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Electrophilic *ipso*-iodination of silylated arylboronic acids

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ABSTRACT

Silylated functionalized arylboronic acids were converted into corresponding iodinated arylboronic acids in good yields via the electrophilic *ipso*-desilylation effected with iodine chloride in refluxing $CHCl_3$. Disilylated arylboronic acids were susceptible to diiodination. In addition, the structural characterization and reactivity of a novel sterically hindered *ortho*-silylated diarylborinic ester were reported. The potential of selected iodinated phenylboronic acids as monomers for the Suzuki–Miyaura cross-coupling polymerization was demonstrated.

1. Introduction

Arylboronic acids are extremely important reagents due to their wide and diverse applications in organic synthesis, catalysis and supramolecular chemistry. Iodinated arylboronic acids are attractive synthetic intermediates as they possess two sites, which can be employed in coupling reactions. Thus, pinacol esters of simple iodophenylboronic acids were used as precursors of magnesium–boron bimetallics followed by the treatment with electrophiles to give functionalized arylboronic esters [1,2]. Recently, 2-iodophenylboronic acid was found to be an effective catalyst for the direct formation of amides from carboxylic acids and amines [3].

Simple iodophenylboronic acids and esters are readily prepared from the corresponding diiodobenzenes via I/Li or I/Mg exchange followed by boronation [4]. Alternative approach based on the treatment of lithium–boron bimetallics with elemental iodine has also been described [5–7]. However, many functionalized iodoarylboronic acids cannot be obtained using these routes due to the limited access to the appropriate aryllithium or arylmagnesium precursors. This has prompted us to investigate the general potential of silylated arylboronic acids as starting materials in the approach involving electrophilic *ipso*-desilylation with ICl [8].

2. Results and discussion

2.1. Synthesis of silylated arylboronic acids

In most cases, the classical approach involving the transmetalation of silylated aryllithiums with trialkyl borate followed by hydrolysis was employed (Scheme 1) as described previously for substrates **8a, 9a, 12a,** and **15a** [9,10]. Alternatively, silylated difluorophenylboronic acids **1a** and **2a** were obtained by the treatment of appropriate lithiated arylboronic derivatives with Me_3SiCl as reported recently [7]. In most cases crude acids were used in subsequent synthetic step as the isolation of well-defined crystalline materials proved problematic.

The reaction of *ortho*-silylated aryllithiums with $B(OMe)_3$ under standard conditions (Et_2O/THF, −70 °C) leads to mixtures of boronic and borinic acid derivatives (Scheme 2) [9]. For the selective formation of arylboronic acids a lower temperature is required during the boronation step. As reported recently, this can be attributed to the decreased stability of the highly strained intermediate anionic *ortho*-silylated boronate. It tends to dissociate to some extent to form the boronic ester which is immediately trapped with excessive aryllithium. Interestingly, the borinic ester **4c** was formed as a major product from the reaction of 3-fluoro-2-(trimethylsilyl)phenyllithium **4-Li** with $B(OMe)_3$ whereas the corresponding 3-chloro and 3-bromo derivatives (**5-Li** and **6-Li**) were converted mainly to boronic acids **5a**–**6a**. Initially, we expected the reversed product distribution as we assumed that larger substituents adjacent to Me_3Si will increase the steric pressure on the

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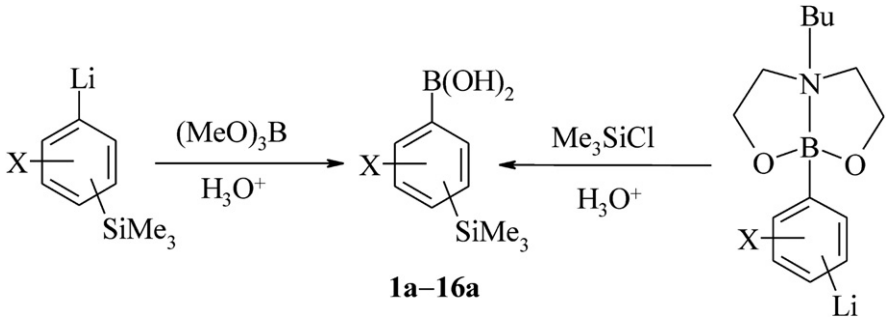


Scheme 1. General synthetic approaches to silylated arylboronic acids **1a**–**16a**.

boronate group. Our results may suggest that irrespective of steric factors the more potent long-range inductive effects of heavier halogens are operative to provide additional electronic stabilization for the intermediate "ate" complex.

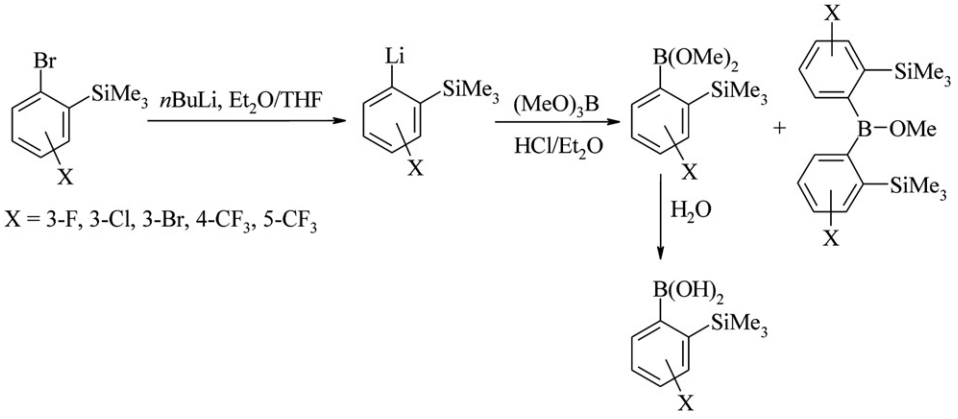
2.2. Structural characterization of bis(3-fluoro-2-(trimethylsilyl) phenyl)methoxyborane (*4c*)

The borinic ester **4c** can be isolated from the reaction mixtures by fractional distillation followed by recrystallization from pentane. It should be noted that unlike other methyl esters of boronic and borinic acids, **4c** is fairly stable towards water and does not rapidly hydrolyze to give corresponding borinic acid and methanol [11]. The ^{1}H NMR spectrum of **4c** shows a broad Me_3Si resonance at 0.35 ppm which splits into two sharp signals at 0.41 and 0.28 ppm on cooling to 227 K. The signal at 0.41 ppm is a doublet, apparently due to the long-range coupling $^{5}J_{H-F} = 2$ Hz. This points to the non-equivalence of aromatic rings, which is also demonstrated by the appropriate changes in the aromatic range of the spectrum. Similarly, broad resonances are also observed in the ^{13}C NMR spectrum of **4c**. This points to the restricted rotation of aryl groups around the B–C bonds.

