A Biphenyl Construction Kit for Modular Chemistry

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The synthesis of a number of telechelic biphenyls with one of the functional groups, $B(OH)_2$, TMS, Br and I, at each ring is presented. These biphenyls constitute a construction kit for modular chemistry using the Suzuki cross-coupling protocol.

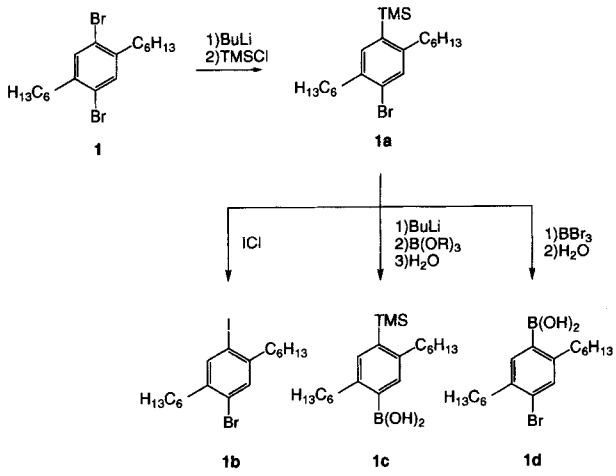
Repetitive strategies are of importance in synthetic organic chemistry whenever structurally defined and monodisperse molecular objects in the nm-range are the targets. Such methods use the same building blocks, coupling reactions and functional groups over and over again to minimize the enormous effort otherwise involved. The growth process can either be linear or exponential. In the latter case, the total number of reaction steps is small, even for compounds whose molecular weights are already in the range of polymers[1-3]. In a long-term project we aim at developing a flexible and versatile route for the synthesis of oligophenylene rods (telechelics)[4] and "giganto" cycles[5] with the help of such growth schemes. This paper lays the foundation of this work in that it describes the multigram-scale syntheses of a number of biphenyl derivatives, all of which have the features required for their usage as building blocks (modules) in molecular constructions[6,7]. Problems of low solubility are circumvented by the introduction of alkyl chains.

Results and Discussion

Our strategy for an efficient synthesis of large objects with phenylene repeating units is described elsewhere[4]. In brief, it involves aromatic nuclei which bear the four functional groups: $B(OH)_2$, trimethylsilyl (TMS), Br and I. It uses the Suzuki cross-coupling of aromatic boronic acids and aromatic halides (Br, I) and Pd(0/II)-catalysis[8], the high selectivity of this coupling method towards iodo functions[9], as well as the relatively high degree of flexibility in interconversions between the four functional groups. Of specific importance in the latter case is the synthesis of biphenyls with the functional group patterns I/Br and TMS/$B(OH)_2$ which are the starting materials for the next coupling step to quaterphenylenes. TMS acts as place holder, ensuring completely *ipso* substitution[10].

Syntheses: Scheme 1 depicts all transformations involving only one benzene nucleus. Schemes 2–5 summarize all cross-couplings to biphenyls and their subsequent transformation into properly functionalized, linear and kinked modules. Schemes 2–4 are organized according to the kind of arylboronic acid used, while Scheme 5 depicts the coupling of boronic acid **1c** with the potentially trifunctional compound **12**. All compounds are new, except for **2** and **3** which are commercially available and **1**[11], **1d**[11], **7**[12], **10**[12] and **12**[13] which have been reported in the literature. Some features are worthly of discussion: The lithiation of dibromobenzene **1** (Scheme 1) was performed in diethyl ether at −78 °C using an excess of butyllithium. In this way a clean monolithiation could be achieved as is indicated by the very high yield of the quenching product **1a**. The iodo function of **1b** was introduced by *ipso* iododesilylation of **1a** with iodine monochloride following a literature procedure[14]. This conversion proceeded cleanly and gave the product in yields of 94–98%. All other iododesilylations proceeded comparably smoothly. With the exception of compound **1d**, the boronic acids were generated from the corresponding bromoarenes by the sequence of lithiation, boronation of the lithiated intermediate with triisopropyl borate, and hydrolysis of the resulting boronic acid ester. The borate employed gave yields that were approximately 20% higher than with the more commonly used trimethyl borate. Compound **1d** was obtained by desilylation of **1a** using boron tribromide. This procedure is not of great importance within the context of this paper but is a very valuable method for the respective conversion of higher oligophenylenes[4].

Scheme 1



The Suzuki cross-couplings were performed in refluxing toluene/water with either sodium carbonate or barium hydroxide as base and 0.5–2.0 mole percent $Pd(PPh_3)_4$ as catalyst precursor. Depending on the *ortho*-substituent of the boronic acid, the isolated yields varied between some 70–80% (*ortho*-alkyl) and 90–100% (*ortho*-hydrogen). In the case of boronic acids with *ortho*-alkyl groups, deboronation occurred during coupling to an extent of 20–30%, which explains the lower yield of coupling product in these instances. The iodo/bromo selectivity of the coupling ex-

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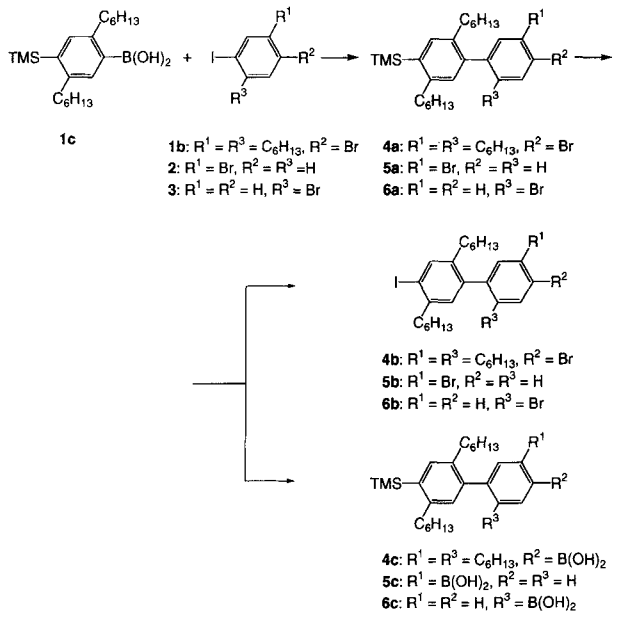
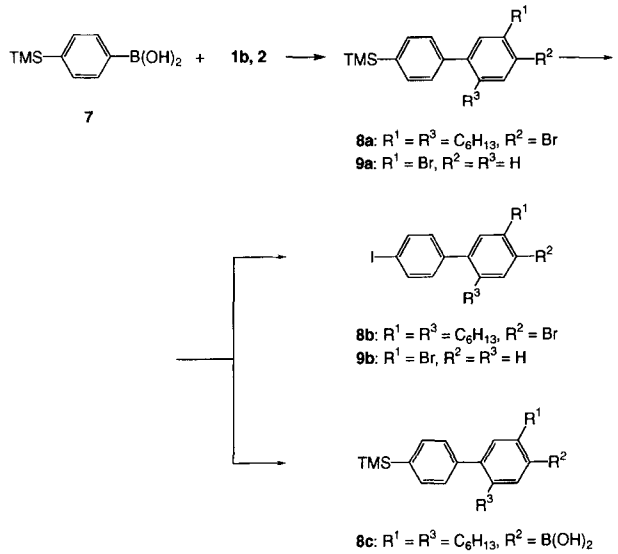
ceeded 98% in all cases but one (**13a**) in favour of coupling at the iodo site. The mass spectra of the crude products did not give any indication of coupling at the bromo site, with the exception of compound **13a**, where a relatively low yield of the desired coupling product (66%) was accompanied by a terphenylene (5%), which was formed through coupling at both the iodo and bromo sites. This phenomenon is not yet understood. There was no indication for coupling at any chloro site.

