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Chemistry of Iminofuran: VIII.* Recyclization of 5-Aryl-3-arylimino-3*H*-furan-2-ones Effected by Cyanoacetic Acid Derivatives

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Abstract—The recyclization of 5-aryl-3-arylimino-3*H*-furan-2-ones under the action of esters, nitriles, and amides of cycnoacetic acids resulted in the corresponding esters, nitriles, and amides of (5*E*)-2-amino-1-aryl-4-oxo-5-(2-oxoethylidene)-1*H*-4,5-dihydropyrrole-3-carboxylic acids.

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The structure of 3-imino-3*H*-furan-2-one underlies their rich synthetic opportunities. The presence of several electron-deficient sites in the molecule of furan-2-ones makes it possible to change the direction of the nucleophile's attack by varying the substituents in the heterocycle and the imino function thus altering the structure of the final reaction products. By now a wide range of OH-, SH-, NH-nucleophiles has been tested in the reactions with 3-imino-3*H*-furan-2-ones [2–7]. Wide synthetic opportunities are contained in the recyclization reactions of 3-imino-3*H*-furan-2-ones which are available and convenient objects for building up versatile acyclic and heterocyclic structures. The transformations of 3-imino-3*H*-furan-2-ones in the reactions with CH-nucleophiles were not yet investigated. According to published data the cyanoacetic acid derivatives as the example of the CH-nucleophile were examined in reactions with diverse four- [8, 9], five- [10–15], and six-membered [16, 17] oxoheterocycles leading as a rule to the formation of recyclization products belonging to new heterocyclic systems. We formerly demonstrated by two examples the synthetic opportunities of 3-(4-bromophenylimino)-5-phenyl-3*H*-furan-2-one in the reactions with malonodinitrile and ethyl cyanoacetate resulting in the ester and the nitrile of (5*E*)-2-amino-1-(4-bromo-phenyl)-4-oxo-5-(2-oxo-2-phenylethylidene)-1*H*-4,5-dihydropyrrole-3-carboxylic acid [18].

In order to test the opportunities of this method and to increase the diversity of the substituted (5*E*)-2-amino-1-aryl-4-oxo-5-(2-oxoethylidene)-1*H*-4,5-dihydropyrrole-3-carboxylic acids we primarily synthesized by the known methods from 4-aryl-2-hydroxy-4-oxobut-2-enoic acids **Ia–Ig** and arylamines **IIa–IIl** 4-aryl-2-arylamino-4-oxobut-2-enoic acids **IIIa–IIIz$_2$**, that treated with acetic anhydride underwent cyclization forming the corresponding 5-aryl-3-arylimino-3*H*-furan-2-ones **IVa– IVz$_2$** (Scheme 1) [1, 19].

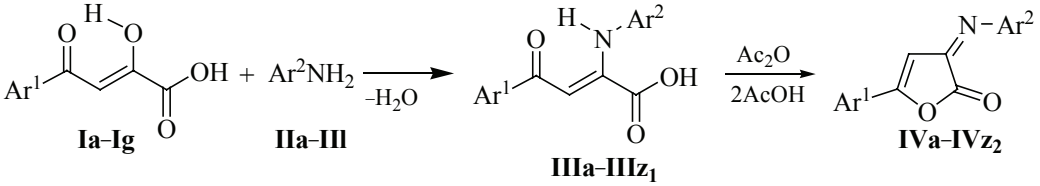
5-Aryl-3-arylimino-3*H*-furan-2-ones **IVa**, **IVh**, **IVl**, **IVm**, **IVo**, **IVr** reacted with malonodinitrile in the presence of triethylamine in dioxane to form nitriles of 2-amino-5-(2-aryl-2-oxoethylidene)-4-oxo-1*H*-4,5-dihydropyrrole-3-carboxylic acids **Va–Vg** (Scheme 2).

Aminopyrroles **Va–Vf** are colorless crystalline substances. Their IR spectra contain absorption bands of NH group in the region 3418–3082 cm^{-1}, of nitrile group at 2212–2207 cm^{-1}, and of carbonyl groups in the region 1691–1639 cm^{-1}. In the ^{1}H NMR spectra the following signals were observed: a singlet of the proton of the NH group in the region 9.13–8.16 ppm, a multiplet of the aromatic protons at 7.60 ppm, and a singlet of vinyl proton at 5.74–5.57 ppm.

5-Aryl-3-arylimino-3*H*-furan-2-ones **IVf, IVh** reacted with cyanoacetamide in the presence of triethylamine in dioxane giving 2-amino-5-(2-aryl-2-oxoethylidene)-4-

*For Communicacion VII, see [1].

Scheme 1.



Ia–Ig **IIa–III** **IIIa–IIIz$_1$** **IVa–IVz$_2$**

I, Ar^1 = Ph (**a**), 4-MeC$_6$H$_4$ (**b**), 4-MeOC$_6$H$_4$ (**c**), 4-ClC$_6$H$_4$ (**d**), 4-FC$_6$H$_4$ (**e**), 2,4-Me$_2$C$_6$H$_3$ (**f**), 1-naphthyl (**g**); **II**, Ar^2 = Ph(**a**), 4-FC$_6$H$_4$ (**b**), 2-ClC$_6$H$_4$ (**c**), 3-ClC$_6$H$_4$ (**d**), 4-ClC$_6$H$_4$ (**e**), 4-BrC$_6$H$_4$ (**f**), 2-IC$_6$H$_4$ (**g**), 3-NO$_2$C$_6$H$_4$ (**h**) 4-NO$_2$C$_6$H$_4$ (**i**), 3-CF$_3$C$_6$H$_4$ (**j**), 2-Me-5-NO$_2$C$_6$H$_3$ (**k**), 4-EtOOCC$_6$H$_4$ (**l**). **III, IV**, Ar^1 = Ph, Ar^2 = Ph (**a**), 4-FC$_6$H$_4$ (**b**), 2-ClC$_6$H$_4$ (**c**), 3-ClC$_6$H$_4$ (**d**), 4-ClC$_6$H$_4$ (**e**), 4-BrC$_6$H$_4$ (**f**), 2-IC$_6$H$_4$ (**g**), 4-NO$_2$C$_6$H$_4$ (**h**), 3-CF$_3$C$_6$H$_4$ (**i**), 2-Me-5-NO$_2$C$_6$H$_3$ (**j**); Ar^1 = 4-MeC$_6$H$_4$, Ar^2 = 4-FC$_6$H$_4$ (**k**), 2-ClC$_6$H$_4$ (**l**), 3-ClC$_6$H$_4$ (**m**), 4-ClC$_6$H$_4$ (**n**), 4-BrC$_6$H$_4$ (**o**), 4-EtOOCC$_6$H$_4$ (**p**), 4-MeC$_6$H$_4$ (**q**), 3-NO$_2$C$_6$H$_4$ (**r**), 4-NO$_2$C$_6$H$_4$ (**s**), 2-Me-5-NO$_2$C$_6$H$_3$ (**t**); Ar^1 = 4-MeOC$_6$H$_4$, Ar^2 = 4-EtOOCC$_6$H$_4$ (**u**), 2-Me-5-NO$_2$C$_6$H$_3$ (**v**); Ar^1 = 4-EtOC$_6$H$_4$, 2-Me-5-NO$_2$C$_6$H$_3$ (**w**); Ar^1 = 4-ClC$_6$H$_4$, Ar^2 = 4-ClC$_6$H$_4$ (**x**), 2-Me-5-NO$_2$C$_6$H$_3$ (**y**); Ar^1 = 4-FC$_6$H$_4$, Ar^2 = 2-Me-5-NO$_2$C$_6$H$_3$ (**z**); Ar^1 = 2,4-Me$_2$C$_6$H$_3$, Ar^2 = 2-Me-5-NO$_2$C$_6$H$_3$ (**z$_1$**); Ar^1 = 1-naphthyl, Ar^2 = 2-Me-5-NO$_2$C$_6$H$_3$ (**z$_2$**).

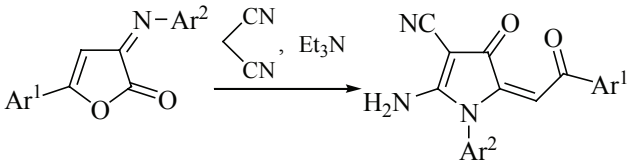
oxo-1*H*-4,5-dihydropyrrole-3-carboxamides **VIa**, **VIb** (Scheme 3).

Aminopyrroles **VIa, VIb** are colorless crystalline substances. Their IR spectra contain absorption bands of NH group in the region 3466–3306 cm^{-1} and of carbonyl groups in the region 1669–1616 cm^{-1}. In the ^{1}H NMR spectra the following signals were observed: singlets of the proton of the NH group in the region 8.68–8.17 ppm, multiplets of the aromatic protons at 7.60 ppm, singlets of the amide group protons at 7.15–6.88 ppm and of vinyl protons at 5.83–5.71 ppm.