The molecular structure of **4c** has been determined by single-crystal X-ray diffraction analysis and is shown in Fig. 1. Two aromatic rings are almost perpendicular to each other due to the steric hindrance of *ortho* trimethysilyl groups. The boron centre adopts trigonal, planar geometry. Interestingly, the C(1)–B(1)–C(7) angle is 120 °, whereas for other sterically hindered borinic derivatives, this angle is close to 125 ° [11–13]. The C(1)–B(1)–O(1) and C(7)–B(1)–O(1) angles are equal to 124.1(1) ° and 115.8(1) °, respectively, which differ significantly from ideal 120 °. Both trimethylsilyl groups show significant deviations either in plane or out of plane of aromatic ring (both Si atoms are out of the least-squares planes of the corresponding phenyl rings by about 0.22 Å). The oxygen atom is involved in the intramolecular C–H···O interactions with selected hydrogen atoms of the adjacent Me_3Si groups (Fig. 1). The geometry of these interactions is presented in Table 1. In order to extend our investigations we performed theoretical calculations at DFT(B3LYP) [14] level of theory using 6 – 311 + G* basis set [15] at the experimental geometry of isolated molecule. The Bond Critical Points and linking bond paths were found in all C–H···O interactions. The values of electron density (ρ) at these BCPs range from 0.06 to 0.08 *e* Å^{-3}. Local potential energy density, which is the quantity proportional to the hydrogen bond energy, is close to −6 kJ mol^{-1} bohr^{-3} and is in good agreement with the literature values [16]. The values of Laplacian of electron density range from 0.8 to 1.0 *e* Å^{-5} and are characteristic for such interactions. The stabilization of the methoxy function via C–H···O interactions may also account for its higher kinetic resistance against hydrolytic cleavage.

2.3. Electrophilic ipso-substitution of silylated arylboronic acids with ICl

There are only a few reported reactions of related silylated pinacol arylboronates and phenyldichloroboranes with iodine chloride [17,18]. They were carried out in dichloromethane at room or lower temperature. We found that the conversion of silylated boronic acids was incomplete using this solvent even under prolonged reflux conditions, which may be due to their limited solubility. Fortunately, good yields of iodinated arylboronic acids were obtained in general using a slight excess of ICl (1.1 equiv.) in refluxing chloroform (Scheme 3). The results are summarized in Table 2. However, in the case of **13a**, the use of excess ICl resulted in the formation of a significant amount of a 3,5-diiodo-2-methoxyphenylboronic acid resulting from electrophilic iodination of the ring at C5 owing to the *para*-activating effect of the methoxy group. The selective synthesis of **13b** was performed using a stoichiometric amount of ICl at 0 °C. Finally, the general protocol was



Scheme 2. Synthesis of ortho-silylated arylboronic acids.

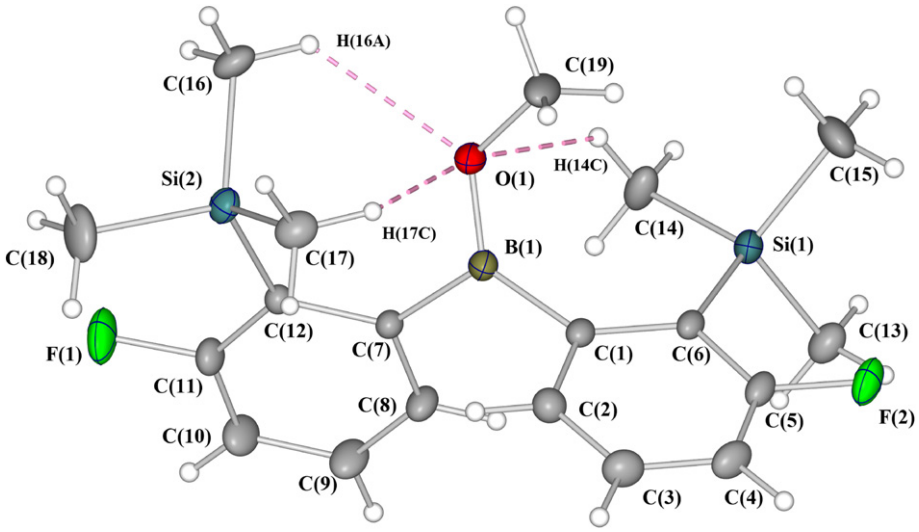


Fig. 1. Molecular structure of **4c**. Labelling of atoms and estimation of atomic thermal motions as Anisotropic Displacement Parameters (ADPs). Ellipsoids are drawn at 50% probability level. Weak intramolecular CeH/O interactions are presented as dashed lines.

successfully extended for the preparation of diiodinated products **14b**–**16b** from their disilylated precursors. Among them, **16b** is the first example of iodinated phenylenediboronic acid.

Iodination of borinic ester was performed in a similar way and the resulting product was isolated after complexation with 8-hydroxyquinoline (Scheme 4).

2.4. Polymerization of 3,5-difluoro-4-iodophenylboronic acid (1b) and 2,5-diiodo-1,4-phenylenediboronic acid (*16b*)

We have probed the potential of **1b** for the synthesis of fluorinated poly(*p*-phenylene) via Pd-catalyzed polymerization. The reaction was performed at room temperature (rt) using $Pd(OAc)_2$ (0.5 mol%)/K_2CO_3 (1.1 equiv) in 2-methoxyethanol/H_2O (3:1) (Scheme 5) [19].

The resulting polymer **1c** was obtained in a good yield as a white powder after removal of palladium black with concentrated HNO_3 and washing with water and acetone. It is completely insoluble in common solvents which preclude the characterization by NMR and ESI MS. The XPRD analysis revealed that **1c** is essentially amorphous. Based on elemental analysis and assuming the presence of iodine and $B(OH)_2$ end groups the average molecular weight was calculated to be ca. 1600, which corresponds to an average value of 13 difluorophenylene units in the polymer chain. IR spectrum of a vacuum-dried sample shows no bands of OH absorption, which indicates that the triangle-shaped polymer with a central boroxine core is formed upon condensation of three $B(OH)_2$ end groups [20,21]. TG/DTA analysis revealed that no significant mass loss occurred when the sample of **1c** was heated up to 300 °C. In the range 300–600 °C the mass loss was ca. 30% followed by extensive degradation in the range 600–700 °C (over 95% of the initial mass).

The polymerization of **16b** was performed using the same catalytic system as that applied for **1b.** The reaction proceeds at room temperature although the mixture was then additionally heated at 100 °C. The resulting product **16c** was isolated as a yellow amorphous powder insoluble in common solvents. Based on elemental analysis data ca. 80% of boronic and iodine groups were involved in the cross-coupling. This indicates that **16c** must have a highly branched structure (Scheme 6). It does not melt up to 425 °C, although partial decomposition manifested by the extrusion of elemental iodine was observed above 370 °C. It seems that the starting boronic acid **1c** could be used as a comonomer for the synthesis of branched poly(phenylenes), e.g., via copolymerization with other phenylenediboronic acids. Further studies on the synthesis and characterization of polymers **1c** and **16c** and their analogues will be reported in due course.

Table 1
Geometry of weak intramolecular interactions (D denotes a donor and A an acceptor of D–H···A interactions; *d* and θ denote distance and angle, respectively).

