

# Synthesis and pharmacological evaluation of 7-substituted 1-ethyl-3,4,10-trimethyl-1,10-dihydro-11H-pyrazolo[3,4-c][1,6]benzodiazocin-11-one. A new ring system

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**Dedicated to Professor Vincenzo Tortorella on the occasion of his “Fuori Ruolo” status**  
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## Abstract

Derivatives of the title ring system of type **10** were obtained in good yield by fusion of the intermediates **12**. Attempt to cyclize the acetylamino derivative **9** under Bischler-Napieralski conditions failed because of the insufficient electronic density in the position 4 of the pyrazole ring created by the adjacent carbonyl moiety. The derivatives of the new ring system, assayed as anxiolytic agents, showed no significant activity.

**Keywords:** Pyrazole, 1,6-benzodiazocine, pyrazolo-1,6-benzodiazocine, Bischler-Napieralski, anxiolytic activity

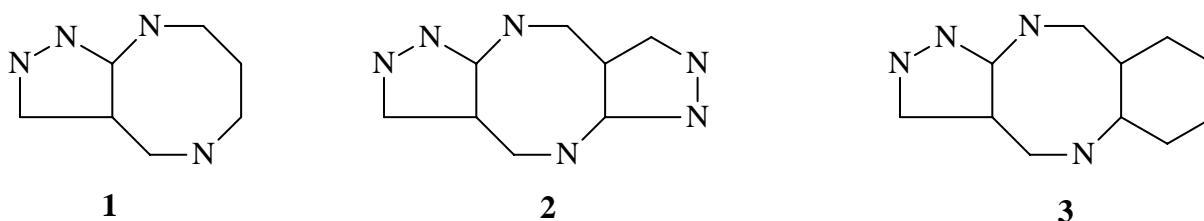
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## Introduction

Since the early eighties the 1,5-benzodiazocine system has acquired remarkable importance because of its interesting analgesic, anticonvulsant, and tranquillizer activities.<sup>1-3</sup> Also annelated benzodiazocines have shown interesting activities. Thus dibenzodiazocines showed to be effective inhibitors of the enzyme thromboxane A2 (TxA2) synthase;<sup>4</sup> or to have intercalating capability between DNA base pairs<sup>5</sup> whilst pyrazolo-benzodiazocines of type **1** exhibited activity on CNS.<sup>6</sup>

In connection with our researches on pyrazole-fused heterocycles with potential pharmaceutical activity we have recently synthesized derivatives of the new ring system

dipyrzolo[3,4-*b*:4',3'-*f*] [1,5]diazocine **2**.<sup>7</sup> Unfortunately, such derivatives assayed to evidence CNS activities showed to be inactive. Continuing our studies in the same field, we became interested in the synthesis of the new ring system pyrazolo[3,4-*c*][1,6]benzodiazocine of type **3**, with the aim to verify whether both the replacement of the pyrazole ring with a benzene nucleus and the shift of the nitrogen of the diazocine moiety from the 5 to the 6 position would produce compounds with some CNS activity.