5-Aryl-3-arylimino-3*H*-furan-2-ones **IVa–IVq, IVs–IVz$_2$** reacted with ethyl cyanoacetate in the presence of triethylamine in dioxane to form ethyl 2-amino-5-(2-aryl-2-oxoethylidene)-4-oxo-1*H*-4,5-dihydropyrrole-3-carboxylates **VIIa–VIIz$_1$** (Scheme 4).

Aminopyrroles **VIIa–VIIz$_1$** are colorless crystalline substances. Their IR spectra contain absorption bands of NH group (3439–3302 cm^{-1}), of ester group (1713–1686 cm^{-1}) and of carbonyl groups (1649–1603 cm^{-1}). In the ^{1}H NMR spectra the following signals were observed: singlets of the proton of the NH group (8.34–7.65 ppm), multiplets of the aromatic protons (7.60 ppm), singlet of vinyl proton (5.72–5.42 ppm), quartet of methylene

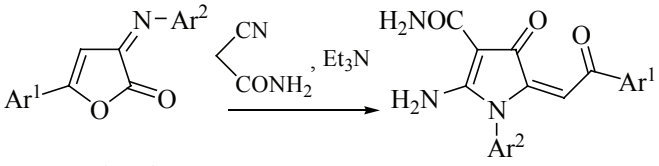
Scheme 2.



IVa, IVh, IVl, IVm, IVn, IVs **Va–Vf**

V, Ar^1 = Ph, Ar^2 = Ph (**a**), 4-NO$_2$C$_6$H$_4$ (**b**); Ar^1 = 4-MeC$_6$H$_4$, Ar^2 = 2-ClC$_6$H$_4$ (**c**), 3-ClC$_6$H$_4$ (**d**), 4-BrC$_6$H$_4$ (**e**), 3-NO$_2$C$_6$H$_4$ (**f**).

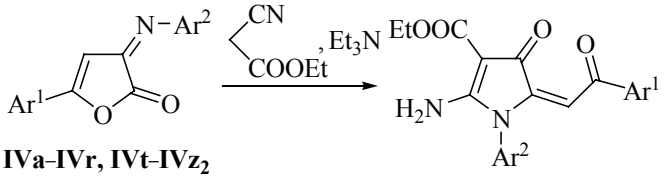
Scheme 3.



IVf, IVh **VIa, VIb**

VI, Ar^1 = Ph, Ar^2 = 4-BrC$_6$H$_4$ (**a**), 4-NO$_2$C$_6$H$_4$ (**b**).

Scheme 4.



IVa–IVr, IVt–IVz$_2$ **VIIa–VIIz$_1$**

VII, Ar^1 = Ph, Ar^2 = Ph (**a**), 4-FC$_6$H$_4$ (**b**), 2-ClC$_6$H$_4$ (**c**), 3-ClC$_6$H$_4$ (**d**), 4-ClC$_6$H$_4$ (**e**), 4-BrC$_6$H$_4$ (**f**), 2-IC$_6$H$_4$ (**g**), 4-NO$_2$C$_6$H$_4$ (**h**), 3-CF$_3$C$_6$H$_4$ (**i**), 2-Me-5-NO$_2$C$_6$H$_3$ (**j**); Ar^1 = 4-MeC$_6$H$_4$, Ar^2 = 4-FC$_6$H$_4$ (**k**), 2-ClC$_6$H$_4$ (**l**), 3-ClC$_6$H$_4$ (**m**), 4-ClC$_6$H$_4$ (**n**), 4-BrC$_6$H$_4$ (**o**), 4-EtOOCC$_6$H$_4$ (**p**), 4-MeC$_6$H$_4$ (**q**), 3-NO$_2$C$_6$H$_4$ (**r**), 2-Me-5-NO$_2$C$_6$H$_3$ (**s**); Ar^1 = 4-MeOC$_6$H$_4$, Ar^2 = 4-EtOOCC$_6$H$_4$ (**t**), 2-Me-5-NO$_2$C$_6$H$_3$ (**u**); Ar^1 =4-EtOC$_6$H$_4$, 2-Me-5-NO$_2$C$_6$H$_3$ (**v**); Ar^1 = 4-ClC$_6$H$_4$, Ar^2 = 4-ClC$_6$H$_4$ (**w**), 2-Me-5-NO$_2$C$_6$H$_3$ (**x**); Ar^1 = 4-FC$_6$H$_4$, Ar^2 = 2-Me-5-NO$_2$C$_6$H$_3$ (**y**); Ar^1=2,4-Me$_2$C$_6$H$_3$, Ar^2 = 2-Me-5-NO$_2$C$_6$H$_3$ (**z**); Ar^1 = 1-naphthyl, Ar^2 = 2-Me-5-NO$_2$C$_6$H$_3$ (**z$_1$**).

(4.13–4.07 ppm) and triplet of methyl (1.20–1.14 ppm) protons of the ethyl carboxylate.

The formation of compounds **V–VII** (Scheme 5) proceeds evidently through the primary nucleophilic attack of the carbanion formed from the cyanoacetic acid derivative under the action of triethylamine [20] on the C^2 atom of the furan ring givng intermediate **A** [15]. Further the charges in the molecule undergo a redistribution with the cleavage of the O^1–C^2 bond and the formation of intermediate **B** with a negative charge on the O atom and a delocalized double bond conjugated with the aromatic ring. The negative charge is apparently delocalized along all conjugation system O–C–C–C–N.

The atom N possessing excess electron density due to the presence of an excessive negative charge in the conjugation system attacks the electro-deficient C atom of the nitrile group with the formation of intermediate **C**. In the next stage apparently a proton goes from the triethylammonium to intermediate **C** giving intermediate **D** suffering subsequently an imino-eHimine tautomeric transformation into compounds **V–VII** due to the formation of a more stable conjugated system.

EXPERIMENTAL

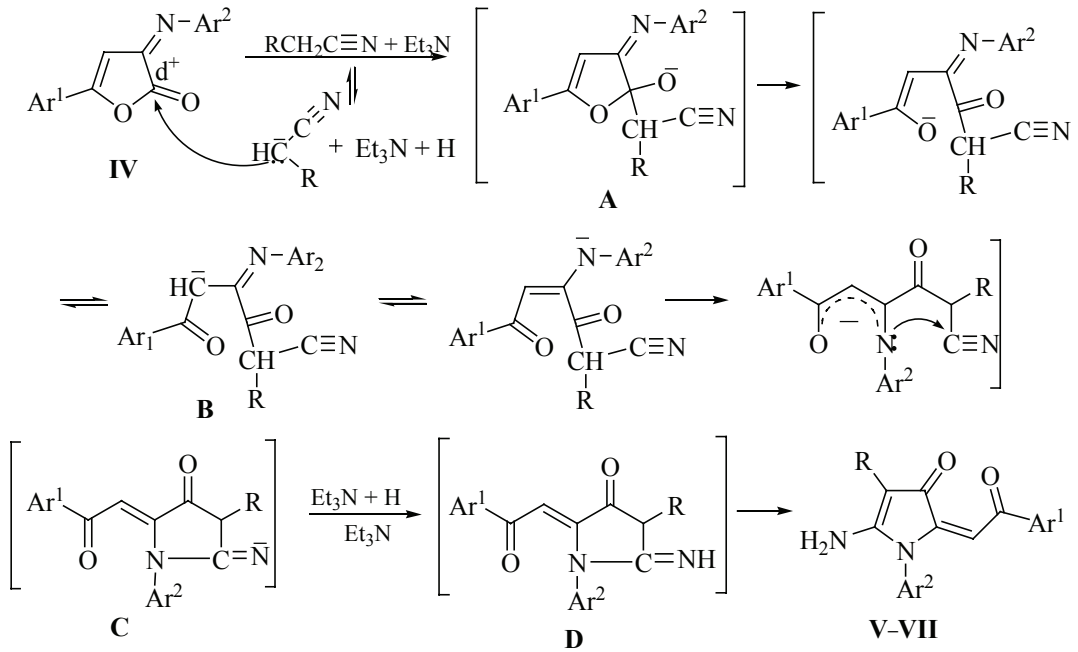
IR spectra were recorded on spectrophotometers FSM-1201 and Specord M-80 from mulls in mineral oil, ^{1}H NMR spectra were registered on spectrometers Varian Mercury Plus-300 (300.05 MHz) and Tesla BS-567A (100 MHz), internal reference HMDS. Elemental analysis was carried out on an analyzer Leco CHNS-932. The monitoring of the reaction progress and checking the compounds purity was performed by TLC on Silufol UV-254 plates, eluent ethyl ether–benzene–acetone, 10 : 9 : 1, spots visualized in iodine vapor. Mass spectrum was registered on an instrument MKh-1310, emission current 1000 mA, ionizing electrons energy 70eV, vaporizer temperature 120°C, ion source temperature 200°C.

