Facile Preparation of [4.4]Metacyclophane- and [5.5]Paracyclophane-Type Macrocycles from Arylboronic Acids and Salicylideneaminoaryl Alcohols

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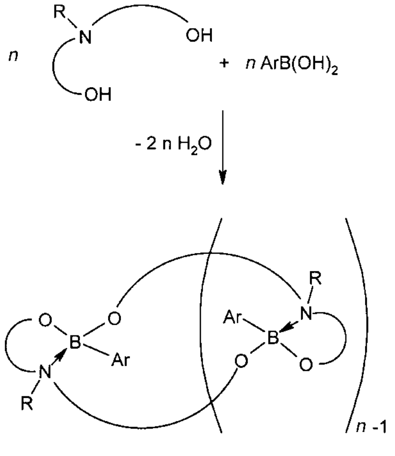
Abstract: Four different salicylideneaminoaryl alcohols have been treated with arylboronic acids in order to prepare air-stable cyclophane-type macrocyclic systems. In two cases, this objective could be realized with the high-yield formation of [4.4]metacyclophane and [5.5]paracyclophane derivatives. The skeleton in these macrocycles is held together by two chiral boron atoms. In the other two cases, monomeric boronates or polymeric material were obtained. The title structures were characterized by spectroscopic techniques and X-ray crystallography. They show transannular C–H ··· O hydrogen bonding, but no intramolecular π–π interactions. A synthetic strategy for the preparation of further boron macrocycles is presented.

Keywords: boron · cyclophane derivatives · macrocycle design · macrocycles · salicylideneamino alcohols · structure elucidation

Introduction

The preparation of macrocyclic and supramolecular structures with reagents from organometallic and coordination chemistry is becoming more and more important.[1] One of the reasons for this development is the circumstance that many of these structures can be prepared by facile one-step syntheses in relatively high yields.

During the last few years, we and others have been interested in the facile preparation of macrocyclic structures, whose skeleton is formed by two or more boron atoms.[2–3] Our strategy thereby has been the formation of complexes, in which the boron atoms are tetracoordinated in order to increase the hydrolytic stability of the products. This goal can be achieved by the carefully designed reaction of arylboronic acids with tridentate amino dialcohols. In order to induce the formation of a macrocyclic structure, the ligands must be constructed in such a way that the boron atom is chelated by only two of the three functional groups of the same ligand (Scheme 1).



n = 2, 3, etc.

Scheme 1. Synthetic strategy for the preparation of macrocycles with tetracoordinated boron atoms.

Since cyclophanes form an important class of organic macrocycles whose synthesis can be quite complex,[4] the preparation of structurally related molecules by means of coordination or organometallic chemistry might be an interesting alternative. Therefore, based on the above strategy, we decided to design some air-stable diboronates that can be considered as cyclophane analogues. To achieve this goal, a

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series of four different tridentate ligands were prepared from salicylaldehyde derivatives and the following aromatic amino alcohols: 4-aminophenol, 4-aminobenzyl alcohol, 4-aminophenethyl alcohol, and 3-aminobenzyl alcohol. When treated with arylboronic acids, these ligands can, in principle, induce the formation of [3.3]paracyclophane-, [4.4]paracyclophane-, [5.5]paracyclophane-, and [4.4]metacyclophane-type ring systems, respectively. However, it has to be considered that electronic effects related to the varying basicity of the ligands as well as steric and transannular strains may be factors that could inhibit the formation of a macrocyclic structure and favor a monomeric or a polymeric complex instead.

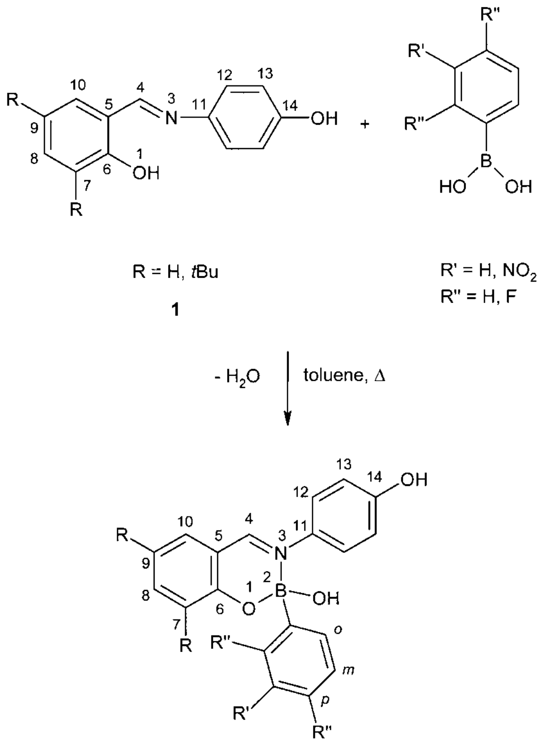
In this contribution, we report on the first results of this investigation and present a [4.4]metacyclophane and a [5.5]paracyclophane derivative, each with two chiral boron atoms. As far as we know, this is the first report on the systematic study of cyclophane derivatives based on a skeleton held together by boron atoms.

Results and Discussion

The ligands used in the present study are salicylideneaminoaryl alcohol derivatives, which have been prepared in high yields according to known methods.[3a, b] Ligands **1**–**4** can be transformed in simple 1:1 stoichiometric condensation reactions with arylboronic acids to the boron chelates, as outlined in Schemes 2–5.

With ligands **1** only monomeric boronates could be obtained, although different reaction conditions were tried, for example, change of solvent, use of different reaction temperatures, use of 2,2-dimethoxypropane or molecular sieves as water-separating reagents, and use of a glass-sealed cylinder for the reaction (Scheme 2). Products **1a**–**d** are quite insoluble in all common organic solvents and decompose before they reach their melting points, so that they could be only characterized by IR spectroscopy, elemental analyses, and, in the case of compound **1d**, by X-ray crystallography.

The molecular structure of **1d** is shown in Figure 1. Crystallographic data as well as selected bond lengths, bond angles, and torsion angles are summarized in Tables 1 and 2. Boronates, such as **1d**, that contain a reactive B–OH function are rare, since they are sensitive to further condensation reactions with alcohols or with each other (vide infra). It is noteworthy that on complexation to boron, the conjugation between the two aromatic ring systems of **1** is lost, as indicated by the C-N-C-C torsion angle of 40.6°. This observation is important because the loss of conjugation might have been an argument to explain the fact that, in this case, no macrocyclic or polymeric structure could be obtained. However, this possibility is ruled out because the conjugation is already lost in the monomeric complex. The N–B bond length, with a value of 1.613 (9) Å, is characteristic of a strong coordinative bond.[5]



1a R = H, R' = H, R'' = H
1b R = *t*Bu, R' = H, R'' = H
1c R = H, R' = H, R'' = F
1d R = H, R' = NO₂, R'' = H

Scheme 2. Preparation of boron chelates **1a**–**d**.

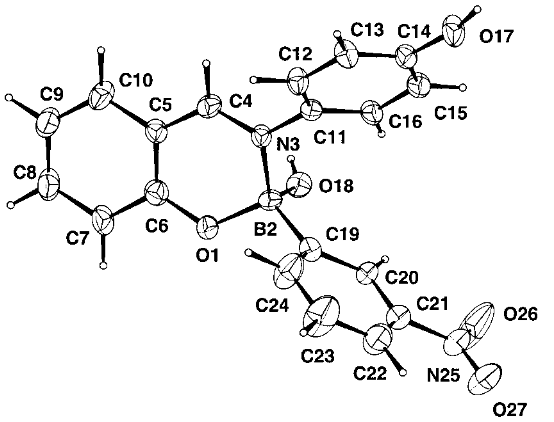


Figure 1. Perspective view of the molecular structure of the monomeric boronate **1d**.

Ligands **2** also react readily with arylboronic acids; however, only oligomeric or polymeric material could be isolated, even under different reaction conditions (vide supra, Scheme 3). In contrast to ligands **1**, in this case both hydroxyl groups react with the B–OH groups in the arylboronic acid, as confirmed by IR and ^{1}H NMR spectroscopy. This may be explained by the higher basicity of the benzyloxy functional group of these ligands compared to that of the phenoxy group of ligands **1**.

If salicylidene-3-aminobenzyl alcohols **3** are used instead of the 4-aminobenzylalcohol derivatives **2**, the dimeric boronates **3a**–**d** are obtained in yields of 70 to 96% (Scheme 4). The reaction is already complete after 10–30 minutes, if a Dean–Stark trap is used to separate the azeotropic toluene/H_2O mixture. The formation of a macrocyclic diboronate was established by mass spectrometry. While for **3a** and **3b** a peak corresponding to $[M - \text{aryl}]^+$ is observed on account of the

Table 1. Crystallographic data for compounds **1d**, **3a**, and **4c**.

