Reactions of Electron-Rich Heterocycles with Ortho-carboxylic Acid Derivatives. 11. Reactions of Carbazole and 4-Methoxycarbazole with Triethyl Orthoformate: Regio-specific Functionalization of the Carbazole Nucleus

H. Witzel and U. Pindur*

Department of Pharmacy, University of Mainz,
Saarstrasse 21, D-6500 Mainz 1, Federal Republic of Germany

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Carbazole (**1a**) and 4-methoxycarbazole (**1b**) can be regioselectively functionalized by reaction with triethyl orthoformate. Whereas the reaction of **1a** with the ortho ester furnishes the amide acetal **2**, the new carbazole derivatives 4-10 are formed, depending on the reaction conditions, in the electrophilic substitution of **1b**. The products of this reaction sequence provide a contribution to studies on the mechanism of the transformation of **1b** to tris-carbazolylmethane **5**. Compound **5** represents a new, three-bladed propeller in the triheteroarylmethane series.

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Introduction.

The interest in the chemistry of carbazoles is beginning to increase steadily since functionalized carbazoles are synthetically interesting building blocks for certain carbazole alkaloids and for pharmacologically attractive carbazole derivatives [1-10]. In continuation of our investigations on the electrophilic substitution of carbazoles [1] and, especially, on the elucidation of analytically exploitable color reactions for use with carbazole drugs [2], we now report on the first reactions of the specifically selected model carbazoles **1a** and **1b** with triethyl orthoformate as an a^1-(formylating)-reagent [11]. On the basis of our initial investigations with indoles [12], interesting functionalization reactions should also be possible between carbazoles and the diethoxycarbenium ion [11] generated *in situ* from the ortho ester [11]. These reactions may also give an insight into the mechanisms of the reaction system "carbazoles/ortho esters".

Results and Discussion.

The parent carbazole **1a** can be functionalized at N-9 by the ortho ester (as solvent and electrophile) in the presence of *p*-toluenesulfonic acid as catalyst. The amide acetal **2** is formed as a viscous oil which, however, cannot be obtained in analytically pure form by chromatography or distillation. Contact of **2** with silica gel results in the formation of the known formyl derivative **3** [1] *via* hydrolysis; acid hydrolysis of **2** with excess hydrochloric acid gives

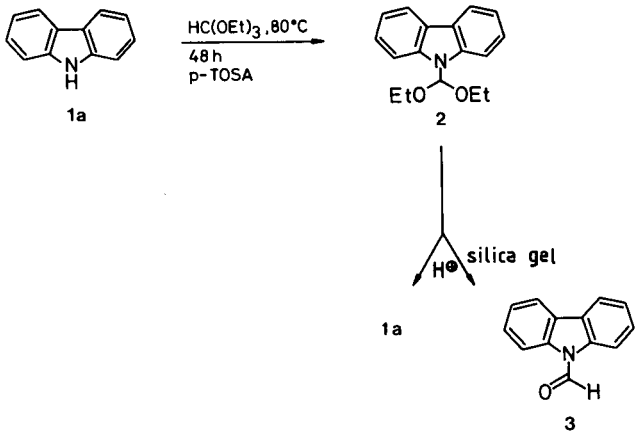
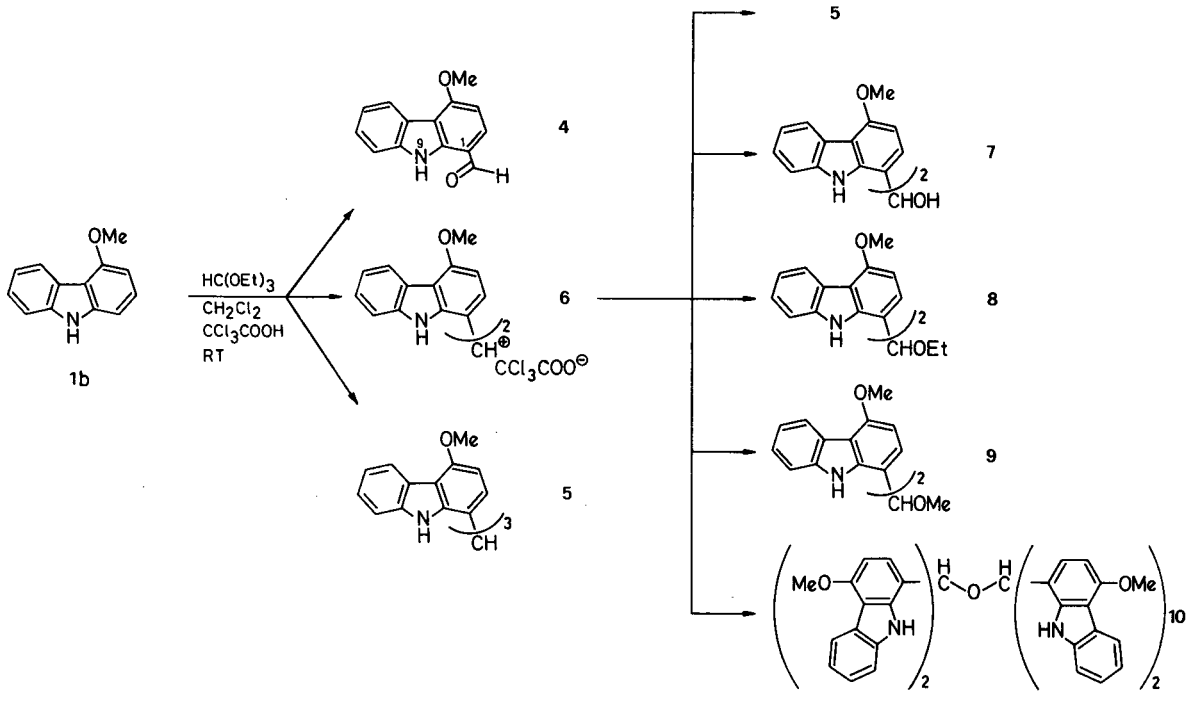


