Fluorine-containing heterocycles: Part II synthesis and reactions of new thieno[2,3-*b*]pyridine derivatives bearing trifluoromethyl group

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Ethyl [3-cyano-6-(2-thienyl)-4-trifluoromethylpyridin-2-ylthio]acetate (**2**) and ethyl 3-amino-6-(2-thienyl)-4-trifluoromethylthieno[2,3-*b*]pyridine-2-carboxylate (**3**) were prepared by reaction of 3-cyano-6-(2-thienyl)-4-trifluoromethylpyridine-2(1*H*)-thione (**1**) with ethyl chloroacetate. The reaction of both **2** and **3** with hydrazine hydrate under different conditions was studied. The main products were [3-cyano-6-(2-thienyl)-4-trifluoromethyl-2-pyridinylthio]acetohydrazide (**4**) and 3-amino-6-(2-thienyl)-4-trifluoromethylthieno[2,3-*b*]pyridine-2-carbohydrazide (**5**). The condensation of acethydrazide **4** with some aromatic or heterocyclic aldehydes yielded the corresponding hydrazones **6a–d** which underwent intramolecular Thorpe–Ziegler cyclisation to give the N^1-aryl or heteroarylmethylene-3-amino-6-(2-thienyl)-4-trifluoromethylthieno[2,3-*b*]pyridine-2-carbohydrazides (**7a–d**). Treatment of **7a–d** with triethyl orthoformate led to the formation of pyridothienopyrimidine derivatives **8a–d**. Heating carbohydrazide **5** with acetic acid gave an unexpected product which was assigned as 3-amino-2-methyl-7-(2-thienyl)-9-trifluoromethylpyrido[3',2':4,5] thieno[3,2-*d*]pyrimidine-4(*3H*)-one (**12**). Moreover, the reaction of **5** with other reagents such as acetic anhydride, formic acid, acetylacetone and/or triethyl orthoformate were carried out and their products were identified. Diazotisation of **5** produced the corresponding acyl azide **18** which underwent Curtius rearrangement to furnish the imidazolone derivative **20**. Hydrolysis of the ester **3** gave the aminoacid **21** which in turn was converted into the oxazinone derivatives **22** and **23**. Recyclisation of **22** and **23** into some pyrimidinone derivatives (**12** and **24–26**) was carried out.

Keywords: cyanotrifluoromethylpyridinethiones, trifluoromethylthienopyridines, trifluoromethylpyridothienopyrimidines, trifluoromethylpyridothieno-oxazine, trifluoromethylimidazolothienopyridine

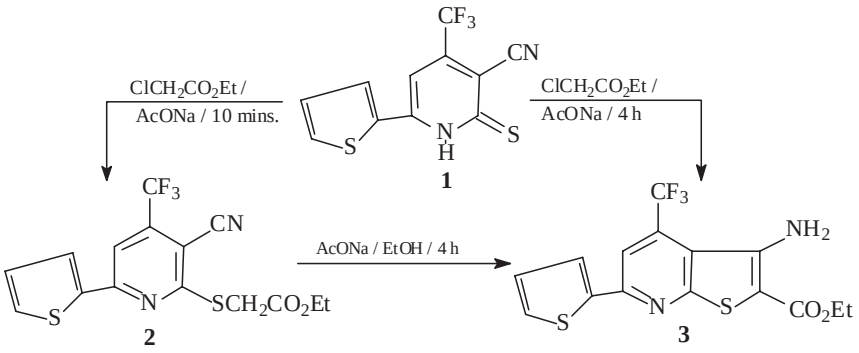
Fluorine-containing compounds, in general, and fluorinated heterocycles, in particular, continue to play an increasing role as pharmaceuticals.[1,2] Utilisation of fluorination as a tool to enhance biological activity and to improve the versatility of a substance has stimulated pharmaceutical researchers to introduce fluorine as a substituent to modify original bioactivity on the basis of rational elucidation of molecular recognition process.[3-6] Recently, it has been demonstrated that selective substitution of fluorine for hydrogen or hydroxyl group in a biologically active compound and introduction of trifluoromethyl, difluoromethyl, fluoromethyl or fluorovinyl substituent are highly effective for discovery of drugs and dianostic agents.[7-9] On the other hand, numerous thieno[2,3-*b*] pyridines have been investigated in relation with their biological and pharmacological activities. Some of them proved to possess antibaterial,[10,11] antiviral,[12] antihypertensive,[13] and immunostimulating[14] activities. Others are useful as gonadtropin-releasing hormone antagonists[15-20] and as lipoxygenases inhibitors.[21] Recently, certain thieno[2,3-*b*] pyridine derivatives were prepared as antinflammatory agents, particularly for treating arthritis and bone resorption inhibiting agents.[22]

