

**SYNTHESIS OF 5-OXO-1,2,3,5,6,7-HEXAHYDROIMIDAZO-  
[1,2-*a*]PYRIDINE-8-CARBONITRILES, 6-OXO-2,3,4,6,7,8-  
HEXAHYDRO-1*H*-PYRIDO[1,2-*a*]PYRIMIDINE-9-  
CARBONITRILES, AND 7-OXO-1,2,3,4,5,7,8,9-  
OCTAHYDROPYRIDO[1,2-*a*][1,3]DIAZEPINE-10-  
CARBONITRILES**

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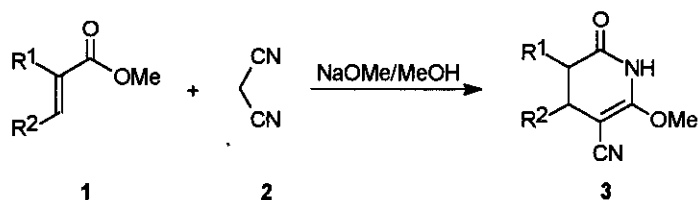
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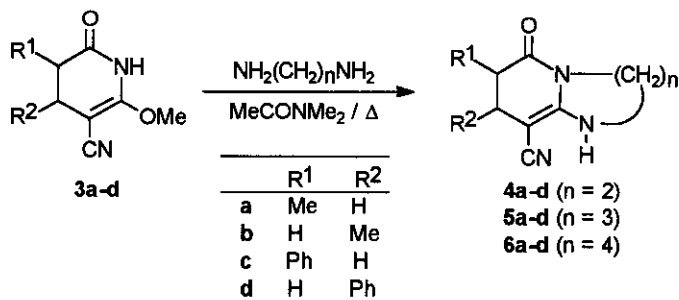
**Abstract-** A simple method for the synthesis of the title compounds is described. Thus,  $\alpha,\beta$ -unsaturated esters (**1**) are transformed in the already described 2-methoxy-6-oxo-1,4,5,6-tetrahydropyridine-3-carbonitriles (**3**) which are treated with  $\text{NH}_2(\text{CH}_2)_n\text{NH}_2$  ( $n = 2, 3, 4$ ) to afford the corresponding bicyclic compounds (**4**, **5**, and **6**). The nitrogen bridged nature of these compounds is determined by an X-ray structure analysis of **4b**. A ring opening-ring closure mechanism is proposed for the formation of structures (**4**–**6**) on the basis of the reaction between **3b** and  $^{15}\text{N},^{15}\text{N}'$ -ethylenediamine which afforded  $^{15}\text{N},^{15}\text{N}'$ -**4b**.

Since the synthesis of the 2-methoxy-4-dimethoxymethyl-6-oxo-1,4,5,6-tetrahydropyridine-3-carbonitrile (**3**,  $\text{R}^1 = \text{H}$ ,  $\text{R}^2 = \text{CH}(\text{OMe})_2$ ) by Victory and Diago in 1978,<sup>1</sup> our group has been using the 2-methoxy-6-oxo-1,4,5,6-tetrahydropyridine-3-carbonitriles (**3**), obtained by the reaction of an  $\alpha,\beta$ -unsaturated ester (**1**) and malononitrile (**2**) in NaOMe/MeOH at reflux (Scheme 1), as starting materials for the synthesis of bicyclic heterocyclic compounds.<sup>2</sup> The formation of the second heterocyclic ring proceeds in most cases by the nucleophilic substitution of the methoxy group by a dibasic system which then undergoes cyclization onto the cyano group. The versatility of the synthesis of compounds (**3**), due to the wide range of substituents which accepts the  $\alpha,\beta$ -unsaturated ester, has allowed us to describe general procedures to obtain pyrazolo[3,4-*b*]pyridines,<sup>3</sup> pyrido[2,3-*d*]pyrimidines,<sup>4</sup> and 1,6-naphthyridines.<sup>5</sup>



