Synthesis of Some 1,3-Dimethyl-6-substituted-1*H*-pyrazolo[3,4-*b*]pyrazin-5(4*H*)-ones

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A series of new 6-substituted-1,3-dimethyl-1*H*-pyrazolo[3,4-*b*]pyrazin-5(4*H*)-ones (**13a** – **e**) and 1,3-dimethyl-5a,6a,7,8-tetrahydro-1*H*-pyrazolo[4,3-*e*]pyrrolo[1,2-*a*]pyrazin-5(4*H*)-one (**15**) have been synthesized. The synthetic strategy involves direct interaction of D,L-α-amino acids with 5-chloro-1,3-dimethyl-4-nitro-1*H*-pyrazole (**10**) to produce the respective *N*-(1,3-dimethyl-4-nitro-1*H*-pyrazol-5-yl) D,L-α-amino acids **11a** – **e** and **14**. The latter compounds underwent reductive lactamization to deliver the corresponding target heterocyclic systems **13a** – **e** and **15**.

Key words: 5-Chloro-1,3-dimethyl-4-nitropyrazole, D,L-α-Amino Acids, S_N-Ar Reactions, Pyrazolo[3,4-*b*]pyrazin-5-ones, Pyrazolo[4,3-*e*]pyrrolo[1,2-*a*]pyrazin-5-one

Introduction

Since the introduction of antipyrine (**1**) [1] as a derivative of pyrazole in 1884 by Knorr as antipyretic agent, several related derivatives have been synthesized as herbicidal [2], antineoplastic [3], antiarrhythmic [4], antiinflammatory [4], antischistosomal [5], and antitumor [6a,b] agents. In recent years, clinically important pyrazoles were also synthesized that exhibit antimicrobial [7], antifungal [8], analgesic, antipyretic [9], ulcerogenic, molluscicidal, and antischistosomal (antibilharzial) [10] activity.

The pyrazole unit is present in a number of natural and synthetic drugs (Fig. 1) with different bioactivities: betazole (**2**) is bioisosteric with histamine and selectively blocks the H_2-receptor [1b], celecoxib (**3**) is a powerful COX-2 inhibitor and exhibits analgesic and antiarthritic effects [11], while difenamizole (**4**) is an analgesic, anti-inflammatory, and antipyretic drug [1b]. Isofezolac (**5**) is a Japanese drug reported to have a good anti-inflammatory activity [9], and Fenpyroximate (**6**) is a novel anti-acaricide agent [12].

Fused pyrazoles have also received considerable attention because of their pharmacological applications as analgesic, anti-inflammatory, antipyretic [13], and antifungal agents [8a]. For instance, the derivatives of pyrazolo[3,4-*b*]pyrazines/pyrazinones **7** – **9** (Fig. 1) are reported to exhibit antifungal, antiparasitic and antitumor activities [6a, 14].

Results and Discussion

The preparation of the new pyrazolo-pyrazinones **13a** – **e** and **15** was achieved by utilizing 5-chloro-1,3-dimethyl-4-nitro-1*H*-pyrazole (**10**) as starting material and constructing the pyrazinone unit thereupon through two-step conversions as illustrated in Scheme 1. Thus, direct interaction of **10** with the appropriate α-amino acid has been conducted in aqueous ethanol containing sodium hydrogen carbonate (or potassium carbonate) at 70 – 80 °C for 2 – 5 d. This reaction follows an S_N-Ar (addition-elimination) path and is facilitated by the presence of the strong electron-withdrawing nitro group at position 4 [15] to yield the corresponding *N*-(4-nitropyrazol-5-yl)-D,L-α-amino acids **11a** – **e** and **14**. In this context, it is worth mentioning that the reaction time required to get optimum yield depends upon the nature of the α-amino acid used. For example, 4 – 5 days are required for glycine, D,L-alanine, D,L-valine, D,L-leucine, and D,L-phenylalanine, and 2 d for D,L-proline. This may be due to differences in their nucleophilicity order:

