Preparation of *trans*- and *cis*-2-allyl-6-alkyl(aryl)-1,2,3,6-tetrahydropyridines based on the reductive *trans*-2,6-dialkylation of pyridine. Synthesis of (±)-epidihydropinidine and (±)-dihydropinidine

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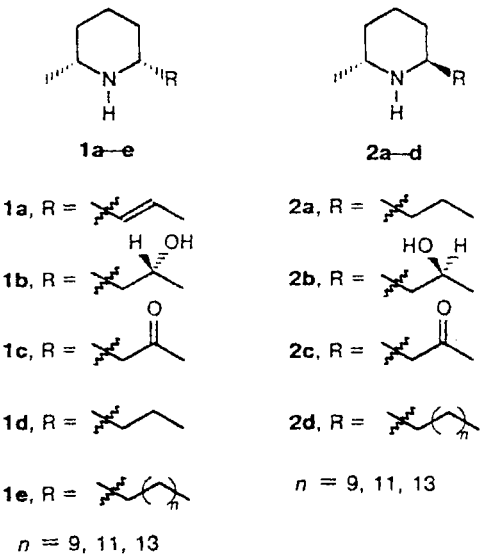
A general method for the preparation of unsymmetrical *trans*-2-allyl-6-alkyl(aryl)-1,2,3,6-tetrahydropyridines **6** based on a combination of 1,2-addition of RLi to pyridine and *trans*-6-allylation with triallylborane in the presence of methanol was elaborated. It was shown that *trans*-piperideines **6** (R = Alk, Ph) isomerize into the corresponding *cis*-2-allyl-6-alkyl(phenyl)-3-piperideines **14** on heating with triallylborane followed by deboronation of aminoborane (**16**) with methanol and an alkali. The stereochemistry of compounds **6** and **14** was determined by two-dimensional NOE spectroscopy. A possible mechanism of the formation of *trans*-amines **6** and their transformation into *cis*-isomers **14** is discussed. Alkaloids (±)-epidihydropinidine (*trans*-2-methyl-6-propylpiperidine **2a**, 70%) and (±)-dihydropinidine (*cis*-2-methyl-6-propylpiperidine **1d**, 71%) were synthesized by hydrogenation of compound **6a** (R = Me) and **14a** (R = Me), respectively, over Raney nickel.

Key words: allylboration; pyridine, 1,2-addition, alkyl(aryl)lithium, triallylborane; *trans*- and *cis*-2-allyl-6-alkyl(aryl)-1,2,3,6-tetrahydropyridines; *trans-cis*-isomerization; stereochemistry; piperidine alkaloids; (±)-epidihydropinidine; (±)-dihydropinidine.

2,6-Disubstituted piperidine alkaloids are produced by many species of plants and insects and play an important role in their vital activity. For example, pinidine (**1a**), epidihydropinidine (**2a**), and their derivatives (**1b—d**, **2b,c**) have been isolated from the needles, bark, and roots of several pine-tree and fir-tree species. In addition, pinidinone (**1c**) has been isolated from lady beetles (*Cryptolaemus montrouziri*)[2] and from Mexican bean beetles (*Epilachna varivestis*)[3]. The latter also produce dihydropinidine **1d**. Isosolenopsins A (n = 9), B (n = 11), and C (n = 13) (**1e**) and solenopsins A (n = 9), B (n = 11), and C (n = 13) (**2d**) are components of the poison of some ants (*Solenopsis geminata* and *Solenopsis invicta*).[4,5] Many of these alkaloids have high teratogenic and embryotoxic activity.[1b] Their biological function is probably to protect the species from antagonists and enemies.

Several laborious methods have been reported to date for the synthesis of such alkaloids,[1,3,6] including chiral ones.[5,7,8]

We recently found that pyridine and its derivatives undergo reductive *trans*-2,6-diallylation on treatment of their triallyl,[9,10] trimethallyl,[11] or tricrotylborane[10a,12] complexes with alcohols, water, or R_2NH. For example, adduct **3** is transformed into amine **4** on heating with methanol, ethanol, or isopropanol at 60—90 °C. The yield of *trans*-amine **4** is 70—97%, and the admixture of *cis*-isomer **5** usually does not exceed 0.5—2% (Scheme 1).



It was also shown that *trans*-amines of type **4** are transformed almost quantitatively to the corresponding *cis*-isomers (**5**) on heating with triallylborane (130—135 °C) followed by deboronation with an alkali.[10]

These reactions, which are a new, much more convenient way for the synthesis of piperidine derivatives, opened up interesting prospects in the chemistry of heterocyclic compounds. Compounds of types **4** and **5**

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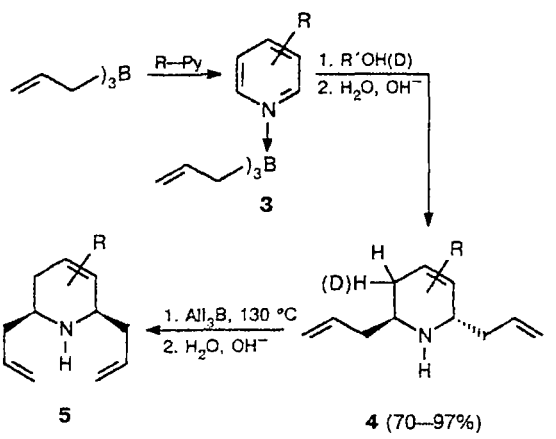
obtained on their basis contain an NH group and three double bonds, which provide various ways for subsequent functionalization. However, the above reactions afford only 2,6-symmetrically disubstituted 3-piperideines and piperidines. On the other hand, as noted above, the majority of natural alkaloids of the piperidine series contain *different substituents* at positions 2 and 6.

Scheme 1

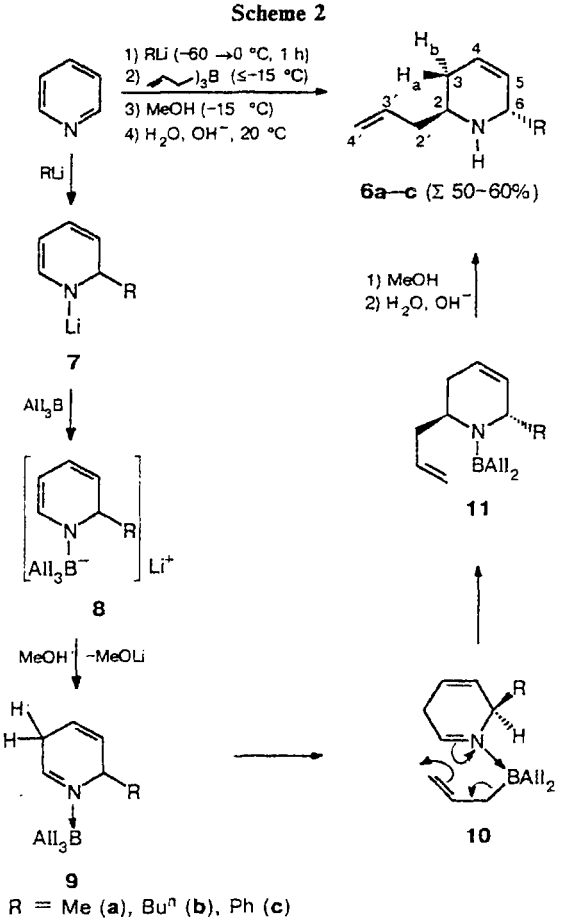


In order to be able to apply the "boron" methodology to the synthesis of both *trans*- and *cis*-2,6-unsymmetrically disubstituted 3-piperideines and use the latter for obtaining alkaloids and their analogs, we developed a convenient procedure for the synthesis of unsymmetrical *trans*-2-allyl-6-alkyl(aryl)-1,2,3,6-tetrahydropyridines (**6**). This procedure is based on a combination of the well-known 1,2-addition of RLi to pyridine[13] and subsequent *trans*-allylboration (Scheme 2; for preliminary communications, see Ref. 14).

