A Cyclotetraicosaphenylene

Volker Hensel and A. Dieter Schlüter*[a]

Abstract: Suzuki cross-coupling of kinked oligophenylene building blocks is used for the repetitive synthesis of large hexagons, which as a result of their substitution with flexible alkyl chains are soluble in common organic solvents. Cycle **15** with its 24 phenylene units is the largest shape persistent cycle known. The last cyclization step proceeds with 68% yield.

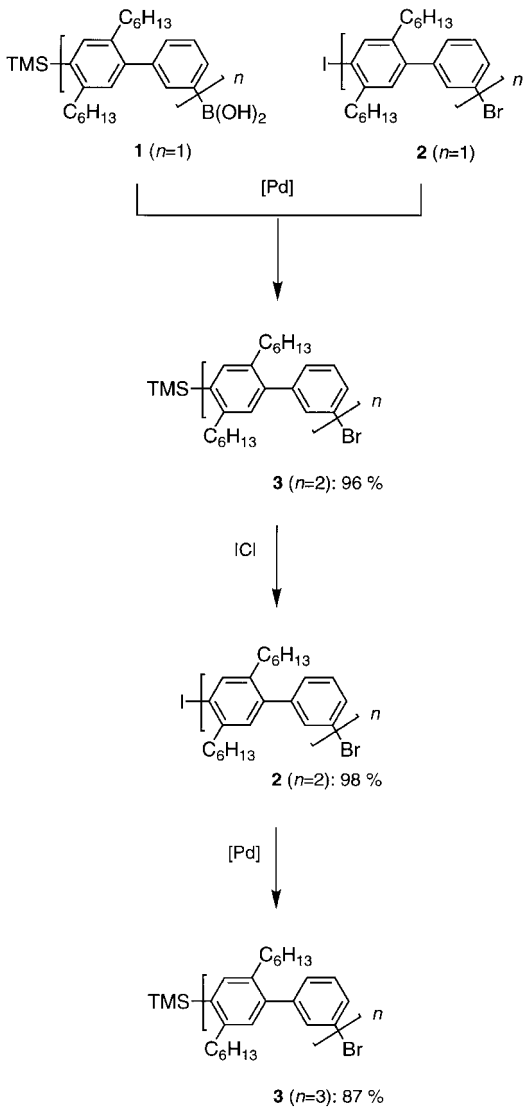
Keywords: cross-coupling · macrocycles · modular chemistry · repetitive synthesis · shape persistence

Introduction

Stimulated by the elegant syntheses of phenylacetylene-based macrocycles by Moore[1] and Höger[2] along with our group's experience with Suzuki cross-coupling reactions,[3] we decided to develop a repetitive synthesis for large, regular, and soluble oligophenylene hexagons and other cycles. The long-range objective of this research is the controlled synthesis of monodisperse macromolecules with dimensions in the nanometer range and to accumulate all necessary knowledge for applying the same protocol to the synthesis of heteroarylenes, which are interesting targets for many reasons.[4] Recently we reported on the synthesis of cycle **6** which consists of twelve phenylene units. Depending on the route this synthesis can be brought about on the gram scale in yields ranging from 17–86%.[5] An essential observation here was that the yields are highest, when the ring is formed from one precursor instead of from two precursors, and when this precursor carries the iodo/boronic acid functional group pattern at its termini instead of bromo/boronic acid. The present contribution gives a full account on this work and describes the application of the same protocol to the synthesis of cyclotetraicosaphenylene **15,** an oligophenylene hexagon with 24 phenylene rings.

Results and Discussion

Synthesis: The routes to cycles **6** and **15** are shown in Schemes 1–3 and Schemes 4 and 5, respectively. The general procedure has already been described.[5, 6] Therefore only a



Scheme 1. Reaction scheme for the formation of **3** ($n = 3$).

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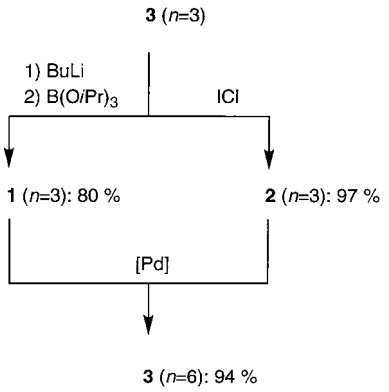
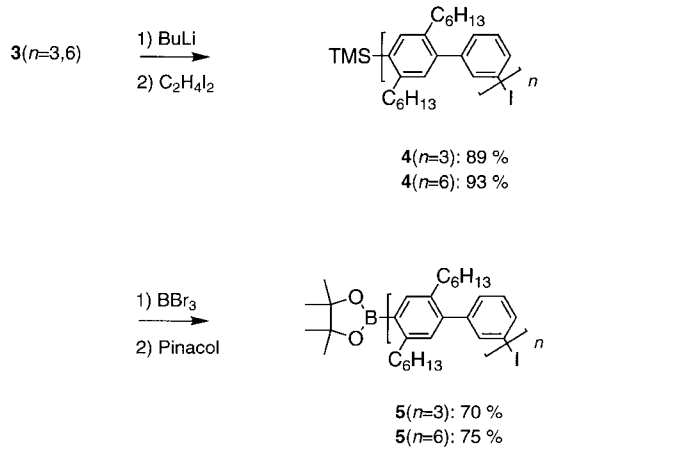


Scheme 2. Reaction scheme for the formation of **3** ($n=6$).



Scheme 3. Reaction scheme for the formation of **6**.

few general remarks are given here, followed by a short description of the ring closures:

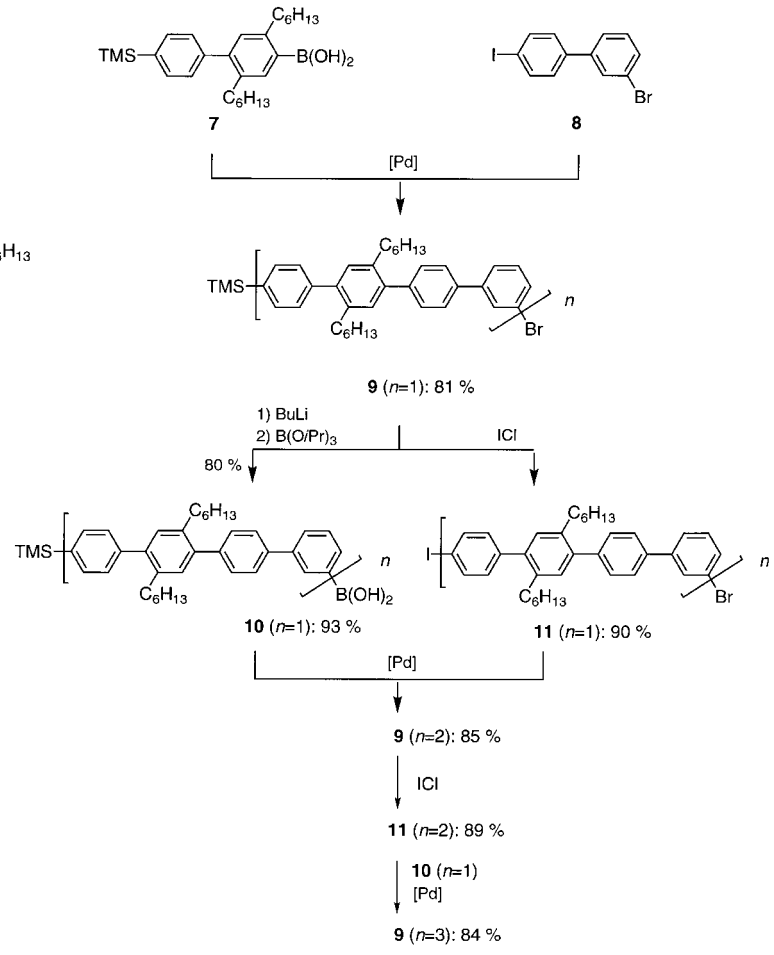
a) According to TLC evidence, the Suzuki cross-coupling reactions proceed in practically all cases virtually quantitatively. During work-up losses of material depend on molecular weight (approximately 5–10% for compounds with up to twelve phenylenes and 10–15% for larger compounds).

b) The cross-coupling proceeds with very high selectivity at C–I over C–Br. In fact, there was not even mass spectrometric evidence for coupling products that contain the iodo function.[7]

c) The conversion of C–Br into C–$B(OH)_2$ was performed with highest yield when tri(isopropyl)borate was used to quench the lithiated precursor. The resulting boronic ester was then hydrolyzed to boronic acid. This quenching process should be done slowly and at low temperature ($-78\,^{\circ}C$). All boronic acids were purified by column chromatography in amounts of up to 10 g, which could be easily done because of the large differences in the R_f values of the acids compared with all other by-products.

d) The C–Br/C–I conversions were done by lithiation with butyllithium followed by treatment with 1,2-diiodoethane. When this reaction was performed with small quantities of substance, undesired protonations of lithiated intermediate caused by traces of water inadvertently present could not be prevented, despite use of a dry-box, water-free solvents, and flame-dried apparatuses. In the case of **9** ($n=6$), which was subjected to this conversion in amounts of 600 mg (0.2 mmol; Scheme 5), the use of a sacrificing agent like bromo benzene in a tenfold excess proved successful. This way the detrimental effect of the remaining last traces of water could be prevented. Yields of iodo product could thus be brought up to 89%.

e) The C–TMS/C–I conversions were done with iodochloride and proceeded in all cases very cleanly in isolated yields of approximately 87–95% with a tendency to the lower value with increasing molecular weight.[8] This conversion could also be performed with compound **10** ($n=3$) to give



Scheme 4. Reaction scheme for the formation of **9** ($n=3$).

