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Synthesis of Sterically Hindered 4a,9a-Disubstituted 1,2,3,4,4a,9a-Hexahydrocarbazoles from 4a-Methyl-1,2,3,4-tetrahydro-4a*H*-carbazole with Organolithium Reagents

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Abstract: The reaction of 4a-methyl-1,2,3,4-tetrahydrocarbazole (**1**) with organolithium reagents affords the sterically hindered alkyl, aryl or alkenyl *cis*-4a-methyl-9a-substituted-1,2,3,4,4a,9a-hexahydrocarbazole derivatives (**2**) in excellent yields. Two diastereomeric pairs were isolated for the 9a-sec-butyl derivative. Evidence for a radical mechanism is supported by epr.

Introduction

The structural diversity exhibited by the *cis*-fused tetrahydrocarbazole system does not detract from the potency of these alkaloids, but instead leads to an impressive array of biological activity.[1]

We previously reported a novel synthesis of 2′-substituted spiro[cycloalkane-1,3′-indolines].[2] This synthesis proceeded by reaction of the C=N bond in a spiro[cycloalkane-1,3′-3′*H*-indole] with an organomagnesium reagent in the presence of copper(I) chloride, to give the 2′-R substituted (R = Me, Ph) derivatives, in nearly quantitative yield.[3] In this way, 4a-methyl-9a-substituted-1,2,3,4,4a,9a-hexahydrocarbazoles have been obtained by reaction of **1** with an organomagnesium-copper(I) chloride reagent to give 4a,9a-disubstituted derivatives.[4] The yield of this reaction is moderate to low (when it takes place) and depends upon the bulk of the Grignard reagent. Thus, the bulkier *sec*-butyl and *tert*-butyl reagents gave only the 9a-H derivative in low yield.

We desired a good preparation of the hexahydrocarbazoles **2a-h** by reaction of the C=N bond in 4a-methyl-1,2,3,4-tetrahydro-4a*H*-carbazole **1** with bulky organometallic reagents, to prepare the corresponding hindered 9a-substituted derivatives. These compounds are used as starting materials for the synthesis of the 9-(3-*N*,*N*-dimethylaminopropyl) derivatives, some of which show efficient dopaminergic and serotoninergic activity in the central nervous system.[5]

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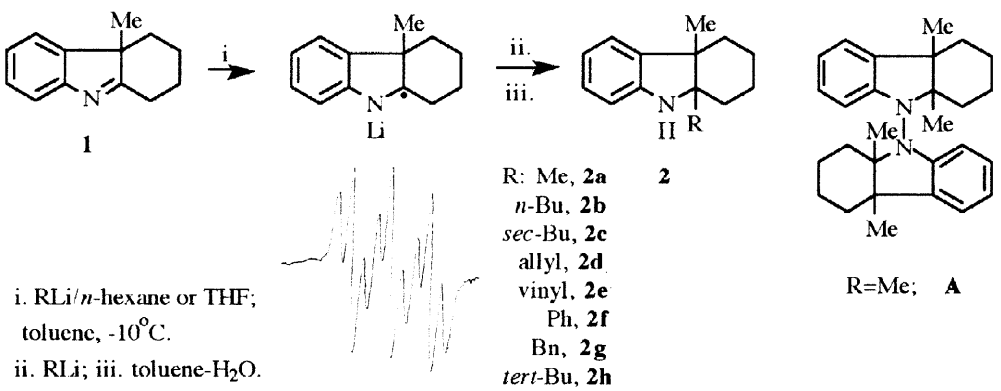
Results and Discussion

The compound **1** was satisfactorily synthesized either by treatment of 1,2,3,4-tetrahydrocarbazolyl magnesium iodide with methyl iodide in dry tetrahydrofuran or by the Fischer reaction from the phenylhydrazone of 2-methylcyclohexanone.[6]

