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Suzuki–Miyaura monocouplings of *p*-dibromobiphenyl and substituted *p*-dibromo(penta-*p*-phenylenes)

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ABSTRACT

The mono/bis ratio for the Suzuki–Miyaura cross coupling of *p*-dibromobiphenyl and *p*-dibromo(penta-*p*-phenylenes) with arylboronic acids and esters has been studied. The coupling reaction is demonstrated to be highly selective for monoarylation when the substrate is a *p*-dibromooligoarene, while selective biarylation is obtained for *p*-diiodoterphenyl. The mono/bis coupling-ratio for these compounds was highly sensitive to the nature of the halogen involved, however steric hindrance or electronic characteristics of the boronic derivative did not affect the selectivity of the reaction. The reaction yields observed were higher at room temperature and when arylboronic pinacol esters were used. These reactions also offer a useful method for the preparation of asymmetrically substituted terphenyls and hexa-*p*-phenylenes, giving good yields.

1. Introduction

Research on π-conjugated poly-*p*-phenylenes has seen a tremendous number of recent developments due to their interesting optoelectronic and electrical properties. Upon doping, they not only act as excellent organic conductors, but also as long-range electron transfer materials.[1,2] They can be used as the active component in optical devices, such as light-emitting diodes,[3] and they display liquid crystalline properties as well as a high degree of thermal stability.[4] Among them, oligo-*p*-phenylenes are of particular interest because, when compared with polymers, they are easily obtained by controlled organic reactions as a monodisperse material of great purity[5–8] and owing to its rigid rod-like molecular structure[9] they have been used in the construction of organic nanostructures.[10–13]. Use in the latter case has been demonstrated with symmetrical penta-*p*-phenylenes, which were rigid enough to be used to form the legs of giant tripod-shaped molecules.[14,15] These molecules have been proposed as adsorbates for controlling the orientation and location of individual molecules on nanostructured surfaces.[16]

The syntheses of oligo-*p*-phenylenes usually involves the palladium-catalyzed Suzuki cross coupling of dihaloaryl derivatives as the key-step. The reaction is a flexible, advantageous synthetic method for constructing C–C biaryl bonds under mild reaction conditions,[17] and has been used for a great number of applications in aryl–aryl bond formation. These include variously substituted derivatives, such as highly substituted biphenyls, heterobiaryls, poly-*p*-phenylenes, polyheterobiaryls, and many other classes of biaryls.[18]

In cases involving poly-haloaromatic precursors in a Suzuki reaction, the most common outcome is exhaustive multiple coupling, and an excess of the boronic acid or ester coupling partner is often employed to drive the reaction to completion. However, a significant number of selective single couplings with di- or tri-haloaromatics have also been reported.[19] In these cases, to encourage single coupling products, a low molar ratio of boronic acid to polyhalobenzenes is employed. However, contradictory to this, it has also been reported that during the selective double coupling of arylboronic acids and esters with symmetrical *p*-dihalobenzene this molar ratio does not affect the selectivity. Even when the ratio is 10/1 the products of double coupling are preferentially obtained.[19] Halogen has also been identified as one of the major factors in determining selectivity, with *p*-dibromobenzene resulting in single couplings with arylboronic acids with high selectivity, while *p*-diiodobenzene results in double-coupled products.[19]

To the best of our knowledge, no study on the selectivity of the *p*-dihalobiphenyl and *p*-dihalo(oligo-*p*-phenylenes) reaction has

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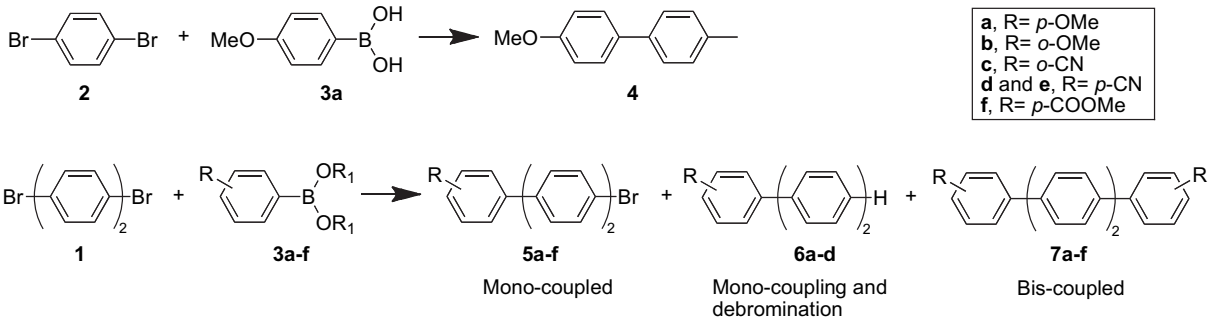
been reported. In this paper we study the selectivity of the Suzuki cross-coupling reaction of the *p*-dibromobiphenyl and *p*-dibromo (penta-*p*-phenylene) derivatives. These are, as mentioned above, compounds of interest in the synthesis of tripod-shaped oligo-*p*-phenylenes. The results also provide a concise, practical, and high-yielding synthesis of asymmetrical ter- and hexa-*p*-phenylenes by employing selective Suzuki–Miyaura reactions for the mono-arylation of symmetrical dibromoarenes.

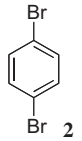
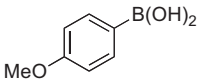
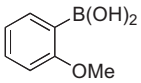
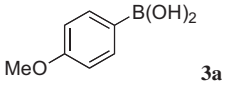
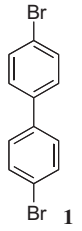
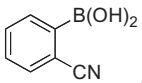
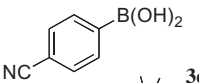
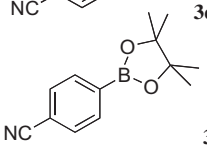
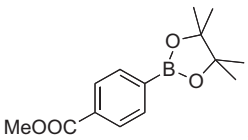
2. Results and discussion

We evaluated the Suzuki cross coupling of *p*-dibromobiphenyl (**1**) under the same optimized conditions reported by Sinclair for *p*-dibromobenzene (**2**).[19] We investigated the reaction of **1** with a number of boronic acids and esters with different substitution patterns (compounds **3a**–**f**, Table 1). Previously, model compound **2** was coupled with *p*-methoxyphenyl boronic acid (**3a**) by using 1.5 equiv of **3a**, 8 mol % of palladium catalyst, 2 equiv of Cs_2CO_3, and a mixture of toluene/methanol as a solvent (Table 1, entry 1). After 12 h refluxing, the reaction was complete and only the mono-coupled compound *p*-methoxybiphenyl (**4**) was isolated in 82% yield. The bis-coupled product was not detected.

