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Synthesis and characterization of boronates derived from non-symmetric amino-bis-phenols

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Abstract

The condensation of 2-[[(2-hydroxyphenyl)amino]methyl]-phenols (**1a**–**1e**) with different arylboronic acids led to 12 new monomeric boronates of the type 2-aryl-dibenzo[d,h]-6-aza-1,3-dioxa-2-boracyclononene (**2a**–**2l**). The boronates were characterized by ^{1}H-, ^{13}C-, ^{11}B- and 2D-NMR experiments, FT infrared, mass spectra and elemental analyses. The stereochemistry of the H–N → B–Ph fusion is always *cis*, as established through the NMR spectra, as well as the X-ray structures of four boronates (**2a**, **2e**, **2f** and **2l**). Hydrogen bonds between the amine proton and the oxygen ester of the five- membered ring are present in three X-ray structures (**2a**, **2e** and **2f**), while the supramolecular structure in the derivative possessing a primary amine (**2l**) is built up through the protons present in this moiety instead of the proton from the H–N → B–Ph fragment.
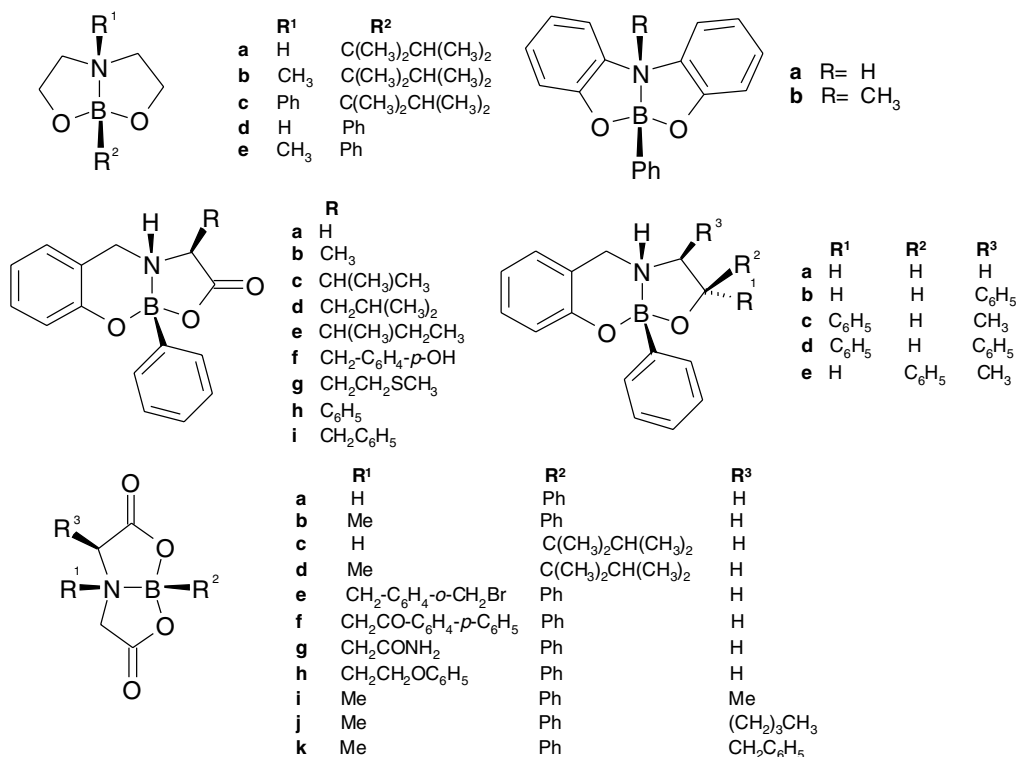© 2005 Elsevier B.V. All rights reserved.

1. Introduction

In previous studies, we described the synthesis of a series of mono-, di-, tri- and tetrameric boronates derived from NO$_2$ tridentate ligands such as *N*-alkyl-diethanolamines [1], *N*-methyl-*N*-(1-methyl-2-phenyl-2-hydroxyethyl)glycines [2], 2-substituted pyridines [3], *N*-(2-hydroxybenzyl)-α-aminoacids [4], *N*-alkyliminodiacetic acids [5], *N*-(2-hydroxyethyl)-*N*-alkyl-glycines [6], *N*-alkyl-2-2′-diphenol-amines [7], 2,6-pyridinedimethanol and 2-salicylideneami-noethanol [8–12], piperidine and piperazine alcohols [13], α-aminoacids [14,15], *N*-alkylaminodiacetic acids [16], ephedrine and pseudoephedrine derivatives [17], tridentate azomethine ligands [18], ethanolamine derivatives [19], aminodialcohols [20] as well as the self assembly of boro-nic-salicylidene Schiff bases [21] (Scheme 1). All of these ligands have one nitrogen and two oxygen donor atoms with strategic variations in the main skeleton that allowed evaluation of steric and electronic effects in the resulting chelate molecules. The studies showed that, in all cases, the boron atom is tetra-coordinated and forms a dative bond with the nitrogen atom; the characteristics of the dative bond as well as the rigidity of the tridentate ligands employed gave rise to monomeric molecules and, through a self-assembly procedure, to specific di-, tri- and tetrameric molecules. For this particular construction, the oxygen atoms build up mainly five- or six- membered rings as well as intermolecular boron-oxygen bonds to achieve the oligomeric-products [22]. As previously mentioned, the structure of the product is mainly determined by the nature of the ligand, however, in some cases it can be modulated by varying the reaction conditions.

The geometrical change between planar trigonal to tetrahedral boron atoms due to donor → acceptor coordination has been quantitatively evaluated by the TetraHedral

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	R^1	R^2
a	H	C(CH$_3$)$_2$CH(CH$_3$)$_2$
b	CH$_3$	C(CH$_3$)$_2$CH(CH$_3$)$_2$
c	Ph	C(CH$_3$)$_2$CH(CH$_3$)$_2$
d	H	Ph
e	CH$_3$	Ph

a	R= H
b	R= CH$_3$

	R
a	H
b	CH$_3$
c	CH(CH$_3$)CH$_3$
d	CH$_2$CH(CH$_3$)$_2$
e	CH(CH$_3$)CH$_2$CH$_3$
f	CH$_2$-C$_6$H$_4$-p-OH
g	CH$_2$CH$_2$SCH$_3$
h	C$_6$H$_5$
i	CH$_2$C$_6$H$_5$

	R^1	R^2	R^3
a	H	H	H
b	H	H	C$_6$H$_5$
c	C$_6$H$_5$	H	CH$_3$
d	C$_6$H$_5$	H	C$_6$H$_5$
e	H	C$_6$H$_5$	CH$_3$

|	R^1	R^2	R^3
a	H	Ph	H
b	Me	Ph	H
c	H	C(CH$_3$)$_2$CH(CH$_3$)$_2$	H
d	Me	C(CH$_3$)$_2$CH(CH$_3$)$_2$	H
e	CH$_2$-C$_6$H$_4$-o-CH$_2$Br	Ph	H
f	CH$_2$CO-C$_6$H$_4$-p-C$_6$H$_5$	Ph	H
g	CH$_2$CONH$_2$	Ph	H
h	CH$_2$CH$_2$OC$_6$H$_5$	Ph	H
i	Me	Ph	Me
j	Me	Ph	(CH$_2$)$_3$CH$_3$
k	Me	Ph	CH$_2$C$_6$H$_5$

Scheme 1. Monomeric boronates derived from tridentate ligands.

Character (THC$_{D \to A}$) [23]. As important structural evidence, it is worth mentioning that for boron compounds constructed from tridentate ligands, the N → B bonds are between 1.6 and 1.7 Å.

A literature search proved that the preferred stereochemistry at the transannular fused rings involving the N → B bonds is cis [1–7,24]. Further studies revealed that it is possible to carry out the stereoselective addition of acetone to the C=N bond in a complete series of [4.3.0] boron heterobicycles derived from salicylideniminophenols (Scheme 2). In these compounds, the polarization, and therefore the selective reactivity of this bond was evidenced by acetolysis of the imine group to produce the corresponding dioxaborocines with a cis fusion and the incoming group placed also on the same side, with full diastereoselec-

tivity [12]. The same behaviour was observed in the case of the boronates derived from N-(2-hydroxybenzyl)-α-amino-acids [4] (possessing a sp^2 carbon atom at the five membered fused ring) and 2-((2-hydroxyethylamino) methyl) phenols [25] (the five-membered fused ring has a sp^3 carbon atom) where the substituents are on the same side and only the exo disastereoisomer is formed.

Continuing our investigations, we describe herein the reactions of 2-[[(2-hydroxyphenyl)amino]methyl]-phenols, nonsymmetric amino-bis-phenols, with different arylboronic acids with the aim to determine the preferred arrangement of these new boronates. Additionally the fusion preference was investigated by changing the design of the tridentate ligands using compounds possessing two phenolic units linked through a methylene-secondary

	R^1	R^2	R^3
a	NO$_2$	H	H
b	CH$_3$	H	H
c	Cl	H	H
d	CH$_3$	H	CH$_3$
e	H	CH$_3$	H
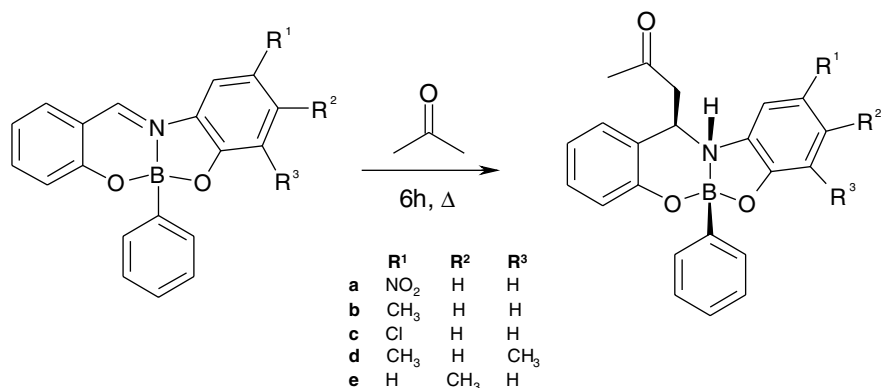
Scheme 2. Synthesis of 2-phenyl-aryl[d]benzo[h]-6-aza-1,3-dioxa-2-boracyclonon-6-enes by acetolysis reaction.