	1d[a]	**3a**[b]	**4c**[b]
formula	$C_{19}H_{15}BN_2O_5 \cdot 2THF$	$C_{20}H_{16}BNO_2$	$C_{21}H_{16}BF_2NO_2 \cdot C_6H_6$
crystal size [mm]	0.5 × 0.5 × 0.5	0.14 × 0.21 × 0.25	0.13 × 0.36 × 0.42
M_r [g mol^{-1}]	506.52	313.15	441.27
space group	*Cc*	$P\bar{1}$	$P\bar{1}$
a [Å]	9.9480(9)	8.5778(7)	6.859(1)
b [Å]	15.081(2)	10.3981(8)	13.584(2)
c [Å]	17.843(1)	10.9940(14)	13.618(2)
α [°]	90	108.392(3)	70.124(4)
β [°]	91.417(6)	112.829(3)	88.603(4)
γ [°]	90	101.751(2)	82.625(4)
V [Å^3]	2676.0(4)	795.77(14)	2769(2)
Z	4	2	2
μ [mm^{-1}]	0.080	0.083	0.088
ρ [g cm^{-3}]	1.26	1.31	1.24
θ limits [°]	$2 < \theta < 28$	$2 < \theta < 24$	$2 < \theta < 26$
hkl limits	$-13 \leq h \leq 13$ $-19 \leq k \leq 0$ $0 \leq l \leq 23$	$-9 \leq h \leq 9$ $-11 \leq k \leq 11$ $-12 \leq l \leq 12$	$-8 \leq h \leq 8$ $-16 \leq k \leq 11$; $-16 \leq l \leq 15$
collected reflections	3436	4047	7693
independent reflections (R_{int})	3215 (0.02)	2293 (0.03)	4659 (0.02)
observed reflections	1514[c]	1169[d]	1791[c]
R	0.059[e]	0.046[f]	0.062[e]
R_w	0.047[g]	0.112[h]	0.066[g]
w	$1/\sigma^2$	[i]	$1/\sigma^2$
GOF	4.28	0.80	1.55
$\Delta\rho_{min}$ [e Å^{-3}]	−0.16	−0.18	−0.28
$\Delta\rho_{max}$ [e Å^{-3}]	0.23	0.21	0.38

[a] Data collection on an Enraf Nonius CAD4 diffractometer. [b] Data collection on a Bruker Smart 6000 diffractometer. [c] $[I > 3\sigma(I)]$. [d] $[F_o > 4\sigma(F_o)]$. [e] $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|)$. [f] $R = \Sigma(F_o^2 - F_c^2)/\Sigma F_o^2$. [g] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o^2]^{1/2}$. [h] $R_w = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$. [i] $w^{-1} = \sigma_c^2 + (0.0484P)^2 + 0.00P$; $P = (F_o^2 + 2F_c^2)/3$.

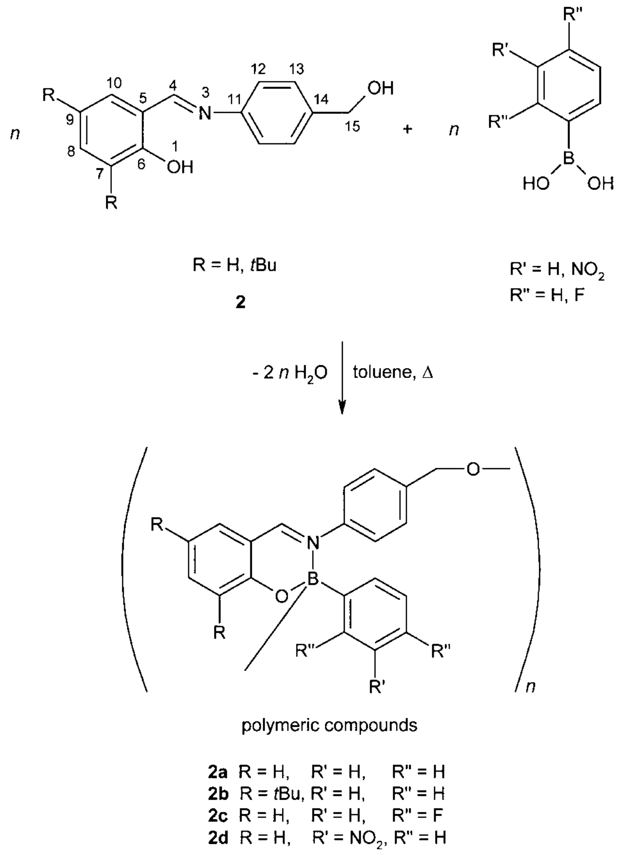
Table 2. Selected bond lengths, bond angles, and torsion angles for compounds **1d**, **3a**, and **4c**.

	1d	**3a**	**4c**
N−B	1.613(9)	1.630(4)	1.631(9)
B−O_{ph}	1.48(1)	1.482(4)	1.480(9)
B−O_{aliph}	1.45(1)	1.437(4)	1.428(9)
B−C	1.61(1)	1.612(4)	1.613(11)
C=N	1.301(8)	1.302(3)	1.297(8)
N−C_{ph}	1.444(8)	1.449(3)	1.454(8)
N-B-O_{ph}	107.0(6)	107.9(2)	107.3(16)
O-B-O	112.3(6)	110.3(3)	111.2(6)
N-B-C	112.1(6)	107.9(2)	110.6(6)
N-B-O_{aliph}	107.1(6)	104.0(2)	108.6(6)
O_{ph}-B-C	106.1(6)	110.0(2)	110.0(6)
O_{aliph}-B-C	112.2(7)	116.3(3)	109.2(6)
B-N-C4	119.5(4)	122.1(2)	122.8(6)
N-C4-C5	122.3(7)	122.5(3)	122.4(7)
B2-O1-C6	122.1(6)	126.4(3)	127.1(6)
C4-N3-C11	118.9(4)	118.3(3)	117.2(6)
B2-N3-C11	121.5(6)	119.4(2)	119.8(6)
O1-B2-C19-C20	124.3	158.6	54.8
O1-B2-N3-C4	28.0	4.0	0.2
C4-N3-C11-C12	40.6	123.6	117.6
B2-N3-C4-C5	8.7	4.0	1.6
C4-N3-B2-C19	144.0	114.7	119.8
C4-N3-B2-O18	92.6	121.2	120.4[a]

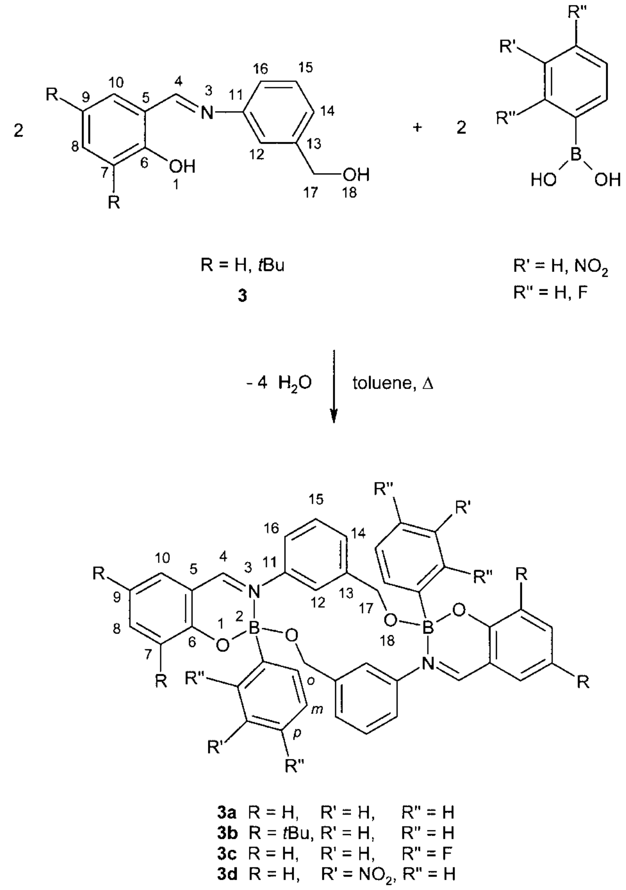
[a] C4-N3-B2-O2.

facile separation of an aryl radical from tetrahedral boronates,[3a–c, 6] in the case of **3c** the molecular ion was also detected. Interestingly, in all four cases a peak corresponding to a dication or a cation with half the molecular weight is observed.

