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A Practical Method for Preparation of Optically Pure Oxazaborolidines from α-Pinene

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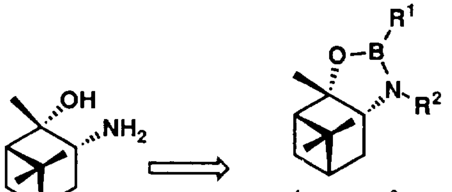
***Abstract*:** : (1S,2S,3R,5S)- and (1S,2S,3R,5S)-3-Amino-2-hydroxypinane (**1** and **2**) were prepared from the corresponding α-pinene in optically pure form. They and their derivatives reacted with various organoborane compounds. A variety of chiral oxazaborolidines **3a-e** and **4** were obtained in high yield.

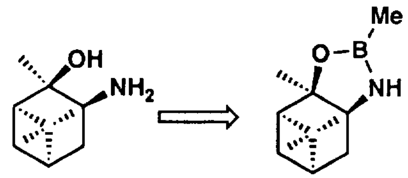
During a past decade, a number of chiral oxazaborolidines have been synthesized and applied to asymmetric synthesis of optically active secondary alcohols. In borane reduction of prochiral ketones,[1] addition of diethyl zinc to aldehydes,[2] rhodium-catalyzed hydroboration of styrenes[3] and alkynylation of aldehydes,[4] oxazaborolidine compounds have proved to be an excellent chiral promoter. The desired secondary alcohols were obtained with high enantioselectivity in every case. Recent progress in the asymmetric borane reduction,[5] aminoalcohols which both enantiomers are available have been used for starting materials to synthesize oxazaborolidines.

α-Pinene is a good chiral source because both enantiomers are commercially available, so its derivatives such as pinanediol,[6] 2-hydroxypinan-3-one,[7] Alpine-Borane®,[8] and B-chlorodiisopinocampheylborane[9] have been used for chiral reagents in asymmetric synthesis. In this paper, we wish to report a practical method for preparation of the optically pure aminoalcohols (**1** and **2**) and the oxazaborolidines (**3a-e** and **4**) from the corresponding α-pinene. These compounds are expected to be useful catalysts for various asymmetric syntheses.



1

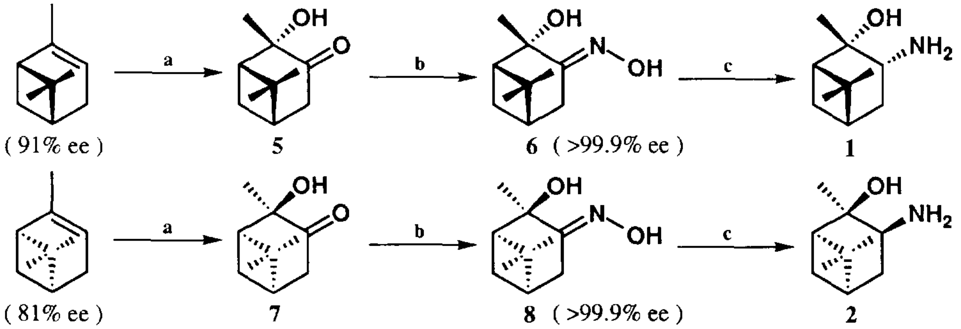
3a R^1 = Me, R^2 = H
3b R^1 = Bu, R^2 = H
3c R^1 = Ph, R^2 = H
3d R^1 = Me, R^2 = Me
3e R^1 = Me, R^2 = Ts



2

4

Although Burak et al. already reported the synthesis of 3-amino-2-hydroxypinane,[10] the enantiomeric purity of the product was not described. We synthesized both enantiomers of 3-amino-2-hydroxypinane in optically pure form according to the Burak's procedure with some modifications. In order to prepare (1S,2S,3R,5S)-3-amino-2-hydroxypinane (**1**), (1R,5R)-α-pinene (91% ee optical purity)[11] was adopted as a starting material because it was available at a relatively low price. Oxidation of the α-pinene with potassium permanganate followed by reaction with 50% aqueous hydroxylamine[12] instead of $NH_2OH{\cdot}HCl\text{-}AcONa$[10] afforded oxime **6** as a white solid in better yield. The optically impure solid was recrystallized fractionally from ethyl ether-hexane to provide the optically pure oxime **6** as white crystals. Reduction of the oxime **6** with lithium aluminum hydride gave the desired aminoalcohol **1**. (1R,2R,3S,5R)-3-Amino-2-hydroxypinane (**2**) was also prepared from (1S,5S)-α-pinene (81% ee optical purity).[11]



