Synthesis of substituted 3-acyl-1-hydroxyindoles and azoles on their basis

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A general approach to the synthesis of new 3-acetyl-substituted pyrrolo[3,4-*f*]indole-5,7-diones, 3-[3-(dimethylamino)acryloyl]-1-methoxypyrrolo[3,4-*f*]indole-5,7-diones and similar indole-5,6-dicarbonitriles has been developed. Dimethylaminoacryloyl derivatives synthesized on their basis regioselectively reacted with hydrazine hydrochlorides and hydroxylamine with the formation of the corresponding 5-substituted azoles.

Key words: 3-acetylpyrrolo[3,4-*f*]indole-5,7-diones and indole-5,6-dicarbonitriles, 3-dimethylaminoacryloyl-substituted indole-5,6-dicarbonitriles and pyrrolo[3,4-*f*]indole-5,7-diones, pyrazoles, isoxazoles.

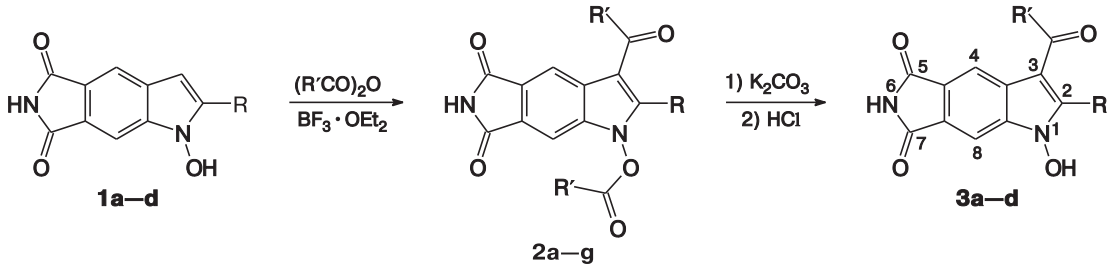
Synthetic availability of 3-acylindoles is of interest from the point of view of application of these compounds as substrates for the design of new heterocyclic systems with different structure. This is frequently accomplished by the transformation of a Me group of acetylindoles to the aminovinyl one by the reaction of the former with dimethylformamide dimethyl acetal (DMF DMA).[1—4] A combination of a carbonyl and an aminovinyl group in one molecule allows one to carry out intramolecular cyclization with the formation of substituted heterocycles: pyrazoles,[1] triazoles,[5] pyrimidines,[6,7] which exhibit different kinds of biological activity.[7—9] It is also known that the indole ring fused with a pyrazole one is a part of natural compounds.[10] However, we did not find publications on the synthesis of 3-isoxazole-substituted indoles from aminovinyl derivatives. Though similar structures can be synthesized by Fischer reaction from 1,3,5-triketones,[11] by the reaction of 6-substituted 4-pyrano-2-carboxylic acids with arylhydrazines,[12] by modification of the corresponding chalcones[13] or indole-substituted 1,3-diketones[9,14,15] with hydrazines or hydroxylamine, by Suzuki reaction.[16,17]

The purpose of the present work is the development of a general approach to the synthesis of 3-acyl-substituted 1-hydroxyindole-5,6-dicarbonitriles and 1-hydroxypyrrolo[3,4-*f*]indole-5,7-diones and the synthesis of new five-membered heterocycles (pyrazoles, isoxazoles) on their basis.

Earlier, we have developed an efficient method for the synthesis of 3-acyl-substituted 1-hydroxyindole-5,6-dicarbonitriles.[18] This method of acylation was used for the preparation of 3-acyl-substituted 1-hydroxypyrrolo[3,4-*f*]indole-5,7-diones **3a—d** from the corresponding indoles **1a—d**[19] (Scheme 1).

The reaction of pyrrolo[3,4-*f*]indole-5,7-diones **1a—d** with anhydrides (Ac_2O, $(C_2H_5CO)_2O$, $(C_3H_7CO)_2O$) was carried out at 65—85 °C for 5—20 min, the yield of compounds **2a—g** was 57—90%. Pyrrolo[3,4-*f*]indole-5,7-diones **1a—d** are acylated similarly to indole-5,6-

Scheme 1



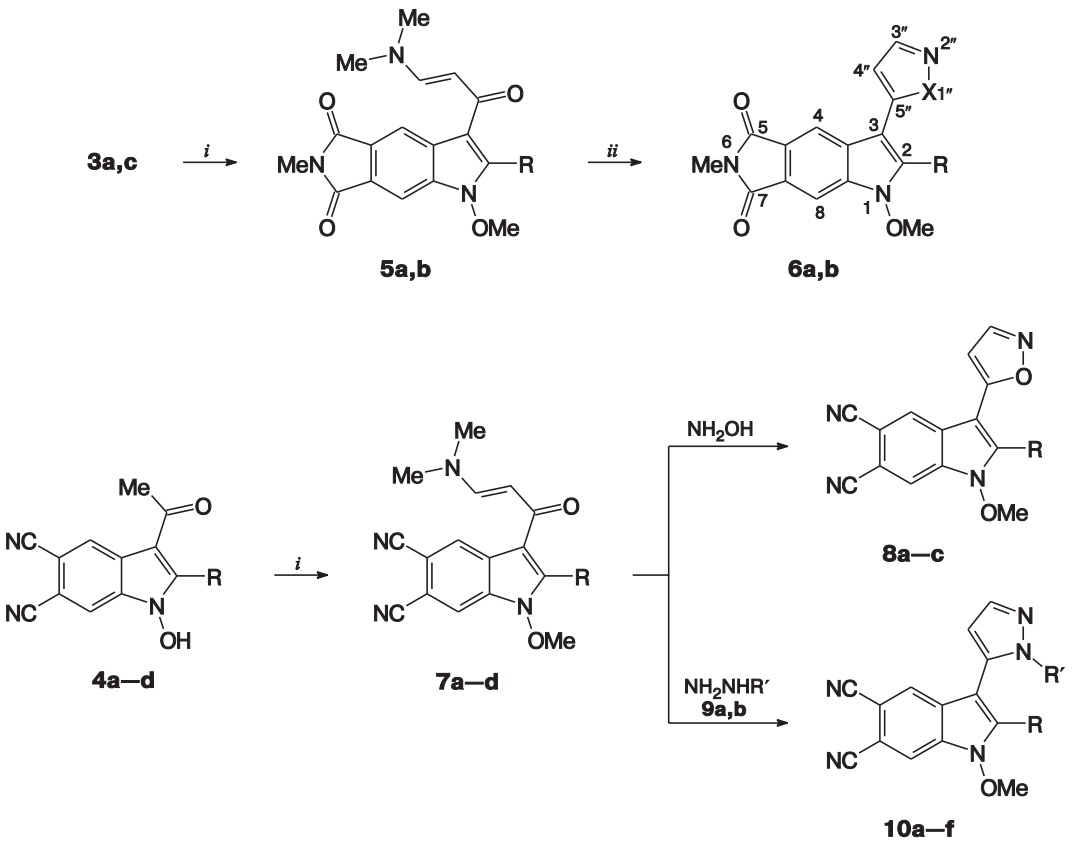
1	R	R′	2, 3
a	Ph	Me	a
b	4-MeC_6H_4	Me	b

1 c	R	R′	2, 3
	4-$MeOC_6H_4$	Me	c
	4-$MeOC_6H_4$	Et	e

1 d	R	R′	2, 3
	2-Thienyl	Me	d
	2-Thienyl	Et	f
	2-Thienyl	Pr	g

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 6, pp. 1018—1023, June, 2017.