The reaction of the compound **1** with *n*-butyllithium in ethereal solvents (THF or diethyl ether) at room temperature gives the 9a-*n*-butyl derivative **2b** in low yield (5 %). However, the use of toluene instead of the ethereal solvent, permits the quantitative transformation of the compound **1** to **2b**, Scheme 1. In this way, the preparation of the 9a-alkyl, alkenyl or aryl derivatives **2a-h** was carried out from **1** with a stoichiometric amount or slight excess of the appropriate organolithium reagent in toluene in excellent yield, Table 1. In all the cases only the *cis* isomer was obtained as the corresponding diastereoisomer pair 4a(S*)-methyl-9a(R*)-substituted (**2a-h**). The reaction is particularly useful for the synthesis of the bulky 9a substituted compounds **2**, such as *n*-butyl, *sec*-butyl, *tert*-butyl, benzyl and phenyl, or the unsaturated allyl and vinyl derivatives, Scheme 1.



Scheme 1

Table 1. Preparation of 9a-Substituted Derivatives 2a-h

RLi	Equiv.	T (°C)	t (h)	2 (%)	RLi	Equiv.	T (°C)	t (h)	2 (%)
Methyl	2	-10	3	87	Allyl	1	-10	4	75
n-Butyl	1.25	0	3	97	Allyl	2	-10	3	95
sec-Butyl	2	0	5	90	Vinyl	1	-10	5	78
Phenyl	1.5	0	2	94	Vinyl	2	-10	4	90
Benzyl	2	0	5	65					

Experimental evidence for the involvement of a radical intermediate in this reaction was found by esr from a sample of **1** and methyllithium in toluene at room temperature. The spectrum of the radical appears as a triplet of triplets showed in Scheme 1, [esr, g factor = 2.0244, a_H = 0.325 mT (1:2:1) and a_N = 0.975 mT (1:1:1)]. This is consistent with the possibility that the reaction proceeds through a single electron transfer mechanism[7] from the RLi reagent giving the 9a radical intermediate which couples with the radical R of the organolithium to the 9a substituted derivative **2**. The radical mechanism agrees well with the low yield found for this reaction in more

polar ethereal solvents, although an alternative ionic mechanism can be considered. In general, some amount of the self-coupling reaction of the R group of the organolithium to the corresponding dimer R-R was detected.

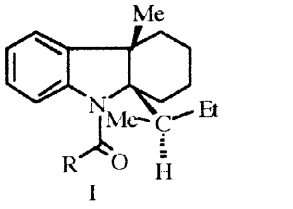
In this reaction only the *cis* isomer of **2** was isolated and in contrast with the reaction of the Grignard/copper(I) chloride system and **1**, the 9a-H derivative was never detected.[4] A radical mechanism for the C=N bond in spiroindolenines with Grignard reagents has recently been proposed.[8]

Afterwards, in the reaction of **1** with methyllithium was obtained the expected *cis* isomer 4a*S**,9a*R**-dimethyl derivative **2a** and exceptionally, only for this case, a byproduct (7 %) which, on the basis of the spectral and elemental analysis was interpreted as the 9,9′ dimer **A**, Scheme 1. Thus, the NH band was not detected in the IR spectrum; by NMR two doublets at 7.05 and 6.00 and a multiplet at 6.78 ppm, all characteristic of the indoline nucleus, were seen, corroborated by the two singlet signals at 1.10 and 1.35 ppm corresponding to the 4a,9a and 4a′,9a′ methyl groups on a symmetrical structure, and the multiplet at 2.29 ppm for the methylene at position 1; the mass spectrum shows the molecular peak at m/z 400 (35 %), the base peak at 200 is assigned to the N-N impact cleavage, and the rest of the spectrum shows identical fragmentation peaks to that of **2a**.[9]