Compounds **3a**, **3c**, and **3d** are quite insoluble in organic solvents, and only **3b** could be characterized by ^{1}H and ^{13}C NMR spectroscopy. The spectroscopic data are summarized in Tables 3 and 4. The ^{1}H NMR spectrum shows some interesting shift displacements, as shown in the ^{1}H,^{1}H-COSY spectrum outlined in Figure 2. The diastereotopic methylene signals at $\delta = 5.04$ and 5.25 indicate the coordination of the benzyloxy group to a boron atom that must be chiral and therefore tetracoordinate. The tetracoordination is further confirmed by ^{11}B NMR spectroscopy ($\delta = 9$).[7] In the aromatic region of this spectrum two signals with unusual chemical shifts are detected, one at very high field ($\delta = 6.19$; H16) and another one at very low field ($\delta = 9.25$; H12). Both hy-



Scheme 3. Reaction of ligands **2** with arylboronic acids.



Scheme 4. Preparation of the [4.4]metacyclophane derivatives **3a**–**d**.

drogens have been assigned unequivocally by COSY and HETCOR spectra. Based on these two-dimensional experiments, it can be excluded that the signal at $\delta = 9.25$ is the imine hydrogen atom; this has a chemical shift of $\delta = 7.16$ and correlates with a ^{13}C NMR signal at $\delta = 164.1$.

To explain these unusual ^{1}H NMR shift displacements, a crystallographic study was necessary; this was performed in the case of compound **3a**. Crystallographic data as well as selected bond lengths, bond angles, and torsion angles are summarized in Tables 1 and 2. The molecular structure is shown in Figure 3. The molecules are located on crystallographic inversion centers in the crystal lattice, so that the configurations of the two chiral boron atoms are *RS* or *SR*, respectively. The central macrocyclic unit consists of a 14-membered $C_8B_2N_2O_2$ heterocyclic ring and it is important to notice that it includes two coordinative N–B bonds. The O18 ··· O18′, B2 ··· B2′ and C12 ··· C12′ distances are 4.29, 6.35, and 3.84 Å, respectively. In this structure the conjugation between the benzyloxy group and the salicylideneamino group is no longer maintained. The mutual rotation of these functional groups by an angle of 56.8° places the H16 hydrogen atom in the anisotropic magnetic field of the imino group, and this location should be responsible for the extreme ^{1}H NMR high-field shift ($\Delta\delta = 0.96$) of this atom ($\delta = 6.19$). The unusual shift of hydrogen H12 can be explained by intramolecular C–H ··· O hydrogen bonding, as outlined in Figure 4. The distance between O18 and H–C12 is 2.34 Å (C–H ··· O = 116.8°); this value is significantly shorter than the sum of the van der Waals radii of oxygen and hydrogen (2.70 Å).[8] Furthermore, there may be an additional interaction between the same hydrogen and the second oxygen atom in the heterocycle (2.60 Å, 92.7°), so that the deshielding effect may still be enhanced, thus explaining the extreme low-field shift of this hydrogen ($\delta = 9.25$). It has been recognized recently that C–H ··· O interactions can act as important control elements in the stabilization of supramolecular structures.[9] In the present case these interactions might contribute to the stabilization of the antiperiplanar conformation of the heterocycle. Figure 4 illustrates that compound **3a** can be considered as a [4.4]metacyclophane derivative. By means of dynamic NMR spectroscopy, theoretical calculations, and X-ray crystallography it has been shown that both antiperiplanar and anticlinal conformers of carbocyclic [4.4]metacyclophanes can be stable depending on the substituents on the aliphatic chain.[10] In compound **3a** the two aromatic rings are joined by two C-O-B-N chains, whereby the N–B bond is coordinative. The N–B bond length is 1.630(4) Å and is typical for an intermediate strength of this type of bonding.[5]

Table 3. ^{1}H (300 MHz) and ^{11}B NMR (96.3 MHz) data for compounds **3b** and **4b** and the corresponding ligands **3** and **4**.

	3[a]	**3b**[b]	**4**[a, c]	**4b**[a]
H4	8.57 (s)	7.16 (m)	8.67 (s)	8.21 (s)
H8	7.38 (m)	7.84 (m)	7.46 (d)	7.62 (d)
H10	7.15 (d)	6.74 (m)	7.22 (d)	7.12 (d)
H12	7.22 (s)	9.25 (s)	7.26 (d)[d]	6.60 (d)
H13	–	–	7.29 (d)[d]	6.99 (d)
H14	7.15 (m)	6.74 (m)	–	–
H15	7.30 (t)	6.74 (m)	7.29 (d)	6.99 (d)
H16	7.15 (m)	6.19 (d)	7.26 (d)	6.60(d)
H17	4.64 (s)	5.04 (d) 5.25 (d)	2.91 (t)	2.57 (dd) 2.96 (dt)
H18	–	–	3.90 (t)	3.36 (t) 4.02 (m)
*t*Bu	1.25 (s) 1.40 (s)	1.36 (s) 1.68 (s)	1.34 (s) 1.49 (s)	1.33 (s) 1.41 (s)
^{11}B NMR	–	9	–	7

[a] $CDCl_3$. [b] C_6D_6. [c] ^{1}H NMR, 400 MHz. [d] Signals may be interchanged.

Table 4. ^{13}C (75 MHz) data for compound **3b** and the corresponding ligand **3**.

	3[a]	**3b**[b]
C4	164.1	164.1
C5	118.4	116.1
C6	158.5	159.2
C7	137.2[c]	139.7[c]
C8	128.3	133.6
C9	140.8[c]	140.7[c]
C10	127.1	127.4
C11	149.1	144.9[d]
C12	119.7	125.9
C13	142.5	146.0[d]
C14	120.6[d]	126.1
C15	129.7	128.5
C16	125.1[d]	122.4
C17	65.1	64.6

[a] $CDCl_3$. [b] C_6D_6. [c] Signals may be interchanged. [d] Signals may be interchanged.

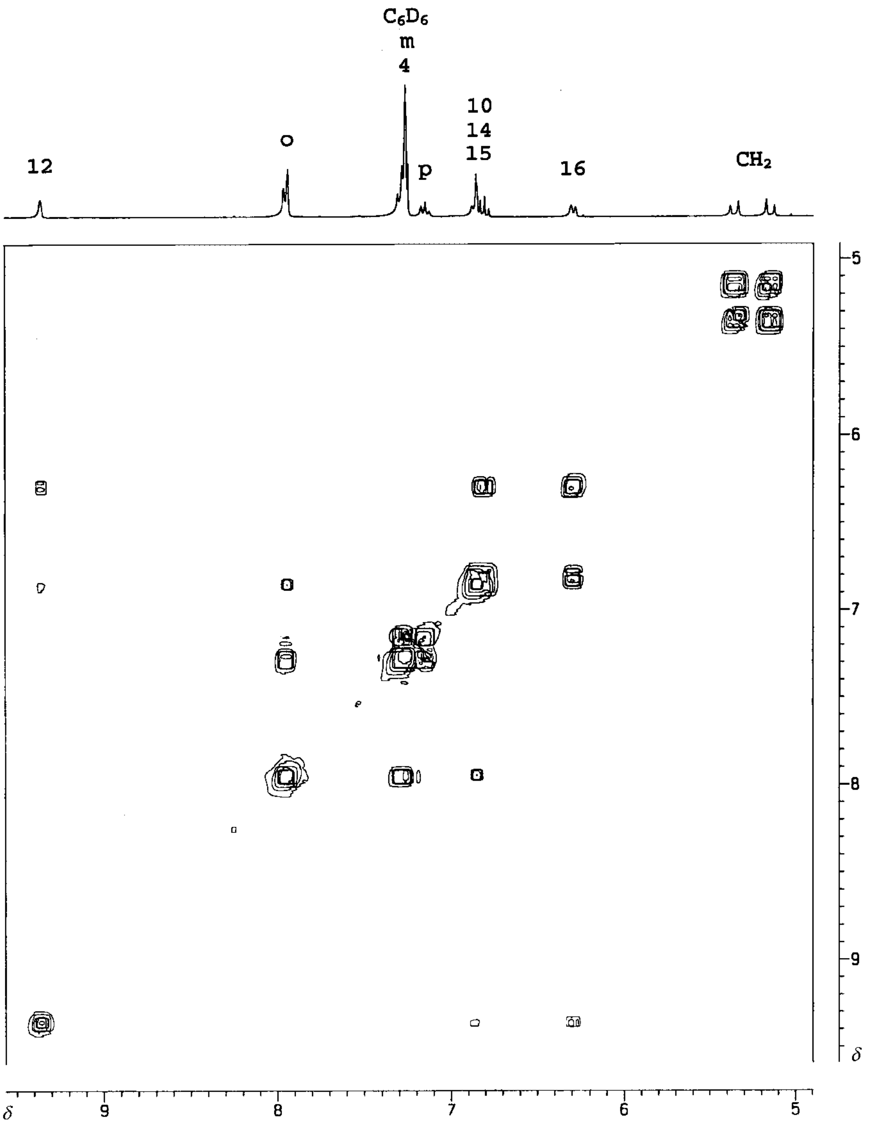


Figure 2. ^{1}H COSY NMR spectrum of compound **3b**.

