

Allylmethallation of benzoazaheterocycles with allylic derivatives of zinc. Synthesis of 1,4-ethano-2,3-dihydroisoquinolines and allylated heterocycles

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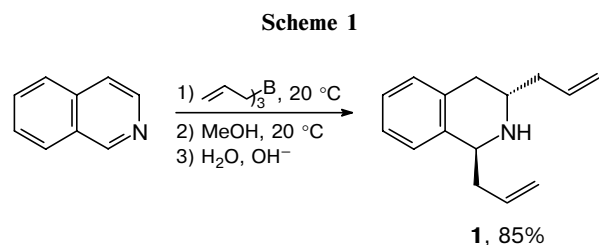
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Allylmethallation of isoquinolines, quinoline, and quinoxaline with allylic derivatives of zinc was examined for the first time. A convenient procedure was discovered and developed for the synthesis of 1,4-ethano-2,3-dihydroisoquinolines based on the reactions of isoquinolines with allylic derivatives of zinc. This multistage process involves double allylmethallation of the heterocyclic ring followed by cyclization through intramolecular carbometallation of the C=C bond. The structures of three key derivatives of 1,4-ethano-2,3-dihydroisoquinoline were established by X-ray diffraction analysis. The reactions of quinoxaline with allyl- and methallylzinc bromide proceeded stereospecifically to form *trans*-2,3-diallylated 1,2,3,4-tetrahydroquinoxalines. Heating of quinoline with methallylzinc bromide in THF afforded 4-methallylquinoline in nearly quantitative yield. The initially formed 1,4-methallation product underwent aromatization through elimination of HZnBr.

Key words: metallation, allylzinc halides, isoquinoline, quinoline, quinoxaline, 1,4-ethano-2,3-dihydroisoquinolines, cyclization, X-ray diffraction analysis, stereochemistry, allylboranes.

The 1,2-addition of organometallic compounds to the C=N bond is a classical reaction widely used in the organic synthesis.^{1,2} Thus, allylboration^{2–7} of imines has long been in use for the preparation of butenylamines with various structures.

Some aromatic nitrogen-containing heterocycles, for example, quinolines and phenanthridine, also readily react with allylboranes (0–20 °C) to give (after deboration) 2-allyl-1,2-dihydroquinolines (85–95%) and 5-allyl-5,6-dihydrophenanthridine, respectively.⁸ When treated successively with triallylborane and methanol, isoquinoline underwent reductive *trans*-1,3-diallylation to form compound **1** (Scheme 1).⁹ It should be emphasized that this unusual transformation involved methanol as a reagent¹⁰ rather than as the solvent.



Allylboration is the key stage in the synthesis of unsymmetrical *trans*-1-R-3-allyl-1,2,3,4-tetrahydro-

isoquinolines (R = Alk or Ar) from isoquinoline, RLi, and triallylborane.¹¹

All the above-mentioned reactions proceeded with the allylic rearrangement, apparently, through the six-membered chair-like transition state.⁷

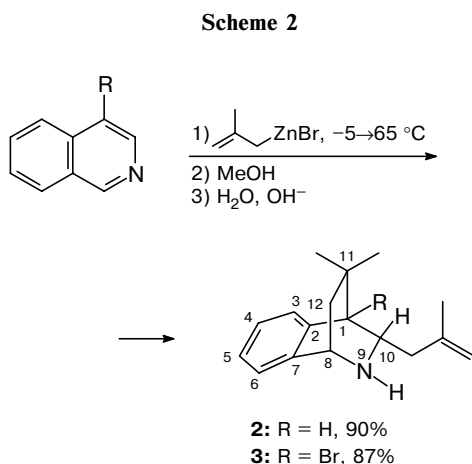
Taking into account that allylzinc halides also add to imines,^{2,12} we decided to perform the above-mentioned reactions with the use of zinc analogs of allylboranes, which are more readily accessible than allylboranes by themselves. These analogs, like the Grignard reagent, can be easily prepared *in situ* from the corresponding allyl halide and activated zinc in THF.¹³ It appeared that allylzinc bromide readily reacted with isoquinoline and its derivatives to form products of reductive *trans*-1,3-diallylation (**1**) or 1,4-ethano-2,3-dihydroisoquinoline derivatives depending on the reaction conditions (see the preliminary communication¹⁴).

The present study was devoted to allylmethallation of isoquinolines, quinoline, and quinoxaline with allyl-, methallyl-, and crotylzinc bromides.

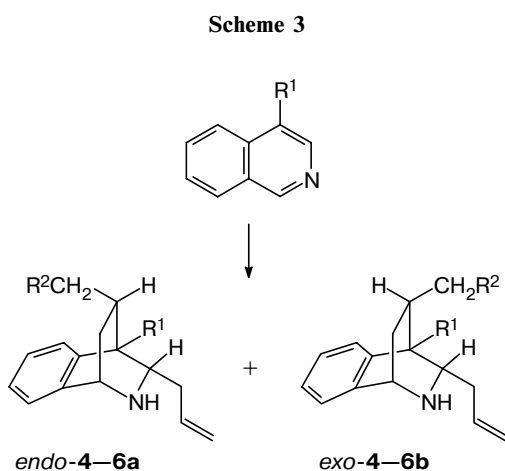
Reactions with isoquinolines

Heating (65 °C, 1 h) of a mixture of isoquinoline and 2.5 equivs. of methallylzinc bromide in THF followed by treatment with methanol and an alkali solution afforded 1,4-ethano-2,3-dihydro-3-methallyl-10,10-

dimethylisoquinoline, or 10-methyl-11,11-dimethyl-9-azatricyclo[6.2.2.0^{2,7}]dodeca-2,4,6-triene (**2**), in 90% yield (Scheme 2). The atomic numbering scheme presented in Scheme 2 corresponds to the latter name and is used in the subsequent consideration and discussion of the data from NMR spectroscopy and X-ray diffraction analysis. Compound **3** was prepared analogously from 4-bromoisoquinoline.



Under the same conditions, the reactions of allylzinc bromide with isoquinoline or 4-bromoisoquinoline afforded mixtures of two diastereomers of ethanoisoquinolines **4a** and **4b** or **5a** and **5b**, respectively, which differ in the orientation of the methyl group (Scheme 3).



Reagents and conditions: 1) $\text{CH}_2=\text{CH}-\text{CH}_2\text{ZnBr}$, $0 \rightarrow 65^\circ\text{C}$, 1 h; 2) MeOR^2 ; 3) H_2O , OH^- .

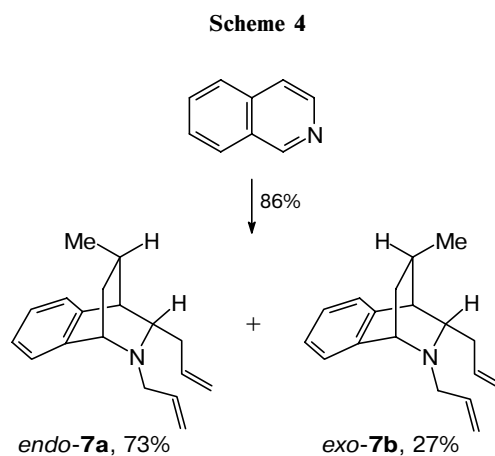
Compound	R ¹	R ²	Total yield (%)	Ratio of the <i>endo/exo</i> isomers
4	H	H	90	73/27
5	Br	H	87	69/31
6	H	D	89	73/27

The ratio of the *endo* and *exo* isomers (**4a** : **4b** \approx 7 : 3) was determined by ¹H NMR spectroscopy and GLC-mass

spectrometry. It appeared that this ratio is virtually independent of the reaction conditions (temperature, the reaction time, and the concentrations of the starting compounds).

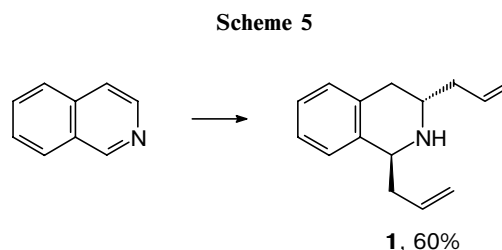
Treatment of the reaction mixture with deuteromethanol MeOD (the cleavage of the C—Zn bonds in the resulting organozinc compounds) afforded a mixture of two deuterium-containing diastereomers (**6a** and **6b**, R² = D).

Successive treatment of isoquinoline with allylzinc bromide ($0 \rightarrow 65^\circ\text{C}$), allyl bromide, methanol, and an alkali solution gave rise to a mixture of *N*-allylated ethanoisoquinolines **7a** and **7b** in a ratio of 7 : 3 in 86% total yield (Scheme 4).