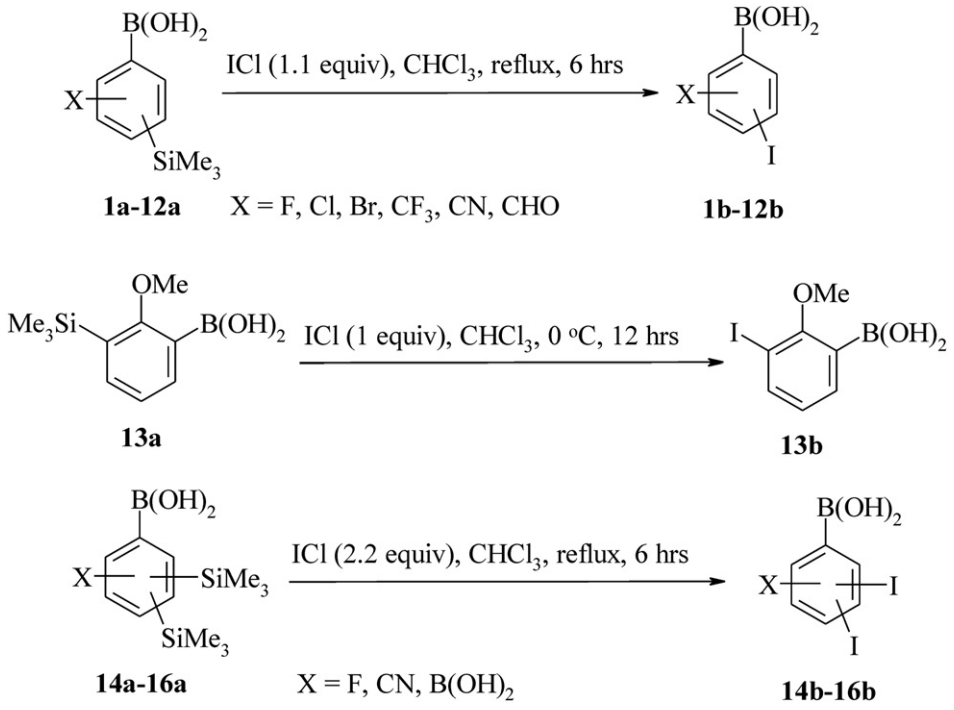
Interaction	$d_{H\cdots A}$/Å	$d_{D\cdots A}$/Å	$\theta_{D-H\cdots A}$/°
C(14)–H(14C)···O(1)	2.525	3.279 (2)	133.7
C(16)–H(16A)···O(1)	2.457	3.170 (1)	129.3
C(17)–H(17C)···O(1)	2.477	3.182 (2)	128.7

3. Conclusions

In conclusion, silylated arylboronic acids can be readily prepared from the appropriate bimetallic aromatic silicon–lithium or boron–lithium precursors by lithium–boron or lithium–silicon transmetalation, respectively. The sterically hindered arylborinic esters are formed to a significant extent from the reactions of *ortho*-silylated aryllithiums with $B(OMe)_3$. Silylated arylboronic acids are efficiently converted into iodinated arylboronic acids using the *ipso*-iododesilylation protocol involving ICl in $CHCl_3$ as the iodinating agent. Similarly, diiodinated arylboronic acids as well as bis(iodoaryl)borinic derivatives were obtained. The preliminary results indicate the potential of iodinated arylboronic acids in the synthesis of boroxine-based and branched poly(phenylenes).

4. Experimental

All reactions involving air- or moisture-sensitive reagents were carried out under argon. Et_2O and THF were stored over sodium wire before use. Key reagents including *n*BuLi (10 M solution in hexanes), diisopropylamine, 2,2,6,6-tetramethylpiperidine, chlorotrimethylsilane, iodine chloride, acyl chlorides, trimethoxyborane, $Pd(OAc)_2$ and solvents were received from Aldrich and used without additional purification. The synthesis of silylated arylboronic acids **1a**, **2a**, **8a**, **9a**, **12a**, and **15a** was described previously [7,9,10]. The remaining silylated arylboronic acids were obtained from appropriate silylated bromobenzenes [22–24], in most cases as crude materials and hence their combustion analyses were not performed. NMR spectra were recorded on a Varian Mercury 400



Scheme 3. Preparation of iodoarylboronic acids **1b**–**16b**.

spectrometer. The NMR chemical shifts are given relative to TMS with the aid of known chemical shifts of residual proton (^{1}H) or carbon (^{13}C) solvent resonances. In the ^{13}C NMR spectra the resonances of boron-bound carbon atoms were not observed in most cases (except for compounds **2b**, **11b** and **16b**), due to their broadening by quadrupolar boron nuclei.

4.1. Synthesis of silylated arylboronic acids

4.1.1. 4-Fluoro-3-(trimethylsilyl)phenylboronic acid (**3a**)

A solution of 1-bromo-4-fluorobenzene-3-(trimethylsilyl)-benzene (6.35 g, 25 mmol) was added at −75 °C to a stirred solution of *n*BuLi (10 M, 2.5 mL, 25 mmol) in Et_2O (30 mL). THF (10 mL) was added. After ca. 30 min of stirring at ca. −75 °C a mixture containing the lithiate was quenched with $B(OMe)_3$ (3.2 g, 3.5 mL, 0.30 mmol). The mixture was stirred for 30 min at −75 °C and was then hydrolyzed with 2 M aq. H_2SO_4 (10 mL). The water phase was separated, followed by extraction with diethyl ether (2 × 15 mL). The extracts were added to the organic phase, which was concentrated under reduced pressure. A solid residue was filtered and washed consecutively with water (2 × 10 mL) and hexane (2 × 10 mL). Drying in vacuo afforded the title compound as a white powder. Yield: 4.9 g (93%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.31 (1H, dd, *J* 6.5, *J* 1.0 Hz, Ph), 8.20 (1H, t, *J* 8.5 Hz, Ph), 7.13 (1H, t, *J* 8.5 Hz, Ph), 0.40 (9H, s, CH_3) ppm. ^{11}B NMR ([D_6]acetone, 64.16 MHz) δ: 30.

4.1.2. 3-Fluoro-2-(trimethylsilyl)phenylboronic acid (**4a**)

The synthesis was performed as described for **3a** starting with 1-bromo-3-fluoro-2-(trimethylsilyl)benzene. The lithiate was quenched with $B(OMe)_3$ below −90 °C. Yield: 4.3 g (80%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.37–7.31 (1H, m, Ph), 7.26–7.21 (1H, m, Ph), 7.02–6.97 (1H, m, Ph), 0.36 (9H, s, CH_3); ^{13}C{^{1}H} NMR ([D_6]acetone, 100.6 MHz) δ: 167.6 (d, *J* 242.0 Hz), 130.8 (d, *J* 8.3 Hz), 128.5 (d, *J* 27.5 Hz), 127.1 (d, *J* 2.3 Hz), 115.8 (d, *J* 27.4 Hz), 0.4 (d, *J* 3.0 Hz); ^{11}B NMR ([D_6]acetone, 64.16 MHz) δ: 28.5.

