Building Blocks for the Construction of Large Chloro-Functionalized, Hexagonal Oligophenylene Cycles

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The synthesis of a variety of kinked oligophenylene building blocks is described. The synthetic strategy is repetitive, utilizes the Suzuki cross-coupling protocol, and involves potentially bifunctional building blocks (modules) which carry one functional group for coupling and one group which serves as place holder. After the coupling, the placeholder is converted into a coupling functionality for the next growth step. The building blocks also carry chloro-substituents which are unaffected by all transformations. For one of the large building blocks it is shown that it actually can be cyclized into an oligophenylene macrocycle with a chloro-substituent at each corner and a pair of hexyl chains at each side.

Introduction

We have recently reported on efficient repetitive syntheses which make oligophenylene hexagons with 12[1] and 24[2] phenylene rings, available on the gramme and several hundred milligramme scale, respectively. A motivation for this research is the production of extended honeycomb-like, two-dimensional networks for which these shape-persistent, geometrically regular molecules may serve as constituents.[3] A prerequisite for their application in such a direction is that these cycles carry regular patterns of functional groups which can be used for further growth. The present contribution describes the synthesis of a number of linear and kinked oligophenylene building blocks which carry not only the functional group pattern required for repetitive growth but also chlorine atoms at positions which after ring closure should lead to cycles with two or six chlorine atoms at the corners. Chloroarenes have been successfully employed in transition-metal-catalyzed cross-coupling reactions.[4] The building blocks also carry varying numbers of alkyl chains, a feature which, at a later stage, should allow the tuning of the solubility and self-assembly properties of the cycles. The paper also presents the synthesis of the hexachlorocyclododecaphenylene **29** which proves that these rings can actually be made. Related work on shape-persistent cycles by other groups is available.[5]

Results and Discussion

The synthetic schemes are organized according to the targeted ring structures, all of which are cyclododecaphenylenes. They contain (a) two chlorine atoms in “para” positions and two pairs of hexyl chains at opposite sides (Scheme 1), (b) two “para” chlorine atoms and a pair of hexyl chains per side (Scheme 2), (c) chlorine atoms at each corner and two opposite pairs of hexyl groups (Scheme 3), and finally (d) six chlorine atoms and 12 hexyl groups (Scheme 4). For better readability black dots are used to indicate phenylenes with two hexyl substituents and circles for those without hexyl chains. The general synthetic procedure has been described elsewhere.[3,6] Some additional synthetically useful comments have also been made.[2] In the present case the regioselectivity of the Suzuki cross-coupling[7] steps needs to be commented on. Normally the selectivity of C−I over C−Br groups in this reaction is very high.[8] In our own work, coupling at C−Br has never been observed, even if C−I was sterically more hindered, e.g. by an *ortho*-alkyl substitution.[2] This, of course, only holds true if the coupling partner was not used in excess. An exception was observed, however, during synthesis of biphenyl **3** (Scheme 1) which involves 1-bromo-3-chloro-5-iodobenzene (**2**); the main product, compound **3**, was accompanied by some chlorodi(trimethylsilyl)-*m*-terphenyl (not shown) in an approximate proportion of 7:1. All other cross-couplings of bromo- and iodo-containing building blocks proceeded regiospecifically. It is not immediately self-evident whether the chloro substituent of **2** or of **3** is responsible for this. If the former case holds true, it must decrease the reactivity of C−I considerably more than that of C−Br in order to allow some couplings to take place first at C−Br before a second coupling at C−I of the same molecule follows. Alternatively if the chloro substituent of **3** is responsible, one must assume that it increases the reactivity of C−Br compared to all other structurally related compounds. This would be in contradiction to the outcome of the reaction between **9** and **10**, as well as related ones and is therefore considered very unlikely. The syntheses of the other buildings blocks is fairly self-explanatory.

The cyclization was done using the “half-ring” **26** as precursor which carries the bromo/boronic acid functional-

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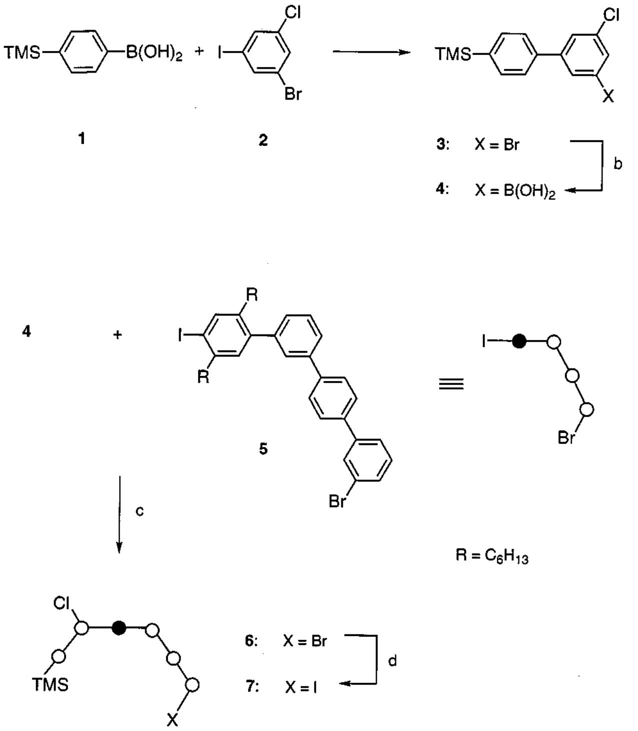
group pattern at the termini. Under high-dilution conditions cycle **29** was obtained in a yield of 15% after chromatographic separation. This experiment shows that the cycles can actually be obtained but that the Br/B(OH)$_2$ functions is not optimal. For non-chlorinated oligophenylene cycles it has been observed that the (easy-to-perform) switch from Br/B(OH)$_2$ to I/B(OR)$_2$[1] improves the yield considerably.

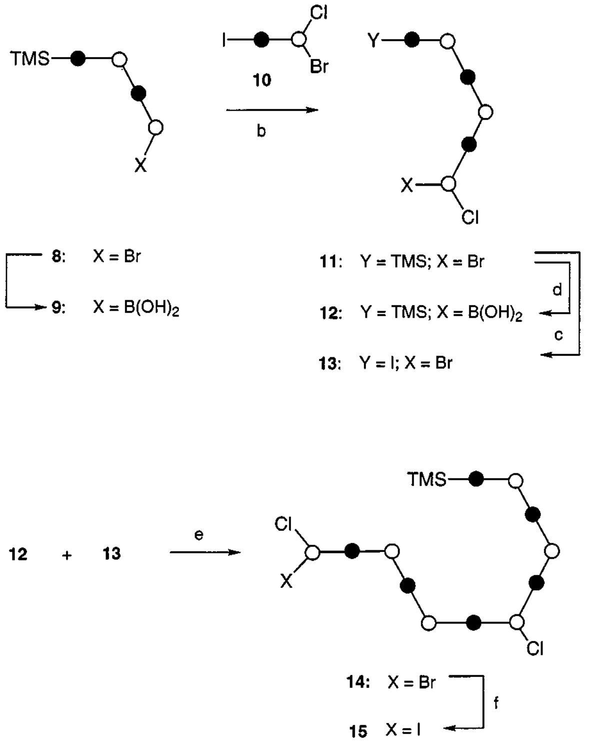


Scheme 1. (a) Pd[PPh$_3$]$_4$/toluene; Ba(OH)$_2$/H$_2$O, 50%, (b) *n*-butyllithium, triisopropyl borate, 79%, (c) Pd[PPh$_3$]$_4$/toluene; Ba(OH)$_2$/H$_2$O, 89%; (d) *n*-butyllithium, 1.2-diiodoethane, 76%

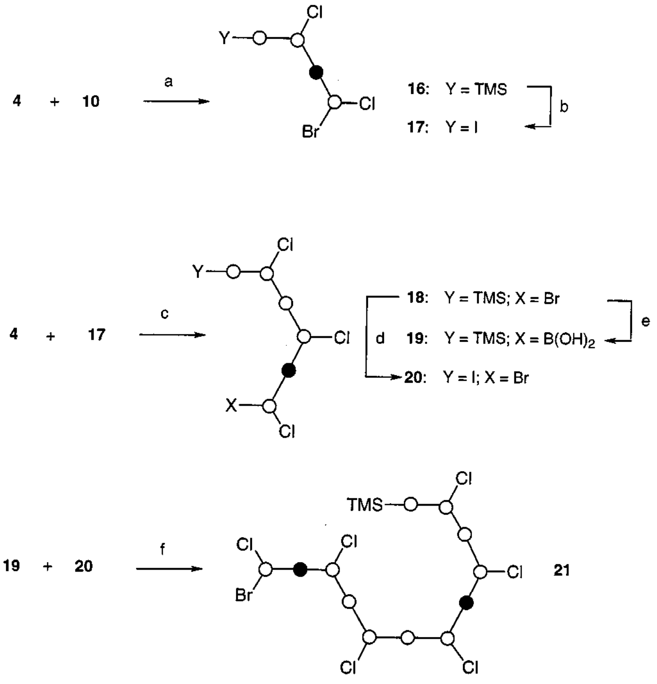
Characterization of Building Blocks and of Cycle 29

All building blocks were obtained as highly viscous, colorless oils. They are highly soluble in common organic solvents and were all therefore fully characterized (see Experimental Section) except for most of the boron compounds for which correct data from elemental analysis could not be obtained, as is normally the case. Boronic acids tend to trimerize to the corresponding boroxines.[9] The NMR shifts given in nonpolar solvents refer to these trimers.

