General synthetic method for *NH*-indoles starting from *N*-hydroxyindoles

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A general and efficient method has been developed for the synthesis of *NH*-indoles bearing electron-accepting substituents *via* the modification of corresponding *N*-hydroxyindoles.

Key words: substituted indole-5,6-dicarbonitriles, pyrrolo[3,4-*f*]indole-5,7-diones, phenacyl bromide.

Substituted *NH*-indoles are much more widely used than the corresponding *N*-hydroxyindoles. Currently, the overwhelming majority of published works are devoted to the synthesis of *NH*-indoles, but not their *N*-hydroxy derivatives. A reductive cyclization of various substrates[1—3] resulting usually in the obtaining of *N*-hydroxy derivatives is one among the known methods for the preparation of indoles bearing acceptor substituents. It is not always possible to obtain *NH*-indoles according to this method even in the case of using a metal catalysis,[3] although some examples have been reported.[4,5]

Methods for the chemical transformation of *N*-hydroxyindoles into the corresponding *NH*-indoles do in most cases not involve a reduction of the OH group: they can formally be considered as a "substitution" of the OH group with a hydrogen atom, which occurs during various rearrangements of intermediates generated *via* a reaction with the hydroxyl group of *N*-hydroxyindoles. The formation of 3-halogenindoles[6] or 3-formylindole[7,8] proceeds probably in this way in the Vilsmeier—Haack reaction or during the formation of *NH*-products upon the reaction of aromatic sulfonyl chlorides or acid chlorides with hydroxyindoles.[9] The mentioned methods are usually not selective and do not always lead to the target product in a satisfactory yield. In addition, the reaction of 1-hydroxyindoles with esters of halogenacetic acid in methanol in the presence of triethylamine (TEA) leading to either *NH*-indoles[10] or a mixture of indoles with the corresponding *NO*-esters[11] has been reported. However, we have previously found[12] that the alkylation of 2-amino-1-hydroxyindole-5,6-dicarbonitriles with methyl bromoacetate in DMF upon using potassium carbonate as the deprotonating agent results in the formation of esters at the NOH group. Such differences in the experimental data are probably related to the reaction conditions. For instance, it is known that 1-hydroxyindoles are mostly represented in alcohols by their *N*-oxide form, while the hydroxy form is major in DMF.[13]

The present work was aimed at the development of simple, non-catalytic method for the synthesis of *NH*-indoles bearing acceptor substituents *via* a modification of the corresponding *N*-hydroxyindoles.

To obtain the desired *NH*-indoles, we have initially chosen our method reported previously,[14] but this method was not very efficient in the case of using *N*-hydroxyindoles **1** as the substrates, since a long-term heating at the boiling point of methanol was required to complete the reaction. The less toxic solvent, isopropyl alcohol, was found to be more appropriate. The modified procedure became applicable to a wide range of substituted *N*-hydroxyindoles (Scheme 1, Table 1).

Scheme 1

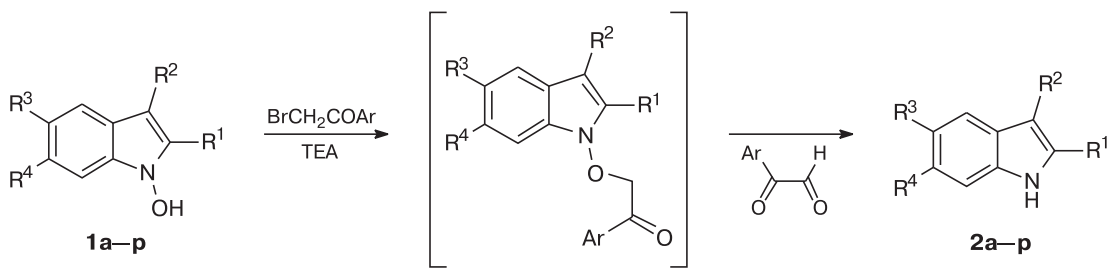

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Table 1. Synthesis of NH-indoles **2a**—**p**: the reaction conditions and product yields

