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3-Aminophenylboronic acid as building block for the construction of calix- and cage-shaped boron complexes

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ABSTRACT

The reactivity of 3-aminophenylboronic acid toward 3,5-disubstituted salicylaldehyde derivatives (R = *t*Bu, MeO, I, Br, NO_2) was analyzed with the aim to synthesize macrocyclic boron compounds having a calix-like structure. The three-component condensation was carried out using different aliphatic alcohols (ROH, R = Me, Et, *n*Pr, *n*Bu, *n*Pn, *n*Hex) in order to replace the free B–OH groups by B–OR moieties and their effect on the structural and physicochemical properties of the resulting compounds was analyzed. When the reaction was carried out under reflux conditions, trimeric calix-like compounds are formed for the 3,5-*t*Butyl salicylaldehyde derivatives. The absence of alcohol molecules during the reaction lead to the condensation of two calixarenes through two of the three B(OH) groups to form two B-O-B moieties, giving place to the formation of a hexanuclear cage. Using the salicylaldehyde derivatives having I, Br and NO_2 groups, the Schiff bases resulting from the condensation reaction of the aldehyde and the boronic acid were isolated providing thus evidence for the previously proposed reaction sequence for the formation of the calix-shaped compounds.

1. Introduction

Over the past two decades the interest in the preparation of macrocycles containing boron atoms has increased considerably [1]. This can be attributed to the – importance of macrocyclic compounds in supramolecular chemistry as molecular receptors [2]. A large variety of synthetic techniques for the construction of boron macrocycles compounds have been reported, involving frequently a direct one-pot synthesis sequence [3]. The ease of boron macrocyclic synthesis is due to the versatility of boron atoms to react with donor atoms (e.g. N and O), thus favoring self-assembly processes; this method has been applied for the construction of molecules with large cavities that might have applications in several fields of chemistry and materials science [4]. Usually, oligomeric compounds containing boron atoms are built through donor–acceptor intermolecular interactions. So far, dimeric, trimeric, tetrameric and pentameric species have been described [5]. Furthermore boronic acids have been used to construct molecular boxes [6] and cages [7] by coupling with transition metals. Recently, a synthetic strategy for the construction of boron-based dendrimers has been described employing a multi-component assembly reaction [8].

On the other hand, the B(OH) groups present in boronic acids can form hydrogen bonds and thus give rise to strong intermolecular interactions [9]. It is well known that hydrogen-bonding interactions permit the control of molecular recognition, and naturally, self-assembly processes from molecular components to superstructures in a well organized manner [10]. For that reason, the boronic acids are considered important building blocks for molecular crystal engineering [11].

Previously, we have used a the three-component reaction strategy to create trimeric calixarenes and hemicarcerands *via* condensation reactions of 3-aminophenylboronic acid with salicylaldehyde derivatives using methanol as solvent [12]. UV–Vis, ^{1}H NMR and X-ray crystallographic studies have shown that these compounds have cone conformations and are capable to include small organic guest molecules in their interior [13].

Continuing with the study of this type of macrocycles, we describe herein the reaction of 3,5-di-*t*butyl salicylaldehyde with 3-aminophenylboronic acid using different alcohols as boronate ester forming reagents, in order to establish the influence that groups of variable size attached to the boron atoms have on the macrocyclic compounds formation (**1b**–**1f**). This study allowed us also to analyze their effect on the physicochemical and structural characteristics such as solubility and conformation. Furthermore, salicylaldehyde derivatives containing MeO, I, Br and NO_2 substituents were reacted with 3-aminophenylboronic acid in order to analyze their effect on the calix-shape structure formation.

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2. Results and discussion

Compounds **1b–1f** were synthesized through three-component condensation reactions as described previously for compound **1a** (Scheme 1) [12a]. 3,5-Di-*t*butylsalicylaldehyde was dissolved in acetonitrile whereupon 3-aminophenylbornic acid was added. After 10 min 2 mL of the corresponding alcohol were added under stirring in order to replace the OH groups attached to the boron atoms. The reaction mixtures were stirred for 1 h under reflux to give yellow solids. Recrystallization in a solvent mixture of $MeOH/CH_2Cl_2$, (1:3 ratio) lead to the formation of yellow powders which were recovered by filtration. In the case of compound **1c**, the yellow crystals formed during the recrystallization process were suitable for X-ray diffraction analysis. Despite of the presence of different boron ester functions (Me, Et, *n*Pr, *n*Bu, *n*Pn, *n*Hex), the yields were almost constant (41–56%). Nonetheless, some interesting changes are observed when comparing the different compounds, for instance, the melting point decreases as the chain size of the B–OR functions increases (298, 297, 247, 229, 213 and 190 °C for **1a**–**1f**, respectively). This observation can be explained taking into account that in the solid state large chains separate the macrocyclic molecules more than small ones, diminishing the intermolecular forces and thus the melting point. Additionally, the solubility of compounds **1b**–**1f** in common organic solvents was higher when compared to compound **1a**. This behavior is reasonable considering that large aliphatic chains allow for a better dispersion of the molecules in the solvent.

