

Synthesis of Heterocycles from Arylation Products of Unsaturated Compounds: XVIII.* 5-Arylfuran-2-carboxylic Acids and Their Application in the Synthesis of 1,2,4-Thiadiazole, 1,3,4-Oxadiazole, and [1,2,4]Triazolo[3,4-*b*][1,3,4]thiadiazole Derivatives

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Abstract—Arylation of furan-2-carboxylic acid or its methyl ester with arenediazonium chlorides in the presence of copper(II) chloride gave the corresponding 5-arylfuran-2-carboxylic acids or methyl 5-arylfuran-2-carboxylates. 5-Arylfuran-2-carbonyl chlorides reacted with potassium thiocyanate and then with 5-methyl-1,2-oxazol-3-amine to give 5-aryl-*N*-[3-(2-oxopropyl)-1,2,4-thiadiazol-5-yl]furan-2-carboxamides as a result of recyclization of intermediate isoxazolylthiourea derivatives. The reactions of 5-arylfuran-2-carbonyl chlorides with 5-(2-furyl)-1*H*-tetrazole involved opening of the tetrazole ring with elimination of nitrogen molecule and led to the formation of 2-(5-arylfuran-2-yl)-5-(2-furyl)-1,3,4-oxadiazoles. 3-Substituted 6-(5-arylfuran-2-yl)-[1,2,4]triazolo[3,4-*b*][1,3,4]thiadiazoles were obtained by condensation of 5-arylfuran-2-carboxylic acids with 5-substituted 4-amino-4*H*-1,2,4-triazole-3-thiols in phosphoryl chloride.

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Interest in arylation of furan derivatives is largely determined by prospects in searching for biologically active substances among compounds of the furan series. It is known that many furan derivatives are used as medicines [2–5]. Arylfuran fragments are present in molecules of such medical agents as Nitrafudan, Dantrolene, Clodanole, and Azimilide. Many arylfuran compounds display a broad spectrum of biological activity [5–11].

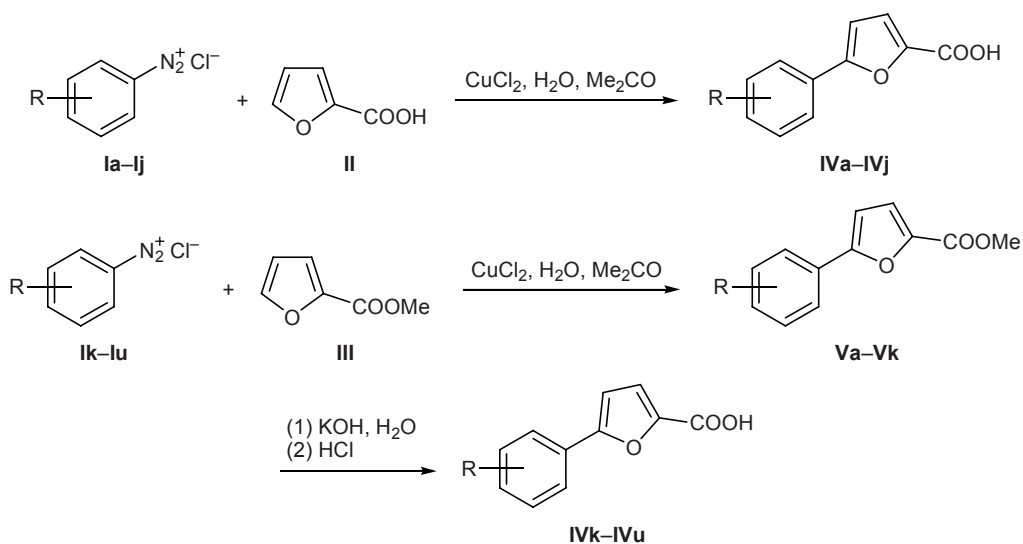
A convenient method for the synthesis of arylfurans is based on catalytic arylation of furan derivatives with arenediazonium salts according to Meerwein [1, 10–12]. Furan-2-carboxylic acid [13–15] and its methyl ester [10, 14] can also be subjected to arylation with arenediazonium salts. In the present work we extended the scope of this reaction with a view to explore synthetic potential of the arylation products. Arenediazonium chlorides **Ia–Iu** reacted with furan-2-carboxylic acid (**II**) or methyl furan-2-carboxylate (**III**) in the presence of copper(II) chloride to give the correspond-

ing 5-aryl-substituted derivatives **IVa–IVj** and **Va–Vh** (Scheme 1) in 40–70% yields which are fairly good for Meerwein reaction. The best yields in the arylation of furan-2-carboxylic acid (**II**) were obtained with arenediazonium salts containing a nitro group or two halogen atoms in the aromatic ring, whereas ester **III** was appropriate for the arylation with monohalo-substituted and trifluoromethylbenzenediazonium chlorides. Alkaline hydrolysis of methyl 5-arylfuran-2-carboxylates **Va–Vh** gave the corresponding acids **IVk–IVu**, and acids **IVa–IVh**, **IVk**, and **IVm–IVt** were converted into 5-arylfuran-2-carbonyl chlorides **VIa–VIh**, **VIk**, and **VI m–VI t** (Scheme 2, see table).

Acid chlorides **VI** were used to synthesize heterocycles having arylfuran fragments. Acyl isothiocyanates **VIIa–VIIk** generated *in situ* from acid chlorides **VIb**, **VIc**, **VIe–VIh**, **VI n–VI p**, **VI r**, and **VI s** and potassium thiocyanate reacted with 5-methyl-1,2-oxazol-3-amine (**VIII**). The expected products of this reaction, *N*-acylthioureas **IXa–IXk**, were not isolated, for they underwent recyclization involving opening of the 1,2-oxazole ring and closure of 1,2,4-thiadiazole

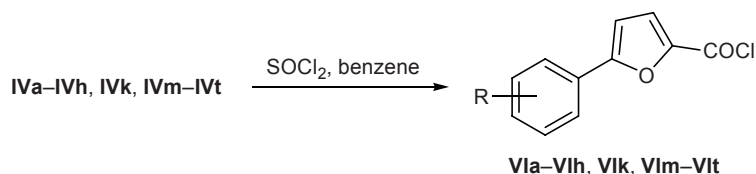
* For communication XVII, see [1].

Scheme 1.



I, IV, R = 2-O₂N (a), 3-O₂N (b), 4-O₂N (c), 2,3-Cl₂ (d), 2,4-Cl₂ (e), 2,5-Cl₂ (f), 3,4-Cl₂ (g), 2-Cl-4-O₂N (h), 2-O₂N-4-MeO (i), 2-O₂N-4-Me (j), 2-F (k), 3-F (l), 4-F (m), 2-Cl (n), 3-Cl (o), 4-Cl (p), 4-Br (q), 2-F₃C (r), 3-F₃C (s), 2-Cl-5-F₃C (t), 3-F₃C-4-Cl (u);
V, R = 2-F (a), 3-F (b), 4-F (c), 2-Cl (d), 3-Cl (e), 4-Cl (f), 4-Br (g), 2-F₃C (h), 3-F₃C (i), 2-Cl-5-F₃C (j), 3-F₃C-4-Cl (k).

Scheme 2.

