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The first preparation of (1*S*,5*R*)-(−)- and (1*R*,5*S*)-(+)-7-phenyl-3-borabicyclo[3.3.1]non-6-enes and their application for synthesis of chiral cyclohexene derivatives

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Abstract

(1*S*,5*R*)-(−)- and (1*R*,5*S*)-(+)-7-phenyl-3-borabicyclo[3.3.1]non-6-enes of 97–98% de that differed only by the location of the double bond were prepared by the resolution of diastereomeric intramolecular chelates with L- and D-prolinol. Deboronation of chiral bicyclic boranes obtained was used for synthesis of optically active 3,5-dimethyl- and 3,5-dihydroxymethyl-1-phenylcyclohexenes.

Keywords: 3-Borabicyclo[3.3.1]non-6-ene derivatives; 2,2-Disubstituted 3-borabicyclo[3.3.1]-nonanes; Chiral auxiliaries; Chelate complexes; Diastereomeric purity

1. Introduction

The thermal reaction (130–140 °C) of triallylborane with terminal acetylenes (allylboron–acetylene condensation) gives rise to 7-substituted 3-allyl-3-borabicyclo[3.3.1]non-6-enes **1** in 70–97% yields. Further treatment of **1** with methanol leads to the corresponding 3-methoxy derivatives **2** [1] (see Scheme 1).

The compounds **1** and **2** have been widely used as starting materials for the directed stereospecific synthesis of various cyclic and cage structures such as *cis*-3,5-dimethyl-1-cyclohexenes, *cis*-3,5-dihydroxymethyl-1-cyclohexenes, methylene cyclohexene derivatives and bis-cyclohexene derivatives [1,2]. However, all the above compounds were previously obtained only as racemate. It is desirable to get the bicyclic boranes **1** and/or **2** in enantiomerically pure form for using them as chiral transfer reagents in asymmetric allyboronation as well as the precursors for the synthesis of natural and related compounds.

Indeed, 7-substituted 3-allyl-3-borabicyclo[3.3.1]non-6-enes **1** and **2** are the compounds of C_1 symmetry, which enantiomers differ only in the location of the double bond. Previously, the resolution of certain boracyclanes such as borolanes [3] allylborane [4] and 10-trimethylsilyl-9-borabicyclo[3.3.2]decane (10-TMS-9-BBD) [5] has been performed via intramolecular complexes with valinol, prolinol or pseudoephedrine.

Herein, we report a methodology for obtaining (1*S*,5*R*)-(+) and (1*R*,5*S*)-(−)-7-phenyl-3-borabicyclo[3.3.1]non-6-enes by the resolution of the corresponding diastereomeric intramolecular complexes with L- and D-prolinol. 3-Borabicyclo-[3.3.1]non-6-enes thus obtained were transformed into optically active cyclohexene derivatives.

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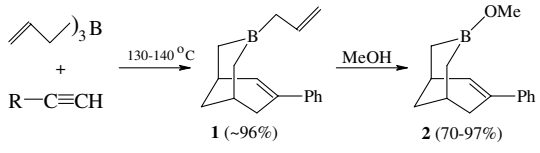


R = H, Alk, Ph, Alkenyl, OR, etc.

Scheme 1.

2. Results and discussion

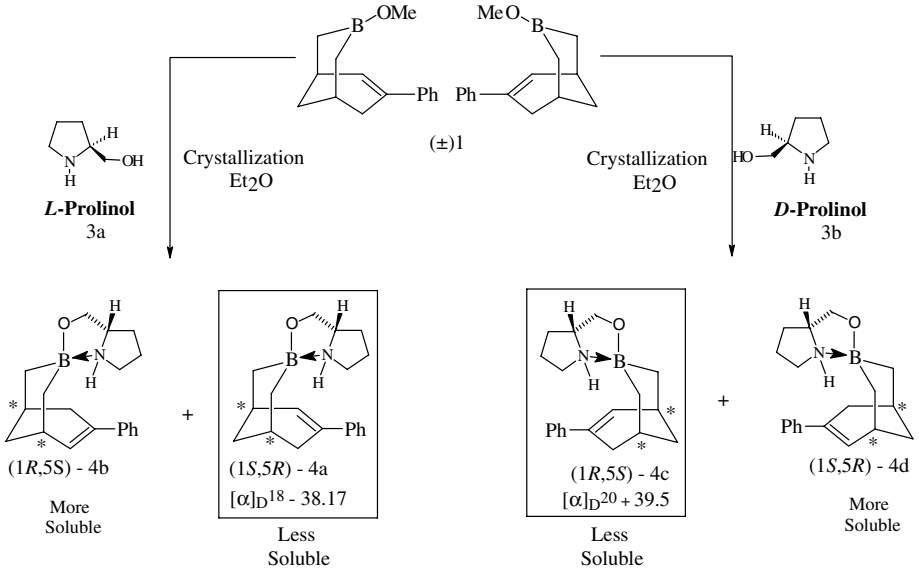
Racemic 3-methoxy-7phenyl-3-borabicyclo[3.3.1] non-6-ene (±) (**1**) was synthesized in 89% yield by interaction between triallylborane and phenylacetylene (135–140 °C) followed by the treatment with methanol [6]. Capacity of diorganylboranes to form air-stable intramolecular adducts with 1,2-aminoalcohols was exploited for resolution of racemate **1**.

