Synthesis of Low Generation Phenylenealkylene Dendrons as Nonpolar Building Blocks for a Dendrimer Construction Set

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Abstract: The gram scale syntheses of first and second generation (G1 and G2) dendrons **1**–**4**, and **35**, based on aryl and alkyl moieties, by Suzuki–Miyaura cross-coupling are presented. Both a divergent and an accelerated convergent route are applied. In addition, first results on the synthesis of hyperbranched oligomers of AB_2 monomer **19** are reported.

Key words: dendrimers, dendrons, Suzuki–Miyaura cross-coupling, iododesilylation, building blocks

Introduction

One of our aims is to develop a construction set consisting of first (G1) and second generation (G2) dendritic building blocks which carry orthogonally protected functional groups to allow a wide range of combinations.[1] Such a set is of considerable interest not only for the modular and combinatorial synthesis of a variety of spherical dendrimers and dendronized polymers[2] but also for surface modifications.[3] Up to now, we have developed G1 and G2 dendrons with the following orthogonal protecting group patterns (periphery/focal point/connectivity): hydroxy/isocyanate/urethane,[4] hydroxy/acid/amides,[5] amines/acid/amides,[6] and amines/olefin (allyl)/amides.[7] Besides these, dendrons with two differently protected amine groups in the periphery were also constructed.[8] Properties of dendrimers like solubility, glass transition temperature, melting behavior, etc., are very dependent on the nature of their periphery. For applications as energy or electron transfer agents or their ability to act as a host for guest uptake (and release), the interior of dendrimers is also important. Recently we started a project aiming at the creation of a polarity gradient in the interior of dendrimers.[6b,9] For such a goal the construction set lacks nonpolar representatives, like hydrocarbons, with appropriate connecting functions in the periphery and/or at the focal point. Unfortunately, the known all-hydrocarbon dendrons on the basis of oligo(phenylene)s,[10] oligo(phenyleneacetylene)s,[11] oligo(phenylenevinylene)s,[12] and oligo(alkylene)s[13] are not suitable, since they are too different in flexibility and/or in spacer lengths between two phenylene branching units in comparison to other dendrons in our set.[14]

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Here we describe gram scale procedures for the synthesis of nonpolar aryl/alkyl G1 and G2 dendrons employing both divergent and convergent routes. The main synthetic tool is the Suzuki–Miyaura cross-coupling of alkyl boranes with aryl bromides and iodides.[15] This tool was also applied to one of the new AB_2 type monomers to test whether hyperbranched polymers with reasonable molar mass and branching degree can be obtained.[16]

Results and Discussion

Figure 1 shows the four main target dendrons **1**–**4**. They are characterized by threefold benzene branching units which are connected by trimethylene (**1**, **2**) and tetramethylene bridges (**3**, **4**), respectively. Dendrons **1** and **2** each carry two trimethylsilyl (TMS) placeholder functions per terminal phenyl unit and a benzyl protected hydroxyethyl group at the focal point. Dendrons **3** and **4** carry two silyl-protected hydroxypropyl groups per terminal phenyl unit and 1-but-3-enyl groups at the focal point which results in a very efficient, step economic growth reaction (see below). The syntheses for **1** and **2** are divergent, that for **3** and **4** convergent.

Divergent Procedure

The synthesis of dendrons **1** and **2** started from 1,3,5-tribromobenzene (**5**) which was silylated to give compound **6**[17,18] in 80% yield by performing twice the metal–halogen exchange sequence and quenching the generated anion with chlorotrimethylsilane (Scheme 1). The ethanol derivative **7** was obtained by reacting parent oxirane with the Grignard derivative of **6**. Its benzyl protection gave **8**. Subsequent *ipso*-iododesilylation[19] at the position carrying the TMS place holder group[20] with iodine monochloride at –60 °C led to the diiodo compound **9** on a 30 g scale.

The G1 dendron **1** was synthesized from bromide **6** (Scheme 2). Its conversion into the terminal olefin **10** was achieved through reductive metalation and allylation with allyl bromide. Isomerization to the conjugated isomer (not shown) was not observed (high-field NMR) under the conditions applied. In situ hydroboration of **10** with 9-BBNH cleanly furnished the expected *anti*-Markownikow[21] borane **11,** which was not isolated. For the following Suzuki–Miyaura cross-coupling 2.2–2.3 equivalents of borane **11** were reacted with the diiodo compound **9** in the presence of 1–3 mol% of $Pd(Ph_3P)_4$ as

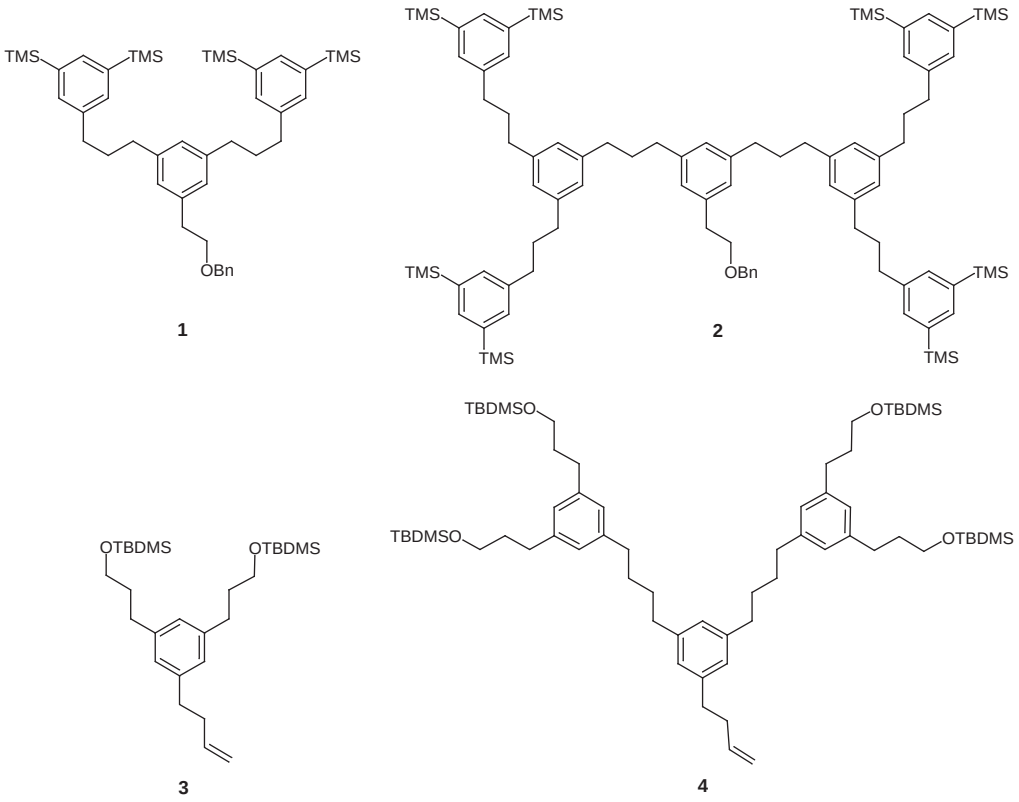
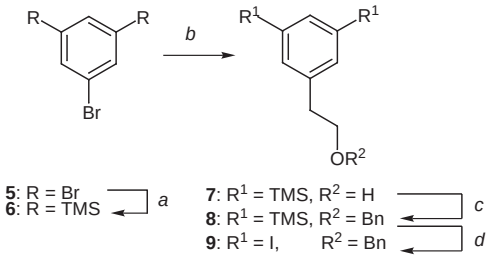
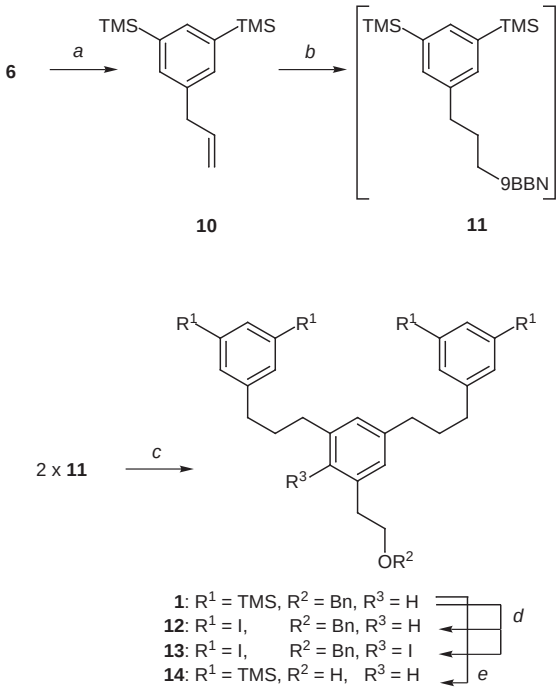


Figure 1 Structures of target dendrons **1**–**4**

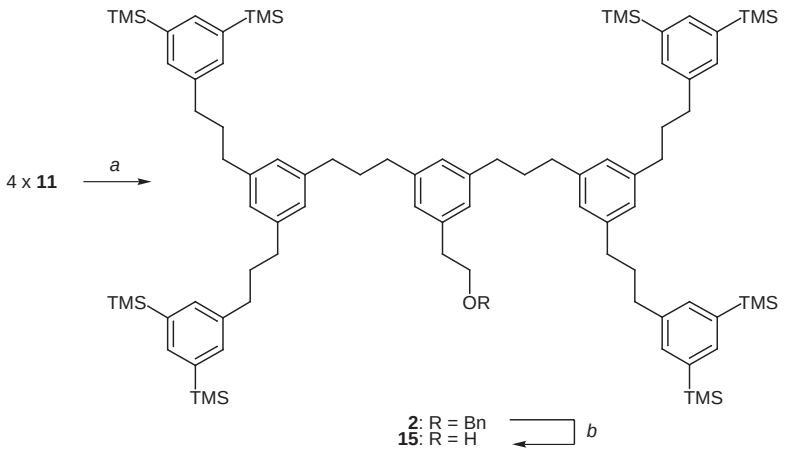


Scheme 1 *Reagents and conditions*: (a) i. BuLi (1 equiv), anhyd Et_2O, –78 °C, ii. TMSCl, –78 °C to r.t., iii. repetition of i and ii, 80%; (b) i. Mg, anhyd THF, reflux, ii. oxirane, 83%; (c) i. *t*-BuONa, anhyd THF, r.t., ii. benzyl bromide, r.t., 95%; (d) ICl, $CHCl_3$, –60 °C, 87%

catalyst precursor to afford G1 dendron **1** in 85–88% yield. The slight excess of borane **11** could easily be separated by column chromatography because it became converted into the more polar corresponding hydroxyborate under the basic coupling conditions. The next step leading to the tetraiodoarene **12** required iododesilylation which is normally conveniently achieved by the addition of iodine monochloride. Even when the reaction was carried out avoiding any excess of ICl and at a temperature as low as –78 °C, the formation of a side product could not be prevented (up to 8% by ^{1}H NMR). Repeated recrystallization or reversed phase HPLC gave the pure byproduct and was characterized as the pentaiodo compound **13** (mass spectrometry, 2D HMQC NMR,[22] see Figure 3 in the experimental section for structure and signal assignment). Obviously the central branching unit is activated by its