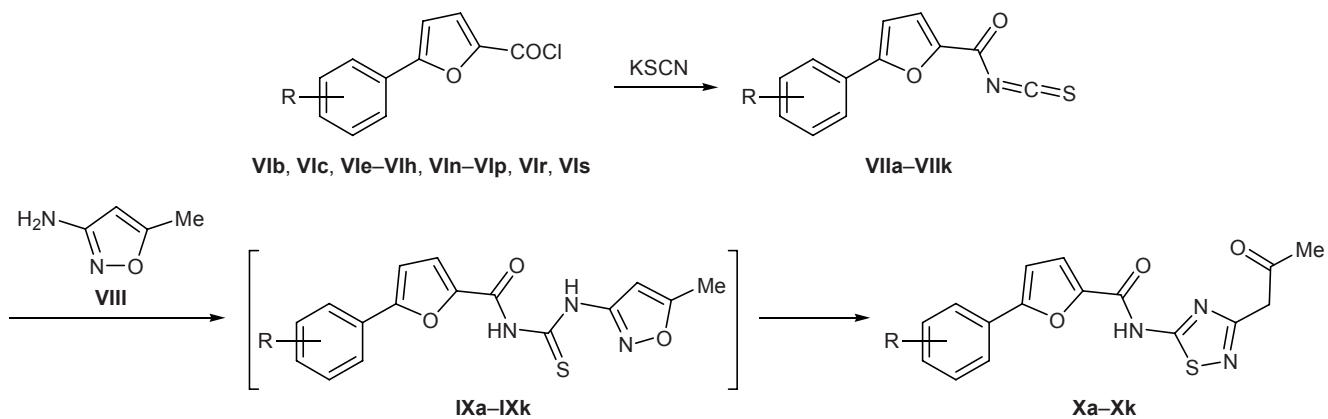


ring [16] to produce finally 5-aryl-*N*-[3-(2-oxopropyl)-1,2,4-thiadiazol-5-yl]furan-2-carboxamides **Xa-Xk** (Scheme 3).

We also tried to synthesize 1,3,4-oxadiazoles having an arylfuran fragment. Derivatives of 1,3,4-oxadiazoles are known as biologically active substances

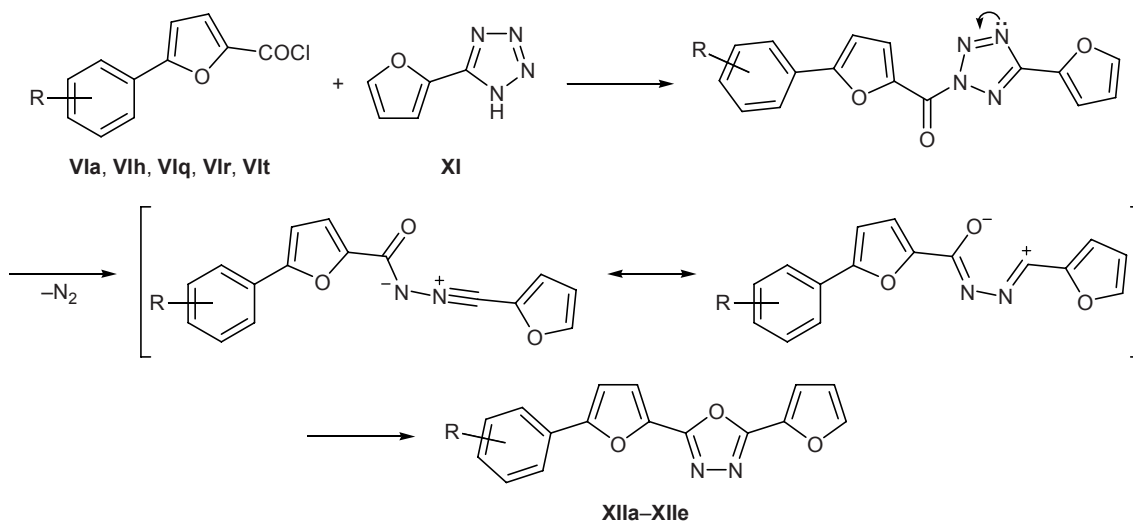
[2, 3] and intermediate products in the preparation of heat-resistant polymers, scintillators, luminophores, dyes, and photochromic materials [17]. For this purpose, we followed an approach based on recyclization of tetrazoles [17, 18]. In fact, 5-arylfuran-2-carbonyl chlorides **VIa, VIh, VIq, VIr, and VI t** reacted with

Scheme 3.



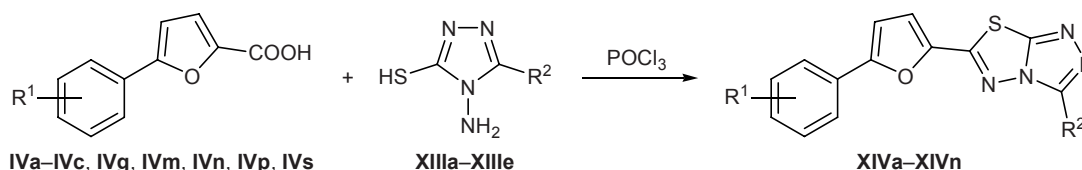
VII, X, R = 3-O₂N (a), 4-O₂N (b), 2-Cl-4-O₂N (c), 2-Cl (d), 3-Cl (e), 4-Cl (f), 2,4-Cl₂ (g), 2,5-Cl₂ (h), 3,4-Cl₂ (i), 2-F₃C (j), 3-F₃C (k).

Scheme 4.



XII, R = 2-O₂N (**a**), 2-Cl-4-O₂N (**b**), 4-Br (**c**), 2-F₃C (**d**), 2-Cl-5-F₃C (**e**).

Scheme 5.



XIII, R² = 2-methylfuran-3-yl (**a**), 2-furyl (**b**), Ph (**c**), PhCH₂ (**d**), Pr (**e**); **XIV**, R¹ = 2-O₂N, R² = 2-methylfuran-3-yl (**a**), Ph (**b**); R¹ = 3-O₂N, R² = 2-methylfuran-3-yl (**c**); R¹ = 4-O₂N, R² = 2-methylfuran-3-yl (**d**), 2-furyl (**e**); R¹ = 2-Cl, R² = Ph (**f**), 2-methylfuran-3-yl (**g**), PhCH₂ (**h**); R¹ = 4-Cl, R² = Pr (**i**), 2-methylfuran-3-yl (**j**), 2-furyl (**k**); R¹ = 4-F, R² = 2-furyl (**l**); R¹ = 3-F₃C, R² = 2-furyl (**m**); R¹ = 3,4-Cl₂, R² = PhCH₂ (**n**).

5-(2-furyl)-1*H*-tetrazole on heating in pyridine to give compounds **XIIa-XIie** (Scheme 4). The reactions were accompanied by evolution of nitrogen. In the first step, acylation of 5-(2-furyl)-1*H*-tetrazole (**XI**) with acid chloride **VI** is likely to afford 2-(5-arylfuran-2-yl)-5-(2-furyl)-2*H*-tetrazole, and decomposition of the latter with elimination of nitrogen molecule and subsequent recyclization leads to the formation of 1,3,4-oxadiazoles **XIIa-XIie**. Presumably, elimination of nitrogen molecule and oxadiazole ring closure follow a concerted mechanism [19].

It is known that fused [1,2,4]triazolo[3,4-*b*][1,3,4]-thiadiazole system is a pharmacophore [20]. Biological activity of some [1,2,4]triazolo[3,4-*b*][1,3,4]thiadiazole derivatives has stimulated further studies in the fields of their synthesis and properties [21]. As follows from published data [21], the most convenient method for building up [1,2,4]triazolo[3,4-*b*][1,3,4]thiadiazole system is cyclization of carboxylic acids with 4-amino-4*H*-1,2,4-triazole-3-thiols. We examined reactions of 5-substituted 4-amino-4*H*-1,2,4-triazole-3-thiols

XIIIa-XIIIe with furancarboxylic acids **IVa-IVc**, **IVg**, **IVm**, **IVn**, **IVp**, and **IVs** in POCl₃ and obtained the corresponding 6-(5-arylfuran-2-yl)[1,2,4]triazolo[3,4-*b*][1,3,4]thiadiazoles **XIVa-XIVn** (Scheme 5).