Scheme 2

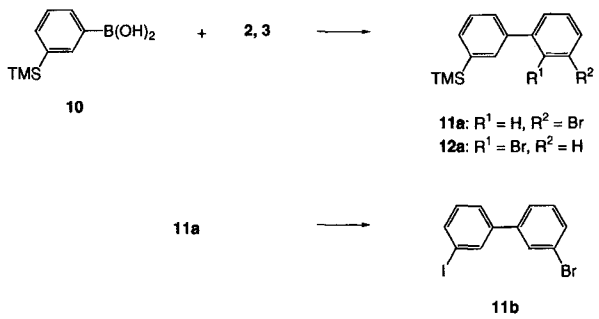


Scheme 3

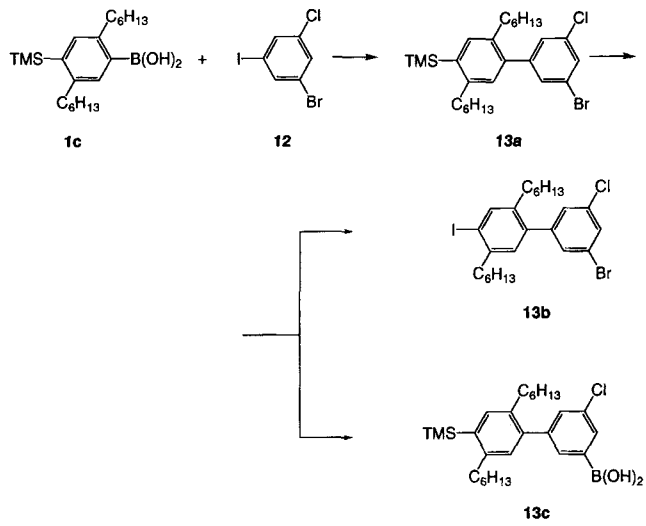


Characterization: All products other than the boronic acids were fully characterized. The iodoaromatics show the expected upfield shift of the iodinated carbon in the ^{13}C-NMR spectrum. The TMS proton shift in silylated compounds is sensitive to substituents in the *ortho*-position. For example, the TMS groups of compounds **4a**–**6a** and **4c**–**6c**, which bear an *ortho*-alkyl group, absorb at approximately $\delta = 0.60$, whereas the signal of the same group in compounds **8a**, **9a**, **11a** and **12a**, which have no alkyl group near the TMS moiety, is shifted considerably upfield to approximately $\delta = -1.10$. Boronic acids tend to form cyclic anhydrides (boroxines) and, depending upon solvent polarity and water content, exist as mixtures of the monomeric and trimeric forms[15]. This, of course, complicates their NMR spectra. The spectra were recorded in either chloroform or DMSO, in which the cyclic trimer and the monomeric species, respectively, are favoured. With the exception of compounds **1c** and **1d**, for which both sets of NMR data are given in the Experimental Section, the listed shifts of all other boronic acids were taken from the trimeric form in $CDCl_3$. The coexistence of differently dehydrated forms becomes very apparent in the case of the boronic acids **6c**[16] and **13c**. Figure 1 shows a series of ^{1}H-NMR spectra of **13c** in chloroform (a) as obtained from synthesis, (b) after the addition of water at 20 °C, and (c) after removal of this water with $MgSO_4$. As can be seen, the low intensity signals in Figure 1(a) increase on addition of water and decrease on addition of a drying agent. This shows that these signals do not stem from impurities but from a less condensed, presumably monomeric form and that the equilibrium can be shifted easily. Correct elemental analysis data could not be obtained for the boronic acids as is typical of this class of compounds. The EI mass spectra invariably showed the correct molecular ion peak of the trimer and no indication of the monomer. For the two representative boronic acids **1c** and **5c**, high resolution mass spectra were also recorded which were in full agreement with the proposed elemental composition. A simple and reliable additional means of charac-

Scheme 4

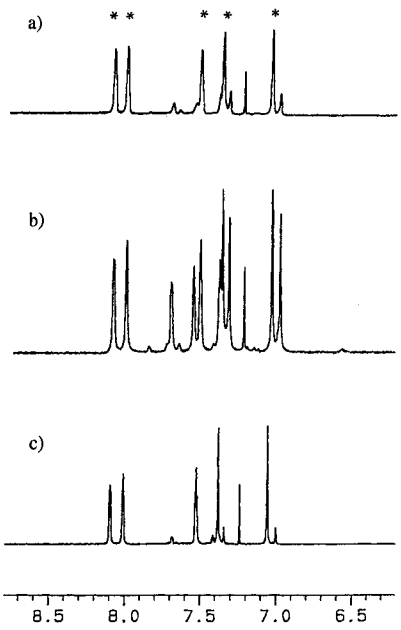


Scheme 5



terization for laboratory use is TLC, using silica and hexane/ethyl acetate (3:1) as eluent. The R_f-value of boronic acids is normally the lowest of all compounds in a reaction mixture and the spot tails very characteristically over approximately 0.2 R_f values. For cross-couplings the boronic acids were used as obtained directly from their syntheses (which involved a drying step in high vacuum at 35 °C for several hours). They were obtained in a 1.0:1.0 stoichiometry, assuming they exist exclusively as trimers.

Figure 1. Aromatic region of the ^{1}H-NMR spectrum of boronic acid **13c** in $CDCl_3$ at 293 K: (a) as obtained from synthesis; (b) after addition of water; (c) after removal of the added water with $MgSO_4$; the marked signals (*) indicate the trimeric anhydride of the boronic acid



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Experimental Section

General: Starting materials were either prepared according to literature procedures or purchased from Fluka, Aldrich or Acros and used without further purification. All solvents were purified and dried by standard methods. All reactions were carried out under N_2. The catalyst was stored under N_2 at −30 °C. It was weighed out on the bench top and transferred in air. – ^{1}H-NMR spectra: Bruker AM 270 spectrometer (270 MHz) (TMS at δ = 0, $CHCl_3$ at δ = 7.24, CH_2Cl_2 at δ = 5.32 or DMSO at δ = 2.49 as internal standard). – ^{13}C-NMR spectra: Bruker AM 270 spectrometer (67.9 MHz) ($CDCl_3$ at δ = 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. – Preparative HPLC: Nucleosil 100 C_{18} (Macherey-Nagel), 5 µm, 250 × 16 mm, UV detection.

