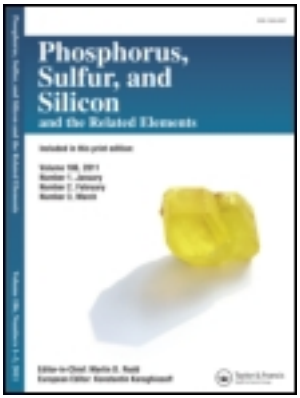

Phosphorus, Sulfur, and Silicon and the Related Elements

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Novel Syntheses and Reactions of Polynuclear Heterocyclic Derivatives Derived From Thioxopyridopyrimidine, With a New Ring System

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Novel Syntheses and Reactions of Polynuclear Heterocyclic Derivatives Derived From Thioxopyridopyrimidine, With a New Ring System

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*Pyridopyrimidine derivatives **2** reacted with hydrazonoylchloride derivatives and yielded triazolopyridopyrimidines **6a–f**. Compound **4b** reacted with aliphatic acids and afforded triazolo-pyridopyrimidines **7a,b**, and the reaction with carbon disulfide afforded 10-mercapto-triazolopyridopyrimidine (**10**). Moreover, the reaction of **4b** with β-ketoesters afforded 10-pyrazolyl-pyridopyrimidines derivatives **11**, **13**, **14**, and **15**. Compound **4b** reacted with nitrous acid to give tetrazolopyridopyrimidine **16**, which reduced to 10-amino-derivative **17**. On the other hand, the reaction of **4b** with aromatic aldehydes afforded arylidines derivatives **18a–c**, which were later cyclized to triazolo-pyridopyrimidines deivatives **19a–c**. Finally, **4b** reacted with α-haloketones to give triazines derivativrs **20**, with new ring systems.*

Keywords New ring system; polynuclear heterocyclic; pyrimido[4,5-b]quinolone derivatives; thioxopyrido pyrimidine

INTRODUCTION

It is known that pyridopyrimidine derivatives have biochemical activities against bacteria.[1,2] Moreover, they are used for the treatment of intestinal, urinary, and biliary tract infection in humans.[3,4] These derivatives also have similar inherent chemotherapeutic properties.[5] Moreover, biological activities of condensed pyrimidine derivatives act as sedatives[6,7] and analgesic,[8] antiinflammatory,[9] anticonvulasnt,[10] and antimicrobial agents.[11]

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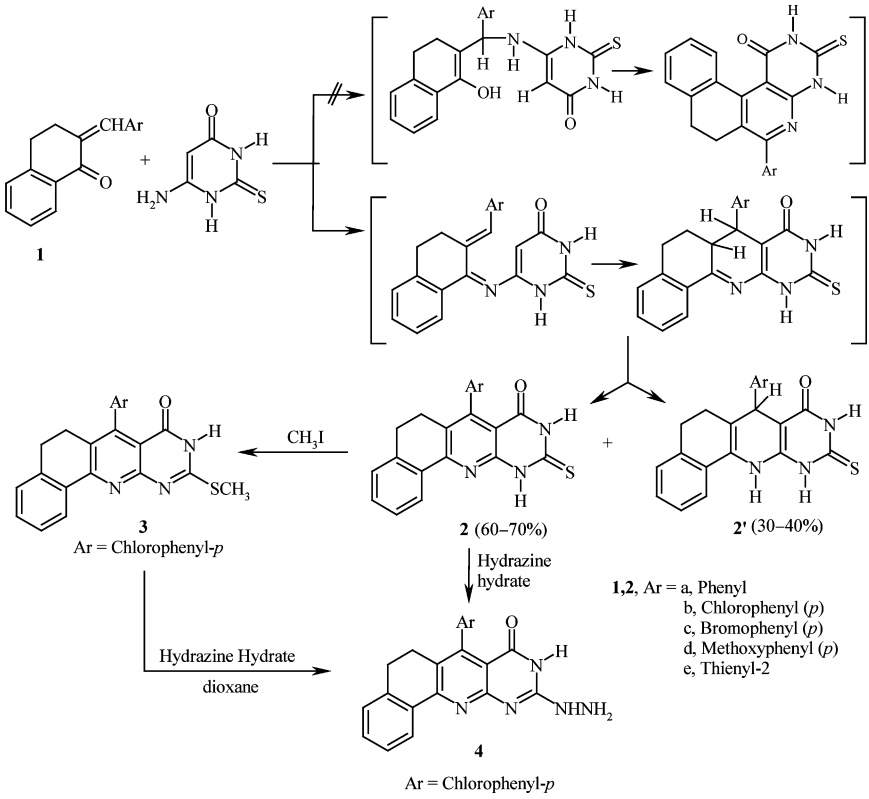
The rapid growth in the literature dealing with the synthesis biological activity of the pyridopyrimidine derivatives prompted us to start a program to synthesize some new pyridopyrimidine derivatives.

This report describes our approach to the synthesis of polyfunctional heterocyclic compounds.[12,13] In addition, we reported convenient methods for the synthesis of triazolopyrido-pyrimidines **7**, **9**, **10**, and **19**; tetrazolopyridopyrimidines **16**; and triazinopyridopyrimidines **20**. Thus, heating under reflux 6-aminothiouracil with chalcones **1a–e** in boiling dimethylformamide for long times afforded a mixture of the oxidizing form of 7-(4-aryl)-10-thioxo-5,6,10,11-tetrahydro-9*H*-benzo[h]pyrimido[4,5-b]quinolin-8-ones **2a–e** (60–70%), and nonoxidizes formed **2′** (30–40%). The oxidized form, which separated by crystalization, reacted with methyl iodide to give the corresponding 10-methylthio derivative **3** (Scheme 1). ^{1}H NMR spectra of the resulting products were agreement with the structures. The ^{1}H-NMR spectrum (DMSO-d_6) of **2d** as an example showed signals at δ 2.42–2.47 (m, 2H, CH_2), 2.75–2.80 (m, 2H, CH_2), 4.15 (s, 3H, OCH_3) 7.18–7.22 (d, 2H, p-pheny), 7.30–7.37 (m, 1H, phenyl), 7.44–7.47 (m, 2H, phenyl), 7.58–7.61 (d, 2H, phenyl), 8.32–8.38 (m, 1H, phenyl), and 12.10, 12.60 (two NH, D_2O exchangable). The oxidized pyridopyrimidine derivative **2b** reacted with hydrazonoyl chlorides **5a–f** to give novel functionalized heterocycles having pyridine rings condensed with other important heterocycles, such as 7-(4-aryl)-5,6-dihydro-9*H*-benzo[h]-1,2,4-triazolo-[4′,3′:1,2]pyrimido[4,5-b]quinolin-8-one derivatives **6a–f** (Scheme 2). The correct values in elemental analysis and IR, ^{1}H NMR, and mass spectra of compounds **6a–f** are in agreement with the assigned structures. The N-3 nitrogen atom and not the N-1 nitrogen atom was involved in the cyclization to form the adduct **6**, not **6**. The ^{1}H NMR spectrum of **6e** as an example showed signals at δ 1.25 (t, 3H, CH_3), 2.35–2.45 (m, 2H, CH_2), 2.65–2.80 (m, 2H, CH_2) 4.40 (q, 2H, CH_2), 7.25–7.30 (d, 2H, phenyl), 7.31–7.35 (m, 1H, phenyl), 7.40–7.75 (m, 7H, 5H (phenyl) +2H (phenyl), 8.05–8.10 (d, 2H, phenyl), and 8.30–8.35 (d, 1H, phenyl). The mass spectrum showed the molecular ion peak at m/z, 547 (100%).

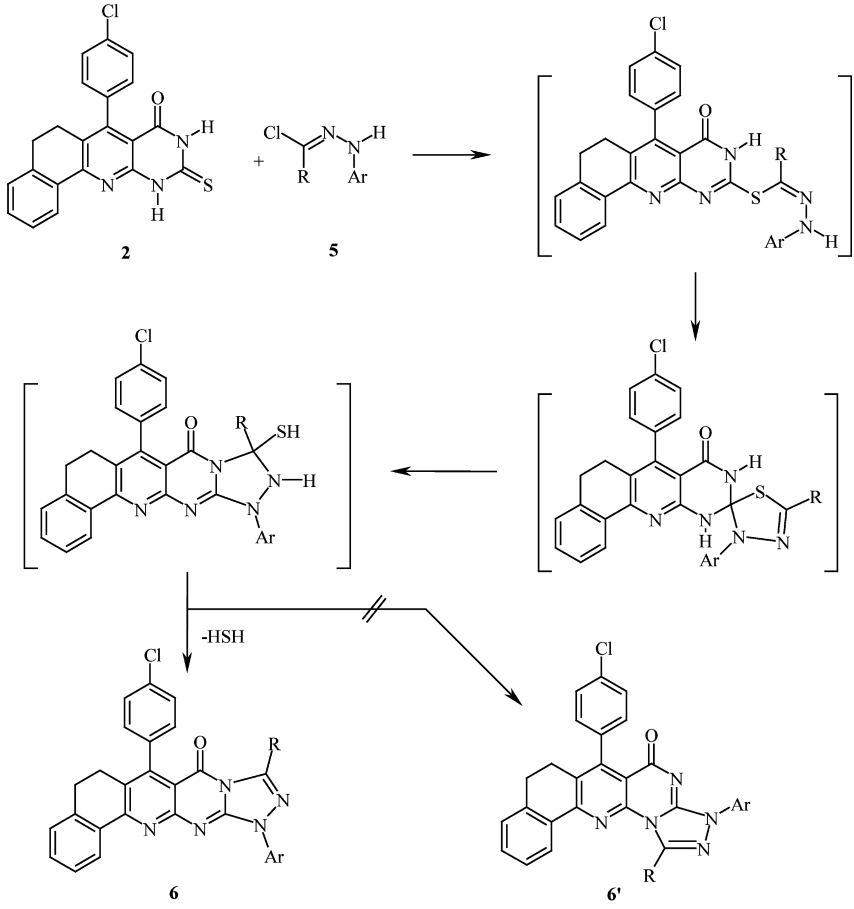
Mercapto groups may be removed in favor of hydrogen by desulfurization using alkaline hydrazine hydrate.[14,15] Therefore, the 7-(4-chlorophenyl)-10-hydrazino-5,6,10,11-tetrahydro-9*H*-benzo[h]pyrimido[4,5-b]quinolin-8-one (**4b**) is a fertile source to enrich the synthesis of heterocyclic chemistry with several new azolopyridopyrimidines, pyridopyrimido-as-triazines, and pyrazolylpyridopyrimidines (Scheme 3). Thus, heating under reflux **4b** with aliphatic acids, mainly, formic and acetic acids, for 6 h yielded 7-(4-chlorophenyl)-5,6-dihydro-9*H*-benzo[h]-1,2,4-triazolo[4′,3′:1,2]pyrimido[4,5-b]quinolin-8-one derivatives **7a,b**. Besides the correct values in elemental analyses,



SCHEME 1

the ^{1}H NMR spectrum of **7a**, as an example, showed signals at δ 2.52–2.60 (m, 2H, CH_2), 2.75–2.85 (m, 2H, CH_2), 7.20–7.25 (d, 2H, phenyl), 7.27–7.33 (m, 1H, phenyl), 7.40–7.45 (m, 2H, phenyl), 7.50–7.55 (d, 2H, phenyl) 8.50–8.55 (m, 1H, phenyl), 9.50 (s, 1H, H triazole), and 12.65 (brs, 1H, NH, D_2O exchangable), and they are in agreement with the assigned structure. On the other hand, heating under reflux compound **4b** with acetic acid for 3 h yielded the 2-acethydrazido derivative **8**. The IR spectrum of **8** displayed absorption bands at 3389, 3100 cm^{-1} (brs, 2NH), 1709 cm^{-1} (CO), and 1686 cm^{-1} (CO).