4.1.3. Bis(3-fluoro-2-(trimethylsilyl)phenyl)methoxyborane (**4c**)

The suspension of **4-Li** was prepared from 1-bromo-3-fluoro-2-(trimethylsilyl)benzene (20.0 g, 0.08 mol) and *n*BuLi (10 M, 8 mL, 0.08 mol) at −70 °C in Et_2O/THF (2:1, 100 mL). Then, $B(OMe)_3$ (10.4 g, 0.1 mol) was added at −60 °C and the resulting mixture was warmed up to the room temperature. 2 M HCl solution in Et_2O (40 mL) was added followed by the filtration of the resulting slurry. The filtrate was concentrated in vacuo and the residue was subjected to vacuum distillation to give impured (3-fluoro-2-(trimethylsilyl)phenyl) dimethoxyborane (5.5 g, b.p. 60–110 °C, 1 Tr) and **4c** (11.0 g, b.p. 130–135 °C, 1 Tr) which slowly crystallized and was purified by recrystallization from pentane at −20 °C, m.p. 78–80 °C. Yield: 9.3 g (62%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.29 (2H, broad, Ph), 7.10–6.98 (4H, m, Ph), 3.64 (3H, s, OMe), 0.35 (18H, broad, $SiMe_3$); ^{13}C{^{1}H} NMR ($CDCl_3$, 100.6 MHz) δ: 167.8 (d, *J* 241 Hz), 147 (broad), 134.7 (broad) 130.9 (broad), 130.0 (broad), 125.4 (broad), 117.5 (broad), 114.5 (broad), 2.1 (broad), 0.1 (broad); ^{11}B NMR ($CDCl_3$, 64.16 MHz) δ: 42. Anal. Calcd. for $C_{19}H_{27}BF_2OSi_2$ (376.40): C, 60.63; H, 7.23. Found: C, 60.45; H, 7.11.

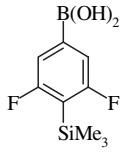
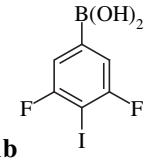
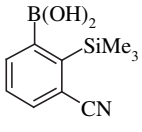
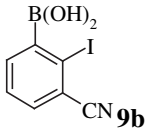
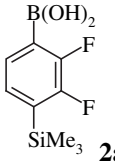
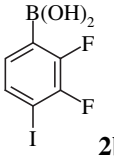
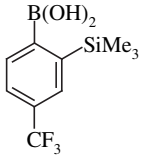
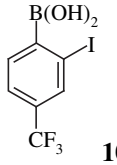
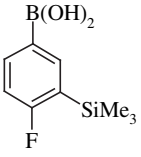
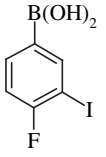
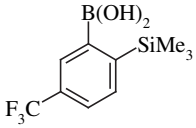
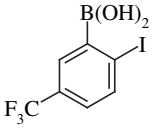
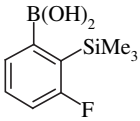
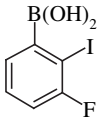
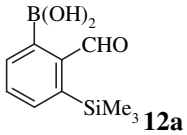
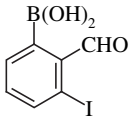
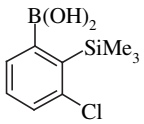
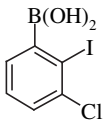
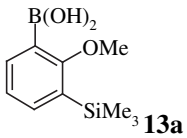
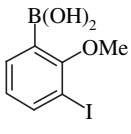
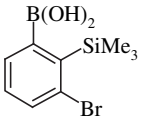
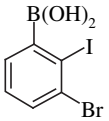
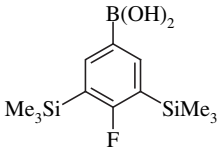
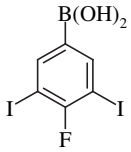
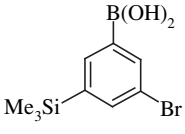
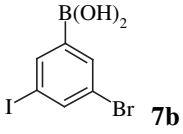
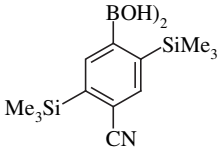
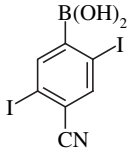
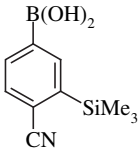
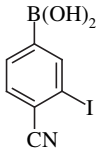
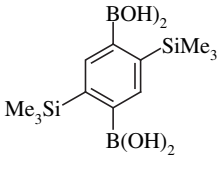
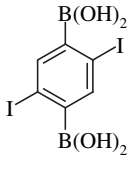
4.1.4. 3-Chloro-2-(trimethylsilyl)phenylboronic acid (**5a**)

The synthesis was performed as described for **3a** starting with 1-bromo-3-chloro-2-(trimethylsilyl)benzene (21.0 g, 0.08 mol). Vacuum distillation gave crude (3-chloro-2-(trimethylsilyl)phenyl) dimethoxyborane (10.5 g, b.p. 75–80 °C, 1 Tr). It was mixed with water (10 mL) and acetone (10 mL). The solvent was removed and the resulting white solid was filtered, washed with water and hexane and dried to give pure boronic acid, m.p. 94–96 °C. Yield: 9.5 g (52%). ^{1}H NMR ([D_6]acetone, 400 MHz) δ: 7.35 (2H, broad, $B(OH)_2$), 7.28 (3H, m, Ph), 0.41 (9H, s, $SiMe_3$); ^{13}C{^{1}H} NMR ([D_6] acetone, 100.6 MHz) δ: 141.9, 140.6, 130.4, 130.3, 129.6, 1.1; ^{11}B NMR ([D_6]acetone, 64.16 MHz) δ: 29.

4.1.5. 3-Bromo-2-(trimethylsilyl)phenylboronic acid (**6a**)

The synthesis was performed as described for **3a** starting with 1,3-dibromo-2-(trimethylsilyl)benzene (15.5 g, 0.05 mol), m.p. 95–97 °C. Yield: 6.5 g (48%). ^{1}H NMR ([D_6]acetone, 400 MHz) δ: 7.49 (1H, dd, *J* 8.0, 1.5 Hz, Ph), 7.35 (2H, broad, $B(OH)_2$), 7.33 (1H, dd, *J* 7.0,

Table 2
Preparation of functionalized iodophenylboronic acids via electrophilic *ipso*-substitution of silylated arylboronic acids with iodine chloride.

Substrate	Product	Yield, %	Substrate	Product	yield, %
 **1a**	 **1b** **1b**	63	 **9a** [9]	 **9b**	64
[7]					
 **2a**	 **2b**	86	 **10a**	 **10b**	72
[7]					
 **3a**	 **3b**	79	 **11a**	 **11b**	79
 **4a**	 **4b**	91	 **12a** [10]	 **12b**	85
 **5a**	 **5b**	88	 **13a**	 **13b**	94
 **6a**	 **6b**	84	 **14a**	 **14b**	87
 **7a**	 **7b**	84	 **15a** [9]	 **15b**	68
 **8a**	 **8b**	79	 **16a**	 **16b**	86
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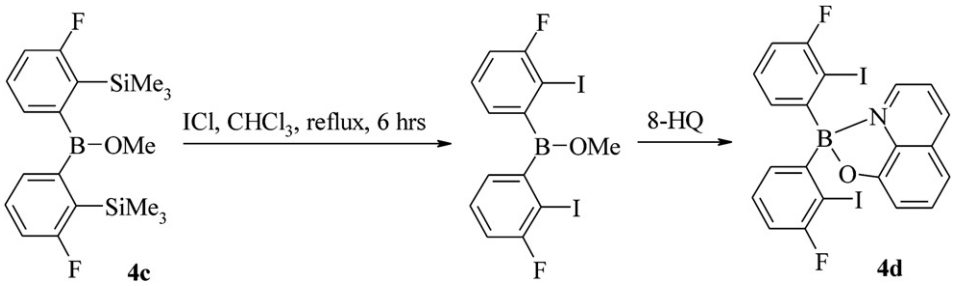


Scheme 4. Electrophilic ipso-iodination of **4c**.