1-Bromo-2,5-di-n-hexyl-4-trimethylsilylbenzene (**1a**): To a suspension of 75 g (185.5 mmol) of **1** in diethyl ether (1000 ml) at −78 °C, 150.75 ml of a 1.6 M solution of *n*-butyllithium in hexane was added over a period of 45 min. and the reaction mixture was allowed to warm to 0 °C. The colourless solution was then cooled once again to −78 °C and 40.3 g (371 mmol) of trimethylchlorosilane was added over a period of 30 min. The reaction mixture was allowed to warm to room temperature over 12 h and then 500 ml of water was added. The layers were separated, the aqueous layer was washed twice with diethyl ether (200 ml) and the combined organic layers were washed twice with water (200 ml). The organic phase was dried over $MgSO_4$. Distillation gave 71.9 g (98%) of **1a** as a colourless oil; b.p. 157 °C/0.25 mbar. – ^{1}H NMR (270 MHz, $CDCl_3$): δ = 0.35 (s, 9H, $SiMe_3$), 0.90 (m, 6H, Me), 1.30–1.45 (m, 12H, γ-, δ-, ε-CH_2), 1.50–1.70 (m, 4H, β-CH_2), 2.60–2.75 (m, 4H, α-CH_2), 7.28 (s, 1H, aromatic H), 7.37 (s, 1H, aromatic H). – ^{13}C NMR (67.9 MHz, $CDCl_3$): δ = 0.39 (3 C), 14.11 (2 C), 22.64, 22.67, 29.18, 29.59, 30.15, 31.68, 31.79, 32.40, 35.60, 35.84, 125.98, 132.53, 136.23, 137.08, 138.29, 148.00. – MS (EI, 70 eV, 80 °C); *m/z* (%): 396 (6.8), 397 (2.7), 398 (7.0), 399 (2.4) [M^+], 73 (100) [$SiMe_3^+$]. – $C_{21}H_{37}BrSi$ (397.51): calcd. C 63.45, H 9.38; found C 63.21, H 9.17.

Typical Procedure for the Conversion of the Trimethylsilyl Function into the Iodo Function: 4-Bromo-2,5-Di-n-hexyl-1-iodobenzene (**1b**): To a solution of 30.0 g (75.47 mmol) of **1a** in CCl_4 (150 ml) at 0 °C, a solution of 13.43 g (82.72 mmol) of ICl in CCl_4 (50 ml) was added over 20 min. The reaction mixture was allowed to warm to room temperature over a period of 30 min. 100 ml of a 1 M aqueous solution of sodium disulfite was then added. The layers were separated, the aqueous layer was washed twice with CCl_4 (50 ml) and the combined organic layers were washed twice with water (50 ml). The organic phase was dried over $MgSO_4$. Chromatographic separation on silica gel with hexane gave 33.1 g (97%) of **1b** as colourless crystals; m.p. 37 °C; R_f = 0.51 (hexane). – ^{1}H NMR (270 MHz, $CDCl_3$): δ = 0.85–0.95 (m, 6H, Me), 1.25–1.45 (m, 12H, γ-, δ-, ε-CH_2), 1.45–1.60 (m, 4H, β-CH_2), 2.55–2.65 (m, 4H, α-CH_2), 7.30 (s, 1H, aromatic H), 7.60 (s, 1H, aromatic H). – ^{13}C NMR (67.9 MHz, $CDCl_3$): δ = 14.09 (2 C), 22.59 (2 C), 28.99, 29.02, 29.82, 30.11, 31.60 (2 C), 35.32, 40.08, 98.82, 124.46, 132.77, 140.27, 141.51, 144.65. – MS (EI, 70 eV, 60 °C); *m/z* (%): 450 (100), 451 (24), 452 (99), 453 (21), 454 (3) [M^+]. – $C_{18}H_{28}IBr$ (451.23): calcd. C 47.91, H 6.25; found C 47.87, H 6.19.

Typical Procedure for the Conversion of the Bromo Function into Boronic Acid: 2,5-Di-n-hexyl-4-trimethylsilylbenzene-1-boronic Acid (**1c**): To a solution of 27.42 g (69.0 mmol) of **1a** in a mixture of diethyl ether (500 ml) and tetrahydrofuran at −78 °C, 129.4 ml (207 mmol) of a 1.6 M solution of *n*-butyllithium in hexane was added over a period of 35 min. and the reaction mixture was allowed to warm to −10 °C. The solution was then cooled once again to −78 °C and 51.90 g (276 mmol) of triisopropyl borate was added over a period of 60 min. The reaction mixture was allowed to warm to room temperature overnight. Thereafter, 400 ml water was added. The layers were separated, the aqueous layer was washed twice with diethyl ether (200 ml) and the combined organic layers were washed twice with water (200 ml). The organic phase was dried over $MgSO_4$. Chromatographic separation on silica gel with (a) hexane and (b) hexane/ethyl acetate (3:1) gave 20.76 g (87%) of **1c** as a colourless oil; R_f = 0.29 (hexane/ethyl acetate, 3:1). – ^{1}H NMR (270 MHz, $CDCl_3$): δ = 0.40 (s, 9H, $SiMe_3$), 0.78–0.88 (t, J = 8 Hz, 3H, Me), 0.88–1.00 (t, J = 8 Hz, 3H, Me), 1.32–1.53 (m, 12H, γ-, δ-, ε-CH_2), 1.59–1.79 (m, 4H, β-CH_2), 2.78 (t, J = 8 Hz, 2H, α-CH_2), 3.21 (t, J = 8 Hz, 2H, α-CH_2), 7.39 (s, 1H, aromatic H), 8.04 (s, 1H, aromatic H). – ^{1}H NMR (270 MHz, [D_6]DMSO): δ = 0.24 (s, 9H, $SiMe_3$), 0.78–0.90 (m, 6H, Me), 1.18–1.33 (m, 12H, γ-, δ-, ε-CH_2), 1.39–1.57 (m, 4H, α-CH_2),

2.78, 7.10 (s, 1H, aromatic H), 7.20 (s, 1H, aromatic H), 7.94 [(s, 2H, $B(OH)_2$]. – ^{13}C NMR (67.9 MHz, $CDCl_3$): δ = 0.44, 14.07, 14.11, 22.70 (2C), 29.26, 29.84, 31.94 (2 C), 32.95, 33.36, 35.22, 36.12, 129.48, 136.05, 137.11, 142.47, 145.16, 146.90. – MS (EI, 70 eV, 150°C); *m/z* (%): 1031 (16), 1032 (59), 1033 (100), 1034 (72), 1035 (35), 1036 (13) [M^+]. – $C_{63}H_{111}B_3O_3Si_3$: calcd. 1032.81202, found 1032.81209 (MS).

4-Bromo-2,5-di-n-hexylbenzene-1-boronic Acid (**1d**): 1 g (2.52 mmol) of **1a** was dissolved in 20 ml dichloromethane. To this solution 3.77 mmol of boron tribromide in 12 ml of dichloromethane was added over a period of 15 min. After stirring this solution for 3 h, 10 ml of water 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 (20 ml). The organic phase was dried over $MgSO_4$. Chromatographic separation on silica gel with (a) hexane and (b) dichloromethane gave 0.83 g (94%) of **1d** as colourless crystals; m.p. 85.5°C (ref. 11: 85–87.5°C); R_f = 0.27 (hexane/ethyl acetate, 3:1). – ^1H NMR (270 MHz, $CDCl_3$): δ = 0.72–0.82 (t, *J* = 8 Hz, 3H, Me), 0.82–0.94 (t, *J* = 8 Hz, 3H, Me), 1.15–1.48 (m, 12H, γ-, δ-, ε-CH_2), 1.48–1.71 (m, 4H, β-CH_2), 2.74 (t, *J* = 8 Hz, 2H, α-CH_2), 3.11 (t, *J* = 8 Hz, 2H, α-CH_2), 7.23 (s, 1H, aromatic H), 7.94 (s, 1H, aromatic H). – ^1H NMR (270 MHz, [D_6]DMSO): δ = 0.78–0.90 (m, 6H, Me), 1.18–1.37 (m, 12H, γ-, δ-, ε-CH_2), 1.40–1.59 (m, 4H, β-CH_2), 2.53–2.70 (m, 4H, α-CH_2), 7.29 (s, 1H, aromatic H), 7.31 (s, 1H, aromatic H), 8.04 [s, 2H, $B(OH)_2$].

