Methyl 3-aroyl-4-oxo-1,4-dihydroquinoline-2-carboxylates: synthesis and molecular and crystal structures

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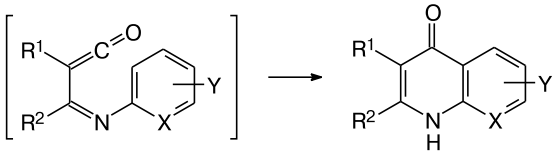
Thermal decarbonylation of methyl 1-aryl-3-(het)aroyl-4,5-dioxo-4,5-dihydro-1*H*-pyrrole-2-carboxylates afforded 8-substituted methyl 3-(het)aroyl-4-oxo-1,4-dihydroquinoline-2-carboxylates. X-ray diffraction studies revealed no hydrogen bonds in the crystals of the compounds obtained. According to spectral data, hydrogen bonding is possible in concentrated solutions of 8-substituted methyl 4-oxo-1,4-dihydroquinoline-2-carboxylates.

Key words: *N*-arylimidoylketenes, decarbonylation, 4,5-dioxo-4,5-dihydro-1*H*-pyrroles, 4-quinolones, hydrogen bonds, X-ray diffraction analysis.

Intramolecular cyclizations of *N*-α-pyridyl- and *N*-arylimidoylketenes are known to produce substituted 4-quinolones or their nitrogen analogs.[1—3] The reaction occurs as [4+2] cyclization involving two π-electrons of the aromatic substituent at the N atom and four π-electrons of the imidoylketene fragment followed by migration of the H atom (Scheme 1). The pathway of the reaction is insensitive to either an acyl group conjugated with the ketene C=C bond or substituents on the aromatic ring involved in the cyclization.[2]

Scheme 1



X = CH, N; Y = Alk, AlkO, Hal, CN

The commercial success of fluoroquinolones as highly effective antibacterial drugs as well as the discovery of other types of activity in 4-quinolone-containing compounds have given impetus to a search for methods of their synthesis and investigations of structural factors that ensure interactions with biological targets.[4]

Thermal decarbonylation of methyl 1-aryl-3-(het)aroyl-4,5-dioxo-4,5-dihydro-1*H*-pyrrole-2-carboxylates (**1**) through the formation of reactive intermediate *N*-arylimidoylketene (**2**) provides a convenient route to methyl 3-(het)aroyl-4-oxo-1,4-dihydroquinoline-2-carboxylates (**3**) (Scheme 2).

Pyrrolediones **1** prepared from methyl (*Z*)-2-arylamino-4-(het)aryl-4-oxobut-2-enoates (**4**) and oxalyl chloride easily and reversibly react with water to give methyl 1-aryl-3-(het)aroyl-2,4-dihydroxy-5-oxo-2,5-dihydro-1*H*-pyrrole-2-carboxylates (**5**). The spectral and physicochemical characteristics of compounds **1** and **5** agree with the literature data,[2,5] with the exception that their ^{1}H NMR spectra feature doublets for the protons of the methyl groups and those for the protons of the substituents at the asymmetric C(2) atom of the dihydropyrrole ring (—COOMe and —OH) and that their ^{13}C NMR spectra show doublets for the C(2) and C(4) atoms and the carbon atoms of the *o*-Me and OMe groups. Apparently, the rotation of the aromatic substituent about the C—N bond in compounds **5** is hindered by the presence of an *ortho*-substituent. This is responsible for the magnetic nonequivalence of the protons and the carbon atoms of the aforementioned groups and, accordingly, for the doubling of their signals in the ^{1}H and ^{13}C NMR spectra.

Thermal decarbonylation of pyrrolediones **1** at 180—200 °C yields methyl 3-(het)aroyl-4-oxo-1,4-di-

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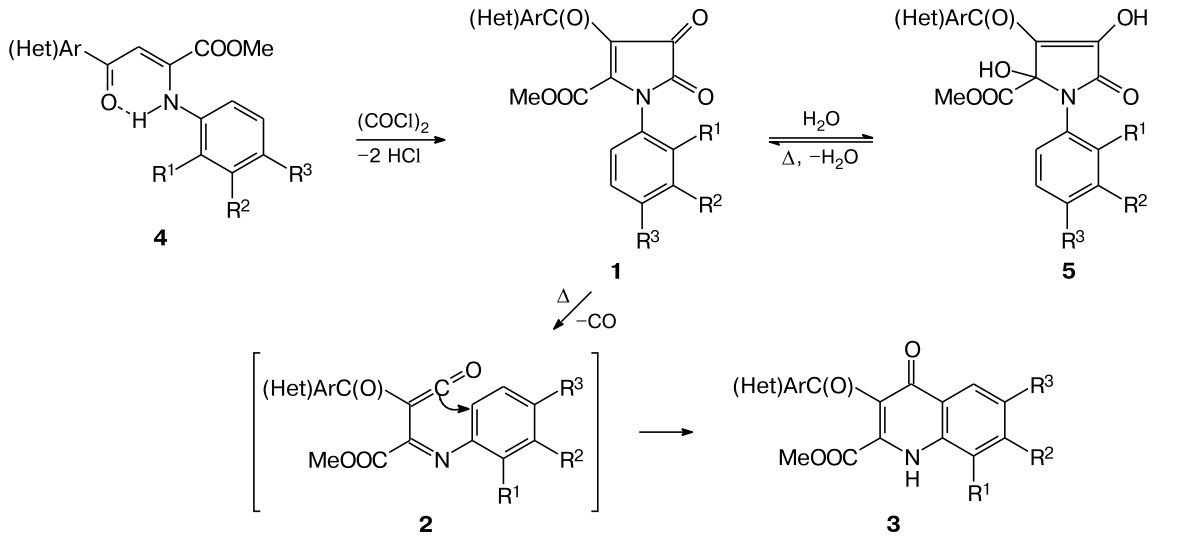
Scheme 2



	Ar	R^1	R^2	R^3		Ar	R^1	R^2	R^3		Ar	R^1	R^2	R^3
a	Ph	H	H	H	**e**	Ph	Me	H	H	**i**	4-$EtOC_6H_4$	Cl	H	Cl
b	Ph	Me	Me	H	**f**	4-BrC_6H_4	Me	H	H	**j**	4-ClC_6H_4	Cl	H	Cl
c	4-$EtOC_6H_4$	Me	Me	H	**g**	Ph	Me	H	Cl	**k**	2-Thienyl	Cl	H	Cl
d	4-ClC_6H_4	Me	Me	H	**h**	Ph	Cl	H	Cl					

hydroquinoline-2-carboxylates (**3**) as a result of intramolecular cyclization of *in situ* generated *N*-arylimidoylketenes. The optimized temperature for the synthesis of quinolones **3** is 190—220 °C. At 155—180 °C, the reaction rate is very low, which substantially extends the reaction time. Thermolysis above 225 °C is often accompanied by intense tarring of the reaction mixture, thus decreasing the yields of quinolones **3**.

The IR spectra of carboxylates **3** recorded in mineral oil show absorption bands characteristic of this type of compounds:[2] 1628—1610 (C(4)=O), 1690—1655 (CO_{aroyl}), 1725—1760 (CO_{ester}), and 3310—3372 cm^{-1} (NH stretching).

The ^1H NMR spectra of compounds **3a**—**j** in DMSO-d_6 (Table 1) contain the signals for aromatic protons, a singlet at δ 3.74—3.77 for the protons of the methoxycarbon-

Table 1. ^1H NMR spectra of compounds **3**[a] (DMSO-d_6, δ, *J*/Hz)

Compound	OMe (c)	H(6)	H(7)	H(3′), (5′)	H(4′) (м)	H(2′), (6′)	H(5)	NH
3a[b]	3.75	7.43—7.46 (m)	8.00 (d, *J* = 8.0)	7.47—7.50 (m)	7.60—7.63	7.81—7.83 (m)	8.07 (d, *J* = 6.5, *J* = 1.0)	12.40
3b	3.74	7.31 (br.d, *J* = 7.5)	—	7.48—7.51 (m)	7.61—7.64	7.78 (d, *J* = 7.0)	7.87 (br.d, *J* = 7.5)	10.70
3c	3.74	7.29 (br.d, *J* = 5.5)	—	6.99 (d, *J* = 9.0)	—	7.73 (d, *J* = 9.0)	7.88 (br.d, *J* = 5.5)	10.65
3d	3.77	7.32 (d, *J* = 7.5)	—	7.56 (d, *J* = 6.8, *J* = 2.0)	—	7.79 d, (*J* = 6.8, *J* = 2.0)	7.89 (d, *J* = 7.5)	10.78
3e	3.75	7.36—7.39 (m)	7.67 (d, *J* = 7.0)	7.49—7.52 (m)	7.62—7.65	7.79—7.81 (m)	7.98 (d, *J* = 6.0)	10.87
3f	3.77	7.37—7.40 (m)	7.67 (d, *J* = 7.0)	7.70—7.74 (m, 4 H)	—	7.70—7.74 (m)	7.96 (d, *J* = 6.0)	10.95
3g	3.75	—	7.88 (br.s)	7.48—7.52 (m)	7.62—7.65	7.80 (d, *J* = 8.0)	8.06 (br.s)	11.08
3h	3.74	—	8.08 (br.s)	7.49—7.52 (m)	7.62—7.66	7.83 (d, *J* = 7.5)	8.22 (d, *J* = 2.5)	11.23
3j	3.77	—	8.07 (br.s)	7.57 (d, *J* = 7.0, *J* = 2.0)	—	7.85 (d, *J* = 7.0, *J* = 2.0)	8.22 (d, *J* = 2.5)	11.29

[a] The signals pertaining to the substituent R are given in text.
[b] The spectrum also contains a signal at δ 7.78—7.80 (m, 1 H, H(8)).

yl group, and a broadened singlet at δ 10.65—11.29 for the NH proton. For 8-unsubstituted analogs, the last signal is shifted downfield[2] (δ 12.40 for **3a**).