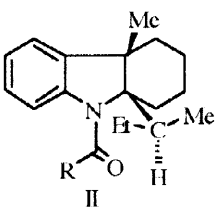
It is well known that the formation of a η^6-chromium tricarbonyl complex enhances the reactivity and selectivity of the conjugated positions by carbanion stabilization on the benzylic position.[10] Hence, to improve the yield of the reaction of **1** with *tert*-butyllithium, the η^6-chromium tricarbonyl complex of **1** was prepared for the ionic *vs* radical addition mechanism enhancement. Thus, the reaction of the complex with *tert*-butyllithium in toluene, after decomplexation with I_2-$Na_2S_2O_3$-H_2O, afforded only the more stable *cis*-ring fused isomer of the 4a(*S**)-methyl,9a(*R**)-*tert*-butyl derivative (**2h**) in low yield (12 %); 4a-methyl appears at 1.45 ppm, while the 9a-tert-butyl group at 1.00 ppm in the NMR spectrum. However, in more polar solvents (THF or diethyl ether instead toluene), the **1**-$Cr(CO)_3$ complex remains untransformed in contrast with an ionic mechanism enhancement of the reaction. The evidence for the *cis*-4a(*S**)-methyl,9a(*R**)-*n*-butyl derivative **2b**, was obtained by reaction of the **1**-$Cr(CO)_3$ complex with *n*-butyllithium reagent.[4] The *cis* isomer of **2b** shows the 4a-methyl group at 1.05 ppm in the NMR spectrum.

On the other hand, in the reaction of **1** with *sec*-butyllithium the *cis*-4a-methyl,9a-*sec*-butyl derivative **2c** was obtained as two diastereomers I and II, which were isolated and identified by ^{1}H-NMR, as the enantiomeric pairs: (4a*S**,9a*R**,2′*R**), diastereomer I and (4a*S**,9a*R**,2′*S**), diastereomer II; the 4a-methyl group appears at 1.15 and 1.12 ppm respectively. Characterization of both diastereomers was performed by means of the anisotropic effect induced by the carbonyl group on the methyl or ethyl groups of the *sec*-butyl chain in 1-acryloyl derivatives **3c**, [5] Table 2.

Table 2. Diastereomers of 9a-sec-butyl derivative 3c



I



II

R= vinyl, **3c**

^{1}H-NMR	**I-3c**	**II-3c**
Me	0.79 (d)	0.97 (d)
Me (Et)	0.71 (t)	0.65 (t)

In the ^{1}H NMR spectrum it was observed that the 9a-phenyl substituent in **2f** shows an important shielding effect on the 4a-methyl group (0.74 ppm). In contrast, any anisotropic effect was observed for the 9a-benzyl substituent in **2g** on the 4a-methyl group (1.28 ppm). Hence, while in **2f** the 4a-methyl is in the plane of the 9a-phenyl substituent, in **2g** the phenyl ring of the 9a-benzyl group probably rotates about the methylene to alleviate

hindrance between the the phenyl ring and the 4a-methyl groups. The diastereotopic effect shown in the methylene hydrogens of the benzyl group can be explained by hindered rotation around C-9a.

Moreover, in general the bulky 9a substitution produces a chair deformation of the trans-fused cyclohexane ring.[4] The axial hydrogen of the methylene at position 1 exhibits a deshielding effect in the NMR among 1.85 to 1.95 vs 1.55 ppm for 9a-H derivative.[4] In the same way, the steric hindrance from the more bulky 9a substitution produces a deshielding effect on the 4a methyl group; 1.28 and 1.45 ppm for 9a-benzyl (**2g**) and 9a-*tert*-butyl (**2h**) respectively.

Experimental Section

Melting points were determined in open capillary tubes or in a hot stage microscope and are uncorrected. Infrared spectra were taken on a FT-IR spectrometer. ^{1}H NMR spectra were recorded at 200 MHz in $CDCl_3$, with TMS as reference. ^{13}C NMR spectra were recorded at 50 MHz, in $CDCl_3$ with TMS as reference. Mass spectra were recorded using electronic impact technique at 70 eV. All reactions were performed in flame-dried glassware under argon atmosphere. All solvents were distilled prior to use; diethyl ether and THF were dried by distillation over sodium benzophenone ketyl and toluene was distilled over calcium hydride. All chemicals were reagent grade.

