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Addition reactions of protonic reagents to optically active 2-phenyl-1,3,2-oxazaborolines

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Abstract

The addition reactions of water and methanol to (4*R*,5*S*)-4-methyl-2,5-diphenyl-1,3,2-oxazaboroline **1** (derived from (+)-norephedrine), (4*R*,5*S*)-(+)-3,4-dimethyl-2,5-diphenyl-1,3,2-oxazaboroline **2** (derived from (+)-ephedrine) and to (4*R*,5*R*)-(+)-3,4-dimethyl-2,5-diphenyl-1,3,2-oxazaboroline **3** (derived from (+)-pseudoephedrine) were studied. The reactions gave the corresponding (N–B)-phenyl(2-aminoethoxy)boronic acids (**4**–**6**) or methyl esters (**7**–**9**). In **4** and **7** the boron atom is a stereogenic center, therefore two diasteromeric derivatives are expected. In compounds **5**, **6**, **8** and **9** both nitrogen and boron atoms are stereogenic centers and four diasteromers are possible. The structures of the addition products have been established by ^{1}H-, ^{11}B- and ^{13}C-NMR, and that of compound **6** by X-ray diffraction analysis. The reactions with methanol gave only one isomer (**7**–**9**). The reaction of **1** with water afforded both boron epimers (50/50 ratio). The reaction of **2** with water observed at −50° showed both B-epimers in 80/20 ratio, whereas the same reaction with **3** gave only one isomer. In all cases the main isomer has the *N*-methyl *trans* to the *C*-methyl group and the B-phenyl *cis* to the *N*-methyl group. The X-ray diffraction molecular structure of compound **6** [(4*R*,5*R*)-(+)-3,4-dimethyl-2,5-diphenyl-2-hydroxy-1,3,2-oxazaborolidine], confirmed the structure assignment made from the NMR data. Addition reactions to 1,3,2-oxazaborolines are an efficient method to introduce stereoselectively functional groups to boron atom in order to obtain new boron heterocycles.

Keywords: Heterocycles; Ephedrine; Boronic acids; Chirality

1. Introduction

Boraheteroazolines are very important heterocycles, used widely as reagents for asymmetric catalysis or as optically active reducing agents [1–9]. In this context we have prepared optically active boron heterocycles [10–20] and studied the nature of bonding between boron and heteroatoms. We are interested especially in the nature of the N–B bond [10–15,17–50] and in its ability to form heterocycles via N–B coordination [10–13,19,22,23,26,30,32,34–36,38,44–47]. We have been working in the synthesis of molecules where boron or nitrogen are stereogenic centers [10–13,19,22,25,27–29,45–47]. On the other hand, borane coordination is an excellent tool to determine the molecular structure of nitrogenated molecules by NMR, by examining the steric or electronic effects of the boron over its neighboring atoms, in this way N-borane groups function as steric probes [10–13,27–29,36,39,41,46]. The borane coordination works also as an anchor to stop the conformational equilibrium in heterocyclohexanes allowing to study anomeric effects [36,40,45,47].

On the preparation of N-borane adducts of oxazolidines derived from ephedrines, we have obtained relatively stable compounds [27–29], Scheme 1. We have also prepared the ephedrine esters of catecholborane, the nitrogen–boron bonding produces spiranic structures. The nitrogen atom configuration was also deduced from NMR data [10], Scheme 2. A similar study was performed in (N–B)-diphenyl(2-aminoethoxy)-boronic acid derivatives of ephedrine and pseudoephedrine. The analysis of the dependence of the

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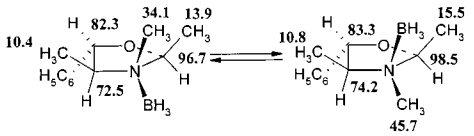
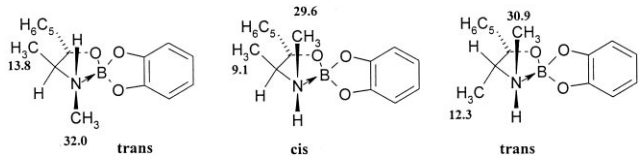


Scheme 1. The structure of the N-epimers derived from optically active N-borane oxazolidine can be deduced from the ^{13}C-NMR data shown here [27–29].