Scheme 2



i. DMF DMA, 100—105 °C; *ii*. NH_2OH or NH_2NH_2, AcOH, 80—100 °C.

Compounds	R	Compounds	R	Starting compounds	Product	R	R′
3a, **5a**, **6a**	Ph	**6a**	O	**7a**, **9a**	**10a**	Ph	H
3c, **5b**, **6b**	4-$MeOC_6H_4$	**6b**	H	**7a**, **9b**	**10e**	Ph	Ph
4a, **7a**, **8a**	Ph			**7b**, **9a**	**10b**	4-MeC_6H_4	H
4b, **7b**, **8b**	4-MeC_6H_4			**7c**, **9a**	**10c**	4-$MeOC_6H_4$	H
4c, **7c**, **8c**	4-$MeOC_6H_4$			**7c**, **9b**	**10f**	4-$MeOC_6H_4$	Ph
4d, **7d**	2-Thienyl			**7d**, **9a**	**10d**	2-Thienyl	H

dicarbonitriles.[20] Hydrolysis of the acetate group in compounds **2a—d** required more prolonged heating in aqueous alcoholic solution of potassium carbonate as compared to indole-5,6-dicarbonitriles. The yield of 3-acetyl-substituted 1-hydroxypyrrolo[3,4-*f*]indole-5,7-diones **3a—d** reached 76%.

The synthesized 3-acetyl-1-hydroxyindoles **3a**,**c** and **4a—d**[18] were used for the preparation of new five-membered heterocycles by a two-stage procedure (Scheme 2).

In the first stage, 3-acetyl-1-hydroxyindoles **3a**,**c** and **4a—d** reacted with DMF DMA at 100—105 °C for 4—6 h with the formation of *E*-isomers of 1-methoxy-3-[3-(dimethylamino)acryloyl]pyrrolo[3,4-*f*]indole-5,7-diones and similar indole-5,6-dicarbonitriles **5a**,**b**, **7a—d** in up to 70% yield. The reaction included initial alkylation of the N—OH group in compounds **3a**,**c** and **4a—d** and also of the NH group of the imide fragment in the case of compounds **3a**,**c**, which followed by the reaction of DMF DMA with 3-acetyl group of the indoles to give *E*-products **5a**,**b** and **7a—d**. The spin-spin coupling constants (J = = 12.5—12.7 Hz) do not unambiguously indicate formation of isomer with the *trans*-arrangement of the protons at the double bond in compounds **5a**,**b** and **7a—d**, therefore, we recorded a NOESY spectrum for compound **5a**, the analysis of which confirmed the formation of only *E*-isomer.

In the second stage, the cyclization of compounds **5a**,**b** and **7a—d** with hydrazine hydrochlorides **9a**,**b** and hydroxylamine hydrochloride in glacial AcOH at 80—100 °C for 0.3—1 h regioselectively gave the target heterocycles in up to 85% yield. According to the literature data, the cyclization of arylaminovinyl compounds with hydrochlorides of hydroxylamine or hydrazines, as a rule, leads to the formation of 5-substituted isoxazoles or pyrazoles (1,5-isomers)[21—23] and is determined by the initial transamination of dimethylamine group, while the use of these reagents in the basic form leads to a predominant formation

of 3-substituted azoles (1,3-azoles), which is explained by the formation in the first step of the corresponding oximes or hydrazones. The NMR studies of 3-(isoxazol-5-yl)-1-methoxy-2-(4-methoxyphenyl)-1*H*-indole-5,6-dicarbonitrile (**8c**) confirmed the indicated position of heteroatoms in the isoxazole ring. From the HMBC spectrum of compound **8c**, it was found that the key signals indicating the mutual arrangement of heteroatoms are the low-field signals for the carbon atoms at the oxygen (C(5′′) δ 162.6) and the nitrogen atoms (C(3′′) δ 151.1). The relatively large spin-spin coupling constant values of the isoxazole ring protons (J = 1.8—1.9 Hz) are also in good agreement with the expected data for 1,5-isomer.[24] The identification of products **6b** and **10a—d** is complicated by the prototropic tautomerism of the pyrazole ring NH proton (the ^{1}H NMR spectra of these compounds exhibit broad signals for the protons of the pyrazole ring). The ^{13}C NMR spectra of compounds **6b** and **10a—d** were recorded in the presence of trifluoroacetic acid, which allowed us to detect the signals for all the carbon atoms. The NOESY spectra of compounds **10e**,**f** exhibited strong cross-peaks between the protons of the aromatic substituents of the pyrazole and indole fragments, that confirmed their 1,5-configuration.

Experimental

IR spectra were recorded on a Perkin—Elmer Fourier RX-1 with a 700—4000 cm^{-1} wavelength. The compounds were analyzed as suspensions in Nujol. NMR spectra were recorded on Bruker DRX-300 or Bruker DRX-500 spectrometers in solutions of $CDCl_3$ or DMSO-d_6 at 30 °C. Signals of residual protons of the deuterated solvents were used as reference for chemical shifts. Mass spectra were recorded on a FINNIGAN MAT.INCOS 50 GC-MS spectrometer, voltage 70 eV, ionization chamber temperature 100—220 °C (N. D. Zelinsky Institute of Organic Chemistry of the Russian Academy of Sciences). Elemental analysis was carried out on a Perkin—Elmer 2400 analyzer in the Laboratory of Microanalysis of the A. N. Nesmeyanov Institute of Organoelement Compounds of the Russian Academy of Sciences. Melting points were determined on a Büchi M-560 apparatus for determination of melting and boiling points.

Synthesis of compounds 2a—g (general procedure). Boron trifluoride diethyl etherate (0.5 g) and compound **1a—d** (2 mmol) were added to an anhydride (Ac_2O, $(C_2H_5CO)_2O$, $(C_3H_7CO)_2O$) (2 mL) and the mixture was stirred at 65—85 °C for 5—20 min and cooled. A precipitate formed was collected by filtration, thoroughly washed with water, crystallized from ethanol, and dried in air.

[3-Acetyl-5,7-dioxo-2-phenyl-6,7-dihydropyrrolo[3,4-*f*]indol-1(5*H*)-yl] acetate (2a). The yield was 0.52 g (72%), m.p. 232—233 °C. IR, ν/cm^{-1}: 3198 (NH); 1819 (OAc); 1766, 1703, 1657 (C=O); 1614, 1502 (H_{arom}); 1135 (C—O). MS (EI, 70 eV), m/z (I_{rel} (%)): 362 [M]$^+$ (52), 320 (100), 305 (14), 43 (16). ^{1}H NMR ($CDCl_3$), δ: 2.01 (m, 3 H, 3-Ac); 2.22 (s, 3 H, Ac); 7.48—7.69 (m, 5 H, Ph); 8.22 (s, 1 H, H(8)); 8.67 (s, 1 H, H(4)); 11.32 (s, 1 H, NH). Found (%): C, 66.04; H, 3.86; N, 7.71. $C_{20}H_{14}N_2O_5$. Calculated (%): C, 66.30; H, 3.89; N, 7.73.

