Dynamic covalent self-assembled macrocycles prepared from 2-formyl-aryl-boronic acids and 1,2-amino alcohols†

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Reaction of 2-formyl-aryl-boronic acids with 1,2-amino alcohols results in dynamic covalent self assembly to quantitatively afford tetracyclic macrocyclic Schiff base boracycles containing bridging boron–oxygen–boron functionality.

Introduction

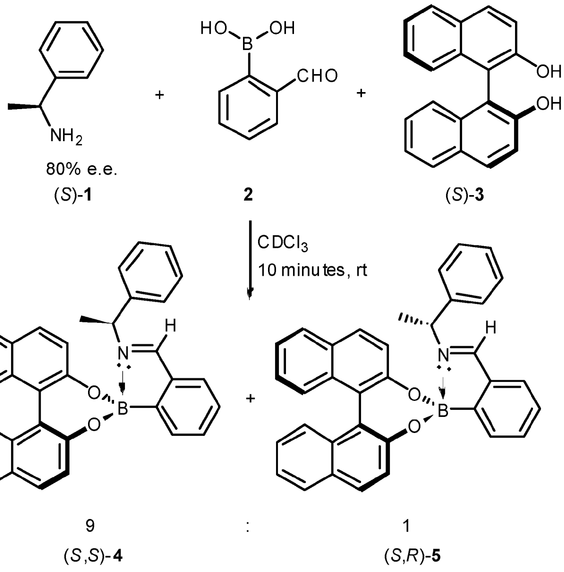
The development of boronic acid based saccharide sensors that rely on the dynamic covalent interaction of boronic acids with diols has been widely investigated.[1–9] Boronic ester formation with diols has also been used for the construction of discrete macrocycles and cages.[10] The reversible nature of boronic acid complexation with diols makes this type of interaction highly suitable for the reversible self-assembly of multicomponent systems. With these types of reversible systems any errors that occur during the assembly process may be corrected because equilibration of the reactive species results in formation of a thermodynamically favoured product. A number of boracycles have been prepared that employ a combination of facile imine formation and boronic acid esterification to afford multicomponent macrocycles.[11–24] For example, Severin has prepared a series of self assembled macrocycles/cages by combining 3- or 4-formyl-phenyl-boronic acids with bis or tris primary amines and pentaerythritol (tetraol).[25,26] Nitschke has also prepared a macrocycle derived from pentaerythritol, 2-formyl-phenyl-boronic acid and *para*-diaminobenzene, as well as a cage compound arising from self assembly of cyclotricatechylene, *meta*-xylylenediamine and 2-formyl-phenyl-boronic acid.[27] Farfan has prepared boracycles from boric acid, 4-diethylamino salicylaldehyde and (*R*)-phenylglycinol **6d**. This complex was formed in two steps involving reaction of 4-diethylamino salicylaldehyde and (*R*)-**6d** to produce an imine, followed by reflux with boric acid in toluene under Dean–Stark conditions for 18 h to produce the observed complex.[28]

We now report herein that simple room temperature mixing of 2-formyl-aryl-boronic acids with 1,2-amino alcohols results in dynamic covalent self assembly to afford stable tetracyclic macrocyclic Schiff base complexes that contain a rigid bridging boron–oxygen–boron functionality.

Results and discussion

We have recently reported the development of versatile three-component derivatization protocols for determining the enantiomeric excess of chiral primary amines, diols or diamines.[29–35] For the case of amines, this approach involves derivatization of a chiral amine **1** with 2-formyl-phenyl-boronic acid **2** and enantiopure BINOL (*S*)-**3** in $CDCl_3$ to quantitatively afford a mixture of diastereoisomeric imino-boronate esters (*S*,*S*)-**4** and (*S*,*R*)-**5**. The diastereoisomeric ratio of (*S*,*S*)-**4**:(*S*,*R*)-**5** is then determined by ^1H NMR spectroscopic analysis, and since no kinetic resolution occurs this value is an accurate reflection of the enantiomeric excess of the parent amine (Scheme 1).

We reasoned that this type of three-component derivatization protocol might also be useful for analyzing the enantiopurity of chiral 1,2-amino alcohols. Therefore, (*S*)-leucinol **6b** was treated with 2-formyl-phenyl-boronic acid **2** and (*S*)-BINOL **3** in $CDCl_3$ and its ^1H NMR spectrum acquired after ten minutes. The resultant ^1H NMR spectra revealed the presence of a complicated mixture of interconverting products



Scheme 1 Three-component protocol for determining the enantiomeric purity of chiral amines by ^1H NMR spectroscopic analysis.

