ISSN NO. 2320-5407

Journal homepage: http://www.journalijar.com

INTERNATIONAL JOURNAL OF ADVANCED RESEARCH

RESEARCH ARTICLE

Synthesis of Some New Fused Azolopyrimidines, Azolotriazines and Pyridines Containing Coumarines Moieties

Abdou O. Abdelhamid[*], Abdelgawad A. Fahmi and Abeer Al-Bahlol Ali
Department of Chemistry, Faculty of Science, Cairo University, Giza 12613, Egypt.

Manuscript Info

Manuscript History:

Received: 17 September 2013
Final Accepted: 22 September 2013
Published Online: October 2013

Key words:
Pyrazolo[1,5-*a*]pyrimidines, Triazolo[4,3-*a*]pyrimidines, Benzo[4,5]-imidazo[1,2-*a*]-pyrimidines, Pyrazolo[5,1-*c*][1,2,4]-triazines, benzo[*f*]chromene-3-one, chromen-2-one

Abstract

Pyrazolo[1,5-*a*]pyrimidines, [1,2,4]triazolo[4,3-*a*]pyrimidines, benzo[4,5]-imidazo[1,2-*a*]pyrimidines, pyrazolo[5,1-*c*][1,2,4]triazines, Triazolo[3,4-*c*][1,2,4]-triazines, benzo[4,5]imidazo[2,1-*c*][1,2,4]triazines, pyridenes are synthesized from each of 3-(3-(dimethylamino)acryloyl)-2*H*-chromen-2-one, and 2-(3-(dimethylamino)acryloyl)-3*H*-benzo[*f*]chromen-3-one and various reagents. The newly synthesized compounds were elucidated by elemental analysis, spectral data, chemical transformation and alternative synthetic route whenever possible.

1. Introduction

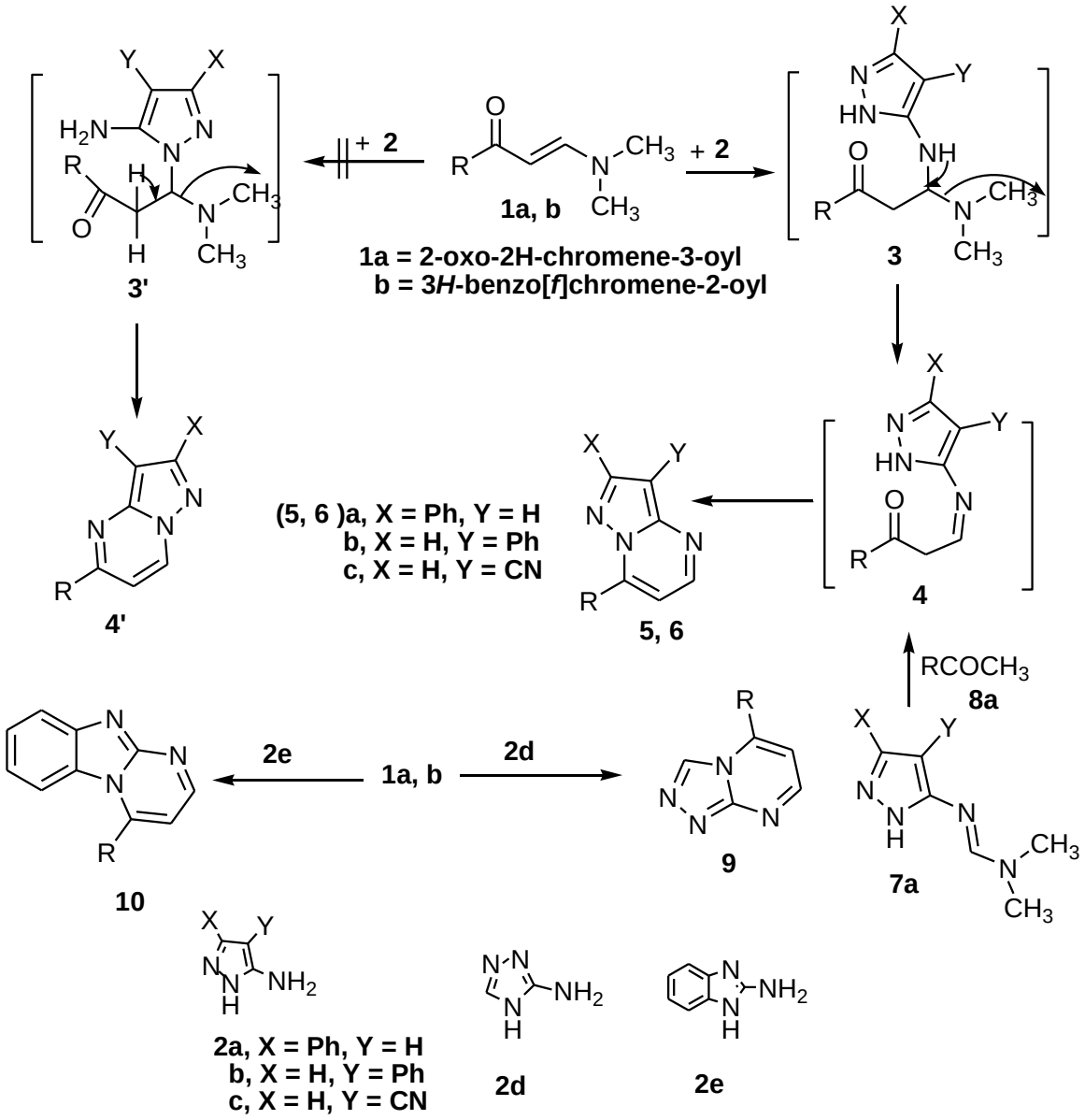
Coumarins constitute an important class of benzopyrones, exhibiting a broad range of biological activities such as anticoagulants [1], antimicrobial [2], antibacterial [3], anticancer [4], and anti-HIV activity [5]. The interesting biological activities of the coumarins make them attractive targets in organic synthesis. Coumarins having pyridine substitution at C-3 are reported to have interesting biological activity. Many 3-(2-pyridyl)- and 3-(3-pyridyl)coumarins are known for their useful bioactivities viz. antifungal [6-9], bactericidal [7], fish toxicity [7] and moth proofing activity [8]. Some of them are also known for their CNS depressant activity [9]. Moreover, pyrazolopyrimidine systems are reported as inhibitors for the synthesis of DNA and RNA in the cells of some types of cancer [10] and viruses [11]. In addition, a large number of thiazole derivatives have been found to exhibit pharmacological activity [12-17]. This work is an extension of an ongoing research program devoted to the synthesis and characterization of different heterocyclic ring systems endowed with potential biological activities [18-24].

2. Results and Discussion

2.1. Chemistry

Treatment of each of enaminones **1a** and **1b** with 3-amino-5-phenylpyrazole in refluxing acetic acid containing ammonium acetate yielded a single product, in each case, that was identified as 3-(2-phenylpyrazolo[1,5-*a*]pyrimidin-7-yl)-2*H*-chromen-2-one (**5a)** and 2-(2-phenylpyrazolo[1,5-*a*]pyrimidin-7-yl)-3*H*-benzo[*f*]chromen-3-one **(6a),** respectively (Scheme 1). The structure of the latter was elucidated on the basis of its spectral data (IR, MS, and ^{1}H NMR) and elemental analysis.

For example, its ^{1}H NMR ($CDCl_3$) spectrum of **5a** revealed signals at: δ = 7.16 (s, 1H, pyrazole H-5), 7.28-7.56 (m, 10H, ArH's), 8.77 (d, 1H, J = 4Hz, ArH,s), 8.82 (s, 1H, ArH). The formation of compounds **5** assumed to take place via an initial Michael addition of the exocyclic amino group in compound **2** to the activated double bond in **1** to give the acyclic non-isolable intermediate **3**, which undergo cyclization and aromatization via loss of both dimethylamine and water molecules producing the final isolable products **5a**. Although the endocyclic imino group in compounds **2a** is the most nucleophilic center, nevertheless, it is the most sterically hindered site [24] as shown in Scheme **1**.



Scheme 1

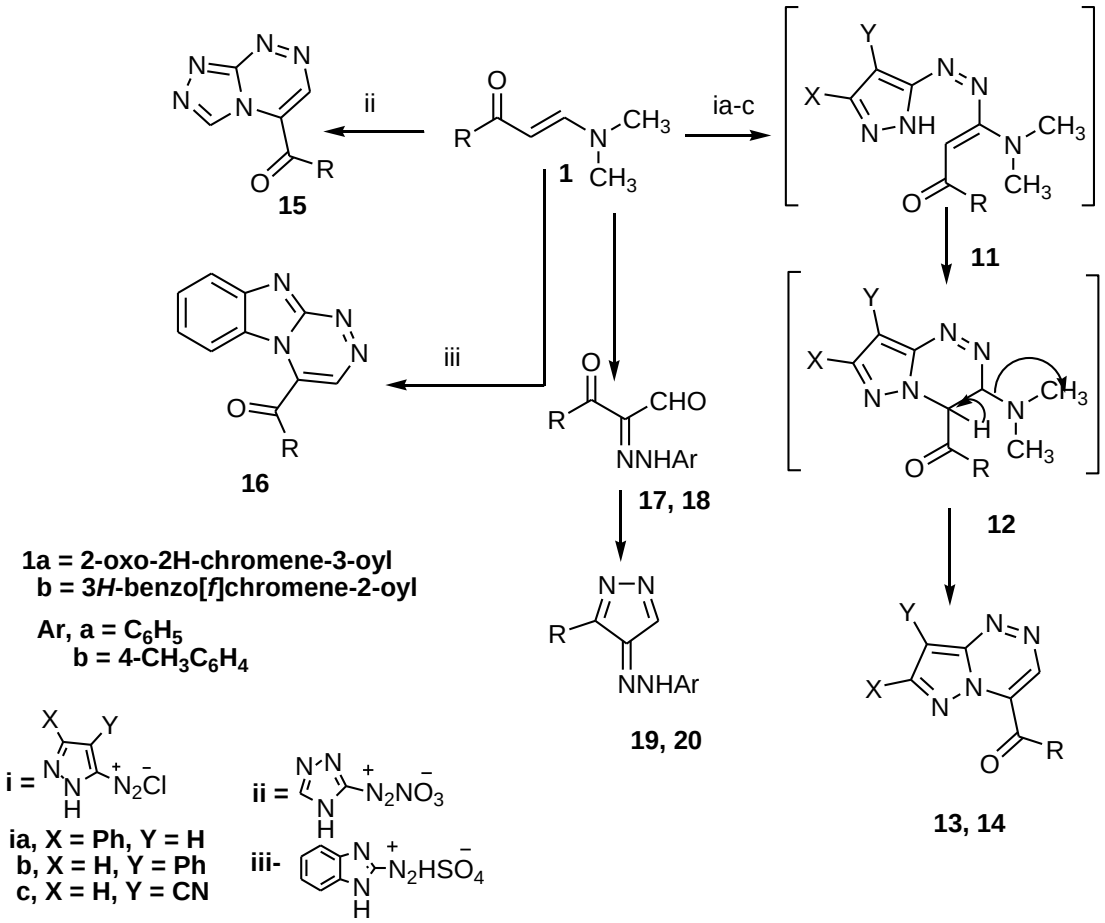
Structure **5a** was further confirmed *via* an independent synthesis by reacting equimolar amounts of *N*,*N*-dimethyl-*N'*-(3-phenyl-1*H*-pyrazol-5-yl)formamidine[24] (**7a**) with 3-acetyl-2*H*-chromen-2-one (**8a)** in ethanol under reflux to provide a product identical in all aspects (m.p., TLC, and spectra) with those of the proposed structure **5a**.

Analogously, compound **1a** was reacted with the appropriate of 3-amino-4-phenylpyrazole (**2b**), 3-amino-4-cyanopyrazole (**2c**), 3-aminotriazole (**2d**) or 2-aminbenzimidazole (**2e**) yilded 3-(3-phenylpyrazolo[1,5-*a*]pyrimidin-7-yl)-2*H*-chromen-2-one (**5b**), 7-(2-oxo-2*H*-chromen-3-yl)pyrazolo[1,5-*a*]pyrimidine-3-carbonitrile (**5c**), 3-([1,2,4]triazolo[4,3-a]pyrimidin-5-yl)-2H-chromen-2-one (**9a**), 3-benzo[4,5]imidazo[1,2-a]pyrimidin-4-yl-chromen-2-one (**10a**) (Scheme 1). Analogously, reactions of **1b** with the appropriate heterocyclic amines **2b-e** in acetic acid containing ammonium acetate gave, 2-(pyrazolo[1,5-a]pyrimidin-7-yl)-3*H*-benzo[*f*]chromen-3-one derivatives **6b, 6c**, 2-([1,2,4]triazolo[4,3-*a*]pyrimidin-5-yl)-*3H*-benzo[*f*]chromen-3-one (**9b**) and 2-benzo[4,5]imidazo[1,2-*a*]pyridin-1-yl-benzo[*f*]chromen-3-one (**10b**), respectively.

