Experimental Evidence for Intramolecular *ipso* Substitution of Alkyl Groups[‡]

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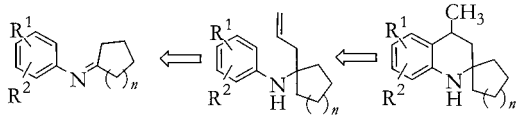
An acid-mediated intramolecular Friedel–Crafts intramolecular alkene alkylation of the *ortho*-alkyl group in the *N*-arylamino moiety of various *N*-(1-allylcycloalkyl)-*N*-arylamines resulting in alkyl-substituted 3′,4′-dihydro-1′*H*-spiro[cycloalkane-1,2′-quinolines] is described. The mechanistic details of this intramolecular Friedel–Crafts alkylation by an alkene moiety can be explained by an intramolecular alkylation with *ipso* substitution of alkyl groups and their 1,2-rearrangement. The scope and limitations of this reaction were determined. As a conclusive proof of the proposed mechanism, previously unknown interesting by-products, dispiro[quino[6,7-*f*]quinoline-3,1′:9,1′′-bis(cycloalkanes), were isolated and characterized.

Introduction

Electrophilic aromatic substitution via Wheland complexes is the classical method for functionalizing aromatic and heteroaromatic compounds. Friedel−Crafts alkylation differs from all other aryl S_E reactions in that the reaction products are better nucleophiles than the starting material. This decreases the synthetic value of this method. However, there is a beautiful possibility for improving this situation. An intramolecular version of the Friedel−Crafts alkylation, promoted by Brønsted or Lewis acids[1] has become an efficient method for the rapid construction of many carbo- and heterocyclic compounds,[2] including many biologically and pharmacologically active quinoline and tetrahydroquinoline derivatives.[3] The most general method to obtain these compounds involves an intramolecular cyclisation starting from a suitably substituted aniline derivative. Moreover, many new methods for the synthesis of tetrahydroquinoline derivatives have been developed.[4] However, there are very few publications that describe the construction of the tetra- or dihydroquinoline rings spiro-annulated at position C-2 with cycloalkanes[4d−4g] or other heterocycles. Thus, the chemistry and biological activity of this type of spiro-heterocyclic compounds remain largely unexplored. As part of our research program towards the preparation of drug-like heterocyclic molecules from imines, we developed a practical synthesis of the 3′,4′-dihydro-4′-methyl-1′*H*-spiro[cycloalkane-1,2′-quinolines] based on the reactivity of accessible ketimines[5] (Scheme 1). The ketimines are transformed into the corresponding *gem*-allyl-*N*-(arylamino)cycloalkanes through an addition of the Grignard reagent, allylmagnesium bromide. These amines, possessing a π-electron-rich aromatic ring, a basic nitrogen atom and an allyl fragment (an electrophilic C_3 synthon), represent versatile synthetic intermediates for the construction of quinolines spiro-annulated at C-2.



n = 1-4

Scheme 1

While the synthetic potential of intramolecular Friedel−Crafts alkylation is well documented, there have been no reports of intramolecular alkene alkylation in which *ipso* attack at a carbon atom attached to an alkyl group plays a pivotal role in the preparation of alkyl-substituted dihydro-1′*H*-spiro[cycloalkane-1,2′-quinolines]. We recently reported an unprecedented intramolecular Friedel−Crafts alkylation with an alkene group in the series

[‡] Intramolecular Friedel−Crafts Alkylation of *N*-(*ortho*-Alkylaryl)-*N*-(1-allylcycloalkyl)amines as an Entry to the Synthesis of Alkyl-Substituted 3′,4′-Dihydro-1′*H*-spiro[cycloalkane-1,2′-quinolines], 1

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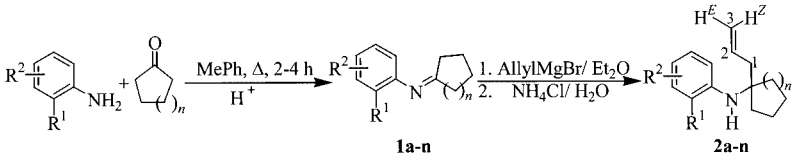


1a-n **2a-n**

2	a	b	c	d	e	f	g	h	i	k	l	m	n
R^1	Me	Me	Me	Me	Me	Et	Et	*i*Pr	Bn	Me	Me	Me	Et
R^2	H	H	H	*p*-Me	*m*-Me	H	H	H	H	*o*'-Me	*o*'-Me	*o*'-Et	*o*'-Et
n	1	2	3	2	2	1	2	2	2	1	2	2	2
Yield (%)	73	81	82	70	82	69	82	65	52	36	65	51	50

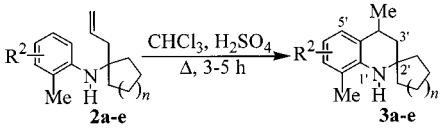
Scheme 2

of *ortho*-methyl(or -ethyl)-substituted *N*-(1-allylcycloalkyl)-*N*-(*ortho*-R-aryl)amines.[6] Now we describe our investigations, which include some mechanistic details on this intramolecular Friedel−Crafts alkylation that easily undergo the *ipso* substitution of methyl or ethyl groups and a practical synthesis of 5′,8′-dimethyl(or -diethyl)-3′,4′-dihydro-1′*H*-spiro[cycloalkane-1,2′-quinolines], which can serve as useful semiproducts in drug preparation.

Results and Discussion

Starting ketimines **1a**−**n** were easily prepared from the corresponding anilines and cycloalkanones in boiling toluene in the presence of catalytic amounts of glacial AcOH (**1a**−**i**) or *p*TsOH (**1k**−**n**) using a Dean−Stark apparatus. According to our approach to 3′,4′-dihydro-1′*H*-spiro[cycloalkane-1,2′-quinolines], the homoallylamines **2a**−**n** were obtained easily from accessible cycloalkanone imines and allylmagnesium bromide in an overall yield of 36−82% (from the anilines, calculated after distillation and purification processes) (Scheme 2).

Cyclisation of the key substrates **2a**−**n** was performed using a seven-fold excess of concd. H_2SO_4 over 3−5 h in boiling chloroform. The cyclisation of (*o*-methylphenyl)-amines **2a**−**e** proceeded smoothly to give 8-alkyl-substituted quinolines **3a**−**e** in 66−84% yields (Scheme 3). The so-obtained 8′-methyl-substituted dihydrospiro[cycloalkane-1,2′-quinolines] are of interest in our investigations into spiro analogs of marine alkaloids.[7] It is noteworthy that in all cases, GC-MS analysis of the crude reaction mixtures in the formation of **3a**−**e** did not show any appreciable amounts of side products.

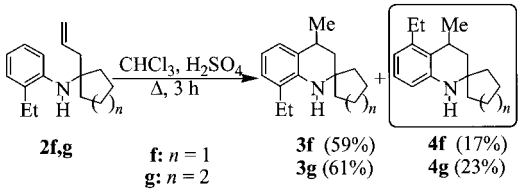


2a-e **3a-e**

3	a	b	c	d	e
R^2	H	H	H	6'-Me	7'-Me
n	1	2	3	2	2
Yield (%)	66	84	79	83	83

Scheme 3

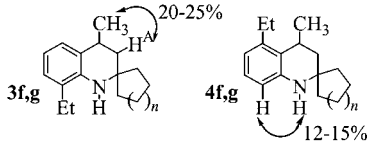
However, cyclisation of the *ortho*-ethyl-substituted analogs **2f**,**g** gave the desired 8-ethyl-substituted tetrahydroquinolines **3f**,**g** (in 59 and 61% yields, respectively) together with the unexpected 5-ethyl-substituted 1,2,3,4-tetrahydroquinolines **4f**,**g** (17 and 23% yields, respectively) (Scheme 4). Compounds **3f**,**g** and **4f**,**g** were purified and separated by alumina column chromatography as colorless oils with similar retention factors. The mass and IR spectra of the isomeric quinolines **3f**,**g** and **4f**,**g** were virtually the same (see Exp. Sect.).



2f,g **f:** *n* = 1 **g:** *n* = 2 **3f** (59%) **3g** (61%) **4f** (17%) **4g** (23%)

Scheme 4

The ^1H and ^{13}C NMR spectroscopic data allowed only an unambiguous statement of the formation of the 4-methyltetrahydroquinoline ring. Thus, the ^1H NMR spectra displayed the signals of the three aromatic protons. The position of the ethyl group could be differentiated between the pairs **3f**/**4f** and **3g**/**4g** using NOE experiments (Figure 1).



3f,g **4f,g**

Figure 1. Results of NOE experiments on **3f**/**4f** and **3g**/**4g**

Moreover, the X-ray crystal structures of hydrochloride **4f**,**g** unambiguously confirmed their structures as the 3′,4′-dihydro-5′-ethyl-4′-methyl-1′*H*-spiro[cycloalkane-1,2′-quinolines]. The salt of **4g** occurs in two forms **A** and **B** (Figure 2).[8] The crystallographically independent cations **A** and **B** have similar geometrical parameters, and differ only in the orientation of the ethyl group [torsion angles C(9)−C(10)−C(16)−C(17) and C(11)−C(10)−C(16)−C(17) have values of 154.6 and −30.3° (**A**), and −123.4 and 53.8° (**B**), respectively]. The projections of forms **A** and **B** with superimposed phenyl groups are shown in Figure 2.

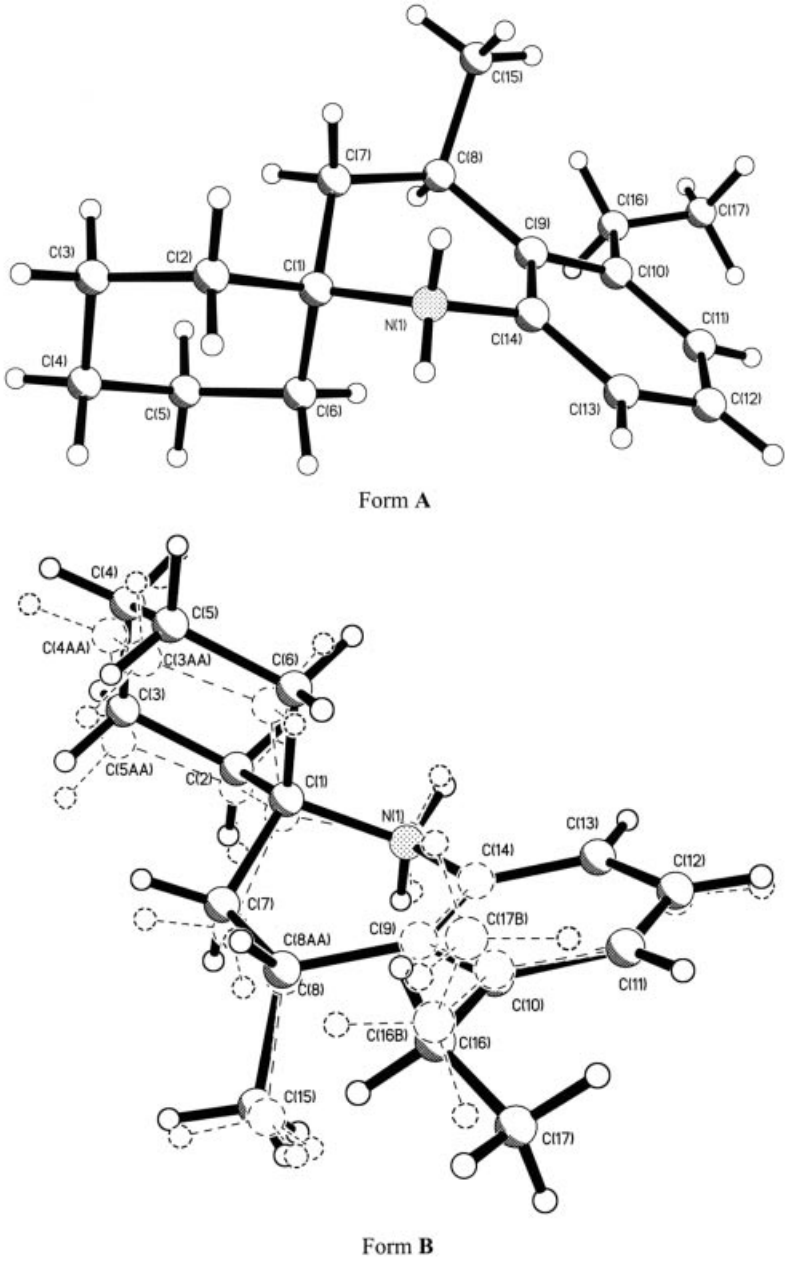
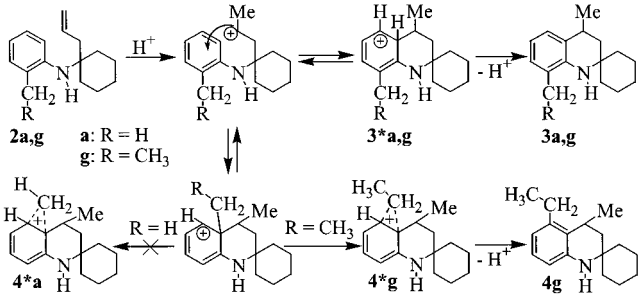


