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Synthesis, characterization and X-ray studies of new six–seven membered rings [4.5.0] heterobicyclic system of monomeric boronates

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ABSTRACT

Different tridentate ligands derived from ethanolamines and 2-hydroxyacetophenone, 2-hydroxybenzophenone and salicylaldehyde were reacted with two equivalents of phenylboronic acid to obtain compounds ***6a–6f*** which are [4.5.0] heterobicyclic systems with a B–O–B structural unit. The boronates were fully characterized and two heterobicyclic [4.5.0] structures have been analyzed by X-ray crystallography, where a series of parameters such as bond distances, bond angles, torsion angles, tetrahedral character at the boron atom and deviation of the boron atom from the mean plane have been evaluated.

1. Introduction

Recently, there has been a considerable interest in the synthesis, characterization and study of organoboron compounds, due to a great variety of applications derived from these complexes in different areas such as supramolecular chemistry [1,2]; boron complexes have found application in medicinal chemistry, as anticancer agents in boron neutron capture therapy [3,4]; as bioactive materials, ^{10}B is employed in the control of nuclear reactors as a shield against the nuclear radiation [5]. Moreover, they also display a wide range of applications in organic synthesis [6], for example, in the synthesis of polyolefins, styrene, and substituted biphenyls by the Suzuki reaction [7–10]; as materials with fluorescence [11], electro optical and nonlinear optical properties which are areas recently explored using boron chemistry [12,13]. In this context, the synthesis and characterization of boron complexes obtained from the condensation of 3-amino-phenylboronic acid and 1,3-diketones [14] and recently the synthesis, characterization and X-ray studies of new fused five–six-membered rings, [4.3.0.] heterobicyclic systems of monomeric boronates derived from optically active tridentate ligands [15] have been reported. Our previous studies have shown that fused five–six membered rings compounds are obtained under strong reaction conditions such as reflux of toluene for 24 h. In turn, dimeric compounds were formed when the ligands have zero, two, five or six methylene units between the imino and hydroxyl group, using mild reactions conditions such as reflux of THF for approximately 30 min [16] (Scheme 1). In this work, tridentate ligands ***5a–5f*** were allowed to react with two equivalents of phenylboronic acid to give six new [4.5.0] heterobicyclic boronates which possess two boron atoms in the structure. The results from X-ray diffraction indicated low strain present in the seven membered rings of the molecules as well as the chair conformation and the tetrahedral character of the boron atoms which is directly associated to the geometry [17,18] and shows deviation from ideal values. The presence of two different boron atoms in the structures suggests that these molecules are intermediates in the reaction. One of the boron atoms (B1) is tetrasubstituted forming a coordination bond to the nitrogen and the other boron atom (B2) is trisubstituted with an empty p orbital. These boronate units are connected by two covalent B–O and a coordinative N → B bond, which are responsible for hydrolytic stability of these molecules [19] (Scheme 2).

2. Experimental

2.1. Instrumentation

NMR spectra were recorded in $CDCl_3$ and DMSO-d_6 solutions on Bruker Avance 300 spectrometer. Chemical shifts (ppm) are

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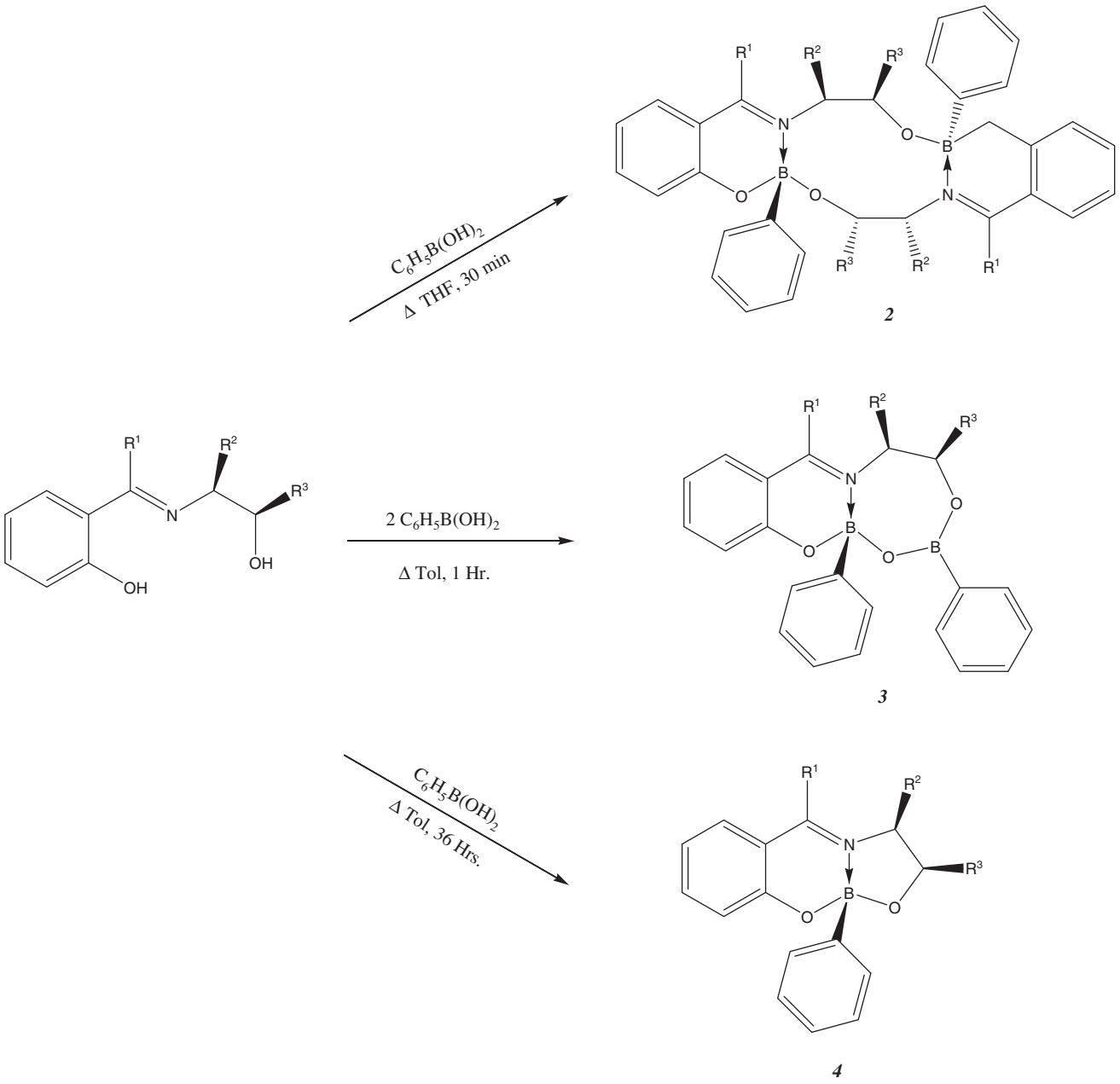


