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# SYNTHETIC APPROACHES FOR NITROGEN BRIDGEHEAD PYRIDO-[1,2-*b*][1,2,4]TRIAZEPINES AND ANNULATED COMPOUNDS USING 4-(8-ALLYLCHROMON-3-YL)-1,6-DIAMINO-2-OXO-1,2-DIHYDRO-PYRIDINE-3,5-DICARBONITRILE

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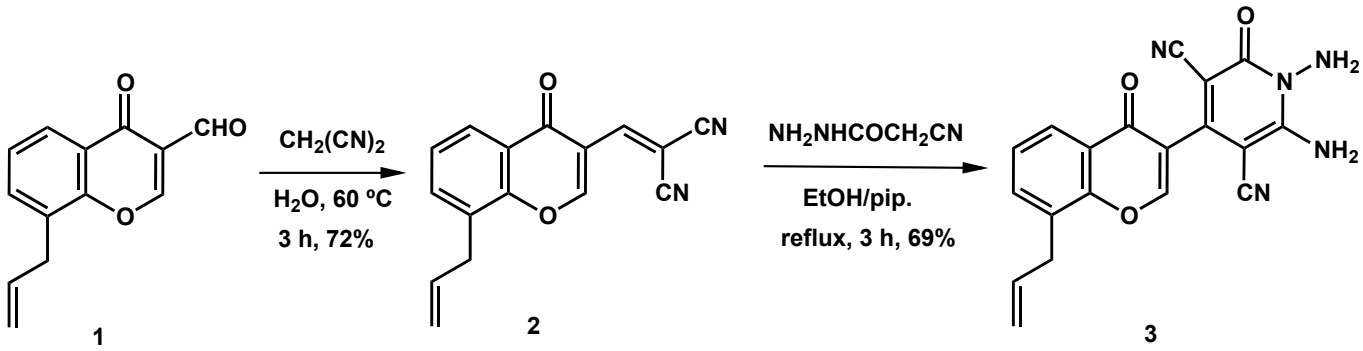
**Abstract** – Some new nitrogen bridgehead pyrido[1,2-*b*][1,2,4]triazepines linked 8-allylchromone moiety have been synthesized from reaction of novel 4-(8-allyl-chromon-3-yl)-1,6-diamino-2-oxo-1,2-dihydropyridine-3,5-dicarbonitrile (**3**) with a variety of α,γ-bifunctional electrophiles including dibenzoylmethane, ethyl benzoylacetate, 3-[*bis*(methylthio)methylidene]pentane-2,4-dione, 2-cyano-3,3-*bis*(methylthio)acrylonitrile, 2-cyano-3,3-*bis*(methylthio)prop-2-enamide, 5-chloro-3-methyl-1-phenylpyrazole-4-carboxaldehyde, 2-chloro-3-formyl-quinoline, (*p*-methoxybenzylidene)malononitrile and ethyl 2-cyano-3-(4-methoxyphenyl)prop-2-enoate. Some novel pyrazolo[3,4-*e*]pyrido[1,2-*b*]-[1,2,4]triazepines were also synthesized. Structures of the newly synthesized products have been deduced upon the help of elemental analysis and spectral data (IR, $^{1}$H NMR, $^{13}$NMR, mass spectra).

Chromones (4-oxo-4*H*-chromenes) are well known natural and synthetic products that possess diverse biological activities namely anticancer,[1] neuroprotective,[2] HIV-inhibitory,[3] antimicrobial,[4] anti-malaria,[5] antioxidant,[6] anti-inflammatory,[7] antibiotic[8] as well as Alzheimer's disease.[9] Recently, chromone derivatives have been used in several opto-electronic applications.[10] Chromones bearing an allyl group at position 8 have a special medicinal importance; 8-allyl-2-styrylchromones were used as inhibitors for the growth of tumors.[11] On the other hand, 1,2-diaminoarenes are very active substrates for building of various heterocyclic systems.[12] In symmetrical diamines, the product will be the same irrespective of which amino group participates first in the reaction. In the case of unsymmetrical diamines, the electron

withdrawing/donating nature of substituents influence the initial participation of a particular amino group in the reaction, resulting in chemoselective products. Some triazolo[1,5-*a*]pyridines, pyrido[1,2-*b*][1,2,4]triazines, and pyrido[1,2-*b*][1,2,4]triazepines were prepared from the reaction of 1,2-diaminopyridines with a diversity of electrophilic reagents.[13] On the basis of above observations and as a part of our aforementioned work directed on the reaction of 8-allylchromone,[14] as well as synthesis of new polynuclear bioactive heterocyclic systems,[15] the present work aims to study the chemical reactivity of the novel 4-(8-allylchromon-3-yl)-1,6-diamino-2-oxo-1,2-dihydropyridine-3,5-dicarbonitrile (**3**) towards various 1,3-bifunctional electrophiles to furnish some new nitrogen bridgehead pyrido[1,2-*b*][1,2,4]triazepines and some annulated compounds bearing 8-allylchromone moiety.

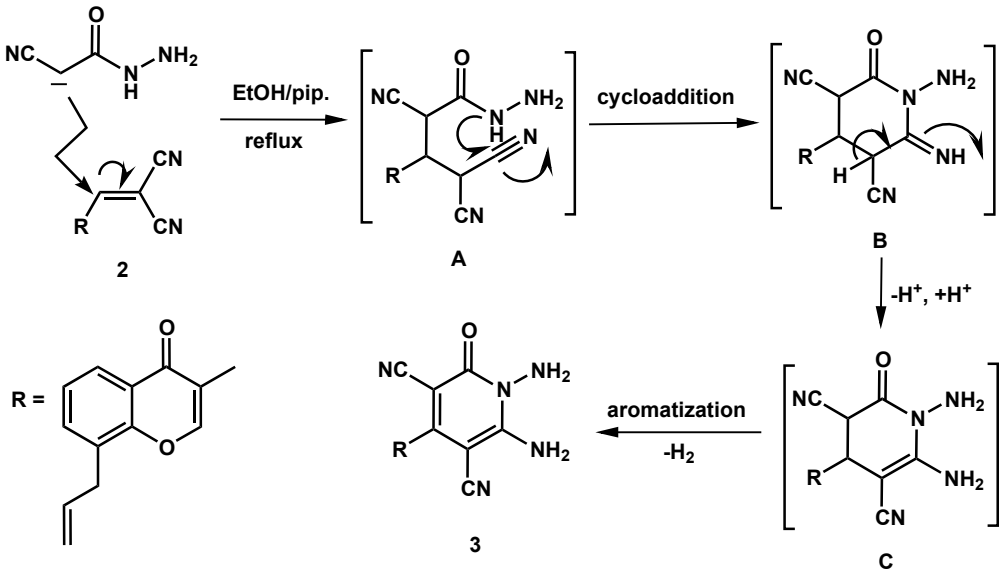
Stirring 8-allyl-3-formylchromone (**1**) with malononitrile in distilled water as a solvent at 60 ºC for 3 hours gave the condensation product; [(8-allylchromon-3-yl)methylene]malononitrile (**2**).[16] In this reaction we must notify the reaction temperature to avoid boiling of water because 8-allyl-3-formylchromone (**1**) melts at 73-74 ºC.[14] Treatment of compound **2** with cyanoacetohydrazide in 1:1 molar ratio, in boiling ethanol containing piperidine as a catalyst, afforded the novel 4-(8-allylchromon-3-yl)-1,6-diamino-2-oxo-1,2-dihydropyridine-3,5-dicarbonitrile (**3**) (Scheme 1).[17]




**Scheme 1.** Formation of the novel 1,6-diamino-2-oxo-1,2-dihydropyridine-3,5-dicarbonitrile **3**

Formation of compound **3** proceeds through nucleophilic addition of the deprotonated cyanoacetohydrazide onto the electron deficient vinyl carbon producing intermediate **A** followed by cycloaddition to the nitrile function giving intermediate **B** which underwent proton transfer furnishing intermediate **C**. Aromatization of the latter intermediate *via* autooxidation under the reaction conditions produced the target product **3** as illustrated in Scheme 2.[17] The IR spectrum of compound **3** showed characteristic absorption bands at 3406, 3336, 3287 ($2NH_2$), 2256 (2 C≡N), 1685 ($C{=}O_{pyridone}$) and 1655 $cm^{-1}$ ($C{=}O_{\gamma\text{-pyrone}}$). The $^1H$ NMR spectrum of compound **3** showed typical singlet signal at δ 9.31 ppm attributed to $H\text{-}2_{chromone}$. In addition, the spectrum showed two exchangeable signals at δ 4.70 and 10.14 ppm due to the *N*-$NH_2$ and *C*-$NH_2$ protons, respectively, that confirms the difference in nucleophilicity between the two amino groups. Thus, it is expected that the hydrazide β-nitrogen (*N*-$NH_2$) is more

nucleophilic and will react more rapidly with the electron deficient center than the second amino group (*C*-$NH_2$). The $^{13}C$ NMR spectrum of compound **3** showed characteristic downfield signal at δ 146.7 (C-$2_{chromone}$), 154.3 (C-$8a_{chromone}$), 160.1 (C-4), 168.8 (C-2 as C=O) and 177.8 ppm (C-$4_{chromone}$ as C=O). The two cyano groups appeared at δ 115.9, 116.4 ppm. The allyl segment appeared as specific signals at δ 31.4 (C-$3_{allyl}$ as $CH_{2\ alkane}$), 112.1 (C-$1_{allyl}$ as $CH_{2\ alkene}$) and 135.2 (C-$2_{allyl}$ as $CH_{alkene}$). Compound **3** was further deduced from its mass spectrum which showed the molecular ion peak, as the base peak, at *m/z* 359 which agrees well with the suggested molecular formula $C_{19}H_{13}N_5O_3$ and supports the identity of the structure.