The results of our present study have demonstrated that Meerwein reaction is suitable for arylation of furan-2-carboxylic acid or its ester and that 5-arylfuran-2-carboxylic acids having various substituents in the benzene ring are convenient reagents for the design of heterocyclic compounds with an arylfuryl fragment.

EXPERIMENTAL

The ¹H NMR spectra were recorded on Varian Mercury (400 MHz; compounds **IV**, **XII**, **XIV**) and Bruker DRX-500 spectrometers (500 MHz; compounds **X**) from solutions in DMSO-*d*₆ or DMSO-*d*₆-CCl₄ (1:3) (**IV**, **XII**). The chemical shifts were measured relative to tetramethylsilane as internal reference. The mass spectra (chemical ionization) were obtained on an Agilent 1100 GC-MS system.

Yields and melting points of 5-arylfuran-2-carbonyl chlorides **VIa–VIh**, **VIk**, and **VI m–VI t**

Comp. no.	Yield, %	bp, °C (mm)	mp, °C (solvent)
VIa	83	–	74–75 (benzene)
VIb	86	–	111–112 (benzene)
VIc	80	–	147–148 (benzene)
VI d	84	177–180 (2)	83–84 (hexane)
VI e	90	170–175 (2)	90–91 (benzene)
VI f	75	175–180 (2)	129–130 (benzene)
VI g	82	189–194 (2)	97–98 (benzene)
VI h	79	–	145–146 (benzene)
VI k	89	140–144 (2)	74–75 (hexane)
VI m	89	144–149 (2)	71–72 (hexane)
VI n	79	154–159 (2)	57–58 (benzene)
VI o	75	170–175 (2)	53–54 (benzene)
VI p	77	166–167 (2)	64–65 (benzene)
VI q	74	183–186 (2)	76–77 (benzene)
VI r	84	155–158 (2)	–
VI s	71	150–155 (2)	77–78 (hexane)
VI t	79	160–165 (2)	91–92 (benzene)

5-Arylfuran-2-carboxylic esters IVa–IVj and methyl 5-arylfuran-2-carboxylates Va–Vk (general procedure). A solution of arenediazonium chloride **Ia–Ij** or **I k–I u**, prepared by diazotization (HCl, NaNO₂) of 0.21 mol of the corresponding aromatic amine, was cooled to 0–5°C and added dropwise under stirring to a solution of 22.4 g (0.2 mol) of furan-2-carboxylic acid (**II**) or 25.2 g (0.2 mol) of methyl furan-2-carboxylate (**III**) and 2 g of copper(II) chloride dihydrate (CuCl₂·2H₂O) in 80 ml of acetone. During the addition, the temperature was maintained in the range from 20 to 30°C so that the rate of evolution of nitrogen was 2–3 bubbles per second. When nitrogen no longer evolved, the mixture was poured into 200 ml water, and the precipitate was filtered off (compounds **IVa–IVj**) or the product was isolated by vacuum distillation (**Va–Vk**) and purified by recrystallization.

5-(2-Nitrophenyl)furan-2-carboxylic acid (IVa). Yield 37%, mp 223–224°C (from EtOH–DMFA); published data [14]: mp 223–224°C. ¹H NMR spectrum, δ, ppm: 6.79 d (1H, 4-H, *J* = 3.4 Hz), 7.19 d (1H, 3-H, *J* = 3.4 Hz), 7.59 t (1H, 4'-H, *J* = 7.8 Hz), 7.72 t (1H, 5'-H, *J* = 7.8 Hz), 7.82 d (1H, 6'-H, *J* = 7.8 Hz), 7.89 d (1H, 3'-H, *J* = 7.8 Hz). Found, %: C 56.78; H 3.15; N 6.20. C₁₁H₇NO₅. Calculated, %: C 56.66; H 3.03; N 6.01.

5-(3-Nitrophenyl)furan-2-carboxylic acid (IVb). Yield 43%, mp 265–267°C (from EtOH–DMF); published data: mp 265–268 [15], 244°C [13]. Found, %: C 56.38; H 3.09; N 6.17. C₁₁H₇NO₅. Calculated, %: C 56.66; H 3.03; N 6.01.

5-(4-Nitrophenyl)furan-2-carboxylic acid (IVc). Yield 68%, mp 252–253°C (from EtOH–DMF); published data [22]: mp 251–252°C.

5-(2,3-Dichlorophenyl)furan-2-carboxylic acid (IVd). Yield 51%, mp 259–260°C (from EtOH–DMF); published data [23]: mp 259–261°C. ¹H NMR spectrum, δ, ppm: 7.20 d (1H, furan, *J* = 3.4 Hz), 7.24 d (1H, furan, *J* = 3.4 Hz), 7.39 pseudotriplet (1H, 5'-H), 7.50 d (1H, 4'-H, *J* = 7.8 Hz), 7.92 d (1H, 6'-H, *J* = 6.8 Hz). Found, %: C 51.18; H 2.22. C₁₁H₆Cl₂O₃. Calculated, %: C 51.39; H 2.35.

5-(2,4-Dichlorophenyl)furan-2-carboxylic acid (IVe). Yield 49%, mp 216°C (from EtOH–DMF). Found, %: C 51.13; H 2.47; Cl 27.65. C₁₁H₆Cl₂O₃. Calculated, %: C 51.39; H 2.35; Cl 27.58.

5-(2,5-Dichlorophenyl)furan-2-carboxylic acid (IVf). Yield 56%, mp 226–227°C (from EtOH–DMF). Found, %: C 51.48; H 2.43; Cl 27.63. C₁₁H₆Cl₂O₃. Calculated, %: C 51.39; H 2.35; Cl 27.58.

5-(3,4-Dichlorophenyl)furan-2-carboxylic acid (IVg). Yield 50%, mp 237–238°C (from EtOH–DMF); published data: mp 232–235 [15], 234–238°C [23].

5-(2-Chloro-4-nitrophenyl)furan-2-carboxylic acid (IVh). Yield 70%, mp 257–258°C (from EtOH–DMF); published data [24]: mp 252–254°C. Found, %: C 49.24; H 2.30; Cl 5.15. C₁₁H₆ClNO₅. Calculated, %: C 49.37; H 2.26; N 5.23.

5-(4-Methoxy-2-nitrophenyl)furan-2-carboxylic acid (IVi). Yield 55%, mp 184–185°C (from EtOH–DMF); published data [25]: mp 182–184°C.

5-(4-Methyl-2-nitrophenyl)furan-2-carboxylic acid (IVj). Yield 45%, mp 199–200°C (from EtOH–DMF); published data [23]: mp 197–200°C.

Methyl 5-(2-fluorophenyl)furan-2-carboxylate (Va). Yield 57%, bp 148–150°C (2 mm), mp 42–43°C (from hexane). Found, %: C 65.26; H 4.04. C₁₂H₉FO₃. Calculated, %: C 65.46; H 4.12.

Methyl 5-(3-fluorophenyl)furan-2-carboxylate (Vb). Yield 46%, bp 151–153°C (2 mm), mp 82–83°C (from hexane); published data [8]: mp 82°C.