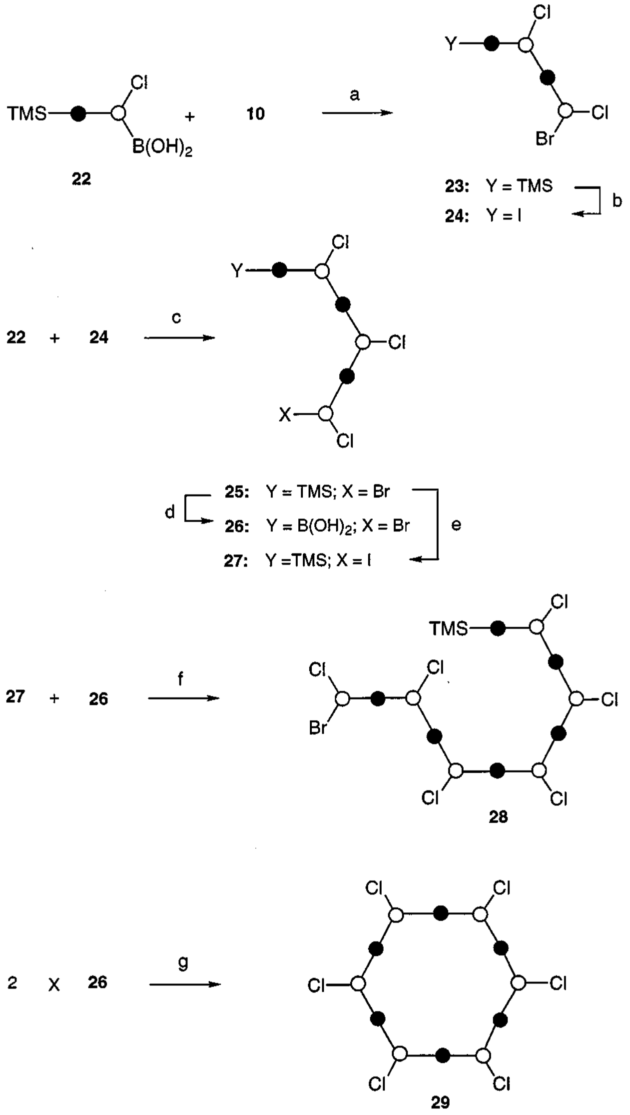
The ^{1}H- and ^{13}C-NMR spectra of cycle **29** are very simple because of its hexagonal symmetry and the few signals observed can be fully assigned. The spectra of precursor **26** are far more complex, which is consistent with the proposed cyclic structure of **29**. For example, the ^{13}C-NMR spectrum of **26** shows 24 aromatic signals including the characteristic absorptions of C−Br at $\delta = 122.3$ whereas that of **29** exhibits only 7 such signals, as expected. Further support for the cyclic nature of **29** comes from SEC co-injection experiments with “half-rings”, deboronified direct precursor and cycle which gave significantly different retention times for all of them. Finally a EI mass spectrum gives the molecular ion at $m/z = 2123$.



Scheme 2. (a) *n*-butyllithium, triisopropyl borate, 75%, (b) Pd[PPh$_3$]$_4$/toluene; Ba(OH)$_2$/H$_2$O, 77%, (c) ICl, 94%, (d) *n*-butyllithium, triisopropyl borate, 52%, (e) Pd[PPh$_3$]$_4$/toluene; Ba(OH)$_2$/H$_2$O, 80%, (f) *n*-butyllithium, 1,2-diiodoethane, 82%



Scheme 3. (a) Pd[PPh$_3$]$_4$/toluene; Ba(OH)$_2$/H$_2$O, 70%, (b) ICl, 83%, (c) Pd[PPh$_3$]$_4$/toluene; Ba(OH)$_2$/H$_2$O, 90%, (d) ICl. 97%, (e) *n*-butyllithium, triisopropyl borate, 44%, (f) Pd[PPh$_3$]$_4$/toluene; Ba(OH)$_2$/H$_2$O, 91%



Scheme 4. (a) Pd[PPh$_3$]$_4$/toluene; Ba(OH)$_2$/H$_2$O, 91%, (b) ICl, 96%, (c) Pd[PPh$_3$]$_4$/toluene; Ba(OH)$_2$/H$_2$O, 90%, (d) BBr$_3$, 80%, (e) *n*-butyllithium, 1,2-diiodoethane, 37%, (f) Pd[PPh$_3$]$_4$/toluene; Ba(OH)$_2$/H$_2$O, 37%, (g) Pd[PPh$_3$]$_4$/toluene; Ba(OH)$_2$/H$_2$O, 15%

Experimental Section

General: Reagents were purchased from Fluka, Aldrich, or Acros and used without further purification. All solvents were purchased from Fluka, Aldrich, or Acros and purified and dried by standard methods. Starting materials **1**,[10] **2**,[11] **5**,[12] **8**,[2] **10**,[6b] and **22**[6b] were prepared according to literature procedures. All reactions were carried out under N$_2$. − ^{1}H-NMR spectra: Bruker AM 270 spectrometer (270 MHz) or Bruker AC 500 spectrometer (500 MHz) (TMS at $\delta = 0$, CHCl$_3$ at $\delta = 7.24$, dichloromethane at $\delta = 5.32$ or DMSO at $\delta = 2.49$ as internal standard). − ^{13}C spectra: Bruker AM 270 spectrometer (67.9 MHz) or Bruker AC 500 spectrometer (126 MHz) (CDCl$_3$ at $\delta = 77.0$ as internal standard). − MS: Varian MAT 711 spectrometer. − Melting points: Büchi 510 (open capillaries, uncorrected values). − Column chromatography: Merck silica gel 60, 0.040−0.063 mm (230-400 mesh). − Analytical TLC: alumina sheets, silica gel Si 60 F$_{254}$ (Merck), detection: UV absorption. − Elemental analyses: Perkin Elmer EA 240.

3-Bromo-5-chloro-4′-(trimethylsilyl)biphenyl (3): Phenylboronic acid **1** (7.99 g, 41.2 mmol) and 1-bromo-3-chloro-5-iodophenyl **2** (12.01 g, 37.8 mmol) were dissolved in toluene (150 mL). The solution was degassed and let down to N$_2$ repeatedly. A saturated aqueous solution of Ba(OH)$_2$ (100 mL) was added.The mixture was degassed again and tetrakis(triphenylphosphane)palladium(0) (440 mg, 0.38 mmol) was added. The mixture was refluxed for 18 h with vigorous stirring and then allowed to cool to room temperature. The layers were separated, the aqueous one was washed twice with toluene (35 mL) and the combined organic layers twice with water (30 mL). The organic phase was dried (MgSO$_4$). Chromatographic separation through silica gel with hexane gave 6.4 g (50%) of **3** as a colorless oil. − $R_f = 0.51$ (hexane). − ^{1}H NMR (270 MHz, CDCl$_3$): $\delta = 0.32$ (s, 9 H, SiMe$_3$), 7.50−7.57 (m, 4 H, aromatic H), 7.61−7.66 (m, 3 H, aromatic H). − ^{13}C NMR (67.9 MHz, CDCl$_3$): $\delta = -1.12$, 123.01, 125.91, 126.20, 128.33, 129.82, 133.94, 135.28, 138.47, 140.72, 144.20. − MS (EI, 70 eV, 60°C); *m/z* (%): 338 (21), 339 (6), 340 (28), 341 (7), 342 (8) [M$^+$], 325 (100) [M − CH$_3$]. − C$_{15}$H$_{16}$BrClSi (339.73): calcd. C 53.03, H 4.74; found C 52.71, H 4.58.

5-Chloro-4′-(trimethylsilyl)biphenyl-3-boronic Acid (4): Bromobiphenyl **3** (5.28 g, 15.54 mmol) was dissolved in diethyl ether (200 mL). A 1.6 M solution of *n*-butyllithium in hexane (11.66 mL, 18.65 mmol) was dropped in at −78°C. After warming to room temperature and cooling again to −78°C, triisopropyl borate (7.30 g, 38.8 mmol) was added within 2 h. The reaction mixture was allowed to come to room temperature overnight. 150 mL water were then added. The layers were separated, the aqueous layer was washed twice with diethyl ether (120 mL) and the combined organic layers were washed twice with water (200 mL). The organic phase was dried with MgSO$_4$. The solvent was removed in vacuo at 35°C. Chromatographic separation through silica gel with hexane/ethyl acetate = 1:1 gave 3.74 g (79%) of **4** as a colorless viscous oil. − $R_f = 0.31$ (hexane/ethyl acetate = 1:1). − ^{1}H NMR (270 MHz, [D$_6$]DMSO): $\delta = 0.27$ (s, 9 H, SiMe$_3$), 7.64 (m, 4 H, aromatic H), 7.72−7.76 (m, 2 H, aromatic H), 8.00 (s, 1 H, aromatic H), 8.38 [s, 2 H, B(OH)$_2$]. − ^{13}C NMR (67.9 MHz, CDCl$_3$): $\delta = -1.07$, 126.45, 131.62, 131.86, 132.14, 133.90, 134.01, 134.87, 139.61, 140.30, 142.70. − MS (EI, 70 eV, 350°C); *m/z* (%): 859 (77), 860 (86), 861 (55), 862 (40), 863 (19) [M$^+$, trimeric anhydride].