We tested D-valinol, D-phenylalaninol and D- and L-prolinol and found prolinols to be chiral auxiliaries of choice. L- (**3a**) and D-prolinol (**3b**) of 98% and 99% enantiomeric purity were used.

The mixture of two diastereomer complexes (1*S*,5*R*)-**4a** and (1*R*,5*S*)-**4b** was obtained by the reaction of **1** with **3a** (double set of signals was observed in ^{1}H and ^{13}C NMR) (Scheme 2). Two successive crystallizations from diethyl ether resulted in (1*S*,5*R*)-**4a** with 96% de, which structure was estimate by ^{1}H NMR spectroscopy (Fig. 1).

An absolute configuration of 3-borabicyclo[3.3.1]-non-6-ene moiety in compounds **4a** was established by X-ray diffraction analysis on the base of the comparison with known stereo structure of L-prolinol as a chiral ligand (Fig. 2).

The conformation of boron containing cycle in **4a** is "distorted *chair*" (the deviations of B(3) and C(9) atoms are −0.39 and 0.74 Å). Due to the presence of the double bond in C(5)C(6)C(7)C(8)C(1)C(9) cycle its conformation is "distorted *sofa*" with the deviation of C(9) atom (0.745(2) Å). The phenyl ring is almost coplanar



Scheme 2.

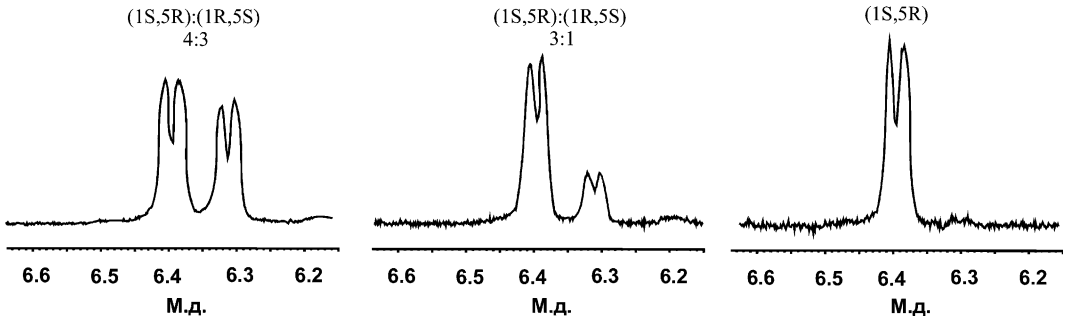


Fig. 1. ^{1}H NMR spectra of 7-phenyl-3-borabicyclo[3.3.1]non-6-ene derivatives with L-prolinol (**4a**) (200.13 MHz, $CDCl_3$, double bonds signals area). (a) The starting diastereomer mixture (~1:1). (b) The product of first crystallization 1*S*,5*R*:1*R*,5*S* – 3:1. (c) The product of second crystallization – separate diastereomer form 1*S*,5*R*.

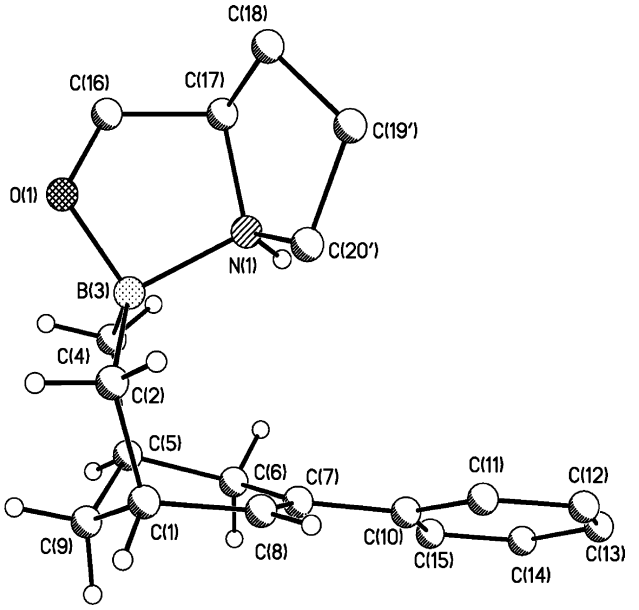


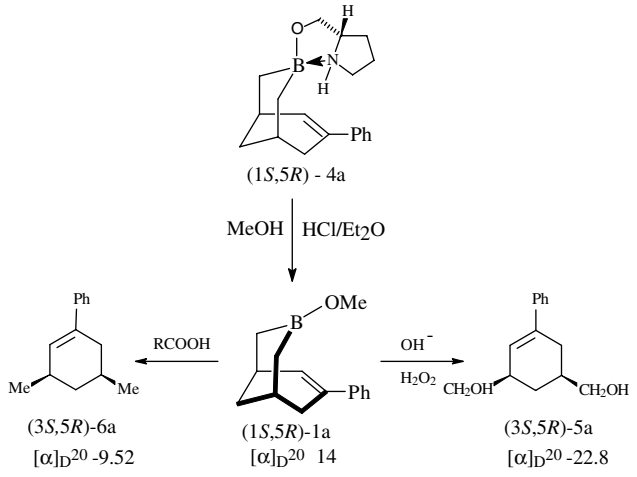
Fig. 2. The general view of 2(*R*)-2[(1*S*,5*R*)7-phebyl-3-borabicyclo[3.3.1]non-6-en-3-iloxymethyl]-tetrahydropyrrole (**4a**). Selected bond lengths (Å): O(1)–B(3) 1.490(5), N(1)–B(3) 1.698(6), C(2)–B(3) 1.618(6), B(3)–C(4) 1.616(6), C(7)–C(8) 1.318(5); bond angles (°): C(16)–O(1)–B(3) 107.1(3) C(20′)–N(1)–B(3) 109.3(8), C(20)–N(1)–B(3) 131.4(8), C(17)–N(1)–B(3) 105.0(4), O(1)–B(3)–C(2) 109.2(4), O(1)–B(3)–C(4) 111.8(4), C(2)–B(3)–C(4) 114.4(4), O(1)–B(3)–N(1) 98.4(3), C(2)–B(3)–N(1) 114.3(4), C(4)–B(3)–N(1) 107.7(4).

