Synthesis of Symmetrically and Unsymmetrically *para*-Functionalized *p*-Quaterphenylenes

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Abstract: Oligo-*p*-phenylenes have proven to be versatile building blocks for the generation of self-assembled nanoaggregates with interesting optical properties via vapor deposition on solid supports. Preliminary studies have shown that both the properties and the morphologies of these aggregates can be influenced by the introduction of functional groups. To this end, we have developed general approaches to the synthesis of symmetrically and unsymmetrically 1,4‴-substituted *p*-quaterphenylenes through the application of a reliable Suzuki cross-coupling strategy.

Key words: cross-coupling reaction, oligo-*p*-phenylenes, rod-like molecules, Suzuki

Materials built up of π-conjugated systems have developed tremendously recently due to their interesting optical, electrical and optoelectrical properties.[1] The use of organic, rather than inorganic compounds to fabricate nanostructures usually has the advantage of providing higher luminescence efficiency at the same material density, more flexible spectroscopic properties and, in general, easier and cheaper processing. Rod-like molecules[2] such as oligothiophenes,[1b,3] perylenes,[4] pentacenes,[5] and oligo-*p*-phenylenes[6,7] have been particularly studied in this context.[8] Among these, the latter type, especially *p*-hexaphenylene, has been found to form very interesting needle-like aggregates upon vapor deposition by a sophisticated high-vacuum surface growth process.[7b,c,9] Owing to their typical nanometer-scale height, and lengths of up to one millimeter, the fibers bridge the gap between microscopic and macroscopic dimensions. These nanofibers show high quantum yields of anisotropic blue luminescence, which makes them promising candidates as new building blocks for optoelectronic devices such as organic light emitting diodes (OLEDs). Waveguides,[10,11] as well as ultraviolet-light pumped organic nanolasers[12] are other potential applications. In addition, electrical properties have been investigated[13,14,15] in view of the potential applications of nanofibers in organic field-effect transistors (OFETs) or electroluminescent nanolasers.

As the shape of the molecular building blocks is altered, the alignment of the nanofibers also change. Chemical functionalization of the molecular building blocks would thus allow access to a range of new materials. Recently, we found that 1,4‴-dimethoxy- and 1,4‴-dichloro-substituted *p*-quaterphenylenes also form mutually aligned nanofibers on muscovite mica substrate under appropriately controlled growth conditions. The linear optical properties and morphologies of these structures were determined by the functional group,[16] which opens up a new dimension to the control of nanoaggregates of photonic importance.

In a next step, well-organized nanoaggregates have been grown on muscovite mica from unsymmetrically functionalized *p*-quaterphenylenes, which are expected to have increased nonlinear optical properties. Such an increase in nonlinear optical activity has indeed been shown by measuring the optical second harmonic generation (SHG) after excitation with near infrared femtosecond laser pulses: the nanofibers act as frequency doublers.[17] Upon irradiation, a strong, true SH peak was observed originating from the bulk of the nanofibers. Thus, these nanoscaled frequency doublers constitute promising candidates for use in devices for up-conversion of light emitted from sub-micronscaled infrared light sources.

Here, we report on the synthesis of a number of these symmetrically and unsymmetrically 1,4‴-disubstituted oligo-*p*-phenylenes via Suzuki cross-coupling reactions. Although the non-substituted *p*-quaterphenylene has been known for more than 125 years[18] and, like its higher oligomers, is even commercially available, 1,4‴-disubstituted derivatives, especially unsymmetrically functionalized compounds, are still rare. This is mainly due to the notoriously low solubility of these compounds that severely restricts (regio)selective functionalization.[19] In order to gain access to substances with a defined substitution pattern it is therefore necessary to initially introduce the desired functional groups into smaller building blocks and then use these precursors to synthesize the *p*-quaterphenylene scaffold. In the past this was achieved by cyclotrimerizations of acetylenes,[20] Diels–Alder reactions of cyclopentadienones and subsequent aromatization,[21] Wittig reactions of cinnamaldehydes followed by Diels–Alder reactions with acetylenic dicarboxylates and subsequent aromatization,[22] addition of Grignard reagents to arines,[23] Grignard reactions with *p*-quinones and subsequent dehydration,[24] or Ullmann-type coupling reactions.[25]

Modern transition-metal-catalyzed homo- and cross-coupling reactions, however, have become ever more

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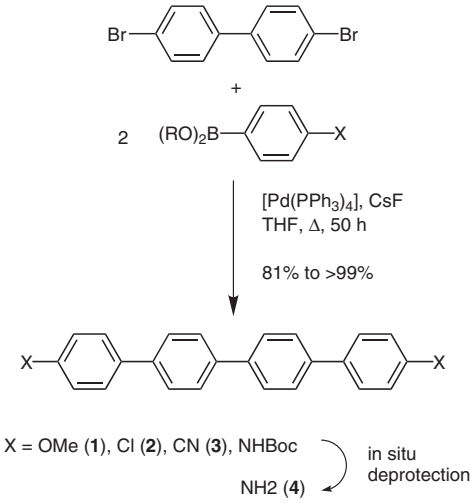
popular over the last 30 years[26] and, today, have come to dominate the synthesis of oligophenylenes. Kharash- and Suzuki-type couplings using Grignard reagents, arylboronic acids or esters, especially, have been used very successfully in this context.[27,28,29] Although most of the compounds prepared in this way carry long alkyl or alkoxy groups that ensure solubility in common organic solvents, a few unmodified 1,4‴-disubstituted *p*-quaterphenylenes could also be prepared.[27b,c,30]

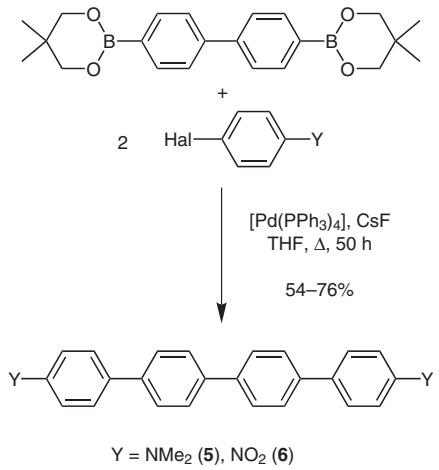
We thus followed a similar approach for our purposes, using Suzuki cross-coupling reactions as the key steps in the synthesis of our target compounds.

