ISSN 1070-4280, Russian Journal of Organic Chemistry, 2016, Vol. 52, No. 6, pp. 848–856. © Pleiades Publishing, Ltd., 2016.
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Chemistry of Iminofurans: XII.[1] Synthesis of 2-(Arylimino)furan-3(2*H*)-ones and Their Reaction with Amines

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Received February 29, 2016

Abstract—2-(Arylimino)-5-(het)arylfuran-3(2*H*)-ones were synthesized by reaction of 5-(het)arylfuran-2,3-diones with *N*-(triphenyl-λ^5-phosphanylidene)anilines, and their aminolysis afforded *N*-aryl-4-amino-4-(het)aryl-2-oxobut-3-enamides.

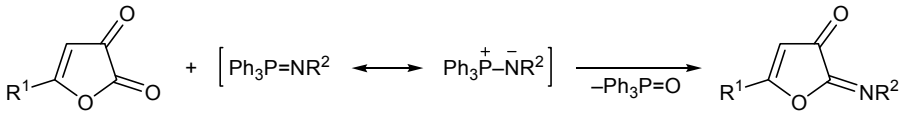
DOI: 10.1134/S1070428016060154

The first data on furan derivatives containing oxo and imino groups in positions *3* and *2*, respectively, were reported more than hundred years ago; specifically, the synthesis of 1-benzofuran-3(2*H*)-one 2-oxime was described [2]. After a century, the diversity of information on the synthesis and chemical transformations of iminofuran derivatives has been considerably extended. It is known that replacement of the lactone carbonyl oxygen atom by less electronegative nitrogen atom in going from 5-arylfuran-2,3-diones to *N*-substituted 2-iminofuran-3(2*H)*-ones reduces the electrophilicity of C^2, so that the reactivity of the latter essentially changes, and their preparative potential extends. However, there are only a few publications concerned with 2-iminofuran-3(2*H*)-ones [3].

The structure of 2-iminofuran-3(2*H*)-ones determines their rich synthetic potential. The presence of several electron-deficient centers in their molecules provides the possibility of controlling the direction of nucleophilic attack by varying substituents on the heterocycle and imino nitrogen atom. Recyclizations of iminofuranones and cycloadditions to the C=N bond therein also provide wide possibilities from the synthetic viewpoint. We were interested in extending the series of substituents on the imino nitrogen atom and studying chemical properties of 5-aryl-2-iminofuran-3(2*H*)-ones. The most convenient method for the synthesis of 5-aryl-2-(aryl-imino)furan-3(2*H*)-ones is based on the Staudinger imination of the lactone carbonyl of 5-arylfuran-2,3-diones [4–7].

5-(Het)arylfuran-2,3-diones **1a**–**1e** reacted with *N*-(triphenyl-λ^5-phosphanylidene)anilines **2a**–**2f** to give 2-(arylimino)-5-(het)arylfuran-3(2*H*)-ones **3a**–**3t** and triphenylphosphine oxide (Scheme 1). Compounds **3a**–**3t** were isolated as yellow crystalline substances. Their IR spectra characteristically showed absorption bands due to C^3=O and C^2=N groups in the region 1697–1721 cm^{-1}. The ^{1}H NMR spectra of **3a**–**3t**

Scheme 1.

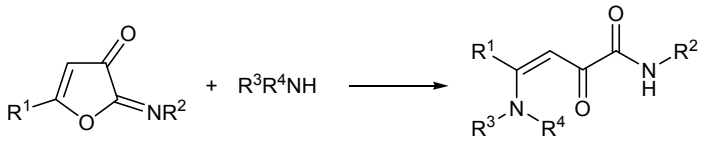


1a–1e **2a–2f** **3a–3t**

1, R^1 = Ph (**a**), 4-MeC_6H_4 (**b**), 4-ClC_6H_4 (**c**), naphthalen-1-yl (**d**), thiophen-2-yl (**e**); **2**, R^2 = Ph (**a**), 3-NCC_6H_4 (**b**), 3-$O_2NC_6H_4$ (**c**), 3-$F_3CC_6H_4$ (**d**), 4-EtOC(O)C_6H_4 (**e**), 4-AcC_6H_4 (**f**); **3**, R^1 = Ph, R^2 = Ph (**a**), 3-NCC_6H_4 (**b**), 3-$O_2NC_6H_4$ (**c**), 3-$F_3CC_6H_4$ (**d**), 4-EtOC(O)C_6H_4 (**e**), 4-AcC_6H_4 (**f**); R^1 = 4-MeC_6H_4, R^2 = Ph (**g**), 3-NCC_6H_4 (**h**), 3-$O_2NC_6H_4$ (**i**), 3-$F_3CC_6H_4$ (**j**), 4-EtOC(O)C_6H_4 (**k**); R^1 = 4-ClC_6H_4, R^2 = Ph (**l**), 3-$O_2NC_6H_4$ (**m**), 3-$F_3CC_6H_4$ (**n**), 4-EtOC(O)C_6H_4 (**o**), 4-AcC_6H_4 (**p**); R^1 = naphthalen-1-yl, R^2 = 3-$O_2NC_6H_4$ (**q**); R^1 = thiophen-2-yl, R^2 = 3-$O_2NC_6H_4$ (**r**), 3-$F_3CC_6H_4$ (**s**), 4-EtOC(O)C_6H_4 (**t**).

[1] For communication XI, see [1].

Scheme 2.



3c, **3k**, **3m**, **3o**, **3t** **4a–4f** **5a–5k**

4, R^3 = H, R^4 = Et (**a**), $PhCH_2$ (**b**), Cy (**c**), 1-Ad (**d**); R^3 = R^4 = Et (**e**); R^3R^4N = morpholin-4-yl (**f**); **5**, R^3 = H, R^4 = Et, R^2 = 3-$O_2NC_6H_4$, R^1 = Ph (**a**), 4-ClC_6H_4 (**b**); R^1 = thiophen-2-yl, R^2 = 4-$EtOC(O)C_6H_4$ (**c**); R^1 = 4-ClC_6H_4, R^2 = 4-$EtOC(O)C_6H_4$, R^3 = H, R^4 = $PhCH_2$ (**d**); R^3 = H, R^4 = Cy: R^1 = 4-ClC_6H_4, R^2 = 3-$O_2NC_6H_4$ (**e**); R^1 = 4-MeC_6H_4, R^2 = 4-$EtOC(O)C_6H_4$ (**f**); R^1 = thiophen-2-yl, R^2 = 4-$EtOC(O)C_6H_4$, R^3 = H, R^4 = 1-Ad (**g**); R^3 = R^4 = Et, R^1 = 4-ClC_6H_4, R^2 = 3-$O_2NC_6H_4$ (**h**); R^1 = 4-MeC_6H_4, R^2 = 4-$EtOC(O)C_6H_4$ (**i**); R^3R^4N = morpholin-4-yl, R^1 = 4-ClC_6H_4, R^2 = 3-$O_2NC_6H_4$ (**j**); R^1 = 4-MeC_6H_4, R^2 = 4-$EtOC(O)C_6H_4$ (**k**).

