Reactions of *N*-Alkyl-*N*-phenyl-1*H*-benzotriazole-1-methanamines with α,β-Unsaturated Ethers. A Novel Route to 1,4- and 1,3-Disubstituted 1,2,3,4-Tetrahydroquinolines

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N-Alkyl-*N*-aryl-1*H*-benzotriazole-1-methanamines **3**, easily accessible from the condensation of anilines with formaldehyde and benzotriazole, undergo acid-catalyzed reactions with ethyl vinyl ether to give 1-alkyl-4-(benzotriazol-1-yl)-1,2,3,4-tetrahydroquinolines **10** and their benzotriazol-2-yl isomers **11**. The reaction mechanism involves formation of 1-alkyl-4-ethoxy-1,2,3,4-tetrahydroquinolines **8** as isolable intermediates, followed by substitution of the ethoxy group in **8** with benzotriazole to produce **10** and **11**. Treatment with Grignard reagents in toluene converts compounds **10** and **11** in good yield to 4-alkyl- or 4-aryltetrahydroquinolines **12**. 2,3-Dihydrofuran and 3,4-dihydro-2*H*-pyran undergo similar reaction sequences giving tetrahydroquinolines additionally substituted by 3-(β-hydroxyethyl) and 3-(γ-hydroxypropyl) groups, respectively. The stereochemistry of 1,3,4-trisubstituted 1,2,3,4-tetrahydroquinolines is assigned on the basis of NOE methodology. An unusual reduction of the benzotriazolyl moiety to a phenylamino group is observed in the case of product **43** obtained from the reaction of 10-(benzotriazol-1-ylmethyl)-4*H*-phenothiazine with ethyl vinyl ether.

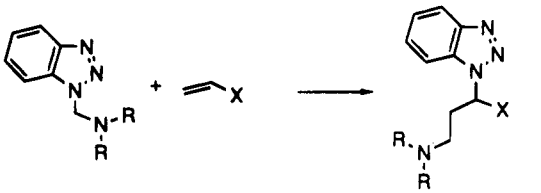
Introduction

In preceeding reports[1,2] we have described additions of 1-[(dialkylamino)methyl]benzotriazoles (**1**) to electron rich vinyl groups of (i) ethyl vinyl ether (producing **2a**), (ii) *N*-vinylamides (**2b**), and (iii) 9-vinylcarbazole (**2c**) (Scheme 1). Treatment of adducts **2** with lithium aluminum hydride or Grignard reagents effected replacement of the benzotriazol-1-yl moiety by a hydrogen atom or by an alkyl (or aryl) group leading to new and versatile synthetic methods for 1,3-amino ethers[1] and 1,3-diamines.[2] In our preliminary communication,[3] we reported that for compounds of type **1** derived from anilines (one of the R substituents is aromatic), the initially formed adducts **2a** react further to give 1,4-disubstituted tetrahydroquinolines. We now report details of this work and the exploitation of these new cyclocondensations.

Results and Discussion

Ethyl Vinyl Ether. *N*-Alkyl-*N*-aryl-1*H*-benzotriazole-1-methanamines **3**[4] undergo reversible equilibration with the benzotriazol-2-yl derivatives **5**. The isomerization has been shown[5a] to proceed via the ion pairs **4** and is slow at room temperature, but rapid upon heating. The rate is also extremely sensitive to pH; even small quantities of acid cause dramatic rate increases.[5b] The acidic catalysis can be explained by protonation of **3** allowing expulsion of benzotriazole rather than of the alternative benzotriazolide anion (Scheme 2).

Scheme 1



1, R = alkyl

2a, X = OEt
2b, X = NR^1COR^2
2c, X = carbazol-9-yl

N-Methylaniline derivative **3a** and ethyl vinyl ether reacted under acidic catalysis to give 4-(benzotriazol-1-yl)-1-methyl-1,2,3,4-tetrahydroquinoline (**10a**) in 48% yield. 1,6-Dimethyl-1,2,3,4-tetrahydroquinoline derivatives **10b** and **11b** were isolated in 62 and 12% yields, respectively, from the product mixture obtained from the reaction of ethyl vinyl ether with *N*-methyl-*N*-(4-methylphenyl)-1*H*-benzotriazole-1-methanamine (**3b**) in toluene. Apart from the main product (**10c**), careful separation of the mixture obtained from the reaction of *N*-ethyl-*N*-phenyl-1*H*-benzotriazole-1-methanamine (**3c**) with ethyl vinyl ether allowed the identification and characterization of four additional products: two isomeric adducts, **6c** and **9c**, and two tetrahydroquinolines, **8c** and **11c**. According to the NMR spectra, when the reaction was carried out in the absence of solvent, the estimated ratio of **6c**:**8c**:**9c**:**10c**:**11c** was 24:8:5:55:8, respectively. Heating the reaction mixture at 150 °C for 30 min caused total disappearance of **8c** with little change in the ratio of the other components.

Interestingly, we have found that the ratio of products **6-11** changes rapidly in the first phase of the reaction. Thus, when the reaction was monitored by NMR, integration of the characteristic signals of ethyl vinyl ether (δ 4.18), **8c** (δ 4.31), **9c** (δ 5.96), and **10c** (δ 6.28) allowed estimation of the ratios between these compounds. Products **6c** and **11c** could not be determined individually due

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(5) (a) Katritzky, A. R.; Yannakopoulou, K.; Kuzmierkiewicz, W.; Aurrecoechea, J. M.; Palenik, G. J.; Koziol, A. E.; Szczesniak, M. *J. Chem. Soc., Perkin Trans. 1* **1987**, 2673. (b) Katritzky, A. R.; Rachwal, S.; Rachwal, B.; Frankenfeld, J. W. *Chem. Kinet.* **1995**, in press.

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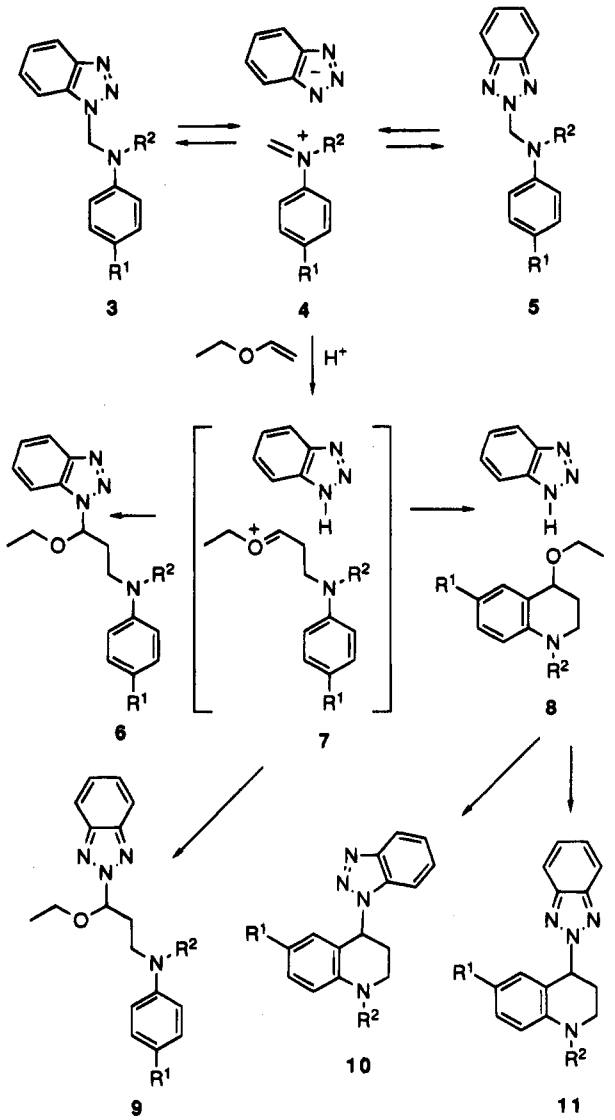
Scheme 2



a, $R^1 = H$, $R^2 = Me$
b, $R^1 = R^2 = Me$
c, $R^1 = H$, $R^2 = Et$

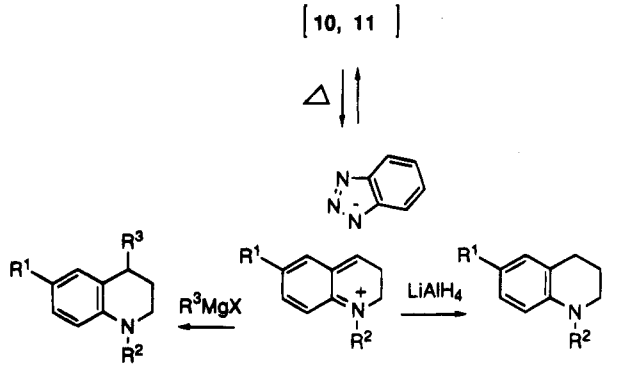
Table 1. Kinetics of the Reaction of 3c with Ethyl Vinyl Ether at 22 °C. Percentage of the Reagent (ethyl vinyl ether) and the Products

time (min)	reagent	8c	9c	10c	6c + 11c
0	100	0	0	0	0
4	63	17	3	3	14
10	55	20	6	7	12
24	44	20	7	13	16
40	37	20	7	21	15
50	34	19	7	24	16
58	29	17	9	26	19
65	28	16	9	28	19
73	25	15	8	29	23
166	10	6	12	41	31
221	5	3	13	42	37

to overlap of their resonances (plus additional overlap with the methylene singlet of **3c**). As can be seen in Table 1, ethoxytetrahydroquinoline **8c** initially dominated among the products, but as the reaction progressed, compound **10c** became the major product.

It is reasonable to accept **7** as an intermediate leading to all of the products identified. Thus, as a strong electrophile, carboxonium cation **7** can react with benzotriazole giving products **6** and **9**. Amino ethers of type **6** and **9** are reported to be the only products from the addition of *N,N*-dialkyl-1*H*-benzotriazole-1-methanamines to ethyl vinyl ether.[1] However, in the present case, the electron rich aniline ring can also be a target for electrophilic attack producing in effect 4-ethoxy-1,2,3,4-tetrahydroquinoline **8**. Substitution of the protonated ethoxy group in **8** by benzotriazole (via the relatively stable immonium cation **13,** Scheme 3) gives derivative **10** or **11**.

