Synthesis of 6,7-benzo-3-borabicyclo[3.3.1]nonane and its 3-aza analog from 2-allylphenyl(diallyl)borane. Intramolecular arylboration of the C=C bond

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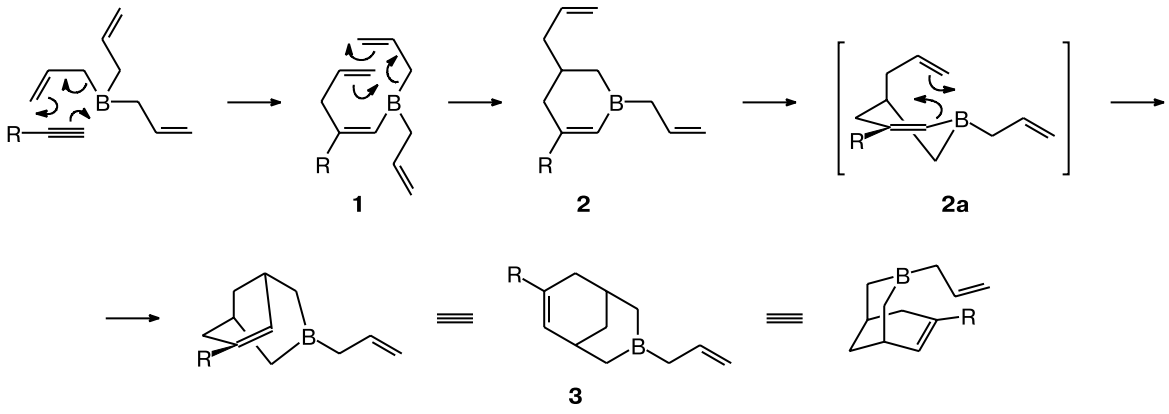
A method was developed for the synthesis of 6,7-benzo-3-borabicyclo[3.3.1]nonane and 6,7-benzo-3-azabicyclo[3.3.1]nonane derivatives based on intramolecular cyclization of 2-allylphenyl(diallyl)borane. Intramolecular arylboration of the double bond in 1,5-diallyl-2,3-benzo-1-boracyclohexane was carried out for the first time. Conventional oxidation (H_2O_2—OH^-) of 6,7-benzo-3-methoxy-3-borabicyclo[3.3.1]nonane afforded *cis*-1,3-di(hydroxymethyl)tetralin. The structure of the latter was established by X-ray diffraction analysis.

Key words: triallylborane, allylboranes, allylboration, intramolecular arylboration, dimethyl 2-allylphenylboronate, benzoazocine, 3-borabicyclo[3.3.1]nonane, 3-azabicyclo[3.3.1]nonane.

Triallylborane and various β,γ-unsaturated boron derivatives possess high reactivity and are widely used in organic synthesis.[1—3] Due to specific structural features, these reagents can add to organic compounds containing multiple bonds (C=O, C=S, C=N, C=C, N=O, C≡C, C≡N). All these reactions involve the allylic rearrangement and proceed, apparently, *via* the six-membered chair-like transition state accompanied by cyclic electron transfer.[3—5]

Allylboron—acetylene condensation, which is the thermal reaction of triallyl derivatives of boron with acetylenes giving rise to 3-borabicyclo[3.3.1]non-6-ene derivatives in yields up to 97%, is one of the most important and promising reactions in organoboron chemistry.[3—6] Earlier, it has been demonstrated that condensation involves three successive steps, which in some cases are clearly separated by temperature ranges (Scheme 1). The first two steps are, respectively, *cis*-allylboration of the triple and terminal carbon—carbon double bonds in adduct **1**. The temperatures of these steps vary from −70 °C to +80 °C depending on the nature of the substituent R in the starting acetylene compound. The third step, *viz.*, vinylboration of the terminal double bond in boracycle **2**, occurs at 125—160 °C (**2a**) and also depends on the nature of R. The products generated in each step were isolated and used as the starting compounds for the synthesis of 1,4-dienes, unsaturated aldehydes and ketones, acyclic alcohols, diols, amines, and cage compounds, such as 1-bora- and 1-azaadamantane.[3,6,7]