In view of these findings and as a part of our strongly developed interest in organo fluoroheterocycles,[6,23] we report here synthesis and reactions of some new thieno[2,3-*b*] pyridines bearing trifluoromethyl group in anticipation of better pharmacological activities.

Results and discussion

Our approach to the synthesis of the target compounds started from 3-cyano-6-(2-thienyl)-4-trifluoromethylpyridine-2(1*H*)-thione (**1**) which upon refluxing with ethyl chloroacetate, in ethanol containing slightly excess amounts of sodium acetate for 4 h, gave ethyl 3-amino-6-(2-thienyl)-4-trifluoromethylthieno[2,3-*b*]pyridine-2-carboxylate (**3**). When the reaction time was reduced to 10 min, the product was identified as pyridine derivative **2** which underwent intramolecular Thorpe–Ziegler cyclisation to give the thienopyridine **3** upon refluxing in ethanol containing sodium acetate for 4 h (Scheme 1).

Heating the ester **2** with hydrazine hydrate in refluxing ethanol for 10 min produced a mixture of the corresponding acethydrazide **4** and ethyl 3-amino-6-(2-thienyl)-4-trifluoromethylthieno[2,3-*b*]pyridine-2-carboxylate (**3**). When the reaction time was increased to 3 h, the product was identified



Scheme 1

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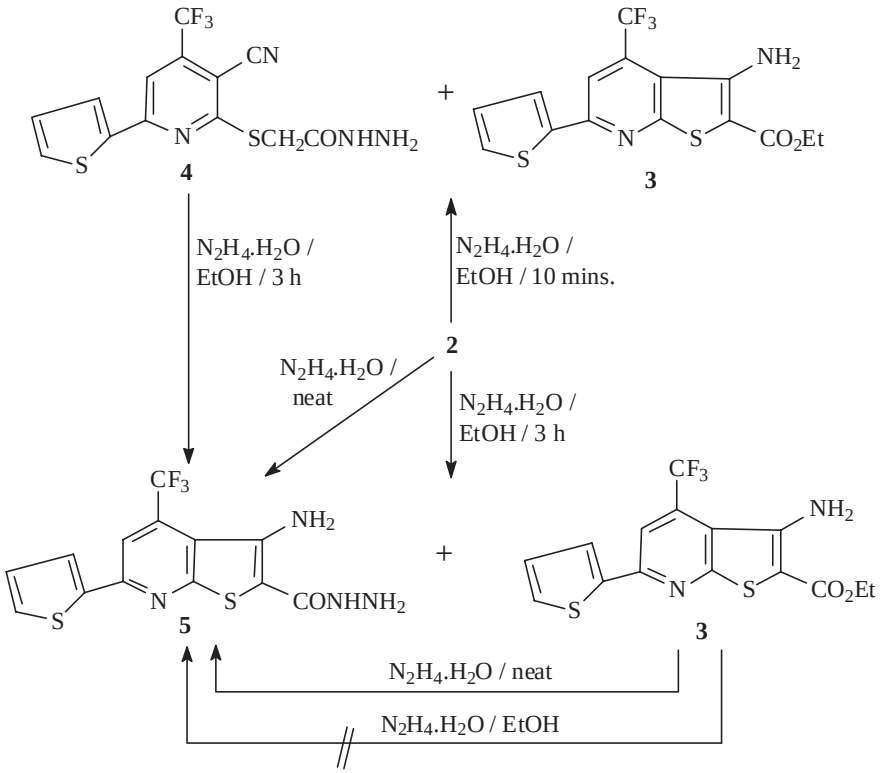


Scheme 2

as a mixture of 3-amino-6-(2-thienyl)-4-trifluoromethylthieno[2,3-*b*]pyridine-2-carbohydrazide (**5**) and the related ester **3**. Moreover, repeating the above reaction under neat conditions produced the carbohydrazide derivative **5** as a sole product. Compound **5** was also obtained by the reaction of *o*-aminoester **3** with hydrazine hydrate under neat conditions or by refluxing the acethydrazide **4** with hydrazine hydrate in ethanol for 3 h. Note that *o*-aminoester **3** did not react with hydrazine hydrate in boiling ethanol. This may be the result of relatively low electronegativity of sulfur atom and / or highly delocalisation of the two electron pairs of the sulfur atom of the thieno moiety (Scheme 2).