A "one-pot" procedure was used for the synthesis of compounds **6**. First, pyridine was added to a solution of RLi at 0 °C (R = Me, Ph) or at −60 °C (R = Bu^n), and the mixture was stirred for 1 h at the same temperature. After that, triallylborane and then methanol were added at a temperature no higher than −15 °C. Final deboronation was carried out by treatment of the reaction mixture with 10—20% NaOH. In the end, all boron and lithium compounds that formed were transferred into the aqueous layer, and amine **6** was extracted with an appropriate solvent. The reagents were taken in the ratio Py : RLi : All$_3$B : MeOH : NaOH = 1 : 1 : 1 : 3 : 1.2. A possible mechanism of the formation of amines **6** is shown in Scheme 2.

The 1,2-addition of organolithium compounds to pyridine results in adduct **7**.[13] The latter reacts with triallylborane to give an enamine *ate*-complex **8**, alcoholysis of which (cleavage of the B—N bond) involves double bond migration[9,10] to give imine complex **9** (a proton from MeOH is added to the C-5 position of the pyridine ring). Subsequent allylboration of the C=N double bond in complex **9** occurs *trans*-stereoselectively with respect to the substituent at the ring (Alk, Ph),

Scheme 2



probably through intermediate **10**, and *this step determines the trans-configuration of the final product* **6**. Alcoholysis of the resulting aminoborane **11** with methanol (cleavage of the B—N bond) gives amine **6**.

According to GLC and NMR data, the yield of compound **6** is 90—94%, and the preparative yield is 50—60%.

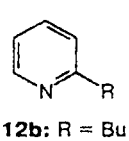
The yield of amines **6** strongly depends on the nature of the solvent used and on the conditions of the synthesis, mainly of its first stage, *i.e.*, 1,2-addition of RLi to pyridine (Table 1). This is caused by the fact that the reaction of RLi with pyridine is accompanied by a number of side processes, the main of which is aromatization of the 1,2-addition product **7** [15] to give the corresponding 2-substituted pyridine **12**. The reaction can completely follow this pathway,[13] hence it is important to control its conditions (see Table 1).*

* It is stated in all books on the chemistry of pyridine that aromatization occurs by elimination of LiH from lithium derivative **7** or by oxidation of the latter, for instance, with air oxygen during work-up of the reaction mixture. However, it was recently shown[15] that 2-R-Py (**12**) is formed due to the reaction of adduct **7** with pyridine, which is reduced to give a mixture of lithium derivatives of 1,2- and 1,4-dihydropyridine (1 : 1); lithium hydride was not found in the reaction products.

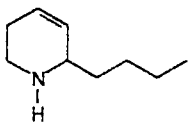
Table 1. Dependence of the ratio of the final products (**6** : **12** : other) on the conditions of transformation of pyridine into piperideines

R	Solvent	*T*/°C[a]			Ratio
		Py+RLi	All_3B	MeOH	**6** : **12** : Other
Me	Ether	−25—0	−30—0	−40—20	0 : 0 : 100[b]
Me	Ether+THF	0—20	−40—0	−40—20	90 : 0 : 10
Me	Ether+THF	0—20	−15—10	−15—20	90 : 0 : 10
Bu	Hexane+Ether	0	0—20	0—20	58 : 41 : 1
Bu	Hexane+Ether	−60	−60—10	−40—20	90 : 9 : 1[c]
Bu	Hexane+Ether	−50—0	−35—20	−30—20	62 : 37 : 1
Bu	Hexane+THF	−50—10	−35—20	−30—20	63 : 23 : 14[c] (**6** : **12** : **13**)
Ph	Ether	0—20	−30—20	−30—20	83 : 16 : 1
Ph	Ether	0	−30—10	−30—20	93 : 6 : 1

[a] The temperature ranges of consecutive treatment of pyridine with RLi, All_3B, and methanol are shown. [b] Only *trans*-2,6-diallyl-1,2,3,6-tetrahydropyridine (**4**) was isolated. [c] 2-Butyl-1,2,5,6-tetrahydropyridine (**13**).



12b: R = Bu
12c: R = Ph



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The reaction of MeLi with pyridine (see Scheme 2) has to be carried out in THF, since the reaction in diethyl ether gives a stable insoluble complex MeLi · Py,[16] which reacts with triallylborane to give *trans*-2,6-diallyl-1,2,3,6-tetrahydropyridine (**4**). In the case of PhLi, ether can be used as the solvent, while the reaction involving BuLi should be carried out in a hexane—ether mixture.

The raw product of the reaction involving BuLi contains compound **6b** (90%), 2-butylpyridine **12b** (9%), and probably 2-butyl-1,2,5,6-tetrahydropyridine **13** (1%) (according to GLC and NMR data). A product analogous to compound **13** (2-*tert*-butyl-1,2,5,6-tetrahydropyridine) has been obtained previously by the reaction of pyridine with Bu^tLi.[17] The ratio of products **6b** : **12b** : **13** depends considerably on the reaction conditions (see Table 1). It is only in a hexane—ether mixture at −60 °C that amine **6b** is formed as the major product (90%). The raw product of the reaction with PhLi contains compound **6c** (93%) and 2-phenylpyridine **12c** (6%) (GLC and NMR data).

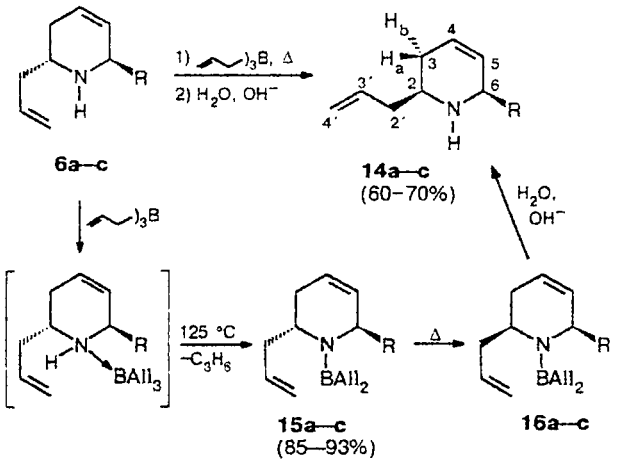
Since compounds **6b** and **12b** (and, correspondingly, **6c** and **12c**) have similar boiling points, we developed a procedure for their separation based on the different basicity of these amines. In fact, amines **6** are stronger bases (pK_a ~ 10) than 2-R-pyridines (pK_a ~ 6).[18] On treatment of a mixture of compounds **6c** (94%) and **12c** (6%) with 2*N* hydrochloric acid (0.95 equiv. with respect to the amount of compound **6c** in the mixture), the resulting salt **6c** · HCl goes into the aqueous solution (the process was monitored by GLC analysis of the organic phase). The organic layer containing compound **12c** and a small amount of **6c** (~5%) was separated, and the aqueous layer was twice extracted with ether. Treatment of the aqueous layer with a solution of NaOH followed by extraction with ether gave amine **6c** in 53% yield. Amine **6b** was obtained similarly in 60% yield.