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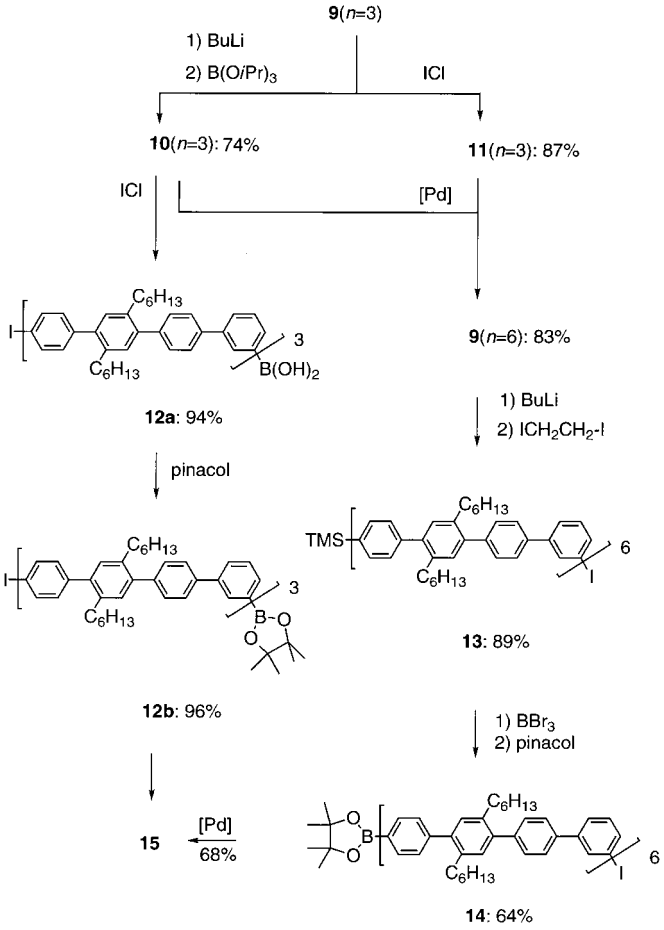
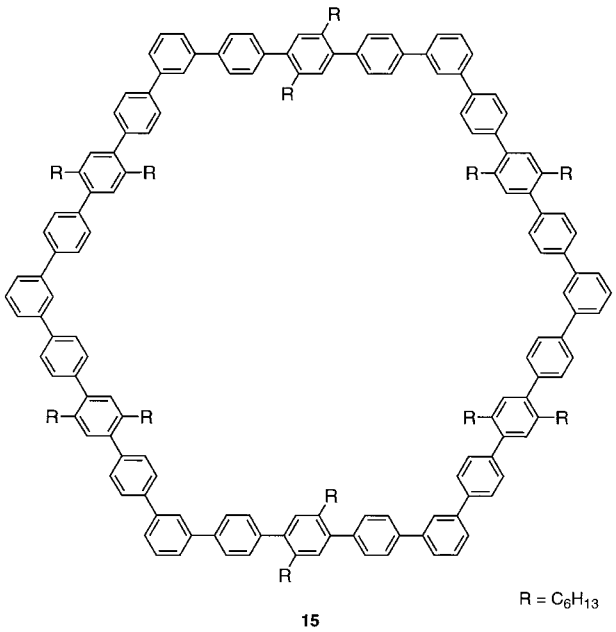
12a without interference of the occasionally quite sensitive boronic acid function (Scheme 5).

f) During several applications of borontribromide it was observed that results were best when this compound was used in freshly prepared, highly concentrated solutions (CH_2Cl_2).



Scheme 5. Reaction scheme for the formation of **15**.

The ring closure leading to cycle **6** has already been described in quite some detail.[5] The larger cycle **15** was prepared independently both from two half-rings **12b** and the direct precursor **14**. The yields for the final steps were 17% and 64%, respectively. The total yields calculated from the last common intermediate **9** ($n = 3$) amount to 11% and 24% which favors the latter route involving six instead of four steps. In both cases high-dilution conditions were applied. For the direct precursor route, for example, a solution of compound **14** and some $[Pd(PPh_3)_4]$ in toluene was syringed during 36 h into a refluxing mixture of the same complex in dimethoxyethane with some toluene and saturated barium hydroxide. Cycle **15** was prepared on the 150–200 mg scale. Isolation was achieved by preparative size exclusion chromatography. The remaining material consists of a few percent of deboronified starting material and mostly linear noncyclic oligomers with a peak molecular weight of 33,000 $g\,mol^{-1}$ versus polystyrene standard.



15

Characterization of building blocks and of cycle 15: All building blocks were fully characterized (see Experimental Section) except for most of the boron compounds, for which it is normal to not be able to obtain correct data from elemental analysis. The ^1H and ^{13}C NMR spectra of cycle **15** are very simple because of its hexagonal symmetry, and the few signals observed can be fully assigned. The spectra of both its precursors (not shown) are far more complex, which supports the proposed cyclic structure of **15**. For example, the ^{13}C NMR spectrum of **14** shows (at least) 17 aromatic signals including the characteristic absorptions of C–I at $\delta = 94.3$, whereas that of **15** exhibits only 11 signals as required. Some of these 17 signals are quite broad; this is due to some almost isochronically absorbing carbons. The situation is even more pronounced in the case of the half-cycle **12b** whose ^{13}C NMR spectrum reveals 23 aromatic signals. Further support for the cyclic nature of **15** comes from size exclusion chromatography (SEC). Co-injection experiments with half-rings, deboronified direct precursor, and cycle gave significantly different retention times for all of them. Finally a MALDI-TOF mass spectrometric investigation with 1,8,9-trihydroxyanthracene as matrix material and AgOAc removed any last doubts. The spectrum shows a signal at 2944 Da, which corresponds to the molecular ion plus one Ag, and a low intensity signal at 3052 Da, which corresponds to the molecular ion plus two Ag (Figure 1).

Cycle **15** gave correct data from elemental analysis (within 0.3). Its purity can be assessed by visual inspection of its 500 MHz ^1H NMR spectrum (Figure 2), which also provides a signal assignment. It crystallizes from toluene and chloroform into single crystals whose structure determination is presently underway.[9] The melting behavior of both cycles is presently under investigation.

On the size of 15: The equilateral hexagon that geometrically describes the structure of cycle **15** has side-to-side and corner-to-corner distances of approximately 3.0 and 3.5 nm, respec-

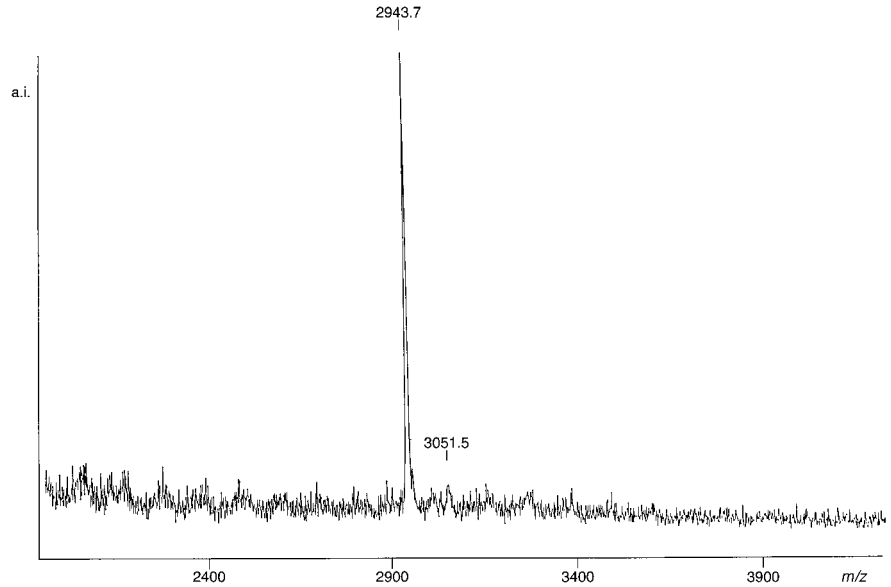


Figure 1. MALDI-TOF mass spectrum of cycle **15** (Dithranol; AgOAc). The signal at 3051.5 indicates the disilver complex.

tively. Disregarding the space demand for the chemical structure, seven C_{60} fullerenes held at van der Waals distance of each other fit into the interior of the hexagon. With these dimensions, **15** is the largest shape-persistent cycle known.[10] Counting the 1,3- and 1,4-phenylenes as three and four chain members, respectively, the cycle consists of 90 chain members altogether. This compares with Sanders' largest dioxoporphyrin cycle with 86,[11] Höger's and Moore's largest phenylacetylene cycle with 82[12] and 66,[1] Vasella's acetylenosaccharide with 64,[13] Tobe's metacyclophandodecaine with 42,[14] and de Meijere and Scott's exploded [6]rotane with 30 ring members.[15] For larger, but more flexible rings see the work by Schill[16] and Wegner[17] who made $(CH_2)_{144}$, $(CH_2)_{192}$, and $(CH_2)_{288}$ rings available using a long α,ω-diacetylene as initial building block and Eglinton reaction for coupling. These syntheses are also repetitive in nature, but do not use protecting groups. The synthetic sequences therefore comprise of the steps: a) linear oligomerization, b) isolation of the required oligomer, c) subjection of this oligomer to further linear oligomerization, and d) isolation of the C_{144}, C_{192}, or C_{288} oligomer as precursor for the final step e), which is cyclization at high-dilution conditions. Large cycles have also been obtained as mixtures from equilibrium condensations like olefin metathesis[18] or from ring-closing depolymerizations.[19]

The repetitive approach, involving protecting groups, used in the present work prevents all undesired oligomerizations and, thus, also prevents the tedious subsequent separations except in the last step. In this step the final, bifunctional ring precursor necessarily has the option to either cyclize or linearly oligomerize.

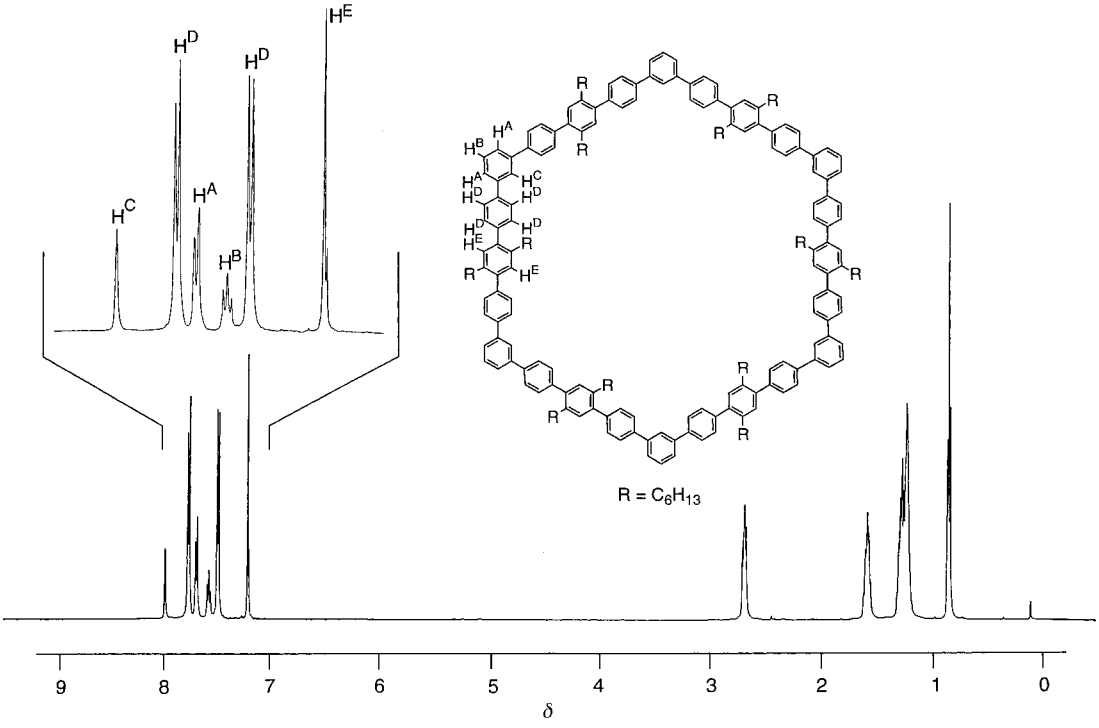


Figure 2. 500 MHz ^{1}H NMR spectrum of cycle **15** in $CDCl_3$ at 20 °C with an expansion of the aromatic region and the signal assignment.

