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Synthesis of carbosilane dendrons and dendrimers derived from 1,3,5-trihydroxybenzene

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ABSTRACT

Several carbosilane wedges of generations 1–3 have been synthesized, following the divergent method, containing at the focal point a C–Br bond and as peripheral functional groups $SiMeCl_2$, $SiMe(C_3H_5)_2$, $SiMe_2Cl$, $SiMe_2H$, and ester units $SiMe_2\{(C_3H_6)N(C_2H_4CO_2Me)_2\}$. The dendrons functionalized with $SiMe(C_3H_5)_2$ and $SiMe_2\{(C_3H_6)N(C_2H_4CO_2Me)_2\}$ groups were used to synthesize spherical dendrimers derived from 1,3,5-$(HO)_3C_6H_3$, leaving the outer groups unchanged. The allyl dendrimers thus obtained were used as precursors to prepare new dendrimers functionalized with $SiMeCl_2$, $SiMe_2Cl$, $SiMe_2H$, amine units $SiMe_2\{(C_3H_6)NH_2\}$ and also ester units $SiMe_2\{(C_3H_6)N(C_2H_4CO_2Me)_2\}$.

1. Introduction

Dendrimer molecules have been studied for several applications as catalysis, material sciences and nano-biotechnology.[1–14] Some of the reasons that have attracted the interest toward these molecules are their well defined and uniform branching structure, multivalency, and variety of typologies.[15–17] For biomedical applications, apart from low cytotoxicity, the surface of the dendrimers has to give adequate solubility in aqueous media.[18–21] Dendrimers functionalized at the periphery with amine groups can fulfill this goal by their own or being transformed to cationic[22–27] or anionic[28–30] functionalities.

One type of dendrimer molecules is formed by a carbosilane scaffold.[31–38] The strength of these dendrimers is related to the high energy of the C–Si bond and also its low polarity. This last characteristic of the C–Si bond endows high hydrophobicity to carbosilane dendrimers. However, this can be modified by functionalization of the periphery with polar moieties, turning them hydrophilic and thus, carbosilane dendrimers have also been used in biomedical applications.[39–44]

Dendrimers are synthesized following two main synthetic methods.[45–47] The divergent approach builds dendrimers from the core to the periphery, whereas the convergent methodology consists in the opposite procedure. This second method generates the so-called dendritic wedges or dendrons, which are cone-shaped molecules with two different functions, one at the periphery and other at the focal point. This last procedure also gives dendrimers with lower dispersity, due to the formation of less damaged branches during their synthesis. Furthermore, dendrons can be employed to synthesize asymmetrical dendrimers by coupling different units.[48–50] Carbosilane dendrimers have been mainly synthesized following the divergent synthesis, although a few examples of carbosilane wedges are known.[51–54]

In this work, we present the synthesis of new carbosilane dendrons synthesized by divergent procedures with a C–Br bond at their focal point. Some of the new dendrons here obtained have been also used as building blocks for spherical dendrimers by coupling with 1,3,5-$(HO)_3C_6H_3$. We are interested to obtain water soluble dendrons and dendrimers for various biomedical applications and, for that reason, precursors for these molecules containing amine or ester groups as terminated units have been synthesized. Furthermore, the presence of the 1,3,5-$(O)_3C_6H_3$ core would lead to carbosilane dendrimers less congested than related dendrimers with a silicon atom core.[41]

2. Results and discussion

2.1. Carbosilane wedges

The synthesis of the carbosilane wedges have been carried out following previous described procedures,[52] consistent in

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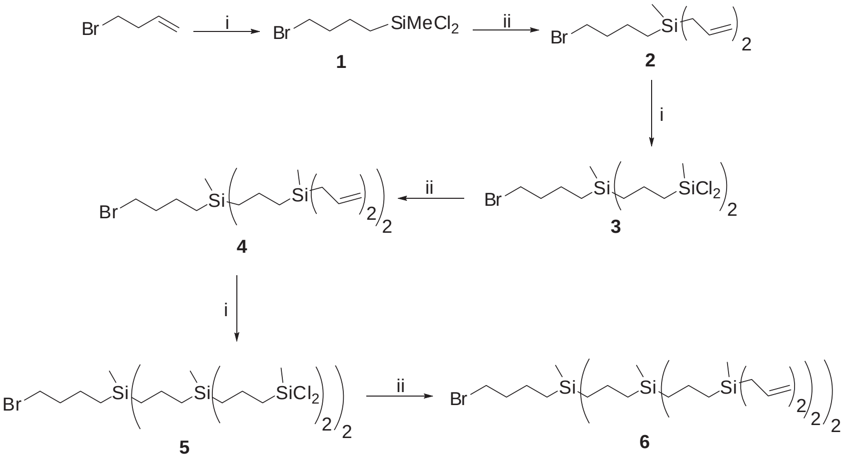
hydrosilylation with chlorosilanes of an alkenyl group and subsequent alkenylation with a Grignard reagent. Thus, starting from 4-Br-butene and employing $HSiCl_2Me$, in the presence of Karstedt Pt catalyst,[55] and $MgBr(C_3H_5)$, the dendritic wedges $BrG_n(SiCl_2)_m$ (n=1, m=1 (**1**); n=2, m=2 (**3**); n=3, m=4 (**5**)) and $BrG_n(C_3H_5)_m$ (n=1, m=2 (**2**); n=2, m=4 (**4**); n=3, m=8 (**6**)) (generations 1–3) were obtained after repeating each pair of steps the number of required times (Scheme 1, Fig. 1). We have considered increase of generation in these dendrons, and also dendrimers, after hydrosilylation with $HSiCl_2Me$. With this procedure, the C–Br bond located at the focal point remained unaltered in the alkenylation reaction of the Si–Cl bond. The yield of these reactions was independent of the dendron generation, being over 95% for the hydrosilylation and over 75% for the alkenylation reaction.



Scheme 1. Synthesis of dendrons **1**–**6**. (i) $HSiMeCl_2$, Karstedt's catalyst; (ii) $MgBr(C_3H_5)$.

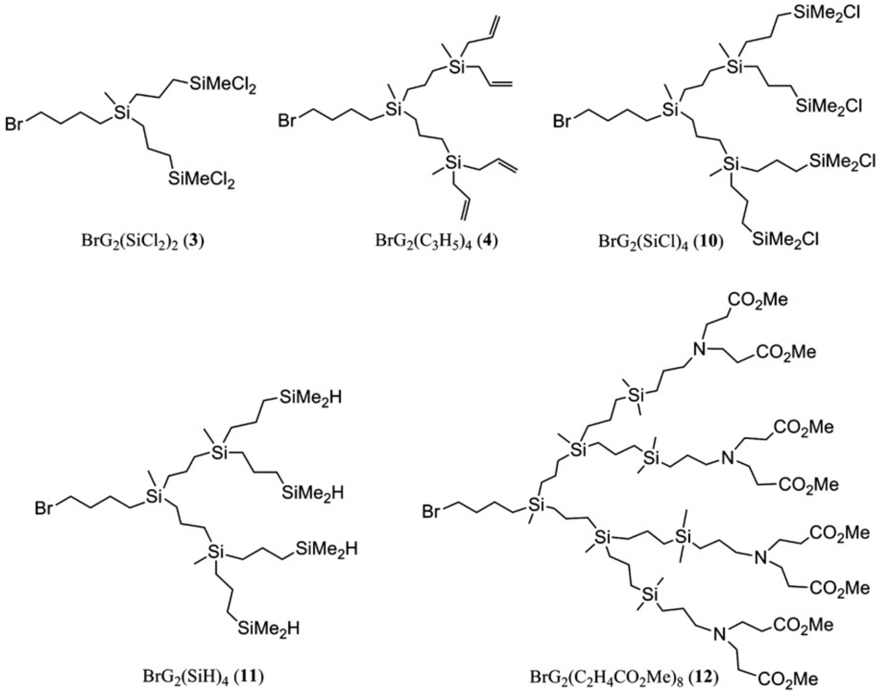
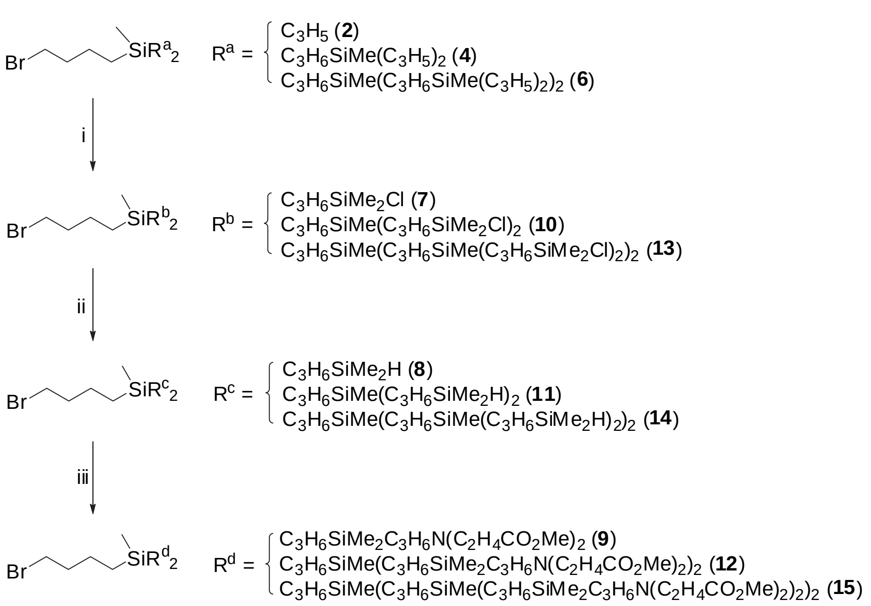


Fig. 1. Drawing of G2 dendrons synthesized in this work.

These compounds were characterized by NMR spectroscopy (^1H, ^{13}C, ^{29}Si) and elemental analysis. Formation of the $BrG_n(SiCl_2)_m$ (**1**, **3**, **5**) dendrons was confirmed in the ^1H NMR spectra by one singlet at ca. δ 0.80 belonging to the $SiMeCl_2$ methyl group and also the disappearance of the resonances belonging to the allyl moiety. In the ^{13}C NMR spectra of these compounds, the resonance of these peripheral $SiMeCl_2$ methyl groups was observed about δ 5.0. On the other hand, the ^1H NMR spectra of the allyl dendrons $BrG_n(C_3H_5)_m$ (**2**, **4**, **6**) showed the characteristics signals of the allyl group, a doublet about δ 1.50 ($SiCH_2$–CH), and two multiplets about δ 4.60 ($CH{=}CH_2$) and δ 5.10 ($CH{=}CH_2$) and also the displacement of the external $SiMe(C_3H_5)_2$ methyl group to lower frequency (δ=−0.50). A similar behavior was observed in the ^{13}C NMR spectra of these compounds with respect to the peripheral $SiMe(C_3H_5)_2$ methyl groups, observing a resonance about δ −5.0. With respect to the allyl moiety, the resonances corresponding to the Csp^2 atoms were observed at ca. δ 113.0 and δ 135.0. In all these compounds, the presence of the Br atom at the focal point was confirmed in the ^1H NMR spectra by a triplet at δ ca. 2.40 and in the ^{13}C NMR spectra by one resonance at δ ca. 31.5. Also, for these two type of compounds,

$^{1}H-^{29}Si$ 2D HMBC spectroscopy was used to determine the presence of the different Si atoms. The resonance corresponding to the Si atom of the $SiMeCl_2$ group was observed about δ 31.0, that to the peripheral $SiMe(allyl)_2$ groups between δ 2–3 and that of the internal $SiMe(CH_2)_3$ about δ 1.0.

The next goal in this work was to transform the periphery of the allyl-terminated $BrG_n(C_3H_5)_m$ dendrons to terminal Si–H units. This was achieved by hydrosilylation the allyl substituents with $HSiMe_2Cl$, also in the presence of Karstedt Pt catalyst, and then by Cl/H substitution with $LiAlH_4$. Dendritic wedges of generation 1–3 $BrG_n(SiCl)_m$ (n=1, m=2 (**7**); n=2, m=4 (**10**); n=3, m=8 (**13**)) and $BrG_n(SiH)_m$ (n=1, m=2 (**8**); n=2, m=4 (**11**); n=3, m=8 (**14**)) (Scheme 2, Fig. 1) were thus synthesized. It is important to note that this last reaction did not affect the Br–C bond at the focal point, as was confirmed by NMR spectroscopy (see above). Again, the yield of these reactions was independent of the dendron generation, being over 95% for the hydrosilylation and over 70% for the substitution reaction. It is important to note that heating the hydrosilylation reaction speed up this process and also reduced the presence of damaged branches by isomerization of the allyl moiety.[56]



Scheme 2. Synthesis of dendrons functionalized with $SiMe_2Cl$, $SiMe_2H$, and $SiMe_2\{(C_3H_6)N(C_2H_4CO_2Me)_2\}$ groups. (i) $HSiMe_2Cl$, Karstedt's catalyst, 60 °C; (ii) $LiAlH_4$; (iii) $(C_3H_5)N(C_2H_4CO_2Me)_2$, Karstedt's catalyst, r. t.