Scheme 1



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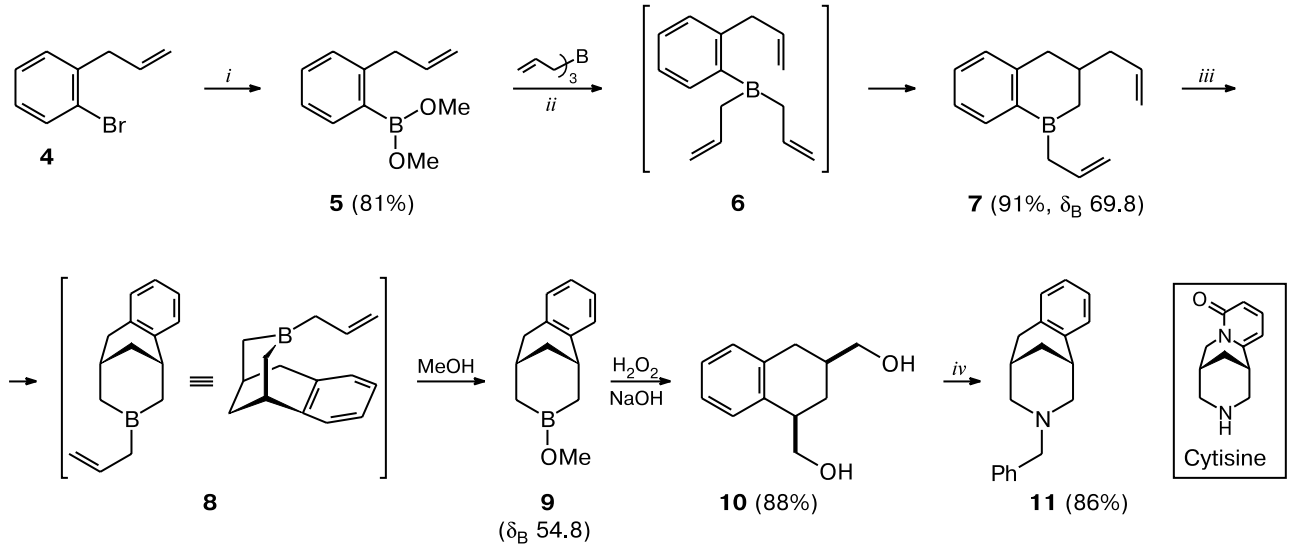
Scheme 2



Reagents and conditions: *i*. 1) Mg; 2) $B(OMe)_3$, –78 °C; 3) TMSCl; *ii*. 60 °C (60 Torr); *iii*. 140 °C, 8 h; *iv*. 1) TsCl, Py; 2) $BnNH_2$, $PhCH_3$, 110 °C.

As part of continuing studies, we carried out thermal cyclization of 2-allylphenyl(diallyl)borane (**6**) and thus performed the previously unknown intramolecular arylboration of the terminal double bond **7** → **8** (Scheme 2).

Results and Discussion

The reaction of 2-allylphenylmagnesium bromide **4** with trimethyl borate at –78 °C followed by treatment of the resulting *ate*-complex with trimethylchlorosilane afforded dimethyl 2-allylphenylboronate **5** (81%) (see Scheme 2). The methoxy groups in **5** were replaced with the allyl groups by the reaction with triallylborane. These exchange reactions are equilibrium processes, and the equilibrium can be shifted in the desired direction, for example, by removing low-boiling products.[8,9] Thus, heating of a mixture of **5** and triallylborane (1 : 2) under reduced pressure (60 °C, 60 Torr) is accompanied by the removal of low-boiling $AllB(OMe)_2$ to form unsymmetrical aryldiallylborane **6**. Under the reaction conditions, the latter undergoes cyclization through intramolecular allylboration of the terminal double bond to give benzoborinane **7** (91%), which is the 2,3-benzo analog of the product that is generated in the second step of allylboron-acetylene condensation (**2**) (see Scheme 1). Heating (140 °C, 8 h) of compound **7** results in its smooth rearrangement into 6,7-benzo-3-borabicyclo[3.3.1]nonane (**8**). This cyclization is similar to the third step of allylboron-acetylene condensation, *viz.*, the rearrangement of vinylic borane **2** into bicyclic compound **3** (see Scheme 1). However, this reaction has not been known earlier for arylboranes. Therefore, this is the first example of intramolecular arylboration of the C=C bond. It should be noted that the intermolecular addition of arylboranes to olefins and acetylenes is also untypical of arylboranes. To our knowledge, only two reactions of this type were described in the literature: the addition of phenyl(dichloro)borane to norbornadiene[10] and butylacetylene.[11]

Compound **8** was not isolated in pure form and was immediately treated with methanol to prepare methoxyorganoborane **9**. Conventional oxidation (H_2O_2—OH^-) of compound **9** produced bicyclic diol **10** (88%), which was purified by chromatography on silica gel. The *cis* arrangement of the hydroxymethyl groups in compound **10** was unambiguously established by X-ray diffraction analysis (Fig. 1).