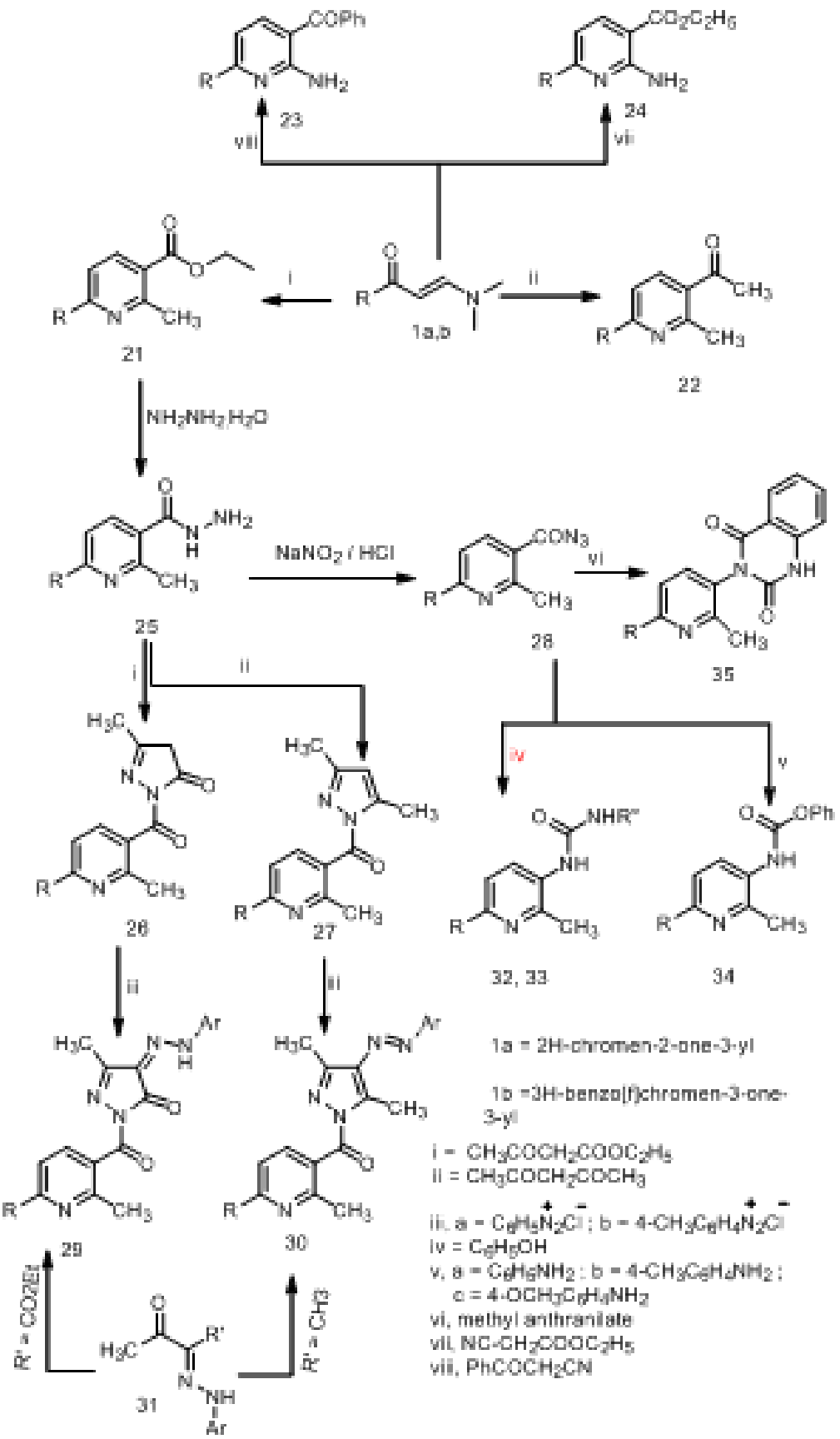
Next, treatment of 5-phenylpyrazole-3-diazonium chloride reacted with the appropriate of enaminones **1a** and **1b** in ethanolic sodium acetate solution afforded product in each case (tlc) that was identified as 1-(7-

phenylpyrazolo[5,1-*c*][1,2,4]triazin-3-yl) ethanone (**13a**) and 2-(7-phenyl-pyrazolo[5,1-*c*][1,2,4]triazine-3-carbonyl)-benzo[*f*]chromen-3-one (**14a**), respectively on the basis of its spectral data and elemental analysis (Scheme 2). For example, ^{1}H NMR spectrum of **13a** revealed signals at δ = 6.89 (s, 1H, pyrazole H-5), 7.31 (t, 1H, *J* = 8 Hz, ArH), 7.45-750 (m, 2H, ArH), 7.62 (m, 2H, ArH's), 7.98 (m, 2H, ArH's), 7.91 (d, 2H, *J* = 8 Hz, ArH's), 8.01 (d, 1H, *J* = 8 Hz, ArH), 10.82 (s, 1H, ArH).

Analogously, reactions of each enaminone **1a** and **1b** with the appropriate diazonium heterocyclic amines **ib,c**, **ii**, **iii** or aryene diazonium chloride in ethanolic sodium acetate afforded (**13, 14**)**b,c** , (**15, 16**)**a, b**, (**18, 19**)**a**, **b** respectively.



Scheme 2


23
24
viii
vii
21
1a,b
22
i
ii
$NH_2NH_2.H_2O$
25
$NaNO_2$ / HCl
28
35
vi
26
27
32, 33
34
iv
v
29
30
31
1a = 2H-chromen-2-one-3-yl
1b =3H-benzo[f]chromen-3-one-3-yl
i = $CH_3COCH_2COOC_2H_5$
ii = $CH_3COCH_2COCH_3$
iii, a = $C_6H_5\overset{+}{N}_2Cl^-$; b = 4-$CH_3C_6H_4\overset{+}{N}_2Cl^-$
iv = C_6H_5OH
v, a = $C_6H_5NH_2$; b = 4-$CH_3C_6H_4NH_2$;
c = 4-$OCH_3C_6H_4NH_2$
vi, methyl anthranilate
vii, $NC\text{-}CH_2COOC_2H_5$
viii, $PhCOCH_2CN$

Scheme 3

On the other hand, treatment enaminones **1a** and **1b** with each of ethyl acetoactate, acetylacetone, benzoylacetonitrile and ethyl cyanoacetate were carried out in acetic acid under reflux in the presence of ammonium acetate afforded **21**-**24**, respectively. Structures **21**-**24** were elucidated by elemental analyses, spectra and chemical transformation. For example, ^{1}H NMR spectrum of **21a**: δ = 1.43 (t, 3H, *J* = 7.5 Hz, $CH_2\underline{CH_3}$), 2.92 (s, 3H, CH_3, pyridine H-2), 4.40 (q, 2H, *J* = 7.5 Hz, $\underline{CH_2}CH_3$), 7.27-7.40 (m, 3H, ArH's), 7.58-7.70 (m, 2H, *J* = 8 Hz, ArH), 8.27-8.37 (m, 2H, ArH's), 8.93 (s, 1H, ArH). Compounds **21a** and **21b** were reacted with hydrazine hydrate to afford 2-methyl-6-(2-oxo-2*H*-chromen-3-yl)pyridine-3-carbohydrazide (**25a**) and 2-methyl-6-(3-oxo-3*H*-benzo[f]chromen-2-yl)pyridine-3-carbohydrazide (**25b**), respectively. The structure of **25** was elucidated by elemental analysis, spectra and chemical transformations. Thus, compounds **25**a and **25b** were reacted with each of ethyl acetoacetate, acetylacetone and nitrous acid, to give 5-methyl-2-[2-methyl-6-(2-oxo-2H-chromen-3-yl)-pyridine-3-carbonyl]-2,4-dihydro-pyrazol-3-one (**26a**), 5-methyl-2-[2-methyl-6-(3-oxo-3H-benzo[*f*]chromen-2-yl)-pyridine-3-carbonyl]-2,4-dihydro-pyrazol-3-one (**26b**), 3-[5-(3,5-dimethyl-pyrazole-1-carbonyl)-6-methyl-pyridin-2-yl]-chromen-2-one (**27a**), 2-[5-(3,5-dimethyl-pyrazole-1-carbonyl)-6-methyl-pyridin-2-yl]-benzo[*f*]chromen-3-one (**27b**), 3-(5-(azidoformyl)-6-methylpyridin-2-yl)-2*H*-chromen-2-one (**28a**) and 2-(5-(azidoformyl)-6-methylpyridin-2-yl)-3*H*-benzo[*f*]chromen-3-one (**28b**), respectively (Scheme 3). Structures **26**-**28** were confirmed by elemental analyses, spectral data and chemical transformations. Thus, treatment the compounds **26a,b** and **27a,b** with the appropriate arene diazonium chlorides gave the corresponding **29a,b** and **30a,b**. Structures **29** and **30** were confirmed by the reaction of of the appropriate **25a,b** with the appropriate **31a-d** in boiling acetic acid under reflux gave identical product in aspects (mp., mixed mp. and spectra) with corresponding compounds (**29, 30**)**a,b**. Structures of **28a** and **28b** were established by elemental analyses, spectra and chemical transformation. Thus, treatment of **28** with each of the appropriate aromatic amine in boiling dioxane and phenol in boiling benzene gave 1-(2-methyl-6-(2-oxo-2*H*-chromen-3-yl)pyridin-3-yl)-3-substituted urea **32a-c**, 1-(2-methyl-6-(3-oxo-3*H*-benzo[*f*]chromen-2-yl)pyridin-3-yl)-3-substituted urea **33a-c**, phenyl 2-methyl-6-(2-oxo-2*H*-chromen-3-yl)pyridin-3-ylcarbamate (**34a**) Structres **32-34** were confirmed by elemental analyses and spectral data.

3. Experimental

Instrumentation

All melting points are uncorrected. IR spectra were recorded in KBr using Pye Unicam SP-1000 Spectrophotometer. ^{1}H NMR and ^{13}C NMR spectra were recorded for DMSO-*d*6 and $CDCl_3$ solutions with TMS as internal reference using a Varian EM-200 MHz spectrometer. Mass spectra were recorded on AEI MS 30 mass spectrometer operating at 70eV. Elemental analyses were carried out at the Microanalytical Centre of Cairo University.

3.1. *Synthesis of pyrazolo[1,5-a]pyrimidines 5a-c, 6a-c, [1,2,4]triazolo[4,3-a]pyrimidines 9a, b and benzo[4,5]imidazo[1,2-a]pyrimidines 10a,b*

Method A: A mixture of the appropriate 3-(3-(dimethylamino)acryloyl)-2*H*-chromen-2-one (**1a**) and 2-(3-(dimethylamino)acryloyl)-3*H*-benzo[*f*]chromen-3-one (**1b**) (5 mmole), the appropriate heterocyclic compounds **2a-e** (5 mmole), ammonium acetate (0.37 g, 5 mmole) in acetic acid (20 mL) was reflux for 4 hrs. The resulting solid which formed was collected and recrystallized from the proper solvent to give pyrazolo[1,5-a]pyrimidines **5a-c**, **6a-c**, triazolo[4,3-*a*]pyrimidines **9a,b** and benzo[4,5]imidazo[1,2-*a*]pyrimidines **10a,b**, respectively.

Method B: Equimolar amount of *N*,*N*-dimethyl-*N'*-(3-phenyl-1*H*-pyrazol-5-yl)formamidine (**7a**) and 3-acetyl-2*H*-chromen-2-one (**8a)** (5 mmole) in ethanol (20 mL) and catalytic amount of piperidine was boiled under reflux for 2 hrs. The resulting solid was collected and recrystallized from acetic to give **5a**.

3.1.1. 3-(2-Phenylpyrazolo[1,5-a]pyrimidin-7-yl)-2H-chromen-2-one (5a). Yellow crystals from AcOH, yield (88%), mp: 268-70°C; IR (KBr): 3065 (CH, aromatic), 1727.9 (C=O), 1602 (C=C); ^{1}H NMR ($CDCl_3$): δ = 7.16 (s, 1H, pyrazole H-5), 7.28-7.56 (m, 10H, ArH's), 8.77 (d, 1H, J = 4Hz, ArH,s), 8.82 (s, 1H, ArH); ^{13}C NMR δ = 98.2, 105, 111, 116, 123, 123.8, 124, 128.2, 128.8, 130, 133, 134, 136, 145, 150, 154, 155, 156, 157; MS: m/z = 340 (M+1, 8.8%), 339 (M^+, 26.9%), 311 (41.1%), 262 (1.03%), 77 (100%), 63 (17.6%); *Anal.* Calcd. for $C_{21}H_{13}N_3O_2$ (339.35) C, 74.33; H, 3.86; N, 12.38. Found: C, 74.12; H, 3.67; N, 12.52 %.

3.1.2. 3-(3-Phenylpyrazolo[1,5-a]pyrimidin-7-yl)-2H-chromen-2-one (5b). Red crystals from AcOH, yield (85 %), mp: 234-36°C; IR (KBr): 3060 (CH, aromatic), 1725 (C=O), 1605 (C=C); ^{1}H NMR ($CDCl_3$): δ = 6.76-6.79 (m, 2H, ArH's), 7.26-7.60 (m, 8H, ArH's), 8.48 (d, 1H, *J* = 4Hz, ArH,s), 8.82 (s, 1H, ArH), 9.05 (s, 1H, pyrazole H-3); MS: m/z = 340 (M+1, 19.45%, 339 (M^+, 76.92%), 311 (20.74%), 142 (71.23%), 127 (41.34%,), 115 (100%), 102 (25.74%), 89 (44.77%), 77 (28.54%), 63 (47.52%); *Anal.* Calcd. for $C_{21}H_{13}N_3O_2$ (339.35) C, 74.33; H, 3.86; N, 12.38. Found: C, 74.28; H, 3.77; N, 12.45 %.

3.1.3. 7-(2-Oxo-2H-chromen-3-yl)pyrazolo[1,5-a]pyrimidine-3-carbonitrile (5c). Yellow crystals from EtOH, yield (82 %), mp: 278-80°C; IR (KBr): 3107 (CH, aromatic), 2233 (CN), 1721 (C=O), 1606 (C=C); ^{1}H NMR ($CDCl_3$): δ = 7.27-7.37 (m, 2H, ArH's), 7.56-7.62 (m, 3H, ArH's), 8.68 (s, 1H, pyrazole H-3), 8.89 (s, 1H, ArH), 9.08 (d, 1H, *J* = 4Hz, ArH,s); MS: m/z = 289 (M+2, 14.54%), 288 (M^+, 76.84%), 260 (100%), 244 (22.29%), 231 (25.76%), 203 (36.23%), 193 (35.0%), 177 (39.72%), 154 (29.0%), 143 (71.23%), 128 (25.4%,), 115 (40.2%), 102 (25.36%), 87 (48.24%), 77 (52.86%), 65 (25.34%); *Anal.* Calcd. for $C_{16}H_8N_4O_2$ (288.26) C, 66.67; H, 2.80; N, 19.44. Found: C, 66.75; H, 2.99; N, 19.62 %.

