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Synthesis of Heterocycles Based on Arylation Products of Unsaturated Compounds: XVII.* Arylation of 2-Acetylfuran and Synthesis of 3-R-6-(5-Aryl-2-furyl)-7*H*-[1,2,4]triazolo[3,4-*b*][1,3,4]thiadiazines

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Abstract—Reaction of 2-acetylfuran with arenediazonium chlorides under Meerwein reaction conditions led to the formation of 5-aryl-2-acetylfurans. The bromination of these compounds gave 2-bromo-1-(5-aryl-2-furyl)-ethanones that reacted with 4-amino-4*H*-5-R-1,2,4-triazole-3-thiols to form 3-R-6-(5-aryl-2-furyl)-7*H*-[1,2,4]triazolo[3,4-*b*][1,3,4]thiadiazines.

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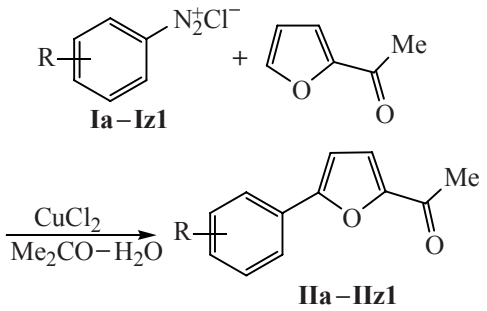
Arylfuran structural fragments are known to be included into the composition of many natural and synthetic substances exhibiting a versatile biological activity [2–6]. Based on the compounds of this class pharmaceuticals were prepared (nitrafudan, dandrolene, clodanolene, azimilide etc.) [7,8]. A convenient procedure for preparation of arylfuran compounds is a catalytic arylation of furan derivatives with arenediazonium salts under the conditions of Meerwein reaction [3,9,]. The furfural arylation is well understood. Thus obtained 5-aryl-furfurals are most commonly used for designing molecules with arylfuran fragments. Arylation of 2-acetylfuran is less investigated although the synthetic potential of 5-aryl-2-acetylfurans is high [11–15].

In this connection in the present study we examined in detail the arylation of the 2-acetylfuran applying arenediazonium salts with various substituents in the aromatic ring. Arenediazonium chlorides **Ia–Iz1** reacted with the acetylfuran in the presence of $CuCl_2$ catalyst providing 5-aryl-2-acetylfurans **IIa– IIz1**. The majority of compounds **IIa–IIz1** were obtained in yields considered to be high for Meerwein reaction (40–70%). In this reaction arenediazonium salts with electron-donor substituents and the benzyldiazonium chloride are less reactive. 2,5-Diarylfurans formed as side products [13].

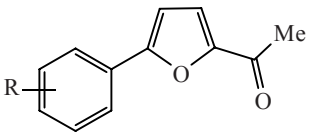
* For communcation XVI, see [1].

In keeping with the results obtained 5-aryl-2-acetylfurans **IIa–IIz1** may be regarded as accessible reagents for building up molecules with the arylfuryl fragment utilizing the synthetic opportunities of the acetyl group. The bromination of compounds **IIj,III, IIr–IIu**, and **IIw** provided a series of 2-bromo-1-(5-aryl-2-furyl)ethanones **IIIa–IIIg**.

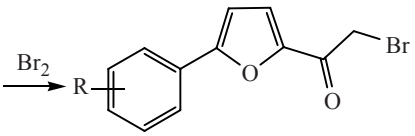


R = H (**a**), 4-Me (**b**), 4-s-Bu (**c**), 4-*i*-Pr (**d**), 2-F (**e**), 3-F (**f**), 4-F (**g**), 2-Cl (**h**), 3-Cl (i), 4-Cl (**j**), 3-NO_2 (**k**), 4-NO_2 (**l**), 2-CF_3 (**m**), 3-CF_3 (**n**), 2-COOMe (**o**), 3-F-4-Cl (**p**), 2,3-Cl_2 (**q**), 2,4-Cl_2 (**r**), 2,5-Cl_2 (**s**), 3,4-Cl_2 (**t**), 3,5-Cl_2 (**u**), 3-Cl-4-Me (**v**), 2-Cl-4-NO_2 (**w**), 2-Cl-5-CF_3 (**x**), 4-Cl-3-CF_3 (**y**), 3,5-$(CF_3)_2$ (**z**), 2-Br-4-Me (**z1**).