3-Bromo-5′′′′-chloro-2′′′,5′′′-di-*n*-hexyl-4′′′′′-(trimethylsilyl)-1,1′:4′,1′′:3′′,1′′′:4′′′,1′′′′:3′′′′,1′′′′′-sexiphenyl (6): The procedure was analogous to the one described for **3**. Compounds **4** (0.75 g, 2.47 mmol), **5** (1.68 g, 2.47 mmol), tetrakis(triphenylphosphane)palladium(0) (29 mg, 0.02 mmol), toluene (100 mL), and a saturated aqueous solution of Ba(OH)$_2$ (55 mL). Chromatographic separation through silica gel with hexane gave 1.79 g (89%) of **6** as a colorless oil. − $R_f = 0.04$ (hexane). − ^{1}H NMR (250 MHz, CD$_2$Cl$_2$): $\delta = 0.30$ (s, 9 H, SiMe$_3$), 0.81−0.86 (m, 6 H, CH$_3$), 1.02−1.43 (m, 12 H, *g*-, *d*-, *e*-CH$_2$), 1.49−1.65 (m, 4 H, b-CH$_2$), 2.56−2.72 (m, 4 H, *a*-CH$_2$), 7.22 (s, 1 H, aromatic H), 7.26 (s, 1 H, aromatic H), 7.28−7.88 (m, 19 H, aromatic H). − ^{13}C NMR (62.9 MHz, CDCl$_3$): $\delta = -1.117$ (SiMe$_3$), 14.07, 22.49, 29.18, 31.50, 32.63, 32.70, 123.00 (C−Br), 125.49, 126.42, 126.94, 127.44, 127.58, 127.95, 128.16, 128.43, 128.60, 129.97, 130.23, 130.76, 131.07, 133.94, 134.35, 137.51, 137.76, 138.53, 139.48, 140.01, 140.13, 140.50, 141.19, 142.36, 142.52, 142.68, 144.04. − MS (EI, 70 eV, 200°C); *m/z* (%): 810 (71), 811 (42), 812 (100), 813 (52), 814 (35) [M$^+$]. − C$_{51}$H$_{56}$BrClSi: calcd. 810.3023 found 810.3044 (MS).

5′-Chloro-2′′,5′′-di-*n*-hexyl-3′′′′′-iodo-4-trimethylsilyl-1,1′:3′,1′′:4′′,1′′′:3′′′,1′′′′:4′′′′,1′′′′′-sexiphenyl (7): The bromotrimethylsilylsexiphenyl **6** (786 mg, 0.97 mmol), and bromobenzene (1.52 g, 9.7 mmol) were dissolved in diethyl ether (6 mL). NaH (10 mg) was added. At −78°C a 1.6 M solution of *n*-butyllithium in hexane (7.0 mL, 11.21 mmol) was dropped in. After warming to room temperature and cooling again 1,2-diiodoethane (6.01 g, 21.35 mmol) disolved in diethyl ether (45 mL) was added. The reaction mixture was allowed to warm to room temperature overnight and water (12 mL) was added. The layers were separated, the aqueous layer was washed twice with diethyl ether (15 mL) and the combined organic layers were washed twice with water (15 mL). The organic phase was dried with $MgSO_4$. The solvent was removed in vacuo. Chromatographic separation through silica gel with hexane gave 589 mg (76%) of **7** as a colorless highly viscous oil. − R_f = 0.05 (hexane). − ^{1}H NMR (270 MHz, $CDCl_3$): δ = 0.49 (s, 9 H, $SiMe_3$), 0.82−0.92 (m, 6 H, CH_3), 1.19−1.38 (m, 12 H, *g*-, *d*-, *e*-CH_2), 1.52−1.69 (m, 4 H, *b*-CH_2), 2.64−2.77 (m, 4 H, *a*-CH_2), 7.21 (tr, ^3J = 7 Hz, 1 H, aromatic H), 7.27 (s, 1 H, aromatic H), 7.30 (s, 1 H, aromatic H), 7.42−7.47 (m, 2 H, aromatic H), 7.54−7.63 (m, 3 H, aromatic H), 7.64−7.75 (m, 10 H, aromatic H), 7.76−7.81 (m, 2 H, aromatic H), 8.05 (mc, 1 H, aromatic H). − ^{13}C NMR (67.9 MHz, $CDCl_3$): δ = −1.12 ($SiMe_3$), 14.03, 22.47, 29.18, 31.47, 32.61, 32.68, 94.93 (C−I), 125.48, 126.22, 126.43, 127.47, 127.60, 127.98, 128.15, 128.42, 128.59, 130.43, 130.75, 131.04, 133.95, 134.30, 135.99, 136.22, 137.53, 137.78, 138.53, 139.48, 140.06, 140.18, 140.54, 141.18, 142.36, 142.53, 142.87, 144.03. − MS (EI, 70 eV, 250°C); *m*/*z* (%): 858 (100), 859 (57.4), 860 (45.8), 861 (15.6), 862 (5.9) [M^+]. − $C_{51}H_{56}ClISi$ (859.44): calcd. C 71.27, H 6.57; found C 71.05, H 6.32.

2′,2′′′,5′,5′′′-Tetra-*n*-hexyl-4′′′-trimethylsilyl-1,1′:4′,1′′:3′′,1′′′-quaterphenyl-3-boronic Acid (9): The procedure was analogous to that described for **4**. Compound **8** (2.36 g, 2.784 mmol), diethyl ether (50 mL), and tetrahydrofurane (50 mL), a 1.6 M solution of *n*-butyllithium in hexane (5.22 mL, 8.35 mmol), triisopropyl borate (3.14 g, 16.7 mmol). Chromatographic separation through silica gel with hexane/ethyl acetate = 3:1 gave 1.53 g (75%) of **9** as a colorless viscous oil. − R_f = 0.25 (hexane/ethyl acetate, 3:1). − ^{1}H NMR (270 MHz, $CDCl_3$): δ = 0.55 (s, 9 H, $SiMe_3$), 0.85−1.12 (m,12 H, Me), 1.24−1.88 (m, 32 H, *b*-, *g*-, *d*-, *e*-CH_2), 2.67−2.94 (m, 8 H, *a*-CH_2), 7.29 (s, 1 H, aromatic H), 7.38 (2s, 2 H, aromatic H), 7.42−7.80 (m, 7 H, aromatic H), 8.36−8.47 (2 s, 2 H, aromatic H). − ^{13}C NMR (67.9 MHz, $CDCl_3$): δ = 0.60, 14.06, 22.52, 22.65, 26.92, 29.30, 29.77, 31.57, 31.84, 32.67, 32.79, 36.06, 127.62, 130.24, 131.00, 133.76, 135.71, 136.29, 136.55, 136.65, 137.61, 137.68, 140.67, 140.93, 141.64, 141.88, 142.47, 145.99. − MS (EI, 70 eV, 350°C); *m*/*z* (%): 2222 (0.18), 2223 (0.21) [M^+, trimeric anhydride]; 713 (6.13), 714 (5.19), 715 (100), 716 (64.03), 717 (22.48), 718 (5.83) [monomer − $B(OH)_2$].

3-Bromo-5-chloro-2′,2′′′,2′′′′′,5′,5′′′,5′′′′′-hexa-*n*-hexyl-4′′′′′-trimethylsilyl-1,1′:4′,1′′:3′′,1′′′:4′′′,1′′′′:3′′′′,1′′′′′-sexiphenyl (11): The procedure was analogous to that described for **3**. Compounds **9** (1.53 g, 2.02 mmol), **10** (1.36 g, 2.42 mmol), tetrakis(triphenylphosphane)palladium(0) (11.6 mg, 0.01 mmol), toluene (40 mL), and a saturated aqueous solution of $Ba(OH)_2$ (40 mL). Reflux for 3 d. Chromatographic separation through silica gel with hexane gave 1.78 g (77%) of **11** as a colorless oil. − R_f = 0.17 (hexane). − ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 0.36 (s, 9 H, $SiMe_3$), 0.78−0.88 (m, 15 H, Me), 0.88−0.92 (m, 3 H, Me), 1.15−1.29 (m, 30 H, CH_2), 1.30−1.36 (m, 4 H, CH_2), 1.40−1.46 (m, 2 H, CH_2), 1.46−1.55 (m, 10 H, *b*-CH_2), 1.59−1.67 (m, 2 H, *b*-CH_2), 2.54−2.60 (m, 2 H, *a*-CH_2), 2.62−2.69 (m, 10 H, *a*-CH_2), 7.11(s, 2 H, aromatic H), 7.20 (s, 1 H, aromatic H), 7.25 (s, 2 H, aromatic H), 7.30−7.38 (m, 6 H, aromatic H), 7.39 (s, 2 H, aromatic H), 7.45−7.51 (m, 3 H, aromatic H), 7.56 (tr, *J* = 2.5 Hz, 1 H, aromatic H). − ^{13}C NMR (67.9 MHz, $CDCl_3$): δ = 0.58 (3 C, $SiMe_3$), 14.05, 22.54, 22.58, 22.66, 29.12, 29.25, 29.32, 29.77, 31.46, 31.58, 31.83, 32.3−32.5 (br), 32.6−32.9 (br), 35.9−36.1 (br), 122.30 (C−Br), 127.4−128.1(br), 128.1−128.4(br), 129.4−129.8 (2 signals), 130.1−130.4(br), 130.5−130.6(br), 130.7−130.8 (br), 130.9−131.1 (br), 131.1−131.2 (br), 131.2−131.3 (br), 134.63, 135.6−135.8 (br), 136.54, 136.65, 137.32, 137.51, 137.54, 137.88, 137.92, 140.58, 140.78, 141.30, 141.58, 141.71, 141.76, 141.83, 142.43, 145.20, 146.01. − MS (EI, 70 eV, 250°C); *m*/*z* (%): 1147 (62.7), 1148 (55.7), 1149 (100.0), 1150 (73.3), 1151 (53.4), 1152 (27.7), 1153 (10.6), 1154 (3.2) [M^+]. $C_{75}H_{104}BrClSi$: calcd. 1146.67793; found 1146.67799 (MS).