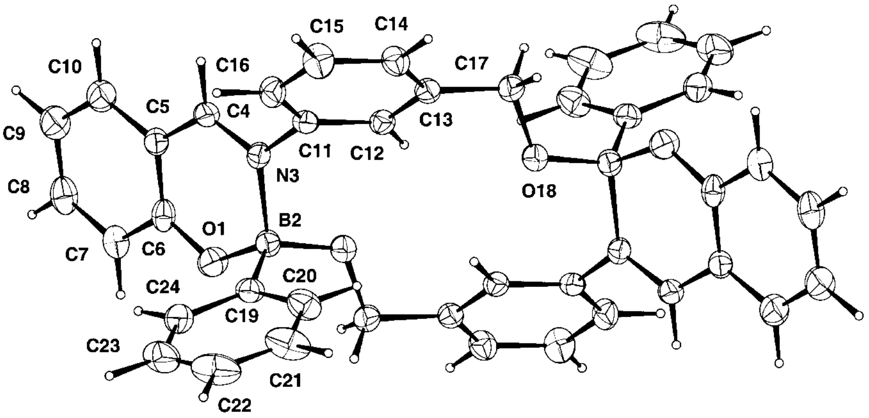


Figure 3. Perspective view of the molecular structure of the [4.4]metacyclophane derivative **3a**.

The central macrocyclic ring of compounds **3a–d** can be expanded if 4-(salicylideneamino)phenethyl alcohols **4** are used as ligands for the reaction with arylboronic acids (Scheme 5). Compounds **4a–d** are air-stable products and are obtained in yields of 69 to 98%. Reaction times are also very short (10–30 min), and the product precipitates because of its low solubility. The formation of macrocycles could be demonstrated by mass spectrometry. In the case of **4b** (HRMS) and **4c** the molecular ion is detected, while for **4a** and **4d** it is the ion that results from the loss of an aryl radical.[6] As for compounds **3a–d**, a peak corresponding to a dication or a cation with half the molecular weight is detected.

Compounds **4a–d** have very low solubility and only **4b** could be characterized by NMR spectroscopy (Table 3). Nevertheless, the solubility was not high enough to obtain a ^{13}C NMR spectrum because decomposition (polymerization) occurred before sufficient transients could be accumulated. The aliphatic region of the ^{1}H NMR spectrum shows an ABCD spin system that is characteristic for ethyleneoxy groups that coordinate to a boron atom which is tetracoordinate, as expected (^{11}B NMR, $\delta = 7$). The rest of the spectrum was assigned by a COSY experiment (Table 3). In contrast to compound **3b**, both hydrogens in the *ortho* positions with respect to the imino group (H12/H16) are now significantly shifted to higher fields ($\Delta\delta = 0.67$). On the timescale of the ^{1}H NMR experiment, H12/H16 as well as H13/H15 have chemical shifts, which are pairwise identical, although all four hydrogen atoms should have different shifts as a result of their different chemical environments. Therefore, the central aromatic rings are rotating rapidly around their central axes in the macrocycles.

The molecular structure of this type of molecule was elucidated by the X-ray crystallographic study of compound **4c**. Crystallographic data as well as selected bond lengths, bond angles, and torsion angles are summarized in Tables 1 and 2. The molecular structure is given in Figure 5. Similar to compound **3a**, it has

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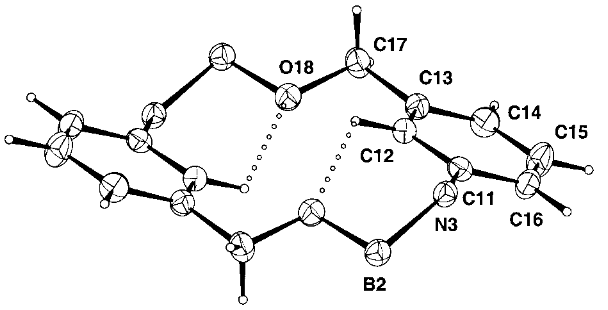
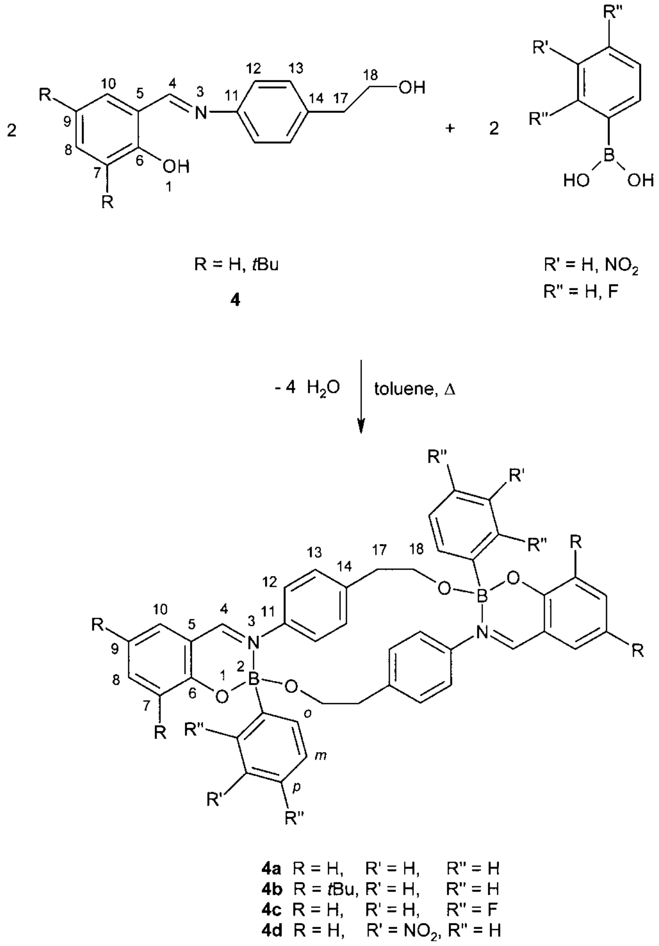


Figure 4. Perspective view of the central 14-membered heterocycle of compound **3a** with intramolecular C–H ··· O hydrogen bonds.



Scheme 5. Preparation of the [5.5]paracyclophane derivatives **4a**–**d**.

an inversion center so that the two chiral boron atoms have different configurations. The central macrocyclic $C_{12}B_2N_2O_2$ ring is 18-membered with a B2 ··· B2′ distance of 8.26 Å, an O2 ··· O2′ distance of 7.02 Å, and an C18 ··· C18′ distance of 7.32 Å, all of which are longer than in compound **3a**. As in compound **3a**, the C4-N3-C11-C16 torsion angle of 62.4° places the H16 hydrogen atom near to the anisotropic magnetic field of the imino group. However, it should be remembered that in solution a free rotation of this phenyl ring is observed, so that in solution both H12 and H16 should be influenced. Furthermore, these two hydrogen atoms are in proximity to aromatic rings: the distance between H12 and the centroid of the B-phenyl group is 3.07 Å and the distance between H16 and the plane formed by the opposite C11′ – C16′ phenyl ring is 3.50 Å. Therefore, at least part of the high-field shift may be attributed to the influence of anisotropic aromatic ring currents.

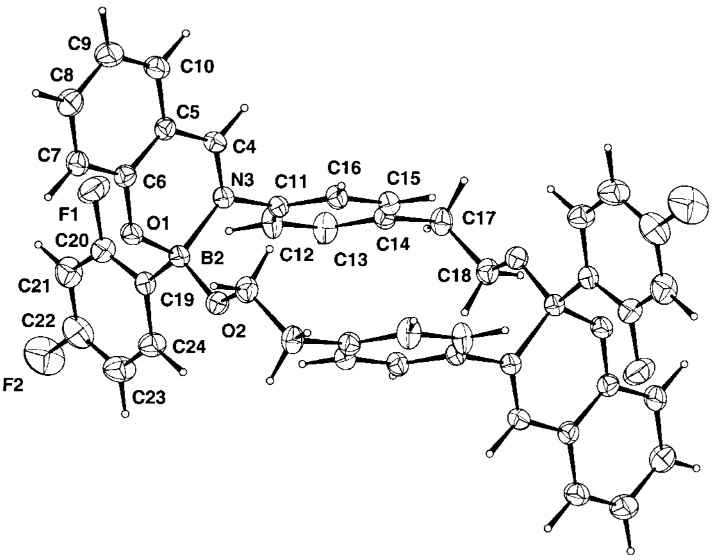


Figure 5. Perspective view of the molecular structure of the [5.5]paracyclophane derivative **4c**.

