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Synthesis of Low-Generation, Aryl-/Alkyl-Type, Nonpolar Dendrons Carrying Protected Hydroxyalkyl Groups in the Periphery

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An efficient convergent synthesis of first- and second-generation aryl-/alkyl-type nonpolar dendrons via Suzuki cross-coupling is described. The dendrons carry either one or two benzyl-protected hydroxyalkyl groups/terminus. Iododesilylation reactions of aryltrimethylsilanes with iodo chloride are used as a tool for the incorporation of iodo, an important functionality for transition-metal-catalyzed cross-coupling reactions. In the case of sensitive aromatics, the addition of some donor solvent like diethyl ether proved effective in suppressing side reactions through electrophilic aromatic iodination.

Introduction

Due to their unique structure and properties, dendrimers have attracted increasing attention in the past decade, and an intensive effort has been expended in their synthesis.[1] The preparation of dendrimers with heteroatom linkages such as aryl ether, aryl ester, aryl amide, alkyl ether, alkyl ester, etc., has been well documented. However, only few examples were described with nonpolar hydrocarbon skeletons. The approaches to this latter kind were described by Newkome et al. and Miller and Neenan, who prepared an all-alkyl representative with peripheral carboxylic groups[2] and a conformationally less flexible hydrocarbon dendrimer based on aryl−aryl linkage using the Suzuki cross-coupling (SCC) reaction,[3] respectively. A whole family of dendrimers comprised of pentaphenylbenzene repeating units were recently prepared by Müllen et al. using an iterative Diels−Alder reaction.[4] Additionally, hydrocarbon dendrimers based on benzene and acetylene[5] or benzene−ethylene[6] were reported.

Highly efficient and robust synthetic methods for CC-coupling are limited. SCC is one of the few true exceptions, specifically as far as aryl/aryl couplings from aryl boronic acids (and esters) and aryl bromides (or iodides) are concerned. Aryl/alkyl couplings[7] also work well, but here occasionally problems with purification were encountered which can render their application in nonsolid-phase iterative synthesis less attractive.[8] We here report on the synthesis of nonpolar dendrons containing both aryl and alkyl subunits using aryl-/aryl-SCC as the growth reaction.[9] Consequently the dendrons synthesized carry (*m*-) terphenylene units. The mode of synthesis is convergent, and the peripheral branching units carry one or two benzyl-protected hydroxyalkyl groups to systematically vary surface polarity in future target structures. On route, conditions were discovered which allowed suppressing undesired iodination side reactions in iododesilylation steps. The reported dendrons are of interest for the synthesis of globular dendrimers[1] as well as cylindrically shaped dendronized polymers.[10] In particular, their combination with other low-generation dendrimers opens the possibilities to design both the interior and exterior of dendritic compounds as required either using a modular or combinatorial type approach.

Results and Discussion

Chart 1 contains the central branching unit **1**, the linear and branched peripheral building blocks **2** and **3**,

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(1) (a) Newkome, G. R.; Moorefield, C. N.; Vögtle, F. *Dendrimers and Dendrons*; Wiley-VCH: Weinheim, Germany, 2001. (b) Fréchet, J. M. J.; Tomalia, D. A. *Dendrimers and other Dendritic Polymers*; Wiley-VCH: Weinheim, Germany, 2001.

(2) Newkome, G. R.; Moorefield, C. N.; Baker, G. R.; Johnson, A. L.; Behera R. K. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1176.

(3) (a) Miller, T. M.; Neenan, T. X. *Chem. Mater.* **1990**, *2*, 346. (b) Miller, T. M.; Neenan, T. X.; Zayas, R.; Bair, H. E. *J. Am. Chem. Soc.* **1992**, *114*, 1018.

(4) Watson, M. D.; Fechtenkötter, A.; Müllen K. *Chem. Rev.* **2001,** *101*, 1267.

(5) (a) Xu, Z.; Moore, J. S. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 246. (b) Xu, Z.; Kahr, M.; Walker, K. L.; Willins, C. L.; Moore, J. S. *J. Am. Chem. Soc.* **1994**, *116*, 4537. (c) Liu, B.; Roy, R. *Tetrahedron* **2001**, *57*, 6909.

(6) (a) Deb, S. K.; Maddux, T. M.; Yu, L. *J. Am. Chem. Soc.* **1997**, *11*99, 9079. (b) Meier, H.; Lehmann, M. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 7, 643. (c) Lehmann, M.; Schartel, B.; Hennecke, M.; Meier, H. *Tetrahedron* **1999**, *55*, 13377. (d) Pillow, J. N. G.; Halim, M.; Lupton, J. M.; Burn, P. L.; Samuel, I. D. W. *Macromolecules* **1970**, *3*, 2, 5985.

(7) Miyaura, N. *Top. Curr. Chem.* **2002**, *219*, 11.

