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Tricyclic keto-indoles were synthesized by photocyclization of easily obtained enaminones in an electrocyclic photochemical reaction. The three methods reported were chosen according to the enaminone structure. The most general procedure using one-step synthesis was carried out in a benzene-methanol solution in the presence of sodium methylate. In the case of base sensitive substrates, the best method was photocyclization followed by oxidation. Besides, *N*-unsubstituted indoles with a five-membered ring were prepared by a photolysis reaction. All three methods are efficient and easy to perform.

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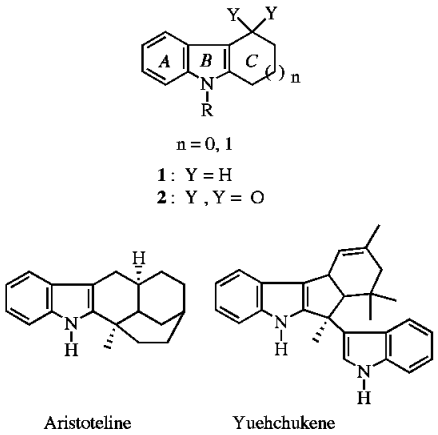
Tricyclic indoles **1** are biologically important compounds [1] because of their specific pharmacological activities and their presence in the structures of various active alkaloids (*e.g.*, aristoteline, yuehchukene). The corresponding keto-compounds **2** are key intermediates in the building of tetra and pentacyclic alkaloid skeletons [2,3].

Scheme 1

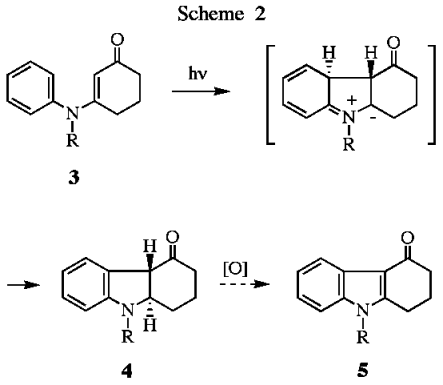


Since the discovery of the Fischer indole synthesis [4] numerous strategies have been developed for the indole ring formation [5a] such as base-initiated cyclization of halogenated imines/enamines [5b], transition metal catalyzed reactions [5c-5e] and radical initiated reactions [5f]. However, the search for new approaches is still a topic of current interest.

We previously described the non-oxidative photocyclization of *N*-arylenaminones **3** leading to *trans*-hexahydrocarbazolones **4** [6], which were intermediates in the synthesis of dihydroindolic *Aspidosperma* alkaloids [7]. The reaction mechanism is similar to that proposed by Grellmann [8] and Chapman [9] for the photocyclization of *N*-arylenamines, which gave *trans* compounds in agreement with the Woodward-Hoffmann rules [10]. It probably involves the n, π* triplet excited state [11].

Attemps were soon made to develop experimental conditions that would direct this reaction towards an oxidative photocyclization leading straight to indole derivatives. Although oxidative products were obtained as by-products when the solution was not thoroughly degassed [6a], pioneering attempts to prepare these compounds in good yields met little success and gave mixtures of compounds owing to incomplete reaction [9, 11].

Scheme 2

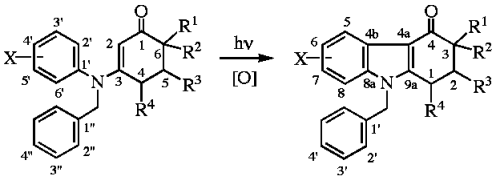


Here we describe two preparative photochemical processes (methods A and B) to synthesize, in good to excellent yield, substituted tricyclic keto-indoles **5,** with a five or six-membered C ring, from *N*-arylenaminones **3** by an oxidative cyclization reaction. Photocyclizations were performed using a 400 W medium pressure Pyrex®-jacketed immersion lamp (> 300 nm).

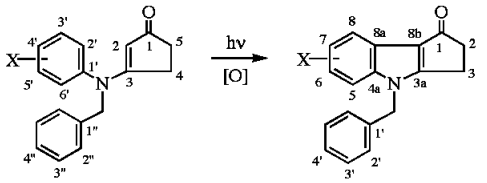
In method A, irradiation was conducted in non-degassed neutral medium and the crude mixture (mixture of compounds **4** and **5**) was oxidized in the presence of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) or manganese (III) acetate dihydrate [12].

In method B we first investigated the oxidative photocyclization of *N*-arylenaminones **3** in the presence of iodine or oxygen [9]. These reactions gave indoles **5** in low yield. In contrast, good to excellent yields of indoles **5** were obtained when irradiation of *N*-arylenaminones **3** was performed in the presence of sodium methoxide. The use

Scheme 3



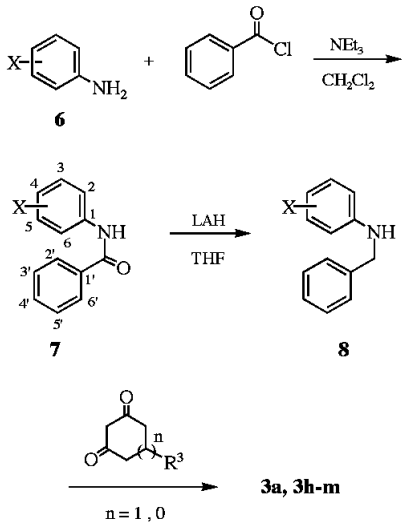
3a: X = H ; $R^1 = R^2 = R^3 = R^4 = H$ **5a**
3b: X = H ; R^1 = Et ; $R^2 = R^3 = R^4 = H$ **5b**
3c: X = H ; $R^1 = R^2$ = Me ; $R^3 = R^4 = H$ **5c**
3d: X = H ; $R^1 = (CH_2)_3Cl$; $R^2 = R^3 = R^4 = H$ **5d**
3e: X = H ; $R^1 = (CH_2)_3Cl$; R^2 = Et ; $R^3 = R^4 = H$ **5e**
3f: X = H ; $R^1 = CO_2Me$; $R^2 = R^3 = R^4 = H$ **5f**
3g: X = H ; $R^1 = R^2 = R^3 = H$; $R^4 = CO_2Me$ **5g**
3h: X = H ; $R^1 = R^2 = R^4 = H$; $R^3 = CO_2Me$ **5h**
3i: X = 4'-Me ; $R^1 = R^2 = R^3 = R^4 = H$ **5i**
3j: X = 3'-OMe ; $R^1 = R^2 = R^3 = R^4 = H$ **5j**
3k: X = 3',5'-diMe ; $R^1 = R^2 = R^3 = R^4 = H$ **5k**



3l: X = H **5l**
3m: X = 3',5'-diMe **5m**

of a strong base was suggested by the oxidation of hexahydrocarbazolones **4** into indoles **5** during alkylation attempts of **4** in strongly basic medium [13]. The same transformation was observed on treatment of **4** with sodium in methanol. These experiments call to mind the oxidation of ketones in basic medium [14,15] as related in the Büchi vindoline synthesis [16]. The reaction certainly proceeds by oxidation of the thermodynamic enolate of the saturated ketone followed by aromatization. After optimization of experimental conditions, the photocyclization of compounds **3** was carried out in the presence of sodium (3 equivalents) in a benzene/methanol (1:1) solution.

Scheme 4



Enaminones **3a** [17], **3h-m** were prepared following the reaction pathway of Scheme 4 and enaminones **3b-g** were obtained by alkylation of **3a** as previously described [17,18].

These thirteen compounds were photocyclized to lead to the expected indoles **5a-m**. The results are collected in the Table.

Table

Experimental Conditions and Results of Enaminone Photocyclization by Different Methods

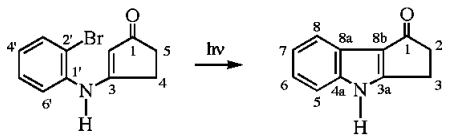
Enaminone	Solvents	Method A		Method B		Indole
		t (h)	%	t (h)	%	
3a	C_6H_6	1.2	49	-	-	**5a**
	C_6H_6 + MeOH	1.0	75 [a]	3.0	80	
3b	C_6H_6	0.7	95 [b]	-	-	**5b**
	C_6H_6 + MeOH	-	-	3.2	81	
3c	C_6H_6	0.5	65 [b]	-	-	**5c**
	C_6H_6 + MeOH	2.5	72 [b]	4.0	63	
3d	C_6H_6	0.5	68	-	-	**5d**
3e	C_6H_6	0.5	66 [b]	-	-	**5e**
	C_6H_6 + MeOH	-	-	2.5	42	
3f	C_6H_6 + MeOH	3.0	40	3.0	traces	**5f**
3g	C_6H_6 + MeOH	1.0	36	2.0	traces	**5g**
3h	C_6H_6 + MeOH	1.5	56	4.0	traces	**5h**
3i	C_6H_6 + MeOH	1.5	63	4.0	54	**5i**
3j	C_6H_6 + MeOH	4.0	78 [a,c]	4.0	56[c]	**5j**
3k	C_6H_6 + MeOH	-	-	7.0	91	**5k**
3l	C_6H_6	76.0	50 [d]	-	-	**5l**
	C_6H_6 + MeOH	-	-	48.0	30	
3m	C_6H_6 + MeOH	-	-	48.0	35	**5m**

[a] Photocyclization followed by oxidative treatment with $Mn(OAc)_3$ (1.1 eq) in dichloromethane + acetic acid at 70°C for 3h; [b] Photocyclization followed by oxidative treatment with DDQ (0.6 eq) in benzene at 80°C for 6h; [c] Formation of two indoles **5j** (5-OMe) and **5j'** (7-OMe), ratio 65:35; [d] Yield relative to converted enaminone **3l**; conversion 25%, real yield 12%.

