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Synthetic Approaches to Zigzag-Shaped Oligophenylene Strands Laterally Decorated with Hydroxy Functions

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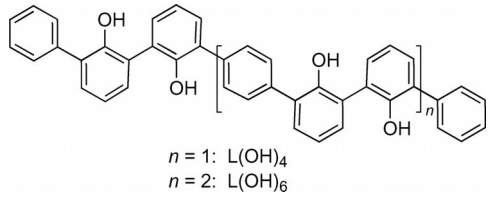
Two nanosized zigzag-shaped oligophenylene strands incorporating 2,2′-biphenol units were prepared by Suzuki–Miyaura coupling methodology. The two strands are made up of ten and seven phenyl rings, respectively. Two synthetic pathways were evaluated. The first involved the preparation of the target oligophenylene molecules by a sequential approach, whereas the second entailed the formation of the precursors of the target compounds in a one-step fashion. The efficiencies of these two approaches are discussed and compared.

Introduction

In the field of organic materials, nanosized polyphenylene structures occupy a particular place.[1] The self-assembling,[2] photophysical,[3] conducting,[4] and mechanical properties,[5] as well as the liquid-crystal behavior,[6] of this very large family of thermally and photochemically stable compounds have been intensively studied. In coordination chemistry, oligophenylenes or oligophenylene backbones substituted with coordinating atoms or groups are an important class of ligands.[7] A large variety of synthetic approaches to oligophenylene structures have been reported; these include, for instance, reductive and oxidative coupling,[1,8] thermolysis or aromatization of appropriate precursors,[1,9] and Diels–Alder cycloaddition.[1,10] Nowadays, however, transition-metal-catalyzed aryl–aryl coupling reactions are certainly the most widely employed.[1,11] In particular, mild palladium(0)-catalyzed couplings of arylboronic acids with aryl halides, known as Suzuki–Miyaura cross-coupling reactions,[12] have allowed the preparation of a large range of molecules containing polyphenylene backbones.[1,13]

Recently, our group has described the ability of a novel tetrahydroxyheptaphenylene strand – $L(OH)_4$ (Scheme 1) – to complex a titanium(IV) center, leading to a non-centrosymmetric double-stranded titanium(IV) helicate.[14]



Scheme 1.

Here we report two synthetic approaches leading to the formation of the zigzag-shaped[15] polyhydroxyoligophenylene strand $L(OH)_4$ and its longer analogue, the strand $L(OH)_6$ (Scheme 1). Both approaches reported here involve the preparation of the nanosized oligophenylene structures by application of Suzuki–Miyaura reactions. A complete description of the procedure for preparing these strands is presented, and the efficiencies of the two strategies are discussed and compared. Furthermore, the solid-state characterization of some target strands and their synthetic intermediates is reported.

Results and Discussion

The molecular strands $L(OH)_4$ and $L(OH)_6$, incorporating two and three 2,2′-biphenol units, respectively, are shown in Scheme 1. The $L(OH)_4$ molecule contains two 3-phenyl-2,2′-biphenol entities linked together through a *para*-phenylene spacer, whereas in $L(OH)_6$ the central core of the molecule is a 3,3′-diphenyl-2,2′-biphenol fragment. Of the large variety of methods described for the preparation of oligophenylene structures, palladium-catalyzed cross-coupling reactions looked the most suitable. Applica-

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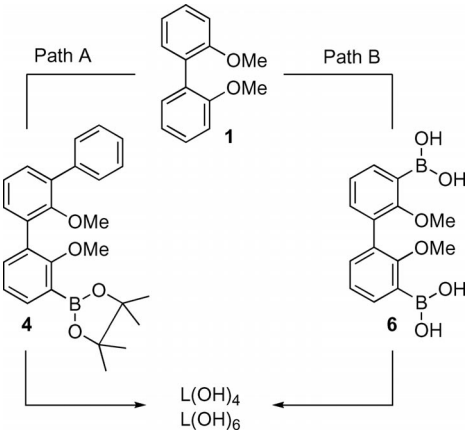
tion of Suzuki–Miyaura condensation reactions to construct our target molecules by two synthetic pathways was thus envisaged, as shown in Scheme 2.



Scheme 2. Two synthetic approaches leading to $L(OH)_4$ and $L(OH)_6$.

Path A involves the preparation of $L(OH)_4$ and $L(OH)_6$ starting from the commercially available 2,2′-dimethoxybiphenyl (**1**; Scheme 2) by a sequential approach. The key intermediate is the dissymmetric boronic ester **4**, obtained in three steps from **1**. Compound **4** proved suitable, after Suzuki–Miyaura coupling with an appropriate spacer and subsequent cleavage of the methoxy groups, for the production of $L(OH)_4$ and $L(OH)_6$. The second approach, path B, is more straightforward. It consists first of the conversion of 2,2′-dimethoxybiphenyl into the bis(boronic acid) adduct **6**, followed by a one-pot Suzuki–Miyaura reaction in the simultaneous presence of bromobenzene and 1,4-dibromobenzene. The isolation of the desired compounds was achieved by careful separation from a crude material composed of a complex mixture of polyphenylene molecules.

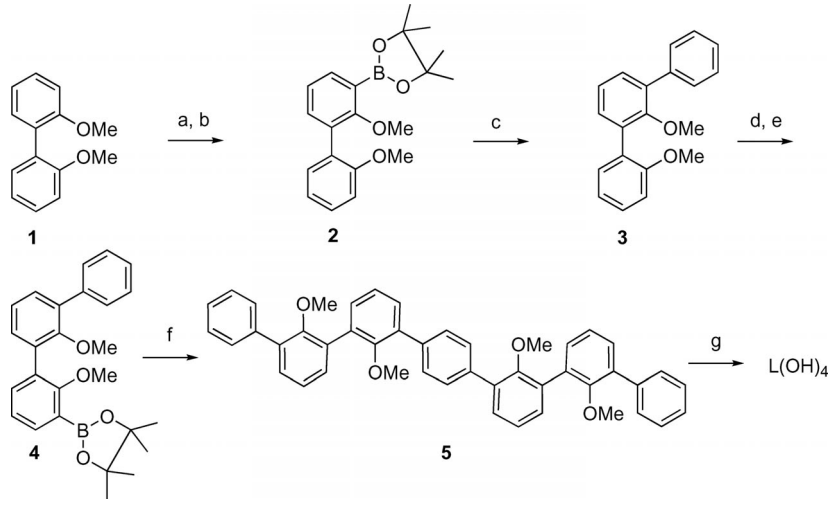
Path A

The compound $L(OH)_4$ was prepared in five steps by starting from 2,2′-dimethoxybiphenyl as shown in Scheme 3. The synthesis of $L(OH)_4$ was performed by application of *ortho*-metalation, metal-catalyzed cross-coupling in the presence of the "classical" $Pd(PPh_3)_4$ catalyst, and ether cleavage methodologies. 2,2′-Dimethoxybiphenyl was first *ortho*-monolithiated and then quenched with $B(OMe)_3$ to give the corresponding monoboronic acid after basic hydrolysis followed by acidification. However, to circumvent tedious characterization of the product due to the possible formation of anhydride products, the boronic acid was directly converted into the pinacol ester **2**. Under Suzuki–Miyaura conditions, **2** was transformed in good yield into the dissymmetric compound **3**.