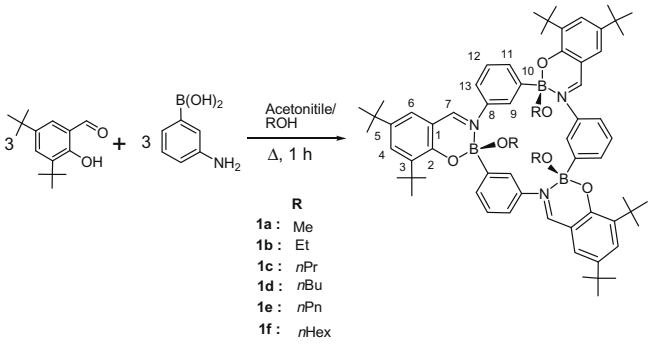
The IR data provide the first evidence for the formation of compounds **1b**–**1f**. The vibration of the C=N stretching band occurs at 1624–1625 cm^{-1}, as observed for compound **1a** and other related compounds [12,13]. Additional evidence was obtained from mass spectrometry using the FAB^+ technique. In all cases, peaks for the molecular and the $[M-OR]^+$ ion, which result from the loss of an alcoxy group, were observed.

The NMR analysis illustrates some interesting observations. In all cases, as a result of their C_3 molecular symmetry, the NMR spectra showed signals for only one third part of the structure, suggesting that the molecules have double *cone* conformation. The number of signals would be enhanced for the case that another conformation was present, according to the loss of the C_3 symmetry. In the ^1H NMR spectrum a single signal was observed at $\delta = 8.0$ ppm, corresponding to the imine hydrogen. The signals for the aromatic moieties appeared in the region of $\delta = 6.93–7.63$ ppm without significant differences between the different compounds. It is important to remark that the hydrogen atoms of the $-CH_2OB-$ group gave diasterotopic signals due the presence of chiral boron atoms in all compounds. This behavior can be enhanced by existence of hydrogen bonding interactions as observed in the solid state between this methylene group and the endocyclic oxygen atom (Fig. S1). The ^{13}C NMR spectra showed that the signals corresponding to imine carbon atoms are shifted downfield, appearing around $\delta = 161$ ppm, in accordance with the chemical shifts observed for related compounds [12,13]. ^{11}B NMR spectroscopy provided evidence for the tetrahedral environment of the boron atoms. In all cases, the chemical shifts are observed as broad signals in the region between $\delta = 2.5$ and 4.2 ppm, which are in the expected region for tetracoordinate boronates [12,13].

For compound **1c** suitable crystals for X-ray diffraction were obtained during the recrystallization process. The crystals diffracted very poorly, as a result of the relatively large quantity of atoms and the fact that the heaviest atom in the molecule is oxygen. As a consequence, the R values are somewhat elevated. Nonetheless, the atomic positions of the non-hydrogen atoms and the overall molecules conformation were clearly defined. The molecular structure is shown in Fig. 1, and the most relevant crystallographic data are described in Table 1. The molecule has double-cone conformation which has been observed for analogous compounds [12a,13]. The –OPr groups attached to the boron atoms in **1c** are oriented to the outer sphere, leaving a hydrophobic interior environment. It is interesting to notice that in the crystal lattice par of a *t*Butyl group of a neighboring molecules is included part inside the cavity (Fig. S2), leading in this way to the formation of supramolecular dimers. It is important to remark that for compound **1a** the inclusion of different solvent molecules has been observed, instead of the self-assembly of two calix-shape molecules. Therefore, in the case of **1c**, as a consequence of the self-assembly process of two trimeric units, the exclusion of solvent molecules from its interior is not surprising. The ^1H NMR analysis recorded at different concentration of **1c** did not show significant changes, indicating that the dimerization process is just a packing effect in the solid state.

On the other hand, when the condensation reaction was realized in the absence of alcohol solvent molecules and under reflux, two calix-shaped molecules were connected to a spherical hexameric boron cage by condensation of four B(OH) groups. It is well known that B–OH groups can condense to give B–O–B moieties [14]. Thus, the reaction of 4-methoxysalicylaldehyde with 3-aminophenylboronic acid using a solvent mixture of DMF/CH_2Cl_2 (1:1 ratio) lead to the formation of cage **2** (Scheme 2). After three days, yellow crystals had formed, which were suitable for X-ray diffraction analysis. The FAB^+ mass spectrum showed a peak at $m/z = 1481$ corresponding to the molecular ion of the proposed hexanuclear boron structure **2**, indicating the condensation of four B–OH moieties giving two –B–O–B– bridges giving the double calix-like structure.

The IR spectrum shows only one broad band at 1621 cm^{-1} corresponding to the stretching band of the C=N group. The ^1H NMR analysis was done using DMSO-d_6 as solvent and it was necessary to heat the NMR tube containing the solution up to 45 °C in order to increase the solubility of **2**. The ^1H NMR spectrum showed only a single set of signals indicating that the compound has symmetry



Scheme 1. Three-component condensation reaction for the formation of calix-shaped boron compounds **1a**–**1f**.

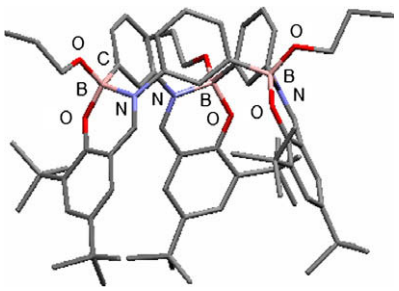
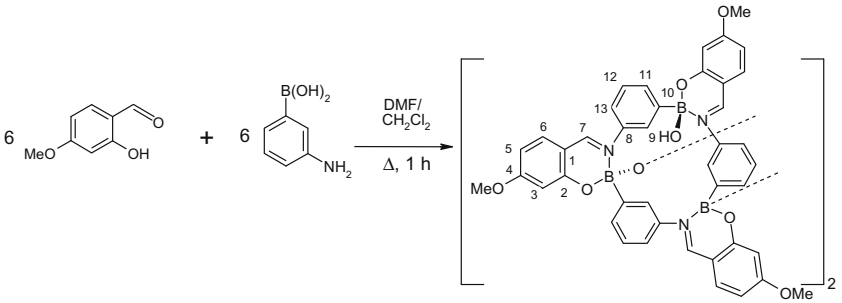


Fig. 1. Lateral view of the molecular structure of compound **1c**. Hydrogen atoms are omitted for clarity.