Indoles **5a-k**, prepared from six-membered ring enaminones **3a-k**, were obtained in good yields using either method A or B. Method B offered the great advantage of being an one-pot synthesis, but could not be used for base-sensitive compounds **3d-h** bearing a chloroalkyl group or ester function. Also, method A gave the best yields in benzene/methanol solution, although the reaction was faster in benzene. Photocyclization of enaminone **3j** afforded two regioisomers **5j** (5-OMe) and **5j'** (7-OMe) in 65:35 ratio as already observed for non-oxidative photocyclization [19].

In contrast, indoles **5l**,**m**, prepared from five-membered ring substrates **3l**,**m**, were generated in moderate yields by methods A or B. These disappointing results are certainly due to the high ring strain in the corresponding indoles **5l**,**m**. *N*-Unsubstituted compound **5n**, with a five-membered C-ring, could, however, be synthesized in good yield by a third approach, namely free radical photocyclization of 2'-bromoaryl enaminone **3n**, according to Kibayashi's method [20] (Scheme 5). The best result (63% yield) was obtained when the photolysis was carried out for 1.5 hour in a methanol solution, in the presence of triethylamine, using a quartz insert.

Scheme 5



3n **5n**

In conclusion, we describe versatile and efficient photochemical methods to obtain tricyclic keto-indoles from readily available enaminones. *N*-substituted indoles **5** with a six-membered C-ring were easily obtained from *N*-arylenaminones using an electrocyclic photochemical reaction. Experimental conditions depend on the enaminone stucture. Photocyclization in the presence of sodium in a benzene/methanol solution (method B) has proved to be a general and useful one-step synthesis to access to indoles **5**. However, photocyclization followed by oxidation (method A) is shown to be more efficient for base-sensitive substrates. *N*-unsubstituted indoles **5n** with a five-membered C ring were prepared by a photolysis reaction.

The three methods described require inexpensive reagents, are complementary, easy to perform and compare favorably with other methods recently reported in the literature.

EXPERIMENTAL

General Methods.

Thin layer chromatography was performed with Merck silica gel 60 F254 and flash column chromatography was carried out with Merck silica gel 0.040-0.063 mm. Melting points were taken on a Reichert hot-stage microscope and are uncorrected. Infrared spectra were run on a Perkin Elmer 377 or 881 spectrophotometer. ^{1}H nmr spectra were recorded on Jeol C60H, Bruker MSL 300 or Bruker AC 400 instrument and ^{13}C nmr spectra on Jeol FX 60, Bruker MSL 300 or Bruker AC 400 spectrometer (δ values are given in ppm and J-values in Hz). Mass spectra were measured on a Varian CH-5 or a Varian VG 30F apparatus. Elemental combustion analysis were obtained from CNRS, Service Central d'Analyse, Vernaison, France.

Preparation of Aromatic Amides **7i-k**.

General Procedure.

To a solution of aromatic amine **6**, triethylamine (1.2 eq) and 4-(dimethylamino)-pyridine (DMAP) (catalytic amount) in dichloromethane (3 ml/mmole) was added dropwise, at 0° and under nitrogen, a solution of benzoyl chloride (1.2 eq) in dichloromethane (4 ml/mmole). The solution was allowed to warm up to room temperature, stirred for 6 hours and washed with brine (1 ml/mmole). The organic layer was dried on magnesium sulfate, filtered and evaporated under reduced pressure. Crystallization of the crude material afforded the pure amide.

N-(4-Methylphenyl)-benzamide (**7i**).

This compound was prepared from *p*-toluidine (**6i**) (3.92 g, 36.7 mmoles), triethylamine (4.44 g, 6.10 ml, 44.0 mmoles), DMAP (3 mg) and benzoyl chloride (6.18 g, 5.10 ml, 44.0 mmoles). The work-up afforded a residue which was crystallized from ethanol as a white solid, 7.43 g (35.2 mmoles, 96%), mp 156° (lit. [21] 154°); ir and ^{1}H nmr spectroscopic data of **7i** have been already reported [21]; ^{13}C nmr (15 MHz, methanol-d_4): δ 20.9 (CH_3), 122.4 (C-2, C-6), 128.7 (C-2', C-6'), 129.6 (C-3', C-5'), 130.3 (C-3, C-5), 132.9 (C-4'), 135.2 (C-4), 136.2 (C-1'), 137.4 (C-1), 168.4 (CO).

N-(3-Methoxyphenyl)-benzamide (**7j**).

This compound was prepared from *meta*-anisidine (**6j**) (4.92 g, 4.50 ml, 40.0 mmoles), triethylamine (4.85 g, 6.66 ml, 48.0 mmoles), DMAP (3 mg) and benzoyl chloride (6.75 g, 5.57 ml, 48.0 mmoles). The work-up afforded a residue which was crystallized from ethanol as a white solid, 8.63 g (38.0 mmoles, 95%), mp 175°; ir (chloroform): 1675 (CO) cm^{-1}; ^{1}H nmr (60 MHz, deuteriochloroform): δ 3.70 (s, 3H, OCH_3), 6.50-8.50 (m, 10H, phenyl protons + NH); ^{13}C nmr (100 MHz, methanol-d_4): δ 55.3 (OCH_3), 106.0 (C-2), 110.5 (C-4), 112.6 (C-6), 127.1 (C-5), 128.7 (C-2', C-6'), 129.7 (C-4'), 131.8 (C-3', C-5'), 134.8 (C-1'), 139.2 (C-1), 160.1 (C-3), 171.4 (CO).

N-(3,5-Dimethylphenyl)-benzamide (**7k**).

This compound was prepared from 3,5-dimethylaniline (**6k**) (4.44 g, 4.57 ml, 36.7 mmoles), triethylamine (4.44 g, 6.10 ml, 44.0 mmoles), DMAP (3 mg) and benzoyl chloride (6.18 g, 5.10 ml, 44.0 mmoles). The work-up afforded a residue which was crystallized from ethanol as a white solid, 8.09g (35.9 mmoles, 98%), mp 144-147°; ir (chloroform): 1670 (CO) cm^{-1}; ^{1}H nmr (60 MHz, methanol-d_4): δ 2.20 (s, 6H, $2CH_3$), 4.90 (s, 1H, NH), 6.85 (m, 1H, H-4), 7.30-7.70 (m, 5H, phenyl protons), 8.15 (m, 2H, H-2, H-6); ^{13}C nmr (15 MHz, methanol-d_4): δ 22.9 (CH_3), 120.1 (C-2, C-6), 120.5 (C-4), 128.9 (C-2', C-5'), 129.8 (C-3', C-5'), 132.8 (C-4'), 136.3 (C-1'), 139.3 (C-1), 141.5 (C-3, C-5), 167.3 (CO).

Preparation of Aromatic Amines **8i-k**.

General Procedure.

To a suspension of lithium aluminium hydride ($LiAlH_4$) (2 eq) in THF (1 ml/mmole) was added dropwise, at 0° and under nitrogen, a solution of aromatic amide **7** (1 eq) in THF (5 ml/mmole). After refluxing for 2 hours the excess of hydride was destroyed by addition of H_2O (0.1 ml/mmole) and a 15% solution of NaOH (0.1 ml/mmole). After filtration, the residue was washed with ethyl acetate (2 x 5 ml/mmole). The organic solution was dried on magnesium sulfate and filtered. Evaporation of the solvant afforded the expected aromatic amine with a satisfying purity.

N-Benzyl-*N*-(4-methylphenyl)amine (**8i**).

This compound was prepared from amide **7i** (10.97 g, 52.0 mmoles) and $LiAlH_4$ (3.95 g, 104.0 mmoles) and isolated as an oil, 7.80 g (39.5 mmoles, 76%); ir (carbon tetrachloride): 3430 (NH) cm^{-1}; nmr spectroscopic data of **8i** have been already reported [22].

N-Benzyl-*N*-(3-methoxyphenyl)amine (**8j**).