The six-membered ring adopts a half-chair conformation with the C(8) and C(9) atoms deviating from the C(10)C(1)C(6)C(7) plane by 0.51 and –0.22 Å, respectively. In the crystal, the hydroxymethyl groups occupy the equatorial (C(12)) and pseudoequatorial (C(11)) po-

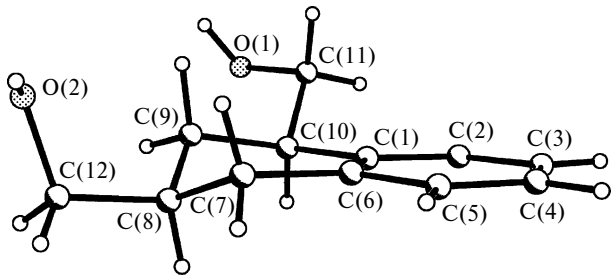


Fig. 1. Overall view of compound **10**.

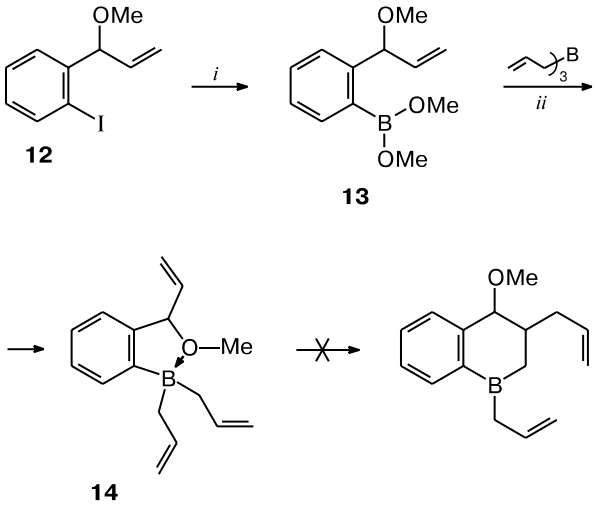
Table 1. Selected bond lengths (*d*) and bond angles (ω) in compound **10**

Parameter	Value	Parameter	Value
Bond	*d*/Å	Bond	*d*/Å
O(1)—C(11)	1.430(2)	C(2)—C(3)	1.385(3)
O(2)—C(12)	1.417(2)	C(3)—C(4)	1.369(3)
C(1)—C(2)	1.394(2)	C(4)—C(5)	1.376(3)
C(1)—C(6)	1.395(2)	C(5)—C(6)	1.399(2)
C(1)—C(10)	1.525(2)		
Angle	ω/deg	Angle	ω/deg
C(2)—C(1)—C(6)	118.3(1)	C(9)—C(8)—C(7)	108.7(1)
C(2)—C(1)—C(10)	120.0(1)	C(12)—C(8)—C(7)	112.7(1)
C(6)—C(1)—C(10)	121.7(1)	C(11)—C(10)—C(9)	110.0(1)
C(1)—C(6)—C(5)	119.0(1)	C(11)—C(10)—C(1)	111.1(1)
C(1)—C(6)—C(7)	121.4(1)	C(9)—C(10)—C(1)	112.8(1)
C(5)—C(6)—C(7)	119.6(2)	O(1)—C(11)—C(10)	111.6(1)
C(9)—C(8)—C(12)	112.0(1)	O(2)—C(12)—C(8)	112.6(1)

sitions in the benzocyclohexane fragment. The bond lengths and bond angles have standard values (Table 1). A slight difference between the O(1)—C(11) and O(2)—C(12) bond lengths is, apparently, attributable to the crystal packing effects. Actually, the molecules of diol **10** in the crystal are linked to each other by strong hydrogen bonds to form chains along the crystallographic *b* axis (Fig. 2).

Treatment of diol **10** with TsCl in pyridine afforded the ditosyl derivative in quantitative yield. The latter was used without additional purification. Refluxing of ditosylate with benzylamine in toluene produced tricyclic amine, *viz.*, benzoazocine **11**,[12] which is a carbocyclic analog of alkaloid cytisine, in 86% yield (see Scheme 2).