Earlier,[6] 4-quinolones have been reported to dimerize in solutions by means of π-hydrogen bonding; those bonds are weakened by a substituent in position 8. Because of this, the signals for the NH proton in the ^{1}H NMR spectra of 8-substituted 4-quinolones are shifted upfield and the stretching vibrations at 3000 cm^{-1} in their IR spectra become more intense.

Based on the spectral characteristics[2] of 8-unsubstituted compounds **3**, we have hypothesized that their molecules in the crystals may be linked by strong intermolecular hydrogen bonds between the C(4)=O group of one molecule and the NH group of another. Later,[7] such bonds have been detected in 2-aryl-4-quinolones by X-ray diffraction.

In dilute solutions, 8-unsubstituted methyl 1,4-dihydroquinoline-2-carboxylates were expected[2] to be stabilized by intramolecular hydrogen bonds between the endocyclic amino group and the carbonyl O atom of the ester group, which is suggested by the lower frequency of the absorption of the ester CO group in the IR spectra of solutions of these compounds compared to their spectra in crystals. For 8-substituted quinolones in both the crystalline state and solutions, intramolecular hydrogen bonding through the NH group seems to be the only possible one because the substituent in position 8 precludes intermolecular hydrogen bonding.

To study the nature of hydrogen bonding in 8-substituted methyl 1,4-dihydroquinoline-2-carboxylates **3**, we recorded their IR spectra in solutions (Table 2).

In the spectra of 0.005 *M* solutions of compounds **3a—f** in $CHCl_3$, the absorption band due to the NH group is shifted by 20—40 cm^{-1} to the higher frequencies compared to their spectra in Nujol. The absorption band due to ester CO group is shifted to the lower frequencies by 10—20 cm^{-1} (see Table 2). In more dilute chloroform solutions (0.5 mmol L^{-1}), the bands of neither the ester nor aroyl CO groups are shifted compared to more concentrated solutions. Therefore, the carbonyl O atom of the ester group and the endocyclic amino group seem to be linked by no intermolecular hydrogen bonds in the crystals of compounds **3a—f**. According to spectroscopic data, the formation of such intermolecular hydrogen bonds is possible in concentrated solutions (by analogy with methyl 1,4-dihydroquinoline-2-carboxylates studied earlier[2]). However, the above comparison of the absorption frequencies of the aroyl CO group and C(4)=O in solutions and in the crystals precludes any conclusion about their participation in hydrogen bonding.

Table 2. IR spectra of compounds **3**

Compound	ν/cm^{-1}			
	NH	COOMe	ArCO	C(4)=O, C=C
3a	—	1746*	1676*	1620*, 1610* sh
	3372	1734	1682	1616
3b	3350*	1750*	1692*	1625*, 1600*
	3396	1730	1682	1618
3c	3310*	1745*	1655*	1610*, 1620*
	3396	1732	1682	1620, 1604
3d	3400*, 3370*	1760*, 1740*, 1725*	1680*	1620*, 1595*
	3396	1732	1682	1622
3e	3360*	1740*	1680*	1588*
	3396	1732	1680	1622, 1612
3f	3368*	1744*	1680*	1624*, 1610*
	3392	1734	1684	1624

Note. The IR spectra were recorded in mineral oil (asterisked values) and $CHCl_3$. The concentration of compounds **3a—f** in $CHCl_3$ is 5 mmol L^{-1}.

An X-ray diffraction study of compound **3f** containing the methyl group in position 8 revealed no hydrogen bonds in its crystal (Fig. 1).

The main geometrical parameters of structure **3f** are very close to standard values for such substituted heterocycles.[8] The quinolone ring is virtually planar; the bromobenzoyl fragment is nearly perpendicular to the plane of the heterocycle (the torsion angle C(6)C(10)C(9)O(4) is 99.1(2)°). Note that the rotation of the aroyl group, which disrupts the conjugation between the above fragments, can be due to two types of intermolecular contacts in the crystal packing. First, this is the Br···O contact between the Br(1) atom and the oxo group of the quinolone ring ([−0.5 + x, 1 − y, −0.5 + z]; Br(1)···O(3), 3.052(2) Å). This distance is shorter by about 0.3 Å than the sum of the van der Waals radii of the corresponding atoms (according to Bondi´s compilation), which indicates a specific intermolecular interaction between them. Nevertheless, the C(14)=O(3) and C(3)—Br(1) bond lengths (1.230(2) and 1.894(2) Å, respectively) do not differ appreciably from standard values. Second, this is the contact between the endocyclic NH group and the O atom of the aroyl group. The distance between the N(1) atom and the nearest carbonyl O atom of the aroyl group ([2 − x, −y, 1 − z]; N(1)···O(4), 3.096(2) Å) is long, and the corresponding

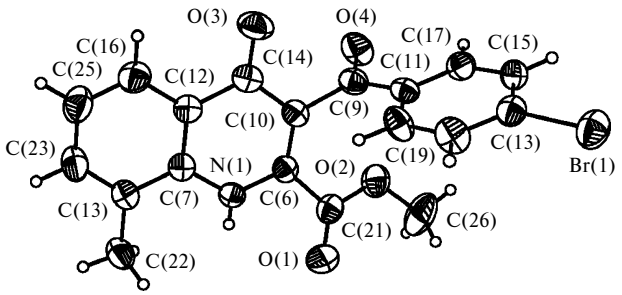


Fig. 1. Structure **3f** with atomic displacement ellipsoids (p = 50%) (X-ray diffraction data).

angle NHO is too acute (125(1)°) to form a normal hydrogen bond. In this case, one can assume the presence of only a dipolar coupling that is crucial for the conformation of the aroyl group relative to the plane of the heterocycle. The methoxycarbonyl group is slightly turned with respect to the plane of the heterocycle (the torsion angle O(1)C(21)C(6)N(1) is −15.6(2)°) and is not involved in specific interactions.

Experimental

The IR spectra of the compounds obtained were recorded on a Specord-M80 instrument in mineral oil. For compounds **3a—f**, both mineral oil and chloroform solutions ($C_{\mathbf{3a—f}}$ = 0.5 and 5 mmol L^{-1}) were used. ^{1}H NMR spectra were recorded on BS-567A (100 MHz, HMDS as an internal standard), Bruker AM-300, Bruker DRX-400, and Bruker Avance-500 spectrometers ($SiMe_4$ as an internal standard). ^{13}C NMR spectra were recorded on a Bruker Avance-500 spectrometer.

The progress of the reactions was monitored and the purity of the compounds obtained was checked by TLC on Sorbfil plates.

An X-ray diffraction study of structure **3f** ($C_{19}H_{14}BrNO_4$, M = 400.22) was carried out on an Xcalibur 3 diffractometer equipped with a CCD detector according to a standard procedure (λ(Mo), graphite monochromator, 295(2) K, ω and φ scan modes, scan step 0.5°, frame exposure time 10 s). A colorless crystal stub (0.212×0.169×0.108 mm) of quinolone **3f** was used for X-ray diffraction. Single crystals of compound **3f** were obtained by crystallization from acetonitrile. The crystals are monoclinic, space group $P2/n$. The unit cell parameters are as follows: a = 12.1557(13) Å, b = 9.5382(12) Å, c = 14.2910(11) Å, β = 91.591(7)°, V = 1656.3(3) Å^3, Z = 4, d_{calc} = 1.605 g cm^{-3}, $F(000)$ = 808. For 2.85 < θ < 31.79°, 26 645 reflections were collected. The number of unique reflections was 5235 (R_{int} = = 0.0283), including 2976 reflections with $I \geq 2\sigma(I)$. The ranges of the Miller indices were $-17 \leq h \leq 17$, $-14 \leq k \leq 13$, and $-20 \leq l \leq 20$. An absorption correction was applied analytically using a multifaceted crystal model[9] (μ = 2.50614 mm^{-1}). The structure was solved by the direct methods with the SHELXS97 program[10] and refined anisotropically by the full-matrix least-squares method on F^2 (for non-hydrogen atoms) with the SHELXL97 program[11] for 242 parameters. The hydrogen atoms were located geometrically and refined with parent-dependent thermal parameters. The final R factors are R_1 = 0.0293 and ωR_2 = 0.0566 (for reflections with $I \geq 2\sigma(I)$) and R_1 = 0.0701 and ωR_2 = 0.0592 (for all reflections); S = 1.000. The maximum and minimum peaks of the residual electron density are 0.261 and −0.544 e Å^{-3}, respectively.

