Open Journal of Synthesis Theory and Applications, **2012, 1, 44-57**
http://dx.doi.org/10.4236/ojsta.2012.13008 Published Online October 2012 (http://www.SciRP.org/journal/ojsta)

A Simple and Convenient Synthesis of Isolated-Fused Heterocycles Based on: 2-Imino-*N*-phenyl-2*H*-chromene-3-carboxamide

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Received June 23, 2012; revised July 26, 2012; accepted August 29, 2012

ABSTRACT

Starting from 2-imino-*N*-phenyl-2*H*-chromene-3-carbox-amide, (**1**) a series of functionalized chromenes were achieved; such as, 2-ethoxy-2,3-dihydro-3-phenylchromeno[2,3-*d*]pyrimidin-4-one (**2**), and 2-hydrazinyl-2,3-dihydro-3-phenyl-chromeno-[2,3-*d*]pyrimidin-4-one (**3**). Furthermore, reactions of (**3**) with some of laboratory available compounds gave pyrazoles (**4 - 9, 12, 13a, 13b**), tetrazoles (**11**), 2-(2-benzylidenehydrazinyl)-3-phenyl-3*H*-chromeno[2,3-*d*]pyrimidin-4(10*H*)-oneisoxazoles (**14**), 5-chloro-1-(4-oxo-3-phenyl-4,10-dihydro-3*H*-chromeno[2,3-*d*]pyrimidin-2-yl)-3-phenyl-2, 3-dihydro-1*H*-pyrazole-4-carbonitrile (**17**), pyrimidines (**28a, b**), pyridines (**29a - 29e, 30, 33a, 33b**), benzo[*b*][1, 4]oxazepin-2- amines (**32a, b**), 3-chloro-4-(2-imino-2H-chromen-3-yl)-1-phenyl-4-(phenylamino) azetidin-2-one (**34a-34e**) and 2-(2- imino-2*H*-chromen-3-yl)-3-phenyl-2-(phenyl amino)thiazolidin-4-onee (**35a -35e**). The structures of these compounds were established by elemental analysis, IR, MS and NMR spectral analysis.

Keywords: 2-Imino-2*H*-chromen-3-yl; Chromeno[2,3-*d*]pyrimidin-4-one; *β*-Lactam; Thiazolidin-4-ones

1. Introduction

Natural and synthetic coumarin derivatives represent, nowadays, an important group of organic compounds that are used as antibiotics [1,2] fungicides [3] anti-inflammatory [4], anticoagulant [5] and antitumor agents [6,7]. Regarding their high fluorescence ability, they are widely used as optical whitening agents, brighteners, laser dyes and also as fluorescent probes [8] in biology and medicine [9]. Also, The 4 *H*-chromene derivatives ethyl 4-((ethoxycarbonyl) (cyano) methyl)-2-amino-6-bromo-4*H*-chromene-3-carboxylate (HA 14-1) has demonstrated promising antifungal activities [10], antiviral agent [11], antiproliferation agent [12]. Due to the unique biological and pharmacological activity, chromene derivatives have attracted considerable attention thus; different processes for the synthesis of chromenes have been reported during the past few years. The importance of the chromone nucleus is evidenced by the continued appearance of new and improved methods for their synthesis, despite the several existing methods for the synthesis of chromene derivatives [13-20], there still is demand for general synthetic strategies which can efficiently provide variously substituted chromene systems.

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2. Experimental

2.1. Instruments

All melting points are measured using Galenkanp melting point apparatus and are uncorrected. Elemental analyses were carried out at the Microanalytical Center of Cairo University. IR (KBr pellets υ = cm^{-1}) spectra were determined in 1650 FT-IR instrument (Cairo University), 1H-NMR spectra (δ = ppm) were accomplished using 300 MHz NMR Spectrometer and mass spectroscopy were recorded on GCMS-QP-1000 EX spectrometer (Cairo University).

2.2. Material and Reagents

Hydrazine hydrate, phenyhydrazine, benzaldehyde and its substituted derivatives, aniline and its substituted derivatives, thioglycolic acid, acetylacetone, phosoryl chloride, ethyl acetoacetate and chloroacetyl chloride were purchased from Alderich Chemical Co.

Triethylamine, thiourea, urea, o-phenylenediamine, o-aminothiophenol and 2-cyanomethy benzimidazole were purchased from British Drug Houses (BDH).

Acetophenone, malononitrile, 2-chloro acetamide, piperidine, ethoxymethylene-malononitrile, sodium azide and

5-amino-(1H)-1,2,4-triazole were purchased from Merck Co., Germany.

2.3. Solvents

Dimethyformamide, benzene, pyridine, ethanol and acetone were purchased from El-Nasr Pharmaceutical and Chemical Co. (ADWIC), Egypt.

2.4. Organic Preparations

Preparation of 2-ethoxy-2, 3-dihydro-3-phenylchromeno[2,3-*d*]pyrimidin-4-one (2). A mixture of **1** (2.64 g, 0.01 mol) and triethoxymethane (1.48 mL, 0.05 mol) in 20 mL of dimethylformamide was refluxed 8 h. Then the reaction mixture was poured into 150 mL of crushed ice then the resultant solid was collected by filtration to provide **2** (1.5 g, 60%) as a pale yellow solid; m.p. 285˚C - 287˚C. ^{1}HNMR ($CDCl_3$): δ 1.2 (*t*, 3H, CH_3), 3.9 (*q*, 2H, CH_2) and 6.7 - 7.9 (*m*, 11H, Ar-H). MS: *m/z* 320 ($[M]^+$, 65%). *Calcd* for $C_{19}H_{16}N_2O_3$ (320.34). *Calcd*: C 71.24, H 5.03, N 8.74 %. *Found*: C 70.14, H 5.01, N 7.88%.

Preparation of 2-hydrazinyl-2, 3-dihydro-3-phenyl chromeno[2,3-*d*]pyrim-idin-4-one (3). A mixture of 2 (3.20 g, 0.01 mol) and hydrazine hydrate (0.5 mL, 0.01 mol) in 30 mL ethanol containing 0.1 mL piperidine was refluxed for 8 hr. The reaction mixture was concentrated under reduced pressure and the residue washed with acidified cold water and then triturated with methanol. The formed pale yellow product was filtered, washed well with methanol. Yield 66%, m.p. 250˚C - 252˚C. IR: 1670 (C=O), 3282 (NH) and 3432 (NH_2). ^{1}H NMR (DMSO): 4.82 (*s*, br, 2H, NH_2, D_2O, exchangeable), 5.1 (*s*, 1H, CH- methine), 6.7 - 7.9 (*m*, 11H, Ar-H) and 8.85 (*s*, br, 1H, NH, D_2O, exchangeable). MS: *m/z* 309($[M+3]^+$, 45%). *Calcd* for $C_{17}H_{14}N_4O_2$ (306.32): C 66.66, H 4.61, N 18.29%. *Found*: C 66.01, H 3.20, N 17.66 %.

Preparation of 3-amino-3-(3-amino-5-oxo-1-(4-oxo-3-phenyl-3,4-dihydro-2*H*-chromeno[2,3-*d*]pyrimidin-2-yl)-1*H*-pyrazol-4(5*H*)-ylidene)propanenitrile (5), and its derivatives, (7 - 10, 12, 13a, b).

General procedure: To a solution of hydrazide **3** (3.06 g, 0.01 mol) and ethyl 3-amino-2,4-dicyanobut-2-enoate (1.79 mL, 0.01 mol) in 30 mL ethanol containing 0.1 mL piperidine was refluxed for 6 h. then allowed to cool. The formed solid was filtered off, washed with methanol to afford the pyrazoile derivative **5**. Analogously, diethyl malonate (1.60 mL, 0.01mol), ethyl 2-cyanoacetate (1.13 mL), ethyl 3-oxobutanoate (1.30 mL), pentane-2,4-dione (1.00 mL), 2-(ethoxymethylene) malononitrile (1.22 gm) and 2-cyano-*N*-phenylacetamide (1.60 gm) were reacted with compound **3** to yield **(7 - 10, 12, 13a, b),** respectively.

3-Amino-3-(3-amino-5-oxo-1-(4-oxo-3-phenyl-3,4-dihdro-2*H*-chromeno-[2,3-*d*]pyrimidin-2-yl)-1*H*-pyrazol-4(5*H*)-ylidene)propanenitrile (5). Yellow crystals (MeOH), yield 70%, m.p. 250˚C - 252˚C. IR: 1699 (CO), 2219 (CN), 3422 (NH_2). ^{1}H NMR (DMSO): 2.9 (*s*, 2H, CH_2), 3.5 (*s*, 2H, NH_2), 3.7 (*s*, 2H, NH_2), 6.7 - 7.9 (*m*, 10H, Ar-H). MS: *m/z* 439 ($[M^+]$, 60%). *Calcd* for $C_{23}H_{17}N_7O_3$ (439.43). C 62.87, H 3.90, N 22.31%. *Found*: C 61.01, H 3.20, N 21.89%.

1-(3,4-dihydro-4-oxo-3-phenyl-2*H*-chromeno[2,3-*d*]-pyrimidin-2-yl)pyrazo-lidine-3,5-dione, (7). Pale yellow crystals (MeOH), yield 66%. m.p. 280˚C -282˚C. IR: υ (cm^{-1}) 1685 - 1705 (C=O), 3212 (NH), ^{1}HNMR ($CDCl_3$): δ 3.2 (*s*, 2H, CH_2), 5.8 (*s*, 1H, CH-methine), 8.1 (*s*, 1H, NH of pyrazole ring) and 6.1 - 7.8 (*m*, 10H, Ar-H). MS: *m/z* 374 ($[M]^+$, 55%). *Calcd* for $C_{20}H_{14}N_4O_4$ (374.35). *Calcd*: C 64.17, H 3.77, N 14.97%. *Found*: C 63.33, H 2.91, N 14.15%.

Compound 5. Yield 70%, m.p. 257˚C - 259˚C. IR: 1699 (CO), 2219 (CN), 3422 (NH_2). ^{1}H NMR (DMSO): 2.9 (*s*, 2H, CH_2), 3.5 (*s*, 2H, NH_2), 3.7 (*s*, 2H, NH_2), 6.7 - 7.9 (*m*, 10H, Ar-H). MS: *m/z* 439 ($[M^+]$, 60%). *Calcd* for $C_{23}H_{17}N_7O_3$ (439.43). C 62.87, H 3.90, N 22.31 %. *Found*: C 61.01, H 3.20, N 21.89%.

Compound 8. Pale green crystals (Ethanol), yield 50%, m.p. 250˚C - 252˚C, IR: υ (cm^{-1}) 1685-1705(C=O), 3432 (NH_2), MS: *m/z* 373 ($[M]^+$,65%). *Calcd* for $C_{20}H_{15}N_5O_3$ (373.36). *Calcd*: C 64.34, H 4.05, N 18.76%. *Found*: C 63.33, H 3.91, N 17.15%.