**Figure 1**

## Results and Discussion

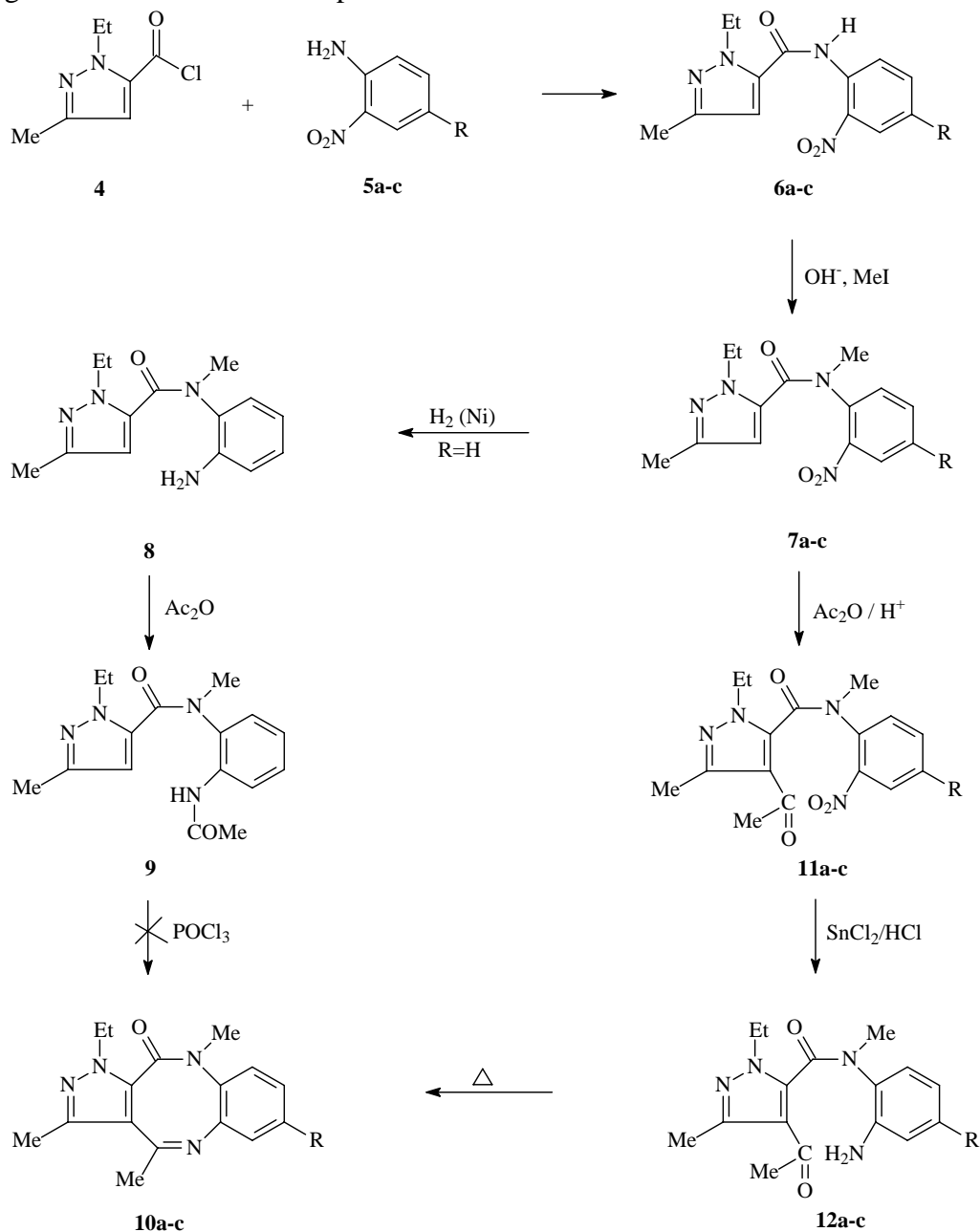
We started our synthesis reacting 5-pyrazolecarbonyl chloride **4** with the substituted 2-nitroanilines **5a-c** to give the corresponding 5-pyrazolecarboxamides **6a-c** in acceptable yields (50-65%). Reaction of these latter with methyl iodide in alkaline medium afforded the methyl derivatives **7a-c** in good yields (70-85%). Catalytic hydrogenation on Raney-nickel of compound **7a** led to the corresponding amine derivative **8** (75%) which was quantitatively converted into **9** by reaction with acetic anhydride.

The attempt to cyclize of the acetamido derivative **9** was carried out in refluxing phosphorous oxychloride. However under the Bischler-Napieralski reaction conditions the expected new ring system pyrazolo[3,4-*c*][1,6]benzodiazocine was not obtained and a very complex reaction mixture was formed from which it was only possible to isolate 1-ethyl-3-methylpyrazole 5-carboxylic acid. The failure of the cyclization involving electrophilic attack on the position 4 of the pyrazole ring, has probably to be ascribed to the presence of the carbonyl group in the position 5 that decreases the electronic density on the reaction centre. In fact, in compound **9**, between positions 4 and 5 of the pyrazole nucleus, there is a larger transmission of electronic effects (hyper ortho) than between the positions 3 and 4 (hypo ortho) due to the high "bond fixation" which give rise to a C-4—C-5 bond with a high  $\pi$  bond order as already pointed out in pyrrole and thiophene rings.<sup>8,9</sup>

We therefore undertook a different synthetic approach to the pyrazolobenzodiazocine ring system. Thus, reaction of acetic anhydride on derivatives **7** led, in excellent yields, to the corresponding acetyl derivatives **11** which were reduced with stannous chloride in hydrochloric acid to the amino derivatives **12** (70-75%). Such amino derivative heated at their melting temperatures for one hour gave the expected new tricyclic ring system pyrazolo[3,4-*c*][1,6]benzodiazocine in good yield (57-70%).