Scheme 1

These results lead us to extend our study to 1,4-, 1,5-, and 1,6-dibasic systems. Then we carried out the reaction between **3a-d** and  $\text{NH}_2(\text{CH}_2)_n\text{NH}_2$  with  $n = 2, 3, 4$  (Scheme 2). In any case a cyclization also took place in which the cyano group was not involved. Thus the reaction with ethylenediamine ( $n = 2$ ), 1,3-diaminopropane ( $n = 3$ ) and 1,4-diaminobutane ( $n = 4$ ) afforded respectively 5-oxo-1,2,3,5,6,7-hexahydroimidazo[1,2-a]pyridine-8-carbonitriles (**4a-d**), 6-oxo-2,3,4,6,7,8-hexahydro-1*H*-pyrido[1,2-a]pyrimidine-9-carbonitriles (**5a-d**), and 7-oxo-1,2,3,4,5,7,8,9-octahydropyrido[1,2-a][1,3]diazepine-10-carbonitriles (**6a-d**) in 14-83% yields (Table 1).



Scheme 2

Table 1. Compounds (**4**, **5**, and **6**)

Compound	R <sup>1</sup>	R <sup>2</sup>	n	Yield <sup>a</sup> (%)	Reaction Time (h)	mp (°C) <sup>b</sup>	Elemental Analysis (%): Found (Calculated)		
							C	H	N
<b>4a</b>	Me	H	2	74	6.5	195-197	61.07 (61.01)	6.53 (6.26)	23.65 (23.71)
<b>4b</b>	H	Me	2	69	5	165-167	61.05 (61.01)	6.24 (6.26)	23.66 (23.71)
<b>4c</b>	Ph	H	2	47	5.5	200-202	70.42 (70.28)	5.39(5.48)	17.67 (17.56)
<b>4d</b>	H	Ph	2	83	5.5	176-179	70.00 (70.28)	5.41 (5.48)	17.74 (17.56)
<b>5a</b>	Me	H	3	45	8	155-158	62.76 (62.81)	6.95 (6.85)	22.10 (21.97)
<b>5b</b>	H	Me	3	51	4.5	140-142	62.49 (62.81)	6.89 (6.85)	21.91 (21.97)
<b>5c</b>	Ph	H	3	14	5	183-185	71.25 (71.14)	6.03(5.97)	16.47 (16.59)
<b>5d</b>	H	Ph	3	78	2.5	148-149	71.13 (71.14)	5.90 (5.97)	16.65 (16.59)
<b>6a</b>	Me	H	4	26	22	145-146	64.35 (64.37)	7.25 (7.37)	20.60 (20.47)
<b>6b</b>	H	Me	4	28	22	171-174	64.13 (64.37)	7.34 (7.37)	20.44 (20.47)
<b>6c</b>	Ph	H	4	16	21	198-201	71.53 (71.89)	6.42 (6.41)	15.54 (15.72)
<b>6d</b>	H	Ph	4	27	15	184-186	71.50 (71.89)	6.81 (6.41)	15.65 (15.72)

<sup>a</sup> Yield of isolated products based on **3**

<sup>b</sup> Uncorrected, measured with a Büchi-Tottoli apparatus

Yields depend both on the nature of the substituents  $R^1$  and  $R^2$  and on length of the diamine chain. Thus, for each family of compounds, they are lower when  $R^1 = \text{Ph}$  and  $R^2 = \text{H}$ . On the other hand, when  $n = 4$  longer reaction times are needed to achieve acceptable yields. Compounds (**4**, **5**, and **6**) were characterized by their ir,  $^1\text{H}$  nmr,  $^{13}\text{C}$  nmr, and ms data (Table 2).

The bicyclic nitrogen bridged structure of these compounds was unequivocally established by an X-ray diffraction study of **4b**. The structure exhibits disorder, the *R* and *S* enantiomers being present in the asymmetric unit with a site occupation factor of 0.5 (Figure).