The derivative **4b** reacted with potassium thiocyanate in boiling acetic acid to give compound **9**. Besides the correct values in elemental analysis, the spectral data of **9** are in agreement with the assigned structure. Similarly, heating **4b** with carbon disulphide in ethanolic potassium hydroxide gave 7-(4-chlorophenyl)-5,6-dihydro-9*H*-10-thioxobenzo[h]-1,2,4-triazolo[4′,3′:1,2]pyrimido[4,5-b]quinolin-8-one



5, 6a, R = Ar = C_6H_5

5, 6b, R = $COCH_3$, Ar = *p*-C_6H_4-Cl

5, 6c, R = $COCH_3$, Ar = *p*-C_6H_4-OCH_3

5, 6d, R = $COCH_3$, Ar = *p*-C_6H_4-NO_2

5, 6e, R = $COOC_2H_5$, Ar = C_6H_5

5, 6f, R = $COOC_2H_5$, Ar = *p*-C_6H_4-CH_3

SCHEME 2

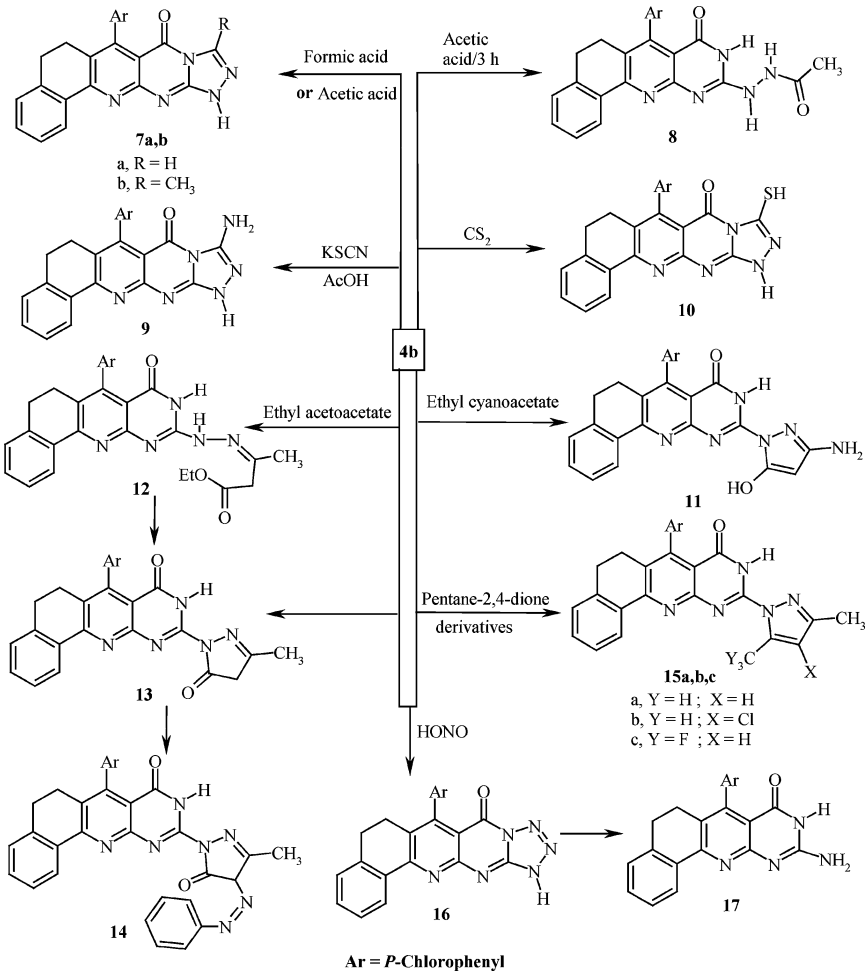
(**10**). The IR spectrum of **10** displayed absorption bands at 3465 cm^{-1} (NH) and 1168 cm^{-1} (CO).

The ^1H NMR spectrum (DMSO-d_6) of **10** showed signals at δ 2.40–2.55 (m, 2H, CH_2), 2.80–3.00 (m, 2H, CH_2), 7.15–7.25 (d, 2H, phenyl), 7.30–7.40 (m, 1H, phenyl), 7.45–7.50 (m, 2H, phenyl), 7.51–7.55 (d,

2H, phenyl), 8.75–8.80 (m, 1H, phenyl), 12.55 (brs, 1H, NH, D_2O exchangable), and 13.65 (brs, 1H, NH, D_2O exchangable). Mass spectra of **10** showed the molecular ion peak at m/z 431.

Moreover, the 10-hydrazino derivative **4b** reacted with some β-cyanoesters, β-ketooesters, and β-diketones to form derivatives **11**, **12**, and **15**. Compound **4b** and ethyl cyanoacetate in hot ethanolic sodium ethoxide solution afforded the 10-(3-amino-5-hydroxy-4H-pyrazol-l-yl) derivative **11**. The IR spectrum of **11** displayed absorption bands at 3318 cm^{-1} (NH) and 1687 cm^{-1} (CO). Its ^1H NMR spectrum (DMSO-d_6) showed signals at δ 2.36–2.43 (m, 2H, CH_2), 2.67–2.75 (m, 2H, CH_2), 3.57 (s, 2H, CH_2), (7.17–7.25 (d, 2H, phenyl), 7.27–7.34 (m, 1H, phenyl), 7.43–7.50 (m, 2H, phenyl), 7.53–7.58 (d, 2H, phenyl), 8.41–8.43 (m, 1H, phenyl), and 12.20, 12.85 (two brs, NH, D_2O exchangable). Similarly, **4b** reacted with ethyl acetoacetate in absolute ethanol and gave the ethylacetoacetate hydrazone derivative **12**, while the 7-(4-chlorophenyl)-10-(3-methyl-4*H*-pyrazol-5-one-1-yl)-5,6,10,11-tetrahydro-9H-benzo-[h]pyrimido[4,5-b]quinolin-8-one (**13**) was produced by heating **4b** with ethyl acetoacetate under reflux in ethanolic sodium ethoxide. Compound **12** could be converted to **13** upon additional heating with ethanolic sodium ethoxide solution. The ^1H NMR spectrum (DMSO-d_6) of **12** showed signals at δ 1.25 (t, 3H, CH_3), 2.00 (s, 3H, CH_3), 2.35–2.45 (m, 2H, CH_2), 2.70–2.85 (m, 2H, CH_2), 3.35 (s, 2H, CH_2), 4.15 (q, 2H, CH_2), 7.15–7.25 (d, 2H, phenyl), 7.25–7.30 (m, 1H, phenyl), 7.30–7.35 (m, 2H, phenyl), 7.40–7.50 (d, 2H, phenyl), 8.20–8.30 (m, 1H, phenyl), 9.80–10.40 (brs, 1H, NH, D_2O exchangable), and 11.15 (brs, NH, D_2O exchangable). The IR spectrum displayed absorption bands 3250 cm^{-1} (brs, NH), 1740, 1680 cm^{-1} (2CO), and 1580 cm^{-1} (C=N). The ^1H NMR spectrum of **13** showed no signals corresponding to ethyl group protons. Compound **13** was coupled with phenyl diazonium salts to afford 7-(4-chlorophenyl)-10-(3-methyl-4-phenylazopyrazol-5-one-1-yl)-5,6,10, 11-tetra-hydro-9*H*-benzo[h]pyrimido[4,5-b]quinolin-8-one**(14)**. The IR spectra of **14** showed absorption bands at 3436 cm^{-1} (OH), 3250 cm^{-1} (NH), 2917 cm^{-1} (CH aliphatic), and 1686 cm^{-1} (CO). The ^1H NMR spectrum showed signals at δ 2.41 (s, 3H, CH_3), 2.49–2.54 (m, 2H, CH_2), 2.80–2.85 (m, 2H, CH_2), 7.19–7.21 (m, 1H, phenyl), 7.25–7.28 (d, 2H, phenyl), 7.30–7.36 (m, 1H, phenyl), 7.38–7.47 (m, 6H, 2H, phenyl +4H, phenyl), 7.49–7.56 (d, 2H, phenyl), 8.40–8.41 (m, 1H, phenyl), and 11.20 (brs, NH, D_2O exchangable). The mass spectrum for **14** showed the molecular ion peak at m/z 560 (100%).