Scheme 2 *Reagents and conditions*: (a) i. Mg, anhyd THF, reflux, ii. allyl bromide, 85%; (b) 9-BBNH, anhyd THF, r.t.; (c) i. aq NaOH, ii. **9**, toluene, degas, iii. cat. $Pd(Ph_3P)_4$, reflux, 87%; (d) ICl, $CHCl_3$, –60 °C, 94% of **12**; (e) cyclohexa-1,4-diene, Pd/C (10%), THF, reflux, quant



Scheme 3 *Reagents and conditions*: (a) i. aq NaOH, ii. **12**, toluene, degas, iii. cat. $Pd(Ph_3P)_4$, reflux, 77%; (b) cyclohexa-1,4-diene, Pd/C (10%), THF, reflux, quant

three alkyl substituents to such a degree that it is attacked by the electrophilic iodine monochloride. Recently, conditions were found which allow suppression of this side reaction by applying a solvent combination.[14]

The coupling procedure was repeated with G1 dendron **12** and 4.5–5.0 equivalents of borane **11** to give the G2 dendron **2** in reproducible isolated yields of 77–78% and quantities of about 8 g (Scheme 3). Thus, every step of this fourfold coupling proceeds with at least 94%.

Preliminary experiments showed that the benzylic protecting group can be cleanly removed in the presence of peripheral TMS group. Catalytic hydrogenation of **1** and **2** with Pd/C and cyclohexa-1,4-diene gave deprotected G1-dendron **14** (Scheme 2) and G2-dendron **15**, respectively (Scheme 3). ^{1}H NMR integration did not indicate any loss of TMS.

Convergent Procedure

Figure 2 shows the general structure of the used A^iB_2 monomer where i denotes the inactivity of the focal function A in the coupling step and its potential for an in situ activation. Here, A is an olefinic group whereas B are halogens. The construction methodology starts with the replacement of the peripheral halogens by protected hydroxyalkyl moieties. Hydroxy groups were chosen mainly for two reasons. First, they can serve as suitable connecting units to already existing other dendritic building blocks in the construction set of which many have benzoic acid groups at their focal point. Secondly, the varying number of protected hydroxy groups in different dendrimer generations should facilitate column purification by polarity differences.

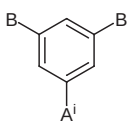
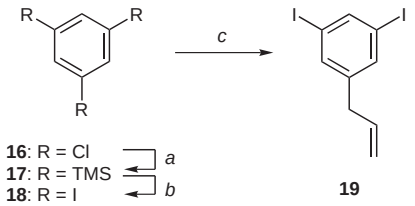


Figure 2 Structure of A^iB_2 monomer

Low generation dendrons were obtained by an accelerated convergent approach whereby every isolated step produces a new generation.[23,24] It uses the fact that the focal olefinic group is inactive during the Pd-catalyzed growth reaction performed at the periphery and can then be easily converted into a coupling functionality by hydroboration. This allows the entire growth step to be performed as a one-pot reaction.

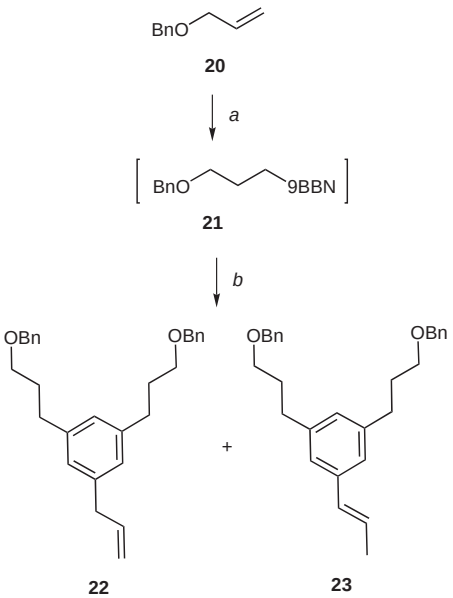
Pd-catalyzed cross-coupling reactions with iodoarenes usually proceed faster and with higher yields than the corresponding bromo compunds. Though 1-allyl 3,5-dibromobenzene has been employed in a convergent dendron synthesis,[7,25] the diiodo derivative **19** was considered superior and synthesized instead (Scheme 4).[26]

1,3,5-Trichlorobenzene (**16**) was silylated threefold in a one-pot reaction in the presence of magnesium and chlorotrimethylsilane to the 1,3,5-tris(trimethylsilyl)benzene (**17**).[27] Subsequent *ipso*-iododesilylation[19] with iodine monochloride at room temperature led to 1,3,5-triiodobenzene (**18**) in an overall yield of 63% on a 100 g scale which was purified by recrystallization. Both this high yield and the simple purification procedure renders this route to triiodobenzene **18** superior to other protocols.[28] Allyl derivative **19** was obtained in up to 86% yield on a 60 g scale by coupling the in situ prepared monolithiation product of **18** with allyl bromide (Scheme 4). The lithiation was performed with butyllithium in toluene. When the same reaction was conducted in diethyl ether or tetrahydrofuran, even at –78 °C, the product always contained butylated and twofold allylated compounds (NMR) which were rather difficult to remove. A reason for this may be the low solubility of the mono lithiated intermediate in toluene which seems to protect it from the side reactions mentioned. It precipitates immediately after addition of butyllithium as finely dispersed particles. This lithiation in toluene is very slow and it took several days to reach completion. Besides small amounts of unaffected **18**, 1,3-diiodobenzene (not shown) was detected as a byproduct, presumably resulting from quenching of unreacted organolithium compound with water.



Scheme 4 *Reagents and conditions*: (a) Mg, TMSCl, anhyd THF, reflux, 70%; (b) ICl, CH_2Cl_2, 0 °C, 90%; (c) i. BuLi (1 equiv), anhyd toluene, r.t., ii. allyl bromide, 86%

Monomer **19** was converted into the G1 dendron **22** in 70% yield by reacting it with the in situ prepared **21**, which is the hydroborated derivative of the benzyl-protected allylic alcohol **20** (Scheme 5). Unfortunately the desired allylic product **22** was accompanied by varying amounts of its styryl isomer **23**. These compounds could easily be differentiated by ^{1}H NMR spectroscopy (see experimental section). Compound **23** was typically formed in yields below 10%, in some cases, however, even 50% was observed. No reaction conditions could be found which suppressed this isomerization in a reproducable manner.[18] Thus, in principle compound **19** should work as a A^iB_2 monomer, the purification requirements for **22**, however, were considered too unattractive to follow this route further.

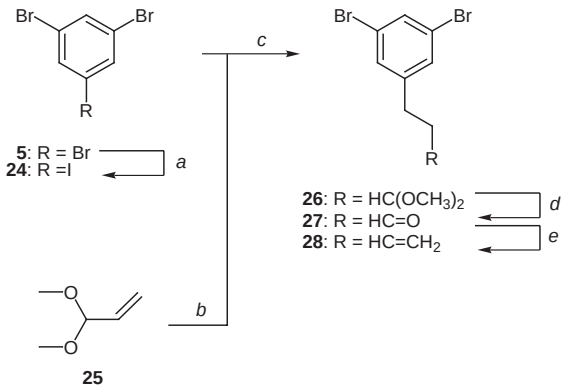


Scheme 5 *Reagents and conditions*: (a) 9-BBNH, anhyd toluene, r.t.; (b) i. aq NaOH, ii. **19**, toluene, degas, iii. cat. $Pd(Ph_3P)_4$, reflux, 70%

Two alternative A^iB_2 monomers were, therefore, considered, one with a methylene group less (a dihalostyrene) and one with an additional methylene group (dihalohomoallylbenzene). Orienting experiments with 3,5-dibromostyrene revealed an unexpectedly high propensity of its bis(hydroxypropyl) functionalized derivative to polymerize. This route was, therefore, not continued.

Finally, the homoallyl variants **28** and **32** led to success (Schemes 6 and 7). The bromo derivative was considered more attractive for lower generation dendrons regarding overall effort, whereas for higher generation the diiodo analogue was also prepared to exploit its generally higher coupling efficiency.

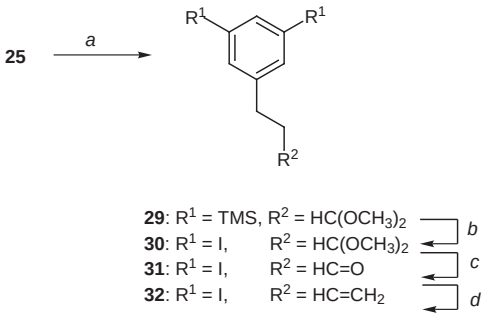
Both compounds were prepared according to four step sequences starting from bromide **5** or **6**. 1,3-Dibromo-5-iodobenzene (**24**)[14,29] was obtained by monolithiation of tribromobenzene **5** in diethyl ether[30] and electrophilic trapping of the resulting organolithium derivative with 1,2-diiodoethane. In situ hydroboration of vinyl acetal **25** with 9-BBNH and Pd-catalyzed coupling of the resulting borane with **24** exploiting the known chemoselectivity of C–I over C–Br groups yielded acetal **26** (Scheme 6). Hydrolysis of **26** to the aldehyde **27** proceeded quantitatively (TLC) with catalytic amounts of DDQ in aqueous acetonitrile solution.[31] Various other conditions, including treatment with acidic resin Amberlyst®-15[32] or tin(II) chloride,[33] only led to partial deprotection. In the case of the dioxolane derivative (not shown) the results were even worse. Aldehyde **27** was unstable on silica gel. The reaction mixture was therefore filtered through Celite to remove DDQ. Standard Wittig reaction produced dibromo olefin **28** in an overall yield of 35% on a 10 g scale.[34] Attempts to obtain aldehyde **27** by selective Heck coupling of iodoarene **24** and allyl alcohol[35] (not shown) yielded a low yield mixture with the twofold coupled byproduct.



