119. Synthesis and Properties of First and Second Generation Chiral Dendrimers with Triply Branched Units: A Spectacular Case of Diastereoselectivity[1])

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Dedicated to Professor *Oskar Jeger* on the occasion of his 80th birthday

(27. V. 97)

Chiral triols (which may be considered as derivatives of tris(hydroxymethyl)methane), without (**3**–**5**) and with aliphatic (**6**) or aromatic (**7**) elongating units, and the 1st- and 2nd-generation benzylic branched bromides, **17**, **18**, **23**, **24**, **29**, and **30** are subjected to *Williamson* etherification conditions (NaH in THF). This gave the first 'fully chiral' dendrimers, with triple branching and with a stereogenic center at each and every branching point (including the central building block; see **33**–**42**, **44**, and **46**–**49**). Higher than 2nd-generation dendrimers of this type could not be prepared. Certain combinations of diastereoisomeric 2nd-generation branched bromides, **23**, **24**, **29**, and **30**, and enantiomeric center-piece triols, **3** and **4**, would smoothly react to give the desired dendrimers (*e.g.*, **44**, and **46**–**49**) and others would not, with the reactions stopping at the dendritic alcohols containing only two branches (*e.g.*, **45**, and **50**–**53**; see *Schemes 4* and *5*). Considering the distance at which the intermediate diastereoisomeric 'doubly coupled' dendritic alcohols differ in their configuration, this diastereodifferentiation or molecular recognition phenomenon (discovered by trying to prepare only 8 out of 2^{39} possible diastereoisomers!) is a most surprising result. All compounds were fully characterized, and the 2nd-generation dendrimers, *e.g.*, **38**, **40**, and **47** with and without elongation were shown to be monodisperse and without defects, by MALDI-TOF mass spectroscopy (*cf. Fig. 4*). A simple, unambiguous nomenclature for identification of the novel dendritic compounds is proposed and applied in the *Exper. Part.*

1. Introduction. – Dendrimers are well-defined highly branched macromolecules of nanoscopic dimensions, emanating from a central core with a branching point at each monomer unit [3]. The interior building blocks are arranged in layers, called 'generations', giving a highly symmetrical, fractal-like architecture to the dendrimer. As a result of the high degree of branching, high-generation dendrimers should adopt a globular shape with cavities inside the superstructure, in the absence of chain entanglements. To date, several syntheses of different types of dendrimers and also potential applications have appeared in the literature. Dendrimers are prepared by using multi-step iterative syntheses either by a divergent or a convergent route and with purification after each step. However, only the convergent approach permits the synthesis of monodisperse,

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

[2]) Part of the Dissertation (No. 12001) of *P.K.M.*, 1996, and of the projected Dissertation of *G.G.*, ETH-Zürich.

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unimolecular high-generation dendrimers[4]). The investigations of physical and material properties are continuing[5]).

Our research in this area aims at the synthesis and study of the physical and chemical properties of *chiral* dendrimers. We are especially interested in the influence of chiral building blocks on the overall shape of the structure, and in the chiroptical properties which may indicate chiral secondary structures within the dendrimer. Because of their well-defined molecular weight and structure, one can expect that chiral dendrimers could be useful as model compounds for disordered and semi-ordered chiral structures (polymers, oligomers, aggregates, clusters, liquid crystals, and other supramolecular structures). Low-generation chiral dendrimers with readily accessible cavities might be used as catalysts or for processes requiring so-called chiral recognition.

We have already reported synthetic accesses to chiral derivatives of 'tris(hydroxymethyl)methanes' [12] which were prepared from PHB[6]) (**1**) through the dioxanone **2** [14] [15], by aldol addition [16–18], reduction to triols **3**–**5** [17–19] which, in turn, could be converted to triols with better separated functional groups (see **6** and **7** [20]). The triols **3**, **6**, and **7** were used as chiral central units of dendrimers with achiral *Fréchet* branches [20] [21]. More recently, we have also prepared CO_2H-functionalized dendrimers from (*R*)-hydroxybutanoic and benzene-1,3,5-tricarboxylic acid [22], and we have attached TADDOL[7]) moieties to dendrimers [24].

Chiral dendritic structures or achiral dendrimers containing on the surface amino acid [25], carbohydrate [26], or nucleotide building blocks [27] have been prepared by other groups. In this paper, we describe the convergent [21] synthesis of what we loosly call 'fully chiral dendrimers', *i.e.*, 1st- and 2nd-generation dendrimers containing a chiral central core and chiral triple branching units, and we report a most surprising diastereoselectivity of the reactions used for coupling dendrons with cores[8]).

2. Synthesis of the Chiral Branch Building Blocks. – For the construction of the branches, we chose triols **11** and **12** with an additional benzylic functional group (*Scheme 1*). All coupling reactions would then be carried out using a *Williamson* etherification with benzylic bromides. For the protection of the benzylic OH group, we found the (*t*-Bu)Ph_2Si group (TBDPS) [30] to be most suitable; it is very stable under the conditions of all the reactions to be performed previous to the transformation providing the bromide; it can be cleaved under mild conditions (Bu_4NF, 20°, THF), even from high-molecular-weight synthetic intermediates.

As outlined in *Scheme 1*, the triols **11** and **12** were prepared by the aldol addition of the enolate from dioxanone **2** to the benzaldehyde derivative **8**, which, in turn, is readily

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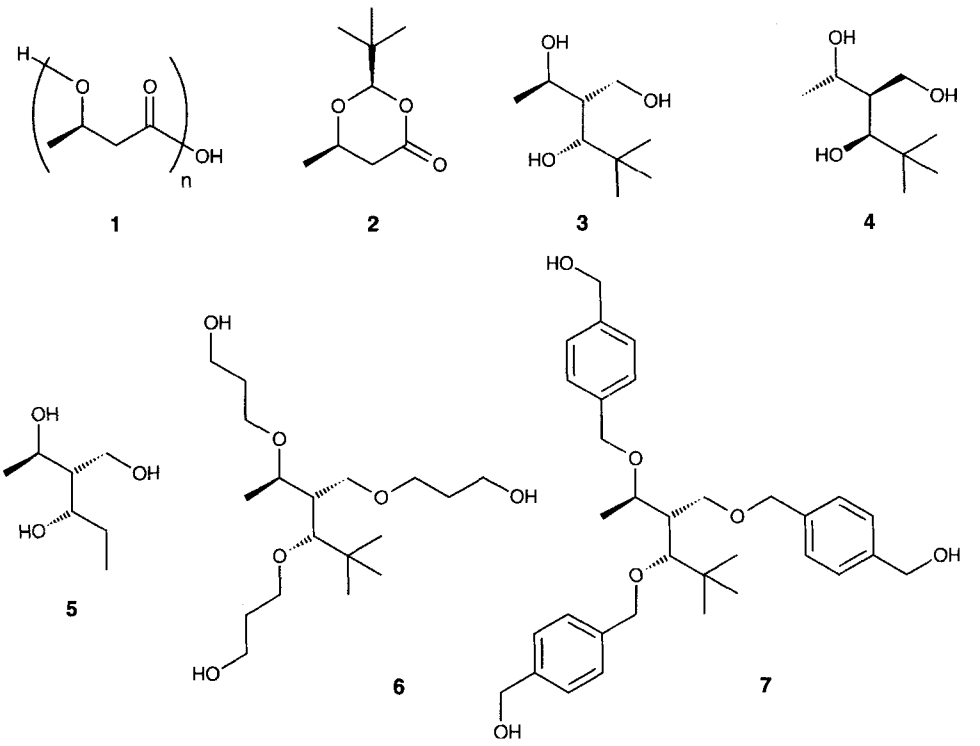
[4]) For representative review articles, see [4].

[5]) Measurements of NMR relaxation parameters [5]; small-angle neutron scattering [6]; rheological [7], photophysical [8], neutron-reflectivity [9] investigations; effects of molecular size and structure on physical properties [10]; theoretical calculations of dendrimer structures [11].

[6]) Poly[(*R*)-3-hydroxybutanoic acid]; for review articles, see [13].

[7]) α,α,α′,α′-*T*etra*a*ryl-1,3-*d*ioxolane-4,5-*d*imetha*n*ol derivatives form chiral *Lewis* acids with TiX_4, useful for enantioselective catalysis (for a review article, see [23]).

[8]) Independent efforts by *Chow et al.* [28], of *K. B. Sharpless* and coworkers [29a] and *McElkanon* and *McGrath* [29b] have led to dendrimers with achiral core and chiral branching units which – like ours – were taken from the pool of chiral building blocks (tartaric acid) or generated by asymmetric dihydroxylation.



available from commercial starting materials (benzene-1,4-dimethanol or 4-formylphenyl acetate, see *Exper. Part*)[9]). As with other aromatic aldehydes, the aldol addition occurs with poor diastereoselectivity, affording a 1.25:1 mixture of the (1′*S*)- and (1′*R*)-isomers **9** and **10**, respectively, separable by medium-pressure liquid chromatography (MPLC), in an overall yield of 86% (10–20-g scale). Configurational assignment of **9** and **10** was originally based on comparative NMR analysis and has been confirmed by X-ray crystal-structure analysis of **9** (*Fig. 1* [31]).

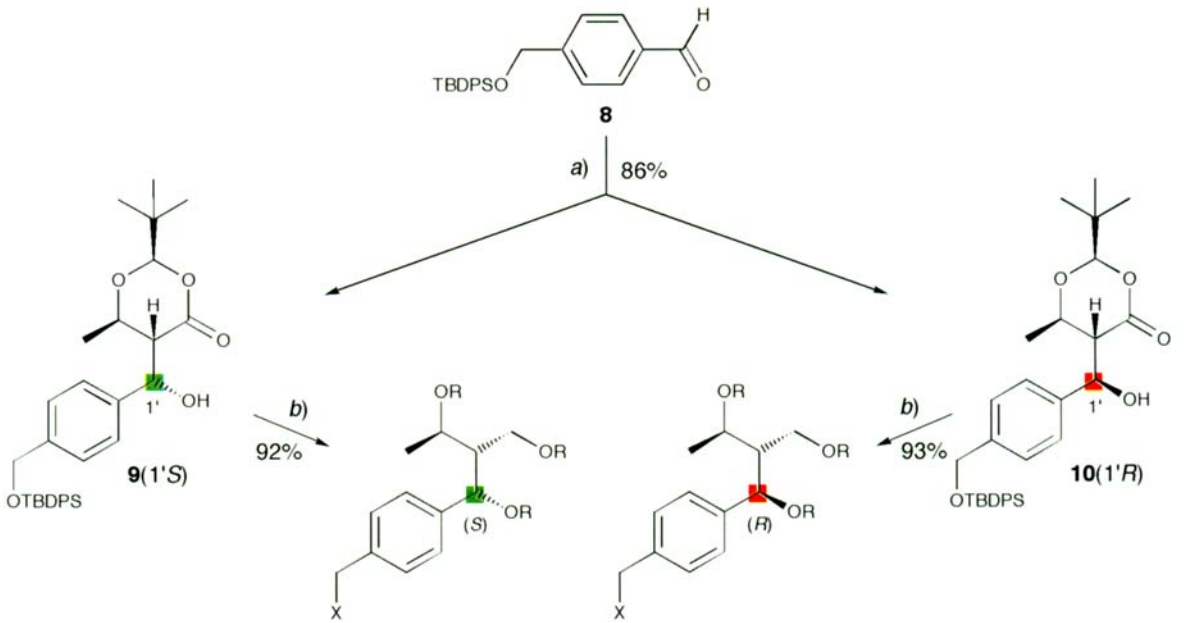
The reduction of the epimeric dioxanones **9** and **10** was easily performed with $NaBH_4$ in THF/MeOH 20:1 [32] and furnished triols **11**(*S*) and **12**(*R*)[10]), respectively, as viscous oils in 90%[11]) yield after flash chromatography. Etherification with MeI afforded the peripheral building blocks (**13**(*S*) and **14**(*R*)), and subsequent removal of the (*t*-Bu)Ph_2Si groups gave the benzylic alcohols **15**(*S*) and **16**(*R*), respectively, in almost quantitative yields. Conversion to the bromides proceeded smoothly upon treatment with Ph_3P/Br_4C

[9]) The route starting from the diol is described herein. It turned out that the route starting from the formyl ester is superior; details will be given in a forthcoming paper on dendritic TADDOLs [31].

[10]) From here on we use (*R*) and (*S*) to identify the diastereoisomers with the corresponding configuration at the benzylic positions. The configurations at the other two stereocenters are identical in all compounds described herein (they were all prepared from (*R*)-3-hydroxybutanoic acid!).

[11]) With $LiAlH_4$, almost complete loss of the (*t*-Bu)Ph_2Si group is observed in large-scale runs.

Scheme 1. *Syntheses of the 1st-Generation Benzylic Bromides* **17** *(*S*) and* **18** *(*R*)*. As in the following *Schemes* and *Figures*, the positions with benzylic (*S*)-configuration, are marked in green, those with (*R*)-configuration in red.



a) LDA, **2**, THF, −78°, 3 h; MPLC separation. *b*) $NaBH_4$, THF/MeOH 20:1, 0° → r.t., 20 h. *c*) NaH, MeI, THF, reflux, 3 h, yields > 95%. *d*) $Bu_4NF \cdot 3H_2O$, THF, r.t., 24 h, yields > 98%. *e*) Ph_3P, Br_4C, THF, r.t., 3 h, yields *ca.* 90%.

(THF/20°) [33], providing the 1st-generation benzylic bromides, **17**(*S*) and **18**(*R*), respectively, in 90% yield.

To further elaborate the branches, the bromides **17**(*S*) and **18**(*R*) were used for etherification of the OH groups of the corresponding triols **11**(*S*) and **12**(*R*). At first, we combined only components of *like* configuration at the benzylic centers (*Scheme 2*).

The coupling reactions were carried out with an excess (3.5 equiv.) of bromide under classical *Williamson* etherification conditions (NaH, THF, reflux) and yielded 59–64% of the 2nd-generation (*t*-Bu)Ph_2Si-protected alcohols **19**(*S*) and **20**(*R*). NMR and FAB-MS analyses of these dendrons gave no indication of impurities with defects that

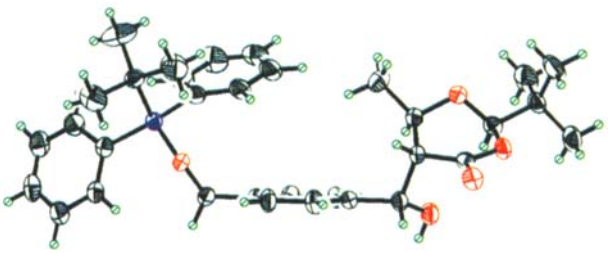


Fig. 1. *ORTEP Representation of dioxanone* (**9**; (5*S*,6*R*,1′*S*)-configuration). The thermal elipsoids are drawn to the 30% probability level. The X-ray structure was determined by *Rheiner* [31].

would have arisen from incomplete coupling. Cleavage of the (*t*-Bu)Ph_2Si groups (→ **21**(*S*) and **22**(*R*), resp.) and OH/Br substitution as described above furnished the 2nd-generation benzylic bromides **23**(*S*) and **24**(*R*), respectively.

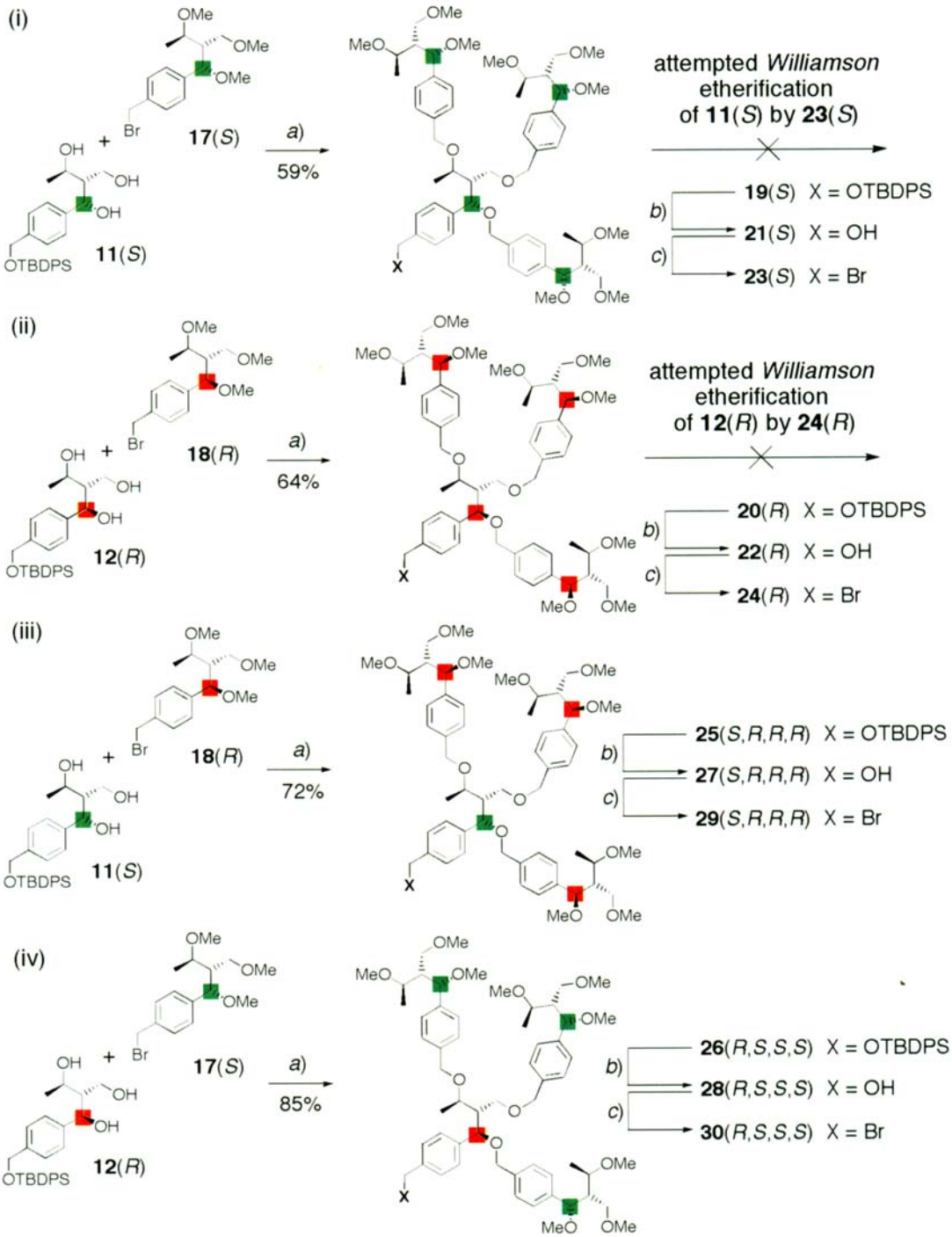
As also shown in *Scheme 2*, we, additionally, prepared the 2nd-generation 'mixed' benzylic bromides **29**(*S*,*R*,*R*,*R*) and **30**(*R*,*S*,*S*,*S*) containing branching units with (*S*)- and (*R*)-configuration of the benzylic centers. Thus, the corresponding benzyloxy-triols **11** and **12** of benzylic (*S*)- or (*R*)-configuration, respectively, were etherified with the benzyl bromides **18**(*R*) and **17**(*S*), respectively, affording the (*t*-Bu)Ph_2Si-protected branches **25**(*S*,*R*,*R*,*R*) and **26**(*R*,*S*,*S*,*S*), which were desilylated (→ **27** and **28**) and finally converted to the bromides **29** and **30**. The yields of these transformations were comparable to those mentioned in the preparation of the bromides **23** and **24** (with identical configuration at all benzylic centers).

With these bromides at our disposal, we were ready for the next coupling step with the triols **11**(*S*) and **12**(*R*). Unfortunately, this further coupling to give 3rd-generation branches did not occur under a variety of conditions (*prolonged reflux*, use of *different solvents* such as Et_2O, DMF, THF/DMPU, THF/DMF, *different bases* such as KH, BuLi, K_2CO_3/18-crown-6, *t*-Bu-P4 [34] [35], TlOEt [36], *increased concentrations* of the components). Instead, complex product mixtures were formed in which the desired compounds could not even be detected by FAB-MS analysis.

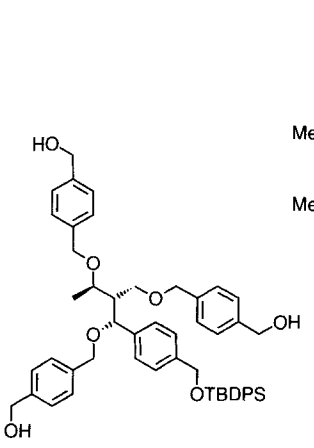
In experiments [2]) not described here we prepared the silyloxy-triol **31** with elongating aromatic spacers (*cf.* [20]), to find that it also did not undergo triple etherification with the benzylic bromide **23** (to a branch unit of 3rd generation). On the other hand, the 3rd-generation-branch (*t*-Bu)Ph_2Si-protected benzylic alcohol **32** was formed readily from the corresponding silyloxy-diol and the bromide **23**(*S*). This observation led to our subsequent work on chiral dendrimers with double-branching units.

The failing attempts towards the synthesis of 3rd-generation branches made us proceed in the following way: concentration of the efforts to 2nd-generation dendrimers with triple branching, use of elongated core building blocks, and then an attempt at dendrimers with non-elongated central moieties (see *Chapts. 3* and *4*). The elaboration of 'fully chiral' higher-generation branches (up to 5th) and dendrimers (up to 4th generation) will be the subject of a separate publication.

Scheme 2. *Preparation of the 2nd-Generation Benzylic Bromide Branches* **23**(S), **24**(R), **29**(S,R,R,R), *and* **30**(R,S,S,S)



a) NaH, THF, reflux. *b*) $Bu_4NF \cdot 3\,H_2O$, THF, r.t., 24 h, yields *ca.* 90%. *c*) Ph_3P, Br_4C, THF, r.t., 24 h, yields 50–80%.



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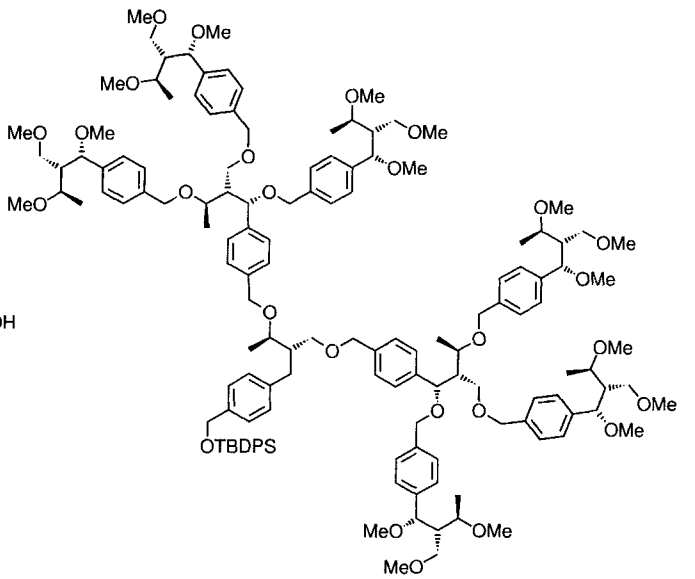

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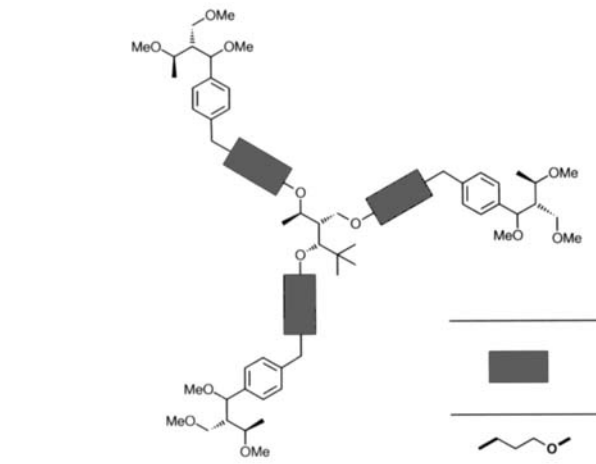
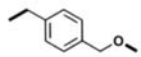
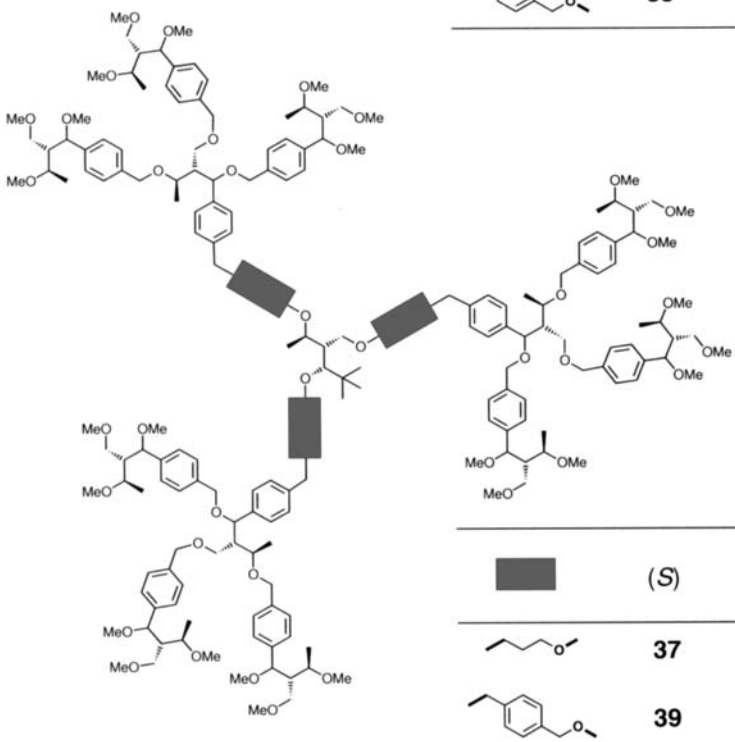
3. Preparation of the Chiral Dendrimers with Elongated Center Pieces. – The elongated triols **6** and **7** reacted smoothly with the 1st- (**17**(*S*), **18**(*R*)) and 2nd-generation branch bromides (**23**(*S*), **24**(*R*)), under the standard *Williamson* etherification conditions specified above to give the 1st- and 2nd-generation dendrimers **33**(*S*), **34**(*R*), **37**(*S*), and **38**(*R*) with aliphatic, as well as **35**(*S*), **36**(*R*), **39**(*S*), and **40**(*R*) with aromatic elongation (*Scheme 3*). The coupling yields ranged from 50% to quantitative for the 1st-generation, and from 40 to 80% for the 2nd-generation products. The molecular weights of these products run from 1102 to 3415, and the largest ones (**37**–**40**) are constructed from nine peripheral, three interior, and one central unit, containing 39 stereocenters (5.5×10^{11} possible stereoisomers!).

