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SYNTHESIS AND CHARACTERIZATION OF SOME NOVEL HETEROANNULATED CHROMENO[4,3-*b*]QUINOLINES

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Abstract – The recently synthesized 1-chloro-11-oxo-3,4-dihydro-11*H*-chromeno[4,3-*b*]quinoline-2-carboxaldehyde (**1**) was efficiently utilized as a key precursor to construct a diversity of polyfused systems containing chromeno[4,3-*b*]quinoline. Reaction of compound **1** with some substituted hydrazines afforded pyrazoles annulated chromeno[4,3-*b*]quinoline. Treatment of compound **1** with a diversity of 1,3-*N*,*N*-binucleophiles led to pyrimidines annulated chromeno[4,3-*b*]quinoline. In addition, a diversity of fused pyridines annulated chromeno[4,3-*b*]quinoline were synthesized from condensation of compound **1** with a variety of 1,3-*C*,*N*-binucleophiles. Finally, the reactivity of compound **1** was tested towards a diversity of 1,4-binucleophilic reagents. Structures of the new compounds were established using spectral and analytical data.

INTRODUCTION

Coumarins are widely dispersed in plants particularly in the roots, leaves, fruits, and seeds.[1] The effect of substituted coumarins in the inhibition of various cancer cells is significant.[2] The pharmacological properties as well as therapeutic uses of coumarins are well determined by governing the substituent in their nucleus.[3] An interesting framework for creating new anti-inflammatory medicines is widely provided by coumarin derivatives.[4] The biological uses of coumarins include antioxidant,[5] anti-HIV,[6] antiviral,[7] antibacterial,[8] antimalarial,[9] antifungal,[10] anti-influenza,[11] antimicrobial,[12] antiproliferative,[13] anticoagulant,[14] antileishmanial,[15] antiplatelet,[16] and antidepressant.[17] Computational studies are used to investigate and recognize the structural, vibrational and optical properties using DFT calculations.[20] The photoluminescence and fluorescence properties were examined for some coumarins.[19]

β-Chloroenaldehydes are well known as good precursors for construction of heterocyclic compounds.[20] The present work is directed to utilize the recently synthesized 1-chloro-11-oxo-3,4-dihydro-11*H*-chromeno[4,3-*b*]quinoline-2-carboxaldehyde (**1**)[21] to construct a novel series of heterocyclic compounds including chromeno[4,3-*b*]quinolines.

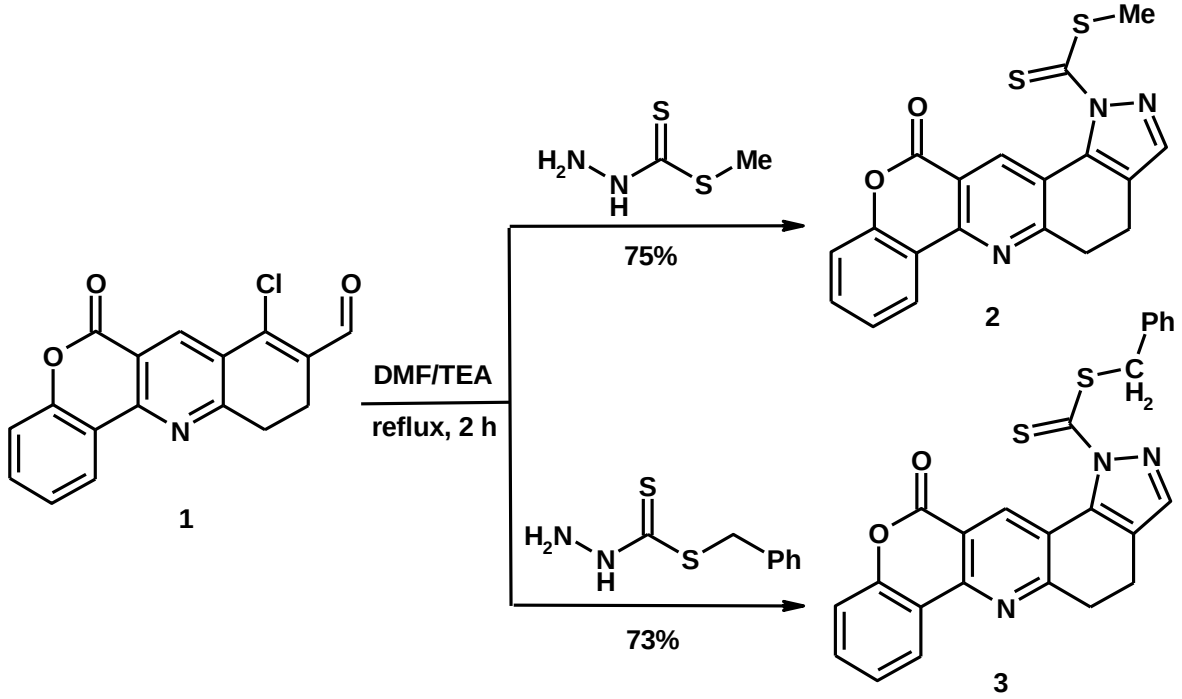
RESULTS AND DISCUSSION

Recently, compound **1** was efficiently synthesized and characterized by different spectroscopic techniques.[21] Compound **1** represents a significant precursor for building a variety of angular annulated chromeno[4,3-*b*]quinolines due to the existence of aldehyde and chloro functions in the beta position to each other. The behavior of cyclic β-chloroenaldehyde **1** was firstly examined towards some 1,2-binucleophilic reagents. So, condensation of compound **1** with *S*-methyl dithiocarbazate, and *S*-benzyl dithiocarbazate, in boiling DMF including triethylamine (TEA), furnished the novel chromeno[4,3-*b*]-pyrazolo[3,4-*f*]quinoline-1-carbodithioate derivatives **2** and **3**, respectively (Scheme 1). These reactions proceed *via* condensation with loss of H_2O and HCl molecules. In the IR spectra of compounds **2** and **3**, the aldehyde function that was presented at 1707 cm^{-1} in the IR spectrum of compound **1** was vanished.[21] The molecular ion peaks at *m/z* 379 ($C_{19}H_{13}N_3O_2S_2$) and 455 ($C_{25}H_{17}N_3O_2S_2$) were shown by the mass spectra of compounds **2** and **3**, respectively, proving the suggested structures. In addition, the singlet signal of aldehyde proton, which was observed at δ 10.36 in the ^{1}H NMR spectrum of compound **1**, was vanished in the spectra of compounds **2** and **3**, and a new singlet due to H-$3_{pyrazole}$ was observed at δ 8.46 and 8.42. Also, singlet signals attributed to Me and CH_2 protons were seen in the ^{1}H NMR spectra of compounds **2** and **3** at δ 2.41 and 2.59, respectively. The ^{13}C NMR spectra of compounds **2** and **3** displayed specific signals due to C=S in the downfield region at δ 194.2 and 195.1, respectively.

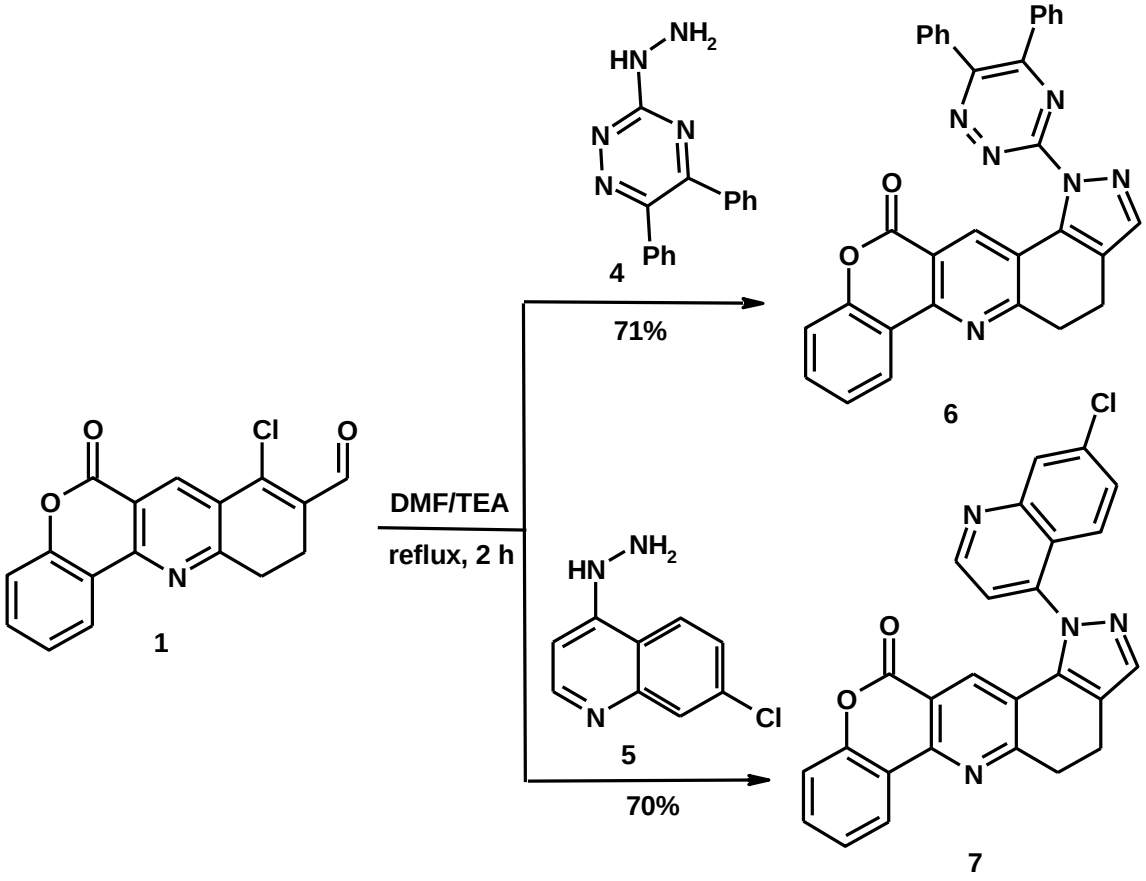
Similarly, treatment of compound **1** with 3-hydrazinyl-5,6-diphenyl-1,2,4-triazine (**4**),[22] and 7-chloro-4-hydrazinylquinoline (**5**),[23] in boiling DMF including TEA, afforded triazinyl/quinolinylchromeno[4,3-*b*]pyrazolo[3,4-*f*]quinolines **6** and **7**, respectively (Scheme 2). Their ^{1}H NMR spectra presented H-$3_{pyrazole}$ as typical signal at δ 8.49 and 8.47. The spectrum of compound **7** presented characteristic singlet signal assigned to H-$8_{quinoline}$ at δ 7.53. Structures **6** and **7** were further confirmed from their mass spectra that exhibited their parent ion peaks at *m/z* 520 ($C_{32}H_{20}N_6O_2$) and 450 ($C_{26}H_{15}ClN_4O_2$), respectively.

