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Synthesis of 4-(5-Nitrophenylfur-2-yl)-1,2,3-thia- and Selenadiazoles

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Abstract—Arylation of 2-acetylfuran with *o*-, *m*-, and *p*-nitrophenyldiazonium salts under the conditions of the Gomberg–Bachmann reaction has afforded the corresponding 5-(nitrophenyl)-2-acetylfurans. Their carboethoxyhydrazones have undergone the cyclization into stable 4-(5-nitrophenylfur-2-yl)-1,2,3-thiadiazoles under the conditions of the Hurd–Mori reaction. Analogous semicarbazones have afforded the corresponding selenadiazoles upon oxidation with selenium dioxide. The analysis of electronic absorption spectra of the obtained hybrid heterocycles has shown that the conjugation of the phenyl and the furan ring in *o*-nitrophenyl derivatives is distorted due to steric hindrance, whereas the effect of direct polar conjugation leading to strong bathochromic shift of the absorption band has been observed in the case of the *p*-nitro derivatives. The position and intensity of the bands in the electronic absorption spectra of the studied compounds are determined by electronic as well as steric factors. The difference in the length of conjugation chain determined by the position of the nitro group in the phenyl fragment also contributes to the observed trend. The introduction of selenadiazole fragment instead of thiadiazole one has caused slight bathochromic shift of the band in the electron absorption spectra.

Keywords: 2-acetylfuran, arylation, hydrazones, Hurd–Mori reaction, 1,2,3-thidiazoles, 1,2,3-selenadiazoles

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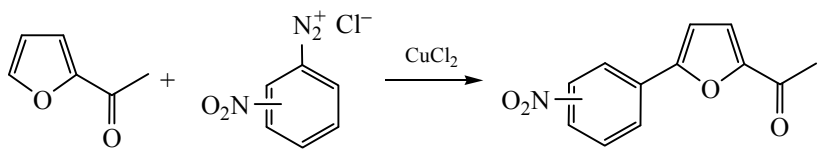
We have recently demonstrated that phenyl substituent containing nitro or ester group and located at position 5 of the furan ring of 4-(3-furyl)-1,2,3-thiadiazole makes this hybrid system thermally stable [1]. This study aimed to verify whether it was possible to stabilize labile 4-(2-furyl)-1,2,3-thia- and selenadiazole systems [2] via the same approach and to elucidate the features of electron density distribution in such molecules.

The first step of the target products synthesis was the arylation of 2-acetylfuran with *o*-, *m*-, or *p*-nitrophenyldiazonium salts in a water–acetone medium under the conditions of the Gomberg–Bachmann reaction, as described elsewhere [3] (Scheme 1).

Compounds **1-3** were obtained in 62, 30, and 70% yield, respectively. The difference in the yields was in line with electrophilicity of aryl carbocations formed via elimination of nitrogen from the nitrophenyldiazonium salts, suggesting that the arylation of acetylfuran proceeded according to the electrophilic mechanism.

Nitrophenylketones **1**–**3** were crystalline substances with distinct melting points. Synthetic protocol and

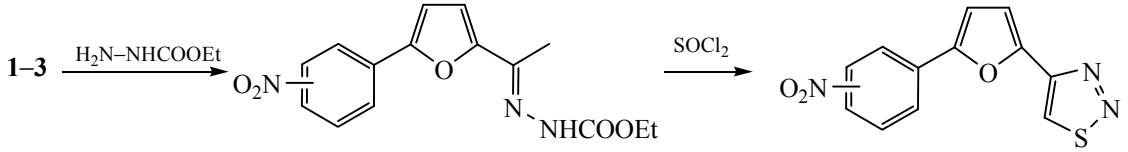
Scheme 1.



1–3

2-NO_2 (**1**), 3-NO_2 (**2**), 4-NO_2 (**3**).

Scheme 2.



4–6 **7–9**

2-NO_2 (**4**, **7**), 3-NO_2 (**5**, **8**), 4-NO_2 (**6**, **9**).

spectral parameters of the obtained compounds are presented in the Experimental.

Carbethoxyhydrazones of compounds **1**–**3** were synthesized via the reaction with carboethoxyhydrazine in 2-propanol in the presence of sulfuric acid at the ketone to hydrazine molar ratio 1 : 1.05 (Scheme 2). The reaction duration was 10 h at 80°C. Yields of *o*- (**4**) and *p*-nitrophenyl compounds **6** were practically equal (56 and 57%, respectively), while the *m*-isomer was prepared in 65% yield. According to ^{1}H and ^{13}C spectral data, those compounds existed in solutions in a single form rather than as a mixture of *syn*- and *anti*-isomers as in the case of hydrazones of methyl derivatives of acetylfuran [2] and acetylfurancarboxylates [4].

