Solvent-free synthesis of indole-based thiosemicarbazones under microwave irradiation

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A rapid, efficient and environmentally friendly methodology has been developed for the synthesis of indole-3-carboxaldehyde thiosemicarbazones by using aluminum oxide as the solid support under microwave assisted solvent-free conditions. Compared with the conventional heating method, this method gave the target products in good yield.

Keywords: solvent-free conditions, microwave irradiation, indole-based thiosemicarbazones

Thiosemicarbazones and their metal complexes have attracted considerable interest due to their antiviral, antibacterial, antimalarial, antifungal, and tumour inhibitory biological activities.[1–6] Moreover, thiosemicarbazones bearing an aromatic heterocyclic moiety seem to possess enhanced biological activities.[7–8]Among them, indole-based thiosemicarbazones have aroused particular interest.

Microwave irradiation has been applied to a large and expanding range of chemical transformations in recent years, and this method of energy transfer to a reaction mixture can provide impressive enhancements in product yield, selectivity, and reaction rate.[9] This method has some obvious advantages: the process is fast and simple; the reaction can be performed under atmospheric pressure in a domestic microwave oven; no high-pressure and high temperature apparatus is needed.[10] Microwave irradiation provides a rapid and homogeneous heating of the entire sample, facilitates formation of uniform nucleation centres, and it is also energy efficient and environmentally friendly. Other advantages of microwave technique include its capability to screen a wide range of experimental conditions (such as time and temperature).[11–15] Moreover, with the development of "green chemistry", the focus has now shifted to less cumbersome solvent-free methods, giving facile reactions to provide high yields of pure products, thus eliminating or minimising the use of organic solvents.[16,17] We report here the synthesis of indole-based thiosemicarbazones under solvent-free irradiation using neutral aluminum oxide as mineral support and microwave organic reaction enhancement in good yields. The synthetic route is shown in Scheme 1.

Results and discussion

As shown in Scheme 1, intermediate **3a–j** were obtained using a prior method.[18] Condensation of **3a–j** with indole-3-carboxaldehyde (**4**) afforded the products **5a–j** under solvent-free conditions using microwave irradiation.

Structure elucidation of **5a–j** were accomplished on the basis of their elemental analysis and spectral data. The IR spectra of compound **5a–j** exhibited a characteristic strong absorption at 3149–3412 cm^{-1} due to N–H stretching vibration; The strong bands between 1500 and 1614 cm^{-1} indicated the absorption of C=N; The strong absorption bands falling within the range of 1193–1291 cm^{-1} were assigned to the C=S. In the ^1H NMR spectra, the singlet peaks between δ 11.59–11.79 ppm were assigned to the protons in the =NH, the CH=N proton appeared as a singlet peaks at δ 8.16–9.00 ppm. Their mass spectra showed the expected molecular ions with a high intensity.

In searching for the best reaction conditions for the reaction, we examined the synthesis of **5a** and varied the microwave irradiation power, time and different supports. The typical results are shown in the tables as follows.

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Table 1 Effect of microwave powers on yields

Power/W	240	280	360	425	460	500
Yield/%	52	64	79	90	81	70

As shown in Table 1, we irradiated the reaction using different powers under the same reaction time (3 min). As a result, 425 W was the optimum power. The yield improved up to this power but it decreased under the highest power, owing to carbonisation of this mixture.

Table 2 Effect of microwave irradiation time on yields

Time/min	1	2	3	4	5
Yield/%	79	82	90	71	65

As shown in Table 2, we irradiated the reaction using different time under the same power (425 W). It was found that 3 min was the optimum time, and more byproducts were identified when the reaction time was increased.

Table 3 Effect of supports on yields

Supporter	Zeolite	K_2CO_3	Neutral Al_2O_3	Silica gel H	Alkaline Al_2O_3
Yield/%	71	75	90	54	69

