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Synthesis, characterization and X-ray studies of new chiral five-six-membered ring, [4.3.0] heterobicyclic system of monomeric boronates

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ABSTRACT

Nine new boronates, six of them chiral, with five-six-membered ring heterobicycles were prepared by reaction of the Schiff bases and phenyl boronic acid. The boronates were fully characterized by spectroscopic techniques, NMR ^{1}H, ^{13}C, ^{11}B, Infrared spectroscopy, mass spectrometry and elemental analysis. The reaction showed high diasteroselectivity, only in the case of compound **4c**, containing a methyl substituent in the aliphatic moiety, the induction is low giving a 2:1 mixture of two diatereoisomers. The results showed that the preferred stereochemistry in the heterocycles is that where all substituents in the five membered ring and the phenyl group attached to boron atom are on the same side.

1. Introduction

In the last years there has been great interest in the study of boron complexes due to the great number of applications found, for example in medicinal chemistry, as anticancer agents directly applied in the technique known as boron neutron capture therapy used for the treatment of certain brain tumors [1], some boron compounds also present cytotoxic activity [2–4]. Moreover, they also display a wide range of applications in organic synthesis [5,6] supramolecular chemistry [7], macrocyclic chemistry [8,9], organometallics [10], dendrimers [11,12] among others. Our group has reported several studies on the N → B coordination bond [13–16] and recently the synthesis and characterization of boron complexes obtained from the condensation of 3-aminophenylboronic acid and 1,3-diketones [17].

In this paper, we describe the synthesis of nine new [4.3.0] heterobicyclic boronates, derived from ethanolamines, as well as the study of the structures and stereochemistry of the six chiral boron complexes which were obtained with high Diastereoselectivity. The results from X-ray diffraction indicated high strain present in the five member rings of the molecules as well as the envelope conformation, the tetrahedral character of the boron atoms which is directly associated to the geometry [18,19] showed deviation from ideal values. The configurational stability at the boron atom is closely related to the size of the substituents attached to the aliphatic carbons in the ethanol amine residues. In previous studies it has been shown that the addition of phenyl boronic acid to salicylidenimino alcohols produces dimeric (**1a**–**1d**) or monomeric (**2**) boronates [20,21] which are stable in air and are obtained in high yields in one step synthesis. (Scheme 1).

These boronate units are connected by two covalent B–O and coordinative N→B bonds, which are responsible for the hydrolytic stability of these molecules [22,23]. Dimeric complexes have been obtained when the ligands have zero (**1a**) [20], two (**1b**) [21], four [24], five (**1c**) or six (**1d**) [21e] methylene units between the imino and the hydroxyl groups. The studies indicated that formation of the dimeric compound is favored because the monomeric systems would be too strained owing to the tetrahedral geometry at the boron atom, as well as its small atomic radius. When the imino alcohol is substituted with three methylene groups, a monomeric specie is obtained because the tridentate ligand permits the formation of a stable [4.4.0] heterobicyclic system (**2**) [21e,25]. However, the use of harder reaction conditions, for example toluene and 24 h of refluxing favored the monomeric especies than the dimeric ones. In the present work, we describe the synthesis of monomeric boronates (**4a**–**4i**) with five-six fused membered rings

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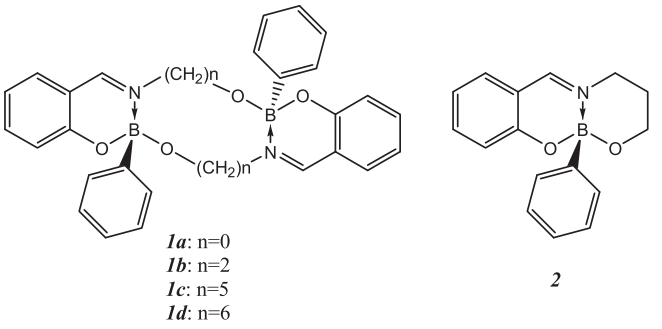
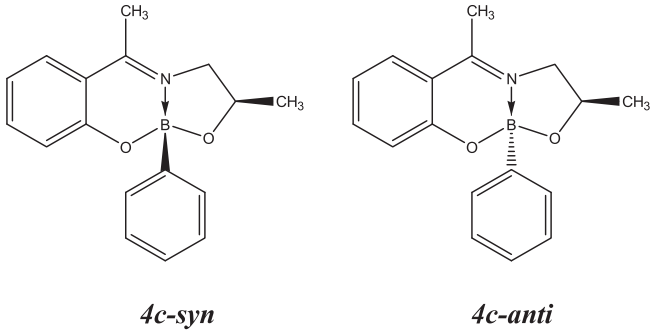


Scheme 1. Monomeric and dimeric boronates obtained with different methylene units in the iminodialcohol moiety.



Scheme 3. Products from the reaction of **3c** with phenyl boronic acid.

derived from optically active ethanolamines (Schemes 2 and 3), as well as the NMR and X-ray studies, this boronates can be apply in assymetric synthesis as catalysts [26].

2. Experimental

2.1. Instrumentation

NMR spectra were recorded in $CDCl_3$ and DMSO-d_6 solutions on Bruker Advance DPX 300 and Jeol Eclipse +400 spectrometers. Chemical shifts (ppm) are relative to $(CH_3)_4Si$ for ^1H and ^{13}C and $BF_3{\cdot}OEt_2$ for ^{11}B. Coupling constants are reported in Hz. Infrared spectra were recorded on a Perkin–Elmer 16F-PC FT-IR spectrometer. Mass spectra were recorded on a Hewlet-Packard model 5989 engine, coupled to an HP 5890 Series II GC. Melting points were obtained on a Gallenkamp MFB-595 apparatus and are uncorrected. Elemental analyses were carried out on a thermo finnigan model Flash 1112. The X-ray diffraction study was determined on an Enraf-Nonius-Fr590 Kappa-CCD ($\lambda_{MoK\alpha}$ = 0.71073 Å, graphite monochromator, T = 293 K, CCD rotating images scan mode) and the crystal was mounted on a LINDEMANN tube. Absorption correction was not necessary. All reflections data set were corrected for Lorentz and Polarization effects. Structure solution and refinement were performed using the SHELX-S-97 program and then SHELX-L-97 program was applied for refinement and output data [26,27]. All software manipulations were done under the WINGX environment program set [28]. Molecular perspectives were drawn under ORTEP-3 [29], and Diamond 2.1e drawing applications.

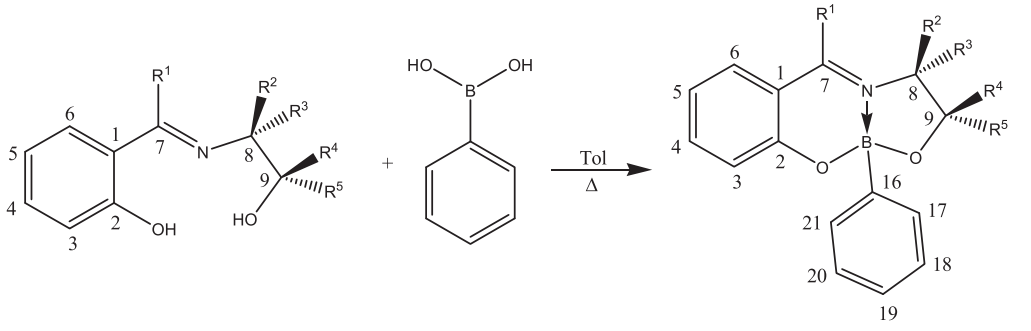
2.2. Reagents

All reactants and solvents were purchased from Aldrich Chemical Co. and solvents were dried previous to use. Single crystals were grown using spectroscopic grade solvents.