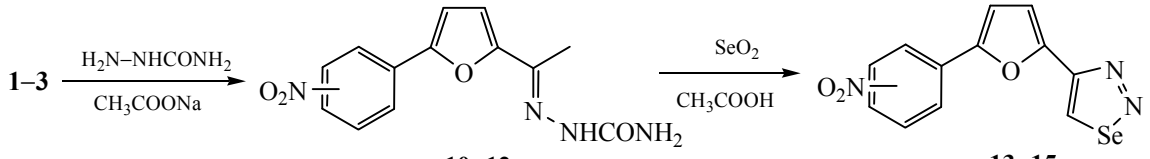
The transformation of carboethoxyhydrazones **4**–**6** into 1,2,3-thiadiazoles **7**–**9** was carried out under the conditions of the Hurd–Mori reaction, in boiling chloroform via treating with 3–4-fold molar excess of thionyl chloride (Scheme 3). Yields of thiadiazoles **7**–**9** were 40, 35, and 76%, respectively. The formation of thiadiazole ring was confirmed by the presence of the H^5 proton signal (8.6–8.8 ppm) in the ^{1}H NMR spectra. The signals of 1,2,3-thiadiazole C^5 and C^4 carbon atoms were located at about 129 and 149–152 ppm, respectively. Compounds **7**–**9** were crystalline substances with mp 107, 102, and 160°C, respectively.

Two-stage synthesis of 1,2,3-selenadiazoles from acetylfurans **1**–**3** was carried out similarly to the procedure described elsewhere [5]. The treatment of acetylfurans with semicarbazide hydrochloride in the presence of sodium acetate in 2-propanol gave semicarbazones **10**–**12** (Scheme 3). The reaction was performed at the ketone : semicarbazide hydrochloride : sodium acetate molar ratio of 1 : 1.2 : 2 at 80°C during 10 h. The yields of the target products after crystallization from ethanol were 87, 89, and 90%, respectively. Oxidation of compounds **10**–**12** with selenium dioxide in acetic acid at 66°C led to the formation of selenadiazoles **13**–**15** (Scheme 3). The reaction was carried out at the semicarbazone : selenium dioxide molar ratio of 1 : 1.1 during 6 h. The target products were obtained in 82, 65, and 77% yield, respectively. The formation of 1,2,3-selenadiazole ring was confirmed by the presence of the proton signal at 9.3–9.6 ppm in $CDCl_3$ (satellite with $^2J_{HSe}$ = 39.2 Hz) or at 10.2 ppm in DMSO-d_6 (satellite with $^2J_{HSe}$ = 37.2 Hz) in the ^{1}H NMR spectra. The signals of the C^5 and C^4 carbon atoms were observed at 135–141 and 149–151 ppm, respectively.

The obtained compounds **13**–**15** were crystalline substances with mp 120, 127, and 116°C, respectively.

Hence, the introduction of nitrophenyl fragment in the structure of 4-(2-furyl)-1,2,3-thiadiazole as well as of 4-(2-furyl)-1,2,3-selenadiazole led to thermal stabilization of the system. The yields of the target products in the Hurd–Mori reaction were significantly stronger dependent on the location of the nitro group in the phenyl ring as compared with the reaction leading to the formation of selenadiazole heterocycle.

Scheme 3.



10–12 **13–15**

2-NO_2 (**10**, **13**), 3-NO_2 (**11**, **14**), 4-NO_2 (**12**, **15**).

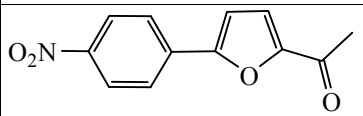
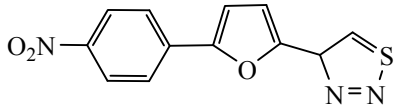
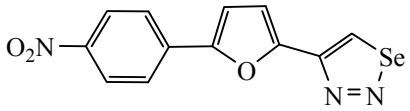
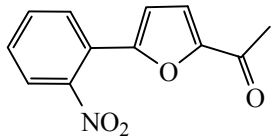
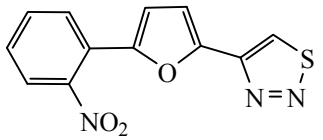
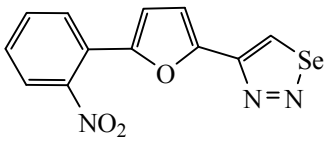
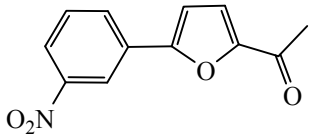
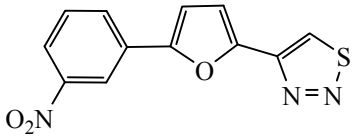
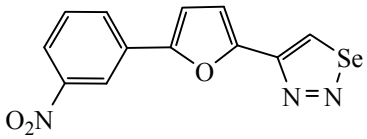
To elucidate the effect of the structure of chromophore groups and their mutual influence, we examined the electronic absorption spectra of ketones **1**–**3**, thiadiazoles **7**–**9**, and selenadiazoles **13**–**15** in chloroform. The positions of the absorption maximums and the extinction coefficients of the above-mentioned compounds at room temperature are listed in the table.

