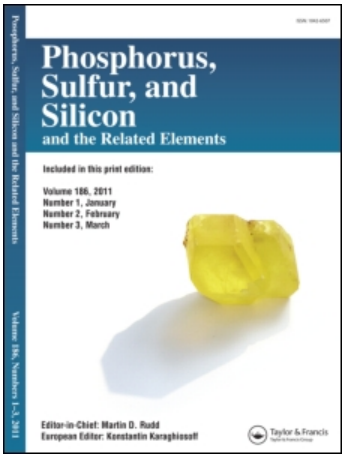

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Synthesis of Heterocycles via 2-Thioxo-1,2-dihydropyridine-3-carbonitrile Derivative

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*The present study aimed to investigate the synthetic potentiality and chemical reactivity of 2-thioxo-1,2-dihydropyridine-3-carbonitrile derivative **1**. This goal performed via its reaction with each of 1-chloroacetone and iodomethane to afford the corresponding 2-alkylthio derivatives **3** and **9**, respectively. Compound **3** underwent intramolecular cyclization to afford the corresponding thieno[2,3-b]pyridine derivative **4** which in turn, reacted with dimethylformamide / dimethylacetal followed by hydrazine hydrate and nitrous acid to afford the corresponding pyridothienopyrimidine and pyridothienopyridazine derivatives **6** and **8**, respectively. On the other hand, Compound **9** reacted with hydrazine hydrate to give 3-aminopyrazolo[3,4-b]pyridine derivative **10**, which diazotized with nitrous acid to give the corresponding diazonium salt **11**. Compound **11** coupled with several active –CH_2- containing reagents to synthesize the corresponding pyridopyrazolo-triazines **15, 24, 29**, and **31**. The formulas of all newly synthesized heterocyclic compounds were elucidated by considering the data of IR, ^1H NMR, Mass spectral data, as well as data from elemental analyses.*

Keywords 2-Thioxohydropyridine-3-carbonitrile; pyridopyrazolotriazine; thieno[2,3-b]pyridine; thienopyridopyridazine; thienopyridopyrimidine

INTRODUCTION

In continuation of our previous efforts,[1–20] we investigate here the synthetic potentiality of 2-thioxo-1,2-dihydropyridine-3-carbonitrile derivative **1**. Compound **1** was obtained by two different procedures[21,22]; on repeating these procedures, we obtained higher yield and different melting points. We are interested in investigating the position and chemical reactivity of functional groups present in **1**. The present study aims to synthesize several new heterocycles via building up new rings—

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e.g., thiophenes, pyrazoles, pyridazines, pyrimidines, or triazines—on the parent pyridine ring. In the course of our investigations on the titled compound **1**, we were interested in the utilization of the reactivity of C=S, NH, and CN groups to carry out different types of heterocyclizations. Based on the nucleophilicity of S-atom of the SH group we have developed new procedures for the synthesis of heterocyclic systems with the aim to find biologically active compounds.[23–28]

Compound **1** was used as a starting point for the present study; thus, it has been found that compound **1** reacted with 1-chloroacetone **(2)** in stirred methanolic sodium methoxide at room temperature, which afforded a reaction product **3** via the dehydrochlorination. The IR (cm^{-1}) of compound **3** showed the bands (2212.2, CN) and (1716, CH_3CO) groups. Further confirmation of **3** arose from its cyclization in ethanolic sodium ethoxide under reflux 5–10 min, which through intramolecular cyclization gave **4**. The IR (cm^{-1}) of compound **4** showed no bands of the CN group, while that of the newly formed NH_2 was detected at 3307.3 and 3471.9;this proved that both -CH_2- and CN groups involved in the cyclization step (cf. Chart 1). The formula of compound **4** elucidated further through its preparation authentically via the reaction of **1** with **2** in ethanolic sodium ethoxide under reflux for 2–3 h. It is important to report here that compound **4** was obtained by two pathways—identical in all physical and chemical properties. The position of NH_2 and its adjacent $COCH_3$ in compound **4** was confirmed via its reaction with both nitrous acid to give the corresponding pyridothienopyridazine derivative **8** and dimethylformamide/dimethyacetal followed by hydrazine to give the corresponding pyridothienopyrimidine derivative **6**.

By considering the data of both elemental analyses, IR, and ^1H NMR, the formulas of compounds **3–8** were elucidated, in addition to the data of mass spectra of compounds **4–6** that gave m/z = 380, 435, and 422, which corresponded to the molecular weights of the formulas $C_{20}H_{16}O_2N_2S_2$, $C_{23}H_{21}O_2N_3S_2$, and $C_{21}H_{18}O_2N_4S_2$ of the assigned formulas, in addition to several peaks that corresponded to fragments, which confirmed the assigned formulas further (Chart 1 and Experimental section). Work was extended to shed more light on the reactivity of SH group in **1** towards the electrophilic C-atom of iodomethane; thus, **1** reacted with iodomethane in methanolic sodium methoxide solution to give the corresponding 2-methylthio derivative **9** in which the nucleophilic substitution reaction of SCH_3 group performed by the reaction with hydrazine hydrate giving a reaction product **10**. The IR (cm^{-1}) of compound **10** showed no bands of CN function and instead that of NH_2 detected at 3194.0, 3290.4, 3433.3, and this proved that the CN function consumed in building a new pyrazole ring.