5-Chloro-2′,2′′′,2′′′′′,5′,5′′′,5′′′′′-hexa-*n*-hexyl-4′′′′′-trimethylsilyl-1,1′:4′,1′′:3′′,1′′′:4′′′,1′′′′:3′′′′,1′′′′′-sexiphenyl-3-boronic Acid (12): The procedure was analogous to that described for **4**. Compound **11** (797 mg, 0.69 mmol), diethyl ether (50 mL), a 1.6 M solution of *n*-butyllithium in hexane (0.65 mL, 1.04 mmol), triisopropyl borate (626 mg, 3.33 mmol). Chromatographic separation through silica gel with hexane/ethyl acetate = 6:1 gave 393 mg (52%) of **12** as a colorless viscous oil. − R_f = 0.14 (hexane/ethyl acetate = 6:1). − ^{1}H NMR (270 MHz, $CDCl_3$): δ = 0.46 (s, 9 H, $SiMe_3$), 0.80−1.03 (m, 18 H, CH_3), 1.19−1.46 (m, 34 H, *g*-, *d*-, *e*-CH_2), 1.46−1.79 (m, 14 H, *b*-, *g*-, *d*-, *e*-CH_2), 2.50−2.89 (m, 12 H, *a*-CH_2), 7.20−7.83 (m, 15 H, aromatic H), 8.15 (mc, 1, aromatic H), 8.26 (mc, 1, aromatic H). − ^{13}C NMR (67.9 MHz, $CDCl_3$): δ = 0.61 ($SiMe_3$), 14.02, 22.53, 22.63, 29.29, 29.74, 31.43, 31.49, 31.58, 31.82, 32.62, 32.83, 36.05, 127.61, 130.23, 130.75, 131.01, 131.24, 134.24, 135.70, 136.54, 136.67, 137.51, 137.54, 137.93, 139.08, 140.69, 140.82, 141.50, 141.70, 141.84, 141.91, 142.49, 143.80, 145.96. − MS (EI, 70 eV, 380°C, max. temp.); *m*/*z* (%): 1069 (100), 1070 (83.7), 1071 (67.4), 1072 (40.0), 1073 (14.9), 1074 (4.9) [$M^+ - B(OH)_2 + H$].

3-Bromo-5-chloro-2′,2′′′,2′′′′′,5′,5′′′,5′′′′′-hexa-*n*-hexyl-4′′′′′-iodo-1,1′:4′,1′′:3′′,1′′′:4′′′,1′′′′:3′′′′,1′′′′′-sexiphenyl (13): The bromotrimethylsilylsexiphenyl **11** (807 mg, 0.70 mmol) was dissolved in dichloromethane (10 mL). ICl (125 mg, 0.77 mmol) in dichloromethane (5 mL) was added at 0°C within 20 min under N_2. After 30 minutes and warming to room temperature a 1 M solution of sodium disulphite (10 mL) was added. The layers were separated, the aqueous layer was washed twice with dichloromethane (15 ml) and the combined organic layers were washed twice with water (20 mL). The organic phase was dried ($MgSO_4$). Chromatographic separation through silica gel with hexane gave 796 mg (94%) of **13** as a colorless oil. − R_f = 0.18 (hexane). − ^{1}H NMR (270 MHz, $CDCl_3$): δ = 0.77−0.94 (m, 18 H, CH_3), 1.10−1.39 (m, 32 H, *g*-, *d*-, *e*-CH_2), 1.39−1.56 (m, 14 H, *b*-, *g*-, *d*-, *e*-CH_2), 1.56−1.68 (m, 2 H, *b*-CH_2), 2.50−2.76 (m, 12 H, *a*-CH_2), 7.09 (s, 2 H, aromatic H), 7.16−7.20 (m, 4 H, aromatic H), 7.25−7.30 (m, 2 H; aromatic H), 7.30−7.39 (m, 5 H, aromatic H), 7.43−7.52 (m, 2 H, aromatic H), 7.55 (mc, 1 H, aromatic H), 7.75 (s, 1 H, aromatic H). − ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 14.01, 22.50, 22.60, 29.10, 29.21, 29.27, 29.70, 30.38, 31.18, 31.41, 31.54, 31.65, 32.34, 32.47, 32.73, 32.79, 40.36, 99.42 (C−I), 122.29 (C−Br), 127.40, 127.56, 127.76, 127.93, 128.29, 129.57, 130.03, 130.20, 130.49, 130.69, 130.94, 131.15, 134.64, 137.32, 137.50, 137.53, 137.87, 137.94, 139.83, 139.94, 140.60, 140.73, 140.87, 141.34, 141.74, 141.82, 141.92, 142.58, 145.24. − MS (EI, 70 eV, 300°C); *m*/*z* (%): 1200 (64.52), 1201 (49.5), 1202 (100), 1203 (66.8), 1204 (44.4), 1205 (21.9), 1206 (7.1), 1207 (1.7) [M^+]. − $C_{72}H_{95}ClBrI$ (1202.80): calcd. C 71.90, H 7.96; found C 72.08, H 7.87.

3-Bromo-5,5′′′′′′-dichloro-2′,2′′′,2′′′′′2′′′′′′′,2′′′′′′′′′,2′′′′′′′′′′′, 5′,5′′′,5′′′′′,5′′′′′′′,5′′′′′′′′′,5′′′′′′′′′-dodeca-*n*-hexyl-4′′′′′′′′′′′-trimethylsilyl-1,1′:4′,1′′:3′′,1′′′:4′′′,1′′′′:3′′′′,1′′′′′:4′′′′′,1′′′′′′:

3′′′′′′,1′′′′′′′:4′′′′′′′,1′′′′′′′′:3′′′′′′′′,1′′′′′′′′′:4′′′′′′′′′,1′′′′′′′′′′:3′′′′′′′′′′,1′′′′′′′′′′′-bideciphenyl (14): The procedure was analogous to the one described for **3**. Compounds **12** (390 mg, 3.56·10^{-4} mol), **13** (446 mg , 3.71·10^{-4} mol), tetrakis(triphenylphosphane)palladium(0) (14 mg, 1.2·10^{-5} mol), toluene (20 mL) and a saturated aqueous solution of Ba(OH)$_2$ (30 mL). Reflux for 3 d. Chromatographic separation through silica gel with first hexane and then hexane/dichloromethane = 10:1 gave 610 mg (80%) of **14** as a colorless oil. − R_f = 0.10 (hexane). − ^{1}H NMR (270 MHz, CDCl$_3$): δ = 0.49 (s, 9 H, SiMe$_3$), 0.75−0.96 (m, 36 H, CH$_3$), 1.12−1.49 (m, 72 H, *g*-, *d*-, *e*-CH$_2$), 1.42−1.64 (m, 24 H, *b*-CH$_2$), 2.52−2.79 (m, 24 H, *a*-CH$_2$), 7.11 (s, 1 H, aromatic H), 7.15 (s, 1 H, aromatic H), 7.18−7.26 (m, 8 H, aromatic H), 7.31−7.43 (m, 16 H, aromatic H), 7.43−7.45 (m, 2 H, aromatic H), 7.48 (mc, 2 H, aromatic H), 7.51 (mc, 2 H, aromatic H), 7.54 (mc, 2 H, aromatic H). − ^{13}C NMR (67.9 MHz, CDCl$_3$): δ = 0.61 (SiMe$_3$), 14.04, 22.53, 29.11, 29.29, 29.74, 31.44, 31.57, 31.83, 32.49, 32.83, 36.05, 122,31 (C−Br), 127.68, 128.31, 128.75, 129.59, 130.24, 130.52, 130.79, 131.00, 133.51, 134.67, 135.70, 136.54, 136.66, 137.34, 137.45, 137.53, 137.75, 137.91, 139.38, 140.69, 140.79, 141.27, 141.36, 141.56, 141.67, 141.77, 142.47, 143.40, 145.26, 145.98. − MS (EI, 70 eV, 380°C, max. temp.); *m/z* (%): 2141 (32.1), 2142 (40.9), 2143 (54.7), 2144 (62.7), 2145 (56.6), 2146 (45.7), 2147 (29.3), 2148 (21.3) [M$^+$]. − C$_{147}$H$_{199}$BrCl$_2$Si (2145.08): calcd. C 82.23, H 9.35; found C 81.95, H 9.12.

5,5′′′′′′-Dichloro-2′,2′′′,2′′′′′,2′′′′′′′,2′′′′′′′′′,5′,5′′′,5′′′′′,5′′′′′′′,5′′′′′′′′′,5′′′′′′′′′-dodecahexyl-4′′′′′′′′′′-(trimethylsilyl)-3-iodo-1,1′:4′,1′′:3′′,1′′′:4′′′,1′′′′:3′′′′,1′′′′′:4′′′′′,1′′′′′′:3′′′′′′,1′′′′′′′:4′′′′′′′,1′′′′′′′′:3′′′′′′′′,1′′′′′′′′′:4′′′′′′′′′,1′′′′′′′′′′:3′′′′′′′′′′,1′′′′′′′′′′′-bideciphenyl (15): The procedure was analogous to that described for **7**. **14** (262 mg, 1.22·10^{-4} mol), diethyl ether (2 mL), NaH (7 mg), a 1.6 M solution of *n*-butyllithium in hexane (0.11 mL, 1.83·10^{-4} mol), 1,2-diiodoethane (172 mg, 6.1·10^{-4} mol). Chromatographic separation through silica gel with hexane/dichloromethane = 96:4 gave 219 mg (82%) of **15** as a colorless oil. − R_f = 0.22 (hexane/dichloromethane, 96:4). − ^{1}H NMR (500 MHz, CDCl$_3$): δ = 0.43 (s, 9 H, SiMe$_3$), 0.82−1.00 (m, 36 H, CH$_3$), 1.16−1.43 (m, 72 H, *g*-, *d*-, *e*-CH$_2$), 1.49−1.65 (m, 20 H, *b*-CH$_2$), 1.65−1.75 (m, 4 H, *b*-CH$_2$), 2.60−2.67 (m, 4 H, *a*-CH$_2$), 2.67−2.83 (m, 20 H, *a*-CH$_2$), 7.18 (s, 1 H, aromatic H), 7.20 (s, 1 H, aromatic H), 7.22 (s, 1 H, aromatic H), 7.24−7.31 (m, 8 H, aromatic H), 7.38−7.49 (m, 17 H, aromatic H), 7.49−7.58 (m, 4 H, aromatic H), 7.71 (mc, 1 H, aromatic H), 7.79 (mc, 1 H, aromatic H). − ^{13}C NMR (125.8 MHz, CDCl$_3$): δ = 0.58 (SiMe$_3$), 14.06, 22.53, 22.64, 29.11, 29.24, 29.30, 29.75, 31.44, 31.56, 31.81, 32.45, 32.67, 32.69, 32.77, 36.02, 93.67 (C−I), 127.61, 127.65, 128.92, 130.20, 130.29, 130.78, 131.00, 131.11, 133.51, 134.53, 135.23, 135.71, 136.54, 137.33, 137.44, 137.52, 137.74, 139.32, 140.63, 140.73, 141.20, 141.48, 141.67, 141.72, 143.32, 146.00. − MS (EI, 70 eV, 380°C, max. temp.); *m/z* (%): 2189 (20.0), 2190 (35.1), 2191 (56.8), 2192 (53.8), 2193 (48.8), 2194 (37.4), 2195 (21.5), 2196 (12.3) [M$^+$], 2120 (100) [M$^+$ − C$_5$H$_{11}$]. − C$_{147}$H$_{199}$Cl$_2$ISi (2192.08): calcd. C 80.55, H 9.15; found: C 80.31, H 8.94.

