A Versatile Palladium-Catalyzed Synthesis of *n*-Alkyl-Substituted Oligo-*p*-phenyls

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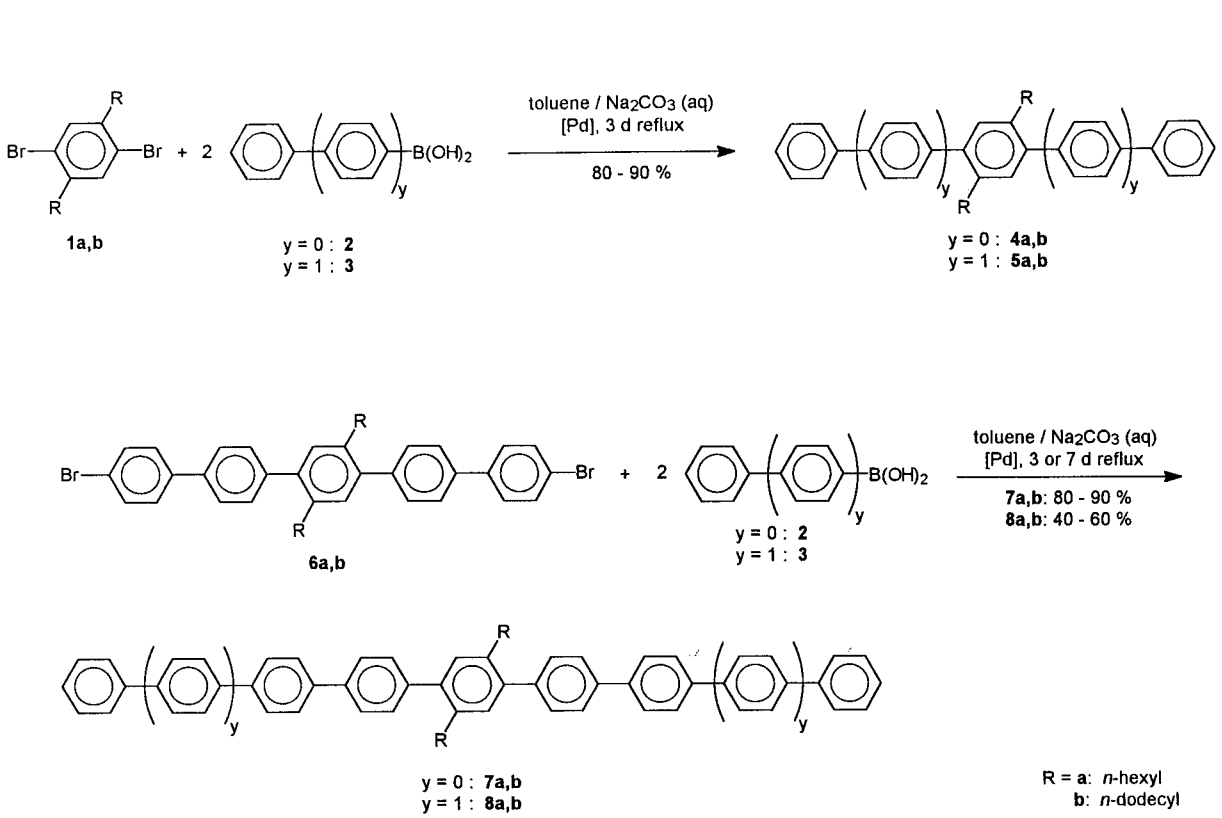
High-yield Pd-catalyzed syntheses of constitutionally homogeneous, *n*-alkyl-substituted oligo-*p*-phenyls having three to fifteen benzene rings connected to each other exclusively in the 1,4-(*para*-) fashion are reported. Most of the oligomers described readily dissolve in common organic solvents. Furthermore, their thermal phase-transition temperatures show that some of these rodlike oligomers can exist in different crystalline modifications and/or form liquid-crystalline mesophases.

Constitutionally homogeneous oligo-*p*-phenyls are materials of considerable current interest for chemists, physicists, and material scientists because, on the one hand, the elaboration of efficient synthetic routes for their preparation is still a challenge.[1] On the other hand, oligo-*p*-phenyls are excellent model compounds for developing a profound understanding of the spectroscopic and redox properties of polyaromatic systems,[2] and of the thermal phase behavior and solution properties of rodlike liquid-crystalline molecules.[3] Furthermore, functionalized oligo-*p*-phenyls have gained some importance as main-chain-stiffening building-blocks in semiflexible polymers like aromatic polyesters[4] and polyimides.[5] Despite considerable advantages, however, parent oligo-*p*-phenyls have a serious drawback with regard to the above applications: their solubility decreases dramatically with the number of benzene rings. For example, although *p*-terphenyl will dissolve in toluene to the extent of 8.5 g · L^{-1}, *p*-sexiphenyl has a solubility less than 10 mg · L^{-1}.[6] From the work of Kern, Heitz and others,[6,7] it is known, fortunately, that the attachment of lateral methyl groups to the oligo-*p*-phenyls increases their solubility. Nevertheless, the solubilizing effect of methyl groups is insufficient in the case of longer oligo-*p*-phenyls, and the concept of solubilizing, flexible side chains was worked out to further increase solubility of rigid-rod molecules such as aromatic polyesters[8] and poly(*p*-phenylene)s (PPPs).[9] By taking advantage of this latter concept, and by simultaneously using the efficient Pd-catalyzed condensation reaction (Suzuki coupling)[10] as the oligomer formation reaction, we developed two straightforward and – with regard to the length and the substitution pattern of the oligomers – general methods of access to constitutionally homogeneous oligo-*p*-phenyls bearing two (route A; Scheme 1) or even more (route B; Scheme 2) hexyl or dodecyl substituents as solubilizing side chains. Except for the starting materials **1, 2, 3, 6,** and **11**, all compounds reported are new.