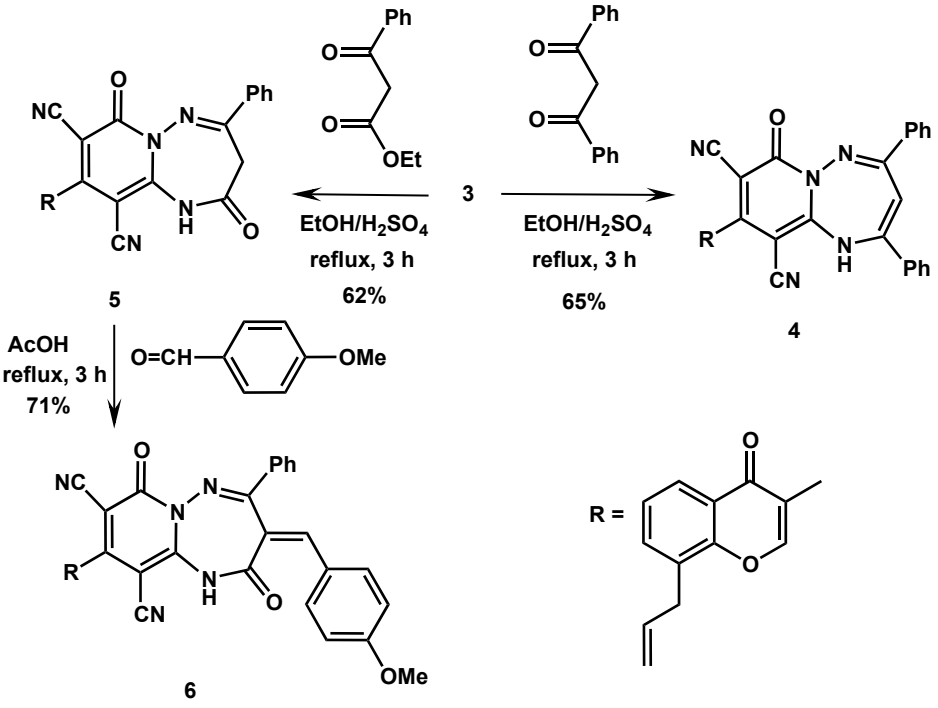



**Scheme 2.** The proposed mechanism for diaminopyridone derivative **3**

The chemical reactivity of 1,6-diaminopyridone **3** was studied towards some α,γ-bifunctional electrophiles.[18] Thus, condensation of compound **3** with dibenzoylmethane and ethyl benzoylacetate in boiling ethanol containing one drop of concentrated $H_2SO_4$ gave pyrido[1,2-*b*][1,2,4]triazepines **4** and **5**, respectively (Scheme 3). The reaction proceeds through condensation of the more nucleophilic amino group (*N*-$NH_2$) with the keto group followed by cyclocondensation of *C*-$NH_2$ with the other keto or ester group. The IR spectrum of compound **4** recorded characteristic absorption bands at 3342 (NH), 2249 (2C≡N), 1682 (C=$O_{pyridone}$), 1651 (C=$O_{\gamma\text{-pyrone}}$) and 1613 $cm^{-1}$ (C=N). Its mass spectrum showed the molecular ion peak at *m/z* 547 and supports the structure. The singlet signals attributed to H-3 and H-$2_{chromone}$ appeared in the $^1H$ NMR spectrum of compound **4** at δ 6.84 and 9.19 ppm. While, the $^1H$ NMR spectrum of compound **5** displayed two characteristic singlet signals at δ 2.84 ($CH_2$), and 9.30 (H-$2_{chromone}$), in addition to an exchangeable signal due to the NH proton at δ 12.31. The $^{13}C$ NMR spectrum

exhibited characteristic signal at δ 43.5 ppm attributed to C-3 as $CH_{2\ triazepine}$.

The presence of active methylene group in compound **5** was further confirmed by its simple condensation reaction with 4-methoxybenzaldehyde, in boiling acetic acid, giving the simple condensation product **6** (Scheme 3). The $^1$H NMR spectrum of compound **6** showed three specific singlets at δ 3.92, 6.37 and 9.12 assignable to OMe, $CH_{vinyl}$, H-$2_{chromone}$, respectively. The mass spectrum of compound **6** showed the molecular ion peak at *m/z* 605 which is coincident with its formula weight (605.60) and supports the identity of the structure.

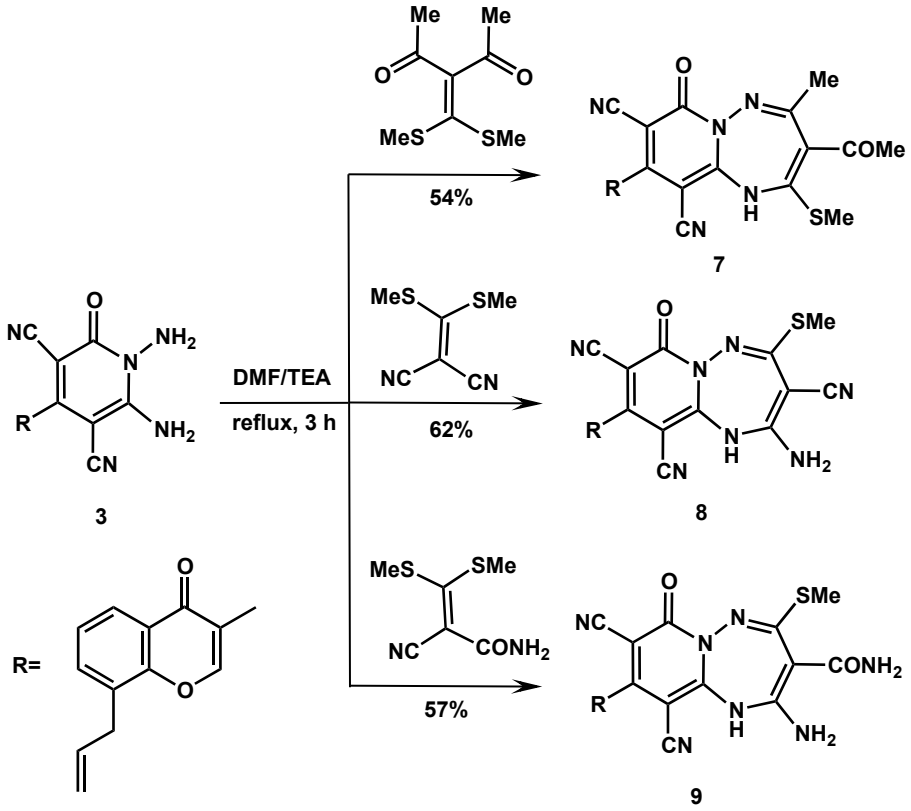



**Scheme 3.** Formation of pyrido[1,2-*b*][1,2,4]triazepine derivatives **4-6**

Condensation of compound **3** with 3-[*bis*(methylthio)methylidene]pentane-2,4-dione in DMF containing TEA gave 3-acetyl-9-(8-allylchromon-3-yl)-4-methyl-2-(methylsulfanyl)-7-oxo-1,7-dihydropyrido[1,2-*b*][1,2,4]triazepine-8,10-dicarbonitrile (**7**) (Scheme 4). The $^1$H NMR spectrum of compound **7** showed four characteristic singlet signals at δ 2.10 (Me), 2.34 (COMe), 2.73 (SMe) and 9.32 (H-$2_{chromone}$). Its $^{13}$C NMR spectrum displayed three upfield signals attributed to three methyl carbons at δ 15.4 (SMe), 17.2 (Me), 23.5 ppm ($Me_{acetyl}$).