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Experimental Section

General: Reagents were purchased from Fluka, Aldrich, or Acros and were used without further purification. All solvents were purchased from Fluka, Aldrich, or Acros and were purified and dried by standard methods. Starting materials **1** ($n=1$), **2** ($n=1$), **7** and **8** were prepared according to literature procedures.[3d] All reactions were carried out under N_2. ^{1}H NMR spectra: Bruker AM270 spectrometer (270 MHz) or Bruker AC500 spectrometer (500 MHz) (TMS at $\delta=0$, $CHCl_3$ at $\delta=7.24$, CH_2Cl_2 at $\delta=5.32$, or DMSO at $\delta=2.49$ as internal standard; mc = centered multiplet). ^{13}C spectra: Bruker AM270 spectrometer (67.9 MHz) or Bruker AC500 spectrometer (126 MHz) ($CDCl_3$ at $\delta=77.0$ as internal standard). MS: Varian MAT711 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.

Compound 3 ($n=2$): Biphenylboronic acid **1** ($n=1$; 14.07g, 33.5 mmol) and bromoiodobiphenyl **2** ($n=2$; 17.65 g, 33.5 mmol) were dissolved in toluene (250 mL). The solution was degased and flushed with N_2 repeatedly. A saturated aqueous solution of $Ba(OH)_2$ (200 mL) was added. The mixture was degased again and tetrakis(triphenylphosphine)palladium(**0**) (190 mg, 1.65×10^{-4} mol) was added. The mixture was refluxed for 3 d with vigorous stirring and then allowed to cool to room temperature. The layers were separated, the aqueous one was washed twice with toluene (20 mL), and the combined organic layers were washed once with water (20 mL). The organic phase was dried ($MgSO_4$). Chromatographic separation through silica gel with hexane in portions of 10 g gave 25.46 g (96 %) of **3** ($n=2$) as a colorless oil. $R_f=0.18$ (hexane); ^{1}H NMR (270 MHz, CD_2Cl_2): $\delta=0.35$ (s, 9H; $SiMe_3$), 0.76–0.85 (m, 9H; Me), 0.85–0.92 (m, 3H; Me), 1.11–1.24 (m, 18H; CH_2), 1.28–1.36 (m, 4H; CH_2), 1.36–1.51 (m, 8H; CH_2), 1.54–1.65 (m, 2H; CH_2), 2.49–2.73 (m, 8H; α-CH_2), 7.08 (s, 1H; aromatic H), 7.09 (s, 1H; aromatic H), 7.15 (s, 1H; aromatic H), 7.26–7.34 (m, 5H; aromatic H), 7.36 (s, 1H; aromatic H), 7.42–7.53 (m, 3H; aromatic H); ^{13}C NMR (67.9 MHz, $CDCl_3$): $\delta=0.61$ ($SiMe_3$), 14.06, 22.52, 22.65, 29.17, 29.25, 29.75, 31.40, 31.56, 31.83, 32.56, 32.65, 32.74, 32.86, 36.04, 122.15 (C–Br), 127.63, 127.97, 129.48, 129.72, 130.15, 130.22, 130.70, 131.06, 132.34, 135.72, 136.54, 136.71, 137.66, 139.22, 141.27, 141.48, 141.91, 142.42, 144.12, 145.99; MS (EI, 70 eV, 220 °C): *m/z* (%): 792 (14.4), 793 (13.7), 794 (17.1), 795 (12.8), 796 (6.9), 797 (1.9) [M^+], 73 (100) [$SiMe_3^+$]; $C_{51}H_{73}SiBr$ (794.13): calcd C 77.14, H 9.27; found C 77.13, H 9.30.

Compound 2 ($n=2$): Bromo(trimethylsilyl)quaterphenyl **3** ($n=2$; 17.06 g, 21.5 mmol) was dissolved in CCl_4 (150 mL), and a solution of ICl (3.84 g, 23.7 mmol) in CCl_4 (20 mL) was added at 0 °C within 20 min under N_2. After 30 min and warming to room temperature, a 1M solution of sodium disulphite (20 mL) was added. The layers were separated, the aqueous layer was washed twice with dichloromethane (25 mL), and the combined organic layers were washed twice with water (30 mL). The organic phase was dried ($MgSO_4$). Chromatographic filtration through silica gel with hexane gave 17.8 g (98 %) of **2** ($n=2$) as a colorless oil. $R_f=0.19$ (hexane); ^{1}H NMR (270 MHz, CD_2Cl_2): $\delta=0.75-0.85$ (m, 9H; Me), 0.85–0.93 (m, 3H; Me), 1.10–1.26 (m, 1.29–1.37 (m, 4H; CH_2), 1.37–1.52 (m, 8H; CH_2), 1.52–1.65 (m, 2H; CH_2), 2.51–2.65 (m, 6H;, α-CH_2), 2.65–2.73 (m, 2H; α-CH_2), 7.08 (s, 1H; aromatic H), 7.10 (s, 1H; aromatic H), 7.24 (s, 1H; aromatic H), 7.23–7.36 (m, 5H; aromatic H), 7.42–7.53 (m, 3H; aromatic H), 7.74 (s, 1H; aromatic H); ^{13}C NMR (67.9 MHz, $CDCl_3$): $\delta=14.01$, 22.48, 22.60, 29.11, 29.21, 30.38, 31.17, 31.36, 31.49, 31.64, 32.33, 32.53, 32.72, 40.35, 99.45 (C–I), 122.14 (C–Br), 127.46, 127.80, 127.88, 127.90, 129.46, 129.73, 129.96, 130.67, 130.70, 130.96, 132.30, 137.43, 137.60, 139.32, 139.84, 139.92, 140.89, 141.03, 141.65, 141.87, 142.58, 144.04; MS (EI, 70 eV, 150 °C): *m/z* (%): 846 (38.9), 847 (21.0), 848 (44.4), 849 (22.5), 850 (5.06) [M^+];$C_{48}H_{64}BrI$ (847.84): calcd C 68.00, H 7.61; found C 68.01, H 7.32.

Compound 3 ($n=3$): The procedure was analogous to the one described for **3** ($n=2$). Compound **2** ($n=2$; 17.30 g, 20.4 mmol), **1** ($n=1$; 8.58 g, 20.4 mmol), tetrakis(triphenylphosphine)palladium(**0**) (112 mg, 0.1 mmol toluene (300 mL), and saturated aqueous solution of $Ba(OH)_2$ (250 mL) were used. Chromatographic separation through silica gel with hexane gave 19.83 g (87 %) of **3** ($n=3$) as a colorless oil. $R_f=0.12$ (hexane); $R_f=0.40$ (hexane/dichloromethane = 9/1); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta=0.46$ (s, 9H; SiMe), 0.87–0.93 (m, 15H; Me), 0.95–0.99 (m, 3H; Me), 1.22–1.36 (m, 30H; CH_2), 1.38–1.43 (m, 4H; CH_2), 1.47–1.53 (m, 2H; CH_2), 1.55–1.64 (m, 10H; CH_2), 1.68–1.76 (m, 2H; CH_2), 2.62–2.67 (m, 2H; α-CH_2), 2.71–2.77 (m, 8H; α-CH_2), 2.77–2.83 (m, 2H; α-CH_2), 7.21 (s, 1H; aromatic H), 7.23 (s, 1H; aromatic H), 7.28 (s, 1H; aromatic H), 7.29 (s, 1H; aromatic H), 7.30 (s, 1H; aromatic H), 7.33–7.37 (t, $^3J=8$ Hz, 1H; aromatic H), 7.37–7.40 (m, 1H; aromatic H), 7.40–7.49 (m, 6H; aromatic H), 7.52–7.58 (m, 3H; aromatic H), 7.62–7.7.64 (m, 1H; aromatic H); ^{13}C NMR (125.8 MHz, $CDCl_3$): $\delta=0.58$ ($SiMe_3$), 14.06, 14.08, 14.10, 14.13, 14.20, 22.39, 22.51, 22.53, 22.57, 22.64, 22.77, 29.17, 29.26, 29.31, 29.77, 31.06, 31.41, 31.43, 31.45, 31.48, 31.55, 31.57, 31.70, 31.76, 31.82, 32.53, 32.67, 32.74, 32.77, 32.79, 32.84, 36.03, 122.13, 127.54, 127.61, 127.65, 127.69, 127.76, 127.96, 129.49, 129.72, 130.19, 130.24, 130.28, 130.71, 130.97, 131.01, 131.05, 132.30, 135.69, 136.54, 136.65, 137.41, 137.51, 137.53, 137.67, 139.21, 140.63, 140.73, 141.23, 141.47, 141.60, 141.71, 141.82, 142.42, 144.06, 146.01; MS (EI, 70 eV, 150 °C): *m/z* (%): 1113 (14.5), 1114 (12.3), 1115 (20.1), 1116 (14.2), 1117 (5.8), 1118 (1.6) [M^+], 73 (100) [$SiMe_3^+$]; $C_{75}H_{105}SiBr$ (1114.64): calcd C 80.82, H 9.49; found C 80.83, H 9.45.