Table 1
Crystallographic data for compounds **1c**, **2** and **3a**.

Identification code	**1c**	**2**	**3a**
Empirical formula	$C_{149}H_{203}B_6N_7O_{15}$	$C_{49}H_{47}B_3N_{5.5}O_{10.5}$	$C_{17}H_{14}B_1I_2N_3O_3$
Formula weight	2397.04	913.35	572.92
Crystal size (mm^3)	$0.36 \times 0.32 \times 0.28$	$0.40 \times 0.26 \times 0.20$	$0.40 \times 0.28 \times 0.20$
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
Unit cell dimensions			
a (Å)	15.063(4)	13.262(3)	4.2801(6)
b (Å)	19.358(5)	13.882(3)	21.944(3)
c (Å)	27.532(7)	14.999(3)	20.376(3)
α (°)	86.444(5)	115.145(3)	90
β (°)	80.791(4)	95.986(3)	94.934(2)
γ (°)	68.649(4)	110.501(3)	90
Volume ($Å^3$)	7380(3)	2234.6(7)	1906.7(4)
Z	2	2	4
ρ_{calcd} (g/cm^3)	1.079	1.357	1.996
μ (mm^{-1})	0.068	0.095	3.320
Collected reflections	29969	19125	9026
Independent reflections [$R_{(int)}$]	19472 (0.0725)	6614 (0.0636)	3275(0.0542)
Parameters	1639	624	291
$R_1[I > 2\sigma(I)]$	0.1209	0.0906	0.048
wR_2 (all data)	0.3839	0.2424	0.1012
GOF	1.068	1.078	1.076



2

Scheme 2. Formation of a cage-shape compound.

(similar to that observed for compounds **1a–1f**). This might indicate that the hexameric compound was hydrolyzed to give a trimeric compound containing OH groups attached to the boron atoms. The ^1H NMR spectrum showed a single signal at $\delta = 8.8$ ppm corresponding to the proton of the iminic group. In addition, a broad signal shifted to low fields ($\delta = 10$ ppm) was assigned to the B–OH groups. In spite of the presence of two boron atoms (in the hexameric compound) with different chemical environments in the molecule, the ^{11}B NMR spectrum showed only one broad signal at $\delta = 2.7$ ppm indicating a tetrahedral environment for the boron atoms. The poor solubility of compound **2** in common organic solvents precluded the ^{13}C NMR analysis.

The X-ray crystallographic study allowed for a detailed analysis of the cage-like boronate (Fig. 2). The crystal quality was low, but the connection and overall geometry could be clearly established. The molecule possesses a C_i symmetry in the solid state, having a bis-double *cone* conformation. As a result of the intermolecular condensation of four B–OH moieties, two BOB moieties act as bridges connecting two calix-like units. Two B–OH groups remain intact and are located at the outer sphere of the molecule. As described above, there are three boron atoms in each calix-like moiety (six in total), of which the boron atoms involved in the BOB bridges have RR or SS configuration while the boron atoms of the B–OH fragment have the opposite configuration (S or R). Whereas the BOB links are located in the interior of the spherical cavity, the B–OH groups are located at the periphery of the molecule. In contrast, in a double calix-shaped compound was reported previously

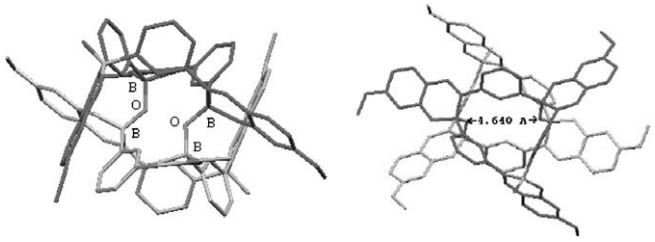
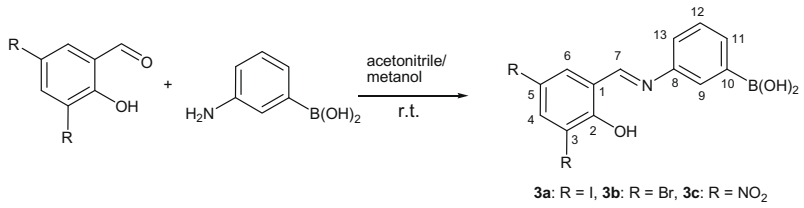


Fig. 2. Molecular structure of compound **2** (side view (left) and top view (right)).

by us, the six boron atoms have the same configuration giving a hemicarcerand structure. In the case of the related compounds **1a–1f**, all three boron atoms present in the molecule have the same configuration. The bridged B–O–B bond angles (127.45°) and B–O bond distances (1.410/1.412 Å) in compound **2** are very similar to those found in related systems [14].