Compound 9. Brown crystals (Ethanol), yield 55%, m.p. 190˚C - 192˚C. IR: υ (cm^{-1}) 1685-1705 (C=O), ^{1}HNMR ($CDCl_3$): δ 1.1 (*s*, 3H, CH_3), 2.5 (*s*, 2H, CH_2), 5.8 (*s*, 1H, CH-methine), 6.7 - 7.9 (*m*, 10H, Ar-H). MS: *m/z* 370 ($[M-2]^+$, 60%). *Calcd* for $C_{23}H_{16}N_4O_3$ (372.38). *Calcd*: C 67.73, H 4.33, N 15.05%. *Found*: C 67.17, H 3.31, N 14.15%.

Compound 10. Pale green crystals (Ethanol), yield 59 %, m.p. 270˚C-2˚C. IR: υ (cm^{-1}) 1685 - 1705(C=O), MS: *m/z* 369 ($[M-1]^+$, 66%). *Calcd* for $C_{22}H_{18}N_4O_2$ (370.4). *Calcd*: C 71.34, H 4.90, N 15.13%. *Found*: C 70.17, H 3.31, N 14.15%.

Preparation of 1-phenyl-tetrazolo[4',5':2,3] pyimido[4,5-*b*]chromen-12-one, (11).

To a stirred cold solution of **3** (0.306 g, 0.001 mol) in 30 mL of glacial acetic acid, a cold solution of sodium nitrite (0.7 g, 0.01 mol) in 10 mL of H_2O was added drop wise stirring at 5˚C. The mixture was stirred for further four hours at room temperature. The solid that precipitated was collected by filtration, washed with water and air dried to afford 55% yield of the tetrazolo derivative **11**. Yield 55%, m.p. 250˚C - 252˚C. IR: 1699 (CO). MS: *m/z* 317 ($[M^+]$, 60%). *Calcd* for $C_{17}H_{11}N_5O_2$ (317.3). C 64.35, H 3.49, N 22.07%. *Found*: C 63.01, H 2.20, N 21.89%.

Compound 12. Yellow crystals (Ethanol), yield 55%, m.p. 259˚C - 261˚C. IR: υ (cm^{-1}) 1685 - 1705(C=O), 2219 (CN), 3212 - 3423 (NH_2), MS: *m/z* 382 ($[M + 1]^+$, 50%). *Calcd* for $C_{21}H_{14}N_6O_2$ (382.37). *Calcd*: C 65.96, H 3.69, N

21.98%. *Found*: C 64.17, H 2.31, N 20.15%.

Compound 13a. Yellow crystals (Ethanol), yield 62%, m.p. 150˚C - 152˚C. IR: υ (cm^{-1}) 1685 - 1705(C=O), 3212 - 3432 (NH_2), ^{1}HNMR ($CDCl_3$): δ 4.1 (*s*, 2H, NH_2), 4.3 (*s*, 1H, NHPh), 6.2 (*s*, 1H, = CH-), 6.7 - 7.9 (*m*, 10H, Ar-H). MS: *m/z* 448([M]$^+$,40%). *Calcd* for $C_{26}H_{20}N_6O_2$ (448.48). *Calcd*: C 69.63, H 4.49, N 18.74%. *Found*: C 68.17, H 3.31, N 17.15%.

Compound 13b. Pale yellow crystals (MeOH), yield 50%, m.p. 180˚C - 182˚C. IR: υ (cm^{-1}) 1685 - 1705(C=O), 3212 - 3432 (NH_2), MS: *m/z* 456 ([M + 1]$^+$, 35%). *Calcd* for $C_{23}H_{17}N_7O_2S$ (455.49). *Calcd*: C 60.65, H 3.76, N 71.53, S 7.04%. *Found*: C 59.17, H 2.66, N 70.26, S 6.54%.

Preparation of 2-(2-benzylidenehydrazinyl)-3-phenyl-3*H*-chromeno[2,3-*d*]pyri-midin-4(10*H*)-one, (14). A mixture of the 2-hydrazinyl-3-phenyl-2*H*-chromeno [2,3-*d*]pyrimidin-4(3*H*)-one **3** (3.06 g, 0.01 mol) and benzaldehyde (1.06, 0.01 mol) in 20 mL ethanol containing 0.1 mL of piperidine was refluxed for 8 hr. The reaction mixture was concentrated, cooled then poured into ice/H_2O mixture the solid product thus so formed was filtered, washed for several times with water to afford **14** (1.66 g, 61%) as a brown solid; m.p. 225˚C - 227˚C. IR: υ (cm^{-1}) 1705 (C=O), 3322 (NH). ^{1}HNMR ($CDCl_3$): δ 6.7 - 7.9 (*m*, 14H, Ar-H), 8.11 (*s*, 1H, CH=) and 10.11 (*s*, 1H, NH). MS: *m/z* 397 ([M]$^+$, 65%). *Calcd* for $C_{24}H_{18}N_4O_2$ (394.43). *Calcd*: C 73.08, H 4.60, N 14.20 %. *Found*: C 72.14, H 4.01, N 13.88%.

Preparation of 5-oxo-1-(4-oxo-3-phenyl-4, 10-dihydro-3*H*-chromeno[2,3-*d*]pyrimidin-2-yl)-3-phenylpyrazolidine-4-carbonitrile, (16). A solution of benzylidenehydrazinyl **14** (3.94 g, 0.01 mol) and ethyl 2-cyanoacetate (1.13 mL) in 30 mL ethanol containing 0.1 mL piperidine was refluxed for 6 h. then allowed to cool. The formed solid was filtered off, washed with methanol to afford the pyrazole derivative **16** (2.45 g, 61%) as a brown solid; m.p. 295˚C - 297˚C. IR: υ (cm^{-1}) 1670 (C=O), 2217 (CN), 3432 (NH). ^{1}HNMR ($CDCl_3$): δ 3.98 (*s*, 1H, NH), 4.12 (*s*, 1H, C-3 pyrazole), 4.21 (*s*, 1H, C-4 pyrazole) and 6.7 - 7.9 (*m*, 14H, Ar-H). MS: *m/z* 462 ([M + 1]$^+$, 55%). *Calcd* for $C_{27}H_{19}N_5O_3$ (461.47). *Calcd*: C 70.27, H 4.15, N 15.18 %. *Found*: C 69.12, H 4.01, N 14.11%.

Preparation of 5-chloro-1-(4-oxo-3-phenyl-4,10-dihydro-3*H*-chromeno[2,3-*d*]pyrimidin-2-yl)-3-phenyl-2, 3-dihydro-1*H*-pyrazole-4-carbonitrile, (17). A suspension of 1.0 g of **16** in 10 ml of phosphoryl chloride was heated at 90˚C for 5 hr and, after cooling, crushed ice was added. The solution was then made basic with concentrated ammonium hydroxide (pH = 8) and the solid that precipitated was collected by filtration, washed with water and purified by crystallization to give **17** as a Yellow solid; m.p. 189˚C - 191˚C. IR: υ (cm^{-1}) 1700 (C=O), 2217 (CN), 3425 (NH). ^{1}HNMR ($CDCl_3$): δ 3.98 (*s*, 1H, NH), 4.61 (*s*, 1H, C-3 pyrazole) and 6.7 - 7.9 (*m*, 14H, Ar-H). MS: *m/z* 478 ([M-1]$^+$, 16%). *Calcd* for $C_{27}H_{18}N_5O_2Cl$ (479.92). *Calcd*: C 67.57, H 3.78, N 14.59%. *Found*: C 66.12, H 3.21, N 14.51%.

Preparation of 2-(4-amino-3-phenyl-2, 3-dihydro-1*H*-pyrazolo[4,3-*e*][1, 2, 4]-triazolo[1,5-*a*] pyrimidin-1-yl)-3-phenyl-3*H*-chromeno[2,3-*d*]pyrimidin-4(10*H*)-one, (18). Amixtuer of **17** (4.79 g, 0.01 mol) and 5-amino-1,2,4-1*H*-triazole (0.84 g) in 30 mL ethanol containing 0.1 mL piperidine was refluxed for 3 hr. then allowed to cool. The formed brownish solid was filtered off, washed with methanol to afford the pyrazoile derivative **18** (2.4 g, 50%) as a brownish solid; m.p. 156˚C - 158˚C. IR: υ (cm^{-1}) 1670 (C=O), 3432 (NH). ^{1}HNMR (DMSO): δ 3.98 (*s*, br, 1H, NH), 5.21 (*s*, 1H, C-3 pyrazole), 6.13 (*s*, br, 2H, NH_2) and 6.7 - 7.9 (*m*, 14H, Ar-H) and 8.71 (*s*, 1H, methine proton of triazole ring). MS: *m/z* 527 ([M]$^+$, 25%). *Calcd* for $C_{29}H_{21}N_9O_2$ (527.54). *Calcd*: C 66.03, H 4.01, N 23.90 %. *Found*: C 65.31, H 3.22, N 22.84%.

Preparation of 4-amino-7-(methylthio)-1-(4-oxo-3-phenyl-4,10-dihydro-3*H*-chromeno[2,3-*d*]pyrimidin-2-yl)-3-phenyl-2,3-dihydro-1*H*-dipyrazolo [1,5-a:4',3'-*e*] pyrimidine-6-carbonitrile, (19). Amixtuer of **17** (4.79 g, 0.01 mol) and 5-amino-3-(methylthio)-1*H*-pyrazole-4- carbonitrile (1.54 g, 0.01 mol) in 30 mL ethanol containing 0.1 mL piperidine was refluxed for 5 h. then allowed to cool. The formed pale yellow solid was filtered off, washed with methanol to afford the pyrazoile derivative **19** (2.4 g, 50%) as a pale yellow solid (MeOH); m.p. 240˚C - 242˚C. IR: υ (cm^{-1}) 1670 (C=O), 2221 (CN), 3432 (NH). ^{1}HNMR (DMSO): δ 3.54 (*s*, 3H, SCH_3), 3.98 (*s*, br, 1H, NH), 5.21 (*s*, 1H, C-3 pyrazole), 6.13 (*s*, br, 2H, NH_2) and 6.7 - 7.9 (*m*, 14H, Ar-H) and 8.71 (*s*, 1H, methine proton of triazole ring). MS: *m/z* 597 ([M]$^+$, 35 %). *Calcd* for $C_{32}H_{23}N_9O_2S$ (597.65). *Calcd*: C 64.31, H 3.88, N 21.09 %. *Found*: C 63.56, H 2.52, N 20.78%.