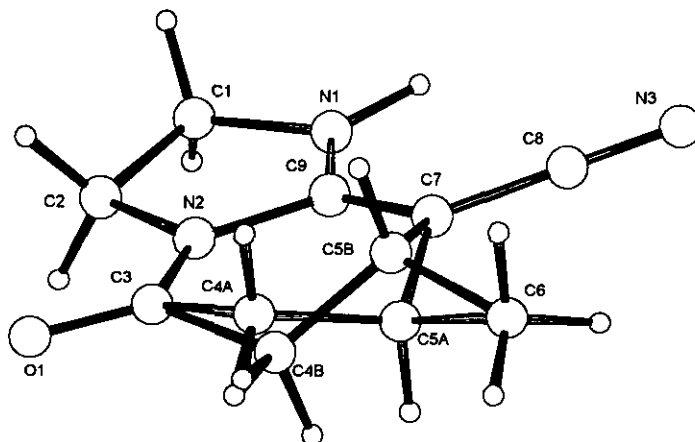
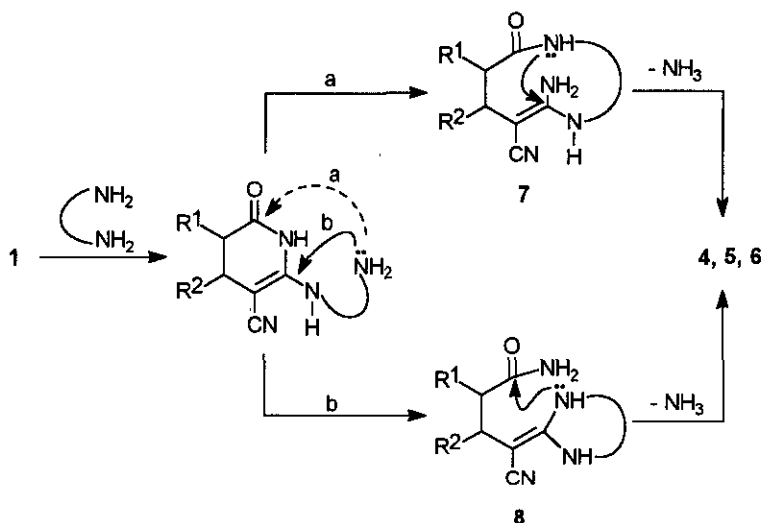


Figure. View of the asymmetric unit of **4b** showing the structural disorder (two enantiomers superimposed) (PC-PLUTO plot<sup>6</sup>)

The fact that, for the first time starting from pyridones (**3**), the formation of the second heterocyclic ring does not involve the cyano group, prompted us to approach the mechanism of this reaction. Firstly, we decided to test if the two nitrogen atoms present in the final bicyclic systems came from the diamine compound. Then, we carried out the reaction between **3b** and  $^{15}\text{N},^{15}\text{N}'$ -ethylenediamine which afforded  $^{15}\text{N},^{15}\text{N}'$ -**4b**, as it was clearly proved by its spectral data. Among them, it has to be pointed out the presence in the  $^{15}\text{N}$  nmr spectrum of a doublet at  $\delta = -303.9$  ppm ( $^1J_{\text{N-H}} = 95.2$  Hz) and a singlet at  $-238.7$  ppm, which respectively correspond to the  $^{15}\text{N1}$  and  $^{15}\text{N4}$  nitrogen atoms. The coupling with the  $^{15}\text{N}$  atoms was also detected in the  $^1\text{H}$  and  $^{13}\text{C}$  nmr spectra. Finally, the mass spectrum showed the  $M^+$  at  $m/z$  179 (24) in agreement with the presence of two  $^{15}\text{N}$  atoms.

