedure furnished the bicyclic compounds **69** in 20% and **70** in 18% yield. The three bicyclic compounds with antiparallel 3-HB oligomer chains were obtained as colorless solids.

[11]) The products (*t*-Bu)Ph_2SiF and 9-methylidene-9*H*-fluorene, resulting from the protecting groups, were removed by trituration in pentane.

Scheme 11

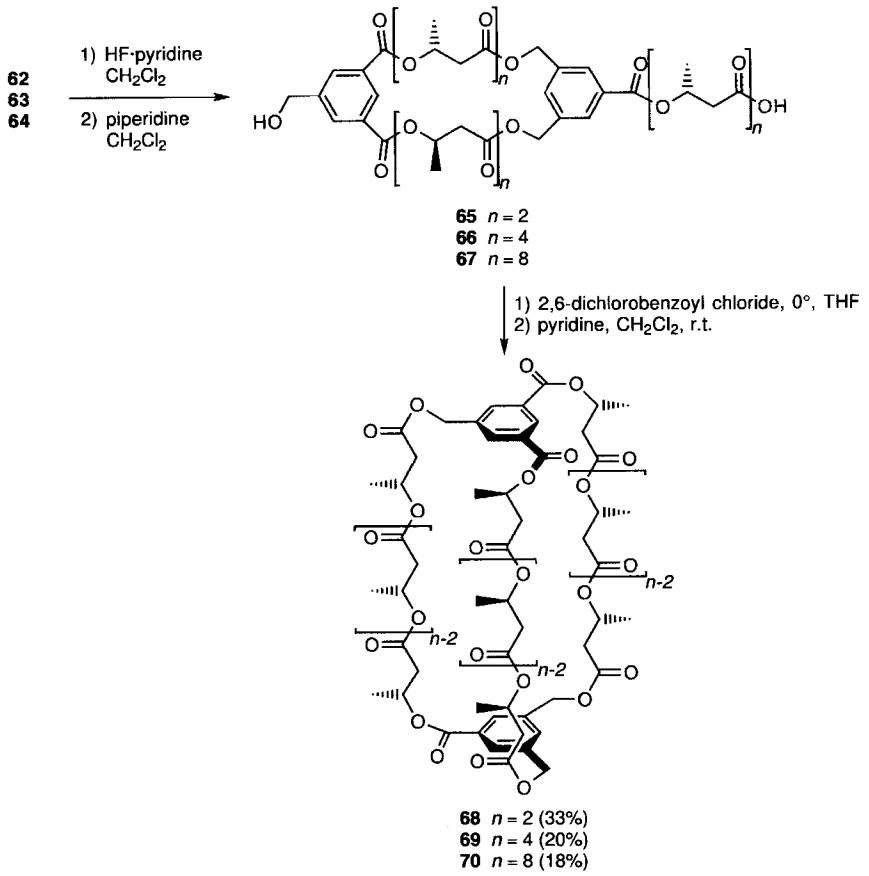


Unfortunately, no single crystals suitable for X-ray analysis were obtained of any of the bicyclic compounds with parallel or antiparallel arrangement of the chains. The crystalline domains of all corresponding samples prepared so far were even too small for observation of powder X-ray diffractions!

2.2. *Synthesis of Dendritic Compounds.* Dendrimers are attracting growing interest in stereoselective synthesis [23], as a new type of material [24] and for their use in biological studies, *e.g.*, as DNA carriers [25]. With regard to these possible applications of dendrimers [26] and in connection with ongoing efforts in our group on the synthesis of monodisperse chiral dendrimers, we decided to employ (*R*)-3-hydroxybutanoic acid and trimesic acid as building blocks for the synthesis of dendrimers with polyanionic peripheral groups.

The synthesis of the first generation dendrimers was based on the bridgehead molecules **21**–**23** (*Scheme 4*) which were employed as the dendritic cores. The branching units **53**–**55** were obtained by desilylation of compounds **45**–**47** (*Scheme 9*). Activation of the dendritic cores **21**–**23** as the acid chlorides and coupling with the branching units **53**–**55** (*Scheme 13*) gave the dendrimers of the first generation **71**–**73** in good-to-moderate yields (52–25%). The selective hydrogenolysis of the terminal $PhCH_2$ groups of the dendrimers **72** and **73** was carried out in DMF with Pd/C as the catalyst and cyclohexa-

Scheme 12



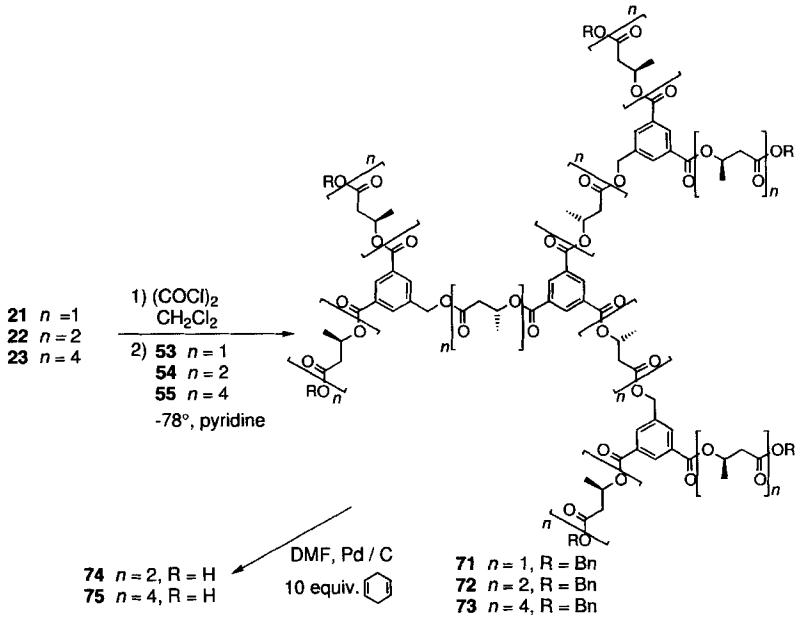
1,4-diene as the hydrogen donor [27] and gave the polyanionic dendrimers of the first generation **74** and **75**, respectively.

The fully protected branches for the dendrimers of the second generation **76**–**78** were synthesized (*Scheme 14*) starting from the silylated diacids **49**–**51**, which were activated as the acid chlorides and subsequently coupled to the desilylated benzyl esters **53**–**55**. Desilylation of the fully protected branches gave the benzyl esters **79**–**81** in quantitative yields.

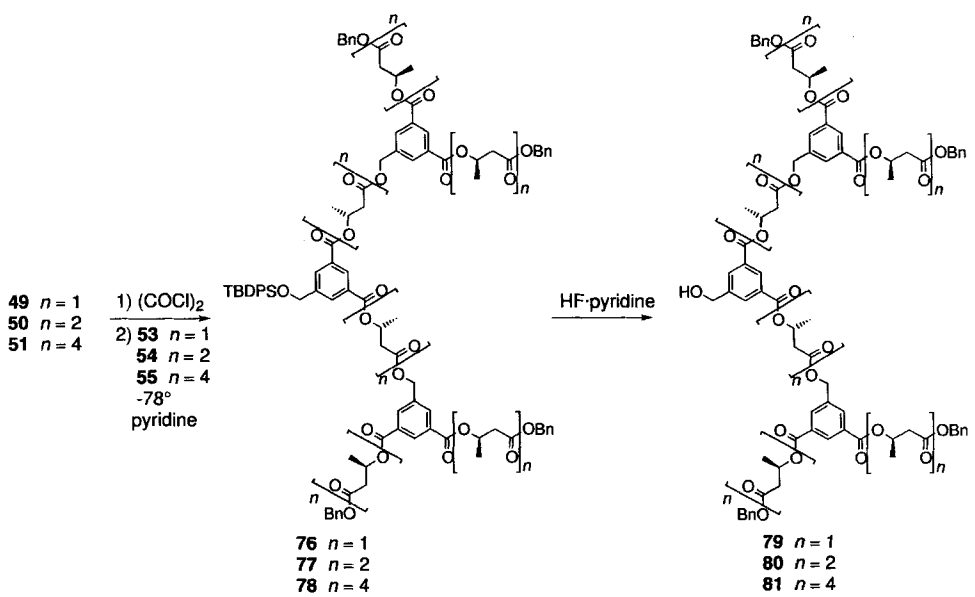
The coupling of **21**–**23** with the desilylated branches **79**–**81** finally gave the dendrimers of the second generation **82**–**84** (*Scheme 15*). The polyanionic dendrimer **85** of the second generation was again obtained by selective hydrogenolysis of the terminal $PhCH_2$ groups of **83**.

The dendritic compounds were obtained in 150 mg (**84**) to 450 mg (**83**) quantities as viscous oils which were soluble in CH_2Cl_2. All compounds were fully characterized (optical rotation, IR, ^1H- and ^{13}C-NMR spectroscopy, MS, elemental analysis). The

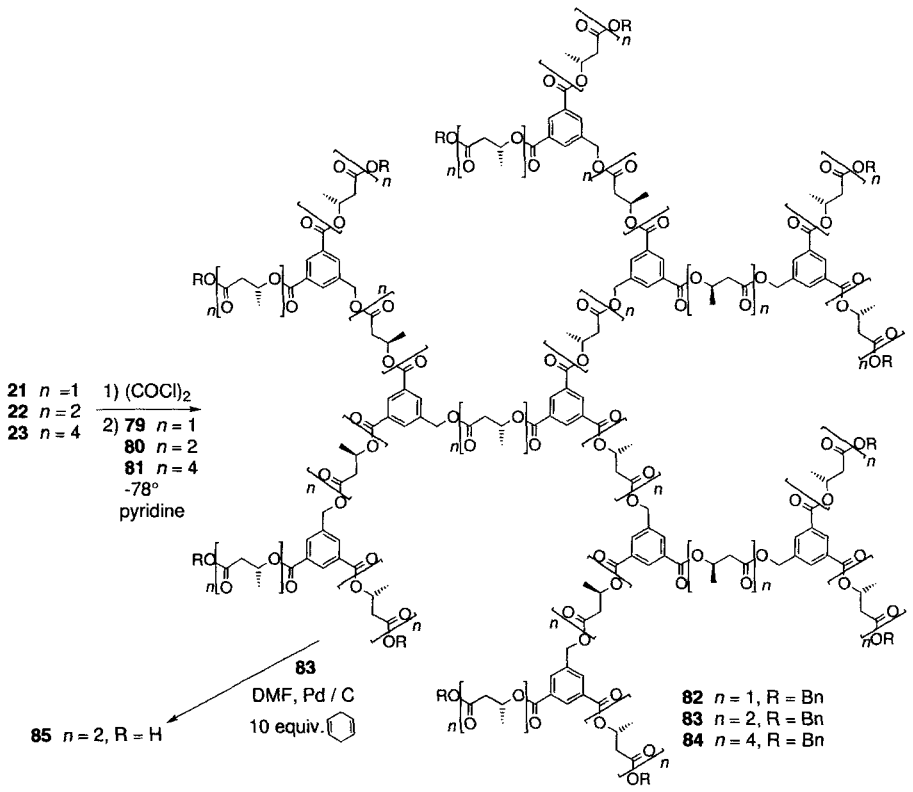
Scheme 13



Scheme 14



Scheme 15



optical rotations of the dendrimers do not exhibit any significant dependence upon their generation or the number of 3-HB molecules in the elongation units (see *Exper. Part*).

2.3. *Use of Mass Spectrometry for Studying Dendritic Structures.* The unambiguous determination of molecular weight and dispersity by mass spectrometry is undoubtedly of primordial importance for analyzing the product dendrimers resulting from a convergent synthesis. With the advent of *m*atrix *a*ssisted *l*aser *d*esorption and *i*onization *t*ime-*o*f-*f*light MS (MALDI-TOF-MS) [28], the required tools and additional benefits through virtually complete absence of fragmentation [12]) in the linear TOF mode became available, allowing the detection of synthetic defects at the sub-percent level. Moreover, MALDI-TOF-MS has a strong preference for singly-charged, mono-sodiated adduct ions. Thus, we have determined the purity and identity of the macrobicyclic and dendritic 3-HB derivatives by this method. Inspite of the fact that these compounds could undergo

[12]) The absence of *prompt* (in-source) fragmentation suggested by linear MALDI-TOF-MS is a matter of debate [29]. In our experience, working with very careful sample preparation and at the lowest possible laser fluence, *prompt* fragmentation with molecules containing no special photoactive groups (*e.g.*, fluorescence markers) can be safely excluded even for the peculiar class of dendrictic macroions.

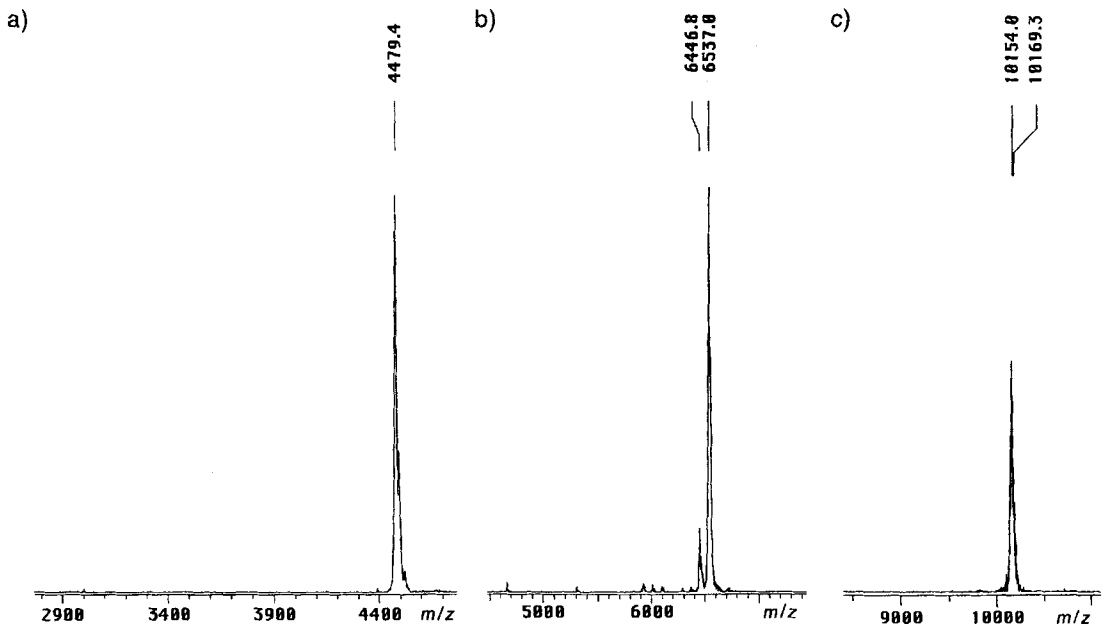


Fig. 2. *Characterization of a bicyclic compound and of two dendrimers by mass spectrometry (MALDI-MS)*: a) *Bicyclic compound* **29** ($C_{210}H_{300}O_{102}$, 4456.6 $gmol^{-1}$; $[M + Na]^+$, 4479); b) *second generation with 'dimeric' 3-HB elongation unit and R = Bn* (**83**: $C_{342}H_{384}O_{126}$, 6510.7 $gmol^{-1}$; $[M + Na]^+$, 6537; the signal at 6447 corresponds to $[M + Na - Bn]^+$); c) *second generation with 'tetrameric' 3-HB elongation unit and R = Bn* (**84**: $C_{510}H_{640}O_{210}$, 10130.5 $gmol^{-1}$; $[M + Na]^+$, 10153).

cleavage with β-elimination (crotonization)[13]), MALDI-MS spectra showing the molecular ion, and not fragment ions, could be observed (examples are shown in *Fig. 2*)[14]). By contrast, electron spray ionization MS (ESI-MS) would not easily create the necessary charge numbers with these compound classes, in order to bring them into the observable m/z range imposed by most quadrupole instruments.

A new technique in *structural* mass spectroscopy, for which the terms post source decay (PSD) [31] and *FAST*™-MS have been coined, may be applied to the structure confirmation of dendrimers of lower mass. By measuring the kinetic energy of metastable fragment ions in a reflectron TOF analyzer, complete sequence information can be obtained from synthetically pure precursors up to 3 kDa. The extension of PSD to even higher m/z values will be a challenge [32]. Preliminary results obtained with two linear 3-HB derivatives and with a core and a branch building block are shown in *Fig. 3*. The fragmentation is induced by the complexed sodium ion, which is retained in all product

[13]) PHB depolymerizes thermally to crotonic acid at 180–200°.

[14]) Even milder conditions can be achieved through the technique of delayed ion extraction (DE) [30]. DE enhances the yield of cationization and improves substantially the linear TOF mass resolution. DE-MALDI holds great promise for the analysis of dendritic macroions. Our MALDI instrument (a *Bruker Reflex*™ TOF-MS) is currently being upgraded for delayed ion extraction, high-resolution operation, and precursor ion preselection, allowing DE-*FAST*™-MS/MS of mixtures.

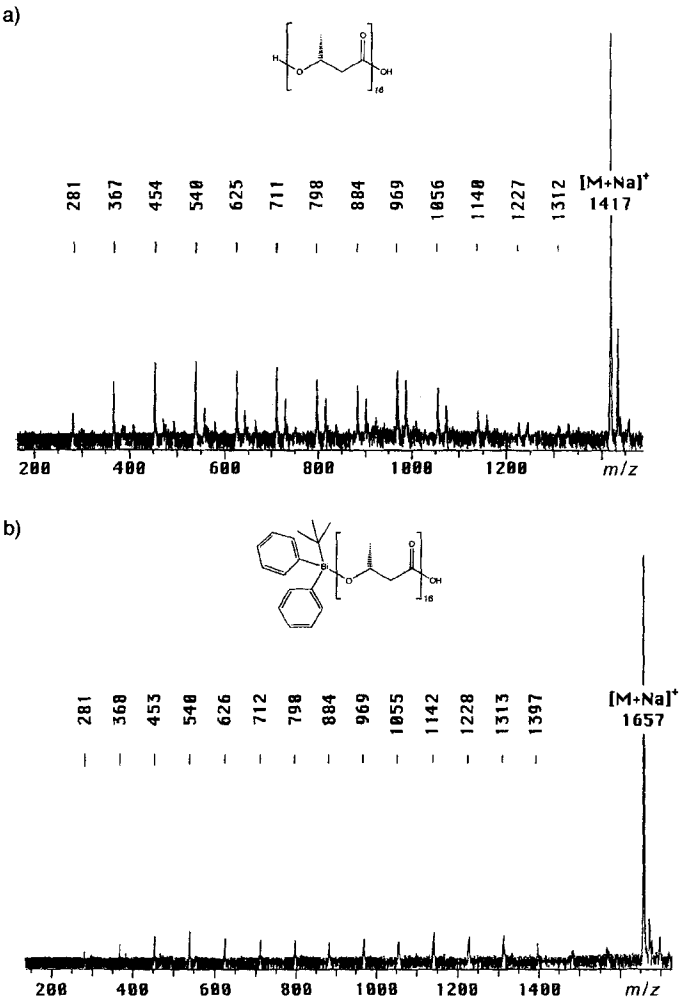
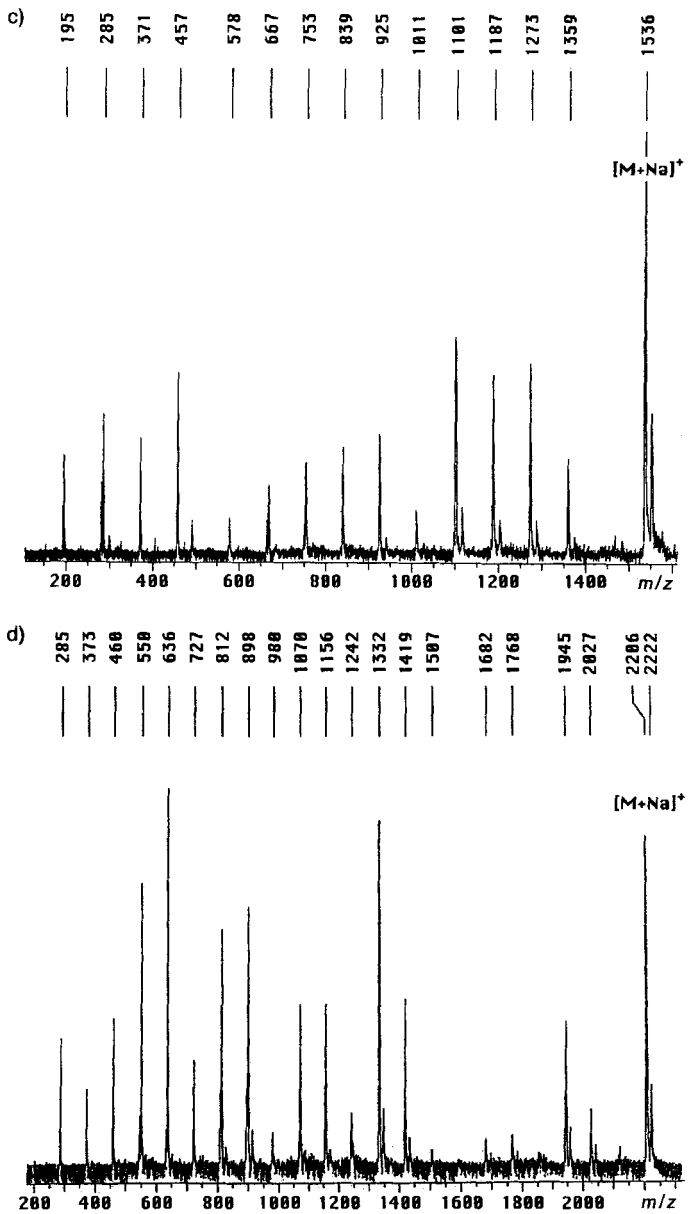


Fig. 3. *PSD-MALDI-MS/MS Spectra of two 16mer 3-HB derivatives and of dendrimer building blocks.* a) *Deprotected 16mer* (as $C_{64}H_{98}O_{33}Na^+$, 1417.6; below the molecular ions $[M + Na]^+$ and $[M + K]^+$, there are fragment ions corresponding to cleavage of 3-HB units ($OCH(Me)CH_2CO$ has a mass of 86), all of which appear as sodiated/potassiated pairs); b) *(t-Bu)Ph_2Si-protected 16mer* (as $C_{80}H_{116}O_{33}SiNa^+$, 1656.6; below the molecular ion, we see the mass peak of $[M + Na - (t\text{-Bu})Ph_2SiOH]^+$ (1397; calc. 1399), and from there on an almost monotonous series of peaks differing by 86 mass units); c) core unit **15** (as $C_{78}H_{96}O_{30}Na^+$, 1537.0; the fragment at highest mass is $[M + Na - BnOCOCH = CHMe]^+$ (1359; calc. 1359.3), and then three 3-HB units (mass 86) are lost; the fragments resulting up to this point all show up as sodiated/potassiated pairs; next a $PhCH_2$ group is lost, followed by a cascade of four HB losses, and all the corresponding signals come from sodiated ions only; the further fragmentation is less clear and is not commented); d) *compound* **78** (as $C_{119}H_{134}O_{37}SiNa^+$, 2206.0); a possible interpretation of the major fragments observed here is as follows: loss of HB-HB-Bn leads to an ion $[M + Na - Me\text{-}CH = CHCOOCHMeCH_2CO_2Bn]^+$ (1945; calc. 1942.0), then the entire rest of the branch falls off, *i.e.*, the branching unit with 4 3-HB units and the attached $PhCH_2$ group (remaining fragment at 1332; calc. 1331.4); further peaks at lower mass can be derived as arising from losses of 3-HB units (86), of $PhCH_2$ groups (91), and loss of $CH_2C_6H_3(CO_2)_2$ (177).



ions, and only lowest-energy pathways are taken (such as crotonate elimination or cleavage of benzylic CO bonds). Most interestingly, the hierarchic organization of the model compounds studied here is revealed by the relative PSD intensities; it is possible to deduce the stepwise loss of units from the oligo(3-HB) chains in these molecules, and it is interesting to note that the K^+ adducts yield much fewer metastable fragments then the Na^+ adducts (see *Fig. 3*).

We would like to express our gratitude to *Zeneca Bio Products* (Billingham, GB) for supplying us with P(3-HB), and we thank *FMC Corporation* (Bessemer City, USA) for a generous donation of (*t*-Bu)Ph_2SiCl. *G.F.H.* would like to thank the *Deutsche Forschungsgemeinschaft* for generous financial support through a *Forschungsstipendium*. We gratefully acknowledge the assistance of *B. Brandenberg*, *M. Bollhalder* and Prof. *B. Jaun* (NMR service) and of *H. U. Hediger* and *R. Häfliger* (MS service). We thank *M. G. Fritz* for supplying generous samples of the tetramer **3** used for the dendrimer syntheses described here. We also gratefully acknowledge the help of *S. Sigrist*, *M. G. Fritz*, *R. Formisano*, *Ch. Krell*, *S. Poenaru*, and *P. Waser* in preparing and proof-reading the manuscript.

Experimental Part

1. *Abbreviations*: CCA (α-Cyano-4-hydroxycinnamic acid), DMAP (4-(dimethylamino)pyridine), EI-MS (electron-ionization mass spectrometry), FAB (fast-atom bombardment), FC (flash chromatography), FmOH ((9*H*-fluoren-9-yl)methanol), *GP* (general procedure), h.v. (high vacuum, 10^{-4}–10^{-6} mbar), *i.v.* (*in vacuo*). LSI-MS (liquid source ionization mass spectrometry), MALDI-MS (matrix-assisted laser desorption ionization mass spectrometry), PSD (post-source decay).

2. *General.* All solvents were either *puriss p.a.* quality or distilled over appropriate drying reagents. CH_2Cl_2 and pyridine (*Fluka, puriss.*) were stored over 4-Å molecular sieves. For h.v. $< 10^{-4}$ mbar a turbomolecular pump *Balzers TSH065* was employed. Compounds **1**–**12** were synthesized as described in [10]. TLC: *Merck* silica gel *60* F_{254} anal. plates; detection either with UV or by dipping into a soln. of I_2 (30 g), KI (2 g), EtOH (200 ml), and H_2O (200 ml), and drying in the air. FC: *Merck* silica gel *60* (40–63 μm). M.p.: open capillaries; uncorrected. Optical rotations: 10-cm, 1-ml cell, at r.t.; *Perkin-Elmer-241* polarimeter. IR Spectra: *Perkin-Elmer-983* or *-1600 FT* spectrophotometer in $CHCl_3$. NMR Spectra: *Bruker-AMX-II-500* (500 (^{1}H) and 125 MHz (^{13}C)), *-AMX-400* (400 (^{1}H) and 100 MHz (^{13}C)), *-ARX-300* (300 (^{1}H) and 75 MHz (^{13}C)), or *Varian-Gemini-200* (200 (^{1}H) and 50 MHz (^{13}C)) spectrometer; in $CDCl_3$ unless other specified. MS: *VG (micromass) TRIBRID* (for EI (70 eV); *VG (micromass) ZAB2-SEQ* for FAB with 3-nitrobenzyl alcohol as matrix; and *Bruker Reflex MALDI-TOF* spectrometer for MALDI-TOF, all PSD spectra in CCA matrix by decreasing the reflector voltage in 10–12 steps with 30–50 laser shots in each segment, data combined and calibrated using *FAST*™ software from *Bruker*. Elemental analyses were conducted by the Microanalytical Laboratory of the Laboratorium für Organische Chemie, ETH-Zürich.