2.3. Synthesis

2.3.1. General method for the preparation of tridentate ligands *3b* and *3g*

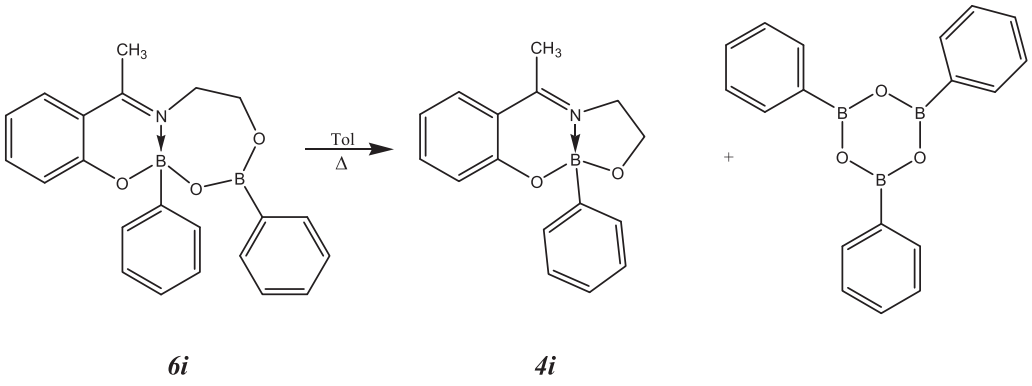
In order to prepare the tridentate ligands **3b** and **3g**, equimolar quantities of the corresponding aminoalcohol and 2-hydroxybenzophenone or 2-hydroxyacetophenone, respectively, were refluxed in ethanol for 1 h. The solvent and the water formed during the reaction were eliminated to yield yellow solids which were washed with methylene chloride and used without further purification. Tridentate ligands **3a**, **3c**, **3d**, **3e**, **3f**, **3h** and **3i** have already been published [21,30–34].



3a-3h

Comp.	R^1	R^2	R^3	R^4	R^5
4a	CH_3	CH_3	H	Ph	H
4b	CH_3	H	Ph	H	H
4c	CH_3	H	H	CH_3	H
4d	H	H	Ph	H	H
4e	H	H	Ph	H	Ph
4f	H	CH_3	H	Ph	H
4g	Ph	H	Ph	H	H
4h	Ph	H	H	H	H
4i	CH_3	H	H	H	H

Scheme 2. Synthesis of monomeric boronates **4a**–**4h** with six and five membered rings, derived from optically active ethanolamines and phenyl boronic acid.



6i *4i*

Scheme 4. Synthesis of boronates with [4.3.0] heterobicycles (**4i**) using as starting materials boronates with [4.5.0] heterobicycles (**6i**).

2.3.1.1. 2-[1-(2-hydroxy-(1R)-phenyl-ethylimino)-ethyl]-phenol ***3b***. Prepared from 2-hydroxyacetophenone (1.00 g, 7.34 mmol) and (R)-(−)-phenylglycinol (1.00 g 7.34 mmol). The product was obtained as a yellow solid (1.85 g, 7.24 mmol), yield 98%, mp: 95–97 °C. IR υ_{max} (KBr): 3059 (OH), 2839, 1611 (C=N), 1449, 1340, 1285, 1149, 1068, 845, 753, 701, 636, 565, 524, 444 cm^{-1} ^{1}H NMR (300 MHz, $CDCl_3$) [δ, ppm]: 2.36 (s, 3H, CH_3), 3.98 (q, 1H, J = 4.9 Hz, H-8), 4.01 (q, 1H, J = 8.3, H-9a), 5.00 (dd, 1H, J = 2.6 Hz, 4.93 Hz, H-9b), 6.80 (t, 1H, J = 7.2 Hz, H-5), 6.98 (d, 1H, J = 8.4 Hz, H-3), 7.26–7.38 (m, 6H, H-4, H-11, H-12, H-13, H-14, H-15), 7.52 (d, 1H, J = 8.1 Hz, H-6). ^{13}C NMR (75.46 MHz, $CDCl_3$) [δ, ppm] 15.6 (CH_3), 65.7 (C-8), 68.6 (C-9), 117.6 (C-5), 119.8 (C-3), 119.5 (C-1), 127.5 (C-12, 14), 128.1 (C-6), 128.8 (C-13), 129.2 (C-11, 15), 133.2 (C-4), 139.3 (C-10), 164.2 (C-2), 174.0 (C-7). MS (*m/z*, %): 255 (M^+, 28), 240 (3), 224 (100), 209(7), 183 (9), 165 (11), 146 (9), 136 (23), 120 (42), 103 (15), 91 (31), 77 (17). Anal. Calc. for $C_{16}H_{17}NO_2$: C, 75.27; H, 6.71; N, 5.49. Found C, 75.11; H, 6.52; N, 5.33%.

2.3.1.2. 2-[(2-hydroxy-1-phenyl-ethylimino)-phenyl-methyl]-phenol ***3g***. Prepared from 2-hydroxybenzophenone (1.00 g, 5.04 mmol) and (R)-(−)-phenylglycinol (1.00 g 5.04 mmol). The product was obtained as a yellow solid (1.48 g, 4.67 mmol), yield 92%, mp: 112–116 °C. IR υ_{max} (KBr): 3048 (OH), 2832, 1605 (C=N), 1438, 1345, 1289, 1152, 1053, 841, 750, 712, 632, 560, 529, 512, 413 cm^{-1} ^{1}H NMR (300 MHz, $CDCl_3$) [δ, ppm]: 3.78 (dd, 1H, J = 4.7 Hz, 6.4 Hz, H-9a), 3.95 (dd, 1H, J = 3.2 Hz, 8.2 Hz, H-9b), 4.5 (dd, 1H, J = 3.5 Hz, 4.7 Hz, H-9a), 6.62 (t, 1H, J = 8.2 Hz, H-5), 6.78 (dd, 1H, J = 1.7 Hz, 6.2 Hz, H-3), 6.98 (d, 1H, J = 8.2 Hz, H-6), 7.18–7.56 (m, 11H, H-4, H-11, H-12, H-13, H-14, H-15, H-17, H-18, H-19, H-20, H-21). ^{13}C NMR (75.46 MHz, $CDCl_3$) [δ, ppm] 67.3 (C-8), 68.0 (C-9), 117.6 (C-5), 118.2 (C-3), 119.2 (C-1), 127.3 (C-12, C-14), 127.8 (C-13), 128.5 (C-18), 128.6 (C-6), 128.9 (C-11, C-15), 129.2 (C-20), 132.0 (C-19), 133.0 (C-17), 133.7 (C-21), 136.5 (C-10), 137.9 (C-16), 139.8 (C-4), 163.6 (C-2), 175.6 (C-7). MS (*m/z*, %): 318 (M^+, 1), 211 (100), 194 (4), 182 (2), 165 (2), 132 (7), 116 (5), 91 (9), 77 (2). Anal. Calc. for $C_{21}H_{19}NO_2$: C, 79.47; H, 6.03; N, 4.41. Found C, 79.27; H, 5.98; N, 4.36%.

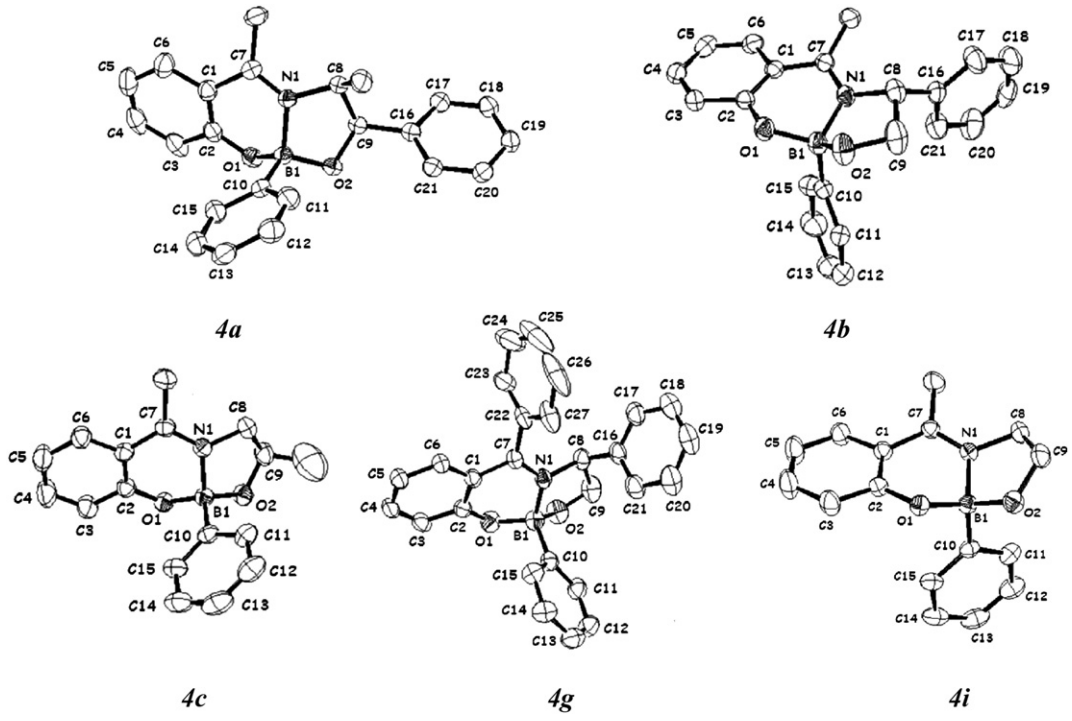
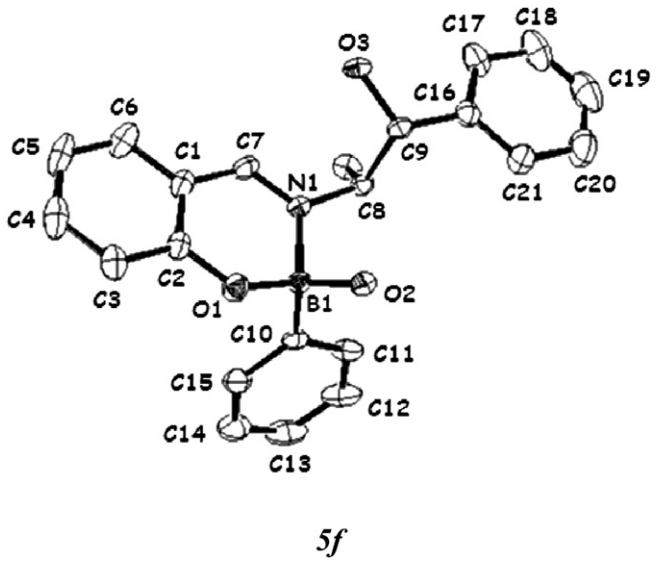