Selectivity of this reaction was then studied for **1** (results are shown in Table 1). Under the above conditions, the cross coupling of **1** with the *p*-methoxy substituted boronic acid **3a** did not give the

Table 1
Pd catalyzed cross coupling of *p*-dibromobiphenyl (**1**) and *p*-dibromobenzene (**2**) with boronic acids or esters (**3a**–**f**)



Entry	Dibromide **1** or **2**	Boronic acid/ester **3a**–**f**	Conditions (a) or (b)	Ratio % Mono/Bis	React. Prod. and yield (%)	
					Mono	Bis
1	 **2**	 **3a**	(a), reflux, 12 h	100/0	**4** (82)	**7a** (0)
2		 **3b**	(a), reflux, 12 h	72[a]/28	**6b** (61)[a]	**7b** (24)
3			(a), rt, 18 h	99/1	**5b** (58)	**7b** (4)
4		 **3a**	(a), reflux, 12 h	100[a]/0	**6a** (83)[a]	—
5			(a), rt, 18 h	100/0	**5a** (93)	—
6	 **1**	 **3c**	(a), reflux, 12 h	74[a]/26	**6c** (43)[a]	**7c** (9)
7			(a), rt, 18 h	73/27	**5c** (61)	**7c** (22)
8		 **3d**	(a), reflux, 12 h	74[a]/26	**6d** (62)[a]	**7d** (16)
9			(a), rt, 18 h	73/27	**5d** (69)	**7d** (25)
10		 **3e**	(b), rt, 18 h	87/13	**5e** (78)	**7e** (11)
11		 **3f**	(b), rt, 18 h	98/2	**5f** (56)	**7f** (5)

(a) 1/1.5 mol ratio boronic acid or ester to dibromide/8 mol % $Pd(PPh_3)_4$/2 equiv Cs_2CO_3/toluene/methanol.
(b) 8 mol % $Pd(PPh_3)_4$/2 equiv Ag_2CO_3/tetrahydrofuran.
[a] Monocoupling and debromination product.

expected mono-coupled product **5a** (Table 1, entry 4). Instead, the only product resulting from the monocoupling and debromination (**6a**) was isolated in 83% yield (entry 4). Similar results were obtained under refluxing conditions when **1** was coupled with phenyl boronic acids **3b**–**d**: monocoupling and debromination products **6b**–**d** were obtained, respectively, as the main reaction products (entries 2, 6, and 8) with 61, 43, and 62% yields, respectively. In these cases, bis-coupled products were also isolated as minor compounds (**7b**–**d**, entries 2, 6, and 8). The debromination reaction under Pd-catalyzed coupling conditions is known to occur as an undesired side reaction, for example, when protic conditions are used.[20]

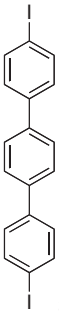
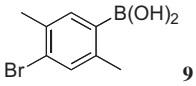
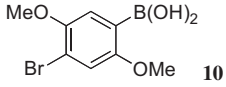
No significant yield or mono/bis coupling differences were found with electron rich (**3a** and **3b**), electron poor (**3c** and **3d**) or sterically hindered (**3b** and **3c**) or unhindered aromatic boronic acids. These results show the monocoupling and debromination processes to be predominant for *p*-dibromobiphenyl (**1**) when the reaction is carried out under reflux.

In order to avoid the debromination process, reactions of **1** with arylboronic acids **3a**–**d** were carried out at room temperature (Table 1, entries 3, 5, 7, and 9). Monocoupling products were obtained in good yields, and the corresponding *p*-bromoterphenyls **5a**–**d** were isolated in good yields too. Small quantities of the bis-coupled products were also isolated; *p*-quaterphenyls **7b**–**d**, as shown in entries 3, 7, and 9. Under room temperature conditions no bis-coupled product (**7a**) was found for the electron rich phenyl boronic acid **3a**, and only a small quantity for the *ortho*-methoxy substituted **3b** (compound **7b**, 4% yield, entry 3).

The Suzuki reaction of *p*-dibromobiphenyl (**1**) was also carried out with phenyl boronic esters **3e** and **3f** (Table 1, entries 10 and 11). Good yields were obtained in both cases under smooth conditions (rt, 18 h) by using 1.5 equiv of ester, 8 mol % of $Pd(PPh_3)_4$, 2 equiv of Ag_2CO_3 as the base and tetrahydrofuran as the solvent. The use of silver carbonate and an aprotic solvent was found to optimize coupling reactions with arylboronic esters.[21] Major compounds were the mono-coupled products **5e** and **5f**, isolated in a mono/bis ratio of 87/13 and 98/2 to the bis-coupled products **7e** and **7f**, respectively.

These results show that the reported monocoupling selectivity for the reaction of *p*-dibromobenzene (**2**) with boronic acids and esters can be extended to *p*-dibromobiphenyl (**1**). However, contrary to the data reported in the literature,[19] yields and selectivity to monocoupling of **1** is more pronounced in pinacolate esters than in the corresponding acid derivatives (Table 1, entries 9 and 10). These results are in agreement with those reported for the coupling of *p*-diiodobiphenyl with pinacolyl 2,6-dimethoxyphenyl boronate, where the bis-coupled product is the main compound (86%), in preference to the mono-coupled compound (14%).[19] In fact, selective multiple couplings appear to be a general trait of polyiodoaryls, while selective monocoupling is a general trait of polybromoaryls. We studied the coupling reaction of *p*-diiodoterphenyl (**8**) with boronic acids **9** and **10** under Suzuki conditions (Table 2), since we used compound **8** as a starting material for phenyl homologation to obtain several substituted oligo-*p*-phenylenes, used as molecular legs in tripodal adsorbates.[14] As for **1**, in this reaction a 1/1.5 mol ratio of boronic acid to diiodide **8** was used. Even with an excess of diiodide we only obtained the bis-coupled products (**11** and **12**), while monocoupling products were not detected. This result means that the selectivity to biscoupling found for *p*-diiodobenzene and *p*-diiodobiphenyl is also extended to *p*-diiodoterphenyl (**8**).