M = Fe(III), Mo(VI)

Ti (IV)
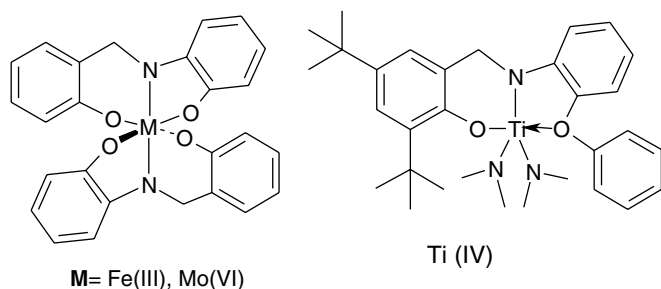
Scheme 3. Application of 2-[[(2-hydroxyphenyl)amino]methyl]-phenols as chelating agents for transition metals.

amine system. These new ligand prototypes are the 2-[[(2-hydroxyphenyl)amino]methyl]-phenols, which were synthesized by a method similar to that described in the literature [26]. Moreover, it has been described that the tridentate ligands synthesized herein have found application as chelating agents for some transition metals [27–31] and as plant growth regulators [32] (Scheme 3).

The tridentate ligands and the monomeric boronates were characterized by ^{1}H, ^{13}C, homo- and hetero-nuclear 2D-NMR experiments, FT-IR, mass spectra, and additionally for the boronates, the ^{11}B NMR spectra. Suitable monocrystals of four boronates were obtained.
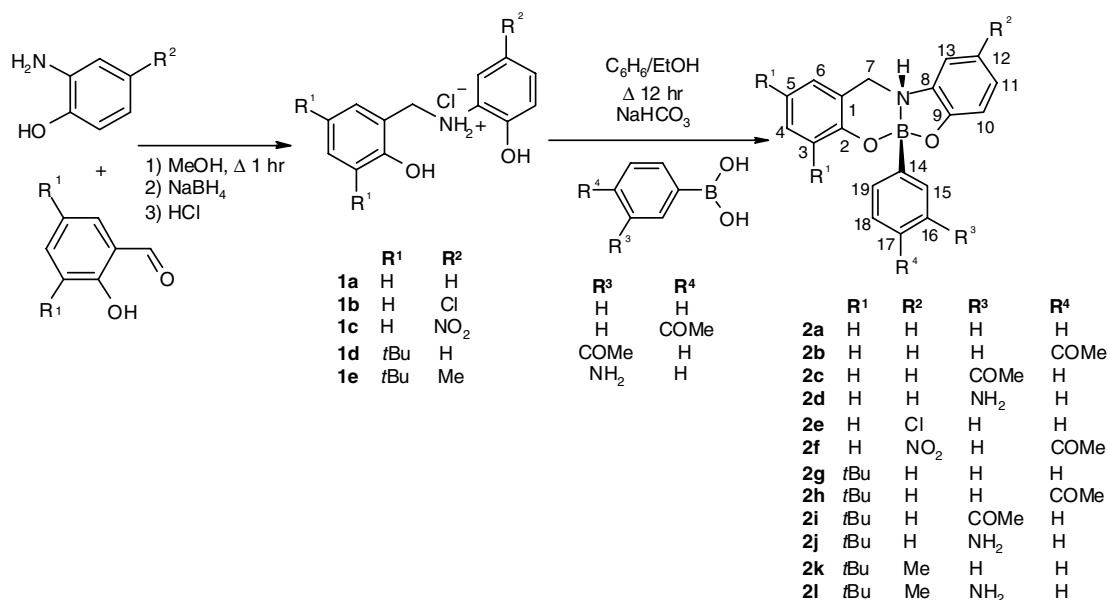
2. Results and discussion

The reaction between 2-[[(2-hydroxyphenyl)amino]methyl]phenols (**1a**–**1e**) and different aryl boronic acids led to 12 new monomeric boronates (**2a**–**2l**). The stereochemistry of the H–N → B–Ph fusion is always *cis*, as established from the NMR spectra, as well as the X-ray structures of four boronates. The results of this contribution are resumed as follows.

2.1. Synthesis of 2-[[(2-hydroxyphenyl)amino]methyl]-phenols

The synthetic route to prepare the 2-[[(2-hydroxyphenyl)amino]methyl]-phenols **1a**–**1e** involved the reaction of 2-aminophenols with an equimolecular ratio of salicylaldehyde or 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde under reflux of methanol during 6 h to give the corresponding Schiff bases. This was followed by in situ reduction of the imine fragment with sodium borohydride and acidulation with hydrochloric acid. The resulting tridentate ligands were obtained in yields ranging from 59% to 91% (Scheme 4).

2.2. NMR data of 2-[[(2-hydroxyphenyl)amino]methyl]-phenol hydrochlorides (1a–1e)

The ^{1}H NMR spectra shows a phenolic OH between 10.42 and 10.79 ppm, followed by the hydrogen atoms from the bridging nitrogen around 8.50 ppm. The coupling system of the salicylidene fragment for compounds **1a**–**1c** is of ABCD type. The **1d** and **1e** ligands show an AM system for the 3,5-di-*tert*-butyl fragment and the protons corresponding to the di-*tert*-butyl groups appear in 1.36 and 1.16 for the 3 and 5 positions, respectively. The protons at position 7 are observed between 4.36 and 4.43 ppm. The ^{13}C NMR spectra present the following trends, the resonance for C-2 shows chemical shifts between 152.4 and 156.9 ppm, for C-9 between 149.3 and 154.2 ppm, always appearing at high frequencies. The chemical shifts for C-7 are between 47.4 and 49.7 ppm. The chemical shifts for the di-*tert*-butyl groups appear between 30.4 and 32.1 for the methyl (C(CH$_3$)$_3$) group and appear between 34.5 and 35.7 ppm for the quaternary carbon (C(CH$_3$)$_3$)).

	R¹	R²
1a	H	H
1b	H	Cl
1c	H	NO₂
1d	*t*Bu	H
1e	*t*Bu	Me

R³	R⁴
H	H
H	COMe
COMe	H
NH₂	H

	R¹	R²	R³	R⁴
2a	H	H	H	H
2b	H	H	H	COMe
2c	H	H	COMe	H
2d	H	H	NH₂	H
2e	H	Cl	H	H
2f	H	NO₂	H	COMe
2g	*t*Bu	H	H	H
2h	*t*Bu	H	H	COMe
2i	*t*Bu	H	COMe	H
2j	*t*Bu	H	NH₂	H
2k	*t*Bu	Me	H	H
2l	*t*Bu	Me	NH₂	H

Scheme 4. Synthesis of 2-[[(2-hydroxyphenyl)-amino]-methyl]-phenols (**1a**–**1e**) and 6-aza-1,3-dioxa-2-bora-[d,h]-di-benzocylononenes (**2a**–**2l**).

2.3. IR and MS data of 2-[[(2-hydroxyphenyl)amino]-methyl]-phenol hydrochlorides (1a–1e)

The IR spectra of compounds 1a–1e show strong N–H and O–H stretching bands. The mass spectra show the ion peak corresponding to loss of hydrochloric acid from the M^+. Cleavage at the CH_2–NH bond, leads to the fragment corresponding to the hydroxytropylium ion in 1a–1c, while the base peak in 1d corresponds to the aminophenol fragment and 1e to the di-*tert*-butylsalicylidene ion.

2.4. Synthesis of 2-aryl-dibenzo[d,h]-6-aza-1,3-dioxa-2-boracyclononenes

The condensation of 2-[[(2-hydroxyphenyl)amino]-methyl]-phenol hydrochlorides (1a–1e) with phenylboronic acid, 3-aminophenylboronic acid, 3-acetylphenylboronic acid and 4-acetylphenylboronic acid in the presence of 1.5 molar equivalents of sodium bicarbonate were carried out at reflux in benzene–ethanol mixtures to give the corresponding boronates (2a–2l) in yields ranging from 55% to 90%. These compounds show transannular N → B bonds with a tetrahedral geometry for both boron and nitrogen atoms as well as five- and six-membered fused rings (Scheme 4).

2.5. NMR data of 2-aryl-dibenzo[d,h]-6-aza-1,3-dioxa-2-boracyclononenes

All compounds show an AB system for the methylene at position 7 in the ^1H NMR spectra. The chemical shift difference for the AB system is in the range from 0.08 to 0.15 ppm for compounds 2b–2g and 2j, which were determined in DMSO-d_6; while boronates 2a, 2h, 2i, 2k and 2l were determined in CDCl₃, and showed an ABX system. In chloroform, the chemical shift difference for the AB system was 0.46 ppm and showed in all cases, a coupling constant of 12.8 Hz and an additional coupling with the amine proton with magnitudes between 3.6 and 1.5 Hz for the A–X and B–X fragments, respectively. The recording of the spectra in these two solvents was due to the lack of solubility depending on the substituents attached to the main boronate skeleton.

The proton signal for the N–H proton is shifted depending on the nature of the solvent employed; for the compounds determined in DMSO-d_6, the proton appears around 9.5 ppm, while for those obtained in CDCl₃, it is around 6.5 ppm. This significant difference in chemical shifts was attributed to the formation of hydrogen bonds, of the type Ph–B ← N–H···O = S(Me)₂ (see Section 2.7 for the crystalline solid state evidence of this finding).

In ^{13}C NMR, the boronates show chemical shifts similar to the tridentate ligands; only carbons C-2 and C-9 are slightly shifted by 4 and 7 ppm, respectively.

The construction of the tetracyclic-fused structure was evidenced by the ^{11}B chemical shift which appears within a range of 9.6–7.4 ppm, characteristic for tetracoordinated boronate esters.

2.6. IR and MS data of 2-aryl-dibenzo[d,h]-6-aza-1,3-dioxa-2-boracyclononenes

The IR spectra of compounds 2a–2l show the characteristic N–H band. The mass spectra show the molecular ion peak for the monomeric boronates and the loss of the aryl groups from M^+ to give tetracyclic structures with a covalent bond between the boron and nitrogen atoms, characteristic for this type of derivatives, as well as the hydroxytropylium ion for 2a–2e and the di-*tert*-butylsalicylidene ion for 2g–2l.

2.7. Molecular structures of 2a, 2e, 2f and 2l

Crystallographic data for boronates 2a, 2e, 2f and 2l are listed in Table 1; selected bond lengths, bond and torsion angles, as well as plane deviations are summarized in Table 2. The corresponding molecular structures are shown in Fig. 1.

Compound 2a crystallized in a non primitive space group (C c m 2₁) which is indicative of the σ_h generated due to disorder in the molecule, hence only half of the molecular entity was refined. This kind of disorder is quite unusual, since similar structures showed a disordered imine fragment where boron and tin atoms are coordinated to the Schiff base and the fused ring moieties remain asymmetric [33]. Due to the high symmetry, in this case, the B(1), C(14), C(17), H(1N), H(7A) and H(7B) atoms are placed in special positions within the crystallographic cell. More accurate models regarding the molecular disorder were performed relative to two aromatic ring moieties with independent occupation factors but were unstable approaches during the refinement of the structure. Hence, the model for the disordered structure presented herein represents the one with better crystal and refinement data parameters.