Fig. 1. Molecular structures for compounds **4a**–**4c**, **4g** and **4i**, hydrogens are omitted for clarity.



5f

Fig. 2. Molecular structure for compound **5f**.

*2.3.2. General method for the preparation of compounds **4a**–**4h***

To prepare compounds **4a**–**4h**, equimolar quantities of the corresponding tridentate ligands **3a**–**3h** and phenyl boronic acid, were refluxed in toluene for 24 h. The solvent and the water formed during the reaction were eliminated to yield yellow solids that were then washed with methylene chloride and purified by recrystallization using chloroform.

*2.3.2.1. (2S,4R,5S)-2-(Phenyl)benzo[j]-4-phenyl-5-methyl-7-methyl-6-aza-1,3-dioxa-2-boracyclononen-6-ene **4a**.* Compound **4a** was synthesized from 0.30 g (1.11 mmol) of **3a** and 0.14 g (1.11 mmol) of phenyl boronic acid. The reaction was carried out in toluene under reflux, using a Dean–Stark trap during 24 h. The product was obtained as a yellow solid 0.21 g (0.59 mmol), yield, 53%, $[\alpha]_D^{25} = +87.4$ (c 0.101 $CHCl_3$), mp: 233–237 °C. IR υ_{max} (KBr): 3062, 2928, 2864, 1638 (C=N), 1553, 1473, 1451, 1314, 1265, 1169, 1076, 1021, 861, 752, 701, 649, 580, 524, 474 cm^{-1} ^1H NMR (300 MHz, DMSO-d_6) [δ, ppm]: 1.02 (d, 3H, $J = 6$ Hz, CH_3), 2.62 (s, 3H, CH_3), 4.35 (m, 1H, H-8), 5.48 (d, 1H, $J = 5$ Hz, H-9), 6.89 (t, 1H, $J = 8.1$ Hz, H-5), 7.08 (d, 1H, $J = 8.4$ Hz, H-3), 7.18–7.26 (m, 3H, H-18, H-20, H-13), 7.31 (t, 1H, $J = 8.1$ Hz, H-4), 7.35–7.39 (m, 2H, H-12, H-14), 7.39–7.44 (m, 2H, H-17, H-21), 7.48–7.54 (m, 4H, H-6, H-19, H-11, H-15). ^{13}C NMR (75.46 MHz, $CDCl_3$) [δ, ppm]: 14.9 (CH_3), 18.4 (CH_3), 63.2 (C-8), 80.3 (C-9), 119.2 (C-5), 120.9 (C-1), 121.5 (C-3), 126.8 (C-18, 20), 127.2 (C-13), 127.5 (C-12, 14), 127.7 (C-19), 128.5 (C-6), 128.6 (C-17, 21), 131.7 (C-11, 15), 137.0 (C-4), 139.9 (C-16), 161.1 (C-2), 167.0 (C-7). ^{11}B NMR (96.29 MHz, $CDCl_3$), [δ, ppm]: 5.6($h_{1/2} = 260$ Hz). MS (*m/z*, %): 354 (M^+, 0.1), 278 (100), 248 (7), 162 (32), 117 (1), 91 (1). Anal. Calc for $C_{23}H_{22}BNO_2$: C, 77.76; H, 6.24; N, 3.94. Found C, 77.39; H, 6.29; N, 3.87%.

*2.3.2.2. (2S,5R)-2-(Phenyl)benzo[j]-5-phenyl-7-methyl-6-aza-1,3-dioxa-2-boracyclononen-6-ene **4b**.* Compound **4b** was synthesized from 0.30 g (1.55 mmol) of **3b** and 0.183 g (1.55 mmol) of phenyl boronic acid. The reaction was carried out in toluene under reflux, using a Dean–Stark trap during 24 h. The product was obtained as a yellow solid 0.29 g (1.04 mmol), yield, 67%, mp: 194–202 °C $[\alpha]_D^{25} = +209.3$ (c 0.097 $CHCl_3$), IR υ_{max} (KBr): 3061, 2930, 2868, 1641 (C=N), 1553, 1472, 1451, 1315, 1263, 1170, 1070, 1022, 859, 753, 702, 650, 526, 474 cm^{-1} ^1H NMR (300 MHz, DMSO-d_6) [δ, ppm]: 2.36 (CH_3), 4.02 (dd, 1H, $J = 7.7$ Hz, 3 Hz, H-9a), 4.58 (dd, 1H, $J = 7.7$ Hz, 3.0 Hz, H-9b), 5.05 (dd, 1H, $J = 7.7$ Hz, 3.0 Hz, H-8), 6.88 (t, 1H, $J = 8.0$ Hz, H-5), 7.01 (d, 1H, $J = 8.0$ Hz, H-3), 7.06–7.09 (m, 2H, H-18, H-20), 7.18–7.20 (m, 3H, H-12, H-13, H-14), 7.24–7.27 (m, 3H, H-17, H-19, H-21), 7.39–7.42 (m, 3H, H-4, H-11, H-15), 7.48 (dd, 1H, $J = 8.0$ Hz, 3.0 Hz, H-6). ^{13}C NMR (75.46 MHz, DMSO-d_6) [δ, ppm]: 18.6 (CH_3), 65.7 (C-8), 70.5 (C-9), 119.2 (C-5), 120.8 (C-1), 121.1 (C-3), 127.3 (C-18, 20), 127.4 (C-13), 127.6 (C-12, 14), 128.2 (C-6), 128.3 (C-19), 129.3 (C-17, 21), 131.1 (C-11, 15), 136.9 (C-4), 138.3 (C-16), 159.7 (C-2), 169.9 (C-7). ^{11}B NMR (96.29 MHz, $CDCl_3$), [δ, ppm]: 6.1 ($h_{1/2} = 396$ Hz). MS (*m/z*, %): 341 (M^+, 0.3), 310 (4), 264 (100), 236 (2), 162 (20). Anal. Calc for $C_{22}H_{20}BNO_2$: C, 77.44; H, 5.91; N, 4.11. Found C, 77.93; H, 5.87; N, 4.11%.

Table 1
Crystallographic data for compounds **4a**, **4b**, **4c**, **4i**, **4g** and **5f**.