We examined α-bromoketones **IIIc–IIIg** with respect to a reaction with S,N-binucleophilic reagents,



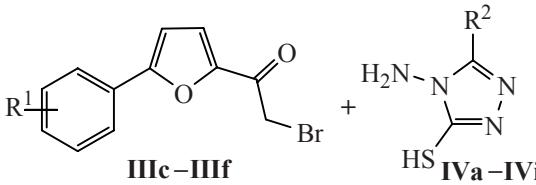
IIj, IIl, IIr–IIu, IIw



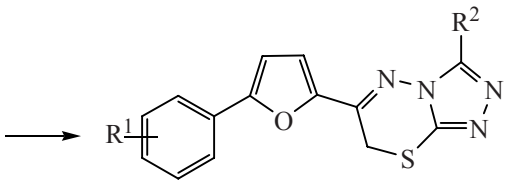
IIIa–IIIg

III, R = 4-Cl (**a**), 4-NO_2 (**b**), 2,4-Cl_2 (**c**), 2,5-Cl_2 (**d**), 3,4-Cl_2 (**e**), 3,5-Cl_2 (**f**), 2-Cl-4-NO_2 (**g**).

4-amino-1,2,4-triazole-3-thiol **IVa–IVi**. 5-Substituted 4-amino-4*H*-1,2,4-triazole-3-thiols are convenient reagents for the synthesis of fused nitrogen and sulfur heterocycles [16, 17]. In particular, these compounds react with α-bromoacetophenones and some other α-bromoketones to form a thiadiazine ring [18, 19]. We established that all the reagents **IVa–IVi** cleanly reacted with α-bromoketones **IIIc–IIIg** in anhydrous ethanol affording 3-substituted 6-(5-aryl-2-furyl)-7*H*-[1,2,4]-triazolo-[3,4-*b*][1,3,4]thiadiazines **Va–Vk** in high yields.



IIIc–IIIf **IVa–IVi**



Va–Vk

IV, R^2 = Me (**a**), Et (**b**), Pr (**c**), 2-furyl (**d**), 2-Me-3-furyl (**e**), $PhCH_2$ (**f**), 2-BrC_6H_4 (**g**), 4-BrC_6H_4 (**h**), 4-$MeOC_6H_4CH_2$ (**i**); **V**, R^1 = 2,4-Cl_2, R^2 = Et (**a**); R^1 = 3,4-Cl_2, R^2 = 4-$MeOC_6H_4CH_2$ (**b**); R^1 = 3,4-Cl_2, R^2 = 2-furyl (**c**); R^1 = 3,5-Cl_2, R^2 = Me (**d**); R^1 = 3,5-Cl_2, R^2 = 2-furyl (**e**); R^1 = 2,5-Cl_2, R^2 = Et (**f**); R^1 = 2,5-Cl_2, R^2 = Pr (**g**); R^1 = 2,5-Cl_2, R^2 = $PhCH_2$ (**h**); R^1 = 2,5-Cl_2, R^2 = 2-BrC_6H_4 (**i**); R^1 = 2,5-Cl_2, R^2 = 4-BrC_6H_4 (**j**); R^1 = 2,5-Cl_2, R^2 = 2-Me-3-furyl (**k**).

Note that many triazolothiadiazines exhibit a biological activity [19,20]. The described reaction makes it possible to synthesize 3-substituted 1,2,4-triazolo[3,4-*b*][1,3,4]-thiadiazines with arylfuran fragments in the position *6* promising for the screening for biological activity.

Hence the 5-aryl-2-acetylfurans are convenient reagents for building up 1,2,4-triazolo[3,4-*b*][1,3,4]thiadiazines.

EXPERIMENTAL

^{1}H NMR spectra of compounds **II** were registered on a spectrometer Varian Mercury (400 MHz) in DMSO-d_6; of compounds **V**, on a spectrometer Bruker DRX-500 (500 MHz) in a mixture DMSO-d_6–CCl_4, 1:3, internal reference TMS.

Compounds **IVa–IVi** were obtained by procedures [21]. **IVe**: yield 70%, mp 162–163°C (ethanol–water); **IVh**: yield 63%, mp 198–199°C (ethanol). Triazoles **IVb–IVd, IVf**, and **IVi** were described in [17].