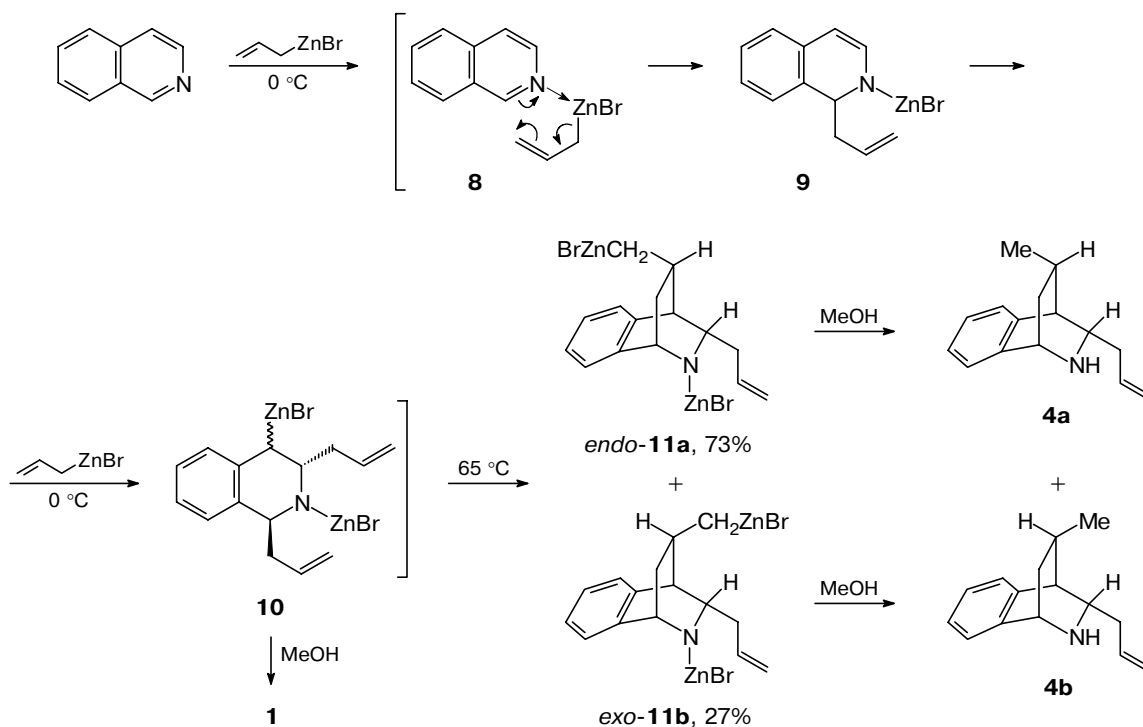
Reagents and conditions: 1) AlI_2ZnBr , 65°C , 30 min; 2) AlI_2Br , 20°C , 24 h; 3) MeOH; 4) H_2O , OH^- .

The results obtained in the reaction of isoquinoline with allylzinc bromide at low temperature ($-5 \rightarrow 0^\circ\text{C}$, 1 h) are of importance for an understanding of the mechanism of formation of 1,4-ethano-2,3-dihydroisoquinolines. Subsequent treatment with methanol and alkali afforded *trans*-1,3-diallyl-1,2,3,4-tetrahydroisoquinoline (**1**) in 60% yield (Scheme 5). Under these conditions, tricyclic compounds **4a** and **4b** were obtained only in trace amounts. It should be noted that the reaction presented in Scheme 5 is the first example of reductive *trans*- α,α' -diallylation of an aromatic heterocycle under the action of allylzinc halide. In this pro-



Reagents and conditions: 1) AlI_2ZnBr , -5°C , 1 h; 2) MeOH, NaOH.

Scheme 6



cess, methanol served only as a demetallating agent in contrast to allylboration of isoquinoline (see Scheme 1) producing the same product (**1**).

The possible pathway of the formation of ethanoisoquinolines is shown in Scheme 6.

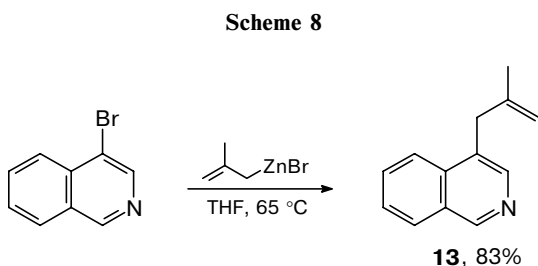
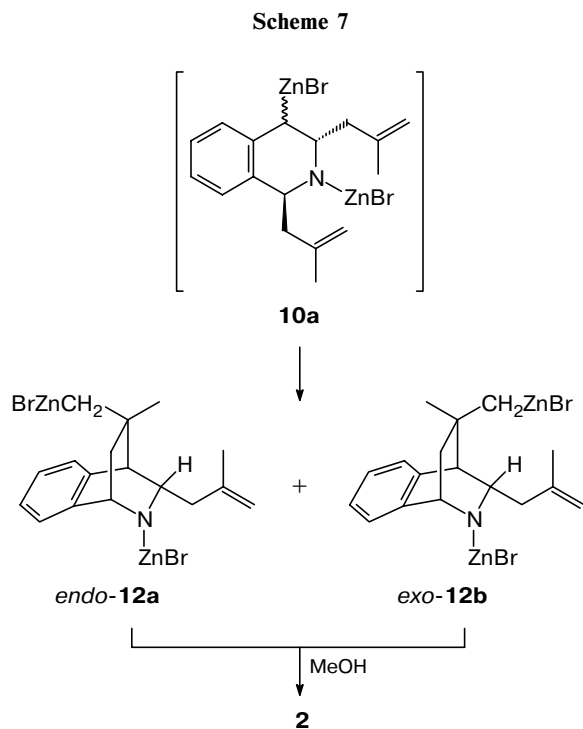
The first stage of this multistep process involves the addition of AllylZnBr at the $\text{C}(1)=\text{N}$ bond of the isoquinoline molecule (apparently, *via* complex **8**). This stage as well as the subsequent stage, *viz.*, the addition of the second allylzinc bromide molecule to the $\text{C}(3)=\text{C}(4)$ double bond (in compound **9**), proceed with the allylic rearrangement, apparently, through the six-membered transition state of type **8** (see below). An important point is that the addition of the second allyl group at the $\text{C}(3)$ atom occurs *trans*-stereospecifically with respect to the allyl group, which is already present in the ring. It should be noted that the stereochemistry of the benzylzinc fragment in intermediate **10** remains unclear and hence, the $\text{C}-\text{Zn}$ bond is indicated by a wavy line. Hydrolysis of dizinc derivative **10** ($0-5\text{ }^\circ\text{C}$) afforded tetrahydroisoquinoline **1**, whereas heating of **10** resulted in its cyclization through the intramolecular addition of the benzylic fragment $\text{C}(4)-\text{ZnBr}$ at the double bond of the allylic group bound to the $\text{C}(1)$ atom of the heterocycle. As a result, two diastereomeric dizinc compounds (**11a** and **11b**) are formed. Demetallation of the latter produces a mixture of diastereomeric ethanoisoquinolines **4a** and **4b**. Apparently, *endo*-isomer **11a** is formed as the major product due to interaction of the zinc atom with the π -electrons of the benzene ring in the transition state (upon cyclization $\mathbf{10} \rightarrow \mathbf{11}$).

All stages of the mechanism presented in Scheme 6 were justified and confirmed by the results obtained in early studies. There are many examples of allylmethallation of imines^{2,12} and olefins,^{12a} including 3,4-dihydroisoquinolines,^{12d} styrene derivatives,¹⁵ and 4-vinylpyridine derivatives¹⁶ as well as of cyclization of 5- and 6-alkenylzinc halides.¹⁷ Allylmethallation of compounds with the $\text{C}=\text{N}$ and $\text{C}=\text{C}$ bonds proceeds as the ene-type reaction (with the rearrangement). Cyclization proceeds through the four-membered transition state, the zinc atom being bound to the $\text{C}(1)$ atom, whereas the organic fragment being attached to the $\text{C}(2)$ atom of the terminal double bond.

It appeared that the reaction of methallylzinc bromide with isoquinoline afforded cyclization product **12** even at $0\text{ }^\circ\text{C}$. We failed to isolate the dimethallyl analog of compound **1**. This fact indicates that the rate of cyclization of intermediate **10a** is higher than the rate of the addition to the $\text{C}=\text{N}$ bond (the slowest stage) and to the $\text{C}(3)=\text{C}(4)$ bond of the initial heterocycle. Apparently, cyclization of intermediate **10a** also gave rise to two tricyclic compounds (*endo*-**12a** and *exo*-**12b**) whose demetallation afforded the same product **2** (Scheme 7).

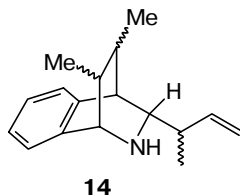
Unexpectedly, we found that the analogous reaction of 4-bromoisoquinoline (see Scheme 2), which was performed by adding a solution of methallylzinc bromide in THF to a boiling solution of 4-bromoisoquinoline in THF, produced 4-methallylisoquinoline (**13**) in 83% yield (Scheme 8).

As expected, the reaction of isoquinoline with crotylzinc bromide ($0 \rightarrow 65\text{ }^\circ\text{C}$, 1 h) yielded a mixture of



diastereomers **14**, which differ in the mutual arrangement of the methyl groups. Consequently, both stages of reductive allylmethylation of isoquinoline occurred with the allylic rearrangement.

We demonstrated by special experiments that diethylzinc (up to 140 °C) and benzylzinc bromide (65 °C, THF) did not add to isoquinoline.



The structures of the key compounds **2** and **7a** were established by X-ray diffraction analysis of their picrates (**15** and **16**, respectively). To reveal the structural characteristics of the ethanoisoquinoline core, *N,N*-dimethyl salt of compound **2** (iodide **17**) was also studied by X-ray diffraction analysis.

The structures of the cations of picrate **15** and salt **17** are shown in Figs. 1 and 2, respectively. According to the data from the X-ray study, NMR spectroscopy, and elemental analysis, crystals of picrate **15**, which were obtained by crystallization from a mixture of ethyl ac-

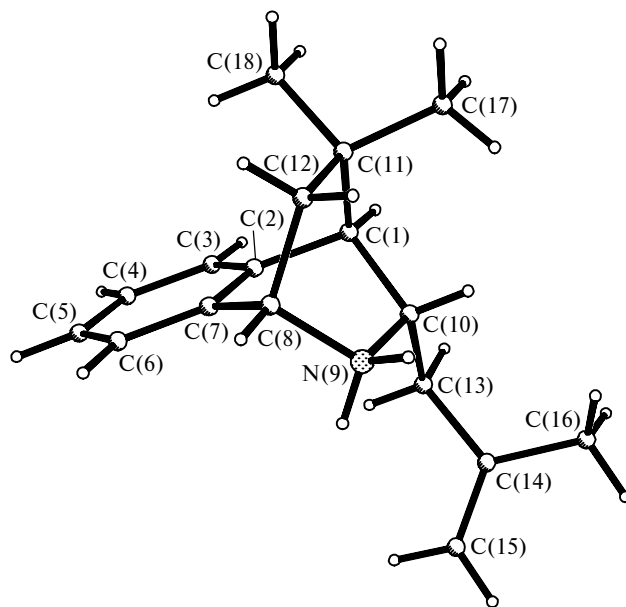
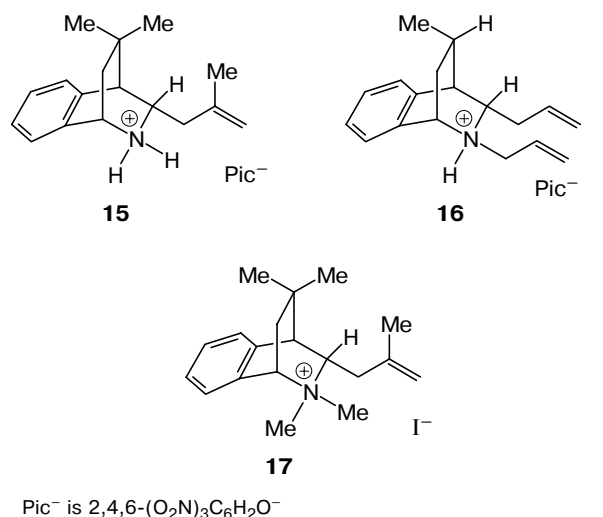


Fig. 1. Structure of the cation of picrate **15**.