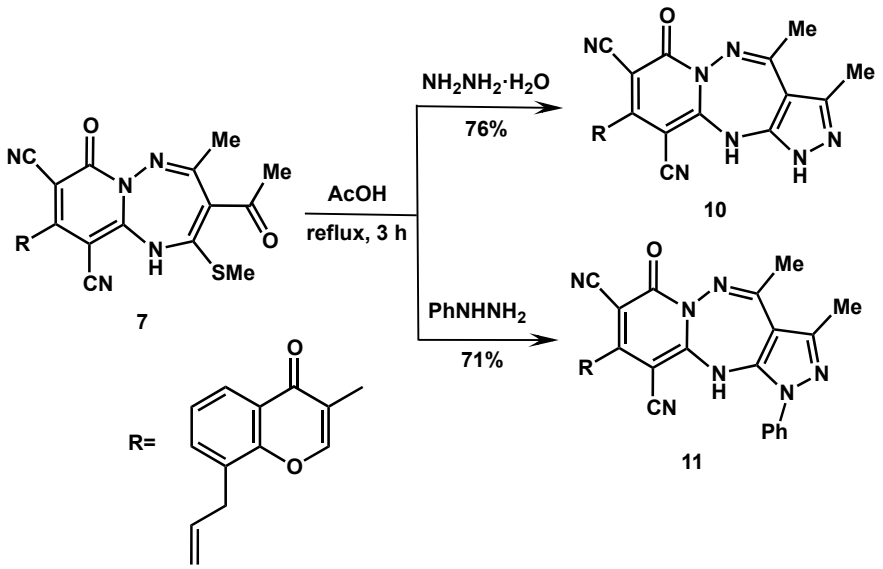
Also, heterocyclization of compound **3** with 2-cyano-3,3-*bis*(methylthio)acrylonitrile and 2-cyano-3,3-*bis*(methylthio)prop-2-enamide, in DMF containing TEA, afforded pyrido[1,2-*b*][1,2,4]triazepines **8** and **9**, respectively (Scheme 4). These reactions proceed *via* nucleophilic displacement of SMe group by the more nucleophilic amino group (*N*-$NH_2$) with concomitant cycloaddition of the other amino group (*C*-$NH_2$) onto nitrile function. The $^1$H NMR spectrum of compound **8** exhibited characteristic singlet signals

δ 2.78 ppm (SMe) and 9.26 ppm (H-$2_{chromone}$). The $^{13}C$ NMR spectrum of compound **9** presented three downfield signals attributed to three carbonyl carbons at δ 165.4 ($C=O_{amide}$), 168.9 (C-7 as C=O) and 177.5 ($C\text{-}4_{chromone}$ as C=O). The molecular ion peaks appeared in the mass spectrum of compounds **8** and **9** at *m/z* 481 and 499 and supports the identity of the structure.



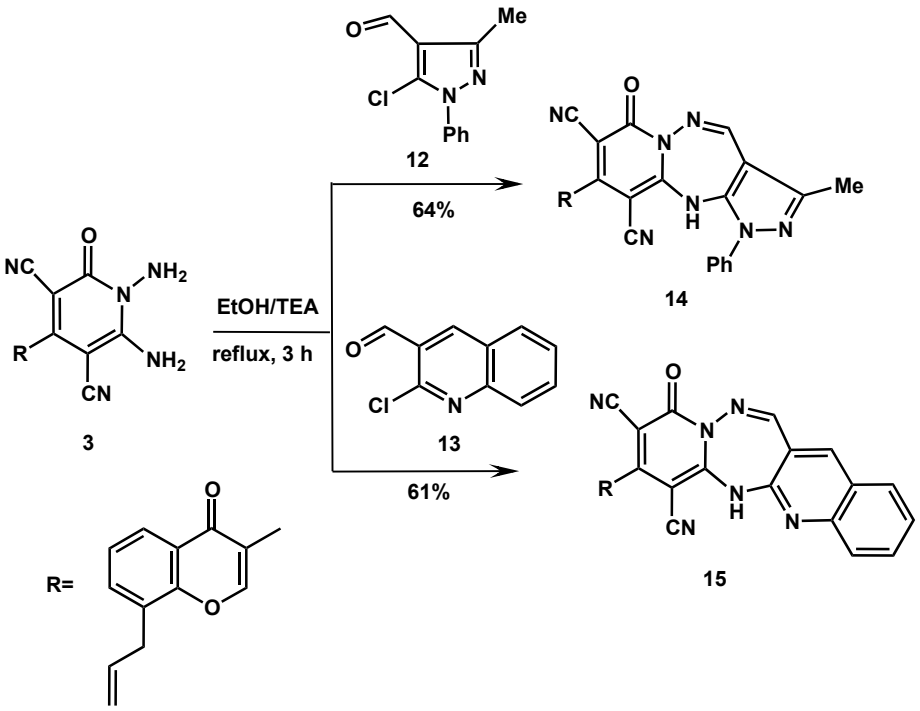

**Scheme 4.** Formation of pyrido[1,2-*b*][1,2,4]triazepine derivatives **7**-**9**

Compound **7** contains acetyl and methylthio function groups adjacent to each other and may serve a precursor for construction of annulated pyridotriazepines. Therefore, treatment of compound **7** with hydrazine hydrate and phenylhydrazine, in boiling acetic acid, afforded the novel pyrazolo[3,4-*e*]-pyrido[1,2-*b*][1,2,4]triazepines **10** and **11**, respectively (Scheme 5). The mass spectrum of compounds **10** and **11** showed their molecular ion peaks at *m/z* 463 and 539, that agree well with their suggested molecular formulas $C_{25}H_{17}N_7O_3$ and $C_{31}H_{21}N_7O_3$ and support the identity of the structures.



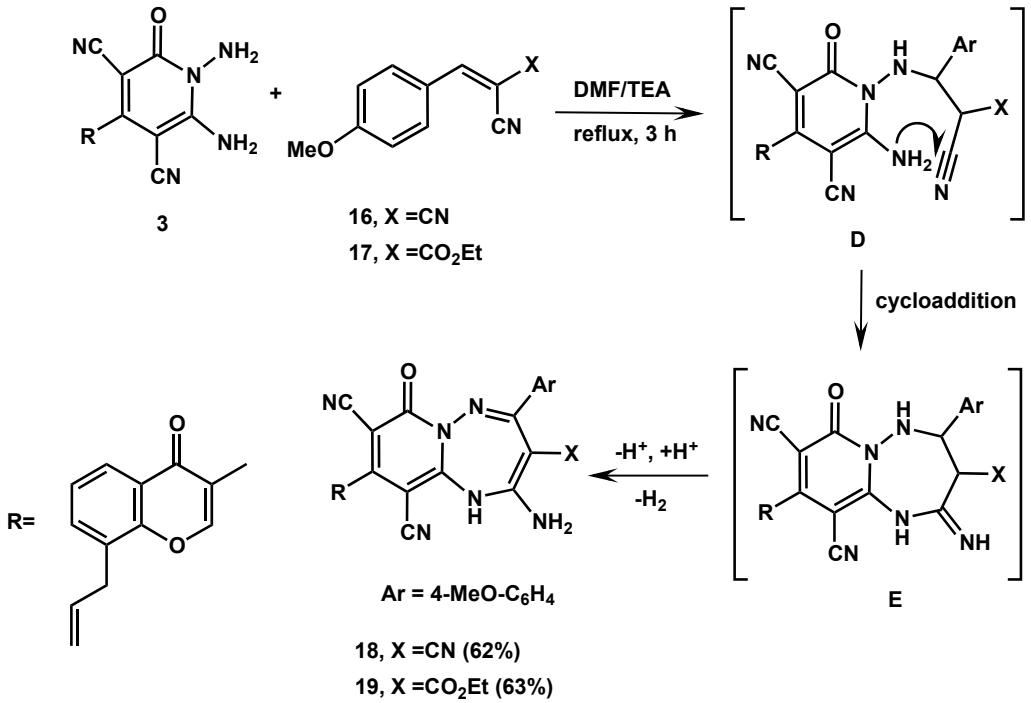

**Scheme 5.** Formation of pyrazolo[3,4-*e*]pyrido[1,2-*b*][1,2,4]triazepines **10** and **11**

On the other hand, 1,6-diaminopyridone **3** was allowed to react with some heterocyclic *o*-chloroaldehydes as α,γ-bifunctional electrophiles.[19] Thus, condensation of compound **3** with 5-chloro-3-methyl-1-phenylpyrazole-4-carboxaldehyde (**12**)[20] and 2-chloro-3-formylquinoline (**13**)[21] in ethanol containing TEA afforded heteroannulated pyrazolo[3,4-*e*]pyrido[1,2-*b*][1,2,4]triazepine **14** and quinolinyl[2,3-*e*]pyrido[1,2-*b*][1,2,4]triazepine **15**, respectively (Scheme 6). The $^{1}$H NMR spectra of compounds **14** and **15** showed characteristic singlet signals due to triazepine ring proton at δ 8.48 and 8.52 ppm, respectively. Also, the spectrum of compound **15** showed characteristic singlet at δ 8.92 ppm attributed to the H-4$_{quinoline}$. Further, the mass spectra of compounds **14** and **15** revealed the molecular ion peaks at *m/z* 525 and 496 corresponding to their molecular formula 525.53 and 496.49 and supports the identity of the structures.