Scheme 1. Monomeric and dimeric boronates obtained using different reactions conditions.

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 Hewlett–Packard model 5989 engine, coupled to a GC 5890 series II. Melting points were obtained on a Gallenkamp MFB-595 apparatus and are uncorrected. Elemental analyses were carried out on a FLASH (EA) 1112 series, thermo Finnigan apparatus. The X-ray diffraction study was determined on an Enraf–Nonius-Fr590 Kappa-CCD ($\lambda_{Mo\ K\alpha}$ = 0.71073 Å, graphite monochromator, T = 293 K, CCD rotating images scan mode) and the crystals were mounted on a LINDEMANN tube. Absorption correction was not necessary. All reflections data set were corrected for Lorentz and Polarizations 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 [20,21]. All software manipulations were done under the WINGX environment program set [22]. Single crystal structure validation was done with PLATON [23]. Molecular perspectives were drawn under ORTEP-3 [24], and DIAMOND 2.1e drawing applications.

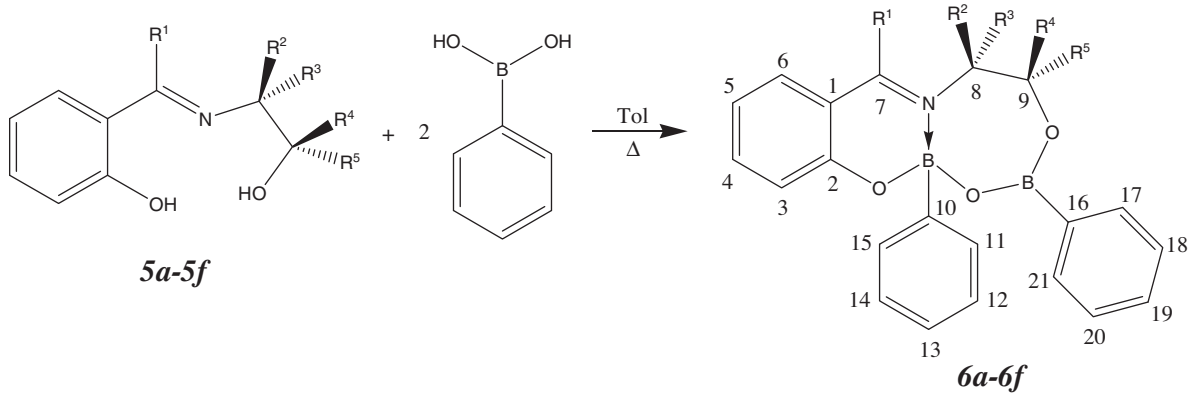
2.2. Reagents

All reactants and solvents were purchased from Aldrich chemical Co. and solvents were dried previous to use [25]. Single crystals were grown using spectroscopic grade solvents.

2.3. Synthesis

2.3.1. General method for the preparation of tridentate ligands ***5a–5f***

In order to prepare the tridentate ligands ***5a–5f***, equimolecular quantities of the corresponding aminoalcohol and 2-hydroxyacetophenone, 2-hydroxybenzophenone or salicylaldehyde, respectively, were refluxed in ethanol for 1 h. The solvent and water formed during the reaction were eliminated with a Dean–Stark



Compounds	R^1	R^2	R^3	R^4	R^5
6a	CH_3	H	H	CH_3	H
6b	CH_3	H	H	H	H
6c	H	H	Ph	H	H
6d	H	H	Ph	H	Ph
6e	H	H	H	CH_3	H
6f	Ph	H	H	CH_3	H

Scheme 2. Synthesis of oligodiboronates ***6a–6f***, derived from tridentate ligands ***5a–5f*** and two equivalents of phenylboronic acid.

trap to yield yellow solids that were washed with methylene chloride and used without further purification. All tridentate ligands ***5a–5f*** have already been published [26–33].

*2.3.2. General method for the preparation of compounds **6a–6f***

To prepare compounds ***6a–6f*** one equivalent of the tridentate ligands ***5a–5f*** and two equivalents of the phenylboronic acid were refluxed in toluene for 1 h. The solvent and water formed during the reaction were eliminated to yield yellow solids that were washed with methylene chloride and purified by recrystallization using a mixture of chloroform hexane 2:1.