After that, cyclic β-chloroenaldehyde **1** was permitted to reacted with a diversity of 1,3-*N*,*N*-binucleophiles. Therefore, boiling compound **1** with cyanoguanidine, in boiling DMF/TEA, yielded chromeno[3`,4`:5,6]pyrido[2,3-*h*]quinazoline derivative **8** (Scheme 3). Its IR spectrum displayed definite absorption bands at 3241 (NH), 2201 (C≡N) and 1722 cm^{-1} (C=$O_{α\text{-pyrone}}$). The ^{1}H NMR spectrum exhibited distinctive signals corresponding to H-$4_{pyrimidine}$ and H-$4_{pyridine}$ at δ 8.59 and 8.89, as well as D_2O vanished signal at δ 11.35 assignable to NH proton. In the ^{13}C NMR spectrum, typical signals were

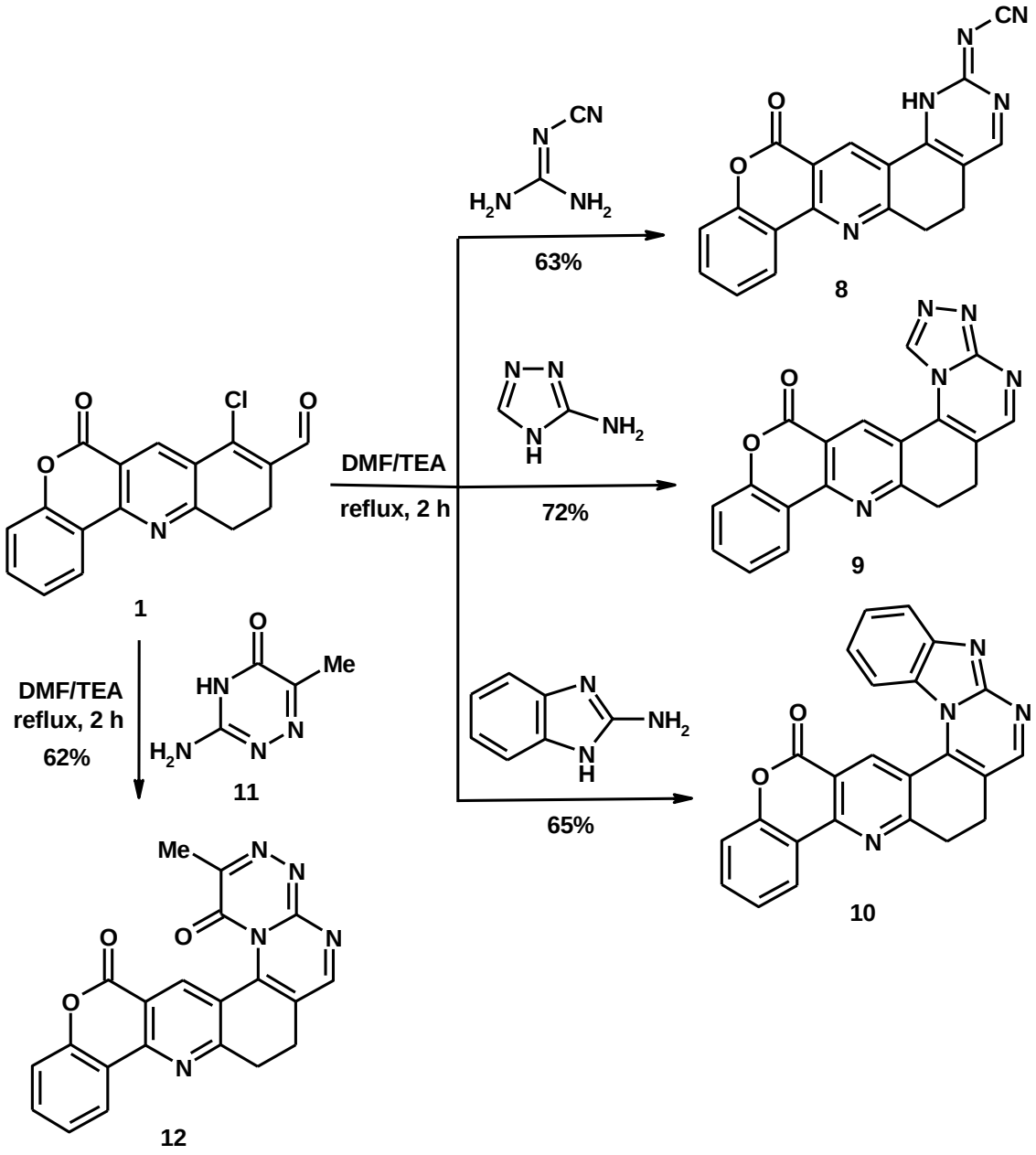
observed at δ 116.8 (C≡N), 156.5 (C-2) and 171.2 ($C{=}O_{\alpha\text{-pyrone}}$). The mass spectrum recorded the parent ion peak, as the base peak, at *m/z* 341.



Scheme 1. Condensation of compound **1** with *S*-methyl/ *S*-benzyl dithiocarbazate



Scheme 2. Formation of poly fused chromeno[4,3-*b*]pyrazolo[3,4-*f*]quinolines **6** and **7**



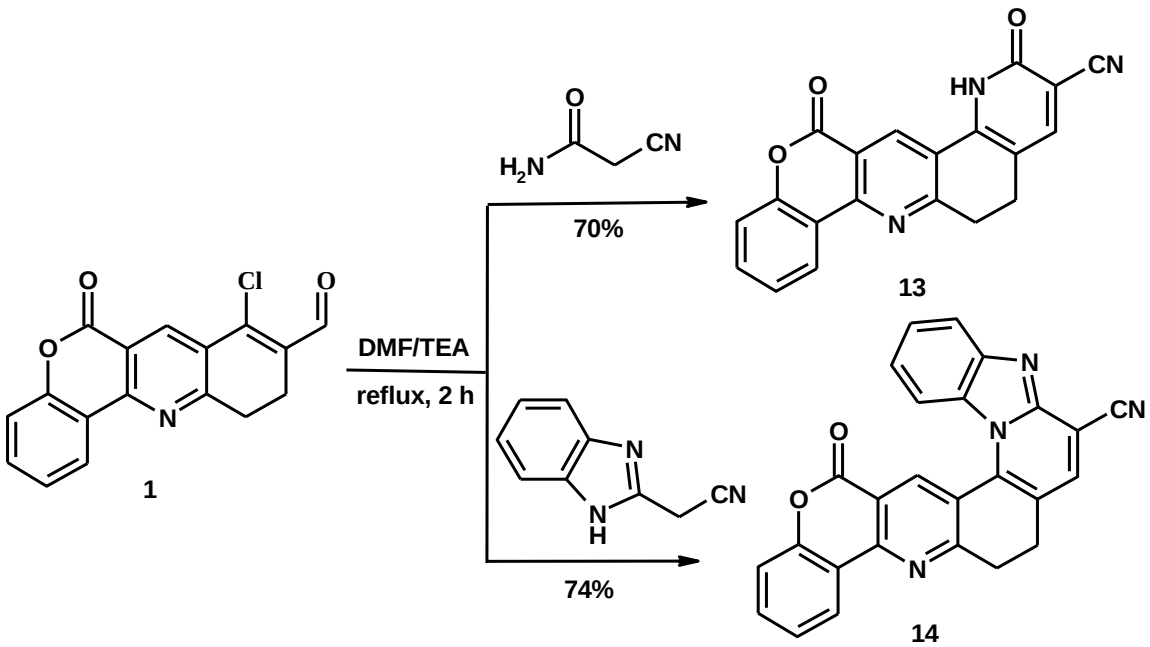
Scheme 3. Reaction of compound **1** with some 1,3-*N*,*N*-binucleophiles

Likewise, reaction of compound **1** with some heterocyclic binucleophiles namely 3-amino-1,2,4-triazole and 2-aminobenzimidazole led to chromeno[3`,4`:5,6]pyrido[2,3-*h*][1,2,4]triazolo[4,3-*a*]quinazoline **9** and chromeno[3`,4`:5,6]pyrido[2,3-*h*]benzimidazo[1,2-*a*]quinazoline **10**, respectively (Scheme 3). Their ^{1}H NMR spectra displayed specific singlet due to H-4$_{\text{pyrimidine}}$ at δ 8.63 and 8.58, respectively. The spectrum of compound **9** showed typical singlet due to H-3$_{\text{triazole}}$ at δ 9.03. Structures **9** and **10** were also verified by the mass spectra that recorded the molecular ion peaks at *m/z* 341 and 390 that agree well with the proposed molecular formulas $C_{19}H_{11}N_5O_2$ and $C_{24}H_{14}N_4O_2$, respectively.

