

A DIRECT CONVERSION OF 5,6,7,8-TETRAHYDRO-2H-1-BENZOPYRAN-2,5-DIONES INTO SUBSTITUTED 1-AMINO-5,6,7,8-TETRAHYDROQUINOLINE-2,5-DIONES[#]

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Abstract – A highly selective transformation of 5,6,7,8-tetrahydro-2H-1-benzopyran-2,5-diones (**1a–c**) with hydrazides, arylhydrazines and heterocyclic hydrazines as nitrogen-containing nucleophiles (**2**) into the corresponding 1-amino-5,6,7,8-tetrahydroquinoline-2,5-diones (**5–17**) was investigated. The reaction was carried out in the mixture of ethanol, water and triethylamine, and the corresponding quinoline-2,5-diones were obtained in 52–89% yields. The compounds (**3**) and (**4**) were proposed to be intermediates in this transformation.

2H-Pyran-2-ones and fused pyran-2-ones are important synthons and building blocks in organic synthesis.¹ For example, they have been used for the preparation of pyridines and their benzo derivatives,^{2a–b} which are also known to be widely applied in the heterocycle synthesis and as constituents of pharmaceuticals, veterinary products, agrochemicals, additives, etc.^{2c} Fused pyran-2-ones, such as 5-, 6-, 7-, or 8-oxo substituted 5,6,7,8-tetrahydro-2H-1-benzopyran-2-ones possess several reactive centers. For example, nucleophiles might react either with the lactone ring or with the carbonyl group. Previous results have shown that *N*-(5,6,7,8-tetrahydro-2,5-dioxo-2H-1-benzopyran-3-yl)benzamides gave the corresponding quinolines^{3a–c} when reacted with nitrogen-containing nucleophiles, such as ammonia, hydroxylamine, aniline, amino acids, hydrazine and *N,N*-dimethylhydrazine. On the other hand, hydrazides, arylhydrazines and heterocyclic hydrazines converted benzopyran-2,5-diones selectively into 5-hydrazonebenzopyrans.^{3c–h} These reactions were carried out in dry ethanol under the influence of acidic catalysts or under microwave irradiation in the absence of a solvent. The hydrazones, when treated with a

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mixture of ethanol, water and triethylamine, were selectively transformed to the corresponding quinoline-2,5-diones *via* an open-ring intermediate.^{3e} In the case of a cyclopenta[*b*]pyran-2,5-dione derivative the corresponding fused pyridines were obtained as the only products.^{3f} Heats of formation of some hydrazone or imine–fused pyridinone product pairs have shown that the isolated products were generally thermodynamically favored over the hypothetical isomers.^{3b,e,f,i} In contrast to the isomeric 5-oxo derivatives, the 5,6,7,8-tetrahydro-2*H*-1-benzopyran-2,8-dione system gave in all the investigated transformations the corresponding 8-hydrazono (or 8-hydroxyimino) derivatives.^{3j} The two-step formation of quinoline-2,5-diones from benzopyran-2,5-diones^{3e} prompted us to investigate their direct formation from 5-oxo-5,6,7,8-tetrahydro-2*H*-1-benzopyran-2-ones and various hydrazine derivatives. Our investigation was carried out with 5-oxobenzopyran derivatives (**1a–c**)⁴ and nitrogen-containing nucleophiles (acetylhydrazine, different arylhydrazines and heterocyclic hydrazines). Acetylhydrazine was used in three equivalent amounts and all other nucleophiles in up to 10% excess; for the transformation we have used previously mentioned^{3e} alkaline reaction condition (mixture of ethanol, water and triethylamine). Upon heating of the reaction mixtures for 4–10.5 h the corresponding quinoline derivatives (**5–17**) were isolated in satisfactory (52–89%) yields (Scheme 1, Table 1).

