# Synthesis of New Guanidine Derivatives from 2',3',4',9'-Tetrahydrospiro[piperidine-4,1'-[1*H*]pyrido[3,4-*b*]indole]



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The reaction of the isothiourea derivative **2** with methylamine or pyrrolidine resulted in guanidines **3a-3b**. Using hydrazine under the same conditions the tetrazole derivative **4** was obtained. On reacting **2** with piperidine, morpholine, methylhydrazine, phenylhydrazine, hydroxylamine or sodium hydroxide, cyclization took place leading to the novel 4-cyanimino-1,2,3,4,6,7,12,12b-octahydro-3,12b-ethanopyrimido[1',6':1,2]pyrido[3,4-*b*]indole (**5**). Some structural aspects of **5** and other model compounds were analysed mainly by $^{13}C$ nmr spectroscopy.

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Spiropiperidine derivatives of type **1** [1] are, due to their three nitrogens of different reactivity, promising objects for further modifications and can also be considered as potential pharmacophores with interesting biological activities [2-8]. In this study our aim was to investigate the reaction of **1b** with a multifunctional carbonic acid derivative, dimethyl *N*-cyanodithioiminocarbonate, in the hope that the product would bear synthetic and/or pharmacological potential.

## Results and Discussion.

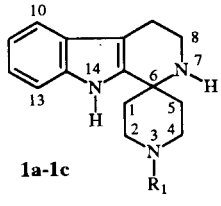
### Synthesis.

The synthesis of our starting material **1b** is known from the literature [4]. However, as an alternative route we prepared **1b** *via* the cyclocondensation of tryptamine hydrochloride and 1-ethoxycarbonyl-4-piperidone which led to **1a**. The ethoxycarbonyl group was then removed under basic conditions to give **1b.**

The reaction of **1b** with dimethyl *N*-cyanodithioiminocarbonate gave **2** as the sole product. The formation of **2** provides further evidence that in nucleophilic reactions N-3 is the most reactive nitrogen in **1a** [8].

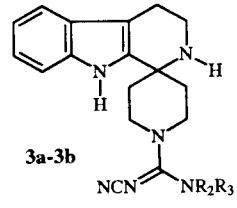
Starting from **2** we prepared cyanoguanidine derivatives **3a** and **3b** using methylamine and pyrrolidine, respectively, as reaction partners. Compound **3b** showed significant antihypoxic activity in a hypobaric hypoxia model in rats. The details of this study will be published elsewhere.

On reacting **2** with hydrazine under the same conditions, substitution of the methylthio group was followed by a cycloaddition step resulting in the 3,5-diamino-1,2,4-triazole derivative **4**. By using piperidine, morpholine, methylhydrazine, phenylhydrazine or hydroxylamine as the nucleophilic partner, in each case the reaction gave the novel cyclic cyanoguanidine derivative **5**. The cyclocondensation resulting in **5** could be elicited by sodium



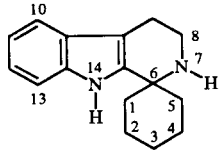
**1a-1c**

| | $R_1$ |
|---|---|
| **1a** | COOEt |
| **1b** | H |
| **1c** | CSOMe |

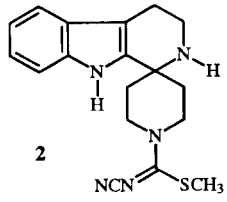


**3a-3b**

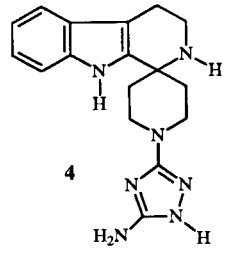
| | $R_2$ | $R_3$ |
|---|---|---|
| **3a** | $CH_3$ | H |
| **3b** | $-(CH_2)_4-$ | |



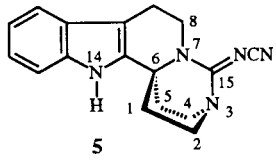
**7**



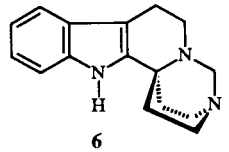
**2**



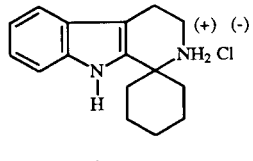
**4**



**5**



**6**



**8**

Figure

hydroxide as well. We assume that cyclocondensation is favoured when the nucleophilic power of the reagent is less than that of N-7.