Also, reaction of compound **1** with 3-amino-6-methyl-1,2,4-triazin-5(4*H*)-one (**11**),[24] in DMF/TEA under reflux, produced chromeno[3`,4`:5,6]pyrido[2,3-*h*][1,2,4]triazino[4,3-*a*]quinazoline **12** (Scheme 3). Its IR

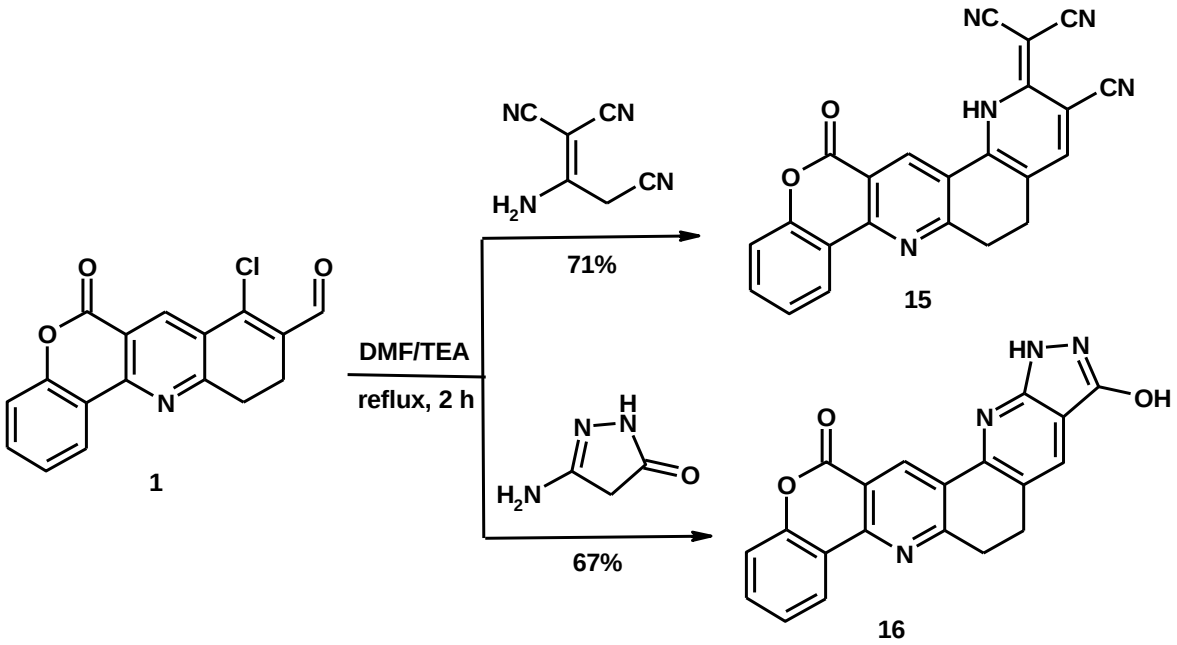
spectrum exhibited typical absorption bands at 1721 ($C=O_{\alpha\text{-pyrone}}$) and 1683 cm^{-1} ($C=O_{triazine}$). The ^1H NMR spectrum presented typical singlet signals at δ 2.86 ($CH_{3\ triazine}$), 8.61 ($H\text{-}4_{pyrimidine}$) and 8.89 ($H\text{-}4_{pyridine}$). Structure **12** was also deduced from its mass spectrum which displayed the molecular ion peak at *m/z* 383.

Next, cyclic β-chloroenaldehyde **1** reacted with some 1,3-*C*,*N*-binucleophiles such as cyanoacetamide and 1*H*-benzimidazol-2-ylacetonitrile giving chromeno[4,3-*J*][1,7]phenanthroline **13** and chromeno[4,3-*J*]-benzoimidazo[1,2-*a*][1,7]phenanthroline **14** (Scheme 4). Their IR spectra showed typical absorption bands due to C≡N functions at 2216 and 2219 cm^{-1}, respectively. In the ^1H NMR spectra of compounds **13** and **14**, two singlet signals appeared in each spectrum due to $2H\text{-}4_{pyridine}$ at δ 8.68/8.85 and 8.54/8.76, respectively. D_2O-vanished signal (due to $NH_{pyridine}$) was observed in the spectrum of compound **13** at δ 11.83. The ^{13}C NMR spectrum of compound **13** showed specific signals at δ 116.4 (C≡N), 167.4 (C-2 as C=O) and 170.6 ($C=O_{\alpha\text{-pyrone}}$). The mass spectra of compounds **13** and **14** confirmed the assigned structures and presented the molecular ion peaks, as the base peaks, at *m/z* 341 and 414, respectively.



Scheme 4. Reaction of compound **1** with some 1,3-*C*,*N* binucleophiles

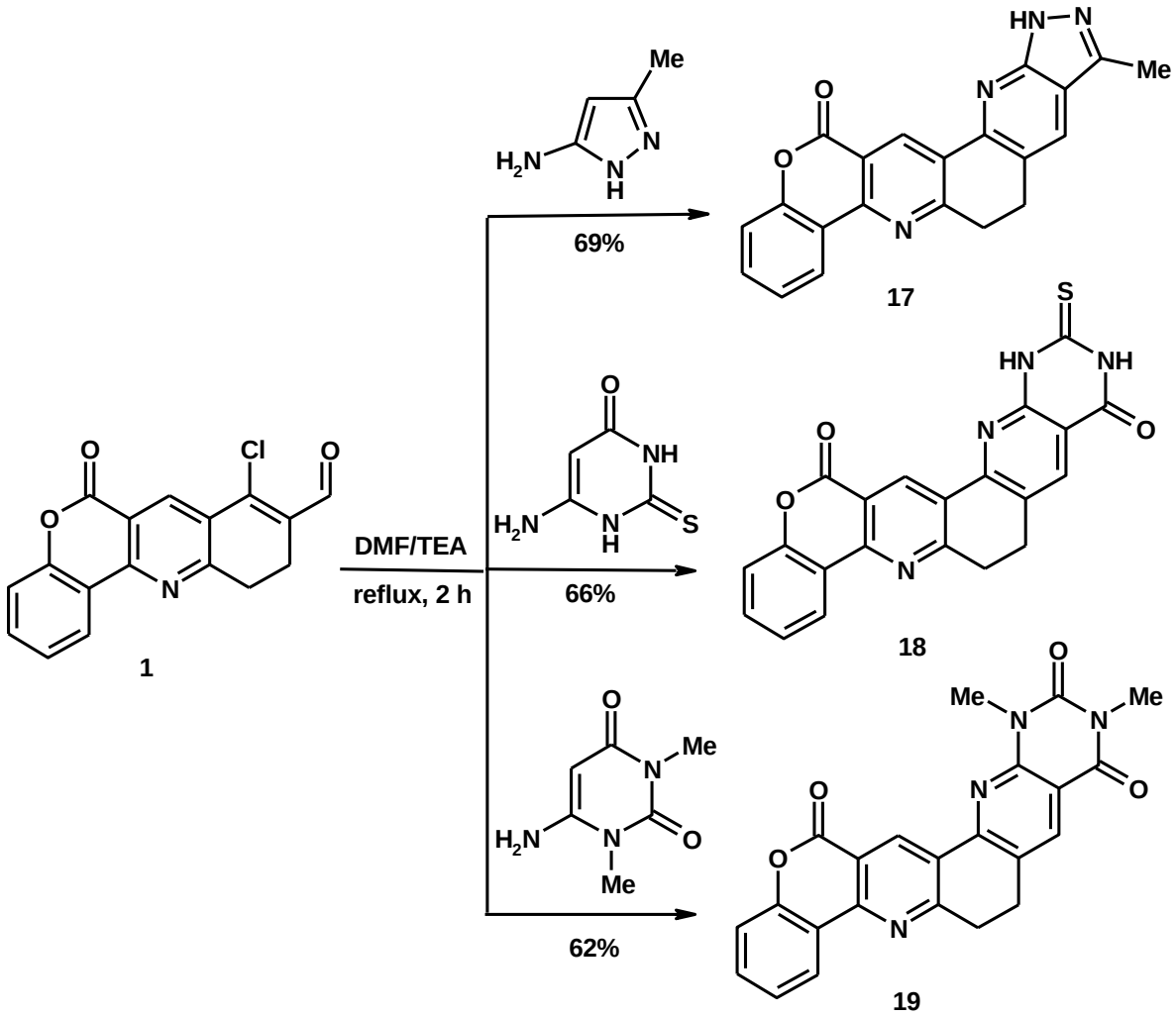
Moreover, treating compound **1** with 2-aminoprop-1-ene-1,1,3-tricarbonitrile and 5-amino-2,4-dihydro-3*H*-pyrazol-3-one, in DMF/TEA, gave chromeno[4,3-*J*][1,7]phenanthroline **15** and chromeno[4,3-*J*]-pyrazolo[3,4-*b*][1,7]phenanthroline **16**, respectively (Scheme 5).[25] The IR spectrum of compound **15** displayed characteristic absorption bands at 3286 (NH), 2223, 2204, 2196 (3C≡N) and 1712 cm^{-1} ($C=O_{\alpha\text{-pyrone}}$). Structures **15** and **16** were also confirmed from their mass spectra which showed the molecular ion peaks at *m/z* 389 and 356.



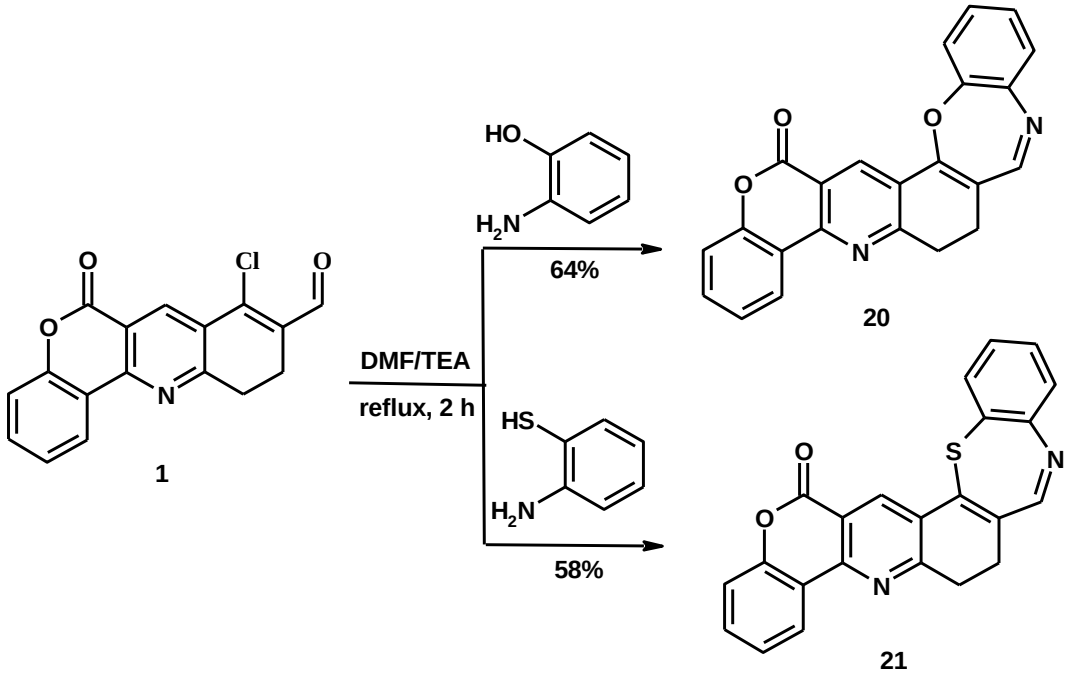
Scheme 5. Formation of heteroannulated compounds **15** and **16**

Further, cyclic β-chloroenaldehyde **1** reacted with a diversity of cyclic enamines, as 1,3-*C*,*N*-binucleophiles. Thus, reaction of compound **1** with 5-amino-3-methyl-1*H*-pyrazole, 6-amino-2-thioxo-2,3-dihydropyrimidin-4(1*H*)-one and 6-amino-1,3-dimethylpyrimidine-2,4(1*H*,3*H*)-dione gave the angular annulated chromeno[4,3-*J*]pyrazolo[3,4-*b*][1,7]phenanthroline **17** and chromeno[4,3-*J*]pyrimido-[4,5-*b*][1,7]phenanthrolines **18**, **19** (Scheme 6). Structures **17**-**19** were proved using the mass spectra which displayed their molecular ion peaks at *m/z* 354, 400 and 412, respectively. The ^{1}H NMR spectra for compounds **17**-**19** showed characteristic singlets due to 2H-4$_{\text{pyridine}}$ at δ 8.69/ 8.81, 8.54/ 8.78 and 8.61/ 8.83, respectively.