The chemical integrities of **2** and **3** were confirmed by various analytical techniques including ^1H and ^{13}C NMR spectroscopy and electrospray ionization mass spectrometry (ESI-MS).

Formation of the key intermediate **4** was possible through *ortho*-lithiation of **3** and subsequent addition of $B(OMe)_3$, acidification, and esterification in the presence of pinacol.

Compounds **2**, **3**, and **4** are crystalline materials. Crystals suitable for X-ray diffraction (XRD) were obtained by slow diffusion of pentane in the case of **2** and of hexane in those of **3** and **4** into CH_2Cl_2 solutions of these compounds. The structures of the dissymmetric compounds **2**, **3**, and **4** are shown in Figure 1. Interestingly, these three compounds crystallized in the same crystal system and the same space group (monoclinic and $P2_1/c$). Torsion angle measurements between the phenyl rings bearing the methoxy groups indicate synclinal conformations between two neighboring cycles for **3** and **4**, with angle values of 66° and 80°, respectively, whereas an anticlinal conformation was found in **2** (measured torsion angle 117°).



Scheme 3. Synthesis of the tetrahydroxyheptaphenylene strand $L(OH)_4$. (a) *n*BuLi, TMEDA, $B(OMe)_3$, HCl; (b) 2,3-dimethylbutane-2,3-diol, toluene, reflux, 34% (based on **1**); (c) bromobenzene, $Pd(PPh_3)_4$, toluene/MeOH/water, 110 °C, Na_2CO_3, 89%; (d) *n*BuLi, TMEDA, $B(OMe)_3$, HCl; (e) 2,3-dimethylbutane-2,3-diol, toluene, reflux, 56% (based on **3**); (f) 1,4-dibromobenzene, $Pd(PPh_3)_4$, toluene/MeOH/water, 110 °C, Na_2CO_3, 75%; (g) BBr_3, dichloromethane, quantitative.

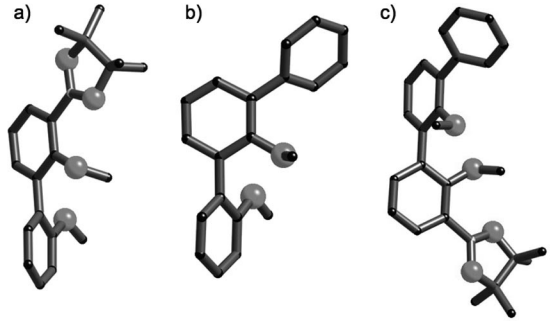


Figure 1. X-ray structures of **2**, **3**, and **4**. Hydrogen atoms are omitted for clarity.

Next, the palladium-catalyzed cross-coupling reaction between **4** and 1,4-dibromobenzene (0.55 equiv.) led to the formation of the tetramethoxyheptaphenylene derivative **5** in good yield (75%).

Finally, upon treatment with BBr_3, **5** was quantitatively deprotected to give the target strand $L(OH)_4$. ^1H and ^{13}C NMR spectroscopy, as well as elemental analysis and ES-MS data, are in full accordance with the expected structure of $L(OH)_4$.

Crystals of $L(OH)_4$ and of its methylated precursor **5** suitable for X-ray analysis were obtained by slow diffusion of pentane into CH_2Cl_2 solutions. Figure 2 shows the X-ray crystallographic structures of **5** and $L(OH)_4$.

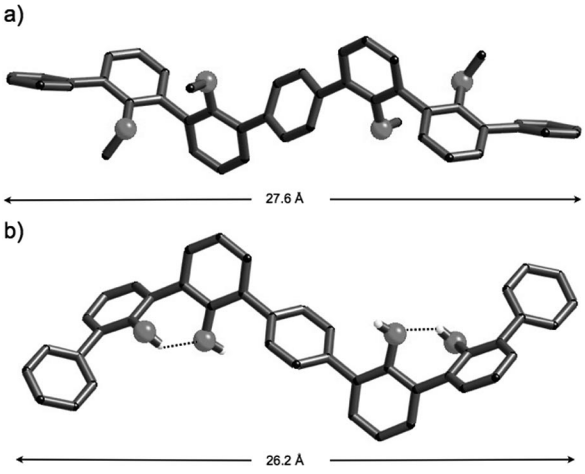


Figure 2. (a) X-ray crystal structure of **5**. (b) X-ray crystal structure of $L(OH)_4$. In both structures, the hydrogen atoms are omitted for clarity except for [in (b)] the hydroxy functions involved in the intramolecular hydrogen bonds (dotted line) ($O_{(OH)}$···O 2.865 Å, O···H···O 130.4°).

A slight size difference can be observed in these structures. In the solid state, lengths of 27.6 Å and 26.2 Å were measured for **5** and $L(OH)_4$, respectively. Another significant difference between these two structures relates to the torsion angles between the pairs of consecutive phenyl rings bearing methoxy or hydroxy groups in **5** and in $L(OH)_4$, respectively. Because of the steric hindrance produced by two adjacent methoxy groups, the two phenyl rings adopt an anticlinal conformation (measured torsion angle: 99°). For $L(OH)_4$ the situation is different, with an intramolecular hydrogen bond between two neighboring hydroxy functions ($O_{(OH)}$···O 2.865 Å, O···H···O 130.4°) allowing a synclinal arrangement of two phenol subunits (measured torsion angle: 63°). Inspection of the monodimensional packing of $L(OH)_4$ is also instructive. In the crystal, $L(OH)_4$ interacts with two nearest neighbors through four intermolecular hydrogen bonds ($O_{(OH)}$···O 2.855 Å, O···H···O 149.9°). Each $L(OH)_4$ molecule behaves both as a hydrogen-bond donor and as a hydrogen-bond acceptor, leading to an infinite ladder-type structure as shown in Figure 3.

