A Versatile Method for the Preparation of Substituted 1,2,3,4-Tetrahydroquinolines†

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N-Alkyl-*N*-aryl-1*H*-benzotriazole-1-methanamines **1** react with acetaldehyde to give 4-(benzotriazol-1-yl)-1,2,3,4-tetrahydroquinolines **11** in good yields along with minor amounts of diamines **12**. Reactions of **1** with higher enolizable aldehydes R^1CH_2CHO lead to 4-(benzotriazol-1-yl)tetrahydroquinolines with an R^1 substituent at C-3 (**17**, **18**). Condensation of *N*-methylaniline with two molecules of aldehyde RCH_2CHO and one molecule of benzotriazole produces 4-(benzotriazol-1-yl)-1,2,3,4-tetrahydroquinolines **34** bearing an R substituent at C-3 and RCH_2 on C-2. In all of these products, the benzotriazol-1-yl moiety can be replaced by a hydrogen atom (by reduction with lithium aluminum hydride) or by an alkyl or aryl group (by reaction with a Grignard reagent). Treatment of **11** with sodium alkoxides leads to 4-alkoxy-1,2,3,4-tetrahydroquinolines **10**. Elimination of a molecule of nitrogen from the benzotriazole system of 4-(benzotriazol-1-yl)-1,2,3,4-tetrahydroquinolines **17**, **18**, and **35** by sodium hydride produces the corresponding 4-(phenylamino)-1,2-dihydroquinolines **26** (R^1 = alkyl) or 4-(phenylimino)-1,2,3,4-tetrahydroquinolines **27** and **38** (R = Ph), depending on the nature of the substituents at C-3 and the workup conditions.

Introduction

Increased interest in 1,2,3,4-tetrahydroquinolines was observed recently due to their biochemical activity, especially as antihypertensives,[1] oxytocin antagonists,[2] vasopressin antagonists,[3] and calcium antagonists.[4] The largest group of classical synthetic methods for 1,2,3,4-tetrahydroquinolines is based on reductions of the heterocyclic ring of quinolines,[5–7] *N*-alkylquinolinium salts,[8,9] 1,2-dihydroquinolines,[10–14] 4-methylene-1,2,3,4-tetrahydroquinolines,[15] or 2,3-dihydro-1*H*-quinolin-4-ones.[16] A second important class of synthetic methods for 1,2,3,4-tetrahydroquinolines involves intramolecular electrophilic attack of an *N*-substituted aniline at the *ortho* position; the most common *N*-substituents are 2-alkenyl,[17,18] 3-alkenyl,[15] and 3-hydroxyalkyl.[19,20] Other less frequent synthetic approaches involve cyclization of [3-(chloroamino)propyl]benzenes,[21] cyclocondensation of 2-benzoyl-*N*-methylanilines with acrolein,[22] cyclocondensation of 2-(3-hydroxyalkyl)anilines,[20] and reactions of *N*-(methoxymethyl)-*N*-methylaniline,[23] *N*,*N*′-dimethyl-*N*,*N*′-diphenylmethanediamine[24] or *N*,*N*-dimethylanilines[25] with vinyl ethers. However, none of these methods are particularly convenient for the synthesis of 1,2,3,4-tetrahydroquinolines bearing complex substituents at C-2, C-3, and/or C-4 of the heterocyclic ring. We now present such an approach.

In previous papers,[26–28] we have reported the synthesis of tetrahydroquinolines **4** by reactions of *N*-alkyl-*N*-aryl-1*H*-benzotriazole-1-methanamines **1** with various electron-rich olefins of type **2** (Scheme 1). The reaction proceeds *via* addition of an immonium cation derived from **1** to the double bond of **2**, followed by an electrophilic aromatic attack of the transition cation **3** on the *ortho* carbon atom of the aniline. We have shown that the vinyl group in **2** can be attached to a conjugated carbon system (X: Ph, C(Me)=CH_2),[29] or a heteroatom (X: OEt, N(Me)Ac, carbazol-9-yl).[26–28] The present paper now reports our

† Dedicated to Ivar Ugi, a brilliant chemist and excellent companion, on the occasion of his 65th birthday.

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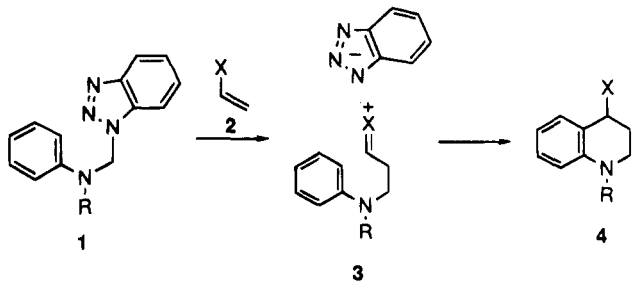
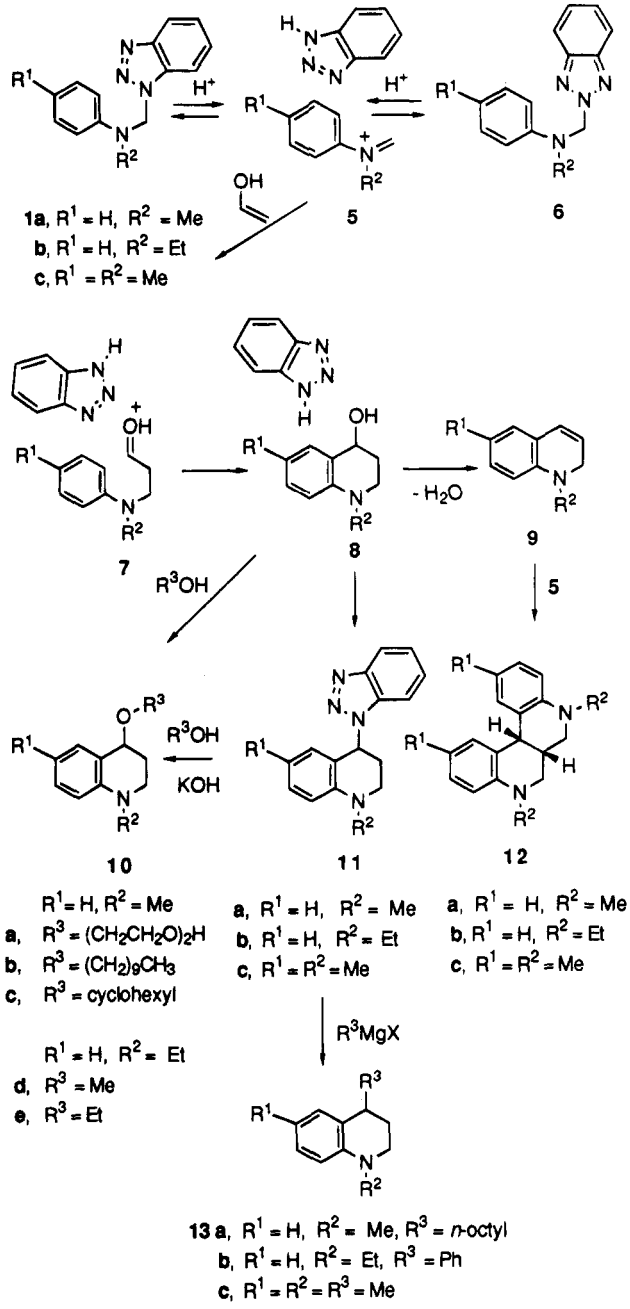
Scheme 1



Scheme 2



recent findings, that **2** can also represent any enolizable aldehyde. This expands dramatically the scope of these reagents and provides considerable potential for the introduction of substituents into the C-2, C-3, and C-4 positions of the tetrahydroquinoline ring.

Results and Discussion

1,4-Disubstituted 1,2,3,4-Tetrahydroquinolines. In the presence of catalytic *p*-toluenesulfonic acid, 1*H*-benzotriazole-1-methanamines **1**[27] react with acetaldehyde at 22 °C to produce tetrahydroquinolines **11** in 64–76% yields (Scheme 2). Additionally, byproducts of type **12** were separated (1–15%) from the reaction mixtures by column chromatography. We envisage that the reaction proceeds as shown in Scheme 2. Protonation of the benzotriazole moiety in 1*H*-benzotriazole-1-methanamine **1** and 2*H*-benzotriazole-2-methanamine **6** facilitates formation of immonium cations **5** as shown by a kinetic study of the effects of acid on the isomerization of such compounds in 1,4-dioxane solution.[30] In analogy to the reaction with enol ethers,[27] it is believed that electrophilic attack of the cation **5** on the enol form of acetaldehyde leads, *via* carboxonium cation **7**, to 4-hydroxy-1,2,3,4-tetrahydroquinolines **8**. Substitution of the protonated hydroxy group in **8** by benzotriazole gives the final products **11**. According to literature reports,[31,32] two diastereomeric 4-hydroxy-2,6-dimethyl-1,2,3,4-tetrahydroquinolines were prepared by condensation of *p*-toluidine with two molecules of acetaldehyde under acidic catalysis; the hydroxy group in these products can be easily substituted by mild nucleophiles, *e.g.* by a methoxy group from methanol.[33]

In an alternative route, 4-hydroxytetrahydroquinoline **8** presumably eliminates water to give 1,2-dihydroquinoline **9**, which reacts with cation **5** on the electron-rich C-3 of **9** and subsequently cyclizes to the tetracyclic product **12**. The relatively small coupling constants between the protons on the tertiary carbon atoms in **12** (4.5 Hz) indicates their *cis* configuration. NMR spectra of the crude reaction mixtures did not show the presence of any of the *trans* isomers of **12**.

An additional finding is the relatively easy substitution of the benzotriazole moiety in **11** by an alkoxy group. Compounds **11** reacted at 140–180 °C with sodium alkoxides (or just excess alcohol and potassium hydroxide) to give the corresponding 4-alkoxy-1,2,3,4-tetrahydroquinolines **10a–c** in good yield. Alternatively, 4-alkoxy derivatives **10** can be obtained from reactions of **1** with acetaldehyde carried out in alcohol as the solvent. 4-Methoxy- (**10d**) and 4-ethoxy- (**10e**) tetrahydroquinolines were prepared in this way. A reported synthesis of 4-ethoxy-1-methyl-1,2,3,4-tetrahydroquinoline (**10e**) is based on a reaction of *N*,*N*′-dimethyl-*N*,*N*′-diphenylmethylenediamine with ethyl vinyl ether *via* a mechanism similar to that given in Scheme 2, involving an electrophilic attack of cation **5** on the β-carbon atom of the vinyl group.[24] Treatment with Grignard reagents converted the benzotriazole adducts **11** into 1,4-dialkyl-1,2,3,4-tetrahydroquinolines **13**, as expected.[27]

1,3,4-Trisubstituted 1,2,3,4-Tetrahydroquinolines. *N*-Methyl-*N*-phenyl-1*H*-benzotriazole-1-methanamine (**1a**) reacted with phenylacetaldehyde, propionaldehyde, valeraldehyde, and β-phenylpropionaldehyde to give, in each case, mixtures of four isomeric tetrahydroquinolines (diastereomers **17** and **18** and their benzotriazol-2-yl analogs). The crude product mixture, obtained from the