Typical Procedure for the Suzuki Coupling: 4-Bromo-2,2',5,5'-tetra-n-hexyl-4'-trimethylsilylbiphenyl (**4a**): 21.88 g (63.53 mmol) of **1c** and 28.67 g (63.54 mmol) of **1b** were dissolved in 200 ml toluene. The solution was degassed and flushed with N_2 repeatedly. 200 ml of a saturated aqueous solution of $Ba(OH)_2$ was then added. The system was degassed again and 367 mg (0.32 mmol) of tetrakis(triphenylphosphane)palladium(0) was added. The mixture was refluxed for 48 h with vigorous stirring. Then the mixture was allowed to cool to room temperature, the layers were separated, the aqueous phase was washed twice with toluene (20 ml) and the combined organic layers once with water (20 ml). The organic layer was dried ($MgSO_4$). The unreacted bromoiodobenzene **1b** was distilled off. Chromatographic separation on silica gel with hexane gave 28.5 g (69%) of **4a** as a colourless oil; R_f = 0.45 (hexane). – ^1H NMR (270 MHz, $CDCl_3$): δ = 0.37 (s, 9H, $SiMe_3$), 0.78–0.94 (m, 12H, Me), 1.08–1.23 (m, 12H, γ-, δ-, ε-CH_2), 1.23–1.47 (m, 12H, γ-, δ-, ε-CH_2 and 4H, β-CH_2), 1.50–1.66 (m, 4H, β-CH_2), 2.19–2.40 (m, 4H, α-CH_2), 2.59–2.79 (m, 4H, α-CH_2), 6.88 (s, 1H, aromatic H), 6.95 (s, 1H, aromatic H), 7.31 (s, 1H, aromatic H), 7.42 (s, 1H, aromatic H). – ^{13}C NMR (67.9 MHz, $CDCl_3$): δ = 0.62 (3C), 14.07 (4C), 22.46, 22.53, 22.64 (2 C), 29.07 (2C), 29.25, 29.64, 29.95, 30.81, 31.09, 31.54, 31.61, 31.71, 31.87, 32.57 (2C), 32.87, 35.66, 35.91, 129.88, 131.51, 132.58, 135.15, 136.61 (2C), 138.53, 140.21, 140.35, 140.66, 145.41. – MS (EI, 70 eV, 120°C); *m/z* (%): 640 (86), 641 (44), 642 (100), 643 (46), 644 (12) [M^+]. – $C_{39}H_{65}SiBr$ (641.93): calcd. C 72.97, H 10.21; found C 72.85, H 10.15.

4-Bromo-2,2',5,5'-tetra-n-hexyl-4'-iodobiphenyl (**4b**): The procedure was analogous to that described for **1b**: 14.8 g (23.06 mmol) of **4a** in 200 ml of CCl_4, 4.09 g (25.20 mmol) of ICl in 40 ml of CCl_4, 80 ml of a 1 M aqueous solution of sodium disulphite. Chromatographic separation on silica gel with hexane gave 15.2 g (95%) of **4b** as a colourless oil; R_f = 0.45 (hexane). – ^1H NMR (270 MHz, $CDCl_3$): δ = 0.75–0.95 (m, 12H, Me), 1.06–1.24 (m, 12H, γ-, δ-, ε-CH_2), 1.24–1.46 (m, 12H, γ-, δ-, ε-CH_2 and 4H, β-CH_2), 1.46–1.68 (m, 4H, β-CH_2), 2.10–2.36 (m, 4H, α-CH_2), 2.57–2.70 (m, 4H, α-CH_2), 6.89 (s, 1H, aromatic H), 6.91 (s, 1H, aromatic H), 7.42 (s, 1H, aromatic H), 7.70 (s, 1H, aromatic H). – ^{13}C NMR (67.9 MHz, $CDCl_3$): δ = 14.06 (4 C), 22.46 (2 C), 22.61 (2 C), 29.03 (2 C), 29.08 (2 C), 29.92, 30.28, 30.71, 30.74, 31.53 (2 C), 31.67 (2 C), 32.32, 32.52, 35.63, 40.24, 99.44, 123.26, 130.42, 131.35, 132.71, 138.77, 139.20, 139.45, 140.01, 140.14, 140.24, 142.14. – MS (EI, 70 eV, 150°C); *m/z* (%): 694 (97), 695 (48), 696 (100), 697 (43), 698 (12) [M^+]. – $C_{36}H_{56}BrI$ (695.65): calcd. C 62.16, H 8.11; found C 62.20, H 8.03.

2,2',5,5'-Tetra-n-hexyl-4'-trimethylsilylbiphenyl-4-boronic Acid (**4c**): The procedure was analogous to that described for **1c**: 19.3 g (30.1 mmol) of **4a** in a mixture of 300 ml diethyl ether and 300 ml THF, 60 ml (96 mmol) of a 1.6 M solution of *n*-butyllithium in hexane, 26.1 g (139 mmol) of triisopropyl borate. Chromatographic separation on silica gel with hexane/ethyl acetate (6:1) gave 13.7 g (77%) of **6c** as a colourless oil; R_f = 0.30 (hexane/ethyl acetate, 3:1). – ^1H NMR (270 MHz, $CDCl_3$): δ = 0.48 (s, 9H, $SiMe_3$), 0.75–0.96 (m, 12H, Me), 1.09–1.80 (m, 32H, β-, γ-, δ-, ε-CH_2), 2.24–2.53 (m, 4H, α-CH_2), 2.62–2.76 (t, *J* = 8 Hz, 2H, α-CH_2), 3.06–3.24 (m, 1H, α-CH_2), 3.32–3.46 (m, 1H, α-CH_2), 7.01 (s, 1H, aromatic H), 7.10 (s, 1H, aromatic H), 7.38 (s, 1H, aromatic H), 8.19 (s, 1H, aromatic H). – ^{13}C NMR (67.9 MHz, $CDCl_3$): δ = 0.69 (3 C), 14.10 (4 C), 22.58 (2 C), 22.70 (2 C), 29.34 (3 C), 29.68, 31.18, 31.36, 31.70 (2 C), 31.94, 32.09, 31.61, 32.90, 33.03, 33.21, 35.18, 36.01, 127.49, 129.78, 131.56, 135.19, 136.43, 136.53, 137.35, 138.27, 141.67, 145.11, 145.37, 148.00. – MS (EI, 70 eV, 300°C); *m/z* (%): 1763 (12), 1764 (37), 1765 (93), 1766 (100), 1767 (72), 1768 (39), 1769 (17) [M^+].

