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# A Versatile Methodology for the Controlled Synthesis of Photoluminescent High-Boron-Content Dendrimers

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**Abstract:** Fluorescent star-shaped molecules and dendrimers with a 1,3,5-triphenylbenzene moiety as the core and 3 or 9 carborane derivatives at the periphery, have been prepared in very good yields by following different approaches. One procedure relies on the nucleophilic substitution of Br groups in 1,3,5-tris(4-(3-bromopropoxy)phenyl)benzene with the monolithium salts of methyl and phenyl-*o*-carborane. The second method is the hydrosilylation reactions on the peripheral allyl ether functions of 1,3,5-tris(4-allyloxyphenyl)benzene and 1,3,5-tris(4-(3,4,5-trisallyloxybenzyloxy)phenyl)benzene with suitable carboranyl-silanes to produce different generations of dendrimers

decorated with carboranyl fragments. This approach is very versatile and allows one to introduce long spacers between the fluorescent cores and the boron clusters, as well as to obtain a high loading of boron clusters. The removal of one boron atom from each cluster leads to high-boron-content water-soluble macromolecules. Thermogravimetric analyses show a higher thermal stability for the three-functionalized compounds than for those con-

taining 9 clusters. All compounds exhibit photoluminescent properties at room temperature under ultraviolet irradiation with high quantum yields; these depend on the nature of the cluster and the substituent on the C<sub>cluster</sub>. Cyclic voltammetry indicates that there is no electronic communication between the core and the peripheral carboranyl fragments. Due to the high boron content of these molecules, we currently focus our research on their biocompatibility, biodistribution in cells cultures, and potential applications for boron neutron capture therapy (BNCT).

**Keywords:** boron • carboranes • cluster compounds • dendrimers • macromolecules • photoluminescence

## Introduction

The search for luminescent materials is continuously expanding due to their applications as light-emitting diodes, semiconductor lasers, probes, or fluorescence sensors, among others.<sup>[1]</sup> In boron chemistry, there are few reports concerning the photophysical properties of boranes and carboranes. Nevertheless, during the last few years, the interest in the development of new photoluminescent materials that incorporate polyhedral boron clusters has increased, as shown by the incorporation of these compounds, which possess special electronic properties and geometry, into fluorescent systems.<sup>[2]</sup> For this reason, different fluorescent carborane-appended star-shaped molecules, in which the carborane is linked to a fluorescent  $\pi$ -conjugated core,<sup>[3]</sup> to  $\pi$ -conjugated organic systems,<sup>[4]</sup> or polymers,<sup>[5,6]</sup> have been recently described, and the influence of the cluster on the emission properties studied.

On the other hand, the interest in the use of different types of platforms for the incorporation of boron-based clusters to obtain high-boron-content molecules for boron neutron capture therapy (BNCT), or for drug delivery, has increased enormously.<sup>[3,7]</sup> During the last decade, our group has contributed to the development of different synthetic strategies for the preparation of boron-rich neutral systems

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that incorporate *closo*-carboranes, and water-soluble anionic macromolecules functionalized with *nido*-carborane and cobaltabisdicarbollide fragments, which provide potential biomedical applications.<sup>[8–10]</sup> Apart from the high boron content, another interesting property that we have considered important for their biological application is their photophysical properties. For this reason, we have prepared Fréchet-type anionic carboranyl-functionalized aryl-ether derivatives that exhibit blue emission under ultraviolet irradiation in different solvents at room temperature,<sup>[11]</sup> as well as other dendrimeric systems that consist of a 1,3,5-triphenylbenzene unit as fluorescent core,<sup>[12,13]</sup> poly(aryl-ether) fragments as connecting groups, and three, six, and twelve terminal cobaltabisdicarbollide anions.<sup>[14]</sup> Nevertheless, in the latter, despite the fluorescence of the starting dendrimers, after functionalization with the metallocarborane, a quenching of the fluorescence was observed. Based on these results, and considering our interest in the preparation of fluorescent boron-rich systems, we wondered if the carborane clusters, unlike the cobaltabisdicarbollide, would produce an improvement of the photoluminescent properties. For that reason, herein we report on the synthesis and characterization of a set of fluorescent high-boron-content star-shaped molecules and dendrimers by using a versatile methodology to control and increase the number of boron atoms. Control of the spacer between the core and the peripheral cages is also sought. The crystal structure of one of the carboranyl-containing star-shaped molecules has been analyzed by X-ray diffraction and is reported herein. The thermal and electrochemical behavior of the compounds has been studied. A comparative revision of the photoluminescent properties for all compounds has been carried out, and the influence of the substituent attached to the second C<sub>cluster</sub> (Me, Ph), the type of spacer, and the number and nature of the clusters have been investigated.

## Results and Discussion

**Synthesis of compounds 1–27:** A set of star-shaped molecules and dendrimers with 1,3,5-triarylbenzene as core and incorporating different terminal groups (see Figure 1, 1–3), has been used as platform to prepare fluorescent high-boron-content macromolecules by functionalization with carboranyl fragments. The synthesis of 1,3,5-tris(4-(3-bromopropoxy)phenyl)benzene (**1**) has been described before,<sup>[15]</sup> however we used a modified procedure by mixing the corresponding 4-(3-bromopropoxy)acetophenone and tetrachlorosilane at room temperature. On the other hand, fluorescent compounds **2** and **3** with terminal allyl ether groups have already been reported by our group, as well as their reaction with cobaltabisdicarbollide units.<sup>[14]</sup> In that previous work, when the periphery of **2** was functionalized with metallocarboranes, a quenching of the fluorescence occurred and we were not able to explain this phenomenon. Besides, a complete periphery functionalization with cobaltabisdicar-

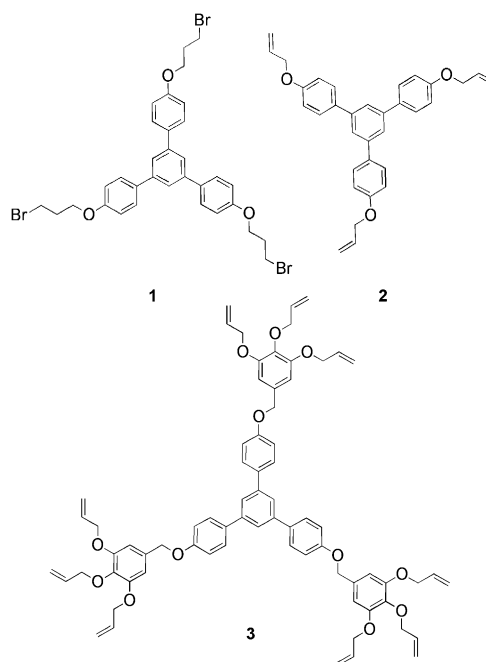
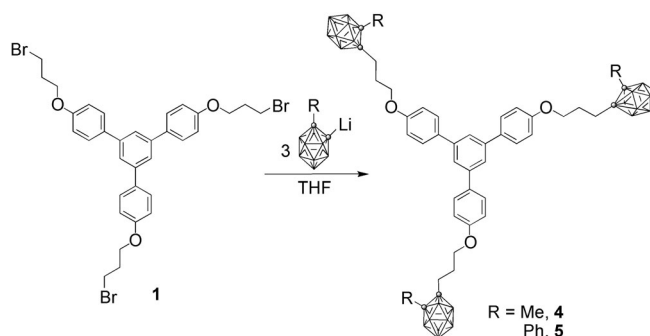


Figure 1. Starting star-shaped molecules and dendrimers with different terminal groups.

bollide clusters was not possible for **3**, which was attributed to steric hindrance.

Thus, because we are interested in the synthesis of fluorescent high-boron-content systems, we explore here the functionalization of these fluorescent starting compounds by using carborane clusters instead of metallocarboranes and study their effect on the observed photoluminescent properties.<sup>[16]</sup>

The different terminal groups on the periphery of the starting compounds **1–3** allow their functionalization by nucleophilic substitution or by catalyzed hydrosilylation reactions, respectively. First, the carborane-containing star-shaped molecules **4** and **5** were synthesized by nucleophilic substitution of the bromine groups in 1,3,5-tris(4-(3-bromopropoxy)phenyl)benzene (**1**), performing the reaction of **1** with 3 equivalents of the monolithium salts of 1-Me-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>11</sub> and 1-Ph-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>11</sub>,<sup>[17]</sup> respectively, in THF heated at reflux overnight (Scheme 1).



Scheme 1. Synthesis of **4** and **5** by nucleophilic substitution.

Compounds **2** and **3** were functionalized with different carboranyl derivatives by catalyzed hydrosilylation reactions. This approach permits a higher versatility and allows us to introduce longer spacers between the fluorescent core and the boron clusters, as well as to further increase the number of carborane clusters. For that purpose, two different sets of carboranyl-containing hydrosilylating agents, **6** and **7**<sup>[9a]</sup> and **8** and **9**, have been used (Figure 2).

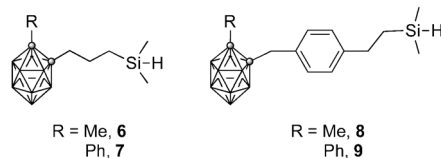
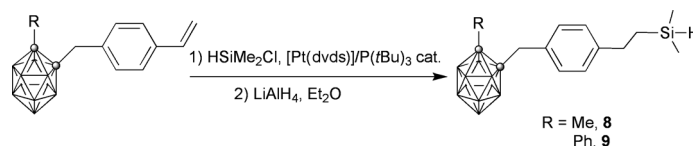


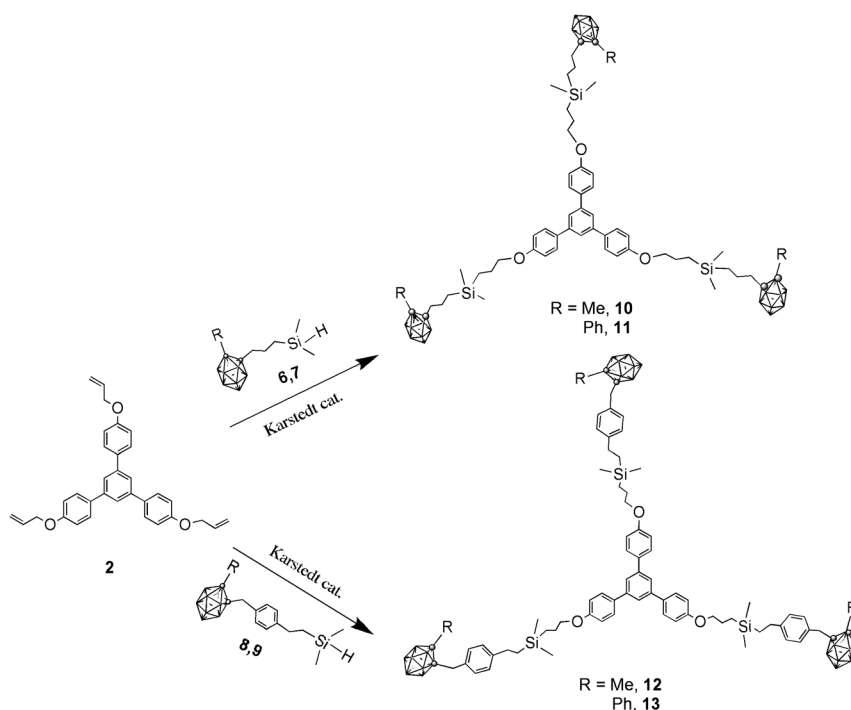
Figure 2. Hydrosilylation agents **6–9**.

Compounds **8** and **9** have been prepared in two steps from two recently developed fluorescent styrene-containing carborane clusters.<sup>[18]</sup> In the first step, a regiospecific hydrosilylation of styrene-containing carborane clusters with an excess of  $\text{HSiMe}_2\text{Cl}$  at RT, in the presence of Karstedt catalyst, led to the formation of the corresponding chlorosilane derivatives. The hydrosilylation is the addition of one Si–H function to a double- or triple bond catalyzed by a transition metal, usually a Pt catalyst,  $[\text{Pt}(\text{dvds})]$  ( $\text{dvds} = 1,3\text{-divinyltetramethyldisiloxane}$ ). Karstedt's catalyst is one of the most regioselective catalysts favoring the anti-Markovnikov addition to obtain mainly the  $\beta$ -adduct. However, according to the  $^1\text{H}$  NMR spectra for **8** and **9**, a mixture of isomers resulted from  $\alpha$ - (20%) and  $\beta$ -additions (80%); this result was different to that of compounds **6** and **7**, which were obtained as 100%  $\beta$ -adducts. To control the catalytic hydrosilylation and produce only the desired isomer, a new  $[\text{Pt}(\text{dvds})]/\text{P}(\text{tBu})_3$  complex was used.<sup>[19]</sup> Thus, the reaction of the styrene-containing carborane clusters with an excess of  $\text{HSiMe}_2\text{Cl}$  at RT in the presence of the  $[\text{Pt}(\text{dvds})]/\text{P}(\text{tBu})_3$  catalyst led to the formation of the corresponding chlorosilane derivatives as 100%  $\beta$ -adducts (Scheme 2). Following evaporation of the solvents, the second step consists of the reduction of the Si–Cl to Si–H by the addition of  $\text{LiAlH}_4$  in  $\text{Et}_2\text{O}$  at RT to obtain compounds **8** and **9** in high yield (Scheme 2).



Scheme 2. Synthesis of **8** and **9** by hydrosilylation reaction and reduction with  $\text{LiAlH}_4$ .

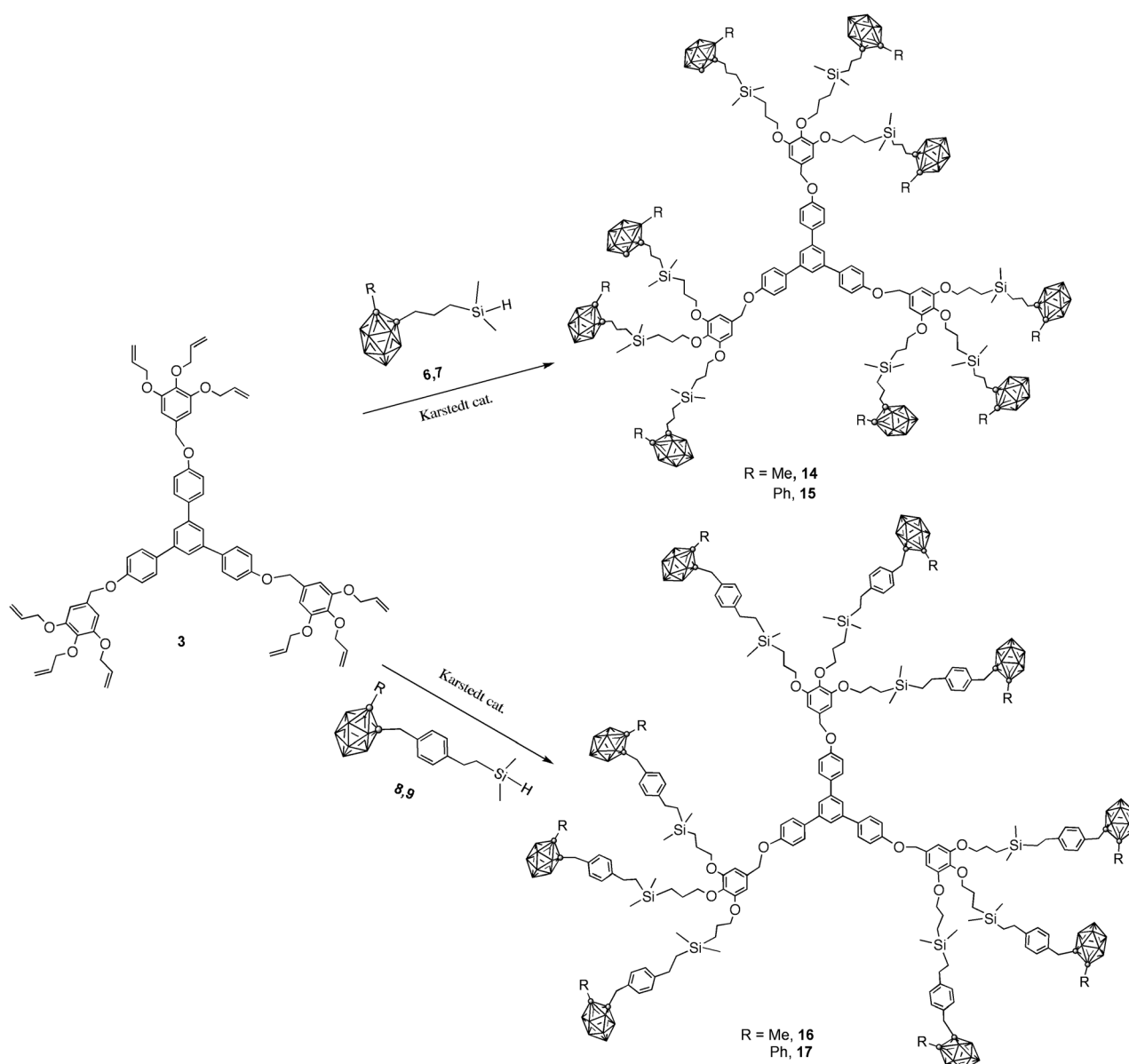
To functionalize the periphery of the fluorescent star-shaped molecule **2** and dendrimer **3** with carborane clusters, hydrosilylation reactions of the allyl ether with the hydrosilylating agents **6–9** were carried out in the minimum amount of dry THF at room temperature in the presence of Karstedt catalyst. The reaction of 3 equivalents of **6–9** with 1 equivalent of **2** leads to the three-functionalized molecules **10–13** (Scheme 3).



Scheme 3. Synthesis of three-functionalized compounds **10–13**.