1.5 Hz, Ph), 7.18 (1H, dd, *J* 8.0, 7.0 Hz, Ph), 0.44 (9H, s, $SiMe_3$); $^{13}C\{^1H\}$ NMR ([D_6]acetone, 100.6 MHz) δ: 142.9, 133.3, 132.1, 130.7, 130.5, 1.4; ^{11}B NMR ([D_6]acetone, 64.16 MHz) δ: 29.

*4.1.6. 3-Bromo-5-(trimethylsilyl)phenylboronic acid (**7a**)*

Yield: 5.9 g (86%), m.p. 145–147 °C. The synthesis was performed as described for **3a** starting with 1,3-dibromo-5-(trimethylsilyl)benzene (7.7 g, 25 mmol). ^1H NMR ([D_6]acetone, 400 MHz) δ: 8.03 (1H, t, *J* 1.0 Hz, Ph), 7.97 (1H, dd, *J* 2.0 Hz, *J* 1.0 Hz, Ph), 7.69 (1H, d, *J* 2.0 Hz, *J* 1.0 Hz, Ph), 0.27 (9H, s, $SiMe_3$); ^{11}B NMR ([D_6]acetone, 64.16 MHz) δ: 29.

*4.1.7. 5-(Trifluoromethyl)-2-(trimethylsilyl)phenylboronic acid (**10a**)*

The synthesis was performed as described for **3a** starting with 1-bromo-5-(trifluoromethyl)-2-(trimethylsilyl)benzene. Yield: 2.8 g (42%). ^1H NMR ($CDCl_3$, 400 MHz) δ: 8.29 (1H, s, Ph), 7.86 (1H, d, *J* 8.0, Ph), 7.74 (1H, d, *J* 8.0, Ph), 0.37 (9H, s, $SiMe_3$); ^{11}B NMR ($CDCl_3$, 64.16 MHz) δ = 29.

*4.1.8. 4-(Trifluoromethyl)-2-(trimethylsilyl)phenylboronic acid (**11a**)*

The synthesis was performed as described for **3a** starting with 1-bromo-4-(trifluoromethyl)-2-(trimethylsilyl)benzene. Yield: 3.0 g (46%). ^1H NMR ($CDCl_3$, 400 MHz) δ: 8.03 (d, *J* 7.5 Hz, 1H, Ph), 7.65 (d, *J* 7.5 Hz, 1H, Ph), 7.46 (s, 1H, Ph), 0.33 (s, 9H, $SiMe_3$); ^{11}B NMR ($CDCl_3$, 64.16 MHz) δ: 29.

*4.1.9. 2-Methoxy-3-(trimethylsilyl)phenylboronic acid (**13a**)*

The synthesis was performed as described for **3a** starting with 1-bromo-2-methoxy-3-(trimethylsilyl)benzene (6.5 g, 25 mmol). Yield: 4.5 g (81%), m.p. 79–82 °C ^1H NMR ([D_6]acetone, 400 MHz) δ: 7.67 (1H, dd, *J* 7.5, *J* 1.5 Hz, Ph), 7.45 (1H, dd, *J* 7.5, *J* 1.5 Hz, Ph), 7.21 (2H, broad, $B(OH)_2$), 7.07 (1H, t, *J* 7.5 Hz, Ph), 3.80 (1H, s, Ph), 0.27 (9H, s, $SiMe_3$); ^{11}B NMR ([D_6]acetone, 64.16 MHz) δ: 29.

*4.1.10. 3,5-Bis(trimethylsilyl)-4-fluorophenylboronic acid (**14a**)*

The synthesis was performed as described for **3a** starting with 1-bromo-4-fluoro-3,5-bis(trimethylsilyl)benzene (25.5 g, 0.08 mol), m.p. 288–291 °C. Yield 20.5 g (90%). ^1H NMR ([D_6]acetone, 400 MHz) δ: 8.03 (2H, d, *J* 1.0 Hz, Ph), 7.29 (2H, s, $B(OH)_2$), 0.30 (18H, d, *J* 1.0 Hz, $SiMe_3$); $^{13}C\{^1H\}$ NMR ([D_6]acetone, 100.6 MHz) δ: 174.7 (d, *J* 236.0, 11.5 Hz), 144.3 (d, *J* 12.0 Hz), 124.3 (d, *J* 34.0 Hz), −0.8; ^{11}B NMR ([D_6]acetone, 64.16 MHz) δ: 28.

*4.1.11. 2,5-Bis(trimethylsilyl)-1,4-phenylenediboronic acid (**16a**)*

The synthesis was performed as described for **3a** starting with 1,4-diiodo-2,5-bis(trimethylsilyl)benzene (4.8 g, 0.01 mol). Yield: 2.5 g (80%), m.p. >310 °C (dec). ^1H NMR ([D_6]acetone, 400 MHz) δ: 7.78 (2H, s, Ph), 7.20 (4H, s, $B(OH)_2$), 0.29 (18H, d, $SiMe_3$); $^{13}C\{^1H\}$ NMR ([D_6]acetone, 100.6 MHz) δ: 143.0, 138.5, 0.5; ^{11}B NMR ([D_6]acetone, 64.16 MHz) δ: 28.0.

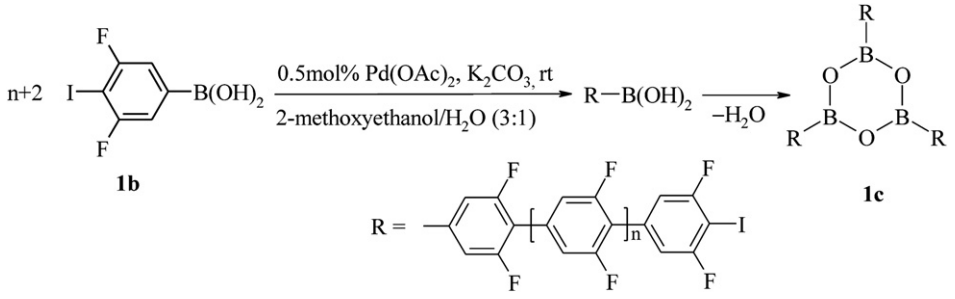
4.2. Synthesis of iodinated arylboronic acids