Compound	R^1	R^2	R^3	R^4	τ/h	*T*/°C	Product (%)	Yield
			R^3—R^4					
1a	Ph	H	CN	CN	8	60	**2a**	34
1b	4-MeC_6H_4	H	CN	CN	7	60	**2b**	73
1c	4-$MeOC_6H_4$	H	CN	CN	7	60	**2c**	71
1d	2-Thienyl	H	CN	CN	8	60	**2d**	64
1e	Ph	Ac	CN	CN	5	50	**2e**	83
1f	4-MeC_6H_4	Ac	CN	CN	4	50	**2f**	75
1g	4-$MeOC_6H_4$	Ac	CN	CN	4	50	**2g**	71
1h	2-Thienyl	Ac	CN	CN	5	50	**2h**	56
1i	Ph	Cl	CN	CN	5	65	**2i**	68
1j	4-MeC_6H_4	Cl	CN	CN	3	65	**2j**	79
1k	4-$MeOC_6H_4$	Cl	CN	CN	4	65	**2k**	74
1l	2-Thienyl	Cl	CN	CN	5	65	**2l**	57
1m	Ph	H	CONHCO		4	40	**2m**	70
1n	4-MeC_6H_4	H	CONHCO		2	40	**2n**	64
1o	4-$MeOC_6H_4$	H	CONHCO		3.5	40	**2o**	77
1p	2-Thienyl	H	CONHCO		4	40	**2p**	48

N-Hydroxyindoles **1a**—**p** were treated in isopropyl alcohol with phenacyl bromide in the presence of TEA at 40—65 °C for 2—8 h. The reaction mixture was then cooled and kept at room temperature for 24 h. Resulting *NH*-indoles **2a**—**p** were isolated in the yields of up to 83%. The mechanism of formation of the target compounds includes the generation of unstable products of the alkylation at the hydroxyl group of indoles **1a**—**p**, which consequently disproportionate under the reaction conditions into *NH*-indoles **2a**—**p** and phenylglyoxal.[14]

It was found that the yield of target compounds **2a**—**p** does not depend on the structure of used phenacyl bromide (Ar = Ph, 4-ClC_6H_4, and 4-MeC_6H_4). Moreover, the temperature and duration of reaction depend on the nature of substituent at the positions 2 and 3 of heterocyclic moiety in substrate **1a**—**p**. A common feature for the preparation of all the compounds is that the reaction practically does not proceed at temperatures below 40 °C. The longest duration and highest reaction temperature were needed in the case of indoles **2a**,**d**.

The structure of synthesized compounds **2a**—**p** was confirmed by the combination of data acquired on IR and NMR spectroscopy and mass spectrometry. For *NH*-indoles **2a**—**p**, their molecular ions of average intensity were usually detected upon the electron impact ionization. ^{1}H NMR spectra of compounds **2a**—**p** were characterized by the presence of NH proton in a field weaker by 0.3—0.6 ppm as compared to the corresponding signal from the hydrogen atom of NOH group. Hydrogen atoms H(4) and H(7) were also slightly (by 0.1—0.2 ppm) shifted upfield in contrast to the atom H(3), which was usually shifted downfield. ^{13}C NMR spectra did not contain any significant changes in the chemical shift values, but there was a common tendency of shifting downfield (by 1—3 ppm) of the corresponding signals from the carbon atoms. HMBC spectra of compounds **2b** and **2p** were recorded in order to assign more accurately the correlation of hydrogen and carbon atoms. The key signals for compound **2b** were the intense cross-peaks between the hydrogen atom of 1-*NH*-group and the carbon atoms C(2), C(3), and C(3a), as well as a weaker interaction with the carbon atom C(7a); and those for compound **2p** were the cross-peaks between the hydrogen atom of 1-*NH*-group and the carbons C(3), C(3a), and C(2′) in addition to a weaker interaction with the atom C(8a).

The synthesized 3-chloroindole-5,6-dicarbonitriles **2i**—**l** were identical to those obtained previously.[6]

Experimental

IR spectra were recorded on a PerkinElmer RX-1 Fourier transform spectrometer at the wavelength of 700—4000 cm^{-1}. The analyzed compounds were introduced as suspensions in Nujol.

NMR spectra were recorded at the N. D. Zelinsky Institute of Organic Chemistry of the Russian Academy of Sciences (IOCh RAS, Moscow) on a Bruker DRX-400 or Bruker DRX-500 instrument in DMSO-d_6 solutions at 30 °C. The references were the solvent residual signals in ^{1}H NMR (δ_H 2.50) and ^{13}C (δ_C 39.5) NMR using the signal of $SiMe_4$ as the marker.

Mass spectra were recorded at IOCh RAS (Moscow) on a Finnigan MAT.INCOS 50 chromato-mass spectrometer at the ionizing voltage of 70 eV and the temperature of ionization chamber of 100—220 °C.