Comprehensive crystallographic data were deposited with the Cambridge Structural Database (CCDC No. 763936) and can be retrieved free of charge from www.ccdc.cam.ac.uk/data_request/cif.

Compounds **1a** and **5a** were synthesized as described earlier.[2,5]

Methyl 3-benzoyl-1-(2,3-dimethylphenyl)-4,5-dioxo-4,5-dihydro-1*H*-pyrrole-2-carboxylate (1b) and methyl 3-benzoyl-1-(2,3-dimethylphenyl)-2,4-dihydroxy-5-oxo-2,5-dihydro-1*H*-pyrrole-2-carboxylate (5b). Enamine **4b** (7 g, 23 mmol) was dissolved in anhydrous $CHCl_3$ (60 mL), and oxalyl chloride (2.02 mL, 24 mmol) was added dropwise. The reaction mixture was refluxed for 2 h (with special care taken to prevent ingress of atmospheric moisture) and then concentrated by half. The precipitate of compound **1b** that formed was filtered off and washed with chloroform. Yield 7.55 g (92%), m.p. 132—134 °C (decomp.). IR, ν/cm^{-1}: 1780 (C(5)=O); 1754 (COO); 1714 (C(4)=O); 1636 (PhCO); 1600 (C=C). Found (%): C, 69.32; H, 4.51; N, 3.82. $C_{21}H_{17}NO_5$. Calculated (%): C, 69.41; H, 4.72; N, 3.85. The mother liquor was concentrated, and the residue was recrystallized from chloroform—hexane (4 : 1) to give compound **5b**. Yield 0.43 g (5%), m.p. 154—156 °C (decomp.). IR, ν/cm^{-1}: 3410, 3340 (OH); 1745 (COO); 1720, 1680 (C(5)=O); 1645 (PhCO); 1600 (C=C). ^{1}H NMR ($CDCl_3$), δ: 1.97, 2.17 (both s, 3 H, C(2)Me); 2.27, 2.31 (both s, 3 H, C(3)Me); 3.62, 3.80 (both s, 3 H, OMe); 4.60, 4.81 (both s, 1 H, C(2)OH); 6.65 (d, 1 H, H(4), J = 7.8 Hz); 7.09—7.23 (m, 2 H, H(4′), H(5)); 7.44—7.46 (m, 2 H, H(3′), H(5′)); 7.55—7.58 (m, 1 H, H(6)); 7.89—7.92 (m, 2 H, H(2′), H(6′)). ^{1}H NMR (DMSO-d_6), δ: 1.93, 2.27 (both s, 3 H, C(2)Me); 2.10, 2.30 (both s, 3 H, C(3)Me); 3.59, 3.76 (both s, 3 H, OMe); 6.67 (d, 1 H, H(6), J = 8.0 Hz); 7.13—7.26 (m, 2 H, H(4), H(5)); 7.50—7.54 (m, 2 H, H(3′), H(5′)); 7.61—7.64 (m, 1 H, H(4′)); 7.79—7.83 (m, 2 H, H(2′), H(6′)). ^{13}C NMR (DMSO-d_6), δ: 13.96, 14.84 (*o*-Me); 20.12 (*m*-Me); 52.44, 52.82 (OMe); 87.83, 88.83 (C(2)); 119.99, 119.14 (C(3)); 125.42, 125.82, 126.03, 127.26, 128.14, 128.92, 129.86, 130.24, 132.31, 132.69, 132.74, 132.82, 135.49, 137.11, 137.59, 137.70, 137.84 (Ar); 151.69 (C(5)); 164.16 (COO); 168.18, 169.02 (C(4)); 188.49 (COPh). Found (%): C, 66.02; H, 4.97; N, 3.60. $C_{21}H_{19}NO_6$. Calculated (%): C, 66.13; H, 5.02; N, 3.67.

Methyl 1-(2,3-dimethylphenyl)-3-(4-ethoxybenzoyl)-4,5-dioxo-4,5-dihydro-1*H*-pyrrole-2-carboxylate (1c) and methyl 1-(2,3-dimethylphenyl)-3-(4-ethoxybenzoyl)-2,4-dihydroxy-5-oxo-2,5-dihydro-1*H*-pyrrole-2-carboxylate (5c). Compound **1c** was obtained in a similar way from enamine **4c** (3.50 g, 9.9 mmol) and oxalyl chloride (1.32 g, 10.4 mmol). Yield 2.49 g (62%), m.p. 148—150 °C. IR, ν/cm^{-1}: 1770 (C(5)=O); 1750 (COO); 1735 (C(4)=O); 1635 (ArCO); 1600 (C=C). ^{1}H NMR ($CDCl_3$), δ: 1.44 (t, 3 H, Me, J = 6.9 Hz); 2.17 (s, 3 H, Me); 2.34 (s, 3 H, Me); 3.68 (s, 3 H, OMe); 4.12 (q, 2 H, CH_2, J = 6.9 Hz); 6.94 (d, 2 H, H(3′), H(5′), J = 9.0 Hz); 6.99 (d, 1 H, H(4), J = 7.8 Hz); 7.13—7.19 (m, 1 H, H(5)); 7.24—7.27 (m, 1 H, H(6)); 7.85 (d, 2 H, H(2′), H(6′), J = 9.0 Hz). Found (%): C, 67.88; H, 5.25; N, 3.35. $C_{23}H_{21}NO_6$. Calculated (%): C, 67.80; H, 5.20; N, 3.44.

Compound **5c**. Yield 0.5 g (12%), m.p. 121—122 °C (decomp.). IR, ν/cm^{-1}: 3390, 3260 (OH); 1745 (COO); 1705, 1675 (C(5)=O); 1620 (ArCO); 1600 (C=C). ^{1}H NMR (DMSO-d_6), δ: 1.36 (t, 3 H, Me, J = 7.0 Hz); 1.93, 2.26 (both s, 3 H, C(2)Me); 2.09, 2.29 (both s, 3 H, C(3)Me); 3.59, 3.76 (both s, 3 H, OMe); 4.12 (q, 2 H, CH_2, J = 7.0 Hz); 6.67 (d, 1 H, H(6), J = 8.0 Hz); 7.03 (d, 2 H, H(3′), H(5′), ^3J = 9.0 Hz); 7.13—7.17 (m, 1 H, H(5)); 7.20—7.26 (m, 1 H, H(4)); 7.82 (dd, 2 H, H(2′), H(6′), ^3J = 8.8 Hz, ^4J = 2.0 Hz). ^{13}C NMR (DMSO-d_6), δ: 14.48, 14.78 (*o*-Me); 20.07 (*m*-Me); 52.33, 52.72 (OMe); 63.50 (CH_2); 87.93, 88.90 (C(2)); 119.51, 119.66 (C(3)); 125.40, 125.50, 125.96, 127.25, 129.76, 129.99, 130.16, 131.48, 131.61, 132.38, 132.81, 135.49, 137.12, 137.64, 137.88 (Ar); 150.32 (C(5)); 164.27 (COO); 168.25, 169.09 (C(4)); 186.68, 186.90 (ArCO). Found (%): C, 64.55; H, 5.46; N, 3.42. $C_{23}H_{23}NO_7$. Calculated (%): C, 64.93; H, 5.45; N, 3.29.

Methyl 3-(4-chlorobenzoyl)-1-(2,3-dimethylphenyl)-4,5-dioxo-4,5-dihydro-1*H*-pyrrole-2-carboxylate (1d) and methyl 3-(4-chlorobenzoyl)-1-(2,3-dimethylphenyl)-2,4-dihydroxy-5-oxo-

2,5-dihydro-1*H*-pyrrole-2-carboxylate (5d). Compound **1d** was obtained in a similar way from enamine **4d** (5 g, 14.5 mmol) and oxalyl chloride (1.94 g, 15.3 mmol). Yield 5.11 g (88%), m.p. 86—88 °C. IR, ν/cm^{-1}: 1775 (C(5)=O); 1740 (COO); 1725 (C(4)=O); 1645 (ArCO); 1590 (C=C). Found (%): C, 63.09; H, 4.10; Cl, 8.70; N, 3.48. $C_{21}H_{16}ClNO_5$. Calculated (%): C, 63.40; H, 4.05; Cl, 8.91; N, 3.52.

Compound **5d**. Yield 0.63 g (10%), m.p. 157—158 °C (decomp.). IR, ν/cm^{-1}: 3390, 3340 (OH); 1750 (COO); 1720, 1680 (C(5)=O); 1650 (ArCO); 1600 (C=C). ^{1}H NMR ($CDCl_3$), δ: 1.98, 2.16 (both s, C(2)Me); 2.27, 2.31 (both s, 3 H, C(3)Me); 3.67, 3.83 (both s, 3 H, OMe); 4.57, 4.78 (both s, 1 H, OH); 6.66 (d, 1 H, H(4), J = 8.1 Hz); 7.06—7.27 (m, 2 H, H(5), H(6)); 7.44 (dd, 2 H, H(3′), H(5′), J = 8.0 Hz, J = 1.8 Hz); 7.87 (d, 2 H, H(2′), H(6′), J = 8.0 Hz). Found (%): C, 60.58; H, 4.44; Cl, 8.41; N, 3.45. $C_{21}H_{18}ClNO_6$. Calculated (%): C, 60.66; H, 4.36; Cl, 8.53; N, 3.37.

