Dendritic TADDOLs: Synthesis, Characterization and Use in the Catalytic Enantioselective Addition of Et_2Zn to Benzaldehyde

P. Beat Rheiner and Dieter Seebach*[a]

Abstract: The versatile chiral ligand for polar metal centers, TADDOL ((*R*,*R*)-$\alpha,\alpha,\alpha',\alpha'$-tetraaryl-1,3-dioxolane-4,5-dimethanol), has been incorporated as core building block into dendrimers by way of benzylation of a fourfold phenolic derivative (hexol **2**) with Fréchet-type branches of up to fourth generation. These carry either benzyl (**3**–**7**) or octyl groups (**33**–**35**) at the periphery, or they contain chiral branching units (**18**–**20**, **36**), derived from (*R*)- or (*S*)-3-hydroxybutanoic acid. The dendritic compounds of molecular weight up to 13626 have been fully characterized, including by MALDI-TOF mass spectrometry, NMR spectroscopy, and optical activity measurements; one of the branch precursors with four octyl groups crystallized in an intriguing packing pattern. From the spectra and from the specific and molar optical rotations, there was no indication for the formation of chiral secondary structures of up to the third generation. The new TADDOLs were converted to Ti TADDOLates, which were employed as catalysts for the addition of Et_2Zn to PhCHO. The stereoselectivities and the reaction rates observed with the novel catalysts were compared with those of the simple Ti TADDOLate: up to the second generation there was no detectable decrease of selectivity (=98:2), and the rates hardly decreased up to the third generation; also, enantiomeric branches caused no change of stereoselectivity within experimental error. Thus, there may be applications for the special properties (such as high molecular weight, good solubility, spacing of central site from cross-linked polymer matrix) of dendritically modified chiral catalyst ligands.

Keywords: alkylations · asymmetric catalysis · catalysts · dendrimers · TADDOLs

Introduction

A variety of chiral dendritic catalysts has been described.[1] In most cases, chiral, catalytically active units have been attached as end groups to the periphery of achiral dendrimers,[2–4] providing high molecular weight catalysts which should be easily removed from a reaction mixture.[5] A second type of chiral dendritic catalysts employs chiral branches, which are attached to an achiral catalytically active core unit,[6] an approach which has, so far, not been very successful.

It is known that only dendrimers of lower generations (below the critical mass) can be suitable carriers for catalytically active sites: if the catalytic sites are at the periphery of high-generation dendrimers (with a densely packed surface) they interfere with each other; this may result in decreased selectivity.[7] If the catalytic site is located inside a high-generation dendrimer, the branches prevent access of substrates.[8] Furthermore, catalytically active sites must not interact with each other or with the dendritic branches,[2, 7] and it is advisable to use inert apolar dendritic branches around the (polar, functionalized) catalytically active site(s).[9] Finally, it is not to be expected that remote chiral units in a dendrimer have a strong influence on the stereoselectivity with which a catalytic site performs.[10]

In view of possible applications of derivatives of TADDOL ((*R*,*R*)-$\alpha,\alpha,\alpha',\alpha'$-tetraaryl-1,3-dioxolane-4,5-dimethanol, Figure 1)[11] in membrane reactors and in dendritically cross-linked polymer particles,[12] we have now prepared compounds with the propeller-type[13] TADDOL moiety in the center[14] carrying four dendritic arms. These, in turn, were of three different types: „classical“ achiral Fréchet dendrimer

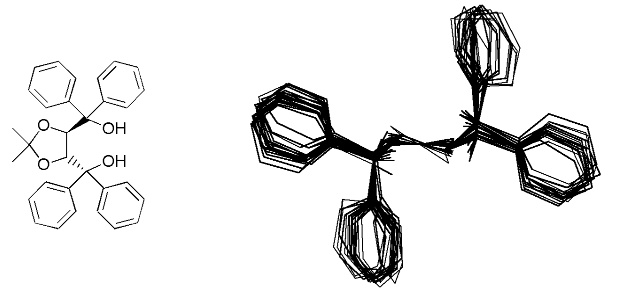

Figure 1. Formula of TADDOL[11] and overlay of 19 X-ray structures of various C_1- and C_2-symmetrical TADDOL derivatives.[13]

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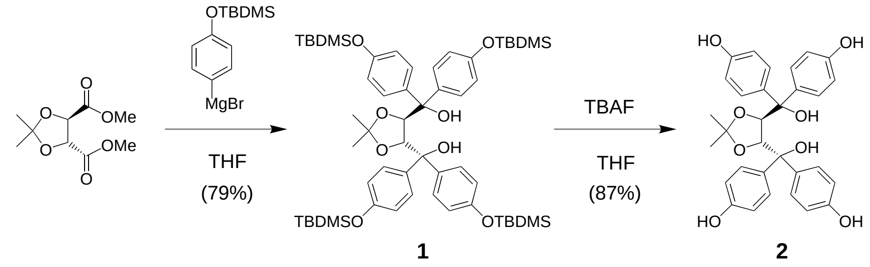
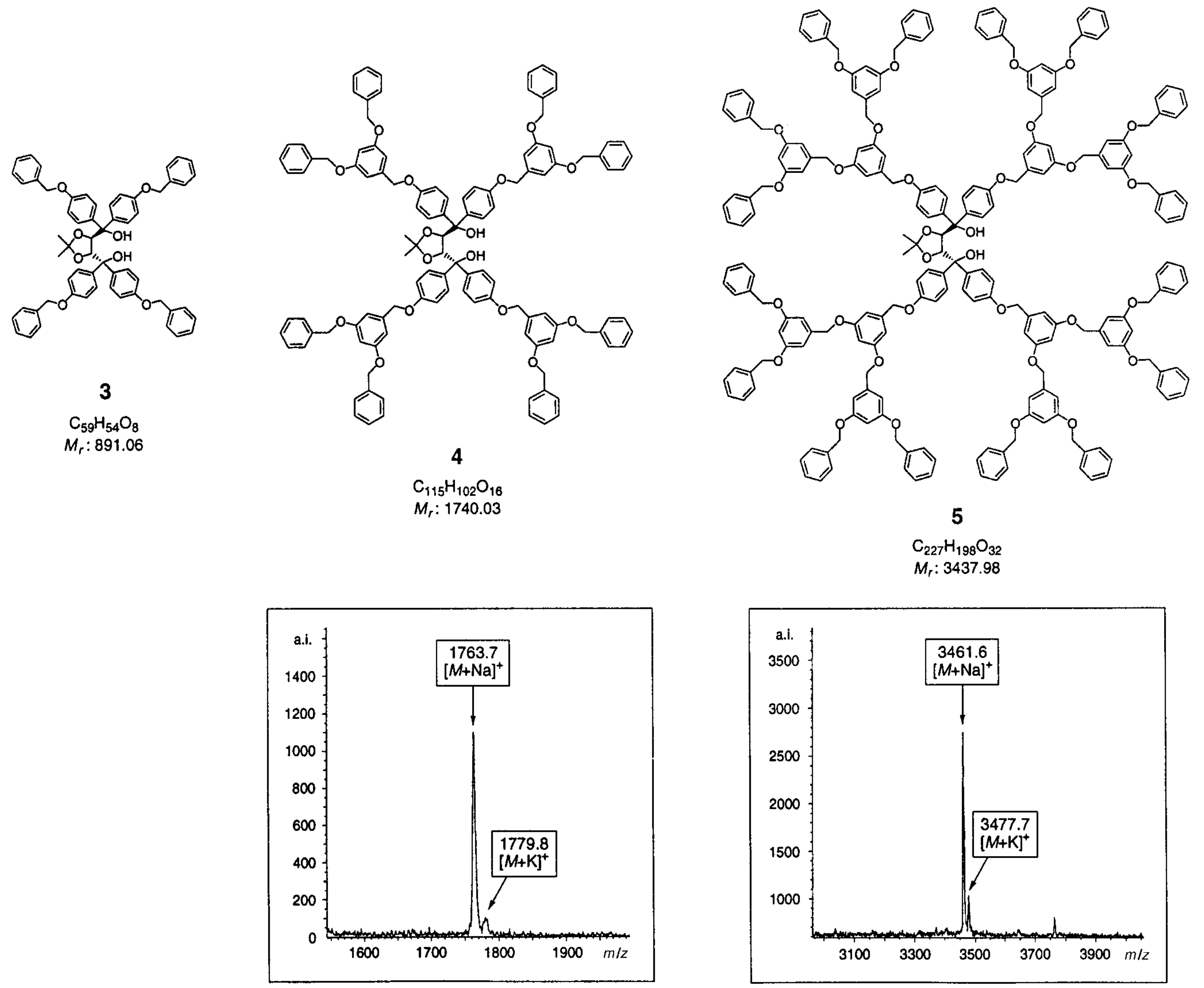
branches,[15] arms with chiral branching units (derived from 3-hydroxybutanoic acid[16]), and branches with peripheral octyl groups (mimicking micelles,[17–19] increasing the molecular weight and the solubility in hydrocarbons). The synthesis and characterization of these compounds, as well as their use as ligands in titanates for the enantioselective catalysis of Et_2Zn addition to benzaldehyde[20] (as a test reaction) are subject of the present paper.



Scheme 1. Synthesis of the TADDOL core building block **2** from (*R*,*R*)-tartrate acetonide.

Results and Discussion

Preparation of the hexol 2 for the TADDOL core units: For the preparation of the new dendritic derivatives, the *para* positions of the four phenyl groups in TADDOL, which point away from the metal-bonding site, were considered ideal for the attachment of dendritic branches. The relatively large distance between the coupling sites should also allow for coupling with sterically demanding branches. The synthesis of the TADDOL core started from the acetal of (*R*,*R*)-dimethyl tartrate,[21] to which was added an excess of the Grignard reagent prepared from 4-*tert*-butyldimethylsilyloxyphenyl bromide. The resulting TADDOL derivative **1** was isolated by crystallization as a 1:1 complex with methanol. Cleavage of the four protecting groups with Bu_4NF gave the hexol **2** in good yield (Scheme 1).

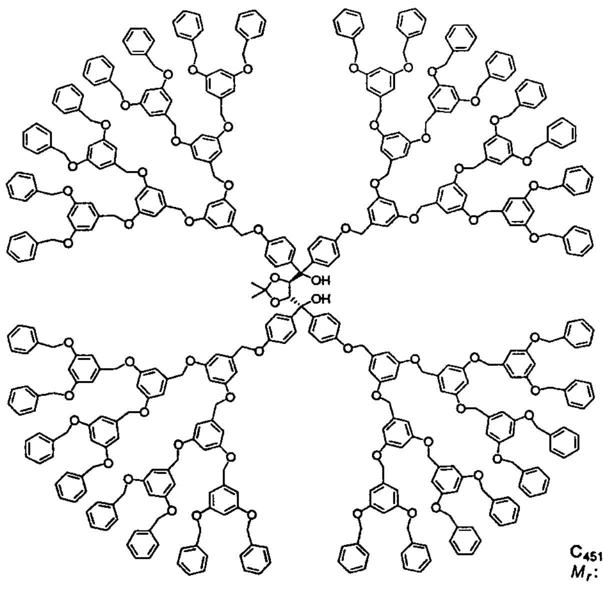


3
$C_{59}H_{54}O_8$
M_r: 891.06

4
$C_{115}H_{102}O_{16}$
M_r: 1740.03

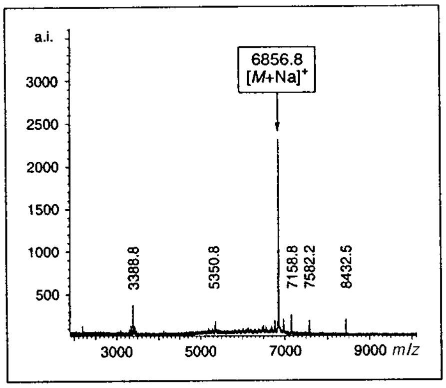
5
$C_{227}H_{198}O_{32}$
M_r: 3437.98

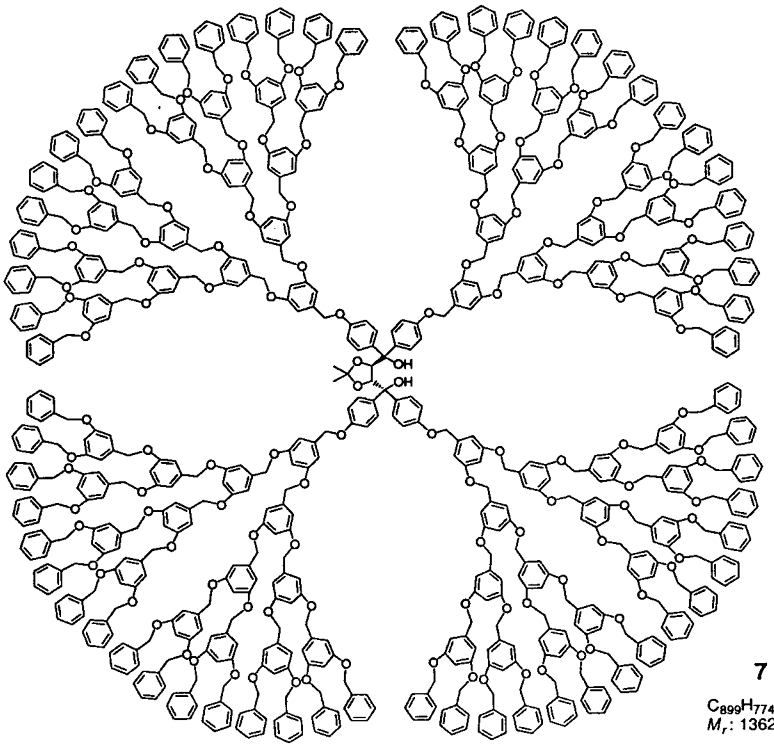
Figure 2. Formulae of TADDOL dendrimers **3**–**5** of 0th, first, and second generation. MALDI-TOF spectra of dendrimers **4** and **5**, demonstrating the monodispersity of the compounds.



6

$C_{451}H_{390}O_{64}$
M_r: 6834.00





7

$C_{899}H_{774}O_{128}$
M_r: 13625.93

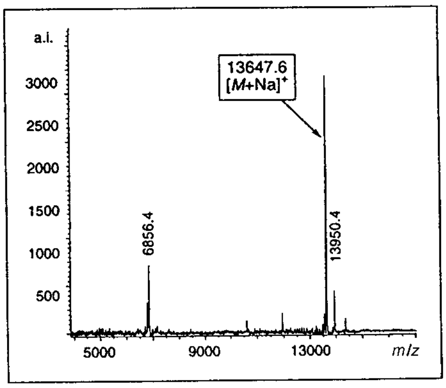


Figure 3. Formulae and MALDI-TOF spectra of TADDOL dendrimers **6** and **7** of third and fourth generation. The signals besides the molecule peaks might stem from molecules which are produced during evaporation and ionization of the molecules from the matrix ("in-source decay"[22]).

Synthesis and characterization of dendrimers with a TADDOL core and achiral branches: For the first series of dendrimers, Fréchet's[15] achiral poly(benzyl ether) branches, up to the fourth generation, were used. For the coupling of the branches with the core hexol **2**, reaction conditions were similar to those for the branch syntheses; etherification of **2** with benzylic bromide gave „dendrimer“ **3** of 0th generation (DMF/K_2CO_3); the coupling reactions of the dendritic branch bromides with the TADDOL unit to give dendrimers **4**–**7** of first to fourth generation were carried out in acetone (50 °C/K_2CO_3). Dendrimers **3**–**7** were all purified by column chromatography and were isolated in yields of up to 87%. They have been fully characterized by ^1H and ^{13}C NMR and IR spectroscopy, MALDI-TOF MS, and elemental analysis (Figures 2, 3).

Besides the major products (dendrimers **4**–**6**), C_1-symmetrical minor products (10–20%) were formed (higher R_f value). It follows from ^1H NMR and MALDI-TOF spectra

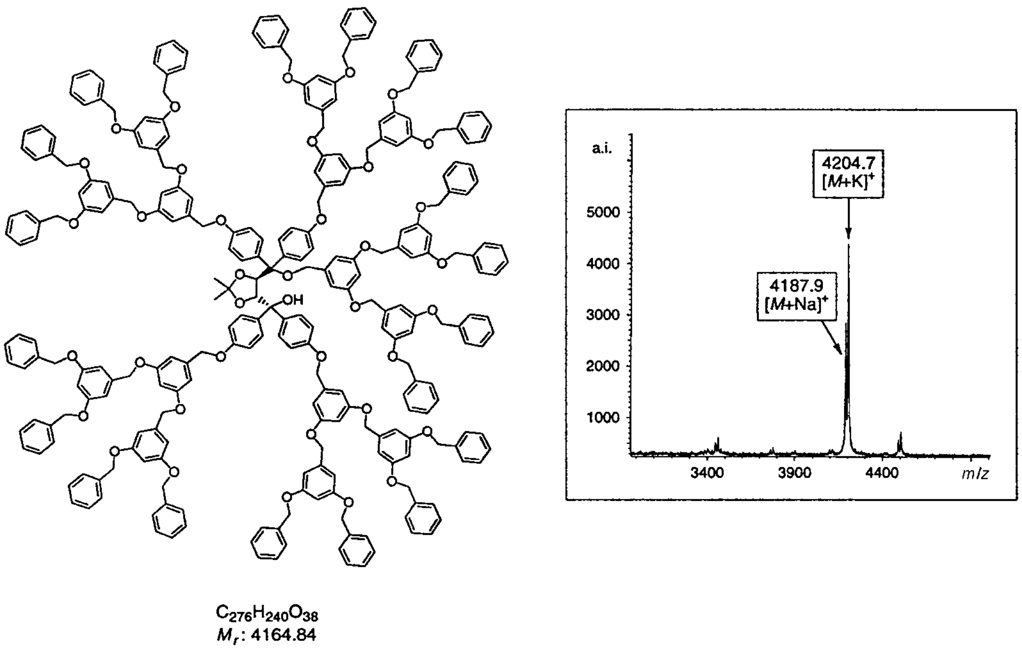


Figure 4. Formula and MALDI-TOF spectrum of the impurity in the desired dendrimer **5**, formed by fivefold coupling of the hexol **2** with the corresponding benzylic branch bromide.

that these are TADDOLs with five branches; see Figure 4 for an example. It is surprising that a tertiary OH group of the TADDOL **2** competes successfully with the four phenolic OH groups in these etherifications.

Figure 5 shows the ^{1}H NMR spectrum of third-generation dendrimer **6**. Specific signals from branch and core hydrogens can be recognized: the TADDOL unit at $\delta = 1.0$ (2 CH$_3$ groups, H), 4.15 (2 tertiary OH groups, G, identified by H/D exchange) and at 4.4 (2 CH groups, F); two doublets (D, E) each from the two diastereotopic *para*-substituted benzene rings. A set of signals at $\delta = 6.5$ (A, B, C) belongs to the aromatic hydrogens between the oxygens in the branches; the three signals belong to the three generations, and they appear at higher fields as we approach the core unit.

