On the Synthesis and Selective Deprotection of Low-Generation Dendrons with Orthogonally Protected Peripheral Amine Groups and a Possible Impact of the Deprotection Conditions on the Stability of Dendronized Polymers' Skeletons

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The synthesis of first- and second-generation dendrons with defined ratios of orthogonally protected amine groups in the periphery ((benzyloxy)carbonyl (Cbz) and (*tert*-butoxy)carbonyl (Boc) protection) and the degree to which they can be selectively removed are described. The reaction conditions required for these deprotections were applied to methacrylic acid (=2-methylprop-2-enoic acid) based dendronized polymers carrying the same peripheral protecting groups to investigate whether they have any detrimental interference with the polymer skeleton. Specifically it was explored whether dendrons attached to the backbone could possibly be cleaved off as a whole (de-dendronization). Finally it was investigated how de-dendronizations can be used for quantifying both the dendron-structure perfection and the polymer-backbone configurations.

Introduction. – The surface functional groups of dendrimers [1][2] and dendronized polymers [3–6] play a key role in the property engineering of these intriguing macromolecules. By the proper choice of these groups, fundamental issues such as solubility in either water or organic media [1][2] and the temperature range at which the glass transition occurs can be addressed [7][8]. More sophisticated aspects have also been treated, including the attachment of cell-targeting units and drugs [2] or compactization of DNA [2][9]. Recently, specifically surface-designed dendronized polymers were used to conduct elementary steps in the so-called bottom-up approach to the nanosciences [10]. So far, most dendrimers and dendronized polymers carry only one kind of peripheral functional group. Therefore, there is an obvious demand for synthetic strategies leading to compounds with individually addressable surface functionalities. This then would allow for a more flexible surface decoration and, thus, considerably widen the application scope. Besides a preliminary disclosure of parts of the present paper's findings [11], there have only been a few reports on dendrons, the key building blocks for dendrimers and dendronized polymers with orthogonally protected functional groups [12–14]. Related studies on desymmetrization during dendron synthesis are also available (see, *e.g.*, [15]).

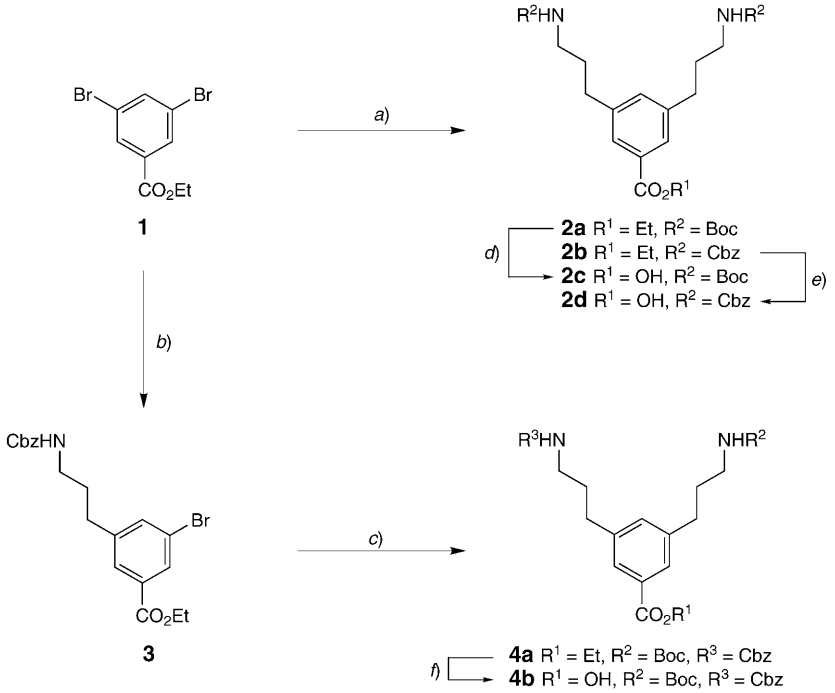
In our laboratory, a several-gram-scale route to first(G1)- through fourth-generation (G4) dendrons with (*tert*-butoxy)carbonyl(Boc)-protected amine groups was developed which proved reliable and useful and was, therefore, applied to the synthesis of a wide variety of dendronized polymers [16–18]. We here report on an extension of this strategy leading to G1 and G2 dendrons with two and four peripheral amines,

respectively, which carry the orthogonal Boc and (benzyloxy)carbonyl (Cbz) protecting groups in all possible combinations. Thus, on the G2 level, the dendrons carry 4 Boc, 3 Boc and 1 Cbz, 2 Boc and 2 Cbz, 1 Boc and 3 Cbz, or, finally, 4 Cbz groups. High-molar-mass dendronized polymers carry easily hundreds if not thousands of protected amine groups per macromolecule. It was, therefore, of utmost importance to check the degree of orthogonality of the chosen protecting groups. Any incomplete deprotection cannot be improved anymore. This is why the present work addresses also this aspect in some depth. At this point, it should be mentioned that another potentially promising pair of protecting groups, namely Boc and (9*H*-fluoren-9-ylmethoxy)carbonyl (Fmoc), could not be reasonably applied because the solubility of polymers which carry many Fmoc units is known to be very low [19].

Deprotection does not only lead to a hopefully complete removal of protecting groups but may also cause defects in the denpol skeleton. In many of these macromolecules, the dendrons are attached to the backbone through benzylic ester linkages which are known to be quite sensitive to conditions also relevant for deprotection. Such a cleavage would result in a loss of complete dendrons (de-dendronization), a process which of course cannot be accepted normally. Another aim of the present work was, therefore, to investigate to what extent certain deprotection conditions are associated with de-dendronizations. This refers specifically to hydrogenolysis, a commonly used protocol for deprotection of Cbz, which is known to also cleave benzylic esters. A point of concern was whether the steric crowding around the backbone caused by the dendrons would be sufficient to shield the internal benzylic ester functions. Finally, the present work addresses the issue of whether de-dendronization can actually be done quantitatively and used for two purposes: *a*) to analyze the structure by NMR spectroscopy of the cleaved-off dendrons and *b*) to determine the configuration of the polymer backbone. Aspect *a*) would be of importance in regard to the otherwise difficult to perform quantification of structure perfection of the dendrons of a dendronized polymer which was synthesized according to the attach-to route. Aspect *b*) is of principal interest in regard to the issue whether the dendritic substitution of macromonomers affects the stereochemical course of the polymerization.

Results and Discussion. – The synthetic sequences to the orthogonally protected dendrons are shown in *Schemes 1–4*. *Scheme 1* depicts the transformations done on the G1 level to provide all necessary starting dendrons for further growth. Some of these transformations have already been described but were improved to provide pure products on a larger scale. *Scheme 2* shows how the orthogonally Cbz- and Boc-protected G1 building block **4** was converted into the G2 dendrons with either 3 Boc and 1 Cbz (**7a**) or 1 Boc and 3 Cbz (**7b**). *Scheme 3* describes the access to the remaining combinations on the G2 level (**9a**: 4 Boc; **9b**: 2 Boc, 2 Cbz; **9c**: 4 Cbz). *Scheme 4*, finally, compiles the deprotections done on the G2 level. All reactions use standard steps of organic and peptide synthesis. The arms of the branching units were attached to the aromatic nucleus by *Suzuki–Miyaura* cross-coupling [20][21], and amides were synthesized by the EDC/HOBt method [22][23] (EDC = *N*-[3-(dimethylamino)propyl]-*N*′-ethylcarbodiimide, HOBt = 1-hydroxy-1*H*-benzotriazole). Deprotection of Boc groups was uniformly done with 25% aqueous HCl solution. The Cbz groups were removed by hydrogenation by using two different methods, *A* (5% aqueous formic acid, Pd/C, Hz

Scheme 1



a) 1. 9-BBN (9-borabicyclo[3.3.1]nonane), CH_2CHCH_2NHBoc or CH_2CHCH_2NHCbz, dry toluene, 0°, then 12 h at r.t.; 2. **1**, $[Pd(PPh_3)_4]$, 1M KOH, toluene, 100°, 14 h (86%). *b*) 1. 9-BBN, CH_2CHCH_2-NHCbz, dry toluene, 0°, then 12 h at r.t.; 2. **1**, $[Pd(PPh_3)_4]$, 1M KOH, toluene, 60°, 48 h, (66%). *c*) 1. 9-BBN, CH_2CHCH_2NHBoc, dry toluene, 0°, then 12 h at r.t.; 2. **3**, $[Pd(PPh_3)_4]$, 1M KOH, toluene, 100°, 14 h (86%). *d*) KOH, 55°, 10 h (92%). *e*) KOH, 55°, 4 h (94%). *f*) $MeOH/H_2O$ (3:1), KOH, 50°, 14 h (93%).

(3.5 bar)) and *B* (cyclohexa-1,4-diene, Pd/C, Hz (3.5 bar)), depending on the respective starting compound. In the following, only a few steps will be commented. The G2 dendrons reported carry hydroxy functions at the focal point, which give the possibility to attach polymerizable units in future polymer applications.

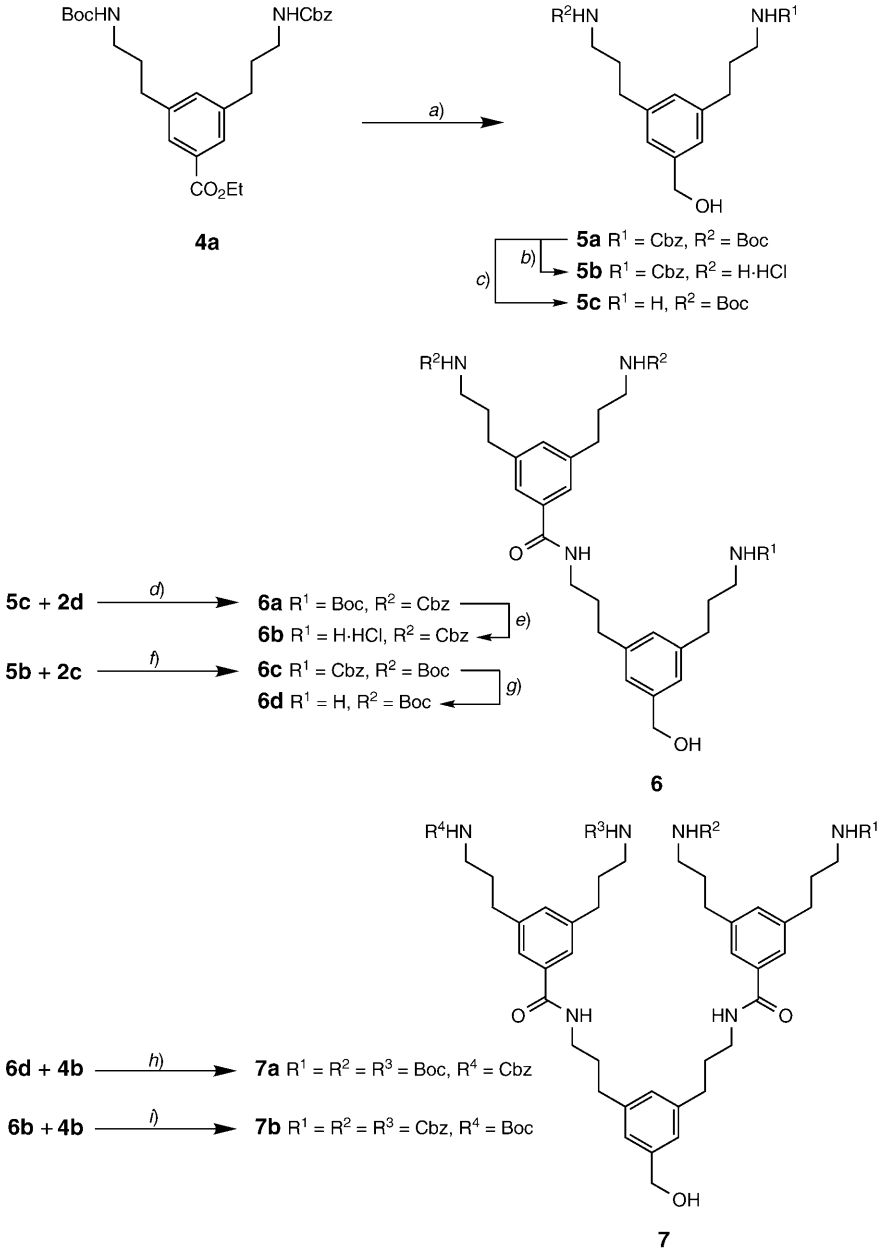
The dibromo ester **1** was converted into both the symmetric G1 dendrons **2a** [16] and **2b** [24] and the non-symmetric analog **4a**. To achieve the important desymmetrization, starting material **1** was first converted into the 'mono-armed' compound **3** which then was reacted further to give **4a** [25][26] (*Scheme 1*). The scale in which these steps were performed was significantly increased. Therefore, the key compound **4a** is now available in the 20-g scale with an overall yield of analytically pure material of 56% referring to **1**.