Methyl 3-benzoyl-1-(2-methylphenyl)-4,5-dioxo-4,5-dihydro-1*H*-pyrrole-2-carboxylate (1e) and methyl 3-benzoyl-2,4-dihydroxy-1-(2-methylphenyl)-5-oxo-2,5-dihydro-1*H*-pyrrole-2-carboxylate (5e). Compound **1e** was obtained in a similar way from enamine **4e** (14.96 g, 50.7 mmol) and oxalyl chloride (6.41 g, 50.5 mmol). Yield 16.07 g (92%), m.p. 60—62 °C (decomp.). IR, ν/cm^{-1}: 1784 (C(5)=O); 1744 (COO); 1728 (C(4)=O); 1640 (ArCO); 1548 (C=C). Found (%): C, 68.70; H, 4.34; N, 3.99. $C_{20}H_{15}NO_5$. Calculated (%): C, 68.96; H, 4.51; N, 4.01.

Compound **5e**. Yield 0.86 g (5%), m.p. 145—146 °C (decomp.). IR, ν/cm^{-1}: 3416, 2952 (OH); 1772, 1744 (COO); 1728 (C(5)=O); 1672 (ArCO); 1604 (C=C). ^{1}H NMR (DMSO-d_6), δ: 2.07, 2.23 (both s, 3 H, Me); 3.56, 3.79 (both s, 3 H, OMe); 6.83 (d, 1 H, H(6), ^3J = 6.0 Hz); 7.25—7.28 (m, 1 H, H(4)); 7.32—7.35 (m, 2 H, H(3), H(5)); 7.51—7.54 (m, 2 H, H(3′), H(5′)); 7.61—7.64 (m, 1 H, H(4′)); 8.81 (d, 2 H, H(2′), H(6′), J = 7.5 Hz). ^{13}C NMR (DMSO-d_6), δ: 17.33, 18.08 (Me); 52.46, 52.91 (OMe); 87.89, 88.77 (C(2)); 119.26 (C(3)); 126.26, 126.77, 127.82, 128.17, 128.57, 129.07, 129.47, 130.91, 132.84, 136.78, 137.59, 137.80, 138.45 (Ar); 151.63 (C(5)); 163.97 (COO); 168.29, 169.07 (C(4)); 188.51 (ArCO). Found (%): C, 65.47; H, 4.69; N, 3.75. $C_{20}H_{17}NO_6$. Calculated (%): C, 65.39; H, 4.66; N, 3.81.

Methyl 3-(4-bromobenzoyl)-1-(2-methylphenyl)-4,5-dioxo-4,5-dihydro-1*H*-pyrrole-2-carboxylate (1f) and methyl 3-(4-bromobenzoyl)-2,4-dihydroxy-1-(2-methylphenyl)-5-oxo-2,5-dihydro-1*H*-pyrrole-2-carboxylate (5f). Compound **1f** was obtained in a similar way from enamine **4f** (3.90 g, 10.4 mmol) and oxalyl chloride (1.32 g, 10.4 mmol). Yield 3.94 g (88%), m.p. 156—158 °C. IR, ν/cm^{-1}: 1782 (C(5)=O); 1734 (COO); 1724 (C(4)=O); 1636 (ArCO); 1588 (C=C). ^{1}H NMR ($CDCl_3$), δ: 2.28 (s, 3 H, Me); 3.70 (s, 3 H, OMe); 7.16—7.79 (m, 8 H, Ar). Found (%): C, 56.01; H, 3.46; Br, 18.78; N, 3.34. $C_{20}H_{14}BrNO_5$. Calculated (%): C, 56.09; H, 3.30; Br, 18.66; N, 3.27.

Compound **5f**. Yield 0.53 g (11%), m.p. 170—172 °C (decomp.). IR, ν/cm^{-1}: 3408, 3320 (OH); 1736 (COO); 1708 (C(5)=O); 1684, 1640 (ArCO); 1592 (C=C). ^{1}H NMR (DMSO-d_6), δ: 2.06, 2.22 (both s, 3 H, Me); 3.58, 3.78 (both s, 3 H, OMe); 6.82 (d, 1 H, H(6), ^3J = 6.0 Hz); 7.25—7.36 (m, 3 H, H(3), H(4), H(5)); 7.72—7.76 (m, 4 H, H(2′), H(3′), H(5′), H(6′)). ^{13}C NMR (DMSO-d_6), δ: 17.25, 18.00 (Me); 52.42, 52.82 (OMe); 87.74, 88.60 (C(2)); 118.80 (C(3)); 126.22, 126.62, 127.75, 128.58, 128.85, 129.34, 130.84, 130.93, 131.23, 132.75, 136.67, 138.34 (Ar); 152.30 (C(5)); 163.76 (COO); 168.12, 168.92 (C(4)); 187.379 (ArCO). Found (%): C, 53.51; H, 3.48; Br, 17.89; N, 3.05. $C_{20}H_{16}BrNO_6$. Calculated (%): C, 53.83; H, 3.61; Br, 17.91; N, 3.14.

Methyl 3-benzoyl-1-(4-chloro-2-methylphenyl)-2,4-dihydroxy-5-oxo-2,5-dihydro-1*H*-pyrrole-2-carboxylate (5g). Yield 0.12 g (3%), m.p. 154—156 °C (decomp.). IR, ν/cm^{-1}: 3440, 3200, (OH); 1746 (COO); 1706, 1682 (C(5)=O); 1646 (PhCO); 1604 (C=C). ^{1}H NMR ($CDCl_3$), δ: 2.10, 2.28 (both s, 3 H, Me); 3.67, 3.84 (both s, 3 H, OMe); 4.68, 4.93 (both s, 1 H, OH); 7.35 (br.s, 2 H, H(3′), H(5′)); 7.46—7.50 (m, 3 H, H(3), H(5), H(6)); 7.58—7.62 (m, 1 H, H(4′)); 7.89—7.91 (m, 2 H, H(2′), H(6′)). ^{1}H NMR (DMSO-d_6), δ: 2.06, 2.23 (both s, 3 H, Me); 3.60, 3.78 (both s, 3 H, OMe); 6.77, 7.37 (both br.s, 1 H, H(6)); 7.49 (m, 3 H, H(3′), H(5′), H(4′)); 7.61—7.64 (m, 2 H, H(3), H(5)); 7.80 (d, 2 H, H(2′), H(6′), J = 7.5 Hz). ^{13}C NMR (DMSO-d_6), δ: 17.03, 17.74 (Me); 52.54, 52.90 (OMe); 87.81, 88.69 (C(2)); 119.26 (C(3)); 128.11, 128.95, 129.34, 129.70, 129.92, 131.25, 132.20, 132.77, 133.44, 137.53, 139.56, 141.31 (Ar); 151.47 (C(5)); 163.91 (COO); 168.12, 168.88 (C(4)); 188.30, 188.33 (C=OPh). Found (%): C, 59.89; H, 4.10; Cl, 8.98; N, 3.53. $C_{20}H_{16}ClNO_6$. Calculated (%): C, 59.78; H, 4.01; Cl, 8.82; N, 3.49.

Methyl 3-benzoyl-1-(2,4-dichlorophenyl)-4,5-dioxo-4,5-dihydro-1*H*-pyrrole-2-carboxylate (1h) and methyl 3-benzoyl-1-(2,4-dichlorophenyl)-2,4-dihydroxy-5-oxo-2,5-dihydro-1*H*-pyrrole-2-carboxylate (5h). Compound **1h** was obtained in a similar way from enamine **4h** (2.00 g, 5.7 mmol) and oxalyl chloride (0.76 g, 6 mmol). Yield 1.22 g (53%), m.p. 120—122 °C. IR, ν/cm^{-1}: 1780 (C(5)=O); 1735 (COO, C(4)=O); 1665 (PhCO); 1605 (C=C). Found (%): C, 56.28; H, 2.79; Cl, 17.62; N, 3.50. $C_{19}H_{11}Cl_2NO_5$. Calculated (%): C, 56.46; H, 2.74; Cl, 17.54; N, 3.47.

Compound **5h**. Yield 0.30 g (12%), m.p. 133—135 °C (decomp.). IR, ν/cm^{-1}: 3500 (OH); 1740 (COO); 1712, 1678 (C(5)=O); 1632 (PhCO); 1598 (C=C). ^{1}H NMR (DMSO-d_6), δ: 3.61, 3.80 (both s, 3 H, OMe); 7.05 (br.s, 1 H, H(6)); 7.50—7.58 (m, 4 H, H(5), H(3′), H(4′), H(5′)); 7.61—7.64 (m, 1 H, H(3)); 7.80 (d, 2 H, H(2′), H(6′), J = 7.0 Hz). ^{13}C NMR (DMSO-d_6), δ: 52.53, 53.04 (OMe); 87.56, 88.61 (C(2)); 119.23, 119.51 (C(3)); 128.11, 128.87, 129.72, 130.27, 131.18, 132.74, 133.16, 134.08, 134.37, 135.40, 137.76 (Ar); 151.42 (C(5)); 163.88 (COO); 167.66, 168.80 (C(4)); 188.32 (C=OPh). Found (%): C, 54.21; H, 3.19; Cl, 16.85; N, 3.38. $C_{19}H_{13}Cl_2NO_6$. Calculated (%): C, 54.05; H, 3.10; Cl, 16.79; N, 3.32.