Scheme 3



Reagents and conditions: *i*. 1) BuLi, –95 °C; 2) $B(OMe)_3$, –78 °C; 3) TMSCl; *ii*. 60 °C (60 Torr).

With the aim of extending the scope of application of intramolecular arylboration, we synthesized borane **14** containing the methoxy group in the side chain (Scheme 3). Iodide **12** was metallated with BuLi to pre-

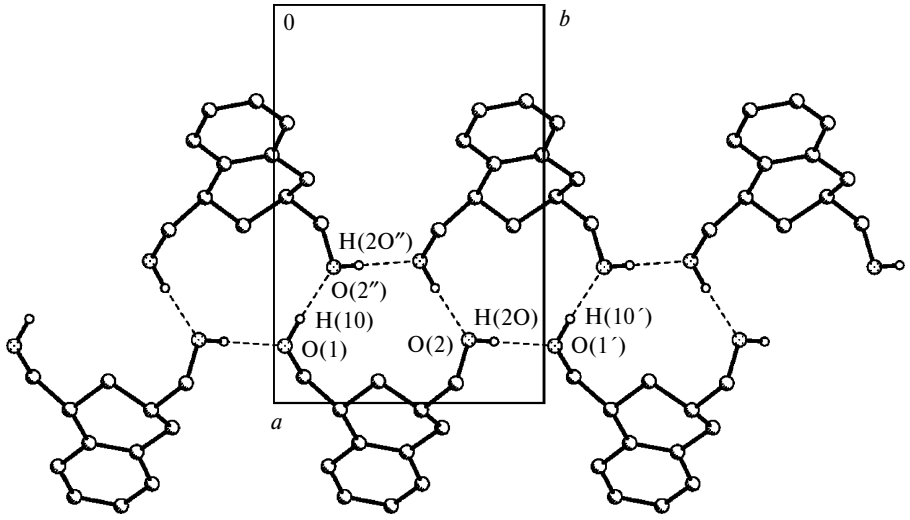


Fig. 2. The O—H...O-bonded chains in the crystal structure of diol **10**.

Parameters of H bonds:

Fragment	Symmetry transformation	Bond	*d*/Å	Angle	ω/deg
O(1)—H(1O)...O(2)	1.5 – *x*, *y* – 0.5, 0.5 – *z*	O(1)...O(2″)	2.653(2)	O(1)—H(1O)—O(2″)	173
		H(1O)...O(2″)	1.77		
O(2)—H(2O)...O(1)	*x*, *y* + 1, *z*	O(2)...O(1′)	2.625(2)	O(2)—H(2O)—O(2′)	168
		H(2O)...O(1′)	1.82		

pare the aryllithium derivative, which was successively treated with trimethyl borate and trimethylchlorosilane. The further replacement of the methoxy groups in **13** with the allyl groups in the presence of triallylborane afforded exclusively compound **14**, which, however, was not subjected to further cyclization even at 100 °C.

This is, apparently, caused by the intramolecular O→B coordination, which blocks the unoccupied orbital of the boron atom. The occurrence of this coordination in compound **14** is evidenced by the fact that the ^{11}B NMR spectrum shows a signal at δ 14.8, which corresponds to the four-coordinate boron atom, whereas the corresponding signal in the ^{11}B NMR spectrum of compound **7** is observed at δ 69.8. We also failed to perform cyclization of borane **14** in the presence of strong Lewis acids, such as $Sc(OTf)_3$ or $BF_3 \cdot OEt_2$ (10 mol.%, CH_2Cl_2, 20 °C, 2 h), which should be coordinated to the oxygen atom of the methoxy group and destroy the O→B coordination. Both reactions produced (^{1}H and ^{13}C NMR spectroscopic data) at least three new compounds, whose structures were not established.

To summarize, we developed a procedure for the preparation of 6,7-benzo-3-borabicyclo[3.3.1]nonane and 6,7-benzo-3-azabicyclo[3.3.1]nonane derivatives based on intramolecular allyl- and arylboration of carbon—carbon double bonds. It was found that heating of 2-allylphenyl(diallyl)borane leads to its cyclization (isomerization) by the mechanism of allylboron-acetylene condensation.