Scheme 3



12 a, $R^1 = H$, $R^2 = R^3 = Me$
b, $R^1 = H$, $R^2 = Me$, $R^3 = Bu$
c, $R^1 = H$, $R^2 = Me$, $R^3 = Ph$
d, $R^1 = H$, $R^2 = Et$, $R^3 = PhCH_2$
e, $R^1 = H$, $R^2 = Et$, $R^3 = BuC{\equiv}C$
f, $R^1 = R^2 = Me$, $R^3 = Et$

At elevated temperatures, ionization of **10** and **11** gives immonium cation **13** which can be trapped by nucleophiles. High yielding conversions of the mixture **10**–**11** to 4-substituted tetrahydroquinolines **12** were achieved on treatment with Grignard reagents in refluxing toluene (Scheme 3). In the case of β-hydrogen donor groups, Grignard reduction may also occur.[6,7] Thus, tetrahydroquinoline **14** was detected by NMR in a crude product obtained from the reaction mixture of **6b**–**11b** with ethylmagnesium bromide. An efficient preparation of **14** (53%) was achieved by reduction of the mixture **6b**–**11b** with lithium aluminum hydride.

There are three main literature methods for the preparation of 1,4-disubstituted 1,2,3,4-tetrahydroquinolines: (i) reduction of the heterocyclic ring of 4-substituted quinolines followed by *N*-alkylation;[8,9] (ii) formation of the (C–4)–(C–10) bond starting from appropriately substituted anilines, eg. reduction of 2-chloro-*N*-(3-buten-1-yl)anilines[10] over a platinum catalyst or treatment of *N*-(3-hydroxyalkyl)anilines[11] with perchloric acid; (iii) reaction of *N*-(methoxymethyl)anilines, obtained electrochemically, with olefins.[12] We have recently reported a modification of method iii using *N*-(benzotriazol-

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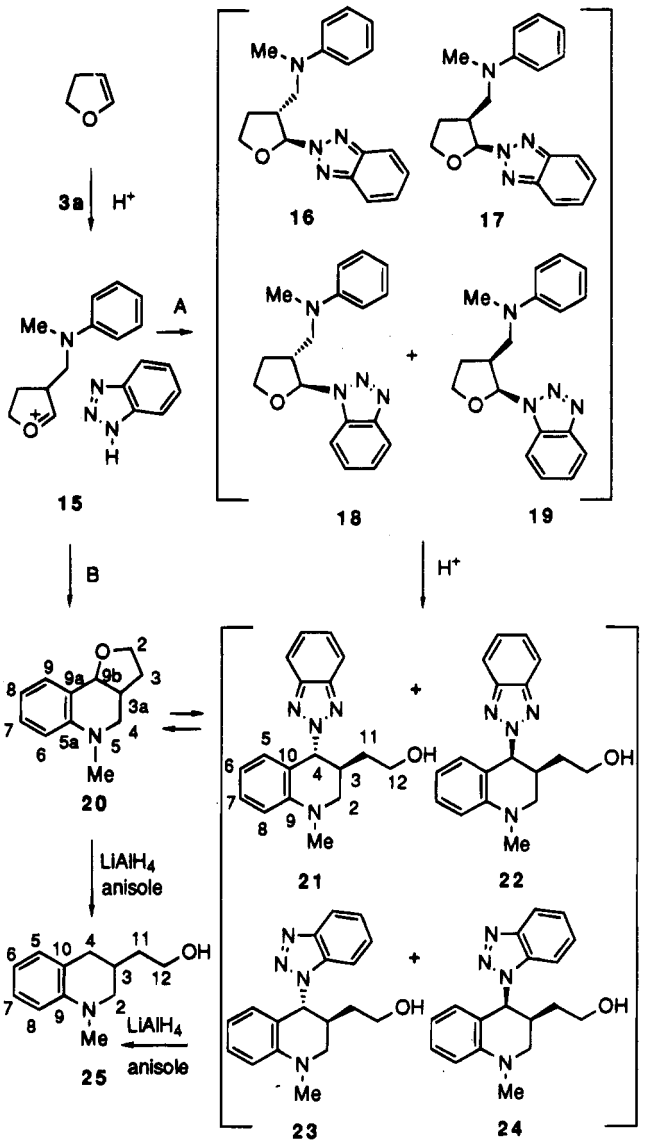
Scheme 4



1-ylmethyl)anilines.[13] None of these methods, however, are as simple and efficient as our new high yielding preparation of tetrahydroquinolines **12** from *N*-alkylanilines in three steps without purification of the intermediates. An additional advantage of the new method is the flexibility regarding the C−4 substituent.

2,3-Dihydrofuran. Addition of *N*-methyl-*N*-phenyl-1*H*-benzotriazole-1-methanamine (**3a**) to 2,3-dihydrofuran allows new possibilities. In analogy to the reaction with ethyl vinyl ether described above, carboxonium cation **15** is formed. In reaction pathway A (Scheme 4), **15** adds to benzotriazole in one of four possible modes leading to a mixture of two diastereomeric pairs **16**−**19** (Scheme 4). In the alternative reaction pathway B, intramolecular electrophilic aromatic attack in species **15** gives heterocyclic amino ether **20**, which, under the reaction conditions of elevated temperature and presence of an acid, undergoes further conversions. Thus, protonation of the oxygen atom in **20** leads to cleavage of the C−O bond followed by electrophilic attack of the immonium cation generated (similar to **13**, Scheme 3) on benzotriazole to give two diastereomeric pairs of tetrahydroquinolines, **21**, **22** and **23**, **24**, respectively. The process outlined in Scheme 4 is analogous to the formation of **10** and **11** described in Scheme 2 except that the alkoxy group is retained rather than eliminated.

Competition between the two reaction modes A and B of Scheme 4 results in a complex product mixture, consisting of tricyclic derivative **20**, four tetrahydrofurans **16-19**, and four 4-benzotriazolyltetrahydroquinolines **21**−**24**. Fortunately, compound **20** can be easily separated from the benzotriazolyl derivatives **16**−**19** and **21**−**24** due to its much lower polarity. We have also found that the whole reaction mixture, upon heating under reduced pressure, is converted in good yield to compound **20**. As tricyclic derivative **20** is the most volatile ingredient, it is readily removed from the mixture by distillation.

The complex reaction mixture of products **16**−**24** was partially separated by column chromatography. The predominant tetrahydrofuran diastereomers **16** and **18** were isolated pure. A sample enriched in diastereomer **17** allowed its characterization by NMR. The most characteristic ^{1}H resonances of compounds **16-19** originate from the tetrahydrofuran H-2 atoms and can easily be distinguished in the ^{1}H NMR spectra as doublets at δ 6.40, 6.56, and 6.28, for **16**, **17**, and **18**, respectively. Small values of $J_{2,3}$ for diastereomers **16** (1.8 Hz) and **18** (2.4 Hz) indicate *trans* configurations, by comparison with the data of similar adducts previously studied.[1] The larger $J_{2,3}$ for **17** (6.3 Hz) is characteristic of *cis*-2-benzotriazolyl-3-(aminomethyl)tetrahydrofurans.[1]

The last fraction from column chromatography gave a mixture of tetrahydroquinolines **21**−**24** easily recognizable in the ^{1}H NMR spectrum by the characteristic doublets arising from the tetrahydropyridinyl H-4 atom resonances at δ 5.92 (6.5 Hz), 6.18 (4.9 Hz), 6.03 (8.0 Hz) and 6.16 (4.5 Hz), for **21**−**24**, respectively. Comparison of the integration of these doublets allowed estimation of the isomers **21**−**24** to be in the ratio 16:5:63:16, respectively. Careful chromatography of this mixture with a new solvent system allowed partial separation and characterization of the components by NMR.

^{1}H and ^{13}C NMR spectra of compounds **21**−**24** were assigned on the basis of selective proton−proton decoupling, 2D proton−carbon correlation (HETCOR) and attached proton test (APT) techniques. Comparison of the chemical shifts and coupling constants of the diastereomers enabled stereochemical assignment. The most obvious difference between the ^{1}H NMR spectra of the more abundant (**21** and **23**) and the less abundant (**22** and **24**) diastereomers was observed in the side chain resonance patterns. Thus, in the case of diastereomer **23**, the H-11 and H-12 resonances are observed as a two proton quartet at δ 1.59 and a two proton triplet at δ 3.62, respectively, whereas diastereomer **24** exhibits the H-11 resonances at δ 1.08 and 1.48 as complex one proton multiplets, and the H-12 resonances as a broad multiplet at δ 3.77. Examination of molecular models suggests that strong differentiation between each of the H-11 and H-12 proton resonances should occur for the sterically more hindered *cis* configuration where additional stiffening of the side chain can be introduced by intramolecular hydrogen bonding between the OH group and one of the benzotriazolyl nitrogen atoms. Free rotation of the CH_2-CH_2OH group in the *trans* diastereomer averages the magnetic field for both protons in each pair. Strong support for these structural assignments was obtained from NOE experiments. Thus, irradiation of the H-4 atom of **23** enhanced the H-11 (1.9%), H-3 (3.2%), H-5

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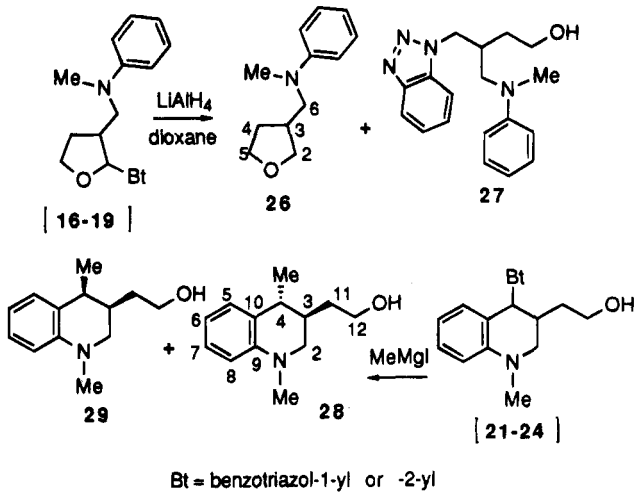
Scheme 5



(5.9%), and benzotriazolyl H-7′ (1.9%) resonances supporting a *trans* configuration of the substituents. Irradiation of the H-4 doublet of **24** gave only enhancement of the H-3 (5%) and benzotriazolyl H-7′ (8.6%) signals in agreement with the *cis* configuration.