Symmetrically substituted compounds were synthesized in a two-fold Suzuki cross-coupling reaction from commercially available *p*-substituted phenylboronic acids (or esters) and 4,4′-dibromobiphenyl or from 4,4′-biphenylbisboronic acid ester and a *p*-substituted arylhalide. Tetrakis(triphenylphosphino)palladium was used as catalyst (5 mol%) in anhyd THF, together with cesium fluoride as base (Scheme 1 and Scheme 2). The desired products were obtained in 54% (**6**), 76% (**5**), 81% (**3**), 92% (**2** and **4**, including in situ deprotection of the amino group in the latter case) and quantitative yield (**1**), after heating at reflux for 50 hours.

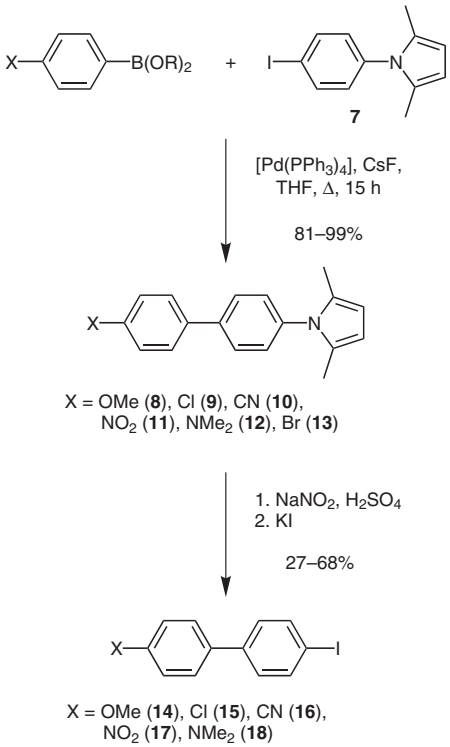


Scheme 1 Synthesis of symmetrically 1,4‴-disubstituted *p*-quaterphenylenes **1**–**4** from 4,4′-dibromobiphenyl and *p*-substituted phenylboronic acid derivatives

The preparation of unsymmetrically disubstituted derivatives was achieved in a multi-step synthesis involving three Suzuki cross-coupling reactions and an iodination as the key steps. The synthesis starts with building block **7**, which consists of a single phenyl ring substituted with a protective group and a *para*-substituted reactive group. Further phenyl rings are added stepwise at the reactive center, using Suzuki cross-coupling reactions, to finally give the *p*-quaterphenylene core bearing functional groups at the 1,4‴-positions (Scheme 3, Scheme 4, and Scheme 5).

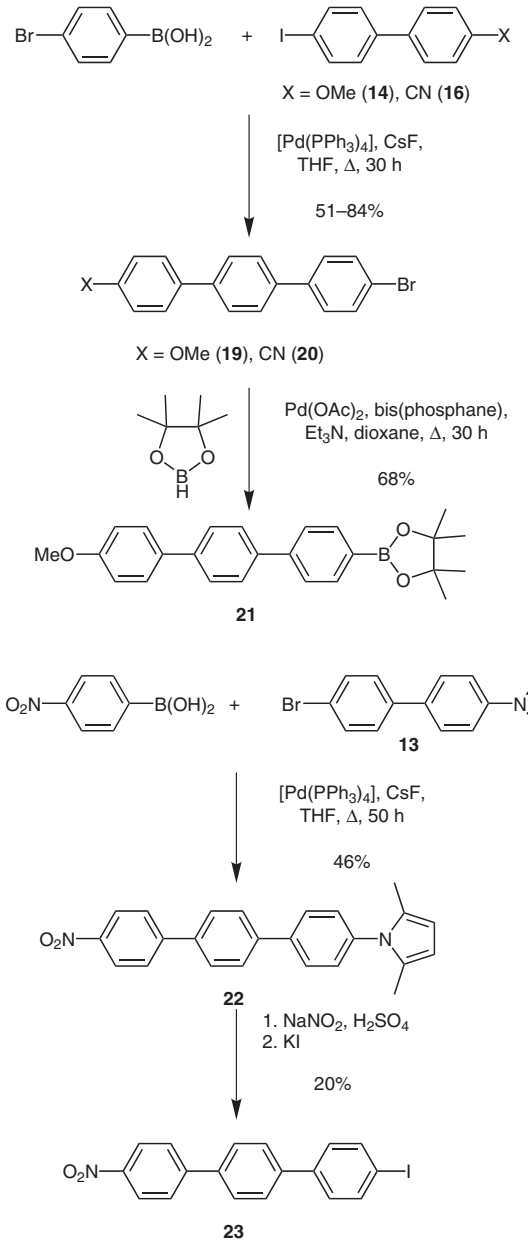


Scheme 2 Synthesis of symmetrically 1,4‴-disubstituted *p*-quaterphenylenes **5** and **6** from biphenyl-4,4′-diboronic acid ester and *p*-substituted phenyl halides



Scheme 3 Synthesis of unsymmetrically 4,4′-disubstituted biphenyl building blocks **8**–**18** (R = H or alkyl)

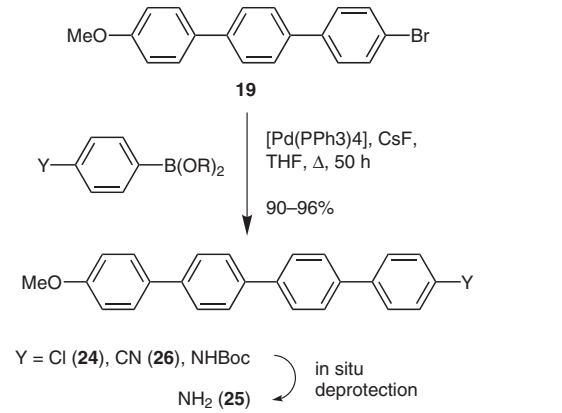
This strategy has the advantage of allowing access to a variety of *p*-quaterphenylenes, with different combinations of functional groups, from the same precursors. Furthermore, it is flexible in the sense that the sequence of Suzuki coupling and iodination reactions can be changed or additional functional group manipulations, such as palladium catalyzed borylations of halogenated compounds, can be performed to synthesize other functionalized oligo-*p*-phenylenes. Such an approach is depicted in Scheme 4.