Table 2. Conditions of isomerization of *trans*-isomers **15** into *cis*-isomers **16** on heating with triallylborane

R	*T*/°C	Heating duration/h	Ratio **15** : **16** (%)
Me	130—135	1	70 : 30[a]
	140—145	+3	20 : 80[a]
	160—165	6.5	1 : 99[b]
Bu^n	135—140	1	80 : 20[a]
	160—165	+3	5 : 95[a]
	200	6	3 : 97[b]
Ph	135—140	1	100 : 0[a]
	160—165	3	75 : 25[a]
	195	+2	20 : 80[a,b]
	195	12	20 : 80[a,b]

[a] Found by ^{13}C NMR of a raw mixture of compounds **15** and **16**. [b] Found by GLC of the deboronated product.

It was then found that, similarly to compounds **4**,[10] *trans*-amines **6a—c** isomerize into the corresponding *cis*-compounds **14a—c** on heating with triallylborane at 140—190 °C followed by deboronation with an alkali (see Table 2).

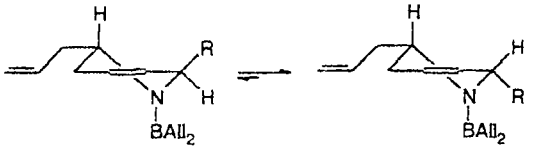


R = Me (**a**), Bu^n (**b**), Ph (**c**)

In order to find the isomerization conditions, it was carried out in two steps. Treatment of amines **6a—c** with triallylborane initially gives the corresponding N→B complex. Its heating (120—130 °C) results in cleavage of one B—C bond (1 mol of propylene is formed) to give aminoboranes **15**, which were isolated by distillation in

85—93% yields. On further heating (Table 2), *trans*-aminoboranes **15** isomerize into the corresponding *cis*-compounds **16**, deboronation of which with methanol (0—20 °C) and 20% NaOH affords compounds **14a—c** in 60—70% yields with respect to compounds **6a—c**. The amines obtained in this way (**14a,b**) contained 1—3% of an admixture of the *trans*-isomer (see Table 2), which can be removed by distillation or chromatography on Al_2O_3 with hexane—ether (10 : 1) as the eluent. In the case of aminoborane **15c** (R = Ph), isomerization remains incomplete even on prolonged heating (195 °C, 12 h). According to ^{13}C NMR and/or GLC data for deboronation products (**6** and **14**), the equilibrium ratio of **15c** : **16c** is probably 20 : 80. An increase in the temperature (>195 °C) results in decomposition of the product. Amine **14c** was isolated in a pure form by chromatography on Al_2O_3 using hexane—ether (20 : 1) as the eluent.

The driving force of the **15**→**16** isomerization is the higher thermodynamic stability of *cis*-isomers (two pseudoequatorial groups) in comparison with the corresponding *trans*-compounds.



R = Alk, Allyl, Ph

It can be assumed that the **15**→**16** transformation occurs by deallylboration—allylboration (elimination—addition of the B—All fragment).

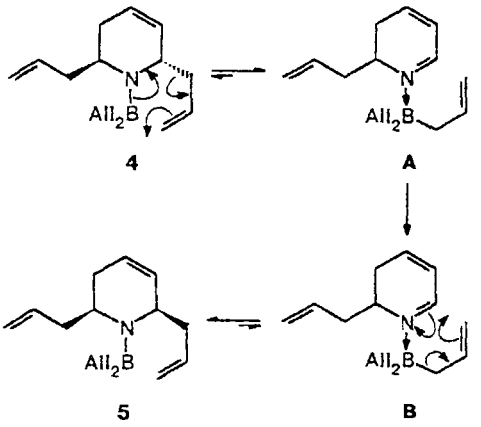
15 **16**

R = Alk, Ph

The **15**→**16** isomerization occurs under more drastic conditions (145—200 °C, Table 2) than in the case of 2,6-diallyl compound **4** (130—135 °C, 2 h).[10] This difference can be explained as shown in Scheme 3.

In the case of compound **4** (R = All), the elimination—addition mainly involves the 6-allyl group (rather than the 2-All group). Its elimination from the ring and migration to the boron atom results in intermediate complex **A** with a system of conjugated bonds (C=C—C=N), which cannot be formed in the case of isomerization involving compounds **15a—c**. Subsequent allylboration of the C=N bond (**B**) results in a *cis*-aminoborane.

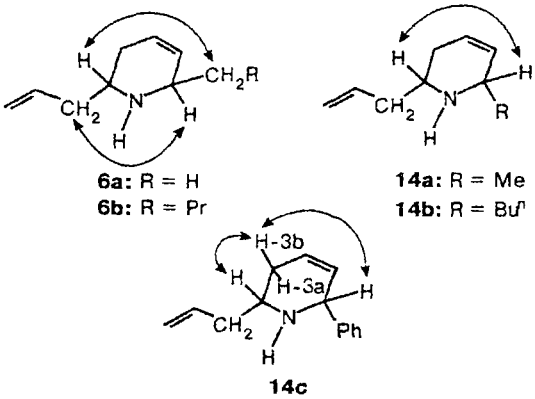
Scheme 3



4 **A** **5** **B**

The structure of compounds **6a—c** and **14a—c** was confirmed by elemental analysis and physicochemical methods (^1H and ^{13}C NMR, IR and mass spectroscopy). Assignment of signals in ^1H NMR spectra was made on the basis of ^1H—^1H COSY spectra.

The mutual arrangement of substituents with respect to the ring in *trans*-(**6a,b**) and *cis*-amines (**14a—c**) was established by two-dimensional 2D NOESY spectroscopy:



6a: R = H
6b: R = Pr

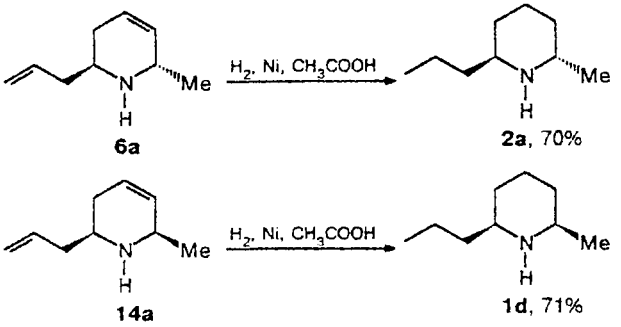
14a: R = Me
14b: R = Bu^n

14c

The presence of positive cross-peaks of H-2 with the CH_3 group (**6a**) and H-2 with butyl group protons (**6b**), as well as those of H-6 with allyl group CH_2, suggests unambiguously the *trans*-arrangement of substituents in compounds **6a** and **6b**. The positive cross-peaks of H-2 with H-6 confirm the *cis*-configuration of amines **14a** and **14b**. The presence of positive cross-peaks of H-2 with H-3b and of H-3b with H-6 in compound **14c** indicates that these three protons are located on the same side of the ring. Hence, the corresponding substituents are also *cis*-arranged.

The *trans*-configuration of 6-phenyl derivative **6c** was established by X-ray diffraction analysis of its hydrochloride.[19]

Hydrogenation of compound **6a** in acetic acid over Raney nickel in an autoclave (100 °C, 100 atm H_2, 10 h) gave an alkaloid (±)-epidihydropinidine **2a** (*trans*-2-methyl-6-propylpiperidine) in 70% yield. The ^1H and ^{13}C NMR spectra of amine **2a** and its salt **2a** · HCl are similar to those reported previously.[1a]



An analogous procedure starting from compound **14a** gave another alkaloid, (±)-dihydropinidine **1d** (*cis*-2-methyl-6-propylpiperidine), and its hydrochloride **1d** · HCl. The spectroscopic characteristics of these compounds coincide with literature data.[6a,b]

The stereoselective reactions described in the present paper can be successfully used as a key stage for the synthesis of many alkaloids and their analogs, not only those belonging to the piperidine series but also more complex bi- and polycyclic nitrogen-containing heterocycles, which are also widespread in nature.