Analysis of the obtained data revealed that the substituion at positions 2 and 5 of the furan ring led to significant bathochromic shift and the increase in the extinction coefficient as compared to the unsubstituted furan (λ_{max} = 200 nm, ε_{max} 1000 L mol^{-1} cm^{-1} [6]).

A transition from *orto*- to *meta*- and *para*-nitro group in the phenyl fragment in the series of acetylfurans, 1,2,3-thia- and -selenadiazoles increased the bathochromic shift in the electronic absorption spectra. The analysis of the Stewart–Brigleb models of nitrophenylfuryl derivatives showed that coplanar location of phenyl and furyl rings was impossible for the *orto*-nitrophenyl-substituted furans **1**, **7**, and **13**. That decreased the degree of conjugation between those structural units and led to shorter-wave absorption maximums as compared to the *para*-substituted derivatives **3**, **9**, and **15**. The *para*-nitrophenyl derivatives **3**, **9**, and **15** exhibited longer-wave absorption due to effect of direct polar conjugation with the electron-accepting *para*-nitro group. The strongest bathochromic shift in the absorption spectra was observed for the furans containing 1,2,3-selenadiazole fragment at position 2 ($\Delta\lambda_{max}$ = 75 and 65 nm between *p*- and *o*-, *m*-nitro derivatives, respectively). The weakest shift was observed for the acetylfuran series ($\Delta\lambda_{max}$ = 51 and 36 nm between *p*- and *o*-, *m*-nitro derivatives, respectively). The transition from thiadiazole to selenadiazole caused slight bathochromic shift of the absorption maximum for all three (*orto*-, *meta*-, and *para*-nitro) chromophore systems, somewhat depending on the structure. Therefore, it could be concluded that 1,2,3-thia- and -selenadiazole cycles similarly affected the electron density distribution in the studied molecules, and the heavy atom effect was minor. Hence, the bands location in the electronic absorption spectra of the studied compounds was determined mainly by the steric factors determined by the position of the nitro group in the phenyl fragment.

The change in the extinction coefficient of the described compounds was nonpredictable. It did not follow the Braude rule (the decrease in the extinction coefficient should be enhanced along with the angle between the planes of phenyl and furyl rings [7]). Such behavior was most probably connected with the more prominent influence of the electronic factors as compared to the steric ones. The presence of strong electron-accepting substituents at the opposite sides of

Electronic absorption spectral data for 5-(nitrophenyl)-2-acetylfurans **1**–**3**, 4-[5-(nitrophenyl)fur-2-yl]-1,2,3-thiadiazoles **7**–**9**, and 4-[5-(nitrophenyl)fur-2-yl]-1,2,3-selenadiazoles **13**–**15** (chloroform, 20°C).

Comp. no.	Formula	λ_{max}, nm	ε, L mol^{-1} cm^{-1}
3		346	13452
9		374	8934
15		385	16673
1		295	17966
7		300	14368
13		310	21911
2		310	22378
8		315	14560
14		320	25680

the π-excessive furan led to the change in the molecule polarity. Overall electron-accepting effect of the nitrophenyl fragment at position 5 and the π-deficient substituents at position 2 (ketones **1**–**3** and heterocycles **7**–**9**, **13**–**15**) on furan possessing the electron-donating character showed complex outcome in the absorption intensity. The molar absorptivity was decreased for the thiadiazole derivatives in comparison with the acetyl and increased in the case of the selenadiazoles. Hence, the position and intensity of the band in the electronic absorption spectra of the studied compounds was determined by electronic as well as steric factors. Further effect was caused by the difference in the length of the conjugation chain caused by different location of the nitro group in the phenyl fragment.

EXPERIMENTAL

^{1}H and ^{13}C NMR spectra were recorded using a Bruker DPX-400 spectrometer [400.13 (^{1}H), 100.61 MHz (^{13}C)] in $CDCl_3$ and DMSO-d_6. Electronic absorption spectra were obtained using an SF-2000 device in 1 cm quartz cells. High-resolution mass spectra were obtained using a Bruker MicrOTOF mass spectrometer. Melting points were measured with a Boëtius apparatus.