Methyl 5-(4-fluorophenyl)furan-2-carboxylate (Vc). Yield 51%, bp 148–151°C (2 mm), mp 70–71°C (from hexane); published data [8]: mp 70°C.

Methyl 5-(2-chlorophenyl)furan-2-carboxylate (Vd). Yield 56%, bp 159–163°C (2 mm), mp 67–68°C (from hexane); published data: mp 68°C [8], 68–69°C [14].

Methyl 5-(3-chlorophenyl)furan-2-carboxylate (Ve). Yield 41%, bp 173–176°C (2 mm), mp 77–78°C (from hexane); published data: mp 76°C [8], 81–82°C [14].

Methyl 5-(4-chlorophenyl)furan-2-carboxylate (Vf). Yield 45%, bp 171–175°C (2 mm), mp 130–131°C (from hexane); published data [14]: mp 131–132°C.

Methyl 5-(4-bromophenyl)furan-2-carboxylate (Vg). Yield 43%, bp 186–190°C (2 mm), mp 129–130°C (from hexane); published data [22]: mp 128–129°C.

Methyl 5-(2-trifluoromethylphenyl)furan-2-carboxylate (Vh). Yield 39%, bp 159–163°C (2 mm). Found, %: C 57.60; H 3.25. $C_{13}H_9F_3O_3$. Calculated, %: C 57.79; H 3.36.

Methyl 5-(3-trifluoromethylphenyl)furan-2-carboxylate (Vi). Yield 45%, bp 155–160°C (2 mm), mp 86–87°C (from hexane); published data [15]: mp 89°C.

Methyl 5-(2-chloro-5-trifluoromethylphenyl)furan-2-carboxylate (Vj). Yield 44%, bp 163–167°C (2 mm), mp 117–118°C (from EtOH). Found, %: C 51.09; H 2.58; Cl 11.54. $C_{13}H_8ClF_3O_3$. Calculated, %: C 51.25; H 2.65; Cl 11.64.

Methyl 5-(4-chloro-3-trifluoromethylphenyl)furan-2-carboxylate (Vk). Yield 41%, bp 180–184°C (2 mm), mp 109–110°C (from EtOH); published data [15]: mp 113°C. Found, %: C 51.03; H 2.55. $C_{13}H_8ClF_3O_3$. Calculated, %: C 51.25; H 2.65.

5-Arylfuran-2-carboxylic acids IVk–IVu (general procedure). A solution of 4.5 g (0.08 mol) of potassium hydroxide in 20 ml of ethanol was added to a solution of 0.05 mol of ester Va–Vk in 30 ml of ethanol. The mixture was heated for 30 min under reflux, diluted with an equal volume of water, and acidified with dilute (1:1) hydrochloric acid. The precipitate was filtered off, washed with water, and recrystallized from appropriate solvent.

5-(2-Fluorophenyl)furan-2-carboxylic acid (IVk). Yield 90%, mp 179–180°C (from EtOH). 1H NMR spectrum, δ , ppm: 6.88–6.92 m (1H, 4-H), 7.15–7.22 m (2H, 3-H, C_6H_4), 7.26 pseudotriplet (1H, C_6H_4), 7.30–7.38 m (1H, C_6H_4), 7.97 t (1H, C_6H_4 , $J =$

7.8 Hz). Mass spectrum: m/z 206 $[M]^+$. Found, %: C 64.27; H 3.48. $C_{11}H_7FO_3$. Calculated, %: C 64.08; H 3.42. M 206.18.

5-(3-Fluorophenyl)furan-2-carboxylic acid (IVl). Yield 92%, mp 142–143°C (from EtOH); published data [15]: mp 142–146°C.

5-(4-Fluorophenyl)furan-2-carboxylic acid (IVm). Yield 88%, mp 198–199°C (from EtOH); published data [23]: mp 199–202°C. Found, %: C 63.87; H 3.34. $C_{11}H_7FO_3$. Calculated, %: C 64.08; H 3.42.

5-(2-Chlorophenyl)furan-2-carboxylic acid (IVn). Yield 93%, mp 227–228°C (from EtOH); published data [14]: mp 230–231°C. Found, %: C 59.19; H 3.11. $C_{11}H_7ClO_3$. Calculated, %: C 59.35; H 3.17.

5-(3-Chlorophenyl)furan-2-carboxylic acid (IVo). Yield 89%, mp 172–173°C (from EtOH); published data [14]: mp 170–171°C.

5-(4-Chlorophenyl)furan-2-carboxylic acid (IVp). Yield 90%, mp 197–198°C (from EtOH); published data [22]: mp 198–201°C. 1H NMR spectrum, δ , ppm: 7.08 d (1H, 4-H, $J = 2.9$ Hz), 7.29 d (1H, 3-H, $J = 2.9$ Hz), 7.46 d (2H, 3'-H, 5'-H, $J = 8.8$ Hz), 7.81 d (2H, 2'-H, 6'-H, $J = 8.8$ Hz). Found, %: C 59.16; H 3.14. $C_{11}H_7ClO_3$. Calculated, %: C 59.35; H 3.17.

5-(4-Bromophenyl)furan-2-carboxylic acid (IVq). Yield 87%, mp 198–199°C (from EtOH); published data [22]: mp 198–200°C.

5-(2-Trifluoromethylphenyl)furan-2-carboxylic acid (IVr). Yield 85%, mp 171–172°C (from EtOH). Found, %: C 56.17; H 2.83. $C_{12}H_7F_3O_3$. Calculated, %: C 56.26; H 2.75.

5-(3-Trifluoromethylphenyl)furan-2-carboxylic acid (IVs). Yield 85%, mp 203–204°C (from EtOH); published data: mp 203–208°C [15], 208–210°C [23]. 1H NMR spectrum, δ , ppm: 7.05 d (1H, 4-H, $J = 3.4$ Hz), 7.18 d (1H, 3-H, $J = 3.4$ Hz), 7.55–7.64 m (2H, 4'-H, 5'-H), 8.00–8.07 m (2H, 2'-H, 6'-H). Mass spectrum: m/z 256 $[M]^+$. Found, %: C 55.94; H 2.71. $C_{12}H_7F_3O_3$. Calculated, %: C 56.26; H 2.75. M 256.18.

5-(2-Chloro-5-trifluoromethylphenyl)furan-2-carboxylic acid (IVt). Yield 89%, mp 230–231°C (from EtOH). Found, %: C 49.40; H 2.02; Cl 12.09. $C_{12}H_6ClF_3O_3$. Calculated, %: C 49.59; H 2.08; Cl 12.20.

5-(4-Chloro-3-trifluoromethylphenyl)furan-2-carboxylic acid (IVu). Yield 87%, mp 213–214°C (from EtOH); published data [15]: mp 213–215°C.

5-Arylfuran-2-carbonyl chlorides VIa–VIh, VIk, and VI m–VI t (general procedure). A mixture of

0.044 mol of acid **IVa–IVh**, **IVk**, or **IVm–IVt** and 3 ml of thionyl chloride in 50 ml of anhydrous benzene was heated under reflux until it became homogeneous. The mixture was cooled, and the precipitate was filtered off and washed with anhydrous hexane (compounds **VIa–VIc** and **VIh**); otherwise, the mixture was evaporated, and the residue was distilled under reduced pressure (**VI d–VIg**, **VIk**, **VI m–VI t**).