Compound 1 ($n=3$): Bromo(trimethylsilyl)sexiphenyl **3** ($n=3$; 4.88 g, 4.38 mmol) was dissolved in diethyl ether (250 mL) and a 1.6M solution of *n*-butyllithium in hexane (27.3 mL, 43.8 mmol) was added at −78 °C over a period of 25 min. After warming to room temperature and cooling again to −78 °C triisopropyl borate (16.46 g, 87.6 mmol) was added within 2 h. The reaction mixture was allowed to warm to room temperature overnight. Water (250 mL) was then added. The layers were separated, the aqueous one was washed twice with diethyl ether (100 mL), and the combined organic layers were washed twice with water (200 mL). The organic phase was dried over $MgSO_4$. The solvent was removed in vacuo at 35 °C. Chromatographic separation through silica gel with hexane/ethyl acetate 3:1 gave 3.72 g (80 %) of **1** ($n=3$) as a colorless, highly viscous oil. $R_f=0.31$ (hexane/ethyl acetate 3:1); ^{1}H NMR (250 MHz, CD_2Cl_2): $\delta=0.38$ (s, 9H; $SiMe_3$), 0.75–0.96 (m, 18H; Me), 1.12–1.40 (m, 36H; γ-, δ-, ε-CH_2), 1.40–1.70 (m, 12H; β-CH_2), 2.58–2.79 (m, 12H; α-CH_2), 7.13 (s, 1H; aromatic H), 7.20–7.29 (m, 4H; aromatic H), 7.29–7.44 (m, 7H; aromatic H), 7.44–7.56 (m, 3H; aromatic H), 7.56–7.67 (m, 2H; aromatic H), 8.32 (s, 1H; aromatic H); ^{13}C NMR (62.9 MHz, CD_2Cl_2): $\delta=0.70$ ($SiMe_3$), 14.22, 14.27, 14.32, 14.44, 22.94, 22.97, 23.00, 23.08, 27.38, 29.66, 29.70, 30.11, 31.92, 32.02, 32.26, 33.05, 33.19, 36.43, 127.98, 128.11, 130.62, 130.72, 131.46, 136.21, 137.03, 137.20, 138.06, 138.12, 138.17, 141.17, 141.25, 141.39, 142.15, 142.19, 142.24, 142.41, 142.90, 146.50; MS (EI, 70 eV, 380 °C, max. temp.): *m/z* (%): 1033 (13.6), 1034 (11.4), 1035 (100), 1036 (96.7), 1037 (85.3), 1038 (20.9), 1039 (5.8) [$M^+-B(OH)_2$], monomer.

Compound 2 ($n=3$): The procedure was analogous to the one described for **2** ($n=2$). Compound **3** ($n=3$; 3.00 g, 2.69 mmol), dichloromethane (8 mL), and ICl (481 mg, 2.69 mmol) in dichloromethane (8 mL) were used. Chromatographic filtration through silica gel with hexane gave 3.04 g (97 %) of **2** ($n=3$) as a colorless oil. $R_f=0$. 13 (hexane); ^{1}H NMR (270 MHz, CD_2Cl_2): $\delta=0.74-0.95$ (m, 18H; Me), 1.08–1.30 (m, 30H; γ-, δ-, ε-CH_2), 1.30–1.38 (m, 6H; γ-, δ-, ε-CH_2), 1.38–1.56 (m, 10H; β-CH_2), 1.56–1.69 (m, 2H; β-CH_2), 2.50–2.77 (m, 12H; α-CH_2), 7.09 (s, 1H; aromatic H), 7.12 (s, 1H; aromatic H), 7.17 (s, 1H; aromatic H), 7.18 (s, 1H; aromatic H), 7.19 (s, 1H; aromatic H), 7.25–7.38 (m, 8H; aromatic H), 7.43–7.55 (m, 4H; aromatic H), 7.75 (s, 1H; aromatic H); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta=14.01$, 14.07, 18.66, 22.47, 22.50, 22.59, 29.11, 29.22, 29.26, 29.68, 30.37, 31.17, 31.40, 31.45, 31.48, 31.53, 31.64, 31.91, 32.31, 32.53, 32.7740.37, 99.44 (C–I), 122.14 (C–Br), 127.36, 127.60, 127.67, 127.74, 127.92, 129.44, 129.69, 130.02, 130.24, 130.68, 130.91, 130.98, 131.01, 132.29, 137.37, 137.45, 137.52, 137.63, 139.21, 139.81, 139.91, 140.53, 140.76, 140.83, 141.21, 141.50, 141.67, 141.80, 141.89, 142.54, 144.06; MS (EI, 70 eV, 300 °C): *m/z* (%): 1166 (77.9), 1167 (58.1), 1168 (100), 1169 (69.9), 1170 (40.7), 1171 (14.4), 1172 (3.8) [M^+]; $C_{72}H_{96}BrI$ (1168.36): calcd C 74.02, H 8.28; found C 74.24, H 8.20.

Compound 3 ($n=6$): The procedure was analogous to the one described for **3** ($n=2$). Compound **2** ($n=3$; 2.70 g, 2.31 mmol), **1** ($n=3$; 2.71 g, 2.55 mmol), tetrakis(triphenylphosphine)palladium(**0**) (56 mg, 4.8×10^{-5} mol), toluene (70 mL), and a saturated aqueous solution of $Ba(OH)_2$ (80 mL) were used. Chromatographic separation through silica gel with hexane gave 4.49 g (93.6 %) of **3** ($n=3$) as a colorless oil. ^{1}H NMR (500 MHz, CD_2Cl_2): $\delta=0.42$ (s, 9H; $SiMe_3$), 0.82–0.87 (m, 33H; Me), 0.89–0.994 (m, 3H; Me), 1.17–1.31 (m, 66H; γ-, δ-, ε-CH_2), 1.33–1.38 (m, 6H; γ-, δ-, ε-CH_2), 1.42–1.59 (m, 22H; β-CH_2), 1.60–1.68 (m, 2H; β-CH_2), 2.58–2.62 (m, 2H; α-CH_2), 2.65–2.77 (m, 22H; α-CH_2), 7.14 (s, 1H;

aromatic H), 7.16 (s, 1H; aromatic H), 7.22–7.27 (m, 9H; aromatic H), 7.32–7.36 (m, 4H; aromatic H), 7.36–7.39 (m, 1H; aromatic H), 7.39–7.43 (m, 5H; aromatic H), 7.48–7.55 (m, 5H; aromatic H), 7.57 (mc, 1H; aromatic H); ^{13}C NMR (125.8 MHz, CD_2Cl_2): $\delta = 0.63$ ($SiMe_3$), 14.25, 22.79, 22.91, 22.94, 22.96, 23.05, 29.51, 29.62, 29.67, 30.09, 31.83, 31.86, 31.90, 31.96, 32.03, 32.21, 32.85, 33.08, 33.13, 33.19, 36.36, 122.34 (C–Br), 127.87, 128.02, 128.10, 128.44, 129.97, 130.44, 130.55, 130.60, 131.12, 131.38, 132.56, 136.12, 136.94, 137.06, 137.84, 137.98, 138.10, 139.58, 141.08, 141.56, 141.87, 142.04, 142.74, 144.44, 146.45.; MS (EI, 70 eV, 350 °C): *m/z* (%): 2073 (8.6), 2074 (19.2), 2075 (31.1), 2076 (47.0), 2077 (42.1), 2078 (37.5), 2079 (26.5), 2080 (15.6) [M^+], 73 (100) [$SiMe_3^+$]; $C_{147}H_{201}SiBr$ (2076.62): calcd C 85.04, H 9.76; found C 85.11, H 9.69.

Compound 4 ($n = 3$): Bromotrimethylsexiphenyl **3** ($n = 3$; 635 mg, 0.57 mmol) was dissolved in diethyl ether (7.5 mL). After cooling to −78 °C, a 1.6 M solution of *n*-butyllithium in hexane (0.71 mL, 1.14 mmol) was added. The solution was allowed to warm to room temperature and then cooled to −78 °C again. At this temperature a solution of 1,2-diiodoethane (406 mg, 1.42 mmol) in diethyl ether (2 mL) was added. The solution was allowed to warm to room temperature within 1 h and water (10 mL) was added. The layers were separated, the aqueous layer was washed twice with diethyl ether (10 mL), and the combined organic layers were washed twice with water (15 mL). The organic phase was dried over $MgSO_4$. The solvent was removed in vacuo. Chromatographic separation through silica gel with hexane gave 589 mg (89%) of **4** ($n = 3$) as a colorless oil. $R_f = 0.07$ (hexane); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 0.49$ (s, 9H; $SiMe_3$), 0.87–0.94 (m, 15H; Me), 0.94–0.99 (mc, 3H; Me), 1.21–1.36 (m, 30H; γ-, δ-, ε-CH_2), 1.37–1.44 (m, 4H; γ-, δ-, ε-CH_2), 1.46–1.53 (m, 2H; γ-, δ-, ε-CH_2), 1.53–1.63 (m, 10H; β-CH_2), 1.68–1.75 (m, 2H; β-CH_2), 2.60–2.65 (mc, 2H; α-CH_2), 2.69–2.76 (m, 8H; α-CH_2), 2.76–2.82 (mc, 2H; α-CH_2), 7.17–7.24 (m, 3H; aromatic H), 7.25–7.31 (m, 3H; aromatic H), 7.39–7.49 (m, 8H; aromatic H), 7.51–7.58 (m, 2H; aromatic H), 7.76 (d, $^3J = 7$ Hz, 1H; aromatic H), 7.83 (s, 1H; aromatic H); ^{13}C NMR (125.8 MHz, $CDCl_3$): $\delta = 0.58$ ($SiMe_3$), 14.07, 14.09, 22.53, 22.56, 22.64, 29.17, 29.26, 29.30, 29.76, 31.44, 31.48, 31.56, 31.80, 32.53, 32.66, 32.73, 32.77, 32.83, 36.02, 94.05 (C–I), 127.60, 127.65, 127.68, 128.55, 129.65, 130.18, 130.23, 130.27, 130.68, 130.96, 131.01, 131.03, 135.69, 136.54, 137.52, 137.65, 138.19, 140.62, 141.20, 141.80, 142.41, 146.00; MS (EI, 70 eV, 160 °C): *m/z* (%): 1160 (2.4), 1161 (100), 1162 (91.6), 1163 (42.9), 1164 (14.2), 1165 (3.7) [M^+]; $C_{75}H_{105}ISi$ (1161.64): calcd C 77.55, H 9.11; found: C 77.34, H 8.83.

Compound 4 ($n = 6$): The procedure was analogous to the one described for **4** ($n = 3$). Compound **3** ($n = 6$; 2.11 g, 1.02 mmol), diethyl ether (10 mL), 1 M butyl lithium in hexane (1.2 mL, 1.92 mmol), and 1,2-diiodoethane (675 mg, 2.4 mmol) in dichloroethane (3 mL) were used. Chromatographic separation through silica gel with hexane gave 2.00 g (93%) of **4** ($n = 6$) as a colorless oil. $R_f = 0.19$ (hexane/dichloromethane = 9/1); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 0.38$ (s, 9H; $SiMe_3$), 0.77–0.85 (m, 33H; Me), 0.85–0.90 (m, 3H; Me), 1.12–1.27 (m, 66H; γ-, δ-, ε-CH_2), 1.27–1.35 (m, 4H; γ-, δ-, ε-CH_2), 1.37–1.41 (m, 2H; γ-, δ-, ε-CH_2), 1.41–1.58 (m, 22H; β-CH_2), 1.58–1.65 (mc, 2H; β-CH_2), 2.50–2.58 (mc, 2H; α-CH_2), 2.60–2.76 (m, 22H; α-CH_2), 7.05 (s, 1H; aromatic H), 7.08 (s, 1H; aromatic H), 7.10–7.16 (m, 2H; aromatic H), 7.16–7.24 (m, 9H; aromatic H), 7.32–7.48 (m, 14H; aromatic H), 7.48–50 (m, 5H; aromatic H), 7.70 (d, $^3J = 7$ Hz, 1H; aromatic H), 7.76 (s, 1H; aromatic H); ^{13}C NMR (125.8 MHz, $CDCl_3$): $\delta =$ 0.63, 14.08. 22.57, 22.66, 29.18, 29.32, 29.78, 31.49, 31.61, 31.85, 32.57, 32.70, 32.85, 36.07, 94.08 (C–I), 127.68, 128.53, 129.61, 130.27, 130.42, 130.73, 131.05, 135.72, 136.55, 136.62, 137.40, 137.53, 137.66, 138.24, 139.19, 140.77, 141.56, 141.75, 141.88, 142.50, 144.17, 145.98; MS (EI, 70 eV, 380 °C, max. temp.): *m/z* (%): 2120 (8.67), 2121 (10.93), 2122 (18.84), 2123 (17.86), 2124 (14.99), 2125 (9.16) [M^+]; $C_{147}H_{201}ISi$ (2123.19): calcd C 83.16, H 9.54; found C 82.97, H 9.32.