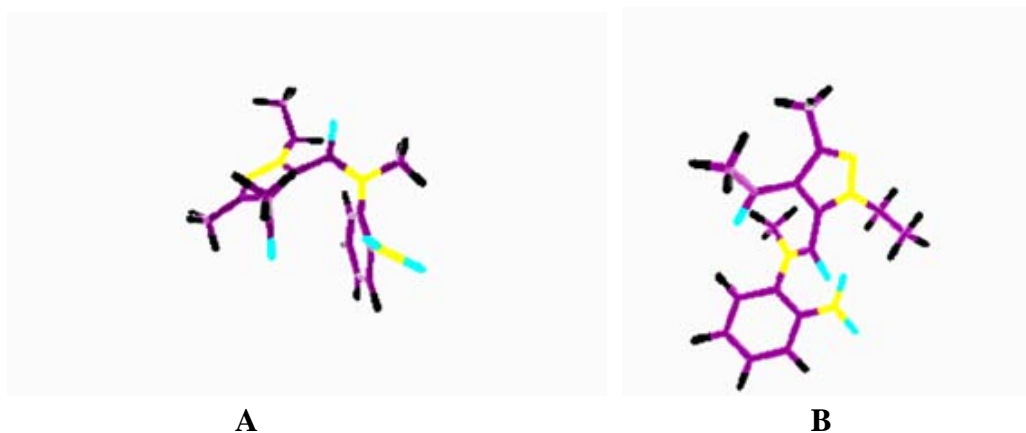
The structure of compounds **6-12** was confirmed by spectroscopic data as well as elemental analysis (see Tables 1 - 3).

In the case of compounds **11** and **12**  $^1\text{H}$  NMR spectra provided evidence for the presence of a rotational isomerism because of the hindered rotation due both to the partial double bond character of the amide C-N bond, and to the steric hindrance of the substituents in position 4 and 2'. In fact two set of signals due to N-methyl, the pyrazole and phenyl substituents were observed. The relative abundance of the more stable conformer was 75-87%. The signals belonging to both conformers are reported in Table 2.



**Scheme 1**

It is interesting to note that, in compounds **11** and **12**, the chemical shifts of the N-methyl signals of the predominant conformers are always upfield to the same signals related to the minor conformers. In accordance with the literature, the downfield resonance should be assigned to the conformer bearing the methyl group *anti* to the carbonyl.<sup>10</sup> Therefore, in our case, the predominant conformer should be the structure **A** bearing the methyl *syn* to the carbonyl. This seems unlikely since two bulky groups would lie on the same side creating a remarkable steric hindrance. However, in our opinion, the predominant conformer is the form **B** bearing the methyl *anti* to the carbonyl and the unusual upfield chemical shift can be justified by the fact that the methyl protons fall inside the conical shielding region of the carbonyl anisotropic field as shown by the Figure 2 that reports the 3D-structure of the two conformers of compound **11a** fully optimized *in vacuo* with semiempirical calculations performed with the VAMP (V 6.5) software, supplied by Oxford Molecular-Accelrys, using the Hamiltonian method PM3.



**Figure 2**

The <sup>1</sup>H and <sup>13</sup>C NMR data for the derivatives of the new ring system **10** are reported in Table 3. For these compounds, two different signals for the N-methylene protons were detected. This behaviour was observed in strictly correlated 1,5-diazocine series.<sup>7,11</sup>

It is interesting to note that compounds **10** undergo ring opening to give compounds **12** at room temperature upon silica gel acid catalysis.