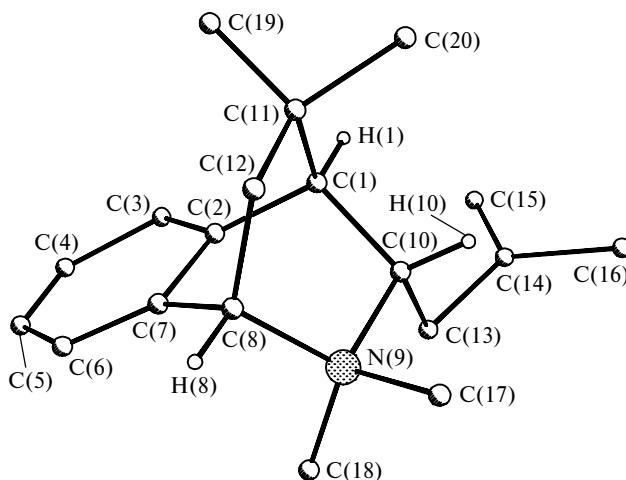


Fig. 2. Structure of the cation of salt **17**.

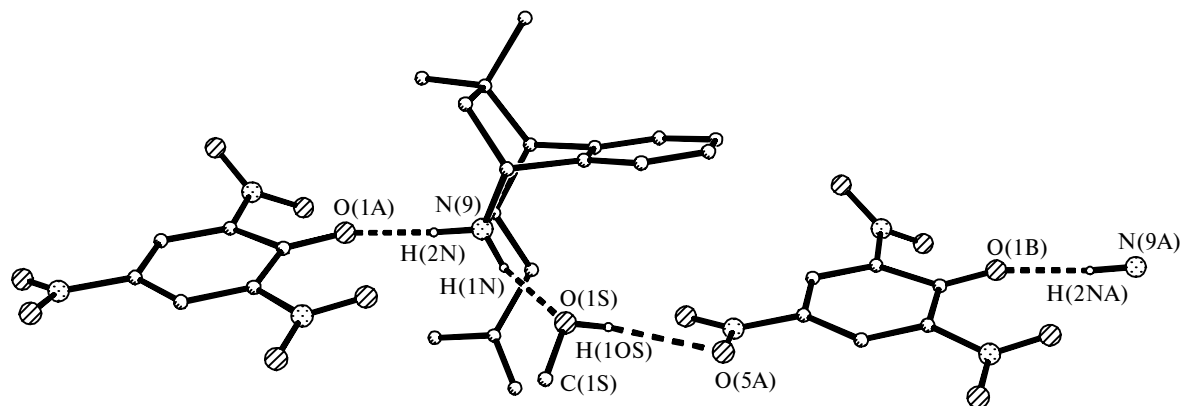


Fig. 3. Structure of the picric acid–amine **2**–methanol chain.

etate and methanol, contain methanol of solvation (Fig. 3).

We failed to separate diastereomers **4a** and **4b** as well as diastereomers **7a** and **7b** by chromatography. At the same time, picrate of the major isomer (**16**) was isolated by fractional crystallization of a mixture of picrates of the *N*-allyl derivatives (*endo*-**7a** and *exo*-**7b**). The structure of the cation of **16** is shown in Fig. 4.

The cyclic systems of all three cations have similar structures. Both nonaromatic six-membered rings adopt a boat conformation. In all three cations, the allylic (methallyl) substituent at the C(10) atom is in the axial position of the C(1)C(2)C(7)C(8)N(9)C(10) ring. The *N*-allylic group in picrate **16** (see Fig. 4) is located in the equatorial position of the same ring.

The bond lengths and bond angles in the salts under study are close to the standard values and are not reported here. Let us only mention the following facts. The carbon atom of the Me group in picrate **16** (see Fig. 4) is at a distance of 4.15 Å from the center of the benzene ring. The introduction of the second methyl group at the C(11) atom leads to a decrease in this distance. In the cations of picrate **15** (see Fig. 1) and

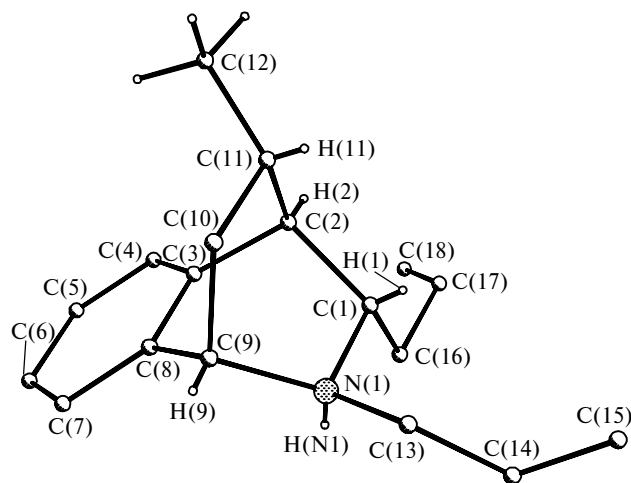


Fig. 4. Structure of the cation of picrate **16**.

N,N-dimethyl salt **17** (see Fig. 2), the corresponding distances are 3.70 and 3.72 Å, respectively, and the distances between the hydrogen atoms (*endo*-CH₃) and the C(2) atom of the benzene ring decrease accordingly from 2.91 Å (in **16**) to 2.50 and 2.55 Å in picrate **15** and *N,N*-dimethyl salt **17**, respectively.

Magnetic anisotropy induced by the benzene ring is responsible for a noticeable difference in the ¹H (~0.7 ppm) and ¹³C (up to 7 ppm) chemical shifts of the *endo*- and *exo*-CH₃ groups in the dimethyl derivatives (**2** and **3**) and in isomers **4**–**7** (see the Experimental section).

The fragment of the ¹H NMR spectrum of a mixture of isomers **4a** and **4b** is shown in Fig. 5. The signals of the *endo*-CH₃ group are observed at higher field (δ 0.62) compared to the signals of the *exo*-CH₃ group (δ 1.23 ppm.). The ratio of isomers **4a** and **4b** (~7 : 3) was determined from the integral intensities of these signals.

The assignments of the signals in the ¹H NMR spectra of tricyclic compounds **2**–**7** were made based on the COSY ¹H–¹H, NOE, and ¹³C APT NMR experiments.

In the mass spectra (electron impact) of ethanoisoquinolines **2**–**7**, molecular ion peaks are virtually absent

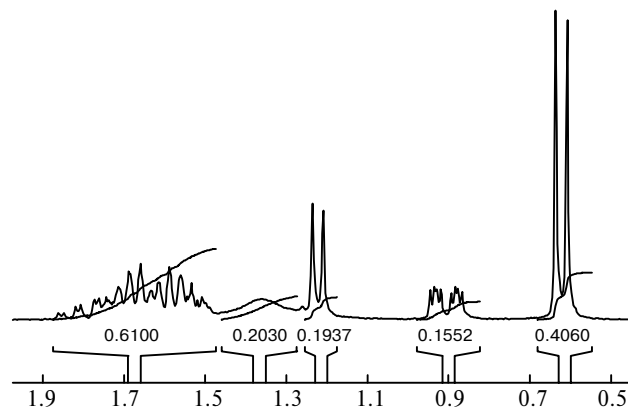


Fig. 5. Fragment of the ¹H NMR spectrum of a mixture of amines **4a** and **4b**.

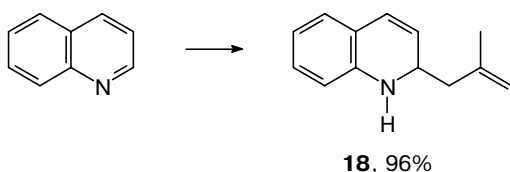
and peaks of the ions generated by elimination of the allyl (methallyl) groups $[M - C_3H_5]^+$ or $[M - C_4H_7]^+$ prevail. The ions of isoquinoline and naphthalene were observed as the final degradation products.

It should be noted that the ethanoisoquinoline systems have been prepared earlier based on the polar cycloaddition of vinyl ethers or cyclopentadiene to isoquinolinium salts.¹⁸ Recently, silicon-containing analogs of compounds **4** and **5** (as mixtures of isomers) were prepared by the reactions of allyltrimethylsilane with isoquinoline acylated with phenyl chloroformate in the presence of silver triflate.¹⁹

Reactions with quinoline and quinoxaline

As mentioned above, quinolines react with triallylborane through the 1,2-addition at the C=N bond of the heterocycle to form (after deboration) 2-allyl-1,2-dihydroquinolines.⁸ Analogously, we prepared 2-methallyl-1,2-dihydroquinoline **18** using trimethallylborane (Scheme 9).