Compound	**4a**	**4b**	**4c**	**4g**	**4i**	**5f**
Chemical formula	$C_{23}H_{22}BNO_2$	$C_{22}H_{20}BNO_2$	$C_{17}H_{18}BNO_2$	$C_{27}H_{22}BNO_2$	$C_{16}H_{16}BNO_2$	$C_{21}H_{22}BNO_2$
Formula weight	355.23	341.20	279.13	403.28	265.11	331.21
Space group	P $2_12_12_1$	P 2_1	P 2_1	P 2_1	P $2_1/n$	P $2_12_12_1$
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Orthorhombic
Crystal size (mm)	0.2 x 0.2 x 0.1	0.1 x 0.1 x 0.1	0.12x0.1x0.1	0.2x0.1x 0.1	0.1x.05x .05	0.12x0.1x0.1
a (Å)	9.7792(4)	8.6473(2)	8.6619(5)	8.3990(3)	8.5671(2)	7.09570(10)
b (Å)	12.7252(6)	10.9323(3)	9.9421(6)	10.7430(3)	9.6308(2)	13.0448(3)
c (Å)	15.3413(6)	10.6276(3)	17.0126(11)	12.0826(4)	17.2100(4)	20.5644(5)
α (°)	90	90	90	90	90	90
β (°)	90	112.5290(10)	92.584(4)	92.7180(10)	92.8220	90
γ (°)	90	90	90	90	90	90
Formula units per cell	4	2	4	3	4	4
δ_{calc} (g cm^{-3})	1.236	1.221	1.267	1.230	1.242	1.156
F (000)	752	360	592	424	560	704
Temperature of measurement (K)	293(2)	293(2)	293(2)	293(2)	293(2)	293(2)
θ Limits (°)	3.47-27.50	4.15-27.49	3.87-27.48	4.15-27.53	3.44-27.46	3.42-27.48
No. of reflections collected	4161	3840	5699	4756	23752	12053
No. of independent reflections	4181	3848	3218	4767	24680	12094
No. of observed reflections, $(F_o)^2 > 4\sigma(F_o)^2$	2534	3108	1921	3416	2166	3366
$R = \sum \lvert F_o \rvert - \lvert F_c \rvert / \sum \lvert F_o \rvert$	0.0447	0.0393	0.0771	0.0494	0.0485	0.0398
$R_w = [\sum_w(\lvert F_o \rvert - \lvert F_c \rvert)^2 / \sum wF_o^2]^{1/2}, w = 1/\sigma^2$	0.0879	0.0883	0.2084	0.1170	0.1127	0.0812
Goodness-of-fit σ	1.002	1.048	1.011	1.033	1.011	1.034
No. of parameters	333	316	190	285	246	305
Maximun Δ/σ	0.014	-0.010	-0.068	0.032	0.055	0.057
$\Delta\rho_{min}$ (e $Å^{-3}$)	-0.115	-0.109	-0.383	-0.141	-0.144	-0.130
$\Delta\rho_{max}$ (e $Å^{-3}$)	0.118	0.102	0.196	0.173	0.231	0.138

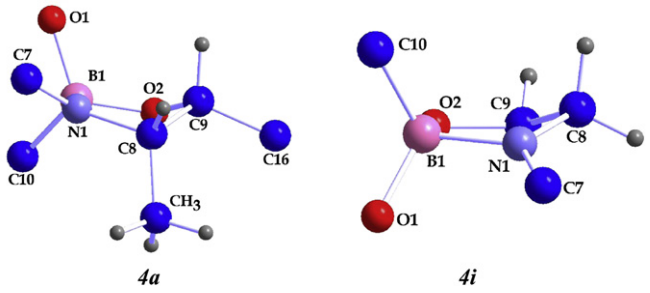


Fig. 3. Envelope conformation for the five membered rings in compounds **4a** and **4i**.

*2.3.2.3. (4R)-2-(Phenyl)benzo[j]-4-methyl-7-methyl-6-aza-1,3-dioxa-2-boracyclononen-6-ene **4c**.* Compound **4c** was synthesized from 0.30 g (1.55 mmol) of the ligand **3c** and 0.19 g (1.55 mmol) of phenyl boronic acid. The reaction was carried out in toluene under reflux, using a Dean–Stark trap during 24 h. The product was obtained as a yellow solid 0.23 g (0.82 mmol), yield, 53%, mp: 148–152 °C $[\alpha]_D^{25} = -216.1$ (c 0.079 $CHCl_3$), IR υ_{max} (KBr): 3065, 2969, 2925, 2856, 1650 (C=N), 1607, 1556, 1476, 1455, 1380, 1349, 1320, 1274, 1181, 1116, 1086, 1029, 997, 943, 874, 846, 751, 705, 642, 581, 523, 486, 450 cm^{-1} ^1H NMR (300 MHz, DMSO-d_6) [δ, ppm]: 1.48 (d, CH_3), 2.42 (s, CH_3), 3.60 and 3.93 (m, 2H, H-8a, 8b), 4.27 (m, 1H, H-9), 6.85 (t, 1H, $J = 7.0$ Hz, H-5), 7.13–7.19 (m, 4H, H-3, H-12, H-13, H-14), 7.45 (m, 2H, H-11, 15), 7.45–7.52 (m, 2H, H-4, H6). ^{13}C NMR (75.46 MHz, $CDCl_3$) [δ, ppm]: 18.3 (CH_3), 20.8 (CH_3), 57.6 (C-8), 71.0 (C-9), 118.8 (C-5), 119.8 (C-1), 120.7 (C-3), 127.1 (C-13), 127.2 (C-12, C-14), 128.5 (C-6), 132.0 (C-11, C-15), 136.6 (C-4), 160.5 (C-2), 166.1 (C-7).^{11}B NMR (96.29 MHz, $CDCl_3$), [δ, ppm]: 6.0 ($h_{1/2} = 241$ Hz). MS (*m/z*, %): 279 (M^+, 0.2), 202 (100), 174 (0.3), 101 (13), 77 (23). Anal. Calc for $C_{17}H_{18}BNO_2$: C, 73.15; H, 6.50; N, 5.02. Found C, 73.42; H, 6.79; N, 4.95%.

*2.3.2.4. (2S,5R)-2-(Phenyl)benzo[j]-5-phenyl-6-aza-1,3-dioxa-2-boracyclononen-6-ene **4d**.* Compound **4d** was synthesized from 0.30 g (1.24 mmol) of the ligand **3d** and 0.15 g (1.24 mmol) of phenyl boronic acid. The reaction was carried out in toluene under reflux, using a Dean–Stark trap during 24 h. The product was obtained as a yellow solid 0.26 g (0.79 mmol), yield, 64%, mp: 210–215 °C $[\alpha]_D^{25} = +189.3$ (c 0.092 $CHCl_3$), IR υ_{max} (KBr): 3059, 2935, 2872, 1635 (C=N), 1548, 1470, 1455, 1319, 1259, 1158, 1067, 1029, 845, 759, 712, 657, 514, 521, 479, 423 cm^{-1} ^1H NMR (300 MHz, DMSO-d_6) [δ, ppm]: 4.23 (dd, 1H, $J = 8.0$ Hz, 5.0 Hz, H-9a), 4.83 (dd, 1H, $J = 8.0$ Hz, 3.0 Hz, H-9b), 5.02 (dd, 1H, $J = 8.0$ Hz, 3.0 Hz, H-8), 7.06 (t, 1H, $J = 8.0$ Hz, H-5), 7.15 (d, 1H, $J = 8.0$ Hz, H-3), 7.18–7.21 (m, 2H, H-18, H-20), 7.21–7.23 (m, 3H, H-12, H-13, H-14), 7.25–7.28 (m, 3H, H-17, H-19, H-21), 7.40–7.42 (m, 3H, H-4, H-11, H-15), 7.61 (dd, 1H, $J = 8.0$ Hz, 2.5 Hz, H-6), 7.84 (s, 1H, H-7). ^{13}C NMR (75.46 MHz, DMSO-d_6) [δ, ppm]: 64.8 (C-8), 71.5 (C-9), 119.8 (C-5), 121.4 (C-1), 122.3 (C-3), 128.1 (C-18, C-20), 127.0 (C-13), 128.2 (C-12, C-14), 128.5 (C-6), 128.6 (C-19), 129.7 (C-17, C-21), 131.8 (C-11, C-15), 137.0 (C-4), 138.5 (C-16), 160.0 (C-2), 165.8 (C-7). ^{11}B NMR (96.29 MHz, $CDCl_3$), [δ, ppm]: 4.7 ($h_{1/2} = 297$ Hz). MS (*m/z*, %): 327 (M^+, 0.1), 251 (100), 223 (0.5), 173 (0.2), 149 (4), 90 (0.1), 78 (0.1). Anal. Calc for $C_{21}H_{18}BNO_2$: C, 77.09; H, 5.55; N, 4.28. Found C, 77.16; H, 5.50; N, 4.26%.