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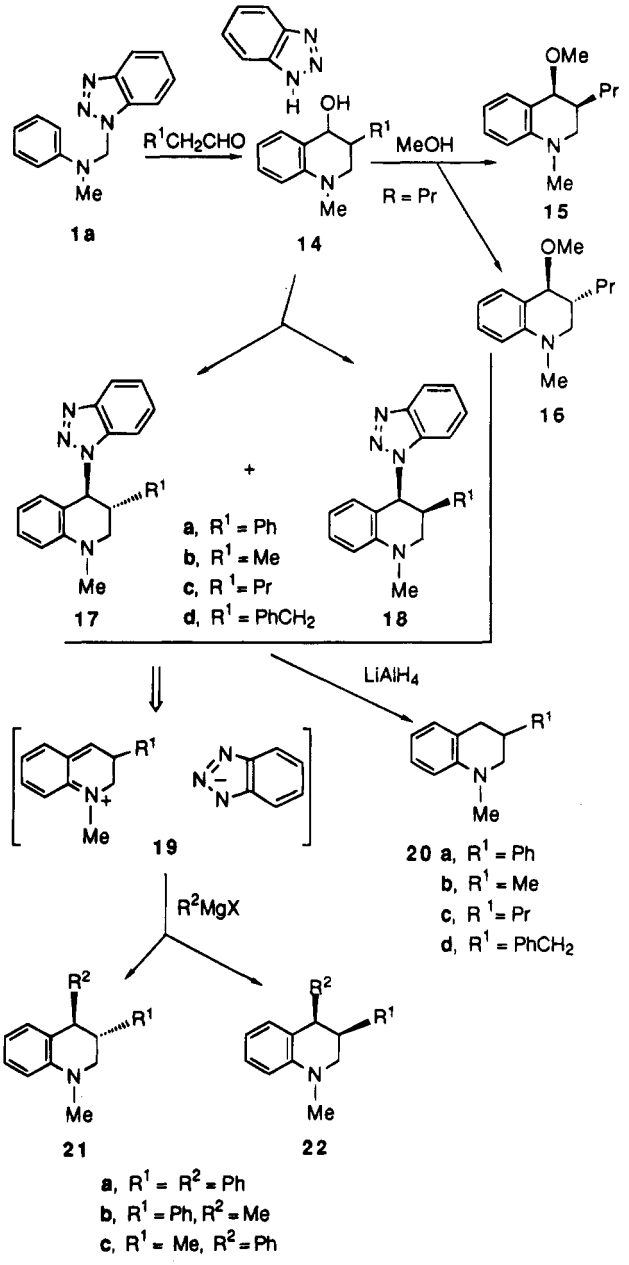
Scheme 3



reaction of **1a** with propionaldehyde, consisted of **17b** (67%, H-4 δ 5.96, $J_{3,4}$ = 9.6 Hz), **18b** (23%, H-4 δ 6.06, $J_{3,4}$ = 4.9 Hz) and their benzotriazol-2-yl isomers (10%). The *trans* configuration of the substituents in the predominant diastereomer **17b** was assigned on the basis of an NOE experiment; thus, irradiation of the methyl group (δ 0.94) produced a 12% enhancement of the H-4 doublet indicating close locations of H-4 to the methyl group. The compositions of the mixtures obtained from the reactions with valeraldehyde and β-phenylpropionaldehyde were similar. The mixtures were enriched in diastereomers **17** to about 90% by column chromatography allowing their full characterization by NMR. The *trans* configuration of the substituents in **17a** (9.8 Hz), **17c** (8.5 Hz), and **17d** (7.1 Hz) was assigned on the basis that their $J_{3,4}$ coupling constants were similar to that in **17b**. In the case of the reaction with phenylacetaldehyde, diastereomer **17a** (R^1 = Ph) was strongly predominant allowing its separation from the product mixture (Scheme 3).

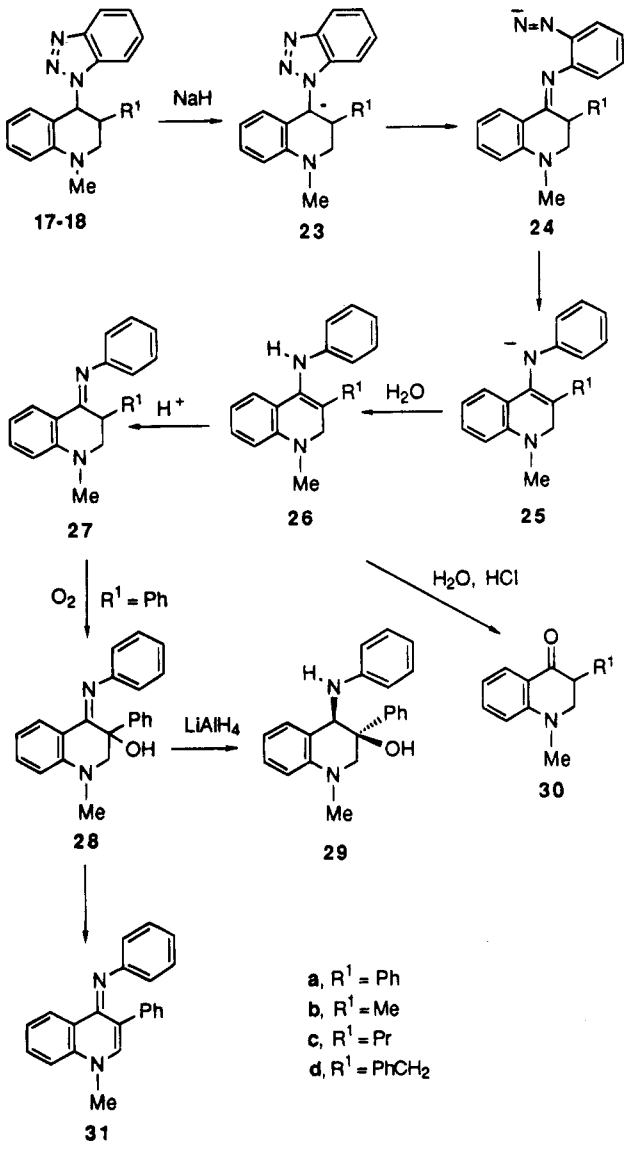
Performing the reaction of **1a** with valeraldehyde in methanol resulted in the formation of diastereomeric 4-methoxy derivatives **15** and **16**. The diastereomers were easily separated by column chromatography and fully characterized. Their stereochemistry was also assigned based on NOE spectroscopy. In this case, irradiation of the signals arising from the methoxy groups provided a convenient diagnostic tool: a 1.6% enhancement of the propyl C-α resonances at δ 1.40 and 1.55 in the minor diastereomer **15** indicated a *cis* configuration, and a 3.7% enhancement of the H-3 resonances at δ 2.02 in the major diastereomer **16** indicated a *trans* configuration of the C-3 and C-4 substituents.

The crude mixture of **17a**+**18a** and their benzotriazol-2-yl isomers was reduced with lithium aluminum hydride to provide the 1,3-disubstituted tetrahydroquinoline **20a** in a yield of 92%. The mixtures of **17b**+**18b**, **17c**+**18c**, and **17d**+**18d** (in each case including the Bt-2 isomers) were similarly reduced to give **20b**, **20c**, and **20d**, respectively, in yields of 68–96%. This preparation from **1a** without isolation of the intermediates appears to be the best available synthetic method for such 1,3-disubstituted tetrahydroquinolines. Tetrahydroquinoline **20b** was previously prepared in 44% yield by methylation of 3-methylquinoline with dimethyl sulfate, followed by reduction of the *N*-methylquinolinium salt with triethylammonium formate.[8] The other tetrahydroquinolines of this group are new compounds.

Reactions of **17a**+**18a** and of **17b**+**18b** with phenylmagnesium bromide each produced exclusively a single *trans*-diastereomer **21a** and **21c**, respectively. However, reaction of **17b**+**18b** with methylmagnesium iodide gave a mixture of the *trans* (**21b**) and *cis* (**22b**) diastereomers in a ratio of 2:1. The stereochemistry was assigned by NMR: in an NOE experiment, irradiation of the methyl doublet of **21c** at δ 0.88 gave a 10% enhancement of the H-4 doublet at δ 3.61 (J = 8.8 Hz) indicating a *trans* location of the R^1 and R^2 substituents. The coupling constants $J_{3,4}$ observed in the spectra of the product (**21a**, 9.1 Hz) obtained from the reaction of **17a**+**18a** with phenylmagnesium bromide and the main diastereomer (**21b**, 9.6 Hz), from a reaction of **17a**+**18a** with methylmagnesium iodide, appeared to be similar to that of **21c** allowing assignment of a *trans* geometry to the molecules of **21a** and **21b**. Application of the NOE or coupling constant approach to the stereochemistry of **17a** (the only pure isomer separated) was not possible because of overlapping of the resonances of interest. However, because the formation of **17**, **18**, and of **21** each had to proceed *via* the same flat ionic transition form **19**, the less hindered *trans* geometry is also assigned to **17a**. Approach of the Grignard reagent to **19** is clearly easier from the less hindered *trans*-face, explaining the exclusive formation of **21** when phenylmagnesium bromide was used.

Reaction of 4-(Benzotriazol-1-yl)-1,2,3,4-tetrahydroquinolines with Sodium Hydride. Treatments of the 4-benzotriazolyltetrahydroquinoline mixtures **17a**+**18a** – **17d**+**18d** (+ the Bt-2 isomers) with sodium hydride in each case led to the single corresponding 4-(phenylamino)-1,2-dihydroquinoline **26a–d** (Scheme 4). The reaction mechanism suggested involves deprotonation at C-4, the resulting anion **23** undergoing ring opening of the triazole to the more stable anion **24** and then nitrogen loss followed by proton transfer from C-3 to the *ortho* carbon atom of the aniline ring to give anion **25**; finally protonation of **25** during workup produces products **26a–d**. Similar reaction mechanisms were previously invoked

Scheme 4



for reactions of various 1-benzylbenzotriazoles with butyllithium.[34,35]

Enamines **26b–d** were separated pure from the reaction mixture, provided the entire workup was done under basic conditions. Attempted column chromatography led to decomposition of **26b–d.** Mild acidification of the solutions of products **26a–d** (diluted acetic acid) caused their rearrangement to the more stable imine isomers **27**. Enamine **26a** appeared to be the least stable undergoing rearrangement to **27a** even during basic workup. Acidic workup (pH 5.5) of the reaction mixtures obtained from reactions of **17a+18a-17d+18d** with sodium hydride led to the direct separation of the imines **27a–d** in good yields. The 3-phenyl derivative **27a** is very sensitive to oxygen, undergoing oxidation to the 3-hydroxy derivative **28**; approximately an equimolar mixture of **27a** and **28** was obtained in one run (reaction under nitrogen) and exclusively product **28** in another run (reaction in air). Dehydration of **28** catalyzed by *p*-toluenesulfonic acid gave compound **31** in good yield.

Treatment with lithium aluminum hydride converted compound **28** into 3-hydroxy-4-(phenylamino)-3-phenyl-

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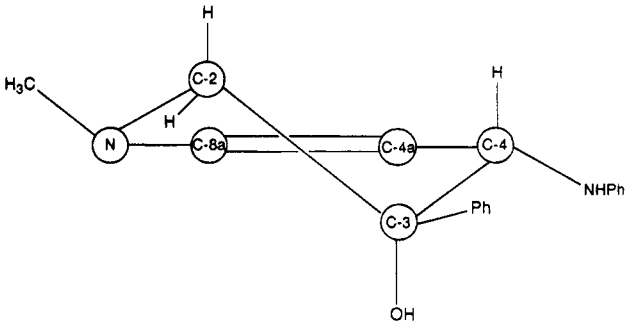


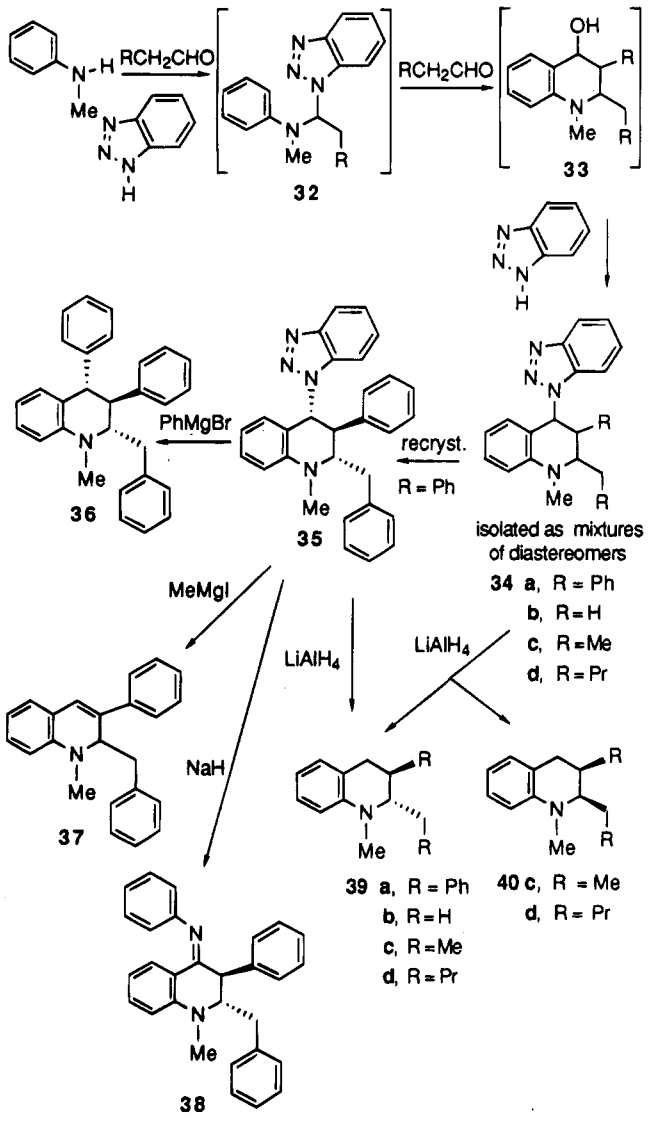
Figure 1.