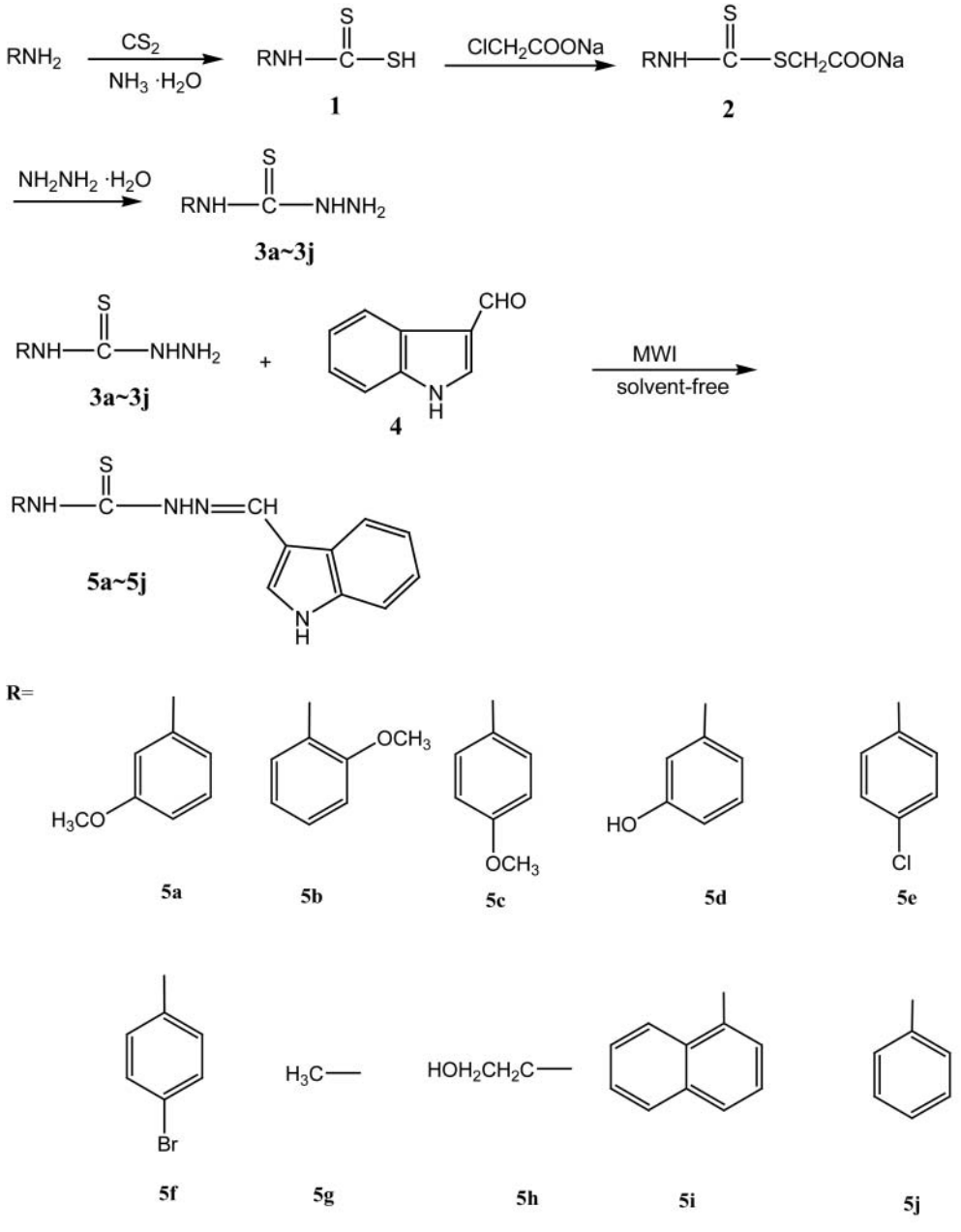
As shown in Table 3, we irradiated the reaction using different supports under the same time (3 min) and power (425 W). This supports significantly affected the yield of products. A low yield was obtained when using silica gel H, zeolite, alkaline Al_2O_3 and K_2CO_3 as supports and irradiating for 3 min. However, the product was obtained in a yield of 90% when using neutral Al_2O_3 as support.