Scheme 9

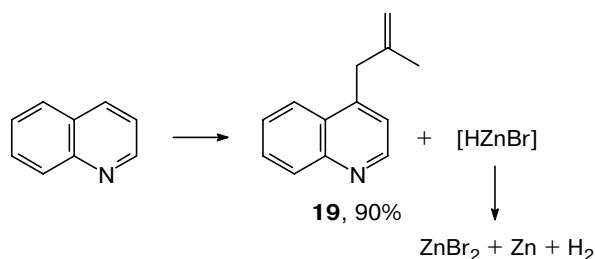


Reagents and conditions: 1) $(CH_2=CH)_3B$, 20–100 °C, 15 min; 2) Pr^iOH ; 3) H_2O , OH^- .

We expected that allylic derivatives of zinc would react with quinoline and its derivatives in a similar manner; however, our expectations were not realized.

Heating of methallylzinc bromide with quinoline afforded 4-methallylquinoline **19** (Scheme 10). The reaction also produced $ZnBr_2$, zinc metal, and gaseous hydrogen.

Scheme 10

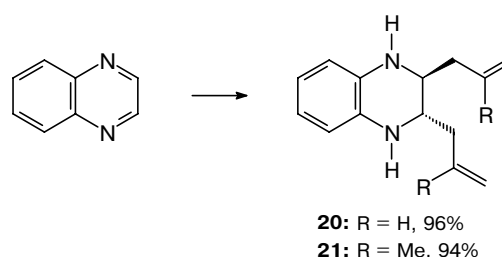


Reagents and conditions: 1) $CH_2=CHCH_2ZnBr$, 65 °C, 6 h; 2) H_2O , OH^- .

We believe that this reaction was accompanied by the 1,4-addition of methallylzinc bromide to the heterocycle followed by elimination of unstable zinc bromide hydride. It should be noted that 4-methallylquinoline has not been described previously. The reaction of allylmagnesium bromide with quinoline afforded 2-allylquinoline.²⁰

Quinoxaline, which acts as diimine, reacted with allyl- and methallylzinc bromide (2 equivs.) even at –30 °C. The subsequent demetallation produced the corresponding racemic *trans*-2,3-diallylated 1,2,3,4-tetrahydroquinoxalines (**20** and **21**) in high yields (Scheme 11).

Scheme 11



Reagents and conditions: 1) $CH_2=CHMgBr$, –35→20 °C, 1 h; 2) $MeOH$; 3) H_2O , OH^- .

The *trans*-stereochemistry of products **20** and **21** was confirmed by the data from ^{13}C NMR spectroscopy of their mixtures with chiral europium fluorocamphorate. Splitting of the signals is indicative of the presence of two enantiomers both of **20** and **21**. This splitting cannot occur in the case of the *cis* isomers (the *meso* form).

At higher temperature (20–50 °C), the above-mentioned reaction with methallylzinc bromide gave rise to the *trans* isomer (65–75%) along with the corresponding *cis*-diallylated product (25–35%). It should be noted that the reaction of quinoxaline with allylmagnesium bromide also yielded 2,3-diallyl-1,2,3,4-tetrahydroquinoxaline, but the stereochemistry of the latter has not been established.²⁰

To summarize, we developed a simple procedure for the construction of ethanoisoquinolines based on the reactions of isoquinolines with allylzinc bromides. This multistage process involves double allylmethallation of the heterocyclic ring followed by intramolecular carbometallation of the terminal C=C bond (cyclization). It was also found that heating of quinoline with methallylzinc bromide afforded 4-methallylquinoline in virtually quantitative yield. The primary allylmethallation product underwent aromatization by elimination of $HZnBr$, which decomposed to give hydrogen, $ZnBr_2$, and zinc metal. It was demonstrated that the reactions of quinoxaline with allyl- or methallylzinc bromide at low temperature proceeded stereospecifically to yield *trans*-2,3-diallylated 1,2,3,4-tetrahydroquinoxalines.

Experimental

All operations with organozinc compounds were carried out under an atmosphere of dry argon. Solutions of allyl-, methallyl-, and crotylzinc halides were prepared according to standard procedures.¹³ The ¹H, NOE, COSY ¹H–¹H, ¹³C, and ¹³C APT NMR spectra were recorded on Bruker DRX 500, Bruker AC-200P, Bruker AMX 400, and Bruker AM 300 instruments. The mass and GLC-mass spectra (EI, 70 eV) were measured on Kratos MS-30 and Varian-MAT instruments. The X-ray diffraction data sets (7083 (**16**), 4737 (**17**) and 22848 (**15**) reflections) were collected on four-circle automated CAD-4 (**16**) and Siemens P3/PC diffractometers (Mo-K α radiation, graphite monochromator, θ_{\max} = 30°) (**17**) at –20 °C and 27 °C for **16** and **17**, respectively, and on a Bruker SMART diffractometer (Mo-K α radiation, graphite monochromator, θ_{\max} = 28.77°) at –63 °C for **15**. After averaging of the equivalent reflections, the X-ray data sets contained 5938 (**15**), 6346 (**16**), and 4430 (**17**) independent reflections, which were used in the subsequent calculations. The structures were solved by direct methods. The positions of the nonhydrogen atoms were refined anisotropically by the least-squares method based on F^2_{hkl} . The positions of the hydrogen atoms were revealed from difference electron density syntheses. In the structure **16**, the positions of the hydrogen atoms were refined isotropically, except for the H(10⁺) atom and the hydrogen atoms of one of the Me groups (at the C(19) atom), which were refined using the riding model. In the structure of picrate **15**, the positions of the hydrogen atoms were refined isotropically, except for the hydrogen atoms of the Me groups (at the C(16), C(17), C(19), and C(20) atoms) and of the methylene groups (at the C(13) and C(15) atoms), which were placed in idealized positions and refined using the riding model; the hydrogen atoms of the molecule of solvation were located from difference electron density syntheses and were included in the refinement with fixed positional parameters. All calculations were carried out using the SHELXTL PLUS 5 program package.²¹ The crystallographic data for the structures of **15**, **16**, and **17** were deposited with the Cambridge Structural Database* (CCDC 142011, CCDC 142012, and CCDC 142013, respectively).

trans-1,3-Diallyl-1,2,3,4-tetrahydroisoquinoline (1). A 1.7 M solution of allylzinc bromide (115 mL, 0.2 mol) in THF was added with intense stirring to a solution of isoquinoline (5 g, 38.8 mmol) in THF (30 mL) at –5–0 °C for 1 h and the reaction mixture was stirred at this temperature for 1 h. Then methanol (6.5 g, 0.2 mol) was added at –15–0 °C with caution in such a way as to maintain the temperature below 0 °C. A 6 M NaOH solution was added to the reaction mixture until the precipitate of Zn(OH)₂ was completely dissolved. The organic layer was separated and the aqueous layer was extracted with ether (3×30 mL) and dried with Na₂CO₃. After distillation, compound **1** was obtained in a yield of 4.8 g (60%), b.p. 110 °C (2 Torr), n_D^{20} 1.5488. ¹H NMR (CDCl₃), δ : 2.10–2.85 (m, 6 H, –CH₂–CH= and C(4)H₂); 3.15 (m, 1 H, C(3)H); 4.05 (dd, 1 H, C(1)H, J = 10.53 Hz, J = 7.02 Hz); 5.05–5.20 (m, 4 H, CH₂=CH–); 5.70–6.00 (m, 2 H, –CH=CH₂); 7.00–7.15 (m, 4 H, C₆H₄). ¹³C NMR (CDCl₃), δ : 35.70 (C(4)); 40.90, 41.21 (–CH₂–CH=); 45.88 (C(3)); 54.80 (C(1)); 117.51, 118.02 (CH₂=CH–); 125.46, 125.97,

126.75, 128.93 (CH arom.); 135.10, 135.84 (–CH=CH₂); 134.40, 138.33 (C_{quater} arom.) (cf. lit.⁹).

11,11-Dimethyl-10-methallyl-9-azatricyclo[6.2.2.0^{2,7}]dodeca-2,4,6-triene (2). A 2.3 M solution of methallylzinc bromide (54 mL, 0.125 mol) in THF was added with stirring to a solution of isoquinoline (6.45 g, 0.05 mol) in THF (20 mL). The reaction mixture was refluxed for 30 min. Then methanol (4.5 g, 0.14 mol) was added carefully at 0–10 °C. Subsequent treatment was carried out as described for compound **1**. Compound **2** was isolated by distillation in a yield of 10.8 g (90%), b.p. 133–135 °C (1 Torr), n_D^{23} 1.5420. Found (%): C, 84.32; H, 9.44; N, 5.78. C₁₇H₂₃N. Calculated (%): C, 84.59; H, 9.60; N, 5.80. MS, m/z ($I_{\text{rel}}(\%)$): 241 [M]⁺ (1), 186 [M – C₄H₇]⁺ (65), 158 [M – (C₄H₇ + HC=NH)]⁺ (14), 143 [M – (C₄H₇ + HC=NH + CH₃)]⁺ (48), 131 [M – (C₄H₇ + C₄H₇)]⁺ (58), 130 [M – (C₄H₇ + C₄H₈)]⁺ (100), 129 [isoquinoline]⁺ = [M – (C₄H₇ + C₄H₆)]⁺ (52), 128 [M – (C₄H₇ + C₄H₁₀)]⁺ (41), 55 [C₄H₇]⁺ (17), 41 [C₃H₅]⁺ (24). ¹H NMR (CDCl₃), δ : 0.50 (s, 3 H, *endo*-CH₃); 1.00 (br.s, NH); 1.22 (s, 3 H, *exo*-CH₃); 1.65 (s, 3 H, CH₃–C=); 2.35 (s, 1 H, C(1)H); 3.55 (m, 1 H, C(10)H); 3.80 (s, 1 H, C(8)H); 1.10–1.85 (m, 4 H, C(12)H₂, –CH₂–C=); 4.45 and 4.65 (both s, 1 H + 1 H, CH₂=C–); 6.95–7.20 (m, 4 H, C₆H₄). ¹³C NMR (CDCl₃), δ : 21.92 (*exo*-CH₃); 28.49 (*endo*-CH₃); 31.30 (C(11)); 31.42 (CH₃–C=); 42.31 (C(12)); 44.64 (–CH₂–C=); 47.91 (C(1)); 49.91 (C(10)); 52.03 (C(8)); 112.47 (CH₂=C–); 121.04, 125.71, 125.90, 127.06 (CH arom.); 138.74, 141.58 (C(2), C(7)); 141.95 (CH₂=C–).