Scheme 1

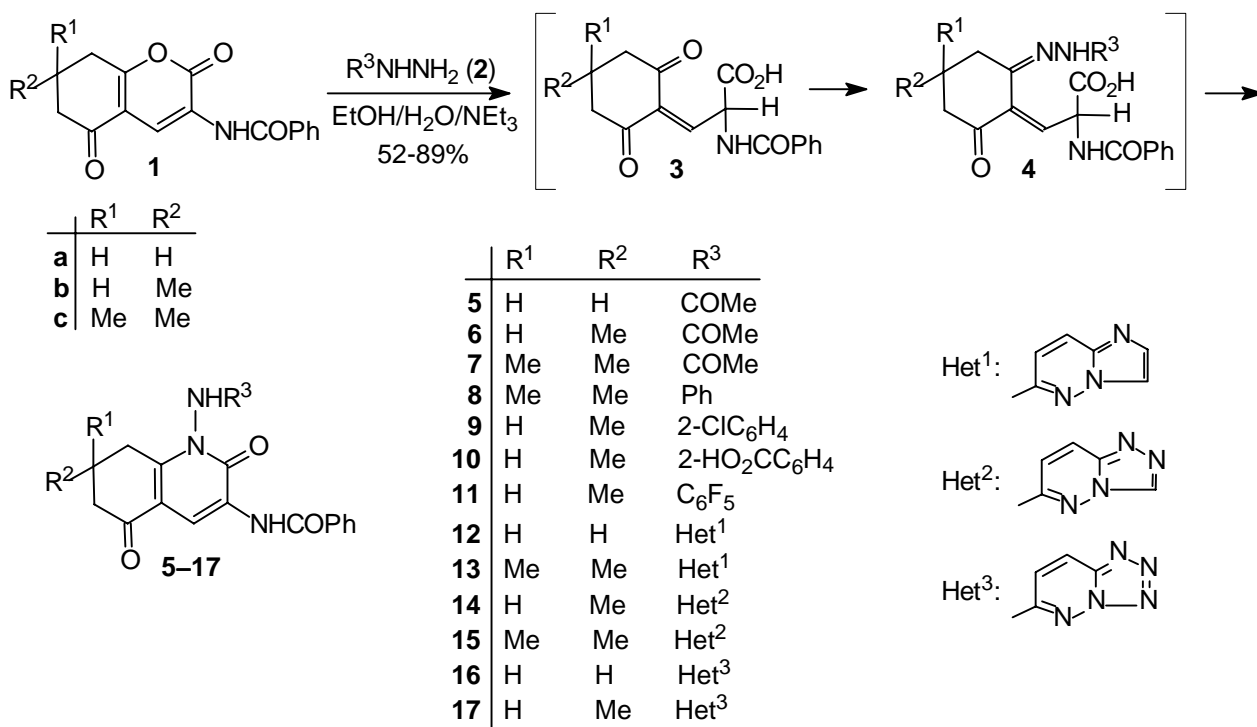


Table 1. Reaction Conditions and Yields of Compounds (**5–17**):

Run	Substrate	R ³ -NHNH ₂ (R ³ , mmol)	Reflux (h)	Product (yield, %) ^a
1	1a	Ac (3)	6	5 (64)
2	1b	Ac (3)	6.5	6 (67)
3	1c	Ac (3)	4	7 (87)
4	1c	Ph (1.1)	5.5	8 (52)
5	1b	2-Cl-C ₆ H ₄ (1)	6	9 (66)
6	1b	2- HO ₂ C-C ₆ H ₄ (1)	7	10 (62)
7	1b	C ₆ F ₅ (1)	8	11 (64)
8	1a	Het ¹ (1.1)	4	12 (74)
9	1c	Het ¹ (1.1)	4	13 (72)
10	1b	Het ² (1.1)	10.5	14 (81)
11	1c	Het ² (1.1)	4	15 (70)
12	1a	Het ³ (1.1)	10	16 (89)
13	1b	Het ³ (1.1)	10	17 (88)

^aYields of isolated products are given.