Compound 5 ($n = 3$): The reaction was carried out under dry conditions (glove box, oxygen and water content < 1ppm). Iodo(trimethylsilyl)sexiphenyl **4** ($n = 3$; 520 mg, 0.45 mmol) was dissolved in dichloromethane (4 mL) and a solution of BBr_3 (146 mg, 0.582 mmol) in dichloromethane (0.3 mL) was then added. After 40 min pinacol (159 mg, 1.35 mmol) was added, and after continued stirring for 30 min water (7 mL) was added. The layers were separated, the aqueous one was washed twice with dichloromethane (5 mL), and the combined organic layers were washed twice with water (20 mL). The organic phase was dried over $MgSO_4$ and the solvent was removed in vacuo at 35 °C. Chromatographic separation through silica gel first with hexane and then with hexane/ethyl acetate 30:1 gave 382 mg (70%) of **5** ($n = 3$) as a colorless, highly viscous oil. $R_f = 0.33$ (hexane/ethyl acetate 30:1); ^{1}H NMR (250 MHz, CD_2Cl_2): $\delta = 0.71–0.86$ (m, 18H; Me), 1.03–1.38 (m, 36H; γ-, δ-, ε-CH_2), 1.39 (s, 12H; pinacol CH_3), 1.41–1.52 (m, 12H; β-CH_2), 2.42–2.63 (m, 10H; α-CH_2), 2.71 (mc, 2H; α-CH_2), 7.02 (s, 1H; aromatic H), 7.04(s, 1H; aromatic H), 7.08–7.21 (m, 5H; aromatic H), 7.23–7.32 (m, 7H; aromatic H), 7.32–7.41 (m, 2H; aromatic H), 7.59–7.63 m, 2H; aromatic H), 7.23 (mc, 1H; aromatic H); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 14.05$, 14.13, 22.51, 22.66, 24.87 (ester-CH_3), 26.73, 28.65, 29.14, 29.29, 29.54, 30.13, 31.43, 31.46, 31.56, 31.81, 32.54, 32.75, 32.78, 33.59, 35.57, 83.23 (ester-C), 94.02 (C–I), 126.82, 127.45, 127.60, 127.66, 128.53, 129.61, 130.08, 130.28, 130.67, 130.99, 135.65, 136.68, 137.22, 137.36, 137.48, 137.51, 137.63, 138.21, 139.13, 140.66, 140.77, 141.23, 141.51, 141.61, 141.76, 141.90, 144.11, 144.17, 147.48; MS (EI, 70 eV, 100 °C): *m/z* (%): 1214 (23.2), 1215 (100), 1216 (77.8), 1217 (33.3), 1218 (9.2) [M^+]; $C_{78}H_{108}BIO_2$ (1215.43): calcd C 77.08, H 8.96; found: C 76.81, H 8.71.

Compound 5 ($n = 6$): The procedure was analogous to the one described for **5** ($n = 3$). Glove box, iodo(trimethylsilyl)bideciphenyl **4** ($n = 6$; 1.65 g, 7.78×10^{-4} mol), dichloromethane (5 mL), BBr_3 (234 mg, 9.34×10^{-4} mol) in dichloromethane (0.29 mL), and pinacol (229 mg, 1.94 mmol) were used. Chromatographic separation through silica gel with hexane/dichloromethane 9:1 gave 1.27 g (75%) of **5** ($n = 6$) as a colorless, highly viscous oil. $R_f = 0.22$ (hexane/dichloromethane 9:1); ^{1}H NMR (500 MHz, CD_2Cl_2): $\delta =$ 0.79–0.88 (m, 32H; Me), 0.88–0.92 (m, 4H; Me), 1.16–1.29 (m, 66H; γ-, δ-, ε-CH_2), 1.29–1.34 (m, 6H; γ-, δ-, ε-CH_2), 1.37 (s, 12H; pinacol CH_3), 1.43–1.60 (m, 24H; β-CH_2), 2.57 (mc, 2H; α-CH_2), 2.59–2.71 (m, 20H; α-CH_2), 2.86 (mc, 2H; α-CH_2), 7.07 (s, 1H; aromatic H), 7.12 (s, 1H; aromatic H), 7.15–7.28 (m, 10 , aromatic H), 7.30–7.32 (m, 2H; aromatic H), 7.32–7.39 (m, 14H; aromatic H), 7.42–7.52 (m, 5H; aromaric H), 7.62 (s, 1H; aromatic H), 7.71 (d, $^3J = 7$ Hz, 1H; aromatic H), 7.73 (mc, 1H; aromatic H); ^{13}C NMR (125.8 MHz, $CDCl_3$): $\delta = 14.04$, 14.14, 22.53, 22.68, 24.88 (ester-CH_3), 29.16, 29.26, 29.30, 29.36, 29.56, 31.45, 31.58, 31.83, 32.56, 32.77, 32.83, 33.59, 35.58, 83.27 (ester-C), 94.03 (C–I), 127.67, 128.56, 129.64, 130.39, 131.01, 136.73, 137.21, 137.40, 137.54, 137.67, 139.16, 140.70, 140.75, 141.26, 141.54, 141.66, 141.73, 141.75, 141.92, 144.14, 144.19, 147.50; MS (EI, 70 eV, 380 °C, max. temp.): *m/z* (%): 2175 (33.0), 2176 (56.9), 2177 (55.4), 2178 (46.3), 2179 (28, 95), 2180 (16.7) [M^+]; $C_{150}H_{204}BIO_2$ (2176.98): calcd C 82.76, H 9.44;found C 82.43, H 9.26.

Compound 6: a) A solution of **5** ($n = 3$; 382 mg, 0.314 mmol) and tris(tri-*p*-tolylphosphine)palladium(**0**) (13 mg, 1.3×10^{-5} mol) in toluene (10 mL) was added through a syringe pump within 72 h to a boiling mixture of the same complex (13 mg, 1.3×10^{-5} mol) in a 1 M aqueous solution of Na_2CO_3 (45 mL), dimethoxyethane (30 mL), and toluene (15 mL). The phases were then separated, and the organic one was washed with water. Removal of the solvent in vacuo gave crude **6** in a conversion of 44% (anal. GPC). Purification by preparative GPC gave 106 mg **6** (35%) as a colorless, solid material.

b) A solution of **5** ($n = 6$; 903 mg, 0.415 mmol) and tris(tri-*p*-tolylphosphine)palladium(**0**) (10 mg, 1×10^{-5} mol) in toluene (25 mL) was added through a syringe pump within 54 h to a boiling mixture of the same complex (11 mg, 1.08×10^{-5} mol) in a 1 M aqueous solution of Na_2CO_3 (90 mL), dimethoxyethane (100 mL), and toluene (50 mL). The phases were then separated, and the organic one was washed with water. Removal of the solvent in vacuo gave crude **6** in a conversion of 89% (anal. GPC). Purification by preparative GPC afforded 678 mg **6** (85%) as a colorless solid material. t_R: 19.3 min (column: water/styragel 7.8 × 300 HR5E and HR6E, flow 1 mL min^{-1} THF): $\lambda_{max} = 254.4$ nm; ^{1}H NMR (270 MHz, $CDCl_3$): $\delta = 0.89$ (t, $^3J = 8$ Hz, 36H; CH_3), 1.32 (mc, 72H; γ-, δ-, ε-CH_2), 1.60 (mc, 24H; α-CH_2), 2.76 (t, $^3J = 8$ Hz, 24H; α-CH_2), 7.30 (s, 12H; H-3), 7.45 (s, 6H; H-2′), 7.48 (d, $^3J = 7$ Hz, 12H; H-4′), 7.59 (t, $^3J = 7$ Hz, 6H; H-5′); ^{13}C NMR (126 MHz, CD_2Cl_3): $\delta = 14.07$ (CH_3), 22.74, 29.47, 31.69, 31.78, 32.95 [5 × CH_2], 127.75 (C-6′), 127.94 (C-5′), 130.69 (C-2′), 131.13 (C-6), 137.76 (C-2), 141.03 (C-1), 141.95 (C-1′); MS (EI, 70 eV, 380 °C, max. temp.): *m/z* (%): 1921 (65.9), 1922 (100), 1923 (94.3), 1924 (47.4), 1925 (27.8), 1926 (12.4), 1927 (4.2) [M^+]; $C_{144}H_{192}$ (1923.10): calcd C 89.94, H 10.06; found C 89.76, H 9.87.