For the characterization of chiral dendrimers, optical rotation values are relevant,[1] because they may indicate conformational changes which occur in the dendritic structures. Normally, the (molar) optical rotation value of each chiral

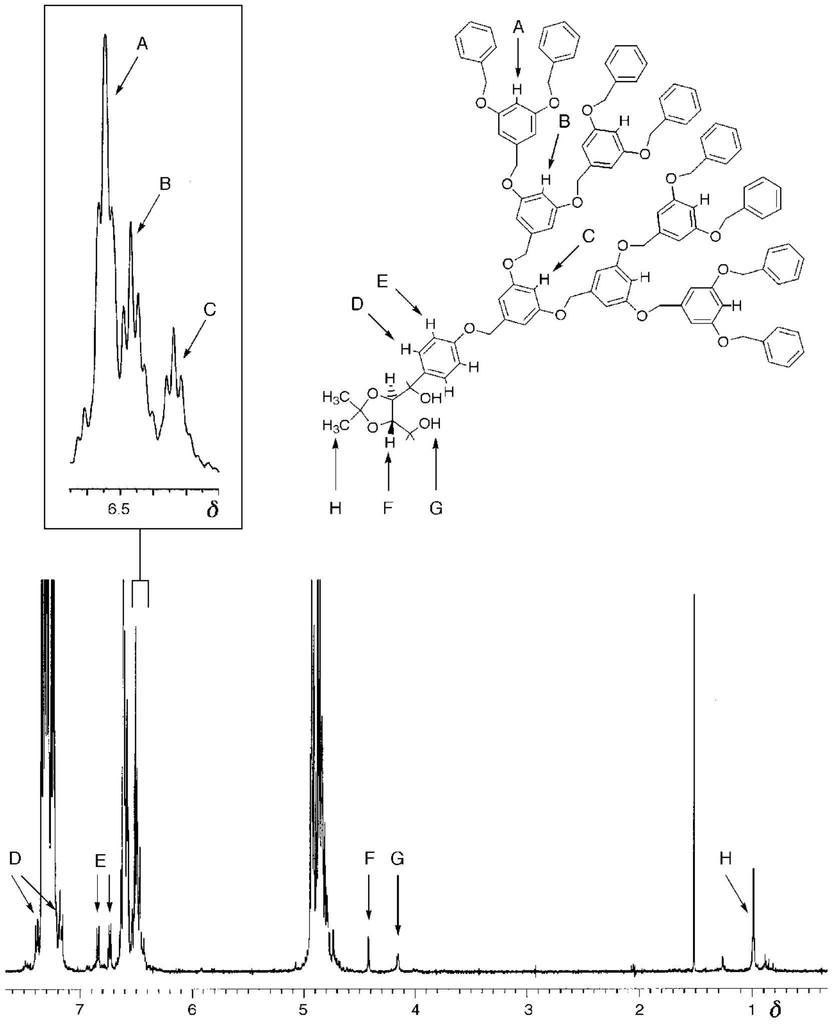


Figure 5. ^{1}H NMR spectrum (500 MHz) of third-generation dendrimer **6**. The individual hydrogens and the signals assigned to them are labelled A–H.

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building block in a dendrimer is constant,[23, 24] and the corresponding contributions of different chiral building blocks can be added up to give the value for the whole molecule.[16, 24] Only serious steric hindrance or interaction with other building blocks (e.g. H bonds in peptide structures) can lead to exceptions to this rule. The dendrimers **3**–**7** of 0th to fourth generation, which contain only one chiral unit in the center, were thus expected to show a decreasing specific rotation value $[\alpha]_D$ with increasing molecular weight, but a constant molar rotation value $[\phi]_D$. This is in fact the case, as can be seen from Table 1.

Table 1. Comparison of the specific ($[\alpha]$) and molar ($[\phi]$) optical rotations of TADDOL dendrimers **3**–**7**.

	M_r	$[\alpha]_D^{RT}$	$[\phi]_D^{RT}$
dendrimer G0 **3**	891	−49.24	−439
dendrimer G1 **4**	1740	−26.55	−462
dendrimer G2 **5**	3438	−13.23	−455
dendrimer G3 **6**	6834	−6.40	−437
dendrimer G4 **7**	13626	−3.36	−458

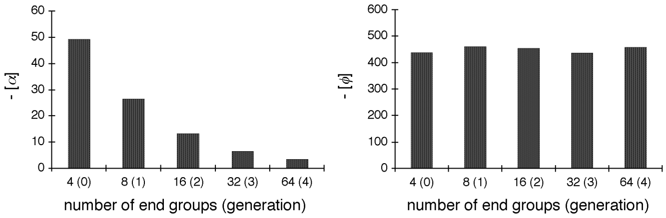
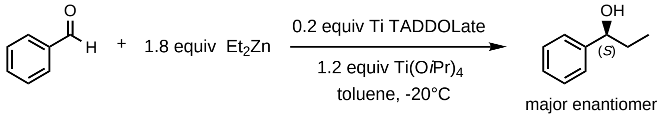
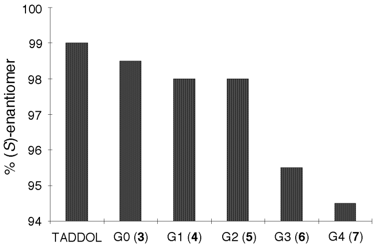


Table 2. Comparison of the selectivity of the TADDOL dendrimers **3**–**7** when employed as ligands on titanium for catalysis of the enantioselective addition of Et_2Zn to PhCHO. Although the difference is not dramatic, there is clearly a sudden decrease (from above 98 to below 96% of *S* enantiomer) from TADDOL and the lower generation dendrimers **3**–**5**, on the one hand, to the higher generation dendrimers **6** and **7**, on the other hand.



	PhCHO [mmol]	Cat* [mg][a]	Conc [mmol mL^{-1}][b]	Conversion [%][c]	*S*/*R*
TADDOL	5.0	447	0.25	quant.	99:1
dendrimer G0 **3**	1.0	178	0.25	98.7	98.5:1.5
dendrimer G1 **4**	1.0	348	0.25	96.8	98:2
dendrimer G2 **5**	1.0	688	0.25	96.5	98:2
dendrimer G3 **6**	1.0	1367	0.25	94.4	95.5:4.5
dendrimer G4 **7**	0.2	545	0.13	46.8	94.5:5.5

[a] Amount of free auxiliary before loading with titanate. [b] Concentration in mmol PhCHO per mL toluene. [c] After 2 h reaction time.



Catalysis with the Ti complexes of dendrimers 3–7 containing achiral branches: To measure the influence of the dendritic branches on the catalytic activity and stereoselectivity of the TADDOL, we tested dendrimers **3**–**7** in the enantioselective addition of Et_2Zn to PhCHO. In order for a comparison of the results with those obtained for the TADDOL to be possible, 20 mol% of the high molecular weight dendritic catalyst had to be employed. The titanium complex of the simple TADDOL catalyzes the reaction with very high enantioselectivity (*S*:*R* 99:1[20]). Table 2 shows that there is a decrease of enantioselectivity with increasing generation number of the dendritic catalyst. While the dendrimers **3**–**5** (up to the second generation) catalyze the reaction with almost the same selectivity as the simple TADDOL, there is a clear-cut decrease from the second to the third generation.

We have also compared the reaction rates (Figure 6) to find that even though all dendritic TADDOLs catalyze the addition at a similarly high rate, the reactions become steadily slower with the generation number. The reactions with the Ti complexes of the dendrimers **3**–**6** were run under the same conditions, while a smaller amount of PhCHO and Et_2Zn and also a lower concentration of the substrate were used for the catalysis with fourth-generation dendrimer **7** (so that the curve for **7** in Figure 6 is not really comparable).

Both the rate and the stereoselectivity of the addition of Et_2Zn to PhCHO catalyzed by Ti TADDOLate are hardly changed when the catalyst is replaced by dendritic analogues **3**–**5** (up to second-generation). The performance decreases when we go from the third- (**6**) to the fourth-generation (**7**) derivatives.[25]

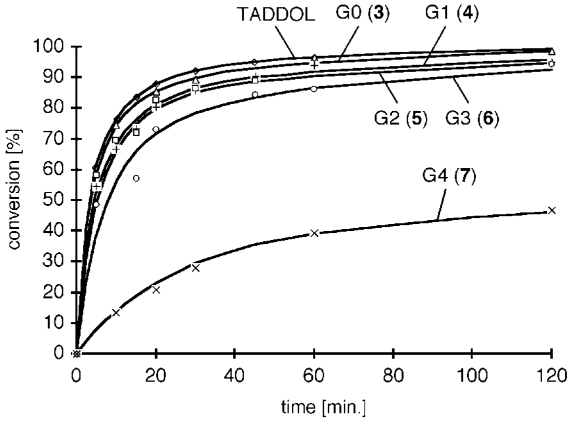
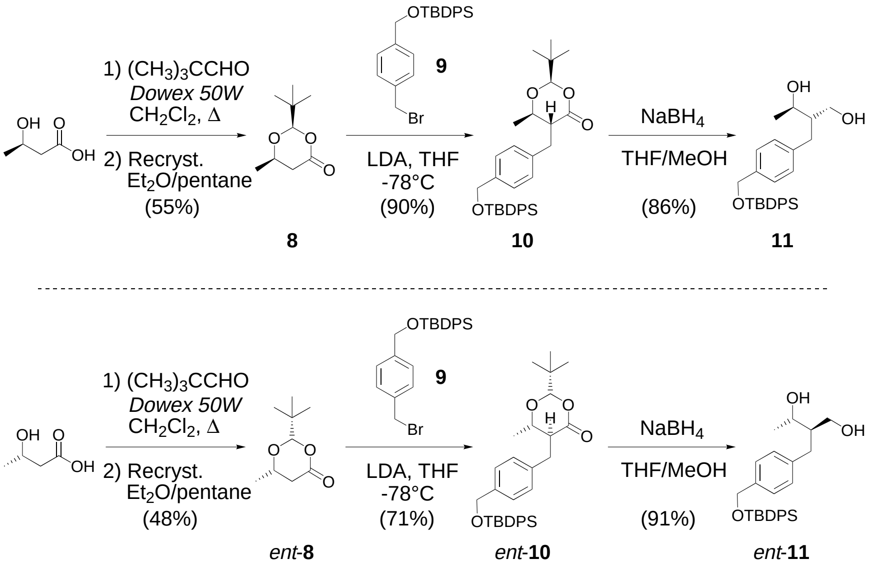
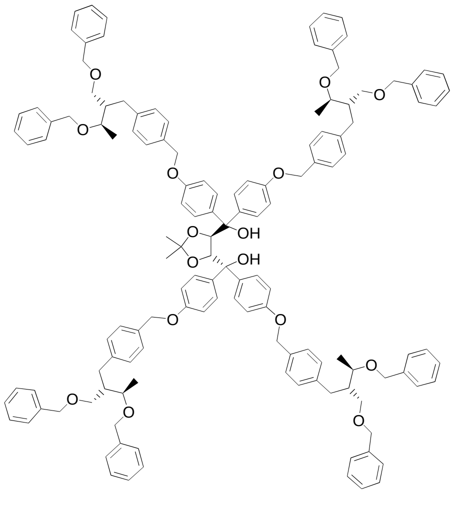


Figure 6. Comparison of the reaction rates of the Et_2Zn addition to PhCHO catalyzed by TADDOL and the dendritic TADDOL derivatives **3**–**7**. Higher dilution was used with the dendritic ligand **7** (see accompanying text and experimental section).

Synthesis and characterization of dendrimers with a TADDOL core and chiral branches. We next investigated whether additional stereogenic centers in the dendritic branches would influence the selectivity of the catalyzed reaction. In our previous work on chiral dendrimers, we reported the synthesis of doubly[16] and triply[26] branching chiral building blocks, which are obtained in a few steps from 3-hydroxybutanoic acid, both enantiomers of which are readily available: the *R* enantiomer by depolymerization of the commercial biopolymer PHB,[27] the *S* enantiomer by yeast reduction of β-keto esters,[28] either one of the two by Noyori hydrogenation.[29] From hydroxybutanoic acid the dioxanones **8** and *ent*-**8** were prepared[16] and stereoselectively alkylated with bromide **9** to give derivatives **10** and *ent*-**10**, reduction of which furnished the chiral diols **11** and *ent*-**11** (Scheme 2), and these, in turn, were converted to the chiral branch units **12**–**17** of the first and second generation (Scheme 3).



Scheme 2. Preparation of the enantiomerically pure diols **11** and *ent*-**11** from the corresponding (*R*)- and (*S*)-3-hydroxybutanoic acids.

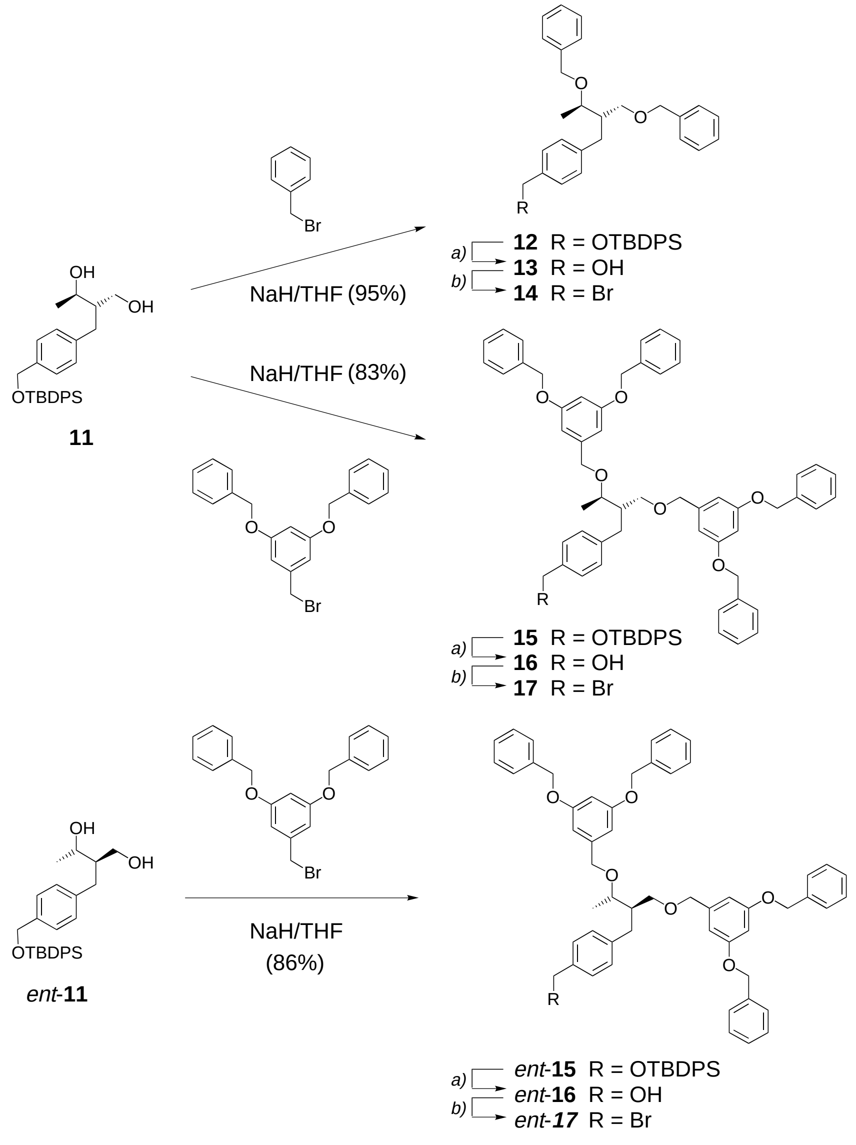


18

$C_{135}H_{142}O_{16}$
M_r: 2020.56

Figure 7. Formula of first-generation dendrimer **18** with chiral branches.

Coupling of the chiral benzylic branch bromides **14** of first and **17** of second generation with the TADDOL core **2** was achieved as for the achiral branches (acetone/K_2CO_3). First-generation dendrimer **18** (Figure 7) and the two diastereomeric dendrimers **19** and **20** were thus obtained in yields of up to 80%. Figure 8 shows the formulae and MALDI-TOF mass spectra of **19** and **20**. Again, the dendrimers were purified by column chromatography and fully characterized.[30] Due to the chiral branching units, the ^1H NMR spectra of the den-



Scheme 3. Preparation of the chiral branches of first and second generation from the diols **11** and *ent*-**11**. Conditions: a) TBAF, THF (84–89%); b) CBr_4, PPh_3, THF (43–47%).

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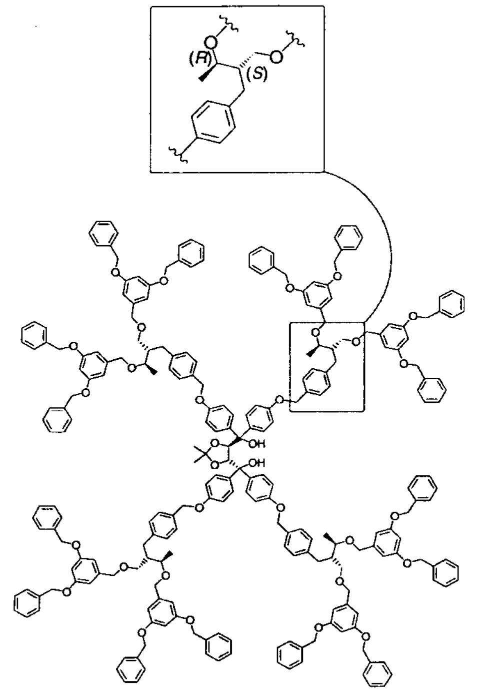
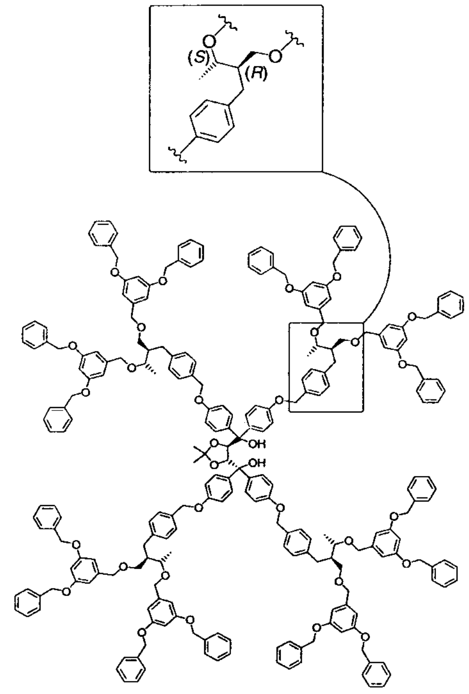
drimers **19** and **20** are more complex, but also easier to interpret. In the ^{1}H NMR spectrum of second-generation dendrimer **19** (Figure 9), the typical TADDOL signals (A, B, H, O) can again be easily recognized. In addition, the signals of the protons close to the stereogenic centers in the branches (F, J–N) all display unique shifts.