Experimental

All operations with organoboron compounds were carried out in a dry argon atmosphere. ^1H and ^{13}C NMR spectra were recorded on a Bruker AC-200P spectrometer. ^1H—^1H COSY and 2D NOESY spectra were obtained on a Bruker AMX-400 instrument. Chemical shifts are given in the δ scale relative to $SiMe_4$. ^{11}B NMR spectra were recorded on a Bruker AC-200P spectrometer; the corresponding chemical shifts are given in the δ scale relative to $BF_3 \cdot OEt_2$. IR spectra were obtained on a UR-20 spectrophotometer, and mass spectra were obtained on a Varian-MAT spectrometer. GLC analysis was carried out on a Khrom-5 instrument, OV-1 column (1 m) on Chromaton, He as the carrier gas.

***trans*-2-Allyl-6-methyl-1,2,3,6-tetrahydropyridine (6a).** A 2.03 *N* solution of methyllithium in ether (100 mL, 203 mmol) was placed in a three-necked flask equipped with a thermometer, a reflux condenser, a dropping funnel, and an inlet for argon. Dry THF (100 mL) and then a solution of pyridine (16.4 mL, 203 mmol) in dry THF (50 mL) were added with cooling (0 °C). The mixture was stirred for 1 h at 20 °C, then triallylborane (27.1 g, 203 mmol) was added at −15 °C, and the mixture was heated to 10 °C. After that, dry methanol (25 mL, 618 mmol) and then 20% NaOH (55 mL) were cautiously added at −15 °C. The mixture was refluxed for 2 h, and the aqueous layer was saturated with K_2CO_3 and extracted with ether (3×25 mL). The extract was dried with K_2CO_3 and concentrated. Distillation of the residue on a column packed with glass spirals gave 14.4 g (52%) of piperideine **6a**, b.p. 55.5—56.5 °C (6 Torr), n_D^{20} 1.4781. Found (%): C, 78.81; H, 11.42; N, 10.57. $C_9H_{15}N$. Calculated (%): C, 78.77; H, 11.02; N, 10.21. MS (EI, 70 eV), *m/z* (I_{rel} (%)): 96 $[M-C_3H_5]^+$. IR (pure compound), ν/cm^{-1}: 3260 (br); 3070, 3010, 2960, 2910, 2820, 1640, 1430, 1365, 1320, 1200, 1125, 1060, 995, 915, 715. ^1H NMR (400 MHz, $CDCl_3$), δ: 1.15 (d, 3 H, CH_3, J = 7 Hz); 1.48 (br.s, 1 H, NH); 1.80 (dddt, 1 H, H-3a, ^2J = 17.3 Hz, ^3J = 8.2 Hz, 2.7 Hz, ^4J = 2.6 Hz); 2.07 (dddt, 1 H, H-3b, ^3J = 5.8 Hz, 5.8 Hz, ^4J = 1.3 Hz); 2.19 (m, 2 H, H-2′); 2.98 (m, 1 H, H-2); 3.54 (m, 1 H, H-6); 5.07 (dm, 1 H, H-4′a, ^3J = 10.1 Hz); 5.11 (dm, 1 H, H-4′b, ^3J = 16.2 Hz); 5.64 (dm, 1 H, H-5, ^3J = 10.0 Hz); 5.70 (dm, 1 H, H-4); 5.80 (ddt, 1 H, H-3′, ^3J = 7.6 Hz). ^{13}C NMR ($CDCl_3$), δ: 21.24 (CH_3); 30.90 (C-3); 39.88 (C-2′); 46.34 and 47.23 (C-2 and C-6); 116.79 (C-4′); 123.69 (C-4); 131.09 (C-5); 135.20 (C-3′).

***trans*-2-Allyl-6-methyl-1,2,3,6-tetrahydropyridine hydrochloride (6a · HCl)** was synthesized by treatment of compound **6a** with a solution of HCl in ether, yield 85%, m.p. 122—123 °C (from an ether—MeOH mixture) and 125.5—126 °C (from ethyl acetate). IR (KBr pellets), ν/cm^{-1}: 3410 (br); 2920, 2760, 2495, 1645, 1590, 1445, 1425, 1200, 1105, 1035, 1000, 980, 925, 725, 555. ^1H NMR (200 MHz, $CDCl_3$), δ: 1.60 (d, 3 H, CH_3); 2.20—2.75 (m, 3 H, H-3a and H-2′); 2.82—3.08 (m, 1 H, H-3b); 3.35—3.55 (m, 1 H, H-2); 3.90—4.15 (m, 1 H, H-6); 5.05—5.33 (m, 2 H, H-4′); 5.52—5.96 (m, 3 H, —CH=); 9.75 (br.s, 2 H, NH_2^+). ^{13}C NMR ($CDCl_3$), δ: 17.91 (CH_3); 26.14 (C-3); 35.56 (C-2′); 47.13 and 48.07 (C-2 and C-6); 119.21 (C-4′); 123.64 (C-4); 125.36 (C-5); 131.61 (C-3′).

***trans*-2-Allyl-6-butyl-1,2,3,6-tetrahydropyridine (6b).** Pyridine (2.65 mL, 33 mmol) was added at −60 °C to a mixture of a solution of *n*-butyllithium in hexane (2.2 *N*, 15 mL, 33 mmol) and dry ether (70 mL). The mixture was stirred for 1 h at −60 °C, and triallylborane (4.42 g, 33 mmol) was then added. The temperature of the solution was brought to 10 °C, and dry methanol (4 mL, 99 mmol) was cautiously added at −40 °C. The reaction mixture was treated with 20% NaOH (10 mL) and refluxed for 2 h. The aqueous layer was extracted with ether (3×10 mL). According to GLC data, the ethereal solution contained 90% of compound **6b**, ~9% of 2-butylpyridine **12b**, and <1% of 2-butyl-1,2,5,6-tetrahydropyridine **13**. 2 *N* HCl (15.3 mL) was added to the solution of these compounds, and the aqueous layer was separated and washed with ether. A NaOH solution (20%, 10 mL) was added to the aqueous layer, and the solution was extracted with ether (3×15 mL). The extract was dried with K_2CO_3 and distilled on a column packed with glass spirals to give 3.32 g (56%) of compound **6b**, b.p. 100—101 °C (6 Torr), n_D^{19} 1.4751. Found (%): C, 80.65; H, 11.95; N, 7.58. $C_{12}H_{21}N$. Calculated (%): C, 80.38; H, 11.81; N, 7.81. MS (EI, 70 eV), *m/z* (I_{rel} (%)): 138 $[M-C_3H_5]^+$, 122 $[M-C_4H_9]^+$, 80 $[M-(C_4H_9 + CH_2{=}CH{-}CH_3)]^+$. IR (pure compound), ν/cm^{-1}: 3250 (br); 3035, 3010, 2960, 2920, 2860, 1640, 1460, 1435, 1000, 915, 710. ^1H NMR (400 MHz, $CDCl_3$), δ: 0.90 (t, 3 H, CH_3, J = 7 Hz); 1.30 (m, 4 H, $CH_2\underline{CH_2}\underline{CH_2}CH_3$); 1.40 (m, 2 H, $\underline{CH_2}Pr$); 1.61 (s, 1 H, NH); 1.80 (ddd, 1 H, H-3a, ^2J = 17.3 Hz, ^3J = 10.5 Hz, 2.3 Hz); 2.05 (dt, 1 H, H-3b, ^3J = 3.7 Hz, 3.7 Hz); 2.16 (m, 2 H, H-2′); 2.92 (m, 1 H, H-2); 3.29 (td, 1 H, H-6, ^3J = 7.2 Hz, 1.9 Hz); 5.07 (dm, 1 H, H-4′a, ^3J = 10.0 Hz); 5.10 (dm, 1 H, H-4′b, ^3J = 15.4 Hz); 5.67 (m, 2 H, closed AB-system of H-4 and H-5); 5.79 (ddt, 1 H, H-3′, ^3J = 7.7 Hz). ^{13}C NMR ($CDCl_3$), δ: 13.72 (CH_3); 22.40 ($C_2H_4\underline{C}H_2CH_3$); 28.34 ($CH_2\underline{C}H_2C_2H_5$); 31.32 (C-3); 34.85 ($\underline{C}H_2Pr$); 39.97 (C-2′); 46.51 and 51.84 (C-2 and C-6); 116.81 (C-4′); 123.94 (C-4); 130.08 (C-5); 135.29 (C-3′).