1,2,3,4-tetrahydroquinoline (**29**). The reaction was stereoselective producing exclusively one diastereomer of the product. NOE experiments showed it to be the *cis* isomer; thus, irradiation of the H-4 doublet at δ 4.49 produced enhancement of the following resonances: 11.8% of the aniline *ortho* proton (δ 6.23), 10.0% of the tetrahydroquinoline H-5 (δ 7.16), 1.5% of the phenyl *ortho* proton (δ 7.54), and 1.2% of one of H-2 (δ 3.31). These results were confirmed by another NOE experiment in which the doublet of doublets originating from the *ortho* protons of the phenyl substituent at C-3 were irradiated giving a 2.5% enhancement of the H-4 doublet and a 7.4% enhancement of another H-2 proton doublet at δ 3.77 (Figure 1). Probably, the reaction mechanism consists of formation of a complex involving coordination of the aluminum atom by the oxygen and nitrogen atoms on one side of the molecule of **28**, followed by nucleophilic attack of another molecule of the aluminum hydride anion on the other side. Compounds **26** and **27** appeared to be inert to lithium aluminum hydride. The crude products **26a–d** on heating with hydrochloric acid in air produced dihydroquinolinones **30**.

Tetrahydroquinolines Substituted at C-2. So far, we have presented the formation of the saturated carbon linkage of the heterocyclic ring of 1,2,3,4-tetrahydroquinolines from two fragments: formaldehyde (C-2) and an aldehyde of type RCH_2CHO (C-3 and C-4). However, this method did not allow introduction of a substituent at C-2. 1-*H*-Benzotriazole-1-methanamines substituted at C-α (**32**) were needed. As previously reported,[28] compounds **32** derived from benzaldehyde and isobutyraldehyde were stable enough to be isolated and characterized, but attempts to condense *N*-methylaniline with normal aliphatic aldehydes and benzotriazole in equimolar amounts produced complex mixtures. We now find that increasing the molar ratio of aldehyde to *N*-methylaniline to 2:1 gave less complex mixtures, and in the case of phenylacetaldehyde, pure tetrahydroquinoline **35** (Scheme 5) was isolated (39%).

Three asymmetric carbon atoms in the molecule of **34a** make possible four stereoisomeric racemates: *trans-trans*, *trans-cis*, *cis-trans*, and *cis-cis*. Molecular models suggest *cis* orientations of the bulky vicinal substituents are less likely due to steric hindrance. The remote location of the H-4 resonance (δ 6.15) allowed application of the NOE methodology to assign the *trans-trans* molecular geometry to the most abundant stereoisomer **35**. Thus, irradiation of H-4 produced positive NOE effects for H-3 (4%), H-2 (3%), and three of the aromatic doublets at δ 6.52, 6.87, and 6.96. Enhancement of the H-2 resonances indicated location of the H-2 and H-4 protons on the same side of the heterocyclic ring. Two of the aromatic doublets belong to tetrahydroquinoline H-5 and

Scheme 5



benzotriazole H-7. The third doublet must originate from the *ortho* proton of the phenyl at C-3 indicating a *trans* orientation of the substituents on C-3 and C-4. Hence, the *trans-trans* geometry applies to the isolated stereoisomer **35**.

Reaction of **35** with phenylmagnesium bromide led to substitution of the benzotriazolyl moiety by a phenyl group giving tetrahydroquinoline **36**. Due to overlapping of the aromatic resonances, NOE experiments did not produce a clear picture for confident assignment of the molecular geometry, but a *trans-trans* configuration of the substituents in **36** seems to be most likely, in analogy to **35**. Unexpectedly, treatment of **35** with methylmagnesium iodide in refluxing toluene caused elimination of benzotriazole producing 1,2-dihydroquinoline **37**. Heating with sodium hydride caused conversion of the benzotriazole moiety in **35** to a phenylimino group giving product **38**. Treatment with lithium aluminum hydride smoothly converted **35** into the 1,2,3-trisubstituted tetrahydroquinoline **39a**.

In the case of the products from aliphatic aldehydes (R = H, Me, and Pr), the complex crude diastereomeric mixtures **34b–d** were each reduced. Only one product **39b** was obtained from reduction of the acetaldehyde derivative **34b**. Tetrahydroquinoline **39b** had been obtained previously[13] in 60% yield by reaction on *N*-methylquinolinium iodide with methylmagnesium iodide followed by hydrogenation of the obtained 1,2-dimethyl-1,2-dihydroquinoline. Reductions of **34c** and **34d** gave separable mixtures of **39c+40c** and **39d+40d**, respectively. *Trans* configurations for the predominant diastereomers **39c,d**, and *cis* for the minor diastereomers **40c,d**, were assigned on the basis of NOE experiments. Thus, irradiation of the H-3 proton of **39c** (δ 2.01) produced, on average, a 2% enhancement of the ethyl multiplets at δ 1.33 and δ 1.62; whereas no such enhancement was observed upon irradiation of H-3 in **40c** (δ 2.19).

Conclusions

Various 1-alkyl-4-(benzotriazol-1-yl)-1,2,3,4-tetrahydroquinolines have been easily prepared by condensations of one molecule of *N*-alkylaniline with two molecules of aldehyde and one molecule of benzotriazole. A stepwise procedure involving condensation of *N*-alkylaniline with formaldehyde and benzotriazole giving the 1-[(phenylamino)methyl]benzotriazole **1** followed by condensation of **1** with acetaldehyde yielded 1,4-disubstituted tetrahydroquinolines **11**. Use of higher aldehydes RCH_2CHO for condensation with **1** provides a simple method for the introduction of R substituents onto the C-3 of the 1,2,3,4-tetrahydroquinoline system. Direct condensation of the *N*-alkylanilines with two molecules of RCH_2CHO and one molecule of benzotriazole provides a convenient method for the synthesis of 1,2,3,4-tetrahydroquinolines bearing R substituents on C-3 and RCH_2 substituents on C-2. The synthetic potential of the 4-(benzotriazolyl)-1,2,3,4-tetrahydroquinolines thus obtained is demonstrated by substitution of the benzotriazole moiety with a hydrogen atom (lithium aluminum hydride), alkyl or aryl group (Grignard reagent), or an alkoxy group (sodium or potassium alkoxide). Additional possibilities are open by elimination of a molecule of nitrogen from the benzotriazole system of 4-(benzotriazol-1-yl)-1,2,3,4-tetrahydroquinoline upon treatment with sodium hydride, yielding appropriate 4-(phenylamino)-1,2-dihydroquinolines or 4-(phenylimino)-1,2,3,4-tetrahydroquinolines.

Experimental Section

General. Melting points were determined on a capillary melting point apparatus and are uncorrected. NMR spectra were recorded in $CDCl_3$ solution with tetramethylsilane as the internal standard for ^1H (300 MHz) and ^{13}C (75 MHz). Solvents for the Grignard reactions and reductions (diethyl ether, THF, dioxane, toluene) were dried by refluxing with sodium benzophenone ketyl under nitrogen and distilling immediately before use. Column chromatography was performed with silica gel (60–200 mesh).

4-[2-(2-Hydroxyethoxy)ethoxy]-1-methyl-1,2,3,4-tetrahydroquinoline (10a). A solution of **11a**[27] (2.64 g, 10 mmol) and KOH (0.56 g, 10 mmol) in diethylene glycol (5 mL) was heated under nitrogen at 160 °C for 3 h. After cooling, the reaction mixture was poured into water (50 mL) and extracted with diethyl ether (50 mL). The extract was washed with water (2 × 20 mL), dried over Na_2CO_3, and evaporated. The residue was subjected to column chromatography (ethyl acetate) to give **10a** (1.53 g, 61%) as a colorless oil: ^1H NMR δ 1.92 (m, 1 H), 2.14 (dq, J = 13.7 and 3.5 Hz, 1 H), 2.85 (bs, 1 H), 2.91 (s, 3 H), 3.12 (dtd, J = 11.4, 3.8 and 0.8 Hz , 1 H), 3.42 (td, J = 12.1, 3.3 Hz, 1 H), 3.56–3.60 (m, 2 H), 3.66 (m, 6 H), 4.38 (t, J = 3.5 Hz, 1 H), 6.63 (m, 2 H), 7.15 (m, 2 H); ^{13}C NMR δ 27.2, 38.8, 46.0, 61.7, 67.0, 70.5, 72.4, 73.6, 11.2, 115.3, 120.4, 129.5, 130.4, 146.2. Anal. Calcd for $C_{14}H_{21}NO_3$: C, 66.91; H, 8.42; N, 5.57. Found: C, 66.59; H, 8.51; N, 5.56.

4-(Decyloxy)-1-methyl-1,2,3,4-tetrahydroquinoline (10b). A mixture of **11a** (2.64 g, 10 mmol), decyl alcohol (19 mL, 100 mmol), and sodium hydride (0.26 g, 11 mmol) was heated under nitrogen at 185 °C for 16 h. After cooling, the mixture was dissolved in diethyl ether (50 mL), washed with 5% NaOH followed by water, and dried over Na_2CO_3. The ether was evaporated, and most of the unreacted decyl alcohol was distilled off under a reduced pressure of 1 Torr. The residue was subjected to column chromatography (toluene) to give analytically pure **10b** (2.40 g, 79%) as a colorless oil: ^{1}H NMR δ 0.89 (t, J = 6.6 Hz, 3 H), 1.27 (m, 14 H), 1.59 (m, 2 H), 1.92 (m, 1 H), 2.11 (dq, J = 13.4 and 3.6 Hz, 1 H), 2.92 (s, 3 H), 3.11 (dt, J = 11.2 and 4.3 Hz, 1 H), 3.41 (dt, J = 11.7 and 3.4 Hz, 1 H), 3.52 (m, 2 H), 4.31 (t, J = 3.8 Hz, 1 H), 6.63 (m, 2 H), 7.16 (m, 2 H); ^{13}C NMR δ 14.1, 22.7, 26.3, 27.3, 29.3, 29.5, 29.58, 29.63, 30.1, 31.9, 38.9, 46.3, 67.9, 73.1, 111.3, 115.6, 121.6, 129.2, 130.3, 146.3; HRMS calcd for $C_{20}H_{33}NO$ 303.256 [M$^+$], found 303.256.

4-(Cyclohexyloxy)-1-methyl-1,2,3,4-tetrahydroquinolines (10c). A procedure analogous to that for **10b** was used. A reaction of **11a** (2.64 g, 10 mmol), cyclohexanol (10.4 mL, 100 mmol), and sodium hydride (0.26 g, 11 mmol) gave **10c** (2.03 g, 83%) as a colorless oil: ^{1}H NMR δ 1.30 (m, 4 H), 1.54 (m, 2 H), 1.75 (m, 2 H), 1.94 (m, 4 H), 2.88 (s, 3 H), 3.09 (dt, J = 11.3 and 4.5 Hz, 1 h), 3.38 (td, J = 11.3 and 3.3 Hz, 1 H), 3.74 (m, 1 H), 4.46 (t, J = 3.9 Hz, 1 H), 6.63 (m, 2 H), 7.13 (m, 2 H); ^{13}C NMR δ 24.4, 24.5, 25.8, 28.2, 32.8, 33.7, 39.0, 46.5, 70.0, 74.7, 111.4, 115.9, 122.6, 128.9, 129.9, 146.4, HRMS calcd for $C_{16}H_{23}NO$ 245.178 [M$^+$], found 245.181.

1-Ethyl-4-methoxy-1,2,3,4-tetrahydroquinoline (10d). A solution of **1b**[27] (2.52 g, 10 mmol), acetaldehyde (0.6 mL, 11 mmol), and *p*-toluenesulfonic acid (20 mg) in methanol (20 mL) was stirred at 22 °C for 1 h and poured into ice–water (100 g). The mixture was extracted with chloroform (50 mL), washed with 5% Na_2CO_3, dried over Na_2CO_3, and evaporated. Column chromatography of the residue (chloroform) gave pure **10d** (0.95 g, 50%) as a colorless oil: ^{1}H NMR δ 1.13 (t, J = 7.1 Hz, 3 H), 1.85 (m, 1 H), 2.12 (dq, J = 13.5 and 3.6 Hz, 1 H), 3.10 (m, 1 H), 3.30 (m, 1 H), 3.57 (s, 3 H), 3.41 (m, 2 H), 4.17 (t, J = 3.3 Hz, 1 H), 6.58 (td, J = 7.2 and 1.0 Hz, 1 H), 6.64 (d, J = 8.3, 1 H), 7.13 (m, 2 H); ^{13}C NMR δ 10.8, 26.6, 42.9, 45.1, 55.1, 74.7, 110.8, 114.5, 120.2, 129.3, 130.8, 144.6. Anal. Calcd for $C_{12}H_{17}NO$: C, 75.35; H, 8.96; N, 7.32. Found: C, 75.01; H, 9.03; N, 7.45.