Experimental

All operations with organoboron compounds were carried out under dry argon. The solvents were dried according to standard procedures. The ^{1}H and ^{13}C NMR spectra were recorded on Bruker AC-200P and Bruker AMX-400 spectrometers. The chemical shifts δ in the ^{1}H and ^{13}C NMR spectra are given relative to the residual signals of the solvent in $CDCl_3$. The chemical shifts in the ^{11}B NMR spectra are given relative to $BF_3 \cdot OEt_2$ as the external standard. 2-Allylbromobenzene **4** was prepared according to procedures described earlier.[13,14]

Dimethyl 2-allylphenylboronate (5). A solution of **4** (10.23 g, 41 mmol) in THF (50 mL) was added to magnesium chips (1.1 g, 45 mmol) activated with 1,2-dibromoethane in THF (20 mL). The addition was carried out at such a rate as to maintain the temperature of the reaction mixture at no higher than 40 °C. Then the reaction mixture was stirred at room temperature for 30 min. The resulting Grignard reagent was added dropwise to a solution of trimethyl borate (10.39 g, 11.15 mL, 0.1 mol) in THF (40 mL) cooled to −78 °C. After completion of the addition, the reaction mixture was stirred until it was warmed to room temperature, treated with TMSCl (3.24 g, 3.77 mL, 30 mmol), stirred for 30 min, and concentrated *in vacuo*. The residue was extracted several times with hexane, filtered off from salts, and concentrated under reduced pressure. Vacuum distillation (59—60 °C (0.5 Torr)) afforded boronate **5** (6.3 g, 81%) as a colorless liquid. $C_{11}H_{15}BO_2$. M = 190.5. ^{1}H NMR (200 MHz), δ: 3.47 (d, 2 H, *J* = 6.7 Hz); 3.64 (s, 6 H); 5.07 (s, 1 H); 5.16 (dd, 1 H, *J* = 1.6 Hz, *J* = 7.6 Hz); 5.90—6.10 (m, 1 H); 7.23—7.37 (m, 4 H). Upon storage in air for one day, boronate **5** was transformed into solid 2-allylphenylboronic acid, whose identity was confirmed by comparing with the ^{1}H NMR spectrum published in the literature.[15]

2,3-Benzo-1,5-diallylborinane (7). A mixture of compound **5** (2.0 g, 10.5 mmol) and triallylborane (2.97 g, 3.86 mL, 22 mmol) was heated at 55—60 °C for 6 h under reduced pressure (60 Torr). Simultaneously, argon was passed through the reaction mixture using a thin capillary tube to remove volatile reaction products. The reaction was monitored by NMR spectroscopy based on the disappearance of the signals of the methoxy group. Subsequent vacuum distillation (95—96 °C; 0.5 Torr) afforded product **7**. The yield was 2 g (91%). Found (%): C, 85.61; H, 9.05; B, 5.06. $C_{15}H_{19}B$. M = 210.12. Calculated (%): C, 85.74; H, 9.11; B, 5.15. ^{1}H NMR (400 MHz), δ: 1.10 (dd, 1 H, *J* = 11.8 Hz, *J* = 18.7 Hz); 2.00 (m, 2 H); 2.22 (t, 2 H, *J* = 6.6 Hz); 2.55—2.66 (m, 3 H); 2.94 (dt, 1 H, *J* = 2.8 Hz, *J* = 15.6 Hz); 5.03—5.14 (m, 4 H); 5.93 (m, 1 H); 6.13 (m, 1 H); 7.29 (d, 1 H, *J* = 7.5 Hz); 7.35 (t, 1 H, *J* = 7.2 Hz); 7.51 (td, 1 H, *J* = 1.2 Hz, *J* = 7.5 Hz); 7.95 (d, 1 H, *J* = 6.8 Hz). ^{13}C NMR (127 MHz), δ: 31.08 (CH_2B); 31.93 (CH_2B); 35.30 (CH); 39.74 (CH_2); 43.04 (CH_2); 114.41 (CH_2=); 115.87 (CH_2=); 125.59 (CH=); 128.69 (CH=); 133.23 (CH); 134.15 (CH); 136.09 (CH); 137.34 (CH); 150.17 (C). ^{11}B NMR (128 MHz), δ: 69.83.