*2.3.2.1. (2R,6R)-2,4-diphenylbenzo[j]-6,9-dimethyl-8-aza-1,3,5,2,4-trioxadiboracycloundec-8-ene. **6a**.* Compound ***6a*** was synthesized from 0.50 g (2.59 mmol) of ***5a*** and two equivalents (0.63 g, 5.18 mmol) of phenylboronic acid. The reaction was carried out under reflux of toluene for 1 h, using a Dean–Stark trap. The product was obtained as a yellow solid 0.78 g. (2.04 mmol), yield, 79%, mp: 95–100 °C. IR υ_{max} (KBr): 3070, 3011, 2976, 2881, 1914, 1830, 1620 (C=N), 1554, 1441, 1408, 1335, 1276, 1156, 1079, 1025, 992, 854, 746, 702, 646, 580, 537, 504, 452 cm^{-1}. ^1H NMR (300 MHz, DMSO-d_6) [δ, ppm]: 1.44 (d, 3H, CH_3), 2.18 (s, 3H, CH_3), 3.67 (dd, 1H, J = 4.7 Hz, J = 9.1 Hz, H-8a), 3.77 (d, 1H, J = 13.9 Hz, H-8b), 4.24 (q, 1H, J = 7.3 Hz, H-9), 6.87 (t, 1H, J = 7.7 Hz, H-5), 7.05 (d, 1H, J = 8.4 Hz, H-3), 7.22–7.31 (m, 3H, H-6, H-12, H-14), 7.33–7.55 (m, 6H, H-4, H-11, H-13, H-15, H-18, H-20), 7.57 (d, 1H, J = 8.4 Hz, H-19), 8.09 (d, 2H, J = 6.6 Hz, H-17, H-21). ^{13}C NMR (75.46 MHz, DMSO-d_6) [δ, ppm]: 15.9 (CH_3), 22.5 (CH_3), 56.2 (C-8), 71.7 (C-9), 116.6 (C-1), 118.6 (C-5), 120.7 (C-3), 127.4 (C-6), 127.6 (C-18, C-20), 127.8 (C-12, C-14), 128.5 (C-19), 130.1 (C-13), 131.4 (C-11, C-15), 135.1 (C-17, C-21), 137.2 (C-4), 159.3 (C-2), 169.3 (C-7). ^{11}B NMR (96.29 MHz, DMSO-d_6), [δ, ppm]: 3.4, 25.7. ($h_{1/2}$ = 286, 596 Hz.). MS (*m/z*,%): 383 (M^+, 0.1), 306 (38), 262 (0.1), 234 (1), 202 (100), 162 (6), 105 (0.2). *Anal.* Calc. for $C_{23}H_{23}B_2NO_3$: C, 72.12; H, 6.05; N, 3.66. Found C, 72.69; H, 6.15; N, 3.71%.

*2.3.2.2. 2,4-diphenylbenzo[j]-9-Methyl-8-aza-1,3,5,2,4-trioxadiboracycloundec-8-ene. **6b**.* Compound ***6b*** was synthesized from 0.50 g. (2.79 mmol) of ***5b*** and 0.68 g. (5.58 mmol) of phenylboronic acid. The reaction was carried under reflux of toluene for 1 h, using a Dean–Stark trap. The product was obtained as a yellow solid 0.87 g. (2.37 mmol), yield, 84%, mp: 203–207 °C. IR υ_{max} (KBr): 3046, 3012, 2881, 1958, 1826, 1617 (C=N), 1556, 1437, 1335, 1272, 1149, 1083, 1026, 995, 951, 838, 747, 702, 641, 577, 506, 464, 420 cm^{-1}. ^1H NMR (300 MHz, DMSO-d_6) [δ, ppm]: 2.57 (s, CH_3), 3.82 (m, 1H, H-8a), 3.97 (m, 2H, H-8b, H-9a), 4.41 (m, 1H, H-9b), 6.86 (t, 1H, J = 7.9 Hz, H-5), 7.21 (d, 1H, J = 8.3 Hz, H-3), 7.21–7.25 (m, 3H, H-6, H-12, H-14), 7.34–7.49 (m, 6H, H-4, H-11, H-13, H-15, H-18, H-20), 7.57 (dd, 1H, J = 1.3 Hz, J = 6.9 Hz, H-19), 8.01 (d, 2H, J = 6.3 Hz, H-17, H-21). ^{13}C NMR (75.46 MHz DMSO-d_6) [δ, ppm]: 16.1 (CH_3), 52.0 (C-8), 63.9 (C-9), 117.0 (C-1), 118.8 (C-5), 120.7 (C-3), 127.3 (C-6), 127.6 (C-18, C-20), 127.8 (C-12, C-14), 128.5 (C-19), 130.3 (C-13), 131.1 (C-11, C-15), 137.2 (C-4), 159.4 (C-2), 170.2 (C-7).^{11}B NMR (96.29 MHz, DMSO-d_6), [δ, ppm]: 3.5, 25.8 ($h_{1/2}$ = 289, 674 Hz.). MS (*m/z*,%): 368 (M^+, 0.2), 312 (3), 292 (46), 188 (100), 160 (2), 104 (1). *Anal.* Calc. for $C_{22}H_{21}B_2NO_3$: C, 71.60; H, 5.74; N, 3.80. Found C, 71.28; H, 5.94; N, 3.86%.

*2.3.2.3. (7R)-2,4-diphenylbenzo[j]-7-phenyl-8-aza-1,3,5,2,4-trioxadiboracyclo-undec-8-ene. **6c**.* Compound ***6c*** was synthesized from 0.50 g. (2.07 mmol) of ***5c*** and two equivalents 0.51 g. (4.14 mmol) of phenylboronic acid. The reaction was carried out under reflux of toluene for 1 h, using a Dean–Stark trap. The product was obtained as a yellow solid 0.81 g. (1.89 mmol), yield, 91%, mp: 98–102 °C. IR υ_{max} (KBr): 3049, 2957, 2932, 1961, 1634 (C=N), 1559, 1442, 1310, 1191, 1151, 1076, 1027, 984, 882, 850, 755, 701, 650, 549, 452 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) [δ, ppm]: 4.22 (dd, 1H, J = 4.7 Hz, 7.7 Hz; H-8a), 4.84 (dd, 1H, J = 2.9 Hz, 9.5 Hz, H-9a), 4.98 (m, 1H, H-9b), 6.78 (t, 1H, J = 6.9 Hz, H-5), 7.09 (d, 1H, J = 8.8 Hz, H-3), 7.21–7.32 (m, 5H, H-6, H-12, H-14, H-23, H-27), 7.38–7.54 (m, 9H, H-4, H-11, H-13, H-15, H-18, H-20, H-24, H-25, H-26), 7.85 (s, 1H, H-7), 8.25 (d, 2H, J = 6.6 Hz, H-17, H-21). ^{13}C