Picrate of amine 2 (15). A solution of amine **2** (1 g, 4.15 mmol) in MeOH (3 mL) was added to a solution of picric acid (0.95 g) in methanol (25 mL) heated to boiling. Then the reaction mixture was concentrated to 8–10 mL and cooled to 0 °C. The precipitate that formed was separated and recrystallized from a methanol–ethyl acetate mixture. The crystal solvate of picrate **2**·MeOH was obtained in a yield of 1.67 g (82%), m.p. 176–177 °C. Found (%): C, 57.24; H, 6.10; N, 11.05. C₂₄H₃₀N₄O₈. Calculated (%): C, 57.36; H, 6.02; N, 11.15. ¹H NMR (CDCl₃), δ : 0.60 (s, 3 H, *endo*-CH₃); 1.35 (s, 3 H, *exo*-CH₃); 1.45 (d, 1 H, *endo*-H–C(12), ³ J = 1.9 Hz); 1.7 (s, 3 H, CH₃–C=); 1.95 (m, 2 H, –CH₂–C=); 2.25 (dd, 1 H, *exo*-H–C(12), ³ J = 14.50 Hz, ³ J = 2.34 Hz); 2.70 (s, 1 H, C(1)H); 3.40 (s, 3 H, CH₃OH), 4.40 (br.s, 1 H, C(10)H); 4.65 and 4.90 (both s, 1 H + 1 H, CH₂=C–); 4.75 (s, 1 H, C(8)H); 7.45–7.65 (m, 4 H, C₆H₄); 5.90 and 10.80 (both br.s, 1 H + 1 H, NH₂⁺); 8.85 (s, 2 H, CH picrate anion). ¹³C NMR (DMF-d₇), δ : 22.01 (*exo*-CH₃); 27.20 (*endo*-CH₃); 31.04 (CH₃–C=); 31.54 (C(11)); 38.10 (–CH₂–C=); 41.20 (C(12)); 48.10 (C(1)); 49.39 (C(10)); 50.63 (MeOH); 52.88 (C(8)); 114.01 (CH₂=C–); 125.70, 127.80, 128.12, 129.23 (CH arom.); 124.63 (2 CH picrate anion); 133.87, 139.01, (C(2), C(7)); 142.66 (CH₂=C–); 126.39, 140.60, 160.66 (picrate anion). The crystals of [C₁₇H₂₄N]⁺[C₆H₂N₃O₇][–]·CH₃OH, C₂₄H₃₀N₄O₈ (M = 502.52), are monoclinic, at –63 °C a = 7.7405(9) Å, b = 29.839(4) Å, c = 10.728(1) Å, β = 94.311(2)°, V = 2470.8(5) Å³, d_{calc} = 1.351 g cm^{–3} for Z = 4, space group $P2_1/c$.

9,9,11,11-Tetramethyl-10-(2-methylallyl)-9-azoniatri-cyclo[6.2.2.0^{2,7}]dodeca-2,4,6-triene iodide (17). Iodomethane (3.5 g, 25 mmol) and K₂CO₃ (6.9 g, 50 mmol) were added to a solution of amine **2** (2 g, 8.3 mmol) in methanol (30 mL). The reaction mixture was refluxed for 5 h (the course of the reaction was monitored by TLC). The methanol was evaporated and the solid residue was extracted with chloroform (3×30 mL). The extract was concentrated *in vacuo* and the solid residue was crystallized from an ethyl acetate–chloro-

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form mixture. Salt **17** was obtained in a yield of 3 g (92%), m.p. 215–216 °C. The crystals of C₂₀H₃₂INO (M = 429.37) are triclinic, at 20 °C $a = 8.754(3)$ Å, $b = 10.278(4)$ Å, $c = 25.491(8)$ Å, $\alpha = 84.45(3)^\circ$, $\beta = 84.00(3)^\circ$, $\gamma = 67.51(3)^\circ$, $V = 2103.4(12)$ Å³, $d_{\text{calc}} = 1.356$ g cm⁻³ for $Z = 2$, space group $P\bar{1}$.

1-Bromo-11,11-dimethyl-10-(2-methylallyl)-9-azatri-cyclo[6.2.2.0^{2,7}]dodeca-2,4,6-triene (3). A 1.61 M solution of methylzinc bromide (43.5 mL, 0.070 mol) in THF was added with stirring to a solution of 4-bromoisoquinoline (6 g, 0.0288 mol) in THF (35 mL) cooled to a temperature from -10 to -5 °C. The reaction mixture was stirred at a temperature from -10 to -5 °C for 30 min, gradually (for 30 min) heated to 20 °C, refluxed for 20 min, and cooled to 0 °C. Then methanol (4.5 g, 0.14 mol) was added. Subsequent treatment was carried out as described for compound **1**. Fractional distillation afforded a substance with the b.p. 136–138 °C (0.5 Torr) in a yield of 7.85 g (85%). According to the ¹H NMR spectral data, this substance contained ~95% of **3**. Column chromatography of the distillate on neutral Al₂O₃ (hexane–ether as the eluent, 2 : 1) afforded compound **3**, n_D^{22} 1.5592. Found (%): C, 63.79; H, 6.82; N, 4.41. C₁₇H₂₂BrN. Calculated (%): C, 63.75; H, 6.92; N, 4.37. MS, m/z ($I_{\text{rel}}(\%)$): 321, 319 [M]⁺ (1), 266, 264 [M - C₄H₇]⁺ (35, 37), 238, 236 [M - (C₄H₇ + HC=NH)]⁺ (22, 23), 223, 221 [M - (C₄H₇ + HC=NH + CH₃)]⁺ (7), 210, 208 [M - (C₄H₇ + C₄H₇)]⁺ (98, 100), 157 [M - (C₄H₇ + Br + HC=NH)]⁺ (83), 142 [M - (C₄H₇ + Br + HC=NH + CH₃)]⁺ (73), 129 [isoquinoline]⁺ = [M - (C₄H₇ + C₄H₉ + Br)]⁺ (79), 128 [M - (C₄H₇ + C₄H₉ + HBr)]⁺ (35), 55 [C₄H₇]⁺ (12), 41 [C₃H₅]⁺ (12). ¹H NMR (CDCl₃), δ : 0.70 (s, 3 H, *endo*-CH₃); 0.95 (dd, 1 H, *endo*-H-C(12), ³J = 16.18 Hz, ³J = 10.95 Hz); 1.45 (s, 3 H, *exo*-CH₃); 1.50 (m, 1 H, -CH₂-C=); 1.65 (s, 4 H, CH₃-C= and NH); 2.15 (dd, 1 H, -CH₂-C=, ³J₁ = 13.98 Hz, ²J₂ = 2.95 Hz); 2.60 (m, 1 H, *exo*-H-C(12)); 3.85 (m, 1 H + 1 H, C(8)H and C(10)H); 4.40 and 4.70 (both s, 1 H + 1 H, CH₂=C-); 7.05 (m, 1 H, CH arom.); 7.25 (m, 2 H, CH arom.); 7.60 (m, 1 H, CH arom.). ¹³C NMR (CDCl₃), δ : 21.81 (*exo*-CH₃); 27.61 (*endo*-CH₃); 29.98 (CH₃-C=); 38.42 (C(11)); 43.97, 44.08 (C(12) and -CH₂-C=); 51.60 (C(10)); 54.74 (C(8)); 81.19 (C(1)); 113.45 (CH₂=C-); 120.86, 126.64, 127.60, 127.89 (CH arom.); 137.53 (C(7)); 140.99 (CH₂=C-); 142.58 (C(2)).

Picrate of compound 3 was prepared from amine **3** (1.5 g) and picric acid (1.1 g); the yield was 2.16 g (87%), m.p. 182–183 °C (from an ethyl acetate–methanol mixture). Found (%): C, 50.20; H, 4.63; N, 10.13. C₂₃H₂₅BrN₄O₇. Calculated (%): C, 50.28; H, 4.59; N, 10.2. ¹H NMR (DMSO-d₆), δ : 0.70 (s, 3 H, *endo*-CH₃); 1.30 (dd, 1 H, *endo*-H-C(12), ³J = 16.18 Hz, ³J = 11.03 Hz); 1.45 (s, 3 H, *exo*-CH₃); 1.55 (dd, 1 H, -CH₂-C=); 1.65 (s, 3 H, CH₃-C=); 2.30 (dd, 1 H, *exo*-H-C(12), ³J = 13.98 Hz, ²J = 2.95 Hz); 2.65 (d, 1 H, -CH₂-C=, ³J = 16.91 Hz); 4.25 (d, 1 H, C(10)H, ³J = 10.30 Hz); 4.75 (s, 1 H, C(8)H); 4.85 (d, 2 H, CH₂=C-, ³J = 5.14 Hz); 7.45–7.65 (m, 4 H, CH arom.); 8.45 and 9.95 (both br.s, 1 H + 1 H, NH₂) 8.60 (s, 2 H, picrate anion). ¹³C NMR (DMSO-d₆), δ : 22.69 (*exo*-CH₃); 25.86 (*endo*-CH₃); 29.29 (CH₃-C=); 37.55 (-CH₂-C=); 38.58 (C(11)); 39.07 (C(12)); 50.81 (C(10)); 54.53 (C(8)); 75.40 (C(1)); 112.47 (CH₂=C-); 124.63 (2 CH picrate anion); 126.97, 128.44, 129.11, 131.55 (CH arom.); 136.52, 138.92 (C(2), C(7)); 141.57 (CH₂=C-); 125.14, 139.12, 160.79 (picrate anion).