Then, compound **1** reacted with some 1,4-binucleophiles such as *o*-aminophenol and *o*-aminothiophenol, in DMF/TEA, producing chromenobenzoxazepinoquinoline **20** and chromenobenzothiazepinoquinoline **21** (Scheme 7). Structures **20** and **21** were confirmed by the mass spectra which presented the molecular ion peaks at *m/z* 366 and 382, corresponding to the suggested formula weights of $C_{23}H_{14}N_2O_3$ and $C_{23}H_{14}N_2O_2S$, respectively. In the ^{1}H NMR spectrum of each compound, two characteristic singlet signals attributed to H-6 and H-4$_{\text{pyridine}}$ were seen at δ 8.37/8.76 and 8.41/8.83, respectively.



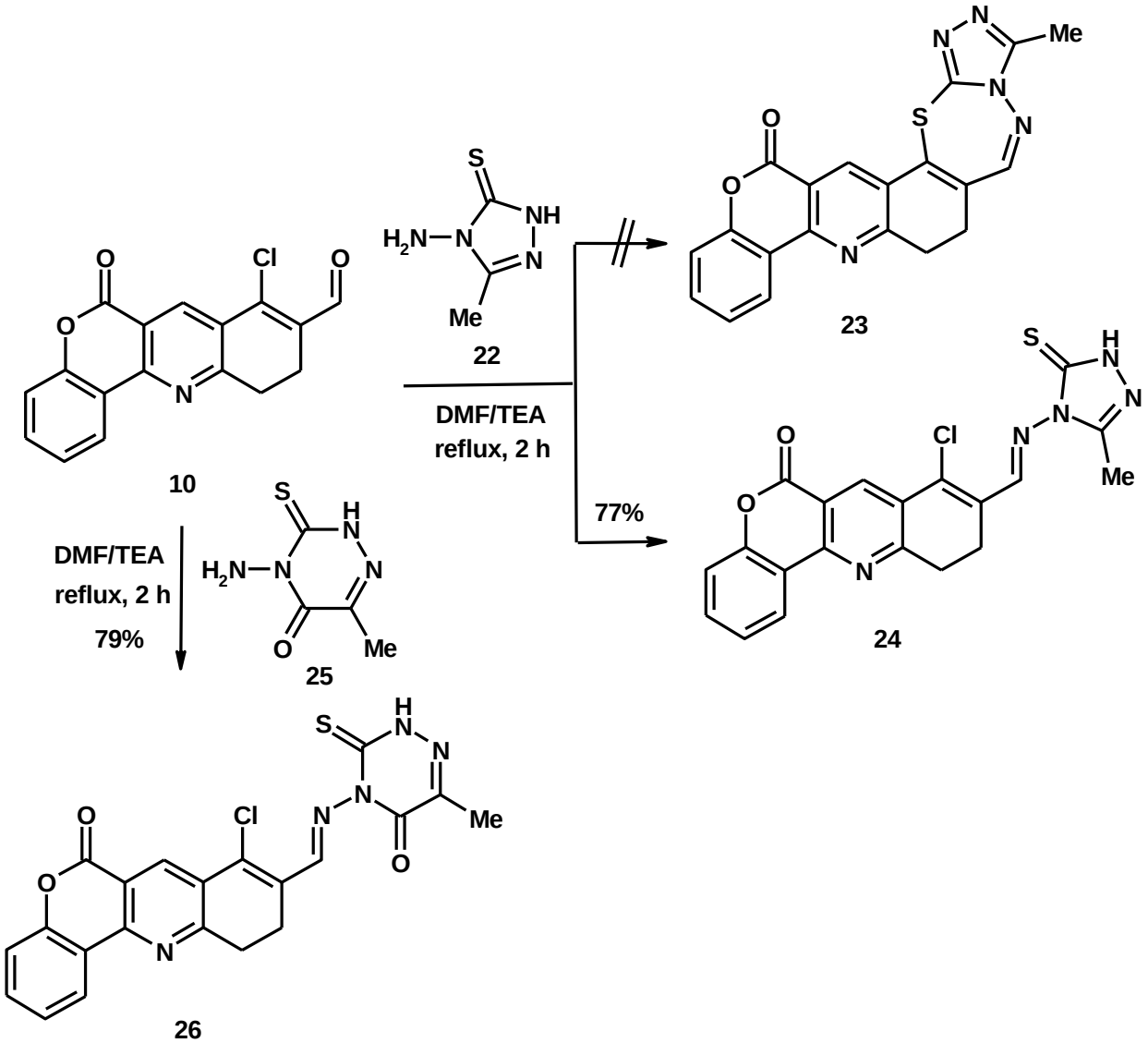
Scheme 6. Reaction of compound **1** with some cyclic 1,3-*C*,*N* binucleophiles



Scheme 7. Reaction of compound **1** with as *o*-aminophenol and *o*-aminothiophenol

Meanwhile, boiling compound **1** with 4-amino-5-methyl-2,4-dihydro-3*H*-1,2,4-triazole-3-thione (**22**) did not afford the cyclized product **23**, but the reaction stops at the stage of the condensation process giving the condensation product **24** (Scheme 8). Its mass spectrum considered as excellent evidence for the structure **24** and presented the parent ion peak with its isotopic peak (M^+/M+2) at *m/z* 423/425 (relative abundance *I* %; 15/5); the base peak was seen at *m/z* 309/311 (*I* %; 100/34). The ^{1}H NMR spectrum displayed characteristic singlet signals at δ 2.46 ($Me_{triazole}$), 8.35 ($CH_{azomethine}$) and 8.85 (H-$4_{pyridine}$), as well as D_2O-vanished signal due to NH proton at δ 11.64. The ^{13}C NMR spectrum showed definite signals at δ 18.2 (Me), 141.6 (C-$5_{triazole}$), 171.3 (C=$O_{\alpha\text{-pyrone}}$) and 189.6 (C=S).

Finally, reaction of compound **1** with 4-amino-6-methyl-3-thioxo-3,4-dihydro-1,2,4-triazin-5(2*H*)-one (**25**) yielded the Schiff base **26** (Scheme 8). Its ^{1}H NMR spectrum showed characteristic singlet signals at δ 2.39 ($Me_{triazine}$), 8.32 ($CH_{azomethine}$) and 8.88 (H-$4_{pyridine}$), the spectrum also revealed D_2O-vanished signal due to NH proton at δ 12.54.



Scheme 8. Formation of Schiff bases **24** and **26**

CONCLUSION

A novel series of angular polyfused systems containing chromeno[4,3-*b*]quinoline moiety were synthesized from condensation reactions of cyclic β-chloroenaldehyde **1** with a diversity of binucleophilic reagents. Some novel chromeno[4,3-*b*]pyrazolo[3,4-*f*]quinolines **2**, **3**, **6** and **7** were prepared from reaction of compound **1** with some hydrazine derivatives. Reaction of compound **1** with cyanoguanidine, 3-amino-1,2,4-triazole, 2-aminobenzimidazole and 3-amino-6-methyl-1,2,4-triazin-5(4*H*)-one afforded a series of chromeno[3`,4`:5,6]pyrido[2,3-*h*]quinazolines **8**-**10** and **12**. A novel series of chromeno[4,3-*J*]-[1,7]phenanthrolines **13-15**, chromeno[4,3-*J*]pyrazolo[3,4-*b*][1,7]phenanthrolines **16**, **17** and chromeno[4,3-*J*]pyrimido[4,5-*b*][1,7]phenanthrolines **18**, **19** were efficiently synthesized from reaction of compound **1** with some acyclic and cyclic 1,3-*C*,*N*-binucleophiles. Treating compound **1** with *o*-aminophenol and *o*-aminothiophenol afforded chromenobenzoxazepinoquinoline **20** and chromenobenzothiazepinoquinoline **21**. Schiff bases **24** and **26** were obtained from reaction of compound **1** with 4-amino-5-methyl-2,4-dihydro-3*H*-1,2,4-triazole-3-thione (**22**) and 4-amino-6-methyl-3-thioxo-3,4-dihydro-1,2,4-triazin-5(2*H*)-one (**25**).