Following the same procedure and to increase the amount of boron, 9 equivalents of **6–9** were mixed with 1 equivalent of **3** to produce compounds **14–17** (Scheme 4). Hydrosilylation reactions were monitored by  $^1\text{H}$  NMR spectroscopy to determine the completion of the reaction upon the disappearance of the allyl proton resonances of the starting large molecules (Scheme 4).

The preparation of pure compounds is a requirement for the development of materials, particularly for biological applications. Therefore, due to the presence of the Karstedt catalyst, a further purification of the functionalized molecules by TLC was necessary. Subsequently, all of the com-



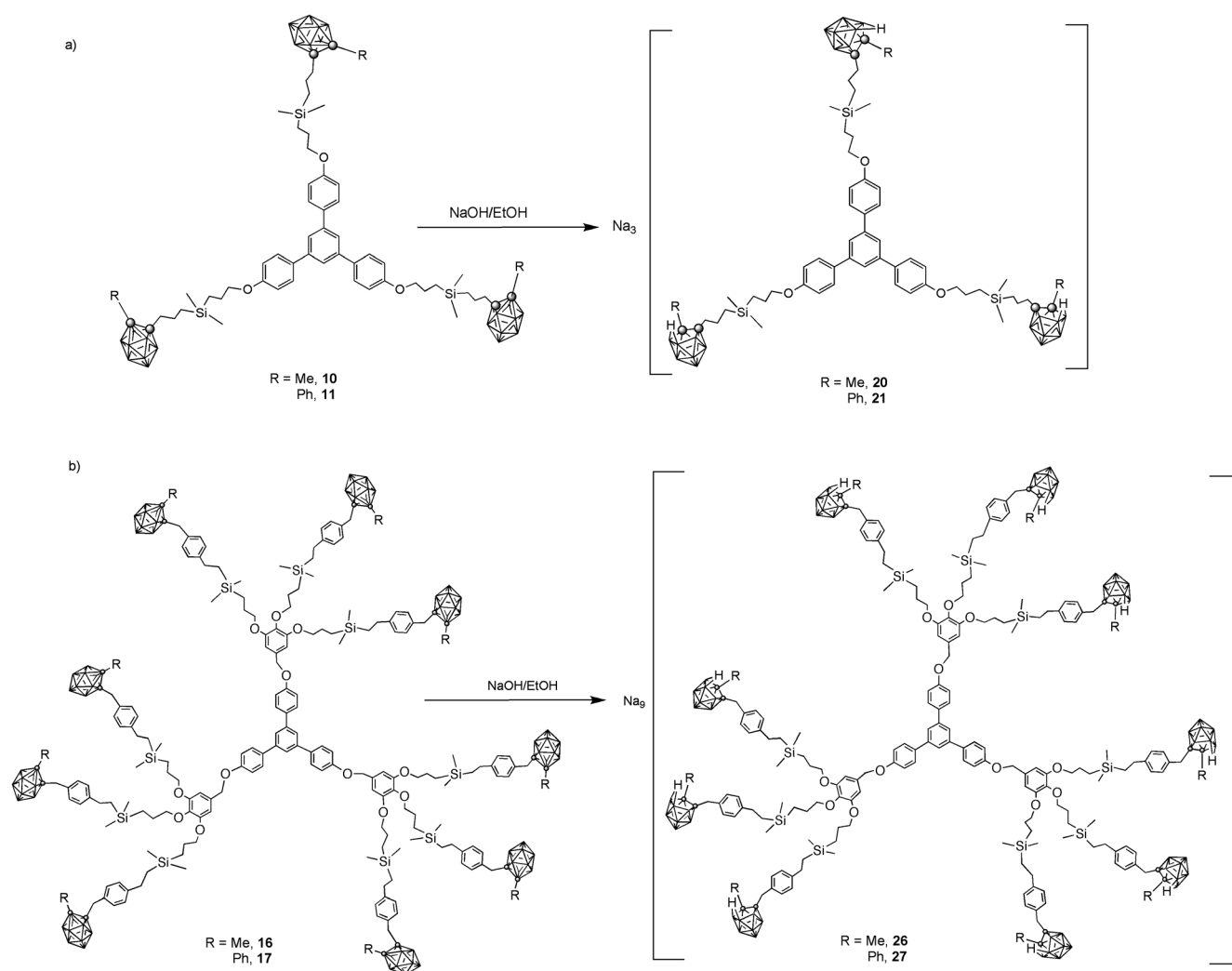
Scheme 4. Synthesis of nine-functionalized compounds **14–17**.

pounds (**10–13** and **14–17**) were obtained with yields in the range 60–85 %.

**Preparation of the water-soluble compounds 18–27:** Anionic carborane clusters have also shown potential for different applications due to their solubility in water depending on the counterion used. Indeed,  $K^+$  and  $Na^+$  have been broadly used as counterions for anionic carborane clusters because of the biocompatibility and solubility of these cluster salts in water. To obtain the corresponding carboranyl-containing dendrimers, the well-known partial degradation method for *closo*-carboranes through nucleophilic attack was performed, by using an excess of NaOH in deoxygenated EtOH. The corresponding polyanionic macromolecules functionalized with *nido*-carboranes **18–27** were isolated as  $Na^+$  salts after the work-up. Polyanionic den-

drimers **18–27** are water-soluble compounds and are therefore good candidates to explore their application as boron-delivery platforms (Scheme 5 and the Supporting Information).

**Characterization of compounds 1–27:** The structures of all the compounds were established by IR,  $^1H$ ,  $^{13}C\{^1H\}$ ,  $^{11}B$ ,  $^{11}B\{^1H\}$ ,  $^{29}Si\{^1H\}$  NMR spectroscopies, elemental analysis, ESI-MS, UV/Vis and fluorescence spectroscopy (and for **4** confirmed by X-ray diffraction analysis). The IR spectra of the *closo*-derivatives, **8–17**, present the typical  $\nu(B-H)$  strong bands for *closo*-clusters between 2554 and 2584  $cm^{-1}$ . For **8** and **9**, a band around 2112  $cm^{-1}$  corresponding to  $\nu(Si-H)$  from the silane function is also observed, which disappeared in compounds **10–17** after the hydrosilylation reaction, indicating total conversion of the alkene. In the



Scheme 5. a) Deboronation reaction for compounds **10** and **11** and b) deboronation reaction for compounds **16** and **17**.

$^1\text{H}$  NMR spectra of **8** and **9**, the resonances due to the vinyl protons have disappeared and new resonances are observed in the aliphatic region that indicate  $\beta$ -addition of the Si–H to the vinyl.<sup>[9a]</sup> In addition, one septuplet at about  $\delta = 3.90$  ppm attributed to the Si–H and a doublet close to  $\delta = 0.0$  ppm from Si–CH<sub>3</sub> confirm the formation of the compounds. The starting compounds **2** and **3** show resonances in the range from  $\delta = 6.20$  to 5.20 ppm attributed to the allyl protons.<sup>[14]</sup> These resonances disappear after the hydrosilylation reaction, indicating the anti-Markovnikov addition of the  $-\mu\text{-SiH}$  function of **6–9** to the double bonds, and subsequently the complete peripheral functionalization. In the latter compounds, the presence of new  $-\text{CH}_2-$  proton resonances corroborates their formation (Figure 3). The  $^1\text{H}$  NMR spectra for dendrimers bearing *closo*-clusters also exhibit resonances at low frequencies, in the  $\delta = -0.11$ –0.08 ppm range for  $\text{C}_c\text{-SiCH}_3$  protons. The  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra show different resonances in the aromatic region, from  $\delta = 160.5$  to 114.0 ppm for all compounds. After functionalization with carboranes, the dendrimers show resonances in the region  $\delta = 84.0$  to 74.6 ppm attributed to the

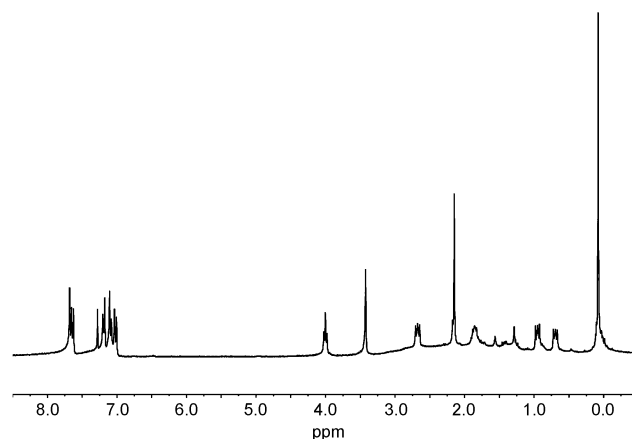


Figure 3.  $^1\text{H}$  NMR spectrum of compound **12**.

$\text{C}_{\text{cluster}}$  The resonances for the Si–CH<sub>3</sub> units bonded to the  $\text{C}_c$  appear around  $\delta = -3.5$  ppm, whereas the  $-\text{CH}_2-$  carbons are displayed in the range  $\delta = 40.0$  to 10.0 ppm.

The  $^{11}\text{B}\{^1\text{H}\}$  NMR resonances for molecules decorated with *closo*-clusters (**4**, **5**, and **10–17**) appear in the region

characteristic for *closo*-compounds, from  $\delta = -3.0$  to  $-11.0$  ppm. In general, all compounds present broad overlapped bands with the patterns 2:8, 1:1:8, or 1:1:4:4. Anionic compounds (**18–27**) that contain *nido*-clusters show broad bands in the region from  $\delta = -7.0$  to  $-37.0$  ppm. All compounds show only one peak in the  $^{29}\text{Si}\{^1\text{H}\}$  NMR spectra, due to the Si nuclei present in the molecules. Compounds **8** and **9** containing a  $-\text{SiH}$  function show a peak at  $\delta = -12.80$  ppm, very similar to that found for **6–7** at  $\delta = -14.10$  ppm.<sup>[9a]</sup> After derivatization, the  $^{29}\text{Si}\{^1\text{H}\}$  resonances appear around  $\delta = +3.0$  ppm. Different mass spectrometry techniques (ESI and MALDI-TOF) have been used for the characterization of compounds. The formula of the smaller dendrimers was well established by using ESI-MS showing the molecular ion peak; nevertheless, for the largest dendrimers neither the ESI nor the MALDI-TOF mass spectra were useful, because an important fragmentation was observed. A similar fragmentation had been previously observed for other boron-containing large molecules.<sup>[10]</sup>

**Crystal structure of 4:** Compound **4** crystallizes with one molecule of hexane. The bonding parameters of **4** do not show any unusual features. The geometry of **4** is shown in Figure 4. The three phenyl groups (C1a-C6a, C1b-C6b and

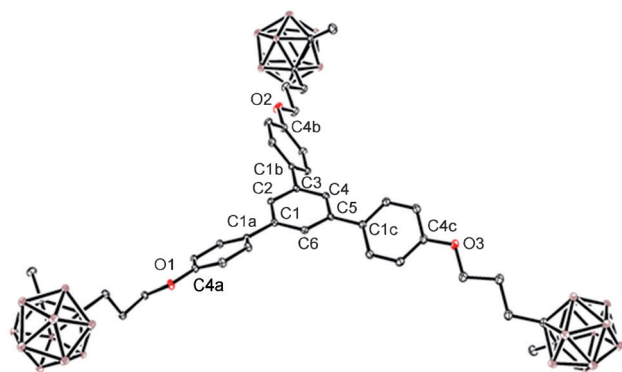


Figure 4. The asymmetric unit of **4**-hexane. The hydrogen atoms and the hexane molecule have been omitted for clarity reasons. Thermal ellipsoids have been presented at the 20% probability level.

C1c-C6c) attached to the central phenyl group (C1-C6) are slightly tilted from the plane of that group (by  $30.5(1)$ ,  $50.6(1)$  and  $34.0(1)^\circ$ ), respectively. The packing of **4** is controlled by weak van der Waals interactions. The packing view, presented in Figure 5, shows a layer-type structure with hexane molecules in the closed holes.

**Thermal properties:** The utilization of carborane clusters for the preparation of thermally stable materials has been explored to improve their final thermal properties. Previously, we had reported an exhaustive study and thermal evolution of carborane-containing sol-gel hybrid materials, showing an enhancement of the thermal stability of xerogels.<sup>[20]</sup> Other silicon-derived polymers, coordination polymers, conducting organic polymers, or high carboranyl-containing

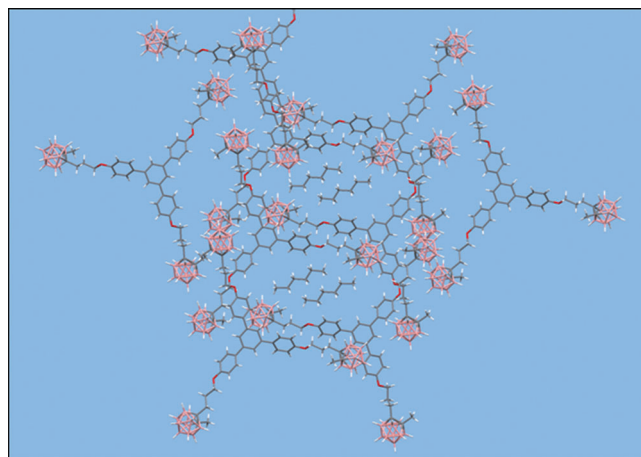


Figure 5. Packing of **4**-hexane showing the location of hexane molecules in the holes.

macromolecules have been used as oxidative protection coatings or ceramic polymeric materials that exhibit outstanding thermal and thermo-oxidative properties.<sup>[3]</sup> To study the thermal stability of the carboranyl-containing macromolecules, different parameters have been considered: the presence of the Si-C bond, the number of clusters, and the percentage boron content (Figure 6). Compounds **4**, **10**, and **12**, which contain three cages, are shown to be thermally stable up to  $350^\circ\text{C}$ , however **14** and **15** with nine clusters start to lose mass at lower temperatures.

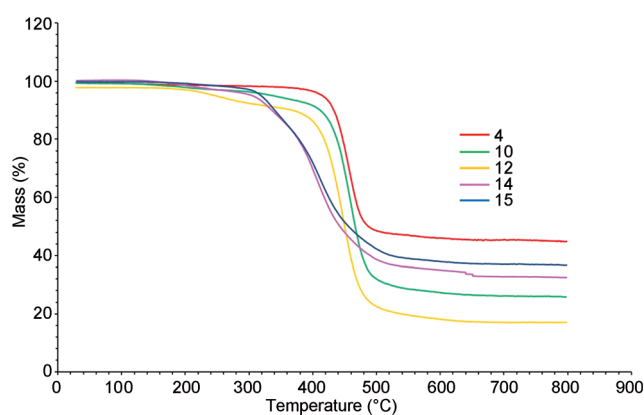


Figure 6. Thermogravimetric analysis (TGA) curves of different dendrimers **4**, **10**, **12**, **14**, and **15** under nitrogen.

By examining the thermogravimetric analysis (TGA) curves of the tri-functionalized **4** and **10** under  $\text{N}_2$ , it can be concluded that the presence of the Si-C bond in **10** does not affect the thermal stability of the dendrimers. Both started to lose weight around the same temperature,  $395$  and  $385^\circ\text{C}$ , respectively. Nevertheless, some differences between **10** and **12** are observed; compound **12** is less stable and its thermal decomposition occurs in two steps: the first one, between  $200$  and  $390^\circ\text{C}$ , results in a mass loss of a 10% that can be due to the decomposition of the peripheral aromatic

ring bonded to the carborane cages; the second step sets up at 390 °C, with a higher decomposition, to give a residue of 17.1%. In addition, for the star-shaped macromolecules with 3 clusters (**4**, **10**, and **12**) the results observed are consistent with their boron content (Table 1). Compound **4**, which is

Table 1. Percentage boron content, mass loss temperatures and final residues [%] from TGA.

Dendrimer	Boron [%]	<i>T</i> [°C]	Residue [%]
<b>4</b>	34.2	395	44.9
<b>10</b>	25.9	385	25.8
<b>12</b>	21.9	365	17.1
<b>14</b>	28.2	300	32.5
<b>15</b>	24.4	300	36.7

the most stable of the three compounds and shows the highest final residual mass, also has the highest percentage of boron content (34.2%), whereas **10** and **12** have 25.9% and 21.9% boron by weight (wt), respectively. When the boron content (wt%) of the macromolecules decreases, the thermal stability decreases as well. Both nine-functionalized dendrimers, compound **14** with nine Me-*o*-carborane and **15** with nine Ph-*o*-carborane, are less thermally stable and the mass loss occurs at about 300 °C with a relative higher final residual mass. For **14**, with 28.2% boron content, the final residual mass is 32.5%, whereas for **15** a 36.7% is recovered at 600 °C. This phenomenon can be attributed to an increase of the organic fragments due to the new –OCH<sub>2</sub>– groups and the number of alkyl chains. The final residual mass of both compounds is in agreement with the wt% boron content, although for **15** a higher residue is obtained. This result indicates that when Ph-*o*-carborane is used other effects may influence the thermal behavior of the dendrimer because even with lower wt% boron the final mass residue is still higher than those with a higher boron content.

Dendrimers **12**, **14**, and **15** start to lose weight earlier than **4** and **10**, this phenomenon is similar to that observed in other macromolecules and branched polymers that contain branching units, apparently decompositions starts in these branches. However, in all our cases an important percentage of the residue is maintained due to the presence of the clusters in the molecule.

**Photophysical properties:** The UV/Vis absorption spectra of compounds **1–5** and **10–17** were performed in acetonitrile and THF, whereas compounds **18–27** were measured in H<sub>2</sub>O. Tables 2 and 3 list the spectroscopic and photophysical data obtained for these compounds. The starting molecules, carboranyl-functionalized star-shaped molecules and dendrimers, **1–5** and **10–27**, display a bathochromic shift and exhibit bands of absorption maxima in the region 266–275 nm, which correspond to the  $\pi$ – $\pi^*$  transitions in the aromatic core, which are 10–20 nm redshifted with respect to the maximum at 254 nm reported for 1,3,5-triphenylsubstituted benzene compounds.<sup>[13d]</sup> In general, neither changes on the substituent at the C<sub>cluster</sub> nor modifications in the electronic

Table 2. Spectroscopic data of star-shaped molecules and neutral dendrimers.