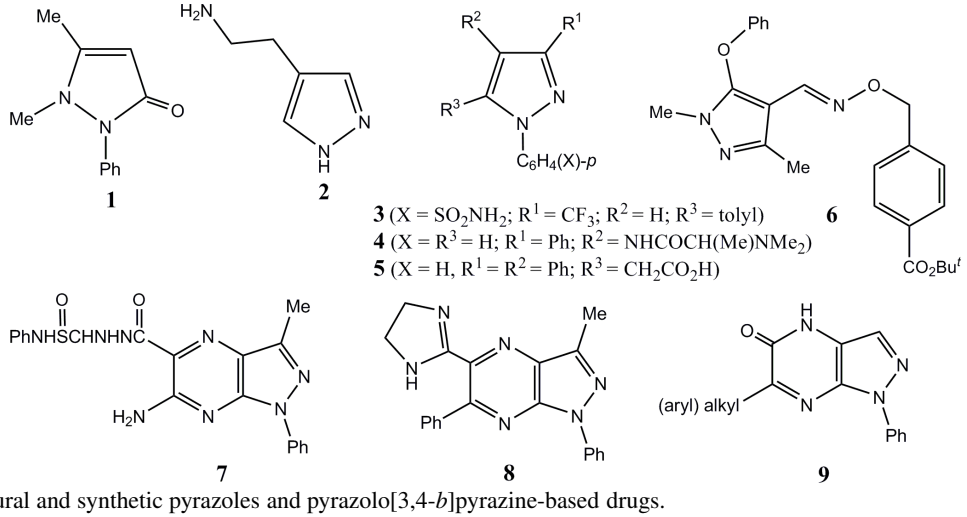
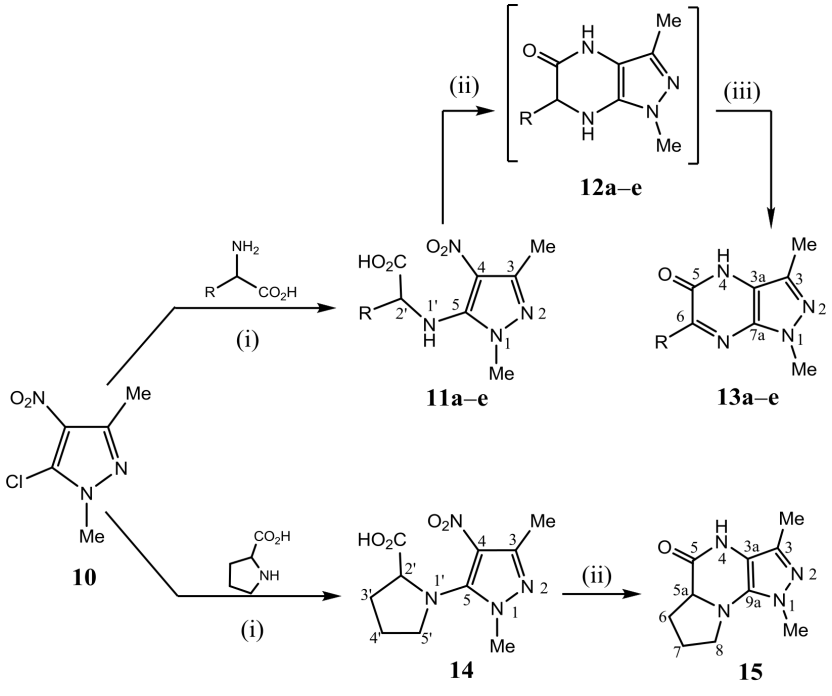
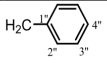


Fig. 1. Natural and synthetic pyrazoles and pyrazolo[3,4-*b*]pyrazine-based drugs.



Compounds **11**–**13**

Entry	a	b	c	d	e
R	H	Me	$CHMe_2$ (1")	CH_2CHMe_2 (1", 2")	

Scheme 1. (i) EtOH + H_2O/$NaHCO_3$, reflux; (ii) H_2, 5 % Pd/C; (iii) air oxidation.

the former primary α-amino acids are weaker nitrogen nucleophiles than the secondary α-amino acid (D,L-proline).