The comparison of the optical rotation values of these dendrimers is especially interesting, because, according to the rule mentioned above, the contributions to the molar optical rotation values by the building blocks should add up to the molar optical rotation value of the entire dendrimer (in the absence of contributing chiral conformations). Since the values of the branches of opposite configuration are of opposite sign, the molar optical rotation value of the dendrimers with achiral branches (such as **5**) should lie in the middle of the values for dendrimers **19** and **20**. The numbers in Table 3 show that these expectations are met when we use a $[\phi]_D$ contribution of ca. 20 from each chiral branching unit (the alcohol **16** has a $[\phi]_D$ of 28). We should keep in mind that in the case of the dendrimers **19** and **20**, a difference of ±1 in the measured specific rotation leads to a difference of ±37 in the molar rotation value.



19
$C_{247}H_{238}O_{32}$
M_r: 3718.51



20
$C_{247}H_{238}O_{32}$
M_r: 3718.51

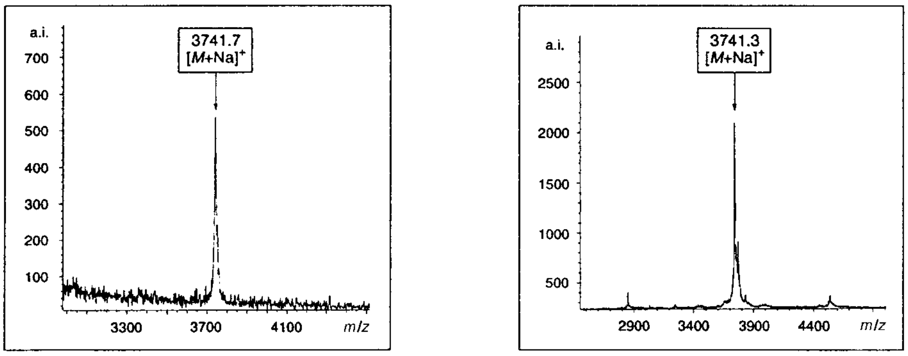


Figure 8. Formulae and MALDI-TOF mass spectra of the diastereomeric second-generation dendrimers **19** and **20**.

Table 3. Comparison of the specific ($[\alpha]$) and molar ($[\phi]$) optical rotations of the TADDOL dendrimers **18**–**20** with chiral branches. To test the addition rule (see accompanying text) the values for the chiral branch unit **16** and for the dendrimer **5** with achiral branches are also included.

	M_r	$[\alpha]$	$[\phi]$
dendrimer G1* **18**[a]	2021	−29.10	−588
dendrimer G1^F–G1*(A) **19**[a]	3719	−14.43	−537
dendrimer G1^F–G1*(B) **20**[a]	3719	−10.85	−404
dendrimer G2^F **5**[a]	3438	−13.23	−455
branch alcohol **16**[a]	815	−3.50	−28

[a] * = chiral; (A) and (B) represent the two enantiomeric diols, F = poly(benzyl ether) branches after Fréchet et al.

Catalysis with the titanium complexes of dendrimers 19 and 20 containing enantiomeric chiral branches: To compare the catalytic activity of the dendrimers with and without chiral branches, the enantioselective addition of Et_2Zn to PhCHO was used as a test. It was especially interesting and informative to see whether the two (*R*,*R*)-TADDOL units in **19** and **20** with enantiomeric branch units would give different results. It was found that neither of the two enantiomeric branches of the dendrimers influenced the *selectivity* of the reaction significantly (Table 4).

Also, the titanates of the second-generation dendrimer **5** and of TADDOLs **19** and **20** all catalyzed the reaction at almost exactly the same *rate*. Obviously, the distance of thirteen bonds from the nearest stereogenic center of the branches to the tertiary OH group of the TADDOL unit is too large to influence the stereochemical outcome of the catalyzed reaction.

In summary we have found that, under the conditions applied, dendritic branches of up to the second generation,

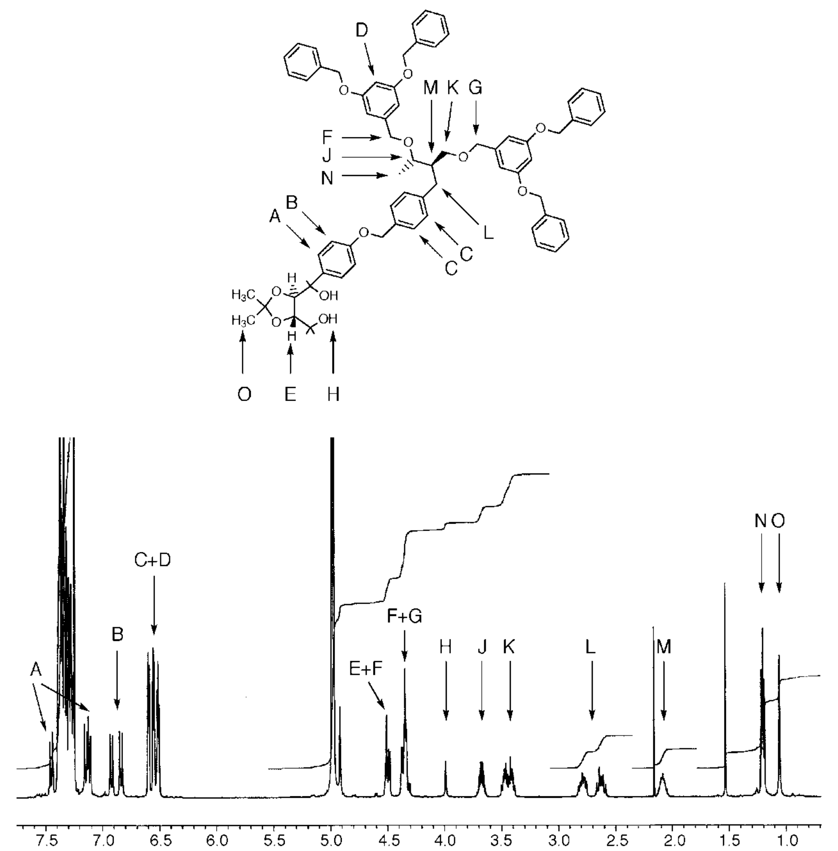
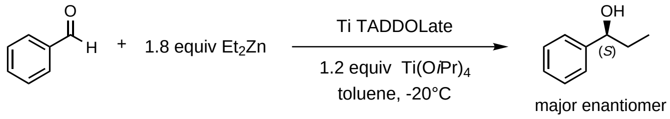


Figure 9. ^{1}H NMR spectrum (500 MHz) of second-generation dendrimer **19**. The signals are well separated, so that more hydrogens (A–O) can be assigned than for the dendrimer **6** (having no chiral branching units).

Table 4. Comparison of the selectivities of TADDOL dendrimers **5** (with achiral branching units) and **19** and **20** (with chiral branching units) when employed as ligands on titanium in the catalytic enantioselective Et_2Zn addition to PhCHO.



	Cat* [mol%]	PhCHO [mmol]	Cat* [mg][a]	Conc [mmol mL^{-1}][b]	Conversion [%][c]	*S*/*R*
monomeric TADDOL	20	5	447	0.25	quant.	98:2
dendrimer G1^F–G1*(A) **19**[d]	20	0.7	521	0.18	n.d.	98:2
dendrimer G1^F–G1*(B) **20**[d]	20	0.7	521	0.18	93.8	98.5:1.5
dendrimer G2^F **5**[d]	20	0.7	688	0.18	96.5	98:2

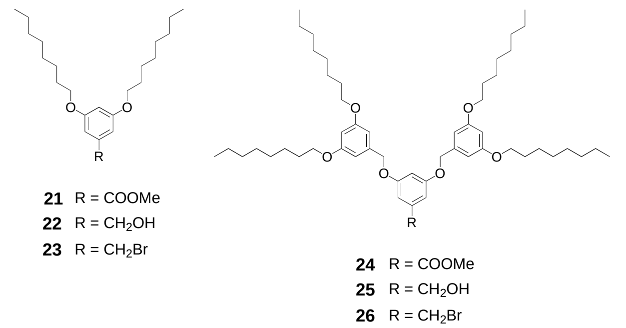
[a] Amount of free auxiliary before loading with titanate. [b] Concentration in mmol PhCHO per mL toluene. [c] After 2 h reaction time. [d] The abbreviations are as in Table 3.

regardless of whether they contain additional stereogenic centers, do not really influence the catalytic performance of the dendritic Ti TADDOLates compared to the simple Ti TADDOLate.

Synthesis and characterization of dendrimers with a TADDOL core and octyl end groups—model for an inverse micelle: In 1985 dendrimers were described as "unimolecular micelles" [17] because of their spherical shape and their large number of aliphatic end groups, which can determine the solubility of the entire molecule. Meijer et al. were the first to describe dendrimers using the model of an inverse micelle.[18] Using the same strategy, we have now attached alkyl chains at the periphery of dendritic TADDOLs, making the TADDOL unit soluble for catalysis in apolar solvents such as hexane.

Achiral branches were again synthesized following the method of Fréchet et al.:[15] starting from octyl bromide and the branching unit 3,5-dihydroxy methyl benzoate, the achiral branches **21**–**23** (first generation) and **24**–**26** (second generation) were prepared (Figure 10). Compared with those for the branches carrying benzylic end groups, the coupling yields were lower and the purification of the oily products by column chromatography was more difficult.

To our surprise, single crystals of the second-generation alcohol **25** were obtained by crystallization from CH_2Cl_2; these were analyzed by X-ray diffraction. Like lipids in membranes, the octyl chains pack in the crystalline state in a highly regular manner. The molecules seem to be held together mainly by hydrophobic interactions rather than by H bonds: there are crystal structures that contain C–H ··· O distances of up to 3.5 Å,[31] which is clearly shorter than the closest neighbourhoods of any carbon and oxygen atoms, as outlined in Figure 11a (an average O–H ··· O hydrogen bond is ca. 2.4 Å long[32]). In the crystal packing the alcohol **25** forms layers as shown in Figure 11b.[33]



21 R = COOMe
22 R = CH_2OH
23 R = CH_2Br

24 R = COOMe
25 R = CH_2OH
26 R = CH_2Br

Figure 10. Achiral dendritic branches **21**–**26** bearing octyl groups at the periphery.

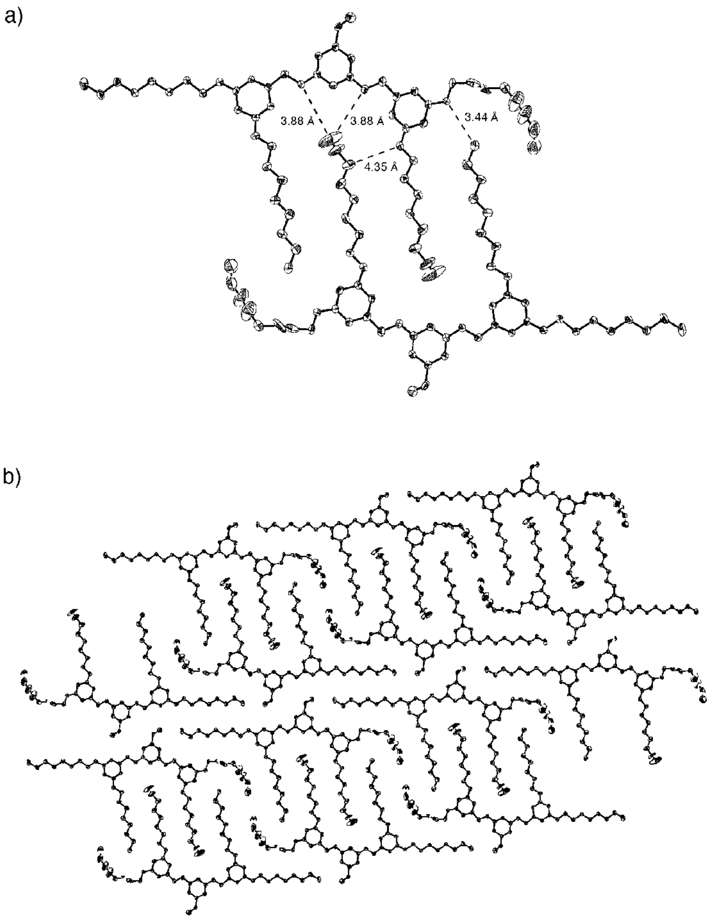


Figure 11. ORTEP plots from the crystal structure of compound **25** showing: a) two molecules and the distances between the atoms which could form weak H bonds, and b) a plane out of the crystal lattice with a highly regular pattern of molecules held together by hydrophobic interaction.

Besides the achiral branch precursors **21**–**26**, we have also prepared the chiral branch derivatives **27**–**29** of the second and **30**–**32** of the third generation (Figure 12); while the coupling of chiral diol **11** with first-generation bromide **23** was almost quantitative, the same reaction with the second-generation bromide **26** gave much poorer yields. The subsequent deprotection and bromination steps gave consistent yields of over 80 %. The achiral branches were coupled with the core hexol **2** under the usual conditions to give dendrimers **33**–**35** of 0th, first, and second generation (Figure 13), and the chiral-branch bromide **32** was used for the preparation of the third-generation dendrimer **36** (Figure 14). The latter compound contains 32 peripheral octyl groups (“inverse micelle”[18]). The coupling yields were mostly moderate, and the dendrimers **33**–**36** were isolated as oils which were difficult to purify; only small amounts of these hexane- and pentane-soluble compounds were synthesized, so that no further experiments have, as yet, been carried out with them.

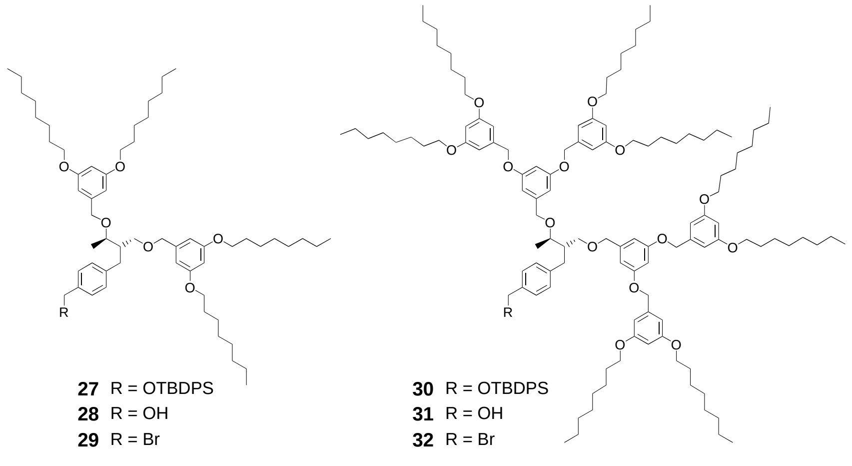


Figure 12. Chiral first- and second-generation branches **27**–**32** with octyl groups at the periphery obtained by benzylation of the diol **11** with the halides **23** and **26**, respectively.

Conclusion

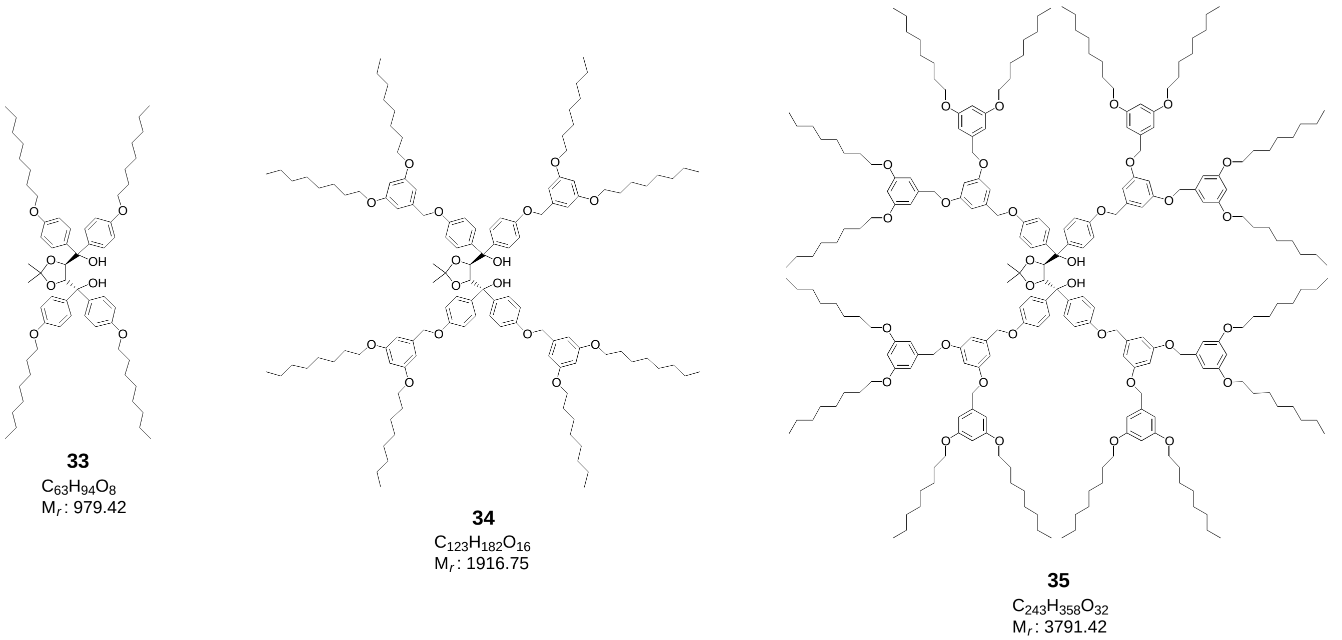
We have shown that dendritic branches attached to a conformationally rigid chiral catalyst moiety, such as the TADDOLate, influence the performance only when the branches become sterically too demanding and access of substrates is therefore hindered. For the TADDOL ligand, we have defined the limiting generation size 2 of Fréchet branches, four of which may be attached without influencing the activity of a catalytic titanium center; we have also shown that additional chiral building blocks in the dendritic structure may not interfere at all with the performance of a TADDOLate site, if placed far enough away from the catalytic center. This knowledge is most important in view of possible applications involving this kind of catalyst. Of course, a dendritically modified catalyst is only of interest if there are advantages, such as the large molecular weight (cf. membrane reactor), better solubility (cf. inverse or unimolecular micelle), simpler recovery and separation from products, or better performance when incorporated in polymers.[12] Experiments along these lines are currently being performed in our laboratory.

Experimental Section

For more details see P. B. Rheiner, Dissertation No. 12773, ETH Zürich, 1998.

General: Starting materials and reagents: (*R*,*R*)-dimethyl tartrate (Chemische Fabrik, Uetikon) and Et_2Zn (Schering, Bergkamen) were used as received without further purification. A 2 M stock solution of Et_2Zn was prepared from Et_2Zn (20.5 mL) and toluene (79.5 mL). $(iPrO)_4Ti$ (Hüls, Troisdorf) and PhCHO were distilled. The solvents used in the reactions were of p.a. quality or purified and dried according to standard methods. All other chemicals were used as commercially available.