Compound	$\lambda_{\text{max,abs}}$ [nm]	$\lambda_{\text{max,em}}$ [nm]	$\Phi_F$	
			CH <sub>3</sub> CN	THF
<b>1</b>	266 <sup>[a]</sup>	366	0.48	0.48
<b>4</b>	266	366	0.59	0.58
<b>5</b>	266	366	0.21	0.23
<b>2</b>	268	366	0.52	0.45
<b>10</b>	268	366	0.55	0.48
<b>11</b>	268	366	0.26	0.32
<b>12</b>	268	366	0.55	0.49
<b>13</b>	268	366	0.13	0.24
<b>3</b>	269	366	0.57	0.55
<b>14</b>	269	366	0.47	0.54
<b>15</b>	269	366	0.17	0.24
<b>16</b>	269	366	0.49	0.51
<b>17</b>	269	366	n.a. <sup>[b]</sup>	0.11

[a] The  $\lambda_{\text{max}}$  of absorption and emission in both solvents are almost the same. [b] Not available; compound was not soluble in acetonitrile.

properties of the cluster (*closo* and *nido*) cause substantial alterations of the absorption wavelengths. This indicates that the absorption properties are dominated by the core as the chromophore, and the introduction of carborane clusters does not influence them.

Figure 7 shows absorption and emission bands of allyl-terminated **2** and carboranyl functionalized star-shaped molecules **10–13** in acetonitrile, whereas Figure 8 exhibits absorp-

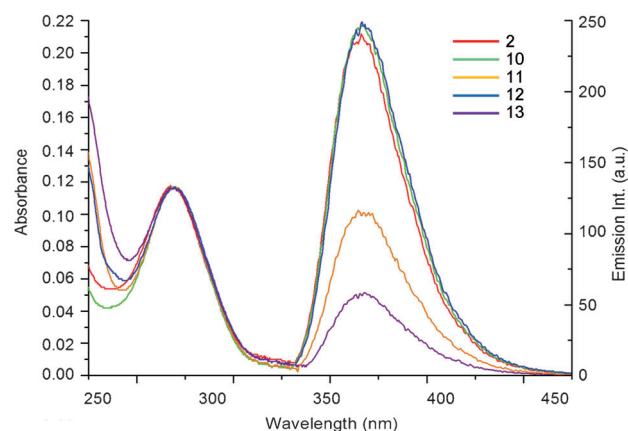


Figure 7. Emission and normalized absorption spectra for the starting compound **2** and the three-functionalized **10–13** in acetonitrile.

tion and emission spectra of dendrimers that contain nine functional groups **14–17** in THF. As is usually the case, the excitation spectra of **1–5** and **10–27** resemble their absorption spectra. All compounds exhibited emission bands in the blue-violet region, with maximum emission intensities ( $\lambda_{\text{em}}$ ) around 366 nm due to the local emission of the chromophore. These maxima  $\lambda_{\text{em}}$  are not influenced by the solvent (Table 2), therefore no solvatochromic effect is observed.

These results are just the opposite to those previously reported by us, in which similar dendrimeric systems were pre-



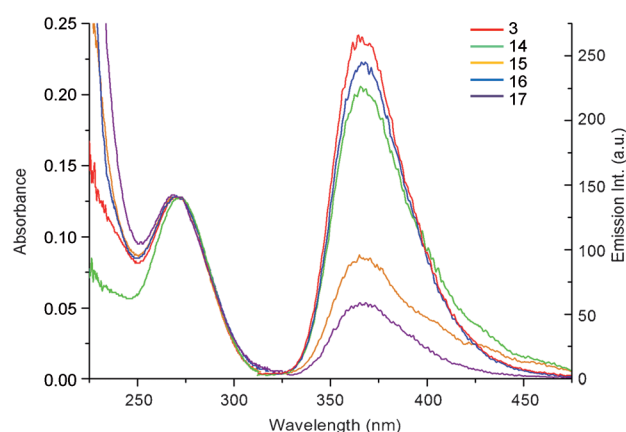


Figure 8. Emission and normalized absorption data for **3** and the nine-functionalized **14–17** in THF.

pared, but in that case the cores were decorated with anionic cobaltabisdicarbollide fragments resulting in the quenching of the fluorescence.<sup>[14]</sup> To measure the fluorescence quantum yields ( $\Phi_F$ ), compounds **1** and **4** and **5** were excited at 266 nm, whereas the rest of the compounds were excited at 269 nm. The  $\Phi_F$  values were calculated by using quinine sulphate in an aqueous solution of  $H_2SO_4$  (0.5 M) as a standard (see Table 2).

To study the influence of the carboranyl fragments on the photoluminescent properties, different compounds have been prepared by changing: 1) the substituent at the  $C_{cluster}$  (Me or Ph); 2) the distance and the type of spacer between the cluster and the chromophore, as well as the generation of the dendrimer; 3) the nature of the cluster, either hydrophobic *closo*-clusters or hydrophilic *nido*-clusters; and 4) the number of carboranyl groups.

**The substituent at the  $C_{cluster}$ :** As a general trend, and independently of the way in which the carboranyl fragment is bonded to the starting molecule, the incorporation of methyl-*o*-carborane produces an enhancement of the emission intensity with respect to the starting compound, with quantum yields ranging from 47 to 59% (Table 2). Conversely, dendrimers bearing phenyl-*o*-carborane clusters exhibited lower fluorescence intensity, with relative quantum yields of 13–26% in acetonitrile, and 11–32% in THF (Table 2). These differences can be clearly observed in Figures 7 and 8, in which the emission spectra of compounds **10–13** and **14–17** are represented. Compounds **10**, **12**, **14**, and **16**, bearing methyl-*o*-carborane, show higher relative quantum yields than compounds **11**, **13**, **15**, and **17**, which contain phenyl-*o*-carborane. These results could be explained by considering our previous work on the photoluminescence properties of carboranyl-containing styrene derivatives, in which it was reported that the introduction of a phenyl group into the electron-withdrawing carboranyl fragment results in an excellent electron-acceptor unit that upon being covalently bonded to an electron-donor produces a quenching of the fluorescence.<sup>[18]</sup> This quenching is the

result of a charge-transfer process from the styrene to the phenyl-carborane unit. In the current compounds, only partial quenching of the fluorescence was observed, however the decrease of the emission intensities for the phenyl-*o*-carborane with respect to the methyl-*o*-carborane derivatives could be due to a process in which the phenyl group would be involved.

**Distance/type of spacer and generation of the dendrimer:** For compounds bearing methyl-*o*-carborane, the fluorescence intensities are very similar and the influence of the distance and type of spacer between the cluster and the chromophore is practically unnoticed in both THF and acetonitrile. Nevertheless, for those molecules containing phenyl-*o*-carborane at the periphery, an important effect of these two factors is observed. If the compounds with 3 clusters are considered (Figure 9), compound **11** is the one with a higher fluores-

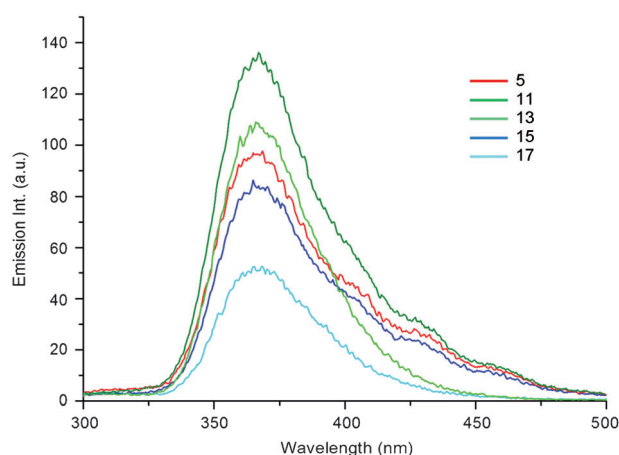


Figure 9. Emission spectra in THF for different compounds bearing phenyl-*o*-carborane clusters.

cence intensity (32% of  $\Phi_F$ ), whereas **5** and **13** show lower relative quantum yields (23 and 24%, respectively). This difference could be due to electron-transfer processes caused by the existence of the phenyl-*o*-carborane, as has been previously discussed,<sup>[18]</sup> which also depends on the type of spacer.<sup>[21]</sup> In the case of compounds with 9 clusters, despite the longer spacer that increases the distance between the cluster and the chromophore, the relative quantum yields of **15** and **17** (24 and 11%) are reduced in relation to their analogues with 3 clusters (Figure 9). This effect could be explained by the fact that after growing the molecule, six additional phenyl rings are introduced to the chromophore, which could facilitate other interactions, such as  $\pi\cdots\pi$  interactions, weakly B–H $\cdots$ H–C<sub>aryl</sub> interactions, among others. This interpretation can be supported by the insolubility of **17** in acetonitrile, this being the reason why this data is not available.

**The nature of the cluster:** Concerning the nature of the cluster, the largest fluorescence quantum yields are always

found for *closo*-compounds, whereas aqueous solutions of *nido*-derivatives **20–26** show comparatively much lower quantum yields, between 9 and 23 % (Table 3). These results are in agreement with previously reported data,<sup>[3,18]</sup> confirming that the presence of the hydrophilic *nido*-carborane clusters produces a decrease of the emission intensities (Figure 10).

Table 3. Spectroscopic data of star-shaped molecules and polyanionic dendrimers.

Compound	$\lambda_{\text{max,abs}}$ [nm]	$\lambda_{\text{max,em}}$ [nm]	$\Phi_{\text{F}}(\text{H}_2\text{O})$
<b>20</b>	275	367	0.09
<b>21</b>	270	367	0.23
<b>22</b>	271	367	0.11
<b>23</b>	275	367	0.11
<b>24</b>	270	366	0.11
<b>25</b>	267	367	0.22
<b>26</b>	267	367	0.13
<b>27</b>	n.a. <sup>[a]</sup>	n.a. <sup>[a]</sup>	n.a. <sup>[a]</sup>

[a] Not available; the compound had low solubility in water.

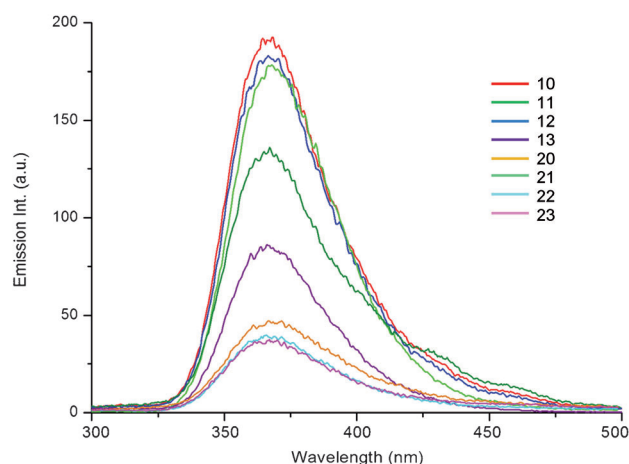


Figure 10. Comparative emission spectra for neutral **10–13** and anionic **20–23** species.

Nevertheless, it is important to notice that the relative quantum yields of **20–26** in water are reasonably good if they are compared with the previously reported star-shaped molecules, which were remarkably lower.<sup>[3a]</sup> We have attributed this difference to a longer distance between the *nido*-carborane clusters and the chromophore, since the increase of the number of charged clusters close to the chromophore diminishes the fluorescence quantum yields.<sup>[3a]</sup>

**The number of carboranyl groups:** The introduction of a larger number of homologous neutral *closo*-carborane clusters into the molecule does not seem to affect the fluorescence behavior of the dendrimers, because the fluorescence quantum yields of **10** and **14**, or **12** and **16** are very similar. The largest difference was found for **17**, with a lower  $\Phi_{\text{F}}$  with respect to its homologous **13**. On the other hand, the

increase in the number of hydrophilic *nido*-carboranes within the molecule provides a better water solubility for the chromophore, but does not affect in general the fluorescence intensity (Table 3). This is a good result because it is known that most water-soluble chromophores show low fluorescence due to the photoinduced electron-transfer in polar solvents.<sup>[22]</sup>

**Electrochemical studies:** Cyclic voltammetry (CV) has been utilized to understand the degree of electronic communication between the triarylbenzene core and the peripheral carboranes separated with 4, 7, or 11 non-conjugated atom spacers. The ratio of carboranes to the triarylbenzene core ranges from 3 in compounds **10–13**, to 9 for compounds **14–17**. The CVs of compounds **1** and **2**, the first terminated with Br and the second with allyl groups, show no redox activity in THF (See the Supporting Information). Conversely, the methyl- and phenyl-*o*-carborane are redox active and have been taken as references. Preliminary CV studies were performed from +3 to –3 V versus SCE. The phenyl-*o*-carborane has displayed a reduction potential around –2.2 V and the methyl near –2.9 V. These values are close to those described in the literature at –1.95 and 2.44 versus SCE from polarographic data;<sup>[23]</sup> probably this corresponds only to 1e<sup>–</sup> reduction of the cage, the difference may result from using THF instead of acetonitrile or DMF. The CVs of the 1,3,5-triarylbenzene dendrimers peripherally decorated with methyl-*o*-carboranes or phenyl-*o*-carboranes are very similar to those obtained for the isolated carboranes in THF. These results indicate that the core does not influence the electroactivity of the peripheral carboranes, so that the 1,3,5-triarylbenzene core and the carboranes are not electronically communicated. This implies that their individual entities in the dendrimers or star-shaped molecules are largely preserved. Therefore, these results corroborate that the absorption and emission data grossly remain unaltered.

## Conclusion

A new family of star-shaped molecules and dendrimers that have the 1,3,5-triphenylbenzene unit as fluorescent core, and three- or nine terminal carboranyl fragments, have been prepared by using various approaches. The methodology used is highly versatile and allows one to introduce different spacers between the nuclei and the boron clusters. It also facilitates to further increase the number of carborane clusters, as well as to modify their nature either neutral or anionic. Thermal stability studies of the compounds indicate that star-shaped molecules with three cages are more stable than dendrimers containing nine terminal clusters. A high percentage of residue is obtained after thermal experiments due to the presence of the carboranes. This quantity of residue fits well with the wt % of boron in the molecules. All compounds exhibit photoluminescence at room temperature in the blue-violet region and relative high quantum yields, even for the anionic species; these depend on the nature of the cluster

and the second substituent on the  $C_{cluster}$ . None of the compounds reported here show total quenching of the fluorescence; these results conflict with other earlier reports for analogue dendrimers functionalized with metallacarboranes. In agreement with the photoluminescent results, the cyclic voltammetry studies have shown that the two electroactive centers, the 1,3,5-triarylbenzene and the carborane, are not electronically communicated; this corroborates that the absorption and emission wavelengths are practically unaffected.

## Experimental Section

**Synthesis of 1,3,5-tris(4-(3-bromopropoxy)phenyl)benzene (1):** 4-(3-bromopropoxy)acetophenone (1.00 g, 3.68 mmol) and tetrachlorosilane (5.64 g, 33.19 mmol) were mixed in absolute ethanol at room temperature for 48 h. The solid obtained was filtered and washed with methanol to give **1** as a white powder. Yield: 0.74 g, 80.0%. M.p. 115–117°C;  $^1H$  NMR ( $CDCl_3$ ):  $\delta$  = 7.65 (s, 3H; C- $H_{aryl}$ ), 7.62 (d,  $^3J(H,H)$  = 8.7 Hz, 6H; C- $H_{aryl}$ ), 7.03 (d,  $^3J(H,H)$  = 8.7 Hz, 6H; C- $H_{aryl}$ ), 4.16 (t,  $^3J(H,H)$  = 6.0 Hz, 6H; O- $CH_2$ ), 3.64 (t,  $^3J(H,H)$  = 6.0 Hz, 6H;  $CH_2$ -Br), 2.37 ppm (quint,  $^3J(H,H)$  = 6.0 Hz, 6H;  $CH_2CH_2CH_2$ );  $^{13}C$  NMR ( $CDCl_3$ ):  $\delta$  = 158.5–114.9 ( $C_{aryl}$ ), 65.4 ( $OCH_2$ ), 32.4 ( $CH_2CH_2CH_2$ ), 30.1 ppm ( $CH_2Br$ ); IR (KBr):  $\tilde{\nu}$  = 3034 (C- $H_{aryl}$  stretching (st)), 2930 (C- $H_{alkyl}$  st), 1509 (C=C st), 1236 (s, C-O-C st), 827  $cm^{-1}$ ; MS (ESI):  $m/z$  calcd for  $C_{33}H_{33}Br_3O_3$ : 715.0 [ $M+H$ ] $^+$ ; found: 715.0057.