Synthesis of 5-aryl-2-acetylfurans IIa–IIz1. To a solution of 0.2 mol (22 g) of 2-acetylfuran and 2 g of $CuCl_2 \cdot 2H_2O$ in 80 ml of acetone was added dropwise at stirring a cooled to 0–5°C solution of arenediazonium chloride **Ia–Iz1** obtained by diazotization (HCl, $NaNO_2$) of 0.21 mol of the corresponding aromatic amine. The temperature of the reaction mixture was maintained in the range 20–30°C to keep the nitrogen evolution at a rate 2–3 babble per second. The reaction was carried out to the end of nitrogen liberation. Then 200 ml of water was added, the precipitate was filtered off or the product was isolated by a vacuum distillation. Solid substances were recrystallized.

2-Acetyl-5-phenylfuran (IIa). Yield 39%, bp 143°C (2 mm Hg). Found, %: C 77.26; H 5.38. $C_{12}H_{10}O_2$. Calculated, %: C 77.40; H 5.41.

2-Acetyl-5-(4-methylphenyl)furan (IIb). Yield 28%, bp 158°C (2 mm Hg). Found, %: C 77.75; H 5.95. $C_{13}H_{12}O_2$. Calculated, %: C 77.98; H 6.04.

2-Acetyl-5-(4-*sec*-butylphenyl)furan (IIc). Yield 30%, bp 183°C (2 mm Hg), n_D^{20} 1.5750. Found, %: C 79.11; H 7.31. $C_{16}H_{18}O_2$. Calculated, %: C 79.31; H 7.49.

2-Acetyl-5-(4-isopropylphenyl)furan (IId). Yield 50%, bp 175°C (2 mm Hg), n_D^{20} 1.5861. Found, %: C 78.71; H 6.98. $C_{15}H_{16}O_2$. Calculated, %: C 78.92; H 7.06.

2-Acetyl-5-(2-fluorophenyl)furan (IIe). Yield 50%, bp 147°C (2 mm Hg), mp 84–85°C (hexane). Found, %: C 70.47; H 4.52. $C_{12}H_9FO_2$. Calculated, %: C 70.58; H 4.44.

2-Acetyl-5-(3-fluorophenyl)furan (IIf). Yield 43%, bp 149°C (2 mm Hg), mp 50–51°C (hexane). Found, %: C 70.61; H 4.57. $C_{12}H_9FO_2$. Calculated, %: C 70.58; H 4.44.

2-Acetyl-5-(4-fluorophenyl)furan (IIg). Yield 45%, bp 147°C (2 mm Hg). ^{1}H NMR spectrum, δ, ppm: 2.51 s (3H, CH_3CO), 7.18 d (1H, H^3, Fu, *J* 3.2 Hz), 7.28–7.36 m (2H, $H^{3,5}$, C_6H_4), 7.50 d (1H, H^4, Fu, *J* 3.2 Hz), 7.85–7.90 m (2H, $H^{2,6}$, C_6H_4). Found, %: C 70.04; H 4.80. $C_{12}H_9FO_2$. Calculated, %: C 70.58; H 4.44.

2-Acetyl-5-(2-chlorophenyl)furan (IIh). Yield 49%, bp 156–160°C (2 mm Hg), mp 76–77°C (hexane). Found, %: C 65.19; H 4.04; Cl 15.93. $C_{12}H_9ClO_2$. Calculated, %: C 65.32; H 4.11; Cl 16.07.

2-Acetyl-5-(3-chlorophenyl)furan (IIi). Yield 52%, bp 173°C (2 mm Hg), n_D^{20} 1.6331. Found, %: C 65.40; H 4.17. $C_{12}H_9ClO_2$. Calculated, %: C 65.32; H 4.11.

2-Acetyl-5-(4-chlorophenyl)furan (IIj). Yield 55%, bp 150°C (2 mm Hg), mp 63–64°C (hexane) (mp 60.5–61.5°C [11], 62–64°C [23]).

2-Acetyl-5-(3-nitrophenyl)furan (IIk). Yield 44%, bp 210°C (2 mm Hg), mp 116–117°C (ethanol) (mp 118°C [24]). ^{1}H NMR spectrum, δ, ppm: 2.50 s (3H, CH_3CO), 7.47 d (1H, H^3 Fu, *J* 3.6 Hz), 7.59 d (1H, H^4, Fu, *J* 3.6 Hz), 7.74–7.79 m (1H, H^5 C_6H_4), 8.20–8.27 m (2H, $H^{4,6}$ C_6H_4), 8.53 s (1H, H^2 C_6H_4). Found, %: C 62.19; H 3.85; N 5.95. $C_{12}H_9NO_4$. Calculated, %: C 62.34; H 3.92; N 6.06.