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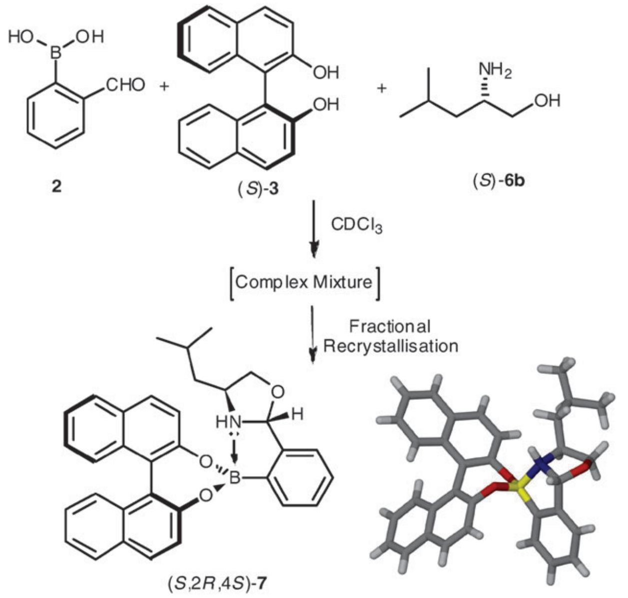
† CCDC reference numbers 694358–694361 [(*S*,2*R*,4*S*)-**7**, **8a**, **8f** and **8h**]. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b815138e

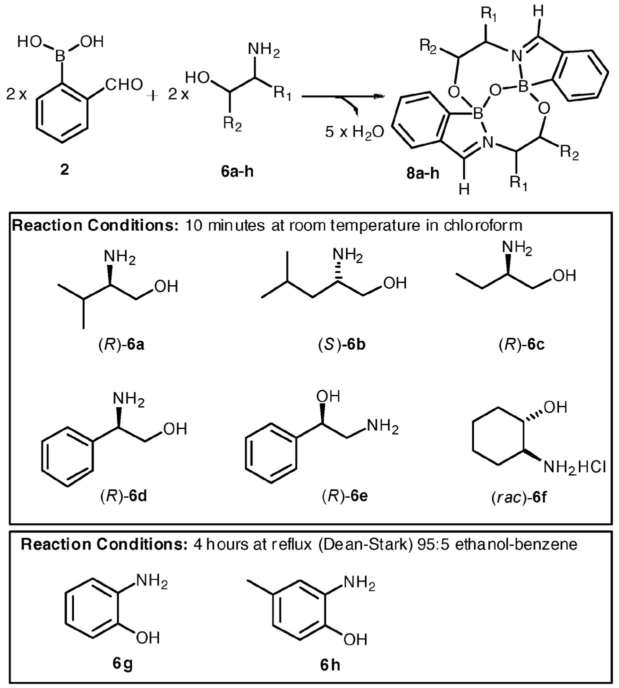


Scheme 2 Formation and X-ray crystal structure of boronic ester (*S*,2*R*,4*S*)-**7**.

that was clearly unsuited for carrying out ee determination. However, on standing overnight, the crude reaction product fractionally crystallised to afford the expected oxazolidine-boronate ester (*S*,2*R*,4*S*)-**7**, whose structure was subsequently confirmed by X-ray crystallographic analysis (Scheme 2).

In order to investigate this complexation reaction further, it was decided to determine what products would be formed when 2-formyl-phenyl-boronic acid **2** was individually reacted with either (*S*)-BINOL **3** or (*R*)-valinol **6a**. Two-component mixing of 2-formyl-phenyl-boronic acid **2** with (*S*)-BINOL **3** in $CDCl_3$ resulted in no reaction occurring. However, reaction of **2** with (*R*)-valinol **6a** at room temperature in chloroform resulted in exclusive formation of a new boracycle (*R*,*R*)-**8a** in quantitative yield (Scheme 3). The structure of symmetrical boracycle (*R*,*R*)-**8a** was confirmed by X-ray crystallographic analysis (Fig. 1), which revealed it to be the condensation product of two equivalents of 2-formyl-phenyl-boronic acid **2** with two equivalents of (*R*)-valinol **6a**, with concomitant elimination of five molecules of water. This complexation reaction results in formation of the densely packed central core of boracycle (*R*,*R*)-**8a** which comprises two fused seven membered rings formed from two tetrahedral sp^3-boron atoms, two imino alcohol fragments, and a central oxygen atom that bridges both boron atoms. This architecture results in its central fused bicyclic ring structure being further appended by two five-membered rings formed from two imino-boronate ester linkages that confer sp^3 character on the boron atoms. The scope and limitation of this four-component condensation reaction was then investigated *via* treatment of a series of five chiral amino alcohols **6b–f** with 2-formyl-phenyl-boronic acid **2**, which resulted in clean formation of their respective boracycles **8b–f** in 84–96% isolated yield (Scheme 3).