This compound was prepared from amide **7j** (16.09 g, 70.9 mmoles) and $LiAlH_4$ (5.39 g, 141.8 mmoles) and isolated as an oil, 13.43 g (63.1 mmoles, 89%); ir (carbon tetrachloride): 3440 (NH) cm^{-1}; ^1H nmr (60 MHz, deuteriochloroform): δ 3.85 (s, 3H, OCH_3), 4.40 (s, 2H, CH_2Ph), 6.27 (br. s, 1H, NH), 6.25-6.45 (m, 2H, phenyl protons), 7.15-7.50 (m, 7H, phenyl protons); ^{13}C nmr (100 MHz, deuteriochloroform): δ 48.2 (NCH_2Ph), 55.0 (OCH_3), 98.8 (C-2), 102.6 (C-4), 105.9 (C-6), 127.2 (C-4'), 127.5 (C-2', C-6'), 128.6 (C-3', C-5'), 130.3 (C-5), 139.3 (C-1'), 149.5 (C-1), 160.8 (C-3).

N-Benzyl-*N*-(3,5-dimethylphenyl)amine (**8k**).

This compound was prepared from amide **7k** (10.37 g, 46.1 mmoles) and $LiAlH_4$ (3.50 g, 92.2 mmoles) and isolated as an oil (9.03 g, 42.8 mmoles, 93%); ir (carbon tetrachloride): 3420 (NH) cm^{-1}; ^1H nmr (60 MHz, deuteriochloroform): δ 2.18 (s, 6H, 2 CH_3), 3.65 (s, 1H, NH), 4.10 (s, 2H, CH_2Ph), 6.13 (s, 2H, H-2, H-6), 6.37 (s, 1H, H-4), 7.45 (s, 5H, phenyl protons); ^{13}C nmr (15 MHz, deuteriochloroform): δ 21.4 (2 CH_3), 48.3 (NCH_2Ph), 110.8 (C-2, C-6), 119.6 (C-4), 127.1 (C-4'), 127.5 (C-2', C-6'), 128.6 (C-3', C-5'), 138.8 (C-3, C-5), 139.7 (C-1'), 148.3 (C-1).

Preparation of Enaminones **3**.

General Procedure.

To a suspension of diketone (1 eq) in toluene (10 ml/mmole) was added *para*-toluenesulfonic acid (PTSA) (5 mg/mmole) and aromatic amine **8** (1.1 eq). The mixture was refluxed overnight in a Dean-Stark apparatus, neutralized with potassium carbonate, filtered and evaporated under reduced pressure. The residual semisolid was purified on a silica gel column.

Compounds **3a** [17], **3b** [17], **3c** [18], **3d** [18], **3e** [17], **3f** [18], and **3g** [18] have been already described.

3-(Benzylphenylamino)-5-oxo-cyclohex-3-ene Carboxylic Acid Methyl Ester (**3h**).

This compound was prepared from methyl 3,5-dioxocyclohexylformiate [23] (1.84 g, 10.8 mmoles), *N*-benzylamine (2.17 g, 11.9 mmoles), and PTSA (54 mg) in toluene (110 ml). Chromatography with ethyl acetate:hexane (70:30, v/v) afforded enaminone **3h**, 2.88 g (8.60 mmoles, 80%); ir (carbon tetrachloride): 1740 (CO ester), 1640 (CO ketone) cm^{-1}; ^1H nmr (400 MHz, deuteriochloroform) [24]: δ 2.47-2.70 (m, 4H, 2H-4, 2H-6), 3.02 (m, 1H, H-5), 3.74 (s, 3H, OCH_3), 4.85 (s, 2H, CH_2Ph), 5.47 (s, 1H, H-2), 7.10-7.42 (m, 10H, phenyl protons); ^{13}C nmr (100 MHz, deuteriochloroform) [24]: δ 30.4 (C-4), 37.5 (C-6), 39.1 (C-5), 52.1 (OCH_3), 57.2 (CH_2Ph), 100.8 (C-2), 127.1 (C-4'), 127.7 (C-4", C-2', C-6'), 128.1 (C-2", C-6"), 128.8 (C-3'', C-5''), 129.9 (C-3', C-5'), 135.7 (C-1''), 143.9 (C-1'), 164.4 (C-3), 176.4 (CO ester), 195.7 (CO ketone) .

Anal. Calcd. for $C_{21}H_{21}NO_3$: C, 75.20; H, 6.31; N, 4.18. Found: C, 75.11; H, 6.20; N, 4.32.

3-[Benzyl-(4-methylphenyl)-amino]-cyclohex-2-enone (**3i**).

This compound was prepared from cyclohexane-1,3-dione (2.24 g, 20.0 mmoles), *N*-benzyl-*p*-methylaniline (**8i**) (4.30 g, 22.0 mmoles), and PTSA (100 mg) in toluene (200 ml). Chromatography with ethyl acetate afforded enaminone **3i**, 4.00 g (14.0 mmol, 70%); ir (carbon tetrachloride): 1635 (CO) cm^{-1}; ^1H nmr (400 MHz, deuteriochloroform): δ 1.86 (quint., 2H, 2H-5, J = 6.3 Hz), 2.24-2.34 (m, 4H, 2H-4, 2H-6), 2.27 (s, 3H, CH_3), 4.76 (s, 2H, CH_2Ph), 5.34 (s, 1H, H-2), 6.90-7.35 (m, 9H, phenyl protons); ^{13}C nmr (100 MHz, deuteriochloroform): δ 21.2 (CH_3), 22.4 (C-5), 28.4 (C-4), 35.9 (C-6), 56.0 (CH_2Ph), 101.4 (C-2), 126.8 (C-2', C-6'), 127.0 (C-2", C6"), 127.2 (C-4"), 128.5 (C-3", C-5"), 129.9 (C-3', C-5'), 136.3 (C-1"), 136.9 (C-4'), 144.2 (C-1'), 165.1 (C-3), 197.3 (CO).

Anal. Calcd. for $C_{20}H_{21}NO$: C, 82.44; H, 7.26; N, 4.81. Found: C, 82.11; H, 7.02; N, 4.63.

3-[Benzyl-(3-methoxyphenyl)-amino]-cyclohex-2-enone (**3j**).

This compound was prepared from cyclohexane-1,3-dione (3.05 g, 27.2 mmoles), *N*-(methoxyphenyl)benzylamine **8j** (6.38 g, 30.0 mmoles) and PTSA (136 mg) in toluene (270 ml). Chromatography with ethyl acetate:methanol (95:5, v/v) afforded enaminone **3j**, 7.26 g (23.7 mmoles, 87%); ir (carbon tetrachloride): 1635 (CO) cm^{-1}; ^1H nmr (400 MHz, deuteriochloroform): δ 1.93 (quint., 2H, 2H-5, J = 6.2 Hz), 2.40 (m, 4H, 2H-4, 2H-6), 3.79 (s, 3H, OCH_3), 4.84 (s, 2H, CH_2Ph), 5.40 (s, 1H, H-2), 6.65-7.45 (m, 9H, phenyl protons); ^{13}C nmr (100 MHz, deuteriochloroform): δ 22.3 (C-5), 28.4 (C-4), 35.8 (C-6), 55.2 (OCH_3), 56.4 (CH_2Ph,), 101.2 (C-2), 112.7 (C-2'), 113.5 (C-4'), 119.7 (C-6'), 126.7 (C-2", C-6"), 127.2 (C-4"), 128.5 (C-3", C-5"), 130.1 (C-5'), 136.1 (C-1"), 145.2 (C-1'), 160.2 (C-3'), 164.8 (C-3), 197.5 (CO).

Anal. Calcd. for $C_{20}H_{21}NO_2$: C, 78.15; H, 6.89; N, 4.56. Found: C, 77.85; H, 7.16; N, 4.70.

3-[Benzyl-(3,5-dimethylphenyl)-amino]-cyclohex-2-enone (**3k**).

This compound was prepared from cyclohexane-1,3-dione (440 mg, 3.93 mmoles), *N*-benzyl-3,5-dimethylaniline **8k** (910 mg, 4.32 mmoles), and PTSA (20 mg) in toluene (40 ml). Chromatography with ethyl acetate:hexane (50:50, v/v) afforded enaminone **3k**, 1.08 g (3.54 mmoles, 90%); crystals (Et_2O), mp 70-71°; ir (carbon tetrachloride): 1640 (CO) cm^{-1}; ^1H nmr (400 MHz, deuteriochloroform): δ 1.97 (quint., 2H, 2H-5, J = 6.3 Hz), 2.34 (s, 6H, 2 CH_3), 2.37 (m, 4H, 2H-4, 2H-6), 4.87 (s, 2H, CH_2Ph), 5.40 (s, 1H, H-2), 6.80 (s, 2H, H-2', H-6'), 6.97 (s, 1H, H-4'), 7.25-7.40 (m, 5H, phenyl protons); ^{13}C nmr (100 MHz, deuteriochloroform): δ 21.1 ($2CH_3$), 22.5 (C-5), 28.6 (C-4), 36.0 (C-6), 56.7 (CH_2Ph), 101.3 (C-2), 125.1 (C-2', C-6'), 126.7 (C-2", C-6"), 127.2 (C-4"), 128.6 (C-3", C-5"), 129.1 (C-4'), 136.4 (C-1"), 139.3 (C-3', C-5'), 144.4 (C-1'), 165.0 (C-3), 197.5 (CO); ms: m/z 305 (17, $M^{+\cdot}$), 249 (11), 234 (5), 186 (3), 134 (4), 91 (100), 65 (12), 28 (25).