Table 1

Reaction Conditions for the Isolation of Compounds **4-10** and their Yields

Carbazole Product	Reactants and Reaction Conditions	Yield (%) [a]
4	200 mg (1 mmole) of carbazole **1b**, 300 mg (2 mmoles) of triethyl orthoformate, dichlormethane, 5% trichloroacetic acid, rt, 0.25 hour	17 [b]
5	60 mg (0.3 mmole) of carbazole **1b**, 90 mg (0.6 mmole) of triethyl orthoformate, dichloromethane, 1% trichloroacetic acid, rt, 4 hours	66
6	200 mg (1 mmole) of carbazole **1b**, 300 mg (2 mmoles) of triethyl orthoformate, dichloromethane, 5% trichloroacetic acid, rt, 0.25 hour	82
7	200 mg (0.35 mmole) of trichloroacetate **6**, dichloromethane, 5% aqueous sodium hydrogen carbonate, rt, 20 minutes	17
8	234 mg (0.41 mmole) of trichloroacetate **6**, dichloromethane, ethanol, 10% aqueous ammonia	66
9	70 mg (0.12 mmole) of trichloroacetate **6**, methanol, rt	60
10	70 mg (0.12 mmole) of trichloroacetate **6**, dichloromethane, concentrated ammonia, rt, 0.25 hour	55

[a] Based on the starting material **1b**. [b] The yield can be increased considerably by using excess ortho ester and acid.

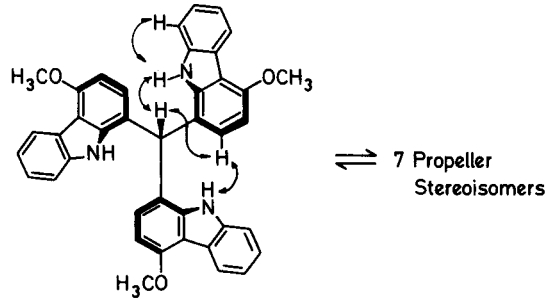


rise to small amounts of the starting material **1a** in additions to **3** [13].

In contrast, the electronically activated 4-methoxycarbazole (**1b**) [14] reacts with triethyl orthoformate in dichloromethane under proton catalysis (trichloroacetic acid) at C-1 to give, depending on the reaction conditions, an interesting mixture of products that could be analyzed by thin layer chromatography. By specific performance of the reaction or treatment of the salt **6**, all of the stable intermediates **4**, **7**, and **8** which, from a mechanistic point of view, play a part in the reaction sequence from **1b** to the final product **5**, could be isolated (Table 1). The dinuclear cyanine **6**, isolated as dark-green crystals, plays a decisive role as the central key structure since - as has been confirmed experimentally - the subsequent products **7** and **8** as well as **5** and the bis[dicarbazolyl]methyl ether **10** [15] (Table 1) are formed directly from this cation.