4-Aryl-2-arylamino-4-oxobut-2-enoic acids IIIa–IIIz$_2$ were obtained by procedure [21] from 0.01 mol of 4-aryl-2-hydroxy-4-oxobut-2-enoi acids **Ia–Ig** and 0.01 mol of substituted anilines **IIa–III**. Compounds **IIIa, IIIe, IIIn, IIIh**) [19] and **IIIf, IIIg, IIIi, IIIj, IIIp, IIIt, IIIu, IIIv**) [21] were described previously.

4-Oxo-4-phenyl-2-(4-fluorophenylamino)but-2-enoic acid (IIIb). Yield 1.92 g (67%), yellow crystals, t.decomp. 189–190°C (acetonitrile). IR spectrum, ν, cm^{-1}: 3256 (NH), 1730 (COOH). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 6.46 s (1H, CH), 7.60 m (9H, Ar), 11.96 s (1H, NH). Found, %: C 67.39; H 4.25; N 4.91. $C_{16}H_{12}FNO_3$. Calculated, %: C 67.36; H 4.24; N 4.93.

4-Oxo-4-phenyl-2-(2-chlorophenylamino)but-2-enoic acid (IIIc). Yield 2.35 g (78%), yellow crystals, t.decomp. 161–162°C (ethanol). IR spectrum, ν,

Scheme 5.



cm^{-1}: 3230 (NH), 1590 sh (COOH, C^4=O, C=C, C=N). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 6.63 s (1H, CH), 7.60 m (9H, Ar), 12.17 s (1H, NH). Found, %: C 63.65; H 4.03; Cl 11.72; N 4.63. $C_{16}H_{12}ClNO_3$. Calculated, %: C 63.68; H 4.02; Cl 11.78; N 4.62.

4-Oxo-4-phenyl-2-(3-chlorophenylamino)but-2-enoic acid (IIId). Yield 2.77 g (92%), yellow crystals, t.decomp. 174–175°C (acetonitrile). IR spectrum, ν, cm^{-1}: 3225 (NH), 1603, 1557 (C^4=O, C=C, C=N). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 6.50 s (1H, CH), 7.50 m (9H, Ar), 11.75 s (1H, NH). Found, %: C 63.68; H 4.02; Cl 11.78; N 4.62. $C_{16}H_{12}ClNO_3$. Calculated, %: C 63.69; H 4.01; Cl 11.75; N 4.64.

4-(4-Methylphenyl)-4-oxo-2-(4-fluorophenylamino)but-2-enoic acid (IIIk). Yield 2 g (69%), yellow crystals, t.decomp. 158–159°C (ethanol). IR spectrum, ν, cm^{-1}: 3199 (NH), 1655, 1607 (C^4=O, C=C, C=N). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.37 s (3H, Me), 6.38 s (1H, CH), 7.60 m (8H, Ar), 11.9 s (1H, NH). Found, %: C 68.22; H 4.71; N 4.68. $C_{17}H_{14}FNO_3$. Calculated, %: C 68.20; H 4.70; N 5.00.

4-(4-Methylphenyl)-4-oxo-2-(2-chlorophenylamino)but-2-enoic acid (IIIl). Yield 2.7 g (85%), yellow crystals, t.decomp. 161–162°C (aceto-nitrile). IR spectrum, ν, cm^{-1}: 3230 (NH), 1605 sh (COOH, C^4=O, C=C, C=N). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.38 s (3H, Me), 6.58 s (1H, CH), 7.40 m (8H, Ar), 12.09 s (1H, NH). Found, %: C 64.65; H 4.48; Cl 11.20; N 4.43. $C_{17}H_{14}ClNO_3$. Calculated, %: C 64.68; H 4.49; Cl 11.22; N 4.42.

4-(4-Methylphenyl)-4-oxo-2-(3-chlorophenylamino)but-2-enoic acid (IIIm). Yield 2.7 g (85%), t.decomp. 160–161°C (acetonitrile). IR spectrum, ν, cm^{-1}: 3202 (NH), 1597, 1554, 1522 (C^4=O, C=C, C=N). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.37 s (3H, Me), 6.48 s (1H, CH), 7.40 m (8H, Ar), 11.73 s (1H, NH). Found, %: C 64.67; H 4.47; Cl 11.23; N 4.44. $C_{17}H_{14}ClNO_3$. Calculated, %: C 64.67; H 4.47; Cl 11.23; N 4.44.

4-(4-Methylphenyl)-2-(4-methylphenylamino)-4-oxobut-2-enoic acid (IIIq). Yield 2.30 g (78%), t.decomp. 154–155°C (benzene). IR spectrum, ν, cm^{-1}: 3229 (NH), 1734 (COOH), 1640, 1600, 1577 (C^4=O, C=C, C=N). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.29 s (3H, Me), 2.43 c (3H, Me), 6.48 c (1H, CH), 7.30 m (8H, Ar), 12.09 c (1H, NH). Found, %: C 73.23; H 5.79; N 4.74. $C_{18}H_{17}NO_3$. Calculated, %: C 73.20; H 5.80; N 4.74.

4-(4-Methylphenyl)-2-(3-nitrophenylamino)-4-oxobut-2-enoic acid (IIIr). Yield 2.48 g (76%), t.decomp. 181–182°C (ethanol). IR spectrum, ν, cm^{-1}: 3217 (NH), 1686, 1678, 1608 (C^4=O, C=C, C=N). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.38 s (3H, Me), 6.61 s (1H, CH), 7.6 m (8H, Ar), 11.65 s (1H, NH). Found, %: C 62.55; H 4.30; N 8.61. $C_{17}H_{14}N_2O_5$. Calculated, %: C 62.57; H 4.32; N 8.59.

4-(4-Methylphenyl)-2-(4-nitrophenylamino)-4-oxobut-2-enoic acid (IIIs). Yield 2.81 g (86%), t.decomp. 144–145°C (ethanol). IR spectrum, ν, cm^{-1}: 3219 (NH), 1755 (COOH), 1651, 1589 (C^4=O, C=C, C=N). ^{1}H NMR spectrum, δ, ppm: 2.44 s (3H, Me), 6.79 s (1H, CH), 7.60 m (8H, Ar), 11.58 s (1H, NH). Found, %: C 62.59; H 4.30; N 8.55. $C_{17}H_{14}N_2O_5$. Calculated, %: C 62.57; H 4.32; N 8.59.

2-(2-Methyl-5-nitrophenylamino)-4-(4-methoxyphenyl)-4-oxobut-2-enoic acid (IIIv). Yield 2.71 g (76%), t.decomp. 168–169°C (dioxane). IR spectrum, ν, cm^{-1}: 3210 br. (NH), 1728 (COOH) 1630, 1604, 1580 (C^4=O, C=C, C=N). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.46 s (3H, Me), 3.82 s (3H, MeO), 6.52 s (1H, CH), 7.50 m (7H, Ar), 11.84 s (1H, NH). Found, %: C 60.59; H 4.48; N 7.91. $C_{18}H_{16}N_2O_6$. Calculated, %: C 60.67; H 4.53; N 7.86.

2-(2-Methyl-5-nitrophenylamino)-4-oxo-4-(4-ethoxyphenyl)but-2-enoic acid (IIIw). Yield 2.99 g (81%), t.decomp. 175–176°C (dioxane). IR spectrum, ν, cm^{-1}: 3244 (NH), 1708, 1648, 1582 (COO, C^4=O, C=C, C=N). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.38 t (3H, Me), 2.45 s (3H, Me), 4.08 q (2H, CH_2), 6.57 s (1H, CH), 7.55 m (7H, Ar), 11.83 s (1H, NH). Found, %: C 61.58; H 4.84; N 7.59. $C_{19}H_{18}N_2O_6$. Calculated, %: C 61.62; H 4.90; N 7.56.

4-Oxo-4-(4-chlorophenyl)-2-(4-chlorophenylamino)-but-2-enoic acid (IIIx). Yield 2.92 g (87%), t.decomp. 198–199°C (ethanol). IR spectrum, ν, cm^{-1}: 3228 (NH), 1647, 1598 (C^4=O, C=C, C=N). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 6.71 s (1H, CH), 7.5 m (8H, Ar), 11.45 s (1H, NH). Found, %: C 57.08; H 3.27; Cl 21.13; N 4.21. $C_{16}H_{11}Cl_2NO_3$. Calculated, %: C 57.17; H 3.30; Cl 21.09; N 4.17.

2-(2-Methyl-5-nitrophenylamino)-4-oxo-4-(4-chlorophenyl)but-2-enoic acid (IIIy). Yield 2.02 g (56%), t.decomp. 174–175°C (dioxane). IR spectrum, ν, cm^{-1}: 3212 (NH), 1670, 1652, 1578 (COOH, C^4=O, C=C, C=N). ^{1}H NMR spectrum, δ, ppm: 2.34 s (3H, Me), 6.49 s (1H, CH), 7.60 m (7H, Ar), 11.87 s (1H, NH). Found, %: C 56.64; H 3.57; Cl 9.87; N 7.69. $C_{17}H_{13}ClN_2O_5$. Calcu-

lated, %: C 56.60; H 3.63; Cl 9.83; N 7.76.