The two central aromatic rings of the complex have a parallel orientation, but are displaced relative to each other. From Figure 6, which shows the central part of the structure, it can be seen that the distance between the centroids of the aromatic rings is 4.16 Å. A repulsive transannular π – π interaction can be therefore excluded.[11] The shortest intermolecular π – π distances observed are those between the centroids of the C5 – C10 aromatic rings (3.94 Å). From Figure 6, the analogy to a [5.5]paracyclophane derivative becomes clear, and it should be mentioned again that the N–B bonds are coordinative. The N–B bond length is 1.631 (9) Å, which indicates an intermediate bond strength for this type of bonding.[5]

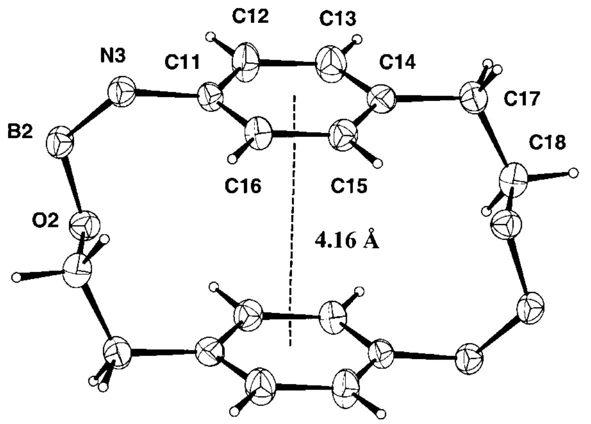


Figure 6. Perspective view of the central 18-membered heterocycle of compound **4c**.

Conclusion

This contribution has shown that certain cyclophane-type diboronates can be readily prepared and in high yields. However, it must be mentioned that the ligand structure is very important for a successful macrocyclization. The [4.4]metacyclophane and [5.5]paracyclophane derivatives discussed in this report are air-stable, but have very low solubilities in organic solvents. This problem could be overcome by the introduction of additional aliphatic substituents on one of the aromatic residues in the structure.

The central macrocycle is formed by a skeleton held together by two boron atoms with a relatively strong N–B bond. Theoretically, this bond can be broken by borophilic reagents in order to expand the macrocyclic ring further, and we are working on this topic at the moment. The cyclophane derivatives described here carry boron atoms that are chiral and, therefore, they may be also interesting for the formation of chiral host–guest complexes.

At the moment, we are designing ligands that give even larger macrocyclic systems; however, it must also be considered that there will be more and more competition with the formation of polymeric molecules.

Experimental Section

Instrumental: NMR studies were carried out with Varian 200, Bruker 300, and Jeol Eclipse +400 instruments. Standards were TMS (^{1}H, ^{13}C) and $BF_3 \cdot OEt_2$ (^{11}B). Chemical shifts are positive if the signal was shifted to higher frequencies than the standard. Two-dimensional COSY, HETCOR, and NOESY experiments were carried out in order to assign the ^{1}H and ^{13}C spectra completely. IR spectra were recorded on a Bruker Vector 22 FT-IR and UV/Vis spectra on a Hewlett Packard 8453 spectrophotometer. Mass spectra were obtained on a HP 5989 A spectrometer and the HRMS analysis of compound **4b** was carried out on the Q-TOF-II of Micromass. Elemental analyses were carried out on a Perkin–Elmer Series II 2400 instrument. It should be mentioned that elemental analyses of boronic acid derivatives are complicated by incombustible residues (boron carbide) and are thus not always within the established limits of exactitude.[12]

General: Commercial starting materials and solvents have been used. Ligands **1**–**4** are Schiff bases and were prepared according to refs. [3a, b]. Boron complexes **1a**–**d**, **3a**–**d**, and **4a**–**d** were obtained as described in ref. [3b]. In the case of **2a**–**d**, the same preparative methods were applied, but only oligomeric or polymeric material could be isolated. These compounds were only characterized by IR and ^{1}H NMR spectroscopy in order to verify whether all the hydroxyl groups of the starting material had reacted.

Preparation of ligands 1

4-(Salicylideneamino)phenol: Prepared from salicylaldehyde (1.00 g, 8.19 mmol) and 4-aminophenol (0.89 g, 8.19 mmol) in ethanol (20 mL). Yield: 98%; m.p. 135–137 °C; ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 6.89$ (AB, 2H; H13), 6.94 (m, 1H; H9), 7.02 (dd, 1H; H7), 7.24 (AB, 2H; H12), 7.37 (m, 2H; H8, H10), 8.61 (s, 1H; H4); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 116.4$ (C13), 117.4 (C7), 119.3 (C9), 119.5 (C5), 122.7 (C12), 132.2, 133.0 (C8, C10), 141.5 (C11), 155.2 (C14), 160.6 (C4), 161.2 (C6); IR (KBr): $\tilde{\nu} = 1617$ (C=N), 1509 cm^{-1}; MS (70 eV, EI): m/z (%): 213 (8) $[M]^+$, 129 (5), 123 (5), 111 (7), 97 (15), 83 (44), 69 (32), 57 (53), 47 (17), 43 (100).

4-(3,5-Di-tert-butylsalicylideneamino)phenol: Prepared from 3,5-di-*tert*-butylsalicylaldehyde (0.50 g, 2.14 mmol) and 4-aminophenol (0.23 g, 2.14 mmol) in ethanol (20 mL) as a viscous oil. Yield: 95%; ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 1.33$, 1.48 (s, 18H; *t*Bu), 6.87 (AB, 2H; H13), 7.22 (m, 3H; H10, H12), 7.43 (d, 1H; H8), 8.61 (s, 1H; H4); ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 29.7$, 31.7 ($C(CH_3)_3$), 34.4, 35.3 ($C(CH_3)_3$), 116.3 (C13), 118.6 (C5), 122.6 (C12), 126.8 (C10), 127.8 (C8), 137.1, 140.7 (C7, C9), 142.1 (C11), 154.7 (C14), 158.2 (C6), 162.1 (C4); IR (KBr): $\tilde{\nu} = 1622$ (C=N), 1507, 1186 cm^{-1}.

Preparation of ligands 2

4-(Salicylideneamino)benzyl alcohol: Prepared from salicylaldehyde (1.00 g, 8.19 mmol) and 3-aminobenzyl alcohol (1.01 g, 8.19 mmol) in ethanol (20 mL). Yield: 94%; m.p. 156–158 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 4.76$ (s, 2H; H15), 6.97 (dt, 1H; H9), 7.05 (d, 1H; H7), 7.30 (AB, 2H; H12), 7.40 (m, 4H; H8, H10, H13), 8.65 (s, 1H; H4), 13.3 (br s, 1H; OH_{ph}); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 65.3$ (C15), 117.7 (C7), 119.5 (C9), 119.6 (C5), 121.8 (C12), 128.5 (C13), 132.7, 133.6 (C8, C10), 140.0 (C14), 148.3 (C11), 161.5 (C6), 163.0 (C4); IR (KBr): $\tilde{\nu} = 1620$ (C=N), 1599, 1570, 1511, 1497, 1456, 1413, 1368, 1282, 1185, 1169, 1158, 1148, 1025 cm^{-1}; MS (70 eV, EI): m/z (%): 227 (100) $[M]^+$, 210 (25), 181 (8), 167 (6), 132 (5), 107 (8), 104 (9), 91 (8), 77 (26), 51 (14).

3-(3,5-Di-tert-butylsalicylideneamino)benzyl alcohol: Prepared from 3,5-di-*tert*-butylsalicylaldehyde (1.00 g, 4.26 mmol) and 4-aminobenzyl alcohol (0.53 g, 4.26 mmol) in toluene (20 mL). Crystals were obtained by cooling to −20 °C. Yield: 93%; m.p. 162–165 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 1.33$, 1.48 (s, 18H; *t*Bu), 4.73 (s, 2H; H15), 7.23 (d, 1H; H10), 7.28 and 7.43 (AB, 4H; H12, H13), 7.46 (d, 1H; H8), 8.65 (s, 1H; H4), 13.7 (br s, 1H; OH_{ph}); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 29.6$, 31.7 ($C(CH_3)_3$), 34.4, 35.3 ($C(CH_3)_3$), 65.1 (C15), 118.5 (C5), 121.5, 128.3 (C12, C13), 127.0, 128.3 (C8, C10), 137.2, 139.4, 140.8 (C7, C9, C14), 148.3 (C11), 158.4 (C6), 163.9 (C4); IR (KBr): $\tilde{\nu} = 1619$ (C=N), 1171 cm^{-1}.