3. *General Procedure for the Generation of Acid Chlorides* (*GP I*) [14]. The acid (1 equiv.) was dissolved in *x* ml of CH_2Cl_2 in a round-bottomed flask with bubble trap, and subsequently oxalyl chloride (1.5 equiv.) was added at r.t. The soln. was stirred until formation of gas had ceased (2 to 8 h). The volatile components were then removed *i.v.* at r.t., and the obtained yellowish oil or solid was dried under h.v. for several hours. The corresponding ^{1}H-NMR exhibited a downfield shift of the signals of the terminal CH_2 compared to the corresponding free acid (*ca.* 0.4 ppm).

4. *General Procedure for the Coupling of the Acid Chlorides with the Corresponding Alcohols* (*GP II*) [15]. The crude, well-dried acid chloride was dissolved in *x* ml of CH_2Cl_2 and subsequently cooled to −78° in an acetone/dry-ice slush or to 0° in an ice bath. After addition of 1 equiv. of alcohol in *y* ml of CH_2Cl_2, 1.5 equiv. of pyridine in *z* ml of CH_2Cl_2 were added dropwise through a syringe in small portions over the given time period. If addition of pyridine took more than 3 h, a syringe pump (ETH) was employed. The reaction was exothermic. Depending on the concentration of the soln., a precipitation of a white solid occurred, which was dissolved by addition of further solvent. Subsequently the mixture was allowed to warm up to r.t. within 12–18 h, followed by stirring at r.t. for 2 to 10 h (monitoring by either TLC (Et_2O/pentane) or ^{1}H-NMR). After addition of Et_2O, the org. layer was washed with 1N HCl, aq. sat. $NaHCO_3$ soln., and aq. sat. NaCl soln., dried ($MgSO_4$), and evaporated. The crude products were purified as described.

5. *General Procedure for the Hydrogenations* (*GP III*). The benzyl-ester-protected oligomer or bicyclic or dendritic structure was dissolved in MeOH, AcOEt, or CF_3CH_2OH, then Pd/C (10%) was added, and hydrogenation was carried out under H_2 (balloon) with vigorous stirring. The reactions went to completion within 2 to 5 h (TLC (Et_2O/pentane 1:1) or ^{1}H-NMR monitoring). The slightly yellow soln. was filtered through *Celite* and dried *i.v.* The obtained oils or solids were used for further coupling without purification.

6. *General Procedure for the Cleavage of the* (t-*Bu*)Ph_2Si *Groups* (*GP IV*) [33]. The fully protected oligomer or bicyclic or dendritic compound was dissolved in *x* ml of CH_2Cl_2 in a polyethylene bottle and cooled to 0°; *y* ml of a 70% HF soln. in pyridine were added with a syringe, and the mixture was vigorously stirred (HF · pyridine does not dissolve in CH_2Cl_2; without vigorous stirring the protective groups are not cleaved). After 20 min, the mixture was diluted with double the amount of H_2O, then Et_2O was added and the soln. washed with H_2O

(3 times), aq. sat. $NaHCO_3$ soln. (2 times), and aq. sat. NaCl soln. After drying ($MgSO_4$) and evaporating the solvents *i.v.* slighlty red oils or solids were obtained, which still contained 1 equiv. of (*t*-Bu)Ph_2SiF and which were used for further coupling mostly without additional purification.

7. *Synthesis of the Bicyclic Structures*[4]) **27–29** *and* **68–70**. *Tris[(1*R*)-(benzyloxy)-1-methyl-3-oxopropyl] Benzene-1,3,5-tricarboxylate* (**13**). As described in *GP II*, trimesoyl trichloride (2.45 g, 9.2 mmol) was dissolved in CH_2Cl_2 (50 ml) and **9** (5.4 g, 27.8 mmol) was added, followed by the dropwise addition of pyridine (2.5 ml). The mixture was then stirred for 12 h at r.t. Workup as described in *GP II*. FC (SiO_2 (300 g), CH_2Cl_2): 5.48 g (6.9 mmol; 75%) of **13**. Colorless, viscous oil. $[\alpha]_D^{r.t.} = -47.4$, $[\alpha]_{365}^{r.t.} = -176.6$ ($c = 1.335$, CH_2Cl_2). IR: 3056*m*, 2989*w*, 1732*vs*, 1607*w*, 1498*w*, 1456*s*, 1383*m*, 1302*s*, 1142*s*, 1102*s*, 1055*vs*, 974*m*, 955*s*, 838*w*. ^{1}H-NMR (300 MHz): 8.69 (*s*, 3 arom. H); 7.32–7.20 (*m*, 15 arom. H); 5.66–5.55 (*m*, 3 CH); 5.14, 5.10 (3 *AB*, $J_{AB} = 12.21$); 2.89, 2.72 (3 *AB* of *ABX*, $J_{AB} = 15.69$, $J_{AX} = 7.74$, $J_{BX} = 5.45$); 1.45 (*d*, $J = 6.33$, 3 Me). ^{13}C-NMR (75 MHz): 169.88; 164.12; 135.54; 134.53; 131.23; 128.51; 128.31; 69.89; 66.61; 40.85; 20.03. LSI-MS: 751.1 (1.4), 545.0 (20), 271.1 (9.4), 193.0 (18), 181.1 (33), 90.9 (100). Anal. calc. for $C_{42}H_{42}O_{12}$: C 68.28, H 5.73; found: C 68.28, H 5.85.

*Tris{(1*R*)-3-[(1*R*)-3-(benzyloxy)-1-methyl-3-propoxy]-1-methyl-3-oxopropyl} Benzene-1,3,5-tricarboxylate* (**14**). As described in *GP II*, trimesoyl trichloride (2.25 g, 8.87 mmol) was dissolved in CH_2Cl_2 (60 ml) and **10** (7.44 g, 26.63 mmol) was added. After dropwise addition of pyridine (4.31 ml), stirring was continued for 27 h at r.t. Workup as described in *GP II*. FC SiO_2 (430 g, CH_2Cl_2/Et_2O 20:1): 6.58 g (6.61 mmol; 74.6%) of **14**. Colorless, viscous oil. R_f 0.67 (CH_2Cl_2/Et_2O 20:1). $[\alpha]_D^{r.t.} = -28.8$ ($c = 1.53$, CH_2Cl_2). IR: 3032*m*, 2986*w*, 2937*w*, 1734*vs*, 1607*w*, 1498*w*, 1456*m*, 1383*s*, 1303*s*, 1248*s*, 1136*s*, 1101*s*, 1056*vs*, 972*m*, 952*s*, 837*w*. ^{1}H-NMR (400 MHz): 8.75 (*s*, 3 arom. H); 7.26–7.36 (*m*, 15 arom. H); 5.54–5.45 (*m*, 3 CH); 5.34–5.26 (*m*, 3 CH); 5.08 (*d*, $J = 1.92$, 3 CH_2); 2.75–2.49 (*m*, 6 CH_2); 1.40 (*d*, $J = 6.32$, 3 Me); 1.24 (*d*, $J = 6.33$, 3 Me). ^{13}C-NMR (100 MHz): 169.87; 169.08; 164.05; 135.70; 134.54; 131.40; 128.58; 128.36; 128.33; 68.83; 67.77; 66.47; 40.89; 40.66; 19.86; 19.83. LSI-MS: 998.7 (2.56), 997.5 (6.0), 541.29 (11.5), 455.2 (21.1), 369.1 (15.3), 271.2 (46.1), 181.1 (100). Anal. calc. for $C_{54}H_{60}O_{18}$: C 65.05, H 6.07; found: C 64.88, H 5.94.

*Tris[(1*R*,5*R*,9*R*,13*R*)-1,5,9,13-tetramethyl-3,7,11,15-tetraoxo-17-phenyl-4,8,12,16-tetraoxaheptadecyl] Benzene-1,3,5-tricarboxylate* (**15**). As described in *GP II*, trimesoyl trichloride (0.53 g, 2 mmol) was dissolved in CH_2Cl_2 (60 ml), and **11** (4.83 g, 7 mmol) was added at 0°. Then, pyridine (1.94 ml) was added in 0.1-ml portions within 30 min, stirring was continued for 24 h at r.t. Workup as described in *GP II*. Two FC (SiO_2 (97 g), CH_2Cl_2/Et_2O 7:1; SiO_2 (100 g), CH_2Cl_2/Et_2O 6:1): 1.33 g (0.88 mmol; 43.9%) of **15**. Colorless, viscous oil. R_f 0.58 (CH_2Cl_2/Et_2O 7:1); 0.49 (CH_2Cl_2/Et_2O 6:1). $[\alpha]_D^{r.t.} = -15.95$ ($c = 1.235$, CH_2Cl_2). IR: 3032*m*, 2986*m*, 2936*w*, 1734*vs*, 1498*w*, 1456*m*, 1383*s*, 1178*s*, 1100*s*, 1057*s*, 977*m*, 826*w*. ^{1}H-NMR (400 MHz): 8.67 (*s*, 3 arom. H); 7.48–7.28 (*m*, 15 arom. H); 5.57–5.49 (*m*, 3 CH); 5.32–5.17 (*m*, 9 CH); 5.11 (*s*, 3 CH_2); 2.83–2.35 (*m*, 12 CH_2); 1.44 (*d*, $J = 6.31$, 3 Me); 1.37–1.21 (*m*, 9 Me). ^{13}C-NMR (100 MHz): 169.92; 169.18; 169.13; 169.06; 164.05; 135.73; 134.54; 134.46; 134.43; 131.4; 130.26; 128.59; 127.9; 68.88; 67.7; 66.47; 58.47; 40.94; 40.68; 26.00; 19.90; 19.80; 19.78; 19.72; 18.44. LSI-MS: 1551.67 (5.3, $[M + K]^+$), 1535.7 (20.5, $[M + Na]^+$), 1515.05 (9.6, $[M + H]^+$), 1513.6 (21.1, M^+), 155.03 (100). MALDI-MS: 1552.4 ($[M + K]^+$), 1536.4 ($[M + Na]^+$). Anal. calc. for $C_{78}H_{96}O_{30}$: C 61.90, H 6.39; found: C 61.68, H 6.46.

*Tris[(1*R*,5*R*,9*R*,13*R*,17*R*,21*R*,25*R*,29*R*)-1,5,9,13,17,21,25,29-octamethyl-3,7,11,15,19,23,27,31-octaoxo-33-phenyl-4,8,12,16,20,24,28,32-octaoxatritriacontyl] Benzene-1,3,5-tricarboxylate* (**16**). As described in *GP II*, to a soln. of trimesoyl trichloride (406 mg, 1.53 mmol) in CH_2Cl_2 (100 ml) was added **12** (4.84 g, 4.59 mmol, containing 1 equiv. (*t*-Bu)Ph_2SiF. At 0°, pyridine (1.0 ml) was added dropwise, the mixture was stirred for 18 h at r.t. Workup as described in *GP II*. FC (SiO_2 (400 g), CH_2Cl_2/Et_2O 4:1): 780 mg (306 μmol; 20%) of **16**. Colorless, viscous oil. $[\alpha]_D^{r.t.} = -35.9$, $[\alpha]_{365}^{r.t.} = -12.6$ ($c = 0.57$, CH_2Cl_2). IR: 3038*w*, 2983*w*, 1738*vs*, 1456*w*, 1383*m*, 1306*m*, 1179*s*, 133*m*, 1102*m*, 1058*s*. ^{1}H-NMR (400 MHz): 8.76 (*s*, 3 arom. H); 7.38–7.30 (*m*, 15 arom. H); 5.59–5.51 (*m*, 3 CH); 5.33–5.20 (*m*, 21 CH); 5.12 (*s*, 3 CH_2); 2.85–2.37 (*m*, 24 CH_2); 1.45 (*d*, $J = 6.32$, 3 Me); 1.29–1.23 (*m*, 21 Me). ^{13}C-NMR (100 MHz): 169.91; 169.15; 169.04; 164.05; 135.72; 134.55; 131.40; 128.60; 128.35; 68.90; 67.71; 67.61; 66.49; 40.96; 40.80; 40.68; 19.92; 19.82; 19.77; 19.73. LSI-MS: 2585.5 (15, $[M + K]^+$), 2569.8 (100, $[M + Na]^+$), 2547.7 (4.9, $[M + Na]^+$). Anal. calc. for $C_{126}H_{168}O_{54}$: C 59.43, H 6.85; found: C 59.40, H 6.47.

*(Benzene-1,3,5-triyl)tris{(methyleneoxy)[(1*R*)-1-methyl-3-oxopropane-3,1-diyl]} Tris-{(3*R*)-3-{[(*tert*-butyl)-diphenylsilyl]oxy}butanoate}* (**17**) *and [5-(Hydroxymethyl)-1,3-phenylene]bis{(methyleneoxy)[(1*R*)-1-methyl-3-oxopropane-3,1-diyl]} Bis{(3*R*)-3-{[(*tert*-butyl)diphenylsilyl]oxy}butanoate}* (**19**). Synthesis of the acid chloride as described in *GP I*, with **6** (6.30 g (14.7 mmol) in CH_2Cl_2 (40 ml). Coupling as described in *GP II*, by adding to the acid chloride (in 30 ml CH_2Cl_2) a soln. of benzene-1,3-5-trimethanol (820 mg, 4.9 mmol; in 10 ml of CH_2Cl_2/MeCN 1:1) at –78°. Two FC (SiO_2 (400 g), CH_2Cl_2/Et_2O 10:1; SiO_2 (300 g), Et_2O/pentane 1.6:1) yielded 5.1 g (3.65 mmol; 74%) of **17** as a colorless, viscous oil and 830 mg (893 μmol; 17%) of **19** as a colorless oil.

Data of **17**: $[\alpha]_D^{r.t.} = +1.24$, $[\alpha]_{365}^{r.t.} = +6.01$ ($c = 1.205$, CH_2Cl_2). IR: 2964*m*, 2932*m*, 2859*m*, 1736*vs*, 1589*w*, 1462*w*, 1428*m*, 1381*m*, 1303*s*, 1177*vs*, 1111*vs*, 1006*s*, 909*m*, 822*m*. ^{1}H-NMR (400 MHz): 7.68–7.64 (*m*, 12 arom. H); 7.43–7.31 (*m*, 21 arom. H); 5.27–5.18 (*m*, 3 CH); 5.07, 5.04 (3 *AB*, $J_{AB} = 12.57$); 4.29–4.21 (*m*, 3 CH); 2.65, 2.50 (3 *AB* of *ABX*, $J_{AB} = 15.67$, $J_{AX} = 6.93$, $J_{BX} = 6.28$); 2.49, 2.35 (3 *AB* of *ABX*, $J_{AB} = 14.50$, $J_{AX} = 5.84$, $J_{BX} = 6.72$); 1.22 (*d*, $J = 6.31$, 3 Me); 1.10 (*d*, $J = 6.12$, 3 Me); 1.03 (*s*, 3 *t*-Bu). ^{13}C-NMR (100 MHz): 170.33; 169.85; 136.62; 135.81; 135.80; 134.22; 133.89; 129.65; 129.59; 127.82; 127.57; 127.51; 67.14; 66.71; 65.76; 44.62; 40.61; 26.90; 23.39; 19.80; 19.15. LSI-MS: 1532.6(3.0), 1421.4(5), 1412.1(53.2), 1341.2(24), 1321.2(23), 503.0(50), 457.0(94), 413.0(59), 323.0(78), 239.0(81), 197.0(85), 135.0(82), 68.9(100).

Data of **19**: $[\alpha]_D^{r.t.} = -0.4$, $[\alpha]_{365}^{r.t.} = 1.37$ ($c = 1.52$, CH_2Cl_2). IR: 3073*w*, 2965*w*, 2932*m*, 2859*w*, 1736*vs*, 1473*w*, 1461*w*, 1428*m*, 1382*m*, 1303*m*, 1179*s*, 1111*s*, 1059*m*, 1005*m*, 822*w*, 612*m*. ^{1}H-NMR (400 MHz): 7.68–7.64 (*m*, 4 arom. H); 7.43–7.33 (*m*, 6 arom. H); 7.28 (*s*, 2 arom. H); 7.19 (*s*, 1 arom. H); 5.27–5.19 (*m*, 2 CH); 5.09, 5.05 (*AB*, $J_{AB} = 12.48$, $2CH_2O$); 4.67 (*s*, CH_2O); 4.28–4.20 (*m*, 2 CH); 2.64, 2.50 (2 *AB* of *ABX*, $J_{AB} = 15.55$, $J_{AX} = 7.21$, $J_{BX} = 5.98$); 2.46, 2.33 (2 *AB* of *ABX*, $J_{AB} = 14.52$, $J_{AX} = 5.82$, $J_{BX} = 6.76$); 1.22 (*d*, $J = 6.32$, 2 Me); 1.09 (*d*, $J = 6.13$, 2 Me); 1.03 (*s*, *t*-Bu). ^{13}C-NMR (100 MHz): 170.42; 169.85; 141.96; 136.42; 135.79; 135.77; 134.20; 133.90; 129.63; 129.57; 127.56; 127.49; 126.99; 126.46; 67.21; 66.69; 65.91; 64.69; 44.60; 40.72; 26.88; 23.34; 19.82; 19.13. Anal. calc. for $C_{57}H_{72}O_{11}Si_2$: C 69.20, H 7.34; found: C 69.26, H 7.17.

*(Benzene-1,3,5-triyl)trimethyl Tris[(3*R*,7*R*,11*R*,15*R*,19*R*,23*R*,27*R*,31*R*)-3,7,11,15,19,23,27,31,34,34-decamethyl-1,5,9,13,17,21,25,29-octaoxo-4,8,12,16,20,24,28,32-octaoxa-33-silapentatriacontanoate]* (**18**) *and [5-(Hydroxymethyl)-1,3-phenylene]dimethyl Bis[(3*R*,7*R*,11*R*,15*R*,19*R*,23*R*,27*R*,31*R*)-3,7,11,15,19,23,27,31,34,34-decamethyl-1,5,9,13,17,21,25,29-octaoxo-4,8,12,16,20,24,28,32-octaoxa-33-silapentatriacontanoate]* (**20**). Synthesis of the acid chloride as described in *GP I*, with **8** (3.57 g, 3.7 mmol) in CH_2Cl_2 (80 ml). Coupling as described in *GP II*, with benzene-1,3-5-trimethanol (207 mg, 1.22 mmol dissolved in MeCN (10 ml) in CH_2Cl_2 (80 ml). The coupling was carried out at −78°. FC (SiO_2 (200 g), CH_2Cl_2/Et_2O 5:1): 1.81 g (596 μmol; 49%) of **18** as a colorless, viscous oil and 580 mg (278 μmol; 23%) of **20** as a colorless oil.

Data of **18**: $[\alpha]_D^{r.t.} = -1.1$, $[\alpha]_{365}^{r.t.} = 5.0$ ($c = 0.855$, CH_2Cl_2). IR: 3010*w*, 2985*m*, 2935*w*, 2858*w*, 1736*vs*, 1459*w*, 1428*w*, 1383*s*, 1304*s*, 1265*s*, 1179*vs*, 1132*m*, 1103*s*, 1058*vs*. ^{1}H-NMR (400 MHz): 7.68–7.65 (*m*, 12 arom. H); 7.44–7.33 (*m*, 18 arom. H); 7.29 (*s*, 3 arom. H); 5.52–5.14 (*m*, 21 CH); 5.12, 5.10 (3 *AB*, $J_{AB} = 12.46$); 4.30–4.22 (*m*, 3 CH); 2.73–2.34 (*m*, $24CH_2$); 1.29–1.21 (*m*, 21 Me); 1.11 (*d*, $J = 6.21$, 3 Me); 1.03 (*s*, 3 *t*-Bu). ^{13}C-NMR (100 MHz): 170.31; 169.81; 169.20; 169.15; 136.67; 135.82; 135.81; 134.26; 133.93; 129.66; 129.59; 127.93; 127.59; 127.51; 67.60; 67.52; 67.18; 66.71; 65.86; 53.43; 44.60; 40.88; 40.86; 40.81; 40.54; 26.91; 23.42; 19.84; 19.77; 19.74; 19.16. LSI-MS: 3081.8 (100, $[M + Cs]^+$), 2972.1(57, $[M + Na]^+$). Anal. calc. for $C_{153}H_{210}O_{51}Si_3 \cdot CH_2Cl_2$: C 60.96, H 7.04; found: C 60.75, H 7.04.

Data of **20**: $[\alpha]_D^{r.t.} = -2.5$, $[\alpha]_{365}^{r.t.} = -0.5$ ($c = 1.46$, CH_2Cl_2). IR: 3034*w*, 2983*w*, 2935*w*, 2851*w*, 1738*vs*, 1458*w*, 1428*w*, 1383*m*, 1305*s*, 1179*vs*, 1133*m*, 1103*s*, 1058*s*. ^{1}H-NMR (400 MHz): 7.68–7.65 (*m*, 8 arom. H); 7.44–7.35 (*m*, 12 arom. H); 7.32 (*s*, 2 arom. H); 7.22 (*s*, 1 arom. H); 5.35–5.14 (*m*, 14 CH); 5.12, 5.10 (2 *AB*, $J_{AB} = 12.44$); 4.70 (*d*, $J = 5.73$, CH_2); 4.30–4.22 (*m*, 2 CH); 2.71–2.34 (*m*, $16CH_2$); 1.29–1.21 (*m*, 14 Me); 1.11, (*d*, $J = 6.11$, 2 Me); 1.03 (*s*, 2 *t*-Bu). ^{13}C-NMR (100 MHz): 170.33; 169.83; 169.24; 169.22; 169.20; 169.17; 169.16; 142.34; 136.38; 135.82; 135.81; 134.26; 133.93; 129.67; 129.59; 127.59; 127.51; 127.09; 126.55; 67.68; 67.62; 67.53; 67.19; 66.71; 66.06; 64.58; 53.43; 44.60; 40.88; 40.80; 40.66; 26.91; 23.42; 19.88; 19.77; 19.73; 19.71; 19.16. LSI-MS: 2154.8 (100, $[M + Cs]^+$), 2047.0 (19, $[M + Na]^+$). Anal. calc. for $C_{105}H_{144}O_{35}Si_2$: C 62.36, H 7.18; found: C 62.60, H 6.91.

*3,3′,3″-[(Benzene-1,3,5-triyl)tris(carbonyloxy)]tris[(3*R*)-butanoic Acid]* (**21**). As described in *GP III*, a soln. of **13** (5.08 g, 6.88 mmol) in $MeOH/CF_3CH_2OH$ 3:7 (100 ml) was hydrogenated. Careful drying at 10^{-5} mbar: 3.13 g (6.67 mmol; 97%) of **21**. White solid (pure according to the ^{1}H-NMR). M.p. 159.5–160.5°. $[\alpha]_D^{r.t.} = -63.1$, $[\alpha]_{365}^{r.t.} = -192.9$ ($c = 1.27$, $CHCl_3$). IR: 3500–2500 (br.), 3040*m*, 2987*m*, 1725*vs*, 1448*w*, 1383*w*, 1141*m*, 1054*s*, 960*m*, 837*w*. ^{1}H-NMR (300 MHz, CD_3OD): 8.75 (*s*, 3 arom. H); 5.58–5.47 (*m*, 3 CH); 2.83, 2.72 (3 *AB* of *ABX*, $J_{AB} = 15.96$, $J_{AX} = 8.00$, $J_{BX} = 5.24$); 1.46 (*d*, $J = 6.33$, 3 Me). ^{13}C-NMR (75 MHz, CD_3OD): 173.95; 165.50; 135.14; 132.97; 70.75; 41.39; 20.03. LSI-MS: 981.2(3.7), 959.2(5.5), 937.2(5.1), 491.1(75), 469.1(13), 365.0(100), 279.0(40), 193.0(39). Anal. calc. for $C_{21}H_{24}O_{12}$: C 53.85, H 5.16; found: C 53.26, H 5.07.

*3,3′,3″-{(Benzene-1,3,5-triyl)tris{(carbonyloxy)[(3*R*)-3-methyl-1-oxopropane-3,1-diyl-1-oxy]}}tris[(3*R*)-butanoic Acid]* (**22**). As described in *GP III*, a soln. of **14** (3.25 g, 3.25 mmol) in CF_3CH_2OH (100 ml) was hydrogenated. Co-evaporation of the CF_3CH_2OH with 1,2-dichloroethane and careful drying for 18 h at 10^{-6} mbar: 2.32 g (3.2 mmol; 98%) of **22**. Wax-like solid (pure according to ^{1}H-NMR). $[\alpha]_D^{r.t.} = -65.95$ ($c = 1.175$, CH_2Cl_2). IR: 3032*m*, 2987*m*, 2936*w*, 1734*vs*, 1448*w*, 1383*m*, 1303*w*, 1248*vs*, 1138*vs*, 1101*s*, 1054*m*, 974*m*. ^{1}H-NMR (400 MHz): 8.75 (*s*, 3 arom. H); 5.60–5.52 (*m*, 3 CH); 5.38–5.30 (*m*, 3 CH); 2.84–2.46 (*m*, $6CH_2$); 1.43 (*d*, $J = 6.31$, 3 Me); 1.28–1.23 (*d*, $J = 6.37$, 3 Me). ^{13}C-NMR (100 MHz): 174.34; 169.66;

164.73; 134.87; 131.10; 69.67; 67.33; 41.15; 40.16; 20.06; 19.93. LSI-MS: 1453.8(2.6, $[2M + H]^+$), 749.4(100, $[M + Na]^+$), 727.4(95, $[M + H]^+$), 537.3(8.46), 451.3(21.91), 365.2(33.96), 279.1(23.91), 193.1(15.7), 137.1(66.11). Anal. calc. for $C_{33}H_{42}O_{18} \cdot C_2H_4Cl_2$ ($C_{34}H_{46}O_{18}Cl_2$): C 51.04, H 5.38; found: C 51.43, H 5.80.

*3,3',3''-{(Benzene-1,3,5-triyl)tris{(carbonyloxy){(3*R*)-3-methyl-3-{(3*R*)-3-methyl-3-[(3*R*)-3-methyl-1-oxopropane-3,1-diyl-1-oxy]}-1-oxopropane-3,1-diyl-1-oxy}-1-oxopropane-3,1-diyl-1-oxy}}tris[(3*R*)-butanoic Acid]* (**23**). As described in *GP III*, a soln. of **15** (660 mg, 0.436 mmol) in CF_3CH_2OH (60 ml) was hydrogenated. Co-evaporation of the CF_3CH_2OH with 1,2-dichloroethane and careful drying for 18 h at 10^{-6} mbar: 480 mg (0.384 mmol; 88%) of **23**. Wax-like solid (pure according to ^{1}H-NMR). $[\alpha]_D^{r.t.} = -23.39$ ($c = 1.265$, CH_2Cl_2). IR: 3032*m*, 2987*m*, 2936*w*, 1735*vs*, 1448*w*, 1383*m*, 1305*m*, 1248*vs*, 1136*m*, 1102*m*, 1055*s*, 975*w*. ^{1}H-NMR (400 MHz): 8.77 (*s*, 3 arom. H); 5.60–5.52 (*m*, 3CH); 5.28–5.18 (*m*, 9CH); 2.86–2.41 (*m*, 12CH_2); 1.45 (*d*, J = 6.31, 3Me); 1.31–1.22 (*m*, 9Me). ^{13}C-NMR (100 MHz): 174.67; 169.55; 169.39; 169.26; 164.18; 134,61; 131.32; 68.89; 67.95; 67.68; 67.62; 40.86; 40.80; 40.74; 40.56; 19.88; 19.81; 19.71. LSI-MS: 1267.7(18.9, $[M + 2H + Na]^+$), 1266.7(25.43, $[M + H + Na]^+$), 1265.6(73.1, $[M + Na]^+$), 519.1(6.17), 451.0(17.30), 365.1(29.83), 279.0(21.17), 195.1(12.67), 155.1(100). Anal. calc. for $C_{57}H_{78}O_{30} \cdot CH_2Cl_2$ ($C_{58}H_{80}O_{30}Cl_2$): C 52.45, H 6.07; found: C 52.28, H 6.03.