NMR (75.46 MHz, $CDCl_3$) [δ, ppm]: 60.5 (C-8), 67.4 (C-9), 118.7 (C-1), 118.9 (C-5), 119.8 (C-3), 127.4 (C-6), 128.1 (C-18, C-20), 129.1 (C-12, C-14), 129.5 (C-19), 129.7 (C-24, C-26), 130.4 (C-13), 131.4 (C-11, C-15), 132.7 (C-25), 135.1 (C-23, C-27), 135.7 (C-17, C-21), 138.6 (C-4), 162.3 (C-2), 165.8 (C-7). ^{11}B NMR (96.29 MHz, $CDCl_3$), [δ, ppm]: 3.9, 28.8. ($h_{1/2}$ = 235, 752 Hz.). MS (*m/z*,%): 430 (M^+, 1), 354 (45), 326 (3), 312 (5), 250 (100), 210 (1), 148 (3), 78 (1). *Anal.* Calc. for $C_{27}H_{23}B_2NO_3$: C, 75.22; H, 5.38; N, 3.25. Found C, 75.39; H, 5.43; N, 3.29%.

2.3.2.4. (6S,7R)-2,4-diphenylbenzo[j]-6,7-diphenyl-8-aza-1,3,5,2,4-trioxadiboracycloundec-8-ene. ***6d***. Compound ***6d*** was synthesized from 0.50 g. (1.58 mmol) of ***5d*** and two equivalents (0.38 g, 3.16 mmol) of phenylboronic acid. The reaction was carried out under reflux of toluene for 1 h, using a Dean–Stark trap. The product was obtained as a yellow solid 0.58 g. (1.15 mmol), yield, 73%, mp: 94–98 °C. IR υ_{max} (KBr): 3029, 3007. 2975, 1958, 1629 (C=N), 1557, 1493, 1454, 1396, 1306, 1185, 1130, 1082, 946, 893, 830, 757, 701, 653, 599, 515, 452 cm^{-1}. ^1H NMR (300 MHz, DMSO-d_6) [δ, ppm]: 5.15 (d, 1H, *J* = 2.9 Hz, H-8), 6.44 (d, 1H, *J* = 2.7 Hz, H-9), 6.82 (t, 1H, *J* = 7.7 Hz, H-5), 6.92 (m, 2H, H-29, H-33), 7.01–7.16 (m, 7H, H-3, H-6, H-12, H-14, H-25, H-30, H-32), 7.23–7.30 (m, 3H, H-19, H-23, H-27), 7.36–7.52 (m, 7H, H-4, H-13, H-18, H-20, H-24, H-26 H-31), 7.74 (dd, 2H, *J* = 1.4 Hz, *J* = 6.4 Hz, H-11, H-15), 8.05 (s, 1H, H-7), 8.09 (dd, 2H, *J* = 1.3 Hz, *J* = 6.3 Hz, H17, H-21). ^{13}C NMR (75.46 MHz, DMSO-d_6) [δ, ppm]: 74.1 (C-8), 75.9 (C-9), 115.7 (C-1), 119.3 (C-5), 120.2 (C-3), 126.4 (C-29, C-33), 127.6 (C-6), 127.8 (C-18, C-20), 128.0 (C-31), 128.3 (C-12, C-14), 129.0 (C-23, C-27), 129.3 (C-19), 130.7 (C-30, C-32), 130.9 (C-13), 131.0 (C-11, C-15), 132.5 (C-25), 133.9 (C-22), 135.6 (C-17, C-21), 139.2 (C-4), 139.3 (C-28), 160.5 (C-2), 165.6 (C-7). ^{11}B NMR (96.29 MHz, DMSO-d_6), [δ, ppm]: 4.4, 28.9 ($h_{1/2}$ = 337, 626 Hz.). MS (*m/z*,%): 507 (M^+, 2), 430 (94), 326 (100), 296 (10), 234 (4), 148 (14), 105 (2), 78 (1). *Anal.* Calc. for $C_{33}H_{27}B_2NO_3$: C, 78.15; H, 5.37; N, 2.76. Found C, 78.23; H, 5.39; N, 2.88%.

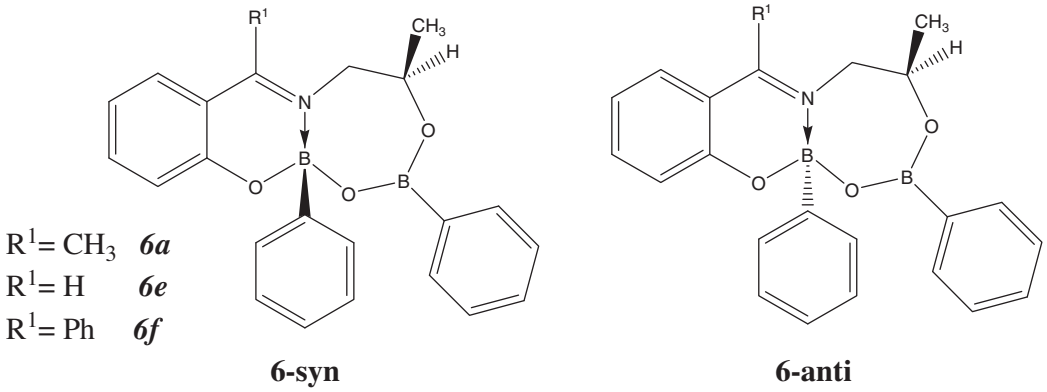
2.3.2.5. (6R)-2,4-diphenylbenzo[j]-6-methyl-8-aza-1,3,5,2,4-trioxadiboracycloundec-8-ene. ***6e***. Compound ***6e*** was synthesized from 0.50 g. (2.79 mmol) of ***5e*** and two equivalents 0.68 g. (5.58 mmol) of phenylboronic acid. The reaction was carried under reflux of toluene for 1 h, using a Dean–Stark trap. The product was obtained as a yellow solid 0.74 g. (2.0 mmol), yield, 72%, mp: 100–104 °C. IR υ_{max} (KBr): 3050, 3016, 2928, 2868, 1901, 1640 (C=N), 1560, 1482, 1441, 1405, 1376, 1346, 1271, 1192, 1155, 1072, 1082, 852, 746, 700, 658, 558, 515, 456, 423 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) [δ, ppm]: 1.25 (d, 3H, CH_3), 3.37 (m, 1H, H-8a), 3.94 (d, 1H, *J* = 13.1 Hz, H-8b), 4.69 (m, 1H, H-9), 6.87 (t, 1H, *J* = 7.7 Hz, H-5), 7.05 (d, 1H, *J* = 8.1 Hz, H-3), 7.24–7.32 (m, 3H, H-6, H-12, H-14), 7.34–7.58 (m, 6H, H-4, H-11, H-13, H-15, H-18, H-20), 7.60 (d, 1H, *J* = 7.7 Hz, H-19), 8.1 (dd, 2H, *J* = 1.5 Hz, *J* = 6.7 Hz, H-17, H-21). ^{13}C NMR (75.46 MHz, $CDCl_3$) [δ, ppm]: 20.1 (CH_3), 64.5 (C-8), 66.7 (C-9), 115.2 (C-1), 119.1 (C-5), 119.8 (C-3), 127.5 (C-6), 127.6 (C-18, C-20), 127.9 (C-12, C-14), 130.5 (C-19), 131.2 (C-13), 131.6 (C-11, C-15), 135.0 (C-17, C-21), 138.6 (C-4), 161.4 (C-2), 164.2 (C-7). ^{11}B NMR (96.29 MHz, $CDCl_3$), [δ, ppm]: 3.7, 25.8. ($h_{1/2}$ = 286, 854 Hz.). MS (*m/z*,%): 369 (M^+, 0.3), 292 (51), 247 (1), 188 (100), 148 (3), 91 (0.2). *Anal.* Calc. for $C_{22}H_{21}B_2NO_3$: C, 71.60; H, 5.74; N, 3.80. Found C, 71.74; H, 5.84; N, 3.86%.