Preparation of ligands 3

3-(Salicylideneamino)benzyl alcohol: Prepared from salicylaldehyde (1.00 g, 8.19 mmol) and 3-aminobenzyl alcohol (1.01 g, 8.19 mmol) in ethanol (20 mL). Yield: 97%; m.p. 58–59 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 4.77$ (s, 2H; H17), 6.97 (dt, 1H; H9), 7.04 (dd, 1H; H7), 7.22, 7.32 (m, 3H; H12, H14, H16), 7.40 (m, 3H; H8, H10, H15), 8.65 (s, 1H; H4), 13.3 (br s, 1H; OH_{ph}); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): $\delta =$ 65.2 (C17), 117.6 (C7), 119.6 (C5, C9), 119.8 (C12), 120.9, 125.7 (C14, C16), 130.0 (C15), 132.8 (C10), 133.7 (C8), 142.8 (C13), 149.0 (C11), 161.5 (C6), 163.2 (C4); IR (KBr): $\tilde{\nu} = 1621$ (C=N), 1602, 1572 cm^{-1}; MS (70 eV, EI): m/z (%): 227 (100) $[M]^+$, 209 (25), 180 (17), 167 (6), 120 (5), 89 (11), 77 (129), 51 (13).

3-(3,5-Di-tert-butylsalicylideneamino)benzyl alcohol: Prepared from 3,5-di-*tert*-butylsalicylaldehyde (1.00 g, 4.27 mmol) and 3-aminobenzyl alcohol (0.46 g, 4.27 mmol) in ethanol (20 mL). Yield: 91%; m.p. 54–56 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 1.25$, 1.40 (s, 18H; *t*Bu), 4.64 (s, 2H; H17), 7.15 (m, 3H; H10, H14, H16), 7.22 (s, 1H; H12), 7.30 (t, 1H; H15), 7.38 (d, 1H; H8), 8.57 (s, 1H; H4), 13.6 (br s, 1H; OH_{ph}); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 29.6$, 31.7 ($C(CH_3)_3$), 34.4, 35.3 ($C(CH_3)_3$), 65.1 (C17), 118.4 (C5), 119.7 (C12), 120.6, 125.1 (C14, C16), 127.1 (C10), 128.3 (C8), 129.7 (C15), 137.2, 140.8 (C7, C9), 142.5 (C13), 149.1 (C11), 158.5 (C6), 164.1 (C4); IR (KBr): $\tilde{\nu} = 1618$ (C=N), 1574, 1466, 1438 cm^{-1}; MS (70 eV, EI): m/z (%): 339 (63) $[M]^+$, 324 (100), 296 (41), 282 (22), 268 (7), 134 (8), 41 (7).

Preparation of ligands 4

4-(Salicylideneamino)phenethyl alcohol: Prepared from salicylaldehyde (1.00 g, 8.19 mmol) and 4-aminophenethyl alcohol (1.12 g, 8.19 mmol) in ethanol (20 mL). Yield: 99%; m.p. 95–96 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 1.83$ (br s, 1H; OH_{aliph}), 2.89 (t, 2H; H17), 3.87 (t, 2H; H18), 6.94 (dt, 1H; H9), 7.02 (dd, 1H; H7), 7.26 and 7.29 (dd, 4H; H12, H13), 7.37 (m, 2H; H8, H10), 8.60 (s, 1H; H4), 13.4 (br s, 1H; OH_{ph}); ^{13}C NMR (100.5 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 38.7$ (C17), 63.6 (C18), 117.2 (C7), 119.1 (C9), 119.2 (C5), 121.3, 130.1 (C12, C13), 132.3, 133.1 (C8, C10), 137.6 (C14), 146.8 (C11), 161.1 (C6), 162.2 (C4); IR (KBr): $\tilde{\nu} =$ 1620 cm^{-1} (C=N); MS (70 eV, EI): m/z (%): 242 (11) $[M]^+$, 241 (60), 210 (100), 91 (23), 77 (13), 31 (13).

4-(3,5-Di-tert-butylsalicylideneamino)phenethyl alcohol: Prepared from 3,5-di-*tert*-butylsalicylaldehyde (2.00 g, 8.55 mmol) and 4-aminophenethyl alcohol (1.17 g, 8.55 mmol) in ethanol (20 mL). Crystals were obtained on cooling to −20 °C. Yield: 95%; m.p. 145–146 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 1.34$, 1.49 (s, 18H; *t*Bu), 2.91 (t, 2H; H17), 3.90 (t, 2H; H18), 7.22 (d, 1H; H10), 7.27 (m, 4H; H12, H13), 7.46 (d, 1H; H8), 8.67 (s, 1H; H4), 13.7 (br s, 1H; OH_{ph}); ^{13}C NMR (100.5 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 29.5$, 31.5 ($C(CH_3)_3$), 34.2, 35.1 ($C(CH_3)_3$), 38.7 (C17), 63.7 (C18), 118.3 (C5), 121.4 (C12), 126.8 (C10), 128.0 (C8), 130.0 (C13), 137.0, 140.6 (C7, C9, C14), 147.1 (C11), 158.2 (C6), 163.4 (C4); IR (KBr): $\tilde{\nu} = 1619$ (C=N), 1582, 1171 cm^{-1}; UV/Vis (CHCl$_3$): λ_{max} (absorbance) = 244 (0.930), 277 (0.987), 312 (1.042), 327 (0.982), 358 nm (0.869 AU); MS (70 eV, EI): m/z (%): 353 (65) [M]$^+$, 338 (100), 310 (41), 296 (20), 282 (6), 148 (4), 91 (6), 57 (6), 41 (7).

Boronate 1a: Prepared from 4-(salicylideneamino)phenol (0.50 g, 2.34 mmol) and phenylboronic acid (0.28 g, 2.34 mmol) in ethyl acetate (8 mL). After 1 h reflux and cooling to room temperature, the yellow product was precipitated with hexane and filtered under vacuum. The product was insoluble in all common organic solvents. Yield: 93 %; m.p. 224–226 °C (decomp); IR (KBr): $\tilde{\nu} = 3357$ (br), 3046 (w), 1625 (s), 1556 (m), 1507 (s), 1478 (m), 1458 (m), 1376 (m), 1263 (m), 1203 (m), 1152 (m), 1125 (m), 1108 (w), 1075 (w), 1028 cm^{-1} (m); elemental analysis calcd (%) for $C_{19}H_{16}BNO_3$ (317.16): C 71.95, H 5.09, N 4.42; found: C 70.76, H 5.28, N 4.27.

Boronate 1b: Prepared from 4-(3,5-di-*tert*-butylsalicylideneamino)phenol (0.70 g, 2.14 mmol) and phenylboronic acid (0.26 g, 2.14 mmol) in toluene/hexane (1:1, 10 mL). After 30 min reflux the hexane was distilled off, and after 90 min a yellow precipitate formed that was filtered under vacuum and washed with toluene. The product was insoluble in all common organic solvents. Yield: 7 %; m.p. 285 °C (decomp); IR (KBr): $\tilde{\nu} = 3433$ (br), 3071 (w), 3047 (w), 3007 (w), 2960 (m), 2909 (m), 2869 (m), 1622 (s), 1562 (m), 1550 (m), 1507 (s), 1467 (m), 1433 (m), 1392 (w), 1362 (m), 1295 (m), 1259 (s), 1184 (s), 1132 (w), 1078 (m), 1049 (m), 1027 (m), 1001 cm^{-1} (m).

Boronate 1c: Prepared from 4-(salicylideneamino)phenol (0.50 g, 2.34 mmol) and 2,5-difluorophenylboronic acid (0.37 g, 2.34 mmol) in ethyl acetate (8 mL). After 1 h reflux and cooling to room temperature, the yellow product was precipitated with hexane and filtered under vacuum. The product was insoluble in all common organic solvents. Yield: 84 %; m.p. 320–323 °C (decomp); IR (KBr): $\tilde{\nu} = 3447$ (w, br), 3045 (w), 2941 (w), 2895 (w), 2860 (w), 1622 (s), 1598 (m), 1553 (m), 1513 (s), 1529 (m), 1478 (m), 1455 (m), 1419 (w), 1376 (m), 1349 (m), 1311 (m), 1274 (w), 1244 (w), 1198 (s), 1161 (w), 1151 (m), 1128 (m), 1081 (w), 1052 (w), 1032 cm^{-1} (m).