**Synthesis of 4:** To a solution of 1- $CH_3$ - $C_{2}B_{10}H_{11}$  (0.15 g, 0.95 mmol) in of dry THF (5 mL) at 0°C, was added dropwise a solution of  $n$ -BuLi (1.6 M) in hexane (0.62 mL, 0.99 mmol). The mixture was stirred for 1 h at room temperature, cooled down at 0°C, and a solution of **1** (0.21 g, 0.31 mmol) in THF was added. The resulting mixture was heated at reflux overnight. The residue was extracted with  $Et_2O$  (10 mL) and washed with  $H_2O$  (3  $\times$  10 mL). The organic layer was dried with  $MgSO_4$ . Evaporation of the volatiles at reduced pressure gave a crude product, which was redissolved with ethyl acetate, and **4** was precipitated with hexane as a white solid. Yield: 0.1 g, 34%.  $^1H$  NMR ( $CDCl_3$ ):  $\delta$  = 7.66 (s, 3H; C- $H_{aryl}$ ), 7.63 (d,  $^3J(H,H)$  = 9.0, 6H; C- $H_{aryl}$ ), 6.98 (d,  $^3J(H,H)$  = 9.0, 6H; C- $H_{aryl}$ ), 4.05 (t,  $^3J(H,H)$  = 6.0; 6H; O- $CH_2$ ), 2.46 (m, 6H;  $CH_2CH_2CH_2$ ), 2.16–1.99 (m, 15H; Cc- $CH_2$ , Cc- $CH_3$ );  $^1H$  NMR ( $CDCl_3$ ):  $\delta$  = 7.66 (s, 3H; C- $H_{aryl}$ ), 7.63 (d,  $^3J(H,H)$  = 9.0, 6H; C- $H_{aryl}$ ), 6.98 (d,  $^3J(H,H)$  = 9.0, 6H; C- $H_{aryl}$ ), 4.05 (t,  $^3J(H,H)$  = 6.0; 6H; O- $CH_2$ ), 2.46 (m, 6H;  $CH_2CH_2CH_2$ ), 2.29 (br s, B-H), 2.22 (br s, B-H), 2.13 (br s, B-H), 2.16–1.99 ppm (m, 15H; Cc- $CH_2$ , Cc- $CH_3$ );  $^{11}B$  NMR ( $CDCl_3$ ):  $\delta$  = -6.0 (d,  $^1J(B,H)$  = 147, 6B), -10.9 (d,  $^1J(B,H)$  = 140, 24B);  $^{13}C$  NMR ( $CDCl_3$ ):  $\delta$  = 158.3–114.8 ( $C_{aryl}$ ), 74.8 (Cc), 66.6 ( $OCH_2$ ), 32.2 ( $CH_2CH_2CH_2$ ), 29.4 (Cc- $CH_2$ ), 23.1 ppm (Cc- $CH_3$ ); IR (KBr):  $\tilde{\nu}$  = 2930 (m, C- $H_{alkyl}$  st), 2588 (s, B-H st), 1236  $cm^{-1}$  (s, C-O-C st); MS (ESI):  $m/z$  calcd for  $C_{42}H_{72}B_{30}O_3$ : 949.3; found: 972.1 [ $M+Na$ ] $^+$ , 982.7; elemental analysis calcd for  $C_{42}H_{72}B_{30}O_3$ : C 53.14, H 7.64; found: C 52.93, H 7.60.

**Synthesis of 5:** The procedure and workup were the same as for **4**, using 1- $C_6H_5$ - $C_{2}B_{10}H_{11}$  (0.38 g, 1.72 mmol) in dry THF (10 mL),  $n$ -BuLi (1.6 M, 1.22 mL, 1.95 mmol) and **1** (0.397 g, 0.56 mmol). The volatiles were removed at reduced pressure to obtain a crude product, which was redissolved with ethyl acetate and **5** was precipitated with hexane as a white solid. Yield: 0.63 g, 41.7%.  $^1H$  NMR ( $CDCl_3$ ):  $\delta$  = 7.67–7.40 (m, 24H; C- $H_{aryl}$ ), 6.78 (d,  $^3J(H,H)$  = 8.4, 6H; C- $H_{aryl}$ ), 3.81 (t,  $^3J(H,H)$  = 6.0, 6H; O- $CH_2$ ), 2.05 ppm (m, 6H;  $CH_2CH_2CH_2$ ), 1.91 (m, 6H;  $CH_2CH_2CH_2$ );  $^1H$  NMR ( $CDCl_3$ ):  $\delta$  = 7.67–7.40 (m, 24H; C- $H_{aryl}$ ), 6.78 (d,  $^3J(H,H)$  = 8.4, 6H; C- $H_{aryl}$ ), 3.81 (t,  $^3J(H,H)$  = 6.0, 6H; O- $CH_2$ ), 2.76 (br, B-H), 2.40 (br, B-H), 2.28 (br, B-H), 2.05 (m, 6H;  $CH_2CH_2CH_2$ ), 1.91 (m, 6H; Cc- $CH_2$ );  $^{11}B$  NMR ( $CDCl_3$ ):  $\delta$  = -3.80 (d,  $^1J(B,H)$  = 140, 6B), -10.47 (d,  $^1J(B,H)$  = 130, 24B);  $^{13}C$  NMR ( $CDCl_3$ ):  $\delta$  = 158.1–114.7 ( $C_{aryl}$ ), 83.9 ( $C_c$ ), 81.8 ( $C_c$ ), 66.3 ( $OCH_2$ ), 31.7 ( $CH_2CH_2CH_2$ ), 29.2 ppm (Cc- $CH_2$ ); IR (KBr):  $\tilde{\nu}$  = 3063 (m, C- $H_{aryl}$  st), 2929 (m, C- $H_{alkyl}$  st), 2585 (s, B-H st), 1236  $cm^{-1}$  (C-O-C st); MS (ESI):  $m/z$  calcd for  $C_{57}H_{78}B_{30}O_3$ : 1135.6 [ $M$ ];

found: 1135.7; elemental analysis calcd for  $C_{57}H_{78}B_{30}O_3$ : C 60.29, H 6.92; found: C 60.25, H 6.86.

**Synthesis of 8:** In a Schlenk flask, 1-( $CH_2C_6H_4$ -4'-( $CH_2=CH_2$ ))-2- $CH_3$ -1,2-*closo*- $C_{2}B_{10}H_{10}$  (200 mg, 0.70 mmol),  $HSiMe_2Cl$  (1 mL, 9 mmol) and [Pt(dvds)]/P( $t$ Bu) $_3$  catalyst system (10  $\mu$ L, 0.02 mmol) were mixed and stirred for 6 h at room temperature. Volatiles and the excess of ( $CH_3$ ) $_2$ HSiCl were evaporated in the vacuum lines to obtain a yellowish oil that was dissolved in diethyl ether (10 mL) and  $LiAlH_4$  (27 mg, 0.70 mmol) were added. The mixture was stirred overnight at room temperature and filtered off through Celite twice. The solvent was removed in vacuo to give **8** as transparent oil. Yield: 218 mg, 89%.  $^1H$  NMR ( $CDCl_3$ ):  $\delta$  = 7.21 (d,  $^3J(H,H)$  = 9 Hz, 2H; C- $H_{aryl}$ ), 7.12 (d,  $^3J(H,H)$  = 9 Hz, 2H; C- $H_{aryl}$ ), 3.95 (sept,  $^3J(H,H)$  = 4.2 Hz, 1H; Si-H), 3.46 (s, 2H; Cc- $CH_2$ ), 2.72 (m, 2H;  $CH_2CH_2Si$ ), 2.18 (s, 3H; Cc- $CH_3$ ), 1.00 (td,  $^3J(H,H)$  = 10.2 Hz,  $^3J(H,H)$  = 3 Hz, 2H;  $CH_2CH_2Si$ ), 0.12 ppm (d,  $^3J(H,H)$  = 3 Hz, 6H; ( $CH_3$ ) $_2$ ).  $^1H$  NMR ( $CDCl_3$ ):  $\delta$  = 7.21 (d,  $^3J(H,H)$  = 9 Hz, 2H; C- $H_{aryl}$ ), 7.12 (d,  $^3J(H,H)$  = 9 Hz, 2H; C- $H_{aryl}$ ), 3.95 (sept,  $^3J(H,H)$  = 4.2 Hz, 1H; Si-H), 3.46 (s, 2H; Cc- $CH_2$ ), 2.72 (m, 2H;  $CH_2CH_2Si$ ), 2.30 (br s, 1H, B-H), 2.22 (br s, 1H, B-H), 2.18 (s, 3H; Cc- $CH_3$ ), 1.00 (td,  $^3J(H,H)$  = 10.2 Hz,  $^3J(H,H)$  = 3 Hz, 2H;  $CH_2CH_2Si$ ), 0.12 (d,  $^3J(H,H)$  = 3 Hz, 6H; ( $CH_3$ ) $_2$ );  $^{11}B$  NMR ( $CDCl_3$ ):  $\delta$  = -4.36 (d,  $^1J(B,H)$  = 148 Hz, 1B), -5.84 (d,  $^1J(B,H)$  = 148 Hz, 1B), -9.80 (d, 4B), -10.62 ppm (d,  $^1J(B,H)$  = 134 Hz, 4B);  $^{13}C$  NMR ( $CDCl_3$ ):  $\delta$  = 144.7 ( $C_{aryl}$ ), 132.2 ( $C_{aryl}$ ), 130.2 ( $C_{aryl}$ ), 128.0 ( $C_{aryl}$ ), 77.9 (Cc- $CH_2$ ), 74.8 (Cc- $CH_3$ ), 40.9 (- $CH_2$ -), 30.2 ( $CH_2CH_2Si$ ), 23.6 (- $CH_3$ ), 16.0 ( $CH_2CH_2Si$ ), -4.4 (Si-( $CH_3$ ) $_2$ );  $^{29}Si$  NMR ( $CDCl_3$ ):  $\delta$  = -12.80. IR (NaCl):  $\tilde{\nu}$  = 3026 (m, C- $H_{aryl}$  st), 2957–2929 (m, C- $H_{alkyl}$  st), 2584 (s, B-H st), 2112  $cm^{-1}$  (s, Si-H st); MS (MALDI-TOF):  $m/z$  calcd for  $C_{14}H_{30}B_{10}Si$ : 334.32 [ $M$ ]; found: 334.70; elemental analysis calcd for  $C_{14}H_{30}B_{10}Si$ : C 50.30, H 9.00; found: C 50.70, H 9.26.

**Synthesis of 9:** The procedure was the same as for **8**, using 1-( $CH_2C_6H_4$ -4'-( $CH_2=CH_2$ ))-2- $C_6H_4$ -1,2-*closo*- $C_{2}B_{10}H_{10}$  (200 mg, 0.6 mmol),  $HSiMe_2Cl$  (1 mL, 9 mmol) and [Pt(dvds)]/P( $t$ Bu) $_3$  catalyst system (10  $\mu$ L, 0.02 mmol) and 23 mg (0.6 mmol) of  $LiAlH_4$ . After work up, compound **9** was obtained as transparent oil. Yield: 207 mg, 88%.  $^1H$  NMR ( $CDCl_3$ ):  $\delta$  = 7.76 (d,  $^3J(H,H)$  = 9 Hz, 2H;  $C_{aryl}$ ), 7.47–7.60 (m, 3H;  $C_{aryl}$ ), 7.10 (d,  $^3J(H,H)$  = 9 Hz, 2H;  $C_{aryl}$ ), 6.76 (d,  $^3J(H,H)$  = 9 Hz, 2H;  $C_{aryl}$ ), 3.92 (sept,  $^3J(H,H)$  = 4.2 Hz, 1H; Si-H), 3.07 (s, 2H; Cc- $CH_2$ ), 2.67 (m, 2H;  $CH_2CH_2Si$ ), 0.96 (td,  $^3J(H,H)$  = 10.2 Hz,  $^3J(H,H)$  = 3 Hz 2H;  $CH_2CH_2Si$ ), 0.11 ppm (d,  $^3J(H,H)$  = 3 Hz, 6H; ( $CH_3$ ) $_2$ );  $^1H$  NMR ( $CDCl_3$ ):  $\delta$  = 7.76 (d,  $^3J(H,H)$  = 9 Hz, 2H;  $C_{aryl}$ ), 7.47–7.60 (m, 3H;  $C_{aryl}$ ), 7.10 (d,  $^3J(H,H)$  = 9 Hz, 2H;  $C_{aryl}$ ), 6.76 (d,  $^3J(H,H)$  = 9 Hz, 2H;  $C_{aryl}$ ), 3.92 (sept,  $^3J(H,H)$  = 4.2 Hz, 1H; Si-H), 3.07 (s, 2H; Cc- $CH_2$ ), 2.75 (br s, 1H; B-H), 2.67 (m, 2H;  $CH_2CH_2Si$ ), 2.24 (br s, 1H; B-H), 2.33 (br s, 1H; B-H), 2.42 (br s, 1H; B-H), 0.96 (td,  $^3J(H,H)$  = 10.2 Hz,  $^3J(H,H)$  = 3 Hz 2H;  $CH_2CH_2Si$ ), 0.11 (d,  $^3J(H,H)$  = 3 Hz, 6H; ( $CH_3$ ) $_2$ );  $^{11}B$  NMR ( $CDCl_3$ ):  $\delta$  = -2.58 (d,  $^1J(B,H)$  = 145 Hz, 2B), -9.14 ppm (d,  $^1J(B,H)$  = 121 Hz, 8B);  $^{13}C$  NMR ( $CDCl_3$ ):  $\delta$  = 144.3 ( $C_{aryl}$ ), 132.4 ( $C_{aryl}$ ), 131.5 ( $C_{aryl}$ ), 130.9 ( $C_{aryl}$ ), 130.7 ( $C_{aryl}$ ), 129.9 ( $C_{aryl}$ ), 129.0 ( $C_{aryl}$ ), 127.8 ( $C_{aryl}$ ), 126.7 ( $C_{aryl}$ ), 83.7 (Cc- $CH_2$ ), 82.4 (Cc- $C_6H_5$ ), 40.6 (- $CH_2$ -), 30.1 ( $CH_2CH_2Si$ ), 15.9 ( $CH_2CH_2Si$ ), -4.4 ppm (Si-( $CH_3$ ) $_2$ );  $^{29}Si$  NMR ( $CDCl_3$ ):  $\delta$  = -12.80 ppm; IR (NaCl):  $\tilde{\nu}$  = 3025 (w, C- $H_{aryl}$  st), 2957–2927 (m, C- $H_{alkyl}$  st), 2582 (s, B-H st), 2112  $cm^{-1}$  (s, Si-H st); MS (MALDI-TOF):  $m/z$  calcd for  $C_{19}H_{32}B_{10}Si$ : 396.40; found: 397.45 [ $M+H$ ] $^+$ ; elemental analysis calcd for  $C_{19}H_{32}B_{10}Si$ : C 57.60, H 8.10; found: C 56.94, H 7.94.

**Synthesis of 10:** In a Schlenk flask, 1- $CH_3$ -2-[ $CH_2CH_2CH_2(CH_3)_2SiH$ ]-1,2- $C_{2}B_{10}H_{10}$  (**6**) (0.37 g, 1.43 mmol), 1,3,5-tris(4-allyloxyphenyl)benzene (**2**) (0.23, 0.48 mmol), Karstedt catalyst (10  $\mu$ L) and dry THF (1 mL) were mixed and stirred at room temperature for 60 h. The volatiles were removed under pressure to obtain a brown oil, which was purified by preparative TLC (ethyl acetate/hexane 1:2) and washed with hexane to obtain compound **10** as a white solid. Yield: 0.52 g, 60.6%.  $^1H$  NMR ( $CDCl_3$ ):  $\delta$  = 7.62 (m, 9H; C- $H_{aryl}$ ), 7.01 (d,  $^3J(H,H)$  = 9.0 Hz, 6H; C- $H_{aryl}$ ), 4.01 (t,  $^3J(H,H)$  = 6.0 Hz, 6H; O- $CH_2$ ), 2.19 (t,  $^3J(H,H)$  = 9.0 Hz, 6H; Cc- $CH_2$ ), 2.01 (s, 9H; Cc- $CH_3$ ), 1.83 (m, 6H;  $CH_2CH_2CH_2$ ), 1.57 (m, 6H;  $CH_2CH_2CH_2$ ), 0.69 (t,  $^3J(H,H)$  = 9.0 Hz, 6H; Si- $CH_2$ ), 0.58 (t,  $^3J(H,H)$  = 9.0 Hz, 6H;  $CH_2$ -Si), 0.07 ppm (s, 18H; Si- $CH_3$ );  $^1H$  NMR ( $CDCl_3$ ):  $\delta$  = 7.62 (m, 9H; C- $H_{aryl}$ ), 7.01 (d,  $^3J(H,H)$  = 9.0 Hz, 6H; C- $H_{aryl}$ ), 4.01 (t,

$^3J(\text{H,H})=6.0$  Hz, 6H; O-CH<sub>2</sub>-), 2.27 (br s, B-H), 2.18 (br s, B-H), 2.19 (t,  $^3J(\text{H,H})=9.0$  Hz, 6H; Cc-CH<sub>2</sub>-), 2.01 (s, 9H; Cc-CH<sub>3</sub>), 1.83 (m, 6H; CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>), 1.57 (m, 6H; CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>), 0.69 (t,  $^3J(\text{H,H})=9.0$  Hz, 6H; Si-CH<sub>2</sub>), 0.58 (t,  $^3J(\text{H,H})=9.0$  Hz, 6H; CH<sub>2</sub>-Si), 0.07 ppm (s, 18H; Si-CH<sub>3</sub>);  $^{11}\text{B}$  NMR (CDCl<sub>3</sub>):  $\delta=-4.7$  (d,  $^1J(\text{B,H})=136$  Hz, 3B),  $-6.6$  (d,  $^1J(\text{B,H})=146$  Hz, 3B),  $-10.7$  ppm (d,  $^1J(\text{B,H})=137$  Hz, 24B);  $^{13}\text{C}\{^1\text{H}\}$  NMR (CDCl<sub>3</sub>):  $\delta=158.8\text{--}114.9$  (C<sub>aryl</sub>), 74.6 (Cc), 70.3 (O-CH<sub>2</sub>), 39.0 (Cc-CH<sub>2</sub>), 24.3 (CH<sub>2</sub>), 23.8 (CH<sub>2</sub>), 23.1 (Cc-CH<sub>3</sub>), 15.3 (Si-CH<sub>2</sub>), 11.2 (Si-CH<sub>2</sub>),  $-3.5$  ppm (Si-CH<sub>3</sub>);  $^{29}\text{Si}\{^1\text{H}\}$  NMR (CDCl<sub>3</sub>):  $\delta=3.57$  ppm; IR (KBr):  $\tilde{\nu}=2930$  (m, C-H<sub>alkyl</sub> st), 2588 (s, B-H st), 1250 (Si-CH<sub>alkyl</sub>), 1236 cm<sup>-1</sup> (s, C-O-C st); MS (ESI):  $m/z$  calcd for C<sub>57</sub>H<sub>108</sub>B<sub>30</sub>O<sub>3</sub>Si<sub>3</sub>: 1250; found: 1273 [M+Na]<sup>+</sup>, 1289 [M+K]<sup>+</sup>; elemental analysis calcd for C<sub>57</sub>H<sub>108</sub>B<sub>30</sub>O<sub>3</sub>Si<sub>3</sub>: C 54.77, H 8.71; found: C 55.64, H 8.60.