Figure 2. X-ray crystal structure of **4g** (Forms **A** and **B**)

The spirocyclohexane ring has a chair conformation, and the piperidine part of the molecule possesses a half-chair conformation with the respective deviations of the C(1) and C(7) atoms from the plane of the four atoms C(8),C(9),C(14),N(1) being −0.85 and −0.20Å in cation **A** and −0.70 and 0.05Å in cation **B**. The bond C(1)−N(1) has a pseudo-equatorial orientation, and C(1)−C(7) is pseudo-axial. These cations are linked to the chloride anions by N−H···Cl hydrogen bonds in this crystal. These structural interactions result in dimeric cation−anion pairs $\{\mathbf{A}\cdots Cl\}_2$ and $\{\mathbf{B}\cdots Cl\}_2$.

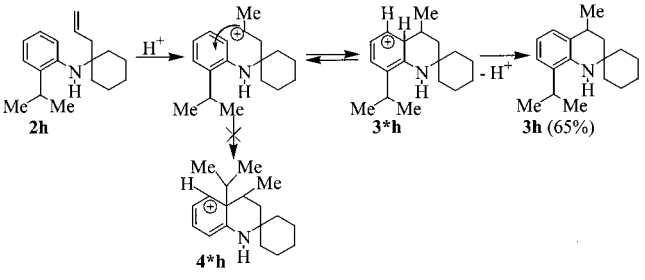
These results could be explained by an intramolecular alkylation with *ipso* substitution of the ethyl group in **2f**,**g**. It is noteworthy that cases of intramolecular *ipso* substitution of the *ortho*-alkyl group in the presence of a second free *ortho′* position have not been observed. Usually, a proton is replaced by the electrophile, but in an *ipso* substitution, another substituent is replaced. In most cases, the nucleophilic carbon atom of the arene has a hydrogen atom attached.[9] Moreover, intermolecular *ipso* attack[10] has mostly been studied for nitration[10a,10b] and halogenation[10c,10d] reactions. A plausible mechanism for this type of intramolecular Friedel−Crafts alkene alkylation promoted by Brønsted acid is proposed in Scheme 5. Thus, the Wheland intermediates **3*a**,**g** were formed as the result of electrophilic attack at the free *ortho* position. Loss of H^+ from C-4a then afforded the 8-alkyl-substituted tetrahydroquinolines **3a**,**g**. However, when the carbocation formed from the allyl fragment attacks at the carbon atom attached to the alkyl group, *ipso* attack occurs, resulting in the for-

mation of the alternative Wheland intermediates **4*a**,**g**. A 1,2-shift of the ethyl group from C-4a to C-5, followed by loss of H^+, gives rise to the isomeric 5-ethyl-substituted tetrahydroquinoline **4g**. We assume that methyl group in the ethyl radical can stabilize the three-center cationic species **4*g** by both induction and hyperconjugation effects.[11] In the case of **2a**, the formation of intermediate **4*a** is difficult because the hydrogen atom cannot stabilize the cationic center (Scheme 5).



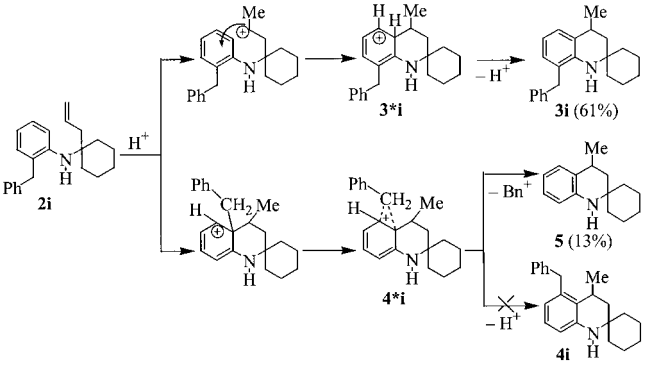
Scheme 5

Next, we tested specially synthesized *ortho*-isopropyl and *ortho*-benzyl derivatives **2h** and **2i** in acid-mediated alkene alkylation. We anticipated that the presence of these groups in the *N*-arylamino moiety of *N*-(1-allylcycloalkyl)-*N*-arylamines would increase the stability of the alkyl cation compared to the ethyl-substituted analogs. However, our experiments gave unexpected results. Thus, acid-mediated cyclisation of **2h** led to the 8-isopropyl-substituted tetrahydroquinoline **3h** in good yield by formation of the Wheland intermediate **3*h** (Scheme 6). No by-products were observed in the crude reaction mixture. In this case, we assume that the *ipso* attack at the carbon atom attached to the bulky isopropyl group does not occur because of the high steric barrier towards the formation of intermediate **4*h**.



Scheme 6

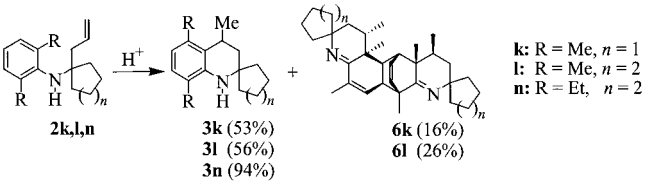
From the cyclisation of *ortho*-benzyl derivative **2i**, in addition to the "common" 8-substituted product **3i** (61% yield), we observed and isolated the debenzylation[12] product **5**[13] (13% yield) (Scheme 7).



Scheme 7

The intermediate **4*i**, resulting from *ipso* attack, would be likely to eliminate a stable benzyl cation rather than a proton. The benzyl elimination process is also favored by the presence of a *peri* interaction between the 5-benzyl and 4-methyl groups in the anticipated structure **4i** (whose formation has not been observed).

These interesting results stimulated us to investigate the intramolecular alkene alkylation process in another series, the *ortho*,*ortho'*-dialkyl-substituted compounds **2k**−**n**. To our surprise, treatment of the *ortho*,*ortho'*-diethyl-substituted allyl(arylamino)cyclohexane **2n** under the same conditions readily afforded the 5,8-diethyl-substituted spirane **3n** in an almost quantitative yield (94%) (Scheme 8). In this case, as both *ortho*-carbon atoms attached to ethyl groups are equivalent, *ipso* attack proceeded smoothly, and was followed by a 1,2-shift of an ethyl group and loss of H^+ to reconstitute the aromatic system.



Scheme 8

We were very surprised by the result of the intramolecular alkylation in the cases of *ortho*,*ortho'*-dimethyl-substituted allyl(arylamino)cyclohexanes **2k**,**l**. Besides the *ipso*-substitution products **3k**,**l**, which were obtained in 53−56% yield, we isolated the polyheterocycles **6k**,**l** (16−26%), which had an unprecedented spiro structure. Their spectroscopic data (^1H and ^{13}C NMR and MS data) did not allow an unambiguous assignment of their structures. However, X-ray analysis of the product **6l**[7] proved its dimeric nature. As shown in Figure 3, the central bicyclo[2.2.2]octene fragment of **6l** is *endo*-fused to a piperidine ring, and *exo*-fused to a cyclohexene moiety. The spirocycloalkane fragments of polyheterocycle **6l** have chair conformations, and the reduced six-membered quinoline rings, unexpectedly spiro-substituted by the cycloalkane moieties at C(1) and C(23),

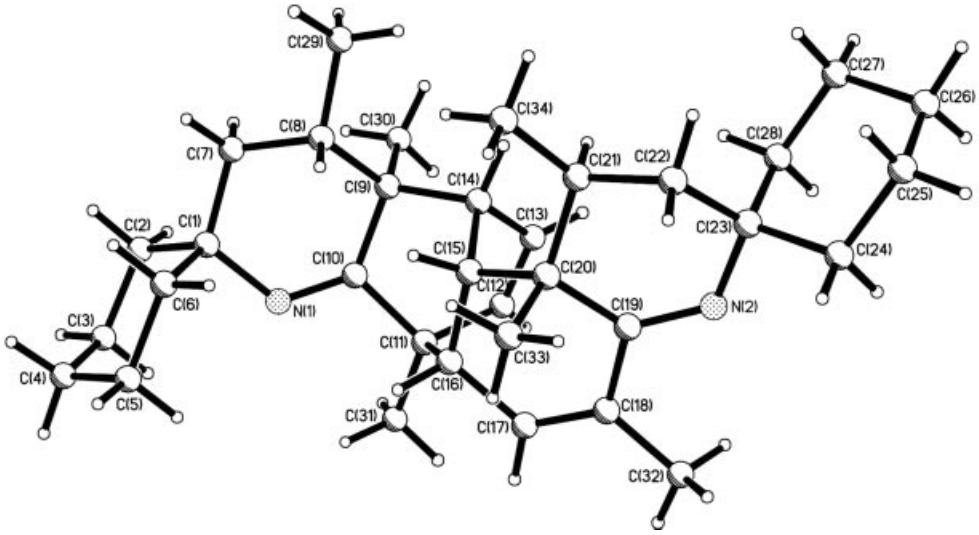
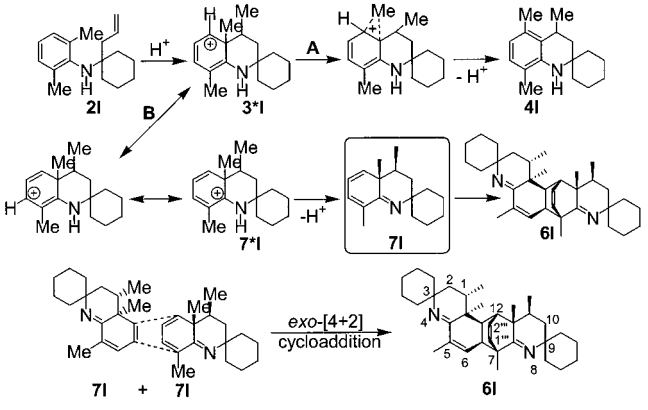


Figure 3. X-ray crystal structure of **6l**

adopt "envelope" conformations in which atoms C(8) and C(21) lie away from the mean planes of the other five atoms in the rings by 0.67 and 0.61Å, respectively (crystallographic numbering is used throughout). The methyl groups attached to C(8) and C(21) are orientated equatorially. They deviate from the corresponding planes by 0.63 and 0.53Å, respectively. The vicinal methyl groups at C(8) and C(9) have a *cis* orientation. The other methyl groups at C(20) and C(21) are orientated in a similar manner.