5-Aryl-*N*-[3-(2-oxopropyl)-1,2,4-thiadiazol-5-yl]furan-2-carboxamides Xa–Xk (general procedure). Acid chloride **VI b**, **VI c**, **VI e–VI h**, **VI n–VI p**, **VI r**, or **VI s**, 3.4 mmol, was dissolved in 10 ml of anhydrous acetonitrile, 0.33 g (3.4 mmol) of potassium thiocyanate was added under stirring, the mixture was heated for 30 min at 60°C, 0.34 g (3.4 mmol) of 5-methyl-1,2-oxazol-3-amine (**VIII**) was added, and the mixture was heated under stirring for 2 h and poured into water. The precipitate was filtered off, washed with several portions of water, and purified by recrystallization.

5-(3-Nitrophenyl)-*N*-[3-(2-oxopropyl)-1,2,4-thiadiazol-5-yl]furan-2-carboxamide (Xa). Yield 88%, mp 255–256°C (from EtOH–DMF). ¹H NMR spectrum, δ, ppm: 2.17 s (3H, CH₃), 3.89 s (2H, CH₂), 7.16 d (1H, 4-H, *J* = 3.3 Hz), 7.54 d (1H, 3-H, *J* = 3.3 Hz), 7.61–7.64 m (1H, 5'-H), 8.14 d (1H, 4'-H, *J* = 7.5 Hz), 8.32 d (1H, 6'-H, *J* = 7.5 Hz), 8.92 s (1H, 2'-H), 13.49 s (1H, NH). Found, %: C 51.76; H 3.28; N 14.94. C₁₆H₁₂N₄O₅S. Calculated, %: C 51.61; H 3.25; N 15.05.

5-(4-Nitrophenyl)-*N*-[3-(2-oxopropyl)-1,2,4-thiadiazol-5-yl]furan-2-carboxamide (Xb, 1:1 complex with DMF). Yield 85%, mp 229–230°C (from EtOH–DMF). ¹H NMR spectrum, δ, ppm: 2.18 s (3H, CH₃), 2.82 s and 2.95 s (3H each, DMF), 3.90 s (2H, CH₂), 7.19 br.s (1H, 4-H), 7.61 d (1H, 3-H, *J* = 3.6 Hz), 7.90 s (1H, NCHO), 8.24 d (2H, C₆H₄, *J* = 9.0 Hz), 8.28 d (2H, C₆H₄, *J* = 9.0 Hz), 13.35 s (1H, NH). Found, %: C 50.89; H 4.45; N 15.48. C₁₆H₁₂N₄O₅S·C₃H₇NO. Calculated, %: C 51.23; H 4.30; N 15.72.

5-(2-Chloro-4-nitrophenyl)-*N*-[3-(2-oxopropyl)-1,2,4-thiadiazol-5-yl]furan-2-carboxamide (Xc). Yield 83%, mp 236–237°C (from EtOH–DMF). ¹H NMR spectrum, δ, ppm: 2.18 s (3H, CH₃), 3.91 s (2H, CH₂), 7.58 d (1H, furan, *J* = 3.6 Hz), 7.65 d (1H, furan, *J* = 3.6 Hz), 8.23 d.d (1H, 5'-H, ⁴*J* = 1.2, ³*J* = 8.5 Hz), 8.32 s (1H, 3'-H), 8.77 d (1H, 6'-H, *J* = 8.5 Hz), 13.49 s (1H, NH). Found, %: C 47.19; H 2.87; N 13.69. C₁₆H₁₁ClN₄O₅S. Calculated, %: C 47.24; H 2.73; N 13.77.

5-(2-Chlorophenyl)-*N*-[3-(2-oxopropyl)-1,2,4-thiadiazol-5-yl]furan-2-carboxamide (Xd). Yield 89%, mp 175–176°C (from EtOH). ¹H NMR spectrum, δ, ppm: 2.21 s (3H, CH₃), 3.99 s (2H, CH₂), 7.37 d (1H, 4-H, *J* = 4.0 Hz), 7.41 d.t (1H, 4'-H, ⁴*J* = 1.2, ³*J* = 7.6 Hz), 7.48 d.t (1H, 5'-H, ⁴*J* = 1.2, ³*J* = 7.6 Hz), 7.54 d.d (1H, 3'-H, ⁴*J* = 1.2, ³*J* = 8.0 Hz), 7.73 d (1H, 3-H, *J* = 3.6 Hz), 8.31 d.d (1H, 6'-H, ⁴*J* = 1.2, ³*J* = 8.0 Hz), 13.63 s (1H, NH). Found, %: C 52.88; H 3.38; N 11.68. C₁₆H₁₂ClN₃O₃S. Calculated, %: C 53.12; H 3.34; N 11.61.

5-(3-Chlorophenyl)-*N*-[3-(2-oxopropyl)-1,2,4-thiadiazol-5-yl]furan-2-carboxamide (Xe). Yield 84%, mp 169–170°C (from EtOH). ¹H NMR spectrum, δ, ppm: 2.21 s (3H, CH₃), 4.05 s (2H, CH₂), 7.40 d (1H, 4-H, *J* = 3.6 Hz), 7.48 d (1H, 4'-H, *J* = 8.0 Hz), 7.53 pseudotriplet (1H, 5'-H), 7.70 d (1H, 3-H, *J* = 3.6 Hz), 7.99 d (1H, 6'-H, *J* = 7.6 Hz), 8.18 s (1H, 2'-H), 13.70 s (1H, NH). Found, %: C 53.24; H 3.22; N 11.49. C₁₆H₁₂ClN₃O₃S. Calculated, %: C 53.12; H 3.34; N 11.61.

5-(4-Chlorophenyl)-*N*-[3-(2-oxopropyl)-1,2,4-thiadiazol-5-yl]furan-2-carboxamide (Xf). Yield 78%, mp 180–181°C (from EtOH). ¹H NMR spectrum, δ, ppm: 2.20 s (3H, CH₃), 3.97 s (2H, CH₂), 7.17 d (1H, 4-H, *J* = 2.9 Hz), 7.37 d (2H, 3'-H, 5'-H, *J* = 8.8 Hz), 7.65 d (1H, 3-H, *J* = 2.9 Hz), 8.03 d (2H, 2'-H, 6'-H, *J* = 8.8 Hz), 13.54 s (1H, NH). Found, %: C 53.27; H 3.38; N 11.75. C₁₆H₁₂ClN₃O₃S. Calculated, %: C 53.12; H 3.34; N 11.61.

5-(2,4-Dichlorophenyl)-*N*-[3-(2-oxopropyl)-1,2,4-thiadiazol-5-yl]furan-2-carboxamide (Xg). Yield 80%, mp 215–216°C (from EtOH–DMF). ¹H NMR spectrum, δ, ppm: 2.20 s (3H, CH₃), 4.01 s (2H, CH₂), 7.40 d (1H, 4-H, *J* = 4.0 Hz), 7.56 d.d (1H, 5'-H, ⁴*J* = 2.0, ³*J* = 8.8 Hz), 7.69 d (1H, 3'-H, *J* = 2.0 Hz), 7.72 d (1H, 3-H, *J* = 4.0 Hz), 8.37 d (1H, 6'-H, *J* = 8.8 Hz), 13.72 s (1H, NH). Found, %: C 48.17; H 2.74; N 10.68. C₁₆H₁₁Cl₂N₃O₃S. Calculated, %: C 48.50; H 2.80; N 10.60.