2-(2-Methyl-5-nitrophenylamino)-4-oxo-4-(4-fluorophenyl)but-2-enoic acid (IIIz). Yield 2.17 g (63%), t.decomp. 169–170°C (dioxane). IR spectrum, ν, cm^{-1}: 3150 br. (NH), 1744 (COOH), 1625, 1608, 1592 (C^4=O, C=C, C=N). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.47 c (3H, Me), 6.60 s (1H, CH), 7.50 m (7H, Ar), 11.84 c (1H, NH). Found, %: C 59.38; H 3.76; N 8.10. $C_{17}H_{13}FN_2O_5$. Calculated, %: C 59.31; H 3.81; N 8.14.

4-(2,4-Dimethylphenyl)-2-(2-methyl-5-nitrophenylamino)-4-oxobut-2-enoic acid (IIIz$_1$). Yield 2.66 g (75%), t.decomp. 171–172°C (dioxane). IR spectrum, ν, cm^{-1}: 3150 br. (NH), 1734 (COOH), 1686, 1668, 1616 (C^4=O, C=C, C=N). ^{1}H NMR spectrum, δ, ppm: 2.31 s (3H, Me), 2.42 s (3H, Me), 2.46 s (3H, Me), 6.18 s (1H, CH), 7.5 m (6H, Ar), 11.61 s (1H, NH). Found, %: C 64.44; H 5.09; N 7.88. $C_{19}H_{18}N_2O_5$. Calculated, %: C64.40; H 5.12; N 7.90.

2-(2-Methyl-5-nitrophenylamino)-1-naphthyl-4-oxobut-2-enoic acid (IIIz$_2$). Yield 2.44 g (65%), t.decomp. 179–180°C (dioxane). IR spectrum, ν, cm^{-1}: 3215 br. (NH), 1732 (COOH), 1612 уш (C^4=O, C=C, C=N). ^{1}H NMR spectrum, δ, ppm: 2.52 s (3H, Me), 6.28 s (1H, CH), 7.90 m (10H, Ar), 11.82 c (1H, NH). Found, %: C 67.08; H 4.32; N 7.48. $C_{21}H_{16}N_2O_5$. Calculated, %: C 67.02; H 4.28; N 7.44.

5-Aryl-3-arylimino-3*H*-furan-2-ones IVb–IVz$_2$ were prepared by procedure [1] from 0.01 mol of 4-aryl-2-hydroxy-4-oxobut-2-enoic acids **IIIa– IIIz$_2$** and acetic anhydride. Compounds **IVg, IVi, IVj, IVo, IVp, IVt**, **IVu**) [1], (IIIn) [19] were described before.

5-Phenyl-3-(4-fluorophenylimino)-3*H*-furan-2-one (IVb). Yield 2.11 g (79%), orange crystals, t.decomp. 169–171°C (toluene). IR spectrum, ν, cm^{-1}: 1801 (C=O$_{lactone}$). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 7.14 s (1H, CH), 7.60 m (9H, Ar). Found, %: C 71.87; H 3.74; N 5.26. $C_{16}H_{10}FNO_2$. Calculated, %: C 71.91; H 3.77; N 5.24.

5-Phenyl-3-(2-chlorophenylimino)-3*H*-furan-2-one (IVc). Yield 1.96 g (69%), orange crystals, t.decomp. 103–105°C (toluene). IR spectrum, ν, cm^{-1}: 1809 (C=O$_{lactone}$). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 7.07 s (1H, CH), 7.60 m (9H, Ar). Found, %: C 67.76; H 3.53; Cl 12.51; N 4.93. $C_{16}H_{10}ClNO_2$. Calculated, %: C 67.74; H 3.55; Cl 12.50; N 4.94.

5-Phenyl-3-(3-chlorophenylimino)-3*H*-furan-2-one (IVd). Yield 2.12 g (75%), orange crystals, t.decomp. 133–134°C (toluene). IR spectrum, ν, cm^{-1}: 1803 (C=O$_{lactone}$). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 7.06 s (1H, CH), 7.60 m (9H, Ar). Found, %: C 67.79; H 3.57; Cl 12.47; N 4.96. $C_{16}H_{10}ClNO_2$. Calculated, %: C 67.74; H 3.55; Cl 12.50; N 4.94.

5-(4-Methylphenyl)-3-(4-fluorophenylimino)-3*H*-furan-2-one (IVk). Yield 2.1 g (77%), orange crystals, t.decomp. 179–180°C (toluene). IR spectrum, ν, cm^{-1}: 1801 (C=O$_{lactone}$). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.39 s (3H, Me), 7.08 s (1H, CH), 7.60 m (8H, Ar). Found, %: C 72.57; H 4.32; N 4.97. $C_{17}H_{12}FNO_2$. Calculated, %: C 72.59; H 4.30; N 4.98.

5-(4-Methylphenyl)-3-(2-chlorophenylimino)-3*H*-furan-2-one (IVl). Yield 2.14 g (72%), orange crystals, t.decomp. 157–158°C (toluene). IR spectrum, ν, cm^{-1}: 1801 (C=O$_{lactone}$). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.36 s (3H, Me), 7.05 s (1H, CH), 7.50 m (8H, Ar). Found, %: C 68.57; H 4.07; Cl 11.95; N 4.68. $C_{17}H_{12}ClNO_2$. Calculated, %: C 68.58; H 4.06; Cl 11.91; N 4.70.

5-(4-Methylphenyl)-3-(3-chlorophenylimino)-3*H*-furan-2-one (IVm). Yield 2.32 g (78%), orange crystals, t.decomp. 154–156°C (toluene). IR spectrum, ν, cm^{-1}: 1801 (C=O$_{lactone}$). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.39 s (3H, Me), 6.99 s (1H, CH), 7.50 m (8H, Ar). Found, %: C 68.56; H 4.03; Cl 11.95; N 4.68. $C_{17}H_{12}ClNO_2$. Calculated, %: C 68.58; H 4.06; Cl 11.91; N 4.70.

5-(4-Methylphenyl)-3-(4-methylphenylimino)-3*H*-furan-2-one (IVq). Yield 2.02 g (73%), orange crystals, t.decomp. 165–167°C (toluene). IR spectrum, ν, cm^{-1}: 1796 (C=O$_{lactone}$). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.26 s (3H, Me), 2.39 s (3H, Me), 7.04 s (1H, CH), 7.40 m (8H, Ar). Found, %: C 77.98; H 5.46; N 5.03. $C_{18}H_{15}NO_2$. Calculated, %: C 77.96; H 5.45; N 5.05.

5-(4-Methylphenyl)-3-(3-nitrophenylimino)-3*H*-furan-2-one (IVr). Yield 2.2 g (73%), orange crystals, t.decomp. 198–199°C (toluene). IR spectrum, ν, cm^{-1}: 1811 (C=O$_{lactone}$). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.39 s (3H, Me), 7.03 s (1H, CH), 7.60 m (8H, Ar). Found, %: C 66.20; H 3.95; N 9.06. $C_{17}H_{12}N_2O_4$. Calculated, %: C 66.23; H 3.92; N 9.09.

5-(4-Methylphenyl)-3-(4-nitrophenylimino)-3*H*-furan-2-one (IVs). Yield 2.62 s (85%), orange crystals, t.decomp. 178–179°C (toluene). IR spectrum, ν, cm^{-1}: 1801 (C=O$_{lactone}$). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.36 s (3H, Me), 7.06 s (1H, CH), 7.60 m (8H, Ar). Found, %: C 66.22; H 3.91; N 9.08. $C_{17}H_{12}N_2O_4$. Calculated, %: C 66.23; H 3.92; N 9.09.

3-(2-Methyl-5-nitrophenylimino)-5-(4-methoxyphenyl)-3*H*-furan-2-one (IVv). Yield 1.76 g

(52%), orange crystals, t.decomp. 154–156°C (toluene). IR spectrum, ν, cm^{-1}: 1808 (C=O$_{lactone}$). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.35 s (3H, Me), 3.85 s (3H, MeO), 6.20 s (1H, CH), 7.50 m (7H, Ar). Found, %: C 63.78; H 4.22; N 8.24. $C_{18}H_{14}N_2O_5$. Calculated, %: C 63.90; H 4.17; N 8.28.

3-(2-Methyl-5-nitrophenylimino)-5-(4-ethoxyphenyl)-3*H*-furan-2-one (IVw). Yield 1.72 g (49%), orange crystals, t.decomp. 164–165°C (toluene). IR spectrum, ν, cm^{-1}: 1816 (C=O$_{lactone}$). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.36 t (3H, Me), 2.28 s (3H, Me), 4.08 q (2H, Me), 6.73 s (1H, CH), 7.50 m (7H, Ar). Found, %: C 64.73; H 4.59; N 7.91. $C_{19}H_{16}N_2O_5$. Calculated, %: C 64.77; H 4.58; N 7.97.