How do 2*H*-1-benzopyran-2,5-diones (**1**) transform to the quinolines under the aqueous basic conditions? On the basis of our previous results one might expect first the formation of *N*-(5-hydrazono-5,6,7,8-tetrahydro-2-oxo-2*H*-1-benzopyran-3-yl)benzamides followed by their further direct conversion into the final quinolines.^{3c} Some additional experiments have shown that this was probably not the case. Namely, *N*-(5-acetylhydrazono-7,7-dimethyl-5,6,7,8-tetrahydro-2-oxo-2*H*-1-benzopyran-3-yl)benzamide^{3c} remained unchanged after heating for 4 h in a mixture of pure ethanol and triethylamine (4:1) and was recovered in 93% yield. Similarly, the same compound remained unchanged when 1 equivalent of water was added to the previous mixture and the starting hydrazono derivative was recovered after 6 h of heating in 82% yield. A heating of the benzopyran derivative (**1c**) and acetylhydrazine for 4 h in a mixture of pure ethanol and triethylamine, resulted in the quinoline derivative (**7**) in 63% yield; no traces of the corresponding hydrazono derivative were detected by TLC. This fact excluded the intermediary formation of the hydrazone derivative in the last transformation. As a consequence of this observation, the conversion of the starting benzopyran (**1c**) to the quinoline had to take place by the nucleophilic attack directly on the pyran-2-one ring. In order to elucidate the structure of the intermediate in this transformation, we carried out an experiment in which the starting compound (**1c**) was heated for 5 h in the mixture of ethanol, water and triethylamine as a solvent, and we isolated in 67% yield a product for which we determined the structure as **3**. When the reaction between the benzopyran (**1c**) and

acetylhydrazine was stopped after 2 h of heating, besides the quinoline derivative (**7**) (40%), the same intermediate (**3**) was isolated in 43% yield. When starting from the compound (**3**) and acetylhydrazine we isolated the same product (**7**) as in a direct conversion. On the basis of these experiments we postulated the reaction pathway as shown in Scheme 1. The proposed intermediate (**3**) might exist in several tautomeric forms; its main structure was determined on the basis of ^1H NMR spectral data. An alternative reaction pathway, which cannot be completely excluded on the basis of our experiments (and for which we have no firm evidence), might be a nucleophilic attack of the hydrazine nitrogen at the position 2 in the pyran-2-one ring followed by the cleavage of O, 2-C single bond and a subsequent cyclization of the hydrazine nitrogen onto the carbonyl group yielding the final quinoline derivative.

In conclusion, we have presented a direct synthesis of 1-aminoquinoline-2,5-diones and postulated the reaction pathway of this conversion.

EXPERIMENTAL

Melting points were determined on a Kofler micro hot stage, and are uncorrected. ^1H and ^{13}C NMR spectra were recorded in $\text{DMSO-}d_6$ with the Bruker Avance DPX 300 spectrometer, using TMS as an internal standard. The coupling constants (J) are given in Hz. IR spectra were obtained with a Perkin Elmer 1310 spectrophotometer. MS spectra were recorded with a VG-Analytical AutoSpec Q instrument. Elemental analyses (C, H, N) were performed with a Perkin Elmer 2400 CHN Analyzer. TLC was carried out on Fluka silica gel TLC-cards.

***N*-Benzoyl-3-(4,4-dimethyl-2,6-dioxocyclohexylidene)alanine (**3**)**. 7,7-Dimethyl derivative (**1c**) (311 mg, 1 mmol) in pure ethanol (2 mL), water (2 mL) and triethylamine (1 mL) was heated under reflux for 5 h. The solvent was removed *in vacuo* and water (2 mL) was added to the residue. The pH value was adjusted to 5 by 9% hydrochloric acid. Upon cooling the product (**3**) was separated by filtration (220 mg, 67% yield); mp 200–202 °C (MeOH); $\nu_{\text{max}}/\text{cm}^{-1}$ 1610 br, 1625; ^1H NMR δ 1.00 (6H, s, two Me), 2.33 (4H, br s, two CH_2), 6.43 (1H, d, $J = 14.9$ Hz, 3-H), 7.51 (3H, m, Ph), 7.94 (3H, m, 2-H, Ph), 10.20 (1H, d, $J = 10.2$ Hz, NH), 11.03 (1H, br s, OH); MS m/z 285 ($\text{M}^+ - \text{CO}_2$, 23%), 105 (100%). Anal. Calcd for $\text{C}_{18}\text{H}_{19}\text{NO}_5$: C, 65.64; H, 5.81. Found: C, 65.50; H, 5.95.