6,7-Benzo-3-methoxy-3-borabicyclo[3.3.1]nonane (9). Borinane **7** (1.30 g, 6.14 mmol) was heated at 140—150 °C for 8 h. The reaction was monitored by NMR spectroscopy. Heating was performed until the ratio of the integral intensities of the signals for the aromatic to allylic (CH=) protons became *ca* 4 : 1. The reaction mixture was treated with an excess of MeOH, and methyl ether **9** was distilled off *in vacuo*, b.p. 114—116 °C (1 Torr). The yield was 1.18 g (96%). $C_{13}H_{17}BO$. M = 200.08. The product contained *ca* 8% of the methanolysis product of compound **7** (^{1}H NMR spectroscopic data). ^{1}H NMR (400 MHz), δ: 1.03 (br.d, 1 H, *J* = 17.4 Hz); 1.12—1.20 (m, 2 H); 1.29 (br.d, 1 H, *J* = 16.3 Hz); 1.91 (br.d, 1 H, *J* = 12.6 Hz); 2.07 (br.d, 1 H, *J* = 12.4 Hz); 2.59 (d, 1 H, *J* = 17.0 Hz); 2.66 (br.s, 1 H); 3.14 (dd, 1 H, *J* = 6.0 Hz, *J* = 17.0 Hz); 3.28 (br.s, 1 H); 3.53 (s, 3 H); 7.14—7.06 (m, 4 H). ^{13}C NMR (50 MHz), δ: 25.43 (CH_2B); 27.23 (CH); 28.94 (br, CH_2B); 32.60 (CH_2); 33.48 (CH); 38.20 (CH_2); 52.96 (OCH_3); 125.57 (CH); 125.79 (CH); 129.05 (CH); 129.68 (CH); 133.47 (C); 143.03 (C). ^{11}B NMR (128 MHz), δ: 54.81.

***cis*-1,3-Di(hydroxymethyl)-1,2,3,4-tetrahydronaphthalene (10).** An excess of 20% NaOH (5 mL) was added to a solution of borane **9** (1.32 g, 6.6 mmol) in THF (5 mL), and then 30% H_2O_2 (0.63 g, 1.9 mL, 18.5 mmol) was added dropwise with stirring and cooling. The reaction mixture was stirred for 1 h, refluxed for 1 h, and cooled. The organic layer was separated, dried with K_2CO_3, and concentrated under reduced pressure. The oil was purified by passing through a short column (20×2 cm) with SiO_2 in the AcOEt—*n*-C_6H_{14} system (3 : 2). After removal of the solvents, diol **10** was obtained as white crystals (1.12 g, 88%), m.p. 92—93 °C (*n*-C_6H_{14}—CH_2Cl_2), R_f = 0.1 (AcOEt—*n*-C_6H_{14}, 1 : 1). Found (%): C, 74.95; H, 8.40. $C_{12}H_{16}O_2$. M = 192.25. Calculated (%): C, 74.97; H, 8.39. ^{1}H NMR (400 MHz), δ: 1.38 (dd, 1 H, *J* = 11.5 Hz, *J* = 23.6 Hz); 1.95 (m, 1 H); 2.12—2.25 (br.m, 2 H); 2.37 (br.s, 1 H,

OH); 2.50 (dd, 1 H, J = 11.8 Hz, J = 15.9 Hz); 2.71 (dd, 1 H, J = 1.9 Hz, J = 15.9 Hz); 3.07 (m, 1 H); 3.60 (dd, 1 H, J = 6.8 Hz, J = 10.6 Hz); 3.65 (dd, 1 H, J = 6.2 Hz, J = 10.6 Hz); 3.90 (dd, 1 H, J = 5.9 Hz, J = 10.9 Hz); 3.95 (dd, 1 H, J = 4.0 Hz, J = 10.9 Hz); 7.10—7.19 (m, 3 H); 7.31 (d, 1 H, J = 7.5 Hz). ^{13}C NMR (127 MHz), δ: 30.14 (CH_2); 33.30 (CH_2); 36.69 (CH); 40.48 (CH); 66.90 (CH_2OH); 67.60 (CH_2OH); 126.09 (2 CH); 126.84 (CH); 129.52 (CH); 136.63 (C); 137.73 (C).