**Scheme 6.** Formation of pyrido[1,2-*b*][1,2,4]triazepine derivatives **14** and **15**

Next, the chemical reactivity of compound **3** was investigated towards some arylidenenitriles. Thus, treating diaminopyridone **3** with (*p*-methoxybenzylidene)malononitrile (**16**) and ethyl 2-cyano-3-(4-methoxyphenyl)prop-2-enoate (**17**), in boiling DMF containing TEA, afforded pyrido[1,2-*b*][1,2,4]triazepine derivatives **18** and **19**, respectively (Scheme 7). Formation of compounds **18** and **19** occur through nucleophilic addition by the more nucleophilic amino group (N-$NH_2$) onto the vinyl carbon producing intermediate **D** followed by cycloaddition onto the nitrile function generating intermediate **E** with concomitant proton transfer with autooxidation under the reaction conditions leading to the final products (Scheme 7).[15] The IR spectrum of compound **18** showed specific absorption bands at 3402, 3243 ($NH_2$, NH), 2242, 3325 (3 C≡N), 1675 ($C=O_{pyridone}$), 1644 ($C=O_{\gamma\text{-pyrone}}$), and 1615 $cm^{-1}$ (C=N). Its $^1H$ NMR spectrum showed two characteristic singlet at δ 3.88 and 9.13 ppm assignable to methoxy and H-2 protons, respectively. The mass spectrum of compound **18** recorded the molecular ion peak at *m/z* 541 which is coincident well with the proposed molecular formula ($C_{30}H_{19}N_7O_4$). The IR spectrum of compound **19** displayed absorption bands at 3355, 3208 ($NH_2$, NH), 2242 (2 C≡N), 1700 ($C=O_{ester}$), 1682 ($C=O_{pyridone}$), 1646 ($C=O_{\gamma\text{-pyrone}}$) and 1614 $cm^{-1}$ (C=N). Its $^1H$ NMR spectrum showed triplet and quartet signals at δ 1.26 and 4.24 ppm attributed to the ethoxy protons, the spectrum also revealed characteristic singlet at δ 3.89 ppm assigned to the methoxy protons. In the $^{13}C$ NMR spectrum the ethoxy carbons appeared at chemical shift 13.2 (Me) and 38.1 ($CH_2$).




**Scheme 7.** Condensation of diaminopyridone **3** with arylidinenitriles **16** and **17**

A new series of nitrogen bridgehead pyrido[1,2-*b*][1,2,4]triazepines linked 8-allylchromone moiety was successfully synthesized through ring closure reactions of the key intermediate 4-(8-allylchromon-3-yl)-1,6-diamino-2-oxo-1,2-dihydropyridine-3,5-dicarbonitrile (**3**) with a diversity of α,γ-bifunctional electrophiles. The reaction proceeds firstly through condensation reactions of the more nucleophilic nitrogen (N-$NH_2$) followed by triazepine ring closure *via* the second amino group (C-$NH_2$) leading to chemoselective products. Some novel derivatives of pyrazolo[3,4-*e*]pyrido[1,2-*b*][1,2,4]triazepine and quinolinyl[2,3-*e*]pyrido[1,2-*b*][1,2,4]triazepine were also synthesized.

## EXPERIMENTAL

***General.*** Melting points were determined on a digital Stuart SMP3 apparatus. Infrared spectra were measured on FTIR Nicolet IS10 spectrophotometer ($cm^{-1}$), using KBr disks. $^1H$ NMR (300 MHz) and $^{13}C$ NMR (75 MHz) spectra were measured on Mercury-300BB, using DMSO-$d_6$ as a solvent and TMS (δ) as the internal standard. Mass spectra were obtained using GC-2010 Shimadzu Gas chromatography instrument mass spectrometer (70 eV). Elemental microanalyses were performed on a Perkin–Elmer CHN-2400 analyzer. The purity of the synthesized compounds was tested using TLC. 8-Allylchromone-3-carboxaldehyde (**1**) was prepared according to the reported method.[14]

**[(8-Allylchromon-3-yl)methylene]malononitrile (2).**

A mixture of 8-allyl-3-formylchromone (**1**) (2.13 g, 10 mmol) and malononitrile (0.66 g, 10 mmol), in water (20 mL) was stirred at 60 ºC for 3 h. The yellow precipitate obtained during heating was filtered and crystallized from MeOH as yellow crystals, yield (1.60 g, 72%), mp 189-190 ºC. IR (KBr, $cm^{-1}$): 3082 ($CH_{arom.}$), 2924, 2890 ($CH_{aliph.}$), 2232 (2 C≡N), 1653 ($C=O_{\gamma\text{-pyrone}}$), 1604 (C=C). $^1$H NMR (DMSO-$d_6$, δ, 300 MHz): 3.59 (d, 2H, *J*=6.2 Hz, $CH_{2\ allyl}$), 5.03-5.09 (m, 2H, $CH_{2\ allyl}$), 5.71 (s, 1H, $CH_{vinyl}$), 6.01-6.12 (m, 1H, $CH_{allyl}$), 7.44 (d, 1H, *J*=7.2 Hz, H-$6_{chromone}$), 7.62 (d, 1H, *J*=7.5 Hz, H-$7_{chromone}$), 8.27 (d, 1H, *J*=7.5 Hz, H-$5_{chromone}$), 9.23 (s, 1H, H-$2_{chromone}$). MS (*m/z*, *I*%): 262 ($M^+$; 72), 234 (100), 208 (56), 157 (19), 132 (11), 117 (8), 78 (12), 51 (32). Anal. Calcd for $C_{16}H_{10}N_2O_2$ (262.27); C, 73.27; H, 3.84; N, 10.68%. Found: C, 73.05; H, 3.62; N, 10.59%.

**4-(8-Allylchromon-3-yl)-1,6-diamino-2-oxo-1,2-dihydropyridine-3,5-dicarbonitrile (3).**

A mixture of (8-allylchromon-3-yl)methylenemalononitrile (**2**) (0.26 g, 1 mmol) and cyanoacetohydrazide, (0.1 g, 1 mmol), in absolute EtOH (10 mL) containing one drop of piperidine, was heated under reflux for 3 h. The orange-yellow precipitate obtained after cooling was filtered and crystallized from EtOH, yield (0.24 g, 69%), mp 217-218 ºC. IR (KBr, $cm^{-1}$): 3406, 3336, 3287 ($2NH_2$), 3062 ($CH_{arom.}$), 2928 ($CH_{aliph.}$), 2256 (2 C≡N), 1685 ($C=O_{pyridone}$), 1655 ($C=O_{\gamma\text{-pyrone}}$), 1602 (C=C). $^1$H NMR (DMSO-$d_6$, δ, 300 MHz): 3.62 (d, 2H, *J*=6.6 Hz, $CH_{2\ allyl}$), 4.70 (bs, 1H, *N*-$NH_2$ exchangeable with $D_2O$), 5.07-5.13 (m, 2H, $CH_{2\ allyl}$), 5.94-6.07 (m, 1H, $CH_{allyl}$), 7.25 (d, 1H, *J*=7.5 Hz, H-$6_{\ chromone}$), 7.42 (d, 1H, *J*=7.5 Hz, H-$7_{chromone}$), 8.24 (d, 1H, *J*=7.2 Hz, H-$5_{chromone}$), 9.31 (s, 1H, H-$2_{chromone}$), 10.14 (bs, 1H, *C*-$NH_2$ exchangeable with $D_2O$). $^{13}$C NMR (DMSO, δ, 75 MHz): 31.4 (C-$3_{allyl}$), 67.8 (C-5), 96.3 (C-3), 112.1 (C-$1_{allyl}$), 115.9, 116.4 (2C≡N), 118.6 (C-3 $_{chromone}$), 120.1 (C-$4a_{chromone}$), 124.0 (C-$6_{chromone}$), 126.3 (C-$5_{chromone}$), 128.8 (C-$8_{chromone}$), 133.5 (C-$7_{chromone}$), 135.2 (C-$2_{allyl}$), 142.3 (C-6), 146.7 (C-$2_{chromone}$), 154.3 (C-$8a_{chromone}$), 160.1 (C-4), 168.8 (C-2 as C=O), 177.8 (C-4 $_{chromone}$ as C=O). MS (*m/z*, *I*%): 359 ($M^+$; 100), 344 (61), 316 (34), 288 (70), 186 (22), 161 (16), 133 (21), 116 (12), 93 (15), 77 (62), 64 (24). Anal. Calcd for $C_{19}H_{13}N_5O_3$ (359.35); C, 63.51; H, 3.65; N, 19.49%. Found: C, 63.32; H, 3.42; N, 19.24%.