with the base of "*sofa*" with the torsion angle C(8)C(7)C(10)C(11) equal to 20.5°. In crystal, the molecules of **4a** are assembled into infinite chains due to the weak N(1)–H(1N)...O(1) $(1-x,\ -1/2+y,\ 1/2-z)$ bond (N...O 3.319(3) Å).

Treatment of (1*S*,5*R*)-diastereomer **4a** with methanol and HCl in diethyl ether led to (1*S*,5*R*)-3-methoxy-7-phenyl-3-borabicyclo[3.3.1]non-6-ene (**1a**) ($[\alpha]_D^{20}$ −14, MeOH). Oxidation of the latter with hydrogen peroxide resulted in (3*S*,5*R*)-3,5-dihydroxymethyl-1-phenylcyclohex-1-ene **(5a)** ($[\alpha]_D^{20}$ −22.8, MeOH) in 60% yield, while hydrocarbon (*3S, 5R*)-**6a** ($[\alpha]_D^{20}$ −9.52, hexane) was synthesized in 78% yield by the protolytic cleavage of (1*S*,5*R*)-**1a** with butyric acid under reflux (see Scheme 3).

The similar simple methodology was utilized for the preparation of (1*R*,5*S*)-diasteromer **2c** ($[\alpha]_D^{20}$ +39.5, MeOH) using D-prolinol as a chiral auxiliary. Further oxidation of **2c** afforded optically active (3*R*,5*S*)-diol **5b**, which was transformed into (3*R*,5*S*)-3,5-dimethyl-1-phenylcyclohex-1-ene **(6b)** ($[\alpha]_D^{20}$ +8.98, hexane) via the reduction of bis-tosylate **7** with $LiAlH_4$ (Scheme 4).

To our best knowledge, cyclohexene derivatives **5a**, **5b** and **6a**, **6b** were prepared in optically active form for the first time. Attempts to determine their optical purity for **5a** and **5b** using europium (III) *tris*[3-(heptafluoropropylhydroxymethylene)-*l*-camphorate] and (+)- and (−)-phenylethylamine as chiral shift reagents were fruitless. We suppose, the above products should have



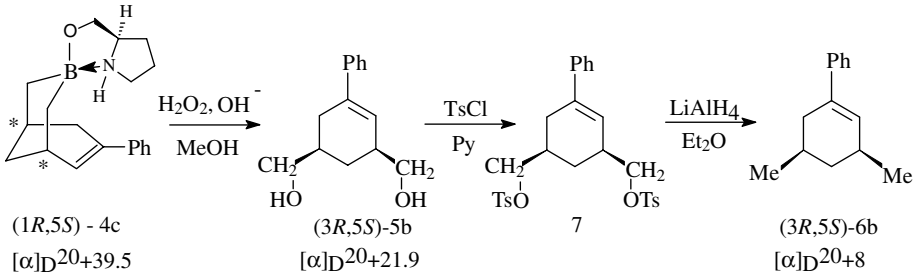
Scheme 3.

optical purity not less than that of their precursors (1*S*,5*R*)-**4a** and (1*R*,5*S*)-**4c** (ca. 96–97%), as soon as oxidation and protolytic cleavage of organoboranes is known to proceed with retention of configuration, without of racemization or epimerization.

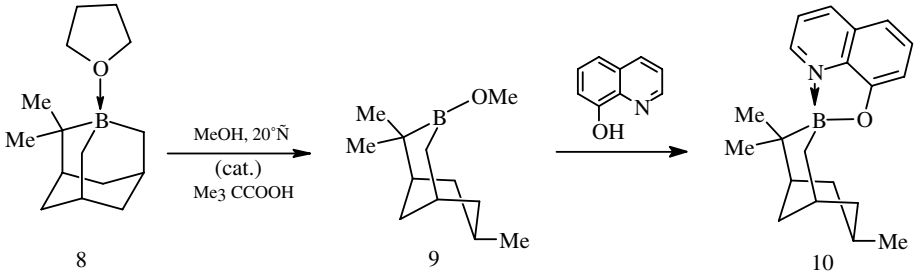
The 2,2-dialkyl-3-borabicyclo[3.3.1]nonane present another interesting member of 3-borabicyclic families with C_1 symmetry suitable for the creation of optically active organoboron derivatives. This compound is readily obtained from 2,2-dimethyl-1-boradamantane (**8**). We have found that THF complex **8** underwent the completely regiospecific cleavage of unsubstituted intracyclic B-C bond under action of methanol in the presence of catalytic amount of pivalic acid and yielded 83% 3-methoxy-2,2,7α-trimethyl-3-borabicyclo-[3.3.1]nonane **9** (according to ^1H and ^{13}C NMR data) (Scheme 5).