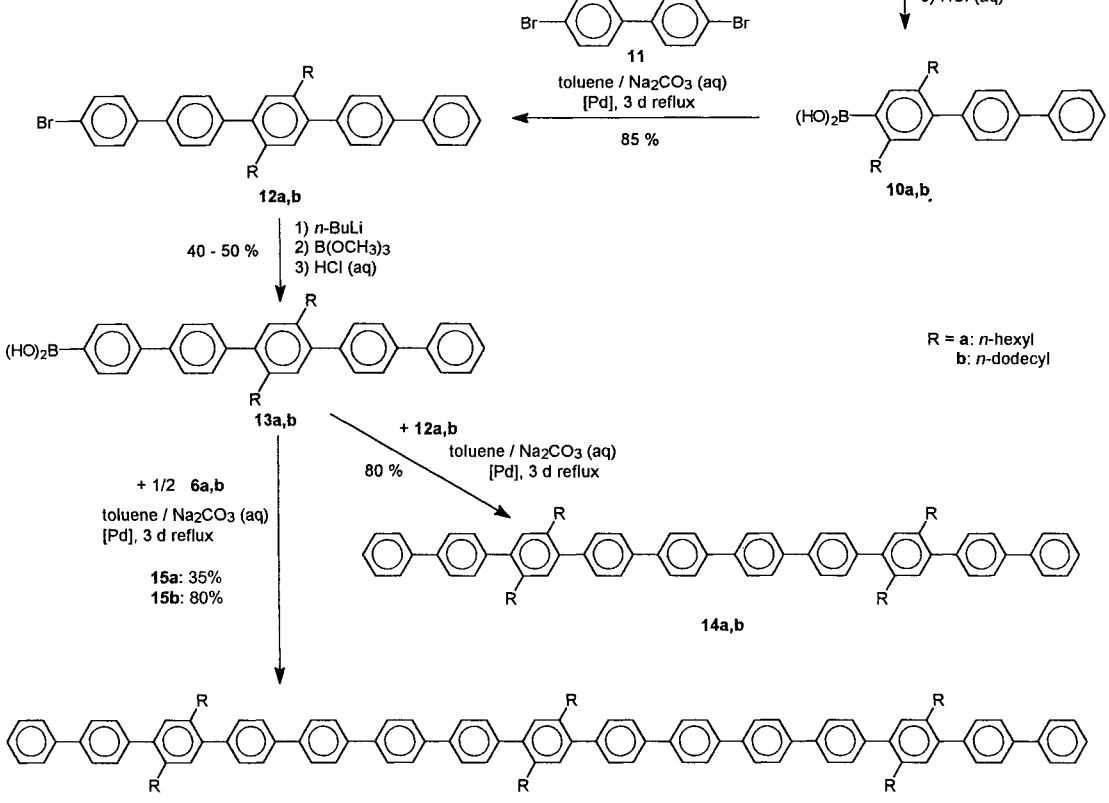
2,5-Dialkyl-1,4-dibromobenzene derivatives **1a, b** are the central starting materials for both routes. They are easily available from *p*-dichlorobenzene in a two-step synthesis (> 80% yield).[11] Following Scheme 1, the 2′,5′-dialkyl-*p*-terphenyls **4a, b** and the 2″,5″-dialkyl-*p*-quinquephen-



Scheme 1

yls **5a, b** having (a) hexyl- or (b) dodecyl side chains are directly available in excellent yields via condensation of one equivalent of 2,5-dialkyl-1,4-dibromobenzenes **1a, b** and two equivalents of either benzeneboronic acid **2** or biphenylboronic acid **3**[12] in the heterogeneous system of toluene/Na_2CO_3 (aq) in the presence of catalytic amounts of $(Ph_3P)_4Pd$. According to NMR spectra of representative product mixtures, almost quantitative conversions were achieved throughout (≥95%), and pure *p*-terphenyls **4a, b** or *p*-quinquephenyls **5a, b** were obtained after purification by recrystallization (80 to 90% yield). For the preparation of the *p*-septiphenyl and *p*-noviphenyl derivatives **7a, b** and **8a, b**, two equivalents of benzeneboronic acid **2** or biphenylboronic acid **3** respectively were reacted with one equivalent of 2″,5″-dialkyl-4,4‴″-dibromo-*p*-quinquephenyls **6a, b**, the latter being prepared from **1a, b** in a two-step synthesis.[13] In the case of *p*-septiphenyls **7a, b**, the coupling reactions occurred without any detectable side reaction (NMR) and gave pure oligomers in excellent yields (60–80%). In contrast, 4-bromo-*p*-septiphenyl intermediates were found as main products when the preparation of *p*-noviphenyl derivatives **8a, b** was tried according to the conventional procedure of the Pd-catalyzed condensation, particularly in the case of the hexyl-substituted *p*-noviphenyl **8a**. This interruption in the condensation reaction after the first coupling step between **6a, b** and **3** was shown to be due to the already very low solubility of the 4-bromo-*p*-septiphenyl intermediates which precipitate from the reaction mixture. Consequently, the second condensation step was dramatically slowed down. Only by prolonging the reaction time from three to seven days could an almost complete second condensation step be achieved. Nevertheless, because also the subsequent workup procedure was aggravated by the low solubility of the products, pure *p*-noviphenyls **8a** and **8b** were finally obtained in yields of only 40% and 60%, respectively.

As is obvious from the above observations, the synthesis of *p*-noviphenyls **8a, b** represents the limit of applicability of route A because only two alkyl side chains are clearly insufficient to solubilize oligo-*p*-phenyls having more than nine benzene rings connected to each other in the *all-para* fashion. Therefore, the supplementary route B was developed (Scheme 2) which allows the introduction of more alkyl side chains into an oligomer. This route is additionally distinguished by the use of the already quite long *p*-quinquephenyls **6**, **12** and **13** as starting materials which simplify formation and purification of higher oligo-*p*-phenyls like **14a, b** and **15a, b**.