Scheme 6 *Reagents and conditions*: (a) i. BuLi (1 equiv) , anhyd Et_2O, –78 °C; ii. 1,2-diiodoethane, –78 °C to r.t., 92%; (b) 9-BBNH, anhyd THF, r.t.; (c) i. THF, aq NaOH, degas, ii. cat. $Pd(Ph_3P)_4$, reflux, 68%; (d) DDQ, MeCN–H_2O (9:1), r.t., 90%; (e) i. Ph_3PCH_2I, BuLi, anhyd THF, 0 °C, ii. **27**, r.t., 63%

A similar strategy was applied for the synthesis of 1-but-3-enyl-3,5-diiodobenzene (**32**) (Scheme 7). The bromoarene **6** was converted into acetal **29**, again by coupling with the hydroboration product of vinylacetal **25**. The iododesilylation step gave the diiodoacetal **30**, which was accompanied by some deprotected aldehyde **31**. It was crucial to perform the iododesilylation at low temperature (–78 °C). At room temperature or 0 °C some α-chlorina-

tion of the alkyl chain occurred as indicated by a ^{13}C NMR signal at δ = 63.8 and the corresponding molecular ion in the mass spectrum. Acetal **30** was not separated, but rather a mixture of **30** and aldehyde **31** was reacted with DDQ to give **31** in a clean conversion. Wittig reaction of **31** resulted in the diiodo olefin **32**.

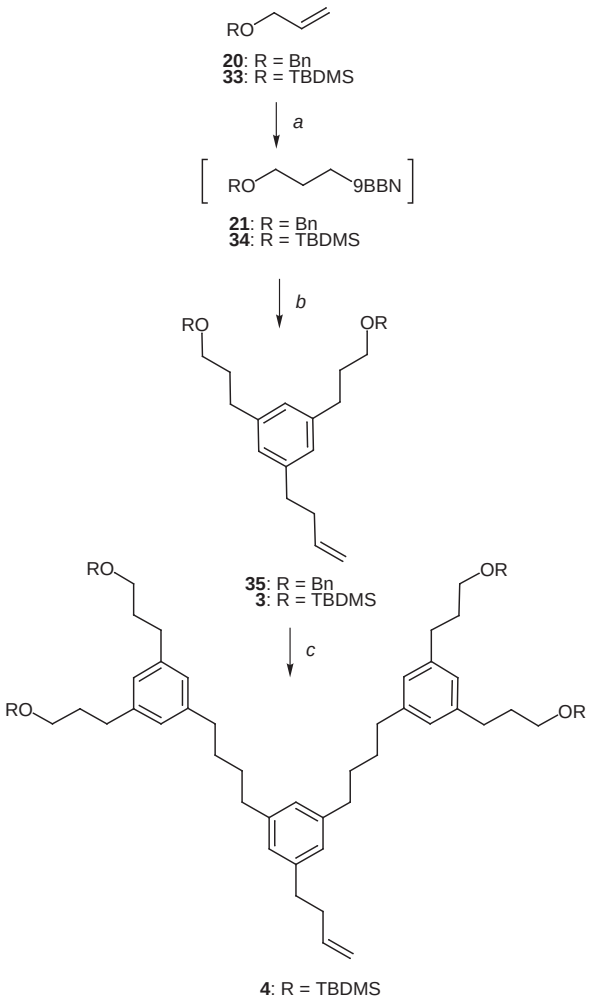


Scheme 7 *Reagents and conditions*: (a) i. 9-BBNH, anhyd THF, r.t., ii. aq NaOH, iii. **6**, degas, iv. cat. $Pd(Ph_3P)_4$, reflux, 76%; (b) ICl, CH_2Cl_2, –78 °C; (c) DDQ, MeCN–H_2O (9:1), r.t.; (d) i. triphenylmethylphosphonium iodide, BuLi, anhyd THF, 0 °C, ii. **31**, r.t., 62%

Both homoallylbenzene derivatives **28** and **32** acted successfully as A^iB_2 monomers. Functionalization of the peripheral halogens proceeded without affecting the homoallyl goup (Scheme 8). Three equivalents of allyl benzyl ether **20** or allyl TBDMS ether **33** were both hydroborated in situ with 9-BBNH to boranes **21** and **34**, respectively, and coupled under standard Suzuki–Miyaura cross-coupling conditions with either the dibromo **28** or the diiodo monomer **32**.[36] The benzylether **35** was isolated in a yield of about 95%, the TBDMS ether **3** 80 (from **28**) and 85% (from **32**). G2 dendron **4** was obtained from G1 building block **3** and iodo monomer **32** in 75% on a 2 g scale. The excess of unreacted borane derivative **34** was easily removed by column chromatography. For the TBDMS ether dendrons **3** and **4**, the desired polarity differences were so small that chromatographic separation of the pure compounds from the monocoupled products resulted in lower isolated yields.[37]

Hyperbranched Oligomer

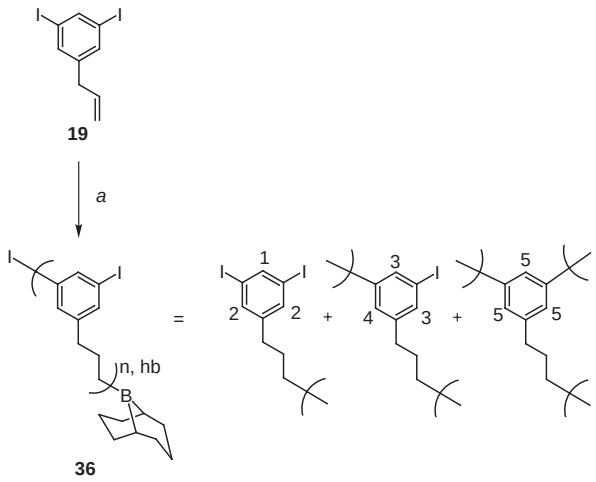
In contrast to dendrons/dendrimers where a few all-hydrocarbon representatives have been reported, there is only one such example for a hyperbranched polymer. This is a poly(phenylene), which was synthesized by Suzuki cross-coupling of 3,5-dibromophenylboronic acid.[38] Considering the importance of unpolar highly branched molecules with a polar surface specifically for transport of unpolar guests in polar media, the A^iB_2 monomer **19** was tested with regard to its ability to polymerize. Activation of its olefinic group by 9-BBN hydroboration followed by typical cross-coupling of the resulting borane [(1–3 d reflux in THF or toluene, NaOH or $Ba(OH)_2$ as base, 1–2 mol% of the freshly prepared catalyst precursor $Pd(Ph_3P)_4$] gave a polymeric material to which tentatively the poly(phenylenepropenylene) structure **36** was assigned



Scheme 8 *Reagents and conditions*: (a) 9-BBNH, anhyd THF, r.t.; (b) i. aq NaOH, ii. **28** or **32** (0.5 equiv), degas, iii. cat. $Pd(Ph_3P)_4$, reflux, 80–95%; (c) i. 9-BBNH, anhyd THF, r.t., ii. aq NaOH, iii. **32**, degas, iv. cat. $Pd(Ph_3P)_4$, reflux, 75%

(Scheme 9). In several runs under different conditions, polymeric material was obtained in yields of 78–95% which was only slightly soluble in common organic solvents. Size exclusion chromatography (SEC) analyses of the THF soluble fractions gave M_n of about 2.000 to 3.000 g/mol, and PDI between 1.35 and 1.50 (polystyrene standard, THF as eluent, r.t.) which corresponds to relatively low degrees of polymerization (DP) of 8–12.[39] In some SEC fractions of masses up to 10 000 g/mol were determined. MALDI TOF mass spectrometric analysis confirmed at least oligomers with a DP of 9. The degree of branching (DB) was determined on the basis of ^1H NMR integration using the method by Frey.[40] The aromatic signals were assigned by comparison with the ones of the parent molecular compounds, diiodotoluene, iodoxylene, and mesitylene. The resonances at δ = 7.82 (H-1) and 7.42 (H-2) stem from the terminal moiety, the signals at δ = 7.30 (H-3) and 6.88 (H-4) from the linear unit and the one at δ = 6.76 (H-5) belong to the dendritic part. Values of about DB = 0.65 were obtained. The compared aromatic signals were not completely baseline separated, and the

DB can therefore only be considered a reasonable estimation. The oligomer **36** shows a broad endothermic transition from 35–55 °C (differential scanning calorimetry) and decomposition at 290 °C (thermogravimetric analysis).



Scheme 9 *Reagents and conditions*: Typical procedure: (a) i. 9-BBNH, anhyd THF, r.t., ii. aq NaOH, degas, iii. cat. $Pd(Ph_3P)_4$, reflux, 94%. Due to its hyperbranched (hb) nature, polymer **36** consists of three different units, the terminal, linear, and dendritic units (from left)

Conclusion and Outlook

The gram scale syntheses of all-hydrocarbon G1 and G2 dendrons by Suzuki–Miyaura cross-coupling of alkyl boranes with aryl halides were presented. Both a divergent and convergent procedure were successfully applied. The latter approach seems to be capable of yielding higher generation dendrons in an accelerated manner since every isolated step yields a new generation. Depending on whether their hydroxy groups are at the periphery or the focal point, the dendrons presented have the promising potential to be used for the construction of higher generations both with a polarity gradient going from the interior to the exterior and the other way around, respectively. For example, the convergently grown dendrons with (protected) hydroxyl groups in the periphery will be connected to some of the dendrons with carboxylic acids at the focal point.[5,6] First results in the synthesis of hyperbranched oligomers of an A^iB_2 monomer by Suzuki–Miyaura cross-coupling were also reported.