Boronate 1d: Prepared from 4-(salicylideneamino)phenol (0.50 g, 2.34 mmol) and 3-nitrophenylboronic acid (0.39 g, 2.34 mmol) in ethyl acetate (8 mL). After 1 h reflux and cooling to room temperature, the yellow product was precipitated with hexane and filtered under vacuum. The product was insoluble in all common organic solvents. Yield: 33 %; m.p. 218–220 °C (decomp); IR (KBr): $\tilde{\nu} = 3448$ (br), 3078 (w), 3039 (w), 2961 (w), 2922 (w), 1625 (s), 1556 (m), 1511 (s), 1478 (m), 1459 (w), 1378 (w), 1347 (s), 1301 (w), 1276 (m), 1204 (m), 1153 (w), 1126 (w), 1099 (w), 1029 cm^{-1} (w).

Boronate 3a: Prepared from 3-(salicylideneamino)benzyl alcohol (0.50 g, 2.20 mmol) and phenylboronic acid (0.27 g, 2.20 mmol) in benzene (8 mL). After 1 h reflux, the yellow precipitate was filtered under vacuum. The product was insoluble in all common organic solvents. Crystals suitable for X-ray crystallography were grown directly from the starting materials in dichloromethane. Yield: 96 %; m.p. 266–267 °C; IR (KBr): $\tilde{\nu} = 3067$ (w), 3046 (w), 3004 (w), 2959 (m), 2869 (w), 1629 (s), 1605 (m), 1588 (w), 1562 (s), 1550 (m), 1469 (m), 1442 (w), 1432 (w), 1415 (w), 1391 (w), 1314 (w), 1263 (m), 1232 (m), 1202 (s), 1184 (s), 1119 (s), 1083 (m), 1020 cm^{-1} (w); MS (70 eV, EI): m/z (%): 549 (51) [$M - C_6H_5$]$^+$, 312 (100) [M/2]$^+$ or [M]$^{2+}$, 282 (10), 262 (20), 236 (52), 225 (14), 165 (10), 152 (12), 91 (11), 77 (30), 51 (22); elemental analysis calcd (%) for $C_{40}H_{32}B_2N_2O_4$ (626.34): C 76.71, H 5.15, N 4.47; found: C 75.36, H 5.19, N 4.04.

Boronate 3b: Prepared from 3-(3,5-di-*tert*-butylsalicylideneamino)benzyl alcohol (0.50 g, 1.47 mmol) and phenylboronic acid (0.18 g, 1.47 mmol) in benzene (10 mL). After 1 h reflux, the yellow precipitate was filtered under vacuum. The product was slightly soluble in benzene. Yield: 70 %; m.p. 278–280 °C; ^{1}H NMR (300 MHz, C_6D_6, 25 °C, TMS): $\delta = 1.36$, 1.68 (s, 36H; *t*Bu), 5.04 and 5.25 (AB, 4H; H17), 6.19 (d, 2H; H16), 6.74 (m, 6H; H10, H14, H15), 7.05 (t, 2H; p-BC$_6$H$_5$), 7.18 (m, 6H; m-BC$_6$H$_5$, H4), 7.84 (m, 6H; H6, H8, o-BC$_6$H$_5$), 9.25 (s, 2H; H12); ^{13}C NMR (75 MHz, C_6D_6, 25 °C, TMS): $\delta = 30.3$, 31.9 (C(CH$_3$)$_3$), 34.7, 35.9 (C(CH$_3$)$_3$), 64.6 (C17), 116.1 (C5), 122.4 (C16), 125.9 (C12), 126.1 (C14), 127.4 (C10, p-BC$_6$H$_5$), 127.8 (m-BC$_6$H$_5$), 128.5 (C15), 133.4 (o-BC$_6$H$_5$), 133.6 (C8), 139.7, 140.7 (C7, C9), 144.9, 146.0 (C11, C13), 159.2 (C6), 164.1 (C4); ^{11}B NMR (96.3 MHz, C_6D_6, 25 °C, BF$_3\cdot$OEt$_2$): $\delta = 9$ ($h_{1/2} = 600$ Hz); IR (KBr): $\tilde{\nu} = 3064$ (w), 2945 (w), 2924 (w), 2892 (w), 2862 (w), 1630 (s), 1605 (s), 1588 (m), 1558 (s), 1508 (m), 1484 (m), 1461 (m), 1405 (m), 1384 (m), 1344 (w), 1320 (m), 1286 (w), 1261 (w), 1232 (m), 1203 (m), 1172 (m), 1154 (m), 1129 (m), 1109 (s), 1090 (m), 1054 (m), 1028 cm^{-1} (m); MS (70 eV, EI): m/z (%): 773 (30) [$M - C_6H_5$]$^+$, 425 (58) [M/2]$^+$ or [M]$^{2+}$, 410 (100), 374 (21), 348 (83), 333 (14), 317 (11), 190 (7), 176 (7), 91 (8), 78 (9), 57 (7); elemental analysis calcd (%) for $C_{56}H_{64}B_2N_2O_4$ (850.77): C 79.06, H 7.58, N 3.29; found: C 78.29, H 7.50, N 3.99.

Boronate 3c: Prepared from 3-(salicylideneamino)benzyl alcohol (0.50 g, 2.20 mmol) and 2,5-difluorophenylboronic acid (0.35 g, 2.20 mmol) in benzene (8 mL). After 1 h reflux, the yellow precipitate was filtered under vacuum. The product was insoluble in all common organic solvents. Yield: 95 %; m.p. 254–255 °C; IR (KBr): $\tilde{\nu} = 3043$ (w), 2912 (w), 2866 (w), 2832 (w), 2718 (w), 1632 (s), 1606 (s), 1587 (m), 1559 (m), 1486 (m), 1463 (w), 1402 (m), 1380 (m), 1302 (m), 1281 (w), 1231 (m), 1178 (m), 1152 (m), 1131 (m), 1081 (m), 1032 (w), 1024 cm^{-1} (w); MS (70 eV, EI): m/z (%): 698 (1) [M]$^+$, 585 (100) [$M - C_6H_3F_2$]$^+$, 349 (29) [M/2]$^+$ or [M]$^{2+}$, 333 (8), 292 (5), 272 (6), 262 (9), 254 (26), 236 (45), 224 (6), 150 (5), 89 (10), 77 (8), 51 (7); elemental analysis calcd (%) for $C_{40}H_{28}B_2F_4N_2O_4$ (698.30): C 68.80, H 4.04, N 4.01; found: C 68.74, H 4.09, N 4.09.

Boronate 3d: Prepared from 3-(salicylideneamino)benzyl alcohol (0.50 g, 2.20 mmol) and 3-nitrophenylboronic acid (0.36 g, 2.20 mmol) in benzene (8 mL). After 1 h reflux, the yellow precipitate was filtered under vacuum. The product was insoluble in all organic solvents. Yield: 86 %; m.p. 255–256 °C; IR (KBr) $\tilde{\nu} = 3133$ (w), 3060 (w), 3038 (w), 2925 (w), 2887 (w), 2836 (w), 1626 (s), 1607 (m), 1585 (w), 1555 (s), 1520 (s), 1479 (m), 1461 (m), 1417 (w), 1383 (m), 1344 (s), 1304 (m), 1289 (w), 1277 (w), 1248 (w), 1225 (m), 1193 (m), 1153 (m), 1114 (m), 1072 (m), 1028 cm^{-1} (w); MS (70 eV, EI): m/z (%): 358 (59) [M/2]$^+$ or [M]$^{2+}$, 357 (100), 342 (2), 327 (3), 310 (7), 298 (3), 282 (27), 254 (9), 225 (25), 208 (9), 196 (6), 178 (5), 165 (5), 152 (8), 141 (8), 120 (7), 105 (8), 89 (8), 77 (29), 63 (7), 51 (22); elemental analysis calcd (%) for $C_{40}H_{30}B_2N_4O_8$ (716.34): C 67.07, H 4.22, N 7.82; found: C 67.38, H 4.42, N 7.39.