*33,33',33''-(Benzene-1,3,5-triyl)tris[(3*R*,7*R*,11*R*,15*R*,19*R*,23*R*,27*R*,31*R*)-3,7,11,15,19,23,27,31-octamethyl-5,9,13,17,21,25,29,33-octaoxo-4,8,12,16,20,24,28,32-octaoxatritriacontanoic Acid]* (**24**). As described in *GP III*, a soln. of **16** (600 mg, 236 µmol) in CF_3CH_2OH (20 ml) was hydrogenated. Careful drying at 10^{-5} mbar: 490 mg (215 µmol; 91%) of **24**. Wax-like solid (pure according to ^{1}H-NMR). $[\alpha]_D^{r.t.} = -16.2$, $[\alpha]_{365}^{r.t.} = -44.8$ ($c = 0.605$, CH_2Cl_2). IR: 3010*w*, 2986*m*, 2937*w*, 1738*vs*, 1458*w*, 1383*s*, 1306*vs*, 1179*vs*, 1137*s*, 1102*m*, 1057*vs*. ^{1}H-NMR (400 MHz): 8.76 (*s*, 3 arom. H); 5.57–5.51 (*m*, 3CH); 5.31–5.20 (*m*, 21 CH); 2.85–2.43 (*m*, 24CH_2); 1.45 (*d*, J = 6.31, 3Me); 1.28–1.23 (*m*, 21 Me). ^{13}C-NMR (100 MHz): 174.71; 169.60; 169.56; 169.41; 169.38; 169.35; 169.30; 169.21; 164.09; 134.57; 131.42; 68.93; 68.31; 67.87; 67.83; 67.77; 67.68; 41.53; 40.94; 40.97; 40.84; 40.80; 19.97; 19.92; 19.82; 19.77; 19.73. LSI-MS: 2342.7(17, $[M - 3 + 3Na]^+$), 2320.7(44, $[M - 2H + 2Na]^+$), 2298.7(100, $[M - H + Na]^+$), 2342.7(0.6, M^+). Anal. calc. for $C_{105}H_{150}O_{54} \cdot 3CF_3CH_2OH$ ($C_{111}H_{159}O_{57}F_9$): C 51.75, H 6.22; found: C 51.48, H 6.19.

*(Benzene-1,3,5-triyl)tris{(methyleneoxy)[(1*R*)-1-methyl-3-oxopropane-3,1-diyl]} Tris[(3*R*)-3-hydroxybutanoate]* (**25**). As described in *GP IV*, to a soln. of **17** (4.52 g, 3.23 mmol) in CH_2Cl_2 (45 ml) was added HF · pyridine (5 ml). Workup and FC (SiO_2 (80 g), Et_2O/pentane 1:1, followed by AcOEt/CH_2Cl_2 5:1): 1.85 g (2.7 mmol; 84%) of **25**. Colorless oil. $[\alpha]_D^{r.t.} = -24.6$, $[\alpha]_{365}^{r.t.} = -72.6$ ($c = 0.96$, CH_2Cl_2). IR: 3534(br.), 3008*m*, 2983*m*, 2935*w*, 1733*vs*, 1613*w*, 1458*m*, 1382*s*, 1303*vs*, 1174*vs*, 1057*vs*, 974*m*, 930*w*, 862*w*. ^{1}H-NMR (400 MHz): 7.30 (*s*, 3 arom. H); 5.39–5.31 (*m*, 3CH); 5.13, 5.12 (3 *AB*, J_{AB} = 12.71); 4.20–4.11 (*m*, 3CH); 3.07 (*s*, 3OH); 2.70, 2.60 (3 *AB* of *ABX*, J_{AB} = 15.68, J_{AX} = 7.95, J_{BX} = 5.07); 2.41, 2.34 (3 *AB* of *ABX*, J_{AB} = 15.88, J_{AX} = 3.65, J_{BX} = 8.60); 1.32 (*d*, J = 6.34, 3Me); 1.20 (*d*, J = 6.30, 3Me). ^{13}C-NMR (100 MHz): 172.00; 170.12; 136.60; 128.03; 67.50; 65.98; 64.40; 43.25; 40.67; 22.50; 19.97. LSI-MS: 707.2(6), 685.2(36), 495.1(7), 305.1(100), 287.1(6), 219.1(37), 203.1(21), 173.1(15), 154.0(36), 137.0(36), 68.9(91). Anal. calc. for $C_{33}H_{48}O_{15}$: C 57.89, H 7.07; found: C 57.81, H 7.10.

*(Benzene-1,3,5-triyl)trimethyl (3*R*,7*R*,11*R*,15*R*,19*R*,23*R*,27*R*,31*R*)-31-Hydroxy-3,7,11,15,19,23,27-heptamethyl-5,9,13,17,21,25,29-heptaoxo-4,8,12,16,20,24,28-heptaoxadotriacontanoate* (**26**). As described in *GP IV*, to a soln. of **18** (1.61 g, 546 µmol) in CH_2Cl_2 (25 ml) was added HF · pyridine (2.5 ml). Workup and FC (SiO_2 (80 g), Et_2O/CH_2Cl_2 1:3 + 0.5 parts MeOH): 1.07 g (480 µmol; 88%) of **26**. White solid. M.p. 53.5–55.0°. $[\alpha]_D^{r.t.} = -11.0$, $[\alpha]_{365}^{r.t.} = -24.2$ ($c = 0.985$, CH_2Cl_2). IR: 3531*w*, 3031*w*, 2986*w*, 2938*w*, 1738*vs*, 1458*w*, 1383*m*, 1304*s*, 1179*s*, 1135*m*, 1058*s*. ^{1}H-NMR (500 MHz): 7.30 (*s*, 3 arom. H); 5.34–5.21 (*m*, 21 CH); 5.12, 5.10 (3 *AB*, J_{AB} = 12.54); 4.20–4.11 (*m*, 3CH); 3.10 (*d*, J = 3.76, 3OH); 2.73–2.37 (*m*, 24CH_2); 1.31–1.25 (*m*, 21 Me); 1.22 (*d*, J = 6.31, 3Me). ^{13}C-NMR (125 MHz): 172.00; 169.83; 169.43; 169.20; 169.17; 136.67; 127.94; 67.75; 67.63; 67.60; 67.54; 65.87; 64.39; 43.27; 40.85; 40.81; 40.54; 22.54; 19.89; 19.84; 19.78; 19.75. LSI-MS: 2257.2(100, $[M + Na]^+$). Anal. calc. for $C_{105}H_{156}O_{51}$: C 56.44, H 7.04; found: C 56.51, H 7.02.

*(6*R*,10*R*,14*R*,28*R*,32*R*,36*R*,43*R*,47*R*,51*R*)-6,10,14,28,32,36,43,47,51-Nonamethyl-5,9,13,17,25,29,33,37,42,46,50,54-dodecaoxatetracyclo[19.19.15.1^{3,38}.1^{19,23}]heptapentaconta-1,3(57),19,21,23(56),39-hexaene-4,8,12,16,26,30,34,38,41,45,49,53-dodecone* (**27**). Synthesis of the acid chloride as described in *GP I*, with **21** (988 mg, 2.1 mmol) in CH_2Cl_2/AcOEt 6:1 (35 ml). After careful drying at 10^{-5} mbar, CH_2Cl_2 (20 ml) and **25** (1.44 g, 2.1 mmol) were added, and a syringe was filled with the soln. Within 10 h, the soln. was added at −78° dropwise to a soln. of pyridine (2 ml) in CH_2Cl_2 (150 ml) such that the tip of the needle was immersed into the cold soln. After warming up to r.t. in 4 h, Et_2O (10 ml) was added, and the org. layer was washed twice with 1N HCl and once with aq. sat. NaCl soln., dried ($MgSO_4$), filtered, and evaporated *i.v.* Two FC (SiO_2 (80 g), CH_2Cl_2/Et_2O 4:1; SiO_2 (60 g), Et_2O/pentane 4:1): 640 mg (687 mmol; 33%) of **27**. White, vitreous foam. M.p. 85.0–88.0°.

$[\alpha]_D^{r.t.} = -39.2$, $[\alpha]_{365}^{r.t.} = -130.3$ ($c = 0.775$, CH_2Cl_2). IR: 3010*w*, 2987*w*, 2936*w*, 1738v*s*, 1449*w*, 1383*m*, 1305*s*, 1138*m*, 1102*m*, 1057*s*, 978*w*, 861*w*. ^{1}H-NMR (500 MHz): 8.72 (*s*, 3 arom. H); 7.26 (*s*, 3 arom. H); 5.62–5.55 (*m*, 3 CH); 5.28–5.20 (*m*, 6 CH); 5.00, 4.93 (3 *AB*, $J_{AB} = 12.47$); 2.83, 2.60 (3 *AB* of *ABX*, $J_{AB} = 16.10$, $J_{AX} = 7.47$, $J_{BX} = 5.67$); 2.59, 2.52 (3 *AB* of *ABX*, $J_{AB} = 15.75$, $J_{AX} = 8.20$, $J_{BX} = 4.64$); 2.53, 2.40 (3 *AB* of *ABX*, $J_{AB} = 15.61$, $J_{AX} = 8.18$, $J_{BX} = 5.22$); 1.42 (*d*, $J = 6.35$, 3 Me); 1.27 (*d*, $J = 5.35$, 3 Me); 1.24 (*d*, $J = 6.32$, 3 Me). ^{13}C-NMR (125 MHz): 169.80, 169.34, 169.29, 164.01, 136.50, 134.47, 131.32, 127.87, 68.65, 67.77, 67.59, 65.67, 40.81, 40.58, 40.56, 19.97, 19.89, 19.83. LSI-MS: 1099.3 (9.7), 669.2 (3.6), 583.1 (2.7), 479.1 (5.0), 411.1 (29.6), 287.1 (26), 155.1 (46). Anal. calc. for $C_{54}H_{66}O_{24}$: C 59.01, H 6.05; found: C 58.83, H 5.97.

(6R,10R,14R,18R,22R,26R,30R,34R,38R,52R,56R,60R,64R,68R,72R,76R,80R,84R,91R,95R,99R,103R,107R,111R,115R,119R,123R)-6,10,14,18,22,26,30,34,38,52,56,60,64,68,72,76,80,84,91,95,99,103,107,111,115,119,123-Heptacosamethyl-5,9,13,17,21,25,29,33,37,41,49,53,57,61,65,69,73,77,81,85,90,94,98,102,106,110,114,118,122,126-triacontaoxatetracyclo[43.43.39.1^{3,87}.1^{43,47}]nonocosahecta-1,3(129),43,45,47(128),87-hexaene-4,8,12,16,20,24,28,32,36,40,50,54,58,62,66,70,74,78,82,86,89,93,97,101,105,109,113,117,121,125-triacontone (**28**). Synthesis of the acid chloride as described in *GP I*, with **21** (198 mg, 423 μmol) in CH_2Cl_2 (10 ml). After careful drying at 10^{-5} mbar, CH_2Cl_2 (8 ml) and **26** (945 mg, 423 μmol) were added, and a syringe was filled with the soln., which was added dropwise at $-78°$ within 4 h to a soln. of pyridine (3 ml) in CH_2Cl_2 (150 ml), such that the tip of the needle was immersed into the cold soln. The soln. was then stirred for 10 h at $-78°$ and for 3 d at r.t. After washing twice with 1N HCl and once with aq. sat. NaCl soln., the org. layer was dried ($MgSO_4$), filtered, and evaporated *i.v.* Two FC (SiO_2 (80 g), CH_2Cl_2/Et_2O/MeOH 20:10:1): 100 mg (37 mmol; 9%) of **28**. White, vitreous foam. $[\alpha]_D^{r.t.} = -11.9$, $[\alpha]_{365}^{r.t.} = -23.0$ ($c = 0.63$, CH_2Cl_2). IR: 3034*w*, 2985*w*, 2937*w*, 1734v*s*, 1458*w*, 1383*s*, 1305*s*, 1179v*s*, 1136*m*, 1101*m*, 1060v*s*, 978*w*. ^{1}H-NMR (500 MHz): 8.76 (*s*, 3 arom. H); 7.30 (*s*, 3 arom. H); 5.58–5.52 (*m*, 3 CH); 5.32–5.20 (*m*, 24 CH); 5.12, 5.10 (3 *AB*, $J_{AB} = 12.55$); 2.84–2.67 (*m*, 3 CH_2); 2.69–2.42 (*m*, 24 H_2C); 1.45 (*d*, $J = 6.31$, 3 Me); 1.29–1.23 (*m*, 24 Me). ^{13}C-NMR (125 MHz): 169.82; 169.16; 169.13; 169.06; 164.02; 136.66; 134.53; 131.38; 127.91; 68.86; 67.70; 67.58; 67.42; 65.84; 40.89; 40.81; 40.76; 40.51; 19.91; 19.83; 19.76; 19.74. LSI-MS: 2649.4 ([*M* + H]$^+$). Anal. calc. for $C_{126}H_{174}O_{60} \cdot 1.5CH_2Cl_2$ ($C_{126.5}H_{175}ClO_{60}$): C 55.16, H 6.46; found: C 55.19, H 6.76.

(6R,10R,14R,18R,22R,26R,30R,34R,38R,42R,46R,50R,54R,58R,62R,66R,80R,84R,88R,92R,96R,100R,104R,108R,112R,116R,120R,124R,128R,132R,136R,140R,147R,151R,155R,159R,163R,167R,171R,175R,179R,183R,187R,191R,195R,199R,203R,207R)-6,10,14,18,22,26,30,34,38,42,46,50,54,58,62,66,80,84,88,92,96,100,104,108,112,116,120,124,128,132,136,140,147,151,155,159,163,167,171,175,179,183,187,191,195,199,203,207-Octatetracontamethyl-5,9,13,17,21,25,29,33,37,41,45,49,53,57,61,65,69,77,81,85,89,93,97,101,105,109,113,117,121,125,129,133,137,141,146,150,154,158,162,166,170,174,178,182,186,190,194,198,202,206,210-henpentacontaoxatetracyclo[71.71.67.1^{3,143}.1^{71,75}]tridecadicta-1,3(213),71,73,75(212),143-hexaene-4,8,12,16,20,24,28,32,36,40,44,48,52,56,60,64,68,78,82,86,90,94,98,102,106,110,114,118,122,126,130,134,138,142,145,149,153,157,161,165,169,173,177,181,185,189,193,197,201,205,209-henpentacontane (**29**). Synthesis of the acid chloride as described in *GP I*, with **24** (400 mg, 175 μmol) in CH_2Cl_2 (50 ml). After careful drying at 10^{-5} mbar, CH_2Cl_2 (10 ml) and **26** (396 mg, 176 μmol) were added, and a syringe was filled with the soln. Within 3 h, it was added dropwise at $-78°$ to a soln. of CH_2Cl_2 (20 ml), containing pyridine (0.4 ml), such that the tip of the needle was immersed into the cold soln. Subsequently, the soln. was stirred for 10 h at $-78°$ and 24 h at r.t. CH_2Cl_2 (30 ml) was added, the org. layer was washed twice with 1N HCl and once with aq. sat. NaCl soln., dried ($MgSO_4$), filtered, and evaporated *i.v.* FC (SiO_2 (80 g), CH_2Cl_2/acetone/MeOH 20:5:0.5): 50 mg of a white solid were obtained, which was recrystallized twice from CH_2Cl_2/pentane. 40 mg (9 μmol; 5%) of **29**. ^{1}H-NMR (500 MHz): 8.76 (*s*, 3 arom. H); 7.29 (*s*, 3 arom. H); 5.58–5.52 (*m*, 3 CH); 5.33–5.20 (*m*, 45 CH); 5.12, 5.10 (3 *AB*, $J_{AB} = 12.58$); 2.85–2.68 (*m*, 3 CH_2); 2.70–2.40 (*m*, 45 H_2C); 1.46 (*d*, $J = 6.32$, 3 Me); 1.30–1.22 (*m*, 45 Me). ^{13}C-NMR (125 MHz): 169.81; 169.22; 169.14; 169.04; 164.03; 136.69; 134.54; 131.41; 127.91; 127.55; 68.89; 67.71; 67.61; 67.44; 65.85; 40.94; 40.85; 40.80; 40.54; 19.92; 19.84; 19.77; 19.61; 19.51; 19.28. MALDI-MS: 4479.4 ([*M* + Na]$^+$).

Dimethyl 5-(Hydroxymethyl)benzene-1,3-dicarboxylate (**30**) *and Methyl 3,5-Bis(hydroxymethyl)benzoate* (**31**). A suspension of $LiAlH_4$ (2.51 g) in THF (900 ml) was cooled to 0°, and a soln. of trimesic acid trimethyl ester (20.22 g, 80.2 mmol) in THF (300 ml) was added quickly. The temp. increased from 1° to 30°. Stirring was continued for 10 min, then H_2O (5 ml) and conc. HCl soln. (10 ml) were added carefully, and the solvent was removed *i.v.* The residue was dissolved in AcOEt (400 ml), washed with 1N HCl and aq. sat. NaCl soln., dried ($MgSO_4$), filtered, and evaporated *i.v.* According to ^{1}H-NMR (300 MHz), the crude product contained 19.9 mmol of starting material, 19.9 mmol of **30**, and 23.9 mmol of **31**. First FC (Et_2O/pentane 1:1.5 (R_f (trimesic acid trimethyl ester) 0.59), then 2:1, then Et_2O/AcOEt 2:1; the crude product was dissolved in acetone) yielded 3.72 g (16.6 mmol; 20.1%) of **30** and 3.56 g (18.1 mmol; 23%) of **31**. Unreacted starting material (4.99 g, 19.8 mmol; 25%) was recovered. **30**: R_f 0.13 (Et_2O/pentane 1:1.5). Anal. data are in good agreement with [18].

*Dimethyl 5-{{[(*tert*-Butyl)diphenylsilyl]oxy}methyl}benzene-1,3-dicarboxylate* (**32**). To a soln. of **30** (11.08 g, 49.4 mmol) in DMF (205 ml), (*t*-Bu)Ph_2SiCl (16.42 g, 60 mmol) and DMAP (7.5 g, 61.4 mmol) were added, and the mixture was stirred for 24 h at r.t. DMF (150 ml) was removed *i.v.*, then AcOEt (250 ml) was added and the org. layer washed twice with 1N HCl and once with aq. sat. NaCl soln., dried ($MgSO_4$), filtered, and evaporated *i.v.* FC (SiO_2 (430 g), CH_2Cl_2/pentane 1:1): 21.92 g (45.87 mmol; 92.8%) of **32**. Colorless oil. R_f 0.37 (CH_2Cl_2/pentane 1:1). IR: 3072*w*, 3008*w*, 2954*s*, 2932*m*, 2893*w*, 2869*m*, 1959*w*, 1897*w*, 1826*w*, 1724*vs*, 1604*w*, 1434*s*, 1335*s*, 1113*vs*, 999*m*. ^{1}H-NMR (300 MHz): 8.58 (*t*, *J* = 1.59, 1 arom. H); 8.21 (*d*, *J* = 1.59, 2 arom. H); 7.70–7.67 (*m*, 4 arom. H); 7.47–7.36 (*m*, 6 arom. H); 4.83 (*s*, CH_2); 3.95 (*s*, 2 MeO); 1.12 (*s*, *t*-Bu). ^{13}C-NMR (75 MHz): 466.32; 142.08; 135.56; 135.42; 133.08; 131.57; 131.47; 130.59; 129.87; 129.35; 128.01; 127.82; 64.74; 52.33; 26.84; 19.31. LSI-MS: 925.4(5.6, [2*M* + H]$^+$), 463.2(49, [*M* + H]$^+$), 405.1(91). Anal. calc. for $C_{27}H_{30}O_5Si$: C 70.10, H 6.54; found: C 70.22, H 6.58.

*Methyl 3,5-Bis{{[(*tert*-butyl)diphenylsilyl]oxy}methyl}benzoate* (**33**). To a soln. of **31** (1.79 g, 9.1 mmol) in DMF (30 ml) (*t*-Bu)Ph_2SiCl (6.03 g, 22 mmol) and (*i*-Pr)$_2$NH (3.23 g, 25 mmol) were added and stirred for 24 h at r.t. Then AcOEt (200 ml) was added and the mixture worked up as described for **32**. FC (SiO_2 (120 g), pentane/CH_2Cl_2 2:1): 5.19 g (7.71 mmol; 85%) of **33**. White solid. M.p. 110.0–111.0°. IR: 3072*w*, 3053*w*, 3008*w*, 2955*m*, 2932*s*, 2892*w*, 2859*vs*, 1964*w*, 1897*w*, 1826*w*, 1718*vs*, 1607*w*, 1589*w*, 1472*m*, 1428*s*, 1308*m*, 1152*m*, 1113*vs*, 998*w*. ^{1}H-NMR (300 MHz, (D_6)acetone): 7.94 (*s*, 2 arom. H); 7.77–7.71 (*m*, 8 arom. H); 7.50–7.39 (*m*, 13 arom. H); 4.89 (*s*, 2 CH_2); 3.87 (*s*, MeO); 1.10 (*s*, 2 *t*-Bu). ^{13}C-NMR (75 MHz, (D_6)acetone): 142.52; 136.27; 135.59; 134.07; 131.19; 130.73; 129.21; 128.69; 128.30; 126.65; 65.96; 52.27; 27.24; 19.82. LSI-MS: 1287.6 (2.8, [2*M* – 57]$^+$), 671.0(26, [*M* – H]$^+$). Anal. calc. for $C_{42}H_{48}O_4Si_2$: C 74.96, H 7.19; found: C 74.76, H 7.36.

*5-{{[(*tert*-Butyl)diphenylsilyl]oxy}methyl}benzene-1,3-dicarboxylic Acid* (**34**). To a soln. of **32** (21.92 g, 45.87 mmol) in MeOH (60 ml), 1,4-dioxane (115 ml) and H_2O (60 ml), LiOH (4.51 g, 187.9 mmol) in H_2O (10 ml) was added. After stirring for 30 min, solvent (100 ml) was removed *i.v.* and AcOEt (50 ml) was added and the pH adjusted to < 2 with conc. HCl soln. The soln. was then extracted twice with AcOEt (100 ml). The combined org. layers were washed with aq. sat. NaCl soln., dried ($MgSO_4$), filtered, and evaporated *i.v.* The obtained solid was triturated in Et_2O (100 ml) for 2 h, filtered, and the org. phase was evaporated *i.v.*: 15.67 g (36 mmol; 78%) of **34**. M.p. 138.0–140.0°. IR: 3500–2300(br.), 3010*m*, 2932*m*, 2859*m*, 1701*vs*, 1606*w*, 1462*w*, 1428*m*, 1113*s*. ^{1}H-NMR (300 MHz, (D_6)acetone): 8.60 (*s*, 1 arom. H); 8.33 (*s*, 2 arom. H); 7.77–7.74 (*m*, 4 arom. H); 7.49–7.41 (*m*, 6 arom. H); 5.00 (*s*, CH_2); 1.13 (*s*, *t*-Bu). ^{13}C-NMR (75 MHz, (D_6)acetone): 166.84; 143.28; 136.30; 133.94; 132.15; 132.01; 130.86; 130.21; 128.79; 65.50; 27.23; 19.87. LSI-MS: 907.3(6.7, [*M* + K – H]$^+$), 433.1(13, [*M* – H]$^+$), 377.1(100, [*M* – 57]$^+$). Anal. calc. for $C_{25}H_{26}O_5Si$: C 69.10, H 6.03; found: C 68.50, H 6.16.

*(*tert*-Butyl)diphenylsilyl 3,5-Bis{{(*tert*-butyl)diphenylsilyl]oxy}methyl}benzoate* (**35**). To a soln. of 3,5-bis(hydroxymethyl)benzoic acid (5.19 g, 28.5 mmol) in DMF (100 ml) (*t*-Bu)Ph_2SiCl (26.7 g, 97.3 mmol) and (*i*-Pr)$_2$NH (14.7 g, 114 mmol) were added and stirred at r.t. for 24 h. Then, DMF (70 ml) were removed *i.v.*, AcOEt (300 ml) was added, and the mixture worked up as described for **32** (^{1}H-NMR: complete conversion). FC (SiO_2 (60 g), Et_2O/pentane 1:3) of the crude product (260 mg) yielded pure **35** for the determination of the anal. data. IR: 3073*w*, 3008*w*, 2960*m*, 2932*m*, 2893*w*, 2860*m*, 1959*w*, 1892*w*, 1921*w*, 1703*m*, 1472*w*, 1428*m*, 1363*w*, 1306*m*, 1114*vs*, 937*w*. ^{1}H-NMR (300 MHz): 8.02 (*s*, 2 arom. H); 7.77–7.70 (*m*, 12 arom. H); 7.59 (*s*, 1 arom. H); 7.45–7.36 (*m*, 18 arom. H); 4.80 (*s*, 2 CH_2); 1.18 (*s*, *t*-Bu); 1.10 (*s*, 2 *t*-Bu). ^{13}C-NMR (75 MHz): 165.83; 141.54; 135.58; 135.46; 135.35; 135.22; 133.27; 131.86; 131.23; 130.05; 129.91; 129.77; 129.68; 128.73; 127.77; 126.73; 65.31; 27.03; 26.88; 19.30. LSI-MS: 896.0(3.0, [*M* – H]$^+$), 819.0(42), 761.0(20), 196.9(78). Anal. calc. for $C_{57}H_{64}O_4Si_3$: C 76.29, H 7.19; found: C 76.09, H 7.42.

*3,5-Bis{{[(*tert*-butyl)diphenylsilyl]oxy}methyl}benzoic Acid* (**36**). To a soln. of **35** (28.3 g, *ca.* 28 mmol, crude) in EtOH (400 ml) 1N KOH (100 ml) was added and stirred for 10 min at r.t. Additional 1N KOH (50 ml) was added, stirred for 10 min, and solvent (200 ml) removed *i.v.* Then, 1N HCl (500 ml) was added and the soln. extracted twice with Et_2O. The combined org. layers were washed with aq. sat. NaCl soln., dried ($MgSO_4$), filtered, and evaporated *i.v.* FC (SiO_2 (400 g), Et_2O/pentane 1:1): 14.89 g (22.6 mmol; 81%) of **36**. Colorless oil. IR: 3500–2400(br.), 3072*w*, 3008*w*, 2959*m*, 2932*s*, 2892*m*, 2859*s*, 2707*w*, 2605*w*, 1959*w*, 1892*w*, 1826*w*, 1694*s*, 1606*w*, 1428*m*, 1112*vs*. ^{1}H-NMR (300 MHz): 7.93 (*s*, 2 arom. H); 7.72–7.69 (*m*, 8 arom. H); 7.66 (*s*, 1 arom. H); 7.46–7.35 (*m*, 12 arom. H); 4.80 (*s*, 2 CH_2); 1.10 (*s*, 2 *t*-Bu). ^{13}C-NMR (75 MHz): 169.99; 141.67; 135.58; 133.27; 129.78; 129.11; 128.91; 127.77; 127.66; 126.48; 113.86; 65.17; 27.08; 26.88; 19.30. LSI-MS: 681.2 (12, [*M* + Na]$^+$), 657.2 (14, [*M* – H]$^+$). Anal. calc. for $C_{41}H_{46}O_4Si_2$: C 74.73, H 7.04; found: C 74.65, H 7.09.