The subsequent reduction of **4a** to **5a** was performed with $LiAlH_4$. It turned out to be essential to strictly keep the reaction temperature below 10° to avoid an attack at Cbz (*Scheme 2*). When the same reaction was carried out at 20°, the yield of **5a** dropped from 81% to *ca.* 25%. All other reactions of *Schemes 1–3* (→ **5b**,**c**, **6a**–**d**, **7a**,**b**, **8a**,**b**, and **9a**–**c**) succeeded as expected. This refers also to the deprotection reactions; the degree

to which they proceeded was monitored either by TLC or NMR spectroscopy. Two of the compounds, **7b** and **9c**, required some attention. Dendron **7b** required prolonged hydrogenation times (*Method B*, 20 h instead of 10 h) to achieve complete deprotection of Cbz and **9c** failed even then to give completely deprotected material. Therefore, the somewhat harsher *Method A* was applied which led to success. All deprotection reactions were performed on a 200–400-mg scale and reached yields above 95% (for Boc groups) and in the range 85–94% (for Cbz). The deprotected compounds were used without further purification. The dendrons **9a**–**c** were obtained on a larger scale (**9a**: 8 g; **9b**: 7 g; **9c**: 4 g) than **7a** and **7b** (0.5–1 g) because of the lower number of steps involved. Some of the amide formations, for example the ones of **6a** and **7a**, were not only performed with HOBt/EDC but also with active-ester chemistry (HOSu/DCC (=*N*-hydroxysuccinimide/dicyclohexylcarbodiimide)). Though the coupling yields increased by *ca.* 10–15% in all cases with the latter reagents, the purification of the products was more tedious, rendering the overall efficiency of the former protocol higher. All dendrons were purified by conventional silica gel column chromatography with loadings of up to 3 g.

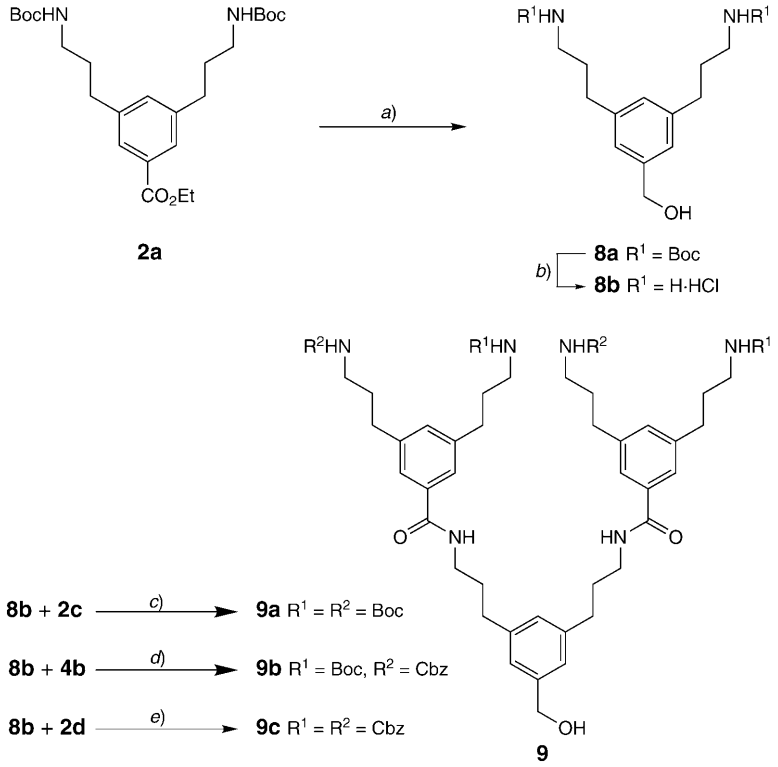
The deprotection reactions of the G2 dendrons **7a**,**b** and **9b**,**c** (*Scheme 4*) were checked by high-field NMR spectroscopy, the one of **9a** has already been reported [16]. Emphasis was of course placed on the orthogonally protected dendrons **7a**,**b** and **9b** to assess the selectivity of their deprotection, but also the deprotection of the all-Cbz decorated **9c** was investigated in some detail. Cbz had occasionally proven a delicate protecting group in polymer applications. In all cases, it was not only checked whether the signals of the respective protecting group had completely disappeared after deprotection, but also the intensity of the NMR signal of the remaining protecting group was compared with the dendritic fragment by integration to make sure that it had stayed unaffected. Finally, the entire dendritic fragment was checked by integration for structural integrity. *Fig. 1* shows three triples of ^{1}H-NMR spectra whereby each triple contains the respective starting dendron at the bottom (**7a**, **7b**, **9b**) followed by the products where Boc (in the middle) and Cbz have been removed (top), respectively. The spectra of the starting materials were recorded in $CDCl_3$, all those of deprotected dendrons, irrespective of the remaining protecting group, were recorded in $CDCl_3$/CD_3-OD mixtures. The signals of the protecting groups appeared as expected at the following chemical shifts: Boc at δ 1.44 and Cbz (CH_2 group) at δ 5.02. As can be seen, the spectra of the deprotected dendrons do not show any indication of the removed protecting groups, even if the relevant shift ranges are amplified considerably. From this, it is concluded that the deprotections are virtually quantitative, and Boc and Cbz are virtually orthogonal. The deprotection of **9c** was investigated with the same rigorosity and also found to be quantitative (NMR spetra not shown). To determine eventual loss of some of the protecting group supposed to remain intact while the other is removed, the integrals of the remaining group were compared with the dendritic skeleton by using NMR spectra recorded with pulse sequences so as to allow for reliable integrations. Exemplary this may be described for the transformations of **7a**, **7b**, and **9b** into **10c**, **10g**, and **10e**, respectively. The remaining Boc signal, which in all cases appeared at δ 1.44, was compared with the dendron signals at δ 2.55 and 4.55 before and after deprotection. Within the accuracy of this method, no reduction of Boc intensity was observed. Also no indication for structural defects could be obtained.

Scheme 2



a) **4a**, $LiAlH_4$, THF, $<10°$, 8.5 h (81%). *b*) 25% HCl soln., THF, r.t. (94%). *c*) AcOEt/EtOH 1.1, Pd/C, cyclohexa-1,4-diene, H_2, 4 h (92%). *d*) 1. **2d**, HOBt, EDC, CH_2Cl_2, $-30°$, 3 h; 2. **5c**, Et_3N, CH_2Cl_2, MeOH, $-20°$, then 14 h at r.t. (69% for both steps). *e*) 25% HCl soln, THF, r.t. (96%). *f*) 1. **2c**, HOBt, EDC, CH_2Cl_2, $-30°$, 3 h; 2. **5b**, Et_3N, CH_2Cl_2, MeOH, $-20°$, then 14 h at r.t. (84% for both steps). *g*) THF/AcOEt/EtOH 1:1:1, Pd/C cyclohexa-1,4-diene, H_2, 5 h (99%). h) 1. **4b**, HOBt, EDC, CH_2Cl_2, $-20°$, 3 h; 2. **6d**, Et_3N, CH_2Cl_2, MeOH, $-20°$, then 15 h at r.t. (80% for both steps). *i*) 1. **4b**, HOBt, EDC, CH_2Cl_2, $-20°$, 3 h; 2. **6b**, Et_3N, CH_2Cl_2, MeOH, $-20°$, then 14 h at r.t. (69% for both steps).

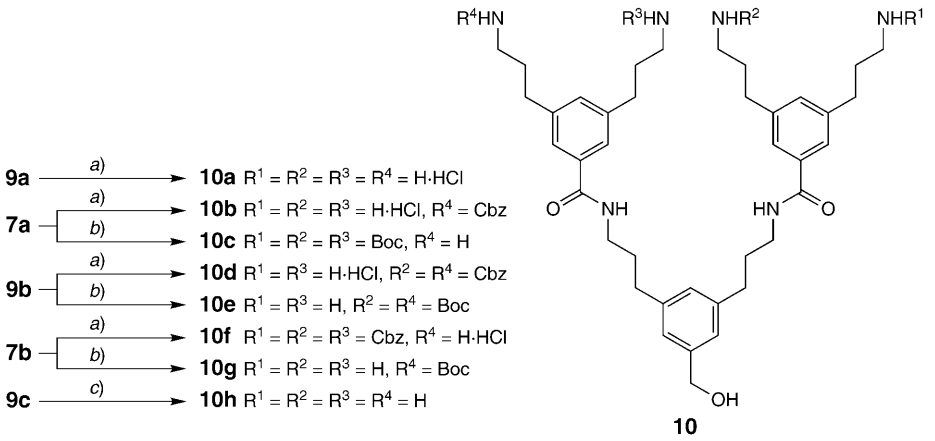
Scheme 3



a) **2a**, $LiAlH_4$, THF, 0°, 10 h (93%). *b*) 25% HCl soln., THF, r.t. (96%). *c*) 1. **2c**, HOBt, EDC, CH_2Cl_2, −30°, 3 h; 2. **8b**, Et_3N, CH_2Cl_2, MeOH, −20°, then 14 h at r.t. (65% for both steps). *d*) 1. **4b**, HOBt, EDC, CH_2Cl_2, −20°, 3 h; 2. **8b**, Et_3N, CH_2Cl_2, MeOH, −20°, then 15 h at r.t. (86% for both steps). *e*) 1. **2d**, HOBt, EDC, CH_2Cl_2, −30°, 3 h; 2. **8b**, Et_3N, CH_2Cl_2, MeOH, −20°, then 14 h at r.t. (72% for both steps).