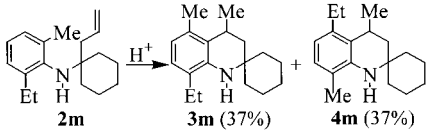
This interesting finding could be also interpreted by the intramolecular *ipso* attack at the carbon atom attached to the methyl group. A plausible mechanistic explanation for the formation of this product **6l** is proposed in Scheme 9. The Wheland intermediate **3*l**, formed by *ipso* attack, can be stabilized not only by a 1,2-shift of the methyl group to give the 5,8-dimethyl-substituted spirane **4l** (route A), but also by loss of H^+ from the resonance-stabilized structure **7*l** (route B), resulting in the 2,3,4,4a-tetrahydroquinoline **7l**, a precursor of polycyclic product **6l**.



Scheme 9

The presence of compound **7l** in the reaction mixture was proved by ^{1}H NMR spectroscopy, but all attempts to isolate it by alumina column chromatography met with failure. As shown in Scheme 9, this compound has a *cis*-diene structure and presumably exists long enough to dimerize, acting as both a diene and a dienophile. It is noteworthy that this dimerization process is highly stereoselective for the *endo* adduct **6l**.

It is noteworthy that the cyclisation of **2m**, which bears two different *ortho* substituents, occurs with no regioselectivity, giving two isomeric tetrahydroquinolines **3m** and **4m** in a ratio of ca. 1:1 in an overall yield of 77% (Scheme 10). The two possible *ipso* attacks are probably equivalent in this case.

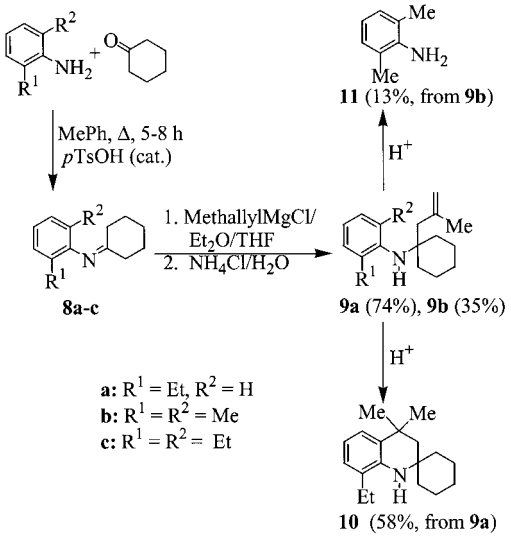


Scheme 10

All attempts to isolate these isomeric products by alumina column chromatography met with failure because their physical and chemical properties are similar. Analysis of their structures was carried out by means of correlation ^{1}H-^{13}C NMR spectra of the isomeric mixture. It is interesting to note that only the *ortho*,*ortho'*-dimethyl derivatives **2k**,**l** could form dimers (**6k**,**l**); the diethyl analogue **2n** and similar derivative **2m** did not give the corresponding dimers. The ethyl group appears to give significant steric hindrance in the transition state of the diene dimerization reaction.

To determine the scope and limitations of acid-mediated intramolecular alkene alkylation of *N*-(arylamino)cyclohexanes bearing an alkene moiety, we synthesized another series of methallyl-substituted (arylamino)cyclohexanes **9a**,**b** from ketimines **8a**,**b** (Scheme 11). The *ortho*,*ortho'*-dimethyl derivative **9a** was prepared by refluxing the corresponding imine (**8a**) and (methallyl)magnesium chloride in

an Et_2O/THF mixture in poor yield (35%). Ketimine **8c** ($R^1 = R^2 = Et$) did not react with (methallyl)magnesium chloride in either THF or dioxane at reflux. Finally, it is noteworthy that a conventional procedure for imine formation (condensation of reagents in boiling toluene in the presence of *p*TsOH) turned out to be more convenient for the synthesis of the hindered ketimines **8a−c** and **1k−m** derived from *o*,*o*′-dialkylanilines than the recently described imine synthesis where the keto form reaction was used.[14]



Scheme 11

The chemical behavior of substrates **9a**,**b** was studied under the previously described conditions of cyclisation. In the case of **9a** ($R^1 = Et$, $R^2 = H$), cyclisation proceeded smoothly at the free *ortho*′ position to give the 8-ethyl-substituted 1,2,3,4-tetrahydroquinoline **10** in good yield, while similar treatment of **9b** ($R^1 = R^2 = Me$) led only to the degradation product 2,6-dimethylaniline **11** in poor yield (Scheme 11). In both cases, we did not observe any *ipso* substitution products. Such an outcome could be due to the poor electrophilic reactivity of the tertiary carbocation generated from the methallyl fragment compared to the secondary carbocation derived from an allyl radical.

Conclusion

We have studied the chemical behavior of the 1-[(*ortho*-alkylaryl)amino]-1-allyl(methallyl)cycloalkanes under acidic conditions. Whilst carrying out classical intramolecular Friedel−Crafts alkene alkylation reactions, we discovered a previously unknown alkylation process in which intramolecular *ipso* substitution of the *ortho*-alkyl group in the *N*-arylamino moiety of the *N*-(1-allylcycloalkyl)-*N*-arylamines takes place. Intramolecular *ipso* attack at the carbon atom attached to the methyl (ethyl) group provides an attractive alternative route to alkyl-substituted C-2-spiro-annulated 1,2,3,4-tetrahydroquinolines. During this study, previously unknown by-products, the dispiro[quino[6,7-*f*]quinoline-3,1′:9,1′′-bis(cycloalkanes)], were isolated and characterized. Efforts are in progress to elucidate the mechanistic details of this intramolecular Friedel−Crafts alkene alkylation and to study the chemical behavior of the dispiro-[quino[6,7-*f*]quinoline-3,1′:9,1′′-bis(cycloalkanes)] **6k** and **6l.**

Experimental Section

General Remarks: All reagents for synthesis were purchased from Acros Chemical Co. All solvents were used without further purification. Melting points were determined using a Fisher−Johns melting point apparatus and are uncorrected. IR spectra were obtained with a UR-20 spectrometer using KBr pellets for solids and thin films for oils. ^1H and ^{13}C NMR spectra were recorded with Bruker WP-200 (^1H 200 MHz), WH-400 or Varian UNITY+400 (^1H 400 MHz, ^{13}C 100.6 MHz) spectrometers with solutions (2%) in deuteriochloroform or [D_6]DMSO at 30 °C, and using TMS as an internal standard. Chemical shifts are reported in ppm, and coupling constants (*J*) are quoted in Hz. Designations [a], [b], [c], [d], [e] indicate possible reverse assignment of the marked signals. Mass spectra were obtained by electron impact at 70 eV with a Varian MAT-112 spectrometer or Finnegan MAT95XL chromatomass spectrometer. Microanalyses were performed with a Perkin−Elmer 2400 Series II analyzer. The purity of the obtained substances and the composition of the reaction mixtures were monitored by TLC Silufol UV_{254} or Sorbfil plates (using hexane/ethyl acetate, 10:1 as eluent). X-ray data of compounds **4g** and **6l** were collected with a "Cad-4" 3-circle diffractometer at 293 K using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å, ω-scan, $2° \le 2\theta \le 60°$). The software packages used were: SMART[15] for collecting frames of data, indexing, integration of intensity of reflections and scaling; SADABS[16] for empirical absorption correction for structure **4g** and **6l**. The structures were solved by direct methods using the SHELXS-97 program and refined against F^2 in an anisotropic approximation for metal and chlorine atoms using the SHELXL-97 package.[16b,16c] The H atoms were located at calculated positions. Atomic coordinates, bond lengths, bond angles and thermal parameters of these molecules have been deposited at the Cambridge Crystallographic Data Centre (CCDC).[8]

Preparation of Homoallylamines 2a−n and Methallyl Derivatives 9a,b. General Procedure: The corresponding aldimine (0.30 mol) (see Discussion − Schemes 2 and 11) was slowly added dropwise to a stirred solution of allylmagnesium bromide, prepared from allyl bromide (39 mL, 0.45 mol) and magnesium turnings (22.0 g, 0.90 mol), in absolute ether (300 mL) at reflux (for amines **2a−n**), or to a solution of (methallyl)magnesium chloride, prepared from methallyl chloride (41 mL, 0.45 mol) and magnesium turnings (22.0 g, 0.90 mol) in a mixture of THF/ether (1:1; 300 mL) at reflux (for amines **9a**,**b**). After the addition of the Schiff base, the reaction mixture was stirred at room temperature for 1 h. The cooled reaction mixture was taken up in saturated aqueous NH_4Cl solution (300 mL) under ice cooling, and the mixture was extracted with diethyl ether (3 × 120 mL). The organic layer was dried with $MgSO_4$ and concentrated. The residue was distilled in vacuo to give the products, **2a−n** or **9a**,**b**, as a colorless oils [except for *N*-(1-allylcyclohexyl)-*N*-(2′-benzylphenyl)amine (**2i**), which was recrystallized from hexane after removal of ether].

***N*-(1-Allylcyclopentyl)-*N*-(2′-methylphenyl)amine (2a):** Yield 73%, R_f = 0.62, b.p. 122−125 °C/1.5 Torr. IR (film): $\tilde{\nu}$ = 3437 (NH), 1635 (C=C) cm^{-1}. ^1H NMR ($CDCl_3$, 200 MHz): δ = 1.55−2.05

(m, 8 H, cycloalkyl H), 2.07 (s, 3 H, 2′-Me), 2.55 (d, J = 7.3 Hz, 2 H, 1-H_{allyl}), 3.53 (br. s, 1 H, NH), 4.92 (m, J = 17.1, 2.4 Hz, 1 H, 3-H^{Z}_{allyl}), 5.00 (m, J = 10.4, 2.4 Hz, 1 H, 3-H^{E}_{allyl}), 5.73 (ddt, J = 17.1, 10.4, 7.3 Hz, 1 H, 2-H_{allyl}), 6.59 (dt, J = 7.3, 0.9 Hz, 1 H, 4′-H), 6.77 (dd, J = 7.3, 0.9 Hz, 1 H, 6′-H), 7.02 (dd, J = 7.3, 0.9 Hz, 1 H, 3′-H), 7.04 (dt, J = 7.3, 0.9 Hz, 1 H, 5′-H) ppm. $C_{15}H_{21}N$ (215.4): calcd. C 83.72, H 9.77, N 6.51; found C 83.81, H 9.95, N 6.61.