The refinement of the crystal structure for 2l revealed two sites of positional disorder, one regarding a chloroform molecule included in the crystallographic cell, and the second one due to a *tert*-butyl moiety of the salicylidene. When both disorders were neglected, the final R_1 was equal to 10.29% with R_2 (all data) equal to 31.48%. When the disorder present at the chloroform molecule was considered, the final indexes were those shown in Table 1, R_1 was equal to 9.33% with R_2 (all data) equal to 30.17%. Moreover, when both, the *tert*-butyl and the chloroform were included as disordered moieties within the model, no satisfactory solution was encountered and a full anisotropic refinement was not possible. Thus, the latter refinement scheme gave R_1 equal to 11.45% with R_2 (all data) equal to 33.62%. Additionally, due to the obtained R values, the trial of twinned refinement was performed, but no significant gain was obtained with this approach. Therefore, the disorder was mainly responsible for the inaccurate statistical refinement of this structure. In any

Table 1
Collection data and refinement parameters for compounds **2a**, **2e**, **2f** and **2l**

Compound	2a	2e	2f	2l
Molecular formula	$C_{18}H_{16}BNO_2$	$C_{19}H_{15}BClNO_2$	$C_{19}H_{15}BN_2O_4$	$C_{28}H_{35}BN_2O_2 \cdot CHCl_3$
Molecular weight	301.14	335.58	346.14	561.76
Crystalline system	Orthorhombic	Monoclinic	Orthorhombic	Triclinic
Space group	$Ccm2_1$	$P2_1/n$	$Pcab$	$P\bar{1}$
Unit cell dimensions				
a (Å)	9.3521(3)	9.1036(4)	10.0342(2)	7.6645(4)
b (Å)	18.3953(7)	9.2801(5)	11.0069(2)	13.7299(6)
c (Å)	9.1534(3)	20.1784(13)	31.1396(5)	16.2540(9)
α (°)	90	90	90	112.226(2)
β (°)	90	100.004(2)	90	91.331(2)
γ (°)	90	90	90	106.195(2)
Volume (Å^3)	1574.70(9)	1678.80(16)	3439.23(11)	1504.51(13)
Z	4	4	8	2
ρ (mg m^{-3})	1.270	1.328	1.337	1.240
μ (mm^{-1})	0.081	0.238	0.094	0.332
θ Range (°)	3.97–27.47	3.44–27.52	3.70–26.01	4.09–23.00
Collected reflections	5900	5723	6201	7608
Independent reflections [R_{int}]	1776 [0.0412]	3617 [0.035]	3332 [0.0378]	4169 [0.0390]
θ Completeness [%]	27.47° [99.3]	27.52° [93.9]	26.01° [98.1]	23.00° [99.3]
Data/restrictions/parameters	1776/43/147	3617/0/278	3332/0/295	4169/66/431
Goodness-of-fit on F^2	1.049	1.007	1.048	1.096
Final indices [$I > \sigma(I)$]R_1	0.0499	0.0534	0.0528	0.0933
Final indices (all data) wR_2	0.1414	0.1241	0.1381	0.3017
$\Delta\rho_{min}$ (e Å^3)	−0.106	−0.225	−0.217	−0.248
$\Delta\rho_{max}$ (e Å^3)	0.116	0.148	0.231	0.435

case, the boronate moiety presents adequate geometrical parameters and structure factors, allowing its further discussion.

The N → B, B–O(1) and B–O(2) distances found are 1.701(4), 1.453(3), 1.453(3) Å for **2a**, 1.665(3), 1.490(3), 1.450(3) Å for **2e**, 1.680(3), 1.505(3), 1.450(3) Å for **2f**, and 1.690(8), 1.503(7), 1.420(7) Å for **2l**, in agreement with the distances found in similar derivatives described in the literature [1–31,33b]. The tetrahedral character (THC$_{D \to A}$) of the boron atoms has magnitudes of

Table 2
Selected geometrical parameters for compounds **2a**, **2e**, **2f** and **2l**

Compound	2a	2e	2f	2l
Bond lengths (Å)				
N(1)–B(1)	1.701(4)	1.665(3)	1.680(3)	1.690(8)
C(14)–B(1)	1.609(4)	1.599(3)	1.579(3)	1.600(8)
Bond angles (°)				
O(1)–B(1)–O(2)	108.0(3)	107.60(16)	110.63(16)	112.6(4)
N(1)–B(1)–C(14)	108.9(2)	110.33(15)	112.13(16)	111.8(4)
N(1)–B(1)–O(1)	118.6(2)[a]	100.41(16)	100.05(14)	99.4(4)
N(1)–B(1)–O(2)	118.6(2)[a]	109.71(18)	108.54(16)	109.4(4)
O(1)–B(1)–C(14)	113.66(18)[a]	113.41(19)	112.29(16)	111.2(4)
O(2)–B(1)–C(14)	113.66(18)[a]	114.44(18)	111.96(17)	111.8(4)
Dihedral angles (°)				
H(1N)–N(1)–B(1)–C(14)	39.24(160)	−21.04(130)	0.72(142)	−8.38(506)
N(1)–C(6)–C(1)–O(1)	13.89(19)	−4.7(2)	−1.4(2)	−0.9(6)
B(1)–O(1)–C(1)–C(2)	20.5(18)	170.3(2)	−177.51(18)	173.5(5)
B(1)–O(2)–C(13)–C(12)	20.5(18)	−140.48(19)	133.8(2)	136.0(5)
C(6)–N(1)–C(7)–C(8)	160.61(19)	163.33(17)	67.9(2)	77.1(6)
Deviation from mean C(7)–C(8)–C(9)–C(10)–C(11)–C(12)–C(13)–O(2) plane (Å)				
B(1)	0.7125(49)	−0.7828(27)	−0.9458(28)	0.9920(74)
N(1)	0.6931(48)	−0.9601(23)	−1.0156(25)	0.8637(64)
Deviation from mean N(1)–C(6)–C(5)–C(4)–C(3)–C(2)–C(1)–O(1) plane (Å)				
B(1)	0.2849(41)	−0.3057(28)	0.0230(26)	0.1655(69)
THC B (%)	68.20	76.80	78.42	78.22

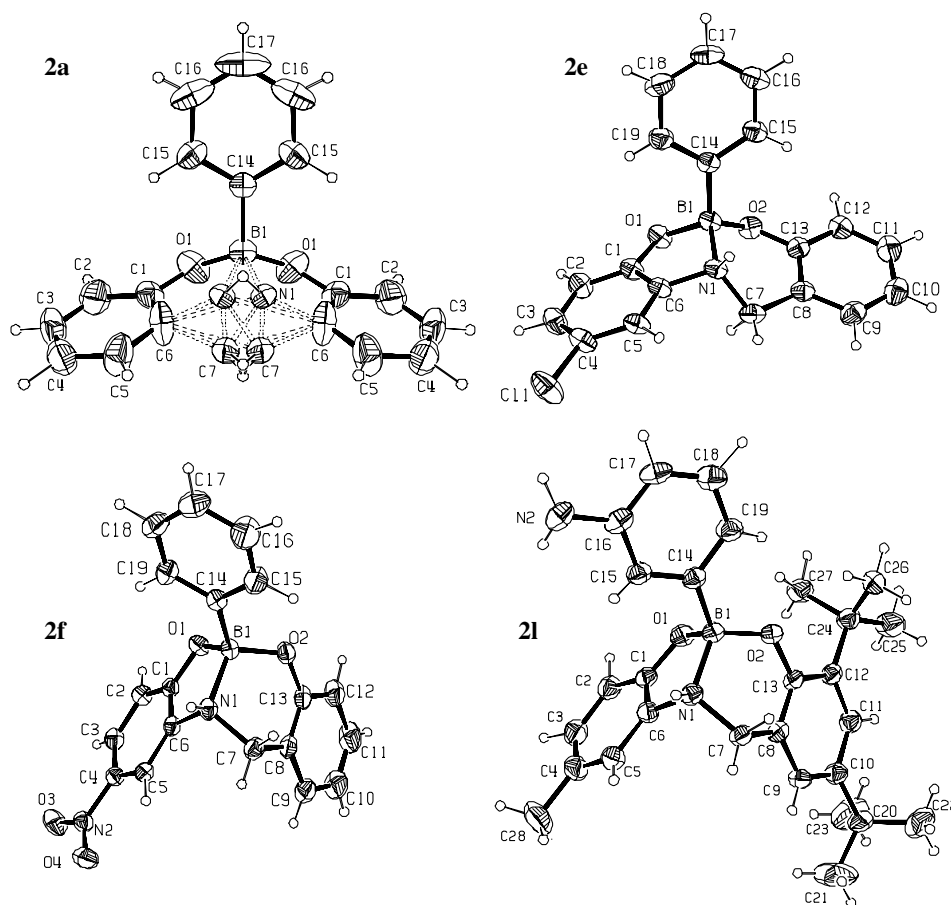[a] The values are the same due to the molecular symmetry.

Fig. 1. ORTEP diagrams of the molecular structures of compounds **2a**, **2e**, **2f** and **2l**.

68.20, 76.80, 78.42 and 78.22% for **2a**, **2e**, **2f** and **2l**. The first value is diminished due to the crystallographic disorder present. For the $THC_{D \rightarrow A}$ measurement it is important to mention that the lowest bond angle measured corresponds to the O(1)–B–N angle with values of 118.6°, 100.41°, 100.05°, 99.4° for **2a**, **2e**, **2f** and **2l**; in this case, the former value is incremented also due to the crystallographic disorder. The decrease in bond angle can be attributed to the ring fusion and strain in the 5-membered ring. The structures possess dihedral angles of 39.24°, 21.04°, 0.72° and 8.38°, respectively for the H–N–B–Ph fragment in **2a**, **2e**, **2f** and **2l**, whereby it is worth mentioning the significant variation of the disordered structure and thus the $THC_{D \rightarrow A}$ value was farther from the mean value for this family of boronates. The five-membered ring containing the B–N–C(6)–C(1)–O(1) fragment presents an almost flat conformation for **2a**, **2e** and **2l** with C(1), B(1) or B(1) slightly displaced from the plane; in the case of **2f**, the conformation of such fragment is the one closer to planarity with a B(1) deviation of only 0.0230(26) Å (Table 2). The six-membered ring containing the B–N–C(7)–C(8)–C(13)–O(2) fragment presents twisted boat conformation for **2a** and boat conformation for the remaining derivatives, with the O(2) and C(7) placed below the plane for **2e**, and above for **2f** and **2l**, leading to distinct conformations.