The next step was to show whether dendronized polymers are sensitive to both deprotection conditions in their main skeleton. Most internal functional groups contained in the denpols in question are the relatively inert amide functions which in the above experiments had proved robust. The focus was put, therefore, on the benzylic ester functions which serve as linkage between the dendrons and the backbone. Very similar to the dendrons observed above, all denpols reported from this group withstood treatment with either trifluoroacetic acid or 25% aqueous HCl solution under the published conditions. Not even slight changes in the highly resolved ^{1}H- and ^{13}C-NMR spectra before and after the treatment with acid were observed. However, in contrast to the above findings for the dendrons with Cbz groups, hydrogenolysis of denpols turned out to be critical. In several attempts, G1 and G2 denpols [16] suffered cleavage of dendrons directly at the benzylic position. Even worse, no hydrogenolysis conditions could be found where de-dendronization would not occur at least partially. To find out whether an increased steric crowding at the sensitive position would help overcome this problem, the G3 denpol **13** (*Scheme 5*) was investigated accordingly. It was synthesized

Scheme 4



a) 25% HCl soln., THF, r.t. *b*) Pd/C, cyclohexa-1,4-diene, H_2, r.t., 3.5 bar. *c*) Pd/C, 5% formic acid, H_2, r.t, 3.5 bar.

by the attach-to route starting from G1 denpol **11** [16]. Reaction of the deprotected form **11** with the active-ester dendron **12** gave polymer **13**, whose coverage was virtually complete (see below). Somewhat against our expectation, subjecting **13** to several hydrogenolysis conditions led again to at least partial de-dendronization. Under certain conditions (10% formic acid for 4 d at 20°), it could even be driven to completion furnishing poly(methacrylic acid) (**14**) and the corresponding dendron **15**. The latter carries a Me group at the focal point, which is indicative for the cleavage process to be actually hydrogenolytic and not solvolytic in nature. The fact that de-dendronization occurs even for a G3 denpol like **13** shows that the steric shielding is insufficient, and any search for conditions to deprotect at a denpols' periphery of this kind must also take the internal functional groups into consideration even if they are located near the backbone and the conditions are heterogeneous. A lesson to be learned from this is that the density around the backbone imposed by the dendritic layer is lower than perhaps expected. At a first glance this is a disappointing finding as it suggests that Cbz is not a good protecting group for denpols based on acrylate polymerizable groups. However, this could be easily escaped by using denpols based on acrylamide polymerizable groups [27]. In this way, the critical linkage between dendron and backbone would be turned into a robust amide.

The initially unwanted de-dendronization opens interesting new options which will be briefly discussed in the following. Denpols prepared by the attach-to route have the intrinsic disadvantage that their structure will have defects due to an incomplete coverage of the starting denpol with dendrons. Though this coverage can be driven to values above 99% [28], it still has to be quantified in each case which is a rather tedious procedure. UV and Fluorescence spectroscopy were used for this purpose after appropriate labelling [27]. Each of these methods has its intrinsic limitations and uncertainties and involves a considerable effort. It was, therefore, of interest to have a third independent and perhaps easier to perform method available. This is where the above de-dendronization comes into play.

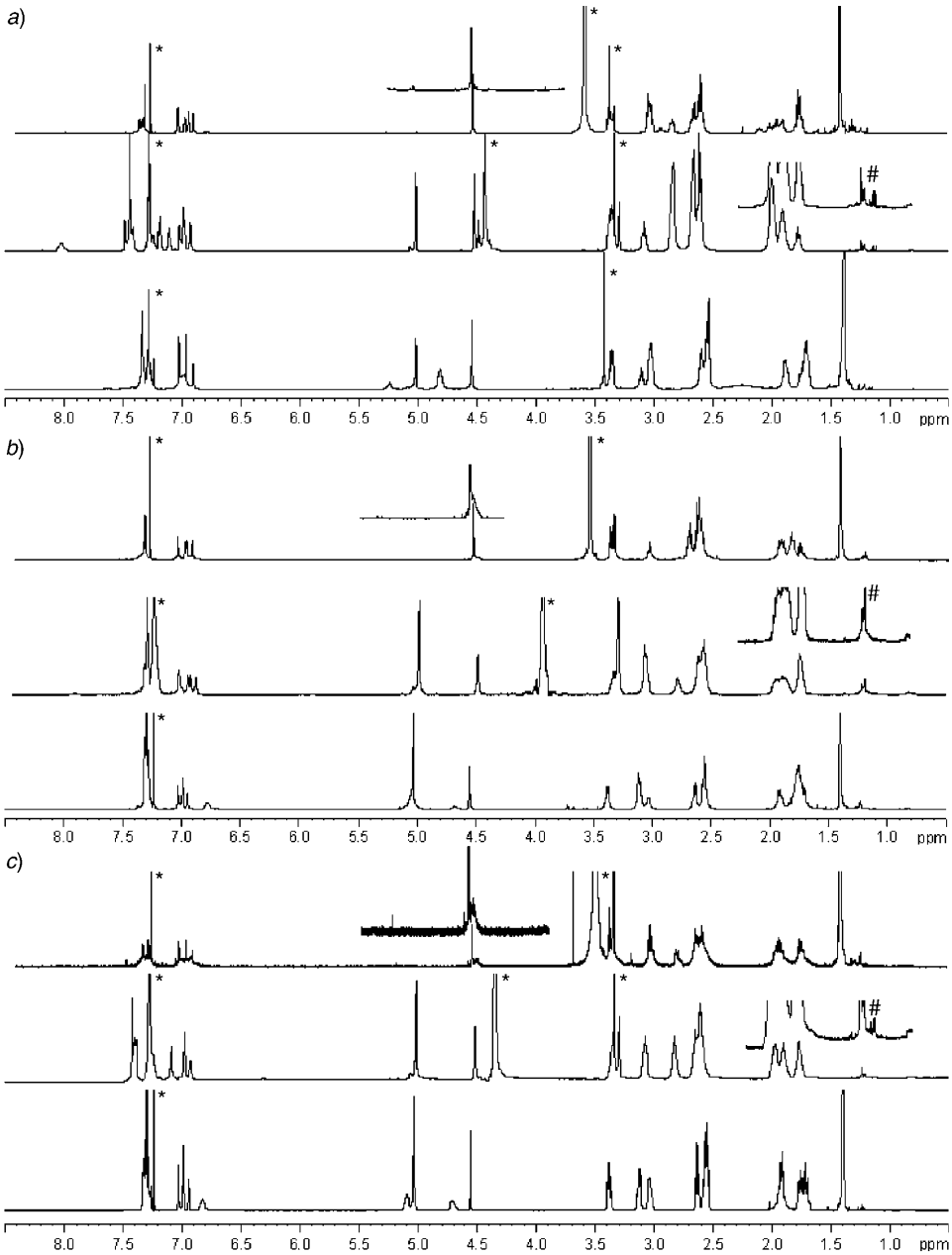


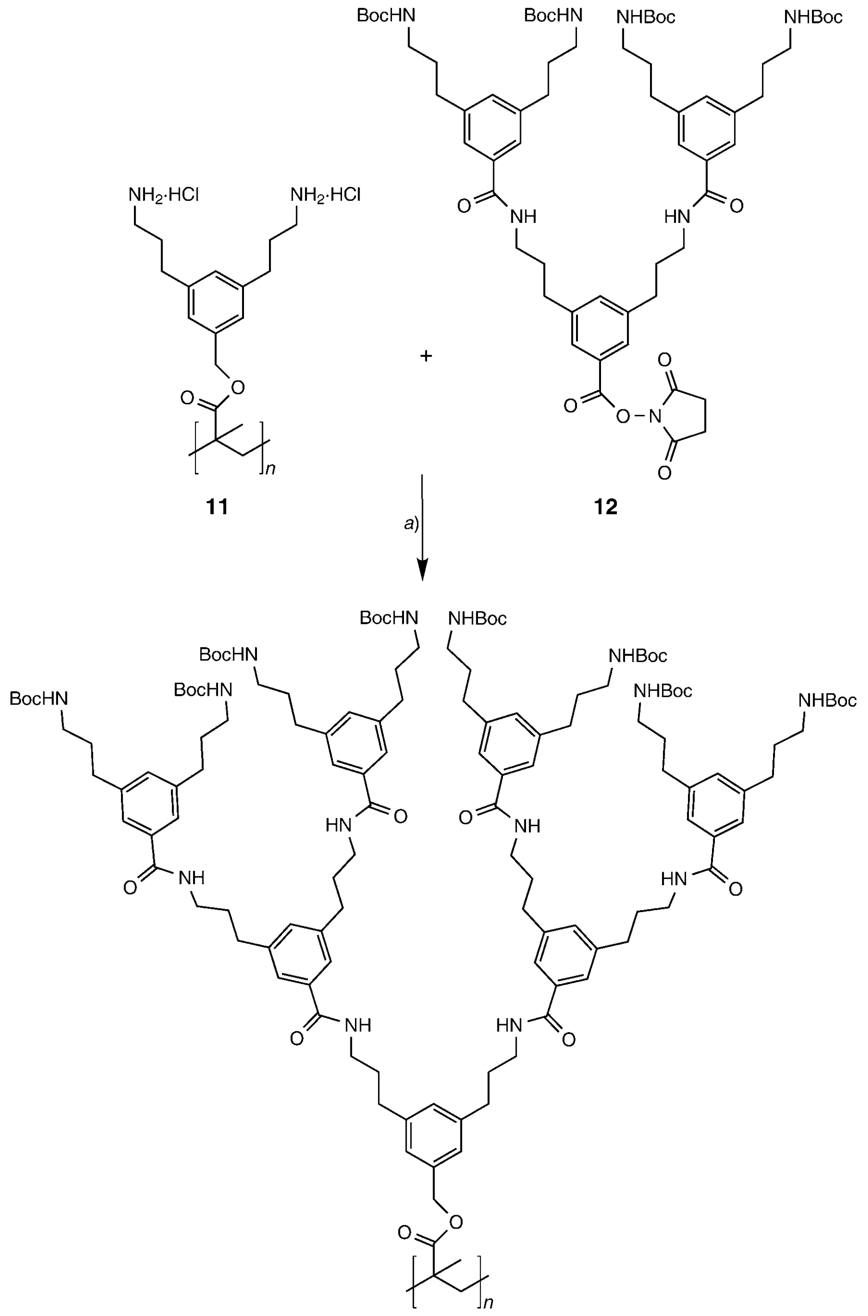
Fig. 1. *^{1}H-NMR Spectra of* a) **7a**, b) **7b**, *and* c) **9b** *and their respective selectively deprotected counterparts* (see text) *to show the degrees to which the deprotections can be achieved*. *: Solvent signals, #: grease signals.

The ^{1}H-NMR chemical shifts of CH_2 groups in α-position to amine or amide groups do not differ much normally. In many cases, however, the difference is large enough to be used for quantification. If a dendronization of a denpol (like the one shown in *Scheme 5*) does not lead to a complete coverage of the terminal amines with dendrons, a product is obtained which contains these unreacted amines next to reacted (amidated) ones. Given the shift difference between the respective CH_2 groups in α-position, this could in principle be used to quantify the degree of coverage by NMR integration. As long as one deals with the entire denpol, NMR signals are too broad to even consider such a method. If, however, the dendrons can be completely cleaved off the backbone prior to the NMR investigation by some simple treatment, highly resolved NMR spectra of the resulting dendrons can be obtained at a reasonable effort, and the quantification can be done. This procedure was tried for denpol **13** whose synthesis is given in the *Exper. Part*. For that purpose, the model compounds **17b** and **19** were prepared from **16** and **18**, respectively (*Scheme 6*). They served as reference points for the relevant chemical shifts of the CH_2 groups in α-position. The de-dendronization of **13** was performed as described above. When driven to completion, it furnished dendron **15** in yields of 80 and 85% (*Run 1* and *2*, resp., in *Fig. 2*) after the crude product had been passed once through a short silica gel column to remove impurities. During this simple step, it was paid attention to not remove any eventually existing incomplete dendron with free amino groups (for details, see *Exper. Part*). For the NMR analysis, the spectra of compounds **19** and **17b,** and of the two samples of **15** which stemmed from independent preparations (*Runs 1* and *2*) were compared (*Fig. 2*).

The critical signal is the one of **17b** at δ 2.85 which represents the protons of a CH_2 group in α-position to a free amino group (arrow in *Fig. 2*, *b*). This signal does, of course, not appear for model compound **19** (*Fig. 2*, *a*). The spectrum of dendron **15** (*Run 1*) shows a low-intensity signal in the relevant shift range whose intensity was estimated by integration to be 1.5% assuming that it represents two protons (*Fig. 2*, *c*). Given the fact that the samples of **15** used for the study had not been carefully purified it was not clear at this point whether this small signal actually stemmed from a CH_2 group in α-position. *Fig. 2*, *d* shows the spectrum of dendron **15** (*Run 2*): Virtually nothing was to be seen in the shift range δ 2.70–2.90, and an integration was, therefore, not performed. It is clear from this experiment that one deals with a level of structure perfection which is at or even below the limit of what NMR spectroscopy can provide. Defects amounting to a few percent would certainly be detected. This finding is in good agreement with the other quantification experiments described earlier which underlines that the attach-to route can be a powerful and reliable tool for the synthesis of structurally defined, high-molar-mass and high-generation dendronized polymers.