Taking into account this result, we have proposed a ring opening-ring closure mechanism for the formation of structures (**4**, **5**, and **6**) according to which, after the initial substitution of the methoxy group of the starting pyridone (**3**) by one of the amino groups of the diamine compound, the formation of the bicyclic system can be rationalized both through a macrocyclic intermediate (**7**) and through a heterocyclic ketene aminal (**8**) (Scheme 3). The macrocycle, formed by the direct attack of the second amino group to the carbonyl atom, would evolve to the bicyclic system through an internal ethylenic nucleophilic substitution, similar to those described for compounds **3**.<sup>2</sup> On the other hand, the nucleophilic attack of the second amino group onto the double bond of the  $\alpha,\beta$ -unsaturated nitrile group would open the ring yielding an intermediate ketene aminal, which would form the final compounds through a nucleophilic acyl substitution on the intermediate amide

group. In fact some ketene aminals have been used as starting materials for the synthesis of compounds referable to 4.<sup>7</sup>



Scheme 3

In any case, the present procedure constitutes a convenient method for the synthesis of the title heterocyclic compounds in two steps from an  $\alpha,\beta$ -unsaturated ester.

#### ACKNOWLEDGMENTS

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#### EXPERIMENTAL

Compounds 3a-d were prepared according to reported procedures.<sup>4</sup>  $^{15}\text{N},^{15}\text{N}'$ -Ethylenediamine-2HCl (99 atom %  $^{15}\text{N}$ ) was purchased from ISOTEC Inc. Cat No. 85-00202. Its spectra were recorded on a Perkin-Elmer 683 spectrophotometer.  $^1\text{H}$  and  $^{13}\text{C}$  nmr spectra were measured on a Bruker AC-80, Varian Gemini 200 and Varian Gemini 300 spectrometers using TMS or as an internal standard. The  $^{15}\text{N}$  nmr spectrum was registered on a Bruker AM-400 spectrometer using  $\text{MeNO}_2$  as the standard. Mass spectra were obtained on a Hewlett-Packard 5995 A spectrometer. Elemental analyses were obtained on a Carlo-Erba CHNS-O/EA 1108 analyzer. Column chromatography was carried out on silica gel (70-230 mesh).

#### 5-Oxo-1,2,3,5,6,7-hexahydroimidazo[1,2-a]pyridine-8-carbonitriles 4a-d; General Procedure:

A mixture of the 2-methoxy-6-oxo-1,4,5,6-tetrahydropyridine-3-carbonitrile (3) (0.006 mol) and ethylenediamine (0.72 g, 0.012 mol) in *N,N*-dimethylacetamide (50 ml) was refluxed for the time stated in Table 1. The solvent was removed in vacuo and  $\text{H}_2\text{O}$  (20 ml) was added. The precipitate was filtered, washed with water and dried over  $\text{P}_2\text{O}_5$ . The compound (4) was crystallized from AcOEt-hexane (Table 1).

#### $^{15}\text{N},^{15}\text{N}'$ -5-Oxo-1,2,3,5,6,7-hexahydroimidazo[1,2-a]pyridine-8-carbonitrile $^{15}\text{N},^{15}\text{N}'$ -(4b):

A mixture of 2-methoxy-4-methyl-6-oxo-1,4,5,6-tetrahydropyridine-3-carbonitrile (3b) (0.12 g, 0.8 mmol),  $^{15}\text{N},^{15}\text{N}'$ -ethylenediamine-2 HCl (0.22 g, 1.63 mmol) and triethylamine (0.42 g, 4.16 mmol) in *N,N*-