Compounds **2a**, **2f** and **2l** crystallized in a roofed conformation with respect to the boron nitrogen bond, while **2e** shows stepper conformation; for the roofed one a bigger H–N–B–Ph dihedral angle is present in comparison to the stepper arrangement.

The acidic nature of the N–H proton was evidenced through NMR experiments realized with DMSO-d_6 and CDCl₃ as solvents. For the former solvent, a significant displacement for the ¹H resonances is indicative of a strong hydrogen bonding for the Ph–B ← N–H···O=SMe₂ interaction. The same behaviour is observed in the solid state crystalline phase, where acid-base intermolecular interactions between the Ph–B ← N–H···O–B fragments take place (Fig. 2). The observed values for the two interactions of **2a** are $d(H\cdots O) = 2.329$ Å, $\theta(N–H\cdots O) = 164.08°$, $\theta(H\cdots O–B) = 95.55°$. The values for the two interactions for **2e** are $d(H\cdots O(1)) = 2.224$ Å, $\theta(N–H\cdots O(1)) = 155.68°$, $\theta(H\cdots O(1)–B) = 103.59°$, $d(H\cdots O(2)) = 2.573$ Å, $\theta(N–H\cdots O(2)) = 139.37°$, $\theta(H\cdots O(2)–B) = 109.06°$, $\theta(H\cdots O(2)–B) = 90.02°$ (Fig. 2).

There are two other types of supramolecular arrangements which depend on the type of substituent attached to the boronate molecule. In the first one, compound **2f** with a NO₂ group, presents a Ph–B ← N–H···O(1)–B interaction that involves the five member ring oxygen atom O(1)) with values of $d(H\cdots O(1)) = 2.321$ Å, $\theta(N–H\cdots O(1)) = 149.90°$,
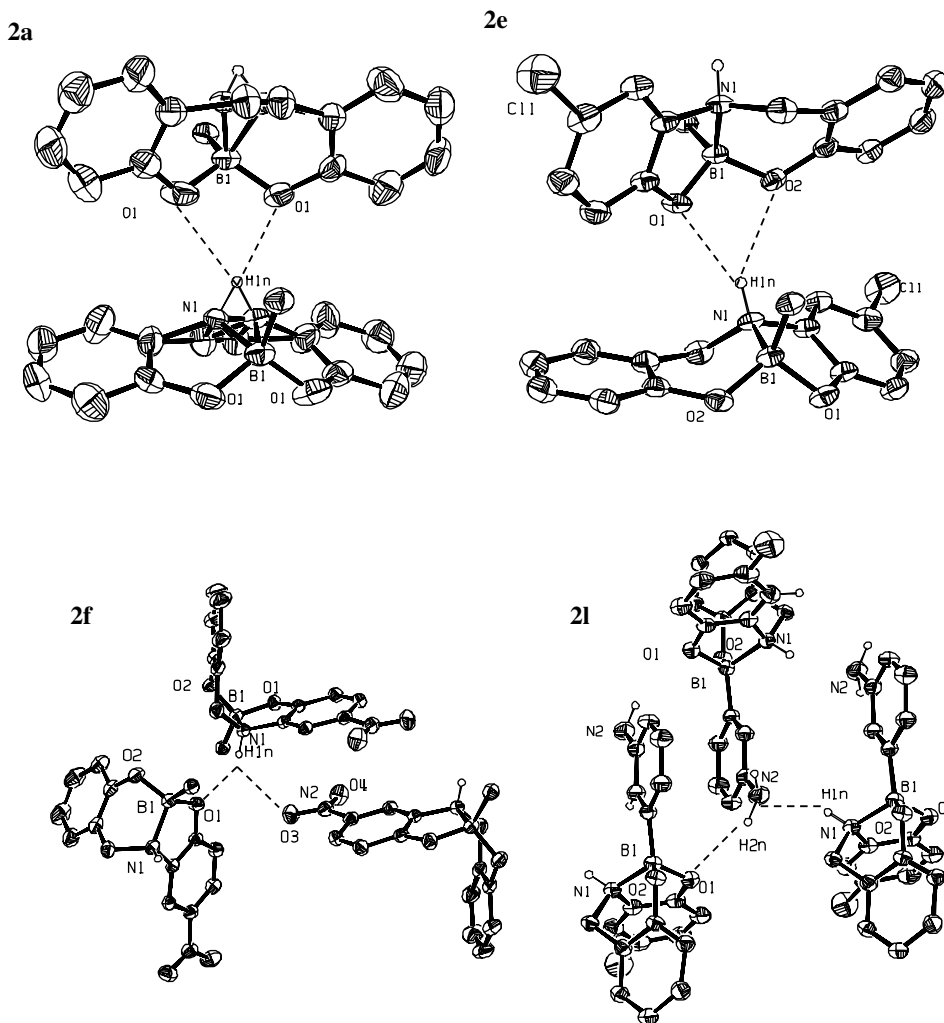
Fig. 2. Intermolecular hydrogen bonds in compounds **2a**, **2e**, **2f** and **2l** (some fragments were omitted for clarity).

$\theta(H \cdots O(1)–B) = 118.55°$; and the Ph–B ← N–H···O–N interaction with values of $d(H \cdots O) = 2.788$ Å, $\theta(N–H \cdots O) = 128.07°$, $\theta(H \cdots O–N) = 121.92°$ (Fig. 2). The second arrangement is present in the X-ray structure of **2l**; in this case, the substituent was a primary amine which acted as a bridging group between the normal Ph–B ← N–H···O–B fragments to construct a more complex supramolecular entity of the type Ph–B ← N–H···N–H···O–B (Fig. 2). The values for the interaction in **2l** are $d(H \cdots N) = 2.214$ Å, $\theta(N–H \cdots N) = 153.83°$, $\theta(H \cdots N–H) = 98.66°$, $d(H \cdots O) = 2.526$, $\theta(N–H \cdots O) = 156.38°$, $\theta(H \cdots O–B) = 109.06°$.

3. Conclusions

The reaction between 2-[[(2-hydroxyphenyl)amino]-methyl]-phenols with different aryl boronic acids led to 12 new monomeric boronates, in all cases.

The stereochemistry of the H–N → B–Ph moiety is always *cis* and was established through the NMR and the X-ray structures of four boronates.

The acidic nature of the N–H proton was evidenced through NMR experiments realized with DMSO-d_6 and

CDCl$_3$ solvents. In the former solvent, a significant shift for the ^{1}H resonances is indicative of a strong hydrogen bonding for the Ph–B ← N–H···O=SMe$_2$ interaction.

The difference in chemical shifts for the AB system varies also depending on the solvent used, the $\Delta\delta$ in CDCl$_3$ around 0.45 ppm while in DMSO-d_6 is 0.15 ppm, this effect is also observed in the N–H proton.

The same behaviour is observed in the crystalline phase, where acid-base intermolecular interactions between the Ph–B ← N–H···O–B fragments are present. The interactions changed significantly when a primary amine is placed within the molecular entity, since this substituent acted as a bridging group between the normal Ph–B ← N–H···O–B fragments to construct a more complex supramolecular entity of the type Ph–B ← N–H···N–H···O–B.

4. Experimental

All starting materials were commercial grade and were used as received. Solvents were purchased from J.T. Baker Co and used without further purification.

(C-2), 151.2 (C-9), 132.2 (C-6), 130.8 (C-4), 129.8 (C-11), 124.5 (C-13), 124.0 (C-8), 119.6 (C-12), 119.2 (C-5), 118.8 (C-1), 117.1 (C-10), 115.9 (C-3), 48.4 (C-7) ppm. The remaining tridentate ligands **1b–1e** were prepared in analogous ways.

4.1.1.2. 2-[[(2-Hydroxyphenyl)amino]methyl]-4-chlorophenol hydrochloride (1b). White solid, yield 59% (1.38 g, 4.48 mmol) m.p. 196–198 °C. IR v_{max} (KBr): 3330, 3167, 2935, 1604, 1562, 1433, 1349, 1274, 1231, 1105, 774 cm^{-1}. MS (20 eV) m/z (%) 251 (M$^+$ – HCl, 5), 249 (14) 145 (37), 143 (100) 114 (11) 107 (37) 80 (26), 78 (13). ^{1}H NMR (300.13 MHz, DMSO-d_6, δ, ppm, J, Hz) 10.81 (OH, bs), 8.24 (NH, bs) 7.28 (1H, H-6, dd, J_o = 7.6, J_m = 1.7), 7.15 (1H, H-4, m), 7.14 (1H, H-13, m), 7.07 (1H, H-10, m), 7.07 (1H, H-11, m), 6.92 (1H, H-3, dd, J_o = 8.0, J_m = 1.0), 6.75 (1H, H-5, ddd, J_o = 8.0, 7.7, J_m = 1.0), 4.36 (2H, H-7, s) ppm. ^{13}C NMR (75.46 MHz, DMSO-d_6) δ: 156.9 (C-2), 149.5 (C-9), 132.0 (C-6), 130.7 (C-4), 128.0 (C-11), 127.0 (C-13), 123.0 (C-8), 123.0 (C-10), 120.0 (C-1), 119.6 (C-5), 118.1 (C-12), 116.0 (C-3), 47.4 (C-7) ppm.

4.1.1.3. 2-[[(2-Hydroxyphenyl)amino]methyl]-4-nitrophenol hydrochloride (1c). White solid, yield 76% (1.85 g, 6.23 mmol) m.p. 176–179 °C. IR v_{max} (KBr, cm^{-1}) 3330, 3167, 2935, 1604, 1562, 1433, 1349, 1274, 1231, 1105, 774 cm^{-1}. MS (20 eV) m/z (%) 260 (M$^+$ – HCl, 16), 154 (97), 124 (10), 107 (100), 85 (45), 78 (47). ^{1}H NMR (300.13 MHz, DMSO-d_6, δ, ppm, J, Hz) 11.98 (OH, bs), 8.62 (NH, bs) 7.77 (1H, H-11, dd, J_o = 8.8, J_m = 2.7), 7.65 (1H, H-13, d, J_m = 2.7), 7.25 (1H, H-6, dd, J_o = 7.5, J_m = 1.4), 7.10-7.16 (1H, H-5, m), 7.10–7.16 (1H, H-10, m), 6.92 (1H, H-3, dd, J_o = 7.5, J_m = 0.6), 6.76 (1H, H-4, ddd, J_o = 7.5, J_m = 0.6), 4.41 (2H, H-7, s). ^{13}C NMR (75.46 MHz, DMSO-d_6, δ, ppm) 155.8 (C-2), 154.2 (C-9), 139.8 (C-12), 131.7 (C-8), 129.9 (C-6), 129.1 (C-4), 121.8 (C-1), 119.0 (C-5), 118.7 (C-11), 115.2 (C-3), 114.2 (C-10), 110.9 (C-13), 44.1 (C-7).