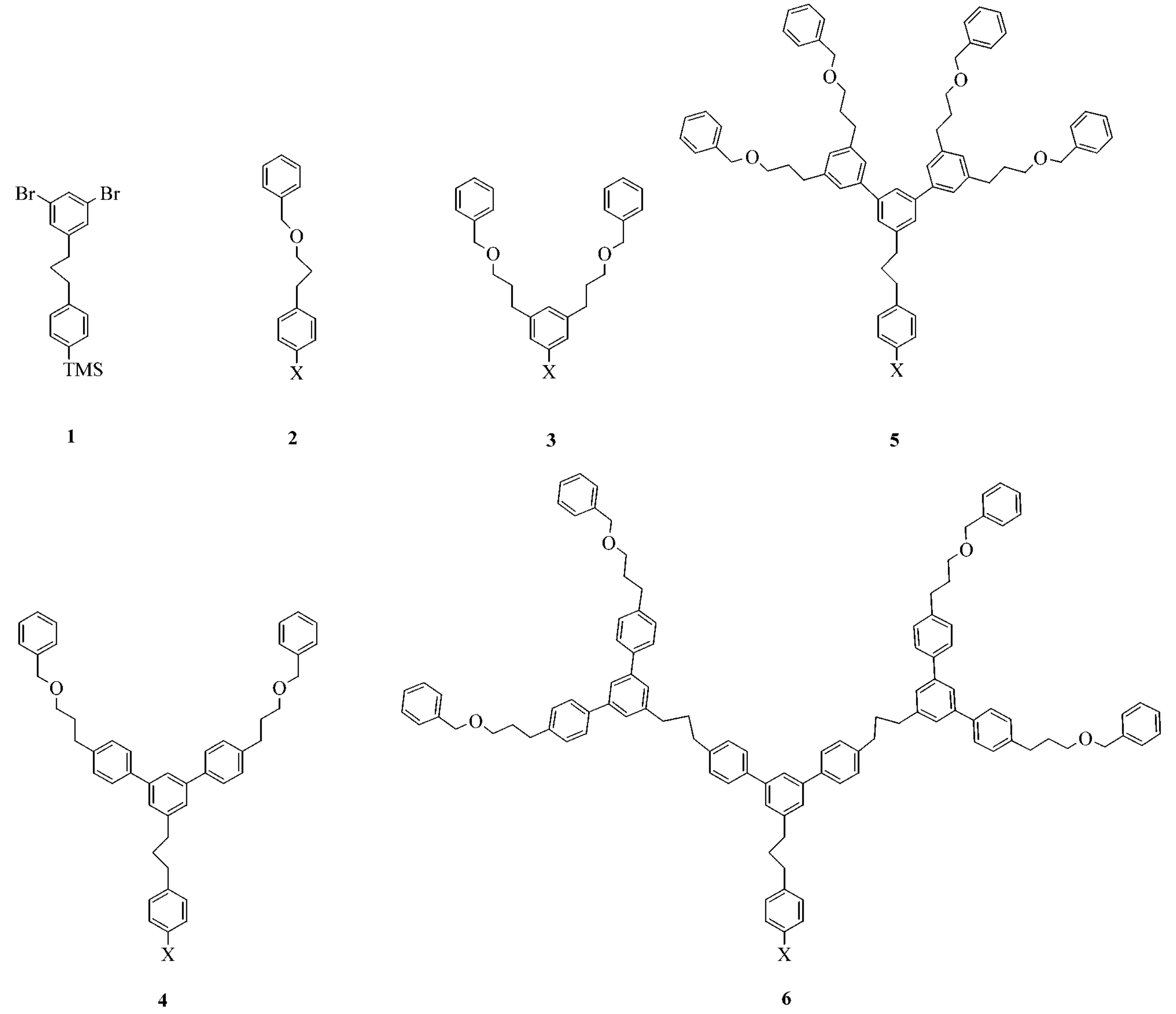
(8) (a) Shu, L.; Schlüter, A. D. *Macromol. Chem. Phys.* **2000**, *201*, *239*. (b) Shu, L.; Schäfer, A.; Schlüter, A. D. *Macromolecules* **2000**, *33*, 4321.

(9) For a related work using aryl/alkyl SCC, see: Beinhoff, M.; Karakaya, B.; Schlüter, A. D. *Synthesis* **2002**, submitted for publication.

(10) (a) Schlüter, A. D.; Rabe, J. P.; *Angew. Chem., Int. Ed.* **2000**, *39*, 864. (b) Shu, L., Schlüter, A. D.; Ecker, C.; Severin, N., Rabe, J. P. *Angew. Chem., Int. Ed.* **2001**, *40*, 4666.

10.1021/jo025742k CCC: $22.00

CHART 1



and the three dendrons **4**−**6** obtained (for X, see Schemes 1−3). Branching unit **1** is of the AB_2-type and, besides the two bromo coupling functionalities, carries a trimethylsilyl (TMS) group as a placeholder for its subsequent conversion into iodo function through iododesilylation chemistry with iodo chloride.[11] Many examples of this kind of reaction have been reported to be very high yielding. Conversion of TMS aryls into aryl boronic acid has also been reported.[3a] The conditions for this reaction, however, were expected to be too harsh for cases such as the present, where protected hydroxy functions are to be considered. This conversion was therefore not applied here. The dendrons carry either TMS or iodo functions at the focal point. Dendron **4** was additionally prepared bearing a boronic acid and the corresponding pinacol ester. Coupling of **1** with either the linear or branched building block **2** or **3** furnishes the dendrons **4** and **5**, respectively, whereas the coupling of **1** with **4** yields the second generation (G2) dendron **6**. The three main reactions involved in these transformations are the following: SCC for the growth step; iododesilylation forthe incorporation of iodo functionality; halogen/lithium exchange for the preparation of boronic acids.