10-Allyl-11-methyl-9-azatri-cyclo[6.2.2.0^{2,7}]dodeca-2,4,6-triene (4) — 1R*,8S*,10S*,11S* isomer (4a) and 1R*,8S*,10S*,11R* isomer (4b). Compound **4** was obtained analogously to compound **2** from a solution of isoquinoline

(5 g, 38.8 mmol) in THF (20 mL) and a 2.3 M solution of allylzinc bromide (42 mL) in THF in a yield of 7.22 g (88%). According to the data from ¹H NMR spectroscopy and GLC-mass spectrometry, the resulting mixture contained isomers **4a** (73%) and **4b** (27%), b.p. 122–123 °C (1.5 Torr), n_D^{20} 1.5504. Found (%): C, 84.35; H, 8.86; N, 6.62. C₁₅H₁₉N. Calculated (%): C, 84.46; H, 8.98; N, 6.57. MS, m/z ($I_{\text{rel}}(\%)$): 213 [M]⁺ (1), 172 [M - C₃H₅]⁺ (100), 41 [C₃H₅]⁺ (28). **Isomer 4a.** ¹H NMR (CDCl₃), δ : 0.60 (d, 3 H, CH₃, ³J₁ = 7.22 Hz); 0.90 (ddd, 1 H, *endo*-H-C(12), ³J = 13.12 Hz, ³J = 3.93 Hz, ³J = 2.62 Hz); 1.36 (br.s, 1 H, NH); 1.45–1.75 (m, 2 H, -CH₂-CH=); 2.10 (m, 1 H, C(11)H); 2.30 (m, 1 H, *exo*-H-C(12)); 2.75 (s, 1 H, C(1)H); 3.22 (dt, 1 H, C(10)H, ³J₁ = 7.22 Hz, ³J_d = 1.97 Hz); 3.90 (m, 1 H, C(8)H); 4.95 (m, 2 H, CH₂=CH-); 5.70 (m, 1 H, -CH=CH₂); 7.05–7.25 (m, 4 H, C₆H₄). ¹³C NMR (CDCl₃), δ : 21.83 (CH₃); 30.35 (C(11)); 35.76 (C(12)); 40.60 (-CH₂-CH=); 44.75 (C(1)); 51.06 (C(10)); 56.27 (C(8)); 116.84 (CH₂=CH-); 121.00, 126.05, 126.14, 127.40 (CH arom.); 134.91 (-CH=CH₂); 140.86, 142.93 (C(2), C(7)). **Isomer 4b.** ¹H NMR (CDCl₃), δ : 0.90 (m, 1 H, *endo*-H-C(12)); 1.20 (d, 3 H, CH₃, ³J₁ = 6.57 Hz); 1.36 (br.s, 1 H, NH); 1.45–1.75 (m, 2 H, -CH₂-CH=); 1.70–2.00 (m, 1 H, C(11)H); 2.40 (m, 1 H, *exo*-H-C(12)); 2.65 (s, 1 H, C(1)H); 3.47 (dt, 1 H, C(10)H, ³J₁ = 7.22 Hz, ³J_d = 1.32 Hz); 3.90 (m, 1 H, C(8)H); 4.95 (m, 2 H, CH₂=CH-); 5.70 (m, 1 H, -CH=CH₂); 7.05–7.25 (m, 4 H, C₆H₄). ¹³C NMR (CDCl₃), δ : 18.85 (CH₃); 29.83 (C(11)); 34.97 (C(12)); 40.60 (-CH₂-CH=); 44.07 (C(1)); 48.57 (C(10)); 51.75 (C(8)); 116.84 (CH₂=CH-); 121.49, 125.04, 125.94, 126.14 (CH arom.); 136.46 (-CH=CH₂); 142.74, 142.93 (C(2), C(7)).

10-Allyl-9,9,11-trimethyl-9-azoniatricyclo[6.2.2.0^{2,7}]dodeca-2,4,6-triene iodide. Iodomethane (1.5 g, 10.4 mmol) and K₂CO₃ (2.76 g, 20 mmol) were added to a solution of a mixture of amines **4a** and **4b** (0.74 g, 3.46 mmol) in methanol (20 mL). The reaction mixture was refluxed for 5 h, the methanol was evaporated, and the solid residue was extracted with chloroform (3×30 mL). The extract was concentrated *in vacuo* and the solid residue was twice recrystallized from an ethyl acetate–chloroform mixture. *N,N*-Dimethyl salt of amine **4a** was obtained in a yield of 0.69 g (54%). The diastereomeric purity was >94% (¹H NMR), m.p. 225–226 °C. Found (%): C, 55.63; H, 6.63; N, 3.97. C₁₇H₂₄NI. Calculated (%): C, 55.29; H, 6.55; N, 3.79. ¹H NMR (CDCl₃), δ : 0.70 (d, 3 H, CH₃, ³J = 7.50 Hz); 1.17 (m, 1 H, *endo*-H-C(12)); 1.85, 2.85 (m, 1 H + 1 H, -CH₂-CH=); 2.80 (m, 1 H, C(11)H); 2.90 (m, 1 H, *exo*-H-C(12)); 2.95, 3.80 (s, 3 H + 3 H, NMe₂); 3.10 (s, 1 H, C(1)H); 3.85 (m, 1 H, C(10)H); 5.15–5.35 (t, 2 H, CH₂=CH-); 5.40 (s, 1 H, C(8)H); 5.85 (m, 1 H, CH₂=C-); 7.30, 7.45, 7.65 (m, 1 H + 2 H + 1 H, C₆H₄). ¹³C NMR (CDCl₃), δ : 20.65 (CH₃); 27.53 (C(11)); 29.08 (C(12)); 33.63 (-CH₂-CH=); 42.51 (C(1)); 48.96, 54.10 (N(CH₃)₂); 69.44 (C(10)); 74.40 (C(8)); 119.76 (CH₂=CH-); 125.56, 127.39, 127.72, 129.37 (CH arom.); 131.86 (CH₂=C-); 132.80, 132.97 (C(2), C(7)).

10-Allyl-1-bromo-11-methyl-9-azatri-cyclo[6.2.2.0^{2,7}]dodeca-2,4,6-triene (5) — 1R*,8S*,10S*,11S* isomer (5a) and 1R*,8S*,10S*,11R* isomer (5b). A mixture of **5a** and **5b** was obtained analogously to compound **3** from a solution of 4-bromoisoquinoline (5 g, 24.0 mmol) in THF (30 mL) and a 1.58 M solution of allylzinc bromide (36.5 mL) in THF in a yield of 6.11 g (87%) in a ratio of 70 : 30 (NMR), b.p. 130–131 °C (0.5 Torr), n_D^{22} 1.5794. Found (%): C, 61.79; H, 6.09; N, 4.62. C₁₅H₁₈BrN. Calculated (%): C, 61.65; H, 6.11; N, 4.59. **Isomer 5a.** ¹H NMR (CDCl₃), δ : 0.75 (d, 3 H, CH₃, ³J = 5.91 Hz); 1.05–1.30 (m, 1 H + 1 H,

—CH₂—CH= and *endo*-H—C(12)); 1.68 (br.s, 1 H, NH); 1.75–2.15 (m, 1 H, —CH₂—CH=); 2.45 (m, 1 H, C(11)H); 2.82 (dd, 1 H, *exo*-H—C(12)H, *J* = 14.44 Hz, *J* = 1.97 Hz); 3.45 (dd, 1 H, C(10)H, *J* = 10.50 Hz, *J* = 3.28 Hz); 3.90 (s, 1 H, C(8)H); 4.90 (m, 2 H, CH₂=CH—); 5.60 (m, 1 H, —CH=CH₂); 7.05 (m, 1 H, CH arom.); 7.25 (m, 2 H, CH arom.); 7.50 (m, 1 H, CH arom.). ¹³C NMR (CDCl₃), δ: 20.99 (CH₃); 37.00, 39.78 (C(12) and —CH₂—CH=); 40.28 (C(11)); 50.80 (C(10)); 62.27 (C(8)); 75.73 (C(1)); 117.65 (CH₂=CH—); 120.80, 126.88, 127.69, 128.02 (CH arom.); 134.77 (—CH=CH₂); 135.22, 141.93 (C(2), C(7)). **Isomer 5b.** ¹H NMR (CDCl₃), δ: 1.05–1.30 (m, 1 H + 1 H, —CH₂—CH= + *endo*-H—C(12)); 1.45 (d, 3 H, CH₃, ³*J* = 6.58 Hz); 1.68 (br.s, 1 H, NH); 1.90 (m, 1 H, —CH₂—CH=); 2.45 (m, 1 H, C(11)H); 2.62 (dd, 1 H, *exo*-H—C(12)H, *J* = 14.44 Hz, *J* = 1.97 Hz); 3.65 (dd, 1 H, C(10)H, *J* = 10.5 Hz, *J* = 2.63 Hz); 3.90 (s, 1 H, C(8)H); 4.90 (m, 2 H, CH₂=CH—); 5.60 (m, 1 H, —CH=CH₂); 7.05 (m, 1 H, CH arom.); 7.25 (m, 2 H, CH arom.); 7.65 (m, 1 H, CH arom.). ¹³C NMR (CDCl₃), δ: 19.21 (CH₃); 37.37, 38.55 (C(12) and —CH₂—CH=); 40.28 (C(11)); 51.17 (C(10)); 54.69 (C(8)); 74.38 (C(1)); 117.67 (CH₂=CH—); 120.91, 126.28, 126.79, 127.51 (CH arom.); 134.77 (—CH=CH₂); 139.26, 142.04 (C(2), C(7)).

Picrate of compound 5, m.p. 153–154 °C (from an ethyl acetate–methanol mixture). Found (%): C, 48.37; H, 3.90; N, 10.64. C₂₁H₂₁BrN₄O₇. Calculated (%): C, 48.38; H, 4.06; N, 10.75.