Preparation 5-methoxy-1-(4-oxo-3-phenyl-4, 10-dihydro-3*H*-chromeno[2,3-*d*]py-rimidin-2-yl)-3-phenyl-2,3-dihydro-1*H*-pyrazole-4-carbonitrile, (20). A solution of 10 mmol of freshly prepared sodium methoxide and 1.0 mmol of the chloro derivatives **17** in 10 ml of anhydrous methanol was refluxed for 4 hr then the reaction mixture was evaporated to dryness in vacuo. The crude residue was treated with water and neutralized with 10% hydrochloric acid, and the solid precipitate, collected by filtration, was purified by crystallization to obtain **20** as yellow crystals (DMSO-HCl); yield 30%. m.p. 288˚C - 290˚C. IR: υ (cm^{-1}) 1699 (C=O), 2219 (CN), 3422 (NH). ^{1}HNMR (DMSO): δ 3.82 (*s*, 3H, OCH_3), 3.98 (*s*, br, 1H, NH), 4.61 (*s*, 1H, C-3 pyrazole) and 6.7 - 7.9 (*m*, 14H, Ar-H). MS: *m/z* 475 ([M]$^+$, 62%). *Calcd* for $C_{28}H_{23}N_9O_2S$ (597.65). *Calcd*: C 64.31, H 3.88, N 21.09 %. *Found*: C 63.56, H 2.52, N 20.78%.

Preparation 5-azido-1-(4-oxo-3-phenyl-4, 10-dihy-

dro-3*H*-chromeno[2,3-*d*]pyri-midin-2-yl)-3-phenyl-2,3-dihydro-1*H*-pyrazole-4-carbonitrile, (21). A solution of the chloro compound **17** (1.437 g, 3 mmol) in acetone (5 mL) was stirred and ice-cooled. The solution of NaN_3 (0.13 g, 2 mmol) in water (1 mL) was added drop wise in the solution and this mixture was stirred for 1 hr at room temperature. After evaporation of acetone, the crude product was separated by filtration and recrystallized from dichlormethane. We have obtained (0.9 g, 62%) of **21** as Yellow solid with mp 150˚C - 152˚C [21, 22]. IR: υ (cm^{-1}) 1699 (C=O), 2217 (CN), 3422 (NH). ^{1}HNMR (DMSO): δ 3.98 (*s*, br, 1H, NH), 4.61 (*s*, 1H, C-3 pyrazole) and 6.7 - 7.9 (*m*, 14H, Ar-H). MS: *m/z* 486 ($[M]^+$, 32%). *Calcd* for $C_{27}H_{18}N_8O_2$ (486.48). *Calcd*: C 66.66, H 3.73, N 23.03%. *Found*: C 65.76, H 2.56, N 22.73%.

Preparation of 2-(4-amino- 3-phenyl-2,3-dihydro-pyrazolo[3,4-*c*]pyrazol-1(6*H*)-yl)-3-phenyl-3*H*-chromeno[2,3-*d*]pyrimidin-4(10*H*)-one, (23). A mixture of **17** (3.20 g, 0.01 mol) and hydrazine hydrate (0.5 mL, 0.01 mol) in 20 mL DMF containing 0.1 mL piperidine was refluxed for 8 hr. The reaction mixture was concentrated under reduced pressure and the residue washed with acidified cold water and then triturated with methanol. The formed yellow product was filtered, washed well with methanol. Yield 58%, m.p. 150˚C - 152˚C. IR: 1670 (C=O), 3432 (NH) and 3455 (NH_2). ^{1}H NMR (DMSO): 3.98 (*s*, br, 1H, NH), 5.21 (*s*, 1H, CH- methine), 6.7 - 7.9 (*m*, 11H, Ar-H) and 9.21 (*s*, 1H, NH). MS: *m/z* 475($[M]^+$, 64%). *Calcd* for $C_{27}H_{21}N_7O_2$ (475.50): C 68.20, H 4.45, N 20.62%. *Found*: C 67.03, H 3.32, N 19.23%.

Preparation of 3-(2-imino-2*H*- chromen-3-yl)-1-phenyl-3-(phenylamino) prop-2-en-1-one, (24a) and its derivatives (24b-e).

General procedure: A mixture of the 2-imino-*N*-phenyl-2*H*-chromene-3-carboxamide **1** (2.64 g, 0.01 mol) and acetophenone (1.2 ml, 0.01 mol), *p*-hydroxyacetophenone (1.36 g, 0.01 mol), *p*-nitroacetophenone (1.65 g, 0.01 mol), *o*-nitroacetophenone (1.65 g, 0.01 mol) and *p*-chloroacetophenone (1.54 g, 0.01 mol) respectively, in 20 mL DMF containing 0.1ml of piperidine was refluxed for 8 hr. The reaction mixture was concentrated, cooled then poured into ice/H_2O mixture the solid product thus so formed was filtered, washed for several times with water to afford **24a - 24e** derivatives.

Compound 24a. Yellow crystals (MeOH), yield 60%. m.p. 182˚C - 184˚C. IR: υ (cm^{-1}) 1665 - 1705 (C=O), 3322 (NH), ^{1}HNMR (DMSO): δ 4.1 (*s*, 1H, NH-amine), 6.5 (*s*, 1H, CH-ethylene), 7.1-7.6 (*m*, 15H, Ar-H), 11.5 (*s*, 1H, =NH). MS: *m/z* 366 ($[M]^+$,40%). *Calcd* for $C_{24}H_{18}N_2O_2$ (366.41). *Calcd*: C 78.67, H 4.95, N 7.65%. *Found*: C 77.17, H 4.01, N 8.15%.

Compound 24b. Pale green crystals (MeOH), yield 55%, m.p. 220˚C - 222˚C. IR: υ (cm^{-1}) 1665 - 1705(C=O), 3445 (OH), ^{1}HNMR ($CDCl_3$): δ 4.1 (*s*, 1H, NH-amine), 6.5 (*s*, 1H, CH-ethylene), 7.1 - 7.6 (*m*, 14H, Ar-H), 11.5 (*s*, 1H, =NH) and 9.9 (s, 1H, phenolic OH). MS: *m/z* 383 ($[M + 1]^+$, 60%). *Calcd* for $C_{24}H_{18}N_2O_3$ (382.41). *Calcd*: C 75.38, H 4.74, N 7.33%. *Found*: C 74.17, H 3.91, N 6.15%.

Compound 24c. Brown crystals (Ethanol), yield 65%, m.p. 190˚C - 192˚C. IR: υ (cm^{-1}) 1665 - 1705(C=O), ^{1}HNMR (DMSO): δ 4.1(*s*, 1H, NH-amine), 6.5(*s*, 1H, CH-ethylene), 7.1 - 7.6 (*m*, 14H, Ar-H), 11.5 (*s*, 1H, =NH). MS: *m/z* 411($[M]^+$, 62%). *Calcd* for $C_{24}H_{17}N_3O_4$ (411.41). *Calcd*: C 70.07, H 4.16, N 10.21%. *Found*: C 69.17, H 3.31, N 9.15%.

Compound 24d. Brown crystals (Ethanol), yield 59 %, m.p. 170˚C -172˚C. IR: υ (cm^{-1}) 1665 - 1705(C=O). MS: *m/z* 410 ($[M-1]^+$, 52%). *Calcd* for $C_{24}H_{17}N_3O_4$ (411.41). *Calcd*: C70.07, H 4.16, N 10.21%. *Found*: C 69.17, H 3.31, N 9.15%.

Compound 24e. Yellow crystals (Ethanol), yield 55%, m.p. 255˚C - 257˚C. IR: υ (cm^{-1}) 1665 - 1705(C=O), ^{1}HNMR (DMSO): δ 4.1 (*s*, 1H, NH-amine), 6.5 (*s*, 1H, CH-ethylene), 7.1 - 7.6 (*m*, 14H, Ar-H), 11.5 (*s*, 1H, =NH). MS: *m/z* 400 ($[M]^+$,60%). *Calcd* for $C_{24}H_{17}N_2O_2Cl$ (400.86). *Calcd*: C 71.91, H 4.27, N 6.99, Cl8.84%. *Found*: C 70.17, H 3.31, N 5.15, Cl7.18%.

Preparation of 2-imino-*N*,*N*′-diphenyl-2*H*-chromene-3-carboxamidines, (25a) and its derivatives (25b-25e).

General procedure: A mixture of equimolar amount of compound **1** (2.64 g, 0.01 mol) and aniline (0.93 ml, 0.01 mol), *p*-hydroxyaniline (1.09 g, 0.01 mol), *p*-nitroaniline (1.38 g, 0.01 mol), *o*-nitroaniline (1.38 g, 0.01 mol and *p*-chloroaniline (1.27 g, 0.01 mol), respectively in 30 mL ethanol containing 0.1 mL of piperidine was refluxed for 5 hr. The reaction mixture was concentrated, poured into ice/H_2O mixture, and the solid product thus formed, filtered, washed for several times with water and crystallized from methanol.

Compound 25a. Pale brown crystals (Methanol), yield 58%, m.p. 205˚C - 207˚C. IR: υ (cm^{-1}) 3380(NH), ^{1}HNMR ($CDCl_3$): δ 4.1 (*s*, 1H, NH-amine), 7.1 - 7.6(*m*, 15H, Ar-H), 11.5(*s*, 1H, =NH). MS: *m/z* 339 ($[M]^+$, 65%). *Calcd* for $C_{22}H_{17}N_3O$(339.39). C 77.86, H 5.05, N 12.38%. *Found*: C 76.66, H 4.52, N 11.12%.

Compound 25b. Yellow crystals (Methanol), yield 60%, m.p. 210˚C - 212˚C. IR: υ (cm^{-1}) 3380(NH), 3445 (OH), ^{1}HNMR (DMSO): δ 4.1(*s*, 1H, NH-amine), 7.1- 7.6(*m*, 14H, Ar-H), 11.5 (*s*, 1H, = NH) and 9.9 (s, 1H, phenolic OH). MS: *m/z* 357 ($[M+2]^+$, 50%). *Calcd* for $C_{22}H_{17}N_3O_2$ (355.39). C 74.35, H 4.82, N 11.82%. *Found*: C 73.45, H 3.52, N 10.12%.

Compound 25c. Pale yellow crystals (Methanol), yield 64%, m.p. 285˚C - 287˚C. ^{1}HNMR (DMSO): δ 4.1 (*s*, 1H, NH-amine), 7.1 - 7.6 (*m*, 14H, Ar-H), 11.5 (*s*, 1H, = NH), MS: *m/z* 385 ($[M + 1]^+$, 55%). *Calcd* for $C_{22}H_{16}N_4O_3Cl$ (384.39). C 68.74, H 4.20, N 14.58%. *Found*: C 67.72, H

3.52, N 13.12%.

Compound 25d. Yellow crystals (Methanol), yield 60%, m.p. 215˚C - 117˚C. MS: *m/z* 384([M]$^+$, 55%). *Calcd* for $C_{22}H_{16}N_4O_3Cl$ (384.39). C 68.74, H 4.20, N 14.58%. *Found*: C 67.72, H 3.52, N 13.12%.