Equipment: TLC: precoated silica gel 25 Durasil UV_{254} plates (Macherey-Nagel); visualization by UV_{254} light, development using phosphomolybdic

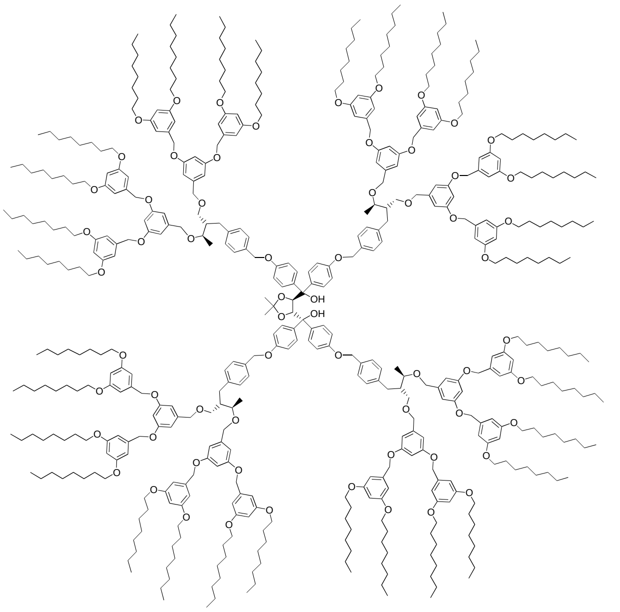


33
$C_{63}H_{94}O_8$
M_r: 979.42

34
$C_{123}H_{182}O_{16}$
M_r: 1916.75

35
$C_{243}H_{358}O_{32}$
M_r: 3791.42

Figure 13. TADDOL dendrimers **33**–**35** of 0th to second generation with achiral branches bearing octyl chains on the periphery.



36
$C_{503}H_{750}O_{64}$
M_r: 7821.30

Figure 14. Formula of third-generation dendrimer **36** with chiral branches and octyl groups at the periphery (cf. the term unimolecular micelle[17]).

acid solution (phosphomolybdic acid (25 g), $Ce(SO_4)_2 \cdot 4H_2O$ (10 g), H_2SO_4 (60 mL), H_2O (940 mL)). Flash column chromatography (FC): SiO_2 60 (0.040–0.063 mm, Fluka), pressure 0.2–0.6 bar. M.p.: open glass capillaries, Büchi 510 (Tottoli apparatus), 50 °C range Anschütz thermometers, uncorrected. $[\alpha]_D$ at RT (ca. 20 °C) Perkin–Elmer 241 polarimeter (p.a. solvents, Fluka). Capillary gas chromatography (GC): Carlo Erba Fractovap 4160 with Carlo Erba DP 700 CE integrator or Hewlett Packard 5890 Series II with HP 6890 Series Injector; column: FS-Hydrodex β-PM (50 m × 0.25 mm) (Macherey–Nagel); injector temp. 220 °C, detector temp. 220 °C (FID), heating rate: 80°, 1 °min^{-1}; pressure: 1.3 bar H_2. ^1H and ^{13}C NMR spectra: Bruker AMX-300, AMX-400, AMX-II-500, Varian-XL-300, Gemini-200 or Gemini-300; δ downfield of TMS ($\delta = 0$), J in Hz; $CDCl_3$ solutions (unless stated otherwise). IR: $CHCl_3$ solutions; Perkin–Elmer FT-IR 1600 (s = strong, m = medium, w = weak). MS: Hitachi–Perkin–Elmer RMU-6M (EI), VG ZAB2-SEQ (FAB); MALDI-TOF spectra: Bruker Reflex® Spectrometer (N_2 laser, 337 nm), matrices: α-cyano-4-hydroxycinnamic acid (CCA), 2,5-dihydroxybenzoic acid (2,5-DHB), 2-(4-hydroxyphenylazo)benzoic acid (HABA), 2,4,6-trihydroxyacetophenone (THA), fragment ions in m/z with relative intensities (%) in parentheses. Elemental analyses were performed by the Microanalytical Laboratory of the Laboratorium für Organische Chemie (ETH Zürich). Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-116051. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk). Nomenclature of dendrimers and dendritic branches is used according to our published convention.[34]

Cleavage of the alcohol protecting groups TBDMS and TBDPS

General procedure I (GP I): A solution of the protected alcohol (1 equiv) in THF was cooled to ice-bath temperature. After addition of 1–2 equiv of tetrabutylammonium fluoride (TBAF) for each protecting group the reaction mixture was stirred for at least 20 h (TLC control). To work the reaction up, H_2O was added under ice-bath cooling and the aqueous layer was extracted (3 × Et_2O, 3 × CH_2Cl_2). The combined organic layers were dried over $MgSO_4$ and the solvents were removed under vacuum.

Coupling of benzylic branch bromides to the TADDOL core

General procedure II (GP II): To a solution of TADDOL in acetone were added bromide (4 equiv) in acetone and K_2CO_3 (4 equiv), and the reaction mixture was stirred at ca. 50 °C for about 60 h (TLC monitoring). After being cooled to RT, the salt was filtered off and most of the acetone was evaporated under vacuum. The remaining solution was diluted with CH_2Cl_2 and washed with H_2O. The organic layer was washed again with H_2O and the combined aqueous layers were extracted (2 × CH_2Cl_2). The combined organic layers were dried over $MgSO_4$ and the solvent evaporated under vacuum. The crude product can be purified by flash column chromatography (20 weight equiv SiO_2, CH_2Cl_2). All by-products are eluted faster than the desired product, which can be obtained from the column by adding a few drops of acetone to the solvent.

Coupling of benzylic branch bromides to the chiral building blocks

General procedure III (GP III): THF was added to NaH (6 equiv) and the mixture was cooled to ice-bath temperature. After addition of a solution of the chiral diol in THF, the suspension was stirred for 1.5 h at RT. A solution of the benzylic bromide (2.5 equiv) in THF was added slowly and the reaction mixture was stirred for 3 h at RT and then heated under reflux for 15 h. After cooling of the mixture to ice-bath temperature, H_2O was added and the layers were separated. The aqueous layer was extracted ($3 \times Et_2O$), saturated with NaCl, and extracted again with CH_2Cl_2. The combined organic layers were dried over $MgSO_4$ and the solvents were evaporated under vacuum.

Bromination of the benzylic branch alcohols

General procedure IV (GP IV): PPh_3 (1.5 equiv) and CBr_4 (1.5 equiv) were added in this order to a solution of benzylic alcohol (1 equiv), which was cooled in an ice bath, and the reaction mixture was stirred for 45 min at 0 °C. Aluminum foil was then wrapped around the flask to prevent exposure to light and the mixture was stirred for an additional 20 h at RT to give a milky white suspension. After addition of H_2O, the layers were separated; the aqueous layer was saturated with NaCl and extracted ($2 \times CH_2Cl_2$). The combined organic layers were dried over $MgSO_4$ and the solvents were evaporated under vacuum.

(4*R*,5*R*)-2,2-Dimethyl-*α*,*α*,*α′*,*α′*-tetra(4-*tert*-butyldimethylsiloxyphenyl)-1,3-dioxolane-4,5-dimethanol (1): Following the usual procedure,[21] a solution of 4-*tert*-butyldimethylsilyloxy phenyl bromide (11.5 g, 40 mmol) in THF (15 mL) was added over 20 min to Mg (1.0 g, 40 mmol) and a few iodine crystals. This mixture was heated under reflux for 1 h before a solution of (*R*,*R*)-dimethyl-*O*,*O*-methylidene tartrate (2.0 g, 8 mmol) in THF (15 mL) was added over 20 min. After heating under reflux for 3 h and stirring overnight at RT, the milky brown reaction mixture was neutralized with saturated NH_4Cl solution (40 mL). Et_2O was added, washed with saturated NaCl solution (3 ×) and the combined aqueous layers were extracted ($3 \times Et_2O$). After drying of the combined organic layers over $MgSO_4$ and evaporation of the solvent, the crude product was dried under high vacuum to yield an orange foam (10.0 g). FC (CH_2Cl_2) yielded the product (6.23 g, 79 %) as a yellowish foam. This was dissolved in Et_2O (60 mL) and MeOH (30 mL), then most of the Et_2O was evaporated, and the flask was put in the refrigerator overnight to give MeOH-containing colorless crystals, which, after drying under high vacuum (24 h, 70 °C), yielded solvent-free **1** (4.82 g, 61 %) as a white solid. M.p. 182.8 – 183.4 °C; R_f (acetone/hexane 1:4): 0.46; $[\alpha]_D^{RT} = -34.6$ ($c = 1.1$, $CHCl_3$); ^1H NMR (400 MHz): $\delta = 0.17$ (s, 12 H, 4 CH_3Si), 0.21 (s, 12 H, 4 CH_3Si), 0.96 (s, 18 H, 2 *t*Bu), 0.99 (s, 18 H, 2 *t*Bu), 3.91 – 3.94 (m, 2 H, 2 OH), 4.44 (s, 2 H, 2 CH), 6.71 (d, $J = 8.8$, 4 H, 4 arom. H), 6.79 (d, $J = 8.8$, 4 H, 4 arom. H), 7.18 (d, $J = 8.7$, 4 H, 4 arom. H), 7.36 (d, $J = 8.7$, 4 H, 4 arom. H); ^{13}C NMR (100 MHz): $\delta = -4.4$, -4.3, 18.2, 18.3, 25.7, 27.1, 77.7, 81.1, 109.2, 118.8, 119.4, 128.8, 129.8, 135.6, 139.0, 154.7, 154.9; IR ($CHCl_3$): $\tilde{\nu} = 3352$ w, 2957 m, 2931 m, 2859 m, 1711 w, 1606 m, 1507 s, 1472 w, 1362 w, 1257 s, 1054 w, 914 s, 842 s cm^{-1}; MALDI-TOF MS (2,5-DHB): *m*/*z*: 1011.3 ($[M+Na]^+$); $C_{55}H_{86}O_8Si_4$ (987.62): calcd C 66.89, H 8.78; found C 66.95, H 8.78.

(4*R*,5*R*)-2,2-Dimethyl-*α*,*α*,*α′*,*α′*-tetra(4-hydroxyphenyl)-1,3-dioxolane-4,5-dimethanol (2): As described in GP I, TBAF (6.39 g, 20 mmol) was added to a solution of **1** (5.0 g, 5 mmol) in THF (90 mL). In the brownish-red suspension a red lump formed after a few minutes, which slowly dissolved again after stirring for 40 h at RT. Workup as in GP I yielded an orange foam (3.60 g) as crude product. FC (acetone/CH_2Cl_2 1:2) yielded **2** (2.32 g, 87 %) as a slightly yellow solid. M.p. > 180 °C (decomp), 214.2 – 215.0 (liq); R_f (acetone/hexane 1:1): 0.32; ^1H NMR (400 MHz): $\delta = 1.01$ (s, 6 H, 2 CH_3), 4.33 (s, 2 H, 2 CH), 6.65 (d, $J = 8.9$, 2 H, 2 arom. H), 6.75 (d, $J = 8.9$, 2 H, 2 arom. H), 7.09 (d, $J = 8.9$, 2 H, 2 arom. H), 7.33 (d, $J = 8.9$, 2 H, 2 arom. H); ^{13}C NMR (100 MHz): $\delta = 27.4$, 78.3, 82.5, 109.6, 114.6, 115.3, 130.4, 131.2, 135.0, 138.7, 157.4, 157.5. Because of its polar nature, the product could not be isolated entirely from the solvent and was used directly for the next reaction steps.

(Bn)$_4$–{[G0]}$_4$–[Phe-TADDOL] (3): Benzyl bromide (0.645 g, 3.77 mmol) was added to a solution of TADDOL **2** (0.503 g, 0.95 mmol) in DMF (10 mL). To this solution was added dried and finely powdered K_2CO_3 (0.52 g, 3.77 mmol), and the resulting suspension was stirred for 18 h at RT, then heated under reflux for 1 h. After cooling to RT, H_2O (20 mL) and CH_2Cl_2 (40 mL) were added, and the solids were filtered off and rinsed with CH_2Cl_2. The two layers of the filtrate were separated, and the aqueous layer was extracted twice with CH_2Cl_2. The combined organic layers were washed with H_2O, then dried over $MgSO_4$, and the solvent was evaporated to yield the crude product as a yellow oil. FC (CH_2Cl_2) yielded **3** (0.50 g, 59 %) as a white solid. M.p. 176.6 – 177.8 °C; R_f (acetone/hexane 1:2): 0.31; $[\alpha]_D^{RT} = -49.24$ ($c = 1.1$, $CHCl_3$); ^1H NMR (500 MHz): $\delta = 1.05$ (s, 6 H, 2 CH_3), 4.00 (s, 2 H, 2 OH), 4.48 (s, 2 H, 2 CH), 5.01 (s, 4 H, 2 CH_2(P)), 5.06 (s, 4 H, 2 CH_2(P)), 6.84 (d, $J = 9.0$, 4 H, 4 arom. H(c)), 6.93 (d, $J = 9.0$, 4 H, 4 arom. H(c)), 7.22 – 7.47 (m, 28 H, 8 arom. H(c), 20 arom. H(P)); ^{13}C NMR (125 MHz): $\delta = 27.2$, 69.9, 70.0, 77.6, 81.1, 109.2, 113.5, 114.3, 127.4, 127.6, 127.9, 128.0, 128.6, 128.9, 129.7, 135.3, 137.0, 138.6, 157.9, 158.0; IR ($CHCl_3$): $\tilde{\nu} = 3357$ w, 3008 w, 1671 w, 1608 m, 1582 w, 1509 s, 1454 w, 1380 w, 1295 w, 1081 w, 1055 w, 1026 m, 885 w, 834 w cm^{-1}; MALDI-TOF MS (CCA): *m*/*z*: 914.3 ($[M+Na]^+$); $C_{59}H_{54}O_8$ (891.07): calcd C 79.53, H 6.11; found C 79.51, H 6.01.

(Bn)$_8$–{[G1]$_F$}$_4$–[Phe-TADDOL] (4): As described in GP II, a solution of first-generation Fréchet-type branch bromide[15] (3.07 g, 8 mmol) in acetone (10 mL) was added to a solution of TADDOL **2** (1.06 g, 2 mmol) in acetone (50 mL). To this solution was added K_2CO_3 (1.11 g, 8 mmol) and the reaction mixture was heated under reflux for 20 h. Workup as described in GP II yielded a brownish foam (3.85 g). FC (CH_2Cl_2) yielded **4** (2.11 g, 61 %) as white foam. M.p. 72.3 – 73.4 °C; R_f (acetone/hexane 1:1): 0.62; $[\alpha]_D^{RT} = -26.55$ ($c = 1.0$, $CHCl_3$); ^1H NMR (400 MHz): $\delta = 1.06$ (s, 6 H, 2 CH_3), 3.98 – 4.02 (m, 2 H, 2 OH), 4.49 (s, 2 H, 2 CH), 4.92 (s, 4 H, 2 CH_2(G1)), 4.99 (s, 12 H, 2 CH_2(G1), 4 CH_2(P)), 5.02 (s, 8 H, 4 CH_2(P)), 6.54 (t, $J = 2.3$, 2 H, 2 arom. H(G1)), 6.57 (t, $J = 2.3$, 2 H, 2 arom. H(G1)), 6.63 (d, $J = 2.3$, 4 H, 4 arom. H(G1)), 6.70 (d, $J = 2.3$, 4 H, 4 arom. H(G1)), 6.80 (d, $J = 9.0$, 4 H, 4 arom. H(c)), 6.91 (d, $J = 9.0$, 4 H, 4 arom. H(c)), 7.20 – 7.47 (m, 44 H, 4 arom. H(c), 40 arom. H(P)); ^{13}C NMR (100 MHz): $\delta = 27.2$, 69.8, 69.9, 70.1, 77.6, 81.1, 101.5, 101.6, 106.3, 106.4, 109.2, 113.5, 114.3, 127.6, 128.0, 128.6, 128.9, 129.7, 135.4, 136.8, 138.7, 139.5, 157.8, 157.9, 160.1, 160.2; IR ($CHCl_3$): $\tilde{\nu} = 3008$ w, 1597 s, 1508 s, 1454 m, 1374 m, 1294 w, 1160 s, 1056 m, 1028 m, 836 w cm^{-1}; MALDI-TOF MS (CCA): *m*/*z*: 1763.7 ($[M+Na]^+$); $C_{115}H_{102}O_{16}$ (1740.06): calcd C 79.38, H 5.91; found C 79.31, H 5.90.

(Bn)$_{16}$–{[G2]$_F$}$_4$–[Phe-TADDOL] (5): As described in GP II, a solution of second-generation Fréchet-type branch bromide[15] (6.46 g, 8 mmol) in acetone (20 mL) was added to a solution of TADDOL **2** (1.06 g, 2 mmol) in acetone (20 mL). To this solution was added K_2CO_3 (1.11 g, 8 mmol) and the reaction mixture was heated to 40 °C for 30 h. Workup as in GP II yielded a brownish foam (7.51 g). Two FC (CH_2Cl_2) yielded **5** (5.95 g, 87 %) as a white foam. M.p. 71.4 – 75.6 (glass CH_2(G2)), 4.97 (s, 16 H, 8 CH_2), 4.98 (s, 16 H, 8 CH_2(P)), 6.49 – 6.56 (m, 12 H, 4 arom. H(G1), 8 arom. H(G2)), 6.59 (d, $J = 2.2$, 4 H, 4 arom. H(G1)), 6.63 (d, $J = 2.3$, 8 H, 8 arom. H(G2)), 6.66 (d, $J = 2.3$, 8 H, 8 arom. H(G2)), 6.66 (d, $J = 2.2$, 4 H, 4 arom. H(G1)), 6.78 (d, $J = 9.0$, 4 H, 4 arom. H(c)), 6.88 (d, $J = 9.0$, 4 H, 4 arom. H(c)), 7.19 (d, $J = 9.0$, 4 H, 4 arom. H(c)), 7.22 – 7.39 (m, 80 H, 80 arom. H(P)), 7.41 (d, $J = 9.0$, 4 H, 4 arom. H(c)); ^{13}C NMR (125 MHz): $\delta = 27.2$, 69.8, 69.9, 70.0, 70.1, 77.5, 101.5, 101.6, 101.7, 106.2, 106.3, 106.4, 106.5, 109.1, 113.5, 114.3, 127.5, 127.6, 127.9, 128.0, 128.5, 128.6, 128.9, 129.7, 135.3, 136.8, 138.6, 139.2, 139.5, 157.8, 157.9, 160.0, 160.1, 160.2; IR ($CHCl_3$): $\tilde{\nu} = 3374$ w, 3009 w, 1596 s, 1508 w, 1453 m, 1374 m, 1295 m, 1158 s, 1054 m, 835.2 w cm^{-1}; MALDI-TOF MS (THA): *m*/*z*: 3461.6 ($[M+Na]^+$); $C_{227}H_{198}O_{32}$ (3438.04): calcd C 79.30, H 5.80; found C 79.04, H 5.85.