Apart from the issue of structure perfection, the observed de-dendronization of **13** opens another interesting possibility which is to determine the backbone's tacticity. It is still an open question whether there is a preorientation of dendronized monomers prior to their polymerization to denpols [29]. Possibly occurring isotactic or syndiotactic backbones may be caused by such phenomena, though a nonoccurrence of tacticity, of course, does not mean that there is no preorientation. The ^{1}H-NMR spectrum of the poly(methacrylic acid) (**14**) obtained by de-dendronization of **13** by comparison with literature spectra of highly iso-, syndio-, and atactic poly(methacrylic acids) (not shown) [30] shows that polymer **14** is mainly atactic with some isotactic units.

Scheme 5



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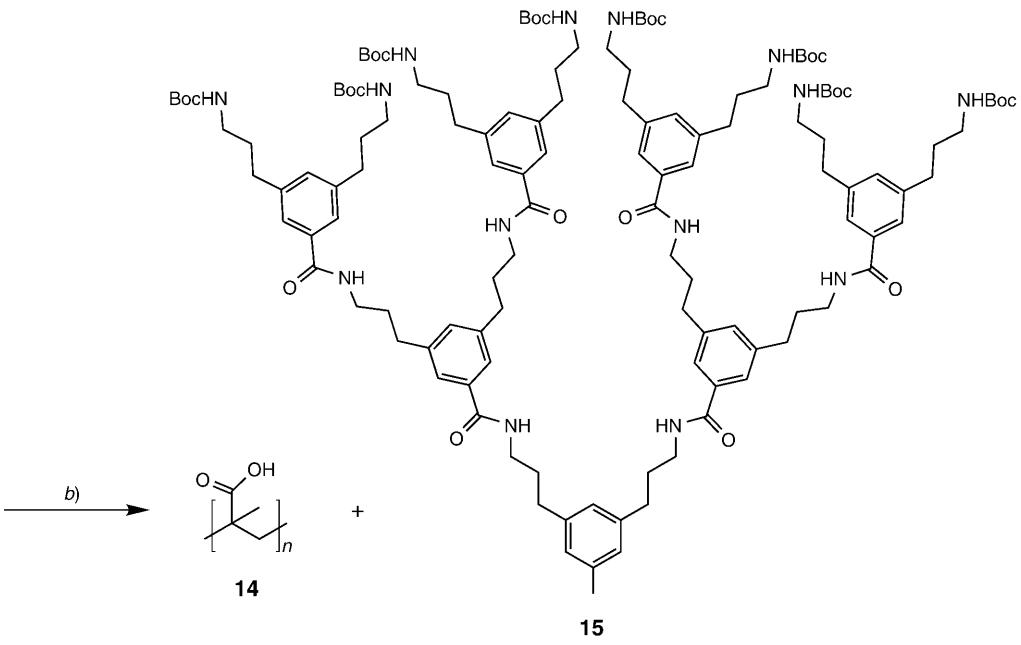
Scheme 5 (cont.)



a) **12**, Et_3N, $MeOH/CH_2Cl_2$, r.t., 60 h (93%). *b*) Pd/C, 10% HCOOH, THF/EtOH/AcOEt, 3.5 bar H_2, r.t., 4 d (84%).

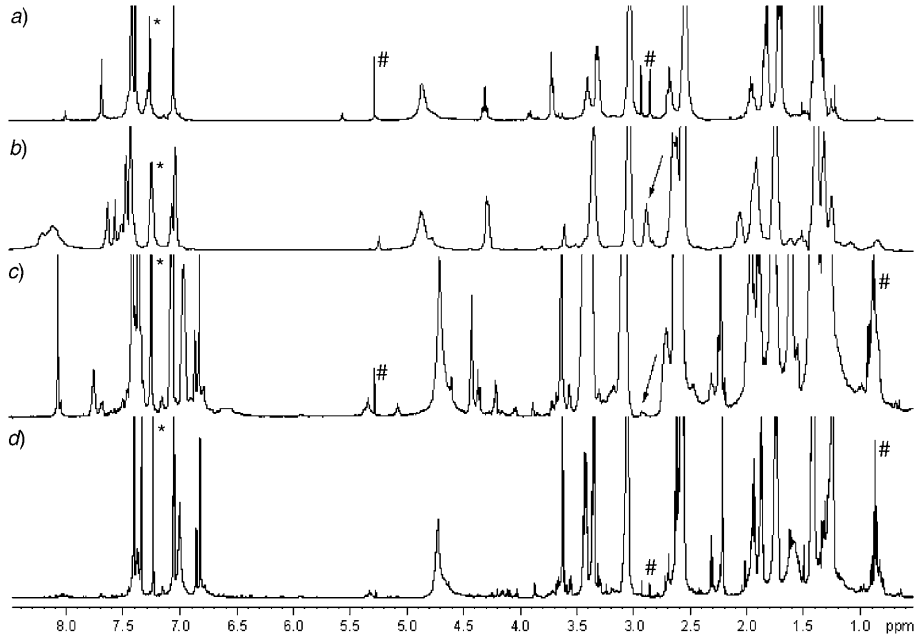
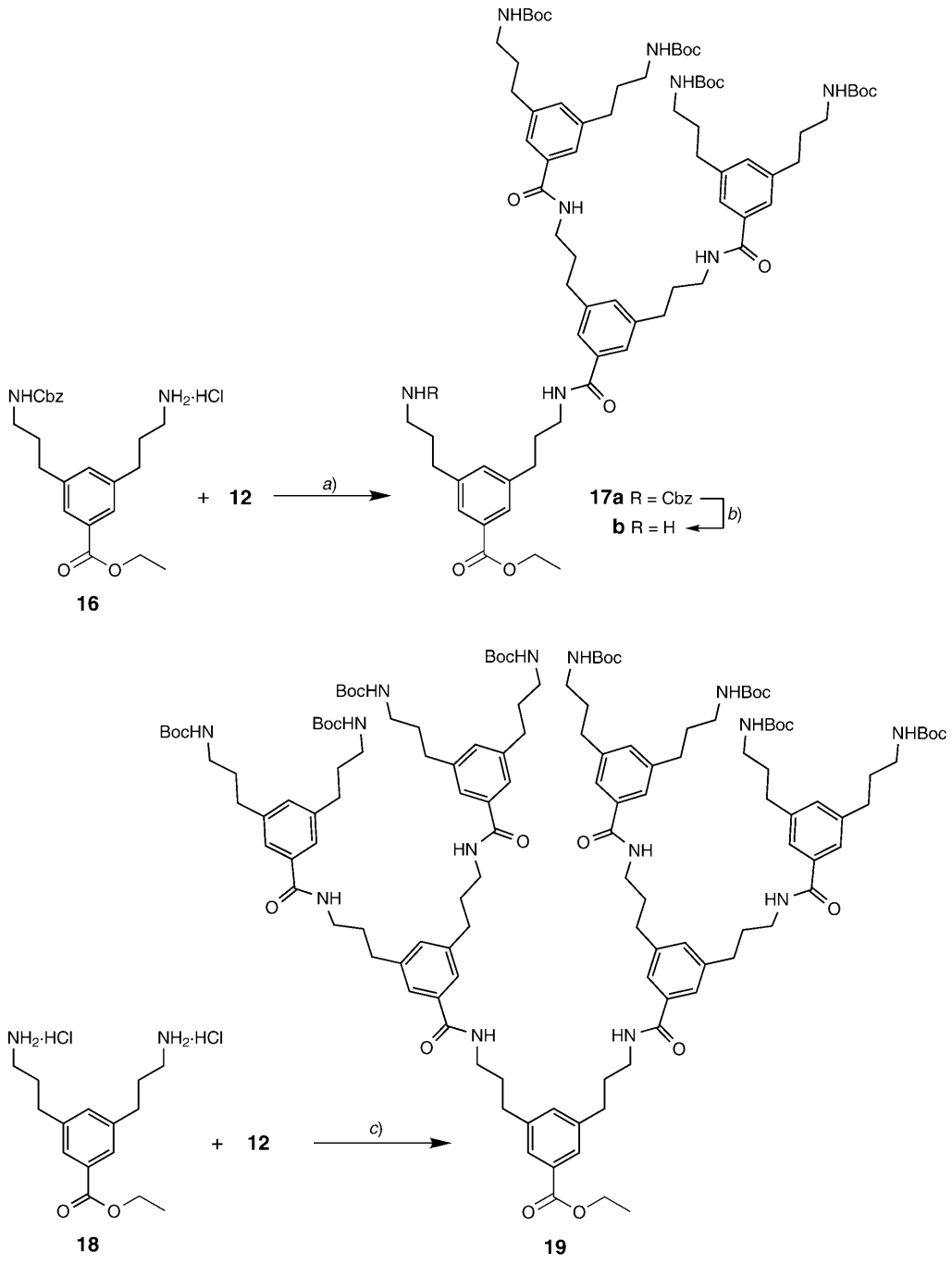


Fig. 2. *^{1}H-NMR Spectra of* a*) model compound* **19**, b*) model compound* **17b***, and* c)d*) crude dendron* **15** *obtained from two independent experiments* (*c*) *Run 1* and *d*) *Run 2*). All spectra were run in $CDCl_3$ which is marked (*). Solvent signals (DMF, CH_2Cl_2, grease) are marked (#).

Scheme 6



a) **12**, Et_3N, $MeOH/CH_2Cl_2$, r.t., 14 h (83%). *b*) Pd/C, 10% HCOOH, THF/EtOH, 3.5 bar H_2, r.t., 48 h (83%). *c*) **12**, Et_3N, $MeOH/CH_2Cl_2$, r.t., 14 h (89%).

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Experimental Part

General. Dendrons **2a**–**d**, **4b**, **8a**,**b**, **9a**, **10a**, and **12** were prepared according to literature procedures [16][24]. Reagents were purchased from *Aldrich*, *Acros*, or *Fluka*. Methacryloyl chloride (=2-methylprop-2-enoyl chloride; MAC) was freshly distilled before use. Tetrahydrofuran (THF) and triethylamine (Et_3N) were refluxed over Na with benzophenone as indicator, CH_2Cl_2 was dried by distilling over CaH_2. All other reagents and solvents were used as received. All reactions were performed under N_2. Column chromatography (CC): silica gel *60 M* (*Macherey–Nagel*; 0.04–0.063 mm, 230–400 mesh); FC = flash chromatography. T_g = Glass-transition temp. ^{1}H- and ^{13}C-NMR Spectra: *Bruker AM-300* (300 (^{1}H) and 75 MHz (^{13}C)), *AV-500* (500 (^{1}H) and 125 MHz (^{13}C)), and *AV-700* (700 MHz (^{1}H)) spectrometers; at r.t. (if not otherwise stated); $CDCl_3$ or CD_3OD as solvent; δ in ppm, J in Hz. ESI-MS: MS-service of the Laboratorium für Organische Chemie, ETH Zürich; *IonSpec-Ultra* instrument; in *m*/*z* (rel. %). Elemental analyses were performed by the Mikrolabor of the Laboratorium für Organische Chemie, ETH Zürich; the samples were dried rigorously under vacuum prior to analysis to remove strongly adhering solvent molecules. Gel permeation chromatography (GPC): *PL-GPC-220* instrument with 2× *PL-Gel Mix-B LS* column set (2×30 cm) equipped with RI (refractive index), viscosity, and LS (light scattering with 15 and 90° angle) detectors (DMF + 1 gl^{-1} LiBr as eluent at 80°); universal calibration with PMMA standards in a range of M_p 2680 to 3900000 (*Polymer Labs. Ltd*, UK).