Compound 25e. Pale brown crystals (methanol), yield 55%, m.p. 230˚C - 232˚C. ^{1}HNMR (DMSO): δ 4.1 (*s*, 1H, NH-amine), 7.1 - 7.6 (*m*, 14H, Ar-H), 11.5 (*s*, 1H, =NH), MS: *m/z* 372([M − 1]$^+$, 70%). *Calcd* for $C_{22}H_{16}N_3OCl$ (373.83). C 70.68, H 4.31, N 11.24, Cl 9.48%. *Found*: C 69.45, H 3.52, N 11.12, Cl 8.48%.

Preparation of 4,5-dihydro-5-(2-imino-2*H*-chromen-3-yl)-*N*,3-diphenyl-1*H*-pyrazol-5-amine, (26a) a- nd its derivatives (26b and 27).

General procedure: A mixture of **24a** (3.66 g, 0.01 mol) and hydrazine hydrate (0.05 ml, 0.01 mol), phenyl hydrazine (1.08 ml, 0.01 mol) and hydroxylamine hydrochloride (0.69 gm, 0.01 mol) containing 0.1 ml piperidine was refluxed for 8 hr. The reaction mixture was concentrated under reduced pressure and the residue washed with acidified cold water and then triturated with methanol, and the solid product thus formed, filtered, washed for several times with water and crystallized from methanol.

Compound 26a. Pale brown crystals (methanol), yield 66%, m.p. 155˚C - 157˚C. IR: 3117 - 3293 (NH). 1H NMR (DMSO): 2.9 (s, 2H, CH_2), 4.1 (s, 1H, NH-amine), 7.1 (s, H, NH hydrazide), 7.2 - 7.8 (m, 15H, Ar-H), 11.5 (s, 1H, =NH). MS: m/z 383([M+3]$^+$, 55%). Calcd for $C_{24}H_{20}N_4O$ (380.44): C 75.77, H 5.30, N 14.73%. Found: C 74.01, H 4.20, N 13.66%.

Compound 26b. Brown crystals (Methanol), yield 50%, m.p. 295˚C - 297˚C. IR: 3117 - 3293 (NH). 1H NMR (DMSO): 1.9 (s, 2H, CH2), 4.1 (s, 1H, NH-amine), 7.1 (s, H, NH hydrazide), 7.2 - 7.8 (m, 20H, Ar-H) and 11.5 (s, 1H, =NH). MS: m/z 456 ([M+], 75%). Calcd for $C_{30}H_{24}N_4O$ (456.54): C 78.92, H 5.30, N 12.27%. Found: C 77.01, H 4.20, N 11.66%.

Compound 27. Pale brown crystals (Methanol), yield 55%, m.p. 230˚C - 232˚C. IR: 3117 - 3293 (NH). ^{1}H NMR (DMSO): 1.9 (*s*, 2H, CH_2), 4.1(*s*, 1H, NH-amine), 7.2 - 7.8 (*m*, 15H, Ar-H) and 11.5 (*s*, 1H, = NH). MS: *m/z* 383 ([M+2]$^+$, 30%). *Calcd* for $C_{24}H_{19}N_3O_2$ (381.43): C 75.57, H 5.02, N 11.02%. *Found*: C 74.01, H 4.20, N 10.66%.

Preparation of 4,5-dihydro-4-(2-imino- 2*H*-chromen-3-yl)-6-phenyl-4-(phenyl-amino) pyrimi-din-2(1-*H*)-one, (28a), and its derivative (28b).

General procedure: A mixture of equimolar amounts of **24a** (3.66 g, 0.01 mol) and urea (0.60 g, 0.01 mol) or thiourea (0.76 g, 0.01 mol) and 0.1 mL piperidine was refluxed for 8 h. in 30 mL of ethanol. The solvent was evaporated under vacuum, and the residue was poured to 30 ml acidified cold water and then triturated with methanol. The product were filtered and crystallized from ethanol.

Compound 28a. Brown crystals (Ethanol); yield 67%, m.p. 196˚C - 198˚C. IR: 1685 - 1705 (C=O), 3063 - 3288 (NH). 1H NMR (DMSO): 2.9 (s, 2H, CH2), 4.1 (*s*, 1H, NH-amine), 7.2 - 7.8 (m, 15H, Ar-H), 8.1 (*s*, H, NH-amide) and 11.5 (s, 1H, = NH), MS: m/z 408 ([M]$^+$, 45%). Calcd for C25H20N4O2 (408.45): C 73.51, H 4.94, N 13.72%. Found: C 72.01, H 3.20, N 12.66%.

Compound 28b. Brown crystals (Methanol), yield 59%, m.p. 210˚C - 112˚C. IR: 1230 (C=S), 3063 - 3288 (NH), MS: *m/z* 422 ([M-2]$^+$, 35%). *Calcd* for $C_{25}H_{20}N_4OS$ (424.52): C 70.73, H 4.75, N 13.20%. *Found*: C 69.01, H 3.20, N 12.66%.

Preparation of 1, 2, 5, 6-tetrahydro-6-(2-imino-2*H*-chromen-3-yl)-2-oxo-4-phenyl-6-(phenylamino) pyrine-carbonitrile, (29a) and its derivatives (29b - 29e) and (30).

General procedure: A mixture of **24a** (3.66 g, 0.01 mol) and cyanoacetamide (0.84 g, 0.01 mol) in 30 ml of ethanol in the presence of 0.1 ml of piperidine was refluxed for 8 h. The reaction mixture was concentrated under vacuum and the residue washed with acidified cold water and then triturated with methanol. The solid product formed was filtered and crystallized from ethanol to afford **29a** in 65% yield. In analogously, the Chalcone **24a** was reacted with cyanothioacetamide (1.0 g, 0.01 mol), 2-cyano-*N*-*p*-tolylacetamide (1.74 g, 0.01 mol), 2-cyanoacetohydrazide (0.99 g, 0.01 mol), 2-cyano-*N*-phenylacetamide (1.6 g, 0.01 mol) and 2-chloroacetamide (0.93 g, 0.01 mol) to yield the pyridine derivatives **29b -29e** and **30** respectively.

Compound 29a. Yellow crystals (Methanol), yield 56%, m.p. 184˚C - 186˚C. IR: 1689 - 1705 (C=O), 2220 (CN), 3188 - 3244(NH). ^{1}H NMR (DMSO): 2.9 (*s*, 2H, CH_2), 4.1 (*s*, 1H, NH-amine), 7.2 - 7.8 (*m*, 15H, Ar-H), 8.1 (*s*, H, NH-amide) and 11.5 (*s*, 1H, =NH), MS: *m/z* 432 ([M]$^+$, 65%). *Calcd* for $C_{27}H_{20}N_4O_2$ (432.47). C 74.98, H 4.66, N 12.95%. *Found*: C 73.01, H 3.20, N 11.66%.

Compound 29b. Pale yellow crystals (Methanol), yield 50%, m.p. 240˚C - 242˚C. IR: 1251 (C=S), 2218 (CN), 3188 - 3244 (NH). MS: *m/z* 448 ([M]$^+$, 45%). *Calcd* for $C_{27}H_{20}N_4OS$ (448.54). C 72.30, H 4.49, N 12.49, S 7.15%. *Found*: C 71.11, H 3.21, N 11.12, S 6.55%.

Compound 29c. Pale red crystals (Methanol), yield 60%, m.p. 235˚C - 238˚C, IR: 1689 – 1705 (C=O), 2210 (CN), 3188 - 3244 (NH), MS: *m/z* 522 ([M]$^+$, 40%). *Calcd* for $C_{34}H_{26}N_4O_2$ (522.6): C 78.14, H 5.01, N 10.72%. *Found*: C 77.01, H 4.20, N 9.66%.

Compound 29d. Pale red crystals (Methanol), yield 75%, m.p. 217˚C - 219˚C. IR: 1689 – 1705 (C=O), 2210 (CN), 3188 - 3344 (NH and NH_2). MS: *m/z* 447 ([M]$^+$, 35%). *Calcd* for $C_{27}H_{21}N_5O_2$ (447.49): C 71.47, H 4.73, N 15.65%. *Found*: C 70.01, H 3.20, N 14.66%.

Compound 29e. Yellow crystals (Methanol), yield 35%,

m.p. 280˚C - 282˚C. IR: 1689 - 1705 (C=O), 2210 (CN), 3188 - 3344 (NH and NH_2). ^{1}H NMR (DMSO): 1.9 (*s*, 2H, CH_2), 2.1 (*s*, 2H, NH_2), 4.1 (*s*, 1H, -NHPh), 7.2 - 7.8 (*m*, 20H, Ar-H) and 11.5 (*s*, 1H, =NH), MS: *m/z* 510 $[M + 2]^+$, 50 %). *Calcd* for $C_{33}H_{24}N_4O_2$ (508.57). C 77.93, H 4.76, N 11.02%. *Found*: C 76.41, H 3.10, N 10.06%.

Compound 30. Brown crystals (Methanol), yield 50%, m.p. 220˚C - 222˚C. IR: 1699 - 1705 (C=O), 3188 - 3244 (NH). ^{1}H NMR (DMSO): 1.9 (*s*, 2H, CH_2), 4.1 (*s*, 1H, NH-amine), 7.2 - 7.8 (*m*, 15H, Ar-H), 8.1 (*s*, H, NH) and 11.5 (*s*, 1H, =NH), MS: *m/z* 441 ($[M]^+$, 55%). *Calcd* for $C_{26}H_{20}N_3O_2Cl$ (441.91). C 70.67, H 4.56, N 9.51, Cl 8.02%. *Found*: C 69.11, H 3.20, N 8.26, Cl 7.61%.

Preparation of 2-(2-imino-2*H*-chromen-3-yl)-4-phenyl-2-(phenylamino)pyrido-[1,2-*a*]benzim-idazo-lo-5-carbonitriles, (31). A mixture of **24a** (3.66 g, 0.01 mol), 2-cyanomethylbenzimidazole (1.57 g, 0.01 mol) and 0.1 mL of piperidine in 30 mL of ethanol was refluxed for 8 h. The solvent was evaporated under vacuum and the residue was washed by acidified cold water and then triturated with methanol. The solid product was filtered and crystallized from ethanol, as brown crystals, yield 65%, m.p. 278˚C - 280˚C. IR: 2220 (CN), 3188 - 3244 (NH). ^{1}H NMR ($CDCl_3$): 2.9 (*s*, 2H, CH_2), 4.1 (*s*, 1H, NH-amine), 6.9 - 7.6 (*m*, 19H, Ar-H) and 11.5 (*s*, 1H, =NH), MS: *m/z* 505 ($[M]^+$, 35%). *Calcd* for $C_{33}H_{23}N_5O$ (505.57): C 78.40, H 4.59, N 13.85%. *Found*: C 77.01, H 3.20, N 12.66%.

Preparation of 2,3-dihydro-2-(2-imino-2*H*-chrom-e-n-3-yl)-*N*,4-diphenyl-benzo[*b*][1,4]oxazepin-2-amine, (32a) and its derivatives, (32b).