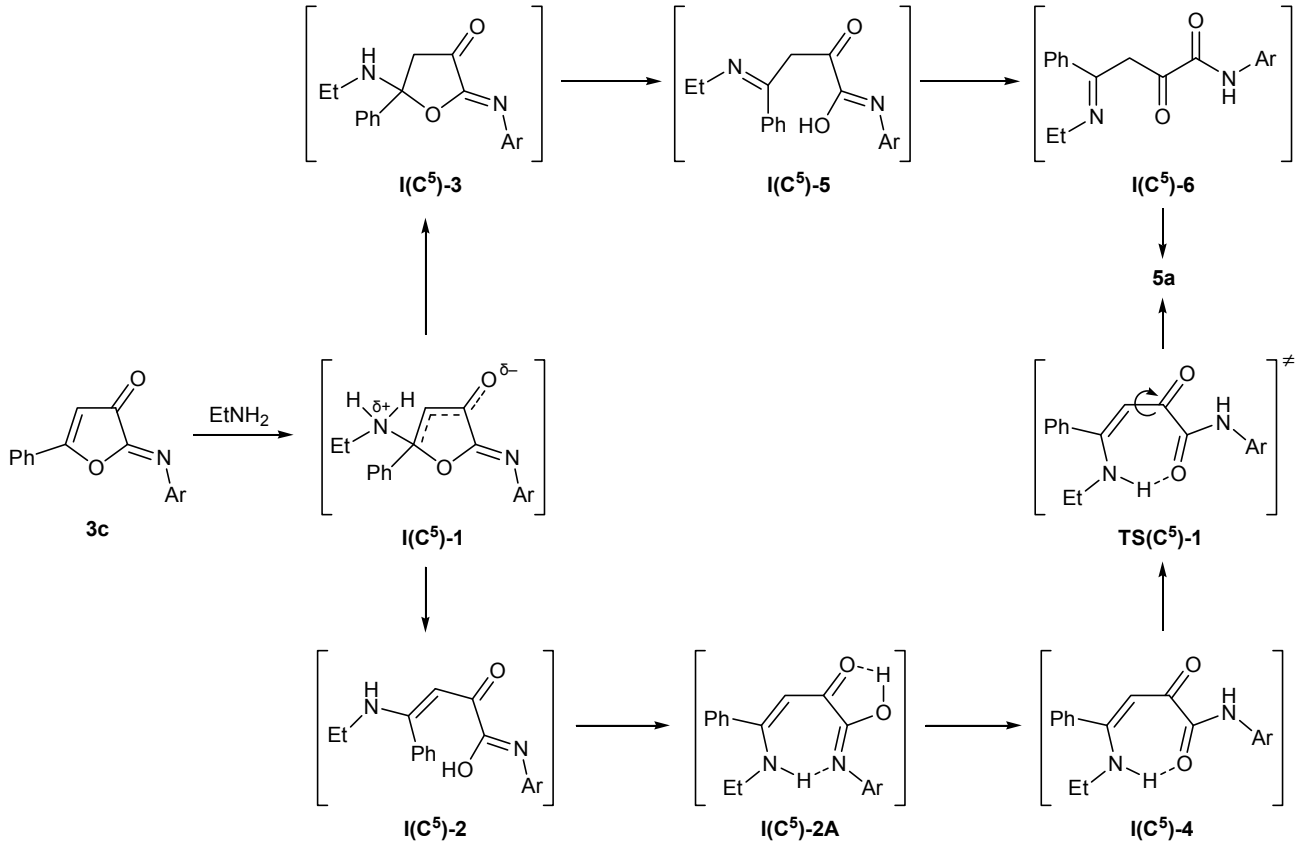
contained a singlet at δ 6.33–6.56 ppm due to 4-H and aromatic proton signals centered at δ 7.6 ppm. Presumably, compounds **3** are formed through a four-center transition state. We found that phosphine imides **2** containing electron-withdrawing groups in the aromatic ring reacted with furandiones **1** more readily and with higher yields, which may be rationalized by additional stabilization of the negative charge on the nitrogen atom.

The reactions of 2-(arylimino)-5-(het)arylfuran-3(2*H*)-ones **3c**, **3k**, **3m**, **3o**, and **3t** with primary and secondary aliphatic amines **4a**–**4f** afforded *N*-aryl-4-amino-4-(het)aryl-2-oxobut-3-enamides **5a**–**5k** (Scheme 2). Amides **5a**–**5k** are yellow crystalline substances. They showed in the IR spectra absorption bands at 3346–3255 (NH), 1697–1676 (C=O, amide), and 1607–1588 cm^{-1} (C^2=O). In the ^1H NMR spectra of **5a**–**5k**, the NH proton resonated as a singlet at δ 9.44–10.95 ppm, signals from aromatic protons were observed at about δ 7.5–7.6 ppm, and the vinylic 3-H proton signal appeared as a singlet at δ 5.92–6.60 ppm.

Compounds **5** are likely to be formed via initial nucleophilic attack by the amino nitrogen atom on C^5 of the furan ring to produce zwitterionic intermediate **I(C^5)-1** which is stabilized by proton transfer from the ammonium nitrogen atom to either O^1 or C^4, leading to intermediates **I(C^5)-2** and **I(C^5)-3**, respectively. Possible further transformation pathways are shown in Scheme 3. This scheme was verified by quantum chemical calculations of the total energies E_{tot} (in hartree units, Ha) and electronic and geometric parameters of possible intermediates at the B3LYP/6-311G(*d*) level of theory. Initial iminofuranone **3c** molecule (E_{tot} = –1026.2546 Ha) possesses three electrophilic centers, C^2, C^3, and C^5, with total Mulliken charges of +0.3445, +0.2542, and +0.2360 a.u., respectively. However, the contributions of $2p_z$ atomic orbitals constituting the LUMO of molecule **3c** turned out to change in the reverse order. Therefore, the charge-controlled reaction should involve nucleophilic attack on C^2, and the orbital-controlled reaction, on C^5.