Anal. Calcd. for $C_{21}H_{23}NO$: C, 82.58; H, 7.59; N, 4.59. Found: C, 82.63; H, 7.67; N, 4.95.

3-(Benzylphenylamino)-cyclopent-2-enone (**3l**).

This compound was prepared from cyclopentane-1,3-dione (0.50 g, 5.10 mmoles), *N*-benzylaniline (1.02 g, 5.60 mmoles, and PTSA (25 mg) in toluene (50 ml). Chromatography with ethyl acetate afforded enaminone **3n**, 1.30 g (4.94 mmoles, 97%); ir (carbon tetrachloride): 1705 (CO), 1675 (N-C=C) cm^{-1}; ^1H nmr (400 MHz, deuteriochloroform): δ 2.20 (m, 2H, 2H-5), 2.40 (m, 2H, 2H-4), 4.70 (s, 2H, N*C*H_2Ph), 5.20 (s, 1H, H-2), 7.00-7.25 (m, 10H, phenyl protons); ^{13}C nmr (100 MHz, deuteriochloroform): δ 28.0 (C-4), 33.8 (C-5), 57.3 (N*C*H_2Ph), 102.5 (C-2), 126.6 (C-2', C-6', C-2", C-6"), 126.8 (C-4'), 127.2 (C-4"), 128.2 (C-3", C-5"), 129.1 (C-3', C-5'), 135.7 (C-1"), 143.2 (C-1'), 176.7 (C-3), 203.7 (CO).

Anal. Calcd. for $C_{18}H_{17}NO$: C, 82.10; H, 6.51; N, 5.32. Found: C, 82.30; H, 6.38; N, 5.16.

3-[Benzyl-(3,5-dimethylphenyl)-amino]-cyclopent-2-enone (**3m**).

This compound was prepared from cyclopentane-1,3-dione (353 mg, 3.60 mmoles), *N*-benzyl-3,5-dimethylaniline (836 mg, 3.96 mmoles), and PTSA (18 mg) in toluene (40 ml). Chromatography with ethyl acetate afforded enaminone **3m**, 922 mg (3.17 mmoles, 88%); ir (carbon tetrachloride): 1695 (CO), 1675 (N-C=C) cm^{-1}; ^1H nmr (400 MHz, deuteriochloroform): δ 2.30 (s, 6H, 2CH_3), 2.35-2.47 (m, 2H, 2H-5), 2.50-2.65 (m, 2H, 2H-4), 4.72 (s, 2H, N*C*H_2Ph), 5.22 (s, 1H, H-2), 6.77 (s, 2H, H-2', H-6'), 6.95 (s, 1H, H-4'), 7.20-7.38 (m, 5H, phenyl protons); ^{13}C nmr (100 MHz, deuteriochloroform): δ 21.6 (2 *C*H_3), 29.7 (C-4), 35.3 (C-5), 59.2 (N*C*H_2Ph), 102.9 (C-2), 125.9 (C-4'), 128.9 (C-4"), 129.0 (C-2", C-6"), 130.0 (C-2', C-6'), 130.8 (C-3", C-5"), 137.7 (C-3', C-5'), 140.9 (C-1"), 144.9 (C-1'), 181.2 (C-3), 207.2 (CO).

Anal. Calcd. for $C_{20}H_{21}NO$: C, 82.44; H, 7.26; N, 4.81. Found: C, 82.72; H, 7.35; N, 4.62.

3-(2-Bromophenylamino)-cyclopent-2-enone (**3n**).

This compound was prepared from cyclopentane-1,3-dione (0.98 g, 10.0 mmoles), *o*-bromoaniline (1.80 g, 10.5 mmoles), and PTSA (50 mg) in toluene (100 ml). Chromatography with ethyl acetate afforded enaminone **3n**, 2.49 g (9.9 mmoles, 99%); yellow crystals (Et_2O), mp 161-163°; ir (carbon tetrachloride): 1695 (CO) cm^{-1}; ^1H nmr (400 MHz, deuteriochloroform): δ 2.40 (m, 2H, 2H-5), 2.80 (m, 2H, 2H-4), 5.55 (s, 1H, H-2), 7.10 (m, 1H, phenyl proton), 7.25-7.62 (m, 3H, phenyl protons); ^{13}C nmr (100 MHz, deuteriochloroform): δ 29.1 (C-4), 33.5 (C-5), 103.7 (C-2), 116.2 (C-2'), 122.7 (C-6'), 126.1 (C-4'), 128.5 (C-5'), 133.2 (C-3'), 137.5 (C-1'), 171.9 (C-3), 205.9 (CO); ms: m/z 253 [40, $M^{+\cdot}$ (^{81}Br)], 251 [41, $M^{+\cdot}$ (^{79}Br)], 224 (11), 222 (12), 196 (4), 172 (100), 157 (5), 89 (12), 28 (49), 27 (12).

Anal. Calcd. for $C_{11}H_{10}BrNO$: C, 52.40; H, 4.00; N, 5.56. Found: C, 52.72; H, 3.78; N, 5.48.

Preparation of Indoles **5**. General Procedure.

Method A.

A solution of enaminone **3** (0.23 to 1.80 mmole) in benzene (150 ml) or benzene:methanol (1:1, v/v) (150 ml) was irradiated at ambient air. When formation of tetrahydrocarbazolone **5** was accompanied by small amounts of hexahydrocarbazolone **4**, two alternative processes were followed after evaporation of the solvents: i) the residue was dissolved in toluene (100 ml/mmole) and refluxed for 5 hours in presence of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (0.5 eq); after removal of part of the solvent (2/3) and filtration of the DDQ reduced form, the solution was concentrated; the crude material was then purified by chromatography; ii) the residue was dissolved in dichloromethane (3 ml/mmole) and the solution added dropwise to a suspension of manganese (III) acetate dihydrate (1.1 eq) in acetic acid (5 ml/mmole); the mixture was warmed at 70° for 3 hours, cooled and filtered; the organic layer was washed successively with saturated solutions of sodium hydrogen carbonate (2 x 20 ml) and brine (2 x 10 ml), dried on magnesium sulfateand concentrated; the crude material then was purified by chromatography.

Method B.

A solution of enaminone (0.72 to 1.08 mmole) in benzene:methanol (1:1, v/v) (150 ml) was irradiated at ambient air and in presence of sodium (3 eq). After evaporation of the solvents, the residue was dissolved in ethyl acetate (50 ml/mmole). The solution was washed with brine (2 x 10 ml) and the aqueous phase extracted a last time with dichloromethane (10 ml). The combined organic layers were dried on magnesium sulfate and concentrated. The residue was purified by chromatography on a silica gel column.

9-Benzyl-1,2,3,9-tetrahydrocarbazol-4-one (**5a**).

This compound was prepared either by method A (solvent: *i)* benzene *ii)* benzene-methanol (1:1, v/v) or by method B.

Method A: i) Irradiation of **3a** (300 mg, 1.08 mmole) was realized in benzene (150 ml, c = 7.22 x 10^{-3} *M*) for 1.2 hour. Chromatography with ethyl acetate:hexane (50:50, v/v) as eluent afforded **5a** (145 mg, 0.53 mmole, 49%); ii) irradiation of **3a** (500 mg, 1.80 mmole) in benzene-methanol 1:1 (150 ml, c = 12.0 x 10^{-3} *M*) for 1 hour was followed by treatment with a suspension of manganese (III) acetate dihydrate (536 mg, 2.00 mmoles) in acetic acid (9 ml). Chromatography with ethyl acetate:hexane (40:60, v/v) as eluent afforded **5a**, 370 mg (1.35 mmole, 75%).

Method B: Irradiation of **3a** (300 mg, 1.08 mmole) in benzene-methanol 1:1 (150 ml, c = 7.22 x 10^{-3} *M*) was performed in presence of sodium (75 mg, 3.24 mmoles) for 3 hours. Chromatography with ethyl acetate:hexane (40:60, v/v) as eluent afforded **5a**, 240 mg (0.87 mmole, 80%).