*4.2.1. 3,5-Difluoro-4-iodophenylboronic acid (**1b**)*

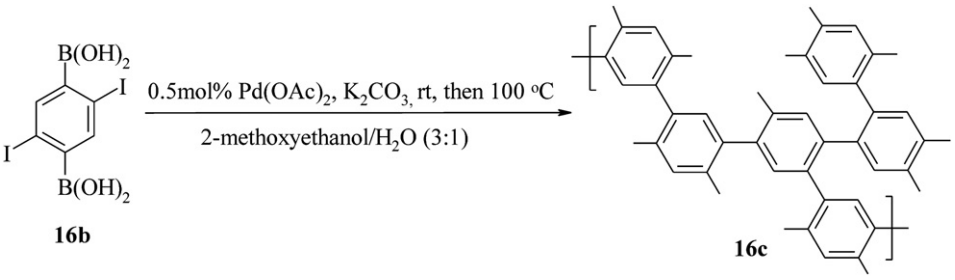
A mixture of **1a** (2.44 g, 10 mmol), ICl (1.8 g, 11 mmol) and $CHCl_3$ (50 mL) was stirred under reflux for 6 h. The resulting mixture was concentrated under reduced pressure. Et_2O (50 mL) was added and the dark-coloured solution was treated with 10% aq. $Na_2S_2O_3$ (10 mL). The almost colourless organic phase was separated and ether was removed under reduced pressure. The crude product was filtered and washed with $CHCl_3$ (5 mL). Yield: 1.80 g (63%), m.p. 304–307 °C ^1H NMR ([D_6]acetone, 400 MHz) δ: 7.63 [2H, broad, $B(OH)_2$], 7.41 (2H, d, *J* 7.0 Hz, Ph); $^{13}C\{^1H\}$ NMR ([D_6]acetone, 100.6 MHz) δ: 163.2 (d, *J* 250.5 Hz), 116.8 (d, *J* 23.0 Hz), 73.9 (t, *J* 29.0 Hz); ^{11}B NMR ([D_6]acetone, 64.16 MHz) δ: 28.5. Anal. Calcd. for $C_6H_4BF_2IO_2$ (283.81): C, 25.39; H, 1.42. Found: C, 25.05; H, 1.39.

*4.2.2. 2,3-Difluoro-4-iodophenylboronic acid (**2b**)*

Yield: 2.45 g (86%), m.p. >400 °C ^1H NMR ([D_6]acetone, 400 MHz) δ: 7.55–7.52 (1H, m, Ph), 7.23–7.20 (1H, m, Ph); $^{13}C\{^1H\}$ NMR ([D_6]acetone, 100.6 MHz) δ: 153.6 (dd, *J* 252.0 Hz, *J* 14.0 Hz), 150.8 (dd, *J* 244.0 Hz, *J* 16.0 Hz), 134.6, 132.5, 125.0 (broad), 84.7 (d, *J* 21.5 Hz); ^{11}B NMR ([D_6]acetone, 64.16 MHz) δ: 23.0. Anal. Calcd. for $C_6H_4BF_2IO_2$ (283.81): C, 25.39; H, 1.42. Found: C, 25.18; H, 1.77.



Scheme 5. Polymerization of **1b**.



Scheme 6. Polymerization of **16b**.

*4.2.3. 4-Fluoro-3-iodophenylboronic acid (**3b**)*

Yield: 2.10 g (79%), m.p. 240–241 °C ^{1}H NMR ([D$_6$]acetone, 400 MHz) δ: 8.30 (1H, dd, *J* 7.5 Hz, *J* 1.5 Hz, Ph), 7.90–7.86 (1H, m, Ph), 7.39 [2H, broad, B(OH)$_2$], 7.17 (1H, t, *J* 8.4 Hz, Ph); ^{13}C{^{1}H} NMR ([D$_6$]acetone, 100.6 MHz): δ: 163.9 (d, *J* 245.5 Hz), 146.4, 137.3 (d, *J* 7.5 Hz), 115.8 (d, *J* 23.0 Hz), 81.26 (d, *J* 24.5 Hz); ^{11}B NMR ([D$_6$] acetone, 64.16 MHz) δ: 29.0; Anal. Calcd. for $C_6H_5BFIO_2$ (265.82): C, 30.81; H 1.85. Found: C, 28.40; H, 1.47.

*4.2.4. 3-Fluoro-2-iodophenylboronic acid (**4b**)*

Yield: 2.42 g (91%), m.p. 199–202 °C ^{1}H NMR ([D$_6$]acetone, 400 MHz) δ: 7.55 [2H, broad, B(OH)$_2$], 7.39–7.34 (1H, m, Ph), 7.17–7.09 (2H, m, Ph); ^{13}C{^{1}H} NMR ([D$_6$]acetone, 100.6 MHz): δ: 161.6 (d, *J* 243.5 Hz), 130.4 (d, *J* 7.0 Hz), 129.9 (d, *J* 3.0 Hz), 116.0 (d, *J* 24.5 Hz), 85.6 (d, *J* 23.5 Hz); ^{11}B NMR ([D$_6$]acetone, 64.16 MHz): δ: 28.7. Anal. Calcd. for $C_6H_5BFIO_2$ (265.82): C, 27.11; H, 1.90. Found: C, 27.76; H, 2.04.

*4.2.5. 3-Chloro-2-iodophenylboronic acid (**5b**)*

Yield: 2.48 g (88%), m.p. 130–132 °C ^{1}H NMR ([D$_6$]acetone, 400 MHz) δ: 7.49 [2H, broad, B(OH)$_2$], 7.47 (1H, dd, *J* 8.0 Hz, *J* 1.5 Hz, Ph), 7.35 (1H, t, *J* 7.2 Hz, Ph), 7.18 (1H, dd, *J* 7.0 Hz, *J* 1.5 Hz, Ph); ^{13}C {^{1}H} NMR ([D$_6$]acetone, 100.6 MHz): δ: 138.6, 131.6, 129.9, 129.7, 101.9; ^{11}B NMR ([D$_6$]acetone, 64.16 MHz): δ: 28.1. Anal. Calcd. for $C_6H_4BF_2IO_2$ (282.27): C, 25.53; H, 1.79. Found: C, 25.86; H, 1.83.

*4.2.6. 3-Bromo-2-iodophenylboronic acid (**6b**)*

Yield: 2.54 g (78%), m.p. 127–128 °C ^{1}H NMR ([D$_6$]acetone, 400 MHz) δ: 7.64 (1H, dd, *J* 7.5 Hz, *J* 2.0 Hz, Ph), 7.48 [2H, broad, B(OH)$_2$], 7.31–7.20 (2H, m, Ph); ^{13}C{^{1}H} NMR ([D$_6$]acetone, 100.6 MHz) δ: 133.1, 132.0, 130.5, 129.9, 104.8; ^{11}B NMR ([D$_6$] acetone, 64.16 MHz) δ: 29.5. Anal. Calcd. for $C_6H_5BBrIO_2$ (326.72): C, 22.06; H, 1.54. Found: C, 21.92; H, 1.70.

*4.2.7. 3-Bromo-5-iodophenylboronic acid (**7b**)*

Yield: 2.75 g (84%), m.p. 323–324 °C ^{1}H NMR ([D$_6$]acetone, 400 MHz) δ: 8.16 (1H, m, Ph) 7.96 (2H, m, Ph), 7.60 [2H, broad, B(OH)$_2$]; ^{13}C{^{1}H} NMR ([D$_6$]acetone, 100.6 MHz) δ: 142.6, 141.5, 136.9, 123.3, 95.2; ^{11}B NMR ([D$_6$]acetone, 64.16 MHz) δ: 28.0. Anal. Calcd. for $C_6H_5BBrIO_2$ (326.72): C, 22.06; H, 1.54. Found: C, 21.85; H, 1.65.