General procedure: A mixture of an equimolar amounts of **24a** (3.66 g, 0.01 mol) and (1.09 g, 0.01 mol) *o*-aminophenol and (1.25 g, 0.01 mol) *o*-aminothiophenol respectively, in 30 mL ethanol containing 0.1 mL of piperidine was refluxed for 8 hr. The reaction mixture was concentrated, cooled then poured into ice/H_2O mixture. The solid product thus so formed was filtered, washed for several times with water and crystallized from ethanol.

Compound 32a. Brown crystals (Ethanol), yield 60%, m.p. 282˚C - 284˚C, IR: 3289(NH), ^{1}H NMR (DMSO): 2.9(*s*, 2H, CH_2), 4.1(*s*, 1H, NH-amine), 6.7 - 7.3 (*m*, 19H, Ar-H) and 11.5(*s*, 1H, = NH), MS: *m/z* 457 ($[M]^+$, 55%). *Calcd* for $C_{30}H_{23}N_3O_2$ (457.52): C 78.75, H 5.07, N 9.18%. *Found*: C 77.01, H 4.20, N 8.66%.

Compound 32b. Yellow crystals (Ethanol), yield 45 %, m.p. 270˚C-272˚C. IR: 3188-3244(NH), ^{1}H NMR ($CDCl_3$): 1.9 (*s*, 2H, CH_2), 4.1 (*s*, 1H, NH-amine), 6.9 - 7.6 (*m*, 19H, Ar-H) and 11.5 (*s*, 1H, =NH), MS: *m/z* 476 ($[M+3]^+$, 45%). *Calcd* for $C_{30}H_{23}N_3OS$ (473.59). C 76.08, H 4.90, N 8.87, S 6.77%. *Found*: C 77.01, H 3.20, N 12.66, S 5.12%.

Preparation of 2-(dicyanomethylene)-1,2,5,6-tetrahydro-6-(2-imino-2*H*-chromen-3-yl)-4-phenyl-6-(phenylamino)pyridine-3-carbonitrile, (33a) and its derivatives (33b).

General procedure: A mixture of **24a** (0.366 g, 0.001 mol) and 2-aminoprop-1-ene-1,1,3-tricarbonitrile (0.132 g, 0.001 mol) in 30 mL of ethanol in the presence of 0.1 mL of piperidine was refluxed for 8 h. The reaction mixture was concentrated under vacuum and the residue washed with acidified cold water and then triturated with methanol. The solid product formed was filtered and crystallized from methanol to afford **33a** in 60% yield. In analogously, the Chalcone **34a** was reacted with ethyl 3-amino-2, 4-dicyanobut-2-enoate (1.79 g, 0.01 mol) to yield the pyridine derivative **33b**.

Compound 33a. Yellow crystals (Methanol), yield 60%, m.p. 184˚C - 186˚C. IR: 2219 (CN), 3289 (NH). ^{1}H NMR (DMSO): 2.9 (*s*, 2H, CH_2), 4.1 (*s*, 1H, NH-amine), 6.7 - 7.3 (*m*, 15H, Ar-H), 8.1 (*s*, H, NH) and 11.5 (*s*, 1H, =NH), MS: *m/z* 482 ($[M+2]^+$, 35%). *Calcd* for $C_{30}H_{20}N_6O$ (480.52). C 74.99, H 4.20, N 17.49%. *Found*: C 73.01, H 3.20, N 16.66%.

Compound 33b. Pale yellow crystals (Methanol), yield 45%, m.p. 240˚C - 242˚C. IR: 2219 (CN), 3289 (NH). ^{1}H NMR (DMSO): δ 1.2 (*t*, 3H, CH_3), 2.2 (*s*, 2H, CH_2), 3.7 (*q*, 2H, CH_2), 4.1 (*s*, 1H, NH-amine), 6.7 - 7.9 (*m*, 15H, Ar-H) and 11.5 (*s*, 1H, =NH), MS: *m/z* 527 ($[M]^+$, 35%). *Calcd* for $C_{32}H_{25}N_5O_3$ (527.57). *Calcd*: C 72.85, H 4.78, N 13.27%. *Found*: C 71.14, H 3.01, N 12.88%.

Preparation of 3-chloro-4- (2-imino-2*H*-chromen-3-yl)-1-phenyl-4-(phenyl-amino) azetidin-2-one, (34a) and its derivatives, (34b - 34e).

Compound 34a. Brown crystals (Methanol) yield 60%, m.p. 280˚C - 282˚C. IR: 1705 (C=O), 3289 (NH). ^{1}H NMR (DMSO): 4.1 (*s*, 1H, NH-amine), 5.2 (*s*, 1H, CH, C-3 of β-lactam ring), 7.1 - 7.6 (*m*, 15H, Ar-H) and 11.5 (*s*, 1H, =NH), MS: *m/z* 415 ($[M]^+$, 40%), *Calcd* for $C_{24}H_{18}N_3O_2Cl$ (415.87): C 69.31, H 4.36, N 10.10, Cl 8.5279%. *Found*: C 68.19, H 3.21, N 9.18, Cl 7.12%.

Compound 34b. Pale yellow crystals (Methanol), yield 63%, m.p. 275˚C - 277˚C. IR: 1705(C=O), 3289 (NH), 3388(OH). ^{1}H NMR (DMSO): 4.1 (*s*, 1H, NH-amine), 5.2 (*s*, 1H, CH, C-3 of β-lactam ring), 7.1 - 7.6 (*m*, 14H, Ar-H), 11.5 (*s*, 1H, =NH) and 10.1 (*s*, 1H, phenolic OH). MS: *m/z* 431($[M]^+$, 55%), *Calcd* for $C_{24}H_{18}N_3O_3Cl$ (431.87): C 66.75, H 4.20, N 9.73, Cl 8.21%. *Found*: C 65.09, H 3.52, N 9.08, Cl 7.12%.

Compound 34c. Pale brown crystals (Methanol), yield 70%, m.p. 210˚C - 212˚C. IR: 1705 (C=O), 3289 (NH). ^{1}H NMR ($CDCl_3$): 4.1 (*s*, 1H, NH-amine), 5.2 (*s*, 1H, CH, C-3 of β-lactam ring), 7.1 - 7.6 (*m*, 14H, Ar-H) and 11.5 (*s*, 1H, =NH). MS: *m/z* 460($[M]^+$, 40%), *Calcd* for $C_{24}H_{17}N_4O_4Cl$ (460.87): C 62.55, H 3.72, N 12.16, Cl 7.69%. *Found*: C 61.07, H 2.22, N 11.18, Cl 6.11%.

Compound 34d. Brown crystals (Ethanol), yield 62%, m.p. 175˚C - 177˚C. IR: 1705 (C=O), 3289 (NH). MS: *m/z* 461 ($[M + 1]^+$, 55%), *Calcd* for $C_{24}H_{17}N_4O_4Cl$ (460.87): C 62.55, H 3.72, N 12.16, Cl 7.69%. *Found*: C 61.17, H 2.25,

N 11.48, Cl 6.21%.

Compound 34e. Yellow crystals (Ethanol), yield 55%, m.p. 250˚C - 252˚C. IR: 1705 (C=O), 3289 (NH). ^{1}H NMR ($CDCl_3$): 4.1 (*s*, 1H, NH-amine), 5.2 (*s*, 1H, CH, C-3 of *β*-lactam ring), 7.1 - 7.6(*m*, 14H, Ar-H) and 11.5 (*s*, 1H, =NH). MS: *m/z* 450([M]$^+$, 65%), *Calcd* for $C_{24}H_{17}N_3O_2Cl_2$ (450.32): C 64.01, H 3.81, N 9.33, Cl 7.11%. *Found*: C 63.07, H 2.82, N 8.18, Cl 6.41%.

Preparation of 2-(2-imino-2*H*- chromen-3-yl)-3-phenyl-2-(phenylamino) thiazolidin-4-one, (35a) and its derivatives (35b - 35e).

General procedure: An equimolar mixture of **25a** (0.99 g, 0.003 mol) and thioglycolic acid (0.276 mL, 0.003 mol) in dry benzene (20 mL) was refluxed for 10 h. The reaction mixture was evaporated to dryness under reduced pressure. The thiazolidinone was separated off, washed with ether and crystallized from ethanol. Analogously, **25b - 25e** reacted with thioglycolic acid to yield **35b - 35e**.

Compound 35a. Yellow crystals (ethanol), yield 60%, m.p. 185˚C - 187˚C. IR: 1230 (CS), 1695 (C=O), 3289 (NH). ^{1}H NMR (DMSO): 3.8 (*s*, 2H, CH_2), 4.1(*s*, 1H, NH-amine), 6.8 - 7.8 (*m*, 15H, Ar-H) and 11.5 (*s*, 1H, =NH). MS: *m/z* 411 ([M − 2]$^+$, 35%). *Calcd* for $C_{24}H_{19}N_3O_2S$ (413.49): C 69.71, H 4.63, N 10.16, S 7.91%. *Found*: C 68.46, H 3.17, N 9.46, S 6.55%.

Compound 35b. Yellow crystals (Methanol), yield 70%, m.p. 215˚C - 117˚C. IR: 1230 (CS), 1695 (C=O), 3289 (NH). ^{1}H NMR (DMSO): 3.8 (*s*, 2H, CH_2), 4.1 (*s*, 1H, NH-amine), 6.8 - 7.8 (*m*, 15H, Ar-H), 11.5 (*s*, 1H, =NH) and 10.1 (*s*, 1H, phenolic OH). MS: *m/z* 429([M]$^+$, 44%). *Calcd* for $C_{24}H_{19}N_3O_3S$ (429.49): C 67.12, H 4.46, N 9.78, S 7.47%. *Found*: C 66.46, H 3.17, N 8.46, S 6.25%.

Compound 35c. Pale brown crystals (Ethanol), yield 76%, m.p. 198˚C - 200˚C. IR: 1230 (CS), 1695 (C=O), 3289 (NH). ^{1}H NMR (DMSO): 3.8 (*s*, 2H, CH_2), 4.1 (*s*, 1H, NH-amine), 6.8 - 7.8 (*m*, 14H, Ar-H) and 11.5 (*s*, 1H, =NH). MS: *m/z* 457 ([M-1]$^+$, 55%). *Calcd* for $C_{24}H_{18}N4O_4S$ (458.49): C 62.87, H 3.96, N 12.22, S 6.99%. *Found*: C 61.66, H 3.17, N 11.16, S 5.55%.

Compound 35d. Yellow crystals (Ethanol), yield 65%, m.p. 290˚C - 292˚C. IR: 1230 (CS), 1695 (C=O), 3289 (NH). MS: *m/z* 458 ([M]$^+$, 55%). *Calcd* for $C_{24}H_{18}N4O_4S$ (458.49): C 62.87, H 3.96, N 12.22, S 6.99%. *Found*: C 61.12, H 3.74, N 11.18, S 6.25%.