Preparation of 9a-substituted 4a-methyl-1,2,3,4,4a,9a-hexahydrocarbazoles, 2a-h. General procedure. To a solution of 4a-methyl-1,2,3,4-tetrahydro-4a*H*-carbazole (**1**) (1.5 g, 8.1 mmol) in dry toluene (19 mL), at -10 °C and shielded from sunlight, was added the appropriate organolithium solution (12.5 mmol) in hexane or THF. The solution mixture was stirred at -10 °C for 3 h and hydrolysed with toluene:water 1:1 (25 mL). The organic layer was separated, extracted with dichloromethane, dried with Na_2SO_4 and filtered. The solvent was evaporated and the residual orange oil, purified by column chromatography using hexane:ethyl acetate 4:1 as the eluent. The corresponding 9a-substituted 4a-methyl-1,2,3,4,4a,9a-hexahydrocarbazole (**2a-h**) was obtained as an oil which was transformed into the respective hydrochloride.

4a,9a-Dimethyl-1,2,3,4,4a,9a-hexahydrocarbazole (2a). **2a** was obtained as a light yellow oil, hydrochloride m.p. 222-224 °C, 1.41 g, 87 % yield. IR (film) 3340, 740 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ 1.10 (s, 3H), 1.18 (s, 3H), 1.3-1.7 (m, 7H, $(CH_2)_3$, 1-H), 1.85 (m, 1H), 3.33 (s, 1H), 6.62 (d, 1H, J = 7.3 Hz), 6.76 (t, 1H, J = 6.8 Hz); 6.98 (m, 2H). ^{13}C-NMR ($CDCl_3$): δ 22.0 (CH_3-4a,9a), 22.3 (C-3), 22.4 (C-2), 34.6 (C-4), 36.4 (C-1), 45.8 (C-4a), 65.7 (C-9a), 110.1 (C-8), 118.4 (C-6), 121.5 (C-5), 126.6 (C-7), 138.1 (C-4b), 148.4 (C-8a). MS (70 eV) m/z 201 (M^+, 30), 186 (100), 158 (19), 146 (49), 144 (73). Anal. Calcd for $C_{14}H_{19}N$: C, 83.53; H, 9.51; N, 6.96. Found: C, 83.41; H, 9.34; N, 7.15.

Compound **A** was also obtained as a yellow oil, 0.23 g, 7 % yield. IR (film) 740 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ 1.10 (s, 6H), 1.35 (s, 6H), 1.4-1.9 (m, 12H, $(CH_2)_3$), 2.29 (m, CH_2-1), 6.00 (d, 2H, J = 7.1 Hz), 6.78 (m, 4H)); 7.05 (d, 2H, J = 6.7 Hz). MS (70 eV) m/z 400 (M^+, 35), 200 (100) 185 (50), 144 (30). Anal. Calcd for $C_{14}H_{19}N$: C, 83.95; H, 9.06; N, 6.99. Found: C, 83.65; H, 9.27; N, 6.88.

4a-Methyl-9a-n-butyl-1,2,3,4,4a,9a-hexahydrocarbazole (2b). **2b** was obtained as a light yellow oil, hydrochloride mp 221-223 °C, 1.9 g, 97 % yield. IR (film) 3350, 730 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ 0.86 (t, 3H, J = 5.0 Hz), 1.05 (s, 3H), 1.2-1.7 (m, 13H), 1.85 (m, 1H), 3.31 (s, 1H), 6.52 (d, 1H, J = 7.8 Hz), 6.66 (t, 1H, J = 7.2 Hz), 6.95 (m, 2H). ^{13}C-NMR ($CDCl_3$) δ 14.1 (CH_3-Bu), 22.2 (CH_3-4a, CH_2-3′), 22.5 (C-3), 23.5 (C-2), 26.4 (CH_2-2′), 31.5 (CH_2-1′), 32.5 (C-4), 34.8 (C-1), 46.8 (C-4a), 67.7 (C-9a), 110.1 (C-8), 118.5 (C-6), 121.4 (C-5), 126.7 (C-7), 138.5 (C-4b), 148.5 (C-8a). MS (70 eV) m/z 243 (M^+, 10), 186 (100), 144 (28), 143 (10), 130 (6). Anal. Calcd for $C_{17}H_{25}N$: C, 83.89; H, 10.35; N, 5.75. Found: C, 83.6; H, 10.45; N, 5.8