[3-Acetyl-5,7-dioxo-2-(*p*-tolyl)-6,7-dihydropyrrolo[3,4-*f*]indol-1(5*H*)-yl] acetate (2b). The yield was 0.60 g (80%), m.p. 216—218 °C. IR, ν/cm^{-1}: 3182 (NH); 1805 (OAc); 1705, 1660 (C=O); 1616, 1593 (H_{arom}); 1155 (C—O). MS (EI, 70 eV), m/z (I_{rel} (%)): 376 [M]$^+$ (41), 334 (100), 319 (82), 303 (18), 43 (11). ^{1}H NMR ($CDCl_3$), δ: 2.01 (s, 3 H, 3-Ac); 2.24 (s, 3 H, Ac); 2.43 (s, 3 H, Me); 7.42 (d, 2 H, H(3′), H(5′), J = 8.1 Hz); 7.45 (d, 2 H, H(2′), H(6′), J = 8.1 Hz); 8.19 (s, 1 H, H(8)); 8.65 (s, 1 H, H(4)); 11.30 (s, 1 H, NH). ^{13}C NMR (DMSO-d_6), δ: 17.5, 21.0, 29.8, 105.5, 112.9, 117.2, 124.2, 125.7, 127.4, 128.5, 129.4 (2 C); 130.0 (2 C); 134.9, 140.5, 145.3, 168.2, 168.8, 169.2, 193.4. Found (%): C, 66.76; H, 4.25; N, 7.41. $C_{21}H_{16}N_2O_5$. Calculated (%): C, 67.02; H, 4.28; N, 7.44.

[3-Acetyl-2-(4-methoxyphenyl)-5,7-dioxo-6,7-dihydropyrrolo[3,4-*f*]indol-1(5*H*)-yl] acetate (2c). The yield was 0.71 g (90%), m.p. 276—277 °C. IR, ν/cm^{-1}: 3186 (NH); 1804 (OAc); 1703, 1658 (C=O); 1611 (H_{arom}); 1153 (C—O). MS (EI, 70 eV), m/z (I_{rel} (%)): 392 [M]$^+$ (59), 350 (100), 335 (55), 333 (40), 319 (21), 318 (21), 43 (13). ^{1}H NMR ($CDCl_3$), δ: 2.03 (s, 3 H, 3-Ac); 2.25 (s, 3 H, Ac); 3.87 (s, 3 H, OMe); 7.16 (d, 2 H, H(3′), H(5′), J = 8.8 Hz); 7.50 (d, 2 H, H(2′), H(6′), J = 8.8 Hz); 8.18 (s, 1 H, H(8)); 8.65 (s, 1 H, H(4)); 11.30 (s, 1 H, NH). ^{13}C NMR (DMSO-d_6), δ: 17.7, 30.0, 55.4, 105.7, 113.1, 114.5 (2 C); 117.3, 119.1, 125.9, 127.6, 128.7, 132.0 (2 C); 135.1, 145.6, 161.1, 168.3, 168.9, 169.5, 193.6. Found (%): C, 64.01; H, 4.08; N, 7.12. $C_{21}H_{16}N_2O_6$. Calculated (%): C, 64.28; H, 4.11; N, 7.14.

[3-Acetyl-5,7-dioxo-2-(thiophen-2-yl)-6,7-dihydropyrrolo[3,4-*f*]indol-1(5*H*)-yl] acetate (2d). The yield was 0.61 g (83%), m.p. 254—256 °C. IR, ν/cm^{-1}: 3227 (NH); 1818 (OAc); 1757, 1661 (C=O); 1616 (H_{arom}); 1150 (C—O). MS (EI, 70 eV), m/z (I_{rel} (%)): 368 [M]$^+$ (43), 326 (100), 311 (64), 309 (37), 295 (43), 223 (19), 43 (98). ^{1}H NMR ($CDCl_3$), δ: 2.16 (s, 3 H, 3-Ac); 2.35 (s, 3 H, Ac); 7.32 (dd, 1 H, H(4′), J = 5.0 Hz, J = 3.7 Hz); 7.55 (dd, 1 H, H(3′), J = 3.7 Hz, J = 1.1 Hz); 8.04 (dd, 1 H, H(5′), J = 5.0 Hz, J = 1.1 Hz); 8.21 (s, 1 H, H(8)); 8.59 (s, 1 H, H(4)); 11.34 (s, 1 H NH). ^{13}C NMR (DMSO-d_6), δ: 17.8, 29.5, 105.7, 114.5, 117.3, 125.4, 125.5, 127.7, 128.1, 129.0, 132.0, 133.7, 135.2, 137.7. 168.4, 168.8, 169.2, 193.6. Found (%): C, 58.41; H, 3.25; N, 7.57. $C_{18}H_{12}N_2O_5S$. Calculated (%): C, 58.69; H, 3.28; N, 7.60.

[2-(4-Methoxyphenyl)-5,7-dioxo-3-propionyl-6,7-dihydropyrrolo[3,4-*f*]indol-1(5*H*)-yl] propionate (2e). The yield was 0.64 g (76%), m.p. 194—196 °C. IR, ν/cm^{-1}: 3197 (NH); 1814 ($OCOC_2H_5$); 1762, 1662 (C=O); 1610 (H_{arom}); 1136 (C—O). MS (EI, 70 eV), m/z (I_{rel} (%)): 420 [M]$^+$ (60), 364 (63), 347 (24), 335 (100), 318 (19), 57 (19). ^{1}H NMR ($CDCl_3$), δ: 0.91 (t, 3 H, CH_3, J = 7.4 Hz); 0.92 (t, 3 H, CH_3, J = 7.3 Hz); 2.36 (q, 2 H, —CH_2—, J = 7.3 Hz); 2.70 (q, 2 H, —CH_2—, J = 7.4 Hz); 3.86 (s, 3 H, OMe); 7.16 (d, 2 H, H(3′), H(5′), J = 8.6 Hz); 7.48 (d, 2 H, H(2′), H(6′), J = 8.6 Hz); 8.18 (s, 1 H, H(8)); 8.67 (s, 1 H, H(4)); 11.30 (s, 1 H, NH). ^{13}C NMR (DMSO-d_6), δ: 8.2, 8.4, 24.3, 34.3, 55.4, 105.5, 112.5, 114.3 (2 C); 117.2, 119.2, 125.9, 127.3, 128.4, 131.7 (2 C); 135.0, 144.8, 160.7, 168.9, 169.3, 171.7, 196.7. Found (%): C, 65.43; H, 4.75; N, 6.63. $C_{23}H_{20}N_2O_6$. Calculated (%): C, 65.71; H, 4.79; N, 6.66.

[5,7-Dioxo-3-propionyl-2-(thiophen-2-yl)-6,7-dihydropyrrolo[3,4-*f*]indol-1(5*H*)-yl] propionate (2f). The yield was 0.54 g (68%), m.p. 178—180 °C. IR, ν/cm^{-1}: 3208 (NH); 1816 ($OCOC_2H_5$); 1760, 1715, 1646 (C=O); 1612 (H_{arom}); 1145 (C—O). MS (EI, 70 eV), m/z (I_{rel} (%)): 396 [M]$^+$ (80), 340 (100), 323 (18), 311 (96), 294 (32), 223 (29), 57 (40). ^{1}H NMR ($CDCl_3$), δ: 0.90 (t, 3 H, CH_3, J = 7.4 Hz); 1.01 (t, 3 H, CH_3, J = 7.3 Hz); 2.53—2.62 (m, 4 H, 2 —CH_2—); 7.32 (dd, 1 H, H(4′), J = 5.0 Hz, J = 3.6 Hz); 7.52 (dd, 1 H, H(3′), J = 3.6 Hz, J = 1.1 Hz); 8.03 (dd, 1 H, H(5′), J = 5.0 Hz, J = 1.1 Hz); 8.23 (s, 1 H, H(8)); 8.62 (s, 1 H, H(4)); 11.34 (s, 1 H, NH).

^{13}C NMR (DMSO-d_6), δ: 8.2, 8.4, 24.4, 34.1, 105.7, 114.3, 117.3, 125.4, 125.8, 127.4, 128.0, 128.9, 131.7, 133.2, 135.2, 136.9, 168.8, 169.2, 171.8, 196.7. Found (%): C, 60.32; H, 4.04; N, 7.03. $C_{20}H_{16}N_2O_5S$. Calculated (%): C, 60.60; H, 4.07; N, 7.07.