5-(4-Chlorophenyl)-3-(4-chlorophenylimino)-3*H*-furan-2-one (IVx). Yield 2.14 g (78%), orange crystals, t.decomp. 234–235°C (toluene). IR spectrum, ν, cm^{-1}: 1803 (C=O$_{lactone}$). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 6.97 s (1H, CH), 7.30 m (8H, Ar). Found, %: C 60.44; H 2.86; Cl 22.27; N 4.43. $C_{16}H_9Cl_2NO_2$. Calculated, %: C 60.40; H 2.85; Cl 22.29; N 4.40.

3-(2-Methyl-5-nitrophenylimino)-5-(4-chlorophenyl)-3*H*-furan-2-one (IVy). Yield 1.44 g (42%), orange crystals, t.decomp. 220–221°C (toluene). IR spectrum, ν, cm^{-1}: 1820 (C=O$_{lactone}$). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.36 s (3H, Me), 6.34 s (1H, CH), 7.70 m (7H, Ar). Found, %: C 59.61; H 3.26; Cl 10.29; N 8.13. $C_{17}H_{11}ClN_2O_4$. Calculated, %: C 59.58; H 3.23; Cl 10.34; N 8.17.

3-(2-Methyl-5-nitrophenylimino)-5-(4-fluorophenyl)-3*H*-furan-2-one (IVz). Yield 1.56 g (48%), orange crystals, t.decomp. 194–195°C (toluene). IR spectrum, ν, cm^{-1}: 1816 (C=O$_{lactone}$). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.30 s (3H, Me), 6.50 s (1H, CH), 7.50 m (7H, Ar). Found, %: C 62.62; H 3.36; N 8.53. $C_{17}H_{11}FN_2O_4$. Calculated, %: C 62.58; H 3.39; N 8.58.

5-(2,4-Dimethylphenyl)-3-(2-methyl-5-nitrophenylimino)-3*H*-furan-2-one (IVz_1). Yield 2.49 g (74%), orange crystals, t.decomp. 171–172°C (toluene). IR spectrum, ν, cm^{-1}: 1808 (C=O$_{lactone}$). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.35 s (3H, Me), 2.37 s (3H, Me), 2.44 s (3H, Me), 6.15 s (1H, CH), 7.50 m (6H, Ar). Found, %: C 67.81; H 4.76; N 8.35. $C_{19}H_{16}N_2O_4$. Calculated, %: C 67.85; H 4.79; N 8.32.

3-(2-Methyl-5-nitrophenylimino)-5-(2-naphthyl)-3*H*-furan-2-one (IV z_2). Yield 1.15 g (32%), orange crystals, t.decomp. 161–162°C (toluene). IR spectrum, ν, cm^{-1}: 1808 (C=O$_{lactone}$). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.35 s (3H, Me), 6.72 s (1H, CH), 7.80 m (10H, Ar). Found, %: C 70.42; H 3.91; N 7.85. $C_{21}H_{14}N_2O_4$. Calculated, %: C 70.39; H 3.94; N 7.82.

(5*E*)-2-Amino-1-aryl-5-(2-arylethylidene-2-oxo)-4-oxo-1*H*-4,5-dihydropyrrole-3-carbonitriles Va–Vf. A solution of 0.01 mol of an appropriate furanone **IV** and 0.66 g (0.01 mol)of malonodinitrile in 30 ml of anhydrous dioxane was heated at 70°C, 1 g (0.01 mol) of triethylamine was added, and the mixture was cooled. The separated precipitate was filtered off and recrystallized from acetonitrile.

(5*E*)-2-Amino-4-oxo-5-(2-oxo-2-phenyl-ethylidene)-1-phenyl-1*H*-4,5-dihydropyrrole-3-carbonitrile (Va). Yield 1.98 g (65%), colorless crystals, mp 240–241°C (acetonitrile). IR spectrum, ν, cm^{-1}: 3356, 3266 (NH), 2207 (C≡N), 1660 (C=O). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 5.51 s (1H, CH), 7.60 m (9H, Ar), 8.53 br.s (2H, NH). Found, %: C 63.33; H 3.36; N 15.55. $C_{19}H_{13}N_3O_2$. Calculated, %: C 72.37; H 4.16; N 13.33.

(5*E*)-2-Amino-1-(4-nitrophenyl)-4-oxo-5-(2-oxo-2-phenylethylidene)-1*H*-4,5-dihydropyrrole-3-carbonitrile (Vb). Yield 2.29 g (75%), colorless crystals, mp 241–242°C (acetonitrile). IR spectrum, ν, cm^{-1}: 3367, 3268 (NH), 2207 (C≡N), 1686, 1658 (C=O). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 5.74 s (1H, CH), 7.60 m (9H, Ar), 8.32 s (1H, NH) 9.13 C (1H, NH). Found, %: C 63.30; H 3.39; N 15.54. $C_{19}H_{12}N_4O_4$. Calculated, %: C 63.33; H 3.36; N 15.55.

(5*E*)-2-Amino-5-[2-(4-methylphenyl)-2-oxoethylidene]-4-oxo-1-(2-chlorophenyl)-1*H*-4,5-dihydropyrrole-3-carbonitrile (Vc). Yield 3.16 g (87%), colorless crystals, mp 226–227°C (ethanol). IR spectrum, ν, cm^{-1}: 3379, 3164 (NH), 2207 (C≡N), 1657 (C=O). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.34 s (3H, Me), 5.62 s (1H, CH), 7.60 m (8H, Ar), 8.21 s (1H, NH) 8.92 s (1H, NH). Found, %: C 66.01; H 3.87; Cl 9.59; N 11.56. $C_{20}H_{14}ClN_3O_2$. Calculated, %: C 66.03; H 3.88; Cl 9.57; N 11.55.

(5*E*)-2-Amino-5-[2-(4-methylphenyl)-2-oxoethylidene]-4-oxo-1-(3-chlorophenyl)-1*H*-4,5-dihydropyrrole-3-carbonitrile (Vd). Yield 2.98 g (83%), colorless crystals, mp 210–211°C (ethanol). IR spectrum, ν, cm^{-1}: 3452, 3278 (NH), 2202 (C≡N), 1691, 1639 (C=O). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.36 s (3H, Me), 5.58 s (1H, CH), 7.60 m (8H, Ar), 8.22 s (1H, NH) 9.04 s (1H, NH). Found, %: C 66.01; H 3.87; Cl 9.59; N 11.56. $C_{20}H_{14}ClN_3O_2$. Calculated, %: C 66.03; H 3.88; Cl 9.57; N 11.55.

(5*E*)-2-Amino-1-(4-bromophenyl)-5-[2-(4-methylphenyl)-2-oxoethylidene]-4-oxo-1*H*-4,5-dihydropyrrole-3-carbonitrile (Ve). Yield 3.6 g (89%) colorless crystals, mp 278–279°C (dioxane). IR spectrum, ν, cm^{-1}: 3380, 3260 (NH), 2208 (C≡N), 16866, 1659 (C=O, C=C). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 2.35 s (3H, Me), 5.58 s (1H, CH), 7.60 m (8H, Ar), 8.17 s (1H, NH), 9.03 s (1H, NH). Found, %: C 58.83; H 3.42; Br 19.54; N 10.31. $C_{20}H_{14}BrN_3O_2$. Calculated, %: C 58.84; H 3.46; Br 19.57; N 10.29.

(5*E*)-2-Amino-5-[2-(4-methylphenyl)-2-oxoethylidene]-1-(3-nitrophenyl)-4-oxo-1*H*-4,5-dihydropyrrole-3-carbonitrile (Vf). Yield 2.73 g (74%) colorless crystals, mp 207–208°C (ethanol). IR spectrum, ν, cm^{-1}: 3418, 3082 (NH), 2212 (C≡N), 1666, 1639 (C=O). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 2.36 s (3H, Me), 5.69 s (1H, CH), 7.70 m (8H, Ar), 8.25 s (1H, NH), 9.08 s (1H, NH). Found, %: C 64.15; H 3.79; N 14.96. $C_{20}H_{14}N_4O_4$. Calculated, %: C 64.17; H 3.77; N 14.97.

(5*E*)-2-Amino-1-aryl-4-oxo-5-(2-oxo-2-phenylethylidene)-1*H*-4,5-dihydropyrrole-3-carboxamides VIa, VIb. A solution of 0.01 mol of an appropriate furanone **IV** and 0.8 g (0.01 mol) of cyanoacetamide in 30 ml of anhydrous dioxane was heated at 70°C, 1 g (0.01 mol) of triethylamine was added, and the mixture was cooled. The separated precipitate was filtered off and recrystallized from acetonitrile.