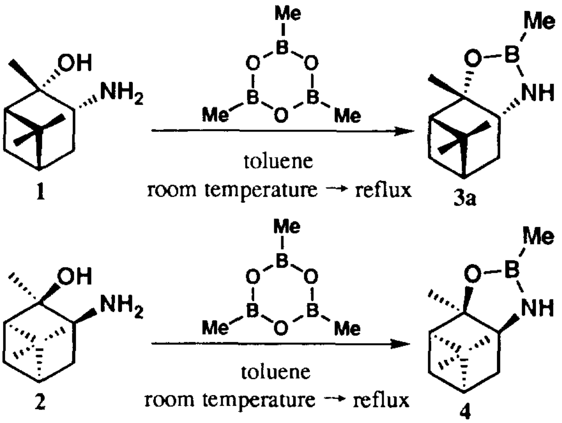
(91% ee) **5** **6** (>99.9% ee) **1**

(81% ee) **7** **8** (>99.9% ee) **2**

(a) $KMnO_4$, 90% aqueous acetone, -10℃; (b) i) 50% aqueous NH_2OH, EtOH, reflux; ii) fractional recrystallizations from Et_2O-hexane; (c) $LiAlH_4$, Et_2O, reflux

Scheme 1

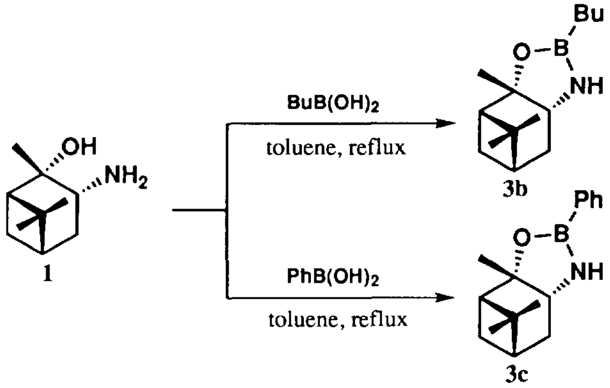
Synthesis of B-methyl oxazaborolidines **3a** and **4** were accomplished by the reaction of the corresponding aminoalcohol **1** and **2** with trimethylboroxine (Scheme 2).[13] B-Butyl and B-phenyl oxazaborolidines **3b** and **3c** were prepared from aminoalcohol **1** by refluxing in toluene with butylboronic acid and phenylboronic acid respectively (Scheme 3).[14] These new oxazaborolidines were obtained in high yield and were characterized by IR, ^{1}H-NMR, ^{13}C-NMR and ^{11}B-NMR spectra.