*2.3.2.5. (4S,5R)-2-(Phenyl)benzo[j]-4-phenyl-5-phenyl-6-aza-1,3-dioxa-2-boracyclononen-6-ene **4e**.* Compound **4e** was synthesized from 0.30 g (0.94 mmol) of the ligand **3e** and 0.11 g (0.94 mmol) of phenyl boronic acid. The reaction was carried out in toluene under reflux, using a Dean–Stark trap during 24 h. The product was obtained as a yellow solid 0.24 g (0.59 mmol), yield, 63%, mp: 122–130 °C $[\alpha]_D^{25} = -14.9$ (c 0.114 $CHCl_3$), IR υ_{max} (KBr): 3063, 2958, 2921, 2869, 1645 (C=N), 1609, 1553, 1494, 1454, 1384, 1291, 1256, 1215, 1176, 1154, 1126, 1050, 1026, 979, 919, 876, 805, 759, 700, 630, 597, 565, 544, 517, 455 cm^{-1} ^1H NMR (300 MHz, DMSO-d_6) [δ, ppm]: 4.52 (d, 1H, $J = 7.0$ Hz, H-8), 5.04 (d, 1H, $J = 7.0$ Hz, H-9), 6.82 (t, 1H, $J = 7.0$ Hz, H-5), 6.95 (d, 1H, $J = 8.0$ Hz, H-3), 7.08 (d, 1H,

Table 2
Selected bond distances (Å), bond angles (°) and dihedral angles (°) for compounds **4a**, **4b**, **4c**, **4g**, **4i** and **5f**.

Compound	4a	4b	4c	4g	4i	5f
Bond distances (Å)						
N(1)-C(8)	1.476(3)	1.482(2)	1.465(3)	1.485(4)	1.466(2)	1.4807(19)
N(1)-C(7)	1.290(3)	1.288(2)	1.294(3)	1.302(4)	1.290(19)	1.2903(19)
O(1)-C(2)	1.335(3)	1.343(2)	1.345(3)	1.336(4)	1.346(19)	1.3320(19)
O(2)-C(9)	1.418(3)	1.420(2)	1.412(4)	1.402(5)	1.412(2)	––
C(8)-C(9)	1.545(3)	1.542(3)	1.523(5)	1.549(6)	1.522(3)	1.547(2)
B(1)-O(1)	1.490(3)	1.475(2)	1.475(3)	1.477(5)	1.484(2)	1.491(2)
B(1)-O(2)	1.440(3)	1.442(2)	1.444(3)	1.440(5)	1.445(2)	1.442(2)
B(1)-N(1)	1.605(3)	1.590(2)	1.588(3)	1.591(5)	1.582(2)	1.607(19)
B(1)-C(10)	1.614(4)	1.608(3)	1.620(4)	1.617(5)	1.615(2)	1.617(2)
Bond angles (°)						
C(8)-N(1)-B(1)	108.96(17)	108.41(14)	108.3(2)	109.2(3)	108.27(13)	117.95(11)
N(1)-B(1)-O(2)	100.64(16)	99.83(14)	101.5(2)	100.6(3)	101.55(12)	104.15(12)
B(1)-O(2)-C(9)	110.46(16)	107.27(14)	112.5(2)	108.4(3)	112.27(13)	––
O(2)-C(9)-C(8)	105.26(18)	106.63(18)	108.3(2)	109.3(3)	108.46(14)	––
C(9)-C(8)-N(1)	99.00(15)	101.98(15)	101.5(2)	101.0(3)	101.28(14)	109.94(12)
C(7)-N(1)-B(1)	123.07(17)	124.07(14)	123.7(2)	123.7(3)	124.38(13)	122.24(13)
N(1)-B(1)-O(1)	102.91(17)	107.07(15)	106.1(19)	107.6(3)	106.00(12)	107.76(11)
B(1)-O(1)-C(2)	116.77(17)	118.03(12)	116.1(2)	119.1(2)	116.89(12)	124.83(12)
C(2)-C(1)-C(7)	117.00(2)	118.11(15)	119.0(2)	118.8(3)	118.61(13)	119.14(14)
C(1)-C(7)-N(1)	116.64(19)	116.91(15)	116.2(2)	117.3(3)	116.39(14)	122.48(15)
Dihedral angles (°)						
O(1)-B(1)-C(10)-C(15)	-5.5(3)	64.9(2)	-0.8(3)	60.1(4)	2.6(2)	-5.74(19)
O(2)-B(1)-C(10)-C(11)	42.1(3)	14.8(2)	-52.3(3)	10.4(4)	-50.0(2)	49.73(19)
N(1)-B(1)-C(10)-C(15)	111.4(2)	55.5(2)	-119.2(3)	-60.0(4	-115.8(16)	112.73(16)
N(1)-B(1)-C(10)-C(11)	-72.6(3)	127.8(17)	60.9(3)	124.4(3)	63.5(19)	-67.73(18)
Deviation from mean plane (Å)						
Plane: C(2)-C(1)-C(7)-N(1)-B(1)-O(1)-B(1)	-0.305	0.228	-0.26	-0.212	0.254	0.100
Plane: B(1)-N(1)-C(8)-C(9)-O(2)	C(9) -0.236	O(2) -0.246	C(8) -0.171	O(2) 0.207	C(8) 0.173	––

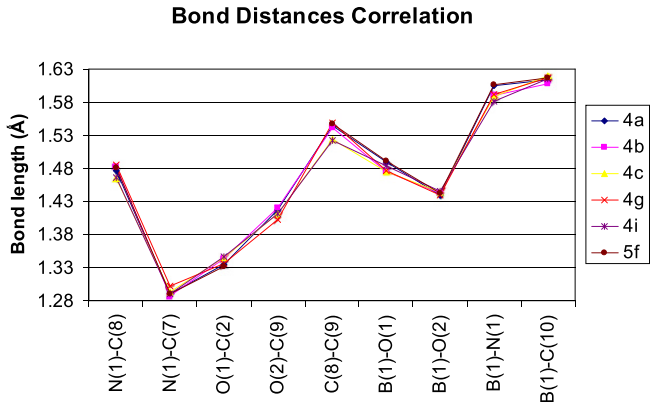


Fig. 4. Bond distances correlation for compounds **4a**–**4c**, **4g**, **4i** and **5f**.

$J = 7.0$ Hz, H-6), 7.25–7.39 (m, 16 H, H-4, H-11, H-12, H-13, H-14, H-15, H-17, H-18, H-19, H-20, H-21, H-23, H-24, H-25, H-26, H-27), 8.07 (s, 1H, H-7). ^{13}C NMR (75.46 MHz, $CDCl_3$) [δ, ppm]: 78.4 (C-8), 80.2 (C-9), 117.0 (C-3), 118.8 (C-5), 119.2 (C-1), 127.3 (C-12, C-14), 128.1 (C-24, C-26), 128.2 (C-13), 128.25 (C-6), 128.27 (C-18, C-20), 128.3 (C-23, C-27), 128.9 (C-11, C-15), 131.8 (C-19), 132.6 (C-25), 138.8 (C-4), 139.5 (C-16), 140.3 (C-22), 160.0 (C-2), 166.0 (C-7). ^{11}B NMR (96.29 MHz, $CDCl_3$), [δ, ppm]: 4.4 ($h_{1/2} = 385$ Hz). MS (*m/z*, %): 402 (M^+, 0.4), 326 (100), 296 (3), 211 (3), 148 (3), 148 (1), 116 (0.2), 91 (0.2), 77 (0.1). Anal. Calc for $C_{27}H_{22}BNO_2$: C, 80.41; H, 5.50; N, 3.47. Found C, 80.23; H, 5.38; N, 3.41%.