4a-Methyl-9a-sec-butyl-1,2,3,4,4a,9a-hexahydrocarbazole (2c). **2c** was obtained as a light yellow oil (mixture of two diastereomers, 1:1), 1.77 g, 90 % yield. The two diastereomeric products were separated by column chromatography using hexane:THF 20:1 as the eluent. The first eluting (**2cI**) was obtained as a light yellow oil, hydrochloride mp 249-251 °C while the second (**2cII**) was obtained as a white solid, mp 57-60 C (hydrochloride mp 239-241 °C).

Diastereomer I: enantiomeric pairs (4a*S**,9a*R**,2′*R**)-9a-sec-butyl-4a-methyl-1,2,3,4,4a,9a-hexahydrocarbazole. IR (film) 3350, 745 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ 0.95 (t, 3H, *J* = 6.9 Hz), 1.05 (d, 3H, *J* = 6.9 Hz), 1.15 (s, 3H), 1.2-2.1 (m, 11H), 3.7 (s, 1H), 6.58 (d, 1H, *J* = 7.6 Hz), 6.73 (td, 1H, *J* = 7.5, 0.8 Hz), 6.96 (d, 1H, *J* = 7.6 Hz), 7.00 (td, 1H, *J* = 7.4, 1.4 Hz). ^{13}C-NMR ($CDCl_3$): δ 12.5, 15.9, 21.9, 23.2, 24.1, 25.4, 31.2, 35.2, 40.7, 47.2, 69.9, 109.7, 118.5, 121.3, 126.8, 138.5, 148.1. MS (70 eV) m/z 243 (M^+, 6), 187 (20), 186 (100), 144 (21), 143 (11). Anal. Calcd for $C_{17}H_{25}N$: C, 83.89; H, 10.35; N, 5.75. Found: C, 83.58; H, 10.17; N, 5.50.

Diastereomer II: enantiomeric pairs (4a*S**, 9a*R**,2′*S**)-9a-sec-butyl-4a-methyl-1,2,3,4,4a,9a-hexahydrocarbazole. IR (KBr) 3350, 745 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ 0.93 (t, 3H, *J* = 6.8 Hz), 0.97 (d, 3H, *J* = 6.7 Hz), 1.12 (s, 3H), 1.2-2.1 (m, 11H), 3.65 (s, 1H), 6.57 (d, 1H, *J* = 7.7 Hz), 6.72 (td, 1H, *J* = 7.5, 0.8 Hz), 6.96 (d, 1H, *J* = 7.7 Hz), 6.99 (td, 1H, *J* = 7.6, 1.3 Hz). ^{13}C-NMR ($CDCl_3$) δ 13.0, 14.4, 22.0, 22.7, 24.1, 26.2, 29.9, 35.4, 40.6, 47.2, 69.8, 109.5, 118.3, 121.2, 126.8, 138.4, 147.9. MS (70 eV) m/z 243 (M^+, 6), 187 (15), 186 (100), 144 (13), 143 (7). Anal. Calcd for $C_{17}H_{25}N$: C, 83.89; H, 10.35; N, 5.75. Found: C, 83.40; H, 10.07; N, 5.40.