4.1.1.4. 2-[[(2-Hydroxy-3,5-di-tertbutylphenyl)amino]methyl]-phenol hydrochloride (1d). White solid, yield 90% (2.78 g, 7.66 mmol) m.p. 194–198 °C. IR v_{max} (KBr, cm^{-1}) 3202, 2958, 2770, 1625, 1565, 1508, 1360, 1282, 1213, 754. MS (20 eV) m/z (%) 327 (M$^+$ – HCl, 10), 219 (40), 203 (38), 161 (15), 109 (100), 91 (10), 80 (21). ^{1}H NMR (399.78 MHz, DMSO-d_6, δ, ppm, J, Hz) 11.05 (OH, bs), 8.62 (NH, bs) 7.31 (1H, H-13, d, J_o = 7.7), 7.21 (1H, H-11, dd, J_o = 8.2, J_m = 1.1), 7.20 (1H, H-4, d, J_m = 2.6), 7.10 (1H, H-10, dd, J_o = 8.2, J_m = 1.1), 6.97 (1H, H-6, d, J_o = 2.6), 6.79 (1H, H-12, ddd, J_o = 8.2, 7.7, J_m = 1.1), 4.43 (2H, H-7, s), 1.36 (9H, tBu-C-3, s), 1.16 (9H, tBu-C-5, s). ^{13}C NMR (75.47 MHz, DMSO-d_6, δ, ppm) 152.4 (C-2), 151.3 (C-9), 142.4 (C-5), 139.6 (C-3), 130.2 (C-11), 127.3 (C-3), 124.8 (C-13), 124.6 (C-4), 123.4 (C-8), 121.9 (C-1), 119.7 (C-12), 117.1 (C-10), 49.2 (C-7), 35.3 (C-tBut-C-3), 34.4 (C-tBu-C-5), 31.8 (CH$_3$-tBu-C-5) 30.4 (CH$_3$-tBu-C-3).

4.1. Instrumentation

NMR experiments were performed on Jeol ECLIPSE-400, Jeol-GSX-270 and Bruker ADVANCE-300 spectrometers. All ^{1}H and ^{13}C chemical shifts [ppm] are reported relative to TMS ($\delta^1H = 0$, $\delta^{13}C = 0$). Coupling constants are quoted in Hz. ^{11}B spectra were obtained relative to BF$_3$ · OEt$_2$ using DMSO-d_6 or CDCl$_3$ as solvent. Infrared spectra were recorder as KBr pellets in a Perkin–Elmer 16F-PC FT-IR and Perkin–Elmer FT-IR System Spectrum GX spectrometers. Mass spectra were recorded on a HP 5989A spectrometer at 20 eV electron impact.

Melting points were measured in open capillary tubes on a Gallenkamp MFB-595 apparatus and have not been corrected.

The X-ray crystal structure determinations for compounds **2a**, **2e**, **2f** and **2l** were obtained on an Enraf Nonius-FR590 and Kappa-CCD ($\lambda_{Mo K\alpha}$ = 0.71073 Å, graphite monochromator, T = 293 K, ω-2θ and CCD rotating images scan modes) respectively. When necessary, absorption correction was performed within the SHELX-A [34] program or by the semiempirical correction through MULTISCAN procedure (PLATON) [35]. All reflection data sets were corrected for Lorentz and polarization effects. The first structure solution was obtained using the SHELX-s-97 program and then SHELX-L-97ver. 34 program [34] was applied for refinement and output data. All software manipulations were done under the WIN-GX [36] environment program set. Molecular perspectives were drawn under ORTEP 3 [37] drawing application. All heavier atoms were found by Fourier map difference and refined anisotropically. Some hydrogen atoms were found by Fourier map difference and refined isotropically, the remaining hydrogen atoms were geometrically modeled and calculated for the refinement.

4.1.1. Preparation of 2-[[(2-hydroxyphenyl)amino]-methyl]-phenol hydrochlorides (1a–1e)

4.1.1.1. 2-[[(2-Hydroxyphenyl)amino]methyl]-phenol hydrochloride (1a). Compound **1a** was prepared from 0.89 g (8.18 mmol) of 2-aminophenol and 1.00 g (8.18 mmol) of salicylaldehyde under reflux in a THF–MeOH mixture for 6 h to give **3a**, followed by reduction with 0.62 g (16.36 mmol) of sodium borohydride, and subsequent addition of 3.4 mL of hydrochloric acid, to obtain a white solid, characterized as **1a** in 91% yield (1.90 g, 7.71 mmol) m.p. 210–213 °C. IR v_{max} (KBr): 3313, 3218, 2840, 2784, 1605, 1564, 1507, 1445, 1270, 1235, 753, 591 cm^{-1}. MS (20 eV) m/z (%) 215 (M$^+$ – HCl, 19), 109 (100), 80 (26), 77 (21), 51 (13). ^{1}H NMR (399.78 MHz, DMSO-d_6, δ, ppm, J, Hz) 11.04 (OH, bs), 10.27 (NH, bs) 7.28 (1H, H-6, dd, J_o = 7.7, J_m = 1.5), 7.25 (1H, H-13, d, J_o = 7.7), 7.10–7.16 (1H, H-4, m), 7.10–7.16 (1H, H-10, m), 7.10–7.16 (1H, H-11, m), 6.96 (1H, H-3, dd, J_o = 8.1, J_m =;1.1), 6.77 (1H, H-12, ddd, J_o = 8.0, 7.4, J_m = 1.4), 6.74 (1H, H-5, ddd, J_o = 8.1, 7.7, J_m = 1.1), 4.38 (2H, H-7, s) ppm. ^{13}C NMR (100.53 MHz, DMSO-d_6) δ: 156.8

4.1.1.5. 2-[[(2-Hydroxy-3,5-di-tertbutylphenyl)amino]-methyl]-4-methylphenol (1e).

White solid, yield 70% (2.24 g, 5.93 mmol) m.p. 228–232 °C. IR ν_{max} (KBr, cm^{-1}) 3202, 2958, 2770, 1625, 1565, 1508, 1360, 1282, 1213, 754 cm^{-1}. MS m/z (%) 327 (M$^+$ − HCl, 10), 218 (27) (100), 161(29), 123 (90). ^{1}H NMR (399.78 MHz, DMSO-d_6, δ, ppm, J, Hz) 10.79 (OH, bs), 8.61 (NH, bs) 7.31 (1H, H-13, d, J_o = 7.7), 7.21 (1H, H-11, dd, J_o = 8.2, J_m = 1.1), 7.20 (1H, H-4, d, J_m = 2.6), 7.10 (1H, H-10, dd, J_o = 8.2), 6.97 (1H, H-6, d, J_o = 2.6), 6.79 (1H, H-12, ddd, J_o = 8.2, 7.7, J_m = 1.1), 4.43 (2H, H-7, s), 1.36 (9H, tBu-C-3, s), 1.16 (9H, tBu-C-5, s). ^{13}C NMR (75.47 MHz, DMSO-d_6, δ, ppm) 152.4 (C-2), 151.3 (C-9), 142.4 (C-5), 139.6 (C-3), 130.2 (C-11), 127.3 (C-3), 124.8 (C-13), 124.6 (C-4), 123.4 (C-8), 121.9 (C-1), 119.7 (C-12), 117.1 (C-10), 49.2 (C-7), 35.3 (C-tBu-C-3), 34.4 (C-tBu-C-5), 31.8 (CH$_3$-tBu-C-5) 30.4, (CH$_3$-tBu-C-3).

4.1.2. General synthesis of 2-aryl-dibenzo[d,h]-6-aza-1,3-dioxa-2-boracyclononones

4.1.2.1. 2-Phenyl-benzo[d]-benzo[h]-6-aza-1,3-bora-cyclononene (2a).

Compound **2a** was prepared by the reaction of 0.50 g (1.98 mmol) of **1a**, 0.283 g (1.98 mmol) phenylboronic acid, and (0.29 g, 2.98 mmol) of sodium bicarbonate in 120 mL of 4:1 benzene: ethanol mixture for 12 h, to give a yellow solid in 80.0% yield (0.56 g, 1.59 mmol) m.p. 210–214 °C. IR ν_{max} (KBr, cm^{-1}) 3116, 1610, 1490, 1460, 1280, 1254, 1230, 1214, 1042, 748. MS (m/z) 301 (M$^+$, 35), 224 (57), 223 (82), 222 (81), 195 (100), 194 (26), 78 (10). ^{1}H NMR (399.78 MHz, CDCl$_3$, δ, ppm, J, Hz) 8.53 (1H, NH, s), 7.59 (2H, H-15, d, J_o = 7.0), 7.16-7.22 (2H, H-16, m), 7.16-7.22 (2H, H-17, m), 7.09 (1H, H-4, t, J_o = 8.8), 7.28 (1H, H-13, d, J_o = 7.7), 6.99 (1H, H-11, t, J_o = 7.7), 6.91 (1H, H-3, d, J_o = 7.1), 7.08 (1H, H-6, d, J_o = 7.3), 6.70 (1H, H-10, d, J_o = 8.0), 6.67 (1H, H-12, t, J_o = 7.3), 6.62 (1H, H-5, t, J_o = 7.7), 4.41 (1H, H-7A, dd, J_{AB} = 13.5, J_{AX} = 3.7), 3.95 (1H, H-7B, dd, J_{AB} = 13.5, J_{BX} = 2.0). ^{13}C NMR (100.53 MHz, CDCl$_3$, δ, ppm) 159.2 (C-9), 157.0 (C-2), 132.0 (C-15, C-19), 129.9 (C-4), 129.8 (C-11), 129.2 (C-8), 127.7 (C-17), 127.6 (C-6), 127.6 (C-16, C-18), 121.2 (C-1), 120.6 (C-13), 120.1 (C-12), 119.4 (C-3), 118.1 (C-5), 112.9 (C-10), 50.2 (C-7). ^{11}B NMR (128.26 MHz, CDCl$_3$, δ, ppm) 7.6. The remaining boronates were prepared using the same procedure.

4.1.2.2. 2-(4-Acetylphenyl)-benzo[d]-benzo[h]-6-aza-1,3-dioxa-2-boracyclononene (2b).