[3-Butyryl-5,7-dioxo-2-(thiophen-2-yl)-6,7-dihydropyrrolo-[3,4-*f*]indol-1(5*H*)-yl] butyrate (2g). The yield was 0.48 g (57%), m.p. 162—164 °C. IR, ν/cm^{-1}: 3196 (NH); 1809 ($OCOC_3H_7$); 1756, 1710, 1641 (C=O); 1602 (H_{arom}); 1147 (C—O). ^{1}H NMR ($CDCl_3$), δ: 0.73 (t, 3 H, CH_3, *J* = 7.3 Hz); 0.77 (t, 3 H, CH_3, *J* = 7.3 Hz); 1.43—1.51 (m, 4 H, 2 —CH_2—); 2.52—2.72 (m, 4 H, 2 —CH_2—); 7.29 (dd, 1 H, H(3′), *J* = 3.8 Hz, *J* = 1.0 Hz); 7.57 (dd, 1 H, H(4′), *J* = 5.0 Hz, *J* = 3.8 Hz); 7.67 (s, 1 H, H(8)); 7.96 (dd, 1 H, H(5′), *J* = 5.0 Hz, *J* = 1.0 Hz); 8.47 (s, 1 H, H(4)); 11.16 (s, 1 H, NH). ^{13}C NMR (DMSO-d_6), δ: 12.9, 13.4, 17.2, 17.3, 32.2, 35.5, 107.9, 108.8, 116.2, 116.5, 123.7, 128.0, 128.6, 131.4, 132.3, 133.0, 133.7, 138.7, 170.4 (2 C); 174.3, 195.9. Found (%): C, 61.97; H, 4.71; N, 6.57. $C_{22}H_{20}N_2O_5S$. Calculated (%): C, 62.25; H, 4.75; N, 6.60.

Synthesis of compounds 3a—d (general procedure). Potassium carbonate (4 mmol) was added to a solution of compound **2a—d** (2 mmol) in ethanol (5 mL) and the mixture was stirred at 60—70 °C for 20—30 min until dissolution of the precipitate. Then the reaction mixture was cooled and diluted with 5% aqueous solution of hydrochloric acid (50 mL). A precipitate formed was collected by filtration, thoroughly washed with water, and dried in air.

3-Acetyl-1-hydroxy-2-phenylpyrrolo[3,4-*f*]indole-5,7-(1*H*,6*H*)-dione (3a). The yield was 0.45 g (70%), m.p. 232—233 °C. IR, ν/cm^{-1}: 3298 (OH); 3210 (NH); 1745, 1701, 1658 (C=O); 1608, 1590 (H_{arom}). MS, *m*/*z* (*I*$_{rel}$ (%)): 320 [M]$^+$ (100), 305 (62), 304 (49), 289 (76), 234 (31), 218 (38), 188 (25), 163 (18), 43 (90). ^{1}H NMR (DMSO-d_6), δ: 1.99 (s, 3 H, Ac); 7.54—7.68 (m, 5 H, Ph); 7.81 (s, 1 H, H(8)); 8.35 (s, 1 H, H(4)); 11.23 (br.s, 1 H, NH); 12.06 (s, 1 H, OH). Found (%): C, 67.28; H, 3.74; N, 8.72. $C_{18}H_{12}N_2O_4$. Calculated (%): C, 67.50; H, 3.78; N, 8.75.

3-Acetyl-1-hydroxy-2-(*p*-tolyl)pyrrolo[3,4-*f*]indole-5,7-(1*H*,6*H*)-dione (3b). The yield was 0.51 g (76%), m.p. 240—241 °C. IR, ν/cm^{-1}: 3375 (OH); 3182 (NH); 1769, 1706, 1660 (C=O); 1616, 1594 (H_{arom}). ^{1}H NMR (DMSO-d_6), δ: 1.98 (s, 3 H, Ac); 2.43 (s, 3 H, Me); 7.42 (d, 2 H, H(3′), H(5′), *J* = 8.1 Hz); 7.54 (d, 2 H, H(2′), H(6′), *J* = 8.1 Hz); 7.83 (s, 1 H, H(8)); 8.64 (s, 1 H, H(4)); 11.23 (s, 1 H, NH); 12.16 (s, 1 H, OH). Found (%): C, 68.03; H, 4.19; N, 8.34. $C_{19}H_{14}N_2O_4$. Calculated (%): C, 68.26; H, 4.22; N, 8.38.

3-Acetyl-1-hydroxy-2-(4-methoxyphenyl)pyrrolo[3,4-*f*]indole-5,7(1*H*,6*H*)-dione (3c). The yield was 0.50 g (72%), m.p. 256—258 °C. IR, ν/cm^{-1}: 3403 (OH); 3182 (NH); 1713, 1644 (C=O); 1607, 1535 (H_{arom}); 1026 (C—O). MS, *m*/*z* (*I*$_{rel}$ (%)): 350 [M]$^+$ (100), 335 (54), 333 (39), 318 (41), 303 (12), 290 (15), 276 (18), 247 (12). ^{1}H NMR (DMSO-d_6), δ: 2.02 (s, 3 H, Ac); 3.89 (s, 3 H, OMe); 7.17 (d, 2 H, H(3′), H(5′), *J* = 8.5 Hz); 7.61 (d, 2 H, H(2′), H(6′), *J* = 8.5 Hz); 7.82 (s, 1 H, H(8)); 8.63 (s, 1 H, H(4)); 11.24 (s, 1 H, NH); 12.18 (br.s, 1 H, OH). ^{13}C NMR (DMSO-d_6), δ: 29.8 (Me), 55.4 (OMe), 104.6, 111.9, 114.0 (2 C); 117.2, 120.4, 125.6, 126.6, 127.4, 132.4 (2 C); 135.4, 145.8, 160.6, 169.1, 169.6, 193.3 (C=O). Found (%): C, 64.87; H, 3.99; N, 7.96. $C_{19}H_{14}N_2O_5$. Calculated (%): C, 65.14; H, 4.03; N, 8.00.

3-Acetyl-1-hydroxy-2-(thiophen-2-yl)pyrrolo[3,4-*f*]indole-5,7(1*H*,6*H*)-dione (3d). The yield was 0.44 g (68%), m.p. 246—247 °C. IR, ν/cm^{-1}: 3346 (OH); 3210 (NH); 1756, 1699, 1665 (C=O); 1620, 1590 (H_{arom}). ^{1}H NMR (DMSO-d_6), δ: 2.16 (s, 3 H, Ac); 7.32 (dd, 1 H, H(4′), *J* = 5.0 Hz, *J* = 3.7 Hz); 7.55 (dd, 1 H, H(3′), *J* = 3.7 Hz, *J* = 1.1 Hz); 8.04 (dd, 1 H, H(5′), *J* = 5.0 Hz, *J* = 1.1 Hz); 8.21 (s, 1 H, H(8)); 8.59 (s, 1 H, H(4)); 11.34 (s, 1 H, NH); 12.20 (br.s, 1 H, OH). Found (%): C, 58.65; H, 3.05; N, 8.51. $C_{16}H_{10}N_2O_4S$. Calculated (%): C, 58.89; H, 3.09; N, 8.58.

Synthesis of compounds 5a,b and 7a—d (general procedure). Compounds **3a,c** and **4a—d** were heated in DMF DMA (2 mL) at 100—105 °C for 4—6 h (TLC monitoring). Then the reaction mixture was cooled and diluted with ethanol (5 mL) with stirring, a precipitate formed was collected by filtration and recrystallized from ethanol.