As shown in Table 4, we carried out a comparison of the synthesis of **5a–j** between microwave irradiation in the

Table 4 Synthetic comparison of thiosemicarbazones **5a–j** between solvent-free conditions under microwave irradiation and conventional heating

Comp.	Conventional method		Microwave method		$t_C{}^a/t_{MW}{}^b$
	t/min	Yield/%	t/min	Yield/%	
5a	360	71	3.0	90	120
5b	240	85	2.0	96	120
5c	360	69	3.0	90	120
5d	360	60	4.0	85	90
5e	240	73	3.0	91	80
5f	300	75	3.0	92	100
5g	240	80	3.0	94	120
5h	300	79	3.0	88	100
5i	300	69	2.0	91	150
5j	360	68	4.0	88	90

$T_C{}^a$ was the time of conventional heating method; $T_{MW}{}^b$ was the time of microwave irradiation method



Scheme 1

solvent-free conditions and conventional heating. Compared to conventional thermal heating, microwave irradiation greatly decreased the reaction time from 240–360 min to 2–4 min. It was obvious that yields were increased from 60–85% to 85–96%. From these data, we conclude that microwave irradiation method is a rapid, efficient, and environmentally friendly methodology for this synthesis.

In conclusion, we have developed a very rapid, efficient and eco-friendly method for the preparation of thiosemicarbazones. The reaction was conducted in the presence of aluminum oxide, without using solvent, and assisted by microwave irradiation. The salient features of this method include the simple reaction set-ups, high yields of products, and short reaction time.

Experimental

Melting points were determined on a micro-melting point apparatus and were uncorrected. IR spectra were obtained on 1700 Perkin-Elmer FTIR using KBr disks. ^{1}H NMR spectra were recorded on a Varian INOVA 400 MHz spectrometer using DMSO-d_6 as solvent and TMS as internal standard. Mass spectra were determined on FinniganL-CQ^{DECA} instrument. Elemental analysis was performed on a Carlo-Erba-1106 autoanalyzer. Microwave irradiation was carried out with a MCL-3 microwave oven which was modified from domestic microwave oven and tested at full power (700 W) to conform to the performance index before use. All the solvents were purified before use.

*General procedure for the preparation of substituted thiosemicarbazides **3a–j***

A typical reaction was carried out as follows: A solution of substituted amine (0.01 mol) in ethanol (10 mL) and concentrated aqueous ammonia (2 mL) and was added carbon disulfide dropwise (0.8 mL), and the mixture was stirred at 15–20 °C for 1–2 h to form a solid. Sodium chloroacetate (1.2 g) was added to the stirred mixture and then 85% hydrazine hydrate(1.2 mL) was added. Stirring continued at 60 °C for 4 h to obtain a solid. The crude product was then recrystallised from ethanol to obtain each thiosemicarbazide in 62–80% yields. The melting point of the thiosemicarbazide **3a–j** is shown in Table 5.

Table 5 The melting point of thiosemicarbazide **3a–j**

Product	Formula	M.p./°C	Lit M.p./°C
3a	$C_8H_{11}N_3OS$	157–158	161[19]
3b	$C_8H_{11}N_3OS$	155–157	159[20]
3c	$C_8H_{11}N_3OS$	147–149	152[21]
3d	$C_7H_9N_3OS$	160–162	160[22]
3e	$C_7H_8N_3ClS$	178–180	178[23]
3f	$C_7H_8N_3BrS$	165–168	163–165[24]
3g	$C_2H_7N_3S$	133–134	136–137[25]
3h	$C_3H_9N_3OS$	113–114	114–115[26]
3i	$C_{11}H_{11}N_3S$	135–137	138–139[27]
3j	$C_7H_{10}N_3OS$	137–139	136–138[28]

General procedure for the preparation of thiosemicarbazones **5a–j**
Conventional method: Five drops of acetic acid were added to a mixture of the substituted thiosemicarbazide (**3**) (1 mmol) and indole-3-carboxaldehyde (**4**) (1 mmol) in refluxing ethanol (10 mL). The solution was refluxed for 4–6 h at 85 °C, and the mixture was allowed to cool to room temperature and filtered. The crude product was then recrystallised from ethyl alcohol in 60–85% yields.

Microwave irradiation method: The substituted thiosemicarbazide (**3**) (1 mmol), indole-3-carboxaldehyde(**4**) (1 mmol) and neutral aluminium oxide (0.8 g) were put in a porcelain mortar, then acetic acid (5 drops) was added. After grinding, the mixture was put in a round-bottom flask (25 mL) and was placed in the microwave oven. Then it was irradiated for 2–4 min at 240–510 W. The reaction mixture was cooled to room temperature and was dissolved in DMSO and filtered. The filtrate was added to water and the product was precipitated. The product was recrystallised from DMSO and H_2O in 85–96% yields. The physical and spectra data of the compounds **5a–j** are as follows.