Pale yellow solid, 80.2% (0.767 g, 1.73 mmol), m.p. 208–211 °C. IR ν_{max} (KBr, cm^{-1}) 3430, 3221, 2762, 2560, 1566, 1481, 1449, 1116. MS (m/z) 343 (M$^+$, 7), 237 (13), 334 (23), 224 (28), 223 (52), 222 (100), 221 (24), 193 (11), 120 (20), 105 (27), 77 (41). ^{1}H NMR (270.16 MHz, DMSO-d_6, δ, ppm, J, Hz) 9.36 (1H, NH, s), 7.89 (2H, H-16, d, J_o = 7.8), 7.70 (2H, H-15, d, J_o = 7.8), 7.33 (1H, H-13, d, J_o = 7.9), 7.14 (1H, H-4, t, J_o = 7.9), 7.06 (1H, H-11, t, J_o = 8.8), 7.04 (1H, H-6, d, J_o = 8.8), 6.85 (1H, H-3, d, J_o = 7.9), 6.70-6.77 (1H, H-5, m), 6.70-6.77 (1H, H-10, m), 6.70–6.77 (1H, H-12, m), 4.45 (1H, H-7A, d, J_{AB} = 13.8), 4.29 (1H, H-7B, d, J_{AB} = 13.8), 2.56 (3H, H–COCH$_3$, s). ^{13}C NMR (67.94 DMSO-d_6, δ, ppm) 198.6 (C=O), 159.1 (C-9), 157.1 (C-2), 150.1 (C-14), 136.6 (C-16), 132.6 (C-15, C-19), 130.0 (C-4), 129.9 (C-8), 129.7 (C-11), 129.0 (C-6), 127.5 (C-16, C-18), 122.2 (C-1) 121.4 (C-13), 120.3 (C-12), 119.0 (C-3), 118.7 (C-5), 112.5 (C-10), 48.7 (C-7), 27.2 (COCH$_3$). ^{11}B NMR (86.68 MHz, CDCl$_3$, δ, ppm) 7.5.

4.1.2.3. 2-(3-Acetylphenyl)-benzo[d]-benzo[h]-6-aza-1,3-dioxa-2-boracyclononene (2c).

Yellow solid, 62% (0.576 g, 1.73 mmol), m.p. 201–204 °C. IR ν_{max} (KBr, cm^{-1}) 3446, 3076, 1661, 1610, 1490, 1281, 1247, 1037, 968, 751. MS (m/z) 343 (M$^+$, 19), 237 (23), 224 (45), 223 (66), 222 (100), 221 (23), 194 (8), 120 (19), 105 (21), 77 (15). ^{1}H NMR (300.13 MHz, DMSO-d_6, δ, ppm, J, Hz) 9.37 (1H, NH, s), 8.15 (1H, H-15, d, J_m = 1.4), 7.89 (1H, H-17, ddd, J_o = 7.5, J_m = 1.1, 1.4), 7.81 (1H, H-19, ddd, J_o = 7.5, J_m = 1.1, 1.4), 7.45 (1H, H-18, t, J_o = 7.5), 7.31 (1H, H-13, d, J_o = 7.4), 7.14 (1H, H-4, dd, J_o = 7.9, J_m = 1.4), 7.03–7.07 (1H, H-6, m), 7.03–7.07 (1H, H-11, m), 6.85 (1H, H-3, d, J_o = 7.9), 6.69-6.72 (3H, H-5, H-10, H-12, m), 4.47 (1H, H-7A, d, J_{AB} = 13.9), 4.33 (1H, H-7B, d, J_{AB} = 13.9), 2.57 (3H, COCH$_3$, s). ^{13}C NMR (75.46 MHz, DMSO-d_6, δ, ppm) 198.6 (C=O), 158.5 (C-9), 156.7 (C-2), 137.0 (C-19), 135.9 (C-16), 131.5 (C-15), 129.4 (C-4), 128.8 (C-11), 128.5 (C-6), 128.5 (C-8), 127.6 (C-17), 127.6 (C-18), 121.9 (C-13), 121.8 (C-1), 120.8 (C-12), 118.5 (C-3), 118.2 (C-5), 111.9 (C-10), 47.9 (C-7), 26.8 (COCH$_3$). ^{11}B NMR (128.26 MHz, CDCl$_3$, δ, ppm) 8.2.

4.1.2.4. 2-(3-Aminophenyl)-benzo[d]-benzo[h]-6-aza-1,3-dioxa-2-boracyclononene (2d).

Yellow solid, 69% (0.47 g, 1.40 mmol), m.p. 224–226 °C. IR ν_{max} (KBr, cm^{-1}) 3427, 3162, 3066, 1608, 1486, 1464, 1248, 1236, 1204, 1076, 1050, 936, 756. EM (m/z, %) 337 (M$^+$ + 2, 13), 336 (11), 335 (37), 258 (55), 257 (66), 256 (66), 231 (35), 229 (100), 228 (26), 107 (16), 78 (14). ^{1}H NMR (300.18 MHz, DMSO-d_6, δ, ppm, J, Hz) 9.12 (1H, NH, s), 7.58 (2H, H-15, H-19, dd, J_o = 7.5), 7.29–7.35 (3H, H-16, H-18, H-17, m), 7.30 (1H, H-13, dd, J_o = 7.4), 7.12 (1H, H-4, t, J_o = 7.4), 6.99–7.04 (1H, H-6, H-11, m), 6.90 (1H, H-3, d, J_o = 7.37), 6.73 (1H, H-5, m,), 6.69 (1H, H-12, t, J_o = 7.4), 6.68-6.72 (1H, H-10, H,12, m), 4.39 (1H, H-7A, d, J_{AB} = 14.0), 4.24 (1H, H-7B, d, J_{AB} = 14.0). ^{13}C NMR (75.47 MHz, DMSO-d_6, δ, ppm) 159.5 (C-9), 157.4 (C-2), 148.1 (C-16), 129.9 (C-8), 129.9 (C-4), 129.0 (C-11), 129.0 (C-18), 128.6 (C-6), 121.8 (C-1), 121.4 (C-13), 120.3 (C-12), 120.0 (C-15), 119.0 (C-3), 118.4 (C-19), 118.3 (C-5), 113.8 (C-17), 112.4 (C-10), 48.7 (C-7). ^{11}B NMR (96.29 MHz, DMSO-d_6, δ, ppm) 9.0.

4.1.2.5. 2-Phenyl-4-chlorobenzo[d]-benzo[h]-6-aza-1,3-dioxa-2-boracyclononene (2e).

Yellow pale solid, 70.0% (0.56 g, 1.59 mmol), m.p. 243–246 °C. IR ν_{max} (KBr, cm^{-1}) 3116, 1610, 1490, 1460, 1280, 1254, 1230, 1214,

1042, 748. MS (*m/z*, %) 301 (M$^+$, 35), 224 (57), 223 (82), 222 (81), 195 (100), 194 (26), 78 (10). ^{1}H NMR (300.18 MHz, DMSO-d_6, δ, ppm, *J*, Hz) 9.49 (1H, NH, s), 7.58 (2H, H-15, H-19, dd, $J_o = 7.5$, $J_m = 2.4$), 7.29–7.35 (3H, H-16, H-18, H-17, m), 7.16 (1H, H-4, t, $J_o = 7.4$), 7.07 (1H, H-6, d, $J_o = 7.6$), 6.90 (1H, H-3, d, $J_o = 7.4$), 6.73–6.79 (1H, H-5, m,), 6.92 (2H, H-11, H-12, d, $J_o = 7.5$), 6.40 (1H, H-13, d, $J_m = 2.4$), 4.45 (1H, H-7A, d, $J_{AB} = 14.0$), 4.38 (1H, H-7B, d, $J_{AB} = 14.0$). ^{13}C NMR (75.47 MHz, DMSO-d_6, δ, ppm) 157.9 (C-9), 156.9 (C-2), 134.2 (C-8), 131.9 (C-15, C-19), 129.7 (C-11), 129.5 (C-4), 128.6 (C-6), 127.8 (C-12), 127.5 (C-17), 127.4 (C-16, C-18) 121.6 (C-13), 121.8 (C-1), 120.0 (C-3), 118.6 (C-5), 113.2 (C-10), 48.1 (C-7). ^{11}B NMR (96.29 MHz, DMSO-d_6, δ, ppm) 9.0.

4.1.2.6. 2-Phenyl-4-nitrobenzo[d]-benzo[h]-6-aza-1,3-dioxa-2-boracyclononene (2f). Yellow pale solid, 75.0% (0.50 g, 1.44 mmol), m.p. 236–238 °C. IR ν_{max} (KBr, cm^{-1}) 3448, 3178, 1604, 1490, 1512, 1494, 1342, 1310, 1286, 1274, 1236, 1050, 1042, 1022, 742. MS (*m/z*, %) 346 (M$^+$, 16), 269 (72), 268 (100), 267 (79), 240 (45), 222 (18), 221 (34), 210 (14), 194 (21), 107 (25), 78 (18). ^{1}H NMR (399.78 MHz, DMSO-d_6, δ, ppm, *J*, Hz) 9.85 (1H, NH, s), 8.38 (1H, H-13, d, $J_m = 2.4$), 8.08 (1H, H-11, dd, $J_o = 8.9$, $J_m = 2.4$), 7.59 (2H, H-15, H-19, dd, $J_o = 7.2$, $J_m = 2.6$), 7.32–7.36 (3H, H-16, H-18, H-17, m), 7.16 (1H, H-4, t, $J_o = 7.4$), 7.11 (1H, H-6, d, $J_o = 7.4$), 6.89 (2H, H-3, H-10, m), 6.79 (1H, H-5, t, $J_o = 7.4$), 4.60 (1H, H-7A, d, $J_{AB} = 13.6$), 4.52 (1H, H-7B, d, $J_{AB} = 13.6$). ^{13}C NMR (100.53 MHz, DMSO-d_6, δ, ppm) 165.2 (C-9), 156.7 (C-2), 139.4 (C-12), 134.6 (C-8), 132 (C-15, C-19), 130.5 (C-4), 130.1 (C-6), 127.8 (C-16, C-18), 127.8 (C-17), 122.2 (C-1), 120.6 (C-3), 119.4 (C-5), 119.1 (C-11), 112.5 (C-13), 112.5 (C-10), 48.5 (C-7). ^{11}B NMR (128.26 MHz, DMSO-d_6, δ, ppm) 8.4.