The reversible nature of macrocycle formation of these boracycles **8a–f** was confirmed by adding one equivalent of amino alcohol (*S*)-**6a** to macrocycle (*S*,*S*)-**8b** in chloroform.



Scheme 3 Condensation of 2-formyl-phenylboronic acid **2** with chiral amino alcohols **6a–f** and achiral amino alcohols **6g, h** affords four-component boracycles **8a–h**.

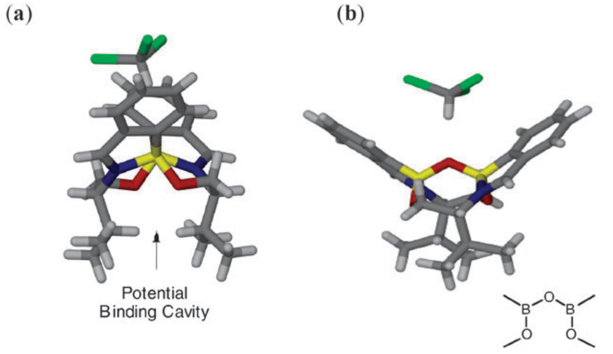


Fig. 1 Crystal structure of macrocycle **8a**. (a) Viewed along the boron–boron axis. (b) Viewed perpendicular to the boron–boron axis.

Mass spectrometry indicated that this solution now contained a mixture of three macrocycles, (*S*,*S*)-**8a** (M + H 431 *m*/*z*), (*S*,*S*)-**8b** (M + H 445 *m*/*z*) and a mixed macrocycle derived from (*S*)-**6a** and (*S*)-**6b** (M + H 417 *m*/*z*) in a statistical 1:1:2 ratio.

Norman and coworkers have previously reported the synthesis of achiral boracycle **8g** derived from condensation of 2-aminophenol with 2-formyl-phenyl-boronic acid **2** in ethanol at reflux.[36] Attempts to repeat this condensation reaction using our mild complexation conditions at room temperature resulted in no reaction occurring. However, heating 2-aminophenol **6g** (or 4-methyl-2-aminophenol **6h**) with 2-formyl-phenyl-boronic acid **2** at reflux in 95:5 ethanol:benzene under Dean–Stark conditions did result in quantitative formation of the boracycles **8g** (or **8h**). Comparison of the X-ray crystal structures of boracycle (*S*)-**8a** with that of boracycle **8h** (Fig. 2) revealed that whilst they belong to the

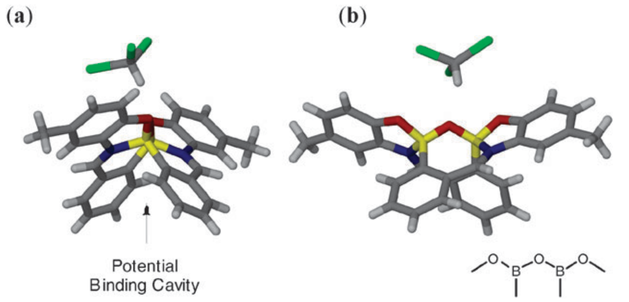
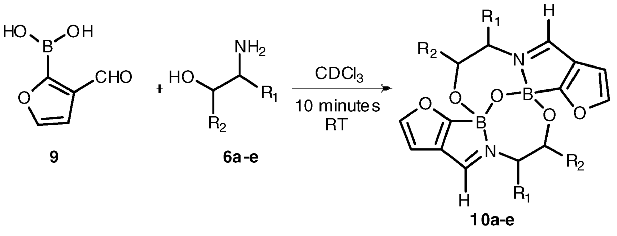


Fig. 2 Crystal structure of macrocycle **8h**. (a) Viewed along the boron–boron axis. (b) Viewed perpendicular to the boron–boron axis.