All chemicals were purchased from Acros, Aldrich, Fluka, Janssen, or Lancaster and used without further purification. Several compounds were prepared according to literature procedures and gave satisfactory NMR and MS data: **17**,[27] **20**,[41] triphenylmethylphosphonium iodide.[42] $Pd(Ph_3P)_4$ was prepared according to Ref.,[43] stored in a glove box (O_2: <2.0 ppm, H_2O: <0.3 ppm) and used without further characterization. Compounds **6**,[17,44] **10**,[14] **18**[28] and **24**[14,29] were prepared in ways different to the literature procedures, and are described in full detail. All other compounds have not been previously reported. Anhyd toluene, Et_2O, and THF were distilled from sodium/benzophenone ketyl or potassium/benzophenone ketyl; in the cross-coupling reactions toluene used was of p.a. quality. The solvents used in the column chromatography were distilled prior to use. Experiments under a protective atmosphere were carried out under N_2 with a purity of 4.0 and 5.0, purchased from Linde or Messer Griesheim. All reactions with moisture sensitive reagents (e. g., lithiations and hydroborations) were performed in dried glassware. The apparatus was evacuated (~15 mbar), heated with an electric dryer (~500 °C), and flushed with N_2. After cooling, this procedure was repeated. All palladium-catalyzed cross-coupling reactions were carried out under oxygen-free conditions. For this a stream of N_2 was run through the stirred mixture (15–30 min). All reactions were monitored by TLC on silica gel alumina sheets. Some of the compounds were spotted by spraying the TLC plate either with an anisaldehyde stain (solution of 0.5 mL *p*-methoxybenzaldehyde, 50 mL glacial AcOH, and 1 mL concd H_2SO_4) and heating it up to ~100 °C (for boranes, alcohols and ethers), or with an aqueous solution of $KMnO_4$ (0.5%, for olefins). Melting points: Büchi SMP 510 (open capillaries, uncorrected values). NMR: Bruker WH 270, AC 500 (^{1}H: $CDCl_3$ at δ = 7.24, ^{13}C: $CDCl_3$ at δ = 77.00 as internal standards, 20 °C). MS: Perkin-Elmer Varian Type MAT 771 and CH6 (EI), Type CH5DF (FAB), or Bruker Reflex (MALDI-TOF) respectively. MALDI-TOF: UV-Laser (337 nm), delayed extraction source, reflector mode. 2,5-Dihydroxybenzoic acid (DHB) was used as matrix. The high resolution mass spectra were obtained according to the peak match method (MAT 771). Elemental analyses: Perkin-Elmer EA 240. Column chromatography: Merck silica gel 60, 0.040–0.063 mm (230–400 mesh). Analytical TLC: Merck silica gel Si 60, F_{254}, on aluminum sheets. Preparative RP-HPLC: Machery-Nagel, Nucleosil® 5µm C_{18}, 32 × 250 mm, UV detection at 254 nm. Analytical SEC: Waters Styragel HR 1 or HR 3 columns, Waters 2487 UV/VIS detector at 254 nm.

1-Bromo-3,5-bis(trimethylsilyl)benzene (6)

To a solution of 1,3,5-tribromobenzene (**5**; 100.0 g, 318.0 mmol) in Et_2O (1.4 L) was added BuLi (210.0 mL of a 1.6 M solution in hexane, 336.0 mmol, 1.06 equiv) within 30 min at –40 °C. After the mixture had been stirred at –78 °C for 30 min, Me_3SiCl (50.0 mL, 400.7 mmol, 1.19 equiv) was added all at once, and the mixture was allowed to warm up to r.t. The suspension was cooled to –78 °C and BuLi (250.0 mL of a 1.6 M solution in hexane, 400.0 mmol, 1.19 equiv) was added within 15 min. After the addition of chlorotrimethylsilane (60.0 mL, 480.8 mmol, 1.43 equiv) all at once, the mixture was allowed to warm up to r.t. Aq 10% $NaHCO_3$ solution (100 mL) was added, followed by extractive workup with Et_2O (3 × 100 mL), drying ($MgSO_4$), evaporation of the volatile components, and distillation through a vigreux column. Recrystallization of the residue from EtOH (70 mL) at –22 °C gave 81.0 g (85%) of the desired **6** as colorless crystals; bp 65 °C/0.02 mbar.

^{1}H NMR (270 MHz, $CDCl_3$): δ = 0.30 (s, 18 H), 7.58 (s, 2 H), 7.65 (s, 1 H).

^{13}C NMR (68 MHz, $CDCl_3$,): δ = –1.16, 123.41, 136.19, 136.33, 142.95.

MS (EI, 70 eV, 40 °C): *m*/*z* (%) = 302 (17, $[M]^+$), 287 (100, $[M - CH_3]^+$).

Anal. Calcd for $C_{12}H_{21}BrSi_2$ (301.37): C, 47.82; H, 7.02. Found: C, 47.59; H, 6.87.

2-[3,5-Bis(trimethylsilyl)phenyl]ethanol (7)

Ethylene oxide (oxirane, 15 mL) was condensed into THF (20 mL), and added dropwise to an ice-cold Grignard solution prepared from 1-bromo-3,5-bis(trimethylsilanyl)benzene (**6**; 65.7 g, 218.0 mmol) and Mg (6.4 g, 263.3 mmol, 1.2 equiv) in THF (150 mL). The solution was stirred overnight, and brine (200 mL) was added. After acidification with AcOH (~ pH 5), the separated aqueous phase was extracted with Et_2O (3 × 100 mL), the combined organic phases

were dried ($MgSO_4$), and evaporated. The crude product was distilled to give the alcohol **7** as a colorless oil in 83% yield (48.2 g); bp 95 °C/0.014 mbar.

^{1}H NMR (270 MHz, $CDCl_3$): δ = 0.30 [s, 18 H, Si(CH_3)$_3$], 1.56 (s, 1 H, OH), 3.38 (t, ^3J = 7.0 Hz, 2 H, Ar-CH_2), 3.88 (t, ^3J = 7.0 Hz, 2 H, CH_2OH), 7.36 (s, 2 H, Ar-H), 7.55 (s, 1 H, Ar-H).

^{13}C NMR (68 MHz, $CDCl_3$,): δ = –1.44, 39.27, 63.26, 134.28, 135.77, 136.69, 138.92.

MS (EI, 70 eV, 40 °C): *m*/*z* (%) = 266 (16, $[M]^+$), 251 (100, $[M - CH_3]^+$).

Anal. Calcd for $C_{14}H_{26}OSi_2$ (266.53): C, 63.09; H, 9.83. Found: C, 62.85; H, 9.69.

1-(2-Benzyloxyethyl)-3,5-bis(trimethylsilyl)benzene (8)

To a stirred solution of alcohol **7** (21.9 g, 82.2 mmol) and *t*-BuONa (21.1 g, 219.5 mmol, 2.7 equiv) in THF (150 mL) was slowly added benzyl bromide (20.0 mL, 168.4 mmol, 2.05 equiv) via a syringe. After stirring overnight, brine (200 mL) was added. The separated aqueous phase was extracted with Et_2O (3 × 100 mL), the combined organic phases were dried ($MgSO_4$), and the resulting oil was distilled in vacuo to give 27.7 g (95%) of a colorless oil; bp 131 °C/0.014 mbar.

^{1}H NMR (270 MHz, $CDCl_3$): δ = 0.39 [s, 18 H, Si(CH_3)$_3$], 3.04 (t, ^3J = 7.0 Hz, 2 H, Ar-CH_2), 3.82 (t, ^3J = 7.0 Hz, 2 H, CH_2CH_2O), 4.62 (s, 2 H, Ar-CH_2), 7.40 (m, 5 H, Ar-H), 7.48 (s, 2 H, Ar-H), 7.63 (s, 1 H, Ar-H).

^{13}C NMR (68 MHz, $CDCl_3$): δ = –1.06, 36.61, 71.50, 72.93, 127.45, 127.54, 128.29, 134.55, 136.06, 137.20, 138.44, 139.41.

MS (EI, 70 eV, 60 °C): *m*/*z* (%) = 356 (22, $[M]^+$), 73 (100, $[SiMe_3]^+$).

Anal. Calcd for $C_{21}H_{32}OSi_2$ (356.65): C, 70.72; H, 9.04. Found: C, 70.40; H, 8.76.

1-(2-Benzyloxyethyl)-3,5-diiodobenzene (9); Typical Procedure

A stirred solution of **8** (27.6 g, 77.4 mmol) in $CHCl_3$ (100 mL) was cooled to –60 °C, and a solution of ICl (26.4 g, 162.6 mmol, 2.1 equiv) in $CHCl_3$ (50 mL) was added dropwise. After stirring 1.5 h at this temperature, a solution of $Na_2S_2O_5$ (20 g) in H_2O (100 mL) was added, and the mixture was stirred for additional 30 min. The separated aqueous phase was washed with $CHCl_3$ (3 × 50 mL), the collected organic phases were dried ($MgSO_4$), and the solvent was evaporated. The diiodo compound **9** was recrystallized from CH_2Cl_2, and 31.1 g (87%) were obtained as colorless, long needles; mp 82 °C.

^{1}H NMR (270 MHz, $CDCl_3$): δ = 2.78 (t, ^3J = 7.0 Hz, 2 H, CH_2CH$_2$O), 3.63 (t, ^3J = 7.0 Hz, 2 H, CH_2CH_2O), 4.49 (s, 2 H, ArCH_2O), 7.29 (m, 5 H, Ar-H), 7.53 (s, 2 H, Ar-H), 7.89 (s, 1 H, Ar-H).

^{13}C NMR (67 MHz, $CDCl_3$): δ = 35.31, 69.95, 72.99, 94.66, 127.58, 127.63, 128.40, 137.25, 137.96, 142.81, 143.40.

MS (EI, 70 eV, 100 °C): *m*/*z* (%) = 464 (29), 91 (100, $[C_7H_7]^+$).

Anal. Calcd for $C_{15}H_{14}I_2O$ (464.08): C, 38.82; H, 3.04. Found: C, 38.71; H, 2.73.