**Synthesis of 11:** The procedure was the same as for **10**, using 1-C<sub>6</sub>H<sub>5</sub>-2-[CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>(CH<sub>3</sub>)<sub>2</sub>SiH]-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub> (**7**) (0.12 g, 0.39 mmol), 1,3,5-tris(4-allyloxyphenyl)benzene (**2**) (0.06 g, 0.13 mmol), Karstedt catalyst (10  $\mu\text{L}$ ) and dry THF (1 mL). After work up, compound **11** was obtained as a white solid. Yield: 0.11 g, 62.1%;  $^1\text{H}$  NMR (CDCl<sub>3</sub>):  $\delta=7.65\text{--}7.40$  (m, 24H; C-H<sub>aryl</sub>), 7.01 (d,  $^3J(\text{H,H})=9.0$  Hz, 6H; C-H<sub>aryl</sub>), 3.95 (t,  $^3J(\text{H,H})=6.0$  Hz, 6H; O-CH<sub>2</sub>), 1.77 (m, 12H; CH<sub>2</sub>), 1.41 (m, 6H; CH<sub>2</sub>), 0.54 (t,  $^3J(\text{H,H})=9.0$  Hz, 6H; CH<sub>2</sub>-Si), 0.32 (t,  $^3J(\text{H,H})=9.0$  Hz, 6H; CH<sub>2</sub>-Si),  $-0.07$  ppm (s, 18H; Si-CH<sub>3</sub>);  $^1\text{H}\{^{11}\text{B}\}$  NMR (CDCl<sub>3</sub>):  $\delta=7.65\text{--}7.40$  (m, 42H; C-H<sub>aryl</sub>), 7.01 (d,  $^3J(\text{H,H})=9.0$  Hz, 6H; C-H<sub>aryl</sub>), 3.95 (t,  $^3J(\text{H,H})=6.0$  Hz, 6H; O-CH<sub>2</sub>), 2.75 (br s, B-H), 2.38 (br s, B-H), 1.77 (m, 12H; CH<sub>2</sub>), 1.41 (m, 6H; CH<sub>2</sub>), 0.54 (t,  $^3J(\text{H,H})=9.0$  Hz, 6H; CH<sub>2</sub>-Si), 0.32 (t,  $^3J(\text{H,H})=9.0$  Hz, 6H; CH<sub>2</sub>-Si),  $-0.07$  ppm (s, 18H; Si-CH<sub>3</sub>);  $^{11}\text{B}$  NMR (CDCl<sub>3</sub>):  $\delta=-3.9$  (d,  $^1J(\text{B,H})=133$ , 6B),  $-10.7$  ppm (d,  $^1J(\text{B,H})=130$ , 24B);  $^{13}\text{C}\{^1\text{H}\}$  NMR (CDCl<sub>3</sub>):  $\delta=158.6\text{--}114.9$  (C<sub>aryl</sub>), 83.4 (Cc), 82.4 (Cc), 70.6 (O-CH<sub>2</sub>), 38.6 (Cc-CH<sub>2</sub>), 23.7 (CH<sub>2</sub>), 22.7 (CH<sub>2</sub>), 14.5 (Si-CH<sub>2</sub>), 10.8 (Si-CH<sub>2</sub>),  $-3.6$  ppm (Si-CH<sub>3</sub>);  $^{29}\text{Si}\{^1\text{H}\}$  NMR (CDCl<sub>3</sub>):  $\delta=3.31$  ppm; IR (KBr):  $\tilde{\nu}=3063$  (m, C-H<sub>aryl</sub> st), 2929 (m, C-H<sub>alkyl</sub> st), 2585 (s, B-H st), 1252 (Si-CH<sub>alkyl</sub>), 1236 ppm (s, C-O-C st); MS (ESI):  $m/z$  calcd for C<sub>72</sub>H<sub>114</sub>B<sub>30</sub>O<sub>3</sub>Si<sub>3</sub>: 1435.7; found: 1459 [M+Na]<sup>+</sup>, 1475 [M+K]<sup>+</sup>; elemental analysis calcd for C<sub>72</sub>H<sub>114</sub>B<sub>30</sub>O<sub>3</sub>Si<sub>3</sub>: C 60.21, H 8.00; found: C 60.27, H 7.91.

**Synthesis of 12:** In a Schlenk flask, compound **8** (0.1 g, 0.30 mmol), 1,3,5-tris(4-allyloxyphenyl)benzene (**2**) (0.04 g, 0.09 mmol) and Karstedt catalyst system (10  $\mu\text{L}$ , 0.02 mmol), were dissolved in diethyl ether (1 mL). The mixture was stirred overnight at room temperature. Evaporation of the volatiles gave a brownish residue, which was purified by preparative TLC (hexane/ethyl acetate, 2:1) to obtain compound **12** as a white solid. Yield: 114 mg, 85%.  $^1\text{H}$  NMR (CDCl<sub>3</sub>):  $\delta=7.68$  (s, 3H; C-H<sub>aryl</sub>), 7.64 (d,  $^3J(\text{H,H})=6$  Hz, 6H; C-H<sub>aryl</sub>), 7.19 (d,  $^3J(\text{H,H})=6$  Hz, 6H; C-H<sub>aryl</sub>), 7.09 (d,  $^3J(\text{H,H})=6$  Hz, 6H; C-H<sub>aryl</sub>), 7.02 (d,  $^3J(\text{H,H})=6$  Hz, 6H; C<sub>6</sub>H<sub>4</sub>-O), 4.00 (t,  $^3J(\text{H,H})=9$  Hz, 6H; O-CH<sub>2</sub>), 3.43 (s, 6H; Cc-CH<sub>2</sub>), 2.68 (t,  $^3J(\text{H,H})=9$  Hz, 6H; SiCH<sub>2</sub>CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>), 2.17 (s, 9H; Cc-CH<sub>3</sub>), 1.85 (m, 6H; CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si), 0.95 (t,  $^3J(\text{H,H})=9$  Hz, 6H; SiCH<sub>2</sub>CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>), 0.70 (t,  $^3J(\text{H,H})=9$  Hz, 6H; CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si), 0.08 ppm (s, 18H; Si(CH<sub>3</sub>)<sub>2</sub>);  $^1\text{H}\{^{11}\text{B}\}$  NMR (CDCl<sub>3</sub>):  $\delta=7.68$  (s, 3H; C-H<sub>aryl</sub>), 7.64 (d,  $^3J(\text{H,H})=6$  Hz, 6H; C-H<sub>aryl</sub>), 7.19 (d,  $^3J(\text{H,H})=6$  Hz, 6H; C-H<sub>aryl</sub>), 7.09 (d,  $^3J(\text{H,H})=6$  Hz, 6H; C-H<sub>aryl</sub>), 7.02 (d,  $^3J(\text{H,H})=6$  Hz, 6H; C<sub>6</sub>H<sub>4</sub>-O), 4.00 (t,  $^3J(\text{H,H})=9$  Hz, 6H; O-CH<sub>2</sub>), 3.43 (s, 6H; Cc-CH<sub>2</sub>), 2.68 (t,  $^3J(\text{H,H})=9$  Hz, 6H; SiCH<sub>2</sub>CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>), 2.20 (s, 1H; B-H), 2.28 (s, 1H; B-H), 2.17 (s, 9H; Cc-CH<sub>3</sub>), 2.09 (s, 1H; B-H), 1.85 (m, 6H; CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si), 0.95 (t,  $^3J(\text{H,H})=9$  Hz, 6H; SiCH<sub>2</sub>CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>), 0.70 (t,  $^3J(\text{H,H})=9$  Hz, 6H; CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si), 0.08 ppm (s, 18H; Si(CH<sub>3</sub>)<sub>2</sub>);  $^{11}\text{B}$  NMR (CDCl<sub>3</sub>):  $\delta=-4.4$  (d,  $^1J(\text{B,H})=136$  Hz, 3B),  $-5.9$  (d,  $^1J(\text{B,H})=148$  Hz, 3B),  $-10.6$  ppm (d,  $^1J(\text{B,H})=130$  Hz, 24B);  $^{13}\text{C}\{^1\text{H}\}$  NMR (CDCl<sub>3</sub>):  $\delta=158.8\text{--}114.9$  (C<sub>aryl</sub>), 78.0 (Cc-CH<sub>2</sub>), 74.9 (Cc-CH<sub>3</sub>), 70.7 (O-CH<sub>2</sub>), 40.3 (-CH<sub>2</sub>-), 29.7 (CH<sub>2</sub>CH<sub>2</sub>Si), 23.8 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 23.6 (Cc-CH<sub>3</sub>), 16.8 (SiCH<sub>2</sub>), 10.8 (SiCH<sub>2</sub>)  $-3.3$  ppm (Si-CH<sub>3</sub>);  $^{29}\text{Si}\{^1\text{H}\}$  NMR (CDCl<sub>3</sub>):  $\delta=2.94$  ppm; IR (KBr):  $\tilde{\nu}=2931$  (m, C-H st), 2574 (s, B-H st), 1608 (m, arC-C st), 1510 (s, arC-C st), 1248 cm<sup>-1</sup> (s, C-O-C st); MS (ESI):  $m/z$  calcd for C<sub>75</sub>H<sub>120</sub>B<sub>30</sub>O<sub>3</sub>Si<sub>3</sub>: 1478; found: 1557 [M+2 K]<sup>+</sup>; elemental analysis calcd for C<sub>75</sub>H<sub>120</sub>B<sub>30</sub>O<sub>3</sub>Si<sub>3</sub>: C 60.93, H 8.18; found: C 61.00, H 8.31.

**Synthesis of 13:** The procedure was the same as for **12**, using **9** (75 mg, 0.19 mmol), 1,3,5-tris(4-allyloxyphenyl)benzene (**2**) (28 mg, 0.06 mmol) and the Karstedt catalyst system (10  $\mu\text{L}$ , 0.02 mmol). After work up, com-

pound **13** was obtained as a white solid. Yield: 68 mg, 70%.  $^1\text{H}$  NMR (CDCl<sub>3</sub>):  $\delta=7.73\text{--}6.73$  (m, 42H, C-H<sub>aryl</sub>), 3.99 (t,  $^3J(\text{H,H})=9$  Hz, 6H; O-CH<sub>2</sub>), 3.05 (s, 6H; Cc-CH<sub>2</sub>), 2.64 (t,  $^3J(\text{H,H})=9$  Hz, 6H; SiCH<sub>2</sub>CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>), 1.85 (m, 6H; CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si), 0.92 (t,  $^3J(\text{H,H})=9$  Hz, 6H; SiCH<sub>2</sub>CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>), 0.68 (t,  $^3J(\text{H,H})=9$  Hz, 6H; CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si), 0.06 ppm (s, 18H; Si(CH<sub>3</sub>)<sub>2</sub>);  $^1\text{H}\{^{11}\text{B}\}$  NMR (CDCl<sub>3</sub>, TMS):  $\delta=7.73\text{--}6.73$  (m, 24H; C-H<sub>aryl</sub>), 3.99 (t,  $^3J(\text{H,H})=9$  Hz, 6H; O-CH<sub>2</sub>), 3.05 (s, 6H; Cc-CH<sub>2</sub>), 2.73 (s, 1H; B-H), 2.64 (t,  $^3J(\text{H,H})=9$  Hz, 6H; SiCH<sub>2</sub>CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>), 2.40 (s, 1H; B-H), 2.23 (s, 1H; B-H), 1.85 (m, 6H; CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si), 0.92 (t,  $^3J(\text{H,H})=9$  Hz, 6H; SiCH<sub>2</sub>CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>), 0.68 (t,  $^3J(\text{H,H})=9$  Hz, 6H; CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si), 0.06 ppm (s, 18H; Si(CH<sub>3</sub>)<sub>2</sub>);  $^{11}\text{B}$  NMR (CDCl<sub>3</sub>):  $\delta=-3.7$  (d,  $^1J(\text{B,H})=132$  Hz, 6B),  $-10.3$  ppm (d,  $^1J(\text{B,H})=114$  Hz, 24B);  $^{13}\text{C}\{^1\text{H}\}$  NMR (CDCl<sub>3</sub>):  $\delta=158.9\text{--}114.9$  (C<sub>aryl</sub>), 83.9 (Cc-CH<sub>2</sub>), 82.5 (Cc-CH<sub>3</sub>), 70.7 (O-CH<sub>2</sub>), 40.6 (-CH<sub>2</sub>-), 30.1 (CH<sub>2</sub>CH<sub>2</sub>Si), 23.9 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 16.8 (SiCH<sub>2</sub>), 10.8 (SiCH<sub>2</sub>)  $-3.4$  ppm (Si-CH<sub>3</sub>);  $^{29}\text{Si}\{^1\text{H}\}$  NMR (CDCl<sub>3</sub>):  $\delta=2.94$  ppm; IR (KBr):  $\tilde{\nu}=2929$  (m, C-H st), 2573 (s, B-H st), 1608 (m, arC-C st), 1510 (s, arC-C st), 1247 cm<sup>-1</sup> (s, C-O-C st); MS (ESI):  $m/z$  calcd for C<sub>90</sub>H<sub>126</sub>B<sub>30</sub>O<sub>3</sub>Si<sub>3</sub>: 1665.2; found: 1688.3 [M+Na]<sup>+</sup>; elemental analysis calcd for C<sub>90</sub>H<sub>126</sub>B<sub>30</sub>O<sub>3</sub>Si<sub>3</sub>: C 64.94; H 7.63; found: C 64.92, H 7.68.

**Synthesis of 14:** The procedure was the same as for **10**, using 1-CH<sub>3</sub>-2-[CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>(CH<sub>3</sub>)<sub>2</sub>SiH]-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub> (**6**) (0.32 g, 1.26 mmol), 1,3,5-tris[4-(3,4,5-tris(allyloxy)benzyloxy)-phenyl]benzene (**3**) (0.16, 0.14 mmol), Karstedt catalyst (10  $\mu\text{L}$ , 0.02 mmol), and dry THF (1 mL). After work up, compound **14** was obtained as a brownish solid. Yield: 0.27 g, 62%.  $^1\text{H}$  NMR (CDCl<sub>3</sub>):  $\delta=7.66$  (m, 9H; C-H<sub>aryl</sub>), 7.10 (m, 6H; C-H<sub>aryl</sub>), 6.67 (s, 6H; C-H<sub>aryl</sub>), 5.02 (s, 6H; O-CH<sub>2</sub>-C<sub>aryl</sub>), 3.98 (t,  $^3J(\text{H,H})=6.0$  Hz, 18H; O-CH<sub>2</sub>), 2.17 (t,  $^3J(\text{H,H})=9.0$  Hz, 18H; Cc-CH<sub>2</sub>-), 1.99 (s, 27H; Cc-CH<sub>3</sub>), 1.80 (m, 18H; CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>), 1.57 (m, 18H; CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>), 0.65 (t,  $^3J(\text{H,H})=9.0$  Hz, 18H; Si-CH<sub>2</sub>), 0.54 (t,  $^3J(\text{H,H})=9.0$  Hz, 18H; CH<sub>2</sub>-Si), 0.04 ppm (s, 54H; Si-CH<sub>3</sub>);  $^1\text{H}\{^{11}\text{B}\}$  NMR (CDCl<sub>3</sub>):  $\delta=7.66$  (m, 9H; C-H<sub>aryl</sub>), 7.10 (m, 6H; C-H<sub>aryl</sub>), 6.67 (s, 6H; C-H<sub>aryl</sub>), 5.02 (s, 6H; O-CH<sub>2</sub>-C<sub>aryl</sub>), 3.98 (t,  $^3J(\text{H,H})=6.0$  Hz, 18H; O-CH<sub>2</sub>), 2.27 (br s, B-H), 2.17 (t,  $^3J(\text{H,H})=9.0$  Hz, 18H; Cc-CH<sub>2</sub>-), 2.14 (br s, B-H), 1.99 (s, 27H; Cc-CH<sub>3</sub>), 1.80 (m, 18H; CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>), 1.57 (m, 18H; CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>), 0.65 (t,  $^3J(\text{H,H})=9.0$  Hz, 18H; Si-CH<sub>2</sub>), 0.54 (t,  $^3J(\text{H,H})=9.0$  Hz, 18H; CH<sub>2</sub>-Si), 0.04 ppm (s, 54H; Si-CH<sub>3</sub>);  $^{11}\text{B}$  NMR (CDCl<sub>3</sub>):  $\delta=-4.9$  (d,  $^1J(\text{B,H})=132$  Hz, 9B),  $-5.9$  (d,  $^1J(\text{B,H})=144$  Hz, 9B),  $-10.8$  (d,  $^1J(\text{B,H})=139$  Hz, 72B);  $^{13}\text{C}\{^1\text{H}\}$  NMR (CDCl<sub>3</sub>):  $\delta=158.8\text{--}106.4$  (C<sub>aryl</sub>), 78.1 (O-CH<sub>2</sub>-C<sub>aryl</sub>), 74.7 (Cc), 71.8 (O-CH<sub>2</sub>), 39.0 (Cc-CH<sub>2</sub>), 24.3 (CH<sub>2</sub>), 23.9 (CH<sub>2</sub>), 23.1 (Cc-CH<sub>3</sub>), 15.3 (Si-CH<sub>2</sub>), 11.1 (Si-CH<sub>2</sub>),  $-3.5$  ppm (Si-CH<sub>3</sub>);  $^{29}\text{Si}\{^1\text{H}\}$  NMR (CDCl<sub>3</sub>):  $\delta=3.51$  ppm; IR (KBr):  $\tilde{\nu}=2931$  (m, C-H<sub>alkyl</sub> st), 2584 (s, B-H st), 1250 (Si-CH<sub>alkyl</sub>), 1236 cm<sup>-1</sup> (s, C-O-C st); elemental analysis calcd for C<sub>144</sub>H<sub>306</sub>B<sub>90</sub>O<sub>12</sub>Si<sub>9</sub>: C 50.05, H 8.93; found: C 50.36, H 8.84.