4. Synthesis of Dendrimers with Non-elongated Cores: Dramatic Case of Diastereoisomer Differentiation (and Recognition). – While there were no problems encountered with the coupling reaction of our favorite center triol **3**((*R*,*S*,*R*)-configuration) with the 1st-generation branch bromides **17**(*S*) and **18**(*R*) (→ **41**(*S*) and **42**(*R*), resp., yields > 90%), we observed a peculiar effect in the reactions of this triol with 2nd-generation bromides (*Schemes 4* and *5*). The triol **3** reacted smoothly with the bromide **23**(*S*) to give the desired dendrimer **44** (56%) by triple etherification, while the diastereoisomeric bromide **24**(*R*) reacted only twice to afford the dendritic alcohol **45** (88%). Under the most forcing conditions (several days of reflux!), we observed products of ether cleavages in **45** and destruction of the bromide **24**, rather than the *Williamson* coupling product. We assign structure **45**, with free OH next to the *t*-Bu group (*Scheme 4*), to the product

Scheme 3. *1st- and 2nd-Generation Dendrimers* **33**–**40** *with Elongated Core Units, and Molecular Weights* (**33**/**34**, **35**/**36**, **37**/**38**, and **39**/**40** differ only in the configuration of the benzylic centers)

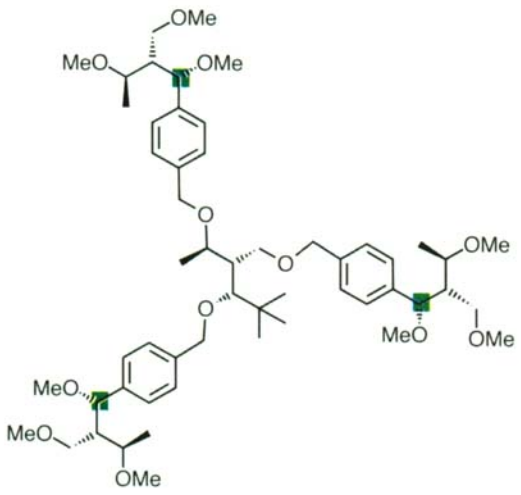


	(*S*)	(*R*)	M_r
	33	**34**	1102
	**35**	**36**	1288

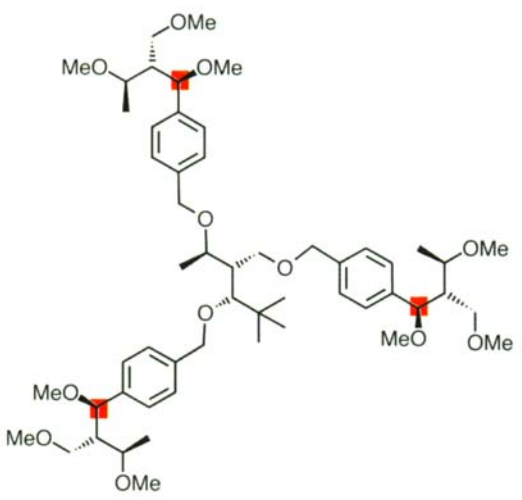


	(*S*)	(*R*)	M_r
	37	**38**	3228
	39	**40**	3415

(*R*) and (*S*) refer to the configurations of the benzylic positions which are not specified in the formulae



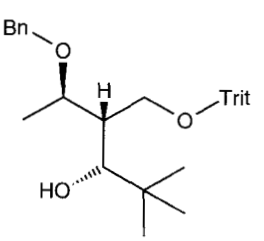
41(*S*)



42(*R*)

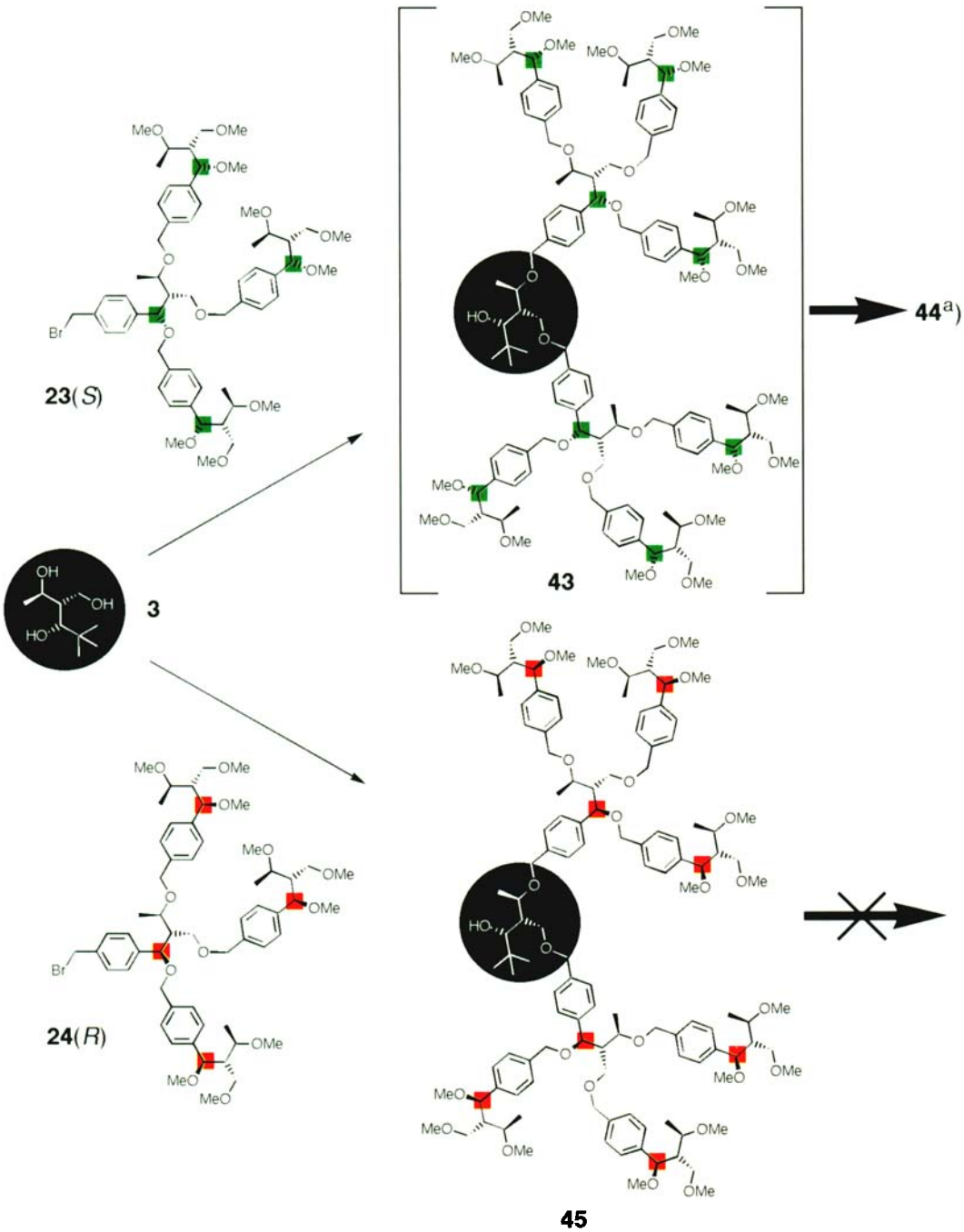
of double coupling for reactivity reasons but without proof[12]): neither the correct molecular-ion peak in the mass spectrum, nor the presence of an OH absorption in the IR spectrum, nor the clear-cut NMR spectra indicating that **45** is a uniform compound (*cf. Fig. 2*) would allow for a distinction between constitutional isomers with the α-*t*-BuOH group etherified and one of the other two OH groups of **3** free. Note that the site of configurational difference between the two bromides is far remote (5, 12, and 14 bonds including *para*-positions on benzene rings) from the site of reaction, and that this is even more true for the OH groups in **43** and **45** (10, 17, and 19 bonds!). Note also that compound **44**, which is formed, and the dendrimer from **3** and **24**(*R*), which is not

[12]) Attempts to oxidize the CHOH to a C=O group failed to give an identifyable carbonyl compound (which would be an aldol ether!): The sequence of reactivity of the OH groups in **3** was proved to be primary > secondary next to methyl > secondary next to *t*-Bu by first allowing **3** to react with 4-(dimethylamino)-1-(triphenylmethyl)pyridinium chloride (→ exclusively CH_2O-trityl), and then treating with 4-fold excess $PhCH_2Br$/NaH to give the benzyloxy-trityloxy-alcohol **i**, the structure of which was assigned by the fact that H/D exchange (CH–OH → CH–OD) led to simplification of the signal from a proton which has only one C,H-coupling neighbor.



i

Scheme 4. *Observed Case of Diastereoselectivity in the Coupling of the Benzylic Bromides* **23**(S) *and* **24**(R) *with the Non-elongated Triol* **3**



[a]) Formula of **44** in *Figs. 2* and *3*.

formed, are just two out of 2^{39} (or *ca.* 5.5×10^{11}) possible diastereoisomers. Thus, the case of diastereoisomer differentiation observed here may – with all due modesty – be called spectacular.

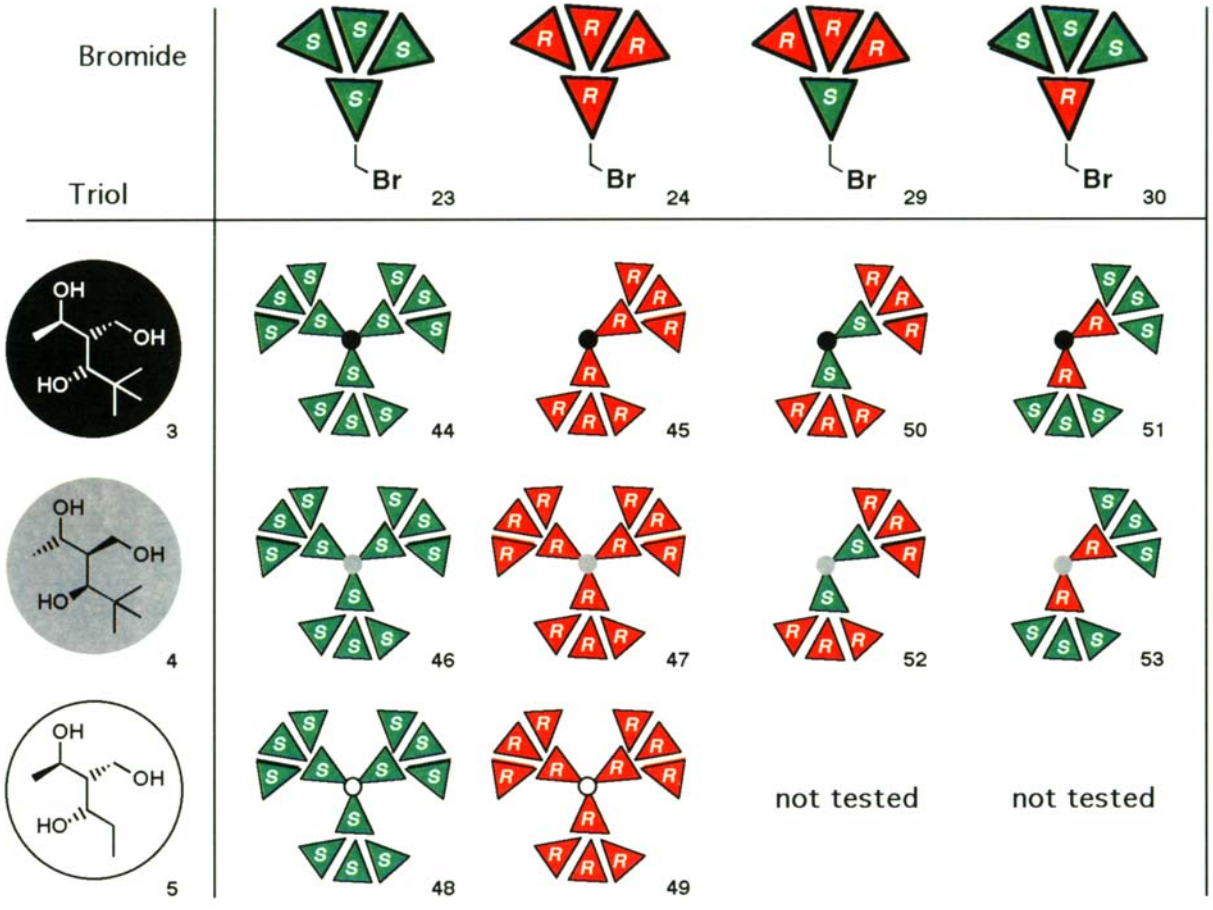
With other triols, such as the enantiomer **4** of our triol **3** and compound **5** from dioxanone **2** and propanal, as well as other bromides (**29** and **30**) available, we tested some additional combinations of center piece and branch building blocks (*Scheme 5*). The enantiomeric triol **4** reacted with both **23**(*S*) (→ **46**, 48% yield) and **24**(*R*) (→ **47**, 50%). Less surprisingly, the triol **5** with less sterically hindered OH groups also gave dendrimers with both diastereoisomeric bromides (→ **48**, 46%, and **49**, 46%). On the other hand, none of the 'mixed' branch bromides **29** and **30** reacted all the way to a dendrimer with either the original triol **3** (→ **50**, **51**) or its enantiomer **4** (→ **52**, **53**); instead, the doubly etherified products were formed in yields ranging from 53 to 65% (all these yields refer to chromatographed, analytically pure materials).

5. Characterization. – The branches, dendritic compounds, and dendrimers are very viscous oils. They are highly soluble in solvents of varying polarity (toluene, Et_2O, CH_2Cl_2, MeCN). As expected, the R_f values decrease as the sizes of the dendrimers or branches increase. In most cases, the R_f differences between the bromide, mono-, doubly-, and triply-coupled products are large enough, allowing to easily follow the progression of the reactions by TLC and even to confirm the absence of unreacted starting materials. The alternating polarity in each step and the large molecular-weight increase, features of the convergent approach, facilitate separations by standard flash chromatography. All new materials exhibited spectral data in agreement with the proposed structures. The purified compounds were characterized by ^{1}H- and ^{13}C-NMR, IR, UV, CD spectroscopy, specific rotation, mass spectrometry (FAB, MALDI-TOF, electrospray (only for **36**)), vapor-pressure osmometry (VPO, only for **44** and **45**), and elemental analysis. By none of these methods did we find evidence for contamination by impurities resulting from incomplete coupling or cleavages. Elemental analyses gave the correct C and H composition within $\pm$ 0.3%. However, because of the oligomeric nature of these dendritic macromolecules, their composition is similar and, therefore, elemental analysis is of little value for confirming structure and purity; for example, 'doubly coupled' 2nd-generation dendritic compound **45** ($C_{123}H_{184}O_{27}$) requires C 70.53, H 8.85, while 'fully coupled' 2nd-generation dendrimer **44** ($C_{180}H_{266}O_{39}$) requires C 70.79, H 8.78, values which are within experimental error of the method.

Instead, 500-MHz ^{1}H-NMR analysis (in $CDCl_3$) was found to be very useful for the characterization of the dendrimers, dendritic compounds, and their branch building blocks. There was no line broadening up to 2nd generation. Obvious features of these spectra are a single, sharp *t*-Bu proton resonance of the core (0.9–1.0 ppm) and of the (*t*-Bu)Ph_2Si group (1.0–1.1 ppm). Other resonances from analogous protons of the peripheral, interior, and central units are always 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 spectra of the 'fully' (**44**) and 'doubly coupled' (**45**) derivatives in *Fig. 2*.

Thus, the signals of the nine peripheral, three interior, and one central Me group (depicted as squares) show distinct sets of signals between 1.2 and 1.4 ppm. The downfield shift between these three layers is even larger in the case of the central C*H* protons of the nine peripheral, three interior, and a single core unit (1.8–2.5 ppm, depicted as circles). In addition, for all 'doubly coupled' dendritic molecules, the central C*H* reso-

Scheme 5. *Combination of Diastereoisomeric 2nd-Generation Benzylic Bromides* (**23**, **24**, **29**, and **30**) *with Different Triols* (**3**, **4** (*ent*-**3**), **5**) *leading to 'Doubly Coupled' Dendritic Derivatives* (**45**, and **50**–**53**) *in 53–88% Yield and to 'Fully Coupled' Dendrimers* (**44**, and **46**–**49**) *in 46–56% Yield.* All reactions were carried out under the same coupling reactions, *i.e.*, 9 equiv. NaH, 3.5 equiv. bromide, THF, reflux.



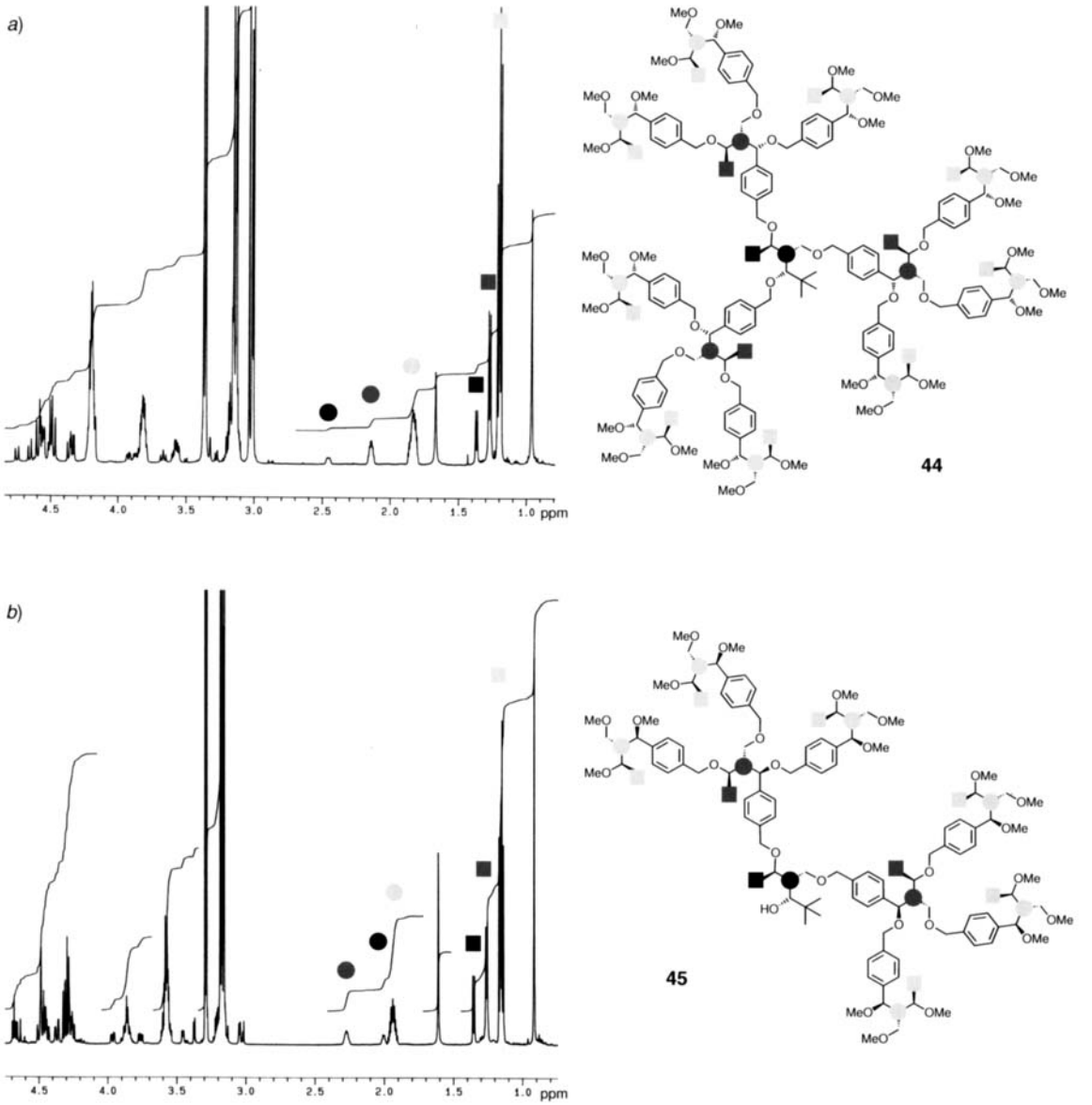


Fig. 2. *Part of the 500-MHz ^{1}H-NMR spectra of the 2nd-generation dendrimer* **44** *(*a*) and the dendritic compound* **45** *(*b*) measured in $CDCl_3$*. The labelling of signals or groups of signals refers to the sets of Me groups (masked as squares) and of CH groups (masked as circles) in the corresponding formulae (see text).

nance (see black circle in *Fig. 2, b*) is shifted upfield (0.4–0.5 ppm) as compared to the 'fully coupled' dendrimers (see black circle in *Fig. 2, a*). This behavior is independent of the configuration of the branching units. Thus, this signal is an excellent probe to detect impurities derived from incomplete coupling. Moreover, the integral ratios of the *t*-Bu

resonance to those of the aforementioned groups is a welcome indicator to track the growth of the dendritic series. For branches, there are, on the other hand, unique resonances of the PhCH_2OH protons at 4.7 ppm (after removal of the (*t*-Bu)Ph_2Si group) and for the PhCH_2Br protons at 4.5 ppm. The observed ratios are in good agreement with the expected values for all systems. In this way, the signals could be unambiguously assigned according to their layer origin. However, given the precision of the measurement, the possibility of contamination by small defects (loss of one monomer unit) cannot be ruled out by integration data alone. The ^{1}H chemical shifts, which appear in all generations, are not much affected by the dendrimer's generation number. The biggest deshielding occurs for the central C*H* protons of the central unit (for **44**, see black circle in *Fig. 2, a*) in the most compact dendrimers **44**, **46**, and **47**, *i.e.*, those with non-elongated core. For all these 2nd-generation dendrimers, a downfield shift by 0.15 ppm is observed when we go from 1st- to 2nd-generation.

Similar structural information was obtained from the 125-MHz ^{13}C-NMR spectra, where the resonances are better separated as compared to ^{1}H-NMR spectra. Each of the resonances was unambiguously assigned using standard theoretical values and equations [37]. Again, the layers of monomers were recognizable from additional peaks separated from one another, as depicted in *Fig. 3* for the dendrimer **44**. Moreover, the *t*-Bu group provides unique resonances at 26.5 ppm and at 37.6 ppm.

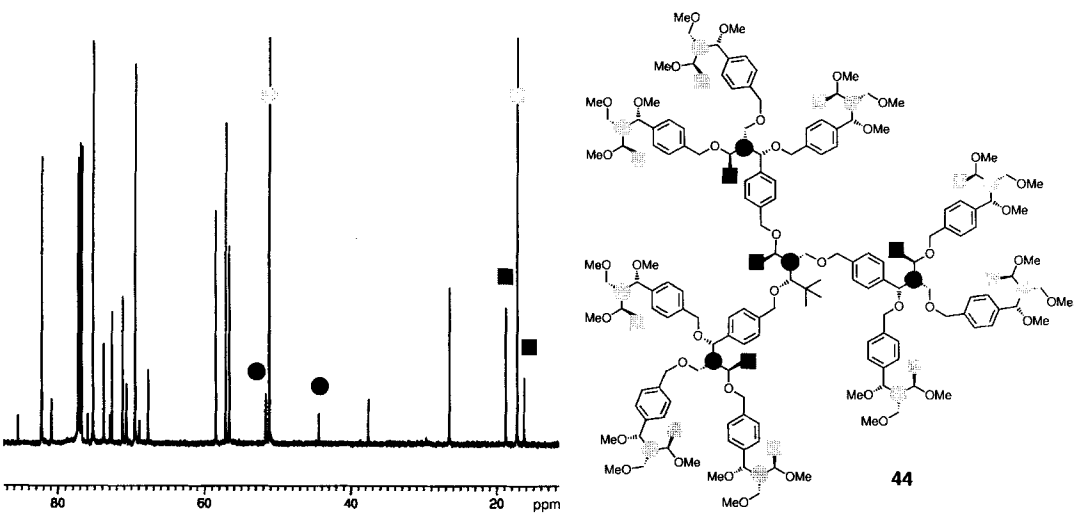


Fig. 3. *Part of the 125-MHz ^{13}C-NMR spectrum of the 2nd-generation dendrimer* **44** *measured in $CDCl_3$.* The labelling of signals or groups of signals refers to the sets of Me groups (depicted as squares) of CH groups (depicted as circles) in the corresponding formula (see text).