(*E*)-3-[3-(Dimethylamino)acryloyl]-1-methoxy-6-methyl-2-phenylpyrrolo[3,4-*f*]indole-5,7(1*H*,6*H*)-dione (5a). The yield was 0.21 g (51%), m.p. 197—199 °C. IR, ν/cm^{-1}: 1759, 1699, 1677 (C=O); 1630 (C=C); 1612 (H_{arom}); 1090 (OCH_3); 972 (*trans*-C=C). MS (EI, 70 eV), *m*/*z* (*I*$_{rel}$ (%)): 403 [M]$^+$ (8), 372 (37), 356 (17), 289 (47), 217 (19), 204 (16), 190 (27), 98 (82), 84 (100), 77 (15). ^{1}H NMR (DMSO-d_6), δ: 2.29 (br.s, 3 H, NMe); 2.99 (br.s, 3 H, NMe); 3.08 (s, 3 H, 6-NMe); 3.87 (s, 3 H, OMe); 4.71 (d, 1 H, H(1′), *J* = 12.6 Hz); 7.48 (d, 1 H, H(2′), *J* = 12.6 Hz); 7.55—7.62 (m, 3 H, Ph); 7.62—7.69 (m, 2 H, Ph); 8.03 (s, 1 H, H(8)); 8.65 (s, 1 H, H(4)). Found (%): C, 68.23; H, 5.22; N, 10.39. $C_{23}H_{21}N_3O_4$. Calculated (%): C, 68.47; H, 5.25; N, 10.42.

(*E*)-3-[3-(Dimethylamino)acryloyl]-1-methoxy-2-(4-methoxyphenyl)-6-methylpyrrolo[3,4-*f*]indole-5,7(1*H*,6*H*)-dione (5b). The yield was 0.26 g (59%), m.p. 203—205 °C. IR, ν/cm^{-1}: 1738, 1697, 1661 (C=O); 1626 (C=C); 1607 (H_{arom}); 1253, 1090 (OCH_3); 976 (*trans*-C=C). MS (EI, 70 eV), *m*/*z* (*I*$_{rel}$ (%)): 433 [M]$^+$ (39), 402 [M – OMe]$^+$ (80), 386 (55), 374 (23), 359 (18), 333 (20), 319 (100). ^{1}H NMR (DMSO-d_6), δ: 2.36 (br.s, 3 H, NMe); 2.99 (br.s, 3 H, NMe); 3.07 (s, 3 H, 6-NMe); 3.86 (s, 3 H, OMe); 3.87 (s, 3 H, OMe); 4.79 (d, 1 H, H(1′), *J* = 12.5 Hz); 7.15 (d, 2 H, H(3′′), H(5′′), *J* = 8.6 Hz); 7.49 (d, 1 H, H(2′), *J* = 12.5 Hz); 7.58 (d, 2 H, H(2′′), H(6′′), *J* = 8.6 Hz); 8.00 (s, 1 H, H(8)); 8.62 (s, 1 H, H(4)). Found (%): C, 66.27; H, 5.33; N, 9.67. $C_{24}H_{23}N_3O_5$. Calculated (%): C, 66.50; H, 5.35; N, 9.69.

(*E*)-3-[3-(Dimethylamino)acryloyl]-1-methoxy-2-phenyl-1*H*-indole-5,6-dicarbonitrile (7a). The yield was 0.24 g (64%), m.p. 207—209 °C. IR, ν/cm^{-1}: 2224 (CN); 1715 (C=O); 1635 (C=C); 1606, 1546 (H_{arom}); 1090 (OCH_3); 975 (*trans*-C=C). MS (EI, 70 eV), *m*/*z* (*I*$_{rel}$ (%)): 370 [M]$^+$ (29), 339 (69), 256 (49), 98 (36), 42 (100). ^{1}H NMR (DMSO-d_6), δ: 2.30 (br.s, 3 H, NMe); 2.99 (br.s, 3 H, NMe); 3.86 (s, 3 H, OMe); 4.70 (d, 1 H, H(1′), *J* = 12.6 Hz); 7.49 (d, 1 H, H(2′), *J* = 12.6 Hz); 7.57—7.70 (m, 5 H, Ph); 8.55 (s, 1 H, H(7)); 8.82 (s, 1 H, H(4)). Found (%): C, 71.08; H, 4.87; N, 15.10. $C_{22}H_{18}N_4O_2$. Calculated (%): C, 71.34; H, 4.90; N, 15.13.

(*E*)-3-[3-(Dimethylamino)acryloyl]-1-methoxy-2-(*p*-tolyl)-1*H*-indole-5,6-dicarbonitrile (7b). The yield was 0.27 g (70%), m.p. 210—211 °C. IR, ν/cm^{-1}: 2223 (CN); 1710 (C=O); 1636 (C=C); 1600 (H_{arom}); 1253, 1152 (OMe); 974 (*trans*-C=C). MS (EI, 70 eV), *m*/*z* (*I*$_{rel}$ (%)): 384 [M]$^+$ (6), 368 (35), 351 (100), 298 (52), 270 (32), 254 (41), 98 (22). ^{1}H NMR (DMSO-d_6), δ: 2.26 (br.s, 3 H, NMe); 2.42 (s, 3 H, Me); 2.98 (br.s, 3 H, NMe); 3.65 (s, 3 H, OMe); 4.61 (d, 1 H, H(1′), *J* = 13.0 Hz); 7.33—7.49 (m, 4 H, Ar); 7.52 (d, 1 H, H(2′), *J* = 13.0 Hz); 8.53 (s, 1 H, H(7)); 8.80 (s, 1 H, H(4)). Found (%): C, 71.67; H, 5.20; N, 14.55. $C_{23}H_{20}N_4O_2$. Calculated (%): C, 71.86; H, 5.24; N, 14.57.

(*E*)-3-[3-(Dimethylamino)acryloyl]-1-methoxy-2-(4-methoxyphenyl)-1*H*-indole-5,6-dicarbonitrile (7c). The yield was 0.27 g (67%), m.p. 222—224 °C. IR, ν/cm^{-1}: 2227 (CN); 1708 (C=O); 1634 (C=C); 1606 (H_{arom}); 1255, 1170 (OMe); 978 (*trans*-C=C). MS (EI, 70 eV), *m*/*z* (*I*$_{rel}$ (%)): 400 [M]$^+$ (6), 369 [M – OMe]$^+$ (32), 286 (100), 254 (27), 228 (20), 97 (27), 84 (31). ^{1}H NMR (DMSO-d_6), δ: 2.37 (br.s, 3 H, NMe), 3.00 (br.s, 3 H, NMe); 3.86 (s, 3 H, OMe); 3.85 (s, 3 H, OMe); 4.78

(d, 1 H, H(1′), J = 12.5 Hz); 7.16 (d, 2 H, H(3′′), H(5′′), J = 8.6 Hz); 7.50 (d, 1 H, H(2′), J = 12.5 Hz); 7.58 (d, 2 H, H(2′′), H(6′′), J = 8.6 Hz); 8.51 (s, 1 H, H(7)); 8.76 (s, 1 H, H(4)). ^{13}C NMR (DMSO-d_6), δ: 35.8, 47.2, 55.3, 66.4, 95.5, 105.7, 106.4, 113.7, 114.0 (2 C); 115.7, 116.7, 117.0, 119.6, 124.5, 128.3, 131.0, 131.8 (2 C); 142.2, 152.3, 160.6, 181.9. Found (%): C, 68.73; H, 5.00; N, 13.97. $C_{23}H_{20}N_4O_3$. Calculated (%): C, 68.99; H, 5.03; N, 13.99.