(5*E*)-2-Amino-1-(4-bromophenyl)-4-oxo-5-(2-oxo-2-phenylethylidene)-1*H*-4,5-dihydro-pyrrole-3-carboxamide (VIa). Yield 3.74 g (91%), colorless crystals, mp 235–236°C. IR spectrum, ν, cm^{-1}: 3402, 3306 (NH), 1674, 1655 (C=O). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 5.71 s (1H, CH), 6.88 s (1H, $CONH_2$), 7.13 s (1H, $CONH_2$), 7.60 m (9H, Ar), 8.35 s (1H, NH) 8.55 s (1H, NH). Found, %: C 55.35; H 3.43; Br 19.39; N 10.18. $C_{19}H_{14}BrN_3O_3$. Calculated, %: C 55.36; H 3.42; Br 19.38; N 10.19.

(5*E*)-2-Amino-1-(4-nitrophenyl)-4-oxo-5-(2-oxo-2-phenylethylidene)-1*H*-4,5-dihydropyrrole-3-carboxamide (VIb). Yield 3.25 g (86%), colorless crystals, mp 242–243°C. IR spectrum, ν, cm^{-1}: 3466, 2954 (NH), 1686, 1658 (C=O). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 5.83 s (1H, CH), 6.92 s (1H, $CONH_2$), 7.15 s (1H, $CONH_2$), 7.60 m (9H, Ar), 8.43 s (1H, NH, 8.68 s (1H, NH). Found, %: C 60.31; H 3.74; N 14.80. $C_{19}H_{14}N_4O_5$. Calculated, %: C 60.32; H 3.73; N 14.81.

Ethyl (5*E*)-2-amino-1-aryl-5-(2-aryl-2-oxoethylidene)-1*H*-4,5-dihydropyrrole-3-carboxylates VIIa–VIIz$_1$. A solution of 0.01 mol of an appropriate furanone **IV** and 1.13 g (0.01 mol) of ethyl cyanoacetate in 30 ml of anhydrous dioxane was heated at 70°C, 1 g (0.01 mol) of triethylamine was added, and the mixture was cooled. The separated precipitate was filtered off and recrystallized.

Ethyl (5*E*)-2-amino-1-phenyl-4-oxo-5-(2-oxo-2-phenylethylidene)-1*H*-4,5-dihydropyrrole-3-carboxylate (VIIa). Yield 2.64 g (73%), colorless crystals, mp 246–248°C (dioxane). IR spectrum, ν, cm^{-1}: 3423, 3225 (NH), 1714 (COOEt), 1646, 1601 (C=C, C=O). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 1.13 t (3H, CMe), 4.03 q (2H, CH_2), 5.57 s (1H, CH), 7.65 m (10H, Ar), 8.12 s (1H, NH), 8.35 s (1H, NH). Found, %: C 69.61; H 5.01; N 7.70. $C_{21}H_{18}N_2O_4$. Calculated, %: C 69.60; H 5.01; N 7.73.

Ethyl (5*E*)-2-amino-4-oxo-5-(2-oxo-2-phenylethylidene)-1-(4-fluorophenyl)-1*H*-4,5-dihydropyrrole-3-carboxylate (VIIb). Yield 2.39 g (86%), colorless crystals, mp 251–252°C (acetonitrile). IR spectrum, ν, cm^{-1}: 3433, 3234 (NH), 1711 (COOEt), 1643, 1603 (C=O). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 1.14 t (3H, CMe), 4.17 q (2H, CH_2), 5.49 s (1H, CH), 7.65 m (9H, Ar), 8.17 s (1H, NH), 8.30 s (1H, NH). Found, %: C 66.34; H 4.52; N 7.38. $C_{21}H_{17}FN_2O_4$. Calculated, %: C 66.31; H 4.50; N 7.36.

Ethyl (5*E*)-2-amino-4-oxo-5-(2-oxo-2-phenylethylidene)-1-(2-chlorophenyl)-1*H*-4,5-dihydropyrrole-3-carboxylate (VIIc). Yield 3.09 g (78%), colorless crystals, mp 239–240°C (dioxane). IR spectrum, ν, cm^{-1}: 3380, 3109 (NH), 1712 (COOEt), 1658 (C=C, C=O). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 1.15 t (3H, CMe), 4.09 q (2H, CH_2), 5.61 s (1H, CH), 7.65 m (9H, Ar), 8.02 s (1H, NH), 8.19 s (1H, NH). Found, %: C 63.53; H 4.30; Cl 8.97; N 7.09. $C_{21}H_{17}ClN_2O_4$. Calculated, %: C 63.56; H 4.32; Cl 8.93; N 7.06.

Ethyl (5*E*)-2-amino-4-oxo-5-(2-oxo-2-phenylethylidene)-1-(3-chlorophenyl)-1*H*-4,5-dihydropyrrole-3-carboxylate (VIId). Yield 2.33 g (59%), colorless crystals, mp 220–221°C (toluene). IR spectrum, ν, cm^{-1}: 3377, 2955 (NH), 1664 (COOEt), 1595 (C=O). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 1.17 t (3H, CMe), 4.11 q (2H, CH_2), 5.56 s (1H, CH), 7.65 m (9H, Ar), 7.68 s (1H, NH), 8.19 s (1H, NH). Found, %: C 63.54; H 4.35; Cl 6.95; N 7.08. $C_{21}H_{17}ClN_2O_4$. Calculated, %: C 63.56; H 4.32; Cl 8.93; N 7.06.

Ethyl (5*E*)-2-amino-4-oxo-5-(2-oxo-2-phenylethylidene)-1-(4-chlorophenyl)-1*H*-4,5-dihydropyrrole-3-carboxylate (VIIe). Yield 2.61 g (66%), colorless crystals, mp 264–265°C (acetonitrile). IR spectrum, ν,

cm^{-1}: 3440, 3260 (NH), 1716 (COOEt), 1645, 1612 (C=O, C=C). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.09 t (3H, CMe), 3.48 q (2H, CH_2), 5.42 s (1H, CH), 7.50 m (9H, Ar), 8.02 br.s (2H, NH_2). Found, %: C 63.53; H 4.34; Cl 8.97; N 7.08. $C_{21}H_{17}ClN_2O_4$. Calculated, %: C 63.56; H 4.32; Cl 8.93; N 7.06.

Ethyl (5*E*)-2-amino-1-(4-bromophenyl)-4-oxo-5-(2-oxo-2-phenylethylidene)-1*H*-4,5-dihydropyrrole-3-carboxylate (VIIf). Yield 3.79 g (86%), colorless crystals, mp 264–266°C (acetonitrile). IR spectrum, ν, cm^{-1}: 3441, 3281 (NH), 1711 (COOEt), 1665, 1645 (C=O). ^{1}H, NMR spectrum (DMSO-d_6), δ, ppm: 1.14 t (3H, CMe), 4.07 q (2H, CH_2), 5.55 s (1H, CH), 7.60 m (9H, Ar), 8.15 s (1H, NH), 8.30 s (1H, NH). ^{13}C NMR spectrum, δ, ppm: 14.52 (CH_3), 58.36 (CH_2), 85.88 (C^3), 108.53 (=CH), 123.32 (C), 128.44 (CH), 128.50 (CH), 131.36 (CH), 132.05 (C), 132.98 (CH), 133.48 (CH), 137.23 (C), 141.79 (C^2), 164.48 (C^5), 166.08 (CO) 174.68 (C^4), 193.62 (CO). Found, %: C 57.12; H 3.85; Br 18.15; N 6.32. $C_{21}H_{17}BrN_2O_4$. Calculated, %: C 57.16; H 3.88; Br 18.11; N 6.35.

Ethyl (5*E*)-2-amino-1-(2-iodophenyl)-4-oxo-5-(2-oxo-2-phenylethylidene)-1*H*-4,5-dihydro-pyrrole-3-carboxylate (VIIg). Yield 4.25 g (86%), colorless crystals, mp 212–213°C (acetonitrile). IR spectrum, ν, cm^{-1}: 3298 (NH), 1682 (COOEt), 1655, 1606 (C=O). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.14 t (3H, CMe), 4.07 q (2H, CH_2), 5.55 s (1H, CH), 7.60 m (9H, Ar), 8.15 s (1H, NH), 8.30 s (1H, NH). Found, %: C 51.68; H 3.54; N 5.72. $C_{21}H_{17}IN_2O_4$. Calculated, %: C 51.66; H 3.51; N 5.74.