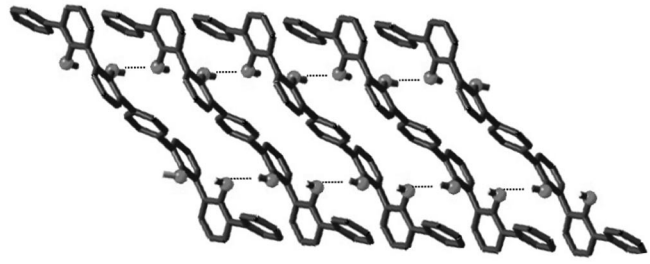
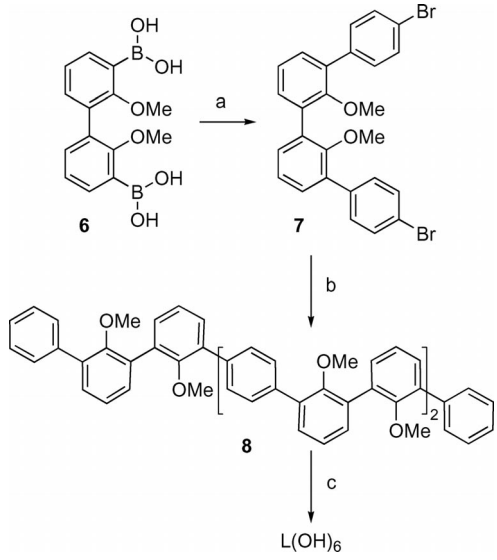


Figure 3. View along *x* of the monodimensional hydrogen-bond networks in the crystal of $L(OH)_4$ ($O_{(OH)}$···O 2.855 Å, O···H···O 149.9°).

With the efficient synthetic route described in Scheme 3 to hand, the synthesis of a second polyphenylene derivative composed of three biphenol units [i.e., $L(OH)_6$] was tackled. The formation of $L(OH)_6$ required the condensation of **4** (2 equiv.) with **7** as shown in Scheme 4, followed by cleavage of the methoxy groups.



Scheme 4. Synthesis of the hexahydroxydecaphenylene strand $L(OH)_6$. (a) 1-Bromo-4-iodobenzene, $Pd(PPh_3)_4$, toluene/MeOH/water, 110 °C, Na_2CO_3, 74%; (b) **4**, $Pd(PPh_3)_4$, toluene/MeOH/water, 110 °C, Na_2CO_3, 30%; (c) BBr_3, dichloromethane, 76%.

The synthesis of **7** was first attempted through a condensation under Suzuki–Miyaura conditions between 1,4-dibromobenzene and **6**, which could be easily obtained on a large scale from the commercially available 2,2′-dimethoxy-

1,1′-biphenyl by a recently described procedure.[7f] In order to disfavor the formation of polymeric species, a large excess of 1,4-dibromobenzene (10 equiv.) was used. However, despite this precaution, **7** was isolated only in a poor yield of 25%.

It is well known that the rate-determining step in the Suzuki reaction is the oxidative addition of the aryl halide to the palladium complex, with a relative reactivity decrease in the order I > Br > Cl.[16] Application of Suzuki conditions to the synthesis of **7** from **6** and 1-bromo-4-iodobenzene (3 equiv.) instead of 1,4-dibromobenzene therefore allowed the isolation of the desired dibromo derivative **7** in good yield (74%). The structure of the expected compound was confirmed by various analytical techniques including XRD as shown in Figure 4.

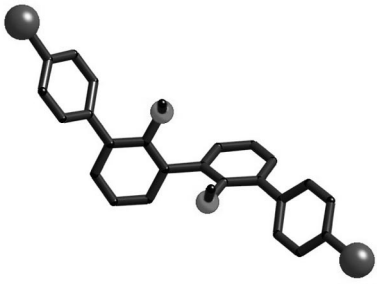
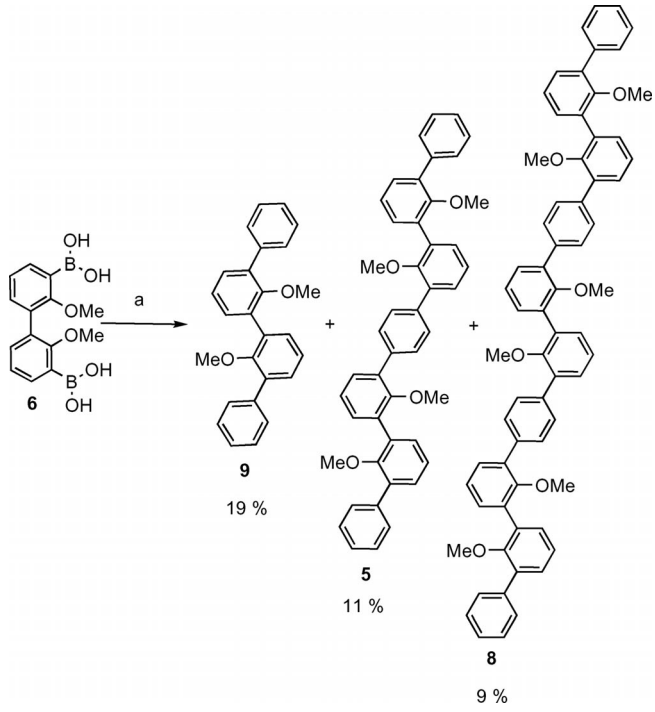


Figure 4. X-ray crystal structure of **7**. Hydrogen atoms are omitted for clarity.



Scheme 5. One-pot procedure allowing the isolation, in one step, of **9** (3,3′-diphenyl-2,2′-dimethoxy-1,1′-biphenyl), **5**, and **8**. (a) $Pd(PPh_3)_4$ (5 mol-%), bromobenzene (0.70 equiv.), 1,4-dibromobenzene (0.33 equiv.).

Under Suzuki–Miyaura conditions, **8** was then prepared through the coupling of 2 equiv. of **4** with **7** (Scheme 4). Compound **8** was isolated in modest yield (30%). Deprotection of **8** with BBr_3 resulted in the formation of the strand $L(OH)_6$, poorly soluble in common organic solvents with the exception of tetrahydrofuran.