5-(*o*-Nitrophenyl)-2-acetylfuran (1). 10.4 mL of 15% hydrochloric acid was added at stirring to a suspension of 2.40 g (17.4 mmol) of *o*-nitroaniline in 14 mL of water. The mixture was heated until complete dissolution of *o*-nitroaniline hydrochloride and cooled to 0°C, 4.2 mL of 30% aqueous solution of sodium nitrite was then added dropwise at 0–3°C. After that, the solutions of 1.91 g (17.4 mmol) of 2-acetylfuran in 9 mL of acetone and of 0.44 g (2.6 mmol) of copper chloride dihydrate in 2 mL of water were added at the same temperature. The obtained mixture was stirred for 20 min, heated to 40°C, and stirred at that temperature for 5 h. Then it was extracted with chloroform, and the extract was dried with calcium chloride. The drying agent was filtered off, and the filtrate was evaporated. The residue was triturated with ethanol, and water was added until the onset of precipitation. The mixture was kept during several hours, the precipitate was filtered off and dried in air. Yield 2.48 g (62%), mp 116°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.48 s (3H, C$\underline{H}_3$–C=O-furan), 6.76 d (1H, H^4-furan, J = 3.6 Hz), 7.24 d (1H, H^3-furan, J = 3.6 Hz), 7.54 t (1H, H^4-phenyl, J = 7.6 Hz), 7.65 t (1H, H^5-phenyl, J = 7.6 Hz), 7.77 br. d (1H, H^{3,6}-phenyl, J = 7.6 Hz), 7.78 br. d (1H, H^{3,6}-phenyl, J = 7.6 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 26.07 ($\underline{C}H_3$–C=O-furan), 111.71 (C^4-furan), 118.20 (C^3-furan), 123.02 (C^1-phenyl), 124.16 (C^3-phenyl), 129.70 (C^4-phenyl), 129.98 (C^6-phenyl), 132.27 (C^5-phenyl), 147.95 (C^5-furan), 151.68 (C^2-furan), 153.08 (C^2-pheny), 186.48 (C=O).

5-(*m*-Nitrophenyl)-2-acetylfuran (2). 12.2 mL of 15% hydrochloric acid was added at stirring to a suspension of 2.50 g (20.3.4 mmol) of *m*-nitroaniline in 16 mL of water. The mixture was heated until complete dissolution of *m*-nitroaniline hydrochloride and cooled to 0°C, 5.5 mL of 30% aqueous solution of sodium nitrite was then added dropwise at 0–3°C. After that, the solutions of 2.30 g (17.4 mmol) of 2-acetylfuran in 10.2 mL of acetone and of 0.51 g (3.0 mmol) of copper chloride dihydrate in 2 mL of water were added at the same temperature. The mixture was stirred for 20 min, heated to 40°C, and stirred at that temperature for 5 h. The evolved organic phase was boiled with ethanol and small amount of silica gel; the solution was filtered and left for crystallization. The formed precipitate was filtered off, washed with ethanol, and dried in air. Yield 1.45 g (30%), mp 117°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.59 s (3H, C$\underline{H}_3$–C=O-furan), 6.97 d (1H, H^4-furan, J = 3.6 Hz), 7.32 d (1H, H^3-furan, J = 3.6 Hz), 7.66 t (1H, H^5-phenyl, J = 8.0 Hz), 8.14 d (1H, H^6-phenyl, J = 8.0 Hz), 8.24 d (1H, H^4-phenyl, J = 8.0 Hz), 8.61 s (1H, H^2-phenyl). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 26.14 ($\underline{C}H_3$-C=O-furan), 109.37 (C^4-furan), 119.18 (C^3-furan), 119.72 (C^4-phenyl), 121.70 (C^1-phenyl), 123.53 (C^2-phenyl), 130.12 (C^5-phenyl), 130.39 (C^6-phenyl), 148.78 (C^5-furan), 152.66 (C^3-phenyl), 154.77 (C^2-furan), 186.59 (C=O).

5-(*p*-Nitrophenyl)-2-acetylfuran (3). 16.2 mL of 15% hydrochloric acid was added at stirring to a suspension of 3.28 g (20.3.4 mmol) of *p*-nitroaniline in 21.6 mL of water. The mixture was heated until complete dissolution of *p*-nitroaniline hydrochloride and cooled to 0°C, 6.5 mL of 30% aqueous solution of sodium nitrite was then added dropwise at 0–3°C. After that, the solutions of 2.93 g (27.0 mmol) of 2-acetylfuran in 13.5 mL of acetone and of 0.69 g (4.0 mmol) of copper chloride dihydrate in 2 mL of water were added at the same temperature. The mixture was stirred for 20 min, heated to 40°C, and stirred at that temperature for 5 h. The evolved organic phase was boiled with ethanol; the solution was