1 **3a**

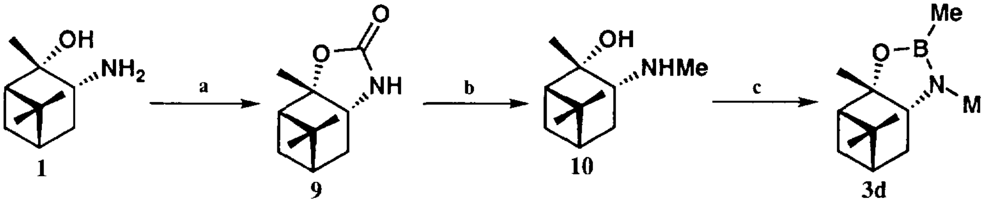
2 **4**

Scheme 2



Scheme 3

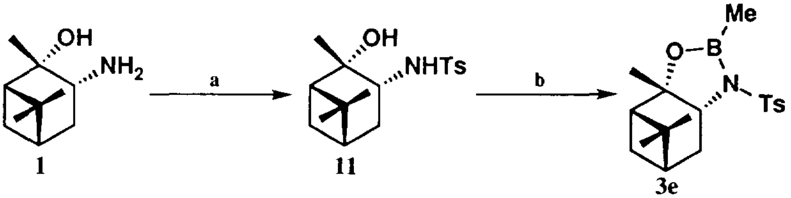
B,N-Dimethyl oxazaborolidine **3d** was synthesized by the following procedure shown in Scheme 4. Reaction of aminoalcohol **1** with 1,1'-carbonyldiimidazole gave oxazolinone **9**, which was reduced with lithium aluminum hydride to afford N-methyl aminoalcohol **10**. Cyclization of the aminoalcohol with trimethylboroxine provided the desired oxazaborolidine **3d** in high yield.



(a) 1,1'- carbonyldiimidazole, THF, room temperature; (b) $LiAlH_4$, THF, reflux; (c) trimethylboroxine, toluene, room temperature → reflux

Scheme 4

In recent papers N-sulfonyl oxazaborolidinone were shown to be efficient catalysts for asymmetric Dields-Alder reactions[15] and asymmetric aldol condensations.[16] We tried to synthesize N-tosyl oxazaborolidine **3e** and it was obtained quantitatively from aminoalcohol **1** (Scheme 5).



(a) *p*-toluenesulfonyl chloride, 1N NaOH, THF, room temperature; (b) trimethylboroxine, toluene, reflux

Scheme 5

Herein we reported the synthesis of new chiral oxazaborolidine compounds whose both enantiomers were available. We are now investigating various asymmetric syntheses using these oxazaborolidines. The results will be published in another paper.

EXPERIMENTAL

Melting points were determined on a Yanagimoto micro melting point apparatus. Infrared spectra were measured with a JASCO FT IR-300 spectrometer. ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a JEOL GSX-270 or JNM A-400 spectrometer with tetramethylsilane as an internal standard. ^{11}B-NMR spectra were recorded on JEOL JNM A-400 spectrometer with BF_3 etherate as an external standard. Optical rotations were measured with a PERKIN-ELMER 241 polarimeter. HPLC was conducted using a Waters Model 510 pumping system with a JASCO UVIDEC-100-IV detector. Silica gel (Fuji Silysia BW-200) was used for column chromatography. All solvents were dried over 3A or 4A molecular sieves before use.

(1S,2S,5S)-2-Hydroxypinan-3-one (5):
Ketoalcohol **5** was prepared in 43% yield from (1R,5R)-α-pinene (91% ee)[11] according to the literature procedure.[17]

(1S,2S,5S)-2-Hydroxypinan-3-one oxime (6):
To a solution of ketoalcohol **5** (58.9 g, 0.35 mol) in 400 ml of ethanol was added 50% aqueous NH_2OH[12] (69.4 g, 1.05 mol). The reaction mixture was refluxed for 24 h, and the volatiles were removed under reduced pressure. The resulting residue was redissolved in 2N NaOH (250 ml), and washed with hexane. The aqueous layer was acidified with 12N HCl, and extracted with ethyl acetate (250 ml x 3). The extracts were washed with water and brine, dried over $MgSO_4$, and the solvent was evaporated *in vacuo*. The crude residue was recrystallized from ethyl acetate-hexane to afford 42.9 g (67%) of **6** as a white solid. The fractional recrystallizations from ethyl ether-hexane provided the optically enriched **6** (29.9 g, 47%). The enantiomeric purity was determined to be >99.9% ee by HPLC analysis using a Chiralcel OD-R chiral column (purchased from Daicel Chemical Industries, Ltd.) with a mixture of CH_3CN-H_2O (2:8) as an eluent: mp 119-120 ℃ (lit.[7a] mp 117-118 ℃); $[\alpha]_D^{22}$ +18.9° (*c* 3.0, $CHCl_3$) (lit.[7a] $[\alpha]_D^{22}$ +16.6° (*c* 3.0, $CHCl_3$)); IR (KBr) ν_{max} cm^{-1}: 3310, 3087, 2978, 1643, 1448, 1386, 1086; ^{1}H-NMR ($CDCl_3$) δ 0.87 (s, 3H), 1.31 (s,3H), 1.55 (s, 3H), 1.57 (d, *J* = 10.4Hz, 1H), 2.00 (m, 2H), 2.29-2.38 (m, 1H), 2.65-2.81 (m, 3H), 8.07 (s, 1H); Anal. Calcd for $C_{10}H_{17}NO_2$: C, 65.54; H,9.35; N,7.64. Found: C,65.45; H,9.26; N,7.68.