(Bn)$_{32}$–{[G3]$_F$}$_4$–[Phe-TADDOL] (6): As described in GP II, a solution of third-generation Fréchet-type branch bromide[15] (4.64 g, 2.8 mmol) in acetone (15 mL) was added to a solution of TADDOL **2** (0.37 g, 0.7 mmol) in acetone (15 mL). K_2CO_3 (0.39 g, 2.8 mmol) was added to this solution and the reaction mixture was heated to 50 °C for 3 d. Workup as described in GP II yielded a brownish foam (5.56 g). FC ($2 \times CH_2Cl_2$) yielded **6** (4.00 g, 84 %) as a white foam. M.p. 76.4 – 78.0 °C (glass), from ca. 90 °C liquid; R_f (acetone/hexane 1:1): 0.42; $[\alpha]_D^{RT} = -6.40$ ($c = 1.00$, $CHCl_3$); ^1H NMR (500 MHz): $\delta = 0.99$ (s, 6 H, 2 CH_3), 4.15 (s, 2 H, 2 OH), 4.42 (s, 2 H, 2 CH), 4.79 – 4.94 (m, 120 H, 60 CH_2), 6.46 – 6.54 (m, 28 H, 4 arom. H(G1), 8 arom. H(G2), 16 arom. H(G3)), 6.57 – 6.63 (m, 56 H, 8 arom. H(G1), 16 arom. H(G2), 32 arom. H(G3)), 6.73 (d, $J = 9.0$, 4 H, 4 arom. H(c)), 6.84 (d, $J = 9.0$, 4 H, 4 arom. H(c)), 7.19 (d, $J = 9.0$, 4 H, 4 arom. H(c)), 7.21 – 7.35 (m, 160 H, 160 arom. H(P)), 7.38 (d, $J = 9.0$, 4 H, 4 arom. H(c)); ^{13}C NMR (125 MHz): $\delta = 27.2$, 69.7, 69.9, 70.0, 101.6, 106.3, 106.4, 106.5, 114.2, 127.5, 127.6, 127.7, 127.9, 128.0, 128.3, 128.4, 128.5, 128.9, 136.8, 139.2, 139.5, 160.0, 160.1; IR ($CHCl_3$): $\tilde{\nu} = 3008$ w, 2875 w, 1596 s, 1498 w, 1453 m, 1374 m, 1296 m, 1158 s, 1056 m, 836 w cm^{-1}; MALDI-TOF MS (IAA): *m*/*z*: 3390.4, 6857.6 ($[M+Na]^+$), 7159.1, 7584.5, 8434.1; $C_{451}H_{390}O_{64}$ (6834.00): calcd C 79.26, H 5.75; found C 79.20, H 5.78.

(Bn)$_{64}$–{[G4]$_F$}$_4$–[Phe-TADDOL] (7): As described in GP II, a solution of fourth-generation Fréchet-type branch bromide[15] (5.42 g, 1.62 mmol) in acetone (15 mL) was added to a solution of TADDOL **2** (0.214 g, 0.404 mmol) in acetone (10 mL). To this solution was added K_2CO_3 (0.223 g, 1.62 mmol) and the reaction mixture was heated to 50 °C for 4 d. Workup as described in GP II yielded a brownish foam (5.79 g). Two FC (CH_2Cl_2) yielded **7** (1.21 g, 22 %) as a white foam (the difficult identification of the product led to a big loss of product after the first column chromatography). M.p. 77.3–78.1 °C (glass), from ca. 90 °C liquid. R_f (acetone/hexane 1:1): 0.41; $[\alpha]_D^{RT} = -3.36$ ($c = 1.00$, $CHCl_3$); ^1H NMR (500 MHz): $\delta = 0.94$ (s, 6 H, 2 CH_3), 4.26 (brs, 2 H, 2 OH), 4.38 (s, 2 H, 2 CH), 4.74–4.82 (m, 120 H, 4 CH_2(G1), 8 CH_2(G2), 16 CH_2(G3), 32 CH_2(G4)), 4.82–4.88 (m, 128 H, 64 CH_2(P)), 6.43–6.48 (m, 60 H, 4 arom. H(G1), 8 arom. H(G2), 16 arom. H(G3), 32 arom. H(G4)), 6.53–6.60 (m, 120 H, 8 arom. H(G1), 16 arom. H(G2), 32 arom. H(G3), 64 arom. H(G4)), 6.68 (d, $J = 8.2$, 4 H, 4 arom. H(c)), 6.79 (d, $J = 8.2$, 4 H, 4 arom H(c)), 7.14 (d, $J = 7.7$, 4 H, 4 arom. H(c)), 7.17–7.30 (m, 320 H, 320 arom. H(P)), 7.36 (d, $J = 7.7$, 4 H, 4 arom. H(c)); ^{13}C NMR (125 MHz): $\delta = 27.2$, 69.9, 70.0, 101.6, 106.4, 127.3, 127.5, 127.6, 127.7, 127.9, 128.0, 128.3, 128.4, 128.5, 136.8, 139.2, 139.4, 160.0, 160.1; IR ($CHCl_3$): $\tilde{\nu} = 3008$ w, 2876 w, 1596 s, 1498 w, 1452 m, 1373 m, 1296 m, 1158 s, 1055 m, 834 w cm^{-1}; MALDI-TOF MS (IAA): m/z: 6856.4, 13647.6 ($[M+Na]^+$), 13950.4; $C_{899}H_{774}O_{128}$ (13625.93): calcd C 79.25, H 5.73; found C 79.03, H 5.76.

The preparation of compounds **8**[35] and **9**–**11**[16] is described in previous publications. The compounds *ent*-**8**, *ent*-**10** and *ent*-**11** were synthesized following the same procedures as for their enantiomers. Analytical data correspond with the literature.

(Bn)$_2$–[G1]*(A)–OTBDPS (12): As described in GP III, NaH (1.28 g, 53.4 mmol) was added to THF (20 mL). After cooling to ice-bath temperature, a solution of diol **11** (4.0 g, 8.9 mmol) in THF (20 mL) was added and the reaction mixture was stirred at 0 °C for 1 h before a solution of benzyl bromide (3.66 g, 21.4 mmol) in THF (20 mL) was added slowly. After stirring at RT for 30 min, the reaction mixture was heated under reflux for 15 h. Workup as described in GP III yielded a slightly yellow oil (9.1 g). FC (acetone/hexane 1:3) yielded **12** (5.31 g, 95 %) as a clear viscous oil. R_f (acetone/hexane 1:3): 0.46; $[\alpha]_D^{RT} = -2.1$ ($c = 1.05$, $CHCl_3$); ^1H NMR (400 MHz): $\delta = 1.10$ (s, 9 H, *t*Bu), 1.23 (d, $J = 6.3$, 3 H, CH_3-C(3)), 2.09–2.16 (m, 1 H, H-C(2)), 2.63 ("dd", *ABX*, $J = 13.5$, 8.9, 1 H, PhCH_2-C(2)), 2.82 ("dd", *ABX*, $J = 13.5$, 5.9, 1 H, PhCH_2-C(2)), 3.44 ("dd", *ABX*, $J = 9.4$, 5.1, 1 H, H-C(1)), 3.70–3.76 (m, 1 H, H-C(3)), 4.41–4.45, 4.57–4.60 (m, 4 H, 2 OCH_2Ph), 4.75 (s, 2 H, CH_2OSi), 7.09 (d, $J = 8.0$, 2 H, 2 arom. H), 7.20–7.44 (m, 18 H, 18 arom. H), 7.69–7.71 (m, 4 H, 4 arom. H); ^{13}C NMR (100 MHz): $\delta = 16.7$, 19.3, 26.9, 33.2, 46.3, 65.4, 69.2, 70.8, 73.0, 74.7, 125.9, 127.4, 127.6, 127.7, 128.3, 129.0, 129.7, 133.6, 135.6, 138.5, 138.7, 139.2, 139.7; IR ($CHCl_3$): $\tilde{\nu} = 3007$ w, 2932 w, 2859 w, 1711 s, 1454 w, 1428 w, 1363 m, 1112 m, 1090 m, 1020 w, 824 w cm^{-1}; MS (EI): m/z: 627 (5, $[M-1]^+$), 479 (6), 404 (8), 403 (23), 373 (14), 301 (7), 297 (16), 295 (7), 269 (8), 265 (18), 247 (19), 241 (5), 237 (6), 236 (20), 235 (100), 199 (25), 181 (9), 157 (8), 91 (31).

(Bn)$_2$–[G1]*(A)–OH (13): As described in GP I, TBAF (6.65 g, 21.1 mmol) was added to a solution of **12** (5.31 g, 8.44 mmol) in THF (90 mL). Workup as described in GP I yielded a brown oil (5.4 g). FC (acetone/hexane 1:3) yielded **13** (2.92 g, 89 %) as a slightly yellow oil. R_f (acetone/hexane 1:3): 0.28; $[\alpha]_D^{RT} = -6.90$ ($c = 1.12$, $CHCl_3$); ^1H NMR (400 MHz): $\delta = 1.22$ (d, $J = 6.4$, 3 H, CH_3-C(3)), 1.68 (t, $J = 5.7$, 1 H, OH), 2.07–2.14 (m, 1 H, H-C(2)), 2.64 ("dd", *ABX*, $J = 13.5$, 8.9, 1 H, PhCH_2-C(2)), 2.81 ("dd", *ABX*, $J = 13.5$, 5.9, 1 H, PhCH_2-C(2)), 3.42 ("dd", *ABX*, $J = 9.4$, 5.6, 1 H, H-C(1)), 3.49 ("dd", *ABX*, $J = 9.4$, 5.2, 1 H, H-C(1)), 3.68–3.74 (m, 1 H, H-C(3)), 4.40–4.44, 4.56–4.59 (m, 4 H, 2 OCH_2Ph), 4.63 (d, $J = 5.3$, 2 H, CH_2OH), 7.11 (d, $J = 8.1$, 2 H, 2 arom. H), 7.22–7.34 (m, 12 H, 12 arom. H); ^{13}C NMR (100 MHz): $\delta = 16.7$, 33.2, 46.3, 65.3, 69.2, 70.8, 73.0, 74.6, 127.1, 127.4, 127.6, 128.3, 129.4, 138.3, 138.7, 139.1, 140.7; IR ($CHCl_3$): $\tilde{\nu} = 3605$ w, 3457 br, 3008 m, 2870 m, 1810 w, 1722 w, 1602 w, 1513 w, 1496 m, 1454 s, 1378 m, 1090 s, 1028 m, 1012 m, 913 w, 820 w cm^{-1}; MS (EI): m/z: 391.2 (0.3, $[M+1]^+$), 299 (6), 282 (14), 252 (6), 227 (22), 191 (15), 176 (46), 175 (21), 161 (19), 148 (12), 147 (18), 145 (22), 144 (23), 135 (16), 134 (11), 131 (30), 121 (18), 117 (24), 92 (11), 91 (100); $C_{26}H_{30}O_3$ (390.52): calcd C 79.97, H 7.74; found C 80.10, H 7.54.

(Bn)$_2$–[G1]*(A)–Br (14): As described in GP IV, PPh_3 (2.9 g, 11 mmol) and CBr_4 (3.7 g, 11 mmol) were added to a solution of alcohol **13** (2.92 g, 7.47 mmol) in THF (40 mL). Workup as described in GP IV yielded a slightly yellow oil (8.84 g). FC (acetone/hexane 1:19) yielded **14** (1.56 g, 28 %) as a colorless oil. R_f (acetone/hexane 1:9): 0.64; $[\alpha]_D^{RT} = +16.91$ ($c = 1.20$, $CHCl_3$); ^1H NMR (400 MHz): $\delta = 1.22$ (d, $J = 6.4$, 3 H, CH_3-C(3)), 2.08–2.13 (m, 1 H, H-C(2)), 2.63 ("dd", *ABX*, $J = 13.5$, 8.9, 1 H, PhCH_2-C(2)), 2.80 ("dd", *ABX*, $J = 13.5$, 5.9, 1 H, PhCH_2-C(2)), 3.42 ("dd", *ABX*, $J = 9.4$, 5.6, 1 H, H-C(1)), 3.48 ("dd", *ABX*, $J = 9.4$, 5.2, 1 H, H-C(1)), 3.67–3.72 (m, 1 H, H-C(3)), 4.40–4.44, 4.55–4.59 (m, 4 H, 2 OCH_2Ph), 4.47 (s, 2 H, CH_2Br), 7.08 (d, $J = 8.1$, 2 H, 2 arom. H), 7.22–7.34 (m, 12 H, 12 arom. H); ^{13}C NMR (100 MHz): $\delta = 16.6$, 33.3, 33.7, 46.2, 69.1, 70.8, 73.0, 74.6, 127.4, 127.5, 127.6, 128.3, 128.5, 129.0, 129.6, 135.2, 138.6, 139.1, 141.6; IR ($CHCl_3$): $\tilde{\nu} = 3002$ w, 1714 s, 1603 w, 1452 m, 1316 m, 1277 s, 1115 m, 1070 m, 1026 w, 910 w cm^{-1}; MS (EI): m/z: 453 (0.4, $[M]^+$), 265 (18), 175 (10), 159 (12), 158 (6), 147 (7), 145 (8), 144 (8), 131 (10), 117 (11), 105 (13), 104 (17), 92 (12), 91 (100); $C_{26}H_{29}O_2Br$ (453.42): calcd C 68.87, H 6.45; found C 68.93, H 6.45.

(Bn)$_4$–[G1]$_F$–[G1]*(A)–OTBDPS (15): As described in GP III, NaH (1.28 g, 53.4 mmol) was added to THF (20 mL). After cooling to ice-bath temperature, a solution of diol **11** (4.0 g, 8.9 mmol) in THF (20 mL) was added and the reaction mixture was stirred at RT for 1 h, before a solution of first-generation Fréchet-type branch bromide[15] (8.2 g, 21.4 mmol) in THF (20 mL) was added slowly. After stirring at RT for 3 h, the reaction mixture was heated under reflux for 15 h. Workup as described in GP III yielded a brownish oil (10.6 g). FC (acetone/hexane 1:1000) yielded **15** (7.8 g, 83 %) as a clear viscous oil. R_f (acetone/hexane 1:3): 0.35; $[\alpha]_D^{RT} = -1.46$ ($c = 1.01$, $CHCl_3$); ^1H NMR (400 MHz): $\delta = 1.09$ (s, 9 H, *t*Bu), 1.21 (d, $J = 6.3$, 3 H, CH_3-C(3)), 2.04–2.14 (m, 1 H, H-C(2)), 2.58–2.67 (m, 2 H, PhCH_2-C(2)), 2.74–2.83 (m, 2 H, PhCH_2-C(2)), 3.38–3.53 (m, 1 H, H-C(1)), 3.64–3.72 (m, 1 H, H-C(3)), 4.31–4.53 (m, 4 H, 2 OCH_2Ph (G2)), 4.73 (s, 2 H, CH_2OSi), 4.98 (d, $J = 5.6$, 8 H, 4 OCH_2Ph (P)), 6.50–6.54 (m, 2 H, 2 arom. H (G2)), 6.57 (d, $J = 2.3$, 2 H, 2 arom. H (G2)), 6.61 (d, $J = 2.3$, 2 H, 2 arom. H (G2)), 7.10 (d, $J = 8.1$, 2 H, 2 arom. H (G1)), 7.22 (d, $J = 7.6$, 2 H, 2 arom. H (G1)), 7.24–7.43 (m, 26 H, 26 arom. H (P)), 7.67–7.72 (m, 4 H, 4 arom. H (P)); ^{13}C NMR (100 MHz): $\delta = 16.8$, 19.3, 26.9, 33.1, 46.3, 65.4, 69.3, 70.0, 70.7, 72.9, 74.7, 101.1, 106.3, 126.0, 127.5, 127.7, 127.9, 128.5, 129.0, 129.6, 133.6, 135.6, 136.9, 138.5, 139.6, 141.2, 141.7, 160.0; IR ($CHCl_3$): $\tilde{\nu} = 3007$ w, 2932 w, 2860 w, 1596 s, 1453 w, 1376 m, 1293 w, 1157 s, 1060 m, 832 w cm^{-1}; MALDI-TOF MS (Dithranol): m/z: 1076.5 ($[M+Na]^+$); $C_{70}H_{72}O_7Si$ (1053.42): calcd C 79.81, H 6.89; found C 79.59, H 6.88.

(Bn)$_4$–[G1]$_F$–[G1]*(A)–OH (16): As described in GP I, TBAF (6.3 g, 20 mmol) was added to a solution of **15** (6.0 g, 5.7 mmol) in THF (75 mL). Workup as described in GP I yielded **16** as a slightly yellow oil (6.0 g). A small amount thereof was purified for analytical data by FC, the rest was used for further reaction steps. R_f (Et_2O/pentane 1:3): 0.43; $[\alpha]_D^{RT} = -3.5$ ($c = 1.50$, $CHCl_3$); ^1H NMR (400 MHz): $\delta = 1.20$ (d, $J = 6.4$, 3 H, CH_3-C(3)), 1.62–1.70 (m, 1 H, OH), 2.04–2.13 (m, 1 H, H-C(2)), 2.61 ("dd", *ABX*, $J = 13.5$, 8.9, 1 H, PhCH_2-C(2)), 2.79 ("dd", *ABX*, $J = 13.5$, 5.9, 1 H, PhCH_2-C(2)), 3.40 ("dd", *ABX*, $J = 9.4$, 5.6, 1 H, H-C(1)), 3.46 ("dd", *ABX*, $J = 9.4$, 5.1, 1 H, H-C(1)), 3.63–3.71 (m, 1 H, H-C(3)), 4.29–4.53 (m, 4 H, 2 OCH_2Ph (G2)), 4.59 (d, $J = 3.4$, 2 H, CH_2OH), 6.50–6.55 (m, 4 H, 4 arom. H (G2)), 6.59 (d, $J = 2.3$, 2 H, 2 arom. H (G2)), 7.22 (d, $J = 8.4$, 2 H, 2 arom. H (G1)), 7.26–7.41 (m, 20 H, 20 arom. H (P)); ^{13}C NMR (100 MHz): $\delta = 16.7$, 33.2, 46.1, 65.2, 69.2, 70.0, 70.7, 72.8, 74.8, 101.0, 101.1, 106.4, 106.5, 127.1, 127.5, 127.9, 128.5, 129.3, 136.9, 138.3, 140.5, 141.1, 141.6, 159.9; IR ($CHCl_3$): $\tilde{\nu} = 3008$ w, 1710 s, 1596 s, 1453 m, 1364 s, 1292 w, 1156 s, 1055 m, 835 w cm^{-1}; MS (FAB): m/z: 816 (11), 815 (33, $[M]^+$), 814 (54), 607 (11), 606 (41), 605 (94), 604 (12), 603 (24), 515 (14), 514 (10), 513 (24), 495 (12), 423 (12), 393 (22), 304 (44), 303 (100), 213 (19), 181 (31), 121 (19), 105 (21); $C_{54}H_{54}O_7$ (815.02): calcd C 79.58, H 6.68; found C 79.69, H 6.94.