dimethylacetamide (10 ml) was refluxed for 3 h. The solvent was removed in vacuo and the residue was chromatographed on silica gel using a mixture AcOEt/hexane (1:0.5) as eluent to afford 38.5 mg (30%) of  $^{15}\text{N}$ ,  $^{15}\text{N}'$ -(4b).  $^1\text{H}$  Nmr ( $\text{CDCl}_3$ ):  $\delta$  = 1.20 (d, 3H,  $^3J$  = 6.6,  $\text{CH}_3$ ), 2.28 and 2.65 (m, 2H,  $^2J_{\text{AB}}$  = 16.5,  $^3J_{\text{trans}}$  = 9,  $^3J_{\text{cis}}$  = 6, 2 H-C6), 2.77 (m, 1H, H-C7), 3.64 (m, 2H, H-C2), 3.91 (m, 2H, H-C3), 5.46 (d, 1H,  $^1J$  = 93.3, NH).  $^{13}\text{C}$  Nmr ( $\text{CDCl}_3$ ):  $\delta$  = 20.5 ( $\text{CH}_3$ ), 26.7 (C7), 39.4 (d,  $J_{\text{CN}}$  = 7, C6), 42.0 (d,  $J_{\text{CN}}$  = 8, C2), 42.9 (d,  $J_{\text{CN}}$  = 9, C3), 57.4 (C8), 120.4 (CN), 154.4 (dd,  $J_{\text{CN}}$  = 17,  $J_{\text{CN}}$  = 15, C8a), 167.9 (d,  $J_{\text{CN}}$  = 13, C5).  $^{15}\text{N}$  Nmr ( $\text{CDCl}_3$ ):  $\delta$  = -303.9 (d,  $^1J_{\text{NH}}$  = 95.2, N1), -238.7 (s, N4). Ms.  $m/z$  = 180 ( $\text{M}^+ + 1$ , 2%), 179 ( $\text{M}^+$ , 24), 178 ( $\text{M}^+ - 1$ , 15), 164 ( $\text{M}^+ - 15$ , 100), 150 (7), 136 (11), 111 (17).

#### 6-Oxo-2,3,4,6,7,8-hexahydro-1H-pyrido[1,2-a]pyrimidine-9-carbonitriles 5a-d; General Procedure:

A mixture of the 2-methoxy-6-oxo-1,4,5,6-tetrahydropyridine-3-carbonitrile (3) (0.006 mol) and 1,3-diaminopropane (0.89 g, 0.012 mol) in *N,N*-dimethylacetamide (50 ml) was refluxed for the time stated in Table 1. The solvent was removed in vacuo and  $\text{H}_2\text{O}$  (20 ml) was added. The precipitate was filtered, washed with water and dried over  $\text{P}_2\text{O}_5$ . The compound (5) was chromatographed on silica gel using a mixture AcOEt/hexane (2:1) as eluent (Table 1).

#### 7-oxo-1,2,3,4,5,7,8,9-octahydropyrido[1,2-a][1,3]diazepine-10-carbonitriles 6a-d; General Procedure:

A mixture of the 2-methoxy-6-oxo-1,4,5,6-tetrahydropyridine-3-carbonitrile (3) (0.006 mol) and 1,4-diaminobutane (1.06 g, 0.012 mol) in *N,N*-dimethylacetamide (50 ml) was refluxed for the time stated in Table 1. The solvent was removed in vacuo and  $\text{H}_2\text{O}$  (20 ml) was added. The precipitate was filtered, washed with water and dried over  $\text{P}_2\text{O}_5$ . The respective compound (6) was chromatographed on silica gel using a mixture AcOEt/hexane (2:1) as eluent (Table 1).