Ethyl 3-Bromo-5-{3-{[(benzyloxy)carbonyl]amino}propyl}benzoate (**3**). A soln. of benzyl prop-2-enylcarbamate (12.50 g, 65.4 mmol) in dry toluene (150 ml) in a *Schlenk* flask under N_2 was degassed (3×), and at 0°, 9-BBN (8.65 g, 71.5 mmol) was added. The mixture was stirred for 12 h at r.t. The resulting mixture was then transferred to 1M KOH (100 ml), **1** (20.00 g, 65.3 mmol), and toluene (50 ml). The soln. was again degassed (3×), and then tetrakis(triphenylphosphine)palladium(0) (2.00 g, 1.7 mmol) was added. The mixture was stirred at 60° for 48 h under N_2. Then, the org. phase was washed with brine (100 ml) and $NaHCO_3$ soln. (100 ml), dried ($MgSO_4$), and evaporated and the residue subjected to CC (silica gel, hexane/AcOEt 15:1, then 8:1), followed by FC (CH_2Cl_2): **3** (16.78 g, 66%). Slightly yellow oil. ^{1}H-NMR ($CDCl_3$): 1.33 (*t*, *Me*CH_2O); 1.75 (*m*, 1 CH_2); 2.60 (*t*, ArCH_2); 3.09 (*m*, NHCH_2); 4.30 (*q*, MeCH_2-O); 4.69 (br. *s*, NH); 5.02 (*s*, PhCH_2O); 7.31 (*m*, 5 arom. H); 7.44 (*s*, 1 arom. H); 7.72 (*s*, 1 arom. H); 7.92 (*s*, 1 arom. H). ^{13}C-NMR ($CDCl_3$): 14.23; 31.32; 32.49; 40.03; 61.24; 66.69; 122.35; 128.09; 128.47; 130.19; 132.43; 135.53; 143.89; 156.39; 165.27. EI-MS: 419 (M^+). Anal. calc. for $C_{20}H_{22}BrNO_4$ (418.8): C 57.15, H 5.25, N 3.33; found: C 57.30, H 5.27, N 3.23.

Ethyl 3-{3-{[(Benzyloxy)carbonyl]amino}propyl}-5-{3-{[(tert-*butoxy)carbonyl]amino}propyl}benzoate* (**4a**). As described for **3**, with *tert*-butyl prop-2-enylcarbamate (8.20 g, 52.3 mmol), toluene (150 ml), and 9-BBN (7.00 g), (12 h at r.t), and then with 1M KOH (100 ml), **3** (16.70 g, 39.8 mmol), toluene (50 ml), and tetrakis(triphenylphosphine)palladium(0) (1.50 g, 1.3 mmol) (14 h at 100°). CC (silica gel, hexane/AcOEt 8:1 then 3:1): **4a** (18.63 g, 86%). Yellow oil. ^{1}H-NMR ($CDCl_3$): 1.35 (*t*, *Me*CH_2O); 1.44 (*s*, Me_3C); 1.78 (*m*, 4 H, CH_2); 2.60 (*m*, 4 H, ArCH_2); 3.09 (2*q*, 4 H, NHCH_2); 4.34 (*q*, MeCH_2O); 4.63 (br. *s*, 1 NH); 4.85 (br. *s*, 1 NH); 5.02 (*s*, PhCH_2O); 7.12 (*s*, 1 arom. H); 7.31 (*m*, 5 arom. H); 7.62 (*s*, 2 arom. H). ^{13}C-NMR ($CDCl_3$): 14.23; 28.32; 31.31; 31.47; 32.61; 32.67; 40.24; 60.89; 66.59; 79.08; 127.07; 127.13; 127.99; 128.42; 130.71; 133.09; 141.76; 141.95; 156.39; 156.79; 165.27. FAB-MS (3 kV): 521 (5.15, $[M+Na]^+$). Anal. calc. for $C_{28}H_{38}N_2O_6$ (498.61): C 67.45, H 7.68, N 5.62; found: C 67.32, H 7.48, N 5.25.

Benzyl tert-*Butyl {[5-(Hydroxymethyl)-1,3-phenylene]dipropane-3,1-diyl}bis[carbamate]* (**5a**). A soln. of **4a** (2.00 g, 4.0 mmol) in abs. THF (30 ml) was added dropwise to a suspension of $LiAlH_4$ (0.36 g, 9.6 mmol) in THF (10 ml) within 30 min under N_2 at 0°. The mixture was stirred for 8 h below 10°, and the reaction was quenched by adding acidified water (4 ml; pH 5). The resulting precipitate was filtered and washed with AcOEt (3×60 ml), and the solvent was evaporated. CC (silica gel, AcOEt/hexane 1:1) yielded **5a** (1.48 g, 81%)). Colorless viscous oil. ^{1}H-NMR ($CDCl_3$): 1.43 (*s*, Me_3C); 1.79 (*m*, 4 H,

CH_2); 2.45 (*t*, 4 H, ArCH_2); 3.10 (*q*, 2 H, CH_2NH); 3.20 (*q*, 2 H, CH_2NH); 4.49 (*s*, HOCH_2); 4.85 (br. *s*, 2 NH); 4.95 (*s*, PhCH_2O); 6.91 (*s*, 1 arom. H); 6.99 (*s*, 2 arom. H); 7.31 (*m*, 5 arom. H). ^{13}C-NMR ($CDCl_3$): 28.19; 31.08; 31.25; 32.54; 32.59; 39.66; 40.12; 64.36; 66.27; 78.85; 124.38; 126.60; 126.99; 127.25; 127.77; 128.10; 128.21; 136.41; 141.39; 141.53; 155.92; 156.38. ESI-MS: 479.3 ($[M+Na]^+$). Anal. calc. for $C_{28}H_{38}N_2O_6$ (456.26): C 68.40, H 7.95, N 6.14; found: C 68.11, H 7.92, N 6.17.

Benzyl {3-[3-(3-Aminopropyl)-5-(hydroxymethyl)phenyl]propyl}carbamate Hydrochloride (**5b**). A soln. of 25% HCl soln. (1.37 ml, 4 equiv.) in THF (3 ml) was added slowly to a soln. of **5a** (1.20 g, 2.6 mmol) in THF (25 ml) under N_2 at 0° (TLC monitoring). After completion of the reaction (*ca.* 3 h), the solvent was evaporated at r.t.: **5b** (0.97 g, 94%). Viscous oil. The product was used for the next step without further purification.

tert-*Butyl {3-[3-(3-Aminopropyl)-5-(hydroxymethyl)phenyl]propyl}carbamate* (**5c**). A mixture of **5a** (1.00 g, 2.2 mmol) in AcOEt/EtOH 1:1 (20 ml), 10% Pd/C (100 mg), and cyclohexa-1,4-diene (1.74 g, 22.0 mmol) was hydrogenated under 3 bar of H_2 at r.t. for 4 h. The soln. was then filtered through *Celite* and the solvent evaporated at r.t.: **5c** (0.7 g, 92%). Viscous oil. The product was used for the next step without further purification.

*Dibenzyl {{5-{{{3-{3-{[(*tert-*Butoxy)carbonyl]amino}propyl}-5-(hydroxymethyl)phenyl}propyl}-amino}carbonyl}-1,3-phenylene}dipropane-3,1-diyl}bis[carbamate]* (**6a**). To a mixture of **5c** (1.13 g, 2.2 mmol) and 1-hydroxy-1*H*-benzotriazol (HOBt; 0.36 g, 2.4 mmol) in CH_2Cl_2 (60 ml) in a *Schlenk* flask was added *N*-(3-dimethylaminopropyl)-*N*′-ethylcarbodiimide hydrochloride (EDC·HCl; 0.47 g, 2.5 mmol) at −30° under N_2. The mixture was stirred until the hydrochloride was dissolved. Then a soln. of **2c** (0.58 g, 1.8 mmol) and Et_3N (0.75 ml, 5.4 mmol) in MeOH/CH_2Cl_2 1:1 (15 ml) was added dropwise at −20°. The mixture was warmed to r.t. and stirred for 14 h, then washed with aq. $NaHCO_3$ soln. (50 ml) and brine (50 ml), dried ($MgSO_4$), and concentrated. CC (silica gel, AcOEt/hexane 3:1) yielded **6a** (1.01 g, 69%). Colorless foam. ^{1}H-NMR ($CDCl_3$): 1.45 (*s*, Me_3C); 1.66 (*m*, 6 H, CH_2); 1.80 (*m*, 2 H, CH_2); 2.44 (*m*, 8 H, ArCH_2); 2.97 (*m*, 6 H, CH_2NH); 3.30 (*q*, 2 H, CH_2NH); 4.45 (*s*, HOCH_2); 4.74 (br. *s*, 1 NH); 4.96 (*s*, 2 PhCH_2O); 5.28 (br. *s*, 2 NH); 6.77 (*s*, 1 arom. H); 6.84 (*s*, 1 arom. H); 6.88 (*s*, 2 arom. H); 6.97 (*s*, 1 arom. H); 7.19 (*m*, 10 arom. H); 7.27 (*s*, 1 arom. H). ^{13}C-NMR ($CDCl_3$): 28.06; 30.55; 30.95; 31.18; 32.45; 32.92; 39.38; 40.18; 64.24; 65.99; 78.60; 124.21; 124.49; 126.98; 127.50; 127.55; 128.03; 131.15; 134.44; 136.37; 141.26; 141.34; 141.41; 141.47; 155.92; 156.34; 167.60. ESI-MS: 831 (M^+). Anal. calc. for $C_{47}H_{60}N_4O_8$ (809.01): C 69.78, H 7.48, N 6.93; found: C 69.63, H 7.68, N 6.94.

Dibenzyl {{5-{{{3-{3-(3-Aminopropyl)-5-(hydroxymethyl)phenyl]propyl}amino}carbonyl}-1,3-phenylene}dipropane-3,1-diyl}bis[carbamate] Hydrochloride (**6b**). To a soln. of **6a** (1.20 g, 2.6 mmol) in THF (25 ml) was slowly added a soln. of 25% HCl soln. (1.37 ml, 4 equiv.) in THF (3 ml) under N_2 at 0°. The mixture was stirred for 3 h. The solvent was evaporated at r.t. to yield **6b** (1.00 g, 96%). Viscous oil. The product was used for the next step without further purification.

*Di(*tert-*butyl) {{5-{{{3-{3-{3-{[(Benzyloxy)carbonyl]amino}propyl}-5-(hydroxymethyl)phenyl}propyl}amino}carbonyl}-1,3-phenylene}dipropane-3,1-diyl}bis[carbamate]* (**6c**). To a soln. of the acid dendron **2c** (1.10 g, 2.5 mmol) in CH_2Cl_2 (30 ml) was added HOBt (0.39 g, 2.7 mmol) at r.t. After 10 min at −30°, EDC·HCl (0.50 g, 2.6 mmol) was added. The mixture was stirred for 3 h. Then a soln. of **5b** (0.82 g, 2.1 mmol) and Et_3N (1.45 ml, 10.4 mmol) in MeOH/CH_2Cl_2 1:1 (15 ml) was added dropwise at −20°. The resulting mixture was warmed to r.t. and stirred for 14 h. It was then washed with brine and aq. $NaHCO_3$ soln. The org. phase was dried ($MgSO_4$) and the solvent evaporated. CC (silica gel, AcOEt/hexane 2:1, then 3:1) yielded **6c** (2.65, 84%). Colorless foam. ^{1}H-NMR ($CDCl_3$): 1.44 (*s*, 2 Me_3-C); 1.76 (*m*, 6 H, CH_2); 1.92 (*m*, 2 H, CH_2); 2.57 (*m*, 8 H, ArCH_2); 3.13 (*m*, 6 H, CH_2NH); 3.40 (*q*, 2 H, CH_2NH); 4.58 (*s*, HOCH_2); 5.2 (br. *s*, 1 NH); 5.06 (*s*, PhCH_2O); 5.29 (br. *s*, 2 NH); 6.89 (*s*, 1 arom. H); 6.97 (*s*, 1 arom. H); 7.01 (*s*, 1 arom. H); 7.07 (*s*, 1 arom. H); 7.32 (*m*, 5 arom. H); 7.39 (*s*, 2 arom. H). ^{13}C-NMR ($CDCl_3$): 28.10; 30.54; 30.76; 31.21; 32.12; 32.57; 32.99; 39.50; 39.80; 64.33; 66.13; 78.66; 124.24; 124.57; 127.04; 127.57; 127.66; 128.11; 131.23; 134.48; 136.30; 141.32; 141.45; 155.90; 156.44; 167.68. ESI-MS: 797 ($[M+Na]^+$). Anal. calc. for $C_{44}H_{62}N_4O_8$ (775.00): C 68.19, H 8.06, N 7.23; found: C 67.92, H 8.23, N 7.12.