(Bn)$_4$–[G1]$_F$–[G1]*(A)–Br (17): As described in GP IV, PPh_3 (2.82 g, 10.7 mmol) and CBr_4 (3.57 g, 10.7 mmol) were added to a solution of alcohol **16** (5.8 g, 7.12 mmol) in THF (75 mL). Workup as described in GP IV yielded a slightly yellow oil (5.7 g). FC (Et_2O/pentane 1:5) yielded **17** (2.95 g, 47 % over two steps) as a colorless oil. R_f (acetone/hexane 1:3): 0.34; $[\alpha]_D^{RT} = -1.33$ ($c = 1.50$, $CHCl_3$); ^1H NMR (400 MHz): $\delta = 1.20$ (d, $J = 6.3$, 3 H, CH_3-C(3)), 2.02–2.12 (m, 1 H, H-C(2)), 2.56–2.66 (m, 1 H, PhCH_2-C(2)), 2.72–2.81 (m, 1 H, PhCH_2-C(2)), 3.36–3.50 (m, 1 H, H-C(1)), 3.62–3.70 (m, 1 H, H-C(3)), 4.28–4.53 (m, 6 H, 2 OCH_2Ph(G2) and CH_2Br), 4.99 (d, $J = 5.0$, 8 H, 4 OCH_2Ph(P)), 6.50–6.53 (m, 2 H, 2 arom. H(G2)), 6.55 (d, $J = 2.2$, 2 H, 2 arom. H(G2)), 6.59 (d, $J = 2.3$, 2 H, 2 arom. H(G2)), 7.05–7.12 (m, 2 H, 2 arom. H(G1)), 7.21–7.25 (m, 2 H, 2 arom. H(G1)), 7.26–7.41 (m, 20 H, 20 arom. H(P)); ^{13}C NMR (100 MHz): $\delta = 16.7$, 33.2, 33.7, 46.1, 46.2, 69.2, 70.0, 70.7, 72.9, 74.6, 101.0, 101.1, 106.4, 106.5, 127.5, 127.9, 128.5, 129.0, 129.5, 129.6, 134.9, 135.2, 136.9, 141.1, 141.5, 160.0; IR ($CHCl_3$): $\tilde{\nu} = 3008$ m, 2870 w, 1597 s, 1498 w, 1453 m, 1375 m, 1292 w, 1157 s, 1048 m, 833 w cm^{-1}; MS (FAB): m/z: 878 (15, $[M]^+$), 877 (10), 876 (12), 832 (11), 606 (24), 605

(49), 393 (14), 319 (15), 305 (14), 304 (63), 303 (100), 213 (36), 212 (12), 211 (25), 183 (15), 182 (13), 181 (61), 175 (15), 167 (14), 165 (17), 155 (20), 154 (49), 152 (13), 141 (14), 139 (23), 138 (20), 137 (28), 136 (45), 131 (18), 129 (16), 117 (15), 115 (17), 107 (29), 105 (40), 104 (24); $C_{54}H_{53}O_6Br$ (877.91): calcd C 73.88, H 6.08; found C 75.43, H 6.27.

The compounds *ent*-**15**, *ent*-**16** and *ent*-**17** were synthesized following the same procedures as for their enantiomers, and the analytical data correspond.

(Bn)$_8$–{[G1]$_F$–[G1]*(A)}$_4$–[Phe-TADDOL] (18): As described in GP II, a solution of **14** (1.10 g, 2.43 mmol) in acetone (15 mL) was added to a solution of TADDOL **2** (0.292 g, 0.55 mmol) in acetone (15 mL). To this solution was added K_2CO_3 (0.336 g, 2.43 mmol), and the reaction mixture was heated under reflux for 12 h. Workup as described in GP II yielded a slightly yellow oil (1.15 g). FC (acetone/hexane 1:4) yielded **18** (0.45 g, 41 %) as a colorless oil. R_f (acetone/hexane 1:4): 0.21; $[\alpha]_D^{RT} = -29.10$ (c = 1.10, $CHCl_3$); ^{1}H NMR (300 MHz): δ = 1.08 (s, 6H, $(CH_3)_2$-C(2)(c)), 1.22–1.26 (m, 12H, 4 CH_3-C(3)(G1)), 2.10–2.19 (m, 4H, 4 H-C(2)(G1)), 2.61–2.72 (m, 4H, 4 PhCH_2-C(2)(G1)), 2.79–2.89 (m, 4H, 4 PhCH_2-C(2)(G1)), 3.42–3.58 (m, 8H, 8 H-C(2)(G1)), 3.69–3.77 (m, 4H, 4 H-C(3)(G1)), 4.02 (brs, 2H, 2 OH), 4.37–4.61 (m, 18H, 8 CH_2(P) and H-C(4), H-C(5)(c)), 4.98 (s, 4H, 2 CH_2O(G1)), 5.03 (s, 4H, 2 CH_2O(G1)), 6.88 (d, J = 8.7, 4H, 4 arom. H(c)), 6.96 (d, J = 8.7, 4H, 4 arom. H(c)), 7.13 (d, J = 8.1, 4H, 4 arom. H(c)), 7.21–7.41 (m, 56H, 16 arom. H(G1) and 40 arom. H(P)), 7.42 (d, J = 8.1, 4H, 4 arom. H(c)); ^{13}C NMR (75 MHz): δ = 16.7, 27.2, 33.3, 46.2, 69.1, 69.9, 70.8, 73.0, 74.6, 75.7, 113.4, 114.2, 127.4, 127.5, 127.6, 127.8, 128.3, 128.9, 129.4, 129.7, 134.3, 138.6, 139.1, 141.1, 158.1, 168.6; IR ($CHCl_3$): $\tilde{\nu}$ = 3374 br, 3007 m, 2864 w, 1607 m, 1508 s, 1454 m, 1379 m, 1090 s, 1017 m, 909 s, 836 m cm^{-1}; MALDI-TOF MS (HABA): m/z: 2043.9 ([M+Na]$^+$); $C_{135}H_{142}O_{16}$ (2020.60): calcd C 80.25, H 7.08; found C 79.33, H 6.92.

(Bn)$_{16}$–{[G1]$_F$–[G1]*(A)}$_4$–[Phe-TADDOL] (19): As described in GP II, a solution of **17** (2.20 g, 2.51 mmol) in acetone (5 mL) was added to a solution of TADDOL **2** (0.302 g, 0.57 mmol) in acetone (20 mL). To that was added K_2CO_3 (0.32 g, 2.28 mmol), and the reaction mixture was heated under reflux for 45 h. Workup as described in GP II yielded a brownish foam (2.73 g). FC (acetone/hexane 1:2) yielded **19** (1.70 g, 80 %) as a slightly yellow foam. R_f (acetone/hexane 2:3): 0.27; $[\alpha]_D^{RT} = -14.43$ (c = 0.98, $CHCl_3$); ^{1}H NMR (500 MHz): δ = 1.06 (s, 6H, $(CH_3)_2$-C(2)(c)), 1.17–1.22 (m, 12H, 4 CH_3-C(3)(G1)), 2.03–2.14 (m, 4H, 4 H-C(2)(G1)), 2.59–2.68 (m, 4H, 4 PhCH_2-C(2)(G1)), 2.75–2.84 (m, 4H, 4 PhCH_2-C(2)(G1)), 3.38–3.51 (m, 8H, 8 H-C(2)(G1)), 3.62–3.72 (m, 4H, 4 H-C(3)(G1)), 4.01 (brs, 2H, 2 OH), 4.28–4.40 (m, 12H, 8 CH_2(G2)), 4.46–4.52 (m, 6H, 8 CH_2(G2) and C(4), C(5)(c)), 4.88–5.03 (m, 40H, 16 CH_2(P) und 4 CH_2O(G1)), 6.49–6.53 (m, 8H, 8 arom. H(G2)), 6.53–6.58 (m, 8H, 8 arom. H(G2)), 6.58–6.61 (m, 8H, 8 arom. H(G2)), 6.84 (d, J = 9.0, 4H, 4 arom. H(c)), 6.92 (d, J = 9.0, 4H, 4 arom. H(c)), 7.11 (d, J = 8.1, 4H, 4 arom. H(c)), 7.14 (d, J = 8.1, 4H, 4 arom. H(c)), 7.21–7.41 (m, 96H, 16 arom. H(G1) and 80 arom. H(P)); ^{13}C NMR (125 MHz): δ = 16.8, 23.5, 26.9, 27.2, 33.3, 46.2, 69.2, 69.9, 69.9, 70.0, 70.7, 72.9, 74.7, 76.8, 77.0, 77.3, 77.6, 101.1, 101.1, 106.4, 106.5, 113.4, 114.2, 126.5, 126.7, 126.9, 127.5, 127.7, 127.8, 127.9, 128.6, 128.9, 129.4, 129.7, 134.3, 134.4, 135.6, 136.9, 138.7, 141.0, 141.2, 141.6, 158.0, 158.1, 160.0; IR ($CHCl_3$): $\tilde{\nu}$ = 3008 w, 2870 w, 1596 s, 1509 w, 1454 m, 1376 m, 1293 w, 1157 s, 1058 m, 833 w cm^{-1}; MALDI-TOF MS (CCA): m/z: 3741.7 ([M+Na]$^+$); $C_{247}H_{238}O_{32}$ (3718.58): calcd C 79.78, H 6.45; found C 79.87, H 6.58.

(Bn)$_{16}$–{[G1]$_F$–[G1]*(B)}$_4$–[Phe-TADDOL] (20): As described in GP II, a solution of *ent*-**17** (1.89 g, 2.16 mmol) in acetone (5 mL) is added to a solution of TADDOL **2** (0.29 g, 0.54 mmol) in acetone (15 mL). To this solution was added K_2CO_3 (0.30 g, 2.16 mmol), and the reaction mixture was heated under reflux for 45 h. Workup as described in GP II yielded a brownish foam (2.3 g). FC (acetone/hexane 1:2) yielded **20** (1.53 g, 76 %) as a slightly yellow foam. R_f (acetone/hexane 2:3): 0.25; $[\alpha]_D^{RT} = -10.85$ (c = 1.10, $CHCl_3$); ^{1}H NMR (400 MHz): δ = 1.06 (s, 6H, $(CH_3)_2$-C(2)(c)), 1.19–1.22 (m, 12H, 4 CH_3-C(3)(G1)), 2.05–2.12 (m, 4H, 4 H-C(2)(G1)), 2.59–2.67 (m, 4H, 4 PhCH_2-C(2)(G1)), 2.77–2.82 (m, 4H, 4 PhCH_2-C(2)(G1)), 3.38–3.50 (m, 8H, 8 H-C(2)(G1)), 3.64–3.71 (m, 4H, 4 H-C(3)(G1)), 3.99 (brs, 2H, 2 OH), 4.30–4.38 (m, 12H, 8 CH_2(G2)), 4.48–4.52 (m, 6H, 8 CH_2(G2) and C(4), C(5)(c)), 4.91–4.99 (m, 40H, 16 CH_2(P) and 4 CH_2O(G1)), 6.50–6.53 (m, 8H, 8 arom. H(G2)), 6.53–6.56 (m, 8H, 8 arom. H(G2)), 6.59–6.61 (m, 8H, 8 arom. H(G2)), 6.84 (d, J = 9.0, 4H, 4 arom. H(c)), 6.92 (d, J = 9.0, 4H, 4 arom. H(c)), 7.11 (d, J = 8.1, 4H, 4 arom. H(c)), 7.14 (d, J = 8.1, 4H, 4 arom. H(c)), 7.22–7.40 (m, 96H, 16 arom. H(G1) and 80 arom. H(P)); ^{13}C NMR (100 MHz): δ = 16.8, 27.2, 33.3, 46.2, 69.2, 69.9, 70.0, 70.7, 72.9, 74.7, 77.6, 101.1, 106.4, 106.5, 113.4, 114.2, 127.5, 127.7, 127.8, 127.9, 128.6, 129.4, 129.8, 134.3, 134.4, 136.9, 141.0, 141.2, 141.6, 160.0; IR ($CHCl_3$): $\tilde{\nu}$ = 3008 w, 2869 w, 1596 s, 1508 m, 1453 m, 1375 m, 1293 m, 1157 s, 1055 m, 834 w cm^{-1}; MALDI-TOF MS (HABA): m/z: 3741.3 ([M+Na]$^+$); $C_{247}H_{238}O_{32}$ (3718.58): calcd C 79.78, H 6.45; found C 79.51, H 6.40.

(Octyl)$_2$–[G1]$_F$–COOMe (21): *n*-Octyl bromide (96 mL, 550 mmol), 18-C-6 (11.6 g, 44 mmol), and K_2CO_3 (76.0 g, 550 mmol) were added to a solution of methyl α-resorcylate (37.0 g, 220 mmol) in acetone (1 L), and the reaction mixture was heated under reflux for 60 h. After cooling to RT the solids were filtered off, and the solvent of the filtrate was evaporated. After addition of CH_2Cl_2 (400 mL) the product was washed with H_2O (200 mL) and the aqueous layer was extracted again with CH_2Cl_2 (2 × 400 mL). The combined organic layers were dried over $MgSO_4$ and the solvent removed to yield a yellow oil. This was placed in the refrigerator overnight, where a white product cristallized. The solid was redissolved in Et_2O and the insoluble parts were filtered off. The solvent of the filtrate was again evaporated to give **21** as a white solid in quantitative yield. M.p. 40.8–41.4 °C; R_f (CH_2Cl_2): 0.64; ^{1}H NMR (300 MHz): δ = 0.89 (t, J = 6.80, 6H, 2 CH_3), 1.28–1.48 (m, 20H, 10 CH_2), 1.72–1.82 (m, 4H, 2 CH_2CH$_2$O), 3.90 (s, 3H, OCH_3), 3.97 (t, J = 6.55, 4H, 2 CH_2O), 6.63 (t, J = 2.34, 1H, 1 arom. H), 7.16 (d, J = 2.34, 2H, 2 arom. H); ^{13}C NMR (75 MHz): δ = 14.2, 22.7, 26.1, 29.3, 29.4, 31.8, 52.2, 68.4, 106.7, 107.7, 131.9, 160.2, 167.0; IR ($CHCl_3$): $\tilde{\nu}$ = 2927 s, 2858 m, 1718 m, 1596 m, 1447 m, 1352 m, 1301 m, 1167 m, 1112 s, 1056 w, 963 m cm^{-1}; MS (EI): m/z: 392 (34.7, [M]$^+$), 364 (6), 361 (4), 280 (10), 248 (4), 221 (4), 181 (4), 168 (100), 137 (16), 111 (5), 83 (5), 69 (18), 57 (20), 43 (27), 28 (7); $C_{24}H_{40}O_4$ (392.57): calcd C 73.43, H 10.27; found C 73.54, H 10.16.

(Octyl)$_2$–[G1]$_F$–OH (22): A solution of **21** (102.0 g, 0.26 mol) in Et_2O (450 mL) was added to a suspension of $LiAlH_4$ (11.0 g, 0.29 mol) in Et_2O (350 mL) over 30 min. The grey mixture was heated under reflux for 4 h and stirred overnight at RT. Hydrolysis by dropwise addition of H_2O (11 mL) followed by 15 % NaOH solution (11 mL) and then once more by H_2O (33 mL) gave a clear supernatant solution, which was separated from the salt. The organic layer was washed (2 × H_2O) and the combined aqueous layers extracted (2 × Et_2O). The combined organic layers were dried over $MgSO_4$ and the solvent was evaporated to give a crude product containing **22** as a colorless oil (107.1 g). A small amount thereof was purified by FC (CH_2Cl_2) for analytical purposes, the rest was used directly for the next reaction steps. R_f (CH_2Cl_2): 0.18; ^{1}H NMR (300 MHz): δ = 0.89 (t, J = 6.8, 6H, 2 CH_3), 1.21–1.49 (m, 20H, 10 CH_2), 1.71–1.80 (m, 4H, 2 CH_2CH$_2$O), 1.98 (t, J = 6.0, 1H, OH), 3.92 (t, J = 6.6, 4H, 2 CH_2O), 4.59 (d, J = 5.8, 2H, CH_2OH), 6.36 (t, J = 2.3, 1H, 1 arom. H), 6.48 (d, J = 2.2, 2H, 2 arom. H); ^{13}C NMR (75 MHz): δ = 14.1, 22.7, 26.1, 29.3, 29.4, 31.8, 65.4, 68.1, 100.6, 105.1, 143.2, 160.5; IR ($CHCl_3$): $\tilde{\nu}$ = 3604 w, 2926 s, 2856 s, 1596 s, 1454 s, 1384 m, 1293 m, 1165 s, 1061 m, 836 w cm^{-1}; MS (EI): m/z: 364 (28.8, [M]$^+$), 252 (7), 221 (6), 141 (46), 140 (100), 138 (10), 123 (15), 111 (21), 71 (14), 69 (24), 57 (26), 55 (23), 43 (28); $C_{23}H_{40}O_3$ (364.56): calcd C 75.78, H 11.06; found C 75.88, H 10.94.

(Octyl)$_2$–[G1]$_F$–Br (23): As described in GP IV, PPh_3 (78.7 g, 0.3 mol), and CBr_4 (99.5 g, 0.3 mol) were added to a solution of alcohol **22** (88.0 g, 0.24 mol) in THF (650 mL). Workup as described in GP IV yielded a yellow oil as crude product containing **23** (149 g). A small amount thereof was purified by FC (CH_2Cl_2) for analytical purposes, the rest was used directly for the next reaction steps. R_f (CH_2Cl_2): 0.85; ^{1}H NMR (300 MHz): δ = 0.89 (t, J = 6.8, 6H, 2 CH_3), 1.21–1.50 (m, 20H, 10 CH_2), 1.71–1.83 (m, 4H, 2 CH_2CH$_2$O), 3.92 (t, J = 6.6, 4H, 2 CH_2O), 4.41 (s, 2H, CH_2Br), 6.38 (t, J = 2.2, 1H, 1 arom. H), 6.51 (d, J = 2.2, 2H, 2 arom. H), ^{13}C NMR (75 MHz): δ = 14.1, 22.7, 26.1, 29.3, 29.4, 31.9, 33.8, 68.2, 101.5, 107.5, 139.6, 160.5; IR ($CHCl_3$): $\tilde{\nu}$ = 2928 s, 2853 s, 1595 s, 1461 s, 1384 m, 1347 m, 1167 s, 1056 m cm^{-1}; MS (EI): m/z: 428 (52.7 [M+1]$^+$), 426 (54), 348 (24), 347 (43), 235 (58), 204 (36), 202 (34), 123 (100), 69 (80), 55 (66), 43 (66); $C_{23}H_{39}O_2Br$ (427.46): calcd C 64.63, H 9.20; found C 64.81, H 9.39.