An analogue of **5** lacking the cyanimino group on C-15 (**6**) has been prepared recently [8] by connecting N-3 and N-7 in **1b** with a $CH_2$ unit by the use of formaldehyde. We obtained **6** from **1b** by using dibromomethane as the connecting agent. Our findings support the observation that in the cyclocondensation reactions of **1b** the ring closure between N-3 and N-7 is favorable [4,8].

Furthermore, we attempted the synthesis of the 1,2,3,4,6,7,12,12b-octahydro-3,12b-ethanopyrimido-[1',6':1,2]pyrido[3,4-*b*]indole skeleton starting from **1b** and thiophosgene, but could isolate only **1c** after work-up of the reaction mixture.

It has been observed that 1,2,3,4,6,7,12,12b-octahydropyrimido[1',6':1,2]pyrido[3,4-*b*]indoles can easily be transformed into the corresponding octahydro-3,6,7a-triazacyclohepta[*j,k*]fluorenes with proton catalysis [9]. Compound **6**, however, did not afford the corresponding rearranged product even by prolonged heating in acidified ethanol solution.

Structural Elucidation.

The structures of compounds **1-6** were verified by $^1H$ and $^{13}C$ nmr measurements. Spectral assignments for **1b**, **5**, **6** and the model compounds **7** and **8** [7] (see below) were confirmed by the concerted use of two-dimensional homo(COSY) and heterocorrelation (HETCOR) as well as $^1H\{^1H\}$ and $^{13}C\{^1H\}$ nuclear Overhauser effect (NOE) difference experiments. In the latter measurements [10] selective irradiation of H-13 gave an enhancement on C-13a, thus providing unambiguous distinction between the signals due to C-13a and C-14a in **5-8** . Assignments for C-9a and C-9b are straightforward by comparison with suitable analogues [11]. The $^1H$ nmr data are collected in the experimental section. The $^{13}C$ chemical shifts for compounds **1b**, **5**, **6**, **7** and **8** are listed in the Table. To aid comparisons, all spectra were recorded in DMSO-$d_6$ solution.

One spectral feature that provides an obvious corroboration of the structure of compound **5** is the NOE measured between N(14)-H and H-13. Clearly, the existence of such a dipolar interaction rules out a possible alternative geometry in which the ring closure involves N-14 and N-3. Further, the observed NOE into the $H_{ax}$-1,5 protons from N(14)-H gives a convenient entry point for identifying the stereopositions (pseudo-axial or pseudo-equatorial) of the relevant ring protons (in the case of **5** that information is not readily accessible from the scalar coupling constants). In particular, $H_{ax}$-2,4 and $H_{eq}$-2,4 could be distinguished by the presence of the strong $H_{ax}$-1,5 $\Leftrightarrow$ $H_{ax}$-2,4 and $H_{eq}$-1,5 $\Leftrightarrow$ $H_{eq}$-2,4 NOE connections. Moreover, $H_{eq}$-1,5 and $H_{ax}$-2,4 were connected by small negative NOEs (three-spin effect); interestingly, such effects were absent in relation to $H_{ax}$-1,5 and $H_{eq}$-2,4.