We failed to calculate geometric and electronic characteristics of **I(C^5)-1**; optimization of its geometric parameters led to increase of the $C^5 \cdots N$ distance, i.e., ethylamine molecule moved apart from the iminofuranone molecule. Insofar as the calculations were performed for the gas phase, intermediate **I(C^5)-1** should be regarded as unstable. Probably, under real experimental conditions, effective solvation stabilizes that intermediate. Therefore, the formation of **I(C^5)-1** in the reaction under study was postulated. Subsequent transformations of **I(C^5)-1** may follow two pathways involving proton transfer from the nitrogen atom to O^1 or C^4 with formation of intermediate **I(C^5)-2** or **I(C^5)-3** (E_{tot} = –1161.4771 Ha), respectively. Geometry optimization of **I(C^5)-2** showed that proton transfer to O^1 (formation of O^1–H bond) is accompanied by internal rotation about the C^2–C^3 bond, leading to structure **I(C^5)-2A** (E_{tot} = –1116.4892 Ha) with an imidic acid fragment. Intermediate **I(C^5)-2A** is stabilized by two intramolecular hydrogen bonds $N–H \cdots N=C^1$ and $C^1O–H \cdots O=C^2$, as follows from the corresponding calculated interatomic distances (1.803 and 1.753 Å, respectively). The transformation of **I(C^5)-2A** into more stable amide **I(C^5)-4** (E_{tot} = –1161.5143 Ha) is also accompanied by internal rotation about the C^1–C^2 bond so that intramolecular hydrogen bond $N–H \cdots O=C^1$ (1.740 Å) is formed. The formation of amide **5a** requires internal rotation about the C^2–C^3 bond in **I(C^5)-4**. This rotation was analyzed by the reaction coordinate method where the reaction coordinate was the dihedral angle Θ ($OC^2C^3C^4$). The maximum on the E_{tot}—Θ curve corresponds to transition state **TS(C^5)-1**. Optimization of its structure by SADPOINT procedure gave E_{tot} = –1161.4866 Ha for Θ = 92.0°. Further decrease of Θ led to amide **5a** (E_{tot} = –1161.5233 Ha). The calculated $N–H \cdots O=C^2$

Scheme 3.



Ar = 3-$O_2NC_6H_4$.

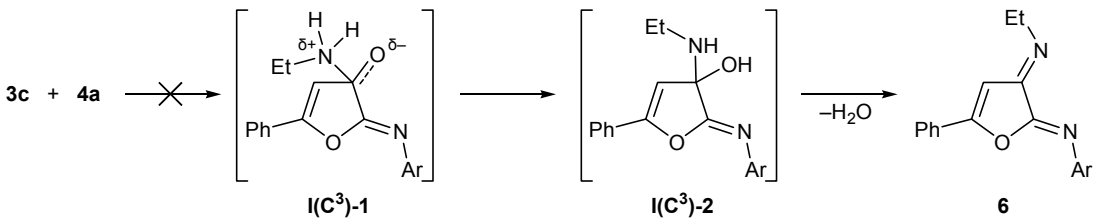
distance (1.866 Å) in **5a** confirms the presence of intramolecular hydrogen bond, which does not contradict the spectral data.

An alternative path for the formation of amide **5a** includes intermediates **I(C^5)-5** and **I(C^5)-6**. Intermediate **I(C^5)-5** (E_{tot} = –1161.4602 Ha) appears as a result of proton transfer from the nitrogen atom to O^1 of the heterocycle. The subsequent proton transfer to the nitrogen atom of the C^1=N fragment in **I(C^5)-5** gives more stable α-oxo amide structure **I(C^5)-6** (E_{tot} = –1161.4989 Ha), and migration of one proton from the methylene group to the imino nitrogen atom yields final product **5a**.

The attack by amine on C^3 (Scheme 4) could lead to diiminofuran **6** through intermediates **I(C^3)-1** and **I(C^3)-2**. Geometry optimization of **I(C^3)-1** failed for the reasons mentioned above. Intermediate **I(C^3)-2** (E_{tot} = –1161.4552 Ha) has a higher energy than **I(C^5)-2a** and **I(C^5)-3**, and its formation seems to be less probable. A hypothetic supermolecule consisting of **6** (E_{tot} = –1085.0099 Ha) and water (E_{tot} = –76.4348 Ha) is also less stable than amide **5a**. Presumably, this is the reason why nucleophilic attack is not directed at C^3 of **3c** and compound **6** is not formed.

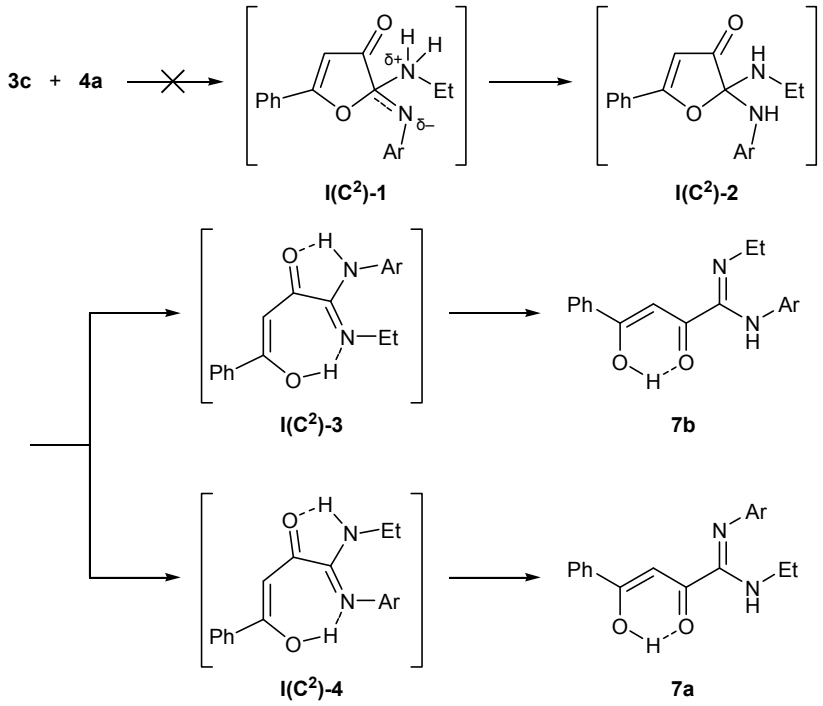
The attack on C^2 (Scheme 5) could give rise to amidine **7a** or **7b**. Zwitterionic intermediate **I(C^2)-1**

Scheme 4.