2.3.2.6. (2S,4R,5S)-2-(Phenyl)benzo[j]-4-phenyl-5-methyl-6-aza-1,3-dioxa-2-boracyclononen-6-ene ***4f***. Compound **4f** was synthesized from 0.30 g (1.17 mmol) of **3f** and 0.14 g (1.17 mmol) of phenyl boronic acid. The reaction was carried out in toluene under reflux, using a Dean–Stark trap during 24 h. The product was obtained as a yellow solid 0.27 g (0.79 mmol), yield, 67%, mp: 236–241 °C $[\alpha]_D^{25} = +65.9$ (c 0.097 $CHCl_3$), IR υ_{max} (KBr): 3065, 2979, 2935, 2864, 1651 (C=N), 1608, 1552, 1474, 1454, 1404, 1292, 1225, 1177, 1145, 1094, 1023, 992, 923, 882, 816, 746, 703, 642, 571, 518, 485, 461, 425 cm^{-1} ^{1}H NMR (300 MHz, DMSO-d_6) [δ, ppm]: 0.92 (d, 3H, $J = 7.0$ Hz, CH_3), 4.19 (m, 1H, H-8), 5.38 (d, 1H, $J = 5.0$ Hz, H-9), 6.85 (t, 1H, $J = 7.5$ Hz, H-5), 6.98 (d, 1H, $J = 8$ 0.0 Hz, H-3), 7.12–7.23 (m, 4H, H-13, H-18, H-19, H-20), 7.28–7.38 (m, 2H, H-17, H-21), 7.32–7.42 (m, 2H, H-4, H-6), 7.48–7.62 (m, 4H, H-11, H-12, H-14, H-15), 8.38 (s, 1H, H-7). ^{13}C NMR (75.46 MHz, $CDCl_3$) [δ, ppm]: 15.4 (CH_3), 66.9 (C-8), 80.0 (C-9), 118.7 (C-1), 119.1 (C-5), 120.5 (C-3), 126.4 (C-18, C-20), 127.4 (C-13), 127.3 (C-12, C-14), 127.1 (C-19), 128.3 (C-17, C-21), 130.8 (C-6), 131.0 (C-11, C-15), 137.6 (C-4), 139.2 (C-16), 158.2 (C-2), 161.5 (C-7). ^{11}B NMR (96.29 MHz, $CDCl_3$), [δ, ppm]: 5.9 ($h_{1/2} = 192$ Hz). MS (*m/z*, %): 341 (M^+, 0.1), 264 (100), 234

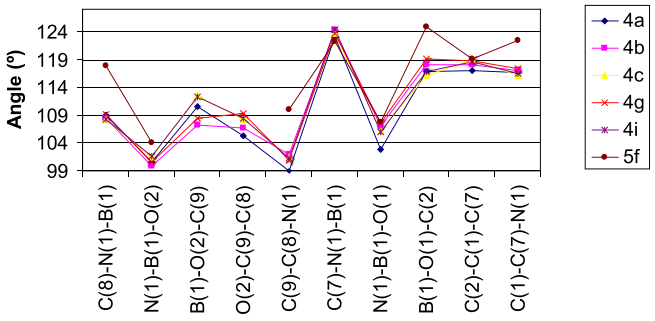


Fig. 5. Bond angles correlation for the compounds **4a**–**4c**, **4g**, **4i** and **5f**.

(0.8), 206 (0.1), 148 (3), 117 (0.2), 78 (0.2). Anal. Calc for $C_{22}H_{20}BNO_2$: C, 77.44; H, 5.91; N, 4.11. Found C, 77.40; H, 6.01; N, 4.06%.

2.3.2.7. (2S,5R)-2-(Phenyl)benzo[j]-5-phenyl-7-phenyl-6-aza-1,3-dioxa-2-boracyclononen-6-ene ***4g***. Compound **4g** was synthesized from 0.30 g (0.94 mmol) of **3g** and 0.11 g (0.94 mmol) of phenyl boronic acid. The reaction was carried out in toluene under reflux, using a Dean–Stark trap during 24 h. The product was obtained as a yellow solid 0.21 g (0.53 mmol), yield, 56%, mp: 221–224 °C $[\alpha]_D^{25} = +381.0$ (c 0.114 $CHCl_3$), IR υ_{max} (KBr): 3066, 3006, 2940, 2864, 1606 (C=N), 1546, 1453, 1393, 1340, 1268, 1192, 1150, 1106, 1015, 951, 844, 818, 741, 701, 651, 619, 533, 499, 437, 406 cm^{-1} ^{1}H NMR (300 MHz, DMSO-d_6) [δ, ppm]: 4.12 (d, 1H, $J = 5.0$ Hz, H-8), 4.44 (d, 1H, $J = 7.0$ Hz, H-9b), 4.64 (d, 1H, $J = 4.0$ Hz, H-9a), 6.79 (t, 1H, $J = 8.0$ Hz, H-5), 7.08–7.13 (m, 2H, H-3, H-23), 7.08–7.23 (m, 8H, H-13, H-17, H-18, H-19, H-20, H-21, H-24, H-25), 7.23–7.25 (m, 2H, H-12, H-14), 7.40–7.55 (m, 6H, H-4, H-6, H-11, H-15, H-26, H-27). ^{13}C NMR (75.46 MHz, $CDCl_3$) [δ, ppm]: 68.4 (C-8), 71.6 (C-9), 118.8 (C-5), 120.5 (C-3), 121.3 (C-1), 127.2 (C-19), 127.4 (C-18, C-20), 127.7 (C-12, C-14), 127.8 (C-13), 128.2 (C-24), 128.5 (C-17, C-21), 128.7 (C-26), 129.1 (C-25), 129.25 (C-23), 131.5 (C-27), 131.6 (C-6), 131.7 (C-11, C-15), 132.3 (C-22), 137.3 (C-4), 140.7 (C-16), 161.4 (C-2), 172.3 (C-7). ^{11}B NMR (96.29 MHz, $CDCl_3$), [δ, ppm]: 6.5. ($h_{1/2} = 257$ Hz). MS (*m/z*, %): 402 (M^+, 0.3), 326 (100), 298 (2), 248 (2), 224 (10), 208 (1), 146 (3), 104 (1). Anal. Calc for $C_{27}H_{22}BNO_2$: C, 80.41; H, 5.50; N, 3.47. Found C, 80.18; H, 5.44; N, 3.42%.

2.3.2.8. (Rac)-2-(Phenyl)benzo[j]-7-phenyl-6-aza-1,3-dioxa-2-boracyclononen-6-ene ***4h***. Compound **4h** was synthesized from 0.30 g (1.24 mmol) of **3h** and 0.15 g (1.24 mmol) of phenyl boronic acid. The reaction was carried out in toluene under reflux, using a Dean–Stark trap during 24 h. The product was obtained as a yellow solid 0.29 g (0.89 mmol), yield, 71%, mp: 151–154 °C, IR υ_{max} (KBr): 3055, 2963, 2928, 2870, 1601 (C=N), 1543, 1490, 1449, 1364, 1323, 1258, 1180, 1090, 1060, 1005, 902, 877, 832, 742, 699, 630, 573, 531, 442 cm^{-1} ^{1}H NMR (300 MHz, DMSO-d_6) [δ, ppm]: 3.04 (dd, 1H, $J = 3.5$ Hz, $J = 9.0$ Hz, H-8b), 3.36 (dd, 1H, $J = 3.0$ Hz, $J = 5.0$ Hz, H-8a), 3.85 (m, 1H, H-9a), 4.18 (m, 1H, H-9b), 6.72 (t, 1H, $J = 6.0$ Hz, H-5), 6.83 (d, 1H, $J = 6.0$ Hz, H-6), 7.04 (d, 1H, $J = 8.0$ Hz, H-3), 7.18–7.31 (m, 4H, H-12, H-13, H-14, H-20), 7.42–7.44 (m, 1H, $J = 7$ Hz, H-4), 7.48–7.57 (m, 2H, H-18, H-21), 7.64 (t, 1H, $J = 8.0$ Hz, H-19), 7.69 (d, 2H, $J = 7.0$ Hz, H-11, H-15), 8.39 (d, 1H, $J = 8.0$ Hz, H-17), ^{13}C NMR (75.46 MHz, $CDCl_3$) [δ, ppm]: 53.1 (C-8), 60.4 (C-9), 118.1 (C-5), 118.2 (C-1), 119.1 (C-3), 126.9 (C-13), 127.4 (C-12, C-14), 128.2 (C-26), 128.5 (C-24), 129.0 (C-25), 129.9 (C-27), 130.3 (C-23), 132.1 (C-11, C-15), 132.5 (C-6), 132.6 (C-22), 136.5 (C-4), 160.7 (C-2), 174.7 (C-7). ^{11}B NMR (96.29 MHz, $CDCl_3$), [δ, ppm]: 3.9($h_{1/2} = 298$ Hz) MS (*m/z*, %): 327 (M^+, 0.1), 250 (100), 224 (0.1), 208 (0.1), 174 (3), 146 (0.1), 78 (0.1). Anal. Calc. for $C_{21}H_{18}BNO_2$: C, 77.09; H, 5.55; N, 4.28. Found C, 77.01; H, 5.68; N, 4.22%.