2-Acetyl-5-(4-nitrophenyl)furan (IIl). Yield 70%, mp 164–165°C (ACOH) (mp 164.5–165.5°C[11], 168–169°C [24]).

2-Acetyl-5-(2-trifluoromethylphenyl)furan (IIm). Yield 51%, bp 165–166°C (2 mm Hg), mp 61–62°C (hexane). ^{1}H NMR spectrum, δ, ppm: 2.46 s (3H, CH_3), 7.01 d (1H, H^3, Fu, *J* 3.6 Hz), 7.51 d (1H, H^4, Fu, *J* 3.6 Hz), 7.70 pseudo t (1H, C_6H_4), 7.81 pseudo t (1H, C_6H_4), 7.87–7.92 m (2H, C_6H_4). Found, %: C 61.37; H 3.42. $C_{13}H_9F_3O_2$. Calculated, %: C 61.42; H 3.57.

2-Acetyl-5-(3-trifluoromethylphenyl)furan (IIn). Yield 43%, bp 152°C (2mm Hg), mp 99–100°C (hexane). ^{1}H NMR spectrum, δ, ppm: 2.50 C (3H, CH_3CO), 7.42 d (1H, H^3, Fu, *J* 3.4 Hz), 7.57 d (1H, H^4, Fu, *J* 3.4 Hz), 7.68–7.78 m (2H, C_6H_4), 8.12–8.15 m (2H, C_6H_4). Found, %: C 61.29; H 3.49. $C_{13}H_9F_3O_2$. Calculated, %: C 61.42; H 3.57.

Methyl 2-(5-acetyl-2-furyl)benzoate (IIo). Yield 48%, mp 78–79°C (ethanol). Found, %: C 68.69; H 4.87. $C_{14}H_{12}O_4$. Calculated, %: C 68.85; H 4.95.

2-Acetyl-5-(3-fluoro-4-chlorophenyl)furan (IIp). Yield 60%, bp 171–175°C (2 mm Hg), mp 83–84°C (hexane). Found, %: C 60.21; H 3.29; Cl 14.98. $C_{12}H_8ClFO_2$. Calculated, %: C 60.40; H 3.38; Cl 14.86.

2-Acetyl-5-(2,3-dichlorophenyl)furan (IIq). Yield 60%, mp 90–91°C (ethanol). Found, %: C 56.25; H 3.09. $C_{12}H_8Cl_2O_2$. Calculated, %: C 56.50; H 3.16.

2-Acetyl-5-(2,4-dichlorophenyl)furan (IIr). Yield 45%, mp 163–164°C (ethanol) Found, %: C 56.62; H 3.18; Cl 27.58. $C_{12}H_8Cl_2O_2$. Calculated, %: C 56.50; H 3.16; Cl 27.80.

2-Acetyl-5-(2,5-dichlorophenyl)furan (IIs). Yield 50%, mp 100–101°C (ethanol) (mp 100–101°C [25]).

2-Acetyl-5-(3,4-dichlorophenyl)furan (IIt). Yield 56%, mp 116–117°C (ethanol). Found, %: C 56.41; H 3.07. $C_{12}H_8Cl_2O_2$. Calculated, %: C 56.50; H 3.16.

2-Acetyl-5-(3,5-dichlorophenyl)furan (IIu). Yield 56%, mp 149–150°C (ethanol). Found, %: C 56.41; H 3.07. $C_{12}H_8Cl_2O_2$. Calculated, %: C 56.50; H 3.16.

2-Acetyl-5-(4-methyl-3-chlorophenyl)furan (IIv). Yield 51%, mp 85–86°C (ethanol). ^{1}H NMR spectrum, δ, ppm: 2.36 s (3H, CH_3), 2.46 C (3H, CH_3CO), 7.26 d (1H, H^3, Fu, *J*.8 Hz), 7.46 d (1H, H^5, C_6H_3, *J* 7.8 Hz), 7.55 d (1H, H^4, Fu, *J* 3.8 Hz), 7.71 d (1H, H^6, C_6H_3, *J*.8 Hz), 7.88 s (1H, H^2, C_6H_3). Found, %: C 66.40; H 4.66; Cl 14.98. $C_{13}H_{11}ClO_2$. Calculated, %: C 66.53; H 4.72; Cl 15.11.