4-Ethoxy-1-ethyl-1,2,3,4-tetrahydroquinoline (10e). Reaction of **1b** with acetaldehyde in ethanol (according to the procedure for **10d**) gave **10e** (1.05 g, 51%) as a colorless oil: ^{1}H NMR δ 1.12 (t, J = 7.1 Hz, 3 H), 1.21 (t, J = 6.9 Hz, 3 H), 1.84 (m, 1H), 2.08 (dq, J = 13.3 and 3.6 Hz, 1 H), 3.10 (dt, J = 11.3 and 3.9 Hz, 1 H), 3.22–3.62 (m, 5 H), 4.29 (t, J = 3.4 Hz, 1 H), 6.58 (td, J = 7.3 and 1.0 Hz, 1 H), 6.63 (d, J = 8.2 Hz, 1 H), 7.12 (m, 2 H); ^{13}C NMR δ 11.0, 15.6, 27.2, 43.2, 45.2, 62.8, 73.0, 111.0, 114.7, 121.1, 129.2, 130.7, 144.7. Anal. Calcd for $C_{13}H_{19}NO$: C, 76.06; H, 9.33; N, 6.82. Found: C, 75.78; H, 9.42; N, 7.00.

4-(Benzotriazol-1-yl)-1-methyl-1,2,3,4-tetrahydroquinoline (11a) and Compound 12a. *p*-Toluenesulfonic acid monohydrate (40 mg, 0.2 mmol) was added to a solution of **1a** (2.38 g, 10 mmol) and acetaldehyde (0.6 mL, 11 mmol) in chloroform (30 mL), and the resulting solution was stirred at 22 °C for 15 min. Molecular sieves (4 Å, 50 g) were added, and the mixture was set aside at 22 °C for 30 min with occasional shaking. The solution was separated, and the molecular sieves were washed with chloroform (30 mL). The combined chloroform solutions were washed with 5% sodium carbonate (50 mL) followed by water (50 mL) and dried over sodium carbonate. The solvent was evaporated, and the residue was subjected to column chromatography (toluene) to give **12a** (0.05 g, 2%) as the first fraction as a colorless oil: ^{1}H NMR δ 2.64 (m, 1 H), 2.89 (s, 6 H), 3.11 (dd, J = 6.9 and 11.4 Hz, 2 H), 3.37 (dd, J = 5.1 and 11.4 Hz, 2 H), 4.00 (d, J = 4.5 Hz, 1 H), 6.64 (m, 4 H), 6.98 (d, J = 6.9 Hz, 2 H), 7.14 (m, 2 H); ^{13}C NMR δ 30.6 (2 C), 38.7, 39.4, 52.5 (2 C), 110.7 (2 C), 115.9 (2 C), 123.9 (2 C), 127.6 (2 C), 130.2 (2 C), 145.0 (2 C). **Picrate**, mp 159 °C. Anal. Calcd for $C_{24}H_{23}N_5O_7$: C, 58.42; H, 4.70; N, 14.19. Found: C, 58.01; H, 4.67; N, 14.32.

The second fraction gave **11a** (1.69 g, 64%): white solid, mp 124 °C, lit.[27] mp 125–126 °C.

4-(Benzotriazol-1-yl)-1-ethyl-1,2,3,4-tetrahydroquinoline (11b) and Compound 12b. Starting from **1b** and following the procedure given above, tetrahydroquinoline **11b** was obtained in 65% yield.[27] Additionally, minor amounts of product **12b** (0.44 g) were isolated in 15% yield as a colorless oil: ^{1}H NMR δ 1.43 (t, J = 7.0 Hz, 6 H), 2.85 (m, 1 H), 3.47 (dd, J = 7.2 and 11.5 Hz, 2 H), 3.56–3.74 (m, 6 H), 4.29 (d, J = 3.9 Hz, 2 H), 6.90 (t, J = 8.3 Hz, 1 H), 6.94 (d, J = 8.0 Hz, 2 H), 7.29 (d, J = 7.3 Hz, 2 H), 7.42 (t, J = 7.7 Hz, 2 H); ^{13}C NMR δ 10.9 (2 C), 29.9, 39.7, 45.0 (2 C), 49.4 (2 C), 110.4 (2 C), 115.2 (2 C), 123.4 (2 C), 127.5 (2 C), 130.6 (2 C), 143.3 (2 C). **Dipicrate**, mp 135–138 °C. Anal. Calcd for $C_{32}H_{30}N_8O_{14}$: C, 51.20; H, 4.03; N, 14.93. Found: C, 51.27; H, 4.08; N, 14.67.

4-(Benzotriazol-1-yl)-1,6-dimethyl-1,2,3,4-tetrahydroquinoline (11c) and Compound 12c. Following the procedure for **11a**, compound **11c**[27] was obtained in 76% yield. Minor amounts of product **12c** were isolated in 1% yield as white needles: mp 106–107 °C; ^{1}H NMR δ 2.22 (s, 6 H), 2.60 (m, 1 H), 2.84 (s, 6 H), 3.00 (dd, J = 7.3 and 11.3 Hz, 2 H), 3.27 (dd, J = 5.1 and 11.3 Hz, 2 H), 3.92 (d, J = 4.5 Hz, 1 H), 6.54 (d, J = 8.2 Hz, 2 H), 6.79 (s, 2 H), 6.93 (dd, J = 1.7 and 8.2 Hz, 2 H); ^{13}C NMR δ 20.5 (2 C), 31.3, 38.9 (2 C), 39.5, 52.9 (2 C), 111.0 (2 C), 124.4 (2 C), 125.2 (2 C), 127.9 (2 C), 130.8 (2 C), 143.1 (2 C). Anal. Calcd for $C_{20}H_{24}N_2$: C, 82.15; H, 8.27; N, 9.58. Found: C, 81.98; H, 8.23; N, 9.73.

1-Methyl-4-octyl-1,2,3,4-tetrahydroquinoline (13a). An ethereal solution of octylmagnesium bromide (10 mmol, 10 mL) was added to a toluene solution of **11a** (1.32 g, 5.0 mmol), and the resulting mixture was heated at reflux for 15 min. After cooling to room temperature, the mixture was poured into ice–water (50 g), neutralized with 20% acetic acid and extracted with diethyl ether (2 × 50 mL). The combined extracts were washed with water followed by 10% NaOH (50 mL) and again with water. The solution was dried over Na_2CO_3 and evaporated under reduced pressure. The residue was subjected to column chromatography (hexane/toluene, 9:1) to give pure **13a** (2.38 g, 92%) as a colorless oil: ^{1}H NMR δ 0.89 (m, 3 H), 1.20–1.55 (m, 13 H), 1.62 (m, 1 H), 1.80 (m, 1 H), 1.97 (m, 1 H), 2.70 (m, 1 H), 2.91 (s, 3 H), 3.12 (dt, J = 11.5 and 4.7 Hz, 1 H), 3.26 (td, J = 10.5 and 3.9 Hz, 1 H), 6.60 (m, 2 H), 6.99 (d, J = 7.5 Hz, 1 H), 7.07 (td, J = 7.7 and 1.7 Hz, 1 H); ^{13}C NMR δ 14.1, 22.7, 26.4, 27.1, 29.4, 29.7, 29.9, 32.0, 36.2, 36.6, 38.9, 47.6, 110.8, 115.9, 127.0, 127.2, 128.5, 146.0; HRMS calcd for $C_{18}H_{29}N$: 259.230 [M$^+$], found 259.231.

1-Ethyl-4-phenyl-1,2,3,4-tetrahydroquinoline (13b). An ethereal solution of phenylmagnesium bromide (30 mL, 60 mmol) was added to a solution of **11a** (5.66 g, 20 mmol) in toluene (100 mL). A part of the ether was distilled off to increase the temperature of the reaction mixture to 95 °C. Reflux at this temperature was continued under nitrogen for 3 h. Workup according to the procedure for **13a** and purification by column chromatography of the crude product (hexane) gave analytically pure **13b** (3.67 g, 77%) as a colorless oil: ^{1}H NMR δ 1.16 (t, J = 7.1 Hz, 3 H), 2.04 (m, 1 H), 2.20 (m, 1 H), 3.19 (m, 2 H), 3.39 (m, 2 H), 4.12 (t, J = 5.8 Hz, 1 H), 6.51 (td, J = 7.4 and 1.1 Hz, 1 H), 6.68 (d, J = 8.2 Hz, 1 H), 6.75 (d, J = 6.9 Hz, 1 H), 7.09–7.30 (m, 6 H); ^{13}C NMR δ 10.7, 30.6, 43.4, 45.1, 45.3, 110.7, 115.4, 124.2, 126.0, 127.5, 128.2 (2 C), 128.6 (2 C), 130.2, 145.1, 146.5. Anal. Calcd for $C_{17}H_{19}N$: C, 86.03; H, 8.07; N, 5.90. Found: C, 85.69; H, 8.07; N, 5.72.

1,4,6-Trimethyl-1,2,3,4-tetrahydroquinoline (13c). Starting from **11c** (0.56 g, 2 mmol) and an ethereal solution of methylmagnesium iodide (6 mmol, 3 mL), compound **13c** (0.28 g, 82%) was obtained, by a procedure similar to that of **13a**, as a colorless oil: ^{1}H NMR δ 1.26 (d, J = 7.0 Hz, 3 H), 1.66 (m, 1 H), 2.02 (m, 1 H), 2.22 (s, 3 H), 2.87 (m, 1 H), 2.85 (s, 3 H), 3.14 (m, 2 H), 6.53 (d, J = 8.7 Hz, 1 H), 6.87 (s, 1 H), 6.88 (d, J = 7.2 Hz, 1 H); ^{13}C NMR δ 20.6, 23.2, 30.5, 31.0, 39.6, 48.6, 111.6, 125.5, 127.7, 128.4, 128.9, 144.3. **Picrate**, mp 138–139 °C (from methanol). Anal. Calcd for $C_{18}H_{20}N_4O_7$: C, 53.46; H, 4.99; N, 13.86. Found: C, 53.50; H, 4.97; N, 13.93.

***cis*- (15) and *trans*- (16) 4-Methoxy-1-methyl-3-propyl-1,2,3,4-tetrahydroquinolines.** Reaction of **1a** (2.38 g, 10

mmol) with valeraldehyde (1.1 mL, 10 mmol) carried out in methanol (procedure analogous for preparation of **10d**, reaction time 15 min only) gave an oily product. Column chromatography (hexanes) of the oil gave **15** (0.42 g, 19%) as the first fraction as a colorless oil: ^{1}H NMR δ 0.94 (t, J = 7.0 Hz, 3 H), 1.30–1.60 (m, 4 H), 1.92 (m, 1 H), 2.90 (s, 3 H), 2.99 (dd, J = 4.9 and 11.0 Hz, 1 H), 3.23 (d, J = 11.5 Hz, 1 H), 3.29 (s, 3 H), 3.98 (d, J = 1.7 Hz, 1 H), 6.58 (m, 2 H), 7.03 (dd, J = 1.2 and 7.2 Hz, 1 H), 7.17 (td, J = 8.8 and 1.8 Hz, 1 H); ^{13}C NMR δ 14.3, 20.2, 31.2, 36.8, 38.4, 51.2, 55.8, 77.6, 110.7, 114.3, 120.4, 129.6, 130.4, 145.7. Anal. Calcd for $C_{14}H_{21}NO$: C, 76.67; H, 9.65; N, 6.39. Found: C, 76.36; H, 9.70; N, 6.45.

The second fraction from column chromatography gave **16** (0.95 g, 43%) as a colorless oil: ^{1}H NMR δ 0.87 (t, J = 7.2 Hz, 3 H), 1.14 (m, 2 H), 1.35 (m, 2 H), 2.02 (m, 1 H), 2.90 (s, 3 H), 2.92 (m, 1 H), 3.33 (s, 3 H), 3.48 (ddd, J = 2.0, 3.4 and 11.5 Hz, 1 H), 3.88 (bs, 1 H), 6.61 (m, 2 H), 7.14 (m, 2 H); ^{13}C NMR δ 14.1, 20.4, 31.4, 35.2, 38.8, 49.8, 55.1, 79.4, 110.8, 115.1, 118.7, 129.3, 131.4, 145.6. Anal. Calcd for $C_{14}H_{21}NO$: C, 76.67; H, 9.65; N, 6.39. Found: C, 76.31; H, 9.62; N, 6.47.