**Synthesis of 15:** The procedure was the same as for **10**, using 1-C<sub>6</sub>H<sub>5</sub>-2-[CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>(CH<sub>3</sub>)<sub>2</sub>SiH]-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub> (**7**) (0.34 g, 1.05 mmol), 1,3,5-tris[4-(3,4,5-tris(allyloxy)benzyloxy)-phenyl]benzene (**3**) (0.13 g, 0.11 mmol), Karstedt catalyst (10  $\mu\text{L}$ ), and dry THF (1 mL). After work up, compound **15** was obtained as a brownish solid. Yield: 0.47 g, 59.1%.  $^1\text{H}$  NMR (CDCl<sub>3</sub>):  $\delta=7.65\text{--}7.40$  (m, 54H; C-H<sub>aryl</sub>), 7.10 (d,  $^3J(\text{H,H})=9.0$  Hz, 6H; C-H<sub>aryl</sub>), 6.67 (s, 6H; C-H<sub>aryl</sub>), 5.04 (s, 6H; O-CH<sub>2</sub>-C<sub>aryl</sub>), 3.93 (t,  $^3J(\text{H,H})=6.0$  Hz, 18H; O-CH<sub>2</sub>), 1.78 (m, 36H; CH<sub>2</sub>), 1.39 (m, 18H; CH<sub>2</sub>), 0.48 (t,  $^3J(\text{H,H})=9.0$  Hz, 18H; CH<sub>2</sub>-Si), 0.30 (t,  $^3J(\text{H,H})=9.0$  Hz, 18H; CH<sub>2</sub>-Si),  $-0.11$  ppm (s, 54H; Si-CH<sub>3</sub>);  $^1\text{H}$  NMR (CDCl<sub>3</sub>):  $\delta=7.65\text{--}7.40$  (m, 54H; C-H<sub>aryl</sub>), 7.01 (d,  $^3J(\text{H,H})=9.0$  Hz, 6H; C-H<sub>aryl</sub>), 6.67 (s, 6H; C-H<sub>aryl</sub>), 5.04 (s, 6H; O-CH<sub>2</sub>-C<sub>aryl</sub>), 3.93 (t,  $^3J(\text{H,H})=6.0$  Hz, 18H; O-CH<sub>2</sub>), 2.73 (s, B-H), 2.37 (s, B-H), 2.25 (s, B-H), 1.78 (m, 36H; CH<sub>2</sub>), 1.39 (m, 18H; CH<sub>2</sub>), 0.48 (t,  $^3J(\text{H,H})=9.0$  Hz, 18H; CH<sub>2</sub>-Si), 0.30 (t,  $^3J(\text{H,H})=9.0$  Hz, 18H; CH<sub>2</sub>-Si),  $-0.11$  ppm (s, 54H; Si-CH<sub>3</sub>);  $^{11}\text{B}$  NMR (CDCl<sub>3</sub>):  $\delta=-3.9$  (d,  $^1J(\text{B,H})=133$ , 18B),  $-10.7$  ppm (d,  $^1J(\text{B,H})=130$ , 72B);  $^{13}\text{C}\{^1\text{H}\}$  NMR (CDCl<sub>3</sub>, TMS):  $\delta=158.6\text{--}106.4$  (C<sub>aryl</sub>), 83.4 (Cc), 82.4 (Cc), 80.1 (O-CH<sub>2</sub>-C<sub>aryl</sub>), 71.8 (O-CH<sub>2</sub>), 38.6 (Cc-CH<sub>2</sub>), 24.5 (CH<sub>2</sub>), 23.8 (CH<sub>2</sub>), 14.9 (Si-CH<sub>2</sub>), 11.0 (Si-CH<sub>2</sub>),  $-3.6$  ppm (Si-CH<sub>3</sub>);  $^{29}\text{Si}\{^1\text{H}\}$  NMR (CDCl<sub>3</sub>):  $\delta=3.35$  ppm; IR (KBr):  $\tilde{\nu}=3063$  (m, C-H<sub>aryl</sub> st), 2926 (m, C-H<sub>alkyl</sub> st), 2583 (s, B-H st), 1252 (Si-CH<sub>alkyl</sub>), 1240 cm<sup>-1</sup> (s, C-O-C st); MS (ESI):  $m/z$  calcd for C<sub>189</sub>H<sub>324</sub>B<sub>90</sub>O<sub>12</sub>Si<sub>9</sub>: 4014.6; found: 4037.9 [M+Na]<sup>+</sup>, 4111.9 [M+Na+EtO]<sup>+</sup>; elemental analysis calcd for C<sub>189</sub>H<sub>324</sub>B<sub>90</sub>O<sub>12</sub>Si<sub>9</sub>: C 56.55, H 8.14; found: C 56.38, H 8.00.

**Synthesis of 16:** The procedure was the same as for **12**, using **8** (69 mg, 0.20 mmol), 1,3,5-tris[4-(3,4,5-tris(allyloxy)benzyloxy)-phenyl]benzene (**3**) (19 mg, 0.017 mmol), and Karstedt catalyst (20  $\mu$ L, 0.04 mmol). After the work up, **16** was obtained as a colorless oil. Yield: 58 mg, 83%.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 7.67 (m, 9H; C- $H_{\text{aryl}}$ ), 7.10 (m, 42H; C- $H_{\text{aryl}}$ ), 6.70 (s, 6H; C- $H_{\text{aryl}}$ ), 5.03 (s, 6H; O- $\text{CH}_2$ - $\text{C}_{\text{aryl}}$ ), 3.98 (t,  $^3J(\text{H,H})$  = 9 Hz, 18H; O- $\text{CH}_2$ ), 3.42 (s, 18H; Cc- $\text{CH}_2$ ), 2.66 (t,  $^3J(\text{H,H})$  = 9 Hz, 18H;  $\text{SiCH}_2\text{CH}_2\text{C}_6\text{H}_4$ ), 2.15 (s, 27H; Cc- $\text{CH}_3$ ), 1.83 (m, 18H;  $\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}$ ), 0.92 (t,  $^3J(\text{H,H})$  = 9 Hz, 18H;  $\text{SiCH}_2\text{CH}_2\text{C}_6\text{H}_4$ ), 0.67 (t,  $^3J(\text{H,H})$  = 9 Hz, 18H;  $\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}$ ), 0.05 ppm (s, 54H;  $\text{Si}(\text{CH}_3)_2$ );  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ),  $\delta$  = 7.67 (m, 9H; C- $H_{\text{aryl}}$ ), 7.10 (m, 48H; C- $H_{\text{aryl}}$ ), 6.70 (s, 6H; C- $H_{\text{aryl}}$ ), 5.03 (s, 6H; O- $\text{CH}_2$ - $\text{C}_{\text{aryl}}$ ), 3.98 (t,  $^3J(\text{H,H})$  = 9 Hz, 18H; O- $\text{CH}_2$ ), 3.42 (s, 18H; Cc- $\text{CH}_2$ ), 2.66 (t,  $^3J(\text{H,H})$  = 9 Hz, 18H;  $\text{SiCH}_2\text{CH}_2\text{C}_6\text{H}_4$ ), 2.28 (s, B-H), 2.20 (s, B-H), 2.15 (s, 27H; Cc- $\text{CH}_3$ ), 2.09 (s, B-H), 1.83 (m, 18H;  $\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}$ ), 0.92 (t,  $^3J(\text{H,H})$  = 9 Hz, 18H;  $\text{SiCH}_2\text{CH}_2\text{C}_6\text{H}_4$ ), 0.68 (t,  $^3J(\text{H,H})$  = 9 Hz, 18H;  $\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}$ ), 0.05 ppm (s, 54H;  $\text{Si}(\text{CH}_3)_2$ );  $^{11}\text{B}$  NMR ( $\text{CDCl}_3$ ),  $\delta$  = -4.4 (d,  $^1J(\text{B,H})$  = 132 Hz, 9B), -5.8 (d,  $^1J(\text{B,H})$  = 157 Hz, 9B), -10.5 ppm (d,  $^1J(\text{B,H})$  = 140 Hz, 72B);  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 158.8–106.4 ( $\text{C}_{\text{aryl}}$ ), 78.1 (O- $\text{CH}_2$ - $\text{C}_{\text{aryl}}$ ), 78.0 (s, Cc- $\text{CH}_2$ ), 74.7 (Cc- $\text{CH}_3$ ), 71.8 (O- $\text{CH}_2$ ), 40.5 (Cc- $\text{CH}_2$ ), 23.9 ( $\text{CH}_2$ ), 23.6 (Cc- $\text{CH}_3$ ), 16.8 (Si- $\text{CH}_2$ ), 10.8 (Si- $\text{CH}_2$ ), -3.4 ppm (Si- $\text{CH}_3$ );  $^{29}\text{Si}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 2.96 ppm; IR (NaCl)  $\tilde{\nu}$  = 2931 (m, C-H $_{\text{alkyl}}$  st), 2577 (s, B-H st), 1591 (m, arC-C st), 1511 (s, arC-C st), 1248  $\text{cm}^{-1}$  (s, C-O-C st); elemental analysis calcd for  $\text{C}_{198}\text{H}_{342}\text{B}_9\text{O}_{12}\text{Si}_9$ : C 57.43, H 8.33; found: C 56.43, H 8.90.

**Synthesis of 17:** The procedure was the same as for **13**, using **9** (75 mg, 0.20 mmol), 1,3,5-tris[4-(3,4,5-tris(allyloxy)benzyloxy)-phenyl]benzene (**3**) (19 mg, 0.017 mmol) and Karstedt catalyst (20  $\mu$ L, 0.04 mmol). After the work up, **17** was obtained as a colorless oil. Yield: 62 mg, 88%.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 7.72–6.73 (m, 102H; C- $H_{\text{aryl}}$ ), 5.00 (s, 6H; O- $\text{CH}_2$ - $\text{C}_{\text{aryl}}$ ), 3.96 (t,  $^3J(\text{H,H})$  = 9 Hz, 18H; O- $\text{CH}_2$ ), 3.03 (s, 18H; Cc- $\text{CH}_2$ ), 2.60 (t,  $^3J(\text{H,H})$  = 9 Hz, 18H;  $\text{SiCH}_2\text{CH}_2\text{C}_6\text{H}_4$ ), 1.83 (m, 18H;  $\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}$ ), 0.88 (t,  $^3J(\text{H,H})$  = 9 Hz, 18H;  $\text{SiCH}_2\text{CH}_2\text{C}_6\text{H}_4$ ), 0.63 (t,  $^3J(\text{H,H})$  = 9 Hz, 18H;  $\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}$ ), 0.02 (s, 54H;  $\text{Si}(\text{CH}_3)_2$ );  $^1\text{H}\{^{11}\text{B}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 7.72–6.73 (m, 102H; C- $H_{\text{aryl}}$ ), 5.00 (s, 6H; O- $\text{CH}_2$ - $\text{C}_{\text{aryl}}$ ), 3.96 (t,  $^3J(\text{H,H})$  = 9 Hz, 18H; O- $\text{CH}_2$ ), 3.03 (s, 18H; Cc- $\text{CH}_2$ ), 2.73 (s, B-H), 2.60 (t,  $^3J(\text{H,H})$  = 9 Hz, 18H;  $\text{SiCH}_2\text{CH}_2\text{C}_6\text{H}_4$ ), 2.41 (s, B-H), 2.31 (s, B-H), 2.22 (s, B-H), 1.83 (m, 18H;  $\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}$ ), 0.88 (t,  $^3J(\text{H,H})$  = 9 Hz, 18H;  $\text{SiCH}_2\text{CH}_2\text{C}_6\text{H}_4$ ), 0.63 (t,  $^3J(\text{H,H})$  = 9 Hz, 18H;  $\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}$ ), 0.02 ppm (s, 54H;  $\text{Si}(\text{CH}_3)_2$ );  $^{11}\text{B}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = -3.7 (d, 18B,  $^1J(\text{B,H})$  = 132 Hz), -10.2 ppm (m, 72B);  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , TMS):  $\delta$  = 158.6–106.4 ( $\text{C}_{\text{aryl}}$ ), 83.4 (Cc- $\text{CH}_2$ ), 82.4 (Cc- $\text{C}_6\text{H}_5$ ), 80.1 (O- $\text{CH}_2$ - $\text{C}_{\text{aryl}}$ ), 71.8 (O- $\text{CH}_2$ ), 40.6 (Cc- $\text{CH}_2$ ), 30.1 (s,  $\text{CH}_2\text{CH}_2\text{Si}$ ), 23.8 ( $\text{CH}_2\text{CH}_2\text{CH}_2$ ), 16.9 (Si- $\text{CH}_2$ ), 10.9 (Si- $\text{CH}_2$ ), -3.5 ppm (Si- $\text{CH}_3$ );  $^{29}\text{Si}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 2.91 ppm; IR (NaCl)  $\tilde{\nu}$  = 2923 (m, C-H $_{\text{alkyl}}$  st), 2579 (s, B-H st), 1591 (m, arC-C st), 1510 (s, arC-C st), 1247  $\text{cm}^{-1}$  (s, C-O-C st); elemental analysis calcd for  $\text{C}_{243}\text{H}_{360}\text{B}_9\text{O}_{12}\text{Si}_9$ : C 62.11; H 7.72; found: C 60.77, H 8.23.

**Synthesis of 18:** A solution of **4** (18.20 mg, 0.02 mmol) in THF (1 mL) was added to a solution of NaOH (23.0 mg, 0.58 mmol) in deoxygenated ethanol (2.5 mL). The mixture was heated at reflux for 16 h. After cooling the mixture, the excess of NaOH was precipitated as sodium carbonate by saturating the solution with a stream of  $\text{CO}_2$  (g). After filtration, the solution was evaporated and treated with cold THF. The precipitate was filtered off through Celite and evaporation of the solvent led **18** as a yellowish oil. Yield: 15.4 mg, 81.4%.  $^1\text{H}$  NMR ( $\text{CD}_3\text{COCD}_3$ ),  $\delta$  (ppm): 7.76 (s, 3H; C- $H_{\text{aryl}}$ ), 7.03 (d, 6H;  $^3J(\text{H,H})$  = 9.0, C- $H_{\text{aryl}}$ ), 6.97 (s, 6H; C- $H_{\text{aryl}}$ ), 4.02 (t, 6H;  $^3J(\text{H,H})$  = 6.0,  $\text{CH}_2$ ), 1.47 (br s, 12H;  $\text{CH}_2\text{CH}_2\text{-Cc}$ ), 1.42 ppm (br s, 9H;  $\text{CH}_3\text{-Cc}$ );  $^1\text{H}\{^{11}\text{B}\}$  NMR ( $\text{CD}_3\text{COCD}_3$ ):  $\delta$  = 7.76 (s, 3H; C- $H_{\text{aryl}}$ ), 7.03 (d, 6H;  $^3J(\text{H,H})$  = 9.0, C- $H_{\text{aryl}}$ ), 6.97 (s, 6H; C- $H_{\text{aryl}}$ ), 4.02 (t, 6H;  $^3J(\text{H,H})$  = 6.0,  $\text{CH}_2$ ), 1.60 (br s, B-H), 1.80 (m, 12H;  $\text{CH}_2\text{CH}_2\text{-Cc}$ ), 1.42 (br s, 9H;  $\text{CH}_3\text{-Cc}$ ), 0.56 (br s, B-H), 0.09 (br s, B-H), -2.54 ppm (br s, B-H-B);  $^{11}\text{B}$  NMR ( $\text{CD}_3\text{COCD}_3$ ):  $\delta$  = -8.2 (d, 3B,  $^1J(\text{B,H})$  = 132 Hz), -9.6 (d, 6B,  $^1J(\text{B,H})$  = 132 Hz), -17.4 (d, 12B,  $^1J(\text{B,H})$  = 132 Hz), -33.7 (dd, 3B,  $^1J(\text{B,H})$  = 126 Hz,  $^1J(\text{B,H})$  = 38 Hz), -36.1 ppm (d, 3B,  $^1J(\text{B,H})$  = 147 Hz);  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CD}_3\text{COCD}_3$ ):  $\delta$  = 159.2–114.9 ( $\text{C}_{\text{aryl}}$ ), 69.1 (OCH $_2$ ), 31.9 ( $\text{CH}_2\text{CH}_2\text{CH}_2$ ), 31.1 (Cc- $\text{CH}_2$ ), 21.5 ppm (Cc- $\text{CH}_3$ ); IR (NaCl)  $\tilde{\nu}$  = 2932 (m, C-H $_{\text{alkyl}}$  st), 2515  $\text{cm}^{-1}$  (s, B-H st).