Elemental analysis was carried out on a PerkinElmer 2400 analyzer in the Analytical laboratory 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 determining melting and boiling points.

Compounds **1a—d**[15], **1e—h**[16], **1i—l**[17], and **1m—p**[18] were prepared according to the known procedures.

Synthesis of compounds 2a—p (general procedure). Compound **1a—p** (1 mmol) in isopropyl alcohol (3 mL) was mixed with phenacyl bromide (1 mmol) and TEA (2.5 mmol). The resulting mixture was stirred at 40—65 °C for 2—8 h. The reaction mixture was then cooled and kept at room temperature for 24 h. Once the reaction was completed (TLC control), water (3 mL) was added; the formed precipitate was filtered, thoroughly washed water, recrystallized from EtOH, and dried in air.

2-Phenyl-1*H*-indole-5,6-dicarbonitrile (2a). The yield was 0.08 g (34%), m.p. 288—290 °C (EtOH). IR, ν/cm^{-1}: 3190 (NH), 2230 (CN), 1603 (Ar). MS (EI, 70 eV), *m/z* (I_{rel} (%)): 244 $[M + 1]^+$ (44), 243 $[M]^+$ (100), 215 (34). ^{1}H NMR (DMSO-d$_6$), δ: 7.23 (s, 1 H, H(3)); 7.45 (t, 1 H, H(4′), *J* = 7.4 Hz); 7.54 (t, 2 H, H(3′), H(5′), *J* = 7.4 Hz); 7.96 (d, 2 H, H(2′), H(6′), *J* = 7.4 Hz); 8.09 (s, 1 H, H(7)); 8.35 (s, 1 H, H(4)); 12.77 (br.s, 1 H, NH). ^{13}C NMR (DMSO-d$_6$), δ: 100.6, 103.8, 104.6, 117.6 (2 C), 117.9, 125.9 (2 C), 127.2, 129.1 (2 C), 129.2, 130.1, 130.8, 136.9, 144.1. Found (%): C, 78.64; H, 3.70; N, 17.24. $C_{16}H_9N_3$. Calculated (%): C, 79.00; H, 3.73; N, 17.27.

2-(4-Methylphenyl)-1*H*-indole-5,6-dicarbonitrile (2b). The yield was 0.19 g (73%), m.p. 300—302 °C (EtOH). IR, ν/cm^{-1}: 3227 (NH), 2230 (CN), 1603 (Ar). MS (EI, 70 eV), *m/z* (I_{rel} (%)): 259 $[M + 2]^+$ (19), 257 $[M]^+$ (100), 229 (11). ^{1}H NMR (DMSO-d$_6$), δ: 2.36 (s, 3 H, CH_3); 7.12 (s, 1 H, H(3)); 7.32 (d, 2 H, H(3′), H(5′), *J* = 7.9 Hz); 7.81 (d, 2 H, H(2′), H(6′), *J* = 7.9 Hz); 8.03 (s, 1 H, H(7)); 8.26 (s, 1 H, H(4)); 12.67 (s, 1 H, NH). ^{13}C NMR (DMSO-d$_6$), δ: 20.8 (4′-Me), 99.9 (C(3)), 103.7 (C(5)), 104.3 (C(6)), 117.6 (2 CN), 117.7 (C(7)), 125.8 (C(2′), C(6′)), 126.9 (C(4)), 127.3 (C(1′)), 129.6 (C(3′), C(5′)), 130.9 (C(3a)), 136.8 (C(7a)), 138.9 (C(4′)), 144.2 (C(2)). Found (%): C, 79.07; H, 4.28; N, 16.27. $C_{17}H_{11}N_3$. Calculated (%): C, 79.36; H, 4.31; N, 16.33.