***trans*-2-Allyl-6-butyl-1,2,3,6-tetrahydropyridine hydrochloride (6b · HCl)** was synthesized by treatment of compound **6b** with a solution of HCl in ether, yield 98%, m.p. 150.5—151.5 °C (from a hexane—chloroform mixture (4 : 1)). Found (%): C, 66.90; H, 10.39; N, 6.32; Cl, 16.53. $C_{12}H_{22}NCl$. Calculated (%): C, 66.80; H, 10.28; N, 6.49; Cl, 16.43. IR (KBr pellets, ν/cm^{-1}): 3420 (br); 3080, 2950, 2940, 2870, 2760, 2720, 2495, 1640, 1585, 1470, 1425, 1040, 1000, 930, 730. ^1H NMR (200 MHz, $CDCl_3$), δ: 0.66—1.13 (m, 3 H, CH_3); 1.15—3.15 (m, 10 H, CH_2); 3.26—3.61 (m, 1 H, H-2); 3.61—4.0 (m, 1 H, H-6); 4.98—5.38 (m, 2 H, H-4′); 5.56—6.15 (m, 3 H, —CH=); 9.71 (br.s, 2 H, NH_2^+). ^{13}C NMR ($CDCl_3$), δ: 13.78 (CH_3); 22.31 ($C_2H_4\underline{C}H_2CH_3$); 26.4 ($CH_2\underline{C}H_2C_2H_5$); 27.51 (C-3); 32.52 ($\underline{C}H_2Pr$); 35.75 (C-2′); 49.01 and 51.18 (C-2 and C-6); 119.39 (C-4′); 123.84 (C-4); 124.62 (C-5); 132.01 (C-3′).

***trans*-2-Allyl-6-phenyl-1,2,3,6-tetrahydropyridine (6c).** Pyridine (14.6 mL, 181.5 mmol) was added at 0 °C to a 0.66 *N* solution of phenyllithium in ether (275 mL, 181.5 mmol), and the mixture was stirred for 1 h at the same temperature (a precipitate formed). The reaction mixture was cooled to −30 °C, triallylborane (26.7 g, 200 mmol) was added, and the mixture was stirred for 0.5 h at 10 °C. Dry MeOH (24 mL, 594 mmol) was added dropwise at −30 °C, and the temperature was brought to 20 °C with stirring. The mixture was treated with 20% NaOH (60 mL), refluxed for 1 h, and extracted with ether. According to GLC data, the ethereal solution contained compound **6c** (94%) and 2-phenylpyridine **12c** (6%). 3 *N* HCl (47 mL) was added to the solution of these compounds, and the aqueous layer was separated and washed with ether. 20% NaOH (60 mL) was added to the aqueous layer, and the solution was extracted with ether (3×30 mL). The extract was dried with K_2CO_3 and concentrated. Distillation gave 19.2 g (53%) of compound **6c**, b.p. 101—103 °C (1 Torr), n_D^{20} 1.5510. Found (%): C, 84.39; H, 8.65; N, 6.75. $C_{14}H_{17}N$. Calculated (%): C, 84.37; H, 8.60; N, 7.03. MS (EI, 70 eV), m/z (I_{rel} (%)): 199 $[M]^+$, 158 $[M-C_3H_5]^+$, 91 $[C_7H_7]^+$. IR (pure compound), ν/cm^{-1}: 3320 (br); 3060, 3030, 2910, 1640, 1490, 1450, 1110, 1000, 920, 900, 760, 740, 705. ^1H NMR ($CDCl_3$), δ: 1.87—2.35 (m, 5 H, CH_2—C= and NH); 2.85—3.08 (m, 1 H, H-2); 4.6 (s, 1 H, H-6); 4.95—5.20 (m, 2 H, CH_2=); 5.55—6.15 (m, 3 H, =CH—); 7.20—7.55 (m, 5 H, Ph). ^{13}C NMR ($CDCl_3$), δ: 31.31 (C-3); 40.27 (C-2′); 45.90 (C-2); 56.27 (C-6); 117.16 (C-4′); 126.23 (C-4); 126.90 (C_p); 127.48 (C-5); 127.54 and 128.20 (C_o and C_m); 134.96 (C-3′); 143.46 (C_i).

***trans*-2-Allyl-6-phenyl-1,2,3,6-tetrahydropyridine hydrochloride (6c · HCl)** was synthesized by treatment of compound **6c** with a solution of HCl in ether, yield 97%, m.p. 145—147 °C. IR (KBr pellets), ν/cm^{-1}: 3440 (br); 2960, 2680, 1640, 1590, 1580, 1475, 1450, 1425, 1060, 1020, 1000, 925, 740, 720, 700. ^1H NMR ($CDCl_3$), δ: 2.32—2.70 (m, 3 H, H-2′ and H-3a); 2.75—2.95 (m, 1 H, H-3b); 3.20—3.48 (m, 1 H, H-2); 4.85 (s, 1 H, H-6); 5.05—5.25 (m, 2 H, H-4′); 5.55—5.90 (m, 2 H, H-3′ and H-4); 6.05—6.25 (m, 1 H, H-5); 7.30—7.70 (m, 5 H, Ph); 9.55 (br.s, 1 H, NH); 10.55 (br.s, 1 H, NH). ^{13}C NMR ($CDCl_3$), δ: 26.79 (C-3); 35.86 (C-2′); 48.32 (C-2); 54.57 (C-6); 119.38 (C-4′); 122.55 (C_p); 126.67 (C-4); 128.81 (Ph); 129.61 (C-5); 130.25 (Ph); 131.87 (C-3′); 133.72 (C_i).

***trans*-2-Methyl-6-propylpiperidine ((±)-epidihydropinidine) (2a).** A mixture of compound **6a** (1.73 g, 12.6 mmol), glacial acetic acid (9.8 mL), and Raney nickel (0.04 g) was placed in a 0.15 L autoclave. Hydrogen was fed to a pressure of 98.5 atm, and the autoclave was heated for 10 h at 100—105 °C. The nickel was removed, 20% NaOH was added until the acid was neutralized completely, and the mixture was extracted with ether. The extract was dried with K_2CO_3, and the residue was distilled *in vacuo* to give 1.21 g (70%) of compound **2a**, b.p. 53—54 °C (7 Torr), n_D^{20} 1.4480. ^1H NMR ($CDCl_3$), δ: 0.8—1.7 (m, 17 H); 2.8—3.2 (m, 2 H, N—CH). ^{13}C NMR ($CDCl_3$), δ: 13.53 ($C_2H_4\underline{C}H_3$); 18.96 and 19.01 ($CH_2\underline{C}H_2CH_3$); 20.63 (C-4); 30.27 (C-3); 32.48 (C-5); 35.73 ($\underline{C}H_2C_2H_5$); 45.20 (C-2); 49.89 (C-6).