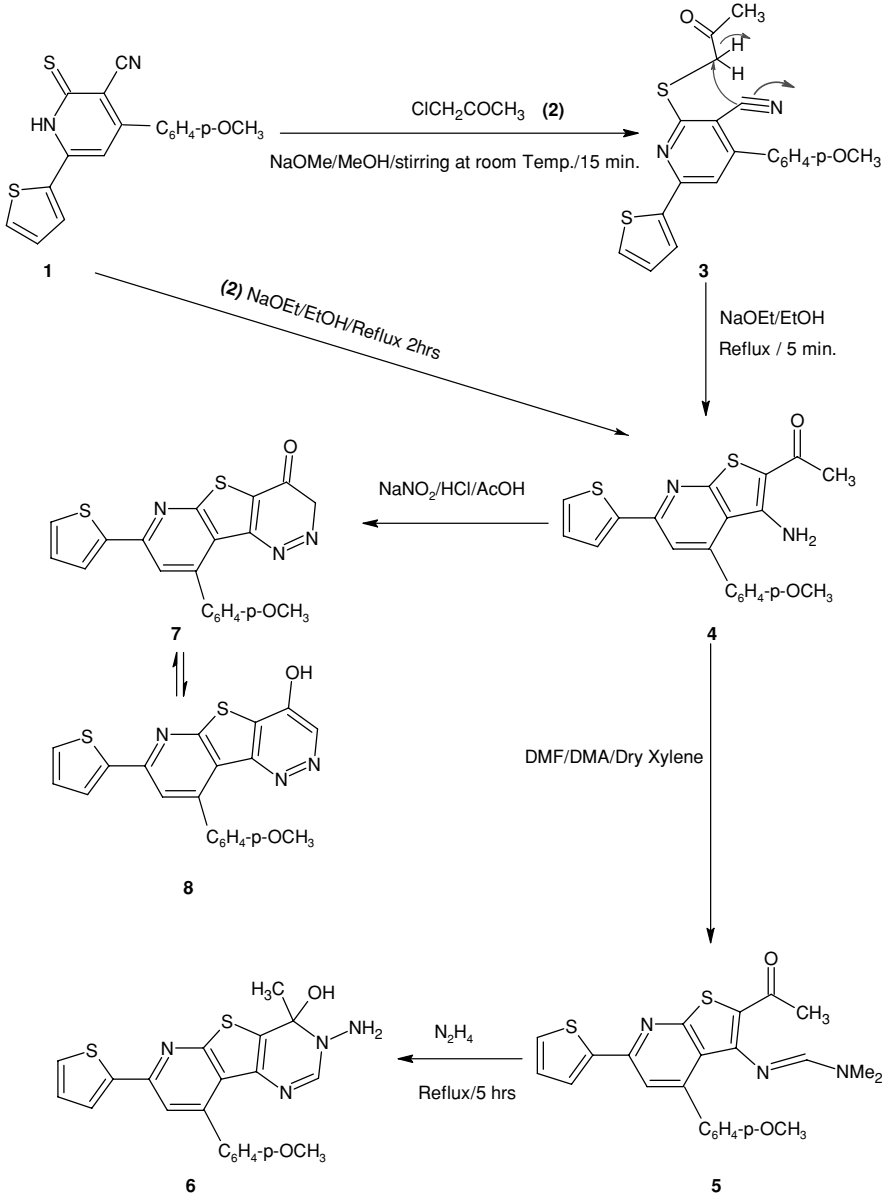


CHART 1

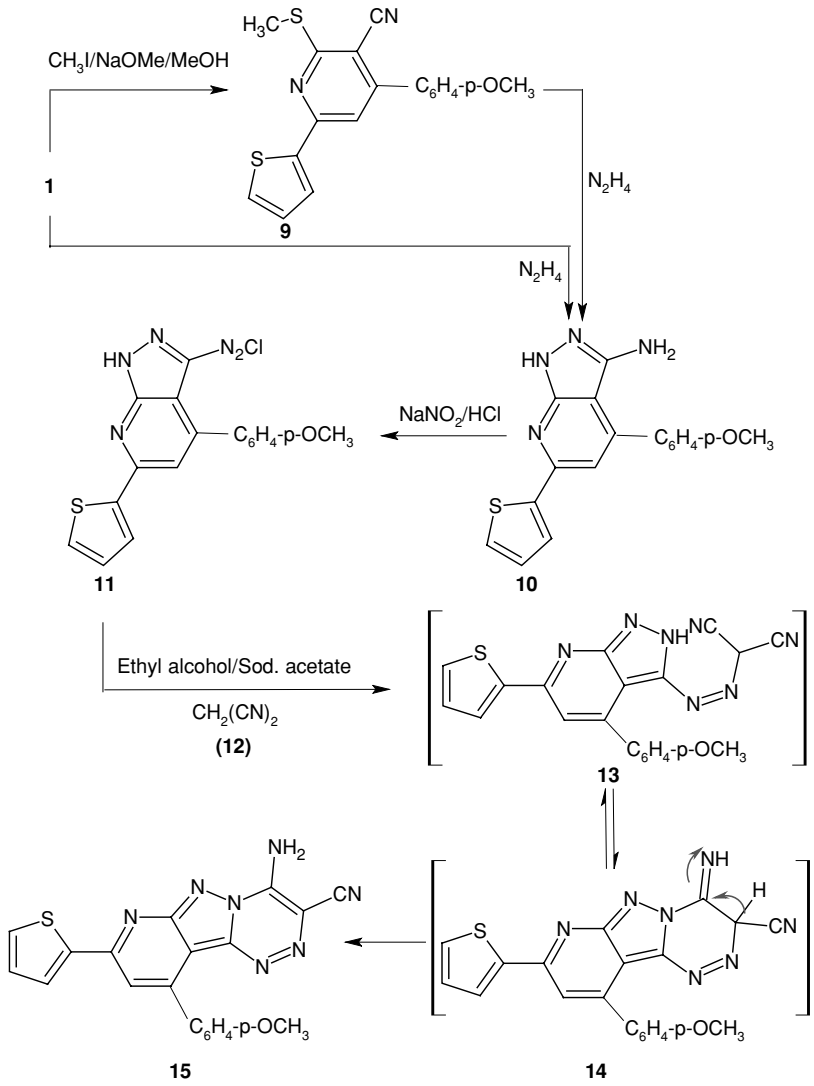


CHART 2

Moreover, the mass spectrum of **9** gave m/z = 338 (36.3%) and this corresponded to the molecular weight of the molecular formula $C_{18}H_{14}ON_2S_2$ of the assigned formula (Chart 2), 337 (100%, M-1), 323 (26.8%, M-CH_3), 291 (2.5%, M-SCH_3). On the other hand, the mass spectrum of **10** gave m/z = 322, which corresponded to a molecular weight of a molecular formula $C_{17}H_{14}ON_4S$ of the assigned formula