3-Bromo-5,5′′-dichloro-2′,5′-di-*n*-hexyl-′′′′-trimethylsilyl-1,1′:4′,1′′:3′′,1′′′-quarterphenyl (16): The procedure was analogous to the one described for **3**. Compounds **4** (1.41 g, 4.63 mmol), **10** (2.60 g, 4.63 mmol), tetrakis(triphenylphosphane)palladium(0) (53 mg, 0.02 mmol), toluene (150 mL), and a saturated aqueous solution of Ba(OH)$_2$ (100 mL). Reflux for 1 d. Chromatographic separation through silica gel with hexane gave 2.24 g (70%) of **116** as a colorless oil. − R_f = 0.36 (hexane). − ^{1}H NMR (270 MHz, CDCl$_3$): δ = 0.30 (s, 9 H, SiMe$_3$), 0.70−0.99 (m, 6 H, CH$_3$), 1.04−1.48 (m, 12 H, *g*-, *d*-, *e*-CH$_2$), 1.48−1.56 (m, 4 H, *b*-CH$_2$), 2.46−2.66 (m, 4 H, *a*-CH$_2$), 7.10 (s, 1 H, aromatic H), 7.16 (s, 1 H, aromatic H), 7.32 (m, 2 H, aromatic H), 7.44 (m, 1 H, aromatic H), 7.48 (m, 2 H, aromatic H), 7.56 (m, 1 H, aromatic H), 7.62 (m, 4 H, aromatic H). − ^{13}C NMR (67.9 MHz, CDCl$_3$): δ = −1.11 (SiMe$_3$), 14.06, 22.51, 29.13, 31.47, 31.76, 32.45, 32.59, 122.39 (C−Br), 125.64, 126.42, 128.06, 128.24, 129.69, 130.65, 130.92, 133.95, 134.43, 134.72, 137.53, 137.82, 138.51, 139.97, 140.16, 140.32, 142.62, 143.71, 145.02. − MS (EI, 70 eV, 250°C); *m/z* (%): 692 (69), 693 (22), 694 (100), 695 (53), 696 (67), 697 (16), 698 (13) [M$^+$]. − C$_{39}$H$_{47}$BrCl$_2$Si (694,70): calcd. C 67.41, H 6.82; found C 67.72, H 6.61.

3-Bromo-5,5′′-dichloro-2′,5′-di-*n*-hexyl-4′′′-iodo-1,1′:4′,1′′:3′′,1′′′-quarterphenyl (17): The procedure was analogous to the one described for **13**. Compunds **16** (2.24 g, 3.21 mmol), dichloromethane(40 mL), ICl (0.57 g, 3.53 mmol), dichloromethane(15 mL), a 1 M aqueous solution of sodium disulfite (15 mL). Chromatographic separation through silica gel with hexane gave 1.99 g (83%) of **17** as a colorless oil. − R_f = 0.33 (hexane). − ^{1}H NMR (270 MHz, CDCl$_3$): δ = 0.73−0.92 (m, 6 H, CH$_3$), 1.03−1.38 (m, 12 H, *g*-, *d*-, *e*-CH$_2$), 1.42−1.57 (m, 4 H, *b*-CH$_2$), 2.48−2.71 (m, 4 H, *a*-CH$_2$), 7.10 (s, 1 H, aromatic H), 7.17 (s, 1 H, aromatic H), 7.30−7.46 (m, 6 H, aromatic H), 7.54−7.59 (m, 2 H, aromatic H), 7.78−7.83 (m, 2 H, aromatic H). − ^{13}C NMR (67.9 MHz, CDCl$_3$): δ = 14.03, 22.46, 29.07, 31.41, 32.38, 32.49, 93.93 (C−I), 122.32 (C−Br), 125.36, 126.00, 128.18, 128.36, 128.86, 129.68, 130.59, 130.80, 134.50, 134.65, 137.56, 137.73, 138.00, 138.55, 139.09, 139.99, 141.43, 143.85, 144.86. − MS (EI, 70 eV, 200°C); *m/z* (%): 746 (60.5), 747 (24.4), 748 (100), 749 (38.5), 750 (52.4), 751 (17.6), 752 (9.8), 753 (2.8) [M$^+$]. − C$_{36}$H$_{38}$BrCl$_2$I (748.41): calcd. C 57.78, H 5.12; found: C 57.51, H 4.95.

3-Bromo-5,5′′,5′′′′-trichloro-2′,5′-di-*n*-hexyl-4′′′′′-(trimethylsilyl)-1,1′:4′,1′′:3′′,1′′′:4′′′,1′′′′:3′′′′,1′′′′′-sexiphenyl (18): The procedure was analogous to the one described for **3**. Compounds **4** (0.79 g, 2.58 mmol), **17** (1.93 g, 2.58 mmol), tetrakis(triphenylphosphane)palladium(0) (30 mg, 0.03 mmol), toluene (100 mL), and a saturated aqueous solution of Ba(OH)$_2$ (45 mL). Reflux for 2 d. Chromatographic separation through silica gel with hexane gave 2.05 g (90%) of **18** as a colorless oil of high viscosity. − R_f = 0.12 (hexane). − ^{1}H NMR (270 MHz, CDCl$_3$): δ = 0.32 (s, 9 H, SiMe$_3$), 0.61−1.00 (m, 6 H, CH$_3$), 1.00−1.42 (m, 12 H, *g*-, *d*-, *e*-CH$_2$), 1.44−1.58 (m, 4 H, *b*-CH$_2$), 2.46−2.70 (m, 4 H, *a*-CH$_2$), 7.12 (s, 1 H, aromatic H), 7.18 (s, 1 H, aromatic H), 7.28−7.40 (m, 2 H, aromatic H), 7.44 (mc, 1 H, aromatic H), 7.52−7.58 (m, 1 H, aromatic H), 7.62−7.69 (m, 7 H, aromatic H), 7.70−7.78 (m, 6 H, aromatic H). − ^{13}C NMR (67.9 MHz, CDCl$_3$): δ = −1.14, 14.02, 22.47, 29.06, 29.11, 31.35, 31.44, 32.42, 32.55, 122.32 (C−Br), 124.21, 125.58, 125.9, 126.22, 126.49, 127.66, 127.69, 128.22, 129.71, 130.63, 130.86, 133.97, 134.47, 134.68, 135.14, 137.59, 137.82, 138.56, 139.26, 139.44, 140.08, 140.19, 140.38, 141.90, 142.60, 143.53, 143.82, 144.95, 156.46. − MS (EI, 70 eV, 250°C); *m/z* (%): 878 (41.5), 879 (25.2), 880 (85.0), 881 (51.2), 882 (65.4), 883 (32.7), 884 (24.8), 885 (10.7), 886 (4.9) [M$^+$]. − C$_{51}$H$_{54}$BrCl$_3$Si: calcd. 878.2243; found: 878.2276 (MS).

5,5′′,5′′′′-Trichloro-2′,5′-di-*n*-hexyl-4′′′′′-trimethylsilyl-1,1′:4′,1′′:3′′,1′′′:4′′′,1′′′′:3′′′′,1′′′′′-sexiphenyl-3-boronic Acid (19): The procedure was analogous to that described for **4**. Compound **18** (1.10 g, 1.25 mmol), diethyl ether (20 mL), a 1.6 M solution of *n*-butyllithium in hexane (1.01 mL, 1.62 mmol), triisopropyl borate (940 mg, 5.00 mmol). Chromatographic separation through silica gel with hexane/ethyl acetate = 3:1 gave 461 mg (44%) of **19** as a colorless viscous oil. − R_f = 0.29 (hexane/ethyl acetate = 3:1).