***N*-(1-Allylcyclohexyl)-*N*-(2′-methylphenyl)amine (2b):** Yield 81%, R_f = 0.65, b.p. 118−122 °C/2 Torr; n_D^{23} = 1.5494. IR (film): $\tilde{\nu}$ = 3445 (NH), 1638 (C=C) cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 1.64−1.32 (m, 8 H, cycloalkyl H), 2.06−2.01 (m, 2 H, cycloalkyl H), 2.19 (s, 3 H, 2′-Me), 2.56 (d, J = 7.3 Hz, 2 H, 1-H_{allyl}), 3.38 (br. s, 1 H, NH), 5.02 (dd, J = 17.4, 2.2 Hz, 1 H, 3-H^{Z}_{allyl}), 5.06 (dd, J = 10.2, 2.2 Hz, 1 H, 3-H^{E}_{allyl}), 5.79 (ddt, J = 17.4, 10.2, 7.3 Hz, 1 H, 2-H_{allyl}), 6.65 (t, J = 7.3 Hz, 1 H, 4′-H), 6.90 (d, J = 7.3 Hz, 1 H, 6′-H), 7.02 (d, J = 7.3 Hz, 1 H, 3′-H), 7.10 (br. t, J = 7.3 Hz, 1 H, 5′-H) ppm. $C_{16}H_{23}N$ (229.4): calcd. C 83.84, H 10.04, N 6.11; found C 83.75, H 10.13, N 6.17.

***N*-(1-Allylcycloheptyl)-*N*-(2′-methylphenyl)amine (2c):** Yield 82%, R_f = 0.62, b.p. 125−127 °C/1.5 Torr. IR (film): $\tilde{\nu}$ = 3439 (NH), 1642 (C=C) cm^{-1}. ^1H NMR ($CDCl_3$, 200 MHz): δ = 1.50−1.78 (m, 10 H, cycloalkyl H), 1.99 (m, 2 H, cycloalkyl H), 2.15 (s, 3 H, 2′-Me), 2.54 (d, J = 7.5 Hz, 2 H, 1-H_{allyl}), 3.39 (br. s, 1 H, NH), 4.98 (br. d, J = 17.1 Hz, 1 H, 3-H^{Z}_{allyl}), 5.00 (br. s, J = 10.6 Hz, 1 H, 3-H^{E}_{allyl}), 5.75 (ddt, J = 17.1, 10.6, 7.5 Hz, 1 H, 2-H_{allyl}), 6.62 (t, J = 7.5 Hz, 1 H, 4′-H), 6.86 (d, J = 7.5 Hz, 1 H, 6′-H), 7.05 (d, J = 7.5 Hz, 1 H, 3′-H), 7.06 (t, J = 7.5 Hz, 1 H, 5′-H) ppm. $C_{17}H_{25}N$ (243.4): calcd. C 83.95, H 10.29, N 5.76; found C 83.80, H 10.17, N 5.59.

***N*-(1-Allylcyclohexyl)-*N*-(2′,4′-dimethylphenyl)amine (2d):** Yield 70%, R_f = 0.61, b.p. 144−145 °C/ 1.5 Torr; n_D^{23} = 1.5461. IR (film): $\tilde{\nu}$ = 3448 (NH), 1639 (C=C) cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 1.60−1.45 (m, 8 H, cycloalkyl H), 1.96 (m, 2 H, cycloalkyl H), 2.12 (s, 3 H, 2′-Me), 2.20 (s, 3 H, 4′-Me), 2.47 (d, J = 7.2 Hz, 2 H, 1-H_{allyl}), 3.19 (br. s, 1 H, NH), 4.97 (m, J = 17.6, 1.2 Hz, 1 H, 3-H^{Z}_{allyl}), 5.01 (m, J = 10.2, 1.2 Hz, 1 H, 3-H^{E}_{allyl}), 5.75 (ddt, J = 17.6, 10.2, 7.2 Hz, 1 H, 2-H_{allyl}), 6.76 (d, J = 7.9 Hz, 1 H, 6′-H), 6.86 (br. s, 1 H, 3′-H), 6.85 (br. d, J = 7.9 Hz, 1 H, 5′-H) ppm. $C_{17}H_{25}N$ (243.4): calcd. C 83.95, H 10.29, N 5.76; found C 83.87, H 10.13, N 5.59.

***N*-(1-Allylcyclohexyl)-*N*-(2′,3′-dimethylphenyl)amine (2e):** Yield 82%, R_f = 0.71, b.p. 161−165 °C/3 Torr; n_D^{20} = 1.5517. IR (film): $\tilde{\nu}$ = 3440 (NH), 1641 (C=C) cm^{-1}. ^1H NMR ($CDCl_3$, 200 MHz): δ = 1.65−1.20 (m, 8 H, cycloalkyl H), 1.99 (m, 2 H, cycloalkyl H), 2.05 (s, 3 H, 2′-Me), 2.26 (s, 3 H, 3′-Me), 2.49 (d, J = 7.3 Hz, 2 H, 1-H_{allyl}), 3.33 (br. s, 1 H, NH), 4.97 (m, J = 16.5, 2.4 Hz, 1 H, 3-H^{Z}_{allyl}), 4.99 (m, J = 10.7, 2.4 Hz, 1 H, 3-H^{E}_{allyl}), 5.75 (ddt, J = 16.5, 10.7, 7.3 Hz, 1 H, 2-H_{allyl}), 6.53 (d, J = 7.6 Hz, 1 H, 4′-H), 6.75 (d, J = 7.6 Hz, 1 H, 6′-H), 6.92 (t, J = 7.6 Hz, 1 H, 5′-H) ppm. $C_{17}H_{25}N$ (243.4): calcd. C 83.95, H 10.29, N 5.76; found C 83.83, H 10.17, N 5.77.

***N*-(1-Allylcyclopentyl)-*N*-(2′-ethylphenyl)amine (2f):** Yield 69%, R_f = 0.80, b.p. 132−133 °C/2.5 Torr; n_D^{23} = 1.5459. IR (film): $\tilde{\nu}$ = 3432 (NH), 1635 (C=C) cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 1.22 (t, J = 7.6 Hz, 3 H, CH_2CH_3), 1.82−1.61 (m, 6 H, cycloalkyl H), 1.98−1.89 (m, 2 H, cycloalkyl H), 2.42 (q, J = 7.6 Hz, 2 H, CH_2CH_3), 2.56 (d, J = 7.3 Hz, 2 H, 1-H_{allyl}), 3.67 (br. s, 1 H, NH), 4.95 (m, J = 17.2, 1.1 Hz, 1 H, 3-H^{Z}_{allyl}), 5.00 (m, J = 10.2, 1.1 Hz, 1 H, 3-H^{E}_{allyl}), 5.74 (ddt, J = 17.2, 10.2, 7.3 Hz, 1 H, 2-H_{allyl}), 6.65 (dt, J = 7.5, 0.5 Hz, 1 H, 4′-H), 6.78 (d, J = 7.5 Hz, 1 H, 6′-H), 7.05 (d, J = 7.5 Hz, 1 H, 3′-H), 7.06 (dt, J = 7.5, 0.5 Hz, 1 H, 5′-H) ppm. $C_{16}H_{23}N$ (229.4): calcd. C 83.84, H 10.04, N 6.11; found C 83.70, H 10.04, N 6.17.

***N*-(1-Allylcyclohexyl)-*N*-(2′-ethylphenyl)amine (2g):** Yield 82%, R_f = 0.71, b.p. 135−136 °C/1.5 Torr; n_D^{22} = 1.5462. IR (film): $\tilde{\nu}$ = 3448 (NH), 1636 (C=C) cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 1.25 (t, J = 7.4 Hz, 3 H, CH_2CH_3), 1.63−1.18 (m, 8 H, cycloalkyl H), 2.00 (m, 2 H, cycloalkyl H), 2.49 (q, J = 7.4 Hz, 2 H, CH_2CH_3), 2.52 (d, J = 7.3 Hz, 2 H, 1-H_{allyl}), 3.45 (br. s, 1 H, NH), 4.97 (d, J = 17.0 Hz, 1 H, 3-H^{Z}_{allyl}), 5.01 (d, J = 9.8 Hz, 1 H, 3-H^{E}_{allyl}), 5.74 (ddt, J = 17.0, 9.8, 7.3 Hz, 1 H, 2-H_{allyl}), 6.67 (br. t, J = 7.7 Hz, 1 H, 4′-H), 6.86 (d, J = 7.7 Hz, 1 H, 6′-H), 7.05 (d, J = 7.7 Hz, 1 H, 3′-H), 7.04 (t, J = 7.5 Hz, 1 H, 5′-H) ppm. $C_{17}H_{25}N$ (243.4): calcd. C 83.95, H 10.29, N 5.76; found C 84.16, H 10.18, N 5.64.

***N*-(1-Allylcyclohexyl)-*N*-(2′-isopropylphenyl)amine (2h):** Yield 65%, R_f = 0.72, b.p. 156−158 °C/4 Torr; n_D^{22} = 1.5420. IR (film): $\tilde{\nu}$ = 3455 (NH), 1644 (C=C) cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 1.26 [d, J = 6.8 Hz, 6 H, $CH(CH_3)_2$], 1.58−1.43 (m, 8 H, cycloalkyl H), 2.03−1.93 (m, 2 H, cycloalkyl H), 2.86 [sept, J = 6.8 Hz, $CH(CH_3)_2$, 1 H], 2.53 (br. d, J = 7.2 Hz, 2 H, 1-H_{allyl}), 3.53 (br. s, 1 H, NH), 4.97 (m, J = 17.5, 1.0 Hz, 1 H, 3-H^{Z}_{allyl}), 5.01 (m, J = 10.3, 1.0 Hz, 1 H, 3-H^{E}_{allyl}), 5.74 (ddt, J = 17.5, 10.3, 7.2 Hz, 1 H, 2-H_{allyl}), 6.68 (dt, J = 7.5, 1.6 Hz, 1 H, 4′-H), 6.87 (dd, J = 7.5, 1.6 Hz, 1 H, 6′-H), 7.13 (dd, J = 7.5, 1.6 Hz, 1 H, 3′-H), 7.02 (br. dt, J = 7.5, 1.6 Hz, 1 H, 5′-H) ppm. $C_{18}H_{27}N$ (257.4): calcd. C 84.05, H 10.51, N 5.45; found C 83.95, H 10.60, N 5.41.

***N*-(1-Allylcyclohexyl)-*N*-(2′-benzylphenyl)amine (2i):** White crystals, yield 52%, R_f = 0.72, m.p. 67−69 °C (from hexane). IR (KBr): $\tilde{\nu}$ = 3429 (NH), 1638 (C=C) cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 1.35−1.15 (m, 8 H, cycloalkyl H), 1.79 (m, 2 H, cycloalkyl H), 2.39 (dd, J = 7.3, 1.0 Hz, 2 H, 1-H_{allyl}), 3.30 (br. s, 1 H, NH), 3.89 (br. s, 2 H, CH_2Ph), 4.84 (m, J = 17.5, 1.5 Hz, 1 H, 3-H^{Z}_{allyl}), 4.82 (m, J = 10.2 and 1.5 Hz, 1.0 Hz, 1 H, 3-H^{E}_{allyl}), 5.39 (ddt, J = 17.5, 10.2, 7.3 Hz, 1 H, 2-H_{allyl}), 6.65 (dt, J = 7.5, 1.1 Hz, 1 H, 4′-H), 6.84 (d, J = 7.5 Hz, 1 H, 6′-H), 7.29−7.08 (m, 7 H, 5′−H, 3′-H, CH_2Ph) ppm. $C_{22}H_{27}N$ (305.5): calcd. C 86.56, H 8.85, N 4.59; found C 86.55, H 8.88, N 4.60.