**Synthesis of 19:** A solution of **5** (70.7 mg, 0.06 mmol) in THF (2 mL) was added to a solution of NaOH (75.0 mg, 1.88 mmol) in deoxygenated

ethanol (5 mL). The mixture was heated at reflux for 16 h. After cooling the mixture, the excess of NaOH was precipitated as sodium carbonate by saturating the solution with a stream of  $\text{CO}_2$  (g). After filtration, the solution was evaporated and treated with cold THF. The precipitate was filtered off through Celite and evaporation of the solvent led **19** as a yellowish oil. Yield: 57.9 mg, 79.4%.  $^1\text{H}$  NMR ( $\text{CD}_3\text{COCD}_3$ ):  $\delta$  = 7.69–7.16 (m, 24H; C- $H_{\text{aryl}}$ ), 6.87 (d,  $^3J(\text{H,H})$  = 8.4, 6H; C- $H_{\text{aryl}}$ ), 3.64 (t,  $^3J(\text{H,H})$  = 6.0, 6H; O- $\text{CH}_2$ ), 1.80 ppm (m, 12H;  $\text{CH}_2\text{CH}_2\text{CH}_2$ );  $^1\text{H}\{^{11}\text{B}\}$  NMR ( $\text{CD}_3\text{COCD}_3$ ):  $\delta$  = 7.69–7.16 (m, 24H; C- $H_{\text{aryl}}$ ), 6.87 (d,  $^3J(\text{H,H})$  = 8.4, 6H; C- $H_{\text{aryl}}$ ), 3.64 (t,  $^3J(\text{H,H})$  = 6.0, 6H; O- $\text{CH}_2$ ), 1.80 (m, 12H;  $\text{CH}_2\text{CH}_2\text{CH}_2$ ), 1.61 (br s, B-H), 0.74 (br s, B-H), 0.25 (br s, B-H), -2.09 ppm (br s, B-H-B);  $^{11}\text{B}$  NMR ( $\text{CD}_3\text{COCD}_3$ ):  $\delta$  = -7.8 (d, 3B,  $^1J(\text{B,H})$  = 149 Hz), -9.6 (d, 3B,  $^1J(\text{B,H})$  = 154 Hz), -12.7 (d, 3B,  $^1J(\text{B,H})$  = 145 Hz), -17.1 (12B), -32.7 (dd, 3B,  $^1J(\text{B,H})$  = 121 Hz,  $^1J(\text{B,H})$  = 33 Hz), -35.5 (d, 3B,  $^1J(\text{B,H})$  = 138 Hz);  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CD}_3\text{COCD}_3$ ):  $\delta$  = 158.9–114.7 ( $\text{C}_{\text{aryl}}$ ), 69.2 (OCH $_2$ ), 32.3 (Cc- $\text{CH}_2$ ), 31.4 ppm ( $\text{CH}_2\text{CH}_2\text{CH}_2$ ); IR (NaCl):  $\tilde{\nu}$  = 3032 (m, C-H $_{\text{aryl}}$  st), 2940 (m, C-H $_{\text{alkyl}}$  st), 2517  $\text{cm}^{-1}$  (s, B-H st).

**Synthesis of 20:** A solution of **10** (150.0 mg, 0.12 mmol) in THF (2 mL) was added to a solution of NaOH (144.0 mg, 3.60 mmol) in deoxygenated ethanol (5 mL). The mixture was heated at reflux for 17 h. After cooling the mixture, the excess of NaOH was precipitated as sodium carbonate by saturating the solution with a stream of  $\text{CO}_2$  (g). After filtration, the solution was evaporated and treated with cold acetone. The precipitate was filtered off through Celite and evaporation of the solvent led **20** as a white oil. Yield: 97.0 mg, 62.8%.  $^1\text{H}$  NMR ( $\text{CD}_3\text{COCD}_3$ ):  $\delta$  = 7.77 (m, 6H, C- $H_{\text{aryl}}$ ), 7.06 (d, 6H,  $^3J(\text{H,H})$  = 9.0 Hz, C- $H_{\text{aryl}}$ ), 6.97 (s, 3H, C- $H_{\text{aryl}}$ ), 4.05 (t, 6H,  $^3J(\text{H,H})$  = 6.0 Hz, O- $\text{CH}_2$ ), 1.87 (m, 12H,  $\text{CH}_2\text{-CH}_2\text{-CH}_2$ ), 1.57 (m, 6H,  $\text{CH}_2\text{-CH}_2\text{-CH}_2$ ), 1.42 (s, 9H, Cc- $\text{CH}_3$ ), 0.71 (t, 6H,  $^3J(\text{H,H})$  = 9.0 Hz, Si- $\text{CH}_2$ ), 0.52 (t, 6H,  $^3J(\text{H,H})$  = 9.0 Hz,  $\text{CH}_2\text{-Si}$ ), 0.05 ppm (s, 18H, Si- $\text{CH}_3$ );  $^1\text{H}\{^{11}\text{B}\}$  NMR ( $\text{CD}_3\text{COCD}_3$ ):  $\delta$  = 7.77 (m, 6H, C- $H_{\text{aryl}}$ ), 7.06 (d, 6H,  $^3J(\text{H,H})$  = 9.0 Hz, C- $H_{\text{aryl}}$ ), 6.97 (s, 3H, C- $H_{\text{aryl}}$ ), 4.05 (t, 6H,  $^3J(\text{H,H})$  = 6.0 Hz, O- $\text{CH}_2$ ), 1.87 (m, 12H,  $\text{CH}_2\text{-CH}_2\text{-CH}_2$ ), 1.57 (m, 6H,  $\text{CH}_2\text{-CH}_2\text{-CH}_2$ ), 1.42 (s, 9H, Cc- $\text{CH}_3$ ), 0.71 (t, 6H,  $^3J(\text{H,H})$  = 9.0 Hz, Si- $\text{CH}_2$ ), 0.52 (t, 6H,  $^3J(\text{H,H})$  = 9.0 Hz,  $\text{CH}_2\text{-Si}$ ), 0.05 ppm (s, 18H, Si- $\text{CH}_3$ ), -2.56 ppm (br s, B-H-B);  $^{11}\text{B}$  NMR ( $\text{CD}_3\text{COCD}_3$ ):  $\delta$  = -8.1 (d, 3B,  $^1J(\text{B,H})$  = 151 Hz), -9.8 (d, 6B,  $^1J(\text{B,H})$  = 149 Hz), -17.2 (d, 12B,  $^1J(\text{B,H})$  = 132 Hz), -33.7 (dd, 3B,  $^1J(\text{B,H})$  = 121 Hz,  $^1J(\text{B,H})$  = 33 Hz), -36.1 ppm (d, 3B,  $^1J(\text{B,H})$  = 136 Hz);  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CD}_3\text{COCD}_3$ ):  $\delta$  = 158.9–115.0 ( $\text{C}_{\text{aryl}}$ ), 70.8 (O- $\text{CH}_2$ ), 40.1 ( $\text{CH}_2$ ), 24.9 ( $\text{CH}_2$ ), 23.8 ( $\text{CH}_2$ ), 21.7 (Cc- $\text{CH}_3$ ), 15.8 (Si- $\text{CH}_2$ ), 11.2 (Si- $\text{CH}_2$ ), -3.5 ppm (Si- $\text{CH}_3$ ); IR (NaCl):  $\tilde{\nu}$  = 2930 (m, C-H $_{\text{alkyl}}$  st), 2515  $\text{cm}^{-1}$  (s, B-H st).

**Synthesis of 21:** A solution of **11** (90.0 mg, 0.06 mmol) in THF (2 mL) was added to a solution of NaOH (144.0 mg, 3.60 mmol) in deoxygenated ethanol (5 mL). The mixture was heated at reflux for 17 h. After cooling the mixture, the excess of NaOH was precipitated as sodium carbonate by saturating the solution with a stream of  $\text{CO}_2$  (g). After filtration, the solution was evaporated and treated with cold acetone. The precipitate was filtered off through Celite and evaporation of the solvent led **21** as a yellowish oil. Yield: 60.0 mg, 65.2%.  $^1\text{H}$  NMR ( $\text{CD}_3\text{COCD}_3$ , TMS):  $\delta$  = 7.78–7.36 (m, 24H; C- $H_{\text{aryl}}$ ), 7.09 (d,  $^3J(\text{H,H})$  = 9.0 Hz, 6H; C- $H_{\text{aryl}}$ ), 4.00 (t,  $^3J(\text{H,H})$  = 6.0 Hz, 6H; O- $\text{CH}_2$ ), 1.70 (m, 12H;  $\text{CH}_2$ ), 0.54 (t,  $^3J(\text{H,H})$  = 9.0 Hz, 6H;  $\text{CH}_2\text{-Si}$ ), 0.05 (m, 6H;  $\text{CH}_2\text{-Si}$ ), -0.11 ppm (s, 18H; Si- $\text{CH}_3$ );  $^1\text{H}\{^{11}\text{B}\}$  NMR ( $\text{CD}_3\text{COCD}_3$ ):  $\delta$  = 7.78–7.36 (m, 24H; C- $H_{\text{aryl}}$ ), 7.09 (d,  $^3J(\text{H,H})$  = 9.0 Hz, 6H; C- $H_{\text{aryl}}$ ), 4.00 (t,  $^3J(\text{H,H})$  = 6.0 Hz, 6H; O- $\text{CH}_2$ ), 1.70 (m, 12H;  $\text{CH}_2$ ), 0.54 (t,  $^3J(\text{H,H})$  = 9.0 Hz, 6H;  $\text{CH}_2\text{-Si}$ ), 0.05 (m, 6H;  $\text{CH}_2\text{-Si}$ ), -0.11 (s, 18H; Si- $\text{CH}_3$ ), -2.13 ppm (br s, B-H-B);  $^{11}\text{B}$  NMR ( $\text{CD}_3\text{COCD}_3$ ):  $\delta$  = -7.6 (d, 3B,  $^1J(\text{B,H})$  = 192 Hz), -9.7 (d, 3B,  $^1J(\text{B,H})$  = 1171 Hz), -12.8 (d, 3B,  $^1J(\text{B,H})$  = 158 Hz), -17.0 (12B), -32.8 (dd, 3B,  $^1J(\text{B,H})$  = 131 Hz,  $^1J(\text{B,H})$  = 33 Hz), -35.6 ppm (d, 3B,  $^1J(\text{B,H})$  = 139 Hz);  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CD}_3\text{COCD}_3$ ):  $\delta$  = 158.2–115.3 ( $\text{C}_{\text{aryl}}$ ), 68.7 (O- $\text{CH}_2$ ), 40.6 ( $\text{CH}_2$ ), 24.5 ( $\text{CH}_2$ ), 23.8 ( $\text{CH}_2$ ), 15.6 (Si- $\text{CH}_2$ ), 11.0 (Si- $\text{CH}_2$ ), -3.9 ppm (Si- $\text{CH}_3$ ); IR (NaCl)  $\tilde{\nu}$  = 3030 (m, C-H $_{\text{aryl}}$  st), 2942 (m, C-H $_{\text{alkyl}}$  st), 2516 (s, B-H st), 1246  $\text{cm}^{-1}$  (Si- $\text{C}_{\text{alkyl}}$ ).

**Synthesis of 22:** A solution of **12** (50.0 mg, 0.033 mmol) in THF (1 mL) was added to a solution of NaOH (88 mg, 2.20 mmol) in deoxygenated ethanol (3 mL). The mixture was heated at reflux overnight. After cooling the mixture, the excess of NaOH was precipitated as sodium carbo-

nate by saturating the solution with a stream of CO<sub>2</sub> (g). After filtration the solution was evaporated and treated with cold THF. The precipitate was filtered off through Celite and evaporation of the solvent led **22** as an orange oil. Yield: 36 mg, 71%. <sup>1</sup>H NMR (CD<sub>3</sub>COCD<sub>3</sub>): δ = 7.76 (s, 3H; C-H<sub>aryl</sub>), 7.74 (d, <sup>3</sup>J(H,H) = 6 Hz, 6H; C-H<sub>aryl</sub>), 7.27 (d, <sup>3</sup>J(H,H) = 6 Hz, 6H; C-H<sub>aryl</sub>), 7.14 (d, <sup>3</sup>J(H,H) = 6 Hz, 6H; C-H<sub>aryl</sub>), 7.06 (d, <sup>3</sup>J(H,H) = 6 Hz, 6H; C<sub>6</sub>H<sub>4</sub>-O), 4.00 (t, <sup>3</sup>J(H,H) = 9 Hz, 6H; O-CH<sub>2</sub>), 3.11 (s, 6H; Cc-CH<sub>2</sub>), 2.66 (t, <sup>3</sup>J(H,H) = 9 Hz, 6H; SiCH<sub>2</sub>CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>), 1.84 (m, 6H; CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si), 1.29 (s, 9H; Cc-CH<sub>3</sub>), 0.95 (t, <sup>3</sup>J(H,H) = 9 Hz, 6H; SiCH<sub>2</sub>CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>), 0.70 (t, <sup>3</sup>J(H,H) = 9 Hz, 6H; CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si), 0.08 ppm (s, 18H; Si(CH<sub>3</sub>)<sub>2</sub>); <sup>1</sup>H [<sup>11</sup>B] NMR (CD<sub>3</sub>COCD<sub>3</sub>): δ = 7.76 (s, 3H; C-H<sub>aryl</sub>), 7.74 (d, <sup>3</sup>J(H,H) = 6 Hz, 6H; C-H<sub>aryl</sub>), 7.27 (d, <sup>3</sup>J(H,H) = 6 Hz, 6H; C-H<sub>aryl</sub>), 7.14 (d, <sup>3</sup>J(H,H) = 6 Hz, 6H; C-H<sub>aryl</sub>), 7.06 (d, <sup>3</sup>J(H,H) = 6 Hz, 6H; C<sub>6</sub>H<sub>4</sub>-O), 4.00 (t, <sup>3</sup>J(H,H) = 9 Hz, 6H; O-CH<sub>2</sub>), 3.11 (s, 6H; Cc-CH<sub>2</sub>), 2.66 (t, <sup>3</sup>J(H,H) = 9 Hz, 6H; SiCH<sub>2</sub>CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>), 2.18 (s, B-H), 2.02 (s, B-H), 1.84 (m, 6H; CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si), 1.56 (s, B-H), 1.29 (s, 9H; Cc-CH<sub>3</sub>), 0.95 (t, <sup>3</sup>J(H,H) = 9 Hz, 6H; SiCH<sub>2</sub>CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>), 0.70 (t, <sup>3</sup>J(H,H) = 9 Hz, 6H; CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si), 0.61 (s, B-H), 0.08 (s, 18H; Si(CH<sub>3</sub>)<sub>2</sub>), -2.40 ppm (s, B-H-B); <sup>11</sup>B NMR (CD<sub>3</sub>COCD<sub>3</sub>): δ = -7.76 (d, <sup>1</sup>J(B,H) = 106 Hz, 3B), -8.51 (d, <sup>1</sup>J(B,H) = 105 Hz, 6B), -15.18 (d, <sup>1</sup>J(B,H) = 134 Hz, 6B), -17.69 (d, <sup>1</sup>J(B,H) = 125 Hz, 3B), -18.70 (d, <sup>1</sup>J(B,H) = 128 Hz, 3B), -33.34 (d, <sup>1</sup>J(B,H) = 139 Hz, 3B), -35.75 ppm (d, <sup>1</sup>J(B,H) = 142 Hz, 3B); <sup>13</sup>C [<sup>1</sup>H] NMR (CD<sub>3</sub>COCD<sub>3</sub>): δ = 158.9–114.9 (C<sub>aryl</sub>), 70.6 (O-CH<sub>2</sub>), 41.9 (-CH<sub>2</sub>), 29.7 (CH<sub>2</sub>CH<sub>2</sub>Si), 23.9 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 22.3 (Cc-CH<sub>3</sub>), 16.8 (CH<sub>2</sub>CH<sub>2</sub>Si), 10.9 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), -3.4 ppm (Si-(CH<sub>3</sub>)<sub>2</sub>); IR (NaCl)  $\tilde{\nu}$  = 2960–2870 (m, C-H st), 2516 cm<sup>-1</sup> (s, B-H st); elemental analysis calcd for C<sub>75</sub>H<sub>120</sub>B<sub>27</sub>O<sub>3</sub>Si<sub>3</sub>Na<sub>3</sub>: C 59.46, H 7.98; found: C 58.31, H 7.84.