2.3.2.6. (6R)-2,4-diphenylbenzo[j]-6-methyl-9-phenyl-8-aza-1,3,5,2,4- trioxadiboracycloundec-8-ene. ***6f***. Compound ***6f*** was synthesized from 0.50 g. (1.96 mmol) of ***5f*** and two equivalents (0.48 g, 3.92 mmol) of phenylboronic acid. The reaction was carried out under reflux of toluene for 1 h, using a Dean–Stark trap. The product was obtained as a yellow solid 0.72 g. (1.63 mmol), yield, 81%, mp: 97–101 °C. IR υ_{max} (KBr): 3049, 3016, 2982, 1963, 1610 (C=N), 1550, 1443, 1407, 1335, 1279, 1189, 1154, 1072, 1029, 951, 841, 757, 702, 647, 569, 529 cm^{-1}. ^1H NMR (300 MHz, DMSO-d_6) [δ, ppm]: 2.18 (s, 3H, CH_3), 3.44 (dd, 1H, *J* = 3.9 Hz, *J* = 8.1 Hz, H-8a), 3.54 (d, 1H, *J* = 6.2 Hz, 8b), 4.13 (dd, 1H, *J* = 4.0 Hz, *J* = 6.9 Hz, H-9), 6.68 (t, 1H, *J* = 7.3 Hz, H-5), 7.09 (d, 1H, *J* = 8.2 Hz, H-3), 7.24–7.36 (m, 4H, H-6, H-12, H-14, H-26), 7.37–7.48 (m, 8H, H-4, H-11, H-13, H-15, H-18, H-20, H-24, H-27), 7.51–7.65 (m, 3H, H-19, H-23, H-25), 8.07 (dd, 2H, *J* = 1.3 Hz, *J* = 7.9 Hz, H-17, H-21). ^{13}C NMR (75.46 MHz, DMSO-d_6) [δ, ppm]: 20.6 (CH_3), 60.7 (C-8), 71.4 (C-9), 118.4 (C-5), 119.9 (C-1), 120.5 (C-3), 126.8 (C-22), 127.3 (C-6), 127.4 (C-18, C-20), 127.6 (C-26), 128.2 (C-12, C-14), 129.2 (C-19), 129.7 (C-24), 131.8 (C-25), 132.1 (C-11, C-15), 132.9 (C-27), 135.2 (C-23), 135.8 (C-17, C-21), 137.1 (C-4), 161.9 (C-2), 168.3 (C-7). ^{11}B NMR (96.29 MHz, DMSO-d_6), [δ, ppm]: 3.8, 25.7 ($h_{1/2}$ = 293, 714 Hz.). MS (*m/z*,%): 444 (M^+, 1), 368 (56), 340 (1), 264 (100), 224 (1), 146 (2), 104 (1). *Anal.* Calc. for $C_{28}H_{25}B_2NO_3$: C, 75.55; H, 5.66; N, 3.15. Found C, 75.28; H, 5.52; N, 3.17%.