*Di(*tert-*butyl) {{5-{{{3-[3-(3-Aminopropyl)-5-(hydroxymethyl)phenyl]propyl}amino}carbonyl}-1,3-phenylene}dipropane-3,1-diyl}bis[carbamate]* (**6d**). Into a hydrogenation flask, **6c** (2.15 g, 2.8 mmol) in THF/AcOEt/EtOH 1:1:1 (30 ml), 10% Pd/C (0.22 g) and cyclohexa-1,4-diene (0.4 ml, 10 equiv.) were

added. The mixture was hydrogenated under 3 bar of H_2 at r.t. (TLC monitoring until the reaction was finished (*ca.* 5 h)). The product was filtered and washed with AcOEt (50 ml). Evaporation of the solvent at r.t. yielded **6d** (1.77 g, 99%). Viscous oil. The product was used for the next step without further purification.

*Benzyl Tri(*tert*-butyl) {[5-(Hydroxymethyl)-1,3-phenylene]bis(propane-3,1-diyliminocarbonylbenzene-5,1,3-triyldipropane-3,1-diyl)}tetrakis[carbamate]* (**7a**). To a soln. of acid dendron **4b** (1.50 g, 3.2 mmol) and HOBt (0.53 g, 3.9 mmol) in CH_2Cl_2 (80 ml) was added EDC·HCl (0.7 g, 3.66 mmol) at $-20°$ under N_2. The mixture was stirred until the hydrochloride was dissolved completely (*ca.* 3 h). To this soln. were added **6d** (1.77 g, 2.7 mmol) and Et_3N (1.4 ml) in CH_2Cl_2/MeOH 1:1 (30 ml) at $-20°$. The mixture was stirred for 15 h at r.t. It was then washed with aq. $NaHCO_3$ soln. (70 ml) and brine (70 ml), the org. phase dried ($MgSO_4$), and the solvent evaporated. CC (silica gel, AcOEt/hexane 3:1) yielded **7a** (2.4 g, 80%). Colorless foam. T_g 35.10°. ^{1}H-NMR ($CDCl_3$, 500 MHz): 1.43 (*s*, 27 H, Me_3C); 1.71 (*m*, 8 H, CH_2); 1.86 (*m*, 4 H, CH_2); 2.55 (*m*, 12 H, ArCH_2); 3.06 (*q*, 6 H, CH_2NH); 3.23 (*q*, 2 H, CH_2-NH); 3.34 (*q*, 4 H, CH_2NH); 4.50 (*s*, HOCH_2); 4.85 (br. *s*, 2 NH); 4.99 (*s*, PhCH_2O); 6.90 (*s*, 1 arom. H); 6.96 (*s*, 2 arom. H); 7.02 (*s*, 2 arom. H); 7.27 (*m*, 5 arom. H); 7.29 (*s*, 2 arom. H); 7.30 (*s*, 2 arom. H). ^{13}C-NMR ($CDCl_3$, 500 MHz): 28.41; 30.77; 31.36; 32.50; 33.29; 39.62; 65.00; 66.59; 78.67; 124.75; 127.66; 128.04; 128.46; 131.48; 134.57; 141.34; 141.41; 141.96; 156.13; 156.35; 167.73. FAB-MS (3 kV): 1115 (100, $[M+Na]^+$). Anal. calc. for $C_{62}H_{88}N_6O_{11}$ (1093.41): C 68.11, H 8.11, N 7.69; found: C 67.92, H 8.25, N 7.51.

Tribenzyl tert*-Butyl {[5-(Hydroxymethyl)-1,3-phenylene]bis(propane-3,1-diyliminocarbonylbenzene-5,1,3-triyldipropane-3,1-diyl)}tetrakis[carbamate]* (**7b**). As described for **7a**, with **4b** (0.72 g, 1.7 mmol), HOBt (0.22 g, 1.7 mmol), CH_2Cl_2 (30 ml), EDC·HCl (0.33 g, 1.73 ml), **6b** (0.85 g, 1.3 mmol), Et_3N (0.93 ml, 6.7 mmol), and MeOH/CH_2Cl_2 1:1 (15 ml). After 14 h at r.t., the mixture was washed with brine (50 ml) and aq. $NaHCO_3$ soln. (50 ml), the org. phase dried ($MgSO_4$), and the solvent evaporated. CC (silica gel, CH_2Cl_2/MeOH 4:1) yielded **7b** (0.91 g, 69%). Colorless foam. T_g 33.10°. ^{1}H-NMR ($CDCl_3$, 500 MHz): 1.44 (*s*, 9 H, Me_3C); 1.75 (*m*, 8 H, CH_2); 1.88 (*m*, 4 H, CH_2); 2.55 (*m*, 12 H, ArCH_2); 3.00 (*t*, 2 H, CH_2NH); 3.10 (*q*, 6 H, CH_2NH); 3.34 (*t*, 4 H, CH_2NH); 4.51 (*s*, HOCH_2); 5.01 (*s*, PhCH_2O); 6.91 (*s*, 1 arom. H); 6.97 (*s*, 2 arom. H); 7.03 (*s*, 1 arom. H); 7.27 (*m*, 20 arom. H). ^{13}C-NMR ($CDCl_3$, 500 MHz): 28.39; 30.64; 31.00; 31.29; 32.44; 33.21; 39.66; 40.14; 64.88; 66.60; 78.60; 124.88; 127.60; 127.99; 128.02; 128.44; 131.53; 134.77; 136.57; 141.55; 141.71; 141.88; 155.92; 156.66; 167.90. FAB-MS (3 kV): 1183 (65.15, $[M+Na]^+$). Anal. calc. for $C_{68}H_{84}N_6O_{11}$ (1161.45): C 70.32, H 7.29, N 7.24; found: C 70.52, H 7.05, N 6.96.

*O,O″-Dibenzyl O′,O‴-Di-(*tert*-butyl) {[5-(Hydroxymethyl)-1,3-phenylene]bis(propane-3,1-diyliminocarbonylbenzene-5,1,3-triyldipropane-3,1-diyl)}tetrakis[carbamate]* (**9b**). As described for **7a**, with **4b** (1.20 g, 2.6 mmol), HOBt (0.35 g, 2.6 mmol), CH_2Cl_2 (30 ml), EDC·HCl (0.53 g, 2.8 mmol), **8b** (0.30 g, 1.0 mmol), Et_3N (0.8 ml), and MeOH (10 ml). After 15 h at r.t., the mixture was washed with aq. $NaHCO_3$ soln. (40 ml) and brine (40 ml), the org. phase dried ($MgSO_4$), and the solvent evaporated. CC (silica gel, AcOEt/hexane 4:1) yielded **9b** (0.98 g, 86%). Colorless foam. T_g 43.90°. ^{1}H-NMR ($CDCl_3$, 500 MHz): 1.43 (*s*, 18 H, Me_3C); 1.71 (*m*, 8 H, CH_2); 1.88 (*m*, 4 H, CH_2); 2.58 (*t*, 8 H, ArCH_2); 2.69 (*t*, 4 H, ArCH_2); 3.06 (*q*, 4 H, CH_2NH); 3.23 (*q*, 4 H, CH_2NH); 3.34 (*q*, 4 H, CH_2NH); 4.52 (*s*, HOCH_2); 4.85 (br., 1 NH); 5.01 (*s*, 2 PhCH_2O); 5.12 (br. *s*, 2 NH); 6.85 (br. *s*, 2 NH); 6.90 (*s*, 1 arom. H); 6.98 (*s*, 2 arom. H); 7.04 (*s*, 2 arom. H); 7.27 (*m*, 14 arom. H). ^{13}C-NMR ($CDCl_3$, 500 MHz): 28.15; 30.55; 30.85; 31.00; 32.23; 32.99; 36.19; 39.44; 39.92; 64.33; 66.17; 78.76; 124.33; 124.62; 127.00; 127.62; 127.77; 128.16; 130.55; 131.27; 134.55; 136.40; 141.44; 141.58; 156.00; 156.49; 167.74. FAB-MS (3 kV): 1149 (100, $[M+Na]^+$). Anal. calc. for $C_{65}H_{86}N_6O_{11}$ (1127.43): C 69.25, H 7.69, N 7.45; found: C 69.03, H 7.87, N 7.52.

Tetrabenzyl {[5-(Hydroxymethyl)-1,3-phenylene]bis(propane-3,1-diyliminocarbonylbenzene-5,1,3-triyldipropane-3,1-diyl)}tetrakis[carbamate] (**9c**). To a soln. of the acid dendron **2d** (1.64 g, 3.3 mmol) in CH_2Cl_2 (30 ml) was added HOBt (0.45 g, 3.3 mmol) at r.t. After 10 min at $-30°$, EDC·HCl (0.66 g, 3.4 mmol) was added. The mixture was stirred for 3 h. Then a soln. of **8b** (0.4 g, 1.4 mmol) and Et_3N (1.5 ml, 10.8 mmol) in MeOH (10 ml) was added dropwise at $-20°$. The resulting mixture was warmed up to r.t. and stirred for 14 h. It was then washed with brine (50 ml) and aq. $NaHCO_3$ soln. (50 ml), the org. phase dried ($MgSO_4$), and the solvent evaporated. CC (silica gel, CH_2Cl_2/MeOH 20:1) yielded **9c**

(1.17 g, 72%). White foam. T_g 32.07°. ^{1}H-NMR ($CDCl_3$, 500 MHz): 1.58 (*m*, 8 H, CH_2); 1.71 (*m*, 4 H, CH_2); 2.39 (*m*, 12 H, ArCH_2); 2.90 (*t*, 8 H, CH_2NH); 3.18 (*t*, 4 H, CH_2NH); 4.40 (*s*, HOCH_2); 4.95 (*s*, 8 H, 4 PhCH_2O); 6.83 (*s*, 1 arom. H); 6.91 (*s*, 2 arom. H); 6.99 (*s*, 2 arom. H); 7.22 (*m*, 20 arom. H); 7.34 (*s*, 4 arom. H). ^{13}C-NMR ($CDCl_3$, 500 MHz): 30.36; 30.77; 30.92; 32.11; 32.29; 32.88; 39.32; 39.44; 39.96; 64.11; 66.25; 78.60; 124.44; 124.49; 127.11; 127.50; 127.77; 128.14; 131.33; 132.00; 134.33; 136.31; 141.11; 141.55; 141.66; 156.82; 168.47. FAB-MS (3 kV): 1217 (100, $[M+Na]^+$). Anal. calc. for $C_{71}H_{82}N_6O_{11}$ (1217.25): C 71.33, H 6.91, N 7.03; found: C 71.07, H 7.16, N 7.30.