Catalytic hydrogenation of **11a** – **e**, using 5 % Pd/C, led to reduction of the nitro to the amino group. It was followed by spontaneous lactamization and air-

oxidation of intermediates **12a – e** to afford good yields of the respective target products (**13a – e**; Scheme 1). Likewise, reductive lactamization of **14** afforded the respective tricyclic system **15**.

The new compounds **11a – e**, **13a – e**, **14** and **15** were characterized by elemental analyses, MS, and NMR spectral data. These data, detailed in the Experimental Section, are consistent with the suggested structures. Thus, their MS spectra displayed the correct molecular ions $[M]^+$ for which the m/z values are in agreement with those calculated from the respective molecular formulas. ^{1}H and ^{13}C signal assignments to the different protons and carbons in the NMR spectra of the new compounds followed from DEPT and 2D (COSY, HMQC, HMBC) experiments which showed correlations that helped in the full assignments.

Experimental Section

D,L-α-Amino acids, 5-chloro-1,3-dimethyl-4-nitro-1*H*-pyrazole, and 5 % Pd/C, employed in this study, were purchased from Acros and were used as received. Melting points were measured on an SMP2 Stuart apparatus. IR spectra were recorded from KBr discs on a Nicolet-MAGNA-IR-560 spectrophotometer. ^{1}H and ^{13}C NMR spectra were obtained with a Bruker DPX-300 ultrashield instrument. Chemical shifts are expressed in ppm with reference to TMS as internal standard. Electron impact mass spectra (EIMS) were measured using a Varian MAT-112S instrument or a Finnigan MAT-312 spectrometer at 70 eV, at an ion source temperature of 200 °C. Elemental analyses were performed on a Euro Vector elemental analyzer, model EA 3000.

*N-(1,3-Dimethyl-4-nitro-1H-pyrazol-5-yl) α-amino acids **11a – e** and **14***

General procedure

A well-stirred mixture of the appropriate D,L-α-amino acid (9 mmol), 5-chloro-1,3-dimethyl-4-nitropyrazole (**10**, 0.53 g, 3 mmol) and sodium hydrogen carbonate (1.5 g, 18 mmol) in aqueous ethanol (140 mL, 1 : 1 v/v) was heated at 70 – 80 °C. The reaction mixture slowly developed a light-yellow color. Progress of the reaction was monitored by TLC and was completed within 4 – 5 d. The resultant yellow solution was first extracted with dichloromethane (40 mL), and the aqueous layer was separated and acidified with 3N HCl to pH = 6 – 7. The precipitated product was collected by suction filtration, washed with water and dried. Compounds **11a – e** and **14** were prepared following the above-described general procedure.

*N-(1,3-Dimethyl-4-nitro-1H-pyrazol-5-yl)glycine (**11a**)*

This compound was prepared from **10** (0.53 g, 3 mmol) and glycine (0.68 g, 9 mmol), m. p. 233 – 235 °C, 94 % yield. – IR (KBr): ν = 3444 (O-H), 3307 (N-H), 1713 (C=O), 1625 cm^{-1} (C=N). – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.25 (s, 3H, C-CH_3), 3.67 (s, 3H, *N*-CH_3), 4.31 (d, 2H, *J*= 6.0 Hz, 2′-H), 7.48 (t, 1H, *J* = 6.0 Hz, N-H), 13.17 (br s, 1H, O-H). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.8 (C-*C*H_3), 37.9 (*N*-CH_3), 45.5 (C-2′), 118.3 (C-5), 144.0 (C-3), 146.9 (C-4), 172.1 (C=O). – MS (EI, 70 eV): m/z (%) = 214 (47) $[M]^+$. – $C_7H_{10}N_4O_4$ (214.07): calcd. C 39.25, H 4.71, N 26.16; found C 38.97, H 4.79, N 25.94.