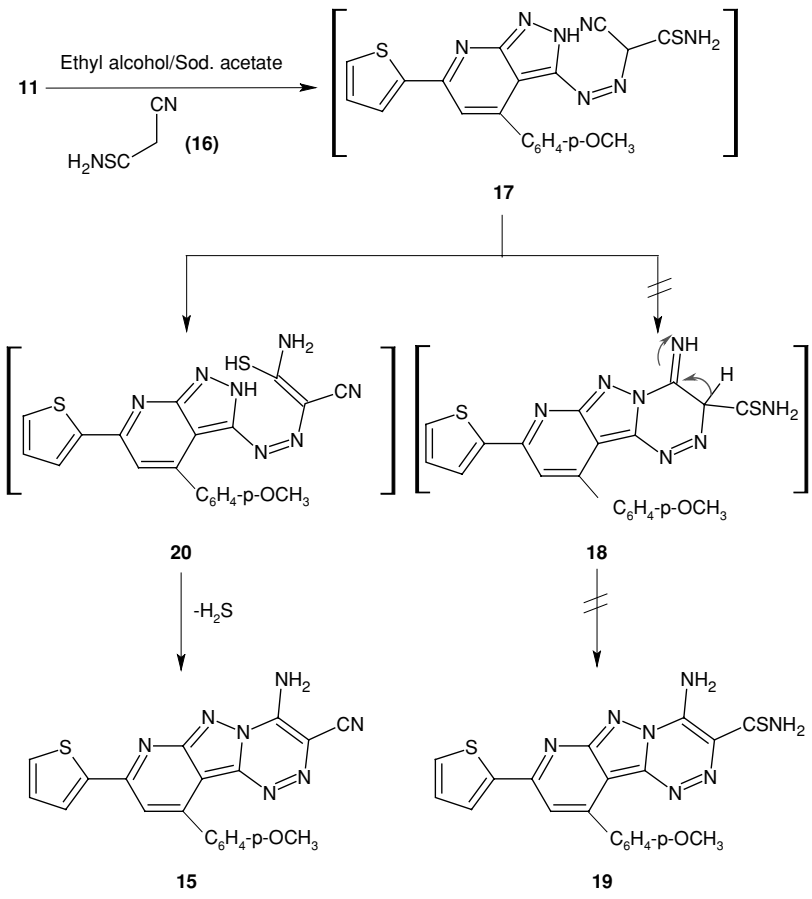


CHART 3

(cf. Chart 2 and Experimental section). The position and chemical reactivity of NH_2 of **10** elucidated through its diazotization with nitrous acid to give the corresponding diazonium salt **11** whose formula was established via its coupling with each of malononitrile **(12)** and/or 1-cyanoethanethioamide **(16)** to give **15**.