The treatment of compound **9** with 8-hydroxyquinoline gave the intramolecular complex **10**, which molecular and crystal structure was proved by X-ray diffraction analysis (Fig. 3).

The boron containing cycle in **10** has conformation of "*chair*" with deviations of B(3) and C(9) atoms by −0.571(2) and 0.762(2) Å. In contrast, C(5)C(6)C(7)C(8)C(1)C(9) cycle has conformation "*boat*" (deviation of C(9) and C(7) atoms are 0.707(2) and 0.625(2) Å, respectively) with the methyl group in equatorial position. Totally, the 3-borabicyclo[3.3.1]nonane fragment in **10** may be described as "*chair-boat*" conformer. The B(3) atom has distorted tetrahedral configuration with the decrease of the O(1)B(3)N(1) angle to 97.3(1)°. The presence of two methyl groups at C(4) atom lead to some shortening of the B(3)–C(4) bond (1.628(2) Å) in comparison to B(3)–C(2) one (1.605(2)Å). The B(3)–N(1) bond length (1.637(2) Å) in **10** is slightly elongated in comparison with the corresponding one in 7-endo-methyl-3-borabicyclo[3.3.1]non-3-yl 8-hydroxyquinolinate (1.607 Å) [6] but significantly shorter than the corresponding value in **4a**.



Scheme 4.



Scheme 5.

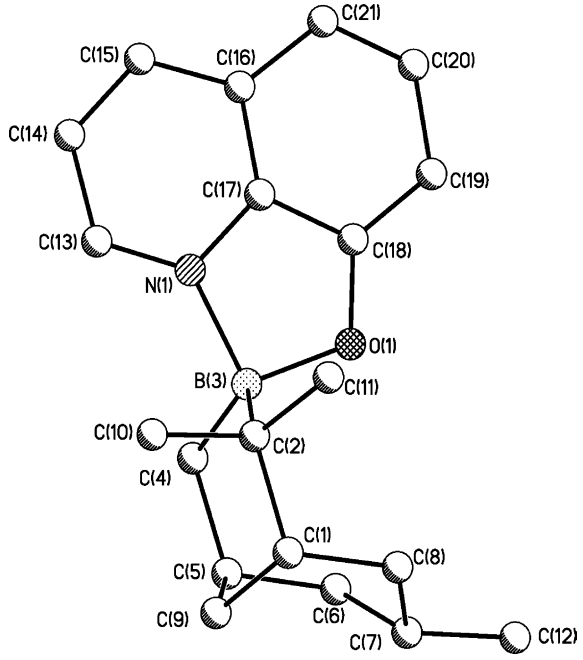


Fig. 3. The general view of (2,2,7α-trimethyl-3-borabicyclo[3.3.1]non-3-yl)-8-hydroxyquinolinate (**10**). Selected bond lengths (Å): N(1)–C(13) 1.320(2), N(1)–C(17) 1.359(2), O(1)–C(18) 1.335(2), O(1)–B(3) 1.544(2), N(1)–B(3) 1.637(2), B(3)–C(4) 1.605(2), C(2)–B(3) 1.628(2); bond angles (°): C(18)–O(1)–B(3) 111.1(1), O(1)–B(3)–C(4) 112.5(1), O(1)–B(3)–C(2) 111.3(1), C(4)–B(3)–C(2) 113.8(1), O(1)–B(3)–N(1) 97.3(1), C(4)–B(3)–N(1) 110.0(1), C(2)–B(3)–N(1) 110.8(1).

We expected that some optically active amino alcohols as chiral auxiliary might be used for resolution of compound **9**. Unfortunately, we failed to resolve compound **9** into enantiomers with D-valinol, D-phenylalaninol and D- and L-prolinol. Probably, in this case, the formation of expected chelate product is impossible because of steric hindrances (due to the presence of two methyl groups).

3. Conclusion

In conclusion, we proposed a novel method for the synthesis of the optically active cyclohexene derivatives using 3-borabicyclo[3.3.1]non-6-ene enantiomers. We have shown that L- and D-prolinol proved to be the most favourable choice of reagents for the enantiomeric resolution of borabicyclic derivatives.

4. Experimental

4.1. General

All operations with organoboron compounds were carried out under dry argon. The solvents were purified according to the standard procedures. The optical rotation was measured on a Perkin–Elmer model 341 polarimeter. The ^{1}H, ^{13}C, and ^{11}B NMR spectra were recorded on Bruker AC-200 instrument (200.13, 50.32 and 64.21 MHz, respectively) or Bruker DRX-500 (500.13 and 125.75 MHz). Compound **8** was prepared according to [7]. L- and D-Prolinol were synthesized as described in [8].

*4.2. (1S,5R)- and (5R,1S)-diastereomers (**4a** + **4b**)*

To a solution of **1** (7.76 g, 34.2 mmol) in diethyl ether (20 ml) was added solution of L-prolinol (3.46 g, 34.2 mmol) in diethyl ether (15 ml) and reaction mixture left to stir at room temperature for 0.5 h. The solvent was removed under reduced pressure to yield the air-stable (5*R*,1*S*)- and (1*S*,5*R*)-diastereomers **4a** and **4b** (9.42 g), ^{11}B NMR ($CDCl_3$): δ = 7.36 ppm. Anal. Calc. for $C_{19}H_{26}BNO$ (%): C, 76.75; H, 8.88; B, 3.36; N, 4.70. Found (%): C, 77.3; H, 8.88; B, 3.66; N, 4.74.