*4.2.8. 3-Cyano-2-iodophenylboronic acid (**8b**)*

Yield: 2.15 g (79%), m.p. 141–143 °C ^{1}H NMR ([D$_6$]acetone, 400 MHz) δ: 7.70 (1H, dd, *J* 5.6 Hz, *J* 4.0 Hz, Ph), 7.68 [2H, broad, B(OH)$_2$], 7.57 (1H, s, Ph), 7.56 (1H, d, *J* 2.0 Hz, Ph). ^{13}C{^{1}H} NMR ([D$_6$] acetone, 100.6 MHz): δ: 147.5, 145.0, 138.6, 131.3, 130.6, 112.3; ^{11}B NMR ([D$_6$]acetone, 64.16 MHz): δ: 29.2. Anal. Calcd. for $C_7H_5BINO_2$ (272.84): C, 30.82; H, 1.85; N, 5.13. Found: C, 30.50; H, 1.85; N, 5.20.

*4.2.9. 4-Cyano-3-iodophenylboronic acid (**9b**)*

Yield: 1.75 g (64%), m.p. 137–138 °C ^{1}H NMR ([D$_6$]acetone, 400 MHz) δ: 7.70 (1H, dd, *J* 5.5 Hz, *J* 3.5 Hz), 7.69 [2H, broad, B(OH)$_2$], 7.57 (1H, s, Ph), 7.56 (1H, d, *J* 7.0 Hz); ^{13}C{^{1}H} NMR ([D$_6$]acetone, 100.6 MHz) δ: 137.5, 134.5, 128.6, 121.3, 120.6; ^{11}B NMR ([D$_6$] acetone, 64.16 MHz) δ: 29.0. Anal. Calcd. for $C_7H_5BINO_2$ (272.84): C, 30.82; H, 1.85; N, 5.13. Found: C, 30.95; H, 2.00; N, 5.07.

*4.2.10. 5-(Trifluoromethyl)-2-iodophenylboronic acid (**10b**)*

Yield: 2.30 g (72%), m.p. 139–142 °C ^{1}H NMR ([D$_6$]acetone, 400 MHz) δ: 8.03 (1H, d, *J* 8.5 Hz, Ph), 7.67 [2H, broad, B(OH)$_2$], 7.64 (1H, d, *J* 2.0 Hz, Ph), 7.17 (1H, dd, *J* 8.5 Hz, *J* 3.0 Hz, Ph); ^{13}C{^{1}H} NMR ([D$_6$]acetone, 100.6 MHz) δ: 140.1, 130.5 (d, *J* 4.0 Hz), 129.5 (q, *J* 32.5 Hz), 127.3, 125.3 (q, *J* 277.0 Hz), 104.0; ^{11}B NMR ([D$_6$]acetone, 64.16 MHz) δ: 28.4. Anal. Calcd. for $C_7H_5BF_3IO_2$ (315.82): C, 26.62; H, 1.60. Found: C, 26.38; H, 1.73.

*4.2.11. 4-(Trifluoromethyl)-2-iodophenylboronic acid (**11b**)*

Yield: 2.50 g (79%), m.p. 205–208 °C ^{1}H NMR ([D$_6$]acetone, 400 MHz) δ: 8.05 (1H, d, *J* 7.5 Hz, Ph), 7.67 (1H, d, *J* 7.5 Hz, Ph), 7.54 (1H, s, Ph); ^{13}C{^{1}H} NMR ([D$_6$]acetone, 100.6 MHz) δ: 139.4 (broad), 135.5, 132.1 (q, *J* 32 Hz), 125.4 (q, *J* 270 Hz), 124.8 (q, *J* 4.0 Hz), 124.3 (q, *J* 4.0 Hz), 98.6; ^{11}B NMR ([D$_6$]acetone, 64.16 MHz): δ: 28.7. Anal. Calcd. for $C_7H_5BF_3IO_2$ (315.82): C, 26.62; H, 1.60. Found: C, 26.87; H, 1.80.

*4.2.12. 3-Iodo-2-formylphenylboronic acid (**12b**)*

Yield: 2.25 g (85%), m.p. 80–83 °C ^{1}H NMR ([D$_6$]acetone, 400 MHz) δ: 7.86 (1H, d, *J* 7.6 Hz, Ph), 7.71 (1H, d, *J* 7.6 Hz, Ph), 7.14 (1H, t, *J* 7.6 Hz, Ph); ^{13}C{^{1}H} NMR ([D$_6$]acetone, 100.6 MHz) δ: 157.4, 141.8, 131.3, 130.7, 99.9, 91.0; ^{11}B NMR ([D$_6$]acetone, 64.16 MHz) δ: 27.5. Anal. Calcd. for $C_7H_6BIO_3$ (275.84): C, 30.48; H, 2.19. Found: C, 30.31; H, 2.04.

*4.2.13. 3-Iodo-2-methoxyphenylboronic acid (**13b**)*

The synthesis was carried out using a stoichiometric amount of ICl at 0 °C. Yield: 2.6 g (94%), m.p. 89–91 °C ^{1}H NMR ([D$_6$]acetone, 400 MHz) δ: 7.88 (1H, dd, *J* 8.0 Hz, *J* 2.0 Hz, Ph), 7.73 (1H, dd, *J* 7.0 Hz, *J* 1.5 Hz, Ph), 7.25 [2H, broad, B(OH)$_2$], 6.93 (1H, t, *J* 7.5 Hz, Ph), 3.83 (3H, s, Ph); ^{13}C{^{1}H} NMR ([D$_6$]acetone, 100.6 MHz) δ: 164.9, 142.6, 136.9, 126.7, 91.6, 62.6; ^{11}B NMR ([D$_6$]acetone, 64.16 MHz) δ: 29.0. Anal. Calcd. for $C_7H_8BIO_3$ (277.85): C, 30.26; H, 2.90. Found: C, 30.10; H, 2.73.

*4.2.14. 4-Fluoro-3,5-diiodophenylboronic acid (**14b**)*

Yield: 3.40 g (87%), m.p. 352–354 °C ^{1}H NMR ([D$_6$]acetone, 400 MHz) δ: 8.24 (2H, d, *J* 6.4 Hz, Ph), 7.61 [2H, broad, B(OH)$_2$]; ^{13}C{^{1}H} NMR ([D$_6$]acetone, 100.6 MHz) δ: 162.1 (d, *J* 242.5 Hz), 146.5, 80.9 (d, *J* 27.7 Hz); ^{11}B NMR ([D$_6$]acetone, 64.16 MHz) δ: 27.5. Anal. Calcd. for $C_6H_4BFI_2O_2$ (391.71): C, 18.39; H, 1.03. Found: C, 18.21; H, 1.10.