1-Allyl-3,5-bis(trimethylsilyl)benzene (10)

To a refluxing Grignard solution prepared from 1-bromo-3,5-bis(trimethylsilyl)benzene (**6**; 36.6 g, 121.4 mmol) and Mg (3.1 g, 127.6 mmol, 1.05 equiv) in THF (100 mL), was added dropwise a solution of allyl bromide (15.0 mL, 181.8 mmol, 1.5 equiv) in THF (50 mL). After refluxing overnight, the mixture was cooled to r.t., and brine (200 mL) was added. The separated aqueous phase was extracted with Et_2O (3 × 100 mL), the combined organic phases were dried ($MgSO_4$), and the resulting oil obtained after evaporation of the solvent was distilled in vacuo to give 27.2 g (85%) of a colorless oil **10**; bp 53 °C/0.010 mbar.

^{1}H NMR (270 MHz, $CDCl_3$): δ = 0.41 [s, 18 H, Si(CH_3)$_3$], 3.54 (d, ^3J = 7.5 Hz, 2 H, Ar-CH_2), 5.19–5.29 (m, 2 H, CH=CH_2), 6.13 (m, 1 H, CH=CH$_2$), 7.41 (s, 2 H, Ar-H), 7.61 (s, 1 H, Ar-H).

^{13}C NMR (68 MHz, $CDCl_3$): δ = -1.03, 40.51, 115.72, 134.15, 135.97, 137.59, 138.22, 139.59.

MS (EI, 80 eV, 20 °C): *m*/*z* (%) = 262 (16; $[M]^+$, 247 (100, $[M - CH_3]^+$).

Anal. Calcd for $C_{15}H_{26}Si_2$ (262.54): C, 68.62; H, 9.98. Found: C, 68.31; H, 9.71.

1-(2-Benzyloxyethyl)-3,5-bis{3-[3,5-bis(trimethylsilyl)phenyl]-propyl}benzene (1); Typical Procedure

A solution of **10** (16.9 g, 64.4 mmol) and 9-BBNH (7.9 g, 64.7 mmol, 1.01 equiv) in THF (180 mL) was stirred overnight. After removing the solvent toluene (130 mL), aq 1 M NaOH (80 mL), and **9** (13.3 g, 28.7 mmol, 0.45 equiv) were added to the degassed solution. The catalyst precursor $Pd(Ph_3P)_4$ (980 mg, 0.85 mg, 1.5 mol%) was added, and the resulting suspension was refluxed overnight. After cooling to r.t., the phases were separated, the aqueous phase was extracted with toluene (3 × 50 mL), the combined organic phases were washed with H_2O (50 mL) and dried ($MgSO_4$). After removal of the solvent, the residual oil was chromatographed on silica gel (EtOAc–hexanes, 1:20) to give **1** as a viscous oil; yield: 18.4 g (87%); R_f 0.64 (EtOAc–hexanes, 1:6).

^{1}H NMR (270 MHz, $CDCl_3$): δ = 0.32 [s, 36 H, Si(CH_3)$_3$], 2.00 (quintet, ^3J = 7.5 Hz, 4 H, CH_2CH_2CH$_2$), 2.70 (m, 8 H, Ar-CH_2), 2.95 (t, ^3J = 7.5 Hz, 2 H, Ar-CH_2), 3.73 (t, ^3J = 7.0 Hz, 2 H, CH_2CH_2O), 4.57 (s, 2 H, Ar-CH_2), 6.95 (s, 3 H, Ar-H), 7.25–7.37 (m, 5 H, Ar-H), 7.41 (s, 4 H, Ar-H), 7.56 (s, 2 H, Ar-H).

^{13}C NMR (68 MHz, $CDCl_3$): δ = –1.00, 33.21, 35.60, 35.89, 36.36, 71.37, 72.95, 126.59, 127.50, 127.60, 128.32, 134.05, 135.63, 138.41, 138.82, 139.34, 140.50, 142.36.

MS (EI, 70 eV, 150 °C): *m*/*z* (%) = 736 (1, $[M]^+$).

Anal. Calcd for $C_{45}H_{68}OSi_4$ (737.38): C, 73.30; H, 9.29. Found: C, 73.09; H, 9.12.

1-(2-Benzyloxyethyl)-3,5-bis[3-(3,5-diiodophenyl)propyl]-benzene (12)

Following the typical procedure described for the preparation of **9**, the reaction was carried out with **1** (12.5 g, 16.9 mmol), ICl (17.0 g, 104.7 mmol, 6.2 equiv), $CHCl_3$ (200 mL), and worked up with $Na_2S_2O_5$ (20 g) in H_2O (100 mL). Recrystallization from Et_2O gave 15.1 g (94%) of the tetraiodo compound **12** as colorless, short needles; mp 83 °C. The pentaiodo compound **13** was obtained as a side product (see below).

^{1}H NMR (270 MHz, $CDCl_3$): δ = 1.92 (m, 4 H, CH_2CH_2CH$_2$), 2.50 (t, ^3J = 7.5 Hz, 4 H, Ar-CH_2), 2.60 (t, ^3J = 7.5 Hz, 4 H, Ar-CH_2), 2.93 (t, ^3J = 7.0 Hz, 2 H, Ar-CH_2), 3.73 (t, ^3J = 7.0 Hz, 2 H, CH_2CH_2O), 4.57 (s, 2 H, Ar-CH_2), 6.83 (s, 1 H, Ar-H), 6.89 (s, 2 H, Ar-H), 7.32 (m, 5 H, Ar-H), 7.49 (s, 4 H, Ar-H), 7.89 (s, 2 H, Ar-H).

^{13}C NMR (68 MHz, $CDCl_3$): δ = 32.38, 34.49, 35.05, 36.25, 71.23, 72.89, 94.83, 126.41, 126.71, 127.48, 127.53, 127.66, 128.25, 139.07, 140.37, 141.61, 142.38, 146,48.

MS (EI, 70 eV, 250 °C): *m*/*z* (%) = 952 (100, $[M]^+$).

Anal. Calcd for $C_{33}H_{32}I_4O$ (952.23): C, 41.62; H, 3.39. Found: C, 41.49; H, 3.27.

1-(2-Benzyloxyethyl)-4-iodo-3,5-bis[3-(3,5-diiodophenyl)-propyl]benzene (13)

Pentaiodo compound **13** (Figure 3) was obtained as a side product in the synthesis of G1 **12**. It was separated either by recrystallization (EtOAc–toluene) or reversed phase HPLC: t_R 5.3 min at 28 mL/min vs t_R 4.7 min of **12**; mp 92–93 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.88 (m, 4 H, H-6, H-6′), 2.52 (m, 4 H, H-5, 7), 2.59 (t, 2 H, ^3J = 7.7 Hz, H-7′), 2.75 (t, ^3J = 7.7 Hz, 2 H, H-5′), 3.12 (t, ^3J = 7.0 Hz, 2 H, H-12), 3.70 (t, ^3J = 7.0 Hz, 2 H, H-13), 4.56 (s, 2 H, H-14), 6.81 (d, ^4J = 2.0 Hz, 1 H, H-4), 6.92 (s, ^4J = 2.0 Hz, 1 H, H-2), 7.31 (m, 5 H, H-16, 17, 18), 7.45 (d, ^4J = 1.3 Hz, 2 H, H-9), 7.53 (d, ^4J = 1.3 Hz, 2 H, H-9′), 7.87 (d, ^4J = 1.3 Hz, 2 H, H-11, 11′).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 31.19 (C-6′), 32.09 (C-6), 34.25, 34.32 (C-5, 7), 34.60 (C-7′), 41.43 (C-5′), 42.13 (C-12), 69.54 (C-13), 72.78 (C-14), 94.87, 94.89 (C-10, 10′), 104.20 (C-2′), 127.49 (C-16, 18), 127.56 (C-4), 128.15 (C-2), 128.27 (C-17), 136.72, 136,76 (C-9, C-9′), 138.21 (C-15), 141.18 (C-3), 142.11 (C-1), 142.36 (C-11, 11′), 144.94 (C-3′), 146.11, 146.14 (C-8, 8′).

MS (EI, 70 eV, 270 °C): *m*/*z* (%) = 1078 (2, $[M]^+$), 987 (3, $[M - C_7H_7]^+$), 972 (2, $[M - C_7H_7O]^+$), 952 (2, $[M - I]^+$), 845 (100, $[M - C_7H_7O - I]^+$).

Anal. Calcd for $C_{33}H_{31}I_5O$ (1078.12): C, 36.76; H, 2.90. Found: C, 36.88; H, 2.88.

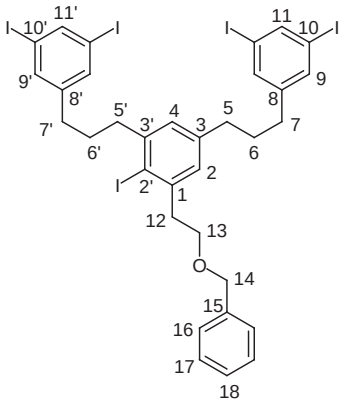


Figure 3 Structure of byproduct **13**, elucidated by 2D NMR

1-(2-Benzyloxyethyl)-3,5-bis[3-(3,5-bis{3-[3,5-bis(trimethylsilyl)phenyl]propyl}phenyl)propyl]benzene (2)

Following the typical procedure described for the preparation of **1**, the reaction was carried out with **10** (8.5 g, 32.4 mmol), 9-BBNH (4.0 g, 32.8 mmol, 1.01 equiv), THF (150 mL), toluene (75 mL), aq 1 M NaOH (75 mL), **12** (6.5 g, 6.8 mmol, 0.21 equiv), and $Pd(Ph_3P)_4$ (844 mg, 0.73 mmol, 2.7 mol%). The resulting viscous oil was dried at 80 °C in high vacuo to give **2** as a resin-like substance; yield: 7.8 g (77%); R_f 0.71 (EtOAc–hexanes, 1:6).

^{1}H NMR (270 MHz, $CDCl_3$): δ = 0.32 [s, 72 H, $Si(CH_3)_3$], 2.03 (m, 12 H, $CH_2CH_2CH_2$), 2.70 (m, 24 H, ArCH_2), 2.93 (t, ^3J = 7.0 Hz, 2 H, Ar-CH_2), 3.72 (t, ^3J = 7.0 Hz, 2 H, CH_2CH_2O), 4.56 (s, 2 H, Ar-CH_2), 7.02 (s, 9 H, Ar-H), 7.42 (m, 5 H, Ar-H), 7.49 (s, 8 H, Ar-H), 7.66 (s, 4 H, Ar-H).