(1S,2S,3R,5S)-3-Amino-2-hydroxypinane (1):
To an ice cooled suspension of lithium aluminum hydride (7.97 g, 0.21 mol) in 500 ml of ethyl ether was added oxime **6** (12.83 g, 0.07 mol). The reaction mixture was refluxed for 14 h and then cooled to about 5 ℃. Ethyl acetate (8 ml), 10% aqueous NaOH (8 ml) and waters (24 ml) were added dropwise, and the resulting mixture was stirred at room temperature for 4 h. The insoluble material was removed by filtration through celite, and the filtrate was evaporated *in vacuo*. The residue was acidified with 10% HCl-methanol, and ethyl ether was added. The resulting white solid was filtered and dried to give 9.0 g (62%) of **1** hydrochloride. The solid was dissolved in 1N NaOH (100 ml), and the solution was extracted with CH_2Cl_2, and dried over $MgSO_4$. Evaporation of the solvent gave 7.36 g (62%) of **1** as a white solid, which was recrystallized from ethyl ether-hexane: mp 45-46.5 ℃; $[\alpha]_D^{22}$ -14.3° (*c* 1.0, $CHCl_3$); IR (KBr) ν_{max} cm^{-1}: 3479, 3419, 3272, 2910, 1566, 1480; ^{1}H-NMR ($CDCl_3$) δ 0.98 (s, 3H), 1.19 (s, 3H), 1.27 (s, 3H), 1.31 (m, 1H), 1.33 (d, *J* = 10.4Hz, 1H), 1.85-1.91 (m, 1H), 2.02 (t, *J* = 5.5Hz, 1H), 2.11-2.20 (m, 1H), 2.39-2.49 (m, 1H), 3.24 (dd, *J* = 6.1, 9.8Hz, 1H); Anal. Calcd for $C_{10}H_{19}NO$: C, 70.96; H, 11.31; N, 8.27. Found: C, 70.56; H, 11.27; N, 8.28.

(1R,2R,5R)-2-Hydroxypinan-3-one (7):
Ketoalcohol **7** was prepared in 43% yield from (1S,5S)-α-pinene (81% ee)[11] according to the literature procedure.[17]

(1R,2R,5R)-2-Hydroxypinan-3-one oxime (8):

Optically pure **8** was prepared from ketoalcohol **7** (81% ee) in 36% yield according to the procedure described for **6**: mp 120-121 ℃; $[\alpha]_D^{22}$ -18.5°(*c* 3.0, $CHCl_3$).

(1R,2R,3S,5R)-3-Amino-2-hydroxypinane (2):

Aminoalcohol **2** was prepared from oxime **8** in 62% yield according to the procedure described for **1**: mp 48-49.5 ℃; $[\alpha]_D^{22}$ +13.1°(*c* 1.0, $CHCl_3$).

(1S,2S,6R,8S)-2,4,9,9-Tetramethyl-5-aza-4-bora-3-oxatricyclo[6,1,1,$0^{2,6}$]decane (3a):