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. ^{1}H 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, ppm) 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 PerkinElmer CHN-2400 analyzer. 1-Chloro-11-oxo-3,4-dihydro-11*H*-chromeno[3,4-*b*]quinoline-2-carboxaldehyde (**1**) was prepared according to the published method.[21]

Methyl 4,5-dihydrochromeno[4,3-*b*]pyrazolo[3,4-*f*]quinoline-1-carbodithioate (2)

A mixture of compound **1** (0.62 g, 2 mmol) and *S*-methyl dithiocarbazate (0.23 g, 2 mmol), in DMF (10 mL) containing TEA (0.1 mL), was heated under reflux for 2 h. The yellow crystals deposited after cooling were filtered and crystallized from *n*-butanol, mp > 300 °C, yield (0.57 g, 75%). IR (KBr, cm^{-1}): 3036 ($CH_{arom.}$), 2958, 2922 ($CH_{aliph.}$), 1716 ($C{=}O_{\alpha\text{-pyrone}}$), 1611 (C=N), 1601 (C=C), 1238 (C=S). ^{1}H NMR (300 MHz, DMSO-d_6, δ): 2.03 (t, 2H, *J*= 6.3 Hz, CH_2), 2.23 (t, 2H, *J*= 6.3 Hz, CH_2), 2.41 (s, 3H, CH_3), 7.06 (t, 1H, *J*= 7.2 Hz, H-8), 7.35 (d, 1H, *J*= 7.5 Hz, H-9), 7.68 (t, 1H, *J*= 7.2 Hz, H-7), 7.97 (d, 1H, *J*= 7.5 Hz, H-10), 8.46 (s, 1H, $H\text{-}3_{pyrazole}$), 8.87 (s, 1H, $H\text{-}4_{pyridine}$). ^{13}C NMR (75 MHz, DMSO-d_6, δ): 20.6 (SCH_3), 22.9 (CH_2), 27.1 (CH_2), 114.3 (C-12a), 115.6 (C-3a), 119.8 (C-13a), 124.6 (C-9), 126.1 (C-7), 127.9 (C-8), 129.2 (C-10), 130.4 (C-6b), 132.8 (C-13b), 137.6 (C-3), 140.1 (C-13), 143.5 (C-6a), 146.2

(C-5a), 149.6 (C-10a), 171.3 (C=$O_{\alpha\text{-pyrone}}$), 194.2 (C=S). Mass spectrum, *m/z* (I_r %): 379 (21), 364 (19), 288 (23), 260 (16), 233 (12), 195 (31), 145 (20), 120 (100), 93 (52), 77 (43), 64 (16). Anal. Calcd for $C_{19}H_{13}N_3O_2S_2$ (379.45): C, 60.14; H, 3.45; N, 11.07; S, 16.90%. Found: C, 59.86; H, 3.32; N, 10.93; S, 16.73%.

Benzyl 4,5-dihydrochromeno[4,3-*b*]pyrazolo[3,4-*f*]quinoline-1-carbodithioate (3)

A mixture of compound **1** (0.62 g, 2 mmol) and *S*-benzyl dithiocarbazate (0.39 g, 2 mmol), in DMF (10 mL) containing TEA (0.1 mL), was heated under reflux for 2 h. The yellow crystals deposited during heating were filtered and crystallized from *n*-butanol, mp > 300 °C, yield (0.66 g, 73%). IR (KBr, cm^{-1}): 3069 ($CH_{arom.}$), 2943, 2915 ($CH_{aliph.}$), 1720 (C=$O_{\alpha\text{-pyrone}}$), 1616 (C=N), 1600 (C=C), 1249 (C=S). ^{1}H NMR (300 MHz, DMSO-d_6, δ): 2.05 (t, 2H, *J*= 6.6 Hz, CH_2), 2.21 (t, 2H, *J*= 6.6 Hz, CH_2), 2.59 (s, 2H, CH_2), 6.92-7.14 (m, 5H, Ph-H), 7.21 (t, 1H, *J*= 7.5 Hz, H-8), 7.41 (d, 1H, *J*= 7.5 Hz, H-9), 7.71 (t, 1H, *J*= 7.5 Hz, H-7), 8.03 (d, 1H, *J*= 7.5 Hz, H-10), 8.42 (s, 1H, H-$3_{pyrazole}$), 8.83 (s, 1H, H-$4_{pyridine}$). ^{13}C NMR (75 MHz, DMSO-d_6, δ): 22.3 (CH_2), 27.8 (CH_2), 35.2 (SCH_2), 113.8 (C-12a), 115.9 (C-3a), 120.3 (C-13a), 122.1 (Ph-C), 124.8 (C-9), 126.3 (C-7), 126.8 (2Ph-C), 128.0 (C-8), 128.7 (2Ph-C), 129.7 (C-10), 130.9 (C-6b), 133.2 (C-13b), 134.5 (Ph-C), 137.4 (C-3), 139.9 (C-13), 143.7 (C-6a), 146.8 (C-5a), 149.3 (C-10a), 170.8 (C=$O_{\alpha\text{-pyrone}}$), 195.1 (C=S). Mass spectrum, *m/z* (I_r %): 455 (24), 332 (18), 288 (31), 233 (17), 196 (25), 170 (11), 145 (14), 121 (26), 91 (100), 77 (63), 64 (13). Anal. Calcd for $C_{25}H_{17}N_3O_2S_2$ (455.55): C, 65.91; H, 3.76; N, 9.22; S, 14.08%. Found: C, 65.85; H, 3.57; N, 9.03; S, 13.86%.

4,5-Dihydro-1-(5,6-diphenyl-1,2,4-triazin-3-yl)-12*H*-chromeno[4,3-*b*]pyrazolo[3,4-*f*]quinolin-12-one (6)

A mixture of compound **1** (0.62 g, 2 mmol) and 3-hydrazinyl-5,6-diphenyl-1,2,4-triazine (**4**) (0.58 g, 2 mmol), in DMF (10 mL) containing TEA (0.1 mL), was heated under reflux for 2 h. The yellow crystals deposited after cooling were filtered and crystallized from AcOH, mp > 300 °C, yield (0.74 g, 71%). IR (KBr, cm^{-1}): 3046 ($CH_{arom.}$), 2937, 2908 ($CH_{aliph.}$), 1719 (C=$O_{\alpha\text{-pyrone}}$), 1608 (C=N), 1593 (C=C). ^{1}H NMR (300 MHz, DMSO-d_6, δ): 2.01 (t, 2H, *J*= 6.3 Hz, CH_2), 2.22 (t, 2H, *J*= 6.3 Hz, CH_2), 6.86-7.15 (m, 11H, 2Ph-H and H-8), 7.43 (d, 1H, *J*= 7.2 Hz, H-9), 7.67 (t, 1H, *J*= 7.5 Hz, H-7), 7.92 (d, 1H, *J*= 7.2 Hz, H-10), 8.49 (s, 1H, H-$3_{pyrazole}$), 8.86 (s, 1H, H-$4_{pyridine}$). Mass spectrum, *m/z* (I_r %): 520 (43), 342 (37), 314 (52), 261 (30), 233 (16), 196 (45), 178 (100), 145 (12), 120 (26), 93 (63), 77 (41), 64 (19). Anal. Calcd for $C_{32}H_{20}N_6O_2$ (520.54): C, 73.84; H, 3.87; N, 16.14%. Found: C, 73.71; H, 3.66; N, 16.02%.

4,5-Dihydro-1-(7-chloroquinolinyl)-12*H*-chromeno[4,3-*b*]pyrazolo[3,4-*f*]quinolin-12-one (7)

A mixture of compound **1** (0.62 g, 2 mmol) and 7-chloro-4-hydrazinylquinoline (**5**) (0.38 g, 2 mmol) in DMF (10 mL) containing TEA (0.1 mL), was heated under reflux for 2 h. The yellow crystals deposited during heating were filtered and crystallized from DMF/H_2O, mp > 300 °C, yield (0.37 g, 70%). IR (KBr, cm^{-1}): 3058 ($CH_{arom.}$), 2927, 2886 ($CH_{aliph.}$), 1715 (C=$O_{\alpha\text{-pyrone}}$), 1613 (C=N), 1599 (C=C). ^{1}H NMR (300

MHz, DMSO-d_6, δ): 2.05 (t, 2H, *J*= 6.0 Hz, CH_2), 2.27 (t, 2H, *J*= 6.0 Hz, CH_2), 6.98-7.17 (m, 2H, H-$5_{quinoline}$ and H-$6_{quinoline}$), 7.26 (t, 1H, *J*= 7.2 Hz, H-9), 7.49 (d, 1H, *J*= 7.5 Hz, H-7), 7.53 (s, 1H, H-$8_{quinoline}$) 7.64 (t, 1H, *J*= 7.5 Hz, H-8), 7.96 (d, 1H, *J*= 7.2 Hz, H-10), 8.04 (d, 1H, *J*= 8.1 Hz, H-$3_{quinoline}$), 8.23 (d, 1H, *J*= 8.1 Hz, H-$2_{quinoline}$), 8.47 (s, 1H, H-$3_{pyrazole}$), 8.83 (s, 1H, H-$4_{pyridine}$). ^{13}C NMR (75 MHz, DMSO-d_6, δ): 21.7 (CH_2), 26.5 (CH_2), 111.9 (C-$4a_{quinoline}$), 114.6 (C-12a), 115.9 (C-3a), 118.3 (C-13a), 121.3 (C-$3_{quinoline}$), 123.7 (C-$5_{quinoline}$), 125.2 (C-9), 126.6 (C-7), 127.5 (C-8), 128.1 (C-$6_{quinoline}$), 129.3 (C-10), 130.1 (C-6b), 131.6 (C-$6_{quinoline}$), 133.5 (C-13b), 135.7 (C-$7_{quinoline}$), 138.2 (C-3), 140.6 (C-13), 143.4 (C-6a), 145.3 (C-8a $_{quinoline}$), 146.4 (C-5a), 147.5 (C-$2_{quinoline}$), 148.9 (C-$4_{quinoline}$), 150.3 (C-10a), 171.8 (C=$O_{α\text{-}pyrone}$). Mass spectrum, *m/z* (I_r %): 450/452 (100/33), 422/424 (58/19), 395/397 (45/15), 232 (17), 196 (34), 163/165 (67/22), 120 (57), 92 (49), 79 (19), 64 (10). Anal. Calcd for $C_{26}H_{15}ClN_4O_2$ (450.88): C, 69.26; H, 3.35; N, 12.43%. Found: C, 68.96; H, 3.25; N, 12.31%.