3.1.4. 2-(2-Phenylpyrazolo[1,5-a]pyrimidin-7-yl)-3H-benzo[f]chromen-3-one (6a). Yellow crystals from DMF, yield (80 %), mp: 310-12°C; IR (KBr): 3062 (CH, aromatic), 1724 (C=O), 1608 (C=C); ^{1}H NMR ($(CD_3)_2SO$): δ = 7.23 (s, 1H, pyrazole H-5), 7.27-7.85 (m, 12H, ArH's), 9.25 (d, 1H, *J* = 8Hz, ArH's), 8.68 (d, 1H, *J* = 8 *H*z, ArH); ^{13}C NMR δ = 100, 107, 113, 113.8, 119, 122, 124.6, 125.8, 127, 127.4, 128, 130, 132, 132.5, 134, 135, 136, 145, 150, 152, 154, 156, 159; MS: m/z = 390 (M^+, 75.36%), 362 (100%), 344 (12.68%), 304 (4.21%), 284 (8.45%), 256 (6.80%), 229 (3.98%), 206 (6.52%), 189 (9.94%), 163 (20.24%), 138 (14.65%,), 114 (12.08%), 76 (77.15%), 51 (28.86%); *Anal.* Calcd. for $C_{25}H_{15}N_3O_2$ (389.41) C, 77.11; H, 3.88; N, 10.79. Found: C, 77.24; H, 4.00; N, 10.97 %.

3.1.5. 2-(3-Phenylpyrazolo[1,5-a]pyrimidin-7-yl)-3H-benzo[f]chromen-3-one (6b). Red crystals from Dioxane, yield (80 %), mp: 310-12°C; IR (KBr): 3058 (CH, aromatic), 1720 (C=O), 1608 (C=C); ^{1}H NMR ($(CD_3)_2SO$): δ = 6.76 (d, 2H, *J* = 8Hz, ArH's), 7.29-7.85 (m, 11H, AH's), 8.35 (d, 1H, *J* = 8Hz, ArH's), 9.08 (s, 1H, pyrazole H-3); MS: m/z = 390 (M^+, 26.4%), 389 (100%), 360 (21.1%), 202 (19.8%), 180 (8.8%), 167 (6.80%), 229 (3.98%), 206 (6.52%), 165 (26.4%), 189 (9.94%), 163 (20.24%), 138 (14.65%,), 114 (7.7%), 89 (36.3%), 76 (24.2%), 51 (22.0%); *Anal.* Calcd. for $C_{25}H_{15}N_3O_2$ (389.41) C, 77.11; H, 3.88; N, 10.79. Found: C, 77.00; H, 3.78; N, 11.0%.

3.1.6. 7-(3-oxo-3H-benzo[f]chromen-2-yl)pyrazolo[1,5-a]pyrimidine-3-carbonitrile (6c). Yellow crystals from DMF, yield (84 %), mp: 350-52°C; IR (KBr): 3116 (CH, aromatic), 2233 (CN), 1712 (C=O), 1616 (C=C); ^{1}H NMR ($(CD_3)_2SO$): δ = 7.38 (d, 1H, *J* = 8Hz, ArH's), 7.59-7.86 (m, 6H, AH's), 8.14 (d, 1H, *J* = 8Hz, ArH's), 8.65 (s, 1H, pyrazole H-3); 9.04 (s, 1H, ArH's); MS: m/z = 340 (M+2, 5.2%), 339 (M+1, 14.9%), 338 (M^+, 64.2%), 309 (28.4%), 310 (100%), 282 (11.09%), 254 (14.90%), 194 (16.4%), 177 (11.9%), 163 (23.1%), 139 (14.2%), 114 (18.7%), 91 (20.9%,), 89 (19.4%), 88 (41.0%), 76 (14.9%), 63 (31.3%), 52 (29.1%); *Anal.* Calcd. for $C_{20}H_{10}N_4O_2$ (338.32) C, 71.00; H, 2.98; N, 16.56. Found: C, 71.12; H, 3.15; N, 16.57%.

3.1.7. 3-([1,2,4]triazolo[4,3-a]pyrimidin-5-yl)-2H-chromen-2-one (9a). Beige crystals from EtOH, yield (80 %), mp: 232-34°C; IR (KBr): 3061 (CH, aromatic), 1726 (C=O), 1602 (C=C); ^{1}H NMR ($CDCl_3$): δ = 6.96 (d, 1H, *J* = 8 Hz, ArH's), 7.22-7.45 (m, 4H, AH's), 8.43 (d, 1H, *J* = 8Hz, ArH's), 8.87 (s, 1H, pyrazole H-3); 9.04 (s, 1H, ArH's); ^{13}C NMR δ = 107, 115, 116, 123.5, 123.8, 128, 132, 136, 143, 149, 155, 156, 157, 169; MS: m/z = 265 (M+1, 16.9%), 264 (M^+, 100%), 236 (60.98%), 221 (2.64%), 209 (7.7%), 182 (7.27%), 169 (20.29%), 156 (10.5%), 132 (18.8%), 127 (42.57), 126 (54.64%), 113 (22.73%), 102 (32.77%), 89 (25.57%), 87 (48.55%), 77 (36.54%), 65 (20.13%); *Anal.* Calcd. for $C_{14}H_8N_4O_2$ (264.24) C, 63.64; H, 3.05; N, 21.20. Found: C, 63.45; H, 3.12; N, 21.35 %.

3.1.8. 2-([1,2,4]triazolo[4,3-a]pyrimidin-5-yl)-3H-benzo[f]chromen-3-one (9b). Brown crystals from EtOH, yield (80 %), mp: 232-34°C; IR (KBr): 3061 (CH, aromatic), 1726 (C=O), 1612 (C=C); ^{1}H NMR ($(CD_3)_2SO$): δ = 7.38 (d, 1H, *J* = 8Hz, ArH's), 7.59-7.86 (m, 6H, AH's), 8.14 (d, 1H, *J* = 8Hz, ArH's), 8.65 (s, 1H, pyrazole H-3); 9.04 (s, 1H, ArH's); MS: m/z = 316 (M+2, 5.2%), 315 (M+1, 14.9%), 314 (M^+, 10.1%), 238 (5%), 225 (19.3%), 223 (24.4%), 211 (14.3%), 102 (27.7%), 76 (19.3%), 51 (48.7%); *Anal.* Calcd. for $C_{18}H_{10}N_4O_2$ (314.3) C, 68.79; H, 3.21; N, 17.83. Found: C, 68.94; H, 3.3.35; N, 17.65 %.

3.1.9. 3-Benzo[4,5]imidazo[1,2-a]pyrimidin-4-yl-chromen-2-one (10a). Brown crystals from EtOH, yield (80 %), mp: 164-66°C; IR (KBr): 3063 (CH, aromatic), 1725 (C=O), 1605 (C=C); ^{1}H NMR ($CDCl_3$): δ = 6.89 (d, 1H, *J* = 8Hz, ArH's), 7.26-7.61 (m, 6H, AH's), 7.80 (d, 1H, *J* = 8Hz, ArH), 8.20 (d, 1H, *J* = 8Hz, ArH); 8.53 (d, 1H, *J* = 8Hz, ArH), 8.75 (s, 1H, ArH); ^{13}C NMR δ= 104.5, 111.2, 114, 116, 119, 122, 122.5, 123.4, 123.8, 127.8, 128, 133, 138, 146.5, 153.7, 154.3, 154.8, 157, 159.7; MS: m/z = 314 (M+1, 18.46%), 313 (M^+, 90.32%), 312 (M-1, 42.34%), 283 (29.89%), 223 (24.4%), 307 (15.84%), 300 (14.76%), 272 (17.38%), 209 (21.13%), 263 (28.23%), 202 (16.9%), 200 (26.79%), 251 (15.84%), 195 (30.36%), 242 (19.27%), 236 (39.73%), 225 (27.87%), 222 (36.06%), 213 (19.73%), 207 (19.95%), 201 (24.88%),189 (50.48%), 173 (77.62%), 164 (26.48%), 155 (36.60%), 145 (28.92%), 134 (20.749%), 122 (26.28%), 116 (26.87%), 111 (27.66), 106 (29.45%), 100 (26.84%), 89 (95.02%), 77 (100%), 65 (19.56%); *Anal.* Calcd. for $C_{19}H_{11}N_3O_2$ (313.31) C, 72.84; H, 3.54; N, 13.41. Found: C, 72.71; H, 3.42; N, 13.58 %.

3.1.10. 2-Benzo[4,5]imidazo[1,2-a]pyrimidin-4-yl-benzo[f]chromen-3-one (10b). Brown crystals from DMF, yield (85 %), mp: 280-82°C; IR (KBr): 3058 (CH, aromatic), 1720 (C=O), 1624 (C=N), 1589 (C=C); ^{1}H NMR ($CDCl_3$): δ = 6.89 (d, 1H, *J* = 8Hz, ArH's), 7.26-7.93 (m, 9H, AH's), 7.80 (d, 1H, *J* = 8Hz, ArH), 8.20 (d, 1H, *J* = 8Hz, ArH); 8.75 (s, 1H, ArH); MS: m/z = 364 (M+1, 7.84%), 363 (M^+, 56.50%), 335 (29.04%), 306 (18.41%), 289 (9.96%), 273 (16.93%), 249 (19.21%), 197 (31.97%), 189 (20.34%), 167 (39.11%), 163 (37.97%), 157 (16.84%), 151

(47.28%), 144 (26.84%), 139 (100%), 127 (68.91%), 114 (65.81%), 102 (27.03%), 89 (39.99%), 75 (60.08%), 62 (61.40%), 50 (71.89%); *Anal.* Calcd. for $C_{23}H_{13}N_3O_2$ (363.37) C, 76.02; H, 3.61; N, 11.56. Found: C, 76.13; H, 3.52; N, 11.68 %.

3.2. Synthesis of pyrazolo[5,1-c]triazines 13a-c, 14a,c, triazolo[3,4-c]triazines 15a,b, benzo[4,5]imidazo[2,1-c][1,2,4]triazine 16a and 2-(2-phenylhydrazono)propanals (17,18)a,b

A solution of the appropriate diazonium salt of heterocyclic amines (3-amino-5-phenylpyrazole (**3a**), 3-amino-4-phenylpyrazole (**3b**), 3-amino-4-cyanopyrazole (**3c**), 3-amino-1,2,4-triazole (**3d**), 2-aminobenzimidazole (**3e**)) (5 mmole) was added to a mixture of the appropriate of 3-(3-(dimethylamino)acryloyl)-2*H*-chromen-2-one (**1a**) or 2-(3-(dimethylamino)acryloyl)-3*H*-benzo[*f*]chromen-3-one (**1b**) (5 mmole), sodium acetate (0.65 g, 5 mmole) in ethanol (30 mL) at 0-5^{o}C while stirring. The resulting solid which formed after 3 hrs was collected, washed with water and recrystallized from acetic acid to give **13a-c**, **14a-c**, **15a,b**, **16a,b** and (**17, 18)a,b**, respectively.

3.2.1. 3-(7-Phenyl-pyrazolo[5,1-c][1,2,4]triazine-4-carbonyl)-chromen-2-one (13a). Olive crystals from EtOH, yield (96 %), mp: 168-70°C; IR (KBr): 3058 (CH, aromatic), 1724 (C=O), 1608 (C=C); ^{1}H NMR δ = 6.89 (s, 1H, pyrazole H-5), 7.31 (t, 1H, *J* = 8 Hz, ArH), 7.45-750 (m, 2H, ArH), 7.62 (m, 2H, ArH's), 7.98 (m, 2H, ArH's), 7.91 (d, 2H, *J* = 8 Hz, ArH's), 8.01 (d, 1H, *J* = 8 Hz, ArH), 10.82 (s, 1H, ArH); MS: m/z = 340 (M-CO, 21.16%), 309 (26.27%), 303 (23.65%), 298 (22.83%), 289 (30.35%), 279 (25.39%), 271 (31.06%), 242 (44.60%), 202 (43.61%), 173 (93.17%), 158 (49.20%), 144 (100%), 129 (54.50%), 116 (62.15%), 105 (49.20%), 89 (78.05%), 77 (57.15%), 65 (25.41%); *Anal.* Calcd. for $C_{21}H_{12}N_4O_3$ (368.34) C, 68.48; H, 3.28; N, 15.21. Found: C, 68.94; H, 3.35; N, 15.65 %.

3.2.2. 3-(8-Phenyl-pyrazolo[5,1-c][1,2,4]triazine-4-carbonyl)-chromen-2-one (13b). Brown crystals from benzene-pet.ether, yield (95 %), mp: 196-98°C; IR (KBr): 3058 (CH, aromatic), 1728 (C=O), 1608 (C=C); ^{1}H NMR ($CDCl_3$): δ = 7.11-7.95 (m, 10H, ArH's), 9.32 (s, 1H, pyrazole H-3), 9.32 (s, 1H, ArH); ^{13}C NMR δ = 103, 116.2, 116.8, 125.4, 126, 127.4, 128, 130, 131, 134, 135, 151.2, 151.8, 152.4, 154, 157, 160, 182; MS: m/z = 341 (28.69%), 327 (14.18%), 302 (10.23%), 271 (16.04%), 261 (11.22%), 251 (15.77%), 245 (12.39%), 239 (18.38%), 221 (18.19%), 134 (25.60%), 128 (14.92%), 125 (22.76%), 112 (22.61%), 103 (40.30%), 97 (29.58%), 89 (61.27%), 76 (21.69%), 69 (28.00 %); *Anal.* Calcd. for $C_{21}H_{12}N_4O_3$ (368.34) C, 68.48; H, 3.28; N, 15.21. Found: C, 68.32; H, 3.30; N, 15.45 %.