− ^{1}H NMR (270 MHz, $CDCl_3$): δ = 0.34 (s, 9 H, $SiMe_3$), 0.79−0.92 (m, 6 H, CH_3), 1.18−1.42 (m, 12 H, *g*-, *d*-, *e*-CH_2), 1.50−1.66 (m, 4 H, *b*-CH_2), 2.53−2.73 (m, 4 H, *a*-CH_2), 7.19−7.31 (m, 2 H, aromatic H), 7.41−7.50 (m, 2 H, aromatic H), 7.52−7.79 (m, 14 H, aromatic H), 8.18−8.24 (m, 1 H, aromatic H). − ^{13}C NMR (67.9 MHz, $CDCl_3$): δ = −1.18 ($SiMe_3$), 13.98, 14.09, 19.07, 20.89, 22.45, 22.61, 26.87, 29.15, 29.66, 31.44, 32.63, 124.05, 125.43, 125.82, 126.14, 126.41, 127.60, 128.26, 130.89, 133.91, 134.24, 134.52, 135.11, 137.52, 137.71, 137.80, 139.14, 139.29, 139.69, 139.96, 140.03, 140.23, 141.84, 142.52, 143.42, 143.51, 143.92, 144.06. − MS (EI, 70 eV, 350°C); *m/z* (%): 800 (86.2), 801 (54.3), 802 (100), 803 (56.8), 804 (45.6), 805 (20.5), 806 (9.7) [M^+ − $B(OH)_2$ + H, monomer].

3-Bromo-5,5′′,5′′′′-trichloro-2′,5′-di-*n*-hexyl-4′′′′′-iodo-1,1′:4′,1′′:3′′,1′′′:4′′′,1′′′′:3′′′′,1′′′′′-sexiphenyl (20): The procedure was analogous to the one described for **13**. Compound **18** (882 mg, 1.00 mmol), dichloromethane (5 mL), ICl (207 mg, 1.30 mmol), dichloromethane (5 mL), 1 м aqueous solution of sodium disulfite (20 mL). Chromatographic separation through silica gel with hexane gave 910 mg (97%) of **20** as a colorless oil. − R_f = 0.14 (hexane). − ^{1}H NMR (270 MHz, $CDCl_3$): δ = 0.72−0.93 (m, 6 H, CH_3), 1.12−1.31 (m, 12 H, *g*-, *d*-, *e*-CH_2), 1.41−1.57 (m, 4 H, *b*-CH_2), 2.46−2.63 (m, 4 H, *a*-CH_2), 7.11 (s, 1 H, aromatic H), 7.18 (s, 1 H, aromatic H), 7.32−7.42 (m, 7 H, aromatic H), 7.45 (mc, 1 H, aromatic H), 7.47−7.63 (m, 7 H, aromatic H), 7.77−7.82 (m, 2 H, aromatic H). − ^{13}C NMR (67.9 MHz, $CDCl_3$): δ = 14.02, 22.45, 29.03, 29.08, 29.67, 31.41, 32.40, 32.54, 93.99 (C−I), 122.33 (C−Br), 123.71, 125.49, 125.82, 126.15, 126.38, 127.59, 128.19, 128.80, 129.66, 130.60, 130.83, 134.49, 134.66, 135.27, 137.55, 137.75, 137.98, 138.53, 139.05, 139.28, 140.13, 141.75, 142.21, 142.67, 143.80, 144.90. − MS (EI, 70 eV, 300°C); *m/z* (%): 932 (24.5), 933 (11.1), 934 (46.5), 935 (21.5), 936 (35.4), 937 (14.6)[M^+]. − $C_{48}H_{45}BrCl_3I$ (935.05): calcd. C 61.66, H 4.85; found C 61.62, H 4.73.

3-Bromo-5,5′′,5′′′′,5′′′′′′,5′′′′′′′′,5′′′′′′′′′′-hexachloro-2′,2′′′′′′′5′,5′′′′′′′-tetra-*n*-hexyl-4′′′′′′′′′′′-trimethylsilyl-1,1′:4′,1′′:3′′,1′′′:4′′′,1′′′′:3′′′′,1′′′′′:4′′′′′,1′′′′′′:3′′′′′′,1′′′′′′′:4′′′′′′′,1′′′′′′′′:3′′′′′′′′,1′′′′′′′′′:4′′′′′′′′′,1′′′′′′′′′′:3′′′′′′′′′′,1′′′′′′′′′′′-bideciphenyl (21): The procedure was analogous to the one described for **3**. **19** (461 mg, $5.57\cdot10^{-4}$ mol), **20** (545 mg, $5.83\cdot10^{-4}$ mol), tetrakis(triphenylphosphane)palladium(0) (13 mg, $1.1\cdot10^{-5}$ mol) mmol), toluene (20 mL), a saturated aqueous solution of $Ba(OH)_2$ (17 mL). Reflux for 2 d. Chromatographic separation through silica gel with hexane/dichloromethane = 9:1 gave 796 mg (91%) of **21** as a colorless oil. − R_f = 0.16 (hexane/dichloromethane, 9:1). − ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 0.31 (s, 9 H, $SiMe_3$), 0.76−0.88 (m, 12 H, CH_3), 1.11−1.30 (m, 24 H, *g*-, *d*-, *e*-CH_2), 1.43−1.58 (m, 8 H, *b*-CH_2), 2.52−2.57 (m, 2 H, *a*-CH_2), 2.57−2.68 (m, 6 H, *a*-CH_2), 7.11 (s, 1 H, aromatic H), 7.19 (s, 1 H, aromatic H), 7.23 (s, 2 H, aromatic H), 7.32 (mc, 1 H, aromatic H), 7.33−7.40 (m, 4 H, aromatic H), 7.44 (mc, 1 H, aromatic H), 7.52−7.59 (m, 5 H, aromatic H), 7.62−7.71 (m, 11 H, aromatic H), 7.73−7.80 (m, 11 H, aromatic H), 7.84 (mc, 1 H, aromatic H). − ^{13}C NMR (125 MHz, $CDCl_3$): δ = −1.14 ($SiMe_3$), 14.08, 22.49, 29.05, 29.15, 29.70, 31.39, 31.46, 32.37, 32.57, 122.33 (C−Br), 123.96, 124.08, 125.46, 125.83, 126.04, 126.16, 126.22, 126.42, 127.62, 128.25, 129.62, 130.57, 130.62, 130.83, 133.93, 134.45, 134.63, 135.08, 135.22, 137.55, 137.68, 137.75, 138.50, 139.21, 139.27, 139.81, 139.96, 140.11, 140.22, 141.77, 142.48, 142.63, 143.39, 143.76, 143.90, 144.86. − MS (MALDI−TOF in dithranol + Ag^+); *m/z* (%): 1716 [M + Ag^+]. − $C_{99}H_{99}BrCl_6Si$ (1609.58): calcd. C 73.88, H 6.20; found C 73.52, H 5.98.

3-Bromo-5,5′′-dichloro-2′,2′′′,5′,5′′′-tetra-*n*-hexyl-4′′′-trimethylsilyl1,1′:4′,1′′:3′′,1′′′-quaterphenyl (23): The procedure was analogous to the one described for **3**. **22** (2.31 g, 5.07 mmol), **10** (2.85 g, 5.07 mmol), tetrakis(triphenylphosphane)palladium(0) (29 mg, $2.5\cdot10^{-5}$ mol), toluene (100 mL), a saturated aqueous solution of $Ba(OH)_2$ (100 mL). Reflux for 2 d. Chromatographic separation through silica gel with hexane gave 3.98 g (91%) of **23** as a colorless oil. − R_f = 0.49 (hexane). − ^{1}H NMR (270 MHz, $CDCl_3$): δ = 0.35 (s, 9 H, $SiMe_3$), 0.78−0.92 (m, 12 H, CH_3), 1.09−1.38 (m, 22 H, *g*-, *d*-, *e*-CH_2), 1.38−1.53 (m, 8 H, *b*-, *g*-, *d*-, *e*-CH_2), 1.59−1.70 (m, 2 H, *b*-CH_2), 2.46−2.56 (m, 2 H, *a*-CH_2), 2.56−2.65 (m, 4 H, *a*-CH_2), 2.65−2.74 (m, 2 H, *a*-CH_2), 7.21−7.38 (mc, 2 H, aromatic H), 7.11 (s, 1 H, aromatic H), 7.18 (mc, 1 H, aromatic H), 7.28 (mc, 1 H, aromatic H), 7.31 (mc, 2 H, aromatic H), 7.36 (mc, 1 H, aromatic H), 7.39 (mc, 1 H, aromatic H), 7.52 (mc, 1 H, aromatic H). − ^{13}C NMR (67.9 MHz, $CDCl_3$): δ = 0.55 ($SiMe_3$), 14.03, 22.50, 22.62, 29.07, 29.15, 29.21, 29.71, 31.36, 31.50, 31.80, 32.44, 32.62, 32.73, 35.99, 122.32 (C−Br), 127.51, 127.71, 128.24, 128.43, 129.67, 129.91, 130.62, 130.93, 133.52, 134.69, 135.81, 136.38, 137.46, 137.52, 137.77, 138.41, 140.32, 140.92, 142.91, 143.61, 145.03, 146.14. − MS (EI, 70 eV, 100°C); *m/z* (%): 860 (36.4), 861 (19.6), 862 (60.1), 663 (36.2), 664 (40.5), 665 (17.8), 666 (7.8) [M^+], 73 (100) [$SiMe_3^+$]. − $C_{51}H_{71}BrCl_2Si$ (863.02): calcd. C 70.98, H 8.29; found: C 70.97, H 8.03.