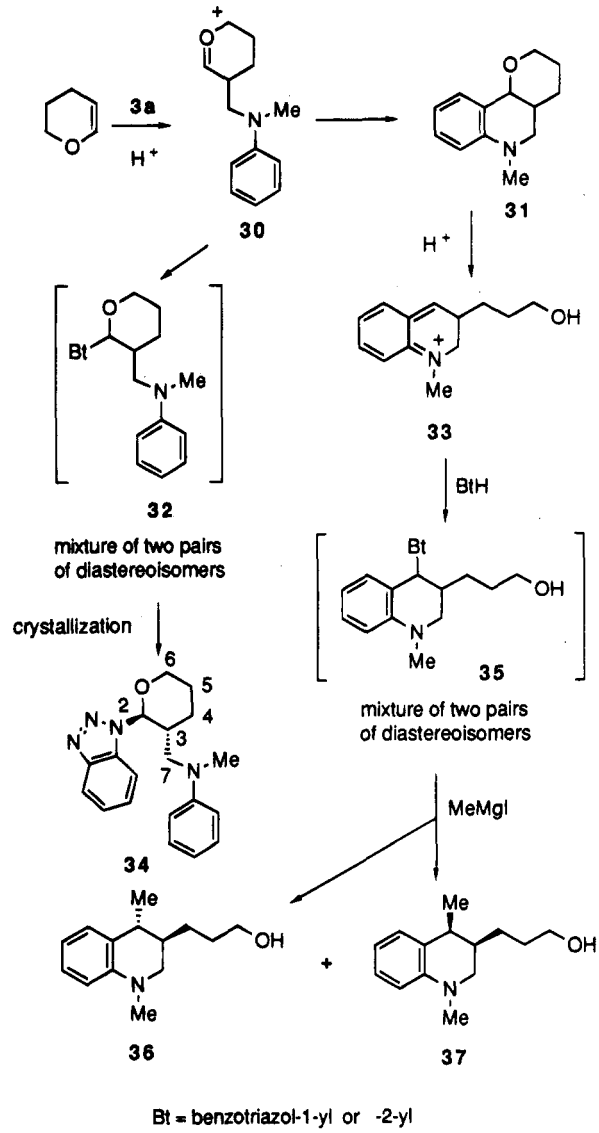
Despite its complexity, the crude reaction mixture of **16**–**24** was converted in 86% yield to tetrahydroquinoline **25** upon heating with lithium aluminum hydride in anisole. Obviously, under these extreme conditions, both the C–O bond of **20** and the C(4)–N bonds of **21**–**24** are cleaved to give a transition state similar to **13** (Scheme 3). Tetrahydrofurans **16**–**19** are probably also first converted into tetrahydroquinolines **21**–**24** under these conditions before reduction to **25**.

By contrast, the crude mixture obtained from the reaction of **3a** with 2,3-dihydrofuran was not completely reduced by $LiAlH_4$ in dioxane. Under these conditions a complex mixture resulted from which two new products, **26** and **27**, were isolated in addition to compounds **20**–**25** (Scheme 5). Products **26** and **27** can reasonably be formed by reduction of adducts **16**–**19**. Cleavage of the C–N(Bt) bond of **16**–**19** would give carboxonium cation **15** which is then reduced to **26**. Alternatively, cleavage of the C–O bond in **16**-**19** gave a cation which is then reduced to product **27**.

Reaction of a mixture of **23** and **24** with methylmagnesium iodide gave an equimolar mixture of the two diastereomeric 4-methyltetrahydroquinolines **28** and **29**, which were separated by careful column chromatography and assigned stereochemically based on their NOE NMR spectra. Thus, in the case of tetrahydroquinoline **28**, irradiation of the C–4 methyl doublet at δ 1.25 gave in addition to H-4 (7%), one of the H-2 signals (5%), and H-5 (10%), a 3% enhancement of the H-3 multiplet at δ 1.81 indicating a *trans* configuration of the C–3 and C–4 substituents. Similar irradiation of the methyl group of **29** gave enhanced signals only from H-2 (13%) and H-5 (6%).

3,4-Dihydro-2*H*-pyran. Addition of **3a** to 3,4-dihydro-2*H*-pyran leads to carboxonium cation **30** (Scheme 6) which, under the reaction conditions, reacts further to afford the tricyclic system **31**. Alternatively, addition of benzotriazole gives 2,3-disubstituted tetrahydropyrans **32**. Interestingly, in this case, isomer **34** comprised about 90% of the mixture and was readily separated from the other tetrahydroquinolines by recrystallization. As the coupling constant, $J_{2,3}$ = 7.7 Hz, does not indicate directly

Scheme 6

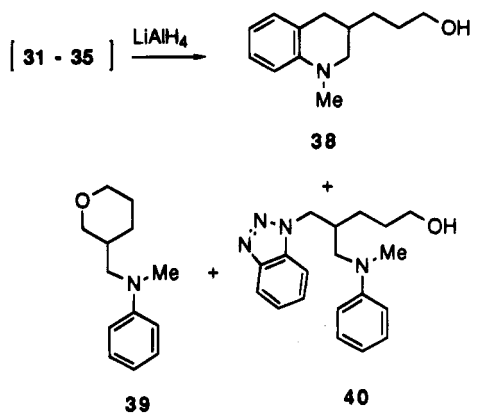


whether **34** is the *cis* or *trans* isomer, the NOE technique was employed once more to establish the stereochemistry. Thus, irradiation of the H-2 doublet at δ 5.86 gave 3% enhancement of the H-7 signal at δ 3.13 (dd) and also the second H-7 signal at δ 3.24 (dd), indicating a *trans* configuration of the C–2 and C–3 substituents.

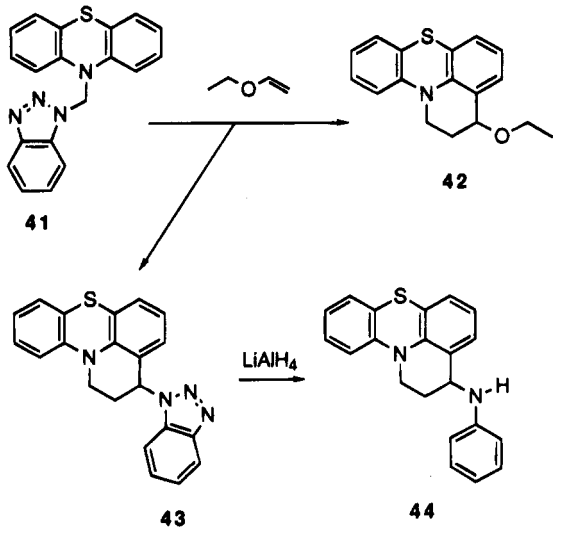
Under the reaction conditions, protonation of the oxygen atom of **31** can cause opening of the tetrahydropyran ring giving immonium cation **33** which then attacks benzotriazole leading to a diastereoisomeric mixture of tetrahydroquinolines **35**. The crude reaction mixture was separated into **31**, **34**, and a mixture of two tetrahydroquinoline **35** diastereomers. Reaction of the mixture **35** with methylmagnesium iodide gave two diastereomeric 4-methyltetrahydroquinolines **36** and **37**. Comparison of the NMR spectra of **36** and **37** with those of compounds **28** and **29** allowed assignment of the *trans* geometry to the less polar isomer **36**.

As for the dihydrofuran case, treatment of the crude reaction mixture obtained from the addition of **3a** to dihydropyran with lithium aluminum hydride in anisole resulted in the formation of compound **38** in 76% yield (Scheme 7). When the reduction was carried out in dioxane, products **39** and **40** from the reduction of tetrahydropyrans **32** were obtained in addition to **38**.

Scheme 7



Scheme 8



Phenothiazine. Application of our method to a heterocyclic amine allows the addition of a new ring to the heterocyclic system. This possibility was tested on phenothiazine derivative **41**[13] (Scheme 8). Thus, reaction of **41** with ethyl vinyl ether gave two main products: ethoxy derivative **42** and benzotriazol-1-yl derivative **43**. An unusual reaction course was observed during reduction of **43** with lithium aluminum hydride. Instead of substitution of the benzotriazolyl group by hydrogen giving an unsubstituted tetrahydroquinoline system in analogy to products **14**, **25**, and **38**, the benzotriazolyl substituent was reduced to aniline.

Conclusions

We have reported a novel and practical synthetic method for the conversion of *N*-alkylanilines into 1,4-disubstituted tetrahydroquinolines. The three-step procedure involves (i) condensation of an aniline with formaldehyde and benzotriazole, (ii) reaction of the product with ethyl vinyl ether, and (iii) replacement of the benzotriazolyl substituent in the tetrahydroquinoline 4-position with a Grignard reagent. No purification of intermediates is required. Although tested on only a few compounds, there is no obvious limitation to the type of alkyl (or aryl) substitution in positions 1 (the *N*-alkyl group from the starting aniline) and 4 (from the Grignard reagent) of the 1,2,3,4-tetrahydroquinoline system. As shown in the case of a *p*-toluidine derivative, ring-substituted anilines can give 1,2,3,4-tetrahydroquinolines bearing a substituent on the aromatic ring. Use of higher α,β-unsaturated ethers allows the introduction of an additional substituent at position 3 of the 1,2,3,4-tetrahydroquinoline system as was shown in the reactions with 2,3-dihydrofuran and 2,3-dihydropyran. The stereochemistry of 1,3,4-trisubstituted 1,2,3,4-tetrahydroquinolines has been clarified.

Experimental Section

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

***N*-Methyl-*N*-phenyl-1*H*-benzotriazole-1-methanamine (3a)**. Formaldehyde (37%, 10 mL) was added to a stirred solution of benzotriazole (11.93 g, 100 mmol) and *N*-methylaniline (10.8 mL, 100 mmol) in ether (200 mL). The obtained mixture was set aside at 22 °C for 2 h and then stored at −5 °C for 16 h. The obtained precipitate was separated by filtration, washed with ether (50 mL), and dried under reduced pressure at 40 °C, to give **3a** (containing 16% isomer **5a**, 18.4 g, 78%): colorless needles, mp 83 °C [lit mp 76–78 °C];[14] ^1H NMR δ 3.00 (s, 3 H), 6.10 (s, 2 H), 6.87–7.08 (m, 3 H), 7.16–7.34 (m, 5 H), 8.00 (m, 1 H); ^{13}C NMR δ 37.4, 66.7, 110.0, 115.1 (2 C), 119.7, 119.9, 123.8, 129.4 (2 C), 132.5, 146.1, 147.8.

***N*-Methyl-*N*-(4-methylphenyl)-1*H*-benzotriazole-1-methanamine (3b)**. By a procedure analogous to that for **3a**, compound **3b** was obtained in 69% yield as the Bt-1 isomer after recrystallization from EtOH as colorless needles, mp 102 °C: ^1H NMR δ 2.27 (s, 3 H), 2.97 (s, 3 H), 6.09 (s, 2 H), 6.90 (d, J = 8.8 Hz, 2 H), 7.09 (d, J = 8.7 Hz, 2 H), 7.16 (m, 1 H), 7.29 (m, 1 H), 8.00 (m, 1 H); ^{13}C NMR δ 20.3, 37.6, 67.1, 110.1, 115.5 (2 C), 119.7, 123.7, 127.3, 129.5, 129.9 (2 C), 132.6, 145.6, 146.1. Anal. Calcd for $C_{15}H_{16}N_4$: C, 71.40; H, 6.39; N, 22.20. Found: C, 71.55; H, 6.49; N, 22.31.