Scheme 2

Table. Oligo-*p*-phenyls and Starting Materials Prepared

Product[a]	Yield[b] (%)	Thermal Transitions[c]	^{1}H NMR ($CDCl_3$/TMS) δ, J (Hz)	^{13}C NMR ($CDCl_3$/TMS) δ
3	60	–[d]	($CDCl_3$/DMSO-d_6, 1 : 1): 7.34 (t, 1 H, H4′, J = 1.7), 7.44 (t, 2 H, H3′, 5′, J = 5.5), 7.58 (d, 2 H, H2′,6′, J = 8.2), 7.63 (d, 2 H, H2,6, J = 7.3), 7.85 [s, 2 H, $B(OH)_2$], 7.91 (d, 2 H, H3,5, J = 8.0)	($CDCl_3$/DMSO-d_6, 1 : 1): 123.95 (d, C3,5), 125.01 (d, C2,6), 125.64 (d, C4′), 127.05 (d, C2′, 6′), 131.34 (s, C4), 133.10 (d, C3′,5′), 138.79, 140.13 (2 s, C1,1′)
4a	82	36 (k → i)	0.81 (t, 6 H, CH_3, J = 6.9), 1.17 (m, 12 H, CH_2), 1.45 (m, 4 H, β-CH_2), 2.57 (t, 4 H, α-CH_2, J = 8.0), 7.13 (s, 2 H, H3′,6′), 7.35–7.43 (m, 10 H, H2-6,2″-6″)	14.01 (q, CH_3), 22.49, 29.20, 31.37, 31.51, 32.64 (5t, CH_2), 126.65 (d, C4,4″), 127.98, 129.34 (2d, C2,3,5,6,2″,3″,5″,6″), 130.87 (d, C3′,6′), 130.87 (d, C3′,6′), 137.44 (s, C2′,5′), 140.79, 142.04 (2s, C1, 1′, 1″, 4)
4b	93	65 (k → i)	0.87 (t, 6 H, CH_3, J = 7.2), 1.16, 1.24 (2 m, 36 H, CH_2), 1.47 (m, 4 H, β-CH_2), 2.56 (t, 4 H, α-CH_2, J = 8.0), 7.12 (s, 2 H, H3′,6′), 7.33–7.43 (m, 10 H, H2-6,2″-6″)	14.10 (q, CH_3), 22.69, 29.30, 29.34, 29.50, 29.64, 31.38, 31.93, 32.63 (8t, CH_2), 126.65 (d, C4,4″), 127.97, 129.34 (2d, C2,3,5,6,2″,3″,5″,6″), 130.87 (d, C3′,6′), 137.44 (s, C2′,5′), 140.77, 142.04 (2s, C1,1′,1″4′)
5a	80	115 (k_1 → i)[e] 103 (k_2 → i)[e]	0.81 (t, 6 H, CH_3, J = 7.1), 1.19, 1.21 [2m, 12 H, $CH_2CH_2(CH_2)_3CH_3$], 1.53 (m, 4 H, β-CH_2), 2.64 (t, 4 H, α-CH_2, J = 7.8), 7.20 (s, 2 H, H3″,6″), 7.32 (dd, 2 H, H4,4‴, J = 1.7), 7.43 (m, 8 H, H3,5,3′,5′, 2‴,6‴,3‴″,5‴″), 7.64 (m, 8 H, H2,6,2′,6′,3‴, 5‴,2‴″,6‴″)	14.04 (q, CH_3), 22.49, 29.22, 31.45, 31.52, 32.69 (5t, CH_2), 126.72, 127.05 (2d, C2,3,5,6,2‴″,3‴″,5‴″,6‴″), 127.23 (d, C4,4‴″), 128.78, 129.76 (2d, C2′,3′,5′,6′,2‴, 3‴,5‴,6‴), 130.96 (d, C3″,6″), 137.60 (s, C2″,5″), 139.52, 140.44, 140.90, 141.01 (4s, C1,1′,1″,1‴,1‴″, 4′,4″,4‴″)
5b	93	66 (k_1 → i)[f] 60 (k_2 → i)[f] (17, 56)	0.81 (t, 6 H, CH_3, J = 7.1), 1.19, 1.22 [2 m, 36 H, $CH_2CH_2(CH_2)_9CH_3$], 1.53 (m, 4 H, β-CH_2), 2.64 (t, 4 H, α-CH_2, J = 7.9), 7.20 (s, 2 H, H3″,6″), 7.34 (dd, 2 H, H4,4‴, J = 1.6), 7.46 (m, 8 H, H3,5,3′,2‴, 6‴,3‴″,5‴″), 7.67 (m, 8 H, H2,6,2′,6′,3‴,5‴, 2‴″,6‴″)	14.11 (q, CH_3), 22.67, 29.33, 29.52, 29.64, 31.49, 31.91, 32.65 (7t, CH_2), 126.71, 127.06 (2d, C2,3,5,6,2‴″,3‴″, 5‴″,6‴″), 127.23 (d, C4,4‴″), 128.78, 129.75 (2d, C2′,3′,5′,6′,2‴, 3‴,5‴,6‴), 130.95 (d, C3″,6″), 137.60 (s, C2″,5″), 139.49, 140.40, 140.88, 140.97 (4s, C1,1′,1″,1‴,1‴″,4′,4″,4‴″)
7a	60	212 (k/n → i) (93, 124, 168, 180)	0.82 (t, 6 H, CH_3, J = 7.2), 1.19, 1.21 [2 m, 12 H, $CH_2CH_2(CH_2)_3CH_3$], 1.53 (m, 4 H, β-CH_2), 2.65 (t, 4 H, α-CH_2, J = 8.0), 7.22 (s, 2 H, H3‴,6‴), 7.37 (dd, 2 H, H4,4′^{6}, J = 1.7), 7.48 (m, 8 H, H3″,5″,2‴″, 6‴″), 7.66–7.77 (m, 16 H, other aromatic H)	14.07 (q, CH_3), 22.51, 29.25, 31.49, 31.53, 32,69 (5t, CH_2), 126.62, 127.05, 127.42, 127.54, 128.83, 129.82 (6d, other aromatic *C*H), 127.60 (d, C4,4′^{6}), 130.98 (d, C3‴,6‴), 137.77 (s, C2‴,5‴), 138.98, 139.79, 140.09, 140.41, 140.70, 141.07 (6s, other aromatic *C*C)