The formation of compound **15** proceeded through dehydrochlorination with intramolecular cyclization via NH_2 addition on the CN function in case of **12** and removal of H_2S in case of **16**. Formula **15** was established by considering the data of IR, ^1H NMR, and elemental analyses, where IR (cm^{-1}) showed the bands 3417.1, 3273.9 (NH_2), 2208.1 (CN), and ^1H NMR (δppm), which revealed the signals 3.884 (s,

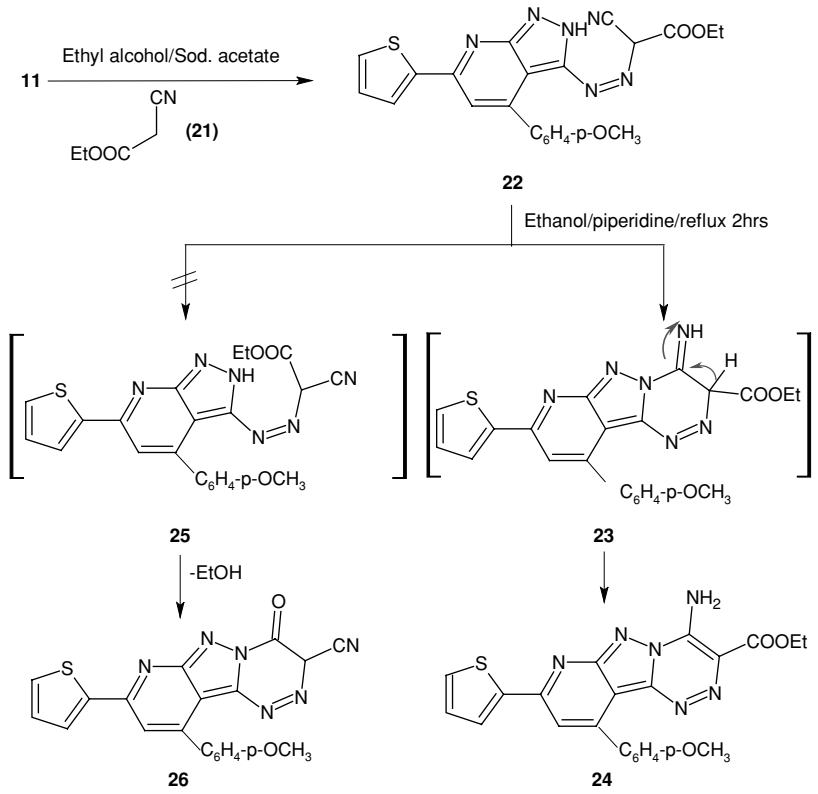
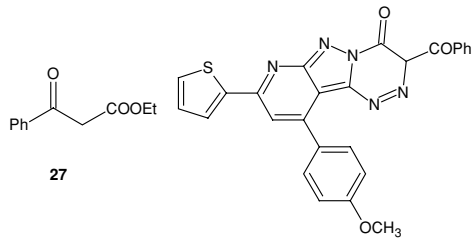


CHART 4

br., 2H, NH_2). Considering the previously mentioned IR and ^1H NMR data, we rejected compound **19**.

Moreover, the mass spectrum of **15** gave m/z = 399 (100%) which corresponded to the molecular weight of the molecular formula $C_{20}H_{13}ON_7S$ of the assigned formula (Charts 2, 3, and Experimental section). It important to report here that all attempts to isolate compounds **13**, **14**, **17**, and **20** failed. On contrast to the behavior of **11** towards each of **12** and **16**, we found that **11** reacted with ethyl cyanoacetate **(21)** to give ethyl cyano{[4-(4-methoxyphenyl)-6-(2-thienyl)-1*H*-pyrazolo[3,4-*b*]pyridin-3-yl]-diazenyl}acetate **(22)**, whose formula was elucidated by considering the data of IR and elemental analyses (Experimental section).