Table 2
Pd-catalyzed coupling of *p*-diiodoterphenyl (**8**) with boronic acids (**9** and **10**)

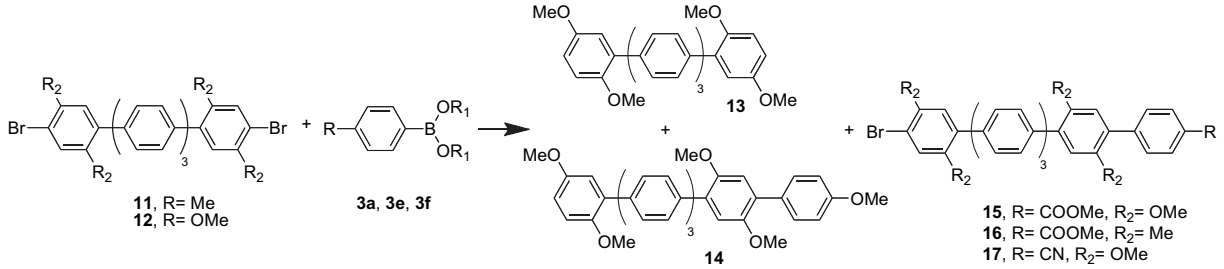
Entry	*p*-Diiodoterphenyl	Boronic acid	Conditions	Yield %	React. Prod. and ratio (%) mono/bis
1	 **8**	 **9**	1/1.5 mol ratio boronic acid to **8**/Reflux 8% $Pd(PPh_3)_4$/2 equiv Cs_2CO_3/toluene/MeOH	94	0/100, **11**
2		 **10**		90	0/100, **12**

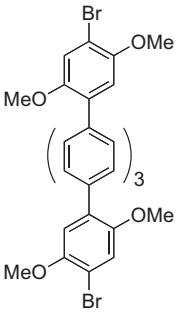
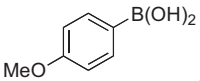
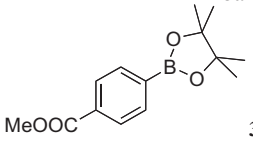
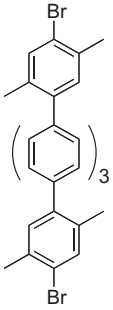
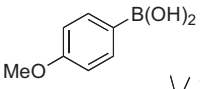
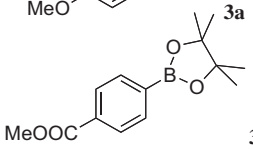
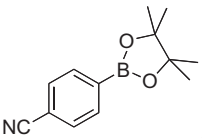
Access to the substituted penta-*p*-phenylenes **11** and **12** allowed us to extend the study of the mono/bis ratio for Suzuki coupling for these products, with a special interest in the monocoupling, since the synthetic use of oligo-*p*-phenylenes of defined length depends on the ability to differentiate both ends of the molecule.[5,12,13] However, any attempt to react the tetramethoxy derivative **12** with the boronic acid **3a** only resulted in the isolation of the debromination product **13**, together with a small quantity of the monocoupling and debromination compound **14** (Table 3, entries 1 and 2). When the reaction was carried out with compound **11** at room temperature or under refluxing conditions, only the starting material was recovered, and no reaction products were isolated (Table 3, entries 4 and 5).

The lack of reactivity of penta-*p*-phenylene **11**, even in refluxing toluene/methanol, can probably be attributed to the remarkably poor solubility of this compound in this mixture of solvents. Also, **11** is less soluble than **12** in usual organic solvents. The coupling reaction with **11** as a substrate was also carried out in ethanol and DMF, both typically used Suzuki solvents. In this case only the starting material was recovered and the expected monocoupling product of **11** was not detected.

However, when we carried out the Suzuki reaction for **11** and **12** using the corresponding phenyl boronic pinacol ester (**3e** and **3f**), good yields of the mono-coupled product were obtained, and the hexa-*p*-phenylenes **15**, **16** and **17** were isolated in yields of 78, 54, and 55%, respectively (Table 3, entries 3, 6, and 7), and bis-coupled products were not detected. The higher yield obtained for the coupling of **12** can be again attributed to the better solubility of this compound in THF compared to **11**. As for compound **1**, coupling reactions with boronic acid pinacol ester derivatives give better reaction yields, together with a higher selectivity to the mono-coupled products.

Table 3
Pd-catalyzed coupling of *p*-dibromo(penta-*p*-phenylenes) **11** and **12** with boronic acids or esters **3a**, **3e**, and **3f**



Entry	Dibromide	Boronic acid/ester	Conditions (a) or (b)	Ratio % Mono/Bis	React. Prod. and yield (%)	
					Debromin.	Mono
1	 **12**	 **3a**	(a), rt, 18 h	NR	—	—
2			(a), reflux, 12 h	—	**13**[a] (80) **14**[b] (14)	—
3		 **3f**	(b), rt, 18 h	100/0	—	**15** (78)
4	 **11**	 **3a**	(a), rt, 18 h	NR	—	—
5			(a), reflux, 12 h	NR	—	—
6		 **3f**	(b), rt, 18 h	100/0	—	**16** (54)
7		 **3e**	(b), rt, 18 h	100/0	—	**17** (55)

(a) 1/1.5 mol ratio boronic acid or ester to dibromide/8 mol % $Pd(PPh_3)_4$/2 equiv Cs_2CO_3/toluene/methanol.
(b) 8 mol % $Pd(PPh_3)_4$/2 equiv Ag_2CO_3/tetrahydrofuran.
[a] Didebromination product.
[b] Monocoupling and debromination product.