Boronate 4a: Prepared from 4-(salicylideneamino)phenethyl alcohol (0.50 g, 2.07 mmol) and phenylboronic acid (0.25 g, 2.07 mmol) in benzene (10 mL). After 1 h reflux, the yellow precipitate was filtered under vacuum. The product was insoluble in all common organic solvents. Yield: 98 %; m.p. 257–260 °C; IR (KBr): $\tilde{\nu} = 3046$ (w), 2942 (w), 2896 (w), 2860 (w), 1621 (s), 1553 (s), 1514 (s), 1478 (m), 1456 (m), 1377 (m), 1348 (s), 1311 (m), 1274 (w), 1244 (w), 1198 (s), 1151 (m), 1128 (s), 1032 cm^{-1} (m); MS (70 eV, EI): m/z (%): 577 (6) [$M - C_6H_5$]$^+$, 500 (17), 428 (11), 329 (47), 327 (30) [M/2]$^+$ or [M]$^{2+}$, 298 (100), 239 (16), 192 (52), 165 (14), 91 (14), 77 (17), 51 (14); elemental analysis calcd (%) for $C_{42}H_{36}B_2N_2O_4$ (654.39): C 77.09, H 5.54, N 4.27; found: C 76.36, H 5.70, N 4.09.

Boronate 4b: Prepared from 4-(3,5-di-*tert*-butylsalicylideneamino)phenethyl alcohol (1.00 g, 2.83 mmol) and phenylboronic acid (0.35 g, 2.83 mmol) in toluene (5 mL). After 1 h reflux, the orange precipitate was filtered under vacuum. The product was slightly soluble in chloroform. Yield: 69 %; m.p. 286–288 °C; ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C, TMS): $\delta = 1.33$, 1.41 (s, 36H; *t*Bu), 2.57 and 2.96 (AB, 4H; H17), 3.36 and 4.02 (AB, 4H; H18), 6.60 and 6.99 (AB, 8H; H12, H13), 7.12 (d, 2H; H10), 7.22 (m, 6H; m-BC$_6$H$_5$, p-BC$_6$H$_5$,), 7.48 (dd, 4H; o-BC$_6$H$_5$,), 7.62 (d, 2H; H8), 8.21 (s, 2H; H4); ^{11}B NMR (96.3 MHz, CDCl$_3$, 25 °C, BF$_3\cdot$OEt$_2$): $\delta = 7$; IR (KBr): $\tilde{\nu} = 3048$ (w), 3003 (w), 2960 (m), 2912 (w), 2872 (w), 1625 (s), 1603 (w), 1562 (m), 1549 (w), 1506 (w), 1468 (w), 1443 (w), 1432 (w), 1412 (w), 1391 (w), 1379 (w), 1362 (w), 1314 (w), 1261 (w), 1199 (s), 1118 (m), 1073 (w), 1056 (w), 1019 cm^{-1} (w); UV/Vis (CHCl$_3$): λ_{max} (absorbance) = 251 (2.249), 310 (2.568), 409 nm (1.307 AU); MS (70 eV, EI): m/z (%): 802 (1) [$M - C_6H_5$]$^+$, 439 (21) [M/2]$^+$ or [M]$^{2+}$, 424 (27), 410 (14), 362 (100) [$M - C_6H_5$]$^{2+}$, 346 (20), 192 (29), 185 (19), 171 (17), 157 (14), 143 (18), 137 (11), 130 (17), 125 (20), 113 (17), 101 (11), 78 (44), 51 (22); HRMS calcd m/z for $C_{58}H_{68}B_2N_2O_4$: 879.5462 [M+H]$^+$; found: 879.5465; error: +0.34; elemental analysis calcd (%) for $C_{58}H_{68}B_2N_2O_4$ (878.54): C 79.27, H 7.80, N 3.19; found: C 79.45, H 7.94, N 4.08.

Boronate 4c: Prepared from 4-(salicylideneamino)phenethyl alcohol (0.50 g, 2.07 mmol) and 2,5-difluorophenylboronic acid (0.33 g, 2.07 mmol) in benzene (10 mL). After 1 h reflux, the green-yellow precipitate was filtered under vacuum. The product was insoluble in all common organic solvents. Crystals suitable for X-ray crystallography were prepared directly from the starting materials in benzene/hexane. Yield: 94 %; m.p. 254–255 °C; IR (KBr): $\tilde{\nu} = 3064$ (w), 2945 (w), 2924 (w), 2892 (w), 2862 (w), 1629 (s), 1605 (s), 1588 (m), 1558 (s), 1508 (m), 1484 (m), 1461 (m), 1405 (m), 1383 (m), 1320 (m), 1232 (m), 1203 (m), 1172 (m), 1154 (m), 1129 (m), 1109 (s), 1090 (m), 1054 (m), 1028 cm^{-1} (m); MS (70 eV, EI): m/z (%): 726 (1) $[M]^+$, 613 (83) $[M - C_6H_3F_2]^+$, 583 (15), 420 (7), 363 (30) $[M/2]^+$ or $[M]^{2+}$, 346 (18), 334 (100), 270 (9), 250 (50), 239 (33), 228 (28), 210 (44), 165 (6), 152 (6), 134 (26), 114 (31), 90 (21), 77 (15), 63 (12), 51 (12), 44 (17), 31 (22); elemental analysis calcd (%) for $C_{42}H_{32}B_2F_4N_2O_4$ (726.35): C 69.45, H 4.44; found: C 69.68, H 4.51.

Boronate 4d: Prepared from 4-(salicylideneamino)phenethyl alcohol (0.50 g, 2.07 mmol) and 3-nitrophenylboronic acid (0.35 g, 2.07 mmol) in benzene (10 mL). After 1 h reflux, the yellow precipitate was filtered under vacuum. The product was insoluble in all common organic solvents. Yield: 74%; m.p. 246–247 °C; IR (KBr): $\tilde{\nu} = 3072$ (w), 2925 (w), 1626 (s), 1588 (m), 1557 (m), 1505 (s), 1491 (m), 1478 (m), 1458 (m), 1403 (m), 1381 (m), 1309 (m), 1257 (m), 1230 (m), 1165 (m), 1132 (m), 1089 (m), 1035 (m), 1017 cm^{-1} (m); MS (70 eV, EI): m/z (%): 622 (30) $[M - C_6H_4NO_2]^+$, 501 (11), 372 (29) $[M/2]^+$ or $[M]^{2+}$, 343 (100), 297 (15), 239 (39), 210 (87), 191 (21), 106 (15), 91 (18), 78 (22), 51 (11); elemental analysis calcd (%) for $C_{42}H_{34}B_2N_4O_8$ (744.34): C 67.77, H 4.60, N 7.53; found: C 68.01, H 4.86, N 7.14.

X-ray crystallography: X-ray diffraction studies of single crystals of compound **1d** were conducted with an Enraf Nonius CAD4 diffractometer ($\lambda_{MoK\alpha} = 0.71069$ Å, monochromator: graphite, $T = 293$ K, $\omega - 2\theta$ scan). Cell parameters were determined by least-squares refinement on diffractometer angles for 24 automatically centered reflections. Absorption correction was not necessary; corrections were made for Lorentz and polarization effects. For data collection of compounds **3a** and **4c**, a Bruker Smart6000 diffractometer was used. After optical alignment the cell parameters were determined with reflections collected on four sets of 20 frames each (program SMART[13]). Data collection was performed in the hemisphere mode. Reflections of a total of 1321 frames were used for data reduction (program SAINT-NT[14]). Data were measured by rotating ψ successively by 0.3° with two different χ settings. Solution and refinement for compounds **1d** and **4c**: direct methods (SHELXS-86[15]) for structure solution and the CRYSTALS (version 9, 1994) software package[16–18] for refinement and data output. Solution and refinement for compound **3a**: structure solution, refinement and data output with the SHELXTL-NT program package.[19] Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were positioned geometrically and one overall isotropic thermal parameter was refined. The riding model was used in the case of **3a**. The benzene molecules in the crystal lattice of **4c** are slightly disordered, so that the C–C bond lengths and C-C-C bond angles were restrained. The X-ray data of compound **1d** were of only poor quality and the reflection/parameter ratio is somewhat lower than 5. However, our interest in this structure has been mainly focused on the confirmation of the molecular structure and the conformation of the molecule, but not in the discussion of particular bond lengths or bond angles. The X-ray data of compounds **3a** and **4c** is better; however, the reflection/parameter ratio is also relatively low (5.4 and 6.0, respectively). The most important crystallographic data are given in Table 1. In the case of compounds **3a** and **4c**, the molecules are located on special positions (inversion center) in the crystal lattice.

Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-167723 (**1d**), CCDC-167724 (**3a**), and CCDC-167725 (**4e**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge, CB21EZ, UK (fax: (+44) 1223-336-033, e-mail: deposit@ccdc.cam.ac.uk).

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