If the condensation reactions between 3-aminophenylboronic acid and salicylaldehyde derivatives are carried out at room temperature, it is possible to isolate the intermediate Schiff bases, giving evidence that the first step in the reaction mechanism is the imine moiety formation as suggested before [3c]. Three Schiff bases were isolated in the course of the present contribution. The combination of the 3,5-disubstituted salicylaldehyde derivatives (R = I **3a**, R = Br **3b** and R = NO_2 **3c**) with 3-aminophenylboronic acid in a solvent mixture of acetonitrile and methanol at room temperature, lead to the formation of **3a–3c** in form of yellow



Scheme 3. Formation of the Schiff base compounds **3a**–**3c**.

solids (Scheme 3). In the mass spectra for **3a**–**3c**, peaks were observed that correspond to the $[M+H]^+$ ions. The IR spectra showed bands for the C=N stretching at 1617, 1622 and 1622 cm^{-1}, for **3a**, **3b** and **3c**, respectively, evidencing the imine formation. Interestingly, neither of the two boronate-ester reactions took place under these conditions, thus allowing the isolation of the macrocycle precursor. It should be noticed that the precursor of the trimeric compounds can be isolated only, if electron-withdrawing substituents are present in the 3,5-positions of the salicylaldehyde. This is reasonable considering that these groups have negative inductive effects and reduce the donor character of the nitrogen and oxygen atoms within the salicylaldehyde moiety thus reducing its ability to coordinate to the boron atom. This statement is supported by the fact that compounds **3b** and **3c** could not be transformed to the corresponding macrocyclic derivatives when using the same reaction conditions as for compounds **1a**–**1f**, even if the reaction times were increased up to 24 h. The macrocyclic compound derived from compound **3a** has been reported previously [13]. A plausible explanation for its formation is that the iodine atoms provide less negative inductive effects on the nitrogen atom. In contrast, the corresponding 3,5-di-*t*butylsalicylaldehyde Schiff base derivative (analogous to **3a–c**) could not be isolated under these reaction conditions.

The ^1H NMR spectra gave additional evidence for the Schiff base formation. A single signal was observed at $\delta = 8.94$, 8.98 and 9.07 ppm for **3a**–**c**, respectively. In agreement with the observation made above, the chemical shift increases according to the electron-withdrawing effect of the substituent. The signals are shifted to lower fields ($\Delta\delta \sim 0.9$ ppm) when compared to those observed in compounds **1a**–**1e**. Nonetheless, the ^{13}C NMR chemical shifts observed for the C=N groups ($\delta = 161.2$, 162.0 and 161.5 for **3a**–**c**, respectively) are very similar to those of compounds **1a**–**1e** and no significant changes are observed. The tri-coordinate character of the boron atoms was evidenced by ^{11}B NMR spectroscopy, wherein the signals are observed at $\delta = 27$, 28 and 30 ppm for **3a**–**c**, respectively.

Suitable crystals for X-ray diffraction analysis were grown for compound **3a** from a mixture of methanol:pyrazine (1:1 ratio), showing that in the solid state compound **3a** cocrystallized with a pyrazine molecule. As shown in Fig. 3, the molecular structure of compound **3a** is almost planar. The B–O bond distances are 1.340(8) and 1.373(11) Å, respectively, and are shorter in comparison to those observed for the calix-like complexes, which are in the range of 1.412(10) to 1.500(7) Å [12]. The difference can be attributed to the higher B–O retrodonation character in the free boronic acid group. Also, since there is no N–B coordination bond, the C=N bond distance is shorter (1.273(9) Å) when compared to the corresponding bond in the calix-like compounds (~1.305(9) Å). The OH group of the phenolic part shows an intramolecular hydrogen bonding interaction with the imine moiety (O–(H)···N, 2.555(6) Å, 154.5°): It is important to remark that the hydrogen atom remains attached to the oxygen atom (O–H, 0.960(8) Å), since it has been reported that in aromatic imines without the $B(OH)_2$ group [15], the hydrogen atom is located at the nitrogen atom (dist. N–H ~ 0.97 Å), giving place to a zwitterionic specie. This is again in agreement with the observation that the electron-donor character of the imine nitrogen atom is reduced. Hydrogen bonding interactions are also found for the B–OH groups, thus giving a dimeric assembly, in which two boronic acids are linked through two BO···O(H)–B hydrogen bonds, forming an eight member ring (O(2)–H···O(3), 2.736 Å, 163.32°). The two OH groups of each boronic acid moiety are in a *syn-anti* disposition (Fig. 3). In the crystal lattice, the molecular dimmers are organized in columns, with a π–π distance between molecular the planes of 3.556 Å.

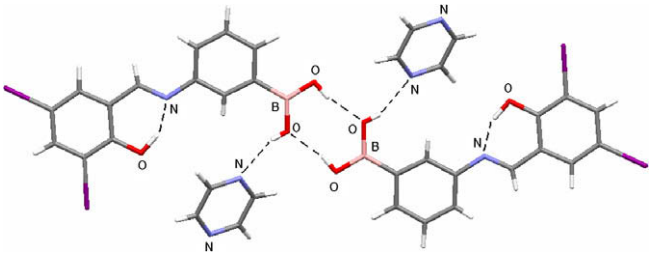


Fig. 3. Molecular structure of compound **3a**. The picture shows hydrogen bonding interactions between two molecules of **3a** and two pyrazine molecules giving a dimeric supramolecular arrangement. Lateral view of molecular structure of compound **1c**. Hydrogen atoms are omitted for clarity.