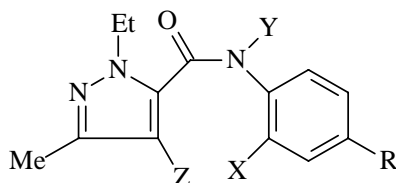
Compounds **10** were evaluated as anxiolytic agents utilizing chlordiazepoxide as reference drug, but none of them showed significant activity.

## Experimental Section

**General Procedures.** Melting points were measured in open capillary tubes using a Buchi-Tottoli immersion apparatus, and are uncorrected. The IR spectra were recorded on a Perkin-Elmer Infracord 137 spectrophotometer as nujol mulls. The <sup>1</sup>H NMR spectra were recorded on

a Bruker AC 200 in deuteriochloroform solutions. TMS was used as an internal standard. Mass spectra were recorded on a JEOL JMS-OI-SG-2 spectrometer at 75 eV(100  $\mu$ A).

**Table 1.**  $^1\text{H}$  NMR chemical shifts of compounds **6-9**:  $\delta_{\text{H}}$  [ppm]



Comp.	N-1-CH <sub>2</sub> CH <sub>3</sub>	3-CH <sub>3</sub>	Z	Y	X	R	Aryl-H
<b>6</b>							
X=NO <sub>2</sub> , Y=Z=H							
<b>a</b> R=H	4.60, 1.47	2.32	6.60	11.23			7.21-8.89 (4H)
<b>b</b> R=OCH <sub>3</sub>	4.59, 1.43	2.33	6.57	10.87		3.88	7.27-8.79 (3H)
<b>c</b> R=Cl	4.51, 1.37	2.02	6.70	10.65			7.79-8.63 (3H)
<b>7</b>							
X=NO <sub>2</sub> , Y= CH <sub>3</sub> , Z=H							
<b>a</b> R=H	4.32, 1.44	2.01	5.22	3.45			7.47-7.94 (4H)
<b>b</b> R=OCH <sub>3</sub>	4.31, 1.44	2.04	5.24	3.39		3.99	7.20-7.42 (3H)
<b>c</b> R=Cl	4.30, 1.44	2.08	5.29	3.43			7.43-7.94 (3H)
<b>8</b>							
X=NH <sub>2</sub> , Y= CH <sub>3</sub> , Z=R=H	4.25, 1.31	1.92	5.57	3.15	5.35		6.39-7.01 (4H)
<b>9</b>							
X=NHAc, Y= CH <sub>3</sub> , Z=R=H	4.25, 1.34	1.69	5.27	3.20	9.51, 2.08		7.06-7.81 (4H)

**General procedure for the synthesis of 1-ethyl-3-methyl-N-(4'-R-2'-nitrophenyl)-1H-pyrazole-5-carboxamide (6a-c)**

A solution of **4** (5 mmol), aniline derivatives **5a-c** (5 mmol), and triethylamine (5 mmol) in toluene (50 mL) was refluxed for 5 h. The solvent was then evaporated under reduced pressure and the residue was recrystallized from ethanol.

Compound **6a** (R = H): yield 60%; mp 120-121°C (yellow crystals); IR: 3350 (NH), 1670 (CO) cm<sup>-1</sup>. Anal. Calcd. for C<sub>13</sub>H<sub>14</sub>N<sub>4</sub>O<sub>3</sub>: C, 56.93; H, 5.15; N, 20.43. Found: C, 56.77; H, 5.35; N, 20.22.

Compound **6b** (R = OCH<sub>3</sub>): yield 65%; mp 135-136°C (orange needles); IR: 3380 (NH), 1680 (CO) cm<sup>-1</sup>. Anal. Calcd. for C<sub>14</sub>H<sub>16</sub>N<sub>4</sub>O<sub>4</sub>: C, 55.25; H, 5.30; N, 18.41. Found: C, 55.34, H, 5.57; N, 18.32.

Compound **6c** (R = Cl): yield 50%; mp 115-116°C (yellow crystals); IR: 3380 (NH), 1690 (CO)  $\text{cm}^{-1}$ . Anal. Calcd. for  $\text{C}_{13}\text{H}_{13}\text{N}_4\text{O}_3\text{Cl}$ : C, 50.58; H, 4.21; N, 18.15. Found: C, 50.39; H, 4.33; N, 18.27.