(Octyl)$_4$–[G2]$_F$–COOMe (24): K_2CO_3 (5.2 g, 37.5 mmol) was added to a mixture of acetonitrile (100 mL) and acetone (50 mL), and the reaction mixture was cooled to ice-bath temperature before bromide **23** (8.0 g, 15 mmol, ca. 80 % pure), methyl α-resorcylate (1.3 g, 7.5 mmol), and 18-C-6 (0.5 g, 1.9 mmol) were added. After stirring for 20 h at RT the salt was filtered off and most of the solvent of the filtrate was evaporated. After addition of CH_2Cl_2 (50 mL) and H_2O (50 mL) and after separation of the layers, the aqueous layer was extracted ($3\times CH_2Cl_2$). The combined organic layers were dried over $MgSO_4$ and the solvent evaporated under vacuum. FC (cyclohexane/CH_2Cl_2 1:1) yielded **24** (4.7 g, 73 %) as a slightly yellow oil. R_f (cyclohexane/CH_2Cl_2 1:1): 0.29; ^{1}H NMR (200 MHz): $\delta=$ 0.8–1.0 (m, 12H, 4 CH_3), 1.2–1.5 (m, 40H, 20 CH_2), 1.7–1.9 (m, 8H, 4 OCH_2CH_2), 3.93 (s, 3H, OCH_3), 3.96 (t, $J=7.06$, 2H, OCH_2), 5.01 (s, 2H, C(arom.)-CH_2O), 6.4 (m, 2H, 2 arom. H), 6.6 (m, 4H, 4 arom. H), 6.8 (m, 1H, 1 arom. H), 7.3 (m, 2H, 2 arom. H).

(Octyl)$_4$–[G2]$_F$–OH (25): A solution of ca. 80 % of compound **23** (148 g, 346 mmol) in THF (250 mL) was added at ice-bath temperature to a solution of 3,5-dihydroxybenzylic alcohol (13.0 g, 93 mmol) in THF (250 mL). Compound 18-C-6 (4.9 g, 18.6 mmol) and K_2CO_3 (32.1 g, 232 mmol) were added to this solution, and the reaction mixture was heated under reflux for 30 h. After cooling to RT the salt was filtered off and most of the solvent of the filtrate was evaporated under vacuum. Et_2O (400 mL) was added to the residue and the solution was washed with H_2O (200 mL). The aqueous layer was extracted (2×600 mL), the combined organic layers were dried over $MgSO_4$, and the solvent was evaporated under vacuum to give a brown crude product. FC (CH_2Cl_2) yielded **25** (42.0 g, 54 %) as a slightly yellow oil. A small amount was purified by FC (CH_2Cl_2) for analytical purposes. M.p. 38.0–38.1 °C; R_f (CH_2Cl_2): 0.28; ^{1}H NMR (400 MHz): $\delta=0.88$ (t, $J=6.9$, 12H, 4 CH_3), 1.22–1.49 (m, 40H, 20 CH_2), 1.65 (t, $J=6.0$, 1H, OH), 1.71–1.80 (m, 8H, 4 CH_2CH_2O), 3.93 (t, $J=6.6$, 8H, 4 CH_2O), 4.62 (d, $J=5.8$, 2H, CH_2OH), 4.95 (s, 4H, 2 benzyl. CH_2), 6.40 (t, $J=2.3$, 2H, 2 arom. H), 6.52–6.56 (m, 5H, 5 arom. H), 6.61 (d, $J=2.3$, 2H, 2 arom. H); ^{13}C NMR (100 MHz): $\delta=14.1$, 22.7, 26.1, 29.2, 29.3, 29.4, 31.8, 65.4, 68.1, 70.1, 100.8, 101.4, 105.7, 139.0, 143.4, 160.2, 160.5; IR ($CHCl_3$): $\tilde{\nu}=3601$ w, 2928 s, 2856 m, 1595 s, 1456 m, 1378 w, 1295 w, 1166 s, 1058 m, 835 w cm^{-1}; MS (FAB): m/z: 834 (36.5, $[M]^+$), 833 (50), 832 (26), 816 (13), 696 (14), 695 (49), 694 (100), 693 (35), 692 (36), 58 (11), 467 (13), 457 (11), 349 (11), 348 (32), 347 (38), 163 (12), 149 (11), 137 (19), 125 (57), 124 (33), 123 (30); $C_{53}H_{84}O_7$ (833.23): calcd C 76.40, H 10.16; found C 76.56, H 9.93.

X-ray crystal structure analysis of 25 ($C_{53}H_{84}O_7$): Determination of the cell parameters and collection of the reflection intensities were performed on an Enraf–Nonius CAD4 four-circle diffractometer (graphite monochromated $Mo_{K\alpha}$ radiation, $\lambda=0.7107$ Å). Colorless cube, $0.3\times0.3\times0.5$ mm, triclinic, space group $P1$, $a=10.578(4)$ Å, $b=16.045(6)$ Å, $c=16.688(6)$ Å, $\alpha=101.67(3)^\circ$, $\beta=105.96(3)^\circ$, $\gamma=100.98(3)^\circ$, $V=2574(2)$ Å^3, $Z=2$, $\rho_{calcd}=1.075$ g cm^{-3}, $\mu=0.069$ mm^{-1}, $F(000)=916$. Number of reflections measured 5585 (ω scan, $2.6<2\theta<44^\circ$, $T=293$ K); 5585 unique reflections, which were used for the determination (direct methods, SHELXS-86). SHELXL-93 was used for structure refinement (full-matrix least-squares). The temperature factors of the non-H atoms were refined anisotropically, the H atoms were added to the molecule with constant isotropic temperature factors on idealized positions and refined according to the riding model (afix 3). The refinement converged at $R=0.0872$ ($wR^2=0.229$), min and max residual electron density 0.438 and -0.215 e Å^{-3}, number of variables 541.

(Octyl)$_4$–[G2]$_F$–Br (26): As described in GP IV, PPh_3 (19.8 g, 76 mmol) and CBr_4 (25.2 g, 76 mmol) were added to a solution of alcohol **25** (42.0 g, 50 mmol) in THF (400 mL). Workup as described in GP IV yielded a brown crude product. This was stirred in petroleum ether (500 mL) for 15 min and the insoluble parts were filtered off to give, after evaporation of the solvent, a brownish oil. This was purified of polar by-products by a short FC (350 g SiO_2, CH_2Cl_2) to yield a yellow oil as **26**-containing product (45.8 g). A small amount was purified again by FC (hexane/Et_2O 19:1) for analytical purposes, the rest was used directly for the next reaction steps. R_f (CH_2Cl_2): 0.86; ^{1}H NMR (400 MHz): $\delta=0.89$ (t, $J=6.9$, 12H, 4 CH_3), 1.22–1.49 (m, 40H, 20 CH_2), 1.71–1.81 (m, 8H, 4 CH_2CH_2O), 3.93 (t, $J=6.6$, 8H, 4 CH_2O), 4.41 (s, 2H, CH_2Br), 4.94 (s, 4H, 2 benzyl. CH_2), 6.40 (t, $J=2.3$, 2H, 2 arom. H), 6.52–6.56 (m, 5H, 5 arom. H), 6.62 (d, $J=2.2$, 2H, 2 arom. H); ^{13}C NMR (100 MHz): $\delta=14.1$, 22.7, 26.1, 29.2, 29.3, 29.4, 31.8, 33.6, 68.1, 70.2, 100.9, 102.2, 105.8, 108.2, 138.8, 139.8, 160.1, 160.6; IR ($CHCl_3$): $\tilde{\nu}=2927$ s, 2856 m, 1595 s, 1454 m, 1378 w, 1296 w, 1166 s, 1055 m, 836 w cm^{-1}; MS (FAB): m/z: 896 (21.1), 817 (12), 816 (19), 815 (10), 814 (13), 696 (16), 695 (55), 694 (100), 693 (40), 692 (51), 666 (13), 581 (22), 579 (20), 469 (20), 468 (18), 467 (32), 466 (14), 457 (29), 361 (27), 355 (16), 349 (18), 348 (51), 347 (84), 345 (22), 163 (28), 149 (25), 137 (40), 125 (79), 123 (61), 107 (22); $C_{53}H_{63}O_6Br$ (896.13): calcd C 71.04, H 9.34; found C 70.94, H 9.45.

(Octyl)$_4$–[G1]$_F$–[G1]*(A)–OTBDPS (27): As described in GP III, NaH (0.24 g, 10 mmol) was added to THF (20 mL). After cooling to ice-bath temperature a solution of diol **11** (1.12 g, 2.5 mmol) in THF (15 mL) was added and the reaction mixture was stirred at RT for 1 h, before a solution of **23** (3.18 g, 7.5 mmol) in THF (15 mL) was added slowly. After stirring at RT for 3 h the reaction mixture was heated under reflux for 15 h. Workup as described in GP III yielded a slightly yellow oil as crude product. FC (CH_2Cl_2/hexane 1:3) yielded **27** (2.83 g, 99 %) as a clear viscous oil. R_f (acetone/hexane 1:9): 0.54; ^{1}H NMR (400 MHz): $\delta=0.88$ (t, $J=6.8$, 12H, 4 CH_3(P)), 1.09 (s, 9H, *t*Bu), 1.23 (d, $J=6.4$, 3H, CH_3-C(3)), 1.23–1.48 (m, 40H, 20 CH_2(P)), 1.70–1.79 (m, 8H, 4 CH_2CH_2O(P)), 2.08–2.17 (m, 1H, H-C(2)), 2.64 ("dd", *ABX*, $J=13.5$, 8.9, 1H, PhCH_2-C(2)), 2.83 ("dd", *ABX*, $J=13.5$, 5.8, 1H, PhCH_2-C(2)), 3.44 ("dd", *ABX*, $J=9.4$, 5.7, 1H, H-C(1)), 3.50 ("dd", *ABX*, $J=9.4$, 5.1, 1H, H-C(1)), 3.68–3.76 (m, 1H, H-C(3)), 3.86–3.95 (m, 8H, 4 CH_2CH_2O(P)), 4.29–4.52 (m, 4H, 2 OCH_2Ph(G2)), 4.74 (s, 2H, CH_2OSi), 6.34–6.37 (m, 2H, 2 arom. H(G2)), 6.45 (d, $J=2.3$, 2H, 2 arom. H(G2)), 6.50 (d, $J=2.3$, 2H, 2 arom. H(G2)), 7.11 (d, $J=8.1$, 2H, 2 arom. H(G1)), 7.23 (d, $J=8.2$, 2H, 2 arom. H(G1)), 7.33–7.44 (m, 6H, 6 arom. H), 7.67–7.72 (m, 4H, 4 arom. H); ^{13}C NMR (100 MHz): $\delta=14.1$, 16.7, 19.3, 22.6, 26.1, 26.8, 29.2, 29.3, 29.4, 31.6, 31.8, 33.1, 46.2, 65.4, 68.0, 69.3, 70.9, 73.0, 74.7, 100.3, 100.4, 105.7, 125.9, 127.7, 129.0, 129.6, 133.6, 135.6, 138.5, 139.7, 141.0, 141.4, 160.3; MALDI-TOF MS (CCA): m/z: 1136.6, 1164.3 ($[M+Na]^+$); $C_{74}H_{112}O_7Si$ (1141.78): calcd C 77.84, H 9.89; found C 77.63, H 9.91.

(Octyl)$_4$–[G1]$_F$–[G1]*(A)–OH (28): As described in GP I, TBAF (2.04 g, 6.46 mmol) was added to a solution of **27** (2.46 g, 2.15 mmol) in THF (25 mL). Workup as described in GP I yielded a yellow oil (6.7 g). This was purified by FC (acetone/hexane 1:4) to yield a slightly yellow oil containing product **28** (2.34 g). A small amount thereof was purified for analytical data by FC, the rest was used for further reaction steps. R_f (acetone/hexane 1:3): 0.32; ^{1}H NMR (400 MHz): $\delta=0.88$ (t, $J=6.8$, 12H, 4 CH_3(P)), 1.23 (d, $J=6.3$, 3H, CH_3-C(3)), 1.23–1.49 (m, 40H, 20 CH_2(P)), 1.68–1.80 (m, 8H, 4 CH_2CH_2O(P)), 2.07–2.18 (m, 1H, H-C(2)), 2.63 ("dd", *ABX*, $J=13.5$, 8.9, 1H, PhCH_2-C(2)), 2.82 ("dd", *ABX*, $J=13.5$, 5.9, 1H, PhCH_2-C(2)), 3.38–3.49 (m, 1H, H-C(1)), 3.66–3.73 (m, 1H, H-C(3)), 3.84–3.94 (m, 8H, 4 CH_2CH_2O(P)), 4.28–4.52 (m, 4H, 2 OCH_2Ph(G2)), 4.64 (d, $J=3.2$, 2H, CH_2OH), 6.34–6.37 (m, 2H, 2 arom. H(G2)), 6.41 (d, $J=2.3$, 2H, 2 arom. H(G2)), 6.47 (d, $J=2.3$, 2H, 2 arom. H(G2)), 7.12 (d, $J=8.1$, 2H, 2 arom. H(G1)), 7.23 (d, $J=8.2$, 2H, 2 arom. H(G1)); ^{13}C NMR (100 MHz): $\delta=$ 14.1, 16.7, 22.7, 26.1, 29.2, 29.3, 29.4, 31.6, 31.8, 33.1, 46.1, 65.3, 68.0, 69.3, 70.9, 73.0, 74.8, 100.3, 100.4, 105.8, 127.7, 129.4, 129.7, 134.8, 140.7, 140.9, 141.3, 160.3.

(Octyl)$_4$–[G1]$_F$–[G1]*(A)–Br (29): As described in GP IV, PPh_3 (0.79 g, 3 mmol) and CBr_4 (1.0 g, 3 mmol) were added to a solution of alcohol **28** (1.94 g, 2.15 mmol) in THF (15 mL). Workup as described in GP IV yielded a yellow oil (2.86 g). FC (acetone/hexane 1:8) yielded **29** (1.89 g, 91 %) as a colorless oil. R_f (acetone/hexane 1:5): 0.56; ^{1}H NMR (400 MHz): $\delta=0.88$ (t, $J=6.5$, 12H, 4 CH_3(P)), 1.21 (d, $J=6.4$, 3H, CH_3-C(3)), 1.22–1.49 (m, 40H, 20 CH_2(P)), 1.70–1.80 (m, 8H, 4 CH_2CH_2O(P)), 2.05–2.13 (m, 1H, H-C(2)), 2.63 ("dd", *ABX*, $J=13.5$, 8.8, 1H, PhCH_2-C(2)), 2.80 ("dd", *ABX*, $J=13.5$, 6.0, 1H, PhCH_2-C(2)), 3.39–3.49 (m, 1H, H-C(1)), 3.65–3.72 (m, 1H, H-C(3)), 3.87–3.94 (m, 8H, 4 CH_2CH_2O(P)), 4.28–4.52 (m, 4H, 2 OCH_2Ph(G2)), 4.48 (d, $J=3.2$, 2H, CH_2Br), 6.34–6.38 (m, 2H, 2 arom. H(G2)), 6.43 (d, $J=2.3$, 2H, 2 arom. H(G2)), 6.48 (d, $J=2.3$, 2H, 2 arom. H(G2)), 7.09 (d, $J=8.1$, 2H, 2 arom. H(G1)), 7.23 (d, $J=8.2$, 2H, 2 arom. H(G1)); ^{13}C NMR (100 MHz): $\delta=14.1$, 16.7, 22.6, 26.1, 29.2, 29.3, 29.4, 31.8, 33.2, 33.7, 46.1, 68.0, 69.2, 70.8, 73.1, 74.6, 100.3, 100.4, 105.7, 105.8, 128.9, 129.6, 135.1, 140.8, 141.3, 141.7, 160.0.

(Octyl)$_8$–[G2]$_F$–[G1]*(A)–OTBDPS (30): As described in GP III, NaH (0.55 g, 23 mmol) was added to THF (25 mL). After cooling to ice-bath temperature, a solution of diol **11** (1.70 g, 3.8 mmol) in THF (25 mL) was added and the reaction mixture was stirred at RT for 1 h, before a solution of **26** (8.14 g, 9.1 mmol) in THF (50 mL) was added slowly. After stirring at RT for 3 h the reaction mixture was heated under reflux for 30 h. Workup as described in GP III gave a brownish oil (10.2 g) as crude product. FC (CH_2Cl_2/hexane 1:2) yielded **30** (6.20 g, 79 %) as a clear viscous oil. R_f (CH_2Cl_2/hexane 3:2): 0.38; $[\alpha]_D^{RT}=-1.39$ ($c=1.15$, $CHCl_3$); ^{1}H NMR (400 MHz): $\delta=0.88$ (t, $J=6.8$, 24H, 8 CH_3(P)), 1.08 (s, 9H, *t*Bu), 1.23 (d, $J=6.3$, 3H, CH_3-C(3)), 1.23–1.48 (m, 80H, 40 CH_2(P)), 1.68–1.79 (m, 16 H, 8 CH_2CH$_2$O(P)), 2.07 – 2.14 (m, 1 H, H-C(2)), 2.63 ("dd", *ABX*, $J = 13.5$, 9.0, 1 H, PhCH_2-C(2)), 2.80 ("dd", *ABX*, $J = 13.5$, 5.9, 1 H, PhCH_2-C(2)), 3.44 ("dd", *ABX*, $J = 9.4$, 5.6, 1 H, H-C(1)), 3.52 ("dd", *ABX*, $J = 9.4$, 4.9, 1 H, H-C(1)), 3.66 – 3.74 (m, 1 H, H-C(3)), 3.86 – 3.94 (m, 16 H, 8 CH$_2$CH_2O(P)), 4.30 – 4.53 (m, 4 H, 2 OCH$_2$Ph(G2)), 4.73 (s, 2 H, CH$_2$O-Si), 4.90 (d, $J = 4.0$, 8 H, 4 OCH_2Ph(G3)), 6.37 – 6.40 (m, 4 H, 4 arom. H(G3)), 6.48 – 6.55 (m, 10 H, 2 arom. H(G2) and 8 arom. H(G3)), 6.57 (d, $J = 2.3$, 2 H, 2 arom. H(G2)), 6.60 (d, $J = 2.3$, 2 H, 2 arom. H(G2)), 7.10 (d, $J = 8.1$, 2 H, 2 arom. H(G1)), 7.22 (d, $J = 8.2$, 2 H, 2 arom. H(G1)), 7.32 – 7.43 (m, 6 H, 6 arom. H), 7.66 – 7.71 (m, 4 H, 4 arom. H); ^{13}C NMR (100 MHz): $\delta = 14.5$, 17.3, 19.7, 23.1, 26.5, 27.3, 29.6, 29.7, 29.8, 32.2, 46.7, 65.8, 68.5, 70.5, 101.2, 101.5, 106.1, 106.7, 106.8, 126.4, 128.1, 129.5, 130.0, 134.0, 136.0, 138.9, 139.5, 140.0, 141.6, 142.0, 160.4, 160.9; IR (CHCl$_3$): $\tilde{\nu} = 3008$ w, 2929 s, 2857 m, 1596 s, 1455 m, 1377 w, 1343 w, 1295 w, 1166 s, 1112 w, 1047 m, 834 w cm^{-1}; MALDI-TOF MS (CCA): *m*/*z*: 2074.9, 2102.7 ($[M+\mathrm{Na}]^+$), 2118.6 ($[M+\mathrm{K}]^+$), 2143.3; $C_{134}H_{200}O_{15}Si$ (2079.14): calcd C 77.41, H 9.70; found C 77.56, H 9.55.