***N*-Ethyl-*N*-phenyl-1*H*-benzotriazole-1-methanamine (3c)**. By a procedure analogous to that for **3a**, compound **3c** was obtained in 86% yield (containing 22% isomer **5c**): prisms, mp 74 °C; ^1H NMR δ 1.19 (t, J = 6.9 Hz, 3 H), 3.42 (q, J = 7.1 Hz, 2 H), 6.10 (s, 2 H), 6.90 (t, J = 7.1 Hz, 1 H), 7.00 (d, J = 8.0 Hz, 2 H), 7.13 (d, J = 8.6 Hz, 1 H), 7.28 (m, 4 H), 8.02 (d, J = 8.1 Hz, 1 H); ^{13}C NMR δ 12.3, 43.9, 65.2, 110.1, 116.2 (2 C), 119.7, 120.1, 123.8, 127.2, 129.4 (2 C), 132.6, 146.1, 147.0. Anal. Calcd for $C_{15}H_{16}N_4$: C, 71.40; H, 6.39; N, 22.20. Found: C, 71.09; H, 6.41; N, 22.46.

4-(Benzotriazol-1-yl)-1-methyl-1,2,3,4-tetrahydroquinoline (10a). A mixture of **3a** (2.38 g, 10 mmol), ethyl vinyl ether (1.2 mL, 12 mmol), and *p*-toluenesulfonic acid monohydrate (10 mg) was stirred at 22 °C for 30 min followed by heating at 120 °C for 10 min. After cooling, the reaction mixture was dissolved in toluene (50 mL). The toluene solution was washed with 10% NaOH (50 mL) followed by water and dried over $MgSO_4$. Evaporation of the solvent and column chromatography (silica gel/CH_2Cl_2) of the residue afforded pure **10a** (1.26 g, 48%). An analytical sample of **10a** was obtained by recrystallization from EtOH: prisms, mp 125–126 °C; ^1H NMR δ 2.35–2.69 (m, 2 H), 2.98 (s, 3 H), 3.29 (m, 2 H), 6.32 (t, J = 6.3 Hz, 1 H), 6.53 (t, J = 7.0 Hz, 1 H), 6.73 (m, 2 H), 6.93 (m, 1 H), 7.23 (m, 1 H), 8.03 (m, 1 H); ^{13}C NMR δ 29.6, 39.3, 48.2, 57.1, 111.0, 119.9, 123.7, 127.0, 129.2, 129.9, 132.4, 146.4, 147.1. Anal. Calcd for $C_{16}H_{16}N_4$: C, 72.70; H, 6.10; N, 21.20. Found: C, 72.76; H, 6.08; N, 21.27.

4-(Benzotriazol-1-yl)-1,6-dimethyl-1,2,3,4-tetrahydroquinoline (10b) and Its Benzotriazol-2-yl Isomer (11b). *p*-Toluenesulfonic acid monohydrate (0.02 g, 0.1 mmol) was added to a solution of **3b** (1.26 g, 5 mmol) and ethyl vinyl ether (0.6 mL, 6 mmol) in toluene (10 mL). The solution was stirred

(14) Lindsay Smith, J. R., Sadd, J. S. *J. Chem. Soc., Perkin Trans. 1* **1975**, 1181.

for 1 h and set aside at 22 °C for 20 h. Evaporation of the solvent and column chromatography of the residue (hexane/ether, 1:1) gave product **11b** (0.17 g, 12%) as an oil: ^{1}H NMR δ 2.12 (s, 3 H), 2.51 (m, 1 H), 2.64 (m, 1 H), 3.00 (s, 3 H), 3.25 (m, 1 H), 3.56 (ddd, J = 3.3, 10.2 and 11.6 Hz, 1 H), 6.15 (t, J = 5.2 Hz, 1 H), 6.69 (d, J = 8.5 Hz, 1 H), 6.74 (s, 1 H), 7.03 (m, 1 H), 7.37 (m, 2 H), 7.88 (m, 2 H); ^{13}C NMR δ 20.1, 29.6, 39.4, 47.4, 62.8, 112.3, 118.3 (2 C), 120.4, 120.7, 126.0 (2 C), 126.4 (2 C), 130.0, 130.6, 144.2. Anal. Calcd for $C_{17}H_{18}N_4$: C, 73.35; H, 6.52; N, 20.12. Found: C, 73.25; H, 6.56; N, 20.22.

The second fraction from column chromatography afforded product **10b** (0.86 g, 62%) as an oil: ^{1}H NMR δ 2.03 (s, 3 H), 2.45 (m, 1 H), 2.55 (m, 1 H), 2.94 (s, 3 H), 3.18 (ddd, J = 3.6, 7.8 and 11.7 Hz, 1 H), 3.28 (ddd, J = 2.4, 7.2 and 11.4 Hz, 1 H), 6.27 (t, J = 6.3 Hz, 1 H), 6.56 (s, 1 H), 6.69 (d, J = 8.4 Hz, 1 H), 6.97 (m, 1 H), 7.03 (d, J = 8.7 Hz, 1 H), 7.26 (m, 2 H), 8.02 (m, 1 H); ^{13}C NMR δ 20.1, 29.9, 39.5, 48.3, 57.0, 111.0, 112.2, 117.5, 119.9, 123.6, 126.2, 126.9, 129.6, 130.6, 132.3, 145.1, 146.4. Anal. Calcd for $C_{17}H_{18}N_4$: C, 73.35; H, 6.52; N, 20.12. Found: C, 73.40; H, 6.51; N, 20.09.

Reaction of *N*-Ethyl-*N*-phenyl-1*H*-benzotriazole-1-methanamine (3c) with Ethyl Vinyl Ether. *p*-Toluenesulfonic acid monohydrate (0.05 g, 0.25 mmol) was added to a solution of **3c** (2.52 g, 10 mmol) and ethyl vinyl ether (1.4 mL, 15 mmol) in chloroform (10 mL). The exothermic reaction caused the solution to boil. The reaction mixture was left at 22 °C for 1 h and then subjected to column chromatography (hexane/ether, 4:1). The first fraction gave 4-ethoxy-1-ethyl-1,2,3,4-tetrahydroquinoline (**8c**) as an oil (0.086 g, 4%): ^{1}H NMR δ 1.13 (t, J = 7.0 Hz, 3 H), 1.22 (t, J = 7.0 Hz, 3 H), 1.86 (m, 1 H), 2.11 (m, 1 H), 3.11 (m, 1 H), 3.24–3.64 (m, 5 H), 4.31 (t, J = 3.3 Hz, 1 H), 6.59 (t, J = 7.3 Hz, 1 H), 6.65 (d, J = 8.2 Hz, 1 H), 7.13 (m, 2 H); ^{13}C NMR δ 11.0, 15.6, 27.2, 43.2, 45.2, 62.8, 73.0, 110.9, 114.7, 121.0, 129.2, 130.7, 144.7; HRMS calcd for $C_{13}H_{19}NO$: 205.147, found 205.144.

The second fraction gave **3-ethoxy-*N*-ethyl-*N*-phenyl-2*H*-benzotriazole-3-propanamine (9c)**: yield 0.088 g (3%) oil; ^{1}H NMR δ 1.13 (t, J = 7.0 Hz, 3 H), 1.18 (t, J = 7.0 Hz, 3 H), 2.48 (m, 1 H), 2.63 (m, 1 H), 3.39 (m, 5 H), 3.56 (dq, J = 9.3 and 7.0 Hz, 1 H), 5.96 (dd, J = 5.3 and 7.6 Hz, 1 H), 6.74 (m, 3 H), 7.21 (m, 2 H), 7.40 (m, 2 H), 7.90 (m, 2 H); ^{13}C NMR δ 12.1, 14.6, 33.6, 45.1, 45.7, 65.3, 93.1, 112.5 (2 C), 116.2, 118.5 (2 C), 126.7 (2 C), 129.2 (2 C), 144.2 (2 C), 147.7. Anal. Calcd for $C_{19}H_{24}N_4O$: C, 70.34; H, 7.46; N, 17.27. Found: C, 70.14; H, 7.57; N, 16.92.

The third fraction gave **3-ethoxy-*N*-ethyl-*N*-phenyl-1*H*-benzotriazole-3-propanamine (6c)**: yield 0.162 g (5%) oil; ^{1}H NMR δ 1.11 (t, J = 7.0 Hz, 3 H), 1.16 (t, J = 7.0 Hz, 3 H), 2.36 (m, 1 H), 2.59 (m, 1 H), 3.28 (dq, J = 9.3 and 7.1 Hz, 1 H), 3.33 (t, J = 7.1 Hz, 2 H), 3.41 (t, J = 7.1 Hz, 2 H), 3.51 (dq, J = 9.3 and 6.9 Hz, 1 H), 6.13 (dd, J = 5.3 and 7.6 Hz, 1 H), 6.68 (m, 3 H), 7.20 (m, 2 H), 7.40 (m, 1 H), 7.48 (m, 1 H), 7.76 (d, J = 8.3 Hz, 1 H), 8.09 (d, J = 8.3 Hz, 1 H); ^{13}C NMR δ 12.0, 14.6, 32.9, 45.1, 45.8, 64.5, 88.5, 111.0, 112.5, 116.2 (2 C), 120.0, 124.1, 127.4, 129.2 (2 C), 131.3, 146.7, 147.5; HRMS calcd for $C_{19}H_{24}N_4O$: 324.1950, found 324.1952.

The fourth fraction gave **4-(benzotriazol-2-yl)-1-ethyl-1,2,3,4-tetrahydroquinoline (11c)**: yield 0.14 g (5%) prisms, mp 97–98 °C; ^{1}H NMR δ 1.19 (t, J = 7.1 Hz, 3 H), 2.49 (m, 1 H), 2.65 (m, 1 H), 3.29 (m, 1 H), 3.41 (t, J = 10.1 Hz, 2 H), 3.56 (m, 1 H), 6.12 (t, J = 5.2 Hz, 1 H), 6.54 (t, J = 7.3 Hz, 1 H), 6.74 (d, J = 8.4 Hz, 1 H), 6.90 (d, J = 7.6 Hz, 1 H), 7.17 (m, 1 H), 7.33 (m, 2 H), 7.86 (m, 2 H); ^{13}C NMR δ 11.1, 29.0, 44.2, 45.5, 63.0, 111.6, 115.7, 117.8, 118.2 (2 C), 126.0 (2 C), 129.9, 130.0, 144.2 (2 C), 145.1. Anal. Calcd for $C_{17}H_{18}N_4$: C, 73.35; H, 6.52; N, 20.13. Found: C, 73.42; H, 6.46; N, 19.90.