6,7-Benzo-3-benzyl-3-azabicyclo[3.3.1]nonane (11). Tosyl chloride (1.75 g, 9.2 mmol) was added to a solution of diol **10** (0.8 g, 4.16 mmol) in pyridine (10 mL) at 0 °C and the mixture was stirred for 2 h. The reaction was monitored by TLC (AcOEt—n-C_6H_{14}, 1 : 1). After consumption of the starting compound **10**, pyridine was evaporated under reduced pressure. The residue was washed successively with water and 3 *N* HCl, extracted with CH_2Cl_2 (10 mL), dried with Na_2SO_4, and concentrated. The ditosyl derivative was dissolved in toluene (40 mL), benzylamine (1.34 g, 1.36 mL, 12.5 mmol) was added, and the mixture was refluxed for 14 h. The reaction was monitored by TLC (AcOEt—n-C_6H_{14}, 1 : 2). After consumption of the starting ditosylate, an excess of 6 *N* NaOH was added. The organic layer was separated, filtered, dried with K_2CO_3, and concentrated *in vacuo*. The product was purified by filtration through a small layer of SiO_2 in the AcOEt—n-C_6H_{14} system (1 : 5), and the nonpolar fraction of amine **11** (yellow oil) was collected. The yield was 0.93 g (86%), R_f = 0.73 (AcOEt—n-C_6H_{14}, 1 : 5). Found (%): C, 86.31; H, 8.14; N, 5.09. $C_{19}H_{21}N$. M = 263.38. Calculated (%): C, 86.65; H, 8.04; N, 5.32. ^{1}H NMR (400 MHz), δ: 1.85 (br.d, 1 H, J = 12.1 Hz); 1.95 (br.d, 1 H, J = 12.1 Hz); 2.23 (m, 1 H); 2.35 (dd, 1 H, J = 1.9 Hz, J = 10.3 Hz); 2.43 (dd, 1 H, J = 1.9 Hz, J = 10.6 Hz); 2.79 (br.d, 1 H, J = 10.3 Hz); 2.86—2.92 (m, 3 H); 3.14 (dd, 1 H, J = 7.2 Hz, J = 17.4 Hz); 3.45 (s, 2 H); 6.94 (m, 2 H); 7.04 (d, 1 H, J = 7.5 Hz); 7.12—7.25 (m, 6 H). ^{13}C NMR (127 MHz), δ: 28.72 (CH_2); 29.93 (CH_2); 34.97 (CH); 35.82 (CH); 60.14 (CH_2); 61.14 (CH_2); 62.16 (CH_2); 124.55 (CH); 125.52 (CH); 126.31 (CH); 127.35 (CH); 127.85 (3 CH); 128.00 (2 CH); 138.80 (C); 139.25 (C); 141.37 (C).

1-Iodo-2-(1-methoxy-2-propenyl)benzene (12). 1-(2-Iodophenyl)-2-propen-1-ol (15.8 g, 60.8 mmol), which was prepared according to a known procedure,[16] and MeI (12.95 g, 5.7 mL, 91.2 mmol) were dissolved in THF (120 mL) under argon and cooled to −40 °C. Then NaH (60%, 3.3 g, 82 mmol) was added. The reaction mixture was slowly warmed to −15—−10 °C. At this temperature, the reaction proceeded rather vigorously. After hydrogen evolution ceased, the reaction mixture was allowed to warm to room temperature. The reaction was monitored by TLC (AcOEt—n-C_6H_{14}, 1 : 4). The reaction mixture was stirred at room temperature for 1 h and then concentrated *in vacuo*. The residue was treated with water and extracted with CH_2Cl_2. The extracts were dried with K_2CO_3 and concentrated. The residue was distilled *in vacuo*. Iodide **12** was obtained in a yield of 14 g (84%), b.p. 77—78 °C (2 Torr), R_f = 0.74 (AcOEt—n-C_6H_{14}, 1 : 4). Found (%): C, 43.93; H, 4.10. $C_{10}H_{11}IO$. M = 274.10. Calculated (%): C, 43.82; H, 4.05. ^{1}H NMR (400 MHz), δ: 3.35 (s, 3 H); 4.95 (d, 1 H, J = 6.2 Hz); 5.25 (d, 1 H, J = 10.3 Hz); 5.38 (d, 1 H, J = 17.1 Hz); 5.88 (ddd, 1 H, J = 6.2 Hz, J = 10.3 Hz, J = 17.1 Hz); 6.99 (t, 1 H, J = 6.9 Hz); 7.40 (m, 2 H); 7.84 (d, 1 H, J = 8.1 Hz). ^{13}C NMR (127 MHz), δ: 56.57 (CH_3); 86.83 (CH); 98.98 (C—I); 116.85 (CH); 127.84 (CH); 128.58 (CH); 129.31 (CH); 136.87 (CH); 139.32 (CH); 142.62 (C).