The two sequential synthetic routes described above led to the isolation of the target nanosized molecular strands $L(OH)_4$ and $L(OH)_6$, incorporating seven and ten aromatic units, respectively. Five synthetic steps starting from 2,2′-dimethoxybiphenyl were necessary to isolate $L(OH)_4$ with an overall yield of 12%, whereas for the longer analogue $L(OH)_6$ seven steps were required. In both cases, the synthetic pathways involve the tedious preparation of the dissymmetric compound **4**. Therefore, in order to improve the accessibility of $L(OH)_4$ and $L(OH)_6$, another protocol based on a much more direct approach was developed.

Path B

The synthesis of the precursors **5** and **8** (Scheme 5) of the target hydroxylated strands was envisaged as starting from the readily available 2,2′-dimethoxy-1,1′-biphenyl-3,3′-bis(boronic acid) (**6**) in a one-pot reaction. Compound **6** was engaged in a palladium(0)-catalyzed double C–C bond formation with bromobenzene and 1,4-dibromobenzene simultaneously present in the reaction mixture in substoichiometric amounts as shown in Scheme 5.

The formation of several polyphenylene structures was indeed expected, and so a careful separation of the crude mixture with chromatographic tools was necessary to isolate the target compounds. In an optimized procedure, bromobenzene (0.70 equiv.) and 1,4-dibromobenzene (0.33 equiv.) reacted with **6** at 50 °C over a period of 53 h with catalysis by $Pd(PPh_3)_4$ (5 mol-%) in a triphasic mixture (toluene/methanol/water). The composition of the reaction mixture was evaluated by analytical silica gel thin layer chromatography (TLC). Development by elution with *n*-pentane/CH_2Cl_2 (50:50) revealed the presence of three major round spots characterized by significant differences in their R_f values (0.52, 0.37, and 0.33). These products could easily be separated by chromatography [SiO_2; *n*-pentane/CH_2Cl_2 (50:50)]. It should be noted that TLC analysis also revealed the presence of more polar products, which could not be isolated as pure samples under our conditions. Compounds **9**, **5**, and **8** were obtained in 19%, 11%, and 9% yields, respectively. These yields, although modest, are satisfactory, especially for the longest rod **8**, containing ten aromatic rings, if we consider that six carbon–carbon bonds were created in one step. It should be noted that slight modifications of the optimized protocol described above have important consequences for the isolated yields, as reported in Table 1.

Finally, a similar synthetic route involving the condensation of benzeneboronic acid and 1,4-benzenediboronic acid with 3,3′-dibromo-2,2′-dimethoxy-1,1′-biphenyl has also been investigated.[17] In that case, only **5** could be isolated in a yield of 8% and as a sample contaminated by a large amount of inseparable impurities (ca. 30% evaluated by ^1H NMR spectroscopy).

Table 1. Reaction conditions tested for the one-step synthesis of **9**, **5**, and **8** starting from **6**. Entry 6 corresponds to the optimized protocol.

Entry	**6** [10^{-3} mol]	Bromobenzene [equiv.]	1,4-Dibromobenzene [equiv.]	Procedure,[a] temperature	Product, yield[b]
1	1.6	0.55	0.27	i, 50 °C	**9**, 0% **5**, 0% **8**, 0%
2	1.6	0.55	0.27	ii, 50 °C	**9**, 0% **5**, 4% **8**, 0%
3	1.6	1.05	0.55	ii, 50 °C	**9**, 11% **5**, 6% **8**, 0%
4	1.6	1.05	0.55	ii, 110 °C	**9**, 13% **5**, 5% **8**, 0%
5	1.6	0.7	0.33	ii, 110 °C	**9**, 14% **5**, 3% **8**, 0%
6	3.3	0.7	0.33	ii, 50 °C	**9**, 19% **5**, 11% **8**, 9%

[a] Procedure (i): $Pd(PPh_3)_4$ (5 mol-%), Na_2CO_3 (1 M), toluene, MeOH, 50 °C. Compound **6** was first treated with bromobenzene. After 24 h, 1,4-dibromobenzene was then added to the reaction mixture. Procedure (ii): $Pd(PPh_3)_4$ (5 mol-%), Na_2CO_3 (1 M), toluene, MeOH, 50 °C. Compound **6** was treated simultaneously with bromobenzene and 1,4-dibromobenzene. [b] Isolated yields obtained after purification of the crude reaction on silica gel (CH_2Cl_2/pentane). For Entries 1, 2, 3, 4, and 5 undesired products corresponding, for instance, to **1** or to strands **5** and **8** with one or two phenyl rings missing were isolated.

Conclusions

Here we have described the synthesis of two new polyphenylene structures incorporating two or three 2,2′-biphenol moieties linked through *para*-phenylene spacers. These two strands were obtained by application of Suzuki–Miyaura C–C bond formation, once again highlighting the crucial role of palladium cross-coupling methodologies in the construction of polyphenylene nanostructures. Two synthetic pathways were applied. The stepwise procedure, which required the synthesis of an unsymmetrically *ortho*-substituted 2,2′-dimethoxy-1,1′-biphenyl intermediate, allowed the preparation of $L(OH)_4$ and $L(OH)_6$ in five and seven steps, respectively. A second synthetic strategy based on an efficient one-pot protocol was also evaluated. In the particular case of the synthesis of our target compounds, the use of the one-pot cross-coupling strategy represented an efficient alternative to the stepwise procedure. We are now focusing on the preparation of other polyphenylene structures that incorporate biphenol units by a similar one-pot approach, for potential applications in coordination chemistry and materials science.