*(9H-Fluoren-9-yl)methyl (R)-3-{[(*tert*-Butyl)diphenylsilyl]oxy}}butanoate* (**37**). Synthesis of the acid chloride as described in *GP I*, with **5** (270 mg, 750 µmol) in CH_2Cl_2 (10 ml). Coupling as described in *GP II*, with

220 mg (1.1 mmol) of 9*H*-fluorene-9-methanol (FmOH) in CH_2Cl_2 (10 ml) at 0°. FC (SiO_2 (80 g), Et_2O/pentane 1:3): 320 mg (615 mmol; 82%) of **37**. Viscous oil. $[\alpha]_D^{r.t.} = -5.2$, $[\alpha]_{365}^{r.t.} = -33.5$ ($c = 0.795$, CH_2Cl_2). IR: 3072*w*, 3008*w*, 2964*m*, 2932*m*, 2894*w*, 2859*m*, 1732*vs*, 1589*w*, 1450*s*, 1428*s*, 1381*m*, 1302*m*, 1177*s*, 1111vs, 1006*s*. ^{1}H-NMR (300 MHz): 7.75–7.25 (*m*, 18 arom. H); 4.35–4.26 (*m*, CH); 4.28 (*d*, $J = 7.11$, CH_2); 4.12 (*t*, $J = 7.11$, CH); 2.63, 2.46 (*AB* of *ABX*, $J_{AB} = 14.56$, $J_{AX} = 6.61$, $J_{BX} = 6.38$); 1.11 (*d*, $J = 6.04$, Me); 1.03 (*s*, *t*-Bu). ^{13}C-NMR (75 MHz): 171.21; 143.89; 141.29; 135.84; 134.18; 133.93; 130.17; 129.68; 129.61; 127.74; 127.55; 127.09; 126.11; 125.08; 125.01; 119.99; 66.81; 66.26; 64.35; 46.73; 44.64; 26.90; 23.57; 19.17. LSI-MS: 518.9 (0.8, $[M - H]^+$), 284.9 (35), 264.9 (26), 198.9 (26), 178.9 (100). Anal. calc. for $C_{34}H_{36}O_3Si$: C 78.42, H 6.97; found: C 78.48, H 7.10.

*9H-Fluoren-9-yl (*R*)-3-Hydroxybutanoate* (**41**). As described in *GP IV*, **37** (150 mg, 288 µmol) was dissolved in CH_2Cl_2 (20 ml), HF · pyridine (2.5 ml) was added at 0°, and the mixture was stirred vigorously for 30 min. Workup and FC (SiO_2 (60 g), Et_2O/pentane 1:1): 61 mg (218 mmol; 76%) of **41**. Viscous oil. $[\alpha]_D^{r.t.} = -17.5$, $[\alpha]_{365}^{r.t.} = -54.3$ ($c = 0.78$, CH_2Cl_2). IR: 3579*w*(br.), 3069*w*, 3008*m*, 2976*w*, 1954*w*, 1913*w*, 1877*w*, 1847*w*, 1805*w*, 1725vs, 1450*s*, 1406*m*, 1386*m*, 1175*vs*. ^{1}H-NMR (300 MHz): 7.79 (*d*, $J = 7.47$, 2 arom. H); 7.60 (*d*, $J = 7.47$, 2 arom. H); 7.43 (*dd*, $J = 7.47$, 7.42, 2 arom. H); 7.33 (*ddd*, $J = 7.47$, 7.42, 1.24, 2 arom. H); 4.49, 4.48 (*AB* of *ABX*, $J_{AB} = 10.79$, $J_{AX} = 7.04$, $J_{BX} = 6.50$); 4.23 (*t*, $J = 6.84$, CH); 4.20–4.12 (*m*, CH); 2.76 (*d*, $J = 4.05$, OH); 2.55, 2.49 (*AB* of ABX, $J_{AB} = 16.63$, $J_{AX} = 3.01$, $J_{BX} = 8.20$); 1.21 (*d*, $J = 6.22$, Me). ^{13}C-NMR (75 MHz): 172.67; 143.57; 141.33; 130.30; 127.90; 127.18; 124.92; 120.10; 66.33; 64.22; 46.78; 42.86; 22.40. EI-MS: 282.2 (2.0), 191.1 (1.3), 178.1 (100), 165.1 (31), 87.1 (8). Anal. calc. for $C_{18}H_{18}O_3$: C 76.57, H 6.43; found: C 76.35, H 6.74.

*(1*R*)-3-[(9H-Fluoren-9-yl)methoxy]-1-methyl-3-oxopropyl (3*R*)-3-{[(*tert*-Butyl)diphenylsilyl]oxy}butanoate* (**38**). Synthesis of the acid chloride as described in *GP I*, with **6** (2.87 g, 6.7 mmol) in CH_2Cl_2 (40 ml). Coupling as described in *GP II*, with FmOH (1.96 g, 10 mmol) in CH_2Cl_2 (40 ml) at −78°. FC (SiO_2 (100 g), Et_2O/pentane 1:4): 3.94 g (6.45 mmol; 96%) of **38**. Colorless oil. $[\alpha]_D^{r.t.} = 1.4$, $[\alpha]_{365}^{r.t.} = 3.2$ ($c = 0.68$, CH_2Cl_2). IR: 3070*w*, 3008*w*, 2961*m*, 2952*m*, 2892*w*, 2859*m*, 1954*w*, 1913*w*, 1736vs, 1450*m*, 1427*m*, 1381*m*, 1303*s*, 1177vs, 1105*vs*. ^{1}H-NMR (300 MHz): 7.79–7.29 (*m*, 18 arom. H); 5.26–5.19 (*m*, CH); 4.38 (*d*, $J = 7.09$, CH_2); 4.31–4.22 (*m*, CH); 4.18 (*t*, $J = 7.09$, CH); 2.70, 2.53 (*AB* of *ABX*, $J_{AB} = 15.53$, $J_{AX} = 6.86$, $J_{BX} = 6.44$); 2.51, 2.37 (*AB* of *ABX*, $J_{AB} = 14.55$, $J_{AX} = 5.95$, $J_{BX} = 6.72$); 1.23 (*d*, $J = 6.36$, Me); 1.11 (*d*, $J = 6.19$, Me); 1.03 (*s*, *t*-Bu). ^{13}C-NMR (75 MHz): 170.40; 170.14; 143.66; 141.31; 135.82; 134.26; 133.89; 130.24; 129.65; 127.84; 127.58; 127.50; 127.14; 125.00; 120.24; 120.05; 67.27; 66.75; 66.51; 46.75; 44.67; 40.70; 26.91; 23.43; 20.01; 19.74; 19.17. LSI-MS: 549.1 (2.3, $[M - 57]^+$), 529.2 (1.1, $[M - 77]^+$), 285.0 (22), 179.0 (100).

*(1*R*)-3-[(9H-Fluoren-9-yl)methoxy]-1-methyl-3-oxopropyl (3*R*)-3-Hydroxybutanoate* (**42**). As described in *GP IV*, **38** (3.70 g, 6.1 mmol) was dissolved in CH_2Cl_2 (40 ml), HF · pyridine (5 ml) was added at 0° and the mixture stirred vigorously for 15 min. Workup and FC (SiO_2 (100 g), Et_2O/pentane 1:1): 2.06 g (5.36 mmol; 89%) of **42**. Colorless oil. $[\alpha]_D^{r.t.} = -14.1$, $[\alpha]_{365}^{r.t.} = -43.8$ ($c = 0.905$, CH_2Cl_2). IR: 3541 (br.), 3008*m*, 2982*w*, 1949*w*, 1913*w*, 1735vs, 1450*s*, 1303*s*, 1177vs, 1141*m*, 1104*m*, 1056*s*. ^{1}H-NMR (300 MHz): 7.78 (*d*, $J = 7.43$, 2 arom. H); 7.60 (*d*, $J = 7.40$, 2 arom. H); 7.42 (*dd*, $J = 7.43$, 7.40, 2 arom. H); 7.33 (*ddd*, $J = 7.43$, 7.40, 1.19, 2 arom. H); 5.37–5.31 (*m*, CH); 4.43 (*d*, $J = 6.99$, CH_2); 4.21 (*t*, $J = 6.99$, CH); 4.23–4.18 (*m*, CH); 3.01 (*d*, $J = 3.43$, OH); 2.73, 2.60 (*AB* of *ABX*, $J_{AB} = 15.66$, $J_{AX} = 7.64$, $J_{BX} = 5.37$); 2.44, 2.38 (*AB* of *ABX*, $J_{AB} = 16.00$, $J_{AX} = 3.84$, $J_{BX} = 8.32$); 1.31 (*d*, $J = 6.36$, Me); 1.21 (*d*, $J = 6.33$, Me). ^{13}C-NMR (75 MHz): 172.08; 170.30; 143.62; 141.33; 127.86; 127.15; 124.98; 120.09; 67.59; 66.64; 64.43; 46.73; 43.20; 40.63; 22.48; 19.87. LSI-MS: 368.2 (0.3, M^+), 191.1 (1.4), 178.1 (100), 165.1 (18).

*(9H-Fluoren-9-yl)methyl (3*R*,7*R*,11*R*,15*R*)-3,7,11,15,18,18-Hexamethyl-5,9,13-trioxo-17,17-diphenyl-4,8,12,16-tetraoxa-17-silanonadecanoate* (**39**). Synthesis of the acid chloride as described in *GP I*, with **7** (3.18 g, 5.3 mmol) in CH_2Cl_2 (30 ml). Coupling as described in *GP II*, with FmOH (1.84 g, 9.3 mmol) in CH_2Cl_2 (60 ml) at −78°. FC (SiO_2 (120 g), Et_2O/pentane 1:3): 3.90 g (5.0 mmol; 94%) of **39**. Colorless oil. $[\alpha]_D^{r.t.} = +2.2$, $[\alpha]_{365}^{r.t.} = +10.4$ ($c = 0.95$, CH_2Cl_2). IR: 3015*w*, 2933*w*, 2859*w*, 1737vs, 1450*m*, 1382*m*, 1304*s*, 1178vs, 1104s, 1059*s*. ^{1}H-NMR (400 MHz): 7.77–7.29 (*m*, 18 arom. H); 5.32–5.21 (*m*, 2 CH); 5.19–5.13 (*m*, CH); 4.40 (*d*, $J = 7.06$, CH_2); 4.29–4.23 (*m*, CH); 4.20 (*t*, $J = 7.06$, CH); 2.75–2.33 (*m*, 4 CH_2); 1.26 (*d*, $J = 6.32$, Me); 1.22 (*d*, $J = 6.32$, Me); 1.206 (*d*, $J = 6.33$, Me); 1.11 (*d*, $J = 6.12$, Me); 1.03 (*s*, *t*-Bu). ^{13}C-NMR (100 MHz): 170.31; 170.03; 169.21; 169.16; 143.67; 143.65; 141.33; 135.83; 135.81; 134.28; 133.95; 129.66; 129.59; 127.85; 127.59; 127.51; 127.15; 125.00; 120.07; 67.66; 67.52; 67.17; 66.72; 66.55; 46.75; 44.60; 40.87; 40.60; 26.91; 23.42; 19.75; 19.73; 19.17. LSI-MS: 801.3 (0.3, $[M + Na]^+$). 721.3 (1.1, $[M - 57]^+$). 701.3 (0.5, $[M - 77]^+$), 179.1 (100). Anal. calc. for $C_{46}H_{54}O_9Si$: C 70.92, H 6.99; found: C 70.85, H 7.17.

*(1*R*)-3-{(1*R*)-3-{(1*R*)-3-[(9H-Fluoren-9-yl)methoxy]-1-methyl 3-oxopropoxy}-1-methyl-3-oxopropoxy}-1-methyl-3-oxopropyl (3*R*)-3-Hydroxybutanoate* (**43**). As described in *GP IV*, **39** (3.90 g, 5.0 mmol) was dissolved in CH_2Cl_2 (40 ml), HF · pyridine (4.5 ml) was added at 0°, and the mixture stirred vigorously for 15 min. Workup

and FC (SiO_2 (120 g), Et_2O/pentane 2:1): 2.06 g (3.81 mmol; 89%) of **43**. Colorless oil. $[\alpha]_D^{r.t.} = -7.4$, $[\alpha]_{365}^{r.t.} = -17.2$ ($c = 1.4$, CH_2Cl_2). IR: 3536*w*, 3007*w*, 2985*m*, 2936*w*, 1949*w*, 1913*w*, 1877*w*, 1736*vs*, 1450*m*, 1383*s*, 1304*s*, 1177*vs*, 1137*s*, 1102*s*, 1057*vs*. ^{1}H-NMR (400 MHz): 7.76 (*d*, $J = 6.53$, 2 arom. H); 7.59 (*d*, $J = 6.84$, 2 arom. H); 7.41 (*dd*, $J = 6.53, 6.84$, 2 arom. H); 7.32 (*ddd*, $J = 6.53, 6.84, 1.18$, 2 arom. H); 5.33–5.22 (*m*, 3 CH); 4.41 (*d*, $J = 7.07$, CH_2); 4.21 (*t*, $J = 7.07$, CH); 4.18–4.12 (*m*, CH); 3.04 (*d*, $J = 3.77$, OH); 2.76–2.33 (*m*, 4 CH_2); 1.28 (*d*, $J = 6.33$, Me); 1.27 (*d*, $J = 6.35$, Me); 1.25 (*d*, $J = 6.34$, Me); 1.21 (*d*, $J = 6.31$, Me). ^{13}C-NMR (100 MHz): 172.02; 170.08; 169.41; 169.22; 143.66; 141.32; 129.09; 127.86; 127.15; 125.01; 124.98; 124.34; 120.08; 67.74; 67.71; 67.52; 66.57; 64.39; 46.75; 43.23; 40.85; 40.80; 40.63; 22.50; 19.86; 19.76. LSI-MS: 1081.6 (0.9, $[2M + H]^+$), 563.2 (9.2, $[M + Na]^+$), 541.3 (22, M^+), 178.1 (100). Anal. calc. for $C_{30}H_{36}O_9$: C 66.65, H 6.71; found: C 66.58, He 7.01.

(9H-Fluoren-9-yl)methyl (3R,7R,11R,15R,19R,23R,27R,31R)-3,7,11,15,19,23,27,31,34,34-Decamethyl-5,9,13,17,21,25,29-heptaoxo-33,33-diphenyl-4,8,12,16,20,24,28,32-octaoxa-33-silapentatriacontanoate (**40**). Synthesis of the acid chloride as described in *GP I*, with **8** (4.53 g, 4.8 mmol) in CH_2Cl_2 (60 ml). Coupling as described in *GP II*, with FmOH (1.57 g, 7.9 mmol) in CH_2Cl_2 (80 ml) at −78°. FC (SiO_2 (200 g), Et_2O/pentane 1:1): 5.02 g (4.47 mmol; 93%) of **40**. Colorless viscous oil. $[\alpha]_D^{r.t.} = 1.5$, $[\alpha]_{365}^{r.t.} = 12.5$ ($c = 0.4$, CH_2Cl_2). IR: 2983*w*, 2934*w*, 2859*w*, 1737*vs*, 1450*w*, 1383*m*, 1305*s*, 1178*vs*, 1134*m*, 1104*s*, 1059*s*, 909*s*. ^{1}H-NMR (400 MHz): 7.78–7.30 (*m*, 18 arom. H); 5.32–5.14 (*m*, 7 CH); 4.41 (*d*, $J = 7.07$, CH_2); 4.30–4.21 (*m*, CH); 4.21 (*t*, $J = 7.07$, CH); 2.76–2.34 (*m*, 8 CH_2); 1.28–1.20 (*m*, 7 Me); 1.11 (*d*, $J = 6.12$, Me); 1.03 (*s*, *t*-Bu). ^{13}C-NMR (100 MHz): 170.31; 170.04; 169.20; 169.18; 169.14; 143.67; 141.33; 135.83; 135.82; 134.29; 133.95; 129.67; 129.59; 127.86; 127.59; 127.52; 127.16; 125.01; 125.00; 120.08; 67.68; 67.81; 67.53; 67.19; 66.72; 66.56; 46.76; 44.61; 40.89; 40.86; 40.80; 40.62; 26.92; 23.43; 19.77; 19.17. LSI-MS: 1145.6 (0.4, $[M + Na]^+$), 1065.5 (0.5, $[M - 57]^+$). Anal. calc. for $C_{62}H_{78}O_{17}Si$: C 66.29, H 7.00; found: C 66.18, H 6.99.

(9H-Fluoren-9-yl)methyl (3R,7R,11R,15R,19R,23R,27R,31R)-31-Hydroxy-3,7,11,15,19,23,27-heptamethyl-5,9,13,17,21,25,29-heptaoxo-4,8,12,16,20,24,28-heptaoxahentricontanoate (**44**). As described in *GP IV*, **40** (4.80 g, 4.27 mmol) was dissolved in CH_2Cl_2 (45 ml) and HF · pyridine (5.5 ml) was added at 0°, and the mixture stirred vigorously for 12 min. Workup and FC (SiO_2 (120 g), Et_2O/CH_2Cl_2 1:3): 3.60 g (4.07 mmol; 95%) of **44**. White solid. $[\alpha]_D^{r.t.} = -5.2$, $[\alpha]_{365}^{r.t.} = -6.5$ ($c = 1.03$, CH_2Cl_2). IR: 3537 (br.), 3026*w*, 2986*w*, 2936*w*, 1736*vs*, 1450*m*, 1383*m*, 1305*s*, 1178*vs*, 1135*m*, 1102*m*, 1058*s*. ^{1}H-NMR (400 MHz): 7.77 (*d*, $J = 7.45$, 2 arom. H); 7.59 (*d*, $J = 7.50$, 2 arom. H); 7.41 (*dd*, $J = 7.54, 7.47$, 2 arom. H); 7.32 (*ddd*, $J = 7.54, 7.47, 1.19$, 2 arom. H); 5.34–5.20 (*m*, 7 CH); 4.41 (*d*, $J = 7.08$, CH_2); 4.20 (*t*, $J = 7.08$, CH); 4.20–4.13 (*m*, CH); 3.06 (*d*, $J = 3.86$, OH); 2.76–2.35 (*m*, 8 CH_2); 1.31–1.24 (*m*, 7 Me); 1.22 (*d*, $J = 6.28$, Me). ^{13}C-NMR (100 MHz): 172.01; 170.04; 169.41; 169.18; 169.16; 143.67; 141.33; 127.86; 127.16; 125.01; 124.99; 120.08; 67.75; 67.68; 67.62; 67.54; 66.56; 64.39; 46.75; 43.26; 40.80; 40.62; 22.53; 19.89; 19.77. LSI-MS: 1769.5 (0.9, $[2M - H]^+$), 885.4 (6.8 M^+), 178.1 (100). Anal. calc. for $C_{46}H_{60}O_{17}$: C 62.43, H 6.83; found: C 62.38, H 6.74.

*Bis[(1R)-3-(benzyloxy)-1-methyl-3-oxopropyl] 5-{{[(*tert*-Butyl)diphenylsilyl]oxy}methyl}benzene-1,3-dicarboxylate* (**45**). To **34** (6.16 g, 14.2 mmol) was added $(COCl)_2$ (40 ml) and the mixture stirred for 20 min. To the suspension, DMF (3 drops) was added and stirred for 14 h. The solid was completely dissolved after *ca.* 20 min. The volatile components were removed *i.v.*, and the residue was dried for 12 h (10^{-4} mbar), then dissolved in CH_2Cl_2 (60 ml), cooled to 0°, and **9** (5.85 g, 30.2 mmol) was added, followed by the dropwise addition of pyridine (5 ml). The mixture was then stirred for 3 h at 0° and 8 h at r.t. The soln. was diluted with Et_2O (100 ml) and the org. layer was washed twice with 1N HCl and once with aq. sat. NaCl soln., dried ($MgSO_4$), filtered and was evaporated *i.v.* FC (SiO_2 (260 g), Et_2O/pentane 1:3): 8.07 g (10.25 mmol; 72%) of **45**. Colorless oil. $[\alpha]_D^{r.t.} = -25.4$, $[\alpha]_{578}^{r.t.} = -26.6$; $[\alpha]_{549}^{r.t.} = -30.6$, $[\alpha]_{436}^{r.t.} = -55.4$, $[\alpha]_{365}^{r.t.} = -94.6$ ($c = 0.97$, CH_2Cl_2). IR: 3071*w*, 3032*w*, 2960*m*, 2933*m*, 2859*w*, 1959*w*, 1892*w*, 1732*vs*, 1606*w*, 1456*m*, 1428*m*, 1363*m*, 1308*s*, 1114*vs*, 1058*s*, 950*m*. ^{1}H-NMR (400 MHz): 8.46 (*t*, $J = 1.65$, 1 arom. H); 8.14 (*d*, $J = 1.65$, 2 arom. H); 7.71–7.69 (*m*, 4 arom H); 7.46–7.35 (*m*, 6 arom. H); 7.30–7.19 (*m*, 10 arom. H); 5.63–5.52 (*m*, 2 CH); 5.12, 5.08 (2 *AB*, $J_{AB} = 12.24$); 4.80 (*s*, CH_2); 2.86, 2.69 (2 *AB* of *ABX*, $J_{AB} = 15.60$, $J_{AX} = 7.55$, $J_{BX} = 5.64$); 1.43 (*d*, $J = 6.33$, 2 Me); 1.13 (*s*, *t*-Bu). ^{13}C-NMR (75 MHz): 169.95; 164.93; 141.98; 135.57; 133.08; 131.20; 130.71; 129.90; 129.39; 128.51; 128.27; 127.87; 68.37; 66.56; 64.55; 40.95; 26.86; 20.04; 19.33. LSI-MS: 785.1 (1.3, $[M - H]^+$), 593.1 (34). Anal. calc. for $C_{47}H_{52}O_9Si$: C 71.73, H 6.40; found: C 71.93, H 6.39.

*3,3′-{{5-{{[(*tert*-Butyl)diphenylsilyl]oxy}methyl}benzene-1,3-diyl}bis(carbonyloxy)}bis[(3R)-butanoic Acid]* (**49**). As described in *GP III*, **45** (1.57 g, 2.0 mmol) was hydrogenated in CF_3CH_2OH (30 ml). Workup and careful drying *i.v.*: 1.04 g (1.71 mmol; 86%) of **49**. Colorless oil. $[\alpha]_D^{r.t.} = -18.6$, $[\alpha]_{365}^{r.t.} = -43.7$ ($c = 0.84$, CH_2Cl_2). IR: 3500–2400 (br.), 3011*m*, 2933*s*, 2859*m*, 1959*w*, 1892*w*, 1720*vs*, 1606*w*, 1428*s*, 1364*m*, 1311*s*, 1114*vs*, 1055*s*, 956*m*. ^{1}H-NMR (400 MHz): 8.45 (*s*, 1 arom. H); 8.17 (*s*, 2 arom. H); 7.68–7.65 (*m*, 4 arom. H); 7.44–7.35 (*m*, 6 arom. H); 5.57–5.47 (*m*, 2 CH); 4.81 (*s*, CH_2); 2.75, 2.69 (2 *AB* of *ABX*, $J_{AB} = 15.65$, $J_{AX} = 7.64$,

J_{BX} = 4.70); 1.44 (*d*, *J* = 6.35, Me); 1.11 (*s*, *t*-Bu). ^{13}C-NMR (125 MHz): 176.39; 165.08; 142.14; 135.53; 133.05; 133.01; 131.35; 130.63; 129.88; 129.38; 127.83; 68.29; 64.55; 40.67; 26.81; 19.91; 19.29. LSI-MS: 629.2 (100, $[M + Na]^+$), 503(34). Anal. calc. for $C_{33}H_{38}O_9Si \cdot 0.5H_2O$ ($C_{33}H_{39}O_{9.5}Si$): C 64.37, H 6.39; found: C 64.33, H 6.33.

*Bis[(1*R*)-3-(benzyloxy)-1-methyl-3-oxopropyl] 5-(Hydroxymethyl)benzene-1,3-dicarboxylate* (**53**). As described in *GP IV*, with **45** (4.88 g, 6.2 mmol) in CH_2Cl_2 (40 ml) and HF · pyridine (5 ml) for 15 min. Workup: 4.85 g (6.02 mmol; 97%; containing 1 equiv. of (*t*-Bu)Ph_2SiF) of **53**. Colorless oil. For the determination of the anal. data, 200 mg were precipitated twice with CH_2Cl_2/pentane. $[\alpha]_D^{r.t.} = -37.2$, $[\alpha]_{578}^{r.t.} = -38.6$, $[\alpha]_{546}^{r.t.} = -44.5$, $[\alpha]_{436}^{r.t.} = -80.0$, $[\alpha]_{365}^{r.t.} = -134.8$ (*c* = 1.67, CH_2Cl_2). IR: 3032*w*, 1732*vs*, 1606*w*, 1498*w*, 1456*m*, 1383*m*, 1362*w*, 1303*m*, 1136*m*, 1102*w*, 1057*s*. ^{1}H-NMR (300 MHz): 8.49 (*t*, *J* = 1.64, 1 arom. H); 8.13 (*d*, *J* = 1.64, 2 arom. H); 7.31–7.23 (*m*, 10 arom. H); 5.63–5.52 (*m*, 2CH); 5.12, 5.10 (2 *AB*, J_{AB} = 12.27); 4.74 (*s*, CH_2); 2.87, 2.71 (2 *AB* of *ABX*, J_{AB} = 15.55, J_{AX} = 7.68, J_{BX} = 5.48); 1.44 (*d*, *J* = 6.33, 2Me). ^{13}C-NMR (75 MHz): 169.99; 164.83; 141.73; 135.60; 131.98; 131.01; 129.91; 128.51; 128.27; 68.53; 66.57; 64.20; 40.95; 20.03. LSI-MS: 1098.0 (0.3, $[M + 2H]^+$), 549.2 (13, $[M + H]^+$), 355.1 (66), 265.1 (45), 181.1 (100). Anal. calc. for $C_{31}H_{32}O_9$: C 67.68, H 5.88; found: C 67.95, H 5.89.

*Bis{(1*R*)-3-[(1*R*)-3-(benzyloxy)-1-methyl-3-oxopropoxy]-1-methyl-3-oxopropyl} 5-{{[(*tert*-Butyl)diphenylsilyl]oxy}methyl}benzene-1,3-dicarboxylate* (**46**). As described for **45**, **34** (15.67 g, 36.06 mmol) was mixed with $(COCl)_2$ (60 ml) and the mixture stirred for 0.5 h. To the suspension DMF (3 drops) was added and the mixture stirred for 14 h. The solid was completly dissolved after *ca.* 20 min. The volatile compounds were then removed *i.v.*, and the residue was dried for 20 h (10^{-4} mbar) and subsequently dissolved in CH_2Cl_2 (150 ml), cooled to 0°, and **10** (20.14 g, 72.12 mmol; containing 1 equiv. of (*t*-Bu)Ph_2SiF) was added, followed by dropwise addition of pyridine (8.73 ml). The mixture was then stirred for 3 h at 0° and for 8 h at r.t. After the reaction was finished, Et_2O (200 ml) was added and the org. layer washed twice with 1N HCl and once with aq. sat. NaCl soln., dried ($MgSO_4$), filtered and evaporated *i.v.* FC (SiO_2 (450 g), Et_2O/pentane 1:1): 18 g (18.78 mmol; 52%) of **46**. Colorless oil. R_f 0.33 (Et_2O/pentane 1:1). $[\alpha]_D^{r.t.} = -18.4$, $[\alpha]_{365}^{r.t.} = -64.4$ (*c* = 0.76, CH_2Cl_2). IR: 3032*m*, 2987*w*, 2934*m*, 2859*w*, 1959*w*, 1887*w*, 1736*vs*, 1606*w*, 1456*m*, 1428*m*, 1383*m*, 1364*m*, 1304*s*, 1135*s*, 1113*vs*, 1059*s*. ^{1}H-NMR (300 MHz): 8.50 (*t*, *J* = 1.31, 1 arom. H); 8.18 (*d*, *J* = 1.31, 2 arom. H); 7.69–7.67 (*m*, 4 arom. H); 7.46–7.29 (*m*, 16 arom. H); 5.52–5.46 (*m*, 2CH); 5.34–5.27 (*m*, 2CH); 5.08 (*s*, $2CH_2$); 4.82 (*s*, CH_2); 2.76–2.48 (*m*, $4CH_2$); 1.39 (*d*, *J* = 6.26, 2Me); 1.22 (*d*, *J* = 6.33, 2Me); 1.13 (*s*, *t*-Bu). ^{13}C-NMR (75 MHz): 169.93; 169.19; 164.89; 142.10; 135.67; 135.54; 153.04; 131.26; 130.75; 129.89; 129.27; 128.57; 128.35; 127.83; 68.29; 67.72; 66.49; 64.54; 41.03; 40.66; 26.84; 19.91; 19.82; 19.33. LSI-MS: 971.4 (6.3, $[M + Na - H]^+$); 957.4 (12, $[M - 2H]^+$). Anal. calc. for $C_{55}H_{62}O_{13}Si \cdot CF_3CH_3OH$ ($C_{57}H_{65}F_3O_{14}Si$): C 64.64, H 6.19; found: C 64.03, H 6.27.