Ar = 3-$O_2NC_6H_4$.

Scheme 5.



Ar = 3-$O_2NC_6H_4$.

could be converted into **I(C^2)-2** via proton migration from the ethylammonium fragment to the imino nitrogen atom. The calculated total energy of **I(C^2)-2** is E_{tot} = –1161.4814 Ha. Its stabilization may be achieved by proton transfer to O^1 either from the NHC_2H_5 nitrogen atom or from the NHAr group with formation of intermediate **I(C^2)-3** or **I(C^2)-4**, respectively. The total energies of **I(C^2)-3** and **I(C^2)-4** are –1161.4884 and –1161.4909 Ha, respectively. Internal rotation about the C^2–C^3 bond could produce more stable structures **7a** and **7b** with intramolecular hydrogen bond C^4–OH···O=C^2. Amidine **7a** (E_{tot} = –1161.4978 Ha) is more stable than **7b** (E_{tot} = –1161.4909 Ha).

As follows from the calculated total energies of key intermediates **I(C^5)-2**, **I(C^3)-2**, and **I(C^2)-2**, the former should be regarded as the most stable. Intermeditate **I(C^5)-4** is also more stable than **I(C^2)-4**. Furthermore, real product **5a** is more stable than hypothetical structure **7a**. Thus, the reaction following the path

3c + $EtNH_2$ → **I(C^5)-1** → **I(C^5)-2A** → **I(C^5)-4** → **5a**

seems to be energetically more favorable. Other iminofuranones should react with amines according to an analogous scheme.

EXPERIMENTAL

The IR spectra were recorded on an FSM-1201 spectrometer from samples dispersed in mineral oil. The ^1H and ^{13}C NMR spectra were measured on Varian Mercury Plus-300 (300 MHz), Bruker Avance III (400 and 100 MHz, respectively), and Bruker 500 instruments (500.13 MHz); the chemical shifts were determined relative to tetramethylsilane as internal standard or solvent signals. The mass spectra (electron impact, 70 eV) were recorded on a Kratos MS-30 mass spectrometer (ion source temperature 200°C). The elemental analyses were obtained on a Leco CHNS-932 analyzer. The purity of compounds was checked, and the progress of reactions was monitored, by TLC on Sorbfil PTSKh P-A-UF-254 plates with diethyl ether–benzene–acetone (10 : 9 : 1) as eluent; spots were detected under UV light or by treatment with iodine vapor. Quantum chemical calculations of reaction intermediates with full optimization of all parameters were performed on a supercomputer (Tesla Center for Parallel and Distributed Computations, Perm State National Research University) using Firefly [8].

Commercially available triphenylphosphine, triethylamine (*Vekton*), 4-methylacetophenone, 4-chloroacetophenone, 2-acetylthiophene (Sigma–Aldrich),

acetophenone, 4-aminoacetophenone, diethyl oxalate, and morpholine (*Reakhim*) were used. Chloroform, methanol, benzene, toluene, dioxane, and acetonitrile of chemically pure grade were subjected to additional purification [9] prior to use; rectified ethanol was of de luxe grade. Compounds **1a**–**1e** were synthesized according to the procedure reported in [10] from the corresponding (het)aroylpyruvic acids which were prepared as described in [11, 12]. Compounds **1a**–**1c** and **1e** were reported previously [10, 13]. Phosphine imides **2a**–**2f** were synthesized according to [14] from the corresponding substituted anilines. Compounds **2a** [14], **2b**, **2e** [15], **2c** [16], and **2f** [17] were reported previously.

5-(Naphthalen-1-yl)furan-2,3-dione (1d). Yield 80%, red–brown crystals, decomposition point 160–162°C (from benzene). IR spectrum, ν, cm^{-1}: 1814 (C^2=O), 1708 (C^3=O). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 6.23 s (1H, 4-H), 7.25–7.87 m (7H, H_{arom}). Found, %: C 75.00; H 3.60. $C_{14}H_8O_3$. Calculated, %: C 75.00; H 3.57.

2-(Arylimino)-5-(het)arylfuran-3(2*H*)-ones 3a–3t (*general procedure*). Phosphine imide **2a**–**2f**, 5 mmol, was added to a solution of 5 mmol of 5-arylfuran-2,3-dione **1a**–**1e** in 10 mL of anhydrous toluene, and the mixture was stirred until it became homogeneous. After 24 h, the precipitate was filtered off and recrystallized from acetonitrile.

5-Phenyl-2-(phenylimino)furan-3(2*H*)-one (3a). Yield 0.94 g (76%), yellow crystals, mp 155–156°C (from MeCN). IR spectrum, ν, cm^{-1}: 1703 (C=O, C=N), 1603 (C=C). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 6.38 s (1H, 4-H), 7.25–7.87 m (10H, H_{arom}). Found, %: C 71.10; H 4.45; N 5.62. $C_{16}H_{11}NO_2$. Calculated, %: C 71.11; H 4.42; N 5.62.

3-[3-Oxo-5-phenylfuran-2(3*H*)-ylideneamino]-benzonitrile (3b). Yield 0.55 g (70%), yellow crystals, mp 178–179°C (from MeCN). IR spectrum, ν, cm^{-1}: 2229 (CN), 1711 (C=O), 1702 (C=N), 1605 (C=C). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 6.45 s (1H, 4-H), 7.57–7.86 m (9H, H_{arom}). Found, %: C 74.45; H 3.67; N 10.21. $C_{17}H_{10}N_2O_2$. Calculated, %: C 74.45; H 3.65; N 10.22.

2-[(3-Nitrophenyl)imino]-5-phenylfuran-3(2*H*)-one (3c). Yield 0.94 g (71%), yellow crystals, mp 174–176°C (from MeCN). IR spectrum, ν, cm^{-1}: 1716 (C=O, C=N), 1598 (C=C). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.46 s (3H, Me), 6.39 s (1H, 4-H), 7.25–8.19 m (9H, H_{arom}). Found, %: C 65.31; H 3.43; N 9.52. $C_{16}H_{10}N_2O_4$. Calculated, %: C 65.30; H 3.40; N 9.52.