(*E*)-3-[3-(Dimethylamino)acryloyl]-1-methoxy-2-(2-thiophen-2-yl)-1*H*-indole-5,6-dicarbonitrile (7d). The yield was 0.18 g (48%), m.p. 204—206 °C. IR, ν/cm^{-1}: 2222 (CN); 1714 (C=O); 1636 (C=C); 1601 (H_{arom}); 1176 (OMe); 972 (*trans*-C=C). ^{1}H NMR (DMSO-d_6), δ: 2.54 (br.s, 3 H, NMe); 3.03 (br.s, 3 H, NMe); 3.99 (s, 3 H, OMe); 5.04 (d, 1 H, H(1′), J = 12.2 Hz); 7.32 (dd, 1 H, H(4′′), J = 4.9 Hz, J = 3.8 Hz); 7.55 (d, 1 H, H(2′), J = 12.2 Hz); 7.68 (dd, 1 H, H(3′′), J = 3.8 Hz, J = 1.0 Hz); 7.98 (dd, 1 H, H(5′′), J = 4.9 Hz, J = 1.0 Hz); 8.54 (s, 1 H, H(7)); 8.59 (s, 1 H, H(4)). Found (%): C, 63.57; H, 4.25; N, 14.84. $C_{20}H_{16}N_4O_2S$. Calculated (%): C, 63.81; H, 4.28; N, 14.88.

Synthesis of compounds 6a,b, 8a—c, and 10a—f (general procedure). Compound **5** or **7** (1 mmol) and hydroxylamine hydrochloride or hydrazine hydrochloride **9a**,**b** (1.5 mmol) were mixed in glacial AcOH (2 mL), the resulting reaction mixture was heated at 80—100 °C for 0.3—1 h. Then it was cooled, diluted with cold water (5 mL), a precipitate formed was collected by filtration and recrystallized from ethanol.

3-(Isoxazol-5-yl)-1-methoxy-6-methyl-2-phenylpyrrolo[3,4-*f*]indole-5,7(1*H*,6*H*)-dione (6a). The yield was 0.29 g (78%), m.p. 187—189 °C. IR, ν/cm^{-1}: 2226 (CN); 1610, 1597 (H_{arom}); 1256, 1229 (OMe); 1027 (C—O—N). MS (EI, 70 eV), m/z (I_{rel} (%)): 373 [M]$^+$ (100), 330 (11), 314 (23), 287 (60), 230 (34), 202 (37). ^{1}H NMR (DMSO-d_6), δ: 3.12 (s, 3 H, 6-Me); 3.94 (s, 3 H, OMe); 6.21 (d, 1 H, H(4′′), J = 1.9 Hz); 7.60—7.75 (m, 5 H, Ph); 8.19 (s, 1 H, H(4)); 8.39 (s, 1 H, H(8)); 8.58 (d, 1 H, H(3′′), J = 1.9 Hz). ^{13}C NMR (DMSO-d_6), δ: 23.9, 67.0, 99.8, 100.8, 105.5, 116.0, 123.6, 125.5, 127.0, 127.1, 129.0 (2 C); 130.2 (2 C); 130.4, 133.4, 139.1, 151.0, 163.4, 167.8, 168.0. Found (%): C, 67.28; H, 4.01; N, 11.21. $C_{21}H_{15}N_3O_4$. Calculated (%): C, 67.56; H, 4.05; N, 11.25.

1-Methoxy-2-(4-methoxyphenyl)-6-methyl-3-(1*H*-pyrazol-5-yl)pyrrolo[3,4-*f*]indole-5,7(1*H*,6*H*)-dione (6b). The yield was 0.33 g (83%), m.p. 190—192 °C. IR, ν/cm^{-1}: 3306 (NH); 1759, 1697 (C=O); 1610 (H_{arom}); 1252, 1178 (OMe); 1027 (C—O—N). MS (EI, 70 eV), m/z (I_{rel} (%)): 402 [M]$^+$ (82), 387 [M – Me]$^+$ (26), 371 (100), 356 (11), 314 (19), 286 (22), 216 (13). ^{1}H NMR (DMSO-d_6), δ: 3.07 (s, 3 H, Me); 3.85 (s, 3 H, OMe); 3.86 (s, 3 H, OMe); 5.80 (d, 1 H, H(4′′), J = 2.0 Hz); 7.12 (d, 2 H, H(3′), H(5′), J = 8.6 Hz); 7.55 (d, 2 H, H(2′), H(6′), J = 8.6 Hz); 7.66 (d, 1 H, H(3′′), J = 2.0 Hz); 7.97 (s, 1 H, H(4)); 8.57 (s, 1 H, H(8)); (N—H in exchange). Found (%): C, 65.38; H, 4.47; N, 13.86. $C_{22}H_{18}N_4O_4$. Calculated (%): C, 65.66; H, 4.51; N, 13.92.

3-(Isoxazol-5-yl)-1-methoxy-2-phenyl-1*H*-indole-5,6-dicarbonitrile (8a). The yield was 0.28 g (82%), m.p. 235—236 °C. IR, ν/cm^{-1}: 2222 (CN); 1613, 1593 (H_{arom}); 1257, 1237 (OMe); 1027 (C—O—N). MS (EI, 70 eV), m/z (I_{rel} (%)): 340 [M]$^+$ (69), 254 (100), 127 (11), 77 (19). ^{1}H NMR (DMSO-d_6), δ: 3.94 (s, 3 H, OMe); 6.46 (d, 1 H, H(4′′), J = 1.8 Hz); 7.57—7.73 (m, 5 H, Ph); 8.62 (d, 1 H, H(3′′), J = 1.8 Hz); 8.70 (s, 1 H, H(4)); 8.73 (s, 1 H, H(7)). Found (%): C, 70.31; H, 3.52; N, 16.40. $C_{20}H_{12}N_4O_2$. Calculated (%): C, 70.58; H, 3.55; N, 16.46.

3-(Isoxazol-5-yl)-1-methoxy-2-(*p*-tolyl)-1*H*-indole-5,6-dicarbonitrile (8b). The yield was 0.27 g (76%), m.p. 195—196 °C. IR, ν/cm^{-1}: 2228 (CN); 1611 (H_{arom}); 1259, 1178 (OMe); 1022 (C—O—N). MS (EI, 70 eV), m/z (I_{rel} (%)): 354 [M]$^+$ (100), 314 (37), 298 (36), 268 (56), 254 (23), 43 (78). ^{1}H NMR (DMSO-d_6), δ: 2.44 (s, 3 H, Me); 3.90 (s, 3 H, OMe); 6.42 (d, 1 H, H(4′′), J = 1.8 Hz); 7.43 (d, 2 H, H(3′), H(5′) J = 8.0 Hz); 7.54 (d, 2 H, H(2′), H(6′), J = 8.0 Hz); 8.58 (d, 1 H, H(3′′), J = 1.8 Hz); 8.65 (s, 1 H, H(4)); 8.66 (s, 1 H, H(7)). Found (%): C, 70.87; H, 3.95; N, 15.76. $C_{21}H_{14}N_4O_2$. Calculated (%): C, 71.18; H, 3.98; N, 15.81.