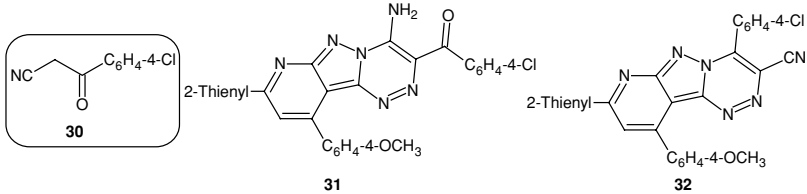
Compound **22**—established via its intramolecular cyclization in ethanol/piperidine under reflux 2 h—afforded a reaction product, where



the IR showed no CN function and showed the newly formed NH_2; this confirmed compound **24** and rejected **26**. The mass spectrum of this reaction product gave m/z = 446 (100%), which corresponded to the molecular weight of the molecular formula $C_{22}H_{18}N_6O_3S$ of the assigned formula **24** and did not give m/z = 400 for the formula **26** with $C_{20}H_{12}N_6O_2S$ (cf. Chart 4 and Experimental section).

Similarly, compound **11** reacted with ethyl 3-oxo-3-phenylpropanoate **(27)**, which gave the reaction product **29**, rather than **28**. The rejection of **28** depends on the appearance of the band at 1727 for CO ester in IR and detection of the signals 1.027 (t, 3H, $\underline{CH_3}CH_2COO$, J = 7.0), 4.201 (q, 2H, $CH_3\underline{CH_2}COO$-, J = 7.1). Furthermore, the mass spectrum of this reaction product gave m/z = 507, which corresponded to the molecular weight of the molecular formula $C_{28}H_{21}N_5O_3S$ of the assigned formula **29** and did not give m/z = 479 for the formula $C_{26}H_{17}N_5O_3S$ **28** (cf. Experimental section).

The work extended to investigate further the reactivity of both chlorine atom and NH-pyrazole in compound **11**. Thus, it was found that **11** reacted with 3-(4-chlorophenyl)-3-oxopropanenitrile **30** to give the reaction product **31**, which formed via the dehydrochlorination followed by intramolecular cyclization that involved both CN and NH-pyrazole groups. Formula of **31** established by considering the data of IR, elemental analyses and mass spectrum (cf. Experimental section) on such data we reject formula **32**.



CONCLUSION

Finally, we concluded that the starting material 4-(4-methoxy-phenyl)-2-[(2-oxopropyl)thio]-6-(2-thienyl)nicotinonitrile **(3)** contained three chemically active groups—e.g., NH, SH, and CN—which was used for several chemical transformations. Furthermore it was used to build a new ring system, i.e., electrophilic attack on nucleophilic S of SH group from the electrophilic C-atom of CH_3I, and the nucleophilic substitution of SCH_3 group by the nucleophilic hydrazine N.

EXPERIMENTAL

All melting points were uncorrected. I.R. (KBr discs) spectra were recorded on a Shimadzu FTIR-8201PC Spectrophotometer. ^1H NMR spectra were recorded on a Varian Mercury 300 MHz., and a Varian Gemini 200 MHz. spectrometers using TMS as an internal standard and $CDCl_3$, DMSO-d_6, and $(CD_3)_2CO$ as solvents. Chemical shifts were expressed as δ (ppm) units. Mass spectra were recorded on Shimadzu GCMS-QP1000EX using an inlet type at 70 eV. The Microanalytical Center of Cairo University performed the microanalyses.

The Synthesis of 3

A solution of each of **1** (0.324 g, 1 mmol) and chloroacetone (**2**, 0.092 g, 1 mmol) in sodium methoxide (prepared from 0.023 g of sodium and methanol 25 mL) was stirred at room temperature for 15 min. The formed precipitate was collected by filtration, washed with water, dried, and recrystallized from ethanol to afford 4-(4-methoxyphenyl)-2-[(2-oxopropyl)thio]-6-(2-thienyl)nicotinonitrile **(3)** as yellow crystals (84%), m.p.=194-196 C°, IR $\upsilon(cm^{-1})$: 3092.5(C-H, aromatic), 2212.2 (CN), 1716 (CO); anal., for $C_{20}H_{16}O_2N_2S_2$ (380), calcd./found(%): C(63.13/63.22), H(4.24/4.31), N(7.36/7.52), S(16.85/16.90).

The Synthesis of 4

Method A

A solution of each of **3** (0.380 g, 1 mmol) in sodium ethoxide solution (prepared from 0.023 g of sodium and 25 mL ethanol) heated under reflux for 30 min. The solid that formed after cooling, collected by filtration, washed with water and ethanol, and recrystallized from chloroform to afford **4**.