The fifth fraction gave **4-(benzotriazol-1-yl)-1-ethyl-1,2,3,4-tetrahydroquinoline (10c)**: yield 1.69 (52%) prisms, mp 73–74 °C; ^{1}H NMR δ 1.19 (t, J = 7.1 Hz, 3 H), 2.44 (m, 1 H), 2.58 (m, 1 H), 3.24 (ddd, J = 3.6, 8.7 and 12.4 Hz, 1 H), 3.33–3.54 (m, 3 H), 6.28 (dd, J = 6.0 and 5.4 Hz, 1 H), 6.53 (t, J = 7.4 Hz, 1 H), 6.79 (t, J = 8.8 Hz, 2 H), 6.90 (m, 1 H), 7.25 (m, 3 H), 8.04 (m, 1 H); ^{13}C NMR δ 10.7, 29.4, 44.9, 45.4, 57.2, 110.9, 111.5, 116.0, 116.7, 119.8, 123.5, 126.8, 129.7, 129.9, 132.5, 145.5, 146.3. Anal. Calcd for $C_{17}H_{18}N_4$: C, 73.35; H, 6.52; N, 20.13. Found: C, 73.62; H, 6.55; N, 20.19.

Tetrahydroquinolines 12. General Procedure. The crude product mixture obtained from the reaction of **3** (10 mmol) with ethyl vinyl ether was dissolved in dry toluene (30 mL). To this stirred solution at 100 °C (oil bath), was added dropwise an ethereal solution of the appropriate Grignard reagent (25 mmol) with simultaneous distillation of the ether. The obtained mixture was then heated at reflux under nitrogen for 1 h (or until TLC showed no starting material remaining). After cooling, the reaction mixture was poured into ice–water (200 mL), neutralized with acetic acid, and extracted with ether (2 × 50 mL). The combined extracts were washed with water, followed by 10% NaOH, and dried over anhydrous Na_2CO_3. The solvent was evaporated, and the residue was purified by column chromatography (hexane/ether, 4:1) or by fractional distillation under reduced pressure.

1,4-Dimethyl-1,2,3,4-tetrahydroquinoline (12a): yield 0.64 g (79%) oil; ^{1}H NMR δ 1.27 (d, J = 7.0 Hz, 3 H), 1.68 (m, 1 H), 2.02 (m, 1 H), 2.87 (m, 1 H), 2.88 (s, 3 H), 3.19 (m, 2 H), 6.62 (m, 2 H), 7.06 (m, 2 H); ^{13}C NMR δ 22.8, 30.1, 30.9, 39.3, 48.4, 111.1, 116.4, 125.8, 127.1, 127.9, 146.2. **Picrate**: mp 105–107 °C. Anal. Calcd for $C_{17}H_{18}N_4O_7$: C, 52.31; H, 4.65; N, 14.35. Found: C, 52.47; H, 4.68; N, 14.13.

4-Butyl-1-methyl-1,2,3,4-tetrahydroquinoline (12b): yield 0.92 g (46%) oil; ^{1}H NMR δ 0.90 (t, J = 7.1 Hz, 3 H), 1.33 (m, 4 H), 1.40 (m, 1 H), 1.48 (m, 1 H), 1.62 (m, 1 H), 1.78 (m, 1 H), 1.95 (m, 1 H), 2.72 (m, 1 H), 2.86 (s, 3 H), 3.12 (dt, J = 11.4 and 4.7 Hz, 1 H), 3.25 (td, J = 7.3 and 1.3 Hz, 1 H), 6.58 (d, J = 8.2 Hz, 1 H), 6.59 (td, J = 7.3 and 1.2 Hz, 1 H), 6.98 (dd, J = 1.2 and 7.3 Hz, 1 H), 7.05 (td, J = 8.3 and 1.6 Hz, 1 H); ^{13}C NMR δ 14.1, 22.9, 26.4, 29.2, 36.2, 36.3, 38.9, 47.6, 110.7, 115.8, 127.0, 127.1, 128.4, 145.9. Anal. Calcd for $C_{14}H_{21}N_4$: C, 82.70; H, 10.41; N, 6.89. Found: C, 82.38; H, 10.41; N, 6.98. **Picrate**: mp 72–73 °C (from MeOH).

1-Methyl-4-phenyl-1,2,3,4-tetrahydroquinoline (12c): yield 0.70 g (62%) oil; ^{1}H NMR δ 2.08 (m, 1 H), 2.22 (m, 1 H), 2.87 (s, 3 H), 3.16 (m, 2 H), 4.08 (t, J = 6.0 Hz, 1 H), 6.55 (t, J = 7.3 Hz, 1 H), 6.63 (d, J = 8.3 Hz, 1 H), 6.72 (d, J = 7.1 Hz, 1 H), 7.05–7.26 (m, 6 H); ^{13}C NMR 31.0, 39.2, 43.3, 48.4, 110.9, 116.2, 124.7, 126.0, 127.5, 128.2 (2 C), 128.6 (2 C), 129.8, 146.5, 146.8. Anal. Calcd. for $C_{16}H_{17}N$: C, 86.40; H, 7.67; N, 6.27. Found: C, 86.04; H, 7.77; N, 6.45. **Picrate**: mp 170–172 °C (from MeOH).

4-Benzyl-1-ethyl-1,2,3,4-tetrahydroquinoline (12d): yield 1.66 g (66%) oil; ^{1}H NMR δ 1.13 (t, J = 7.1 Hz, 3 H), 1.71 (m, 1 H), 1.80 (m, 1 H), 2.68 (dd, J = 12.2 and 9.0 Hz, 1 H), 2.96–3.14 (m, 3 H), 3.22–3.47 (m, 3 H), 6.56 (td, J = 7.3 and 1.1 Hz, 1 H), 6.62 (d, J = 8.2 Hz, 1 H), 6.98 (dd, J = 7.4 and 1.4 Hz, 1 H), 7.06 (ddd, J = 8.6, 7.2 and 1.7 Hz, 1 H), 7.18 (m, 3 H), 7.28 (m, 2 H); ^{13}C NMR δ 10.7, 25.0, 38.3, 43.0, 44.2, 45.2, 110.6, 115.2, 125.6, 125.9, 127.3, 128.3 (2 C), 128.9, 129.3 (2 C), 140.4, 144.3. Anal. Calcd for $C_{18}H_{21}N$: C, 86.01; H, 8.42; N, 5.57. Found: C, 85.82; H, 8.42; N, 5.47. **Picrate**: mp 131–132 °C (from MeOH).

1-Ethyl-4-(1-hexyn-1-yl)-1,2,3,4-tetrahydroquinoline (12e): yield 1.48 g (62%) oil; ^{1}H NMR δ 0.90 (t, J = 7.1 Hz, 3 H), 1.13 (t, J = 7.1 Hz, 3 H), 1.44 (m, 4 H), 1.99 (m, 1 H), 2.09 (m, 1 H), 2.19 (td, J = 6.9 and 2.0 Hz, 2 H), 3.23 (m, 1 H), 3.33 (m, 3 H), 3.71 (m, 1 H), 6.58 (m, 2 H), 7.07 (td, J = 8.0 and 1.1 Hz, 1 H), 7.28 (d, J = 7.2 Hz, 1H); ^{13}C NMR δ 10.9, 13.6, 18.5, 21.9, 29.1, 30.1, 31.1, 45.3, 46.1, 82.4, 82.5, 110.7, 115.5, 122.4, 127.8, 128.9, 143.9. Anal. Calcd for $C_{17}H_{23}N$: C, 84.59; H, 9.60; N, 5.80. Found: C, 84.95; H, 9.94; N, 6.10.

1,6-Dimethyl-4-ethyl-1,2,3,4-tetrahydroquinoline (12f): yield 1.16 g (61%) oil; ^{1}H NMR δ 0.97 (t, J = 7.4 Hz, 3 H), 1.51 (m, 1 H), 1.70 (m, 1 H), 1.81 (m, 1 H), 1.96 (m, 1 H), 2.22 (s, 3 H), 2.59 (m, 1 H), 2.84 (s, 3 H), 3.07 (dt, J = 11.2 and 4.5 Hz, 1 H), 3.18 (td, J = 11.0 and 3.9 Hz, 1 H), 6.52 (d, J = 8.2 Hz, 1 H), 6.84 (d, J = 1.7 Hz, 1 H), 6.88 (dd, J = 8.2 and 2.2 Hz, 1 H); ^{13}C NMR δ 11.6, 20.3, 26.1, 29.4, 37.8, 39.3, 47.9, 111.1, 125.0, 127.1, 127.4, 129.3, 144.0. Anal. Calcd for $C_{13}H_{19}N$: C, 82.48; H, 10.12; N, 7.40. Found: C, 82.14; H, 10.09; N, 7.37. **Picrate**: mp 144–146 °C (from MeOH).

1,6-Dimethyl-1,2,3,4-tetrahydroquinoline (14). A solution of crude **6b–11b** (obtained from 10 mmol of **3b**) and $LiAlH_4$ (0.38 g, 10 mmol) in dry THF (20 mL) was heated at reflux for 2 h. After cooling, the reaction mixture was poured

into ice-cold NaOH (20%, 100 mL) and extracted with ether (2 × 50 mL). The combined extracts were washed with water, dried over Na_2CO_3, and evaporated. Purification by column chromatography (hexane/ether, 5:1) gave product **14** (0.86 g, 53%) as a colorless oil: ^{1}H NMR δ 1.97 (m, 2 H), 2.20 (s, 3 H), 2.73 (t, J = 6.6 Hz, 2 H), 2.84 (s, 3 H), 3.15 (t, J = 5.8 Hz, 2 H), 6.53 (d, J = 8.2 Hz, 1 H), 6.78 (s, 1 H), 6.87 (d, J = 8.2 Hz, 1 H); ^{13}C NMR δ 20.2, 22.6, 27.7, 39.4, 51.5, 111.4, 123.0, 125.5, 127.3, 129.6, 144.7. **Picrate**: mp 142–143 °C (from MeOH). Anal. Calcd for $C_{17}H_{18}N_4O_7$: C, 52.31; H, 4.65; N, 14.35. Found: C, 51.98; H, 4.60; N, 14.42.