Scheme 4 Synthesis of unsymmetrically 1,4″-disubstituted *p*-terphenylene building blocks **19**–**23**

Since we have already shown that the methoxy group is tolerated in the formation of nanofiber-like structures, we prepared three different compounds **24**–**26**, also carrying a methoxy group at the 1-position, and a chloro, amino or cyano substituent in the 4‴-position as a first set of unsymmetrically substituted *p*-quaterphenylenes in 90% (**25**), 92% (**24**), and 96% (**26**) yield (Scheme 5).

As in the case of the symmetrical analogues, the final products precipitated from the reaction mixture and were purified by repeated washing with water and organic solvents. However, this process led to retention of residual water and organic solvents in the products which could only be removed by out-gassing under ultrahigh vacuum. Nevertheless, the desired functionalized compounds were



Scheme 5 Synthesis of unsymmetrically 1,4‴-disubstituted *p*-quaterphenylenes **24**–**26** from *p*-terphenylene **19** (R = H or alkyl)

obtained in sufficient purity for the vapor deposition experiments.

In conclusion we have developed a versatile new approach to the synthesis of symmetrically and unsymmetrically 1,4‴-disubstituted *p*-quaterphenylenes employing Suzuki cross-coupling reactions. These constitute promising molecular building blocks for the formation of defined nanoaggregates via vapor deposition techniques.

Solvents were dried, distilled and stored under argon according to standard procedures. Reactions with air- and moisture-sensitive transition-metal compounds were performed under an argon atmosphere in oven-dried glassware using standard Schlenk techniques.

Thin-layer chromatography was performed on aluminum TLC plates (silica gel 60 F_{254}) from Merck and the products were visualized under UV-light (254 or 366 nm). Products were purified either by column chromatography on silica gel 60 (70–230 mesh or 230–400 mesh) from Merck or by extraction and washing procedures. ^{1}H NMR and ^{13}C NMR spectra were recorded at 300 K in $CDCl_3$ solutions on a Bruker Avance 500 spectrometer at 500 MHz and 125 MHz, respectively. ^{1}H NMR and ^{13}C NMR chemical shifts are reported on the δ-scale in ppm relative to residual non-deuterated solvent as internal standard. Mass spectra were recorded on a Finnigan MAT 95 with data system DEC-Station 5000 (EI, HiRes-EI, CI, HiRes-CI, isobutane or NH_3). UV/Vis spectra were measured on a Jena Analytic Specord 200 spectrometer in a 1 cm quartz cuvette. Since all of the *p*-quaterphenylenes were obtained as amorphous solids they generally did not give satisfactory elemental analyses due to residual amounts of solvents within the powder-like solids. Unfortunately, these could not be completely removed even after heating for longer periods of time under standard laboratory high vacuum (10^{-3} mbar). Thus, we give high-resolution MS data instead.

4,4,5,5-Tetramethyl-1,3,2-dioxaborolane, 4-bromophenylboronic acid, 4-chlorophenylboronic acid, 4-methoxyphenylboronic acid, 4-nitrophenylboronic acid, 4-cyanophenylboronic acid, *tert*-butyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenylcarbamate, 1-(diphenylphosphino)-2-[2-(diphenylphosphino)phenoxy]benzene, 4,4′-biphenyldiboronic acid bis(neopentylglycol)ester, 4,4′-dibromobiphenyl, 4-iodonitrobenzene, cesium fluoride, and tetrakis(triphenylphosphino)palladium(0) [$Pd(PPh_3)_4$] were purchased from ABCR, Sigma–Aldrich, or Atlantic Scientific Co. and used as received. 4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolyl)-*N*,*N*-di-

methylaniline[31] and 4-(2,5-dimethyl-1*H*-pyrrol-1-yl)iodobenzene (**7**)[32] were prepared following published procedures.

Synthesis of 2,5-Dimethyl-1*H*-pyrrole Protected 4-Aminobiphenyls: General Procedure 1 (GP1)

A two-neck flask equipped with a condenser was charged with 4-(2,5-dimethyl-1*H*-pyrrol-1-yl)iodobenzene (**7**; 600 mg, 2.0 mmol), a 4-substituted phenylboronic acid or ester (2.1 mmol, 1.05 equiv), CsF (912 mg, 6.0 mmol, 3 equiv) and $[Pd(PPh_3)_4]$ (69 mg, 0.06 mmol, 3 mol% Pd) and the solids were dissolved in anhyd THF (40 mL) under an argon atmosphere. The solution was refluxed for 15 h then allowed to cool to r.t., diluted with CH_2Cl_2 (50 mL) and washed with H_2O. The organic layer was taken, dried (Na_2SO_4) and concentrated in vacuo. The resulting residue was purified by column chromatography on silica to obtain the desired functionalized biphenyl.

4-(2,5-Dimethyl-1*H*-pyrrole)-4′-methoxybiphenyl (8)

Treatment of 4-methoxyphenylboronic acid with **7** according to GP1 gave **8** after purification by column chromatography (*n*-hexane–EtOAc, 3:1).

Yield: 549 mg (99%).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.07 (6 H, s), 3.86 (3 H, s), 5.92 (2 H, s), 7.00 (2 H, d, *J* = 8.7 Hz), 7.24 (2 H, d, *J* = 8.2 Hz), 7.57 (2 H, d, *J* = 8.7 Hz), 7.62 (2 H, d, *J* = 8.2 Hz).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.1, 55.3, 105.7, 114.3, 127.1, 128.1, 128.4, 128.8, 132.7, 137.5, 140.1, 159.4.

MS (CI, isobutane): *m*/*z* = 278.2 [M + H$^+$].

HRMS (EI): *m*/*z* calcd for $C_{19}H_{19}NO$: 277.1467; found: 277.1467.

4-(2,5-Dimethyl-1*H*-pyrrole)-4′-chlorobiphenyl (9)

Treatment of 4-chlorophenylboronic acid with **7** according to GP1 gave **9** after purification by column chromatography (*n*-hexane–EtOAc, 3:1).

Yield: 535 mg (95%).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.12 (6 H, s), 5.98 (2 H, s), 7.32 (2 H, d, *J* = 8.3 Hz), 7.47 (2 H, d, *J* = 8.5 Hz), 7.59 (2 H, d, *J* = 8.5 Hz), 7.67 (2 H, d, *J* = 8.3 Hz).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.0, 105.9, 127.5, 128.3, 128.5, 128.7, 128.9, 133.7, 138.4, 138.6, 139.1.

MS (CI, isobutane): *m*/*z* = 282.2 [M + H$^+$].