General procedure for the preparation of quinoline-2,5-diones (**5**–**17**).

A mixture of a benzamide (**1a–c**, 1 mmol) and a substituted hydrazine (**2**, 1–3 mmol) in pure ethanol (2 mL), water (2 mL) and triethylamine (1 mL) was heated under reflux. The solvent was removed *in vacuo* and water (2 mL) was added to the residue. The pH value was adjusted to 6 by 9% hydrochloric acid. Upon cooling, the products were separated by filtration. Reaction conditions and yields are given in Table

1.

Analytical and spectroscopic data of products (5–17):

***N*-(1-Acetylamino-2,5-dioxo-1,2,5,6,7,8-hexahydro-3-quinolinyl)benzamide (5):** mp 204–206 °C (EtOH); $\nu_{\max}/\text{cm}^{-1}$ 1645 br, 1695; $^1\text{H NMR } \delta$ 2.05 (2H, m, 7-CH₂), 2.12 (3H, s, COMe), 2.53 (2H, m, 6-CH₂), 2.71 (1H, ddd, $J = 18.0, 6.0, \text{ and } 6.0$ Hz) and 2.93 (1H, ddd, $J = 18.0, 6.0, \text{ and } 6.0$ Hz) (8-CH₂), 7.58 (3H, m, Ph), 7.93 (2H, m, Ph), 8.61 (1H, s, 4-H), 9.42 (1H, s, NH), 11.14 (1H, s, NH); MS m/z 339 (M^+ , 22%), 105 (100%). Anal. Calcd for C₁₈H₁₇N₃O₄: C, 63.71; H, 5.05; N, 12.38. Found: C, 63.48; H, 5.08; N, 12.50.

***N*-(1-Acetylamino-7-methyl-2,5-dioxo-1,2,5,6,7,8-hexahydro-3-quinolinyl)benzamide (6):** mp 195–196 °C (EtOH); $\nu_{\max}/\text{cm}^{-1}$ 1645 br, 1685; $^1\text{H NMR (90 }^\circ\text{C)}$ δ 1.09 (3H, d, $J = 4.6$ Hz, Me), 2.11 (3H, s, COMe), 2.33 (2H, m) and 2.45–3.12 (3H, m) (6-CH₂, 7-H, 8-CH₂), 7.56 (3H, m, Ph), 7.90 (2H, m, Ph), 8.62 (1H, s, 4-H), 9.16 (1H, s, NH), 10.80 (1H, br s, NH). Anal. Calcd for C₁₉H₁₉N₃O₄: C, 64.58; H, 5.42; N, 11.89. Found: C, 64.41; H, 5.42; N, 11.86.

***N*-(1-Acetylamino)-7,7-dimethyl-2,5-dioxo-1,2,5,6,7,8-hexahydro-3-quinolinyl)benzamide (7):** mp 140–141 °C (DMF/MeOH) (lit.,^{3e} mp 140–141 °C).

***N*-(1-Anilino-7,7-dimethyl-2,5-dioxo-1,2,5,6,7,8-hexahydro-3-quinolinyl)benzamide (8):** mp 144–145 °C (EtOH); $\nu_{\max}/\text{cm}^{-1}$ 1640 br, 1684; $^1\text{H NMR } \delta$ 1.05 (6H, s, two Me), 2.48 (2H, deg dd, 6-CH₂), 2.75 (1H, d, $J = 18.0$ Hz) and 3.15 (1H, d, $J = 18.0$ Hz) (8-CH₂), 6.66 (2H, m, *N*-Ph), 6.88 (1H, m, *N*-Ph), 7.23 (2H, m, *N*-Ph), 7.56 (3H, m, Ph), 7.92 (2H, m, Ph), 8.71 (1H, s, 4-H), 9.27 (1H, s, NH), 9.38 (1H, s, NH); MS m/z 401 (M^+ , 49%), 105 (100%). Anal. Calcd for C₂₄H₂₃N₃O₃ × 0.25 H₂O: C, 71.01; H, 5.83; N, 10.35. Found: C, 70.94; H, 6.01; N, 10.36.