Compound **5a** was obtained as white crystals (ethyl acetate), mp 160-161°; ir (chloroform): 1640 (CO) cm^{-1}; ^1H nmr (400 MHz, deuteriochloroform): δ 2.25 (quint, 2H, 2H-2, J = 6.4 Hz), 2.60 (t, 2H, 2H-3, J = 6.4 Hz,), 2.90 (t, 2H, 2H-1, J = 6.2 Hz), 5.37 (s, 2H, NC*H*$_2$Ph), 7.05 (dd, 2H, H-2', H-6', J = 7.6, 1.2 Hz), 7.21-7.34 (m, 6H, phenyl protons), 8.31 (dt, 1H, H-5, J = 7.4, 1.2 Hz); ^{13}C NMR (100 MHz, deuteriochloroform): δ 22.1 (C-2), 23.3 (C-1), 37.8 (C-3), 46.9 (N*C*H_2Ph), 109.7 (C-8), 112.9 (C-4a), 121.5 (C-5), 122.9 (C-6), 123.1 (C-7), 124.8 (C-4b), 126.0 (C-2', C-6'), 127.8 (C-4'), 128.9 (C-3', C-5') , 136.0 (C-1'), 137.0 (C-9a), 151.9 (C-8a), 193.9 (CO); ms: m/z 275 (80, $M^{+\cdot}$), 247 (30), 218 (18), 156 (8), 128 (13), 91 (100), 65 (12).

Anal. Calcd. for $C_{19}H_{17}NO$: C, 82.88; H, 6.22; N, 5.09. Found: C, 82.49; H, 6.38; N, 5.14.

9-Benzyl-3-ethyl-1,2,3,9-tetrahydrocarbazol-4-one (**5b**).

This compound was prepared either by method A or method B.

Method A: Irradiation of **3b** (160 mg, 0.52 mmole) in benzene (150 ml, c = 3.5 x 10^{-3} *M*) for 0.7 hour was followed by treat-

ment with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (60 mg, 0.26 mmole, 0.5 eq) in toluene (52 ml). Chromatography with ethyl acetate:cyclohexane (20:80, v/v) as eluent afforded **5b**, 151 mg (0.50 mmole, 95%).

Method B: irradiation of **3b** (160 mg, 0.52 mmole) in benzene:methanol (1:1, v/v) (150 ml, c = 3.5 x10^{-3} *M*) was performed in presence of sodium (36 mg, 1.57 mmole, 3 eq) for 3.2 hours. Chromatography with ethyl acetate:cyclohexane (20:80, v/v) as eluent afforded **5b**, 129 mg (0.42 mmole, 81%).

Compound **5b** was obtained as white crystals (ethyl acetate), mp 135-137°; ir (carbon tetrachloride): 1660 (CO) cm^{-1}; ^{1}H nmr (400 MHz, deuteriochloroform): δ 1.04 (t, 3H, CH_3, J = 7.5 Hz), 1.58 (ddq, 1H, C*H*$_B$-Me,J = 15.0, 7.5, 7.5 Hz), 1.97-2.09 (m, 2H, C*H*$_A$-Me, H-2ax), 2.32 (dddd, 1H, H-2eq, J = 13.3, 5.0, 5.0, 5.0 Hz), 2.42 (dddd, 1H, H-3, J = 9.5, 7.5, 7.5, 5.0 Hz), 2.85 (ddd, 1H, H-1ax, J = 17.0, 8.5, 5.0 Hz), 2.96 (ddd, 1H, H-1eq,J = 17.0, 5.0, 5.0 Hz), 5.30 (s, 2H, NC*H*$_2$Ph), 7.04 (dd, 2H, H-2', H-6', J = 7.2, 1.8 Hz), 7.20-7.34 (m, 6H, phenyl protons), 8.32 (dt, 1H, H-5, J = 7.8, 1.0 Hz); ^{13}C nmr (100 MHz, deuteriochloroform): δ 12.0 (CH_3), 21.2 (C-1), 22.5 (*C*H$_2$Me), 27.8 (C-2), 47.0 (N*C*H$_2$Ph), 47.8 (C-3), 109.7 (C-8), 112.8 (C-4a), 121.8 (C-5), 122.7 (C-6), 123.2 (C-7), 125.2 (C-4b), 126.1 (C-2', C-6'), 127.9 (C-4'), 129.1 (C-3', C-5'), 136.2 (C-1'), 137.4 (C-9a), 151.1 (C-8a), 196.3 (CO); ms: m/z 303 (38, $M^{+\cdot}$), 275 (100), 246 (18), 218 (26), 184 (7), 156 (8), 128 (19), 115 (6), 91 (83), 77(6), 65 (19); hrms calcd. for $C_{21}H_{21}NO$: 303.1623, found 303.1620.

Anal. Calcd. for $C_{21}H_{21}NO$: C, 83.13; H, 6.98; N, 4.62. Found: C, 82.67; H, 6.95; N, 4.69.

9-Benzyl-3,3-dimethyl-1,2,3,9-tetrahydrocarbazol-4-one (**5c**).

This compound was prepared either by method Aor method B.

Method A: Irradiation of **3c** (160 mg, 0.52 mmole) in benzene (150 ml, c = 3.5 x 10^{-3} *M*) for 0.5 hour or benzene:methanol (1:1, v/v) (150 ml, c = 3.5 x 10^{-3} *M*) for 2.5 hours was followed by treatment with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (60 mg, 0.26 mmole, 0.5 eq) in toluene (52 ml). Chromatography with ethyl acetate:cyclohexane (10:90, v/v) afforded **5c**, 103 mg (0.34 mmole, 65%) (irradiation in benzene) or 115 mg (0.38 mmole, 72%) (irradiation in benzene:methanol).

Method B: Irradiation of **3c** (160 mg, 0.52 mmole) in benzene:methanol (1:1, v/v) (150 ml, c = 3.5 x 10^{-3} *M*) was performed in presence of sodium (36 mg, 1.57 mmole, 3 eq) for 4 hours. Chromatography with ethyl acetate:cyclohexane (10:90, v/v) afforded **5c**, 101 mg (0.33 mmole, 63%).

Compound **5c** was obtained as white crystals (ethyl acetate), mp 171-172°; ir (carbon tetrachloride): 1640 (CO) cm^{-1}; ^{1}H nmr (400 MHz, deuteriochloroform): δ 1.25 (s, 6H, 2CH_3), 2.08 (t, 2H, 2H-2, J = 6.3 Hz), 2.90 (t, 2H, 2H-1, J = 6.3 Hz), 5.33 (s, 2H, NC*H*$_2$Ph), 7.03 (dd, 2H, H-2', H-6', J = 6.4, 1.7 Hz), 7.20-7.35 (m, 6H, phenyl protons), 8.34 (d, 1H, H-5, *J* = 7.8 Hz); ^{13}C nmr (100 MHz, deuteriochloroform): δ 19.7 (C-1), 24.5 (2 CH_3), 37.1 (C-2), 41.6 (C-3), 46.8 (N*C*H$_2$Ph), 109.6 (C-8), 111.3 (C-4a), 121.7 (C-5), 122.6 (C-6), 123.1 (C-7), 125.5 (C-4b), 126.0 (C-2', C-6'), 127.9 (C-4'), 129.1 (C-3', C-5'), 127.9 (C-4'), 136.1 (C-1'), 137.5 (C-9a), 150.3 (C-8a), 199.2 (CO); ms: m/z 303 (100, $M^{+\cdot}$), 232 (7), 218 (24), 128 (13), 101 (6), 91 (70), 77 (4), 65 (24), 56 (10), 41 (16), 29 (8); hrms calcd. for $C_{21}H_{21}NO$: 303.1623, found 303.1630.

Anal. Calcd. for $C_{21}H_{21}NO$: C, 83.13; H, 6.98; N, 4.62. Found: C, 83.50; H, 6.97; N, 4.53.

9-Benzyl-3-(3-chloropropyl)-1,2,3,9-tetrahydrocarbazol-4-one (**5d**).