3-Bromo-2',5'-di-n-hexyl-4'-trimethylsilylbiphenyl (**5a**): The procedure was analogous to that described for **4a**: 28.5 g (82.8 mmol) of **1c**, 23.4 g (82.8 mmol) of **2** and 390 mg (0.34 mmol) tetrakis(triphenylphosphane)palladium(0) in a mixture of 400 ml toluene and 400 ml of a saturated aqueous solution of $Ba(OH)_2$. Reflux for 1 d. The unreacted bromoiodobenzene **2** was distilled off. Chromatographic separation on silica gel with hexane gave 32.2 g (82%) of **5a** as a colourless oil; R_f = 0.35 (hexane). – ^1H NMR (270 MHz, $CDCl_3$): δ = 0.38 (s, 9H, $SiMe_3$), 0.85 (t, *J* = 8 Hz, 3H, Me), 0.9 (t, *J* = 8 Hz, 3H, Me), 1.15–1.25 (m, 6H, γ-, δ-, ε-CH_2), 1.25–1.35 (m, 4H, γ-, δ-, ε-CH_2), 1.35–1.55 (m, 2H, γ-, δ-, ε-CH_2 and 2H, β-CH_2), 1.6–1.7 (m, 2H, β-CH_2), 2.57 (t, *J* = 8 Hz, 2H, α-CH_2), 2.75 (t, *J* = 8 Hz, 2H, α-CH_2), 7.05 (s, 1H, aromatic H), 7.26–7.30 (m, 2H, aromatic H), 7.39 (s, 1H, aromatic H), 7.45–7.53 (m, 2H, aromatic H). – ^{13}C NMR (67.9 MHz, $CDCl_3$): δ = 0.58 (3 C), 14.07 (2 C), 22.53, 22.64, 29.14, 29.70, 31.48 (2 C), 31.82, 32.61 (2 C), 35.98, 122.11, 127.81, 129.43, 129.70, 129.90, 132.19, 135.76, 136.38, 137.36, 140.95, 144.28, 146.05. – MS (EI, 70 eV, 120°C); *m/z* (%): 472 (14), 473 (5), 474 (15), 475 (5), 476 (2) [M^+], 73 (100) [$SiMe_3^+$]. – $C_{27}H_{41}BrSi$ (473.61): calcd. C 68.47, H 8.73; found C 68.23, H 8.44.

3'-Bromo-2,5-di-n-hexyl-4-iodobiphenyl (**5b**): The procedure was analogous to that described for **1b**: 7.10 g (15.0 mmol) of **5a** in 40 ml of CCl_4, 2.68 g (16.5 mmol) of ICl in 20 ml of CCl_4, 30 ml of a 1 M aqueous solution of sodium disulfite. Chromatographic filtration through silica gel with hexane gave 7.65 g (97%) of **5b** as a colourless oil; R_f = 0.42 (hexane). – ^1H NMR (270 MHz, CD_2Cl_2): δ = 0.85 (t, *J* = 8 Hz, 3H, Me), 0.9 (t, *J* = 8 Hz, 3H, Me), 1.15–1.25 (m, 6H, γ-, δ-, ε-CH_2), 1.25–1.50 (m, 6H, γ-, δ-, ε-CH_2 and 2H, β-CH_2), 1.5–1.65 (m, 2H, β-CH_2), 2.47 (t, *J* = 8 Hz, 2H, α-CH_2), 2.7 (t, *J* = 8 Hz, 2H, α-CH_2), 7.0 (s, 1H, aromatic H), 7.20–7.32 (m, 2H, aromatic H), 7.43–7.52 (m, 2H, aromatic H), 7.74 (s, 1H, aromatic H). – ^{13}C NMR (67.9 MHz, $CDCl_3$): δ = 14.03, 14.09, 22.43, 22.59, 28.93, 29.06, 30.29, 31.12, 31.35, 31.60, 32.02, 40.27, 100.06, 122.20, 127.59, 129.46, 129.94, 130.24,

131.95, 139.628, 139.88, 140.26, 142.62, 143.11. – MS (EI, 70 eV, 120°C); *m/z* (%): 526 (100), 527 (25), 528 (95), 529 (24), 530 (3) [M^+]. – $C_{24}H_{32}BrI$ (527.33): calcd. C 54.66, H 6.11; found C 54.77, H 6.03.

2',5'-Di-n-hexyl-4'-trimethylsilylbiphenyl-3-boronic Acid (**5c**): The procedure was analogous to that described for **1c**: 9.70 g (20.5 mmol) of **5a** in a mixture of 150 ml diethyl ether and 150 ml THF, 38.4 ml (61.4 mmol) of a 1.6 M solution of *n*-butyllithium in hexane, 15.3 g (81.7 mmol) of triisopropyl borate. Chromatographic separation on silica gel with hexane/ethyl acetate (6:1) gave 6.57 g (76%) of **5c** as a colourless oil; R_f = 0.24 (hexane/ethyl acetate, 3:1). – ^{1}H NMR (270 MHz, $CDCl_3$): δ = 0.36 (s, 9H, $SiMe_3$), 0.71–0.79 (m, 3H, Me), 0.83–0.92 (m, 3H, Me), 1.10–1.20 (m, 6H, γ-, δ-, ε-CH_2), 1.28–1.38 (m, 4H, γ-, δ-, ε-CH_2), 1.38–1.51 (m, 2H, γ-, δ-, ε-CH_2 and 2H, β-CH_2), 1.51–1.69 (m, 2H, β-CH_2), 2.50–2.60 (t, *J* = 9 Hz, 2H, α-CH_2), 2.67–2.76 (t, *J* = 9 Hz, 2H, α-CH_2), 7.10 (s, 1h, aromatic H), 7.40 (s, 1H, aromatic H), 7.53–7.58 (m, 2H, aromatic H), 8.17 (d, *J* = 2 Hz, 1H, aromatic H), 8.19–8.25 (m, 1H, aromatic H). – ^{13}C NMR (67.9 MHz, $CDCl_3$): δ = 0.60 (3 C), 14.07 (2 C), 22.52, 22.63, 29.25, 29.75, 31.48, 31.59, 31.81, 32.61, 32.77, 36.01, 127.67, 129.76, 130.20, 133.50, 134.13, 135.70, 136.21, 136.67, 136.83, 141.71, 142.37, 146.01. – MS (EI, 70 eV, 300°C); *m/z* (%): 1260 (11), 1261 (24), 1262 (18), 1263 (10), 1264 (5) [M^+], 73 (100) [$SiMe_3^+$]. – $C_{81}H_{123}B_3O_3Si_3$: calcd. 1260.9059, found 1260.9065 (MS).

2-Bromo-2',5'-di-n-hexyl-4'-trimethylsilylbiphenyl (**6a**): The procedure was analogous to that described for **4a**: 7.72 g (22.4 mmol) of **1c**, 6.34 g (22.4 mmol) of **3** and 129 mg (0.11 mmol) tetrakis(triphenylphosphane)palladium(0) in a mixture of 150 ml toluene and 150 ml of a saturated aqueous solution of $Ba(OH)_2$. Reflux for 2 d. The unreacted bromoiodobenzene **3** was distilled off. Chromatographic separation on silica gel with hexane gave 7.13 g (67%) of **6a** as a colourless oil; R_f = 0.32 (hexane). – ^{1}H NMR (270 MHz, $CDCl_3$): δ = 0.39 (s, 9H, $SiMe_3$), 0.85 (t, *J* = 8 Hz, 3H, Me), 0.9 (t, *J* = 8 Hz, 3H, Me), 1.17–1.29 (m, 6H, γ-, δ-, ε-CH_2), 1.29–1.56 (m, 6H, γ-, δ-, ε-CH_2 and 2H, β-CH_2), 1.58–1.70 (m, 2H, β-CH_2), 2.31–2.59 (m, 2H, α-CH_2), 2.70–2.80 (m, 2H, α-CH_2), 6.99 (s, 1H, aromatic H), 7.17–7.39 (m, 3H, aromatic H), 7.41 (s, 1H, aromatic H), 7.69 (dd, J_1 = 8 Hz, J_2 = 1 Hz, 1H, aromatic H). – ^{13}C NMR (67.9 MHz, $CDCl_3$): δ = 0.64 (3 C), 14.08 (2 C), 22.48, 22.66, 29.13, 29.57, 30.78, 31.47, 31.85, 32.41, 32.85, 35.89, 123.95, 126.81, 128.46, 129.76, 131.22, 132.51, 135.19, 136.49, 137.29, 141.32, 142.67, 145.57. – MS (EI, 70 eV, 120°C); *m/z* (%): 472 (60), 473 (22), 474 (65), 475 (21), 476 (5) [M^+], 73 (100) [$SiMe_3^+$]. – $C_{27}H_{41}BrSi$ (473.61): calcd. C 68.47, H 8.73; found C 68.29, H 8.64.