The condensation of acetohydrazide **4** with some aromatic aldehydes or thiophene-2-carboxaldehyde yielded the corresponding hydrazones **6a–d** which underwent intramolecular Thorpe–Ziegler cyclisation upon heating in ethanol containing sodium acetate to furnish N^1-aryl- or N^1-(2-thienyl) methylene-3-amino-6-(2-thienyl)-4-trifluoromethylthieno[2,3-*b*]pyridine-2-carbohydrazides (**7a–d**). The compounds **7a–d** were also synthesised through direct condensation of **5** with an equimolar amount of the respective aldehydes in boiling ethanol. Treatment of **7a–d** with triethyl orthoformate in refluxing acetic anhydride led to the formation of 3-aryl- or 3-(2-thienyl)methyleneamino-7-(2-thienyl)-9-trifluoromethyl pyrido[3',2':4,5]thieno[3,2-*d*] pyrimidine-4(3*H*)-ones (**8a–d**). The latter compounds were also prepared by direct condensation of aminopyrimidinone derivative **24** with the respective aldehydes (Scheme 3).

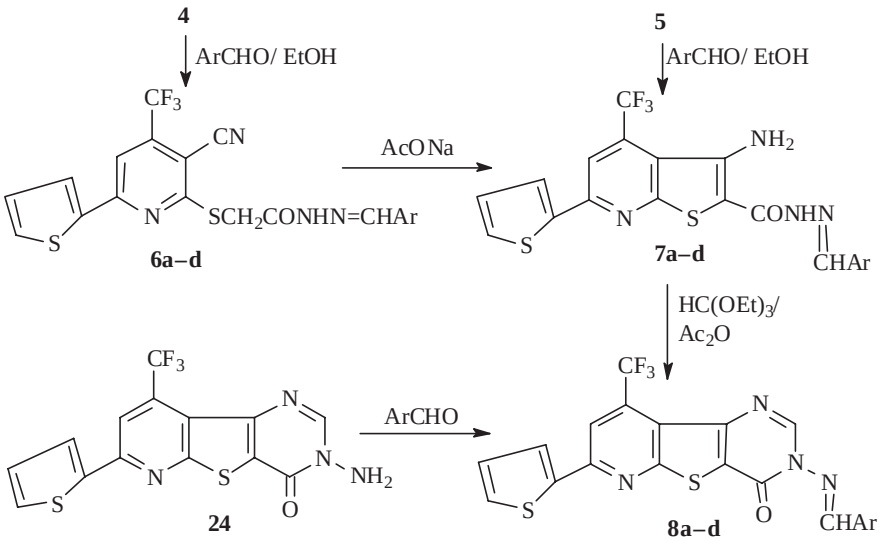
On heating of carbohydrazide **5** with acetic acid at reflux temperature for 4 h, the product was identified as pyrimidinone derivative **12** rather than the expected triazipine **9**, pyrazolothienopyridine **10**[24] or oxadiazolylthienopyridine **11** (Scheme 4). Two pathways were proposed for the formation of the final compound. Path a involves the acetylation of the amino group attached to thienopyridine moiety followed by cyclisation *via* elimination of a molecule of water. In Path b the acetylation occurs at the most active amino group of carbohydrazide and then the intermediate losses a molecule of water to give the non isolated triazepine derivative **9**. The intermediate **9** underwent recyclisation (or Dimroth rearrangement-type) to give the final product **12**. In our opinion, path b is more favourable since the carbohydrazide group is more basic than the amino group attached to thienopyridine moiety in compound **5**. The structure of compound **12** was also confirmed by an independent method of preparation *via* treatment of oxazinone derivative **23** with hydrazine hydrate in refluxing ethanol.

The mechanism of recyclisation of compound **9** into **12** was given in Scheme 5.[25] The rearrangement is promoted here by aqueous acid (acetic acid 96 %). It involves initially covalent hydration of **9**. The hydroxy group enters position 2, then the triazepine ring opens and forms the intermediate **A** which loses a molecule of water to give 3-aminopyrimidinone derivative **12**.