The constitutions of the carbazole derivatives and hence the regiochemistry of the electrophilic attack were clarified above all by 400 MHz ^{1}H-nmr spectroscopy. As examples, differential ^{1}H{^{1}H}-nOe measurements were performed on **4** and **5**. Thus, on irradiation of the formyl proton, a positive nOe was observed for the protons at N-9 and C-2 and *vice versa* of compound **4**. As expected, a positive nOe was also detected for the proton at C-8 when the proton at N-9 was irradiated. The nuclear Overhauser effects that confirm the structure of product **5** are shown in Scheme 1. The tricarbazolylmethane **5** belongs to the class of heteroaromatic molecular propellers that have been only little investigated to date [16].

Scheme 1



I

(P-Helix, ^{1}H {^{1}H} NOE)

As a consequence of the three constitutionally identical blades without local C_2 axes, a maximum of eight chiral, stereoisomeric propellers (four *dl* pairs, two with C_3 and two with C_1 symmetry) are conceivable as stable ground state conformations according to Mislow [16]. In the nmr spectra, compound **5** exhibits C_3 symmetry at 20° as an averaged spectrum on the nmr time scale; accordingly the barrier to stereoisomerization should be less than 16 kcal/mole. In the ^{1}H-nmr spectrum of the carbinol **7**, however, a significant coupling (^{3}J = 2.3 Hz, dideuteriodichloromethane) for the "C*H*-O*H*" group can be observed. As expected, this coupling disappears as a result of deuterium exchange in the presence of deuterium oxide. The ir (potassium bromide) spectrum of **7** contains, in addition to

the carbazole NH bands (3440 cm^{-1}), an OH_{assoc} absorption at 3600-3200 cm^{-1}. The trichloroacetate **6** [λ max (1% trichloroacetic acid in dichloromethane) = 660 nm: log ε = 5.0] is difficult to purify as a result of its instability and its high electrophilicity towards nucleophilic solvents. The structure, however, is sufficiently confirmed by the direct solvolysis reactions to give compounds **7**, **8**, and **9** (Table 1). Further analytical data confirming the structures of the new carbazole derivatives are given in the Experimental.

As examples, we have also allowed **1a** and **1b** to react with the Vilsmeier reagent (*N*-methylformanilide/phosphoryl chloride). Compound **1a** was formylated exclusively at N-9 and compound **1b** exclusively at C-1 to yield the corresponding carboxaldehydes [17]. A subsequent reaction, as observed in the reaction of **1b** with the ortho ester, did not take place.

EXPERIMENTAL

Materials and Techniques.

The proton magnetic resonance spectra were recorded on Bruker WH-90, WM-200, and WM-400 spectrometers using tetramethylsilane as internal standard (δ scale). The infrared spectra were recorded on a Beckman IR 4200 spectrophotometer. The ei and fab mass spectra were measured on a Varian CH 7A instrument. Elemental analyses were performed using a Carlo Erba Strumentazione apparatus. Melting points were determined on a Büchi SMP 20 apparatus and are not corrected. Merck silica gel (grain size: 0.063-0.200 mm) was used for column chromatography and Merck silica gel (grain size: 0.040-0.063 mm) for "flash" chromatography. Preparative layer chromatography was performed with a Harrison Research Chromatotron Type 7924T apparatus on Merck silica gel 60PF.

4-Methoxycarbazole (**1b**).

4-Hydroxycarbazole [18] (1100 mg, 6 mmoles) was dissolved in 20 ml of water-free acetone. After addition of 360 mg of coarsely powdered potassium hydroxide, the reaction mixture was treated dropwise with a solution of 760 mg (6 mmoles) of dimethyl sulfate dissolved in 20 ml of acetone and stirred for 1 hour at room temperature. The mixture was then concentrated on a rotary evaporator, the residue was treated with water, and extractively shaken twice with dichloromethane. The organic phase was dried with sodium sulfate, evaporated, and the residue was purified by flash chromatography (eluent: petroleum ether/ethyl acetate, 85/15). The product **1b** was obtained as colorless crystals in 77% yield (910 mg), mp 134° (petroleum ether); ir (potassium bromide): 3400 cm^{-1} (NH); ms: m/e (%) 197 (M^+, 100); ^{1}H-nmr (200 MHz, deuteriochloroform): 4.08 (s, 3H, OCH_3), 6.68 (d, ^3J = 8 Hz, 1H), 7.03 (d, ^3J = 8.2 Hz, 1H), 7.2-7.4 (m, 4H), 8.02 (s, 1H, NH), 8.32 (d, ^3J = 7.7 Hz, 1H, H-5).