All these new compounds were also characterized by NMR spectroscopy (^{1}H, ^{13}C, ^{29}Si) and elemental analysis. The ^{1}H NMR spectra of dendrons **7**, **10** and **13** showed one singlet at ca. δ 0.40 belonging to the $SiMe_2Cl$ methyl groups while the ^{1}H NMR spectra of the hydride dendrons **8**, **11**, and **14** showed one multiplet at about δ 4.80 corresponding to the SiH proton and one doublet at about δ 0.04 for the $SiMe_2H$ methyl groups. A similar behavior was observed in the ^{13}C NMR spectra of these compounds with respect to the Me_2Si group, observing a resonance about δ 2.0 for compounds **7**, **10**, and **13** and about δ −4.0 for compounds **8**, **11**, and **14**. The presence of the $SiMe_2Cl$ group was also confirmed in the $^{1}H-^{29}Si$ HMBC spectra by one cross peak at about δ 31.0 for this Si atom, whereas the $SiMe_2H$ groups gave a resonance clearly a lower frequency (δ ca. −14.0) than any other silyl group in the molecule.

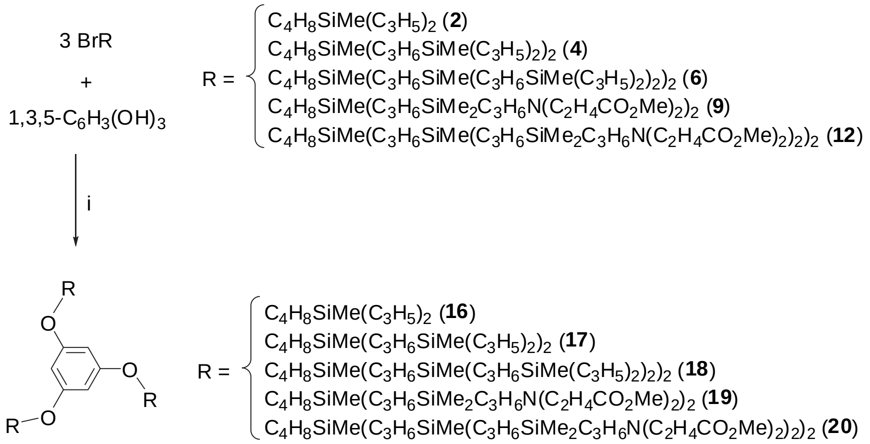
As it has been comment before, dendrimers containing NH_2 groups on the surface can be employed as precursors of cationic NH_3^+ and also anionic dendrimers. Thus, we tried to obtain dendrons with peripheral NH_2 groups by hydrosilylation of allylamine $(C_3H_5)NH_2$ with compounds $BrG_n(SiH)_m$ (**8**, **11**, **14**), following previously reported procedure.[41] Unfortunately, the presence of the C–Br bond at the focal point favored the quaternization of the N atom instead of hydrosilylation of the amine, leading to a mixture of compounds.

However, with the aim to obtain a dendritic wedge with terminal ester groups, we studied the reaction of Si–H dendrons **8**, **11**, and **14** with $(C_3H_5)N(C_2H_4CO_2Me)_2$.[57] In this case, the hydrosilylation in the presence of Pt catalyst proceeded smoothly giving the desired compounds $BrG_n(C_2H_4CO_2Me)_m$ (n=1, m=4 (**9**); n=2, m=8 (**12**); n=3, m=16 (**15**)) (Scheme 2, Fig. 1) in high yields (over 90%). It is important to note that the ester moiety remained unaltered in this reaction, not observing hydrosilylation of the C=O bond. The reaction was followed by NMR spectroscopy. The disappearance of the doublet belonging to the starting $SiMe_2H$ methyl groups and the multiplet of the SiH proton was indicative of the outcome of the reaction. The main resonances of the ^{1}H NMR spectra of compounds **9**, **12** and **15** are the singlets at ca. δ 3.60 belonging to the OMe methyl groups, the two triplets about δ 2.40 and δ 2.70 for the CH_2 groups of the chain $NC_2H_4CO_2Me$ and the triplet about δ 2.35 for the innermost CH_2N groups. A $^{1}H-^{1}H$ TOCSY NMR experiment showed clearly the presence of the new $Si(CH_2)_3N$ chain, with three cross peaks about δ 2.35, δ 1.35, and δ 0.35. In the ^{13}C NMR spectroscopy, the main resonances were the corresponding to the CO groups at δ ca. 173.0 and those for both C–N (δ ca. 49.2 and 57.5) and C–CO (δ ca. 32.5) carbon atoms. With respect to the ^{29}Si NMR spectroscopy, the disappearance of the low frequency resonance of the $SiMe_2H$ silicon atom at δ ca. −14.0 and the observation of a new one at δ ca. −4.0 belonging to a new $SiMe_2$ silicon atom also confirmed this reaction.

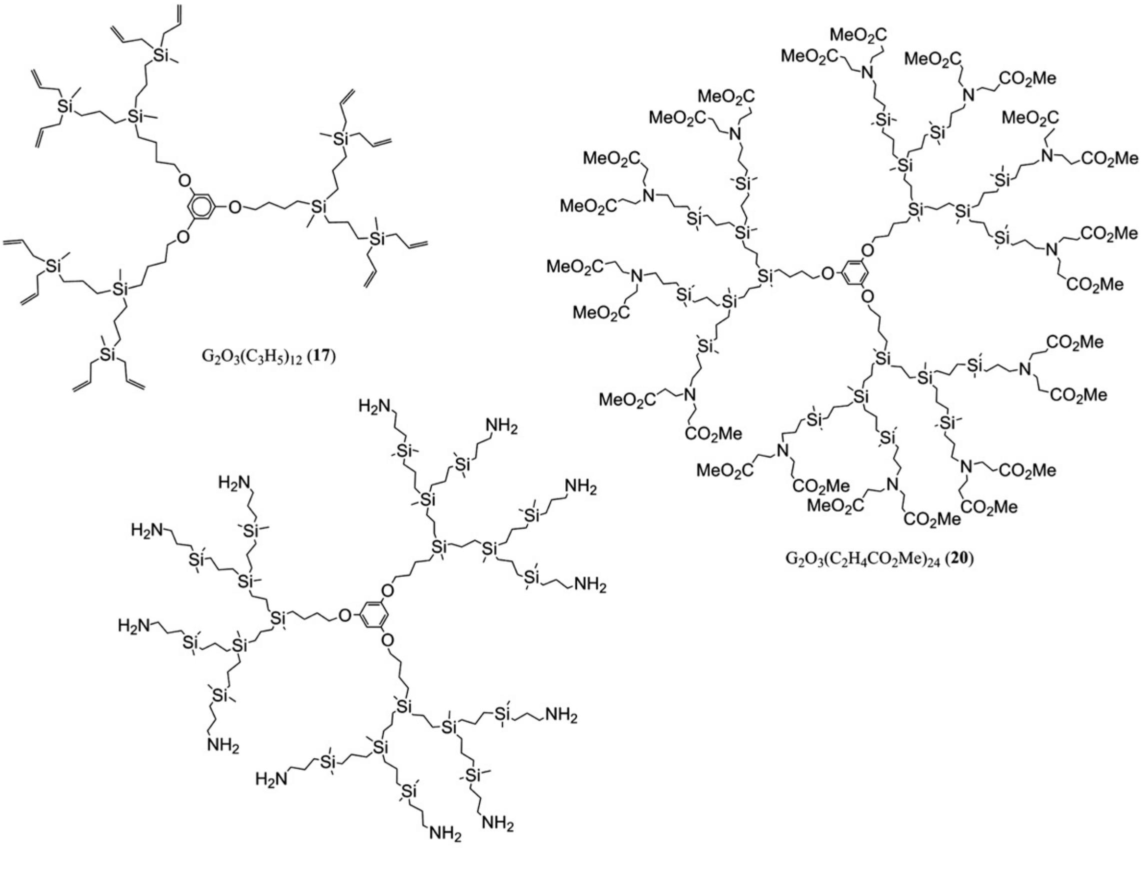
2.2. Carbosilane dendrimers

The new dendrons synthesized were employed as synthons for generation of new spherical dendrimers via convergent methodology. The core selected for this purpose was the polyphenolic derivative 1,3,5-$(HO)_3C_6H_3$, as the introduction of Br–C bond containing ligands to this type of units is well documented and proceed through a simple methodology.[47,58] The dendritic wedges with Si–Cl terminal groups $BrG_n(SiCl_2)_m$ and $BrG_n(SiCl)_m$ were discharged for this reaction, due to the high reactivity of this bond. The reaction with the Si–H terminated dendrons $BrG_n(SiH)_m$ failed probably due to side-reactions of this bond with the base K_2CO_3 or even with the CO_2 released during this process. However, the reaction was successful with the allyl $BrG_n(C_3H_5)_m$ (**3**, **4**, and **6**) and ester $BrG_n(C_2H_4CO_2Me)_m$ (**9**, **12**) wedges, obtaining the respective allyl $G_nO_3(C_3H_5)_m$ (n=1, m=6 (**16**); n=2, m=12 (**17**); n=3, m=24 (**18**)) and ester $G_nO_3(C_2H_4CO_2Me)_m$ (n=1, m=12 (**19**); n=2, m=24 (**20**)) dendrimers (Scheme 3, Fig. 2). In contrast with the synthesis of the dendritic wedges, now the reaction time is clearly dependent on the generation wedge, lasting from few days for G1 to ca. 3 weeks for G3. In the particular case of the ester wedges, the corresponding G_2 dendrimer $G_2O_3(C_2H_4CO_2Me)_{24}$ was obtained with rather low yield and the reaction to synthesize the G_3 dendrimer was unsuccessful.

The main NMR data that confirm formation of these compounds are the resonances of the newly formed CH_2—O groups, which are observed in the ^{1}H NMR spectra at δ ca. 3.80 and in the ^{13}C NMR spectra at δ ca. 67.0. Furthermore, the C_6H_3 core gave in the ^{1}H NMR spectra one singlet about δ 6.00 and in the ^{13}C NMR spectra two resonances about δ 94.0 and δ 161.0 for the CH and i-C carbon atoms, respectively, indicating the total substitution of the phenol groups. The rest of resonances in the NMR spectroscopy are essentially the same as those described for the corresponding dendrons.



Scheme 3. Synthesis of dendrimers with peripheral $SiMe(C_3H_5)_2$ and $SiMe_2\{(C_3H_6)N(C_2H_4CO_2Me)_2\}$ groups. (i) K_2CO_3, crown ether 18C6, 90 °C.

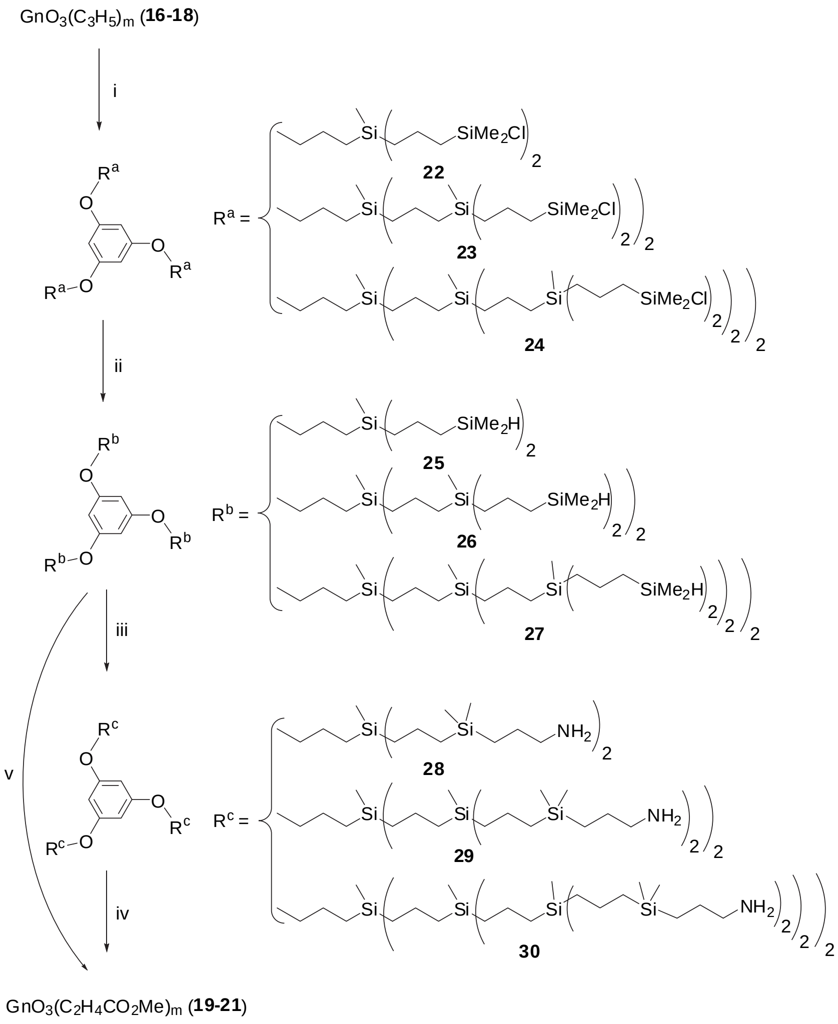

$G_2O_3(C_3H_5)_{12}$ (**17**)

$G_2O_3(C_2H_4CO_2Me)_{24}$ (**20**)

$G_2O_3(NH_2)_{12}$ (**29**)

Fig. 2. Drawing of representative examples of G2 dendrimers synthesized in this work.

With this convergent procedure, we have been able to obtain ester dendrimers, precursors of anionic derivatives, although with low yields for higher generations, but not NH_2 functionalized ones, precursors of cationic dendrimers. For this purpose, we adopted the synthetic strategy described previously to synthesize functionalized amine spherical dendrimers[41] using the allyl dendrimers $G_nO_3(C_3H_5)_m$ **16**–**18**. Thus, hydrosilylation of **16**–**18** with $HSiMe_2Cl$ afforded spherical dendrimers with $SiMe_2Cl$ terminated groups, $G_nO_3(SiCl)_m$ (n=1, m=6 (**22**); n=2, m=12 (**23**); n=3, m=24 (**24**)), and then Cl/H exchange with $LiAlH_4$ led to dendrimers with $SiMe_2H$ groups, $G_nO_3(SiH)_m$ (n=1, m=6 (**25**); n=2, m=12 (**26**); n=3, m=24 (**27**)) (Scheme 4). The NMR data of all these dendrimers are the expected, as they have been described in the related dendrons (see above and also Experimental part).