HRMS (EI): *m*/*z* calcd for $C_{18}H_{16}ClN$: 281.0971; found: 281.0971.

4-(2,5-Dimethyl-1*H*-pyrrole)-4′-cyanobiphenyl (10)

Treatment of 4-cyanophenylboronic acid with **7** according to GP1 gave **10** after purification by column chromatography (*n*-hexane–EtOAc, 3:1).

Yield: 502 mg (92%).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.10 (6 H, s), 5.95 (2 H, s), 7.34 (2 H, d, *J* = 8.3 Hz), 7.70 (2 H, d, *J* = 8.3 Hz), 7.75 (2 H, d, *J* = 8.5 Hz), 7.77 (2 H, d, *J* = 8.3 Hz).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.0, 105.9, 111.2, 118.6, 127.6, 127.8, 128.6, 128.8, 132.6, 138.2, 139.3, 144.5.

MS (EI): *m*/*z* = 272.1 [M$^{+\cdot}$].

HRMS (EI): *m*/*z* calcd for $C_{19}H_{16}N_2$: 272.1313; found: 272.1314.

4-(2,5-Dimethyl-1*H*-pyrrole)-4′-nitrobiphenyl (11)

Treatment of 4-nitrophenylboronic acid with **7** according to GP1 gave **11** after purification by column chromatography (*n*-hexane–EtOAc, 3:1).

Yield: 473 mg (81%).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.09 (6 H, s), 5.94 (2 H, s), 7.35 (2 H, d, *J* = 8.3 Hz), 7.73 (2 H, d, *J* = 8.3 Hz), 7.79 (2 H, d, *J* = 8.8 Hz), 8.33 (2 H, d, *J* = 8.8 Hz).

^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 13.0, 106.2, 124.2, 127.8, 128.0, 128.7, 128.8, 137.9, 139.7, 146.5, 147.3.

MS (CI, isobutane): *m*/*z* = 293.3 [M + H$^+$].

HR-MS (EI): *m*/*z* calcd for $C_{18}H_{16}N_2O_2$: 292.1212; found: 292.1211.

4-(2,5-Dimethyl-1*H*-pyrrole)-4′-*N*,*N*-dimethylaminobiphenyl (12)

Treatment of 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolyl)-*N*,*N*-dimethylaniline with **7** according to GP1 gave **12** after purification by column chromatography (*n*-hexane–EtOAc, 3:1 + 0.5% Et_3N).

Yield: 540 mg (93%).

^{1}H NMR (500 MHz, $CDCl_3$,): δ = 2.09 (6 H, s), 3.02 (6 H, s), 5.93 (2 H, s), 6.83 (2 H, d, *J* = 8.7 Hz), 7.23 (2 H, d, *J* = 8.3 Hz), 7.56 (2 H, d, *J* = 8.7 Hz), 7.63 (2 H, d, *J* = 8.3 Hz).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.1, 40.5, 105.5, 112.7, 126.6, 127.6, 128.0, 128.3, 128.9, 136.8, 140.5, 150.1.

MS (CI, isobutane): *m*/*z* = 291.1 [M + H$^+$], 198.1 [M – C_6H_7N]$^+$.

HRMS (EI): *m*/*z* calcd for $C_{20}H_{22}N_2$: 290.1783; found: 290.1788.

4-(2,5-Dimethyl-1*H*-pyrrole)-4′-bromobiphenyl (13)

Treatment of 4-chlorophenylboronic acid with **7** according to GP1 gave **13** after purification by column chromatography (*n*-hexane–EtOAc, 3:1).

Yield: 639 mg (98%).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.07 (6 H, s), 5.92 (2 H, s), 7.27 (2 H, d, *J* = 8.3 Hz), 7.49 (2 H, d, *J* = 8.5 Hz), 7.59 (2 H, d, *J* = 8.3 Hz), 7.63 (2 H, d, *J* = 8.3 Hz).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.0, 105.9, 121.9, 127.5, 128.6, 128.7, 128.8, 131.9, 138.5, 139.0, 139.2.

MS (CI, isobutane): *m*/*z* = 326.1 [M + H$^+$], 328.1 [M + H$^+$].

HRMS (EI): *m*/*z* calcd for $C_{18}H_{16}BrN$: 325.0466; found: 325.0467.

Synthesis of 4-Iodobiphenyls from 4-Aminobiphenyls: General Procedure 2 (GP2)

A 4′-substituted 4-(2,5-dimethyl-1*H*-pyrrol-1-yl)biphenyl (1.9 mmol) was dissolved in a mixture of H_2SO_4 (2 N, 20 mL) and MeCN (20 mL) and the solution was cooled to –5 °C. $NaNO_2$ (400 mg, 5.9 mmol, 3 equiv) dissolved in H_2O (5 mL) was added dropwise at the same temperature. After stirring for 30 min, NaI (1.30 g, 7.6 mmol, 4 equiv) dissolved in H_2O (5 mL) was added dropwise at –5 °C then the reaction was allowed to warm to r.t. over 1 h. The reaction mixture was briefly heated to 60 °C then stirred at r.t. for 5 h. After neutralization with sat. aq Na_2CO_3, the mixture was repeatedly extracted with CH_2Cl_2 and the combined organic layers were washed with H_2O (100 mL), aq $Na_2S_2O_3$ (1 M, 2 × 100 mL) and H_2O (100 mL), dried (Na_2SO_4) and concentrated in vacuo. The crude product was purified by flash chromatography on silica (*n*-hexane–EtOAc, 3:1).

4-Iodo-4′-methoxybiphenyl (14)[25,33]

Treatment of **8** according to GP2 gave **14**.

Yield: 324 mg (55%); yellow microcrystalline solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.84 (3 H, s), 6.96 (2 H, d, *J* = 8.7 Hz), 7.27 (2 H, d, *J* = 8.3 Hz), 7.47 (2 H, d, *J* = 8.7 Hz), 7.72 (2 H, d, *J* = 8.3 Hz).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 55.3, 92.1, 114.3, 127.9, 128.6, 132.5, 137.7, 140.3, 159.4.

MS (EI): *m*/*z* = 310.0 [$M^{+\cdot}$], 184.1 [M – I]$^+$.

HRMS (EI): *m*/*z* calcd for $C_{13}H_{11}IO$: 309.9854; found: 309.9853.

4-Chloro-4′-iodobiphenyl (15)[34]
Treatment of **9** according to GP2 gave **15** (191 mg, 0.61 mmol, 32%).