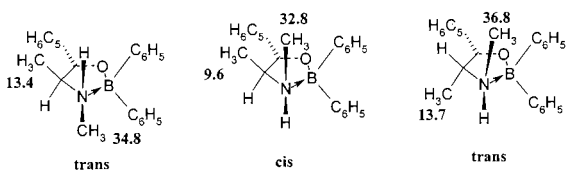


Scheme 2. The two N-epimers derived from catecholborane and ephedrine, and the main isomer derived from pseudoephedrine and catecholborane [10].

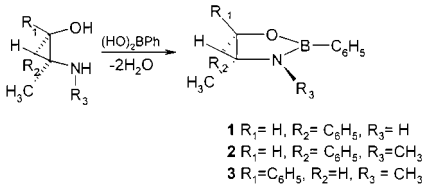
stereochemistry and the energy of the N–B bond on the nitrogen substitution and the nature of the ligands was reported [19]. In all cases their stereochemistry was deduced from the NMR data based on steric and electronic effects produced by neighboring groups, Scheme 3.

Herein we report the study of addition reactions of water and methanol to the N–B bond to 2-phenyl-1,3,2-oxazaborolines derived from (1*S*,2*R*)-(+)-norephedrine **1**, (1*S*,2*R*)-(+)-ephedrine **2** and (1*R*,2*R*)-(+)-pseudoephedrine **3**. The syntheses of compounds **1** [8] and **2** [2] have been reported. They have been used as catalyzing agents for reduction or alkylations [2,3,6–9]. Compounds **1**–**3** were prepared from the reactions of phenylboronic acid and the corresponding ethanolamines in dry toluene in a Dean–Stark trap, Scheme 4. The compounds were purified by distillation. Their NMR data are listed in Tables 1 and 2.

In heteroborolines, the heteroatoms provide electronic density by π-donation to the electronic deficient boron atom [21,42,48–50]. This gives some double bond character to the boron sp^2 bonds, and makes them susceptible to addition reactions that result in tetracoordinated boron structures. Presumably, the addition reactions are favored because the electronic deficiency at boron atom is better relieved in the tetrahedral structures resulting from nucleophilic addition, relative to stabilization by π-donation in three-co-



Scheme 3. ^{13}C-NMR data of diphenylborinic esters derived from ephedrine and pseudoephedrine [19].



Scheme 4. Preparation of phenylboronic esters derived from ethanolamines.

ordinate boron compounds. There are some previous examples of addition reactions to the B–N bond in boroxazolines. We have reported phenol addition reaction to benzoxazaboroline, to give a phenol ester bearing a N–B coordination bond [50], as is depicted in Scheme 5. In this reaction the nucleophilic oxygen atom of phenol adds to boron and the proton transfers to nitrogen. We have also investigated on borane addition to the covalent nitrogen–boron of 1,3,2-oxazaborolines derived from ephedrine [15,17,18,20], Scheme 6. In this addition the boron in borane coordinates to the nitrogen atom, and a BH_3 hydride bridges to the endocyclic boron. The assignment of stereochemistry for these compounds is based on their earlier observations of empirical chemical shifts correlations with structure [10,14,15,17–20,27–29].

Compounds **1**–**3** react rapidly with water **4**–**6** or methanol **7**–**9** to give the corresponding boroxazolidines. Compound **1** could form two boron epimers I–II, whereas compounds **2** and **3** could give four diasteromers III–VI, because the products have nitrogen and boron stereogenic centers. The stereochemistry of all possible compounds is shown in Scheme 7.