Method B

A solution of each of **1** (0.324 g, 1 mmol) and chloroacetone (2, 0.092 g, 1 mmol) in sodium ethoxide solution (prepared from 0.023 g of sodium and 25 mL ethanol) heated under reflux for 2 h. The solid product that formed after cooling, collected by filtration, washed with water and ethanol, recrystallized from chloroform to afford 1-[3-amino-4-(4-methoxyphenyl)-6-(2-thienyl)thieno[2,3-*b*]pyridin-2-yl]ethanone (4) as orange crystals (89%), m.p. = 162–164°C, **IR** $\upsilon(cm^{-1})$, 3471.9, 3307.3 (NH_2), 1615.3 (CO); **MS**: 380 (M^+, 100%, which corresponded to the molecular weight of the molecular formula $C_{20}H_{16}O_2N_2S_2$ of the assigned formula), 379 (M^+-H, 51.5%), 365 (M^+-CH_3, 43.0%), 364 (379-NH, 4.0%), 337 (M+-$COCH_3$, 14.3%), 297 (M^+-$CH_3COC{=}C$-NH_2, 2.9%), and 83 ($CH_3COC{=}C$-NH_2, 1.2 %); anal., for $C_{20}H_{16}O_2N_2S_2$ (380) calcd./found(%): C(63.13/63.31), H(4.24/4.40), N(7.36/7.40), S(16.85/16.91).

The Synthesis of 5

A solution of each of **4** (0.190 g, 0.5 mmol) and dimethyl formamide-dimethylacetal (0.106 g, 1 mmol) in dry xylene (30 mL) heated under reflux for 5 h. The excess solvent evaporated, and the solid that formed after cooling was collected by filtration, dried, and recrystallized from dioxane to afford 1-3-[ethylideneamino]-4-(4-methoxyphenyl)-6-(2-thienyl)thieno[2,3-*b*]pyridin-2-ylethanone **(5)**: as yellow crystals (91%), m.p. = 230°C, **IR** υ (cm^{-1}): 2995.5, 2920 (aliphatic CH), 1641.3 (CO acetyl); **MS**: 435 (M^+, 100%, which corresponded to the molecular weight of the molecular formula $C_{23}H_{21}O_2N_3S_2$ of the assigned formula), 420 (M+-CH_3, 20.1%), 392 (M^+-$COCH_3$, 65.5%), 391 (M^+-$N(CH_3)_2$, 54.1%), 378 (M+-$CHN(CH_3)_2$, 8.3%), 364 (M+-$N{=}CHN(CH_3)_2$, 5.6%) 351 (M^+-C_4H_3S, 41%); anal., for $C_{23}H_{21}O_2N_3S_2$ (435) calcd./found: C(65.00/64.62), H(4.46/4.50), N(6.89/7.10), S(15.78/15.91).

The Synthesis of 6

A solution of each of **5** (0.478 g, 1.1 mmol) and hydrazine hydrate (10 mL) in ethanol (20 mL) heated under reflux for 5 h. The excess solvent evaporated, and the solid formed after cooling collected by filtration, dried and recrystallized from ethanol to afford 3-amino-9-(4-methoxy-phenyl)-4-methyl-7-(2-thienyl)-3,4-dihydropyrido[3′,2′:4,5]thieno[3,2-*d*]pyrimi- din-4-ol **(6)** as red crystals (89%), m.p. = 120°C, **IR** υ (cm^{-1}): 3454, (NH_2), broad

3320–3454 (H-bonded OH) and 1615.1 (C=N); **MS**: 422 (M^+, 39.4%, which corresponded to the molecular weight of the molecular formula $C_{21}H_{18}O_2N_4S_2$ of the assigned formula), 421 (M^+-H, 54.5%), 406 (M^+-NH_2, 33.3%), 405 (M^+- OH, 77.8%), 335 (M^+-CH_3(OH)C-N(NH_2)CH, 70.7%), 321 (M^+ - CH_3(OH)C-N(NH_2)CH=N, 47.5%); **^{1}H NMR**(δ ppm): 1.915 (s, 3H, CH_3), 3.866 (s, 3H, OCH_3), 5.558 (s, br., 2H, NH_2), 8.66 (s, br., 1H, OH), 7.144–8.031 (m, 9H, ArH's, Thiophene, Pyridine, Pyrimidine-H's); anal., for $C_{21}H_{18}O_2N_4S_2$ (422) calcd./found: C(59.69/60.11), H(4.29/4.31), N(13.26/13.33), S(15.18/15.20).

The Synthesis of 7

A solution of each of **4** (0.380 g, 1 mmol) in concentrated hydrochloric acid (5 mL) and glacial acetic acid (5 mL) stirred in an ice bath. Add sodium nitrite solution (0.138 g, 2 mmol) dropwise with stirring along 30 min. The solid that formed was collected by filtration, washed with water, dried, and recrystallized from dioxane to afford 9-(4-methoxyphenyl)-7-(2-thienyl)pyrido[3',2':4,5]thieno[3,2-*c*]pyridazin-4-ol **(7)** as red crystals (91%), m.p. = 115°C; **IR** υ(cm^{-1}) 3250–3505 (H-bonded OH), 3100.9 (=C-H), 2928.6 (aliphatic C-H); **^{1}H NMR** ($CDCL_3$, δppm): 3.652 (s, 3H, OCH_3), 7.016–7.644 (m, 9H, ArH's, Thiophene, Pyridine, Pyridazine H's), and 13.597 (s, 1H, OH); anal., for $C_{20}H_{13}O_2N_3S_2$ (391): calcd./found (%): C(61.36/61.41), H(3.35/3.37), N(10.73/10.81), S(16.38/16.41).