Reaction of *N*-(Benzotriazol-1-ylmethyl)-*N*-methylaniline (3a) with 2,3-Dihydrofuran. *p*-Toluenesulfonic acid monohydrate (10 mg) was added to a mixture of **3a** (2.35 g, 10 mmol) and dihydrofuran (0.84 g, 12 mmol) in a 10 mL flask equipped with a reflux condenser and preheated in an oil bath to 140 °C. The reaction mixture was heated at 140–150 °C for 30 min until distillation of dihydrofuran stopped. After cooling, the obtained oil was dissolved in chloroform and the solution was washed carefully with water, followed by 10% Na_2CO_3, and then water again. Drying over Na_2CO_3 and evaporation of the solvent afforded an oily product, which by NMR consisted of several different compounds, mainly Bt-1 and Bt-2 derivatives of tetrahydroquinoline (**21–24**) and tetrahydrofuran (**16–19**), and polycycle **20**. The molar ratio of all of the benzotriazolyl derivatives to cycloether **20** was 2:1. Column chromatography (ethyl ether/hexane, 1:2) allowed separation of the first fraction, a mixture of adducts **16** and **17** in a ratio of 2:1 (0.28 g, 9%).

Fractional recrystallization of the mixture from toluene gave the predominant diastereomer **16** as colorless prisms, mp 106 °C; ^{1}H NMR δ 1.94 (m, 1 H), 2.63 (m, 1 H), 2.97 (s, 3 H), 3.50 (m, 3 H), 4.32 (m, 2 H), 6.40 (d, J = 1.8 Hz, 1 H), 6.74 (m, 3 H), 7.21 (m, 2 H), 7.38 (m, 2 H), 7.86 (m, 2 H); ^{13}C NMR δ 28.4, 38.9, 44.8, 55.0, 69.7, 96.6, 112.7 (2 C), 117.2, 118.4 (2 C), 126.6 (2 C), 129.2 (2 C), 144.2 (2 C), 149.4 (Ph). Anal. Calcd for $C_{18}H_{20}N_4O$: C, 70.11; H, 6.54; N, 18.17. Found: C, 69.90; H, 6.54; N, 17.95.

After separation of **16,** the residue appeared to be a mixture enriched in diastereomer **17** (80%). This allowed for full NMR characterization of **17**: ^{1}H NMR δ 2.30 (m, 1 H), 2.65 (m, 1 H), 2.74 (s, 3 H), 2.84 (dd, J = 7.5 and 14.7 Hz, 1 H), 3.09 (m, 1 H), 3.25 (dd, J = 5.7 and 14.7 Hz, 1 H), 4.12 (m, 1 H), 4.60 (m, 1 H), 6.56 (d, J = 6.3 Hz, 1 H), 6.61 (d, J = 8.7 Hz, 2 H), 6.96 (m, 1 H), 7.19 (m, 2 H), 7.41 (m, 2 H), 7.91 (m, 2 H); ^{13}C NMR δ 28.5, 39.1, 43.6, 50.9, 70.3, 95.1, 112.3 (2 C), 116.6, 118.4 (2 C), 126.7 (2 C), 129.2 (2 C), 144.1 (2 C), 149.2.

The second fraction from column chromatography was cycloether **20** (0.57 g, 30%) as a colorless oil. The compound was additionally purified by vacuum distillation: bp 122 °C/0.25 Torr; ^{1}H NMR δ 1.72 (m, 1 H), 2.20 (m, 1 H), 2.49 (m, 1 H), 2.75 (t, J = 11.0 Hz, 1 H), 2.85 (s, 3 H), 2.94 (dd, J = 5.4 and 11.2 Hz, 1 H), 3.77 (td, J = 8.6 and 6.3 Hz, 1 H), 3.91 (td, J= 8.3 and 5.9 Hz, 1 H), 4.56 (d, J = 5.4 Hz, 1 H), 6.68 (d, J = 8.2 Hz, 1 H), 6.74 (t, J = 7.4 Hz, 1 H), 7.17 (td, J = 7.5 and 1.5 Hz, 1 H), 7.32 (d, J = 7.4 Hz, 1 H); ^{13}C NMR δ 29.9, 35.8, 39.2, 52.4, 65.0, 75.7, 111.7, 117.3, 121.6, 128.9, 131.0, 147.0; HRMS calcd for $C_{12}H_{15}NO$ 189.115, found 189.115. **Picrate**: mp 62–64 °C. Anal. Calcd for $C_{18}H_{18}N_4O_8$: C, 51.68; H, 4.34; N, 13.39. Found: C, 51.36; H, 4.09; N, 13.76.

The third fraction gave a diastereomeric mixture of adducts **18** and **19** (4:1) as an oil (0.50 g, 16%). Careful column chromatography (hexane/ether, 9:1) of this mixture allowed separation of pure **18**: ^{1}H NMR δ 1.93 (m, 1 H), 2.57 (m, 1 H), 2.93 (s, 3 H), 3.39 (dd, J = 6.8 and 14.7 Hz, 1 H), 3.63 (dd, J = 9.6 and 14.6 Hz, 1 H) 3.90 (m, 1 H), 4.05 (m, 1 H), 4.24 (m, 1 H), 6.28 (d, J = 2.4 Hz, 1 H), 6.75 (m, 3 H), 7.22 (m, 2 H), 7.36 (m, 1 H), 7.44 (m, 1 H), 7.53 (d, J = 8.1 Hz, 1 H), 8.05 (d, J = 8.3 Hz, 1 H); ^{13}C NMR δ 28.6, 38.5, 43.1, 55.1, 68.6, 90.1, 110.2, 112.9 (2 C), 117.4, 119.7, 124.1, 127.5, 129.3 (2 C), 132.8, 146.2, 149.7. Anal. Calcd for $C_{18}H_{20}N_4O$: C, 70.11; H, 6.54; N, 18.17. Found: C, 69.82; H, 6.55; N, 18.19.

The minor diastereomer **19** was not isolated.

The last fraction from column chromatography was eluted with ether giving a mixture of tetrahydroquinolines **21–24** (0.77 g, 22%) in a ratio of 16:5:63:16, respectively. The mixture was separated by careful column chromatography (toluene/ethyl acetate, 1:1).

The first fraction gave a mixture of tetrahydroquinolines **21** and **22** in a ratio of 4:1 as an oil. This allowed for full NMR characterization of **21**: ^{1}H NMR δ 1.63 (m, 2 H), 2.01 (bs, 1 H), 2.93 (m, 1 H), 2.99 (s, 3 H), 3.14 (dd, J = 7.1 and 11.9 Hz, 1 H), 3.57 (dd, J = 3.6 and 11.9 Hz, 1 H), 3.65 (m, 2 H), 5.92 (d, J = 6.5 Hz, 1 H), 6.57 (m, 1 H), 6.72 (d, J = 8.1 Hz, 2 H), 7.20 (m, 1 H), 7.35 (m, 2 H), 7.85 (m, 2 H); ^{13}C NMR δ 33.6, 35.7, 52.3, 60.1, 68.2, 111.8, 116.8, 118.2 (2 C), 126.3 (2 C), 129.3, 129.7, 144.1 (2 C), 146.1. Anal. Calcd for $C_{18}H_{20}N_4O$: C, 70.11; H, 6.54; N, 18.17. Found: C, 69.86; H, 6.57; N, 18.22.

The main resonances of the minor diastereomer **22** in this mixture were as follows: ^{1}H NMR δ 1.20 (m, 2 H), 2.22 (bs, 1 H), 2.72 (m, 2 H), 3.08 (s, 3 H), 3.80 (m, 1 H), 6.18 (d, J = 4.9 Hz, 1 H); ^{13}C NMR δ 31.7, 34.9, 39.3, 51.0, 60.5, 66.0, 111.6, 116.0, 118.2 (2 C), 126.0 (2 C), 130.2, 130.3, 143.8, 146.2.

The second fraction gave a mixture of **23** and **24** (5:1) as an oil. This allowed for full NMR characterization of **23**: ^{1}H NMR δ 1.59 (q, J = 6.3 Hz, 2 H), 2.33 (bs, 1 H), 2.82 (m, 1 H), 2.99 (s, 3 H), 3.18 (dd, J = 8.3 and 12.1 Hz, 1 H), 3.38 (dd, J = 3.8 Hz and 12.1 Hz, 1 H), 3.62 (t, J = 6.3 Hz, 2 H), 6.03 (d, J = 8.0 Hz, 1 H), 6.53 (t, J = 7.7 Hz, 1 H), 6.60 (d, J = 7.7 Hz, 1 H), 6.75 (d, J = 8.3 Hz, 1 H), 6.96 (m, 1 H), 7.14–7.30 (m, 3 H), 7.99 (m, 1 H); ^{13}C NMR δ 33.3, 35.6, 39.3, 53.2, 59.7, 62.4, 111.0, 111.7, 117.0, 117.2, 119.7, 123.8, 127.0, 129.0, 129.6, 131.9, 146.2, 146.7. Anal. Calcd for $C_{18}H_{20}N_4O$: C, 70.11; H, 6.54; N, 18.17. Found: C, 69.92; H, 6.56; N, 18.27.

The third fraction was a mixture of **23** and **24** in a ratio of 1:2. This allowed characterization of diastereomer **24** by NMR: ^{1}H NMR δ 1.08 (m, 1 H), 1.48 (m, 1 H), 2.80 (m, 1 H), 3.06 (s, 3 H), 3.26 (m, 2 H), 3.77 (m, 2 H), 6.16 (d, J = 4.5 Hz, 1 H), 6.52 (m, 2 H), 6.77 (d, J = 8.6 Hz, 1 H), 6.92 (d, J = 7.6 Hz, 1 H), 7.08 (m, 1 H), 7.24 (m, 3 H), 7.95 (m, 1 H); ^{13}C NMR δ 32.0, 35.4, 38.9, 51.9, 59.98, 60.01, 110.6, 111.3, 116.4, 116.8, 119.7, 123.6, 127.1, 128.1, 129.1, 130.1, 133.7, 146.4, 146.7.

2,3,3a,4,5,9b-Hexahydro-5-methylquino[4,3-*b*]furan (20). The crude mixture **16–24** obtained from the reaction of **3a** (14.00 g, 59 mmol) with dihydrofuran was subjected to fractional vacuum distillation (0.3 Torr) to give a fraction distilling at 134–135 °C. According to NMR the fraction consisted of compound **20** and benzotriazole. Washing of an ethereal solution of this mixture with 10% NaOH, drying over Na_2CO_3, and evaporation of the solvent gave pure **20** (6.88 g, 61%).