Experimental Section

General: All chemicals were of the best commercially available grade and were used without further purification. Column chromatography was performed with silica gel 60 (Merck 9385, 230–400 mesh) or aluminium oxide 90 (neutral, activity II–III, Merck 1097). ^1H and ^{13}C NMR spectra were recorded with a Bruker Avance 300 (300 MHz) spectrometer with use of a deuterated solvent as the lock. The chemical shifts were referenced to residual solvent protons as internal standards (^1H NMR: $CDCl_3$: δ = 7.24 ppm, CD_2Cl_2: δ = 5.32 ppm, [D_8]THF: δ = 3.31 ppm; ^{13}C NMR: $CDCl_3$: δ = 77.23 ppm, CD_2Cl_2: δ = 54.00 ppm). Mass spectra were obtained with a VG-BIOQ triple quadrupole in positive mode (ES-MS). Microanalyses were performed by the Service de Microanalyses de la Fédération de Recherche de Chimie, Université de Strasbourg, Strasbourg. Crystallography data were collected at 173(2) K with a Bruker APEX8 CCD diffractometer equipped with an Oxford Cryosystem liquid N_2 device, with use of graphite-monochromated Mo-K_α (λ = 0.71073) radiation. For all structures, diffraction data were corrected for absorption, and structural determination was achieved by using the APEX (1.022) package. The hydrogen atoms were introduced at calculated positions and not refined (riding model). CCDC-783150 (**2**), -783151 (**3**), -783389 (**4**), -783152(**5**), -783153 (**6**), and -783388 (**7**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Compound 2: The reaction was conducted under nitrogen. 2,2′-Dimethoxy-1,1′-biphenyl (5 g, 2.34×10^{-2} mol) and freshly distilled TMEDA (5.23 mL, 3.51×10^{-2} mol) were dissolved in dry diethyl ether. The resulting mixture was cooled to –78 °C, and *n*BuLi solution (1.35 M, 26 mL, 3.51×10^{-2} mol) was added. The solution was allowed to come to room temperature and stirred for 3 h. The resulting milky solution was cooled again to –78 °C, and $B(OMe)_3$ (22.3 mL, 1.96×10^{-1} mol) was slowly added. After the mixture had been stirred at room temperature overnight, an aqueous solution of NaOH (6 N, 100 mL) was added. After 5 h, the white suspension had disappeared, and the aqueous layer was extracted, washed with CH_2Cl_2, and acidified with concentrated HCl to pH = 1. The resulting yellowish aqueous layer was then washed with CH_2Cl_2, and the isolated organic layer was dried with $MgSO_4$ and concentrated under reduced pressure to yield a yellow oil. The monoboronic acid was separated from the crude material by silica gel column chromatography (Ø = 4.5 cm, *l* = 35 cm; CH_2Cl_2/MeOH, 99:1) to yield a yellow oil (4.06 g). In order to facilitate the characterization, the resulting product was used directly in the next step. The resulting oil and pinacol (3.66 g, 3.10×10^{-2} mol) were dissolved in

toluene (150 mL). Water formed during the reaction was removed by use of a Dean–Stark apparatus. The mixture was heated to 110 °C, left overnight, and concentrated under reduced pressure. Purification was performed by silica gel chromatography (Ø = 3.2 cm, l = 43 cm; CH_2Cl_2) and crystallization from CH_2Cl_2/pentane to yield transparent crystals (2.74 g, 34% based on **1**). M.p. 110 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.72 (dd, ^3J = 7.3, ^4J = 1.8 Hz, 1 H), 7.37 (dd, ^3J = 7.4, ^4J = 1.9 Hz, 1 H), 7.32 (complex, 2 H), 7.14 (t, ^3J = 7.3 Hz, 1 H), 6.97 (td, ^3J = 7.7 Hz, 2 H), 3.76 (s, 3 H, OMe), 3.49 (s, 3 H, OMe), 1.36 (s, 12 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 136.0, 135.1, 131.8, 131.7, 128.5, 123.0, 120.1, 110.7, 83.5, 61.8, 55.5, 24.8 ppm. IR: $\tilde{\nu}$ = 3069, 2995, 2978, 2969, 2932, 1591, 1496, 1470, 1458, 1412, 1389, 1371, 1309, 1298, 1273, 1254, 1236, 1224, 1200, 1165, 1148, 1134, 1120, 1078, 1057, 1036, 1024, 1008 cm^{-1}. $C_{20}H_{25}BO_4$ (340.18): calcd. C 70.61, H 7.41; found C 70.43, H 7.41. MS (ES): calcd. for $[M + Li]^+$ 347.200, found 347.200. Crystals were obtained by slow diffusion of pentane into a CH_2Cl_2 solution of **2**. X-ray data for **2**: empirical formula: $C_{20}H_{25}BO_4$; formula mass: 340.21; crystal system: monoclinic; space group: $P2_1/c$; unit cell dimensions: a = 11.0075(5) Å, b = 11.3215(5) Å, c = 15.5545(12) Å; V = 1867.85(15) Å^3; Z = 4; density (calcd.): 1.201 Mg m^{-3}; crystal size: 0.18 × 0.14 × 0.12 mm; θ range for data collection: 2.88–27.59°; reflections collected: 16537; independent reflections: 4320 [R(int) = 0.0451]; refinement method: full-matrix least squares on F^2; data/restraints/parameters: 4320/0/232; goodness-of-fit on F^2: 1.025; final R indices [$I > 2\sigma(I)$]: $R1$ = 0.0425, $wR2$ = 0.0952; R indices (all data): $R1$ = 0.0759, $wR2$ = 0.1106.

2′,2″-Dimethoxy-1,1′:3′,1″-triphenyl (3): Under nitrogen, an aqueous solution of Na_2CO_3 (1 M, 15 mL) was transferred by cannula to toluene (40 mL) containing bromobenzene (2.79 mL, 2.65×10^{-2} mol) and tetrakis(triphenylphosphane)palladium(0) (70 mg, 0.06 mmol). After addition of an MeOH solution of **2** (1.5 g, 4.41×10^{-3} mol), the mixture was heated overnight at 110 °C. After cooling, the aqueous phase was extracted with CH_2Cl_2 (3×). The combined organic phases were dried with $MgSO_4$, concentrated under reduced pressure, and purified by silica gel chromatography (Ø = 3.2 cm, l = 24.5 cm; n-pentane/CH_2Cl_2, 50:50) to yield a white solid (1.14 g, 89%). M.p. 70 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.63–7.59 (complex, 2 H), 7.45–7.26 (complex, 7 H), 7.25–7.18 (complex, 2 H), 7.05–6.97 (complex, 2 H), 3.81 (s, 3 H, OMe), 3.18 (s, 3 H, OMe) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 157.0, 155.5, 139.1, 135.0, 132.6, 131.4, 131.0, 130.4, 129.2, 128.7, 128.3, 128.0, 127.1, 123.7, 120.5, 111.1, 60.4, 55.6 ppm. IR: $\tilde{\nu}$ = 3050, 3037, 2985, 2952, 2929, 2895, 2833, 1599, 1581, 1495, 1465, 1459, 1434, 1410, 1331, 1297, 1282, 1272, 1256, 1238, 1221, 1174, 1131, 1104, 1082, 1071, 1053, 1021, 1014, 1005 cm^{-1}. MS (ES): calcd. for $[M + Li]^+$ 297.146, found 297.145. $C_{20}H_{18}O_2$ (290.13): calcd. C 82.73, H 6.25; found C 80.66, H 6.25. Crystals were obtained by slow diffusion of pentane into a CH_2Cl_2 solution of **3** at +4 °C. X-ray data for **3**: empirical formula: $C_{20}H_{18}O_2$; formula mass: 290.34; crystal system: monoclinic; space group: $P2_1/c$; unit cell dimensions: a = 14.071(4) Å, b = 7.2788(19) Å, c = 15.767(5) Å; V = 1576.6(7) Å^3; Z = 4; density (calcd.): 1.223 Mg m^{-3}; crystal size: 0.06 × 0.04 × 0.03 mm; θ range for data collection: 2.65–27.51°; reflections collected: 10524; independent reflections: 3583 [R(int) = 0.0862]; refinement method: full-matrix least squares on F^2; data/restraints/parameters: 3583/0/201; goodness-of-fit on F^2: 1.246; final R indices [$I > 2\sigma(I)$]: $R1$ = 0.1005, $wR2$ = 0.1644; R indices (all data): $R1$ = 0.1500, $wR2$ = 0.1934.