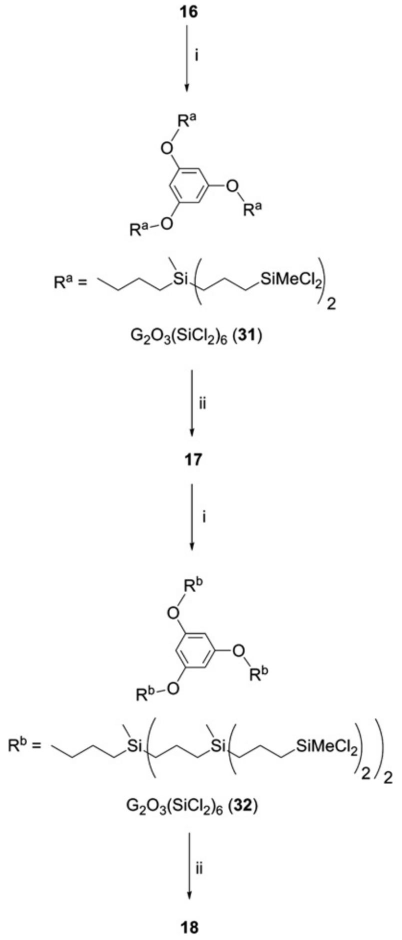


Scheme 4. Synthesis of dendrimers functionalized with $SiMe_2Cl$, $SiMe_2H$, $SiMe_2\{(C_3H_6)NH_2\}$, and $SiMe_2\{(C_3H_6)N(C_2H_4CO_2Me)_2\}$. (i) $HSiMe_2Cl$, Karstedt's catalyst, 60 °C; (ii) $LiAlH_4$; (iii) $(C_3H_5)NH_2$, Karstedt's catalyst, 120 °C; (iv) $C_2H_3CO_2Me$, rt; (v) $(C_3H_5)N(C_2H_4CO_2Me)_2$, Karstedt's catalyst.

Dendrimers **25**–**27** reacted with $(C_3H_5)NH_2$, in the presence of Karstedt's catalyst, to afford the amine dendrimers $G_nO_3(NH_2)_m$ (n=1, m=6 (**28**); n=2, m=12 (**29**); n=3, m=24 (**30**)) (Scheme 4, Fig. 2), after several days over 120 °C. In this case, the yield was much lower for the G_3 **30** (30%) than for G_1 and G_2, 85% and 70%, respectively. The difficulty to hydrosilylate amines would be increased in the G_3 compound **27** by higher congestion of functional groups. Formation of compounds **28**–**30** was confirmed by NMR spectroscopy. In the ^1H NMR spectra the disappearance of the doublet belonging to the starting $SiMe_2H$ methyl groups and the multiplet belonging to the SiH proton was indicative of the outcome of the reaction. Furthermore, a new resonance about δ 2.65 corresponding to the CH_2N group was observed. The presence of the new $Si(CH_2)_3N$ chain was also confirmed by a ^1H TOCSY-1D experiment, with three resonances about δ 2.63, δ 1.40 and δ 0.48. In the ^{13}C NMR spectroscopy, the main resonance was that belonging to the CH_2N carbon atom that gave a signal at δ ca. 45.0. The ^{29}Si NMR spectroscopy showed the disappearance of the low frequency resonance of the $SiMe_2H$ silicon atom at δ ca. −14.0 and the observation of a new one at δ ca. −4.0 belonging to the new $SiMe_2$ silicon atom.

These dendrimers **28**–**30** reacted with methyl acrylate $C_2H_3CO_2Me$ (room temperature, 16 h) to give the respective ester dendrimers $G_nO_3(C_2H_4CO_2Me)_m$ **19**–**21** (Scheme 4, Fig. 2). However, they could also be obtained in one-step from the Si–H functionalized dendrimers $G_nO_3(SiH)_m$ **25**–**27** by reaction with $(C_3H_5)N(C_2H_4CO_2Me)_2$ in THF (Scheme 4), in the presence of Karstedt's catalyst, after 16 h at room temperature for G_1 and G_2 and at 40 °C for G3. In this case, this hydrosilylation proceeded smoothly even in the case of G_3 dendrimer **27**, obtaining the respective ester dendrimers with high yields.

Finally, the allyl dendrimers $G_nO_3(C_3H_5)_m$ (n=2, m=12 (**17**); n=3, m=24 (**18**)) could be also obtained following a divergent synthetic strategy from the lower generation allyl dendrimer (**16** for **17** and **17** for **18**) by an analogous procedure described for the corresponding allyl dendrons (Scheme 5), namely hydrosilylation of the allyl dendrimer with $HSiMeCl_2$ and then alkenylation with MgBr(C_3H_5). With this method, the new dendrimers $G_nO_3(SiCl_2)_m$ (n=2, m=6 (**31**); n=3, m=12 (**32**)) functionalized with $SiMeCl_2$ groups were isolated. These dendrimers were characterized by NMR spectroscopy, being their NMR spectra very similar to those described in the related dendrons $BrG_n(SiCl_2)_m$ (**1**, **3**, **5**) (see above and also Experimental part).



Scheme 5. Synthesis of dendrimers functionalized with $SiMeCl_2$ and $SiMe(C_3H_5)_2$. (i) $HSiMeCl_2$, Karstedt's catalyst; (ii) $MgBr(C_3H_5)$.

2.3. Characterization by gel permeation chromatography (GPC) and mass spectrometry

The GPC analyses have been performed for the most relevant dendrimers. The allyl dendrimers $G_nO_3(C_3H_5)_m$ showed narrow polydispersity values (1.05 for **16**, 1.10 for **17**, 1.16 for **18**; Fig. 3). Similar values were obtained for the ester dendrimers $G_nO_3(C_2H_4CO_2Me)_m$ (**19**–**21**) synthesized by hydrosilylation of $(C_3H_5)N(C_2H_4CO_2Me)_2$ with dendrimers $G_nO_3(SiH)_m$ **25**–**27** (1.06 for **19**, 1.11 for **20**, 1.18 for **21**) and slightly higher for the amine dendrimers $G_nO_3(NH_2)_m$ (1.13 for **28**, 1.21 for **29**, 1.40 for **30**). These values confirm the high monodispersity degree of these systems.

Two different mass spectrometry techniques were used for characterization of dendrons and dendrimers ESI and MALDI-TOF. The first one allowed us to determine the $[M+H]^+$ peak of the dendrons $BrG_n(C_2H_4CO_2Me)_m$ (**9**, **12**, **15**), whereas MALDI-TOF technique was useful to find the $[M+H]^+$ peak of dendrimers $G_1O_3(C_3H_5)_6$ (**16**), $G_1O_3(C_2H_4CO_2Me)_{12}$ (**19**), and $G_nO_3(SiH)_m$ (n=1, m=6 (**25**); n=2, m=12 (**26**)) and the $[M+Na]^+$ peak of dendrimers $G_nO_3(C_3H_5)_m$ (n=2, m=12 (**17**); n=3, m=24 (**18**)). For the rest of compounds we could not observed the corresponding molecular peak.

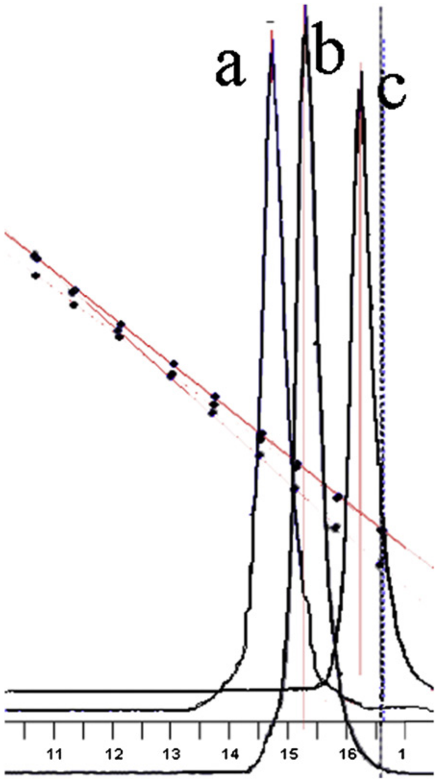


Fig. 3. GPC diagram of $G_nO_3(C_3H_5)_m$ (**16** (a), **17** (b), **18** (c)).

3. Conclusions

Dendritic wedges of generations 1–3 with a C–Br bond at the focal point can be synthesized by iterative stepwise hydrosilylation and alkenylation reactions with $HSiCl_2Me$ and $MgBr(C_3H_5)$, respectively. The allylic dendrons were also precursors of SiH functionalized dendrons after hydrosilylation with $HSiClMe_2$ and then Cl/H exchange with $LiAlH_4$. Nor the alkenylation neither the reaction with $LiAlH_4$ affected the C–Br bond. Ester dendritic wedges can be also obtained from the SiH dendrons hydrosilylating with the allyl ester compound $(C_3H_5)N(C_2H_4CO_2Me)_2$. However, this procedure can not be employed with $(C_3H_5)NH_2$ to obtain analogous dendrons terminated in amine groups, because the presence of the C–Br bond gave rise to quaternization of the amine.

The C–Br bond of the focal point has been useful to introduce the allyl and ester wedges at the polyphenolic core 1,3,5-$(HO)_3C_6H_3$, generating spherical dendrimers. However, the reaction time for the synthesis of the G3 allyl dendrimer has resulted too long (over 20 days) compared with G1 and G2 (2–6 days), whereas the reaction for the synthesis of G3 ester dendrimers was unsuccessful. The allyl dendrimers thus synthesized were used as precursors for amine dendrimers, after hydrosilylation with $HSiMe_2Cl$, exchange the Cl atom by a H atom with $LiAlH_4$ and then hydrosilylation with $(C_3H_5)NH_2$. However, in this last case, this method gave low yield for the G3 dendrimer.

Ester dendrimers could be also obtained by adding the acrylate $C_2H_3CO_2Me$ to the amine dendrimers or from the SiH dendrimers by hydrosilylation with $(C_3H_5)N(C_2H_4CO_2Me)_2$, being the ester moiety unaffected. The later procedure clearly shortens synthetic times of ester derivatives with respect to the synthesis from amines, requiring smoother conditions than hydrosilylation of primary amines and also giving higher overall yields.

4. Experimental section

4.1. General considerations

All reactions were carried out under inert atmosphere and solvents were purified from appropriate drying agents. NMR spectra were recorded on a Varian Unity VXR-300 (300.13 (^{1}H) and 75 (^{13}C) MHz) or on a Bruker AV400 (400.13 (1H) and 79.49 (^{29}Si) MHz). Chemical shifts (δ) are given in parts per million. ^{1}H and ^{13}C resonances were measured relative to solvent peaks considering TMS=0 ppm, meanwhile ^{29}Si resonance were measured relative to external TMS. When necessary, assignment of resonances was done from HSQC, HMBC, COSY, TOCSY, and NOESY NMR experiments. Elemental analyses were performed on a Perkin–Elmer 240C. Mass Spectra were obtained from an Agilent 6210 (ESI) and a Bruker Ultraflex III (MALDI-TOF). GPC analyses were carried out in a Varian HPLC with Plgel Mixed-D (300×7.5 mm) columns from Polymer Laboratories and a GPC Pl-ELS 1000 detector from Polymer Laboratories. Compounds 4-Br-butene, Karstedt's Pt catalyst, MgBr(C_3H_5), $LiAlH_4$, $(C_3H_5)NH_2$ and $C_2H_3CO_2Me$ (Aldrich), $HSiCl_2Me$, and $HSiClMe_2$ (ABCR) were obtained from commercial sources.

4.2. Synthesis of compounds

4.2.1. $(C_3H_5)N(C_2H_4CO_2Me)$. $(C_3H_5)NH_2$ (0.76 mL, 0.017 mol) and $C_2H_3CO_2Me$ (3.30 mL, 0.040 mol) were stirred in MeOH (5 mL) at 60 °C for 20 h. Afterward, volatiles were removed under vacuum and $(C_3H_5)N(C_2H_4CO_2Me)$ (2.99 g, 98%,) was obtained as a colorless liquid. Anal. Calcd for $C_{11}H_{19}NO_4$ (229.27): C, 57.62; H, 8.35; N, 6.11; Obt.: C, 57.69; H, 8.25; N, 6.05.

^{1}H NMR ($CDCl_3$): 2.46 (t, 4H, *J*=7.2 Hz, NC*H*$_2$CH$_2$), 2.79 (t, 4H, *J*=7.2 Hz, C*H*$_2$CO$_2$Me), 3.10 (d, 2H, *J*=6.6 Hz, CHC*H*$_2$N), 3.67 (s, 6H, CO$_2$*Me*), 5.15 (m, 2H, C*H*$_2$=CH), 5.80 (m, 2H, CH$_2$=C*H*); ^{13}C NMR {^{1}H} ($CDCl_3$): 32.3 (*C*H$_2$CO), 48.7 (*C*H$_2$N), 51.3 (O*Me*), 56.7 (CH*C*H$_2$N), 117.2 (CH$_2$=CH), 135.2 (*C*H$_2$=H), 172.7 (*C*O).