7b	80	167 (k → i) (111, 157)	0.85 (t, 6 H, CH_3, J = 6.9), 1.19 [m, 36 H, $CH_2CH_2(CH_2)_9CH_3$], 1.54 (m, 4 H, β-CH_2), 2.65 (t, 4 H, α-CH_2, J = 7.9), 7.21 (s, 2 H, H3‴,6‴), 7.35 (dd, 2 H, H4,4′^{6}, J = 1.6), 7.47 (m, 8 H, H3″,5″,2‴″, 6‴″), 7.66–7.77 (m, 16 H, other aromatic H)	14.11 (q, CH_3), 22.69, 29.36, 29.52, 29.66, 31.51, 31.92, 32.67 (7t, CH_2), 126.61, 127.04, 127.40, 127.53, 128.82, 129.83 (6d, other aromatic *C*H), 130.98 (d, C3‴,6‴), 137.64 (s, C2‴,5‴), 138.97, 139.78, 140.10, 140.41, 140.71, 141.08 (6s, other aromatic *C*C)
8a	40	301 (k → n)[g] (130, 247, 285)	($C_2D_2Cl_4$): 0.83 (t, 6 H, CH_3, J = 7.1), 1.23 [m, 12 H, $CH_2CH_2(CH_2)_3CH_3$], 1.54 (m, 4 H, β-CH_2), 2.65 (t, 4 H, α-CH_2, J = 7.9), 7.17 (s, 2 H, H3‴″,6‴″), 7.34 (dd, 2 H, H4,4′^{8}, J = 1.7), 7.48 (m, 8 H, H3‴,5‴,2′^{5},6′^{5}), 7.63–7.76 (m, 24 H, other aromatic H)	($C_2D_2Cl_4$): 14.13 (q, CH_3), 22.66, 29.36, 31.51, 31.76, 33.05 (5t, CH_2), 126.70, 127.22, 127.52, 127.59, 127.70, 129.05, 130.12 (7d, other aromatic *C*H), 131.15 (d, C3‴″,6‴″), 137.77 (s, C2‴″,5‴″), 138.97, 139.25, 139.76, 140.13, 140.42, 140.65, 140.89, 141.54, 141.70 (9s, other aromatic *C*C)
8b	60	243 (k → n) [335 (n → i, dec)] (143, 175, 208)	($C_2D_2Cl_4$): 0.86 (t, 6 H, CH_3, J = 7.0), 1.21 [m, 36 H, $CH_2CH_2(CH_2)_9CH_3$], 1.54 (m, 4 H, β-CH_2), 2.64 (t, 4 H, α-CH_2, J = 7.8), 7.18 (s, 2 H, H3‴″,6‴″), 7.33 (dd, 2 H, H4,4′^{8}, J = 1.7), 7.47 (m, 8 H, H 3‴,5‴,2′^{5},6′^{5}), 7.63–7.78 (m, 24 H, other aromatic H)	($C_2D_2Cl_4$): 14.18 (q CH_3), 21.80, 22.80, 29.46, 29.53, 29.70, 29.81, 29.83, 31.53, 31.53, 32.08, 33.03 (10 t, CH_2), 126.68, 127.22, 127.52, 127.58, 127.71, 129.05 130.13 (7 d, other aromatic *C*H), 131.16 (d, C3‴″,6‴″), 137.77 (s, C2‴″,5‴″), 138.96, 139.74, 139.81, 140.11, 140.43, 140.66, 140.91, 141.69 (8 s, other aromatic *C*C)
9a	96	28 (k → i)	0.80, 0.88 (2 m, 6 H, CH_3), 1.17, 1.30 [2 m, 12 H, $CH_2CH_2(CH_2)_3CH_3$], 1.38, 1.45, 1.63 (3 m, 4 H, β-CH_2), 2.52, 2.70 (2 t, 4 H, α-CH_2, J = 7.6), 7.08 (s, 1 H, H6), 7.34 (m, 3 H, H2′,6′,4″), 7.45 (m, 3 H, H3,3″,5″), 7.64 (m, 4 H, H3′,5′,2″,6″)	14.05, 14.10 (2 q, CH_3), 22.47, 22.63, 29.03, 29.17, 30.03, 31.17, 31.45, 31.67, 32.42, 35.78 (10 t, CH_2), 123.38 (s, C4), 126.71, 126.94 (2d, C2″,3″,5″,6″), 127.26 (d, C4″), 128.74, 129.51 (2d, C2′,3′,5′,6′), 131.60 (d, C6), 133.10 (d, C3), 139.14 (s, C2), 139.71 (s, C1″), 139.76 (s, C5), 140.04 (s, C1), 140.57, 140.63 (2s, C1′,4′)
9b	99	42 (k → i)	0.84 (m, 6 H, CH_3), 1.17–1.25 [m, 36 H, $CH_2CH_2(CH_2)_9CH_3$], 1.48, 1.62 (2 m, 4 H, β-CH_2), 2.54, 2.80 (2 t, 4 H, α-CH_2, J = 7.2), 7.08 (s, 1 H, H6), 7.33 (m, 3 H, H2′,6′,4″), 7.45 (m, 3 H, H3,3″,5″),7.64 (m, 4 H, H3′,5′, 2″,6″)	14.13 (q, CH_3), 22.70, 29.27, 29.36, 29.48, 29.67, 30.05 31.24, 31.93, 33.41, 35.75 (10 t, CH_2), 123.34, (s, C 4), 126.76, 127.03 (2 d, C2″,3″,5″,6″), 127.32 (d, C4″), 128.79, 129.54 (2d, C2′,3′,5′,6′), 131.64 (d, C6), 133.09 (d, C3), 139.18 (s, C2), 139.76 (s, C1″), 139.84 (s, C5), 140.09 (s, C1), 140.58, 140.72 (2s, C1′, 4′)