2-(4-Methoxyphenyl)-1*H*-indole-5,6-dicarbonitrile (2c). The yield was 0.19 g (71%), m.p. 311—313 °C (EtOH). IR, ν/cm^{-1}: 3300 (NH), 2230, 2216 (CN), 1609 (Ar), 1256, 1188 (OMe). MS (EI, 70 eV), *m/z* (I_{rel} (%)): 274 $[M + 1]^+$ (19), 273 $[M]^+$ (100), 258 (33), 230 (22). ^{1}H NMR (DMSO-d$_6$), δ: 3.83 (s, 3 H, OMe); 7.07 (s, 1 H, H(3)); 7.09 (d, 2 H, H(3′), H(5′), *J* = 8.8 Hz); 7.89 (d, 2 H, H(2′), H(6′), *J* = 8.8 Hz); 8.02 (s, 1 H, H(7)); 8.26 (s, 1 H, H(4)); 12.64 (br.s, 1 H, NH). ^{13}C NMR (DMSO-d$_6$), δ: 55.3, 99.2, 103.7, 103.9, 114.5 (2 C), 117.5, 117.7, 117.7, 122.6, 126.6, 127.4 (2 C), 131.0, 136.8, 144.2, 160.0. Found (%): C, 74.42; H, 4.03; N, 15.32. $C_{17}H_{11}N_3O$. Calculated (%): C, 74.71; H, 4.06; N, 15.38.

2-(Thiophen-2-yl)-1*H*-indole-5,6-dicarbonitrile (2d). The yield was 0.16 g (64%), m.p. 321—323 °C (EtOH). IR, ν/cm^{-1}: 3187 (NH), 2230 (CN), 1604 (Ar). MS (EI, 70 eV), *m/z* (I_{rel} (%)): 250 $[M + 1]^+$ (31), 249 $[M]^+$ (100), 204 (12). ^{1}H NMR (DMSO-d$_6$), δ: 6.98 (s, 1 H, H(3)); 7.22 (dd, 1 H, H(4′), *J* = 4.9 Hz, *J* = 3.9 Hz); 7.70—7.73 (m, 2 H, H(3′), H(5′)); 8.05 (s, 1 H, H(7)); 8.28 (s, 1 H, H(4)); 12.79 (br.s, 1 H, NH). ^{13}C NMR (DMSO-d$_6$), δ: 100.3, 104.0, 104.7, 117.6, 117.7, 117.8, 126.3, 126.9, 128.0, 128.6, 130.8, 133.0, 136.7, 138.6. Found (%): C, 67.28; H, 2.80; N, 16.81. $C_{14}H_7N_3S$. Calculated (%): C, 67.45; H, 2.83; N, 16.86.

3-Acetyl-2-phenyl-1*H*-indole-5,6-dicarbonitrile (2e). The yield was 0.24 g (83%), m.p. 320—322 °C (EtOH). IR, ν/cm^{-1}: 3152 (NH), 2232 (CN), 1618 (C=O), 1562 (Ar). MS (EI, 70 eV), *m/z* (I_{rel} (%)): 285 $[M]^+$ (42), 270 (100), 215 (16). ^{1}H NMR (DMSO-d$_6$), δ: 2.12 (s, 3 H, Ac); 7.53—7.64 (m, 3 H, Ph); 7.70 (d, 2 H, Ph, *J* = 7.5 Hz); 8.16 (s, 1 H, H(7)); 8.72 (s, 1 H, H(4)); 13.21 (br.s, 1 H, NH). ^{13}C NMR (DMSO-d$_6$), δ: 30.0, 106.3, 106.7, 114.9, 116.9, 117.2, 118.6, 128.1, 128.6 (2 C), 129.1, 130.0 (2 C), 130.3, 130.7, 135.6, 149.7, 193.7. Found (%): C, 75.46; H, 3.86; N, 14.69. $C_{18}H_{11}N_3O$. Calculated (%): C, 75.78; H, 3.89; N, 14.73.

3-Acetyl-2-(4-methylphenyl)-1*H*-indole-5,6-dicarbonitrile (2f). The yield was 0.22 g (75%), m.p. 334—336 °C (EtOH). IR, ν/cm^{-1}: 3145 (NH), 2232 (CN), 1618 (C=O), 1561 (Ar). MS (EI, 70 eV), *m/z* (I_{rel} (%)): 299 $[M]^+$ (44), 284 (100), 254 (13). ^{1}H NMR (DMSO-d$_6$), δ: 2.13 (s, 3 H, Ac); 2.43 (s, 3 H, 4′-Me); 7.41 (d, 2 H, H(3′), H(5′), *J* = 8.0 Hz); 7.59 (d, 2 H, H(2′), H(6′), *J* = 8.0 Hz); 8.16 (s, 1 H, H(7)); 8.71 (s, 1 H, H(4)); 13.16 (br.s, 1 H, NH). ^{13}C NMR (DMSO-d$_6$), δ: 21.1, 30.1, 106.3, 106.7, 114.9, 117.1, 117.3, 118.5, 127.9, 128.1, 129.3 (3 C), 130.0 (2 C), 135.7, 140.3, 149.9, 193.8. Found (%): C, 75.96; H, 4.36; N, 13.99. $C_{19}H_{13}N_3O$. Calculated (%): C, 76.24; H, 4.38; N, 14.04.