The reaction of compound **1** with D_2O in an NMR tube generates two compounds (**4a** and **4b)** in a 1/1 ratio with one ^{11}B-NMR signal at +6.7 ppm, which is characteristic for tetrahedral boron. The boron-epimers are in equilibrium as is denoted by the two sets of broad signals in ^{1}H- and ^{13}C-NMR spectra. If the mixture is sublimed then **4a** is enriched (70%), but equilibration of the chloroform solution gives **4b** as the predominant isomer (70%). In Scheme 8 the NMR data

Table 1
^{13}C-NMR data of **1–5**, **7–9** in $CDCl_3$ and **6** in toluene–d_8

Compound	C-5	C-4	CH_3–C	CH_3–N	CH_3–O
1	82.8	54,6	20.5		
2	81.5	61.8	15.6	31.0	
3	85.6	66.4	19.2	30.5	
4a	77.1	51.9	17.9		
4b	77.2	53.0	16.0		
5a	76.3	60.0	12.0	33.0	
5b	77.0	59.0	9.0	31.3	
6	80.8	67.6	11.9	35.6	
7	77.6	53.8	16.0		50.0
8	77.3	61.1	13.5	33.0	50.2
9	80.7	68.0	13.5	36.5	50.1

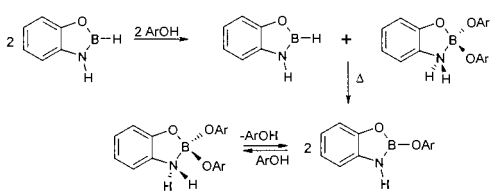
Table 2
^{1}H-NMR data of compounds **1–5**, **7–9** in $CDCl_3$ and **6** in toluene-d_8

Compound	H-5	H-4	CH_3–C	CH_3–N	N–H	OH	CH_3–O
1	5.63	4.06	0.66		3.84		
2	5.61	3.78	0.70	2.90			
3	4.89	3.36	1.28	2.80			
4a	4.40	3.05	0.87				
4b	4.73	3.21	0.72				
5a	5.22	2.11	0.58	1.70			
5b	5.39	3.07	0.41	1.75			
6	4.88	1.77	0.54	1.31	5.6	6.6	
7	5.35	3.70	0.80				3.25
8	5.36	3.40	0.77	2.34			3.33
9	4.6	3.25	1.26	2.09			3.32

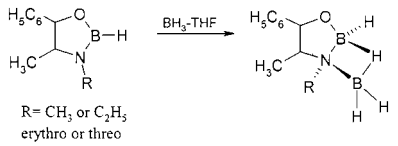
assigned to each isomer is shown. On the other hand, the reaction of **1** with methanol is stereoselective and only one isomer (**7**, $^{11}B = +6.7$ ppm) whose structure is similar to that of compound **4a** was detected (Scheme 8).

The reaction product of compound **2** with water in a NMR tube shows one set of broad signals in the ^{1}H- and ^{13}C-NMR spectra in toluene at room temperature ($^{11}B = +7.8$ ppm). If the solution is cooled to -50°C two sets of sharp signals appear in a ratio 20/80. These resonances were assigned to compounds **5a** and **5b**, respectively, and the NMR data is shown in Scheme 9. The reaction of **2** with methanol gives only one isomer **8** whose structure is the same as that of compound **5b** ($^{11}B = +7.8$ ppm, Scheme 9). The sharp NMR resonances undicate that compound **8** is not in equilibrium with isomeric structures.

The reaction of compound **3** with water gives one set of broad signals when the compound is observed at room temperature. At -50° (400 MHz, in toluene) one set of sharp signals appear that was assigned to heterocycle **6**. Its molecular structure was obtained by an X-ray diffraction study, Figs. 1–3. The structure corresponds to that deduced from the NMR spectra, Scheme 10. The reaction of compound **3** with methanol was also stereoselective, as it gave only one compound, **9**. Compounds **6** and **9** present similar structures, with methyl groups in *trans* position and N–methyl and B–phenyl also *trans*, Scheme 10. The structure assignment was done by comparison with the analogous diphenylborinic esters, Scheme 3 [19].



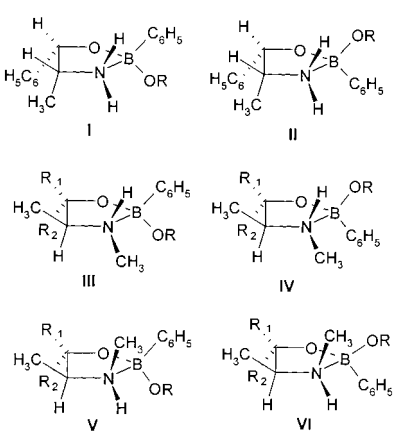
Scheme 5. Phenol addition to benz-1,3,2-oxazaborole affords tetracoordinated nitrogen and boron atoms [50].