Anal. Calcd. for $C_{13}H_{11}NO$ (197.24): C, 79.16; H, 5.62; N, 7.10. Found: C, 79.33; H, 5.76; N, 6.94.

9-(Diethoxymethyl)carbazole (**2**).

Carbazole (**1a**) (1 g, 6 mmoles) was suspended in 10 ml of triethyl orthoformate, treated with 100 mg of *p*-toluenesulfonic acid, and the mixture was stirred at 80° for 48 hours. The reaction mixture was then poured into ammoniacal ice/water and extractively shaken several times with dichloromethane. The organic phase was distilled under reduced pressure (15 torr) to separate the larger portion of the ortho ester. The precipitated starting material **1a** was separated from the distillation residue. The viscous residue was purified using the Chromatotron apparatus (eluent: petroleum ether/acetone, 9/1). A viscous, easily cleavable oil was obtained in 65% yield. Hydrolysis by hydrochloric acid and longer contact with silica gel both led to the formation of the known product **3** [17]; ms: m/e (%) 269 (M^+, 2), 47 (100); ^{1}H-nmr (90 MHz, deuteriochloroform): 1.2 (t, ^3J = 8 Hz, 6H, CH_3), 3.2-3.8 (m, 4H, CH_2CH_3), 6.54 [s, 1H, $CH(OC_2H_5)_2$], 7.1-7.5 (m, 4H, ArH), 7.73 (d, ^3J = 7.6 Hz, 2H, ArH), 8.04 (m, 2H, ArH).

Bis[4-methoxycarbazol-1-yl]methylium Trichloroacetate (**6**).

4-Methoxycarbazole (**1b**) (200 mg, 1 mmole) was dissolved in 20 ml of dichloromethane, 1 g, of trichloroacetic acid followed by 300 mg (2 mmoles) of triethyl orthoformate were added. The resultant, dark green-colored solution was shaken at room temperature several times within 15 minutes. After further 15 minutes reaction time, the dark-green, metallic shining precipitate was separated and washed several times with dichloromethane. The polymethine product **6** was obtained in 81% yield (294 mg) and its structure was confirmed by several subsequent reactions (see below). As a result of its insolubility, no structurally informative data could be obtained from the nmr spectra of compound **6**.

4-Methoxycarbazole-1-carboxaldehyde (**4**).

The aldehyde **4** was isolated by flash chromatography (eluent: petroleum ether/ethyl acetate, 85/15) of the mother liquor remaining after isolation of compound **6**. Product **4** was obtained as colorless crystals in 18% yield (40 mg). The yield of the aldehyde **4** could be increased considerably by using an excess of triethyl orthoformate in the above reaction.

Preparation of **4** by the Vilsmeier Formylation Reaction.

4-Methoxycarbazole (**1b**) (200 mg, 1 mmole) was dissolved in 1 ml (8 mmoles) of *N*-methylformanilide, the solution was cooled in ice, and slowly treated with 0.1 ml (1.06 mmoles) of phosphoryl chloride. The mixture was stirred at room temperature for 1 hour, then heated to 50°, and stirring was continued for a total of 24 hours. The mixture was then treated with a little ice/water, stirred for a short time, and extracted with dichloromethane. The aldehyde **4** was isolated using the Chromatotron apparatus (Merck silica gel 60; eluent: petroleum ether/ethyl acetate, 85/15 in 29% yield (66 mg); mp 179°; ir (potassium bromide): 3395 (NH), 1655 (CO) cm^{-1}; ^{1}H-nmr (400 MHz, dideuteriodichloromethane): 4.17 (s, 3H, OCH_3), 6.83 (d, ^3J = 8.4 Hz, 1H, H-3), 7.29 (dt, ^3J = 7.5 Hz, ^4J = 1 Hz, 1H, H-6), 7.45 (dt, ^3J = 7.6 Hz, ^4J = 1.2 Hz, 1H, H-7), 7.55 (ddd, ^3J = 8.1 Hz, ^4J,^5J < 1 Hz, 1H, H-8), 7.81 (d, ^3J = 8.4 Hz, 1H, H-2), 8.28 (dd, ^3J = 8.0 Hz, ^4J < 1 Hz, 1H, H-5), 10.03 (s, 1H, CHO), 10.32 (s, 1H, NH).

Anal. Calcd. for $C_{14}H_{11}NO_2$ (225.25): C, 74.65; H, 4.92; N, 6.22. Found: C, 74.68; H, 4.93; N, 6.45.