The analytical data were in agreement with those published by R. N. Young.[33a]

4-Cyano-4′-iodobiphenyl (16)[35]
Treatment of **10** according to GP2 gave **16**.

Yield: 336 mg (58%).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.31 (2 H, d, *J* = 8.4 Hz), 7.63 (2 H, d, *J* = 8.3 Hz), 7.72 (2 H, d, *J* = 8.3 Hz), 7.80 (2 H, d, *J* = 8.4 Hz).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 94.8, 111.3, 118.6, 127.4, 128.9, 132.6, 138.2, 138.5, 144.4.

MS (CI, isobutane): *m*/*z* = 306.2 [M + H$^+$], 280.2 [M – I + H]$^+$.

HRMS (CI, isobutane): *m*/*z* calcd for $C_{13}H_9IN$: 305.9779; found: 305.9779.

4-Iodo-4′-nitrobiphenyl (17)[25,36]
Treatment of **11** according to GP2 gave **17**.

Yield: 167 mg (27%).

^{1}H NMR (500 MHz $CDCl_3$): δ = 7.35 (2 H, d, *J* = 8.3 Hz), 7.70 (2 H, d, *J* = 8.8 Hz), 7.83 (2 H, d, *J* = 8.3 Hz), 8.29 (2 H, d, *J* = 8.8 Hz).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 95.1, 124.2, 127.6, 129.0, 138.2, 138.3, 146.4, 147.3.

MS (CI, isobutane): *m*/*z* = 326.1 [M + H$^+$], 200.1 [M – I + H]$^+$.

HRMS (CI, isobutane): *m*/*z* calcd for $C_{12}H_9NO_2I$: 325.9678; found: 325.9678.

4-*N*,*N*-Dimethylamino-4′-iodobiphenyl (18) [37]
Treatment of **12** according to GP2 but using 3 N H_2SO_4 instead of 2 N gave **18** after purification by flash chromatography (*n*-hexane–EtOAc, 3:1 + 0.5% Et_3N).

Yield: 443 mg (68%).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.99 (6 H, s), 6.78 (2 H, d, *J* = 8.7 Hz), 7.29 (2 H, d, *J* = 8.3 Hz), 7.45 (2 H, d, *J* = 8.7 Hz), 7.69 (2 H, d, *J* = 8.3 Hz).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 40.4, 91.1, 112.7, 125.9, 127.4, 128.1, 137.6, 140.7, 150.2.

MS (CI, isobutane): *m*/*z* = 323.9 [M + H$^+$], 198.1 [M – I + H]$^+$.

HRMS (EI): *m*/*z* calcd for $C_{14}H_{14}NI$: 323.0171; found: 323.0170.

1-Bromo-4″-methoxy-4,1′:4′,1″-terphenylene (19)
Under an argon atmosphere, **14** (700 mg, 2.25 mmol), 4-bromophenylboronic acid (452 mg, 2.4 mmol, 1.1 equiv), CsF (1026 mg, 6.75 mmol, 3.0 equiv) and [$Pd(PPh_3)_4$] (78 mg, 0.067 mmol, 3 mol% Pd) were dissolved in anhyd THF (50 mL) and the mixture was refluxed for 30 h. After cooling to r.t. the reaction mixture was diluted with *n*-hexane (20 mL) and H_2O (20 mL) and the precipitate was collected by filtration. The crude product was thoroughly washed with THF, EtOAc, and H_2O to give **19** (641 mg, 1.89 mmol, 84%) as a light brown amorphous solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.85 (3 H, s), 6.99 (2 H, d, *J* = 8.4 Hz), 7.48 (2 H, d, *J* = 8.2 Hz), 7.56 (4 H, d, *J* = 8.2 Hz), 7.59 (2 H, d, *J* = 8.2 Hz), 7.62 (2 H, d, *J* = 8.2 Hz).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 55.3, 114.3, 121.4, 127.1, 127.2, 128.0, 128.4, 131.9, 133.0, 138.2, 139.1, 140.1, 159.3.

MS (CI, isobutene): *m*/*z* = 339.1 [M + H$^+$], 340.1 [M + H$^+$].

HRMS (EI): *m*/*z* calcd for $C_{19}H_{15}BrO$: 338.0306; found: 338.0305.

1-Cyano-4″-bromo-4,1′:4′,1″-terphenylene (20)[38]
Under an argon atmosphere, **16** (470 mg, 1.5 mmol), 4-bromophenylboronic acid (452 mg, 1.6 mmol, 1.1 equiv), CsF (684 mg, 4.5 mmol, 3.0 equiv), and [$Pd(PPh_3)_4$] (52 mg, 0.045 mmol, 3 mol% Pd) were dissolved in anhyd THF (50 mL) and refluxed for 30 h. After cooling to r.t. the reaction mixture was diluted with *n*-hexane (20 mL) and H_2O (20 mL) and the precipitate was collected by filtration. The crude product was thoroughly washed with THF, EtOAc, and H_2O to give **20** (255 mg, 0.76 mmol, 51%) as a colorless amorphous solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.49 (2 H, d, *J* = 8.5 Hz), 7.58 (2 H, d, *J* = 8.5 Hz), 7.66 (4 H, s), 7.71 (2 H, d, *J* = 8.6 Hz), 7.73 (2 H, m).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 111.1, 118.8, 122.0, 127.5, 127.6, 127.7, 128.6, 132.0, 132.6, 138.3, 139.1, 140.3, 144.9.

MS (EI): *m*/*z* = 332.6 [M$^+$], 334.6 [M$^+$].

HRMS (EI): *m*/*z* calcd for $C_{19}H_{12}Br$: 333.0153; found: 333.0152.

1-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolyl)-4″-methoxy-4,1′:4′,1″-terphenylene (21)
A two-neck flask was charged with **19** (244 mg, 0.72 mmol), $Pd(OAc)_2$ (8 mg, 0.036 mmol, 5 mol% Pd) and 1-(diphenylphosphino)-2-[2-(diphenylphosphino)phenoxy]benzene (39 mg, 0.072 mmol, 10 mol%) under an argon atmosphere. Anhyd 1,4-dioxane (20 mL), anhyd Et_3N (0.4 mL, 2.9 mmol, 4 equiv), and 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.21 mL, 1.44 mmol, 2 equiv) were added via syringe. The reaction mixture was heated to 100 °C for 30 h, then allowed to cool to r.t. and quenched with sat. aq NH_4Cl (20 mL). The aqueous phase was extracted repeatedly with CH_2Cl_2 and the organic phases were combined, dried (Na_2SO_4) and concentrated in vacuo. The crude product was purified by column chromatography on silica (*n*-hexane–EtOAc,1:1 + 5% Et_3N) to give **23**.