**9-[8-Allylchromon-3-yl]-2,4-diphenyl-7-oxo-1,7-dihydropyrido[1,2-*b*][1,2,4]triazepine-8,10-dicarbonitrile (4).**

A mixture of compound **3** (0.72 g, 2 mmol) and dibenzoylmethane (0.45 g, 2 mmol) in EtOH (30 mL) containing one drop of concentrated sulfuric acid was heated under reflux for 3 h. The solid obtained after cooling was filtered, washed with EtOH and crystallized from *n*-BuOH, yield (0.70 g, 65%), mp 260-261 ºC. IR (KBr, $cm^{-1}$): 3342 (NH), 3058 ($CH_{arom.}$), 2249 (2 C≡N), 1682 ($C=O_{pyridone}$), 1651 ($C=O_{\gamma\text{-pyrone}}$), 1613 (C=N), 1594 (C=C). $^1$H NMR (DMSO-$d_6$, δ, 300 MHz): 3.55 (d, 2H, *J*=6.0 Hz, $CH_{2\ allyl}$),

5.03-5.11 (m, 2H, $CH_{2\ allyl}$), 5.97-6.05 (m, 1H, $CH_{allyl}$), 6.84 (s, 1H, H-3), 6.97-7.54 (m, 12H, Ar-H, H-6 $_{chromone}$ and H-7$_{chromone}$), 8.29 (d, 1H, *J*=7.2 Hz, H-5$_{chromone}$), 9.19 (s, 1H, H-2$_{chromone}$), 10.62 (bs, 1H, NH exchangeable with $D_2O$). MS (*m/z*, *I*%): 547 ($M^+$; 46), 519 (31), 491 (12), 342 (31), 314 (62), 157 (14), 132 (16), 117 (49), 77 (100), 64 (57). Anal. Calcd for $C_{34}H_{21}N_5O_3$ (547.58): C, 74.58; H, 3.87; N, 12.79%. Found: C, 74.45; H, 3.65; N, 12.71%.

**9-[8-Allylchromon-3-yl]-4-phenyl-2,7-dioxo-1,2,3,7-tetrahydropyrido[1,2-*b*][1,2,4]triazepine-8,10-dicarbonitrile (5).**

A mixture of compound **3** (0.72 g, 2 mmol) and ethyl benzoylacetate (0.38 g, 2 mmol) in EtOH (30 mL) containing one drop of $H_2SO_4$ was heated under reflux for 3 h. The solid obtained after cooling was filtered, washed with ethanol and crystallized from EtOH to give **5** as yellow crystals, yield (0.63 g, 62%), mp 242-243 ºC. IR (KBr, $cm^{-1}$): 3326 (NH), 3049 ($CH_{arom.}$), 2235 (2 C≡N), 1680 (C=O$_{pyridone}$), 1668 (C=O$_{cyclic\ amide}$), 1639 (C=O$_{\gamma\text{-pyrone}}$), 1611 (C=N), 1599 (C=C). $^1$H NMR (DMSO-$d_6$, δ, 300 MHz): 2.84 (s, 2H, $CH_2$), 3.53 (d, 2H, *J*=6.6 Hz, $CH_{2\ allyl}$), 5.02-5.08 (m, 2H, $CH_{2\ allyl}$), 6.01-6.08 (m, 1H, $CH_{allyl}$), 6.88-7.39 (m, 7H, 5Ph-H, H-6$_{chromone}$ and H-7$_{chromone}$), 8.33 (d, 1H, *J*=7.2 Hz, H-5$_{chromone}$), 9.30 (s, 1H, H-2$_{chromone}$), 12.31 (bs, 1H, NH exchangeable with $D_2O$). $^{13}$C NMR (DMSO, δ, 75 MHz): 31.7 (C-3$_{allyl}$), 43.2 (C-3 as $CH_2$), 68.5 (C-10), 95.9 (C-8), 111.4 (C-1$_{allyl}$), 114.3 (2C-Ph), 116.1, 116.7 (2C≡N), 117.9 (C-Ph), 119.2 (C-3$_{chromone}$), 120.6 (C-4a$_{chromone}$), 112.5 (2C-Ph), 124.2 (C-6$_{chromone}$), 126.1 (C-5$_{chromone}$), 127.6 (C-Ph), 128.9 (C-8$_{chromone}$), 133.2 (C-7$_{chromone}$), 135.7 (C-2$_{allyl}$), 145.4 (C-2$_{chromone}$), 152.1 (C-8a$_{chromone}$), 160.3 (C-4), 162.1 (C-9), 166.3 (C-2 as C=O), 169.4 (C-7 as C=O), 178.2 (C-4$_{chromone}$ as C=O). MS (*m/z*, *I*%): 487 ($M^+$; 44), 459 (26), 416 (31), 339 (15), 311 (14), 260 (33), 233 (8), 185 (12), 161 (100), 133 (17), 103 (7), 77 (100), 65 (36). Anal. Calcd for $C_{28}H_{17}N_5O_4$ (487.48): C, 68.99; H, 3.52; N, 14.37%. Found: C, 68.74; H, 3.33; N, 14.14%.

**9-[8-Allylchromon-3-yl]-3-(4-methoxybenzylidene)-4-phenyl-2,7-dioxo-1,2,3,7-tetrahydropyrido[1,2-*b*][1,2,4]triazepine-8,10-dicarbonitrile (6).**

A mixture of compound **5** (0.49 g, 1 mmol) and 4-methoxybenzaldehyde (0.14 mL, 1 mmol) in glacial acetic acid (10 mL) was heated under reflux for 3 h. The solid obtained during heating was filtered and crystallized from AcOH as yellow crystals, yield (0.43 g, 71%), mp 296-297 ºC. IR (KBr, $cm^{-1}$): 3340 (NH), 3032 ($CH_{arom.}$), 2233 (2 C≡N), 1675 (C=O$_{pyridone}$), 1660 (C=O$_{cyclic\ amide}$), 1634 (C=O$_{\gamma\text{-pyrone}}$), 1607 (C=N), 1584 (C=C). $^1$H NMR (DMSO-$d_6$, δ, 300 MHz): 3.55 (d, 2H, *J*=6.9 Hz, $CH_{2\ allyl}$), 3.92 (s, 3H, OMe), 5.01-5.06 (m, 2H, $CH_{2\ allyl}$), 6.02-6.07 (m, 1H, $CH_{allyl}$), 6.37 (s, 1H, CH $_{vinyl}$), 6.58 (d, 2H, *J*=7.8 Hz, Ar-H), 7.02-7.51 (m, 7H, 5Ph-H, H-6$_{chromone}$ and H-7$_{chromone}$), 7.86 (d, 2H, *J*=7.8 Hz, Ar-H), 8.24 (d, 1H, *J*=8.1 Hz, H-5$_{chromone}$), 9.12 (s, 1H, H-2$_{chromone}$), 12.20 (bs, 1H, NH exchangeable with $D_2O$). MS (*m/z*,

*I*%): 605 ($M^+$; 32), 502 (18), 474 (25), 446 (10), 340 (21), 315 (17), 287 (9), 247 (33), 233 (8), 184 (8), 161 (24), 132 (9), 106 (100), 77 (68), 64 (13). Anal. Calcd for $C_{36}H_{23}N_5O_5$ (605.60): C, 71.40; H, 3.83; N, 11.56%. Found: C, 71.19; H, 3.60; N, 11.33%.

**3-Acetyl-9-(8-allylchromon-3-yl)-4-methyl-2-(methylthio)-7-oxo-1,7-dihydropyrido[1,2-*b*]-[1,2,4]triazepine-8,10-dicarbonitrile (7).**