2-Bromo-2',5'-di-n-hexyl-4'-iodobiphenyl (**6b**): The procedure was analogous to that described for **1b**: 2.52 g (5.32 mmol) of **6a** in 15 ml of CCl_4, 0.95 g (5.85 mmol) of ICl in 10 ml of CCl_4, 10 ml of a 1 M aqueous solution of sodium disulfite. Preparative reversed phase HPLC [Nucleosil 100 C_{18}, 5 μm, 250 × 16 mm flow: 20 ml/min, methanol/dichloromethane (7:3)] gave 2.38 g (85%) of **6b** as a colourless oil; R_f = 0.34 (hexane). – ^{1}H NMR (270 MHz, CD_2Cl_2): δ = 0.85 (t, *J* = 8 Hz, 3H, Me), 0.93 (t, *J* = 8 Hz, 3H, Me), 1.16–1.25 (m, 6H, γ-, δ-, ε-CH_2), 1.25–1.50 (m, 6H, γ-, δ-, ε-CH_2 and 2H, β-CH_2), 1.5–1.67 (m, 2H, β-CH_2), 2.20–2.50 (m, 2H, α-CH_2), 2.68–2.77 (m, 2H, α-CH_2), 6.95 (s, 1H, aromatic H), 7.21–7.28 (m, 2H, aromatic H), 7.33–7.40 (m, 1H, aromatic H), 7.65–7.69 (m, 1H, aromatic H), 7.76 (s, 1H, aromatic H). – ^{13}C NMR (67.9 MHz, $CDCl_3$): δ = 14.05, 14.10, 22.38, 22.60, 28.91 (2 C), 30.09, 30.38, 31.34, 31.61, 32.23, 40.20, 100.19, 123.71, 126.84, 128.71, 130.23, 130.93, 132.48, 139.44, 140.00, 140.65, 141.47, 142.15. – MS (EI, 70 eV, 120°C); *m/z* (%): 526 (59), 527 (21), 528 (60), 529 (18) [M^+]. – $C_{24}H_{32}BrI$ (527.33): calcd. C 54.66, H 6.11; found C 54.77, H 5.84.

2',5'-Di-n-hexyl-4'-trimethylsilylbiphenyl-2-boronic Acid (**6c**): The procedure was analogous to that described for **1c**: 8.00 g (16.9 mmol) of **6a** in a mixture of 150 ml diethyl ether and 150 ml THF, 37.0 ml (59.1 mmol) of a 1.6 M solution of *n*-butyllithium in hexane, 22.2 g (118 mmol) of triisopropyl borate. Chromatographic separation on silica gel with hexane/ethyl acetate (6:1) gave 5.43 g (76%) of **6c** as a colourless oil; R_f = 0.40 (hexane/ethyl acetate, 6:1). – ^{1}H NMR (270 MHz, $CDCl_3$): δ = 0.29–0.39 (3 s, 9H, $SiMe_3$), 0.68–0.95 (m, 6H, Me), 0.99–1.23 (m, 8H, CH_2), 1.23–1.50 (m, 6H, CH_2), 1.52–1.64 (m, 2H, $-CH_2$), 2.28–2.52 (m, 2H, α-CH_2), 2.58–2.72 (m, 2H, α-CH_2), 6.69–6.78 (m, 0.75H, aromatic H), 6.83–6.88 (2 s, 0.75H, aromatic H), 7.01–7.16 (m, 2.1H, aromatic H), 7.31–7.48 (m, 2.2H, aromatic H), 7.95–8.05 (m, 0.2H, aromatic H). – ^{13}C NMR (67.9 MHz, $CDCl_3$): δ = 0.56, 0.81, 13.87, 14.01, 19.15, 22.45, 22.61, 29.06, 29.62, 30.91, 31.44, 31.53, 31.74, 32.46, 32.73, 32.90, 33.58, 35.90, 36.02, 62.39, 125.80, 126.59, 126.71, 129.19, 129.34, 129.79, 129.93, 130.22, 130.66, 135.10, 135.34, 135.68, 136.17, 136.93, 137.16, 136.93, 137.16, 137.93, 138.19, 142.48, 142.70, 144.42, 145.20, 146.643, 146.57, 146.72, 147.07, 149.11. – MS (EI, 70 eV, 200°C); *m/z* (%): 1259 (8), 1260 (42), 1261 (78), 1262 (66), 1263 (35), 1264 (13), 1265 (3) [M^+], 421 (100) [1/3 M^+].

4-Bromo-2,5-di-n-hexyl-4'-trimethylsilylbiphenyl (**8a**): The procedure was analogous to that described for **4a**: 13.6 g (77.2 mmol) of **7**, 34.85 g (77.2 mmol) of **1b** and 446 mg (0.39 mmol) tetrakis(triphenylphosphane)palladium(0) in a mixture of 200 ml toluene and 150 ml of an aqueous 1 M solution of Na_2CO_3. Reflux for 2 d. Chromatographic separation on silica gel with hexane gave 33.4 g (91%) of **8a** as a colourless oil; R_f = 0.59 (hexane). – ^{1}H NMR (270 MHz, $CDCl_3$): δ = 0.33 (s, 9H, $SiMe_3$), 0.84 (m, 3H, Me), 0.91 (m, 3H, Me), 1.15–1.25 (m, 6H, γ-, δ-, ε-CH_2), 1.31–1.42 (m, 6H, γ-, δ-, ε-CH_2), 1.48 (m, 2H, β-CH_2), 1.63 (m, 2H, β-CH_2), 2.53 (t, *J* = 2H, α-CH_2), 2.72 (t, *J* = 8 Hz, 2H, α-CH_2), 7.07 (s, 1H, aromatic H), 7.29 (dd, J_1 = 8 Hz, J_2 = 2 Hz, 2H, aromatic H), 7.47 (s, 1H, aromatic H), 7.58 (dd, J_1 = 8 Hz, J_2 = 2 Hz, 2H, aromatic H). – ^{13}C NMR (67.9 MHz, $CDCl_3$): δ = −1.06 (3 C), 14.08 (2 C), 22.44, 22.61, 28.98, 29.15, 29.99, 31.16, 31.43, 31.67, 32.32, 35.75, 123.26, 128.45 (2 C), 131.65 (2 C), 133.06 (2 C), 138.81, 139.09, 139.76, 140.99, 141.49. – MS (EI, 70 eV, 100°C); *m/z* (%): 472 (94), 473 (38), 474 (100), 475 (24), 476 (10) [M^+]. – $C_{27}H_{41}BrSi$ (473.61): calcd. C 68.47, H 8.73; found C 68.38, H 8.59.