Yield: 188 mg (68%); fawn solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.38 (12 H, s), 3.86 (3 H, s), 7.00 (2 H, d, *J* = 8.3 Hz), 7.59 (2 H, d, *J* = 8.3 Hz), 7.63–7.70 (6 H, m), 7.92 (2 H, d, *J* = 7.8 Hz).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 24.8, 55.3, 83.7, 114.2, 127.0, 127.5, 128.0, 128.0, 133.1, 134.7, 135.2, 140.0, 140.7, 143.3, 159.2.

MS (CI, isobutene): *m*/*z* = 387.5 [M + H$^+$].

HRMS (EI): *m*/*z* calcd for $C_{25}H_{27}BO_3$: 386.2053; found: 386.2052.

1-(2,5-Dimethyl-1*H*-pyrrole)-4″-nitro-4,1′:4′,1″-terphenylene (22)
Under an argon atmosphere, **13** (620 mg, 1.9 mmol), 4-nitrophenylboronic acid (350 mg, 2.0 mmol, 1.05 equiv), CsF (866 mg, 5.7 mmol, 3.0 equiv) and [$Pd(PPh_3)_4$] (66 mg, 0.057 mmol, 3 mol% Pd) were dissolved in anhyd THF (50 mL) and refluxed for 30 h. After this time, the reaction mixture was diluted with CH_2Cl_2 (50 mL), washed with H_2O (2 × 100 mL), dried (Na_2SO_4) and concentrated in vacuo. The crude product was purified by flash chromatography on silica (*n*-hexane–EtOAc–CH_2Cl_2, 10:5:1 + 5% Et_3N) to give **21**.

Yield: 320 mg (46%); brown amorphous solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.09 (6 H, s), 5.93 (2 H, s), 7.31 (2 H, d, *J* = 8.2 Hz), 7.72 (2 H, d, *J* = 8.2 Hz), 7.75 (4 H, d, *J* = 6.9 Hz), 7.80 (2 H, d, *J* = 8.8 Hz), 8.32 (2 H, d, *J* = 8.8 Hz).

^{13}C NMR ($CDCl_3$, 125 MHz): δ = 13.1, 105.9, 124.2, 127.6, 127.6, 127.8, 127.9, 128.9, 137.9, 138.7, 139.4, 140.8, 146.9, 147.2.

MS (EI): m/z = 368.1 [M^+], 275.1 [$M - C_6H_7N]^+$.

HRMS (EI): m/z calcd for $C_{24}H_{20}N_2O_2$: 368.1524; found: 368.1521.

1-Iodo-4″nitro-4,1′:4′,1″-terphenylene (23)[39]

To a solution of **21** (320 mg, 0.87 mmol) dissolved in a mixture of H_2SO_4 (2 N, 20 mL) and MeCN (20 mL) and cooled to –5 °C was added, dropwise, a solution of $NaNO_2$ (180 mg, 2.6 mmol, 3 equiv) in H_2O (5 mL). After stirring for 30 min, KI (722 mg, 4.4 mmol, 5 equiv), dissolved in H_2O (5 mL) was added dropwise at –5 °C. After removing of the cooling bath, the reaction mixture was stirred for 1 h at r.t., briefly heated to 60 °C and then stirred at r.t. for additional 8 h. The reaction mixture was neutralized with sat. aq Na_2CO_3 and the aqueous layer was extracted repeatedly with CH_2Cl_2. The combined organic layers were washed with H_2O (100 mL), aq $Na_2S_2O_3$ (1 M, 2 × 100 mL) and H_2O (100 mL), dried (Na_2SO_4) and concentrated in vacuo. The crude product was purified by flash chromatography on silica (first *n*-hexane–EtOAc, 5:1 and then *n*-hexane–CH_2Cl_2, 1:5 containing 5% Et_3N) to give **22**.

Yield: 70 mg (20%); yellow amorphous solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.41 (2 H, d, J = 8.4 Hz), 7.72 (2 H, d, J = 8.4 Hz), 7.75 (2 H, d, J = 8.8 Hz), 7.82 (2 H, d, J = 8.8 Hz), 7.84 (2 H, d, J = 8.4 Hz), 8.36 (2 H, d, J = 8.8 Hz).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 93.6, 124.2, 127.5, 127.6, 127.9, 128.8, 138.0, 138.0, 139.6, 140.6, 145.6, 146.9.

MS (EI): m/z = 401.0 [M^+].

HRMS (EI): m/z calcd for $C_{18}H_{12}INO_2$: 400.9913; found: 400.9914.

1,4‴-Dimethoxy-4,1′:4′,1″:4″,1‴-quaterphenylene (1)[25,27b,c,40]

Under an argon atmosphere, 4,4′-dibromobiphenyl (1.1 g, 3.4 mmol), 4-methoxyphenylboronic acid (1.14 g, 7.48 mmol, 2.2 equiv), CsF (1.93 g, 12.68 mmol, 4 equiv), and [$Pd(PPh_3)_4$] (110 mg, 0.10 mmol, 3 mol% Pd) were dissolved in anhyd THF (60 mL) and refluxed for 50 h. The product precipitated from the reaction mixture and was collected by filtration. The crude product was washed repeatedly with CH_2Cl_2 and H_2O to give **1**.

Yield: 1.26 g (100%); colorless amorphous solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.86 (6 H), 6.99 (4 H, d, J = 8.5 Hz), 7.58 (4 H, d, J = 8.5 Hz), 7.64 (4 H, d, J = 8.3 Hz), 7.69 (4 H, d, J = 8.3 Hz).

MS (CI, isobutane): m/z = 367.1 [$M + H^+$].

HRMS (EI): m/z calcd for $C_{26}H_{22}O_2$: 366.1620; found: 366.1622.

UV/Vis (CH_2Cl_2): λ_{max} = 310 nm.