5-(2,5-Dichlorophenyl)-*N*-[3-(2-oxopropyl)-1,2,4-thiadiazol-5-yl]furan-2-carboxamide (Xh). Yield 86%, mp 223–224°C (from EtOH–DMF). ¹H NMR spectrum, δ, ppm: 2.21 s (3H, CH₃), 4.00 s (2H, CH₂), 7.42–7.47 m (2H, 4-H, 4'-H), 7.58 d (1H, 3'-H, *J* = 7.5 Hz), 7.69 d (1H, 3-H, *J* = 3.6 Hz), 8.44 d (1H, 6'-H, *J* = 2.0 Hz), 13.68 s (1H, NH). Found, %: C 48.38; H 2.67; N 10.69. C₁₆H₁₁Cl₂N₃O₃S. Calculated, %: C 48.50; H 2.80; N 10.60.

5-(3,4-Dichlorophenyl)-*N*-[3-(2-oxopropyl)-1,2,4-thiadiazol-5-yl]furan-2-carboxamide (Xi). Yield

87%, mp 202–203°C (from EtOH–DMF). ¹H NMR spectrum, δ , ppm: 2.21 s (3H, CH₃), 3.99 s (2H, CH₂), 7.33 d (1H, 4-H, $J = 3.2$ Hz), 7.63 d (1H, 3-H, $J = 3.2$ Hz), 7.67 d (1H, 5'-H, $J = 8.8$ Hz), 7.98 d.d (1H, 6'-H, $^4J = 2.0$, $^3J = 8.8$ Hz), 8.33 d (1H, 2'-H, $J = 2.0$ Hz), 13.61 s (1H, NH). Found, %: C 48.24; H 2.73; N 10.72. C₁₆H₁₁Cl₂N₃O₃S. Calculated, %: C 48.50; H 2.80; N 10.60.

N-[3-(2-Oxopropyl)-1,2,4-thiadiazol-5-yl]-5-(2-trifluoromethylphenyl)furan-2-carboxamide (Xj). Yield 84%, mp 97–98°C (from EtOH). ¹H NMR spectrum, δ , ppm: 2.20 s (3H, CH₃), 3.99 s (2H, CH₂), 6.98 d (1H, 4-H, $J = 3.2$ Hz), 7.68 pseudotriplet (1H, 4'-H), 7.75–7.85 m (2H, 3-H, 5'-H), 7.87 d (1H, 3'-H, $J = 8.0$ Hz), 8.08 d (1H, 6'-H, $J = 8.0$ Hz), 13.58 s (1H, NH). Found, %: C 51.40; H 3.12; N 10.74. C₁₇H₁₂F₃N₃O₃S. Calculated, %: C 51.65; H 3.06; N 10.63.

N-[3-(2-Oxopropyl)-1,2,4-thiadiazol-5-yl]-5-(3-trifluoromethylphenyl)furan-2-carboxamide (Xk). Yield 86%, mp 233–234°C (from EtOH). ¹H NMR spectrum, δ , ppm: 2.21 s (3H, CH₃), 3.99 s (2H, CH₂), 7.36 d (1H, 4-H, $J = 3.9$ Hz), 7.65–7.73 m (3H, 3-H, C₆H₄), 8.26–8.32 m (1H, C₆H₄), 8.35 s (1H, 2'-H), 13.60 s (1H, NH). Found, %: C 51.46; H 3.10; N 10.50. C₁₇H₁₂F₃N₃O₃S. Calculated, %: C 51.65; H 3.06; N 10.63.

2-(5-Arylfuran-2-yl)-5-(2-furyl)-1,3,4-oxadiazoles XIIa–XIIe (general procedure). Acid chloride **Vla**, **Vlh**, **VIq**, **Vir**, or **VIt**, 3.4 mmol, was dissolved in 15 ml of anhydrous pyridine, 0.46 g (3.4 mmol) of 5-(2-furyl)-1H-tetrazole (**XI**) was added, and the mixture was heated for 3 h on a boiling water bath. The precipitate was filtered off, washed with several portions of water, and recrystallized from appropriate solvent.

2-(2-Furyl)-5-[5-(2-nitrophenyl)furan-2-yl]-1,3,4-oxadiazole (XIIa). Yield 73%, mp 139–140°C (from EtOH–DMF). ¹H NMR spectrum, δ , ppm: 6.75 d.d (1H, 4-H, $J = 3.6$, 1.6 Hz), 7.07 d (1H, 3'-H, $J = 3.8$ Hz), 7.33 d (1H, 3-H, $J = 3.6$ Hz), 7.47 d (1H, 4'-H, $J = 3.8$ Hz), 7.67 pseudotriplet (1H, 4''-H), 7.80 pseudotriplet (1H, 5''-H), 7.92–7.96 m (2H, 3''-H, 6''-H), 7.98 d (1H, 5-H, $J = 1.8$ Hz). Found, %: C 59.30; H 2.74; N 12.77. C₁₆H₉N₃O₅. Calculated, %: C 59.45; H 2.81; N 13.00.

2-[5-(2-Chloro-4-nitrophenyl)furan-2-yl]-5-(2-furyl)-1,3,4-oxadiazole (XIIb). Yield 77%, mp 208–209°C (from EtOH–DMF). ¹H NMR spectrum, δ , ppm: 6.76 pseudodoublet (1H, 4-H), 7.37 d (1H, 3-H,

$J = 2.4$ Hz), 7.54 d (1H, 3'-H, $J = 3.6$ Hz), 7.65 d (1H, 4'-H, $J = 3.6$ Hz), 7.98 br.s (1H, 5-H), 8.22–8.33 m (2H, 5''-H, 6''-H), 8.35 s (1H, 3''-H). Found, %: C 53.85; H 2.30; N 11.87. C₁₆H₈ClN₃O₅. Calculated, %: C 53.72; H 2.25; N 11.75.

2-[5-(4-Bromophenyl)furan-2-yl]-5-(2-furyl)-1,3,4-oxadiazole (XIIc). Yield 79%, mp 184–185°C (from EtOH–DMF). ¹H NMR spectrum, δ , ppm: 6.75 d.d (1H, 4-H, $J = 3.6$, 1.4 Hz), 7.24 d (1H, 3'-H, $J = 3.8$ Hz), 7.35 d (1H, 3-H, $J = 3.6$ Hz), 7.42 d (1H, 4'-H, $J = 3.8$ Hz), 7.62 d (2H, 3''-H, 5''-H, $J = 8.6$ Hz), 7.80 d (2H, 2''-H, 6''-H, $J = 8.6$ Hz), 7.98 d (1H, 5-H, $J = 1.4$ Hz). Found, %: C 53.55; H 2.44; N 7.79. C₁₆H₉BrN₂O₃. Calculated, %: C 53.81; H 2.54; N 7.84.

2-(2-Furyl)-5-[5-(2-trifluoromethyl)furan-2-yl]-1,3,4-oxadiazole (XII d). Yield 76%, mp 108–109°C (from EtOH). ¹H NMR spectrum, δ , ppm: 6.75 d.d (1H, 4-H, $J = 3.6$, 1.2 Hz), 7.01 d (1H, 3'-H, $J = 3.6$ Hz), 7.33 d (1H, 3-H, $J = 3.6$ Hz), 7.46 d (1H, 4'-H, $J = 3.6$ Hz), 7.66 t (1H, 4''-H, $J = 7.6$ Hz), 7.79 t (1H, 5''-H, $J = 7.6$ Hz), 7.86 d (1H, 3''-H, $J = 7.6$ Hz), 7.91 d (1H, 6''-H, $J = 7.6$ Hz), 7.98 d (1H, 5-H, $J = 1.2$ Hz). Found, %: C 58.71; H 2.78; N 8.01. C₁₇H₉F₃N₂O₃. Calculated, %: C 58.97; H 2.62; N 8.09.