A mixture of compound **3** (0.72 g, 2 mmol) and 3-[*bis*(methylthio)methylidene]pentane-2,4-dione (0.41 g, 2 mmol) in DMF (15 mL) containing two drops of triethylamine was heated under reflux for 3 h. The yellow crystals obtained after cooling was filtered and crystallized from DMF/MeOH, yield (0.53 g, 54%), mp 249-250 ºC. IR (KBr, $cm^{-1}$): 3310 (NH), 3057 ($CH_{arom.}$), 2962, 2922 ($CH_{aliph.}$), 2242 (2C≡N), 1683 ($C=O_{pyridone}$), 1667 ($C=O_{aceyl}$), 1642 ($C=O_{\gamma\text{-pyrone}}$), 1608 (C=N), 1598 (C=C). $^1$H NMR (DMSO-$d_6$, δ, 300 MHz): 2.10 (s, 3H, Me), 2.34 (s, 3H, COMe), 2.73 (s, 3H, SMe), 3.52 (d, 2H, *J*=6.0 Hz, $CH_{2\ allyl}$), 5.04-5.13 (m, 2H, $CH_{2\ allyl}$), 6.04-6.15 (m, 1H, $CH_{allyl}$), 7.32 (d, 1H, *J*=6.9 Hz, H-$6_{chromone}$), 7.56 (d, 1H, *J*=7.2 Hz, H-$7_{chromone}$), 8.26 (d, 1H, *J*=7.2 Hz, H-$5_{chromone}$), 9.32 (s, 1H, H-$2_{chromone}$), 11.74 (bs, 1H, NH exchangeable with $D_2O$). $^{13}$C NMR (DMSO, δ, 75 MHz): 15.4 (SMe), 17.2 (Me), 23.5 ($Me_{\ acetyl}$), 31.5 (C-$3_{allyl}$), 69.3 (C-10), 96.2 (C-8), 111.8 (C-$1_{allyl}$), 116.2, 116.9 (2C≡N), 119.6 (C-$3_{chromone}$), 120.4 (C-$4a_{\ chromone}$), 124.3 (C-$6_{chromone}$), 126.0 (C-$5_{chromone}$), 128.5 (C-$8_{chromone}$), 132.6 (C-$7_{chromone}$), 134.9 (C-$2_{allyl}$), 145.8 (C-$2_{chromone}$), 151.7 (C-$8a_{chromone}$), 155.6 (C-2), 159.4 (C-4), 162.3 (C-9), 169.6 (C-7 as C=O), 178.1 (C-$4_{chromone}$ as C=O). MS (*m/z*, *I*%): 497 ($M^+$; 17), 454 (24), 424 (41), 396 (36), 300 (51), 274 (8), 161 (100), 133 (60), 116 (23), 92 (31), 77 (74), 65 (25). Anal. Calcd for $C_{26}H_{19}N_5O_4S$ (497.53): C, 62.77; H, 3.85; N, 14.08; S, 6.44%. Found: C, 62.48; H, 3.74; N, 13.94; S, 6.28%.

**9-(8-Allylchromon-3-yl)-2-amino-4-methylthio-7-oxo-1,7-dihydropyrido[1,2-*b*][1,2,4]triazepine-3,8,10-tricarbonitrile (8).**

A mixture of compound **3** (0.72 g, 2 mmol) and 2-cyano-3,3-*bis*(methylthio)acrylonitrile (0.34 g, 2 mmol) in DMF (15 mL) containing two drops of triethylamine was heated under reflux for 3 h. The yellow crystals obtained after cooling was filtered and crystallized from DMF/EtOH, yield (0.55 g, 62%), mp 271-272 ºC. IR (KBr, $cm^{-1}$): 3315, 3240, 3184 ($NH_2$, NH), 3052 ($CH_{arom.}$), 2921, 2883 ($CH_{aliph}$), 2254, 2238 (3 C≡N), 1681 ($C=O_{pyridone}$), 1642 $C=O_{\gamma\text{-pyrone}}$), 1609 (C=N), 1601 (C=C). $^1$H NMR (DMSO-$d_6$, δ, 300 MHz): 2.78 (s, 3H, SMe), 3.56 (d, 2H, *J*=6.6 Hz, $CH_{2\ allyl}$), 5.06-5.11 (m, 2H, $CH_{2\ allyl}$), 6.01-6.09 (m, 1H, $CH_{\ allyl}$), 7.43 (d, 1H, *J*=7.8, H-$6_{chromone}$), 7.62 (d, 1H, *J*=7.5 Hz, H-$7_{chromone}$), 7.87 (bs, 2H, $NH_2$ exchangeable with $D_2O$), 8.31 (d, 1H, *J*=7.5 Hz, H-$5_{chromone}$), 9.26 (s, 1H, H-$2_{chromone}$), 10.84 (bs, 1H, NH exchangeable with $D_2O$). $^{13}$C NMR (DMSO, δ, 75 MHz): 15.2 (SMe), 31.0 (C-$3_{allyl}$), 69.7 (C-10), 78.3 (C-3), 96.5 (C-8), 111.6 (C-$1_{allyl}$), 116.2, 116.9, 117.4 (3C≡N), 119.2 (C-$3_{chromone}$), 120.7 (C-$4a_{\ chromone}$),

124.2 (C-6$_{chromone}$), 126.4 (C-5$_{chromone}$), 128.1 (C-8$_{chromone}$), 132.3 (C-7$_{chromone}$), 134.6 (C-2$_{allyl}$), 145.9 (C-2$_{chromone}$), 148.3 (C10a), 151.2 (C-8a$_{chromone}$), 157.1 (C-2), 159.3 (C-4), 162.1 (C-9), 169.4 (C-7 as C=O), 178.4 (C-4$_{chromone}$ as C=O). MS (*m/z*, *I*%): 481 ($M^+$; 29), 434 (46), 406 (30), 380 (13), 288 (60), 194 (38), 161 (100), 120 (14), 91 (25), 77 (41), 65 (11). Anal. Calcd for $C_{24}H_{15}N_7O_3S$ (481.50): C, 59.87; H, 3.14; N, 20.36; S, 6.66%. Found: C, 59.80; H, 3.07; N, 20.13; S, 6.58%.

**9-(8-Allylchromon-3-yl)-2-amino-8,10-dicyano-4-(methylthio)-7-oxo-1,7-dihydropyrido[1,2-*b*]-[1,2,4]triazepine-3-carboxamide (9).**

A mixture of compound **3** (0.72 g, 2 mmol) and 2-cyano-3,3-*bis*(methylthio)prop-2-enamide (0.38 g, 2 mmol) in DMF (15 mL) containing two drops of triethylamine was heated under reflux for 4 h. The solid obtained after cooling was filtered, washed with EtOH and crystallized from DMF, yield (0.57 g, 57%), mp 283-284 ºC. IR (KBr, $cm^{-1}$): 3426, 3362, 3287, 3175 (2$NH_2$, NH), 2244 (2C≡N), 1693 (C=O$_{amide}$), 1684 (C=O$_{pyridone}$), 1649 (C=O$_{\gamma\text{-pyrone}}$), 1608 (C=N), 1592 (C=C). $^1$H NMR (DMSO-$d_6$, δ, 300 MHz): 2.75 (s, 3H, SMe), 3.58 (d, 2H, *J*=6.4 Hz, $CH_{2\ allyl}$), 5.04-5.10 (m, 2H, $CH_{2\ allyl}$), 6.03-6.08 (m, 1H, $CH_{allyl}$), 7.36 (d, 1H, *J*=7.8 Hz, H-6$_{chromone}$), 7.58 (d, 1H, *J*=7.8 Hz, H-7$_{chromone}$), 7.92 (bs, 2H, $NH_2$ exchangeable with $D_2O$), 8.24 (d, 1H, *J*=7.8 Hz, H-5$_{chromone}$), 8.93 (s, 1H, H-2$_{chromone}$), 10.74 (bs, 1H, NH exchangeable with $D_2O$). $^{13}$C NMR (DMSO, δ, 75 MHz): 15.6 (SMe), 31.2 (C-3$_{allyl}$), 69.4 (C-10), 83.6 (C-10), 96.7 (C-8), 111.9 (C-1$_{allyl}$), 116.0, 116.8 (2C≡N), 118.9 (C-3$_{chromone}$), 120.5 (C-4a$_{chromone}$), 124.5 (C-6$_{chromone}$), 126.3 (C-5$_{chromone}$), 128.6 (C-8$_{chromone}$), 132.6 (C-7$_{chromone}$), 134.9 (C-2$_{allyl}$), 146.2 (C-2$_{chromone}$), 148.2 (C10a), 151.6 (C-8a$_{chromone}$), 156.8 (C-2), 160.2 (C-4), 162.4 (C-9), 165.4 (C=O$_{amide}$), 168.9 (C-7 as C=O), 177.5 (C-4$_{chromone}$ as C=O). MS (*m/z*, *I*%): 499 ($M^+$; 26), 471 (31), 452 (19), 427 (42), 408 (11), 316 (91), 288 (47), 133 (100), 117 (23), 77 (12). Anal. Calcd for $C_{24}H_{17}N_7O_4S$ (499.51): C, 57.71; H, 3.43; N, 19.63; S, 6.42%. Found: C, 57.74; H, 3.40; N, 19.55; S, 6.40%.