*3,3'-{5-{{[(*tert*-Butyl)diphenylsilyl]oxy}methyl}benzene-1,3-diyl}bis{(carbonyloxy)[(3*R*)-3-methyl-1-oxopropane-3,1-diyl-1-oxy]}bis[(3*R*)-butanoic Acid]* (**50**). As described in *GP III*, **46** (2.87 g, 3 mmol) was hydrogenated in CF_3CH_2OH (80 ml). Workup and careful drying under h.v.: 2.32 g (2.98 mmol; 98%) of **50**. Colorless oil. $[\alpha]_D^{r.t.} = -48.2$, $[\alpha]_{365}^{r.t.} = -140.9$ (*c* = 0.56, CH_2Cl_2). IR: 3500–2300(br.), 3011*m*, 2988*w*, 2934*m*, 2859*w*, 1734*vs*, 1607*w*, 1450*w*, 1428*m*, 1383*m*, 1303*s*, 1136*m*, 1114*s*, 1056*m*. ^{1}H-NMR (300 MHz): 8.45 (*t*, *J* = 1.46, 1 arom. H); 8.21 (*d*, *J* = 1.46, 2 arom. H); 7.73–7.67 (*m*, 4 arom. H); 7.47–7.35 (*m*, 6 arom. H); 5.55–5.48 (*m*, 2CH); 5.35–5.29 (*m*, 2CH); 4.85 (*s*, CH_2); 2.82–2.43 (*m*, $4CH_2$); 1.42 (*d*, *J* = 6.26, 2Me); 1.24 (*d*, *J* = 6.36, 2Me); 1.14 (*s*, *t*-Bu). ^{13}C-NMR (75 MHz): 175.20; 169.70; 165.17; 141.91; 135.52; 134.80; 133.04; 132.99; 132.56; 131.36; 130.91; 130.60; 130.17; 129.92; 129.64; 129.43; 127.86; 127.71; 69.10; 68.93; 67.61; 67.25; 64.60; 64.28; 40.20; 26.89; 20.19; 19.92; 19.83; 19.36. LSI-MS: 1580.2 (5.9, $[2M + Na]^+$), 823 (16, $[M + 2Na - H]^+$), 801.3 (100, $[M + Na]^+$), 779.3 (14, M^+).

*Bis{(1*R*)-3-[(1*R*)-3-(benzyloxy)-1-methyl-3-oxopropoxy]-1-methyl-3-oxopropyl} 5-(Hydroxymethyl)benzene-1,3-dicarboxylate* (**54**). As described in *GP IV*, **46** (3.35 g, 3.5 mmol) was dissolved in CH_2Cl_2 (50 ml) and HF · pyridine (5 ml) was added at 0°, and the mixture was stirred vigorously for 15 min. Workup and FC (SiO_2 (82 g), Et_2O/pentane 3:1; R_f((*t*-Bu)Ph_2 SiF) 1): 2.33 g (3.23 mmol; 92.5%) of **54**. Colorless oil. R_f 0.34 (Et_2O/pentane 3:1). $[\alpha]_D^{r.t.} = -19.6$ (*c* = 2.05, CH_2Cl_2). IR: 3500–3200(br.), 3011*m*, 2988*w*, 2937*m*, 2878*w*, 1723*vs*, 1606*w*, 1498*w*, 1455*s*, 1382*m*, 1306*s*, 1133*m*, 1101*s*, 1056*m*, 974*s*, 908*m*. ^{1}H-NMR (400 MHz): 8.53 (*m*, 1 arom. H); 8.16 (*m*, 2 arom. H); 7.36–7.27 (*m*, 10 arom. H); 5.52–5.43 (*m*, 2CH); 5.34–5.25 (*m*, 2CH); 5.06 (*s*, $2CH_2$); 4.75 (*d*, *J* = 6.06, CH_2); 2.73–2.50 (*m*, $4CH_2$); 1.40 (*d*, *J* = 6.32, 2Me); 1.24 (*d*, *J* = 6.34, 2Me). ^{13}C-NMR (100 MHz): 170.06; 169.24; 164.79; 142.03; 135.62; 132.00; 131.06; 129.88; 128.59; 128.47; 128.34; 68.44; 67.73; 66.53; 64.19; 40.98; 40.73; 19.87; 19.83. LSI-MS: 721.4 (36.18, $[M + H]^+$), 419.2 (37.55), 333.1 (56.2), 265.1 (68.55), 181.1 (100), 155.1 (73). Anal. calc. for $C_{39}H_{44}O_{13}$: C 64.99, H 6.15; found: C 64.82, H 5.90.

(1R)-3-{(1R)-3-[(9H-Fluoren-9-yl)methoxy]-1-methyl-3-oxopropoxy}-1-methyl-3-oxopropyl 3,5-Bis-{{[(tert-Butyl)diphenylsilyl]oxy}methyl}benzoate (**56**). Synthesis of the acid chloride as described in *GP I*, with **36** (2.64 g, 4.0 mmol) in CH_2Cl_2 (10 ml) with $(COCl)_2$ (2 ml), and with DMF (3 drops). Coupling as described in *GP II*, in CH_2Cl_2 (20 ml) with **42** (1.80 g, 4.89 mmol) at 0°. Workup and FC (SiO_2 (120 g), Et_2O/pentane 1:3): 1.82 g (1.8 mmol; 37%) of **56**. Colorless oil. $[\alpha]_D^{r.t.} = -10.0$, $[\alpha]_{365}^{r.t.} = -37.7$ ($c = 1.15$, CH_2Cl_2). IR: 3072*w*, 3007*w*, 2932*m*, 2859*m*, 1595*w*, 1603*w*, 1735*vs*, 1606*w*, 1472*w*, 1450*m*, 1428*m*, 1304*s*, 1178*s*, 1113*vs*, 1059*s*. ^{1}H-NMR (400 MHz): 7.85–7.26 (*m*, 28 arom. H); 5.53–5.45 (*m*, CH); 5.31–5.23 (*m*, CH); 4.82 (*s*, $2CH_2$); 4.36 (*d*, $J = 7.11$, CH_2); 4.16 (*t*, $J = 7.11$, CH); 2.73–2.49 (*m*, $2CH_2$); 1.38 (*d*, $J = 6.29$, Me); 1.20 (*d*, $J = 6.32$, Me); 1.09 (*s*, 2 *t*-Bu). ^{13}C-NMR (100 MHz): 170.04; 169.24; 165.69; 143.64; 141.50; 141.29; 135.57; 134.81; 133.32; 130.13; 129.76; 128.17; 127.81; 127.77; 127.13; 125.83; 124.99; 120.21; 120.02; 67.78; 67.63; 66.52; 65.16; 46.72; 41.24; 40.60; 26.86; 26.57; 19.97; 19.74; 19.31. LSI-MS: 1007.3 (3.5, $[M - 2H]^+$), 641.1 (22), 385.0 (12), 197.0 (38), 179.0 (100). Anal. calc. for $C_{63}H_{68}O_8Si_2$: C 74.96, H 6.79; found: C 74.94, H 6.87.

(1R)-3-{(1R)-3-[(9H-Fluoren-9-yl)methoxy]-1-methyl-3-oxopropoxy}-1-methyl-3-oxopropyl 3,5-Bis(hydroxymethyl)benzoate (**59**). As described in *GP IV*, **56** (1.45 g, 1.44 mmol) was dissolved in CH_2Cl_2 (35 ml), mixed with HF · pyridine (4.5 ml) at 0°, and the mixture stirred vigorously for 15 min. Workup and FC (SiO_2 (80 g), Et_2O): 770 mg (1.41 mmol; 98%) of **59**. Colorless oil. $[\alpha]_D^{r.t.} = -14.1$, $[\alpha]_{365}^{r.t.} = -46.8$ ($c = 0.87$, CH_2Cl_2). IR: 3428*w*, 3008*m*, 2937*w*, 2878*w*, 1949*w*, 1918*w*, 1736*vs*, 1608*w*, 1450*s*, 1383*s*, 1305*vs*, 1177*vs*, 1137*m*, 1103*s*, 1058*s*. ^{1}H-NMR (400 MHz): 7.87–7.86 (*m*, 2 arom. H); 7.76–7.50 (*m*, 5 arom. H); 7.42–7.28 (*m*, 4 arom. H); 5.54–5.46 (*m*, CH); 5.34–5.26 (*m*, CH); 4.67 (*s*, $2CH_2$); 4.32, 4.28 (*AB* of *ABX*, $J_{AB} = 10.77$, $J_{AX} = 7.341$, $J_{BX} = 6.76$); 4.13 (*dd*, $J = 7.34$, 6.76, CH); 2.73, 2.60 (*AB* of *ABX*, $J_{AB} = 16.42$, $J_{AX} = 8.16$, $J_{BX} = 5.00$); 2.70, 2.55 (*AB* of *ABX*, $J_{AB} = 15.69$, $J_{AX} = 7.87$, $J_{BX} = 5.21$); 1.39 (*d*, $J = 6.32$, Me); 1.23 (*d*, $J = 6.32$, Me). ^{13}C-NMR (100 MHz): 170.36; 169.47; 165.48; 143.62; 143.59; 141.69; 141.28; 141.27; 130.77; 129.77; 127.87; 127.85; 127.18; 127.15; 127.06; 125.00; 124.96; 120.05; 109.16; 68.20; 67.70; 66.64; 64.61; 46.65; 41.16; 40.76; 19.94; 19.81. LSI-MS: 1597.5 (0.2, $[3M + H]^+$), 1065.3 (1.4, $[2M + H]^+$), 555.1 (2.3, $[M + Na]^+$), 533.1 (14, $[M + H]^+$), 325.0 (24), 251.0 (12), 178.0 (100).

(1R)-3-{(1R)-3-[(9H-Fluoren-9-yl)methoxy]-1-methyl-3-oxopropoxy}-1-methyl-3-oxopropyl (4R,8R,22R,26R)-31-{{[(tert-Butyl)diphenylsilyl]oxy}methyl}-4,8,22,26-tetramethyl-2,6,10,20,24,28-hexaoxo-3,7,11,19,23,27-hexaoxatricyclo[27.3.1.1^{13,17}]tetratriaconta-1(32),13,15,17(34),29(33),30-hexaene-15-carboxylate (**62**). Synthesis of the acid chloride as described in *GP I*, with **50** (1.40 g, 1.8 mmol) in CH_2Cl_2 (20 ml). After drying of the acid chloride (h.v., 10^{-5} mbar), **59** (959 mg, 1.80 mmol) and CH_2Cl_2 (10 ml) were added to the residue, and a syringe was filled with the soln. The soln. was then added dropwise within 3 h at −78° to a soln. of pyridine (1 ml) in CH_2Cl_2 (20 ml). Then, the mixture was stirred for 5 h at −78° and 36 h at r.t.; Et_2O (50 ml) was added and the org. layer washed twice with 1N HCl and once with aq. sat. NaCl soln., dried ($MgSO_4$), filtered, and evaporated *i.v.* FC (SiO_2 (120 g), Et_2O/pentane 3:1): 1.15 g (902 μmol; 50%) of **62**. White, foamy solid. $[\alpha]_D^{r.t.} = -21.4$, $[\alpha]_{578}^{r.t.} = -22.7$, $[\alpha]_{546}^{r.t.} = -25.8$, $[\alpha]_{436}^{r.t.} = -44.9$, $[\alpha]_{365}^{r.t.} = -73.3$ ($c = 0.445$, CH_2Cl_2). IR: 3011*w*, 2929*w*, 2858*w*, 1737*vs*, 1606*w*, 1450*m*, 1428*w*, 1384*m*, 1304*s*, 1178*vs*, 1104*s*, 1057*s*. ^{1}H-NMR (500 MHz): 8.46 (*t*, $J = 1.66$, 1 arom. H); 8.15 (*d*, $J = 1.66$, 2 arom. H); 7.84 (*d*, $J = 1.67$, 2 arom. H); 7.75–7.28 (*m*, 19 arom. H); 5.53–5.45 (*m*, 3CH); 5.34–5.25 (*m*, 3CH); 5.03, 5.02 (2 *AB*, $J_{AB} = 12.70$); 4.80 (*s*, CH_2); 4.36 (*d*, $J = 7.02$, CH_2); 4.17 (*t*, $J = 7.02$, CH); 2.79–2.49 (*m*, $6CH_2$); 1.39 (*d*, $J = 6.34$, Me); 1.38 (*d*, $J = 6.35$, 2Me); 1.24 (*d*, $J = 6.34$, 2Me); 1.21 (*d*, $J = 6.31$, Me); 1.11 (*s*, *t*-Bu). ^{13}C-NMR (125 MHz): 170.03; 169.72; 169.36; 169.26; 164.89; 164.86; 143.65; 143.63; 142.03; 141.28; 136.59; 135.54; 133.05; 133.01; 132.21; 131.24; 130.95; 130.71; 129.89; 129.16; 129.07; 127.83; 127.83; 127.13; 124.99; 124.96; 120.05; 68.37; 68.16; 67.65; 67.63; 66.53; 65.53; 64.50; 46.70; 41.07; 40.81; 40.67; 40.61; 40.44; 26.85; 19.91; 19.89; 19.86; 19.76; 19.32. LSI-MS: 1297.6 (57, $[M + Na - H]^+$), 1275.5 (4.2, M^+). Anal. calc. for $C_{72}H_{76}O_{19}Si$: C 67.91, H 6.02; found: C 67.67, H 6.11.

(1R)-3-[(1R)-2-Carboxy-1-methylethoxy]-1-methyl-3-oxopropyl(4R,8R,22R,26R)-31-(Hydroxymethyl)-4,8,22,26-tetramethyl-2,6,10,20,24,28-hexaoxo-3,7,11,19,23,27-hexaoxatricyclo[27.3.1.1^{13,17}]tetratriaconta-1(32),13,15,17(34),29(33),30-hexaene-15-carboxylate (**65**). As described in *GP IV*, **62** (1.05 g, 823 μmol) was dissolved in CH_2Cl_2 (30 ml), mixed with HF · pyridine (3.3 ml) at 0° and stirred vigorously for 13 min. Workup yielded 1.04 g (818 μmol, 99%; containing 1 equiv. of (*t*-Bu)Ph_2SiF) of a white foam, which was dissolved in CH_2Cl_2 (20 ml). After addition of piperidine (4 ml) and stirring for 80 min at r.t., Et_2O (50 ml) was added and the org. layer was washed twice with 1N HCl and once with aq. sat. NaCl soln., dried ($MgSO_4$), filtered, and evaporated *i.v.* The viscous crude product was dissolved twice in CH_2Cl_2, precipitated with pentane and the solvent was carefully decanted: 640 mg (757 μmol; 91%) of **65**. $[\alpha]_D^{r.t.} = -44.1$, $[\alpha]_{578}^{r.t.} = -46.3$, $[\alpha]_{546}^{r.t.} = -52.5$, $[\alpha]_{436}^{r.t.} = -89.4$, $[\alpha]_{365}^{r.t.} = -140.7$ ($c = 0.905$, CH_2Cl_2). IR: 3520*w*, 3032*w*, 2987*w*, 2923*w*, 1735*vs*, 1606*w*, 1456*m*, 1384*s*, 1304*vs*, 1136*s*, 1102*m*, 1056*vs*. ^{1}H-NMR (400 MHz): 8.50 (*t*, $J = 1.64$, 1 arom. H); 8.13 (*d*, $J = 1.64$, 2 arom. H); 1.76 (*d*, $J = 1.66$, 2 arom. H); 7.29 (*t*, $J = 1.66$, 1 arom. H); 5.53–5.44 (*m*, 3CH); 5.36–5.28 (*m*, 3CH);

4.98, 4.97 (2 *AB*, J_{AB} = 12.54); 4.73, 4.72 (*AB*, J_{AB} = 12.51); 2.83–2.49 (*m*, 6 CH_2); 1.41 (*d*, *J* = 6.31, Me); 1.38 (*d*, *J* = 6.34, 2 Me); 1.29 (*d*, *J* = 6.34, 2 Me); 1.28 (*d*, J = 6.32, Me). ^{13}C-NMR (100 MHz): 172.41; 170.19; 169.61; 169.53; 165.13; 164.76; 142.01; 136.41; 132.53; 132.11; 130.97; 130.91; 129.70; 129.33; 68.66; 68.41; 67.68; 67.64; 65.66; 64.07; 40.99; 40.93; 40.71; 40.22; 19.98; 19.90; 19.85. LSI-MS: 881.2 (28, $[M + Na]^+$), 859.2 (100, $[M + H]^+$). Anal. calc. for $C_{42}H_{50}O_{19}$: C 58.74, H 5.87; found: C 58.52, H 5.87.

(6R,10R,22R,26R,35R,39R)-6,10,22,26,35,39-Hexamethyl-5,9,13,21,25,29,34,38,42-nonaoxatetracyclo[15.15.11.1^{3,31}.1^{15,29}]pentatetraconta-1,3(45),15,17,19(44),31-hexaene-4,8,12,20,24,28,33,37,41-nonone (**68**). To a soln. of **65** (269 mg, 313 µmol) in THF (10 ml was added, at 0°, 2,6-dichlorobenzoyl chloride (50 µl, 350 µmol). After stirring for 30 min, pyridine (150 µl, 1.8 mmol) was added, and the mixture was then stirred for 2 h at 0° and for 1 h at r.t., followed by addition of CH_2Cl_2 (20 ml) and stirring for additional 45 h. Workup as described in *GP II*, and FC (SiO_2 (40 g), Et_2O/pentane 5:1): 140 mg (166.5 µmol; 53%) of **68**. White foam. $[\alpha]_D^{r.t.} = -53.5$, $[\alpha]_{578}^{r.t.} = -56.2$, $[\alpha]_{546}^{r.t.} = -64.5$, $[\alpha]_{436}^{r.t.} = -116.6$, $[\alpha]_{365}^{r.t.} = -201.5$ (*c* = 0.61, CH_2Cl_2). IR: 2011*w*, 2986*w*, 2937*w*, 1736v*s*, 1610*w*, 1456*m*, 1384*s*, 1303v*s*, 1140*s*, 1101*s*, 1056v*s*, 972*w*, 908*w*. ^{1}H-NMR (500 MHz): 8.45 (*s*, 1 arom. H); 8.08 (*s*, 1 arom. H); 7.91 (*s*, 1 arom. H); 7.81 (*s*, 1 arom. H); 7.71 (*s*, 1 arom. H); 7.28 (*s*, 1 arom. H); 5.61–5.54 (*m*, 1 CH); 5.49–5.29 (*m*, 5 CH); 5.11, 4.85 (*AB*, J_{AB} = 12.81); 5.03, 4.96 (*AB*, J_{AB} = 12.63); 5.02, 4.94 (*AB*, J_{AB} = 12.81); 2.81–2.47 (*m*, 6 CH_2); 1.40 (*d*, *J* = 6.38, Me); 1.35 (*d*, *J* = 6.37, Me); 1.33 (*d*, *J* = 6.36, Me); 1.32 (*d*, *J* = 6.39, Me); 1.31 (*d*, *J* = 6.41, Me); 1.30 (*d*, *J* = 6.35, Me). ^{13}C-NMR (125 MHz): 169.75; 169.72; 169.70; 169.58; 169.49; 169.40; 164.49; 164.25; 164.22; 136.78; 136.46; 136.00; 133.78; 132.23; 131.87; 131.38; 131.10; 130.71; 130.31; 129.34; 128.14; 68.56; 68.37; 68.29; 67.61; 67.53; 65.59; 65.38; 65.24; 41.12; 40.94; 40.89; 40.79; 40.49; 20.02; 19.93; 19.90; 19.78; 19.72. LSI-MS: 1681.5 (0.6, $[2M + H]^+$), 841.3 (100, $[M + H]^+$), 669.2 (6.8), 411.1 (15). Anal. calc. for $C_{42}H_{48}O_{18} \cdot CH_2Cl_2$ ($C_{43}H_{50}Cl_2O_{18}$): C 55.79, H 5.44; found: C 56.10, H 5.54.

*Bis[(1R,5R,9R,13R)-1,5,9,13-tetramethyl-3,7,11,15-tetraoxo-17-phenyl-4,8,12,16-tetraoxaheptadecyl] 5-{{[(*tert*-Butyl)diphenylsilyl]oxy}methyl}benzene-1,3-dicarboxylate* (**47**). After stirring a suspension of **34** (6.86 g, 15.79 mmol) in $(COCl)_2$ (30 ml) for 30 min, DMF (3 drops) was added, followed by an additional stirring over 20 h. The solid was completely dissolved after *ca.* 20 min. The volatile components were removed *i.v.* and dried for 21 h at h.v. (10^{-6} mbar). The residue was dissolved in CH_2Cl_2 (100 ml), and **11** (14.29 g, 31.5 mmol) was added, the soln. cooled to 0°, and pyridine (3.8 ml) was added dropwise. The soln. was then stirred for 3 h at 0° and for 21 h at r.t. After addition of CH_2Cl_2 (80 ml) the org. layer was washed twice with 1N HCl and once with aq. sat. NaCl soln., dried ($MgSO_4$), filtered, and evaporated *i.v.* FC (SiO_2 (360 g), CH_2Cl_2/Et_2O 12:1): 4.1 g (3.14 mmol; 19.8 %) of **47**. Colorless oil. R_f 0.57 (CH_2Cl_2/Et_2O 12:1). $[\alpha]_D^{r.t.} = -14.1$, $[\alpha]_{365}^{r.t.} = -47.2$ (*c* = 0.77, CH_2Cl_2). $[\alpha]_D = -14.8$ (c = 1.47, CH_2Cl_2). IR: 3041*w*, 2996*w*, 2935*w*, 2859*w*, 1735v*s*, 1606*w*, 1456*w*, 1427*w*, 1383*m*, 1305*s*, 1179v*s*, 1132*s*, 1103*s*, 1058*s*. ^{1}H-NMR (500 MHz): 8.49 (*t*, *J* = 1.66, 1 arom. H); 8.17 (*d*, *J* = 1.66, 2 arom. H); 7.68–7.66 (*m*, 4 arom, H); 7.45–7.29 (*m*, 16 arom. H); 5.55–5.48 (*m*, 2 CH); 5.32–5.18 (*m*, 6 CH); 5.11 (*s*, 2 CH_2); 4.82 (*s*, CH_2); 2.80–2.35 (*m*, 8 CH_2); 1.42 (*d*, *J* = 6.30, 2 Me); 1.26 (*d*, *J* = 6.33, 2 Me); 1.22 (*d*, *J* = 6.32, 2 Me); 1.21 (*d*, *J* = 6.31, 2 Me); 1.12 (*s*, *t*-Bu). ^{13}C-NMR (125 MHz): 169.91; 169.17; 169.15; 169.11; 164.87; 142.08; 135.71; 135.54; 133.05; 131.26; 130.76; 129.89; 129.28; 128.59; 128.34; 127.83; 68.31; 67.69; 67.63; 67.56; 66.48; 64.55; 41.06; 40.79; 40.77; 40.67; 26.84; 19.94; 19.81; 19.77; 19.72; 19.32. LSI-MS: 1325.8 (13, $[M + Na - H]^+$), 531.0 (60), 385.0 (43), 267.0 (62). Anal. calc. for $C_{71}H_{86}O_{21}Si$: C 65.42, H 6.65; found: C 65.14, H 6.69.

*3,3′-{5-{{[(*tert*-Butyl)diphenylsilyl]oxy}methyl}benzene-1,3-diyl}bis{(carbonyloxy){(3R)-3-methyl-{(3R)-{3-methyl-[(3R)-3-methyl-1-oxopropane-3,1-diyl-1-oxy]-1-oxopropane-3,1-diyl-1-oxy}-1-oxopropane-3,1-diyl-1-oxy}}}bis[(3R)-butanoic Acid]* (**51**). As described in *GP III*, **47** (1.70 g, 1.30 mmol) was hydrogenated in CF_3CH_2OH (100 ml). Workup, precipitation with Et_2O/pentane, and careful drying under h.v.: 1.42 g (1.26 mmol; 97%) of **51**. Colorless oil. $[\alpha]_D^{r.t.} = -16.7$, $[\alpha]_{365}^{r.t.} = -46.8$ (*c* = 0.21, CH_2Cl_2). $[\alpha]_D = -18.18$ (*c* = 1.655, CH_2Cl_2). IR: 3500–2400 (br.), 3011*w*, 2986*w*, 2936*w*, 1736v*s*, 1606*w*, 1449*w*, 1383*m*, 1305*s*, 1136*m*, 1103*m*, 1056*s*. ^{1}H-NMR (400 MHz): 8.48 (*s*, 1 arom. H); 8.18 (*s*, 2 arom. H); 7.69–7.66 (*m*, 4 arom. H); 7.44–7.36 (*m*, 6 arom. H); 5.57–5.51 (*m*, 2 CH); 5.30–5.21 (*m*, 6 CH); 4.83 (*s*, CH_2); 2.83–2.39 (*m*, 8 CH_2); 1.45 (*d*, *J* = 6.33, Me); 1.43 (*d*, *J* = 6.33, Me); 1.28–1.20 (*m*, 6 Me); 1.12 (*s*, *t*-Bu). ^{13}C-NMR (100 MHz): 175.26; 174.71; 169.70; 169.64; 169.57; 169.40; 169.24; 164.99; 164.18; 142.11; 135.55; 134.98; 134.87; 133.04; 131.41; 131.32; 130.72; 129.90; 129.30; 127.84; 68.93; 68.37; 68.00; 67.93; 67.87; 67.69; 67.54; 64.55; 41.05; 40.98; 40.90; 40.81; 40.46; 26.85; 20.00; 19.94; 19.84; 19.78; 19.74; 19.70; 19.33. LSI-MS: 1167.4 (17, $[M + 2Na - 2H]^+$), 1145.5 (100, $[M + Na - H]^+$), 921.2 (24).

