Synthesis and Properties of Monodisperse Chiral Dendrimers (up to Fourth Generation) with Doubly Branched Building Blocks[1]): An Intriguing Solvent Effect

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'Fully chiral' dendrimers, containing a stereogenic center at each and every branching point, have been prepared using a chiral core triol with aromatic elongating units (*cf.* **27**) and chiral branch diols (*cf.* **8**, **12**, and **24**) as building blocks. The biggest dendrimer prepared is of the 4th generation (**33**: 46 building blocks, 93 stereogenic centers, 10^{28} possible stereoisomers), and has been obtained by a convergent growth approach in 32 steps starting from the biopolymer poly[(*R*)-3-hydroxybutanoic acid] (P(3-HB)). All compounds were shown to be monodisperse by MALDI-TOF mass spectrometry. Spin-lattice relaxation-time (T_1) measurements and size-exclusion chromatography show typical features of structurally related achiral dendrimers. The influence of the chiral building blocks on the shape of the whole dendrimer has been investigated by chiroptical measurements: the specific rotation can be considered as average of all chiroptical properties of its constituent chiral units, independent of the solvent, the concentration, and the temperature. On the other hand, regularity in the circular dichroism (CD) spectra is completely lost with variation of the solvent (*cf. Fig. 13*).

1. Introduction. – Chirality, a characteristic property of biological systems, plays an important role in several highly selective recognition processes and reactions [3][4]. Furthermore, in a biomacromolecule the 'chirality' of the monomer is often 'amplified', and a chiral superstructure, *e.g.*, a helix is formed [5]. Similar observations have been made with synthetic polymers [6–8] or lipid aggregates [9–11].

Because of their well-defined molecular weight and structure, one can expect that chiral dendrimers[3]) could be useful as model compounds for studying how 'chirality is expressed' in a macromolecular system. It can be anticipated that introducing chiral branching units into the dendrimer should result in a non-symmetrical, non-spherical overall shape and should provide chiral cavities. These structures might also be useful for asymmetric catalysis, chiral recognition, and resolution processes.

In our preceding paper on 'fully chiral' dendrimers with triple branching units, we reported on a diastereoselective effect in the reactions used for coupling dendrons with cores [14]. All chiral building blocks, *e.g.*, core triol **2** [15–17] and branch triol **3** [1][14][18], were prepared from the dioxanone **1** [19][20], which is easily accessible from the biopolymer P(3-HB)[4]) by aldol addition and reduction.

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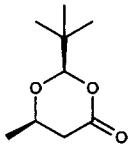
[1]) Partially published in preliminary communications [1][2].

[2]) Part of the Dissertation (No. 12001) of *P.M.*, ETH-Zürich, 1996. Present address: Department of Chemistry, University of California Berkeley, Berkeley, CA 94720-1460, USA.

[3]) For reviews, see [12][13].

[4]) Poly[(*R*)-3-hydroxybutanoic acid]; for review articles, see [21][22].



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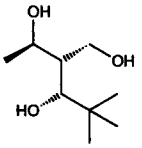

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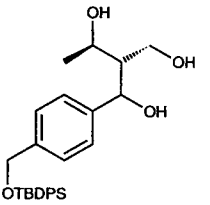

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However, higher than 2nd-generation dendrimers of this type could not be prepared. This limitation led to the present work on chiral dendrimers with analogous double branching units. Here, we describe the convergent synthesis of 'fully chiral' higher-generation branches (up to 5th) and dendrimers (up to 4th generation) containing up to 93 stereogenic centers, and we report an intriguing solvent effect of their chiroptical properties.

2. Synthesis of the Chiral Building Blocks. – For the convergent [23] construction of the branches, diols **8** and **12** were prepared with an additional benzylic OH group, protected with a MOM[5]) or a TBDPS[6]) group, respectively. As outlined in *Scheme 1*, the Li-enolate of the dioxanone **1** was allowed to react with benzyl-bromide derivatives **4** or **5**, furnishing adducts **6** or **7**, respectively, in 65–90% yield[7]) (10–20-g scale) with a diastereoselectivity greater than 99:1.

Configurational assignment has been confirmed by an X-ray crystal-structure analysis of **7** (*Fig. 1*) and by comparative NMR analysis of the MOM-protected compound **6**.

Reduction of **6** was easily accomplished with $LiAlH_4$ and furnished the MOM-protected diol **8**. Etherification with MeI (→ **9**), removal of the MOM protecting group with $LiBF_4$ in $MeCN/H_2O$ 25:1 [24] (→ **10**), and treatment with Ph_3P/Br_4C gave the 1st-generation benzyl bromide **11**. Additionally, a TBDPS-protected diol **12** was prepared, which was obtained by $NaBH_4$ reduction of **7** in THF/MeOH 20:1 [25] (see *Scheme 1*).

To start the growth steps for the dendritic branches, the benzylic bromide **11** was used for the etherification of the OH groups of the corresponding diol **8** (→ **14**) (*Scheme 2*). However, the MOM group could only be removed in the presence of a large excess of $LiBF_4$, and with extensive reaction times. Therefore, only the TBDPS-protected diol **12** was used for further elaborations of the branches.

Reaction of the diol **12** with bromide **11** was carried out under *Williamson* etherification conditions (NaH, THF, reflux; → **13**). Quantitative cleavage of the TBDPS protective group with $Bu_4NF \cdot 3\,H_2O$ (→ **15**) and OH/Br substitution provided 2nd-generation benzyl bromide **16**. Repetition of this reaction cycle, including coupling of diol **12** with **16** (→ **17**), deprotection (→ **18**), and OH/Br exchange, gave 3rd-generation branched benzyl bromide **19**. Unfortunately, a further reaction of **19** with **12** under a variety of

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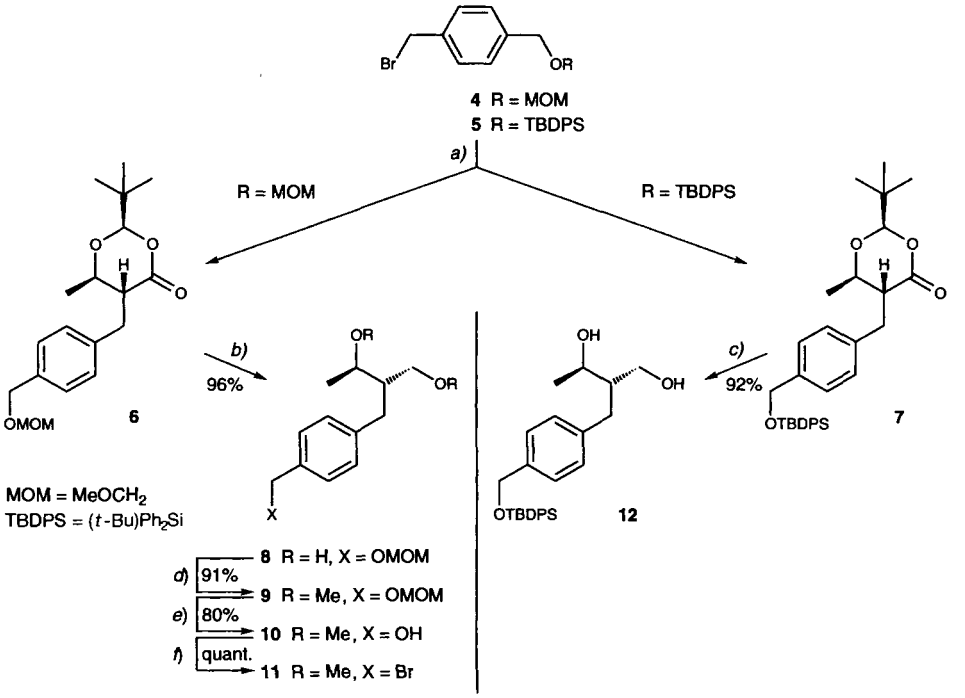
[5]) MOM = Methoxymethyl.

[6]) TBDPS = (*tert*-butyl)diphenylsilyl; the trimethylsilyl (TMS) and the (*tert*-butyl)dimethylsilyl (TBDMS) groups were not stable enough under the reaction conditions described later for the assembly of branches.

[7]) The excess bromide used in these reactions could be recovered quantitatively in the course of flash-chromatographic isolation and purification of the products.

Scheme 1. *Syntheses of the 1st-Generation Benzyl Bromide* **11** *and of Diol* **12**



a) LDA, **1**, THF, −78°, 20–30 h. *b*) $LiAlH_4$, Et_2O, reflux, *c*) $NaBH_4$, THF/MeOH 20:1, 0° → r.t., 15 h. *d*) NaH, MeI, THF, r.t., 19 h. *e*) $LiBF_4$, MeCN/H_2O 25:1, 72°, *f*) Ph_3P, Br_4C, THF, r.t., 28 h.

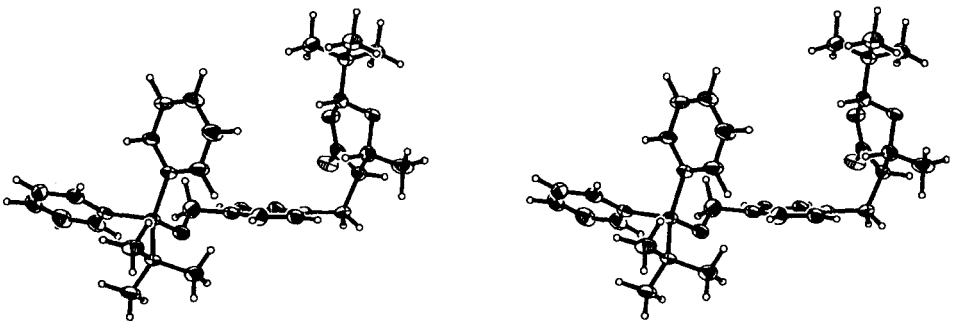
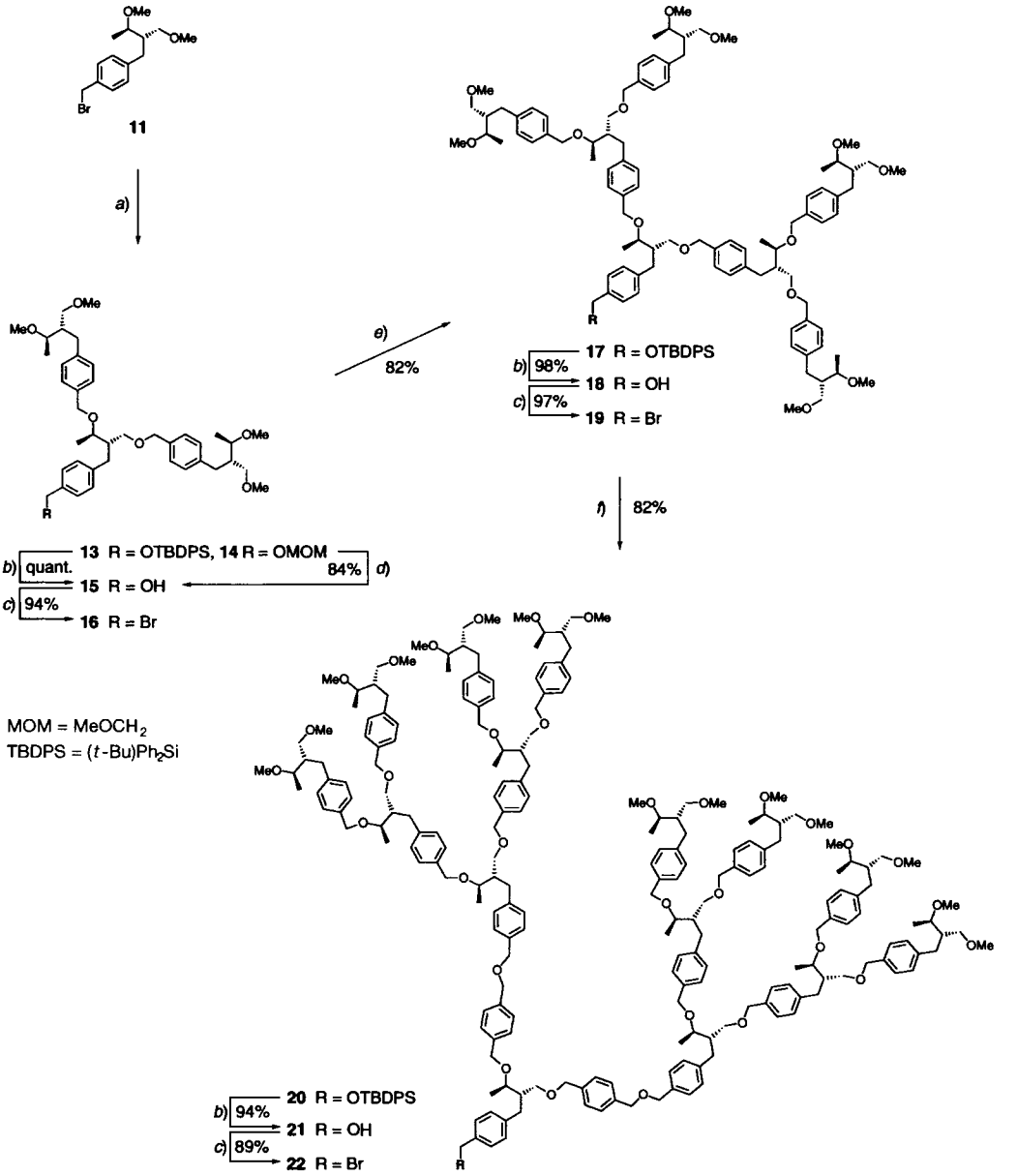


Fig. 1. *ORTEP Stereo representation of the crystal structure of dioxanone* 7. The thermal ellipsoids are drawn to the 30% probability level.

conditions furnished a mixture of mono and doubly etherified products, from which the fully coupled 4th-generation branch could be isolated in only moderate yield.

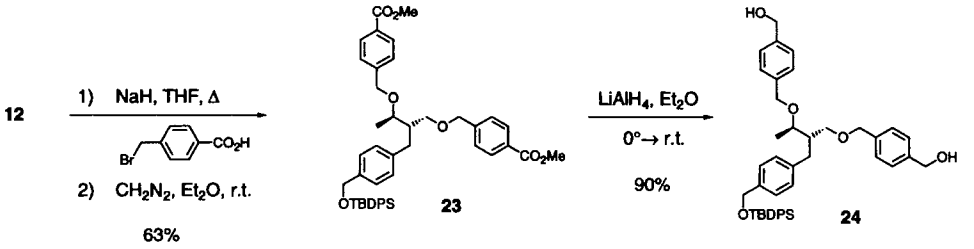
Thus, for the successful synthesis of higher-generation branches, we prepared the silyloxy diol **24** with elongating aromatic units, which was obtained by etherification of diol **12** with 4-(bromomethyl)benzoic acid, esterification with CH_2N_2 (→ **23**), and $LiAlH_4$ reduction (*Scheme 3*).

Scheme 2. *Preparation of the 2nd-, 3rd-, and 4th-Generation Benzyl-Bromide Branches* **16**, **19**, *and* **22**



a) NaH, THF, reflux; with **12** (see *Scheme 1*): 88% yield; with **8** (see *Scheme 1*): 75% yield. *b*) $Bu_4NF \cdot 3\,H_2O$, THF, r.t. *c*) Ph_3P, Br_4C, THF, r.t. *d*) $LiBF_4$, $MeCN/H_2O$ 25:1, 72°, 2.5 d. *e*) NaH, **12**, THF, reflux. *f*) NaH, **24** (see *Scheme 3*), THF, reflux.

Scheme 3. *Synthesis of the Aromatically Elongated Diol* **24**



With diol **24** at our disposal, we succeeded in repeating the previously described three-step reaction cycle (etherification of diol[8]) (→ **20**, **25**), deprotection[9]) (→ **21**), OH/Br substitution[9])) twice, which provided the 4th-generation benzyl bromide **22** (see *Scheme 2*) and even the 5th-generation benzyl alcohol **26**, in high yields (*Scheme 4*).

Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrometry [26][27] not only confirmed the expected molecular weights but also revealed the high purity of the samples obtained through the efficient reaction cycle discussed before, even on scales up to 20 g[10])[11]). *Fig. 2* shows the quality of the spectra of 3rd- to 5th-generation branched alcohols achieved with excellent signal-to-noise ratios[12]).

However, for the biggest branched compound, the 5th-generation benzyl alcohol **26** we observed a 'ghost' signal of a $[M+59]^+$ ion, the origin of which could not be determined (calculated mass of the weighted average M^+ ion is 7148 Da; see *Fig. 2, c*). Moreover, a small peak at m/z 6957 appeared in the same spectrum, corresponding to a sodium-ion adduct of a defect structure ($C_{438}H_{590}O_{67}$, MW 6927 Da) with one missing peripheral building block[13]).

3. Preparation of the Chiral Dendrimers with Elongated Center Piece. – After very pure branches had been obtained, coupling with the aromatically elongated triol **27** was carried out under *Williamson* etherification conditions[14]) to give the 1st- to 4th-genera-

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[8]) Best results were obtained by using 6 equiv. of NaH and 2.5 equiv. of branched bromides for the synthesis of **20** and **25**.

[9]) These two steps proceeded only in yields of > 90% when the concentration of branches was chosen as follows: 0.01M–0.1M in the case of the deprotection step, and > 0.02M for reactions with Ph_3P/Br_4C.

[10]) For the construction of dendritic compounds, 20 g of 2nd-generation compound **13**, 14 g of 3rd-generation **17**, 6.5 g of 4th-generation **20** and 0.8 g of 5th-generation **25** were prepared.

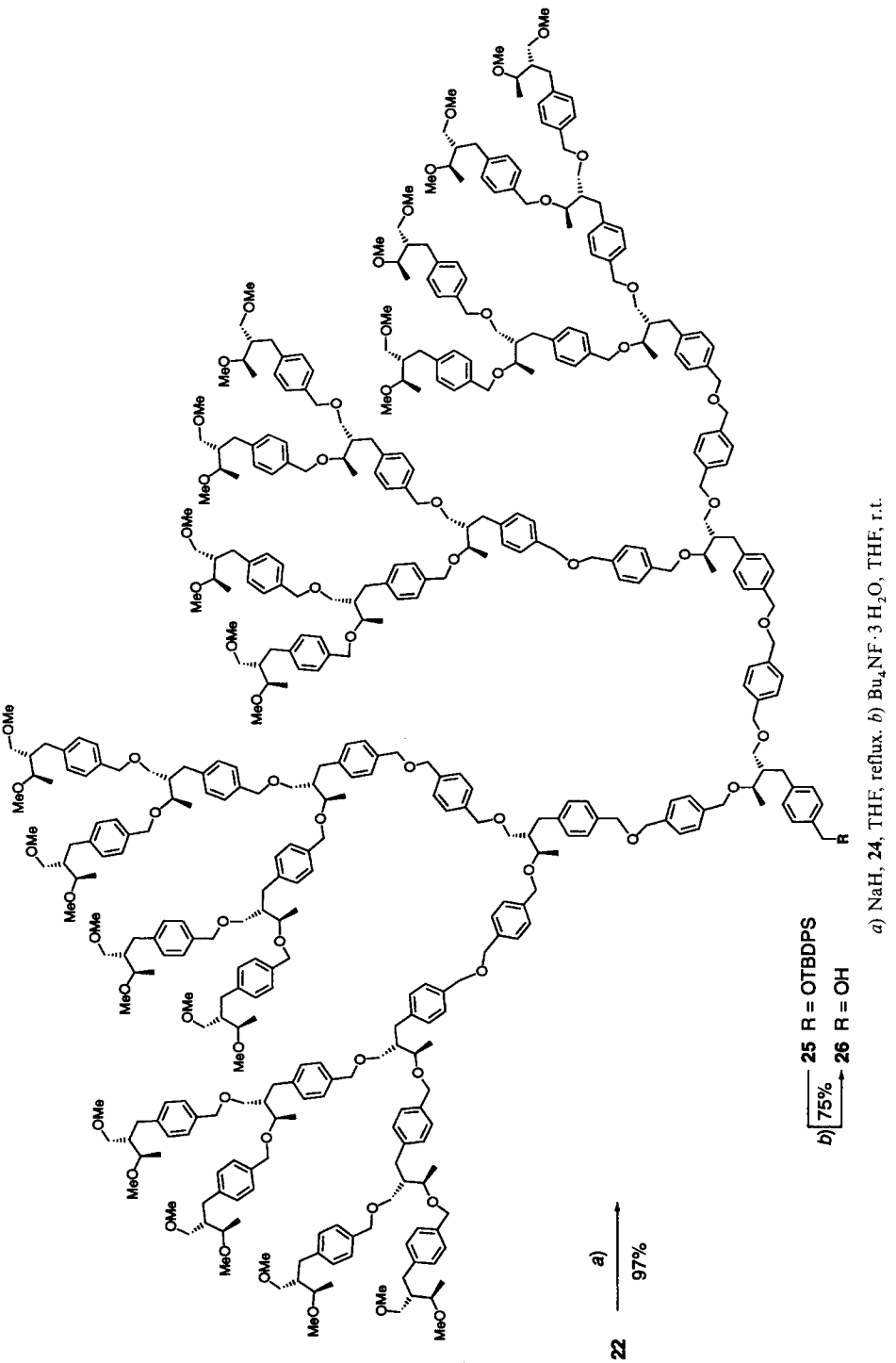
[11]) Purification was performed by standard flash chromatography in the case of benzyl alcohols and bromides, by medium-pressure liquid chromatography (MPLC) after coupling steps.