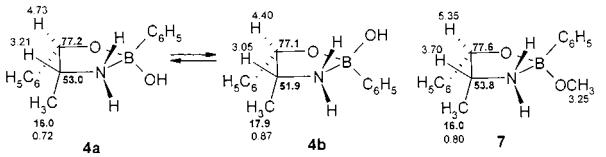
Scheme 6. Borane adds to the B–N bond giving two tetrahedral boron and nitrogen atoms [15,17,18,20].

2. Variable temperature experiment in compound 6

The mobility of the two protons B–OH and N–H in heterocycle **6** was calculated by variable temperature NMR experiments. The temperature dependence of the proton chemical shifts ($\Delta\delta/\Delta T$) was calculated. These data give information about the nature of N–H and O–H bonds. It is accepted that ($\Delta\delta/\Delta T$) values higher than 4×10^{-3} ppm K^{-1} correspond to intermolecular or solvent interactions, whereas lower values than 3×10^{-3} ppm K^{-1} indicate that the proton is less labile or is coordinated intramolecularly [51,52]. Calculations performed in compound **6** in toluene gave values of 13.7×10^{-3} ppm K^{-1} for O–H and 3.8×10^{-3} ppm K^{-1} for N–H. Theses results indicate that the proton in N–H is attached strongly to the nitrogen atom, and therefore the proton is not as acidic as in a normal amine, whereas the O–H is labile. The OH value is consistent with intermolecular O–D bonding observed in the packing diagrams of compound **6**, Fig. 3.



Scheme 7. The two possible B-epimers from reaction addition of water or methanol to the phenylborinic ester derived from norephedrine I–II and the four diasteromers derived from ephedrine or pseudopehedrine III–VI are shown.



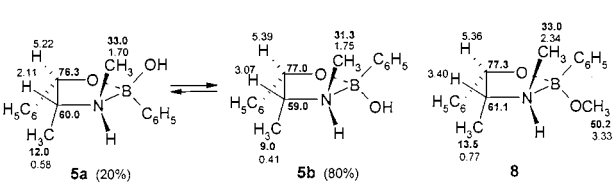
Scheme 8. ^{13}C- and ^{1}H-NMR data of B-epimers obtained from reaction of water and compound **1.**

3. X-ray diffraction molecular structure of compound 6

Compound **6** was prepared directly in an NMR tube by addition of one equivalent of D_2O to a solution of **3** in toluene-d8. The NMR tube was let aside for some weeks, crystals were obtained, and the X-ray structure obtained (Figs. 1–3, Tables 3–7). It shows a cyclic compound with a coordinating B–N bond [bond length 1.692(6)] similar to that found in the analogous compound derived from diphenylborinic ester (B–N) = 1.66(1) [19]. The two phenyl groups and C-methyl are in pseudoequatorial positions as shown by the dihedral angles, Table 5. The bond length B–O1 is 1.450(6) Å, whereas B–O2 of the hydroxyl group is slightly shorter 1.441(6) Å in accord with its pseudoaxial conformation. The B–C bond length is 1.595(7) Å. The large value for C5–N1–B1 117.8(4) can be attributed to the steric compression between phenyl and methyl groups and also from ring distortion in order to put the C-methyl group in pseudoequatorial position. The endocyclic angle B–N1–C3 is very close 104.6 (3). The boron atom has also distorted angles. The angle O1–B–N1 99.5(3) is more acute because is an endocyclic angle in a five membered ring, and the O2–B–N1 small angle 106.1(4) is due to the pseudoaxial position of the B–OH group. The C12–B–N1 wide angle 113.7(4) is due to the steric compression between the N–Me and the B–phenyl groups. The packing diagram indicates a deuterium bonding between the deuterium of the OD and the endocyclic oxygen atom of another molecule (OD—O atomic distance = 3.24 Å), Fig. 3.