2-[5-(2-Chloro-5-trifluoromethyl)furan-2-yl]-5-(2-furyl)-1,3,4-oxadiazole (XIIe). Yield 82%, mp 169–170°C (from EtOH–DMF). ¹H NMR spectrum, δ , ppm: 6.76 d.d (1H, 4-H, $J = 3.6$, 1.4 Hz), 7.36 d (1H, 3-H, $J = 3.6$ Hz), 7.50 d (1H, 4'-H, $J = 3.8$ Hz), 7.51 d (1H, 3'-H, $J = 3.8$ Hz), 7.71 d.d (1H, 4''-H, $^3J = 8.4$, $^4J = 1.6$ Hz), 7.81 d (1H, 3''-H, $J = 8.4$ Hz), 7.99 d (1H, 5-H, $J = 1.4$ Hz), 8.18 d (1H, 6''-H, $J = 1.6$ Hz). Found, %: C 53.78; H 2.20; N 7.48. C₁₇H₈ClF₃N₂O₃. Calculated, %: C 53.63; H 2.12; N 7.36.

3-Substituted 6-(5-arylfuran-2-yl)[1,2,4]triazolo[3,4-b][1,3,4]thiadiazoles XIVa–XIVn (general procedure). A mixture of 5 mmol of triazole **XIIIa–XIIIe**, 5 mmol of acid **IVa–IVc**, **IVg**, **IVm**, **IVn**, **IVp**, or **IVs**, and 7 ml of phosphoryl chloride was heated under reflux until hydrogen chloride no longer evolved and for 3 h more. The mixture was cooled and poured onto 100 g of crushed ice, an aqueous solution of ammonia was added to pH 8 under effective external cooling, and the precipitate was filtered off, washed on a filter with warm water (up to 500 ml), dried in air, and recrystallized from appropriate solvent.

3-(2-Methylfuran-3-yl)-6-[5-(2-nitrophenyl)furan-2-yl][1,2,4]triazolo[3,4-b][1,3,4]thiadiazole (XIVa). Yield 80%, mp 219–220°C (from EtOH–DMF). ¹H NMR spectrum, δ , ppm: 2.70 s (3H, CH₃),

7.11 d (1H, 4-H, $J = 2.0$ Hz), 7.25 d (1H, 3'-H, $J = 4.0$ Hz), 7.65 d (1H, 4'-H, $J = 4.0$ Hz), 7.67–7.71 m (2H, 5-H, 4''-H), 7.80 pseudotriplet (1H, 5''-H), 7.93–7.98 m (2H, 3''-H, 6''-H). Found, %: C 54.30; H 2.72; N 17.97. $C_{18}H_{11}N_5O_4S$. Calculated, %: C 54.96; H 2.82; N 17.80.

6-[5-(2-Nitrophenyl)furan-2-yl]-3-phenyl[1,2,4]-triazolo[3,4-*b*][1,3,4]thiadiazole (XIVb). Yield 85%, mp 194–195°C (from EtOH–DMF). 1H NMR spectrum, δ , ppm: 7.33 d (1H, 3-H, $J = 3.9$ Hz), 7.55–7.65 m (3H, H_{arom}), 7.72 t (1H, H_{arom} , $J = 7.8$ Hz), 7.75 d (1H, 4-H, $J = 3.9$ Hz), 7.84 t (1H, H_{arom} , $J = 7.8$ Hz), 8.01 t (2H, H_{arom} , $J = 8.8$ Hz), 8.27 d (2H, H_{arom} , $J = 7.8$ Hz). Found, %: C 58.42; H 2.70; N 17.77. $C_{19}H_{11}N_5O_3S$. Calculated, %: C 58.61; H 2.85; N 17.99.

3-(2-Methylfuran-3-yl)-6-[5-(3-nitrophenyl)furan-2-yl][1,2,4]triazolo[3,4-*b*][1,3,4]thiadiazole (XIVc). Yield 77%, mp 262–263°C (from EtOH–DMF). 1H NMR spectrum, δ , ppm: 2.70 s (3H, CH_3), 7.20 d (1H, 4-H, $J = 1.6$ Hz), 7.58 d (1H, 3'-H, $J = 3.8$ Hz), 7.64 d (1H, 4'-H, $J = 3.8$ Hz), 7.69 d (1H, 5-H, $J = 1.6$ Hz), 7.79 t (1H, 5''-H, $J = 8.0$ Hz), 8.22 d (1H, 4''-H, $J = 8.0$ Hz), 8.27 d (1H, 6''-H, $J = 8.0$ Hz), 8.60 s (1H, 2''-H). Found, %: C 54.72; H 2.88; N 17.61. $C_{18}H_{11}N_5O_4S$. Calculated, %: C 54.96; H 2.82; N 17.80.

3-(2-Methylfuran-3-yl)-6-[5-(4-nitrophenyl)furan-2-yl][1,2,4]triazolo[3,4-*b*][1,3,4]thiadiazole (XIVd). Yield 75%, mp 294–295°C (from EtOH–DMF). 1H NMR spectrum, δ , ppm: 2.71 s (3H, CH_3), 7.14 br.s (1H, 4-H), 7.62 d (1H, 3'-H, $J = 3.2$ Hz), 7.66–7.71 m (2H, 5-H, 4'-H), 8.12 d (2H, 3''-H, 5''-H, $J = 8.4$ Hz), 8.33 d (2H, 2''-H, 6''-H, $J = 8.4$ Hz). Found, %: C 55.12; H 2.90; N 17.69. $C_{18}H_{11}N_5O_4S$. Calculated, %: C 54.96; H 2.82; N 17.80.

3-(2-Furyl)-6-[5-(4-nitrophenyl)furan-2-yl]-[1,2,4]triazolo[3,4-*b*][1,3,4]thiadiazole (XIVe). Yield 81%, mp 300–301°C (from EtOH–DMF). 1H NMR spectrum, δ , ppm: 6.78 d.d (1H, 4-H, $J = 3.6, 1.4$ Hz), 7.34 d (1H, 3'-H, $J = 3.6$ Hz), 7.64 d (1H, 3-H, $J = 3.6$ Hz), 7.73 d (1H, 4'-H, $J = 3.6$ Hz), 7.97 d (1H, 5-H, $J = 1.4$ Hz), 8.14 d (2H, 3''-H, 5''-H, $J = 8.8$ Hz), 8.35 d (2H, 2''-H, 6''-H, $J = 8.8$ Hz). Found, %: C 53.61; H 2.48; N 18.53. $C_{17}H_9N_5O_4S$. Calculated, %: C 53.83; H 2.39; N 18.46.

6-[5-(2-Chlorophenyl)furan-2-yl]-3-phenyl[1,2,4]-triazolo[3,4-*b*][1,3,4]thiadiazole (XIVf). Yield 84%, mp 235–236°C (from EtOH–DMF). 1H NMR spectrum, δ , ppm: 7.38 d (1H, 3-H, $J = 2.9$ Hz), 7.43 t (1H,

H_{arom} , $J = 7.8$ Hz), 7.50 t (1H, H_{arom} , $J = 7.8$ Hz), 7.55–7.62 m (4H, H_{arom}), 7.65 d (1H, 4-H, $J = 2.9$ Hz), 7.91 d (1H, H_{arom} , $J = 6.8$ Hz), 8.25 d (2H, H_{arom} , $J = 6.8$ Hz). Found, %: C 59.97; H 2.91; N 14.87. $C_{19}H_{11}ClN_4OS$. Calculated, %: C 60.24; H 2.93; N 14.79.