Picrate of isomer 5b. ¹H NMR (CDCl₃), δ: 0.85 (d, 3 H, CH₃, ³*J* = 6.72 Hz); 1.35 (m, 1 H, *endo*-H—C(12)); 1.75 (m, 1 H, —CH₂—CH=); 2.75 (m, 1 H, C(11)H); 3.00 (m, 1 H, —CH₂—CH=); 3.10 (m, 1 H, *exo*-H—C(12)H); 4.25 (dd, 1 H, C(10)H, *J* = 10.18 Hz, *J* = 3.47 Hz); 4.85 (m, 1 H, C(8)H); 5.10 (m, 2 H, CH₂=CH); 5.50 (m, 1 H, —CH=CH₂); 7.33 (d, 1 H, CH arom., ³*J* = 7.39 Hz); 7.50 (m, 2 H, CH arom.); 7.72 (d, 1 H, CH arom., ³*J* = 7.47 Hz); 8.87 (s, 2 H, CH picrate anion). ¹³C NMR (DMF-d₇), δ: 20.80 (CH₃); 33.24, 36.04 (C(12) and —CH₂—CH=); 38.83 (C(11)); 51.68 (C(10)); 62.50 (C(8)); 70.33 (C(1)); 119.45 (CH₂=CH—); 126.01 (2 CH picrate anion); 126.31, 128.10, 129.39, 130.05 (CH arom.); 132.55 (—CH=CH₂); 133.66, 135.27 (C(2), C(7)); 124.78, 142.50, 161.12 (picrate anion). **Picrate of isomer 5a.** ¹H NMR (CDCl₃), δ: 1.55 (d, 3 H, CH₃, ³*J* = 6.54 Hz); 1.75 (m, 1 H, —CH₂—CH=); 2.10 (m, 1 H, —CH₂—CH=); 2.20 (m, 1 H, C(11)H); 2.35 (m, 1 H, *endo*-H—C(12)); 3.10 (m, 1 H, *exo*-H—C(12)H); 4.43 (dd, 1 H, C(10)H, *J* = 10.20 Hz, *J* = 3.44 Hz); 4.85 (m, 1 H, C(8)H); 5.10 (m, 2 H, CH₂=CH—); 5.50 (m, 1 H, —CH=CH₂); 7.36 (d, 1 H, CH arom., ³*J* = 7.36 Hz); 7.50 (m, 2 H, CH arom.); 7.83 (d, 1 H, CH arom., ³*J* = 7.55 Hz); 8.87 (s, 2 H, CH picrate anion). ¹³C NMR (DMF-d₇), δ: 18.02 (CH₃); 33.04, 36.22 (C(12) and —CH₂—CH=); 38.15 (C(11)); 52.07 (C(10)); 55.89 (C(8)); 69.55 (C(1)); 119.48 (CH₂=CH—); 126.01 (2 CH picrate anion); 126.42, 128.10, 129.13, 130.05 (CH arom.); 132.55 (—CH=CH₂); 133.88, 139.06 (C(2), C(7)); 124.78, 142.50, 161.12 (picrate anion).

10-Allyl-11-(deuteromethyl)-9-azatricyclo[6.2.2.0^{2,7}]dodeca-2,4,6-triene (6) — the 1*R,8*S**,10*S**,11*S** isomer (6a) and the 1*R**,8*S**,10*S**,11*R** isomer (6b).** Analogously to the synthesis of **4**, a mixture of **6a** and **6b** was obtained in a yield of 7.15 g (84%) from a solution of isoquinoline (5 g, 38.8 mmol) in THF (10 mL) and a 2.2 *M* solution of allylzinc bromide (51 mL, 0.112 mol) in THF using MeOD (4 mL) for decomposition of the reaction mixture, b.p. 117–119 °C (1 Torr), *n*_D²⁰ 1.5495. The ¹H and ¹³C NMR spectra are similar to those of the mixture of **4a** and **4b** (the isomers

1*R**,8*S**,10*S**,11*S**-**6** : 1*R**,8*S**,10*S**,11*R**-**6** ≈ 7 : 3), ¹H NMR (CDCl₃), δ: 0.62 and 1.21, respectively; ¹³C NMR (C(11)H₂D), δ: 21.15 and 18.55, respectively, triplets, ¹*J*_{CD} = 19 Hz.

9,10-Diallyl-11-methyl-9-azatricyclo[6.2.2.0^{2,7}]dodeca-2,4,6-triene (7) — the 1*R,8*S**,10*S**,11*S** isomer (7a) and the 1*R**,8*S**,10*S**,11*R** isomer (7b).** A 1.2 *M* solution of allylzinc bromide (77 mL, 93 mmol) in THF was added with stirring to a solution of isoquinoline (4 g, 31 mmol) in THF (15 mL) at 20 °C. The reaction mixture was refluxed for 30 min and cooled to 20 °C. Then allyl bromide (13.4 mL, 0.155 mol) was added. After one day, the reaction mixture was decomposed with methanol (3.2 g, 0.1 mol). Then the reaction mixture was treated as described for compound **2**. After distillation, a mixture of compounds **7a** and **7b** was obtained in a yield of 6.7 g (86%), b.p. 131–133 °C (2 Torr), *n*_D^{23.5} 1.5275. The ratio of the diastereomers 1*R**,8*S**,10*S**,11*S**-**7** : 1*R**,8*S**,10*S**,11*R**-**7** = 73 : 27 (determined by GLC-mass spectrometry). MS, *m/z* (*I*_{rel}(%)): 253 [M]⁺ (1), 212 [M - C₃H₅]⁺ (33), 170 [M - (C₃H₅ + C₃H₆)]⁺ (100), 128 [M - (C₃H₅ + C₃H₆ + C₃H₆)]⁺ (11), 41 [C₃H₅]⁺ (34). **Isomer 7a.** ¹H NMR (CDCl₃), δ: 0.58 (d, 3 H, CH₃, ³*J* = 7.43 Hz); 0.63 (ddd, 1 H, *endo*-H—C(12), *J* = 13.52 Hz, *J* = 3.91 Hz, *J* = 2.65 Hz); 1.60 and 1.95 (both m, 1 H + 1 H, CH₂ in 10-allyl); 1.90 (m, 1 H, C(11)H); 2.45 (m, 1 H, *exo*-H—C(12)); 2.72 (s, 1 H, C(1)H); 3.30 (m, 1 H, C(10)H); 3.35–3.45 (m, 2 H, CH₂ in N-allyl); 3.80 (m, 1 H, C(8)H); 4.90–5.00 (m, 2 H, CH₂= in 10-allyl); 5.10, 5.23 (both m, 1 H + 1 H, CH₂= in N-allyl); 5.70 (m, 1 H, CH= in 10-allyl); 5.92 (m, 1 H, CH= in N-allyl); 7.07 and 7.16 (both m, 2 H + 2 H, CH arom.). ¹³C NMR (CDCl₃), δ: 21.87 (CH₃); 29.80 (C(12)); 30.66 (C(11)); 40.77 (CH₂ in 10-allyl); 44.47 (C(1)); 55.15 (C(10)); 57.61 (CH₂ in N-allyl); 64.93 (C(8)); 116.41, 116.67 (CH₂= in allyl); 122.07, 126.17, 126.38, 127.12 (CH arom.); 136.06, 137.33 (—CH= in allyls). **Isomer 7b.** ¹H NMR (CDCl₃), δ: 0.63 (ddd, 1 H, *endo*-H—C(12), *J* = 13.52 Hz, *J* = 3.91 Hz, *J* = 2.65 Hz); 1.18 (d, 3 H, CH₃, ³*J*₁ = 7.42 Hz); 1.60 and 1.95 (both m, 1 H + 1 H, CH₂ in 10-allyl); 1.90 (m, 1 H, C(11)H); 2.67 (s, 1 H, C(1)H); 2.75 (m, 1 H, *exo*-H—C(12)); 3.30 (m, 1 H, C(10)H); 3.35–3.45 (m, 2 H, CH₂ in N-allyl); 3.75 (m, 1 H, CH(8)); 4.90–5.00 (m, 2 H, CH₂= in 10-allyl); 5.10, 5.23 (both m, 1 H + 1 H, CH₂= in N-allyl); 5.70 (m, 1 H, CH= in 10-allyl); 5.92 (m, 1 H, CH= in N-allyl); 7.07 and 7.16 (both m, 2 H + 2 H, CH arom.). ¹³C NMR (CDCl₃), δ: 18.53 (CH₃); 27.40 (C(12)); 30.37 (C(11)); 40.44 (CH₂ in 10-allyl); 44.09 (C(1)); 55.89 (C(10)); 56.49 (CH₂ in N-allyl); 64.93 (C(8)); 116.41, 116.67 (CH₂= in allyls); 122.42, 124.70, 125.98, 126.49 (CH arom.); 136.06, 137.33 (CH= in allyls).

Picrate of amine 7a (16). A solution of a 7 : 3 mixture of isomers **7a** and **7b** (1 g, 3.95 mmol) in MeOH (3 mL) was added to a solution of picric acid (0.8 g) in methanol (20 mL) heated to boiling. The solution was concentrated to 10 mL and cooled to 0 °C. The crystals that precipitated were separated. Picrate **16** was obtained by double crystallization from a methanol–ethyl acetate mixture, m.p. 126–126.5 °C (according to the ¹H NMR spectral data, an admixture of diastereomer **7b** was less than 4%). Found (%): C, 59.73; H, 5.66; N, 11.89. C₂₄H₂₆N₄O₇. Calculated (%): C, 59.75; H, 5.43; N, 11.61. The crystals of C₂₄H₂₆N₄O₇ (*M* = 482.49) are monoclinic, at 20 °C *a* = 8.436(2) Å, *b* = 17.504(4) Å, *c* = 16.931(3) Å, β = 103.52(3)°, *V* = 2431.0(8) Å³, *d*_{calc} = 1.318 g cm⁻³ for *Z* = 4, space group *P*₂₁/*n*.

9,10-Diallyl-9,11-dimethyl-9-azoniatricyclo[6.2.2.0^{2,7}]dodeca-2,4,6-triene iodide was obtained analogously to the *N,N*-dimethylated salt of amine **4a**. The yield was 2.7 g (47%), the diastereomeric purity was 97%, m.p. 156.5–157 °C.