3-(Isoxazol-5-yl)-1-methoxy-2-(4-methoxyphenyl)-1*H*-indole-5,6-dicarbonitrile (8c). The yield was 0.26 g (74%), m.p. 205—207 °C. IR, ν/cm^{-1}: 2228 (CN); 1610 (H_{arom}); 1259, 1177 (OMe); 1021 (C—O—N). MS (EI, 70 eV), m/z (I_{rel} (%)): 370 [M]$^+$ (100), 345 (13), 314 (19), 311 (35), 284 (56), 241 (15). ^{1}H NMR (DMSO-d_6), δ: 3.89 (s, 3 H, OMe); 3.90 (s, 3 H, OMe); 6.47 (d, 1 H, H(4′′), J = 1.8 Hz); 7.19 (d, 2 H, H(3′), H(5′), J = 8.6 Hz); 7.61 (d, 2 H, H(2′), H(6′), J = 8.6 Hz); 8.62 (d, 1 H, H(3′′), J = 1.8 Hz); 8.66 (s, 1 H, H(4)); 8.68 (s, 1 H, H(7)). ^{13}C NMR (DMSO-d_6), δ: 55.4, 66.9, 99.8, 100.5, 106.4, 107.3, 114.4 (2 C); 116.5, 116.8, 117.0, 118.2, 122.1, 127.1, 131.3, 131.7 (2 C); 140.8, 151.1, 160.9, 162.6. Found (%): C, 67.88; H, 3.78; N, 15.06. $C_{21}H_{14}N_4O_3$. Calculated (%): C, 68.10; H, 3.81; N, 15.13.

1-Methoxy-2-phenyl-3-(1*H*-pyrazol-5-yl)-1*H*-indole-5,6-dicarbonitrile (10a). The yield was 0.24 g (72%), m.p. 202—203 °C. IR, ν/cm^{-1}: 3314 (NH); 2224 (CN); 1607 (H_{arom}); 1234, 1174 (OMe); 1030 (C—O—N). MS (EI, 70 eV), m/z (I_{rel} (%)): 339 [M]$^+$ (59), 308 [M – OMe]$^+$ (100), 281 (35), 254 (41), 154 (19), 77 (20). ^{1}H NMR (DMSO-d_6), δ: 3.85 (s, 3 H, OMe); 5.74 (br.s, 1 H, H(4′′)); 7.51—7.65 (m, 5 H, Ph); 7.67 (br.s, 1 H, H(3′′)); 8.54 (s, 1 H, H(4)); 8.82 (s, 1 H, H(7)); 12.98 (br.s, 1 H, NH). Found (%): C, 70.51; H, 3.84; N, 20.60. $C_{20}H_{13}N_5O$. Calculated (%): C, 70.79; H, 3.86; N, 20.64.

1-Methoxy-3-(1*H*-pyrazol-5-yl)-2-(*p*-tolyl)-1*H*-indole-5,6-dicarbonitrile (10b). The yield was 0.30 g (85%), m.p. 288—289 °C. IR, ν/cm^{-1}: 3344 (NH); 2216 (CN); 1605 (H_{arom}); 1235, 1174 (OMe); 1048 (C—O—N). MS (EI, 70 eV), m/z (I_{rel} (%)): 353 [M]$^+$ (58), 322 [M – OMe]$^+$ (100), 286 (35), 91 (17). ^{1}H NMR (DMSO-d_6), δ: 2.43 (s, 3 H, Me); 3.67 (s, 3 H, OMe); 5.54 (br.s, 1 H, H(4′′)); 7.39 (s, 4 H, Ar); 7.59 (br.s, 1 H, H(3′′)); 8.52 (s, 1 H, H(4)); 8.84 (s, 1 H, H(7)); 12.87 (br.s, 1 H, NH). Found (%): C, 71.09; H, 4.25; N, 19.79. $C_{21}H_{15}N_5O$. Calculated (%): C, 71.38; H, 4.28; N, 19.82.

1-Methoxy-2-(4-methoxyphenyl)-3-(1*H*-pyrazol-5-yl)-1*H*-indole-5,6-dicarbonitrile (10c). The yield was 0.31 g (84%), m.p. 200—201 °C. IR, ν/cm^{-1}: 3356 (NH); 2231 (CN); 1609 (H_{arom}); 1252, 1173 (OMe); 1019 (C—O—N). MS (EI, 70 eV), m/z (I_{rel} (%)): 369 [M]$^+$ (62), 338 [M – OMe]$^+$ (100), 323 (20), 295 (33), 268 (26), 241 (17), 169 (12). ^{1}H NMR (DMSO-d_6), δ: 3.85 (s, 3 H, OMe); 3.86 (s, 3 H, OMe); 5.82 (br.s, 1 H, H(4′′)); 7.13 (d, 2 H, H(3′), H(5′), J = 8.8 Hz); 7.55 (d, 2 H, H(2′), H(6′), J = 8.8 Hz); 7.67 (br.s, 1 H, H(3′′)); 8.48 (s, 1 H, H(4)); 8.74 (s, 1 H, H(7)); 12.96 (br.s, 1 H, NH). ^{13}C NMR (DMSO-d_6), δ: 55.3, 66.6, 102.9, 104.9, 106.1, 114.3 (2 C); 115.8, 117.3, 117.5, 119.6, 123.3, 128.6, 129.1, 131.2, 131.8 (2 C); 138.8, 138.9, 143.8, 160.4. Found (%): C, 67.99; H, 4.07; N, 18.92. $C_{21}H_{15}N_5O_2$. Calculated (%): C, 68.28; H, 4.09; N, 18.96.

1-Methoxy-3-(1*H*-pyrazol-5-yl)-2-(thiophen-2-yl)-1*H*-indole-5,6-dicarbonitrile (10d). The yield was 0.24 g (69%), m.p. 240—242 °C. IR, ν/cm^{-1}: 3306 (NH), 2220 (CN), 1606, 1594 (H_{arom}), 1276, 1173 (OMe). MS (EI, 70 eV), m/z (I_{rel} (%)): 345 [M]$^+$ (78), 314 (100), 287 (66), 281 (75), 260 (20), 157 (17), 130 (12). ^{1}H NMR (DMSO-d_6), δ: 4.03 (s, 3 H, OMe); 6.14 (br.s, 1 H, H(4′′)); 7.27 (dd, 1 H, H(4′), J = 4.9 Hz, J = 3.7 Hz); 7.63 (br.s, 1 H, H(3′′)); 7.79 (s, 1 H, H(4)); 7.92 (dd, 1 H, H(5′), J = 4.9 Hz, J = 1.0 Hz); 8.54 (s, 2 H, H(3′),

H(7)); 13.10 (br.s, 1 H, NH). ^{13}C NMR (DMSO-d_6), δ: 66.9, 104.4, 105.4, 106.7, 115.9, 116.3, 117.2, 117.3, 123.8, 126.9, 127.8, 128.0, 130.5, 130.6, 131.1, 131.5, 132.1, 141.5. Found (%): C, 62.36; H, 3.18; N, 20.26. $C_{18}H_{11}N_5OS$. Calculated (%): C, 62.60; H, 3.21; N, 20.28.

1-Methoxy-2-phenyl-3-(1-phenyl-1*H*-pyrazol-5-yl)-1*H*-indole-5,6-dicarbonitrile (10e). The yield was 0.29 g (71%), m.p. 205—206 °C. IR, ν/cm^{-1}: 2228 (CN); 1614, 1598 (H_{arom}); 1240, 1227 (OMe); 1028 (C—O—N). ^{1}H NMR (DMSO-d_6), δ: 3.79 (s, 3 H, OMe); 6.74 (d, 2 H, H(2′′′), H(6′′′), J = 7.6 Hz); 6.82 (br.s, 1 H, H(4′′)); 6.99—7.18 (m, 5 H, 2-Ph); 7.30 (t, 2 H, H(3′′′), H(5′′′), J = 7.6 Hz); 7.38 (t, 1 H, H(4′′′), J = 7.6 Hz); 7.85 (br.s, 1 H, H(3′′)); 8.21 (s, 1 H, H(4)); 8.59 (s, 1 H, H(7)). Found (%): C, 74.89; H, 4.08; N, 16.82. $C_{26}H_{17}N_5O$. Calculated (%): C, 75.17; H, 4.12; N, 16.86.