4-(Benzotriazol-1-yl)-3-phenyl-1,2,3,4-tetrahydroquinoline (17a). Reaction of **1a** (2.38 g, 10 mmol) with phenylacetaldehyde (1.20 g, 10 mmol) and purification according to the procedure given for **11a** (with chloroform as the eluent for column chromatography) afforded **17a** (2.85 g, 83%) as yellowish grains; mp 154 °C: ^{1}H NMR δ 3.00 (s, 3 H), 3.42 (dd, J = 4.0 and 11.9 Hz, 1 H), 3.71 (t, J = 11.5 Hz, 1 H), 3.99 (td, J = 10.6 and 3.8 Hz, 1 H), 6.43–6.53 (m, 3 H), 6.80 (d, J = 8.5 Hz, 1 H), 7.00 (m, 2 H), 7.10–7.35 (m, 7 H), 7.98 (m, 1 H); ^{13}C NMR δ 39.3, 44.4, 56.1, 63.0, 110.6, 112.0, 117.2, 119.4, 120.1, 123.5, 126.9, 127.1 (2 C), 127.5, 127.8, 128.7 (2 C), 129.4, 131.8, 138.9, 146.3, 146.5. Anal. Calcd for $C_{22}H_{20}N_4$: C, 77.62; H, 5.92; N, 16.46. Found: C, 77.59; H, 6.04; N, 16.35.

General Procedure for 17+18 (b–d). *p*-Toluenesulfonic acid monohydrate (0.02 g, 0.1 mmol) was added to a solution of **1a** (2.38 g, 10 mmol) and the appropriate aldehyde (10 mmol) in THF (20 mL). After an exothermic reaction, the mixture was set aside at 22 °C for 1 h, before the solvent was evaporated. Toluene (30 mL) was added to the residue and evaporated under reduced pressure to remove water from the reaction mixture. The obtained crude product (a mixture of **17** and **18**, 3:1) was used directly for further conversions.

Column chromatography (chloroform) enriched the samples to 90% of the more abundant *trans* isomer **17**, allowing its characterization by NMR.

17b: glassy material; ^{1}H NMR δ 0.94 (d, J = 6.7 Hz, 3 H), 2.81 (m, 1 H), 3.00 (s, 3 H), 3.20 (dd, J - 9.3 and 11.9 Hz, 1 H), 3.28 (dd, J = 4.4 and 11.9 Hz, 1 H), 5.96 (d, J = 9.6 Hz, 1 H), 6.51 (m, 2 H), 6.75 (d, J = 8.4 Hz, 1 H), 6.99 (d, J = 7.1 Hz, 1 H), 7.17–7.35 (m, 3 H), 8.07 (d, J = 7.0 Hz, 1 H); ^{13}C NMR δ 16.3, 33.2, 39.4, 56.3, 64.2, 111.1, 111.8, 117.2, 118.2, 120.1, 123.7, 126.9, 128.3, 129.4, 130.7, 131.7, 146.7. Anal. Calcd for $C_{17}H_{18}N_4$: C, 73.35; H, 6.52; N, 20.13. Found: C, 73.68; H, 6.64; N, 19.76.

17c: glassy material; ^{1}H NMR δ 0.78 (t, J = 7.2 Hz, 3 H), 1.14–1.44 (m, 4 H), 2.65 (m, 1 H), 2.99 (s, 3 H), 3.13 (m, 1 H), 3.31 (m, 1 H), 5.99 (d, J = 8.5 Hz, 1 H), 6.48–6.59 (m, 2 H), 6.75 (d, J = 8.3 Hz, 1 H), 6.98 (m, 1 H), 7.14–7.30 (m, 3 H), 8.05 (m, 1 H); ^{13}C NMR δ 13.8, 19.5, 32.6, 37.8, 39.3, 53.4, 62.5, 110.8, 111.6, 116.9, 117.8, 119.8, 123.5, 126.8, 128.7, 129.4, 131.8, 146.4, 146.7. Anal. Calcd for $C_{19}H_{22}N_4$: C, 74.48; H, 7.24; N, 18.28. Found: C, 74.79; H, 7.41; N, 18.09.

17d: glassy material; ^{1}H NMR δ 2.54 (dd, J = 9.1 and 13.5 Hz, 1 H), 2.70 (dd, J = 5.0 and 13.6 Hz, 1 H), 2.90 (m, 1 H), 2.92 (s, 3 H), 3.02 (dd, J = 7.4 and 12.0 Hz, 1 H), 3.18 (dd, J = 3.3 and 12.1 Hz, 1 H), 6.03 (d, J = 7.1 Hz, 1 H), 6.54 (t, J = 7.4 Hz, 1 H), 6.67 (d, J = 7.2 Hz, 1 H), 6.75 (d, J = 8.2 Hz, 1 H), 6.88 (d, J = 7.9 Hz, 1 H), 7.04 (d, J = 7.6 Hz, 2 H), 7.22 (m, 6 H), 8.04 (d, J = 8.1 Hz, 1 H); ^{13}C NMR δ 36.6, 39.1, 40.0, 52.0, 61.5, 110.6, 111.6, 117.0, 119.9, 123.6, 126.3, 126.9, 128.3 (2 C), 128.9 (2 C), 129.3, 129.7, 132.0, 138.3, 146.3, 146.6; HRMS calcd for $C_{23}H_{22}N_4$ 354.184 [M$^+$], found 354.184.

1-Methyl-3-phenyl-1,2,3,4-tetrahydroquinoline (20a). Lithium aluminum hydride (0.23 g, 6 mmol) was added to a solution of **17a** (1.02 g, 3 mmol) in anisole (10 mL), and the resulting mixture was refluxed under nitrogen for 30 min. After cooling, methanol (5 mL) was added dropwise. The reaction mixture was poured into ice cold NaOH (20%, 50 mL) and extracted with diethyl ether (2 × 50 mL). The combined extracts were washed with NaOH (10%, 50 mL) and dried over Na_2CO_3. The solvent was evaporated under reduced pressure (1 Torr). Column chromatography (hexane/toluene, 9:1) of the residue afforded **20a** (0.62 g, 92%) as a colorless oil: ^{1}H NMR δ 2.87 (s, 3 H), 2.96 (m, 3 H), 3.18 (m, 1 H), 3.27 (m, 2 H), 6.62 (m, 2 H), 6.97 (d, J = 7.8 Hz, 1 H), 7.10 (dd, J = 7.1 and 7.8 Hz, 1 H), 7.21 (m, 2 H), 7.29 (m, 2 H); ^{13}C NMR δ 35.3, 38.8, 38.9, 57.5, 110.8, 116.3, 122.5, 126.6, 127.1 (2 C), 127.2, 128.5 (2 C), 128.9, 143.6, 146.0. Anal. Calcd for $C_{16}H_{17}N$: C, 86.05; H, 7.67; N, 6.27. Found: C, 86.21; H, 7.76; N, 6.03.

1,3-Dimethyl-1,2,3,4-tetrahydroquinoline (20b). Reaction of **1a** (2.38 g, 10 mmol) with propionaldehyde (0.75 mL, 10 mmol), according to the procedure for **11a**, gave a mixture of **17b** and **18b** (and their benzotriazol-2-yl isomers). Reduction of the crude reaction mixture with lithium aluminum hydride, according to the procedure given for **20a**, afforded pure **20b** (1.55 g, 96%) as a colorless oil: ^{1}H NMR δ 1.01 (d, J = 6.6 Hz, 3 H), 2.09 (m, 1 H), 2.41 (dd, J = 10.6 and 15.9 Hz, 1 H), 2.75 (ddd, J = 1.9, 4.8 and 15.8 Hz, 1 H), 2.84 (s, 3 H), 2.84 (m, 1 H), 3.11 (ddd, J = 2.1, 3.9 and 11.0 Hz, 1 H), 6.57 (d, J = 8.1 Hz, 1 H), 6.59 (t, J = 7.5 Hz, 1 H), 6.92 (d, J = 7.3 Hz, 1 H), 7.06 (t, J = 8.2 Hz, 1 H); ^{13}C NMR δ 19.1, 27.3, 36.2, 38.9, 58.2, 110.6, 116.1, 122.3, 126.9, 128.8, 146.1. Anal. Calcd for $C_{11}H_{15}N$: C, 81.94; H, 9.38; N, 8.69. Found: C, 81.62; H, 9.34; N, 8.66.

1-Methyl-3-propyl-1,2,3,4-tetrahydroquinoline (20c). Reaction of **1a** (2.38 g, 10 mmol) with valeraldehyde (1.06 mL, 10 mmol) according to the procedure given for **11a** gave a mixture of **17c** and **18c** (and their benzotriazol-2-yl isomers). Reduction of the crude reaction mixture with lithium aluminum hydride according to the procedure given for **20a** afforded pure **20c** (1.28 g, 68%) as a colorless oil: ^{1}H NMR δ 0.93 (t, J = 7.2 Hz, 3 H), 1.30 (m, 2 H), 1.39 (m, 2 H), 1.96 (m, 1 H), 2.39 (dd, J = 10.4 and 15.9 Hz, 1 H), 2.80 (m, 1 H), 2.83 (s, 3 H), 2.83 (m, 1 H), 3.13 (ddd, J = 2.0, 4.1 and 11.0 Hz, 1 H), 6.54 (d, J = 8.2 Hz, 1 H), 6.58 (t, J = 7.3 Hz, 1 H), 6.92 (d, J = 7.1 Hz, 1 H), 7.04 (t, J = 7.3 Hz, 1 H); ^{13}C NMR δ 14.2, 19.9, 32.1, 34.3, 36.1, 38.9, 56.8, 110.6, 116.1, 122.3, 126.9, 128.8, 146.4. Anal. Calcd for $C_{13}H_{19}N$: C, 82.48; H, 10.12; N, 7.40. Found: C, 82.17; H, 10.10; N, 7.44.

1-Methyl-3-(phenylmethyl)-1,2,3,4-tetrahydroquinoline (20d). *p*-Toluenesulfonic acid monohydrate (0.04 g, 0.2 mmol) was added to a solution of **1a** (4.76 g, 20 mmol) and hydrocinnamaldehyde (2.68 g, 20 mmol) in THF (25 mL). After stirring for 30 min at 22 °C, toluene (50 mL) was added, and the solvent was evaporated under reduced pressure. The residue was dissolved in anisole (50 mL). Lithium aluminum hydride (0.76 g, 20 mmol) was added to the solution, and the resulting mixture was heated at reflux under nitrogen for 1 h. Workup was similar to that of **20a** to give pure **20d** (3.58 g, 75%), with no need for column chromatography, as a colorless oil: ^{1}H NMR δ 2.28 (m, 1 H), 2.50 (dd, J = 9.1 and 15.7 Hz, 1 H), 2.62 (d, J = 7.4 Hz, 2 H), 2.77 (m, 1 H), 2.81 (s, 3 H), 2.89 (dd, J = 8.6 Hz and 10.8 Hz, 1 H), 3.12 (ddd, J = 1.7, 3.6 and 11.0 Hz, 1 H), 6.58 (m, 2 H), 6.91 (d, J = 7.1 Hz, 1 H), 7.06 (t, J = 8.0 Hz, 1 H), 7.17 (m, 3 H), 7.28 (m, 2 H); ^{13}C NMR δ 34.0, 34.3, 39.0, 40.0, 55.8, 110.6, 116.2, 121.7, 126.0, 127.0, 128.3 (2 C), 129.0 (3 C), 140.1, 146.3. Anal. Calcd for $C_{17}H_{19}N$: C, 86.03; H, 8.07; N, 5.90. Found: C, 85.94; H, 8.18; N, 5.87.

***trans*-3,4-Diphenyl-1-methyl-1,2,3,4-tetrahydroquinoline (21a).** An ethereal solution of phenylmagnesium bromide (20 mL, 30 mmol) was added to a solution of a crude mixture of **17a+18a** (3.40 g, 10 mmol) in benzene (50 mL), and was stirred at reflux for 3 h. Workup and purification, analogous to **13a**, gave tetrahydroquinoline **21a** (2.85 g, 95%) as white needles (from hexane): mp 83 °C; ^{1}H NMR δ 2.97 (s, 3 H), 3.32 (m, 1 H), 3.34 (bd, J = 8.2 Hz, 1 H), 3.46 (dd, J = 11.3 and 11.1 Hz, 1 H), 4.25 (d, J = 9.1 Hz, 1 H), 6.57 (t, J = 7.4 Hz, 1 H), 6.69 (d, J = 7.5 Hz, 1 H), 6.73 (d, J = 8.3 Hz, 1 H), 6.99 (d, J = 7.7 Hz, 2 H), 7.05 (d, J = 7.7 Hz, 2 H), 7.14 (m, 7 H); ^{13}C NMR δ 39.5, 47.6, 51.0, 56.4, 111.2, 116.7, 126.1, 126.2, 126.5, 127.7, 127.8 (2 C), 128.1 (2 C), 128.3 (2 C), 129.2 (2 C),

130.4, 142.6, 145.0, 146.8. Anal. Calcd for $C_{22}H_{21}N$: C, 88.25; H, 7.07; N, 4.68. Found: C, 88.14; H, 7.15, N, 4.68.