[12]) MALDI-TOF-MS was performed on samples obtained after one chromatographic separation step. The use of the α-cyano-4-hydroxycinnamic acid (CCA) matrix afforded the $[M + Na]^+$ or $[M + K]^+$ ion, or both, with mass accuracies of 0.05% and a resolving power ($m/\Delta m$) of 700.

[13]) This can be assigned to imperfect synthesis.

[14]) In a typical coupling reaction, triol **27** was deprotonated with 9 equiv. of NaH in THF and heated at reflux with 3.5 equiv. bromide to obtain the 1st- as well as 2nd-generation dendrimers **30** and **31**, respectively. A larger excess (4.5–5 equiv.) of bromide was used for the synthesis of the 3rd- and 4th-generation dendrimers **32** and **33**. The excess bromide could be recovered almost quantitatively by flash chromatography.

Scheme 4. *Preparation of the 5th-Generation Benzyl-Alcohol Branch* **26**



a) NaH, **24**, THF, reflux. *b*) $Bu_4NF \cdot 3\,H_2O$, THF, r.t.

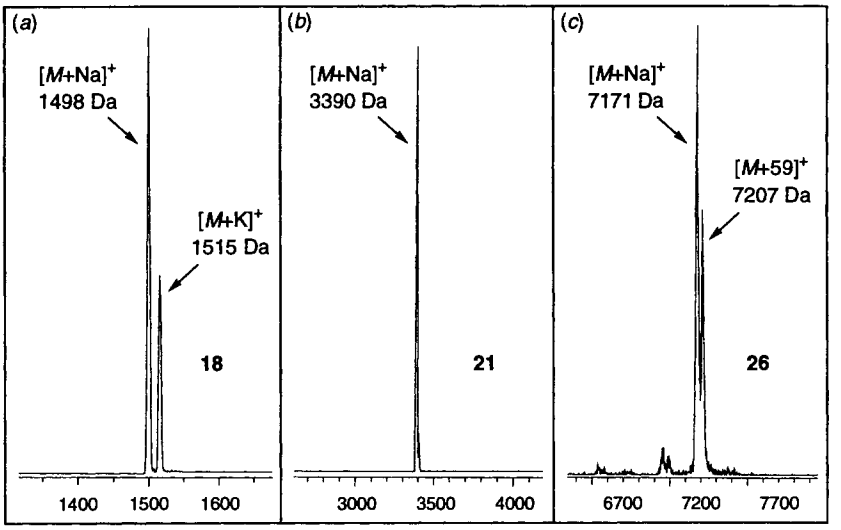


Fig. 2. *Part of the MALDI-TOF-mass spectra of the benzyl-alcohol branches*: a) **18** *(3rd generation)*, b) **21** *(4th generation)*, *and* c) **26** *(5th generation)*

tion dendrimers **30**–**33**[15]). The coupling yields ranged from 90% to quantitative for the 1st- to 3rd-generation dendrimers **30**–**32**, and decreased to 67% for the 4th-generation dendrimer **33** as purification became more difficult[16]). The molecular weights of these products range from 1198 ($C_{75}H_{104}O_{12}$) to 10582 ($C_{669}H_{908}O_{102}$), and the largest one, the 4th-generation dendrimer **33**, is constructed from 24 peripheral, 21 interior, and one central unit, containing 93 stereocenters (10^{28} possible stereoisomers!).

Most of the new materials are very viscous oils (> 2nd-generation) and dissolve readily in common organic solvents. They were fully characterized by a combination of ^{1}H- and ^{13}C-NMR, IR[17]), UV, CD spectroscopy, specific rotation, mass spectrometry (FAB, MALDI-TOF), size exclusion chromatography (SEC), and elemental analysis[18]). These measurements allowed us to unambiguously assign the structures to the new chiral dendrimers as having no major defects[19]).

Among these techniques, MALDI-TOF-MS was the only method to find evidence of minor impurities such as molecules with one or two missing peripheral building

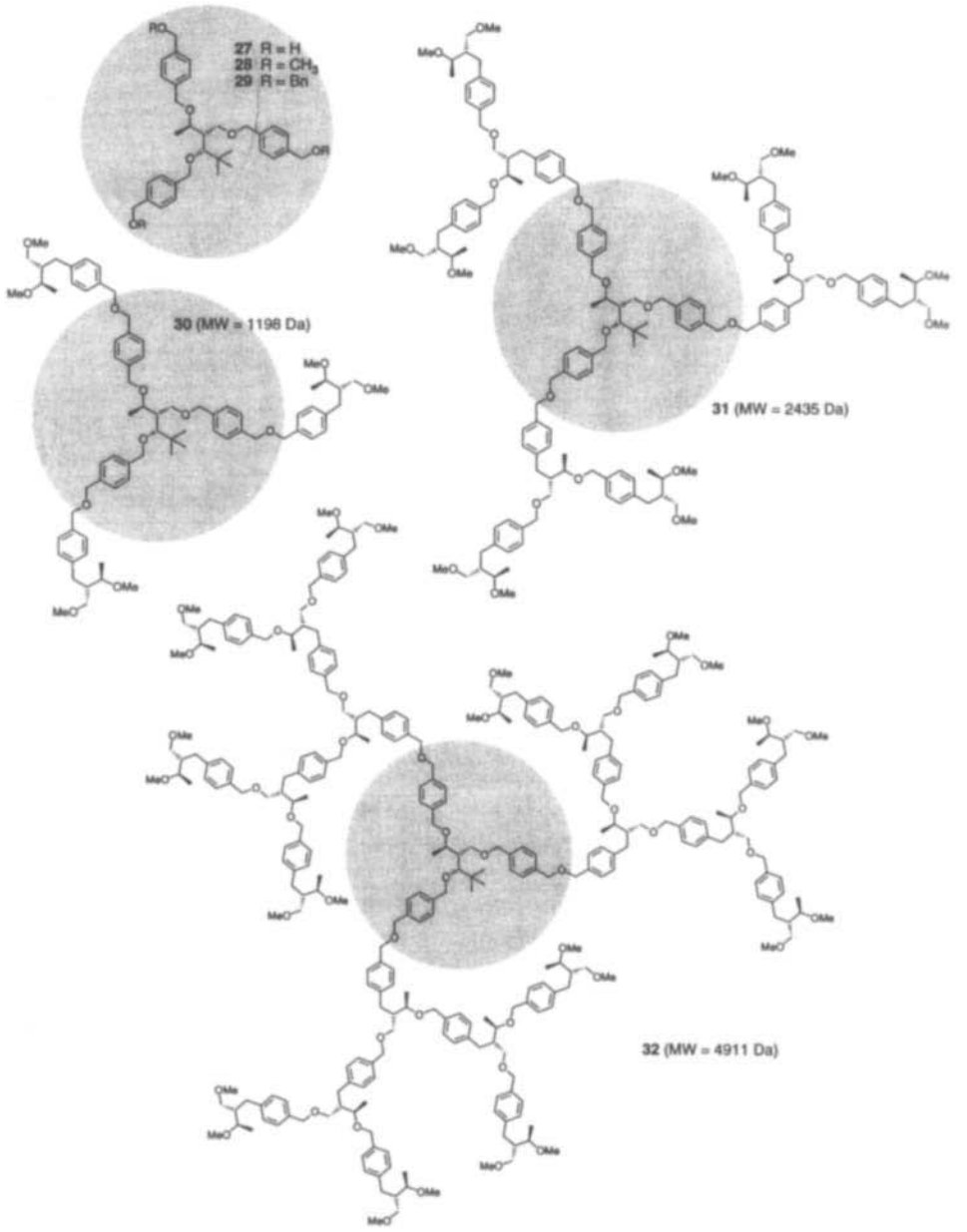
[15]) Since the solubilities of all dendritic compounds discussed here in solvents such as toluene, Et_2O, or CH_2Cl_2 were quite high, chromatographic purification was straightforward, although band broadening and tailing became more severe as the molecular weight increased. Attempts to decrease band broadening by using a more polar solvent composition gave rapid elution with no separation.

[16]) All these yields refer to chromatographed, analytically pure materials.

[17]) The IR spectra of the dendritic compounds are almost identical with increasing generation number, differing only in the relative intensities of selected absorption bands (mainly aromatic and ether groups).

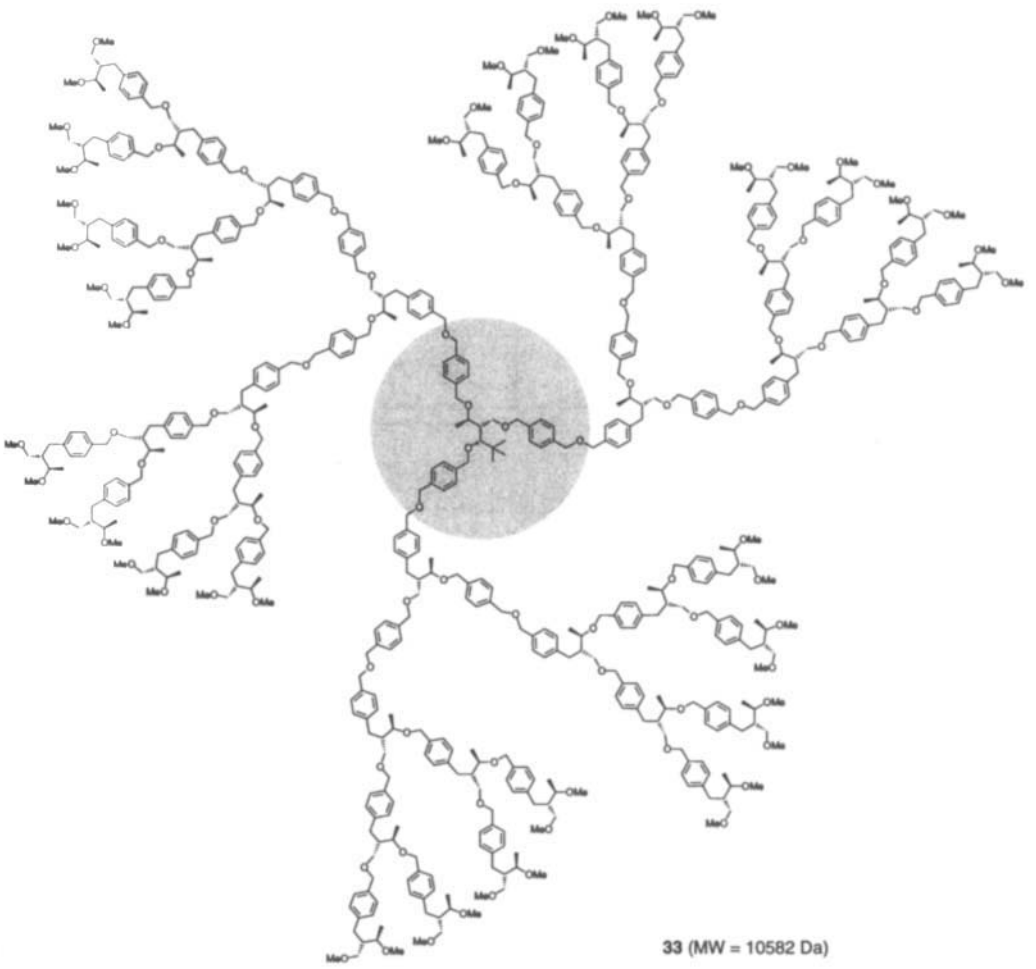
[18]) Elemental analyses gave the correct C and H composition within $\pm$ 0.3%. However, the accuracy of this method is not high enough to reliably detect subtle changes in the molecular structure of these dendritic macromolecules (see comment in [14]).

[19]) Major defects result, for example, from incomplete coupling. Under non-optimized coupling conditions, we also found peaks at higher masses than that of the molecular ion (MALDI-TOF-MS).



blocks[20]). The matrix system of α-cyano-4-hydroxycinnamic acid (CCA) in MeCN/EtOH/H_2O 50:45:5 was found to be most generally applicable for a variety of our

[20]) MALDI-TOF-MS is known to produce little ion fragmentation in the linear TOF mode [28]. In our experience, working with careful sample preparation and at the lowest possible laser fluence, *prompt* fragmentation can be avoided for most classes of dendritic macro-ions.



poly(benzyl ether) dendrimers and molecular weights of up to 10 kDa. Mass accuracies were typically of 0.05%. As shown in *Fig. 3*, the 1st- to 4th-generation dendrimers **30**–**33** exhibit excellent MALDI-TOF mass spectra which contain peaks for both $[M + Na]^+$ and $[M + K]^+$ ions. Furthermore, in the spectra of the 2nd- to 4th-generation dendrimers **31**–**33** minor peaks were detected at *m/z* 2237, 4716, and 10381, respectively, in all of these cases corresponding to the sodium-ion adduct of defect structures (see *Fig. 3, b*: $C_{139}H_{192}O_{22}$, MW 2215 Da; *Fig. 3, c*: $C_{295}H_{408}O_{46}$, MW 4690 Da; *Fig. 3, d*: $C_{655}H_{888}O_{100}$, MW 10362 Da) with one lost peripheral building block.

Additionally, in the spectra of the 4th-generation dendrimer **33** another small peak at *m/z* 9971 appeared which corresponds to the sodium-ion adduct of a defect structure ($C_{629}H_{852}O_{96}$, MW 9950 Da) with three missing peripheral building blocks. According to these measurements, reasonably monodisperse samples of fully chiral dendrimers

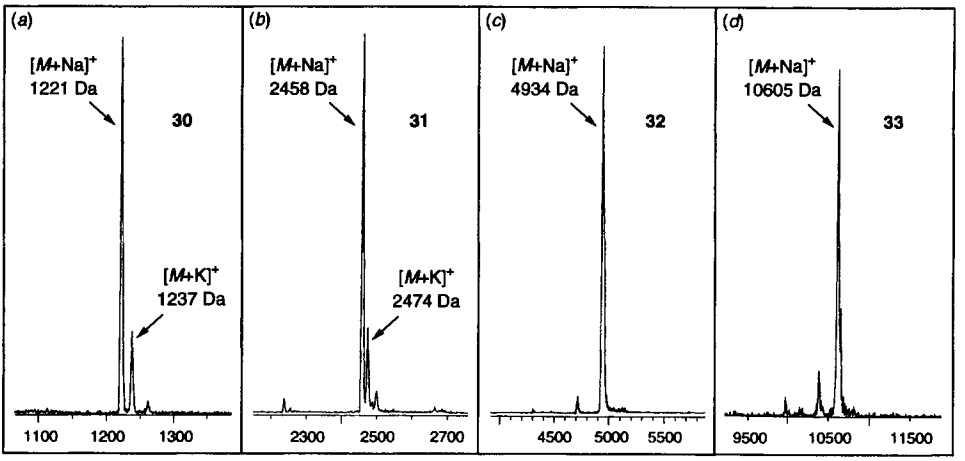


Fig. 3. *Part of the MALDI-TOF mass spectra of the dendrimers*: a) **30** *(1st generation)*, b) **31** *(2nd generation)*, c) **32** *(3rd generation), and* d) **33** *(4th generation)*

up to generation four were at our disposal for a more thorough study of the properties[21]).

4. NMR Characterization: Spin-Lattice Relaxation Time (T_1) Measurements. – 500-MHz ^{1}H-NMR analysis (in $CDCl_3$) was found to be very useful for the characterization of dendritic compounds. Surprisingly, compared to the size of the molecules, no line broadening of the spectral lines is observed with increasing number of generation[22]). Obvious features of these spectra are a single, sharp *t*-Bu resonance of the core (0.94 ppm) for dendrimers and of the (*t*-Bu)Ph_2Si group (1.1 ppm) for branches[23]). Other resonances from analogous protons of the peripheral, interior, and central units are well-separated and shifted towards lower field as we go from outside to inside. This is well-documented by the 500-MHz ^{1}H-NMR spectrum of the 4th-generation dendrimer **33** in *Fig. 4*. The 24 peripheral, the 21 interior, and the single central Me groups (depicted as squares) give rise to distinct sets of signals between 1.1 and 1.3 ppm; the downfield shift observed when going from outside to inside along the three layers is even more pronounced in the case of the central C*H* protons of the peripheral, the interior, and the core units (1.9–2.4 ppm, depicted as circles).

The chemical shifts of the signals of comparable ^{1}H nuclei are not affected by the dendrimer's generation number which is in contrast to our observation made on dendrimers with triply branched units and a non-elongated core unit [14].

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[21]) At least 0.9-g amounts were prepared of each generation.

[22]) The reason for this is found in the substantial conformational freedom in these doubly branched dendrimers.

[23]) Moreover, there are unique resonances of the PhCH_2OH protons at 4.6–4.7 ppm after removal of the (*t*-Bu)Ph_2Si group, and the PhCH_2Br protons at 4.5 ppm. The integral ratios of all these focal groups to peripheral and interior functional groups is a useful tool to track the growth of the dendritic series. The observed ratios are in good agreement with the expected values.