*N-(1,3-Dimethyl-4-nitro-1H-pyrazol-5-yl) D,L-α-alanine (**11b**)*

This compound was prepared from **10** (0.53 g, 3 mmol) and D,L-α-alanine (0.80 g, 9 mmol), m. p. 162 – 164 °C, 91 % yield. – IR (KBr): ν = 3442 (O-H), 3309 (N-H), 1719 (C=O), 1613 cm^{-1} (C=N). – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.56 (d, 3H, *J* = 6.8 Hz, C(2′)-CH_3), 2.35 (s, 3H, C(3)-CH_3), 3.72 (s, 3H, *N*-CH_3), 4.40 (m, 1H, 2′-H), 7.18 (d, 1H, *J* = 5.2 Hz, N-H), 12.13 (br s, 1H, O-H). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.2 (C-*C*H_3), 20.0 (C(2′)-*C*H_3), 37.6 (*N*-CH_3), 53.1 (C-2′), 119.7 (C-5), 145.7 (C-3), 146.2 (C-4), 176.2 (C=O). – MS (EI, 70 eV): m/z (%) = 228 (32) $[M]^+$. – $C_8H_{12}N_4O_4$ (228.09): calcd. C 42.10, H 5.30, N 24.50; found C 42.35, H 5.39, N 24.36.

*N-(1,3-Dimethyl-4-nitro-1H-pyrazol-5-yl) D,L-valine (**11c**)*

This compound was prepared from **10** (0.53 g, 3 mmol) and D,L-valine (1.05 g, 9 mmol), m. p. 115 – 116 °C, 95 % yield. – IR (KBr): ν = 3446 (O-H), 3319 (N-H), 1726 (C=O), 1606 cm^{-1} (C=N). – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.97 (d, 3H, *J* = 6.8 Hz, C(1″)-CH_3), 1.02 (d, 3H, *J* = 6.9 Hz, C(1″)-CH_3), 2.17 (m, 1H, 1″-H), 2.37 (s, 3H, C-CH_3), 3.68 (s, 3H, *N*-CH_3), 4.12 (dd 1H, *J* = 5.7, 9.2 Hz, 2′-H), 7.36 (d, 1H, *J* = 5.7 Hz, N-H), 11.94 (br s, 1H, O-H). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.6 (C-*C*H_3), 17.9/18.9 (C(1″)-2*C*H_3), 31.9 (C-1″), 38.0 (*N*-CH_3), 63.8 (C-2′), 119.0 (C-5), 145.2 (C-3), 147.3 (C-4), 174.9 (C=O). – MS (EI, 70 eV): m/z (%) = 256 (63) $[M]^+$. – $C_{10}H_{16}N_4O_4$ (256.12): calcd. C 46.87, H 6.29, N 21.86; found C 46.86, H 6.36, N 21.63.

*N-(1,3-Dimethyl-4-nitro-1H-pyrazol-5-yl) D,L-leucine (**11d**)*

This compound was prepared from **10** (0.53 g, 3 mmol) and D,L-leucine (1.18 g, 9 mmol), m. p. 132 – 133 °C, 98 % yield. – IR (KBr): ν = 3437 (O-H), 3304 (N-H), 1717 (C=O), 1591 cm^{-1} (C=N). – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.93 (d, 3H, *J* = 6.0 Hz, C(2″)-CH_3), 0.97 (d, 3H, *J* = 6.1 Hz, C(2″)-CH_3), 1.78 (m, 3H, 1″-H/2″-H_2), 2.38 (s, 3H, C(3)-CH_3), 3.72 (s, 3H, *N*-CH_3), 4.32 (m, 1H, 2′-H), 6.91 (d, *J* = 5.5 Hz, 1H, N-H), 11.53 (br s, 1H, O-H). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.2 (C-*C*H_3), 21.8/22.7 (C(2″)-2*C*H_3), 24.8 (C-2″), 37.7 (*N*-CH_3), 42.5 (C-1″), 56.1

(C-2′), 119.7 (C-5), 145.7 (C-3), 146.5 (C-4), 176.2 (C=O). – MS (EI, 70 eV): m/z (%) = 270 (30) $[M]^+$. – $C_{11}H_{18}N_4O_4$ (270.13): calcd. C 48.88, H 6.71, N 20.73; found C 48.56, H 6.70, N 20.72.