filtered and left for crystallization. The formed precipitate was filtered off, washed with ethanol, and dried in air. Yield 3.84 g (70%), mp 196°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.58 s (3H, $C\underline{H}_3$–C=O-furan), 7.00 d (1H, H^4-furan, J = 3.6 Hz), 7.31 d (1H, H^3-furan, J = 3.6 Hz), 7.95 d (2H, H^2-phenyl, J = 9.0 Hz), 8.31 d (2H, H^3-phenyl, J = 9.0 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 26.16 ($\underline{C}H_3$–C=O-furan), 110.62 (C^4-furan), 119.18 (C^3-furan), 124.40 (C^{3,5}-phenyl), 125.40 (C^{2,6}-phenyl), 134.95 (C^1-phenyl), 147.65 (C^2-furan), 153.06 (C^4-phenyl), 154.71(C^5-furan), 186.50 (C=O-furan).

5-Nitrophenyl-2-acetylfuran carboethoxyhydrazones (*general procedure*). 6 mmol of 5-nitrophenyl-2-acetylfuran **1**–**3** and 6.3 mmol of carboethoxyhydrazine were dissolved in a mixture of 50 mL of 2-propanol and 0.25 mL of concentrated sulfuric acid. The solution was refluxed with stirring for 10 h. The formed precipitate was filtered off at cooling, washed with small amount of 2-propanol, and crystallized from ethanol.

Carboethoxyhydrazone of 5-(*o*-nitrophenyl)-2-acetylfuran (4). Yield 56%, mp 119°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.26 t (3H, CH_3-ethyl, J = 7.0 Hz), 2.14 s (3H, CH_3-hydrazone), 4.18 q (2H, $OC\underline{H}_2$-ethyl, J = 7.0 Hz), 6.94 d (1H, H^4-furan, J = 3.6 Hz), 6.99 d (1H, H^3-furan, J = 3.6 Hz), 7.59 t (1H, H^4-phenyl, J = 7.6 Hz), 7.74 t (1H, H^5-phenyl, J = 7.6 Hz), 7.89 d (1H, H^6-phenyl, J = 7.6 Hz), 7.91 d (1H, H^3-phenyl, J = 7.6 Hz), 10.18 s (1H, NH). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 13.43 ($\underline{C}H_3C$=N), 15.00 (CH_3-ethyl), 61.14 ($O\underline{C}H_2$-ethyl), 111.51 (C^4-furan), 112.36 (C^3-furan), 122.79 (C^1-phenyl), 124.39 (C^3-phenyl), 129.17 (C^4-phenyl), 129.82 (C^6-phenyl), 132.91 (C^5-phenyl), 141.37 (C=N), 147.38 (C^5-furan), 148.65 (C^2-furan), 153.77 (C^2-phenyl), 154.37 br (C=O).

Carboethoxyhydrazone of 5-(*m*-nitrophenyl)-2-acetylfuran (5). Yield 65%, mp 110°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.39 br. t (3H, CH_3-ethyl, J = 7.0 Hz), 2.26 s (3H, CH_3-hydrazone), 4.36 br. q (2H, $OC\underline{H}_2$-ethyl, J = 7.0 Hz), 6.88 d (1H, H^4-furan, J = 3.6 Hz), 6.93 d (1H, H^3-furan, J = 3.6 Hz), 7.57 t (1H, H^5-phenyl, J = 8.0 Hz), 8.11 d (1H, H^6-phenyl, J = 8.0 Hz), 8.35 d (1H, H^4-phenyl, J = 8.0 Hz), 8.50 s (1H, H^2-phenyl, J = 8.0 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 12.14 ($\underline{C}H_3C$=N), 14.54 (CH_3-ethyl), 62.37 ($O\underline{C}H_2$-ethyl), 109.42 (C^4-furan), 112.16 (C^3-furan), 118.73 (C^4-phenyl), 121.62 (C^1-phenyl), 122.18 (C^2-phenyl), 129.60 (C^5-phenyl), 129.81 (C^6-phenyl), 143.33(C= N), 148.70 (C^2-furan), 148.70 (C^5-furan), 152.18 (C^2-furan), 152.28 (C^3-phenyl), 152.46 (C=O).