#### X-Ray Structure Determination of 4b:

Suitable colourless crystals were obtained by slow evaporation from an AcOEt solution (0.47 × 0.18 × 0.07 mm). The compound ( $\text{C}_9\text{H}_{11}\text{N}_3\text{O}$ ),  $M_r$  = 177.21, crystallizes in the monoclinic space group  $P2_1/n$  (14),  $a$  = 7.417(2),  $b$  = 7.602(4),  $c$  = 15.953(3) Å,  $\beta$  = 100.07(2)°,  $Z$  = 4,  $V$  = 885.6 Å<sup>3</sup>,  $\rho_{\text{cal}}$  = 1.330 g cm<sup>-3</sup>,  $F(000)$  = 376. A total number of 1755 reflections was collected in the range  $-8 < h < 8$ ,  $0 < k < 9$ ,  $0 < l < 18$  at 25°C on an Enraf-Nonius CAD-4 diffractometer. Graphite-monochromated Mo  $K_\alpha$  radiation ( $\lambda$  = 0.71069 Å),  $\mu$  = 0.9 cm<sup>-1</sup>. Lorentz and polarization but no absorption correction. The structure was solved by direct methods (SHELXS-86)<sup>8</sup> and refined by least-squares method on  $F^2$  for all reflections (SHELXL-93)<sup>9</sup>;  $R(F)$  = 0.072 for 815 data  $F_o > 4\sigma(F_o)$ ,  $R(F)$  = 0.123 for all the data (1549),  $R(F^2)$  = 0.221,  $w$  = [ $\sigma^2(F_o^2) + (0.1239P)^2$ ]<sup>-1</sup> where  $P$  = ( $\text{Max}(F_o^2, 0) + 2F_c^2$ )/3. Number of parameters = 142. Hydrogens bonded to carbon atoms in calculated positions and three overall isotropic temperature factors refined.

Further details of the X-ray structure determination may be obtained through the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, W-7514 Eggenstein-Leopoldshafen 2, on quoting the depository number CSD-401487, the authors and the bibliographical data.

Table 2. Spectroscopic Data of Compounds (4a-d, 5a-d, and 6a-d)