3. Conclusions

In summary, we studied the Suzuki cross-coupling reaction behavior of *p*-dibromobiphenyl (**1**) showing that monocoupling is preferentially obtained in good yields when the reaction is carried out at room temperature. As expected, the selectivity does not depend on the electronic or steric characteristics of the boronic derivative, but better yields were obtained with arylboronic pinacol ester derivatives. Suzuki cross coupling was also studied with *p*-diiodoterphenyl (**8**) as the substrate. In this case only bis-coupled products were obtained in good yields, showing that the coupling is highly sensitive to the nature of the halogen involved. Finally, the analysis was extended to substituted *p*-dibromo(penta-*p*-phenylenes) (**11** and **12**) where monocoupling was found to be selective when arylboronic pinacol esters were used at room temperature with THF as the solvent. The results reported for the Suzuki monocoupling of **1**, **11**, and **12** provides a practical protocol for preparing asymmetrically substituted *p*-terphenyls and hexa-*p*-phenylenes, compounds of interest in the synthesis of giant tripod-shaped molecules.

4. Experimental

4.1. General

p-Dibromobenzene (**2**), *p*-dibromobiphenyl (**1**), and arylboronic acids and esters (**3a**–**f**) were purchased from Aldrich, and they were used without purification. *p*-Diiodoterphenyl (**8**) was prepared from terphenyl following reported procedures.[22] Melting points were determined with a Gallenkamp instrument and are given uncorrected. IR spectra were recorded on Beckman Aculab IV and Perkin–Elmer 883 spectrophotometers. Mass spectrometry was done with a Thermo Finnigan instrument, using the direct injection and electron-impact (EI) modes. HRMS were recorded

with a Micromass (Autospec-Q) spectrometer. ^{1}H NMR and ^{13}C NMR spectra were recorded in a 400 MHz ARX 400 Bruker spectrometer, using the residual solvent peak in $CDCl_3$ (δ_H 7.24 ppm for ^{1}H and δ_C 77.0 ppm for ^{13}C). TLC analyses were performed on Merck silica gel 60 F_{254} plates, and column chromatography on silica gel 60 (0.040–0.063 mm).

4.2. General procedure for the $Pd(PPh_3)_4$ catalyzed coupling reaction

Under an argon atmosphere, an oven-dried round bottom flask was charged with the appropriate phenyl boronic acid [or ester] (1.00 mmol), *p*-dihaloarene (1.50 mmol), cesium carbonate [or silver carbonate] (2.00 mmol), and $Pd(PPh_3)_4$ (8 mol %). The flask was evacuated and re-filled with argon three times, then toluene/methanol [or tetrahydrofuran] was added.

The reaction mixture was heated to reflux for 12 h or stirred for 18 h at room temperature (see Tables 1–3). When the reaction was complete (TLC), inorganic solids were removed by filtration through Celite, and washed with several portions of dichloromethane. The organic filtrates were then concentrated to dryness. The crude product was purified by column chromatography.

*4.2.1. 4-Bromo-4′-methoxybiphenyl (**4**)[23].* The reaction was carried out by following the reflux-12 h procedure, using *p*-dibromobenzene (**2**, 0.50 g, 2.12 mmol), 4-methoxyphenyl boronic acid (**3a**, 0.22 g, 1.41 mmol), cesium carbonate (0.92 g, 2.82 mmol), $Pd(PPh_3)_4$ (0.13 g, 0.11 mmol), toluene (20 mL), and methanol (10 mL). Compound **4** was isolated by column chromatography (silica gel, cyclohexane/AcOEt 8/2) as a white solid (0.31 g, 82% yield), mp: 143–145 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.53 (dd, 4H, *J*=7.6, 8.8 Hz, ArH), 7.40 (d, 2H, *J*=8.3 Hz, ArH), 6.97 (d, 2H, *J*=8.8 Hz, ArH), 3.84 (s, 3H, OCH_3) ppm; MS *m*/*z* (%): 264 (M^+, 0.2), 262 (0.2), 184 (100), 169 (47), 152 (5).

*4.2.2. 4-Bromo-4″-methoxy-p-terphenyl (**5a**)[24].* The reaction was carried out by following the rt-18 h procedure, using *p*-dibromobiphenyl (**1**, 0.62 g, 1.98 mmol), 4-methoxyphenyl boronic acid (**3a**, 0.20 g, 1.32 mmol), cesium carbonate (0.86 g, 2.64 mmol), $Pd(PPh_3)_4$ (0.12 g, 0.11 mmol), toluene (20 mL), and methanol (20 mL). Compound **5a** was isolated by column chromatography (silica gel, cyclohexane/AcOEt 9.8/0.2) as a white solid (0.42 g, 93% yield), mp: 145–146 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.63–7.60 (m, 4H, ArH), 7.56 (d, 4H, *J*=8.4 Hz, ArH), 7.48 (d, 2H, *J*=8.8 Hz, ArH), 6.98 (d, 2H, *J*=8.8 Hz, ArH), 3.85 (s, 3H, OCH_3) ppm; MS *m*/*z* (%): 338 (M^+, 0.1), 336 (0.1), 258 (100).

*4.2.3. 4-Methoxy-p-terphenyl (**6a**)[25].* The reaction was carried out by following the reflux-12 h procedure, using *p*-dibromobiphenyl (**1**, 1.86 g, 5.95 mmol), 4-methoxyphenyl boronic acid (**3a**, 0.60 g, 3.97 mmol), cesium carbonate (2.59 g, 7.94 mmol), $Pd(PPh_3)_4$ (0.37 g, 0.32 mmol), toluene (30 mL), and methanol (20 mL). Compound **6a** was isolated by column chromatography (silica gel, cyclohexane/CH_2Cl_2 8/2) as a white solid (0.86 g, 83% yield), mp: 222–224 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.63 (m, 4H, ArH), 7.57 (d, 2H, *J*=8.8 Hz, ArH), 7.45 (d, 2H, *J*=7.2 Hz, ArH), 7.43 (d, 2H, *J*=8 Hz, ArH), 7.35 (q, 1H, *J*=7.2 Hz, ArH), 6.98 (d, 2H, *J*=8.4 Hz, ArH), 3.85 (s, 3H, OCH_3) ppm; MS *m*/*z* (%): 260 (100), 246 (8), 245 (42).