4.1.2.7. 2-Phenyl-benzo[d]-3,5-ditertbutylbenzo[h]-6-aza-1,3-dioxa-2-boracyclononene (2g). Yellow pale solid, 88.0% (0.50 g, 1.21 mmol), m.p. 208–211 °C. FW = 413. IR ν_{max} (KBr, cm^{-1}) 3221, 2762, 2560, 1566, 1481, 1449, 1116. MS (*m/z*, %) 413 (M$^+$, 11), 398 (6), 336 (5), 320 (11), 203 (18), 195 (100), 146 (7), 91 (5), 57 (23). ^{1}H NMR (300.18 MHz, DMSO-d_6, δ, ppm, *J*, Hz) 9.16 (1H, NH, s), 7.59 (2H, H-15, H-19, dd, $J_o = 7.5$, $J_m = 2.1$), 7.24–7.33 (2H, H-16, H-18, m), 7.24–7.33 (1H, H-17, m), 7.24–7.33 (1H, H-13, m), 7.12 (1H, H-4, d, $J_m = 2.0$), 7.04 (1H, H-11, ddd, $J_o = 8.0$, 7.5, $J_m = 1.1$), 6.90 (1H, H-6, d, $J_o = 2.0$), 6.70 (1H, H-12, dd, $J_o = 8.0$, $J_o = 7.54$), 6.68 (1H, H-10, d, $J_o = 7.95$), 4.37 (1H, H-7A, d, $J_{AB} = 13.7$), 4.22 (1H, H-7B, d, $J_{AB} = 13.7$), 1.37 (9H, *t*Bu-C-3, s), 1.18 (9H, *t*Bu-C-5, s). ^{13}C NMR (75.47 MHz, DMSO-d_6, δ, ppm) 159.2 (C-9), 152.9 (C-2), 140.7 (C-5), 137.2 (C-3), 131.8 (C-15, C-19), 129.4 (C-8), 129.3 (C-11), 127.2 (C-16, C-18), 127.2 (C-17), 123.0 (C-6), 122.8 (C-4), 121.4 (C-13), 120.9 (C-1), 117.7 (C-12), 111.8 (C-10), 49.1 (C-7), 34.6 (C-*t*Bu-C-3), 33.8 (C-*t*Bu-C-5), 31.4 (CH$_3$-*t*Bu-C-

5) 29.7 (CH$_3$-*t*Bu-C-3). ^{11}B NMR (86.68 MHz, DMSO-d_6, δ, ppm) 8.1.

4.1.2.8. 2-(4-Acetylphenyl)-benzo[d]-3,5-ditertbutylbenzo[h]-6-aza-1,3-dioxa-2-boracyclononene (2h). Yellow solid, 55% (0.48 g, 1.06 mmol), m.p. 204–207 °C. FW = 455. IR ν_{max} (KBr, cm^{-1}) 3449, 3139, 2593, 1648, 1610, 1492, 1281, 1241, 1047, 993, 743. MS (*m/z*, %) 455 (M$^+$, 28), 440 (13), 339(14), 336 (19), 335 (34), 320 (38), 237 (100), 222 (19), 203 (55), 57 (21). ^{1}H NMR (300.18 MHz, CDCl$_3$, δ, ppm, *J*, Hz) 7.92 (2H, H-16, H-18, d, $J_o = 7.9$), 7.74 (2H, H-15, H-19, d, $J_o = 7.9$), 7.27 (1H, H-13, d, $J_o = 7.6$) 7.27 (1H, H-4, d, $J_m = 1.8$), 7.14 (1H, H-11, t, $J_o = 7.7$), 6.84 (1H, H-10, d, $J_o = 7.7$), 6.80 (1H, H-6, d, $J_m = 1.8$), 6.74 (1H, NH, s), 6.73 (1H, H-12, t, $J_o = 7.7$), 4.65 (1H, H-7A, dd, $J_{AB} = 13.7$, $J_{AX} = 3.6$), 4.20 (1H, H-7B, dd, $J_{AB} = 13.7$, $J_{BX} = 1.4$), 2.58 (3H, COCH_3, s), 1.45 (9H, *t*Bu-C-3, s), 1.24 (9H, *t*Bu-C-5, s). ^{13}C NMR (75.47 MHz, CDCl$_3$, δ, ppm) 199.1 (C=O), 159.9 (C-9), 153.6 (C-2), 141.7 (C-5), 138.1 (C-3), 136.9 (C-17), 132.9 (C-15, C-19), 130.3 (C-11), 129.8 (C-8), 124.0 (C-6), 123.8 (C-4), 121.8 (C-13), 112.7 (C-1), 118.8 (C-12), 112.8 (C-10), 49.9 (C-7), 35.2 (C-*t*Bu-C-3), 34.7 (C-*t*Bu-C-5), 32.3 (CH$_3$-*t*Bu-C-5) 30.5 (CH$_3$-*t*Bu-C-3), 27.4 (COCH_3). ^{11}B NMR (96.29 MHz, CDCl$_3$, δ, ppm) 7.4.

4.1.2.9. 2-(3-Acetylphenyl)-benzo[d]-3,5-ditertbutylbenzo[h]-6-aza-1,3-dioxa-2-boracyclononene (2i). Yellow solid, 89.8% (0.48 g, 1.06 mmol), m.p. 237–239 °C. FW = 455. IR ν_{max} (KBr, cm^{-1}) 3449, 3139, 2593, 1648, 1610, 1492, 1281, 1241, 1047, 993, 743. MS (*m/z*, %) 455 (M$^+$, 38), 440 (13), 335 (23), 334 (23), 320 (23), 237 (100), 222 (23), 203 (63), 161 (13), 57 (16). ^{1}H NMR (300.18 MHz, CDCl$_3$, δ, ppm, *J*, Hz) 8.08 (1H, H-15, s), 7.92 (1H, H-17, d, $J_o = 7.2$), 7.23 (1H, H-19, d, $J_o = 7.9$), 7.36 (1H, H-18, dd, $J_o = 7.9$, 7.2) 7.27 (1H, H-4, d, $J_m = 2.3$), 7.27 (1H, H-13, d, $J_o = 7.6$), 7.13 (1H, H-11, dd, $J_o = 7.6$, $J_m = 1.2$), 6.84 (1H, H-10, d, $J_o = 7.6$), 6.81 (1H, H-6, d, $J_m = 2.3$), 6.77 (1H, H-12, td, $J_o = 7.6$, $J_m = 1.2$), 6.71 (1H, N–H, s), 4.65 (1H, H-7A, dd, $J_{AB} = 12.9$, $J_{AX} = 3.6$), 4.20 (1H, H-7B, dd, $J_{AB} = 12.9$, $J_{AX} = 1.5$), 2.32 (3H, COCH_3, s), 1.45 (9H, *t*Bu-C-3, s), 1.24 (9H, *t*Bu-C-5, s). ^{13}C NMR (75.47 MHz, CDCl$_3$, δ, ppm) 200.7 (C=O), 159.8 (C-9), 153.1 (C-2), 142.5 (C-5), 139.2 (C-3), 137.5 (C-19), 136.5 (C-16), 132.4 (C-15), 130.6 (C-11), 128.2 (C-18), 128.0 (C-8), 127.9 (C-17), 124.6 (C-6), 123.2 (C-4), 120.8 (C-13), 119.8 (C-1), 118.6 (C-12), 113.6 (C-10), 51.2 (C-7), 35.1 (C-*t*Bu-C-3), 34.4 (C-*t*Bu-C-5), 31.8 (CH$_3$-*t*Bu-C-5) 30.0 (CH$_3$-*t*Bu-C-3), 26.8 (COCH_3). ^{11}B NMR (96.29 MHz, CDCl$_3$, δ, ppm) 8.6.

4.1.2.10. 2-(3-Aminophenyl)-benzo[d]-3,5-ditertbutylbenzo[h]-6-aza-1,3-dioxa-2- boracyclononene (2j). Yellow solid, 82.0% (0.48 g, 1.06 mmol), m.p. 237–239 °C. FW = 428. IR (*v*) (KBr, cm^{-1}) 3351, 3184, 2958, 1610, 1490, 1441, 1242, 1041, 771. MS (*m/z*, %) 428 (M$^+$, 20), 335 (60), 334 (23), 320 (50), 210 (100), 209 (25), 93 (21), 57 (14). ^{1}H NMR

(300.18 MHz, DMSO-d_6, δ, ppm, J, Hz) 9.12 (1H, NH, s), 7.30 (1H, H-13, d, $J_o = 7.5$), 7.12 (1H, H-4, d, $J_m = 1.3$), 7.03 (1H, H-11, t, $J_o = 7.7$), 6.98 (1H, H-18, t, $J_o = 7.5$), 6.88 (1H, H-6, d, $J_m = 1.3$), 6.83 (1H, H-15, m), 6.83 (1H, H-19, m), 6.68 (1H, H-12, t, $J_o = 7.7$), 6.61 (1H, H10, d, $J_o = 7.7$), 6.50 (1H, H-17, d, $J_o = 7.4$), 4.77 (2H, NH$_2$, s), 4.32 (1H, H-7A, d, $J_{AB} = 13.6$), 4.19 (1H, H-7B, d, $J_{AB} = 13.6$), 1.38 (9H, tBu-C-3, s), 1.18 (9H, tBu-C-5, s). ^{13}C NMR (75.47 MHz, DMSO-d_6, δ, ppm) 159.4 (C-9), 153.1 (C-2), 147.5 (C-16), 145.0 (C-14), 140.6 (C-5), 137.2 (C-3), 129.3 (C-11), 129.3 (C-8), 127.8 (C-18), 123.3 (C-6), 123.0 (C-4) 121.4 (C-13), 121.0 (C-1), 119.9 (C-15), 117.9 (C-19), 117.5 (C-12), 113.3 (C-17), 111.8 (C-10), 49.1 (C-7), 34.5 (C-tBu-C-3), 33.9 (C-tBu-C-5), 31.5 (CH$_3$-tBu-C-5) 29.8 (CH$_3$-tBu-C-3). ^{11}B NMR (86.68 MHz, DMSO-d_6, δ, ppm) 9.0.