Methyl 1-(2,4-dichlorophenyl)-3-(4-ethoxybenzoyl)-4,5-dioxo-4,5-dihydro-1*H*-pyrrole-2-carboxylate (1i) and methyl 1-(2,4-dichlorophenyl)-3-(4-ethoxybenzoyl)-2,4-dihydroxy-5-oxo-2,5-dihydro-1*H*-pyrrole-2-carboxylate (5i). Compound **1i** was obtained in a similar way from enamine **4i** (0.60 g, 1.5 mmol) and oxalyl chloride (0.20 g, 1.64 mmol). Yield 0.54 g (79%), m.p. 138—140 °C. IR, ν/cm^{-1}: 1784 (C(5)=O); 1755, 1745, 1730 (COO, C(4)=O); 1632 (ArCO); 1606 (C=C). Found (%): C, 56.38; H, 3.41; Cl, 15.71; N, 3.18. $C_{21}H_{15}Cl_2NO_6$. Calculated (%): C, 56.27; H, 3.37; Cl, 15.82; N, 3.12.

Compound **5i**. Pyrroledione **1i** (0.09 g, 0.2 mmol) was dissolved in CH_2Cl_2 (4 mL). The resulting solution was heated with water (0.1 mL) and concentrated. The precipitate that formed was recrystallized from dichloromethane—hexane. Yield 0.06 g (67%), m.p. 152—154 °C (decomp.). IR, ν/cm^{-1}: 3850, 3640 (OH); 1760 sh, 1740 sh, 1730 sh, 1714 (COO); 1672 (C(5)=O); 1632 (ArCO); 1600 (C=C). ^{1}H NMR ($CDCl_3$), δ: 1.42 (t, 3 H, Me, J = 6.5 Hz); 3.66 (s, 3 H, OMe); 4.10 (q, 2 H, CH_2, J = 6.9 Hz); 4.80 (br.s, 1 H, OH); 6.84 (d, 2 H, H(3′), H(5′), J = 8.4 Hz);

7.16—7.21 (m, 2 H, H(5), H(6)); 7.43 (s, 1 H, H(3)); 7.83 (d, 2 H, H(2′), H(6′), J = 8.4 Hz). Found (%): C, 54.25; H, 3.74; Cl, 15.28; N, 3.03. $C_{21}H_{17}Cl_2NO_7$. Calculated (%): C, 54.09; H, 3.67; Cl, 15.21; N, 3.00.

Methyl 3-(4-chlorobenzoyl)-1-(2,4-dichlorophenyl)-4,5-dioxo-4,5-dihydro-1*H*-pyrrole-2-carboxylate (1j) and methyl 3-(4-chlorobenzoyl)-1-(2,4-dichlorophenyl)-2,4-dihydroxy-5-oxo-2,5-dihydro-1*H*-pyrrole-2-carboxylate (5j). Compound **1j** was obtained in a similar way from enamine **4j** (2.28 g, 5.9 mmol) and oxalyl chloride (0.79 g, 6.2 mmol). Yield 1.63 g (63%), m.p. 162—164 °C. IR, ν/cm^{-1}: 1780 (C(5)=O); 1750 sh, 1732 (COO, C(4)=O); 1658 (ArCO); 1590 (C=C). Found (%): C, 52.24; H, 2.27; Cl, 24.26; N, 3.17. $C_{19}H_{10}Cl_3NO_5$. Calculated (%): C, 52.02; H, 2.30; Cl, 24.25; N, 3.19.

Compound **5j** was obtained as described for pyrrolone **5b**. Yield 0.28 g (14%), m.p. 152—153 °C (decomp.). IR, ν/cm^{-1}: 3750, 3640 (OH); 1740 sh, 1706 (COO, C(5)=O); 1678 (C(5)=O); 1642 (ArCO); 1586 (C=C). ^{1}H NMR (DMSO-d_6), δ: 3.62, 3.81 (both s, 3 H, OMe); 7.04 (br.s, 1 H, H(6)); 7.54 (br.s, 1 H, H(5)); 7.60 (d, 2 H, H(3′), H(5′), J = 8.5 Hz); 7.80 (d, 2 H, H(2′), H(6′), J = 8.5 Hz); 7.85 (br.s, 1 H, H(3)). ^{13}C NMR (DMSO-d_6), δ: 52.52, 52.98 (OMe); 87.41, 88.55 (C(2)); 118.88, 119.19 (C(3)); 128.30, 129.68, 130.23, 130.71, 131.16, 133.11, 134.03, 134.38, 135.36, 136.21, 136.49, 137.53 (Ar); 152.06 (C(5)); 163.74 (COO); 167.55, 168.70 (C(4)); 187.08 (ArCO). Found (%): C, 49.75; H, 2.57; Cl, 23.50; N, 3.21. $C_{19}H_{12}Cl_3NO_6$. Calculated (%): C, 49.97; H, 2.65; Cl, 23.29; N, 3.07.

Methyl 1-(2,4-dichlorophenyl)-4,5-dioxo-3-thenoyl-4,5-dihydro-1*H*-pyrrole-2-carboxylate (1k) and methyl 1-(2,4-dichlorophenyl)-2,4-dihydroxy-5-oxo-3-thenoyl-2,5-dihydro-1*H*-pyrrole-2-carboxylate (5k). Compound **1k** was obtained in a similar way from enamine **4k** (2.38 g, 6.7 mmol) and oxalyl chloride (0.89 g, 7 mmol). Yield 2.14 g (78%), m.p. 83—84 °C. IR, ν/cm^{-1}: 1784 (C(5)=O); 1740 (COO, C(4)=O); 1616 (PhCO, C=C). ^{1}H NMR ($CDCl_3$), δ: 3.71 (s, 3 H, OMe); 7.16—7.27 (m, 3 H, H(4′), H(5), H(6)); 7.47 (s, 1 H, H(3)); 7.66 (m, 1 H, H(3′)); 7.89 (m, 1 H, H(5′)). Found (%): C, 49.61; H, 2.23; Cl, 17.23; N, 3.44. $C_{17}H_9Cl_2NO_5S$. Calculated (%): C, 49.77; H, 2.21; Cl, 17.28; N, 3.41.

Compound **5k** was obtained as described for pyrrolone **5i**. Yield 0.13 g (70%), m.p. 162—164 °C (decomp.). IR, ν/cm^{-1}: 3180 (OH); 1750 (COO); 1724, 1708 (C(5)=O); 1638 (HetCO); 1600 (C=C). ^{1}H NMR (DMSO-d_6), δ: 3.59, 3.78 (both s, 3 H, OMe); 7.03 (br.s, 1 H, H(6)); 7.24 (m, 1 H, H(4′)); 7.50—7.57 (m, 1 H, H(5)); 7.82 (s, 1 H, H(3)); 8.04 (d, 1 H, H(3′), J = 4.5 Hz); 8.14 (s, 1 H, H(5′)). ^{13}C NMR (DMSO-d_6), δ: 52.49, 53.00 (OMe); 87.53, 88.56 (C(2)); 119.12 (C(3)); 128.43, 129.70, 130.20, 131.21, 133.15, 134.15, 134.36, 135.14, 143.72 (Ar); 150.63 (C(5)); 163.85 (COO); 167.63, 168.82 (C(4)); 179.05 (COHet). Found (%): C, 47.74; H, 2.68; Cl, 16.87; N, 3.23. $C_{17}H_{11}Cl_2NO_6S$. Calculated (%): C, 47.68; H, 2.59; Cl, 16.56; N, 3.27.

Methyl 3-benzoyl-4-oxo-1,4-dihydroquinoline-2-carboxylate (3a) was obtained as described earlier.[2] Found (%): C, 70.34; H, 4.28; N, 4.52. $C_{18}H_{13}NO_4$. Calculated (%): C, 70.35; H, 4.26; N, 4.56. ^{1}H NMR (DMSO-d_6), δ: 3.75 (s, 3 H, OMe); 7.43—7.46 (m, 1 H, H(6)); 7.47—7.50 (m, 2 H, H(3′), H(5′)); 7.60—7.63 (m, 1 H, H(4′)); 7.78—7.80 (m, 1 H, H(8)); 7.81—7.83 (m, 2 H, H(2′), H(6′)); 8.00 (br.d, 1 H, H(7), J = 8.0 Hz); 8.07 (dd, 1 H, H(5), J = 6.5 Hz, J = 1.0 Hz); 12.40 (s, 1 H, NH). ^{13}C NMR (DMSO-d_6), δ: 53.40 (OMe); 119.57, 122.69, 124.62, 124.67, 125.53, 128.48, 128.54, 132.90, 133.08, 135.83, 137.19, 139.35 (Ar); 161.92 (COO); 175.71 (C(4)); 193.90 (<u>C</u>OPh).