Compound 9 ($n = 1$): The procedure was analogous to the one described for **3** ($n = 2$). Biphenylboronic acid **7** (5.03 g, 12.0 mmol), bromo-iodobiphenyl **8** (4.29 g, 11.9 mmol), tetrakis(triphenylphosphine)palladium(**0**) (138 mg, 0.12 mmol), toluene (120 mL), and a saturated aqueous solution of $Ba(OH)_2$ (100 mL) were used. After work-up, chromatographic separation through silica gel with hexane gave 6.08 g (81%) of **9** ($n = 1$) as a colorless

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oil. $R_f = 0.12$ (hexane); ^{1}H NMR (270 MHz, CD_2Cl_2): $\delta = 0.36$ (s, 9H; $SiMe_3$), 0.72–0.88 (m, 6H; CH_3), 1.09–1.29 (m, 12H; γ-, δ-, ε-CH_2), 1.43–1.56 (m, 4H; β-CH_2), 2.54–2.68 (m, 4H; α-CH_2), 7.14 (s, 1H; aromatic H), 7.17 (s, 1H; aromatic H), 7.31–7.41 (m, 3H; aromatic H), 7.42–7.45 (m, 1H; aromatic H), 7.45–7.49 (m, 1H; aromatic H), 7.49–7.55 (m, 1H; aromatic H), 7.55–7.70 (m, 5H; aromatic H), 7.84 (mc, 1H; aromatic H); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = -0.99$ (3C; $SiMe_3$), 14.11 (2C; CH_3), 29.18 (1C; CH_2), 29.24 (1C; CH_2), 31.44 (2C; CH_2), 31.49 (1C; CH_2), 31.54 (1C; CH_2), 32.55 (1C; CH_2), 32.65 (1C; CH_2), 122.97 (1C; C-3, C–Br), 125.59 (1C), 126.69 (2C), 128.67 (2C), 129.88 (2C), 130.10 (2C), 130.26 (1C), 130.82 (1C), 131.01 (1C), 133.05 (2C) [14 × tertiary C], 137.44 (1C), 137.55 (1C), 137.92 (1C), 138.42 (1C), 140.06 (1C), 140.91 (1C), 141.65 (1C), 142.28 (1C), 142.99 (1C) [9 × quaternary C]; MS (EI, 70 eV, 180 °C): *m/z* (%): 624 (4.1), 625 (45.0), 626 (86.2), 627 (42.1), 628 (15.1), 629 (5.2), 630 (2.2) [M^+], 73 [TMS^+]; $C_{39}H_{49}BrSi$ (625.81): calcd C 74.85, H 7.89; found C 74.63, H 7.73.

Compound 10 (***n* = 1**): The procedure was analogous to that described for **1** (*n* = 3). Bromoquaterphenyl **9** (*n* = 1; 5.05 g, 8.07 mmol) was dissolved in a mixture of diethyl ether (200 mL) and THF (200 mL). A 1.6 M solution of *n*-butyllithium in hexane (17.3 mL, 24 mmol) was added at −78 °C. After warming to room temperature and cooling again to −78 °C, triisopropyl borate (9.1 g, 48 mmol) was added within 2 h. After work-up, chromatographic separation through silica gel with hexane/ethyl acetate 3:1 gave 4.30 g (93%) of **10** (*n* = 1) as a colorless viscous oil. $R_f = 0.38$ (hexane/ethyl acetate 3:1); ^{1}H NMR (270 MHz, $CDCl_3$): $\delta = 0.40$ (s, 9H; $SiMe_3$), 0.82–0.91 (m, 6H; CH_3), 1.18–1.38 (m, 12H; γ-, δ-, ε-CH_2), 1.52–1.67 (m, 6H; β-CH_2), 2.60–2.78 (m, 4H; α-CH_2), 7.22–7.31 (m, 2H; aromatic H), 7.41–7.48 (m, 2H; aromatic H), 7.48–7.62 (m, 2H; aromatic H), 7.62–7.77 (m, 3H; aromatic H), 7.77–8.01 (m, 3H; aromatic H), 8.23 (mc, 1–2H; aromatic H), 8.38 (mc, 1–2H; aromatic H), 8.51 (mc, 1–2H; aromatic H), 8.65 (mc, 1–2H; aromatic H); ^{13}C NMR (67.9 MHz, $CDCl_3$): $\delta = -1.02$ ($SiMe_3$), 14.06, 22.47, 29.19, 30.66, 31.42, 31.48, 32.55, 32.65, 126.83, 128.67, 129.83, 130.90, 133.02, 134.09, 137.51, 138.41, 139.39, 140.29, 140.47, 140.83, 141.14, 142.35; MS (EI, 70 eV, 350 °C): *m/z* (%): 1717 (13.5), 1718 (14.8), 1719 (10.5), 1720 (6.2), 1721 (2.4) [M^+] trimer, 546 (100), 547 (60.8), 548 (18.6), 549 (4.2) [$M^+ - B(OH)_2$] monomer.

Compound 11 (***n* = 1**): The procedure was analogous to the one described for **2** (*n* = 2). Compound **9** (*n* = 1; 2.30 g, 3.68 mmol), CH_2Cl_2 (15 mL), ICl 690 mg (4.25 mmol), and CH_2Cl_2 (8 mL) were used. Chromatographic separation through silica gel with hexane gave 2.25 g (90%) of **11** (*n* = 1) as a colorless oil. $R_f = 0.14$ (hexane); ^{1}H NMR (270 MHz, CD_2Cl_2): $\delta = 0.70$–0.94 (m, 6H; CH_3), 1.06–1.35 (m, 12H; γ-, δ-, ε-CH_2), 1.37–1.57 (m, 4H; β-CH_2), 2.48–2.66 (m, 4H; α-CH_2), 7.10–7.14 (m, 2H; aromatic H), 7.14–7.19 (m, 2H; aromatic H), 7.32–7.55 (m, 4H; aromatic H), 7.60–7.70 (m, 3H; aromatic H), 7.74–7.82 (m, 2H; aromatic H), 7.82–7.87 (m, 1H; aromatic H); ^{13}C NMR (67.9 MHz, $CDCl_3$): $\delta = 14.05$ (2C; CH_3), 22.46 (2C; CH_2), 29.14 (2C; CH_2), 31.36 (2C; CH_2), 31.46 (2C; CH_2), 32.54 (2C; CH_2), 92.45 (1C; C-4‴, C–I), 122.95 (1C; C-3, C–Br), 125.58 (1C), 126.70 (2C), 129.79 (2C) 130.10 (2C), 130.25 (1C), 130.68 (1C), 130.91 (1C), 131.23 (2C), 137.10 (2C) [14 × tertiary C], 137.36 (1C), 137.63 (1C), 138.00 (1C), 139.68 (1C), 140.43 (1C), 141.36 (1C), 141.44 (1C), 142.93 (1C) [8 × quaternary C]; MS (EI, 70 eV, 160 °C): *m/z* (%): 676 (1.0), 677 (0.4), 678 (90.8), 679 (35.9), 680 (100), 681 (36.2), 682 (7.0), 683 (0.6) [M^+]; $C_{36}H_{40}BrI$ (679.52): calcd C 63.63, H 5.93; found C 63.69, H 5.75.

Compound 9 (***n* = 2**): The procedure was analogous to the one described for **3** (*n* = 3). Compound **10** (*n* = 1; 1.93 g, 3.37 mmol), **11** (*n* = 1; 2.22 g, 3.27 mmol), tetrakis(triphenylphosphine)palladium(**0**) (76 mg, 0.07 mmol), toluene (50 mL), and a saturated aqueous solution of $Ba(OH)_2$ (50 mL) were used. After work-up, chromatographic separation through silica gel with hexane/dichloromethane 9:1 gave 3.07 g (85%) of **9** (*n* = 2) as a colorless vicous oil. $R_f = 0.25$ (hexane/dichloromethane 1:9); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 0.33$ (s, 9H; $SiMe_3$), 0.79–0.89 (m, 12H; CH_3), 1.12–1.32 (m, 24H; γ-, δ-, ε-CH_2), 1.48–1.61 (m, 8H; β-CH_2), 2.56–2.70 (m, 8H; α-CH_2), 7.18–7.25 (m, 4H; aromatic H), 7.32 (t, $^3J = 8$ Hz, 1H; aromatic H), 7.40 (d, $^3J = 8$ Hz, 2H; aromatic H), 7.45–7.53 (m, 7H; aromatic H), 7.56–7.66 (m, 6H; aromatic H), 7.66–7.70 (d, $^3J = 8$ Hz, 2H; aromatic H), 7.72–7.78 (m, 4H; aromatic H), 7.82 (s, 1H; aromatic H), 7.99 (s, 1H; aromatic H); ^{13}C NMR (125.8 MHz, $CDCl_3$): $\delta = -1.02$ ($SiMe_3$), 13.94 (CH_3), 14.09 (CH_3), 22.47 (CH_2), 22.50 (CH_2), 29.17(CH_3), 29.24 (CH_3), 31.44 (CH_2), 31.48 (CH_2), 31.53 (CH_2), 32.52 (CH_2), 32.65 (CH_2), 122.94 (1C; C-3), 125.63 (1C), 126.01 (2C), 126.72 (2C), 126.83 (2C), 126.85 (2C), 128.65 (2C), 129.29 (1C), 129.79 (2C), 129.81 (2C), 129.87 (2C), 130.12 (2C), 130.29 (2C), 130.87 (1C), 130.91 (1C), 130.99 (2C), 133.03 (2C) [28 × tertiary C], 137.51 (1C), 137.54 (1C), 137.57 (1C), 137.66 (1C), 137.97 (1C), 138.43 (1C), 139.42 (1C), 139.49 (1C), 140.17 (1C), 140.25 (1C), 140.49 (1C; quart), 140.80 (1C), 141.04 (1C), 141.14 (1C), 141.43 (1C), 141.47 (1C), 141.60 (1C), 142.28 (1C), 142.99 (1C) [19 × quaternary C]; MS (EI, 70 eV, 270 °C): m/z (%): 1096 (30.6), 1097 (27.9), 1098 (41.9), 1099 (30.4), 1100 (13.5), 1101 (4.0) [M^+], 73 [TMS^+]; $C_{75}H_{89}BrSi$ (1098.52): calcd C 82.00, H 8.17; found C 81.92, H 8.14.

Compound 11 (***n* = 2**): The procedure was analogous to the one described for **2** (*n* = 2). Compound **9** (*n* = 2; 3.00 g, 2.73 mmol), $CHCl_3$ (25 mL), ICl (510 mg, 3.14mmol), and $CHCl_3$ (10 mL) were used. Chromatographic separation through silica gel with hexane/dichloromethane 9:1 gave 2.80 g (89%) of **11** (*n* = 2) as a colorless viscous oil. $R_f = 0.27$ (hexane/dichloromethane 9:1); ^{1}H NMR (270 MHz, CD_2Cl_2): $\delta = 0.79$–0.92 (m, 12H; CH_3), 1.19–1.40 (m, 24H; γ-, δ-, ε-CH_2), 1.49–1.70 (m, 8H; β-CH_2), 2.7–2.79 (m, 8H; α-CH_2), 7.16–7.22 (m, 3H; aromatic H), 7.24–7.32 (m, 3H; aromatic H), 7.37 (mc, 1H; aromatic H), 7.51–7.60 (m, 7H; aromatic H), 7.60–7.77 (m, 6H; aromatic H), 7.77–7.85 (m, 6H; aromatic H), 7.89 (mc, 1H; aromatic H), 8.04 (mc, 1H; aromatic H); ^{13}C NMR (67.9 MHz, $CDCl_3$): $\delta =$ 14.08 (CH_3), 22.50 (CH_2), 29.21 (CH_2), 31.51 (CH_2), 32.67 (CH_2), 92.44 (C-4‴‴‴, C–I), 122.97 (C-3, C–Br), 125.60, 126.71, 126.85, 129.28, 129.75, 129.78, 129.86, 130.11, 130.26, 130.69, 130.92, 130.99, 131.26, 137.11 (14 × tertiary C) 137.35, 137.55, 137.64, 137.70, 137.96, 139.52, 139.61, 140.19, 140.49, 140.67, 140.96, 141.09, 141.41, 141.62, 142.99 (15 × quaternary C); MS (EI, 70 eV, 250 °C): *m/z* (%): 1150 (81.9), 1151 (62.69), 1152 (100), 1153 (68.9), 1154 (25.4), 1155 (6.4), 1156 (1.6) [M^+], 1198 (26.6), 1199 (21.0), 1200 (8.5), 1201 (1.2) [$C_{72}H_{80}I_2^+$], 1102 (9.9), 1103 (8.0), 1104 (22.2), 1105 (16.0), 1106 (15.6), 1107 (9.9), 1108 (3.7), 1109 (1.0) [$C_{72}H_{80}Br_2^+$]; $C_{72}H_{80}BrI$ (1152.23): calcd C 75.05,H 7.00; found: C 74.95, H 7.02.