Table

$^{13}C$ Chemical Shifts (DMSO-$d_6$) for Compounds **1b** and **5-8**

| | **1b** | **5** | **6** | **7** | **8** |
|---|---|---|---|---|---|
| C-1,5 | 36.3 | 34.2 | 30.5 | 35.6 | 33.2 |
| C-2,4 | 41.2 | 47.2 | 47.3 | 20.9 | 20.0 |
| C-3 | - | - | - | 25.5 | 24.1 |
| C-6 | 50.7 | 56.0 | 48.4 | 51.6 | 57.4 |
| C-8 | 38.5 | 40.8 | 43.6 | 38.7 | 37.9 |
| C 9 | 22.8 | 18.8 | 21.2 | 22.8 | 18.2 |
| C-9a | 106.5 | 105.6 | 105.5 | 106.2 | 104.8 |
| C-9b | 126.9 | 125.7 | 126.5 | 126.9 | 125.6 |
| C-10 | 117.3 | 118.0 | 117.4 | 117.3 | 118.0 |
| C-11 | 117.9 | 118.8 | 118.1 | 117.9 | 118.8 |
| C-12 | 120.1 | 121.4 | 120.1 | 120.0 | 121.6 |
| C-13 | 110.8 | 111.3 | 110.8 | 110.7 | 111.3 |
| C-13a | 135.4 | 136.2 | 135.9 | 135.3 | 136.0 |
| C-14a | 141.8 | 133.2 | 138.5 | 142.3 | 135.3 |
| C-15 | - | 170.9 | 72.5 | - | - |
| other | - | 162.2 (NCN) | - | - | - |

Evaluation of the $^{13}C$ chemical shifts (see the Table) reveals some interesting features of compounds **1b**, **5** and **6**. As compared to **1b**, compound **6** shows the following characteristic shift differences: C-1,5 is shifted -5.5 ppm upfield ($\gamma$-gauche steric effect due to C(15)-H2); C-2,4 and C-8 are +6.1 ppm and +5.1 ppm downfield (a mainly $\beta$ shift increment of C-15); C-9 is -1.6 ppm upfield (a mainly $\gamma$-anti shift increment of C-15). More interestingly, the following notable shift differences are observed in **5** relative to **6**: C-14a: -5.3 ppm; C-1,5: +3.7 ppm; C-2,4: -0.1 ppm C-6: +7.6 ppm; C-8: -2.8 ppm; C-9: -2.4 ppm. Further, all aromatic CH carbons show slight downfield shifts in going from **6** to **5**.

These effects can be rationalized as follows. It is noted that the geometrical arrangement of **5** allows for the rapid inversion of N-7, while no inversion takes place in the fixed pyramidal structure of N-3. Consequently, delocalization within the cyanoguanidine moiety mainly affects N-7 as opposed to N-3, and as a result N-7 becomes significantly more positive than in **6**. This ensues a distortion of the aromatic $\pi$-electrons which in turn affects $^{13}C$ shifts. In order to model these effects we also listed in the Table the $^{13}C$ chemical shifts for compound **7** and its protonated analogue **8**. In that case the $\pi$-polarization effect [12] due to $N^+(7)$ shifts the aromatic electrons towards C-14a which thus assumes higher charge density, while the C-10,11,12,13 carbons become more positive. Since $^{13}C$ chemical shifts are directly indicative of ground state electronic distributions in aromatic systems [13], in **8** the above effect causes C-14a to be shifted -7.1 ppm upfield, while the C-10,11,12,13 carbons move slightly downfield of their values in **7**. These results are consistent with similar observations reported for systems of the type $Ph(CH_2)_nN^+H_3$ by Reynolds *et al.* [12]. It should be

pointed out that the above noted shift differences in the aromatic carbons for **5** and **6** are entirely similar to those in the model compounds **7** and **8**; this indeed suggests a considerable delocalization of N-7 in **5**.