It is interesting to note that neither the signals from the central C*H* nor those from the center piece *t*-Bu group in the 500-MHz ^{1}H-NMR spectra are probes which would indicate diastereoisomerism of the dendritic compounds or of the 2nd-generation dendrimers (*Fig. 4*); it is striking to us that the C*H* protons of the central, internal, and peripheral building blocks (ratio 1:3:9) of the two dendrimers (**44** and **46**) with the same (*S*)-branches and enantiomeric center pieces are isochronous (2.45 ppm).

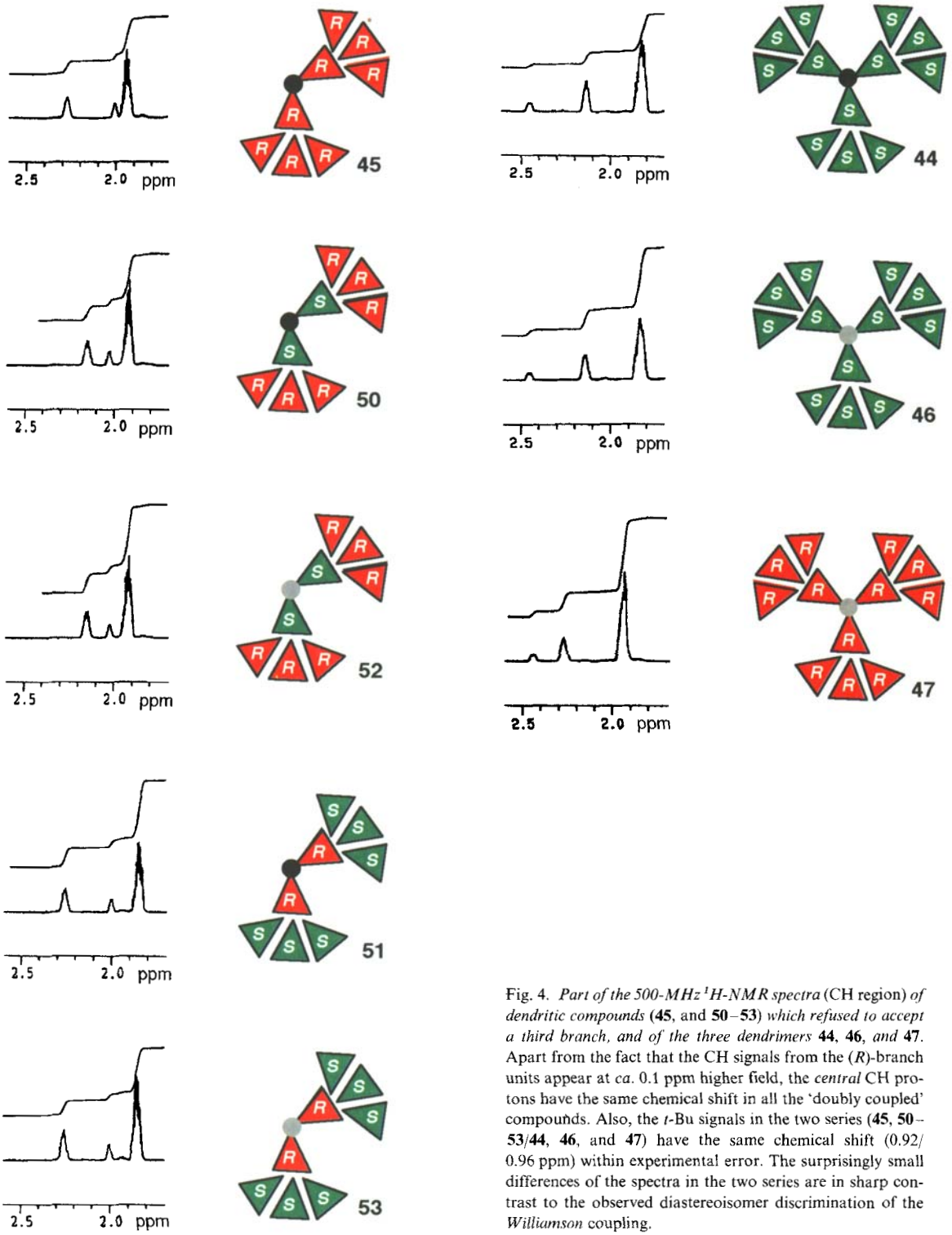


Fig. 4. *Part of the 500-MHz ^{1}H-NMR spectra* (CH region) *of dendritic compounds* (**45**, and **50**–**53**) *which refused to accept a third branch, and of the three dendrimers* **44**, **46**, *and* **47**. Apart from the fact that the CH signals from the (*R*)-branch units appear at *ca.* 0.1 ppm higher field, the *central* CH protons have the same chemical shift in all the 'doubly coupled' compounds. Also, the *t*-Bu signals in the two series (**45**, **50**–**53**/**44**, **46**, and **47**) have the same chemical shift (0.92/0.96 ppm) within experimental error. The surprisingly small differences of the spectra in the two series are in sharp contrast to the observed diastereoisomer discrimination of the *Williamson* coupling.

The nominal molecular weights of all the products were confirmed by *FAB-MS analysis* [38]. Recognizing the inability of NMR and FAB-MS analyses to detect minute amounts of structurally related impurities, we turned to matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrometry [39]. Due to the combination of mild ionization and absence of fragmentation, even for high-molecular-weight molecules, MALDI-TOF-MS proved to be the only analytical method for revealing the purity of our poly(benzyl ether) dendrimers. We applied this technique to some 1st-generation dendrimers (**33**–**36**) as well as to all 2nd-generation dendrimers with molecular weights up to 3500 Da. In most cases, the use of the α-cyano-4-hydroxycinnamic acid (CCA) matrix afforded the $[M + Na]^+$ or $[M + K]^+$ ion, or quite often both, with mass accuracies of 0.05% and a resolving power ($m/\Delta m$) of 700. In *Fig. 5*, we show four typical spectra which prove the high degree of purity of the products obtained. However, in the spectrum of the 'doubly coupled' dendritic compound **45** (see *Fig. 5, a*) additional peaks appear which correspond to the loss of 53, 68, 135, and 227 mass units; we do not know the origin of these signals.

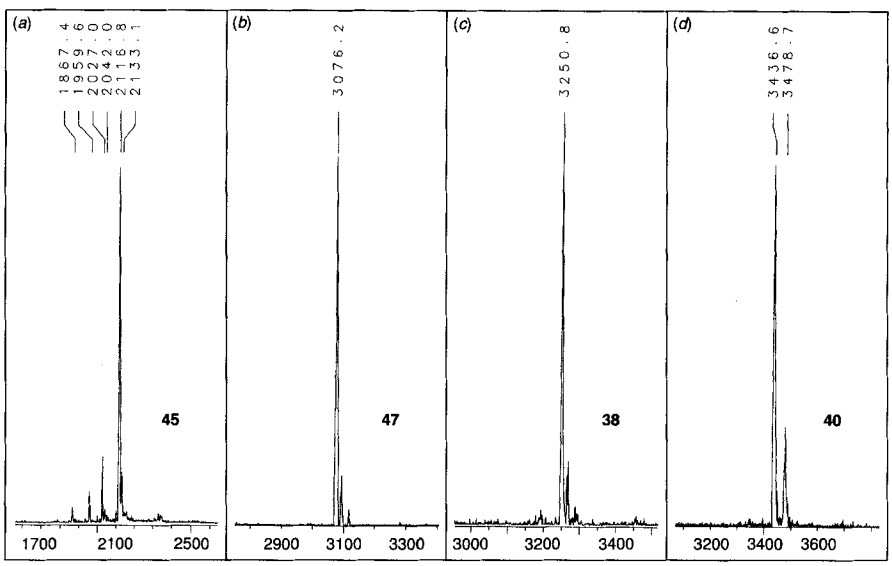
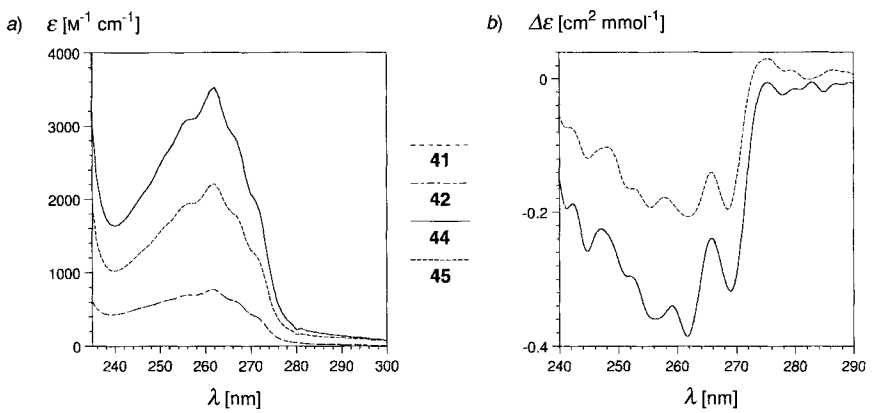


Fig. 5. *Part of the MALDI-TOF mass spectra of the 2nd-generation compounds* **45**, **47**, **38**, *and* **40**

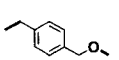
The UV spectra (see *Fig. 6, a*) for 1st- and 2nd-generation dendrimers **41**/**42** and **44**/**45** with non-elongated central unit exhibit an absorption maximum at 262 nm which corresponds to one of the $\pi \rightarrow \pi^*$ electronic transition of the benzene chromophore [40]. The molar absorptivity (ε) is smaller than $4000\,M^{-1}\,cm^{-1}$ and proportional to the number of benzene chromophores[13]). This transition can be used as a probe for investigating possible 'chiral perturbation' of the Ph rings in these dendrimers by measuring

[13]) 1st-generation dendrimers **41** and **42** with three benzene chromophores: $\varepsilon_{max} = 774$ and $772\,M^{-1}\,cm^{-1}$, respectively; 2nd-generation dendrimers **44** ('fully coupled') and **45** ('doubly coupled'): $\varepsilon_{max} = 3520$ and $2211\,M^{-1}\,cm^{-1}$, respectively.

the circular dichroism (CD) spectra (see *Fig. 6, b;* for **44** and **45**). In fact, all these dendrimers show either a negative or a positive *Cotton* effect the maximum of which coincides with the position of the maximum in the absorption spectra (261–263 nm) with a differential dichroic absorption $|\Delta\varepsilon| < 0.5\ cm^2\ mmol^{-1}$.



c)

Entry		(*S*)[a]	$[\theta]_{max}(\cdot 10^2)$[b]	(*R*)[a]	$[\theta]_{max}(\cdot 10^2)$[b]
1	no spacer	**44**	–12.7	**45**[c]	–6.8
2		**37**	+6.1	**38**	–8.8
3		**39**	+15.8	**40**	–8.7

[a]) Configuration at the benzylic positions of branch units.

[b]) Molecular Ellipticity $[\theta]_{max}$ [deg cm² dmol⁻¹] at λ_{max} (261–263 nm).

[c]) Doubly coupled 2nd-generation dendritic compound with (*R*)-configuration of the benzylic centers in the branching units.

Fig. 6. a) *UV Spectra of the 1st-generation dendrimers* **41**/**42** *and of the 2nd-generation compounds* **44**/**45**. b) *CD Spectra of the 2nd-generation compounds* **44**/**45**. c) *Molecular ellipticities of compounds* **37**–**40**, **44**, *and* **45**. All values were measured in MeCN at room temperature.

Both, the 'fully coupled' **44** as well as the 'doubly coupled' **45** provide a negative molecular ellipticity [*θ*] (see *Fig. 6, c, Entry 1*). However, for dendrimers with elongated central units (*Entries 2* and *3*) and (*S*)-configuration in the branches positive *Cotton* effects are observed. If branches with benzylic stereogenic centers of (*R*)-configuration are present, the *Cotton* effects are negative.

The difficulty in interpreting the chiroptical properties of this type of dendrimer comes from the fact that the individual chiral building blocks of different layers are in different environments. Thus, for 2nd-generation dendrimers, the observed specific rotation should be the sum of contributions of the peripheral, interior, and central units. To calculate the theoretical $[\alpha]_D$ values of the dendrimers, we chose the following model compounds (the $[\alpha]_D$ values given in brackets were measured with a concentration of $c = 1$ in $CHCl_3$): 0th-generation dendrimers **54** ($[\alpha]_D = +16.6$) and **55** ($[\alpha]_D = +18.8$) for

the central units; compound **31**(*R*) ($[\alpha]_D = +10.9$) for interior units containing benzylic (*R*)-centers; compound **15**(*S*) ($[\alpha]_D = -47.5$) for (*S*)-peripheral units; compound **16**(*R*) ($[\alpha]_D = +87.7$) for (*R*)-peripheral units (*Fig. 7*). Since the specific rotations of the model peripheral units are much higher than those of the central and interior units, 2nd-generation dendrimers are expected to reflect the specific rotation of the peripheral units. Actually, for all dendrimers with (*R*)-peripheral units, experimental $[\alpha]_D$ values between +48 and +76 are observed; for all dendrimers with (*S*)-peripheral units, the $[\alpha]_D$ values are between −29 and −55. The only exception from this trend is the dendrimer **44** with a positive value $[\alpha]_D = +11.8$ (compare with the results of CD measurements in *Fig. 6, c*). In contrast, the dendrimer **46** – with the same branches, but an enantiomeric central unit – has the expected value.

6. Conclusion. – Triply branching, 2nd-generation dendrimers, containing chiral building blocks in the core and at each and every branching point, can be prepared with

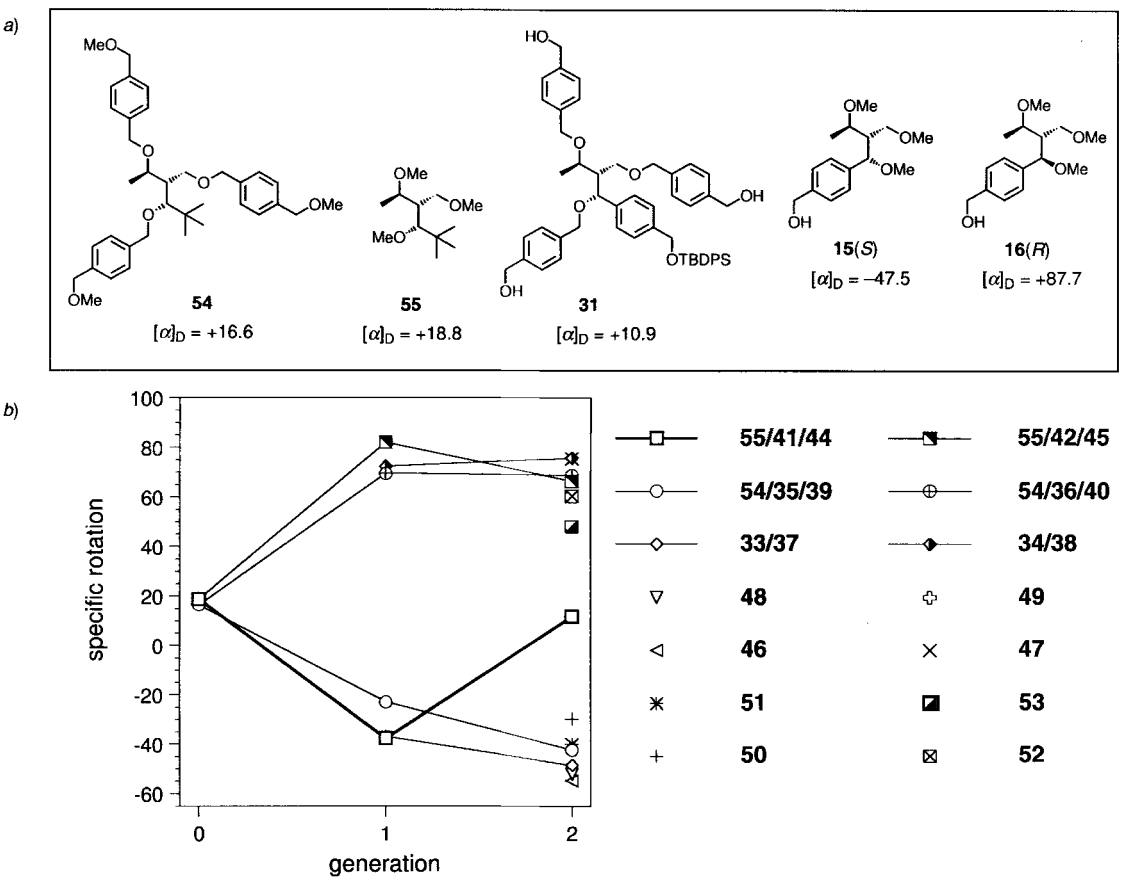


Fig. 7. *Specific rotation* $[\alpha]_D$ a) *of the model compounds for the central, interior, and peripheral building blocks in the dendritic compounds,* b) *of the 1st- and 2nd-generation dendritic compounds.* All values were measured in $CHCl_3$ at room temperature. The 0th-generation dendrimers were represented by compounds **54** and **55**.

and without elongation of the center piece. Diastereoisomeric benzylic branch bromides may react only twice with the non-elongated triol **3** to give such dendrimers[14]). Thus, we were lucky enough to be able to demonstrate that there is a delicate molecular recognition between various diastereoisomeric doubly etherified intermediates and diastereoisomeric branch bromides which allows or prevents the third etherification. The components can be said to discriminate between each other, to exhibit a fit or a misfit, to be matched or mismatched. We used the word lucky because, as pointed out above, such behavior could by no means have been predicted, and furthermore, because we happened to test only eight out of a huge number of possible combinations. Since the numerous single bonds in our dendritic structures have low barriers to rotation, and hence the molecules have shallow conformational energy surfaces, we claim that it is, at present, impossible to reproduce – and thus rationalize (!) – the observed phenomenon by molecular modelling.

The properties of the dendrimers and dendritic compounds prepared do not show irregularities when analogous 0th-, 1st-, and 2nd-generation derivatives are compared, with one exception: the specific rotation of the dendrimers without center-piece elongation jumps from a negative to a positive value, when we go to 2nd-generation (**55** → **41** → **44**), while we seem to approach a constant value in all other cases (see *Fig. 7*). This behavior may indicate a contribution to the optical activity (of **44**) by preferred chiral conformations which, in turn, might be induced by the steric crowding in the dendritic structure.

In a forthcoming paper, we will show that, with elongated center piece and elongated branching units, it is possible to go to 5th-generation branches and to 4th-generation dendrimers which exhibit 'dendritic effect' more clearly.

This work was supported by the *Swiss National Science Foundation* (project No. 2100-040659.94/1). We thank *B. Rusterholz* for preparing compounds **15** and **16**, as well as *P. B. Rheiner* for his help in preparing *Scheme 5*. We gratefully acknowledge the assistance of *H.-U. Hediger*, *R. Häfliger*, and Dr. *W. Amrein* (MS service). We also thank *Zeneca Bio Products*, Billingham (UK), for the generous supply of PHB, *FMC Corporation*, Bessemer City (USA) for (*t*-Bu)Ph_2SiCl, and *BASF AG*, Ludwigshafen (D), for pivalaldehyde. Continuing support by *Novartis AG*, Basel (CH), is gratefully acknowledged.

Experimental Part

1. *General.* All reactions were carried out 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 was freshly distilled from sodium benzophenone ketyl radical. The compounds **2**–**7** were prepared according to literature procedures [20]. TLC: glass-plated TLC silica gel *60* F_{254} (*Merck*). Flash chromatography (FC): silica 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*); Silica gel *Europrep 60-20*

[14]) One explanation of this phenomenon, where only two branches are introduced, is that the branching unit is not symmetrical. According to geometry rules, a three-way branching point that is symmetrical leads to equal distances of the three branches. In our case, this is not true. Therefore, the result is a distorted, fractal-like arrangement of the branches. By alternating (*R*)- and (*S*)-building blocks in the construction of the branches, it is possible that we damaged this fractal character, thus totally changing the conformation of the branch. It becomes very difficult to compare results at this point, since the (*R*)- and (*S*)-branches may differ substantually in their shape and size from the mixed branches.

(*Eurochrom Knauer*) 15–25 μm; *Büchi* 36 × 230 mm standard column; 22 bar; UV detection 245 nm. M.p. *Büchi 510*, uncorrected. Optical rotations: *Perkin-Elmer-241* polarimeter, 10-cm cells. IR: *Perkin-Elmer-1600-FTIR*, in cm^{-1}. UV/VIS: *Kontron Uvikon 931* spectrophotometer, 1-cm cells; 0.3–0.4 mM in MeCN, 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 in MeCN, $[\theta]$ 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. ^{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 matrix (3-NOBA); Electrospray ionization (ESI) on a *SSQ710C* instrument. Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) on a *Bruker-Reflex*^{TM} instrument with a N_2 laser system (337 nm), positive-ion mode, α-cyano-4-hydroxycinnamic acid (CCA); 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. Abbreviations: TBDPS-Cl ((*t*-Bu)Ph_2SiCl), LAH ($LiAlH_4$), TBAF ($Bu_4NF \cdot 3H_2O$), PDC (pyridinium dichromate), r.e. (rotary evaporator).

2. *Nomenclature.* The nomenclature convention developed and used for identification of the dendrimers, dendritic compounds, and dendritic branches is outlined in *Fig. 8*. A systematic application of the current *IUPAC* nomenclature recommendations to these dendritic derivatives would lead to extremely complicated names; apparently, the limits of a systematic nomenclature are met with the type of complex structures containing repeating units arranged in generations or layers.

*4-{[(*tert*-Butyl)diphenylsilyloxy]methyl}benzaldehyde* (**8**). To a soln. of benzene-1,4-dimethanol (5.4 g, 39 mmol) and imidazole (5.4 g, 78 mmol) in DMF (150 ml) was added TBDPS-Cl (10.7 g, 10 ml, 39 mmol) at 0°. After 30 min, the ice-bath was removed, and the mixture was stirred for 20 h at r.t. Then, H_2O (300 ml) was added, the phases were separated, and the aq. phase was extracted with Et_2O (2 × 200 ml). The combined org. extracts were washed with sat. aq. NaCl (2 × 150 ml), dried ($MgSO_4$), and concentrated *in vacuo*. FC (Et_2O/hexane 1:1) gave the monoprotected alcohol in almost pure form (7.7 g, 53%). The alcohol (7.7 g, 20.6 mmol) was dissolved in CH_2Cl_2 (35 ml) and added slowly to a suspension of PDC (19.3 g, 51.2 mmol) in CH_2Cl_2 (130 ml). After stirring for 3 h at r.t., Et_2O (130 ml) was added, and the mixture was filtered through silica. After washing the silica with CH_2Cl_2 (3 × 200 ml), the combined org. extracts were dried ($MgSO_4$) and concentrated *in vacuo*. FC (hexane/Et_2O 4:1) gave **8** (6.7 g, 87%) as a colorless oil, that crystallized in the refrigerator. ^{1}H-NMR (200 MHz): 1.13 (*s*, *t*-Bu); 4.85 (*s*, PhCH_2); 7.38–7.53 (*m*, 8 arom. H); 7.66–7.71 (*m*, 4 arom. H); 7.86 (*d*, J = 6.02, 2 arom. H); 10.02 (*s*, CHO).

*(2*R*,5*R*,6*R*)-2-(*tert*-Butyl)-5-{(S)-{4-{[(*tert*-Butyl)diphenylsilyloxy]methyl}phenyl}hydroxymethyl}-6-methyl-1,3-dioxan-4-one* (**9**) *and (2*R*,5*R*,6*R*)-2-(*tert*-Butyl)-5-{(R)-{4-{[(*tert*-butyl)diphenylsilyloxy]methyl}phenyl}hydroxymethyl}-6-methyl-1,3-dioxan-4-one* (**10**). An ice-cold soln. of $(i\text{-}Pr)_2NH$ (5.55 ml, 39.6 mmol) in THF (100 ml) was treated with BuLi (30.5 ml, 1.6M, 39.6 mmol), kept at 0° for 15 min, then cooled to −78°. The dioxanone **2** (5.98 g, 34.7 mmol) in THF (50 ml) was added at such a rate that the inner temp. never exceeded −70°, and the mixture was subsequently kept at −78° for 45 min. Compound **8** (15.6 g, 41.7 mmol) in THF (50 ml) was slowly added, the mixture kept at −78° for 3 h, then quenched with sat. aq. NH_4Cl (200 ml)/Et_2O (200 ml). The phases were separated, and the aq. phase was extracted with Et_2O (2 × 200 ml). The combined org. extracts were dried ($MgSO_4$) and concentrated *in vacuo*. ^{1}H-NMR of the crude product showed a ratio **9**/**10** of 1.2:1. Separation of the two epimers was achieved using MPLC (33% Et_2O/hexane) and gave 10 g (53%) of pure **9** and 6.45 g (34%) of pure **10**, both as slightly yellow oils. Since the R_f values (0.35 for **9**, 0.32 for **10**) of the two diastereoisomers are similar, their separation by MPLC proved to be superior to FC. After one separation, both isomers were obtained with high diastereoisomer enrichment according to 500 MHz ^{1}H-NMR (major isomer: d.r. 120:1, 99.2% ds; minor isomer: d.r. 545:1, 99.8% ds). Upon slow recrystallization from hexane, low melting (52–54°) crystals of the main isomer **9**, suitable for X-ray analysis were isolated.