same class of bridging boracycle, their three dimensional architectures are very different. In the case of boracycle **8a**, the central bridging oxygen atom lies on the *opposite* side to the other two oxygen atoms about the plane bisected by the two boron atoms. This results in the alkyl side-chains of their amino alcohol fragments adopting a conformation that creates the walls of a potential binding cavity centred around its bridging oxygen atom, with its aryl rings acting as buttressing elements to contribute structural rigidity. Conversely, for the case of macrocycle **8h**, the presence of the more rigid aminophenol fragments results in the three oxygen atoms now being presented on the *same* face of the plane bisected by the boron atoms. This, in turn, results in the aryl rings of the boronic acid fragment forming the walls of a cavity centred around the bridging oxygen atom, with its aminophenol derived fragments now adopting the role of buttressing substituents to confer structural rigidity.

We have also varied the nature of the boronic acid template used for supramolecular assembly, demonstrating that complexation of 2-formyl-furanyl-boronic acid **9** with chiral aminoalcohols **6a–e** in chloroform quantitatively affords their corresponding four-component boracycles **10a–e** in 85–92% isolated yield (Scheme 4). ^{11}B NMR spectroscopic analysis of these macrocycles reveals that the boron atoms of the furan derived boracycles **10a–e** (δ 4.6–5.4 ppm) have more tetrahedral character than their corresponding phenyl derived boracycles **8a–f** (δ 10.5–11.5 ppm). This increased tetrahedral character may be a consequence of the need to incorporate a more geometrically constrained five-membered furan ring into these complexes. It may also explain why reaction of achiral amino alcohols **6g–h** with 2-formyl-furanyl-boronic acid **9** did not result in clean formation of their corresponding four component boracycles, which may be precluded by the opposing steric demands of incorporating tetrahedral sp^3 boron atoms and vicinal sp^2 aryl carbon atoms into the central boracyclic core of the macrocyclic ring system.



Scheme 4 Preparation of boracycles **10a–e**.

Conclusions

In conclusion, a range of covalent self-assembled macrocycles **8** and **10** containing bridging O–B–O–B–O have been prepared and fully characterised. Their ease of preparation suggests that this class of boracycle is well suited for the reversible self-assembly of multicomponent systems, and we are currently investigating the recognition properties of this structurally diverse class of macrocycle.

Experimental

General synthetic methods

The solvents and reagents were reagent grade unless otherwise stated and were purchased from Acros Organics, Alfa Aesar, Fisher Scientific UK, Frontier Scientific Europe Ltd., TCI Europe or Sigma-Aldrich Company Ltd., and were used without further purification. Infra-red spectra were recorded on a Perkin Elmer Spectrum RX spectrometer between 4400 cm^{-1} and 450 cm^{-1}. Samples were evaporated from CHCl$_3$ on to a NaCl disc (film). Nuclear magnetic resonance spectra were run in either chloroform-d. A Bruker AVANCE 300 was used to acquire ^{1}H-NMR spectra and recorded at 300 MHz, ^{11}B-NMR spectra at 100 MHz and ^{13}C{^{1}H} NMR spectra at 75 MHz. Chemical shifts (δ) are expressed in parts per million and are reported relative to the residual solvent peak or to tetramethylsilane as an internal standard in ^{1}H and ^{13}C{^{1}H} NMR spectra. Boron trifluoride diethyl etherate was used as an external standard in ^{11}B NMR spectra. Mass spectra were acquired with a micrOTOFQ electrospray time-of-flight (ESI-TOF) mass spectrometer (Bruker Daltonik GmbH).

General procedure for the preparation of boracycles 8a-f and 10a–e

2-Formyl-phenyl-boronic acid **2** (60 mg, 0.4 mmol) or 3-formyl-furanyl-2-boronic acid **9** (56 mg, 0.4 mmol) was stirred with a chiral 1,2-amino alcohol **6a–f** or **6a–e** (0.4 mmol) in chloroform (5 mL) for 10 min. The solvent was then removed under reduced pressure to afford boracycles **8a–f** or **10a–e** in 84–96% yield.