***N*-(1-Allylcyclopentyl)-*N*-(2′,6′-dimethylphenyl)amine (2k):** Yield 36%, R_f = 0.78, b.p. 145−147 °C/4 Torr; n_D^{25} = 1.5430. IR (film): $\tilde{\nu}$ = 3440 (NH), 1638 (C=C) cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 1.22 (t, J = 7.6 Hz, 3 H, CH_2CH_3), 1.82−1.61 (m, 6 H, cycloalkyl H), 1.98−1.89 (m, 2 H, cycloalkyl H), 2.42 (q, J = 7.6 Hz, 2 H, CH_2CH_3), 2.56 (d, J = 7.3 Hz, 2 H, 1-H_{allyl}), 3.67 (br. s, 1 H, NH), 4.95 (m, J = 17.2, 1.1 Hz, 1 H, 3-H^{Z}_{allyl}), 5.00 (m, J = 10.2, 1.1 Hz, 1 H, 3-H^{E}_{allyl}), 5.74 (ddt, J = 17.2, 10.2, 7.3 Hz, 1 H, 2-H_{allyl}), 6.65 (dt, J = 7.5, 0.5 Hz, 1 H, 4′-H), 6.78 (d, J = 7.5 Hz, 1 H, 6′-H), 7.05 (d, J = 7.5 Hz, 1 H, 3′-H), 7.06 (dt, J = 7.5, 0.5 Hz, 1 H, 5′-H) ppm. $C_{16}H_{23}N$ (229.4): calcd. C 83.84, H 10.04, N 6.11; found C 83.92, H 10.18, N 6.22.

***N*-(1-Allylcyclohexyl)-*N*-(2′,6′-dimethylphenyl)amine (2l):** Yield 65%, R_f = 0.70, b.p. 135−136 °C/2 Torr. IR (film): $\tilde{\nu}$ = 3360 (NH), 1640 (C=C) cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 1.71−1.42 (m, 10 H, cycloalkyl H), 2.35 (s, 6 H, 2′-Me and 6′-Me), 2.40 (d, J = 7.4 Hz, 2 H, 1-H_{allyl}), 2.78 (br. s, 1 H, NH), 5.09 (m, J = 17.4 Hz, 1 H, 3-H^{Z}_{allyl}), 5.11 (m, J = 10.3 Hz, 1 H, 3-H^{E}_{allyl}), 5.96 (ddt, J = 17.4, 10.3, 7.4 Hz, 1 H, 2-H_{allyl}), 6.86 (t, J = 7.4 Hz, 1 H, 4′-H), 6.99 (d, J = 7.4 Hz, 2 H, 3′-H, 5′-H) ppm. $C_{17}H_{25}N$ (243.4): calcd. C 83.95, H 10.29, N 5.76; found C 83.89, H 10.10, N 5.77.

***N*-(1-Allylcyclohexyl)-*N*-(2′-ethyl-6′-methylphenyl)amine (2m):** Yield 51%, R_f = 0.71, b.p. 145−148 °C/3.5 Torr. IR (film): $\tilde{\nu}$ = 3365 (NH), 1643 (C=C) cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 1.16 (t, J = 7.5 Hz, 3 H, CH_2CH_3), 1.48−1.38 (m, 6 H, cycloalkyl H), 1.63−1.57 (m, 4 H, cycloalkyl H), 2.33 (s, 3 H, 6′-Me), 2.35 (q, J = 7.5 Hz, 2 H, CH_2CH_3), 2.35 (d, J = 7.5 Hz, 2 H, 1-H_{allyl}), 2.88 (br. s, 1 H, NH), 5.11 (m, J = 17.1 Hz, 1 H, 3-H^Z_{allyl}), 5.12 (m, J = 10.6 Hz, 1 H, 3-H^E_{allyl}), 5.96 (m, J = 17.1, 10.6, 7.5 Hz, 1 H, 2-H_{allyl}), 6.93 (t, J = 7.3 Hz, 1 H, 4′-H), 7.00 (d, J = 7.3 Hz, 1 H, 3′-H), 7.04 (d, J = 7.3 Hz, 1 H, 5′-H) ppm. $C_{18}H_{27}N$ (257.4): calcd. C 84.05, H 10.51, N 5.45; found C 84.10, H 10.61, N 5.62.

***N*-(1-Allylcyclohexyl)-*N*-(2′,6′-diethylphenyl)amine (2n):** Yield 50%, R_f = 0.73, b.p. 147−157 °C/4 Torr. IR (film): $\tilde{\nu}$ = 3378 (NH), 1641 (C=C) cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 1.17 (t, J = 7.5 Hz, 6 H, CH_2CH_3), 1.37−1.48 (m, 6 H, cycloalkyl H), 1.64−1.54 (m, 4 H, cycloalkyl H), 2.35 (d, J = 7.5 Hz, 2 H, 1-H_{allyl}), 2.74 (q, J = 7.5 Hz, 4 H, CH_2CH_3), 2.89 (br. s, 1 H, NH), 5.11 (m, J = 16.1 Hz, 1 H, 3-H^Z_{allyl}), 5.12 (m, J = 10.7 Hz, 1 H, 3-H^E_{allyl}), 5.95 (m, J = 16.1, 10.7, 7.5 Hz, 1 H, 2-H_{allyl}), 7.06−6.97 (m, 3 H, 3′-H, 4′-H, 5′-H) ppm. $C_{19}H_{29}N$ (271.4): calcd. C 84.13, H 10.70, N 5.17; found C 84.21, H 10.78, N 5.13.

***N*-(2′-Ethylphenyl)-*N*-(1-methallylcyclohexyl)amine (9a):** Yield 74%, R_f = 0.66, b.p. 139−143 °C/2.5 Torr; n_D^{23} = 1.5470. IR (film): $\tilde{\nu}$ = 3367 (NH), 1646 (C=C) cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 1.25 (t, J = 7.5 Hz, 3 H, CH_2CH_3), 1.62−1.40 (m, 8 H, cycloalkyl H), 1.72 (br. s, 2 H, 1-H_{allyl}), 2.10−2.06 (m, 2 H, cycloalkyl H), 2.48 (q, J = 7.5 Hz, 2 H, CH_2CH_3), 2.50 (br. s, 3 H, 2-M^E_{allyl}), 3.47 (br. s, 1 H, NH), 4.59 (m, J = 1.4 Hz, 1 H, 3-H^A_{allyl}), 4.83 (m, J = 1.4 Hz, 1 H, 3-H^B_{allyl}), 6.63 (br. t, J = 7.5 Hz, 1 H, 5′-H), 6.86 (d, J = 7.5 Hz, 1 H, 6′-H), 7.04 (t, J = 7.5 Hz, 1 H, 4′-H), 7.05 (d, J = 7.5 Hz, 1 H, 3′-H) ppm. $C_{18}H_{27}N$ (257.4): calcd. C 84.05, H 10.51, N 5.45; found C 84.23, H 10.62, N 5.68.

***N*-(2′,6′-Dimethylphenyl)-*N*-(1-methallylcyclohexyl)amine (9b):** Yield 35%, R_f = 0.74, b.p. 175−185 °C/9 Torr. IR (film): $\tilde{\nu}$ = 3345 (NH), 1648 (C=C) cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 1.75−1.41 (m, 10 H, cycloalkyl H), 1.97 (s, 3 H, 2-Me_{allyl}), 2.35 (s, 6 H, 2′-Me and 6′-Me), 2.38 (br. s, 2 H, 1-H_{allyl}), 2.93 (br. s, 1 H, NH), 4.87 (br. s, J = 1.3 Hz, 1 H, 3-H^A_{allyl}), 5.00 (m, J = 1.3 Hz, 1 H, 3-H^B_{allyl}), 6.90 (t, J = 7.4 Hz, 1 H, 4′-H), 7.03 (d, J = 7.4 Hz, 2 H, 3′-H and 5′-H) ppm. $C_{18}H_{27}N$ (257.4): calcd. C 84.05, H 10.51, N 5.45; found C 83.92, H 10.49, N 5.49.

4′-Methyl-3′,4′-dihydro-1′*H*-spiro[cycloalkane-1,2′-quinolines] 3a−n, 4f, 4g, 5, 10, Aniline 11 and Cycloadducts 6k,l. Typical Procedure: Sulfuric acid (97%; 37 mL, 0.7 mol) was added rapidly to a stirred solution of the homoallylamine **2a−n** (0.1 mol) (or methallyl derivatives **9a**,**b**) in $CHCl_3$ (80 mL) at 50−60 °C. The resulting mixture was heated at 60−65 °C for 3−5 h while stirring vigorously. The reaction progress was monitored by TLC (until the disappearance of the starting material spot). At the end of the reaction, ice (ca. 200 mL) was added to the cooled reaction mixture, and then concentrated ammonium hydroxide solution (ca. 110 mL) was added until pH = 10−11. Three 70-mL extractions with chloroform were performed. The organic layers were combined, dried ($MgSO_4$) and concentrated. The oily residue was distilled in vacuo to give the products **3a−h**, **10** as pale yellow oils or was purified by column chromatography on alumina to give the products **3i**, **3k**, **3l**, **3n**, **3m**, **4m**, **5**, **6k**, **6l**, **11**.

3′,4′-Dihydro-4′,8′-dimethyl-1′*H*-spiro[cyclopentane-1,2′-quinoline] (3a): Yield 66%, R_f = 0.60, b.p. 128−129 °C/1.5 Torr, m.p. (× HCl) 176−178 °C; n_D^{20} = 1.5621. IR (film): $\tilde{\nu}$ = 390 (NH) cm^{-1}. EI-MS (70 eV): *m*/*z* (%) = 215 (36) [M^+], 214 (7), 201 (13), 200 (100), 187 (14), 186 (79), 172 (15), 158 (8), 157 (14). ^1H NMR ($CDCl_3$, 200 MHz): δ = 1.85−1.59 (m, 8 H, cycloalkyl H), 1.41 (d, J = 6.8 Hz, 3 H, 4′-Me), 1.65 (dd, J = 12.8, 11.4 Hz, 1 H, 3′-H^B), 1.84 (dd, J = 12.8, 5.6 Hz, 1 H, 3′-H^A), 2.12 (s, 3 H, 8′-Me), 3.01 (ddq, J = 11.4, 6.8, 5.6 Hz, 1 H, 4′-H), 3.60 (br. s, 1 H, NH), 6.63 (t, J = 7.5 Hz, 1 H, 6′-H), 6.93 (d, J = 7.5 Hz, 1 H, 7′-H), 7.10 (d, J = 7.5 Hz, 1 H, 5′-H) ppm. $C_{15}H_{21}N$ (215.4): calcd. C 83.72, H 9.77, N 6.51; found C 83.82, H 9.67, N 6.32.

3′,4′-Dihydro-4′,8′-dimethyl-1′*H*-spiro[cyclohexane-1,2′-quinoline] (3b): Yield 84%, R_f = 0.62, b.p. 125−128 °C/1.5 Torr. IR (film): $\tilde{\nu}$ = 3415 (NH) cm^{-1}. EI-MS (70 eV): *m*/*z* (%) = 229 (39) [M^+], 214 (41), 200 (8), 186 (100), 173 (9), 170 (7), 158 (12), 143 (10), 130 (5), 115 (5). ^1H NMR ($CDCl_3$, 200 MHz): δ = 1.85−1.40 (m, 10 H, cycloalkyl H), 1.46 (d, J = 6.7 Hz, 3 H, 4′-Me), 1.50 (t, J = 12.7, 12.5 Hz, 1 H, 3′-H^B), 1.98 (dd, J = 12.7, 5.4 Hz, 1 H, 3′-H^A), 2.23 (s, 3 H, 8′-Me), 3.05 (ddq, J = 12.5, 6.7, 5.4 Hz, 1 H, 4′-H), 3.84 (br. s, 1 H, NH), 6.64 (t, J = 8.0 Hz, 1 H, 6′-H), 6.95 (d, J = 8.0 Hz, 1 H, 7′-H), 7.11 (d, J = 8.0 Hz, 1 H, 5′-H) ppm. $C_{16}H_{23}N$ (229.4): calcd. C 83.84, H 10.04, N 6.11; found C 83.68, H 9.95, N 6.12.