Deprotection of the Boc Group of the Orthogonally Protected Second-Generation Dendrons: General Procedure 1 (*G.P. 1*). A soln. of the G2-dendron in THF was cooled to 0° in an ice bath. Then 25% HCl soln. (4 equiv. per Boc group) in THF was added dropwise, and the mixture was stirred at 0° for 1 h and at r.t. for another 2 h. Then, the mixture was evaporated and the residue dried *in vacuo* at r.t. affording the deprotected dendrons in quantitative yield.

Benzyl {3-{3-(3-Aminopropyl)-5-{{{3-{3-{3-{[3,5-bis(3-aminopropyl)benzoyl]amino}propyl}-5-(hydroxymethyl)phenyl}propyl}amino}carbonyl}phenyl}propyl}carbamate Trihydrochloride (**10b**). According to the *G.P. 1*, with **7a** (0.23 g, 0.21 mmol), THF (10 ml), 25% HCl soln. (0.50 ml, 18 equiv.), and THF (6 ml) at 0° for 1 h and at r.t. for another 4 h: **10b** (0.18 g, 93%). Colorless viscous oil. ^{1}H-NMR (CD_3OD, 500 MHz): 1.78 (*m*, 2 H, CH_2); 1.92 (*m*, 4 H, CH_2); 2.01 (*m*, 6 H, CH_2); 2.62 (*m*, 4 H, ArCH_2); 2.66 (*m*, 8 H, ArCH_2); 3.08 (*t*, 2 H, CH_2NH); 3.33 (*m*, 10 H, CH_2NH); 4.52 (*s*, HOCH_2); 5.02 (*s*, PhCH_2O); 6.93 (*s*, 1 arom. H); 6.96 (*s*, 2 arom. H); 7.18 (*s*, 2 arom. H); 7.25 (*m*, 5 arom. H); 7.43 (*s*, 2 arom. H); 7.48 (*s*, 2 arom. H). ^{13}C-NMR (CD_3OD, 500 MHz): 30.05; 32.22; 33.26; 34.33; 40.29; 40.88; 66.85; 67.33; 126.33; 126.71; 127.88; 128.64; 129.44; 139.02; 142.66; 143.05; 156.33; 170.09.

Dibenzyl {[5-(Hydroxymethyl)-1,3-phenylene]bis{propane-3,1-diyliminocarbonyl[5-(3-aminopropyl)-3,1-phenylene]propane-3,1-diyl}}bis[carbamate] Dihydrochloride (**10d**). According to the *G.P. 1*, with **9b** (0.40 g, 0.4 mmol), THF (15 ml), 25% HCl soln. (0.5 ml, 11 equiv.), and THF (5 ml) at 0° for 1 h and at r.t. for another 3 h: **10d** (0.34 g, 97%). Viscous oil. ^{1}H-NMR ($CDCl_3$/CD_3OD, 500 MHz): 1.77 (*m*, 4 H, CH_2); 1.90 (*m*, 4 H, CH_2); 1.98 (*m*, 4 H, CH_2); 2.61 (*m*, 12 H, ArCH_2); 2.82 (*q*, 4 H, CH_2-NH); 3.08 (*q*, 4 H, CH_2NH); 3.34 (*q*, 4 H, CH_2NH); 4.52 (*s*, HOCH_2); 5.02 (*s*, 2 PhCH_2O); 6.93 (*s*, 1 arom. H); 6.98 (*s*, 2 arom. H); 7.09 (*s*, 2 arom. H); 7.27 (*m*, 10 arom. H); 7.39 (*s*, 2 arom. H); 7.42 (*s*, 2 arom. H).^{13}C-NMR ($CDCl_3$/CD_3OD, 500 MHz): 30.09; 31.55; 32.60; 38.55; 39.17; 65.88; 78.76; 124.11; 124.79; 127.00; 127.35; 127.88; 128.16; 130.55; 131.27; 134.55; 136.40; 141.33; 141.76; 156.88; 168.21.

Dibenzyl {{5-{{{3-{3-{3-{{3-(Aminopropyl)-5-{3-{[(benzyloxy)carbonyl]amino}propyl}benzoyl}amino}propyl}-5-(hydroxymethyl)phenyl}propyl}amino}carbonyl}-1,3-phenylene}dipropane-3,1-diyl}bis[carbamate] Hydrochloride (**10f**). According to the *G.P. 1*, with **7b** (0.18 g, 0.16 mmol), THF (10 ml), 25% HCl soln. (0.12 ml, 6 equiv.), and THF (4 ml) at 0° for 1 h and at r.t. for 3 h: **10f** (0.16 g, 98%). Colorless solid. ^{1}H-NMR ($CDCl_3$/CD_3OD, 500 MHz): 1.70 (*m*, 8 H, CH_2); 1.86 (*m*, 4 H, CH_2); 2.53 (*m*, 10 H, ArCH_2); 2.75 (*t*, 2 H, CH_2NH); 3.03 (*q*, 6 H, CH_2NH); 3.27 (*t*, 4 H, CH_2NH); 4.51 (*s*, HOCH_2); 4.96 (*s*, 3 PhCH_2O); 6.86 (*s*, 1 arom. H); 6.90 (*s*, 2 arom. H); 6.99 (*s*, 1 arom. H); 7.27 (*m*, 20 arom. H). ^{13}C-NMR ($CDCl_3$/CD_3OD, 500 MHz): 30.64; 31.11; 31.29; 32.44; 33.21; 39.66; 40.14; 66.66; 78.60; 124.88; 127.60; 127.99; 128.02; 128.44; 131.53; 134.77; 136.57; 141.55; 141.71; 141.88; 156.92; 167.90.

Deprotection of the Cbz Group of the Orthogonally Protected Second-Generation Dendrons. General 2 (*G.P. 2*). The G2-dendron was dissolved in THF/AcOEt/EtOH (1:1:1). Then cyclohexa-1,4-diene (*Method B*) or 5% formic acid (*Method A*) and Pd/C were added, and the soln. was transferred into a hydrogenation flask. The mixture was hydrogenated under 3.5 bar of H_2 at r.t. overnight. The product was filtered through *Celite*, and the solvent was evaporated at r.t. to yield the deprotected dendrons.

*Di(*tert*-butyl) {{5-{{{3-{3-{3-{{3-(3-Aminopropyl)-5-{3-{[(*tert*-butyl)carbonyl]amino}propyl}benzoyl}-amino}propyl}-5-(hydroxymethyl)phenyl}propyl}amino}carbonyl}-1,3-phenylene}dipropane-3,1-diyl}bis-[carbamate]* (**10c**). According to the *G.P. 2*, with **7a** (0.17 g, 0.2 mmol), THF/AcOEt/EtOH 2:1:1 (20 ml), cyclohexa-1,4-diene (0.06 ml, 0.6 mmol), and 10% Pd/C (20 mg): **10c** (0.14 g, 94%). Slightly pale solid. ^{1}H-NMR ($CDCl_3$, 500 MHz): 1.39 (*s*, 27 H, Me_3C); 1.82 (*m*, 8 H, CH_2); 1.90 (*m*, 4 H, CH_2); 2.52 (*m*, 8 H, ArCH_2); 2.59 (*t*, 4 H, ArCH_2); 2.88 (*t*, 2 H, CH_2NH); 3.02 (*q*, 6 H, CH_2NH); 3.29 (*q*, 4 H, CH_2-NH); 4.50 (*s*, HOCH_2); 6.88 (*s*, 1 arom. H); 6.93 (*s*, 1 arom. H); 6.96 (*s*, 1 arom. H); 7.02 (*s*, 2 arom. H); 7.31 (*s*, 4 arom. H). ^{13}C-NMR ($CDCl_3$): 28.30; 30.66; 31.47; 32.44; 33.03; 39.44; 65.75; 78.67; 124.66 124.76; 127.66; 128.04; 128.44; 131.48; 134.55; 141.34; 141.44; 141.96; 156.33; 167.73.

*Di(*tert-*butyl) {[5-(Hydroxymethyl)-1,3-phenylene]bis{propane-3,1-diyliminocarbonyl[5-(3-aminopropyl)-3,1-phenylene]propane-3,1-diyl}}bis[carbamate]* (**10e**). According to the *G.P. 2*, with **9b** (0.40 g, 0.3 mmol), THF/AcOEt/EtOH 1:1:1 (21 ml), cyclohexa-1,4-diene (0.68 ml, 7.01 mmol), and 10% Pd/C (40 mg): **10e** (0.29 g, 95%). Pale solid. ^{1}H-NMR ($CDCl_3$, 500 MHz): 1.43 (*s*, 18 H, Me_3C); 1.73 (*m*, 8 H, CH_2); 1.88 (*m*, 4 H, CH_2); 2.60 (*m*, 12 H, ArCH_2); 2.69 (*t*, 4 H, ArCH_2); 3.03 (*q*, 4 H, CH_2NH); 3.23 (*q*, 4 H, CH_2NH); 4.52 (*s*, HOCH_2); 6.93 (*s*, 1 arom. H); 7.00 (*s*, 2 arom. H); 7.04 (*s*, 2 arom. H); 7.29 (*s*, 2 arom. H); 7.46 (*s*, 2 arom. H). ^{13}C-NMR ($CDCl_3$): 28.11; 30.44; 31.03; 32.22; 32.54; 32.99; 39.36; 40.44; 64.01; 78.86; 124.22; 124.48; 127.00; 131.14; 134.55; 141.48; 141.88; 156.02; 167.70.

tert-*Butyl {3-{3-(3-Aminopropyl)-5-{{{3-{3-{3-{[3,5-bis(3-aminopropyl)benzoyl]amino}propyl}-5-(hydroxymethyl)phenyl}propyl}amino}carbonyl}phenyl}propyl}carbamate* (**10g**). According to the *G.P. 2*, with **7b** (0.20 g, 0.2 mmol), THF/AcOEt/EtOH 1:1:1 (15 ml), cyclohexa-1,4-diene (0.40 g, 5.2 mmol), and 10% Pd/C (50 mg). The NMR of the product showed that there were still some Cbz-protecting groups present. Therefore, the product was treated for another night by the same procedure: **10g** (0.10 g, 85%). Slightly yellow viscous oil. ^{1}H-NMR ($CDCl_3$/CD_3OD, 500 MHz): 1.44 (*s*, Me_3C); 1.78 (*m*, 2 H, CH_2); 1.82 (*m*, 6 H, CH_2); 1.92 (*m*, 4 H, CH_2); 2.68 (*m*, 8 H, ArCH_2); 2.72 (*m*, 10 H, ArCH_2, CH_2NH); 3.04 (*t*, 2 H, CH_2NH); 3.34 (*t*, 4 H, CH_2NH); 4.51 (*s*, HOCH_2); 6.95 (*s*, 1 arom. H); 6.97 (*s*, 2 arom. H); 7.23 (*s*, 1 arom. H); 7.26 (*s*, 1 arom. H); 7.40 (*s*, 1 arom. H); 7.42 (*s*, 3 arom. H). ^{13}C-NMR ($CDCl_3$/CD_3OD, 500 MHz): 28.39; 31.00; 31.29; 33.99; 34.31; 39.99; 41.78; 65.22; 79.50; 125.77; 125.91; 128.55; 132.77; 132.88; 142.89; 143.22; 143.68; 156.66; 170.30.