Data of **9**: M.p. 52–54°. $[\alpha]_D^{r.t.} = -40.8$ (c = 2.48, $CHCl_3$). IR ($CHCl_3$): 3400*w*, 3070*s*, 2960*s*, 2860*s*, 1725*s*, 1590*w*, 1450*m*, 1430*s*, 1350*s*, 1260*s*, 1110*s*. ^{1}H-NMR (300 MHz): 0.84 (*d*, J = 6.2, Me–C(6)); 0.95 (*s*, *t*-Bu–C(2)); 1.09 (*s*, *t*-BuSi); 2.82 (*dd*, J = 9.1, 3.3, H–C(5)); 3.28 (*d*, J = 5.3, OH); 4.00 (*dq*, J = 9.1, 6.2, H–C(6)); 4.77 (*s*, CH_2OSi); 4.89 (*s*, H–C(2)); 5.40–5.45 (*m*, H–C(1′)); 7.30–7.70 (*m*, 14 arom. H). ^{13}C-NMR (75 MHz): 19.33; 21.14; 23.83; 26.86; 34.93; 55.32; 65.23; 71.05; 72.74; 107.70; 125.59; 126.34; 127.74; 129.74; 133.48; 135.57; 139.42; 141.02; 171.24. EI-MS: 546 (< 1, M^+), 317 (100), 287 (12), 239 (12), 183 (34), 91 (30), 69 (16), 57 (22), 41 (16). Anal. calc. for $C_{33}H_{42}O_5Si$ (546.78): C 72.49 H 7.74; found: C 72.18, H 7.80.

Data of **10**: $[\alpha]_D^{r.t.} = -16.6$ (c = 4.47, $CHCl_3$). IR ($CHCl_3$): 3450*w*, 3070*m*, 3005*m*, 2960*s*, 2860*s*, 1720*s*, 1480*m*, 1430*s*, 1350*s*, 1250*s*, 1110*s*. ^{1}H-NMR (300 MHz): 0.92 (*s*, *t*-Bu – C(2)); 1.01 (*d*, J = 6.1, Me–C(6));

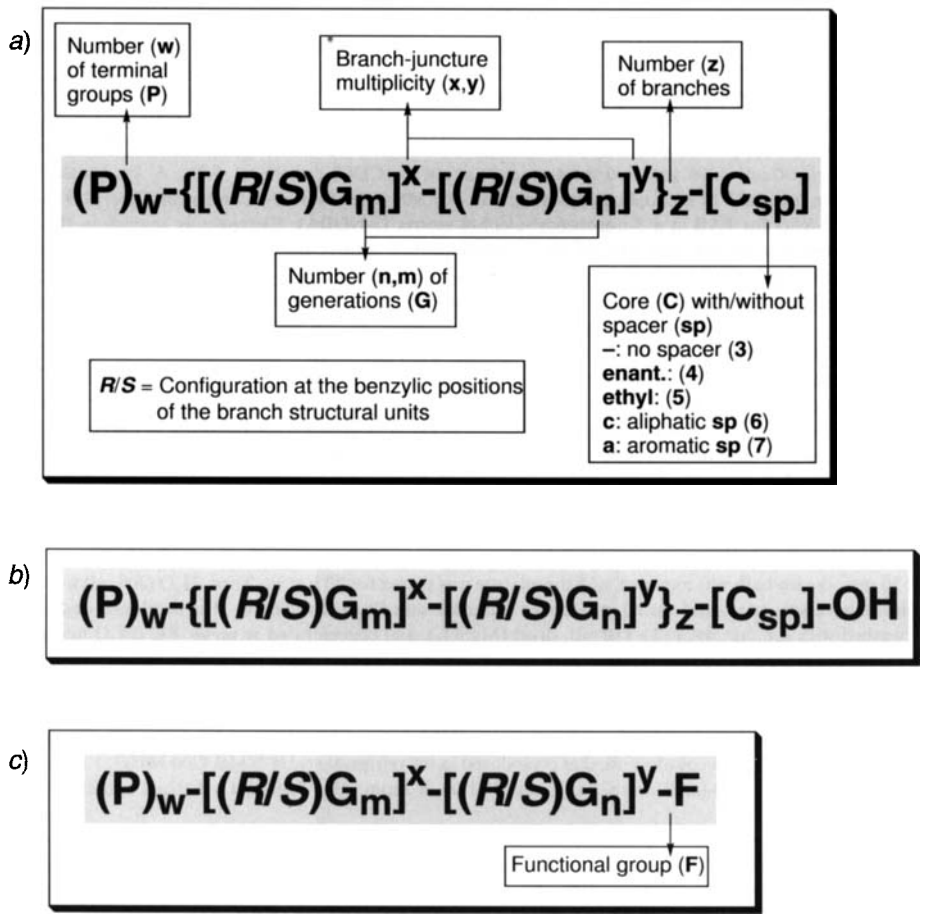


Fig. 8. *Nomenclature convention proposed and used for unambiguous identification* a) *of dendrimers,* b) *of 'doubly coupled' derivatives, and* c) *of dendritic branches*

1.09 (*s*, *t*-BuSi); 2.82 (*dd*, J = 9.0, 6.4, H–C(5)); 3.58 (*d*, J = 2.7, OH); 3.77 (*dq*, J = 9.0, 6.1, H–C(6)); 4.63 (*s*, H–C(2)); 4.77 (*s*, CH_2OSi); 5.12 (*dd*, J = 6.4, 2.7, H–C(1')); 7.30–7.70 (*m*, 14 arom. H). ^{13}C-NMR (75 MHz): 19.33; 21.27; 23.76; 26.85; 35.00; 55.26; 65.24; 72.64; 73.16; 107.76; 126.30; 126.55; 127.74; 129.74; 133.48; 135.56; 138.84; 141.47; 170.56. EI-MS: 471 (< 1, $[M - C_6H_5 + 1]^+$), 317 (100), 287 (15), 239 (14), 211 (13), 199 (10), 183 (38), 91 (33), 87 (12), 69 (33), 57 (33), 41 (19). Anal. calc. for $C_{33}H_{42}O_5Si$ (546.78): C 72.49, H 7.74; found: C 72.17, H 7.87.

*(1S,2S,3R)-1-{4-[[(*tert*-Butyl)diphenylsilyloxy]methyl}phenyl}-2-(hydroxymethyl)butane-1,3-diol* (**11**). To $NaBH_4$ (2.8 g, 75.3 mmol) in THF (200 ml)/MeOH (10 ml) was added **9** (8.23 g, 15.1 mmol) in THF (50 ml) at 0°. The mixture was stirred at r.t. for 18 h, then diluted with H_2O (150 ml) and saturated with NaCl. The mixture was extracted with Et_2O (3 × 250 ml), and the combined org. extracts were dried ($MgSO_4$) and concentrated *in vacuo*. The crude product was purified by FC (Et_2O): 6.41 g (92%) of pure **11**. Colorless, viscous oil. $[\alpha]_D^{r.t.} = -20.3$ (c = 3.06, $CHCl_3$). IR ($CHCl_3$): 3420*m*, 3070*w*, 3005*s*, 2930*s*, 2860*s*, 1470*m*, 1430*s*, 1080*s*. ^{1}H-NMR (300 MHz): 1.09 (*s*, *t*-Bu); 1.26 (*d*, J = 6.6, Me–C(3)); 1.68–1.74 (*m*, H–C(2)); 2.65 (br. *s*, OH); 3.16 (br. *s*, OH); 3.50 (br. *s*, OH); 3.68–3.76 (*m*, 1 H, CH_2OH); 4.04–4.11 (*m*, 1 H, CH_2OH); 4.20–4.35 (*m*, H–C(3)); 4.77 (*s*, CH_2OSi); 5.17–5.21 (*m*, H–C(1)); 7.30–7.70 (*m*, 14 arom. H). ^{13}C-NMR (75 MHz): 19.33; 21.27; 26.87; 51.11; 61.45; 65.32; 67.34; 74.81; 125.92; 126.18; 127.73; 129.71; 133.52; 135.60; 140.46; 141.59. EI-MS: 464

(< 1, M^+), 407 (9), 389 (8), 345 (10), 335 (15), 317 (25), 311 (16), 257 (29), 229 (24), 199 (100), 147 (45), 91 (57), 57 (17). Anal. calc. for $C_{28}H_{36}O_4Si$ (464.68): C 72.37, H 7.81; found: C 72.37, H 7.99.

*(1R,2S,3R)-1-{4-{[(*tert*-Butyl)diphenylsilyloxy]methyl}phenyl}-2-(hydroxymethyl)butane-1,3-diol* (**12**). To $NaBH_4$ (2.2 g, 58.9 mmol) in THF (200 ml)/MeOH (10 ml) was added **10** (6.45 g, 11.8 mmol) in THF (50 ml) at 0°. The mixture was stirred at r.t. for 20 h, then diluted with H_2O (150 ml) and saturated with NaCl. The mixture was extracted with Et_2O (3 × 250 ml) and the combined org. extracts were dried ($MgSO_4$) and concentrated *in vacuo*. The crude product was purified by FC (Et_2O): 5.07 g (93%) of pure **12**. Colorless, viscous oil. $[\alpha]_D^{r.t.} = +20.0$ ($c = 4.36$, $CHCl_3$). IR ($CHCl_3$): 3410*m*, 3070*w*, 3005*s*, 2930*s*, 2860*s*, 1430*s*, 1110*s*, 1070*s*. ^{1}H-NMR (300 MHz): 1.09 (*s*, *t*-Bu); 1.33 (*d*, $J = 6.5$, Me–C(3)); 1.56–1.62 (*m*, H–C(2)); 2.83 (br. *s*, OH); 3.04 (br. *s*, OH); 3.50 (br. *s*, OH); 3.90–4.15 (*m*, CH_2OH, H–C(3)); 4.77 (*s*, CH_2OSi); 5.09–5.13 (*m*, H–C(1)); 7.30–7.70 (*m*, 14 arom. H). ^{13}C-NMR (75 MHz): 19.33; 22.14; 26.87; 51.70; 59.79; 65.33; 69.58; 75.98; 125.86; 126.21; 127.74; 129.71; 133.52; 135.60; 140.46; 141.71. EI-MS: 464 (< 1, M^+), 407 (2), 389 (5), 359 (10), 335 (13), 317 (24), 257 (25), 199 (100), 143 (39), 91 (54), 41 (8). Anal. calc. for $C_{28}H_{36}O_4Si$ (464.68): C 72.37, H 7.81; found: C 72.54, H 7.85.

*1-{[(*tert*-Butyl)diphenylsilyloxy]methyl}-4-[(1S,2S,3R)-1,3-dimethoxy-2-(methoxymethyl)butyl]benzene* (**13**). To a soln. of **11** (0.37 g, 0.81 mmol) in THF (10 ml) was added NaH (0.17 g, 7.3 mmol), and the mixture was stirred at r.t. for 30 min, prior to the addition of MeI (0.46 ml, 7.3 mmol). The mixture was heated to reflux for 3 h, then quenched with H_2O (10 ml). The mixture was extracted with Et_2O (3 × 10 ml), and the combined org. extracts were dried ($MgSO_4$) and concentrated *in vacuo*. The crude product was purified by FC (hexane/Et_2O 4:1): 0.40 g (98%) of pure **13**. Colorless, viscous oil. $[\alpha]_D^{r.t.} = -24.0$ ($c = 2.14$, $CHCl_3$). IR ($CHCl_3$): 3005*s*, 2930*s*, 1470*m*, 1430*m*, 1090*s*. ^{1}H-NMR (300 MHz): 1.10 (*s*, *t*-Bu); 1.23 (*d*, $J = 6.5$, Me–C(3)); 1.82–1.90 (*m*, H–C(2)); 3.05 (*s*, MeO); 3.18 (*s*, MeO); 3.12–3.22 (*m*, CH_2OMe); 3.39 (*s*, MeO); 3.85 (*dq*, $J = 6.5$, 3.0, H–C(3)); 4.22 (*d*, $J = 9.2$, H–C(1)); 4.78 (*s*, CH_2OSi); 7.25–7.70 (*m*, 14 arom. H). ^{13}C-NMR (75 MHz): 17.28; 19.33; 26.87; 51.21; 56.64; 57.17; 58.49; 65.45; 69.47; 75.30; 82.37; 125.83; 127.54; 127.69; 129.68; 133.60; 135.60; 139.58; 140.39. EI-MS: 506 (< 1, M^+), 449 (3), 389 (32), 363 (40), 243 (12), 212 (27), 161 (74), 143 (36), 129 (36), 59 (100). Anal. calc. for $C_{31}H_{42}O_4Si$ (506.76): C 73.48, H 8.35; found: C 73.67, H 8.51.

*1-{[(*tert*-Butyl)diphenylsilyloxy]methyl}-4-[(1R,2S,3R)-1,3-dimethoxy-2-(methoxymethyl)butyl]benzene* (**14**). To a soln. of **12** (0.29 g, 0.63 mmol) in THF (10 ml) was added NaH (0.14 g, 5.7 mmol), and the mixture was stirred at r.t. for 30 min, prior to the addition of MeI (0.36 ml, 5.7 mmol). The mixture was heated under reflux for 3 h, then quenched with H_2O (10 ml). The mixture was extracted with Et_2O (3 × 10 ml), and the combined org. extracts were dried ($MgSO_4$) and concentrated *in vacuo*. The crude product was purified by FC (hexane/Et_2O 4:1): 0.30 g (95%) of pure **14**. Colorless, viscous oil. $[\alpha]_D^{r.t.} = +51.9$ ($c = 1.55$, $CHCl_3$). IR ($CHCl_3$): 3070*w*, 3005*m*, 2930*m*, 1470*m*, 1430*m*, 1110*s*. ^{1}H-NMR (300 MHz): 1.10 (*s*, *t*-Bu); 1.17 (*d*, $J = 6.4$, Me–C(3)); 1.90–1.99 (*m*, H–C(2)); 3.18 (*s*, MeO); 3.19 (*s*, MeO); 3.15–3.22 (*m*, 1 H of CH_2OMe); 3.31 (*s*, MeO); 3.58–3.61 (*m*, 1 H of CH_2OMe, H–C(3)); 4.30 (*d*, $J = 6.7$, H–C(1)); 4.78 (*s*, CH_2OSi); 7.20–7.70 (*m*, 14 arom. H). ^{13}C-NMR (75 MHz): 16.22; 19.36; 26.90; 50.87; 56.13; 56.87; 58.71; 65.42; 69.44; 75.48; 82.06; 125.87; 127.07; 127.70; 129.68; 133.56; 135.63; 139.78; 140.20. EI-MS: 506 (< 1, M^+), 449 (5), 417 (6), 389 (39), 363 (66), 213 (34), 199 (28), 161 (45), 144 (67), 59 (100), 45 (11). Anal. calc. for $C_{31}H_{42}O_4Si$ (506.76): C 73.48, H 8.35; found: C 73.43, H 8.28.

4-[(1S,2S,3R)-1,3-Dimethoxy-2-(methoxymethyl)butyl]benzenemethanol (**15**). The compound **13** (0.32 g, 0.62 mmol) in THF (5 ml) was treated with TBAF (0.39 g, 1.2 mmol) for 24 h at r.t. The mixture was concentrated *in vacuo*, and the residue was purified by FC (hexane/Et_2O 1:1): 0.16 g (99%) of pure **15**. Colorless, viscous oil. $[\alpha]_D^{r.t.} = -47.5$ ($c = 1.31$, $CHCl_3$). IR ($CHCl_3$): 3600*w*, 3430*w*, 3005*s*, 2930*s*, 1465*m*, 1375*m*, 1090*s*. ^{1}H-NMR (300 MHz): 1.22 (*d*, $J = 6.5$, Me–C(3)); 1.80–2.00 (*m*, H–C(2), OH); 3.04 (*s*, MeO); 3.16 (*s*, MeO); 3.11–3.21 (*m*, CH_2OMe); 3.37 (*s*, MeO); 3.83 (*dq*, $J = 6.5$, 3.0, H–C(3)); 4.23 (*d*, $J = 9.2$, H–C(1)); 4.70 (*d*, $J = 5.3$, CH_2OH); 7.29–7.37 (*m*, 4 arom. H). ^{13}C-NMR (75 MHz): 17.28; 51.21; 56.68; 57.17; 58.49; 65.20; 69.53; 75.30; 82.32; 126.89; 127.93; 140.23; 140.53. EI-MS: 236 (< 1), 218 (1), 199 (3), 177 (2), 151 (100), 91 (5), 59 (13). Anal. calc. for $C_{15}H_{24}O_4$ (268.35): C 67.14, H 9.01; found: C 66.89, H 9.16.

4-[(1R,2S,3R)-1,3-Dimethoxy-2-(methoxymethyl)butyl]benzenemethanol (**16**). The compound **14** (0.23 g, 0.45 mmol) in THF (5 ml) was treated with TBAF (0.29 g, 0.91 mmol) for 24 h at r.t. The mixture was concentrated *in vacuo*, and the residue was purified by FC (hexane/Et_2O 1:1): 0.11 g (99%) of pure **16**. Colorless, viscous oil. $[\alpha]_D^{r.t.} = +87.7$ ($c = 1.64$, $CHCl_3$). IR ($CHCl_3$): 3605*w*, 3440*w*, 3005*s*, 2930*s*, 1465*m*, 1380*m*, 1095*s*. ^{1}H-NMR (300 MHz): 1.16 (*d*, $J = 6.4$, Me–C(3)); 1.81 (br. *s*, OH); 1.90–1.98 (*m*, H–C(2)); 3.17 (*s*, MeO); 3.18 (*s*, MeO); 3.14–3.22 (*m*, 1 H, CH_2OMe); 3.30 (*s*, MeO); 3.55–3.60 (*m*, 1 H of CH_2OMe, H–C(3)); 4.32 (*d*, $J = 6.6$, H–C(1)); 4.70 (*d*, $J = 5.4$, CH_2OH); 7.25–7.45 (*m*, 4 arom. H). ^{13}C-NMR (75 MHz): 16.15; 50.86; 56.10; 56.87; 58.69; 65.20; 69.37; 75.42; 81.96; 126.96; 127.44; 139.98; 140.76. EI-MS: 236 (< 1), 204 (2), 199 (5), 191 (3),

177 (3), 151 (100), 131 (1), 91 (4), 59 (12), 45 (5). Anal. calc. for $C_{15}H_{24}O_4$ (268.35): C 67.14, H 9.01; found: C 67.44, H 9.16.

1-(Bromomethyl)-4-[(1S,2S,3R)-1,3-dimethoxy-2-(methoxymethyl)butyl]benzene (**17**). To a soln. of **15** (3.06 g, 11.4 mmol) in THF (50 ml), Ph_3P (6 g, 22.8 mmol) and Br_4C (7.6 g, 22.8 mmol) were added. The mixture was stirred at r.t. for 3 h, then poured into H_2O (50 ml). The mixture was extracted with Et_2O (3 × 100 ml), and the combined org. extracts were dried ($MgSO_4$) and concentrated *in vacuo*. The crude product was purified by FC (hexane/Et_2O 2:1): 2.94 g (78%) of pure **17**. Colorless, viscous oil. $[\alpha]_D^{r.t.} = -39.3$ ($c = 1.04$, $CHCl_3$). IR ($CHCl_3$): 3010*m*, 2930*m*, 2825*m*, 1665*m*, 1095*s*. ^{1}H-NMR (300 MHz): 1.21 (*d*, $J = 6.5$, Me–C(3)); 1.79–1.86 (*m*, H–C(2)); 3.03 (*s*, MeO); 3.11–3.21 (*m*, CH_2OMe); 3.18 (*s*, MeO); 3.37 (*s*, MeO); 3.82 (*dq*, $J = 6.5$, 3.0, H–C(3)); 4.24 (*d*, $J = 9.1$, H–C(1)); 4.51 (*s*, CH_2Br); 7.25–7.45 (*m*, 4 arom. H). ^{13}C-NMR (75 MHz): 17.22; 33.44; 51.27; 56.78; 57.14; 58.46; 69.40; 75.23; 82.25; 128.06; 128.87; 136.99; 141.59. EI-MS: 331(< 1, M^+), 253 (19), 219 (30), 213 (100), 199 (6), 161 (35), 134 (68), 91 (31), 59 (70), 45 (19). Anal. calc. for $C_{15}H_{23}O_3Br$ (331.25): C 54.39, H 7.00; found: C 54.59, H 7.09.

1-(Bromomethyl)-4-[(1R,2S,3R)-1,3-dimethoxy-2-(methoxymethyl)butyl]benzene (**18**). To a soln. of **16** (0.79 g, 3 mmol) in THF (25 ml), Ph_3P (1.55 g, 6 mmol) and Br_4C (1.96 g, 6 mmol) were added. The mixture was stirred at r.t. for 3 h, then poured into H_2O (25 ml). The mixture was extracted with Et_2O (3 × 25 ml), and the combined org. extracts were dried ($MgSO_4$) and concentrated *in vacuo*. The crude product was purified by FC (hexane/Et_2O 2:1), giving 0.88 g (90%) of pure **18**. Colorless, viscous oil. $[\alpha]_D^{r.t.} = +77.6$ ($c = 1.32$, $CHCl_3$). IR ($CHCl_3$): 3005*m*, 2930*m*, 2825*m*, 1465*w*, 1095*s*. ^{1}H-NMR (300 MHz): 1.17 (*d*, $J = 6.4$, Me–C(3)); 1.90–1.98 (*m*, H–C(2)); 3.17 (*s*, MeO); 3.18 (*s*, MeO); 3.16–3.23 (*m*, 1 H, CH_2OMe); 3.29 (*s*, MeO); 3.50–3.60 (*m*, 1 H, CH_2OMe, H–C(3)); 4.32 (*d*, $J = 6.3$, H–C(1)); 4.51 (*s*, CH_2Br); 7.25–7.45 (*m*, 4 arom. H). ^{13}C-NMR (75 MHz): 16.11; 33.42; 50.76; 56.10; 56.97; 58.69; 69.24; 75.36; 81.74; 127.57; 128.93; 136.77; 141.79. EI-MS: 299 (1), 268 (2), 253 (7), 219 (14), 215 (100), 213 (99), 199 (9), 161 (13), 134 (36), 59 (32). Anal. calc. for $C_{15}H_{23}O_3Br$ (331.25): C 54.39, H 7.00; found: C 54.73, H 6.92.

(MeO)$_9$-[(S)G$_2$]^3-OTBDPS (**19**). To NaH (146 mg, 6.1 mmol) in THF (10 ml) was added **11** (134 mg, 0.68 mmol) in THF (5 ml), and the mixture was stirred for 30 min at r.t. The bromide **17** (784 mg, 2.37 mmol) in THF (5 ml) was then added at 0°, and the mixture was stirred under reflux for 18 h. The reaction was quenched by the addition of H_2O (10 ml), and the mixture was extracted with Et_2O (3 × 25 ml). The combined org. extracts were dried ($MgSO_4$) and concentrated *in vacuo*. The crude product was purified by FC (hexane/Et_2O 2:3): 480 mg (59%) of pure **19**. Slightly yellow, viscous oil. $[\alpha]_D^{r.t.} = -26.6$ ($c = 2.52$, $CHCl_3$). IR ($CHCl_3$): 3005*m*, 2930*m*, 2825*m*, 1465*w*, 1375*w*, 1260*m*, 1090*s*. ^{1}H-NMR (300 MHz): 1.11 (*s*, *t*-Bu); 1.19 (*d*, $J = 6.5$, Me(G$_2$)); 1.20 (*d*, $J = 6.5$, Me(G$_2$)); 1.22 (*d*, $J = 6.5$, Me(G$_2$)); 1.30 (*d*, $J = 6.5$, Me(G$_1$)); 1.78–1.90 (*m*, 3 H–C(2)(G$_2$)); 2.11–2.20 (*m*, H–C(2)(G$_1$)); 3.01, 3.03, 3.04, 3.12, 3.14, 3.16 (6*s*, 6 MeO(P)); 3.10–3.25 (*m*, 3 CH_2OMe(P)); 3.33–3.35 (*m*, 1 H, OCH_2–C(2)(G$_1$)); 3.36, 3.37, 3.38 (*s*, 3 MeO(P)); 3.57–3.64 (*m*, 1 H, OCH$_2$–C(2)(G$_1$)); 3.78–3.89 (*m*, 3 H–C(3)(G$_2$)); 4.10–4.64 (*m*, H–C(3)(G$_1$), 3 OCH_2Ph, 3 H–C(1)(G$_2$), H–C(1)(G$_1$)); 4.81 (*s*, CH_2OSi); 7.05–7.50 (*m*, 22 arom. H); 7.64–7.70 (*m*, 4 arom. H). ^{13}C-NMR (75 MHz): 17.32; 18.76; 19.39; 26.93; 51.23; 51.74; 56.67; 57.14; 58.47; 65.52; 67.84; 69.57; 70.63; 71.28; 72.71; 73.96; 75.30; 81.12; 82.36; 125.98; 127.23; 127.59; 127.82; 129.71; 133.61; 135.63; 137.97; 138.03; 138.91; 139.75; 140.07; 140.26; 140.55. FAB-MS: 1216 (17, $[M + 1]^+$), 1215 (34, M^+), 1214 (46, $[M - 1]^+$), 1123 (17), 1098 (28), 1007 (31), 903 (53), 691 (71), 605 (35), 531 (100), 429 (52). Anal. calc. for $C_{73}H_{102}O_{13}Si$ (1215.69): C 72.12, H 8.46; found: C 72.39, H 8.39.