Bis[(1R,5R,9R,13R)-1,5,9,13-tetramethyl-3,7,11,15-tetraoxo-17-phenyl-4,8,12,16-tetraoxaheptadecyl] 5-(Hydroxymethyl)benzene-1,3-dicarboxylate (**55**). As described in *GP IV*, **47** (1.39 g, 1.07 mmol) was dissolved in CH_2Cl_2 (15 ml), and HF · pyridine (1.5 ml) was added at 0° and the mixture stirred vigorously for 15 min. Workup

and FC (SiO_2 (80 g), CH_2Cl_2/Et_2O 5:1; R_f ((*t*-Bu)Ph_2SiF) 1): 0.86 g (0.807 mmol; 75.6%) of **55**. Colorless oil. R_f 0.4 (CH_2Cl_2/Et_2O 5:1). $[\alpha]_D^{r.t.} = -9.86$ (*c* = 1.5, CH_2Cl_2). IR: 3535(br.), 3032*m*, 2986*m*, 2937*w*, 2878*w*, 1729*vs*, 1606*w*, 1498*w*, 1456*s*, 1383*m*, 1306*s*, 1174*m*, 1101*s*, 1057*m*, 977*s*, 908*m*. ^{1}H-NMR (400 MHz): 8.53 (*m*, 1 arom. H); 8.18 (*m*, 2 arom. H); 7.37–7.29 (*m*, 10 arom. H); 5.56–5.48 (*m*, 2CH); 5.31–5.23 (*m*, 4CH); 5.22–5.13 (*m*, 2CH); 5.10 (*s*, $2CH_2$); 4.78 (*d*, *J* = 6.05, $1CH_2$); 2.80–2.34 (*m*, $8CH_2$); 1.42 (*d*, *J* = 6.33, 2Me); 1.25 (*d*, *J* = 6.31, 2Me); 1.23 (*d*, *J* = 6.31, 2Me); 1.19 (*d*, *J* = 6.31, 2Me). ^{13}C-NMR (100 MHz): 169.93; 169.26; 169.25; 169.21; 164.80; 142.22; 135.66; 131.97; 130.98; 129.80; 128.57; 128.32; 68.42; 67.71; 67.59; 66.47; 64.08; 40.96; 40.81; 40.74; 40.63; 19.88; 19.76; 19.66. LSI-MS: 1065.5(24.46, $[M + H]^+$), 591.2(16.44), 505.2(21.1), 419.2(44.03), 333.1(34.43), 265.1(25.43), 192.1(8.13), 155.1(100).

*(1*R*,5*R*,9*R*,13*R*)-17-(9*H*-Fluoren-9-yl)-1,5,9,13-tetramethyl-3,7,11,15-tetraoxo-4,8,12,16-tetraoxaheptadecyl 3,5-Bis{{[(*tert*-Butyl)diphenylsilyl]oxy}methyl}benzoate* (**57**). Synthesis of the acid chloride as described in *GP I*, with **36** (2.67 g, 4.05 mmol) in CH_2Cl_2 (10 ml), with $(COCl)_2$ (2 ml) and DMF (3 drops). Coupling as described in *GP II*, in CH_2Cl_2 (20 ml) with **43** (1.85 g, 3.4 mmol) at 0°. Workup and FC (SiO_2 (220 g), Et_2O/pentane 1:2): 1.87 g (1.56 mmol; 46%) of **57**. Colorless oil. $[\alpha]_D^{r.t.} = -7.6$, $[\alpha]_{365}^{r.t.} = -28.5$ (*c* = 0.165, CH_2Cl_2). IR: 3008*w*, 2933*m*, 2859*w*, 1717*vs*, 1606*w*, 1472*w*, 1450*w*, 1428*m*, 1382*m*, 1305*s*, 1178*s*, 1113*vs*, 1059*s*. ^{1}H-NMR (500 MHz): 7.84 (*s*, 2 arom. H); 7.75 (*d*, *J* = 3.55, 2 arom. H); 7.70–7.68 (*m*, 8 arom. H); 7.61 (*s*, 1 arom. H); 7.58 (*d*, *J* = 3.55, 2 arom. H); 7.44–7.29 (*m*, 16 arom. H); 5.52–5.44 (*m*, CH); 5.30–5.19 (*m*, 3CH); 4.78 (*s*, CH_2); 4.78 (*s*, CH_2); 4.39 (*d*, *J* = 7.10, CH_2); 4.19 (*t*, *J* = 7.10, CH); 2.77 (*m*, $4CH_2$); 1.39 (*d*, *J* = 6.31, Me); 1.25 (*d*, *J* = 6.31, Me); 1.21 (*d*, *J* = 6.31, Me); 1.17 (*d*, *J* = 6.31, Me); 1.09 (*s*, 2 *t*-Bu). ^{13}C-NMR (125 MHz): 170.04; 169.17; 165.66; 143.65; 143.63; 141.48; 141.29; 135.56; 133.29; 130.11; 129.76; 128.12; 127.83; 127.76; 127.13; 125.80; 125.00; 124.99; 120.05; 67.76; 67.64; 67.57; 67.54; 66.54; 65.14; 46.71; 41.14; 40.81; 40.76; 40.58; 26.85; 19.96; 19.73; 19.30. LSI-MS: 1203.9(0.8, $[M + Na - H]^+$), 1123.9(1.3, $[M - 57]^+$), 385.2(13), 247.2(15), 199.1(35), 179.1(100). Anal. calc. for $C_{71}H_{80}O_{12}Si_2$: C 72.17, H 6.82; found: C 72.00, H 7.06.

*(1*R*,5*R*,9*R*,13*R*)-17-(9*H*-Fluoren-9-yl)-1,5,9,13-tetramethyl-3,7,11,15-tetraoxo-4,8,12,16-tetraoxaheptadecyl 3,5-Bis(hydroxymethyl)benzoate* (**60**). As described in *GP IV*, **57** (1.80 g, 1.52 mmol) was dissolved in CH_2Cl_2 (40 ml), and mixed, at 0°, with HF · pyridine (4 ml), and the mixture stirred vigorously for 15 min. Workup and FC (SiO_2 (80 g), Et_2O): 870 mg (1.23 mmol; 81%) of **60**. Colorless oil. $[\alpha]_D^{r.t.} = -7.1$, $[\alpha]_{365}^{r.t.} = -21.9$ (*c* = 0.17, CH_2Cl_2). IR: 3517*w*, 3008*w*, 2937*w*, 1737*vs*, 1608*w*, 1450*m*, 1383*m*, 1305*s*, 1178*s*, 1136*m*, 1102*m*, 1058*s*. ^{1}H-NMR (400 MHz): 7.91 (*s*, 1 arom. H); 7.76 (*d*, *J* = 7.53, 2 arom. H); 7.59–7.56 (*m*, 3 arom. H); 7.42–7.29 (*m*, 4 arom. H); 5.54–5.46 (*m*, CH); 5.29–5.19 (*m*, 2CH); 5.18–5.10 (*m*, CH); 4.72 (*d*, *J* = 5.02, $2CH_2$); 4.40 (*d*, *J* = 7.04, CH_2); 4.19 (*t*, *J* = 7.04, CH); 2.77–2.37 (*m*, $4CH_2$); 2.26 (*t*, *J* = 5.02, 2OH); 1.41 (*d*, *J* = 6.32, Me); 1.22 (*d*, *J* = 6.30, Me); 1.21 (*d*, *J* = 6.45, Me); 1.18 (*d*, *J* = 6.33, Me). ^{13}C-NMR (100 MHz): 170.17; 169.42; 169.40; 169.37; 165.53; 143.64; 141.80; 141.32; 130.80; 129.85; 127.87; 127.16; 127.10; 125.00; 124.98; 120.08; 68.19; 67.78; 67.67; 67.57; 66.59; 67.64; 46.73; 41.07; 40.89; 40.82; 40.58; 19.94; 19.81; 19.70. LSI-MS: 1410.0(6.0, $[2M + 2H]^+$), 705.4 (44, $[M + H]^+$), 479.3 (23), 393.2 (20), 251.3 (21), 178.1(100).

*(1*R*,5*R*,9*R*,13*R*)-17-(9*H*-Fluoren-9-yl)-1,5,9,13-tetramethyl-3,7,11,15-tetraoxo-4,8,12,16-tetraoxaheptadecyl (4*R*,8*R*,12*R*,16*R*,30*R*,34*R*,38*R*,42*R*)-47-{{[(tert-Butyl)diphenylsilyl]oxy}methyl)}-4,8,12,16,30,34,38,42-octamethyl-2,6,10,14,18,28,32,36,40,44-decaoxo-3,7,11,15,19,27,31,35,39,43-decaoxatricyclo[41.3.1.1^{21,25}]pentaconta-1(48),21,23,25(50),45(49),46-hexaene-23-carboxylate* (**63**). Synthesis of the acid chloride as described in *GP I*, with **51** (1.21 g, 1.08 mmol) in CH_2Cl_2 (20 ml). After drying of the acid chloride (h.v., 45°), a soln. of **60** (780 mg, 1.1 mmol) in CH_2Cl_2 (10 ml) was added. A syringe was filled with the soln. and added dropwise, within 2.5 h, to a soln. of pyridine (1 ml) in CH_2Cl_2 (10 ml) at −78°. After stirring for 2 h at −78° and 1 h at r.t., Et_2O (50 ml) was added and the org. layer washed twice with 1N HCl and once with aq. sat. NaCl soln., dried ($MgSO_4$), filtered, and evaporated *i.v.* FC (SiO_2 (100 g), Et_2O/CH_2Cl_2 1:5): 360 mg (201 μmol; 19%) of **63**. White, foamy solid. $[\alpha]_D^{r.t.} = -14.9$, $[\alpha]_{365}^{r.t.} = -47.6$ (*c* = 0.535, CH_2Cl_2). IR: 3032*w*, 2987*w*, 2935*w*, 1737*vs*, 1605*w*, 1450*w*, 1428*w*, 1383*m*, 1305*s*, 1178*vs*, 1134*m*, 1103*m*, 1058*s*. ^{1}H-NMR (400 MHz): 8.47 (*t*, *J* = 1.60, 1 arom. H); 8.18 (*d*, *J* = 1.60, 2 arom. H); 7.92 (*d*, *J* = 1.59, 2 arom. H); 7.76 (*d*, *J* = 7.54, 2 arom. H); 7.69–7.66 (*m*, 4 arom. H); 7.59 (*d*, *J* = 7.49, 2 arom. H); 7.54 (*t*, *J* = 1.59, 1 arom. H); 7.45–7.29 (*m*, 19 arom. H); 5.56–5.45 (*m*, 3CH); 5.32–5.16 (*m*, 9CH); 5.13 (*s*, $2CH_2$); 4.82 (*s*, CH_2); 4.40 (*d*, *J* = 7.06, CH_2); 4.20 (*t*, *J* = 7.06, CH); 2.80–2.37 (*m*, $12CH_2$); 1.41 (*d*, *J* = 6.31, 2Me); 1.41 (*d*, *J* = 6.30, Me); 1.26 (*d*, *J* = 6.31, Me); 1.26 (*d*, *J* = 6.34, 2Me); 1.23 (*d*, *J* = 6.45, Me); 1.21 (*d*, *J* = 6.41, 2Me); 1.21 (*d*, *J* = 6.23, 2Me); 1.20 (*d*, *J* = 6.42, Me); 1.12 (*s*, *t*-Bu). ^{13}C-NMR (100 MHz): 170.03; 169.77; 169.19; 169.17; 164.92; 164.84; 143.66; 142.07; 141.31; 136.75; 135.54; 133.06; 132.23; 131.25; 131.05; 130.77; 129.89; 129.24; 129.03; 127.85; 127.83; 127.14; 125.00; 124.98; 120.07; 68.37; 68.26; 67.67; 67.63; 67.60; 67.56; 66.55; 65.54; 64.55; 46.74; 41.03; 40.97; 40.83; 40.76; 40.61; 40.51; 26.84; 19.93; 19.91; 19.80; 19.75; 19.72; 19.32. LSI-MS: 1814.5(21, $[M + Na]^+$), 1792.2(8.6, $[M + H]^+$), 319.1(23), 178.1(100). Anal. calc. for $C_{96}H_{114}O_{31}Si$: C 64.34, H 6.41; found: C 64.24, H 6.29.

17-[(4R,8R,12R,16R,30R,34R,38R,42R)-47-(Hydroxymethyl)-4,8,12,16,30,34,38,42-octamethyl-2,6,10,14,18,28,32,36,40,44-decaoxo-3,7,11,15,19,27,31,35,38,43-decaoxatricyclo[41.3.1.1^{21,25}]pentaconta-1(48),21,23,25(50),45(49),46-hexaen-23-yl]-3,7,11,15-tetramethyl-5,9,13,17-tetraoxo-4,8,12,16-tetraoxaheptadecanoic Acid (**66**). As described in *GP IV*, **63** (295 mg, 164 µmol) was dissolved in CH_2Cl_2 (20 ml) and HF · pyridine (3 ml) was added at 0°, and the mixture was stirred vigorously for 11 min. After workup, 270 mg of an oil were obtained, which was dissolved in CH_2Cl_2 (12 ml). After adding of piperidine (4 ml) at 0°, the soln. was stirred for 30 min. After addition of Et_2O (50 ml) the org. layer was washed twice with 1N HCl and once with aq. sat. NaCl soln., dried ($MgSO_4$), filtered, and evaporated *i.v.* The viscous crude product was dissolved twice in CH_2Cl_2, precipitated with pentane, and the solvent was decanted: 160 mg (116 µmol; 71%) of **66**. $[\alpha]_D^{r.t.} = -17.7$, $[\alpha]_{365}^{r.t.} = -53.1$ ($c = 0.435$, CH_2Cl_2). IR: 3524*w*, 3011*w*, 2986*w*, 2937*w*, 1736*vs*, 1606*w*, 1458*w*, 1383*m*, 1305*s*, 1178*vs*, 1136*s*, 1102*m*, 1058*s*. ^{1}H-NMR (500 MHz): 8.51 (*t*, $J = 1.64$, 1 arom. H); 8.16 (*d*, $J = 1.64$, 2 arom. H); 7.90 (*d*, $J = 1.60$, 2 arom. H); 7.52 (*t*, $J = 1.60$, 1 arom. H); 5.55–5.47 (*m*, 3CH); 5.35–5.20 (*m*, 6CH); 5.18–5.07 (*m*, 3CH); 5.12 (*s*, $2CH_2$); 4.77 (*s*, CH_2); 2.82–2.37 (*m*, $12CH_2$); 1.42 (*d*, $J = 6.24$, Me); 1.41 (*d*, $J = 6.31$, 2Me); 1.28 (*d*, $J = 6.34$, Me); 1.24 (*d*, $J = 6.34$, 3 Me); 1.24 (*d*, $J = 6.23$, 2Me); 1.22 (*d*, $J = 6.29$, Me); 1.19 (*d*, $J = 6.33$, 2Me). ^{13}C-NMR (125 MHz): 171.84; 169.96; 169.81; 169.40; 169.38; 169.36; 169.11; 165.11; 164.80; 142.30; 136.68; 132.35; 132.01; 130.95; 130.92; 129.75; 129.09; 68.44; 68.13; 67.77; 67.69; 67.67; 67.64; 67.62; 67.60; 67.02; 41.09; 40.91; 40.88; 40.76; 40.50; 40.34; 19.94; 19.91; 19.81; 19.78; 19.75; 19.68; 19.66. LSI-MS: 1397.8 (26, $[M + Na - H]^+$), 1375.8 (30, M^+), 319.1 (22), 155.1 (51). Anal. calc. for $C_{66}H_{88}O_{31} \cdot H_2O$ ($C_{66}H_{90}O_{32}$): C 56.89, H 6.37; found: C 56.87, H 6.50.

(6R,10R,14R,18R,30R,34R,38R,42R,51R,55R,59R,63R)-6,10,14,18,30,34,38,42,51,55,59,63-Dodecamethyl-5,9,13,17,21,29,33,37,41,45,50,54,58,62,66-pentadecaoxatetracyclo[23.23.19.1^{3,47}.1^{23,27}]nonahexaconta-1,3(69),23,25,27(68),47-hexaene-4,8,12,16,20,28,32,36,40,44,49,53,57,61,65-pentadecane (**69**). To **66** (126.7 mg, 92.1 µmol; dissolved in THF (10 ml)) was added, at 0°, 2,6-dichlorobenzoyl chloride (15.8 µl, 110.5 µmol), and the soln. was stirred for 30 min, followed by addition of pyridine (50 µl, 600 µmol). The soln. was stirred for 2 h at 0° and for 1 h at r.t. Then CH_2Cl_2 (20 ml) was added and the soln. stirred for another 45 h. Workup as described in *GP II*, and FC (SiO_2 (60 g), Et_2O/CH_2Cl_2 1:6): 25 mg (18.4 µmol; 20%) of **69**. White foam. $[\alpha]_D^{r.t.} = -12.7$, $[\alpha]_{365}^{r.t.} = -45.2$ ($c = 0.11$, CH_2Cl_2). IR: 3032*w*, 2987*w*, 2933*w*, 1738*vs*, 1605*w*, 1458*w*, 1383*m*, 1304*s*, 1178*s*, 1137*m*, 1102*m*, 1058*s*. ^{1}H-NMR (400 MHz): 8.50 (*t*, $J = 1.59$, 1 arom. H); 8.10 (*d*, $J = 1.59$, 2 arom. H); 7.86 (*d*, $J = 1.60$, 2 arom. H); 7.44 (*t*, $J = 1.60$, 1 arom. H); 5.53–5.45 (*m*, 3CH); 5.29–5.17 (*m*, 9CH); 5.11 (*s*, $2CH_2$); 5.07 (*s*, CH_2); 2.81–2.38 (*m*, $12CH_2$); 1.41 (*d*, $J = 6.31$, 2Me); 1.40 (*d*, $J = 6.25$, Me); 1.27 (*d*, $J = 6.32$, 2Me); 1.26 (*d*, $J = 6.22$, 3Me); 1.23 (*d*, $J = 6.43$, 3Me); 1.21 (*d*, $J = 6.33$, 1Me). ^{13}C-NMR (100 MHz): 169.77; 169.73; 169.22; 164.86; 164.43; 136.80; 136.68; 133.19; 132.12; 131.23; 131.13; 130.35; 128.97; 68.60; 68.39; 67.66; 67.59; 67.57; 65.51; 65.23; 40.90; 40.77; 40.51; 40.42; 19.90; 19.82; 19.74. LSI-MS: 1379.8 (11, $[M + Na\text{-}H]^+$), 1357.8 (100, M^+).

Bis[(1R,5R,9R,13R,17R,21R,25R,29R)-1,5,9,13,17,21,25,29-octamethyl-3,7,11,15,19,23,27,31-octaoxo-33-phenyl-4,8,12,16,20,24,28,32-octaoxatritriacontyl] 5-{{[(tert-Butyl)diphenylsilyl]oxy}methyl}benzene-1,3-dicarboxylate (**48**). To **34** (1.65 g, 5.0 mmol) was added $(COCl)_2$ (20 ml), and the soln. stirred for 30 min. Then, DMF (3 drops) was added to the suspension, and the soln. stirred for additional 4 h. A clear soln. was formed after *ca.* 20 min. The org. phase was evaporated *i.v.* and the residue dried at h.v. (10^{-4} mbar) for 12 h. The residue was then dissolved in CH_2Cl_2 (25 ml), **12** (5.50 g, 6.9 mmol) was added, the soln. cooled to 0°, pyridine (1 ml) was added dropwise, and the soln. was stirred for 30 min at 0° followed by 52 h at r.t. Et_2O (80 ml) was added, and the org. layer washed twice with 1N HCl and once with aq. sat. NaCl soln., dried ($MgSO_4$), filtered, and evaporated *i.v.* The crude product was dissolved in CH_2Cl_2 (50 ml), cooled to 0°, and DMAP (300 mg, 2.5 mmol) was added. After stirring for 4 h at 0° and for 6 h at r.t., workup as described. FC (SiO_2 (300 g), CH_2Cl_2/Et_2O 7:1): 2.40 g (1.16 mmol; 34%) of **48**. Colorless oil. ^{1}H-NMR (300 MHz): 8.49 (*s*, 1 arom. H); 8.18 (*s*, 2 arom. H); 7.69–7.66 (*m*, 4 arom. H); 7.46–7.32 (*m*, 16 arom. H); 5.56–5.49 (*m*, 2CH); 5.33–5.20 (*m*, 14CH); 5.12 (*s*, $2CH_2$); 4.83 (*s*, CH_2); 2.83–2.36 (*m*, $16CH_2$); 1.43 (*d*, $J = 6.30$, 2Me); 1.29–1.21 (*m*, 14Me); 1.12 (*s*, *t*-Bu). ^{13}C-NMR (75 MHz): 169.91; 169.15; 164.86; 142.07; 135.70; 135.53; 133.03; 131.25; 130.74; 129.89; 129.28; 128.59; 128.35; 127.83; 76.35; 68.32; 67.60; 66.49; 64.51; 41.07; 40.79; 40.67; 26.84; 19.96; 19.77; 19.54; 19.33. LSI-MS: 2015.4 (100, $[M + Na]^+$), 1992.5 (72, M^+).

33,33'-{5-{{[(tert-Butyl)diphenylsilyl]oxy}methyl}benzene-1,3-diyl}bis[(3R,7R,11R,15R,19R,23R,27R,31R)-3,7,11,15,19,23,27,31-octamethyl-5,9,13,17,21,25,29,33-octaoxo-4,8,12,16,20,24,28,32-octaoxatritriacontanoic Acid (**52**). As described in *GP III*, **48** (2.19 g, 1.10 mmol) was hydrogenated in CF_3CH_2OH (30 ml). Workup, precipitation with Et_2O/pentane, and careful drying at h.v.: 1.87 g (1.03 mmol; 94%) of **52**. Colorless oil. $[\alpha]_D^{r.t.} = -13.1$, $[\alpha]_{365}^{r.t.} = -25.6$ ($c = 0.72$, CH_2Cl_2). IR: 3400–2500 (*br.*), 3010*w*, 2985*m*, 2935*w*, 1736*vs*, 1606*w*, 1458*w*, 1383*s*, 1306*s*, 1178*vs*, 1134*s*, 1102*s*, 1057*vs*, 977*w*. ^{1}H-NMR (500 MHz): 8.49 (*t*, $J = 1.60$, 1 arom. H);

8.18 (*d*, *J* = 1.60, 2 arom. H); 7.69–7.67 (*m*, 4 arom. H); 7.45–7.35 (*m*, 6 arom. H); 5.58–5.49 (*m*, 2CH); 5.35–5.19 (*m*, 14CH); 4.83 (*s*, CH_2); 2.81–2.42 (*m*, 16CH_2); 1.43 (*d*, *J* = 6.31, 2Me); 1.31–1.21 (*m*, 14Me); 1.12 (*s*, *t*-Bu). ^{13}C-NMR (125 MHz): 173.05; 169.64; 169.43; 169.35; 169.29; 169.23; 169.17; 169.11; 164.85; 164.09; 142.06; 135.49; 135.34; 135.28; 132.98; 131.22; 130.68; 129.86; 129.25; 128.56; 128.32; 127.85; 127.80; 127.71; 68.74; 68.30; 67.99; 67.89; 67.84; 67.71; 67.64; 67.62; 67.58; 64.49; 41.02; 40.83; 40.74; 40.40; 26.79; 19.91; 19.88; 19.72; 19.67; 19.63; 19.28. LSI-MS: 1856.2(36, $[M + 2Na - H]^+$), 1834.7(100, $[M + Na - H]^+$). Anal. calc. for $C_{89}H_{122}O_{37}Si$: C 58.99, H 6.79; found: C 58.33, H 6.88.

*(1R,5R,9R,13R,17R,21R,25R,29R)-33-(9H-Fluoren-9-yl)-1,5,9,13,17,21,25,29-octamethyl-3,7,11,15,19,23,27,31-octaoxo-4,8,12,16,20,24,28,32-octaoxatritriacontyl 3,5-Bis{{[(*tert*-butyl)diphenylsilyl]oxy}methyl}benzoate* (**58**). Synthesis of the acid chloride as described in *GP I*, with **36** (2.29 g, 5.0 mmol) in CH_2Cl_2 (30 ml), with $(COCl)_2$ (3 ml) and DMF (3 drops). Coupling as described in *GP II* in CH_2Cl_2 (20 ml) with **44** (3.04 g, 3.8 mmol) at 0°. Workup and FC (SiO_2 (200 g), Et_2O/pentane 1:1): 3.77 g (2.4 mmol; 63%) of **58**. Colorless oil. $[\alpha]_D^{r.t.} = -3.7$, $[\alpha]_{365}^{r.t.} = -17.1$ (*c* = 0.145, CH_2Cl_2). IR: 2988*w*, 2933*m*, 2859*w*, 1728*vs*, 1603*w*, 1450*w*, 1428*w*, 1383*m*, 1305*s*, 1178*s*, 1105*vs*, 1059*s*. ^{1}H-NMR (400 MHz): 7.84 (*s*, 2 arom. H); 7.76 (*d*, *J* = 7.51, 2 arom. H); 7.70–7.65 (*m*, 8 arom. H); 7.61–7.58 (*m*, 3 arom. H); 7.45–7.29 (*m*, 16 arom. H); 5.53–5.47 (*m*, CH); 5.31–5.20 (*m*, 7CH); 4.78 (*s*, 2CH_2); 4.41 (*d*, *J* = 7.05, CH_2); 4.20 (*t*, *J* = 7.05, CH); 2.78–2.40 (*m*, 8CH_2); 1.40 (*d*, *J* = 6.32, Me); 1.28–1.18 (*m*, 7Me); 1.09 (*s*, 2 *t*-Bu). ^{13}C-NMR (125 MHz): 170.04; 169.27; 169.17; 169.15; 165.67; 143.66; 141.48; 141.32; 135.97; 135.57; 133.32; 130.20; 130.14; 130.08; 129.80; 129.76; 128.18; 127.97; 127.85; 127.82; 127.76; 127.15; 126.11; 126.07; 125.84; 125.00; 124.98; 67.78; 67.67; 67.60; 66.55; 65.17; 46.75; 41.17; 40.90; 40.85; 40.78; 40.61; 26.87; 19.96; 19.75; 19.30. LSI-MS: 1524.5 (6.3, $[M - H]^+$), 641.4 (49), 179.1(94), 155.1(100).

(1R,5R,9R,13R,17R,21R,25R,29R)-33-(9H-Fluoren-9-yl)-1,5,9,13,17,21,25,29-octamethyl-3,7,11,15,19,23,27,31-octaoxo-4,8,12,16,20,24,28,32-octaoxatritriacontyl 3,5-Bis(hydroxymethyl)benzoate (**61**). As described in *GP IV*, **58** (3.36 g, 2.2 mmol) was dissolved in CH_2Cl_2 (40 ml), HF · pyridine (5 ml) was added at 0°, and the mixture stirred vigorously for 15 min. Workup and precipitation with CH_2Cl_2/pentane 2.16 g (2.06 mmol; 81%) of **61**. Colorless oil. $[\alpha]_D^{r.t.} = -5.4$, $[\alpha]_{365}^{r.t.} = -10.1$ (*c* = 0.765, CH_2Cl_2). IR: 3528*w*, 2987*w*, 2936*w*, 2878*w*, 1742*vs*, 1608*w*, 1450*w*, 1383*m*, 1305*vs*, 1178*vs*, 1136*m*, 1102*s*, 1059*vs*, 979*w*. ^{1}H-NMR (400 MHz): 7.92 (*d*, *J* = 1.60, 2 arom. H); 7.77 (*d*, *J* = 7.54, 2 arom. H); 7.60–7.58 (*m*, 3 arom. H); 7.45–7.30 (*m*, 4 arom, H); 5.55–5.47 (*m*, CH); 5.31–5.10 (*m*, 7CH); 4.73 (*s*, 2CH_2); 4.40 (*d*, *J* = 7.03, CH_2); 4.20 (*t*, *J* = 7.03, CH); 2.78–2.39 (*m*, 8CH_2); 1.42 (*d*, *J* = 6.32, Me), 1.28–1.19 (*m*, 7Me). ^{13}C-NMR (100 MHz): 170.09; 169.42; 169.38; 169.34; 169.28; 169.24; 165.55; 143.66; 141.89; 141.32; 130.76; 129.86; 127.87; 127.16; 127.06; 125.01; 124.99; 120.08; 68.17; 67.71; 67.67; 67.65; 67.59; 66.57; 64.60; 46.74; 41.07; 40.90; 40.84; 40.76; 40.61; 19.94; 19.82; 19.75; 19.71. LSI-MS: 1071.1(30, $[M + Na - H]^+$), 1049.1(26, M^+), 478.9(100), 392.9(93). Anal. calc. for $C_{55}H_{70}O_{21} \cdot H_2O$ ($C_{55}H_{72}O_{22}$): C 61.9, H 6.61; found: C 61.87, H 6.46.