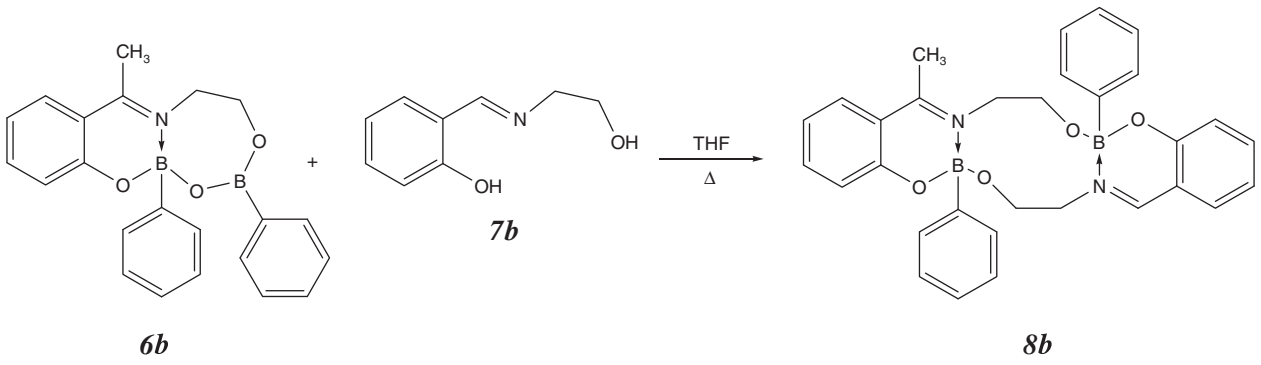
2.3.2.7. 2,11-diphenyl-dibenzo[h,j]-16-methyl-6,15-diaza-1,3,10,12-tetraoxa-2,11-diboracyclooctadeca-6,15-diene. ***8b***. Compound ***8b*** was synthesized from 0.50 g (1.37 mmol) of ***6b*** and 0.22 g. (1.37 mmol) of. 2-[(2-hydroxy-ethylimino)-methyl]-phenol ***7b***. The reaction was carried out under reflux of THF. The product was obtained as a white solid 0.49 g. (0.94 mmol), yield, 70%, mp: 203–207 °C. IR υ_{max} (KBr): 3044, 2932, 2871, 2755, 1966, 1640 (C=N), 1610, 1555, 1482, 1458, 1437, 1343, 1313, 1273, 1200, 1111, 1075, 1017, 962, 927, 873, 825, 752, 709, 652, 629, 455, 410 cm^{-1}. MS (*m/z*,%): 516 (M^+, 0.2), 439 (M^+–C_6H_5, 1), 425 (3), 250 (3), 220 (4), 188 (27), 174 (100), 148 (13), 132 (4), 91 (3), 77 (23). *Anal.* Calc. for $C_{31}H_{30}B_2N_2O_4$: C, 72.13; H, 5.86; N, 5.43. Found C, 72.29; H, 6.03; N, 5.39%.

2.4. Results and discussion

Reacting different ethanolamines with 2-hydroxyacetophenone, salicylaldehyde or 2-hydroxybenzophenone afforded tridentate ligands ***5a***–***5f*** in high yields. The subsequent reaction of these ligands ***5a***–***5f*** with two equivalents of phenylboronic acid under reflux of toluene for 1 h gave compounds ***6a***–***6f*** in yields between 72% and 91% (Scheme 2). All compounds (***6a***–***6f***) were soluble in common solvents and were characterized by mass spectrometry, IR, ^1H, ^{13}C, ^{11}B NMR and elemental analysis. Due to the formation of a new chiral center at the boron atom it is possible to induce its stereochemistry [15]. All compounds except ***6b*** have a chiral center at the aliphatic carbons of the ethanolamine moiety, which favors the formation of only one diastereoisomer. In the case of compounds ***6a***, ***6e*** and ***6f*** that have a methyl group at the aminoacid fragment and afforded a pair of diastereoisomers in a 2:1 ratio, as established by ^1H NMR spectroscopy (Scheme 3). The major product has the methyl and the phenyl groups on the same side, this is attributed to the small size of the methyl group that could not induce high diastereoselectivity, in consequence the attack of phenylboronic acid took place from both faces of the molecule. This observation is in agreement with previous results that have shown that the preferred product possesses the stereochemistry with all the substituents on the same side (syn) [15]. Compound ***6a*** crystallized in a non centrosymmetric P_{212121} space group and the X-ray diffraction showed that the preferred stereochemistry is that where the methyl and phenyl group are on the same side. As we mentioned earlier, we found that reaction of ethanolamines with phenylboronic acid in THF during 30 min, leads to the formation of a very insoluble solid that corresponds to the dimeric compounds, however, changing the reaction conditions to toluene 24 h the product obtained was a monomeric [4.3.0] heterobicyclic system. Surprisingly, we could obtain six–seven membered rings



Scheme 3. Diatereoisomers obtained by reaction of ligands ***5a***, ***5e*** and ***5f*** with phenylboronic acid.



Scheme 4. Synthesis of noncentrosymmetric dimeric compound ***8b***.

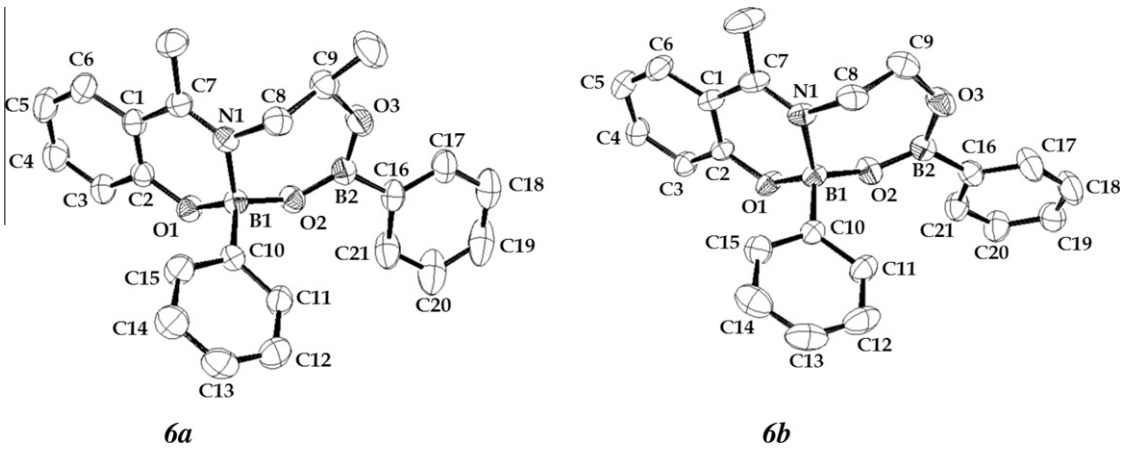


Fig. 1. Molecular structures for compounds ***6a*** and ***6b***, hydrogens are omitted for clarity.

[4.5.0] heterobicyclic systems using toluene after 1 h of reaction. These results indicate that reaction of tridentate ligands ***5a***-***5f*** can lead to the synthesis of the kinetic compound **2** (THF 1/2 h), the thermodynamic compound **4** (Toluene 36 h) and the intermediate of the reaction **3** (toluene 1 h) (Scheme 1). This was confirmed when compound ***8b*** was obtained by reaction of ***6b*** and tridentate ligand ***7b*** in THF for 1 h (Scheme 4).