When equimolar amounts of **4b** and pentane-2,4-dione derivatives were heated under reflux in ethanol, the 7-(4-chlorophenyl)-10-(3-methyl-4-(un)substituted-5-substituted pyrazol-1-yl)-5,6,10,



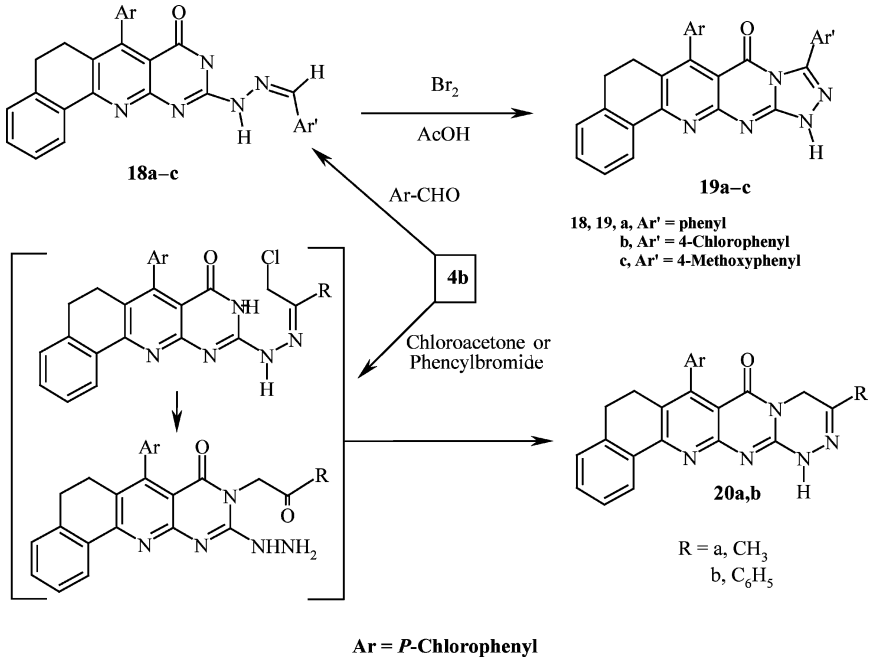
SCHEME 3

11-tetrahydro-9*H*-benzo[h]pyrimido[4,5-b]quinolin-8-ones (**15a–c**) were obtained in good yield. Besides the correct values in elemental analysis, the spectral data of **15a–c** are in agreement with the assigned structure. The ^{1}H NMR spectrum (DMSO-d_6) of **15a**, as an example, showed signals at δ 2.25 (s, 3H, CH_3), 2.45–2.55 (m, 2H, CH_2), 2.65 (s, 3H, CH_3), 2.70–2.85 (m, 2H, CH_2), 6.40 (s, 1H,pyrazol proton), 7.20–7.25 (d, 2H, phenyl), 7.27–7.35 (m, 1H, phenyl), 7.45–7.50 (m, 2H, phenyl), 7.52–7.57 (d, 2H, phenyl), 8.35–8.40 (m, 1H, phenyl), and 11.90, (brs, NH, D_2O exchangable). Its IR spectrum displayed absorption bands at 3320 cm^{-1} (brs, NH), 3054 cm^{-1} (CH aryl), 2943 cm^{-1}

(CH alkyl), 1693 cm^{-1} (CO), 1600 cm^{-1} (C=N), and 1550 cm^{-1} (C=C). Its mass spectrum showed the molecular ion peak at m/z 453.

The treatment of compound **4b** with nitrous acid at 0°C led to the formation of 7-(4-chlorophenyl)-5,6,12-trihydro-9*H*-benzo[h]-tetrazolo[4′,5′:1,2]pyrimido[4,5-b]quinolin-8-one (**16**). IR spectra for compound **16** showed absorption bands at 3243 cm^{-1} (brs, NH), 2934 cm^{-1} (CH alkyl), 1700 cm^{-1} (CO), 1629 cm^{-1} (N=N), and 1582 cm^{-1} (C=N). The ^1H NMR spectrum of **16** (DMSO-d_6) showed signals at δ 2.45–2.50 (m, 2H, CH_2), 2.80–2.90 (m, 2H, CH_2), 7.20–7.25 (d, 2H, phenyl), 7.27–7.31 (m, 1H, phenyl), 7.40–7.60 (m, 4H, 2H phenyl + 2H phenyl), 8.25–8.35 (m, 1H, phenyl), and 13.25, (brs, NH, D_2O exchangable). Compound **16** was reduced to 10-amino-7-(4-Chlorophenyl)-5,6,10,11-tetrahydro-9*H*-benzo[h]pyrimido-[4,5-b]quinolin-8-one (**17**) by zinc dust in acetic acid. The ^1H NMR spectrum (DMSO-d_6) of **17** showed signals at δ 2.30–2.40 (m, 2H, CH_2), 2.80–2.90 (m, 2H, CH_2), 3.55–3.60 (brs, 2H, NH_2 D_2O exchangable), 4.45 (brs, NH, D_2O exchangable), 7.15–7.30 (m, 1H, phenyl), 7.35–7.40 (d, 2H, phenyl), 7.45–7.50 (m, 3H, 2H phenyl + 1H phenyl), and 7.70–7.75 (m, 1H, phenyl). Its IR spectrum displayed absorption band at 3310 cm^{-1} (NH_2). The mass spectrum for the same compound showed the molecular ion peak at m/z 374 (100%).

According to Shishoo and Jain,[15] 10-hydrazinobenzo[h]pyrimido[4,5-b]quinolin-8-one (**4b**) gave 7-(4-chlorophenyl)-10-(aryl-methylenehydrazone)-5,6,10,11-tetrahydro-9*H*-benzo[h]pyri-mido[4,5-b]quinolin-8-one derivatives **18a–c** when **4b** was treated with the appropriate aldehyde in boiling dioxane in the presence of catalytic amounts of piperidine. Compounds **18a–c** gave compatible spectral and analytical data. The ^1H NMR (DMSO-d_6) spectrum of compound **18c**, as an example, showed signals at δ 2.45–2.50 (m, 2H, CH_2), 2.75–2.85 (m, 2H, CH_2), 3.85 (s, 3H, OCH_3), 6.95–7.05 (d, 2H, phenyl), 7.20–7.25 (d, 2H, phenyl), 7.26–7.30 (m, 1H, phenyl), 7.40–7.45 (m, 2H, phenyl), 7.47–7.50 (d, 2H, phenyl),7.85–7.95 (d, 2H, phenyl) 8.05–8.11 (s, 1H, methylenic proton), 8.30–8.40 (m, 1H, phenyl), and 11.20 (brs, NH, D_2O exchangable). The arylhydrazones **18a–c** could be cyclized into the corresponding 10-aryl-7-(4-chlorophenyl)-5,6-dihydro-9*H*-benzo[h]-1,2,4-triazolo[4′,3′:1,2]pyrimido[4,5-b]quinolin-8-one **19a–c**, when treated with excess bromine in acetic acid in presence of anhydrous sodium acetate. IR spectra of compounds **19** displayed absorption bands around 3290 cm^{-1} (NH) and 1690 cm^{-1} (CO). The ^1H NMR (DMSO-d_6) spectrum of compound **19b**, as an example, showed signals at δ 2.43–2.50 (m, 2H, CH_2), 2.75–2.83 (m, 2H, CH_2), 7.15–7.20 (d, 2H, phenyl), 7.25–7.30 (m, 1H, phenyl), 7.35–7.45 (m, 2H, phenyl), 7.45–7.55 (two



SCHEME 4

d, 4H, phenyl), 7.98–8.15 (d, 2H, phenyl), 8.29–8.38 (m, 1H, phenyl), and 11.65 (brs, NH, D_2O exchangable).

Finally, the 10-hydrazino derivative **4b** was used for the preparation of 7-(4-chlorophenyl)-5,6-dihydro-9*H*-11-(methyl or phenyl)benzo [h]-1,2,4-triazino[4′,3′:1,2]pyri-mido[4,5-b]quinolin-8-one derivatives **20a,b**. Thus, heating **4b** under reflux with chloro-acetone or phenacyl bromide in dry xylene yielded directly the triazino derivatives **20a,b** (Scheme 4). IR spectra of **19** displayed absorption bands around 3420 cm^{-1} (NH) and 1687 cm^{-1} (CO). The ^1H NMR (DMSO-d_6) spectrum of compound **20a**, as an example, showed signals at δ 2.05 (s, 3H, CH_3), 2.50–2.55 (m, 2H, CH_2), 2.70–2.85 (m, 2H, CH_2), 4.80 (s, 2H, CH_2), 7.20–7.30 (d, 2H, phenyl), 7.35–7.40 (m, 1H, phenyl), 7.45–7.55 (m, 4H, 2H phenyl + 2H phenyl), 8.25–8.40 (m, 1H, phenyl), and 11.05 (brs, NH, D_2O exchangable). Its mass spectrum showed the molecular ion peak at m/z 427 (100%).

EXPERIMENTAL

All melting points were uncorrected. ^1H NMR and ^{13}C NMR spectra were recorded on Bruker (WM-250 MHz), Bruker (AC-250 MHz)

spectrometers, and a Varian 300 MHz Oxford-Mercury spectrometer (National Research Center, Giza, Egypt). Chemical shifts were expressed as δ values aganist $SiMe_4$ as internal standards. IR spectra were recorded as potassium bromide pellets on a Perkin-Elmer 1430 spectrometer, (National Research Center and the Department of chemistry Cairo University, Giza, Egypt). Mass spectra were recorded on GCMS-QP 1000 EX Shimadzu Japan (gas chromatography-mass spectrometer). Microanalytical data were obtained by the Microanalytical Center at Cairo University and National Research Center (Egypt). The starting materials are prepared according to Quiroga et al.[15] and El-Gazzar.[16]

7-Aryl-10-thioxo-5,6,10,11-tetrahydro-9H-benzo[h]pyrimido-[4,5-b]quinolin-8-one (2a–e)

General Procedure

A mixture of compound **1** (10 mmol) and 6-aminothiouracil (1.43 g, 10 mmol) was refluxed in 50 mL of dimethylformamide for 20 h (TLC analyses). The reaction mixture was cooled and the deposited precipitate was filtered off, washed with ethanol, dried, and crystallized from appropriate solvent to produce **2a–e** in a good yield. The filtrate was concentrated and left overneight at 0°C. A precipitate formed, was filtered off, and crystallized from an appropriate solvent to afford **2′a–e** in a low yield.

7-Phenyl-10-thioxo-5,6,10,11-tetrahydro-9H-benzo[h]-pyrimido[4,5-b]quinolin-8-one (2a)

The compound (**2a**) was obtained from compound **1a** (2.34, 10 mmol) as a yellow powder and crystallized from dimethylformamide (61%), m.p. 369–371°C; IR (KBr) cm^{-1}: 3370 (brs, NH), 3047 (CH aryl), 2919 (CH alkyl), 1688 (CO), 1615 (C=N). ^1H NMR (DMSO-d_6) ppm: δ 2.43–2.46 (m, 2H, CH_2), 2.72–2.88 (m, 2H, CH_2), 7.16–7.19 (m, 2H, phenyl), 7.29–7.31 (m, 1H, phenyl), 7.39–7.46 (m, 5H, phenyl + phenyl), 8.27–8.30 (m, 1H, phenyl) and 9.70, 11.20 (two NH, D_2O exchangable). Its MS, [M^+], m/z 357 (100%). Analysis: $C_{21}H_{15}N_3OS$ (357.4). Requires: C, 70.57; H, 4.23; N, 11.75. Found: C, 70.47; H, 4.21; N, 11.69.

7-(4-Chloro-phenyl)-10-thioxo-5,6,10,11-tetrahydro-9H-benzo[h]pyrimido[4,5-b]quinolin-8-one (2b)

The compound (**2b**) was obtained from compound **1b** (2.68 g, 10 mmol) as a yellow powder and crystallized from dimethylformamide (51%), m.p. > 400°C; IR (KBr) cm^{-1}: 3345 (brs, NH), 3037 (CH aryl), 2920 (CH

alkyl), 1687 (CO), 1608 (C=N). ^{1}H NMR (DMSO-d_6) ppm: δ 2.50–2.53 (m, 2H, CH_2), 2.76–2.79 (m, 2H, CH_2), 6.97–6.99 (d, 2H, p-sub-pheny), 7.09–7.12 (d, 2H, phenyl), 7.29–7.41 (m, 1H, phenyl), 7.42–7.44 (m, 2H, phenyl), 8.26–8.30 (m, 1H, phenyl) and 12.17, 12.93 (two NH, D_2O exchangable). Its MS, [M^+], m/z 391 (100%). Analysis: $C_{21}H_{14}ClN_3OS$ (391.76). Requires: C, 64.36; H, 3.60; N, 10.73. Found: C, 64.35; H, 3.57; N, 10.69.