Compound 9 (***n* = 3**): The procedure was analogous to the one described for **3** (*n* = 2). Compound **10** (*n* = 1; 620 mg, 1.08 mmol), **11** (*n* = 2; 1.24 g, 1.08 mmol), tetrakis(triphenylphosphine)palladium(**0**) (25 mg, 0.02 mmol), toluene (30 mL), and a saturated aqueous solution of $Ba(OH)_2$ (30 mL) were used. Chromatographic separation through silica gel with hexane/dichloromethane 8:2 gave, after lyophilization, 1.43 g (84%) of **9** (*n* = 3) as a colorless solid amorphous material. $R_f = 0.33$ (hexane/dichloromethane 8:2); M.p. 68 °C; ^{1}H NMR (500 MHz, CD_2Cl_2): $\delta = 0.32$ (s, 9H; $SiMe_3$), 0.78–0.85 (m, 18H; CH_3), 1.14–1.30 (m, 36H; γ-, δ-, ε-CH_2), 1.47–1.58 (m, β-CH_2), 2.58–2.69 (m, 12H; α-CH_2), 7.15 (s, 1H; aromatic H), 7.20 (s, 2H; aromatic H), 7.22 (s, 1H; aromatic H), 7.23 (s, 2H; aromatic H), 7.34–7.39 (m, 3H; aromatic H), 7.45–7.53 (m, 11H; aromatic H), 7.58–7.62 (m, 4H; aromatic H), 7.62–7.68 (m, 3H; aromatic H), 7.68–7.72 (m, 4H; aromatic H), 7.76–7.81 (m, 8H; aromatic H), 7.86 (mc, 1H; aromatic H), 8.00 (mc, 2H; aromatic H); ^{13}C NMR (125.8 MHz, $CDCl_3$): $\delta = -1.02$ ($SiMe_3$), 14.09, 22.37, 22.47, 22.50, 22.52, 29.17, 29.24, 29.26, 31.44, 31.46, 31.48, 31.54, 31.67, 32.52, 32.65, 32.68, 122.94 (C–Br), 125.63, 126.02, 126.72, 126.86, 128.65, 129.30, 129.81, 129.87, 130.14, 130.30, 130.87, 130.92, 130.99, 133.03, 137.51, 137.55, 137.63, 137.66, 137.98, 138.43, 139.43, 139.47, 139.49, 140.18, 140.25, 140.40, 140.49, 140.80, 141.05, 141.11, 141.13, 141.45, 141.47, 141.60, 142.28, 143.00; MS (EI, 70 eV, 350 °C): *m/z* (%): 1569 (54.3), 1570 (71.0), 1571 (100), 1572 (88.3), 1573 (50.8), 1574 (20.1), 1575 (6.3); $C_{111}H_{129}BrSi$ (1571.23): calcd C 84.85, H 8.27; found: C 84.83, H 8.22.

Compound 10 (***n* = 3**): The procedure was analogous to that described for **1** (*n* = 3). Compound **9** (*n* = 3; 1.31 g, 8.36×10^{-4} mol), diethyl ether (3 mL), toluene (30 mL), 1.6 M solution of *n*-butyl lithium in hexane (1.57 mL, 2.5×10^{-3} mol, −78 °C), and triisopropyl borate (786 mg, 4.2×10^{-3} mol) were used. Chromatographic separation through silica gel with a) hexane and b) hexane/ethyl acetate 3:1 gave, after lyophilization, 933 mg (74%) of **10** (*n* = 3) as a colorless solid material. $R_f = 0.21$ (hexane/ethyl acetate 3:1); softening point 75 °C; ^{1}H NMR (270 MHz, $CDCl_3$): $\delta = 0.37$ (s, 9H; $SiMe_3$), 0.82–0.98 (m, 18H; CH_3), 1.17–1.40 (m, 36H; γ-, δ-, ε-CH_2), 1.52–1.66 (m, 12H; β-CH_2), 2.62–2.76 (m, 12H; α-CH_2), 7.21–7.45 (m, 9H; aromatic H), 7.52–7.62 (m, 11H; aromatic H), 7.62–7.68 (m, 2H; aromatic H) 7.68–7.78 (m, 7H; aromatic H), 7.81–7.95 (m, 10H; aromatic H), 8.02–8.13 (m, 2H; aromatic H), 8.44 (mc, aromatic H), 8.64 (mc, aromatic H); ^{13}C NMR (67.9 MHz, $CDCl_3$): $\delta = -1.02$ ($SiMe_3$), 22.47, 29.23, 31.49, 32.66, 126.03, 126.74, 126.84, 128.57, 129.30, 129.31, 129.82, 129.88, 130.30, 130.67, 131.01, 137.18, 137.39, 137.61, 137.68, 137.99, 139.32, 139.89, 140.34, 140.67, 141.03, 141.15, 141.44, 141.86; MS (MALDI-TOF): *m/z* (%): 1727 [M^++dithranol − $(H_2O)_2$].

Compound 11 ($n=3$): The procedure was analogous to the one described for **2** ($n=2$). Compound **9** ($n=3$; 530 mg, 3.38×10^{-4} mol), CH_2Cl_2 (8 mL), ICl (66 mg, 4.05×10^{-4} mol), and CH_2Cl_2 (3 mL) were used. Chromatographic separation through silica gel with hexane/dichloromethane 8:2 gave, after lyophilization, 477 mg (87%) of **11** ($n=3$) as a colorless solid material. $R_f=0.29$ (hexane/dichloromethane 8:2); m.p. 72°C; ^{1}H NMR (270 MHz, $CDCl_3$): $\delta=0.80-0.95$ (m, 18H; CH_3), 1.13–1.48 (m, 36H; γ-, δ-, ε-CH_2), 1.49–1.68 (m, 12H; β-CH_2), 2.52–2.77 (m, 12H; α-CH_2), 7.13–7.18 (m, 3H; aromatic H), 7.22–7.28 (m, 5H; aromatic H), 7.35 (t, $^3J=8$ Hz, 1H; aromatic H), 7.47–7.56 (m, 11H; aromatic H), 7.58–7.67 (m, 4H; aromatic H), 7.67–7.74 (m, 5H; aromatic H), 7.74–7.83 (m, 10H; aromatic H), 7.85 (mc, 1H; aromatic H), 8.01 (mc, 2H; aromatic H); ^{13}C NMR (67.9 MHz, $CDCl_3$): $\delta=14.05$, 22.29, 29.23, 31.52, 32.69, 92.39 (C–I), 122.96 (C–Br), 125.64, 126.03, 126.73, 126.86, 129.29, 129.82, 130.16, 130.28, 130.70, 130.99, 131.29, 137.14, 137.38, 137.64, 138.01, 139.51, 140.22, 140.44, 140.53, 140.70, 141.01, 141.18, 141.50, 141.68, 143.06; MS (EI, 70 eV, 380°C, max. temp.): *m/z* (%): 1623 (1.5), 1624 (2.2), 1625 (2.6), 1626 (2.4), 1627 (2.3), 1628 (1.0) [M^+]; $C_{108}H_{120}BrI$ (1624.94): calcd C 79.83, H 7.44; found C 79.68, H 7.31.

Compound 9 ($n=6$): The procedure was analogous to the one described for **3** ($n=2$). Compound **10** ($n=3$; 385 mg, 2.54×10^{-4} mol), **11** ($n=3$; 412 mg, 2.54×10^{-4} mol), tetrakis(triphenylphosphine)palladium(**0**) (12 mg, 1.04×10^{-5} mol) toluene (20 mL), and a saturated aqueous solution of $Ba(OH)_2$ (15 mL) were used. Chromatographic separation through silica gel with hexane/dichloromethane 8:2 gave, after lyophilization, 629 mg (83%) of **9** ($n=6$) as a colorless solid material. $R_f=0.16$ (hexane/dichloromethane 8:2); m.p. 98°C; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta=0.42$ (s, 9H; $SiMe_3$), 0.87–1.00 (m, 36H; CH_3), 1.22–1.43 (m, 72H; γ-, δ-, ε-CH_2), 1.60–1.72 (m, 24H; β-CH_2), 2.66–2.82 (m, 24H; α-CH_2), 7.23 (s, 1H; aromatic H), 7.29 (s, 2H; aromatic H), 7.31–7.37 (m, 9H; aromatic H), 7.49 (mc, 3H; aromatic H), 7.56–7.74 (m, 32H; aromatic H), 7.75–7.80 (m, 11H; aromatic H), 7.81–7.92 (m, 22H; aromatic H), 8.06 (mc, 4H; aromatic H); ^{13}C NMR (125.8 MHz, $CDCl_3$): $\delta=-1.02$ ($SiMe_3$), 14.89, 22.38, 22.53, 22.66, 23.29, 29.05, 29.17, 29.26, 31.49, 31.55, 32.54, 32.70, 122.96 (C–Br), 125.61, 126.01, 126.72, 126.86, 127.05, 128.66, 129.30, 129.82, 130.11, 130.28, 130.88, 130.99, 133.03, 137.51, 137.53, 137.57, 137.63, 139.48, 140.42, 141.12, 141.47, 142.99; MS (MALDI-TOF in dithranol with Ag): *m/z* (%): 3097 ([M^++Ag], 3018 [M^++Ag − Br]; $C_{219}H_{249}BrSi$ (2989.37): calcd C 87.99, H 8.40; found: C 87.71, H 8.24.