*4.2.1. 2(R)-2[(1S,5R)7-Phenyl-3-borabicyclo[3.3.1]-non-6-en-3-yloxymethyl]-tetrahydropyrrole (**4a**)*

The (1*S*,5*R*)-diastereomer **4a** (2.7 g, 28.6%) with (97% de) was isolated from the diastereomers mixture of **4a** + **4b** by fractional crystallizations from diethyl ether using the sample of 1*S*,5*R*-isomer as a seed. $[\alpha]_D^{18}$ − 38.17 (*c* = 4.2, MeOH), m.p. 105–107 °C. 500.13 MHz; ^{1}H NMR ($CDCl_3$): δ = 0.54 (br. d, 2H, H-2α, 4α, ^2J(H-2α, H-2β) = 14.34 Hz), 0.72 (dd, 2H, H-2β, 4β, ^2J(H-2α, H-2β) = 14.34 Hz, ^2J(H-2β, H-1) = 6.1 Hz), 1.42, 1.88 (m, 2H, $NHCH_2CH_2$), 1.57, 2.05 (m, 2H, $CH_2CH_2CH_2$), 1.69 (br.dd, 2H, H-9*syn*, H-9*anti*, ^2J(H-9*syn*, H-9*anti*) = 11.59 Hz), 2.29 (d, 1H, H-8β, ^3J(H-8β, H-8α) = 17.7 Hz), 2.49 (s, 1H, H-1), 2.65 (s, 1H, H-5), 2.82 (m, 3H, H-8α, $NHCH_2$), 3.49 (br.d, 1H, OCH_2), 3.66 (s, 1H, N*H*). 3.74 (a, 1H, OCH_2CH), 4.2 (m, 1H, OCH_2), 6.62 (d, 1H, H-6, ^3J(H-6,H-5) = 4.58 Hz), 7.21 (t, 1H, *p*-Ph, *J* = 7.02 Hz), 7.31 (t, 2H, *m*-Ph, *J* = 7.94 Hz), 7.39 (d, 2H, *o*-Ph, *J* = 7.94 Hz) ppm. 125.75 MHz; ^{13}C NMR ($CDCl_3$): δ = 27.16 ($NH-CH_2-CH_2$), 28.47 (C-1), 31.25 (C-5), 32.37 (CH_2-CH_2-CH), 33.89 (C-9), 36.12 (C-8), 48.30 ($NH-CH_2$), 60.68 ($CH-CH_2-O$), 67.88 (CH_2-O), 124.51 (*o*-Ph), 126.93 (*p*-Ph), 128.61 (*m*-Ph), 132.13 (C-7), 134.30 (C-6), 141.78 (*ipso*-Ph) ppm.

*4.2.2. 2(R)-2[(5S,1R)7-Phenyl-3-borabicyclo[3.3.1]-non-6-en-3-yloxymethyl]-tetrahydropyrrole (**4b**)*

500.13 MHz; ^{1}H NMR ($CDCl_3$): δ = 0.54 (br. d, 2H, H-2α, 4α, ^2J(H-2α, H-2β) = 14.34 Hz), 0.72 (dd, 2H, H-2β, 4β, ^2J(H-2α, H-2β) = 14.34 Hz, ^3J(H-2β, H-1) = 6.1 Hz), 1.42, 1.88 (m, 2H, $NHCH_2CH_2$), 1.57, 2.05 (m, 2H, $CH_2CH_2CH_2$), 1.69 (br.dd, 2H, H-9*syn*, H-9*anti*, ^2J(H-9*syn*, H-9*anti*) = 11.59 Hz), 2.09 (d, 1H, H-8β, ^2J(H-8β, H-8α) = 17.7 Hz), 2.49 (s, 1H, H-1), 2.65 (s, 1H, H-5), 2.82 (m, 3H, H-8α, $NHCH_2$), 3.41 (d, 1H, OCH_2, ^3J(H-CH_2,H-CH) = 9.15 Hz), 3.66 (s, 1H, N*H*). 3.74 (a, 1H, OCH_2CH), 3.98 (m, 1H, OCH_2), 6.41 (d, 1H, H-6, ^3J(H-6,H-5) = 4.58 Hz), 7.21 (t, 1H, *p*-Ph, *J* = 7.02 Hz), 7.31 (t, 2H, *m*-Ph, *J* = 7.94 Hz), 7.39 (d, 2H, *o*-Ph, *J* = 7.94 Hz) ppm. 125.75 MHz; ^{13}C NMR ($CDCl_3$): δ = 27.03 ($NH-CH_2-CH_2$), 28.47 (C-1), 31.31 (C-5), 32.41 (CH_2-CH_2-CH), 33.79 (C-9), 36.31 (C-8), 48.20 ($NH-CH_2$), 60.40 ($CH-CH_2-O$), 67.52 (CH_2-O), 124.19 (*o*-Ph), 126.74 (*p*-Ph), 128.61 (*m*-Ph), 132.34 (C-7), 134.30 (C-6), 141.78 (*ipso*-Ph) ppm.