3.2.3. 4-(2-Oxo-2H-chromene-3-carbonyl)-pyrazolo[5,1-c][1,2,4]triazine-8-carbonitrile (13c). Yellow crystals from EtOH, yield (90 %), mp: 200-202°C; IR (KBr): 3067 (CH, aromatic), 2228 (CN), 1725.9 (C=O), 1609 (C=C); ^{1}H NMR ($CDCl_3$): δ = 7.11-7.95 (m, 5H, ArH's), 8.10 (s, 1H, pyrazole H-3), 9.54 (s, 1H, ArH); MS: m/z = 289 (M-CO, 15.72%), 275 (17.94%), 260 (29.50%), 244 (21.57%), 198 (20.46%), 173 (67.07%), 145 (52.78%), 130 (26.85%), 118 (41.60%), 108 (100%), 89 (78.41%), 77 (38.24%), 65 (27.18 %); *Anal.* Calcd. for $C_{16}H_7N_5O_3$ (317.26) C, 60.57; H, 2.22; N, 22.07. Found: C, 60.57; H, 2.22; N, 22.07 %.

3.2.4. 2-(8-Phenyl-pyrazolo[5,1-c][1,2,4]triazine-4-carbonyl)-benzo[f]chromen-3-one (14a). Yellow crystals from EtOH, yield (90 %), mp: 280-82°C; IR (KBr): 3067 (CH, aromatic), 1720.4 (C=O), 1627 (C=N), 1589 (C=C); ^{1}H NMR ($CDCl_3$): δ = 6.91 (s, 1H, pyrazple H-4), 7.32-7.95 (m, 11H, ArH's), 8.45 (d, 1H, *J* = 8 Hz, ArH), 9.54 (s, 1H, ArH); ^{13}C NMR δ = 104, 109, 120, 122, 125, 126, 127.2, 127.6, 128, 128.3, 129.5, 130.8, 132, 134, 151.5, 151.7, 151.9, 153.5, 160, 182; MS: m/z = 420 (M+2, 3.75%), 418 (M^+, 30.30%), 391 (5.89%), 195 (30.79%), 163 (14.17%), 150 (10.69%), 139 (97.33%), 127 (19.50%), 113 (11.95%), 102 (23.91%), 88 (34.25%), 76 (100%), 65 (11.91%); *Anal.* Calcd. for $C_{25}H_{14}N_4O_3$ (418.4) C, 71.77; H, 3.37; N, 13.39. Found: C, 71.68; H, 3.29; N, 13.45 %.

3.2.5. 4-(3-Oxo-3H-benzo[f]chromene-2-carbonyl)-pyrazolo[5,1-c][1,2,4]triazine-8- carbonitrile (14c).

Yellow crystals from EtOH, yield (91.5 %), mp: 260-63°C; IR (KBr): 3058 (CH, aromatic), 2225 (CN), 1712 (C=O), 1639 (C=N), 1600 (C=C); ^{1}H NMR ($CDCl_3$): δ = 7.32-7.95 (m, 7H, ArH's), 8.42 (d, 1H, *J* = 8 Hz, ArH), 9.62 (s, 1H, ArH); MS: m/z = 366 (M-1, 5.79%), 223 (10.63%), 168 (9.85%), 151 (19.47%), 143 (12.75%), 139 (100%), 126 (11.20%), 115 (10.68%), 89 (17.08%), 77 (38.64%), 63 (40.53%); *Anal.* Calcd. for $C_{20}H_9N_5O_3$ (367.32) C, 65.40; H, 2.47; N, 19.07. Found: C, 65.22; H, 2.53; N, 19.24 %.

3.2.6. 3-([1,2,4]Triazolo[3,4-c][1,2,4]triazine-5-carbonyl)-chromen-2-one (15a). Red crystals from AcOH, yield (89 %), mp: 180-82°C; IR (KBr): 3058 (CH, aromatic), 1724 (C=O), 1628 (C=N), 1604 (C=C); ^{1}H NMR ($CDCl_3$): δ = 7.32-7.95 (m, 5H, ArH's), 8.78 (s, 1H, ArH), 9.48 (s, 1H, triazole H-5); *Anal.* Calcd. for $C_{14}H_7N_5O_3$ (293.24) C, 57.34; H, 2.41; N, 23.88. Found: C, 57.45; H, 2.34; N, 24.00 %.

3.2.7. 3-([1,2,4]Triazolo[3,4-c][1,2,4]triazine-5-carbonyl)-benzo[h]chromen-2-one (15b). Yellow crystals from EtOH, yield (90 %), mp: 200-202°C; IR (KBr): 3058 (CH, aromatic), 1724 (C=O), 1628 (C=N), 1604 (C=C); ^{1}H NMR ($(CD_3)_2SO$): δ = 7.25-7.61 (m, 3H, ArH's), 7.98-8.02 (m, 2H, ArH's), 8.9-8.41 (m, 2H, AH's), 9.05 (s, 1H, ArH), 9.28 (s, 1H, triazole H-5); MS: m/z = 344 (M+1, 20.52%), 315 (10.51%), 205 (15.45%), 195 (18.33%), 176

(9.50%), 151 (15.94%), 148 (10.91%), 139 (1%), 126 (8.38%), 75 (13.95%), 65 (13.60%); *Anal.* Calcd. for $C_{18}H_9N_5O_3$ (343.3) C, 62.98; H, 2.64; N, 20.40 Found: C, 62.98; H, 2.64; N, 20.40 %.

3.2.8. 3-(Benzo[4,5]imidazo[2,1-c][1,2,4]triazine-4-carbonyl)-chromen-2-one (16a). Yellow crystals from EtOH, yield (83 %), mp: 164-66°C; IR (KBr): 3128 (CH, aromatic), 1716 (C=O), 1639 (C=N), 1604 (C=C); ^{1}H NMR ($(CD_3)_2SO$): δ = 7.25-7.35 (m, 1H, ArH), 7.47-7.50 (m, 1H, ArH), 7.72-7.92 (m, 5H, AH's), 8.72 (d, 1H, *J* = 8Hz, ArH), 8.95 (d, 1H, *J* = 8Hz, ArH), 9.13 (s, 1H, ArH); *Anal.* Calcd. for $C_{19}H_{10}N_4O_3$ (342.31) C, 66.67; H, 2.94; N, 16.37 Found: C, 66.75; H, 3.00; N, 16.25 %.

3.2.9. 2-(2-Phenylhydrazono)-3-oxo-3-(2-oxo-2H-chromen-3-yl)propanal (17a). Orange crystals from AcOH, yield (96 %), mp: 150-52°C; IR (KBr): 3280 (NH), 3058 (CH, aromatic), 2858, 2795 (CHO), 1728, 1681 (C=O), 1608 (C=C); ^{1}H NMR ($CDCl_3$): δ = 6.62 (t, 1H, *J* = 8Hz, ArH), 7.15-7.42 (m, 7H, ArH's), 7.76 (d, 1H, *J* = 8Hz, ArH), 8.22 (s, 1H, ArH), 10.73 (s, 1H, CHO), 14.56 (s, br. 1H, NH); ^{13}C NMR δ = 113, 116.2, 116.6, 118, 125, 128, 130, 132.4, 135, 150, 151, 157, 159, 162, 181, 193; MS: m/z = 320 (M^+, 1.57%), 314 (25.91%), 302 (10.45%), 300 (32.17%), 255 (23.63%), 243 (37.72%), 229 (15.53%), 212 (57.97%), 199 (24.13%), 188 (84.64%), 163 (30.07%), 151 (47.68%), 136 (32.84%), 126 (34.20%), 112 (49.21%), 93 (76.73%), 88 (63.72%), 76 (100%), 65 (31.58%); *Anal.* Calcd. for $C_{18}H_{12}N_2O_4$ (320.3) C, 67.50; H, 3.78; N, 8.75 Found: C, 67.38; H, 3.85; N, 8.57 %.

3.2.10. 2-(2-p-Tolylhydrazono)-3-oxo-3-(2-oxo-2H-chromen-3-yl)propanal (17b). Brown crystals from AcOH, yield (95 %), mp: 170-72°C; IR (KBr): 3270 (NH), 3058 (CH, aromatic), 2858, 2750 (CHO), 1724, 1681 (C=O), 1604 (C=C); ^{1}H NMR ($CDCl_3$): δ = 2.32 (s, 3H, $CH_3C_6H_4$-*p*), 7.15-7.32 (m, 7H, ArH's), 7.73 (d, 1H, *J* = 8Hz, ArH), 8.32 (s, 1H, ArH), 10.72 (s, 1H, CHO), 14.66 (s, br. 1H, NH); MS: m/z = 344 (M+1, 1.88%), 329 (28.06%), 328 (86.93%), 300 (44.63%), 271 (42.13%), 255 (21.33%), 245 (11.57%), 243 (39.28%), 225 (42.73%), 213 (47.86%), 200 (20.83%), 188 (100%), 173 (46.22%), 165 (15.69%), 145 (16.20%), 139 (20.75%), 126 (25.67%), 106 (71.39%), 100 (62.49%), 91 (49.82%), 88 (87.74%), 76 (86.78%), 65 (30.20%), 62 (71.82%); *Anal.* Calcd. for $C_{19}H_{14}N_2O_4$ (334.33) C, 68.26; H, 4.22; N, 8.38 Found: C, 68.12; H, 4.18; N, 8.24 %.

3.2.11. 2-(2-Phenylhydrazono)-3-oxo-3-(3-oxo-3H-benzo[f]chromen-2-yl)propanal (18a). Orange crystals from EtOH, yield (96 %), mp: 250-52°C; IR (KBr): 3180 (NH), 3058 (CH, aromatic), 2858, 2750 (CHO), 1724, 1681 (C=O), 1627 (C=N), 1596 (C=C); ^{1}H NMR ($CDCl_3$): δ = 6.68 (t, 1H, J = 8 Hz, ArH), 7.15-7.68 (m, 9H, ArH's), 8.06 (d, 1H, *J* = 8 Hz, ArH), 8.32 (s, 1H, ArH), 10.72 (s, 1H, CHO), 14.66 (s, br. 1H, NH); MS: m/z = 371 (M+1, 2.19%), 370 (M^+, 2.57%), 168 (13.94%), 152 (37.31%), 151 (33.92%), 149 (18.46%), 139 (73.98%), 128 (12.36%), 115 (19.65%), 104 (11.52%), 93 (12.58%), 89 (24.27%), 87 (13.97%), 77 (100%), 65 (18.77%); *Anal.* Calcd. for $C_{22}H_{14}N_2O_4$ (370.36) C, 71.35; H, 3.81; N, 7.56 Found: C, 71.51; H, 3.75; N, 7.69 %.

3.2.12. 2-(2-p-Tolylhydrazono)-3-oxo-3-(3-oxo-3H-benzo[f]chromen-2-yl)propanal (18b). Deep brown crystals from EtOH, yield (95 %), mp: 180-82°C; IR (KBr): 3230 (NH), 3055 (CH, aromatic), 2858, 2750 (CHO), 1724, 1681 (C=O), 1627 (C=N), 1585 (C=C); ^{1}H NMR ($CDCl_3$): δ = 2.23 (s, 3H, $CH_3C_6H_4$-*p*), 7.35-7.83 (m, 9H, ArH's), 8.06 (d, 1H, *J* = 8 Hz, ArH), 8.32 (s, 1H, ArH), 10.72 (s, 1H, CHO), 14.66 (s, br. 1H, NH); ^{13}C NMR δ = 20.5, 110, 117, 120, 122, 125, 126, 127, 130.2, 130.8, 132, 137, 142, 151, 153, 156, 162, 181, 193; MS: m/z = 385 (M+1, 0.23%), 384 (M^+, 0.73%), 223 (31.12%), 151 (28.30%), 139 (100%), 112 (12.19%), 106 (29.81%), 91 (31.79%), 77 (29.57%), 65 (15.43%); *Anal.* Calcd. for $C_{23}H_{16}N_2O_4$ (384.38) C, 71.87; H, 4.20; N, 7.29 Found: C, 71.99; H, 4.18; N, 7.42 %.

*3.3. Synthesis of pyrazol***es**

A mixture of the appropriate **(17, 18)a-c** (5 mmole) and hydrazine hydrate (1 mL, 20 mmole) in ethanol (15 mL) was refluxed for 2 hrs. The resulting solid was collected and recrystallized to give (**19, 20)a,b**, respectively.