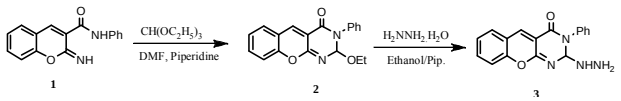
Compound 35e. Brown crystals (Methanol), yield 62%, m.p. 235˚C - 237˚C. IR: 1230 (CS), 1695 (C=O), 3289 (NH). ^{1}H NMR (DMSO): 3.8 (*s*, 2H, CH_2), 4.1 (*s*, 1H, NH-amine), 6.8 - 7.8 (*m*, 14H, Ar-H) and 11.5 (*s*, 1H, =NH). MS: *m/z* 447 ([M]$^+$, 65%). *Calcd* for $C_{24}H_{18}N3O_2SCl$ (447.94): C 64.35, H 4.05, N 9.38, S 7.91%. *Found*: C 63.63, H 3.57, N 9.16, S 6.55%.

3. Results and Discussion

The synthetic procedures adopted to obtain the target compounds are depicted in **Schemes 1 - 10**. The starting compound, 2-imino-*N*-phenyl-2*H*-chromene-3-carboxamide **1**, was prepared according to the previously reported procedure [18]. Thus, refluxing of compound **1** with triethyl orthoformate in dimethylformamide affording 2-ethoxy-2,3-dihydro-3-phenylchromeno[2,3-*d*]pyrimidin-4-one **2**, (**Scheme 1**). The structure of the later product was based on IR, ^{1}H NMR, and mass spectra. The IR spectrum of **2** showed the lack of any absorption of the NH functions, and the ^{1}H NMR spectrum ($CDCl_3$) displayed a triplet at *δ* 1.2 and a quartet at 3.9 ppm due to the ethoxy protons and a multiplet at 6.7 - 7.9 ppm due to aromatic protons, respectively. The MS of **2** showed the [M]$^+$ ion at *m/z* 320 (65%). Furthermore, compound **2** was allowed to react with hydrazine hydrate in ethanolic solution using piperidine as a catalyst yielding 2-hydrazinyl-2, 3-dihydro-3-phenyl-chromeno[2,3-*d*] pyrimidin-4-one, **3**. The structure of **3** was confirmed based on elemental and spectroscopic analysis. The IR spectrum of **3** showed the presence of absorption bands at *υ* 1670, 3282 and 3432 cm^{-1} due to CO, NH and NH_2 groups, respectively. The ^{1}H NMR spectrum (DMSO) displayed three signals at *δ* 4.82, 5.1 and 8.85 due to NH_2, pyrimidine proton and NH respectively, and a multiplet at 6.7 - 7.9 ppm, for aromatic protons. While, the MS of **3** showed *m/z* at 309 ([M + 3]$^+$, 45%).

Compound **3** was utilized as a key intermediate for the synthesis of some new pyrazole derivatives based on mild and efficient reaction of compound **3** with some of laboratory available compounds. Thus, Compound **3** reacted with ethyl 3-amino-2,4-dicyanobut-2-enoate in boiling DMF containing a catalytic amount of piperidine. Two isomeric products seemed possible for this reaction **5** or **6**, (**Scheme 2**). Structure **6** ruled out based on analytical and spectroscopic data (IR, ^{1}H NMR and MS). Thus, the IR spectra of the product **5** showed the presence of absorption bands at υ 1699, 2219 and 3422 cm^{-1} due to C=O, CN and NH_2 groups, respectively. Accordingly, the ^{1}H NMR spectrum (DMSO) of the product **5** showed three singlet signals at *δ* 2.9, 3.5 and 3.7 due to the methylene and two NH_2 groups respectively, and a multiplet at 6.7 - 7.9 ppm, due to aromatic protons. The MS of **5** displayed [M]$^+$ at *m/z* 439 (60%). It is note worth that, trial to cyclise **5** in boiling pyridine was unsuccessful, (**Scheme 2**).

Also, compound **3** reacted with diethyl malonate in boiling DMF containing a catalytic amount of piperidine afforded 1-(3,4-dihydro-4-oxo-3-phenyl-2*H*-chromeno[2,3-*d*]pyrimidin-2-yl)pyrazolidine-3,5-dione **7**, (**Scheme 3**). The structure of **7** was confirmed based on elemental and



Schemes 1. Synthetic route to variously substituted 2, 3-dihydro-3-phenylchromeno[2,3-*d*] pyrimidin-4-one.

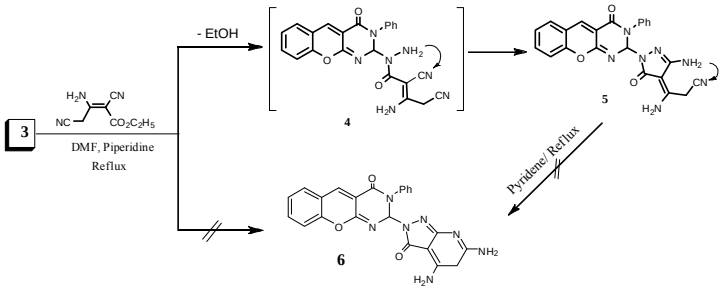
spectroscopic analysis. The IR spectra **7** showed the presence of absorption band centered between υ 1685 - 1705, 3212 cm^{-1} due to CO and NH functions respectively. Accordingly, the ^1H NMR spectrum ($CDCl_3$) of **7** showed three singlet signals at δ 3.2, 5.8 and 8.1 ppm due to the methylene, methine and NH pyrazole ring protons respectively, and a multiplet at δ 6.1 - 7.8 for aromatic protons. The MS of **7** displayed *m/z* at 374 ($[M]^+$, 55%).

Similarly, compound **3** was allowed to react with ethyl 2-cyanoacetate, ethyl 3-oxobutanoate and pentane-2,4-dione to afford the corresponding pyrazole derivatives **8 - 10** respectively, (**Schemes 3**).

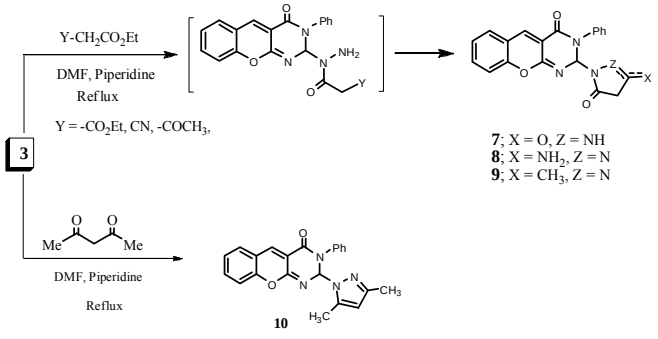
Likewise, compound **3** was reacted with 2-(ethoxymethylene) malononitrile and 2-cyano-*N*-phenylacetamide gave the corresponding pyrazole derivatives **12, 13a, b** respectively, (**Scheme 4**). While the reaction of compound **3** with nitrous acid afforded the tetrazolo[1,5-*a*]pyrimidine derivatives **11,** (**Scheme 4**). The structure of these compounds was in agreement with analytical and spectroscopic data. The IR spectrum of **11** showed the presence of absorption bands at υ 1699 cm^{-1} due to CO group. While, the MS of compound **11** showed *m/z* at 317($[M]^+$, 60%), (**Scheme 4**).

On the other hand, the hydrazine **3** reacted with aromatic aldehydes afforded 2-(2-benzylidenehydrazinyl)-3-phenyl-3*H*-chromeno[2,3-*d*]pyrimidin-4-one **14**, which was cyclized to 5-oxo-1-(4-oxo-3-phenyl-4,10-dihydro-3*H*-chromeno[2,3-*d*]pyrimi-din-2-yl)-3-phenylpyrazolidine-4-carbonitrile **16** by treatment with ethyl cyanoacetate. It seemed that the addition of active methylene hydrogen of ethyl cyanoacetate to the imino carbon of **14** gave the intermediate **15**, which subsequently cyclized *via* elimination of ethanol molecule yielding **16**. The MS of **16** showed *m/z* at 462 $(M + 1)^+$, 55%. Its IR spectrum revealed absorption bands at υ 3432 cm^{-1} (NH), 2217cm^{-1} (CN) and 1670 cm^{-1} (CO). The ^1H NMR spectrum showed a multiplet signals at δ 6.71 - 7.92 for aromatic protons and three singlet signals at δ 3.98, 4.12 and 4.21 due to -NH, the two methine protons of pyrazole ring, respectively, (**Scheme 5**). The compound **16** was transformed in to the chloro derivatives **17**, by treatment with phosphoryl chloride (**Scheme 5**). The MS of **17** showed at *m/z* at 478 ($[M - 1]^+$, 16%). The IR spectrum of **17** showed the presence of absorption band at ν 1700 cm^{-1} due to C=O, 2217 cm^{-1} due to CN and 3425 cm^{-1} due to NH function. The ^{1}HNMR of compound **17** showed singlet signals at δ ppm 3.98 and 4.61 due to NH and methane proton of pyrazole ring.

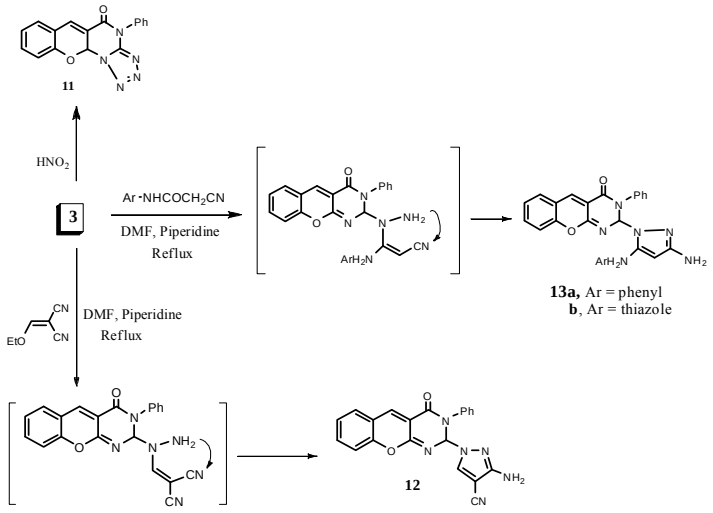
Compound **17** was utilized as a useful starting material for the synthesis of a variety heterocycle-isolated coumarin derivatives based on mild and efficient reaction of compound **17** with some of laboratory available compounds. Thus, compound **17** reacted with 5-amine-1*H*-1,2,4-triazole in boiling DMF containing a catalytic amount of piperidine afforded 2-(4-amino-3-phenyl-2,3-dihydro-1*H*-pyrazolo[4,3-*e*][1,2,4]triazolo[1,5-*a*]pyrimidin-1-yl)-3-phenyl-3*H*-chromeno[2,3-*d*]pyrimidin-4(10*H*)-one **18**, (**Scheme 6**). Similarly, compound **17** reacted with 5-amino-3-(methylthio)-1*H*-pyrazole-4-carbonitrile yielded 4-amino-7-(methylthio)-1-(4-oxo-3-phenyl-4,10-dihydro-3*H*-chromeno[2,3-*d*]pyrimidin-2-yl)-3-phenyl-2, 3-dihydro-1*H*-dipyrazolo[1,5-a:4',3'-*e*]pyrimidine-6-carbonitrile **19.** The



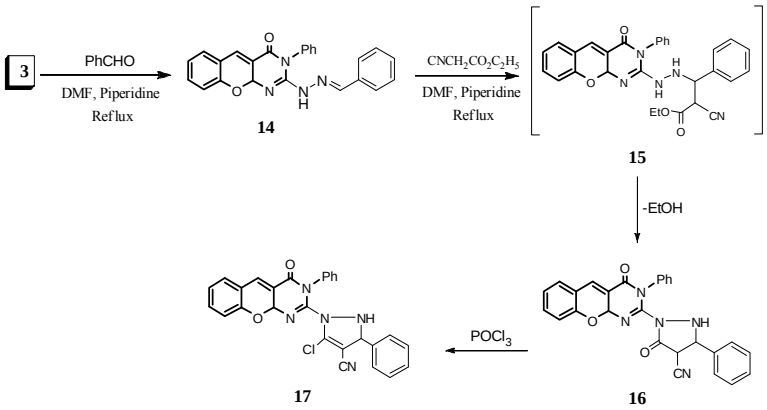
Scheme 2. Synthetic rpute to prepare isolated pyrazole derivatives and reaction conditions.