Found (%): C, 57.78; H, 6.60; N, 32.29. $C_{19}H_{26}NI$. Calculated (%): C, 57.73; H, 6.63; N, 32.10. 1H NMR ($CDCl_3$), δ : 0.65 (d, 3 H, CH_3 , $J = 6.82$ Hz); 1.15 (dd, 1 H, *endo*-H-C(12), $J = 15.69$ Hz, $J = 3.12$ Hz); 1.70, 2.62 (both m, 1 H + 1 H, CH_2 in 10-allyl); 2.70 (m, 1 H, C(11)H); 2.73 (s, 3 H, N- CH_3); 2.95 (m, 1 H + 1 H, C(12)H₂); 3.15 (s, 1 H, C(1)H); 4.10 (dd, 1 H, C(10)H); 4.50, 4.65 (ABX, 1 H + 1 H, CH_2 in N-allyl, $J_{AB} = 12.89$ Hz, $J_{AX} = 6.93$ Hz, $J_{BX} = 7.57$ Hz); 5.15–5.25 (m, 2 H, $CH_2=$ in 10-allyl); 5.20 (s, 1 H, C(8)H); 5.70 and 6.00 (both m, 1 H + 1 H, $CH_2=$ in N-allyl); 5.80 (m, 1 H, $CH=$ in 10-allyl); 6.20 (m, 1 H, $CH=$ in N-allyl); 7.20, 7.35, and 7.55 (all m, 1 H + 2 H + 1 H, CH arom.). ^{13}C NMR ($CDCl_3$), δ : 21.13 (CH_3); 27.78 (C(11)); 29.42 (C(12)); 34.61 (CH_2 in 10-allyl); 42.62 (C(1)); 45.64 (N- CH_3); 66.70 (CH_2 in N-allyl); 68.62 (C(10)); 73.19 (C(8)); 120.27 ($CH_2=$ in 10-allyl); 125.28 ($CH_2=$ in N-allyl); 133.22, 133.90 ($CH=$ in allyls); 126.05, 127.83, 128.25, 129.52 (CH arom.); 133.22, 133.90 (C(2), C(7)); 129.84, 131.87 (CH= in allyls).

4-(2-Methylallyl)isoquinoline (13). A 1.61 M solution of methylallylzinc bromide (16 mL, 26 mmol) in THF was added with stirring to a solution of 4-bromoisoquinoline (4.5 g, 21.6 mmol) in THF (20 mL) heated to boiling. The reaction mixture was refluxed for 1 h and then treated as described for compound 3. After distillation, compound 13 was obtained in a yield of 3.63 g (92%), b.p. 119–120 °C (1 Torr), n_D^{20} 1.5821. MS, m/z ($I_{rel}(\%)$): 183 [M]⁺ (90), 182 [$M - H$]⁺ (97), 168 [$M - CH_3$]⁺ (100), 167 [$M - (CH_3 + H)$]⁺ (60), 142 [$M - C_3H_5$]⁺ (32), 141 [$M - (C_3H_5 + H)$]⁺ (48). 1H NMR ($CDCl_3$), δ : 1.80 (s, 3 H, CH_3); 3.70 (s, 2 H, CH_2); 4.62 (s, 1 H, = CH_2); 4.88 (s, 1 H, = CH_2); 7.63 and 8.00 (both m, 2 H + 2 H, C(5)H and C(8)H); 8.40 (br.s, 1 H, C(3)H); 9.16 (br.s, 1 H, C(1)H). ^{13}C NMR ($CDCl_3$), δ : 22.59 (CH_3); 38.45 (CH_2); 112.60 (= CH_2); 123.34, 126.73, 128.01, 130.01 (C(5)–C(8)); 120.80, 126.71, 128.62 (C_{quater} arom.); 135.05 ($CH_2=C-$); 143.57 (C(3)); 151.55 (C(1)).

4-(2-Methylallyl)quinoline (19). Quinoline (13.5 g) was added to a 2.5 M solution of methylallylzinc bromide (250 mL, 6 equiv., 0.625 mol) and the mixture was refluxed for 6 h, a spongy precipitate of Zn being formed. The reaction mixture was cooled to 0 °C and methanol (26 mL, 0.625 mol) was added with stirring, the temperature being maintained at 0–10 °C. Then the mixture was treated as described for compound 2. After distillation, compound 16 was obtained in a yield of 18.2 g (95%), b.p. 115–116 °C (1 Torr), n_D^{20} 1.5866. MS, m/z ($I_{rel}(\%)$): 183 [M]⁺ (91), 182 [$M - H$]⁺ (94), 168 [$M - CH_3$]⁺ (100), 167 [$M - (CH_3 + H)$]⁺ (51), 142 [$M - C_3H_5$]⁺ (29), 141 [$M - (C_3H_5 + H)$]⁺ (47). 1H NMR ($CDCl_3$), δ : 1.75 (s, 3 H, CH_3); 3.75 (s, 2 H, CH_2); 4.65 (s, 1 H, = CH_2); 4.90 (s, 1 H, = CH_2); 7.21 (d, 1 H, C(3)H, $^3J = 4.38$ Hz); 7.50 (m, 1 H, C(6)H); 7.65 (m, 1 H, C(7)H); 8.00 (d, 1 H, C(5)H, $^3J = 8.37$ Hz); 8.12 (d, 1 H, C(8)H, $^3J = 8.40$ Hz); 8.82 (d, 1 H, C(2)H, $^3J = 4.38$ Hz). ^{13}C NMR ($CDCl_3$), δ : 22.65 (CH_3 , $J = 122.0$ Hz); 40.48 (CH_2 , $J = 126.5$ Hz); 113.41 (= CH_2 , $J = 155.7$ Hz); 121.77 (C(3), $J = 161.3$ Hz); 123.90 (C(6), $J = 159.05$ Hz); 126.22 (C(7), $J = 160.0$ Hz); 128.00 (C(5), $J = 159.4$ Hz); 130.00 (C(8), $J = 161.00$ Hz); 129.36 (C(4')_{quater}); 145.48 (C(8')_{quater}); 142.80 (C_{quater} in methylallyl); 150.09 (C(2), $J = 177.0$ Hz).

Picrate of compound 19, m.p. 154–155 °C. Found (%): C, 55.38; H, 3.85; N, 13.57. $C_{19}H_{16}N_4O_7$. Calculated (%): C, 55.34; H, 3.91; N, 13.59. 1H NMR ($DMSO-d_6$), δ : 1.80 (s, 3 H, CH_3); 4.10 (s, 2 H, CH_2); 4.70 and 5.00 (both s, 1 H + 1 H, $CH_2=$); 7.90–8.50 (m, 2 H + 1 H + 1 H + 1 H, C(2)H + C(5)H–C(8)H); 8.55 (s, 2 H, picrate anion). ^{13}C NMR ($DMSO-d_6$), δ : 22.48 (CH_3); 40.23 (CH_2); 114.32

($CH_2=$); 125.13 (CH picrate anion); 158.21 (C(2)); 121.47, 122.54, 124.62, 125.50, 127.71, 129.37, 134.02, 137.46, 141.55, 141.83, 144.40 (C arom.)

trans-2,3-Diallyl-1,2,3,4-tetrahydroquinoxaline (20). A 1.83 M solution of allylzinc bromide (55 mL, 0.1 mol) in THF was added with stirring to a solution of quinoxaline (5.2 g, 0.04 mol) in THF (60 mL) cooled to a temperature from –35 to –30 °C. The reaction mixture was stirred at this temperature for 30 min, gradually (30 min) heated to 20 °C, stirred at this temperature for 1 h, and cooled to 0 °C. Then methanol (4 mL, 0.1 mol) was added. Subsequent treatment was carried out analogously to the synthesis of 1. Distillation afforded compound 20 in a yield of 8.2 g (96%), b.p. 121–122 °C (0.5 Torr), n_D^{20} 1.5866 (cf. Ref.²⁰). 1H NMR ($CDCl_3$), δ : 2.19 and 2.51 (both m, 2 H + 2 H, $CH_2-CH=CH_2$); 3.15 (br.s, 2 H, N–CH); 3.75 (br.s, 2 H, NH); 5.23 (m, 4 H, $CH=CH_2$); 5.88 (m, 2 H, $CH=CH_2$); 6.60 (m, 4 H, C_6H_4). ^{13}C NMR ($CDCl_3$), δ : 37.88 ($CH_2-CH=CH_2$); 52.66 (N–CH); 114.01 ($CH=CH_2$); 118.44 (C_6H_4); 132.50 (C_{quater} arom.); 134.63 ($CH=CH_2$).

trans-2,3-Bis(2-methylallyl)-1,2,3,4-tetrahydroquinoxaline (21). Analogously to the synthesis of 20, compound 21 was obtained from a solution of quinoxaline (5.2 g, 0.04 mmol) in THF (60 mL) and a 2.38 M solution of methylallylzinc bromide (42 mL) in THF; crystallization from heptane afforded diamine 21 in a yield of 7.22 g (94%), m.p. 75–76 °C. Found (%): C, 79.44; H, 9.18; N, 11.60. $C_{16}H_{22}N_2$. Calculated (%): C, 79.29; H, 9.15; N, 11.56. 1H NMR ($CDCl_3$), δ : 1.70 (s, 6 H, CH_3); 2.10 (dd, 2 H, $CH_2-C=CH_2$, $J = 13.02$ Hz, $J = 9.59$ Hz); 2.40 (d, 2 H, $CH_2-C=CH_2$, $J = 13.00$ Hz); 3.15 (m, 2 H, N–CH); 3.85 (br.s, 2 H, NH); 4.85 and 5.00 (both s, 1 H + 1 H, $CH_2-C=CH_2$); 5.88 (m, 2 H, $CH=CH_2$); 6.50 (m, 4 H, C_6H_4). ^{13}C NMR ($CDCl_3$), δ : 22.23 (CH_3); 41.59 ($CH_2-C=CH_2$); 51.31 (N–CH); 113.64 ($CH_2-C=CH_2$); 113.93 and 118.29 (C_6H_4); 132.36 (C_{quater} arom.); 141.77 ($CH_2-C=CH_2$).

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