To a solution of aminoalcohol **1** (5.92 g, 35.0 mmol) in 70 ml of toluene was added trimethylboroxine (3.30 g, 26.3 mmol), and the mixture was stirred under N_2 at room temperature for 0.5 h. The solution was concentrated (at 1 atm) to a volume of ca. 20 ml. Toluene (50 ml) was added and the solution was concentrated again. This process was repeated once more, and the solvent was removed under reduced pressure to yield 6.03 g (89%) of **3a** as a colorless oil, which was changed to wet solid after a few months:[18] bp 100 ℃ (2 mmHg, Kugelrohr); $[\alpha]_D^{23}$ +7.7°(*c* 1.0, $CHCl_3$); IR (neat) ν_{max} cm^{-1}: 3484, 3411, 2917, 1478, 1345, 1082; ^1H-NMR ($CDCl_3$) δ 0.18 (s, 3H), 0.87 (s, 3H), 1.24 (d, *J* = 10.2Hz, 1H), 1.27 (s, 3H), 1.33 (s, 3H), 1.51 (dt, *J* = 13.2, 2.9Hz, 1H), 1.87 (m, 1H), 2.01 (t, *J* = 5.6Hz, 1H), 2.16 (dddd, *J* = 2.0, 5.6, 6.3, 10.2Hz, 1H), 2.22 (dddd, *J* = 2.0, 2.9, 8.8, 13.2Hz, 1H), 3.42 (brs, 1H), 3.47 (ddd, *J* = 2.0, 2.9, 8.8Hz, 1H); ^{13}C-NMR ($CDCl_3$) δ -5.65 (br), 23.63, 26.19, 27.25, 29.21, 38.04, 38.42, 39.79, 51.88, 54.97, 86.19; ^{11}B-NMR ($CDCl_3$) δ 33.2; Anal. Calcd for $C_{11}H_{20}BNO$: C, 68.42; H, 10.44; N, 7.25. Found: C, 68.05; H, 10.46; N, 7.59. High mass calcd for $C_{11}H_{20}{}^{11}BNO$: 193.1638. Obsd: 193.1628.

(1R,2R,6S,8R)-2,4,9,9-Tetramethyl-5-aza-4-bora-3-oxatricyclo[6,1,1,$0^{2,6}$]decane (4):

Oxazaborolidine **4** was prepared from aminoalcohol **2** in 85% yield according to the procedure described for **3a**: bp 100 ℃ (2 mmHg, Kugelrohr); $[\alpha]_D^{22}$ -8.2°(*c* 1.0, $CHCl_3$).

(1S,2S,6R,8S)-4-Butyl-2,9,9-trimethyl-5-aza-4-bora-3-oxatricyclo[6,1,1,$0^{2,6}$]decane (3b):

To a solution of aminoalcohol **1** (1.0 g, 5.9 mmol) was added butylboronic acid (0.63 g, 6.2 mmol). The reaction mixture was refluxed under N_2 for 5 h. The solution was concentrated at 1 atm to the volume of ca. 5 ml. Toluene (20 ml) was added, and the solution was concentrated again. This process was repeated once more, and the solvent was removed under reduced pressure to yield 1.34 g (96%) of **3b** as a colorless oil: bp 150 ℃ (2 mmHg, Kugelrohr); $[\alpha]_D^{22}$ 0° (*c* 1.0, $CHCl_3$); $[\alpha]_{365}^{22}$ -11.0°(*c* 1.0, $CHCl_3$); IR (neat) ν_{max} cm^{-1}: 3484, 3411, 2921, 1464, 1342, 1081; ^1H-NMR ($CDCl_3$) δ 0.73 (t, *J* = 7.6Hz, 2H), 0.86 (s, 3H), 0.88 (t, *J* = 6.8Hz, 3H), 1.24 (d, *J* = 10.3Hz, 1H), 1.25-1.40 (m, 4H), 1.27 (s, 3H), 1.32 (s, 3H), 1.50 (dt, *J* = 13.4, 2.9Hz, 1H), 1.86 (m, 1H), 2.01 (t, *J* = 5.6Hz, 1H), 2.15 (dddd, *J* = 2.2, 5.6, 6.1, 10.3Hz, 1H), 2.23 (dddd, *J* = 2.2, 2.7, 8.6, 13.4Hz, 1H), 3.42 (brs, 1H), 3.46 (ddd, *J* = 2.2, 2.9, 8.6Hz, 1H); ^{13}C-NMR ($CDCl_3$) δ 11.19 (br), 13.91, 23.64, 25.55, 26.21, 27.23, 27.26, 29.23, 38.04, 38.52, 39.81, 51.88, 54.84, 86.06; ^{11}B-NMR ($CDCl_3$) δ 33.8; Anal. Calcd for $C_{14}H_{26}BNO$: C, 71.50; H, 11.14; N, 5.96. Found: C, 71.03; H, 11.15; N, 5.91. High mass calcd for $C_{14}H_{26}{}^{11}BNO$: 235.2107. Obsd: 235.2113.