7-(4-Bromo-phenyl)-10-thioxo-5,6,10,11-tetrahydro-9H-benzo-[h]pyrimido[4,5-b]quinolin-8-one (2c)

The compound (**2c**) was obtained from compound **1c** (3.13 g, 10 mmol) as a pale yellow powder and crystallized from dimethylformamide (53%), m.p. 397–399°C; IR (KBr) cm^{-1}: 3400 (brs, NH), 3019 (CH aryl), 2921 (CH alkyl), 1683 (CO), 1603(C=N). ^{1}H NMR (DMSO-d_6) ppm: δ 2.44–2.47 (m, 2H, CH_2), 2.78–2.80 (m, 2H, CH_2), 7.15–7.18 (d, 2H, p-sub-pheny), 7.32–7.43 (m, 1H, phenyl), 7.43–7.45 (m, 2H, phenyl), 7.61–7.63 (d, 2H, phenyl), 8.26–8.30 (m, 1H, phenyl) and 12.25, 13.00 (two NH, D_2O exchangable). Its MS, [M^+], m/z 436 (100%). Analysis: $C_{21}H_{14}BrN_3OS$ (436.3). Requires: C, 57.81; H, 3.23; N, 9.63. Found: C, 57.79; H, 3.19; N, 9.57.

7-(4-Methoxy-phenyl)-10-thioxo-5,6,10,11-tetrahydro-9H-benzo[h]pyrimido[4,5-b]quinolin-8-one (2d)

The compound (**2d**) was obtained from compound **1d** (2.64 g, 10 mmol) as a pale yellow powder and crystallized from dimethylformamide (57%), m.p. 361-363°C; IR (KBr) cm^{-1}: 3356 (brs, NH), 3021 (CH aryl), 2920 (CH alkyl), 1679 (CO), 1617 (C=N). ^{1}H NMR (DMSO-d_6) ppm: δ 2.42–2.47 (m, 2H, CH_2), 2.75–2.80 (m, 2H, CH_2), 4.15 (s, 3H, OCH_3) 7.18–7.22 (d, 2H, p-sub-pheny), 7.30–7.37 (m, 1H, phenyl), 7.44–7.47 (m, 2H, phenyl), 7.58–7.61 (d, 2H, phenyl), 8.32–8.38 (m, 1H, phenyl) and 12.10, 12.60 (two NH, D_2O exchangable). Its MS, [M^+], m/z 387 (100%). Analysis: $C_{22}H_{17}N_3O_2S$ (387.4). Requires: C, 68.20; H, 4.42; N, 10.85. Found: C, 68.18; H, 4.39; N, 10.81.

7-(2-Thienyl)-10-Thioxo-5,6,10,11-tetrahydro-9H-benzo[h]-pyrimido[4,5-b]quinolin-8-one (2e)

The compound (**2e**) was obtained from compound **1e** (2.72 g, 10 mmol) as a yellow powder and crystallized from dimethylformamide (63%), m.p. 334–336°C; IR (KBr) cm^{-1}: 3380 (brs, NH), 3038 (CH aryl), 2909 (CH alkyl), 1678 (CO), 1601 (C=N). ^{1}H NMR (DMSO-d_6) ppm: δ 2.43–

2.48 (m, 2H, CH_2), 2.68–2.79 (m, 2H, CH_2), 7.14–7.17 (t, 1H, thiophene), 7.45–7.46 (d, 1H, disub-penyl), 7.47–7.78 (d, 1H, thiophene), 7.59–7.76 (m, 2H, phenyl), 8.24–8.27 (m, 2H , 1H for thiophene = 1H for phenyl), 12.41, 13.05 (two brs, 2NH, D_2O exchangeable). Its MS, [M^+], m/z 363 (100%). Analysis: $C_{19}H_{13}N_3OS_2$ (363.4.4). Requires: C, 62.79; H, 3.60; N, 11.56. Found: C, 62.76; H, 3.56; N, 11.54.

7-(4-Chloro-phenyl)-10-methylthio-5,6,10,11-tetrahydro-9H-benzo[h]pyrimido[4,5-b]quinolin-8-one (3)

To a warmed ethanolic potassium hydroxide solution (prepared by dissolving 0.56 g, 10 mmol of potassium hydroxide in 50 mL of ethanol) compound **2b** (3.91 g, 10 mmol) was added, and heating was continued for 30 min. The mixture was allowed to cool to r.t., and methyl iodide (20 mmol) was added. The mixture was stirred under reflux for 5 h, allowed to cool to r.t., and finally poured into cold water (100 mL). The solid product precipitated was filtered off and washed with 100 mL of water. The compound was obtained as pale white crystals, crystallized from dioxane (87%), m.p. 313–315°C (melted); IR (KBr) cm^{-1}: 3403 (brs, NH), 2950 (CH alkyl), 1676 (CO), 1580 (C=N), 1500 (C=C). ^1H NMR (DMSO-d_6) ppm: δ 2.40–2.45 (m, 2H, CH_2), 2.55 (s, 3H, SCH_3), 2.65–2.70 (m, 2H, CH_2), 7.15–7.25 (d, 2H, phenyl), 7.30–7.35 (m, 1H, phenyl), 7.40–7.45 (m, 2H, phenyl), 7.45–7.55 (d, 2H, phenyl) 8.30–8.35 (m, 1H, phenyl) and 12.50 (brs, NH, D_2O exchangable). Its MS, [M^+], m/z 405 (100%). Analysis: $C_{22}H_{16}ClN_3OS$ (405.9). Requires: C, 65.10; H, 3.97; N, 10.35. Found: C, 65.08; H, 3.96; N, 10.32.

7-(4-Chlorophenyl)-10-hydrazino-5,6,10,11-tetrahydro-9H-benzo[h]pyrimido[4,5-b]quinolin-8-one (4)

Method A

A suspention of dry compound **2b** (3.91 g, 10 mmol) in hydrazine hydrate (80–90%) (25 mL) was stirred under gentle reflux. The insoluble solid dissolved within 10 min with a copious evolution of methyl mercaptan to form a clear solution. After 30 min when the solid product started separating out, heating was continued for 8 h. The reaction mixture was then allowed to cool to r.t. The solid was filtered, washed with ethanol, dried, and crystallized from dimethylformamide (81%), m.p. 307–309°C.

Method B

A suspention of compound **3** (4.05, 10 mmol) and hydrazine hydrate (99–100%, 25 mL) was stirred under reflux in dioxane (20 mL) for 12 h.

The reaction mixture was allowed to cool to r.t. and poured into cold water. The precipitate was filtered off, washed with water and ethanol, and then dried and crystallized from dioxane (72%), yield, m.p. 306–308°C; IR (KBr) cm^{-1}: 3365 (brs, NH), 2917 (CH alkyl), 1680 (CO). ^1H NMR (DMSO-d_6) ppm: δ 2.38–2.43 (m, 2H, CH_2), 2.69–2.75 (m, 2H, CH_2), 7.09–7.15 (d, 2H, phenyl), 7.20–7.30 (m, 1H, phenyl), 7.34–7.38 (m, 2H, phenyl), 7.59–7.64 (d, 2H, phenyl) 8.30–8.35 (m, 1H, phenyl) and 10.60, 11.85 (two brs, 2NH, D_2O exchangable). Its MS, [M^+], m/z 389 (100%). Analysis: $C_{21}H_{16}ClN_5O$ (389.8). Requires: C, 64.70; H, 4.14; N, 17.97. Found: C, 64.67; H, 4.09; N, 17.95.

7-(4-Chloro-phenyl)-5,6-dihydro-9H-benzo[h]-1,2,4-triazolo-[4′,3′:1,2]pyrimido[4,5-b]quinolin-8-one Derivatives (6a–f)

General Procedure

A mixture from compound **2b** (3.91 g, 10 mmol) and the appropriate hydrazonoyl chlorides **5a–f** (10 mmol) was stirred under reflux in dry chloroform (30 mL) and 4 drops of triethylamine for 5 h. The solvent was evaporated under reduced pressure. The solid produced was washed three times with 30 mL of methanol and crystallized form an appropriate solvent to produce **6a–f** in high yields.

7-(4-Chlorophenyl)-5,6-dihydro-9H-10,12-diphenyl-benzo[h]-1,2,4-triazolo[4′,3′:1,2]-pyrimido[4,5-b]quinolin-8-one (6a)

Compound (**6a**) was obtained from the reaction of compound **2b** (3.91 g, 10 mmol) and N-phenylbenzene-carbo-hydrazonoyl chloride **5a** (2.31 g, 10 mmol) as a white needles and crystallized from dimethylformamide (70%), m.p. 348–350°C; IR (KBr) cm^{-1}: 3046 (CH aryl), 2920 (CH alkyl), 1687 (CO), 1611 (C=N), 1596 (C=C). ^1H NMR (DMSO-d_6) ppm: δ 2.40–2.45 (m, 2H, CH_2), 2.75–2.85 (m, 2H, CH_2), 7.20–7.25 (d, 2H, phenyl), 7.26–7.30 (m, 1H, phenyl), 7.40–7.52 (m, 8H, phenyl protons), 7.60–7.70 (m, 4H, phenyl protons), 8.30–8.35 (d, 2H, phenyl) and 8.40 (m, 1H, phenyl). Its MS, [M^+], m/z 552 (100%). Analysis: $C_{34}H_{22}ClN_5O$ (552.0). Requires: C, 73.97; H, 4.02; N, 12.69. Found: C, 73.95; H, 4.00; N, 12.58.

10-Acetyl-7-(4-chlorophenyl)-5,6-dihydro-9H-12-(4-chlorophenyl)-benzo[h]-1,2,4-triazolo[4′,3′:1,2]pyrimido-[4,5-b]quinolin-8-one (6b)

Compound (**6b**) was obtained from the reaction of compound **2b** (3.91 g, 10 mmol) and 2-oxo-N-(4-chlorophenyl)-propane hydrazonoyl chloride **5b** (1.96 g, 10 mmol) as a brown powder and crystallized from

dimethylformamide (77%), m.p. 332–334°C; IR (KBr) cm^{-1}: 3032 (CH aryl), 2923 (CH alkyl), 1682 (CO), 1580 (C=N), 1556 (C=C). ^1H NMR (DMSO-d_6) ppm: δ 2.46–2.51 (m, 2H, CH_2), 2.62 (s, 3H, CH_3) 2.73–2.79 (m, 2H, CH_2), 6.99–7.05 (d, 2H, p-subpheny), 7.10–7.15 (d, 2H, phenyl), 7.30–7.35 (m, 1H, phenyl), 7.42–7.44 (m, 2H, phenyl), 7.65–7.68 (d, 2H, phenyl), 8.20–8.24 (d, 2H, phenyl) and 8.34–8.38 (m, 1H, phenyl). Its MS, [M^+], m/z 552 (100%). Analysis: $C_{30}H_{19}Cl_2N_5O_2$ (552.4). Requires: C, 65.22; H, 3.47; N, 12.65. Found: C, 65.18; H, 3.45; N, 12.59.