4-(m-Methoxyphenyl)-3-thiosemicarbazone of indole-3-carboxaldehyde (**5a**): Pale yellow crystal; yield 90%, m.p. 192–194 °C; IR (KBr) (cm^{-1}): 3411, 3315, 1598, 1557, 1291, 1196, 735; ^1H NMR (DMSO-d_6, 400 MHz) δ: 3.76 (s, 3H, OCH_3), 6.78 (dd, J = 2 Hz, J = 2 Hz, 1H, ArH), 7.14 (t, J = 7.2 Hz, 1H, ArH), 7.19 (t, J = 6.8 Hz, 2H, ArH), 7.26 (t, J = 8.4 Hz, 1H, ArH), 7.44 (d, J = 8.4 Hz, 2H, ArH), 7.93 (d, J = 2.8 Hz, 1H, indole-CH in 2-moiety), 8.22 (d, J = 7.6 Hz, 1H, ArH), 8.41 (s, 1H, NCH), 9.59 (s, 1H, NH), 11.63 (s, 1H, NH), 11.70 (s, 1H, indole-NH); ESI-MS *m/z* (%): 671 ($[2M+Na]^+$, 100). Ana1.Calcd for $C_{17}H_{16}N_4OS$: C, 62.94; H, 4.97; N, 17.27. Found: C, 62.93; H, 4.97; N 17.25%.

4-(o-Methoxyphenyl)-3-thiosemicarbazone of indole-3-carboxaldehyde (**5b**): Pale yellow crystal; yield 96%, m.p. 178–180 °C; IR (KBr) (cm^{-1}): 3391, 3280, 1600, 1549, 1241, 1193, 744; ^1H NMR (DMSO-d_6, 400 MHz) δ: 4.03 (s, 3H, OCH_3), 6.96–7.00 (m, 1H, ArH), 7.10–7.17 (m, 2H, ArH), 7.24–7.29 (m, 2H, ArH), 7.48–7.52 (m, 1H, ArH), 7.93(d, J = 2.4 Hz, 1H, indole-CH in 2-moiety), 8.25–8.28 (m, 1H, ArH), 8.43 (s, 1H, NCH), 9.00 (d, J = 7.6 Hz, 1H, ArH), 10.03 (s, 1H, NH), 11.76 (s, 1H, indole-NH), 11.79 (s, 1H, NH); ESI-MS *m/z* (%): 325 ($[M+1]^+$, 100). Ana1.Calcd for $C_{17}H_{16}N_4OS$: C, 62.94; H, 4.97; N, 17.27. Found: C, 62.81; H, 4.98; N, 17.21%.

4-(p-Methoxyphenyl)-3-thiosemicarbazone of indole-3-carboxaldehyde (**5c**): Pale yellow crystal; yield 90%, m.p. 207–209 °C; IR (KBr) (cm^{-1}): 3307, 3149, 2983,1607, 1553, 1513, 1242, 744; ^1H NMR (DMSO-d_6, 400 MHz) δ: 3.77 (s, 3H, OCH_3), 6.93 (d, J = 8.8 Hz, 2H, ArH), 7.12 (t, J = 6.8 Hz, 1H, ArH), 7.18 (t, J = 6.8 Hz, 1H, ArH), 7.42 (dd, J = 8.8 Hz, J = 10.4 Hz, 3H, ArH), 7.90 (d, J = 2.4 Hz, 1H, indole-CH in 2-moiety), 8.25 (d, J = 8 Hz, 1H, ArH), 8.39 (s, 1H, NCH), 9.47 (s, 1H, NH), 11.50 (s, 1H, NH), 11.67 (s, 1H, indole-NH); ESI-MS *m/z* (%): 671 ($[2M+Na]^+$, 100). Ana1.Calcd for $C_{17}H_{16}N_4OS$: C, 62.94; H, 4.97; N, 17.27. Found: C, 62.83; H, 4.95; N, 17.25%.