Interpretation of the $^{13}C$ shift differences of the aliphatic carbons between **8** and **7** is less straightforward, since on protonating N-7 these chemical shifts may be affected by a variety of factors such as the σ-inductive and field-effect [14] as well as shifts due to geometrical changes. Moreover, secondary effects influencing the σ-framework, such as C-6 being affected by the altered electronic density about C-14a, should not be ignored. Nevertheless, the large downfield shift of C-6 (+5.8 ppm) as well as the -4.6 ppm upfield shift of C-9 in **8** relative to **7** can be regarded as typical indicators of the protonation of N-7 in these systems. Analogous values were observed for **5** as compared to **6** (see above), and once again this points to N-7 being more positive in **6** than in **7**.

## EXPERIMENTAL

Melting points were taken on a Büchi 535 capillary apparatus and are uncorrected. Infrared spectra were obtained using potassium bromide pellets on a Nicolet 20 DXC FT-IR spectrophotometer. Nuclear magnetic resonance spectra were recorded at 300 MHz on a VARIAN VXR-300 spectrometer using tetramethylsilane as the internal standard. The 2D and NOE measurements were carried out by using the standard spectrometer software package. Irradiation times for the homonuclear and heteronuclear NOEs (non-degassed samples) were 4 s and 6 s, respectively. All new compounds were analyzed for C, H, N on a Heraeous C, H, N rapid model.

1-Ethoxycarbonyl-2',3',4',9'-tetrahydrospiro[piperidine-4,1'-[1*H*]pyrido[3,4-*b*]indole] (**1a**).

A solution of tryptamine hydrochloride (20 g, 0.1 mole) and 1-ethoxycarbonyl-4-piperidone (16 ml, 17.1 g, 0.1 mole) in 1-butanol (100 ml) was heated at reflux for 6 hours with stirring. The reaction mixture was allowed to stand overnight at room temperature, the precipitated solid was filtered off, washed with diethyl ether and dried. It was then suspended in 1*M* aqueous sodium carbonate solution (200 ml) and stirred for 1 hour at room temperature. The solid was filtered and washed with water to yield 26.4 g (84%) of **1a**, mp 239-240° (2-propanol); ir: 3269, 2734, 1667, 1579, 1441, 1231, 739 $cm^{-1}$; $^1H$ nmr (DMSO-$d_6$): 1.22 t (3H) [$OCH_2CH_3$], 1.63 brd (2H) [$H_e$-1,5], 1.94 td (2H) [$H_a$-1,5], 2.56 t (2H) [$H_2$-9], 2.97 t (2H) [$H_2$-8], 3.22 brm (2H) [$H_a$-2,4], 3.86 brd (2H) [$H_e$-2,4], 4.07 q (2H) [$OCH_2CH_3$], 6.92 td (1H) [H-11], 7.00 td (1H) [H-12], 7.24 d (1H) [H-13], 7.34 d (1H) [H-10], 10.73 s (1H) [N(14)-H].

*Anal.* Calcd. for $C_{18}H_{23}N_3O_2$ (323.40): C, 68.98; H, 7.40; N, 13.41. Found: C, 68.90; H, 7.31; N, 13.39.

2',3',4',9'-Tetrahydrospiro[piperidine-4,1'-[1*H*]pyrido[3,4-*b*]-indole] (**1b**).

Compound **1a** (27.6 g, 0.088 mole) and a solution of potassium hydroxide (27 g, 0.41 mole) in water (40 ml) was added to dimethyl sulfoxide (150 ml). The reaction mixture was heated at 100° for 2 hours with stirring, then evaporated under reduced pressure. The residue was suspended in water, the solid filtered off and washed with water to yield 20.4 g (96%) of **1b**, mp 265-267° (lit [4b] mp 252-254°). This product can be used as a starting material for further reactions without purification.

1-Cyanoimino(methylthio)methyl-2',3',4',9'-tetrahydrospiro[piperidine-4,1'-[1*H*]pyrido[3,4-*b*]indole] (**2**).