***N*-[1-(2-Chloroanilino)-7-methyl-2,5-dioxo-1,2,5,6,7,8-hexahydro-3-quinolinyl]benzamide (9):** mp 261–263 °C (MeOH/DMF); $\nu_{\max}/\text{cm}^{-1}$ 1655 br, 1680; $^1\text{H NMR } \delta$ 1.08 (3H, d, $J = 5.9$ Hz, Me), 2.37 (2H, m), 2.55 (1H, m), 3.00 (1H, m) and 3.40 (1H, m) (6-CH₂, 7-H, 8-CH₂), 6.45 (1H, deg dd, *N*-C₆H₄), 6.92 (1H, deg ddd, *N*-C₆H₄), 7.15 (1H, deg ddd, *N*-C₆H₄), 7.44 (1H, deg dd, *N*-C₆H₄), 7.55 (3H, m, Ph), 7.92 (2H, m, Ph), 8.72 (1H, s, 4-H), 8.79 (1H, s, NH), 9.40 (1H, s, NH). Anal. Calcd for C₂₃H₂₀N₃O₃Cl: C, 65.48; H, 4.78; N, 9.96. Found: C, 65.35; H, 4.82; N, 9.69.

2-[(3-Benzoylamino-7-methyl-2,5-dioxo-5,6,7,8-tetrahydro-1(2*H*)-quinolinyl)amino]benzoic acid (10): mp 292–294 °C (MeOH/DMF); $\nu_{\max}/\text{cm}^{-1}$ 1653 br, 1687; $^1\text{H NMR } \delta$ 1.07 (3H, d, $J = 6.0$ Hz, Me), 2.38 (2H, m), 2.57 (1H, m), 2.90 (1H, m) and 3.42 (1H, m) (6-CH₂, 7-H, 8-CH₂), 6.49 (1H, m, *N*-C₆H₄), 6.97 (1H, m, *N*-C₆H₄), 7.41 (1H, m, *N*-C₆H₄), 7.55 (3H, m, Ph), 7.92 (2H, m, Ph), 7.97 (1H, deg dd, *N*-C₆H₄), 8.71 (1H, s, 4-H), 9.37 (1H, s, NH), 10.19 (1H, s, NH), 13.42 (1H, br s, OH). Anal. Calcd for C₂₄H₂₁N₃O₅ × 0.25 H₂O: C, 66.12; H, 4.97; N, 9.64. Found: C, 66.00; H, 4.99; N, 9.33.

***N*-[7-Methyl-2,5-dioxo-1-(2,3,4,5,6-pentafluoroanilino)-1,2,5,6,7,8-hexahydro-3-quinolinyl]-**

benzamide (11): mp 217–218 °C (MeOH); $\nu_{\max}/\text{cm}^{-1}$ 1645 br, 1680; $^1\text{H NMR}$ δ 1.13 (3H, d, $J = 6.0$ Hz, Me), 2.40 (2H, m), 2.58 (1H, m), 2.78 (1H, m) and 3.40 (1H, m) (6-CH₂, 7-H, 8-CH₂), 7.56 (3H, m, Ph), 7.91 (2H, m, Ph), 8.64 (1H, s, 4-H), 9.39 (1H, s, NH), 9.51 (1H, s, NH). Anal. Calcd for C₂₃H₁₆N₃O₃F₅: C, 57.87; H, 3.38; N, 8.80. Found: C, 57.65; H, 3.35; N, 8.97.