5-Phenyl-2-{[(3-(trifluoromethyl)phenyl]imino}-furan-3(2*H*)-one (3d). Yield 0.49 g (32%), yellow crystals, mp 141–143°C (from MeCN). IR spectrum, ν, cm^{-1}: 1711 (C=O, C=N), 1600 (C=C). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 6.41 s (1H, 4-H), 7.27–8.02 m (9H, H_{arom}). Found, %: C 64.36; H 3.18; N 4.41. $C_{17}H_{10}F_3NO_2$. Calculated, %: C 64.35; H 3.15; N 4.42.

Ethyl 4-[3-oxo-5-phenylfuran-2(3*H*)-ylideneamino]benzoate (3e). Yield 0.48 g (31%), yellow crystals, mp 120–122°C (from MeCN). IR spectrum, ν, cm^{-1}: 1724 (C=O, ester), 1710 (C=O, C=N), 1600 (C=C). ^{1}H NMR spectrum, δ, ppm: 1.40 t (3H, Me, J = 7.1 Hz), 4.38 q (2H, OCH_2, J = 7.1 Hz), 6.39 s (1H, 4-H) 7.25–8.14 m (9H, H_{arom}). Found, %: C 71.02; H 4.71; N 4.36. $C_{19}H_{15}NO_4$. Calculated, %: C 71.03; H 4.67; N 4.36.

2-[(4-Acetylphenyl)imino]-5-phenylfuran-3(2*H*)-one (3f). Yield 0.83 g (57%), yellow crystals, mp 155–157°C (from MeCN). IR spectrum, ν, cm^{-1}: 1710 (C=O, C=N), 1677 (C=O, Ac), 1597 (C=C). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.64 s (3H, Me), 6.42 s (1H, 4-H), 7.30–8.07 m (9H, H_{arom}). Found, %: C 74.22; H 4.50; N 4.81. $C_{18}H_{13}NO_3$. Calculated, %: C 74.23; H 4.47; N 4.81.

5-(4-Methylphenyl)-2-(phenylimino)furan-3(2*H*)-one (3g). Yield 0.6 g (46%), yellow crystals, mp 176–177°C (from MeCN). IR spectrum, ν, cm^{-1}: 1700 (C=O, C=N), 1605 (C=C). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.45 s (3H, Me), 6.33 s (1H, 4-H), 7.31–7.40 m (4H, H_{arom}), 7.45 m (1H, H_{arom}, J = 7.6 Hz), 7.59 m (2H, H_{arom}, J = 8.1 Hz), 7.75 m (2H, H_{arom}, J = 8.1 Hz). Found, %: C 77.55; H 4.98; N 5.32. $C_{17}H_{13}NO_2$. Calculated, %: C 77.57; H 4.94; N 5.32.

3-[5-(4-Methylphenyl)-3-oxofuran-2(3*H*)-ylideneamino]benzonitrile (3h). Yield 0.60 g (78%), yellow crystals, mp 189–191°C (from MeCN). IR spectrum, ν, cm^{-1}: 2224 (CN), 1715 (C=O), 1698 (C=N), 1603 (C=C). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.48 s (3H, Me), 6.39 s (1H, 4-H), 7.37–7.80 m (8H, H_{arom}). Found, %: C 74.99; H 4.20; N 9.72. $C_{18}H_{12}N_2O_2$. Calculated, %: C 75.00; H 4.17; N 9.72.

5-(4-Methylphenyl)-2-[(3-nitrophenyl)imino]-furan-3(2*H*)-one (3i). Yield 1.18 g (77%), yellow crystals, mp 190–192°C (from MeCN). IR spectrum, ν, cm^{-1}: 1716 (C=O, C=N), 1598 (C=C). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.46 s (3H, Me), 6.39 s (1H, 4-H), 7.25–8.19 m (8H, H_{arom}). Found, %: C 66.23;

H 3.92; N 9.09. $C_{17}H_{12}N_2O_4$. Calculated, %: C 66.23; H 3.90; N 9.09.

5-(4-Methylphenyl)-2-[(3-trifluoromethylphenyl)imino]furan-3(2*H*)-one (3j). Yield 0.57 g (36%), yellow crystals, mp 139–140°C (from MeCN). IR spectrum, ν, cm^{-1}: 1717 (C=O, C=N), 1606 (C=C). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.4 s (3H, Me), 6.36 s (1H, 4-H), 7.24–7.84 m (8H, H_{arom}). Found, %: C 65.26; H 3.65; N 4.23. $C_{18}H_{12}F_3NO_2$. Calculated, %: C 65.25; H 3.63; N 4.23.

Ethyl 4-[5-(4-methylphenyl)-3-oxofuran-2(3*H*)-ylideneamino]benzoate (3k). Yield 0.64 g (38%), yellow fibers, mp 112–114°C (from MeCN). IR spectrum, ν, cm^{-1}: 1717 (C=O, ester), 1703 (C=O, C=N), 1603 (C=C). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.39 t (3H, Me, J = 6.9 Hz), 2.45 s (3H, Me), 4.38 q (2H, CH_2, J = 6.9 Hz), 6.35 s (1H, 4-H), 7.25–8.14 m (8H, H_{arom}). Found, %: C 71.63; H 5.11; N 4.18. $C_{20}H_{17}NO_4$. Calculated, %: C 71.64; H 5.07; N 4.18.

5-(4-Chlorophenyl)-2-(phenylimino)furan-3(2*H*)-one (3l). Yield 0.95 g (60%), yellow crystals, mp 224–226°C (from MeCN). IR spectrum, ν, cm^{-1}: 1721 (C=O, C=N), 1606 (C=C). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 6.38 s (1H, 4-H), 7.27–7.98 m (9H, H_{arom}). Found, %: C 67.74; H 3.55; N 4.94. $C_{16}H_{10}ClNO_2$. Calculated, %: C 67.84; H 3.53; N 4.95.

5-(4-Chlorophenyl)-2-[(3-nitrophenyl)imino]furan-3(2*H*)-one (3m). Yield 0.77 g (47%), yellow crystals, decomposition point 224–226°C (from MeCN). IR spectrum, ν, cm^{-1}: 1716 (C=O, C=N), 1599 (C=C). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 6.42 s (1H, 4-H), 7.25–8.21 m (8H, H_{arom}). Found, %: C 58.46; H 2.76; N 8.52. $C_{16}H_9ClN_2O_4$. Calculated, %: C 58.53; H 2.74; N 8.54.