(1S,2S,6R,8S)-2,9,9-Trimethyl-4-phenyl-5-aza-4-bora-3-oxatricyclo[6,1,1,$0^{2,6}$]decane (3c):

Oxazaborolidine **3c** was prepared from aminoalcohol **1** (1.0 g, 5.9 mmol) and phenylboronic acid (0.76 g, 6.2 mmol) according to the procedure described for **3b**, affording 1.49 g (99%) of **3c** as a colorless oil: bp 180 ℃ (2 mmHg, Kugelrohr); $[\alpha]_D^{22}$ -9.4° (*c* 1.0, $CHCl_3$); IR (neat) ν_{max} cm^{-1}: 3460, 3414, 2919, 1603, 1463, 1336, 1088; ^1H-NMR ($CDCl_3$) δ 0.91 (s, 3H), 1.29 (s, 3H), 1.34 (d, *J* = 10.3Hz, 1H), 1.43 (s, 3H), 1.62

(dt, J = 13.6, 2.9Hz, 1H), 1.90 (m, 1H), 2.13 (t, J = 5.6Hz, 1H), 2.19 (dddd, J = 2.0, 5.6, 6.1, 10.3Hz, 1H), 2.31 (dddd, J = 2.0, 2.7, 8.1, 13.6Hz, 1H), 3.66 (ddd, J = 2.0, 2.9, 8.1Hz, 1H), 3.90 (brs, 1H), 7.32-7.41 (m, 3H), 7.65 (dd, J = 1.7, 8.0Hz, 2H); ^{13}C-NMR ($CDCl_3$) δ 23.73, 26.31, 27.31, 29.29, 38.17, 38.48, 39.81, 52.00, 55.49, 86.99, 127.67 x 2, 129.99, 133.55 x 2 (*C* - B not detected); ^{11}B-NMR ($CDCl_3$) δ 31.1; Anal. Calcd for $C_{16}H_{22}BNO$: C,75.31; H, 8.69; N, 5.49. Found: C, 75.09; H, 8.75; N, 5.50. High mass calcd for $C_{16}H_{22}{}^{11}BNO$: 255.1794. Obsd: 255.1781.

(1S,2S,6R,8S)-2,9,9-Trimethyl-4-oxo-5-aza-3-oxatricyclo[6,1,1,0^{2,6}]decane (9):
Aminoalcohol **1** (4.73 g, 27.9 mmol) and 1,1'-carbonyldiimidazole (4.98 g, 30.7 mmol) were dissolved in 100 ml of tetrahydrofuran. The reaction mixture was stirred at room temperature for 1 h. After water was added, the mixture was extracted with ethyl acetate (50 ml x 3). The extracts were washed with 1N HCl, water and brine, and dried over $MgSO_4$, and concentrated *in vacuo*. The residue was recrystallized from ethyl acetate-hexane to afford 4.71 g (86%) of **9** as white crystals: mp 138-140 ℃; $[\alpha]_D^{22}$ +5.6° (*c* 1.0, $CHCl_3$); IR (KBr) ν_{max} cm^{-1}: 3326, 2949, 2914, 1694, 1427, 1293; ^{1}H-NMR ($CDCl_3$) δ 0.88 (s, 3H), 1.31 (s, 3H), 1.35 (d, J = 11.0Hz, 1H), 1.50 (s, 3H), 1.73 (dt, J = 13.4, 2.8Hz, 1H), 1.97 (m, 1H), 2.15 (t, J = 5.5Hz, 1H), 2.22-2.36 (m, 2H), 3.74 (dd, J = 1.8, 8.6Hz, 1H), 5.50 (br, 1H); Anal. Calcd for $C_{11}H_{17}NO_2$: C, 67.66; H, 8.78; N, 7.17. Found: C, 67.59; H, 8.70; N, 7.14.