(5,6-Dihydro-13-oxo-13*H*-chromeno[3`,4`:5,6]pyrido[2,3-*h*]quinazolin-2(1*H*)-ylidene)cyanamide (8)

A mixture of compound **1** (0.62 g, 2 mmol) and cyanoguanidine (0.16 g, 2 mmol), in DMF (10 mL) containing TEA (0.1 mL), was heated under reflux for 2 h. The yellow crystals deposited after cooling were filtered and crystallized from toluene, mp 268-269 °C, yield (0.43 g, 63%). IR (KBr, cm^{-1}): 3241 (NH), 3029 ($CH_{arom.}$), 2936, 2902 ($CH_{aliph.}$), 2201 (C≡N), 1722 (C=$O_{α\text{-}pyrone}$), 1617 (C=N), 1587 (C=C). ^{1}H NMR (300 MHz, DMSO-d_6, δ): 1.98 (t, 2H, *J*= 6.6 Hz, CH_2), 2.21 (t, 2H, *J*= 6.3 Hz, CH_2), 7.22 (t, 1H, *J*= 7.2 Hz, H-10), 7.47 (d, 1H, *J*= 7.2 Hz, H-8), 7.69 (t, 1H, *J*= 7.2 Hz, H-9), 8.06 (d, 1H, *J*= 7.2 Hz, H-11), 8.59 (s, 1H, H-$4_{pyrimidine}$), 8.89 (s, 1H, H-$4_{pyridine}$), 11.35 (bs, 1H, NH exchangeable with D_2O). ^{13}C NMR (75 MHz, DMSO-d_6, δ): 22.3 (CH_2), 26.7 (CH_2), 113.9 (C-13a), 115.3 (C-4a), 116.8 (C≡N), 120.3 (C-14a), 123.7 (C-10), 126.4 (C-8), 127.2 (C-9), 129.0 (C-11), 130.6 (C-7b), 132.4 (C-14b), 136.9 (C-4), 139.6 (C-14), 142.8 (C-7a), 145.7 (C-6a), 149.1 (C-11a), 156.5 (C-2), 171.2 (C=$O_{α\text{-}pyrone}$). Mass spectrum, *m/z* (I_r %): 341 (100), 290 (68), 261 (51), 233 (18), 195 (22), 144 (15), 120 (57), 105 (23), 93 (35), 77 (41), 64 (24). Anal. Calcd for $C_{19}H_{11}N_5O_2$ (341.32): C, 66.86; H, 3.25; N, 20.52%. Found: C, 66.53; H, 3.08; N, 20.36%.

6,7-Dihydrochromeno[3`,4`:5,6]pyrido[2,3-*h*][1,2,4]triazolo[4,3-*a*]quinazolin-14(14*H*)-one (9)

A mixture of compound **1** (0.62 g, 2 mmol) and 3-amino-1,2,4-triazole (0.16 g, 2 mmol), in DMF (10 mL) containing TEA (0.1 mL), was heated under reflux for 2 h. The pale-yellow crystals deposited after cooling were filtered and crystallized from AcOH/H_2O, mp > 300 °C, yield (0.49 g, 72%). IR (KBr, cm^{-1}): 3046 ($CH_{arom.}$), 2953, 2921 ($CH_{aliph.}$), 1716 (C=$O_{α\text{-}pyrone}$), 1608 (C=N), 1578 (C=C). ^{1}H NMR (300 MHz, DMSO-d_6, δ): 2.03 (t, 2H, *J*= 6.0 Hz, CH_2), 2.28 (t, 2H, *J*= 6.0 Hz, CH_2), 7.25 (t, 1H, *J*= 7.8 Hz, H-10), 7.52 (d, 1H, *J*= 7.5 Hz, H-8), 7.71 (t, 1H, *J*= 7.5 Hz, H-9), 8.04 (d, 1H, *J*= 7.8 Hz, H-11), 8.63 (s, 1H, H-$4_{pyrimidine}$), 8.87 (s, 1H, H-$4_{pyridine}$), 9.03 (s, 1H, H-$3_{triazole}$). ^{13}C NMR (75 MHz, DMSO-d_6, δ): 21.7 (CH_2), 26.4 (CH_2), 113.6 (C-14a), 115.5 (C-5a), 118.7 (C-15a), 122.4 (C-11), 125.1 (C-9), 127.3 (C-10),

129.5 (C-12), 131.2 (C-8b), 132.8 (C-15b), 135.8 (C-5), 137.3 (C-15), 139.7 (C-1), 141.6 (C-8a), 145.9 (C-7a), 147.6 (C-12a), 150.2 (C-3a), 170.8 (C=$O_{\alpha\text{-pyrone}}$). Mass spectrum, *m/z* (I_r %): 341 (100), 286 (75), 233 (52), 196 (32), 145 (20), 120 (42), 92 (29), 77 (23), 64 (9). Anal. Calcd for $C_{19}H_{11}N_5O_2$ (341.32): C, 66.86; H, 3.25; N, 20.52%. Found: C, 66.82; H, 3.14; N, 20.29%.

8,9-Dihydrochromeno[3`,4`:5,6]pyrido[2,3-*h*]benzimidazo[1,2-*a*]quinazolin-16(16*H*)-one (10)

A mixture of compound **1** (0.62 g, 2 mmol) and 2-aminobenzimidazole (0.27 g, 2 mmol), in DMF (10 mL) containing TEA (0.1 mL), was heated under reflux for 2 h. The pale-brown crystals deposited during heating were filtered and crystallized from DMF/H_2O, mp > 300 °C, yield (0.51 g, 65%). IR (KBr, cm^{-1}): 3062 ($CH_{arom.}$), 1714 (C=$O_{\alpha\text{-pyrone}}$), 1619 (C=N), 1602 (C=C). ^{1}H NMR (300 MHz, DMSO-d_6, δ): 2.06 (t, 2H, *J*= 6.3 Hz, CH_2), 2.29 (t, 2H, *J*= 6.3 Hz, CH_2), 7.15-7.50 (m, 6H, Ar-H, H-13 and H-11), 7.73 (t, 1H, *J*= 7.5 Hz, H-12), 8.09 (d, 1H, *J*= 7.2 Hz, H-14), 8.58 (s, 1H, H-$4_{pyrimidine}$), 8.82 (s, 1H, H-$4_{pyridine}$). Mass spectrum, *m/z* (I_r %): 390 (100), 362 (46), 307 (31), 256 (43), 195 (17), 171 (12), 145 (16), 120 (56), 92 (33), 77 (24), 64 (13). Anal. Calcd for $C_{24}H_{14}N_4O_2$ (390.39): C, 73.84; H, 3.61; N, 14.35%. Found: C, 73.59; H, 3.41; N, 14.20%.

2-Methyl-7,8-dihydrochromeno[3`,4`:5,6]pyrido[2,3-*h*][1,2,4]triazino[4,3-*a*]quinazoline-1,15-(1*H*,15*H*)-dione (12)

A mixture of compound **1** (0.62 g, 2 mmol) and 3-amino-6-methyl-1,2,4-triazin-5(4*H*)-one (**11**) (0.25 g, 2 mmol), in DMF (10 mL) containing TEA (0.1 mL), was heated under reflux for 2 h. The pale-brown crystals deposited during heating were filtered and crystallized from AcOH, mp > 300 °C, yield (0.47 g, 62%). IR (KBr, cm^{-1}): 3028 ($CH_{arom.}$), 2944, 2917 ($CH_{aliph.}$), 1721 (C=$O_{\alpha\text{-pyrone}}$), 1683 (C=$O_{triazine}$), 1613 (C=N), 1592 (C=C). ^{1}H NMR (300 MHz, DMSO-d_6, δ): 1.95 (t, 2H, *J*= 6.0 Hz, CH_2), 2.24 (t, 2H, *J*= 6.0 Hz, CH_2), 2.86 (s, 3H, $CH_{3\ triazine}$), 7.27 (t, 1H, *J*= 7.2 Hz, H-12), 7.55 (d, 1H, *J*= 7.2 Hz, H-10), 7.68 (t, 1H, *J*= 7.2 Hz, H-11), 8.05 (d, 1H, *J*= 7.2 Hz, H-13), 8.61 (s, 1H, H-$4_{pyrimidine}$), 8.89 (s, 1H, H-$4_{pyridine}$). Mass spectrum, *m/z* (I_r %): 383 (59), 355 (47), 300 (35), 257 (18), 171 (26), 146 (14), 120 (35), 93 (100), 77 (67), 64 (16). Anal. Calcd for $C_{21}H_{13}N_5O_3$ (383.36): C, 65.79; H, 3.42; N, 18.27%. Found: C, 65.46; H, 3.32; N, 18.06%.

2,13-Dioxo-1,2,5,6-tetrahydro-13*H*-chromeno[4,3-*J*][1,7]phenanthroline-3-carbonitrile (13)

A mixture of compound **1** (0.62 g, 2 mmol) and cyanoacetamide (0.16 g, 2 mmol) in DMF (10 mL) containing TEA (0.1 mL), was heated under reflux for 2 h. The pale-yellow crystals deposited after cooling were filtered and crystallized from DMF/H_2O, mp > 300 °C, yield (0.48 g, 70%). IR (KBr, cm^{-1}): 3315 (NH), 3036 ($CH_{arom.}$), 2216 (C≡N), 1713 (C=$O_{\alpha\text{-pyrone}}$), 1618 (C=N), 1603 (C=C). ^{1}H NMR (300 MHz, DMSO-d_6, δ): 2.01 (t, 2H, *J*= 6.3 Hz, CH_2), 2.26 (t, 2H, *J*= 6.3 Hz, CH_2), 7.28 (t, 1H, *J*= 7.8 Hz, H-10), 7.54 (d, 1H, *J*= 7.5 Hz, H-8), 7.78 (t, 1H, *J*= 7.5 Hz, H-9), 8.12 (d, 1H, *J*= 7.8 Hz, H-11), 8.68 (s, 1H, H-$4_{pyridine}$), 8.85 (s, 1H, H-$4_{pyridine}$), 11.83 (bs, 1H, NH exchangeable with D_2O). ^{13}C NMR (75 MHz,

DMSO-d_6, δ): 22.1 (CH_2), 26.9 (CH_2), 102.3 (C-3), 111.6 (C-13a), 114.2 (C-4a), 116.4 (C≡N), 119.8 (C-14a), 122.9 (C-10), 125.7 (C-8), 127.4 (C-9), 129.3 (C-11), 130.4 (C-7b), 131.9 (C-14b), 135.8 (C-4), 139.1 (C-14), 142.6 (C-7a), 145.9 (C-6a), 149.3 (C-11a), 167.4 (C-2 as C=O), 170.6 ($C=O_{\alpha\text{-pyrone}}$). Mass spectrum, *m/z* (I_r %): 341 (100), 313 (63), 234 (39), 196 (18), 170 (23), 146 (16), 120 (31), 93 (51), 77 (33), 64 (16). Anal. Calcd for $C_{20}H_{11}N_3O_3$ (341.32): C, 70.38; H, 3.25; N, 12.31%. Found: C, 70.25; H, 3.10; N, 12.15%.