Dimethyl 2-(1-methoxy-2-propenyl)phenylboronate (13). A solution of **12** (7.5 g, 27.4 mmol) in THF (30 mL) was cooled to −95—−100 °C and BuLi (2.5 mol L^{-1}, 12 mL, 30.0 mmol) was added with stirring using a syringe. After 1 min, the lithium derivative precipitated, and the temperature rapidly increased to −70 °C. Then the mixture was cooled to −90 °C and a solution of trimethyl borate (4.68 g, 5.1 mL, 45 mmol) in Et_2O (4 mL) was added. The mixture was gradually warmed to 0 °C, after which TMSCl (3.8 g, 4.4 mL, 35 mmol) was added, the mixture was stirred for 30 min, and the solvents were removed under reduced pressure. The residue was treated with hexane and the clean solution was decanted. Vacuum distillation afforded compound **13** in a yield of 4.7 g (79%), b.p. 77—78 °C (2 Torr). Found (%): C, 65.60; H, 7.80. $C_{12}H_{17}BO_3$. M = 220.07. Calculated (%): C, 65.49; H, 7.79. ^{1}H NMR (400 MHz), δ: 3.43 (s, 3 H); 3.53 (s, 6 H); 4.69 (d, 1 H, J = 8.1 Hz); 5.40 (m, 2 H); 5.84 (m, 1 H); 7.16—7.35 (m, 4 H). ^{13}C NMR (127 MHz), δ: 52.05 (2 CH_3); 55.76 (CH_3); 84.59, 118.92 (CH); 124.98 (CH); 126.68 (CH); 127.80 (CH); 130.54 (CH); 137.41 (CH); 143.49 (C).

Diallyl-[2-(1-methoxy-2-propenyl)phenyl]borane (14). A mixture of compound **13** (1.8 g, 8.2 mmol) and triallylborane (2.4 g, 3.2 mL, 18 mmol) was heated for 6 h in a flask for distillation under a stream of Ar at 55—60 °C and 60 Torr. Vacuum distillation afforded compound **14** in a yield of 1.6 g (82%), b.p. 109—110 °C (2 Torr). Found (%): C, 80.05; H, 8.74. $C_{16}H_{21}BO$. M = 240.15. Calculated (%): C, 80.02; H, 8.81. ^{1}H NMR (400 MHz), δ: 1.60—1.67 (m, 3 H); 1.73—1.79 (m, 1 H); 3.69 (s, 3 H); 4.70 (d, 2 H, J = 9.8 Hz); 4.81 (t, 2 H, J = 17.2 Hz); 5.28 (d, 1 H, J = 8.9 Hz); 5.57—5.62 (m, 2 H); 5.69—5.77 (m, 1 H); 5.77—5.84 (m, 2 H); 6.96 (d, 1 H, J = 1.6 Hz, J = 5.7 Hz); 7.20 (td, 1 H, J = 1.6 Hz, J = 7.6 Hz); 7.28—7.32 (m, 2 H). ^{13}C NMR (127 MHz), δ: 30.58 (br, 2 CH_2); 55.12 (CH_3); 93.72 (CH); 110.69 (CH_2); 111.18 (CH_2); 121.06 (CH); 122.65 (CH); 125.57 (CH); 127.55 (CH); 128.09 (CH); 134.84 (CH); 138.26 (C); 141.25 (CH); 141.38 (CH). ^{11}B NMR (128 MHz), δ: 14.8.

X-ray diffraction study of compound 10. Crystals of diol **10** at −100 °C are monoclinic, space group $P2_1/n$, a = 11.552(2), b = 7.729(1), c = 11.704(2)E, β = 99.92(3)°, V = 1029.4(4) Å^3, Z = 4, d_{calc} = 1.240 g cm^{-3}, μ(Mo-Kα) = 0.83 cm^{-1}, F(000) = 416. The intensities of 2360 reflections were measured at −110 °C on a Syntex $P2_1$ diffractometer (λ(Mo-Kα) = 0.71072 Å, θ/2θ scanning technique, 2θ < 54°); 2251 independent reflections (R_{int} = 0.0414) were used in the refinement.

The structure was solved by direct methods using successive difference electron density maps. All hydrogen atoms were localized from difference electron density maps. The structure was refined against F^2_{hkl} with anisotropic displacement parameters for nonhydrogen atoms and isotropic displacement parameters for hydrogen atoms. The final R factors for **10** are R_1 = 0.0430 (based on F_{hkl} for 1393 reflections with $I > 2\sigma(I)$), wR_2 = 0.1128 (based on F^2_{hkl} for reflections), GOOF = 0.837. All calculations were carried out using the SHELXTL 5.10 program package.[17]

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