Synthesis of 9

A solution of each of **1** (0.324 g, 1 mmol) and methyl iodide (0.3 g, 2 mmol) in sodium methoxide (prepared from 0.023 g of sodium and methanol 25 mL) was stirred at room temperature for 15 min. The formed precipitate was collected by filtration, washed with water, dried, and recrystallized from chloroform to afford 4-(4-methoxyphenyl)-2-(methylthio)-6-(2-thienyl)-nicotinonitrile **(9)**: as white crystals (90%), m.p. = 192°C, **IR** υ(cm^{-1}): 3058.6 (Aromatic C-H), 2956.5–2917.7(Aliphatic C-H), and 2212.3 (CN); **MS**: 337 (M^+, 100%), 323 (M^+-CH_3, 26.8%), 308 (M^+-2CH_3, 2.4%), 292 (M^+-CH_3-OCH_3, 5.4%), 291 (M^+-SCH_3, 2.5%), 260 (M^+-OCH_3-SCH_3, 5.5%); anal., for $C_{18}H_{14}ON_2S_2$ (338) calcd./found (%):C(63.88/64.00), H(4.17/4.21), N(8.28/8.31), S(18.95/19.11).

Synthesis of 10

Method A

A solution of each of **1** (0.324 g, 1 mmol) in hydrazine hydrate (10 mL), ethanol (20 mL), and pyridine (10 mL) heated under reflux for 96 h. The excess solvent evaporated, and the solid formed after cooling was collected by filtration, dried, and recrystallized from ethanol to afford **10**.

Method B

A solution of each of **9** (0.338 g, 1 mmol) in hydrazine hydrate (10 mL) in ethanol (20 mL) heated under reflux for 96 h. The excess solvent evaporated, and the solid formed after cooling was collected by filtration, dried, and recrystallized from ethanol to afford 4-(4-methoxyphenyl)-6-(2-thienyl)-1*H*-pyrazolo[3,4-*b*]pyridin-3-amine **(10)** as yellow crystals, (81%), m.p. =210°C, **IR** $\upsilon(cm^{-1})$: 3433, 3290 (NH_2), 3194 (NH); **MS**: 322 (M^+, 100%), 321 (M^+-H, 21.8%), 307 (M^+-CH_3, 7.2%), 306 (M^+-NH_2, 3.8%), 305 (306-H, 291 (M^+-OCH_3, 1.5%); anal., for $C_{17}H_{14}ON_4S$ (322) calcd./found (%): C(63.33/63.21), H(4.38/4.41), N(17.38/17.40), S(9.95/10.11).

Synthesis of 11

A solution of each of **10** (0.322 g, 1 mmol) in concentrated hydrochloric acid (5 mL) and glacial acetic acid (5 mL) was stirred in an ice bath. Add sodium nitrite solution (0.14 g, 2 mmol) dropwise with stirring for 30 min. The solid that formed was collected by filtration, washed with water, and dried to afford 4-(4-methoxyphenyl)-6-(2-thienyl)-1*H*-pyrazolo[3,4-*b*]pyridine-3-diazonium chloride **(11)** as pale yellow crystals crystallized from ethanol (81%), m.p. =>330°C, **IR** $\upsilon(cm^{-1})$: 3194 (NH), 2156,(N=N); anal., for $C_{17}H_{12}ON_5SCl$ (369) calcd./found (%): C(61.06/60.97), H(3.62/3.71), N(20.94/21.11), S(9.59/9.61).

Reaction of the Diazonium Chloride (11) with Active Methylene—General Procedure

A solution of each of **12**, **16**, **21**, **27**, and **30** (0.066 g, 0.1 g, 0.113 g, 0.192 g, 0.179 g respectively, 1 mmole of each) in ethanol (30 mL) containing 2.0g sodium acetate and **11** (0.369 g, 1 mmole) was stirred at room temperature for 1 h and poured onto ice-cold water. The formed precipitate collected by filtration, washed with water, and dried to afford **15**, **24**, **29**, and **31** respectively.