Compound 12a: The procedure was analogous to the one described for **2** ($n=2$). Compound **10** ($n=3$; 212 mg, 1.40×10^{-4} mol), CH_2Cl_2 (5 mL), and ICl (34 mg, 2.09×10^{-4} mol) in CH_2Cl_2 (1 mL) were used. Chromatographic separation through silica gel with hexane/ethyl acetate 3:1 gave after lyophilization 206 mg (94%) of **12a** as a colorless solid material. $R_f=0.19$ (hexane/ethyl acetate 3:1); softening point 74–76°C; ^{1}H NMR (270 MHz, $CDCl_3$): $\delta=0.83-1.02$ (m, 18H; CH_3), 1.19–1.42 (m, 36H; γ-, δ-, ε-CH_2), 1.50–1.73 (m, 12H; β-CH_2), 2.57–2.84 (m, 12H; aromatic H), 7.17–7.43 (m, 10H; aromatic H), 7.51–7.67 (m, 12H; aromatic H), 7.67–7.78 (m, 6H; aromatic H), 7.78–7.93 (m, 11H; aromatic H), 7.98–8.11 (m, 2H; aromatic H) 8.41 (mc, aromatic H), 8.69 (mc, aromatic H); ^{13}C NMR (67.9 MHz, $CDCl_3$): $\delta=14.05$, 22.49, 29.22, 31.51, 32.70, 92.39 (C–I), 126.02, 126.85, 128.52, 129.29, 129.81, 130.69, 130.99, 131.28, 137.13, 137.36, 137.62, 137.71, 139.49, 140.44, 140.70, 141.00, 141.19, 141.83; MS (MALDI-TOF in dithranol): *m/z* (%): 1781 [M^++H+dithranol − $(H_2O)_2$].

Compound 12b: Iodobideciphenylboronic acid **12a** (183 mg, 1.16×10^{-4} mol) and pinacol (35 mg, 3×10^{-4} mol) were dissolved in dichloromethane (15 mL). The solution was refluxed for 2 d, while simultaneously removing water. Work-up and chromatographic separation through silica gel with hexane/ethyl acetate 20:1 gave after lyophilization 186 mg (96%) of **12b** as a colorless solid material. $R_f=0.38$ (hexane/ethyl acetate 20:1); softening point 68–70°C; ^{1}H NMR (270 MHz, $CDCl_3$): $\delta=0.78-0.95$ (m, 18H; CH_3), 1.13–1.37 (m, 36H; γ-, δ-, ε-CH_2), 1.40 (s, 12H; ester-CH_3), 1.49–1.68 (m, 12H; β-CH_2), 2.53–2.76 (m, 12H; α-CH_2), 7.12–7.18 (m, 3H; aromatic H), 7.22–7.29 (m, 5H; aromatic H), 7.46–7.57 (m, 11H; aromatic H), 7.57–7.64 (m, 2H; aromatic H), 7.68–7.74 (m, 5H; aromatic H), 7.74–7.88 (m, 13H; aromatic H), 8.01 (mc, 2H; aromatic H), 8.18 (mc, 1H; aromatic H); ^{13}C NMR (67.9 MHz, $CDCl_3$): $\delta=14.04$, 22.49, 24.89 (ester-CH_3), 29.23, 31.45, 31.53, 32.71, 83.86 (ester-C), 92.38 (C–I), 126.03, 126.85, 128.21, 129.29, 129.82, 130.70, 130.98, 131.29, 133.53, 137.14, 137.38, 137.64, 137.73, 139.49, 140.23, 140.44, 140.55, 140.71, 140.89, 141.01, 141.20, 141.51; MS (MALDI-TOF in dithranol): *m/z* (%): 1671 [M^+]; $C_{114}H_{132}BIO_2$ (1672.01): calcd C 81.89, H 7.96; found C 81.71, H 7.82.

Compound 13: The procedure was similar to the one described for **4** ($n=3$). Compound **9** ($n=6$; 610 mg, 2.04×10^{-4} mol) and bromobenzene (320 mg, 2.03×10^{-3} mol) were dissolved in a mixture of diethyl ether (1 mL) and toluene (8 mL). NaH (8 mg) was added. At −78°C a 1.6 M solution of *n*-butyllithium in hexane (2.8 mL, 2.28 mmol) was added. After warming to room temperature and cooling again to −78°C, 1,2-diiodoethane (2.53 g, 9.0 mmol) dissolved in toluene (5 mL) was added. The reaction mixture was allowed to warm to room temperature over 2 h. A 1 M aqueous solution of sodium disulfite (15 mL) was added. Chromatographic separation through silica gel with hexane/dichloromethane 7:3 gave 551 mg (89%) of **13** as a colorless solid material. M.p. 101°C; $R_f=0.26$ (hexane/dichloromethane 7:3); UV/Vis: $\lambda_{max}=283.6$ nm; ^{1}H NMR (270 MHz, $CDCl_3$): $\delta=0.47$ (s, 9H; $SiMe_3$), 0.89–1.06 (m, 36H; CH_3), 1.25–1.51 (m, 72H; γ-, δ-, ε-CH_2), 1.61–1.81 (m, 24H; β-CH_2), 2.69–2.91 (m, 24H; α-CH_2), 7.27–7.41 (m, 14H; aromatic H), 7.48–7.54 (m, 2H; aromatic H), 7.54–7.66 (m, 24H; aromatic H), 7.66–7.74 (m, 8H; aromatic H), 7.74–7.85 (m, 12H; aromatic H), 7.85–7.97 (m, 20H; aromatic H), 8.12 (mc, 4H; aromatic H); ^{13}C NMR (67.9 MHz, $CDCl_3$): $\delta=-1.01$ ($SiMe_3$), 14.07 (CH_3), 22.51, 29.24, 31.47, 31.54, 32.70, 94.36 (C–I), 126.03, 126.86, 127.41, 128.67, 129.29, 129.82, 130.20, 130.98, 131.89, 137.45, 137.63, 139.50, 140.43, 141.17, 141.50; MS (MALDI-TOF in dithranol with Ag): *m/z* (%): 3143 [M^++Ag], 3017 [M^++Ag − I]; $C_{219}H_{249}ISi$ (3036.37): calcd C 86.63, H 8.27; found C 86.41, H 8.03.

Compound 14: The procedure was analogous to the one described for **5** ($n=3$). Glove box, **13** (530 mg, 1.75×10^{-4} mol), dichloromethane (5 mL), BBr_3 (53 mg, 2.11×10^{-4} mol), dichloromethane (0.15 mL), pinacol (110 mg, 0.93 mmol), and water were used. Chromatographic separation through silica gel with hexane/ethyl acetate 30:1 gave 345 mg (64%) of **14** as a colorless solid material. $R_f=0.21$ (hexane/ethyl acetate 30:1); softening point 105–108°C; ^{1}H NMR (270 MHz, $CDCl_3$): $\delta=0.82-1.00$ (m, 36H; CH_3), 1.23–1.41 (m, 72H; γ-, δ-, ε-CH_2), 1.43 (s, 12H; pinacol CH_3), 1.58–1.80 (m, 24H; β-CH_2), 2.72–2.97 (m, 24H; α-CH_2), 7.31–7.43 (m, 14H; aromatic H), 7.45–7.66 (m, 26H; aromatic H), 7.66–7.77 (m, 9H; aromatic H), 7.77–7.83 (m, 11H; aromatic H), 7.83–8.02 (m, 20H; aromatic H), 8.15 (m, 4H; aromatic H); ^{13}C NMR (67.9 MHz, $CDCl_3$): $\delta=14.05$ (CH_3), 22.49, 22.56, 24.86 (ester-CH_3), 29.19, 29.32, 31.54, 31.61, 32.70, 32.84, 83.81 (ester-C), 94.34 (C–I), 126.09, 126.79, 127.41, 127.56, 128.76, 129.31, 129.47, 130.31, 131.04, 131.96, 137.67, 137.84, 139.61, 140.41, 141.24, 141.61; MS (MALDI-TOF in dithranol with Ag): *m/z* (%): 3199 [M^++Ag]; $C_{222}H_{252}BIO_2$ (3090.15): calcd C 86.29, H 8.22; found C 85.92, H 8.01.

Compound 15: a) A solution of **12b** (182 mg, 0.111 mmol) and tris(tri-*p*-tolylphosphine)palladium(**0**) (2.3 mg, 2.6×10^{-6} mol) in toluene (3.3 mL) was added through a syringe pump within 30 h to a boiling mixture of tris(tri-*p*-tolylphosphine)palladium(**0**) (2.5 mg, 2.5×10^{-6} mol), a saturated aqueous solution of $Ba(OH)_2$ (10 mL), dimethoxyethane (12 mL), and toluene (3 mL). The phases were then separated, and the organic one was washed with water. Removal of the solvent in vacuo gave crude **15** in a conversion of 20% (anal. GPC). Purification by preparative GPC gave 27 mg **15** (17%).

b) A solution of **14** (270 mg, 8.74×10^{-5} mol) and tris(tri-*p*-tolylphosphine)-palladium(**0**) (2.3 mg, 2.6×10^{-6} mol) in toluene (7 mL) was added through a syringe pump within 36 h to a boiling mixture of tris(tri-*p*-tolylphosphine)palladium(**0**) (2.3 mg, 2.6×10^{-6} mol), a saturated aqueous solution of $Ba(OH)_2$ (20 mL), dimethoxyethane (15 mL), and toluene (4 mL). The phases were then separated, and the organic one was washed with water. Removal of the solvent in vacuo gave crude **15** in a conversion of 75% (anal. GPC). Purification by preparative GPC gives 168 mg **15** (68%) as a colorless solid material. t_R: 18.2 min (column: water/styragel 7.8×300 HR5E and HR6E, flow 1 mL min^{-1} THF); UV/Vis: $\lambda_{max}=283.6$ nm; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta=0.79-0.86$ (m, 36H; CH_3), 1.15–1.31 (m, 72H; γ-, δ-, ε-CH_2), 1.51–1.60 (m, 24H; β-CH_2), 2.65 (mc, 24H; α-CH_2), 7.25 (s, 12H; H-3′), 7.42 (d, $^3J=9$ Hz, 24H; H-5), 7.60 (mc, 6H; H-5‴), 7.69–7.73 (m, 12H; H-6‴), 7.79 (d, $^3J=9$ Hz, H-6), 8.00 (s, 12H; H-9); ^{13}C NMR (67.9 MHz, $CDCl_3$): $\delta=14.09$ (CH_3), 22.51 (CH_2), 29.26 (CH_2), 31.48 (CH_2), 31.54 (CH_2), 32.67 (CH_2), 125.88 (C-6‴), 126.24 (C-2‴), 126.83 (C-3), 129.32 (C-5‴), 129.81 (C-2), 130.97 (C-6′), 137.64 (C-2′), 139.43 (C-4), 140.40 (C-5‴), 141.11 (C-1), 141.43 (C-1‴); MS (MALDI-

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TOF in dithranol with Ag): *m/z* (%): 2944 [M^++Ag]; $C_{216}H_{240}$ (2836.27): calcd C 91.47, H 8.53; found: C 91.23, H 8.39.

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