3-Bromo-5,5′′-dichloro-2′,2′′′,5′,5′′′-tetra-*n*-hexyl-4′′′-iodo-1,1′:4′,1′′:3′′,1′′′-quaterphenyl (24): The procedure was analogous to the one described for **13**. Compound **23** (3.60g, 4.17 mmol), $CHCl_3$ (25 mL), ICl (0.75 g, 4.62 mmol), $CHCl_3$ (10 mL), a 1 м aqueous solution of sodium disulfite (20 mL). Chromatographic separation through silica gel with hexane gave 3.67 g (96%) of **24** as a colorless oil. − R_f = 0.49 (hexane). − ^{1}H NMR (270 MHz, $CDCl_3$): δ = 0.77−0.91 (m, 12 H, CH_3), 1.11−1.24 (m, 20 H, *g*-, *d*-, *e*-CH_2), 1.24−1.35 (m, 4 H, *g*-, *d*-, *e*-CH_2), 1.35−1.50 (m, 6 H, *b*-CH_2), 1.50−1.63 (m, 2 H, *b*-CH_2), 2.46−2.61 (m, 6 H, *a*-CH_2), 2.63−2.70 (m, 2 H, *a*-CH_2), 7.02 (s, 1 H, aromatic H), 7.05 (s, 1 H, aromatic H), 7.10 (s, 1 H, aromatic H), 7.12 (mc, 1 H, aromatic H), 7.25−7.29 (m, 2 H, aromatic H), 7.32 (mc, 1 H, aromatic H), 7.39 (mc, 1 H, aromatic H), 7.51 (tr, ^3J = 8 Hz, 1 H, aromatic H), 7.72 (s, 1 H, aromatic H). − ^{13}C NMR (67.9 MHz, $CDCl_3$): δ = 14.01, 22.49, 22.60, 29.05, 29.10, 30.36, 31.17, 31.34, 31.42, 31.48, 31.63, 32.22, 32.43, 32.60, 40.34, 100.04 (C−I), 122.34 (C−Br), 127.55, 127.83, 128.27, 129.69, 130.34, 130.62, 130.87, 133.70, 134.69, 137.57, 137.72, 138.51, 139.74, 140.01, 140.10, 140.40, 142.56, 142.83, 143.11, 144.95. − MS (EI, 70 eV, 110°C); *m/z* (%): 914 (61.2), 915 (31.2), 916 (100), 917 (51.4), 918 (57.3), 919 (24.3), 920 (10.9), 921 (3.7) [M^+]. − $C_{48}H_{62}BrCl_2I$ (916.73): calcd.: C 62.89, H 6.82; found: C 62.95, H 6.69.

3-Bromo-5,5′′,5′′′′-trichloro-2′,2′′′,2′′′′′,5′,5′′′,5′′′′′-hexa-*n*-hexyl-4′′′′′-trimethylsilyl-1,1′:4′,1′′:3′′,1′′′:4′′′,1′′′′:3′′′′,1′′′′′-sexiphenyl (25): The procedure was analogous to the one described for **3**. Compounds **22** (1.79 g, 3.93 mmol), **24** (3.60 g, 3.93 mmol), tetrakis(triphenylphosphane)palladium(0) (45 mg, $3.9\cdot10^{-5}$ mol), toluene (80 mL), a saturated aqueous solution of $Ba(OH)_2$ (70 mL). Reflux for 2 d. Chromatographic separation through silica gel with hexane gave 4.31 g (90%) of **25** as a colorless oil. − R_f = 0.28 (hexane). − ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 0.32 (s, 9 H, $SiMe_3$), 0.80−0.85 (m, 15 H, CH_3), 0.88−0.91(m, 3 H, CH_3), 1.13−1.27 (m, 30 H, *g*-, *d*-, *e*-CH_2), 1.29−1.34 (m, 4 H, *g*-, *d*-, *e*-CH_2), 1.37−1.52 (m, 12 H, *b*-, *g*-, *d*-, *e*-CH_2), 1.56−1.63 (m, 2 H, *b*-CH_2), 2.53−2.58 (m, 2 H, *a*-CH_2), 2.58−2.64 (m, 8 H, *a*-CH_2), 2.67−2.72 (m, 2 H, *a*-CH_2), 7.07 (s, 1 H, aromatic H), 7.10 (s, 1 H, aromatic H), 7.15 (mc, 3 H, aromatic H), 7.19 (mc, 1 H, aromatic H), 7.22 (mc, 1 H, aromatic H), 7.31 (mc, 2 H, aromatic H), 7.34 (m, 2 H, aromatic H), 7.37 (m, 2 H, aromatic H), 7.43 (mc, 1 H, aromatic H), 7.54 (mc, 1 H, aromatic H). − ^{13}C NMR (125.8) MHz, $CDCl_3$): δ = 0.52, 14.05, 22.52, 22.56, 22.64, 29.08, 29.17, 29.22, 29.73, 31.40, 31.51, 31.79, 32.41, 32.63, 32.68, 35.97, 122.32 (C−Br), 127.55, 127.62, 127.78, 128.22, 128.47, 128.51, 129.67, 129.93, 130.61, 130.83, 130.91, 133.45, 134.66, 135.80, 136.39, 137.54, 137.60, 137.64, 137.77, 138.42, 143.02, 143.51, 144.95, 146.16. − MS (EI, 70 eV, 300°C); *m/z* (%): 1214 (46.1), 1215 (44.8), 1216 (100), 1217 (84.2), 1218 (86.2), 1219 (59.4), 1220 (43.1), 1221 (30.1), 1222 (11.3), 1223 (4.8), 1224 (1.7) [M^+]. − $C_{75}H_{102}BrCl_3Si$: calcd. 1214.6000; found 1214.6007 (MS).

3′′′′′-Bromo-5′,5′′′,5′′′′′-trichloro-2,2′′,2′′′′,5,5′′,5′′′′-hexa-*n*-hexyl-1,1′:3′,1′′:4′′,1′′′:3′′′,1′′′′:4′′′′,1′′′′′-sexiphenyl-4-boronic Acid (26): The bromotrimethylsexiphenyl **25** (970 mg, $7.96 \cdot 10^{-4}$ mol) was dissolved in dichloromethane (7 mL) under N_2 (glove box). To this solution boron tribromide (240 mg, $9.56 \cdot 10^{-4}$ mol) in dichloromethane (1 mL) was added within 10 min. After stirring this solution for 2 h, water (6 mL) was added. The layers were separated, the aqueous layer was washed twice with dichloromethane (5 mL) and the combined organic layers were washed twice with water (15 mL). The organic phase was dried over $MgSO_4$ and the solvent was removed in vacuo at 35°C. Chromatographic separation through silica gel with hexane/ethyl acetate = 3:1 gave 743 mg (80%) of **26** as a colorless oil. − R_f = 0.32 (hexane/ethyl acetate, 3:1). − ^{1}H NMR (270 MHz, $CDCl_3$): δ = 0.78−0.98 (m, 18 H, CH_3), 1.12−1.39 (m, 36 H, *g*-, *d*-, *e*-CH_2), 1.39−68 (m, 10 H, *b*-CH_2), 1.71−1.83 (m, 2 H, *b*-CH_2), 2.51−2.80 (m, 10 H, *a*-CH_2), 3.22−3.35 (m, 2 H, *a*-CH_2), 7.10 (s, 1 H, aromatic H), 7.16−7.23 (m, 4 H, aromatic H), 7.25−7.30 (m, 2 H, aromatic H), 7.33 (mc, 1 H, aromatic H), 7.36 (m, 5 H, aromatic H), 7.54 (mc, 1 H, aromatic H), 8.20 (s, 1 H, aromatic H). − ^{13}C NMR (67.9 MHz, $CDCl_3$): δ = 14.02, 22.52, 22.63, 29.08, 29.22, 29.37, 29.68, 30.20, 31.42, 31.52, 31.95, 32.45, 32.68, 33.26, 35.18, 122.33 (C−Br), 127.67, 127.80, 128.24, 128.52, 129.70, 130.63, 130.90, 131.37, 133.63, 134.70, 136.87, 137.57, 137.67, 137.79, 138.47, 138.66, 139.81, 140.26, 143.03, 143.24, 143.88, 145.00, 148.58. − MS (MALDI−TOF); *m/z* (%): 1380 [M^+ + dithranol − $(H_2O)_2$, "monomer"].

5,5′′,5′′′′-Trichloro-2′,2′′′,2′′′′′,5′,5′′′,5′′′′′-hexa-*n*-hexyl-3-iodo-4′′′′′-trimethylsilyl-1,1′:4′,1′′:3′′,1′′′:4′′′,1′′′′:3′′′′,1′′′′′-sexiphenyl (27): The procedure was analogous to the one described for **7**. Compound **25** (785 mg, 0.64 mmol), diethyl ether (5 mL), a 1.6 M solution of *n*-butyllithium in hexane (0.53 mL, 0.85 mmol), 1,2-diiodoethane (472 mg 1.68 mmol), and dichloromethane (5 mL). Chromatographic separation through silica gel with hexane gave 296 mg (37%) of **27** as a colorless oil. − R_f = 0.30 (hexane). − ^{1}H NMR (270 MHz, $CDCl_3$): δ = 0.41 (s, 9 H, $SiMe_3$), 0.78−0.98 (m, 18 H, CH_3), 1.17−1.29 (m, 30 H, *g*-, *d*-, *e*-CH_2), 1.29−1.41 (m, 6 H, *g*-, *d*-, *e*-CH_2), 1.41−1.59 (m, 12 H, *b*-CH_2), 1.59−71 (m, 2 H, *b*-CH_2), 2.52−2.60 (m, 2 H, *a*-CH_2), 2.60−2.71 (m, 8 H, *a*-CH_2), 2.71−2.79 (m, 2 H, *a*-CH_2), 7.14 (s, 1 H, aromatic H), 7.15 (s, 1 H, aromatic H), 7.19−7.23 (m, 3 H, aromatic H), 7.28 (m, 2 H, aromatic H), 7.38−7.42 (m, 4 H, aromatic H), 7.42−7.46 (m, 2 H, aromatic H), 7.68 (mc, 1 H, aromatic H), 7.78 (mc, 1 H, aromatic H). − ^{13}C NMR (67.9 MHz, $CDCl_3$): δ = 0.56 ($SiMe_3$), 14.04, 22.52, 29.09, 29.21, 29.72, 31.40, 31.53, 31.81, 32.46, 32.65, 35.99, 93.67 (C−I), 127.64, 127.80, 128.51, 128.90, 129.93, 130.61, 130.91, 133.50, 133.61, 134.55, 135.34, 135.81, 136.40, 136.50, 137.44, 137.62, 137.77, 138.33, 139.72, 139.91, 140.26, 140.97, 143.08, 143.27, 143.59, 145.11, 146.14. − MS (EI, 70 eV, 300°C); *m/z* (%): 1262 (12.8), 1263 (10.8), 1264 (18.9), 1265 (13.9), 1266 (10.9) [M^+], 73 (100) [$SiMe_3^+$].