*4.2.2. BrG$_1$(SiCl$_2$) (**1**).* $HSiMeCl_2$ (7.67 g, 0.067 mol) was added to a cooled solution of 4-Br-1-butene (4.50 g, 0.033 mol) in hexane (3 mL) in the presence of Karstedt's catalyst (3% mol) and stirred overnight at 40 °C. Afterward, volatiles were removed under vacuum, hexane was added (10 mL) and the solution was filtered through active carbon. Removal of volatiles under vacuum (caution: compound **1** is slightly volatile) gave **1** as a colorless liquid (7.76 g, 94%) (compound **1** is moisture sensitive and has to be stored under inert atmosphere).

^{1}H NMR ($CDCl_3$): 0.77 (s, 3H, *Me*SiCl$_2$), 1.11 (m, 2H, C*H*$_2$Si), 1.65 (m, 2H, C*H*$_2$CH$_2$Si), 1.93 (m, 2H, BrCH$_2$C*H*$_2$), 3.41 (t, *J*=6.6 Hz, 2H, BrC*H*$_2$); ^{13}C NMR{^{1}H} ($CDCl_3$): 5.1 (*Me*SiCl$_2$), 20.6 (*C*H$_2$CH$_2$Si), 21.1 (CH$_2$*C*H$_2$Si), 32.8 (Br*C*H$_2$CH$_2$), 34.9 (BrCH$_2$*C*H$_2$); ^{29}Si NMR ($CDCl_3$): 32.3 (Me*Si*Cl$_2$). Anal. Calcd for $C_5H_{11}BrCl_2Si$ (250.04): C, 24.02; H, 4.43; Obt.: C, 24.23; H, 4.61.

*4.2.3. BrG$_1$(C$_3$H$_5$)$_2$ (**2**).* BrMg(C_3H_5) (0.061 mol) was slowly added to a cooled Et_2O solution (30 mL) of **1** (7.00 g, 0.028 mol) and stirred overnight at room temperature. Afterward, a water solution of NH_4Cl was added (12%, 50 mL), the organic phase was separated and the aqueous phase was extracted twice with Et_2O. The organic phase was washed with brine, dried over $MgSO_4$, and SiO_2. The solution was filtered through active carbon and the volatiles were removed under vacuum, yielding **2** as a colorless liquid (5.85 g, 80%).

^{1}H NMR ($CDCl_3$): −0.02 (s, 3H, *Me*Si(CH$_2$CHCH$_2$)$_2$), 0.53 (m, 2H, C*H*$_2$Si), 1.44 (m, 2H, C*H*$_2$CH$_2$Si), 1.54 (d, *J*=8.5 Hz, 4H, SiC*H*$_2$CH), 1.85 (m, 2H, BrCH$_2$C*H*$_2$), 3.40 (t, *J*=6.6 Hz, 2H, BrC*H*$_2$), 4.84 (m, 4H, CH=C*H*$_2$), 5.74 (m, 2H, C*H*=CH$_2$); ^{13}C NMR{^{1}H} ($CDCl_3$): −5.9 (*Me*Si), 12.0 (Si*C*H$_2$), 21.2 (*C*H$_2$CH=CH$_2$), 22.1 (*C*H$_2$), 33.5 (Br*C*H$_2$), 36.2 (BrCH$_2$*C*H$_2$), 113.3 (CH=*C*H$_2$), 134.5 (*C*H=CH$_2$); ^{29}Si NMR ($CDCl_3$): 0.99 (Me*Si*). Anal. Calcd $C_{11}H_{21}BrSi$ (261.27 g/mol): C, 50.57; H, 8.10; Exp.: C, 50.41; H, 7.93.

*4.2.4. BrG$_2$(SiCl$_2$)$_2$ (**3**).* Following the procedure described for compound **1**, compound **3** was obtained as a colorless liquid (7.60 g, 94%) from **2** (4.30 g, 0.016 mol) and $HSiMeCl_2$ (7.58 g, 0.066 mol).

^{1}H NMR ($CDCl_3$): −0.03 (s, 3H, *Me*Si), 0.53 (m, 2H, SiC*H*$_2$), 0.66 (m, 4H, SiC*H*$_2$), 0.75 (s, 6H, *Me*SiCl$_2$), 1.19 (m, 4H, C*H*$_2$SiCl$_2$), 1.50 (m, 6H, C*H*$_2$), 1.85 (m, 2H, BrCH$_2$C*H*$_2$), 3.40 (t, *J*=6.6 Hz, 2H, BrC*H*$_2$); ^{13}C NMR{^{1}H} ($CDCl_3$): −5.1 (*Me*Si), 5.1 (*Me*SiCl$_2$), 12.5 (Si*C*H$_2$), 17.3 (*C*H$_2$), 17.9 (*C*H$_2$), 22.3 (BrCH$_2$CH$_2$*C*H$_2$), 25.9 (*C*H$_2$SiCl$_2$), 33.7 (Br*C*H$_2$), 36.4 (BrCH$_2$*C*H$_2$); ^{29}Si NMR ($CDCl_3$): 2.3 (Me*Si*), 32.1 (Me*Si*Cl$_2$).

*4.2.5. BrG$_2$(C$_3$H$_5$)$_4$ (**4**).* Following the procedure described for compound **2**, compound **4** was obtained as a colorless liquid (5.10 g, 78%) from **3** (6.25 g, 0.013 mol) and BrMg(C_3H_5) (0.055 mol).

^{1}H NMR ($CDCl_3$): δ −0.08 (s, 3H, *Me*Si), −0.04 (s, 6H, *Me*Si), 0.56 (m, 10H, SiC*H*$_2$), 1.25 (m, 6H, C*H*$_2$), 1.52 (d, *J*=8.4 Hz, 8H, C*H*$_2$CH=CH$_2$), 1.84 (m, 2H, BrCH$_2$C*H*$_2$), 3.40 (t, *J*=6.6 Hz, 2H, BrC*H*$_2$), 4.84 (m, 8H, CH=C*H*$_2$), 5.74 (m, 4H, C*H*=CH$_2$); ^{13}C NMR{^{1}H} ($CDCl_3$): δ −5.7 (*Me*Si), −5.1 (*Me*Si), 12.9 (Si*C*H$_2$), 17.9, 18.2y 18.6 (*C*H$_2$), 21.4 (*C*H$_2$CH=CH$_2$), 22.5 (BrCH$_2$CH$_2$*C*H$_2$), 33.6 (Br*C*H$_2$), 36.3 (BrCH$_2$*C*H$_2$), 113.0 (CH=*C*H$_2$), 134.8 (*C*H=CH$_2$); ^{29}Si NMR ($CDCl_3$): δ 0.1 (Me*Si*), 1.8 (Me*Si*). Anal. Calcd $C_{25}H_{49}BrSi_3$ (513.82 g/mol): C, 58.44; H, 9.61; Exp.: C, 58.11; H, 9.54.

*4.2.6. BrG$_3$(SiCl$_2$)$_4$ (**5**).* Following the procedure described for compound **1**, compound **5** was obtained as a colorless liquid (4.45 g, 94%) from **4** (2.50 g, 4.86 mmol) and $HSiMeCl_2$ (3.80 g, 0.033 mol).

^{1}H NMR ($CDCl_3$): δ −0.07 (s, 3H, *Me*Si), −0.04 (s, 6H, *Me*Si), 0.58 (m, 18H, SiC*H*$_2$), 0.75 (s, 12H, *Me*SiCl$_2$), 0.87 (m, 8H, C*H*$_2$), 1.16 (m, 8H, C*H*$_2$SiCl$_2$), 1.52 (m, 6H, C*H*$_2$), 1.85 (m, 2H, BrCH$_2$C*H*$_2$), 3.40 (t, *J*=6.6 Hz, 2H, BrC*H*$_2$); ^{13}C NMR{^{1}H} ($CDCl_3$): δ −5.2 (*Me*Si), 5.5 (*Me*SiCl$_2$), 12.9 (Si*C*H$_2$), 17.3y 17.5 (*C*H$_2$), 18.4, 18.6y 18.7 (*C*H$_2$), 22.6 (BrCH$_2$CH$_2$*C*H$_2$), 25.9 (*C*H$_2$SiCl$_2$), 33.6 (Br*C*H$_2$), 36.3 (BrCH$_2$*C*H$_2$); ^{29}Si NMR ($CDCl_3$): δ 1.4 (Me*Si*), 1.8 (Me*Si*), 32.1 (Me*Si*Cl$_2$).

*4.2.7. BrG$_3$(C$_3$H$_5$)$_8$ (**6**).* Following the procedure described for compound **2**, compound **6** was obtained as a colorless liquid (2.62 g, 76%) from **5** (3.30 g, 3.39 mmol) and BrMg(C_3H_5) (3.45 mmol).

^{1}H NMR ($CDCl_3$): δ −0.10 (s, 3H, *Me*Si), −0.08 (s, 6H, *Me*Si), −0.04 (s, 12H, *Me*Si), 055 (m, 26H, SiC*H*$_2$), 1.31 (m, 16H, C*H*$_2$), 1.52 (d, *J*=8.4 Hz, 16H, C*H*$_2$CH=CH$_2$), 1.84 (m, 2H, BrCH$_2$C*H*$_2$), 3.40 (t, *J*=6.6 Hz, 2H, BrC*H*$_2$), 4.84 (m, 16H, CH=C*H*$_2$), 5.73 (m, 8H, C*H*=CH$_2$); ^{13}C NMR{^{1}H} ($CDCl_3$): δ −5.7 (*Me*Si), −5.1 (*Me*Si), −4.9 (*Me*Si), 13.0 (Si*C*H$_2$), 17.9, 18.3, 18.5, 18.8y 18.9 (*C*H$_2$), 21.5 (*C*H$_2$CH=CH$_2$), 22.6 (BrCH$_2$CH$_2$*C*H$_2$), 33.6 (Br*C*H$_2$), 36.4 (BrCH$_2$*C*H$_2$), 113.1 (CH=*C*H$_2$), 134.9 (*C*H=CH$_2$); ^{29}Si NMR ($CDCl_3$): δ 0.1 (Me*Si*), 0.9 (Me*Si*), 1.8(Me*Si*). Anal. Calcd $C_{53}H_{105}BrSi_7$ (1018.90 g/mol): C, 62.48; H, 10.39; Exp.: C, 62.22; H, 10.31.

*4.2.8. BrG$_1$(SiCl)$_2$ (**7**).* Following the procedure described for compound **1** but heating at 60 °C, compound **7** was obtained as a colorless liquid (4.96 g, 96%) from the reaction of **2** (3.00 g, 0.011 mol) and $HSiMe_2Cl$ (4.35 g, 0.046 mol).

^{1}H NMR ($CDCl_3$): −0.05 (s, 3H, *Me*Si), 0.38 (s, 12H, *Me*$_2$SiCl), 0.52 (m, 2H, SiC*H*$_2$), 0.58 (m, 4H, SiC*H*$_2$), 0.88 (m, 4H, C*H*$_2$SiCl), 1.42 (m, 6H, C*H*$_2$), 1.85 (m, 2H, BrCH$_2$C*H*$_2$), 3.40 (t, *J*=6.6 Hz, 2H, BrC*H*$_2$); ^{13}C NMR{^{1}H} ($CDCl_3$): −5.2 (*Me*Si), 1.9 (*Me*$_2$Si), 12.8 (Si*C*H$_2$), 17.7 (*C*H$_2$), 17.9 (*C*H$_2$), 22.4 (BrCH$_2$CH$_2$*C*H$_2$), 23.5 (*C*H$_2$SiCl), 33.6 (Br*C*H$_2$), 36.3 (BrCH$_2$*C*H$_2$); ^{29}Si NMR ($CDCl_3$): 2.1 (Me*Si*), 31.1 (Me$_2$*Si*Cl).

*4.2.9. BrG$_1$(SiH)$_2$ (**8**).* An Et_2O solution (40 mL) of **7** (2.00 g, 4.44 mmol) was slowly added to an Et_2O solution (20 mL) of $LiAlH_4$ (7.76 mmol) at 0 °C and stirred overnight at room temperature. Afterward, the mixture was added over a saturated water solution of Na_2SO_4 (50 mL) at 0 °C, the organic phase was separated and the aqueous phase was extracted twice with Et_2O. The organic phase was dried over $MgSO_4$, and SiO_2, the solution was filtered and the volatiles were removed under vacuum, yielding **8** as colorless oil (1.44 g, 85%).

^{1}H NMR ($CDCl_3$): δ −0.08 (s, 3H, *Me*Si), 0.04 (d, *J*=4.2 Hz, 12H, Me_2SiH), 0.52 (m, 2H, SiCH_2), 0.58 (m, 8H, SiCH_2), 1.38 (m, 6H, CH_2), 1.85 (m, 2H, $BrCH_2CH_2$), 3.40 (t, *J*=6.6 Hz, 2H, BrCH_2), 3.82 (m, 2H, Si*H*); ^{13}C NMR{^{1}H} ($CDCl_3$): δ −5.1 (*Me*Si), −4.3 (Me_2SiH), 12.9 (SiCH_2), 17.9 (CH_2), 18.8y 19.0 (CH_2), 22.5 ($BrCH_2CH_2CH_2$), 33.7 (BrCH_2), 36.4 ($BrCH_2CH_2$); ^{29}Si NMR ($CDCl_3$): δ −14.6 (Me_2*Si*H), 2.1 (Me*Si*). Anal. Calcd $C_{15}H_{37}BrSi_3$ (381.61 g/mol): C, 47.21; H, 9.77; Obt.: C, 47.59; H, 9.53.