***N*-[1-(Imidazo[1,2-*b*]pyridazin-6-ylamino)-2,5-dioxo-1,2,5,6,7,8-hexahydro-3-quinolinyl]benzamide (12):** mp 191–194 °C (DMF/MeOH); $\nu_{\max}/\text{cm}^{-1}$ 1645 br, 1690; $^1\text{H NMR}$ δ 2.08 (2H, m, 7-CH₂), 2.55 (2H, m, 6-CH₂), 2.90 (1H, deg ddd) and 3.19 (1H, deg ddd) (8-CH₂), 7.05 (1H, d, $J = 9.7$ Hz, 7'-H), 7.55 (4H, m, 3'-H, Ph) and 7.93 (3H, m, 2'-H, Ph), 8.03 (1H, deg dd, $J_1 = 9.7$ Hz, 8'-H), 8.69 (1H, s, 4-H), 9.46 (1H, s, NH), 10.32 (1H, br s, NH); $^{13}\text{C NMR}$ (75.5 MHz) δ 20.7, 24.8, 36.1, 109.8, 112.7, 116.9, 121.5, 126.6, 127.1, 127.4, 128.5, 131.9, 132.0, 133.6, 136.6, 152.6, 155.1, 157.1, 165.2, 193.8. Anal. Calcd for C₂₂H₁₈N₆O₃: C, 63.76; H, 4.38; N, 20.28. Found: C, 63.53; H, 4.27; N, 20.34.

***N*-[1-(Imidazo[1,2-*b*]pyridazin-6-ylamino)-7,7-dimethyl-2,5-dioxo-1,2,5,6,7,8-hexahydro-3-quinolinyl]benzamide (13):** mp 210–212 °C (DMF/MeOH); $\nu_{\max}/\text{cm}^{-1}$ 1652 br, 1678; $^1\text{H NMR}$ δ 1.04 (3H, s, Me), 1.07 (3H, s, Me), 2.44 (2H, deg dd, 6-CH₂), 2.79 (1H, d, $J = 18.0$ Hz) and 3.10 (1H, d, $J = 18.0$ Hz) (8-CH₂), 7.05 (1H, d, $J = 9.7$ Hz, 7'-H), 7.55 (4H, m, 3'-H, Ph), 7.92 (3H, m, 2'-H, Ph), 8.04 (1H, deg dd, $J_1 = 9.7$ Hz, 8'-H), 8.69 (1H, s, 4-H), 9.45 (1H, s, NH), 10.34 (1H, br s, NH); $^{13}\text{C NMR}$ (75.5 MHz) δ 27.0, 28.2, 32.4, 38.1, 49.5, 109.8, 111.7, 116.8, 121.2, 126.5, 127.1, 127.3, 128.6, 131.9, 132.0, 133.6, 136.6, 152.5, 153.5, 157.4, 165.3, 193.8; MS m/z 442 (M^+ , 46%), 105 (100%); HRMS: Calcd: 442.1753. Found: 442.1763. Anal. Calcd for C₂₄H₂₂N₆O₃ × 0.5 H₂O: C, 63.85; H, 5.13; N, 18.61. Found: C, 64.09; H, 5.00; N, 18.95.

***N*-[7-Methyl-2,5-dioxo-1-([1,2,4]triazolo[4,3-*b*]pyridazin-6-ylamino)-1,2,5,6,7,8-hexahydro-3-quinolinyl]benzamide (14):** mp 197–199 °C (EtOH); $\nu_{\max}/\text{cm}^{-1}$ 1645 br; $^1\text{H NMR}$ (90 °C) δ 1.08 (3H, d, $J = 7.0$ Hz, Me), 2.34 (2H, m), 2.61 (2H, m) and 3.17 (1H, m) (6-CH₂, 7-H, 8-CH₂), 7.16 (1H, d, $J = 9.8$ Hz, 7'-H), 7.53 (3H, m, Ph), 7.90 (2H, m, Ph), 8.19 (1H, dd, $J = 9.8$ and 0.6 Hz, 8'-H), 8.69 (1H, s, 4-H), 9.08 (1H, d, $J = 0.6$ Hz, 3'-H), 9.16 (1H, s, NH), 10.72 (1H, br s, NH); $^{13}\text{C NMR}$ (75.5 MHz, 90 °C) δ 20.4, 28.1, 32.5, 44.2, 112.9, 114.6, 120.9, 125.7, 126.9, 127.2, 128.6, 132.0, 134.0, 138.5, 142.6, 153.6, 153.8, 157.2, 165.4, 193.4; MS m/z 429 (M^+ , 24%), 105 (100%); HRMS: Calcd: 429.1549. Found: 429.1559. Anal. Calcd for C₂₂H₁₉N₇O₃ × 0.25 H₂O: C, 60.89; H, 4.53; N, 22.59. Found: C, 60.91; H, 4.39; N, 22.57.