2-Acetyl-5-(4-nitro-2-chlorophenyl)furan (IIw). Yield 62%, mp 129–130°C (ethanol). ^{1}H NMR spectrum, δ, ppm: 2.52 s (3H, CH_3CO), 7.58 d (1H, H^3, Fu, *J* 4.0 Hz), 7.64 d (1H, H^4, Fu, *J* 4.0 Hz), 8.19 d (1H, H^6, C_6H_3, *J* 8.8 Hz), 8.31 d.d (1H, H^5, C_6H_3, ^3J 8.8, ^4J 2.0 Hz), 8.42 d (1H, H^3, C_6H_3, *J* 2.0 Hz). Found, %: C 54.33; H 2.94; N 5.35. $C_{12}H_8ClNO_4$. Calculated, %: C 54.26; H 3.04; N 5.27.

2-Acetyl-5-(5-trifluoromethyl-2-chlorophenyl)-furan (IIx). Yield 52%, mp 85–86°C (ethanol). ^{1}H NMR spectrum, δ, ppm: 2.51 s (3H, CH_3CO), 7.42 d (1H, H^3, Fu, *J* 3.6 Hz), 7.60 d (1H, H^4, Fu, *J* 3.6 Hz), 7.80 d.d (1H, H^4 C_6H_3, ^3J 8.6, ^4J 2.0 Hz), 7.85 d (1H, H^3, C_6H_3, *J* 8.6 Hz), 8.13 d (1H, H^6, C_6H_3, *J* 2.0 Hz). Found, %: C 53.92; H 2.82. $C_{13}H_8ClF_3O_2$. Calculated, %: C 54.09; H 2.79.

2-Acetyl-5-(3-trifluoromethyl-4-chlorophenyl)-furan (IIy). Yield 55%, mp 121–122°C (ethanol). ^{1}H NMR spectrum, δ, ppm: 2.50 s (3H, CH_3CO), 7.45 d (1H, H^3, Fu, *J* 3.6 Hz), 7.58 d (1H, H^4, Fu, *J* 3.6 Hz), 7.82 d (1H, H^5, C_6H_3, *J* 8.6 Hz), 8.10 d (1H, H^6, C_6H_3, *J* 8.6 Hz), 8.17 s (1H, H^2, C_6H_3). Found, %: C 53.79; H 2.68. $C_{13}H_8ClF_3O_2$. Calculated, %: C 54.09; H 2.79.

2-Acetyl-5-[3,5-bis(trifluoromethyl)phenyl]-furan (IIz). Yield 60%, mp 116–117°C (ethanol). Found, %: C

52.04; H 2.41. $C_{14}H_8F_6O_2$. Calculated, %: C 52.19; H 2.50.

2-Acetyl-5-(2-bromo-4-methylphenyl)furan (IIz1). Yield 43%, mp 74–75°C (hexane). Found, %: C 55.82; H 3.80; Br 28.33. $C_{13}H_{11}BrO_2$. Calculated, %: C 55.94; H 3.97; Br 28.63.

2-Bromo-1-(5-aryl-2-furyl)ethanones IIIa–IIIe. To a solution of 0.05 mol of an appropriate ketone **IIj,III, IIr–IIu**, and **IIw** in glacial acetic was gradually added at vigorous stirring 0.05 mol (8 g) of bromine. After the decoloration of the reaction mixture the separated precipitate was filtered off, washed with ethanol, and recrystallized.

2-Bromo-1-[5-(4-chlorophenyl)-2-furyl]ethanone (IIIa). Yield 66%, mp 111–112°C (benzene) (mp 112–113°C [12]).

2-Bromo-1-[5-(4-nitrophenyl)-2-furyl]ethanone (IIIb). Yield 63%, mp 161–162°C (AcOH) (mp 160–161°C [12]).

2-Bromo-1-[5-(2,4-dichlorophenyl)-2-furyl]-ethanone (IIIc). Yield 46%, mp 101–102°C (AcOH). Found, %: Cl+Br.22. $C_{12}H_7BrCl_2O_2$. Calculated, %: Cl + Br.15.