***trans*-2-Methyl-6-propylpiperidine hydrochloride (2a · HCl).** The reaction of compound **2a** (0.35 g, 2.5 mmol) and a solution of HCl in ether gave 0.42 g (96%) of hydrochloride **2a** · HCl with m.p. 136.5—137.5 °C. IR (pure compound), ν/cm^{-1}: 3410 (br); 2940, 2820, 2760, 2550, 1590, 1460, 1395, 1380, 1190, 1020, 640, 500, 470. ^1H NMR ($CDCl_3$), δ: 0.75—1.0 (t, 3 H, CH_3); 1.15—2.05 (m, 13 H); 3.1—3.35 (m, 1 H, N—C(2)H); 3.35—3.6 (m, 1 H, N—C(6)H). ^{13}C NMR ($CDCl_3$), δ: 13.61 ($C_2H_4\underline{C}H_3$); 16.67 and 17.23 (CH_3, $CH_2\underline{C}H_2CH_3$); 18.90 (C-4); 26.11 (C-3); 28.70 (C-5); 32.65 ($\underline{C}H_2C_2H_5$); 47.81 (C-2); 51.36 (C-6).

***trans*-2-Allyl-1-diallylboryl-6-methyl-1,2,3,6-tetrahydropyridine (15a).** Compound **6a** (4.5 g, 32.8 mmol) was placed in a distilling flask, and triallylborane (5.3 g, 6.9 mL, 39.6 mmol) was added. The mixture was heated at 115 °C for 0.5 h, during which time 32.5 mmol of propylene evolved. The excess triallylborane was distilled off. Subsequent distillation gave 6.94 g (92%) of compound **15a**, b.p. 90—92 °C (1 Torr), n_D^{19} 1.5091. ^1H NMR (CD_3COCD_3), δ: 0.85—1.25 (d, 3 H, CH_3); 1.5—2.35 (m, 8 H, —CH_2—); 3.55—3.8 (m, 1 H, H-2); 3.85—4.1 (m, 1 H, H-6); 4.5—5.0 (m, 6 H, CH_2=); 5.3—5.9 (m, 5 H, —CH=). ^{13}C NMR (CD_3COCD_3), δ: 27.4 (CH_3); 29.44 (C-3, B—CH_2—); 44.27 (C-2′); 51.06 and 55.27 (C-2 and C-6); 115.77 and 115.99 (B—CH_2—CH=$\underline{C}H_2$); 118.64 (C-4′); 125.43 (C-4); 135.49 (C-5); 138.26, 138.64, 138.93 (—CH= in All). ^{11}B NMR ($CDCl_3$), δ: 44.66.

Isomerization of *trans*-2-allyl-1-diallylboryl-6-methyl-1,2,3,6-tetrahydropyridine (15a) into *cis*-2-allyl-1-diallylboryl-6-methyl-1,2,3,6-tetrahydropyridine (16a). Compound **15a** (6.94 g) was placed in a three-necked flask equipped with a thermometer, a reflux condenser, and an inlet for argon. Heating for 6.5 h at 160—165 °C gave compound **16a** (content of compound **15a** ~1%), n_D^{19} 1.4998. ^1H NMR ($CDCl_3$), δ: 1.15—1.35 (d, 3 H, CH_3); 1.75—2.45 (m, 8 H, —CH_2—); 3.9—4.05 (m, 1 H, H-2); 4.1—4.3 (m, 1 H, H-6); 4.75—5.15 (m, 6 H, CH_2=); 5.55—6.05 (m, 5 H, —CH=). ^{13}C NMR ($CDCl_3$), δ: 24.32 (CH_3); 26.2 and 26.95 (B—CH_2—); 28.15 (C-3); 40.18 (C-2′); 48.64 and 50.81 (C-2 and C-6); 113.36 and 113.58 (B—CH_2—CH=$\underline{C}H_2$); 116.33 (C-4′); 121.16 (C-4); 129.96 (C-5); 136.52, 136.69, 136.86 (—CH= in All). ^{11}B NMR ($CDCl_3$), δ: 43.08.

***cis*-2-Allyl-6-methyl-1,2,3,6-tetrahydropyridine (14a).** Dry MeOH (1.5 mL) and 20% NaOH (12 mL) were added consecutively at 0 °C to the reaction mixture obtained after isomerization of compound **15a** into **16a**. The reaction mixture was refluxed for 2 h with vigorous stirring and extracted with ether. The extract was dried with K_2CO_3. Distillation gave 3.24 g (72% with respect to compound **6a**) of *cis*-isomer **14a**, b.p. 46—47 °C (6 Torr). The admixture of *trans*-isomer **6a** (~1%) was removed by repeated distillation. n_D^{19} 1.4755. Found (%): C, 78.89; H, 11.14; N, 9.87. $C_9H_{15}N$. Calculated (%): C, 78.77; H, 11.02; N, 10.21. MS (EI, 70 eV), m/z (I_{rel} (%)): 96 $[M-C_3H_5]^+$. IR (pure compound), ν/cm^{-1}: 3280 (br), 3070, 3020, 2960, 2910, 2830, 2790, 1640, 1465, 1430, 1370, 1310, 1125, 995, 920, 790, 725, 685. ^1H NMR (400 MHz, $CDCl_3$), δ: 1.08 (d, 3 H, CH_3, ^3J = 6.8 Hz); 1.42

(br.s, 1 H, NH); 1.80 (dm, 1 H, H-3b, ^2J = 17.2 Hz); 1.94 (dm, 1 H, H-3a, ^2J = 17.2 Hz); 2.18 (m, 2 H, H-2′); 2.79 (m, 1 H, H-2); 3.46 (m, 1 H, H-6); 5.05 (dd, 1 H, H-4′a, ^3J = 11.3 Hz, ^2J = 1.0 Hz); 5.09 (dd, 1 H, H-4′b, ^3J = 17.1 Hz, ^2J = 1.0 Hz); 5.50 (dm, 1 H, H-5, ^3J = 10.0 Hz); 5.64 (dm, 1 H, H-4, ^3J = 10.0 Hz); 5.78 (m, 1 H, H-3′). ^{13}C NMR ($CDCl_3$), δ: 20.84 (CH_3); 30.76 (C-3); 39.91 (C-2′); 49.14 and 51.16 (C-2 and C-6); 115.92 (C-4′); 123.23 (C-4); 130.76 (C-5); 133.87 (C-3′).

***cis*-2-Allyl-6-methyl-1,2,3,6-tetrahydropyridine hydrochloride (14a · HCl)** was synthesized by treatment of compound **14a** with a solution of HCl in ether, yield 85%, m.p. 199—200 °C (from an ether—methanol mixture). IR (KBr pellets), ν/cm^{-1}: 3420 (br); 2940, 2800, 2740, 2670, 2500, 2340, 1640, 1600, 1585, 1460, 1430, 1390, 1380, 1160, 1100, 1025, 920, 760, 695, 555, 480. ^{1}H NMR (200 MHz, $CDCl_3$), δ: 1.65 (d, 3 H, CH_3, J = 6.71 Hz); 2.20—2.85 (m, 3 H, H-3a and H-2′); 2.9—3.4 (m, 2 H, H-3b and H-2); 3.85—4.1 (m, 1 H, H-6); 5.0—5.35 (m, 2 H, H-4′); 5.45—6.05 (m, 3 H, —CH=); 9.25—9.8 (br.s, 1 H, NH); 9.8—10.4 (br.s, 1 H, NH). ^{13}C NMR ($CDCl_3$), δ: 18.61 (CH_3); 27.58 (C-3); 37.21 (C-2′); 51.39 and 54.04 (C-2 and C-6); 119.25 (C-4′); 125.30 (C-4); 125.94 (C-5); 131.66 (C-3′).