Table. (continued)

Product[a]	Yield[b] (%)	Thermal Transitions[c]	^{1}H NMR ($CDCl_3$/TMS) δ, J (Hz)	^{13}C NMR ($CDCl_3$/TMS) δ
10a	60	–[d]	($CDCl_3$/DMSO-d_6): 0.79, 0.87 (2 m, 6 H, CH_3), 1.16, 1.29 [2 m, 12 H, $CH_2CH_2(CH_2)_3CH_3$], 1.43, 1.55 (2 m, 4 H, β-CH_2), 2.55, 2.77 (2 t, 4 H, α-CH_2, J = 7.7), 5.05 [s, 2 H, $B(OH)_2$], 6.96 (s, 1 H, H6), 7.35 (m, 3 H, H2′,6′,4″), 7.44 (m, 3 H, H3,3″,5″), 7.65 (m, 4 H, H3′,5′,2″,6″)	($CDCl_3$/DMSO-d_6): 12.15, 12.23 (2 q, CH_3), 20.29, 20.48, 26.96, 27.24, 29.24, 29.25, 29.56, 30.39, 30.60, 33.47 (10 t, CH_2), 124.52, 124.82 (2 d, C2″,3″,5″,6″), 125.46 (d, C4″), 127.02, 127.61 (2 d, C2′,3′,5′,6′), 128.04 (d, C6), 132.82 (d, C3), 133.00 (s, C4), 133.81 (s, C5), 136.89 (s, C2), 138.34 (s, C1), 139.23, 139.31 (2s, C1′,4′), 142.15 (s, C1″)
10b	40	–[d]	($CDCl_3$/DMSO-d_6): 0.86 (m, 6 H, CH_3), 1.15–1.28 [m, 36 H, $CH_2CH_2(CH_2)_9CH_3$], 1.45, 1.56 (2 m, 4 H, β-CH_2), 2.54, 2.76 (2 t, 4 H, α-CH_2, J = 7.8), 6.96 (s, 1 H, H 6), 7.35 (m, 3 H, H2′,6′,4″), 7.40 (s, 1 H, H3), 7.46 (m, 2 H, H3″,5″), 7.65 (m, 4 H, H3′,5′,2″,6″), 7.79 [s, 2 H, $B(OH)_2$]	($CDCl_3$/DMSO-d_6): 12.30 (q, CH_3), 20.60, 27.13, 27.25, 27.41, 27.56, 28.64, 29.82, 30.49, 30.73, 33.61 (10 t, CH_2), 124.60, 124.91 (2 d, C2″, 3″,5″,6″), 125.52 (d, C4″), 127.07, 127.71 (2 d, C2′,3′,5′,6′), 128.11 (d, C6), 132.81 (d, C3), 133.20 (s, C4), 133.97 (s, C5), 137.01 (s, C2), 138.47 (s, C1), 139.24, 139.36 (2 s, C1′,4′), 142.11 (s, C1″)
12a	85	178 (k → i)	0.81 (m, 6 H, CH_3), 1.19 [m, 12 H, $CH_2CH_2(CH_2)_3CH_3$], 1.52 (m, 4 H, β-CH_2), 2.62 (t, 4 H, α-CH_2, J = 7.9), 7.19 (2 s, 2 H, H3″,6″), 7.37 (m, 1 H, H4‴), 7.44–7.69 (m, 16 H, other aromatic H)	14.04 (q, CH_3), 22.48, 29.21, 31.44, 31.50, 32.64 (5 t, CH_2), 121.51 (s, C4), 126.53 (d, C3,5), 126.74 (d, C3‴,5‴), 127.08 (d, C2‴,6‴), 127.26 (d, C4‴), 128.65 (d, C2,6), 128.80 (d, C3‴,5‴), 129.74 (d, C2‴,6‴), 129.90 (d, C2′,6′), 130.90, 130.98 (2 d, C3″,6″), 131.91 (d, C3′,5′), 137.56 (s, C2″), 137.66 (s, C5″), 138.28, 139.82, 140.20, 141.43 (4 s, C1,1′,1″,4′), 139.54, 140.52, 140.91 (3 s, C1‴,1⁗,4″,4‴)
12b	85	128 (k → i)	0.86 (m, 6 H, CH_3), 1.21 [m, 36 H, $CH_2CH_2(CH_2)_9CH_3$], 1.52 (m, 4 H, β-CH_2), 2.62 (t, 4 H, α-CH_2, J = 7.9), 7.19 (2 s, 2 H, H3″,6″), 7.35 (m, 1 H, H4‴), 7.44–7.68 (m, 16 H, other aromatic H).	14.12 (q, CH_3), 22.68, 29.33, 29.50, 29.64, 31.47, 31.91, 32.63 (7 t, CH_2), 121.51 (s, C4), 126.51 (d, C3,5), 126.72 (d, C3‴,5‴), 127.05 (d, C2‴,6‴), 127.25 (d, C4‴), 128.62 (d, C2,6), 128.79 (d, C3‴,5‴), 129.73 (d, C2‴,6‴), 129.90 (d, C2′,6′), 130.90, 130.98 (2 d, C3″,6″), 131.89 (d, C3′,5′), 137.55 (s, C2′), 137.65 (s, C5″), 138.24, 139.78, 140.19, 141.42 (4 s, C1,1′,1″,4″), 139.52, 140.51, 140.86, 140.90 (4 s, C1‴,1⁗,4″,4‴)
13a	40	–[d]	($CDCl_3$/DMSO-d_6): 0.80 (m, 6 H, CH_3), 1.18 [m, 12 H, $CH_2CH_2(CH_2)_3CH_3$], 1.50 (m, 4 H, β-CH_2), 2.62 (t, 4 H, α-CH_2, J = 8.0) 7.15 (2 s, 2 H, H3″,6″), 7.35 (m, 1 H, H4⁗), 7.45 (m, 6 H, H2‴,3‴,5‴,6‴,2⁗,6⁗), 7.70 [m, 10 H, other aromatic H, $B(OH)_2$], 7.97 (d, 2 H, H3⁗,5⁗, J = 8.1)	($CDCl_3$/DMSO-d_6): 12.59 (q, CH_3), 20.80, 27.45, 29.78, 30.94 (4 t, CH_2), 124.30, 125.04, 125.32, 127.39, 128.18 (5 d, other aromatic *C*H), 125.84 (d, C4⁗), 129.35 (d, C3″,6″), 133.10 (s, C4), 133.47 (2 d, C2″,5″), 135.81, 137.58, 138.66, 138.92, 139.28, 139.39, 140.34 (7 s, other aromatic *C*C)
13b	50	–[d]	($CDCl_3$/DMSO-d_6): 0.85 (m, 6 H, CH_3), 1.18 [m, 36 H, $CH_2CH_2(CH_2)_9CH_3$], 1.49 (m, 4 H, β-CH_2), 2.55 (t, 4 H, α-CH_2, J = 7.8), 7.14 (2 s, 2 H, H3″,6″), 7.36 (m, 1 H, H4⁗), 7.45 (m, 6 H, H2‴,3‴,5‴,6‴,2⁗,6⁗), 7.69 (m, 10 H, other aromatic H) 7.83 [s, 2 H, $B(OH)_2$], 7.93 (d, 2 H, H3⁗,5⁗, J = 8.1)	($CDCl_3$/DMSO-d_6): 12.38 (q, CH_3), 20.67, 27.20, 27.30, 27.42, 27.61, 29.42, 29.88, 30.57 (8t, CH_2), 123.96, 124.77, 125.02, 127.16 (4 d, other aromatic *C*H), 125.51 (d, C4⁗), 129.10 (d, C3″,6″), 133.21 (s, C4), 133.47 (2 d, C2″,5″), 135.48, 137.24, 138.37, 138.56, 138.98, 139.07, 139.91 (7 s, other aromatic *C*C)
14a	82	178 (k → n) 219 (n → i) (106)	0.84 (m, 12 H, CH_3), 1.20 [m, 24 H, $CH_2CH_2(CH_2)_3CH_3$], 1.55 (m, 8 H, β-CH_2), 2.65 (t, 8 H, α-CH_2, J = 8.0), 7.22 (2 s, 4 H, H3″,6″,3′^{7},6′^{7}), 7.37 (m, 2 H, H4,4′^{9}), 7.48 (m, 12 H, H3,5,3′,5′,2‴,6‴,3′^{6}, 5′^{6},2′^{8},6′^{8},3′^{9},5′^{9}), 7.68 (m, 8 H, H2,6,2′,6′,3′^{8}, 2′^{9},6′^{9}) 7.74 (2 s, 4 H, H3⁗,5⁗,2′^{5},6′^{5}), 7.78 (m, 8 H, H3‴,5‴,2⁗,6⁗,3′^{5},5′^{5},2′^{6},6′^{6})	14.07 (q, CH_3), 22.50, 29.24, 31.52, 32.68 (4 t, CH_2), 126.62, 127.40 (2 d, C2⁗,3⁗,5⁗,6⁗,2′^{5},3′^{5},5′^{5},6′^{5}), 126.74, 127.07, (2 d, C2,3,5,6,2′^{9},3′^{9},5′^{9},6′^{9}), 127.25 (d, C4,4′^{9}), 127.47, 129.84 (2 d, C2‴,3‴,5‴,6‴,2′^{6},3′^{6},5′^{6}, 6′^{6}), 128.80, 129.76 (2 d, C2′,3′,5′,6′,2′^{8},3′^{8},5′^{8},6′^{8}), 130.97 (d, C3″,6″,3′^{7},6′^{7}), 137.63 (s, C2″,5″,2′^{7},5′^{7}), 138.93, 139.82, 140.43, 141.10, 139.51, 140.38, 140.88, 140.95 (7 s, other aromatic *C*C)
14b	80	123 (k → n) 141 (n → i) (42)	0.87 (m, 12 H, CH_3), 1.19–1.28 [m, 72 H, $CH_2CH_2(CH_2)_9CH_3$], 1.53 (m, 8 H, β-CH_2), 2.64 (t, 8 H, α-CH_2, J = 7.9), 7.22 (2 s, 4 H, H3″,6″,3′^{7},6′^{7}), 7.37 (m, 2 H, H4,4′^{9}), 7.48 (m, 12 H, H3,5,3′,5′,2‴,6‴,3′^{6}, 5′^{6},2′^{8},6′^{8},3′^{9},5′^{9}), 7.68 (m, 8 H, H2,6,2′,6′,3′^{8}, 5′^{8},2′^{9},6′^{9}), 7.73 (2 s, 4 H, H3⁗,5⁗,2′^{5},5′^{5}), 7.78 (m, 8 H, H3‴,5‴,2⁗,6⁗,3′^{5}, 5′^{5},2′^{6},6′^{6})	14.14 (q, CH_3), 22.70, 29.36, 29.54, 29.67, 31.52, 31.93, 32.67 (7 t, CH_2), 126.61, 127.39 (2 d, C2⁗,3⁗,5⁗,6⁗, 2′^{5},3′^{5},5′^{5},6′^{5}), 126.73, 127.07 (2 d, C2,3,5,6,2′^{9},3′^{9}, 6′^{9}), 127.25 (d, C4,4′^{9}), 127.46, 129.85 (2 d, C2‴,3‴, 5‴,6‴,2′^{6},3′^{6},5′^{6},6′^{6}), 128.80, 129.77 (2 d, C2′,3′,5′,6′, 2′^{8},3′^{8},5′^{8},6′^{8}), 130.99 (d,C3″,6″,3′^{7},6′^{7}), 137.63 (s, C2″,5″,2′^{7},5′^{7}), 138.93, 139.52, 139.85, 140.40, 141.12, 139.52, 140.39, 140.88, 140.95 (7 s, other aromatic *C*C)