3′,4′-Dihydro-4′,8′-dimethyl-1′*H*-spiro[cycloheptane-1,2′-quinoline] (3c): Yield 79%, R_f = 0.67, b.p. 128−130 °C/1.5 Torr. IR (film): $\tilde{\nu}$ = 3370 (NH) cm^{-1}. EI-MS (70 eV): *m*/*z* (%) = 243 (33) [M^+], 228 (62), 186 (100), 200 (19), 173 (10), 158 (13). ^1H NMR ($CDCl_3$, 400 MHz): δ = 1.85−1.40 (m, 12 H, cycloalkyl H), 1.32 (d, J = 6.7 Hz, 3 H, 4′-Me), 1.76 (dd, J = 12.6, 8.6 Hz, 1 H, 3′-H^B), 1.91 (dd, J = 12.6, 5.5 Hz, 1 H, 3′-H^A), 2.09 (s, 3 H, 8′-Me), 2.91 (ddq, J = 8.6, 6.7, 5.5 Hz, 1 H, 4′-H), 3.65 (br. s, 1 H, NH), 6.59 (t, J = 7.5 Hz, 1 H, 6′-H), 6.89 (d, J = 7.5 Hz, 1 H, 7′-H), 7.06 (d, J = 7.5 Hz, 1 H, 5′-H) ppm. $C_{17}H_{25}N$ (243.4): calcd. C 83.95, H 10.29, N 5.76; found C 84.15, H 10.15, N 5.82.

3′,4′-Dihydro-4′,6′,8′-trimethyl-1′*H*-spiro[cyclohexane-1,2′-quinoline] (3d): Yield 83%, R_f = 0.48, b.p. 154−155 °C/2.5 Torr; n_D^{23} = 1.5560. IR (film): $\tilde{\nu}$ = 3440 (NH) cm^{-1}. EI-MS (70 eV): *m*/*z* (%) = 243 (33) [M^+], 228 (35), 214 (4), 200 (100), 187 (10), 184 (9), 172 (16), 157 (11). ^1H NMR ($CDCl_3$, 400 MHz): δ = 1.75−1.45 (m, 10 H, cycloalkyl H), 1.43 (d, J = 6.9 Hz, 3 H, 4′-Me), 1.52 (dd, J = 12.9, 12.0 Hz, 1 H, 3′-H^B), 1.96 (dd, J = 12.9, 5.4 Hz, 1 H, 3′-H^A), 2.20 (s, 3 H, 8′-Me), 2.32 (s, 3 H, 6′-Me), 3.01 (ddq, J = 12.0, 6.9, 5.4 Hz, 1 H, 4′-H), 3.77 (br. s, 1 H, NH), 6.83 (s, 1 H, 7′-H), 6.98 (s, 1 H, 5′-H) ppm. $C_{17}H_{25}N$ (243.4): calcd. C 83.95, H 10.29, N 5.76; found C 84.05, H 10.33, N 5.81.

3′,4′-Dihydro-4′,7′,8′-trimethyl-1′*H*-spiro[cyclohexane-1,2′-quinoline] (3e): Yield 83%, R_f = 0.73, b.p. 151−153 °C/2 Torr; n_D^{19} = 1.5620. IR (film): $\tilde{\nu}$ = 3428 (NH) cm^{-1}. EI-MS (70 eV): *m*/*z* (%) = 243 (46) [M^+], 228 (36), 214 (3), 200 (100), 187 (6), 172 (10), 157 (6). ^1H NMR ($CDCl_3$, 400 MHz): δ = 1.75−1.40 (m, 10 H, cycloalkyl H), 1.40 (d, J = 6.8 Hz, 3 H, 4′-Me), 1.42 (dd, J = 12.8, 12.1 Hz, 1 H, 3′-H^B), 1.94 (dd, J = 12.8, 5.5 Hz, 1 H, 3′-H^A), 2.12 (s, 3 H, 8′-Me), 2.33 (s, 3 H, 7′-Me), 3.01 (ddq, J = 12.1, 6.8, 5.5 Hz, 1 H, 4′-H), 3.91 (br. s, 1 H, NH), 6.60 (d, J = 7.9 Hz, 1 H, 6′-H), 7.04 (d, J = 7.9 Hz, 1 H, 5′-H) ppm. $C_{17}H_{25}N$ (243.4): calcd. C 83.95, H 10.29, N 5.76; found C 84.13, H 10.18, N 5.88.

8′-Ethyl-3′,4′-dihydro-4′-methyl-1′*H*-spiro[cyclopentane-1,2′-quinoline] (3f) and 5′-Ethyl-3′,4′-dihydro-4′-methyl-1′*H*-spiro[cyclopentane-1,2′-quinoline] (4f): After fractional distillation of the reaction mixture, separation of the products **3f**, **4f** was carried out by column chromatography on Al_2O_3 (using hexane/ethyl acetate, 20:1 as eluent). **3f:** Yield 59%, R_f = 0.72, b.p. 139−140 °C/3 Torr, m.p. (× HCl) 164−166 °C (acetone). IR (film): $\tilde{\nu}$ = 3428 (NH) cm^{-1}. EI-MS (70 eV): *m*/*z* (%) = 229 (39) [M^+], 214 (100), 200 (80), 186 (12),

172 (10), 156 (8). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.33 (t, J = 7.5 Hz, 3 H, CH_2CH_3), 1.9−1.6 (m, 8 H, cycloalkyl H), 1.45 (d, J = 6.8 Hz, 3 H, 4′-Me), 1.72 (dd, J = 12.6, 11.9 Hz, 1 H, 3′-H^B), 1.87 (dd, J = 12.6, 5.5 Hz, 1 H, 3′-H^A), 2.51 (q, J = 7.5 Hz, 2 H, CH_2CH_3), 3.06 (m, J = 11.9, 6.8, 5.5 Hz, 1 H, 4′-H), 3.82 (br. s, 1 H, NH), 6.74 (t, J = 7.6 Hz, 1 H, 6′-H), 7.00 (dd, J = 7.6, 1.1 Hz, 1 H, 7′-H), 7.16 (br. d, J = 7.6 Hz, 1 H, 5′-H) ppm. ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 60.6 (C-2′ spiro), 42.2[(a)] (C-3′), 28.70 (C-4′), 126.0[(b)] (C-4a′), 124.5 (C-5′), 116.0 (C-6′), 125.3 (C-7′), 125.2[(b)] (C-8′), 141.0 (C-8a′), 20.6 (4′-Me), 23.6 (MeCH_2), 12.7 (MeCH$_2$), 41.1[(a)], 39.0, 23.6, 23.3 (C cycloalkyl) ppm. $C_{16}H_{23}N$ (229.4): calcd. C 83.84, H 10.04, N 6.11; found C 84.01, H 10.18, N 6.41. **4f:** Yield 17%, R_f = 0.44, b.p. 139−140 °C/3 Torr, m.p. (× HCl) 201−204 °C (acetone). IR (film): $\tilde{\nu}$ = 3380 (NH) cm^{-1}. EI-MS (70 eV): m/z (%) = 229 (32) [M$^+$], 214 (100), 200 (90), 186 (19), 172 (13), 156 (12), 143 (8). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.32 (t, J = 7.6 Hz, 3 H, CH_2CH_3), 1.6−1.9 (m, 8 H, cycloalkyl H), 1.39 (d, J = 7.1 Hz, 3 H, 4′-Me), 1.88 (dd, J = 13.4, 3.5 Hz, 1 H, 3′-H^B), 2.17 (dd, J = 13.4, 6.0 Hz, 1 H, 3′-H^A), 2.66 and 2.75 (m, J = 7.6 Hz, 2 H, CH_2CH_3), 3.26 (m, J = 7.1, 6.0, 3.5 Hz, 1 H, 4′-H), 3.77 (br. s, 1 H, NH), 6.38 (br. d, J = 7.9 Hz, 1 H, 8′-H), 6.62 (br. d, J = 7.7 Hz, 1 H, 6′-H), 7.01 (t, J = 7.8 Hz, 1 H, 7′-H) ppm. ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 60.1 (C-2′ spiro), 41.1 (C-3′), 27.6 (C-4′), 124.1 (C-4a′), 142.0 (C-5′), 116.8 (C-6′), 126.3 (C-7′), 111.8 (C-8′), 143.2 (C-8a′), 21.8 (4′-Me), 24.6 (MeCH_2), 15.5 (MeCH$_2$), 41.9, 40.9, 24.0, 22.5 (C cycloalkyl) ppm. $C_{16}H_{23}N$ (229.4): calcd. C 83.84, H 10.04, N 6.11; found C 84.10, H 10.12, N 6.38.

8′-Ethyl-3′,4′-dihydro-4′-methyl-1′*H*-spiro[cyclohexane-1,2′-quinoline] (3g) and 5′-Ethyl-3′,4′-dihydro-4′-methyl-1′*H*-spiro[cyclohexane-1,2′-quinoline] (4g): After fractional distillation of the reaction mixture, separation of the products **3g**, **4g** was carried out by column chromatography on Al_2O_3 (using hexane/ethyl acetate, 20:1, as eluent). **3g**: Yield 61%, R_f = 0.70, b.p. 142−143 °C/2 Torr, m.p. (× HCl) 172−174 °C (acetone). IR (film): $\tilde{\nu}$ = 3433 (NH) cm^{-1}. EI-MS (70 eV): m/z (%) = 243 (22) [M$^+$], 228 (30), 200 (100), 214 (5), 187 (8), 172 (10). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.34 (t, J = 7.5 Hz, 3 H, CH_2CH_3), 1.74−1.42 (m, 10 H, cycloalkyl H), 1.41 (d, J = 6.8 Hz, 3 H, 4′-Me), 1.40 (t, J = 12.8 Hz, 1 H, 3′-H^B), 1.94 (dd, J = 12.8, 5.5 Hz, 1 H, 3′-H^A), 2.54 (q, J = 7.5 Hz, 2 H, CH_2CH_3), 3.00 (ddq, J = 12.8, 6.8, 5.5 Hz, 1 H, 4′-H), 3.97 (br. s, 1 H, NH), 6.70 (t, J = 7.5 Hz, 1 H, 6′-H), 6.99 (dd, J = 7.5, 1.1 Hz, 1 H, 7′-H), 7.13 (dd, J = 7.5, 1.1 Hz, 1 H, 5′-H) ppm. ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 50.25 (C-2′ spiro), 42.70 (C-3′), 26.80 (C-4′), 125.90 (C-4a′), 124.38 (C-5′), 115.82 (C-6′), 125.35 (C-7′), 125.27 (C-8′), 140.68 (C-8a′), 20.48 (4′-Me), 23.69 (MeCH_2), 12.66 (MeCH$_2$), 40.02, 35.88, 25.87, 21.82, 22.12 (C cycloalkyl) ppm. $C_{17}H_{25}N$ (243.4): calcd. C 83.95, H 10.29, N 5.76; found C 83.91, H 10.33, N 5.82. **4g:** Yield 23%, R_f = 0.42, b.p. 142−143 °C/2 Torr, m.p. (× HCl) 208−210 °C (acetone). IR (film): $\tilde{\nu}$ = 3385 (NH) cm^{-1}. EI-MS (70 eV): m/z (%) = 243 (21) [M$^+$], 228 (31), 214 (4), 200 (100), 187 (7), 172 (9). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.26 (t, J = 7.6 Hz, 3 H, CH_2CH_3), 1.69−1.38 (m, 10 H, cycloalkyl H), 1.33 (d, J = 7.2 Hz, 3 H, 4′-Me), 1.83 (dd, J = 13.6, 4.9 Hz, 1 H, 3′-H^B), 1.88 (dd, J = 13.6, 6.4 Hz, 1 H, 3′-H^A), 2.65 (m, J = 7.6 Hz, 2 H, CH_2CH_3), 3.18 (ddq, J = 7.2, 6.4, 4.9 Hz, 1 H, 4′-H), 3.56 (br. s, 1 H, NH), 6.41 (dd, J = 7.2, 1.2 Hz, 1 H, 6′-H), 6.99 (t, J = 7.2 Hz, 1 H, 7′-H), 6.60 (dd, J = 7.2, 1.2 Hz, 1 H, 8′-H) ppm. ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 50.95 (C-2′ spiro), 42.06 (C-3′), 26.90 (C-4′), 125.40 (C-4a′), 142.05 (C-5′), 117.61 (C-6′), 126.23 (C-7′), 112.60 (C-8′), 143.52 (C-8a′), 22.07 (4′-Me), 24.89 (MeCH_2), 15.49 (MeCH$_2$), 39.51, 38.75, 25.57, 22.31, 22.06 (C cycloalkyl) ppm. $C_{17}H_{25}N$ (243.4): calcd. C 83.95, H 10.29, N 5.76; found C 83.97, H 10.17, N 5.83.