(MeO)$_9$-[(R)G$_2$]^3-OTBDPS (**20**). As described for **19**, with **12** (604 mg, 1.29 mmol), NaH (279 mg, 11.60 mmol, 9 equiv.), and **18** (1.49 g, 4.5 mmol, 3.5 equiv.), reaction time 23 h. FC (hexane/Et_2O 1:1 → 1:2) of the residual orange oil: **20** (1.01 g, 64%). Slightly yellow, viscous oil. $[\alpha]_D^{r.t.} = +64.5$ ($c = 1.10$, $CHCl_3$). IR ($CHCl_3$): 3007*m*, 2931*s*, 2895*s*, 1512*w*, 1463*m*, 1449*m*, 1428*w*, 1377*m*, 1092*s*, 1020*m*, 957*w*, 824*m*. ^{1}H-NMR (400 MHz): 1.11 (*s*, *t*-Bu); 1.15 (*d*, $J = 6.4$, Me(G$_2$)); 1.16 (*d*, $J = 6.3$, 2 Me(G$_2$)); 1.28 (*d*, $J = 7.0$, Me(G$_1$)); 1.90–1.98 (*m*, 3 H–C(2)(G$_2$)); 2.27–2.32 (*m*, H–C(2)(G$_1$)); 3.15, 3.16 (2*s*, 2 MeO(P)); 3.17, 3.18 (*s*, 4 MeO(P)); 3.11–3.23 (*m*, 3 H–C(3)(G$_2$)); 3.29, 3.30 (*s*, 3 MeO(P)); 3.53–3.62 (*m*, 3 CH_2OMe(P), H–C(3)(G$_1$)); 3.85–3.91 (*m*, OCH$_2$–C(2)(G$_1$)); 4.18–4.54 (*m*, 3 OCH_2Ph, 3 H–C(1)(G$_2$)); 4.68 (*d*, $J = 6.0$, H–C(1)(G$_1$)); 4.80 (*s*, CH_2OSi); 7.22–7.45 (*m*, 22 arom. H); 7.68–7.74 (*m*, 4 arom. H). ^{13}C-NMR (100 MHz): 16.16; 17.18; 19.35; 26.89; 50.83; 51.03; 56.13; 56.90; 58.72; 65.38; 67.63; 69.35; 70.23; 70.59; 72.78; 74.37; 75.43; 80.04; 81.97; 127.07; 127.10; 127.12; 127.14; 127.37; 127.39; 127.72; 129.71; 135.60; 137.82; 137.94; 138.36; 140.33; 140.34. FAB-MS: 1238 (20, $[M + 23]^+$), 1228 (22, $[M + 14]^+$), 1215 (70, $[M + 1]^+$), 1214 (83, M^+), 1183 (20), 1124 (51), 1098 (100), 1034 (26), 1008 (79), 962 (32). Anal. calc. for $C_{73}H_{102}O_{13}Si$ (1215.69): C 72.12, H 8.46; found: C 72.41, H 8.24.

(MeO)$_9$-[(S)G$_2$]^3-OH (**21**). To a soln. of **19** (384 mg, 0.32 mmol) in THF (10 ml) at 0°, TBAF (202 mg, 0.64 mmol) was added at once. After stirring for 24 h at r.t., H_2O (10 ml) was added. Extraction with Et_2O

(3 × 50 ml), drying ($MgSO_4$), evaporation, and FC (hexane/Et_2O 1:9) gave 270 mg (86%) of pure **21**. Slightly yellow, viscous oil. $[\alpha]_D^{r.t.} = -58.8$ ($c = 1.02$, $CHCl_3$). IR ($CHCl_3$): 3425*w*, 3005*m*, 2930*m*, 2825*m*, 1465*w*, 1260*m*, 1095*s*. ^{1}H-NMR (400 MHz): 1.19 (*d*, $J = 6.3$, Me(G_2)); 1.21 (*d*, $J = 6.5$, Me(G_2)); 1.22 (*d*, $J = 6.1$, Me(G_2)); 1.30 (*d*, $J = 6.5$, Me(G_1)); 1.80–1.89 (*m*, 3 H–C(2)(G_2)); 2.00 (br. *s*, OH); 2.11–2.18 (*m*, H–C(2)(G_1)); 3.01, 3.03, 3.04 (*s*, 3 MeO(P)); 3.05–3.25 (*m*, 3 CH_2OMe(P)); 3.13, 3.14, 3.16 (*s*, 3 MeO(P)); 3.33 (*dd*, $J = 9.9$, 4.7, 1 H, OCH_2–C(2)(G_1)); 3.36, 3.37, 3.38 (*s*, 3 MeO(P)); 3.59 (*dd*, $J = 9.9$, 4.6, 1 H, OCH_2–C(2)(G_1)); 3.79–3.87 (*m*, 3 H–C(3)(G_2)); 4.10–4.62 (*m*, 3 OCH_2Ph, H–C(3)(G_1), 3 H–C(1)(G_2), H–C(1)(G_1)); 4.70 (*s*, CH_2OH); 7.03–7.45 (*m*, 16 arom. H). ^{13}C-NMR (100 MHz): 17.21; 17.24; 18.56; 51.13; 51.15; 51.18; 51.64; 56.61; 56.68; 57.16; 58.46; 58.51; 65.08; 67.53; 69.50; 69.52; 70.62; 71.23; 72.48; 73.82; 75.22; 81.16; 82.22; 82.27; 126.87; 127.09; 127.22; 127.44; 127.58; 128.11; 137.81; 137.83; 138.78; 139.92; 140.07; 140.26; 140.47; 140.53. FAB-MS: 977 (1, M^+), 944 (2), 689 (3), 306 (20), 219 (49), 186 (18), 160 (78), 153 (50), 135 (41), 58 (100). Anal. calc. for $C_{57}H_{84}O_{13}$ (977.29): C 70.05, H 8.66; found: C 69.89, H 8.48.

*(MeO)$_9$-[(*R*)G_2]^3-OH* (**22**). To a soln. of **20** (1.01 g, 0.83 mmol) in THF (25 ml) at 0°, TBAF (0.53 g, 1.68 mmol) was added at once. After stirring for 24 h at r.t., H_2O (15 ml) was added. Extraction with Et_2O (3 × 60 ml), drying ($MgSO_4$), evaporation, and FC (hexane/Et_2O 1:9) gave **22** (0.78 g, 96%). Slightly yellow, viscous oil. $[\alpha]_D^{r.t.} = +80.4$ ($c = 1.01$, $CHCl_3$). IR ($CHCl_3$): 3439*w*, 3007*s*, 2929*m*, 2823*m*, 1512*w*, 1449*w*, 1377*w*, 1349*w*, 1094*s*, 1020*w*, 958*w*, 830*w*. ^{1}H-NMR (400 MHz): 1.15 (*d*, $J = 6.5$, Me(G_2)); 1.16 (*d*, $J = 6.4$, Me(G_2)); 1.17 (*d*, $J = 6.5$, Me(G_2)); 1.27 (*d*, $J = 6.4$, Me(G_1)); 1.90–1.98 (*m*, 3 H–C(2)(G_2)); 2.01 (*t*, $J = 5.8$, OH); 2.26–2.31 (*m*, H–C(2)(G_1)); 3.16, 3.17 (*s*, 2 MeO(P)); 3.18 (*s*, 2 MeO(P)); 3.19 (*s*, 2 MeO(P)); 3.15–3.24 (*m*, 3 H–C(3)(G_2)); 3.29–3.30 (*s*, 3 MeO(P)); 3.54–3.65 (*m*, 3 CH_2OMe(P), 3 H–C(3)(G_1)); 3.80–3.90 (*m*, OCH_2–C(2)(G_1)); 4.24–4.53 (*m*, 3 OCH_2Ph, 3 H–C(1)(G_2)); 4.68 (*d*, $J = 5.8$, CH_2OH); 4.69 (*d*, $J = 6.0$, H–C(1)(G_1)); 7.21–7.34 (*m*, 16 arom. H). ^{13}C-NMR (100 MHz): 16.14; 17.17; 50.79; 51.03; 56.13; 56.66; 56.90; 58.72; 65.06; 67.41; 69.33; 70.13; 70.70; 72.70; 74.08; 75.43; 75.46; 79.90; 81.92; 81.98; 127.00; 127.04; 127.06; 127.11; 127.39; 127.58; 137.69; 137.83; 138.23; 140.16; 140.29; 140.35; 140.41; 140.80. FAB-MS: 1110 (< 1, $[M + 133]^+$), 1000 (1, $[M + 23]^+$), 945 (< 1), 665 (2), 457 (2), 402 (1), 307 (8), 219 (37), 161 (62). Anal. calc. for $C_{57}H_{84}O_{13}$ (977.29): C 70.05, H 8.66; found: C 69.82, H 8.54.

*(MeO)$_9$-[(*S*)G_2]^3-Br* (**23**). To a soln. of **21** (2.15 g, 2.20 mmol) in THF (50 ml) at 0°, Ph_3P (1.15 g, 4.4 mmol) and Br_4C (1.46 g, 4.4 mmol) were added. After stirring at r.t. for 8 h, another 1 equiv. Ph_3P/Br_4C was added. After stirring for 14 h, H_2O (50 ml) was added to the suspension. Extraction with CH_2Cl_2 (3 × 100 ml), drying ($MgSO_4$), and evaporation, followed by FC (hexane/Et_2O 1:2), yielded **23** (1.87 g, 82%). Slightly yellow oil. $[\alpha]_D^{r.t.} = -43.0$ ($c = 1.16$, $CHCl_3$). IR ($CHCl_3$): 3007*m*, 2929*m*, 2892*m*, 2823*m*, 1513*w*, 1449*w*, 1420*w*, 1376*m*, 1093*s*, 1020*m*, 969*w*, 877*w*, 829*w*. ^{1}H-NMR (400 MHz): 1.20 (*d*, $J = 6.5$, Me(G_2)); 1.21 (*d*, $J = 6.5$, Me(G_2)); 1.21 (*d*, $J = 6.5$, Me(G_2)); 1.29 (*d*, $J = 6.5$, Me(G_1)); 1.80–1.88 (*m*, 3 H–C(2)(G_2)); 2.09–2.15 (*m*, H–C(2)(G_1)); 3.03–3.04 (3*s*, 3 MeO(P)); 3.14–3.16 (3*s*, 3 MeO(P)); 3.10–3.21 (*m*, 3 CH_2OMe(P)); 3.36–3.38 (3*s*, 3 MeO(P)); 3.34 ('*dd*', *ABX*, $J = 10.1$, 5.0, 1 H, OCH_2–C(2)(G_1)); 3.59 ('*dd*', *ABX*, $J = 9.9$, 4.4, 1 H, OCH_2–C(2)(G_1)); 3.78–3.86 (*m*, 3 H–C(3)(G_2)); 4.11–4.25 (*m*, 3 H–C(1)(G_2), H–C(3)(G_1)); 4.11–4.25 (*m*, 3 H, OCH_2Ph); 4.32 (*AB*, $J = 11.4$, 1 H, OCH_2Ph); 4.45 (*AB*, $J = 11.8$, 1 H, OCH_2Ph); 4.52 (*s*, CH_2Br); 4.54 (*d*, $J = 8.9$, H–C(1)(G_1)); 4.61 (*AB*, $J = 11.8$, 1 H, OCH_2Ph); 7.05 (*d*, $J = 8.1$, 1 arom. H); 7.19–7.39 (*m*, 15 arom. H). ^{13}C-NMR (100 MHz): 17.24; 18.56; 33.36; 51.15; 51.18; 51.71; 56.67; 57.17; 58.50; 67.54; 69.49; 70.76; 71.21; 72.64; 73.79; 75.23; 81.05; 82.24; 127.21; 127.50; 127.57; 127.58; 128.32; 128.98; 137.10; 137.72; 137.73; 138.72; 140.04; 140.10; 140.33; 141.66. FAB-MS: 1173 (< 1, $[M + 133]^+$), 1064 (< 1, $[M + 24]^+$), 1054 (< 1, $[M + 14]^+$), 1040 (< 1, M^+), 1009 (< 1), 829 (< 1), 739 (5), 637 (< 1), 577 (1), 521 (1), 387 (3), 307 (4), 219 (43), 187 (21), 175 (13), 161 (64). Anal. calc. for $C_{57}H_{83}O_{12}Br$ (1040.18): C 65.82, H 8.04; found: C 66.00, H 7.81.

*(MeO)$_9$-[(*R*)G_2]^3-Br* (**24**). To a soln. of **22** (0.97 g, 0.99 mmol) in THF (25 ml) at 0°, Ph_3P (0.6 g, 2.29 mmol) and Br_4C (0.76 g, 2.29 mmol) were added. After stirring at r.t. for 4 h, another 2 equiv. Ph_3P/Br_4C was added. After stirring for 2 h, H_2O (25 ml) was added to the suspension. Extraction with CH_2Cl_2 (3 × 50 ml), drying ($MgSO_4$), and evaporation followed by FC (hexane/Et_2O 1:2), yielded **24** (0.53 g, 51%): Slightly yellow oil. $[\alpha]_D^{r.t.} = +67.3$ ($c = 1.05$, $CHCl_3$). IR ($CHCl_3$): 3005*m*, 2930*m*, 2892*m*, 2823*m*, 1512*w*, 1448*w*, 1376*w*, 1093*s*, 1020*w*, 956*w*, 829*w*. ^{1}H-NMR (500 MHz): 1.15 (*d*, $J = 6.4$, Me(G_2)); 1.16 (*d*, $J = 6.4$, Me(G_2)); 1.17 (*d*, $J = 6.5$, Me(G_2)); 1.27 (*d*, $J = 6.4$, Me(G_1)); 1.90–1.99 (*m*, 3 H–C(2)(G_2)); 2.26–2.31 (*m*, H–C(2)(G_1)); 3.16–3.19 (5*s*, 6 MeO(P)); 3.15–3.23 (*m*, 3 H–C(3)(G_2)); 3.29–3.30 (3*s*, 3 MeO(P)); 3.53–3.68 (*m*, 3 CH_2OMe(P), H–C(3)(G_1)); 3.80–3.86 (*m*, OCH_2–C(2)(G_1)); 4.24–4.49 (*m*, 3 OCH_2Ph, 3 H–C(1)(G_2)); 4.51 (*s*, CH_2Br); 4.71 (*d*, $J = 5.5$, H–C(1)(G_1)); 7.22–7.40 (*m*, 16 arom. H). ^{13}C-NMR (125 MHz): 16.15; 17.09; 33.35; 50.84; 50.93; 56.14; 56.91; 58.73; 67.37; 69.34; 69.49; 70.19; 70.78; 72.77; 74.17; 75.42; 127.10; 127.13; 127.35; 127.39; 127.57; 129.08; 136.86; 137.57; 137.78; 138.20; 140.35; 140.41; 140.48; 141.98. FAB-MS: 1063 (< 1, $[M + 24]^+$), 1053 (< 1, $[M + 14]^+$), 1039 (< 1, M^+), 1008 (< 1), 829 (< 1), 739 (4), 639 (< 1), 577 (< 1), 521 (< 1), 387 (2), 357 (2),

307 (5), 251 (15), 219 (36), 161 (65). Anal. calc. for $C_{57}H_{83}O_{12}Br$ (1040.18): C 65.82, H 8.04; found: C 66.12, H 7.89.

(MeO)$_9$-[(S)G$_1$]^3-[(R)G$_2$]^3-OTBDPS (**25**). As described for **19**, with **11** (0.98 g, 2.11 mmol), NaH (0.46 g, 18.99 mmol, 9 equiv.), and **18** (2.45 g, 7.39 mmol, 3.5 equiv.), reaction time 17 h. FC (pentane/Et_2O 1:2): **25** (1.84 g, 72%). Slightly yellow, viscous oil. $[\alpha]_D^{r.t.} = +47.8$ ($c = 2.10$, $CHCl_3$). IR ($CHCl_3$): 3006*s*, 2931*s*, 2896*s*, 2823*m*, 1512*w*, 1463*m*, 1428*m*, 1376*m*, 1091*s*, 1019*m*, 957*m*. ^{1}H-NMR (500 MHz): 1.11 (*s*, *t*-Bu); 1.13 (*d*, $J = 6.4$, Me(G_2)); 1.14 (*d*, $J = 6.4$, Me(G_2)); 1.15 (*d*, $J = 6.4$, Me(G_2)); 1.32 (*d*, $J = 6.5$, Me(G_1)); 1.88–1.96 (*m*, 3 H–C(2)(G_2)); 2.14–2.18 (*m*, H–C(2)(G_1)); 3.12–3.18 (4*s*, 6 MeO(P)); 3.12–3.21 (*m*, 3 H–C(3)(G_2)); 3.27, 3.28, 3.29 (3*s*, 3 MeO(P)); 3.32–3.38 (*m*, 1 H, OCH_2–C(2)(G_1)); 3.52–3.63 (*m*, 3 CH_2OMe(P), 1 H of OCH_2–C(2)(G_1)); 4.14–4.63 (*m*, 3 OCH_2Ph, 3 H–C(1)(G_2), H–C(1)(G_1), H–C(3)(G_1)); 4.81 (*s*, CH_2OSi); 7.11–7.43 (*m*, 22 arom. H); 7.70–7.72 (*m*, 4 arom. H). ^{13}C-NMR (125 MHz): 16.15; 18.72; 19.36; 26.91; 50.80; 50.83; 50.87; 51.67; 56.11; 56.12; 65.45; 67.85; 69.33; 69.35; 70.57; 71.22; 72.68; 73.90; 75.41; 81.06; 81.95; 81.98; 125.93; 127.02; 127.09; 127.29; 127.33; 127.36; 127.68; 127.72; 127.79; 127.82; 129.71; 133.54; 135.61; 137.72; 137.77; 138.64; 139.68; 140.04; 140.29; 140.35; 140.50; 140.55. FAB-MS: 1347 (5, $[M + 133]^+$), 1213 (27, M^+), 1097 (20), 903 (43), 813 (20), 691 (25), 531 (16), 385 (16), 251 (27), 219 (75), 197 (26), 161 (75), 80 (100). Anal. calc. for $C_{73}H_{102}O_{13}Si$ (1215.69): C 72.12, H 8.46; found: C 72.24, H 8.46.

(MeO)$_9$-[(R)G$_1$]^3-[(S)G$_2$]^3-OTBDPS (**26**). As described for **19**, with **12** (0.76 g, 1.64 mmol), NaH (0.35 g, 14.75 mmol, 9 equiv.), and **17** (1.90 g, 5.74 mmol, 3.5 equiv.), reaction time 17 h. FC (pentane/Et_2O 1:2): **26** (1.68 g, 85%). Slightly yellow, viscous oil. $[\alpha]_D^{r.t.} = -25.4$ ($c = 2.10$, $CHCl_3$). IR ($CHCl_3$): 3001*s*, 2931*s*, 2894*s*, 2823*m*, 1512*w*, 1463*m*, 1427*m*, 1376*m*, 1252*w*, 1091*s*, 1019*m*, 968*w*, 826*w*. ^{1}H-NMR (500 MHz): 1.11 (*s*, *t*-Bu); 1.21 (*d*, $J = 6.5$, Me(G_2)); 1.22 (*d*, $J = 6.5$, Me(G_2)); 1.23 (*d*, $J = 6.5$, Me(G_2)); 1.26 (*d*, $J = 6.4$, Me(G_1)); 1.82–1.88 (*m*, 3 H–C(2)(G_2)); 2.26–2.30 (*m*, H–C(2)(G_1)); 3.02, 3.03, 3.04 (3*s*, 3 MeO(P)); 3.15, 3.16, 3.17 (3*s*, 3 MeO(P)); 3.12–3.24 (*m*, 3 CH_2OMe(P)); 3.36, 3.37, 3.38 (3*s*, 3 MeO(P)); 3.56–3.60 (*m*, H–C(3)(G_1)); 3.80–3.89 (*m*, 3 H–C(3)(G_2), OCH_2–C(2)(G_1)); 4.19–4.58 (*m*, 3 OCH_2Ph, 3 H–C(1)(G_2)); 4.66 (*d*, $J = 6.1$, H–C(1)(G_1)); 4.79 (*s*, CH_2OSi); 7.25–7.44 (*m*, 22 arom. H); 7.69–7.71 (*m*, 4 arom. H). ^{13}C-NMR (125 MHz): 17.20; 17.26; 19.35; 26.90; 51.09; 51.18; 51.21; 56.62; 56.67; 57.18; 58.50; 65.40; 67.57; 69.51; 69.54; 70.24; 70.56; 72.19; 72.77; 74.38; 75.26; 79.99; 82.30; 82.32; 126.00; 127.02; 127.16; 127.33; 127.34; 127.55; 127.59; 127.72; 127.77; 128.22; 129.71; 133.51; 135.61; 138.04; 138.15; 138.61; 140.00; 140.11; 140.12; 140.32; 140.55. FAB-MS: 1347 (5, $[M + 133]^+$), 1213 (36, M^+), 1097 (34), 903 (30), 813 (14), 691 (19), 531 (13), 385 (12), 219 (42), 187 (37), 161 (75), 80 (100). Anal. calc. for $C_{73}H_{102}O_{13}Si$ (1215.69): C 72.12, H 8.46; found: C 72.06, H 8.25.

(MeO)$_9$-[(S)G$_1$]^3-[(R)G$_2$]^3-OH (**27**). To a soln. of **25** (1.81 g, 1.49 mmol) in THF (30 ml) at 0°, TBAF (0.94 g, 2.98 mmol) was added at once. After stirring for 24 h at r.t., H_2O (20 ml) was added. Extraction with Et_2O (3 × 100 ml), drying ($MgSO_4$), evaporation, and FC (pentane/Et_2O 1:9) gave **27** (1.30 g, 90%). Slightly yellow, viscous oil. $[\alpha]_D^{r.t.} = +53.6$ ($c = 1.8$, $CHCl_3$). IR ($CHCl_3$): 3450*w*, 3004*s*, 2929*s*, 2905*s*, 2823*m*, 1512*w*, 1463*m*, 1420*m*, 1376*m*, 1093*s*, 1020*m*, 956*m*, 827*m*. ^{1}H-NMR (500 MHz): 1.14 (*d*, $J = 6.4$, Me(G_2)); 1.15 (*d*, $J = 6.4$, Me(G_2)); 1.16 (*d*, $J = 6.4$, Me(G_2)); 1.32 (*d*, $J = 6.5$, Me(G_1)); 1.89–1.96 (*m*, 3 H–C(2)(G_2)); 2.01 (*t*, $J = 5.9$, OH); 2.13–2.18 (*m*, H–C(2)(G_1)); 3.13–3.18 (5*s*, 6 MeO(P)); 3.13–3.23 (*m*, 3 H–C(3)(G_2)); 3.27, 3.28 (2*s*, 3 MeO(P)); 3.27–3.33 (*m*, 1 H, OCH_2–C(2)(G_1)); 3.52–3.63 (*m*, 3 CH_2OMe(P), 1 H of OCH_2–C(2)(G_1)); 4.12–4.63 (*m*, 3 OCH_2Ph, 3 H–C(1)(G_2), H–C(1)(G_1), H–C(3)(G_1)); 4.70 (*d*, $J = 5.8$, CH_2OH); 7.03–7.40 (*m*, 16 arom. H). ^{13}C-NMR (125 MHz): 16.09; 16.11; 18.52; 50.74; 50.78; 50.83; 51.64; 56.10; 56.85; 58.68; 65.06; 67.50; 69.28; 69.30; 70.59; 71.17; 72.43; 73.75; 75.20; 75.39; 75.42; 81.11; 81.88; 81.93; 126.87; 126.93; 127.06; 127.06; 127.12; 127.33; 127.57; 127.68; 128.12; 137.60; 138.54; 140.15; 140.36; 140.45; 140.51; 140.53. FAB-MS: 1109 (3, $[M + 133]^+$), 999 (7, $[M + 23]^+$), 975 (6, M^+), 944 (15), 709 (11), 690 (23), 665 (32), 575 (11), 457 (23), 307 (50), 251 (46), 219 (74), 161 (60), 80 (100). Anal. calc. for $C_{57}H_{84}O_{13}$ (977.28): C 70.05, H 8.66; found: C 69.95, H 8.40.

(MeO)$_9$-[(R)G$_1$]^3-[(S)G$_2$]^3-OH (**28**). To a soln. of **26** (1.65 g, 1.36 mmol) in THF (28 ml) at 0°, TBAF (0.86 g, 2.72 mmol) was added at once. After stirring for 24 h at r.t., H_2O (20 ml) was added. Extraction with Et_2O (3 × 100 ml), drying ($MgSO_4$), evaporation, and FC (pentane/Et_2O 1:9) gave **28** (1.23 g, 93%). Slightly yellow, viscous oil. $[\alpha]_D^{r.t.} = -35.0$ ($c = 2.1$, $CHCl_3$). IR ($CHCl_3$): 3450*w*, 3003*s*, 2929*s*, 2905*s*, 2823*m*, 1512*w*, 1463*m*, 1421*m*, 1376*m*, 1092*s*, 1020*m*, 969*m*, 828*m*. ^{1}H-NMR (500 MHz): 1.20–1.23 (*m*, 3 Me(G_2)); 1.25 (*d*, $J = 6.4$, Me(G_1)); 1.83–1.90 (*m*, 3 H–C(2)(G_2)); 1.93 (*t*, $J = 5.9$, OH); 2.25–2.29 (*m*, H–C(2)(G_1)); 3.01, 3.02, 3.03 (3*s*, 3 MeO(P)); 3.15, 3.16, 3.17 (3*s*, 3 MeO(P)); 3.11–3.24 (*m*, 3 CH_2OMe(P)); 3.37 (3*s*, 3 MeO(P)); 3.59–3.64 (*m*, H–C(3)(G_1)); 3.80–3.87 (*m*, 3 H–C(3)(G_2), OCH_2–C(2)(G_1)); 4.19–4.51 (*m*, 3 OCH_2Ph, 3 H–C(1)(G_2), H–C(1)(G_1)); 4.68 (*d*, $J = 5.8$, CH_2OH); 7.20–7.33 (*m*, 16 arom. H). ^{13}C-NMR (125 MHz): 17.20; 17.25; 51.09; 51.18; 51.21; 51.24; 56.64; 56.67; 57.17; 58.48; 58.50; 65.10; 67.41; 69.52; 69.54; 70.14; 70.65; 72.73; 74.05; 75.25; 79.84; 82.30; 82.35; 126.98; 127.00; 127.11; 127.34; 127.36; 127.45; 127.55; 127.56; 127.59; 137.91; 138.06;

138.47; 140.00; 140.13; 140.18; 140.79. FAB-MS: 1109 (3, $[M + 133]^+$), 999 (5, $[M + 23]^+$), 975 (6, M^+), 709 (13), 689 (17), 665 (26), 575 (11), 457 (36), 307 (94), 251 (56), 219 (100), 161 (75), 80 (91). Anal. calc. for $C_{57}H_{84}O_{13}$ (977.28): C 70.05, H 8.66; found: C 69.91, H 8.47.