The key branching unit **1** was synthesized according to the sequence in Scheme 1. The TMS-substituted compound **8**,[12] obtained from the commercial dibromide **7**, contained a small amount of 1,4-bis(trimethylsilyl)-benzene as an impurity that could not be removed even after repeated vacuum distillation (approximately 3−4% by ^{1}H NMR). Compound **8** was therefore used without further purification. For the allylation of aryl halides, the known methods comprise the following: (a) Pd-catalyzed reaction of aromatic tin compound with allyl bromide;[13] (b) CuCN·2LiCl-catalyzed reaction of arylmagnesium with allyl bromide;[14] (c) the same reaction like (b) but with $Pd(PPh_3)_4$ as catalyst precursor.[15] Because of the hazardous potential of some of the reagents used in

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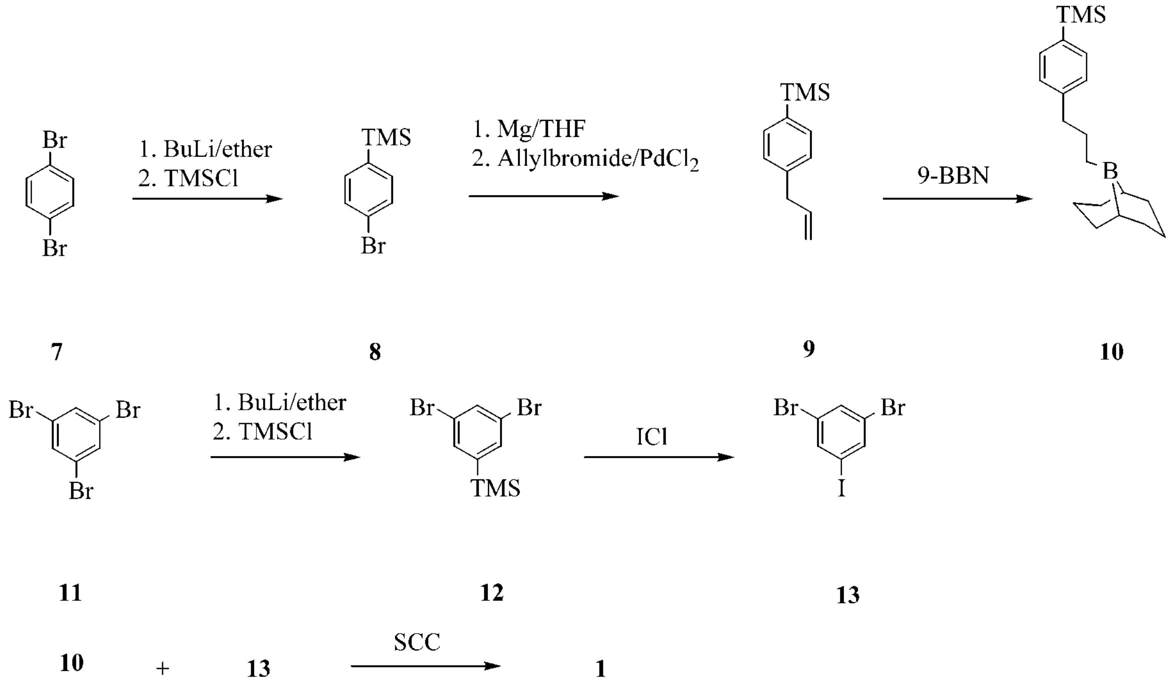
[11] For example: (a) Hensel, V.; Schlüter, A. D. *Chem.—Eur. J.* **1999**, 5, 421. (b) Hensel, V.; Schlüter, A. D. *Eur. J. Org. Chem.* **1999**, 451.

[12] For example: Rehm, J. D. D.; Ziemer, B.; Szeimies, G. *Eur. J. Org. Chem.* **1999**, 2079.

[13] Sheffy, F. K.; Godschalx, J. P.; Stille, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 4833.

SCHEME 1. Synthesis of the Branching Unit 1



methods a and b, method c was chosen with a modification: $PdCl_2$ was used as catalyst precursor instead of $Pd(PPh_3)_4$. This proved to give slightly superior results regarding achievable yield. Applied to the Grignard derivative of compound **8** the reaction gave **9** in 82% yield. Compound **9** still contained traces of 1,4-bis(trimethylsilyl)benzene as impurity, which came from the starting material **8**. No isomerization of the double bond was observed (500 MHz ^1H NMR of raw mixture). Standard hydroboration of **9** with 9-BBN gave compound **10**. The coupling partner of **10**, the dibromoiodobenzene **13**, was obtained from the commercially available tribromobenzene **11**, which was monosilylated to **12** followed by iododesilylation.[11] In the final step, SCC of **10** and **13** proceeded highly selectively at the iodinated carbon of **13** and gave the pure key branching unit **1** free of impurity 1,4-bis(trimethylsilyl)benzene in a yield of 77%. This entire route was scaled up to the degree that compound **1** is now available on the 30 g scale.[16]