***trans*- (21b) and *cis*- (22b) 1,4-Dimethyl-3-phenyl-1,2,3,4-tetrahydroquinolines.** Starting from a crude mixture of **17b+18b** (6.80 g, 20 mmol) and an ethereal solution of methylmagnesium iodide (20 mL, 40 mmol), and following the procedure given for **21a**, a mixture of **21b** and **22b** (2 :1), (3.75 g, 79%) was obtained as a fluorescent oily substance. Anal. Calcd for $C_{17}H_{19}N$: C, 86.03; H, 8.07; N, 5.90. Found: C, 85.70; H, 8.16; N, 5.84.

***trans*-1,3-Dimethyl-4-phenyl-1,2,3,4-tetrahydroquinoline (21c).** An ethereal solution of phenylmagnesium bromide (20 mL, 30 mmol) was added to a solution of **17b+18b** (2.78 g, 10 mmol) in toluene (50 mL). The obtained solution was stirred and heated at reflux for 1 h. Work-up and purification similar to that for **13a** gave pure tetrahydroquinoline **21c** (1.90 g, 80%) as an oil. The oil was crystallized from hexane to give white prisms: mp 84 °C; ^{1}H NMR δ 0.88 (d, J = 6.6 Hz, 3 H), 2.20 (m, 1 H), 2.89 (s, 3 H), 2.93 (dd, J = 8.4 and 11.2 Hz, 1 H), 3.15 (dd, J = 3.8 and 11.2 Hz, 1 H), 3.61 (d, J = 8.8 Hz, 1 H), 6.50 (td, J = 7.4 and 1.1 Hz, 1 H), 6.61 (m, 2 H), 7.09 (m, 3 H), 7.23 (m, 3 H); ^{13}C NMR δ 18.1, 34.9, 39.3, 51.7, 56.6, 110.7, 116.4, 125.3, 126.1, 127.2, 128.2 (2 C), 129.1 (2 C), 130.2, 145.7, 146.5. Anal. Calcd for $C_{17}H_{19}N$: C, 86.03; H, 8.07; N, 5.89. Found: C, 86.25; H, 8.12; N, 5.89.

1,3-Dimethyl-4-(phenylamino)-1,2-dihydroquinoline (26b). Sodium hydride (1.44 g, 60 mmol) was added to a solution of **17b+18b** (8.34 g, 30 mmol) in dioxane (50 mL). The resulting mixture was refluxed under nitrogen for 30 min, cooled, poured into ice-cold NaOH (20%, 100 g), and extracted with toluene (2 × 50 mL). The extracts were washed with NaOH (10%, 50 mL), dried over Na_2CO_3, and evaporated. The crude material was recrystallized from toluene to give pure **26b** (5.40 g, 72%) as orange needles: mp 112–113 °C; ^{1}H NMR δ 1.77 (s, 3 H), 2.82 (s, 3 H), 3.94 (s, 2 H), 4.88 (bs, 1 H), 6.54 (d, J = 8.8 Hz, 1 H), 6.61 (m, 3 H), 6.71 (td, J = 7.3 and 1.1 Hz, 1 H), 7.08 (m, 2 H), 7.15 (t, J = 7.4 Hz, 2 H); ^{13}C NMR δ 16.4, 37.5, 56.9, 110.1, 113.6 (2 C), 117.3, 117.9, 122.2, 122.9, 126.0, 128.3, 128.4, 129.2 (2 C), 146.2, 146.5. Anal. Calcd for $C_{17}H_{18}N_2$: C, 81.56; H, 7.25; N, 11.19. Found: C, 81.23; H, 7.36; N, 11.06.

1-Methyl-4-(phenylamino)-3-propyl-1,2-dihydroquinoline (26c). By a procedure analogous to that for **26b**, compound **26c** (4.18 g, 65%) was obtained from a mixture of **17c+18c** (6.12 g, 20 mmol) and sodium hydride (0.96 g, 40 mmol) as a complex with dioxane: yellow prisms, mp 95–97 °C; ^{1}H NMR δ 0.89 (t, J = 7.2 Hz, 6 H), 1.46 (sextet, J = 7.2 Hz, 4 H), 2.18 (t, J = 7.7 Hz, 4 H), 2.81 (s, 6 H), 3.69 (s, 8 H), 3.90 (s, 4 H), 4.89 (bs, 2 H), 6.59 (m, 8 H), 6.70 (t, J = 7.1 Hz, 2 H), 7.09 (m, 8 H); ^{13}C NMR δ 14.1 (2 C), 20.5 (2 C), 32.4 (2 C), 37.7 (2 C), 55.1 (2 C), 67.0 (4 C), 110.3 (2 C), 113.8 (4 C), 117.4 (2 C), 117.9 (2 C), 122.3 (2 C), 123.5 (2 C), 128.2 (2 C), 129.1 (4 C), 130.3 (4 C), 146.4 (2 C), 146.8 (2 C). Anal. Calcd for $C_{42}H_{52}N_4O_2$: C, 78.22; H, 8.13; N, 8.69. Found: C, 78.43; H, 7.98; N, 9.02.

1-Methyl-4-(phenylamino)-3-(phenylmethyl)-1,2-dihydroquinoline (26d). By a procedure analogous to **26b**, compound **26d** (2.45 g, 75%) was obtained from **17d+18d** (3.54 g, 10 mmol) and sodium hydride (0.72 g, 30 mmol) as an orange oil: ^{1}H NMR δ 2.72 (s, 3 H), 3.56 (s, 2 H), 3.86 (s, 2 H), 5.00 (s, 1 H), 6.50–6.75 (m, 3 H), 7.19 (m, 11 H); ^{13}C NMR δ 36.2, 37.5, 54.8, 110.3, 113.8 (2 C), 117.3, 118.1, 121.8, 123.7, 126.3, 128.3, 128.5 (4 C), 129.2 (2 C), 130.2, 138.4, 146.5 (2 C). Anal. Calcd for $C_{23}H_{22}N_2$: C, 84.63; H, 6.79; N, 8.58. Found: C, 84.44; H, 6.88; N, 8.27.

1-Methyl-3-phenyl-4-(phenylimino)-1,2,3,4-tetrahydroquinoline (27a). Sodium hydride (0.19 g, 8 mmol) was added to a solution of **17a+18a** (1.36 g, 4 mmol) in dioxane (5 mL), and the resulting mixture was heated at reflux under nitrogen for 4 h. After cooling, the reaction mixture was poured into ice–water (10 g), acidified with 20% acetic acid to pH 5.5, and extracted with toluene (2 × 10 mL). The combined extracts were washed with 2% acetic acid (10 mL), dried over sodium sulfate, and evaporated under reduced pressure. The residue was subjected to column chromatography (toluene) to give **27a** (0.35 g, 28%) as an orange oil: ^{1}H NMR δ 2.83 (s, 3 H), 3.26 (dd, J = 12.1 and 2.4 Hz, 1 H), 3.66 (dd, J = 12.1 and 3.7 Hz, 1 H), 3.94 (t, J = 2.6 Hz, 1 H), 6.54 (d, J = 8.3 Hz, 2 H), 6.68 (d, J = 8.5 Hz, 1 H), 6.84 (t, J = 7.1 Hz, 1 H), 6.98 (m, 3 H), 7.16–7.25 (m, 6 H), 8.28 (dd, J = 1.6 and 8.0 Hz, 1 H); ^{13}C NMR δ 39.4, 42.8, 57.4, 112.6, 117.4, 120.0, 120.6, 123.0, 126.7, 127.2, 127.7 (2 C), 128.3, 128.4 (2 C), 128.5 (2 C), 132.6, 140.3, 149.4, 150.7, 163,0; HRMS calcd for $C_{22}H_{20}N_2$: 313.171 [M$^+$], found 313.171.

The second fraction from column chromatography gave **28** (0.42 g, 32%).

1,3-Dimethyl-4-(phenylimino)-1,2,3,4-tetrahydroquinoline (27b). A solution of **26b** (0.50 g, 2 mmol) in toluene (10 mL) was shaken with 5% acetic acid (10 mL) for 15 min. The toluene phase was separated, washed with water (2 × 10 mL), dried over $MgSO_4$, and evaporated. The residue was recrystallized from toluene to give pure **27b** (0.44 g, 88%) as yellow needles: mp 117–118 °C; ^{1}H NMR δ 1.12 (d, J = 6.9 Hz, 3 H), 2.87 (m, 1 H), 2.95 (dd, J = 2.3 and 11.9 Hz, 1 H), 2.97 (s, 3 H), 3.45 (dd, J = 3.0 and 11.9 Hz, 1 H), 6.70 (d, J = 8.3 Hz, 1 H), 6.79 (m, 3 H), 7.05 (t, J = 7.4 Hz, 1 H), 7.33 (m, 3 H), 8.14 (dd, J = 7.4 Hz, 1 H); ^{13}C NMR δ 16.6, 31.4, 39.5, 57.1, 112.4, 117.2, 119.7 (2 C), 122.7, 127.5, 128.9 (2 C), 132.4, 146.3, 148.7, 151.4, 166.6. Anal. Calcd for $C_{17}H_{18}N_2$: C, 81.56; H, 7.25; N, 11.19. Found: C, 81.49; H, 7.30; N, 11.05.

1-Methyl-4-(phenylimino)-3-propyl-1,2,3,4-tetrahydroquinoline (27c). Sodium hydride (0.24 g, 10 mmol) was added to a solution of **17c+18c** (1.53 g, 5 mmol) in dioxane (20 mL), and the resulting mixture was heated under nitrogen at reflux for 30 min. After cooling, the mixture was poured into ice–water (50 g), acidified with 20% acetic acid to pH 5.5, and extracted with toluene (2 × 50 mL). The extracts were combined, washed with water (2 × 50 mL), dried with $MgSO_4$, and evaporated under reduced pressure. The residue was subjected to column chromatography (toluene) to give **27c** (1.01 g, 72%) as an orange oil: ^{1}H NMR δ 0.69 (t, J = 7.3 Hz, 3 H), 0.90 (m, 1 H), 1.05–1.45 (m, 2 H), 1.58 (m, 1 H), 2.80 (m, 1 H), 2.94 (s, 3 H), 3.13 (dd, J = 12.3 and 2.2 Hz, 1 H), 3.38 (dd, J = 12.1 and 2.8 Hz, 1 H), 6.67 (d, J = 8.5 Hz, 1 H), 6.78 (m, 3 H), 7.03 (t, J = 7.5 Hz, 1 H), 7.31 (m, 3 H), 8.12 (dd, J = 7.9 and 1.7 Hz, 1 H); ^{13}C NMR δ 13.7, 20.1, 31.5, 35.8, 39.4, 53.9, 112.2, 117.0, 119.6, 119.8 (2 C), 122.6, 127.3, 128.8 (2 C), 132.2, 148.7, 151.3, 166.5. Anal. Calcd for $C_{19}H_{22}N_2$: C, 81.97; H, 7.97; N, 10.06. Found: C, 81.74; H, 8.17; N, 10.04.

1-Methyl-4-(phenylimino)-3-(phenylmethyl)-1,2,3,4-tetrahydroquinoline (27d). Starting from a mixture of **17d+18d** (3.58 g, 10 mmol) and sodium hydride (0.60 g, 25 mmol), and applying a procedure analogous to that for **27c**, compound **27d** (1.85 g, 57%) was obtained as yellow prisms (diethyl ether), mp 124–126 °C: ^{1}H NMR δ 2.66–2.88 (m, 3 H), 2.90 (s, 3 H), 2.95 (m, 1 H), 3.19 (dd, J = 12.1 and 2.5 Hz, 1 H), 6.77 (m, 6 H), 7.08 (t, J = 7.3 Hz, 1 H), 7.16 (m, 3 H), 7.33 (m, 3 H), 8.20 (d, J = 7.7 Hz, 1 H); ^{13}C NMR δ 35.2, 38.9, 39.1, 52.4, 112.4, 117.3, 119.3, 119.6 (2 C), 122.8, 126.3, 127.4, 128.3 (2 C), 128.9 (2 C), 129.0 (2 C), 132.5, 139.0, 148.9, 151.2, 165.6. Anal. Calcd for $C_{23}H_{22}N_2$: C, 84.63; H, 6.79; N, 8.58. Found: C, 84.61; H, 6.93; N, 8.35.