A solution of **1b** (12 g, 0.05 mole) and dimethyl *N*-cyanodithioiminocarbonate (8.0 g, 0.05 mole) in a mixture of *N,N*-dimethylformamide (100 ml) and ethanol (400 ml) was heated at reflux for 6 hours with stirring. After cooling the precipitated solid was filtered off and washed with diethyl ether to yield 10 g (59%) of **2**, mp 270-272° (1-butanol); ir: 3277, 2189, 1561, 1447, 1433, 1273, 739 $cm^{-1}$; $^1H$ nmr (DMSO-$d_6$): 1.78 brd (2H) [$H_e$-1,5], 2.05 brddd (2H) [$H_a$-1,5], 2.58 brt (2H) [$H_2$-9], 2.76 s (3H) [SMe], 2.99 brt (2H) [$H_2$-8], 3.57 brddd (2H) [$H_a$-2,4], 4.34 brd (2H) [$H_e$-2,4], 6.94 td (1H) [H-11], 7.03 td (1H) [H-12], 7.26 d (1H) [H-13], 7.36 d (1H) [H-10], 10.78 s (1H) [N(14)-H].

*Anal.* Calcd. for $C_{18}H_{21}N_5S$ (339.47): C, 63.69; H, 6.24; N, 20.63. Found: C, 63.78; H, 6.45; N, 20.53.

1-Cyanoimino(methylamino)methyl-2',3',4',9'-tetrahydrospiro-[piperidine-4,1'-[1*H*]pyrido[3,4-*b*]indole] (**3a**).

Compound **2** (3.4 g, 0.01 mole) was suspended in 40% aqueous methylamine solution (30 ml) and was stirred at 50° for 4 hours. After cooling the precipitated solid was filtered off and washed with water to yield 3.10 g (96%) of **3a**, mp 255-256° (2-propanol); ir: 3200, 2966, 2173, 1576, 1450, 1437, 1311, 747 $cm^{-1}$; $^1H$ nmr (DMSO-$d_6$): 1.66 brd (2H) [$H_{eq}$-1,5], 2.01 ddd (2H) [$H_{ax}$-1,5], 2.56 brt (2H) [$H_2$-9], 2.90 d (3H) [NH*Me*], 2.98 brt (2H) [$H_2$-8], 3.35 ddd (2H) [$H_{ax}$-2,4], 3.88 brd (2H) [$H_{eq}$-2,4], 6.92 td (1H) [H-11], 7.01 td (1H) [H-12], 7.21 q (1H) [N*H*Me], 7.25 d (1H) [H-13], 7.35 d (1H) [H-10], 10.80 s (1H) [indole NH].

*Anal.* Calcd. for $C_{18}H_{22}N_6$ (322.42): C, 67.06; H, 6.88; N, 26.06. Found: C, 67.44; H, 6.67; N, 25.93.

1-Cyanoimino(pyrrolidino)methyl-2',3',4',9'-tetrahydrospiro[piperidine-4,1'-[1*H*]pyrido[3,4-*b*]indole] (**3b**).

A solution of **2** (4.0 g, 0.012 mole) in pyrrolidine (30 ml) was heated at reflux for 2 hours. After cooling the precipitated solid was filtered off and washed with diethyl ether to yield 3.3 g (76%) of **3c**, mp 280-281° (nitromethane); ir: 3291, 2915, 2158, 1516, 1458, 1351, 1162, 742 $cm^{-1}$; $^1H$ nmr (DMSO-$d_6$): 1.71 brd (2H) [$H_{eq}$-1,5], 1.85 m (4H) [pyrrole], 2.09 ddd (2H) [$H_{ax}$-1,5], 2.58 brt (2H) [$H_2$-9], 2.99 brt (2H) [$H_2$-8], 3.40-3.60 m (8H) [$H_{ax}$-2,4, $H_{eq}$-2,4, pyrrole], 6.93 td (1H) [H11], 7.02 td (1H) [H-12], 7.28 d (1H) [H-13], 7.36 d (1H) [H-10], 10.80 s (1H) [indole NH].