^{13}C NMR (68 MHz, $CDCl_3$): δ = –1.00, 33.21, 35.60, 35.69, 35.86, 36.32, 71.39, 72.91, 125.84, 126.09, 126.52, 126.89, 127.46, 127.57, 128.29, 128.66, 134.06, 135.60, 138.39, 138.70, 139.30, 139.69, 139.82, 140.50, 142.25, 142.32.

MS (EI, 70 eV, 350 °C): *m*/*z* (%) = 1489 (1, $[M]^+$), 325 (100), 73 (70, $[TMS]^+$).

Anal. Calcd for $C_{93}H_{140}OSi_8$ (1498.79): C, 74.53; H, 9.41. Found: C, 74.35; H, 9.16.

Cleavage of Benzyl Group; General Procedure

A mixture of the respective benzyl ether **1** or **2**, cyclohexa-1,4-diene and 10% Pd/C in THF was refluxed overnight. The cooled suspension was filtered through Celite, and the volatile components were evaporated at elevated temperature in high vacuo to give an analytically pure, colorless, highly viscous oil in virtually quantitative yield.

2-(3,5-Bis{3-[3,5-bis(trimethylsilyl)phenyl]propyl}phenyl)-ethanol (14)

This compound was prepared starting from **1** (3.0 g, 4.1 mmol), cyclohexa-1,4-diene (6.4 g, 80 mmol), and 10% Pd/C (0.3 g); yield: 2.63 g (99%).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.38 [s, 36 H, $Si(CH_3)_3$], 1.77 (s, 1 H, OH), 2.13 (m, 4 H, $CH_2CH_2CH_2$), 2.83 (m, 8 H, Ar-CH_2), 2.97 (t, ^3J = 7.0 Hz, 2 H, Ar-CH_2), 3.98 (t, ^3J = 7.0 Hz, 2 H, CH_2CH_2O), 7.06 (s, 2 H, Ar-H), 7.10 (s, 4 H, Ar-H), 7.48 (s, 4 H, Ar-H), 7.67 (s, 2 H, Ar-H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = –1.01, 33.19, 35.62, 35.87, 39.15, 63.68, 126.09, 126.57, 134.05, 135.61, 139.33, 140.50, 142.27, 142.67.

MS (EI, 70 eV, 180 °C): *m*/*z* (%) = 646 (6, $[M]^+$).

Anal. Calcd for $C_{38}H_{62}OSi_4$ (647.25): C, 70.52; H, 9.65. Found: C, 70.30; H, 9.30.

2-{3,5-Bis[3-(3,5-bis{3-[3,5-bis(trimethylsilyl)phenyl]propyl}-phenyl)propyl]phenyl}ethanol (15)

This compound was prepared strating from **2** (3.0 g, 2.0 mmol), cyclohexa-1,4-diene (3.2 g, 40 mmol), and 10% Pd/C (0.3 g); yield: 2.80 g (99%).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.36 [s, 72 H, $Si(CH_3)_3$], 1.45 (s, 1 H, OH), 2.05 (m, 12 H, $CH_2CH_2CH_2$), 2.70 (m, 24 H, Ar-CH_2), 2.80 (t, ^3J = 7.0 Hz, 2 H, Ar-CH_2), 3.87 (t, ^3J = 7.0 Hz, 2 H, CH_2CH_2O), 6.95 (m, 9 H, Ar-H), 7.43 (s, 8 H, Ar-H), 7.60 (s, 4 H, Ar-H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = –0.98, 31.21, 31.73, 32.46, 35.66, 35.54, 35.86, 39.13, 63.63, 126.61, 126.66, 126.81, 126.87, 134.01, 138.33, 138.93, 139.07, 139.58, 139.82, 141.52, 142.34.

MS (EI, 70 eV, 350 °C): *m*/*z* (%) = 1408 (4, $[M]^+$).

Anal. Calcd for $C_{86}H_{134}OSi_8$ (1408.69): C, 73.33; H, 9.59. Found: C, 73.21; H, 9.36.

1,3,5-Triiodobenzene (18)

To a solution of **17** (66.0 g, 224.0 mmol) in CH_2Cl_2 (1000 mL) was added a solution of ICl (122.4 g, 754.0 mmol, 3.4 equiv) in CH_2Cl_2 (400 mL) at r.t. within 3 h. Cooling with an ice/water bath was necessary. The product precipitated, and the suspension was stirred overnight. After removal of excess ICl with aq $Na_2S_2O_5$ solution, the layers were separated and the aqueous layer was washed with CH_2Cl_2. The combined organic layers were dried ($MgSO_4$) and filtered. Some of the solvent was evaporated and the precipitated product was filtered under suction. Recrystallization from the concentrated filtrate was repeated three times to yield 91.7 g (90%) of **18** as colorless crystals. The product was stored under exclusion of light to avoid brownish discoloring; mp. 183 °C (Lit.[28a] mp 184 °C, Lit.[28c] mp 183 °C).

^{1}H NMR (270 MHz, $CDCl_3$): δ = 7.98 (s).

^{13}C NMR (63 MHz, $CDCl_3$): δ = 95.21, 144.42.

MS (EI, 80 eV, 50 °C): *m*/*z* (%) = 456 (100, $[M]^+$).

anal. Calcd for $C_6H_3I_3$ (455.80): C, 15.81; H, 0.66. Found: C, 15.98; H, 0.60.

1-Allyl-3,5-diiodobenzene (19)

To a suspension of 1,3,5-triiodobenzene (**18**; 84.4 g, 185.2 mmol) in toluene (1000 mL) was added a 1.6 M solution of BuLi in hexane (116.0 mL, 185.6 mmol, 1.00 equiv) within 60 min at r.t. After 3 d, allyl bromide (25.0 mL, 303.6 mmol, 1.64 equiv) was added all at once and the mixture was stirred for an additional one day with a mechanical stirrer. H_2O (500 mL) was added, the phases separated, and the aqueous layer was extracted with toluene twice. The combined organic layers were dried ($MgSO_4$), and evaporated to give 70 g of a brownish oil. Distillation utilizing a vigreux column gave 58.7 g (86%) of the desired **19** as a colorless, mobile oil. Long, colorless needles were obtained by recrystallization from EtOH at –22 °C, but these crystals were not stable at r.t. (22 °C); bp 75 °C/0.008 mbar. 1,3-Diiodobenzene was identified as a side product.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.25 (d, ^3J = 6.5 Hz, 2 H), 5.03–5.14 (m, 2 H), 5.86 (m, 1 H), 7.49 (d, ^4J = 1.3 Hz, 2 H), 7.87 (d, ^4J = 1.3 Hz, 1 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 39.08, 94.91, 117.22, 135.57, 136.87, 142.72, 144.11.

MS (EI, 70 eV, 25 °C): *m*/*z* (%) = 370 (100, $[M]^+$).

Anal. Calcd for $C_9H_8I_2$ (369.97): C, 29.22; H, 2.18. Found: C, 28.92; H, 1.69.

1-Allyl-3,5-bis(3-benzyloxypropyl)benzene (22); Typical Procedure

Allyl benzyl ether (**20**; 7.6 g, 51.1 mmol, 2.07 equiv) and 9-BBNH (6.3 g, 51.4 mmol, 2.08 equiv) were suspended in toluene (100 mL) and stirred for one day at r.t. After addition of aq NaOH (1 M, 60 mL) and 1-allyl-3,5-diiodobenzene (**19**; 9.1 g, 24.7 mmol), the suspension was degassed. The catalyst precursor $Pd(Ph_3P)_4$ (1.07 g, 9.3 × 10^{-4} mol, 1.8 mol% per coupling) was added and the suspension was stirred under gentle reflux for 16 h. Usual extractive workup with toluene and purification by column chromatography on silica gel (hexanes–EtOAc, 20:1) yielded 7.1 g (70%) of **22** as a colorless oil; R_f 0.52 (hexanes–EtOAc, 6:1). The product was accompanied by varying amounts of the styrene derivative **23**, identified by the signals in the ^{1}H NMR spectra [δ = 1.88 (d, 3 H), 6.21 (m, 1 H), 6.38 (d, ^3J = 15 Hz, 1 H)].

^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.96 (m, 4 H), 2.71 (t, ^3J = 6.5 Hz, 4 H), 3.37 (d, ^3J = 6.5 Hz, 2 H), 3.53 (t, ^3J = 7.0 Hz, 4 H), 4.58 (s, 4 H), 5.06–5.17 (m, 2 H), 6.00 (m, 1 H), 6.89 (s, 3 H), 7.27–7.44 (m, 10 H).

^{13}C NMR (63 MHz, $CDCl_3$): δ = 31.35, 32.01, 40.12, 69.53, 72.81, 115.54, 126.17, 126.38, 127.42, 127.55, 128.26, 137.54, 138.52, 139.90, 142.03.

MS (EI, 80 eV, 170 °C): *m*/*z* (%) = 414 (2, $[M]^+$), 91 (100, $[C_7H_7]^+$).

Anal. Calcd for $C_{29}H_{34}O_2$ (414.58): C, 84.02; H, 8.27. Found: C, 83.59; H 7.98.

1,3-Dibromo-5-iodobenzene (24)

To a solution of 1,3,5-tribromobenzene (**5**; 13.4 g, 42.7 mmol) in Et_2O (300 mL) was added BuLi (27.0 mL of a 1.6 M solution in hexane, 43.2 mmol, 1.01 equiv) within 30 min at –78 °C. After an additional hour, solid 1,2-diiodoethane (12.2 g, 43.1 mmol, 1.01 equiv) was added all at once, and the mixture was allowed to warm up to r.t. H_2O (100 mL) was added, followed by usual extractive workup with CH_2Cl_2. Recrystallization from Et_2O gave 14.2 g (92%) of the desired **24** as colorless crystals. The product was stored under exclusion of light to avoid brownish discoloring; mp 118 °C.[45]

^{1}H NMR (270 MHz, $CDCl_3$): δ = 7.62 (s, ^4J = 1.7 Hz, 1 H), 7.77 (s, ^4J = 1.7 Hz, 2 H).

^{13}C NMR (63 MHz, $CDCl_3$): δ = 94.43, 123.34, 133.60, 138.46.

MS (EI, 80 eV, 60 °C): *m*/*z* (%) = 362 (100, $[C_6H_3{}^{79}Br^{81}BrI]^+$).