**Synthesis of 23:** A solution of **13** (50.0 mg, 0.03 mmol) in THF (1 mL) was added to a solution of NaOH (80 mg, 2.00 mmol) in deoxygenated ethanol (3 mL). The mixture was heated at reflux overnight. After cooling the mixture, the excess of NaOH was precipitated as sodium carbonate by saturating the solution with a stream of CO<sub>2</sub> (g). After filtration the solution was evaporated and treated with cold THF. The precipitate was filtered off through Celite and evaporation of the solvent led **23** as an orange oil. Yield: 33 mg, 65%. <sup>1</sup>H NMR (CD<sub>3</sub>COCD<sub>3</sub>): δ = 7.76 (s, 3H; C-H<sub>aryl</sub>), 7.74 (d, <sup>3</sup>J(H,H) = 6 Hz, 6H; C-H<sub>aryl</sub>), 7.32–6.83 (m, 33H), 4.03 (t, <sup>3</sup>J(H,H) = 9 Hz, 6H; O-CH<sub>2</sub>), 3.05 (s, 6H; Cc-CH<sub>2</sub>), 2.62 (t, <sup>3</sup>J(H,H) = 9 Hz, 6H; SiCH<sub>2</sub>CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>), 1.84 (m, 6H; CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si), 0.96 (t, <sup>3</sup>J(H,H) = 9 Hz, 6H; SiCH<sub>2</sub>CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>), 0.72 (t, <sup>3</sup>J(H,H) = 9 Hz, 6H; CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si), 0.08 ppm (s, 18H; Si(CH<sub>3</sub>)<sub>2</sub>); <sup>1</sup>H [<sup>11</sup>B] NMR (CD<sub>3</sub>COCD<sub>3</sub>): δ = 7.76 (s, 3H; C-H<sub>aryl</sub>), 7.74 (d, <sup>3</sup>J(H,H) = 6 Hz, 6H; C-H<sub>aryl</sub>), 7.32–6.83 (m, 33H), 4.03 (t, <sup>3</sup>J(H,H) = 9 Hz, 6H; O-CH<sub>2</sub>), 3.11 (s, 6H; Cc-CH<sub>2</sub>), 2.62 (t, <sup>3</sup>J(H,H) = 9 Hz, 6H; SiCH<sub>2</sub>CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>), 1.84 (m, 6H; CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si), 0.96 (t, <sup>3</sup>J(H,H) = 9 Hz, 6H; SiCH<sub>2</sub>CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>), 0.72 (t, <sup>3</sup>J(H,H) = 9 Hz, 6H; CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si), 0.28 (s, B-H), 0.08 (s, 18H; Si(CH<sub>3</sub>)<sub>2</sub>), -2.05 ppm (s, B-H-B); <sup>11</sup>B NMR (CD<sub>3</sub>COCD<sub>3</sub>): δ = -7.74 (d, <sup>1</sup>J(B,H) = 86 Hz, 3B), -8.49 (d, <sup>1</sup>J(B,H) = 113 Hz, 3B), -12.32 (d, <sup>1</sup>J(B,H) = 148 Hz, 3B), -15.69 (d, <sup>1</sup>J(B,H) = 130 Hz, 3B), -16.94 (d, <sup>1</sup>J(B,H) = 125 Hz, 3B), -17.77 (d, <sup>1</sup>J(B,H) = 129 Hz, 6B), -32.74 (d, <sup>1</sup>J(B,H) = 128 Hz, 3B), -35.39 ppm (d, <sup>1</sup>J(B,H) = 140 Hz, 3B); <sup>13</sup>C [<sup>1</sup>H] NMR (CD<sub>3</sub>COCD<sub>3</sub>): δ = 158.9–114.9 (C<sub>aryl</sub>), 70.7 (O-CH<sub>2</sub>), 41.8 (-CH<sub>2</sub>), 30.1 (CH<sub>2</sub>CH<sub>2</sub>Si), 23.9 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 16.8 (CH<sub>2</sub>CH<sub>2</sub>Si), 10.6 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), -3.4 ppm (Si-(CH<sub>3</sub>)<sub>2</sub>); IR (NaCl)  $\tilde{\nu}$  = 2959–2868 (m, C-H st), 2515 cm<sup>-1</sup> (s, B-H st); elemental analysis calcd for C<sub>90</sub>H<sub>126</sub>B<sub>27</sub>O<sub>3</sub>Si<sub>3</sub>Na<sub>3</sub>: C 63.55, H 7.17; found: C 62.77, H 7.92.

**Synthesis of 24:** A solution of **14** (150.0 mg, 0.04 mmol) in THF (2 mL) was added to a solution of NaOH (156.0 mg, 3.9 mmol) in deoxygenated ethanol (5 mL). The mixture was heated at reflux for 19 h. After cooling the mixture, the excess of NaOH was precipitated as sodium carbonate by saturating the solution with a stream of CO<sub>2</sub> (g). After filtration the solution was evaporated and treated with cold acetone. The precipitate was filtered off through Celite and evaporation of the solvent led **24** as an orange oil. Yield: 97.7 mg, 63.2%. <sup>1</sup>H NMR (CD<sub>3</sub>COCD<sub>3</sub>, TMS): δ = 7.77–6.97 (m, 21H, C-H<sub>aryl</sub>), 5.11 (s, 6H, O-CH<sub>2</sub>-C<sub>aryl</sub>), 4.05 (m, 18H, O-CH<sub>2</sub>), 1.87 (m, 36H, CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>), 1.57 (m, 18H, CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>), 1.42 (s, 27H, Cc-CH<sub>3</sub>), 0.72 (m, 18H, Si-CH<sub>2</sub>), 0.54 (m, 18H, CH<sub>2</sub>-Si), 0.05 ppm (s, 54H, Si-CH<sub>3</sub>); <sup>1</sup>H [<sup>11</sup>B] NMR (CD<sub>3</sub>COCD<sub>3</sub>): δ = 7.77 (m, 9H, C-H<sub>aryl</sub>), 7.09 (m, 12H, C-H<sub>aryl</sub>), 6.97 (s, 6H, C-H<sub>aryl</sub>), 5.11 (s, 6H, O-CH<sub>2</sub>-C<sub>aryl</sub>), 4.05 (m, 18H, O-CH<sub>2</sub>), 1.87 (m, 36H, CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>), 1.57 (m,

18H, CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>), 1.42 (s, 27H, Cc-CH<sub>3</sub>), 0.72 (m, 18H, Si-CH<sub>2</sub>), 0.54 (m, 18H, CH<sub>2</sub>-Si), 0.05 (s, 54H, Si-CH<sub>3</sub>), -2.56 ppm (br s, B-H-B); <sup>11</sup>B NMR (CDCl<sub>3</sub>): δ = -8.1 (d, 9B, <sup>1</sup>J(B,H) = 151 Hz), -9.8 (d, 18B, <sup>1</sup>J(B,H) = 149 Hz), -17.2 (d, 36B, <sup>1</sup>J(B,H) = 99 Hz), -33.7 (dd, 9B, <sup>1</sup>J(B,H) = 121 Hz, <sup>1</sup>J(B,H) = 33 Hz), -36.1 ppm (d, 9B, <sup>1</sup>J(B,H) = 136 Hz); <sup>13</sup>C [<sup>1</sup>H] NMR (CD<sub>3</sub>COCD<sub>3</sub>): δ = 158.9 (C<sub>aryl</sub>), 106.4 (C<sub>aryl</sub>), 78.1 (O-CH<sub>2</sub>-C<sub>aryl</sub>), 71.1 (O-CH<sub>2</sub>), 40.1 (CH<sub>2</sub>), 24.9 (CH<sub>2</sub>), 23.9 (CH<sub>2</sub>), 21.7 (Cc-CH<sub>3</sub>), 15.3 (Si-CH<sub>2</sub>), 11.2 (Si-CH<sub>2</sub>), -3.5 ppm (Si-CH<sub>3</sub>); IR (NaCl)  $\tilde{\nu}$  = 2933 (m, C-H<sub>alkyl</sub> st), 2513 cm<sup>-1</sup> (s, B-H st).

**Synthesis of 25:** A solution of **15** (100.0 mg, 0.03 mmol) in THF (2 mL) was added to a solution of NaOH (89.7 mg, 2.2 mmol) in deoxygenated ethanol (5 mL). The mixture was heated at reflux for 19 h. After cooling the mixture, the excess of NaOH was precipitated as sodium carbonate by saturating the solution with a stream of CO<sub>2</sub> (g). After filtration the solution was evaporated and treated with cold THF. The precipitate was filtered off through Celite and evaporation of the solvent led **25** as an orange oil. Yield: 74.0 mg, 72.0%. <sup>1</sup>H NMR (CD<sub>3</sub>COCD<sub>3</sub>, TMS): δ = 7.77–6.83 (m, 66H, C-H<sub>aryl</sub>), 5.13 (s, 6H, O-CH<sub>2</sub>-C<sub>aryl</sub>), 3.97 (m, 18H; O-CH<sub>2</sub>), 1.70 (m, 36H; CH<sub>2</sub>), 0.52 (m, 18H; CH<sub>2</sub>-Si), 0.04 (m, 36H; CH<sub>2</sub>), -0.11 (s, 54H; Si-CH<sub>3</sub>), -2.10 ppm (br s, B-H-B); <sup>1</sup>H [<sup>11</sup>B] NMR (CD<sub>3</sub>COCD<sub>3</sub>): δ = 7.77–6.83 (m, 66H, C-H<sub>aryl</sub>), 5.13 (s, 6H, O-CH<sub>2</sub>-C<sub>aryl</sub>), 3.97 (m, 18H; O-CH<sub>2</sub>), 1.70 (m, 36H; CH<sub>2</sub>), 0.52 (m, 18H; CH<sub>2</sub>-Si), 0.04 (m, 36H; CH<sub>2</sub>), -0.11 (s, 54H; Si-CH<sub>3</sub>), -2.10 ppm (s, B-H-B); <sup>11</sup>B NMR (CD<sub>3</sub>COCD<sub>3</sub>): δ = -7.7 (d, 9B, <sup>1</sup>J(B,H) = 192 Hz), -9.9 (d, 9B, <sup>1</sup>J(B,H) = 1171 Hz), -12.9 (d, 9B, <sup>1</sup>J(B,H) = 158 Hz), -17.1 (36B), -32.9 (dd, 9B, <sup>1</sup>J(B,H) = 131 Hz, <sup>1</sup>J(B,H) = 33 Hz), -35.6 ppm (d, 9B, <sup>1</sup>J(B,H) = 139 Hz); <sup>13</sup>C [<sup>1</sup>H] NMR (CD<sub>3</sub>COCD<sub>3</sub>): δ = 153.2–106.45 (C<sub>aryl</sub>), 75.7 (O-CH<sub>2</sub>-C<sub>aryl</sub>), 71.6 (O-CH<sub>2</sub>), 40.6 (CH<sub>2</sub>), 24.5 (CH<sub>2</sub>), 23.9 (CH<sub>2</sub>), 15.6 (Si-CH<sub>2</sub>), 11.1 (Si-CH<sub>2</sub>), -3.9 ppm (Si-CH<sub>3</sub>); IR (NaCl)  $\tilde{\nu}$  = 3029 (m, C-H<sub>aryl</sub> st), 2940 (m, C-H<sub>alkyl</sub> st), 2515 (s, B-H st), 1245 cm<sup>-1</sup> (Si-C<sub>alkyl</sub>).

**Synthesis of 26:** A solution of **16** (50.0 mg, 0.012 mmol) in THF (1 mL) was added to a solution of NaOH (34 mg, 0.85 mmol) in deoxygenated ethanol (3 mL). The mixture was heated at reflux overnight. After cooling the mixture, the excess of NaOH was precipitated as sodium carbonate by saturating the solution with a stream of CO<sub>2</sub> (g). After filtration the solution was evaporated and treated with cold THF. The precipitate was filtered off through Celite and evaporation of the solvent led **26** as an orange oil. Yield: 39 mg, 76%. <sup>1</sup>H NMR (CD<sub>3</sub>COCD<sub>3</sub>): δ = 7.67 (m, 9H, C-H<sub>aryl</sub>), 7.10 (m, 42H, C-H<sub>aryl</sub>), 6.82 (s, 6H, C-H<sub>aryl</sub>), 5.09 (s, 6H, O-CH<sub>2</sub>-C<sub>aryl</sub>), 4.03 (m, 18H, O-CH<sub>2</sub>), 3.42 (m, 18H; Cc-CH<sub>2</sub>), 2.62 (m, 18H; SiCH<sub>2</sub>CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>), 2.15 (s, 27H; Cc-CH<sub>3</sub>), 1.83 (m, 18H; CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si), 0.92 (m, 18H; SiCH<sub>2</sub>CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>), 0.67 (m, 18H; CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si), 0.05 ppm (m, 54H; Si(CH<sub>3</sub>)<sub>2</sub>); <sup>1</sup>H [<sup>11</sup>B] NMR (CD<sub>3</sub>COCD<sub>3</sub>): δ = 7.67 (m, 9H, C-H<sub>aryl</sub>), 7.10 (m, 42H, C-H<sub>aryl</sub>), 6.82 (s, 6H, C-H<sub>aryl</sub>), 5.09 (s, 6H, O-CH<sub>2</sub>-C<sub>aryl</sub>), 4.03 (m, 18H, O-CH<sub>2</sub>), 3.42 (m, 18H; Cc-CH<sub>2</sub>), 2.62 (m, 18H; SiCH<sub>2</sub>CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>), 2.15 (s, 27H; Cc-CH<sub>3</sub>), 1.83 (m, 18H; CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si), 0.92 (m, 18H; SiCH<sub>2</sub>CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>), 0.67 (m, 18H; CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si), 0.05 (m, 54H; Si(CH<sub>3</sub>)<sub>2</sub>), -2.43 ppm (s, B-H-B); <sup>11</sup>B NMR (CD<sub>3</sub>COCD<sub>3</sub>): δ = -7.77 (d, <sup>1</sup>J(B,H) = 105 Hz, 9B), -8.60 (d, <sup>1</sup>J(B,H) = 102 Hz, 18B), -15.30 (d, <sup>1</sup>J(B,H) = 132 Hz, 18B), -17.79 (d, <sup>1</sup>J(B,H) = 124 Hz, 9B), -18.78 (d, <sup>1</sup>J(B,H) = 126 Hz, 9B), -33.43 (d, <sup>1</sup>J(B,H) = 137 Hz, 9B), -35.87 (d, <sup>1</sup>J(B,H) = 141 Hz, 9B); <sup>13</sup>C [<sup>1</sup>H] NMR (CD<sub>3</sub>COCD<sub>3</sub>, TMS): δ = 158.8–106.4 (C<sub>aryl</sub>), 78.1 (O-CH<sub>2</sub>-C<sub>aryl</sub>), 70.9 (O-CH<sub>2</sub>), 41.4 (Cc-CH<sub>2</sub>), 29.7 (CH<sub>2</sub>CH<sub>2</sub>Si), 23.9 (CH<sub>2</sub>), 22.3 (Cc-CH<sub>3</sub>), 16.8 (Si-CH<sub>2</sub>), 10.8 (Si-CH<sub>2</sub>), -3.4 ppm (Si-CH<sub>3</sub>); IR (NaCl)  $\tilde{\nu}$  = 2960–2870 (m, C-H<sub>alkyl</sub> st), 2517 cm<sup>-1</sup> (s, B-H st).

**Synthesis of 27:** A solution of **17** (50.0 mg, 0.010 mmol) in THF (1 mL) was added to a solution of NaOH (31 mg, 0.76 mmol) in deoxygenated ethanol (3 mL). The mixture was heated at reflux overnight. After cooling the mixture, the excess of NaOH was precipitated as sodium carbonate by saturating the solution with a stream of CO<sub>2</sub> (g). After filtration the solution was evaporated and treated with cold acetone. The precipitate was filtered off through Celite and evaporation of the solvent led **27** as an orange oil. Yield: 37 mg, 72%. <sup>1</sup>H NMR (CD<sub>3</sub>COCD<sub>3</sub>): δ = 7.74–6.81 (m, 102H; C-H<sub>aryl</sub>), 5.00 (s, 6H; O-CH<sub>2</sub>-C<sub>aryl</sub>), 3.96 (m, 18H; O-CH<sub>2</sub>), 3.22 (s, 18H; Cc-CH<sub>2</sub>), 2.60 (m, 18H; SiCH<sub>2</sub>CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>), 1.83 (m, 18H; CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si), 0.88 (m, 18H; SiCH<sub>2</sub>CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>), 0.63 (m, 18H; CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si), 0.02 ppm (s, 54H; Si(CH<sub>3</sub>)<sub>2</sub>); <sup>1</sup>H [<sup>11</sup>B] NMR



(CD<sub>3</sub>COCD<sub>3</sub>):  $\delta$  = 7.74–6.81 (m, 9H; C-H<sub>aryl</sub>), 5.00 (s, 6H; O-CH<sub>2</sub>-C<sub>aryl</sub>), 3.96 (m, 18H; O-CH<sub>2</sub>), 3.22 (s, 18H; Cc-CH<sub>2</sub>), 2.73 (s, B-H), 2.60 (t, <sup>3</sup>J-(H,H) = 9 Hz, 18H; SiCH<sub>2</sub>CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>), 2.41 (s, 1H, B-H), 2.31 (s, 1H, B-H), 2.22 (s, 1H, B-H), 1.83 (m, 18H; CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si), 0.88 (m, 18H, SiCH<sub>2</sub>CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>), 0.63 (m, 18H; CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si), 0.02 (s, 54H; Si(CH<sub>3</sub>)<sub>2</sub>), -2.09 ppm (s, B-H-B); <sup>1</sup>B NMR (CD<sub>3</sub>COCD<sub>3</sub>):  $\delta$  = -7.68 (d, <sup>1</sup>J(B,H) = 92 Hz, 9B), -8.42 (d, <sup>1</sup>J(B,H) = 108 Hz, 9B), -12.28 (d, <sup>1</sup>J(B,H) = 156 Hz, 9B), -15.70 (d, <sup>1</sup>J(B,H) = 132 Hz, 9B), -16.88 (d, <sup>1</sup>J(B,H) = 118 Hz, 9B), -17.68 (d, <sup>1</sup>J(B,H) = 123 Hz, 18B), -32.81 (d, <sup>1</sup>J(B,H) = 128 Hz, 9B), -35.47 (d, <sup>1</sup>J(B,H) = 138 Hz, 9B); <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>3</sub>COCD<sub>3</sub>):  $\delta$  = 158.6–106.4 (C<sub>aryl</sub>), 80.1 (O-CH<sub>2</sub>-C<sub>aryl</sub>), 71.8 (O-CH<sub>2</sub>), 41.8 (Cc-CH<sub>2</sub>), 30.1 (s, CH<sub>2</sub>CH<sub>2</sub>Si), 23.8 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 16.9 (Si-CH<sub>2</sub>), 10.9 (Si-CH<sub>2</sub>), -3.5 ppm (Si-CH<sub>3</sub>); IR (NaCl):  $\tilde{\nu}$  = 2962–2871 (m, C-H st), 2516 cm<sup>-1</sup> (s, B-H st).

**X-ray structure determinations:** Crystallographic data for compound **4**-hexane was collected at 123 K with a Bruker Nonius-Kappa CCD area detector diffractometer, using graphite-monochromatized MoK $\alpha$  radiation ( $\lambda$  = 0.71073 Å). The structure was solved by direct methods by use of the SHELXS-97 program.<sup>[24]</sup> The full-matrix, least-squares refinements on F<sup>2</sup> were performed using SHELXL-97 program.<sup>[24]</sup> The non-hydrogen atoms were refined with anisotropic thermal displacement parameters. Hydrogen atoms were treated as riding atoms using the SHELX97 default parameters.

CCDC-906346 (**4**-hexane) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

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