Using **1** as the branching unit, dendrons **5** (Scheme 2) as well as **4** and **6** were synthesized (Scheme 3). Hydroboration of **14**[17] gave **15**, which was subjected to SCC with compound **12** to furnish the first generation (G1) dendron **3a** in 79% yield. Its iododesilylation to **3b** was done in virtually quantitative yield by treatment with ICl in CH_2Cl_2 at 0 °C without noticeable side reaction. Iodo/lithium exchange on **3b** with BuLi at -78 °C in ether and subsequent quenching of the anion with trimethyl borate gave the boronic acid **3c** (87%) whose esterification with pinacol cleanly furnished the corresponding boronic acid ester **3d**. The G2 dendron **5a** was obtained in 88% yield by SCC of **1** and **3d** under standard conditions using $Pd(PPh_3)_4$ as catalyst precursor in the biphasic system THF/aqueous $NaHCO_3$. Flash chromatography afforded also a side product, **16**, which had formed in approximately 5% yield. This most likely is the result of ligand scrambling occasionally observed in transition-metal-catalyzed cross-coupling reactions.[18] Its structure was confirmed by ^1H and ^{13}C NMR spectroscopy as well as elemental analysis. The next important step was the transformation of **5a** into its iodo analog **5b**. This was attempted under the same conditions that had been proved successful when applied to **3b**. This time, however, a side reaction was observed. Careful column chromatography workup afforded, besides the desired product, also some of the diiodo compound **17**, where one of the internal rings carrying benzyloxypropyl chains had undergone iodination. The structure of **17** was proved by all standard techniques. Obviously two alkyl substituents on the outer phenyl rings of the terphenylene units in **5a** and/or **5b** activate these phenyls sufficiently strongly to allow an electrophilic attack by iodochloride to occur. **17** only formed to a few percent, and both products, **5b** and **17**, could be cleanly separated by column chromatography. This side reaction was nevertheless considered detrimental in regard to all potentially interesting higher generation compounds because of both increasing purification difficulty with increasing molar mass and the statistical factor, which increasingly works in favor of the side reaction. We therefore sought for a way out of this dilemma. The presence of donors should influence the electrophilicity of iodochloride. If the iododesilylation was performed not in pure methylene chloride (as above) but rather in a mixture with a donor solvent, its reactivity

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[14] (a) Knochel, P.; Yeh, M. C. P.; Berk, S. C.; Talbert, J. *J. Org. Chem.* **1988**, *53*, 2390. (b) Boymond, L.; Rottländer, M.; Cahiez, G.; Knochel, P. *Angew. Chem.* **1998**, *110*, 1801. (c) Kitagawa, K.; Inoue, A.; Shinokubo, H.; Oshima, K. *Angew. Chem., Int. Ed.* **2000**, *39*, 2481.

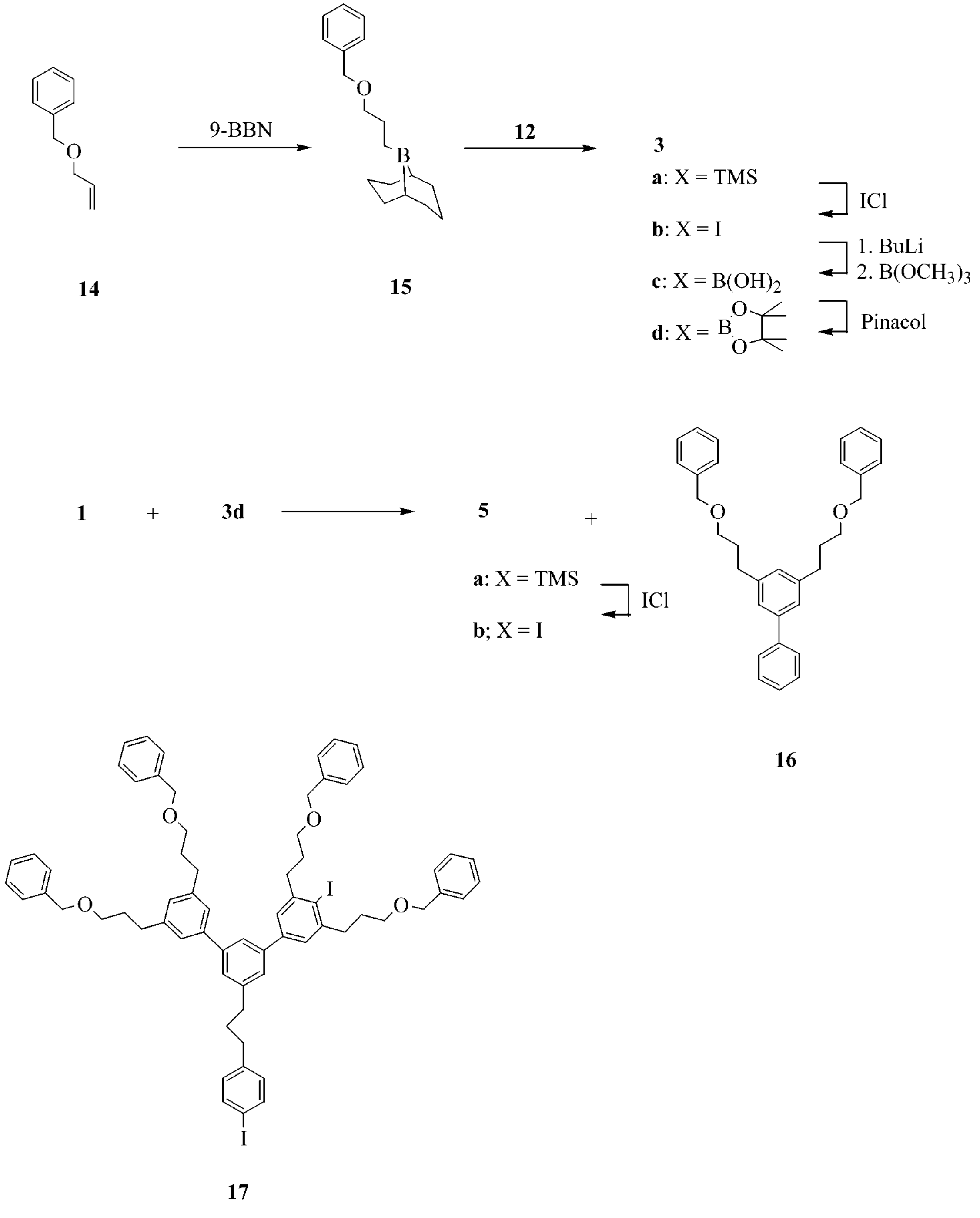
[15] Bumagin, N. A.; Kasatkin, A. N.; Beletskaya, I. P. *Bull. Acad. Sci. USSR Div. Chem. Sci. (Engl. Transl.)* **1984**, *33*, 1696.