5-(4-Chlorophenyl)-2-[(3-trifluoromethylphenyl)imino]furan-3(2*H*)-one (3n). Yield 0.54 g (31%), yellow crystals, mp 155.5–157°C (from MeCN). IR spectrum, ν, cm^{-1}: 1703 (C=O, C=N), 1598 (C=C). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 6.39 s (1H, 4-H), 7.24–8.81 m (8H, H_{arom}). Found, %: C 58.06; H 2.58; N 3.98. $C_{17}H_9ClF_3NO_2$. Calculated, %: C 58.11; H 2.56; N 3.99.

Ethyl 4-[5-(4-chlorophenyl)-3-oxofuran-2(3*H*)-ylideneamino]benzoate (3o). Yield 1.3 g (93%), yellow crystals, mp 180–182°C (from MeCN). IR spectrum, ν, cm^{-1}: 1711 (C=O, ester, C^3=O, C=N), 1604 (C=C). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.40 t (3H, Me, J = 7.0 Hz), 4.38 q (2H, CH_2, J = 7.0 Hz), 6.39 s (1H, 4-H), 7.47–7.54 m (4H, H_{arom}), 7.62 d (2H, H_{arom}, J = 8.4 Hz), 8.13 d (2H, H_{arom}, J = 8.4 Hz). Found, %: C 64.14; H 3.97; N 3.94. $C_{19}H_{14}ClNO_4$. Calculated, %: C 64.22; H 3.94; N 3.94.

2-[(4-Acetylphenyl)imino]-5-(4-chlorophenyl)furan-3(2*H*)-one (3p). Yield 0.59 g (36%), yellow crystals, mp 185–187°C (from MeCN). IR spectrum, ν, cm^{-1}: 1697 (C=O, C=N), 1672 (MeC=O), 1598 (C=C). Found, %: C 66.37; H 3.71; N 4.30. $C_{18}H_{12}ClNO_3$. Calculated, %: C 66.46; H 3.69; N 4.31.

5-(Naphthalen-1-yl)-2-[(3-nitrophenyl)imino]furan-3(2*H*)-one (3q). Yield 1.13 g (66%), yellow crystals, mp 160–161°C (from MeCN). IR spectrum, ν, cm^{-1}: 1713 (C=O, C=N), 1592 (C=C). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 6.53 s (1H, 4-H), 7.24–8.48 m (11H, H_{arom}). Found, %: C 74.28; H 3.84; N 6.66. $C_{26}H_{16}N_2O_4$. Calculated, %: C 74.29; H 3.81; N 6.67.

2-[(3-Nitrophenyl)imino]-5-(thiophen-2-yl)furan-3(2*H*)-one (3r). Yield 0.83 g (55%), yellow crystals, mp 202–203°C (from MeCN). IR spectrum, ν, cm^{-1}: 1715 (C=O, C=N), 1598 (C=C). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 6.26 s (1H, 4-H), 7.25–8.50 m (7H, H_{arom}, C_4H_3S). Found, %: C 56.00; H 2.69; N 9.33; S 10.68. $C_{14}H_8N_2O_4S$. Calculated, %: C 56.00; H 2.67; N 9.33; S 10.67.

5-(Thiophen-2-yl)-2-[(3-trifluoromethylphenyl)imino]furan-3(2*H*)-one (3c). Yield 0.75 g (53%), yellow crystals, mp 162–164°C (from MeCN). IR spectrum, ν, cm^{-1}: 1708 (C=O, C=N), 1583 (C=C). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 6.24 s (1H, 4-H), 7.25–7.86 m (7H, H_{arom}, C_4H_3S). Found, %: C 55.73; H 2.49; N 4.33; S 9.92. $C_{15}H_8F_3NO_2S$. Calculated, %: C 55.73; H 2.48; N 4.33; S 9.91.

Ethyl 4-[3-oxo-5-(thiophen-2-yl)furan-2(3*H*)-ylideneamino]benzoate (3t). Yield 0.98 g (61%), yellow crystals, mp 139–141°C (from MeCN). IR spectrum, ν, cm^{-1}: 1707 (C=O, ester), 1707 (C=O, C=N), 1597 (C=C). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.41 t (3H, Me, J = 7.0 Hz), 4.39 q (2H, CH_2, J = 7.0 Hz), 6.23 s (1H, 4-H), 7.26–8.13 m (7H, H_{arom}, C_4H_3S). Found, %: C 62.37; H 4.00; N 4.28; S 9.79. $C_{17}H_{13}NO_4S$. Calculated, %: C 62.38; H 3.98; N 4.28; S 9.79.

***N*-Aryl-4-(ethylamino)-4-(het)aryl-2-oxobut-3-enamides 5a–5c (*general procedure*).** A solution of 0.41 g (5 mmol) of ethylamine (**4a**) hydrochloride in 5 mL of 5% aqueous alkali was added to a solution of 5 mmol of iminofuranone **3c**, **3m**, or **3t** in 10 mL of toluene, and the mixture was stirred for 3 h. The precipitate was filtered off and recrystallized from acetonitrile.

4-(Ethylamino)-*N*-(3-nitrophenyl)-2-oxo-4-phenylbut-3-enamide (5a). Yield 1.02 g (89%), yellow crystals, mp 167–169°C (from MeCN). IR spectrum, ν, cm^{-1}: 3317 (N–H), 1685 (C=O, amide), 1602 (C^2=O). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.24 t (3H, Me, J = 7.1 Hz), 3.36 q (2H, CH_2, J = 7.1 Hz), 6.22 s (1H, 3-H), 7.40–8.04 m (8H, H_{arom}), 8.60 s (1H, H_{arom}), 9.70 s (1H, NH), 11.31 br.s (1H, NH). Found, %: C 63.71; H 5.05; N 12.38. $C_{18}H_{17}N_3O_4$. Calculated, %: C 63.72; H 5.01; N 12.39.

4-(4-Chlorophenyl)-4-(ethylamino)-*N*-(3-nitrophenyl)-2-oxobut-3-enamide (5b). Yield 1.38 g (74%), yellow crystals, mp 142–143°C (from MeCN). IR spectrum, ν, cm^{-1}: 3309 (N–H), 1682 (C=O, amide), 1598 (C^2=O). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.25 t (3H, Me, J = 7.2 Hz), 3.35 q (2H, CH_2, J = 7.2 Hz), 6.17 s (1H, 3-H), 7.34–8.05 m (7H, H_{arom}), 8.57 s (1H, H_{arom}), 9.62 s (1H, NH), 11.25 br.s (1H, NH). Mass spectrum, *m*/*z* (I_{rel}, %): 373 (29) $[M]^+$, 286 (28), 210 (49), 208 (100), 138 (51), 102 (26), 92 (27), 72 (42), 43 (28). Found, %: C 57.84; H 4.31; N 11.24. $C_{18}H_{16}ClN_3O_4$. Calculated, %: C 57.90; H 4.29; N 11.26. *M* 373.80.