4-Bromo-2,5-di-n-hexyl-4'-iodobiphenyl (**8b**): See ref.[4].

2,5-Di-n-hexyl-4'-trimethylsilylbiphenyl-4-boronic Acid (**8c**): See ref.[4].

3-Bromo-4'-trimethylsilylbiphenyl (**9a**): The procedure was analogous to that described for **4a**: 4.54 g (25.8 mmol) of **7**, 7.00 g (25.8 mmol) of **2** and 298 mg (0.26 mmol) tetrakis(triphenylphosphane)-palladium(0) in a mixture of 150 ml toluene and 150 ml of an aqueous 1 M solution of Na_2CO_3. Reflux for 3 d. Chromatographic separation on silica gel with hexane gave 7.55 g (96%) of **9a** as a colourless oil; R_f = 0.27 (hexane). – ^{1}H NMR (270 MHz, $CDCl_3$): δ = 0.42 (s, 9H, $SiMe_3$), 7.28–7.36 (m, 1H, aromatic H), 7.44–7.68 (m, 6H, aromatic H), 7.78–7.82 (m, 1H, aromatic H). – ^{13}C NMR (67.9 MHz, $CDCl_3$): δ = −1.13 (3 C), 122.87, 125.72, 126.38 (2 C), 130.22 (3 C), 133.90 (2 C), 139.98, 140.06, 143.26. – MS (EI, 70 eV, 50°C); *m/z* (%): 304 (27), 305 (6), 306 (28), 307 (6)

[M^+], 289 (98), 290 (21), 291 (100), 292 (20), 293 (5) [$M - CH_3$]. – $C_{15}H_{17}BrSi$ (305.29): calcd. C 59.01, H 5.61; found C 58.86, H 5.43.

3-Bromo-4'-iodobiphenyl (**9b**): The procedure was analogous to that described for **1b**: 6.58 g (21.6 mmol) of **9a** in 100 ml of CCl_4, 3.67 g (22.6 mmol) of ICl in 30 ml of CCl_4, 30 ml of a 1 M aqueous solution of sodium disulfite. Chromatographic separation on silica gel with hexane gave 7.16 g (93%) of **9b** as a colourless oil; R_f = 0.32 (hexane). – ^{1}H NMR (270 MHz, $CDCl_3$): δ = 7.26–7.38 (m, 3H, aromatic H), 7.44–7.56 (m, 2H, aromatic H), 7.76 (s, 1H, aromatic H), 7.78–7.88 (m, 2H, aromatic H). – ^{13}C NMR (67.9 MHz, $CDCl_3$): δ = 93.79, 123.03, 125.48, 128.87 (2 C), 129.91, 130.39, 130.61, 137.98 (2 C), 139.18, 142.15. – MS (EI, 70 eV, 60°C); *m/z* (%): 358 (100), 359 (14), 360 (97), 361 (13) [M^+]. – $C_{12}H_8BrI$ (359.00): calcd. C 40.15, H 2.25; found C 40.21, H 2.34.

3-Bromo-3'-trimethylsilylbiphenyl (**11a**): The procedure was analogous to that described for **4a**: 3.83 g (21.8 mmol) of **10**, 6.1 g (21.74 mmol) of **2** and 125 mg (0.11 mmol) tetrakis(triphenylphophane)palladium(0) in a mixture of 100 ml toluene and 100 ml of an aqueous 1 M solution of Na_2CO_3. Reflux for 3 d. Chromatographic separation on silica gel with hexane gave 6.30 g (95%) of **11a** as a colourless oil; R_f = 0.28 (hexane). – ^{1}H NMR (270 MHz, $CDCl_3$): δ = 7.18–7.25 (m, 1H, aromatic H), 7.28–7.47 (m, 5H, aromatic H), 7.56–7.61 (m, 1H, aromatic H), 7.63–7.67 (m, 1H, aromatic H). – ^{13}C NMR (67.9 MHz, $CDCl_3$): δ = –1.09 (3 C), 122.87, 125.87, 127.66, 128.22, 130.07, 130.28, 130.27, 131.94, 132.84, 139.05, 141.28, 143.78. – MS (EI, 70 eV, 40°C); *m/z* (%): 304 (29), 305 (6), 306 (30), 307 (6), 308 (2) [M^+], 289 (99), 290 (21), 291 (100), 292 (20), 293 (5) [$M^+ - CH_3$]. – $C_{15}H_{17}BrSi$ (305.29): calcd. C 59.01, H 5.61; found C 58.79, H 5.54.

3-Bromo-3'-iodobiphenyl (**11b**): The procedure was analogous to that described for **1b**: 5.54 g (18.2 mmol) of **11a** in 100 ml of CCl_4, 3.24 g (19.9 mmol) of ICl in 30 ml of CCl_4, 30 ml of a 1 M aqueous solution of sodium disulfite. Chromatographic separation on silica gel with hexane gave 6.38 g (98%) of **11b** as a colourless oil which slowly solidified; m.p. 56°C; R_f = 0.30 (hexane). – ^{1}H NMR (270 MHz, CD_2Cl_2): δ = 7.16–7.24 (m, 1H, aromatic H), 7.29–7.37 (m, 1H, aromatic H), 7.47–7.57 (m, 3H, aromatic H), 7.68–7.74 (m, 2H, aromatic H), 7.91–7.95 (m, 1H, aromatic H). – ^{13}C NMR (67.9 MHz, $CDCl_3$): δ = 94.83, 122.90, 125.61, 126.26, 130.02, 130.29, 130.43, 130.69, 135.96, 136.69, 141.53, 141.72. – MS (EI, 70 eV, 60°C); *m/z* (%): 358 (71), 359 (10), 360 (70), 361 (9) [M^+], 150 (13), 151 (19), 152 (100), 153 (14) [$C_{12}H_8^+$]. – $C_{12}H_8BrI$ (359.00): calcd. C 40.15, H 2.25; found C 40.15, H 2.22.

2-Bromo-3'-trimethylsilylbiphenyl (**12a**): The procedure was analogous to that described for **4a**: 7.00 g (39.8 mmol) of **10**, 11.25 g (39.8 mmol) of **3**, 229 mg (0.2 mmol) tetrakis(triphenylphosphane)-palladium(0) in a mixture of 150 ml toluene and 100 ml of a saturated aqueous solution of $Ba(OH)_2$; reflux 40 h. Chromatographic separation on silica gel with hexane gave 11.2 g (92%) of **12a** as a colourless oil; R_f = 0.27 (hexane). – ^{1}H NMR (270 MHz, $CDCl_3$): δ = 7.28–7.36 (m, 1H, aromatic H), 7.44–7.56 (m, 2H, aromatic H), 7.57–7.63 (m, 2H, aromatic H), 7.70–7.77 (m, 1H, aromatic H), 7.79–7.87 (m, 2H, aromatic H). – ^{13}C NMR (67.9 MHz, $CDCl_3$): δ = –1.09 (3 C), 122.70, 127.29, 127.35, 128.60, 129.72, 131.31, 132.49, 133.14, 134.36, 140.12, 140.26, 142.79. – MS (EI, 70 eV, 40°C); *m/z* (%): 304 (38), 305 (11), 306 (38), 307 (10) [M^+], 289 (99), 290 (28), 291 (100), 292 (26) [$M^+ - CH_3$]. – $C_{15}H_{17}BrSi$ (305.29): calcd. C 59.01, H 5.61; found C 58.81, H 5.58.