3′,4′-Dihydro-8′-isopropyl-4′-methyl-1′*H*-spiro[cyclohexane-1,2′-quinoline] (3h): Yield 65%, R_f = 0.67, b.p. 173−177 °C/4 Torr; n_D^{23} = 1.5526. IR (film): $\tilde{\nu}$ = 3432 (NH) cm^{-1}. EI-MS (70 eV): m/z (%) = 257 (25) [M$^+$], 242 (34), 228 (4), 214 (100), 201 (6), 198 (7), 186 (10), 170 (6), 162 (6). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.26 [d, J = 6.8 Hz, 3 H, CH(CH_3)$_2$], 1.27 [d, J = 6.8 Hz, 3 H, CH(CH_3)$_2$], 1.67−1.44 (m, 10 H, cycloalkyl H), 1.34 (d, J = 6.7 Hz, 3 H, 4′-Me), 1.35 (dd, J = 12.9, 11.8 Hz, 1 H, 3′-H^B), 1.87 (dd, J = 12.9, 5.1 Hz, 1 H, 3′-H^A), 2.83 [sept, J = 6.8 Hz, 1 H, CH(CH$_3$)$_2$], 2.93 (m, J = 11.8, 6.7, 5.1 Hz, 1 H, 4′-H), 4.00 (br. s, 1 H, NH), 6.66 (dd, J = 7.6, 1.3 Hz, 1 H, 6′-H), 6.99 (t, J = 7.6 Hz, 1 H, 7′-H), 7.05 (dd, J = 7.6, 1.3 Hz, 1 H, 5′-H) ppm. $C_{18}H_{27}N$ (257.4): calcd. C 84.05, H 10.51, N 5.45; found C 84.18, H 10.63, N 5.38.

8′-Benzyl-3′,4′-dihydro-4′-methyl-1′*H*-spiro[cyclohexane-1,2′-quinoline] (3i) and 3′,4′-Dihydro-4′-methyl-1′*H*-spiro[cyclohexane-1,2′-quinoline] (5): After the removal of chloroform, the residue crystallized. The resulting crystals of **3i** were recrystallized from a hexane/ethyl acetate mixture. The mother liquor was concentrated and the resulting residue was purified by column chromatography on Al_2O_3 (using hexane/ethyl acetate, 20:1, as eluent) to give compound **5**. **3i**: white crystals, yield 61%, R_f = 0.67, m.p. 125−127 °C (from hexane/ethyl acetate). IR (KBr): $\tilde{\nu}$ = 3430 (NH) cm^{-1}. EI-MS (70 eV): m/z (%) = 305 (41) [M$^+$], 290 (39), 262 (100), 234 (7), 156 (10), 130 (14), 91 (13). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.47 (br. q, 1 H, cycloalkyl H), 1.36−1.10 (m, 8 H, cycloalkyl H), 1.48 (m, 1 H, cycloalkyl H), 1.31 (d, J = 6.7 Hz, 3 H, 4′-Me), 1.4 (br. t, J = 13.0 Hz, 1 H, 3′-H^B), 1.71 (dd, J = 13.0, 5.3 Hz, 1 H, 3′-H^A), 2.91 (m, J = 12.1, 6.7, 5.3 Hz, 1 H, 4′-H), 3.81 (d, J = 15.7 Hz, 1 H, CH_AH$_B$Ph), 3.91 (d, J = 15.7 Hz, 1 H, CH$_A$$H_B$Ph), 3.84 (br. s, 1 H, NH), 6.65 (t, J = 7.5 Hz, 1 H, 6′-H), 6.95 (br. d, J = 7.5 Hz, 1 H, 7′-H), 7.11 (br. d, J = 7.5 Hz, 1 H, 5′-H), 7.30−7.18 (m, 5 H, CH$_2$*Ph*) ppm. $C_{22}H_{27}N$ (305.5): calcd. C 86.56, H 8.85, N 4.59; found C 86.48, H 8.89, N 4.62. **5:** Pale yellow oil, yield 13%, R_f = 0.80. Its constants are in agree to those reported in the ref.[13]

3′,4′-Dihydro-4′,5′,8′-trimethyl-1′*H*-spiro[cyclopentane-1,2′-quinoline] (3k) and 1,2,3,6a,7,9,10,11,11a,12,12a,12b-Dodecahydro-1,5,7,11,11a,12b-hexamethyl-7,12-ethenodispiro[quino[6,7-*f*]quinoline-3,1′:9,1′′-bis(cyclopentane)] (6k): After the removal of chloroform, the residue was purified by column chromatography on Al_2O_3 (using hexane as eluent) to give compound **3k**. The polycycle **6k** was eluted with chloroform. **3k:** Pale yellow oil, yield 53%, R_f = 0.78. IR (film): $\tilde{\nu}$ = 3430 (NH) cm^{-1}. EI-MS (70 eV): m/z (%) = 229 (50) [M$^+$], 214 (100), 200 (84), 186 (17), 184 (18), 171 (29), 158 (10), 156 (9), 130 (7), 115 (7). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.85−1.64 (m, 8 H, cycloalkyl H), 1.29 (d, J = 7.2 Hz, 3 H, 4′-Me), 1.78 (dd, J = 13.3, 3.7 Hz, 1 H, 3′-H^B), 2.09 (dd, J = 13.3, 6.4 Hz, 1 H, 3′-H^A), 2.05 (s, 3 H, 8′-Me), 2.26 (s, 3 H, 5′-Me), 3.13 (ddq, J = 7.2, 6.4, 3.7 Hz, 1 H, 4′-H), 3.66 (br. s, 1 H, NH), 6.42 (d, J = 7.5 Hz, 1 H, 6′-H), 6.78 (d, J = 7.5 Hz, 1 H, 7′-H) ppm. $C_{16}H_{23}N$ (229.4): calcd. C 83.84, H 10.04, N 6.11; found C 83.98, H 9.88, N 6.07. **6k:** White crystals, yield 16%, m.p. 172−175 °C (chloroform). IR (KBr): $\tilde{\nu}$ = 1649 and 1622 (N=C and C=C) cm^{-1}. LC-MS: m/z (%) = 459 ([M + H]$^+$, 100), 230 (13). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.67 (s, 3 H, 11a-Me), 0.84 (d, J = 6.8 Hz, 3 H, 1-Me), 0.86 (d, J = 6.7 Hz, 3 H, 11-Me), 0.88 (s, 3 H, 12b-Me), ca. 1.37 (m, 2 H, 2-H), 1.43 (dd, J = 12.8, 13.8 Hz, 1 H, 10-H^B), 1.39 (s, 3 H, 7-Me), 1.53 (dd, J = 4.5, 13.8 Hz, 1 H, 10-H^A), 1.72 (m, 3 H, 5-Me), 1.88 (m, 1 H, 11-H), 2.13 (m, 1 H, 1-H), 2.25 (d, J = 8.3 Hz, 1 H, 12a-H), 2.33 (m, 1 H, 6a-H), 2.74 (d, J = 6.6 Hz, 1 H, 12-H), 5.69 (dd, J = 1.4, 8.1 Hz, 1 H, 1′′′-H), 5.77

(dq, J = 4.1, 1.4 Hz, 1 H, 6-H), 6.04 (dd, J = 6.6, 8.1 Hz, 1 H, 2′′′-H), 1.8−1.2 (m, 16 H, cycloalkyl H) ppm. ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 29.6 (C-1), 38.2 (C-2), 65.4[a] (C-3), 166.1 (C-4a), 135.4 (C-5), 129.3 (C-6), 48.2 (C-6a), 49.1 (C-7), 176.2 (C-7a), 55.8[a] (C-9), 38.8 (C-10), 28.2 (C-11), 39.7[b] (C-11a), 41.5 (C-12), 41.6 (C-12a), 42.1[b] (C-12b), 136.6 (C-1′′′), 130.6 (C-2′′′), 15.44 (1-Me), 19.8 (5-Me), 18.8 (7-Me), 15.48 (11-Me), 17.7 (11a-Me), 22.7 (12b-Me), 43.5, 42.7, 42.4, 40.0, 24.8, 24.5, 23.98, 23.19 (C-cyclopentyl) ppm. $C_{32}H_{46}N_2$ (458.7): calcd. C 83.84, H 10.04, N 6.11; found C 83.59, H 10.00, N 6.21.