*N-(1,3-Dimethyl-4-nitro-1H-pyrazol-5-yl) D,L-α-phenylalanine (**11e**)*

This compound was prepared from **10** (0.53 g, 3 mmol) and D,L-α-phenylalanine (0.68 g, 9 mmol), m. p. 188 – 190 °C, 91 % yield. – IR (KBr): ν = 3447 (O-H), 3298 (N-H), 1737 (C=O), 1605 cm^{-1} (C=N). – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.37 (s, 3H, C(3)-CH_3), 3.19 (m, 2H, -CH_2Ph), 3.53 (s, 3H, *N*-CH_3), 4.53 (m, 1H, 2′-H), 7.08 (d, J = 10.0 Hz, N-H), 7.30 ((m)$_c$, 5H, C_6H_5), 8.50 (br s, 1H, O-H). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.3 (C-CH_3), 37.5 (*N*-CH_3), 39.7 (C-1″), 58.8 (C-2′), 127.4 (C-3″ + C-5″), 128.7 (C-4″), 129.2 (C-2″ + C-6″), 135.6 (C-5), 136.9 (C-1″), 144.5 (C-3), 146.3 (C-4), 172.8 (C=O). – MS (EI, 70 eV): m/z (%) = 304 (47) $[M]^+$. – $C_{14}H_{16}N_4O_4$ (304.12): calcd. C 55.26, H 5.30, N 18.41; found C 55.04, H 5.56, N 18.18.

*N-(1,3-Dimethyl-4-nitro-1H-pyrazol-5-yl) D,L-proline (**14**)*

A mixture of 5-chloro-1,3-dimethyl-4-nitro-1*H*-pyrazole (**10,** 1.76 g, 10 mmol), D,L-proline (1.77 g, 0.015 mol) and sodium hydrogen carbonate (1.85 g, 22 mmol) or potassium carbonate (3.1 g, 22 mmol) in aqueous ethanol (30 mL, 2:1 v/v) was heated at 70 – 80 °C for 2 d. The reaction mixture was then cooled, acidified with 4N HCl to pH ≈ 6, and extracted with dichloromethane (2 × 30 mL) and ethyl acetate (2 × 30 mL); evaporation of the combined organic extracts gave the title product as a colorless solid, m. p. 126 – 127 °C, 95 % yield. – IR (KBr): ν = 3443 (O-H), 1719 (C=O), 1637 cm^{-1} (C=N). – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.06 (m, 2H, 4′-H_2), 2.38 (m, 2H, 3′-H_2), 2.44 (s, 3H, C(3)-CH_3), 3.28 (m, 2H, 5′-H_2), 3.76 (s, 3H, *N*-CH_3), 4.38 (dd, 1H,J = 4.2, 9.3 Hz, 2′-H), 10.39 (br s, 1H, O-H). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.8 (C-CH_3), 25.4 (C-4′), 30.7 (C-3′), 35.8 (*N*-CH_3), 53.0 (C-5′), 62.7 (C-2′), 125.8 (C-5), 145.1 (C-3), 146.4 (C-4), 179.1 (C=O). – MS (EI, 70 eV): m/z (%) = 254 (12) $[M]^+$. – $C_{10}H_{14}N_4O_4$ (254.10): calcd. C 47.24, H 5.55, N 22.04; found C 47.19, H 5.80, N 21.75.