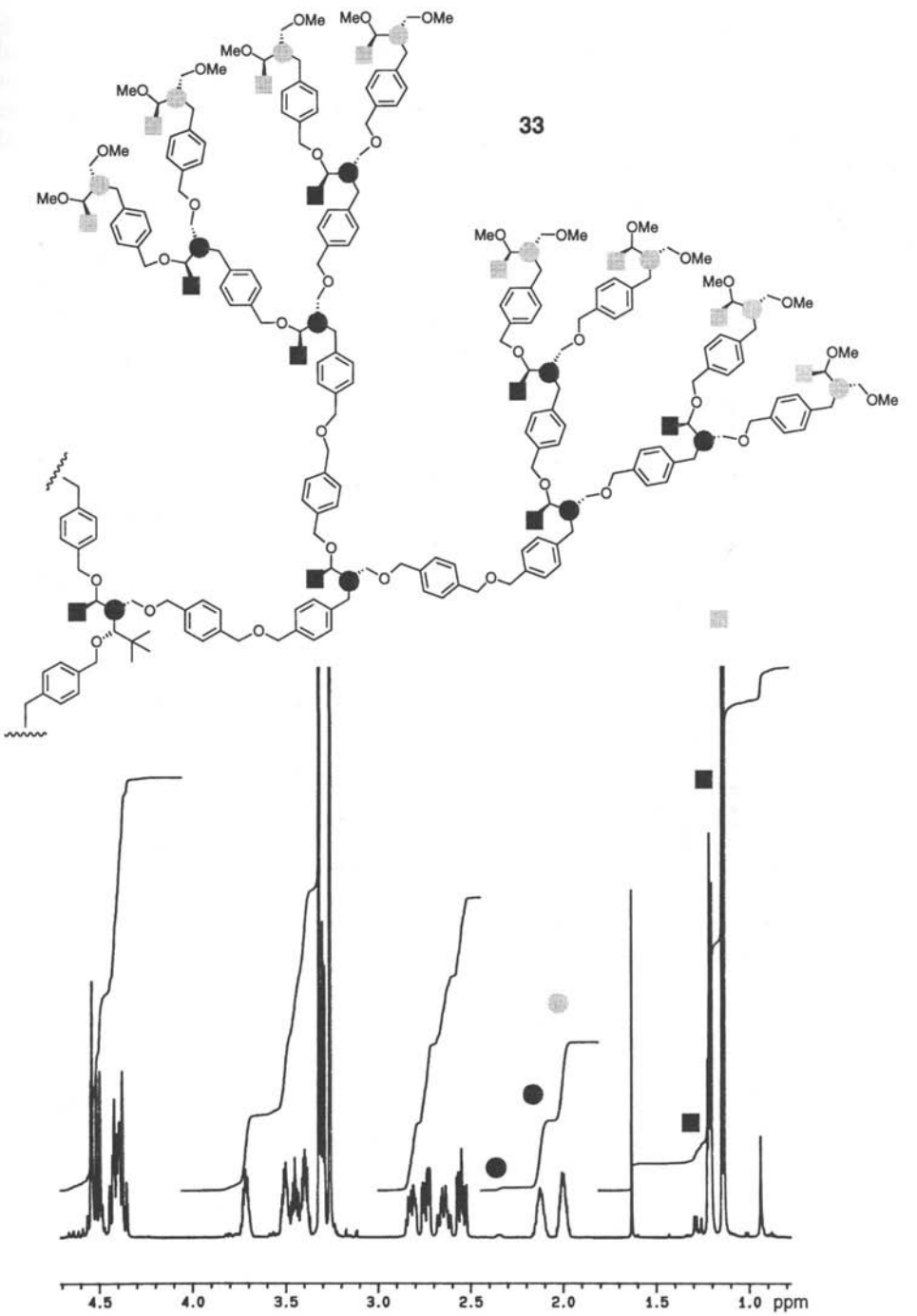

Fig. 4. *Part of the 500-MHz ^{1}H-NMR spectrum of the 4th-generation dendrimer* **33** *measured in $CDCl_3$.* The labelling of signals or groups of signals refers to the sets of Me groups (depicted as rectangles) and of CH groups (depicted as circles) in the corresponding formula.

Similar features were observed in the 125-MHz ^{13}C-NMR spectra, where the resonances are again well-resolved for analogous C-atoms of the peripheral, interior, and central units, as depicted in *Fig. 5* for the 4th-generation dendrimer **33**[24]). Even at this high generation number the signals of the core unit are still clearly separated from the baseline (see, *e.g.*, small signals from the Me and CH group of the core unit depicted as a square and a circle, resp., in *Figs. 4* and *5*).

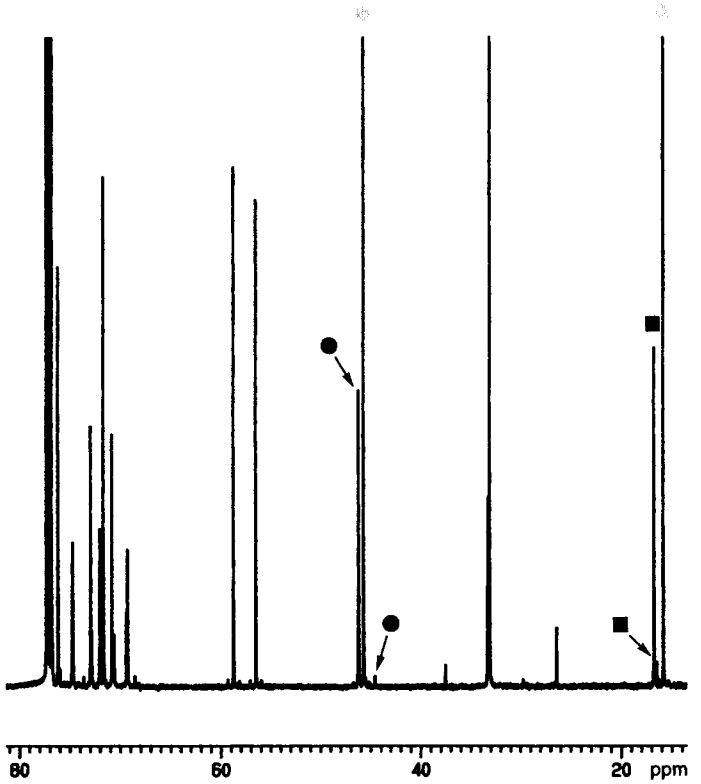

Fig. 5. *Part of the 125-MHz ^{13}C-NMR spectrum of the 4th-generation dendrimer* **33** *measured in $CDCl_3$*. The labelling of signals or groups of signals refers to the sets of Me groups (depicted as rectangles) and of CH groups (depicted as circles) in the formula shown in *Fig. 6*.

Since no overlapping was evident for the signals of, *e.g.*, the three types of central *C*H C-atoms (depicted as circles in *Figs. 5* and *6*), we were able to apply ^{13}C-NMR relaxation measurements on 1st- to 4th-generation dendrimers **30**–**33** to study the segmental mobility of these groups. All of the spin-lattice relaxation-time (T_1) measurements were performed using the standard inversion-recovery method [29][30] with a pulse sequence (180°, variable delay τ, 90°, fixed delay) at eleven different delays τ between 62.5 ms and 64 s. A typical inversion-recovery experiment from which T_1 values were calculated is

[24]) Moreover, the *t*-Bu group provides unique resonances at 26.4–26.7 ppm and at 37.4–37.5 ppm.

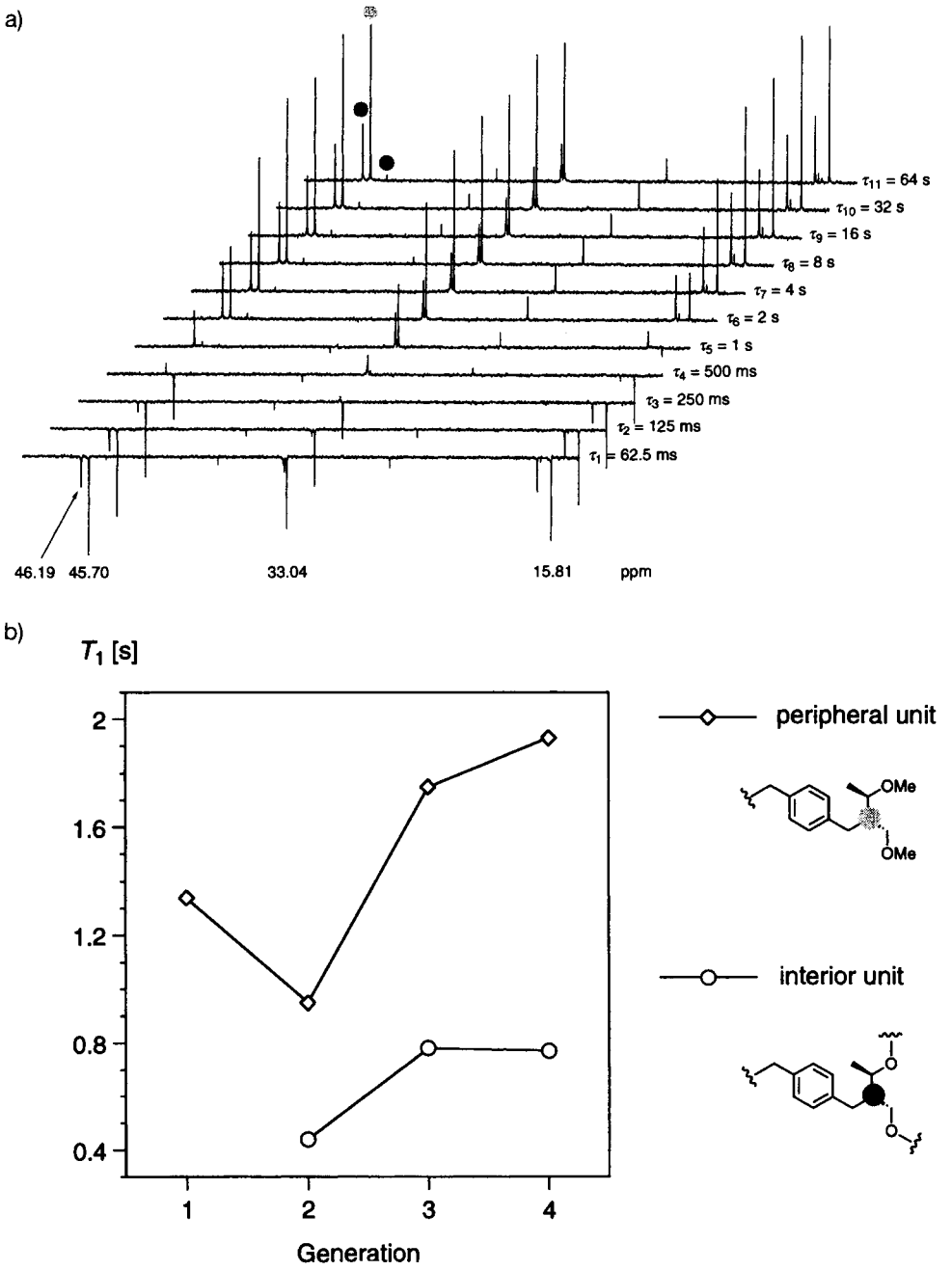

Fig. 6. a) *Part of an inversion-recovery measurement* (14–50 ppm) *of the 3rd-generation dendrimer* **32** (125-MHz ^{13}C-NMR) *with labelling of the resonances for the central CH C-atoms of the core* (black circle, 44.58 ppm), *the interior units* (dark grey, 46.19 ppm), *and the peripheral units* (grey, 45.70 ppm). b) *Dependence of* T_1 *of the central CH C-atoms* (depicted as circles) *of peripheral and interior units on generation number of dendrimers* **30**–**33**

illustrated in *Fig. 6, a*, and T_1 for the central *C*H C-atoms of peripheral and interior units is plotted as a function of generation number of dendrimers **30**–**33** in *Fig. 6, b*[25]).

Due to the small signal intensity of the central *C*H C-atom of the core unit for 3rd- and 4th-generation dendrimers, it was only possible to obtain an estimated value of a short relaxation time $T_1 < 0.3$. Moreover, as a result of identical chemical shifts of analogous C-atoms in the interior layers, T_1 values for interior central *C*H C-atoms are averages over all interior layers of a specific dendrimer[26]). From these measurements, it can be concluded that the segmental mobility at the peripheral units of all the dendrimers (1st- up to 4th-generation) is higher than that of the corresponding interior units. Additionally, the T_1 value of the interior units does not change from the 3rd- to the 4th-generation dendrimer[27]) (*Fig. 6, b*), whereas the T_1 value of the peripheral units increases with increasing molecular weight. Similar observations were made previously on achiral dendrimers [32][33].

5. Characterization by Size-Exclusion Chromatography. – With the invention of low-angle laser light scattering (LALLS)[28]) and differential viscosity detector (DV) for size-exclusion chromatography (SEC), in addition to a refractive-index detector (RI)[29]), a complete structure characterization of polymers in terms of the molecular mass, polydispersity, hydrodynamic radius, and intrinsic viscosity is performed with one single SEC run [34][35]. In such an experiment, the polymer is injected into a chromatographic column which separates the sample components on the basis of size. A comparison of the SEC chromatograms of a polystyrene standard and the 4th-generation dendrimer **33** in *Fig. 7* shows that the peaks generated by the three detectors coincide, which is typical for a very narrow distribution of molecular weights.

The agreement between nominal (MW) and weight average molecular weight (M_w) measured by LALLS of dendrimer **33** is within the experimental error of the technique (Mol. Wt. 10582 Da, M_w 11600 Da, standard deviation 10–15%[30])). The data obtained from the two other detectors, RI and DV, are collected in the *Table*.

Furthermore, the SEC chromatograms, obtained with the DV detector, of 0th- to 4th-generation dendrimers, are shown in an overlay in *Fig. 8, a*. Since calculation of molecular weights from the DV detector requires a universal calibration with narrow molecular-weight-distribution polystyrene standards, absolute values as M_w and M_n[31]),

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[25]) T_1 Values were calculated from the slope of a semi-logarithmic plot of $(I_\infty - I_\tau)$ *vs.* τ according to the equation $\ln(I_\infty - I_\tau) = \ln(2I_\infty) - \tau/T_1$ [31], where I corresponds to the intensity of a spectral line. For I_∞, the magnetization in equilibrium, we chose the value at $\tau = 32$ s. Correlation coefficients of such calculations were typically $r^2 > 0.998$.

[26]) One layer of three interior units in 2nd-generation dendrimer **31**, two layers of a total of nine interior building blocks in 3rd-generation dendrimer **32**, and three layers of a total of 21 interior building blocks in 4th-generation dendrimer **33**.

[27]) This fact is often an indication that the correlation time, which is determinant for the relaxation time, is mainly influenced by the self-motion of the nuclei, rather than by the re-orientation of the whole molecule [31].

[28]) The LALLS detector allows the direct measurement of the weight average molecular weight M_w.

[29]) The RI detector measures dn/dc, the refractive index increment.

[30]) The lower-molecular-weight dendrimers provided only weak scattering signals and, therefore, high uncertainty in the LALLS experiment.

[31]) M_n = number average molecular weight.

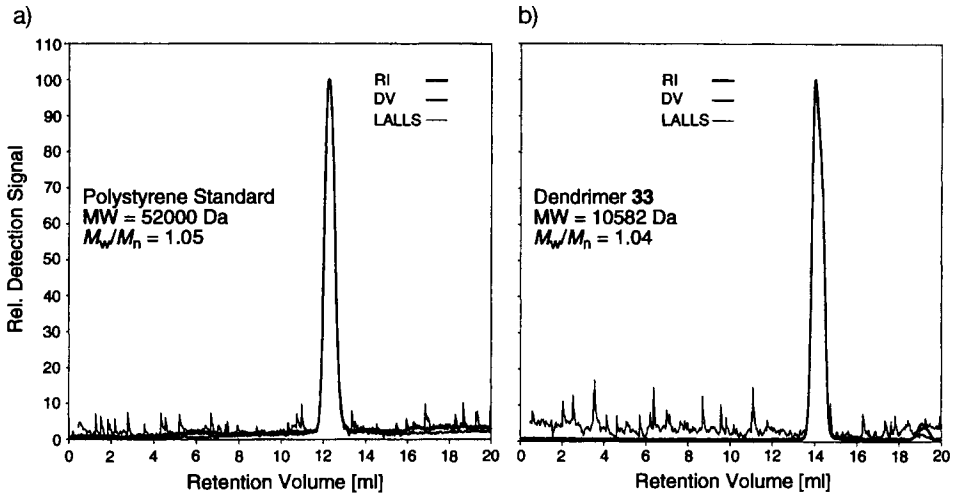

Fig. 7. *Overlay of SEC traces* (three detectors: RI, DV, and LALLS; see text) *of* a) *a polystyrene standard and* b) *the 4th-generation dendrimer* **33**

Table. *Size-Exclusion Chromatography* (SEC). *Data* (for abbreviations, see text).

Dendrimer	MW [Da]	M_w [Da]	M_n [Da]	M_w/M_n	d*n*/d*c* [ml/g]	[η] [dl/g]	r_{SEC} [nm]	r_H [nm]
28	579	450	420	1.07	0.20	0.025	0.73	0.61
30	1198	1150	920	1.25	0.15	0.043	1.13	0.93
31	2435	2450	2170	1.13	0.15	0.057	1.65	1.30
32	4911	5580	5090	1.10	0.15	0.068	2.32	1.74
33	10582	11800	11300	1.04	0.20	0.092	3.36	2.49

or, therefore, also polydispersities M_w/M_n, given in the *Table* are somehow meaningless ('polystyrene-equivalent values'). However, there are reasonable correlations with the nominal molecular weights. The same is true for the hydrodynamic radius (r_{SEC}) which was determined from the elution volume by comparison to the standards (see *Table*). Alternatively, according to the equation described by *Hester* and *Mitchell*[32]) [36] for spherical objects, the hydrodynamic radius (r_H) can be directly derived from the intrinsic viscosity [η] (see *Table*). These radii are 20–25% lower compared to the r_{SEC} values and increase approximately linearly with the generation number; a diameter of *ca.* 5 nm results for the 4th-generation dendrimer **33**.

Similar to other dendrimers [37], a nonlinear dependence is observed in the double logarithmic plot of intrinsic viscosity [η] against the molecular weight of the dendrimers (see *Fig. 8, b*).

[32]) $r_H = 1/2(240/\pi N_A)^{1/3}$ (MW[η])$^{1/3}$; r_H = hydrodynamic radius in cm; N_A = *Avogadro* number; [η] = intrinsic viscosity in dl/g.

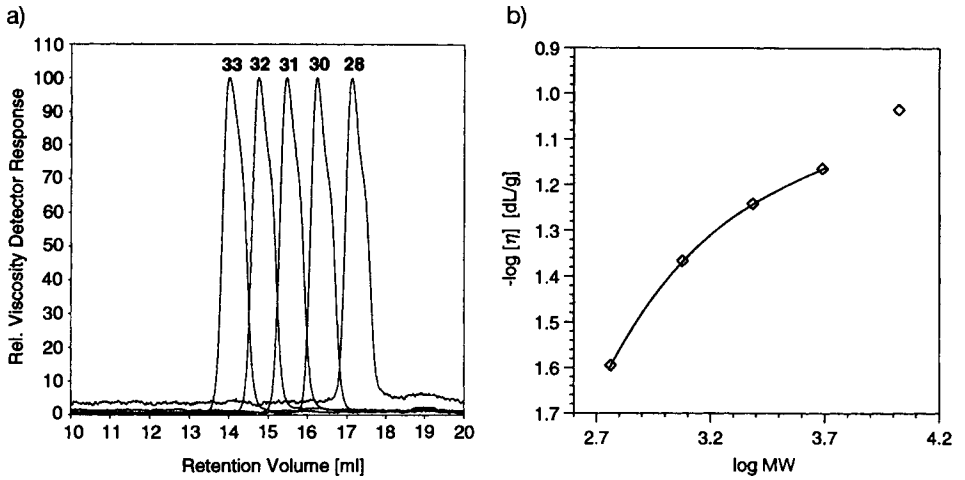

Fig. 8. a) *Superposition of the relative viscosity detector responses of the 0th- to 4th-generation dendrimers* **28**, **30**, **31**, **32**, *and* **33**. b) *Intrinsic viscosity of dendrimers* (0th to 4th generation) *in THF*

6. Chiroptical Properties. – Finally, we turned our attention to the chiroptical properties of our 'fully chiral' dendrimers in order to investigate the influence of the chiral building blocks on the structure of the whole dendrimer. It is well-known that optical activity is very sensitive to conformational changes. Accordingly, chiroptical techniques are often used for structural investigations, mainly in solution[33]) [38–40].

Polarimetry showed that, even for dendrimers with up to 93 stereogenic centers, the overall specific rotation $[\alpha]_D$ can be correlated with the arithmetic sum of the values of suitable model compounds resembling the building blocks. As illustrated in *Fig. 9, a*, compound **29** was used as reference for the elongated central unit ($[\alpha]_D = + 12.2$), **24** for the interior ($[\alpha]_D = - 4.6$), and **10** for the peripheral building blocks ($[\alpha]_D = + 15.9$) (the $[\alpha]_D$ values given in brackets were measured with a concentration of $c = 1$ in $CHCl_3$).

A comparison of the thus calculated (see *Fig. 9, b*) with the measured specific rotations of benzyl-alcohol branches (0th up to 5th generation; *Fig. 10, a*) and dendrimers (0th up to 4th generation; *Fig. 10, c*) of this kind gave a close resemblance, with a curve approaching asymptotically a limiting value with increasing generation number. It was also shown that this observation is independent of solvent (*Fig. 10, b*), concentration, and temperature (*Fig. 10, c*).