2.3.2.9. (Rac)-2-(Phenyl)benzo[j]-7-methyl-6-aza-1,3-dioxa-2-boracyclononen-6-ene ***4i***. Compound **4i** was synthesized from 0.30 g (0.81 mmol) of **6i**. The reaction was carried out in toluene under reflux, using a Dean–Stark trap during. The product was obtained as a yellow solid 0.18 g (0.49 mmol), yield, 60%, mp: 180–184 °C. IR υ_{max} (KBr): 3044, 3000, 2936, 1612 (C=N), 1553, 1479, 1454, 1400, 1325, 1274, 1143, 1106, 1036, 985, 954, 865, 814, 784, 754, 704, 657, 634, 614, 567, 499, 441 cm^{-1} ^{1}H NMR (300 MHz, $CDCl_3$) [δ, ppm]: 2.53 (s, CH_3), 3.99 (m, 2H, H-8), 4.12 (m, 1H, H-9a), 4.30 (m, 1H, H-9b), 6.86 (t, 1H, $J = 7.0$ Hz, H-5), 7.13 (d, 1H, $J = 7.1$ Hz, H-3), 7.14–7.19 (m, 3H, H-12, H-13, H-14), 7.33–7.37 (m, 2H, H-11, H-15), 7.41–7.50 (m, 2H, H-4, H-6). ^{13}C NMR (75.46 MHz, $CDCl_3$) [δ, ppm]: 18.3 (CH_3), 50.0 (C-8), 62.8 (C-9), 119.1 (C-5), 119.7 (C-1), 121.0 (C-3), 127.2 (C-

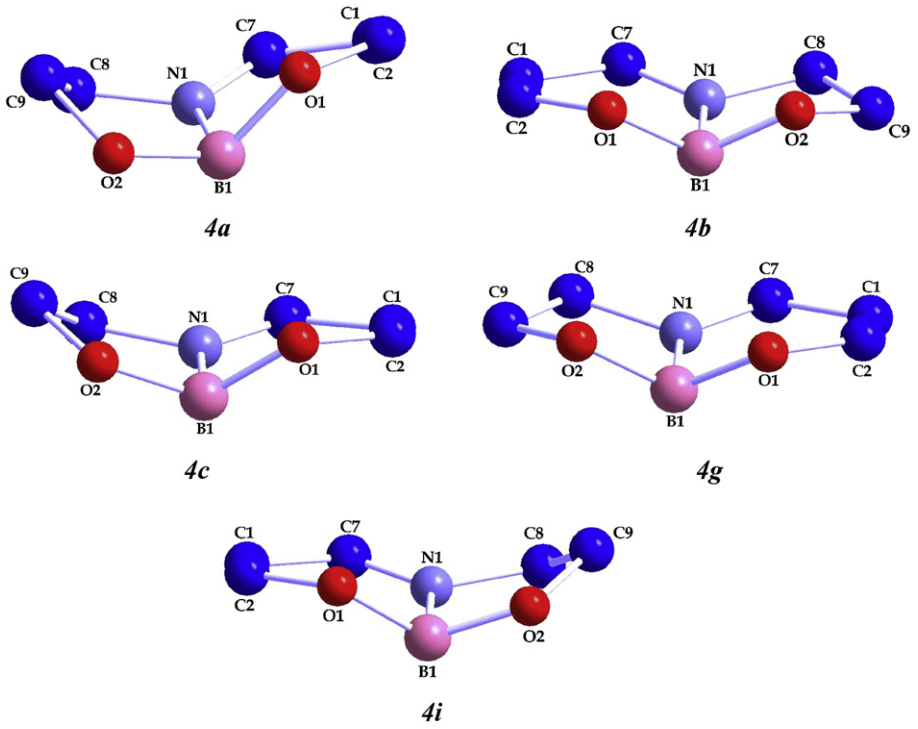


Fig. 6. Conformations of the [4.3.0] heterobicycles in compounds **4a**, **4b**, **4c**, **4g** and **4i**.

13), 127.4 (C-12, C-14), 128.4 (C-6), 131.6 (C-11, C-15), 136.8 (C-4), 160.0 (C-2), 166.9 (C-7). ^{11}B NMR (96.29 MHz, $CDCl_3$), [δ, ppm]: 5.9. ($h_{1/2} = 221$ Hz). MS (*m/z*, %): 264 (M^+, 0.2), 234 (0.3), 188 (100), 162 (16), 146 (7), 117 (3), 91 (3), 77 (13). Anal. Calc. for $C_{16}H_{16}BNO_2$: C, 72.49; H, 6.08; N, 5.28. Found C, 72.11; H, 5.92; N, 5.18%.

2.4. Results and discussion

Reaction of ethanolamines with salicylaldehyde, 2-hydroxyacetophenone or 2-hydroxybenzophenone afforded tridentate ligands **3a**–**3i** in high yields. Subsequent reaction of these ligands **3a**–**3h** with phenyl boronic acid under reflux of toluene for 24 h gave boronates **4a**–**4h** in yields between 53 and 71% (Scheme 2), All compounds including the tridentate ligands were characterized by mass spectrometry, IR, ^{1}H, ^{13}C, elemental analysis and ^{11}B NMR for boron compounds. Due to the formation of a new chiral center at the boron atom it is possible to induce its stereochemistry. Compounds **4a**, **4b**, **4d**, **4e**, **4f**, and **4g** all have a phenyl group at the aliphatic carbons (Scheme 2) hence the formation of only one diastereoisomer can be attributed to the big size of the phenyl group that induces the attack of the boron atom just in one face of the molecule. In the case of compound **4c** we observed in ^{1}H NMR spectroscopy the formation of two different compounds in 2:1 a ratio which correspond to the pair of diastereoisomers **4c-syn** and **4c-anti** (Scheme 3), where the major product has the methyl and phenyl group in the same side. The methyl group in compound **4c** could not induce diastereoselectivity because of its small size, in consequence the attack took place in both faces of the molecule. It is worth to mention that the preferred stereochemistry is that where all substituents are on the same side (*syn*), in the case of compounds **4h** and **4i** they do not have chiral atoms and the products correspond to the enantiomeric mixture.

In the preparation of compound **4i** following the same method failed because the formation of the dimeric compound is very fast, therefore it was necessary to prepare the compound **6i**, which was obtained from the reaction between the ligand **3i** and 2 equivalents of phenyboronic acid, refluxing **6i** in toluene for one day gave **4i** and 2,4,6-triphenylboroxine (Scheme 4).

In the attempts to crystallize compound **4f**, the hydrolysis product **5f** was obtained (Fig. 2). The structure of **5f** showed that the five member ring has been opened, most likely as the result of its greater reactivity owing to ring strain.

2.4.1. Spectroscopic Properties

The existence of the N→B bond in compounds **4a**–**4i** was established by ^{11}B NMR which shows the signals between 6.5 and 3.9 ppm, characteristic for the tetracoordinated boron atom [14–24]. The characteristic signal in the ^{13}C NMR spectra for the imine group appears between 161.5 and 174.7 ppm, and it was confirmed by the band for (C=N) in the infrared spectra, between 1601 and 1651 cm^{-1}. The mass spectra give the molecular ions in low abundance, and a base peak corresponds to the [M^+–C_6H_5] ion in agreement with previous results [21]. In the case of compound **4c** the reaction provides a 2:1 mixture of both diastereomers **4c-syn** and **4c-anti**, this behavior was attributed to the small size of the methyl group compared with the other substituents, which causes that asymmetric induction was poor, and the new chiral center generated on the boron atom is R in **4c-syn** in the case of major product. (Scheme 3)

2.4.2. X-ray analyses of *4a*, *4b*, *4c*, *4g*, *4i* and *5f*

The compounds **4a**, **4b**, **4c**, **4g**, **4i** and **5f** provided crystals suitable for X–ray analyses. The X-ray structures for these compounds are shown in Figs. 1 and 2. The crystallographic data are summarized in the (Table 1). The structures of compounds **4a**, **4b**, **4c**, **4g**, **4i** showed that the phenyl group attached to the boron atom prefers the position in the same face of the other substituents, and the phenyl group in the five membered ring is big enough to induce the configuration at the boron atom (Fig. 3). In compounds **4a** and **4i**, the position of C(9) deviates by −0.236 Å from the mean plane B