10-Acetyl-7-(4-chlorophenyl)-5,6-dihydro-9H-12-(4-methoxyphenyl)benzo[h]-1,2,4-triazolo[4′,3′:1,2]pyrimido[4,5-b]-quinolin-8-one (6c)

Compound (**6c**) was obtained from the reaction of compound **2b** (3.91 g, 10 mmol) and 2-oxo-N-(4-methoxyphenyl)-propane hydrazonoyl chloride **5c** (1.91 g, 10 mmol) as a green powder and crystallized from ethanol (68%), m.p. 273–275°C; IR (KBr) cm^{-1}: 3040 (CH aryl), 2918 (CH alkyl), 1687 (CO), 1600 (C=N), 1587 (C=C). ^1H NMR (DMSO-d_6) ppm: δ 2.45–2.55 (m, 2H, CH_2), 2.60 (s, 3H, CH_3) 2.75–2.85 (m, 2H, CH_2), 3.85 (s, 3H, OCH_3), 7.15–7.20 (d, 2H, p-subpheny), 7.20–7.25 (d, 2H, phenyl), 7.30–7.35 (m, 1H, phenyl), 7.45–7.55 (m, 2H, phenyl), 7.57–7.63 (d, 2H, phenyl), 8.00–8.05 (d, 2H, phenyl) and 8.30–8.35 (m, 1H, phenyl). Its MS, [M^+], m/z 547 (100%). Analysis: $C_{31}H_{22}ClN_5O_3$ (547.98). Requires: C, 67.94; H, 4.05; N, 12.78. Found: C, 67.91; H, 4.06; N, 12.69.

10-Acetyl-7-(4-chlorophenyl)-5,6-dihydro-9H-12-(4-nitrophenyl)benzo[h]-1,2,4-triazolo-[4′,3′:1,2]pyrimido-[4,5-b]quinolin-8-one (6d)

Compound (**6d**) was obtained from the reaction of compound **2b** (3.91 g, 10 mmol) and 2-oxo-N-(4-nitrophenyl)-propane hydrazonoyl chloride **5d** (2.06 g, 10 mmol) as a pale red crystals and crystallized from ethanol (71%), m.p. 272–274°C; IR (KBr) cm^{-1}: 3045 (CH aryl), 2913 (CH alkyl), 1680 (CO), 1598 (C=N), 1565 (C=C). ^1H NMR (DMSO-d_6) ppm: δ 2.55–2.60 (m, 2H, CH_2), 2.80–2.90 (m, 2H, CH_2) 2.95 (s, 3H, CH_3), 7.15–7.20 (d, 2H, pheny), 7.25–7.35 (m, 1H, phenyl), 7.50–7.55 (m, 2H, phenyl), 7.56–7.60 (d, 2H, phenyl), 8.35–8.50 (m, 3H, one for disub, two for phenyl) and 8.55–8.60 (d, 2H, phenyl). Its MS, [M^+], m/z 562 (100%). Analysis: $C_{30}H_{19}ClN_6O_4$ (562.9). Requires: C, 64.00; H, 3.40; N, 14.93. Found: C, 64.02; H, 3.32; N, 14.88.

7-(4-Chlorophenyl)-5,6-dihydro-9H-10-ethylcarboxylate-12-phenyl-benzo[h]-1,2,4-triazolo-[4′,3′:1,2]pyrimido[4,5-b]quinolin-8 one (6e)

Compound (**6e**) was obtained from the reaction of compound **2b** (3.91 g, 10 mmol) and chloro(phenylhydrazono)-ethylacetate **5e** (2.27 g, 10 mmol) as a white powder and crystallized from dimethylformamide (70%), m.p. 278–279°C; IR (KBr) cm^{-1}: 3039 (CH aryl), 2913 (CH aliphatic), 1689 (CO), 1588 (C=N), 1553 (C=C). ^1H NMR (DMSO-d_6) ppm: δ 1.25 (t, 3H, CH_3), 2.35–2.45 (m, 2H, CH_2), 2.65–2.80 (m, 2H, CH_2) 4.40 (q, 2H, CH_2), 7.25–7.30 (d, 2H, p-subpheny), 7.31–7.35 (m, 1H, phenyl), 7.40-7.75 (m, 7H, 5H (phenyl) + 2H (phenyl), 8.05–8.10 (d, 2H, phenyl) and 8.30–8.35 (d, 1H, phenyl). Its MS, [M^+], m/z 547 (100%). Analysis: $C_{31}H_{22}ClN_5O_3$ (547.9). Requires: C, 67.94; H, 4.05; N, 12.78. Found: C, 67.89; H, 4.07; N, 12.69.

7-(4-Chlorophenyl)-5,6-dihydro-9H-10-ethylcarboxylate-12-(4-methylphenyl)benzo[h]-1,2,4-triazolo[4′,3′:1,2]-pyrimido[4,5-b]quinolin-8-one (6f)

Compound (**6f**) was obtained from the reaction of compound **2b** (3.91 g, 10 mmol) and chloro(4-tolylhydrazono)-ethylacetate **5f** (2.41 g, 10 mmol) as a yellow powder and crystallized from ethanol/dioxane (60%), m.p. 316–319°C (dec.); IR (KBr) cm^{-1}: 3029 (CH aryl), 2923 (CH aliphatic), 1685 (CO), 1596 (C=N), 1543 (C=C). ^1H NMR (DMSO-d_6) ppm: δ 1.28 (t, 3H, CH_3), 2.35 (s, 3H, CH_3), 2.40–2.45 (m, 2H, CH_2), 2.75–2.85 (m, 2H, CH_2) 4.38 (q, 2H, CH_2), 7.25–7.35 (m, 3H, 2H p-subpheny + 1H phenyl), 7.40–7.55 (m, 4H, 2H for phenyl + 2H phenyl), 8.00–8.05 (d, 2H, phenyl) and 8.35–8.45 (m, 1H, phenyl). Its MS, [M^+], m/z 562 (100%). Analysis: $C_{32}H_{24}ClN_5O_3$ (562.0). Requires: C, 68.38; H, 4.30; N, 12.46. Found: C, 68.34; H, 4.23; N, 12.39.

7-(4-Chlorophenyl)-5,6-dihydro-9H-benzo[h]-1,2,4-zriazolo-[4′,3′:1,2]pyrimido[4,5-b]-quinolin-8-one (7a)

A mixture of compound **4** (3.89 g, 10 mmol), formic acid (10 mL), and catalytic amount of concentrated hydrochloric acid was heated under reflux for 6 h. The reaction mixture was allowed to cool to r.t. and was poured into water (100 mL). The formed solid was collected by filtration, washed with ethanol (20 mL), dried, and crystallized from dimethylformamide (75%), m.p. 382–385 °C; IR (KBr) cm^{-1}: 3350 (brs, NH), 2980 (CH alkyl), 1685 (CO), 1580 (C=N), 1500 (C=C). ^1H NMR (DMSO-d_6) ppm: δ 2.52–2.60 (m, 2H, CH_2), 2.75–2.85 (m, 2H, CH_2), 7.20–7.25 (d, 2H, phenyl),

7.27–7.33 (m, 1H, phenyl), 7.40–7.45 (m, 2H, phenyl), 7.50–7.55 (d, 2H, phenyl) 8.50–8.55 (m, 1H, phenyl), 9.50 (s, 1H, H triazole) and 12.65 (brs, 1H, NH, D_2O exchangable). Its MS, [M^+], m/z 399 (100%). Analysis: $C_{22}H_{14}ClN_5O$ (399.8). Requires: C, 66.08; H, 3.53; N, 17.52. Found: C, 66.10; H, 3.49; N, 17.43.

7-(4-Chlorophenyl)-5,6-dihydro-9H-10-methyl-benzo[h]-1,2,4-triazolo[4′,3′:1,2]pyrimido-[4,5-b]quinolin-8-one (7b)

A mixture of **4** (3.89 g, 10 mmol) and glacial acetic acid (30 mL) was stirred under reflux for 6 h (under TLC analysis). The reaction mixture was allowed to cool to r.t. and was poured into water (100 mL). The solid formed was collected by filtration, washed with ethanol (20 mL), dried, and crystallized from dimethylformamide (70%), m.p. 370°C (dec.); IR (KBr) cm^{-1}: 3316 (brs, NH), 2986 (CH alkyl), 1678 (CO), 1583 (C=N), 1507 (C=C). ^1H NMR (DMSO-d_6) ppm: δ 2.45–2.55 (m, 2H, CH_2), 2.70–2.85 (m, 2H, CH_2), 3.05 (s, 3H, CH_3), 7.15–7.20 (d, 2H, phenyl), 7.25–7.30 (m, 1H, phenyl), 7.35–7.45 (m, 2H, phenyl), 7.50–7.55 (d, 2H, phenyl) 8.20–8.25 (m, 1H, phenyl) and 12.55 (brs, 1H, NH, D_2O exchangable). Its MS, [M^+], m/z 413 (100%). Analysis: $C_{23}H_{16}ClN_5O$ (413.8). Requires: C, 66.75; H, 3.90; N, 16.92. Found: C, 66.78; H, 3.88; N, 16.87.

7-(4-Chlorophenyl)-10-acethydrazido)-5,6,10,11-tetrahydro-9H-benzo[h]pyrimido[4,5-b]-quinolin-8-one (8)

A solution of compound **4** (3.89 g, 10 mmol) in glacial acetic acid was refluxed for 3 h. The reaction mixture was then allowed to cool to r.t. and was poured into cold water (100 mL); the solid formed was collected by filtration, dried, and crystallized from ethanol (47%), m.p. 350°C (dec.): IR (KBr) cm^{-1}: 3389, 3100 (brs, 2NH), 2922 (CH alkyl), 1709 (CO), 1686 (CO), 1612 (C=N). Its MS, [M^+], m/z 431 (100%). Analysis: $C_{23}H_{18}ClN_5O_2$ (431.8). Requires: C, 63.96; H, 4.20; N, 16.22. Found: C, 63.89; H, 4.17; N, 16.14.