*4.2.4. 2-Methoxy-p-terphenyl (**6b**)[26].* The reaction was carried out by following the reflux-12 h procedure, using *p*-dibromobiphenyl (**1**, 0.62 g, 1.98 mmol), 2-methoxyphenyl boronic acid (**3b**, 0.20 g, 1.32 mmol), cesium carbonate (0.86 g, 2.64 mmol), $Pd(PPh_3)_4$ (0.12 g, 0.11 mmol), toluene (20 mL), and methanol (20 mL). Compound **6b** was isolated by column chromatography (silica gel, cyclohexane/AcOEt 9.8/0.2) as a white solid (0.27 g, 61% yield), mp: 116–118 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.67–7.71 (m, 6H, ArH), 7.50 (t, 2H, J_1=7.9 Hz, ArH), 7.36–7.44 (m, 3H, ArH), 7.10 (t, 1H, *J*=7.2 Hz, ArH), 7.05 (d, 1H, *J*=8.4 Hz, ArH), 3.88 (s, 3H, OCH_3) ppm; MS *m*/*z* (%): 260 (M^+, 100%), 245 (12), 227 (22), 215 (14).

*4.2.5. 2-Cyano-p-terphenylene (**6c**)[27].* The reaction was carried out by following the reflux-12 h procedure, using *p*-dibromobiphenyl (**1**, 0.48 g, 1.54 mmol), 2-cyanophenyl boronic acid (**3c**, 0.15 g, 1.03 mmol), cesium carbonate (0.67 g, 2.06 mmol), $Pd(PPh_3)_4$ (0.10 g, 0.08 mmol), toluene (20 mL), and methanol (20 mL). Compound **6c** was isolated by column chromatography (silica gel, cyclohexane/AcOEt 9.8/0.2) as a white solid (0.11 g, 43% yield), mp: 160–162 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.77 (d, 1H, *J*=7.6 Hz, ArH), 7.71 (d, 2H, *J*=8.4 Hz, ArH), 7.64 (d, 4H, *J*=8 Hz, ArH), 7.56 (d, 1H, *J*=7.6 Hz, ArH), 7.48–7.43 (m, 4H, ArH), 7.37 (dd, 1H, *J*=7.6, 7.2 Hz, ArH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 145.0 (C), 141.5 (C), 140.3 (C), 136.9 (C), 133.8 (CH), 132.8 (CH), 130.0 (CH), 129.1 (2×CH), 128.8 (2×CH), 127.6 (CH), 127.5 (2×CH), 127.4 (2×CH), 127.1 (CH), 118.8 (CN), 111.1 (C) ppm; IR (KBr) ν: 2226 ν_{CN} cm^{-1}; MS *m*/*z* (%): 255 (M^+, 100), 254 (48).

*4.2.6. 4-Cyano-p-terphenylene (**6d**)[28].* The reaction was carried out by following the reflux-12 h procedure, using *p*-dibromobiphenyl (**1**, 0.73 g, 2.34 mmol), 4-cyanophenyl boronic acid (**3d**, 0.23 g, 1.56 mmol), cesium carbonate (1.00 g, 3.12 mmol), $Pd(PPh_3)_4$ (0.14 g, 0.13 mmol), toluene (20 mL), and methanol (20 mL). Compound **6d** was isolated by column chromatography (silica gel, cyclohexane/CH_2Cl_2 5/5) as a pale yellow solid (0.25 g, 62% yield), mp: 195–197 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.73 (m, 4H, ArH), 7.66 (m, 4H, ArH), 7.40 (m, 1H, ArH), 7.29 (br s, 4H, ArH) ppm; IR (KBr) ν: 2229 ν_{CN} cm^{-1}; MS *m*/*z* (%): 255 (M^+, 100), 254 (10).

*4.2.7. 2,2‴-Dimethoxy-p-quaterphenylene (**7b**)[29].* From the same reaction where **6b** was obtained, compound **7b** was isolated as a brown solid (60 mg, 24% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.87–7.76 (m, 4H, ArH), 7.56–7.38 (m, 4H, ArH), 7.19–7.11 (m, 8H, ArH), 3.92 (s, 6H, 2×OCH_3) ppm; MS *m*/*z* (%): 366 (100), 336 (12), 306 (28), 282 (13). This compound was also obtained in 4% yield from the reaction where **5b** was isolated (Table 1, entry 3).

*4.2.8. 2,2‴-Dicyano-p-quaterphenylene (**7c**).* From the same reaction where **6c** was obtained, compound **7c** was isolated as a pale yellow solid (20 mg, 9% yield), mp: 167–170 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.79 (d, 2H, *J*=8.4 Hz), 7.77 (d, 4H *J*=8 Hz), 7.67 (d, 4H, *J*=8.0 Hz, ArH), 7.66 (dd, 2H, *J*=7.6 Hz, ArH), 7.57 (d, 2H, *J*=7.6 Hz, ArH), 7.46 (dd, 2H, *J*=6.8, 7.2 Hz, ArH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 141.2 (2×C), 137.9 (2×C), 137.0 (2×C), 134.5 (2×CH), 133.9 (2×CH), 129.0 (8×CH), 128.1 (2×CH), 128.0 (2×CH), 118.1 (2×CN), 107.9 (2×C) ppm; IR (KBr) ν: 2224 ν_{CN} cm^{-1}; MS *m*/*z* (%): 356 (M^+, 100), 178 (23), 164 (13); HRMS calcd for $C_{26}H_{16}N_2$: 356.1313, Found: 356.1314. This compound was also obtained in 22% yield from the reaction where **5c** was isolated (Table 1, entry 7).

*4.2.9. 4,4‴-Dicyano-p-quaterphenylene (**7d**/**7e**)[5].* From the same reaction where **6d** was obtained, compound **7d** was isolated as a white solid (44 mg, 16% yield), mp: 185 °C dec; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.74–7.76 (m, 8H, ArH), 7.70 (br s, 8H, ArH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 144.9 (2×C), 140.5 (2×C), 138.4 (2×C), 132.7 (4×CH), 127.7 (4×CH) 127.6 (8×CH), 118.9 (2×CN), 111.0 (2×C) ppm; IR (KBr) ν: 2224 ν_{CN} cm^{-1}; MS *m*/*z* (%): 356 (M^+, 100), 178 (15), 152 (11). This compound was obtained in 25% and 11% yields from the reactions where **5d** and **5e** was isolated (Table 1, entries 9 and 10).