[16] Bo, Z. S., Schlüter, A. D. Manuscript in preparation.

[17] Cookson, R. C.; Wallis, S. R. *J. Chem. Soc. B* **1966**, 1245.

[18] (a) Kong, K. C.; Cheng, C. H. *J. Am. Chem. Soc.* **1991**, *113*, 6313. (b) O'Keefe, D. F.; Marcuccio, S. M. *Tetrahedron Lett.* **1992**, *33*, 6679. (c) Koch, F.; Heitz, W. *Macromol. Chem. Phys.* **1997**, *198*, 1531.

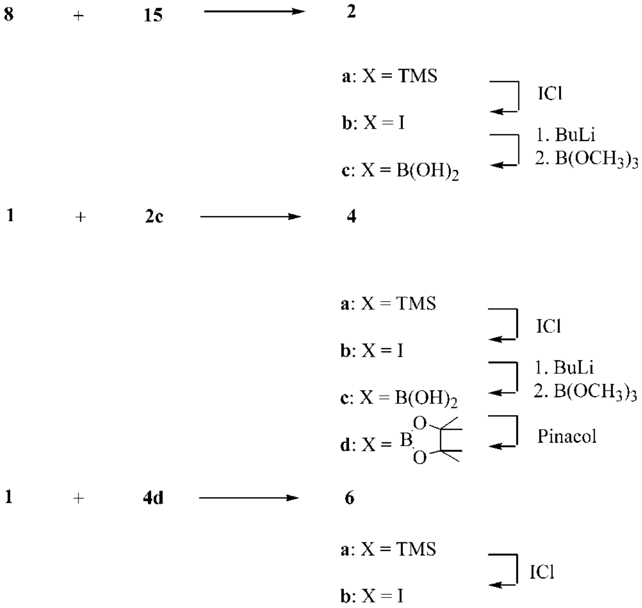
SCHEME 2. Synthesis of the Dendrons 3 and 5



could possibly be fine-tuned. The same reaction was therefore tried in a 20:1 mixture of methylene chloride and diethyl ether, and in fact, the conversion of **5a** to **5b** in this mixture went absolutely cleanly. No side product was observed as judged by visual inspection of a high-field ^{1}H NMR spectrum with an excellent signal-to-noise ratio of the raw mixture. The methylene protons of the alkyls ortho to the iodo function appear as an easy to detect, baseline-separated singlet at $\delta = 4.53$ ppm. Along the same line, if the reaction was tried in ether as the only solvent, no reaction was observed; not even the sensitive TMS function was replaced.

SCC of **8** and **15** afforded the linear peripheral unit **2a,** which was easily converted to the iodide **2b** and the boronic acid **2c**. Coupling of **2c** with the key branching unit **1** afforded the G1 dendron **4a** in a yield of 88%. The iodo desilylation of **4a** did not require the above-described precautions, which is not surprising because its terphenylene carries only one alkyl chain on each side. **4b** wasobtained in a yield of 99%. Its subsequent conversion to **4c** using BuLi and B(O-iso-Pr)$_3$ did not proceed so well and gave the product in a yield of 41%. Pinacolization proceeded cleanly. Pure ester **4d** was obtained by flash chromatography on silica gel, though the separation has

SCHEME 3. Synthesis of Dendrons 4 and 6



to be carried out quickly because of partial decomposition on the column (hydrolysis of ester). Finally, SCC of the G1 dendron **4d** with the branching unit **1** afforded the G2 dendron **6a** in 75% yield. Iododesilylation of **6a** gave **6b** in 99% yield without any side reaction.

Compounds **1** and **4**−**6** will be used for synthesis of hyperbranched polymers (**1**[15]), dendrimers (**4**, **5**), and dendronized polymers (**5**, **6**).