10-Amino-7-(4-chlorophenyl)-5,6-dihydro-9H-benzo[h]-1,2,4-triazolo[4′,3′:1,2]pyrimido-[4,5-b]quinolin-8-one (9)

A mixture of compound **4** (3.89 g, 10 mmol) and potassium thiocyanate (0.97 g, 10 mmol) was heated under reflux in acetic acid for 6 h. The reaction mixture was allowed to cool to r.t. and was poured into water. The precipitate formed was collected by filtration, dried, and crystallized from dimethylformamide to produce a white powder (67%), m.p.

402–403°C. IR spectrum (KBr) cm^{-1}: 3412 (NH) and 1678 (CO). ^1H NMR (DMSO-d_6) ppm: δ 2.43 (brs, 2H, NH_2, D_2O exchangable), 2.50–2.56 (m, 2H, CH_2), 2.73–2.88 (m, 2H, CH_2), 3.31 (brs, 1H, NH, D_2O exchangable), 7.20–7.24 (d, 2H, phenyl), 7.33–7.36 (m, 1H, phenyl), 7.46–7.49 (m, 2H, phenyl), 7.50–7.52 (d, 2H, phenyl) and 8.28–8.31 (m, 1H, phenyl). Its MS, [M^+], m/z 414 (100%). Analysis: $C_{22}H_{15}ClN_6O$ (414.8). Requires: C, 63.69; H, 3.64; N, 20.26. Found: C, 63.64; H, 3.59; N, 20.14.

7-(4-Chlorophenyl)-5,6-dihydro-9H-10-thioxo-benzo[h]-1,2,4-triazolo[4′,3′:1,2]pyrimido[4,5-b]quinolin-8-one (10)

To a warmed ethanolic sodium hydroxide solution (prepared by dissolving (0.40 g, 10 mmol) sodium hydroxide in ethanol (50 mL) (3.89 g, 10 mmol) of compound **4b** and excess carbon disulphide (10 mL) was added. The mixture was heated on a waterbath at 80°C under reflux for 10 h, then allowed to cool to r.t. poured into water (100 mL), and neutralized by dilute acetic acid; the formed precipitate was filtered off and dried. The product was crystallized from benzene (65%), m.p. 349–350°C; IR (KBr) cm^{-1}: 3465 (brs, NH), 2933 (CH alkyl), 1686 (CO), 1625 (C=N), 1530 (C=C), ^1H NMR (DMSO-d_6) ppm: δ 2.40–2.55 (m, 2H, CH_2), 2.80–3.00 (m, 2H, CH_2), 7.15–7.25 (d, 2H, phenyl), 7.30–7.40 (m, 1H, phenyl), 7.45–7.50 (m, 2H, phenyl), 7.51–7.55 (d, 2H, phenyl), 8.75–8.80 (m, 1H, phenyl) and 12.55 (brs, 1H, NH, D_2O exchangable), 13.65 (brs, 1H, NH, D_2O exchangable). Its MS, [M^+], m/z 431 (100%). Analysis: $C_{22}H_{14}ClN_5OS$ (431.8). Requires: C, 61.18; H, 3.27; N, 16.22. Found: C, 61.13; H, 3.24; N, 16.19.

10-(3-Amino-5-hydroxy-4H-pyrazol-5-one-1-yl)-7-(4-chlorophenyl)-5,6,10,11-tetrahydro-9H-benzo[h]pyrimido-[4,5-b]quinolin-8-one (11)

To a warmed ethanolic sodium ethoxide solution (prepared by dissolving (0.23 g, 10 mmol) sodium metal in absolute ethanol (30 mL)) each of compound **4b** (3.89 g, 10 mmol) and ethylcyanoacetate (1.13 g, 10 mmol) was added. The mixture was stirred under reflux for 8 h. The reaction mixture was allowed to cool to r.t. poured into cold water (100 mL), and neutralized with acetic acid. The solid product precipitated was filtered off, washed with water and ethanol, dried, and crystallized from dioxane (56%), m.p. 280–282°C (dec.); IR (KBr) cm^{-1}: 3318 (brs, NH), 2921 (CH alkyl), 1687 (CO), 1601 (C=N), 1520 (C=C). ^1H NMR (DMSO-d_6) ppm: δ 2.36–2.43 (m, 2H, CH_2), 2.67–2.75 (m, 2H, CH_2), 3.57 (s, 2H, CH_2), 7.17–7.25 (d, 2H, phenyl), 7.27–7.34 (m, 1H, phenyl), 7.43–7.50

(m, 2H, phenyl), 7.53–7.58 (d, 2H, phenyl), 8.41–8.43 (m, 1H, phenyl) and 12.20, 12.85 (2 brs, NH, D_2O exchangable). Its MS, [M^+], m/z 456 (100%). Analysis: $C_{24}H_{17}ClN_6O_2$ (456.8). Requires: C, 63.09; H, 3.75; N, 18.40. Found: C, 63.07; H, 3.71; N, 18.36.

7-(4-Chlorophenyl)-10-(ethylacetoacetatehydrazone)-5,6,10,11-tetrahydro-9H-benzo[h]pyrimido[4,5-b]quinolin-8-one (12)

A mixture of compound **4b** (3.89 g, 10 mmol) and ethylacetoacetate (1.30 g, 10 mmol) was refluxed in absolute ethanol (30 mL) for 5 h. The reaction mixture was allowed to cool to r.t. and the solid precipitate produced was filtered off and crystallized from ethanol to produce a pale brown powder (87%), m.p. 201–203°C; IR (KBr) cm^{-1}: 3250 (brs, NH), 2942 (CH alkyl), 1740, 1680 (2CO), 1580 (C=N), 1500 (C=C), ^1H NMR (DMSO-d_6) ppm: δ 1.25 (t, 3H, CH_3), 2.00 (s, 3H, CH_3), 2.35–2.45 (m, 2H, CH_2), 2.70–2.85 (m, 2H, CH_2), 3.35 (s, 2H, CH_2), 4.15 (q, 2H, CH_2), 7.15–7.25 (d, 2H, phenyl), 7.25–7.30 (m, 1H, phenyl), 7.30–7.35 (m, 2H, phenyl), 7.40–7.50 (d, 2H, phenyl), 8.20–8.30 (m, 1H, phenyl), 9.80–10.40 (brs, 1H, NH, D_2O exchangable) and 11.15 (brs, NH, D_2O exchangable). Its MS, [M^+], m/z 501 (100%). Analysis: $C_{27}H_{24}ClN_5O_3$ (501.9). Requires: C, 64.60; H, 4.82; N, 13.95. Found: C, 64.56; H, 4.79; N, 13.92.

7-(4-Chlorophenyl)-10-(3-methyl-4H-pyrazol-5-one-1-yl)-5,6,10,11-tetrahydro-9H-benzo[h]pyrimido[4,5-b]quinolin-8-one (13)

Method A

A solution of compound **4b** (3.89 g, 10 mmol) and ethylacetoacetate (1.30 g, 10 mmol) in sodium ethoxide solution (prepared by dissolving 0.23 g, 10 mmol of sodium metal in absolute ethanol (30 mL) was heated under reflux with stirring for 6 h. The reaction mixture was allowed to cool, poured into cold water (100 mL) and neutralized by acetic acid, whereby a solid was precipitated, which was filtered off and crystallized from dimethylformamide to produce a white powder (61%), m.p. 356–358°C (dec.).

Method B

A solution of compound **12** (5.02 g, 10 mmol) was heated under reflux with sodium ethoxide solution (0.23 g, 10 mmol) of sodium metal in absolute ethanol (30 mL) for 3 h. The reaction mixture was allowed to cool, poured into water (100 mL) and neutralized by acetic acid; the precipitate formed was filtered off and crystallized from dimethylformamide

(72%). IR (KBr) cm^{-1}: 3400 (brs, NH), 2936 (CH alkyl), 1698, 1684 (2CO), 1550 (C=N), 1500 (C=C), ^1H NMR (DMSO-d_6) ppm: δ 2.35–2.45 (m, 2H, CH_2), 2.50 (s, 3H, CH_3), 2.65–2.75 (m, 2H, CH_2), 3.45 (s, 2H, CH_2), (7.15–7.25 (d, 2H, phenyl), 7.25–7.30 (m, 1H, phenyl), 7.35–7.40 (m, 2H, phenyl), 7.45–7.50 (d, 2H, phenyl), 8.35–8.45 (m, 1H, phenyl) and 14.3 (brs, NH, D_2O exchangable). Its MS, [M^+], m/z 455 (100%). Analysis: $C_{25}H_{18}ClN_5O_2$ (455.8). Requires: C, 65.86; H, 3.98; N, 15.36. Found: C, 65.64; H, 3.89; N, 15.29.

7-(4-Chlorophenyl)-10-(3-methyl-4-phenylazo-pyrazol-5-one-1-yl)-5,6,10,11-tetrahydro-9H-benzo[h]pyrimido[4,5-b]-quinolin-8-one (14)

To an ice-cold solution of the appropriate aromatic amine (10 mmol) in concentrated hydrochloric acid (3 mL) was added dropwise a solution of sodium nitrite (1.03 g, 0.01 mole) dissolved in the least amount of water in an ice bath at −5°C. This previously prepared diazonium salt was added dropwise to a mixture of **13** (4.56 g, 10 mmol) and anhydrous sodium acetate in ethanol. The reaction mixture was allowed to stand over night at r.t. and then it was poured into water. The formed solid was filtered off and washed with water. The product was recrystallized from dioxane to produce a brown powder (47%), m.p. 269–270°C. IR spectrum (KBr) cm^{-1}: 3436 (OH), 3250 (NH), 2917 (CH aliphatic) and 1686 (CO). ^1H NMR (DMSO-d_6) ppm: δ 2.41 (s, 3H, CH_3), 2.49–2.54 (m, 2H, CH_2), 2.80–2.85 (m, 2H, CH_2), 7.19–7.21 (m, 1H, phenyl), 7.25–7.28 (d, 2H, phenyl), 7.30–7.36 (m, 1H, phenyl), 7.38–7.47 (m, 6H, 2H phenyl + 4H phenyl), 7.49–7.56 (d, 2H, phenyl), 8.40–8.41 (m, 1H, phenyl) and 11.20 (brs, NH, D_2O exchangable). Its MS, [M^+], m/z 560 (100%). Analysis: $C_{31}H_{22}ClN_7O_2$ (560.0). Requires: C, 66.48; H, 3.96; N, 17.51. Found: C, 66.48; H, 3.87; N, 17.46.

7-(4-Chloro-phenyl)-10-(3-methyl-4-(un)substituted-5-substituted Pyrazol-1-yl)-5,6,10,11-tetrahydro-9H-benzo[h]pyrimido[4,5-b]-quinolin-8-one (15a–c)

General Procedure

A mixture of compound **4b** (3.89 g, 10 mmol and 10 mmol) of either β-diketone in absolute ethanol (30 mL) was stirred under reflux for 5 h. The reaction mixture was allowed to cool to 0°C for 3 h, the deposited precipitate was filtered off, dried, and crystallized from the appropriate solvent to produce **15a–c** in high yields.