(1S,2S,3R,5S)-N-Methyl-3-amino-2-hydroxypinane (10):
To an ice cooled suspension of lithium aluminum hydride (0.87 g, 22.9 mmol) in 20 ml of ethyl ether was added oxazolinone **9** (1.50 g, 7.68 mmol). The reaction mixture was refluxed for 48 h and then cooled to about 5 ℃. Ethyl acetate (0.9 ml), 10% aqueous NaOH (0.9 ml) and waters (2.7 ml) were added dropwise, and the resulting mixture was stirred at room temperature for 5 h. The insoluble material was removed by filtration through celite, and the filtrate was evaporated *in vacuo*. The residue was acidified with 10% HCl-methanol, and ethyl ether was added. The resulting white solid was filtered and dried to give **10** hydrochloride. The solid was dissolved in 1N NaOH (100 ml), and the solution was extracted with CH_2Cl_2, washed with brine, dried over $MgSO_4$. Evaporation of the solvent gave 1.18 g (84%) of **10** as a white solid, which was recrystallized from hexane: mp 58-59 ℃; $[\alpha]_D^{23}$ -35.8° (*c* 1.0, $CHCl_3$); IR (KBr) ν_{max} cm^{-1}: 3319, 3186, 2968, 2905, 1382, 1106; ^{1}H-NMR ($CDCl_3$) δ 0.97 (s, 3H), 1.21-1.27 (m, 2H), 1.25 (s, 3H), 1.27 (s, 3H), 1.86 (m, 1H), 1.96 (t, J = 5.8Hz, 1H), 2.09-2.15 (m, 1H), 2.45-2.53 (m, 1H), 2.50 (s, 3H), 2.74 (dd, J = 5.8, 9.8Hz, 1H); Anal. Calcd for $C_{11}H_{21}NO$: C, 72.08; H, 11.55; N, 7.64. Found: C, 71.83; H, 11.59; N,7.73.

(1S,2S,6R,8S)-2,4,5,9,9-Pentamethyl-5-aza-4-bora-3-oxatricyclo[6,1,1,0^{2,6}]decane (3d):
Oxazaborolidine **3d** was prepared from aminoalcohol **10** (0.85 g, 4.64 mmol) and trimethylboroxine (0.61 g, 3.52 mmol) according to the procedure described for **3a**, affording 0.80 g (83%) of **3d** as a colorless oil: bp 85 ℃ (2 mmHg, Kugelrohr); $[\alpha]_D^{22}$ -16.2° (*c* 1.0, $CHCl_3$); IR (neat) ν_{max} cm^{-1}: 2968, 1500, 1370, 1347, 1241; ^{1}H-NMR ($CDCl_3$) δ 0.17 (s, 3H), 0.88(s, 3H), 1.18 (d, J = 10.3Hz, 1H), 1.27 (s, 3H), 1.30 (s, 3H), 1.70 (dt, J = 13.4, 2.9Hz, 1H), 1.90 (m, 1H), 1.96-2.03 (m, 1H), 1.99 (t, J = 5.4Hz, 1H), 2.14 (dddd, J = 2.2, 2.9, 8.5, 10.2Hz, 1H), 2.65 (s, 3H), 3.17 (dd, J = 2.9, 8.5Hz, 1H); ^{13}C-NMR ($CDCl_3$) δ -6.53 (br), 23.70, 26.48, 27.29, 29.53, 30.11, 32.52, 37.62, 39.90, 51.78, 61.67, 84.68; ^{11}B-NMR ($CDCl_3$) δ 32.4; Anal. Calcd for $C_{12}H_{22}BNO$: C, 69.59; H, 10.71; N, 6.76. Found: C, 69.30; H, 10.70; N, 6.84. High mass calcd for $C_{12}H_{22}{}^{11}BNO$: 207.1794. Obsd: 207.1790.