Bis[4-methoxycarbazol-1-yl]methanol (**7**).

The trichloroacetate **6** [200 mg, corresponding to 170 mg (0.86 mmole) of **1b**] was suspended in 10 ml of dichloromethane, treated with a 5% aqueous sodium hydrogen carbonate solution, and vigorously shaken in a separatory funnel until the organic phase became clear and practically colorless (about 20 minutes). The organic phase was separated, dried, and evaporated, and the residue was subjected to flash chromatographic separation (eluent: petroleum ether/ethyl acetate, 80/20). The product **7** was obtained as colorless crystals, yield, 30 mg (17% based on **1b**), mp 130° (petroleum ether); ir (potassium bromide): 3440 (NH), 3600-3200 (OH_{assoc}) cm^{-1}; ms (fab technique, dichloromethane/tetraethylene glycol): m/e (%) 422 (M^+, 29), 405 ($M^+ + 1 - H_2O$, 100); ^{1}H-nmr (400 MHz, dideuteriodichloromethane): 2.89 (d, ^3J = 2.3 Hz, 1H, OH), 4.06 (s, 6H, OCH_3), 6.55 (d, ^3J = 2.3 Hz, 1H, CHOH), 6.59 (d, ^3J = 8.2 Hz, 2H, H-3), 7.04 (d, ^3J = 8.2 Hz, 2H, H-2), 7.21 (dt, ^3J = 7.2 Hz, ^4J = 1.8 Hz, 2H, H-6), 7.37 (m, 4H, H-7, H-8), 8.29 (d, ^3J = 7.9 Hz, 2H, H-5), 8.92 (s, 2H, NH).

Anal. Calcd. for $C_{27}H_{22}N_2O_3$ (422.49): C, 76.76; H, 5.25; N, 6.63. Found: C, 76.67; H, 5.34; N, 6.47.

Bis[4-methoxycarbazol-1-yl]methyl Ethyl Ether (**8**).

The trichloroacetate **6** (234 mg) was suspended in 10 ml of dichloromethane and treated with 0.5 ml of ethanol; 10 ml of 10% aqueous ammonia solution were then added and the mixture was stirred until the precipitate had dissolved in the organic phase. The dichloromethane

phase was separated, dried, evaporated to dryness, and the residue was recrystallized from petroleum ether. The product **8** was obtained as colorless crystals, yield, 150 mg (66% based on 4-methoxycarbazole); mp 110° (petroleum ether); ir (potassium bromide): 3440 (NH) cm^{-1}; ms: m/e (%) 450 (M^+, 46), 389 (100); ^{1}H-nmr (400 MHz, dideuteriodichloromethane): 1.38 (t, ^3J = 7 Hz, 3H, OCH_2CH_3), 3.67 (q, ^3J = 7 Hz, 2H, OCH_2CH_3), 4.05 (s, 6H, OCH_3), 6.12 (s, 1H, CH), 6.58 (d, ^3J = 8.2 Hz, 2H, H-3), 7.01 (d, ^3J = 8.3 Hz, 2H, H-2), 7.22 (dt, ^3J = 7.3 Hz, ^4J = 1.3 Hz, 2H, H-6), 7.36 (dt, ^3J = 7.4 Hz, ^4J = 1.1 Hz, 2H, H-7), 7.4 (d, ^3J = 7.5 Hz, 2H, H-8), 8.3 (d, ^3J = 7.7 Hz, 2H, H-5), 8.89 (s, 2H, NH).

Anal. Calcd. for $C_{29}H_{26}N_2O_3$ (450.54): C, 77.31; H, 5.82; N, 6.22. Found: C, 76.90; H, 5.83; N, 5.84.

Bis[4-methoxycarbazol-1-yl]methyl Methyl Ether (**9**).

Under gentle warming, 70 mg of the trichloroacetate **6** were dissolved in 100 ml of methanol, then a few drops of 10% aqueous ammonia solution were added, and the mixture was concentrated on a rotary evaporator. The concentrated solution was treated with water and extractively shaken with dichloromethane several times. The organic phase was separated, dried, and evaporated on a rotary evaporator. The product **9** was precipitated as an amorphous powder by addition of *n*-hexane; yield: 40 mg (61% based on 4-methoxycarbazole), mp 190° dec; ir (potassium bromide): 3440 (NH) cm^{-1}; ms: m/e (%) 436 (M^+, 3), 74 (100); ^{1}H-nmr (400 MHz, dideuteriodichloromethane): 3.52 (s, 3H, OCH_3), 4.05 (s, 6H, OCH_3), 6.01 (s, 1H, CH), 6.58 (d, ^3J = 8.2 Hz, 2H, H-3), 7.01 (d, ^3J = 8.3 Hz, 2H, H-2), 7.22 (dt, ^3J = 7.3 Hz, ^4J = 1.3 Hz, 2H, H-6), 7.36 (dt, ^3J = 7.5 Hz, ^4J = 1.2 Hz, 2H, H-7), 7.4 (d, ^3J = 7.5 Hz, 2H, H-8), 8.3 (d, ^3J = 7.8 Hz, 2H, H-5), 8.87 (s, 2H, NH).