1,4‴-Dichloro-4,1′:4′,1″:4″,1‴-quaterphenylene (2)[30a,41]

Under an argon atmosphere, 4,4′-dibromobiphenyl (631 mg, 2.0 mmol), 4-chlorophenylboronic acid (655 mg, 4.2 mmol, 2.1 equiv), CsF (1.22 g, 8.0 mmol, 4 equiv) and [$Pd(PPh_3)_4$] (110 mg, 0.10 mmol, 5 mol% Pd) were dissolved in anhyd THF (60 mL) and refluxed for 50 h. The product precipitated from the reaction mixture and was collected by filtration. The crude product was washed repeatedly with CH_2Cl_2 and H_2O to give **2**.

Yield: 690 mg (92%); colorless amorphous solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.42 (4 H, d, J = 8.4 Hz), 7.57 (4 H, d, J = 8.4 Hz), 7.64 (4 H, d, J = 8.1 Hz), 7.71 (4 H, d, J = 8.1 Hz).

MS (CI, isobutane): m/z = 375.1 [$M + H^+$].

HRMS (EI): m/z calcd for $C_{24}H_{16}Cl_2$: 374.0629; found: 366.0623.

UV/Vis (CH_2Cl_2): λ_{max} = 304 nm.

1,4‴-Dicyano-4,1′:4′,1″:4″,1‴-quaterphenylene (3)

Under an argon atmosphere, 4,4′-dibromobiphenyl (452 mg, 1.45 mmol), 4-cyanophenylboronic acid (450 mg, 3.05 mmol, 2.1 equiv), CsF (881 mg, 5.8 mmol, 4 equiv), and [$Pd(PPh_3)_4$] (84 mg, 0.07 mmol, 5 mol% Pd) were dissolved in anhyd THF (50 mL) and refluxed for 50 h. After cooling to r.t., the reaction mixture was diluted with *n*-hexane (20 mL) and H_2O (20 mL). The precipitate was collected by filtration and washed repeatedly with EtOAc and H_2O to give **3**.

Yield: 421 mg (81%); colorless amorphous solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.70 (4 H, d, J = 8.2 Hz), 7.72–7.77 (12 H, m).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 111.1, 118.8, 127.6, 127.7, 127.7, 132.6, 138.4, 140.5, 144.9.

MS (CI, isobutane): m/z = 357.4 [$M + H^+$].

HRMS (EI): m/z calcd for $C_{26}H_{16}N_2$: 356.1313; found: 356.1312.

UV/Vis (CH_2Cl_2): λ_{max} = 303 nm.

1,4‴-Diamino-4,1′:4′,1″:4″,1‴-quaterphenylene (4)[19b]

Under an argon atmosphere, 4,4′-dibromobiphenyl (308 mg, 1.0 mmol), *tert*-butyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenylcarbamate (668 mg, 2.1 mmol, 2.1 equiv), CsF (608 mg, 4.0 mmol, 4 equiv) and [$Pd(PPh_3)_4$] (56 mg, 0.05 mmol, 5 mol% Pd) were dissolved in anhyd THF (40 mL) and refluxed for 50 h. The precipitate was collected by filtration and washed repeatedly with THF and H_2O to give a light yellow amorphous solid. This was suspended in CH_2Cl_2 (100 mL) and cooled to 0 °C. TFA (12 mL) was added dropwise and the resulting solution was stirred at r.t. for 6 h. The mixture was filtered and the filtrate was made alkaline through dropwise addition of aq NaOH (2 M, 20 mL) to precipitate the product from the reaction mixture. The residue was collected by filtration and washed repeatedly with H_2O and CH_2Cl_2 to give **7**. No mass spectra could be obtained.

Yield: 310 mg (92%); off-white amorphous solid.

^{1}H NMR (500 MHz, $CDCl_3$–TFA, 3:1): δ = 7.47 (4 H, d, J = 8.3 Hz), 7.68 (4 H, d, J = 8.3 Hz), 7.76 (4 H, d, J = 8.3 Hz), 7.79 (4 H, d, J = 8.3 Hz), 8.77 (6 H, br s).

^{13}C NMR (125 MHz, $CDCl_3$–TFA, 3:1): δ = 123.1, 127.2, 127.8, 127.9, 129.2, 138.2, 140.6, 143.6.

UV/Vis (CH_2Cl_2): λ_{max} = 324 nm.

UV/Vis (CH_2Cl_2–TFA, 10:1): λ_{max} = 300 nm.

1,4‴-Di-*N*,*N*-dimethylamino-4,1′:4′,1″:4″,1‴-quaterphenylene (5)[42]

Under an argon atmosphere, 4,4′-biphenyldiboronic acid bis(neopentylglycol)ester (567 mg, 1.50 mmol), 4-bromo-*N*,*N*-dimethylaniline (549 mg, 3.19 mmol, 2.2 equiv), CsF (684 mg, 4.5 mmol, 3 equiv) and [$Pd(PPh_3)_4$] (87 mg, 0.075 mmol, 5 mol% Pd) were dissolved in anhyd THF (60 mL) and refluxed for 50 h. The gray precipitate was filtered off and washed with THF (30 mL) and H_2O (30 mL). After suspending the precipitate in CH_2Cl_2 (100 mL), TFA (5 mL) was added in small portions and the remaining gray-black residue was removed by filtration. Small portions of aq NaOH (10 M) were added to the filtrate and the precipitated crude product was collected by filtration and washed repeatedly with CH_2Cl_2 and H_2O to give **6** (569 mg, 1.45 mmol, 96%) as a light yellow amorphous solid (slightly contaminated with a by-product). For further purification, the crude product was dissolved in CH_2Cl_2 (100 mL) containing a few milliliters of TFA, and *n*-hexane (100 mL) was added to give a colorless precipitate. After 2 h of sedimentation, the precipitate was collected by filtration and washed repeatedly with CH_2Cl_2 and H_2O to give **7**.

Yield: 318 mg (54%); colorless amorphous solid.

^{1}H NMR (500 MHz, $CDCl_3$–TFA, 3:1): δ = 3.40 (6 H, s), 7.58 (4 H, d, *J* = 8.6 Hz), 7.68 (4 H, d, *J* = 8.2 Hz), 7.78 (4 H, d, *J* = 8.2 Hz), 7.84 (4 H, d, *J* = 8.6 Hz), 10.0 (2 H, br s).

^{13}C NMR (125 MHz, $CDCl_3$–TFA, 3:1): δ = 120.2, 127.8, 127.9, 129.6, 137.8, 140.6, 140.8, 144.3.

MS (EI): *m*/*z* = 392.2 [M^+].