(1R,5R,9R,13R,17R,21R,25R,29R)-33-(9H-Fluoren-9-yl)-1,5,9,13,17,21,25,29-octamethyl-3,7,11,15,19,23,27,31-octaoxo-4,8,12,16,20,24,28,32-octaoxatritriacontyl (4R,8R,12R,16R,20R,24R,28R,32R,46R,50R,54R,58R,62R,66R,70R,74R)-79-{{[(tert-Butyl)diphenylsilyl]oxy}methyl}-4,8,12,16,20,24,28,32,46,50,54,58,62,66,70,74-hexadecamethyl-2,6,10,14,18,22,26,30,34,44,48,52,56,60,64,68,72,76-octadecaoxo-3,7,11,15,19,23,27,31,35,43,47,51,55,59,63,67,71,75-octadecaoxatricyclo[75.3.1.1^{37,41}]dooctaconta-1(80),37,39,41(82),77(81),78-hexaene-39-carboxylate (**64**). Synthesis of the acid chloride as described in *GP I*, with **52** (1.74 g, 961 μmol) in CH_2Cl_2 (20 ml). After drying of the acid chloride (h.v., 45°), **61** (1.01 g, 960 μmol) and CH_2Cl_2 (5 ml) were added. A syringe was filled with the soln., the soln. added dropwise, within 2 h, to a soln. of pyridine (0.5 ml) in CH_2Cl_2 (15 ml) at −78°. The soln. was stirred for 8 h at −78° and additional 12 h at r.t. Then, CH_2Cl_2 (50 ml) was added and the org. layer was washed twice with 1N HCl and once with aq. sat. NaCl soln., dried ($MgSO_4$), filtered, and evaporated *i.v.* FC (SiO_2 (100 g), Et_2O/CH_2Cl_2 1:3): 950 mg (330 μmol; 35%) of **64**. White, foamy solid. $[\alpha]_D^{r.t.} = -8.8$, $[\alpha]_{365}^{r.t.} = -28.0$ (*c* = 0.2, CH_2Cl_2). IR: 3006*w*, 2964*w*, 2892*w*, 1738*vs*, 1603*w*, 1459*w*, 1382*m*, 1305*s*, 1178*vs*, 1135*m*, 1102*m*, 1060*s*. ^{1}H-NMR (500 MHz): 8.48 (*t*, *J* = 1.64, 1 arom. H); 8.18 (*d*, *J* = 1.64, 2 arom. H); 7.94 (*d*, *J* = 1.64, 2 arom. H); 7.77, (*d*, *J* = 7.56, 2 arom. H); 7.69–7.66 (*m*, 4 arom. H); 7.59 (*d*, *J* = 8.22, 2 arom. H); 7.54 (*t*, *J* = 1.64, 1 arom. H); 7.47–7.30 (*m*, 10 arom. H); 5.54–5.48 (*m*, 3CH); 5.31–5.21 (*m*, 21CH); 5.16, 5.14(2 *AB*, J_{AB} = 12.65); 4.83 (*s*, CH_2); 4.41 (*d*, *J* = 7.12, CH_2); 4.21 (*t*, *J* = 7.12, CH); 2.81–2.41 (*m*, 24CH_2); 1.43 (*d*, *J* = 6.39, 3Me); 1.30–1.21 (*m*, 21 Me); 1.12 (*s*, *t*-Bu). ^{13}C-NMR (125 MHz): 170.05; 169.79; 169.18; 169.15; 164.92; 164.85; 143.65; 142.08; 141.32; 136.71; 135.54; 133.05; 132.25; 131.26; 131.13; 130.76; 129.89; 129.26; 129.08; 127.86; 127.83; 127.15; 125.01; 124.99; 120.08; 68.41; 68.30; 67.68; 67.63; 67.60; 66.56; 65.57; 64.55; 46.74; 41.04; 40.82; 40.78; 40.61; 40.79; 26.84; 19.95; 19.83; 19.76; 19.32. LSI-MS: 2847.6(62, $[M + Na - H]^+$), 2825.3(26, M^+).

(3R,7R,11R,15R,19R,23R,27R,31R)-33-[(4R,8R,12R,16R,20R,24R,28R,32R,46R,50R,54R,58R,62R,66R,70R,74R)-79-(Hydroxymethyl)-4,8,12,16,20,24,28,32,46,50,54,58,62,66,70,74-hexadecamethyl-2,6,10,14,18,22,26,30,34,44,48,52,56,60,64,68,72,76-octadecaoxo-3,7,11,15,19,23,27,31,35,43,47,51,55,59,63,67,71,75-octadecaoxatricyclo[75.3.1.1^{41,47}]dooctaconta-1(80),37,39,41(82),77(81),78-hexaen-39-yl]-3,7,11,15,19,23,27,31-octamethyl-5,9,13,17,21,25,29,33-octaoxo-4,8,12,16,20,24,28,32-octaoxatritriacontanoic Acid (**67**). As described in *GP IV*, **64** (870 mg, 308 μmol) was dissolved in CH_2Cl_2 (20 ml), HF · pyridine (2 ml) was added at 0°, and the mixture stirred vigorously for 11 min. After workup, 870 mg of a viscous oil were obtained, which was dissolved in CH_2Cl_2 (30 ml). At 0°, piperidine (3 ml) was added, and the soln. stirred for 25 min. After addition of Et_2O (50 ml), the org. layer was washed twice with 1N HCl and once with aq. sat. NaCl soln., dried ($MgSO_4$), filtered and evaporated *i.v.* The oily crude product was dissolved twice in CH_2Cl_2 (each 8 ml), precipitated with pentane (110 ml) and the solvent was decanted: 540 mg (224 μmol; 73%) of **67**. $[\alpha]_D^{r.t.} = -12.0$, $[\alpha]_{578}^{r.t.} = -12.6$, $[\alpha]_{546}^{r.t.} = -13.9$, $[\alpha]_{436}^{r.t.} = -21.4$, $[\alpha]_{365}^{r.t.} = -28.4$ ($c = 0.635$, CH_2Cl_2). IR: 3535*w*, 3032*w*, 2968*m*, 2937*w*, 2878*w*, 1739*vs*, 1606*w*, 1458*m*, 1383*s*, 1306*vs*, 1178*vs*, 1136*s*, 1101*m*, 1058*s*, 978*w*. ^{1}H-NMR (400 MHz): 8.52 (*t*, $J = 1.60$, 1 arom. H); 8.19 (*d*, $J = 1.60$, 2 arom. H); 7.93 (*d*, $J = 1.62$, 2 arom. H); 7.54 (*t*, $J = 1.62$, 1 arom. H); 5.56–5.48 (*m*, 3CH); 5.35–5.19 (*m*, 21CH); 5.16, 5.14 (2 *AB*, $J_{AB} = 12.66$); 4.79 (*s*, CH_2); 2.81–2.41 (*m*, 24CH_2); 1.43 (*d*, $J = 6.31$, 3Me); 1.31–1.21 (*m*, 21Me). ^{13}C-NMR (100 MHz): 169.84; 169.78; 169.42; 169.40; 169.35; 169.30; 169.27; 169.23; 169.10; 164.97; 164.84; 142.45; 136.73; 132.28; 132.00; 131.12; 130.99; 129.73; 129.08; 68.45; 68.15; 67.79; 67.75; 67.72; 67.64; 65.59; 63.99; 41.06; 40.98; 40.91; 40.79; 40.50; 40.39; 19.97; 19.93; 19.83; 19.81; 19.77; 19.74; 19.66. LSI-MS: 2431.3(56, $[M + Na]^+$), 2409.5(39, $[M + H]^+$). Anal. calc. for $C_{114}H_{158}O_{55} \cdot H_2O$ ($C_{114}H_{160}O_{56}$): C 56.43, H 6.65; found: C 56.15, H 6.66.

(6R,10R,14R,18R,22R,26R,30R,34R,46R,50R,54R,58R,62R,66R,70R,74R,83R,87R,91R,95R,99R,103R,107R,111R)-6,10,14,18,22,26,30,34,46,50,54,58,62,66,70,74,83,87,91,95,99,103,107,111-tetracosamethyl-5,9,13,17,21,25,29,33,37,45,49,53,57,61,65,69,73,77,82,86,90,94,98,102,106,110,114-heptacosaoxatetracyclo[39.39.35.1^{3,79}.1^{39,43}]heptadecahecta-1,3(117),39,41,43(116),79-hexaene-4,8,12,16,20,24,28,32,36,44,48,52,56,60,64,68,72,76,81,85,89,93,97,101,105,109,113-heptacosone (**70**). In THF (10 ml), **67** (500 mg, 207 μmol) was dissolved, and 2,6-dichlorobenzoyl chloride (32.7 μl, 228 μmol) was added at 0°. After the soln. was stirred for 10 min, pyridine (150 μl, 1.8 mmol) was added, and stirring was continued for 3 h at 0° and for 1 h at r.t. Then, CH_2Cl_2 (20 ml) was added, and the soln. was stirred for additional 48 h. Workup as described in *GP II*, and FC (SiO_2 (60 g), Et_2O/CH_2Cl_2 1:2): 90 mg (37.7 μmol; 18%) of **70**. White solid. $[\alpha]_D^{r.t.} = -9.3$, $[\alpha]_{365}^{r.t.} = -25.6$ ($c = 0.215$, CH_2Cl_2). IR: 3026*w*, 2986*w*, 2933*w*, 2872*w*, 1739*vs*, 1458*w*, 1383*m*, 1305*m*, 1178*vs*, 1135*m*, 1102*m*, 1058*s*, 978*w*, 909*w*. ^{1}H-NMR (400 MHz): 8.54 (*t*, $J = 1.62$, 1 arom. H); 8.16 (*d*, $J = 1.62$, 2 arom. H); 7.93 (*d*, $J = 1.66$, 2 arom. H); 7.53 (*t*, $J = 1.66$, 1 arom. H); 5.32–5.46 (*m*, 3CH); 5.32–5.12 (*m*, 21CH, CH_2); 5.16, 5.14 (*AB*, $J_{AB} = 12.73$); 2.82–2.42 (*m*, 24CH_2); 1.44 (*d*, $J = 6.42$, 2Me); 1.42 (*d*, $J = 6.61$, Me); 1.30–1.21 (*m*, 21 Me). ^{13}C-NMR (125 MHz): 169.78; 169.74; 169.14; 169.10; 164.88; 164.46; 133.26; 132.22; 131.27; 131.19; 130.39; 129.06; 68.65; 68.41; 67.67; 67.60; 65.56; 65.27; 41.02; 40.97; 40.82; 40.79; 40.48; 40.43; 19.92; 19.82; 19.76. LSI-MS: 2413.0 (24, $[M + Na - H]^+$); 2391.0(100, $[M + H]^+$).

8. *Synthesis of the Dendrimers* **71**–**85**. *Tris{(1R)-3-{{3,5-bis{[(1R)-3-(benzyloxy)-1-methyl-3-oxopropoxy]-carbonyl}phenyl}methoxy}-1-methyl-3-oxopropyl} Benzene-1,3,5-tricarboxylate* (**71**). Synthesis of the acid chloride as described in *GP I*, with **21** (234 mg, 500 μmol) in CH_2Cl_2 (10 ml). Coupling as described in *GP II*, at −78° with **53** (1.21 g, 1.5 mmol; containing 1 equiv. of (*t*-Bu)Ph_2SiF) in CH_2Cl_2 (10 ml). Two FC (SiO_2 (100 g), Et_2O/CH_2Cl_2 1:20; SiO_2 (80 g), Et_2O/CH_2Cl_2 1:10): 540 mg (262 mol; 52%) of **71**. Colorless, viscous oil. $[\alpha]_D^{r.t.} = -45.3$, $[\alpha]_{578}^{r.t.} = -47.4$, $[\alpha]_{546}^{r.t.} = -54.2$, $[\alpha]_{436}^{r.t.} = -97.3$, $[\alpha]_{365}^{r.t.} = -163.7$ ($c = 0.775$, CH_2Cl_2). IR: 3032*w*, 2987*w*, 1732*vs*, 1607*w*, 1456*m*, 1384*m*, 1303*s*, 1140*s*, 1102*m*, 1056*s*. ^{1}H-NMR (400 MHz): 8.72 (*s*, 3 arom. H); 8.46 (*t*, $J = 1.63$, 3 arom. H); 8.08 (*d*, $J = 1.63$; 6 arom. H); 7.29–7.20 (*m*, 15 arom. H); 5.62–5.51 (*m*, 9CH); 5.18, 5.13 (3 *AB*, $J_{AB} = 12.80$); 5.11, 5.10 (6 *AB*, $J_{AB} = 12.27$); 2.93, 2.72 (3 *AB* of *ABX*, $J_{AB} = 15.86$, $J_{AX} = 7.00$, $J_{BX} = 6.19$); 2.86, 2.69 (6 *AB* of *ABX*, $J_{AB} = 15.57$, $J_{AX} = 7.59$, $J_{BX} = 5.58$); 1.46 (*d*, $J = 6.33$, 3Me); 1.43 (*d*, $J = 6.32$, 6Me). ^{13}C-NMR (100 MHz): 169.92; 169.68; 164.47; 164.06; 136.59; 135.60; 134.57; 133.22; 131.28; 131.17; 130.49; 128.51; 128.39; 128.34; 128.27; 68.75; 68.68; 66.55; 65.34; 40.89; 40.59; 20.03; 20.01. LSI-MS: 2060.6 (9.0, M^+). Anal. calc. for $C_{114}H_{114}O_{36}$: C 66.46, H 5.58; found: C 66.38, H 5.66.

Tris{(1R)-3-{(1R)-3-{{3,5-bis{{(1R)-3-[(1R)-3-(benzyloxy)-1-methyl-3-oxopropoxy]-1-methyl-3-oxopropoxy}carbonyl}phenyl}methoxy}-1-methyl-3-oxopropoxy}-1-methyl-3-oxopropyl} Benzene-1,3,5-tricarboxylate (**72**). Synthesis of the acid chloride as described in *GP I*, with **22** (777 mg, 1.07 mmol) in CH_2Cl_2 (10 ml) and subsequent drying for 15 h at h.v. (10^{-6} mbar). Coupling as described in *GP II*, at −78° with **54** (2.3 g, 3.23 mmol) and pyridine (1 ml) in CH_2Cl_2 (10 ml). Two FC (SiO_2 (82 g), CH_2Cl_2/Et_2O 3:1, R_f(**54**) 0.58; SiO_2 (85 g), CH_2Cl_2/Et_2O 5:1, R_f(**54**) 0.39): 1.51 g (0.532 mmol; 49.7%) of **72**. Colorless, viscous oil. R_f 0.88 (CH_2Cl_2/Et_2O 3:1); 0.59 (CH_2Cl_2/Et_2O 5:1). $[\alpha]_D^{r.t.} = -27.43$ ($c = 1.305$, CH_2Cl_2). IR: 3035*w*, 2987*w*, 1735*vs*, 1607*w*, 1498*m*,

1383*m*, 1303*s*, 1248*s*, 1135*m*, 1102*m*, 1057*s*. ^{1}H-NMR (400 MHz): 8.77 (*s*, 3 arom. H); 8.56 (*t*, *J* = 1.63, 3 arom. H); 8.16 (*d*, *J* = 1.62, 6 arom. H); 7.37–7.29 (*m*, 15 arom. H); 5.58–5.45 (*m*, 9 CH); 5.36–5.27 (*m*, 9 CH); 5.18 (*d*, *J* = 2.25, 3 CH_2); 5.10 (*s*, 6 CH_2); 2.85–2.51 (*m*, 18 CH_2); 1.45 (*d*, *J* = 6.30, 3 Me); 1.41 (*d*, *J* = 6.32, 6 Me); 1.27 (*d*, *J* = 6.35, 3 Me); 1.25 (*d*, *J* = 6.34, 6 Me). ^{13}C-NMR (100 MHz): 169.87; 166.71; 169.13; 169.05; 164.48; 164.05; 136.80; 135.71; 134.54; 133.25; 131.41; 131.26; 130.40; 128.57; 128.34; 128.32; 68.91; 68.60; 67.73; 67.60; 66.45; 65.26; 40.95; 40.66; 40.41; 29.71; 19.87; 19.82. MALDI-MS: 2857.1 ([*M* + Na]$^+$), 2873.3 ([*M* – H + K]$^+$). Anal. calc. for $C_{150}H_{168}O_{54}$: C 63.55, H 5.97; found: C 63.33, H 5.83.

Tris{(1R,5R,9R,13R)-17-{3,5-bis[(3R,7R,11R,15R)-3,7,11,15-tetramethyl-1,5,9,13,17-pentaoxo-19-phenyl-2,6,10,14,18-pentaoxanonadecyl]phenyl}-1,5,9,13-tetramethyl-3,7,11,15-tetraoxo-4,8,12,16-tetraoxaheptadecyl} Benzene-1,3,5-tricarboxylate (**73**). Synthesis of the acid chloride as described in *GP I*, with **23** (290 mg, 0.232 mmol) in CH_2Cl_2 (20 ml) and subsequent drying for 15 h at h.v. (10^{-6} mbar). Coupling as described in *GP II*, at –78° with **55** (0.91 g, 0.7 mmol; containing 1 equiv. of (*t*-Bu)Ph_2SiF) and pyridine (1 ml) in CH_2Cl_2 (20 ml). Workup and three FC (SiO_2 (80 g), CH_2Cl_2/Et_2O 3:1, R_f(**55**) 0.4; SiO_2 (20 g), CH_2Cl_2/Et_2O 3:1; SiO_2 (15 g), CH_2Cl_2/Et_2O 5:1): 240.6 mg (54.7 µmol; 23.6%) of **73**. Colorless, viscous oil. R_f 0.4 (CH_2Cl_2/Et_2O 3:1); 0.13 (CH_2Cl_2/Et_2O 5:1). $[\alpha]_D^{r.t.}$ = –16.12 (*c* = 1.203, CH_2Cl_2). IR: 3035*w*, 2986*w*, 2936*w*, 1737*vs*, 1497*w*, 1456*m*, 1383*m*, 1304*s*, 1178*s*, 1135*m*, 1102*m*, 1057*s*. ^{1}H-NMR (400 MHz): 8.75 (*s*, 3 arom. H); 8.54 (*t*, *J* = 1.61, 3 arom. H); 8.15 (*d*, *J* = 1.66, 6 arom. H); 7.37–7.28 (*m*, 30 arom. H); 5.56–5.47 (*m*, 9 CH); 5.32–5.20 (*m*, 27 CH); 5.18 (*d*, *J* = 3.01, 3 CH_2); 5.10 (*s*, 6 CH_2); 2.84–2.35 (*m*, 36 CH_2); 1.45–1.21 (*m*, 36 Me). ^{13}C-NMR (100 MHz): 169.88; 169.72; 169.14; 169.11; 169.08; 169.01; 164.46; 164.02; 136.78; 135.70; 134.53; 133.25; 131.37; 131.23; 130.39; 128.57; 128.32; 68.88; 68.62; 67.67; 67.64; 67.60; 67.57; 67.50; 66.45; 65.24; 40.96; 40.76; 40.65; 40.40; 19.90; 19.79; 19.76; 19.70. MALDI-MS: 4412.6([*M* + Na]$^+$). Anal. calc. for $C_{222}H_{282}O_{90} \cdot 1.5\ CH_2Cl_2$ ($C_{223.5}H_{285}Cl_3O_{90}$):C 59.57, H 6.33; found: C 59.92, H 6.23.

Tris{(1R)-3-{(1R)-3-{{3,5-bis{{(1R)-3-[(1R)-2-carboxy-1-methylethoxy]-1-methyl-3-oxopropoxy}carbonyl}phenyl}methoxy}-1-methyl-3-oxopropoxy}-1-methyl-3-oxopropyl} Benzene-1,3,5-tricarboxylate (**74**). To a soln. of **72** (71.4 mg, 25.2 µmol) and cyclohexa-1,4-diene (0.16 ml, 1.42 mmol) in DMF (5 ml) was added Pd/C (70 mg). After the mixture was stirred for 29 h, the soln. was filtered over *Celite* and, after removing the volatile components *i.v.*, the residue was dried at h.v. (10^{-6} mbar). Two FC (SiO_2 (5 g), CH_2Cl_2/Et_2O 1:1 + 5% AcOH): 34 mg (14.82 µmol, 58.8%) of **74**; (SiO_2 (5 g), AcOEt/hexane 3:1): 8.3 mg (3.6 µmol; 14.3%) of **74**. Colorless, viscous oil. R_f 0.03 (CH_2Cl_2/Et_2O 1:1 + 5% AcOH); 0.01 (AcOEt/hexane 3:1). $[\alpha]_D^{r.t.}$ = –16.26 (*c* = 0.375, CH_2Cl_2). IR: 3642*w*(br.), 3032*w*, 2985*m*, 1735*vs*, 1608*w*, 1449*m*, 1383*s*, 1303*s*, 1248*vs*, 1137*m*, 1102*m*, 1055*s*, 974*w*. ^{1}H-NMR (500 MHz, (D_6)acetone): 8.72 (*m*, 3 arom. H); 8.48 (*t*, *J* = 1.63, 3 arom. H); 8.19 (*m*, 6 arom. H); 5.54–5.45 (*m*, 9 CH); 5.38–5.28 (*m*, 3 CH); 5.27–5.19 (*m*, 6 CH); 5.23 (*s*, 3 CH_2); 2.87–2.50 (*m*, 18 CH_2); 1.46 (*d*, *J* = 6.35, 3 Me); 1.44 (*d*, *J* = 6.32, 6 Me); 1.26 (*d*, *J* = 6.33, 3 Me); 1.22 (*d*, *J* = 6.29, 6 Me). ^{13}C-NMR (75 MHz, CD_3OD): 171.58; 129.06; 70.43; 69.88; 64.14; 41.98; 30.85; 22.64; 20.17. MALDI-MS: 2333.7 ([*M* + K]$^+$); 2317.3 ([*M* + Na]$^+$).

Tris{(1R,5R,9R,13R)-17-{3,5-bis[(3R,7R,11R,15R)-16-carboxy-3,7,11,15-tetramethyl-1,5,9,13-tetraoxo-2,6,10,14-tetraoxahexadecyl]phenyl-1,5,9,13-tetramethyl-3,7,11,15-tetraoxo-4,8,12,16-tetraoxaheptadecyl} Benzene-1,3,5-tricarboxylate (**75**). To a soln. of **73** (34.4 mg, 7.83 µmol) and cyclohexa-1,4-diene (43.2 µl, 470 µmol) in DMF (5 ml) was added Pd/C (35 mg). After the mixture was stirred for 21 h, the mixture was filtered over *Celite* and after removing the volatile components *i.v.*, the residue was dried at h.v. (10^{-6} mbar; obtained: 29 mg of crude **75**). Two FC (SiO_2 (2 g), first CH_2Cl_2/Et_2O 5:1; then CH_2Cl_2/MeOH 2:1 obtained **75**: 24.5 mg (6.36 µmol, 81.3%); SiO_2 (1 g), CH_2Cl_2/MeOH 6:1): 14.3 mg (3.71 µmol; 47.4%) of **75**. Colorless, viscous oil. R_f 0.00 (CH_2Cl_2/Et_2O 5:1); 0.87 (CH_2Cl_2/MeOH 2:1); 0.53 (CH_2Cl_2/MeOH 6:1). $[\alpha]_D^{r.t.}$ = –21.04 (*c* = 0.575, CH_2Cl_2/MeOH = 2:1). IR: 3038*w*, 2983*m*, 1735*vs*, 1383*m*, 1304*s*, 1261*vs*, 1134*m*, 1101*m*, 1057*s*. ^{1}H-NMR (400 MHz, $CDCl_3$/CD_3OD 2:1): 8.49 (*s*, 3 arom. H); 8.27 (*t*, *J* = 1.55, 3 arom. H); 7.92 (*d*, *J* = 1.54, 6 arom. H); 5.32–5.22 (*m*, 9 CH); 5.09–4.97 (*m*, 27 CH); 4.96 (*d*, *J* = 1.99, 3 CH_2); 2.67–2.12 (*m*, 36 CH_2); 1.20–1.15 (*m*, 9 Me); 1.04–0.94 (*d*, 27 Me). ^{13}C-NMR (100 MHz, $CDCl_3$/CD_3OD = 2:1): 169.91; 169.68; 169.61; 169.22; 169.15; 169.06; 164.27; 163.73; 136.64; 134.05; 132.88; 131.00; 130.76; 129.87; 128.10; 127.88; 127.82; 68.62; 68.36; 68.07; 67.45; 67.42; 67.35; 67.30; 66.09; 64.84; 41.99; 40.40; 40.36; 40.25; 40.12; 39.90; 36.11; 35.99; 35.69; 31.44; 29.17; 28.85; 19.21; 19.12; 19.07; 19.05. MALDI-MS: 3957.3 ([*M* – 4H + Bn + Na]$^+$); 3868.3 ([*M* – 4H + Na]$^+$).

Bis{(1R)-3-{{3,5-bis{[(1R)-3-(benzyloxy)-1-methyl-3-oxo-propoxy]carbonyl}phenyl}methoxy}-1-methyl-3-oxopropyl} 5-{{[(tert-Butyl)diphenylsilyl]oxy}methyl}benzene-1,3-dicarboxylate (**76**). Synthesis of the acid chloride as described in *GP I*, with **49** (910 mg, 1.5 mmol) in CH_2Cl_2 (20 ml), coupling as described in *GP II*, at –78° with **53** (1.65 g, 3.0 mmol; containing 1 equiv. of (*t*-Bu)Ph_2SiF) in CH_2Cl_2 (30 ml). FC (SiO_2 (120 g), CH_2Cl_2/Et_2O 15:1): 1.61 g (965 µmol; 64%) of **76**. Colorless, viscous oil. $[\alpha]_D^{r.t.}$ = –39.7, $[\alpha]_{578}^{r.t.}$ = –41.6, $[\alpha]_{546}^{r.t.}$ = –47.6,

$[\alpha]_{436}^{r.t.} = -85.5$, $[\alpha]_{365}^{r.t.} = -144.0$ ($c = 0.865$, CH_2Cl_2). IR: 3032*m*, 2967*w*, 2935*w*, 2859*w*, 1732*vs*, 1607*w*, 1456*m*, 1382*m*, 1304*s*, 1133*s*, 1114*s*, 1057*vs*, 950*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 8.49 (*t*, $J = 1.54$, 1 arom. H); 8.48 (*t*, $J = 1.54$, 2 arom. H); 8.16 (*d*, $J = 1.54$, 2 arom. H); 8.09 (*d*, $J = 1.54$, 4 arom. H); 7.67–7.65 (*m*, 4 arom. H); 7.44–7.34 (*m*, 6 arom. H); 7.29–7.20 (*m*, 10 arom. H); 5.60–5.52 (*m*, 6CH); 5.16, 5.11 (2 *AB*, $J_{AB} = 12.76$); 5.11, 5.10 (4 *AB*, $J_{AB} = 12.25$); 4.82 (*s*, CH_2); 2.89, 2.70 (2 *AB* of *ABX*, $J_{AB} = 15.62$, $J_{AX} = 6.82$, $J_{BX} = 5.65$); 2.86, 2.70 (4 *AB* of *ABX*, $J_{AB} = 15.62$, $J_{AX} = 7.59$, $J_{BX} = 5.65$); 1.44 (*d*, $J = 5.34$, 2Me); 1.43 (*d*, $J = 6.31$, 4Me); 1.11 (*s*, *t*-Bu). ^{13}C-NMR (100 MHz, $CDCl_3$): 169.92; 169.74; 164.90; 164.50; 142.08; 136.63; 135.60; 135.54; 133.19; 133.06; 131.25; 131.17; 130.69; 130.50; 129.90; 129.38; 128.51; 128.39; 128.27; 127.84; 68.67; 68.18; 66.56; 65.29; 64.55; 40.90; 40.67; 26.84; 20.05; 20.01; 19.32. LSI-MS: 1690.3 (34, $[M - H]^+$); 1622.1 (100, $[M - 57 - H]^+$). Anal. calc. for $C_{95}H_{98}O_{25}Si$: C 68.41, H 5.92; found: C 68.31, H 5.86.