2-Bromo-1-[5-(2,5-dichlorophenyl)-2-furyl]-ethanone (IIId). Yield 41%, mp 125–126°C (AcOH). Found, %: Cl+Br.96. $C_{12}H_7BrCl_2O_2$. Calculated, %: Cl+Br.15.

2-Bromo-1-[5-(3,4-dichlorophenyl)-2-furyl]-ethanone (IIIe). Yield 41%, mp 97–98°C (AcOH). Found, %: Cl+Br44.89. $C_{12}H_7BrCl_2O_2$. Calculated, %: Cl + Br.15.

2-Bromo-1-[5-(3,5-dichlorophenyl)-2-furyl]-ethanone (IIIg). Yield 41%, mp 104–105°C (AcOH). Found, %: Cl+Br.94. $C_{12}H_7BrCl_2O_2$. Calculated, %: Cl + Br45.15.

2-Bromo-1-[5-(4-nitro-2-chlorophenyl)-2-furyl]-ethanone (IIIg). Yield 54%, mp 162–163°C (AcOH). Found, %: Cl + Br.30. $C_{12}H_7BrClNO_4$. Calculated, %: Cl + Br.48.

3-R-6-(5-Aryl-2-furyl)-7*H*-[1,2,4]triazolo-[3,4-*b*][1,3,4]thiadiazines Va–Vk. To a hot solution of 3 mmol of an appropriate 2-bromo-1-(5-aryl-2-furyl)ethanone **IIIc–IIIf** in 15 ml of anhydrous ethanol was added a solution of 3 mmol of triazole **IVa–IVi** in 15 ml of anhydrous ethanol. The mixture was heated till the start of precipitation. On cooling the solution was neutralized with aqueous ammonia, the precipitate was filtered off and recrystallized from a mixture ethanol–DMF.

6-[5-(2,4-Dichlorophenyl)-2-furyl]-3-ethyl-7*H*-[1,2,4]triazolo[3,4-*b*][1,3,4]thiadiazine (Va). Yield 75%, mp 238–239°C. ^{1}H NMR spectrum, δ, ppm: 1.39 t (3H, CH_3, *J* 7.8 Hz), 2.94 q (2H, CH_2, *J* 7.8 Hz), 4.23 s (2H, CH_2 thiadiazine), 7.33 d (1H, H^3, Fu, *J*.6 Hz), 7.44 d (1H, H^5, C_6H_3, *J* 7.8 Hz), 7.48 d (1H, H^4, Fu, *J* 3.6 Hz), 7.54 s (1H, H^3 C_6H_3), 8.01 d (1H, H^6, C_6H_3, *J* 7.8 Hz). Found, %: C 50.53; H 3.01; N 14.52. $C_{16}H_{12}Cl_2N_4OS$. Calculated, %: C 50.67; H 3.19; N 14.77.

6-[5-(3,4-Dichlorophenyl)-2-furyl]-3-(4-methoxybenzyl)-7*H*-[1,2,4]triazolo[3,4-*b*][1,3,4]-thiadiazine (Vb). Yield 80%, mp 275–276°C. ^{1}H NMR spectrum, δ, ppm: 3.74 s (3H, CH_3), 4.18–4.20 m (4H, $2CH_2$), 6.81 d (2H, $H^{3,5}$, C_6H_4, *J* 7.8 Hz), 7.20 d (1H, H^3, Fu, *J* 3.6 Hz), 7.29 d (2H, $H^{2,6}$, C_6H_4, *J* 7.8 Hz), 7.44 d (1H, H^4, Fu, *J* 3.6 Hz), 7.61 d (1H, H^5, C_6H_3, *J* 7.9 Hz), 7.78 d (1H, H^6, C_6H_3, *J* 7.9 Hz), 8.03 s (1H, H^2, C_6H_3). Found, %: C 55.88; H 3.21; N 11.67. $C_{22}H_{16}Cl_2N_4O_2S$. Calculated, %: C 56.06; H 3.42; N 11.89.