1-Methoxy-2-(4-methoxyphenyl)-3-(1-phenyl-1*H*-pyrazol-5-yl)-1*H*-indole-5,6-dicarbonitrile (10f). The yield was 0.32 g (75%), m.p. 242—243 °C. IR, ν/cm^{-1}: 2226 (CN); 1607, 1499 (H_{arom}); 1256, 1175 (OMe); 1028 (C—O—N); 834 (1,4-sub.). MS (EI, 70 eV), m/z (I_{rel} (%)): 445 $[M]^+$ (99), 414 $[M - OMe]^+$ (100), 371 (26), 343 (32), 307 (37), 279 (22), 254 (26), 240 (18), 226 (16), 207 (44), 133 (23), 77 (72). ^{1}H NMR (DMSO-d_6), δ: 3.78 (s, 3 H, 4′-OMe); 3.79 (s, 3 H, 1-OMe); 6.77 (d, 2 H H(2′′′), H (6′′′), J = 7.8 Hz); 6.78 (d, 2 H, H(3′), H(5′), J = 8.6 Hz); 6.80 (d, 1 H, H(4′′), J = 1.8 Hz); 6.87 (d, 2 H, H(2′), H(6′), J = 8.6 Hz); 7.09—7.14 (m, 3 H, H(3′′′), H(4′′′), H(5′′′); 7.85 (d, 1 H, H(3′′), J = 1.8 Hz); 8.15 (s, 1 H, H(4)); 8.54 (s, 1 H, H(7)). ^{13}C NMR (DMSO-d_6), δ: 55.3, 66.5, 101.5, 105.6, 106.5 110.2, 114.2 (2C), 116.2, 117.0, 117.1, 118.5, 123.6 (2 C); 124.4, 126.4, 126.9, 128.5 (2 C); 130.4 (2 C); 131.3, 132.7, 139.2, 139.5, 140.6, 160.2. Found (%): C, 72.56; H, 4.28; N, 15.69. $C_{27}H_{19}N_5O_2$. Calculated (%): C, 72.80; H, 4.30; N, 15.72.

References

1. J.T. Gupton, N. Telang, D. F. Gazzo, P. J. Barelli, K. E. Lescalleet, J. W. Fagan, B. J. Mills, K. L. Finzel, R. P. F. Kanters, K. R. Crocker, S. T. Dudek, C. M. Lariviere, S. Q. Smith, K. M. Keertikar, *Tetrahedron*, 2013, **69**, 5829.
2. B. M. Ramalingam, V. Saravanan, A .K. Mohanakrishnan, *Org. Lett.*, 2013, **15**, 3726.
3. F. Giraud, G. Alves, E. Debiton, L. Nauton, V. Thery, E. Durieu, Y. Ferandin, O. Lozach, L. Meijer, F. Anizon, E. Pereira, P. Moreau, *J. Med. Chem.*, 2011, **54**, 4474.
4. A. Lange, M. Gunther, F. M. Buttner, M. O. Zimmermann, J. Heidrich, S. Hennig, S. Zahn, Ch. Schall, A. Sievers-Engler, F. Ansideri, P. Koch, M. Laemmerhofer, Th. Stehle, S. A. Laufer, F. M. Boeckler, *J. Am. Chem. Soc.*, 2015, **137**, 14640.
5. J. Thomas, V. Goyvaerts, S. Liekens, W. Dehaen, *Chem. Eur. J.,* 2016, **22**, 9966.
6. K. N. More, H. W. Jang, V. S. Hong, J. Lee, *Bioorg. Med. Chem. Lett.*, 2014, **24**, 2424.
7. R. R. Yadav, S. Sharma, P. Joshi, A. Wani, R. A. Vishwakarma, A. Kumar, S. B. Bharate, *Bioorg. Med. Chem. Lett.*, 2015, **25**, 2948.
8. D. Zhang, G. Wang, G. Zhao, W. Xu, L. Huo, *Eur. J. Med. Chem.*, 2011, **46**, 5868.
9. P. Diana, A. Carbone, P. Barraja, G. Kelter, H.-H. Fiebig, G. Cirrincione, *Bioorg. Med. Chem.*, 2010, **18**, 4524.
10. Y. J. Esvan, F. Giraud, E. Pereira, V. Suchaud, L. Nauton, V. Théry, L.G. Dezhenkova, D. N. Kaluzhny, V. N. Mazov, A. A. Shtil, F. Anizon, P. Moreau, *Bioorg. Med. Chem.*, 2016, **24**, 3116.
11. S. H. Kim, S. Lee, S. H. Kim, K. H. Kim, J. N. Kim, *Bull. Korean Chem. Soc.*, 2013, **34**, 3415.
12. D. L. Obydennov, B. I. Usachev, V. Ya. Sosnovskikh, *Chem. Heterocycl. Compd.* (*Engl. Tramsl.*), 2015, **50**, 1388 [*Khim. Geterotsikl. Soedin.*, 2014, 1510].
13. S. B. Somappa, J. S. Biradar, P. Rajesab, S. Rahber, M. Sundar, *Monatsh Chem.*, 2015, **146**, 2067.
14. V. P. Gorbunova, N. N. Suvorov, *Chem. Heterocycl. Compd.*, 1978, **14**, 754.
15. S. V. Kumar, S. K. Yadav, B. Raghava, B. Saraiah, H. Ila, K. S. Rangappa, A. Hazra, *J. Org. Chem.*, 2013, **78**, 4960.
16. T. A. Khan, S. Kumar, Ch. Venkatesh, H. Ila, *Tetrahedron*, 2011, **67**, 2961.
17. T. Delaunay, P. Genix, M. Es-Sayed, J.-P. Vors, N. Monteiro, G. Balme, *Org. Lett.*, 2010, **12**, 3328.
18. Zh. V. Chirkova, M. V. Kabanova, S. I. Filimonov, I. G. Abramov, A. V. Samet, G. A. Stashina, K. Yu. Suponitsky, *Tetrahedron Lett.*, 2017, **58**, 755.
19. Zh. V. Chirkova, M. V. Kabanova, S. I. Filimonov, I. G. Abramov, A. Petzer, J. P. Petzer, K. Yu. Suponitsky, *Bioorg. Med. Chem. Lett.*, 2016, **26**, 2214.
20. S. I. Filimonov, Zh. V. Chirkova, I. G. Abramov, S. I. Firgang, G. A. Stashina, Yu. A. Strelenko, D. V. Khakimov, T. S. Pivina, A. V. Samet, K. Yu. Suponitsky, *Tetrahedron*, 2012, **68**, 5991.
21. Ya. Lin, S. A. Lang, *J. Org. Chem.*, 1980, **45**, 4857.
22. S. Chimichi, M. Boccalini, M. M. M. Hassan, G. Viola, F. Dall′Acqua, M. Curini, *Tetrahedron*, 2006, **62**, 90.
23. F. A. Rosa, P. Machado, H. G. Bonacorso, N. Zanatta, M. A. P. Martins, *J. Heterocycl. Chem.*, 2008, **45**, 879.
24. E. Pretsch, P. Buhlmann, M. Badertscher, in *Structure Determination of Organic Compounds*, Revised and Enlarged Editionin Tables of Spectral Data; Springer: Berlin Heidelberg, 2009, p. 184.

Received February 28, 2017;
in revised form April 05, 2017