This compound was prepared according to the procedure of method A. Irradiation of **3d** (185 mg, 0.52 mmole) in benzene (150 ml, c = 3.5 x 10^{-3} *M*) for 0.5 hour was followed by treatment with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (60 mg, 0.26 mmole, 0.5 eq) in toluene (52 ml). Chromatography with ethyl acetate:cyclohexane (15:85, v/v) afforded **5d**, 114 mg (0.32 mmole, 62%); white solid (ethyl acetate), mp 118-119°; ir (carbon tetrachloride): 1660 (CO) cm^{-1}; ^{1}H nmr (400 MHz, deuteriochloroform): δ 1.71 (dddd, 1H, C*H*$_B$-C$_2$H$_5$Cl, J = 14.0, 7.0, 7.0, 7.0 Hz), 1.91-2.15 (m, 4H, C*H*$_A$-C$_2$H$_5$Cl, C*H*$_2$-CH$_2$Cl, H-2ax), 2.30 (dddd, 1H, H-2eq, J = 13.0, 5.0, 5.0, 5.0 Hz), 2.50 (dddd, 1H, H-3, J = 9.0, 7.0, 5.0, 5.0 Hz), 2.84 (ddd, 1H, H-1ax,J = 17.0, 9.0, 5.0 Hz), 2.95 (ddd, 1H, H-1eq, J = 17.0, 5.0, 5.0 Hz), 3.60 (m, 2H, C*H*$_2$Cl), 5.30 (s, 2H, NC*H*$_2$Ph), 7.03 (dd, 2H, H-2', H-6', J = 7.0, 1.7 Hz), 7.21-7.34 (m, 6H, phenyl protons), 8.30 (d, 1H, H-5, J = 7.7 Hz); ^{13}C nmr (100 MHz, deuteriochloroform): δ 21.3 (C-1), 27.2 (*C*H$_2$-C$_2$H$_5$Cl), 28.7 (C-2), 30.5 (*C*H$_2$-CH$_2$Cl), 45.3 (*C*H$_2$Cl), 45.6 (C-3), 46.9 (N*C*H$_2$Ph), 109.7 (C-8), 112.5 (C-4a), 121.6 (C-5), 122.7 (C-6), 123.2 (C-7), 125.1 (C-4b), 126.1 (C-2', C-6'), 127.9 (C-4'), 129.1 (C-3', C-5'), 136.0 (C-1'), 137.3 (C-9a), 151.0 (C-8a), 195.5 (CO); ms: m/z 353 [4, $M^{+\cdot}$ (^{37}Cl)], 351 [12, $M^{+\cdot}$ (^{35}Cl)], 316 (64), 288 (11), 275 (36), 246 (10), 218 (15), 167 (7), 128 (15), 91 (100), 65 (21).

Anal. Calcd. for $C_{22}H_{22}NOCl$: C, 75.09; H, 6.30; N, 3.98; Cl, 10.07. Found: C, 74.80; H, 6.28; N; 4.04; Cl, 9.72.

9-Benzyl-3-(3-chloropropyl)-3-ethyl-1,2,3,9-tetrahydrocarbazol-4-one (**5e**).

This compound was prepared either by method A or method B.

Method A: Irradiation of **3e** (200 mg, 0.52 mmole) in benzene (150 ml, c = 3.5 x 10^{-3} *M*) for 0.5 hour was followed by treatment with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (60 mg, 0.26 mmole, 0.5 eq) in toluene (52 ml). Chromatography with ethyl acetate/cyclohexane (10:90, v/v) afforded **5e**, 132 mg (0.35 mmole, 66%) as a foam.

Method B: Irradiation of **3e** (200 mg, 0.52 mmole) in benzene (150 ml, c = 3.5 x 10^{-3} *M*) was performed in presence of sodium (36 mg, 1.57 mmole, 3 eq) for 2.5 hours. The aqueous phase was extracted with dichloromethane (2 x 5 ml). Chromatography with ethyl acetate:cyclohexane (10:90, v/v) afforded **5e**, 83 mg (0.22 mmole, 42%).

Compound **5e** was obtained as beige foam; ir (carbon tetrachloride): 1650 (CO) cm^{-1}; ^{1}H nmr (400 MHz, deuteriochloroform): δ 0.93 (t, 3H, CH_3, J = 7.5 Hz), 1.62-1.91 (m, 6H, C*H*$_2$Me, C*H*$_2$-C*H*$_2$-CH$_2$Cl), 2.13 (t, 2H, 2H-2, J = 6.3 Hz), 2.91 (t, 2H, 2H-1, J = 6.3 Hz,), 3.53 (m, 2H, C*H*$_2$Cl), 5.32 (s, 2H, NC*H*$_2$Ph), 7.03 (dd, 2H, H-2', H-6', *J* = 7.8, 1.6 Hz), 7.19-7.34 (m, 6H, phenyl protons), 8.33 (d, 1H, H-5, *J* = 7.6 Hz); ^{13}C nmr (100 MHz, deuteriochloroform): δ 8.6 (CH_3), 19.2 (C-1), 27.5 (CH$_2$Me), 27.6 (*C*H$_2$-CH$_2$Cl), 31.3 (C-2), 31.8 (*C*H$_2$-C$_2$H$_4$Cl), 45.9 (*C*H$_2$Cl), 46.8 (NCH$_2$Ph), 47.5 (C-3), 109.7 (C-8), 112.0 (C-4a), 121.8 (C-5), 122.6 (C-6), 123.2 (C-7), 125.4 (C-4b), 126.0 (C-2', C-6'), 127.9 (C-4'), 129.1 (C-3', C-5'), 136.0 (C-1'), 137.4 (C-9a), 149.9 (C-8a), 197.7 (CO); ms: m/z 381 [14, $M^{+\cdot}$ (^{37}Cl)], 379 [42, $M^{+\cdot}$ (^{35}Cl)], 351 (25), 344 (69), 303 (47), 288 (14), 247 (28), 218 (17), 128 (11), 91 (100), 65 (14), 40 (42), 36 (22), 29 (28); hrms calcd. for $C_{24}H_{26}NOCl$: 379.1697, found 379.1693.

Anal. Calcd. for $C_{24}H_{26}NOCl$: C, 75.87; H, 6.90; N, 3.69; Cl, 9.33. Found: C, 75.77; H, 7.12; N, 3.39; Cl, 8.98.

9-Benzyl-3-methoxycarbonyl-1,2,3,9-tetrahydrocarbazol-4-one (**5f**).

This compound was prepared according to the procedure of method A.Irradiation of **3f** (500 mg, 1.49 mmole) was performed in benzene (150 ml, c = 10.6 x 10^{-3} *M*) for 3 hours. Chromatography with ethyl acetate afforded **5f**, 200 mg (0.60 mmole, 40 %); ir (carbon tetrachloride): 1735 (CO ester), 1665 (CO enaminone) cm^{-1}; ^1H nmr (400 MHz, deuteriochloroform): δ 2.35 (m, 1H, H-2ax), 2.52 (ddd, 1H, H-1ax, J = 13.0, 9.0, 5.4 Hz), 2.76 (m, 1H, H-2eq), 3.00 (ddd, 1H, H-1eq, J = 13.0, 5.4, 5.4 Hz), 3.55 (dd, 1H, H-3, J = 10.0, 5.4 Hz), 3.75 (s, 3H, OCH_3), 5.20 (s, 2H, C*H*$_2$Ph), 7.00 (d, 2H, H-2', H-6', J = 6.8 Hz,), 7.20-7.30 (m, 6H, phenyl protons), 8.27 (d, 1H, H-5, J = 7.6 Hz); ^{13}C nmr (100 MHz, deuteriochloroform): δ 20.5 (C-1), 26.2 (C-2), 46.9 (N*C*H$_2$Ph), 52.2 (O*C*H$_3$), 53.0 (C-3), 109.8 (C-8), 111.9 (C-4a), 121.5 (C-5), 122.9 (C-6), 123.5 (C-7), 124.8 (C-4b), 126.0 (C-2', C-6'), 127.8 (C-4'), 128.9 (C-3', C-5'), 135.6 (C-1'), 137.2 (C-9a), 151.6 (C-8a), 171.1 (CO ester), 187.9 (C-4).

Anal. Calcd. for $C_{21}H_{19}NO_3$: C, 75.65; H, 5.74; N, 4.20. Found: C, 75.90; H, 5.65; N, 4.40.

9-Benzyl-1-methoxycarbonyl-1,2,3,9-tetrahydrocarbazol-4-one (**5g**).

This compound was prepared according to the procedure of method A. Irradiation of **3g** (170 mg, 0.51 mmole) was performed in benzene:methanol (1:1, v/v) (150 ml, c = 3.4 x 10^{-3} *M*) for 1 hour. Chromatography with ethyl acetate:hexane (30:70, v/v) afforded **5g**, 60 mg (0.18 mmole, 36%); white crystals (ethyl acetate), mp 133-135°; ir (carbon tetrachloride): 1735 (CO ester), 1670 (CO enaminone) cm^{-1}; ^1H nmr (400 MHz, deuteriochloroform): δ 2.42 (dddd, 1H, H-2ax, J = 14.0, 14.0, 5.5, 4.5 Hz), 2.57 (ddd, 1H, H-3eq, J = 17.0, 4.5, 2.5 Hz), 2.62 (dddd, 1H, H-2eq, J = 14.0, 5.0, 2.5, 2.5 Hz), 2.89 (ddd, 1H, J= 17.0, 14.0, 5.0 Hz, H-3ax), 3.55 (s, 3H, OCH_3), 4.02 (dd, 1H, J = 5.5, 2.5 Hz, H-1eq), 5.45 (s, 2H, C*H*$_2$Ph), 7.00 (dd, 2H, H-2', H-6', J = 7.0, 1.5 Hz), 7.25-7.35 (m, 6H, phenyl protons), 8.37 (d, 1H, H-5, J = 8.0 Hz); ^{13}C nmr (100 MHz, deuteriochloroform): δ 27.4 (C-2), 34.9 (C-3), 38.3 (C-1), 47.3 (N*C*H$_2$Ph), 52.6 (O*C*H$_3$), 110.2 (C-8), 113.5 (C-4a), 122.1 (C-5), 123.0 (C-6), 123.8 (C-7), 124.5 (C-4b), 125.9 (C-2', C-6'), 127.8 (C-4'), 128.9 (C-3', C-5'), 135.8 (C-1'), 137.4 (C-9a), 146.6 (C-8a), 170.4 (CO ester), 193.5 (C-4); ms: m/z 333 (34, $M^{+\cdot}$), 305 (10), 274 (19), 246 (11), 154 (8), 127 (5), 91 (100), 65 (27), 59 (27), 39 (11), 29 (11) 15 (45).