***trans*-2-Allyl-1-diallylboryl-6-butyl-1,2,3,6-tetrahydropyridine (15b).** Similarly to the synthesis of compound **15a**, the reaction of compound **6b** (3.6 g, 20.1 mmol) and triallylborane (3.25 g, 4.2 mL, 24.2 mmol) carried out by heating for 1 h at 120 °C followed by distillation gave 5.02 g (93%) **16b**, b.p. 100—102 °C (1 Torr), n_D^{19} 1.5056. ^{1}H NMR (CD_3COCD_3), δ: 0.2—0.4 (m, 3 H, CH_3); 0.55—0.85 (m, 4 H, $CH_2C\underline{H}_2C\underline{H}_2CH_3$); 0.85—1.15 (m, 2 H, $C\underline{H}_2Pr$); 1.15—1.4 (m, 4 H, B—CH_2—); 1.4—1.85 (m, 4 H, H-2′ and H-3); 3.15—3.3 (m, 1 H, H-2); 3.3—3.5 (m, 1 H, H-6); 4.15—4.45 (m, 6 H, CH_2=); 4.95—5.45 (m, 5 H, —CH=). ^{13}C NMR (CD_3COCD_3), δ: 14.32 (CH_3); 23.15 ($C_2H_4\underline{C}H_2CH_3$); 27.37 (B—$CH_2$—); 27.84 ($CH_2\underline{C}H_2C_2H_5$); 28.93 (C-3); 40.71 and 42.66 (C-2′ and $\underline{C}H_2Pr$); 53.25 and 53.77 (C-2 and C-6); 113.77 and 113.92 (B—CH_2—CH=$\underline{C}H_2$); 116.58 (C-4′); 124.53 (C-4); 132.12 (C-5); 136.32 (C-3′); 136.75, 136.92 (B—CH_2—$\underline{C}$H=). ^{11}B NMR (CD_3COCD_3), δ: 49.87.

Isomerization of *trans*-2-allyl-1-diallylboryl-6-butyl-1,2,3,6-tetrahydropyridine (15b) into *cis*-2-allyl-1-diallylboryl-6-butyl-1,2,3,6-tetrahydropyridine (16b). Similarly to the synthesis of compound **16a**, heating of compound **15b** for 6 h at 200 °C gave compound **16b** (content of compound **15b** ~3%), n_D^{19} 1.4983. ^{1}H NMR (CD_3COCD_3), δ: 0.55—0.85 (m, 3 H, CH_3); 0.95—2.25 (m, 14 H, CH_2); 3.55—3.85 (m, 2 H, NCH); 4.5—4.85 (m, 6 H, CH_2=); 5.3—5.8 (m, 5 H, —CH=). ^{13}C NMR (CD_3COCD_3), δ: 13.66 (CH_3); 22.53 ($C_2H_4\underline{C}H_2CH_3$); 25.98 and 26.81 (B—$CH_2$—); 28.37 ($CH_2\underline{C}H_2C_2H_5$); 29.2 (C-3); 39.37 and 39.88 (C-2′ and $\underline{C}H_2Pr$); 50.42 and 53.24 (C-2 and C-6); 113.01 and 113.25 (B—CH_2—CH=$\underline{C}H_2$); 115.89 (C-4′); 121.00 (C-4); 127.24 (C-5); 135.9, 136.02, 136.22 (—CH= in All). ^{11}B NMR (CD_3COCD_3), δ: 48.87.

***cis*-2-Allyl-6-butyl-1,2,3,6-tetrahydropyridine (14b).** Dry MeOH (1.5 mL) and 20% NaOH (8 mL) were added consecutively to the reaction mixture obtained after isomerization of compound **15b** into **16b** (the content of compound **15b** in the mixture was ~3%). The reaction mixture was refluxed for 2 h with vigorous stirring, extracted with ether, and dried with K_2CO_3. Distillation gave 2.34 g (65% with respect to compound **6b**) of compound **14b**, b.p. 94—95 °C (6 Torr). The admixture of *trans*-isomer **6b** (~3%) was separated on a column with Al_2O_3 (hexane : ether = 10 : 1 as the eluent). n_D^{19} 1.4757. Found (%): C, 80.15; H, 11.71; N, 7.82. $C_{12}H_{21}N$. Calculated (%): C, 80.38; H, 11.81; N, 7.81. MS (EI, 70 eV), m/z (I_{rel} (%)): 179 $[M]^+$, 138 $[M-C_3H_5]^+$, 122 $[M-C_4H_9]^+$, 80 $[M-(C_4H_9 + CH_2=CH-CH_3)]^+$. IR (pure compound), ν/cm^{-1}: 3300 (br); 3070, 3020, 2960, 2930, 2860, 1640, 1455, 1430, 1320, 1125, 995, 920, 825, 730. ^{1}H NMR (400 MHz, $CDCl_3$), δ: 0.89 (t, 3 H, CH_3); 1.31 (m, 6 H, $(C\underline{H}_2)_3CH_3$); 1.60 (br.s, 1 H, NH); 1.83 (dm, 1 H, H-3b, ^2J = 16.9 Hz); 1.94 (dm, 1 H, H-3a, ^2J = 16.9 Hz); 2.17 (m, 2 H, H-2′); 2.78 (dddd, 1 H, H-2); 3.31 (m, 1 H, H-6); 5.08 (m, 2 H, H-4′); 5.54 (dm, 1 H, H-5, ^3J = 10.0 Hz); 5.67 (dm, 1 H, H-4, ^3J = 10.0 Hz); 5.77 (m, 1 H, H-3′). ^{13}C NMR ($CDCl_3$), δ: 13.16 (CH_3); 21.99 ($C_2H_4\underline{C}H_2CH_3$); 27.1 ($CH_2\underline{C}H_2C_2H_5$); 31.68 (C-3); 35.5 ($\underline{C}H_2Pr$); 40.35 (C-2′); 51.50 and 54.25 (C-2 and C-6); 116.43 (C-4′); 123.96 (C-4); 130.07 (C-5); 134.35 (C-3′).

***cis*-2-Allyl-6-butyl-1,2,3,6-tetrahydropyridine hydrochloride (14b · HCl)** was synthesized by treatment of compound **14b** with a solution of HCl in ether, yield 87%, m.p. 193—194 °C (from an ethyl acetate—methanol mixture). IR (KBr pellets), ν/cm^{-1}: 3400 (br); 2930, 2860, 2800, 2500, 2340, 1640, 1580, 1460, 1430, 1395, 1035, 1000, 925, 760, 700, 500. ^{1}H NMR ($CDCl_3$), δ: 0.7—1.1 (m, 3 H, CH_3); 1.1—1.6 (m, 4 H, $CH_2C\underline{H}_2C\underline{H}_2CH_3$); 1.6—2.8 (m, 5 H, $C\underline{H}_2Pr$, H-2′ and H-3a); 2.85—3.35 (m, 2 H, H-2 and H-3b); 3.6—3.9 (m, 1 H, H-6); 4.9—5.3 (m, 2 H, H-4′); 5.5—6.0 (m, 3 H, —CH=); 9.1—9.5 (br.s, 1 H, NH); 9.65—10.1 (br.s, 1 H, NH). ^{13}C NMR ($CDCl_3$), δ: 13.60 (CH_3); 22.05 ($C_2H_4\underline{C}H_2CH_3$); 27.13 ($CH_2\underline{C}H_2C_2H_5$); 27.58 (C-3); 31.64 ($\underline{C}H_2Pr$); 37.03 (C-2′); 53.88 and 55.17 (C-2 and C-6); 118.86 (C-4′); 123.52 (C-4); 125.35 (C-5); 131.55 (C-3′).