4-Amino-10-(4-methoxyphenyl)-8-(2-thienyl)-pyrido[2′,3′:3,4]pyrazolo-[5,1-c][1,2,4]triazine-3-carbonitrile (15)

Orange crystals crystallized from ethanol (81%), m.p. =>330°C, **IR** $\upsilon(cm^{-1})$: 3417.1, 3273.9 (NH_2), 2208.1 (CN); **MS**: 399 (M^+, 100%, which corresponded to the molecular formula $C_{20}H_{13}ON_7S$ of the assigned formula), 398 (M^+-H, 13.8%), 305 (M^+-$NH_2C{=}CCN$, 5.8%), 290 (305-CH_3, 10.6%); **^{1}H NMR** (δppm): 3.602 (s, 3H, OCH_3), 3.884 (s, br., 2H, NH_2), and 7.14–8.08 (m, 8H, ArH's and PyridineH's); anal., for $C_{20}H_{13}ON_7S$ (339) calcd./found(%): C(60.14/60.22), H(3.28/3.32), N(24.55/24.61), S(8.03%).

Ethyl 2-Cyano{[4-(4-methoxyphenyl)-6-(2-thienyl)-1H-pyrazolo[3,4-b]-pyridin-3-yl]hydrazono}acetate (22)

Yellow crystals crystallized from ethanol (83%), m.p. = 160°C, **IR** $\upsilon(cm^{-1})$: 3188.7(NH), 2956.5, 2853 (Aliphatic CH), 2221.9 (CN), 1694.4 (CO); anal., for $C_{22}H_{18}O_3N_6S$ (446) calcd./found (%): C(59.18/59.22), H(4.06/4.00), N(18.82/18.91), S(7.18/7.21).

Ethyl 4-Amino-10-(4-methoxyphenyl)-8-(2-thienyl)-pyrido[2′,3′:3,4]pyr-azolo[5,1-c][1,2,4]triazine-3-carboxylate (24)

Yellow crystals from ethanol (70%), m.p. = 280 C°, **IR** $\upsilon(cm^{-1})$: 3422.6, 3269.3(NH_2), 2921.5, 2849.8 (Aliphatic CH), 1696(CO); **MS**: 446 (M^+, 100% , which corresponded to the molecular weight of the molecular formula $C_{22}H_{18}O_3N_6S$ of the assigned formula), 373 (M^+-COOEt, 11.7%); **^{1}H NMR** (DMSO, δppm): 1.387 (t, 3H, $\underline{CH_3}CH_2$-, J = 7.2), 4.436 (q, 2H, $CH_3\underline{CH_2}$-, J = 7.2), 3.875 (s, 3H, OCH_3), 7.104–8.125(m, 8H, ArH, thienyl, and pyridine H's); anal., for $C_{22}H_{18}O_3N_6S$ (446) calcd./found(%): C(59.18/59.22), H(4.06/4.11), N(18.82/18.85), S(7.18/7.21).

Ethyl 10-(4-Methoxyphenyl)-4-phenyl-8-(2-thienyl)pyrido-[2′,3′:3,4]-pyrazolo[5,1-c][1,2,4]triazine-3-carboxylate (29)

Yellow crystals crystallized from ethanol (83%), m.p. = 300°C, **IR** $\upsilon(cm^{-1})$: 3067.1 (Aromatic C-H), 2956.2, 2929.1 (Aliphatic C-H), 1727 (CO); **MS**: 507 (M^+, 44.7% , which corresponded to the molecular weight of the molecular formula of the assigned formula), 434 (M^+- COOEt, 100%), 101 (COOEt, N_2, 18.4%); **^{1}H NMR** (DMSO, δppm): 1.027 (t, 3H, $\underline{CH_3}CH_2$-, J = 7.0), 3.858 (s, 3H, OCH_3), 4.201 (q, 2H, $CH_3\underline{CH_2}$-, J = 7.1), 7.096–8.080 (m, 13H, ArH's, thienyl and pyridine H's); anal., for $C_{28}H_{21}O_3N_5S$ (507) calcd./found(%): C(66.26/66.32), H(4.17/4.22), N(13.80/13.91), S(6.32/6.33).

{*4-Amino-10-(4-methoxyphenyl)-8-(2-thienyl)pyrido[2′,3′:3,4]-pyrazolo[5,1-c][1,2,4]triazin-3-yl*}*(4-chlorophenyl)methanone (31)*

Yellow crystals crystallized from ethanol (81%), m.p. = 300°C, **IR** $\upsilon(cm^{-1})$: 3381.8, 3240.6 (NH_2), 2923.4, 2837.4 (Aliphatic C—H), 1635.6 (CO); **MS**: 512 (M^+, 24.9%, which corresponded to the molecular weight of the molecular formula $C_{26}H_{17}ClN_6O_2S$ of the assigned formula), 511 (M^+-H, 11.5%), 496 (M^+-NH_2, 23.3%), 494 (M+-H_2O, 24.7%), 139 (COC_6H_4-p-Cl, 67.0%); anal., for $C_{26}H_{17}ClN_6O_2S$ (512) calcd./found (%): C(60.88/60.91), H(3.34/3.40), Cl(6.91/7.00), N(16.38/16.41), S(6.25/6.3).

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