3.3.1. 3-(4-Phenylazo-1H-pyrazol-3-yl)-chromen-2-one (19a). Pale brown crystals from AcOH, yield (85 %), mp: > 300°C; IR (KBr): 3275 (NH), 3066 (CH, aromatic), 1678, (C=O), 1608 (C=C); ^{1}H NMR ($CDCl_3$): 7.25-7.83 (m, 9H, ArH's), 8.85 (s, 1H, ArH), 8.64 (s, 1H, pyrazol, H-5), 11.66 (s, br. 1H, NH); MS: m/z = 317 (M+1, 16.49%), 297 (11.56%), 201 (10.39%), 189 (14.55%), 182 (9.83%), 156 (13.42%), 154 (17.32%), 146 (11.95%), 129 (12.59%), 116 (15.83%), 104 (23.25%), 99 (19.08%), 90 (35.24%), 77 (100^), 65 (31.32%); *Anal.* Calcd. for $C_{18}H_{12}N_4O_2$ (316.31) C, 68.35; H, 3.82; N, 17.71 Found: C, 68.14; H, 3.99; N, 17.67 %

3.3.2. 3-(4-p-Tolylazo-1H-pyrazol-3-yl)-chromen-2-one (19b). Beige crystals from AcOH, yield (85 %), mp: 240-42°C; IR (KBr): 3230 (NH), 3055 (CH, aromatic), 1681 (C=O), 1608 (C=C); ^{1}H NMR ($CDCl_3$): δ = 2.24 (s, 3H, $CH_3C_6H_4$-*p*), 7.05-7.75 (m, 8H, ArH's), 8.06 (d, 1H, *J* = 8 Hz, ArH), 8.32 (s, 1H, ArH), 14.66 (s, br. 1H, NH); MS: m/z = 331 (M+1, 1.05%), 330 (M^+, 2.27%), 284 (34.62%), 253 (100%), 225 (44.05%), 197 (53.94%), 180 (9.58%), 168 (21.60%), 151 (48.34%), 140 (60.18%),128 (14.28%), 115 (92.37%), 101 (27.45%), 91 (18.71%), 75 (60.47%), 62 (58.95%); *Anal.* Calcd. for $C_{19}H_{14}N_4O_2$ (330.34) C, 69.08; H, 4.27; N, 16.96 Found: C, 69.15; H, 4.35; N, 17.15 %

3.3.3. 2-(4-Phenylazo-1H-pyrazol-3-yl)-benzo[f]chromen-3-one (20a). Beige crystals from EtOH, yield (87 %), mp: 250-52°C; IR (KBr): 3250 (NH), 3055 (CH, aromatic), 1685 (C=O), 1612 (C=C)); ^{1}H NMR ($CDCl_3$): δ = 7.30-7.78 (m, 11H, ArH's), 8.15 (d, 1H, *J* = 8 Hz, ArH), 8.45 (s, 1H,Pyrazole H-5), 11.66 (s, br. 1H, NH); MS: m/z = 365 (M-1, 0.21%), 362 (42.91%), 234 (21.04%), 205 (25.84%), 178 (33.84%), 176 (44.84%), 163 (15.55%), 151 (100%), 139 (26.82%), 127 (9.90%), 126 (21.89%), 113 (13.58%), 111 (18.82%), 98 (28.29%), (89 (21.49%), 86 (49.58%), 77 (21.50%), 66 (28.92%) ; *Anal.* Calcd. for $C_{22}H_{14}N_4O_2$ (366.37) C, 72.12; H, 3.85; N, 15.29 Found: C, 72.00; H, 4.15; N, 15.37 %

3.3.4. 2-(4-p-Tolylazo-1H-pyrazol-3-yl)-benzo[f]chromen-3-one (20b). Brown crystals from AcOH, yield (87 %), mp: 300-302°C; IR (KBr): 3230 (NH), 3055 (CH, aromatic), 1701 (C=O), 1620 (C=N), 1604 (C=C); ^{1}H NMR ($CDCl_3$): δ = 2.23 (s, 3H, $CH_3C_6H_4$-*p*), 7.00-7.87 (m, 10H, ArH's), 8.06 (d, 1H, *J* = 8 Hz, ArH), 8.78 (s, 1H, pyrazole H-5), 11.66 (s, br. 1H, NH); MS: m/z = 380 (M^+, 0.01%), 323 (3.70%), 171 (4.67%), 141 (22.27%), 127 (22.02%), 114 (100%), 88 (21.60%), 77 5.40%), 65 (4.34%); *Anal.* Calcd. for $C_{23}H_{16}N_4O_2$ (380.4) C, 72.62; H, 4.24; N, 14.73 Found: C, 72.80; H, 4.35; N, 14.65 %.

3.5. Ethyl 2-methyl-6-(2-oxo-2H-chromen-3-yl)pyridine-3-carboxylate (21a), ethyl 2-methyl-6-(3-oxo-3H-benzo[f]chromen-2-yl)pyridine-3-carboxylate (21b), 3-(5-acetyl-6-methylpyridin-2-yl)-2H-chromen-2-one (22a), 2-(5-acetyl-6-methylpyridin-2-yl)-3H-benzo[f]chromen-3-one (22b), 3-(6-Amino-5-benzoyl-pyridin-2-yl)chromen-2-one (23a), 2-(6-Amino-5-benzoyl-pyridin-2-yl)-benzo[f]chromen-3-one (23b), ethyl 2-amino-6-(2-oxo-2H-chromen-3-yl)pyridine-3-carboxylate (24) and ethyl 2-amino-6-(3-oxo-3H-benzo[f]chromen-2-yl)pyridine-3-carboxylate (24b).

A mixture of the appropriate of acetylacetone, ethyl acetoacetate, benzoylacetonitrile, ethyl cyanoacetate (5 mmole), 3-(3-(dimethylamino)acryloyl)-2*H*-chromen-2-one (**1a**) or 2-(3-(dimethylamino)acryloyl)-3H-benzo[*f*]chromen-3-one (**1b**) (5 mmole), ammonium acetate (0.37 g, 5 mmole) in acetic acid (15 mL) was reflux for 4 hrs. The resulting solid which formed was collected and recrystallized from ethanol to give **21a,b , 22, 23** and **24,** respectively.

3.5.1. Ethyl 2-methyl-6-(2-oxo-2H-chromen-3-yl)pyridine-3-carboxylate (21a). Pale yellow crystals from EtOH, yield (82 %), mp: 156-58°C; IR (KBr): 3042, 2987 (CH), 1721 (C=O), 1604 (C=C); ^{1}H NMR ($CDCl_3$): δ = 1.43 (t, 3H, *J* = 7.5 Hz, $CH_2\underline{CH_3}$), 2.92 (s, 3H, CH_3, pyridine H-2), 4.40 (q, 2H, *J* = 7.5 Hz, $\underline{CH_2}CH_3$), 7.27-7.40 (m, 3H, ArH's), 7.58-7.70 (m, 2H, ArH), 8.27-8.37 (m, 1H, ArH's), 8.93 (s, 1H, ArH); *Anal.* Calcd. for $C_{18}H_{15}NO_4$ (309.32) C, 69.89; H, 4.89; N, 4.53 Found: C, 70.12; H, 4.71; N, 4.67 %.

3.5.2. Ethyl 2-methyl-6-(3-oxo-3H-benzo[f]chromen-2-yl)pyridine-3-carboxylate (21b). Yellow crystals from EtOH, yield (84 %), mp: 180-82°C; IR (KBr): 3042, 2981 (CH), 1716 (C=O), 1624 (C=N), 1589 (C=C); ^{1}H NMR ($(CD_3)_2SO$): δ = 1.35 (t, 3H, *J* = 7.5 Hz, $CH_2\underline{CH_3}$), 2.85 (s, 3H, CH_3, pyridine H-2), 4.33 (q, 2H, *J* = 7.5 Hz, $\underline{CH_2}CH_3$), 7.58-7.79 (m, 4H, ArH's), 8.05-8.7 (d, 2H, *J* = 6 Hz, ArH), 8.22-8.29 (m, 1H, ArH's), 8.51-8.54 (d, 2H, ArH's), 9.61 (s, 1H, ArH); *Anal.* Calcd. for $C_{22}H_{17}NO_4$ (359.37) C, 73.53; H, 4.77; N, 3.90 Found: C, 73.68; H, 4.91; N, 4.14 %.

3.5.3. 3-(5-Acetyl-6-methylpyridin-2-yl)-2H-chromen-2-one (22a). Beige crystals from EtOH, yield (81 %), mp: 180-82°C; IR (KBr): 3065, 2923 (CH), 1725, 1676 (C=O), 1605 (C=C); ^{1}H NMR ($CDCl_3$): δ = 2.20 (s, 3H, CH_3), 2.40 (s, 3H, CH_3, pyridine H-2), 6.84-7.98 (m, 6H, ArH's), 8.50 (s, 1H, ArH); MS: m/z = 279 (M^+, 53.1%), 278 (28.6%), 270 (15.01%), 266 (14.01%), 254 (15.63%), 250 (18.50%), 242 (18.64%), 239 (14.00%), 236 (48.13%), 227 (13.90%), 223 (22.13%), 221 (19.70%), 214 (25.46%), 209 (16.61%), 204 (13.78%), 198 (12.17%), 195 (49.86%), 173 (82.30%), 167 (30.87%), 163 (33.30%), 152 (35.54%), 147 (22.66%), 142 (26.87%), 140 (30.12%), 139 (72.15%), 131 (19.05%), 127 (22.80%), 126 (38.37%), 121 (20.27%), 101 (50.91%), 89 (100%), 78 (48.23%), 66 (20.43%); *Anal.* Calcd. for $C_{17}H_{13}NO_3$ (279.29) C, 73.11; H, 4.69; N, 5.02 Found: C, 73.30; H, 4.75; N, 5.20 %.

3.5.4. 2-(5-Acetyl-6-methylpyridin-2-yl)-3H-benzo[f]chromen-3-one (22b). Beige crystals from EtOH, yield (81 %), mp: 242-44°C; IR (KBr): 3065, 2920 (CH), 1724, 1681 (C=O), 1558 (C=C); ^{1}H NMR ($CDCl_3$): δ = 2.20 (s, 3H, CH_3), 2.40 (s, 3H, CH_3, pyridine H-2), 7.41-8.28 (m, 8H, ArH's), 8.55 (s, 1H, ArH); MS: m/z = 330 (M+1, 17%), 329 (M^+, 100%), 328 (27.5%), 314 (60.%), 301 (54.2%), 287 (69.3%), 256 (9.2%), 230 (16.3%), 228 (15.7%), 189 (17.0%), 157 (35.9%), 139 (30.7%), 129 (26.8%), 103 (17.6%), 101 (29.4%), 99 (11.8%), 88 (25.5%), 86 (12.4%), 77 (21.6%), 65 (13.7%); *Anal.* Calcd. for $C_{21}H_{15}NO_3$ (329.35) C, 76.58; H, 4.59; N, 4.25 Found: C, 76.71; H, 4.65; N, 4.38 %.

3.5.5. 3-(6-Amino-5-benzoyl-pyridin-2-yl)chromen-2-one (23a). Brown crystals from EtOH, yield (92 %), mp: 172-74°C; IR (KBr): 3421, 3320 (NH_2), 3062, 2920 (CH), 1724, 1674 (C=O), 1604 (C=N), 1566 (C=C); ^{1}H NMR ($CDCl_3$): δ = 7.25-7.32 (m, 2H, ArH's), 7.52-7.74 (m, 8H, ArH's), 8.15 (s, 1H, ArH), 8.65 (s, 1H, ArH), 10.12 (s, br., 2H, NH_2); MS: m/z = 344 (M+2, 20.83%), 342 (M^+, 75.98%), 329 (37.20%), 313 (19.06), 300 (7.08%), 273 8.25%), 271 (50.24.%), 255 (9.21%), 240 (23.46%), 215 (12.68%), 213 (16.30%), 188 (20.27%), 179 (7.29%), 173 (7.65%),

171 (11.53%), 154 (16.94%), 151 (22.07%), 138 (18.73%), 120 (13.09%), 114 (28.99%), 107 (18.86%), 105 (63.04%), 100 (27.19%), 94 (16.67%), 88 (35.79%), 76 (100%),63 (24.72%); *Anal.* Calcd. for $C_{21}H_{14}N_2O_3$(342.35): C, 73.68; H, 4.12; N, 8.18. Found: C, 73.85; H, 4.24; N, 8.32 %.

3.5.6. 2-(6-Amino-5-benzoyl-pyridin-2-yl)-benzo[f]chromen-3-one (23b): Brown crystals from DMF, yield (86 %), mp: 280-82°C; IR (KBr): 3421, 3320 (NH_2), 3062, 2920 (CH), 1724, 1666 (C=O), 1604 (C=N), 1562 (C=C); ^{1}H NMR ($CDCl_3$): δ = 7.38-8.24 (m, 14H, ArH's), 10.12 (s, br., 2H, NH_2); MS: m/z = 394 (M+2, 22.53%), 393 (M+1, 35.68%), 367 (9.46%), 364 (12.52), 350 (10.89%), 222 (13.68%), 289 (7.17.%), 233 (10.84%), 223 (19.93%), 205 (8.05%), 196 (11.14%), 181 (8.02%), 176 (12.11%), 171 (14.76%), 168 (11.48%), 163 (10.44%), 151 (12.06%), 139 (37.20%), 115 (19.24%), 105 (74.48%), 89 (13.24%), 77 (100%), 73 (16.98%), 63 (11.18%); *Anal.* Calcd. for $C_{25}H_{16}N_2O_3$ (392.41): C, 76.52; H, 4.11; N, 7.14. Found: C, 76.372; H, 4.20; N, 7.33 %.

3.5.7. Ethyl 2-amino-6-(2-oxo-2H-chromen-3-yl)pyridine-3-carboxylate (24a). Brown crystals from EtOH, yield (82 %), mp: 166-68°C; IR (KBr): 3379, 3360 (NH_2), 3062, 2920 (CH), 1724 (C=O), 1627 (C=N), 1562 (C=C); ^{1}H NMR ($CDCl_3$): δ = 1.31 (t, 3H, $CH_2\underline{CH_3}$), 4.42 (q, 2H, $\underline{CH_2}CH_3$), 7.25-7.60 (m, 6H, ArH's), 8.65 (s, 1H, ArH), 10.12 (s, br., 2H, NH_2); MS: m/z = 265 (M-OC_2H_5, 2.13%), 173 (7.55%), 166 (3.65%), 151 (4.79%), 139 (6.66%), 118 (6.45%), 105 (26.17%), 102 (11.28%), 102 (10.53%), 91 (17.25%), 90 (28.41%), 89 (47.45%), 77 (100%), 67 (10.45%), 62 (99.03%); *Anal.* Calcd. For $C_{17}H_{14}N_2O_4$ (310.3): C, 65.80; H, 4.55; N, 9.03. Found: C, 65.80; H, 4.55; N, 9.03%.