*4.3. 2(R)-2[(5S,1R)7-Phenyl-3-borabicyclo[3.3.1]non-6-en-3-yloxymethyl]-tetrahydropyrrole (**4c**) and 2(R)-2[(1S,5R)7-Phenyl-3-borabicyclo[3.3.1]non-6-en-3-yloxymethyl]-tetrahydropyrrole (**4d**)*

The mixture of **4c** and **4d** was synthesized analogously to the mixture of **4a** and **4b** from D-prolinol (4.00 g, 39.5 mmol) in diethyl ether (20 ml) and a solution of **1** (9.01 g, 39.5 mmol) in diethyl ether (25 ml). The (1*R*,5*S*)-diastereomer **4c** (3.49 g, 30%) with (98% de) was isolated from the diastereomers mixture of **4c** + **4d** by fractional crystallizations from diethyl ether using the sample of 1*R*,5*S*-isomer as a seed.

$[\alpha]_D^{20}$ + 39.5 (*c* = 1.7, MeOH), m.p. 105–107 °C. The parameters of ^{1}H NMR and ^{13}C NMR are identical to data for (1*S*,5*R*)-diastereomer **4a**.

*4.4. (1S,5R)-3-Methoxy-7-phenyl-3-borabicyclo[3.3.1]-non-6-ene (**1a**)*

To the solution of compound **4a** (1.13 g, 3.82 mmol) in a mixture of diethyl ether (10 ml) and MeOH (0.36 g,11.46 mmol) was cooled and the solution of HCl (3.67 N, 2.08 ml) in diethyl ether was added. The reaction mixture was stirred for 3 h. The solvent was evaporated and the residue was extracted with pentane (20 ml). Removal of the solvent and distillation of the residue gave (0.82 g, 95.9%) of **1a**, b.p. 114–115 °C (1.5 mmHg), $[\alpha]_D^{20}$ − 14.0 (*c* = 20.3, MeOH). ^{11}B NMR ($CDCl_3$, δ): δ = 54.67 ppm. ^{1}H NMR ($CDCl_3$): δ = 0.90–1.39 (m, 5H, H-2α, H-2β, H-4α, H-4β, H-8β), 1.90 (dd, 2H, H-9*anti*, H-9*syn*, ^2J(H-9*syn* -H-9*anti*) = 11.62 Hz), 2.29 (d, 1H, H-8α, ^2J(H-8α, H-8β) = 16.64 Hz), 2.70 (br.s, 1H, H-1), 2.79 (br.s, 1H, H-5), 3.69 (s, 3H, O*Me*), 6.21 (d, 1H, H-6, ^3J(H-6, H-5) = 5.8 Hz), 7.24–7.45 (m, 5H, H-Ph) ppm. 50.32 MHz; ^{13}C NMR ($CDCl_3$): δ = 24.30 (C-2), 25.58, (C-4), 27.43 (C-1), 29.76 (C-5), 32.31 (C-8), 36.62 (C-9), 52.96 (O*Me*), 125.16 (*o*-Ph), 126.63 (*p*-Ph), 128.16 (*m*-Ph), 131.35 (C-7), 132.82 (C-6), 142.52 (*ipso*-Ph) ppm.

4.5. Cyclohex-1-ene derivatives

*4.5.1. (3S,5R)-3,5-cis-Dihydroxymethyl-1-phenylcyclohex-1-ene (**5a**)*

To a mixture of **1a** (0.5 g, 2.2 mmol) in MeOH (2 ml) and NaOH (10%, 0.78 ml) was added H_2O_2 (25%, 1.5 ml) under cooling. The resulting solution was stirred for 6 h and after was heated under reflux for 1 h, then cooled to room temperature. The solvent was removed,

the residue was dissolved in THF (5 ml). Precipitate was filtered off and dried in vacuo and compound **5a** (0.29 g, 60%) was obtained, m.p. 122–124 °C, $[\alpha]_D^{20}$ − 22.8 (c = 1, MeOH). ^{1}H NMR (CD_3OD): δ = 0.86–2.60 (m, intricate multiplet of aliphatic protons), 3.68 (br.s, 4H, OCH_2), 6.06 (s, 1H, H-2), 7.24–7.45 (m, 5H, H-Ph) ppm. ^{13}C NMR ($CDCl_3$): δ = 30.37 (C-6); 32.30 (C-4); 38.40 (C-5); 41.27 (C-3); 67.86 (CH_2-CH-CH_2-OH); 68.30 (CH-CH-CH_2-OH); 126.20 (*o*-Ph); 126.74 (*p*-Ph); 127.86 (C-2); 129.21 (*m*-Ph); 138.65 (C-1); 143.47 (*ipso*-Ph) ppm. Anal. Calc. for $C_{14}H_{18}O_2$(%): C, 76.85; H, 8.13. Found (%): C, 77.03; H, 8.31.

4.5.2. (3R,5S)-3,5-Dihydroxymethyl-1-phenylcyclohex-1-ene (**5b**)

To a mixture of **4c** (1 g, 3.3 mmol) and NaOH (10%.1.21 ml) was added H_2O_2(25%, 3 ml) under cooling. Then resulting mixture was extracted with THF (10 ml). Precipitate was filtered off and dried in vacuo and compound **5b** (0.69 g, 93%) was obtained, m.p. 122–124 °C,. $[\alpha]_D^{20}$ + 21.9 (c = 1, MeOH). The parameters of ^{1}H NMR and ^{13}C NMR are identical to data for (1*S*,5*R*)-diastereomer **5a**.