However, examination of the circular dichroism (CD) spectra of our dendrimers revealed effects that were not found in the polarimetric studies. In *Fig. 11*, the UV (plots on the left side) and the corresponding CD spectra (plots on the right side) of 0th- to 4th-generation dendrimers (**28** and **30**–**33**) are shown. We have recorded the spectra in three different solvents. In CH_2Cl_2 and *t*-BuOMe (*Fig. 11, a* and *b*), the differential dichroic absorption ($\Delta\varepsilon$) increases, as expected, linearly with the generation number and is proportional to the number of benzene chromophores in the dendrimer.

[33]) Theoretical interpretation of optical activity is very complex, and satisfying theories are not yet available.

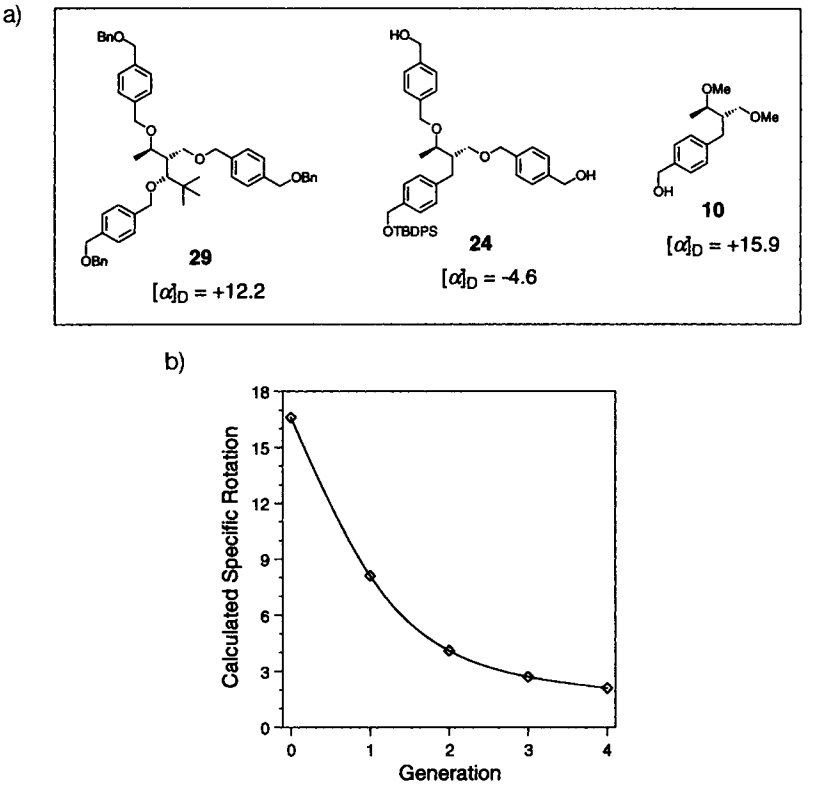

Fig. 9. a) *Specific rotation* ($[\alpha]_D$) *of model compounds for the central, interior, and peripheral building blocks in the dendritic compounds* (measured in $CHCl_3$ at room temperature). b) *Calculated specific rotation as a function of the generation of dendrimers*

All dendrimers exhibit a negative *Cotton* effect with a fine structure having a maximum at *ca.* 262 nm which corresponds to one of the two formally forbidden $\pi \rightarrow \pi^*$ electronic transitions of the benzene chromophore. In these two solvents, the shapes of the CD curves follow the vibrational contour of the absorption curves. By changing to a more polar solvent such as MeCN (*Fig. 11, c*), we observed a remarkable phenomenon with a loss of regularity in the spectra: the curves measured for 0th- to 3rd-generation dendrimers change their shape *and* sign from generation to generation; particularly large differences appear in going from the 2nd to the 3rd generation. Furthermore, the 4th-generation dendrimer **33** is not soluble in MeCN, although the compounds of lower generations are very soluble in this solvent. To date, this effect could not be rationalized.

7. Conclusions. – In the current investigation, we have demonstrated that the synthesis of 'fully chiral' dendrimers and branches up to generation four and five can be achieved, using double branched building blocks. As determined by MALDI-TOF-MS, these chiral macromolecular compounds possess uniform structures and a distinct molecular weight.

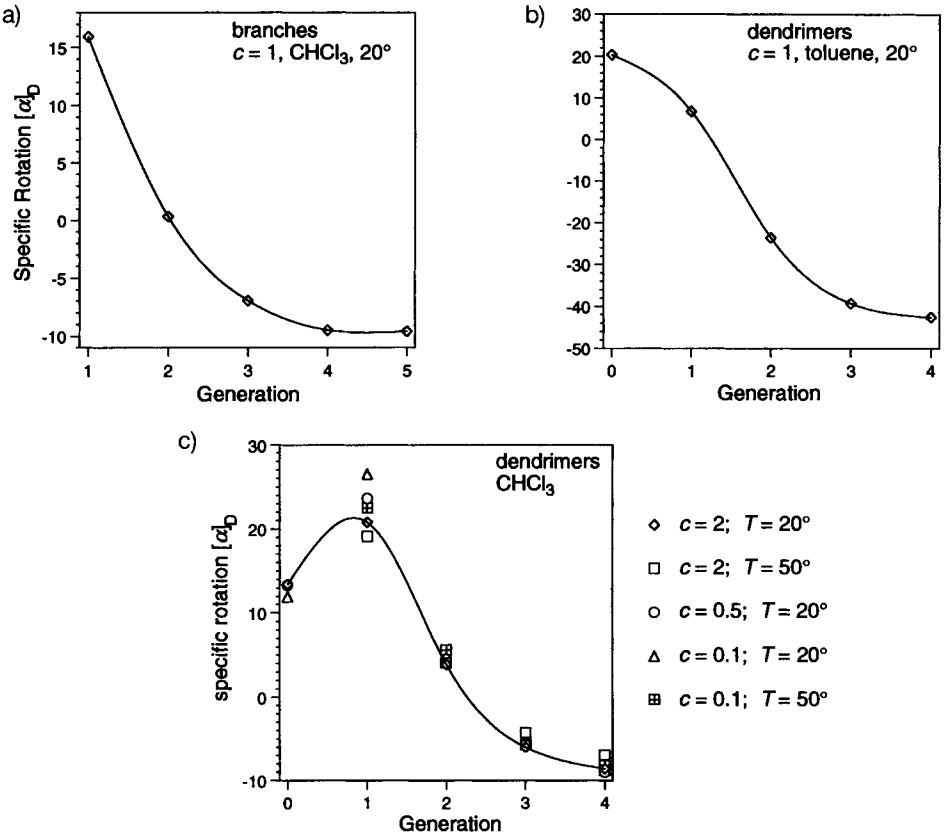

Fig. 10. *Specific rotations* ($[\alpha]_D$) a) *of benzyl-alcohol branches* (1st to 5th generation) *in* $CHCl_3$, b) *of dendrimers* (0th to 4th generation) *in toluene and* c) *in* $CHCl_3$, *at different temperatures and concentrations*

The properties of these chiral dendrimers are similar when compared to achiral dendrimers through ^{13}C-NMR relaxation measurements and size-exclusion chromatography. Furthermore, the specific rotation approaches asymptotically a limiting value with increasing generation number suggesting that the chiral segments contribute as independent, noninteracting units. This is in contrast to the findings made by CD measurements, which revealed a solvent effect with increasing polarity of the solvent. Therefore, contributions of chiral substructures might be very sensitive to the conditions used, especially in relatively flexible dendrimers such as the ones presented in this paper.

This is one of the issues we are currently pursuing in more detail by testing chiral dendrimers as solvent additives for catalytic enantioselective reactions.

We gratefully acknowledge the financial support of the *Swiss National Science Foundation* (project No. 2100-040659.94/1). We thank Dr. *P. Neuenschwander* and *M. Colussi* of Institut für Polymere, ETH, for SEC measurements. We are indebted to Prof. *B. Jaun* and *B. Brandenberger* for spin-lattice relaxation-time measurements. The teams of our MS, NMR, and elemental-analysis services are acknowledged for competent and efficient help. The X-ray of compound **7** was determined as part of the requirements in the crystallography course at ETH, directed by Prof. Dr. *V. Gramlich*. We also thank *Zeneca Bio Products*, Billingham (UK), for the generous supply of

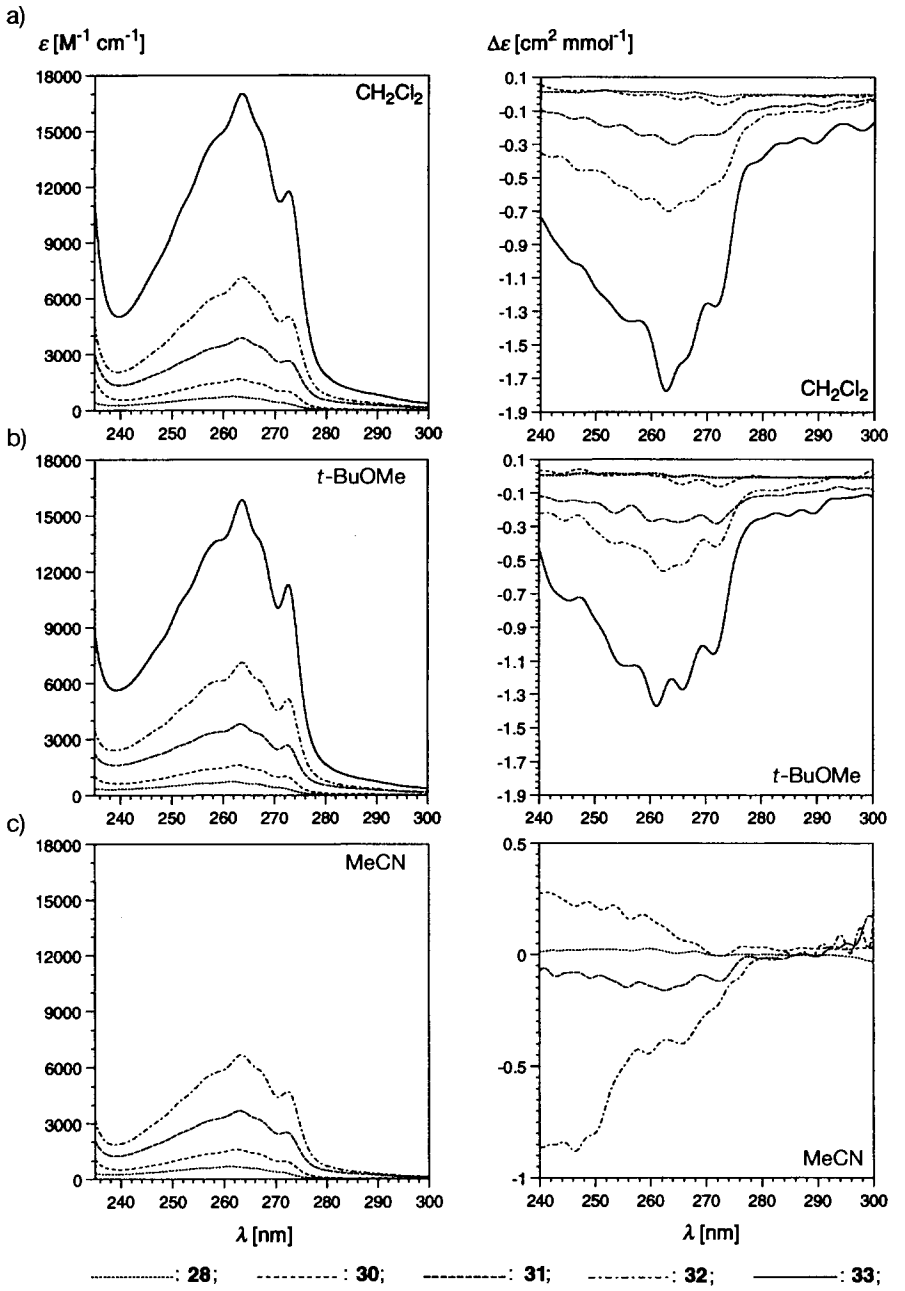

Fig. 11. *UV* (left) *and CD spectra* (right) *of dendrimers* **28**, **30**, **31**, **32**, *and* **33** *of 0th to 4th generation in* a) CH_2Cl_2, b) *t*-BuOMe, *and* c) MeCN. $c = 10^{-3}$–10^{-4} M at room temperature.

P(3-HB), *FMC Corporation*, Bessemer City (USA) for (*t*-Bu)Ph_2SiCl, and *BASF AG*, Ludwigshafen (D), for 2,2-dimethylpropanal and tetrahydrofuran. Continuing support of our research by *Novartis AG*, Basel (CH), is greatly appreciated.

Experimental Part

General. All reactions were carried out in standard glassware under Ar. Reagent-grade chemicals were purchased from *Fluka* or *Aldrich*, and used without further purification unless otherwise stated. Crude solvents for chromatography and for workup were distilled from sikkon (Et_2O from KOH/$FeSO_4$). THF and Et_2O for reactions were freshly distilled from sodium benzophenone ketyl radical. The compounds **1**, **2**, **5**, **27**, **28**, and **29** were prepared according to literature procedures [14–16]. TLC: Glass-plated TLC silica gel *60* F_{254} (*Merck*). Flash chromatography (FC): silical gel *60* (*Merck*), 40–63 μm. Medium pressure liquid chromatography (MPLC): *Büchi* system *B-680* (*Büchi-681 Chromatography Pump*, *Büchi-687 Gradient Former*, *Büchi-686 Peak Detector*, *Büchi-684 Fraction Collector*); Kieselgel *Europrep 60-20* (*Eurochrom Knauer*), 15–25 μm; *Büchi* 36 × 230 mm standard column; 20 bar; UV detection 245 nm; eluant in parantheses. Gel permeation chromatography (GPC): *Knauer* GPC system (pump model *64*; column oven (25–150°); *KMX-6* LALLS detector (*Chromatix*); *VISCOTEK* model *H502B* viscosity detector; *Knauer* high-temperature differential refractometer (35–150°); one *PL-gel mixed D*, 5 μm, 7.5 × 600 mm (*Polymer Laboratories Ltd.*)); THF (distilled from KOH, stabilized with 0.25% jonol); measuring temp: 45°; flow rate: 1.1 ml/min; narrow-molecular-weight-distributed polystyrene standards: 2025/3550/9000/19650/52000/111000/233000 (*Polymer Laboratories Ltd.*); dendrimer-injection concentration: 4–5 mg/ml; injection volume: 100 μl. M.p. *Büchi 510*, uncorrected. Microbalance: *Mettler AT20*. Optical rotations: *Perkin-Elmer-241* polarimeter or *JASCO-DIP-370* digital polarimeter, 10-cm cells. UV/VIS: *Kontron Uvikon 931* spectrophotometer, 1-cm cells; 0.3–0.4 mM, λ_{max} in nm (ε in M^{-1} cm^{-1}); scan speed 20 nm/min, data interval 0.1 nm. CD: *JASCO-J-710* spectropolarimeter, 1-cm cells; 0.3–0.4 mM, [θ] in deg cm^2 $dmol^{-1}$ (λ in nm); band width 1.0 nm, sensitivity 10 mdeg, response 2 s, scan speed 20 nm/min, step resolution 0.1 nm, accumulate 1. IR: *Perkin-Elmer-1600-FTIR*, in cm^{-1}; in $CHCl_3$. ^{1}H- and ^{13}C-NMR: *Bruker AMX-II-500*, *AMX-400*, *AMX-300*, *Varian-Gemini-200*, and *-300* spectrometers at r.t.; in $CDCl_3$; chemical shifts, δ, are quoted in ppm downfield from internal TMS, coupling constants, *J* in Hz. MS (*m/z* (%)): *Hitachi-Perkin-Elmer RMU-6M* for EI; *VG-ZAB2-SEQ* for FAB in a 3-nitrobenzyl-alcohol (3-NOBA) matrix; matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) on a *Bruker-Reflex*™ instrument with a N_2 laser system (337 nm), positive-ion mode; the sample was dissolved in CH_2Cl_2 (*ca.* 10^{-6} M) and mixed with the same volume of a soln. of α-cyano-4-hydroxycinnamic acid (CCA, 0.1M) in MeCN/EtOH/H_2O 50:45:5; spectra were processed and printed using the *XMASS* program on a *SUN* workstation. Elemental analyses and vapor pressure osmometry (VPO) measurements were performed by the Mikroanalytisches Laboratorium der ETH-Zürich.

Nomenclature *of Dendrimers and Dendritic Branches*: according to our convention published in [14].

1-(Bromomethyl)-4-[(methoxymethoxy)methyl]benzene (**4**). To a suspension of benzene-1,4-dimethanol (30.0 g, 217 mmol) in THF (300 ml) was added NaH (10.9 g, 456 mmol) in several portions. The resulting suspension was stirred for 10 min at 0° and for 1 h at r.t. After dropwise addition of $ClCH_2OMe$ (17.5 g, 16.5 ml, 217 mmol) at 0°, stirring was continued for 30 min at 0°, 1 h at 50°, and finally for 24 h at r.t. The white suspension was carefully treated with H_2O (150 ml) at 0°, the phases were separated, and the aq. phase was extracted with Et_2O (3 × 300 ml). The combined org. extracts were dried ($MgSO_4$) and concentrated *in vacuo*. FC (hexane/Et_2O 1:8) gave the monoprotected alcohol in pure form (19.5 g, 49%) as a light-yellow solid. The alcohol (19.5 g, 107 mmol) was dissolved in THF (300 ml) and successively treated with Ph_3P (35.1 g, 134 mmol) and Br_4C (44.4 g, 134 mmol) at 0°. After a precipitate had been formed, an Al foil was wrapped around the flask, and stirring was continued for 15 h at r.t. The resulting suspension was carefully treated at 0° with H_2O (110 ml), followed by extraction with CH_2Cl_2 (3 × 150 ml), drying ($MgSO_4$), and evaporation. FC (hexane/Et_2O 3:1) gave **4** (21.6 g, 82%). Colorless oil. R_f 0.39 (hexane/Et_2O 2:1). B.p. 130–140°/0.2 Torr. ^{1}H-NMR (200 MHz): 3.42 (*s*, MeO); 4.50 (*s*, CH_2Br); 4.60 (*s*, $PhCH_2O$); 4.71 (*s*, OCH_2O); 7.30–7.42 (*m*, 4 arom. H).

*1-(Bromomethyl)-4-{[(*tert*-butyl)diphenylsilyloxy]methyl}benzene* (**5**). To a soln. of (4-{[(*tert*-butyl)diphenylsilyloxy]methyl}phenyl)methanol [14] (10.0 g, 26.6 mmol) in THF (200 ml) at 0° was added Ph_3P (8.36 g, 31.9 mmol, 1.2 equiv.) and Br_4C (10.6 g, 31.9 mmol, 1.2 equiv.). After a precipitate had been formed, an Al foil was wrapped around the flask, and stirring was continued for 13 h at r.t. The resulting suspension was carefully treated at 0° with H_2O (110 ml), followed by extraction with CH_2Cl_2 (3 × 150 ml), drying ($MgSO_4$), and evaporation. FC (hexane/Et_2O 30:1) gave **5** (14.2 g, quant.). White solid. R_f 0.42 (hexane/Et_2O 30:1). M.p. 53–54°. IR: 3072*w*, 3008*m*, 2932*m*, 2859*m*, 1514*w*, 1472*w*, 1428*m*, 1376*w*, 1112*s*, 1086*s*, 1019*w*, 1006*w*, 939*w*. ^{1}H-NMR

(300 MHz): 1.10 (*s*, *t*-Bu); 4.51 (*s*, CH_2Br); 4.76 (*s*, CH_2OSi); 7.31–7.47 (*m*, 10 arom. H); 7.66–7.71 (*m*, 4 arom. H). ^{13}C-NMR (75 MHz): 19.30; 26.87; 33.53; 65.23; 126.38; 127.74; 128.96; 129.74; 133.43; 135.57; 135.92; 136.36; 141.53. EI-MS: 383 (62, $[M - (t\text{-Bu})]^+$), 353 (7), 303 (42), 273 (4), 261 (6), 223 (10), 199 (78), 183 (17), 151 (17), 135 (12), 121 (3), 104 (100), 91 (4), 77 (14), 51 (4), 28 (21), 18 (5). Anal. calc. for $C_{24}H_{27}BrOSi$ (439.47): C 65.59, H 6.19; found: C 65.65, H 6.17.