Anal. Calcd. for $C_{21}H_{19}NO_3$: C, 75.65; H, 5.74; N, 4.20. Found: C, 75.95; H, 5.90; N, 4.38.

9-Benzyl-2-methoxycarbonyl-1,2,3,9-tetrahydrocarbazol-4-one (**5h**).

This compound was prepared according to the procedure of method A. Irradiation of **3h** (231 mg, 0.69 mmole) was performed in benzene:methanol (1:1, v/v) (150 ml, c = 4.6 x 10^{-3} *M*) for 1.5 hour. Chromatography with ethyl acetate:hexane (50:50, v/v) afforded **5h**, 128 mg (0.39 mmole, 56 %); ir (carbon tetrachloride): 1735 (CO ester), 1665 (CO enaminone) cm^{-1}; ^1H nmr (400 MHz, deuteriochloroform): δ 2.81 (ABX spectrum, AB part, 2H, 2H-3, J= 16.6, 8.9, 5.8Hz), 3.12 (A'B'X spectrum, A'B' part, 2H, 2H-1, J = 16.8, 8.0, 6.2 Hz,), 3.28 (ABX+A'B'X spectrum, X part, 1H, H-2), 3.68 (s, 3H, OCH_3), 5.30 (s, 2H, C*H*$_2$Ph), 7.05 (d, 2H, H-2', H-6', J = 7.0 Hz,), 7.20-7.30 (m, 6H, phenyl protons), 8.28 (d, 1H, H-5, J = 8.0 Hz); ^{13}C nmr (100 MHz, deuteriochloroform): δ 24.5 (C-1), 39.7 (C-3), 40.5 (C-2), 47.0 (N*C*H$_2$Ph), 52.3 (O*C*H$_3$), 109.8 (C-8), 112.6 (C-4a), 121.6 (C-5), 122.8 (C-6), 123.4 (C-7), 124.5 (C-4b), 126.1 (C-2', C-6'), 127.9 (C-4'), 129.0 (C-3', C-5'), 135.6 (C-1'), 137.3 (C-9a), 149.5 (C-8a), 173.2 (CO ester), 190.6 (C-4).

Anal. Calcd. for $C_{21}H_{19}NO_3$: C, 75.65; H, 5.74; N, 4.20. Found: C, 75.51; H, 5.85; N, 3.95.

9-Benzyl-6-methyl-1,2,3,9-tetrahydrocarbazol-4-one (**5i**).

This compound was prepared either by method Aor method B.

Method A: Irradiation of **3i** (400 mg, 1.37 mmole) was performed in benzene:methanol (1:1, v/v) (150 ml, c = 9.1 x 10^{-3} *M*) for 1.5 hour. Chromatography with ethyl acetate afforded **5i**, 250 mg (0.86 mmole, 63%).

Method B: Irradiation of **3i** (300 mg, 1.03 mmoles) in benzene:methanol (1:1, v/v) (150 ml, c = 6.9 x 10^{-3} *M*) was performed in presence of sodium (71 mg, 3.09 mmoles, 3 eq) for 4 hours. Chromatography with ethyl acetate afforded **5i**, 160 mg (0.55 mmole, 54%).

Compound **5i** was obtained as white crystals; mp 146-148° (acetone); ir (carbon tetrachloride): 1660 (CO) cm^{-1}; ^1H nmr (400 MHz, deuteriochloroform): δ 2.20 (quint, 2H, 2H-2, J = 6.4 Hz), 2.46 (s, 3H, CH_3), 2.56 (t, 2H, 2H-3, J= 6.4 Hz), 2.83 (t, 2H, 2H-1, J = 6.4 Hz), 5.25 (s, 2H, N*C*H$_2$Ph), 7.04 (d, 2H, H-2', H-6', J = 7.2 Hz), 7.19-7.34 (m, 5H, phenyl protons), 8.15 (s, 1H, H-5); ^{13}C nmr (100 MHz, deuteriochloroform): δ 21.4 (*C*H$_3$), 22.2 (C-2), 23.3 (C-1), 37.8 (C-3), 47.0 (N*C*H$_2$Ph), 109.3 (C-8), 112.6 (C-4a), 121.6 (C-5), 123.5 (C-7), 124.5 (C-4b), 126.1 (C-2', C-6'), 127.8 (C-4'), 129.0 (C-3', C-5'), 132.3 (C-6), 135.4 (C-9a), 136.1 (C-1'), 151.8 (C-8a), 194.0 (CO).

Anal. Calcd. for $C_{20}H_{19}NO$: C, 83.01; H, 6.62; N, 4.84. Found: C, 82.90; H, 6.75; N, 4.68.

9-Benzyl-5-methoxy-1,2,3,9-tetrahydrocarbazol-4-one (**5j**) and 9-Benzyl-7-methoxy-1,2,3,9-tetrahydrocarbazol-4-one (**5j'**).

These compounds were prepared either by method A or method B.

Method A: Irradiation of **3j** (200 mg, 0.65 mmole) in benzene:methanol (1:1, v/v) (150 ml, c = 4.33 x 10^{-3} *M*) for 4 hours was followed by treatment with a suspension of manganese (III) acetate dihydrate (193 mg, 0.72 mmole) in acetic acid (3.3 ml). Chromatography with ethyl acetate:hexane (40:60, v/v) as eluent afforded **5j**, 101 mg (0.33 mmole, 51%,) and **5j'**, 54 mg (0.18 mmole, 27%).

Method B: Irradiation of **3j** (252 mg, 0.82 mmole) in benzene:methanol (1:1, v/v) (150 ml, c = 5.5 x 10^{-3} *M*) was performed in presence of sodium (57 mg, 2.46 mmole) for 4 hours. Chromatography with ethyl acetate:hexane (40:60, v/v) as eluent afforded **5j**, 90 mg (0.30 mmole, 36%) and **5j'**, 50 mg (0.16 mmole, 20%).

Compound **5j** was obtained as white crystals (acetone), mp 167-168°C; ir (carbon tetrachloride): 1670 (CO) cm^{-1}; ^1H nmr (300 MHz, deuteriochloroform): δ 2.21 (quint, 2H, 2H-2, J = 6.0 Hz), 2.65 (t, 2H, 2H-3, J= 6.0 Hz), 2.87 (t, 2H, 2H-1, J= 6.0 Hz), 4.05 (s, 3H, OCH_3), 5.32 (s, 2H, N*C*H$_2$Ph), 6.75 (d, 1H, H-8, J = 8.2 Hz), 6.90 (d, 1H, H-6, J = 8.2 Hz), 7.05 (dd, 2H, H-2', H-6', J = 8.2, 2.0 Hz), 7.20 (t, 1H, H-7, J = 8.0 Hz), 7.30 (m, 3H, H-3', H-4', H-5'); ^{13}C nmr (75 MHz, deuteriochloroform): δ 22.7 (C-2), 22.9 (C-1), 38.9 (C-3), 47.1 (N*C*H$_2$Ph), 56.1 (O*C*H$_3$), 102.9 (C-8), 104.8 (C-6), 113.7 (C-4b), 114.5 (C-4a), 124.5 (C-7), 125.9 (C-2', C-6'), 127.8 (C-4'), 129.0 (C-3', C-5'), 135.9 (C-1'), 139.3 (C-9a), 151.2 (C-8a), 154.5. (C-5), 191.9 (CO); ms: m/z 305

(100, $M^{+\cdot}$), 248 (19), 218 (11), 186 (20), 171 (11), 128 (13), 115 (11), 103 (10), 91 (75), 65 (17), 27 (29).

Anal. Calcd. for $C_{20}H_{19}NO_2$: C, 78.66; H, 6.27; N, 4.59. Found: C, 78.61; H, 6.20; N, 4.41.