2.4.1. Spectroscopic properties

The existence of the N → B coordination bond was established by ^{11}B NMR which shows the signals between 3.40 and 4.40 ppm, characteristic for the tetracoordinated boron atom and signals between 25.7 and 28.9 ppm, for the tricoordinated boron atom [26–40]. The signals in the ^{13}C NMR spectra for the imine group appear at 169.3, 170.2, 165.5, 165.6, 164.2 and 168.3 ppm for ***6a–6f***, respectively, and it was confirmed by the band for (C=N) in the infrared spectra at 1610 and 1640 cm^{-1}.The mass spectrometric analysis gave the molecular ions in low abundance and the base peak corresponds to the [M$^+$–C_6H_5] fragment ions [16,26,27]. Compound ***8b*** was insoluble in all common solvents and the structure was confirmed by IR (C=N at1640 cm^{-1}), mass spectrometry and elemental analysis. The mass spectra gave the molecular ion at 516 (M$^+$, 0.2) which corresponds to the molecular weight of ***8b***.

*2.4.2. X-ray analyses of **6a** and **6b***

Compounds **6a** and **6b** crystallized and the X-ray structures for these compounds are shown in Fig. 1. The crystallographic data are summarized in Table 1. The structure of compound **6a** showed that the phenyl group attached to the tetracoordinated boron atom is in the same face as the methyl group, is in agreement with previous results [15]. The N → B bond distances for **6a** and **6b** are 1.587(5) and 1.597(3) Å, respectively, similar to those observed in boron complexes [26–30]. Significant differences are found between the B(1)–O(1) (1.470(4) and 1.469(3) Å) and B(1)–O(2) (1.449(4)–1.438(3) Å) bond distances for **6a** and **6b**, respectively, and show that the shorter bonds length correspond to the aliphatic oxygen in the seven member rings (Table 2). The bond angles around the tetracoordinated boron atom are in the range from 107.1° to 113.2° and the bond angles around the tricoordinated boron atom are in the range from 114.7° to 125.8° for compounds **6a** and **6b** (Table 2). The average value for the bond angles in the seven membered rings are 120.78° and 120.88° for **6a** and **6b**, respectively, which are larger than those observed in five–six membered rings values, indicating lower ring strain [16,26]. The values for the tetrahedral character (THC) [18] of the tetracoordinated boron atoms are 93% and 90% for **6a** and **6b**, respectively, these values show that the boron atom is less distorted than in five–six membered ring compounds [15]. The deviations of the boron atom from the mean plane of the six membered rings C(2)–C(1)–C(7)–N(1)–B(1)–O(1) in **6a** and **6b** are −0.052 and −0.048 Å, respectively, showing that the largest deviation corresponds to compound **6a**, which has a methyl group in the iminic carbon. The dihedral angles for the O1–B1–C10–C15 fragment in compounds **6a** and **6b** are −59.0(4)° and 52.8(2)° which are indicative that the gauche conformation is the preferred one around the C–B bond. Compound **6a** crystallized in the non centrosymmetric space group P_{212121} and it presents weak intermolecular interactions between O1–H13 with a distance of 2.635 Å and between O2–H13 with a distance of 2.688 Å, the angles between O1–H13–C13 and O2–H13–C13 are 152.8° and 143.9°, respectively [41,42] (Fig. 2). The conformation in the seven member ring in molecules **6a** and **6b** is chair, in **6a** C8 is above the plane formed by C9, O3, B1 and N1, B2, O2 (Fig. 3).

Table 1
Crystallographic data for compounds **6a** and **6b**.

Compound	**6a**	**6b**
Chemical formula	$C_{23}H_{23}B_2NO_3$	$C_{22}H_{21}B_2NO_3$
Formula weight	383.04	369.02
Space group	P_{212121}	Cc
Crystal system	Orthorhombic	Monoclinic
Crystal size (mm^3)	0.2 × 0.1 × 0.1	0.2 × 0.1 × 0.1
Unit cell dimensions		
a (Å)	8.2208(3)	14.8600(3)
b (Å)	14.6103(6)	14.4010(4)
c (Å)	17.4739(8)	10.8940(3)
α (°)	90	90
β (°)	90	122.5560(10)
γ (°)	90	90
Formula units per cell	4	3
δ_{calc} (g cm^{-3})	1.212	0.936
F(000)	808	582
T (K)	293(2)	293(2)
θ (°)	3.64–27.47	3.60–27.46
Reflections collected	4680	4013
Independent reflections	4700	4095
Observed reflections, $(F_o)^2 > 4\sigma(F_o)^2$	2690	3104
$R = \sum\|\|F_o\| - \|F_c\|\|/\sum\|F_o\|$	0.0538	0.0415
$R_w = [\sum w(\|F_o\| - \|F_c\|)^2/\sum wF_o^2]^{1/2}$, $w = 1/\sigma^2$ (all data)	0.1191	0.0619
Goodness-of-fit (GOF)	1.077	0.992
No. of parameters	265	270
Maximum Δ/σ	−0.041	0.047
$\Delta\rho_{min}$ (e $Å^{-3}$)	−0.119	−0.108
$\Delta\rho_{max}$ (e $Å^{-3}$)	0.122	0.157

Table 2
Selected bond distances (Å) and bond angles (°) for compounds **6a** and **6b**.