*(2*R*,5*R*,6*R*)-2-(*tert*-Butyl)-6-methyl-5-{4-[(methoxymethoxy)methyl]benzyl}-1,3-dioxan-4-one* (**6**). An ice-cold soln. of $(i\text{-Pr})_2NH$ (5.27 ml, 37.2 mmol, 1.14 equiv.) in THF (80 ml) was treated with BuLi (24.8 ml, 1.5M, 37.2 mmol, 1.14 equiv.), kept at 0° for 15 min, and then cooled to −78°. Dioxanone **1** (5.62 g, 32.6 mmol) in THF (40 ml) was added at such a rate that the temp. never exceeded −75°. After stirring at this temp. for 45 min a soln. of **4** (16.0 g, 65.3 mmol, 2 equiv.) in THF (40 ml) was added, again, so that the temp. did not rise above −75°. The mixture was kept at −78° for 30 h, then quenched at −78° with 200 ml of sat. aq. NH_4Cl (200 ml)/Et_2O (200 ml). The two phases were separated, and the aq. phase was extracted with Et_2O (2 × 200 ml). The combined org. extracts were dried ($MgSO_4$), and evaporation yielded a yellow oil. FC (hexane/Et_2O 2:1), subsequent evaporation and drying under h.v. gave **6** (8.44 g, 77%). White, crystalline solid. R_f 0.24 (hexane/Et_2O 2:1). M.p. 44–45°. $[\alpha]_D^{r.t.} = -45.8$ (*c* = 1.13, $CHCl_3$). IR: 3008*m*, 2962*m*, 2884*m*, 1729*s*, 1515*w*, 1484*m*, 1380*m*, 1354*m*, 1286*m*, 1149*s*, 1103*m*, 1044*s*, 999*m*, 969*m*, 916*m*. ^{1}H-NMR (CD_2Cl_2, 400 MHz): 0.91 (*s*, *t*-Bu); 1.23 (*d*, *J* = 6.1, Me–C(6)); 2.65 (*ddd*, $J_{1,2}$ = 10.3, J_3 = 5.3, H–C(5)); 2.98 ('*dd*', *ABX*, *J* = 14.4, 5.2, 1 H, CH_2–C(5)); 3.24 ('*dd*', *ABX*, *J* = 14.3, 5.4, 1 H, CH_2–C(5)); 3.37 (*s*, MeO); 3.70 (*dq*, *J* = 10.1, 6.1, H–C(6)); 4.54 (*s*, CH_2O); 4.67 (*s*, OCH_2O); 4.69 (*s*, H–C(2)); 7.17–7.30 (*m*, 4 arom. H). ^{13}C-NMR (CD_2Cl_2, 100 MHz): 20.16; 23.97; 33.77; 35.00; 49.84; 55.50; 69.23; 74.47; 96.22; 108.18; 128.30; 129.74; 137.00; 137.98; 170.85. EI-MS: 335 (< 1, $[M - 1]^+$), 306 (< 1, $[M - CH_2O]^+$), 275 (7, $[M - C_2H_5O_2]^+$), 250 (57), 233 (6), 217 (28), 203 (6), 188 (100), 171 (90), 159 (8), 143 (40), 131 (17), 119 (21), 104 (35), 91 (36), 77 (4), 69 (6), 57 (12), 45 (45), 29 (4). Anal. calc. for $C_{19}H_{28}O_5$ (336.43): C 67.83, H 8.39; found: C 68.06, H 8.26.

*(2*R*,5*R*,6*R*)-2-(*tert*-Butyl)-5-(4-{[(*tert*-butyl)diphenylsilyloxy]methyl}benzyl)-6-methyl-1,3-dioxan-4-one* (**7**). As described for **6**, with $(i\text{-Pr})_2NH$ (4.04 ml, 28.5 mmol, 1.14 equiv.), BuLi (19.0 ml, 1.5M in hexane, 28.5 mmol, 1.14 equiv.), **1** (4.31 g, 25.0 mmol), and **5** (22.0 g, 50.1 mmol, 2 equiv.) in THF (80 ml, 40 ml, 40 ml), reaction time 24 h. FC (hexane/Et_2O 3:1) gave **7** (11.9 g, 90%). White solid. R_f 0.42 (hexane/Et_2O 2:1). M.p. 91–92°. $[\alpha]_D^{r.t.} = -29.0$ (*c* = 1.11, $CHCl_3$). IR: 3008*m*, 2962*m*, 2933*m*, 2860*m*, 1729*s*, 1514*w*, 1484*w*, 1428*m*, 1379*m*, 1150*w*, 1112*s*, 1082*m*, 1030*m*, 998*m*, 968*w*, 939*w*. ^{1}H-NMR (400 MHz): 0.93 (*s*, *t*-Bu–C(2)); 1.09 (*s*, *t*-BuSi); 1.24 (*d*, *J* = 6.1, Me–C(6)); 2.63–2.70 (*m*, H–C(5)); 2.98 ('*dd*', *ABX*, *J* = 14.3, 5.5, 1 H, CH_2–C(5)); 3.32 ('*dd*', *ABX*, *J* = 14.3, 5.0, 1 H, CH_2–C(5)); 3.70 (*dq*, *J* = 10.1, 6.1, H–C(6)); 4.66 (*s*, H–C(2)); 4.75 (*s*, CH_2O); 7.14–7.45 (*m*, 10 arom. H); 7.65–7.69 (*m*, 4 arom. H). ^{13}C-NMR (100 MHz): 19.32; 20.04; 23.85; 26.86; 33.50; 35.12; 49.46; 65.24; 73.93; 107.92; 126.35; 127.71; 129.25; 129.71; 133.49; 135.58; 136.33; 139.71; 170.95. EI-MS: 529 (< 1, $[M - 1]^+$), 473 (20, $[M - (t\text{-Bu})]^+$), 427 (9), 387 (18), 343 (34), 309 (52), 267 (100), 231 (28), 211 (11), 199 (65), 185 (15), 171 (10), 145 (25), 130 (6), 117 (8), 104 (13), 91 (7), 77 (4), 57 (7), 28 (4). Anal. calc. for $C_{33}H_{42}O_4Si$ (530.78): C 74.68, H 7.98; found: C 74.51, H 7.68.

*(2*S*,3*R*)-2-{4-[(Methoxymethoxy)methyl]benzyl}butane-1,3-diol* (**8**). To a suspension of LAH (3.46 g, 91.1 mmol, 5 equiv.) in Et_2O (150 ml) was added **6** (6.13 g, 18.2 mmol) in Et_2O (30 ml). The mixture was stirred at 0° for 15 min, at r.t. for 30 min, then heated under reflux for 16 h. After cooling to 0°, 3.46 ml of H_2O, 3.46 ml of 15% aq. NaOH, and 10.4 ml of H_2O were added consecutively, and the resulting mixture was stirred vigorously, until a white precipitate formed. Addition of $MgSO_4$, stirring, filtration, evaporation, and FC (Et_2O) gave **8** (4.43 g, 96%) as a colorless oil. R_f 0.19 (Et_2O). $[\alpha]_D^{r.t.} = +13.0$ (*c* = 1.33, $CHCl_3$). IR: 3622*w*, 3450*w*, 3008*m*, 2934*m*, 2888*m*, 1615*w*, 1514*w*, 1448*w*, 1421*w*, 1379*w*, 1149*s*, 1101*m*, 1045*s*, 1021*m*, 914*w*. ^{1}H-NMR (300 MHz): 1.30 (*d*, *J* = 6.4, Me–C(3)); 1.65–1.75 (*m*, H–C(2)); 2.64 ('*dd*', *ABX*, *J* = 13.7, 9.1, 1 H, $C_6H_4CH_2C(2)$); 2.81 ('*dd*', *ABX*, *J* = 13.7, 6.0, 1 H, $C_6H_4CH_2C(2)$); 2.90–3.05 (br., 2 OH); 3.41 (*s*, MeO); 3.51–3.60 (br., H–C(3)); 3.84–3.96 (*m*, $OCH_2C(2)$); 4.56 (*s*, $OCH_2C_6H_4$); 4.70 (*s*, OCH_2O); 7.16–7.30 (*m*, 4 arom. H). ^{13}C-NMR (75 MHz): 22.14; 34.76; 47.85; 55.35; 63.09; 69.11; 70.96; 95.72; 128.19; 129.23; 135.62; 139.94. EI-MS: 254 (< 1, M^+), 236 (27), 205 (16), 193 (10), 181 (15), 175 (14), 156 (6), 143 (59), 131 (19), 117 (35), 104 (100), 91 (48), 77 (7), 45 (66), 28 (4). Anal. calc. for $C_{14}H_{22}O_4$ (254.33): C 66.12, H 8.72; found: C 66.05, H 8.80.

(MeO)$_2$-[G$_I^*$]^2-OMOM (= *1-[(Methoxymethoxy)methyl]-4-[(2*S*,3*R*)-3-methoxy-2-(methoxymethyl)butyl]benzene*; **9**). To NaH (6.44 g, 268 mmol, 6 equiv.) in THF (100 ml) was added **8** (11.4 g, 44.7 mmol) in THF (100 ml), and the mixture stirred at r.t. for 30 min, then at 40° for 15 min. The suspension was then cooled to 0°, and MeI (16.7 ml, 268 mmol, 6 equiv.) was added dropwise. After stirring for 19 h at r.t., the mixture was quenched with H_2O (200 ml) and saturated with NaCl. Extraction with Et_2O (3 × 400 ml), drying ($MgSO_4$), evaporation, and FC (hexane/Et_2O 2:1) gave **9** (11.5 g, 91%). Colorless oil. R_f 0.63 (Et_2O). $[\alpha]_D^{r.t.} = +16.8$ (*c* = 1.02, $CHCl_3$). IR: 3007*m*, 2977*m*, 2933*m*, 2890*m*, 2826*w*, 1515*w*, 1449*w*, 1379*w*, 1148*s*, 1100*s*, 1045*s*, 1021*m*,

915*w*. ^{1}H-NMR (300 MHz): 1.15 (*d*, *J* = 6.4, Me–C(3)); 1.95–2.06 (*m*, H–C(2)); 2.56 ('*dd*', *ABX*, *J* = 13.5, 8.7, 1 H, $C_6H_4CH_2C(2)$); 2.75 ('*dd*', *ABX*, *J* = 13.5, 6.2, 1 H, $C_6H_4CH_2C(2)$); 3.27 (*s*, MeO); 3.30 (*d*, *J* = 5.8, $OCH_2C(2)$); 3.33 (*s*, MeO); 3.40 (*dq*, H–C(3)); 3.42 (*s*, OCH_2OMe); 4.56 (*s*, OCH_2Ph); 4.71 (*s*, OCH_2O); 7.15–7.30 (*m*, 4 arom. H). ^{13}C-NMR (75 MHz): 15.83; 33.11; 45.77; 55.32; 56.47; 58.70; 69.20; 71.70; 76.21; 95.75; 128.03; 129.33; 135.31; 140.71. FAB-MS: 283 (40, $[M + 1]^+$), 250 (37), 235 (9), 221 (79), 205 (23), 189 (95), 175 (17), 157 (29), 145 (38), 131 (27), 117 (38), 105 (50), 85 (33). Anal. calc. for $C_{16}H_{26}O_4$ (282.38): C 68.06, H 9.28; found: C 68.29, H 9.02.

(MeO)$_2$-[G$_1^*$]^2-OH (= *4-[(2S,3R)-3-Methoxy-2-(methoxymethyl)butyl]benzenemethanol*; **10**). To a soln. of **9** (8.40 g, 29.8 mmol) in MeCN (250 ml) was added $LiBF_4$ (13.9 g, 149 mmol, 5 equiv.) and H_2O (10 ml). The mixture was heated at 60–70° for 14 h, then at 70° for 6 h, quenched by the addition of H_2O (200 ml), and extracted with E_2O (3 × 400 ml). The combined org. extracts were dried ($MgSO_4$) and evaporated. FC (hexane/Et_2O 1:2) gave **10** (3.56 g, 50%) and 3.43 g of a dimeric product. Repetition of the same reaction sequence as described before with the dimeric product and $LiBF_4$ (7.97 g, 85 mmol, 7 equiv.), MeCN (120 ml) and H_2O (4.8 ml), reaction time 21 h. FC (hexane/Et_2O 1:2) gave **10** (1.97 g, 68%). Total yield of **10**: 80%. Viscous oil. R_f 0.30 (hexane/Et_2O 1:4). $[\alpha]_D^{r.t.} = +15.9$ (*c* = 1.09, $CHCl_3$). IR: 3615*w*, 3434*w*, 3008*s*, 2976*m*, 2932*m*, 2891*m*, 2827*w*, 1514*w*, 1449*w*, 1379*m*, 1448*s*, 1099*s*, 1046*s*, 914*w*, 878*w*. ^{1}H-NMR (300 MHz): 1.15 (*d*, *J* = 6.4, Me–C(3)); 1.90 (*t*, *J* = 5.2, OH); 1.94–2.06 (*m*, H–C(2)); 2.56 ('*dd*', *ABX*, *J* = 13.5, 8.7, 1 H, $C_6H_4CH_2C(2)$); 2.75 ('*dd*', *ABX*, *J* = 13.5, 6.2, 1 H, $C_6H_4CH_2C(2)$); 3.27 (*s*, MeO); 3.30 (*d*, *J* = 5.7, $OCH_2C(2)$); 3.33 (*s*, OMe); 3.40 (*dq*, *J* = 4.5, 6.3, H–C(3)); 4.65 (*d*, *J* = 4.6, CH_2OH); 7.14–7.30 (*m*, 4 arom. H). ^{13}C-NMR (75 MHz): 15.83; 33.08; 45.77; 56.49; 58.72; 65.26; 71.70; 76.27; 127.12; 129.45; 138.42; 140.62. EI-MS: 206 (17, $[M - 36]^+$), 177 (4), 161 (13), 151 (16), 144 (22), 131 (36), 117 (10), 104 (5), 91 (14), 85 (22), 77 (8), 59 (100), 45 (15), 28 (7). Anal. calc. for $C_{14}H_{22}O_3$ (238.33): C 70.56, H 9.30; found: C 70.69, H 9.08.

(MeO)$_2$-[G$_1^*$]^2-Br (= *1-(Bromomethyl)-4-[(2S,3R)-3-methoxy-2-(methoxymethyl)butyl]benzene*; **11**). As described for **5**, with **10** (8.84 g, 37.1 mmol), Ph_3P (12.2 g, 46.4 mmol, 1.25 equiv.), and Br_4C (15.4 g, 46.4 mmol, 1.25 equiv.) in THF (200 ml), reaction time 28 h. FC (hexane/Et_2O 3:1) gave **11** (11.1 g, quant.). Colorless oil. R_f 0.36 (hexane/Et_2O 3:1). $[\alpha]_D^{r.t.} = +17.9$ (*c* = 1.11, $CHCl_3$). IR: 3007*s*, 2974*s*, 2931*m*, 2896*m*, 2825*w*, 1513*w*, 1448*m*, 1420*w*, 1385*m*, 1446*m*, 1090*s*, 1049*m*, 952*w*, 877*w*. ^{1}H-NMR (300 MHz): 1.15 (*d*, *J* = 6.4, Me–C(3)); 1.95–2.05 (*m*, H–C(2)); 2.56 ('*dd*', *ABX*, *J* = 13.5, 8.6, 1 H, $C_6H_4CH_2C(2)$); 2.75 ('*dd*', *ABX*, *J* = 13.5, 6.2, 1 H, $C_6H_4CH_2C(2)$); 3.28 (*s*, MeO); 3.30 (*d*, *J* = 5.7, $OCH_2C(2)$); 3.33 (*s*, MeO); 3.39 (*dq*, *J* = 4.5, 6.4, H–C(3)); 4.50 (*s*, CH_2Br); 7.13–7.32 (*m*, 4 arom. H). ^{13}C-NMR (75 MHz): 15.83; 33.15; 33.67; 45.71; 56.49; 58.75; 71.67; 76.23; 129.00; 129.68; 135.25; 141.69. EI-MS: 302 (< 1, $[M + 2]^+$), 285 (< 1), 270 (49), 239 (9), 225 (31), 213 (33), 189 (90), 157 (19), 144 (79), 131 (53), 117 (33), 104 (47), 85 (27), 59 (100), 45 (15), 28 (7). Anal. calc. for $C_{14}H_{21}BrO_2$ (301.22): C 55.82, H 7.03; found: C 55.83, H 6.97.

(2S,3R)-2-(4-{[(tert-Butyl)diphenylsilyloxy]methyl}benzyl)butane-1,3-diol (**12**). To $NaBH_4$ (2.00 g, 52.8 mmol, 5 equiv.) in THF (50 ml)/MeOH (5 ml) was added **7** (5.61 g, 10.6 mmol) in THF (50 ml) at 0°. The mixture was stirred at 0° for 2 h, then at r.t. for 14.5 h. H_2O (100 ml) was added and the mixture saturated with NaCl, extracted with Et_2O (3 × 200 ml), and the combined org. extracts were dried ($MgSO_4$) and evaporated. FC (Et_2O) gave **12** (4.37 g, 92%). Viscous oil. R_f 0.33 (Et_2O). $[\alpha]_D^{r.t.} = +9.3$ (*c* = 1.07, $CHCl_3$). IR: 3616*w*, 3434*w*, 3072*w*, 3007*m*, 2931*m*, 2889*m*, 2859*m*, 1514*w*, 1472*w*, 1428*m*, 1377*w*, 1112*s*, 1020*w*, 907*w*. ^{1}H-NMR (300 MHz): 1.09 (*s*, *t*-Bu); 1.33 (*d*, *J* = 6.4, Me–C(3)); 1.69–1.79 (*m*, H–C(2)); 2.55–2.63 (*m*, OH); 2.64 ('*dd*', *ABX*, *J* = 13.8, 9.2, 1 H, $C_6H_4CH_2C(2)$); 2.82 ('*dd*', *ABX*, *J* = 13.8, 6.0, 1 H, $C_6H_4CH_2C(2)$); 3.55–3.64 (*m*, H–C(3)); 3.87–4.00 (*m*, OH, $OCH_2C(2)$); 4.75 (*s*, CH_2OSi); 7.15–7.46 (*m*, 10 arom. H); 7.67–7.71 (*m*, 4 arom. H). ^{13}C-NMR (75 MHz): 19.33; 22.20; 26.88; 34.73; 47.92; 63.25; 65.42; 71.09; 126.21; 127.70; 128.93; 129.67; 133.63; 135.60; 138.81; 138.90. EI-MS: 391 (3, $[M - (t\text{-Bu})]^+$), 373 (14), 301 (11), 241 (25), 229 (13), 199 (100), 175 (82), 145 (25), 117 (42), 104 (23), 91 (26), 45 (15), 28 (24). Anal. calc. for $C_{28}H_{36}O_3Si$ (448.68): C 74.96, H 8.09; found: C 75.08, H 8.04.