Table. (continued)

Product[a]	Yield[b] (%)	Thermal Transitions[c]	^{1}H NMR ($CDCl_3$/TMS) δ, J (Hz)	^{13}C NMR ($CDCl_3$/TMS) δ
15a	35	249 (k → n) (109)	0.77 (m, 18H, CH_3), 1.15 [m, 36H, $CH_2CH_2(CH_2)_3CH_3$], 1.48 (m, 12H, β-CH_2), 2.56 (t, 12H, α-CH_2, J = 8.0), 7.16 (2s, 6H, H3″,6″,3′^{7},6′^{7},3′^{12},6′^{12}), 7.32 (m, 2H, H4,4′^{14}), 7.43 (m, 12H, H3′,5′,2‴,6‴, 3′^{6},5′^{6},2′^{8},6′^{8},3′^{11},5′^{11},2′^{13},6′^{13}), 7.64 (m, 8H, H2,6,2′,6′,3′^{13},5′^{13},2′^{14},6′^{14}), 7.70 (2s, 8H, H3⁗,5⁗,2′^{5},6′^{5},3′^{9},5′^{9},2′^{10},6′^{10}), 7.77 (s, 12H, other aromatic H)	14.54 (q, CH_3), 22.89, 29.60, 31.85, 33.01 (4t, CH_2), 126.82, 126.93, 127.30, 127.71, 129.23, 130.13, 131.21, 131.26 (8d, aromatic *C*H), 137.82, 138.68, 139.51, 139.90, 140.42, 141.41, 139.26, 140.42, 140.88, 141.26 (10s, aromatic *C*C)
15b	80	148 (k → n) 279 (n → i)	0.87 (m, 18H, CH_3), 1.19–1.28 [m, 108H, $CH_2CH_2(CH_2)_9CH_3$], 1.53 (m, 12H, β-CH_2), 2.64 (t, 12H, α-CH_2, J = 7.9), 7.22 (2s, 6H, H3″,6″,3′^{7},6′^{7},3′^{12},6′^{12}), 7.37 (m, 2H, H4,4′^{14}), 7.48 (m, 12H, H3′,5′, 2‴,6‴,3′^{6},5′^{6},2′^{8},6′^{8},3′^{11},5′^{11},2′^{13},6′^{13}), 7.68 (m, 8H, H2,6,2′6′,3′^{13},2′^{14},6′^{14}), 7.73 (2s, 8H, H3⁗,5⁗,2′^{5},6′^{5},3′^{9},5′^{9},2′^{10},6′^{10}), 7.78 (s, 12H, other aromatic H)	14.14 (q, CH_3), 22.70, 29.36, 29.54, 29.67, 31.52, 31.93, 32.67 (7t, CH_2), 126.60, 126.72, 127.06, 127.37, 127.45, 128.79, 129.77, 129.86, 130.99 (9d, aromatic *C*H), 137.64, 138.90, 139.49, 139.82, 140,40, 141.10, 139.49, 140.40, 140.86, 140.96 (10s, aromatic *C*C)

[a] Satisfactory microanalyses were obtained (boronic acid derivatives were not analyzed because of their variable water content): C ± 0.24, H ± 0.27, Br ± 0.31

[b] Isolated yields after purification as described in the experimental part. The conversions were > 95% throughout (NMR) for all compounds described except for the boronic acid derivatives **3**, **10a, b**, and **13a, b**.

[c] Abbreviations of phases observed: k = crystalline ($k_{1,2}$ = crystalline modifications 1 or 2); n = nematic; s = smectic; i = isotropic melt. Values additionally given in brackets correspond to further phase transitions observed with DSC and WAXS, the origin of which has not yet been clarified, however.

[d] For boronic acid derivatives, no well-defined melting points were observed because the melting process is accompanied by decomposition (dehydration).