(MeO)$_9$-[(S)G$_1$]^3-[(R)G$_2$]^3-Br (**29**). To a soln. of **27** (1.30 g, 1.33 mmol) in THF (14 ml) at 0°, Ph_3P (0.52 g, 1.99 mmol) and Br_4C (0.66 g, 1.99 mmol) were added. After stirring at r.t. for 20 h, another 1.5 equiv. Ph_3P/Br_4C was added. After stirring for 24 h, H_2O (14 ml) was added to the suspension. Extraction with CH_2Cl_2 (3 × 70 ml), drying ($MgSO_4$), and evaporation, followed by FC (pentane/Et_2O 1:2), yielded **29** (0.98 g, 71%). Slightly yellow oil. $[\alpha]_D^{r.t.} = +52.5$ ($c = 2.1$, $CHCl_3$). IR ($CHCl_3$): 3005*s*, 2929*s*, 2905*s*, 2823*m*, 1603*w*, 1512*w*, 1463*m*, 1420*m*, 1376*m*, 1350*m*, 1092*s*, 1020*m*, 956*m*, 830*m*. ^{1}H-NMR (500 MHz): 1.14 (*d*, $J = 6.4$, Me(G$_2$)); 1.15 (*d*, $J = 6.4$, Me(G$_2$)); 1.16 (*d*, $J = 6.4$, Me(G$_2$)); 1.31 (*d*, $J = 6.5$, Me(G$_1$)); 1.89–1.96 (*m*, 3 H–C(2)(G$_2$)); 2.10–2.14 (*m*, H–C(2)(G$_1$)); 3.13–3.18 (5*s*, 6 MeO(P)); 3.13–3.23 (*m*, 3 H–C(3)(G$_2$)); 3.27, 3.28 (2*s*, 3 MeO(P)); 3.32–3.35 (*m*, 1 H, OCH$_2$–C(2)(G$_1$)); 3.52–3.62 (*m*, 3 CH$_2$OMe(P), 1 H of OCH$_2$–C(2)(G$_1$)); 4.52 (*s*, CH$_2$OH); 4.11–4.62 (*m*, 3 OCH$_2$Ph, 3 H–C(1)(G$_2$), H–C(1)(G$_1$), H–C(3)(G$_1$)); 7.04–7.40 (*m*, 16 arom. H). ^{13}C-NMR (125 MHz): 16.13; 18.52; 33.34; 50.82; 50.86; 51.72; 56.13; 56.88; 58.71; 67.62; 69.30; 69.33; 69.35; 70.73; 71.18; 72.65; 73.77; 75.24; 75.40; 75.43; 75.44; 81.06; 81.91; 81.95; 127.02; 127.10; 127.29; 127.35; 127.50; 127.59; 127.67; 128.35; 128.98; 137.12; 137.50; 137.54; 138.49; 140.31; 140.42; 140.63; 141.67. FAB-MS: 1039 (3, M^+), 1037 (3), 1008 (6), 1006 (5), 829 (8), 827 (7), 739 (51), 737 (47), 251 (21), 219 (50), 161 (74), 50 (100). Anal. calc. for $C_{57}H_{84}O_{12}Br$ (1040.18): C 65.82, H 8.04; found: C 65.56, H 8.30.

(MeO)$_9$-[(R)G$_1$]^3-[(S)G$_2$]^3-Br (**30**). To a soln. of **28** (1.22 g, 1.25 mmol) in THF (13 ml) at 0°, Ph_3P (0.49 g, 1.87 mmol) and Br_4C (0.62 g, 1.87 mmol) were added. After stirring at r.t. for 20 h, another 1.5 equiv. Ph_3P/Br_4C was added. After stirring for 24 h, H_2O (13 ml) was added to the suspension. Extraction with CH_2Cl_2 (3 × 70 ml), drying ($MgSO_4$), and evaporation, followed by FC (pentane/Et_2O 1:2), yielded **30** (0.91 g, 70%). Slightly yellow oil. $[\alpha]_D^{r.t.} = -36.7$ ($c = 1.6$, $CHCl_3$). IR ($CHCl_3$): 3005*s*, 2929*s*, 2905*s*, 2823*m*, 1612*w*, 1511*w*, 1463*m*, 1420*m*, 1376*m*, 1350*m*, 1092*s*, 1020*m*, 969*m*, 828*m*. ^{1}H-NMR (500 MHz): 1.21–1.23 (*m*, 3 Me(G$_2$)); 1.25 (*d*, $J = 6.4$, Me(G$_1$)); 1.83–1.89 (*m*, 3 H–C(2)(G$_2$)); 2.25–2.29 (*m*, H–C(2)(G$_1$)); 3.02, 3.03, 3.05 (3*s*, 3 MeO(P)); 3.15, 3.16, 3.17 (3*s*, 3 MeO(P)); 3.12–3.24 (*m*, 3 CH$_2$OMe(P)); 3.37–3.38 (3*s*, 3 MeO(P)); 3.60–3.64 (*m*, H–C(3)(G$_1$)); 3.81–3.87 (*m*, 3 H–C(3)(G$_2$), OCH$_2$–C(2)(G$_1$)); 4.50 (*s*, CH$_2$Br); 4.19–4.52 (*m*, 3 OCH$_2$Ph, 3 H–C(1)(G$_2$)); 4.69 (*d*, $J = 5.6$, H–C(1)(G$_1$)); 7.20–7.33 (*m*, 16 arom. H). ^{13}C-NMR (125 MHz): 17.10; 17.26; 33.36; 50.98; 51.19; 51.22; 56.64; 56.69; 57.18; 58.51; 67.31; 69.51; 69.54; 70.21; 70.75; 72.76; 74.18; 75.26; 79.62; 82.31; 127.00; 127.10; 127.33; 127.59; 127.60; 128.24; 129.07; 136.86; 137.78; 138.00; 138.45; 140.07; 140.18; 140.26; 141.98. FAB-MS: 1063 (6, $[M + 23]^+$), 1039 (3, M^+), 1037 (3), 1008 (6), 1006 (5), 829 (8), 827 (7), 739 (51), 737 (47), 251 (21), 219 (50), 161 (74), 50 (100). Anal. calc. for $C_{57}H_{84}O_{12}Br$ (1040.18): C 65.82, H 8.04; found: C 65.90, H 8.02.

(MeO)$_9$-{[(S)G$_1$]^3}$_3$-[C$_c$] (**33**). To NaH (30.8 mg, 1.28 mmol, 9 equiv.) in THF (4 ml) was added **6** (50 mg, 0.14 mmol) in THF (2 ml), and the mixture was stirred under reflux for 30 min. The bromide **17** (165 mg, 0.50 mmol, 3.5 equiv.) in THF (3 ml) was then added at 0°, and the mixture was stirred under reflux for 5 h. The reaction was quenched by the addition of H_2O (10 ml), and the mixture was extracted with Et_2O (3 × 25 ml). The combined org. extracts were dried ($MgSO_4$) and concentrated *in vacuo*. The crude product was purified by FC (hexane/Et_2O 1:3): **33** (88 mg, 56%). Colorless, glassy oil. $[\alpha]_D^{r.t.} = -36.8$ ($c = 1.18$, $CHCl_3$). IR ($CHCl_3$): 3006*m*, 2929*m*, 2892*m*, 2824*w*, 1513*w*, 1482*w*, 1464*w*, 1446*w*, 1363*w*, 1093*s*, 1020*w*, 969*w*, 831*w*. ^{1}H-NMR (400 MHz): 0.89 (*s*, *t*-Bu); 1.19 (*d*, $J = 6.4$, Me(C)); 1.21 (*d*, $J = 6.5$, 3 Me(G$_1$)); 1.80–1.92 (*m*, 3 H–C(2)(G$_1$), 6 H–C(2$_{propyl}$)); 2.08–2.13 (*m*, H–C(3)(C)); 3.04 (2*s*, 3 MeO(P)); 3.16 (*s*, 3 MeO(P)); 3.12–3.20 (*m*, 3 CH$_2$OMe(P), H–C(4)(C)); 3.37 (*s*, 3 MeO(P)); 3.39–3.70 (*m*, 6 H–C(3$_{propyl}$), 6 H–C(1$_{propyl}$), CH$_2$(C), H–C(2)(C)); 3.82 (*dq*, $J = 12.9$, 3.1, 3 H–C(3)(G$_1$)); 4.22 (*d*, $J = 9.2$, 3 H–C(1)(G$_1$)); 4.47–4.52 (*m*, 5 H, OCH$_2$Ph); 4.57–4.61 (*m*, 1 H, OCH$_2$Ph); 7.27–7.36 (*m*, 12 arom. H). ^{13}C-NMR (100 MHz): 16.29; 17.24; 26.27; 30.18; 30.54; 30.76; 37.23; 44.44; 51.17; 56.65; 57.18; 58.50; 65.86; 67.88; 67.92; 68.59; 68.79; 69.45; 72.85; 73.18; 75.24; 76.53; 77.24; 82.25; 85.64; 127.22; 127.43; 127.47; 127.61; 127.63; 127.69; 137.84; 137.86; 140.16; 140.29; 140.32; 140.44. FAB-MS: 1234 (< 1, $[M + 133]^+$), 1124 (< 1, $[M + 23]^+$), 1100 (< 1, $[M - 1]^+$), 1069 (< 1), 992 (3), 832 (1), 799 (11), 595 (1), 402 (2), 219 (68), 191 (19), 187 (33), 175 (21), 161 (78). MALDI-TOF-MS: 1123 ($[M + 22]^+$). Anal. calc. for $C_{63}H_{104}O_{15}$ (1101.51): C 68.70, H 9.52; found: C 68.83, H 9.60.

(MeO)$_9$-{[(R)G$_1$]^3}$_3$-[C$_c$] (**34**). As described for **33**, with **6** (50 mg, 0.14 mmol), NaH (30.8 mg, 1.28 mmol, 9 equiv.), and **18** (165 mg, 0.50 mmol, 3.5 equiv.), reaction time 5 h. FC (hexane/Et_2O 1:3): **34** (79 mg, 50%). Colorless, glassy oil. $[\alpha]_D^{r.t.} = +72.4$ ($c = 1.08$, $CHCl_3$). IR ($CHCl_3$): 3007*m*, 2932*m*, 2824*w*, 1513*w*, 1464*w*, 1421*w*, 1364*w*, 1292*w*, 1094*s*, 1020*w*, 957*w*, 830*w*. ^{1}H-NMR (400 MHz): 0.90 (*s*, *t*-Bu); 1.15 (*d*, $J = 6.4$, Me(G$_1$)); 1.18 (*d*, $J = 6.4$, Me(C)); 1.81–1.96 (*m*, 3 H–C(2)(G$_1$), 6 H–C(2$_{propyl}$)); 2.08–2.13 (*m*, H–C(3)(C)); 3.17 (2*s*, 6 MeO(P)); 3.15–3.21 (*m*, 3 H–C(3)(G$_1$), H–C(4)(C)); 3.29 (*s*, 3 MeO(P)); 3.32–3.71 (*m*, 6 H–C(3$_{propyl}$),

6 H–C(1_{propyl}), 3 CH_2OMe(P), CH_2(C), H–C(2)(C)); 4.30 (*d*, *J* = 6.6, 3 H–C(1)(G_1)); 4.46–4.51 (*m*, 5 H, OCH_2Ph); 4.58–4.61 (*m*, 1 H, OCH_2Ph); 7.24–7.38 (*m*, 12 arom. H). ^{13}C-NMR (100 MHz): 16.15; 16.30; 26.28; 30.19; 30.55; 30.77; 37.25; 44.46; 50.86; 56.12; 56.88; 58.71; 65.87; 67.88; 67.95; 67.99; 68.61; 68.79; 69.35; 72.88; 73.22; 75.41; 76.54; 77.24; 81.99; 85.65; 127.23; 127.53; 127.59; 127.71; 137.35; 137.65; 137.66; 138.18; 140.43; 140.55; 140.57; 140.70. FAB-MS: 1234 (< 1, $[M + 133]^+$), 1124 (< 1, $[M + 23]^+$), 1100 (1, M^+), 984 (< 1), 889 (< 1), 832 (< 1), 799 (2), 595 (2), 461 (< 1), 402 (5), 251 (37), 220 (22), 219 (66), 191 (23), 187 (36), 175 (25). MALDI-TOF-MS: 1138 ($[M + 37]^+$), 1124 ($[M + 23]^+$). Anal. calc. for $C_{63}H_{104}O_{15}$ (1101.51): C 68.70, H 9.52; found: C 68.85, H 9.58.

(MeO)$_9$-{[(S)G$_1$]^3}$_3$-[C$_a$] (**35**). As described for **33**, with **7** (80 mg, 0.15 mmol), NaH (32.2 mg, 0.13 mmol, 9 equiv.), and **17** (177 mg, 0.53 mmol, 3.5 equiv.), reaction time 6.5 h. FC (hexane/Et_2O 1:2): **35** (157 mg, 82%). Colorless, glassy oil. $[\alpha]_D^{r.t.} = -22.7$ (*c* = 1.08, $CHCl_3$). IR ($CHCl_3$): 3007*m*, 2931*m*, 2892*m*, 2821*w*, 1514*w*, 1464*w*, 1446*w*, 1421*w*, 1380*w*, 1361*w*, 1092*s*, 1020*w*, 969*w*, 928*w*. ^{1}H-NMR (400 MHz): 0.94 (*s*, *t*-Bu); 1.21 (*d*, *J* = 6.5, 3 Me(G_1)); 1.29 (*d*, *J* = 6.4, Me(C)); 1.82–1.89 (*m*, 3 H–C(2)(G_1)); 2.29–2.35 (*m*, H–C(3)(C)); 3.04 (3*s*, 3 MeO(P)); 3.16, 3.17 (*s*, 3 MeO(P)); 3.12–3.21 (*m*, 3 CH_2OMe(P), H–C(4)(C)); 3.37 (*s*, 3 MeO(P)); 3.57 ('*dd*', *ABX*, *J* = 10.1, 8.9, 1 H, CH_2(C)); 3.74 (*dq*, *J* = 13.2, 3.6, H–C(2)(C)); 3.79 ('*dd*', *ABX*, *J* = 10.2, 3.1, 1 H, CH_2(C)); 3.83 (*dq*, *J* = 13.0, 3.1, 3 H–C(1)(G_1)); 4.23 (*d*, *J* = 9.2, 3 H–C(1)(G_1)); 4.38–4.66 (*m*, 9 OCH_2Ph); 7.20–7.37 (*m*, 24 arom. H). ^{13}C-NMR (100 MHz): 16.60; 17.23; 26.33; 37.43; 44.71; 51.18; 56.66; 57.17; 58.51; 68.37; 69.48; 70.57; 71.84; 71.91; 71.93; 72.10; 72.15; 72.85; 73.62; 75.24; 76.21; 77.24; 82.27; 86.11; 127.02; 127.63; 127.66; 127.72; 127.79; 136.94; 137.29; 137.35; 137.54; 137.56; 137.58; 138.40; 138.52; 139.08; 140.45; 140.46. FAB-MS: 1420 (< 1, $[M + 133]^+$), 1310 (< 1, $[M + 23]^+$), 1300 (< 1, $[M + 13]^+$), 1286 (< 1, $[M - 1]^+$), 807 (< 1), 703 (< 1), 661 (< 1), 557 (< 1), 499 (< 1), 407 (2), 307 (3), 295 (4), 285 (27), 281 (17), 255 (20), 219 (39), 187 (19), 175 (19), 161 (63). MALDI-TOF-MS: 1310 ($[M + 22]^+$). Anal. calc. for $C_{78}H_{110}O_{15}$ (1287.72): C 72.75, H 8.61; found: C 72.75, H 8.42.

(MeO)$_9$-{[(R)G$_1$]^3}$_3$-[C$_a$] (**36**). As described for **33**, with **7** (80 mg, 0.15 mmol), NaH (32.2 mg, 0.13 mmol, 9 equiv.), and **18** (176 mg, 0.53 mmol, 3.55 equiv.), reaction time 6.5 h. FC (hexane/Et_2O 1:2): **36** (161 mg, 84%). Colorless, glassy oil. $[\alpha]_D^{r.t.} = +69.5$ (*c* = 1.00, $CHCl_3$). IR ($CHCl_3$): 3007*m*, 2931*m*, 2882*m*, 2824*w*, 1510*w*, 1464*w*, 1419*w*, 1362*m*, 1093*s*, 1020*w*. ^{1}H-NMR (400 MHz): 0.94 (*s*, *t*-Bu); 1.16 (*d*, *J* = 6.4, 3 Me(G_1)); 1.29 (*d*, *J* = 6.4, Me(C)); 1.91–1.97 (*m*, 3 H–C(2)(G_1)); 2.29–2.34 (*m*, H–C(3)(C)); 3.17 (3*s*, 6 MeO(P)); 3.15–3.22 (*m*, 3 H–C(3)(G_1)); 3.29 (2*s*, 3 MeO(P)); 3.54–3.62 (*m*, 3 CH_2OMe(P), 1 H of CH_2(C)); 3.74 (*dq*, *J* = 13.0, 3.9, H–C(2)(C)); 3.79 ('*dd*', *ABX*, *J* = 10.1, 3.5, 1 H, CH_2(C)); 4.31 (*d*, *J* = 6.62, 3 H–C(1)(G_1)); 4.39–4.67 (*m*, 9 OCH_2Ph); 7.21–7.38 (*m*, 24 arom. H). ^{13}C-NMR (100 MHz): 16.16; 16.61; 26.34; 37.44; 44.71; 50.86; 56.15; 56.89; 58.71; 68.39; 69.36; 70.58; 71.86; 71.93; 71.95; 72.19; 72.23; 72.86; 73.63; 75.40; 76.21; 77.24; 82.00; 86.12; 127.03; 127.26; 127.64; 127.68; 127.74; 127.79; 136.95; 137.30; 137.36; 137.38; 137.41; 138.41; 138.53; 139.09; 140.68; 140.70. FAB-MS: 1420 (< 1, $[M + 133]^+$), 1310 (< 1, $[M + 23]^+$), 1300 (< 1, $[M + 13]^+$), 703 (< 1), 557 (< 1), 499 (< 1), **441** (1), 383 (2), 285 (**44**), 281 (21), 255 (22), 219 (44), 187 (24), 175 (25), 162 (16). ESI-MS: 1310 ($[M + Na]^+$), 667 ($[M + 2\,Na]^{2+}$). MALDI-TOF-MS: 1327 ($[M + 39]^+$), 1311 ($[M + 23]^+$). Anal. calc. for $C_{78}H_{110}O_{15}$ (1287.72): C 72.75, H 8.61; found: C 72.61, H 8.62.

(MeO)$_{27}$-{[(S)G$_2$]^3}$_3$-[C$_c$] (**37**). As described for **33**, with **6** (19.2 mg, 50 µmol), NaH (16 mg, 0.66 mmol, 12 equiv.), and **23** (203 mg, 0.20 mmol, 3.5 equiv.), in THF (3 ml, 5 ml, 5 ml), reaction time 46 h. FC (hexane/Et_2O 1:9): **37** (88 mg, 50%). Slightly yellow, glassy oil. $[\alpha]_D^{r.t.} = -48.5$ (*c* = 1.05, $CHCl_3$). CD (·10^2): 4.8 (255.5), 3.1 (259.0), 6.1 (262.5), 5.0 (266.0), 5.6 (269.5). IR ($CHCl_3$): 3003*m*, 2930*m*, 2892*m*, 2823*m*, 1718*w*, 1605*w*, 1511*w*, 1463*w*, 1420*w*, 1376*w*, 1093*s*, 1020*w*, 870*w*, 828*w*. ^{1}H-NMR (500 MHz): 0.91 (*s*, *t*-Bu); 1.19 (*d*, *J* = 6.6, Me(G_2)); 1.20 (*d*, *J* = 6.5, Me(G_2)); 1.21 (*d*, *J* = 6.6, Me(G_2)); 1.28 (*d*, *J* = 6.5, 3 Me(G_1)); 1.29 (*d*, *J* = 6.4, Me(C)); 1.80–1.94 (*m*, 9 H–C(2)(G_2), 3 H–C(2)(G_1), 3 H–C(2_{propyl})); 2.12–2.16 (*m*, 3 H–C(2_{propyl}), H–C(3)(C)); 3.02–3.04 (7*s*, 9 MeO(P)); 3.13–3.16 (7*s*, 9 MeO(P)); 3.11–3.21 (*m*, 9 CH_2OMe(P), H–C(4)(C)); 3.36–3.38 (7*s*, 9 MeO(P)); 3.33–3.38 (*m*, 3 H, OCH_2–C(2)(G_1)); 3.43–3.69 (*m*, 6 H–C(3_{propyl}), 6 H–C(1_{propyl}), CH_2(C), H–C(2)(C), 3 H of OCH_2–C(2)(G_1)); 3.79–3.86 (*m*, 9 H–C(3)(G_2)); 4.15–4.26 (*m*, 9 H–C(1)(G_2), 12 H of OCH_2Ph); 4.34 (*d*, *J* = 11.4, 3 H–C(1)(G_1)); 4.46–4.63 (*m*, 12 H of OCH_2Ph, 3 H–C(3)(G_1)); 7.10 (*d*, *J* = 7.7, 6 arom. H); 7.21–7.41 (*m*, 42 arom. H). ^{13}C-NMR (125 MHz): 16.20; 17.22; 18.72; 26.30; 30.16; 30.53; 30.76; 37.26; 44.31; 51.14; 51.68; 56.59; 56.63; 56.64; 56.85; 57.14; 58.46; 58.47; 65.88; 67.66; 67.89; 68.13; 68.20; 68.62; 68.76; 69.45; 69.49; 70.62; 71.20; 72.62; 72.86; 73.78; 75.20; 76.35; 80.92; 82.19; 82.21; 82.23; 85.44; 126.98; 127.05; 127.17; 127.20; 127.28; 127.45; 127.53; 127.72; 127.88; 127.96; 137.85; 137.98; 138.80; 139.99; 140.21; 140.44. FAB-MS: 3361 (39, $[M + 135]^+$), 3251 (100, $[M + 25]^+$), 2998 (12), 2410 (19), 2291 (15), 1959 (20). MALDI-TOF-MS: 3254 ($[M + 26]^+$). Anal. calc. for $C_{189}H_{284}O_{42}$ (3228.30): C 70.32, H 8.87; found: C 70.38, H 8.70.

(MeO)$_{27}$-{[(R)G$_2$]^3}$_3$-[C$_c$] (**38**). As described for **33**, with **6** (19.2 mg, 55 µmol), NaH (16 mg, 0.66 mmol, 12 equiv.), and **24** (200 mg, 0.19 mmol, 3.5 equiv.), in THF (3 ml, 5 ml, 5 ml), reaction time 50 h. FC (hexane/Et_2O

1:9): **38** (87 mg, 49%). Sligthly yellow, glassy oil. $[\alpha]_D^{r.t.} = +75.7$ ($c = 0.86$, $CHCl_3$). CD ($\cdot 10^2$): −4.8 (247.5), −8.8 (261.0), −6.5 (265.5), −8.2 (269.0), −1.3 (276.5). IR ($CHCl_3$): 3007*m*, 2930*m*, 2824*m*, 1513*w*, 1464*w*, 1420*w*, 1377*w*, 1092*s*, 1020*w*, 956*w*, 829*w*. ^{1}H-NMR (500 MHz): 0.91 (*s*, *t*-Bu); 1.14 (*d*, $J = 6.4$, $Me(G_2)$); 1.15 (*d*, $J = 6.4$, $Me(G_2)$); 1.16 (*d*, $J = 6.4$, $Me(G_2)$); 1.26 (*d*, $J = 6.4$, 3 $Me(G_1)$, Me(C)); 1.81–1.97 (*m*, 9 H–C(2)(G_2), 6 H–C(2_{propyl})); 2.10–2.15 (*m*, H–C(3)(C)); 2.25–2.30 (*m*, 3 H–C(2)(G_1)); 3.15–3.18 (8*s*, 18 MeO(P)); 3.13–3.22 (*m*, 9 H–C(3)(G_2), H–C(4)(C)); 3.28–3.30 (5*s*, 9 MeO(P)); 3.49–3.69 (*m*, 9 CH_2OMe(P), CH_2(C), 3 H–C(3)(G_1), H–C(2)(C), 6 H–C(3_{propyl}), 6 H–C(1_{propyl})); 3.82–3.90 (*m*, 3 OCH_2–C(2)(G_1)); 4.23–4.51 (*m*, 9 H–C(1)(G_2), 12 OCH_2Ph); 4.68 (*d*, $J = 5.9$, 3 H–C(1)(G_1)); 7.23–7.34 (*m*, 48 arom. H). ^{13}C-NMR (125 MHz): 16.16; 16.24; 17.16; 17.25; 26.33; 30.19; 30.56; 30.80; 37.29; 44.38; 50.83; 50.85; 51.10; 51.18; 51.21; 56.11; 56.13; 56.85; 56.89; 57.17; 58.69; 58.70; 58.71; 65.91; 67.55; 67.91; 68.19; 68.24; 68.63; 68.79; 69.35; 69.37; 69.50; 70.18; 70.65; 72.78; 72.89; 74.27; 75.25; 75.41; 75.43; 75.45; 76.42; 80.01; 81.96; 82.01; 82.31; 85.52; 127.01; 127.07; 127.09; 127.11; 127.29; 127.38; 127.56; 127.58; 127.67; 127.72; 137.73; 137.78; 137.80; 137.92; 138.11; 138.34; 140.30; 140.36; 140.40; 140.82; 140.83. FAB-MS: 3361 (29, $[M + 135]^+$), 3250 (100, $[M + 24]^+$). MALDI-TOF-MS: 3252 ($[M + 23]^+$). Anal. calc. for $C_{189}H_{284}O_{42}$ (3228.30): C 70.32, H 8.87; found: C 70.51, H 8.76.