4.5.3. (3S,5R)-3,5-cis-Dimethyl-1-phenylcyclohex-1-ene (**6a**)

To the compound **1a** (0.87 g, 3.8 mmol) was added butyric acid (0.34 g, 3.8 mmol) and the mixture was heated under reflux for 9 h and stirred at room temperature for 48 h. The distillation of the residue gave compound **6a** (0.56 g, 78%), b.p. 50–52 °C (1.5 mmHg), $[\alpha]_D^{20}$ − 9.52 (c = 1.7, hexane). ^{1}H NMR ($CDCl_3$): δ = 0.9–1.05 (m, 2H, CH-CH_2-CH), 1.09–1.20 (d, 6H, 2Me, ^2J = 6.83 Hz), 1.8–2.6 (m, intricate multiplet of aliphatic protons) ppm. ^{13}C NMR ($CDCl_3$): δ = 22.00 (*C*H$_3$); 22.40 (*C*H$_3$); 29.62 (C-5); 32.21 (C-3); 36.24 (C-6); 40.41 (C-4); 125.04 (*o*-Ph); 126.56 (*p*-Ph); 128.13 (*m*-Ph); 130.81 (C-2); 135.69 (C-1); 142.24 (*ipso*-Ph) ppm.

4.5.4. (3R,5S)-3,5-cis-Dimethyl-1-phenylcyclohex-1-ene (**6b**)

To a solution of $LiAlH_4$(0.42 g, 11.1 mmol) in diethyl ether (10 ml) the solution of **7** (1.27 g, 2.78 mmol) in THF (10 ml) was added and the reaction mixture was heated for 10 h. The solvent was removed and the residue was dissolved in diethyl ether (10 ml). Then the solution was decomposed by NaOH (15%) under cooling. Precipitate was filtered off, decomposed by H_2SO_4 (10%) and extracted with diethyl ether (3 × 15 ml) The organic extracts were dried over Na_2SO_4. The solvent was evaporated and distillation of the residue gave **6b** (0.45 g, 87%), b.p. 50–52 °C (1.5 mmHg),. $[\alpha]_D^{20}$ − 8.98 (c = 1.5, hexane). The parameters of ^{1}H NMR and ^{13}C NMR are identical to data for (1*S*,5*R*)-diastereomer **6a**.

4.5.5. (3R,5S)-3,5-cis-Di-p-toluenesulfoxymethyl-1-phenylcyclohex-1-ene (**7**)

To a solution of compound **5b** (0.69 g, 3.1 mmol) in pyridine (10 ml) was added *p*-toluoenesulfonyl chloride (1.77 g, 9.3 mmol) at 0 °C and the reaction mixture was stirred at this temperature for 12 h. Then this mixture was dissolved in ice water (50 ml) and extracted with benzene (3 × 15 ml). The extracts were combined and washed with HCl (10%) and dried over Na_2SO_4. Removal of the solvent and distillation of the residue gave compound **7** (1.27 g, 90%), m.p. 107–108 °C. Anal. Calc. for $C_{28}H_{30}O_6S_2$ (%): C, 63.85; H, 5.74; S, 12.18. Found (%): C, 64.58; H, 6.18; S, 11.6. ^{1}H NMR ($CDCl_3$): δ = 0.96 (dt, 2H, H-4, ^2J = 11.79 Hz), 1.87 (m, 1H, H-5), 2.11 (m, 1H, H-3), 2.45 (d, 6H, 2*Me*, ^2J = 5.2 Hz), 3.95 (m, 4H, OCH_2), 5.76 (s, 1H, H-2), 7.24–7.40 (m, 8H, H-Ts), 7.76–7.83 (m, 5H, H-Ph) ppm. ^{13}C NMR ($CDCl_3$): δ = 21.78 (C-*C*H$_3$), 28.10 (C-6), 30.33 (C-4), 33.84 (C-5), 36.52 (C-3), 73.64 (C-CH_2CH*C*H$_2$O), 74.15 (C-CHCH*C*H$_2$O), 122.89, 125.26, 127.55, 128.42, 130.01, 130.08, 132.85, 138.12, 140.86, 145.05 (Ph-, Ts-moiety) ppm.

4.6. 2,2,7α-Trimethyl-3-methoxy-3-borabicyclo[3.3.1]nonane (**9**)