4.1.2.11. 2-Phenyl-4-methylbenzo[d]-3,5-ditertbutylbenzo-[h]-6-aza-1,3-dioxa-2-boracyclononene (2k). Compound **2k** was prepared by the reaction of 0.51 g (1.35 mmol) of **1e**, 0.165 g (1.35 mmol) phenylboronic acid, and (0.243 g, 1.925 mmol) of sodium bicarbonate to give **2k** as a yellow solid 80.0% (0.46 g, 1.08 mmol) m.p. 227–231 °C. FW = 428. IR ν_{max} (KBr, cm^{-1}) 3221, 2762, 2560, 1566, 1481, 1449, 1116. MS (*m/z*, %) 427 (M^{+1}, 11), 349 (8), 209 (100), 153 (7), 57 (14). ^{1}H NMR (270.16 MHz, CDCl$_3$, δ, ppm, J, Hz) 7.67 (2H, H-15, H-17, dd, $J_o = 6.30$, $J_m = 2.2$), 7.29–7.33 (2H, H-16, H-18, m), 7.29–7.33 (1H, H-17, m), 7.25 (1H, H-4, d, $J_m = 2.2$), 6.92 (1H, H-13, s), 6.91 (1H, H-11, d, $J_o = 7.9$), 6.74 (1H, H-6, d, $J_o = 2.2$), 6.65 (1H, H-10, d, $J_o = 7.9$), 5.47 (1H, NH, s), 4.48 (1H, H-7A, dd, $J_{AB} = 12.6$, $J_{AX} = 3.7$), 4.02 (1H, H-7B, dd, $J_{AB} = 12.6$, $J_{AX} = 1.7$), 2.23 (3H, CH3-C-12, s), 1.44 (9H, tBu-C-3, s), 1.23 (9H, tBu-C-5, s). ^{13}C NMR (67.94 MHz, CDCl$_3$, δ, ppm) 157.8 (C-9), 153.3 (C-2), 142.2 (C-5), 139.2 (C-3), 132.1 (C-15, C-19), 131.2 (C-11), 128.3 (C-17), 128.1 (C-16, C-18), 127.8 (C-12), 127.2 (C-8), 124.6 (C-6), 123.2 (C-4), 121.1 (C-13), 119.5 (C-1), 113.2 (C-10), 50.8 (C-7), 35.1 (C-tBu-C-3), 34.4 (C-tBu-C-5), 30.1 (CH$_3$-tBu-C-5) 29.3 (CH$_3$-tBu-C-3). ^{11}B NMR (86.68 MHz, DMSO-d_6, δ, ppm) 8.7.

4.1.2.12. 2-(3-Aminophenyl)-4-methylbenzo[d]-3,5-ditertbu-tylbenzo[h]-6-aza-1,3-dioxa-2-boracyclononene (2l). Compound **2l** was prepared by the reaction of 0.9 g (2.66 mmol) of **1e**, 0.37 g (1.35 mmol) 3-aminophenylboronic acid, and (0.30 g, 3.57 mmol) of sodium bicarbonate to give **2o** as a yellow solid 78.0% (0.82 g, 1.86 mmol) m.p. 202–204 °C. FW = 428. IR ν_{max} (KBr, cm^{-1}) 3348, 3224, 2959, 1648, 1507, 1482, 1436, 1276, 1192, 1048, 789. MS (*m/z*, %) 442 (M$^+$, 34), 350 (37), 349 (100), 348 (40), 334 (40), 224 (76), 93 (8), ^{1}H NMR (300.18 MHz, CDCl$_3$, δ, ppm, J, Hz) 7.10 (1H, H-4, d), 7.08–7.10 (1H, H-15, m), 6.95 (1H, H-18, t, $J_o = 7.6$), 6.87 (1H, H-6, d, $J_m = 1.7$), 6.80–6.83 (1H, H-19, m), 6.82 (1H, H-11, d, $J_o = 8.1$), 6.80 (1H, H-13, s), 6.54 (1H, H-10, d, $J_o = 8.1$), 6.48 (1H, H-17, d, $J_o = 7.4$), 6.44 (1H, NH, s), 3.99 (2H, NH$_2$, s), 4.37 (1H, H-7A, d,

$J_{AB} = 13.6$, $J_{AX} = 3.6$), 3.95 (1H, H-7B, d, $J_{AB} = 13.6$, $J_{BX} = 1.7$), 1.33 (9H, tBu-C-3, s), 1.18 (9H, tBu-C-5, s). ^{13}C NMR (75.47 MHz, CDCl$_3$, δ, ppm) 158.1 (C-9), 154.0 (C-2), 148.4 (C-16), 146.1 (C-14), 141.3 (C-5), 138.0 (C-3), 130.4 (C-11), 130.1 (C-8), 128.6 (C-18), 127.1 (C-12), 123.9 (C-6) 123.6 (C-4), 122.4 (C-13), 121.7 (C-1), 120.7 (C-15), 118.7 (C-19), 114.0 (C-17), 113.2 (C-10), 49.9 (C-7), 34.7 (C-tBu-C-3), 34.3 (C-tBu-C-5), 32.3 (CH$_3$-tBu-C-5) 30.6 (CH$_3$-tBu-C-3), 21.2 (C-Me). ^{11}B NMR (96.29 MHz, CDCl$_3$, δ, ppm) 9.6.

5. Supplementary material

Acknowledgements

References

[1] R. Contreras, C. García, T. Mancilla, B. Wrackmeyer, J. Organomet. Chem. 246 (1983) 213.
[2] N. Farfán, T. Mancilla, D. Castillo, G. Uribe, L. Carrillo, P. Joseph-Nathan, R. Contreras, J. Organomet. Chem. 381 (1990) 1.
[3] N. Farfán, R. Contreras, J. Chem. Soc., Perkin Trans. 2 (1988) 1787.
[4] H.I. Beltrán, L.S. Zamudio-Rivera, T. Mancilla, R. Santillán, N. Farfán, J. Organomet. Chem. 657 (2002) 194.
[5] T. Mancilla, R. Contreras, B. Wrackmeyer, J. Organomet. Chem. 307 (1986) 1.
[6] T. Mancilla, R. Contreras, J. Organomet. Chem. 321 (1987) 191.
[7] N. Farfán, P. Joseph-Nathan, L.M. Chiquete, R. Contreras, J. Organomet. Chem 348 (1988) 149.
[8] H. Höpfl, N. Farfán, J. Organomet. Chem. 547 (1997) 71.
[9] N. Farfán, H. Hopfl, V. Barba, M.E. Ochoa, R. Santillán, E. Gómez, A. Gutiérrez, J. Organomet. Chem. 581 (1999) 70.
[10] V. Barba, R. Luna, D. Castillo, R. Santillán, N. Farfán, J. Organomet. Chem. 604 (2000) 273.
[11] V. Barba, D. Cuahutle, M.E. Ochoa, R. Santillán, N. Farfán, Inorg. Chim. Acta 303 (2000) 7.
[12] V. Barba, D. Cuahutle, R. Santillán, N. Farfán, Can. J. Chem. 79 (2001) 1229.
[13] H. Höpfl, N. Farfán, D. Castillo, R. Santillán, A. Gutiérrez, J.C. Darán, J. Organomet. Chem. 553 (1998) 221.
[14] N. Farfán, D. Silva, R. Santillán, Heteroatom Chem. 4 (1993) 533.
[15] J. Trujillo, H. Höpfl, D. Castillo, R. Santillán, N. Farfán, J. Organomet. Chem. 571 (1998) 21.
[16] T. Mancilla, L. Carrillo, M. de la P. Reducindo, Polyhedron 15 (1996) 3777.

[17] H. Höpfl, N. Farfán, D. Castillo, R. Santillán, R. Contreras, F.J. Martínez-Martínez, M. Galván, R. Álvarez, L. Fernández, S. Halut, J.C. Darán, J. Organomet. Chem. 544 (1997) 175.

[18] H. Höpfl, M. Sanchez, N. Farfán, V. Barba, Can. J. Chem. 76 (1998) 1352.

[19] H. Höpfl, M. Sanchez, V. Barba, N. Farfán, Inorg. Chem. 37 (1998) 1679.

[20] H. Höpfl, M. Galván, N. Farfán, R. Santillán, J. Mol. Struct. Theochem. 427 (1998) 1.

[21] (a) V. Barba, E. Gallegos, R. Santillán, N. Farfán, J. Organomet. Chem. 622 (2001) 259;
(b) V. Barba, H. Höpfl, N. Farfán, R. Santillán, H.I. Beltrán, L.S. Zamudio-Rivera, Chem. Commun. (2005) 2834.

[22] N. Farfán, R. Santillán, H. Höpfl, Main Group Chem. News 7 (1999) 3.

[23] H. Höpfl, J. Organomet. Chem. 581 (1999) 129.

[24] S.J. Rettig, J. Trotter, Can. J. Chem. 53 (1975) 1393;
S.J. Rettig, J. Trotter, Can. J. Chem. 54 (1976) 3130;
W. Kliegel, G. Lubkowitz, S.J. Rettig, J. Trotter, Can. J. Chem. 70 (1992) 2033.

[25] H.I. Beltrán, S.J. Alas, R. Santillán, N. Farfán, Can. J. Chem. 80 (2002) 801.

[26] H.I. Beltrán, A. Abreu, L.S. Samudio-Rivera, T. Mancilla, R. Santillán, N. Farfán, Rev. Soc. Quim. Mex. 45 (2001) 152.

[27] D.C.H. Oakes, B.S. Kimberley, V.C. Gibson, D.J. Jones, A.J.P. White, D.J. Williams, Chem. Commun. 19 (2004) 2174.

[28] E.W. Ainscough, A.M. Brodie, J.E. Plowman, K.L. Brown, A.W. Addison, A.R. Gainsford, Inorg. Chem. 19 (1980) 3655.

[29] O.A. Rajan, J.T. Spence, C. Leman, M. Minelli, M. Sato, J.H. Enemark, P.M.H. Kroneck, K. Sulger, Inorg. Chem. 22 (1983) 3065.

[30] M. Thirumavalavan, S.M. Rayappan, P. Akilan, M. Kandaswamy, Ind. J. Chem. Technol. 11 (2004) 29.

[31] V.T. Kasumov, A.A. Medzhidov, Russian J. Coord. Chem. 21 (1995) 747.

[32] H.D. Grimmecke, S. Huneck, K. Schreiber, Ch. Schulze, G. Sembdner, Ger. (East) (1976) 16;
S.J. Rettig, J. Trotter, Can. J. Chem. 51 (1973) 1288;
W. Kliegel, U. Riebe, S.J. Rettig, J. Trotter, Can. J. Chem. 73 (1995) 835.

[33] (a) N. Farfán, T. Mancilla, R. Santillán, A. Gutiérrez, L.S. Zamudio-Rivera, H.I. Beltrán, J. Organomet. Chem. 689 (2004) 3481;
(b) V. Barba, J. Vázquez, F. López, R. Santillán, N. Farfán, J. Organomet. Chem. 690 (2005) 2351.

[34] G.M. Sheldrick, SHELX-97, Program for Crystal Structure Solution, University of Göttingen, Göttingen, 1993.

[35] PLATON (PARST subset): A.L. Spek, J. Appl. Crystallogr. 36 (2003) 7.

[36] WinGX program set: L. Farrugia, J. Appl. Crystallogr. 32 (1999) 837.

[37] ORTEP 3 program: L. Farrugia, J. Appl. Crystallogr. 30 (1997) 565.