9a-Allyl-4a-methyl-1,2,3,4,4a,9a-hexahydrocarbazole (2d). The allyllithium reagent was prepared *in situ* from allyl chloride with lithium in hexane at -78 °C and titrated with *N*-pivaloyl-*o*-toluidine.[11]

a) molar ratio of (**1**):allyllithium 1:1. According to the general procedure, treatment of (**1**), 5.5 mmol, with allyllithium, 5.5 mmol, after 3 h of reaction, give only **2d**, 231 mg, 75 % yield, as a yellow oil, hydrochloride m.p. 157-158 °C.

b) molar ratio of (**1**):allyllithium 1:2. Following the general procedure, treatment of (**1**), 5.5 mmol with allyllithium, 5.5 mmol, after 2 h of reaction, give only **2d**, 292 mg, 95 % yield, was obtained as a green oil, hydrochloride m.p. 157-158 °C.

^{1}H-NMR: 1.09 (s, 3H, CH_3-4a), 1.1-1.7 (m, 7H, $(CH_2)_n$), 1.90 (m, 1H, H-1), 2.05 (m, 2H, CH_2-9a), 4.95 (m, 1H, $=CH_2$), 5.05 (m, 1H, $=CH_2$), 5.80 (m, 1H, CH=), 6.61 (d, 1H, *J* = 8.4 Hz, ArH); 6.76 (t, 1H, *J* = 7.6Hz, ArH), 7.01 (m, 2H, ArH); IR (KBr) 3360 (NH), 1640 (C=C), 910 ($CH=CH_2$), 750 (ArH 1,2-disubst.); MS (70eV) m/z 228 (M^+, 1), 186 (100), 144 (19), 143 (9), 130 (3). Anal. Calcd. for $C_{16}H_{21}N$: C, 84.53; H, 9.31; N, 6.16%. Found: C, 84.30; H, 9.42; N, 6.28%.

4a-Methyl-9a-vinyl-1,2,3,4,4a,9a-hexahydrocarbazole (2e). The vinyllithium reagent was prepared *in situ* from vinyl bromide with *n*-butyllithium in hexane at -78 °C.[12]

a) molar ratio of (**1**):vinyllithium 1:1. According to the general procedure, treatment of (**1**), 5.5 mmol, with vinyllithium, 5.5 mmol, after 5 h of reaction, give **2e**, 224 mg, 78 % yield, as a yellow oil, hydrochloride m.p. 172-174 °C.

b) molar ratio of (**1**):vinyllithium 1:2. The treatment of (**1**), 5.5 mmol with vinyllithium, 5.5 mmol, after 4 h of reaction, give only **2e**, 258 mg, 90 % yield, as a yellow oil, hydrochloride m.p. 172-174 °C.

IR (film) 3360 (NH), 1605 (Ar, C=C), 920 (C=C), 750 (ArH 1,2-disubst.), ^{1}H-nmr: 1.05 (s, 3H, CH_3-4a), 1.2-1.7 (m, 6H, $(CH_2)_n$), 1.95 (m, 2H, H-1), 5.10 (dd, 1H, *J*= 10.6 Hz and 1.6 Hz, $CH=CH_2$), 5.35 (dd, 1H, *J*= 16.3 Hz and 1.6Hz, $CH=CH_2$), 6.10 (dd, 1H, J= 16.3 and 10.6 Hz, $CH=CH_2$), 6.75 (m, 2H, H-6, H-8), 7.0 (m,

2H, H-5, H-7); MS (70eV) m/z 213 (M^+, 5), 186 (100), 144 (18), 133 (13), 105 (20), 91 (26). Anal. Calcd. for $C_{15}H_{19}N$: C, 84.46; H, 8.98; N, 6.57%. Found: C, 84.32; H, 9.15; N, 6.49 %.