*Anal.* Calcd. for $C_{21}H_{26}N_6$ (362.48): C, 69.59; H, 7.23; N, 23.18. Found: C, 69.60; H, 7 40; N, 23.19.

1-[5-(3-Amino-1,2,4-triazolyl)]-2',3',4',9'-tetrahydrospiro-[piperidine-4,1'-[1*H*]pyrido[3,4-*b*]indole] (**4**).

To a suspension of **2** (6.46 g, 0.019 mole) in a mixture of ethanol (50 ml) and *N,N*-dimethylformamide (20 ml) hydrazine monohydrate (2.0 ml, 2.0 g, 0.04 mole) was added. The reaction mixture was heated at reflux for 6 hours with stirring. After cooling the precipitated solid was filtered off and washed with ethanol to yield 2.06 g (34%) of **4**, mp >270°, ir: 3330, 3170, 1656, 1538, 1052, 899, 739 $cm^{-1}$; $^1H$ nmr (DMSO-$d_6$): 1.63 brd

(2H) [$H_e$-1,5], 2.05 brddd (2H) [$H_a$-1,5], 2.56 m (2H) [$H_2$-9]; 2.99 m (2H) [$H_2$-8]; 3.18 brddd (2H) [$H_a$-2,4], 3.65 brd (2H) [$H_e$-2,4], 6.91 td (1H) [H-11], 6.99 td (1H) [H-12]; 7.23 d (1H) [H-13], 7.35 d (1H) [H-10], 10.72 s (1H) [N(14)-H].

*Anal.* Calcd. for $C_{17}H_{21}N_7$ (323.40): C, 63.13; H, 6.55; N, 30.32. Found: C, 63.22; H, 6.49; N, 30.40.

4-Cyanoimino-1,2,3,4,6,7,12,12b-octahydro-3,12b-ethanopyrimido[1',6':1,2]pyrido[3,4-*b*]indole (**5**).

To the solution of **2** (1.7 g, 0.005 mole) in a mixture of ethanol (15 ml) and *N,N*-dimethylformamide (15 ml) methylhydrazine (0.3 ml, 0.25 g, 0.0056 mole) was added, and the reaction mixture was heated at reflux for 7 hours with stirring. After cooling under 10° the precipitated solid was filtered off and washed with ethanol to yield 1.03 g (67%) of **5**, mp >270°; ir: 3225, 2184, 1591, 1440, 1051, 968, 732 $cm^{-1}$; $^1H$ nmr (DMSO-$d_6$): 1.87 m (2H) [$H_e$-1,5], 2.37 m (2H) [$H_a$-1,5], 2.87 m (2H) [$H_2$-9], 3.03 m (2H) [$H_e$-2,4], 3.30 m (2H) [$H_a$-2,4], 3.79 m (2H) [$H_2$-8], 7.02 td (1H) [H-11], 7.11 td (1H) [H-12], 7.37 d (1H) [H-13], 7.49 d (1H) [H-10], 11.26 s (1H) [N(14)-H].

*Anal.* Calcd. for $C_{17}H_{17}N_5$ (291.36): C, 70.08; H, 5.88; N, 24.04. Found: C, 70.17; H, 5.94; N, 23.96.

1,2,3,4,6,7,12,12b-Octahydro-3,12b-ethanopyrimido-[1',6':1,2]pyrido[3,4-*b*]indole (**6**).