Anal. Calcd. for $C_{28}H_{24}N_2O_3$ (436.52): C, 77.04; H, 5.54; N, 6.42. Found: C, 76.86; H, 5.83; N, 6.11.

Di[bis(4-methoxycarbazol-1-yl)]methyl Ether (**10**).

The trichloroacetate **6**, prepared from 70 mg (0.3 mmole) of 4-methoxycarbazole (**1b**), was suspended in 5 ml of dichloromethane and treated with 2-3 ml of 25% aqueous ammonia solution. The mixture was stirred for about 15 minutes until the organic phase became clear. The dichloromethane phase was separated, dried, and evaporated. The analytically pure substance **10** was obtained in a crude yield of 55% (based on 4-methoxycarbazole). Reprecipitation with petroleum ether gave 26 mg (35% yield based on 4-methoxycarbazole) of the product, mp 212° (petroleum ether); ir (potassium bromide): 3410 (NH) cm^{-1}; ms (fab technique, dichloromethane/tetraethylene glycol): m/e (%) 826 (M^+, 1), 405 (M^+ − bis[4-methoxycarbazol-1-yl]methanol); ^{1}H-nmr (400 MHz, dideuteriodichloromethane): 4.08 (s, 12H, OCH_3), 5.58 (s, 2H, CH), 6.72 (d, ^3J = 8.2 Hz, 4H, H-3), 6.96 (s, ^3J = 8 Hz, 4H, H-2), 7.17 (dt, ^3J = 7.5 Hz, ^4J = 0.9 Hz, 4H, H-6), 7.24 (dt, ^3J = 7.6 Hz, ^4J = 1.2 Hz, 4H, H-7), 7.39 (d, ^3J = 8.2 Hz, 4H, H-8), 8.19 (s, 4H, NH), 8.26 (d, ^3J = 7.7 Hz, 4H, H-5).

Anal. Calcd. for $C_{54}H_{42}N_4O_5$ (826.96): C, 78.43; H, 5.12; N, 6.78. Found: C, 78.00; H, 4.95; N, 6.44.

Tris[4-methoxycarbazol-1-yl]methane (**5**).

4-Methoxycarbazole (**1b**) (60 mg, 0.3 mmole) was dissolved in 6 ml of dichloromethane and 60 mg of trichloroacetic acid were added. Then, 90 mg (0.6 mmole) of triethyl orthoformate were added dropwise and the mixture was stirred at room temperature for 4 hours. The mixture was made alkaline with 10% aqueous ammonia solution and extractively shaken with dichloromethane several times. The organic phase was separated and concentrated. The resultant precipitate was separated and washed three times with petroleum ether/2-propanol (8/1). Compound **5** was obtained as colorless crystals in 66% yield (40 mg), mp 190° dec; ir (potassium bromide): 3440, 3405 (NH) cm^{-1}; ms: m/e (%) 601 (M^+, 3), 43 (100); ^{1}H-nmr (400 MHz, dideuteriodichloromethane): 4.05 (s, 9H, OCH_3), 6.34 (s, 1H, CH), 6.61 (d, ^3J = 8.2 Hz, 3H, H-3), 6.97 (d, ^3J = 8.2 Hz, 3H, H-2), 7.20 (dt, ^3J = 7.3 Hz, ^4J = 1.05 Hz, 3H, H-6), 7.25 (d, ^3J = 7.85 Hz, 3H, H-8), 7.30 (dt, ^3J = 7.5 Hz, ^4J = 1 Hz, 3H, H-7), 7.94 (s, 3H, NH), 8.29 (d, ^3J = 7.8 Hz, 3H, H-5).

Anal. Calcd. for $C_{40}H_{31}N_3O_3$ (601.71): C, 79.85; H, 5.19; N, 6.98. Found: C, 79.69; H, 5.22; N, 7.12.

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