8,9-Dihydro-16-oxo-16*H*-chromeno[4,3-*J*]benzoimidazo[1,2-*a*][1,7]phenanthroline-6-carbonitrile (14)

A mixture of compound **1** (0.62 g, 2 mmol) and 1*H*-benzimidazol-2-ylacetonitrile (0.31 g, 2 mmol), in DMF (10 mL) containing TEA (0.1 mL), was heated under reflux for 2 h. The yellow crystals deposited during heating were filtered and crystallized from DMF, mp > 300 °C, yield (0.61 g, 74%). IR (KBr, cm^{-1}): 3043 ($CH_{arom.}$), 2219 (C≡N), 1723 ($C=O_{\alpha\text{-pyrone}}$), 1612 (C=N), 1593 (C=C). ^{1}H NMR (300 MHz, DMSO-d_6, δ): 2.03 (t, 2H, *J*= 6.0 Hz, CH_2), 2.25 (t, 2H, *J*= 6.0 Hz, CH_2), 7.08-7.34 (m, 5H, Ar-H and H-13), 7.56 (d, 1H, *J*= 7.5 Hz, H-11), 7.70 (t, 1H, *J*= 7.5 Hz, H-12), 7.98 (d, 1H, *J*= 7.5 Hz, H-14), 8.54 (s, 1H, $H\text{-}4_{pyridine}$), 8.76 (s, 1H, $H\text{-}4_{pyridine}$). Mass spectrum, *m/z* (I_r %): 414 (100), 386 (55), 335 (41), 309 (27), 219 (20), 196 (13), 120 (56), 93 (38), 77 (28), 64 (12). Anal. Calcd for $C_{26}H_{14}N_4O_2$ (414.41): C, 75.35; H, 3.41; N, 13.52%. Found: C, 75.11; H, 3.26; N, 13.27%.

(3-Cyano-5,6-dihydrochromeno[4,3-*J*][1,7]phenanthrolin-2(1*H*)-ylidene)propanedinitrile (15)

A mixture of compound **1** (0.62 g, 2 mmol) and 2-aminoprop-1-ene-1,1,3-tricarbonitrile (0.26 g, 2 mmol), in DMF (10 mL) containing TEA (0.1 mL), was heated under reflux for 2 h. The orange crystals deposited during heating were filtered and crystallized from DMF/EtOH, mp > 300 °C, yield (0.55 g, 71%). IR (KBr, cm^{-1}): 3286 (NH), 3021 ($CH_{arom.}$), 2223, 2204, 2196 (3C≡N), 1712 ($C=O_{\alpha\text{-pyrone}}$), 1608 (C=N), 1594 (C=C). ^{1}H NMR (300 MHz, DMSO-d_6, δ): 2.10 (t, 2H, *J*= 6.3 Hz, CH_2), 2.31 (t, 2H, *J*= 6.3 Hz, CH_2), 7.18 (t, 1H, *J*= 7.2 Hz, H-10), 7.44 (d, 1H, *J*= 7.2 Hz, H-8), 7.65 (t, 1H, *J*= 7.2 Hz, H-9), 8.02 (d, 1H, *J*= 7.2 Hz, H-11), 8.56 (s, 1H, $H\text{-}4_{pyridine}$), 8.79 (s, 1H, $H\text{-}4_{pyridine}$), 10.86 (bs, 1H, NH exchangeable with D_2O). Mass spectrum, *m/z* (I_r %): 389 (100), 361 (76), 335 (66), 285 (43), 259 (47), 196 (18), 171 (27), 145 (22), 120 (42), 93 (52), 77 (34), 64 (17). Anal. Calcd for $C_{23}H_{11}N_5O_2$ (389.36): C, 70.95; H, 2.85; N, 17.99%. Found: C, 70.88; H, 2.65; N, 17.74%.

5,6-Dihydro-3-hydroxy-1*H*-chromeno[4,3-*J*]pyrazolo[3,4-*b*][1,7]phenanthrolin-13(13*H*)-one (16)

A mixture of compound **1** (0.62 g, 2 mmol) and 5-amino-2,4-dihydro-3*H*-pyrazol-3-one (0.20 g, 2 mmol) in DMF (10 mL) containing TEA (0.1 mL), was heated under reflux for 2 h. The brown crystals deposited during heating were filtered and crystallized from DMF/H_2O, mp > 300 °C, yield (0.48 g, 67%). IR (KBr, cm^{-1}): 3403 (OH), 3316 (NH), 3009 ($CH_{arom.}$), 2926, 2905 ($CH_{aliph.}$), 1715 ($C=O_{\alpha\text{-pyrone}}$), 1616 (C=N), 1596 (C=C). ^{1}H NMR (300 MHz, DMSO-d_6, δ): 2.06 (t, 2H, *J*= 6.0 Hz, CH_2), 2.29 (t, 2H, *J*= 6.0 Hz,

CH_2), 7.32-7.46 (m, 2H, H-10 and H-8), 7.72 (t, 1H, *J*= 7.2 Hz, H-9), 8.03 (d, 1H, *J*= 7.2 Hz, H-11), 8.73 (s, 1H, H-$4_{pyridine}$), 8.83 (s, 1H, H-$4_{pyridine}$), 11.43 (bs, 1H, NH exchangeable with D_2O), 12.62 (bs, 1H, OH exchangeable with D_2O). Mass spectrum, *m/z* (I_r %): 356 (100), 331 (47), 285 (53), 245 (64), 195 (31), 170 (25), 120 (63), 93 (46), 77 (41), 64 (20). Anal. Calcd for $C_{20}H_{12}N_4O_3$ (356.33): C, 67.41; H, 3.39; N, 15.72%. Found: C, 67.18; H, 3.21; N, 15.54%.

5,6-Dihydro-3-methyl-1*H*-chromeno[4,3-*J*]pyrazolo[3,4-*b*][1,7]phenanthrolin-13(13*H*)-one (17)

A mixture of compound **1** (0.62 g, 2 mmol) and 5-amino-3-methyl-1*H*-pyrazole (0.20 g, 2 mmol), in DMF (10 mL) containing TEA (0.1 mL), was heated under reflux for 2 h. The pale brown crystals deposited during heating were filtered and crystallized from DMF/H_2O, mp > 300 °C, yield (0.49 g, 69%). IR (KBr, cm^{-1}): 3315 (NH), 3016 ($CH_{arom.}$), 2962, 2934 ($CH_{aliph.}$), 1716 ($C{=}O_{\alpha\text{-pyrone}}$), 1613 (C=N), 1596 (C=C). ^{1}H NMR (300 MHz, DMSO-d_6, δ): 1.96 (t, 2H, *J*= 6.3 Hz, CH_2), 2.25 (t, 2H, *J*= 6.3 Hz, CH_2), 2.42 (s, 3H, CH_3), 7.26 (t, 1H, *J*= 7.5 Hz, H-10), 7.51 (d, 1H, *J*= 7.2 Hz, H-8), 7.68 (t, 1H, *J*= 7.2 Hz, H-9), 7.95 (d, 1H, *J*= 7.5 Hz, H-11), 8.69 (s, 1H, H-$4_{pyridine}$), 8.81 (s, 1H, H-$4_{pyridine}$), 11.57 (bs, 1H, NH exchangeable with D_2O). ^{13}C NMR (75 MHz, DMSO-d_6, δ): 16.7 (CH_3), 21.8 (CH_2), 26.5 (CH_2), 110.4 (C-3a), 112.1 (C-13a), 114.6 (C-4a), 120.3 (C-14a), 122.5 (C-10), 125.2 (C-8), 127.9 (C-9), 129.7 (C-11), 130.3 (C-7b), 132.1 (C-14b), 135.6 (C-4), 137.9 (C-3), 139.8 (C-14), 142.3 (C-7a), 144.7 (C-6a), 148.4 (C-11a), 155.2 (C-15a), 171.5 ($C{=}O_{\alpha\text{-pyrone}}$). Mass spectrum, *m/z* (I_r %): 354 (100), 326 (86), 285 (63), 244 (53), 195 (25), 146 (11), 120 (55), 93 (37), 77 (25), 64 (11). Anal. Calcd for $C_{21}H_{14}N_4O_2$ (354.36): C, 71.18; H, 3.98; N, 15.81%. Found: C, 71.03; H, 3.86; N, 15.56%.

6,7-Dihydro-2-thioxo-1*H*-chromeno[4,3-*J*]pyrimido[4,5-*b*][1,7]phenanthroline-4,14(3*H*,14*H*)-dione (18)

A mixture of compound **1** (0.62 g, 2 mmol) and 6-amino-2-thioxo-2,3-dihydropyrimidin-4(1*H*)-one (0.29 g, 2 mmol), in DMF (10 mL) containing TEA (0.1 mL), was heated under reflux for 2 h. The pale brown crystals deposited during heating were filtered and crystallized from AcOH, mp > 300 °C, yield (0.53 g, 66%). IR (KBr, cm^{-1}): 3356, 3279 (2NH), 3041 ($CH_{arom.}$), 1712 ($C{=}O_{\alpha\text{-pyrone}}$), 1662 ($C{=}O_{pyrimidine}$), 1615 (C=N), 1585 (C=C), 1244 (C=S). ^{1}H NMR (300 MHz, DMSO-d_6, δ): 2.03 (t, 2H, *J*= 6.3 Hz, CH_2), 2.28 (t, 2H, *J*= 6.3 Hz, CH_2), 7.22 (t, 1H, *J*= 7.2 Hz, H-11), 7.57 (d, 1H, *J*= 7.2 Hz, H-9), 7.73 (t, 1H, *J*= 7.2 Hz, H-10), 7.98 (d, 1H, *J*= 7.2 Hz, H-12), 8.54 (s, 1H, H-$4_{pyridine}$), 8.78 (s, 1H, H-$4_{pyridine}$), 11.13 (bs, 2H, 2NH exchangeable with D_2O). Mass spectrum, *m/z* (I_r %): 400 (62), 357 (100), 329 (36), 285 (51), 244 (53), 195 (10), 170 (14), 145 (17), 120 (38), 92 (27), 77 (28), 64 (15). Anal. Calcd for $C_{21}H_{12}N_4O_3S$ (400.41): C, 62.99; H, 3.02; N, 13.99%. Found: C, 62.84; H, 2.85; N, 13.72%.