(Octyl)$_8$–[G2]$_\mathrm{F}$–[G1]*(A)–OH (31): As described in GP I, TBAF (1.20 g, 3.84 mmol) was added to a solution of **30** (4.00 g, 1.92 mmol) in THF (40 mL). Workup as described in GP I yielded a brownish oil (4.4 g). FC (Et$_2$O/hexane 1:2) yielded **31** (2.88 g, 81 %) as a slightly yellow oil. A small amount thereof was purified again for analytical data by FC, the rest was used for further reaction steps. R_f (Et$_2$O/hexane 1:2): 0.18; ^{1}H NMR (500 MHz): $\delta = 0.88$ (t, $J = 6.9$, 24 H, 8 CH$_3$(P)), 1.27 (d, $J = 1.8$, 3 H, CH$_3$-C(3)), 1.27 – 1.38 (m, 64 H, 32 CH$_2$(P)), 1.38 – 1.47 (m, 16 H, 8 CH_2CH$_2$CH$_2$O(P)), 1.69 – 1.78 (m, 16 H, 8 CH_2CH$_2$O(P)), 2.06 – 2.13 (m, 1 H, H-C(2)), 2.61 ("dd", *ABX*, $J = 13.6$, 8.8, 1 H, PhCH_2-C(2)), 2.79 ("dd", *ABX*, $J = 13.5$, 5.8, 1 H, PhCH_2-C(2)), 3.42 ("dd", *ABX*, $J = 9.4$, 5.6, 1 H, H-C(1)), 3.47 ("dd", *ABX*, $J = 9.4$, 5.1, 1 H, H-C(1)), 3.66 – 3.72 (m, 1 H, H-C(3)), 3.86 – 3.94 (m, 16 H, 8 CH$_2$CH_2O(P)), 4.30 – 4.52 (m, 4 H, 2 OCH$_2$Ph(G2)), 4.61 (d, $J = 5.8$, 2 H, CH$_2$OH), 4.90 (d, $J = 6.9$, 8 H, 4 OCH$_2$Ph(G3)), 6.35 – 6.40 (m, 4 H, 4 arom. H(G3)), 6.49 – 6.56 (m, 12 H, 4 arom. H(G2) and 8 arom. H(G3)), 6.58 (d, $J = 2.3$, 2 H, 2 arom. H(G2)), 7.10 (d, $J = 8.1$, 2 H, 2 arom. H(G1)), 7.22 (d, $J = 8.2$, 2 H, 2 arom. H(G1)); ^{13}C NMR (125 MHz): $\delta = 14.1$, 16.8, 22.7, 26.1, 29.3, 29.4, 31.8, 46.2, 65.3, 68.1, 69.4, 70.1, 72.9, 74.9, 100.8, 101.1, 105.7, 106.4, 106.5, 127.1, 129.4, 138.4, 139.0, 139.1, 140.6, 141.1, 141.6, 160.0, 160.5; MALDI-TOF MS (CCA): *m*/*z*: 1836.0, 1864.2 ($[M+\mathrm{Na}]^+$), 1879.9 ($[M+\mathrm{K}]^+$), 1904.3; $C_{118}H_{182}O_{15}$ (1840.73): calcd C 77.00, H 9.97; found C 77.02, H 10.04.

(Octyl)$_8$–[G2]$_\mathrm{F}$–[G1]*(A)–Br (32): As described in GP IV, PPh$_3$ (0.56 g, 2.12 mmol) and CBr$_4$ (0.7 g, 2.12 mmol) were added to a solution of alcohol **31** (2.60 g, 1.41 mmol) in THF (15 mL). Workup as described in GP IV yielded a yellow oil (4.02 g). FC (CH$_2$Cl$_2$/hexane 8:1) yielded **32** (1.13 g, 42 %) as a colorless oil. R_f (CH$_2$Cl$_2$/hexane 8:1): 0.74; ^{1}H NMR (500 MHz): $\delta = 0.88$ (t, $J = 6.9$, 24 H, 8 CH$_3$(P)), 1.21 (d, $J = 6.3$, 3 H, CH$_3$-C(3)), 1.27 – 1.38 (m, 64 H, 32 CH$_2$(P)), 1.38 – 1.46 (m, 16 H, 8 CH_2CH$_2$CH$_2$O(P)), 1.71 – 1.77 (m, 16 H, 8 CH_2CH$_2$O(P)), 2.04 – 2.09 (m, 1 H, H-C(2)), 2.61 ("dd", *ABX*, $J = 13.6$, 8.7, 1 H, PhCH_2-C(2)), 2.77 ("dd", *ABX*, $J = 13.5$, 5.9, 1 H, PhCH_2-C(2)), 3.42 ("dd", *ABX*, $J = 9.4$, 4.0, 1 H, H-C(1)), 3.47 ("dd", *ABX*, $J = 9.4$, 5.0, 1 H, H-C(1)), 3.64 – 3.69 (m, 1 H, H-C(3)), 3.88 – 3.98 (m, 16 H, 8 CH$_2$CH_2O(P)), 4.30 – 4.51 (m, 6 H, 2 OCH_2Ph(G2) and CH$_2$Br), 4.90 (d, $J = 6.9$, 8 H, 4 OCH$_2$Ph(G3)), 6.37 – 6.39 (m, 4 H, 4 arom. H(G3)), 6.50 – 6.56 (m, 4 H, 4 arom. H(G2) and 8 arom. H(G3)), 6.58 (d, $J = 2.3$, 2 H, 2 arom. H(G2)), 7.07 (d, $J = 8.2$, 2 H, 2 arom. H(G1)), 7.24 (d, $J = 8.2$, 2 H, 2 arom. H(G1)); ^{13}C NMR (125 MHz): $\delta = 14.1$, 16.8, 22.7, 26.1, 29.3, 29.4, 31.8, 33.3, 33.7, 46.2, 68.1, 69.3, 70.1, 70.8, 73.0, 74.7, 100.8, 101.1, 105.7, 106.4, 106.5, 127.7, 129.0, 129.6, 135.2, 139.1, 140.6, 141.1, 141.5, 141.6, 160.0, 160.5; MALDI-TOF MS (HABA): *m*/*z*: 1846.8, 1927.9 ($[M+\mathrm{Na}]^+$), 2102.8; $C_{118}H_{181}O_{14}Br$ (1903.62): calcd C 74.45, H 9.58; found C 75.10, H 9.52.

(Octyl)$_4$–{[G0]}$_4$–[Phe-TADDOL] (33): *n*-Octyl bromide (1.45 g, 7.53 mmol) was added to a solution of TADDOL **2** (1.00 g, 1.88 mmol) in DMF (5 mL). To this solution was added previously dried, finely powdered K$_2$CO$_3$ (1.04 g, 7.53 mmol), and the resulting suspension was heated under reflux for 2 h. After cooling to RT, H$_2$O (30 mL) and CH$_2$Cl$_2$ (100 mL) were added, and the solids were filtered off and rinsed with CH$_2$Cl$_2$. The two layers of the filtrate were separated; the aqueous layer was extracted (2 × Et$_2$O). The combined organic layers were washed with H$_2$O. The combined organic layers were dried over MgSO$_4$ and the solvent was evaporated to yield a yellow oil (1.70 g). FC (acetone/hexane 1:19) yielded **33** (0.477 g, 26 %) as a clear viscous oil. R_f (acetone/hexane 1:2): 0.44; ^{1}H NMR (400 MHz): $\delta = 0.85 – 0.91$ (m, 12 H, 4 CH$_3$(P)), 1.06 (s, 6 H, (CH$_3$)$_2$-C(2)(c)), 1.22 – 1.51 (m, 40 H, 20 CH$_2$(P)), 1.71 – 1.83 (m, 8 H, 4 CH_2CH$_2$O(P)), 3.89 (t, $J = 6.6$, 4 H, 2 CH$_2$O(P)), 3.96 (t, $J = 6.6$, 4 H, 2 CH$_2$O(P)), 4.02 (s, 2 H, 2 OH), 4.47 (s, 2 H, 2 CH), 6.75 (d, $J = 9.0$, 4 H, 4 arom. H(c)), 6.84 (d, $J = 9.0$, 4 H, 4 arom. H(c)), 7.21 (d, $J = 9.0$, 4 H, 4 arom. H(c)), 7.41 (d, $J = 9.0$, 4 H, 4 arom. H(c)); ^{13}C NMR (125 MHz): $\delta = 14.1$, 22.6, 26.0, 26.1, 27.2, 29.2, 29.3, 29.4, 31.8, 67.9, 77.6, 81.1, 109.1, 113.0, 113.8, 128.8, 129.7, 134.8, 138.2, 158.2, 158.3; MS (FAB): *m*/*z*: 944 (0.7), 493 (13), 451 (9), 441 (8), 440 (36), 439 (100), 437 (17), 436 (13), 435 (36), 424 (15), 423 (47), 327 (13), 311 (10), 233 (33), 211 (16), 199 (19), 121 (77); $C_{63}H_{94}O_8$ (979.43): calcd C 77.26, H 9.67; found C 77.10, H 9.47.

(Octyl)$_8$–{[G1]$_\mathrm{F}$}$_4$–[Phe-TADDOL] (34): As described in GP II, a solution of **23** (1.61 g, 3.77 mmol) in acetone (5 mL) was added to a solution of TADDOL **2** (0.5 g, 0.94 mmol) in acetone (10 mL). To this solution was added K$_2$CO$_3$ (0.52 g, 3.77 mmol) and the reaction mixture was heated under reflux for 30 h. Workup as described in GP II yielded a yellow oil (2.6 g). FC (acetone/hexane 1:1) yielded **34** (1.73 g, 95 %) as a slightly yellow oil. R_f (acetone/hexane 1:2): 0.44; $[\alpha]_\mathrm{D}^\mathrm{RT} = -26.0$ ($c = 1.21$, CHCl$_3$); ^{1}H NMR (500 MHz): $\delta = 0.86 – 0.91$ (m, 24 H, 8 CH$_3$(P)), 1.05 (s, 6 H, (CH$_3$)$_2$-C(2)(c)), 1.23 – 1.40 (m, 128 H, 64 CH$_2$(P)), 1.40 – 1.48 (m, 16 H, 8 CH_2CH$_2$CH$_2$O(P)), 1.72 – 1.83 (m, 16 H, 8 CH_2CH$_2$O(P)), 3.88 – 3.96 (m, 16 H, 8 CH$_2$O(P)), 4.49 (s, 2 H, 2 CH(c)), 4.93 (s, 4 H, 2 PhCH_2O(G1)), 4.99 (s, 4 H, 2 PhCH_2O(G1)), 6.38 (t, $J = 2.2$, 2 H, 2 arom. H(G1)), 6.41 (t, $J = 2.2$, 2 H, 2 arom. H(G1)), 6.52 (s, 4 H, 4 arom. H(G1)), 6.58 (s, 2 H, 2 arom. H(G1)), 6.84 (d, $J = 9.1$, 4 H, 4 arom. H(c)), 6.92 (d, $J = 9.1$, 4 H, 4 arom. H(c)), 7.24 (d, $J = 9.0$, 4 H, 4 arom. H(c)), 7.43 (d, $J = 9.0$, 4 H, 4 arom. H(c)); ^{13}C NMR (125 MHz): $\delta = 14.1$, 22.7, 26.1, 27.2, 29.2, 29.3, 29.4, 31.8, 68.1, 70.0, 77.6, 81.1, 100.8, 100.9, 105.7, 105.8, 109.2, 113.5, 114.3, 128.9, 129.7, 135.3, 138.7, 139.2, 157.9, 158.0, 160.5; IR (CHCl$_3$): $\tilde{\nu} = 3364$ w, 2933 s, 2872 s, 1718 w, 1600 s, 1508 m, 1456 s, 1380 m, 1297 m, 1169 s, 1107 s, 1062 s, 907 m, 836 m cm^{-1}; MALDI-TOF MS (CCA): *m*/*z*: 1940.2 ($[M+\mathrm{Na}]^+$); $C_{123}H_{182}O_{16}$ (1916.78): calcd C 77.07, H 9.57; found C 77.11, H 9.40.

(Octyl)$_{16}$–{[G2]$_\mathrm{F}$}$_4$–[Phe-TADDOL] (35): As described in GP II, a solution of **26** (2.95 g, 3.3 mmol) in acetone (20 mL) was added to a solution of TADDOL **2** (0.4 g, 0.75 mmol) in acetone (20 mL). To this solution was added K$_2$CO$_3$ (0.42 g, 3 mmol) and the reaction mixture was heated under reflux for 30 h. Workup as described in GP II yielded a yellow oil (2.46 g). FC (acetone/hexane 1:19) yielded **35** (0.80 g, 28 %) as a colorless oil. R_f (acetone/hexane 1:2): 0.61; $[\alpha]_\mathrm{D}^\mathrm{RT} = -16.4$ ($c = 1.21$, CHCl$_3$); ^{1}H NMR (400 MHz): $\delta = 0.66 – 0.82$ (m, 48 H, 16 CH$_3$(P)), 1.06 (s, 6 H, (CH$_3$)$_2$-C(2)(c)), 1.24 – 1.48 (m, 320 H, 160 CH$_2$(P)), 1.40 – 1.65 (m, 32 H, 16 CH_2CH$_2$O(P)), 3.77 – 3.96 (m, 32 H, 16 CH_2O(P)), 4.46 (s, 2 H, 2 CH(c)), 4.80 – 4.96 (m, 8 H, 4 PhCH_2O(G1)), 6.35 – 6.41 (m, 12 H, 4 arom. H(G1) and 8 arom. H(G2)), 6.55 – 6.59 (m, 20 H, 4 arom. H(G1) and 16 arom. H(G2)), 6.81 (d, $J = 8.2$, 4 H, 4 arom. H(c)), 6.93 (d, $J = 8.2$, 4 H, 4 arom. H(c)), 7.23 (d, $J = 9.0$, 4 H, 4 arom. H(c)), 7.46 (d, $J = 9.0$, 4 H, 4 arom. H(c)); ^{13}C NMR (125 MHz): $\delta = 14.1$, 22.7, 26.1, 27.2, 29.2, 29.4, 30.9, 31.8, 68.1, 70.2, 100.9, 105.7, 105.8, 128.9, 129.8, 138.9, 160.1, 160.2, 160.5; IR (CHCl$_3$): $\tilde{\nu} = 2928$ s, 2857 m, 1596 s, 1508 w, 1456 m, 1372 m, 1296 m, 1167 s, 1057 m, 836 w cm^{-1}; MALDI-TOF MS (HABA): *m*/*z*: 3346.8, 3580.3, 3814.9 ($[M+\mathrm{Na}]^+$); $C_{243}H_{358}O_{32}$ (3791.48): calcd C 76.98, H 9.52; found C 76.96, H 9.37.

(Octyl)$_{32}$–{[G2]$_\mathrm{F}$–[G1]*(A)}$_4$–[Phe-TADDOL] (36): As described in GP II, a solution of **32** (1.21 g, 0.636 mmol) in acetone (10 mL) was added to a solution of TADDOL **2** (76.6 mg, 0.145 mmol) in acetone (30 mL). To this solution was added K$_2$CO$_3$ (0.1 g, 0.722 mmol), and the reaction mixture was heated under reflux for 110 h. Workup as described in GP II yielded a brownish oil (0.70 g) as crude product. Three FC runs (acetone/hexane 1:4, acetone/hexane 1:99, hexane) yielded **36** (54 mg, 5 %) as a colorless oil (the difficulty in identification of the product led to a big loss of product after the first column chromatographies). R_f (acetone/hexane 1:3): 0.75; ^{1}H NMR (500 MHz): $\delta = 0.85 – 0.88$ (m, 96 H, 32 CH$_3$(P)), 1.07 (s, 6 H, (CH$_3$)$_2$-C(2)(c)), 1.20 – 1.38 (m, 259 H, 128 CH$_2$(P) and CH$_3$-C(3)), 1.38 – 1.46 (m, 64 H, 32 CH_2CH$_2$CH$_2$O(P)), 1.70 – 1.75 (m, 64 H, 32 CH_2CH$_2$O(P)), 2.06 – 2.13 (m, 1 H, H-C(2)), 2.62 – 2.67 (m, 1 H, PhCH_2-C(2)), 2.76 – 2.83 (m, 1 H, PhCH_2-C(2)), 3.42 – 3.46 (m, 1 H, H-C(1)), 3.46 – 3.53 (m, 1 H, H-C(1)), 3.67 – 3.72 (m, 1 H, H-C(3)), 3.87 – 3.91 (m, 64 H, 32 CH$_2$CH_2O(P)), 4.30 – 4.53 (m, 24 H, 8 OCH$_2$Ph(G2) and 4 OCH$_2$Ph(G1)), 4.87 – 5.00 (m, 32 H, 16 OCH$_2$Ph(G3)), 6.36 – 6.38 (m, 16 arom. H(G3)), 6.49 – 6.56 (m, 48 H, 16 arom. H(G2) and 32 arom. H(G3)), 6.58 – 6.59 (m, 8 H, 8 arom. H(G2)), 6.83 (d, $J = 8.7$, 4 H, 4 arom. H(c)), 6.92 (d, $J = 9.0$, 4 H, 4 arom. H(c)), 7.13 – 7.18 (m, 8 H, 8 arom. H(G1)), 7.22 – 7.28

(m, 8H, 8 arom. H(G1)), 7.31–7.46 (2*d*, $J = 8.7$, 8H, 8 arom. H(c)); ^{13}C NMR (125 MHz): $\delta = 14.1$, 16.9, 19.0, 22.7, 26.1, 29.2, 29.3, 29.4, 31.8, 68.1, 69.3, 69.9, 70.1, 70.8, 73.0, 74.8, 100.8, 101.1, 105.7, 106.3, 106.4, 127.7, 128.9, 129.4, 129.7, 134.8, 135.2, 139.1, 141.1, 141.6, 160.0, 160.5.

The general procedure for carrying out TADDOL-catalyzed Et_2Zn additions to PhCHO has been previously published.[13]

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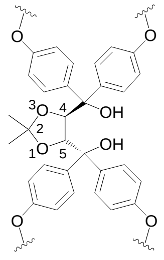
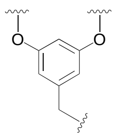
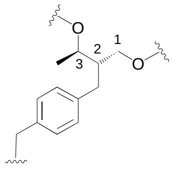


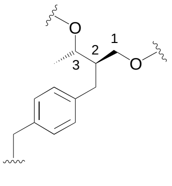
[Phe-TADDOL]



[G1]$_F$



[G1]*(A)



[G1]*(B)

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