4-(m-Hydroxyphenyl)-3-thiosemicarbazone of indole-3-carboxaldehyde (**5d**): Pale green crystal; yield 85%, m.p. 211–212 °C; IR (KBr) (cm^{-1}): 3386, 3303, 3236, 3079, 1611, 1553, 1233, 740; ^1H NMR (DMSO-d_6, 400 MHz) δ: 6.61 (dd, J = 1.6 Hz, J = 2 Hz, 1H, ArH), 7.06 (d, J = 8.4 Hz, 1H, ArH), 7.13–7.23 (m, 4H, ArH), 7.46 (d, J = 8 Hz, 1H, ArH), 7.91 (d, J = 2.8 Hz, 1H, indole-CH in 2-moiety), 8.20 (d, J = 7.6 Hz, 1H, ArH), 8.40 (s, 1H, NCH), 9.48 (s, 1H, OH), 9.49 (s, 1H, NH), 11.57 (s, 1H, NH), 11.69 (s, 1H, indole-NH); ESI-MS *m/z* (%): 643 ($[2M+Na]^+$, 100). Ana1.Calcd for $C_{16}H_{14}N_4OS$: C, 61.92; H, 4.55; N, 18.05. Found: C, 61.78; H, 4.56; N, 18.07%.

4-(p-Chlorophenyl)-3-thiosemicarbazone of indole-3-carboxaldehyde (**5e**): Yellow crystal; yield 91%, m.p. 200–202 °C; IR (KBr) (cm^{-1}): 3405, 3307, 1613, 1543, 1492, 1268, 741; ^1H NMR (DMSO-d_6, 400 MHz) δ: 7.13–7.23 (m, 2H, ArH), 7.41–7.45 (m, 3H, ArH), 7.67–7.71 (m, 2H, ArH), 7.92 (d, J = 2.8 Hz, 1H, indole-CH in 2-moiety), 8.25 (d, J = 7.6 Hz, 1H, ArH), 8.41 (s, 1H, NCH), 9.67 (s, 1H, NH), 11.67 (s, 1H, NH), 11.70 (s, 1H, indole-NH); ESI-MS *m/z* (%): 367 ($[M+K]^+$, 100). Ana1.Calcd for $C_{16}H_{13}ClN_4S$: C, 58.44; H, 3.98; N, 17.07. Found: C, 58.42; H, 3.97; N, 17.14%.

4-(p-Bromophenyl)-3-thiosemicarbazone of indole-3-carboxaldehyde (**5f**): Pale yellow crystal; yield 92%, m.p. 191–192 °C; IR (KBr) (cm^{-1}): 3398, 3294, 3182, 1614, 1547, 1199, 741; ^1H NMR (DMSO-d_6, 400 MHz) δ: 7.16 (t, J = 7.2 Hz, 1H, ArH), 7.23 (t, J = 7.2 Hz, 1H, ArH), 7.43–7.48 (m, 1H, ArH), 7.57 (dd, J = 2.8 Hz, J = 1.6 Hz, 2H, ArH), 7.65 (d, J = 8.8 Hz, 2H, ArH), 7.92 (d, J = 3.2 Hz, 1H, indole-CH in 2-moiety), 8.24 (d, J = 7.6 Hz, 1H, ArH), 8.41 (s, 1H, NCH), 9.66 (s, 1H, NH), 11.67 (s, 1H, NH), 11.70 (s, 1H, indole-NH); ESI-MS *m/z* (%): 371 ($[M-1]^-$, 100). Ana1.Calcd for $C_{16}H_{13}BrN_4S$: C, 51.48; H, 3.51; N, 15.01. Found: C, 51.40; H, 3.50; N, 14.97%.

4-Methyl-3-thiosemicarbazone of indole-3-carboxaldehyde (**5g**): Pale yellow crystal; yield 94%, m.p. 209–210 °C; IR (KBr) (cm^{-1}): 3365, 3236, 1606, 1544, 1441, 1237, 735; ^1H NMR (DMSO-d_6, 400 MHz) δ: 3.08 (d, J = 4.8 Hz, 3H, CH_3), 7.12 (t, J = 7.2 Hz, 1H, ArH), 7.18 (t, J = 8 Hz, 1H, ArH), 7.43 (d, J = 8.4 Hz, 1H, ArH), 7.80 (d, J = 2.4 Hz, 1H, indole-CH in 2-moiety), 7.91 (m, 1H, NH), 8.28 (d, J = 8 Hz, 1H, ArH), 8.29 (s, 1H, NCH), 11.17 (s, 1H, NH), 11.59 (s, 1H, indole-NH); ESI-MS *m/z* (%): 233 ($[M+1]^+$, 100). Ana1.Calcd for $C_{11}H_{12}N_4S$: C, 56.87; H, 5.21; N, 24.12. Found: C, 56.83; H, 5.20; N, 24.10%.