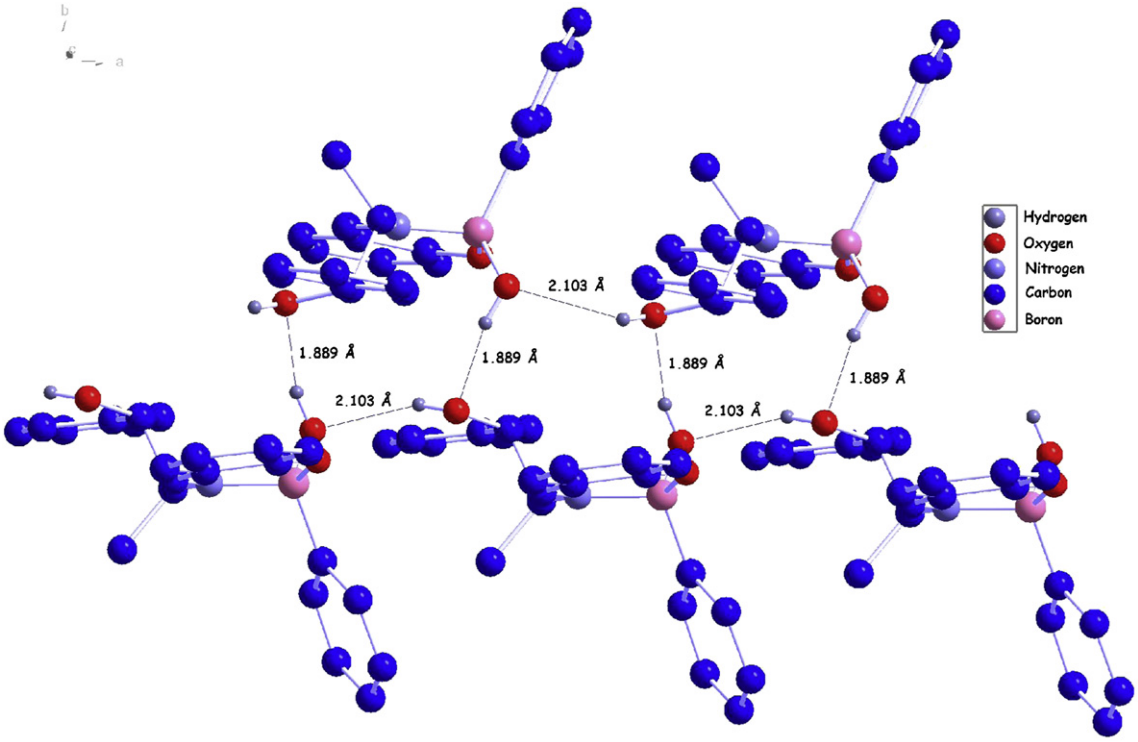


Fig. 7. Intermolecular interactions in structure **5f**.

(1)–N(1)-C(8)-C(9)-O(2), and that of C(8) deviates by 0.173 Å from the same plane, respectively. The N → B bond distances for **4a**, **4b**, **4c**, **4g** and **4i** are 1.605(3), 1.590(2), 1.588(3), 1.591(5) and 1.582(2) and they are similar to those observed in boron complexes [21]. Significant differences were between B(1)–O(1) 1.490(3)-1.475(2) Å and B(1)-O(2) 1.440(3)-1.445(2) Å bond distances, and showed that the shorter bond lengths correspond to the aliphatic oxygen in the five member rings (Table 2). The bond angles around the boron atom for compounds **4a**, **4b**, **4c**, **4g** and **4i** are in the range between 99.83° and 116.04° (Table 2). The average value for the bond angles in five membered rings are 104.92°, 104.82°, 106.42°, 105.68° and 106.36° for **4a**, **4b**, **4c**, **4g** and **4i** respectively, which are better than those observed in six and seven membered rings values, due to the higher strain of five membered rings, while the values observed for similar 6 and 7 member rings heterocycles are 117.1° (3) and 118.8° (3) which indicate lower ring strain [35]. Figs. 4 and 5 show that bond lengths and angles in five and six member rings are similar.

The values for the tetrahedral character (THC) [19] for boron atoms are 66.5%, 74.2%, 75.7%, 77.1% and 75.3% for **4a**, **4b**, **4c**, **4g** and **4i** respectively, these values show that the boron atom is more distorted in the derivative of ephedrine because it has two substituents in the aliphatic carbons directly bonded to the five membered ring, consequently it presents the largest ring strain and the lower THC.

The deviations of the boron atom from the mean plane of the six-membered ring C(2)–C(1)-C(7)–N(1)-B(1)–O(1) in **4a**, **4b**, **4c**, **4g** and **4i** are 0.305, −0.228, 0.261, 0.100 and 0.212 Å respectively, showing again that the largest deviation of the boron atom from the mean plane corresponds to compound **4a**, which has two substituents on the aliphatic carbons and presents the less THC.

The dihedral angles for the O1-B1-C10-C15 fragment in compounds **4a**, **4b**, **4c**, **4g** and **4i** are −5.5°, −64.9°, −0.8°, 60.1° and 2.6° which are indicative of two conformations preferred around C–B bond, eclipsed and gauche.

In the Fig. 6 are shown the different conformations of the [4.3.0] heterobicycle for **4a**, **4b**, **4c**, **4g** and **4i**, the six-members ring is almost planar and the boron atom is deviated from the mean plane −0.305, 0.228, −0.26, −0.212, 0.254, 0.100 Å for **4a**, **4b**, **4c**, **4g** and **4i**, respectively (Table 2) and the five member ring has an envelope conformation with different atoms out of the mean plane for **4a** C(9) −0.236 Å, for **4b** O(2) −0.246 Å for **4c** C(8) −0.171 Å for **4g** O(2) 0.207 Å and **4i** C(8) 0.173 Å. Fig. 4 shows that the bond lengths are very similar, in all compounds. However, in the Fig. 5 shows that bond angles have small differences in the compounds **4a**, **4b**, **4c**, **4g** and **4i**.

The structure for compound **5f** is shown in the Fig. 2, this compound corresponds to the open five membered ring, which was obtained by reaction of water with **4f** and proved that the five member ring is less stable than the six member ring. The THC value for compound **5f** is close to a tetrahedral (85.2%) due to loss of ring strain.

The deviations of the boron atom from the mean plan of six membered ring in **5f** is 0.254 Å The N→B bond length for **5f** is 1.607 (19), and is larger than the **4a**, **4b**, **4c**, **4g** and **4i**, Fig. 4 show that bond lengths are similar to the compounds **4a**, **4b**, **4c**, **4g** and **4i**, but the bond angles are expectedly rather different.

Structure **5f** shows intermolecular hydrogen bond interactions of O2 with H3A with a distance of 1.889 Å and O3 with H2A with a distance of 2.103 Å, in both cases the distances are less than the sum of the van der Walls radii (Fig. 7) [36].

2.5. Conclusions

Two new tridentate ligands and nine boronates (six of them chiral) were synthesized in good yields. The reaction of the tridentate ligands with phenyl boronic acid lead to monomeric boronates (**4a**–**4h**), with exception of compound **4i**, which was obtained from compound **6i**. Although, it was possible to obtain boronates with six and seven membered rings employing two

equivalents of phenyl boronic acid, an adequate control of the reaction conditions, lead to the preparation of boronates with six and five membered rings, which were thermodynamically more stable. However, six and seven membered rings heterobicycles are intermediates which upon heating conduce to the monomeric compounds with six and five member heterobicyclic rings. We conclude that five membered rings are strained as revealed through the bond angles in five member rings which were 104.92°, 104.82°, 106.42°, 105.68° and 106.36° for **4a**, **4b**, **4c**, **4g** and **4i**, respectively. Ring opening in compound **5f** is due to the presence of water in the solvent used to crystallize the compound. This kind of compounds could have some applications as chiral inductors.

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Appendix A. Supplementary material

CCDC no. 264752, 259940, 264751, 264749, 264753 and 264750 for **4a**, **4b**, **4c**, **4g**, **4i** and **5f** respectively, contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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