Ethyl (5*E*)-2-amino-1-(4-nitrophenyl)-4-oxo-5-(2-oxo-2-phenylethylidene)-1*H*-4,5-dihydropyrrole-3-carboxylate (VIIh). Yield 3.46 g (85%), colorless crystals, mp 295–296°C (ethanol). IR spectrum, ν, cm^{-1}: 3439, 3237 (NH), 1709 (COOEt), 1637, 1605 (C=O, C=C). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.20 t (3H, CMe), 4.13 q (2H, CH_2), 5.72 s (1H, CH), 7.65 m (9H, Ar), 8.13 s (1H, NH), 8.29 s (1H, NH). Found, %: C 61.92; H 4.21; N 10.33. $C_{21}H_{17}N_3O_6$. Calculated, %: C 61.91; H 4.21; N 10.31.

Ethyl (5*E*)-2-amino-4-oxo-5-(2-oxo-2-phenylethylidene)-1-(3-tpifluoromethylphenyl)-1*H*-4,5-dihydropyrrole-3-carboxylate (VIIi). Yield 2.97 g (69%), colorless crystals, mp 256–257°C (2-propanol). IR spectrum, ν, cm^{-1}: 3422, 3242 (NH), 1717 (COOEt), 1667, 1642, 1612 (C=O, C=C). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.15 t (3H, CMe), 2.36 s (3H, Me), 4.08 q (2H, CH_2), 5.52 c (1H, CH), 7.70 m (9H, Ar), 8.25 s (1H, NH), 8.42 s (1H, NH). Mass spectrum, *m*/*z* (I_{rel}, %): 430 (22) [*M*]$^+$, 385 (9) [*M* – EtO]$^+$, 357 (9.2) [*M* – EtOCO]$^+$, 290 (15.0) [*M* – EtOCO – CF_3]$^+$, 253 (3.0) [*M* – EtOCO –PhCO]$^+$, 212 (29.0), [*M* – EtOCO – $CF_3C_6H_4$]$^+$, 145 (11.0) [$CF_3C_6H_4$]$^+$, 105 (100) [PhCO]$^+$, 77 (58) [Ph]$^+$, 68 (19) [CF_3]$^+$. Found, %: C 61.43; H 3.96; N 6.55. $C_{22}H_{17}F_3N_2O_4$. Calculated, %: C 61.40; H 3.98; N 6.51. *M* 430.38.

Ethyl (5*E*)-2-amino-1-(2-methyl-5-nitrophenyl)-4-oxo-5-(2-oxo-2-phenylethylidene)-1*H*-4,5-dihydropyrrole-3-carboxylate (VIIj). Yield 3.20 g (76%), colorless crystals, mp 222–223°C (2-propanol). IR spectrum, ν, cm^{-1}: 3304 (NH), 1697 (COOEt), 1648, 1600 (C=O, C=C). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.10 t (3H, CMe), 2.24 s (3H, Me), 3.99 q (2H, CH_2), 5.40 s (1H, CH), 7.80 m (8H, Ar), 8.24 s (1H, NH), 8.32 s (1H, NH). Found, %: C 62.73; H 4.56; N 9.94. $C_{22}H_{19}N_3O_6$. Calculated, %: C 62.70; H 4.54; N 9.97.

Ethyl 5*E*)-2-amino-5-[2-(4-methylphenyl)-2-oxoethylidene]-4-oxo-1-(4-fluorophenyl)-1*H*-4,5-dihydropyrrole-3-carboxylate (VIIk). Yield 3.07 g (78%), colorless crystals, mp 233–234°C (2-propanol). IR spectrum, ν, cm^{-1}: 3439, 3317 (NH), 1713 (COOEt), 1631, 1606 (C=O). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.14 t (3H, CMe), 2.36 s (3H, Me), 4.08 q (2H, CH_2), 5.42 s (1H, CH), 7.65 m (8H, Ar), 8.15 s (1H, NH), 8.27 s (1H, NH). Found, %: C 67.02; H 4.84; N 7.12. $C_{22}H_{19}FN_2O_4$. Calculated, %: C 67.00; H 4.86; N 7.10.

Ethyl (5*E*)-2-amino-5-[2-(4-methylphenyl)-2-oxoethylidene]-4-oxo-1-(2-chlorophenyl)-1*H*-4,5-dihydropyrrole-3-carboxylate (VIIl). Yield 3.06 g (75%), colorless crystals, mp 226–227°C (ethanol). IR spectrum, ν, cm^{-1}: 3376, 3114 (NH), 1674, 1662, 1602 (COOEt, C=C, C=O). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.51 t (3H, CMe), 2.36 s (3H, Me), 4.07 q (2H, CH_2), 5.51 s (1H, CH), 7.60 m (8H, Ar), 8.12 s (1H, NH) 8.31 s (1H, NH). Found, %: C 64.30; H 4.65; Cl 8.67; N 6.79. $C_{22}H_{19}ClN_2O_4$. Calculated, %: C 64.31; H 4.66; Cl 8.63; N 6.82.

Ethyl (5*E*)-2-amino-5-[2-(4-methylphenyl)-2-oxoethylidene]-4-oxo-1-(3-chlorophenyl)-1*H*-4,5-dihydropyrrole-3-carboxylate (VIIm). Yield 3.24 g (79%), colorless crystals, mp 228–229°C (ethanol). IR spectrum, ν, cm^{-1}: 3302 (NH), 1686 (COOEt), 1649, 1637 (C=O). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.51 t (3H, CMe), 2.36 s (3H, Me), 4.07 q (2H, CH_2), 5.51 s (1H, CH), 7.60 m (8H, Ar), 8.17 s (1H, NH), 8.34 s (1H, NH). Found, %: C 64.29; H 4.63; Cl 8.66; N 6.80.

$C_{22}H_{19}ClN_2O_4$. Calculated, %: C 64.31; H 4.66; Cl 8.63; N 6.82.

Ethyl (5*E*)-2-amino-5-[2-(4-methylphenyl)-2-oxoethylidene]-4-oxo-1-(4-chlorophenyl)-1*H*-4,5-dihydropyrrole-3-carboxylate (VIIn). Yield 2.58 g (63%), colorless crystals, mp 263–264°C (ethanol). IR spectrum, ν, cm^{-1}: 3445, 3293 (NH), 1725 (COOEt), 1658, 1642, 1618 (C=O, C=C). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 1.14 t (3H, CMe), 2.36 s (3H, Me), 4.07 q (2H, CH_2), 5.51 s (1H, CH), 7.60 m (8H, Ar), 8.16 s (1H, NH), 8.32 s (1H, NH). Found, %: C 64.33; H 4.64; Cl 8.66; N 6.80. $C_{22}H_{19}ClN_2O_4$. Calculated, %: C 64.31; H 4.66; Cl 8.63; N 6.82.

Ethyl 5*E*)-2-amino-1-(4-bromophenyl)-5-[2-(4-methylphenyl)-2-oxoethylidene]-4-oxo-1*H*-4,5-dihydropyrrole-3-carboxylate (VIIo). Yield 3.54 g (78%), colorless crystals, mp 275–276°C (acetonitrile). IR spectrum, ν, cm^{-1}: 3302 (NH), 1686 (COOEt), 1649, 1637 (C=C, C=O). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 1.14 t (3H, CMe), 2.36 s (3H, Me), 4.07 q (2H, CH_2), 5.51 s (1H, CH), 7.60 m (8H, Ar), 8.16 C (1H, NH), 8.32 s (1H, NH). Found, %: C 58.02; H 4.24; Br 17.53; N 6.12. $C_{22}H_{19}CrN_2O_4$. Calculated, %: C 58.04; H 4.21; Br 17.55; N 6.15.

Ethyl (5*E*)-2-amino-5-[2-(4-methyl-phenyl)-2-oxoethylidene]-4-oxo-1-(4-ethoxycarbonylphenyl)-1*H*-4,5-dihydropyrrole-3-carboxylate (VIIp). Yield 3.85 g (86%), colorless crystals, mp 178–180°C (ethanol). IR spectrum, ν, cm^{-1}: 3308 (NH), 1714, 1682 (COOEt), 1604 (C=O). Found, %: C 66.92; H 5.36; N 6.22. $C_{25}H_{24}N_2O_6$. Calculated, %: C 66.95; H 5.39; N 6.25.

Ethyl (5*E*)-2-amino-1-(4-methylphenyl)-5-[2-(4-methylphenyl)-2-oxoethylidene]-4-oxo-1*H*-4,5-dihydropyrrole-3-carboxylate (VIIq). Yield 3.04 g (78%), colorless crystals, mp 222–223°C (ethanol). IR spectrum, ν, cm^{-1}: 3322, 3145 (NH), 1696 (COOEt), 1662, 1615 (C=O, C=C). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 1.08 t (3H, CMe), 2.28 s (3H, Me), 2.32 s (3H, Me), 4.52 q (2H, CH_2), 5.29 s (1H, CH), 7.60 m (8H, Ar), 7.92 br.s (2H, NH). Found, %: C 70.72; H 5.66; N 7.22. $C_{23}H_{22}N_2O_4$. Calculated, %: C 70.75; H 5.67; N 7.18.