*4.2.10. $BrG_1(C_2H_4CO_2Me)_4$ (**9**).* $C_3H_5N(C_2H_4CO_2Me)_2$ (1.23 g, 5.26 mmol) was added to a hexane solution (5 mL) of **8** (1.00 g, 2.62 mmol) in the presence of Karstedt's catalyst (3% mol) and stirred overnight at room temperature. Afterward, hexane (10 mL) was added, the solution was filtered through active carbon and the volatiles were removed under vacuum. Compound **9** was purified by Gel Permeation Chromatography, obtaining **9** as colorless oil (2.04 g, 92%).

^{1}H NMR ($CDCl_3$): δ −0.10 (s, 3H, *Me*Si), −0.08 (s, 12H, Me_2Si), 0.33 (m, 4H, SiCH_2), 0.52 (m, 10H, SiCH_2), 1.27 (m, 4H, CH_2), 1.35 (m, 6H, CH_2), 1.83 (m, 2H, $BrCH_2CH_2$), 2.33 (m, 4H, CH_2N), 2.41 (t, *J*=7.3 Hz, 8H, CH_2N), 2.74 (t, *J*=7.3 Hz, 8H, CH_2CO), 3.39 (t, *J*=6.6 Hz, 2H, BrCH_2), 3.61 (s, 12H, O*Me*); ^{13}C NMR{^{1}H} ($CDCl_3$): δ −5.1 (*Me*Si), −3.3 (Me_2Si), 12.8 (SiCH_2), 12.9 (SiCH_2), 18.4 (CH_2), 18.6y 20.1 (CH_2), 21.5 (CH_2CH_2N), 22.5 ($BrCH_2CH_2CH_2$), 32.5 (CH_2CO), 33.7 (BrCH_2), 36.4 ($BrCH_2CH_2$), 49.2 (CH_2N), 51.6 (O*Me*), 57.5 (CH_2N), 173.1 (CO); ^{29}Si NMR ($CDCl_3$): δ 1.0 (Me_2*Si*), 2.1 (Me*Si*). MS $[M+H]^+$: 839.41. Anal. Calcd $C_{37}H_{75}BrN_2O_8Si_3$ (840.16 g/mol): C, 52.89; H, 9.00; Obt.: C, 52.29; H, 8.63.

*4.2.11. $BrG_2(SiCl)_4$ (**10**).* Following the procedure described for compound **7**, compound **10** was obtained as a colorless oil (4.08 g, 94%) from the reaction of **4** (2.50 g, 4.86 mmol) and $HSiMe_2Cl$ (3.31 g, 0.035 mol).

^{1}H NMR ($CDCl_3$): −0.08 (s, 3H, *Me*Si), −0.07 (s, 6H, *Me*Si), 0.38 (s, 24H, Me_2SiCl), 0.54 (m, 18H, SiCH_2), 0.86 (m, 8H, CH_2SiCl), 1.28 (m, 4H, CH_2), 1.42 (m, 10H, CH_2), 1.85 (m, 2H, $BrCH_2CH_2$), 3.40 (t, *J*=6.6 Hz, 2H, BrCH_2); ^{13}C NMR{^{1}H} ($CDCl_3$): −5.1 (2 *Me*Si), 1.8 (Me_2SiCl), 12.9 (SiCH_2), 17.7, 18.1, 18.4, 18.7 (CH_2), 22.5 ($BrCH_2CH_2CH_2$), 23.5 (CH_2SiCl), 33.7 (BrCH_2), 36.3 ($BrCH_2CH_2$); ^{29}Si NMR ($CDCl_3$): 1.0 (Me*Si*), 2.0 (Me*Si*), 31.2 (Me_2*Si*Cl).

*4.2.12. $BrG_2(SiH)_4$ (**11**).* Following the procedure described for compound **8**, compound **11** was obtained as a colorless oil (2.18 g, 82%) from the reaction of **10** (3.15 g, 3.53 mmol) and $LiAlH_4$ (10.60 mmol).

^{1}H NMR ($CDCl_3$): δ −0.10 (s, 6H, *Me*Si), −0.08 (s, 3H, *Me*Si), 0.04 (d, *J*=4.2 Hz, 12H, Me_2SiH), 0.54 (m, 26H, SiCH_2), 1.35 (m, 14H, CH_2), 1.85 (m, 2H, $BrCH_2CH_2$), 3.40 (t, *J*=6.6 Hz, 2H, BrCH_2), 3.82 (m, 4H, Si*H*); ^{13}C NMR{^{1}H} ($CDCl_3$): δ −5.0 (*Me*Si), −4.38 (Me_2SiH), 13.0 (SiCH_2), 18.2, 18.5, 18.7, 18.8, 19.0 (CH_2), 22.5 ($BrCH_2CH_2CH_2$), 33.6 (BrCH_2), 36.4 ($BrCH_2CH_2$); ^{29}Si NMR ($CDCl_3$): δ −14.1 (Me_2*Si*H), 1.0 (Me*Si*), 1.8 (Me*Si*). Anal. Calcd $C_{33}H_{81}BrSi_7$ (754.50 g/mol): C, 52.53; H, 10.82; Obt.: C, 52.80; H, 10.45.

*4.2.13. $BrG_2(C_2H_4CO_2Me)_8$ (**12**).* Following the procedure described for compound **9**, compound **12** was obtained as a colorless oil (0.60 g, 91%) from the reaction of **11** (0.30 g, 0.40 mmol) and $C_3H_5N(C_2H_4CO_2Me)_2$ (0.40 g, 1.75 mmol).

^{1}H NMR ($CDCl_3$): δ −0.10 (s, 6H, *Me*Si), −0.08 (s, 3H, *Me*Si), −0.07 (s, 24H, Me_2Si), 0.37 (m, 8H, SiCH_2), 0.52 (m, 26H, SiCH_2), 1.33 (m, 22H, CH_2), 1.83 (m, 2H, $BrCH_2CH_2$), 2.33 (m, 8H, CH_2N), 2.41 (t, *J*=7.3 Hz, 16H, CH_2N), 2.74 (t, *J*=7.3 Hz, 16H, CH_2CO), 3.39 (t, *J*=6.6 Hz, 2H, BrCH_2), 3.61 (s, 24H, O*Me*); ^{13}C NMR{^{1}H} ($CDCl_3$): δ −5.1 (*Me*Si), −4.9 (*Me*Si), −3.3 (Me_2Si), 12.9 (SiCH_2), 13.0 (SiCH_2), 18.4, 18.5, 18.8, 18.9, 20.1 (CH_2), 21.6 (CH_2CH_2N), 22.5 ($BrCH_2CH_2CH_2$), 32.6 (CH_2CO), 33.5 (BrCH_2), 36.4 ($BrCH_2CH_2$), 49.3 (CH_2N), 51.5 (O*Me*), 57.6 (CH_2N), 173.0 (CO); ^{29}Si NMR ($CDCl_3$): δ 0.87 (Me*Si*), 1.7 (Me*Si*), 1.9 (Me_2*Si*). MS $[M+H]^+$: 1669.92. Anal. Calcd $C_{77}H_{157}BrN_4O_{16}Si_7$ (1671.59 g/mol): C, 55.33; H, 9.47; N, 3.35; Obt.: C, 55.98; H, 9.60; N, 3.28.

*4.2.14. $BrG_3(SiCl)_8$ (**13**).* Following the procedure described for compound **7**, compound **13** was obtained as a colorless oil (4.29 g, 94%) from the reaction of **6** (2.62 g, 2.57 mmol) and $HSiMe_2Cl$ (3.31 g, 0.035 mol).

^{1}H NMR ($CDCl_3$): −0.07 (s.a., 21H, *Me*Si), 0.38 (s, 48H, Me_2SiCl), 0.50 (m, 26H, SiCH_2), 0.85 (m, 16H, CH_2SiCl), 1.24 (m, 12H, CH_2), 1.40 (m, 18H, CH_2), 1.82 (m, 2H, $BrCH_2CH_2$), 3.40 (t, *J*=6.6 Hz, 2H, BrCH_2); ^{13}C NMR{^{1}H} ($CDCl_3$): −5.0y −4.9 (*Me*Si), 1.8 (Me_2SiCl), 13.0 (SiCH_2), 17.7, 18.1, 18.5, 18.8 and 18.9 (SiCH_2), 22.6 ($BrCH_2CH_2CH_2$), 23.5 (CH_2SiCl), 33.6 (BrCH_2), 36.3 ($BrCH_2CH_2$); ^{29}Si NMR ($CDCl_3$): 0.9 and 1.2 (Me*Si*), 31.2(Me_2*Si*Cl).

*4.2.15. $BrG_3(SiH)_8$ (**14**).* Following the procedure described for compound **8**, compound **14** was obtained as a colorless oil (1.32 g, 78%) from the reaction of **13** (2.00 g, 1.13 mmol) and $LiAlH_4$ (6.75 mmol).

^{1}H NMR ($CDCl_3$): δ −0.10 (s, 21H, *Me*Si), 0.04 (d, *J*=4.2 Hz, 48H, Me_2SiH), 0.58 (m, 58H, SiCH_2), 1.31 (m, 30H, CH_2), 1.82 (m, 2H, $BrCH_2CH_2$), 3.40 (t, *J*=6.6 Hz, 2H, BrCH_2), 3.83 (m, 8H, Si*H*); ^{13}C NMR {^{1}H} ($CDCl_3$): δ −5.0 to −4.8 (*Me*Si), −4.3 (Me_2SiH), 13.0 (SiCH_2), 18.2–19.0 (CH_2), 22.6 ($BrCH_2CH_2CH_2$), 33.5 (BrCH_2), 36.5 ($BrCH_2CH_2$); ^{29}Si NMR ($CDCl_3$): δ −14.6 (Me_2*Si*H), 1.4 (Me*Si*). Anal. Calcd $C_{69}H_{169}BrSi_{15}$ (1500.27 g/mol): C, 55.24; H, 11.35; Obt.: C, 55.88; H, 11.73.

*4.2.16. $BrG_3(C_2H_4CO_2Me)_{16}$ (**15**).* Following the procedure described for compound **9**, compound **15** was obtained as a colorless oil (0.98 g, 88%) from the reaction of **14** (0.50 g, 0.33 mol) and $C_3H_5N(C_2H_4CO_2Me)_2$ (0.63 g, 0.34 mol).

^{1}H NMR ($CDCl_3$): δ −0.10 (s, 18H, *Me*Si), −0.06 (s, 51H, *Me*Si and Me_2Si), 0.35 (m, 16H, SiCH_2), 0.53 (m, 58H, SiCH_2), 1.27 (m, 30H, CH_2), 1.37 (m, 16H, CH_2), 1.83 (m, 2H, $BrCH_2CH_2$), 2.37 (m, 16H, CH_2N), 2.42 (t, *J*=7.3 Hz, 32H, CH_2N), 2.75 (t, *J*=7.3 Hz, 32H, CH_2CO), 3.40 (t, *J*=6.6 Hz, 2H, BrCH_2), 3.64 (s, 48H, O*Me*); ^{13}C NMR{^{1}H} ($CDCl_3$): δ −5.0 (*Me*Si), −4.9 (*Me*Si), −3.3 (Me_2Si), 12.7 (SiCH_2), 12.8 (SiCH_2), 18.4, 18.8, 19.0, 20.1 (CH_2), 21.5 (CH_2CH_2N), 22.5 ($BrCH_2CH_2CH_2$), 32.5 (CH_2CO), 33.5 (BrCH_2), 36.4 ($BrCH_2CH_2$), 49.2 (CH_2N), 51.5 (O*Me*), 57.5 (CH_2N), 1731 (CO); ^{29}Si NMR ($CDCl_3$): δ 0.87 (Me*Si*), 1.7 (Me*Si*), 1.9 (Me_2*Si*). MS $[M+H]^+$: 3330.87. Anal. Calcd $C_{157}H_{321}BrN_8O_{32}Si_{15}$ (3334.45 g/mol): C, 56.55; H, 9.70; N, 3.36; Obt.: C, 56.79; H, 9.41; N, 3.28.

*4.2.17. $G_1O_3(C_3H_5)_6$ (**16**).* 1,3,5-$(HO)_3C_6H_3$ (0.48 g, 3.82 mmol), **2** (3.00 g, 11.48 mmol), K_2CO_3(3.20 g, 23.00 mmol) and crown ether 18-C-6 (0.30 g, 1.14 mmol) were stirred in acetone (70 mL) at 90 °C into a sealed ampoule for 3 days under vacuum. Afterward, volatiles were removed under vacuum and a water solution of NH_4Cl (12%, 50 mL) and Et_2O were added. The organic phase was separated and the aqueous phase was extracted twice with Et_2O. The organic phase was dried over $MgSO_4$, and for extra 10 min also with SiO_2. The solution was filtered and the volatiles were removed under vacuum, yielding **16** as colorless oil (2.02 g, 80%).

^{1}H NMR ($CDCl_3$): δ −0.02 (s, 9H, *Me*Si), 0.58 (m, 6H, CH_2Si), 1.44 (m, 6H, $OCH_2CH_2CH_2$), 1.54 (d, *J*=8.5 Hz, 12H, $CH_2CH{=}CH_2$), 1.76 (m, 6H, OCH_2CH_2), 3.89 (t, *J*=6.4 Hz, 6H, OCH_2), 4.84 (m, 12H, $CH{=}CH_2$), 5.78 (m, 6H, $CH{=}CH_2$), 6.04 (s, 3H, C_6H_3); ^{13}C NMR{^{1}H} ($CDCl_3$): δ −5.9 (*Me*Si), 12.7 (SiCH_2), 20.1 ($OCH_2CH_2CH_2$), 21.3 ($CH_2CH{=}CH_2$), 32.9 (OCH_2CH_2), 67.4 (OCH_2), 93.7 (C_6H_3 (CH)), 113.1 ($CH{=}CH_2$), 134.7 ($CH{=}CH_2$), 160.9 (*i*-C_6H_3); ^{29}Si NMR ($CDCl_3$): δ 0.8 (Me*Si*). MS $[M+H]^+$: 667.44. Anal. Calcd $C_{39}H_{66}O_3Si_3$ (667.20 g/mol): C, 70.21; H, 9.97; Obt.: C, 69.83; H, 9.22.