*4.2.10. 4″-Bromo-2-methoxy-p-terphenyl (**5b**).* The reaction was carried out by following the rt-18 h procedure, using *p*-

dibromobiphenyl (**1**, 1.00 g, 3.19 mmol), 2-methoxyphenyl boronic acid (**3b**, 0.32 g, 2.13 mmol), cesium carbonate (1.39 g, 4.26 mmol), $Pd(PPh_3)_4$ (0.20 g, 0.17 mmol), toluene (50 mL), and methanol (50 mL). Compound **5b** was isolated by column chromatography (silica gel, cyclohexane/AcOEt 9.8/0.2) as a white solid (0.42 g, 58% yield), mp: 205–210 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.69–7.51 (m, 8H, ArH), 7.43–7.36 (m, 2H, ArH), 7.14–7.03 (m, 2H, ArH), 3.88 (s, 3H, OCH_3) ppm; MS *m*/*z* (%): 340 (5), 338 (6), 260 (100); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 154.0 (C), 140.10 (C), 140.07 (C), 137.0 (C), 132.0 (C), 131.0 (CH), 130.6 (CH), 130.5 (CH), 127.9 (CH), 127.5 (2×CH), 127.1 (2×CH), 122.4 (2×CH), 122.3 (CH), 122.1 (C), 115.2 (CH), 58.0 (OCH_3) ppm; HRMS calcd for $C_{19}H_{15}BrO$: 338.0306, Found: 338.0312.

*4.2.11. 4″-Bromo-2-cyano-p-terphenylene (**5c**).* The reaction was carried out by following the rt-18 h procedure, using *p*-dibromobiphenyl (**1**, 0.48 g, 1.54 mmol), 2-cyanophenyl boronic acid (**3c**, 0.15 g, 1.03 mmol), cesium carbonate (0.67 g, 2.06 mmol), $Pd(PPh_3)_4$ (0.10 g, 0.08 mmol), toluene (20 mL), and methanol (20 mL). Compound **5c** was isolated by column chromatography (silica gel, cyclohexane/AcOEt 9.8/0.2) as a white solid (0.21 g, 61% yield), mp: 120–123 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.73 (m, 4H, ArH), 7.66 (s, 4H, ArH), 7.58 (d, 2H, *J*=8.4 Hz, ArH), 7.49 (d, 2H, *J*=8.4 Hz, ArH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 95.1, 96.8, 99.0, 102.7, 111.4, 111.5, 113.2, 113.9, 116.8, 117.7, 121.2, 124.6, 128.8 ppm; IR (KBr) ν: 2224 ν_{CN} cm^{-1}; MS *m*/*z* (%): 335 (M^+, 83), 333 (100), 255 (26), 254 (54), 253 (42); HRMS calcd for $C_{19}H_{12}BrN$: 333.0153, Found: 333.0150.

*4.2.12. 4″-Bromo-4-cyano-p-terphenylene (**5d**/**5e**)*[5]. The reaction was carried out by following the rt-12 h procedure, using *p*-dibromobiphenyl (**1**, 0.54 g, 1.73 mmol), 4-cyanophenyl boronic acid pinacol ester (**3e**, 0.26 g, 1.15 mmol), silver carbonate (0.91 g, 3.30 mmol), $Pd(PPh_3)_4$ (0.11 g, 0.09 mmol), and tetrahydrofuran (50 mL). Compound **5e** was isolated by column chromatography (silica gel, cyclohexane/AcOEt 9.8/0.2) as a white solid (0.30 g, 78% yield), mp: 115–120 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.73 (m, 4H, ArH), 7.66 (s, 4H, ArH), 7.58 (d, 2H, *J*=8.4 Hz), 7.49 (d, 2H, *J*=8.4 Hz) ppm; IR (KBr) ν: 2229 ν_{CN} cm^{-1}; MS *m*/*z* (%): 335 (M^+, 96), 333 (100), 255 (1), 254 (10), 253 (30).

Compound **5d** was also obtained by following the rt-18 h procedure, using *p*-dibromobiphenyl (**1**, 0.48 g, 1.54 mmol), 4-cyanophenyl boronic acid (**3d**, 0.15 g, 1.03 mmol), cesium carbonate (0.67 g, 2.06 mmol), $Pd(PPh_3)_4$ (0.10 g, 0.08 mmol), toluene (20 mL), and methanol (20 mL). Compound **5d** was isolated by column chromatography (silica gel, cyclohexane/AcOEt 9.8/0.2) as a white solid (0.26 g, 69% yield).

*4.2.13. 4″-Bromo-4-methoxycarbonyl-p-terphenylene (**5f**).* The reaction was carried out by following the rt-12 h procedure, using *p*-dibromobiphenyl (**1**, 0.40 g, 1.28 mmol), 4-(methoxycarbonyl) phenyl boronic acid pinacol ester (**3f**, 0.22 g, 0.85 mmol), silver carbonate (0.47 g, 1.70 mmol), $Pd(PPh_3)_4$ (0.08 g, 0.07 mmol), and tetrahydrofuran (40 mL). Compound **5f** was isolated by column chromatography (silica gel, cyclohexane/AcOEt 9.8/0.2) as a white solid (0.17 g, 56% yield), mp: 120–123 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.09 (d, 2H, *J*=8.2 Hz, ArH), 7.70–7.46 (m, 10H, ArH), 3.93 (s, 3H, $COOCH_3$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 167.0 (CO), 142.2 (C), 140.1 (C), 140.0 (2×C), 131.3 (2×CH), 127.3 (C), 127.2 (2×CH), 127.0 (2×CH), 126.9 (4×CH), 121.0 (C), 120.8 (2×CH), 58.0 (OCH_3); IR (KBr) ν: 1734 ν_{CO} cm^{-1}; HRMS calcd for $C_{20}H_{15}BrO_2$: 366.0255, Found: 366.0257.

*4.2.14. 4,4″-Di(methoxycarbonyl)-p-quaterphenylene (**7f**)*[30]. From the same reaction as for **5f**, compound **7f** was isolated as a white solid (9 mg, 5% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.11 (d, 4H, *J*=8.0 Hz, ArH), 7.71–7.60 (m, 8H, ArH), 7.53–7.40 (m, 4H, ArH), 3.93 (s, 6H, $COOCH_3$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 167.1 (2×CO), 145.7 (2×C), 140.1 (4×C), 130.2 (4×CH), 129.0 (4×CH), 128.2 (2×C), 127.4 (4×CH), 127.2 (4×CH), 52.2 (OCH_3); IR (KBr) ν: 1734 ν_{CO} cm^{-1}; MS *m*/*z* (%): 422 (M^+, 25).