To a solution of THF complex of 2,2-dimethyl-1-boraadamantane (1.05 g, 4.3 mmol) in tetrahydrofurane (5 ml) was added MeOH (0.14 g, 4.3 mmol) and pivalic acid (0.1 g, 0.9 mmol). The reaction mixture was refluxed for 1 h. Removal of the solvent and distillation of the residue gave compound **9** (0.69 g, 83%), b.p. 75–77 °C (1.5 mmHg). 500 MHz; ^{1}H NMR ($CDCl_3$): δ = 0.89 (d, 3H, *Me*-7α, ^2J = 4.13 Hz), 0.91 (s, 9H, 2*Me*), 0.97 (dd, 1H, H-4α, ^2J(H-4α, H-4β) = 16.39 Hz), 1.04–1.1 (br.m, 2H, H-4β, H-6α), 1.38 (br. s, 1H, H-1), 1.45 (dm, 1H, H-8α, ^2J(H-8α, H-8β) = 14.21 Hz), 1.5 (dm, 1H, H-9*anti*, ^2J(H-9*anti*, H-9*syn*) = 13.28 Hz), 1.72 (dt, 1H, H-8β, ^2J(H-8β, H-8α) = 14.21 Hz, ^3J(H-8β, H-1) = 6.41 Hz), 1.81–1.87 (m, 2H, H-7β, H-9*syn*), 1.94 (dt, 1H, H-6β, ^2J(H-6β, H-6α) = 13.52 Hz, ^3J(H-6β, H-5) = 6.64 Hz), 2.25 (br.s, 1H, H-5), 3.62 (s, 3H, O*Me*) ppm. 125.75 MHz; ^{13}C NMR ($CDCl_3$): δ = 23.66, 23.89 (*Me*-2), 25.97 (C-7), 26.93 (*Me*-7), 28.52 (C-5), 30.23 (C-9), 34.76 (C-8), 40.43 (C-6), 42.13 (C-1), 53.11 (O*Me*) ppm. Anal. Calc. for $C_{12}H_{23}BO$: C, 74.25; H, 11.94; B, 5.57%. Found: C, 73.99; H, 11.05; B, 5.89%.

4.7. (2,2,7α-Trimethyl-3-borabicyclo[3.3.1]non-3-yl)-8-hydroxyquinolinate (**10**)

To a solution of **9** (0.266 g, 1.3 mmol) in diethyl ether (4 ml) was added 8-hydroxyquinoline (0.19 g, 1.3 mmol) in diethyl ether (6 ml) and mixture was stirred for 1 h. Then the solvent was evaporated and compound **10**

Table 1
Crystal data and structure refinement parameters for **4a** and **10**

Molecular formula	**4a** $C_{19}H_{26}BNO$	**10** $C_{20}H_{26}BNO$
Formula weight	295.22	307.23
Colour, shape	Yellow, prism	Colorless, prism
Diffractometer	SMART CCD	Siemens P3/PC
Temperature (K)	120(2)	293(2)
Crystal system	Orthorhombic	Monoclinic
Space group	$P2_12_12_1$	$C2/c$
a (Å)	6.7253(4)	31.572(8)
b (Å)	10.4345(9)	8.006(2)
c (Å)	24.076(6)	15.379(5)
β (°)		117.08(2)
V (Å^3)	1689.6(5)	3460.9(16)
$Z(Z')$	4(1)	8(1)
$F(000)$	640	1328
ρ_{calc} (gcm^{-1})	1.161	1.179
Linear absorption, μ (cm^{-1})	0.69	0.70
θ Range (°)	2.13–26.03	2.65–27.05
Measured	5964	3861
Unique	3245 [R(int) = 0.0540]	3800 (0.0130)
With [$I > 2\sigma(I)$]	1252	2093
Parameters	236	312
Final $R(F_{hkl})$: R_1	0.0590	0.0377
wR_2	0.1720	0.0948
GOF	0.950	0.952
ρ_{max}/ρ_{min} (e Å^{-3})	0.137/−0.165	0.138/−0.146

(0.36 g, 85.5%) was obtained as yellow crystalls, m.p. 140–142 °C. ^{1}H NMR (C_6D_6): δ = 0.79 (s, 3H, *Me*-2), 0.93 (dd, 1H, H-4α, ^2J(H-4α, H-4β)=13.35 Hz), 1.03 (s, 3H, *Me*-2), 1.83–2.41 (m, intricate multiplet of aliphatic protons), 2.73 (br.s, 1H, H-5), 6.42–7.66 (m, 6H, intricate multiplet of 8-hydroxyquinolinate fragment). ^{13}C NMR (C_6D_6): δ = 23.40, 23.72 (*Me*-2), 26.56 (C-7), 27.20 (*Me*-7), 27.29 (C-9), 28.60 (C-5), 33.20 (C-8), 38.21 (C-6), 43.09 (C-1), 108.52 (C-5′), 110.50 (3′), 121.58 (C-7′), 128.25 (C-4′), 132.62 (C-6′), 137.12 (C-2′), 138.49 (C-9′), 138.75 (C-1′), 159.88 (C-8′) ppm. Anal. Calc. for $C_{20}H_{26}BNO$ (%): C, 78.19; H, 8.53; B, 3.52. Found: C, 78.38; H, 8.63; B, 3.21.

4.8. X-ray diffraction

X-ray diffraction experiments were carried out with a Bruker SMART 1000 CCD area detector for **4a** and Siemens P3/Pc for **10** using graphite monochromated Mo Kα radiation (λ = 0.71073 Å, ω and $\theta/2\theta$-scans for **4a** and **10**, respectively). The structures were solved by direct method and refined by the full-matrix least-squares against F^2 in anisotropic approximation for non-hydrogen atoms. The analysis of Fourier density synthesis in **4a** have revealed that C(19) and C(20) atoms are disordered by two positions, which were refined with equal occupancies. Crystal data and structure refinement parameters for **4a** and **10** are given in Table 1. All calculations were performed on an IBM PC/AT using the SHELXTL software [11].

4.9. Supplementary material

The crystallographic data have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 253148 for **4a** and No. 253147 for **10**. Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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