Methyl 3-benzoyl-7,8-dimethyl-4-oxo-1,4-dihydroquinoline-2-carboxylate (3b). A solution of compound **1b** (7.88 g, 22 mmol) in Dowtherm A (10 mL) was kept at 190 °C for 50 min. The precipitate that formed was cooled, filtered off, and recrystallized. The yield of compound **3b** was 3.78 g (52%), m.p. 222—224 °C (decomp.) (from dioxane). Found (%): C, 71.60; H, 5.13; N, 4.22. $C_{20}H_{17}NO_4$. Calculated (%): C, 71.53; H, 5.11; N, 4.18. IR, ν/cm^{-1}: 3355 (NH); 1745 (COO); 1690 (Bz); 1625 (C(4)=O); 1600 (C=C). ^{1}H NMR (DMSO-d_6), δ: 2.45 (s, 3 H, Me); 2.49 (s, 3 H, Me); 3.74 (s, 3 H, OMe); 7.31 (br.d, 1 H, H(6), J = 7.5 Hz); 7.48—7.51 (m, 2 H, H(3′), H(5′)); 7.61—7.64 (m, 1 H, H(4′)); 7.78 (d, 2 H, H(2′), H(6′), J = 7.0 Hz); 7.87 (br.d, 1 H, H(5), J = 7.5 Hz); 10.70 (s, 1 H, NH). ^{13}C NMR (DMSO-d_6), δ: 12.73 (Me(8)); 20.37 (Me(7)); 53.34 (OMe); 120.79, 122.14, 124.23, 127.83, 127.18, 128.46, 128.66, 132.98, 137.28, 137.41, 138.73, 141.81 (Ar); 162.35 (COO); 175.49 (C(4)); 193.97 (<u>C</u>OPh).

Methyl 3-(4-ethoxybenzoyl)-7,8-dimethyl-4-oxo-1,4-dihydroquinoline-2-carboxylate (3c) was obtained in a similar way from compound **1c** (2.27 g, 5.6 mmol). Yield 1.08 g (51%), m.p. 185—187 °C (decomp.) (from dioxane). Found (%): C, 69.74; H, 5.77; N, 3.72. $C_{22}H_{21}NO_5$. Calculated (%): C, 69.64; H, 5.58; N, 3.69. IR, ν/cm^{-1}: 3310 (NH); 1745 (COO); 1655 (ArCO); 1620 (C(4)=O); 1610 (C=C). ^{1}H NMR (DMSO-d_6), δ: 1.34 (t, 1 H, Me, J = 7.0 Hz); 2.43 (s, 3 H, Me); 2.48 (s, 3 H, Me); 3.74 (s, 3 H, OMe); 4.10 (q, 2 H, CH_2, J = 7.0 Hz); 6.99 (d, 2 H, H(3′), H(5′), J = 9.0 Hz); 7.29 (br.d, 1 H, H(6), J = 5.5 Hz); 7.73 (d, 2 H, H(2′), H(6′), J = 9.0 Hz); 7.88 (br.d, 1 H, H(5), J = 5.5 Hz); 10.65 (s, 1 H, NH). ^{13}C NMR (DMSO-d_6), δ: 12.78 (Me(8)); 14.47 (<u>Me</u>CH_2); 20.43 (Me(7)); 53.33 (OMe); 63.51 (CH_2); 118.56, 121.19, 122.21, 124.18, 124.78, 127.13, 130.21, 131.19, 137.44, 138.56, 141.72 (Ar); 162.43 (COO); 175.50 (C(4)); 192.30 (<u>C</u>OPh).

Methyl 3-(4-chlorobenzoyl)-7,8-dimethyl-4-oxo-1,4-dihydroquinoline-2-carboxylate (3d) was obtained in a similar way from compound **1d** (5.83 g, 15 mmol). Yield 3.66 g (68%), m.p. 230—232 °C (decomp.) (from MeCN). Found (%): C, 64.75; H, 4.43; Cl, 10.03; N, 3.66. $C_{20}H_{16}ClNO_4$. Calculated (%): C, 64.96; H, 4.36; Cl, 9.59; N, 3.79. IR, ν/cm^{-1}: 3400, 3370 (NH); 1755 (COO); 1680 (ArCO); 1620 (C(4)=O); 1595 (C=C). ^{1}H NMR (DMSO-d_6), δ: 2.44 (s, 3 H, Me); 2.49 (s, 3 H, Me, masked by the signal of DMSO); 3.77 (s, 3 H, OMe); 7.32 (d, 1 H, H(6), J = 7.5 Hz); 7.56 (dd, 2 H, H(3′), H(5′), J = 6.8 Hz, J = 2.0 Hz); 7.79 (dd, 2 H, H(2′), H(6′), J = 6.8 Hz, J = 2.0 Hz); 7.89 (d, 1 H, H(5), J = 7.5 Hz); 10.78 (s, 1 H, NH). ^{13}C NMR (DMSO-d_6), δ: 12.77 (Me(8)); 20.37 (Me(7)); 53.35 (OMe); 119.96, 121.96, 124.15, 125.06, 127.39, 128.63, 130.53, 136.06, 137.45, 137.86, 139.28, 141.76 (Ar); 162.46 (COO); 175.47 (C(4)); 193.03 (Ar<u>C</u>O).

Methyl 3-benzoyl-8-methyl-4-oxo-1,4-dihydroquinoline-2-carboxylate (3e) was obtained in a similar way from compound **1e** (1.47 g, 4.2 mmol). Yield 0.65 g (52%), m.p. 206—208 °C (decomp.) (from dioxane). Found (%): C, 71.16; H, 4.78; N, 4.31. $C_{19}H_{15}NO_4$. Calculated (%): C, 71.02; H, 4.71; N, 4.36. IR, ν/cm^{-1}: 3360 (NH); 1740 (COO); 1680 (PhCO); 1588 (C(4)=O, C=C). ^{1}H NMR (DMSO-d_6), δ: 2.63 (s, 3 H, Me); 3.75 (s, 3 H, OMe); 7.36—7.39 (m, 1 H, H(6)); 7.49—7.52 (m, 2 H, H(3′), H(5′)); 7.62—7.65 (m, 1 H, H(4′)); 7.67 (d, 1 H, H(7), J = 7.0 Hz); 7.80 (d, 2 H, H(2′), H(6′)); 7.98 (d, 1 H, H(5), J = 6.0 Hz); 10.87 (s, 1 H, NH). ^{13}C NMR (DMSO-d_6), δ: 16.94

(Me); 53.33 (OMe); 121.17, 122.85, 124.60, 125.85, 127.45, 128.48, 128.70, 133.03, 134.07, 137.25, 137.48, 138.95 (Ar); 162.35 (COO); 175.56 (C(4)); 193.93 (COPh).

Methyl 3-(4-bromobenzoyl)-8-methyl-4-oxo-1,4-dihydroquinoline-2-carboxylate (3f) was obtained in a similar way from compound **1f** (3.59 g, 8.4 mmol). Yield 2.84 g (85%), m.p. 204—206 °C (decomp.) (from MeCN). Found (%): C, 57.30; H, 3.50; Br, 19.87; N, 3.48. $C_{19}H_{14}BrNO_4$. Calculated (%): C, 57.02; H, 3.53; Br, 19.96; N, 3.50. IR, ν/cm^{-1}: 3368 (NH); 1744 (COO); 1680 (ArCO); 1624 (C(4)=O); 1584 (C=C). ^{1}H NMR (DMSO-d_6), δ: 2.62 (s, 3 H, Me); 3.77 (s, 3 H, OMe); 7.37—7.40 (m, 1 H, H(6)); 7.67 (d, 1 H, H(7), J = 7.0 Hz); 7.70—7.74 (m, 4 H, H(2′), H(3′), H(5′), H(6′)); 7.97 (d, 1 H, H(5), J = 6.0 Hz); 10.95 (s, 1 H, NH). ^{13}C NMR (DMSO-d_6), δ: 16.98 (Me); 53.43 (OMe); 120.50, 122.86, 124.74, 125.99, 127.09, 127.52, 130.68, 131.63, 134.23, 136.34, 137.53, 139.51, 162.31 (COO); 175.51 (C(4)); 193.21 (ArCO).

Methyl 3-benzoyl-6-chloro-8-methyl-4-oxo-1,4-dihydroquinoline-2-carboxylate (3g). Oxalyl chloride (1.62 g, 12.8 mmol) was added to a solution of enamine **4g** (4.00 g, 12.1 mmol) in anhydrous dichloroethane (30 mL). The reaction mixture was refluxed for 50 min (monitoring by TLC) and concentrated *in vacuo*. After addition of diphenyl ether (10 mL), the resulting mixture was kept at 205—210 °C for 7 min and cooled. The precipitate that formed was washed with hot light petroleum and recrystallized from dioxane. The yield of compound **3g** was 2.78 g (72%), m.p. 222—224 °C (decomp.). Found (%): C, 64.28; H, 3.90; Cl, 9.69; N, 3.86. $C_{19}H_{14}ClNO_4$. Calculated (%): C, 64.14; H, 3.97; Cl, 9.97; N, 3.94. IR, ν/cm^{-1}: 3372 (NH); 1732 (COO); 1672 (PhCO); 1618 (C(4)=O); 1594 (C=C). ^{1}H NMR (DMSO-d_6), δ: 2.63 (s, 3 H, Me); 3.75 (s, 3 H, OMe); 7.48—7.52 (m, 2 H, H(3′), H(5′)); 7.62—7.65 (m, 1 H, H(4′)); 7.80 (d, 2 H, H(2′), H(6′), J = 8.0 Hz); 7.88 (br.s, 1 H, H(7)); 8.06 (br.s, 1 H, H(5)); 11.08 (s, 1 H, NH). ^{13}C NMR (DMSO-d_6), δ: 16.75 (Me); 53.36 (OMe); 117.52, 121.27, 124.69, 127.08, 128.51, 128.75, 130.91, 133.17, 136.16, 137.06, 139.71 (Ar); 162.20 (COO); 174.15 (C(4)); 193.55 (COPh).