3. Conclusions

For the formation of calix-shaped compounds using 3-aminophenylboronic acid and salicylaldehyde derivatives, different reaction conditions have been examined in order to investigate the factors that influence the macrocyclization process. It was found that the reaction of 3,5-di-*t*butyl-salicylaldehyde with 3-aminophenyl boronic acid using different alcohols leads to the formation of calix-shape structures. Therefore the presence of large alkyl groups attached to the boron atoms does not have a significant effect over the macrocyclization process aside from increasing the solubility of the system. Additionally, calix compound **1c** gave rise to a self complementary supramolecular structure in the solid state consisting in the formation of a dimeric assembly. If solvents different from alcohols are used during the assembly process, the B–OH groups condense to B–O–B moieties and, therefore, dimeric hexanuclear spherical structures are obtained. Interestingly, for the condensation reaction between two boron-calixarenes a partial inversion of the boron configuration is required which evidences the reversibility of the boronate condensation reactions that is indispensable for the assembly process. At room temperature, the self assembly process can be stopped after the first step (imine formation), even in the presence of alcohol solvent molecules.

4. Experimental

4.1. Materials

All reagents and solvents were acquired from commercial suppliers and used without further purification.

4.2. Instrumentation

^{1}H, ^{13}C and ^{11}B NMR spectra were recorded at room temperature using a Varian Gemini 200 spectrophotometer. As standard references were used TMS (internal, ^{1}H, $\delta = 0.00$ ppm, ^{13}C, $\delta = 0.0$ ppm) and $BF_3 \cdot OEt_2$ (external, ^{11}B, $\delta = 0.0$ ppm). 2D COSY and HECTOR experiments have been carried out for the unambiguous assignment of the ^{1}H and ^{13}C NMR spectra. Infrared spectra have been recorded on a Bruker Vector 22 FT-IR spectrophotometer. Mass spectra were obtained with a Jeol JMS 700 equipment. Melting points were determined with a Büchi B-540 digital apparatus.

4.3. X-ray crystal-structure determination

X-ray diffraction studies were performed on a Bruker-APEX diffractometer with a CCD area detector, using Mo Kα-radiation, ($\lambda = 0.71073$ Å) and a graphite monochromator. Frames were collected at $T = 100$ K for compounds **1c** and **2** and at 293 K for **3a**, by ω/ϕ-rotation ($\Delta/\omega = 0.3°$) at 10 s per frame. The measured intensities were reduced to F^2 [16]. Structure solution, refinement and data output were carried out with the SHELXTL-NT program package [17]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in geometrically calculated positions using a riding model. For compounds **1c** and **2** somewhat elevated R and wR_2 values are observed owing to several factors: the disorder of solvent molecules, the relatively large quantity of atoms in the unit cell and the fact that the heaviest atom is oxygen.

4.4. General method for the preparation of boron complexes *1b–1f*

Compounds **1b–1f** were synthesized from the equimolecular reaction of 3,5-di-*t*butylsalicylaldehyde with 3-aminophenylboronic acid monohydrate using 20 mL of acetonitrile as solvent and 2 mL of the corresponding alcohol. The reaction mixtures were stirred for 1 h under reflux. After that, part of the solvent and the water formed through the triple condensation reaction were removed using a Dean-Star k trap. The final products were recovered by filtration and purified by recrystallization in a solvent mixture $MeOH/CH_2Cl_2$ (1:3 ratio).

4.4.1. Compound *1b*

Compound **1b** was prepared from 0.20 g (1.29 mmol) of 3-aminophenylboronic acid monohydrate and 0.30 g (1.29 mmol) of 3,5-di-*t*butyl salicylaldehyde in acetonitrile using 2 mL of ethanol. The product was obtained as a yellow powder. Yield: 0.26 g (55%); m.p. = 297–300 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.10 (3H, s, H7), 7.62 (3H, d, $J = 2.0$, H4), 7.34 (3H, d, $J = 7.7$, H11), 7.24 (3H, d, $J = 7.7$, H13), 6.99 (3H, t, $J = 7.7$, H12), 6.96 (3H, d, $J = 2.0$, H6), 6.48 (3H, s, H9), 3.45 (3H, dt, $J = 2.3$, 9.4, H14a), 3.33 (3H, dt, $J = 2.3$, 9.4, H14b), 1.42 (27H, s, Me_3-C5), 1.27 (27H, s, Me_3-C3), 1.26 (9H, t, $J = 7.1$ H15) ppm. ^{13}C NMR (50 MHz $CDCl_3$) δ: 161.3 (C-7), 158.3 (C-2), 145.5 (C-8), 140.5 (C-3), 138.3(C-5), 132.7 (C-4), 131.9 (C-11), 127.4 (C-9), 126.5(C-12), 125.6 (C-6), 122.7(C-13), 115.6(C-1), 57.3(C-14), 35.0 (Me_3-*C*-C5), 34.1 (Me_3-*C*-C3), 31.3 (Me_3-C5), 29.3 (Me_3-C3), 17.9 (C-15) ppm. ^{11}B NMR (64 MHz, $CDCl_3$) δ: 2.7 ppm ($h_{1/2} = 1560$ Hz). IR (KBr) $\nu(cm^{-1}) = 3433$, 2961, 1625 (C=N), 1560, 1469, 1207, 1117, 972, 906. FAB-MS *m/z* (%): 1089 (M^+, 25), 1060 ([M−Et]$^+$, 15), 1044 ([M−OEt]$^+$, 70), 1028(15), 1016(35), 1001 (15), 988(15).