Experimental Section

Compounds **8**,[12] **12**,[12] and **14**[17] were prepared according to literature procedures. Compounds **7** and **11** were purchased from Acros. The catalyst precursor Pd(PPh$_3$)$_4$ was prepared according to the literature[19] and stored under nitrogen in a high-quality glovebox. All solvents were purified or dried by standard methods. ^{1}H and ^{13}C NMR spectra were recorded at 270 and 68 MHz in CDCl$_3$, respectively. For the boronic acids, **2c**, **3c**, and **4c,** combustion analysis and NMR measurements were not performed, because boronic acids always contain water or form boroxines.

(4-Allylphenyl)trimethylsilane (9). A mixture of Mg (14.0 g, 0.57 mol), iodine (50 mg), and THF (700 mL) was refluxed until it was colorless. Approximately 20 g of **8** was then added, and the mixture was heated to reflux until the reaction kept refluxing without heating; the rest of **8** (total amount: 114.5 g, 0.5 mol) was added dropwise to keep the reaction mixture refluxing smoothly. After the addition was completed, the mixture was heated to reflux for 6 h, cooled to room temperature, and the transferred to a flask which was already charged with allyl bromide (66.54 g, 0.55 mol) and Pd(PPh$_3$)$_4$ (5.13 g, 4.43 mmol). The resulting mixture was stirred at room temperature for 2 h. Removal of the solvent and vacuum distillation of the residue (65 °C, 4.2 × 10^{-2} mbar) afforded **9** as a colorless liquid (78.3 g, 82%). ^{1}H NMR: δ 7.30 (AB system, 4H), 5.85−6.05 (m, 1H), 3.38 (d, 2H), 0.22 (s, 9H). ^{13}C NMR: δ 140.67, 137.71, 137.24, 133.47, 127.98, 115.83, 40.19, −1.10.

1,3-Dibromo-5-iodobenzene (13). A solution of **12** (37.10 g, 120.4 mmol) in 300 mL of CH$_2$Cl$_2$ was cooled to 0 °C under stirring, and a solution of ICl in CH$_2$Cl$_2$ (1.0 M, 132 mL) was added dropwise over 10 min. After the addition, the reaction was kept at 0 °C for 2 h. A concentrated aqueous solution of NaOH was then added to quench the reaction. The organic layer was separated, the aqueous one extracted with CH$_2$Cl$_2$, and the combined organic layer dried over MgSO$_4$ and evaporated to dryness. The residue was redissolved in hexane and filtered through a short silica gel pad. After removal of solvent, recrystallization from hexane afforded **13** as white needles (37.0 g, 85%): mp 124.4−124.7 °C; ^{1}H NMR δ 7.77 (s, 1H), 7.61 (s, 2H); ^{13}C NMR δ 138.44, 133.59, 123.34, 94.47. Anal. Calcd for $C_6H_3Br_2I$: C, 19.92; H, 0.84. Found: C, 19.77; H, 0.68.

{4-[3-(3,5-Dibromophenyl)propyl]phenyl}trimethylsilane (1). To a stirred solution of **9** (3.01 g, 15.8 mmol) in THF (40 mL) was added a solution of 9-BBN (31.5 mL, 15.8 mmol, 0.5 M in THF) at room temperature under N$_2$ over 0.5 h. The mixture was stirred for further 3 d at room temperature. The obtained adduct (**10**) was used for next reaction without purification.

To this solution were added **13** (9.05 g, 25.0 mmol), NaOH solution (4.0 g in 30 mL of water), and Pd(PPh$_3$)$_4$ (0.48 g, 0.42 mmol). The mixture was carefully degassed, recharged with N$_2$, and stirred at room temperature for 1 d and then at 35 °C for 6 h, and finally refluxed for 16 h. The organic layer was separated, the aqueous phase extracted with ether, and the combined organic layer dried over MgSO$_4$ and evaporated to dryness. Chromatography on silica gel using hexane as an eluent gave the product as a colorless oil (5.2 g, 77%): ^{1}H NMR δ 7.48 (s, 1H), 7.30 (AB system, 4H), 7.23 (s, 2H), 2.62 (t, 2H), 2.57 (t, 2H), 1.91 (p, 2H), 0.25 (s, 9H); ^{13}C NMR δ 146.23, 142.17, 137.65, 133.49, 131.45, 130.29, 127.86, 122.74, 35.19, 34.77, 32.29, −1.08. Anal. Calcd for $C_{18}H_{22}Br_2Si$: C, 50.72; H, 5.20. Found: C, 50.40; H 5.07.

[3,5-Bis(3-(benzyloxy)propyl)phenyl]trimethylsilane (3a). To a stirred solution of **14** (15.6 g, 106 mmol) in THF (50 mL) was added a solution of 9-BBN in THF (0.5 M, 211 mL, 106 mmol) at room temperature under N$_2$, and the mixture was stirred for 3 d. The formed borane adduct (**15**) was used without further purification.