Anal. Calcd for $C_6H_3Br_2I$ (361.80): C, 19.92; H, 0.84. Found C, 19.82; H, 0.89.

1,3-Dibromo-5-(3,3-dimethoxypropyl)benzene (26); Typical Procedure

3,3-Dimethoxypropene (**25**;10.2 mL, 88.6 mmol) was added to a 0.5 M solution of 9-BBNH in THF (200.0 mL, 100.0 mmol, 1.13 equiv) at 0 °C, and the mixture was stirred for 20 h at r.t. After addition of 1,3-dibromo-5-iodobenzene (**24**; 32.1 g, 88.7 mmol, 1.00 equiv), the catalyst precursor $Pd(Ph_3P)_4$ (1.00 g, 8.65 × 10^{-4} mol, 0.98 mol%), aq NaOH (3 M, 85 mL) and additional THF (50 mL), the suspension was stirred under reflux for 20 h. The mixture was cooled with ice/water, and 30% aq H_2O_2 (35 mL) was added carefully. Extractive workup with Et_2O and column chromatography on silica gel (hexanes, then hexanes–EtOAc, 15:1) gave 20.4 g (68%) of **26** as a colorless oil; R_f 0.23 (hexanes–EtOAc, 10:1).

^{1}H NMR (270 MHz, $CDCl_3$): δ = 1.85 (m, 2 H), 2.59 (d, ^3J = 7.5 Hz, 2 H), 3.33 (s, 6 H), 4.39 (t, ^3J = 6.0 Hz, 1 H), 7.25 (s, 2 H), 7.48 (s, 1 H).

^{13}C NMR (63 MHz, $CDCl_3$): δ = 30.17, 33.58, 52.80, 103.26, 122.76, 130.25, 131.56, 145.58.

MS (EI, 80 eV, 40 °C): *m*/*z* (%) = 338 (7, $[C_{11}H_{14}{}^{79}Br^{81}BrO_2]^+$), 75 (100, $[HC(OCH_3)_2]^+$).

HRMS: *m*/*z* Calcd for $C_{11}H_{14}Br_2O_2$ 335.97605; found 335.93298.

3-(3,5-Dibromophenyl)propionaldehyde (27)

1,3-Dibromo-5-(3,3-dimethoxypropyl)benzene (**26**; 9.4 g, 27.8 mmol) was dissolved in a mixture of MeCN (120 mL) and H_2O (13 mL). After addition of DDQ (0.6 g, 2.7 mmol, 0.1 equiv), the dark red suspension was stirred at r.t. for 18 h. After filtration of the mixture through Celite to remove DDQ and elution with CH_2Cl_2 the product was not further purified, since aldehyde **27** was unstable on silica gel. The solvent was evaporated to give 7.3 g (90%) of **27** as a colorless oil; R_f 0.20 (hexanes–EtOAc, 6:1).

^{1}H NMR (270 MHz, $CDCl_3$): δ = 2.78 (m, 4 H), 7.24 (s, 2 H), 7.44 (s, 1 H), 9.74 (s, 1 H).

^{13}C NMR (63 MHz, $CDCl_3$): δ = 27.13, 44.38, 122.80, 130.10, 131.81, 144.30, 199.98.

1-But-3-enyl-3,5-dibromobenzene (28); Typical Procedure

To a suspension of triphenylmethylphosphonium iodide (9.3 g, 23.1 mmol) in THF (100 mL) was added BuLi (14.3 mL of a 1.6 M solution in hexane, 22.9 mmol, 0.99 equiv) at 0 °C within 5 min, and the resulting orange solution was stirred for an additional 45 min. A solution of 3-(3,5-dibromophenyl)propionaldehyde (**27**; 6.1 g, 20.9 mmol, 0.90 equiv) in THF (20 mL) was added dropwise and the reaction mixture was stirred at r.t. for 2 h. The solution was decanted, the residue was washed with Et_2O (3 ×), the combined organic layers were dried ($MgSO_4$). Purification by column chromatography on silica gel (hexanes) gave 3.8 g (63%) of **28** as a colorless oil; R_f 0.58 (hexanes); bp 65 °C/0.01 mbar.

^{1}H NMR (270 MHz, $CDCl_3$): δ = 2.33 (q, ^3J = 8.0 Hz, 2 H), 2.64 (t, ^3J = 8.0 Hz, 2 H), 5.02 (m, 2 H), 5.78 (m, 1 H), 7.25 (s, 2 H), 7.47 (s, 1 H).

^{13}C NMR (63 MHz, $CDCl_3$): δ = 34.63, 34.79, 115.70, 122.67, 130.27, 131.48, 136.84, 145.65.

MS (EI, 80 eV, 40 °C): *m*/*z* (%) = 290 (30, $[C_{10}H_{10}{}^{79}Br^{81}Br]^+$), 249 (100, $[C_7H_5{}^{79}Br^{81}Br]^+$).

Anal. Calcd for $C_{10}H_{10}Br_2$ (289.99): C, 41.42; H, 3.48. Found: C, 41.41; H, 3.07.

1,3-Bis(trimethylsilyl)-5-(3,3-dimethoxypropyl)benzene (29)
Following the typical procedure described for the preparation of **26**, the reaction was carried out with 3,3-dimethoxypropene (**25**; 17.0 mL, 147.7 mmol), 9-BBNH (18.1 g, 148.6 mmol, 1.01 equiv), THF (200 mL), 1-bromo-3,5-bis(trimethylsilyl)benzene (**6**; 41.9 g, 139.0 mmol, 0.94 equiv), $Pd(Ph_3P)_4$ (1.60 g, 1.39 mmol, 1.0 mol%), aq NaOH (3 M, 100 mL), and 30% aq H_2O_2 (60 mL); yield: 36.6 g (76%); colorless oil; R_f 0.26 (hexanes–EtOAc, 10:1).

^{1}H NMR (270 MHz, $CDCl_3$): δ = 0.27 (s, 18 H), 1.95 (m, 2 H), 2.68 (m, 2 H), 3.46 (s, 6 H), 4.42 (t, ^3J = 6.0 Hz, 1 H), 7.35 (s, 2 H), 7.51 (s, 1 H).

^{13}C NMR (63 MHz, $CDCl_3$): δ = –1.06, 31.15, 34.47, 52.80, 104.03, 133.99, 135.77, 139.54, 139.82.

MS (EI, 80 eV, 130 °C): *m*/*z* (%) = 324 (2, $[M]^+$), 291 (4, $[M - HOCH_3]^+$), 276 (17, $[M - CH_3 - HOCH_3]^+$), 73 (100, $[SiMe_3]^+$).

HRMS: *m*/*z* Calcd for $C_{11}H_{12}Br_2O_2$: 324.194087. Found: 324.19732.

Anal. Calcd for $C_{11}H_{12}Br_2O_2$ (324.60): C, 62.90; H, 9.94. Found: C, 62.46; H, 9.95.

3-(3,5-Diiodophenyl)propionaldehyde (31)
To a solution of 1,3-bis(trimethylsilyl)-5-(3,3-dimethoxypropyl)benzene (**29**; 30.8 g, 94.9 mmol) in CH_2Cl_2 (250 mL) at 0 °C was added a solution of ICl (42.9 g, 264.4 mmol, 2.79 equiv) in CH_2Cl_2 (50 mL) within 2 h. After stirring for an additional 30 min, an aq sat. solution of $Na_2S_2O_5$ was added, and the layers were separated. The aqueous layer was washed with CH_2Cl_2 (2 × 20 mL) and the combined organic layers were dried ($MgSO_4$), filtered and the solvent was removed. ^{1}H NMR analysis of the residue indicated formation of a mixture of acetal **30** and aldehyde **31**. It was not further purified, but dissolved in a mixture of MeCN (250 mL) and H_2O (30 mL). After addition of DDQ (2.15 g, 9.5 mmol, 0.10 equiv based on **29**), the dark red suspension was stirred at r.t. for 4 h. Chromography through a short column of silica gel (hexanes–EtOAc, 20:1) and precipitation from CH_2Cl_2–MeOH yielded 9.2 g (25%) of **31** as a pale yellow solid; mp 65–66 °C; R_f 0.23; (hexanes–EtOAc, 6:1). Compound **31** was not stable on silica gel leading to considerable loss. The mass spectra indicated the formation of the corresponding acid.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.74 (m, 2 H), 2.80 (m, 2 H), 7.48 (s, 2 H), 7.86 (s, 1 H), 9.77 (s, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 26.09, 44.62, 94.86, 136.67, 142.96, 144.58, 200.31.

MS (EI, 80 eV, 90 °C): *m*/*z* (%) = 386 (100, $[M]^+$).

Anal. Calcd for $C_9H_8I_2O$ (385.97): C, 28.01; H, 2.09. Found: C, 27.99; H, 2.05.

1-But-3-enyl-3,5-diiodobenzene (32)
Following the typical procedure described for the preparation of **28**, the reaction was carried out with triphenylmethylphosphonium iodide (0.70 g, 1.73 mmol), THF (20 mL), BuLi (1.05 mL of a 1.6 M solution in hexane, 1.68 mmol, 1.14 equiv), and 3-(3,5-diiodophenyl)propionaldehyde (**31**; 0.57 g, 1.48 mmol) in THF (10 mL); yield: 0.53 g (62%); oil; R_f 0.70 (hexanes–EtOAc, 6:1).

^{1}H NMR (270 MHz, $CDCl_3$): δ = 2.32 (m, 2 H), 2.57 (t, ^3J = 8.0 Hz, 2 H), 5.01 (m, 2 H), 5.78 (m, 1 H), 7.50 (s, 2 H), 7.86 (s, 1 H).

^{13}C NMR (63 MHz, $CDCl_3$): δ = 34.36, 34.85, 94.76, 115.68, 136.79, 136.89, 142.51, 145.96.

MS (EI, 80 eV, 40 °C): *m*/*z* (%) = 384 (66, $[M]^+$), 343 (100, $[M - C_3H_5]^+$).

Anal. Calcd for $C_{10}H_{10}I_2$ (384.00): C, 31.28; H, 2.62. Found: C, 31.52; H, 2.48.