HRMS (EI): *m*/*z* calcd for $C_{28}H_{28}N_2$: 392.2252; found: 392.2251.

UV/Vis (CH_2Cl_2–TFA, 10:1): λ_{max} = 303 nm.

1,4‴-Dinitro-4,1′:4′,1″:4″,1‴-quaterphenylene (6)[19,25]
Under an argon atmosphere, 4,4′-biphenyldiboronic acid bis(neopentylglycol) ester (378 mg, 1.00 mmol), 4-iodonitrobenzene (548 mg, 2.2 mmol, 2.2 equiv), CsF (608 mg, 4.08 mmol, 4 equiv) and $[Pd(PPh_3)_4]$ (58 mg, 0.05 mmol, 5 mol% Pd) were dissolved in anhyd THF (50 mL) and refluxed for 50 h. After cooling to r.t. the reaction mixture was diluted with *n*-hexane (20 mL) and H_2O (20 mL) and the precipitate was collected by filtration and washed repeatedly with THF and H_2O to give **4**.

Yield: 303 mg (76%); yellow amorphous solid.

^{1}H NMR (500 MHz, $CDCl_3$–TFA, 3:1): δ = 7.78 (4 H, d, *J* = 8.4 Hz), 7.83 (4 H, d, *J* = 8.4 Hz), 7.86 (4 H, d, *J* = 8.8 Hz), 8.36 (4 H, d, *J* = 8.8 Hz).

^{13}C NMR (125 MHz, $CDCl_3$–TFA, 3:1): δ = 124.7, 128.2, 128.2, 128.3, 138.3, 141.4, 146.8, 148.6.

MS (CI, isobutane): *m*/*z* (%) = 397.1 (100) [M + H^+], 398.1 (26) [M + H^+].

HRMS (EI): *m*/*z* calcd for $C_{24}H_{16}N_2O_4$: 396.1109; found: 366.1110.

UV/Vis (CH_2Cl_2): λ_{max} = 347 nm.

1-Chloro-4‴-methoxy-4,1′:4′,1″:4″,1‴-quaterphenylene (24)
Under an argon atmosphere, **19** (300 mg, 0.9 mmol), 4-chlorophenylboronic acid (142 mg, 0.91 mmol, 1.2 equiv), CsF (347 mg, 2.23 mmol, 3 equiv) and $[Pd(PPh_3)_4]$ (43 mg, 0.058 mmol, 5 mol% Pd) were dissolved in anhyd THF (60 mL) and refluxed for 50 h. The product precipitated from the reaction mixture and was collected by filtration. The crude product was washed repeatedly with THF and H_2O to give **24**.

Yield: 260 mg (92%); off-white amorphous solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.86 (6 H, s), 6.99 (2 H, d, *J* = 8.3 Hz), 7.42 (2 H, d, *J* = 8.1 Hz), 7.55–7.60 (4 H, m), 7.62–7.66 (4 H, m), 7.67–7.72 (4 H, m).

MS (CI, isobutane): *m*/*z* = 371.1 [M + H^+].

HRMS (EI): *m*/*z* calcd for $C_{25}H_{19}ClO$: 370.1124; found: 370.1124.

UV/Vis (CH_2Cl_2): λ_{max} = 309 nm.

1-Amino-4‴-methoxy-4,1′:4′,1″:4″,1‴-quaterphenylene (25)
Under an argon atmosphere, **19** (577 mg, 1.70 mmol), *tert*-butyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenylcarbamate (575 mg, 1.80 mmol, 1.05 equiv), CsF (800 mg, 5.3 mmol, 3 equiv) and $[Pd(PPh_3)_4]$ (57 mg, 0.05 mmol, 3 mol% Pd) were dissolved in anhyd THF (50 mL) and refluxed for 50 h. After cooling to r.t., the Boc-protected product precipitated from the reaction mixture and was collected by filtration. The solid was washed repeatedly with THF and H_2O to give a light yellow amorphous solid which was suspended in CH_2Cl_2 and cooled to 0 °C. TFA (6 mL) was added dropwise and the resulting solution was stirred at r.t. for 12 h. Upon treatment with aq NaOH (2 M, ~8 mL) the product precipitated from the solution and was collected by filtration. Repeated washing with H_2O and CH_2Cl_2 gave **25**.

Yield: 537 mg (90%); off-white amorphous solid.

^{1}H NMR (500 MHz, $CDCl_3$–TFA, 3:1): δ = 4.00 (3 H, s), 7.10 (2 H, d, *J* = 8.5 Hz), 7.48 (2 H, d, *J* = 8.3 Hz), 7.64 (2 H, d, *J* = 8.5 Hz), 7.67 (4 H, d, *J* = 8.2 Hz), 7.73 (2 H, d, *J* = 8.2 Hz), 7.78 (2 H, d, *J* = 8.2 Hz), 7.81 (2 H, d, *J* = 8.3 Hz), 8.73 (3 H, br s).

MS (EI): *m*/*z* = 351.1 [M^+].

HRMS (EI): *m*/*z* calcd for $C_{25}H_{21}NO$: 351.1623; found: 351.1622.

UV/Vis (CH_2Cl_2): λ_{max} = 317 nm.

UV/Vis (CH_2Cl_2–TFA, 10:1): λ_{max} = 307 nm.

4-Cyano-4‴-methoxy-1,1′:4′,1″:4″,1‴-quaterphenylene (26)
Under an argon atmosphere, **19** (851 mg, 2.5 mmol), 4-cyanophenylboronic acid (393 mg, 2.7 mmol, 1.1 equiv), CsF (1.14 g, 7.5 mmol, 3.0 equiv) and $[Pd(PPh_3)_4]$ (86 mg, 0.116 mmol, 4 mol% Pd) were dissolved in anhyd THF (60 mL) and refluxed for 50 h. The product precipitated from the reaction mixture and was collected by filtration. Repeated washing with THF and H_2O gave **26**.

Yield: 867 mg (96%); off-white amorphous solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.86 (3 H, s), 7.00 (2 H, d, *J* = 8.6 Hz), 7.58 (2 H, d, *J* = 8.6 Hz), 7.63–7.71 (6 H, m), 7.73–7.77 (6 H, m).

ESI MS (positive): *m*/*z* = 362.3 [M + H^+].

HRMS (EI): *m*/*z* calcd for $C_{26}H_{19}NO$: 361.1466; found: 361.1467.

UV/Vis (CH_2Cl_2): λ_{max} = 317 nm.

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