**9-(8-Allylchromon-3-yl)-3,4-dimethyl-7-oxo-7,11-dihydro-1*H*-pyrazolo[3,4-*e*]pyrido[1,2-*b*][1,2,4]-triazepine-8,10-dicarbonitrile (10)**

A mixture of compound **7** (0.50 g, 1 mmol) and hydrazine hydrate (0.10 g, 2 mmol) in glacial acetic acid (15 mL) was heated under reflux for 3 h. The yellow crystals obtained during heating were filtered and crystallized from DMF, yield (0.35 g, 76%), mp 269-270 ºC. IR (KBr, $cm^{-1}$): 3381, 3268 (2NH), 3041 (CH$_{arom.}$), 2984, 2910 (CH$_{aliph.}$), 2238 (2C≡N), 1679 (C=O$_{pyridone}$), 1637 (C=O$_{\gamma\text{-pyrone}}$), 1604 (C=N), 1579 (C=C). $^1$H NMR (DMSO-$d_6$, δ, 300 MHz): 2.07 (s, 3H, Me), 2.16 (s, 3H, Me), 3.47 (d, 2H, *J*=6.3 Hz, $CH_{2\ allyl}$), 5.00-5.07 (m, 2H, $CH_{2\ allyl}$), 5.89-5.96 (m, 1H, $CH_{allyl}$), 7.24 (d, 1H, *J*=7.2 Hz, H-6$_{chromone}$), 7.52 (d, 1H, *J*=7.2 Hz, H-7$_{chromone}$), 8.17 (d, 1H, *J*=7.2 Hz, H-5$_{chromone}$), 9.24 (s, 1H, H-2$_{chromone}$), 9.97 (bs, 1H, NH exchangeable with $D_2O$), 11.43 (bs, 1H, NH exchangeable with $D_2O$). MS (*m/z*, *I*%): 463 ($M^+$; 46), 435

(21), 394 (13), 366 (17), 325 (10), 299 (8), 261 (23), 161 (100), 116 (51), 92 (26), 77 (19), 64 (11). Anal. Calcd for $C_{25}H_{17}N_7O_3$ (463.45): C, 64.79; H, 3.70; N, 21.16%. Found: C, 64.50; H, 3.65; N, 20.95%.

**9-(8-Allylchromon-3-yl)-3,4-dimethyl-7-oxo-7,11-dihydro-1-phenyl-1*H*-pyrazolo[3,4-*e*]pyrido[1,2-*b*]-[1,2,4]triazepine-8,10-dicarbonitrile (11)**

A mixture of compound **7** (0.50 g, 1 mmol) and phenylhydrazine (0.12 mL, 1 mmol) in glacial acetic acid (15 mL) was heated under reflux for 3 h. The orange-yellow crystals obtained during heating were filtered and crystallized from DMF, yield (0.38 g, 71%), mp 291-292 ºC. IR (KBr, $cm^{-1}$): 3301 (NH), 3062 ($CH_{arom.}$), 2993, 2925 ($CH_{aliph.}$), 2231 (2C≡N), 1681 ($C=O_{pyridone}$), 1640 ($C=O_{\gamma\text{-pyrone}}$), 1609 (C=N), 1583 (C=C). $^1$H NMR (DMSO-$d_6$, δ, 300 MHz): 2.11 (s, 3H, Me), 2.20 (s, 3H, Me), 3.48 (d, 2H, *J*=6.6 Hz, $CH_{2\ allyl}$), 5.05-5.13 (m, 2H, $CH_{2\ allyl}$), 5.81-5.92 (m, 1H, $CH_{allyl}$), 6.80-7.16 (m, 6H, Ph-H and H-$6_{chromone}$), 7.48 (d, 1H, *J*=7.5 Hz, H-$7_{chromone}$), 8.26 (d, 1H, *J*=7.6 Hz, H-$5_{chromone}$), 9.22 (s, 1H, H-$2_{chromone}$), 10.57 (bs, 1H, NH exchangeable with $D_2O$). MS (*m/z*, *I*%): 539 ($M^+$; 22), 498 (16), 470 (19), 429 (14), 401 (13), 324 (19), 286 (31), 260 (24), 220 (9), 161 (43), 133 (9), 116 (11), 93 (8), 77 (100), 64 (47). Anal. Calcd for $C_{31}H_{21}N_7O_3$ (539.54): C, 69.01; H, 3.92; N, 18.17%. Found: C, 68.85; H, 3.77; N, 18.02%.

**9-(8-Allylchromon-3-yl)-3-methyl-7-oxo-7,11-dihydro-1-phenyl-1*H*-pyrazolo[3,4-*e*]pyrido[1,2-*b*]-[1,2,4]triazepine-8,10-dicarbonitrile (14).**

A mixture of compound **3** (0.72 g, 2 mmol) and 5-chloro-3-methyl-1-phenylpyrazole-4-carbaldehyde (**12**) (0.44 g, 2 mmol) in absolute EtOH (30 mL) containing few drops of triethylamine was heated under reflux for 3 h. The yellow solid obtained during heating was filtered and crystallized from DMF, yield (0.67 g, 64%), mp 258-259 ºC. IR (KBr, $cm^{-1}$): 3321 (NH), 3054 ($CH_{arom.}$), 2929, 2856 ($CH_{aliph.}$), 2238 (2C≡N), 1680 ($C=O_{pyridone}$), 1641 ($C=O_{\gamma\text{-pyrone}}$), 1610 (C=N), 1597 (C=C). $^1$H NMR (DMSO-$d_6$, δ, 300 MHz): 2.09 (s, 3H, $Me_{pyrazole}$), 3.53 (d, 2H, *J*=6.2 Hz, $CH_{2\ allyl}$), 5.03-5.10 (m, 2H, $CH_{2\ allyl}$), 6.02-6.08 (m, 1H, $CH_{allyl}$), 7.35 (d, 1H, *J*=7.8 Hz, H-$6_{chromone}$), 7.59 (d, 1H, *J*=7.8 Hz, H-$7_{chromone}$), 8.25 (s, 1H, H-$5_{chromone}$), 8.48 (s, 1H, H-$7_{triazepine}$), 9.31 (s, 1H, H-$2_{chromone}$), 11.19 (bs, 1H, NH exchangeable with $D_2O$). $^{13}$C NMR (DMSO, δ, 75 MHz): 15.3 (Me), 31.8 (C-$3_{allyl}$), 68.7 (C-10), 88.2 (C-3a), 96.3 (C-8), 111.6 (C-$1_{allyl}$), 114.5 (2C-Ph), 115.8, 116.4 (2C≡N), 117.8 (C-Ph), 119.5 (C-$3_{chromone}$), 121.2 (C-$4a_{chromone}$), 122.6 (2C-Ph), 124.8 (C-$6_{chromone}$), 126.0 (C-$5_{chromone}$), 127.9 (C-Ph), 129.3 (C-$8_{chromone}$), 132.7 (C-$7_{chromone}$), 134.8 (C-$2_{allyl}$), 138.7 (C-11a), 141.5 (C-10a), 143.6 (C-3), 146.1 (C-$2_{chromone}$), 152.9 (C-$8a_{chromone}$), 158.4 (C-4), 163.3 (C-9), 169.1 (C-7 as C=O), 178.5 (C-$4_{chromone}$ as C=O). MS (*m/z*, *I*%): 525 ($M^+$; 100), 493 (53), 416 (32), 375 (39), 335 (13), 308 (12), 284 (8), 186 (26), 161 (62), 145 (14), 133 (21), 77 (46), 65 (11). Anal. Calcd for $C_{30}H_{19}N_7O_3$ (525.53): C, 68.57; H, 3.64; N, 18.66%. Found: C, 68.51; H, 3.63; N, 18.47%.

**2-(8-Allylchromon-3-yl)-4-oxo-4*H*-quinolino[2,3-*e*]pyrido[1,2-*b*][1,2,4]triazepine-1,3-dicarbonitrile (15).**

A mixture of compound **3** (0.72 g, 2 mmol) and 3-formyl-2-chloroquinoline (**13**) (0.38 g, 2 mmol) in EtOH (30 mL) containing few drops of triethylamine was heated under reflux for 3 h. The yellow solid obtained during heating was filtered and crystallized from AcOH, yield (0.61 g, 61%), mp 268-269 ºC. IR (KBr, $cm^{-1}$): 3385 (NH), 3056 ($CH_{arom.}$), 2922, 2860 ($CH_{aliph.}$), 2237 (2 C≡N), 1679 ($C=O_{pyridone}$), 1637 ($C=O_{\gamma\text{-pyrone}}$), 1603 (C=N and C=C). $^1$H NMR (DMSO-$d_6$, δ, 300 MHz): 3.56 (d, 2H, *J*=6.4 Hz, $CH_{2\ allyl}$), 5.00-5.07 (m, 2H, $CH_{2\ allyl}$), 5.98-6.02 (m, 1H, $CH_{allyl}$), 7.32 (d, 1H, *J*=7.5 Hz, H-$6_{chromone}$), 7.56 (d, 1H, *J*=7.5 Hz, H-$7_{chromone}$), 7.76 (t, 1H, *J*=7.2 Hz, H-$6_{quinoline}$), 8.01 (d, 1H, *J*=7.2 Hz, H-$8_{quinoline}$), 8.17 (d, 1H, *J*=7.2 Hz, H-$5_{quinoline}$), 8.42 (s, 1H, H-$5_{chromone}$), 8.52 (s, 1H, H-$7_{triazepine}$), 8.92 (s, 1H, H-$4_{quinoline}$), 9.27 (s, 1H, H-$2_{chromone}$), 9.86 (bs, 1H, NH exchangeable with $D_2O$). $^{13}$C NMR (DMSO, δ, 75 MHz): 31.5 (C-$3_{allyl}$), 68.8 (C-1), 96.3 (C-3), 111.2 (C-$1_{allyl}$), 116.4, 117.1 (2C≡N), 118.7 (C-$3_{chromone}$), 120.2 (C-$4a_{chromone}$), 122.5 (C-8a), 124.7 (C-$6_{chromone}$), 126.3 (C-$5_{chromone}$), 127.1, 127.4, 128.1, 128.9 (C-9, C-10, C-11 and C-12 as Ar-C), 129.8 (C-$8_{chromone}$), 133.4 (C-$7_{chromone}$), 135.1 (C-$2_{allyl}$), 137.3 (C-7a), 138.6 (C-12a), 140.7 (C-13a), 142.3 (C-14a), 144.1 (C-8), 146.1 (C-$2_{chromone}$), 152.1 (C-7), 153.7 (C-$8a_{chromone}$), 161.3 (C-2), 166.3 (C-4 as C=O), 178.0 (C-$4_{chromone}$ as C=O). MS (*m/z*, *I*%): 496 ($M^+$; 100), 468 (39), 314 (54), 286 (23), 154 (22), 132 (19), 116 (18), 77 (81), 64 (43). Anal. Calcd for $C_{29}H_{16}N_6O_3$ (496.49): C, 70.16; H, 3.25; N, 16.93%. Found: C, 70.03; H, 3.18; N, 16.75%.