***(R,R)*-8a.** Yellow oil (70 mg, 84%); $[\alpha]_D^{20}$ +22.0 (*c* 1.0, CH$_2$Cl$_2$); ν_{max} (film) 1628 (C═N); δ_H (300 MHz; CDCl$_3$) 8.08 (2H, s, C*H*═N), 7.51 (2H, d, *J* 7.4, Ar*H*), 7.35–7.27 (4H, m, Ar*H*), 7.11 (2H, dt, *J* 7.4 and 1.1, Ar*H*), 4.26 (2H, dd, *J* 12.2 and 1.3, C*H*$_A$H$_B$(O)), 3.98 (2H, dd, *J* 12.2 and 1.3, CH$_A$*H*$_B$(O)), 3.13 (2H, m, C*H*(^{i}Pr)–N), 2.96–2.83 (2H, m, C*H*(CH$_3$)$_2$), 1.02 (6H, d, *J* 6.8, C(C*H*$_3$)(CH$_3$)) and 0.88 (6H, d, *J* 6.8, C(CH$_3$)(C*H*$_3$)); δ_C (75 MHz; CDCl$_3$) 167.3 (*C*═N), 136.8, 133.6, 129.4, 127.2, 127.0, 126.2, 76.0, 60.9, 27.0, 21.1 and 19.4; δ_B (100 MHz; CDCl$_3$) 10.7; *m*/*z* LRMS (ESI$^+$) 418 [(M + H)$^+$, 13%], 283.2 (100), 200.1 (2); HRMS (ESI$^+$) found 417.2531 ([M + H]$^+$ C$_{24}$H$_{30}$B$_2$N$_2$O$_3$ requires 417.2515).

***(S,S)*-8b.** Yellow solid (79 mg, 89%); m.p. 206–210 °C (dec); $[\alpha]_D^{20}$ −26.1 (*c* 1.0, CH$_2$Cl$_2$); ν_{max} (film) 1628 (C═N); δ_H (300 MHz; CDCl$_3$) 8.16 (2H, s, C*H*═N), 7.51 (2H, d, *J* 7.4, Ar*H*), 7.36–7.27 (4H, m, Ar*H*), 7.11 (2H, dt, *J* 7.4 and 1.1, Ar*H*), 4.35 (2H, dd, *J* 11.9 and 1.7, CH_AH_B(O)), 3.81–3.73 (4H, m, CH_AH_B(O) and C*H*–N), 2.16–2.06 (2H, m, CH_AH_BC(N)), 2.02–1.92 (2H, m, CH_AH_BC(N)), 1.72–1.63 (2H, m, C*H*(CH_3)$_2$) and 0.90 (12H, app t, *J* 6.8, C(CH_3)$_2$); δ_C (75 MHz; $CDCl_3$) 166.9 (*C*=N), 136.9, 133.5, 133.1, 129.4, 127.2, 126.1, 66.7, 62.5, 40.4, 24.8, 23.0 and 22.9; δ_B (100 MHz; $CDCl_3$) 11.5; *m*/*z* LRMS (ESI$^+$) 445 [(M + H)$^+$, 14%], 412.4 (100), 292.2 (66), 227.2 (15); HRMS (ESI$^+$) found 445.2873 ([M + H]$^+$ $C_{26}H_{34}B_2N_2O_3$ requires 445.2828).

(*R*,*R*)-8c. Yellow oil (69 mg, 88%); $[\alpha]_D^{20}$ +14.7 (*c* 1.0, CH_2Cl_2); ν_{max} (film) 1628 (C=N); δ_H (300 MHz; $CDCl_3$) 8.13 (2H, s, C*H*=N), 7.50 (2H, t, *J* 7.4, Ar*H*), 7.3–7.26 (4H, m, Ar*H*), 7.12–7.07 (2H, m, Ar*H*), 4.33 (2H, dd, *J* 12.0 and 1.7, CH_AH_B(O)), 3.78 (2H, dd, *J* 12.0 and 1.7, CH_AH_B(O)), 3.51 (2H, m, C*H*(Et)–N), 2.20–2.09 (4H, m, CH_AH_BMe) and 0.93 (6H, t, *J* 7.6, CH_3); δ_C (75 MHz; $CDCl_3$) 167.3 (*C*=N), 136.9, 133.5, 133.3, 129.3, 127.2, 126.2, 70.7, 62.4, 24.8 and 11.5; δ_B (100 MHz; $CDCl_3$) 11.2; *m*/*z* LRMS (CI$^+$) 389 [(M + H)$^+$, 6%], 188.2 (50), 106.0 (46), 72.0 (100); HRMS (EI$^+$) found 388.2126 (2 × ^{11}B) (M$^{+\bullet}$ $C_{22}H_{26}B_2N_2O_3$ requires 388.2124).