3-Bromo-5-chloro-2',5'-di-n-hexyl-4'-trimethylsilylbiphenyl (**13a**): The procedure was analogous to that described for **4a**: 4.12 g (12.0 mmol) of **1c**, 3.80 g (12.0 mmol) of **12** and 276 mg (0.24 mmol) tetrakis(triphenylphosphane)palladium(0) in a mixture of 75 ml toluene and 75 ml of a saturated aqueous solution of $Ba(OH)_2$. Reflux for 2 d. The unreacted bromoiodobenzene **12** was distilled off. Preparative reversed phase HPLC [Nucleosil 100 C_{18}, 5 μm, 250 × 16 mm flow: 25 ml/min, methanol/dichloroemthane (7:3)] gave 4.03 g (66%) of **6b** as a colourless oil; R_f = 0.50 (hexane). – ^{1}H NMR (270 MHz, $CDCl_3$): δ = 0.40 (s, 9H, $SiMe_3$), 0.90 (t, *J* = 8 Hz, 3H, Me), 0.97 (t, *J* = 8 Hz, 3H, Me), 1.17–1.31 (m, 6H, γ-, δ-, ε-CH_2), 1.31–1.41 (m, 4H, γ-, δ-, ε-CH_2), 1.41–1.58 (m, 2H, γ-, δ-, ε-CH_2 and 2H, β-CH_2), 1.58–1.73 (m, 2H, β-CH_2), 2.58 (t, *J* = 8 Hz, 2H, α-CH_2), 2.74 (t, *J* = 8 Hz, 2H, α-CH_2), 7.03 (s, 1H, aromatic H), 7.26–7.30 (m, 1H, aromatic H), 7.37–7.41 (m, 2H, aromatic H), 7.49–7.55 (m, 1H, aromatic H). – ^{13}C NMR (67.9 MHz, $CDCl_3$): δ = 0.51 (3 C), 14.08 (2 C), 22.54, 22.64, 29.09, 29.70, 31.47 (2 C), 31.80, 32.49, 32.63, 35.93, 122.25, 128.14, 129.53, 129.63, 130.55, 134.60, 135.86, 136.27, 138.02, 139.60, 145.36, 146.22. – MS (EI, 70 eV, 150°C); *m/z* (%): 506 (5.5), 507 (2.4), 508 (7.1), 509 (2.8), 510 (2.4) [M^+], 73 (100) [$SiMe_3^+$]. – $C_{27}H_{40}BrClSi$ (508.06): calcd. C 63.83, H 7.94; found C 63.71, H 7.96.

3-Bromo-5-chloro-2',5'-di-n-hexyl-4'-iodobiphenyl (**13b**): The procedure was analogous to that described for **1b**: 2.16 g (4.25 mmol) of **13a** in 25 ml of CCl_4, 0.76 g (4.68 mmol) of ICl in 15 ml of CCl_4, 15 ml of a 1 M aqueous solution of sodium disulfite. Chromatographic separation on silica gel with hexane gave 2.31 g (97%) of **13b** as a colourless oil; R_f = 0.55 (hexane). – ^{1}H NMR (270 MHz, $CDCl_3$): δ = 0.85 (t, *J* = 8 Hz, 3H, Me), 0.9 (t, *J* = 8 Hz, 3H, Me), 1.09–1.26 (m, 6H, γ-, δ-, ε-CH_2), 1.26–1.49 (m, 6H, γ-, δ-, ε-CH_2 and 2H, β-CH_2), 1.49–1.64 (m, 2H, β-CH_2), 2.44 (t, *J* = 8 Hz, 2H, α-CH_2), 2.67 (t, *J* = 8 Hz, 2H, α-CH_2), 6.94 (s, 1H, aromatic H), 7.18 (dd, J_1 = 2 Hz, J_2 = 2 Hz, 1H, aromatic H), 7.30 (dd, J_1 = 2 Hz, J_2 = 2 Hz, 1H, aromatic H), 7.49 (dd, J_1 = 2 Hz, J_2 = 2 Hz, 1H, aromatic H), 7.70 (s, 1H, aromatic H). – ^{13}C NMR (67.9 MHz, $CDCl_3$): δ = 14.02, 14.07, 22.45, 22.60, 28.92, 29.07, 30.31, 31.14, 31.37, 31.61, 31.96, 40.28, 100.53, 122.38, 127.99, 129.86, 130.03, 130.38, 134.74, 139.04, 139.59, 140.07, 142.93, 144.27. – MS (EI, 70 eV, 120°C); *m/z* (%): 560 (77), 561 (28), 562 (100), 563 (31), 564 (29), 565 (9) [M^+]. – $C_{24}H_{31}BrClI$ (561.77): calcd. C 51.31, H 5.56; found C 51.36, H 5.50.

5-Chloro-2',5'-di-n-hexyl-4'-trimethylsilylbiphenyl-3-boronic Acid (**13c**): The procedure was analogous to that described for **1c**: 5.50 g (10.8 mmol) of **13a** in 100 ml diethyl ether, 7.27 ml (10.8 mmol) of a 1.5 M solution of *n*-butyllithium in hexane, 3.06 g (16.3 mmol) of triisopropyl borate. Chromatographic separation on silica gel with hexane/ethyl acetate (3:1) gave 3.68 g (75%) of **13c** as a colourless/slightly yellow oil; R_f = 0.25 (hexane/ethyl acetate, 3:1). – ^{1}H NMR (270 MHz, $CDCl_3$): δ = 0.38 (s, 9H, $SiMe_3$), 0.77 (t, *J* = 7 Hz, 3H, Me), 0.89 (t, *J* = 9 Hz, 3H, Me), 1.09–1.27 (m, 6H, γ-, δ-, ε-CH_2), 1.27–1.38 (m, 4H, γ-, δ-, ε-CH_2), 1.38–1.53 (m, 2H, γ-, δ-, ε-CH_2 and 2H, β-CH_2), 1.53–1.69 (m, 2H, β-CH_2), 2.56 (t, *J* = 8 Hz, 2H, α-CH_2), 2.72 (t, *J* = 8 Hz, 2H, α-CH_2), 7.06 (s, 1H, aromatic H), 7.39 (s, 1H, aromatic H), 7.53 (dd, J_1 = 2 Hz, J_2 = 2 Hz, 1H, aromatic H), 8.05 (dd, J_1 = 1 Hz, J_2 = 1 Hz, 1H, aromatic H), 8.14 (dd, J_1 = 2 Hz, J_2 = 1 Hz, 1H, aromatic H). – ^{13}C NMR (67.9 MHz, $CDCl_3$): δ = 0.62 (3 C), 14.08, 14.12, 22.59, 22.70, 29.26, 29.81, 31.49, 31.65, 31.86, 32.67, 32.75, 36.05, 129.95, 131.34, 133.73, 134.22, 134.22, 134.45, 135.91, 136.56, 137.70, 140.80, 143.93, 146.25. – MS (EI, 70 eV, 300°C); *m/z* (%): 1362 (0.5), 1363 (0.7), 1364 (0.8), 1365 (0.9), 1366 (0.7), 1367 (0.5) [M^+], 73 (100) [$SiMe_3^+$].

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