To a solution of **1b** (1.2 g, 0.005 mole) in *N,N*-dimethylformamide (10 ml) potassium carbonate (1.5 g, 0.011 mole) and dibromomethane (0.35 ml, 0.87 g, 0.005 mole) was added. The reaction mixture was heated at 100° for 4 hours with stirring. After cooling the inorganic salts were removed by filtration, and the filtrate was diluted with water (20 ml). The precipitated solid was filtered off and washed with water to yield 1.16 g (92%) of **6**, mp 222-225° (lit [8] mp 218-220°). For **1b** physical parameters, including $^1H$ nmr data measured in deuteriochloroform solution, were reported elsewhere [8]. However, for completeness our $^1H$ nmr assignments in DMSO-$_6$ are also given here: 1.84 m (2H) [$H_a$-1,5], 1.98 m (2H) [$H_e$-1,5], 2.61-2.72 m (4H) [$H_2$-8, $H_2$-9], 2.87 m (2H) [$H_a$-2,4], 3.00 m (2H) [$H_e$-2,4], 3.69 s (2H) [$H_2$-15], 6.93 td (1H) [H-11], 7.00 td (1H) [H-12], 7.26 d (1H) [H-13], 7.34 d (1H) [H-10], 10.66 s (1H) [N(14)-H].

1-Methoxythiocarbonyl-2',3',4',9'-tetrahydrospiro[piperidine-4,1'-[1*H*]pyrido[3,4-*b*]indole] (**1c**).

To a solution of **1b** (1.7 g, 0.005 mole) in tetrahydrofuran (10 ml) thiophosgene (0.4 ml, 0.005 mole) was added, and the reaction mixture was heated at reflux with stirring. After cooling the precipitated solid was filtered off and recrystallized in methanol to yield 0.55 g (31%) of **1c** (salt), mp 137-139°; ir: 3233, 2950, 1580, 1451, 1291, 747 $cm^{-1}$; $^1H$ nmr (DMSO-$d_6$): 2.15-2.45 m (4H) [$H_2$-1,5], 2.98 t (2H) [$H_2$-9], 3.50 t (2H) [$H_2$-8], 3.60-4.00 m (2H) [$H_a$-2,4], 4.01 s (3H) [OMe], 4.49 brd (1H) and 4.93 brd (1H) [$H_e$-2,4 (amide rotamers)], 7.02 td (1H) [H-11], 7.12 td (1H) [H-12], 7.33 d (1H) [H-13], 7.47 d (1H) [H-10], 10.28 (2H) [$N^+(7)H_2$], 11.23 s (1H) [N(14)-H].

*Anal.* Calcd. for $C_{17}H_{22}ClN_3OS$ (351.89): C, 58.03; H, 6.30; N, 11.94; S, 9.11. Found: C, 58.11;H, 6.25; N, 11.85; S, 9.06.

Compound **7** had $^1H$ nmr (DMSO-$d_6$): 1.28 m (1H) [$H_a$-3], 1.50 brd (2H) [He-2,4]; 1.64-1.88m (7H) [$H_a$-2,4, $H_e$-3, $H_2$-1,5], 2.55 t (2H) [$H_2$-9], 2.97 t (2H) [$H_2$-8], 6.92 td (1H) [H-11], 7.00 td (1H) [H-12]; 7.27 d (1H) [H-13], 7.33 d (1H) [H-10], 10.67 s (1H) [N(14)-H].

Compound **8** had $^1H$ nmr (DMSO-$d_6$): 1.38 m (1H) [$H_a$-3], 1.60-1.78 m (3H) [$H_e$-2,4, $H_e$-3], 1.90 m (2H) [$H_a$-2,4], 2.06-2.18 m (4H) [$H_2$-1,5], 2.95 t (2H) [$H_2$-9], 3.43 m (2H) [$H_2$-8], 7.00 td (1H) [H-11], 7.10 td (1H) [H-12], 7.35 d (1H) [H-13], 7.43 d (1H) [H-10], 9.69 brs (2H) [$N^+(7)H_2$], 11.33 s (1H) [N(14)-H].

## REFERENCES AND NOTES


[1] To facilitate spectroscopic comparisons, we adopt the skeletal numbering used by Mokrosz *et al.* [8] as depicted in the Figure.

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