4.2.18. $G_2O_3(C_3H_5)_{12}$ (***17***). Following the procedure described for compound **16**, compound **17** was obtained as a colorless oil (2.07 g, 76%) from the reaction of 1,3,5-$(HO)_3C_6H_3$ (0.24 g, 1.94 mmol), **4** (3.00 g, 5.84 mmol), K_2CO_3 (1.62 g, 11.68 mmol), and 18-C-6 (0.15 g, 0.59 mmol) during 7 days.

^{1}H NMR ($CDCl_3$): δ −0.08 (s, 9H, *Me*Si), −0.04 (s, 18H, *Me*Si), 0.57 (m, 30H, $SiCH_2$), 1.30 (m, 12H, CH_2), 1.41 (m, 6H, $OCH_2CH_2CH_2$), 1.52 (d, *J*=7.9 Hz, 24H, $CH_2CH{=}CH_2$), 1.75 (m, 6H, OCH_2CH_2), 3.88 (t, *J*=6.3 Hz, 6H, OCH_2), 4.84 (m, 24H, $CH{=}CH_2$), 5.74 (m, 12H, $CH{=}CH_2$), 6.04 (s, 3H, C_6H_3); ^{13}C NMR{^{1}H} ($CDCl_3$): δ −5.7 (*Me*Si), −5.1 (*Me*Si), 13.8 ($SiCH_2$), 17.9, 18.2y 18.6 (CH_2), 20.6 ($OCH_2CH_2CH_2$), 21.5 ($CH_2CH{=}CH_2$), 33.3 (OCH_2CH_2), 67.6 (OCH_2), 93.7 (C_6H_3 (CH)), 113.1 ($CH{=}CH_2$), 134.9 ($CH{=}CH_2$), 160.9 (*i*-C_6H_3); ^{29}Si NMR ($CDCl_3$): δ 0.1 (Me*Si*), 1.5 (Me*Si*). $[M+Na]^+$: 1446.9. Anal. Calcd $C_{81}H_{150}O_3Si_9$ (1424.83 g/mol): C 68.28; H 10.61; Obt.: C, 68.01; H, 10.31.

4.2.19. $G_3O_3(C_3H_5)_{24}$ (***18***). Following the procedure described for compound **16**, compound **17** was obtained as a colorless oil (1.00 g, 68%) from the reaction of 1,3,5-$(HO)_3C_6H_3$ (0.061 g, 0.49 mmol), **6** (1.50 g, 1.47 mmol), K_2CO_3 (0.41 g, 2.94 mmol), and 18-C-6 (0.039 g, 0.14 mmol) during 20 days.

^{1}H NMR ($CDCl_3$): δ −0.10 (s, 18H, *Me*Si), −0.07 (s, 9H, *Me*Si), −0.04 (s, 36H, *Me*Si), 0.55 (m, 78H, $SiCH_2$), 1.31 (m, 42H, CH_2), 1.52 (d, *J*=7.9 Hz, 48H, CH_2CHCH_2), 1.75 (m, 6H, OCH_2CH_2), 3.88 (t, *J*=6.3 Hz, 6H, OCH_2), 4.84 (m, 48H, $CH{=}CH_2$), 5.74 (m, 24H, $CH{=}CH_2$), 6.04 (s, 3H, C_6H_3); ^{13}C NMR{^{1}H} ($CDCl_3$): δ −5.7 (*Me*Si), −5.0 (*Me*Si), 13.9 (CH_2Si), 17.9, 18.2, 18.5, 18.8, 18.9 (CH_2), 20.6 ($OCH_2CH_2CH_2$), 21.5 ($CH_2CH{=}CH_2$), 33.3 (OCH_2CH_2), 67.7 (OCH_2), 93.6 (C_6H_3 (CH)), 113.0 ($CH{=}CH_2$), 134.9 ($CH{=}CH_2$), 160.9 (*i*-C_6H_3); ^{29}Si NMR ($CDCl_3$): δ 0.1 (Me*Si*), 0.9 (Me*Si*), 1.7 (Me*Si*). $[M+Na]^+$: 2962.9. Anal. Calcd $C_{165}H_{318}O_3Si_{21}$ (2940.08 g/mol): C, 67.41; H, 10.90; Obt.: C, 66.56; H, 10.87.

4.2.20. $G_1O_3(C_2H_4CO_2Me)_{12}$ (***19***). *Method* (*A*): Following the procedure described for compound **16**, compound **19** was obtained as a colorless oil (0.32 g, 61%) from the reaction of 1,3,5-$(HO)_3C_6H_3$ (0.027 g, 0.21 mmol), **9** (0.55 g, 0.65 mmol), K_2CO_3 (0.18 g, 1.30 mmol), and 18-C-6 (0.017 g, 0.06 mmol) during 4 days in acetone (15 mL). *Method* (*B*): Reaction of **25** (1.00 g, 0.95 mmol) and $C_3H_5N(C_2H_4CO_2Me)_2$ (1.44 g, 6.08 mmol) in THF (5 mL) in the presence of Karstedt's catalyst (3% mol) was stirred overnight at 40 °C. Next, THF was added (15 mL), the solution was filtered through active carbon and the volatiles were removed under vacuum. The remaining oil was washed with cold hexane (10 mL) obtaining compound **19** as a pale yellow oil (2.14 g, 91%). *Method* (C): $C_2H_3CO_2Me$ (0.25 g, 2.85 mmol) was added to a solution of **28** (0.25 g, 0.18 mmol) in methanol (5 mL) and stirred at room temperature for 16 h. Afterward, the volatiles were removed under vacuum and the residue was washed with cold hexane (5 mL) yielding **19** as a yellowish oil (0.39 g, 90%).

^{1}H NMR ($CDCl_3$): δ −0.09 (s, 9H, *Me*Si), −0.07 (s, 36H, *Me*$_2$Si), 0.40 (m, 12H, $SiCH_2$), 0.53 (m, 30H, $SiCH_2$), 1.27 (m, 12H, CH_2), 1.36 (m, 18H, CH_2), 1.75 (m, 6H, OCH_2CH_2), 2.39 (m, 12H, CH_2N), 2.41 (t, *J*=7.3 Hz, 24H, CH_2N), 2.74 (t, *J*=7.3 Hz, 24H, CH_2CO), 3.64 (s, 36H, O*Me*), 3.87 (t, *J*=6.6 Hz, 6H, OCH_2), 6.03 (s, 3H, C_6H_3); ^{13}C NMR{^{1}H} ($CDCl_3$): δ −5.1 (*Me*Si), −3.3 (*Me*$_2$Si), 12.8 ($SiCH_2$), 13.9 ($SiCH_2$), 18.4, 18.6y 20.1 (CH_2), 20.5 ($OCH_2CH_2CH_2$), 21.5 (CH_2CH_2N, 32.5 (CH_2CO)), 33.7 (OCH_2CH_2), 49.2 (CH_2N), 51.6 (O*Me*), 57.5 (CH_2N), 67.7 (OCH_2), 93.6 (C_6H_3 (CH)), 160.9 (*i*-C_6H_3), 173.1 (*C*O); ^{29}Si NMR ($CDCl_3$): δ 1.6 (Me*Si*), 1.9 (Me_2*Si*). $[M+H]^+$: 2404.5. Anal. Calcd $C_{117}H_{228}N_6O_{27}Si_9$ (2403.86 g/mol): C 58.46, H 9.56, N, 3.50; Obt.: C, 58.09, H 9.13, N, 3.02.

4.2.21. $G_2O_3(C_2H_4CO_2Me)_{24}$ (***20***). *Method* (B): Compound **20** was obtained as a pale yellow oil (2.10 g, 88%) from the reaction of **26** (1.05 g, 0.48 mmol) and $C_3H_5N(C_2H_4CO_2Me)_2$ (1.34 g, 5.94 mmol) as described for compound **19**. *Method* (C): Starting from $C_2H_3CO_2Me$ (0.25 g, 2.92 mmol) and **29** (0.30 g, 0.11 mmol) compound **20** was isolated as a yellowish oil (0.46 g, 89%) following the procedure described for **19** (method C).

^{1}H NMR ($CDCl_3$): δ −0.10 (s, 27H, *Me*Si), −0.07 (s, 72H, *Me*$_2$Si), 0.39 (m, 24H, $SiCH_2$), 0.53 (m, 78H, $SiCH_2$), 1.30 (m, 66H, CH_2), 1.75 (m, 6H, OCH_2CH_2), 2.39 (m, 24H, CH_2N), 2.41 (t, *J*=7.3 Hz, 48H, CH_2N), 2.74 (t, *J*=7.3 Hz, 48H, CH_2CO), 3.64 (s, 72H, O*Me*), 3.87 (t, *J*=6.6 Hz, 6H, OCH_2), 6.03 (s, 3H, C_6H_3); ^{13}C NMR{^{1}H} ($CDCl_3$): δ −5.1 (*Me*Si), −3.3 (*Me*$_2$Si), 12.8 ($SiCH_2$), 13.9 ($SiCH_2$), 18.4, 18.8, 19.0y 20.1, 20.5, 21.5 (CH_2), 32.5 (NCH_2), 33.7 (OCH_2CH_2), 49.2 (CH_2CO), 51.2 (O*Me*), 57.5 (CH_2N), 67.7 (OCH_2), 93.6 (C_6H_3 (CH)), 160.9 (*i*-C_6H_3), 173.1 (CO); ^{29}Si NMR ($CDCl_3$): δ 0.9 (Me*Si*), 1.7 (Me*Si*), 1.9 (Me_2*Si*). Anal. Calcd $C_{237}H_{474}N_{12}O_{51}Si_{21}$ (4898.14 g/mol): C, 58.11; H, 9.75; N, 3.43; Obt.: C, 57.89; H, 10.01; N, 3.63.

4.2.22. $G_3O_3(C_2H_4CO_2Me)_{48}$ (***21***). *Method* (*B*): Following the procedure described for compound **19** (method B), compound **21** was obtained as a pale yellow oil (0.31 g, 88%) from the reaction of **26** (0.15 g, 0.037 mmol) and $C_3H_5N(C_2H_4CO_2Me)_2$ (0.22 g, 0.93 mmol) at 40 °C *Method* (C): Reaction of $C_2H_3CO_2Me$ (0.13 g, 1.44 mmol) and **30** (0.15 g, 0.026 mmol) yielded **21** as a yellowish oil (0.23 g, 86%) as described for **19** (method C).

^{1}H NMR ($CDCl_3$): δ −0.12 (s.a., 54H, *Me*Si), −0.07 (s, 144H, *Me*$_2$Si), 0.38 (m, 48H, $SiCH_2$), 0.52 (m, 174H, $SiCH_2$), 1.26 (m, 84H, CH_2), 1.38 (m, 54H, CH_2), 1.75 (m, 6H, OCH_2CH_2), 2.45 (m, 144H, CH_2N), 2.74 (s.a., 98H, CH_2CO), 3.63 (s, 144H, O*Me*), 3.87 (s.a., 6H, OCH_2), 6.00 (s, 3H, C_6H_3); ^{13}C NMR{^{1}H} ($CDCl_3$): δ −4.8 (*Me*Si), −3.3 (*Me*$_2$Si), 12.8 ($SiCH_2$), 14.1 ($SiCH_2$), 18.4–20.5 (CH_2), 32.3 (NCH_2), 33.6 (OCH_2CH_2), 49.2 (CH_2CO), 51.6 (O*Me*), 57.4 (CH_2N), 67.8 (OCH_2), 93.6 (C_6H_3 (CH)), 160.9 (*i*-C_6H_3), 172.8 (CO); ^{29}Si NMR ($CDCl_3$): δ 0.9, 1.8 (Me*Si*), 1.9 (Me_2*Si*). Anal. Calcd $C_{477}H_{966}N_{24}O_{99}Si_{45}$ (9886.72 g/mol): C, 57.95; H, 9.85; N, 3.40; Obt.: C, 57.09; H, 10.10; N, 3.63.

4.2.23. $G_1O_3(SiCl)_6$ (***22***). Following the procedure described for compound **7**, compound **22** was obtained as a colorless oil (1.77 g, 95%) from the reaction of **16** (1.01 g, 1.51 mmol) and $HSiMe_2Cl$ (1.46 g, 0.015 mol).

^{1}H NMR ($CDCl_3$): −0.05 (s, 9H, *Me*Si), 0.38 (s, 36H, *Me*$_2$SiCl), 0.58 (m, 18H, $SiCH_2$), 0.86 (m, 12H, CH_2SiCl), 1.42 (m, 18H, CH_2), 1.78 (m, 6H, OCH_2CH_2), 3.88 (t, *J*=6.6 Hz, 6H, OCH_2), 6.04 (s, 3H, C_6H_3); ^{13}C NMR{^{1}H} ($CDCl_3$): −5.1 (*Me*Si), 1.9 (*Me*$_2$SiCl), 13.6 ($SiCH_2$), 17.7 (CH_2), 17.9 (CH_2), 20.5 ($OCH_2CH_2CH_2$), 23.5 (CH_2SiCl), 33.1 (OCH_2CH_2), 67.5 (OCH_2), 93.7 (C_6H_3 (CH)), 160.9 (*i*-C_6H_3); ^{29}Si NMR ($CDCl_3$): 2.1 (Me*Si*), 31.1 (Me_2*Si*Cl).