Product	Ir (film KBr) $\nu$	$^1\text{H}$ Nmr (CDCl <sub>3</sub> /TMS) $\delta$ , J (Hz)	$^{13}\text{C}$ Nmr (solvent/TMS) $\delta$	Ms (70 eV) $m/z$ (%)
4a	3320 (NH), 2180 (C=N), 1680 (C=O), 1640	5.51 (br s, 1H, NH), 3.91 (m, 2H, H-C2), 3.64 (m, 2H, H-C3), 2.57 (m, 2H, H-C7), 2.28 (m, 1H, H-C6), 1.26 (d, 3H, $^3J = 6.9$ , Me)	(CDCl <sub>3</sub> ): 42.1 (C2), 43.0 (C3), 171.0 (C5), 35.6 (C6), 28.3 (C7), 47.5 (C8), 155.1 (C8a), 121.7 (CN), 15.3 (Me)	177 (M <sup>+</sup> , 100), 162 (22), 137 (19), 134 (17)
4b	3330 (NH), 2180 (C=N), 1680 (C=O), 1650	5.40 (br s, 1H, NH), 3.93 (m, 2H, H-C2), 3.70 (m, 2H, H-C3), 2.72 (m, 2H, H-C6), 2.30 (m, 1H, H-C7), 1.21 (d, 3H, $^3J = 7.2$ , Me)	(CDCl <sub>3</sub> ): 42.0 (C2), 42.8 (C3), 167.7 (C5), 39.2 (C6), 26.5 (C7), 55.0 (C8), 154.7 (C8a), 121.1 (CN), 20.6 (Me)	177 (M <sup>+</sup> , 37), 162 (100), 134 (10)
4c	3440 (NH), 2195 (C=N), 1690 (C=O), 1665	5.41 (br s, 1H, NH), 3.97 (m, 2H, H-C2), 3.63 (m, 2H, H-C3), 3.78 (m, $^3J = 7.2$ , 1H, H-C6), 2.74 and 2.82 (m, $^2J = 15.3$ , $^3J = 9.3$ , 2H, H-C7), 7.29 (m, 5H, Ph)	(DMSO- <i>d</i> <sub>6</sub> ): 42.1 (C2), 43.3 (C3), 169.0 (C5), 47.1 (C6), 29.1 (C7), 47.7 (C8), 155.1 (C8a), 121.5 (CN), 139.3, 128.6, 128.5 and 127.3 (Ph)	239 (M <sup>+</sup> , 82), 199 (12), 118 (100)
4d	3240 (NH), 2190 (C=N), 1700 (C=O), 1650	5.60 (br s, 1H, NH), 3.94 (m, 2H, H-C2), 3.66 (m, 2H, H-C3), 3.94 (m, $^3J = 7.1$ , 1H, H-C7), 2.73 and 2.93 (m, $^2J = 16.8$ , $^2J = 6.8$ , 2H, H-C6), 7.29 (m, 5H, Ph)	(DMSO- <i>d</i> <sub>6</sub> ): 42.0 (C2), 42.9 (C3), 167.0 (C5), 39.6 (C6), 37.7 (C7), 53.3 (C8), 155.3 (C8a), 121.3 (CN), 143.6, 129.0, 127.2 and 127.0 (Ph)	239 (M <sup>+</sup> , 100), 162 (79)
5a	3320 (NH), 2180 (C=N), 1690 (C=O), 1630	5.17 (br s, 1H, NH), 3.74 (m, 2H, H-C2), 3.32 (m, 2H, H-C4), 2.57 (m, 1H, H-C7), 2.17 and 2.45 (m, $^2J = 14.7$ , $^3J = 11.7$ , $^3J = 6.7$ , 2H, H-C8), 1.97 (m, 2H, H-C3), 1.23 (d, 3H, $^3J = 6.9$ , Me)	(CDCl <sub>3</sub> ): 39.4 (C2), 22.0 (C3), 40.1 (C4), 173.0 (C6), 36.1 (C7), 27.5 (C8), 50.9 (C9), 153.3 (C9a), 122.9 (CN), 15.8 (Me)	191 (M <sup>+</sup> , 98), 176 (100)
5b	3360 (NH), 2170 (C=N), 1690 (C=O), 1610	5.21 (br s, 1H, NH), 3.75 (m, 2H, H-C2), 3.45 (m, 2H, H-C4), 2.66 (m, 2H, H-C8, H-C7), 2.30 (m, $^2J = 17.1$ , $^3J = 11.1$ , 1H, H-C7), 1.97 (m, 2H, H-C3), 1.16 (d, 3H, $^3J = 6.6$ , Me)	(DMSO- <i>d</i> <sub>6</sub> ): 39.6 (C2), 21.4 (C3), 39.3 (C4), 169.2 (C6), 39.1 (C7), 24.8 (C8), 57.8 (C9), 152.6 (C9a), 121.8 (CN), 20.3 (Me)	191 (M <sup>+</sup> , 21), 176 (100)