4.4.2. Compound *1c*

Compound **1c** was prepared from 0.20 g (1.29 mmol) of 3-aminophenylboronic acid monohydrate and 0.30 g (1.29 mmol) of 3,5-di-*t*butyl salicylaldehyde in acetonitrile using 2 mL of *n*-propanol. The product was obtained as a yellow powder. Yield: 0.24 g (49%); m.p. = 247–250 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.12 (3H, s, H7), 7.63 (3H, d, $J = 7.5$, H11), 7.59 (3H, d, $J = 2.3$, H4), 7.35 (3H, d, $J = 7.55$, H13), 6.98 (3H, t, $J = 7.5$, H12), 6.96 (3H, d, $J = 2.3$, H6), 6.51 (3H, s, H9), 3.35 (3H, dt, $J = 4.8$, 9.4, H14a), 3.22 (3H, dt, $J = 4.8$, 9.4, H14b), 1.65 (6H, sex, $J = 4.8$, H15), 1.45(27H, s, Me_3-C5), 1.30(27H, s, Me_3-C3), 0.94(9H, t, $J = 4.8$, H16) ppm. ^{13}C NMR (100 MHz $CDCl_3$) δ: 161.4 (C-7), 158.6 (C-2), 143.7 (C-8), 140.6(C-3), 138.4 (C-5), 132.9 (C-4), 132.7 (C-11), 127.5 (C-9), 126.6 (C-12), 125.8 (C-6), 122.8 (C-13), 115.8 (C-1), 63.5(C-14), 35.4 (Me_3-*C*-C5), 34.3 (Me_3-*C*-C3), 31.4 (Me_3-C5), 29.4 (Me_3-C3), 25.6.8 (C-15), 11.3 (C-16) ppm. ^{11}B NMR (64 MHz, $CDCl_3$) δ: 3.9 ppm ($h_{1/2} = 608$ Hz). IR (KBr) $\nu(cm^{-1}) = 3445$, 2959, 1624 (C=N), 1559, 1468, 1207, 1119. FAB-MS *m/z* (%): 1132 ([M+H]$^+$, 45), 1072 ([M−OPr]$^+$, 100), 1031 (50), 656 (20), 756 (25), 404 (60), 378 (100), 362 (85), 320 (65).

4.4.3. Compound *1d*

Compound **1d** was prepared from 0.20 g (1.29 mmol) of 3-aminophenylboronic acid monohydrate and 0.30 g (1.29 mmol) of 3,5-di-*t*butyl salicylaldehyde in acetonitrile using 2 mL of *n*-butanol. The product was obtained as a yellow powder. Yield: 0.26 g (52%); m.p. = 229–231 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.07 (3H, s, H7), 7.57 (3H, d, $J = 7.8$, H11), 7.55 (3H, d, $J = 2.2$, H4), 7.29–7.34 (3H, *m*, H13), 6.94 (3H, t, $J = 7.8$, H12), 6.95 (3H, d, $J = 2.2$, H6), 6.46 (3H, s, H9), 3.40–3.20 (3H, m, H14), 1.60–1.30 (12H, m, H15, H16), 1.42 (27H, s, 1.42 (27H, s, Me_3-C5), 1.27 (27H, s, Me_3-C3), 0.93 (9H, t, $J = 7.3$, H17) ppm. ^{13}C NMR (100 MHz $CDCl_3$) δ: 160.7 (C-7), 158.1 (C-2), 143.3 (C-8), 140.1 (C-3), 137.9 (C-5), 132.5 (C-4), 132.3 (C-11), 127.1 (C-9), 126.1 (C-12), 125.4 (C-6), 122.4 (C-13), 115.4 (C-1), 62.8 (C-14), 61.6 (C-15), 35.3 (Me_3-*C*-C5), 34.2 (Me_3-*C*-C3), 31.4 (Me_3-C5), 29.4 (Me_3-C3), 19.8 (C-16), 14.0 (C-17) ppm. ^{11}B NMR (64 MHz, $CDCl_3$) δ: 3.3 ppm ($h_{1/2} = 896$ Hz). IR (KBr) $\nu(cm^{-1}) = 2959$, 1624 (C=N), 1561, 1468, 1207, 1181, 1112, 971, 900, 705. FAB-MS *m/z* (%):1174 ([M + H]$^+$, 20), 1101 ([M−OBu]$^+$, 65), 1045 (40), 972 (20), 653 (25), 468 (100), 362 (95), 346 (95), 219 (80).