(MeO)$_4$-[G$_2^*$]^2-OTBDPS (**13**). A suspension of NaH (2.05 g, 85.4 mmol, 6 equiv.) in THF (100 ml) was cooled to 0°, and **12** (6.38 g, 14.2 mmol) in THF (50 ml) was added. The mixture was stirred at 0° for 15 min, at r.t. for 15 min, then heated up to 70° for 30 min, and the resulting suspension cooled to r.t. during 15 min. The bromide **11** (9.00 g, 29.9 mmol, 2.1 equiv.) was added dropwise at 0° in THF (50 ml), the mixture was stirred at r.t. for 1.5 h, kept at reflux for 1 h, then at r.t. for 20 h, and again heated under reflux for 4 h (pale-beige suspension). The reaction was quenched with H_2O (150 ml), saturated with NaCl, and the mixture extracted with Et_2O (3 × 300 ml). The combined org. extracts were dried ($MgSO_4$) and evaporated. FC (hexane/Et_2O 2:1) gave **13** (12.2 g, 97%). MPLC (33% Et_2O/hexane) yielded pure **13** (11.1 g, 88%). Colorless, very viscous oil. R_f 0.31 (hexane/Et_2O 1:1). $[\alpha]_D^{r.t.} = +1.8$ (*c* = 1.06, $CHCl_3$). IR: 3008*m*, 2977*m*, 2932*m*, 2896*m*, 1514*w*, 1463*w*, 1428*w*, 1377*w*, 1108*s*, 1091*s*, 1020*w*, 909*w*. ^{1}H-NMR (400 MHz): 1.10 (*s*, *t*-Bu); 1.15 (*d*, *J* = 6.3, 2 Me(G_2)); 1.23

(*d*, *J* = 6.3, Me(G_1)); 1.98–2.06 (*m*, 2 H–C(2)(G_2)); 2.10–2.18 (*m*, H–C(2)(G_1)); 2.53 ('*dd*', *ABX*, *J* = 8.7, 3.7, 1 H), 2.57 ('*dd*', *ABX*, *J* = 8.7, 3.6, 1 H), 2.63 ('*dd*', *ABX*, *J* = 13.5, 8.9, 1 H), 2.73 ('*dd*', *ABX*, *J* = 6.2, 2.5, 1 H), 2.77 ('*dd*', *ABX*, *J* = 6.1, 2.5, 1 H), 2.83 ('*dd*', *ABX*, *J* = 13.5, 5.9, 1 H, $C_6H_4CH_2C(2)$); 3.27 (2*s*, 2 MeO(P)); 3.30 ('*dd*', *ABX*, *J* = 5.7, 3.5, 4 H, $OCH_2C(2)(G_2)$); 3.32, 3.33 (2*s*, 2 MeO(P)); 3.36–3.43 (*m*, 2 H–C(3)(G_2)); 3.45 ('*dd*', *ABX*, *J* = 9.4, 5.8, 1 H, $OCH_2C(2)(G_1)$); 3.51 ('*dd*', *ABX*, *J* = 9.5, 5.2, 1 H, $OCH_2C(2)(G_1)$); 3.70–3.77 (*m*, H–C(3)(G_1)); 4.38, 4.43 (*AB*, *J* = 11.8, 3 H, OCH_2Ph); 4.55 (*d*, *AB*, *J* = 11.5, 1 H, OCH_2Ph); 4.75 (*s*, CH_2OSi); 7.10–7.17 (*m*, 6 arom. H); 7.21–7.28 (*m*, 6 arom. H); 7.35–7.44 (*m*, 6 arom. H); 7.68–7.71 (*m*, 4 arom. H). ^{13}C-NMR (100 MHz): 15.80; 16.71; 19.33; 26.87; 33.02; 33.15; 45.68; 46.16; 56.49; 58.73; 65.41; 69.35; 70.80; 71.66; 72.92; 74.72; 76.14; 76.16; 125.97; 127.59; 127.62; 127.69; 127.92; 129.06; 129.18; 129.20; 129.66; 133.59; 135.60; 136.13; 136.58; 138.49; 139.71; 140.23; 140.30. FAB-MS: 902 (1, $[M + 14]^+$), 888 (5, M^+), 668 (7), 429 (2), 349 (2), 323 (3), 281 (3), 221 (21), 189 (100), 157 (46), 145 (35), 135 (53), 131 (52), 117 (67), 104 (51), 59 (82). Anal. calc. for $C_{56}H_{76}O_7Si$ (889.30): C 75.63, H 8.61; found: C 75.73, H 8.44.

(MeO)$_4$-[G$_2^*$]^2-OMOM (**14**). A suspension of NaH (54.4 mg, 2.27 mmol, 9 equiv.) in THF (3 ml) was cooled to 0°, and **8** (167 mg, 0.56 mmol, 2.2 equiv.) in THF (5 ml) was added. The mixture was stirred under reflux for 30 min. Then, **11** (167 mg, 0.56 mmol) in THF (5 ml) was slowly added at r.t., and the mixture was kept at reflux for 23 h. The reaction was quenched with H_2O (15 ml), saturated with NaCl, and the mixture was extracted with Et_2O (3 × 40 ml). The combined org. extracts were dried ($MgSO_4$) and evaporated. FC (hexane/Et_2O 1:1) gave **14** (130 mg, 75%). Colorless, viscous oil. A second FC gave an anal. pure sample. R_f 0.39 (hexane/Et_2O 1:1). ^{1}H-NMR (400 MHz): 1.15 (*d*, *J* = 6.4, 2 Me(G_2)); 1.22 (*d*, *J* = 6.3, Me(G_1)); 1.96–2.04 (*m*, 2 H–C(2)(G_2)); 2.08–2.16 (*m*, H–C(2)(G_1)); 2.55 ('*dd*', *ABX*, *J* = 13.5, 6.3, 1 H, $C_6H_4CH_2C(2)(G_2)$); 2.56 ('*dd*', *ABX*, *J* = 13.4, 8.7, 1 H, $C_6H_4CH_2C(2)(G_2)$); 2.65 ('*dd*', *ABX*, *J* = 13.5, 8.8, 1 H, $C_6H_4CH_2C(2)(G_1)$); 2.75('*dd*', *ABX*, *J* = 13.5, 6.1, 1 H, $C_6H_4CH_2C(2)(G_2)$); 2.76 ('*dd*', *ABX*, *J* = 13.5, 6.1, 1 H, $C_6H_4CH_2C(2)(G_2)$); 2.82 ('*dd*', *ABX*, *J* = 13.5, 6.0, 1 H, $C_6H_4CH_2C(2)(G_1)$); 3.27 (2*s*, 2 MeO(P)); 3.30 ('*dd*', *ABX*, *J* = 5.8, 2.6, 4 H, $OCH_2C(2)(G_2)$); 3.33 (2*s*, 2 MeO(P)); 3.38–3.43 (*m*, 2 H–C(3)(G_2)); 3.42 (*s*, OCH_2OMe); 3.44 ('*dd*', *ABX*, *J* = 9.6, 5.7, 1 H, $OCH_2C(2)(G_1)$); 3.50 ('*dd*', *ABX*, *J* = 9.5, 5.3, 1 H, $OCH_2C(2)(G_1)$); 3.68–3.74 (*m*, H–C(3)(G_1)); 4.35–4.44 (*m*, 3 H, $OCH_2C_6H_4$); 4.54 (*d*, *AB*, *J* = 12.9, 1 H, $OCH_2C_6H_4$); 4.56 (*s*, $C_6H_4CH_2OCH_2$); 4.71 (*s*, OCH_2O); 7.11–7.28 (*m*, 12 arom. H). ^{13}C-NMR (100 MHz): 15.80; 16.70; 33.02; 33.21; 45.69; 46.19; 55.34; 56.49; 58.73; 69.15; 69.26; 70.79; 71.66; 72.92; 74.65; 76.14; 76.16; 95.70; 127.60; 127.61; 128.02; 129.18; 129.20; 129.32; 135.20; 136.08; 136.54; 140.25; 140.31; 140.76. FAB-MS: 693 (6, $[M - 1]^+$), 633 (1), 569 (1), 473 (5), 441 (3), 409 (3), 381 (2), 349 (4), 323 (4), 221 (30), 189 (100), 161 (45), 131 (43), 117 (56), 104 (46), 91 (26). Anal. calc. for $C_{42}H_{62}O_8$ (694.95): C 72.59, H 8.99; found: C 72.48, H 9.02.

(MeO)$_4$-[G$_2^*$]^2-OH (**15**). *a) TBDPS Deprotection*: To a soln. of **13** (20.1 g, 22.6 mmol) in THF (250 ml) was added, at 0°, Bu_4NF (14.3 g, 45.2 mmol, 2 equiv.) at once. After stirring for 24 h at r.t., H_2O (170 ml) was added. Extraction with Et_2O (3 × 340 ml, 200 ml), drying ($MgSO_4$), evaporation, and FC (hexane/Et_2O 1:5) yielded **15** (16.1 g, quant.). Light-yellow, viscous oil. *b) MOM Deprotection*: To a soln. of **14** (82 mg, 0.12 mmol) in MeCN (7 ml) was added $LiBF_4$ (79 mg, 0.84 mmol, 7.14 equiv.) and H_2O (0.28 ml). The mixture was heated at 70° for 15 h, then additional 7.14 equiv. $LiBF_4$ were added, and the mixture was heated again at 70° for 49 h. The mixture was quenched with H_2O (47 ml), extracted with Et_2O (3 × 90 ml), dried ($MgSO_4$), and evaporated. FC (hexane/Et_2O 1:2) gave **15** (66 mg, 84%). Viscous oil. R_f 0.18 (hexane/Et_2O 1:2). $[\alpha]_D^{r.t.} = +0.3$ (*c* = 0.87, $CHCl_3$). IR: 3449*w*, 3008*s*, 2930*m*, 1614*w*, 1514*w*, 1449*w*, 1420*w*, 1378*w*, 1146*w*, 1092*s*, 1020*w*, 830*w*. ^{1}H-NMR (400 MHz): 1.15 (*d*, *J* = 6.4, 2 Me(G_2)); 1.22 (*d*, *J* = 6.4, Me(G_1)); 1.83–1.90 (*m*, OH); 1.97–2.05 (*m*, 2 H–C(2)(G_2)); 2.08–2.15 (*m*, H–C(2)(G_1)); 2.54 ('*dd*', *ABX*, *J* = 13.5, 8.8, 1 H, $C_6H_4CH_2C(2)(G_2)$); 2.55 ('*dd*', *ABX*, *J* = 13.5, 8.7, 1 H, $C_6H_4CH_2C(2)(G_2)$); 2.62 ('*dd*', *ABX*, *J* = 13.5, 8.9, 1 H, $C_6H_4CH_2C(2)(G_1)$); 2.74 ('*dd*', *ABX*, *J* = 13.5, 6.0, 1 H, $C_6H_4CH_2C(2)(G_2)$); 2.75 ('*dd*', *ABX*, *J* = 13.6, 6.1, 1 H, $C_6H_4CH_2C(2)(G_2)$); 2.82 ('*dd*', *ABX*, *J* = 13.5, 5.9, 1 H, $C_6H_4CH_2C(2)(G_1)$); 3.27 (2*s*, 2 MeO(P)); 3.30 (*d*, *J* = 5.7, 4 H, $OCH_2C(2)(G_2)$); 3.33 (*s*, 2 MeO(P)); 3.38–3.95 (*m*, 2 H–C(3)(G_2), $OCH_2C(2)(G_1)$); 3.68–3.74 (*m*, H–C(3)(G_1)); 4.35–4.43 (*m*, 3 H, $OCH_2C_6H_4$); 4.55 (*d*, *AB*, *J* = 11.5, 1 H, $OCH_2C_6H_4$); 4.65 (*d*, *J* = 4.8, CH_2OH); 7.11–7.26 (*m*, 12 arom. H). ^{13}C-NMR (100 MHz): 15.78; 16.69; 33.00; 33.16; 45.68; 46.14; 56.49; 58.73; 65.20; 69.17; 70.77; 71.67; 72.89; 74.62; 76.15; 76.19; 127.02; 127.64; 127.65; 129.17; 129.20; 129.40; 136.04; 136.51; 138.38; 140.26; 140.33; 140.61. FAB-MS: 673 (1, $[M + 23]^+$), 649 (3, $[M - 1]^+$), 549 (1), 429 (10), 409 (3), 381 (1), 349 (2), 323 (4), 289 (3), 261 (2), 221 (34), 189 (100), 161 (40), 117 (58). Anal. calc. for $C_{40}H_{58}O_7$ (650.90): C 73.81, H 8.98; found: C 74.04, H 8.99.

(MeO)$_4$-[G$_2^*$]^2-Br (**16**). As described for **5**, with **15** (16.1 g, 24.7 mmol), Ph_3P (9.73 g, 37.1 mmol, 1.5 equiv.), and Br_4C (12.3 g, 37.1 mmol, 1.5 equiv.) in THF (250 ml), reaction time 27 h. FC (hexane/Et_2O 1:1) gave **16** (16.5 g, 94%). Colorless, viscous oil. R_f 0.54 (hexane/Et_2O 1:4). $[\alpha]_D^{r.t.} = +1.2$ (*c* = 1.03, $CHCl_3$). IR: 3008*m*, 2930*m*, 2892*m*, 2821*w*, 1614*w*, 1514*w*, 1448*w*, 1377*w*, 1092*s*, 1021*w*. ^{1}H-NMR (400 MHz): 1.15 (*d*, *J* = 6.4, 2 Me(G_2)); 1.22 (*d*, *J* = 6.3, Me(G_1)); 1.98–2.05 (*m*, 2 H–C(2)(G_2)); 2.08–2.16 (*m*, H–C(2)(G_1)); 2.53

('*dd*', *ABX*, J = 8.8, 2.9, 1 H), 2.57 ('*dd*', *ABX*, J = 8.7, 2.8, 1 H), 2.63 ('*dd*', *ABX*, J = 13.5, 8.8, 1 H), 2.72 ('*dd*', *ABX*, J = 13.5, 6.1, 1 H), 2.73 ('*dd*', *ABX*, J = 13.6, 6.2, 1 H), 2.81 ('*dd*', *ABX*, J = 13.6, 5.9, 1 H, $C_6H_4CH_2C(2)$); 3.27, 3.28 (2*s*, 2 MeO(P)); 3.31 ('*dd*', *ABX*, J = 5.8, 2.6, 4 H, $OCH_2C(2)(G_2)$); 3.33 (*s*, 2 MeO(P)); 3.37–3.46 (*m*, 2 H–C(3)(G_2), 1 H, $OCH_2C(2)(G_1)$); 3.49 ('*dd*', *ABX*, J = 9.4, 5.3, 1 H, $OCH_2C(2)(G_1)$); 3.68–3.74 (*m*, H–C(3)(G_1)); 4.35–4.43 (*m*, 3 H, $OCH_2C_6H_4$); 4.49 (*s*, CH_2Br); 4.54 (*d*, *AB*, J = 11.5, 1 H, $OCH_2C_6H_4$); 7.10–7.29 (*m*, 12 arom. H). ^{13}C-NMR (100 MHz): 15.80; 16.67; 33.02; 33.24; 33.73; 45.68; 46.06; 56.50; 58.74; 69.21; 70.76; 71.67; 72.92; 74.62; 76.14; 76.17; 127.61; 127.62; 128.97; 129.19; 129.21; 129.64; 135.17; 136.00; 136.47; 140.29; 140.36; 141.71. FAB-MS: 713 (4, $[M+1]^+$), 605 (< 1), 577 (< 1), 491 (6), 429 (2), 409 (3), 323 (2), 239 (2), 237 (8), 221 (17), 189 (100), 157 (29), 145 (20), 131 (40), 117 (56), 104 (43), 59 (80).

(MeO)$_8$-[G$_3^*$]^2-OTBDPS (**17**). A suspension of NaH (321 mg, 13.4 mmol, 6 equiv.) in THF (15 ml) was cooled to 0°, and **12** (1.0 g, 2.2 mmol) in THF (15 ml) was added dropwise *via* syringe. The mixture was stirred at 0° for 15 min, at r.t. for 15 min, and then heated up to reflux for 30 min. Then, the suspension was cooled to 0°. The bromide **16** (3.5 g, 4.9 mmol, 2.2 equiv.) was added dropwise *via* syringe at 0° in THF (20 ml), stirred at 0° for 15 min, at r.t. for 30 min, and kept under reflux for 22 h, then at r.t. for 22 h (pale-beige suspension). The reaction was quenched with H_2O (50 ml), saturated with NaCl, and the mixture extracted with Et_2O (3 × 130 ml). The combined org. extracts were dried ($MgSO_4$) and evaporated. FC (hexane/Et_2O 1:1) yielded **17** (3.13 g, 82%). Colorless, viscous oil. R_f 0.31 (hexane/Et_2O 1:2). $[\alpha]_D^{r.t.} = -5.1$ (c = 1.25, $CHCl_3$). IR: 3007*m*, 2980*m*, 2930*m*, 2892*m*, 2862*m*, 1514*w*, 1448*w*, 1428*w*, 1377*w*, 1091*s*, 1020*w*, 909*w*. ^{1}H-NMR (400 MHz): 1.09 (*s*, *t*-Bu); 1.14 (*d*, J = 6.3, 4 Me(G_3)); 1.21 (*d*, J = 6.3, 2 Me(G_2)); 1.23 (*d*, J = 6.4, Me(G_1)); 1.96–2.04 (*m*, 4 H–C(2)(G_3)); 2.08–2.19 (*m*, 2 H–C(2)(G_2), H–C(2)(G_1)); 2.53 ('*dd*', *ABX*, J = 8.7, 2.8, 2 H), 2.56 ('*dd*', *ABX*, J = 13.6, 6.10, 2 H), 2.61 ('*dd*', *ABX*, J = 9.3, 4.7, 1 H), 2.66 ('*dd*', *ABX*, J = 7.9, 3.6, 2 H), 2.73 ('*dd*', *ABX*, J = 13.6, 6.1, 2 H), 2.74 ('*dd*', *ABX*, J = 13.5, 6.1, 2 H), 2.79–2.86 (*m*, 3 H, $C_6H_4CH_2C(2)$); 3.26, 3.27 (2*s*, 4 MeO(P)); 3.30 ('*dd*', *ABX*, J = 5.7, 3.2, 8 H, $OCH_2C(2)(G_3)$); 3.32 (2*s*, 4 MeO(P)); 3.36–3.48 (*m*, 4 H, $OCH_2C(2)(G_2)$, 2 H, $OCH_2C(2)(G_1)$); 3.49–3.54 (*m*, 4 H–C(3)(G_3)); 3.69–3.78 (*m*, 2 H–C(3)(G_2), H–C(3)(G_1)); 4.34–4.45 (*m*, 9 H, $OCH_2C_6H_4$); 4.51–4.56 (*m*, 3 H, $OCHC_6H_4$); 4.75 (*s*, CH_2OSi); 7.10–7.16 (*m*, 14 arom. H); 7.20–7.28 (*m*, 14 arom. H); 7.34–7.43 (*m*, 6 arom. H); 7.68–7.71 (*m*, 4 arom. H). ^{13}C-NMR (100 MHz): 15.81; 16.72; 19.33; 26.87; 33.02; 33.20; 45.68; 46.13; 46.18; 56.49; 58.73; 65.41; 69.28; 69.50; 70.79; 71.66; 72.91; 74.68; 74.82; 76.13; 76.16; 125.98; 127.58; 127.69; 129.07; 129.18; 129.19; 129.66; 133.58; 135.60; 136.13; 136.57; 138.49; 139.72; 140.22; 140.29; 140.31; 140.39. FAB-MS: 1738 (< 1, $[M+25]^+$), 1727 (< 1, $[M+14]^+$), 1490 (< 1), 1078 (< 1), 857 (< 1), 667 (< 1), 323 (1), 189 (100), 157 (42), 131 (60), 117 (81), 104 (48), 91 (35), 59 (77). Anal. calc. for $C_{108}H_{148}O_{15}Si$ (1714.43): C 75.66, H 8.70; found: C 75.63, H 8.52.