3-Acetyl-2-(4-methoxyphenyl)-1*H*-indole-5,6-dicarbonitrile (2g). The yield was 0.22 g (71%), m.p. 347—349 °C (EtOH). IR, ν/cm^{-1}: 3187 (NH), 2226 (CN), 1615 (C=O), 1501 (Ar), 1258, 1182 (CO). MS (EI, 70 eV), *m/z* (I_{rel} (%)): 315 $[M]^+$ (52), 300 (100). ^{1}H NMR (DMSO-d$_6$), δ: 2.16 (s, 3 H, Ac); 3.86 (s, 3 H, OMe); 7.15 (d, 2 H, H(3′), H(5′), *J* = 8.8 Hz); 7.65 (d, 2 H, H(2′), H(6′), *J* = 8.8 Hz); 8.15 (s, 1 H, H(7)); 8.71 (s, 1 H, H(4)); 13.09 (br.s, 1 H, NH). ^{13}C NMR (DMSO-d$_6$), δ: 29.9, 55.4, 106.1, 106.4, 114.0 (2 C), 114.5, 116.9, 117.2, 118.3, 122.5, 127.8, 129.3, 131.5 (2 C), 135.5, 149.7, 160.8, 193.7. Found (%): C, 72.04; H, 4.14; N, 13.27. $C_{19}H_{13}N_3O_2$. Calculated (%): C, 72.37; H, 4.16; N, 13.33.

3-Acetyl-2-(thiophen-2-yl)-1*H*-indole-5,6-dicarbonitrile (2h). The yield was 0.16 g (56%), m.p. 338—340 °C (EtOH). IR, ν/cm^{-1}: 3104 (NH), 2233 (CN), 1618 (C=O), 1554 (Ar). MS (EI, 70 eV), *m/z* (I_{rel} (%)): 291 $[M]^+$ (59), 276 (100). ^{1}H NMR (DMSO-d$_6$), δ: 2.42 (s, 3 H, Me); 7.32 (dd, 1 H, H(4′), *J* = 4.9 Hz, *J* = 3.1 Hz); 7.79 (d, 1 H, H(3′), *J* = 3.1 Hz); 7.95 (d, 1 H, H(5′), *J* = 4.9 Hz); 8.08 (s, 1 H, H(7)); 8.61 (s, 1 H, H(4)); 13.20 (br.s, 1 H, NH). ^{13}C NMR (DMSO-d$_6$), δ: 30.3, 106.1, 106.8, 114.9, 116.8. 117.1, 118.3, 127.7, 127.8, 128.7, 130.1, 131.0, 131.8, 135.7, 141.6, 193.4. Found (%): C, 65.68; H, 3.09; N, 14.37. $C_{16}H_9N_3OS$. Calculated (%): C, 65.96; H, 3.11; N, 14.42.

2-Phenylpyrrolo[3,4-*f*]indole-5,7(1*H*,6*H*)-dione (2m). The yield was 0.18 g (70%), m.p. 342—344 °C (EtOH). IR, ν/cm^{-1}: 3314, 3207 (NH), 1746, 1733, 1704, 1692 (CO), 1609, 1588 (Ar). MS (EI, 70 eV), *m/z* (I_{rel} (%)): 262 $[M]^+$ (100). ^{1}H NMR (DMSO-d$_6$), δ: 7.21 (s, 1 H, H(3)); 7.40 (t, 1 H, H(4′), *J* = 7.7 Hz); 7.51 (t, 2 H, H(3′), H(5′), *J* = 7.7 Hz); 7.76 (s, 1 H, H(8)); 7.93 (d, 2 H, H(2′), H(6′), *J* = 7.7 Hz); 7.98 (s, 1 H, H(4)); 10.98 (s, 1 H, 6-NH); 12.57 (s, 1 H, 1-NH). Found (%): C, 72.97; H, 3.82; N, 10.65. $C_{16}H_{10}N_2O_2$. Calculated (%): C, 73.27; H, 3.84; N, 10.68.