4.4.4. Compound *1e*

Compound **1e** was prepared from 0.20 g (1.29 mmol) of 3-aminophenylboronic acid monohydrate and 0.30 g (1.29 mmol) of 3,5-di-*t*butyl salicylaldehyde in acetonitrile using 2 mL of *n*-pentanol. The product was obtained as a yellow powder. Yield: 0.24 g (46%); m.p. = 213–216 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.01(3H, s, H7), 7.61 (3H, d, $J = 7.2$, H11), 7.57 (3H, s, H4), 7.33 (3H, d, $J = 7.7$, H13), 6.96 (3H, t, $J = 7.4$, H12), 6.93 (3H, s, H6), 6.47 (3H, s, H9), 3.32 (3H, dt, $J = 2.5$, 9.4, H14a), 3.22 (3H, dt, $J = 2.5$, 9.4, H14b), 1.7–1.22 (18H, m, H15, H16,H17), 1.42 (27H, s, Me_3-C5), 1.26 (27H, s, Me_3-C3), 0.82 (9H, t, $J = 6.4$, H18) ppm. ^{13}C NMR (100 MHz $CDCl_3$) δ: 161.1 (C-7) 158.5 (C-2), 143.5 (C-8),140.3 (C-3), 138.2 (C-5) 132.7 (C-4), 132.5 (C-11), 127.3 (C-9), 126.4 (C-12), 125.6 (C-6), 122.7 (C-13), 115.6 (C-1), 61.8 (C-14), 35.2 (Me_3-*C*-C5), 34.1 (Me_3-*C*-C3), 31.3 (Me_3-C5), 29.3 (Me_3-C3), 28.8(C-16), 22.7 (C-17), 14.3 (C-18) ppm. ^{11}B NMR (64 MHz, $CDCl_3$) δ: 2.5 ppm ($h_{1/2} = 1733$ Hz). IR (KBr) $\nu(cm^{-1}) = 3380$, 2956, 1624 (C=N), 1558, 1468, 1362,1255, 1208, 1181, 1167, 972, 904, 773. FAB-MS *m/z* (%):1216(M+H]$^+$, 45), 1129 ([M−OPn]$^+$, 100), 1059 (50), 1042 ([M−2(OPn)]$^+$, 40), 956 ([M−3(OPn)]$^+$, 30), 812 (30), 724 (35), 561 (35), 361 (80), 346 (75).

4.4.5. Compound *1f*

Compound **1f** was prepared from 0.20 g (1.29 mmol) of 3-aminophenylboronic acid monohydrate and 0.30 g (1.29 mmol) of 3,5-di-*t*butyl salicylaldehyde in acetonitrile using 2 mL of *n*-hexanol. The product was obtained as a yellow powder. Yield: 0.22 g (41%); m.p. = 190–193 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.10 (3H, s, H7), 7.56 (3H, d, $J = 2.2$, H4), 7.55 (3H, d, $J = 7.2$, H11), 7.35 (3H,

d, J = 7.2, H13), 6.98 (3H, t, J = 7.2), 6.96 (3H, d, J = 2.2, H6), 6.48 (3H, d, J = 2.0, H9), 3.33 (3H, dt, J = 2.8, 9.4, H14a), 3.23 (3H, dt, J = 2.8, 9.6, H14b), 1.62–1.54 (24H, *m*, H15, H16, H17, H18), 1.43 (27H, s, Me_3-C5), 1.26 (27H, s, Me_3-C3), 0.84 (9H, t, J = 0.84, H19) ppm; ^{13}C NMR (100 MHz $CDCl_3$) δ: 160.9 (C-7), 158.3 (C-2), 146.3 (C-8), 140.3 (C-3), 138.2 (C-5), 133 (C-10), 132.7 (C-4), 132.5 (C-11), 127.3 (C-9), 126.4 (C-12), 125.6 (C-6), 122.7 (C-13), 115.6 (C-1), 62 (C-14), 35.5 (Me_3-*C*-C5), 34.4 (Me_3-*C*-C3), 32.6 (C-15), 32.2 (C17), 31.6 (Me_3-C5), 29.6 (Me_3-C3), 26.5 (C-16), 23.1 (C-18), 14.5 (C-19) ppm. ^{11}B NMR (64 MHz, $CDCl_3$) δ: 4.2 ppm ($h_{1/2}$ = 1603 Hz). IR (KBr) ν(cm^{-1}) = 2957, 2864, 1624 (C=N), 1559, 1466, 1443, 1254, 1206, 1181. FAB-MS *m/z* (%): 1257 (M^+, 20), 1156 ([M−Ohex]$^+$, 100), 1055 ([M−2(Ohex)]$^+$, 21), 954 ([M−3(Ohex)]$^+$, 15), 446 (35), 362 (100), 346 (90), 307 (65), 260 (50).

4.5. Synthesis of compound **2**

Compound **2** was synthesized from 0.20 g (1.29 mmol) of 3-aminophenylboronic acid monohydrate and 0.20 g (1.29 mmol) of 2-hydroxy-4-methoxybenzaldehyde using 20 ml of a solvent mixture of DMF/CH_2Cl_2 (1:1 ratio). The reaction mixture was stirred for 1 h under reflux. After three days, yellow crystals had formed which were suitable for X-ray diffraction. Yield: 0.14 g (42%); m.p. = >350 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 10.0 (2H, s, B-OH), 8.88 (6H, s, H-7), 8.23 (6H, d, J = 8.0 Hz, H-11), 7.95 (6H, s, H-9), 7.68 (6H, dt, J = 8.0, 2.8 Hz, H-13), 7.55 (6H, d, J = 8.4 Hz, H-6), 7.41 (6H, t, J = 8.0 Hz, H-12), 6.55 (6H, dd, J = 8.4, 2.4 Hz, H-5), 6.49 (6H, d, J = 2.4 Hz, H-3), 3.8 (18H, s, Ar-OMe). ^{11}B NMR (64 MHz, DMSO-d_6) δ: 2.7 ppm ($h_{1/2}$ = 3328 Hz). IR (KBr) ν(cm^{-1}) = 3450 (s), 1621 (C=N) (s), 1543 (m), 1498 (w), 1441 (w), 1375 (w), 1308 (w), 1258 (m), 1215 (m), 1169 (w), 1119 (w), 1023 (w), 983 (w), 895 (w), 843 (w), 796 (w), 704 (w), 521 (w). FAB-MS *m/z* (%): 1481 ([M−1]$^+$, 7), 1465 (18), 1255 (2.8), 1012 (5), 877 (3), 710 (3.2), 563 (4), 489 (12), 328 (28), 307 (100), 254 (12).