(*R*,*R*)-8d. Yellow oil (88 mg, 91%); $[\alpha]_D^{20}$ +21.1 (*c* 1.0, CH_2Cl_2); ν_{max} (film) 1627 (C=N); δ_H (300 MHz; $CDCl_3$) 7.66–7.63 (4H, m, C*H*=N and Ar*H*), 7.43–7.30 (12H, m, Ar*H*), 7.20 (2H, br t, *J* 7.4, Ar*H*), 7.09 (2H, dt, *J* 7.4 and 0.8, Ar*H*), 5.25 (2H, m, CH_AH_B(O)), 4.65 (2H, dd, *J* 11.9 and 10.4, C*H*(Ph)-N), 3.95 (2H, m, CH_AH_B(O)); δ_C (75 MHz; $CDCl_3$) 166.1 (*C*=N), 137.0, 135.7, 133.9, 133.5, 132.3, 130.0, 129.9, 129.7, 129.5, 127.2, 126.8, 126.7, 71.4, and 69.1; δ_B (100 MHz; $CDCl_3$) 11.3; *m*/*z* LRMS (ESI$^+$) 485 [(M + H)$^+$, 9%], 368.2 (10), 312.1 (100), 278.2 (16); HRMS (ESI$^+$) found 485.2230 ([M + H]$^+$ $C_{30}H_{26}B_2N_2O_3$ requires 485.2202).

(*R*,*R*)-8e. Yellow solid (140 mg, 95%); m.p. 125–129 °C (dec); $[\alpha]_D^{20}$ +19.4 (*c* 1.0, CH_2Cl_2); ν_{max} (film) 1635 (C=N); δ_H (300 MHz; $CDCl_3$) 8.25 (2H, s, C*H*=N), 7.64 (2H, d, *J* 7.0, Ar*H*), 7.48–7.14 (16H, m, Ar*H*), 5.46 (2H, br d, *J* 9.8, CH_AH_B(N)), 4.50–4.42 (2H, m, C*H*(Ph)(O)) and 4.03 (2H, br d, *J* 9.8, CH_AH_B(N)); δ_C (75 MHz; $CDCl_3$) 166.0, 137.0, 135.6, 133.9, 133.5, 132.3, 130.0, 129.9, 129.7, 129.4, 128.0, 127.3, 126.8, 71.3 and 65.8; δ_B (100 MHz; $CDCl_3$) 10.5; *m*/*z* LRMS (ESI$^+$) 485 [(M + H)$^+$, 100%], 312.1 (99); HRMS (ESI$^+$) found 485.2219 ([M + H]$^+$$C_{30}H_{26}B_2N_2O_3$ requires 485.2202).

(*rac*)-8f. Yellow solid (85 mg, 96%); m.p. 142–144 °C (dec); ν_{max} (film) 1625 (C=N); δ_H (300 MHz; $CDCl_3$) 8.20 (2H, d, *J* 3.0, C*H*=N), 7.47 (2H, d, *J* 6.8, Ar*H*), 7.35 (2H, d, *J* 7.4, Ar*H*), 7.28 (2H, app dt, *J* 7.5 and 1.1, Ar*H*), 7.10 (2H, app dt, *J* 7.5 and 1.1, Ar*H*), 3.96–3.88 (2H, m, C*H*(N)), 3.79–3.70 (2H, m, C*H*(O)), 2.26 (2H, br d, *J* 12.0, CH_AH_BC–O), 1.88–1.81 (4H, m, CH_AH_BC–O and CH_AH_BC–N), 1.71–1.66 (2H, m, CH_AH_BC–N) and 1.50–1.12 (8H, m, 2×(CH_2)$_2$); δ_C (75 MHz; $CDCl_3$) 164.0 (*C*=N), 137.2, 133.2, 129.9, 129.1, 126.9, 126.3, 65.6, 36.3, 29.8, 27.3, 24.9 and 24.8; δ_B (100 MHz; $CDCl_3$) 10.8; *m*/*z* LRMS (ESI$^+$) 440 [(M + H)$^+$, 100%], 290.2 (15); HRMS (ESI$^+$) found 441.2549 ([M + H]$^+$ $C_{26}H_{30}B_2N_2O_3$ requires 441.2515).