Compound 4: The reaction was conducted under nitrogen. Compound **3** (1 g, 3.44×10^{-3} mol) and freshly distilled TMEDA (0.52 mL, 3.51×10^{-3} mol) were dissolved in dry diethyl ether (10 mL). The resulting mixture was cooled to –78 °C, and nBuLi solution (1.4 M, 3.3 mL, 4.13×10^{-3} mol) was added. After 5 min at –78 °C, the solution was allowed to come to room temperature and stirred for 3 h. The resulting solution was cooled again to –78 °C, and $B(OMe)_3$ (4.3 mL, 0.037 mol) was slowly added. A white precipitate appeared and redissolved when the reaction mixture was allowed to come to room temperature. After stirring at room temperature overnight, the reaction was quenched by addition of water (25 mL) at 0 °C. The mixture was then acidified with concentrated HCl to pH = 1, and diethyl ether was added (55 mL). The organic layer was isolated, dried with $MgSO_4$, and concentrated under reduced pressure. The resulting oil (1.68 g) was used directly in the next step without further characterization. The oil (1.68 g) and pinacol (1.19 g, 1.01×10^{-2} mol) were dissolved in toluene (35 mL). Water formed during the reaction was removed by use of a Dean–Stark apparatus. The mixture was heated to 110 °C, left overnight, and concentrated under reduced pressure. Purification was performed by silica gel chromatography (Ø = 3.2 cm, l = 21 cm; pentane/CH_2Cl_2, 70:30). Compound **4** was isolated as a yellowish solid (814 mg, 56% based on **3**). M.p. 169 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.74 (dd, ^3J = 7.3, ^4J = 1.9 Hz, 1 H), 7.61 (complex, 2 H), 7.50 (dd, ^3J = 7.6, ^4J = 1.9 Hz, 1 H), 7.44–7.30 (complex, 5 H), 7.18 (t, 1 H), 7.16 (t, 1 H), 3.60 (s, 3 H, OMe), 3.16 (s, 3 H, OMe), 1.37 (s, 12 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 136.3, 135.1, 134.9, 131.3, 130.4, 129.2, 128.2, 128.1, 127.0, 123.5, 123.1, 83.6, 62.0, 60.4, 24.9 ppm. IR: $\tilde{\nu}$ = 2977, 2930, 1592, 1497, 1461, 1413, 1389, 1358, 1306, 1263, 1226, 1142, 1114, 1078, 1044, 1004 cm^{-1}. MS (ES): calcd. for $[M + Li]^+$ 423.232, found 423.229. $C_{26}H_{29}BO_4$ (416.21): calcd. C 75.01, H 7.02; found C 75.03, H 7.34. Crystals were obtained by slow diffusion of hexane into a CH_2Cl_2 solution of **4**. X-ray data for **4**: empirical formula: $C_{26}H_{29}BO_4$; formula mass: 416.30; crystal system: monoclinic; space group: $P2_1/c$; unit cell dimensions: a = 7.1425(3) Å, b = 10.3652(4) Å, c = 31.1487(12) Å; V = 2303.17(16) Å^3; Z = 4; density (calcd.): 1.201 Mg m^{-3}; crystal size: 0.11 × 0.10 × 0.09 mm; θ range for data collection: 2.07–27.06°; reflections collected: 16081; independent reflections: 5297 [R(int) = 0.0412]; refinement method: full-matrix least squares on F^2; data/restraints/parameters: 5297/0/286; goodness-of-fit on F^2: 1.030; final R indices [$I > 2\sigma(I)$]: $R1$ = 0.0688, $wR2$ = 0.1467; R indices (all data): $R1$ = 0.0985, $wR2$ = 0.1600.

2′,2″,2‴,2⁗,2⁗′-Tetramethoxy-1,1′:3′,1″:3″,1‴:4‴,1⁗:3⁗,1⁗′:3⁗′,1⁗′′-heptaphenyl (5): The reaction was conducted under nitrogen. An aqueous solution of Na_2CO_3 (1 M, 15 mL) was first transferred by cannula into a degassed solution of 1,4-dibromobenzene (86 mg, 3.65×10^{-4} mol) and $Pd(PPh_3)_4$ (37 mg) in toluene (20 mL), followed by **4** (0.304 g, 7.30×10^{-4} mol) dissolved in MeOH (5 mL). The resulting mixture was then heated to 100 °C and left overnight. After cooling, the solution was filtered through Celite. The collected organic layers were combined, dried with $MgSO_4$, and concentrated under reduced pressure. The crude product was purified by silica gel chromatography (Ø = 3.2 cm, l = 23 cm; CH_2Cl_2) to afford **5** as a white solid (177 mg, 75%). M.p. 230 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.70 (s, 4 H), 7.63 (dd, ^3J = 8.1, ^4J = 1.2 Hz, 4 H), 7.46–7.32 (complex, 7 H), 7.27–7.20 (complex, 4 H), 3.32 (s, 6 H, OMe), 3.27 (s, 6 H, OMe) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 155.6, 155.5, 139.0, 137.7, 135.3, 134.9, 133.1, 131.0, 130.7, 129.4, 129.2, 128.3, 127.2, 123.8, 60.7, 38.4 ppm. IR: $\tilde{\nu}$ = 2932, 1560, 1509, 1459, 1410, 1226, 1079, 1002 cm^{-1}. MS (MALDI-TOF): calcd. for $[M]^+$ 654.277, found 654.282. $C_{46}H_{38}O_4$ (654.27): calcd. C 84.38, H 5.85; found C 83.01, H 5.59. X-ray data for **5**: empirical formula: $C_{46}H_{38}O_4$; formula mass: 654.76; crystal system: triclinic; space group: $P\bar{1}$; unit cell