**General procedure for the synthesis of 1-ethyl-N,3-dimethyl-N-(4'-R-2'-nitrophenyl)-1H-pyrazole-5-carboxamide (7a-c)**

To the solution of compounds **6a-c** (3 mmol) in warm acetone (10 mL) was added powdered potassium hydroxide (10 mmol) or sodium carbonate (in the case of **6c**). The mixture was gently refluxed while methyl iodide (42 mmol) in acetone (5 mL) was added. After 30 minutes the solution was filtered, concentrated, diluted with water and cooled. The solid precipitate was collected, air dried and purified by flash chromatography on column of silica gel (eluant petroleum ether-ethyl acetate, 80:20)

Compound **7a** (R = H): yield 75%; mp 134-135°C (pale yellow crystals from toluene); IR: 1640 (CO)  $\text{cm}^{-1}$ . Anal. Calcd. for  $\text{C}_{14}\text{H}_{16}\text{N}_4\text{O}_3$ : C, 58.32; H, 5.59; N, 19.44. Found: C, 58.25; H, 5.47; N, 19.35.

Compound **7b** (R =  $\text{OCH}_3$ ): yield of 85%; mp 62-63°C (pale yellow crystals from toluene-petroleum ether); IR: 1660 (CO)  $\text{cm}^{-1}$ . Anal. Calcd. for  $\text{C}_{15}\text{H}_{18}\text{O}_4\text{N}_4$ : C, 56.59; H, 5.70; N, 17.60. Found: C, 56.41; H, 5.65; N, 17.49.

Compound **7c** (R = Cl): yield 70%; mp 103-104°C (pale yellow crystals from toluene); IR: 1655 (CO)  $\text{cm}^{-1}$ . Anal. Calcd. for  $\text{C}_{14}\text{H}_{15}\text{N}_4\text{O}_3\text{Cl}$ : C, 52.10; H, 4.68; N, 17.36. Found: C, 52.23; H, 4.84; N, 17.56.

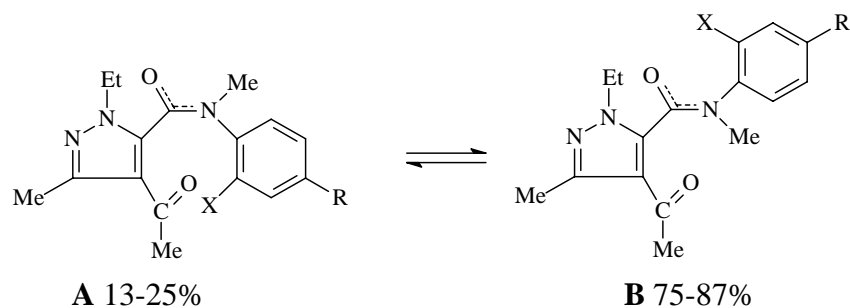
**Synthesis of 1-ethyl-N,3-dimethyl-N-(2'-aminophenyl)-1H-pyrazole-5-carboxamide (8).** A mixture of **7a** (3 mmol) in ethanol (50 mL) and of W-2 Raney-nickel (1 g) was hydrogenated in a Parr apparatus at 45 psi for 24 h at r.t. Removal of the catalyst and evaporation of the solvent under reduced pressure left the crude product which was recrystallized from ethanol (white needles).

Compound **8**: yield 75%; mp 152-153°C; IR: 3420, 3833 ( $\text{NH}_2$ ), 1642 (CO)  $\text{cm}^{-1}$ . Anal. Calcd. for  $\text{C}_{14}\text{H}_{18}\text{ON}_4$ : C, 65.09; H, 7.02; N, 21.69. Found: C, 65.27; H, 7.18; N, 21.45.

**Synthesis of 1-ethyl-N,3-dimethyl-N-(2'-acetamidophenyl)-1H-pyrazole-5-carboxamide (9).**

A mixture of **8** (3 mmol) and acetic anhydride (20 mL) was stirred at r.t. for 20 h. The reaction mixture was then poured onto crushed ice, neutralized with sodium bicarbonate and extracted with diethyl ether (2 x 60 mL). The organic layers were washed with water, dried (magnesium sulfate) and evaporated under reduced pressure to dryness to give a residue which was recrystallized from ethanol (white needles).