3-(2-Hydroxyethyl)-1-methyl-1,2,3,4-tetrahydroquinoline (25). Lithium aluminum hydride (1.14 g, 30 mmol) was added portionwise to an anisole (20 mL) solution of the crude mixture obtained from the reaction of **3a** (3.32 g, 14 mmol) with 2,3-dihydrofuran. The obtained mixture was stirred under nitrogen and heated at reflux for 4 h. After cooling to room temperature, the mixture was added in small portions to a stirred mixture of 20% NaOH (100 mL) and crushed ice (50 g). After 1 h at room temperature, the obtained mixture was extracted with ether (2 × 100 mL). The combined extracts were washed with 20% NaOH and water and then dried over anhydrous Na_2CO_3. After evaporation of the ether at atmospheric pressure, the anisole was evaporated using a vacuum pump. The residue was diluted with ether (5 mL) and stored at −5 °C for 20 h. The obtained precipitate was separated, washed with hexane (10 mL), and dried in a vacuum oven to give **25** (2.30 g, 86%) as colorless needles: mp 63 °C; ^{1}H NMR δ 1.60 (m, 2 H), 1.85 (bs, 1 H, OH), 2.16 (m, 1 H), 2.47 (dd, J = 9.9 and 16.0 Hz, 1 H), 2.78–2.97 (m, 5 H), 3.20 (ddd, J = 1.8, 3.6 and 11.1 Hz, 1 H), 3.73 (t, J = 6.3 Hz, 2 H), 6.60 (m, 2 H), 6.93 (d, J = 6.6 Hz, 1 H), 7.06 (m, 1 H); ^{13}C NMR δ 29.2, 34.1, 36.5, 39.1, 56.5, 60.5, 110.8, 116.4, 121.9, 127.0, 129.0, 146.3. Anal. Calcd for $C_{12}H_{17}NO$: C, 75.35; H, 8.96; N, 7.32. Found: C, 75.49; H, 9.16; N, 7.51.

Reduction of a Mixture of 16–24 with $LiAlH_4$ in Dioxane. A dioxane solution (25 mL) of the reaction mixture obtained from the reaction between **3a** (10 mmol), 2,3-dihydrofuran, and $LiAlH_4$ (0.46 g, 12 mmol) was heated at reflux for 8 h. After cooling, the mixture was poured into ice-cold 20% NaOH (50 mL) and extracted with ether (2 × 50 mL). The combined extracts were washed with water, dried over

Na_2CO_3, and evaporated. Column chromatography (hexane/ether, 1:1) of the residue gave compound **20** (0.38 g, 20%) as the first fraction. The second fraction was tetrahydrofuran **26** (0.21 g, 11%): ^{1}H NMR δ 1.62 (m, 1 H), 2.00 (m, 1 H), 2.65 (m, 1 H), 2.93 (s, 3 H), 3.29 (dd, J = 8.0 and 5.3 Hz, 2 H), 3.57 (dd, J = 5.4 and 8.7 Hz, 1 H), 3.72 (m, 1 H), 3.76 (dd, J = 7.0 and 8.6 Hz, 1 H), 3.90 (td, J = 8.1 and 5.2 Hz, 1 H), 6.71 (m, 3 H), 7.22 (m, 2 H); ^{13}C NMR δ 30.1, 38.3, 39.0, 55.6, 67.6, 71.5, 112.5 (2 C), 116.6, 129.2 (2 C), 149.6; HRMS calcd for $C_{12}H_{17}NO$: 191.131, found 191.136.

The third fraction (eluted with ether) gave a mixture of tetrahydroquinolines **21**–**24** (0.46 g, 15%).

The last fraction gave the aniline derivative **27** (0.40 g, 13%) as an oil: ^{1}H NMR δ 1.65 (q, J = 6.2 Hz, 2 H), 2.79 (m, 1 H), 2.92 (s, 3 H), 3.28 (dd, J = 7.5 and 14.7 Hz, 1 H), 3.40 (dd, J = 7.2 and 14.7 Hz, 1 H), 3.69 (t, J = 6.3 Hz, 2 H), 4.66 (m, 2 H), 6.67 (d, J = 8.0 Hz, 2 H), 6.73 (t, J = 7.5 Hz, 1 H), 7.18 (dd, J = 7.4 and 8.2 Hz, 2 H), 7.38 (m, 3 H), 8.03 (d, J = 8.1 Hz, 1 H); ^{13}C NMR δ 33.2, 35.5, 40.2, 50.1, 55.8, 60.2, 109.4, 113.5 (2 C), 117.7, 119.8, 123.9, 127.4, 129.2 (2 C), 133.2, 145.6, 149.4; HRMS calcd for $C_{18}H_{23}N_4O$ (M^+ + H): 311.187, found 311.181.

1,4-Dimethyl-3-(2-hydroxyethyl)-1,2,3,4-tetrahydroquinolines 28 and 29. Reaction of a mixture of **21**–**24** (400 mg, 1.3 mmol) with methylmagnesium iodide according to the procedure given for **12** gave a mixture of **28** and **29** (1:1, 220 mg). Column chromatography (hexanes/ether, 1:1) of this mixture gave compound **28** (98 mg, 37%) as the first fraction, as an oil: ^{1}H NMR δ 1.25 (d, J =7.1 Hz, 3 H), 1.55 (q, J = 6.3 Hz, 2 H), 1.81 (m, 1 H), 2.40 (bs, 1 H), 2.60 (m, 1 H), 2.85 (s, 3 H), 2.90 (m, 1 H), 3.33 (dd, J = 3.6 and 11.7 Hz, 1 H), 3.66 (t, J = 6.3 Hz, 2 H), 6.61 (m, 2 H), 7.06 (m, 2 H); ^{13}C NMR δ 25.0, 35.2, 35.9, 36.7, 39.7, 51.0, 60.9, 111.3, 116.8, 126.9, 127.2, 129.8, 145.7. Anal. Calcd for $C_{13}H_{19}NO$: C, 76.06; H, 9.33; N, 6.82. Found: C, 75.72; H, 9.33; N, 6.82.

Compound **29** (85 mg, 32%) was obtained as an oil from the second fraction: ^{1}H NMR δ 1.10 (d, J = 7.1 Hz, 3 H), 1.62 (m, 4 H), 2.17 (m, 1 H), 2.90 (m, 4 H), 3.11 (m, 1 H), 3.74 (t, J = 6.7 Hz, 2 H), 6.59 (m, 2 H), 6.98 (d, J = 7.2 Hz, 1 H), 7.07 (m, 1 H); ^{13}C NMR δ 17.4, 32.9, 33.0, 35.2, 38.7, 52.0, 61.0, 110.5, 115.9, 127.2, 128.3, 129.2, 145.1. Anal. Calcd for $C_{13}H_{19}NO$: C, 76.06; H, 9.33; N, 6.82. Found: C, 75.75; H, 9.36; N, 6.87.

Reaction of 3a with 3,4-Dihydro-2*H*-pyran. By a procedure similar to the reaction of **3a** with 2,3-dihydrofuran described above, the reaction of **3a** (4.70 g, 20 mmol) with 3,4-dihydro-2*H*-pyran (2.0 mL, 22 mmol) produced a mixture of adducts **32** and tetrahydroquinolines **31** and **35**. The mixture was subjected to column chromatography (hexanes/ether, 2:1) to give a mixture of two diastereomeric Bt-2 derivatives of tetrahydropyran **32** (0.32 g, 5%) as the first fraction.

The second fraction gave compound **31** (1.22 g, 27%) as an oil: ^{1}H NMR δ 1.45 (m, 1 H), 1.70–1.95 (m, 3 H), 2.15 (m, 1 H), 2.89 (s, 3 H), 2.95 (dd, J = 4.0 and 1.0 Hz, 1 H), 3.53 (t, J = 10.8 Hz, 1 H), 3.66 (td, J = 10.2 and 2.4 Hz, 1 H), 3.95 (m, 1 H), 4.42 (d, J = 3.0 Hz, 1 H), 6.62 (d, J = 8.7 Hz, 1 H), 6.68 (dd, J = 0.9 and 7.9 Hz, 1 H), 7.10–7.25 (m, 2 H); ^{13}C NMR δ 22.6, 25.5, 32.4, 39.0, 51.2, 67.3, 74.2, 111.4, 116.4, 121.7, 129.4, 130.6, 146.5; HRMS calcd for $C_{13}H_{17}NO$: 203.131, found 203.135. **Picrate**: yellow needles, mp 109–110 °C. Anal. Calcd for $C_{19}H_{20}N_4O_8$: C, 52.78; H, 4.66; N, 12.96. Found: C, 52.51; H, 4.67; N, 13.03.

The third fraction gave a diastereomeric mixture of benzotriazol-1-yl adducts **32** (1.77 g, 27%) as an oil. Upon cooling of a concentrated solution of this mixture in hexanes/ether (1:1) to −5 °C, the predominant diastereomer **34** (1.10 g, 17%) precipitated as colorless prisms: mp 113–114 °C; ^{1}H NMR δ 1.55 (m, 1 H), 1.77 (m, 2 H), 2.32 (m, 1 H), 2.78 (s, 3 H), 3.05 (m, 1 H), 3.13 (dd, J = 7.9 and 13.9 Hz, 1 H), 3.24 (dd, J = 5.6 and 13.9 Hz, 1 H), 3.74 (ddd, J = 3.8, 9.0 and 12.4 Hz, 1 H), 3.95 (dt, J = 11.5 and 4.1 Hz, 1 H), 5.86 (d, J = 7.7 Hz, 1 H), 6.46 (d, J = 8.5 Hz, 2 H), 6.63 (t, J = 7.2 Hz, 1 H), 7.08 (t, J = 7.6 Hz, 2 H), 7.37 (m, 1 H), 7.46 (m, 1 H), 7.67 (dd, J = 0.9 and 8.3 Hz, 1 H), 8.08 (dd, J = 1.0 and 8.2 Hz, 1 H); ^{13}C NMR δ 24.0, 26.4, 37.1, 39.6, 54.1, 66.9, 88.0, 110.9, 112.0 (2 C), 116.4, 120.0, 124.3, 127.6, 129.0 (2 C), 132.3, 146.4, 149.0. Anal. Calcd for $C_{19}H_{22}N_4O$: C, 70.78; H, 6.88; N, 17.38. Found: C, 70.95; H, 6.93; N, 17.46.

The fourth fraction gave a mixture of tetrahydroquinolines **35** (1.41 g, 22%).