[e] Two crystalline modifications, k_1 and k_2, are observed in the solid state: when the melt is cooled down quickly (20 K · min^{-1}), modification 1 is formed. When, on the other hand, the cooling rate was only 1 K · min^{-1}, modification 2 is found. Upon crystallization from solution, a mixture of both modifications is found.

[f] Only mixtures of both crystalline modifications, k_1 and k_2, were obtained from both, melt and solution.

[g] The isotropic melt cannot be achieved (> 320°C, decomposition). Therefore, the transition temperature into the nematic mesophase is reported here.

The monofunctional starting materials **12a, b** and **13a, b** were prepared according to Scheme 2. First, 2,5-dialkyl-4-bromo-*p*-terphenyl derivatives **9a, b** were prepared by converting 4-biphenylboronic acid **(3)** with a tenfold molar excess of dibromobenzene derivative **1a, b** under the standard conditions of the Pd-catalyzed condensation reaction (> 95% yield). The excess of **1a, b** used for the reaction **1a, b** → **9a, b** was necessary to suppress the competitive formation of *p*-quinquephenyls **5a, b** (cf. Scheme 1). Subsequently, **9a, b** were converted into the 2,5-dialkyl-*p*-terphenyl-4-boronic acids **10a, b** via halogen-metal exchange using butyllithium, conversion of the lithiated intermediate with trimethyl borate, and finally acidic hydrolysis. Pure **10a, b** were obtained in 40 to 60% yield and subsequently converted under Pd-catalysis into the 2″,5″-dialkyl-4-bromo-*p*-quinquephenyl derivatives **12a, b**. For this conversion as well, a tenfold molar excess of 4,4′-dibromobiphenyl **(11)** was used to suppress the formation of *p*-octiphenyl. During workup, this excess can be recycled almost quantitatively by sublimation, and pure *p*-quinquephenyls **12a, b** were obtained in about 85% yield. Conversion of **12a, b** into the *p*-quinquephenylboronic acids **13a, b** (40 to 50% yield) was performed in analogy to the conversion **9a, b** → **10a, b**. Finally, *p*-deciphenyl derivatives **14a, b** were prepared via Pd-catalyzed condensation of equimolar amounts of **12a, b** and **13a, b** while *p*-quindeciphenyl derivatives **15a, b** were obtained from two equivalents of *p*-quinquephenyl-4-boronic acid derivatives **13a, b** and one equivalent of 4,4⁗-dibromoquinquephenyls **6a, b**. All conversions occurred nearly quantitatively and without any detectable side reaction (NMR). After purification, *p*-deciphenyls **14a, b** and *p*-quindeciphenyl **15b** were obtained in about 80% yield as colorless crystals. In the case of the hexyl-substituted *p*-quindeciphenyl **15a** on the other hand, lower yields were obtained because of its lower solubility which affected the workup. Pure **15a** was obtained in only about 30–35% yield after removing last traces of inorganic compounds, catalyst residues, starting materials and oligophenyl intermediates by filtration over silica gel. Obviously, six hexyl side chains are not sufficient any more to efficiently solubilize such a long oligo-*p*-phenyl oligomer.

The molecular structures of all oligomers shown in Schemes 1 and 2 were finally proven with high-resolution ^{1}H and ^{13}C NMR spectroscopy. All observed absorptions support the constitution of the products (Table).

Furthermore, all oligomers except those having boronic acid functionalities were analyzed by elemental analyses, and characterized with regard to their thermal properties with polarization microscopy, differential scanning calorimetry (DSC), and wide angle X-ray scattering (WAXS). The isotropization temperatures and/or the temperatures of solid-solid and solid-mesophase transitions are summarized in the Table. A detailed analysis of the phase behavior of the presented oligo-*p*-phenyls, however, will be published separately.

In conclusion, the Pd-catalyzed synthesis of oligo-*p*-phenyls is shown to occur highly regioselectively and without any detectable side reaction in all cases under consideration: no resonances were found in the NMR spectra which point towards, for example, the formation of bent structures. Reductive dehalogenation, hydrolysis of boronic acid species, or side products due to the decomposition of the catalyst[14] were found to be minimal. Only the restricted solubility of intermediates and/or final products affected the syntheses in some cases. While the more convenient route A (Scheme 1) proved to be well appropriate for the preparation of oligomers having up to nine phenyl rings, longer oligomers are advantageously prepared via the complementary route B (Scheme 2) which allows the introduction of two alkyl side chains per five phenyl rings of an oligomer. Thus, combination of Pd-catalyzed condensation with the concept of solubilizing side chains is a powerful, and for sure further expansible, strategy for the preparation of well-defined, monodisperse oligo-*p*-phenyls.

All reagents were purchased from Aldrich, Fluka and Lancaster Chemical Co. (p.a. quality); $PdCl_2$ was a gift from Degussa AG. 4-Bromobiphenyl and 4,4′-dibromobiphenyl were purified by sublimation. Et_2O was dried over Na and distilled under N_2. All other chemicals and solvents were used without further purification. All reactions reported were carried out under an atmosphere of N_2. $(Ph_3P)_4Pd$,[15] 2,5-dialkyl-1,4-dibromobenzenes **1a, b**,[11] and 2″,5″-dialkyl-4,4‴-dibromo-*p*-quinquephenyls **6a, b**[13] were prepared according to the literature. ^1H and ^{13}C NMR spectra were recorded with a Bruker AM400 spectrometer (400 MHz for ^1H, 100 MHz for ^{13}C). TMS was used as the internal standard. Melting points were determined using a Zeiss-Ikon microscope equipped with a Mettler heating-desk FP82 and are uncorrected. DSC measurements were performed using a Mettler DSC-30. The heating rate was $2\ K \cdot min^{-1}$. WAXS investigations were carried out with a Siemens D5000 diffractometer using unfiltered Cu-K_α radiation ($\lambda = 1.542$ Å).

4-Biphenylboronic Acid (3):
BuLi (4.8 mL, 7.7 mmol, 1.6 M solution in hexane) was added to a cooled (−78 °C) solution of 4-bromobiphenyl (1.15 g, 5 mmol) in anhyd Et_2O (30 mL). The mixture was allowed to warm up to r.t. and stirred at 25 °C for 1 h. The resulting solution was added dropwise to a cooled (−78 °C) solution of trimethyl borate (2.3 mL 20.4 mmol) in Et_2O (30 mL). After complete addition, the mixture was allowed to warm up to r.t. and stirred for a further 12 h at 25 °C. Subsequently, 3 M HCl (30 mL) was added. The organic layer was separated, washed with H_2O (2 × 100 mL) and dried ($MgSO_4$). The crude product was dissolved in hot toluene (50 mL) and the resulting solution was filtered through a column of silica gel with toluene as the eluent to remove all the impurities. Subsequently, pure product **3** was eluted with acetone as the mobile phase. The solvent was removed in vacuo and the residue was dissolved in hot toluene (100 mL). After cooling down to r.t., dil HCl (50 mL) was added, and the mixture was stirred for a further 12 h. Finally, the solid was filtered and dried in vacuo (P_4O_{10}).