Compound **9**: yield 100%; mp 170-171°C; IR: 3249 (NH), 1663, 1642 (CO)  $\text{cm}^{-1}$ . Anal. Calcd. for  $\text{C}_{16}\text{H}_{20}\text{N}_4\text{O}_2$ : C, 63.98; H, 6.71; N, 18.65. Found: C, 63.77; H, 6.84; N, 18.60.

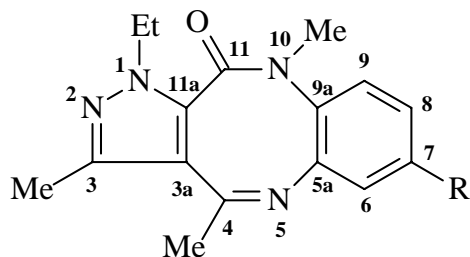
**Table 2.**  $^1\text{H}$  NMR chemical shifts of compounds **11**, **12**:  $\delta_{\text{H}}$  [ppm]

Comp	N-1-CH <sub>2</sub> CH <sub>3</sub>	3-CH <sub>3</sub>	COCH <sub>3</sub>	NCH <sub>3</sub>	X	R	Aryl-H
<b>11</b>							
X=NO <sub>2</sub>							
<b>a</b> R=H	4.16, 1.36 ( <b>A</b> )	2.29 ( <b>A</b> )	2.22 ( <b>A</b> )	3.52 ( <b>A</b> )			7.29-8.13
	4.19, 1.52 ( <b>B</b> )	2.56 ( <b>B</b> )	2.50 ( <b>B</b> )	3.19 ( <b>B</b> )			(4H) ( <b>A+B</b> )
<b>b</b> R=OCH <sub>3</sub>	4.15, 1.36 ( <b>A</b> )	2.32 ( <b>A</b> )	2.27 ( <b>A</b> )	3.48 ( <b>A</b> )		3.82 ( <b>A</b> )	7.27-7.72
	4.20, 1.52 ( <b>B</b> )	2.54 ( <b>B</b> )	2.49 ( <b>B</b> )	3.15 ( <b>B</b> )		3.91 ( <b>B</b> )	(3H) ( <b>A+B</b> )
<b>c</b> R=Cl	3.98, 1.40 ( <b>A</b> )	2.35 ( <b>A</b> )	2.26 ( <b>A</b> )	3.49 ( <b>A</b> )			7.27-8.12
	4.13, 1.55 ( <b>B</b> )	2.54 ( <b>B</b> )	2.50 ( <b>B</b> )	3.17 ( <b>B</b> )			(3H) ( <b>A+B</b> )
<b>12</b>							
X=NH <sub>2</sub>							
<b>a</b> R=H	4.14, 1.30 ( <b>A</b> )	2.33 ( <b>A</b> )	2.29 ( <b>A</b> )	3.41 ( <b>A</b> )	4.80		6.53-7.27
	4.20, 1.51 ( <b>B</b> )	2.54 ( <b>B</b> )	2.43 ( <b>B</b> )	3.12 ( <b>B</b> )	( <b>A+B</b> )		(4H) ( <b>A+B</b> )
<b>b</b> R=OCH <sub>3</sub>	4.07, 1.30 ( <b>A</b> )	2.35 ( <b>A</b> )	2.33 ( <b>A</b> )	3.38 ( <b>A</b> )	4.81	3.68 ( <b>A</b> )	6.07-7.27
	4.16, 1.49 ( <b>B</b> )	2.54 ( <b>B</b> )	2.49 ( <b>B</b> )	3.09 ( <b>B</b> )	( <b>A+B</b> )	3.77 ( <b>B</b> )	(3H) ( <b>A+B</b> )
<b>c</b> R=Cl	4.12, 1.23 ( <b>A</b> )	2.36 ( <b>A</b> )	2.32 ( <b>A</b> )	3.37 ( <b>A</b> )	4.96		6.47-7.27
	4.20, 1.50 ( <b>B</b> )	2.54 ( <b>B</b> )	2.49 ( <b>B</b> )	3.09 ( <b>B</b> )	( <b>A+B</b> )		(3H) ( <b>A+B</b> )