4. Conclusions

In phenyl 1,3,2-oxazaboroline the addition reactions of H_2O and methanol are favored. The reaction products are stable but they can be completely hydrolyzed in an excess of water. The water addition to the norephedrine derivatives is not selective but in the ephedrine derivative one isomer predominates. The pseudoephedrine heterocycle gives completely stereoselective reactions. In all cases the methanol additions are 100% stereoselective. In the preferred configuration of all compounds the N-methyl is in *trans* position to C-methyl group. At the same time the N-methyl group drives the more stable configuration at the boron atom, thus the B-phenyl group is placed *cis* to the N-methyl group. In these compounds it seems that the phenyl group prefers a pseudoequatorial position with the plane of the phenyl orthogonal to the main ring plane, inducing the stereoselectivity of water or methanol addition. The addition reactions to the B–N bond of boroxazolines present interesting perspectives for the stereoselective synthesis of boron heterocycles. Some other addition reactions are under investigation in our group.



Scheme 9. Structure, ^{13}C- and ^{1}H-NMR data of compounds **5a**, **5b** and **8**.

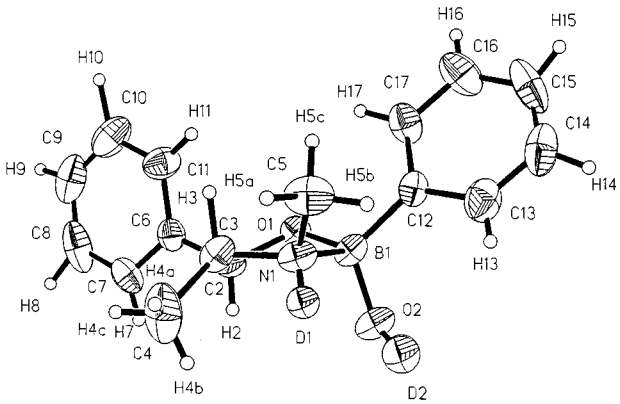


Fig. 1. View of the molecular structure of **6**.

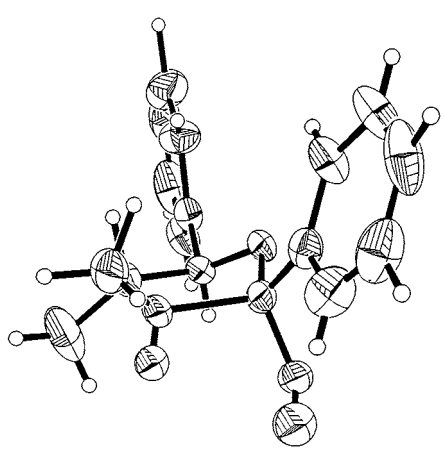


Fig. 2. View of the molecular structure of **6**. The phenyl group conformation is shown.

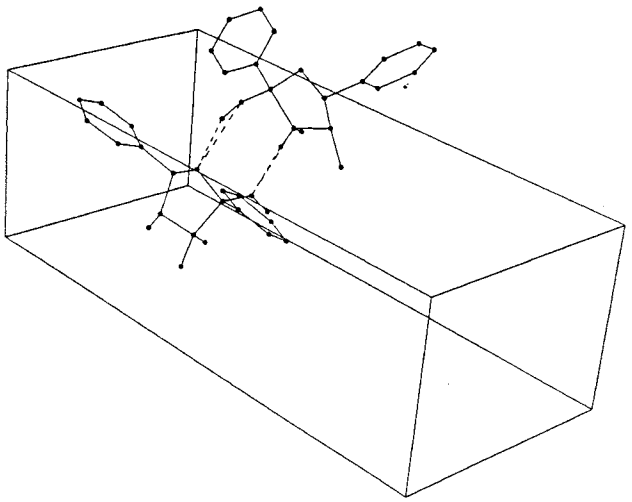
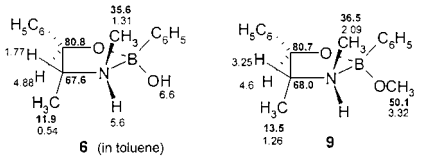


Fig. 3. View of the deuterium bonds between two molecules of compound **6**. The OD–O atomic distance is 3.24 Å.