3-Hydroxy-1-methyl-3-phenyl-4-(phenylimino)-1,2,3,4-tetrahydroquinoline (28). Sodium hydride (0.24 g, 10 mmol) was added to a solution of **17a** (2.00 g, 5.9 mmol) in dioxane (20 mL). The resulting mixture was stirred and heated at reflux under nitrogen for 3 h. After cooling, the reaction mixture was poured onto crushed ice (50 g) and extracted with chloroform (3 × 20 mL). The chloroform solution was washed with water, dried over Na_2CO_3, and evaporated under reduced pressure. The residue was triturated with toluene to give **28** (1.15 g, 62%) as yellow needles: mp 148–149 °C; ^{1}H NMR δ 3.00 (s, 3 H), 3.78 (d, J = 12.6 Hz, 1 H), 3.96 (d, J = 12.6 Hz, 1 H), 5.98 (d, J = 1.0 Hz, 1 H), 6.25 (t, J = 7.7 Hz, 1 H), 6.52 (d, J = 8.5 Hz, 1 H), 6.89 (d, J = 8.0 Hz, 1 H), 6.94 (d, J = 8.2 Hz, 2 H), 7.08 (m, 2 H), 7.20–7.35 (m, 5 H), 7.47 (d, J = 8.2 Hz, 2 H); ^{13}C NMR δ 38.9, 60.6, 70.2, 112.6, 113.0, 115.6, 119.9 (2 C), 123.6, 126.0 (2 C), 127.3, 128.2 (2 C), 129.4 (2 C), 130.0, 132.6, 141.8, 149.1, 149.9, 164.6. Anal. Calcd for $C_{22}H_{20}N_2O$: C, 80.46; H, 6.14; N, 8.53. Found: C, 80.58; H, 6.34; N, 8.47.

***cis*-3-Hydroxy-1-methyl-3-phenyl-4-(phenylamino)-**

1,2,3,4-tetrahydroquinoline (29). A solution of **28** (0.40 g, 1.2 mmol) and $LiAlH_4$ (0.08 g, 2 mmol) in THF (5 mL) was stirred at 22 °C for 30 min. The solution was poured into NaOH (10%, 10 mL) and extracted with diethyl ether (10 mL). The extract was washed with water, dried over Na_2CO_3, and evaporated. The crude product obtained was purified by column chromatography (toluene) to give **29** (0.30 g, 76%) as an orange glassy material: ^1H NMR δ 2.98 (s, 3 H), 3.16 (s, 1 H), 3.31 (d, J = 11.6 and 1.5 Hz, 1 H), 3.57 (d, J = 7.7 Hz, 1 H), 3.77 (d, J = 11.6 Hz, 1 H), 4.49 (d, J = 7.1 Hz, 1 H), 6.23 (d, J = 7.6 Hz, 2 H), 6.57 (t, J = 7.2 Hz, 1 H), 6.69 (td, J = 7.5 and 1.0 Hz, 1 H), 6.74 (d, J = 8.2 Hz, 1 H), 6.93 (t, J = 7.4 Hz, 2 H), 7.10–7.29 (m, 5 H), 7.54 (d, J = 8.0 Hz, 2 H); ^{13}C NMR δ 38.9, 58.0, 62.0, 72.1, 111.6, 113.1 (2 C), 117.7, 118.0, 123.8, 126.1 (2 C), 127.3, 128.0 (2 C), 128.76, 128.82 (2 C), 130.0, 142.0, 144.3, 147.6. Anal. Calcd for $C_{22}H_{22}N_2O$: C, 79.97; H, 6.71; N, 8.48. Found: C, 80.11, H, 6.84; N, 8.30.

1-Methyl-3-phenyl-2,3-dihydro-4-quinolinone (30a). A solution of **27a** (1.00 g, 3.0 mmol) in 36% HCl (10 mL) was heated at reflux for 10 min and poured into ice-water (50 g). The mixture was extracted with chloroform (2 × 30 mL). The extract was washed with water (50 mL), dried over Na_2CO_3, and evaporated. Column chromatography of the residue (chloroform) and recrystallization of the main fraction from toluene gave **30a** (0.56 g, 78%) as yellow needles: mp 107 °C; ^1H NMR δ 3.02 (s, 3 H), 3.60–3.73 (m, 2 H), 3.88 (dd, J = 6.3 and 9.4 Hz, 1 H), 6.76 (m, 2 H), 7.26 (m, 5 H), 7.43 (m, 1 H), 7.98 (d, J = 7.9 Hz, 1 H); ^{13}C NMR δ 39.0, 52.6, 57.3, 113.0, 117.0, 119.7, 127.2, 128.4 (2 C), 128.5 (3 C), 135.3, 137.1, 152.1, 193.4. Anal. Calcd for $C_{16}H_{15}NO$: C, 80.98; H, 6.37; N, 5.90. Found: C, 80.93; H, 6.40; N, 5.91.

1,3-Dimethyl-2,3-dihydro-4-quinolinone (30b). Hydrolysis of crude **26b** obtained from **17b+18b** (2.78 g, 10 mmol) with 36% HCl, according to the procedure given for **30a**, afforded **30b** (1.36 g, 78%) as a yellow oil: ^1H NMR δ 1.22 (d, J = 6.9 Hz, 3 H), 2.74 (m, 1 H), 3.00 (s, 3 H), 3.20 (t, J = 11.9 Hz, 1 H), 3.42 (dd, J = 5.5 and 12.0 Hz, 1 H), 6.70–6.78 (m, 2 H), 7.40 (ddd, J = 1.7, 7.1 and 8.7 Hz, 1 H), 7.92 (dd, J = 1.9 and 8.0 Hz, 1 H); ^{13}C NMR δ 12.4, 39.2, 41.1, 58.0, 113.0, 116.9, 119.2, 128.2, 135.1, 152.3, 196.3. Anal. Calcd for $C_{11}H_{13}NO$: C, 75.40; H, 7.48; N, 7.99. Found: C, 75.69; H, 7.56; N, 7.99.

1-Methyl-3-propyl-2,3-dihydro-4-quinoline (30c). A solution of **26c** (2.34 g, 8 mmol) in 35% HCl (5 mL) was heated at reflux under nitrogen for 30 min. After cooling, the reaction mixture was poured onto crushed ice (20 g), neutralized with 10% NaOH, and extracted with diethyl ether (2 × 20 mL). The extract was dried over Na_2CO_3 and evaporated. The residue was recrystallized from hexane/diethyl ether (1:1) to give pure **30c** (1.85 g, 91%) as yellow prisms: mp 62 °C; ^1H NMR δ 0.95 (t, J = 7.2 Hz, 3 H), 1.43 (m, 3 H), 1.86 (m, 1 H), 2.57 (m, 1 H), 3.00 (s, 3 H), 3.23 (dd, J = 12.1 and 9.2 Hz, 1 H), 3.49 (dd, J = 12.1 and 4.9 Hz, 1 H), 6.70 (d, J = 9.0 Hz, 1 H), 6.74 (td, J = 7.9 and 0.9 Hz, 1 H), 7.39 (ddd, J = 1.8, 7.1 and 8.7 Hz, 1 H), 7.92 (dd, J = 1.8 and 7.9 Hz, 1 H); ^{13}C NMR δ 14.1, 20.3, 29.5, 39.3, 46.1, 55.7, 112.9, 117.0, 119.5, 128.3, 135.1, 152.1, 196.2. Anal. Calcd for $C_{13}H_{17}NO$: C, 76.81; H, 8.43; N, 6.89. Found: C, 77.18; H, 8.65; N, 6.86.

1-Methyl-3-(phenylmethyl)-2,3-dihydro-4-quinolinone (30d). Reaction of **17d+18d** (3.54 g, 10 mmol) with sodium hydride (0.48 g, 20 mmol) in refluxing dioxane (30 mL) for 60 min and workup according to the procedure for **26b**, afforded crude **26d**. Hydrolysis of the obtained material with 36% HCl according to the procedure for **30a**, afforded **30d** (1.56 g, 62%) as a yellow oil: ^1H NMR δ 2.64 (dd, J = 10.7 and 13.7 Hz, 1 H), 2.82 (m, 1 H), 2.92 (s, 3 H), 3.09 (dd, J = 8.9 and 12.3 Hz, 1 H), 3.29 (m, 2 H), 6.71 (d, J = 8.5 Hz, 1 H), 6.77 (t, J = 7.0 Hz, 1 H), 7.23 (m, 4 H), 7.31 (d, J = 7.6 Hz, 1 H), 7.33 (m, 1 H), 7.41 (ddd, J = 1.8, 7.1 and 8.8 Hz, 1 H); ^{13}C NMR δ 33.5, 39.1, 48.2, 54.4, 113.0, 117.1, 119.1, 126.4, 128.6 (3 C), 129.1 (2 C), 135.3, 139.2, 152.2, 195.2. Anal. Calcd for $C_{17}H_{17}NO$: C, 81.24; H, 6.82; N, 5.57. Found: C, 81.21; H, 6.81; N, 5.51.

1-Methyl-3-phenyl-4-(phenylimino)-1,4-dihydroquinoline (31). A solution of **28** (0.99 g, 3 mmol) and p-toluenesulfonic acid monohydrate (0.01 g) in toluene (10 mL) was heated at reflux using a Dean–Stark trap for 1 h. The solution was concentrated to 5 mL and stored at 0 °C. The resulting crystals were separated and dried to give analytically pure **31** (0.80 g, 86%) as yellow needles: mp 179 °C; ^1H NMR δ 3.57 (s, 3 H), 6.50 (m, 3 H), 6.88 (m, 3 H), 6.92 (m, 5 H), 7.19 (t, J = 8.2 Hz, 1 H), 7.24 (m, 1 H), 7.48 (t, J = 7.1 Hz, 1 H), 8.65 (bs, 1 H); ^{13}C NMR δ 39.5, 114.0, 117.5, 120.2 (2 C), 120.5, 123.1, 125.6, 126.4, 127.4 (2 C), 127.8 (3 C), 128.9 (2 C), 130.3, 138.2, 139.3, 141.9, 150.9, 152.0. Anal. Calcd for $C_{22}H_{18}N_2$: C, 85.13; H, 5.85; N, 9.02. Found: C, 85.04; H, 5.92; N, 8.87.

Tetrahydroquinolines 34. General Procedure. Molecular sieves (10 g) were added to a solution of N-methylaniline (1.07 g, 10 mmol), an aldehyde (20 mmol), and p-toluenesulfonic acid monohydrate (0.02 g, 0.1 mmol) in THF (30 mL). The resulting mixture was occasionally shaken for 1 h. The solution was separated, and the molecular sieves were washed with THF (2 × 10 mL). The combined THF solutions were evaporated under reduced pressure. The resulting crude product was directly used for further reactions.

4-(Benzotriazol-1-yl)-1-methyl-3-phenyl-2-(phenylmethyl)-1,2,3,4-tetrahydroquinoline (35). Molecular sieves (5A, 50 g) were added to a solution of **1a** (5.35 g, 50 mmol), phenylacetaldehyde (12.02 g, 100 mmol), benzotriazole (5.96 g, 50 mmol), and p-toluenesulfonic acid monohydrate (200 mg, 1 mmol) in diethyl ether (200 mL), and the resulting mixture was gently shaken for 1 h. The solution was filtered, and the sieves were washed with diethyl ether (2 × 50 mL). The combined filtrate and washings were washed with Na_2CO_3 (10%, 100 mL), followed by water (100 mL), and dried over Na_2CO_3. Evaporation of the solvent gave mixture **34** which upon trituration with diethyl ether afforded pure isomer **35** (8.40 g, 39%) as fine yellowish needles: mp 194–195 °C; ^1H NMR δ 2.67 (dd, J = 7.4 and 14.0 Hz, 1 H), 2.84 (dd, J = 5.2 and 14.3 Hz, 1 H), 3.10 (s, 3 H), 3.80 (m, 1 H), 3.92 (m, 1 H), 6.15 (d, J = 7.4 Hz, 1 H), 6.52 (d, J = 7.5 Hz, 1 H), 6.66 (t, J = 7.4 Hz, 1 H), 6.79 (m, 2 H), 6.87 (m, 2 H), 6.96 (m, 2 H), 7.07–7.18 (m, 5 H), 7.25–7.37 (m, 3 H), 8.03 (m, 1 H); ^{13}C NMR δ 37.5, 38.1, 49.8, 61.8, 65.8, 110.4, 112.7, 117.3, 119.6, 120.0, 123.6, 126.2, 126.96, 127.0, 127.39, 127.44 (2 C), 128.2 (2 C), 128.5 (2 C), 129.2 (2 C), 129.6, 132.8, 137.7, 141.3, 145.8, 146.0. Anal. Calcd for $C_{29}H_{26}N_4$: C, 80.90; H, 6.09; N, 13.01. Found: C, 81.27; H, 6.17; N, 12.97.