***trans*-2-Allyl-1-diallylboryl-6-phenyl-1,2,3,6-tetrahydropyridine (15c).** Similarly to the synthesis of compound **15a**, heating of *trans*-isomer **6c** (5.05 g, 25.3 mmol) and triallylborane (4.1 g, 5.34 mL, 30.66 mmol) for 3 h at 130 °C followed by distillation gave 6.25 g (85%) of *trans*-aminoborane **15c**, b.p. 134—136 °C (1 Torr), n_D^{19} 1.5295. ^{1}H NMR (200 MHz, CD_3COCD_3), δ: 0.75 (d, 2 H, B—CH_2—, J = 7.31 Hz); 1.2 (d, 2 H, B—CH_2—, J = 7.31 Hz); 1.25—1.75 (m, 4 H, H-2′ and H-3); 3.25—3.5 (m, 1 H, H-2); 3.75—4.4 (m, 7 H, H-6, CH_2=); 4.55—5.3 (m, 5 H, —CH=); 6.15—6.55 (m, 5 H, Ph). ^{13}C NMR (CD_3COCD_3), δ: 27.65, 28.60, 29.49 (B—CH_2— and C-3); 41.54 (C-2′); 53.23 (C-2); 58.74 (C-6); 114.06 and 114.26 (B—CH_2—CH=$\underline{C}H_2$); 117.27 (C-4′); 121.30 (C-4); 126.45, 126.6, 128.9 ($C_{o,m,p}$); 132.18 (C-5); 136.59, 136.65, 136.95 (—CH=); 147.59 (C_i). ^{11}B NMR ($CDCl_3$), δ: 45.43.

Isomerization of *trans*-2-allyl-1-diallylboryl-6-phenyl-1,2,3,6-tetrahydropyridine (15c) into *cis*-2-allyl-1-diallylboryl-6-phenyl-1,2,3,6-tetrahydropyridine (16c). Similarly to the synthesis of compound **16a**, heating of compound **15c** for 3.5 h at 195 °C gave compound **16c** (the content of **15c** was ~20%).

***cis*-2-Allyl-6-phenyl-1,2,3,6-tetrahydropyridine (14c).** Dry MeOH (20 mL) and KOH (5 g, 89 mmol) were added at 0 °C to the reaction mixture obtained after isomerization of compound **15c** into **16c** (the content of **15c** was ~20%), and the mixture was refluxed for 2 h with vigorous stirring. Water (30 mL) was added, and the mixture was extracted with ether. The ethereal layer was washed with saturated NaCl and dried with K_2CO_3 to give 3.8 g (75% with respect to compound **6c**) of a product containing compounds **14c** (80%) and **6c** (20%). The admixture of the *trans*-isomer was separated on a column with Al_2O_3 (a hexane—ether mixture (20 : 1) as the eluent). The b.p. of the pure product **14c** was 90—92 °C (1 Torr), n_D^{19} 1.5492. MS (EI, 70 eV), m/z (I_{rel} (%)): 199 $[M]^+$, 158 $[M-C_3H_5]^+$. IR (pure compound), ν/cm^{-1}: 3200 (br); 3060,

3030, 2910, 2820, 1640, 1490, 1450, 1290, 995, 920, 855, 760, 705. ^{1}H NMR ($CDCl_3$), δ: 1.6—1.85 (br.s, 1 H, NH); 1.85—2.4 (m, 4 H, $-CH_2-$); 2.85—3.1 (m, 1 H, H-2); 4.35—4.6 (m, 1 H, H-6); 4.9—5.25 (m, 2 H, $CH_2=$); 5.55—5.95 (m, 3 H, =CH—); 7.1—7.5 (m, 5 H, Ph). ^{13}C NMR ($CDCl_3$), δ: 32.00 (C-3); 40.94 (C-2′); 52.63 (C-2); 60.21 (C-6); 117.40 (C-4′); 125.45 (C-4); 127.1 (C_p); 127.45 and 128.32 (C_o and C_m); 130.34 (C-5); 135.07 (C-3′); 143.92 (C_i).

***cis*-2-Allyl-6-phenyl-1,2,3,6-tetrahydropyridine hydrochloride (14c · HCl)** was synthesized by treatment of compound **14c** with a solution of HCl in ether, yield 94%, m.p. 176—178 °C. Found (%): C, 71.63; H, 7.76; N, 5.77; Cl, 15.01. $C_{14}H_{18}NCl$. Calculated (%): C, 71.33; H, 7.69; N, 5.94; Cl, 15.04. IR (KBr pellets), ν/cm^{-1}: 3410 (br); 2910, 2890, 2700, 2490, 1640, 1575, 1495, 1440, 1425, 1410, 1310, 1180, 1040, 990, 970, 930, 760, 705, 690, 535. ^{1}H NMR (400 MHz, $CDCl_3$), δ: 1.82 (dd, 1 H, H-2′b); 2.33 (m, 2 H, H-2′a and H-3a); 2.45 (m, 1 H, H-3b); 3.16 (m, 1 H, H-2); 4.81 (br.s, 1 H, H-6); 4.97 (d, 1 H, H-4′a, ^3J = 17.0 Hz); 5.08 (d, 1 H, H-4′b, ^3J = 10.1 Hz); 5.45 (m, 1 H, H-3′); 5.61 (d, 1 H, H-4, ^3J = 10.2 Hz); 6.0 (m, 1 H, H-5); 7.23 (m, 3 H, Ph); 7.59 (m, 2 H, Ph); 9.25 (br.s, 2 H, NH). ^{13}C NMR ($CDCl_3$), δ: 27.15 (C-3); 35.29 (C-2′); 55.05 (C-2); 59.32 (C-6); 119.10 (C-4′); 124.6 (C-4), 126.56 (C_p); 128.42 (C_o); 129.90 (C-5 and C_m); 132.33 (C-3′); 139.79 (C_i).

***cis*-2-Methyl-6-propylpiperidine ((±)-dihydropinidine) (1d)** was obtained, in analogy to the synthesis of (±)-epidihydropinidine **2a**, by hydrogenation of compound **14a** (1.15 g, 8.4 mmol) over Raney nickel. Yield 0.84 g (71%), b.p. 46 °C (6 Torr), n_D^{19} 1.4467. ^{1}H NMR ($CDCl_3$), δ: 0.8—1.9 (m, 17 H); 2.4—2.8 (m, 2 H, N—CH). ^{13}C NMR ($CDCl_3$), δ: 13.42 ($C_2H_4\underline{C}H_3$); 18.30 (CH_3); 22.28 ($CH_2\underline{C}H_2CH_3$); 24.12 (C-4); 31.52 (C-3); 33.7 (C-5); 38.93 ($\underline{C}H_2C_2H_5$); 51.65 (C-2); 56.01 (C-6).

***cis*-2-Methyl-6-propylpiperidine hydrochloride (1d · HCl).** The reaction of compound **14a** (0.21 g, 1.49 mmol) with an HCl solution in ether gave 0.22 g (82%) of hydrochloride **1d** · HCl, m.p. 210—211 °C.

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