Ethyl 4-{[4-(ethylamino)-2-oxo-4-(thiophen-2-yl)but-3-enoyl]amino}benzoate (5c). Yield 1.54 g (83%), yellow crystals, mp 117–119°C (from MeCN). IR spectrum, ν, cm^{-1}: 3254 (N–H), 1705 (C=O, ester), 1687 (C=O, amide), 1605 (C^2=O). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.24 m (6H, Me), 3.63 q (2H, CH_2, J = 6.8 Hz), 4.27 q (2H, CH_2, J = 6.9 Hz), 6.19 s (1H, 3-H), 7.27–8.02 m (7H, H_{arom}), 10.69 s (1H, NH), 11.47 t (1H, NH, J = 6.2 Hz). Found, %: C 61.27; H 5.41; N 7.52; S 8.61. $C_{19}H_{20}N_2O_4S$. Calculated, %: C 61.29; H 5.38; N 7.53; S 8.60.

Ethyl 4-{[4-(benzylamino)-4-(4-chlorophenyl)-2-oxobut-3-enoyl]amino}benzoate (5d). Benzylamine, 0.55 mL (5 mmol), was added to a solution of 1.77 g (5 mmol) of iminofuranone **3o** in 10 mL of toluene, and the mixture was stirred for 1 h at 30°C. The mixture was evaporated by half under reduced pressure, and the precipitate was filtered off. Yield 1.36 g (59%), light yellow crystals, mp 140–142°C (from toluene). IR spectrum, ν, cm^{-1}: 3291 (N–H), 1714 (C=O, ester), 1691 (C=O, amide), 1606 (C^2=O). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.37 t (3H, Me, J = 7.0 Hz), 3.37 s (2H, CH_2), 4.36 q (2H, CH_2, J = 7.0 Hz), 5.93 s (1H, 3-H), 7.23–8.13 m (8H, H_{arom}), 9.44 s (1H, NH), 10.97 t (1H, NH, J = 6.2 Hz). Found, %: C 67.46; H 5.01; N 6.05. $C_{26}H_{23}ClN_2O_4$. Calculated, %: C 67.53; H 4.98; N 6.06.

***N*,4-Diaryl-4-(cyclohexylamino)-2-oxobut-3-enamides 5e and 5f (*genral procedure*).** Cyclohexylamine (**4c**), 0.6 mL (5 mmol), was added to a solution of 5 mmol of compound **3k** or **3m** in 10 mL of toluene, and the mixture was stirred for 3 h at 60°C. The mixture was evaporated by half under reduced pressure, and the precipitate was filtered off.

4-(4-Chlorophenyl)-4-(cyclohexylamino)-*N*-(3-nitrophenyl)-2-oxobut-3-enamide (5e). Yield 1.73 g (81%), yellow crystals, mp 187–189°C (from toluene). IR spectrum, ν, cm^{-1}: 3308 (N–H), 1678 (C=O, amide), 1588 (C^2=O). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.24–2.52 m (10H, CH_2, Cy), 3.43 m (1H, NHC**H**), 5.92 s (1H, 3-H), 7.35–7.65 m (5H, H_{arom}), 7.96 m (1H, H_{arom}, J = 8.1 Hz), 8.24 m (1H, H_{arom}, J = 7.5 Hz), 8.89 s (1H, H_{arom}), 10.95 s (1H, NH), 11.54 d (1H, NH, J = 8.7 Hz). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 23.2, 24.6, 33.0, 39.0, 39.2, 39.6, 39.8, 39.9, 40.0, 52.31, 91.50, 114.20, 118.43, 126.19, 129.0, 129.2, 130.0, 135.0, 139.4, 147.9, 162.6, 167.0, 178.4. Mass spectrum, *m*/*z* (I_{rel}, %): 427 (29) $[M]^+$, 286 (42), 264 (98), 262 (100), 180 (51), 139 (22), 55 (17). Found, %: C 61.76; H 5.18; N 9.82. $C_{22}H_{22}ClN_3O_4$. Calculated, %: C 61.83; H 4.65; N 9.84. *M* 427.89.

Ethyl 4-{[4-(cyclohexylamino)-4-(4-methylphenyl)-2-oxobut-3-enoyl]amino}benzoate (5f). Yield 1.34 g (63%), light yellow crystals, mp 148–149°C (from toluene). IR spectrum, ν, cm^{-1}: 3284 (N–H), 1725 (C=O, ester), 1676 (C=O, amide), 1604 (C^2=O). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.23–2.34 m (10H, CH_2, Cy), 1.37 t (3H, Me, J = 7.0 Hz), 2.40 s (3H, Me), 3.50 m (1H, NHC**H**), 4.35 q (2H, CH_2, J = 7.0 Hz), 6.17 s (1H, 3-H), 7.17–7.30 m (4H, H_{arom}), 7.68 m (2H, H_{arom}, J = 7.8 Hz), 8.03 m (2H, H_{arom}, J = 7.8 Hz), 9.62 s (1H, NH), 11.50 d (1H, NH, J = 8.7 Hz). Mass spectrum, *m*/*z* (I_{rel}, %): 434 (33) $[M]^+$, 286 (55), 243 (100), 160 (47), 135 (32), 120 (24), 55 (24), 43 (43). Found, %: C 71.87; H 6.96; N 6.45. $C_{26}H_{30}N_2O_4$. Calculated, %: C 71.89; H 6.28; N 6.91. *M* 434.54.