N,N′*-{[5-(Hydroxymethyl)-1,3-phenylene]dipropane-3,1-diyl}bis[3,5-bis(3-aminopropyl)benzamide]* (**10h**). According to the *G.P. 2*, with **9c** (0.31 g, 0.3 mmol), THF/AcOEt/EtOH 1:1:1 (15 ml), 5% formic acid (0.5 ml), and 10% Pd/C (70 mg) for 48 h: **10h** (0.12 mg, 85%). Viscous brown oil. ^{1}H-NMR ($CDCl_3$/CD_3OD, 500 MHz): 1.58 (*m*, 8 H, CH_2); 1.71 (*m*, 4 H, CH_2); 2.39 (*m*, 12 H, ArCH_2); 2.90 (*t*, 8 H, CH_2-NH); 3.18 (*t*, 4 H, CH_2NH); 4.40 (*s*, HOCH_2); 6.83 (*s*, 1 arom. H); 6.91 (*s*, 2 arom. H); 6.99 (*s*, 2 arom. H); 7.22 (*m*, 20 arom. H); 7.34 (*s*, 4 arom. H). ^{13}C-NMR ($CDCl_3$/CD_3OD, 500 MHz): 29.29; 31.66; 31.71; 33.11; 33.39; 33.99; 40.44; 40.55; 78.60; 125.44; 125.76; 128.22; 132.34; 135.77; 142.20; 142.44; 142.73; 169.67.

*Poly{3,5-bis{3-{{3,5-bis{3-{{3,5-bis{3-{[(*tert-*butoxy)carbonyl]amino}propyl}benzoyl}amino}propyl}-benzoyl}amino}propyl}benzyl 2-Methylprop-2-enoate}* (**13**). A soln. of **11** (0.04 g, 0.1 mmol) and Et_3N (0.23 ml) in MeOH (5 ml) was added dropwise to a soln. of **12** (0.23 g, 0.2 mmol, 1.75 equiv. per amine group) in CH_2Cl_2/MeOH (15 ml) at $-20°$. The mixture was stirred at r.t. for 48 h. The solvent was evaporated, and then another portion of **12** (0.03 g, 0.03 mmol) and Et_3N (0.20 ml) in DMF (10 ml) was added and the mixture stirred for further 12 h. The polymer was then washed with brine, the solvent evaporated, and the crude product purified 3 times by dissolving it in $CHCl_3$ followed by precipitation with AcOEt/hexane 1:1 until all excess of **12** had been completely removed: **13** (0.25 g, 93%). Colorless solid. ^{1}H-NMR ($CDCl_3$, 700 MHz): 0.66 (br., 3 H, Me); 0.80 (br., 2 H, CH_2); 1.35 (br., 72 H, Me); 1.65 (br., 28 H, CH_2); 2.35 (br., 28 H, ArCH_2); 2.89 (br., 28 H, NHCH_2); 4.85 (br., 10 H, CH_2O, NH); 7.11 (br., 10 arom. H); 7.28 (br., 11 arom. H). ^{13}C-NMR ($CDCl_3$, 500 MHz): 28.23; 31.44; 32.95; 40.55; 66.69; 79.29; 125.22; 128.03; 128.22; 128.73; 132.00; 135.05; 137.11; 142.41; 157.00; 157.50; 168.86. GPC: M_n $3.9 \cdot 10^6$; *PDI* 3.23.

*Octa(*tert-*butyl) {(5-Methyl-1,3-phenylene)bis[propane-3,1-diyliminocarbonylbenzene-5,1,3-triylbis-(propane-3,1-diyliminocarbonylbenzene-5,1,3-triyldipropane-3,1-diyl)]}octakis[carbamate]* (**15**). To a soln. of **13** (0.04 g, 0.02 mmol) THF/AcOEt/EtOH 1:1:1 (32 ml). 10% Formic acid (1 ml) and 10% Pd/C (80 mg) were added, and the soln. was transferred into a hydrogenation flask. The mixture was hydrogenated under 3.5 bar of H_2 at r.t. for 4 d. The mixture was filtered, the solvent evaporated at r.t., and the product purified by CC (silica gel, 7.5% MeOH/CH_2Cl_2): **15** (0.03 g, 84%). Pale solid. ^{1}H-NMR ($CDCl_3$, 700 MHz): 1.39 (*s*, 72 H, Me); 1.76 (*m*, 18 H, CH_2); 1.87 (*m*, 8 H, CH_2); 1.95 (*m*, 4 H, CH_2); 2.22 (*s*, 3 H, Me); 2.52 (*m*, 24 H, ArCH_2); 2.68 (*t*, 4 H, ArCH_2); 3.08 (*q*, 18 H, CH_2NH); 3.37 (*q*, 8 H, CH_2NH); 3.42 (*q*, 4 H, CH_2NH); 4.78 (br., 6 H, NH); 6.82 (*s*, 2 arom. H); 6.85 (*s*, 1 arom. H); 7.04 (*s*, 2 arom. H); 7.06 (*s*, 4 arom. H); 7.36 (*s*, 4 arom. H); 7.41 (*s*, 8 arom. H). ^{13}C-NMR ($CDCl_3$, 500 MHz): 23.09; 28.88; 30.10; 31.11; 31.75; 32.11; 32.32; 32.88; 34.80; 37.00; 37.53; 40.00; 79.53; 125.33; 128.90; 132.00; 133.43; 135.11; 142.20; 156.55; 168.03.

*Ethyl 3-{3′-{[(Benzyloxy)carbonyl]amino}propyl}-5-{3-{{3,5-bis{3-{{3,5-bis{3-{[(*tert*-butoxy)carbonyl]amino}propyl}benzoyl}amino}propyl}benzoyl}amino}propyl}benzoate* (**17a**). A soln. of **16** (0.05 g, 0.1 mmol) and Et_3N (0.12 ml) in CH_2Cl_2/MeOH 1:1 (5 ml) was added dropwise to a soln. of **12** (0.16 g, 0.1 mmol) in CH_2Cl_2 (20 ml) at $-20°$. The mixture was stirred at r.t. overnight. It was then washed with brine (30 ml) and aq. $NaHCO_3$ soln. (30 ml). The org. phase was dried ($MgSO_4$), and the solvent evaporated. CC (silica gel, CH_2Cl_2/MeOH 20:1) yielded **17a** (0.14 g, 83%). White foam. ^{1}H-NMR ($CDCl_3$, 700 MHz): 1.32 (*t*, *Me*CH_2O); 1.38 (*s*, 36 H, Me); 1.72 (*m*, 8 H, CH_2); 1.87 (*m*, 4 H, CH_2); 1.95 (*m*, 2 H, CH_2); 2.52 (*t*, 8 H, ArCH_2); 2.59 (*t*, 6 H, ArCH_2); 2.68 (*t*, 2 H, ArCH_2); 3.01 (*q*, 8 H, CH_2-NH); 3.11 (*q*, 2 H, CH_2NH); 3.35 (*q*, 4 H, CH_2NH); 3.43 (*q*, 2 H, CH_2NH); 4.29 (*q*, MeCH_2O); 4.90 (br., 4 NH); 5.01 (*s*, PhCH_2O); 5.38 (br., 2 NH); 7.03 (*s*, 2 arom. H); 7.07 (*s*, 1 arom. H); 7.16 (*s*, 1 arom. H); 7.26 (*m*, 5 arom. H); 7.38 (*s*, 4 arom. H); 7.41 (*s*, 2 arom. H); 7.61 (*s*, 1 arom. H); 7.66 (*s*, 1 arom. H). ^{13}C-NMR ($CDCl_3$, 500 MHz): 14.58; 28.83; 31.00; 31.37; 31.77; 32.87; 33.00; 33.20; 34.00; 39.55; 39.66; 40.00; 40.88; 66.85; 79.45; 125.22; 127.48; 127.55; 128.36; 128.33; 128.84; 131.00; 131.94; 132.00; 133.68; 135.11; 135.15; 137.00; 142.15; 142.11; 142.29; 142.55; 156.58; 156.99; 167.22; 168.33; 168.45. HR-MALDI-MS: 1575 ($[M+Na]^+$).

*Ethyl 3-(3-Aminopropyl)-5-{3-{{3,5-bis{3-{{3,5-bis{3-{[(*tert*-butoxy)carbonyl]amino}propyl}-benzoyl}amino}propyl}benzoyl}amino}propyl}benzoate* (**17b**). According to *G.P. 2*, with **17a** (0.08 g, 0.055 mmol), THF/EtOH 2:1 (15 ml). 10% Formic acid (0.5 ml), and 10% Pd/C (80 mg) for 48 h: **17b** (60 mg, 83%). Slightly pale solid. ^{1}H-NMR ($CDCl_3$/CD_3OD, 700 MHz): 1.32 (*t*, *Me*CH_2O); 1.39 (*s*, 36 H, Me); 1.74 (*m*, 8 H, CH_2); 1.91 (*m*, 6 H, CH_2); 2.05 (*m*, 2 H, CH_2); 2.56 (*m*, 8 H, ArCH_2); 2.65 (*m*, 8 H, ArCH_2); 2.88 (*q*, 2 H, CH_2NH); 3.04 (*q*, 8 H, CH_2NH); 3.35 (*q*, 6 H, CH_2NH); 3.37 (*q*, 4 H, CH_2NH); 4.29 (*q*, MeCH_2O); 4.95 (br., 4 NH); 7.03 (*s*, 2 arom H); 7.07 (*s*, 1 arom. H); 7.25 (*s*, 1 arom. H); 7.43 (*s*, 4 arom. H); 7.51 (*s*, 2 arom H); 7.57 (*s*, 1 arom. H); 7.63 (*s*, 1 arom. H); 8.12 (br., 4 NH). ^{13}C-NMR ($CDCl_3$/CD_3OD, 500 MHz): 14.56; 28.68; 30.66; 30.81; 31.55; 32.29; 32.88; 33.18; 34.00; 39.23; 39.66; 39.91; 79.10; 125.22; 127.53; 128.00; 131.04; 132.11; 132.28; 133.55; 134.65; 134.88; 140.74; 142.22; 142.39; 142.55; 156.92; 167.22; 169.05; 169.22.

*Ethyl 3,5-Bis{3-{{3,5-bis{3-{{3,5-bis{3-{[(*tert*-butoxy)carbonyl]amino}propyl}benzoyl}amino}propyl}benzoyl}amino}propyl}benzoate* (**19**). A soln. of **18** (15 mg, 0.05 mmol) and Et_3N (0.07 ml) in CH_2Cl_2/MeOH 1:1 (5 ml) was added dropwise to a soln. of **12** (0.13 g, 0.1 mmol) in CH_2Cl_2 (15 ml) at $-20°$. The mixture was stirred at r.t. overnight. It was then washed with brine (25 ml) and aq. $NaHCO_3$ soln. (25 ml). The org. phase was dried ($MgSO_4$), and the solvent evaporated. CC (silica gel, CH_2Cl_2/MeOH 15:1) yielded **19** (94 mg, 89%). White foam. ^{1}H-NMR ($CDCl_3$): 1.30 (*t*, *Me*CH_2O); 1.38 (*s*, 72 H, Me); 1.71 (*m*, 18 H, CH_2); 1.83 (*m*, 8 H, CH_2); 1.96 (*m*, 4 H, CH_2); 2.52 (*m*, 24 H, ArCH_2); 2.68 (*t*, 4 H, ArCH_2); 3.08 (*q*, 18 H, CH_2NH); 3.31 (*q*, 8 H, CH_2NH); 3.37 (*q*, 4 H, CH_2NH); 4.30 (*q*, 2 H, MeCH_2O); 4.95 (br., 8 NH); 7.03 (*s*, 6 arom. H); 7.25 (*s*, 1 arom. H); 7.36 (*s*, 4 arom. H); 7.40 (*s*, 8 arom. H); 7.66 (*s*, 2 arom. H). ^{13}C-NMR ($CDCl_3$): 14.32; 25.58; 28.49; 30.55; 30.61; 31.33; 32.50; 32.88; 32.92; 36.44; 39.26; 39.44; 39.67; 67.99; 79.10; 124.88; 124.96; 127.22; 130.68; 131.55; 131.50; 131.66; 133.43; 134.77; 141.74; 141.88; 142.04; 156.11; 166.82; 167.99; 168.03. HR-MALDI-MS: 2397 ($[M+Na]^+$).

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