4a-Methyl-9a-phenyl-1,2,3,4,4a,9a-hexahydrocarbazole (2f). **2f** was obtained as a white solid, mp 88-90 °C (hydrochloride mp 265-267 °C), 2.0 g, 94 % yield. IR (Film) 3340 (NH), 760, 755, 705 (ArH) cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 0.74 (s, 3H), 1.4-1.9 (m, 6H), 2.10 (m, 2H), 3.91 (s, 1H), 6.74 (d, 1H, J = 7.4 Hz), 6.77 (t, 1H, J = 7.3 Hz), 6.99 (d, 1H, J = 6.8 Hz), 7.08 (td, 1H, J = 7.5, 1.2 Hz), 7.30 (m, 3H), 7.70 (m, 2H); ^{13}C-NMR ($CDCl_3$) δ 21.4 (CH_3-4a), 22.4 (C-3), 26.3 (C-2), 33.7 (C-4), 37.4 (C-1), 47.5 (C-4a), 71.0 (C-9a), 109.6 (C-8), 118.7 (C-6), 122.1 (C-5), 126.3 (C-7), 126.6 (C-2′), 127.1 (C-4′), 127.7 (C-3′), 136.5 (C-4b), 145.3 (C-1′), 148.4 (C-8a); MS (70 eV) m/z 263 (M^+, 100), 220 (61), 207 (83), 186 (57), 144 (15), 130 (21). Anal. Calcd for $C_{19}H_{21}N$: C, 86.64; H, 8.04; N, 5.32. Found: C, 86.45; H, 8.15; N, 5.4.

9a-Benzyl-4a-methyl-1,2,3,4,4a,9a-hexahydrocarbazole (2g). The benzyllithium reagent was prepared *in situ* from toluene with *n*-butyllithium in hexane at -78 °C as reported previously.[13] Thus, **2g** was obtained as a white solid, mp 88-90 °C, 1.46 g, 65 % yield. IR (KBr) 3350, 750, 715 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ 1.28 (s, 3H), 1.3-1.6 (m, 6H), 1.80 (m, 2H), 2.73 (AB system, d, 2H, J = 12.8 Hz), 3.55 (s, 1H), 6.63 (dd, 1H, J = 7.2, 1.1 Hz), 6.75 (td, 1H, J = 7.3, 1.0 Hz), 7.03 (d, 1H, J = 7.2 Hz), 7.1-7.4 (m, 6H). ^{13}C-NMR ($CDCl_3$) δ 20.3, 21.9, 30.9, 36.4, 37.9, 39.3, 46.7, 67.8, 109.9, 118.5, 121.5, 125.8, 126.2, 127.0, 128.1, 130.4, 138.1, 148.1. MS (70 eV) m/z 277 (M^+, 3), 186 (100), 130 (4), 91 (11). Anal. Calcd for $C_{20}H_{23}N$: C, 86.59; H, 8.36; N, 5.05. Found: C, 86.35; H, 8.45; N, 5.20.

9a-tert-Butyl-4a-methyl-1,2,3,4,4a,9a-hexahydrocarbazole (2h). **2h** was obtained as a light yellow oil (hydrochloride mp 187-190 °C), 0.9 g, 45 % yield. IR (film) 3400, 735 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ 1.00 (s, 9H), 1.45 (s, 3H), 1.3-1.9 (m, 8H), 3.80 (s, 1H), 6.52 (d, 1H, J = 7.2 Hz), 6.65 (t, 1H, J = 6.5 Hz), 6.85 (d, 1H, J = 6.5 Hz), 6.98 (t, 1H, J = 7.3 Hz). ^{13}C-NMR ($CDCl_3$) δ 21.4, 22.4, 23.3, 28.4, 29.0, 39.8, 41.1, 48.3, 72.7, 107.5, 117.3, 119.8, 126.6, 140.0, 149.3. MS (70 eV) m/z 243 (M^+, 1), 186 (100), 144 (40), 130 (11), 93 (19). Anal. Calcd for $C_{17}H_{25}N$: C, 83.89; H, 10.35; N, 5.75. Found: C, 83.54; H, 10.20; N, 5.45.

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