To the solution of **15** were added **12** (15.9 g, 51.7 mmol), an aqueous NaOH solution (15 g in 100 mL water), and Pd(PPh$_3$)$_4$ (2.46 g, 2.13 mmol). The mixture was carefully degassed, recharged with N$_2$, and refluxed for 2 d. The organic layer was separated, the aqueous layer extracted with ether three times, and the combined organic layer dried over MgSO$_4$ and evaporated to dryness. Chromatography on silica gel eluting with hexane/ethyl acetate (100:4) gives **3a** as a colorless oil (18.2 g, 79.2%): ^{1}H NMR δ 7.36−7.28 (m, 10H), 7.15 (s, 2H), 6.98 (s, 1H), 4.50 (s, 4H), 3.50 (t, 4H), 2.65 (t, 4H), 1.90 (p, 2H), 0.22 (s, 9H); ^{13}C NMR δ 141.20, 140.35, 138.61, 130.95, 129.25, 128.36, 127.63, 127.51, 72.95, 69.75, 32.47, 31.54, −1.03. Anal. Calcd for $C_{29}H_{38}O_2Si$: C, 77.97; H, 8.57. Found: C, 77.75; H, 8.50.

1,3-Bis(3-(benzyloxy)propyl)-5-iodobenzene (3b). To a solution of **3a** (15 g, 33.5 mmol) in CH$_2$Cl$_2$ (150 mL) was added dropwise a solution of ICl in CH$_2$Cl$_2$ (1 M, 50 mL) at 0 °C over 5 min. The reaction was kept stirring for 0.5 h at this temperature. A concentrated aqueous solution of NaOH was added. The organic layer was separated, the aqueous one extracted with CH$_2$Cl$_2$, and the combined organic layer dried over MgSO$_4$ and evaporated to dryness. Filtration through a short silica gel pad eluting with CH$_2$Cl$_2$ gave the product as a colorless oil (15.8 g, 94%): ^{1}H NMR δ 7.35−7.25 (m, 12H), 6.90 (s, 1H), 4.46 (s, 4H), 3.45 (t, 4H), 2.60 (t, 4H), 1.85 (p, 4H); ^{13}C NMR δ 144.27, 138.47, 134.93, 128.36, 128.18, 127.62, 127.56, 94.46, 72.92, 69.22, 31.89, 31.17. Anal. Calcd for $C_{26}H_{29}IO_2$: C, 62.40; H, 5.84. Found: C, 61.96; H, 5.67.

3,5-Bis(3-(benzyloxy)propyl)phenylboronic acid (3c). A solution of **3b** in ether (250 mL) was cooled to −78 °C under N$_2$ and a solution of BuLi in hexane (1.6 M, 18.75 mL) added dropwise over 10 min. The reaction was stirred for further 50 min at −78 °C, and then B(O-isopropyl)$_3$ (7.5 g, 40 mmol) was added. The reaction was stirred overnight and allowed to warm to room temperature gradually. Dilute HCl was added, the organic layer separated, the aqueous one extracted with ether

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[19] Clouson, D. *Inorg. Synth.* **1972**, *13*, 121.

three times, and the combined organic layer dried over Na_2SO_4 and evaporated to dryness. Chromatography on silica gel eluting with CH_2Cl_2 increasing to CH_2Cl_2/ethyl acetate (5:1) gave the product as a colorless oil (9.2 g, 87%): ^{1}H NMR δ 8.12 (AB system, 2H), 7.39−7.25 (m, 11H), 4.50 (s, 2H), 3.50 (t, 2H), 2.80 (t, 2H), 1.97 (p, 2H).

3,5-Bis(3-(benzyloxy)propyl)phenylboronic Acid Pinacol Ester (3d). A mixture of **3c** (9.0 g, 21.5 mmol), pinacol (2.7 g, 23.0 mmol), and dry CH_2Cl_2 (500 mL) was refluxed for 2 h. Removal of the solvent and flash chromatography of the remaining mass on silica gel eluting with CH_2Cl_2 gave the product as a colorless oil (7.3 g, 68%). Further eluting with ethyl acetate recovered the hydrolyzed boronic ester as the corresponding boronic acid (2.3 g): ^{1}H NMR δ 7.50 (S, 2H), 7.36−7.28 (m, 10H), 7.12 (s, 1H), 4.51 (s, 4H), 3.49 (t, 4H), 2.70 (t, 4H), 1.94 (p, 4H), 1.35 (s, 12H); ^{13}C NMR δ 141.30, 138.59, 132.34, 131.77, 128.30, 127.61, 127.44, 83.62, 72.84, 69.65, 32.21, 31.43, 24.83. Anal. Calcd for $C_{32}H_{41}BO_4$: C, 76.80; H, 8.26. Found: C, 76.60; H, 8.12.