Carboethoxyhydrazone of 5-(*m*-nitrophenyl)-2-acetylfuran (6). Yield 57%, mp 166°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.27 t (3H, CH_3-ethyl, J = 7.0 Hz), 2.21 s (3H, CH_3-hydrazone), 4.19 q (2H, $OC\underline{H}_2$-ethyl, J = 7.0 Hz), 7.02 d (1H, H^4-furan, J = 2.8 Hz), 7.39 d (1H, H^3-furan, J = 3.6 Hz), 7.96 d (2H, H^{2,6}-phenyl, J = 8.4 Hz), 8.29 d (2H, H^{3,5}-phenyl, J = 8.4 Hz), 10.23 s (1H, NH). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 13.75 ($\underline{C}H_3C$=N), 15.04 (CH_3-ethyl), 61.18 ($O\underline{C}H_2$-ethyl), 112.38 (C^4-furan), 113.11 (C^3-furan), 124.71 (C^{3,5}-phenyl), 125.95 (C^{2,6}-phenyl), 135.95 (C^1-phenyl), 141.27 br (C=N), 146.51 (C^5-furan), 151.78 (C^2-furan), 154.03 (C^4-phenyl), 154.39 (C=O).

4-[5-(*o*-Nitrophenyl)fur-2-yl]-1,2,3-thiadiazole (7). 0.84 mL (11.6 mmol) of thionyl chloride was added at stirring to a suspension of 0.92 g (2.9 mmol) of 5-(*o*-nitrophenyl)-2-acetylfuran carboethoxyhydrazone in 20 mL of chloroform. The mixture was stirred for 10 h at 64–66°C and left overnight. On the next day, the formed precipitate was filtered off, and the filtrate was evaporated. The residue was dissolved in ethyl acetate and precipitated with hexane. The formed precipitate was removed, the filtrate was boiled with silica gel, the solid phase was removed, and the filtrate was slowly evaporated. The formed precipitate was filtered off and crystallized from ethanol. Yield 0.43 g (40%), mp 106°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 6.88 d (1H, H^4-furan, J = 3.6 Hz), 7.27 d (1H, H^3-furan, J = 3.6 Hz), 7.49 t (1H, H^4-phenyl, J = 7.6 Hz), 7.64 t (1H, H^5-phenyl, J = 7.6 Hz), 7.75 d (1H, H^6-phenyl, J = 7.6 Hz), 7.78 d (1H, H^3-phenyl, J = 7.6 Hz), 8.77 s (1H, H^5-thiadiazole). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 111.34 (C^4-furan), 111.71 (C^3-furan), 123.28 (C^1-phenyl), 123.99 (C^3-phenyl), 128.83 (C^4-phenyl), 128.93 (C^6-phenyl), 129.39 (C^5-thiadiazole), 131.98 (C^5-phenyl), 147.67 (C^5-furan), 149.27 (C^2-furan), 150.90 (C^4-thiadiazole), 153.99 (C^2-phenyl). Mass spectrum: found m/z: 274.0290, calculated for $C_{12}H_7N_3O_3S$: 274.0281 [M + H].

4-[5-(*m*-Nitrophenyl)fur-2-yl]-1,2,3-thiadiazole (8) was obtained similarly from 0.74 g (2.33 mmol) of 5-(*m*-nitrophenyl)-2-acetylfuran carboethoxyhydrazone and 0.7 mL (9.65 mmol) of thionyl chloride. The precipitate was filtered off, and the filtrate was evaporated. The residue was triturated with hexane, the formed precipitate was filtered off and recrystallized from ethanol. Yield 0.22 g (35%), mp 101°C. ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 109.56 (C^4-furan), 111.92 (C^3-furan), 118.70 (C^4-phenyl), 122.37 (C^2-phenyl), 123.07 (C^1-phenyl), 129.17 (C^5-thiadiazole),

129.51 (C^5-phenyl), 129.98 (C^6-phenyl), 147.29 (C^2-furan), 148.26 (C^5-furan), 148.83 (C^4-thiadiazole), 152.24 (C^3-phenyl). Mass spectrum: found *m/z*: 274.0289, calculated for $C_{12}H_7N_3O_3S$: 274.0281 [*M* + H].

4-[5-(*p*-Nitrophenyl)fur-2-yl]-1,2,3-thiadiazole (9) was obtained similarly from 1.19 g (3.75 mmol) of 5-(*p*-nitrophenyl)-2-acetylfuran carboethoxyhydrazone and 1.0 mL (15 mmol) of thionyl chloride. Tar-like precipitate was filtered off, and the filtrate was evaporated. The residue was triturated with hexane, the formed precipitate were filtered off and recrystallized from ethanol. Yield 0.78 g (76%). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 7.08 d (1H, H^4-furan, *J* = 3.6 Hz), 7.33 d (1H, H^3-furan, *J* = 3.6 Hz), 7.91 d (2H, $H^{2,6}$-phenyl, *J* = 8.8 Hz), 8.31 d (2H, $H^{3,5}$-phenyl, *J* = 8.8 Hz), 8.77 s (1H, H^5-thiadiazole). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 111.13 (C^4-furan), 112.20 (C^3-furan), 124.25 ($C^{3,5}$-phenyl), 124.47 ($C^{2,6}$-phenyl), 129.37 (C^5-thiadiazole), 135.16 (C^1-phenyl), 146.82 (C^5-furan), 147.96 (C^2-furan), 152.42 (C^4-thiadiazole), 154.01 (C^4-phenyl). Mass spectrum: found *m/z*: 274.0290, calculated for $C_{12}H_7N_3O_3S$: 274.0281 [*M* + H].