(MeO)$_8$-[G$_3^*$]^2-OH (**18**). As described for **15**, with **17** (3.50 g, 2.04 mmol) and Bu_4NF (1.29 g, 4.08 mmol, 2 equiv.) in THF (40 ml) reaction time 41 h. FC (hexane/Et_2O 1:4) gave **18** (2.96 g, 98%). Colorless, viscous oil. R_f 0.18 (hexane/Et_2O 1:4). $[\alpha]_D^{r.t.} = -7.0$ (c = 1.02, $CHCl_3$). IR: 3438*w*, 3007*m*, 2978*m*, 2931*m*, 2872*m*, 1718*w*, 1613*w*, 1514*w*, 1448*w*, 1420*w*, 1377*w*, 1091*s*, 1020*w*, 954*w*. ^{1}H-NMR (400 MHz): 1.14 (*d*, J = 6.4, 4 Me(G_3)); 1.21 (*d*, J = 6.3, 2 Me(G_2)); 1.23 (*d*, J = 6.2, Me(G_1)); 1.88 (*t*, J = 5.8, OH); 1.97–2.04 (*m*, 4 H–C(2)(G_3)); 2.09–2.18 (*m*, 2 H–C(2)(G_2), H–C(2)(G_1)); 2.53 ('*dd*', *ABX*, J = 8.7, 3.6, 2 H), 2.57 ('*dd*', *ABX*, J = 8.7, 3.6, 2 H), 2.60–2.67 (*m*, 3 H), 2.73 ('*dd*', *ABX*, J = 6.1, 2.8, 2 H), 2.76 ('*dd*', *ABX*, J = 6.1, 2.7, 2 H), 2.80–2.86 (*m*, 3 H), $C_6H_4CH_2C(2)$); 3.26, 3.27 (2*s*, 4 MeO(P)); 3.30 ('*dd*', *ABX*, J = 5.7, 3.4, 8 H, $OCH_2C(2)(G_3)$); 3.32, 3.33 (2*s*, 4 MeO(P)); 3.36–3.52 (*m*, 4 H–C(3)(G_3), 4 H, $OCH_2C(2)(G_2)$, 2 H, $OCH_2C(2)(G_1)$); 3.68–3.75 (*m*, 2 H–C(3)(G_2), H–C(3)(G_1)); 4.34–4.45 (*m*, 9 H, $OCH_2C_6H_4$); 4.52–4.56 (*m*, 3 H, $OCH_2C_6H_4$); 4.62 (*d*, J = 5.47, CH_2OH); 7.09–7.27 (*m*, 28 arom. H). ^{13}C-NMR (100 MHz): 15.80; 16.69; 33.02; 33.18; 45.68; 46.14; 46.17; 56.49; 58.73; 65.17; 68.16; 69.30; 69.34; 70.79; 71.66; 72.92; 74.70; 76.14; 76.17; 127.04; 127.60; 127.62; 128.81; 129.18; 129.20; 129.39; 130.89; 136.03; 136.08; 136.10; 136.51; 136.55; 138.41; 140.23; 140.30; 140.31; 140.36; 140.43; 140.62. FAB-MS: 1498 (< 1, $[M+23]^+$), 1488 (< 1, $[M+13]^+$), 1252 (< 1), 1015 (< 1), 839 (< 1), 603 (< 1), 391 (8), 221 (16), 189 (90), 161 (36), 157 (45), 145 (34), 117 (72), 104 (54), 59 (100). MALDI-TOF-MS: 1515 ($[M+39]^+$), 1498 ($[M+22]^+$). Anal. calc. for $C_{92}H_{130}O_{15}$ (1476.03): C 74.86, H 8.88; found: C 75.01, H 8.65.

(MeO)$_8$-[G$_3^*$]^2-Br (**19**). As described for **5**, with **18** (2.96 g, 2.00 mmol), Ph_3P (0.79 g, 3.00 mmol, 1.5 equiv.) and Br_4C (1.00 g, 3.00 mmol, 1.5 equiv.), in THF (40 ml). An additional equiv. of Ph_3P/Br_4C was added after 13 h to complete the reaction, and the mixture was stirred at r.t. for 10 h. FC (hexane/Et_2O 1:2) gave **19** (2.99 g, 97%). Colorless, viscous oil. R_f 0.49 (hexane/Et_2O 1:4). $[\alpha]_D^{r.t.} = -7.2$ (c = 1.48, $CHCl_3$). IR: 3007*s*, 2979*s*, 2930*s*, 1907*w*, 1722*w*, 1614*w*, 1514*m*, 1448*m*, 1377*m*, 1090*s*, 1021*m*, 953*w*. ^{1}H-NMR (400 MHz): 1.15 (*d*, J = 6.4, 4 Me(G_3)); 1.21 (*d*, J = 6.3, 2 Me(G_2)); 1.22 (*d*, J = 6.3, Me(G_1)); 1.97–2.04 (*m*, 4 H–C(2)(G_3)); 2.09–2.18 (*m*, 2 H–C(2)(G_2), H–C(2)(G_1)); 2.53 ('*dd*', *ABX*, J = 8.8, 2.9, 2 H), 2.56 ('*dd*', *ABX*, J = 8.7, 2.8, 2 H), 2.60–2.68 (*m*, 3 H), 2.73 ('*dd*', *ABX*, J = 6.1, 2.0, 2 H), 2.77 ('*dd*', *ABX*, J = 6.1, 2.0, 2 H), 2.79–2.86 (*m*, 3 H, $C_6H_4CH_2C(2)$); 3.27

(2*s*, 4 MeO(P)); 3.30 ('*dd*', *ABX*, *J* = 5.8, 3.0, 8 H, $OCH_2C(2)(G_3)$); 3.32, 3.33 (*s*, 4 MeO(P)); 3.36–3.53 (*m*, 4 H–C(3)(G_3), 4 H, $OCH_2C(2)(G_2)$, 2 H, $OCH_2C(2)(G_1)$); 3.68–3.75 (*m*, 2 H–C(3)(G_2), H–C(3)(G_1)); 4.35–4.44 (*m*, 9 H, $OCH_2C_6H_4$); 4.47 (*s*, CH_2Br); 4.54 (*d*, *AB*, *J* = 11.5, 3 H, $OCH_2C_6H_4$); 7.08–7.27 (*m*, 28 arom. H). ^{13}C-NMR (100 MHz): 15.80; 16.66; 16.70; 33.02; 33.19; 33.24; 33.71; 45.68; 46.02; 46.81; 56.49; 58.73; 69.28; 69.34; 70.79; 71.66; 72.91; 74.68; 76.13; 76.16; 127.58; 127.60; 128.97; 129.18; 129.20; 129.64; 135.16; 135.98; 136.10; 136.46; 136.55; 140.23; 140.30; 140.38; 140.45; 141.71. FAB-MS: 1552 (< 1, $[M + 15]^+$), 1315 (< 1), 1236 (< 1), 1093 (< 1), 903 (< 1), 823 (< 1), 770 (< 1), 681 (< 1), 603 (< 1), 221 (18), 189 (100), 175 (23), 161 (40), 157 (48), 145 (32), 131 (60), 117 (69), 103 (50), 91 (29), 71 (23), 59 (70). MALDI-TOF-MS: 1577 ($[M + 38]^+$), 1562 ($[M + 23]^+$). Anal. calc. for $C_{92}H_{129}BrO_{14}$ (1538.93): C 71.80, H 8.45; found: C 72.07, H 8.19.

(MeO)$_{16}$-[G$_3^*$]^2-[G$_{1\,(a)}^*$]^2-OTBDPS (**20**). A soln. of **24** (0.71 g, 1.03 mmol) in THF (20 ml) was added at 0° to a suspension of NaH (149 mg, 6.19 mmol, 6 equiv.), and the resulting mixture heated to reflux for 30 min. Then, **19** (3.97 g, 2.58 mmol, 2.5 equiv.) in THF (27 ml) was slowly added at 0°, and the mixture was kept at reflux for 24 h. Workup as described for **9** and FC (hexane/Et_2O 1:4) gave **20** (3.06 g, 82%) as colorless, very viscous oil. R_f 0.35 (hexane/Et_2O 1:4). $[\alpha]_D^{r.t.} = -7.8$ (*c* = 1.77, $CHCl_3$). IR: 3007*m*, 2931*m*, 2872*m*, 1698*w*, 1608*w*, 1514*w*, 1449*w*, 1377*m*, 1090*s*, 1020*m*, 616*w*. ^{1}H-NMR (500 MHz): 1.09 (*s*, *t*-Bu); 1.14 (*d*, *J* = 6.4, 8 Me(G_4)); 1.21 (*d*, *J* = 6.2, 4 Me(G_3)); 1.22 (*d*, *J* = 6.2, 2 Me(G_2)); 1.23 (*d*, *J* = 6.3, Me(G_1)); 1.97–2.03 (*m*, 8 H–C(2)(G_4)); 2.09–2.18 (*m*, 4 H–C(2)(G_3), 2 H–C(2)(G_2), H–C(2)(G_1)); 2.53 ('*dd*', *ABX*, *J* = 8.8, 3.7, 4 H), 2.56 ('*dd*', *ABX*, *J* = 9.0, 3.9, 4 H), 2.60–2.69 (*m*, 7 H), 2.73 (1*dd*', *ABX*, *J* = 6.1, 2.7, 4 H), 2.76 ('*dd*', *ABX*, *J* = 6.1, 2.7, 4 H), 2.79–2.86 (*m*, 7 H, $C_6H_4CH_2C(2)$); 3.26 (3*s*, 8 MeO(P)); 3.30 ('*dd*', *ABX*, *J* = 5.7, 4.3, 16 H, $OCH_2C(2)(G_4)$); 3.32 (3*s*, 8 MeO(P)); 3.36–3.52 (*m*, 8 H–C(3)(G_4), 8 H, $OCH_2C(2)(G_3)$, 4 H, $OCH_2C(2)(G_2)$, 2 H, $OCH_2C(2)(G_1)$); 3.68–3.74 (*m*, 4 H–C(3)(G_3), 2 H–C(3)(G_2), H–C(3)(G_1)); 4.35–4.46 (*m*, 20 H, $OCH_2C_6H_4$); 4.49–4.59 (*m*, 14 H, $OCH_2C_6H_4$); 4.74 (*s*, CH_2OSi); 7.08–7.42 (*m*, 74 arom. H); 7.69 (*m*, arom. H). ^{13}C-NMR (125 MHz): 15.82; 16.72; 16.74; 19.33; 26.89; 33.04; 33.21; 33.25; 45.70; 46.19; 56.48; 58.72; 65.43; 69.29; 69.43; 70.64; 70.80; 70.84; 71.67; 71.97; 72.02; 72.83; 72.92; 72.95; 74.68; 74.70; 74.78; 74.82; 76.16; 76.18; 125.99; 126.94; 127.59; 127.63; 127.69; 127.80; 127.81; 127.87; 128.58; 129.05; 129.17; 129.19; 129.28; 129.66; 129.84; 129.89; 133.60; 135.60; 135.69; 135.71; 136.12; 136.14; 136.58; 137.48; 137.55; 138.14; 138.49; 138.63; 138.68; 140.23; 140.30; 140.40; 140.63. MALDI-TOF-MS: 3628 ($[M + Na]^+$). Anal. calc. for $C_{228}H_{308}O_{33}Si$ (3605.01): C 75.96, H 8.61; found: C 76.06, H 8.56.

(MeO)$_{16}$-[G$_3^*$]^2-[G$_{1\,(a)}^*$]^2-OH (**21**). As described for **15**, with **20** (3.50 g, 0.97 mmol) and Bu_4NF (0.61 g, 1.94 mmol, 2 equiv.) in THF (65 ml), reaction time 43 h. FC (Et_2O) gave **21** (3.08 g, 94%). Colorless, very viscous oil. R_f 0.33 (Et_2O). MALDI-TOF-MS for $C_{212}H_{290}O_{33}$ (3366.60): 3390 ($[M + Na]^+$).

(MeO)$_{16}$-[G$_3^*$]^2-[G$_{1\,(a)}^*$]^2-Br (**22**). As described for **5**, with **21** (3.08 g, 0.92 mmol), Ph_3P (0.72 g, 2.75 mmol, 3 equiv.), and Br_4C (0.91 g, 2.75 mmol, 3 equiv.), in THF (40 ml), reaction time 19 h. FC (hexane/Et_2O 1:8) gave **22** (2.80 g, 89%). R_f 0.40 (hexane/Et_2O 1:8). MALDI-TOF-MS for $C_{212}H_{289}BrO_{32}$ (3429.50): 3452 ($[M + Na]^+$).

*Methyl 4-{{{(1*R,2*S*)*-2-{4-{[(*tert*-Butyl)diphenylsilyloxy]methyl}benzyl}-3-[4-(methoxycarbonyl)benzyloxy]}-1-methylpropyloxy}methyl}benzoate* (**23**). To NaH (1.84 g, 76.7 mmol) in THF (60 ml) at 0° was added **12** (4.00 g, 8.92 mmol) in THF (40 ml), and the mixture stirred under reflux for 30 min. The suspension was then cooled to 0°, and 4-(bromomethyl)benzoic acid (4.98 g, 23.2 mmol) in THF (40 ml) was added dropwise. After stirring for 24 h at r.t., the suspension was heated under reflux for 1 h and then kept at r.t. overnight. H_2O (50 ml) was carefully added at 0°, the resulting mixture acidified with 10% aq. HCl, and extraction with Et_2O (3 × 200 ml), drying ($MgSO_4$), and evaporation gave a yellow solid. The crude product obtained was diluted in Et_2O (150 ml), and treated with a CH_2N_2 soln. to stand overnight and then carefully evaporated. FC (hexane/Et_2O 2:1) gave **23** (4.19 g, 63%). Colorless, viscous oil. R_f 0.43 (hexane/Et_2O 1:1). $[\alpha]_D^{r.t.} = -9.2$ (*c* = 1.39, $CHCl_3$). IR: 3008*w*, 2954*w*, 2859*w*, 1718*s*, 1614*w*, 1513*w*, 1437*m*, 1377*w*, 1283*s*, 1112*s*, 1020*m*, 968*w*, 616*w*. ^{1}H-NMR (300 MHz): 1.09 (*s*, *t*-Bu); 1.26 (*d*, *J* = 6.3, Me–C(1)); 2.09–2.20 (*m*, H–C(2)); 2.65 ('*dd*', *ABX*, *J* = 13.5, 9.0, 1 H, CH_2–C(2)); 2.83 ('*dd*', *ABX*, *J* = 13.5, 5.9, 1 H, CH_2–C(2)); 3.45 ('*dd*', *ABX*, *J* = 9.3, 5.7, H–C(3)); 3.54 ('*dd*', *ABX*, *J* = 9.3, 5.0, H–C(3)); 3.74 (*m*, H–C(1)); 3.90, 3.91 (*s*, 2 MeO); 4.48, 4.65 (*AB*, *J* = 12.3, $OCH_2C_6H_4$); 4.46 (*s*, $OCH_2C_6H_4$); 4.75 (*s*, CH_2OSi); 7.09–7.46 (*m*, 14 arom. H); 7.68–7.72 (*m*, 4 arom. H); 7.97–8.06 (*m*, 4 arom. H). ^{13}C-NMR (75 MHz): 16.67; 19.35; 26.89; 33.30; 46.36; 52.05; 65.42; 69.47; 70.19; 72.42; 75.05; 126.06; 127.04; 127.28; 127.70; 129.00; 129.19; 129.26; 129.36; 129.47; 129.65; 129.81; 133.60; 135.60; 138.68; 139.37; 143.21; 143.95; 144.44; 166.96. FAB-MS: 744 (15, M^+), 687 (100, $[M - (t\text{-Bu})]^+$), 667 (11), 489 (9), 323 (16), 199 (14), 149 (46), 135 (30), 121 (10), 104 (13). Anal. calc. for $C_{46}H_{52}O_7Si$ (745.00): C 74.16, H 7.04; found: C 74.30, H 7.03.

*4-{{{(1*R,2*S*)*-2-{4-{[(*tert*-Butyl)diphenylsilyloxy]methyl}benzyl}-3-[4-(hydroxymethyl)benzyloxy]-1-methylpropyloxy}methyl}benzenemethanol* (**24**). To an ice-cold suspension of LAH (1.07 g, 28.1 mmol, 5 equiv.) in THF (50 ml) was added **23** (4.19 g, 5.62 mmol) in THF (50 ml). The mixture was stirred at 0° and then allowed to warm

to r.t. during 5 h. After cooling to 0°, H_2O (1.07 ml), 15% aq. NaOH (1.07 ml) and H_2O (3.21 ml) were added consecutively, and the resulting mixture was stirred vigorously until a white precipitate formed. Addition of $MgSO_4$, filtration and evaporation of the volatiles yielded a colorless, viscous oil. FC (Et_2O) gave pure diol **24** (3.48 g, 90%). R_f 0.36 (Et_2O). $[\alpha]_D^{r.t.} = -4.6$ ($c = 1.36$, $CHCl_3$). IR: 3606*w*, 3434 (br.), 3052*w*, 3008*m*, 2932*m*, 2860*m*, 1514*w*, 1472*w*, 1428*m*, 1377*m*, 1112*s*, 1085*s*, 1019*m*, 608*w*. ^{1}H-NMR (300 MHz): 1.09 (*s*, *t*-Bu); 1.24 (*d*, $J = 6.3$, Me–C(1)); 1.80–1.89 (br. *s*, 2 OH); 2.09 (*m*, H–C(2)); 2.62 ('*dd*', *ABX*, $J = 13.6$, 9.2, 1 H, $C_6H_4CH_2C(2)$); 2.81 ('*dd*', *ABX*, $J = 13.4$, 5.7, 1 H, $C_6H_4CH_2C(2)$); 3.38 ('*dd*', *ABX*, $J = 9.3$, 5.5, H–C(3)); 3.52 ('*dd*', *ABX*, $J = 9.3$, 4.8, H–C(3)); 3.67–3.74 (*m*, H–C(1)); 4.40 (*s*, $OCH_2C_6H_4$); 4.42, 4.59 (*AB*, $J = 11.8$, $OCH_2C_6H_4$); 4.61–4.68 (br. *s*, 2 CH_2OH); 4.75 (*s*, CH_2OSi); 7.10 (*d*, $J = 8.1$, 2 arom. H); 7.21–7.46 (*m*, 16 arom. H); 7.68–7.73 (*m*, 4 arom. H). ^{13}C-NMR (75 MHz): 16.70; 19.36; 26.90; 33.22; 46.32; 65.15; 65.45; 68.98; 70.42; 72.69; 74.51; 126.00; 126.99; 127.70; 129.06; 129.68; 133.63; 135.63; 138.19; 138.55; 138.61; 129.59; 140.04; 140.10. FAB-MS: 687 (40, $[M - 1]^+$), 672 (17), 629 (8), 567 (26), 415 (60), 223 (9), 199 (35), 181 (21), 175 (16), 145 (13), 135 (53), 121 (100). Anal. calc. for $C_{44}H_{52}O_5Si$ (688.98): C 76.71, H 7.61; found: C 76.89, H 7.51.

(MeO)$_{32}$-[G$_3^*$]^2-[G$_{2\,(a)}^*$]^2-OTBDPS (**25**). A soln. of **24** (62.1 mg, 90 µmol) in THF (4 ml) was added at 0° to a suspension of NaH (13 mg, 0.54 mmol, 6 equiv.), and the resulting mixture stirred at r.t. for 1 h. Then, **22** (0.77 g, 0.23 mmol, 2.5 equiv.) in THF (4 ml) was slowly added at 0°, and the mixture was kept at reflux for 20 h. After stirring at r.t. for 20 h, the light-yellow suspension was worked up as usual and FC (hexane/Et_2O 1:10) gave **25** (645 mg, 97%) as colorless, very viscous oil. R_f 0.28 (hexane/Et_2O 1:10). MALDI-TOF-MS for $C_{468}H_{628}O_{69}Si$ (7386.15): 7446 ($[M + 69]^+$), 7409 ($[M + Na]^+$).