7-(4-Chlorophenyl)-10-(3,5-dimethyl-4H-pyrazol-1-yl)-5,6,10,11-tetrahydro-9H-benzo[h]-pyrimido[4,5-b]quinolin-8-one (15a)

Compound **4b** (3.89 g, 10 mmol) and pentan-2,4-dione (1.00 g, 10 mmol). The compound was obtained as a pale light crystals and crystallized from dimethylformamide (70%), m.p. 356–358°C; IR (KBr) cm^{-1}: 3320 (brs, NH), 3054 (CH aryl), 2943 (CH alkyl), 1693 (CO), 1600 (C=N), 1550 (C=C), ^1H NMR (DMSO-d_6) ppm: δ 2.25 (s, 3H, CH_3), 2.45–2.55 (m, 2H, CH_2), 2.65 (s, 3H, CH_3), 2.70–2.85 (m, 2H, CH_2), 6.40 (s, 1H, pyrazol proton), 7.20–7.25 (d, 2H, phenyl), 7.27–7.35 (m, 1H, phenyl), 7.45–7.50 (m, 2H, phenyl), 7.52–7.57 (d, 2H, phenyl), 8.35–8.40 (m, 1H, phenyl) and 11.90, (brs, NH, D_2O exchangable). Its MS, [M^+], m/z 453 (100%). Analysis: $C_{26}H_{20}ClN_5O$ (453.9). Requires: C, 68.79; H, 4.44; N, 15.43. Found: C, 68.76; H, 4.38; N, 15.37.

7-(4-Chlorophenyl)-10-(3,5-dimethyl-4-chloropyrazol-1-yl)-5,6,10,11-tetrahydro-9H-benzo-[h]pyrimido[4,5-b]quinolin-8-one (15b)

Compound **4b** (3.89 g, 10 mmol) and 3-chloropentan-2,4-dione (1.34 g, 10 mmol). The compound was obtained as light white crystals and crystallized from ethanol (68%), m.p. 309–312°C; IR (KBr) cm^{-1}: 3230 (brs, NH), 2953 (CH alkyl), 1685 (CO), 1609 (C=N), 1576 (C=C), ^1H NMR (DMSO-d_6) ppm: δ 2.25 (s, 3H, CH_3), 2.50–2.55 (m, 2H, CH_2), 2.65 (s, 3H, CH_3), 2.70–2.85 (m, 2H, CH_2), 7.20–7.25 (d, 2H, phenyl), 7.27–7.35 (m, 1H, phenyl), 7.40–7.45 (m, 2H, phenyl), 7.50–7.55 (d, 2H, phenyl), 8.30–8.35 (m, 1H, phenyl), and 12.10, (brs, NH, D_2O exchangable). Its MS, [M^+], m/z 488 (100%). Analysis: $C_{26}H_{19}Cl_2N_5O$ (488.3). Requires: C, 63.94; H, 3.92; N, 14.34. Found: C, 63.87; H, 3.90; N, 14.31.

7-(4-Chlorophenyl)-10-(3-methyl,4H-50trifluromethylpyrazol-1-yl) 5,6,10,11-tetrahydro-9H-benzo[h]pyrimido[4,5-b]quinolin-8-one (15c)

Compound **4b** (3.89 g, 10 mmol) and 1,1,1-trifluro-2,4-pentandione (1.54 g, 10 mmol). The compound was obtained as pale light colorless crystals and crystallized from ethanol (56%), m.p. 244–246°C; IR (KBr) cm^{-1}: 3260 (brs, NH), 2935 (CH alkyl), 1689 (CO), 1600 (C=N), 1554 (C=C),^1H NMR (DMSO-d_6) ppm: δ 2.10 (s, 3H, CH_3), 2.45–2.55 (m, 2H, CH_2), 2.75–2.85 (m, 2H, CH_2), 7.15–7.20 (d, 2H, phenyl), 7.21–7.25 (m, 1H, phenyl), 7.40–7.48 (m, 2H, phenyl), 7.50–7.55 (d, 2H, phenyl), 8.30–8.40 (m, 1H, phenyl), 8.75 (s, 1H, pyrazol proton) and 11.40 (brs, NH, D_2O

exchangable). Its MS, [M^+], m/z 507 (100%). Analysis: $C_{26}H_{17}ClF_3N_5O$ (507.8). Requires: C, 61.48; H, 3.37; N, 13.79. Found: C, 61.46; H, 3.29; N, 13.52.

7-(4-Chlorophenyl)-5,6,12-trihydro-9H-benzo[h]tetrazolo[4′,5′:1,2]pyrimido[4,5-b]quinolin-8-one (16)

To an ice-cold solution of compound **4b** (3.89 g, 10 mmol) in acetic acid (10 mL) was added dropwisely a solution of sodium nitrite (1.04 g, 15 mmol) in the least amount of water in an ice bath at −5°C. The reaction mixture was allowed to stand overnight at r.t. and then it was poured into water (100 mL). The solid precipitated was filtered off and crystallized from dixane to produced pale yellow powder (54%), m.p. 269–270°C; IR (KBr) cm^{-1}: 3243 (brs, NH), 2934 (CH alkyl), 1700 (CO), 1629 (N=N), 1582 (C=N), 1506 (C=C), ^{1}H NMR (DMSO-d_6) ppm: δ 2.45–2.50 (m, 2H, CH_2), 2.80–2.90 (m, 2H, CH_2), 7.20–7.25 (d, 2H, phenyl), 7.27–7.31 (m, 1H, phenyl), 7.40–7.60 (m, 4H, 2H phenyl + 2H phenyl), 8.25–8.35 (m, 1H, phenyl), and 13.25, (brs, NH, D_2O exchangable). Its MS, [M^+], m/z 400 (100%). Analysis: $C_{21}H_{13}ClN_6O$ (400.8). Requires: C, 62.92; H, 3.27; N, 20.97. Found: C, 62.89; H, 3.21; N, 20.78.

10-Amino-7-(4-chlorophenyl)-5,6,10,11-tetrahydro-9H-benzo[h]-pyrimido[4,5-b]quinolin-8-one (17)

To a well-stirred solution the appropriate tetrazolothienopyrimidine **16** (4.01 g, 10 mmol) in glacial acetic acid (30 mL) was added protionwise activated zinc dust (10.00 g) at r.t. over a period of 30 min. Stirring was continued for an additional 3 h. Thereafter, the reaction mixture was heated on a waterbath (80–90°C) for 3 h. The progress of reduction was monitored by TLC. After allowing the reaction mixture to cool to r.t. it was poured into cold water (100 mL). The insoluble solid that separated was filterd, washed with water, and dried. The crude solid was extracted with hot benzene and the solid obtained after the removel of benzene under reduced pressure was crystallized from dioxane (72%), m.p. 286–288°C; IR (KBr) cm^{-1}: 3310 (brs, NH_2), 2910 (CH alkyl), 1687 (CO), 1589 (C=N), 1551 (C=C), ^{1}H NMR (DMSO-d_6) ppm: δ 2.30–2.40 (m, 2H, CH_2), 2.80–2.90 (m, 2H, CH_2), 3.55–3.60 (brs, 2H, NH_2 D_2O exchangable), 4.45 (brs, NH, D_2O exchangable), 7.15–7.30 (m, 1H, phenyl), 7.35–7.40 (d, 2H, phenyl), 7.45–7.50 (m, 3H, 2H phenyl + 1H phenyl) and 7.70–7.75 (m, 1H, phenyl). Its MS, [M^+], m/z 374 (100%). Analysis: $C_{21}H_{15}ClN_4O$ (374.8). Requires: C, 67.29; H, 4.03; N, 14.95. Found: C, 67.23; H, 4.00; N, 14.86.

7-(4-Chlorophenyl)-10-(arylmethylenehydrazone)-5,6,10,11-tetrahydro-9H-benzo[h]-pyrimido[4,5-b]quinolin-8-one (18a–c)

General Procedure

A mixture from compound **4b** (3.89 g, 10 mmol), the appropriate aromatic aldehyde (10 mmol), and anhydrous sodium acetate (1.64 g, 20 mmol) was stirred under reflux in glacial acetic acid (30 mL) for 5 h. The reaction mixture was allowed to cool to r.t. and was poured into water (100 mL), whereby a solid was filtered off and crystallized from an appropriate solvent to produce **18a–c** in high yields.

7-(4-Chlorophenyl)-10-(phenylmethylenehydrazone)-5,6,10,11-tetrahydro-9H-benzo[h]-pyrimido[4,5-b]quinolin-8-one (18a)

Compound **4** (3.89 g, 10 mmol) and benzaldehyde (1.06 g, 10 mmol). The compound was obtained as yellow crystals and crystallized from dimethylformamide (63%), m.p. 337–339°C (melted); IR (KBr) cm^{-1}: 3250 (brs, NH), 3040 (CH aryl), 2920 (CH alkyl), 1670 (CO), 1600 (C=N), 1500 (C=C), ^{1}H NMR (DMSO-d_6) ppm: δ 2.35–2.50 (m, 2H, CH_2), 2.65–2.75 (m, 2H, CH_2), 7.10–7.15 (d, 2H, phenyl), 7.16–7.20 (m, 1H, phenyl), 7.35–7.50 (m, 5H, 2H phenyl + 3H phenyl), 7.90–7.95 (d, 2H, phenyl), 7.96–8.05 (s, 1H, methylenic proton) 8.35–8.40 (m, 1H, phenyl), 11.20 (brs, NH, D_2O exchangable) and 11.60 (brs, NH, D_2O exchangable). Its MS, [M^+], m/z 477 (100%). Analysis: $C_{28}H_{20}ClN_5O$ (477.9). Requires: C, 70.63; H, 4.22; N, 14.65. Found: C, 70.58; H, 4.19; N, 14.54.

7-(4-Chlorophenyl)-10-(4-chlorophenyllmethylenehydrazone)-5,6,10,11-tetrahydro-9H-benzo[h]pyrimido[4,5-b]quinolin-8-one (18b)

Compound **4** (3.89 g, 10 mmol) and 4-chlorobenzaldehyde (1.40 g, 10 mmol). The compound was obtained as pale yellow crystals and crystallized from dimethylformamide (67%) yield, m.p. 349–351°C; IR (KBr) cm^{-1}: 3368 (brs, NH), 3044 (CH aryl), 2916 (CH alkyl), 1676 (CO), 1605 (C=N), 1517 (C=C), ^{1}H NMR (DMSO-d_6) ppm: δ 2.40–2.50 (m, 2H, CH_2), 2.75–2.85 (m, 2H, CH_2), 7.20–7.25 (d, 2H, phenyl), 7.26–7.30 (m, 1H, phenyl), 7.40–7.45 (m, 2H, phenyl), 7.46–7.53 (2d, 4H, phenyl), 7.95–8.05 (d, 2H, phenyl) 8.10–8.15 (s, 1H, methylenic proton), 8.30–8.40 (m, 1H, phenyl) and 11.35 (brs, NH, D_2O exchangable). Analysis: $C_{28}H_{19}ClN_5O$ (512.3). Requires: C, 65.63; H, 3.74; N, 13.67. Found: C, 65.56; H, 3.67; N, 13.53.