Compound	**6a**	**6b**
Bond distances (Å)		
N(1)–C(8)	1.467(4)	1.468(3)
N(1)–C(7)	1.294(4)	1.305(3)
C(1)–C(7)	1.451(5)	1.449(3)
C(7)–C(22)	1.510(5)	1.505(3)
B(1)–O(1)	1.470(4)	1.469(3)
B(1)–O(2)	1.449(4)	1.438(3)
B(1)–N(1)	1.587(5)	1.597(3)
B(1)–C(10)	1.590(5)	1.614(3)
B(2)–O(2)	1.341(5)	1.332(3)
B(2)–O(3)	1.371(5)	1.367(3)
B(2)–C(16)	1.556(5)	1.569(4)
Bond angles (°)		
N(1)–B(1)–O(1)	109.1(3)	109.0(15)
N(1)–B(1)–O(2)	108.4(3)	109.0(17)
N(1)–B(1)–C(10)	109.5(3)	108.1(15)
O(1)–B(1)–C(10)	110.0(3)	110.3(17)
O(2)–B(1)–C(10)	112.2(3)	113.2(17)
O(1)–B(1)–O(2)	107.6(3)	107.1(16)
C(7)–N(1)–B(1)	125.0(3)	124.5(16)
C(8)–N(1)–C(7)	121.3(3)	122.9(18)
B(1)–O(2)–B(2)	142.4(3)	142.3(18)
O(2)–B(2)–O(3)	125.8(4)	125.0(2)
O(2)–B(2)–C(16)	119.5(4)	119.7(2)
O(3)–B(2)–C(16)	114.7(3)	115.2(2)
Deviation from mean plane (Å)		
Plane: C(2)–C(1)–C(7)–N(1)–B(1)–O(1)	B(1) – 0.052	B(1) – 0.048

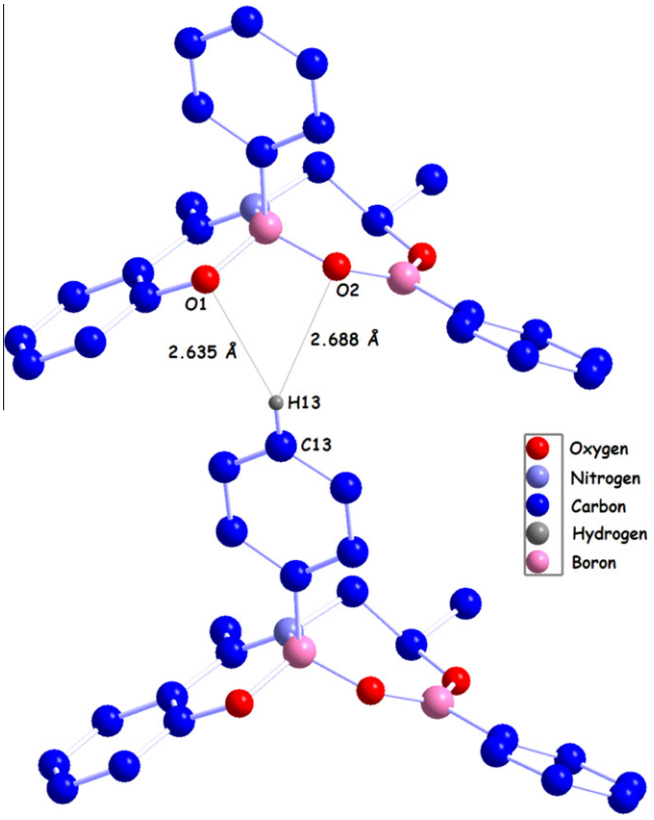


Fig. 2. Intermolecular interactions for compound **6a**, hydrogens are omitted for clarity.

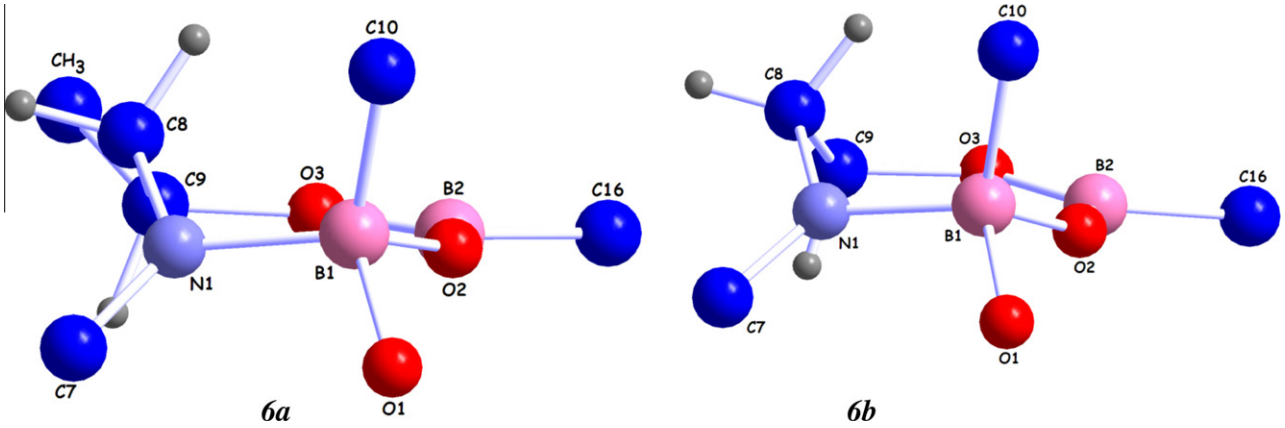


Fig. 3. Chair conformation in the seven member ring in compounds ***6a*** and ***6b***.

2.5. Conclusions

Six new heterobicyclic systems of monomeric boronates with two fused rings, one of which is seven-membered while the other is six-membered were prepared in good yields. The reaction of tridentate ligands with two equivalents of phenylboronic acid leads to oligoboronates (***6a–6f***). It is possible to obtain boronates with fused five–six membered rings by heating oligoboronates ***6a–6f***, or by reacting only one equivalent of the phenylboronic acid and one equivalent of the tridentate ligands under reflux of toluene during 24 h. Reacting compounds ***6a–6f*** with tridentate ligands gave to dimeric compounds (kinetic compounds). These results allow to conclude that boronates with fused six–seven membered rings are very stable, as evidenced by the bond angles in the seven member rings; in turn, dimeric compounds can be obtained by the reaction of compounds ***6a–6f*** with tridentate ligands. This kind of compounds could find application as chiral inductors in the Suzuki reaction.

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Appendix A. Supplementary material

CCDC 270362 and 270360; contains 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. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ica.2012.03.055.

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