Methyl 3-benzoyl-6,8-dichloro-4-oxo-1,4-dihydroquinoline-2-carboxylate (3h) was obtained in a similar way from compound **1h** (1.00 g, 2.5 mmol). Yield 0.17 g (18%), m.p. 224—226 °C (decomp.) (from toluene). Found (%): C, 57.21; H, 2.88; Cl, 18.91; N, 3.73. $C_{18}H_{11}Cl_2NO_4$. Calculated (%): C, 57.47; H, 2.95; Cl, 18.85; N, 3.72. IR, ν/cm^{-1}: 3365 (NH); 1730 (COO); 1680 (PhCO); 1625 (C(4)=O). ^{1}H NMR (DMSO-d_6), δ: 3.74 (s, 3 H, OMe); 7.49—7.52 (m, 2 H, H(3′), H(5′)); 7.62—7.66 (m, 1 H, H(4′)); 7.83 (d, 2 H, H(2′), H(6′), J = 7.5 Hz); 8.08 (br.s, 1 H, H(7)); 8.22 (d, 1 H, H(5), J = 2.5 Hz); 11.23 (s, 1 H, NH). ^{13}C NMR (DMSO-d_6), δ: 53.39 (OMe); 121.66, 123.03, 125.20, 126.62, 128.09, 128.54, 128.80, 129.63, 132.61, 133.33, 136.83 (Ar); 162.36 (COO); 171.38 (C(4)); 193.01 (COPh).

Methyl 6,8-dichloro-3-(4-ethoxybenzoyl)-4-oxo-1,4-dihydroquinoline-2-carboxylate (3i) was obtained in a similar way from compound **1i** (0.30 g, 0.7 mmol). Yield 0.12 g (43%), m.p. 189—190 °C (decomp.) (from dioxane). Found (%): C, 57.26; H, 3.63; Cl, 16.91; N, 3.37. $C_{20}H_{15}Cl_2NO_5$. Calculated (%): C, 57.16; H, 3.60; Cl, 16.87; N, 3.33. IR, ν/cm^{-1}: 3348 (NH); 1730 (COO); 1680 (ArCO); 1628 (C(4)=O); 1604 (C=C). ^{1}H NMR (DMSO-d_6), δ: 1.34 (t, 3 H, Me, J = 6.9 Hz); 3.72 (s, 3 H, OMe); 4.12 (q, 2 H, CH_2, J = 6.9 Hz); 6.98 (dd, 2 H, H(3′), H(5′), J = 6.9 Hz, J = 2.1 Hz); 7.73 (dd, 2 H, H(2′), H(6′), J = 6.9 Hz, J = 2.1 Hz); 8.07 (br.s, 1 H, H(7)); 8.16 (d, 1 H, H(5), J = 2.7 Hz); 11.00 (br.s, 1 H, NH).

Methyl 6,8-dichloro-3-(4-chlorobenzoyl)-4-oxo-1,4-dihydroquinoline-2-carboxylate (3j) was obtained in a similar way from compound **1j** (1.11 g, 2.5 mmol). Yield 0.29 g (28%), m.p. 220—222 °C (decomp.) (from MeCN). Found (%): C, 52.59; H, 2.50; Cl, 25.81; N, 3.40. $C_{18}H_{10}Cl_3NO_4$. Calculated (%): C, 52.65; H, 2.45; Cl, 25.90; N, 3.41. IR, ν/cm^{-1}: 3352 (NH); 1734 (COO); 1684 (ArCO); 1626 (C(4)=O); 1600, 1590 (C=C). ^{1}H NMR (DMSO-d_6), δ: 3.77 (s, 3 H, OMe); 7.57 (dd, 2 H, H(3′), H(5′), J = 7.0 Hz, J = 2.0 Hz); 7.85 (dd, 2 H, H(2′), H(6′), J = 7.0 Hz, J = 2.0 Hz); 8.07 (br.s, 1 H, H(7)); 8.22 (d, 1 H, H(5), J = 2.5 Hz); 11.29 (s, 1 H, NH). ^{13}C NMR (DMSO-d_6), δ: 53.46 (OMe); 121.14, 123.05, 126.76, 128.73, 129.70, 130.67, 132.67, 135.60, 138.25 (Ar); 162.30 (COO); 172.59 (C(4)); 192.08 (ArCO).

Methyl 6,8-dichloro-4-oxo-3-thenoyl-1,4-dihydroquinoline-2-carboxylate (3k) was obtained in a similar way from compound **1k** (2.42 g, 5.9 mmol). Yield 0.59 g (26%), m.p. 206—208 °C (decomp.) (from dioxane). Found (%): C, 50.36; H, 2.41; Cl, 19.00; N, 3.63. $C_{16}H_9Cl_2NO_4S$. Calculated (%): C, 50.28; H, 2.37; Cl, 18.55; N, 3.66. IR, ν/cm^{-1}: 3344 (NH); 1730 (COO); 1662 (C_4H_3SCO); 1622, 1608 (C(4)=O). ^{1}H NMR (DMSO-d_6), δ: 3.77 (s, 3 H, OMe); 7.19 (dd, 1 H, H(4′), J = 4.9 Hz, J = 3.8 Hz); 7.65 (d, 1 H, H(3′), J = 3.4 Hz); 8.07 (dd, 1 H, H(5′), J = 4.9 Hz, J = 1.1 Hz); 8.10 (br.s, 1 H, H(7)); 8.21 (d, 1 H, H(5), J = 2.4 Hz); 11.15 (br.s, 1 H, NH). ^{13}C NMR (DMSO-d_6), δ: 53.51 (OMe); 121.40, 123.20, 126.84, 128.63, 129.68, 132.71, 135.27, 135.53, 143.87 (Ar); 162.26 (COO); 173.26 (C(4)); 184.69 (COHet).

Methyl (*Z*)-2-(2,3-dimethylphenylamino)-4-oxo-4-phenylbut-2-enoate (4b). Methyl benzoylpyruvate (6 g, 29 mmol) and 2,3-xylidine (3.52 g, 29 mmol) were dissolved in benzene (50 mL). The reaction mixture was refluxed with a Dean—Stark trap for 6 h and concentrated by half. The precipitate that formed was filtered off and recrystallized from EtOH. Yield 7.60 g (84%), m.p. 74—76 °C. IR, ν/cm^{-1}: 1740 (COO); 1600 (PhCO, C=C). ^{1}H NMR ($CDCl_3$), δ: 2.22 (s, 6 H, 2 Me); 3.56 (s, 3 H, OMe); 6.26 (s, 1 H, CH); 6.59—8.23 (m, 8 H, Ar); 11.85 (s, 1 H, NH). Found (%): C, 73.70; H, 6.15; N, 4.55. $C_{19}H_{19}NO_3$. Calculated (%): C, 73.77; H, 6.19; N, 4.53.

Methyl (*Z*)-2-(2,3-dimethylphenylamino)-4-(4-ethoxyphenyl)-4-oxobut-2-enoate (4c) was obtained in a similar way from methyl (4-ethoxybenzoyl)pyruvate (5 g, 20 mmol) and 2,3-xylidine (2.42 g, 20 mmol). Yield 3.79 g (54%), m.p. 100—102 °C (from EtOH). IR, ν/cm^{-1}: 1725 (COO); 1605 (ArCO); 1585 (C=C). ^{1}H NMR ($CDCl_3$), δ: 1.35 (t, 3 H, Me, J = 7.2 Hz); 2.22 (s, 6 H, 2 Me); 3.56 (s, 3 H, OMe); 4.01 (q, 2 H, CH_2, J = 7.2 Hz); 6.24 (s, 1 H, CH); 6.52—7.83 (m, 7 H, Ar); 11.73 (s, 1 H, NH). Found (%): C, 71.26; H, 6.50; N, 3.84. $C_{21}H_{23}NO_4$. Calculated (%): C, 71.37; H, 6.56; N, 3.96.

Methyl (*Z*)-4-(4-chlorophenyl)-2-(2,3-dimethylphenylamino)-4-oxobut-2-enoate (4d) was obtained in a similar way from methyl (4-chlorobenzoyl)pyruvate (6 g, 24.9 mmol) and 2,3-xylidine (3.02, 24.9 mmol). Yield 5.95 g (69%), m.p. 105—106 °C (from EtOH). IR, ν/cm^{-1}: 1745 (COO); 1605 (ArCO); 1575 (C=C). ^{1}H NMR ($CDCl_3$), δ: 2.30 (s, 3 H, Me); 2.31 (s, 3 H, Me); 3.65 (s, 3 H, OMe); 6.30 (s, 1 H, CH); 6.72—6.77 (m, 1 H, H(5)); 6.98—7.04 (m, 2 H, H(4), H(6)); 7.41 (dd, 2 H, H(3′), H(5′), J = 6.8 Hz, J = 1.9 Hz); 7.88 (dd, 2 H, H(2′), H(6′), J = 6.8 Hz, J = 1.9 Hz); 12.02 (s, 1 H, NH). Found (%): C, 66.21; H, 5.35; Cl, 10.09; N, 4.09. $C_{19}H_{18}ClNO_3$. Calculated (%): C, 66.38; H, 5.28; Cl, 10.31; N, 4.07.