***N*-[7,7-Dimethyl-2,5-dioxo-1-([1,2,4]triazolo[4,3-*b*]pyridazin-6-ylamino)-1,2,5,6,7,8-hexahydro-3-quinolinyl]benzamide (15):** mp 180–182 °C (EtOH); $\nu_{\max}/\text{cm}^{-1}$ 1650 br; $^1\text{H NMR}$ δ 1.03 (3H, s, Me), 1.06 (3H, s, Me), 2.46 (2H, deg dd, 6-CH₂), 2.80 (1H, d, $J = 18.0$ Hz) and 3.05 (1H, d, $J = 18.0$ Hz) (8-CH₂), 7.19 (1H, d, $J = 9.8$ Hz, 7'-H), 7.56 (3H, m, Ph), 7.93 (2H, m, Ph), 8.28 (1H, dd, $J = 9.8$ and 0.6 Hz, 8'-H), 8.68 (1H, s, 4-H), 9.24 (1H, d, $J = 0.6$ Hz, 3'-H), 9.47 (1H, s, NH), 10.70 (1H, br s, NH). Anal.

Calcd for C₂₃H₂₁N₇O₃: C, 62.29; H, 4.77; N, 22.11. Found: C, 62.06; H, 4.51; N, 22.03.

***N*-[2,5-Dioxo-1-(tetrazolo[1,5-*b*]pyridazin-6-ylamino)-1,2,5,6,7,8-hexahydro-3-quinolinyl]benzamide (16):** mp 256–258 °C (EtOH); $\nu_{\max}/\text{cm}^{-1}$ 1647 br; ¹H NMR δ 2.06 (2H, m, 7-CH₂), 2.56 (2H, m, 6-CH₂), 2.92 (1H, ddd, *J* = 18.5, 6.0, and 6.0 Hz) and 3.13 (1H, ddd, *J* = 18.5, 6.0, and 6.0 Hz) (8-CH₂), 7.56 (4H, m, 7'-H, Ph), 7.93 (2H, m, Ph), 8.64 (1H, d, *J* = 9.7 Hz, 8'-H), 8.70 (1H, s, 4-H), 9.50 (1H, s, NH), 11.23 (1H, br s, NH); MS *m/z* 416 (M⁺, 2%), 105 (100%). Anal. Calcd for C₂₀H₁₆N₈O₃: C, 57.69; H, 3.87; N, 26.91. Found: C, 57.64; H, 3.71; N, 27.10.

***N*-[7-Methyl-2,5-dioxo-1-(tetrazolo[1,5-*b*]pyridazin-6-ylamino)-1,2,5,6,7,8-hexahydro-3-quinolinyl]benzamide (17):** mp 199–201 °C (EtOH/DMF); $\nu_{\max}/\text{cm}^{-1}$ 1655 br; ¹H NMR (90 °C) δ 1.07 (3H, d, *J* = 5.9 Hz, Me), 2.35 (2H, m), 2.62 (2H, m) and 3.12 (1H, br) (6-CH₂, 7-H, 8-CH₂), 7.53 (4H, m, 7'-H, Ph), 7.90 (2H, m, Ph), 8.54 (1H, d, *J* = 9.7 Hz, 8'-H), 8.70 (1H, s, 4-H), 9.21 (1H, s, NH), 10.92 (1H, br s, NH); ¹³C NMR (75.5 MHz, 90 °C) δ 20.4, 28.1, 28.8, 44.1, 113.0, 118.5, 121.2, 125.7, 127.0, 127.3, 128.6, 131.9, 134.0, 141.3, 153.4, 155.4, 157.0, 165.4, 193.4; MS FAB⁺ *m/z* 431 (MH⁺, 57%), 105 (100%). Anal. Calcd for C₂₁H₁₈N₈O₃ × 0.25 H₂O: C, 57.99; H, 4.29; N, 25.76. Found: C, 57.99; H, 4.01; N, 25.99.

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