**Reaction of phosphorus oxychloride with compound 9.** A mixture of **9** (2 mmol) and phosphorus oxychloride (30 mL) was refluxed at 165-175°C for 24 h.. The excess of phosphorus oxychloride was evaporated under reduced pressure and the mixture was poured onto crushed ice, the solution was adjusted to pH 3.5 with solid sodium bicarbonate and extracted with chloroform (2x50 mL). The organic layers were washed with water, dried with magnesium

sulfate and evaporated to give a solid which was identified as 1-ethyl-3-methylpyrazole 5-carboxylic acid. Subsequently, the aqueous mother liquor was adjusted to pH 8.3 with solid sodium bicarbonate, extracted with chloroform (2x50 mL) to give an intractable material.

**Table 3.**  $^{13}\text{C}$  NMR and ( $^1\text{H}$  NMR) chemical shifts of compounds **10**:  $\delta_{\text{H}}$  [ppm]



Position	a, R=H	b, R=OCH <sub>3</sub>	c, R=Cl
3	147.3	148.3	148.7
3a	115.6	115.9	15.4
4	162.0	162.4	161.8
5a	133.7	134.7	134.6
6	122.2 (6.82)	106.1 (6.33)	121.7 (6.91)
7	124.6 (7.06)	158.3	132.1
8	126.7 (7.19)	110.9 (6.65)	124.5 (7.14)
9	128.0 (7.35)	127.6 (7.27)	128.6 (7.44)
9a	134.8	127.1	132.8
11	164.5	164.6	166
11a	142.6	142.6	142.8
N-	44.6 (4.05*), 12.3	44.5 (4.04*), 12.4	44.7 (4.04*), 12.3
CH <sub>2</sub> CH <sub>3</sub>	(1.18)	(1.18)	(1.19)
3-CH <sub>3</sub>	15.5 (2.22)	15.5 (2.15)	15.5 (2.17)
4-CH <sub>3</sub>	27.2 (2.48)	27.2 (2.39)	27.2 (2.42)
R		55.2 (3.70)	
NCH <sub>3</sub>	36.0 (3.33)	36.1 (3.18)	36.0 (3.21)

\* in proton spectra, recorded at 25°C, two different resonances are detected for the methylene protons: **10a**, 4.04 and 4.11 ppm; **10b**, 4.04 and 4.11 ppm; **10c**, 4.04 and 4.12 ppm, respectively.

**General procedure for the synthesis of 1-ethyl-N,3-dimethyl-4-acetyl-N-(4'-R-2'-nitrophenyl)-1H-pyrazole-5-carboxamide (11a-c)**

A mixture of **7a-c** (3 mmol), acetic anhydride (30 mL) and a few drops of sulfuric acid was refluxed for 6 hours. After cooling, the reaction mixture was poured into crushed ice, neutralized with solid sodium bicarbonate and extracted with ethyl ether (2x50 mL). The organic layers were



washed with water, dried with magnesium sulfate and concentrated to dryness under reduced pressure to give a residue which was purified by flash chromatography on column of silica gel (elution with petroleum ether(40-70)-ethyl acetate, 80:20) to give the desired products which were recrystallized from ethanol.

Compound **11a** (R = H): yield 75%; mp 105-106°C (white crystals); IR: 1660 (CO) cm<sup>-1</sup>; Anal. Calcd. for C<sub>16</sub>H<sub>18</sub>N<sub>4</sub>O<sub>4</sub>: C, 58.17; H, 5.49; N, 16.96. Found: C, 58.38; H, 5.33; N, 16.75.

Compound **11b** (R = OCH<sub>3</sub>): yield 85%; mp 137-138° (pale yellow crystals); IR: 1665 (CO) cm<sup>-1</sup>. Anal. Calcd. for C<sub>17</sub>H<sub>20</sub>N<sub>4</sub>O<sub>5</sub>: C, 56.66; H, 5.59; N, 15.55. Found: C, 56.57; H, 5.41; N, 15.33.