5-(*o*-Nitrophenyl)-2-acetylfuran semicarbazone (10). A mixture of 0.92 g (3.98 mmol) of 5-(*o*-nitrophenyl)-2-acetylfuran and 0.52 g (4.70 mmol) of semicarbazide hydrochloride was dissolved at stirring and cooling in 12 mL of 2-propanol. After complete dissolution of the reagents, 0.79 g (9.60 mmol) of sodium acetate was added. The mixture was refluxed with stirring for 10 h and left overnight. The formed precipitate was filtered off, washed with small amount of 2-propanol, and recrystallized from ethanol. Yield 1.00 g (87%), mp 121°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.09 s (3H, CH_3-semicarbazone), 6.53 br. s (2H, NH_2), 7.05 br. s (1H, H^4-furan), 7.10 br. s (1H, H^3-furan), 7.55 br. t (1H, H^4-phenyl, *J* = 7.2 Hz), 7.71 br. t (1H, H^5-phenyl, *J* = 7.2 Hz), 7.83 d (1H, H^6-phenyl, *J* = 7.2 Hz), 7.93 d (1H, H^3-phenyl, *J* = 7.2 Hz), 9.55 s (1H, NH). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 12.84 ($\underline{C}H_3C$=N), 111.16 (C^4-furan), 112.19 (C^3-furan), 122.21 (C^1-phenyl), 124.05 (C^3-phenyl), 128.41 (C^4-phenyl), 129.50 (C^6-phenyl), 132.46 (C^5-phenyl), 135.89 (C=N), 147.26 (C^5-furan), 148.18 (C^2-furan), 153.90 (C^2-phenyl), 157.45 (C=O).

5-(*m*-Nitrophenyl)-2-acetylfuran semicarbazone (11) was prepared similarly from 0.44 g (1.90 mmol) of 5-(*m*-nitrophenyl)-2-acetylfuran, 0.25 g (2.25 mmol) of semicarbazide hydrochloride, and 0.37 g (4.60 mmol) of sodium acetate. Yield 0.49 g (89%), mp 124°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.20 s (3H, CH_3-semicarbazone), 6.54 br. s (2H, NH_2), 7.10 d (1H, H^4-furan, *J* = 3.4 Hz), 7.36 d (1H, H^3-furan, *J* = 3.4 Hz), 7.73 t (1H, H^5-phenyl, *J* = 7.2 Hz), 8.12 d (1H, H^6-phenyl, *J* = 7.2 Hz), 8.22 d (1H, H^4-phenyl, *J* = 7.2 Hz), 8.50 s (1H, H^2-phenyl), 9.52 s (1H, NH). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 12.84 ($\underline{C}H_3C$=N), 110.96 (C^4-furan), 111.82 (C^3-furan), 118.20 (C^4-phenyl), 122.39 (C^2-phenyl), 124.32 (C^1-phenyl),130.10 (C^5-phenyl), 131.16 (C^6-phenyl), 136.57 (C=N), 147.65 (C^2-furan), 148.96 (C^5-furan), 151.16 (C^3-phenyl), 157.42 (C=O).

5-(*p*-Nitrophenyl)-2-acetylfuran semicarbazone (12) was prepared similarly from 1.72 g (7.6 mmol) of 5-(*p*-nitrophenyl)-2-acetylfuran, 1.00 g (9.00 mmol) of semicarbazide hydrochloride, and 1.50 g (18.3 mmol) of sodium acetate. Yield 1.93 g (90%), mp 126°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.20 s (3H, CH_3-semicarbazone), 6.59 br. s (2H, NH_2), 7.14 d (1H, H^4-furan, *J* = 3.4 Hz), 7.39 d (1H, H^3-furan, *J* = 3.4 Hz), 8.02 d (2H, $H^{2.6}$-phenyl, *J* = 8.8 Hz), 8.26 d (2H, $H^{3,5}$-phenyl, *J* = 8.8 Hz), 9.62 s (1H, NH). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 13.16 ($\underline{C}H_3C$=N), 112.13 (C^4-furan), 112.89 (C^3-furan), 124.66 ($C^{3,5}$-phenyl), 124.86 ($C^{2,6}$-phenyl), 136.10 (C^1-phenyl), 136.41 (C=N), 146.51 (C^5-furan), 151.34 (C^2-furan), 154.03 (C^4-phenyl), 157.40 (C=O).