dimensions: a = 7.2091(3) Å, b = 13.1829(4) Å, c = 19.46625(8) Å; V = 1711.78(18) Å^3; Z = 2; density (calcd.): 1.270 Mg m^{-3}; crystal size: 0.20 × 0.15 × 0.14 mm; θ range for data collection: 1.65–29.91°; reflections collected: 17330; independent reflections: 9789 [R(int) = 0.0306]; refinement method: full-matrix least squares on F^2; data/restraints/parameters: 9789/0/455; goodness-of-fit on F^2: 1.082; final R indices [$I > 2\sigma(I)$]: $R1$ = 0.0580, $wR2$ = 0.1155; R indices (all data): $R1$ = 0.1183, $wR2$ = 0.1251.

2′,2″,2‴,2⁗,2⁗′-Tetrahydroxy-1,1′:3′,1″:3″,1‴:4‴,1⁗:3⁗′,1⁗′:3⁗′,1⁗′′-heptaphenyl [L(OH)$_4$]: The reaction was conducted under nitrogen. Compound **5** (167 mg, 2.55 × 10^{-4} mol) was dissolved in anhydrous CH_2Cl_2 (20 mL). At –78 °C, BBr_3 (1 M in CH_2Cl_2, 1.32 mL) was added to the solution. The resulting mixture was allowed to come to room temperature and stirred for 12 h. Water (60 mL) was then added, and the organic layer was isolated, dried with $MgSO_4$, and concentrated under reduced pressure. The product was obtained as a yellowish solid (157 mg, quantitative). M.p. > 270 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.68 (s, 4 H), 7.58–7.34 (complex, 18 H), 7.15 (td, J = 5.3, J = 2.4 Hz, 4 H), 5.92 (s, 2 H, OH), 5.83 (s, 2 H, OH) ppm. ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 150.0, 149.7, 137.4, 136.9, 131.1, 138.7, 129.7, 129.5, 129.5, 129.3, 129.1, 128.8, 127.7, 125.2, 124.8, 121.4 ppm. IR: $\tilde{\nu}$ = 3521, 1444, 1427, 1325, 1217, 1166, 1071 cm^{-1}. MS (MALDI-TOF): calcd. for [M]$^+$ 598.214, found 598.208. $C_{42}H_{30}O_4$ (598.21)·CH_3OH (analyzed sample was obtained by crystallization from MeOH): calcd. C 81.35, H 5.17; found C 81.88, H 5.43. Crystals were obtained by slow diffusion of pentane into a CH_2Cl_2 solution of L(OH)$_4$. X-ray data for L(OH)$_4$: empirical formula: $C_{42}H_{30}O_4$; formula mass: 598.66; crystal system: triclinic; space group: $P\bar{1}$; unit cell dimensions: a = 5.6618(8) Å, b = 10.7721(15) Å, c = 12.4561(16) Å; V = 742.36(18) Å^3; Z = 1; density (calcd.): 1.339 Mg m^{-3}; crystal size: 0.05 × 0.03 × 0.03 mm; θ range for data collection: 2.36–27.06°; reflections collected: 8356; independent reflections: 3199 [R(int) = 0.0358]; refinement method: full-matrix least squares on F^2; data/restraints/parameters: 3199/0/211; goodness-of-fit on F^2: 1.039; final R indices [$I > 2\sigma(I)$]: $R1$ = 0.1100, $wR2$ = 0.2404; R indices (all data): $R1$ = 0.1625, $wR2$ = 0.2814.

4,4‴-Dibromo-2′,2″-dimethoxy-1,1′:3′,1″:3″,1‴-tetraphenyl (7): The reaction was conducted under nitrogen. A degassed toluene solution (80 mL) of 1-bromo-4-iodobenzene (5.62 g, 19.8 × 10^{-3} mmol) was placed in a 250 mL two-necked round-bottomed flask. $Pd(PPh_3)_4$ (3.6 mol-%) was then added, and a degassed aqueous solution of Na_2CO_3 (15 mL, 1 M) and a degassed solution of 2,2′-dimethoxy-1,1′-biphenyl-3,3′-bis(boronic acid) (0.5 g, 1.66 mmol) in methanol (30 mL) were transferred into the mixture by cannula. The resulting solution was heated to 120 °C and left for 22 h. After 6 h of heating, a further quantity of $Pd(PPh_3)_4$ (1.4 mol-%) was added to the reaction mixture. The solution was cooled to room temperature, and then water (150 mL) and dichloromethane (150 mL) were added. The organic layer was isolated, dried with $MgSO_4$, and concentrated under reduced pressure. The crude product was purified on silica gel (Ø = 3.5 cm, l = 30 cm; pentane/CH_2Cl_2, 70:30) to yield a white solid (59%). M.p. 177 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.61–7.49 (complex, 8 H), 7.37–7.32 (complex, 4 H), 7.23–7.20 (complex, 2 H), 3.25 (s, 6 H, OMe) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 137.7, 134.1, 133.0, 131.5, 131.4, 131.0, 130.5, 124.0, 121.5, 60.8, 29.9 ppm. IR: $\tilde{\nu}$ = 2931, 1490, 1454, 1415, 1385, 1227, 1173, 1075, 1009 cm^{-1}. MS (ES): calcd. for [M + H]$^+$ 524.988, found 525.030; calcd. for [M + Na]$^+$ 546.970, found 547.014; calcd. for [M + K]$^+$ 562.944, found 563.229. $C_{26}H_{20}Br_2O_2$ (521.98): calcd. C 59.57, H 3.85; found C 60.11, H 3.83. X-ray data for **7**: empirical formula: $C_{26}H_{20}Br_2O_2$; formula mass: 524.24; crystal system: monoclinic; space group: $C2/c$; unit cell dimensions: a = 30.8980(11) Å, b = 7.7851(4) Å, c = 23.5903(15); V = 4423.4(4) Å^3; Z = 4; density (calcd.): 1.574 Mg m^{-3}; crystal size: 0.12 × 0.06 × 0.06 mm; θ range for data collection: 2.75–27.54°; reflections collected: 17316; independent reflections: 5032 [R(int) = 0.0607]; refinement method: full-matrix least squares on F^2; data/restraints/parameters: 5032/0/273; goodness-of-fit on F^2: 1.005; final R indices [$I > 2\sigma(I)$]: $R1$ = 0.0433, $wR2$ = 0.0788; R indices (all data): $R1$ = 0.1054, $wR2$ = 0.0962.