Ethyl 4-{[4-(1-adamantylamino)-2-oxo-4-(thiophen-2-yl)but-3-enoyl]amino}benzoate (5g). Adamantan-1-amine (**4d**), 0.76 g (5 mmol), was added to a solution of 1.64 g (5 mmol) of iminofuranone **3t** in 10 mL of toluene, and the mixture was refluxed for 1 h. The precipitate was filtered off. Yield 1.53 g (64%), yellow crystals, mp 172–173°C (from toluene). IR spectrum, ν, cm^{-1}: 3299 (N–H), 1702 (C=O, ester), 1687 (C=O, amide), 1605 (C^2=O). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.53–2.05 m (15H, Ad), 1.37 t (3H,

Me, J = 7.0 Hz), 4.36 (2H, CH_2, J = 7.0 Hz), 6.21 s (1H, 3-H), 7.06 m (1H, Th, J = 5.1 Hz), 7.23 m (1H, Th, J = 5.1 Hz), 7.46 m (1H, Th, J = 5.1 Hz), 7.4 m (2H, H_{arom}, J = 8.4 Hz), 8.02 m (2H, H_{arom}, J = 8.4 Hz), 9.57 s (1H, NH), 11.54 s (1H, NH). Mass spectrum, m/z (I_{rel}, %): 478 (15) $[M]^+$, 286 (100), 135 (70), 93 (14), 44 (14). Found, %: C 67.76; H 6.32; N 5.85; S 6.70. $C_{27}H_{30}N_2O_4S$. Calculated, %: C 67.78; H 6.28; N 5.86; S 6.69. M 478.62.

***N*,4-Diaryl-4-(diethylamino)-2-oxobut-3-enamides 5h and 5i (*general procedure*).** Diethylamine (**4e**), 0.51 mL (5 mmol), was added to a solution of 5 mmol of compound **3m** or **3k** in 10 mL of toluene, and the mixture was stirred for 2–4 h at 60°C. The mixture was evaporated, the residue was treated with hexane, and the precipitate was filtered off.

4-(4-Chlorophenyl)-4-(diethylamino)-*N*-(3-nitrophenyl)-2-oxobut-3-enamide (5h). Yield 1.56 g (78%), yellow crystals, mp 148–149°C (from toluene). IR spectrum, ν, cm^{-1}: 3346 (N–H), 1689 (C=O, amide), 1619 (C^2=O). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.06 t (3H, Me, J = 6.8 Hz), 1.40 t (3H, Me, J = 6.9 Hz), 3.13 q (2H, CH_2, J = 6.8 Hz), 3.63 q (2H, CH_2, J = 6.8 Hz), 6.47 s (1H, 3-H), 7.13–8.65 m (8H, H_{arom}), 9.54 s (1H, NH). Mass spectrum, m/z (I_{rel}, %): 401 (14) $[M]^+$, 346 (15), 286 (26), 237 (38), 236 (100), 181 (58), 139 (44), 72 (18), 56 (20), 43 (41). Found, %: C 59.78; H 5.02; N 10.46. $C_{20}H_{20}ClN_3O_4$. Calculated, %: C 59.85; H 4.99; N 10.47.

Ethyl 4-{[4-(diethylamino)-4-(4-methylphenyl)-2-oxobut-3-enoyl]amino}benzoate (5i). Yield 1.71 g (84%), light yellow crystals, mp 141–143°C (from toluene). IR spectrum, ν, cm^{-1}: 3292 (N–H), 1701 (C=O, ester, amide), 1603 (C^2=O). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.03 t (3H, Me, J = 6.9 Hz), 1.33–1.43 m (6H, Me), 3.14 q (2H, CH_2, J = 6.9 Hz), 3.62 q (2H, CH_2, J = 7.2 Hz), 4.33 (2H, CH_2, J = 6.9 Hz), 6.48 s (1H, 3-H), 7.08 m (2H, H_{arom}, J = 8.1 Hz), 7.30 m (2H, H_{arom}, J = 8.1 Hz), 7.62 m (2H, H_{arom}, J = 8.7 Hz), 7.93 m (2H, H_{arom}, J = 8.7 Hz), 9.57 s (1H, NH). Mass spectrum, m/z (I_{rel}, %): 408 (8) $[M]^+$, 363 (8), 216 (100), 115 (8), 101 (9), 59 (10), 56 (14), 43 (27). Found, %: C 70.57; H 6.91; N 6.86. $C_{24}H_{28}N_2O_4$. Calculated, %: C 70.59; H 6.86; N 5.86. M 408.50.

***N*,4-Diaryl-4-(morpholin-4-yl)-2-oxobut-3-enamides 5j and 5k (*general procedure*).** Morpholine (**4f**), 0.43 mL (5 mmol), was added to a solution of 5 mmol of compound **3m** or **3k** in 10 mL of toluene. The mixture was stirred for 0.5–1 h at 60°C, and the precipitate was filtered off and recrystallized from acetonitrile.

4-(4-Chlorophenyl)-4-(morpholin-4-yl)-*N*-(3-nitrophenyl)-2-oxobut-3-enamide (5j). Yield 1.76 g (85%), yellow crystals, mp 166–168°C (from MeCN). IR spectrum, ν, cm^{-1}: 3306 (N–H), 1688 (C=O, amide), 1606 (C^2=O). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.07–3.80 (8H, morpholine), 6.60 s (1H, 3-H), 7.44–8.21 m (7H, H_{arom}), 8.87 s (1H, H_{arom}), 10.70 s (1H, NH). Mass spectrum, m/z (I_{rel}, %): 415 (2) $[M]^+$, 346 (12), 286 (44), 252 (42), 250 (100), 181 (64), 135 (13), 111 (15), 43 (49). Found, %: C 57.77; H 4.36; N 10.10. $C_{20}H_{18}ClN_3O_5$. Calculated, %: C 57.76; H 4.33; N 10.11. M 415.84.

Ethyl 4-{[4-(4-methylphenyl)-4-(morpholin-4-yl)-2-oxobut-3-enoyl]amino}benzoate (5k). Yield 1.84 g (87%), light yellow crystals, mp 146–148°C (from MeCN). IR spectrum, ν, cm^{-1}: 3285 (N–H), 1709 (C=O, ester), 1691 (C=O, amide), 1607 (C^2=O). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.36 t (3H, Me, J = 7.1 Hz), 2.42 s (3H, Me), 3.19–3.86 m (8H, morpholine), 4.33 q (2H, CH_2, J = 7.1 Hz), 6.55 s (1H, 3-H), 7.11 m (2H, H_{arom}, J = 7.5 Hz), 7.30 m (2H, H_{arom}, J = 7.5 Hz), 7.63 m (2H, H_{arom}, J = 9.0 Hz), 7.99 m (2H, H_{arom}, J = 9.0 Hz), 9.46 s (1H, NH). Mass spectrum, m/z (I_{rel}, %): 422 (8) $[M]^+$, 286 (61), 230 (100), 145 (18), 119 (23), 43 (18). Found, %: C 68.23; H 6.20; N 6.63. $C_{24}H_{26}N_2O_5$. Calculated, %: C 68.25; H 6.16; N 6.63. M 422.49.

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