(MeO)$_{32}$-[G$_3^*$]^2-[G$_{2\,(a)}^*$]^2-OH (**26**). As described for **15**, with **25** (645 mg, 87 µmol) and Bu_4NF (110 mg, 0.35 mmol, 4 equiv.) in THF (15 ml), reaction time 63 h. FC (hexane/Et_2O 1:10) gave **26** (470 mg, 75%). Colorless, very viscous oil. R_f 0.31 (Et_2). $[\alpha]_D^{r.t.} = -9.6$ ($c = 1.32$, $CHCl_3$). IR: 3456 (br.), 3007*s*, 2930*s*, 2872*s*, 1908*w*, 1805*w*, 1615*w*, 1514*m*, 1449*m*, 1420*w*, 1377*m*, 1090*vs*, 1021*m*, 624*w*. ^{1}H-NMR (500 MHz): 1.14 (*d*, $J = 6.4$, 16 Me(G_5)); 1.20–1.23 (*m*, 8 Me(G_4), 4 Me(G_3), 2 Me(G_2), Me(G_1)); 1.96–2.04 (*m*, 16 H–C(2)(G_5)); 2.09–2.17 (*m*, 8 H–C(2)(G_4), 4 H–C(2)(G_3), 2 H–C(2)(G_2), H–C(2)(G_1)); 2.53 ('*dd*', *ABX*, $J = 8.8$, 3.7, 8 H), 2.56 ('*dd*', *ABX*, $J = 8.7$, 3.6, 8 H), 2.60–2.69 (*m*, 15 H), 2.73 ('*dd*', *ABX*, $J = 6.1$, 2.7, 8 H), 2.76 ('*dd*', *ABX*, $J = 6.1$, 2.6, 8 H), 2.79–2.86 (*m*, 15 H, $C_6H_4CH_2C(2)$); 3.26 (3*s*, 16 MeO(P)); 3.30 ('*dd*', *ABX*, $J = 5.7$, 4.3, 32 H, $OCH_2C(2)(G_5)$); 3.32 (3*s*, 16 MeO(P)); 3.37–3.52 (*m*, 16 H–C(3)(G_5), 16 H, $OCH_2C(2)(G_4)$, 8 H, $OCH_2C(2)(G_3)$, 4 H, $OCH_2C(2)(G_2)$, 2 H, $OCH_2C(2)(G_1)$); 3.68–3.74 (*m*, 8H–C(3)(G_4), 4 H–C(3)(G_3), 2 H–C(3)(G_2), H–C(3)(G_1)); 4.35–4.60 (*m*, 86 H, 42 $OCH_2C_6H_4$, CH_2OH); 7.07–7.35 (*m*, 148 arom. H). ^{13}C-NMR (125 MHz): 15.81; 16.68; 16.72; 16.74; 33.04; 33.21; 33.25; 45.69; 46.19; 46.23; 56.48; 58.72; 65.10; 69.29; 69.37; 69.41; 70.59; 70.64; 70.79; 70.83; 71.67; 72.01; 72.07; 72.83; 72.91; 72.95; 74.68; 74.69; 74.72; 74.77; 76.15; 76.18; 127.04; 127.31; 127.59; 127.64; 127.65; 127.79; 127.81; 127.87; 128.22; 128.58; 129.17; 129.19, 129.28; 129.34; 129.81; 135.66; 135.69; 135.71; 136.12; 136.13; 136.58; 137.48; 137.51; 137.55; 138.05; 138.11; 138.44; 138.56; 138.61; 140.23; 140.29; 140.30; 140.32; 140.39; 140.49; 140.59; 140.62; 140.63. MALDI-TOF-MS: 7207 ($[M + 59]^+$), 7171 ($[M + 23]^+$). Anal. calc. for $C_{452}H_{610}O_{69}$ (7147.75): C 75.95, H 8.60; found: C 75.95, H 8.72.

(MeO)$_6$-{[G$_3^*$]^2]}$_3$-[C$_a$] (**30**). To NaH (293 mg, 12.2 mmol, 9 equiv.) in THF (15 ml) at 0° was added dropwise *via* syringe **27** (0.73 g, 1.36 mmol) in THF (15 ml), and the mixture stirred at r.t. for 1.5 h, then cooled to 0° and treated with **11** (1.43 g, 4.76 mmol, 3.5 equiv.) in THF (20 ml). The suspension was stirred at r.t. for 1 h, then at reflux for 4 h and at r.t. overnight. Workup as described for **9** and FC (hexane/Et_2O 1:1) gave **30** (1.24 g, 76%). Colorless, viscous oil. R_f 0.16 (hexane/Et_2O 1:1). $[\alpha]_D^{r.t.} = +6.2$ ($c = 1.01$, $CHCl_3$). IR: 3006*m*, 2928*s*, 2855*s*, 1634*s*, 1455*m*, 1446*m*, 1367*w*, 1313*w*, 1057*m*, 1034*m*, 895*w*, 625*w*. CD (MeCN) ($\cdot 10^3$): 4.12 (206.3), −1.82 (213.6), −3.59 (218.0), 1.53 (221.0), −1.51 (224.5), 5.18 (229.5). ^{1}H-NMR (400 MHz): 0.94 (*s*, *t*-Bu); 1.15 (*d*, $J = 6.4$, 3 Me(G_1)); 1.28 (*d*, $J = 6.4$, Me(C)); 1.97–2.04 (*m*, 3 H–C(2)(G_1)); 2.28–2.32 (*m*, H–C(3)(C)); 2.56 ('*dd*', *ABX*, $J = 13.5$, 8.7, 3 H, $C_6H_4CH_2C(2)(G_1)$); 2.75 ('*dd*', *ABX*, $J = 13.5$, 6.2, 3 H, $C_6H_4CH_2C(2)(G_1)$); 3.20 (*d*, $J = 1.9$, H–C(4)(C); 3.37–3.54 (*m*, 3 H–C(3)(G_1), 6 H, $OCH_2C(2)$); 3.57 ('*dd*', *ABX*, $J = 10.0$, 8.7, 1 H, $CH_2(C)$); 3.70–3.76 (*m*, H–C(2)(C)); 3.79 ('*dd*', *ABX*, $J = 10.1$, 3.5, 1 H, $CH_2(C)$); 4.39–4.65 (*m*, 9 $OCH_2C_6H_4$); 7.14–7.33 (*m*, 24 arom. H). ^{13}C-NMR (100 MHz): 15.82; 16.62; 26.35; 26.57; 33.07; 37.44; 44.75; 45.71; 56.49; 58.73; 68.38; 70.60; 71.68; 71.90; 71.99; 72.05; 72.88; 73.66; 76.17; 76.23; 77.23; 86.16; 127.02; 127.64; 127.66; 127.77; 127.79; 127.83; 127.88; 129.28; 135.70; 135.72; 135.75; 137.04; 137.40; 137.46; 138.37; 138.49; 139.05; 140.53; 140.55. FAB-MS: 1210 (26, $[M + 14]^+$). MALDI-TOF-MS: 1221 ($[M + Na]^+$), 1237 ($[M + K]^+$). Anal. calc. for $C_{75}H_{104}O_{12}$ (1197.64): C 75.22, H 8.75; found: C 75.25, H 8.77.

(MeO)$_{12}$-{[G$_2^*$]^2}$_3$-[C$_a$] (**31**). To NaH (130 mg, 5.40 mmol, 9 equiv.) in THF (10 ml) at 0° was added dropwise *via* syringe **27** (322 mg, 0.60 mmol) in THF (12 ml), and the mixture heated to reflux for 30 min. Then, **16** (1.50 g, 2.10 mmol, 3.5 equiv.) in THF (12 ml) was slowly added at 0°, and the mixture kept at reflux for 15 h. Workup of the white suspension as described for **9** and FC (hexane/Et_2O 1:3) gave **31** (1.29 g, 88%) as colorless,

viscous oil. R_f 0.16 (hexane/Et_2O 1:2). $[\alpha]_D^{r.t.} = +3.8$ ($c = 1.00$, $CHCl_3$). IR: 3009*m*, 2977*m*, 2934*m*, 2872*m*, 1721*w*, 1514*w*, 1450*w*, 1378*w*, 1362*w*, 1091*s*, 1021*w*. CD (MeCN) ($\cdot 10^3$): −16.83 (205.9), −5.80 (215.1), 2.03 (217.9), 8.94 (222.6), −7.05 (227.2). ^{1}H-NMR (400 MHz): 0.94 (*s*, *t*-Bu); 1.14 (*d*, $J = 6.3$, 6 Me(G_2)); 1.21 (*d*, $J = 6.3$, 3 Me(G_1)); 1.29 (*d*, $J = 6.4$, Me(C)); 1.97–2.04 (*m*, 6 H–C(2)(G_2)); 2.08–2.16 (*m*, 3H–C(2)(G_1)); 2.29–2.35 (*m*, H–C(3)(C)); 2.53 ('*dd*', *ABX*, $J = 8.8, 3.0$, 3 H), 2.63 ('*dd*', *ABX*, $J = 13.6, 9.0$, 3 H), 2.72 ('*dd*', *ABX*, $J = 6.1, 2.4$, 3 H), 2.76 ('*dd*', *ABX*, $J = 6.1, 2.3$, 3 H), 2.81 ('*dd*', *ABX*, $J = 13.5, 5.9$, 3 H, $C_6H_4CH_2C(2)$); 3.22 (*d*, $J = 1.8$, H–C(4)(C)); 3.26, 3.27 (*s*, 6 MeO(P)); 3.30 ('*dd*', *ABX*, $J = 5.8, 3.2$, 12 H, $OCH_2C(2)(G_2)$); 3.32 (2*s*, 6 MeO(P)); 3.37–3.52 (*m*, 6 H–C(3)(G_2), 6 H, $OCH_2C(2)(G_1)$); 3.57 ('*dd*', *ABX*, $J = 9.8$, 9.0, 1 H, $CH_2(C)$); 3.68–3.75 (*m*, 3 H–C(3)(G_1), H–C(2)(C)); 3.80 ('*dd*', *ABX*, $J = 10.1$, 3.4, 1 H, $CH_2(C)$); 4.34–4.66 (*m*, 15 $OCH_2C_6H_4$); 7.10–7.35 (*m*, 48 arom. H). ^{13}C-NMR (100 MHz): 15.82; 16.56; 16.72; 26.73; 33.04; 33.24; 37.46; 44.66; 45.69; 46.20; 56.49; 58.73; 68.17; 68.45; 69.29; 70.59; 70.80; 71.68; 71.91; 72.00; 72.05; 72.92; 73.65; 74.68; 76.16; 76.19; 86.01; 127.01; 127.60; 127.66; 127.76; 127.87; 128.81; 129.11; 129.18; 129.20; 129.27; 130.89; 135.68; 135.69; 135.72; 136.11; 136.57; 137.05; 137.40; 137.45; 138.36; 138.48; 139.04; 140.24; 140.31; 140.61. FAB-MS: 2458 (< 1, $[M + 24]^+$), 2448 (< 1, $[M + 15]^+$), 391 (5), 221 (11), 189 (100), 175 (16), 157 (36), 149 (31), 131 (46), 117 (59), 104 (46), 91 (28), 59 (70). MALDI-TOF-MS: 2474 ($[M + 39]^+$), 2458 ($[M + 23]^+$). Anal. calc. for $C_{153}H_{212}O_{24}$ (2435.34): C 75.46, H 8.77; found: C 75.81, H 8.56.

(MeO)$_{24}$-{[G$_3^*$]^2}$_3$-[C$_a$] (**32**). As described for **31**, with **27** (34.9 mg, 65 μmol), NaH (14.0 mg, 0.59 mmol, 9 equiv.) and **19** (500 mg, 0.32 mmol, 5 equiv.) in THF (3 ml, 4 ml, 4 ml). The pale-beige suspension was kept at reflux for 36 h and stirred at r.t. for 26 h. FC (hexane/Et_2O 1:4) gave **32** (296 mg, 93%). Colorless, very viscous oil. R_f 0.23 (hexane/Et_2O 1:4). R_f 0.34 (hexane/acetone 7:3). $[\alpha]_D^{r.t.} = -5.0$ ($c = 1.03$, $CHCl_3$). IR: 3009*s*, 2978*m*, 2933*m*, 2872*m*, 1706*w*, 1615*w*, 1514*w*, 1449*w*, 1420*w*, 1378*w*, 1364*w*, 1090*s*, 1021*w*, 949*w*, 897*w*, 846*w*, 628*w*. CD (MeCN) ($\cdot 10^3$): 14.60 (209.2), 8.47 (217.4), 14.51 (222.4), −7.11 (230.9). ^{1}H-NMR (500 MHz): 0.94 (*s*, *t*-Bu); 1.14 (*d*, $J = 6.4$, 12 Me(G_3)); 1.19–1.23 (*m*, 6 Me(G_2), 3 Me(G_1)); 1.29 (*d*, $J = 6.4$, Me(C)); 1.97–2.03 (*m*, 12 H–C(2)(G_3)); 2.09–2.17 (*m*, 6 H–C(2)(G_2), 3 H–C(2)(G_1)); 2.31–2.36 (*m*, H–C(3)(C)); 2.53 ('*dd*', *ABX*, $J = 8.7, 3.6$, 6 H), 2.56 ('*dd*', *ABX*, $J = 9.0, 3.9$, 6 H), 2.60–2.69 (*m*, 9 H), 2.73 ('*dd*', *ABX*, $J = 6.1, 2.6$, 6 H), 2.75 ('*dd*', *ABX*, $J = 6.1, 2.7$, 6 H), 2.80–2.86 (*m*, 9 H, $C_6H_4CH_2C(2)$); 3.22 (*d*, $J = 1.6$, H–C(4)(C)); 3.26 (3*s*, 12 MeO(P)); 3.28–3.32 (*m*, 24 H–C(1)(G_3)); 3.32 (3*s*, 12 MeO(P)); 3.36–3.53 (*m*, 12 H–C(3)(G_3), 6 H, $OCH_2C(2)(G_1)$, 12 H, $OCH_2C(2)(G_2)$); 3.57 ('*dd*', *ABX*, $J = 9.8$, 9.0, 1 H, $CH_2(C)$); 3.69–3.75 (*m*, 6 H–C(3)(G_2), 3 H–C(3)(G_1), H–C(2)(C)); 3.80 ('*dd*', *ABX*, $J = 10.0$, 3.2, 1 H, $CH_2(C)$); 4.34–4.66 (*m*, 27 $OCH_2C_6H_4$); 7.10–7.34 (*m*, 96 arom. H). ^{13}C-NMR (125 MHz): 14.12; 15.81; 16.48; 16.72; 16.75; 22.66; 26.38; 33.04; 33.21; 37.48; 44.58; 45.70; 46.19; 56.48; 58.72; 68.54; 69.29; 69.41; 70.59; 70.80; 70.84; 71.67; 71.94; 72.03; 72.08; 72.92; 72.95; 73.63; 74.68; 74.78; 76.03; 76.16; 76.18; 85.85; 127.00; 127.56; 127.59; 127.65; 127.74; 127.76; 127.87; 129.17; 129.19; 129.28; 135.70; 136.12; 136.13; 136.58; 137.06; 137.41; 137.44; 138.36; 138.48; 139.03; 140.23; 140.30; 140.39; 140.61. VPO ($c = 5.463$ g/kg in CH_2CCl_2): 4569 ± 2%. MALDI-TOF-MS: 4934 ($[M + Na]^+$). Anal. calc. for $C_{309}H_{428}O_{48}$ (4910.75): C 75.58, H 8.78; found: C 75.31, H 8.72.

(MeO)$_{48}$-{[G$_3^*$]^2-[G$_{1\,(a)}^*$]^2}$_3$-[C$_a$] (**33**). To NaH (28.0 mg, 1.17 mmol, 9 equiv.) in THF (7 ml) was added dropwise *via* syringe **27** (69.6 mg, 0.13 mmol) in THF (8 ml), and the mixture stirred at r.t. for 1 h. Then, **22** (2.0 g, 0.58 mmol, 4.5 equiv.) in THF (11 ml) was slowly added at 0°, and the mixture kept at reflux for 31 h. Workup of the white suspension as described for **9** and FC (hexane/acetone 5:2 → 7:3) gave **33** (1.09 g, 79%) as colorless, very viscous oil. A second FC (3 × 90 cm column, hexane/acetone 5:2) afforded anal. pure **33** (915 mg, 67%). R_f 0.24 (hexane/acetone 7:3). $[\alpha]_D^{r.t.} = -8.2$ ($c = 1.28$, $CHCl_3$). IR: 3008*s*, 2976*m*, 2930*m*, 2872*m*, 1908*w*, 1733*w*, 1615*w*, 1514*w*, 1449*w*, 1420*w*, 1377*w*, 1090*vs*, 1020*w*, 634*w*. ^{1}H-NMR (500 MHz): 0.94 (*s*, *t*-Bu); 1.14 (*d*, $J = 6.4$, 24 Me(G_4)); 1.21, 1.22 (2*d*, $J = 6.3$, 12 Me(G_3), 6 Me(G_2), 3 Me(G_1)); 1.29 (*d*, $J = 6.4$, Me(C)); 1.97–2.04 (*m*, 24 H–C(2)(G_4)); 2.09–2.17 (*m*, 12 H–C(2)(G_3), 6 H–C(2)(G_2), 3H–C(2)(G_1)); 2.32–2.37 (*m*, H–C(3)(C)); 2.53 ('*dd*', *ABX*, $J = 8.7$, 3.6, 12 H), 2.56 ('*dd*', *ABX*, $J = 8.7$, 3.6, 12 H), 2.60–2.69 (*m*, 21 H), 2.73 ('*dd*', *ABX*, $J = 6.1, 2.7$, 12 H), 2.75 ('*dd*', *ABX*, $J = 6.0, 2.7$, 12 H), 2.80–2.86 (*m*, 21 H, $C_6H_4CH_2C(2)$); 3.26 (3*s*, 24 MeO(P)); 3.28–3.32 (*m*, 48 H, $OCH_2C(2)(G_4)$, H–C(4)(C)); 3.32 (3*s*, 24 MeO(P)); 3.36–3.53 (*m*, 24 H, $OCH_2C(2)(G_3)$, 12 H, $OCH_2C(2)(G_2)$, 6 H, $OCH_2C(2)(G_1)$, 24 H–C(3)(G_4)); 3.54–3.59 (*m*, 1 H, $CH_2(C)$); 3.69–3.74 (*m*, 12 H–C(3)(G_3), 6 H–C(3)(G_2), 3 H–C(3)(G_1)); 3.75–3.79 (*m*, H–C(2)(C)); 3.80–3.83 (*m*, 1 H, $CH_2(C)$); 4.34–4.67 (*m*, 63 $OCH_2C_6H_4$); 7.10–7.35 (*m*, 216 arom. H). ^{13}C-NMR (125 MHz): 15.81; 16.45; 16.72; 16.75; 26.38; 33.03; 33.20; 33.25; 37.48; 44.54; 45.69; 46.19; 46.25; 56.48; 58.72; 68.56; 69.28; 69.33; 69.39; 70.59; 70.65; 70.79; 70.83; 71.66; 71.98; 72.02; 72.04; 72.83; 72.91; 72.94; 73.62; 74.67; 74.68; 74.76; 76.00; 76.15; 76.17; 85.79; 126.99; 127.33; 127.58; 127.65; 127.73; 127.75; 127.78; 127.80; 127.86; 128.21; 128.54; 128.97; 129.17; 129.18; 129.27; 129.79; 135.69; 135.71; 135.74; 136.11; 136.13; 136.57; 137.06; 137.41; 137.44; 137.47; 137.55; 138.12; 138.35; 138.47; 138.61; 139.03; 140.22; 140.29; 140.30; 140.39; 140.55; 140.61; 140.62. MALDI-TOF-MS: 10605 ($[M + Na]^+$). Anal. calc. for $C_{669}H_{908}O_{102}$ (10582.47): C 75.93, H 8.65; found: C 75.80, H 8.41.

X-Ray Crystal-Structure Analysis of ($C_{33}H_{42}O_4Si$). Determination of the cell parameters and collection of the reflection intensities were performed on an *Picker-Stoe* four-circle diffractometer (graphite monochromatized MoK_α radiation, $\lambda = 0.71073$ Å). Colorless prism, $0.5 \times 0.5 \times 0.5$ mm, orthorhombic, space group $P2_12_12_1$, $a = 10.316(11)$, Å, $b = 19.16(3)$ Å, $c = 31.53(4)$ Å, $V = 6234(13)$ Å^3, $Z = 8$, $\rho_{calc.} = 1.041$ gcm^{-3}, $\mu = 0.105$ mm^{-1}, $F(000) = 1952$. Number of reflections measured 3321 ($\omega/2\theta$ scan, $3 < 2\theta < 40°$, T 293 K); 3294 unique reflections, which were used for the determination (direct methods, SHELXTL PLUS). SHELXS-93 was used for structure refinement (full-matrix least squares). The non-H-atoms were refined anisotropically, the H-atoms were added to the molecule with constant isotropic temp. factors on idealized positions and refined according to the riding model. The refinement converged at $R = 0.0786$ ($wR^2 = 0.0859$), min. and max. rest electron density 0.27, -0.24 eÅ^{-3}, number of variables 685.

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