1-But-3-enyl-3,5-bis-(3-benzyloxypropyl)benzene (35)
Following the typical procedure described for the preparation of **22**, the reaction was carried out with allyl benzyl ether (**20**; 1.51 g, 10.19 mmol, 3.08 equiv), 9-BBNH (20.0 mL of a 0.5 M solution in THF, 10.0 mmol, 3.7 equiv), aq NaOH (1 M, 20 mL), 1-but-3-enyl-3,5-dibromobenzene (**28**; 0.78 g, 2.69 mmol), and $Pd(Ph_3P)_4$ (0.23 g, 0.11 mmol, 2.04 mol% per coupling) by refluxing for 5 d; yield: 1.10 g (95%); colorless oil; R_f 0.34 (hexanes–EtOAc, 10:1).

^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.84 (m, 4 H, $CH_2CH_2CH_2O$), 2.26 (m, 2 H, CH_2CH_2CH), 2.59 (m, 6 H, Ar-CH_2), 3.37 (t, ^3J = 7.0 Hz, 4 H, $CH_2CH_2CH_2O$), 4.39 (s, 2 H, $PhCH_2O$), 4.86–4.98 (m, 2 H, $CH{=}CH_2$), 5.77 (m, 1 H, $CH{=}CH_2$), 6.92 (s, 3 H, Ar-H), 7.32–7.44 (m, 10 H, Ar-H).

^{13}C NMR (63 MHz, $CDCl_3$): δ = 31.33, 32.27, 35.27, 35.47, 69.45, 72.81, 114.75, 125.76, 125.88, 127.53, 128.16, 128.57, 138.04, 138.55, 141.86, 141.86.

MS (EI, 80 eV, 130 °C): *m*/*z* (%) = 428 (2, $[M]^+$), 337 (100, $[M - C_7H_7]^+$).

HRMS: *m*/*z* Calcd for $C_{30}H_{36}O_2$: 428.27153. Found: 428.27158.

1-But-3-enyl-3,5-bis[3-(*tert*-butydimethylsiloxy)propyl]benzene (3)
Following the typical procedure described for the preparation of **22**, the reaction was carried out with (allyloxy)(*tert*-butyl)dimethylsilane (**33**; 11.0 mL, 51.8 mmol, 3.01 equiv), 9-BBNH (6.3 g, 51.7 mmol, 3.01 equiv), THF (60 mL), aq NaOH (1 M, 150 mL), 1-but-3-enyl-3,5-dibromobenzene (**28**; 5.0 g, 17.2 mmol), $Pd(Ph_3P)_4$ (0.44 g, 3.8×10^{-4} mol, 1.1 mol% per coupling), and an additional amount THF (100 mL) by refluxing for 17 h; yield: 8.8 g (85%); colorless oil; R_f 0.64 (hexanes–EtOAc, 20:1).

^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.08 [s, 12 H, $Si(CH_3)_2$], 0.94 [s, 18 H, *t*-C_4H_9], 1.86 (m, 4 H, $CH_2CH_2CH_2O$), 2.36 (m, 2 H, CH_2CH_2CH), 2.66 (m, 6 H, Ar-CH_2), 3.66 (t, ^3J = 7.0 Hz, 4 H, $CH_2CH_2CH_2O$), 4.98–5.11 (m, 2 H, $CH{=}CH_2$), 5.89 (m, 1 H, $CH{=}CH_2$), 6.87 (s, 3 H, Ar-H).

^{13}C NMR (63 MHz, $CDCl_3$): δ = –5.26, 18.35, 25.99, 32.03, 34.49, 35.41, 35.62, 62.48, 114.69, 126.03, 126.24, 138.31, 141.75, 142.14.

MS (EI, 80 eV, 60 °C): *m*/*z* (%) = 476 (<1, $[M]^+$), 418 (33, $[M - t\text{-Bu}]^+$), 346 (61, $[M - OSi(CH_3)_2Bu\text{-}t]^+$, 75 (100, $[OSi(CH_3)_2]^+$).

Anal. Calcd for $C_{28}H_{52}O_2Si_2$ (476.88): C, 70.52; H, 10.99. Found: C, 70.74; H, 10.75.

1-But-3-enyl-3,5-bis(3-{3,5-bis-[3-(*tert*-butyldimethylsiloxy)-propyl]phenylpropyl)benzene (4)
Following the general procedure described for the preparation of **22**, the reaction was carried out with G1 dendron **3** (3.1 g ,6.5 mmol, 3.09 equiv), 9-BBNH (13.0 mL of a 0.5 M solution in THF, 6.5 mmol, 3.09 equiv), aq NaOH (1 M, 25 mL), 1-but-3-enyl-3,5-dibromobenzene (**28**; 0.61 g, 2.10 mmol), and $Pd(Ph_3P)_4$ (0.15 g, 1.3×10^{-4} mol, 3.09 mol% per coupling) in additional THF (20 mL); yield: 1.7 g (75%); colorless oil; R_f 0.38 (hexanes–EtOAc, 20:1).

^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.01 [s, 24 H, $Si(CH_3)_2$], 0.96 (s, 36 H, *t*-C_4H_9), 1.70 (m, 8 H, $CH_2CH_2CH_2CH_2$), 1.86 (m, 8 H, $CH_2CH_2CH_2O$), 2.40 (m, 2 H, CH_2CH_2CH), 2.63–2.70 (m, 18 H, Ar-CH_2), 3.68 (t, ^3J = 7.0 Hz, 8 H, $CH_2CH_2CH_2O$), 5.00–5.10 (m, 2 H, $CH{=}CH_2$), 5.91 (m, 1 H, $CH{=}CH_2$), 6.87–6.88 (m, 9 H, Ar-H).

^{13}C NMR (63 MHz, $CDCl_3$): δ = –5.27, 18.33, 25.98, 26.19, 31.34, 32.03, 34.47, 35.38, 35.61, 35.81, 62.48, 114.70, 125.75, 125.91, 126.02, 126.68, 138.28, 141.67, 142.07, 142.53 (2 signals missing).

MS (EI, 80 eV, 200 °C): *m*/*z* (%) = 1085 (1, $[M]^+$), 1070 (8, $[M - CH_3]^+$), 1028 (100, $[M - t\text{-Bu}]^+$).

Anal. Calcd. for $C_{66}H_{116}O_4Si_4$ (1085.97): C, 73.00; H, 10.77. Found: C, 72.97; H, 10.69.

Poly-{9-[3-(3,5-diiodophenyl)propyl]-9-borabicyclo[3.3.1]-nonane} (36); Typical Procedure

A mixture of 9-BBNH (3.20 mL of a 0.5 M solution in THF, 1.60 mmol, 1.02 equiv) and 1-allyl-3,5-diiodobenzene (**19**; 0.58 g, 1.57 mmol) was stirred for one day at r.t. After addition of aq NaOH (3 M, 1.50 mL, 4.50 mmol, 2.87 equiv) and additional THF (10 mL), the suspension was degassed. The catalyst precursor $Pd(Ph_3P)_4$ (38.3 mg, 3.31×10^{-5} mol, 1.05 mol% per coupling) was added and the suspension was stirred under gentle reflux for 20 h. The reaction mixture was poured into MeOH (200 mL), and the polymer was allowed to stand for one day for precipitatation. The turbid suspension was centrifuged, and the resulting solid was lyophilized from benzene to yield 0.38 g (94%) of polymer **36** as a creamy white solid. The solubilty of polymer **36** was too low to obtain a well resolved ^{13}C NMR spectra.

^1H NMR (500 MHz, $CDCl_3$): δ = 1.85 (s, 2 H, H-7), 2.52 (s, br, 4 H, H-6), 6.76 (s, br, H-5), 6.88 (s, br, H-4), 7.30 (s, br, H-3), 7.42 (s, br, H-2), 7.82 (s, br, H-1).

MS (MALDI-TOF, DHB): *m*/*z* = 2333 $[M_n (n = 9)]^+$, 2207 $[M_n (n = 9) - I]^+$, 2089 $[M_n (n = 8)]^+$, 1963 $[M_n (n = 8) - I]^+$, 1845 $[M_n (n = 7)]^+$, 1719 $[M_n (n = 7) - I]^+$, 1601 $[M_n (n = 6)]^+$, 1475 $[M_n (n = 6) - I]^+$, 1357 $[M_n (n = 5)]^+$, 1231 $[M_n (n = 5) - I]^+$, 1113 $[M_n (n = 4)]^+$, 987 $[M_n (n = 4) - I]^+$, 869 $[M_n (n = 3)]^+$, 743 $[M_n (n = 3) - I]^+$.

Anal. Calcd for $(C_{10}H_{11}I)_n$ (258.20): C, 44.29; H, 3.72. Found: C, 46.46; H, 3.89.

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(36) The Suzuki–Miyaura cross-coupling of **34** with vinylic halides has been previously described: (a) Ridgway, B. H.; Woerpel, K. A. *J. Org. Chem.* **1998**, *63*, 458. (b) Trost, B. M.; Probst, G. D.; Schoop, A. *J. Am. Chem. Soc.* **1998**, *120*, 9228.
(37) Preliminary investigations on the corresponding G3 dendron (not shown) encountered the additional problem that the molar mass of this molecule could not be confirmed, since the applied methods (EI, FAB, MALDI-TOF) only showed much smaller fragments. The mass spectral analyses of TBDMS-protected dendrons **3** and **4** point to the sensitivity of the silyl group with the loss of methyl and *tert*-butyl groups.
(38) Kim, Y. H.; Webster, O. W. *Macromolecules* **1992**, *25*, 5561.
(39) The molar mass distribution of hyperbranched poly(phenylene)s, obtained by Suzuki cross-coupling of 3,5-dibromophenylboronic acid, was reported to show a large dependence from the used solvent system. The average number of repeating units was between 13 and 42 (7 examples), in one example 206 repeating units were achieved.[38]
(40) According to: Hölter, D.; Burgath, A.; Frey, H. *Acta Polym.* **1997**, *48*, 30.
(41) Nicolaou, K. C.; Patron, A. P.; Ajito, K.; Richter, P. K.; Khatuya, H.; Bertinato, P.; Miller, R. A.; Tomaszewski, M. J. *Chem.–Eur. J.* **1996**, *2*, 847.
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(44) For an analogous procedure, see: Chen, G. J.; Tamborski, C. *J. Organomet. Chem.* **1983**, *251*, 149.
(45) No reference data were found.