3.5.8. Ethyl 2-amino-6-(3-oxo-3H-benzo[f]chromen-2-yl)pyridine-3-carboxylate (24b): Brown crystals from DMF, yield (86 %), mp: 230-32°C; IR (KBr): 3379, 3360 (NH_2), 3062, 2920 (CH), 1724 (C=O), 1624 (C=N), 1562 (C=C); ^{1}H NMR ($CDCl_3$): δ = 1.31 (t, 3H, $CH_2\underline{CH_3}$), 4.42 (q, 2H, $\underline{CH_2}CH_3$), 7.25-7.60 (m, 8H, ArH's), 8.65 (s, 1H, ArH), 10.12 (s, br., 2H, NH_2); MS: m/z = 314 (M-OC_2H_5, 17.02%), 265 (15.45%), 222 (19.38%), 219 (15.16%), 206 (21.69%), 205 (18.02%), 202 (27.97%), 199 (18.06%), 194 (20.38%), 189 (25.75%), 182 (19.781%), 178 (23.97%), 177 (26.83%), 167 (133.97%), 169 (16.28%), 140 (75.27%), 139 (87.40%), 138 (39.99%), 127 (22.67%), 115 (40.19%), 105 (50.72%), 98 (34.45%), 77 (63.34%), 69 (34.37%), 61 (23.36%); *Anal.* Calcd. For $C_{21}H_{16}N_2O_4$ (360.36): C, 69.99; H, 4.48; N, 7.77. Found: C, 70.12; H, 4.65; N, 7.82 %.

3.6. 2-Methyl-6-(2-oxo-2H-chromen-3-yl)pyridine-3-carbohydrazide (25a) and 2-methyl-6-(3-oxo-3H-benzo[f]chromen-2-yl)pyridine-3-carbohydrazide (25b).

Equimolar amounts of the appropriate **21a,b** and hydrazine hydrate (5 mmol for each) in ethanol (10 mL) were refluxed for 3 hrs. The resulting solid, was collected and recrystallized from ethanol to give **25a** and **25b**

3.6.1. 2-Methyl-6-(2-oxo-2H-chromen-3-yl)pyridine-3-carbohydrazide (25a). Beige crystals from EtOH, yield (82 %), mp: 180-82°C; IR (KBr): 3320, 3174 (NH_2, NH), 3066, (CH), 1662 (C=O), 1593 (C=C); ^{1}H NMR ($CDCl_3$): δ = 2.48 (s, 3H, CH_3, pyridine H-2), 6.23 (s, br., 3H, NH, NH_2), 7.27-8.04 (m, 4H, ArH's), 8.05-8.15 (m, 2H, ArH's), 8.55 (s, 1H, ArH); *Anal.* Calcd. for $C_{16}H_{13}N_3O_3$ (295.29) C, 65.08; H, 4.44; N, 14.23 Found: C, 65.21; H, 4.53; N, 14.32 %.

3.6.3. 2-methyl-6-(3-oxo-3H-benzo[f]chromen-2-yl)pyridine-3-carbohydrazide (25b). Beige crystals from EtOH, yield (84 %), mp: 240-42°C; IR (KBr): 3313, 3201 (NH_2, NH), 3058, (CH), 1647 (C=O), 1595 (C=C); ^{1}H NMR (($CD_3)_2SO$): δ = 3.30 (s, 3H, CH_3, pyridine H-2), 7.96-8.10 (m, 8H, ArH's), 8.86 (s, 1H, ArH), 9.50 (s, br., 1H, NH), 12.80 (s, br., 2H, NH_2); *Anal.* Calcd. for $C_{20}H_{15}N_3O_3$ (345.35) C, 69.56; H, 4.38; N, 12.17 Found: C, 69.45; H, 4.51; N, 12.32 %.

3.7. 5-Methyl-2-[2-methyl-6-(2-oxo-2H-chromen-3-yl)-pyridine-3-carbonyl]-2,4-dihydro-pyrazol-3-one (26a), 5 -Methyl-2-[2-methyl-6-(3-oxo-3H-benzo[f]- chromen-2-yl)-pyridine-3-carbonyl]-2,4-dihydro-pyrazol-3-one (26b), 3-[5-(3,5-dimethyl-pyrazole-1-carbonyl)-6-methyl-pyridin-2-yl]-5,6-dihydro-chromen-2-one (27a) and 2-[5-(3,5-dimethyl-pyrazole-1-carbonyl)-6-methyl-pyridin-2-yl]-benzo[f]-chromen-3-one (27b)

Equimolar amounts of the appropriate **25a** or **25b** and ethyl acetoacetate or acetyl acetone (4 mmol for each) in ethanol (10 mL) with two drops of acetic acid were refluxed for 4 hrs. The resulting solid, so formed, was collected and recrystallized from dilute acetic acid to give the corresponding **26** and **27**, respectively.

3.7.1. 5-Methyl-2-[2-methyl-6-(2-oxo-2H-chromen-3-yl)-pyridine-3-carbonyl]-2, 4-dihydro-pyrazol-3-one (26a). Yellow crystals from EtOH, yield (84 %), mp: 148-50°C; IR (KBr): 3065, 2920 (CH), 1626 (C=O), 1550 (C=C); ^{1}H NMR (($CD_3)_2SO$): δ = 2.19 (s, 3H, CH_3, pyrazole), 3.41 (s, 3H, CH_3, pyridine H-2), 5.25 (s, 2H, CH_2), 7.22-7.67 (m, 6H, ArH's), 9.31 (s, 1H, ArH); *Anal.* Calcd. for $C_{20}H_{15}N_3O_4$ (361.35) C, 66.48; H, 4.18; N, 11.63 Found: C, 66.55; H, 4.27; N, 11.48 %.

3.7.2. 5-Methyl-2-[2-methyl-6-(3-oxo-3H-benzo[f]-chromen-2-yl)-pyridine-3-carbonyl]-2,4-dihydro-pyrazol-3-one (26b). Beige crystals from dioxane, yield (86 %), mp: 210-12°C; IR (KBr): 3065, 2920 (CH), 1622 (C=O), 1577

(C=C); ^{1}H NMR ($(CD_3)_2SO$): δ = 2.00 (s, 3H, CH_3, pyrazole), 2.84 (s, 3H, CH_3, pyridine H-2), 5.25 (s, 2H, CH_2), 7.22-7.78 (m, 8H, ArH's), 9. 01 (s, 1H, ArH); MS: m/z = 412 (M+1, 0.20%), 411 (M^+, 0.79%), 170 (26.24%), 141 (20.24.%), 127 (37.91%), 115 (100%), 88 (17.45%); *Anal.* Calcd. for $C_{24}H_{17}N_3O_4$ (411.41) C, 70.07; H, 4.16; N, 10.21 Found: C, 70.20; H, 4.23; N, 10.15 %.

3.7.3. 3-[5-(3,5-Dimethyl-pyrazole-1-carbonyl)-6-methyl-pyridin-2-yl]-5,6-dihydro-chromen-2-one (27a). Yellow crystals from EtOH, yield (91 %), mp: 164-66°C; IR (KBr): 3040, 2920 (CH), 1648 (C=O), 1618 (C=C), 1386 (CH_3); ^{1}H NMR ($(CD_3)_2SO$): δ = 2.23 (s, 3H, CH_3, pyrazole), 2.33 (s, 3H, CH_3, pyrazole), 2.86 (s, 3H, CH_3, pyridine H-2), 6.45 (s, 1H, pyrazole H-4), 7.22-7.78 (m, 6H, ArH's), 9.58 (s, 1H, ArH); *Anal.* Calcd. for $C_{21}H_{17}N_3O_3$ (359.38) C, 70.18; H, 4.77; N, 11.69 Found: C, 70.18; H, 4.77; N, 11.69 %.

3.7.4. 2-[5-(3,5-Dimethyl-pyrazole-1-carbonyl)-6-methyl-pyridin-2-yl]-benzo[f]-chromen-3-one (27b). Yellow crystals from dioxane, yield (92 %), mp: 226-28°C; IR (KBr): 3065, 2920 (CH), 1622 (C=O), 1577 (C=C); ^{1}H NMR ($(CD_3)_2SO$): δ = 2.30 (s, 3H, CH_3, pyrazole), 2.33 (s, 3H, CH_3, pyrazole), 2.84 (s, 3H, CH_3, pyridine H-2), 6.65 (s, 1H, pyrazole H-4), 7.41-8.82 (m, 9H, ArH's); MS: m/z = 409 (M^+, 0.04%), 255 (16.99%), 247 (18.35%), 238 (18.35%), 230 (18.36%), 178 (9.12%), 170 (9.12%), 162 (9.12%), 101 (38.75%), 88 (100%), 76 (46.60%), 65 (17.24%); *Anal*. Calcd. for $C_{25}H_{19}N_3O_3$ (409.44) C, 73.34; H, 4.68; N, 10.26 Found: C, 73.34; H, 4.68; N, 10.26 %.

3.8. 5-Methyl-2-[2-methyl-6-(2-oxo-2H-chromen-3-yl)-pyridine-3-carbonyl]-4-(phenyl-hydrazono)-2,4-dihydro-pyrazol-3-one (28a),5 -methyl-2-[2-methyl-6-(3-oxo-3H-benzo[f]chromen-2-yl)-pyridine-3-carbonyl]-4-(phenyl-hydrazono)-2,4-dihydro-pyrazol-3-one(28b), 3-[5-(3,5-dimethyl-4-phenylazo-pyrazole-1-carbonyl)-6-methyl-pyridin-2-yl]-chromen-2-one (29a) and 2-[5-(3,5-dimethyl-4-phenylazo-pyrazole-1-carbonyl)-6-methyl-pyridin-2-yl]-benzo[f]chromen-3-one (29b).

Method A: Method A: *Appropriate arene* diazonium chloride (5 mmole), which is prepared via reaction of the appropriate aromatic amines (5 mmole), hydrochloric acid (3 mL, 6 M) and sodium nitrite (0.37 gm, 5 mmole) at 0-5°C, was added to a mixture of the appropriate **26** or **27** (2.51 gm, 5 mmole) and sodium acetate (0.41 gm, 5 mmole) in ethanol (30 mL) at 0-5°C, while stirring. The reaction mixture was stirred for 3 hrs. The resulting solid, was collected, washed with water and recrystallized from acetic acid to give (**28**, **29**)**a,b**

Method B: A mixture of the appropriate **25a,b** and ethyl 2-substituted phenylazo-3-oxo-4-butanoate (5 mmol for each) in ethanol (20 mL) and catalytic amount of acetic acid (2 drops) was refluxed for 3 hrs. The resulting solid, so formed, was collected and recrystallized from acetic acid to give products identical in all aspects obtained from method A.

3.8.1. 5-Methyl-2-[2-methyl-6-(2-oxo-2H-chromen-3-yl)-pyridine-3-carbonyl]-4-(phenyl-hydrazono)-2,4-dihydro-pyrazol-3-one (29a). Orange crystals from EtOH, yield (87 %), mp: 180-82°C; IR (KBr): 3174 (NH), 3065, 2920 (CH), 1662 (C=O), 1593 (C=C); ^{1}H NMR ($(CD_3)_2SO$): δ = 2.14 (s, 3H, CH_3, pyrazole), 2.67 (s, 3H, CH_3, pyridine H-2), 6.83-8.79 (m, 12H, ArH's), 11.53 (s, br., 1H, NH); *Anal.* Calcd. for $C_{26}H_{19}N_5O_4$ (465.46) C, 67.09; H, 4.11; N, 15.05 Found: C, 66.89; H, 4.21; N, 14.84 %.

3.8.2. 5-Methyl-2-[2-methyl-6-(3-oxo-3H-benzo[f]chromen-2-yl)-pyridine-3-carbonyl]-4-(phenyl-hydrazono)-2,4-dihydro-pyrazol-3-one(29b). Yellow crystals from DMF, yield (88 %), mp: 300-302°C; IR (KBr): 3185 (NH), 3065, 2920 (CH), 1728, 1670 (C=O's), 1612 (C=C); ^{1}H NMR ($(CD_3)_2SO$): δ = 2.12 (s, 3H, CH_3, pyrazole), 2.54 (s, 3H, CH_3, pyridine H-2), 6.83-8.24 (m, 15H, ArH's); MS: m/z = 515 (M^+, 0.09%), 170 (35.31%), 141 (18.40%), 127 (28.76.35%), 115 (100%), 88 (17.57%); *Anal.* Calcd. for $C_{30}H_{21}N_5O_4$ (515.52) C, 69.89; H, 4.11; N, 13.59 Found: C, 70.00; H, 4.24; N, 13.71 %.

3.8.3. 3-[5-(3,5-Dimethyl-4-phenylazo-pyrazole-1-carbonyl)-6-methyl-pyridin-2-yl]-chromen-2-one (30a). Yellow crystals from EtOH, yield (90 %), mp: 150-52°C; IR (KBr): 3065, 2920 (CH), 1720, 1662 (C=O's), 1593 (C=C); ^{1}H NMR ($(CD_3)_2SO$): δ = 2.12 (s, 3H, CH_3, pyrazole), 2.63 (s, 3H, CH_3, pyrazole), 2.84 (s, 3H, CH_3, pyridine H-2), 7.27-8.82 (m, 11H, ArH's), 8.95 (s, 1H, ArH); *Anal.* Calcd. for $C_{27}H_{21}N_5O_3$ (463.49) C, 69.97; H, 4.57; N, 15.11 Found: C, 70.27; H, 4.75; N, 15.00%.

3.8.4. 2-[5-(3,5-Dimethyl-4-phenylazo-pyrazole-1-carbonyl)-6-methyl-pyridin-2-yl]-benzo[f]chromen-3-one (30b). Orange crystals from DMF, yield (93 %), mp: 210-12°C; IR (KBr): 3065, 2920 (CH), 1728, 1670 (C=O's), 1581 (C=C); ^{1}H NMR ($(CD_3)_2SO$): δ = 2.12 (s, 3H, CH_3, pyrazole), 2.62 (s, 3H, CH_3, pyrazole), 2.73 (s, 3H, CH_3, pyridine H-2), 7.32-8.82 (m, 14H, ArH's); MS: m/z = 515 (M+1, 0.09%), 342 (0.38%), 170 (35.31%), 141 (18.40%), 127 (28.67%), 115 (100%), 88 (17.56%); *Anal.* Calcd. for $C_{31}H_{23}N_5O_3$ (513.55) C, 72.50; H, 4.51; N, 13.64 Found: C, 72.37; H, 4.39; N, 13.45 %.