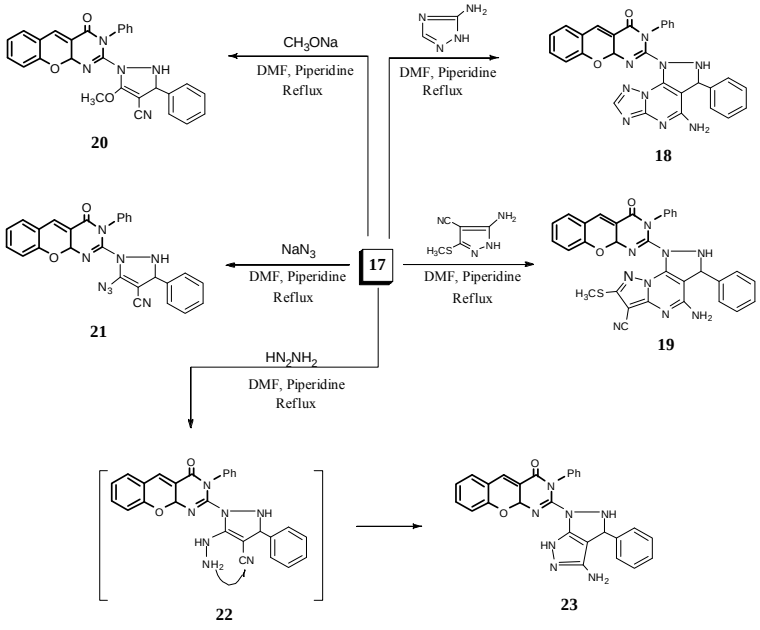
Scheme 3. Synthetic rpute to isolated oxazole 7 and pyrazole derivatives 8 - 10, and reaction conditions.



Scheme 4. Synthetic rpute to isolated pyrazole derivatives and reaction conditions.



Scheme 5. Synthetic rpute to isolated pyrazole derivatives and reaction conditions.



Scheme 6. Synthetic rpute to isolated and/or fused pyrazole derivatives 18 - 23, and reaction conditions.

structure of these compounds was confirmed based on elemental and spectroscopic analysis. (*See experimental section*). Also, the chloro derivative **17** was converted to the 5-methoxy-1-(4-oxo-3-phenyl-4,10-dihydro-3*H*-chromeno[2,3-*d*]pyrimidin-2-yl)-3-phenyl-2,3-dihy-dro-1*H*-pyrazole-4-carbonitrile **20** by refluxing with MeONa, (**Scheme 6**). Structure **20** confirmed based on analytical and spectroscopic data (IR, ^{1}H NMR and MS). Thus, the IR spectra of the product **20** showed the presence of absorption bands at υ 1699, 2219 and 3422 cm^{-1} due to C=O, CN and NH groups, respectively. Accordingly, the ^{1}H NMR spectrum (DMSO) of the product **20** showed three singlet signals at δ 3.82, 3.98 and 4.61 due to the -OCH_3, -NH, and methine protons respectively, and a multiplet at 6.7 - 7.9 ppm, due to aromatic protons. The MS of **20** displayed $[M]^+$ at *m/z* 475 (62%). We prepared 5-azido-1-(4-oxo-3-phenyl-4,10-dihydro-3*H*-chromeno[2,3-*d*]pyrimidin-2-yl)-3-phenyl-2, 3-dihydro-1*H*-pyrazole-4-carbonitrile **21** from the chloro compound **17** by reaction with NaN_3 in acetone [21, 22] .The structure of **21** was in agreement with analytical and spectroscopic data. The IR spectrum of **21** showed the presence of absorption bands at υ 1699 cm^{-1} due to CO, 2217 cm^{-1} due to CN and 3422 cm^{-1} due to NH groups. While, the MS of compound **21** showed *m/z* at 486($[M]^+$, 32%). In further reactions, chloro compound **17** on treatment with hydrazine hydrate in DMF containing a catalytic amount of piperidine at reflux temperature afforded 2-(4-amino-3-phenyl-2,3-dihydro-pyrazolo[3,4-*c*]pyrazol-1(6*H*)-yl)-3-phenyl-3*H*-chromeno[2,3-*d*] pyrimidin-4(10*H*)-one **23**, The formation of **23** may be proceeded *via* an initial elimination of HCl molecule to give the intermediate **22**, which cyclized by nucleophilic addition of the amino function into the cyano group yielded **23,** (**Scheme 6**). The IR spectrum of **23** showed the presence of absorption bands at υ 1670 cm^{-1} due to (CO) and 3432 - 3455 cm^{-1} due to (NH, NH_2) with the absence of any characteristic absorption of (CN) group. The ^{1}H NMR spectrum of **23** showed four singlet at δ 3.98, 5.21, 6.53 and 9.21 ppm due to the -NH amine, methine of pyrazole ring, amino and imino group respectively, and a multiplet at δ 6.97 - 7.81 for aromatic protons. The MS of **23** displayed *m/z* at 475 (M^+, 15%).

On the other hand, the carboxamide **1** easily condensed with acetophenone derivatives in DMF containing a catalytic amount of piperidine at reflux temperature to afford chromenochalcones **24a - 24e** *via* elimination of water (**Scheme 7**). The IR spectrum of **24a** showed absorption bands at υ 1665 - 1705 and 3322 due to CO and NH groups respectively, the Ms of **24a** showed *m/z* at 366 ($[M]^+$, 40%). While, the ^{1}HNMR spectrum of **24a** (DMSO) showed three singlet signals at δ 4.1, 6.5 and 11.5 ppm due to the NH- amine, methylene and NH-imino groups respectively, and a multiplet at δ 7.1 - 7.6 for aromatic protons.

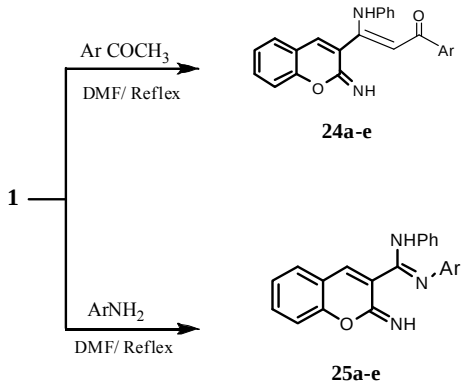
Likewise, compound **1** reacts with some aromatic amines to afford the corresponding Schiff's base **25a - 25e,** (**Scheme 7**). The IR spectrum of **25a** showed the presence of absorption bands at υ 3380, due to NH function, with the absence of any characteristic absorption of a C=O group. The ^{1}H NMR spectrum ($CDCl_3$) displayed two signals at δ 4.1, 3.7 and 11.5 due to NH-amine, and NH-imino groups respectively, and a multiplet at 7.1 - 7.6 ppm, for aromatic protons. While, the MS of **25a** showed *m/z* at 339($[M]^+$, 65%).

The reactivity of exocyclic C = C conjugated with the carbonyl group in **24a - 24e** was investigated by reaction with hydrazines, hydroxylamine, urea, thiourea and some laboratory available active methylene compounds. The nature of the products obtained characterized by elemental and spectroscopic data, indicates that the reaction proceeded *via* condensation followed by a nucleophilic attack through α, β-unsaturated ketonic group. Pyrazoles/isoxazole derivatives **26a - 26b** and **27** were synthesized by treating **24a** with equimolar ratios of hydrazine hydrate (or phenylhydrzine or hydroxylamine respectively) in ethanol containing a catalytic amount of piperidine, (**Scheme 8**). The structure of these compounds was established based on analytical and spectroscopic data. The IR spectra **26a** showed the presence of absorption band centered between υ 3117 - 3293 cm^{-1} due to NH function, with the absence of any characteristic absorption of a C=O group. Accordingly, the ^{1}H NMR spectrum (DMSO) of **26a** showed four singlet signals at δ 2.9, 4.1, 7.1 and 11.5 ppm due to the proton at C-4 of pyrazole, NH- amine, NH- hydrazide and =NH imino respectively, and a multiplet at δ 7.2 - 7.8 for aromatic protons. The MS of **26a** displayed *m/z* at 383 ($[M+3]^+$, 55%). The activation exerted by the carbonyl group on the exocyclic double bond in **24a** renders them available for the cyclocondensation addition of various amino compounds such as urea and thiourea. Thus, when the chalcone **24a** was reacted with an equimolar quantity of urea or thiourea respectively, (**Scheme 7**) an initial condensation of one amino group with the carbonyl function occurred releasing water, followed by a nucleophilic addition of the second amino group to the double bond forming 4,5-dihydro-4-(2-imino-2*H*-chromen-3-yl)-6-phenyl-4-(phenylamino)pyrimidin-2(1*H*)-ones, **28a** and/or thione **28b**. The structures of the synthesized compounds were confirmed by analytical and spectroscopic data (IR, ^{1}H NMR and MS). The IR spectra **28a** showed the presence of absorption bands centered between υ 1685 - 1705, 3063 - 3288 cm^{-1} due to C=O and NH functions, respectively. The ^{1}H NMR spectrum (DMSO) of **28a** showed four singlet signals at δ 2.9, 4.1, 8.1 and 11.5 ppm due to the proton at C-4 of pyrimidine, NH-amine, NH-amide and NH-imino protons , respectively and a multiplet at δ 7.2 - 7.8 for aromatic protons. The MS of **28a** showed a peak at *m/z* 408 ($[M]^+$, 45%). New pyridine derivatives

have been prepared *via* condensation of **24a** with the active methylene groups of cyanoacetamide, cyanothioacetamide, 2-cyano-*N*-*p*-tolylacetamide, 2-cyanoacetohy-drazide and 2-cyano-*N*-phenylacetamide respectively, followed by a nucleophilic addition of the amino/imino group to the double bond, afforded 1,2,5,6-tetrahydro-6-(2-imino-2*H*-chromen-3-yl)-2-oxo(thioxo)-4-phenyl-6-(phenylamino) pyridine-3-carbonitriles **29a - 29e** , respectively (**Scheme 8**). The IR spectrum of **29a** showed the presence of absorption bands at υ 1689 - 1705, 2220 and 3188 - 3244 cm^{-1} due to C=O, CN, and NH functions, respectively, and the ^1H NMR spectrum (DMSO) displayed three singlet signals at δ 2.9, 4.1 and 8.1 due to the proton at C-5 of pyridine, NH-amine and NH amide, respectively, and a multiplet at 7.2 - 7.6 ppm, respectively. The MS of **29a** showed a peak at *m/z* 432 ($[M]^+$, 65%).