3′,4′-Dihydro-4′,5′,8′-trimethyl-1′*H*-spiro[cyclohexane-1,2′-quinoline] (3l) and 1,2,3,6a,7,9,10,11,11a,12,12a,12b-Dodecahydro-1,5,7,11,11a,12b-hexamethyl-7,12-ethenodispiro[quino[6,7-*f*]quinoline-3,1′:9,1′′-bis(cyclohexane)] (6l): After the removal of chloroform, the residue was purified by column chromatography on Al_2O_3 (using hexane as eluent) to give compound **3l**. The polycycle **6l** was eluted with chloroform. **3l:** Pale yellow oil, yield 56%, R_f = 0.73. IR (film): $\tilde{\nu}$ = 3433 (NH) cm^{-1}. EI-MS (70 eV): m/z (%) = 243 (25) [M$^+$], 228 (38), 214 (6), 200 (100), 187 (8), 184 (9), 172 (22), 158 (12). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.69−1.33 (m, 10 H, cycloalkyl H), 1.28 (d, J = 7.0 Hz, 3 H, 4′-Me), 1.76 (dd, J = 13.5, 5.4 Hz, 1 H, 3′-H^B), 1.88 (dd, J = 13.5, 7.1 Hz, 1 H, 3′-H^A), 2.11 (s, 3 H, 8′-Me), 2.26 (s, 3 H, 5′-Me), 3.09 (tq, J = 7.0, 5.4 Hz, 1 H, 4′-H), 3.76 (br. s, 1 H, NH), 6.45 (d, J = 7.5 Hz, 1 H, 6′-H), 6.80 (d, J = 7.5 Hz, 1 H, 7′-H) ppm. $C_{17}H_{25}N$ (243.4): calcd. C 83.95, H 10.29, N 5.76; found C 84.01, H 10.44, N 5.89. **6l:** White crystals, yield 26%, m.p. 173−175 °C (chloroform). IR (KBr): $\tilde{\nu}$ = 1656 and 1616 (N=C and C=C) cm^{-1}. LC-MS: m/z (%) = 487 (100) [M + H]$^+$, 244 (32). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.67 (s, 3 H, 11a-Me), 0.83 (d, J = 6.8 Hz, 3 H, 1-Me), 0.85 (d, J = 6.8 Hz, 3 H, 11-Me), 0.87 (s, 3 H, 12b-Me), 1.09 (t, $J \approx$ 13.2 Hz, 1 H, 2-H^B), 1.22 (t, J = 12.8, 13.9 Hz, 1 H, 10-H^B), 1.38 (s, 3 H, 7-H), 1.58 (dd, J = 4.2, 13.9 Hz, 1 H, 10-H^A), 1.61 (dd, J = 3.1, 13.6 Hz, 1 H, 2-H^A), 1.72 (m, 3 H, 5-Me), 1.86 (m, 1 H, 11-H), 2.12 (m, 1 H, 1-H), 2.24 (d, J = 8.2 Hz, 1 H, 12a-H), 2.32 (m, 1 H, 6a-H), 2.73 (d, J = 6.8 Hz, 1 H, 12-H), 5.69 (dd, J = 1.1, 8.1 Hz, 1 H, 1′′′-H), 5.79 (dq, J = 4.1, 1.4 Hz, 1 H, 6-H), 6.02 (dd, J = 6.6, 8.1 Hz, 1 H, 2′′′-H), 1.8−1.2 (m, 20 H, cyclohexyl H) ppm. ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 27.1 (C-1), 36.5 (C-2), 55.9[a] (C-3), 166.4 (C-4a), 135.5 (C-5), 129.3 (C-6), 48.5 (C-6a), 49.2 (C-7), 176.3 (C-7a), 56.4[a] (C-9), 38.3 (C-10), 27.4 (C-11), 40.1[b] (C-11a), 41.6 (C-12), 41.6 (C-12a), 42.6[b] (C-12b), 136.5 (C-1′′′), 130.7 (C-2′′′), 15.58 (1-Me), 19.8 (5-Me), 18.9 (7-Me), 15.5 (11-Me), 17.9 (11a-Me), 22.9 (12b-Me), 42.1, 40.9, 39.7, 36.9, 26.3, 26.0, 22.5, 22.3, 22.0, 21.8 (C cyclohexyl) ppm. $C_{34}H_{50}N_2$ (486.8): calcd. C 83.95, H 10.29, N 5.76; found C 83.91, H 10.42, N 5.79.

8′-Ethyl-3′,4′-dihydro-4′,5′-dimethyl-1′*H*-spiro[cyclohexane-1,2′-quinoline] (3m) and 5′-Ethyl-3′,4′-dihydro-4′,8′-dimethyl-1′*H*-spiro[cyclohexane-1,2′-quinoline] (4m): Yellow oil, an inseparable mixture of isomers, ca. 1:1, yield 77%, R_f = 0.70. IR (film): $\tilde{\nu}$ = 3430 (NH) cm^{-1}. EI-MS (70 eV): m/z (%) = 257 (47) [M$^+$], 242 (61), 228 (12), 214 (100), 186 (9), 157 (5), 130 (4). $C_{18}H_{27}N$ (257.4): calcd. C 84.05, H 10.51, N 5.45; found C 83.89, H 10.49, N 5.48. ^{1}H and ^{13}C NMR spectra were recorded for a mixture of isomers **3m** and **4m**. **3m:** ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.33 (t, J = 7.5 Hz, 3 H, CH_2CH_3), 1.4−1.8 (m, 10 H, cycloalkyl H), 1.39 (d, J = 7.1 Hz, 3 H, 4′-Me), 1.85 (dd, J = 13.5, 5.3 Hz, 1 H, 3′-H^B), 1.94 (dd, J = 13.5, 7.0 Hz, 1 H, 3′-H^A), 2.34 (s, 3 H, 5′-Me), 2.54 (q, J = 7.5 Hz, 2 H, CH_2CH_3), 3.19 (ddq, J = 7.1, 7.0, 5.3 Hz, 1 H, 4′-H), 3.94 (br. s, 1 H, NH), 6.57 (d, J = 7.6 Hz, 1 H, 6′-H), 6.90 (d, J = 7.6 Hz, 1 H, 7′-H) ppm. ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 50.7[a] (C-2′ spiro), 42.2 (C-3′), 27.0 (C-4′), 124.7[b] (C-4a′), 133.6 (C-5′), 118.7[c] (C-6′), 125.0[d] (C-7′), 124.3 (C-8′), 139.7 (C-8a′), 21.3[e] (4′-Me), 23.5 (MeCH_2), 13.0 (MeCH$_2$), 19.4 (5-Me) ppm. **4m:** ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.28 (t, J = 7.6 Hz, 3 H, CH_2CH_3), 1.4−1.8 (m, 10 H, cycloalkyl H), 1.36 (d, J = 7.1 Hz, 3 H, 4′-Me), 1.89 (d, J = 5.7 Hz, 2 H, 3′-H), 2.19 (s, 3 H, 8′-Me), 2.63 and 2.71 (m, J = 7.6 Hz, 2 H, CH_2CH_3), 3.24 (m, J = 7.6, 5.7 Hz, 1 H, 4′-H), 3.84 (br. s, 1 H, NH), 6.57 (d, J = 7.6 Hz, 1 H, 6′-H), 6.93 (d, J = 7.6 Hz, 1 H, 7′-H) ppm. ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 50.9[a] (C-2′ spiro), 42.2 (C-3′), 27.4 (C-4′), 125.1[b] (C-4a′), 140.7 (C-5′), 116.6[c] (C-6′), 127.5[d] (C-7′), 118.4 (C-8′), 141.3 (C-8a′), 22.1[e] (4′-Me), 24.8 (MeCH_2), 15.6 (MeCH$_2$), 17.0 (8′-Me) ppm. Spirocyclohexane carbon signals of the isomers **3m** and **4m** in the ^{13}C NMR spectrum: δ = 39.7, 39.4, 39.1, 38.3, 25.6, 25.57, 22.52, 22.4, 22.2, 22.1 ppm.

5′,8′-Diethyl-3′,4′-dihydro-4′-methyl-1′*H*-spiro[cyclohexane-1,2′-quinoline] (3n): Colorless oil, yield 94%, R_f = 0.78. IR (film): $\tilde{\nu}$ = 3420 (NH) cm^{-1}. EI-MS (70 eV): m/z (%) = 271 (38) [M$^+$], 256 (41), 242 (6), 228 (100), 200 (12), 184 (8), 170 (6), 156 (4). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.21 (t, J = 7.5 Hz, 3 H, 5′-CH_2CH_3), 1.26 (t, J = 7.5 Hz, 3 H, 8′-CH_2CH_3), 1.72−1.33 (m, 10 H, cycloalkyl H), 1.28 (d, J = 7.1 Hz, 3 H, 4′-Me), 1.79 (dd, J = 13.6, 6.2 Hz, 1 H, 3′-H^B), 1.83 (dd, J = 13.6, 4.7 Hz, 1 H, 3′-H^A), 2.47 (q, J = 7.5 Hz, 2 H, 8′-CH_2CH_3), 2.68−2.51 (m, J = 7.5 Hz, 2 H, 5′-CH_2CH_3), 3.18 (m, J = 7.1, 6.2, 4.7 Hz, 1 H, 4′-H), 3.86 (br. s, 1 H, NH), 6.55 (d, J = 7.7 Hz, 1 H, 6′-H), 6.88 (d, J = 7.7 Hz, 1 H, 7′-H) ppm. $C_{19}H_{29}N$ (271.5): calcd. C 84.13, H 10.70, N 5.17; found C 84.14, H 10.74, N 5.22.

8′-Ethyl-3′,4′-dihydro-4′,4′-dimethyl-1′*H*-spiro[cyclohexane-1,2′-quinoline] (10): Yield 68%, R_f = 0.78, b.p. 141−144 °C/1.5 Torr; n_D^{23} = 1.5539. IR (film): $\tilde{\nu}$ = 3427 (NH) cm^{-1}. EI-MS (70 eV): m/z (%) = 257 (30) [M$^+$], 242 (41), 228 (18), 214 (100), 200 (46), 186 (11), 172 (11), 143 (10), 130 (10), 115 (10). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.27 (t, J = 7.6 Hz, 3 H, CH_2CH_3), 1.58−1.36 (m, 10 H, cycloalkyl H), 1.32 (s, 6 H, 4′-Me), 1.73 (s, 2 H, 3′-H), 2.49 (q, J = 7.6 Hz, 2 H, CH_2CH_3), 3.94 (br. s, 1 H, NH), 6.67 (t, J = 7.6 Hz, 1 H, 6′-H), 6.91 (br. d, J = 7.6 Hz, 1 H, 7′-H), 7.09 (dd, J = 7.6, 1.3 Hz, 1 H, 5′-H) ppm. $C_{18}H_{27}N$ (257.4): calcd. C 84.05, H 10.51, N 5.45; found C 83.78, H 10.33, N 5.48.

2,6-Dimethylaniline (11): Yield 33%. Spectroscopic data are in agreement with those reported in the literature.

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[8] Crystallographic data for structures **4g** and **6l** have been deposited with the Cambridge Crystallographic Data Centre (CCDC) as supplementary publication numbers CCDC-220116 (**4g**) and -220117 (**6l**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK [Fax: (internat.) + 44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk]. Crystal data for **4g**: Crystal dimensions: 0.30 × 0.45 × 0.85 mm, colorless prisms, $C_{17}H_{26}ClN$, M = 279.84, space group $P\bar{1}$, triclinic, a = 11.002(3), b = 12.954(6), c = 14.058(8) Å, α = 90.51(3), β = 112.40(3), γ = 113.73(3)°, Z = 4, V = 1664.3(13) Å^3, $\rho_{calcd.}$ = 1.117 g × cm^{-3}, μ = 0.219 cm^{-1}, $F(000)$ = 608. Intensities of 8882 reflections with $I \geq 0.5\sigma(I)$ (8349 are independent of symmetry) were measured. Final R_1 value 0.0539 [$wR_2(F^2)$ = 0.2041] for 2013 reflections with $I \geq 2\sigma(I)$ (R_{int} = 0.0223), GOOF = 0.998. Crystal data for **6l**: Crystal dimensions: 0.81 × 0.31 × 0.12 mm, colorless rhombuses, $C_{34}H_{50}N_2$, M = 486.76, space group $P2(1)/c$ monoclinic, a = 12.510(3), b = 10.140(2), c = 22.570(5) Å, β = 102.16(3)°, Z = 4, V = 2798.8(11) Å^3, $\rho_{calcd.}$ = 1.155 g × cm^{-3}, μ = 0.660 cm^{-1}, $F(000)$ = 1072. Intensities of 4407 reflections with $I \geq 0.5\sigma(I)$ (4212 are independent of symmetry) were measured. The final R_1 value was 0.0747 [$wR_2(F^2)$ = 0.2359] for 1614 reflections with $I \geq 2\sigma(I)$ ($R_{int.}$ = 0.1238), GOOF = 1.096.

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