2′,2″,2⁗,2⁗′,2⁗′′,2⁗′′′-Hexamethoxy-1,1′:3′,1″:3″,1‴:4‴,1⁗:3⁗′,1⁗′:3⁗′,1⁗′′:4⁗′′,1⁗′′′:3⁗′′′,1⁗′′′′:3⁗′′′′-decaphenyl (8): The reaction was conducted under nitrogen. $Pd(PPh_3)_4$ (26 mg) and an aqueous solution of Na_2CO_3 (6 mL, 1 M) was added to a degassed toluene solution of **7**. The resulting mixture was stirred for 30 min, and compound **4** dissolved in a degassed mixture of toluene/MeOH (5:3, 8 mL), was added. The reaction mixture was heated at 90 °C for 24 h, and a further addition of $Pd(PPh_3)_4$ catalyst (20 mg) was performed. The mixture was heated for an additional 12 h. The reaction mixture was then cooled to room temperature, and then water and dichloromethane were added. The organic layer was isolated, dried with $MgSO_4$ and concentrated under reduced pressure. The crude material was purified on silica gel (pentane/CH_2Cl_2, 70:30) to yield a white solid (30%). M.p. > 270 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.70–7.21 (complex), 3.33 (s, 3 H, OMe), 3.32 (s, 3 H, OMe), 3.27 (s, 3 H, OMe) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 155.5, 155.4, 138.8, 137.6, 135.1, 134.8, 133.0, 132.9, 130.9, 130.6, 129.2, 129.1, 128.2, 127.0, 123.6, 60.6 ppm. IR: $\tilde{\nu}$ = 3054, 3025, 2933, 2820, 1463, 1455, 1410, 1392, 1386, 1227, 1078, 1013, 1003 cm^{-1}. MS (MALDI-TOF): calcd. for [M]$^+$ 942.392, found 942.345. $C_{66}H_{54}O_6$ (942.39): calcd. C 84.05, H 5.77; found C 84.30, H 8.40.

2′,2″,2⁗,2⁗′,2⁗′′,2⁗′′′-Hexahydroxy-1,1′:3′,1″:3″,1‴:4‴,1⁗:3⁗′,1⁗′:3⁗′,1⁗′′:4⁗′′,1⁗′′′:3⁗′′′,1⁗′′′′:3⁗′′′′-decaphenyl [L(OH)$_6$]: The reaction was conducted under nitrogen. Compound **8** (41 mg, 4.35 × 10^{-5} mol) was dissolved in anhydrous CH_2Cl_2 (10 mL). At –78 °C, BBr_3 (1 M in CH_2Cl_2, 0.4 mL) was added to the solution. The resulting mixture was allowed to come to room temperature and stirred for 54 h. Water (30 mL) and dichloromethane (60 mL) were then added. The organic layer was isolated, dried with $MgSO_4$, and concentrated under reduced pressure. The resulting solid was then taken up with THF and precipitated with pentane to afford a poorly soluble compound as yellowish solid. L(OH)$_6$ was obtained in 76% yield. M.p. > 270 °C. ^{1}H NMR (400 MHz, [D$_8$]THF): δ = 7.90 (2 br. s, 4 H), 7.78 (br. s, 2 H), 7.73 (s, 8 H), 7.66 (multiplet, 4 H), 7.4 (complex, 8 H), 7.25 (complex, 10 H), 7.15 (complex, 6 H) ppm. ^{13}C NMR (75 MHz, [D$_8$]THF): δ = 149.8, 135.3, 129.2, 128.3, 127.6, 127.3, 126.0, 125.9, 125.5, 125.4, 125.4, 124.6, 123.1, 118.6 ppm. IR: $\tilde{\nu}$ = 3496, 3375, 2956, 2926, 1440, 1426, 1359, 1247, 1214, 1181, 1172, 1130, 1086 cm^{-1}. HRMS (ESI): calcd. for $C_{60}H_{42}NaO_6$ [M]$^+$ 881.287, found 881.291. $C_{60}H_{42}O_6$ (858.30)·2CH_2Cl_2: calcd. C 72.38, H 4.51; found C 73.44, H 6.17.

Optimized One-Pot Procedure: The reaction was conducted under nitrogen. 1,4-Dibromobenzene (260 mg, 1.1 10^{-3} mol) and bromobenzene (0.240 mL, 2.27 10^{-3} mol) in toluene (80 mL) were placed in a three-necked flask (250 mL), followed by $Pd(PPh_3)_4$ (140 mg). An aqueous solution of Na_2CO_3 (30 mL, 1 M) and a solution of **6** (1 g, 0.003 mol) in methanol (60 mL) were then transferred into the mixture by cannula. The reaction mixture was heated at 50 °C for 5 h, and further $Pd(PPh_3)_4$ (70 mg) was added. The reaction was monitored by TLC analysis (SiO_2; n-pentane/CH_2Cl_2,50:50), and after a total of 48 h, the mixture was allowed to come to room temperature and filtered through Celite. Next, dichloromethane

(50 mL) and methanol (60 mL) were added. The organic layer was isolated, dried with Na_2CO_3, and concentrated under reduced pressure. Compounds **9**, **5**, and **8** were isolated by purification by silica gel chromatography (Ø = 5.5 cm, *l* = 25 cm; pentane/CH_2Cl_2,50:50). **9**: 19% yield, R_f = 0.52 (SiO_2; pentane/CH_2Cl_2,50:50); **5**: 11%, R_f = 0.37 (SiO_2; pentane/CH_2Cl_2, 50:50); **8**: 9%, R_f = 0.33 (SiO_2; pentane/CH_2Cl_2,50:50).

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