Similarly, compound **24a** reacted with 2-chloroacetamide to afford 3-chloro-5, 6-dihydro-6-(2-imino-2*H*-chromen-3-yl)-4-phenyl-6-(phenylamino)pyridin-2(1*H*)-one **30**, (**Scheme 9**). Also, 2-(cyanomethyl) benzimidazole, reacted with the chalcone **24a,** in ethanol using piperidine as a catalyst gave the 2-(2-imino- 2*H*-chromen-3-yl)-4-phenyl-2-(phenylamino) pyrido[1,2-*a*]ben-zimidazolo-5-carbonitriles, derivative probably *via* initial condensation of the activated methylene group with the carbonyl function releasing water, followed by a nucleophilic addition of the NH group at the double bond of compound **24a** to afford **31**, (**Scheme 9**). The structure of **31** was assigned based on IR, ^1H NMR, and mass spectra. The IR spectrum showed the presence of absorption bands at υ 2220 cm^{-1} and 3188 - 3244 cm^{-1} due to CN and NH functions respectively, while that due to C=O was completely disappeared, and the ^1H NMR spectrum ($CDCl_3$) displayed three singlet at δ 2.9, 4.1 and 11.5 due to the C-3 proton, NH-amine and NH-imino protons respectively, and a multiplet at δ 6.9 - 7.6 ppm, for aromatic protons. The MS showed the $[M]^+$ ion at *m/z* 505 (35%). Similarly, the chalcone **24a** was reacted with amino phenols in ethanolic solution containing a catalytic amount of piperidine to give 2,3-dihydro-2-(2-imino-2*H*-chromen-3-yl)-*N*,4-diphenyl-benzo[*b*][1,4]azepine derivatives , **32a, b** (**Scheme 9**). The IR spectrum of **32a** showed the presence of absorption bands at υ 3289 cm^{-1} due to NH function, the ^1H NMR spectrum (DMSO) of **32a** displayed three singlet signals at δ 2.9, 4.1 and 11.5 due to the C-3 protons, NH-amine and NH-imino protons respectively, and a multiplet at 6.7 - 7.3 ppm for aromatic protons. While, the MS of **32a** showed a peak at *m/z* 457 ($[M]^+$, 55%). Also, comund **24a** was reacted with 2-aminoprop-1-ene-1, 1,3-tricarbonitrile and/or ethyl 3-amino-2,4-dicyanobut-2-enoate to afford 2-(dicyano- methylene)-1,2,5,6-tetrahydro-6-(2-imino-2*H*-chromen-3-yl)-4-phenyl-6-(phenylamino)pyridine-3-carbonitrile, **33a** and 2-(1-cyano-2-oxobutylidene)-1,2,5,6-tetrahydro-6-(2-imino-2*H*-chromen-3-yl)-4-phenyl-6-(phenylamino) pyridine-3-carbonitrile **33b,** respectively. The structure of these products was established based on the IR spectrum of **33a** which showed the presence of absorption bands at υ 2219 and 3289 cm^{-1} due to C=O and NH functions, respectively. The ^1H NMR spectrum (DMSO) of **33a** displayed two singlet signals at δ 2.9 and 4.1 due to the C-3 protons and NH-amine and a multiplet at 6.7 - 7.3 ppm for aromatic protons. While, the MS of **33a** showed a peak at *m/z* 482 ($[M + 2]^+$, 35%).

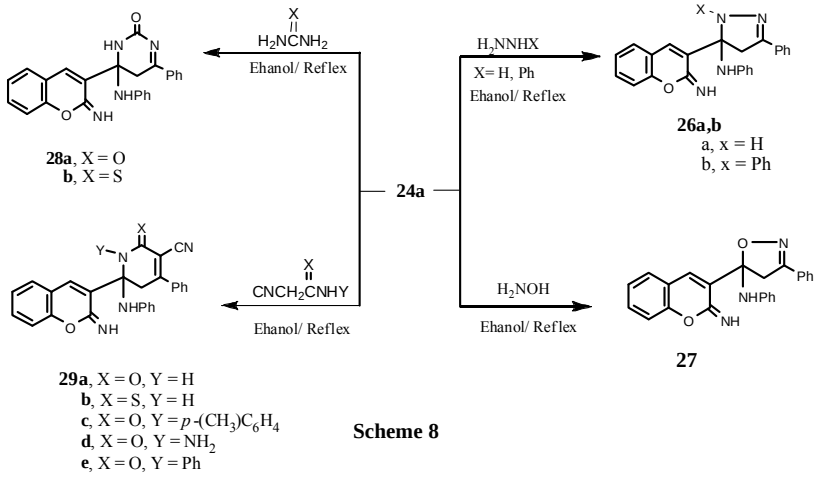
On the other hand, the new synthesized Schiff's bases 2-imino-*N*, *N'*-diphenyl-2*H*-chromene-3-carboxamidines, **25a - 25e**, were used to prepare new compounds. Thus, cycloaddition of chloroacetyl chloride to **25a - 25e** proceeded smoothly in ethanolic solution containing triethylamine as a catalyst to give the β-lactam, derivatives **34a - 34e**, (**Scheme 10**). The IR spectra of **34a - 34e** showed the



a, Ar = Ph
b, Ar = *p*-$(OH)C_6H_4$
c, Ar = *p*-$(NO_2)C_6H_4$
d, Ar = *o*- $(NO_2)C_6H_4$
e, Ar = *p*-$(Cl)C_6H_4$

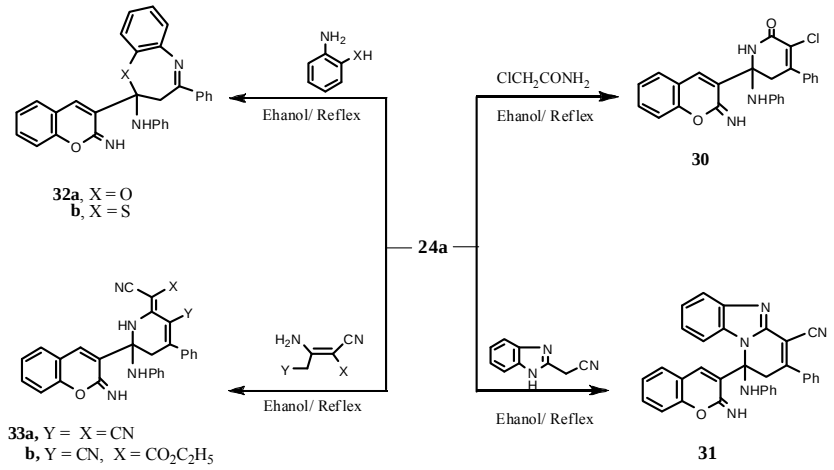
Scheme 7

Scheme 7. Synthetic rpute to chalcones 24a - e and Schiff's bases 25a - e.

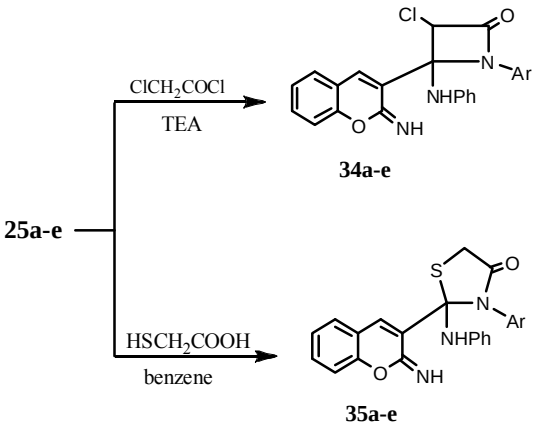


Scheme 8

Scheme 8. Synthetic rpute to isolated pyrazole, isoxazole, pyrimidine and pyridine derivatives 26ab, 27, 28a,b and 29a - e.



Scheme 9. Synthetic rpute for the preparation of compounds 30 - 33a,b.



Scheme 10

a, Ar = Ph
b, Ar = *p*-(OH)C_6H_4
c, Ar = *p*-(NO_2)C_6H_4
d, Ar = *o*- (NO_2)C_6H_4
e, Ar = *p*-(Cl)C_6H_4

Scheme 10. Synthetic rpute for the preparation of *β*-latame 34a,b. and thiazolodinone derivatives 35a - e.

presence of absorption bands due to C=O and NH functions respectively. The ^{1}H NMR spectrum (DMSO) of **34c** showed three singlet signals at δ 4.1, 5.2 and 11.5 ppm for NH-amine, the proton at C3 of the β-lactam unit and NH-imino protons respectively and a multiplet at δ 7.1 - 7.6 for aromatic protons. The MS of **34c** showed the $[M]^+$ ion at *m/z* 460 (40%). Also, the Schiff's bases **25a - 25e** were reacted with equimolar ratio of thioglycolic acid in boiling benzene using water separator system, the thiol group of thioglycolic acid could be added to the imino carbon atoms of Schiff's bases **25a - 25e** followed by smooth cyclization to afford 2-(2-imino-2*H*-chromen-3-yl)-3-phenyl-2-(phenylamino) thiazolidin-4-ones, **35a - 35e** (**Scheme 10**). The IR spectra of **35** showed bands due to CS, CO and NH groups, respectively. While, the ^{1}HNMR spectrum of **35a** (DMSO) showed three singlet signals at δ 3.8, 4.1 and 5.8 for the methylene of thiazolidinone, NH-amine and NH-imino protons respectively and a multiplet at δ 6.8 - 7.8 for aromatic protons. In the MS of **35a** showed *m/z* at 411 ($[M-2]^+$, 35%).

4. Conclusion

Despite the several existing methods for the synthesis of chromene derivatives, there still is demand for general strategies, which can efficiently provide variously substituted chromene systems. Thus, this work opened a new avenue for the synthesis of a variety of 2-imino-*N*-phenyl-2*H*-chromene-3-carboxamide, derivatives.

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