Trimethyl(4-{3-[3,5,3″,5″-tetrakis(3-(benzyloxy)propyl)-[1,1′:3′,1″]terphenyl-5′-yl]propyl}phenyl)silane (5a). A mixture of **3d** (5.48 g, 10.9 mmol), **1** (2.33 g, 5.47 mmol), $NaHCO_3$ (4.2 g, 50 mmol), and $Pd(PPh_3)_4$ (250.6 mg, 0.217 mmol) in THF (50 mL) and H_2O (30 mL) was carefully degassed and recharged with N_2. The reaction was refluxed for 3 d. The mixture was extracted with CH_2Cl_2 three times, and the combined organic layer was dried over $MgSO_4$ and evaporated to dryness. Chromatography on silica gel eluting with hexane/ethyl acetate (5:1) gives **5a** as a colorless oil (4.89 g, 88%): $R_f = 0.61$ (5:1 hexane/ethyl acetate 5:1); ^{1}H NMR δ 7.55 (s, 1H), 7.45−7.18 (m, 30H), 7.00 (s, 2H), 4.51 (s, 8H), 3.55 (t, 8H), 2.80−2.70 (three sets of signals superimpose each other, 12H), 2.12−1.92 (two sets of signals superimpose each other, 10H), 0.25 (s, 9H); ^{13}C NMR δ 143.03, 142.88, 142.48, 142.00, 141.50, 138.55, 133.40, 128.34, 127.94, 127.64, 127.50, 126.28, 125.08, 123.84, 72.94, 69.63, 35.76, 35.60, 32.92, 32.47, 31.50, −1.07. Anal. Calcd for $C_{70}H_{80}O_4Si$: C, 82.96; H, 7.96. Found: C, 82.77; H, 7.92.

The side product **16** was separated from the same silica gel column eluting with hexane/ethyl acetate (5:1) as a colorless oil (0.25 g, 5%): $R_f = 0.71$ (hexane/ethyl acetate 5:1); ^{1}H NMR δ 7.60−7.22 (m, 17H), 7.05 (s, 1H), 4.55 (s, 4H), 3.55 (t, 4H), 2.78 (t, 4H), 2.00 (p, 4H); ^{13}C NMR δ 142.45, 141.39, 141.25, 138.55, 128.60, 128.33, 127.61, 127.49, 127.14, 127.06, 124.91, 72.90, 69.55, 32.41, 31.42. Anal. Calcd for $C_{32}H_{34}O_2$: C, 85.29; H, 7.61. Found: C, 85.07; H, 7.64.

3,5,3″,5″-Tetrakis(3-(benzyloxy)propyl)-5′-[3-(4-iodophenyl)propyl][1,1′:3′,1″]terphenyl (5b). To a solution of **5a** (3.40 g, 3.35 mmol) in CH_2Cl_2 (50 mL) was added dropwise ICl (7.0 mL) at 0 °C. The reaction was stirred at 0 °C for 50 min. An aqueous solution of $NaHSO_3$ was added, and the color disappeared. The organic layer was separated, the aqueous one extracted with CH_2Cl_2, and the combined organic layer dried over $MgSO_4$ and evaporated to dryness. Filtration through a short silica gel pad eluting with CH_2Cl_2 gave **5b** as a mixture with **17** (total amount: 3.40 g, 95%). Pure **5b** was obtained as a colorless oil by careful chromatography on silica gel eluting with CH_2Cl_2: $R_f = 0.61$ (CH_2Cl_2); ^{1}H NMR δ 7.62 (s, 1H), 7.59 (s, 2H), 7.36−7.28 (m, 26H), 7.03 (s, 2H), 6.96 (one set of AB system, 2H), 4.53 (s, 8H), 3.54 (t, 8H), 2.81−2.65 (three sets of signals superimpose each other, 12H), 2.04−1.97 (two sets of signals superimpose each other, 10H); ^{13}C NMR δ 142.72, 142.50, 142.04, 141.79, 141.42, 138.53, 137.30, 130.59, 128.33, 127.75, 127.63, 127.50, 126.25, 125.05, 123.91, 72.94, 69.61, 35.53, 35.02, 32.81, 32.46, 31.50. Anal. Calcd for $C_{67}H_{71}IO_4$: C, 75.41; H, 6.71. Found: C, 74.33; H, 6.62.

Side product **17** was obtained as a colorless oil from the same silica gel column eluting with CH_2Cl_2: $R_f = 0.74$ (CH_2Cl_2); ^{1}H NMR δ 7.61 (s, 1H), 7.59 (s, 2H), 7.35−7.28 (m, 26H), 7.05 (s, 1H), 6.95 (one set of a AB system, 2H), 4.55 (s, 4H), 5.52 (s, 4H), 3.58 (t, 4H), 3.53 (t, 4H), 3.00 (t, 4H), 2.77 (two sets of signals superimpose each other, 6H), 2.68 (t, 2H), 2.05−1.95 (m, 10H); ^{13}C NMR δ 145.79, 142.93, 142.73, 142.54, 142.29, 141.66, 141.23, 140.96, 140.74, 138.49, 137.29, 132.79, 130.53, 129.52, 129.48, 128.29, 127.83, 127.57, 127.45, 126.65, 125.95, 125.32, 125.03, 123.70, 72.89, 69.55, 38.88, 35.47, 34.98, 32.73, 32.43, 31.47, 30.19, 29.30. Anal. Calcd for $C_{67}H_{70}I_2O_4$: C, 67.45; H, 5.91. Found: C, 67.42; H, 5.87.

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Supporting Information Available: Experimental procedures for the preparation of **2a**−**c**, **4a**−**d**, and **6a**,**b**, spectra and physical data for **2a**−**c**, **4a**−**d**, and **6a**,**b**, and copies of ^{1}H NMR spectra for key compounds **3d**, **4d**, **5a**,**b**, **17**, and **6a**,**b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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