*1,3-Dimethyl-6-substituted-1H-pyrazolo[3,4-b]pyrazin-5(4H)-ones **13a – e** and **15***

General procedure

A solution of the appropriate pyrazolo-amino acid **11a – e** or **14** in MeOH (~ 50 mL) was hydrogenated in the presence of 5 % Pd/C (20 – 25 % by mass) at 4 bar for 6 d. The catalyst was then filtered off, and the filtrate was concentrated. The solid obtained was purified on silica gel TLC plates with dichloromethane and methanol (8.5/1.5: v/v) as eluent to afford the respective compounds **13a – e** and **15**.

*1,3-Dimethyl-1H-pyrazolo[3,4-b]pyrazin-5(4H)-one (**13a**)*

This compound was obtained by reductive cyclization of **11a** (0.2 g, 0.93 mmol) with 5 % Pd/C (0.04 g), m. p. = 239 – 242 °C, 66 % yield. – IR (KBr): ν = 3416 (N-H), 1644 (C=O), 1614 (C=N), 1424 cm^{-1} (C=C). – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.49 (s, 3H, C(3)-CH_3), 4.08 (s, 3H, *N*-CH_3), 8.04 (s, 1H, 6-H), 13.20 (s, 1H, N-H). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = 11.1 (C-CH_3), 34.4 (*N*-CH_3), 114.0 (C-7a), 130.4 (C-3a), 136.9 (C-3), 146.3 (C-6), 155.4 (C-5). – MS (EI, 70 eV): m/z (%) = 164 (8) $[M]^+$. – $C_7H_8N_4O$ (164.09): calcd. C 51.21, H 4.91, N 34.13; found C 51.12, H 4.81, N 34.02.

*1,3,6-Trimethyl-1H-pyrazolo[3,4-b]pyrazin-5(4H)-one (**13b**)*

This compound was obtained by reductive cyclization of **11b** (0.2 g, 0.88 mmol) with 5 % Pd/C (0.04 g), m. p. = 174 – 176 °C, 73 % yield. – IR (KBr): ν = 3444 (N-H), 1644 (C=O), 1627 (C=N), 1455 cm^{-1} (C=C). – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.26 (s, 3H, C(6)-CH_3), 2.83 (s, 3H, C(3)-CH_3), 4.19 (s, 3H, *N*-CH_3), 13.05 (s, 1H, N-H). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = 11.0 (C-CH_3), 22.7 (C(6)-CH_3), 34.2 (*N*-CH_3), 114.6 (C-7a), 130.9 (C-3a), 137.0 (C-3), 158.0 (C-6), 163.9 (C-5). – MS (EI, 70 eV): m/z (%) = 178 (9) $[M]^+$. – $C_8H_{10}N_4O$ (178.10): calcd. C 53.92, H 5.66, N 31.44; found C 53.74, H 5.46, N 31.24.

*6-Isopropyl-1,3-dimethyl-1H-pyrazolo[3,4-b]pyrazin-5(4H)-one (**13c**)*

This compound was obtained by reductive cyclization of **11c** (0.2 g, 0.78 mmol) with 5 % Pd/C (0.04 g), m. p. = 241 – 243 °C, 71 % yield. – IR (KBr): ν = 3426 (N-H), 1649 (C=O), 1599 (C=N), 1459 cm^{-1} (C=C). – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.28 (d, 6H, J = 6.8, C(1″)-2CH_3), 2.43 (s, 3H, C(3)-CH_3), 3.56 (m, 1H, 1″-H), 3.96 (s, 3H, *N*-CH_3), 13.10 (s, 1H, N-H). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = 11.1 (C-CH_3), 20.2 (C(1″)-2CH_3), 31.0 (C-1″), 34.2 (*N*-CH_3), 114.0 (C-7a), 131.1 (C-3a), 137.0 (C-3), 156.7 (C-6), 163.3 (C-5). – MS (EI, 70 eV): m/z (%) = 206 (48) $[M]^+$. – $C_{10}H_{14}N_4O$ (206.13): calcd. C 58.24, H 6.84, N 27.17; found C 58.47, H 6.64, N 27.16.