Methyl (*Z*)-2-(2-methylphenylamino)-4-oxo-4-phenylbut-2-enoate (4e) was obtained in a similar way from methyl benzoylpyruvate (10 g, 48.5 mmol) and *o*-toluidine (5.20 g, 48.5 mmol).

Yield 11.66 g (80%), m.p. 47—49 °C (from Pr^iOH). IR, ν/cm^{-1}: 1730 (COO); 1618 (PhCO); 1586 (C=C). ^{1}H NMR ($CDCl_3$), δ: 2.40 (s, 3 H, Me); 3.67 (s, 3 H, OMe); 6.41 (s, 1 H, CH); 6.86 (dd, 1 H, H(3), J = 8.0 Hz, J = 1.5 Hz); 7.05—7.14 (m, 2 H, H(4), H(5)); 7.21—7.24 (m, 1 H, H(6)); 7.41—7.53 (m, 3 H, H(3′), H(4′), H(5′)); 7.95 (d, 2 H, H(2′), H(6′), J = 7.7 Hz); 11.98 (s, 1 H, NH). Found (%): C, 73.29; H, 5.83; N, 4.79. $C_{18}H_{17}NO_3$. Calculated (%): C, 73.20; H, 5.80; N, 4.74.

Methyl (*Z*)-4-(4-bromophenyl)-2-(2-methylphenylamino)-4-oxobut-2-enoate (4f) was obtained in a similar way from methyl (4-bromobenzoyl)pyruvate (10 g, 35.1 mmol) and *o*-toluidine (3.76 g, 35.1 mmol). Yield 7.04 g (54%), m.p. 99—100 °C (from Pr^iOH). IR, ν/cm^{-1}: 1740 (COO); 1605 sh, 1580 (ArCO, C=C). ^{1}H NMR ($CDCl_3$), δ: 2.39 (s, 3 H, Me); 3.67 (s, 3 H, OMe); 6.32 (s, 1 H, CH); 6.86 (d, 1 H, H(3), J = 8.3 Hz); 7.07—7.12 (m, 2 H, H(4), H(6)); 7.21—7.24 (m, 1 H, H(5)); 7.57 (dd, 2 H, H(3′), H(5′), J = 6.8 Hz, J = 2.0 Hz); 7.81 (dd, 2 H, H(2′), H(6′), J = 6.8 Hz, J = 2.0 Hz); 12.00 (s, 1 H, NH). Found (%): C, 57.62; H, 4.39; Br, 21.42; N, 3.68. $C_{18}H_{16}BrNO_3$. Calculated (%): C, 57.77; H, 4.31; Br, 21.35; N, 3.74.

Methyl (*Z*)-2-(4-chloro-2-methylphenylamino)-4-oxo-4-phenylbut-2-enoate (4g) was obtained in a similar way from methyl benzoylpyruvate (6 g, 29.1 mmol) and 4-chloro-2-methylaniline (4.12 g, 29.1 mmol). Yield 6.34 g (66%), m.p. 114—116 °C (from CCl_4). IR, ν/cm^{-1}: 1732 (COO); 1616 (PhCO, C=C). ^{1}H NMR ($CDCl_3$), δ: 1.56 (s, 3 H, Me); 3.73 (s, 3 H, OMe); 6.48 (s, 1 H, CH); 6.71 (d, 1 H, H(6), J = 8.4 Hz); 7.24—7.26 (m, 1 H, H(5)); 7.37 (d, 1 H, H(3), J = 2.0 Hz); 7.45—7.49 (m, 2 H, H(3′), H(5′)); 7.52—7.54 (m, 1 H, H(4′)); 7.95—7.97 (m, 2 H, H(2′), H(6′)); 11.91 (s, 1 H, NH). Found (%): C, 65.50; H, 4.76; Cl, 10.72; N, 4.20. $C_{18}H_{16}ClNO_3$. Calculated (%): C, 65.56; H, 4.89; Cl, 10.75; N, 4.21.

Methyl (*Z*)-2-(2,4-dichlorophenylamino)-4-oxo-4-phenylbut-2-enoate (4h) was obtained in a similar way from methyl benzoylpyruvate (3 g, 14.7 mmol) and 2,4-dichloroaniline (2.38 g, 14.7 mmol). Yield 2.65 g (50%), m.p. 139—141 °C (from CCl_4). IR, ν/cm^{-1}: 1730 (COO); 1630, 1600 (PhCO, C=C). ^{1}H NMR ($CDCl_3$), δ: 3.77 (s, 3 H, OMe); 6.62 (s, 1 H, CH); 6.85 (d, 1 H, H(6), J = 8.6 Hz); 7.17 (dd, 1 H, H(5), J = 8.6 Hz, J = 2.4 Hz); 7.44 (m, 1 H, H(4′)); 7.48 (m, 2 H, H(3′), H(5′)); 7.53 (m, 1 H, H(3)); 7.98 (m, 2 H, H(2′), H(6′)); 11.94 (s, 1 H, NH). Found (%): C, 58.21; H, 3.68; Cl, 20.21; N, 4.05. $C_{17}H_{13}Cl_2NO_3$. Calculated (%): C, 58.31; H, 3.74; Cl, 20.25; N, 4.00.

Methyl (*Z*)-2-(2,4-dichlorophenylamino)-4-(4-ethoxyphenyl)-4-oxobut-2-enoate (4i) was obtained in a similar way from methyl (4-ethoxybenzoyl)pyruvate (5 g, 21.3 mmol) and 2,4-dichloroaniline (3.46 g, 21.3 mmol). Yield 1.37 g (17%), m.p. 144—146 °C (from EtOH). IR, ν/cm^{-1}: 1728 (COO); 1630, 1608 (ArCO, C=C). ^{1}H NMR ($CDCl_3$), δ: 1.40—1.46 (m, 3 H, Me); 3.75 (s, 3 H, OMe); 4.06—4.13 (m, 2 H, CH_2); 6.58 (s, 1 H, CH); 6.80 (d, 1 H, H(6), J = 8.6 Hz); 6.92 (dd, 2 H, H(3′), H(5′), J = 6.7 Hz, J = 2.2 Hz); 7.13 (dd, 1 H, H(5), J = 8.6 Hz, J = 2.5 Hz); 7.40 (d, 1 H, H(3), J = 2.5 Hz); 7.95 (dd, 2 H, H(2′), H(6′), J = 6.7 Hz, J = 2.2 Hz); 11.83 (s, 1 H, NH). Found (%): C, 57.71; H, 4.27; Cl, 18.03; N, 3.58. $C_{19}H_{17}Cl_2NO_4$. Calculated (%): C, 57.88; H, 4.35; Cl, 17.99; N, 3.55.

Methyl (*Z*)-4-(4-chlorophenyl)-2-(2,4-dichlorophenylamino)-4-oxobut-2-enoate (4j) was obtained in a similar way from methyl (4-chlorobenzoyl)pyruvate (6 g, 24.9 mmol) and 2,4-dichloroaniline (4.04 g, 24.9 mmol). Yield 6.33 g (66%), m.p. 140—141 °C (from Pr^iOH). IR, ν/cm^{-1}: 1740 (COO); 1610 (ArCO); 1590 (C=C). ^{1}H NMR ($CDCl_3$), δ: 3.69 (s, 3 H, OMe); 6.28 (s, 1 H, CH); 7.31 (m, 8 H, Ar); 11.81 (s, 1 H, NH). Found (%): C, 53.15; H, 3.19; Cl, 27.62; N, 3.48. $C_{17}H_{12}Cl_3NO_3$. Calculated (%): C, 53.08; H, 3.14; Cl, 27.65; N, 3.64.

Methyl (*Z*)-2-(2,4-dichlorophenylamino)-4-oxo-4-(2-thienyl)but-2-enoate (4k) was obtained in a similar way from methyl thenoylpyruvate (6 g, 28.3 mmol) and 2,4-dichloroaniline (4.58 g, 28.3 mmol). Yield 3.73 g (37%), m.p. 132—133 °C (from benzene). IR, ν/cm^{-1}: 1730 (COO); 1625, 1615, 1605 (C_4H_3SCO, C=C). ^{1}H NMR ($CDCl_3$), δ: 3.78 (s, 3 H, OMe); 6.47 (s, 1 H, CH); 6.82 (d, 1 H, H(6), J = 8.4 Hz); 7.14—7.18 (m, 2 H, H(4′), H(5)); 7.43 (d, 1 H, H(3), J = 2.4 Hz); 7.64 (dd, 1 H, H(3′), J = 5.3 Hz, J = 1.2 Hz); 7.75 (dd, 1 H, H(5′), J = 3.6 Hz, J = 1.2 Hz); 11.63 (s, 1 H, NH). Found (%): C, 50.56; H, 3.12; Cl, 19.92; N, 3.95. $C_{15}H_{11}Cl_2NO_3S$. Calculated (%): C, 50.58; H, 3.18; Cl, 19.90; N, 3.88.

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