3.9. 3-(5-(azidoformyl)-6-methylpyridin-2-yl)-2H-chromen-2-one (28a) and 2-(5-(azidoformyl)-6-methylpyridin-2-yl)-3H-benzo[f]chromen-3-one (28b).

A stirred solution of the appropriate **21a** or **21b** (5 mmole) in acetic acid (15 mL) at 0-5°C, sodium nitrite was added portionwise tell effervescence ended. The reaction mixture was stirred for 1 hr. The resulting solid, was collected, filtered, washed with water and recrystallized from acetic acid to give **28a** and **28b**, respectively.

3.9.1. 3-(5-(azidoformyl)-6-methylpyridin-2-yl)-2H-chromen-2-one (28a). Beige crystals from acetone, yield (84 %), mp: 208-210°C; IR (KBr): 3065, 2920 (CH), 2641 (C-N_3), 1728, 1612 (C=C); ^{1}H NMR ($(CD_3)_2SO$): δ = 2.65 (s, 3H, CH_3, pyridine H-2), 7.32-8.15 (m, 6H, ArH's), 8.59 (s, 1H, ArH); MS: m/z = 306 (M^+, 0.13%), 240 (9.26%), 149 (16.54%), 147 (12.06%), 120 (52.77%), 105 (35.25%), 92 (95.68%), 87 (12.57%), 76 (94.86%), 65 (100%)62 (62.01%); *Anal.* Calcd. for $C_{16}H_{10}N_4O_3$ (306.28) C, 62.74; H, 3.29; N, 18.29 Found: C, 62.74; H, 3.29; N, 18.29 %.

3.9.2. 2-(5-(Azidoformyl)-6-methylpyridin-2-yl)-3H-benzo[f]chromen-3-one (28b). Beige crystals from DMF, yield (93 %), mp: 308-310°C; IR (KBr): 3065, 2920 (CH), 1728, 1670 (C=O's), 1581 (C=C); ^{1}H NMR ($(CD_3)_2SO$): δ = 2.68 (s, 3H, CH_3, pyridine H-2), 7.32-8.14 (m, 9H, ArH's); MS: m/z = 356 (M^+, 0.01%), 323 (4.10%), 170 (41.21%), 154 (3.63%), 141 (28.80%), 127 (28.10%), 115 (100%), 88 (15.73%),75 (7.27%), 62 (6.91%); *Anal.* Calcd. for $C_{20}H_{12}N_4O_3$ (356.33) C, 67.41; H, 3.39; N, 15.72 Found: C, 67.35; H, 3.48; N, 15.95 %.

3.10. 1-(2-Methyl-6-(2-oxo-2H-chromen-3-yl)pyridin-3-yl)-3-substituted urea 32a-c and 1-(2-Methyl-6-(3-oxo-3H-benzo[f]chromen-2-yl)pyridin-3-yl)-3-substituted urea 31a-c and Quinazoline-2,4(1H,3H)-dione 33a-c.

A mixture of the appropriate **26a** or **26b** and appropriate aniline, *p*-toluidine, *p*-anisidine or methyl anthranilate (5 mmol) in dioxane (20 mL) was refluxed for 4 hrs. The resulting solid, so formed, was collected and recrystallized from DMF to give **32a-c** and **33a-c** respectively.

3.10.1. 1-(2-Methyl-6-(2-oxo-2H-chromen-3-yl)pyridin-3-yl)-3-phenylurea (32a). Beige crystals from DMF, yield (95 %), mp: 288-90°C; IR (KBr): 3436 (NH), 3039, 2920 (CH), 16701724, 1678 (CO's), 1620 (C=N), 1596 (C=C); ^{1}H NMR ($(CD_3)_2SO$): δ = 2.24 (s, 3H, CH_3, pyridine H-2), 7.12-8.14 (m, 13H, ArH's and 2NH), 9.54 (s, 1H, ArH); MS: m/z = 373 (M+2, 0.38%), 372 (M+1, 0.42%), 358 (11.52%), 357 (100%), 329 (25.47%), 271 (8.72%), 215 (7.96%), 189 (4.37%), 142 (3.74%), 63 (7.71%); *Anal.* Calcd. for $C_{22}H_{17}N_3O_3$ (371.39) C, 71.15; H, 4.61; N, 11.31 Found: C, 71.00; H, 4.45; N, 11.42 %.

3.10.2. 1-(2-Methyl-6-(2-oxo-2H-chromen-3-yl)pyridin-3-yl)-3-p-tolylurea (32b). Beige crystals from DMF, yield (95 %), mp: 224-26°C; IR (KBr): 3320 (NH), 3065, 2920 (CH), 1728, 1681 (CO's), 1620 (C=N), 1570 (C=C); ^{1}H NMR ($(CD_3)_2SO$): δ = 2.10 (s, 3H, CH_3), 2.24 (s, 3H, CH_3), 7.12-8.14 (m, 12H, ArH's and 2NH), 9.54 (s, 1H, ArH); MS: m/z = 387 (M+2, 1.1%), 386 (1.24%), 270 (16.54%), 269 (13.54%), 226 (48.82%), 207 (24.21%), 193 (25.64%), 191 (91.72%), 179 (26.50%), 165 (53.93%), 163 (100%), 152 (12.26%), 141 (68.34%), 137 (32.78%), 117 (96.19%), 92 (16.00%), 99 (46.87%), 77 (20.69%), 64 (54.97%), 62 (56.20%); *Anal.* Calcd. for $C_{23}H_{19}N_3O_3$ (385.42) C, 71.67; H, 4.97; N, 10.90 Found: C, 71.81; H, 5.11; N, 11.00 %.

3.10.3. 1-(4-Methoxyphenyl)-3-(2-methyl-6-(2-oxo-2H-chromen-3-yl)pyridin-3-yl)urea (32c). Yellow crystals from AcOH, yield (96 %), mp: 230-32°C; IR (KBr): 3320 (NH), 3065, 2920 (CH), 1728, 1670 (C=O's), 1605 (C=C); ^{1}H NMR ($(CD_3)_2SO$): δ = 2.10 (s, 3H, CH_3), 3.78 (s, 3H, OCH_3), 7.12-8.14 (m, 12H, ArH's and 2NH), 9.54 (s, 1H, ArH); MS: m/z = 400 (M-1, 4.67%), 242 (8.36%), 241 (48.78%), 240 (20.60%), 223 (20.68%), 212 (12.02%), 185 (24.35%), 184 (22.03%), 147 (84.56%), 134 (17.48%), 120 (46.30%), 105 (46.26%), 93 (100%), 91 (59%), 77 (77.57%), 65 (34.65%), 63 (61.49%); *Anal.* Calcd. for $C_{23}H_{19}N_3O_4$ (401.41) C, 68.82; H, 4.77; N, 10.47 Found: C, 68.95; H, 4.66; N, 10.52 %.

3.10.4. 1-(2-Methyl-6-(3-oxo-3H-benzo[f]chromen-2-yl)pyridin-3-yl)-3-phenylurea (33a). Yellow crystals from DMF, yield (93 %), mp: > 300°C; IR (KBr): 3320 (NH), 3065, 2920 (CH), 1728, 1670 (C=O's), 1605 (C=C); ^{1}H NMR ($(CD_3)_2SO$): δ = 2.10 (s, 3H, CH3), 7.12-8.14 (m, 15H, ArH's and 2NH), 9.32 (s, 1H, ArH); MS: m/z = 423 (M+1, 0.23%), 341 (39.20%), 170 (75.03%), 143 (10.57%), 127 (28.49%), 114 (100%), 88 (20.08%), 62 (20.50%); *Anal.* Calcd. for $C_{26}H_{19}N_3O_3$ (421.45) C, 74.10; H, 4.54; N, 9.97 Found: C, 74.18; H, 4.62; N, 10.05 %.

3.10.5. 1-(2-Methyl-6-(3-oxo-3H-benzo[f]chromen-2-yl)pyridin-3-yl)-3-p-tolylurea (33b). Yellow crystals from DMF, yield (93 %), mp: 326-28°C; IR (KBr): 3320 (NH), 3065, 2920 (CH), 1728, 1670 (C=O's), 1605 (C=C); ^{1}H NMR ($(CD_3)_2SO$): δ = 2.10 (s, 3H, CH_3), 2.25 (s, 3H, CH_3), 7.12-8.14 (m, 12H, ArH's and NH), 9.32 (s, 1H, ArH), 8.47 (s, br., 2H, 2NH); MS: m/z = 435 (M^+, 0.29%), 341 (30.55%), 324 (18.76%), 170 (82.76%), 154 (5.85%), 127 (17.17%), 115 (100%), 88 (7.04%); *Anal.* Calcd. for $C_{27}H_{21}N_3O_3$ (435.47) C, 74.47; H, 4.86; N, 9.65 Found: C, 74.54; H, 4.75; N, 9.82 %.

3.10.6. 1-(4-Methoxyphenyl)-3-(2-methyl-6-(3-oxo-3H-benzo[f]chromen-2-yl)pyridin-3-yl)urea (33c). Orange crystals from DMF, yield (94 %), mp: > 300°C; IR (KBr): 3320 (NH), 3065, 2920 (CH), 1728, 1670 (C=O's), 1605 (C=C); ^{1}H NMR ($(CD_3)_2SO$): δ = 2.10 (s, 3H, CH_3), 3.77 (s, 3H, OCH_3), 7.12-8.14 (m, 14H, ArH's and NH), 9.32 (s, 1H, ArH); MS: m/z = 453 (M+2, 0.02%), 341 (3.79%), 170 (32.06%), 154 (4.39%), 141 (27.91%), 127 (26.21%),

115 (100%), 88 (13.92%),76 (6.70%), 62 (7.55%); *Anal.* Calcd. for $C_{27}H_{21}N_3O_4$ (451.47) C, 71.83; H, 4.69; N, 9.31 Found: C, 72.05; H, 4.82; N, 9.54 %.

3.10.7. 3-(2-Methyl-6-(2-oxo-2H-chromen-3-yl)pyridin-3-yl)quinazoline-2,4(1H,3H)-dione (35a). Beige crystals from DMF, yield (82 %), mp: 230-32°C; IR (KBr): 3320 (NH), 3034, 2920 (CH), 1693 (CO), 1624 (C=N); ^{1}H NMR ($(CD_3)_2SO$): δ = 2.49 (s, 3H, CH_3), 6.94-7.65 (m, 10H, ArH's), 8.94 (s, 1H, ArH), 11.17 (s, br., 1H, NH); MS: m/z = 396 (M-1, 0.11%), 240 (21.73%), 223 (13.05%), 147 (17.10%), 120 (62.85%), 105 (18.68%), 102 (28.54%), 93 (83.69%), 91 (52.88%), 76 (55.01%), 64 (100%); *Anal.* Calcd. for $C_{23}H_{15}N_3O_4$ (397.38) C, 69.52; H, 3.80; N, 10.57 Found: C, 69.65; H, 3.92; N, 10.73 %.

3.10.8. 3-(2-methyl-6-(3-oxo-3H-benzo[f]chromen-2-yl)pyridin-3-yl)quinazoline-2,4(1H,3H)-dione (35b).
Yellow crystals from AcOH, yield (91 %), mp: 280-82°C; IR (KBr): 3320 (NH), 3034, 2920 (CH), 1693 (CO), 1624 (C=N); ^{1}H NMR ($(CD_3)_2SO$): δ = 2.49 (s, 3H, CH_3), 7.11-8.22 (m, 12H, ArH's), 8.84 (s, 1H, ArH), 11.15 (s, br., 1H, NH); *Anal.* Calcd. for $C_{27}H_{17}N_3O_4$ (447.44) C, 72.48; H, 3.83; N, 9.39 Found: C, 72.58; H, 3.97; N, 9.51 %.

3.11. Synthesis pf carbamate 34a, b

A mixture of each **26a** and **26b** (5 mmol) and phenol (0.5 g, 5 mmol) in dry benzene (20 mL) was refluxed for 4 hrs. The resulting solid, so formed, was collected and recrystallized from DMF to give **34**.

3.11.1. Phenyl 2-methyl-6-(2-oxo-2H-chromen-3-yl)pyridin-3-ylcarbamate (34a). Beige crystals from DMF, yield (94 %), mp: 263-38°C; IR (KBr): 3535 (NH), 3043, 2920 (CH), 1693 (CO), 1620 (C=N); ^{1}H NMR ($(CD_3)_2SO$): δ = 2.39 (s, 3H, CH_3), 6.95-7.61 (m, 9H, ArH's), 6.78 (m, 1H, ArH), 8.36 (s, 1H, ArH), 8.38 (d, 1H, ArH), 11.13 (s, br., 1H, NH); MS: m/z = 356 (M^+, 100%), 329 (45.91%), 300 (15.75%), 272 (16.41%), 243 (15.53%), 226 (14.86%), 215 (23.95%), 213 (18.20%), 189 (13.77%), 163 (11.84%), 150 (16.95%); 142 (10%), 126 (12.80%), 113 (20.59%),100 (22.11%), 94 (13.99%), 75 (27.14%), 62 (23.37%); *Anal.* Calcd. for $C_{22}H_{16}N_2O_4$ (372.37) C, 70.96; H, 4.33; N, 7.52 Found: C, 71.05; H, 4.12; N, 7.56 %.

3.11.2. Phenyl 2-methyl-6-(3-oxo-3H-benzo[f]chromen-2-yl)pyridin-3-ylcarbamate (34b).
Beige crystals from DMF, yield (94 %), mp: 320-24°C; IR (KBr): 3560 (NH), 3065, 2920 (CH), 1693 (CO), 1612 (C=N), 1596 (C=C); ^{1}H NMR ($(CD_3)_2SO$): δ = 2.49 (s, 3H, CH_3), 7.26-7.29 (m, 14H, ArH's), 7.89-7.93 (m, 1H, ArH), 8.01 (d, 1H, *J* = 8Hz, ArH), 8.63 (d, 1H, *J* = 8Hz, ArH), 9.98 (s, 1H, ArH), 12.88 (s, br., 1H, NH); MS: m/z = 420 (M-2, 0.01%), 357 (4.55%), 341 (77.07%), 324 (22.26%), 170 (100%), 152 (10.40%), 143 (9.55%), 128 (13.51%), 127 (16.12%), 115 (84.35%); *Anal.* Calcd. for $C_{26}H_{18}N_2O_4$ (422.43) C, 73.92; H, 4.29; N, 6.63 Found: C, 74.10; H, 4.35; N, 6.84 %.