6-[5-(2-Chlorophenyl)furan-2-yl]-3-(2-methylfuran-3-yl)[1,2,4]triazolo[3,4-*b*][1,3,4]thiadiazole (XIVg). Yield 70%, mp 174–175°C (from EtOH–DMF). 1H NMR spectrum, δ , ppm: 2.67 s (3H, CH_3), 7.12 br.s (1H, 4-H), 7.42 d (1H, 3'-H, $J = 3.2$ Hz), 7.46 t (1H, 4''-H, $J = 7.6$ Hz), 7.53 t (1H, 5''-H, $J = 7.6$ Hz), 7.63 d (1H, 3''-H, $J = 8.0$ Hz), 7.71 d (1H, 4'-H, $J = 3.2$ Hz), 7.78 br.s (1H, 5-H), 7.94 d (1H, 6''-H, $J = 7.6$ Hz). Found, %: C 56.68; H 2.92; N 14.52. $C_{18}H_{11}ClN_4O_2S$. Calculated, %: C 56.47; H 2.90; N 14.64.

3-Benzyl-6-[5-(2-chlorophenyl)furan-2-yl][1,2,4]-triazolo[3,4-*b*][1,3,4]thiadiazole (XIVh). Yield 74%, mp 185–186°C (from EtOH–DMF). 1H NMR spectrum, δ , ppm: 4.43 s (2H, CH_2), 7.22 t (1H, H_{arom} , $J = 6.8$ Hz), 7.27–7.48 m (8H, H_{arom} , 3-H, 4-H), 7.52 d (1H, H_{arom} , $J = 7.8$ Hz), 7.94 d (1H, H_{arom} , $J = 7.8$ Hz). Found, %: C 60.78; H 3.12; N 14.02. $C_{20}H_{13}ClN_4OS$. Calculated, %: C 61.15; H 3.34; N 14.26.

6-[5-(4-Chlorophenyl)furan-2-yl]-3-propyl[1,2,4]-triazolo[3,4-*b*][1,3,4]thiadiazole (XIVi). Yield 60%, mp 192–193°C (from EtOH–DMF). 1H NMR spectrum, δ , ppm: 1.10 t (3H, CH_3 , $J = 7.8$ Hz), 1.91–1.97 m (2H, CH_2CH_3), 3.05 t (2H, 3- CH_2 , $J = 7.8$ Hz), 7.04 d (1H, 3-H, $J = 3.4$ Hz), 7.31 d (1H, 4-H, $J = 3.4$ Hz), 7.43 d (2H, 3'-H, 5'-H, $J = 8.3$ Hz), 7.78 d (2H, 2'-H, 6'-H, $J = 8.3$ Hz). Found, %: C 55.58; H 3.72; N 16.08. $C_{16}H_{13}ClN_4OS$. Calculated, %: C 55.73; H 3.80; N 16.25.

6-[5-(4-Chlorophenyl)furan-2-yl]-3-(2-methylfuran-3-yl)[1,2,4]triazolo[3,4-*b*][1,3,4]thiadiazole (XIVj). Yield 78%, mp 263–264°C (from EtOH–DMF). 1H NMR spectrum, δ , ppm: 2.70 s (3H, CH_3), 7.13 br.s (1H, 4-H), 7.32 d (1H, 3'-H, $J = 3.2$ Hz), 7.52 d (2H, 3''-H, 5''-H, $J = 8.2$ Hz), 7.60 d (1H, 4'-H, $J = 3.2$ Hz), 7.69 br.s (1H, 5-H), 7.86 d (2H, 2''-H, 6''-H, $J = 8.2$ Hz). Found, %: C 56.68; H 2.82; N 14.52. $C_{18}H_{11}ClN_4O_2S$. Calculated, %: C 56.47; H 2.90; N 14.64.

6-[5-(4-Chlorophenyl)furan-2-yl]-3-(2-furyl)-[1,2,4]triazolo[3,4-*b*][1,3,4]thiadiazole (XIVk). Yield 73%, mp 244–245°C (from EtOH–DMF). 1H NMR spectrum, δ , ppm: 6.77 d.d (1H, 4-H, $J = 3.6, 1.4$ Hz),

7.31–7.34 m (2H, 3'-H, 4'-H), 7.52 d (2H, 3''-H, 5''-H, $J = 8.4$ Hz), 7.64 d (1H, 3-H, $J = 3.6$ Hz), 7.88 d (2H, 2''-H, 6''-H, $J = 8.4$ Hz), 7.96 d (1H, 5-H, $J = 1.4$ Hz). Found, %: C 55.07; H 2.55; N 15.32. $C_{17}H_9ClN_4O_2S$. Calculated, %: C 55.37; H 2.46; N 15.19.

6-[5-(4-Fluorophenyl)furan-2-yl]-3-(2-furyl)-[1,2,4]triazolo[3,4-*b*][1,3,4]thiadiazole (XIVl). Yield 79%, mp 253–254°C (from EtOH–DMF). 1H NMR spectrum, δ , ppm: 6.77 d.d (1H, 4-H, $J = 3.6, 1.2$ Hz), 7.24–7.35 m (4H, 3'-H, 3''-H, 4'-H, 5''-H), 7.62 d (1H, 3-H, $J = 3.6$ Hz), 7.92 d.d (2H, 2''-H, 6''-H, $J_{HH} = 8.8, J_{HF} = 5.6$ Hz), 7.96 d (1H, 5-H, $J = 1.2$ Hz). Found, %: C 57.80; H 2.66; N 15.75. $C_{17}H_9FN_4O_2S$. Calculated, %: C 57.95; H 2.57; N 15.90.

3-(2-Furyl)-6-[5-(3-trifluoromethyl)furan-2-yl]-[1,2,4]triazolo[3,4-*b*][1,3,4]thiadiazole (XIVm). Yield 70%, mp 225–226°C (from EtOH–DMF). 1H NMR spectrum, δ , ppm: 6.81 br.s (1H, 4-H), 7.32 br.s (1H, 3-H), 7.55 d (1H, 3'-H, $J = 3.9$ Hz), 7.71 d (1H, 4'-H, $J = 3.9$ Hz), 7.74–7.80 m (2H, C_6H_4), 8.03 s (1H, 5-H), 8.12–8.16 m (2H, C_6H_4). Found, %: C 55.09; H 2.03; N 13.17. $C_{18}H_9F_3N_4O_2S$. Calculated, %: C 53.73; H 2.25; N 13.92.

3-Benzyl-6-[5-(3,4-dichlorophenyl)furan-2-yl]-[1,2,4]triazolo[3,4-*b*][1,3,4]thiadiazole (XIVn). Yield 79%, mp 265–266°C (from EtOH–DMF). 1H NMR spectrum, δ , ppm: 4.42 s (2H, CH_2), 7.22 t (1H, *p*-H, C_6H_5 , $J = 7.8$ Hz), 7.26–7.38 m (4H, C_6H_5), 7.42 d (1H, 3-H, $J = 2.9$ Hz), 7.60 d (1H, C_6H_3 , $J = 7.8$ Hz), 7.76 d.d (1H, C_6H_3 , $J = 8.8, 1.9$ Hz), 7.90 br.s (1H, 4-H), 7.99 d (1H, C_6H_3 , $J = 1.9$ Hz). Found, %: C 55.99; H 2.85; N 12.90. $C_{20}H_{12}Cl_2N_4OS$. Calculated, %: C 56.22; H 2.83; N 13.11.

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