(MeO)$_{27}$-{[(S)G$_2$]^3}$_3$-[C$_a$] (**39**). As described for **33**, with **7** (33 mg, 61 µmol), NaH (18 mg, 0.74 mmol, 12 equiv.), and **23** (224 mg, 0.22 µmol, 3.5 equiv.), in THF (3 ml, 5 ml, 5 ml), reaction time 20 h. FC (hexane/Et_2O 1:9): **39** (83 mg, 40%). Slightly yellow, glassy oil. $[\alpha]_D^{r.t.} = -42.3$ ($c = 1.07$, $CHCl_3$). CD ($\cdot 10^2$): 12.2 (244.0), 15.7 (250.0), 16.9 (256.0), 15.8 (262.5), 12.1 (269.5). IR ($CHCl_3$): 3004*m*, 2929*m*, 2824*w*, 1513*w*, 1464*w*, 1421*w*, 1376*w*, 1091*s*, 1020*w*, 969*w*. ^{1}H-NMR (500 MHz): 0.94 (*s*, *t*-Bu); 1.20 (*d*, $J = 6.8$, $Me(G_2)$); 1.21 (*d*, $J = 6.7$, $Me(G_2)$); 1.27–1.31 (*m*, 3 $Me(G_1)$, Me(C)); 1.80–1.88 (*m*, 9 H–C(2)(G_2)); 2.12–2.17 (*m*, 3 H–C(2)(G_1)); 2.33–2.38 (*m*, H–C(2)(C)); 3.01–3.04 (3*s*, 9 MeO(P)); 3.13–3.15 (3*s*, 9 MeO(P)); 3.10–3.21 (*m*, 9 CH_2OMe(P), H–C(4)(C)); 3.36–3.37 (3*s*, 9 MeO(P)); 3.33–3.39 (*m*, 3 H, OCH_2–C(2)(G_1)); 3.54–3.62 (*m*, 3 H of OCH_2–C(2)(G_1), 1 H of CH_2(C)); 3.75–3.86 (*m*, 9 H–C(3)(G_2), H–C(2)(C), 1 H of CH_2(C)); 4.14–4.68 (*m*, 9 H–C(1)(G_2), 18 OCH_2Ph, 3 H–C(3)(G_1), 3 H–C(1)(G_1)); 7.05–7.08 (*m*, 6 arom. H); 7.17–7.41 (*m*, 54 arom. H). ^{13}C-NMR (125 MHz): 16.69; 17.26; 18.70; 18.72; 26.38; 37.49; 44.57; 50.82; 51.16; 51.19; 51.68; 56.62; 56.66; 56.68; 57.16; 58.48; 58.49; 58.50; 67.70; 68.59; 69.35; 69.49; 69.53; 70.51; 70.60; 70.66; 71.24; 71.92; 71.98; 72.01; 72.29; 72.32; 72.37; 72.65; 72.86; 72.90; 73.63; 73.84; 75.24; 75.40; 76.07; 76.60; 81.01; 81.98; 82.24; 82.26; 82.28; 85.86; 126.80; 126.88; 127.03; 127.07; 127.12; 127.21; 127.32; 127.49; 127.57; 127.61; 127.69; 127.73; 127.78; 127.80; 127.85; 127.93; 127.96; 136.96; 137.30; 137.33; 137.75; 137.88; 138.45; 138.57; 138.83; 139.12; 140.01; 140.04; 140.25; 140.60. FAB-MS: 3547 (20, $[M + 135]^+$), 3437 (100, $[M + 25]^+$), 2477 (20), 1955 (17), 1117 (44). MALDI-TOF-MS: 3439 ($[M + 24]^+$). Anal. calc. for $C_{204}H_{290}O_{42}$ (3414.51): C 71.76, H 8.56; found: C 72.00, H 8.58.

(MeO)$_{27}$-{[(R)G$_2$]^3}$_3$-[C$_a$] (**40**). As described for **33**, with **7** (29.5 mg, 55 µmol), NaH (16 mg, 0.66 mmol, 12 equiv.), and **24** (200 mg, 0.19 mmol, 3.5 equiv.), reaction time 41 h. FC (hexane/Et_2O 1:9): **40** (140 mg, 75%). Slightly yellow, glassy oil. A second FC (hexane/Et_2O 1:9) gave an anal. pure sample. $[\alpha]_D^{r.t.} = +68.7$ ($c = 1.00$, $CHCl_3$). CD ($\cdot 10^2$): −6.7 (256.0), −6.2 (258.5), −8.7 (262.5), −6.1 (266.0), −7.4 (269.0). IR ($CHCl_3$): 3007*m*, 2931*m*, 2823*m*, 1512*w*, 1464*w*, 1421*w*, 1377*w*, 1359*w*, 1093*s*, 1019*w*, 957*w*, 827*w*. ^{1}H-NMR (500 MHz): 0.94 (*s*, *t*-Bu); 1.14 (*d*, $J = 6.2$, $Me(G_2)$); 1.15 (*d*, $J = 6.7$, $Me(G_2)$); 1.16 (*d*, $J = 6.1$, $Me(G_2)$); 1.16 (*d*, $J = 6.4$, $Me(G_2)$); 1.26 (*d*, $J = 6.4$, 3 $Me(G_1)$); 1.30 (*d*, $J = 6.4$, Me(C)); 1.90–1.98 (*m*, 9 H–C(2)(G_2)); 2.25–2.30 (*m*, 3 H–C(2)(G_1)); 2.33–2.38 (*m*, H–C(3)(C)); 3.15–3.18 (5*s*, 18 MeO(P)); 3.12–3.21 (*m*, 9 H–C(3)(G_2), H–C(4)(C)); 3.28–3.29 (3*s*, 9 MeO(P)); 3.53–3.62 (*m*, 9 CH_2OMe(P), 3 H–C(3)(G_1), 1 H of CH_2(C)); 3.78 (*m*, H–C(2)(C)); 3.80–3.91 (*m*, 3 OCH_2–C(2)(G_1), 1 H of CH_2(C)); 4.24–4.70 (*m*, 18 OCH_2Ph, 9 H–C(1)(G_2), 3 H–C(1)(G_1)); 7.22–7.36 (*m*, 60 arom. H). ^{13}C-NMR (125 MHz): 16.16; 16.49; 17.17; 17.25; 26.38; 37.49; 44.57; 50.83; 50.85; 51.09; 51.21; 56.12; 56.13; 56.85; 56.90; 57.17; 58.69; 58.71; 58.72; 67.56; 68.58; 69.35; 69.37; 69.50; 70.19; 70.60; 70.66; 71.91; 71.97; 72.00; 72.35; 72.39; 72.78; 72.89; 73.63; 74.27; 75.26; 75.42; 75.43; 75.45; 76.08; 80.00; 81.97; 82.01; 85.88; 127.02; 127.08; 127.09; 127.12; 127.33; 127.38; 127.61; 127.68; 127.77; 127.79; 127.85; 136.95; 137.30; 137.33; 137.54; 137.55; 137.57; 137.74; 137.91; 138.33; 138.45; 138.57; 139.13; 140.30; 140.36; 140.40; 140.93. FAB-MS: 3439 (100, $[M + 27]^+$), 3428 (21, $[M + 16]^+$), 1159 (20), 1134 (21), 1118 (32), 1103 (26), 1095 (25). MALDI-TOF-MS: 3438 ($[M + 23]^+$). Anal. calc. for $C_{204}H_{290}O_{42}$ (3414.52): C 71.76, H 8.56; found: C 71.81, H 8.48.

(MeO)$_9$-{[(S)G$_1$]^3}$_3$-[C] (**41**). As described for **33**, with **3** (134 mg, 0.76 mmol), NaH (164 mg, 6.82 mmol, 9 equiv.), and **17** (879 mg, 2.65 mmol, 3.5 equiv.), reaction time 4 h. FC (hexane/Et_2O, 1:1): 670 mg (95%) of pure **41**. Colorless, viscous oil. $[\alpha]_D^{r.t.} = -37.5$ ($c = 1.91$, $CHCl_3$). UV (MeCN): 262 (774). IR ($CHCl_3$): 3005*m*, 2930*m*, 2825*m*, 1465*w*, 1375*w*, 1095*s*. ^{1}H-NMR (400 MHz): 0.93 (*s*, *t*-Bu); 1.21 (*d*, $J = 6.5$, 3 $Me(G_1)$); 1.30 (*d*, $J = 6.4$, Me(C)); 1.81–1.89 (*m*, 3 H–C(2)(G_1)); 2.29–2.34 (*m*, H–C(3)(C)); 3.01, 3.02, 3.04 (3*s*, 3 MeO(P)); 3.10–3.25

(*m*, 3 CH_2OMe(P), H–C(4)(C)); 3.15, 3.16, 3.17 (3*s*, 3 MeO(P)); 3.37 (*s*, 2 MeO(P)); 3.38 (*s*, MeO(P)); 3.61 ('*dd*', *ABX*, J = 10.0, 8.5, 1 H, CH_2(C)); 3.71–3.77 (*m*, H–C(2)(C)); 3.79–3.87 (*m*, 3 H–C(3)(G_1), 1 H of CH_2(C)); 4.19–4.24 (*m*, 3 H–C(1)(G_1)); 4.35–4.65 (*m*, 3 OCH_2Ph); 7.20–7.40 (*m*, 12 arom. H). ^{13}C-NMR (100 MHz): 16.63; 17.11; 17.24; 26.32; 37.38; 44.81; 45.09; 51.15; 51.19; 56.65; 57.18; 58.49; 67.89; 68.30; 69.49; 70.77; 70.95; 72.90; 73.26; 73.71; 75.25; 79.92; 82.27; 86.21; 126.69; 127.40; 127.44; 127.59; 127.61; 127.71; 137.32; 137.90; 138.20; 138.29; 138.91; 139.68; 140.11; 140.18; 140.43; 140.54. FAB-MS: 927 (< 1, M^+), 715 (14), 625 (74), 583 (16), 463 (100), 407 (75), 219 (60), 161 (85), 134 (59), 91 (24). Anal. calc. for $C_{54}H_{86}O_{12}$ (927.27): C 69.95, H 9.35; found: C 70.17, H 9.27.

*(MeO)$_9$-{[(*R*)G_1]^3}$_3$-[C]* (**42**). As described for **33**, with **3** (134 mg, 0.76 mmol), NaH (164 mg, 6.82 mmol, 9 equiv.), and **18** (879 mg, 2.65 mmol, 3.5 equiv.), reaction time 4 h. FC (hexane/Et_2O, 1:1): 700 mg (98%) of pure **42**. Colorless, viscous oil. $[\alpha]_D^{r.t.}$ = + 82.1 (c = 2.99, $CHCl_3$). UV (MeCN): 262 (772). IR ($CHCl_3$) 3005*s*, 2930*s*, 2825*s*, 1465*m*, 1360*m*, 1095*s*. ^{1}H-NMR (300 MHz): 0.94 (*s*, *t*-Bu); 1.15 (*d*, J = 6.4, 2 Me(G_1)); 1.16 (*d*, J = 6.4, Me(G_1)); 1.32 (*d*, J = 6.4, Me(C)); 1.90–1.98 (*m*, 3 H–C(2)(G_1)); 2.29–2.35 (*m*, H–C(3)(C)); 3.10–3.25 (*m*, 3 H–C(3)(G_1), H–C(4)(C)); 3.15 (*s*, MeO(P)); 3.16 (*s*, 2 MeO(P)); 3.17 (*s*, 2 MeO(P)); 3.18 (*s*, MeO(P)); 3.29 (*s*, 2 MeO(P)); 3.30 (*s*, MeO(P)); 3.50–3.90 (*m*, 3 CH_2OMe(P), H–C(2)(C), CH_2–C(3)(C)); 4.28–4.32 (*m*, 3 H–C(1)(G_1)); 4.42–4.67 (*m*, 3 OCH_2Ph); 7.20–7.40 (*m*, 12 arom. H). ^{13}C-NMR (75 MHz): 16.19; 16.67; 26.35; 37.42; 44.96; 50.88; 56.10; 56.84; 58.66; 68.37; 69.41; 69.56; 70.79; 72.93; 73.77; 75.30; 75.46; 76.52; 82.06; 82.38; 86.36; 126.80; 126.96; 127.15; 127.31; 127.51; 127.67; 138.06; 138.13; 138.71; 140.04; 140.49. FAB-MS: 926 (6, [M – 1]$^+$), 715 (15), 629 (10), 625 (63), 463 (42), 407 (27), 363 (16), 321 (100), 307 (42). Anal. calc. for $C_{54}H_{86}O_{12}$ (927.27): C 69.95, H 9.35; found: C 70.23, H 9.53.

*(MeO)$_{27}$-{[(*S*)G_2]^3}$_{13}$-[C]* (**44**). As described for **33**, with **3** (9.3 mg, 0.05 mmol), NaH (11.5 mg, 0.47 mmol, 9 equiv.), and **23** (192 mg, 0.18 mmol, 3.5 equiv.), reaction time 28 h. FC (hexane/Et_2O 1:5): **44** (90.2 mg, 56%). Slightly yellow, glassy oil. $[\alpha]_D^{r.t.}$ = + 11.8 (c = 1.03, $CHCl_3$). UV (MeCN): 262 (3520). CD (· 10^2): –8.5 (244.7), –11.9 (256.3), –12.7 (261.7), –7.9 (265.8), –10.5 (269.0). IR ($CHCl_3$): 3007*m*, 2928*m*, 2892*m*, 2823*w*, 1514*w*, 1464*w*, 1420*w*, 1377*w*, 1092*s*, 1020*w*, 955*w*, 829*w*. ^{1}H-NMR (500 MHz): 0.96 (*s*, *t*-Bu); 1.17–1.22 (*m*, 9 Me(G_2)); 1.27 (*d*, J = 6.5, 3 Me(G_1)); 1.37 (*d*, J = 6.4, Me(C)); 1.80–1.88 (*m*, 9 H–C(2)(G_2)); 2.11–2.17 (*m*, 3 H–C(2)(G_1)); 2.43–2.49 (*m*, H–C(3)(C)); 3.00–3.03 (7*s*, 9 MeO(P)); 3.13–3.15 (5*s*, 9 MeO(P)); 3.10–3.21 (*m*, 9 CH_2OMe(P), H–C(4)(C)); 3.36–3.37 (3*s*, 9 MeO(P)); 3.32–3.39 (*m*, 3 H, OCH_2–C(2)(G_1)); 3.54–3.61 (*m*, 3 H, OCH_2–C(2)(G_1)); 3.67 (*t*, J = 9.6, 1 H, CH_2(C)); 3.78–3.85 (*m*, 9 H–C(3)(G_2)); 3.88 ('*dd*', *ABX*, J = 6.5, 3.6, 1 H, CH_2(C)); 3.92 (*dd*, J = 10.1, 3.2, H–C(2)(C)); 4.15–4.78 (*m*, 12 OCH_2Ph, 9 H–C(1)(G_2), 3 H–C(3)(G_1), 3 H–C(1)(G_1)); 7.11–7.39 (*m*, 48 arom. H). ^{13}C-NMR (125 MHz): 16.29; 17.25; 17.26; 18.82; 26.48; 37.59; 44.38; 51.19; 51.63; 51.68; 51.71; 56.62; 56.65; 56.67; 57.15; 57.16; 58.49; 58.50; 67.75; 68.93; 69.49; 69.53; 70.68; 70.74; 71.24; 72.68; 72.98; 73.76; 73.83; 75.22; 75.93; 80.86; 80.90; 80.93; 82.24; 82.27; 82.28; 85.51; 126.79; 127.19; 127.26; 127.42; 127.50; 127.56; 127.61; 127.69; 127.80; 127.82; 137.92; 137.95; 138.34; 138.42; 138.84; 138.85; 139.00; 139.94; 140.02; 140.04; 140.07; 140.24; 140.26; 140.32; 140.34. FAB-MS: 3187 (15, [M + 135]$^+$), 3076 (40, [M + 24]$^+$), 689 (59), 673 (55), 499 (55). VPO (c = 3.900 g/kg in CH_2Cl_2): 3183 ± 11%. Anal. calc. for $C_{180}H_{266}O_{39}$ (3054.07): C 70.79, H 8.78; found: C 70.93, H 8.90.

*(MeO)$_{18}$-{[(*R*)G_2]^3}$_2$-[C]-OH* (**45**). As described for **33**, with **3** (10 mg, 0.05 mmol), NaH (12 mg, 0.50 mmol, 9 equiv.), and **24** (200 mg, 0.19 mmol, 3.5 equiv.), reaction time 21 h. FC (hexane/Et_2O 1:5): **45** (105 mg, 88%). Slightly yellow, glassy oil. $[\alpha]_D^{r.t.}$ = + 66.4 (c = 1.01, $CHCl_3$). UV (MeCN): 262 (2211). CD (· 10^2): –3.9 (244.9), –5.4 (252.0), –6.4 (255.4), –6.8 (261.9), –4.6 (265.8), –6.5 (268.6). IR ($CHCl_3$): 3464*w*, 3007*m*, 2929*m*, 2824*m*, 1512*w*, 1464*w*, 1421*w*, 1377*w*, 1265*m*, 1093*s*, 1020*w*, 956*w*, 829*w*. ^{1}H-NMR (500 MHz): 0.92 (*s*, *t*-Bu); 1.12–1.18 (*m*, 6 Me(G_2)); 1.26 (*d*, J = 6.4, 2 Me(G_1)); 1.35 (*d*, J = 6.3, Me(C)); 1.90–1.98 (*m*, 6 H–C(2)(G_2)); 1.99–2.02 (*m*, H–C(3)(C)); 2.25–2.30 (*m*, 2 H–C(2)(G_1)); 3.16–3.19 (9*s*, 12 MeO(P)); 3.14–3.23 (*m*, 6 H–C(3)(G_2), H–C(4)(C)); 3.28–3.30 (4*s*, 6 MeO(P)); 3.45 ('*dd*', *ABX*, J = 5, 1.8, 1 H, CH_2(C)); 3.54–3.62 (*m*, 6 CH_2OMe(P), 2 H–C(3)(G_1)); 3.76 ('*dd*', *ABX*, J = 10, 5, 1 H, CH_2(C)); 3.83–3.90 (*m*, 2 OCH_2–C(2)(G_1), OH); 3.95–3.99 (*m*, H–C(2)(C)); 4.22–4.71 (*m*, 8 OCH_2Ph, 6 H–C(1)(G_2), 2 H–C(1)(G_1)); 7.22–7.36 (*m*, 32 arom. H). ^{13}C-NMR (125 MHz): 16.16; 17.00; 17.15; 17.25; 26.54; 35.74; 45.01; 50.83; 50.86; 51.09; 56.12; 56.13; 56.85; 56.89; 56.90; 58.69; 58.81; 58.72; 67.53; 67.56; 67.99; 68.17; 69.35; 69.37; 69.50; 70.19; 70.65; 70.91; 72.78; 73.24; 74.28; 75.25; 75.42; 75.43; 75.45; 77.94; 79.95; 79.99; 80.13; 81.96; 82.01; 82.31; 127.01; 127.08; 127.10; 127.12; 127.35; 127.37; 127.56; 127.59; 127.65; 127.75; 127.78; 128.81; 137.38; 137.71; 137.77; 137.91; 138.33; 138.34; 140.31; 140.36; 140.41; 140.98; 140.99. FAB-MS: 2227 (100, [M + 134]$^+$), 2117 (58, [M + 24]$^+$), 1976 (29), 1172 (27), 816 (33), 689 (50), 499 (48). VPO (5.270 g/kg in CH_2Cl_2): 1885 ± 11%. MALDI-TOF-MS: 2133 [M + 38]$^+$), 2117 ([M + 22]$^+$). Anal. calc. for $C_{123}H_{184}O_{27}$ (2094.79): C 70.53, H 8.85; found: C 70.61, H 8.73.

*(MeO)$_{27}$-{[(*S*)G_2]^3}$_{13}$-[C$_{enant.}$]* (**46**). As described for **33**, with **4** (18 mg, 0.11 mmol), NaH (22 mg, 0.92 mmol, 9 equiv.), and **23** (370 mg, 0.36 mmol, 3.5 equiv.), reaction time 25 h. FC (pentane/Et_2O 1:9): **46** (160 mg, 48%).

Slightly yellow, glassy oil. $[\alpha]_D^{r.t.} = -54.8$ ($c = 1.60$, $CHCl_3$). IR ($CHCl_3$): 3002*s*, 2928*s*, 2823*m*, 1602*w*, 1513*w*, 1463*w*, 1449*w*, 1421*w*, 1376*m*, 1093*s*, 969*m*, 832*m*. ^{1}H-NMR (500 MHz): 0.96 (*s*, *t*-Bu); 1.18–1.22 (*m*, 9 Me(G_2)); 1.26–1.28 (*m*, 3 Me(G_1)); 1.37 (*d*, $J = 6.3$, Me(C)); 1.81–1.87 (*m*, 9 H–C(2)(G_2)); 2.13–2.15 (*m*, 3 H–C(2)(G_1)); 2.44–2.46 (*m*, H–C(3)(C)); 3.00–3.04 (7*s*, 9 MeO(P)); 3.12–3.15 (6*s*, 9 MeO(P)); 3.10–3.23 (*m*, 9 CH_2OMe(P), H–C(4)(C)); 3.32–3.37 (*m*, 3 H, OCH$_2$–C(2)(G_1)); 3.36–3.37 (4*s*, 9 MeO(P)); 3.56–3.60 (*m*, 3 H, OCH$_2$–C(2)(G_1)); 3.67 (*t*, $J = 9.6$, 1 H, CH$_2$(C)); 3.79–3.89 (*m*, 9 H–C(3)(G_2), 1 H of CH$_2$(C)); 3.92 (*dd*, $J = 10.0$, 3.3, H–C(2)(C)); 4.17–4.22, 4.32–4.37, 4.46–4.77 (*m*, 12 OCH_2Ph, 9 H–C(1)(G_2), 3 H–C(3)(G_1), 3 H–C(1)(G_1)); 7.09–7.40 (*m*, 48 arom. H). ^{13}C-NMR (125 MHz): 16.28; 16.76; 17.26; 18.83; 26.49; 37.58; 44.40; 51.02; 51.19; 51.64; 51.68; 51.72; 56.62; 56.65; 56.67; 57.15; 58.49; 67.74; 68.90; 69.49; 69.53; 70.67; 71.24; 72.69; 72.96; 73.76; 73.84; 75.23; 75.90; 80.88; 80.95; 82.24; 82.28; 85.53; 126.77; 126.94; 127.19; 127.25; 127.38; 127.51; 127.56; 127.62; 127.70; 127.81; 128.19; 137.89; 137.92; 137.94; 137.96; 138.35; 138.42; 138.87; 139.01; 139.94; 140.03; 140.05; 140.07; 140.25; 140.27; 140.31; 140.33. MALDI-MS: 3075.7 ([M + 23]$^+$). Anal. calc. for $C_{180}H_{266}O_{39}$ (3054.07): C 70.79, H 8.78; found: C 70.62, H 8.71.