Oligo-*p*-phenyls 4, 5, 7, and 8; General Procedure:
Boronic acid derivatives **2** or **3** (10 mmol), dibromo compounds **1** or **6** (5 mmol), toluene (30 mL), aq Na_2CO_3 (30 mL, 1 M), and $(Ph_3P)_4Pd$ (0.29 g, 1 mol%) were intensively stirred and refluxed for 3 d (7 d in the case of **8**). The organic layer was separated, and the aqueous phase extracted with toluene (2 × 100 mL). The combined organic layers were washed with H_2O (2 × 100 mL), dried ($MgSO_4$), dissolved in hot toluene (100 mL), and filtered over Al_2O_3 (type: 100–125 mesh; activity 1). Further workups were done as follows: 2′,5′-Dihexyl-*p*-terphenyl **(4a)**, 2′,5′-Didodecyl-*p*-terphenyl **(4b)**, 2″,5″-Dihexyl-*p*-quinquephenyl **(5a)**: recrystallization from EtOH; 2″,5″-Didodecyl-*p*-quinquephenyl **(5b)**: recrystallization from a mixture of EtOH and hexane (1 : 1) at 0 °C; 2‴,5‴-Dihexyl-*p*-heptaphenyl **(7a)**: recrystallization from toluene at 0 °C; 2‴,5‴-Didodecyl-*p*-heptaphenyl **(7b)**: recrystallization from a mixture of toluene and hexane (1 : 10) at 0 °C; 2⁗,5⁗-Dihexyl-*p*-noaphenyl **(8a)**: recrystallization from toluene (500 mL); 2⁗,5⁗-Didodecycl-*p*-novaphenyl **(8b)**: recrystallization from toluene.

2,5-Dialkyl-4-bromo-*p*-terphenyls 9a, b:
Dibromobenzene derivative **1** (20.2 g, **1a**, 28.6 g **1b**, 50 mmol each), 4-biphenylboronic acid (**3**; 0.99 g, 5 mmol), toluene (30 mL), aq Na_2CO_3 (30 mL, 1 M), and $(Ph_3P)_4Pd$ (0.15 g, 0.5 mol%) were vigorously stirred and refluxed for 3 d. The workup was the same as described for oligo-*p*-phenyls **4a, b**. Pure **9a, b** were obtained by column filtration (silica gel, eluent: hexane).

2,5-Dialkyl-*p*-terphenyl-4-boronic Acids 10a, b:
Monobromo derivative **9a, b** (2.38 g **9a**, 3.23 g **9b**, 5 mmol each) was dissolved in anhyd Et_2O (30 mL) and cooled down to −78 °C. BuLi (6.25 mL, 10 mmol, 1.6 M in hexane) was added dropwise to this mixture and it was allowed to warm up to r.t., stirred at 25 °C for 2 h, and is subsequently cooled down to −78 °C. Trimethyl borate (5.47 g, 50 mmol) in Et_2O (30 mL) was added, and the mixture allowed to warm up to r.t. After stirring for 10 h at r.t., 3 M HCl (100 mL) was added under stirring. The precipitate formed was filtered and stirred for a further 12 h in a mixture of toluene and dil HCl (1 : 1, 100 mL). The solid was dissolved in hot toluene and purified further in the same way as described above for compound **3**.

2″,5″-Dialkyl-4-bromo-*p*-quinquephenyls 12a, b:
A mixture of boronic acid **10** (2.21 g **10a**, 3.05 g **10b**, 5 mmol each), 4,4′-dibromobiphenyl (**11**; 15.6 g, 50 mmol), toluene (30 mL), aqueous Na_2CO_3 (30 mL, 1 M), and $(Ph_3P)_4Pd$ (0.15 g, 0.5 mol%) was vigorously stirred and refluxed for 3 d. The initial workup was the same as described for oligo-*p*-phenyls **4a, b**. To purify the obtained crude product, excess **11** was first removed by sublimation (150 °C, oil bath, 0.01 mbar, 24 h). The residue was dissolved in petroleum ether (bp 60–80 °C) **(12a)** or in a mixture of petroleum ether (bp 60–80 °C) and toluene (8 : 1, **12b**) and purified chromatographically (silica gel) using the same solvents as the mobile phase. Last traces of **11** were eluted in the first fraction followed by pure products **12a, b**. Solvents were removed and the products dried in vacuo.

2″-5″-Dialkyl-*p*-quinquephenyl-4-boronic Acids 13a, b:
Synthesis, workup and purification procedure were identical to those described above for compounds **10a, b**. Starting materials were monobromo derivatives **12** (3.15 g **12a**, 3.99 g **12b**, 5 mmol each), Et_2O (30 mL), BuLi (6.25 mL, 10 mmol, 1.6 M in hexane), and trimethyl borate (5.47 g, 50 mmol) in Et_2O (30 mL).

2″,5″,2‴,5‴-Tetraalkyl-*p*-decaphenyls 14a, b:
Bromo derivative **12** (3.15 g **12a**, 3.99 g **12b**, 5 mmol each), boronic acid **13** (3.27 g **13a**, 4.20 g **13b**, 5.5 mmol each), toluene (30 mL), aq Na_2CO_3 (30 mL, 1 M), and $(Ph_3P)_4Pd$ (0.15 g, 0.5 mol%) were vigorously stirred and refluxed for 3 d. Workup was done as described for **4a, b**. Finally, **14a, b** were recrystallized from toluene and dried in vacuo.

2″,5″,2‴,5‴,2⁽¹²⁾,5⁽¹²⁾-Hexa-x-alkyl-*p*-quindeciphenyls 15a, b:
Dibromo derivatives **6** (3.54 g **6a**, 4.38 g **6b**, 5 mmol each), monoboronic acid derivative **13** (6.54 g **13a**, 8.39 g **13b**, 11 mmol each),

toluene (30 mL), aq Na_2CO_3 (30 mL, 1 M), and $(Ph_3P)_4Pd$ (0.15 g, 0.5 mol%) were vigorously stirred and refluxed for 3 d. Further workup was carried out as described for **4a, b**. Finally, the oligo-*p*-phenyls **15a, b** were recrystallized from toluene and dried in vacuo.

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