*6-Isobutyl-1,3-dimethyl-1H-pyrazolo[3,4-b]pyrazin-5(4H)-one (**13d**)*

This compound was obtained by reductive cyclization of **11d** (0.3 g, 1.1 mmol) with 5 % Pd/C (0.05 g), m. p. = 173 – 175 °C, 62 % yield. – IR (KBr): ν = 3442 (N-H), 1659 (C=O), 1629 (C=N), 1437 cm^{-1} (C=C). – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.00 (d, , 6H, J = 6.7 Hz, C(2″)-2CH_3), 2.00 (m, 1H, 2″-H), 2.47 (s, 3H, C(3)-CH_3), 2.81 (d, 2H, J = 7.0 Hz, 1″-H_2), 4.06 (s, 3H, *N*-CH_3), 12.87 (s, 1H, N-H). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = 11.0 (C-CH_3), 22.2 (C(2″)-2CH_3), 27.0 (C-2″), 34.2 (*N*-CH_3), 42.3

(C-1″), 114.2 (C-7a), 131.1 (C-3a), 137.0 (C-3), 158.7 (C-6), 163.7 (C-5). – MS (EI, 70 eV): m/z (%) = 220 (42) $[M]^+$. – $C_{11}H_{16}N_4O$ (220.15): calcd. C 59.98, H 7.32, N 25.44; found C 59.64, H 7.23, N 25.18.

*6-Benzyl-1,3-dimethyl-1H-pyrazolo[3,4-b]pyrazin-5(4H)-one (**13e**)*

This compound was obtained by reductive cyclization of **11e** (0.2 g, 0.66 mmol) with 5 % Pd/C (0.04 g), m. p. = 182 – 184 °C, 89 % yield. – IR (KBr): ν = 3422 (N-H), 1655 (C=O), 1624 (C=N), 1426 cm^{-1} (C=C). – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.46 (s, 3H, C-CH_3), 4.05 (s, 3H, *N*-CH_3), 4.23(s, 2H, CH_2Ph), 7.27 ((m)$_c$, 5H, C_6H_5), 13.10 (s, 1H, N-H). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = 10.9 (C-CH_3), 34.3 (*N*-CH_3), 40.2 (C-1″), 118.2 (C-7a), 126.8 (C-3″ + C-5″), 128.4 (C-4″), 129.4 (C-2″ + C-6″), 131.1 (C-3a), 136.7 (C-3), 137.1 (C-1″), 157.9 (C-6), 163.5 (C-5). – MS (EI, 70 eV): m/z (%) = 254 (68) $[M]^+$. – $C_{14}H_{14}N_4O$ (254.13): calcd. C 66.13, H 5.55, N 22.03; found C 66.28, H 5.41, N 21.83.

*1,3-Dimethyl-5a,6,7,8-tetrahydro-1H-pyrazolo[4,3-e]pyrrolo[1,2-a]pyrazin-5(4H)-one (**15**)*

This compound was obtained by reductive cyclization of **14** (0.3 g, 1.2 mmol) with 5 % Pd/C (0.05 g), m. p. = 180 – 183 °C, 84 % yield. – IR (KBr): ν = 3445 (N-H), 1672 (C=O), 1644 (C=N), 1452 cm^{-1} (C=C). – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.06 (m, 2H, 7-H_2), 2.15 (s, 3H, C(3)-CH_3), 2.52 (m, 2H, 6-H_2), 3.62 (m, 2H, 8-H_2), 3.72 (s, 3H, *N*-CH_3), 4.03 (s, 1H, 5a-H), 12.80 (s, 1H, N-H). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = 11.0 (C-CH_3), 24.9 (C-7), 28.5 (C-6), 35.2 (*N*-CH_3), 53.2 (C-8), 61.9 (C-5a), 109.0 (C-3a), 130.9 (C-9a), 135.3 (C-3), 167.7 (C-5). – MS (EI, 70 eV): m/z (%) = 206 (6) $[M]^+$. – $C_{14}H_{14}N_4O$ (206.13): calcd. C 66.13, H 5.55, N 22.03; found C 66.02, H 5.44, N 22.12.

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