(MeO)$_{27}$-{[(R)G$_2$]^3}$_3$-[C$_{enant.}$] (**47**). As described for **33**, with the **4** (18 mg, 0.11 mmol), NaH (22 mg, 0.92 mmol, 9 equiv.), and **24** (370 mg, 0.36 mmol, 3.5 equiv.), reaction time 25 h. FC (hexane/Et$_2$O 1:9): **47** (168 mg, 50%). Slightly yellow, glassy oil. $[\alpha]_D^{r.t.} = +75.4$ ($c = 1.90$, $CHCl_3$). IR ($CHCl_3$): 3005*s*, 2933*s*, 2882*s*, 2820*m*, 1697*w*, 1605*w*, 1512*w*, 1461*m*, 1374*m*, 1348*m*, 1256*m*, 1092*s*, 1020*m*, 830*m*. ^{1}H-NMR (500 MHz): 0.97 (*s*, *t*-Bu); 1.14–1.17 (*m*, 9 Me(G_2)); 1.24–1.27 (*m*, 3 Me(G_1)); 1.38 (*d*, $J = 6.4$, Me(C)); 1.91–1.97 (*m*, 9 H–C(2)(G_2)); 2.25–2.28 (*m*, 3 H–C(2)(G_1)); 2.43–2.46 (*m*, H–C(3)(C)); 3.15–3.19 (12*s*, 18 MeO(P)); 3.15–3.28 (*m*, 9 H–C(3)(G_2), H–C(4)(C)); 3.28–3.29 (5*s*, 9 MeO(P)); 3.28–3.31 (*m*, 1 H, CH$_2$(C)); 3.54–3.63 (*m*, 9 CH_2OMe(P), 3 H–C(3)(G_1)); 3.66–3.70 (*m*, 1 H, CH$_2$(C)); 3.85–3.98 (*m*, 3 OCH$_2$–C(2)(G_1), H–C(2)(C)); 4.21–4.75 (*m*, 12 OCH_2Ph, 9 H–C(1)(G_2), 3 H–C(1)(G_1)); 7.23–7.48 (*m*, 48 arom. H). ^{13}C-NMR (125 MHz): 16.14; 16.30; 17.15; 17.17; 26.46; 37.58; 44.37; 50.82; 50.85; 51.08; 51.14; 51.17; 51.21; 56.10; 56.65; 56.83; 56.87; 57.14; 58.47; 58.67; 58.69; 67.56; 68.93; 69.33; 69.49; 70.18; 70.63; 70.74; 72.77; 72.99; 73.73; 74.26; 74.33; 75.40; 75.41; 75.43; 75.92; 79.97; 80.05; 81.94; 81.99; 96.08; 126.89; 127.06; 127.09; 127.13; 127.23; 127.28; 127.34; 127.37; 127.51; 127.58; 127.66; 127.79; 127.99; 137.70; 137.72; 137.76; 137.91; 138.14; 138.19; 138.33; 138.36; 138.77; 140.31; 140.32; 140.34; 140.36; 140.39; 140.42; 140.67; 140.99. MALDI-MS: 3076.2 ([M + 23]$^+$). Anal. calc. for $C_{180}H_{266}O_{39}$ (3054.06): C 70.79, H 8.78; found: C 70.84, H 8.70.

(MeO)$_{27}$-{[(S)G$_2$]^3}$_3$-[C$_{ethyl}$] (**48**). As described for **33**, with the **5** (15 mg, 0.11 mmol), NaH (22 mg, 0.92 mmol, 9 equiv.), and **23** (370 mg, 0.36 mmol, 3.5 equiv.), reaction time 25 h. FC (hexane/Et$_2$O 1:9): **48** (155 mg, 46%). Slightly yellow, glassy oil. $[\alpha]_D^{r.t.} = -52.1$ ($c = 1.60$, $CHCl_3$). IR ($CHCl_3$): 3000*s*, 2928*s*, 2823*m*, 1513*w*, 1463*w*, 1449*w*, 1420*w*, 1376*m*, 1093*s*, 1019*m*, 969*m*, 826*m*. ^{1}H-NMR (500 MHz): 1.00 (*t*, $J = 7.4$, H–C(6)(C)), 1.18–1.22 (*m*, 9 Me(G_2)); 1.26–1.28 (*m*, 3 Me(G_1)); 1.34 (*d*, $J = 6.4$, Me(C)); 1.63–1.76 (*m*, 2 H–C(5)(C)); 1.81–1.86 (*m*, 9 H–C(2)(G_2)); 2.12–2.17 (*m*, 3 H–C(2)(G_1)); 2.34–2.35 (*m*, H–C(3)(C)); 3.00–3.03 (9*s*, 9 MeO(P)); 3.12–3.15 (5*s*, 9 MeO(P)); 3.10–3.23 (*m*, 9 CH_2OMe(P)); 3.30–3.37 (*m*, 3 H, OCH$_2$–C(2)(G_1)); 3.35–3.37 (7*s*, 9 MeO(P)); 3.57–3.61 (*m*, 3 H, OCH$_2$–C(2)(G_1)); 3.69–3.72 (*m*, 1 H, CH$_2$(C)); 3.79–3.86 (*m*, 9 H–C(3)(G_2), 1 H of CH$_2$(C), H–C(4)); 3.91–3.98 (*m*, H–C(2)(C)); 4.17–4.21, 4.32–4.36, 4.46–4.69 (*m*, 12 OCH_2Ph, 9 H–C(1)(G_2), 3 H–C(3)(G_1), 3 H–C(1)(G_1)); 7.10–7.39 (*m*, 48 arom. H). ^{13}C-NMR (125 MHz): 17.22; 17.42; 17.52; 18.72; 18.78; 45.94; 50.98; 51.16; 51.64; 56.58; 56.62; 56.63; 57.11; 58.46; 67.70; 68.55; 69.46; 69.50; 70.42; 70.64; 71.20; 72.65; 72.94; 73.79; 74.26; 74.74; 75.20; 75.82; 80.17; 80.89; 82.21; 82.25; 126.90; 127.16; 127.21; 127.36; 127.47; 127.53; 127.79; 127.82; 127.95; 128.15; 137.89; 138.20; 138.54; 138.82; 139.99; 140.02; 140.19; 140.22; 140.35; 140.78. MALDI-MS: 3048.5 ([M + 23]$^+$). Anal. calc. for $C_{178}H_{262}O_{39}$ (3026.0): C 70.65, H 8.73; found: C 70.37, H 8.96.

(MeO)$_{27}$-{[(R)G$_2$]^3}$_3$-[C$_{ethyl}$] (**49**). As described for **33**, with **5** (15 mg, 0.11 mmol), NaH (22 mg, 0.92 mmol, 9 equiv.), and **24** (370 mg, 0.36 mmol, 3.5 equiv.), reaction time 25 h. FC (hexane/Et$_2$O 1:9): **49** (155 mg, 46%). Slightly yellow, glassy oil. $[\alpha]_D^{r.t.} = +66.6$ ($c = 1.80$, $CHCl_3$). IR ($CHCl_3$): 3005*s*, 2929*s*, 2823*s*, 1512*w*, 1463*m*, 1419*w*, 1377*m*, 1256*w*, 1094*s*, 1019*m*, 957*m*, 826*m*. ^{1}H-NMR (500 MHz): 1.01 (*t*, $J = 7.4$, H–C(6)(C)); 1.14–1.20 (*m*, 9 Me(G_2)); 1.21–1.27 (*m*, 3 Me(G_1)); 1.34 (*d*, $J = 6.4$, Me(C)); 1.68–1.77 (*m*, 2 H–C(5)(C)); 1.90–1.97 (*m*, 9 H–C(2)(G_2)); 2.26–2.27 (*m*, 3 H–C(2)(G_1)); 2.33–2.34 (*m*, H–C(3)(C)); 3.12–3.20 (16*s*, 18 MeO(P)); 3.12–3.23 (*m*, 9 H–C(3)(G_2)); 3.28–3.29 (9*s*, 9 MeO(P)); 3.28–3.31 (*m*, 1 H, CH$_2$(C)); 3.54–3.60 (*m*, 9 CH_2OMe(P), 3 H–C(3)(G_1)); 3.80–4.01 (*m*, 1 H of CH$_2$(C), 3 OCH$_2$–C(2)(G_1), H–C(4)(C), H–C(2)(C)); 4.22–4.70 (*m*, 12 OCH_2Ph, 9 H–C(1)(G_2), 3 H–C(1)(G_1)); 7.23–7.38 (*m*, 48 arom. H). ^{13}C-NMR (125 MHz): 16.16; 17.16; 17.56; 45.88; 48.32; 50.84; 50.86; 51.12; 56.12; 56.85; 56.90; 58.71; 67.57; 67.88; 68.62; 69.35; 69.50; 70.20; 70.45; 70.65; 71.01; 71.25; 72.80; 72.98; 73.47; 74.29; 74.87; 75.25; 75.42; 75.43; 75.94; 80.03; 80.24; 81.95; 82.07; 126.49; 127.08; 127.10; 127.24; 127.35; 127.37; 127.48; 127.59; 127.72; 127.79; 137.26; 137.69; 137.73; 137.75; 137.93; 138.03; 138.33; 138.36; 140.33; 140.38; 140.42; 140.60; 140.67; 140.73; 141.04; 141.13. MALDI-MS: 3048.3 ([M + 23]$^+$). Anal. calc. for $C_{178}H_{262}O_{39}$ (3026.00): C 70.65, H 8.73; found: C 70.51, H 8.85.

(MeO)$_{18}$-{[(S)G$_1$]^3-[(R)G$_2$]^3}$_2$-[C]-OH (**50**). As described for **33**, with **3** (21.8 mg, 0.12 mmol), NaH (26.7 mg, 1.12 mmol, 9 equiv.), and **29** (450 mg, 0.43 mmol, 3.5 equiv.), reaction time 25 h. FC (pentane/Et_2O 1:5 → 1:9): **50** (135 mg, 53%). Slightly yellow, glassy oil. $[\alpha]_D^{r.t.} = +48$ ($c = 1.5$, $CHCl_3$). IR ($CHCl_3$): 3500*w*, 3004*s*, 2929*s*, 2905*s*, 2823*m*, 1602*w*, 1511*w*, 1464*m*, 1376*m*, 1094*s*, 1020*m*, 956*m*, 828*m*. ^{1}H-NMR (500 MHz): 0.91 (*s*, *t*-Bu); 1.13–1.16 (*m*, 6 Me(G$_2$)); 1.24–1.31 (*m*, 2 Me(G$_1$)); 1.35 (*d*, $J = 6.3$, Me(C)); 1.89–1.95 (*m*, 6 H–C(2)(G$_2$)); 2.02–2.04 (*m*, H–C(3)(C)); 2.13–2.16 (*m*, 2 H–C(2)(G$_1$)); 3.13–3.18 (9*s*, 12 MeO(P)); 3.13–3.22 (*m*, 6 H–C(3)(G$_2$), H–C(4)(C)); 3.27–3.29 (4*s*, 6 MeO(P)); 3.35–3.37 (*m*, 2 H, OCH_2–C(2)(G$_1$)); 3.52–3.63 (*m*, 6 CH_2OMe(P), 2 H of OCH_2–C(2)(G$_1$)); 3.45–3.47, 3.74–3.78, 3.82–3.88, 3.96–3.98 (*m*, CH_2–(C), OH, H–C(2)(C)); 4.12–4.71 (*m*, 8 OCH_2Ph, 6 H–C(1)(G$_2$), 2 H–C(1)(G$_1$), 2 H–C(3)(G$_1$)); 7.10–7.41 (*m*, 32 arom. H). ^{13}C-NMR (125 MHz): 16.14; 16.99; 17.26; 18.55; 18.73; 26.23; 26.52; 35.77; 44.96; 50.83; 50.86; 51.65; 51.67; 56.11; 56.85; 56.87; 58.70; 67.79; 68.04; 69.32; 69.35; 70.65; 70.95; 71.21; 72.67; 73.26; 73.82; 75.41; 75.45; 77.90; 79.93; 80.93; 80.97; 81.93; 81.97; 126.45; 127.02; 127.09; 127.30; 127.32; 127.34; 127.58; 127.65; 127.68; 127.95; 127.98; 137.61; 137.66; 137.71; 138.08; 138.60; 140.29; 140.35; 140.54; 140.60; 140.67. MALDI-MS: 2118.4 ([M + 23]$^+$). Anal. calc. for $C_{123}H_{184}O_{27}$ (2094.79): C 70.53, H 8.85; found: C 70.62, H 8.87.

(MeO)$_{18}$-{[(R)G$_1$]^3-[(S)G$_2$]^3}$_2$-[C]-OH (**51**). As described for **33**, with **3** (18.4 mg, 0.10 mmol), NaH (22.6 mg, 0.94 mmol, 9 equiv.), and **30** (380 mg, 0.36 mmol, 3.5 equiv.), reaction time 25 h. FC (pentane/Et_2O 1:5 → 1:9): **51** (130 mg, 59%). Slightly yellow, glassy oil. $[\alpha]_D^{r.t.} = -40.0$ ($c = 1.7$, $CHCl_3$). IR ($CHCl_3$): 3500*w*, 3004*s*, 2930*s*, 2905*s*, 2823*m*, 1614*w*, 1512*w*, 1464*m*, 1376*m*, 1092*s*, 1020*m*, 968*m*, 828*m*. ^{1}H-NMR (500 MHz): 0.92 (*s*, *t*-Bu); 1.20–1.22 (*m*, 6 Me(G$_2$)); 1.24 (*d*, $J = 6.4$, 2 Me(G$_1$)); 1.35 (*d*, $J = 6.3$, 2 Me(C)); 1.82–1.88 (*m*, 6 H–C(2)(G$_2$)); 1.99–2.00 (*m*, H–C(3)); 2.22–2.30 (*m*, 2 H–C(2)(G$_1$)); 3.02–3.05 (6*s*, 6 MeO(P)); 3.15–3.18 (4*s*, 6 MeO(P)); 3.12–3.24 (*m*, 6 CH_2OMe(P), H–C(4)(C)); 3.36–3.38 (3*s*, 6 MeO(P)); 3.55–3.59 (*m*, 2 H–C(3)(G$_1$)); 3.80–3.88 (*m*, 6 H–C(3)(G$_2$), 2 OCH_2–C(2)(G$_1$), 1 H of CH_2–C(2), OH); 3.75–3.78, 3.95–3.98 (*m*, 1 H of CH_2–C(2), H–C(2)(C)); 4.19–4.69 (*m*, 8 OCH_2Ph, 6 H–C(1)(G$_2$), 2 H–C(1)(G$_1$)); 7.21–7.39 (m, 32 arom. H). ^{13}C-NMR (125 MHz): 17.01; 17.16; 17.26; 26.55; 35.75; 45.03; 51.13; 51.19; 51.22; 56.13; 56.63; 56.67; 57.17; 58.50; 67.48; 68.00; 69.51; 69.54; 70.20; 70.61; 70.93; 72.78; 73.25; 74.29; 75.26; 77.93; 79.89; 79.93; 80.13; 82.32; 126.99; 127.32; 127.35; 127.56; 127.59; 127.74; 127.77; 127.88; 137.38; 137.46; 137.78; 137.91; 138.12; 138.57; 140.03; 140.12; 140.17; 140.98. MALDI-MS: 2116.9 ([M + 23]$^+$). Anal. calc. for $C_{123}H_{184}O_{27}$ (2094.79): C 70.53, H 8.85; found: C 70.52, H 8.76.

(MeO)$_{18}$-{[(S)G$_1$]^3-[(R)G$_2$]^3}$_2$-[C$_{enant.}$]-OH (**52**). As described for **33**, with **4** (21.8 mg, 0.12 mmol), NaH (26.7 mg, 1.12 mmol, 9 equiv.), and **29** (450 mg, 0.43 mmol, 3.5 equiv.), reaction time 25 h. FC (pentane/Et_2O 1:5 → 1:9): **52** (166 mg, 64%). Slightly yellow, glassy oil. $[\alpha]_D^{r.t.} = +60.3$ ($c = 1.4$, $CHCl_3$). IR ($CHCl_3$): 3500*w*, 3005*s*, 2929*s*, 2905*s*, 2823*m*, 1603*w*, 1511*w*, 1464*m*, 1376*m*, 1094*s*, 1020*m*, 957*m*, 825*m*. ^{1}H-NMR (500 MHz): 0.91 (*s*, *t*-Bu); 1.13–1.16 (*m*, 6 Me(G$_2$)); 1.25–1.31 (*m*, 2 Me(G$_1$)); 1.35 (*d*, $J = 6.3$, Me(C)); 1.89–1.95 (*m*, 6 H–C(2)(G$_2$)); 2.01–2.02 (*m*, H–C(3)(C)); 2.13–2.16 (*m*, 2 H–C(2)(G$_1$)); 3.13–3.18 (6*s*, 12 MeO(P)); 3.13–3.22 (*m*, 6 H–C(3)(G$_2$), H–C(4)(C)); 3.27–3.29 (3*s*, 6 MeO(P)); 3.34–3.37 (*m*, 2 H, OCH_2–C(2)(G$_1$)); 3.52–3.62 (*m*, 6 CH_2OMe(P), 2 H of OCH_2–C(2)(G$_1$)); 3.46–3.48, 3.75–3.78, 3.82–3.88, 3.95–3.98 (*m*, CH_2–(C), OH, H–C(2)(C)); 4.15–4.71 (*m*, 8 OCH_2Ph, 6 H–C(1)(G$_2$), 2 H–C(1)(G$_1$), 2 H–C(3)(G$_1$)); 7.10–7.41 (*m*, 32 arom. H). ^{13}C-NMR (125 MHz): 16.14; 16.95; 17.26; 18.72; 18.74; 26.54; 35.76; 45.00; 50.83; 50.86; 51.66; 56.11; 56.85; 56.87; 58.70; 67.79; 67.99; 69.32; 69.34; 70.64; 70.89; 71.21; 72.44; 72.66; 73.25; 73.81; 75.24; 75.40; 75.44; 77.94; 80.06; 80.92; 80.96; 81.93; 81.97; 127.02; 127.08; 127.23; 127.29; 127.34; 127.57; 127.66; 127.94; 127.98; 137.61; 137.70; 137.70; 138.05; 138.60; 140.29; 140.35; 140.54; 140.60; 140.66; 140.71. MALDI-MS: 2117.3 ([M + 23]$^+$). Anal. calc. for $C_{123}H_{184}O_{27}$ (2094.79): C 70.53, H 8.85; found: C 70.48, H 8.72.

(MeO)$_{18}$-{[(R)G$_1$]^3-[(S)G$_2$]^3}$_2$-[C$_{enant.}$]-OH (**53**). As described for **33**, with **4** (18.4 mg, 0.10 mmol), NaH (22.6 mg, 0.94 mmol, 9 equiv.), and **30** (380 mg, 0.36 mmol, 3.5 equiv.), reaction time 25 h. FC (pentane/Et_2O 1:5 → 1:9): **53** (140 mg, 64%). Slightly yellow, glassy oil. $[\alpha]_D^{r.t.} = -29.6$ ($c = 1.4$, $CHCl_3$). IR ($CHCl_3$): 3500*w*, 3004*s*, 2930*s*, 2905*s*, 2823*m*, 1610*w*, 1512*w*, 1463*m*, 1376*m*, 1261*m*, 1093*s*, 1020*m*, 968*m*, 828*m*. ^{1}H-NMR (500 MHz): 0.92 (*s*, *t*-Bu); 1.20–1.22 (*m*, 6 Me(G$_2$)); 1.24 (*d*, $J = 6.4$, 2 Me(G$_1$)); 1.35 (*d*, $J = 6.3$, 2 Me(C)); 1.82–1.88 (*m*, 6 H–C(2)(G$_2$)); 1.99–2.00 (*m*, H–C(3)); 2.25–2.27 (*m*, 2 H–C(2)(G$_1$)); 3.02–3.04 (4*s*, 6 MeO(P)); 3.15–3.18 (3*s*, 6 MeO(P)); 3.12–3.23 (*m*, 6 CH_2OMe(P), H–C(4)(C)); 3.36–3.38 (3*s*, 6 MeO(P)); 3.55–3.58 (*m*, 2 H–C(3)(G$_1$)), 3.80–3.88 (*m*, 6 H–C(3)(G$_2$), 2 OCH_2–C(2)(G$_1$), 1 H of CH_2–C(2), OH); 3.75–3.78, 3.96–3.98 (*m*, 1 H of CH_2–C(2), H–C(2)(C)); 4.19–4.69 (*m*, 8 OCH_2Ph, 6 H–C(1)(G$_2$), 2 H–C(1)(G$_1$)); 7.21–7.39 (*m*, 32 arom. H). ^{13}C-NMR (125 MHz): 17.03; 17.16; 17.27; 26.55; 35.76; 45.03; 51.13; 51.19; 51.22; 56.62; 56.67; 57.17; 58.50; 67.49; 68.03; 69.36; 69.52; 69.55; 70.21; 70.62; 70.95; 72.46; 72.77; 73.26; 74.29; 75.26; 77.84; 79.93; 80.05; 82.32; 126.99; 127.32; 127.34; 127.36; 127.56; 127.59; 127.73; 127.77; 127.88; 137.38; 137.46;

137.81; 137.92; 138.12; 138.57; 140.03; 140.12; 140.18; 140.93; 140.98. MALDI-MS: 2116.5 ($[M + 23]^+$). Anal. calc. for $C_{123}H_{184}O_{27}$ (2094.79): C 70.53, H 8.85; found: C 70.39, H 8.59.

(MeO)$_3$-[G$_0$]-[C$_a$] (**54**). As described for **33** with **7** (91 mg, 0.17 mmol), NaH (37 mg, 1.5 mmol, 9 equiv.), and MeI (0.1 ml, 1.5 mmol, 9 equiv.). The suspension was stirred at 40° for 3 h, then kept at reflux for 7.5 h. Workup and FC (hexane/Et_2O 1:1): **54** (95 mg, 97%). Colorless, viscous oil. $[\alpha]_D^{r.t.} = +16.6$ ($c = 1.51$, $CHCl_3$). UV (MeCN): 261 (712). IR ($CHCl_3$): 3007*m*, 2931*m*, 2871*m*, 2824*w*, 1514*w*, 1467*w*, 1420*w*, 1380*w*, 1364*w*, 1095*s*, 1021*w*, 961*w*, 916*w*. ^{1}H-NMR (500 MHz): 0.94 (*s*, *t*-Bu); 1.27 (*d*, $J = 6.4$, Me–C(2)); 2.27–2.31 (*m*, H–C(3)); 3.19 (*d*, $J = 2.0$, H–C(4)); 3.36, 3.37 (3*s*, 3 MeO(P)); 3.55 ('*dd*', *ABX*, $J = 10.1$, 8.6, H–C(1')); 3.71 (*dq*, $J = 6.4$, 3.8, H–C(2)); 3.76 ('*dd*', *ABX*, $J = 10.1$, 3.6, H–C(1')); 4.38–4.48 (*m*, 5 OCH_2Ph); 4.61 (*d*, *AB*, $J = 11.6$, OCH_2Ph); 7.18–7.34 (*m*, 12 arom. H). ^{13}C-NMR (125 MHz): 16.62; 26.33; 37.41; 44.78; 57.97; 58.01; 58.03; 68.28; 70.55; 72.85; 73.64; 74.49; 74.50; 74.56; 76.22; 86.24; 127.00; 127.58; 127.63; 127.68; 127.78; 136.86; 137.22; 137.29; 138.36; 138.50; 139.07. EI-MS: 579 (1, $[M + 1]^+$), 547 (4), 443 (3), 355 (8), 291 (3), 255 (3), 225 (3), 193 (4), 157 (8), 135 (100), 104 (11), 91 (6). Anal. calc. for $C_{36}H_{50}O_6$ (578.79): C 74.71, H 8.71; found: C 74.87, H 8.87.

(MeO)$_3$-[G$_0$]-[C] (**55**). As described for **33** with **3** (159 mg, 0.90 mmol), NaH (195 mg, 8.14 mmol, 9 equiv.), and MeI (0.51 ml, 8.14 mmol, 9 equiv.). The suspension was kept at reflux for 4 h. Workup and FC (hexane/Et_2O 3:1): **55** (179 mg, 91%). Colorless oil. $[\alpha]_D^{r.t.} = +18.8$ ($c = 2.12$, $CHCl_3$). IR: 3005*s*, 2975*s*, 2932*s*, 2826*m*, 1479*m*, 1465*m*, 1395*m*, 1366*m*, 1153*m*, 1097*s*, 988*w*, 959*w*, 920*w*. ^{1}H-NMR (500 MHz): 0.92 (*s*, *t*-Bu); 1.20 (*d*, $J = 6.5$, Me–C(2)); 2.08–2.12 (*m*, H–C(3)); 2.88 (*d*, $J = 1.8$, H–C(4)); 3.30 ('*dd*', *ABX*, $J = 10.0$, 8.6, H–C(1')); 3.30 (*s*, MeO(P)); 3.33 (*s*, MeO(P)); 3.39 (*s*, MeO(P)); 3.40 (*dq*, $J = 6.5$, 3.7, H–C(2)); 3.55 ('*dd*', *ABX*, $J = 10.1$, 3.5, H–C(1')). ^{13}C-NMR (125 MHz): 15.80; 26.20; 37.21; 43.87; 56.63; 58.73; 60.67; 70.45; 78.24; 88.30. EI-MS: 219 (< 1, $[M + 1]^+$), 187 (< 1), 171 (1), 161 (38), 141 (2), 127 (10), 113 (10), 101 (100), 85 (14), 71 (97), 59 (33).

*Crystal-Structure Analysis: (2R,5R,6R)-2-(*tert*-Butyl)-5-{(S)-{4-{[(*tert*-Butyl)diphenylsilyloxy]methyl}-phenyl}hydroxymethyl}-1,3-dioxan-4-one* (**9**; $C_{33}H_{42}O_5Si$). Determination of the cell parameters and collection of the reflection intensities were performed on an *Enraf-Nonius-CAD4* four-circle diffractometer (graphite monochromatized MoK_α radiation, $\lambda = 0.7107$ Å). Colorless prism, 0.4 × 0.4 × 0.6 mm, orthorhombic, space group $P2_12_12_1$, $a = 9.115(9)$ Å, $b = 34.500(9)$ Å, $c = 10.222(5)$ Å, $V = 3215(4)$ Å^3, $Z = 4$, $\rho_{calc.} = 1.130$ gcm^{-3}, $\mu = 0.109$ mm^{-1}, $F(000) = 1176$. Number of reflections measured 1756 ($\omega/2\theta$ scan, $2 < 2\theta < 40°$, $T = 295$ K); 1756 unique reflections, which were used for the determination (direct methods, SHELXS-86). 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 (afix 3). The refinement converged at $R = 0.032$ ($wR^2 = 0.085$), min. and max. rest electron density −0.14, 0.27 eÅ^{-3}, number of variables 352.

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