5c	3310 (NH), 2180 (C=N), 1690 (C=O), 1630	5.30 (br s, 1H, NH), 3.68 (m, 2H, H-C2), 3.25 (m, 2H, H-C4), 3.68 (m, 1H, H-C7), 2.66 (m, 2H, H-C8), 1.93 (m, 2H, H-C3), 7.30 (m, 5H, Ph)	(CDCl <sub>3</sub> ): 39.6 (C2), 21.6 (C3), 39.6 (C4), 170.5 (C6), 47.4 (C7), 26.6 (C8), 52.6 (C9), 152.7 (C9a), 121.8 (CN), 137.6, 128.7, 127.9 and 127.5 (Ph)	253 (M <sup>+</sup> , 94), 136 (100)
5d	3330 (NH), 2180 (C=N), 1690 (C=O), 1620	5.38 (br s, 1H, NH), 3.76 (m, 2H, H-C2), 3.36 (m, 2H, H-C4), 3.76 (m, 1H, H-C8), 2.80 and 2.95 (m, $^2J = 15.8$ , $^3J = 6.7$ , $^3J = 6.6$ , 2H, H-C7), 1.99 (m, 2H, H-C3), 7.26 (m, 5H, Ph)	(DMSO- <i>d</i> <sub>6</sub> ): 39.7 (C2), 21.4 (C3), 39.3 (C4), 168.4 (C6), 39.2 (C7), 36.1 (C8), 55.7 (C9), 153.2 (C9a), 122.1 (CN), 143.2, 128.9, 127.6 and 127.0 (Ph)	253 (M <sup>+</sup> , 100), 176 (91)
6a	3320 (NH), 2180 (C=N), 1700 (C=O), 1630	4.67 (br s, 1H, NH), 3.85 (m, 2H, H-C2), 3.12 (m, 2H, H-C5), 2.55 (m, 1H, H-C8), 2.16 and 2.35 (m, $^2J = 15.2$ , $^3J = 11.7$ , $^3J = 6.1$ , 2H, H-C9), 1.67 (m, 4H, H-C3 and H-C4), 1.22 (d, 3H, $^3J = 7.1$ , Me)	(CDCl <sub>3</sub> ): 44.2 (C2), 27.5 (C3), 27.5 (C4), 46.5 (C5), 173.6 (C7), 36.9 (C8), 28.3 (C9), 61.7 (C10), 158.6 (C10a), 120.9 (CN), 14.8 (Me)	205 (M <sup>+</sup> , 70), 190 (100)
6b	3330 (NH), 2190 (C=N), 1690 (C=O), 1620	4.66 (br s, 1H, NH), 3.85 (m, 2H, H-C2), 3.13 (m, 2H, H-C5), 2.30 (m, 1H, $^2J = 17.3$ , $^3J = 11.1$ , H-C8), 2.60 (m, 2H, H-C8 and H-C9), 1.70 (m, 4H, H-C3 and H-C4), 1.16 (d, 3H, $^3J = 6.8$ , Me)	(CDCl <sub>3</sub> ): 43.9 (C2), 28.3 (C3), 27.5 (C4), 46.2 (C5), 170.3 (C7), 40.8 (C8), 25.3 (C9), 69.0 (C10), 158.5 (C10a), 120.1 (CN), 18.7 (Me)	205 (M <sup>+</sup> , 19), 190 (100)
6c	3340 (NH), 2200 (C=N), 1700 (C=O), 1630	4.67 (br s, 1H, NH), 3.76 (m, 2H, H-C2), 3.10 (m, 2H, H-C5), 3.76 (m, 1H, H-C8), 2.65 (m, 2H, H-C9), 1.66 (m, 4H, H-C3 and H-C4), 7.25 (m, 5H, Ph)	(CDCl <sub>3</sub> ): 44.4 (C2), 27.7 (C3), 26.9 (C4), 48.1 (C5), 171.2 (C7), 47.5 (C8), 28.4 (C9), 63.8 (C10), 158.8 (C10a), 120.0 (CN), 136.8, 128.7, 127.8 and 127.5 (Ph)	267 (M <sup>+</sup> , 74), 150 (100)
6d	3320 (NH), 2180 (C=N), 1680 (C=O), 1610	4.85 (br s, 1H, NH), 3.72 (m, 2H, H-C2), 3.19 (m, 2H, H-C5), 3.76 (m, 1H, H-C9), 2.86 and 2.94 (m, $^2J = 15.3$ , $^3J = 6.2$ , $^3J = 6.1$ , 2H, H-C8), 1.70 (m, 4H, H-C3 and H-C4), 7.30 (m, 5H, Ph)	(CDCl <sub>3</sub> ): 44.0 (C2), 28.1 (C3), 27.5 (C4), 46.3 (C5), 169.7 (C7), 40.5 (C8), 36.3 (C9), 66.2 (C10), 159.4 (C10a), 120.6 (CN), 141.1, 128.9, 127.3 and 127.1 (Ph)	267 (M <sup>+</sup> , 100), 190 (67)

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