1,4-Dimethyl-3-(3-hydroxypropyl)-1,2,3,4-tetrahydroquinolines 36 and 37. Starting from the mixture of tetrahydroquinolines **35** (1.05 g, 3.2 mmol) and methylmagnesium iodide (10.0 mmol), and following the procedure for **12a** (reaction time 30 min), an equimolar mixture of **36** and **37** was obtained as an oily product (0.59 g, 84%). The first fraction from column chromatography (hexane/ether, 2:1) gave diastereomer **36** as an oil (0.32 g, 45%): ^{1}H NMR δ 1.24 (d, J = 7.1 Hz, 3 H), 1.33 (m, 2 H), 1.58 (m, 3 H), 2.12 (bs, 1 H), 2.60 (m, 1 H), 2.88 (m, 4 H), 3.31 (dq, J = 11.6 and 3.3 Hz, 1 H), 3.55 (t, J = 6.6 Hz, 2 H), 6.61 (m, 2 H), 7.03 (m, 2 H); ^{13}C NMR δ 24.6, 28.8, 30.6, 36.6, 38.3, 39.3, 51.1, 63.0, 110.9, 116.3, 126.8, 126.9, 129.4, 145.6. Anal. Calcd for $C_{14}H_{21}NO$: C, 76.77; H, 9.65; N, 6.39. Found: C, 76.38; H, 9.59; N, 6.40.

The second fraction was found to be a mixture of **37** and **36** in a ratio of 4:1 (oil, 0.21 g, 30%). This allowed for NMR characterization of **37**: ^{1} H NMR δ 1.07 (d, J = 6.8 Hz, 3 H), 1.35 (m, 2 H), 1.65 (m, 2 H), 1.90 (bs, 1 H), 2.00 (m, 1 H), 2.85 (m, 1 H), 2.88 (s, 3 H), 3.06 (m, 1 H), 3.67 (t, J = 6.6 Hz, 2 H), 6.58 (m, 2 H), 6.98 (dd, J = 1.2 and 7.3 Hz, 1 H), 7.05 (m, 1 H); ^{13}C NMR δ 17.3, 26.2, 30.3, 35.1, 35.7, 39.3, 51.9, 63.0, 110.4, 115.8, 127.2, 128.4, 128.5, 145.3. Anal. Calcd for $C_{14}H_{21}NO$: C, 76.77; H, 9.65; N, 6.39. Found: C, 76.42; H, 9.54; N, 6.55.

Reduction of a Mixture of 31–35 with $LiAlH_4$ in Dioxane. A solution of the crude product mixture obtained from the reaction of **3a** (2.7 mmol) with dihydropyran (3.0 mmol) and $LiAlH_4$ (0.12 g, 3.2 mmol) in dioxane (5 mL) was heated at reflux under nitrogen for 5 h. After cooling, the reaction mixture was poured into 20% NaOH (20 mL) and extracted with ether (2 × 20 mL). The combined extracts were washed with 20% NaOH (10 mL) followed by water and dried over Na_2CO_3. After evaporation of the solvent, the residue was subjected to column chromatography (toluene/AcOEt, 9:1). The first fraction gave tetrahydropyran **39** (0.19 g, 26%) as an oil: ^{1}H NMR δ 1.21 (m, 1 H), 1.56 (m, 2 H), 1.78 (m, 1 H), 2.02 (m, 1 H), 2.87 (s, 3 H), 3.10 (m, 2 H), 3.20 (dd, J = 8.8 and 11.0 Hz, 1 H), 3.40 (ddd, J = 3.6, 9.1 and 12.8 Hz, 1 H), 3.78 (m, 2 H), 6.64 (m, 3 H), 7.19 (dd, J = 7.1 and 8.6 Hz, 2 H); ^{13}C NMR δ 24.9, 27.3, 34.8, 39.0, 54.9, 68.2, 71.1, 111.8 (2 C), 115.8, 128.9 (2 C), 149.2; HRMS calcd for $C_{13}H_{19}NO$ 205.147, found 205.146.

The second fraction gave alcohol **38** (0.47 g, 45%) as an oil: ^{1}H NMR δ 1.36 (m, 2 H), 1.61 (m, 2 H), 1.97 (m, 1 H), 2.42 (dd, J = 9.9 and 15.6 Hz, 1 H), 2.65 (bs, 1 H), 2.82 (m, 2 H), 2.84 (s, 3 H), 3.16 (ddd, J = 1.8, 3.9 and 11.1 Hz, 1 H), 3.61 (t, J = 6.0 Hz, 2 H), 6.59 (m, 2 H), 6.93 (d, J = 7.2 Hz, 1 H), 7.05 (t, J = 7.5 Hz, 1 H); ^{13}C NMR δ 29.8 (2 C), 32.1, 34.2, 39.0, 56.6, 62.6, 110.7, 116.3, 122.1, 126.9, 128.8, 146.2. Anal. Calcd for $C_{13}H_{19}NO$: C, 76.06; H, 9.33; N, 6.82. Found: C, 75.91; H, 9.40; N, 7.03.

The third fraction gave alcohol **40** (0.092 g, 10%) as an oil: ^{1}H NMR δ 0.87 (m, 1 H), 1.48 (m, 2 H), 1.63 (m, 2 H), 2.64 (m, 1 H), 2.98 (s, 3 H), 3.30 (dd, J = 8.3 and 14.6 Hz, 1 H), 3.41 (dd, J = 6.6 and 14.6 Hz, 1 H), 3.57 (t, J = 6.4 Hz, 2 H), 4.62 (d, J = 6.9 Hz, 2 H), 6.68 (d, J = 8.2 Hz, 1 H), 6.74 (t, J = 7.2 Hz, 1 H), 7.21 (m, 2 H), 7.30–7.46 (m, 4 H), 8.06 (d, J = 8.2 Hz, 1 H); ^{13}C NMR δ 26.6, 29.5, 37.8, 39.9, 50.0, 55.6, 62.7, 109.3, 113.0 (2 C), 117.1, 120.1, 123.9, 127.4, 129.3 (2 C), 133.2, 145.9, 149.5; HRMS calcd for $C_{19}H_{25}N_4O$ (M^+ + 1) 325.203, found 325.203.

3-(3-Hydroxypropyl)-1-methyl-1,2,3,4-tetrahydroquinoline (38). The crude product mixture obtained from the reaction of **3a** (2.38 g, 10 mmol) with 3,4-dihydro-2*H*-pyran was reduced with $LiAlH_4$ (0.76 g, 20 mmol) in anisole (10 mL) following the procedure given for **25**. Column chromatography of the crude product (hexane/ether, 2:1) gave analytically pure **38** (1.56 g, 76%) as an oil.

Reaction of 41 with Ethyl Vinyl Ether. A solution of **41** (3.30 g, 10 mmol), ethyl vinyl ether (2.0 mL), and *p*-toluenesulfonic acid monohydrate (20 mg) in chloroform (50 mL) was stirred under nitrogen for 30 min. The reaction mixture was added to water, and washed with 10% Na_2CO_3,

followed by water and dried. Evaporation of the solvent afforded a dark orange oil which consisted (by NMR) mainly of **42** and **43** in a molar ratio of 1:1. Trituration with toluene and cooling gave **43** (1.50 g, 42%) as a solid, which was additionally purified by column chromatography (chloroform), mp 253–255 °C dec; ^{1}H NMR δ 2.66 (m, 1 H), 2.84 (m, 1 H), 3.76 (ddd, J = 3.6, 7.8 and 12.3 Hz, 1 H), 3.85 (ddd, J = 3.9, 8.1 and 12.6 Hz, 1 H), 6.29 (dd, J = 4.5 and 7.5 Hz, 1 H), 6.58 (dd, J = 0.9 and 7.8 Hz, 1 H), 6.77 (t, J = 7.5 Hz, 1 H), 6.84 (dd, J = 1.2 and 8.1 Hz, 1 H), 7.00 (m, 2 H), 7.15 (m, 3 H), 7.30 (m, 2 H), 8.08 (m, 1 H); ^{13}C NMR δ 28.4, 43.1, 56.6, 110.5, 113.4, 120.1, 120.3 (2 C), 121.0, 121.9, 122.5, 123.2, 123.9, 127.3 (2 C), 127.4, 127.5, 127.7, 127.9, 132.3, 142.1. Anal. Calcd for $C_{21}H_{16}N_4S$: C, 70.76; H, 4.52; N, 15.72. Found: C, 71.00; H, 4.54; N, 15.71.

The solvent was evaporated from the filtrate described above, and the oily residue was subjected to column chromatography (toluene) to give **42** (0.99 g, 35%) as an oil: ^{1}H NMR δ 1.19 (t, J = 6.8 Hz, 3 H), 2.09 (m, 1 H), 2.30 (m, 1 H), 3.57 (m, 3 H), 3.79 (td, J = 12.0 and 3.3 Hz, 1 H), 4.29 (t, J = 3.2 Hz, 1 H), 6.83 (m, 3 H), 7.03 (m, 4 H); ^{13}C NMR δ 15.4, 26.8, 40.8, 63.2, 72.1, 113.0, 118.1, 119.8, 121.2, 122.5, 123.3, 126.7, 127.1, 127.3, 128.7, 141.1, 144.0. Anal. Calcd for $C_{17}H_{17}NOS$: C, 72.05; H, 6.05; N, 4.94. Found: C, 72.05; H, 6.06; N, 4.98.

Compound 44. Compound **43** (1.10 g, 3 mmol) was reduced with $LiAlH_4$ in refluxing THF for 2 h to give aniline derivative **44** as an oil (0.75 g, 76%): ^{1}H NMR δ 2.17 (m, 1 H), 2.33 (m, 1 H), 3.68 (m, 2 H), 3.82 (m, 1 H), 4.55 (bs, 1 H), 6.65 (d, J = 7.5 Hz, 2 H), 6.73 (t, J = 7.5 Hz, 1 H), 6.83 (m, 2 H), 6.89 (td, J = 7.5 and 0.9 Hz, 1 H), 6.98 (dd, J = 1.5 and 7.5 Hz, 1 H), 7.09 (m, 3 H), 7.19 (dd, J = 7.2 and 8.1 Hz, 2 H); ^{13}C NMR δ 26.2, 41.9, 49.3, 112.9, 113.0, 117.7, 120.1, 121.6, 122.1, 122.7, 125.1, 126.8, 127.0, 127.4, 128.1, 128.2, 129.4 (2 C), 141.3, 144.0, 146.4. Anal. Calcd for $C_{21}H_{18}N_2S$: C, 76.53; H, 5.49; N, 8.48. Found: C, 76.22; H, 5.53; N, 8.25.

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