*4.2.15. 4,4‴″-Dibromo-2,2‴″,5,5‴″-tetramethyl-(penta-p-phenylene) (**11**).* The reaction was carried out by following the reflux-12 h procedure, using *p*-diiodoterphenyl (**8**, 0.50 g, 1.00 mmol), boronic acid **9** (0.16 g, 0.69 mmol), cesium carbonate (0.45 g, 1.38 mmol), $Pd(PPh_3)_4$ (0.064 g, 0.055 mmol), toluene (10 mL), and methanol (10 mL). Compound **11** was isolated by column chromatography (silica gel, cyclohexane/CH_2Cl_2 5/5) as a pale yellow solid (0.19 g, 94% yield), mp: 256–260 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.73 (s, 4H, ArH), 7.68 (d, 4H, *J*=8.3 Hz, ArH), 7.46 (s, 2H, ArH), 7.37 (d, 4H, *J*=8.3 Hz, ArH), 7.14 (s, 2H, ArH), 2.39 (s, 6H, 2×CH_3), 2.26 (s, 6H, 2×CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 140.6 (2×C), 140.0 (2×C), 139.7 (2×C), 139.3 (2×C), 135.1 (2×C), 134.7 (2×C), 133.8 (2×CH), 132.0 (2×CH), 129.5 (4×CH), 127.4 (4×CH), 126.7 (4×CH), 123.6 (2×C), 22.3 (2×CH_3), 19.8 (2×CH_3); HRMS calcd for $C_{34}H_{28}Br_2$: 594.0558, Found: 594.0555.

*4.2.16. 4,4‴″-Dibromo-2,2‴″,5,5‴″-tetramethoxy-(penta-p-phenylene) (**12**).* The reaction was carried out by following the reflux-12 h procedure, using *p*-diiodoterphenyl (**8**, 0.50 g, 1.00 mmol), boronic acid **10** (0.18 g, 0.69 mmol), cesium carbonate (0.45 g, 1.38 mmol), $Pd(PPh_3)_4$ (0.064 g, 0.055 mmol), toluene (10 mL), and methanol (10 mL). Compound **12** was isolated by column chromatography (silica gel, cyclohexane/CH_2Cl_2 5/5) as a pale yellow solid (0.20 g, 90% yield), mp: >300 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.72 (s, 4H, ArH), 7.69 (d, 4H, *J*=8.2 Hz, ArH), 7.60 (d, 4H, *J*=8.2 Hz, ArH), 7.19 (s, 2H, ArH), 6.95 (s, 2H, ArH), 3.89 (s, 6H, 2×OCH_3), 3.79 (s, 6H, 2×OCH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 150.9 (2×C), 150.3 (2×C), 139.71 (4×C), 139.69 (2×C), 136.8 (2×C), 129.8 (4×CH), 127.5 (4×CH), 126.5 (4×CH), 117.7 (2×CH), 114.0 (2×CH), 110.6 (2×C), 57.0 (2×OCH_3), 56.5 (2×OCH_3); HRMS calcd for $C_{34}H_{28}Br_2O_4$: 658.0354, Found: 658.0359.

*4.2.17. 2,2‴″,5,5‴″-Tetramethoxy-(penta-p-phenylene) (**13**).* The reaction was carried out by following the reflux-12 h procedure, using **12** (0.12 g, 0.18 mmol), 4-methoxyphenyl boronic acid (**3a**, 0.018 g, 0.12 mmol), cesium carbonate (0.078 g, 0.24 mmol), $Pd(PPh_3)_4$ (0.011 g, 0.010 mmol), toluene (18 mL), and methanol (15 mL). Compound **13** was isolated by column chromatography (silica gel, cyclohexane/AcOEt 9.8/0.2) as a white solid (0.048 g, 80% yield), mp: 220–225 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.72 (s, 4H, ArH), 7.69 (d, 4H, *J*=8.4 Hz, ArH), 7.62 (d, 4H, *J*=8.4 Hz, ArH), 6.97–6.83 (m, 6H, ArH), 3.79 (s, 6H, 2×OCH_3), 3.76 (s, 6H, 2×OCH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 153.8 (2×C), 150.8 (2×C), 139.8 (2×C), 139.4 (2×C), 137.4 (2×C), 131.1 (2×C), 129.9 (4×CH), 127.5 (4×CH), 126.7 (4×CH), 116.6 (2×CH), 113.2 (2×CH), 112.6 (2×CH), 56.5 (2×OCH_3), 56.2 (2×OCH_3); HRMS calcd for $C_{34}H_{30}O_4$: 502.2144, Found: 502.2147.

*4.2.18. 2′,2‴″,4,5′,5‴″-Pentamethoxy-(hexa-p-phenylene) (**14**).* From the same reaction as for **13**, compound **14** was isolated as a yellowish syrup (0.010 g, 14% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.73–7.52 (m, 15H, ArH), 7.02–6.87 (m, 6H, ArH), 3.85 (s, 3H, OCH_3), 3.82 (s, 3H, OCH_3), 3.82 (s, 3H, OCH_3), 3.80 (s, 3H, OCH_3), 3.79 (s, 3H, OCH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.1 (C), 154.1 (C), 151.1 (3×C), 140.1 (4×C), 139.7 (C), 137.8 (2×C), 131.4 (2×C), 130.8 (C), 130.2 (CH), 129.7 (CH), 127.8 (2×CH), 127.7 (4×CH), 127.1 (2×CH), 127.0 (4×CH), 116.9 (CH), 114.9 (CH), 114.8 (CH), 113.9 (CH), 113.5 (CH), 112.9 (2×CH), 56.8 (OCH_3), 56.7 (OCH_3), 56.6 (OCH_3), 56.1 (OCH_3), 55.6 (OCH_3) ppm; HRMS calcd for $C_{41}H_{36}O_5$: 608.2563, Found: 608.2565.