4-[5-(*o*-Nitrophenyl)fur-2-yl]-1,2,3-selenadiazole (13). 0.35 g (3.15 mmol) of selenium dioxide was added at stirring to a suspension of 0.82 g (2.85 mmol) of 5-(*o*-nitrophenyl)-2-acetylfuran semicarbazone in 12.3 mL of glacial acetic acid. The mixture was heated for 6 h at 66°C protecting from light. After the process was complete, 10 mL of warm water was added, the formed precipitate was filtered off and washed with warm water. Yield 0.75 g (82%), mp 119°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 6.90 d (1H, H^4-furan, *J* = 3.6 Hz), 7.23 d (1H, H^3-furan, *J* = 3.6 Hz), 7.49 t (1H, H^4-phenyl, *J* = 8.0 Hz), 7.64 t (1H, H^5-phenyl, *J* = 8.0 Hz), 7.74 d (1H, H^6-phenyl, *J* = 8.0 Hz) 7.81 d (1H, H^3-phenyl, *J* = 8.0 Hz), 9.38 s (1H, H^5-selenadiazole, satellite $^2J_{HSe}$ = 39.2 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 111.23 (C^4-furan), 111.74 (C^3-furan), 123.38 (C^1-phenyl), 123.97 (C^3-phenyl), 128.74 (C^4-phenyl), 128.77 (C^6-phenyl), 131.93 (C^5-phenyl), 136.12 (C^5-selenadiazole), 147.58 (C^5-furan), 148.78 (C^2-furan),148.88 (C^4-selenadiazole), 154.23 (C^2-phenyl). Mass spectrum: found *m/z*: 321.9710, calculated for $C_{12}H_7N_3O_3Se$: 321.9725 [*M* + H].

4-[5-(*m*-Nitrophenyl)fur-2-yl]-1,2,3-selenadiazole (14) was prepared similarly from 0.46 g (1.59 mmol) of 5-(*m*-nitrophenyl)-2-acetylfuran semicarbazone and 0.2 g (1.80 mmol) of selenium dioxide. Yield 0.33 g (65%), mp 127°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 7.01 d (1H, H^4-furan, J = 3.6 Hz), 7.28 d (1H, H^3-furan, J = 3.6 Hz), 7.63 t (1H, H^5-phenyl, J = 8 Hz), 8.06 d (1H, H^6-phenyl, J = 8.0 Hz), 8.17 d (1H, H^4-phenyl, J = 8.0 Hz), 8.60 s (1H, H^2-phenyl), 9.53 s (1H, H^5-selenadiazole, satellite $^2J_{HSe}$ = 39.2 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 109.56 (C^4-furan), 111.79 (C^3-furan), 118.64 (C^4-phenyl), 122.23 (C^2-phenyl), 129.41 (C^5-phenyl), 129.92 (C^6-phenyl), 131.69 (C^1-phenyl), 135.76 (C^5-selenadiazole), 148.39 (C^2-furan), 148.84 (C^5-furan), 151.86 (C^4-selenadiazole), 154.37 (C^3-phenyl). Mass spectrum: found *m/z*: 321.9733, calculated for $C_{12}H_7N_3O_3Se$: 321.9725 [M + H].

4-[5-(*p*-Nitrophenyl)fur-2-yl]-1,2,3-selenadiazole (15) was obtained similarly from 1.05 g (3.64 mmol) of 5-(*p*-nitrophenyl)-2-acetylfuran semicarbazone and 0.44 g (3.96 mmol) of selenium dioxide. Yield 0.9 g (77%), mp 116°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 7.35 br. d (1H, H^4-furan, J = 2.4 Hz), 7.54 br. d (1H, H^3-furan, J = 2.4 Hz), 8.13 d (2H, H^{2,6}-phenyl, J = 8.2 Hz), 8.32 d (2H, H^{3,5}-phenyl, J = 8.2 Hz), 10.17 s (1H, H^5-selenadiazole, satellite $^2J_{HSe}$ = 37.2 Hz). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 112.20 (C^4-furan), 112.88 (C^3-furan), 124.85 (C^{3,5}-phenyl), 124.94 (C^{2,6}-phenyl), 135.92 (C^1-phenyl), 140.60 (C^5-selenadiazole), 146.62 (C^5-furan), 149.31 (C^2-furan), 151.80 (C^4-selenadiazole), 153.97 (C^4-phenyl). Mass spectrum: found *m/z*: 321.9710, calculated for $C_{12}H_7N_3O_3Se$: 321.9725 [M + H].

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CONFLICT OF INTEREST

No conflict of interest was declared by the authors.

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