7-(4-Chlorophenyl)-10-(4-methoxyphenylmethyl-enehydrazone)-5,6,10,11-tetrahydro-9H-benzo [h]pyrimido[4,5-b]quinolin-8-one (18c)

Compound **4** (3.89 g, 10 mmol) and 4-methoxybenzaldehyde (1.36 g, 10 mmol). The compound was obtained as yellow powder and crystallized from dimethylformamide (72%), m.p. 329–330°C; IR (KBr) cm^{-1}: 3368 (brs, NH), 3044 (CH aryl), 2916 (CH alkyl), 1676 (CO), 1605 (C=N), 1517 (C=C), ^1H NMR (DMSO-d_6) ppm: δ 2.45–2.50 (m, 2H, CH_2), 2.75–2.85 (m, 2H, CH_2), 3.85 (s, 3H, OCH_3), 6.95–7.05 (d, 2H, phenyl), 7.20–7.25 (d, 2H, phenyl), 7.26–7.30 (m, 1H, phenyl), 7.40–7.45 (m, 2H, phenyl), 7.47–7.50 (d, 2H, phenyl), 7.85–7.95 (d, 2H, phenyl) 8.05–8.11 (s, 1H, methylenic proton), 8.30–8.40 (m, 1H, phenyl) and 11.20 (brs, NH, D_2O exchangable). Its MS, [M^+], m/z 507 (100%). Analysis: $C_{29}H_{22}ClN_5O_2$ (507.9). Requires: C, 68.57; H, 4.36; N, 13.79. Found: C, 68.53; H, 4.35; N, 13.69.

10-Aryl-7-(4-chloro-phenyl)-5,6-dihydro-9H-benzo[h]-1,2,4-triazolo[4′,3′:1,2]pyrimido[4,5-b]quinolin-8-one (19a-c)

General Procedure

A mixture of compound (**18a–c**) (10 mmol), anhydrous sodium acetate (1.64 g, 20 mmol), and bromine (1.60 g, 10 mmol) was heated gently in glacial acetic acid (30 mL) in a wasterbath at 80°C for a long time (under TLC control). The reaction mixture was allowed to cool to r.t. and was poured into water (100 mL) and the solid formed was collected by filtration and crystallized from an appropriate solvent to produce **19a–c**.

7-(4-Chloro-phenyl)-5,6-dihydro-9H-10-phenyl-benzo[h]-1,2,4-Triazolo[4′,3′:1,2]pyrimido-[4,5-b]quinolin-8-one (19a)

Compound (**19a**) was obtained from the reaction of compound **18a** (4.78 g, 10 mmol) as a dark yellow powder and crystallized from dimethylformamide (62%), m.p. 328–330°C (dec.); IR (KBr) cm^{-1}: 3290 (brs, NH), 3039 (CH aryl), 2919 (CH alkyl), 1693 (CO), 1563 (C=N), 1506 (C=C). ^1H NMR (DMSO-d_6) ppm: δ 2.37–2.50 (m, 2H, CH_2), 2.68–2.76 (m, 2H, CH_2), 7.09–7.15 (d, 2H, phenyl), 7.18–7.22 (m, 1H, phenyl), 7.34–7.47 (m, 5H, 2H phenyl + 3H phenyl), 7.96–8.06 (d, 2H, phenyl), 8.33–8.40 (m, 1H, phenyl) and 11.16 (brs, NH, D_2O exchangable). Its MS, [M^+], m/z 475 (100%). Analysis: $C_{28}H_{18}ClN_5O$ (475.9). Requires: C, 70.66; H, 3.81; N, 14.72. Found: C, 70.56; H, 3.73; N, 14.53.

7,10-Di(4-chlorophenyl)-5,6-dihydro-9H-10-benzo[h]-1,2,4-Triazolo[4′,3′:1,2]pyrimido-[4,5-b]quinolin-8-one (19b)

Compound (**19b**) was obtained from the reaction of compound **18b** (5.12 g, 10 mmol) as brown crystals and crystallized from dimethylformamide (61%), m.p. 359°C (dec.); IR (KBr) cm^{-1}: 3287 (brs, NH), 3052 (CH aryl), 2920 (CH alkyl), 1693 (CO), 1606 (C=N), 1559 (C=C), ^1H NMR (DMSO-d_6) ppm: δ 2.43–2.50 (m, 2H, CH_2), 2.75–2.83 (m, 2H, CH_2), 7.15–7.20 (d, 2H, phenyl), 7.25–7.30 (m, 1H, phenyl), 7.35–7.45 (m, 2H, phenyl), 7.45–7.55 (2d, 4H, phenyl), 7.98–8.15 (d, 2H, phenyl), 8.29–8.38 (m, 1H, phenyl) and 11.65 (brs, NH, D_2O exchangable). Its MS, [M^+], m/z 330 (100%). Analysis: $C_{28}H_{17}Cl_2N_5O$ (330.8). Requires: C, 65.89; H, 3.36; N, 13.72. Found: C, 65.81; H, 3.29; N, 13.59.

7-(4-Chlorophenyl)-5,6-dihydro-9H-10-(4-methoxyphenyl)-benzo[h]-1,2,4-triazolo-[4′,3′:1,2]pyrimido[4,5-b]quinolin-8-one (19c)

Compound (**19c**) was obtained from the reaction of compound **18c** (5.08 g, 10 mmol) as light yellow powder and crystallized from dimethylformamide (65%), m.p. 343–346°C; IR (KBr) cm^{-1}: 3290 (brs, NH), 3053 (CH aryl), 2918 (CH alkyl), 1689 (CO), 1549 (C=N), 1499 (C=C). ^1H NMR (DMSO-d_6) ppm: δ 2.40–2.50 (m, 2H, CH_2), 2.75–2.80 (m, 2H, CH_2), 3.89 (s, 3H, OCH_3), 6.97–7.08 (d, 2H, phenyl), 7.17–7.25 (d, 2H, phenyl), 7.25–7.30 (m, 1H, phenyl), 7.37–7.46 (m, 2H, phenyl), 7.50–7.55 (d, 2H, phenyl), 7.85–8.00 (d, 2H, phenyl), 8.34–8.40 (m, 1H, phenyl) and 11.42 (brs, NH, D_2O exchangable). ^{13}C NMR (DMSO-d_6) ppm: δ 24.42, 26.44 ($2CH_2$, SP^3), 56.83 (OCH_3 SP^3), 109.6, 110.5, 112.2, 122.2, 126.2, 126.8, 128.1, 128.3, 129.4, 130.1, 130.6, 131.0, 131.5, 132.1, 132.3, 134.7, 136.3, 139.3, 144.9, 151.2, 154.0, 157.0 (SP^2) 159.0 (CO). Its MS, [M^+], m/z 505 (100%). Analysis: $C_{29}H_{20}ClN_5O_2$ (505.94). Requires: C, 68.84; H, 3.98; N, 13.84. Found: C, 68.79; H, 3.94; N, 13.68.

7-(4-Chlorophenyl)-5,6-dihydro-9H-11-(methyl or phenyl)-benzo[h]-1,2,4-triazino-[4′,3′:1,2]pyrimido[4,5-b]quinolin-8-one (20a,b)

General Procedure

A mixture of compound **4b** (3.89 g, 10 mmol) with chloroacetone or phenacylbromide (10 mmol) was heated under reflux 5 h in 30 mL of dry xylene. The solid precipitated that separated upon cooling was filtered off and crystallized from an appropriate solvent to produce **20a,b** in high yields.

7-(4-Chlorophenyl)-5,6-dihydro-9H-11-methyl-benzo[h]-1,2,4-triazino[4′,3′:1,2]pyrimido[4,5-b]quinolin-8-one (20a)

Compound **4b** (3.89 g, 10 mmol) and chloroacetone (0.93 g, 10 mmol). The compound was obtained as pale white crystals and crystallized from benzene (67%), m.p. 377–379°C; IR (KBr) cm^{-1}: 3420 (brs, NH), 2950 (CH alkyl), 1687 (CO), 1600 (C=N), 1543 (C=C); ^1H NMR (DMSO-d_6) ppm: δ 2.05 (s, 3H, CH_3), 2.50–2.55 (m, 2H, CH_2), 2.70–2.85 (m, 2H, CH_2), 4.80 (s, 2H, CH_2), 7.20–7.30 (d, 2H, phenyl), 7.35–7.40 (m, 1H, phenyl), 7.45–7.55 (m, 4H, 2H phenyl + 2H phenyl), 8.25–8.40 (m, 1H, phenyl) and 11.05 (brs, NH, D_2O exchangable). Its MS, [M^+], m/z 427 (100%). Analysis: $C_{24}H_{18}ClN_5O$ (427.8). Requires: C, 67.37; H, 4.24; N, 16.37. Found: C, 67.33; H, 4.27; N, 16.29.

7-(4-Chlorophenyl)-5,6-dihydro-9H-11-phenyl-benzo[h]-1,2,4-triazino[4′,3′:1,2]pyrimido[4,5-b]quinolin-8-one (20b)

Compound **4b** (3.89 g, 10 mmol) and phenacylbromide (1.99 g, 10 mmol). The compound was obtained as a yellow powder and crystallized from dimethylformamide (59%), m.p. 334–337°C; IR (KBr) cm^{-1}: 3279 (brs, NH), 3039 (CH aryl), 2916 (CH alkyl), 1686 (CO), 1647 (C=N), 1600 (C=C), ^1H NMR (DMSO-d_6+TFA (1:1)) ppm: δ 2.55–2.60 (m, 2H, CH_2), 2.80–2.90 (m, 2H, CH_2), 5.45 (s, 2H, CH_2 for triazine), 7.20–7.25 (d, 2H, phenyl), 7.35–7.40 (m, 1H, phenyl), 7.45–7.65 (m, 7H, 2H phenyl + 5H phenyl), 7.95–8.05 (m, 1H, phenyl) and 9.05 (brs, NH). Its MS, [M^+], m/z 489 (100%). Analysis: $C_{29}H_{20}ClN_5O$ (489.9). Requires: C, 71.09; H, 4.11; N, 14.29. Found: C, 71.12; H, 4.07; N, 14.23.

CONCLUSION

The prepared new ring systems seem to be interesting for biological activity studies. Furthermore, the present investigation offers rapid and effective new procedures for the synthesis of the polycondensed new heterocyclic ring systems.

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