4.2.24. $G_2O_3(SiCl)_{12}$ (***23***). Following the procedure described for compound **7**, compound **23** was obtained as a pale yellow oil (3.41 g, 95%) from the reaction of **17** (2.00 g, 1.40 mmol) and $HSiMe_2Cl$ (2.71 g, 0.029 mol).

^{1}H NMR ($CDCl_3$): −0.07 (s, 18H, *Me*Si), −0.01 (s, 9H, *Me*Si), 0.38 (s, 72H, *Me*$_2$SiCl), 0.54 (m, 54H, $SiCH_2$), 0.86 (m, 24H, CH_2SiCl), 1.28 (m, 12H, CH_2), 1.42 (m, 30H, CH_2), 1.77 (m, 6H, OCH_2CH_2), 3.87 (t, *J*=6.6 Hz, 6H, OCH_2), 6.04 (s, 3H, C_6H_3); ^{13}C NMR{^{1}H} ($CDCl_3$): −5.0 (*Me*Si), −4.8 (*Me*Si), 1.9 (*Me*$_2$SiCl), 13.9 ($SiCH_2$), 17.7, 18.1 (CH_2), 18.5, 18.7, 18.8 (CH_2), 20.6 ($OCH_2CH_2CH_2$), 23.5 (CH_2SiCl), 33.3 (OCH_2CH_2), 67.7 (OCH_2), 93.7 (C_6H_3 (CH)), 160.9 (*i*-C_6H_3); ^{29}Si NMR ($CDCl_3$): 1.0 (Me*Si*), 2.0 (Me*Si*), 31.2 (Me_2*Si*Cl).

*4.2.25. $G_3O_3(SiCl)_{24}$ (**24**).* Following the procedure described for compound **7**, compound **24** was obtained as a yellowish oil (4.21 g, 95%) from the reaction of **18** (2.50 g, 0.85 mmol) and $HSiMe_2Cl$ (3.28 g, 0.034 mol).

^{1}H NMR ($CDCl_3$): −0.09 (s, 27H, *Me*Si), −0.07 (s, 36H, *Me*Si), 0.38 (s, 144H, Me_2SiCl), 0.54 (m, 126H, SiCH_2), 0.86 (m, 48H, CH_2SiCl), 1.25 (m, 36H, CH_2), 1.42 (m, 54H, CH_2), 1.77 (m, 6H, OCH_2CH_2), 3.87 (t, *J*=6.6 Hz, 6H, OCH_2), 6.03 (s, 3H, C_6H_3); ^{13}C NMR{^{1}H} ($CDCl_3$): −5.0, −4.8 (*Me*Si), 1.9 (Me_2SiCl), 13.9 (CH_2Si), 17.7, 18.1, 18.5, 18.8, 18.9, 19.1 (CH_2), 20.6 ($OCH_2CH_2CH_2$), 23.5 (CH_2SiCl), 33.4 (OCH_2CH_2), 67.7 (OCH_2), 93.6 (C_6H_3 (CH)), 160.9 (*i*-C_6H_3); ^{29}Si NMR ($CDCl_3$): 1.0, 1.6 (Me*Si*), 31.1 (Me_2*Si*Cl).

*4.2.26. $G_1O_3(SiH)_6$ (**25**).* Following the procedure described for compound **8**, compound **25** was obtained as a colorless oil (1.18 g, 80%) from the reaction of **22** (1.77 g, 1.43 mmol) and $LiAlH_4$ (6.45 mmol).

^{1}H NMR ($CDCl_3$): δ −0.08 (s, 9H, *Me*Si), 0.04 (d, *J*=4.2 Hz, 36H, Me_2SiH), 0.55 (m, 18H, SiCH_2), 0.63 (m, 12H, CH_2SiH), 1.25 (m, 18H, CH_2), 1.77 (m, 6H, OCH_2CH_2), 3.82 (m, 6H, Si*H*), 3.88 (t, *J*=6.6 Hz, 6H, OCH_2), 6.04 (s, 3H, C_6H_3); ^{13}C NMR{^{1}H} ($CDCl_3$): δ −5.1 (*Me*Si), −4.4 (Me_2SiH), 13.7 (SiCH_2), 18.0, 18.8y 18.9 (CH_2), 20.5 ($OCH_2CH_2CH_2$), 33.2 (OCH_2CH_2), 67.6 (OCH_2), 93.8 (C_6H_3 (CH)), 161.0 (*i*-C_6H_3); ^{29}Si NMR ($CDCl_3$): δ −14.0 (Me_2*Si*H), 1.9 (Me*Si*). MS $[M+H]^+$: 1027.68. Anal. Calcd $C_{51}H_{114}O_3Si_9$ (1028.22 g/mol): C, 59.57; H, 11.18; Obt.: C, 59.89; H, 11.53.

*4.2.27. $G_2O_3(SiH)_{12}$ (**26**).* Following the procedure described for compound **8**, compound **26** was obtained as a colorless oil (0.95 g, 79%) from the reaction of **23** (1.45 g, 0.57 mmol) and $LiAlH_4$ (5.10 mmol).

^{1}H NMR ($CDCl_3$): δ −0.10 (s, 18H, *Me*Si), −0.08 (s, 9H, *Me*Si), 0.03 (d, *J*=4.2 Hz, 72H, Me_2SiH), 0.55 (m, 54H, SiCH_2), 0.63 (m, 24H, CH_2SiH), 1.35 (m, 42H, CH_2), 1.77 (m, 6H, OCH_2CH_2), 3.82 (m, 12H, Si*H*), 3.88 (t, *J*=6.6 Hz, 6H, OCH_2), 6.04 (s, 3H, C_6H_3); ^{13}C NMR{^{1}H} ($CDCl_3$): δ −5.1 (*Me*Si), −5.0 (*Me*Si), −4.4 (Me_2SiH), 13.9 (SiCH_2), 18.2, 18.5, 18.8y 19.0 (CH_2), 20.5 ($OCH_2CH_2CH_2$), 33.3 (OCH_2CH_2), 67.7 (OCH_2), 93.7 (C_6H_3 (CH)), 160.9 (*i*-C_6H_3); ^{29}Si NMR ($CDCl_3$): δ −14.2 (Me_2*Si*H), 0.8 (Me*Si*), 1.9 (Me*Si*). $[M+H]^+$: 2147.4. Anal. Calcd $C_{105}H_{246}O_3Si_{21}$ (2146.87 g/mol): C, 58.74; H, 11.55; Obt.: C, 58.29; H, 11.53.

*4.2.28. $G_3O_3(SiH)_{24}$ (**27**).* Following the procedure described for compound **8**, compound **27** was obtained as a colorless oil (0.93 g, 74%) from the reaction of **24** (1.50 g, 0.29 mmol) and $LiAlH_4$ (5.00 mmol).

^{1}H NMR ($CDCl_3$): δ −0.10 (s.a., 54H, *Me*Si), 0.03 (d, *J*=4.2 Hz, 144H, Me_2SiH), 0.58 (m, 174H, SiCH_2), 1.35 (m, 90H, CH_2), 1.77 (m, 6H, OCH_2CH_2), 3.82 (m, 30H, Si*H* y OCH_2), 6.03 (s, 3H, C_6H_3); ^{13}C NMR{^{1}H} ($CDCl_3$): δ −5.0 (*Me*Si), −4.3 (Me_2SiH), 13.9 (CH_2Si), 18.2, 18.5, 18.8, 18.9 (CH_2), 20.6 ($OCH_2CH_2CH_2$), 33.2 (OCH_2CH_2), 67.7 (OCH_2), 94.5 (C_6H_3 (CH)), 160.9 (*i*-C_6H_3); ^{29}Si NMR ($CDCl_3$): δ −14.2 (Me_2*Si*H), 1.0, 1.2 (Me*Si*). Anal. Calcd $C_{213}H_{510}O_3Si_{45}$ (4384.17 g/mol): C, 58.35; H, 11.73; Obt.: C, 58.85; H, 10.97.

*4.2.29. $G_1O_3(NH_2)_6$ (**28**).* $C_3H_5NH_2$ (0.37 g, 6.42 mmol) was added to a THF solution (3 mL) of compound **25** (0.50 g, 0.49 mmol) in the presence of Karstedt catalyst (3% mol) and stirred at 120 °C for 3 days into a sealed ampoule. The volatiles were removed under vacuum, CH_2Cl_2 was added to the residue and the solution was filtered through active carbon. After removal of volatiles compound **28** was obtained as a yellowish oil (0.59 g, 89%).

^{1}H NMR ($CDCl_3$): −0.09 (s, 9H, *Me*Si), −0.06 (s, 36H, Me_2SiH), 0.48 (m, 12H, SiCH_2), 0.54 (m, 30H, SiCH_2), 1.29 (m, 18H, CH_2), 1.40 (m, 24H, NH_2, CH_2), 1.74 (m, 6H, OCH_2CH_2), 2.63 (t, *J*=7.1 Hz, 12H, CH_2N), 3.87 (t, *J*=6.3 Hz, 6H, OCH_2), 6.04 (s, 3H, C_6H_3); ^{13}C NMR{^{1}H} ($CDCl_3$): −5.1 (*Me*Si), −3.3 (Me_2Si), 12.3 ($NCH_2CH_2CH_2$), 13.8 (SiCH_2), 18.4, 18.6, 20.0 (CH_2), 20.5 ($OCH_2CH_2CH_2$), 33.2 (OCH_2CH_2), 45.6 (NCH_2), 67.6 (OCH_2), 93.7 (C_6H_3 (CH)), 160.9 (*i*-C_6H_3); ^{29}Si NMR ($CDCl_3$): 1.8 (Me*Si*), 2.1 (Me_2*Si*). Anal. Calcd $C_{69}H_{156}N_6O_3Si_9$ (1370.78 g/mol): C, 60.46, H, 11.47, N, 6.13; Obt.: C, 60.91, H, 11.26, N, 5.86.

*4.2.30. $G_2O_3(NH_2)_{12}$ (**29**).* Following the procedure described for compound **28**, compound **29** was obtained as a colorless oil (0.47 g, 72%) from the reaction of **26** (0.50 g, 0.23 mmol) and $C_3H_5NH_2$ (0.32 g, 5.59 mmol).

^{1}H NMR ($CDCl_3$): −0.11 (s, 18H, *Me*Si), −0.09 (s, 9H, *Me*Si), −0.07 (s, 72H, Me_2SiH), 0.43 (m, 26H, CH_2), 0.54 (m, 72H, CH_2), 1.21 (s, 24H, NH_2), 1.28 (m, 36H, CH_2), 1.38 (m, 30H, CH_2), 1.74 (m, 6H, OCH_2CH_2), 2.63 (t, *J*=7.1 Hz, 24H, CH_2N), 3.85 (t, *J*=6.3 Hz, 6H, OCH_2), 6.04 (s, 3H, C_6H_3); ^{13}C NMR{^{1}H} ($CDCl_3$): −4.9(*Me*Si), −4.7 (*Me*Si), −3.3 (Me_2Si), 12.3 (SiCH_2), 13.8 (SiCH_2), 18.4, 18.6, 18.8, 20.0, 20.1 (CH_2), 20.6 ($OCH_2CH_2CH_2$), 28.3 (CH_2CH_2N), 33.3 (OCH_2CH_2), 45.7 (CH_2N), 67.6 (OCH_2), 93.7 (C_6H_3 (CH)), 160.9 (*i*-C_6H_3); ^{29}Si NMR ($CDCl_3$): 0.9 (Me*Si*), 1.7 (Me*Si*), 1.9 (Me_2*Si*). Anal. Calcd $C_{141}H_{330}N_{12}O_3Si_{21}$ (2832.00 g/mol): C, 59.80; H, 11.75; N, 5.94; Obt.: C, 60.92; H, 10.03; N, 5.44.

*4.2.31. $G_3O_3(NH_2)_{24}$ (**30**).* Following the procedure described for compound **28**, compound **30** was obtained as a colorless oil (0.24 g, 36%) from the reaction of **27** (0.50 g, 0.12 mmol) and $C_3H_5NH_2$ (0.62 g, 5.50 mmol).

^{1}H NMR ($CDCl_3$): −0.11 (s.a., 54H, *Me*Si), −0.07 (s, 144H, Me_2Si), 0.52 (m, 222H, SiCH_2), 1.21–1.50 (m, 186H, NH_2, CH_2), 1.74 (m, 6H, OCH_2CH_2), 2.63 (t, *J*=7.1 Hz, 48H, CH_2N), 3.85 (t, *J*=6.3 Hz, 6H, OCH_2), 6.04 (s, 3H, C_6H_3); ^{13}C NMR{^{1}H} ($CDCl_3$): −4.9 (*Me*Si), −3.3 (Me_2Si), 12.8 ($CH_2CH_2CH_2N$), 14.1 (SiCH_2), 17.9–20.6 (CH_2), 27.1 (CH_2CH_2N), 33.4 (OCH_2CH_2), 45.1 (CH_2N), 67.8 (OCH_2), 93.7 (C_6H_3 (CH)), 161.0 (*i*-C_6H_3); ^{29}Si NMR ($CDCl_3$): 0.9 (Me*Si*), 1.7 (Me*Si*), 1.9 (Me_2*Si*). Anal. Calcd $C_{285}H_{678}N_{24}O_3Si_{45}$ (5754.44 g/mol): C, 59.49; H, 11.88; N, 5.84; Obt.: C, 58.50; H, 11.67; N, 5.34.