*Bis{(1*R*)-3-{{3,5-bis{[(1*R*)-3-(benzyloxy)-1-methyl-3-oxopropoxy]carbonyl}phenyl}methoxy}-1-methyl-3-oxopropyl} 5-(Hydroxymethyl)benzene-1,3-dicarboxylate* (**79**). As described in *GP IV*, **76** (1.50 g, 900 µmol) was dissolved in CH_2Cl_2 (40 ml), HF · pyridine (5 ml) was added at 0°, and the mixture stirred vigorously for 11 min. Workup and precipitation from CH_2Cl_2/pentane: 1.28 g (800 µmol; 88%) of **79**. Colorless, viscous oil. $[\alpha]_D^{r.t.} = -41.4$, $[\alpha]_{578}^{r.t.} = -44.3$, $[\alpha]_{546}^{r.t.} = -50.6$, $[\alpha]_{436}^{r.t.} = -90.5$, $[\alpha]_{365}^{r.t.} = -151.8$ ($c = 0.515$, CH_2Cl_2). IR: 3537*w*, 3036*w*, 2988*w*, 1732*vs*, 1607*w*, 1456*m*, 1383*m*, 1303*s*, 1136*m*, 1102*m*, 1057*s*. ^{1}H-NMR (400 MHz, $CDCl_3$): 8.41 (*t*, $J = 1.61$, 2 arom. H); 8.40 (*t*, $J = 1.62$, 1 arom. H); 8.09 (*d*, $J = 1.62$, 2 arom. H); 8.06 (*d*, $J = 1.61$, 4 arom. H); 7.30–7.21 (*m*, 10 arom. H); 5.59–5.51 (*m*, 6CH); 5.18–5.06 (*m*, $6CH_2$); 4.71 (*d*, $J = 5.61$, OH); 2.87, 2.72 (*AB* of *ABX*, $J_{AB} = 15.54$, $J_{AX} = 7.65$, $J_{BX} = 5.46$); 2.86, 2.70 (*AB* of *ABX*, $J_{AB} = 15.59$, $J_{AX} = 7.61$, $J_{BX} = 5.53$); 1.44 (*d*, $J = 6.32$, 6Me). ^{13}C-NMR (100 MHz, $CDCl_3$): 169.97; 169.80; 164.72; 164.60; 142.20; 136.57; 135.58; 133.41; 131.84; 131.08; 130.80; 130.48; 129.69; 128.52; 128.40; 128.36; 128.28; 68.73; 68.37; 66.59; 65.34; 64.06; 40.89; 40.82; 20.06; 20.00. LSI-MS: 1452.1 (10, $[M + Na]^+$). Anal. calc. for $C_{79}H_{80}O_{25}$: C 66.38, H 5.64; found: C 66.40, H 5.68.

*Bis{(1*R*)-3-{(1*R*)-3-{{3,5-bis{{(1*R*)-3-[(1*R*)-3-(benzyloxy)-1-methyl-3-oxopropoxy]-1-methyl-3-oxopropoxy}carbonyl}phenyl}methoxy}-1-methyl-3-oxopropoxy}-1-methyl-3-oxopropyl} 5-{{[(*tert*-Butyl)diphenylsilyl]oxy}methyl}benzene-1,3-dicarboxylate* (**77**). Synthesis of the acid chloride as described in *GP I*, with **50** (1.96 g, 2.69 mmol) and $(COCl)_2$ (2 ml) in CH_2Cl_2 (40 ml), coupling as described in *GP II*, at −78° with **54** (83.89 g, 5.39 mmol; containing 1 equiv. of (*t*-Bu)Ph_2SiF) in CH_2Cl_2 (40 ml) and dropwise addition of pyridine (2 ml). Workup and two FC (SiO_2 (85 g), CH_2Cl_2/Et_2O 7:1, R_f(**54**) 0.44; SiO_2 (85 g), CH_2Cl_2/Et_2O 8:1): 4.95 g (2.26 mmol; 84.2%) of **77**. Colorless, viscous oil. R_f 0.6 (CH_2Cl_2/Et_2O 7:1). $[\alpha]_D^{r.t.} = -21.05$ ($c = 1.04$, CH_2Cl_2). IR: 3032*m*, 2935*w*, 1736*vs*, 1456*m*, 1383*m*, 1303*s*, 1133*s*, 1058*m*, 973*m*. ^{1}H-NMR (400 MHz): 8.58–8.53 (*m*, 2 arom. H); 8.49 (*t*, $J = 1.63$, 1 arom. H); 8.19–8.17 (*m*, 2 arom. H); 8.14–8.13 (*m*, 4 arom. H); 7.72–7.64 (*m*, 6 arom. H); 7.46–7.26 (*m*, 20 arom. H); 5.54–5.43 (*m*, 6CH); 5.33–5.25 (*m*, 6CH); 5.14 (*d*, $J = 1.55$, $2CH_2$); 5.07 (*s*, $4CH_2$); 4.81 (*s*, $1CH_2$); 2.80–2.49 (*m*, $12CH_2$); 1.44–1.36 (*m*, 2Me); 1.29–1.18 (*m*, 6Me); 1.10–1.07 (*m*, 4Me); 1.06 (*s*, *t*-Bu). ^{13}C-NMR (100 MHz): 169.88; 169.73; 169.14; 164.88; 164.49; 142.10; 136.79; 135.71; 135.54; 134.82; 134.46; 133.27; 133.07; 132.75; 131.26; 130.77; 130.42; 130.26; 129.89; 129.31; 128.58; 128.34; 127.91; 127.83; 127.72; 68.60; 68.33; 67.74; 67.53; 66.46; 65.25; 64.56; 58.48; 26.84; 26.00; 19.92; 19.87; 19.82; 19.32; 19.13. MALDI-MS: 2207.2 ($[M + Na]^+$), 2222.8 ($[M + K]^+$). Anal. calc. for $C_{119}H_{134}O_{37}Si$: C 64.05, H 6.43; found: C 64.14, H 6.23.

*Bis{(1*R*)-3-{(1*R*)-3-{{3,5-bis{{(1*R*)-3-[(1*R*)-3-(benzyloxy)-1-methyloxopropoxy]-1-methyl-3-oxopropoxy}carbonyl}phenyl}methoxy}-1-methyl-3-oxopropoxy}-1-methyl-3-oxopropyl} 5-(Hydroxymethyl)benzene-1,3-dicarboxylate* (**80**). As described in *GP IV*, **77** (2.401 g, 1.1 mmol) was dissolved in CH_2Cl_2 (30 ml), HF · pyridine (3 ml) was added at 0°, and the mixture stirred vigorously for 10 min. Workup and FC (SiO_2 (85 g), CH_2Cl_2/Et_2O 7:1): 1.31 g (670 µmol; 60.9%) of **80**. Colorless, viscous oil. R_f 0.15 (CH_2Cl_2/Et_2O 7:1). $[\alpha]_D^{r.t.} = -34.0$ ($c = 1.0$, CH_2Cl_2). IR: 3541*w*, 3032*m*, 2986*w*, 1736*vs*, 1607*w*, 1498*m*, 1456*m*, 1383*s*, 1303*vs*, 1248*vs*, 1134*s*, 1102*m*, 1057*s*. ^{1}H-NMR (400 MHz): 8.53–8.52 (*t*, 2 arom. H); 8.51 (*t*, $J = 1.63$, 1 arom. H); 8.17–8.16 (*m*, 2 arom. H); 8.13 (*d*, $J = 1.63$, 4 arom. H); 7.35–7.26 (*m*, 20 arom. H); 5.53–5.43 (*m*, 6CH); 5.33–5.25 (*m*, 6CH); 5.13 (*s*, $2CH_2$); 5.07 (*s*, $4CH_2$); 4.77 (*d*, $J = 6.2$, $1CH_2$); 2.78–2.49 (*m*, $12CH_2$); 1.41–1.38 (*m*, 6Me); 1.24 (*d*, $J = 6.33$, 2Me); 1.22 (*d*, $J = 6.32$, 4Me). ^{13}C-NMR (100 MHz): 169.90; 169.84; 169.23; 169.17; 164.80; 164.53; 142.25; 136.77; 135.70; 133.26; 131.99; 131.23; 131.01; 130.40; 129.75; 128.58; 128.34; 68.63; 68.44; 67.76; 67.56; 66.47; 65.28; 64.08; 41.02; 40.95; 40.67; 40.49; 19.89; 19.87; 19.82. MALDI-MS: 1985.7 ($[M + K]^+$), 1969.2 ($[M + Na]^+$). Anal. calc. for $C_{103}H_{116}O_{37} \cdot 2H_2O$ ($C_{103}H_{120}O_{39}$): C 62.41, H 6.10; found: C 62.21, H 6.04.

*Bis{(1*R*,5*R*,9*R*,13*R*)-17-{3,5-bis[(3*R*,7*R*,11*R*,15*R*)-3,7,11,15-tetramethyl-1,5,9,13,17-pentaoxo-19-phenyl-2,6,10,14,18-pentaoxanonadecyl]phenyl}-1,5-9,13-tetramethyl-3,7,11,15-tetraoxo-4,8,12,16-tetraoxaheptadecyl}*

5-{{[(tert-Butyl)diphenylsilyl]oxy}methyl}benzene-1,3-dicarboxylate (**78**). Synthesis of the acid chloride as described in *GP I*, with **51** (0.6 g, 0.403 mmol) and $(COCl)_2$ (3 ml) in CH_2Cl_2 (30 ml), coupling as described in *GP II*, at −78° with **55** (0.86 g, 0.807 mmol) in CH_2Cl_2 (20 ml) and dropwise addition of pyridine (1 ml). Workup and FC (SiO_2 (80 g), CH_2Cl_2/Et_2O 8:1): 0.9 g (0.276 mmol; 68.7%) of **78**. Colorless, viscous oil. R_f 0.22 (CH_2Cl_2/Et_2O 8:1). $[\alpha]_D^{r.t.} = -16.03$ ($c = 1.135$, CH_2Cl_2). IR: 3032*m*, 2986*m*, 2936*m*, 2878*w*, 1736*vs*, 1607*w*, 1497*w*, 1456*s*, 1383*s*, 1302*s*, 1177*m*, 1134*s*, 1101*m*, 1056*s*, 976*m*. ^{1}H-NMR (400 MHz): 8.54 (*t*, $J = 1.63$, 2 arom. H); 8.48 (*s*, 1 arom. H); 8.17 (*s*, 2 arom. H); 8.15 (*d*, $J = 1.59$, 4 arom. H); 7.67–7.65 (*d*, $J = 7.02$, 4 arom. H); 7.42–7.30 (*m*, 26 arom. H); 5.54–5.49 (*m*, 6CH); 5.30–5.18 (*m*, 18CH); 5.17 (*d*, $J = 3.13$, $2CH_2$); 5.10 (*s*, $4CH_2$); 4.82 (*s*, $1CH_2$); 2.81–2.35 (*m*, $24CH_2$); 1.42 (*d*, $J = 6.31$, 3Me); 1.41 (*d*, $J = 6.26$, 3Me); 1.28–1.20 (*m*, 18Me); 1.11 (*s*, *t*-Bu). ^{13}C-NMR (100 MHz): 169.88; 169.71; 169.14; 169.11; 169.07; 164.46; 136.76; 135.69; 135.51; 133.24; 131.22; 130.39; 129.86; 128.57; 128.31; 127.80; 68.61; 68.29; 67.66; 67.63; 67.56; 67.49; 66.44; 65.23; 40.96; 40.75; 40.64; 40.39; 26.81; 19.89; 19.78; 19.75; 19.69. MALDI-MS: 3256.0([*M* + K]$^+$), 3240.7([*M* + Na]$^+$). Anal. calc. for $C_{167}H_{206}O_{61}Si$: C 61.73, H 6.39; found: C 61.80, H 6.39.

Bis{(1R,5R,9R,13R)-17-{3,5-bis[(3R,7R,11R,15R)-3,7,11,15-tetramethyl-1,5,9,13,17-pentaoxo-19-phenyl-2,6,10,14,18-pentaoxanonadecyl]phenyl}-1,5,9,13-tetramethyl-3,7,11,15-tetraoxo-4,8,12,16-tetraoxaheptadecyl} 5-(Hydroxymethyl)benzene-1,3-dicarboxylate (**81**). As described in *GP IV*, **78** (813 mg, 0.252 mmol) was dissolved in CH_2Cl_2 (10 ml), HF · pyridine (1 ml) was added at 0°, and the mixture stirred vigorously for 15 min. Workup and FC (SiO_2 (20 g), CH_2Cl_2/Et_2O 3:1): 430 mg (142 µmol; 56.7%) of **81**. Colorless, viscous oil. R_f 0.48 (CH_2Cl_2/Et_2O 3:1). $[\alpha]_D^{r.t.} = -12.9$ ($c = 1.085$, CH_2Cl_2). IR: 3547*w*, 3032*m*, 2986*w*, 1736*vs*, 1607*w*, 1497*w*, 1456*m*, 1383*s*, 1304*vs*, 1134*s*, 1101*m*, 1059*s*. ^{1}H-NMR (400 MHz): 8.54 (*m*, 3 arom. H); 8.18 (*s*, 2 arom. H); 8.15 (*d*, $J = 1.01$, 4 arom. H); 7.35–7.26 (*m*, 20 arom. H); 5.53–5.51 (*m*, 6CH); 5.32–5.20 (*m*, 18CH); 5.18 (*s*, $2CH_2$); 5.11 (*s*, $4CH_2$); 4.78 (*s*, CH_2); 2.78–2.37 (*m*, $24CH_2$); 1.43–1.21 (*m*, 24Me). ^{13}C-NMR (75 MHz): 169.92; 169.78; 169.19; 169.15; 164.49; 133.30; 133.25; 131.25; 128.58; 128.35; 103.32; 67.61; 66.47; 65.29; 40.97; 40.76; 40.65; 40.38; 19.78; 19.62. MALDI-MS: 3018.2([*M* + K]$^+$), 3001.3([*M* + Na]$^+$).

Tris{(1R)-3-{{3,5-bis{{(1R)-3-{{bis{[(1R)-3-(benzyloxy)-1-methyl-3-oxopropoxy]carbonyl}phenyl}methoxy}-1-methyl-3-oxopropoxy}carbonyl}phenyl}methoxy}-1-methyl-3-oxopropyl} Benzene-1,3,5-tricarboxylate (**82**). Synthesis of the acid chloride as described in *GP I*, with **21** (118.2 mg, 252 µmol) in CH_2Cl_2 (20 ml). Coupling as described in *GP II*, at −78° with **79** (1.07 g, 750 µmol) in CH_2Cl_2 (20 ml). Workup (addition of Et_2O omitted) and FC (SiO_2 (90 g), CH_2Cl_2/Et_2O 4:1): 560 mg (119 µmol; 47%) of **82**. Glassy solid. $[\alpha]_D^{r.t.} = -46.4$, $[\alpha]_{578}^{r.t.} = -49.0$, $[\alpha]_{546}^{r.t.} = -56.2$, $[\alpha]_{436}^{r.t.} = -100.6$, $[\alpha]_{365}^{r.t.} = -169.0$ ($c = 0.84$, CH_2Cl_2). IR: 3011*w*, 2985*w*, 2964*w*, 1733*vs*, 1456*w*, 1384*m*, 1303*m*, 1139*m*, 1101*m*, 1056*s*, 1003*m*. ^{1}H-NMR (500 MHz): 8.72 (*s*, 3 arom. H); 8.49 (*t*, $J = 1.61$, 3 arom. H); 8.45 (*t*, $J = 1.63$, 6 arom. H); 8.12 (*d*, $J = 1.61$, 6 arom. H); 8.08 (*d*, $J = 1.63$, 12 arom. H); 7.29–7.21 (*m*, 60 arom. H); 5.59–5.52 (*m*, 21 CH); 5.25–5.07 (*m*, $21CH_2$); 2.96–2.67 (*m*, $21CH_2$); 1.45 (*d*, $J = 6.28$, 3 Me); 1.45 (*d*, $J = 6.33$, 6 Me); 1.43 (*d*, $J = 6.34$, 12 Me). ^{13}C-NMR (125 MHz): 169.91; 169.72; 169.68; 164.47; 164.44; 164.31; 164.05; 156.95; 136.73; 136.60; 135.59; 134.78; 134.56; 133.92; 133.32; 133.21; 131.40; 131.28; 131.15; 131.13; 130.46; 128.50; 128.39; 128.33; 128.30; 128.26; 68.77; 68.68; 68.49; 66.54; 65.31; 40.88; 40.63; 40.54; 20.03; 20.00. MALDI-MS: 4740.7(60, [*M* + K]$^+$), 4724.8(100, [*M* + Na]$^+$). Anal. calc. for $C_{258}H_{258}O_{84}$: C 65.89, H 5.53; found: C 65.14, H 5.61.

Tris{(1R)-3-{(1R)-3-{{3,5-bis{{(1R)-3-{{3,5-bis{{(1R)-3-(benzyloxy)-1-methyl-3-oxopropoxy]-1-methyl-3-oxopropoxy}carbonyl}phenyl}methoxy}-1-methyl-3-oxopropoxy}-1-methyl-3-oxopropoxy}carbonyl}phenyl}-methoxy}-1-methyl-3-oxopropoxy}-1-methyl-3-oxopropyl} Benzene-1,3,5-tricarboxylate (**83**). Synthesis of the acid chloride as described in *GP I*, with **22** (242 mg (224 µmol) in CH_2Cl_2 (20 ml)). Coupling as described in *GP II*, at −78° with **80** (1.31 g, 670 µmol) in CH_2Cl_2 (20 ml). Workup (addition of Et_2O omitted) and two FC (SiO_2 (86 g), CH_2Cl_2/Et_2O 4:1, R_f(**80**) 0.8; SiO_2 (50 g), CH_2Cl_2/Et_2O 5:1, R_f(**80**) 0.5): 449.8 mg (69.05 µmol; 30.8%) of **83**. Glassy solid. R_f 0.48 (CH_2Cl_2/Et_2O 4:1); 0.25 (CH_2Cl_2/Et_2O 5:1). $[\alpha]_D^{r.t.} = -32.9$ ($c = 1.275$, CH_2Cl_2). IR: 3035*w*, 2986*w*, 1735*vs*, 1607*w*, 1498*w*, 1455*m*, 1383*m*, 1303*s*, 1248*s*, 1135*s*, 1101*m*, 1057*s*, 973*w*. ^{1}H-NMR (500 MHz): 8.75 (*s*, 3 arom. H); 8.53 (*t*, $J = 1.57$, 9 arom. H); 8.15 (*d*, $J = 1.58$, 6 arom. H); 8.14 (*d*, $J = 1.60$, 12 arom. H); 7.34–7.27 (*m*, 60 arom. H); 5.55–5.44 (*m*, 21 CH); 5.34–5.26 (*m*, 21 CH); 5.18–5.10 (*m*, $9CH_2$); 5.09–5.05 (*m*, $12CH_2$); 2.88–2.50 (*m*, $42CH_2$); 1.44–1.38 (*m*, 21 Me); 1.25–1.21 (*m*, 21 Me). ^{13}C-NMR (125 MHz): 169.83; 169.69; 169.09; 169.00; 164.44; 136.75; 135.67; 133.21; 131.21; 130.35; 128.54; 128.30; 128.28; 68.89; 68.63; 68.57; 67.69; 67.56; 67.52; 66.41; 65.22; 40.98; 40.91; 40.62; 40.36; 19.83; 19.78. MALDI-MS: 6537.0([*M* + 3H + Na]$^+$). Anal. calc. for $C_{342}H_{384}O_{126}$: C 63.06, H 5.99; found: C 62.99, H 6.20.

Tris{(1R,5R,9R,13R)-17-{3,5-bis[(3R,7R,11R,15R)-19-{3,5-bis[(3R,7R,11R,15R)-3,7,11,15-tetramethyl-1,5,9,13,17-pentaoxo-19-phenyl-2,6,10,14,18-pentaoxanonadecyl]phenyl}-3,7,11,15-tetramethyl-1,5,9,13,17-pentaoxo-2,6,10,14,18-pentaoxanonadecyl}phenyl}-1,5,9,13-tetramethyl-3,7,11,15-tetraoxo-4,8,12,16-tetraoxaheptadecyl} Benzene-1,3,5-tricarboxylate (**84**). Synthesis of the acid chloride as described in *GP I*, with **23** (60.54 mg,

48.7 μmol) in CH_2Cl_2 (20 ml). Coupling as described in *GP II*, at −78° with **81** (440 mg, 146 μmol) in CH_2Cl_2 (20 ml). The soln. was allowed to warm up in 14 h to −60°, and then to 0° in additional 5 h. Workup (addition of Et_2O omitted; obtained: 480 mg of crude **84**) and FC (SiO_2 (15 g), CH_2Cl_2/Et_2O 2.5:1, R_f(**81**) 0.39): 152 mg (15 μmol; 31%) of **84**. For obtaining an anal. pure sample, **84** was chromatographed three more times: SiO_2 (10 g), CH_2Cl_2/Et_2O first: 4:1, then 3:1; obtained **84**: 85.2 mg (8.41 μmol; 17.2%); SiO_2 (2 g), AcOEt/hexane; 1.6:1; obtained **84**: 32.8 mg (3.23 μmol; 6.64%); SiO_2 (3 g), first CH_2Cl_2/Et_2O 3:1, then AcOEt/hexane 3:1; obtained **84**: 20.4 mg (2.01 μmol; 4%) **84**. Glassy solid. R_f 0.61 (CH_2Cl_2/Et_2O 2.5:1); 0.40 (CH_2Cl_2/Et_2O 4:1); 0.12 (AcOEt/hexane 1.6:1); 0.9 (AcOEt/hexane 3:1). $[\alpha]_D^{r.t.} = -19.36$ ($c = 0.94$, CH_2Cl_2). IR: 3032*w*, 2987*w*, 2936*w*, 1731*vs*, 1607*w*, 1497*s*, 1456*w*, 1383*m*, 1304*m*, 1178*m*, 1135*s*, 1101*m*, 1057*s*, 976*w*, 908*w*, 860*w*, 826*w*. ^{1}H-NMR (500 MHz): 8.76 (*s*, 3 arom. H); 8.54 (*t*, $J = 1.56$, 9 arom. H); 8.15 (*d*, $J = 1.55$, 18 arom. H); 7.37–7.29 (*m*, 60 arom. H); 5.56–5.47 (*m*, 21 CH); 5.29–5.19 (*m*, 63 CH); 5.18 (*d*, $J = 4.13$, 9 CH_2); 5.10 (*s*, 12 CH_2); 2.84–2.36 (*m*, 84 CH_2); 1.45–1.42 (*m*, 21 Me); 1.29–1.21 (*m*, 63 Me). ^{13}C-NMR (125 MHz): 169.90; 169.74; 169.16; 169.13; 169.10; 169.03; 164.48; 164.03; 136.79; 135.72; 134.54; 133.91; 133.26; 132.66; 131.39; 131.25; 130.40; 129.74; 129.20; 128.97; 128.59; 128.47; 128.41; 128.33; 127.98; 127.70; 125.52; 68.90; 68.63; 68.21; 67.68; 67.66; 67.62; 67.59; 67.52; 67.04; 66.46; 65.26; 53.42; 41.80; 40.98; 40.81; 40.78; 40.77; 40.66; 40.42; 39.98; 31.93; 30.33; 29.70; 29.36; 29.24; 22.69; 20.42; 20.28; 19.91; 19.80; 19.78; 19.74; 19.72; 19.40; 19.28; 18.26. MALDI-MS: 10154.9 ($[M + Na]^+$), 8235.8 ($[M - 1894.65]^+$). Anal. calc. for $C_{510}H_{640}O_{210}$: C 59.9, H 6.31; found: C 57.84, H 5.92.

Tris{(1R)-3-{(1R)-3-{{3,5-bis{{(1R)-3-{(1R)-3-{(1R)-3-{{3,5-bis{{(1R)-3-[(1R)-2-carboxy-1-methylethoxy]-1-methyl-3-oxopropoxy}carbonyl}phenyl}methoxy}-1-methyl-3-oxopropoxy}-1-methyl-3-oxopropoxy}carbonyl}phenyl}methoxy}-1-methyl-3-oxopropoxy}-1-methyl-3-oxopropyl} Benzene-1,3,5-tricarboxylate (**85**). To a soln. of **83** (55 mg, 8.44 μmol) and cyclohexa-1,4-diene (113 μl, 1.01 mmol) in DMF (4 ml) was added Pd/C (55 mg). After stirring was continued for 21 h, the soln. was filtered over *Celite* and, after removing the volatile components *i.v.*, the residue was dried at h.v. (10^{-6} mbar). FC (SiO_2 (2 g), first CH_2Cl_2/Et_2O 3:1 + 2% AcOH; then CH_2Cl_2/MeOH 2:1): 31 mg (5.7 μmol; 67.6%) of **85**. Colorless, viscous oil. R_f 0.83 (CH_2Cl_2/MeOH 2:1); 0.00 (CH_2Cl_2/Et_2O 3:1 + 2% AcOH). $[\alpha]_D^{r.t.} = -36.80$ ($c = 1.285$, CH_2Cl_2/MeOH 2:1). IR: 3032*w*, 2988*m*, 1732*vs*, 1383*s*, 1302*s*, 1248*vs*, 1132*m*, 1056*s*, 974*w*. ^{1}H-NMR (400 MHz, CD_2Cl_2/CD_3OD 2:1): 8.73 (*s*, 3 arom. H); 8.51 (*s*, 9 arom. H); 8.17 (*d*, $J = 1.53$, 18 arom. H); 5.52–5.44 (*m*, 21 CH); 5.37–5.21 (*m*, 21 CH); 5.18 (*s*, 9 CH_2); 2.84–2.43 (*m*, 42 CH_2); 1.44–1.39 (*m*, 21 Me); 1.27–1.16 (*m*, 21 Me). ^{13}C-NMR (100 MHz, CD_2Cl_2/CD_3OD 2:1): 170.42; 170.36; 170.17; 168.87; 169.75; 165.02; 164.90; 164.40; 137.41; 134.55; 133.45; 131.75; 131.49; 130.46; 69.32; 69.16; 69.05; 68.83; 67.99; 65.52; 41.17; 41.08; 40.57; 19.71; 19.66. MALDI-MS: 5546.2 ($[M + 2H + Bn + Na]^+$), 5454.8 ($[M + Na]^+$).

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