**9-(8-Allylchromon-3-yl)-2-amino-4-(4-methoxyphenyl)-7-oxo-1,7-dihydropyrido[1,2-*b*]-[1,2,4]triazepine-3,8,10-tricarbonitrile (18).**

A mixture of compound **3** (0.72 g, 2 mmol) and (*p*-methoxybenzylidene)malononitrile (**16**) (0.36 g, 2 mmol) in DMF (15 mL) containing two drops of triethylamine was heated under reflux for 2 h. The orange crystals obtained during heating was filtered and crystallized from DMF/MeOH, yield (0.68 g, 62%), mp 236-237 ºC. IR (KBr, $cm^{-1}$): 3402, 3243 ($NH_2$, NH), 3053 ($CH_{arom.}$), 2925, 2874 ($CH_{aliph.}$), 2242, 3325 (3 C≡N), 1675 ($C=O_{pyridone}$), 1644 ($C=O_{\gamma\text{-pyrone}}$), 1615 (C=N), 1601 (C=C). $^1$H NMR (DMSO-$d_6$, δ, 300 MHz): 3.53 (d, 2H, *J*=6.6 Hz, $CH_{2\ allyl}$), 3.87 (s, 3H, $OCH_3$), 5.01-5.08 (m, 2H, $CH_{2\ allyl}$), 5.99-6.05 (m, 1H, $CH_{allyl}$), 7.20 (d, 2H, *J*=8.4 Hz, Ar-H), 7.42 (d, 1H, *J*=7.5 Hz, H-$6_{chromone}$), 7.50 (d, 1H, *J* = 7.5 Hz, H-$7_{chromone}$), 7.78 (d, 2H, *J*=8.4 Hz, Ar-H), 8.26 (d, 1H, H-$5_{chromone}$), 8.86 (bs, 2H, $NH_2$ exchangeable with $D_2O$), 9.13 (s, 1H, H-$2_{chromone}$), 10.54 (bs, 1H, NH exchangeable with $D_2O$). $^{13}$C NMR (DMSO, δ, 75 MHz): 32.1 (C-$3_{allyl}$), 55.8 ($OCH_3$), 62.3 (C-3), 70.3 (C-10), 97.1 (C-8), 112.1 (C-$1_{allyl}$), 115.3, 115.8, 116.3 (3C≡N), 117.6 (2C-Ar), 118.5 (C-$3_{chromone}$), 121.5 (C-$4a_{chromone}$), 123.9 (C-$6_{chromone}$), 125.3 (C-Ar), 126.9 (C-$5_{chromone}$), 127.7 (2C-Ar), 128.7 (C-$8_{chromone}$), 130.6 (C-Ar), 132.7 (C-$7_{chromone}$), 135.1 (C-$2_{allyl}$), 144.6 (C-$2_{chromone}$), 148.3 (C-10a), 152.3 (C-$8a_{chromone}$), 156.5 (C-2), 160.8 (C-4), 163.1 (C-9), 168.9 (C-7

as C=O), 177.2 (C-4$_{chromone}$ as C=O). MS (*m/z*, *I*%): 541 ($M^+$; 16), 513 (28), 435 (48), 419 (26), 404 (9), 343 (9), 314 (15), 285 (6), 161 (58), 132 (23), 116 (64), 107 (100), 77 (39), 65 (28). Anal. Calcd for $C_{30}H_{19}N_7O_4$ (541.53): C, 66.54; H, 3.54; N, 18.11%. Found: C, 66.36; H, 3.56; N, 18.14%.

**Ethyl 9-(8-allylchromon-3-yl)-2-amino-8,10-dicyano-4-(4-methoxyphenyl)-7-oxo-1,7-dihydropyrido-[1,2-*b*][1,2,4]triazepine-3-carboxylate (19).**

A mixture of compound **3** (0.72 g, 2 mmol) and ethyl 2-cyano-3-(4-methoxyphenyl)prop-2-enoate (**17**) (0.46 g, 2 mmol) in DMF (20 mL) containing two drops of triethylamine was heated under reflux for 4 h. The orange crystals obtained during heating was filtered and crystallized from DMF/EtOH, yield (0.75 g, 63%), mp 272-273 ºC. IR (KBr, $cm^{-1}$): 3355, 3208 ($NH_2$, NH), 3041 ($CH_{arom.}$), 2926, 2873 ($CH_{aliph.}$), 2242 (2 C≡N), 1700 ($C=O_{ester}$), 1682 ($C=O_{pyridone}$), 1646 ($C=O_{\gamma\text{-pyrone}}$), 1614 (C=N), 1596 (C=C). $^1$H NMR (DMSO-$d_6$, δ, 300 MHz): 1.26 (t, 3H, *J*=7.0 Hz, $CH_2CH_3$), 3.55 (d, 2H, *J* = 6.0 Hz, $CH_{2\ allyl}$), 3.89 (s, 3H, OMe), 4.24 (q, 2H, *J*=7.2 Hz, $CH_2CH_3$), 5.00-5.10 (m, 2H, $CH_{2\ allyl}$), 6.03-6.11 (m, 1H, $CH_{\ allyl}$), 7.12 (d, 2H, *J*=8.1 Hz, Ar-H), 7.33 (d, 1H, *J*=7.8 Hz, H-6$_{chromone}$), 7.62 (d, 1H, *J*=7.8 Hz, H-7$_{chromone}$), 7.84 (d, 2H, *J*=8.1 Hz, Ar-H), 8.32 (s, 1H, H-5$_{chromone}$), 8.68 (bs, 1H, NH exchangeable with $D_2O$), 8.74 (bs, 1H, NH exchangeable with $D_2O$), 9.32 (s, 1H, H-2$_{chromone}$), 10.46 (bs, 1H, NH exchangeable with $D_2O$). $^{13}$C NMR (DMSO, δ, 75 MHz): 13.2 (Me), 31.6 (C-3$_{allyl}$), 38.1 ($CH_2$), 55.6 (OMe), 69.5 (C-10), 74.2 (C-3), 96.5 (C-8), 112.3 (C-1$_{allyl}$), 115.6, 116.1 (2C≡N), 117.8 (2C-Ar), 118.9 (C-3$_{chromone}$), 120.9 (C-4a$_{chromone}$), 123.6 (C-6$_{chromone}$), 125.7 (C-Ar), 127.1 (C-5$_{chromone}$), 128.3 (2C-Ar), 128.2 (C-8$_{chromone}$), 130.3 (C-Ar), 132.5 (C-7$_{chromone}$), 135.2 (C-2$_{allyl}$), 144.3 (C-2$_{chromone}$), 147.9 (C-10a), 152.0 (C-8a$_{chromone}$), 156.2 (C-2), 161.1 (C-4), 163.4 (C-9), 169.2 (C-7 as C=O), 177.5 (C-4$_{chromone}$ as C=O), 183.6 ($C=O_{ester}$). MS (*m/z*, *I*%): 588 ($M^+$; 35), 543 (13), 515 (20), 407 (11), 379 (18), 352 (32), 284 (10), 186 (40), 161 (100), 133 (19), 109 (46), 91 (71), 77 (52), 64 (33). Anal. Calcd for $C_{32}H_{24}N_6O_6$ (588.58): C, 65.30; H, 4.11; N, 14.28%. Found: C, 65.15; H, 4.02; N, 14.13%.

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