Compound **5j'** was obtained as white crystals (ethyl acetate:hexane), mp 137-138°; ir (carbon tetrachloride): 1650 (CO) cm^{-1}; ^1H nmr (300 MHz, deuteriochloroform): δ 2.22 (quint, 2H, 2H-2, J = 6.0 Hz), 2.57 (t, 2H, 2H-3, J = 6.0 Hz), 2.85 (t, 2H, 2H-1, J = 6.0 Hz), 3.82 (s, 3H, OCH_3), 5.27 (s, 2H, NCH_2Ph), 6.75 (d, 1H, H-8, J = 2.0 Hz), 6.94 (dd, 1H, H-6, J = 8.0, 2.0 Hz), 7.05 (dd, 2H, H-2', H-6', J = 8.0, 1.0 Hz), 7.30 (m, 3H, H-3', H-4', H-5'), 8.20 (d, 1H, H-5, J = 8.0 Hz); ^{13}C nmr (75 MHz, deuteriochloroform): δ 22.3 (C-2), 23.5 (C-1), 37.8 (C-3), 47.0 (NCH_2Ph), 55.7 (OCH_3), 94.4 (C-8), 110.9 (C-6), 113.1 (C-4a), 118.9 (C-4b), 122.3 (C-5), 126.1 (C-2', C-6'), 127.9 (C-4'), 129.0 (C-3', C-5'), 136.0 (C-1'), 137.9 (C-9a), 151.3 (C-8a), 157.1 (C-7), 193.9 (CO); ms: m/z 305 (100, $M^{+\cdot}$), 290 (17), 277 (16), 248 (15), 214 (13), 186 (27), 158 (15), 91 (65), 65 (12).

Anal. Calcd. for $C_{20}H_{19}NO_2$: C, 78.66; H, 6.27; N, 4.59. Found: C, 78.31; H, 6.20; N, 4.23.

9-Benzyl-5,7-dimethyl-1,2,3,9-tetrahydrocarbazol-4-one (**5k**).

This compound was prepared by method B. Irradiation of **3k** (300 mg, 0.98 mmole) in benzene:methanol (1:1, v/v) (150 ml, c = 6.6 x 10^{-3} *M*) was performed in presence of sodium (68 mg, 2.95 mmoles, 3 eq) for 7 hours. Chromatography with ethyl acetate afforded **5k,** 270 mg (0.89 mmole, 91%); white crystals (acetone), mp 145-146°; ir (carbon tetrachloride): 1665 (CO) cm^{-1}; ^1H nmr (400 MHz, deuteriochloroform): δ 2.18 (quint., 2H, 2H-2, J = 6.4 Hz), 2.39 (s, 3H, CH_3), 2.59 (t, 2H, 2H-3, J = 6.4 Hz), 2.84 (t, 2H, 2H-1, J = 6.4 Hz), 2.97 (s, 3H, CH_3), 5.30 (s, 2H, NCH_2Ph), 6.88 (s, 1H, H-8), 6.90 (s, 1H, H-6), 7.02 (dd, 2H, H-2', H-6', J = 6.6, 1.5 Hz,), 7.26-7.35 (m, 5H, phenyl protons); ^{13}C nmr (100 MHz, deuteriochloroform): δ 21.4 (CH_3), 22.6 (C-2), 22.8 (C-1), 23.0 (CH_3), 38.9 (C-3), 46.6 (NCH_2Ph), 107.0 (C-8), 114.1 (C-4a), 122.1 (C-4b), 125.8 (C-2', C-6'), 126.2 (C-6), 127.6 (C-4'), 128.9 (C-3', C-5'), 132.6 (C-5), 133.2 (C-7), 136.0 (C-1'), 138.1 (C-9a), 151.7 (C-8a), 192.6 (CO).

Anal. Calcd. for $C_{21}H_{21}NO$: C, 83.13; H, 6.98; N, 4.62. Found: C, 83.40; H, 7.12; N, 4.55.

4-Benzyl-3,4-dihydro-2*H*-cyclopenta[b]indol-1-one (**5l**).

This compound was prepared either by method A or method B.

Method A: Irradiation of **3l** (526 mg, 2.00 mmole) in benzene (150 ml, c = 13.3 x 10^{-3} *M*) was performed for 4 days. Chromatography with ethyl acetate:hexane (50:50, v/v) as eluent afforded **5l,** 65 mg (0.25 mmole, 12%, 50% yield based on consumed product)**.**

Method B: Irradiation of **3l** (263 mg, 1.0 mmole) in benzene:methanol (1:1, v/v) (150 ml, c = 6.7 x 10^{-3} *M*) was performed in presence of sodium (69 mg, 3.0 mmoles) for 48 hours. Chromatography with ethyl acetate:hexane (50:50, v/v) as eluent afforded **5l**, 79 mg (0.30 mmole, 30%).

Compound **5l** was obtained as crystals (ethyl acetate:hexane), mp 140-142°; ir (carbon tetrachloride): 1695 (CO) cm^{-1}; ^1H nmr (400 MHz, deuteriochloroform): δ 2.80-2.90 (m, 4H, 2H-2, 2H-3), 5.25 (s, 2H, NCH_2Ph), 7.12 (d, 2H, H-2', H-6', *J* = 7.5 Hz,), 7.18-7.35 (m, 6H, phenyl protons), 7.95 (d, 1H, H-8, *J* = 7.0 Hz); ^{13}C nmr (100 MHz, deuteriochloroform): δ 20.8 (C-3), 40.8 (C-2), 48.1 (NCH_2Ph), 110.6 (C-5), 120.9 (C-8), 121.5 (C-8b), 122.4 (C-7), 123.5 (C-6), 123.7 (C-8a), 126.7 (C-2', C-6'), 128.1 (C-4'), 129.0 (C-3', C-5'), 135.5 (C-1'), 142.6 (C-3a), 168.1 (C-4a), 195.3 (CO); ms: m/z 261 (89, $M^{+\cdot}$), 170 (38), 120 (21), 116 (10), 91 (100), 65 (13), 28 (100).

Anal. Calcd. for $C_{18}H_{15}NO$: C, 82.73; H, 5.79; N, 5.36. Found: C, 82.46; H, 5.92; N, 5.18.

4-Benzyl-6,8-dimethyl-3,4-dihydro-2*H*-cyclopenta[*b*]indol-1-one (**5m**).

This compound was prepared by method B. Irradiation of **3m** (291 mg, 1.00 mmole) in benzene:methanol (1:1, v/v) (150 ml, c = 6.7 x 10^{-3} *M*) was performed in presence of sodium (69 mg, 3.00 mmoles) for 48 hours. Chromatography with ethyl acetate:hexane (50:50, v/v) afforded **5m**, 100 mg (0.35 mmole, 35%); ir (carbon tetrachloride): 1665 (CO) cm^{-1}; ^1H nmr (400 MHz, deuteriochloroform): δ 2.40 (s, 3H, CH_3), 2.85 (s, 3H, CH_3), 2.88 (m, 2H, 2H-2), 2.92 (m, 2H, 2H-3), 5.23 (s, 2H, NCH_2Ph), 6.90 (d, 2H, H-2', H-6', *J* = 7.3 Hz), 7.15-7.40 (m, 5H, phenyl protons); ^{13}C nmr (100 MHz, deuteriochloroform): δ 20.7 (C-3), 20.8 (CH_3), 21.8 (CH_3), 40.8 (C-2), 47.9 (NCH_2Ph), 107.7 (C-5), 123.5 (C-2', C-6'), 124.9 (C-8b), 126.7 (C-4'), 127.0 (C-7), 128.1 (C-8a), 129.0 (C-3', C-5'), 132.4 (C-8), 134.0 (C-6), 135.8 (C-1'), 142.6 (C-3a), 167.5 (C-4a), 194.6 (CO).

Anal. Calcd. for $C_{20}H_{19}NO$: C, 83.01; H, 6.62; N, 4.84. Found: C, 83.22; H, 6.48; N, 4.65.

3,4-Dihydro-2*H*-cyclopenta[*b*]indol-1-one (**5n**).

A solution of bromo-enaminone **3n** (251 mg, 1.0 mmole) and triethylamine (101 mg, 140 µl, 1.0 mmole) was irradiated for 1.5 hour in methanol (150 ml, c = 6.7 x 10^{-3} *M*) in a quartz apparatus. After evaporation of the solvent, addition of water and extraction with dichloromethane, the crude mixture was purified by chromatography. Elution with ethyl acetate gave compound **5n**, 107 mg (0.63 mmole; 63%); crystals (ethanol), mp 250° (lit. [25] 247-248°); ir (carbon tetrachloride): 1675 (CO) cm^{-1}; ^1H nmr (400 MHz, deuteriochloroform): δ 2.99 (m, 2H, 2H-3), 3.09 (m, 2H, 2H-2), 7.10-7.45 (m, 3H, 3 Ar-H), 7.92 (dd, 1H, *J* = 6.7, 2.3 Hz, H-8), 9.20 (br.s, 1H, NH); ^{13}C nmr (100 MHz, deuteriochloroform): δ 21.7 (C-3), 41.1 (C-2), 111.9 (C-5), 121.1 (C-8), 122.6 (C-7), 123.9 (C-6), 130.0 (C-8b), 141.0 (C-8a), 154.9 (C-3a), 166.6 (C-4a), 196.0 (CO).

Anal. Calcd. for $C_{11}H_9NO$: C, 77.17; H, 5.30; N, 8.18. Found: C, 76.90; H, 5.42; N, 8.31.

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