*4.2.19. 4‴″-Bromo-2′,2‴″,5′,5‴″-tetramethoxy-4-methoxycarbonyl-(hexa-p-phenylene) (**15**).* The reaction was carried out by following

the rt-12 h procedure, using **12** (0.20 g, 0.30 mmol), 4-(methoxycarbonyl)phenyl boronic acid pinacol ester (**3f**, 0.052 g, 0.20 mmol), silver carbonate (0.11 g, 0.40 mmol), $Pd(PPh_3)_4$ (0.018 g, 0.016 mmol), and tetrahydrofuran (50 mL). Compound **15** was isolated by column chromatography (silica gel, cyclohexane/AcOEt 9.2/0.8) as a white solid (0.30 g, 78% yield), mp: 230 °C dec; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.10 (d, 2H, J=8.4 Hz, ArH), 7.73–7.66 (m, 12H, ArH), 7.61 (d, 2H, J=8 Hz, ArH), 7.19 (s, 1H, ArH), 7.04 (s, 1H, ArH), 6.99 (s, 1H, ArH), 6.95 (s, 1H, ArH), 3.94 (s, 3H, OCH_3), 3.90 (s, 3H, OCH_3), 3.83 (s, 3H, OCH_3), 3.81 (s, 3H, OCH_3), 3.79 (s, 3H, OCH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 168.5 (CO), 150.9 (C), 150.8 (C), 150.7 (C), 150.4 (C), 143.0 (C), 139.9 (C), 139.7 (C), 139.6 (2×C), 137.2 (2×C), 136.8 (2×C), 129.9 (2×CH), 129.8 (C), 129.5 (3×CH), 129.4 (3×CH), 127.5 (3×CH), 126.8 (3×CH), 117.0 (CH), 114.8 (2×CH), 114.7 (2×CH), 114.5 (C), 57.0 (2×OCH_3), 56.5 (OCH_3), 56.5 (OCH_3), 52.1 (OCH_3) ppm; IR (KBr) ν: 1729 ν_{CO} cm^{-1}; HRMS calcd for $C_{42}H_{35}BrO_6Na$: 737.1515, Found: 737.1520.

*4.2.20. 4‴″-Bromo-2′,2‴″,5′,5‴″-tetramethyl-4-methoxycarbonyl-(hexa-p-phenylene) (**16**).* The reaction was carried out by following the rt-12 h procedure, using **11** (0.46 g, 0.77 mmol), 4-(methoxycarbonyl)phenyl boronic acid pinacol ester (**3f**, 0.135 g, 0.51 mmol), silver carbonate (0.28 g, 1.02 mmol), $Pd(PPh_3)_4$ (0.047 g, 0.041 mmol), and tetrahydrofuran (50 mL). Compound **16** was isolated by column chromatography (silica gel, cyclohexane/CH_2Cl_2 9/1) as a white solid (0.18 g, 54% yield), mp: >300 °C dec; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.09 (d, 2H, J=8.6 Hz, ArH), 7.75 (s, 4H, ArH), 7.71–7.70 (m, 4H, ArH), 7.48–7.43 (m, 5H, ArH), 7.37 (d, 2H, J=8.6 Hz, ArH), 7.22 (s, 1H, ArH), 7.17 (s, 1H, ArH), 7.14 (s, 1H, ArH), 3.94 (s, 3H, $COOCH_3$), 2.39 (s, 3H, CH_3), 2.34 (s, 3H, CH_3), 2.30 (s, 3H, CH_3), 2.26 (s, 3H, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 168.4 (CO), 142.0 (C), 139.5 (C), 138.9 (C), 138.7 (C), 138.5 (C), 136.1 (2×C), 135.70 (C), 135.69 (C), 133.9 (2×C), 132.8 (C), 131.7 (C), 130.2 (2×CH), 129.9 (C), 129.8 (3×CH), 129.0 (3×CH), 128.1 (3×CH), 126.1 (3×CH), 119.5 (CH), 117.8 (2×CH), 114.9 (2×CH), 114.5 (C), 52.0 (OCH_3), 29.2 (CH_3), 23.5 (CH_3), 19.5 (CH_3), 14.2 (CH_3) ppm; IR (KBr) ν: 1730 ν_{CO} cm^{-1}; HRMS calcd for $C_{42}H_{35}BrO_2Na$: 673.1718, Found: 673.1720.

*4.2.21. 4‴″-Bromo-4-cyano-2′,2‴″,5′,5‴″-tetramethyl-(hexa-p-phenylene) (**17**).* The reaction was carried out by following the rt-12 h procedure, using **11** (0.52 g, 0.87 mmol), 4-cyanophenyl boronic acid pinacol ester (**3e**, 0.133 g, 0.58 mmol), silver carbonate (0.32 g, 1.16 mmol), $Pd(PPh_3)_4$ (0.054 g, 0.046 mmol), and tetrahydrofuran (50 mL). Compound **17** was isolated by column chromatography (silica gel, cyclohexane/CH_2Cl_2 9/1) as a white solid (0.20 g, 55% yield), mp: >300 °C dec; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.76–7.67 (m, 12H, ArH), 7.48 (d, 2H, J=8.2 Hz, ArH), 7.45 (d, 2H, J=8.2 Hz, ArH), 7.39 (s, 1H, ArH), 7.35 (s, 1H, ArH), 7.14 (s, 1H, ArH), 7.13 (s, 1H, ArH), 2.39 (s, 3H, CH_3), 2.34 (s, 3H, CH_3), 2.26 (s, 6H, 2×CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 143.6 (C), 139.8 (2×C), 139.4 (2×C), 133.9 (C), 133.2 (2×C), 133.0 (2×C), 132.5 (C), 132.3 (C), 132.1 (2×CH), 131.7 (2×C), 130.1 (2×CH), 129.7 (2×CH), 129.6 (6×CH), 128.0 (4×CH), 127.6 (2×CH), 126.9 (2×CH), 120.0 (C), 118.5 (CN), 112.6 (C), 30.4 (CH_3), 22.4 (CH_3), 19.9 (CH_3), 14.2 (CH_3) ppm; IR (KBr) ν: 2220 ν_{CN} cm^{-1}; HRMS calcd for $C_{41}H_{32}BrNNa$: 640.1616, Found: 640.1623.

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Supplementary data

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.tet.2011.02.025.

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