*4.2.32. $G_2O_3(SiCl_2)_6$ (**31**).* Following the procedure described for compound **1**, compound **31** was obtained as a colorless liquid (4.20 g, 94%) from **17** (2.20 g, 3.30 mmol) and $HSiMeCl_2$ (3.87 g, 0.033 mol).

^{1}H NMR ($CDCl_3$): −0.03 (s, 9H, *Me*Si), 0.53 (m, 6H, SiCH_2), 0.66 (m, 12H, SiCH_2), 0.75 (s, 18H, *Me*$SiCl_2$), 1.16 (m, 12H, CH_2SiCl_2), 1.50 (m, 18H, CH_2), 1.76 (m, 6H, OCH_2CH_2), 3.89 (t, *J*=6.6 Hz, 6H, OCH_2), 6.04 (s, 3H, C_6H_3); ^{13}C NMR{^{1}H} ($CDCl_3$): −5.2 (*Me*Si), 5.5 (*Me*$SiCl_2$), 13.4 (SiCH_2), 17.4 (CH_2), 20.4 ($OCH_2CH_2CH_2$), 25.9 (CH_2SiCl_2), 33.1 (OCH_2CH_2), 67.5 (OCH_2), 93.8 (C_6H_3 (CH)), 160.9 (*i*-C_6H_3); ^{29}Si NMR ($CDCl_3$): 2.0 (Me*Si*), 32.2 (Me*Si*Cl_2).

*4.2.33. $G_3O_3(SiCl_2)_{12}$ (**32**).* Following the procedure described for compound **1**, compound **32** was obtained as a colorless liquid (4.26 g, 95%) from **18** (2.30 g, 1.61 mmol) and $HSiMeCl_2$ (3.90 g, 0.034 mol).

^{1}H NMR ($CDCl_3$): −0.07 (s, 9H, *Me*Si), −0.05 (s, 18H, *Me*Si), 0.59 (m, 54H, SiCH_2), 0.75 (s, 36H, *Me*$SiCl_2$), 1.16 (m, 24H, CH_2SiCl_2), 1.29 (m, 18H, CH_2), 1.50 (m, 24H, CH_2), 1.76 (m, 6H, OCH_2CH_2), 3.87 (t, *J*=6.6 Hz, 6H, OCH_2), 6.04 (s, 3H, C_6H_3); ^{13}C NMR{^{1}H} ($CDCl_3$): −5.1 (*Me*Si), 5.5 (*Me*$SiCl_2$), 13.8 (CH_2Si), 17.3, 17.5, 18.5, 18.6, 18.8 (CH_2), 20.6 ($OCH_2CH_2CH_2$), 25.9 (CH_2SiCl_2), 33.3 (OCH_2CH_2), 67.7 (OCH_2), 93.7 (C_6H_3 (CH)), 161.0 (*i*-C_6H_3); ^{29}Si NMR ($CDCl_3$): 1.8 (Me*Si*), 32.1 (Me*Si*Cl_2).

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Supplementary data

Selected NMR spectra of dendrons and dendrimers. Supplementary data associated with this article can be found in online version at doi:10.1016/j.tet.2010.09.063. These data include MOL files and InChIKeys of the most important compounds described in this article.

References and notes

1. Astruc, D.; Boisselier, E.; Ornelas, C. *Chem. Rev.* **2010**, *110*, 1857.
2. Villaraza, A. J. L.; Bumb, A.; Brechbiel, M. W. *Chem. Rev.* **2010**, *110*, 2921.
3. Dutta, T.; Jain, N. K.; McMillan, N. A. J.; Parekh, H. S. *Nanomed.-Nanotechnol. Biol. Med.* **2010**, *6*, 25.
4. Paleos, C. M.; Tsiourvas, D.; Sideratou, Z.; Tziveleka, L. *Curr. Top. Med. Chem.* **2008**, *8*, 1204.
5. Cheng, Y. Y.; Xu, Z. H.; Ma, M. L.; Xu, T. W. *J. Pharm. Sci.* **2008**, *97*, 123.
6. Andrés, R.; de Jesús, E.; Flores, J. C. *New J. Chem.* **2007**, *31*, 1161.
7. Fu, Y.; Nitecki, D. E.; Maltby, D.; Simon, G. H.; Berejnoi, K.; Raatschen, H. J. *Bioconjugate Chem.* **2006**, *17*, 1043.
8. Jang, W. D.; Kataoka, K. *J. Drug Deliv. Sci. Technol.* **2005**, *15*, 19.
9. Yokoyama, S.; Otomo, A.; Nakahama, T.; Okuno, Y.; Mashiko, S. Dendrimers for optoelectronic applications In. *Dendrimers V: Functional and Hyperbranched Building Blocks, Photophysical Properties, Applications in Materials and Life Sciences*; 2003; Vol. 228, p 205.
10. Reek, J. N. H.; de Groot, D.; Oosterom, G. E.; Kamer, P. C. J.; van Leeuwen, P. W. N. M. *C.R. Chim.* **2003**, *6*, 1061.
11. Kobayashi, H.; Brechbiel, M. W. *Mol. Imaging* **2003**, *2*, 1.
12. Niu, Y. H.; Crooks, R. M. *C.R. Chim.* **2003**, *6*, 1049.
13. Twyman, L. J.; King, A. S. H.; Martin, I. K. *Chem. Soc. Rev.* **2002**, *31*, 69.
14. Dykes, G. M. *J. Chem. Technol. Biotechnol.* **2001**, *76*, 903.
15. Newkome, G. R.; Moorefield, C. N.; Vögtle, F. *Dendrimers and Dendrons: Concepts, Syntheses, Applications*; Wiley-VCH: Weinheim, Germany, 2001.
16. Newkome, G. R.; Moorefield, C. N.; Vögtle, F. *Dendritic Molecules: Concepts, Syntheses, Perspectives*; VCH: Weinheim, Germany, 1996.
17. Cuadrado, I.; Morán, M.; Losada, J.; Casado, C. M.; Pascual, C.; Alonso, B.; Lobete, F. In *Advances in Dendritic Macromolecules*; Newkome, G. R., Ed.; Jai: Greenwich, 1999; 3, p 151.
18. Duncan, R.; Izzo, L. *Adv. Drug Deliv. Rev.* **2005**, *57*, 2215.
19. Jevprasesphant, R.; Penny, J.; Jalal, R.; Attwood, D.; McKeown, N. B.; D'Emanuele, A. *Int. J. Pharm.* **2003**, *252*, 263.
20. Malik, N.; Wiwattanapatapee, R.; Klopsch, R.; Lorenz, K.; Frey, H.; Weener, J. W.; Meijer, E. W.; Paulus, W.; Duncan, R. *9th International Symposium on Recent Advances in Drug Delivery Systems*; Utah: Salt Lake City, 1999; p 133.
21. Brazeau, G. A.; Attia, S.; Poxon, S.; Hughes, J. A. *Pharm. Res.* **1998**, *15*, 680.
22. Pietersz, G. A.; Tang, C. K.; Apostolopoulos, V. *Mini-Rev. Med. Chem.* **2006**, *6*, 1285.
23. Caminade, A. M.; Majoral, J. P. *Prog. Polym. Sci.* **2005**, *30*, 491.
24. Blanzat, M.; Turrin, C. O.; Aubertin, A. M.; Couturier-Vidal, C.; Caminade, A. M.; Majoral, J. P.; Rico-Lattes, I.; Lattes, A. *Chembiochem* **2005**, *6*, 2207.
25. Solassol, J.; Crozet, C.; Perrier, V.; Leclaire, J.; Beranger, F.; Caminade, A. M.; Meunier, B.; Dormont, D.; Majoral, J. P.; Lehmann, S. *J. Gen. Virol.* **2004**, *85*, 1791.
26. Lee, J. H.; Lim, Y. B.; Choi, J. S.; Choi, M. U.; Yang, C. H.; Park, J. S. *Bull. Korean Chem. Soc.* **2003**, *24*, 1637.
27. Kleij, A. W.; van de Coevering, R.; Gebbink, R. J. M. K.; Noordman, A. M.; Spek, A. L.; van Koten, G. *Chem. Eur. J.* **2001**, *7*, 181.
28. Mumper, R. J.; Bell, M. A.; Worthen, D. R.; Cone, R. A.; Lewis, G. R.; Paull, J. R. A.; Moench, T. R. *Drug Develop. Ind. Pharm.* **2009**, *35*, 515.
29. Meyers, S. R.; Juhn, F. S.; Griset, A. P.; Luman, N. R.; Grinstaff, M. W. *J. Am. Chem. Soc.* **2008**, *130*, 14444.
30. Hussain, M.; Shchepinov, M. S.; Sohail, M.; Benter, I. F.; Hollins, A. J.; Southern, E. M.; Akhtar, S. *J. Control. Release* **2004**, *99*, 139.
31. Made, A. W. v. d.; Leeuwen, P. W. N. M. v. *J. Chem. Soc., Chem. Commun.* **1992**, 1400.
32. Zhou, L. L.; Hadjichristidis, N.; Toporowski, P. M.; Roovers, J. *Rubber Chem. Technol.* **1992**, *65*, 303.
33. Roovers, J.; Toporowski, P. M.; Zhou, L. L. *Abstr. Pap. Am. Chem. Soc.* **1992**, *203*, 200.
34. Van der Made, A. W.; Van Leeuwen, P. N. M. W.; de Wilde, J. C.; Brandes, R. A. C. *Adv. Mater.* **1993**, *5*, 466.
35. Seyferth, D.; Son, D. Y.; Rheingold, A. L.; Ostrander, R. L. *Organometallics* **1994**, *13*, 2682.
36. Bruning, K.; Lang, H. *J. Organomet. Chem.* **1998**, *571*, 145.
37. Krska, S. W.; Seyferth, D. *J. Am. Chem. Soc.* **1998**, *120*, 3604.
38. Schlenk, C.; Frey, H. *Monatsh. Chem.* **1999**, *130*, 3.
39. Rasines, B.; Hernández-Ros, J. M.; de las Cuevas, N.; Copa-Patiño, J. L.; Soliveri, J.; Muñoz-Fernández, M. A.; Gómez, R.; de la Mata, F. J. *Dalton Trans.* **2009**, 8704.
40. Weber, N.; Ortega, P.; Clemente, M. I.; Shcharbin, D.; Bryszewska, M.; de la Mata, F. J.; Gómez, R.; Muñoz-Fernández, M. A. *J. Control. Release* **2008**, *132*, 55.
41. Bermejo, J. F.; Ortega, P.; Chonco, L.; Eritja, R.; Samaniego, R.; Mullner, M.; de Jesús, E.; de la Mata, F. J.; Flores, J. C.; Gómez, R.; Muñoz-Fernández, A. *Chem.—Eur. J.* **2007**, *13*, 483.
42. Yamada, A.; Hatano, K.; Matsuoka, K.; Koyama, T.; Esumi, Y.; Koshino, H.; Hino, K.; Nishikawa, K.; Natori, Y.; Terunuma, D. *Tetrahedron* **2006**, *62*, 5074.
43. Nishikawa, K.; Matsuoka, K.; Watanabe, M.; Igai, K.; Hino, K.; Hatano, K.; Yamada, A.; Abe, N.; Terunuma, D.; Kuzuhara, H.; Natori, Y. *J. Infect. Dis.* **2005**, *191*, 2097.
44. Matsuoka, K.; Terabatake, M.; Esumi, Y.; Terunuma, D.; Kuzuhara, H. *Tetrahedron Lett.* **1999**, *40*, 7839.
45. Maraval, V.; Pyzowski, J.; Caminade, A. M.; Majoral, J. P. *J. Org. Chem.* **2003**, *68*, 6043.
46. Grayson, S. M.; Fréchet, J. M. J. *Chem. Rev.* **2001**, *101*, 3819.
47. Hawker, C. J.; Fréchet, J. M. J. *J. Chem. Soc., Chem. Commun.* **1990**, 1010.
48. Kang, T.; Amir, R. J.; Khan, A.; Ohshimizu, K.; Hunt, J. N.; Sivanandan, K.; Montáñez, M. I.; Malkoch, M.; Ueda, M.; Hawker, C. J. *Chem. Commun.* **2010**, *46*, 1556.
49. Carlmark, A.; Hawker, C. J.; Hult, A.; Malkoch, M. *Chem. Soc. Rev.* **2009**, *38*, 352.
50. Wu, P.; Malkoch, M.; Hunt, J. N.; Vestberg, R.; Kaltgrad, E.; Finn, M. G.; Fokin, V. V.; Sharpless, K. B.; Hawker, C. J. *Chem. Commun.* **2005**, 5775.
51. Rodríguez, L. I.; Rossell, O.; Seco, M.; Müller, G. *Organometallics* **2008**, *27*, 1328.
52. van Heerbeek, R.; Kamer, P. C. J.; van Leeuwen, P. N. M. W.; Reek, J. N. H. *Org. Biomol. Chem.* **2006**, *4*, 211.
53. Andrés, R.; de Jesús, E.; de la Mata, F. J.; Flores, J. C.; Gómez, R. *Eur. J. Inorg. Chem.* **2005**, 3742.
54. Tuchbreiter, A.; Werner, H.; Gade, L. H. *Dalton Trans.* **2005**, 1394.
55. Karstedt, B.D. Fr. 19681206 (to General Electric Co.), 1968. *Chem. Abstr.* **1969**, *71*, 91641.
56. Krupková, A.; Čermák, J.; Walterová, Z.; Horský, J. *Macromolecules* **2010**, *43*, 4511.
57. Although this compounds is commercial available, its synthesis is not described in bibliography (see Experimental).
58. Hawker, C. J.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **1990**, *112*, 7638.