8g. 2-Aminophenol **6g** (200 mg, 1.83 mmol) and 2-formylphenylboronic acid **2** (275 mg, 1.83 mmol) were dissolved in 95:5 ethanol–benzene (25 mL) in a round bottom flask fitted with a Dean–Stark condenser and stirred at reflux for 4 h. The reaction mixture was cooled and the solvent removed under reduced pressure. Washing with a little cold methanol afforded **8g** as a yellow powder (709 mg, 90%): m.p. 182–183 °C (dec.) (Lit. 180 °C (dec.)[36]); δ_H (300 MHz, $CDCl_3$) 8.65 (s, 2H), 7.49 (2H, d, *J* = 7.5 Hz), 7.40–7.37 (2H, m, Ar), 7.29–7.12 (8H, m), 6.92 (4H, m); δ_C (75 MHz, $CDCl_3$) δ = 160.9, 155.5, 135.1, 134.2, 134.13, 133.1, 132.9, 131.5, 127.9, 118.7, 115.8, 113.7; δ_B (96.3 MHz, $CDCl_3$) 9.6; *m*/*z* HRMS (ESI$^+$) found 429.1571. ([M + H]$^+$ $C_{26}H_{19}B_2N_2O_3$ (M + H$^+$) requires 429.1582).

8h. 2-Hydroxy-5-methylaniline **6h** (123 mg, 1.0 mmol) and 2-formyl-phenyl-boronic acid **1** (150 mg, 1.0 mmol) were dissolved in 95:5 ethanol–benzene (20 mL) in a round bottom flask fitted with a Dean–Stark condenser and stirred at reflux for 4 h. The reaction mixture was cooled and the solvent removed under reduced pressure. Washing with a little cold methanol afforded **8h** as a orange powder (374 mg, 82%): m.p. 231–232 °C (dec.); δ_H (300 MHz, $CDCl_3$) 8.64 (2H, s, C*H*=N), 7.42 (2H, m, Ar*H*), 7.36 (2H, s, Ar*H*), 7.29–7.16 (6H, m, Ar*H*), 7.11 (2H, d, *J* 8.4 Ar*H*), 6.85 (2H, d, *J* 8.4), 2.35 (6H, s, CH_3); δ_C (75 MHz, $CDCl_3$) 158.24, 154.9, 148.8, 134.9, 134.1, 133.9, 132.9, 131.2, 128.2, 127.8, 115.3, 113.8, 21.5; δ_B (100 MHz, $CDCl_3$) 8.9; *m*/*z* HRMS (ESI$^+$) found 457.2011. ([M + H]$^+$ $C_{28}H_{23}B_2N_2O_3$ (M + H$^+$) requires 457.1889).

(*S*,*S*)-10a. Dark brown solid (74 mg, 93%); m.p. 131–140 °C (dec); $[\alpha]_D^{20}$ −36.8 (*c* 1.0, CH_2Cl_2); ν_{max} (film) 1649 (C=N); δ_H (300 MHz; $CDCl_3$) 8.13 (2H, d, *J* 3.0 C*H*=N), 7.35 (2H, d, *J* 1.9, Ar*H*), 6.33 (2H, d, *J* 1.9, Ar*H*), 4.39 (2H, dd, *J* 9.4 and 6.2, CH_AH_B(O)), 4.15 (2H, dd, *J* 9.4 and 4.0, CH_AH_B(O)), 3.90–3.84 (2H, m, C*H*=N), 2.28–2.17 (2H, m, C*H*(CH_3)$_2$) and 1.06 (12H, app dd, *J* 6.8 and 7.2, C(CH_3)$_2$); δ_C (75 MHz; $CDCl_3$) 157.2, 144.5, 132.6, 123.3, 110.2, 69.3, 63.5, 32.6, 20.0 and 17.4; δ_B (100 MHz; $CDCl_3$) 4.7; *m*/*z* LRMS (ESI$^+$) 397 [(M + H)$^+$, 9%], 345.2 (100), 283.2 (36); HRMS (ESI$^+$) found 397.2122 ([M + H]$^+$$C_{20}H_{26}B_2N_2O_5$ requires 397.2100).

(*S*,*S*)-10b. Red oil (76 mg, 90%); $[\alpha]_D^{20}$ −34.0 (*c* 1.0, CH_2Cl_2); ν_{max} (film) 1649 (C=N); δ_H (300 MHz; $CDCl_3$) 8.13 (2H, d, *J* 3.0, C*H*=N), 7.36 (2H, d, *J* 1.9, Ar*H*), 6.32 (2H, d, *J* 1.9, Ar*H*), 4.39 (2H, dd, *J* 8.9 and 6.0, CH_AH_B(O)), 4.24–4.15 (2H, m, C*H*–N), 3.99 (2H, dd, *J* 8.9 and 7.4, CH_AH_B(O)), 1.77–1.65 (6H, m, CH_AH_BC*H*(CH_3)$_2$) and 1.00 (12H, app t, *J* 5.5, C(CH_3)$_2$); δ_C (75 MHz; $CDCl_3$) 157.2, 144.7, 132.7, 122.8, 110.0, 71.9, 52.2, 32.6, 20.5, 8.9 and 8.1; δ_B (100 MHz; $CDCl_3$) 4.6; *m*/*z* LRMS (ESI$^+$) 425 [(M + H)$^+$, 32%], 412.4 (27), 389.3 (35), 375.2 (100); HRMS (ESI$^+$) found 425.2452 ([M + H]$^+$ $C_{22}H_{30}B_2N_2O_5$ requires 425.2419).