3,4-Diphenyl-1-methyl-2-(phenylmethyl)-1,2,3,4-tetrahydroquinoline (36). Starting from **35** (4.30 g, 10 mmol) and phenylmagnesium bromide (15 mL, 30 mmol), and following the procedure given above for **13a** (except the reaction time extended to 1 h), crude product **36** was obtained. Column chromatography (hexane–ether, 9:1) afforded analytically pure **36** (3.52 g, 90%) as yellowish prisms (from hexane): mp 112–113 °C; ^1H NMR δ 2.59 (dd, J = 8.3 and 13.9 Hz, 1 H), 2.78 (dd, J = 5.2 and 13.9 Hz, 1 H), 2.97 (s, 3 H), 3.24 (dd, J = 4.3 and 5.7 Hz, 1 H), 3.68 (dt, J = 7.9 and 4.8 Hz, 1 H), 4.21 (d, J = 5.6 Hz, 1 H), 6.63–6.79 (m, 4 H), 6.93 (m, 2 H), 7.05–7.25 (m, 13 H); ^{13}C NMR δ 37.9, 38.3, 48.3, 50.6, 67.4, 111.7, 116.6, 124.7, 125.9, 126.1 (2 C), 127.6, 127.7 (2 C), 128.15 (2 C), 128.22 (4 C), 129.3 (2 C), 129.5 (2 C), 129.7, 138.9, 144.8, 145.7, 146.1. Anal. Calcd for $C_{29}H_{27}N$: C, 89.42; H, 6.99; N, 3.60. Found: C, 89.78; H, 7.13; N, 3.57.

1-Methyl-3-phenyl-2-(phenylmethyl)-1,2-dihydroquinoline (37). To a toluene solution of **35** (4.30 g, 10 mmol) was added MeMgI (ethereal solution, 15 mL, 30 mmol), and the diethyl ether was distilled off. The reaction mixture was then refluxed for 2 h under nitrogen. After cooling, it was poured into ice–water (50 mL) and extracted with diethyl ether (50 mL). The extract was washed with 10% Na_2CO_3 and dried over anhydrous Na_2CO_3, and the solvents evaporated under reduced pressure to give a crude oily product, which after trituration with a mixture of hexane/ether (2:1) and cooling at 0 °C gave **37** (2.76 g, 89%) as yellow grains: mp 97–98 °C; ^1H NMR δ 2.70 (s, 3 H), 2.76 (dd, J = 4.2 and 13.9 Hz, 1 H), 2.86 (dd, J = 8.3 and 13.7 Hz, 1 H), 4.70 (dd, J = 4.2 and 8.1 Hz, 1 H), 6.49 (d, J = 8.0 Hz, 1 H), 6.81 (t, J = 7.4 Hz, 1 H), 6.83 (s, 1 H), 7.05–7.20 (m, 8 H), 7.24 (t, J = 7.4 Hz, 1 H), 7.36 (t, J = 7.5 Hz, 1 H), 7.54 (d, J = 8.3 Hz, 2 H); ^{13}C NMR δ 38.9, 39.1, 64.5, 111.4, 116.6, 122.05, 122.10, 125.3 (2 C), 126.1, 127.2, 127.3, 128.1 (2 C), 128.6 (2 C), 129.0, 129.5 (2

C), 134.2, 138.4, 139.1, 143.6. Anal. Calcd for $C_{23}H_{21}N$: C, 88.71; H, 6.80; N, 4.50. Found: 89.04; H, 6.94; N, 4.30.

1-Methyl-3-phenyl-4-(phenylimino)-2-(phenylmethyl)-1,2,3,4-tetrahydroquinoline (38). Starting from **35** (3.00 g, 7.0 mmol) and sodium hydride (0.34 g, 10 mmol), and following a procedure analogous to that given above for **27**, compound **38** (1.60 g, 57%) was obtained as yellow needles (from diethyl ether): mp 138 °C; ^{1}H NMR δ 2.61 (s, 3 H), 2.70 (dd, J = 7.9 and 13.4 Hz, 1 H), 3.04 (dd, J = 6.9 and 13.3 Hz, 1 H), 3.52 (td, J = 7.2 and 1.7 Hz, 1 H), 3.75 (d, J = 1.4 Hz, 1 H), 6.54 (d, J = 7.3 Hz, 2 H), 6.87 (m, 2 H), 6.95 (t, J = 7.3 Hz, 1 H), 7.12 (m, 12 H), 7.38 (m, 1 H), 8.30 (dd, J = 1.6 and 7.9 Hz, 1 H); ^{13}C NMR δ 37.0, 39.0, 45.8, 69.6, 112.2, 116.6, 120.3 (2 C), 123.1, 126.4, 126.6, 127.1, 127.6 (2 C), 128.3 (2 C), 128.4 (2 C), 128.5 (2 C), 129.2 (2 C), 133.0 (2 C), 138.2, 140.9, 146.5, 150.4, 161.8. Anal. Calcd for $C_{29}H_{26}N_2$: C, 86.53; H, 6.51; N, 6.96. Found: C, 86.82; H, 6.58; N, 6.98.

1-Methyl-3-phenyl-2-(phenylmethyl)-1,2,3,4-tetrahydroquinoline (39a). A solution of **35** (4.30 g, 10 mmol) and $LiAlH_4$ (0.68 g, 20 mmol) in anisole (30 mL) was heated at reflux under nitrogen for 1 h. Workup as for **20a** gave analytically pure **39a** (2.35 g, 78%) as white prisms (from diethyl ether): mp 103 °C; ^{1}H NMR δ 2.68 (dd, J = 8.4 and 13.5 Hz, 1 H), 2.76 (s, 3 H), 2.86 (d, J = 16.2 Hz, 1 H), 3.02 (m, 2 H), 3.35 (dd, J = 6.9 and 17.0 Hz, 1 H), 3.51 (m, 1 H), 6.53 (d, J = 7.8 Hz, 1 H), 6.66 (t, J = 7.2 Hz, 1 H), 6.96 (m, 2 H), 7.04–7.31 (m, 10 H); ^{13}C NMR δ 28.7, 38.3, 38.7, 38.8, 66.8, 110.7, 116.0, 120.2, 126.0, 126.3, 127.2, 127.4 (2 C), 128.1 (2 C), 128.6 (2 C), 129.0, 129.2 (2 C), 139.2, 144.9, 145.5. Anal. Calcd for $C_{23}H_{23}N$: C, 88.14; H, 7.40; N, 4.47. Found: C, 88.02; H, 7.48; N, 4.45.

1,2-Dimethyl-1,2,3,4-tetrahydroquinoline (39b). Starting from **34b** (2.78 g, 10 mmol) and $LiAlH_4$ (0.68 g, 20 mmol), and following the procedure for **39a**, crude product **39b** was obtained. Column chromatography of the crude material (hexane) gave analytically pure **39b** (1.42 g, 88%) as a colorless oil: ^{1}H NMR δ 1.10 (d, J = 6.4 Hz, 3 H), 1.64–1.77 (m, 2 H), 1.96 (tt, J = 12.1 and 5.0 Hz, 1 H), 2.65 (dt, J = 16.0 and 4.8 Hz, 1 H), 2.79 (dd, J = 5.4 and 11.9 Hz, 1 H), 2.86 (s, 3 H), 6.52 (d, J = 8.2 Hz, 1 H), 6.57 (t, J = 7.1 Hz, 1 H), 6.94 (d, J = 7.1 Hz, 1 H), 7.06 (t, J = 8.2 Hz, 1 H); ^{13}C NMR δ 17.6, 23.8, 28.1, 36.9, 53.8, 110.6, 115.4, 122.0, 127.1, 128.5, 145.4. Anal. Calcd for $C_{11}H_{15}N$: C, 81.94; H, 9.38; N, 8.69. Found: 82.22; H, 9.42; N, 8.60.

1,3-Dimethyl-2-ethyl-1,2,3,4-tetrahydroquinolines (39c and 40c). Starting from **34c** (3.06 g, 10 mmol) and $LiAlH_4$ (0.68 g, 20 mmol), and following the procedure for **39a**, a mixture of **39c** and **40c** was obtained. Column chromatography (hexane) gave **39c** (0.85 g, 45%) as the first fraction as a colorless oil: ^{1}H NMR δ 0.88 (t, J = 7.4 Hz, 3 H), 0.92 (d, J = 6.9 Hz, 3 H), 1.33 (m, 1 H), 1.62 (m, 1 H), 2.01 (m, 1 H), 2.33 (d, J = 16.0 Hz, 1 H), 2.76 (m, 1 H), 2.91 (dd, J = 5.5 and 16.1 Hz, 1 H), 2.99 (s, 3 H), 6.48 (d, J = 8.2 Hz, 1 H), 6.56 (td, J = 7.3 and 1.0 Hz, 1 H), 6.94 (d, J = 6.9 Hz, 1H), 7.07 (t, J = 7.3 Hz, 1 H); ^{13}C NMR δ 10.5, 19.5, 25.6, 27.1, 30.3, 38.7, 66.9, 109.8, 115.1, 119.7, 126.9, 129.4, 144.3. Anal. Calcd for $C_{13}H_{19}N$: C, 82.48; H, 10.12; N, 7.40. Found: C, 82.07, H, 10.07, N, 7.32.

The second fraction from column chromatography gave **40c** (0.66 g, 35%) as a colorless oil: ^{1}H NMR δ 1.00 (t, J = 7.5 Hz, 3 H), 1.05 (d, J = 6.9 Hz, 3 H), 1.28–1.61 (m, 2 H), 2.19 (m, 1 H), 2.58 (dd, J = 12.6 and 16.5 Hz, 1 H), 2.66 (dd, J = 6.0 and 16.5 Hz, 1 H), 3.02 (m, 1 H), 3.05 (s, 3 H), 6.55 (d, J = 8.4 Hz, 1 H), 6.60 (td, J = 7.5 and 1.2 Hz, 1 H), 6.98 (d, J = 7.2 Hz, 1 H), 7.11 (t, J = 7.2 Hz, 1 H); ^{13}C NMR δ 12.8, 18.6, 21.3, 30.7, 32.2, 40.4, 66.2, 110.8, 115.1, 121.5, 126.9, 128.7, 144.6. Anal. Calcd for $C_{13}H_{19}N$: C, 82.48; H, 10.12; N, 7.40. Found: C, 82.08; H, 10.06; N, 7.40.

2-Butyl-1-methyl-3-propyl-1,2,3,4-tetrahydroquinolines (39d and 40d). Starting from **34d** (3.62 g, 10 mmol) and $LiAlH_4$ (0.68 g, 20 mmol), and following the procedure for **39a**, gave crude mixture of **39d** and **40d**. The mixture was separated by column chromatography (hexane), and the first fraction gave **39d** (1.35 g, 55%) as a colorless oil: ^{1}H NMR δ 0.87 (m, 6 H), 1.17–1.39 (m, 10 H), 1.58 (m, 1 H), 1.82 (m, 1 H), 2.43 (d, J = 16.5 Hz, 1 H), 2.92 (dd, J = 5.7 and 15.0 Hz, 1 H), 2.94 (s, 3 H), 6.47 (d, J = 8.1 Hz, 1 H), 6.56 (td, J = 7.5 and 1.0 Hz, 1 H), 6.95 (d, J = 7.5 Hz, 1 H), 7.07 (t, J = 7.2 Hz, 1 H); ^{13}C NMR δ 14.1, 14.2, 20.5, 22.9, 28.3, 28.5, 32.4, 32.6, 35.1, 38.6, 63.6, 109.7, 115.0, 119.6, 126.9, 129.4, 144.5. Anal. Calcd for $C_{17}H_{27}N$: C, 83.20; H, 11.09; N, 5.71. Found: C, 82.90; H, 11.31; N, 5.68.

The second fraction from chromatography was identified as **40d** (0.82 g, 33%) as a colorless oil: ^{1}H NMR δ 0.89 (t, J = 7.2 Hz, 3 H), 0.95 (t, J = 6.9 Hz, 3 H), 1.24–1.52 (m, 10 H), 2.00 (m, 1 H), 2.52 (dd, J = 12.6 and 16.5 Hz, 1 H), 2.69 (dd, J = 5.4 and 16.5 Hz, 1 H), 3.02 (s, 3 H), 3.11 (m, 1 H), 6.52 (d, J = 8.1 Hz, 1 H), 6.59 (td, J = 8.4 and 1.0 Hz, 1 H), 6.97 (d, J = 7.5 Hz, 1 H), 7.09 (t, J = 7.5 Hz, 1 H); ^{13}C NMR δ 14.2, 14.3, 20.5, 23.2, 28.5, 30.5, 30.7, 35.7, 35.8, 40.5, 63.4, 110.9, 115.1, 121.5, 126.9, 128.9, 144.7. Anal. Calcd for $C_{17}H_{27}N$: C, 83.20; H, 11.09; N, 5.71. Found: C, 83.00; H, 11.40; N, 5.73.

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