(1S,2S,3R,5S)-N-(*p*-Toluenesulfonyl)-3-amino-2-hydroxypinane (11):
To an ice cooled solution of aminoalcohol **1** (2.0 g, 11.8 mmol) in 30 ml of tetrahydrofuran was added *p*-

toluenesulfonyl chloride (2.48 g, 13.0 mmol). After 1N NaOH was added dropwise, the reaction mixture was stirred at room temperature for 1 h. Water was added, and the resulting mixture was extracted with ethyl acetate (50 ml x 3). The extracts were washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by silica gel column chromatography to afford 3.75 g (98%) of **11** as a white solid, which was recrystallized from ethyl acetate-hexane: mp 143-144 °C; $[\alpha]_D^{22}$ -5.7° (*c* 1.0, $CHCl_3$); IR (KBr) ν_{max} cm^{-1}: 3481, 3330, 2926, 1598, 1321, 1151, 1091; ^{1}H-NMR ($CDCl_3$) δ 0.94 (s, 3H), 1.08 (s, 3H), 1.23 (s, 3H), 1.30 (d, J = 9.8Hz, 1H), 1.46-1.56 (m,1H), 1.85 (m, 1H), 1.95 (t, J = 5.8Hz, 1H), 2.13-2.24 (m, 2H), 2.43 (s, 3H), 3.65 (ddd, J = 6.7, 7.9, 8.5Hz, 1H), 5.20 (d, J = 8.5Hz, 1H), 7.30 (d, J = 7.9Hz, 2H), 7.79 (d, J = 7.9Hz, 2H); Anal. Calcd for $C_{17}H_{25}NO_3S$: C, 63.13; H, 7.79; N, 4.33. Found: C, 63.15; H, 7.74; N, 4.31.

(1S,2S,6R,8S)-2,4,9,9-Tetramethyl-5-(*p*-toluenesulfonyl)-5-aza-4-bora-3-oxatricyclo-[6,1,1,$0^{2,6}$]decane (3e):

To a suspension of sulfonamide **11** (1.0 g, 3.1 mmol) in 20 ml of toluene was added trimethylboroxine (0.40 g, 2.3 mmol). The reaction mixture was refluxed under N_2 for 2 h. The solution was concentrated at 1atm to the volume of ca. 5 ml. Toluene (20 ml) was added, and the solution was concentrated again. This process was repeated once more, and the solvent was removed under reduced pressure to yield 1.07 g (100%) of **3e** as a white solid: mp 78-79 °C (hexane); $[\alpha]_D^{23}$ -101.4° (*c* 1.0, $CHCl_3$); IR (neat) ν_{max} cm^{-1}: 2940, 2909, 1598, 1366, 1168; ^{1}H-NMR ($CDCl_3$) δ 0.63 (s, 3H), 0.86 (s, 3H), 1.09 (d, J = 10.7Hz, 1H), 1.11 (s, 3H), 1.26 (s, 3H), 1.87-1.95 (m, 2H), 2.02 (t, J = 5.6Hz, 1H), 2.17-2.24 (m, 1H), 2.34-2.45 (m, 1H), 2.43 (s, 3H), 3.77 (dd, J = 3.4, 9.2Hz, 1H), 7.32 (d, J = 8.0Hz, 2H), 7.76 (d, J = 8.0Hz, 2H); ^{13}C-NMR ($CDCl_3$) δ -3.30 (br), 21.51, 23.82, 27.09, 27.28, 28.98, 36.45, 37.72, 39.65, 51.10, 59.30, 86.64, 126.77 x 2, 129.69 x 2, 138.26, 143.60; ^{11}B-NMR ($CDCl_3$) δ 35.0; Anal. Calcd for $C_{18}H_{26}BNO_3S$: C, 62.25; H, 7.55; N, 4.03. Found: C, 61.90; H, 7.53; N, 4.11. High mass calcd for $C_{18}H_{26}{}^{11}BNO_3S$: 347.1726. Obsd: 347.1730.

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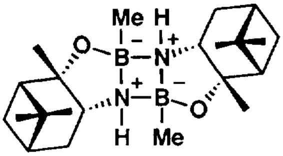
18. This change might be attributed to the partial formation of the dimer **12**.



12

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