5,5′′,5′′′′,5′′′′′′,5′′′′′′′′,5′′′′′′′′′′-Hexachloro-2′,2′′′,2′′′′′2′′′′′′′, 2′′′′′′′′′,2′′′′′′′′′′′,5′,5′′′,5′′′′′,5′′′′′′′,5′′′′′′′′′,5′′′′′′′′′′′-dodeca-*n*-hexyl-4′′′′′′′′′′′-trimethylsilyl-3-Iodo-1,1′:4′,1′′:3′′,1′′′:4′′′,1′′′′:3′′′′,1′′′′′:4′′′′′,1′′′′′′:3′′′′′′,1′′′′′′′:4′′′′′′′,1′′′′′′′′:3′′′′′′′′, 1′′′′′′′′′:4′′′′′′′′′,1′′′′′′′′′′:3′′′′′′′′′′,1′′′′′′′′′′′-bideciphenyl (28): The procedure was analogous to that described for **3**. Compounds **26** (292 mg, 0.245 mmol), **27** (296 mg, 0.234 mmol), tetrakis(triphenylphosphane)palladium(0) (8 mg, $7 \cdot 10^{-6}$ mol), toluene (25 mL), a saturated aqueous solution of $Ba(OH)_2$ (20 mL). Reflux for 2 d. Chromatographic separation through silica gel with hexane gave 192 mg (36%) of **28** as a colorless oil. − R_f = 0.11 (hexane). − ^{1}H NMR (270 MHz, $CDCl_3$): δ = 0.28 (s, 9 H, $SiMe_3$), 0.68−0.80 (m, 36 H, CH_3), 1.00−1.24 (m, 72 H, *g*-, *d*-, *e*-CH_2), 1.32−1.49 (m, 22 H, *b*-CH_2), 1.49−1.59 (m, 2 H, *b*-CH_2), 2.43−2.65 (m, 22 H, *a*-CH_2), 2.65-2.74 (m, 2 H, *a*-CH_2), 7.00 (s, 2 H, aromatic H), 7.05−7.11 (m, 10 H, aromatic H), 7.13−7.20 (3 H, aromatic H), 7.22−7.30 (m, 13 H, aromatic H), 7.33 (s, 1 H, aromatic H), 7.45 (s, 1 H, aromatic H). − ^{13}C NMR (125 MHz, $CDCl_3$): δ = 0.35 ($SiMe_3$), 14.02, 22.52, 22.63, 29.08, 29.21, 29.72, 31.41, 31.53, 31.81, 32.46, 32.69, 35.99, 122.35 (C−Br), 127.59, 127.73, 128.25, 128.53, 128.59, 129.71, 129.94, 130.64, 130.89, 133.50, 133.61, 134.72, 135.82, 137.44, 137.59, 137.66, 137.80, 139.85, 143.05, 143.10, 143.23, 146.15. − MS (MALDI−TOF in dithranol + Ag^+); *m/z* (%): 2391 [$M+Ag^+$]. − $C_{147}H_{195}BrCl_6Si$ (2282.87): calcd. C 77.34, H 8.61; found C 77.03, H 8.37.

5,5′′,5′′′′,5′′′′′′,5′′′′′′′′,5′′′′′′′′′′-Hexachloro-2′,2′′′,2′′′′′, 2′′′′′′′,2′′′′′′′′′,2′′′′′′′′′′′,5′,5′′′,5′′′′′,5′′′′′′′,5′′′′′′′′′,5′′′′′′′′′′′-dodeca-*n*-hexyl-1,1′:4′,1′′:3′′,1′′′:4′′′,1′′′′:3′′′′,1′′′′′:4′′′′′, 1′′′′′′:3′′′′′′,1′′′′′′′:4′′′′′′′,1′′′′′′′′:3′′′′′′′′,1′′′′′′′′′:4′′′′′′′′′, 1′′′′′′′′′′:3′′′′′′′′′′,1′′′′′′′′′′′:4′′′′′′′′′′′,3-dodecaphenylene (29): Bromosexiphenylboronic acid **26** (287 mg, 0.245 mmol) and tetrakis(triphenylphosphane)palladium(0) (22 mg, $1.9 \cdot 10^{-5}$ mol) were refluxed for 2 d in a mixture of toluene (20 mL) and a saturated aqueous solution of $Ba(OH)_2$ (15 mL). The phases were then separated, the organic one was washed with water. Removal of the solvent in vacuo gave crude **26** in a conversion of 15% (anal. GPC). Purification of a part by analytic GPC gave 16 mg of **26** as a colorless oil. − ret. time: 14.8 min. (columns: waters/styragel 7.8 × 300 mm, HR3 and HR1, flow: 1 mL/min THF). − ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 0.73−0.84 (m, 36 H, CH_3), 1.10−1.22 (m, 72 H, *g*-, *d*-, *e*-CH_2), 1.41−1.51 (m, 24 H, *b*-CH_2), 2.56−2.66 (m, 24 H, *a*-CH_2), 7.13 (s, 12 H, H-3′,H-3′′′,...H-3′′′′′′′′′′′, H-6′, H-6′′′,...H-6′′′′′′′′′′′), 7.15 (tr, *J* = 2 Hz, 6 H, H-2, H-2′′,...H-2′′′′′′′′′′), 7.38 (d, *J* = 2 Hz, 12 H, H-4, H-4′′,...H-4′′′′′′′′′′, H-6, H-6′′,...H-6′′′′′′′′′′). − ^{13}C NMR (125.8 MHz, CD_2Cl_2): δ = 14.13 (CH_3), 22.80, 29.43 , 31.68, 31.80, 32.84 (5× CH_2), 127.81 (C-4, C-4′′,...C-4′′′′′′′′′′, C-6, C-6′′,...C-6′′′′′′′′′′), 129.14 (C-5, C-5′′,...C-5′′′′′′′′′′), 131.07 (C-3′,C-3′′′,...C-3′′′′′′′′′′′, C-6′, C-6′′′,...C-6′′′′′′′′′′′), 133.71 (C-2, C-2′′,...C-2′′′′′′′′′′), 137.94 (C-2′, C-2′′′,...C-2′′′′′′′′′′′,C-5′, C-5′′′, C-5′′′′′′′′′′′), 140.11 (C-1′, C-1′′′,...C-1′′′′′′′′′′′,C-4′, C-4′′′,..., C4′′′′′′′′′′′), 143.52 (C-1, C-1′′,...C-1′′′′′′′′′′, C-3, C-3′′, C-3′′′′′′′′′′). − MS (EI, 70 eV, 380°C, max. temp.); *m/z*(%): 2123 (2.5), 2124 (18.2), 2125 (36.5), 2126 (59.0), 2127 (87.8), 2128 (94.2), 2129 (100), 2130 (89.0), 2131 (74.0), 2132 (58.3), 2133 (39.6), 2134 (20.5), 2135 (9.9), 2136 (3.1), 2137 (2.7) [M^+].

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[1] V. Hensel, K. Lützow, J. Jakob, K. Geßler, W. Saenger, A.-D. Schlüter, *Angew. Chem*. **1997**, *109*, 2768; *Angew. Chem., Int. Ed. Engl*. **1997**, *36*, 2654
[2] V. Hensel, A. D. Schlüter, *Chem. Eur. J.*, in press.
[3] A.-D. Schlüter, V. Hensel, P. Liess, K. Lützow, *Towards Oligophenylene Cycles and Related Structures: A Repetitive Approach* in *Modular Chemistry* (Ed.: J. Michl), Nato ASI Series C, Kluwer, Dordrecht, **1997**, Vol 499, 241.
[4] W. A. Herrmann, C. Brossmer, C.-P. Reisinger, T. H. Riermeier, K. Öfele, M. Beller, *Chem. Eur. J.* **1997**, *3*, 1357.
[5] J. S. Moore, J. Zhang, *Angew. Chem*. **1992**, *104*, 873, *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 922; J. S. Moore, *Acc. Chem. Res.* **1997**, 30, 402; S. Höger, V. Enkelmann, *Angew. Chem*. **1995**, *107*, 2917, *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2917.
[6] [6a] P. Liess, V. Hensel, A.-D. Schlüter, *Liebigs Ann*. **1996**, 1037. – [6b] V. Hensel, A.-D. Schlüter, *Liebigs Ann.* **1997**, 303.
[7] N. Miyaura, A. Suzuki, *Chem. Rev.* **1995**, *95*, 2457.
[8] G. W. Gray, M. Hird, D. Lacey, K. J. Toyne, *J. Chem. Soc., Perkin Trans. 2* **1989**, 2041.
[9] *Boron and Oxygen, Gmelin Handbook of Inorganic and Organometallic Chemistry*, Springer, Berlin, **1987**; B 3rd Supplement, Vol. 2, p. 247.
[10] D. Kaufmann, *Chem. Ber.* **1987**, *120*, 901.
[11] G. B. Heisig, *J. Am. Chem. Soc*. **1928**, *50*, 139.
[12] V. Hensel, PhD Thesis, Freie Universität Berlin, **1998**.

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