2-(4-Methylphenyl)pyrrolo[3,4-*f*]indole-5,7(1*H*,6*H*)-dione (2n). The yield was 0.18 g (64%), m.p. 353—355 °C (EtOH). IR, ν/cm^{-1}: 3270, 3203 (NH), 1757, 1742, 1715, 1697 (CO), 1616, 1592 (Ar). MS (EI, 70 eV), *m/z* (I_{rel} (%)): 276 $[M]^+$ (100), 205 (23). ^{1}H NMR (DMSO-d$_6$), δ: 2.36 (s, 3 H, Me); 7.15 (s, 1 H, H(3)); 7.33 (d, 2 H, H(3′), H(5′), *J* = 8.0 Hz); 7.71 (s, 1 H, H(8)); 7.81 (d, 2 H, H(2′), H(6′), *J* = 8.0 Hz); 7.95 (s, 1 H, H(4)); 10.96 (s, 1 H, 6-NH); 12.39 (s, 1 H, 1-NH). ^{13}C NMR (DMSO-d$_6$), δ: 20.9, 100.7, 106.7, 115.6, 124.2, 125.4 (2 C), 125.6, 128.1, 129.7 (2 C), 132.5, 138.2, 139.1, 142.2, 169.8, 169.9.

Found (%): C, 73.59; H, 4.37; N, 10.10. $C_{17}H_{12}N_2O_2$. Calculated (%): C, 73.90; H, 4.38; N, 10.14.

2-(4-Methoxyphenyl)pyrrolo[3,4-*f*]indole-5,7(1*H*,6*H*)-dione (2o). The yield was 0.22 g (77%), m.p. 357—359 °C (EtOH). IR, ν/cm^{-1}: 3346, 3248 (NH), 1761, 1716 (CO), 1609, 1587 (Ar), 1254, 1192 (C—O). MS (EI, 70 eV), *m*/*z* (I_{rel} (%)): 292 $[M]^+$ (100), 277 (43), 262 (30), 249 (10). ^{1}H NMR (DMSO-d_6), δ: 3.82 (s, 3 H, OMe); 7.07 (s, 1 H, H(3)); 7.08 (d, 2 H, H(3′), H(5′), *J* = 8.8 Hz); 7.70 (s, 1 H, H(8)); 7.86 (d, 2 H, H(2′), H(6′), *J* = 8.8 Hz); 7.93 (s, 1 H, H(4)); 10.93 (s, 1 H, 6-NH); 12.33 (s, 1 H, 1-NH). ^{13}C NMR (DMSO-d_6), δ: 55.3, 100.1, 106.5, 114.6 (2 C), 115.4, 124.2, 123.5, 125.3, 127.1 (2 C), 132.7, 139.1, 142.3, 159.7, 169.8, 170.0. Found (%): C, 69.52; H, 4.11; N, 9.55. $C_{17}H_{12}N_2O_3$. Calculated (%): C, 69.86; H, 4.14; N, 9.58.

2-(Thiophen-2-yl)pyrrolo[3,4-*f*]indole-5,7(1*H*,6*H*)-dione (2p). The yield was 0.13 g (48%), m.p. 322—324 °C (EtOH). IR, ν/cm^{-1}: 3307, 3228 (NH), 1764, 1740, 1722, 1701 (CO), 1616, 1595 (Ar). MS (EI, 70 eV), *m*/*z* (I_{rel} (%)): 268 $[M]^+$ (100), 224 (14), 197 (35). ^{1}H NMR (DMSO-d_6), δ: 6.98 (s, 1 H, H(3)); 7.21 (dd, 1 H, H(4′), *J* = 4.9 Hz, *J* = 4.0 Hz); 7.65 (d, 1 H, H(3′), *J* = 4.0 Hz); 7.66 (d, 1 H, H(5′), *J* = 4.9 Hz); 7.69 (s, 1 H, H(8)); 7.95 (s, 1 H, H(4)); 10.97 (s, 1 H, 6-NH); 12.46 (s, 1 H, 1-NH). ^{13}C NMR (DMSO-d_6), δ: 101.2 (C(3)), 106.6 (C(4)), 115.7 (C(8)), 124.4 (C(4a)), 125.3(C(5′)), 125.9 (C(7a)), 126.9 (C(2′)), 128.5 (C(4′)), 132.4 (C(3a)), 134.0 (C(2)), 136.6 (C(2′)), 139.0 (C(8a)), 169.7 (C(7)), 169.9 (C(5)). Found (%): C, 62.39; H, 2.99; N, 10.39. $C_{14}H_8N_2O_2S$. Calculated (%): C, 62.67; H, 3.01; N, 10.44.

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