6-[5-(3,4-Dichlorophenyl)-2-furyl]-3-(2-furyl)-7*H*-[1,2,4]triazolo[3,4-*b*][1,3,4]thiadiazine (Vc). Yield 77%, mp 279–280°C. ^{1}H NMR spectrum, δ, ppm: 4.45 s (2H, CH_2), 6.79 d.d (1H, H^4, Fu, *J* 3.9 and 1.9 Hz), 7.33 d (1H, Fu, *J* 3.9 Hz), 7.49 d (1H, Fu, *J* 3.9 Hz), 7.68 d (1H, Fu, *J* 3.9 Hz), 7.79 d (1H, H^5, C_6H_3, *J* 7.8 Hz), 7.86 d.d (1H, H^6, C_6H_3, ^3J 7.8, ^4J 1.9 Hz), 8.00 s (1H, H^5, Fu), 8.16 d (1H, H^2, C_6H_3, *J* 2.0 Hz). Found, %: C 51.59; H 2.21; N 13.22. $C_{18}H_{10}Cl_2N_4O_2S$. Calculated, %: C 51.81; H 2.42; N 13.43.

6-[5-(3,5-Dichlorophenyl)-2-furyl]-3-methyl-7*H*-[1,2,4]triazolo[3,4-*b*][1,3,4]thiadiazine (Vd). Yield 74%, mp 283–284°C. ^{1}H NMR spectrum, δ, ppm: 2.5 s (3H, CH_3), 4.37 C (2H, CH_2), 7.49 br.s (1H, H^3, Fu), 7.54 br.s (1H, H^4, Fu), 7.60 s (1H, H^4, C_6H_3), 7.91 s (2H, $H^{2,6}$, C_6H_3). Found, %: C 49.10; H 2.53; N 15.12. $C_{15}H_{10}Cl_2N_4OS$. Calculated, %: C 49.33; H 2.76; N 15.34.

6-[5-(3,5-Dichlorophenyl)-2-furyl]-3-(2-furyl)-7*H*-[1,2,4]triazolo[3,4-*b*][1,3,4]thiadiazine (Ve). Yield 82%, mp 237–238°C. ^{1}H NMR spectrum, δ, ppm: 4.35 s (2H, CH_2), 6.64 d.d (1H, Fu, *J* 3.9 and 2.0 Hz), 7.29 d (1H, Fu, *J* 3.9 Hz), 7.34 d (1H, Fu, *J* 3.9 Hz), 7.37 s (1H, H^4, C_6H_3), 7.54 d (1H, Fu, *J* 3.9 Hz), 7.79 br.s (1H, H^5, Fu), 7.85 d (2H, $H^{2,6}$, C_6H_3, *J* 2.0 Hz). Found, %: C 51.53; H 2.11; N 13.25. $C_{18}H_{10}Cl_2N_4O_2S$. Calculated, %: C 51.81; H 2.42; N 13.43.

6-[5-(2,5-Dichlorophenyl)-2-furyl]-3-ethyl-7*H*-[1,2,4]triazolo[3,4-*b*][1,3,4]thiadiazine (Vf). Yield 87%, mp 210–211°C. ^{1}H NMR spectrum, δ, ppm: 1.42 t

(3H, CH_3, *J* 7.3 Hz), 2.94 q (2H, CH_2, *J* 7.3 Hz), 4.21 s (2H, CH_2 thiadiazine), 7.29 d.d (1H, H^4, C_6H_3, ^3J 8.8, ^4J 2.0 Hz), 7.36 d (1H, H^3, Fu, *J* 2.9 Hz), 7.41 C (1H, H^4, Fu), 7.45 d (1H, H^3, C_6H_3, *J* 8.8 Hz), 7.98 d (1H, H^6, C_6H_3, *J* 2.0 Hz). Found, %: C 50.52; H 3.03; N 14.50. $C_{16}H_{12}Cl_2N_4OS$. Calculated, %: C 50.67; H 3.19; N 14.77.

6-[5-(2,5-Dichlorophenyl)-2-furyl]-3-propyl-7*H*-[1,2,4]triazolo[3,4-*b*][1,3,4]thiadiazine (Vg). Yield 82%, mp 239–240°C. ^{1}H NMR spectrum, δ, ppm: 1.00 t (3H, CH_3, *J* 6.8 Hz), 1.77–1.82 m (2H, $CH_2CH_2CH_3$), 2.91 t (2H, $CH_2CH_2CH_3$, *J* 6.8 Hz), 4.46 s (2H, CH_2 thiadiazine), 7.48–7.52 m (2H, H^4, C_6H_3 + H^3, Fu), 7.63–7.67 m (2H, H^4, Fu + H^3, C_6H_3), 7.99C (1H, H^6, C_6H_3). Found, %: C 51.73; H 3.48; N 14.07. $C_{17}H_{14}Cl_2N_4OS$. Calculated, %: C 51.92; H 3.59; N 14.25.