4.6. General method for the preparation of imines **3a–3c**

Compounds **3a–3c** were synthesized from the equimolecular reaction of the corresponding 3,5-disubstituted salicylaldehyde derivative (R = I, Br, NO_2) with 3-aminophenylboronic acid monohydrate using 20 mL of acetonitrile and 2 mL of methanol as solvents. The reaction mixtures were stirred for 1 h at room temperature. After 12 h, yellow powders had precipitated which were filtered and dried under high vacuum.

4.6.1. Compound **3a**

Compound **3a** was prepared from 0.31 g (2.01 mmol) of 3-aminophenylboronic acid monohydrate and 0.75 g (2.01 mmol) of 3,5-diiodosalicylaldehyde. An orange powder was obtained. Yield: 80% (0.78 g). m.p. = 285 °C. IR (KBr) ν(cm^{-1}) = 3434, 30453, 2923, 1617 (C=N), 1589, 1532, 1472, 1377, 1268, 1295, 732, 696. EI-MS *m/z* = 493. ^{1}H NMR (300 MHz, $CDCl_3$), δ 8.94 (1H, s, H-7), 8.14 (1H, d, J = 2.1 Hz, H-4), 8.02 (1H, d, J = 2.1 Hz, H-6), 7.92 (1H, s, H-9), 7.75 (1H, d, J = 6.5 Hz, H-11), 7.52 (1H, d, J = 6.5 Hz,H-13), 7.47 (1H, t, J = 6.5 Hz, H-12). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 161.2 (C-7), 160.4 (C-2), 148.1 (C-4), 144.2 (C-8), 140.8 (C-6), 133.4 (C-11), 128.6 (C-12), 127.1 (C-9), 122.7 (C-13), 120.5 (C-1), 88.6 (C-5), 79.0 (C-3). ^{11}B NMR (96 MHz, $CDCl_3$) δ: 27.0 ($h_{1/2}$ = 660 Hz) ppm.

4.6.2. Compound **3b**

Compound **3b** was prepared from 0.31 g (2.01 mmol) of 3-aminophenylboronic acid monohydrate and 0.56 g (2.01 mmol) of 3,5-dibromosalicylaldehyde. A yellow powder was obtained. Yield: 65% (0.51 g), m.p. = 294 °C. IR (KBr) ν(cm^{-1}) = 3376, 3304, 3048, 2960, 1622 (C=N), 1606, 1512, 1470, 1282, 1268, 1226, 1216, 898, 764, 748, 742. EI-MS *m/z* = 397. ^{1}H NMR (300 MHz, $CDCl_3$), δ 8.98 (1H, s, H-7), 7.89 (1H, d, J = 2.3 Hz, H-4), 7.86 (1H, d, J = 2.3 Hz, H-6), 7.82 (1H, s, H-9), 7.75 (1H, d, J = 7.5 Hz, H-11), 7.52 (1H, d, J = 7.5 Hz, H-13), 7.46 (1H, t, J = 7.5 Hz, H-12). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 162.0 (C-7), 158.3 (C-2), 145.0 (C-8), 137.9 (C-6), 134.7 (C-4), 134.1 (C-11), 129.3 (C-12), 127.5 (C-13), 123.3 (C-9), 121.2 (C-1), 112.2 (C-5), 109.6 (C-3). ^{11}B NMR (96 MHz, $CDCl_3$) δ 28.0 ($h_{1/2}$ = 706 Hz) ppm.

4.6.3. Compound **3c**

Compound **3c** was prepared from 0.21 g (1.35 mmol) of 3-aminophenylboronic acid monohydrate and 0.29 g (1.35 mmol) of 3,5-dinitrosalicylaldehyde. A yellow powder was obtained. Yield: 74% (0.15 g), m.p. = 282 °C. IR (KBr) ν(cm^{-1}) = 3558, 3384, 2916, 1622 (C=N), 1560, 1426, 1368, 1332, 1316, 1236, 704; EI-MS *m/z* 331. ^{1}H NMR (300 MHz, $CDCl_3$), δ 9.07 (1H, s, H-7), 8.80 (1H, d, J = 2.0 Hz, H-6), 8.26 (1H, d, J = 2.0 Hz, H-4), 8.10 (1H, s, H-9), 7.90 (1H, d, J = 7.6 Hz, H-11), 7.64 (1H, d, J = 7.6 Hz, H-13), 7.61 (1H, t, J = 7.6 Hz, H-12). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 169.8 (C-2), 161.5 (C-7), 141.3 (C-5), 137.9 (C-8), 135.6 (C-3), 133.1 (C-11), 129.0 (C-4), 129.0 (C-6), 127.1 (C-12), 126.2 (C-9), 122.6 (C-13), 118.1 (C-1). ^{11}B NMR (96 MHz, $CDCl_3$) δ: 30.6 ($h_{1/2}$ = 1680 Hz) ppm.

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Appendix A. Supplementary material

CCDC 706335, 706336 and 706337 contain the supplementary crystallographic data for **1c**, **2** and **3a**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2009.02.025.

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