4-Hydroxyethyl-3-thiosemicarbazone of indole-3-carboxaldehyde (**5h**): Pale yellow crystal; yield 88%, m.p. 204–206 °C; IR (KBr) (cm^{-1}): 3380, 3170, 1614, 1549, 1236, 749; ^1H NMR (DMSO-d_6, 400 MHz) δ: 3.59–3.70 (m, 4H, CH_2), 4.91 (t, J = 4.8 Hz, 1H, OH), 7.15 (t, J = 7.2 Hz, 1H, ArH), 7.22 (t, J = 7.2 Hz, 1H, ArH), 7.44 (d, J = 8 Hz, 1H, ArH), 7.82 (d, J = 2.8 Hz, 1H, indole-CH in 2-moiety), 7.96 (t, J = 4.4 Hz, 1H, NH), 8.16 (d, J = 7.6 Hz, 1H, ArH), 8.30 (s, 1H, NCH), 11.28 (s, 1H, NH), 11.62 (s, 1H, indole-NH); ESI-MS *m/z* (%): 263 ($[M+1]^+$, 100). Ana1.Calcd for $C_{12}H_{14}N_4OS$: C, 54.94; H, 5.34; N, 21.36. Found: C, 54.97; H, 5.33; N, 21.42%.

4-(α-Naphthyl)-3-thiosemicarbazone of indole-3-carboxaldehyde (**5i**): Pale yellow crystal; yield 91%, m.p. 212–213 °C; IR (KBr) (cm^{-1}): 3261, 3149, 3054, 1602, 1544, 1490, 1221; ^1H NMR (DMSO-d_6, 400 MHz) δ: 7.09 (t, J = 7.6 Hz, 1H, ArH), 7.20 (t, J = 7.6 Hz, 1H, ArH), 7.45 (d, J = 8 Hz, 1H, ArH), 7.53–7.59 (m, 3H, ArH), 7.68 (d, J = 7.2 Hz, 1H, ArH), 7.88 (d, J = 8.4 Hz, 1H, ArH), 7.92 (d, J = 2.8 Hz, 1H, indole-CH in 2-moiety), 7.94–7.96 (m, 1H, ArH), 7.97–8.01 (m, 1H, ArH), 8.36 (d, J = 8 Hz, 1H, ArH), 8.48 (s, 1H, NCH), 9.85 (s, 1H, NH), 11.68 (s, 1H, NH), 11.68 (s, 1H, indole-NH); ESI-MS *m/z* (%): 367 ($[M+Na]^+$, 100). Ana1.Calcd for $C_{20}H_{16}N_4S$: C, 69.74; H, 4.68; N, 16.27. Found: C, 69.73; H, 4.66; N, 16.26%.

4-Phenyl-3-thiosemicarbazone of indole-3-carboxaldehyde (**5j**): Yellow crystal; yield 88%, m.p. 197–199 °C; IR (KBr) (cm^{-1}): 3412, 3320, 3119, 2965, 1601, 1545, 1278; ^1H NMR (DMSO-d_6, 400 MHz) δ: 7.13–7.22 (m, 3H, ArH), 7.40 (t, J = 7.6 Hz, 2H, ArH), 7.45 (d, J = 8 Hz, 1H, ArH), 7.66 (d, J = 7.6 Hz, 2H, ArH), 7.92 (d, J = 2.8 Hz, 1H, indole-CH in 2-moiety), 8.23 (d, J = 7.6 Hz, 1H, ArH), 8.41 (s, 1H, NCH), 9.61 (s, 1H, NH), 11.60 (s, 1H, NH), 11.69 (s, 1H, indole-NH); ESI-MS *m/z* (%): 295 ($[M+1]^+$, 100). Ana1.Calcd for $C_{16}H_{14}N_4S$: C, 65.28; H, 4.79; N, 19.03. Found: C, 65.27; H, 4.78; N, 19.00%.

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