3-Benzyl-6-[5-(2,5-dichlorophenyl)-2-furyl]-7*H*-[1,2,4]triazolo[3,4-*b*][1,3,4]thiadiazine (Vh). Yield 82%, mp 255–256°C. ^{1}H NMR spectrum, δ, ppm: 4.23 s (2H, CH_2), 4.25 s (2H, CH_2), 7.18 pseudo t (1H, H^4, C_6H_5), 7.29 pseudo t (2H, $H^{3,5}$, C_6H_5), 7.33–7.40 m (4H, $H^{2,6}$, C_6H_5 + H^4, C_6H_3 + H^3, Fu), 7.48 d (1H, H^4, Fu, *J* 2.9 Hz), 7.51 d (1H, H^3, C_6H_3, *J* 7.8 Hz), 8.03 s (1H, H^6, C_6H_3). Found, %: C 56.98; H 3.01; N 12.52. $C_{21}H_{14}Cl_2N_4OS$. Calculated, %: C 57.15; H 3.20; N 12.69.

3-(2-Bromophenyl)-6-[5-(2,5-dichlorophenyl)-2-furyl]-7*H*-[1,2,4]triazolo[3,4-*b*][1,3,4]thiadiazine (Vi). Yield 88%, mp >300°C. ^{1}H NMR spectrum, δ, ppm: 4.34 s (2H, CH_2), 7.29–7.36 m (2H, H^4, C_6H_3 + H^3, Fu), 7.39 d (1H, H^4, Fu, *J* 3.9 Hz), 7.45–7.49 m (2H, H^3, C_6H_3 + H^4, C_6H_4), 7.53 pseudo t (1H, H^5, C_6H_4), 7.63 d (1H, H^3, C_6H_4, *J* 7.8 Hz), 7.75 d (1H, H^6, C_6H_4, *J*.8 Hz), 7.93 s (1H, H^6, C_6H_3). Found, %: C 47.33; H 2.01; N 10.90. $C_{20}H_{11}BrCl_2N_4OS$. Calculated, %: C 47.46; H 2.19; N 11.07.

3-(4-Bromophenyl)-6-[5-(2,5-dichlorophenyl)-2-furyl]-7*H*-[1,2,4[triazolo[3,4-*b*][1,3,4]thiadiazine (Vj). Yield 85%, mp >300°C. ^{1}H NMR spectrum, δ, ppm: 4.43 s (2H, CH_2), 7.46–7.54 m (2H, H^4, C_6H_3 + H^3, Fu), 7.59–7.68 m (2H, H^3, C_6H_3 + H^4 Fu), 7.78 d (2H, $H^{3,5}$, C_6H_4, *J* 7.8 Hz), 8.00 s (1H, H^6, C_6H_3), 8.09 d (2H, $H^{2,6}$, C_6H_4, *J* 7.8 Hz). Found, %: C 47.32; H 2.03; N 10.91. $C_{20}H_{11}BrCl_2N_4OS$. Calculated, %: C 47.46; H 2.19; N 11.07.

6-[5-(2,5-Dichlorophenyl)-2-furyl]-3-(2-methyl-3-furyl)-7*H*-[1,2,4]triazolo[3,4-*b*][1,3,4]thiadiazine (Vk). Yield 89%, mp 267–268°C. ^{1}H NMR spectrum, δ, ppm: 2.63 s (3H, CH_3), 4.44 s (2H, CH_2), 7.09 br.s (1H, H^4, Fu), 7.47–7.55 m (2H, H^3, Ar-Fu + H^4, C_6H_3), 7.62 d (1H, H^4, Ar-Fu, *J* 2.9 Hz), 7.66 d (1H, H^3, C_6H_3, *J* 7.8 Hz), 7.71 br.s (1H, H^5, Fu), 8.01 s (1H, H^6, C_6H_3). Found, %: C 52.73; H 2.72; N 12.89. $C_{19}H_{12}Cl_2N_4O_2S$. Calculated, %: C 52.91; H 2.80; N 12.99.

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