*4.2.15. 4-Cyano-2,5-diiodophenylboronic acid (**15b**)*

Yield: 2.70 g (68%), m.p. 151–153 °C ^{1}H NMR ([D$_6$]acetone, 400 MHz) δ: 8.13 (1H, s, Ph), 7.92 (1H, s, Ph); ^{13}C{^{1}H} NMR ([D$_6$] acetone, 100.6 MHz) δ: 144.2, 143.7, 122.3, 118.5, 97.9, 97.5; ^{11}B NMR ([D$_6$]acetone, 64.16 MHz) δ: 28.5. Anal. Calcd. for $C_7H_4BI_2NO_2$ (398.73): C, 21.08; H, 1.01, N, 3.51. Found: C, 21.31; H, 1.12; N, 3.28.

4.2.16. 2,5-Diiodo-1,4-phenylenediboronic acid (**16b**)

Yield: 2.3 g (86%), m.p. >400 °C ^{1}H NMR ([D$_6$]acetone, 400 MHz) δ: 7.72 (s, 2H, Ph), 7.48 (s, 4H, B(OH)$_2$); ^{13}C{^{1}H} NMR ([D$_6$]acetone, 100.6 MHz) δ: 148.0 (broad), 144.3, 98.9; ^{11}B NMR ([D$_6$]acetone, 64.16 MHz) δ: 28.0; Anal. Calcd. for $C_6H_6B_2I_2O_4$ (417.54): C, 17.26; H, 1.45. Found: C, 17.14; H, 1.53.

4.2.17. Bis(3-fluoro-2-iodophenyl)borinic acid 8-hydroxyquinoline ester (**4d**)

The borinic ester **4c** was iodinated as described for **1b**. The crude iodinated borinic ester was dissolved in Et$_2$O (50 mL) followed by the addition of 8-hydroxyquinoline (1.45 g, 0.01 mol). The mixture was stirred for 12 h and a yellow suspension was formed. The resulting yellow solid was filtered and washed with Et$_2$O (10 mL) and hexane (10 mL). Yield: 3.50 g (58%), m.p. 211–212 °C ^{1}H NMR ([D$_6$]acetone, 400 MHz) δ: 9.00 (1H, d, *J* 5.5 Hz, Q), 8.90 (1H, d, *J* 8.0 Hz, Q), 8.00 (1H, dd, *J* 8.5 Hz, *J* 5.0 Hz, Q), 7.74 (1H, t, *J* 8.0 Hz, Q), 7.50 (1H, d, *J* 8.5 Hz, Q), 7.21 (3H, m, Ph, Q), 7.01 (2H, m, Ph), 6.73 (2H, dd, *J* 7.5 Hz, *J* 1.6 Hz, Ph); ^{13}C{^{1}H} NMR ([D$_6$]acetone, 100.6 MHz) δ: 160.2 (d, *J* 241.0 Hz), 159.4, 157.1, 142.6, 141.2, 137.1, 132.5, 129.9, 129.3 (d, *J* 7.5 Hz), 128.0, 124.4, 113.8, 109.8, 89.4 (d, *J* 23.0 Hz); ^{11}B NMR ([D$_6$]acetone, 64.16 MHz) δ: 9.5. Anal. Calcd. for $C_{21}H_{12}BF_2I_2NO$ (596.94): C, 42.25; H, 2.03; N; 2.35. Found: C, 42.18; H, 1.98; N, 2.42.

4.3. Polymerization of **1b**

A mixture of **1b** (1.5 g, 5.3 mmol), K_2CO_3 (0.85 g, 6.1 mmol) and $Pd(OAc)_2$ (5 mg, 0.03 mmol) in 2-methoxyethanol/H_2O (3:1, 10 mL) was stirred for 24 h at rt. A clear solution turned gradually turbid and a grey suspension was formed. The crude product was filtered and washed with water and Et$_2$O. Then it was heated with conc. HNO_3 (3 mL) to remove palladium. Water (5 mL) was added and the white suspension was filtered and washed with water (3 × 5 mL) and acetone (3 × 5 mL) and dried in air. Yield of polymer **1c**: 420 mg. It was obtained as a white powder insoluble in common solvents, which precluded characterization by the solution NMR spectroscopy. IR (KBr) ν/cm^{-1}: 3105 (w), 1634 (s), 1584 (s), 1457 (m), 1391 (s), 1350 (w), 1272 (m), 1009 (s), 868 (s), 736 (m), 564 (m). Anal. found: C, 57.57; H, 1.94.

4.4. Polymerization of **16b**

A mixture of **16b** (1.5 g, 3.6 mmol), K_2CO_3 (1.38 g, 10 mmol) and $Pd(OAc)_2$ (5 mg, 0.03 mmol) in 2-methoxyethanol/H_2O (3:1, 12 mL) was stirred for 12 h at rt and then for 12 h at 100 °C. The crude product was filtered and washed with conc. aq. HCl (3 mL), water (3 × 5 mL) and acetone (3 × 5 mL). Yield of polymer **16c**: 470 mg. IR (KBr) ν/cm^{-1}: 3430 (m), 1448 (m), 1372 (m), 1083 (m), 997 (s), 822 (s), 763 (s). Anal. found: C, 51.40; H, 2.21.

4.5. Crystal structure determination of **4c**

Monocrystals of **4c** were grown from pentane at 4 °C. Single-crystal X-ray measurement for **4c** was performed on Bruker Kappa APEX II Ultra diffractometer with TXS rotating anode (MoK_α radiation, λ = 0.71073 Å), multi-layer optics and equipped with an Oxford Cryosystems nitrogen gas-flow apparatus. A single crystal (0.20 mm × 0.12 mm × 0.12 mm) was attached to a cactus spine using *Paratone N* oil and mounted on a goniometer head in a general position at 50 mm from the APEX II CCD camera. The data collection strategy was optimised and monitored using the appropriate algorithms applied in APEX2 program [25]. Data reduction and analysis were carried out with the Bruker SAINT suit of programs. The data set was corrected for Lorentz and polarization effects. The structure was solved by direct methods using SHELXS-97 and refined using SHELXL-97 [26]. The refinement was based on F^2 for all reflections except those with very negative F^2. Weighted *R* factors (*wR*) and all goodness-of-fit (*GooF*) values are based on F^2. Conventional *R* factors are based on *F* with *F* set to zero for negative F^2. The $F_o^2 > 2\sigma(F_o^2)$ criterion was used only for calculating *R* factors and is not relevant to the choice of reflections for the refinement. The *R* factors based on F^2 are about twice as large as those based on *F*. Scattering factors were taken from International Tables for Crystallography [27]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms of C–H bond were placed in idealized positions (all these hydrogen atoms were visible on difference density map).

4.6. DFT study of **4c**

Calculations were carried out with Gaussian 03 suite of programs [28]. Electron density calculations were performed with Becke-style 3-parameter density functional method using the Lee-Yang-Parr correlation functional [14] (B3LYP) with 6 − 311 + G* basis set [15]. Topological analysis of electron density distributions was investigated in terms of Bader's Quantum-Theory-of-Atoms-In-Molecules [29] (QTAIM) using AIM2000 programs [30].

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Appendix A. Supplementary material

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC No 776555 for compound **4c**. Copies of this information may be obtained free of charge from: The Director, CCDC 12 Union Road, Cambridge, CB2 1EZ UK, Fax. (int code) +44(1223)336 033 or Email: deposit@ccdc.cam.ac.uk or www:http://www.ccdc.cam.ac.uk.

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