Scheme 10. Stereochemistry and NMR data of compounds **6** and **9** obtained by the addition of water and methanol to the phenylboronic ester derived from pseudoephedrine.

5. Experimental

All solvents were distilled freshly and dried before use according to established procedures. The aminoalcohols and phenylboronic acids were commercially available reagents. All reactions were handled under a nitrogen atmosphere using dried glassware and solvents. NMR spectra were obtained on a Jeol GXS 270 $Et_2O–BF_3$ or 400 MHz Eclipse spectrometers. The X-ray diffraction study was performed on an Enraf–Nonius CAD4 diffractometer ($\lambda_{Mo-K_\alpha} = 0.71069$, monochromator: graphite $T = 293$ K, $-2q$ scan). Cell parameters were determined by least-squares refinement on diffractometer angles for 24 automatically centred reflections. Absorption correction was not necessary, corrections were made for Lorentz and polarization effects. Solution and refinement: direct method (SHELXS-86) for structure solutions SHELXS (Sheldrick) [53] package was used for refinement and data output. All hydrogen and deuterium atoms were found and refined (Tables 5–7).

Table 3
Selected bond lengths (Å) of compound **6**

O1–C2	1.402(5)	B1–C12	1.595(7)	O2–B2	1.441(6)
O2–D2	0.88(5)	C2–C3	1.523(6)	N1–C5	1.481(6)
N1–D1	0.87(5)	C3–C4	1.508(7)	N1–B1	1.692(6)
N1–C3	1.508(6)	O1–B1	1.450(6)	C2–C6	1.493(6)
C2–H2	0.855(4)	C3–H3	1.095(5)		

5.1. General procedure to 4-methyl-2,5-diphenyl-1,3,2-oxazaborolines

A solution of the corresponding aminoalcohol in dry toluene was treated with one equivalent of phenylboronic acid and heated under reflux for three hours. The solution was evaporated to dryness under reduced pressure and the crude product distilled under vacuum. The compounds were dissolved in $CDCl_3$ or toluene and the structure identified by NMR.

5.2. (4R,5S)-4-methyl-2,5-diphenyl-1,3,2-oxazaboroline, *1*

(+)-Norephedrine 0.6 g (3.9 mmol), phenylboronic acid 0.483 g (3.9 mmol) and 25 ml of toluene. The distillation afforded a transparent viscous liquid **1** (0.81 g, 87%).

5.3. (4R,5S)-(+)-3,4-dimethyl-2,5-diphenyl-1,3,2-oxazaboroline, *2*

(+)-Ephedrine 1.2 g (7.2 mmol), phenylboronic acid 0.885 g (7.2 mmol) and 40 ml of toluene. The distillation afforded a transparent viscous liquid **2** (1.53 g, 84%).

Table 4
Selected bond angles (°) of compound **6**

C2–O1–B1	109.2 (3)	C6–C2–H2	109.6 (4)	O2–B1–N1	106.1 (4)
D1–N1–C5	114.1 (29)	C4–C3–N1	112.5 (4)	C12–B1–N1	113.7 (4)
C5–N1–C3	110.7 (4)	N1–C3–C2	103.7 (3)	O1–C2–C3–	105.7 (4)
C5–N1–B1	117.8 (4)	N1–C3–H3	96.5 (4)	O1–C2–H2	111.7 (4)
O2–B1–O1	109.1 (4)	D2–O2–B1	130.0 (33)	C3–C2–H2	104.9 (4)
O1–B1–C12	111.6 (4)	D1–N1–C3	104.2 (30)	C4–C3–C2	114.8 (5)
O1–B1–N1	99.5 (3)	D1–N1–B1	104.1 (30)	C4–C3–H3	122.8 (5)
O1–C2–C6	112.7 (3)	C3–N1–B1	104.6 (3)	C2–C3–H3	103.6 (4)
C6–C2–C3	112.0 (4)	O2–B1–C12	115.5 (4)		