4. Biological evaluation

This work was carried out in Microanalytical Center Faculty of Science, Cairo University, Giza, Egypt.

Antimicrobial activity of the tested samples was determined using a modified Kirby-Bauer disc diffusion method[205]**.** Briefly, 100 µl of the test bacteria/fungi were grown in 10 ml of fresh media until they reached a count of approximately 108 cells/ml for bacteria or 105 cells/ml for fungi[206] 100 µl of microbial suspension was spread onto agar plates corresponding to the broth in which they were maintained.

Isolated colonies of each organism that might be playing a pathogenic role should be selected from primary agar plates and tested for susceptibility by disc diffusion method [207]**.**

Of the many media available, NCCLS recommends Mueller-Hinton agar due to: it results in good batch-to-batch reproducibility

Disc diffusion method for filamentous fungi tested by using approved standard method (M38-A) developed by the [208] for evaluating the susceptibilities of filamentous fungi to antifungal agents.

Disc diffusion method for yeasts developed by using approved standard method (M44-P) by the[209].

Plates inoculated with filamentous fungi *as* ***Aspergillus flavus*** at 25°C for 48 hours; Gram (+) bacteria as ***Staphylococcus aureus, Bacillus subtilis;*** Gram (-) bacteria as ***Escherichia coli, Pseudomonas aeuroginosa*** they were incubated at 35-37°C for 24-48 hours and yeast as ***Candida albicans*** incubated at 30°C for 24-48 hours and, then the diameters of the inhibition zones were measured in millimeters [205]**.**

Standard discs of **Tetracycline** (Antibacterial agent), **Amphotericin B** (Antifungal agent) served as positive controls for antimicrobial activity but filter discs impregnated with 10 µl of solvent (distilled water, chloroform, DMSO) were used as a negative control.

The agar used is Meuller-Hinton agar that is rigorously tested for composition and pH. Further the depth of the agar in the plate is a factor to be considered in the disc diffusion method. This method is well documented and standard zones of inhibition have been determined for susceptible and resistant values.

Blank paper disks (Schleicher & Schuell, Spain) with a diameter of 8.0 mm were impregnated l0µ, of tested concentration of the stock solutions.

When a filter paper disc impregnated with a tested chemical is placed on agar the chemical will diffuse from the disc into the agar. This diffusion will place the chemical in the agar only around the disc. The solubility of the chemical and its molecular size will determine the size of the area of chemical infiltration around the disc. If an organism is placed on the agar it will not grow in the area around the disc if it is susceptible to the chemical. This area of no growth around the disc is known as a **"Zone of inhibition"** or" **Clear zone".**

For the disc diffusion, the zone diameters were measured with slipping calipers of the National Committee for Clinical Laboratory Standards [210].

Agar-based methods such as Etest and disk diffusion can be good alternatives because they are simpler and faster than broth-based methods[211, 212]**.**

Sample	**Inhibition zone diameter (mm / mg Sample)**			
	Bacillus Subtilis **(G^+)**	*Escherichia coli* **(G^-)**	*Pseudomonas aeruginosa* **(G)**	*Staphylococcus Aureus* **(G^+)**
Control: DMSO	0.0	0.0	0.0	0.0
Standard: Tetracycline Antibacterial agent	30	31	30	29
1a	13	13	12	15
1b	11	10	14	10
5a	0.0	0.0	0.0	0.0
5b	0.0	0.0	0.0	0.0
5c	0.0	0.0	0.0	0.0
6a	10	11	13	0.0
6b	0.0	0.0	0.0	0.0
6c	0.0	0.0	0.0	0.0
9a	0.0	0.0	0.0	0.0
9b	0.0	0.0	0.0	0.0
10a	0.0	0.0	12	12
13a	12	13	14	14
13b	15	13	14	13

Sample	Inhibition zone diameter (mm / mg Sample)			
	Bacillus Subtilis **(G^+)**	*Escherichia coli* **(G^-)**	*Pseudomonas aeruginosa* (**G**)	*Staphylococcus Aureus* **G^+)**
13c	20	19	20	21
14a	19	15	18	19
14c	0.0	0.0	12	11
15a	15	13	14	13
15b	14	15	14	13
16a	12	12	12	12
16b	12	0.0	14	15
17a	14	13	13	14
17b	15	14	13	13
18a	13	14	15	15
18b	13	12	12	13
19a	0.0	0.0	0.0	0.0
19b	16	15	15	14
20a	0.0	0.0	0.0	0.0
20b	12	0.0	0.0	0.0
21a	15	15	16	15
23a	0.0	0.0	0.0	0.0
23b	0.0	0.0	0.0	0.0
25a	12	0.0	0.0	0.0
25b	17	19	18	20
26a	9	9	0.0	0.0
26b	10	10	9	0.0
27a	9	10	9	9
27b	10	9	9	0.0

Sample	Inhibition zone diameter (mm / mg Sample)			
	Bacillus Subtilis **(G^+)**	*Escherichia coli* **(G^-)**	*Pseudomonas aeruginosa* (**G**)	*Staphylococcus Aureus* **(G^+)**
28a	17	16	17	21
28b	0.0	10	10	0.0
29a	0.0	0.0	0.0	0.0
29b	0.0	0.0	9	0.0
30a	0.0	0.0	0.0	0.0
30b	10	10	9	0.0
32a	0.0	0.0	0.0	0.0
32b	0.0	0.0	0.0	0.0
32c	0.0	9	0.0	0.0
33a	0.0	0.0	0.0	0.0
33b	0.0	0.0	0.0	0.0
33c	0.0	0.0	0.0	0.0
34a	0.0	0.0	0.0	0.0
34b	0.0	0.0	0.0	0.0
35a	0.0	0.0	0.0	0.0
35b	0.0	12	10	0.0

- **G: Gram reaction**
- **Solvent: DMSO**

These compounds give different effects against different types of bacteria included as shown:

Compounds 13a, 16b, 17a and 18b give strong effect against *Bacillus Subtilis* (G^+), *Escherichia coli* (G^-), *Pseudomonas aeruginosa* (G) and *Staphylococcus Aureus* (G^+).

Compound 27a give weak effect against *Bacillus Subtilis* (G^+), *Escherichia coli* (G^-), *Pseudomonas aeruginosa* (G) and *Staphylococcus Aureus* (G^+).

5. Conclusion

In summary, we have developed a simple, efficient procedure for the synthesis of Pyrazolo[1,5-*a*]pyrimidines, [1,2,4]triazolo[4,3-*a*]pyrimidines, benzo[4,5]-imidazo[1,2-*a*]pyrimidines, pyrazolo[5,1-*c*][1,2,4]triazines, Triazolo[3,4-*c*][1,2,4]-triazines, benzo[4,5]imidazo[2,1-*c*][1,2,4]triazines, pyridenes. The newly synthesized compounds were elucidated by elemental analysis, spectral data, chemical transformation and alternative synthetic route whenever possible.

6. References

1. Manolov, I.; Maichle-Moessmer, C.; Danchev, N. (2006): Synthesis, structure, toxicological and pharmacological investigations of 4-hydroxycoumarin derivatives. Eur. J. Med. Chem. 41: 882-890.

2. Khan, I.; Kulkarni, M.; Sun, C. (2005): One pot synthesis of oxygenated tri-heterocycles as anti-microbial agents. Eur. J. Med. Chem. 40: 1168-1172.

3. Nawrot-Morankaa, J.; Nawrotb, E.; Graczykb, J. (2006): In vivo antitumor, in vitro antibacterial activity and alkylating properties of phosphorohydrazine derivatives of coumarin and chromone. Eur. J. Med. Chem. 41: 1301-1309.

4. Reddy, N.; Reddy, M. M.; Cosenza, S.; Gumireddy, K.; Bell, C. S.; Reddy, P.; Reddy, M. R. (2004): Synthesis of new coumarin 3-(*N*-aryl) sulfonamides and their anticancer activity. Bioorg. Med. Chem. Lett. 14: 4093-4097.

5. Donglei, Y.; Suzuki, M.; Lan, X.; Morris-Natschke, S.; Lee, K. (2003): Recent progress in the development of coumarin derivatives as potent anti-HIV agents. Med. Res. Rev. 23: 322-345

6. Moffett, R. B. (1646): Pyridylcoumarins U. S. Patent 3, 156, 697; *Chem. Abstr*. 1965, *62*, 5257f.

7. Sreenivasulu, B.; Sundaramurthy, V.; Rao, N. V. Subba. (1974): Search for physiologically active compounds. XXIII. Synthesis of 3-(3-pyridyl)- and 3-(3-pyridyl)-4-methylcoumarins. Proc. Ind. Acad. Sci., Sec. A, 79: 41-47.

8. Moffett, R. B. (1965): Pyridylcoumarins, U. S. Patent, 3, 201, 406; *Chem. Abstr*. 1965, 63, 13220f.

9. Moffett, R. B. (1964): Central Nervous System Depressants. VII. Pyridyl Coumarins. J. Med. Chem. 7: 446-449.

10. Tominaga, Y.; Honkawa, Y.; Hara, M.; Hosomi, A. (1990): Synthesis of pyrazolo[3,4-***d***]pyrimidine derivatives using ketene dithioacetals. J. Heterocycl. Chem., 27: 775–783

11. Moukha-chafiq, O.; Taha, M. L.; Lazrek, H. B.; Vasseur, J.-J.; Pannecouque, C.; Witvrouw, M.; De Clercq, E. (2002): Synthesis and biological activity of some 4-substituted 1-[1-(2,3-dihydroxy-1-propoxy)methyl-1,2,3-triazol-(4& 5)-ylmethyl]-1*H*-pyrazolo[3,4-*d*]pyrimidines. II Farmaco, 57: 27–32; Chem. Abstr., 2002, 137, 93724z.

12. Lowe, P. A. (1980): Aromatic and heteroaromatic chemistry; In Heterocyclic Chemistry; H. Suschitzky, O. Meth-Cohn (Eds.); Chemical Society: London, vol. 1, pp. 119–139.

13. Metzger, J. V. (1984): Thiazols and their benzo derivatives. In Comprehensive Heterocyclic Chemistry; A. R. Katritzky, C. W. Rees (Eds.); Pergamon Press: Oxford, UK, vol. 6, p. 328.

14. Brown, H. D. (1966): 2-Pyronyl and 2-thiopyronyl benzazoles. US Patent, 3,278,547; Chem. Abstr. 1966, 65, 18593.

15. Singh, S. P.; Segal, S. (1988): Synthesis and phototoxicity of some 2-(phenyl or 2- or 3-thienyl)-4-substituted thiazoles. Indan J. Chem. B, 27, 941.

16. Usui, Y.; Yamano, T. Fungicides, X. X. (1969): Antifungal activity of 3-aminothiazoline-2-thione and 4*H*-1,3,4-thidiazine derivatives. Yakugaku Zasshi 89, 099; Chem. Abstr. 1969, 71, 69601.

17. Goursot, P.; Westrum, E. F. Jr. (1969): Heat capacity and thermodynamic properties of benzothiazol from 5 to 320 K. J. Chem. Eng. Data, 14, 1

18. Abdelhamid, A. O.; Afifi, M. A. (2010): Synthesis Of Some New Thiazoles and Pyrazolo[1,5-*a*]pyrimidines Containing Antipyrine Moiety. Synthetic Communication, 40: 1539–1550.

19. Abdelhamid, A. O.; Abdelall, E. K. A.; Zaki, Y. H. (2010): Reactions with Hydrazonoyl Halides 62: Synthesis of some new Imidazo[1,2-*a*]pyrimidine, imidazo[1,2-*a*]pyridine, imdazo[1,2-*b*]pyrazole and quanazoline derivatives. J. Heterocyclic Chem. 47: 477- 482.

20. Abdelhamid, A. O. (2009): Convenient Synthesis of Some new Pyrazolo[1,5-*a*]pyrimidine, Pyridine, Thieno[2,3-*b*]pyridine and Isoxazolo[3,4-*d*]pyridazine Derivatives Containing Benzofuran Moiety. J. Heterocycl. Chem., 46, 680-686 (2009).

21. Abdelhamid**,** A. O.; Abdelall, E. K. A.; Abdel-Riheem, N. A.; Ahmed, S. A. (2010): Synthesis and Antimicrobial Activity of Some New 5-Arylazothiazole, Pyrazolo[1,5-*a*]pyrimidine, [1,2,4]triazolo[4,3-*a*]pyrimidine and Pyrimido[1,2-*a*]benzimidazole Derivatives Containing the thiazole Moiety. Phosphorus, Sulfur, Silicon and Related Element, 185: 709–718.

22. Abdelall, E. K. A.: Mohamed, M. A.; Abdelhamid, A. O**.** Reactions with Hydrazonoyl Halides 63: (2010): Synthesis and Anticancer Activity of Some New 1,3,4-Thiadiazoles, 1,3,4-Selenadiazoles and 1,2,4-Triazolo[4,3-*a*]pyrimidines. Phosphorus, Sulfur, Silicon and Related Element, 185: 1862-1874.

23. Abdelhamid, A. O.; Afifi, M. A. (2010): Utility of 4-formylantipyrine in heterocyclic synthesis. J. Advance Chemistry. 1: 137.

24. Abdelhamid, A. O.; Shokry A. S.; Tawfiek, S., M. (2012): A new approach for the synthesis of some pyrazolo[5,1-*c*]triazines and pyrazolo[1,5-*a*]pyrimidines. J. Heterocycl Chem., 49: 116 -124.