(*R*,*R*)-10c. Red oil (134 mg, 91%); $[\alpha]_D^{20}$ +33.0 (*c* 1.0, CH_2Cl_2); ν_{max} (film) 1656 (C=N); δ_H (300 MHz; $CDCl_3$) 8.13 (2H, s, C*H*=N), 7.34 (2H, d, *J* 1.9, Ar*H*), 6.31 (2H, d, *J* 1.9, Ar*H*), 4.42–4.39 (2H, m, CH_AH_B(O)), 4.09–3.99 (4H, m, CH_AH_B(O) and C*H*–N), 2.05–1.90 (4H, m, CH_2Me) and 1.07 (6H, t, *J* 7.0, CH_3); δ_C (75 MHz; $CDCl_3$) 156.3, 144.5, 132.6, 123.3 110.2, 67.7, 65.7, 26.4 and 10.4; δ_B (100 MHz; $CDCl_3$)

4.8; *m*/*z* LRMS (ESI$^+$) 369 [(M+H)$^+$, 65%], 288.2 (100), 201.1 (34); HRMS (ESI$^+$) found 369.1791 ([M+H]$^+$ $C_{18}H_{22}B_2N_2O_5$ requires 369.1785).

***(R,R)*-10d.** Red solid (79 mg, 85%); m.p. 115–118 °C (dec); $[\alpha]_D^{20}$ +39.6 (*c* 1.0, CH_2Cl_2); ν_{max} (film) 1657 (C═N); δ_H (300 MHz; $CDCl_3$) 7.83 (2H, d, *J* 3.0, C*H*═N), 7.53–7.44 (10H, m, Ar*H*), 7.42 (2H, d, *J* 1.9, Ar*H*), 6.24 (2H, d, *J* 1.9, Ar*H*), 5.35–5.28 (2H, m, C*H*(Ph)–N) and 4.57–4.45 (4H, m, CH_AH_B(O)); δ_C (75 MHz; $CDCl_3$) 158.3, 144.9, 136.6, 131.4, 129.8, 129.60, 129.59, 129.55, 129.50, 124.6, 110.3, 71.3 and 70.4; δ_B (100 MHz; $CDCl_3$) 5.4; *m*/*z* LRMS (ESI$^+$) 465 [(M + H)$^+$, 100%], 415.2 (33), 335.2 (36), 292.1 (32), 215.1 (10); HRMS (ESI$^+$) found 465.1833 ([M + H]$^+$ $C_{26}H_{22}B_2N_2O_5$ requires 465.1787).

***(R,R)*-10e.** Dark brown solid (85 mg, 92%); m.p. 124–126 °C (dec); $[\alpha]_D^{20}$ +18.5 (*c* 1.0, CH_2Cl_2); ν_{max} (film) 1662 (C═N); δ_H (300 MHz; $CDCl_3$) 8.26 (2H, br s, C*H*═N), 7.56 (4H, br d, Ar*H*), 7.45 (2H, d, *J* 1.9, Ar*H*), 7.39–7.26 (6H, m, Ar*H*), 6.34 (2H, d, *J* 1.9, Ar*H*), 5.56–5.51 (2H, m, CH_AH_B(N)) and 4.11–4.08 (4H, m, CH_AH_B(N)) and C*H*(Ph)(O)); δ_C (75 MHz; $CDCl_3$) 157.7, 145.1, 142.1, 129.7, 128.8, 128.6, 128.1, 126.7, 124.5, 110.4, 76.2 and 63.7; δ_B (100 MHz; $CDCl_3$) 5.0; *m*/*z* LRMS (ESI$^+$) 465 [(M + H)$^+$, 65%], 415.2 (100), 323.2 (83); HRMS (ESI$^+$) found 465.1841 ([M + H]$^+$ $C_{26}H_{22}B_2N_2O_5$ requires 465.1787).

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