Compound **11c** (R = Cl): yield 85%; mp 154-155°C (prazel crystals); IR: 1655 (CO) cm<sup>-1</sup>. Anal. Calcd. for C<sub>16</sub>H<sub>17</sub>N<sub>4</sub>O<sub>4</sub>Cl: C, 52.68; H, 4.70; N, 15.36. Found: C, 52.51; H, 4.88; N, 15.39.

### General procedure for the synthesis of 1-ethyl-N,3-dimethyl-4-acetyl-N-(4'-R-2'-aminophenyl)-1H-pyrazole-5-carboxamide (**12a-c**)

Compounds **11a-c** (10 mmol) were added to a magnetically stirred suspension of finely powdered stannous chloride (30 mmol) in hydrochloric acid (36%, 5 mL) at such a rate so that the temperature of the slurry was maintained below 5°C. After the complete addition of the nitro compounds, the mixture was allowed to stir for 24 hours. The white slurry thus obtained was diluted with cold water and aqueous sodium hydroxide (40%) was added till the salts of tin were dissolved. The solution was extracted with ethyl acetate (3x50 mL), the extracts were dried (magnesium sulphate) and evaporated under reduced pressure to give a residue which was recrystallized from ethanol.

Compound **12a** (R = H): yield 75%; mp 165-166°C (white crystals); IR: 3446, 3362 (NH<sub>2</sub>), 1654, 1640 (CO) cm<sup>-1</sup>. Anal. Calcd. for C<sub>16</sub>H<sub>20</sub>N<sub>4</sub>O<sub>2</sub>: C, 63.98; H, 6.71; N, 18.65 Found: C, 63.77; H, 6.78; N, 18.74.

Compound **12b** (R = OCH<sub>3</sub>): yield 75%; mp 140-141°C (pale yellow crystals); IR: 3437, 3353 (NH<sub>2</sub>), 1656, 1634 (CO) cm<sup>-1</sup>. Anal. Calcd. for C<sub>17</sub>H<sub>22</sub>N<sub>4</sub>O<sub>3</sub>: C, 61.80; H, 6.71; N, 16.96. Found: C, 61.80; H, 6.57; N, 16.75.

Compound **12c** (R = Cl): yield 70%; mp 194-195°C (yellow crystals); IR: 3443, 3354 (NH<sub>2</sub>), 1655, 1635 (CO) cm<sup>-1</sup>. Anal. Calcd. for C<sub>16</sub>H<sub>19</sub>N<sub>4</sub>O<sub>2</sub>Cl: C, 57.40; H, 5.72; N, 16.74. Found: C, 57.46; H, 5.89; N, 16.93.

### General procedure for the synthesis of 7-R-1-ethyl-3,4,10-trimethyl-1,10-dihydro-11H-pyrazolo[3,4-c][1,6]benzodiazocin-11-ones (**10 a-c**)

Compounds **12a-c** were heated for one hour at their melting temperature. After cooling the crude solid was recrystallized from dioxane or, in the case of **10b**, purified by sublimation at 165°C/1mmHg.

Compound **10a** (R = H): yield 57%; mp: 100-101°C (white needles); IR: 1660 (CO) cm<sup>-1</sup>; ms: m/z 282 (M<sup>+</sup>). Anal. Calcd for C<sub>16</sub>H<sub>18</sub>N<sub>4</sub>O: C, 68.06; H, 6.43; N, 19.85. Found: C, 68.34; H, 6.12; N, 19.73.

Compound **10b** (R = OCH<sub>3</sub>): yield 62%, mp: 60-61°C (white glassy solid); IR: 1657 (CO) cm<sup>-1</sup>; ms: m/z 312 (M<sup>+</sup>). Anal. Calcd for C<sub>17</sub>H<sub>20</sub>N<sub>4</sub>O<sub>2</sub>: C, 65.36; H, 6.45; N, 17.94. Found: C, 65.12; H, 6.29; N, 17.74.

Compound **10c** (R = Cl): yield 70%; mp: 108-109°C (white crystals); IR: 1657 (CO) cm<sup>-1</sup>; ms: m/z 316 (M<sup>+</sup>). Anal. Calcd. for C<sub>16</sub>H<sub>17</sub>N<sub>4</sub>OCl: C, 60.66; H, 5.41; N, 17.69. Found: C, 60.49; H, 5.35; N, 17.82.

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