Table 5
Selected dihedral angles (°) of compound **6**

C6–C2–O1–B1	167.47	C6–C2–C3–C4	80.16	C4–C3–N1–B1	136.68
O1–C2–C3–C4	−156.72	C2–C3–N1–C5	139.94	C12–B1–O1–C2	−154.39
C6–C2–C3–N1	−156.69	C4–C3–N1–C5	−95.42	O1–B1–N1–C5	−111.79
C12–B1–N1–C3	130.47				

Table 6
Atomic coordinates ($\times 10^4$) of compound **6**

	x	*y*	*z*	*U*(eq)
O1	−4389(3)	−4177(3)	−5319.8(12)	50.0(8)
O2	−2812(4)	−2216(3)	−4927(2)	65.1(10)
N1	−1098(5)	−4446(4)	−5168(2)	56.2(10)
B1	−3052(6)	−3722(5)	−4884(2)	52.0(12)
C2	−3529(6)	−4202(5)	−5870(2)	52.6(11)
C3	−1649(6)	−4907(5)	−5774(2)	65.0(13)
C4	−192(8)	−4549(10)	−6225(3)	120(3)
C5	−223(7)	−5626(5)	−4844(3)	82(2)
C6	−4662(6)	−4950(5)	−6320(2)	55.7(11)
C7	−5013(8)	−4405(6)	−6867(2)	77.2(15)
C8	−6026(11)	−5167(11)	−7272(2)	110(2)
C9	−6697(9)	−6459(10)	−7134(4)	99(2)
C10	−6332(9)	−7026(7)	−6599(4)	100(2)
C11	−5347(8)	−6277(6)	−6200(3)	77(2)
C12	−3567(6)	−4302(5)	−4250(2)	55.7(11)
C13	−2728(9)	−3813(7)	−3751(3)	89(2)
C14	−3232(11)	−4212(8)	−3194(3)	102(2)
C15	−4634(11)	−5167(10)	−3126(3)	109(3)
C16	−5533(8)	−5711(8)	−3609(3)	100(2)
C17	−4977(7)	−5295(7)	−4162(2)	76.1(15)
D1	−367(67)	−3729(49)	−5225(19)	59(13)
D2	−1940(78)	−1666(54)	−4778(23)	80(17)

Table 7
Crystal data and data collection parameters

Formula	$C_{16}H_{18}BD_2NO_2$
Weight	271.14
Size	$0.22 \times 0.31 \times 0.53$
System	Orthorhombic
Space group	$P2_1\ 2_1\ 2_1$
Unit cell dimensions	
a (Å)	7.1868 (10)
b (Å)	9.473 (2)
c (Å)	22.877 (5)
α (°)	90.00
β (°)	90.00
γ (°)	90.00
V (Å^3)	1557.5 (5)
Z	4
$\rho_{calc.}$ (Mg m^{-3})	1.156
[mm^{-1}]	0.007
F(000)	576
Index range	$0 \le h \le 8,\ -11 \le k \le 0,\ -28 \le l \le 0$
2θ (°)	52.58
Temp (K)	293(2)
Refl. collected	1231
Refl. unique	1231
Refl. observed (4σ)	1111
R(int.)	0.0000
No. variables	189
Weight scheme *x*/*y*	0.1084/0.0998
w^{-1}	$\sigma^2 F_o^2 + (xP)^2 + yP$
P	$(F_o^2 + 2F_c^2)/3$
GOF	1.088
Final R (4σ)	0.0568
Final wR_2	0.1478
Larg. Res. Peak (e/Å^3)	0.215

5.4. (4R,5R)-(+)-3,4-dimethyl-2,5-diphenyl-1,3,2-oxazaboroline, ***3***

(−)-Pseudoephedrine 0.6 g (3.6 mmol), phenylboronic acid 0.442 g (3.6 mmol) and 25 ml of toluene. The distillation afforded a transparent viscous liquid **3**, (0.87 g, 91%).

Preparation of compounds **4–9** was performed directly in NMR tubes in $CDCl_3$ or toluene-d_8 by addition of one equivalent of water or deuterated water or methanol to the corresponding compounds. The reaction products were observed directly.

Compound **6** after adding D_2O and standing for several weeks in the tube crystallized from the $CDCl_3$ solution and the X-ray diffraction molecular structure was obtained.

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