1,3-Dimethyl-6,7-Dihydro-1*H*-chromeno[4,3-*J*]pyrimido[4,5-*b*][1,7]phenanthroline-2,4,14(3*H*,14*H*)-trione (19)

A mixture of compound **1** (0.62 g, 2 mmol) and 6-amino-1,3-dimethylpyrimidine-2,4(1*H*,3*H*)-dione (0.31 g, 2 mmol), in DMF (10 mL) containing TEA (0.1 mL), was heated under reflux for 2 h. The pale brown crystals deposited during heating were filtered and crystallized from AcOH/H_2O, mp > 300 °C, yield (0.51 g, 62%). IR (KBr, cm^{-1}): 3041 ($CH_{arom.}$), 2963, 2941 ($CH_{aliph.}$), 1718 ($C{=}O_{\alpha\text{-pyrone}}$), 1673, 1658 ($2C{=}O_{pyrimidine}$), 1619 (C=N), 1582 (C=C). ^{1}H NMR (300 MHz, DMSO-d_6, δ): 1.94 (t, 2H, *J*= 6.0 Hz, CH_2), 2.23 (t, 2H, *J*= 6.0 Hz, CH_2), 3.41 (s, 3H, NCH_3), 3.63 (s, 3H, NCH_3), 7.29 (t, 1H, *J*= 7.5 Hz, H-10), 7.53-7.65 (m, 2H, H-8 and H-9), 7.91 (d, 1H, *J*= 7.5 Hz, H-11), 8.61 (s, 1H, H-$4_{pyridine}$), 8.83 (s, 1H, H-$4_{pyridine}$). Mass spectrum, *m/z* (I_r %): 412 (63), 356 (100), 342 (41), 300 (28), 285 (32), 246 (17), 195 (18), 170 (24), 120 (27), 92 (22), 77 (25), 64 (8). Anal. Calcd for $C_{23}H_{16}N_4O_4$ (412.39): C, 66.99; H, 3.91; N, 13.59%. Found: C, 66.68; H, 3.74; N, 13.42%.

7,8-Dihydrochromeno[4,3-*b*][1,4]benzoxazepino[2,3-*f*]quinolin-15(15*H*)-one (20)

A mixture of compound **1** (0.62 g, 2 mmol) and *o*-aminophenol (0.22 g, 2 mmol) in DMF (10 mL) containing TEA (0.1 mL), was heated under reflux for 2 h. The brown crystals deposited during heating were filtered and crystallized from xylene, mp > 300 °C, yield (0.47 g, 64%). IR (KBr, cm^{-1}): 3032 ($CH_{arom.}$), 1719 ($C{=}O_{\alpha\text{-pyrone}}$), 1616 (C=N), 1586 (C=C). ^{1}H NMR (300 MHz, DMSO-d_6, δ): 2.03 (t, 2H, *J*= 6.3 Hz, CH_2), 2.28 (t, 2H, *J*= 6.3 Hz, CH_2), 6.92-7.41 (m, 6H, Ar-H, H-12 and H-10), 7.62 (t, 1H, *J*= 7.2 Hz, H-11), 7.98 (d, 1H, *J*= 7.2 Hz, H-13), 8.37 (s, 1H, H-$4_{oxazepine}$), 8.76 (s, 1H, H-$4_{pyridine}$). Mass spectrum, *m/z* (I_r %): 366 (49), 339 (43), 311 (35), 209 (29), 195 (16), 171 (37), 120 (47), 105 (26), 93 (100), 77 (53), 64 (23). Anal. Calcd for $C_{23}H_{14}N_2O_3$ (366.37): C, 75.40; H, 3.85; N, 7.65%. Found: C, 75.21; H, 3.56; N, 7.43%.

7,8-Dihydrochromeno[4,3-*b*][1,4]benzothiazepino[2,3-*f*]quinolin-15(15*H*)-one (21)

A mixture of compound **1** (0.62 g, 2 mmol) and *o*-aminothiophenol (0.25 g, 2 mmol) in DMF (10 mL) containing TEA (0.1 mL), was heated under reflux for 2 h. The brown crystals deposited after cooling were filtered and crystallized from xylene, mp > 300 °C, yield (0.44 g, 58%). IR (KBr, cm^{-1}): 3056 ($CH_{arom.}$), 1701 ($C{=}O_{\alpha\text{-pyrone}}$), 1609 (C=N), 1596 (C=C). ^{1}H NMR (300 MHz, DMSO-d_6, δ): 2.07 (t, 2H, *J*= 6.0 Hz, CH_2), 2.24 (t, 2H, *J*= 6.0 Hz, CH_2), 6.88-7.29 (m, 5H, Ar-H and H-12), 7.54 (d, 1H, *J*= 7.5 Hz, H-10), 7.68 (t, 1H, *J*= 7.5 Hz, H-11), 8.05 (d, 1H, *J*= 7.5 Hz, H-13), 8.41 (s, 1H, H-$4_{thiazepine}$), 8.83 (s, 1H, H-$4_{pyridine}$). Mass spectrum, *m/z* (I_r %): 382 (58), 354 (63), 327 (31), 251 (40), 195 (10), 170 (12), 145 (14), 120 (100), 105 (21), 93 (39), 77 (34), 64 (10). Anal. Calcd for $C_{23}H_{14}N_2O_2S$ (382.43): C, 72.23; H, 3.69; N, 7.33; S, 8.38%. Found: C, 72.00; H, 3.42; N, 7.26; S, 8.34%.

1-Chloro-2-{[(3-methyl-5-thioxo-1,5-dihydro-4*H*-1,2,4-triazol-4-yl)imino]methyl}-3,4-dihydro-chromeno[4,3-*b*]quinolin-1(1*H*)-one (24)

A mixture of compound **1** (0.62 g, 2 mmol) and 4-amino-5-methyl-2,4-dihydro-3*H*-1,2,4-triazole-3-thione (**22**) (0.26 g, 2 mmol), in DMF (10 mL) containing TEA (0.1 mL), was heated under reflux for 2 h.

The yellow crystals deposited during heating were filtered and crystallized from AcOH, mp > 300 °C, yield (0.65 g, 77%). IR (KBr, cm^{-1}): 3268 (NH), 3047 ($CH_{arom.}$), 2958, 2934 ($CH_{aliph.}$), 1702 ($C=O_{\alpha\text{-pyrone}}$), 1613 (C=N), 1591 (C=C), 1248 (C=S). ^{1}H NMR (300 MHz, DMSO-d_6, δ): 2.01 (t, 2H, *J*= 6.0 Hz, CH_2), 2.24 (t, 2H, *J*= 6.0 Hz, CH_2), 2.46 (s, 3H, $CH_{3\ triazole}$), 7.28 (t, 1H, *J*= 7.8 Hz, H-8), 7.51 (d, 1H, *J*= 7.5 Hz, H-6), 7.72 (t, 1H, *J*= 7.5 Hz, H-7), 8.03 (d, 1H, *J*= 7.5 Hz, H-9), 8.35 (s, 1H, $CH_{azomethine}$), 8.85 (s, 1H, H-$4_{pyridine}$), 11.64 (bs, 1H, NH exchangeable with D_2O). ^{13}C NMR (75 MHz, DMSO-d_6, δ): 18.2 (CH_3), 22.1 (CH_2), 27.3 (CH_2), 113.7 (C-11a), 121.4 (C-12a), 123.6 (C-8), 125.7 (C-6), 127.4 (C-7), 129.5 (C-9), 130.6 (C-5b), 131.9 (C-2), 135.3 (C-1), 137.6 (C=N), 139.7 (C-12), 141.6 (C-$5_{triazole}$), 142.7 (C-5a), 146.1 (C-4a), 149.8 (C-9a), 171.3 ($C=O_{\alpha\text{-pyrone}}$), 189.6 (C=S). Mass spectrum, *m/z* (I_r %): 423/425 (15/5), 309/311 (100/34), 281/283 (51/17), 254/254 (40/13), 194 (15), 120 (73), 105 (46), 93 (55), 77 (37), 64 (18). Anal. Calcd for $C_{20}H_{14}ClN_5O_2S$ (423.88): C, 56.67; H, 3.33; N, 16.52; S, 7.56%. Found: C, 56.57; H, 3.12; N, 16.28; S, 7.46%.

1-Chloro-2-{[(6-methyl-5-oxo-3-thioxo-2,5-dihydro-1,2,4-triazin-4(3*H*)-yl)imino]methyl}-3,4-dihydrochromeno[4,3-*b*]quinolin-1(1*H*)-one (26)

A mixture of compound **1** (0.62 g, 2 mmol) and 4-amino-6-methyl-3-thioxo-3,4-dihydro-1,2,4-triazin-5(2*H*)-one (**25**) (0.32 g, 2 mmol) in DMF (10 mL) containing TEA (0.1 mL), was heated under reflux for 2 h. The yellow crystals deposited during heating were filtered and crystallized from AcOH, mp > 300 °C, yield (0.71 g, 79%). IR (KBr, cm^{-1}): 3325 (NH), 3063 ($CH_{arom.}$), 2943, 2922 ($CH_{aliph.}$), 1709 ($C=O_{\alpha\text{-pyrone}}$), 1617 (C=N), 1581 (C=C), 1239 (C=S). ^{1}H NMR (300 MHz, DMSO-d_6, δ): 2.04 (t, 2H, *J*= 6.6 Hz, CH_2), 2.23 (t, 2H, *J*= 6.6 Hz, CH_2), 2.39 (s, 3H, $CH_{3\ triazine}$), 7.31 (t, 1H, *J*= 7.2 Hz, H-8), 7.54 (d, 1H, *J*= 7.2 Hz, H-6), 7.75 (t, 1H, *J*= 7.2 Hz, H-7), 8.02 (d, 1H, *J*= 7.2 Hz, H-9), 8.32 (s, 1H, $CH_{azomethine}$), 8.88 (s, 1H, H-$4_{pyridine}$), 12.54 (bs, 1H, NH exchangeable with D_2O). ^{13}C NMR (75 MHz, DMSO-d_6, δ): 17.6 (CH_3), 22.3 (CH_2), 27.9 (CH_2), 112.5 (C-11a), 120.3 (C-12a), 123.8 (C-8), 125.4 (C-6), 127.2 (C-7), 129.1 (C-9), 130.7 (C-5b), 132.3 (C-2), 134.6 (C-1), 136.9 (C=N), 138.5 (C-12), 140.9 (C-$6_{triazine}$), 142.3 (C-5a), 145.6 (C-4a), 148.5 (C-9a), 168.7 ($C=O_{triazine}$) 172.1 ($C=O_{\alpha\text{-pyrone}}$), 188.9 (C=S). Mass spectrum, *m/z* (I_r %): 451/453 (13/4), 309/311 (100/33), 281/283 (35/12), 254/256 (24/8), 194 (19), 170 (15), 146 (11), 120 (66), 92 (30), 77 (23), 64 (10). Anal. Calcd for $C_{21}H_{14}ClN_5O_3S$ (451.89): C, 55.82; H, 3.12; N, 15.50; S, 7.10%. Found: C, 55.56; H, 3.07; N, 15.35; S, 6.97%.

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