Ethyl (5*E*)-2-amino-5-[2-(4-methylphenyl)-2-oxoethylidene]-1-(3-nitrophenyl)-4-oxo-1*H*-4,5-dihydropyrrole-3-carboxylate (VIIr). Yield 3.07 g (82%), colorless crystals, mp 256–257°C (ethanol). IR spectrum, ν, cm^{-1}: 3309, 3172 (NH), 1673, 1648, 1608 (COOEt, C=O, C=C). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 1.08 t (3H, CMe), 2.26 s (3H, Me), 3.94 q (2H, CH_2), 5.36 s (1H, CH), 7.80 m (8H, Ar), 8.25 s (1H, NH), 8.32 s (1H, NH). Found, %: C 62.72; H 4.66; N 9.95. $C_{22}H_{19}N_3O_6$. Calculated, %: C 62.70; H 4.54; N 9.97.

Ethyl (5*E*)-2-amino-1-(2-methyl-5-nitrophenyl)-5-[2-(4-methylphenyl)-2-oxoethylidene]-4-oxo-1*H*-4,5-dihydropyrrole-3-carboxulate (VIIs). Yield 2.09 g (48%), colorless crystals, mp 251–252°C (ethanol). IR spectrum, ν, cm^{-1}: 3303, 3168 (NH), 1672, 1646, 1608 (COOEt, C=O, C=C). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 1.09 t (3H, CMe), 2.25 s (3H, Me), 2.28 s (3H, Me), 3.92 q (2H, CH_2), 5.34 s (1H, CH), 7.80 m (7H, Ar), 8.24 s (1H, NH), 8.34 s (1H, NH). Found, %: C 63.40; H 4.89; Cl 8.63; N 9.62. $C_{23}H_{21}N_3O_6$. Calculated, %: C 63.44; H 4.86; N 9.65.

Ethyl (5*E*)-2-amino-5-[2-(4-methoxyphenyl)-2-oxoethylidene]-4-oxo-1-(4-ethoxycarbonylphenyl)-1*H*-4,5-dihydropyrrole-3-carboxylate (VIIt). Yield 3.07 g (75%), colorless crystals, mp 194–196°C (ethanol). IR spectrum, ν, cm^{-1}: 3352, 3229 (NH), 1720, 1674 (COOEt), 1647, 1601 (C=O). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 1.51 t (3H, CMe), 2.36 s (3H, Me), 4.07 q (2H, CH_2), 5.51 s (1H, CH), 7.60 m (8H, Ar), 8.16 s (1H, NH), 8.32 s (1H, NH). Found, %: C 64.62; H 5.24; N 6.02. $C_{25}H_{24}N_2O_7$. Calculated, %: C 64.65; H 5.21; N 6.03.

Ethyl (5*E*)-2-amino-1-(2-methyl-5-nitrophenyl)-5-[2-(4-methoxyphenyl)-2-oxoethylidene]-4-oxo-1*H*-4,5-dihydropyrrole-3-carboxylate (VIIu). Yield 2.07 g (46%), colorless crystals, mp 255–256°C (ethanol). IR spectrum, ν, cm^{-1}: 3312, 3184 (NH), 1676, 1650, 1602 (COOEt, C=O, C=C). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 1.16 t (3H, CMe), 2.28 s (3H, Me), 3.77 s (3H, OMe), 4.0 q (2H, CH_2), 5.38 s (1H, CH), 7.80 m (7H, Ar), 8.26 s (1H, NH), 8.35 s (1H, NH). Found, %: C 61.22; H 4.66; N 9.34. $C_{23}H_{21}N_3O_7$. Calculated, %: C 61.19; H 4.69; N 9.31.

Ethyl (5*E*)-2-amino-1-(2-methyl-5-nitrophenyl)-4-oxo-5-[2-oxo-2-(4-ethoxyphenylethylidene)]-1*H*-4,5-dihydropyrrole-3-carboxylate (VIIv). Yield 3.39 g (73%), colorless crystals, mp 222–223°C (ethanol). IR spectrum, ν, cm^{-1}: 3292, 3244 (NH), 1678, 1648, 1606 (COOEt, C=C, C=O). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 1.16 t (3H, CMe), 1.33 t (3H, Me), 4.12 m (4H, $2CH_2$), 5.38 s (1H, CH), 7.60 m (7H, Ar), 8.29 s (1H, NH), 8.38 s (1H, NH). Found, %: C 61.96; H 4.94; N 9.01. $C_{24}H_{23}N_3O_7$. Calculated, %: C 61.93; H 4.98; N 9.03.

Ethyl (5*E*)-2-amino-1-(4-chlorophenyl)-4-oxo-5-[2-oxo-2-(4-chlorophenylethylidene)]-1*H*-4,5-dihydropyrrole-3-carboxylate (VIIw). Yield 2.46 g (57%), colorless crystals, mp 266–267°C (ethanol). IR spectrum,

ν, cm^{-1}: 3301, 3186 (NH), 1676 1652, 1593 (COOEt, C=C, C=O). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.16 t (3H, CMe), 4.05 q (2H, CH_2), 5.41 s (1H, CH), 7.50 m (8H, Ar), 8.31 s (1H, NH), 8.39 s (1H, NH). Found, %: C 58.55; H 3.76; Cl 16.41; N 6.47. $C_{21}H_{16}Cl_2N_2O_4$. Calculated, %: C 58.49; H 3.73; Cl 16.44; N 6.50.

Ethyl (5*E*)-2-amino-1-(2-methyl-5-nitrophenyl)-4-oxo-5-[2-oxo-2-(4-chlorophenylethylidene)]-1*H*-4,5-dihydropyrrole-3-carboxylate (VIIx). Yield 2.32 g (51%), colorless crystals, mp 265–266°C (ethanol). IR spectrum, ν, cm^{-1}: 3296, 3172 (NH), 1670 (COOEt), 1650, 1596 (C=O). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.16 t (3H, CMe), 2.29 s (3H, Me), 4.0 q (2H, CH_2), 5.43 s (1H, CH), 7.80 m (7H, Ar), 8.34 s (1H, NH), 8.40 s (1H, NH). Found, %: C 57.95; H 3.96; Cl 7.73; N 9.26. $C_{22}H_{18}ClN_3O_6$. Calculated, %: C 57.97; H 3.98; Cl 7.77; N 9.22.

Ethyl (5*E*)-2-amino-1-(2-methyl-5-nitrophenyl) 4-oxo-5-[2-oxo-2-(4-fluorophenylethylidene)]-1*H*-4,5-dihydropyrrole-3-carboxylate (VIIy). Yield 2.50 g (57%), colorless crystals, mp 258–259°C (ethanol). IR spectrum, ν, cm^{-1}: 3308, 3184 (NH), 1672 (COOEt), 1648, 1596 (C=O). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.16 t (3H, CMe), 2.29 s (3H, Me), 4.0 q (2H, CH_2), 5.43 s (1H, CH), 7.70 m (8H, Ar), 8.31 s (1H, NH), 8.40 s (1H, NH). Found, %: C 60.18; H 4.09; N 9.51. $C_{22}H_{18}FN_3O_6$. Calculated, %: C 60.14; H 4.13; N 9.56.

Ethyl (5*E*)-2-amino-5-[2-(2,4-dimethylphenyl)-2-oxoethylidene]-1-(2-methyl-5-nitrophenyl)-4-oxo-1*H*-4,5-dihydropyrrole-3-carboxylate (VIIz). Yield 3.06 g (68%), colorless qpandCтал-лы, mp 242–243°C (ethanol). IR spectrum, ν, cm^{-1}: 3296 (NH), 1676 (COOEt), 1650, 1612 (C=O). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.16 t (3H, CMe), 2.26 s (3H, Me), 2.26 s (3H, Me), 2.26 s (3H, Me), 4.0 q (2H, CH_2), 5.43 s (1H, CH), 7.80 m (8H, Ar), 8.32 s (1H, NH), 8.40 s (1H, NH). Found, %: C 64.12; H 5.19; N 9.39. $C_{24}H_{23}N_3O_6$. Calculated, %: C 64.13; H 5.16; N 9.35.

Ethyl (5*E*)-2-amino-1-(2-methyl-5-nitrophenyl)-5-[2-(1-naphthyl)-2-oxoethylidene]-4-oxo-1*H*-4,5-dihydropyrrole-3-carboxylate (VIIz$_1$). Yield 2.21 g (47%), colorless crystals, mp 249–250°C (ethanol). IR spectrum, ν, cm^{-1}: 3288, 3216 (NH), 1676, 1646, 1612 (COOEt, C=C, C=O). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.10 t (3H, CMe), 2.31 s (3H, Me), 4.02 q (2H, CH_2), 5.71 s (1H, CH), 7.90 m (10H, Ar), 8.73 s (1H, NH), 8.80 s (1H, NH). Found, %: C 66.22; H 4.44; N 8.94. $C_{26}H_{21}N_3O_6$. Calculated, %: C 66.24; H 4.49; N 8.91.

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