The reactivity of the amino group of compound **12** was tested *via* reaction with acetic anhydride and / or benzaldehyde wherein the biacetylated compound **13** or azomethine derivative **14** was obtained respectively. The structure of compounds **13** and **14** was also confirmed *via* an independent method of preparation by refluxing the carbohydrazide **5** or hydrazone **7a** with acetic anhydride (Scheme 6).

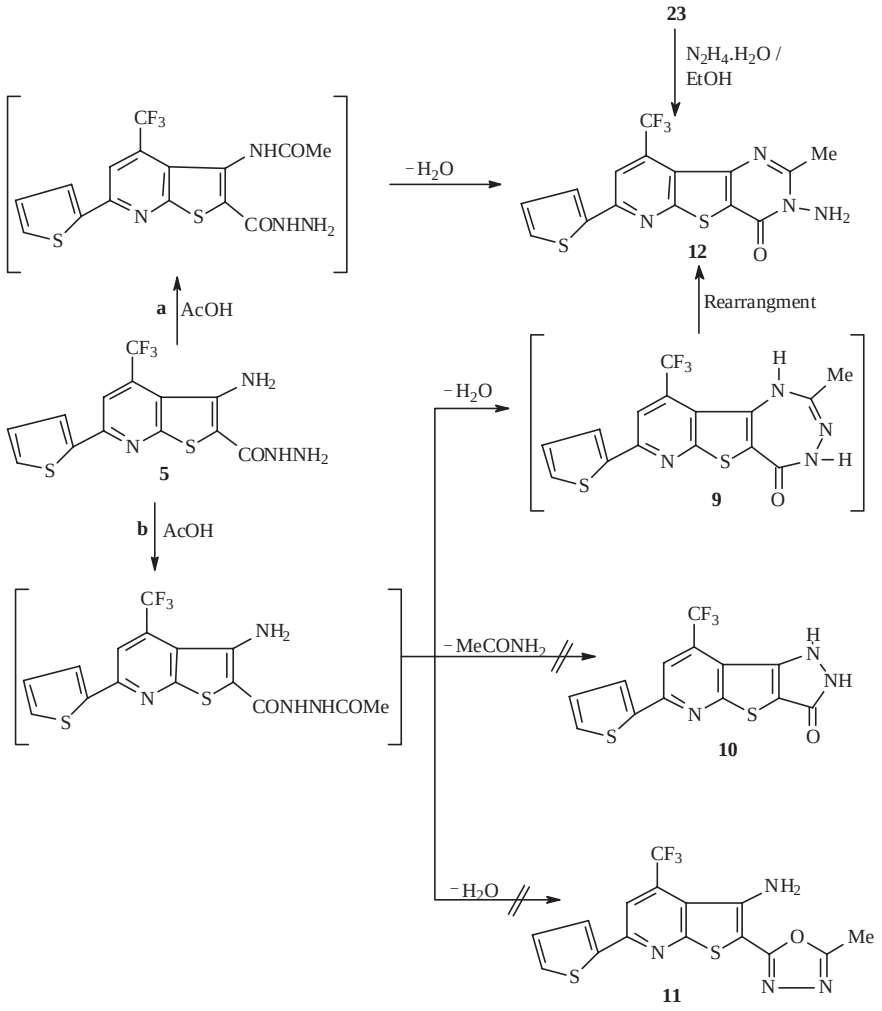
The interaction of carbohydrazide derivative **5** with formic acid led to the formation of *N*-formylaminopyrimidinone derivative **15**. When compound **5** was allowed to react with acetylacetone, the dimethylpyrazolyl derivative **16** was obtained. The cyclocondensation of **5** with triethyl orthoformate by heating in DMF produced 3-ethoxymethyleneaminopyrimidin-4(3*H*)-one derivative **17**. Diazotisation of **5** in acetic acid with sodium nitrite solution at room temperature resulted in the formation of the acid azide **18** (Scheme 7).

On heating of **18** in dry toluene at reflux temperature, it underwent Curtius rearrangement forming the isocyanate intermediate **19** followed by intramolecular cycloaddition reaction to afford the imidazolone derivative **20** (Scheme 8).

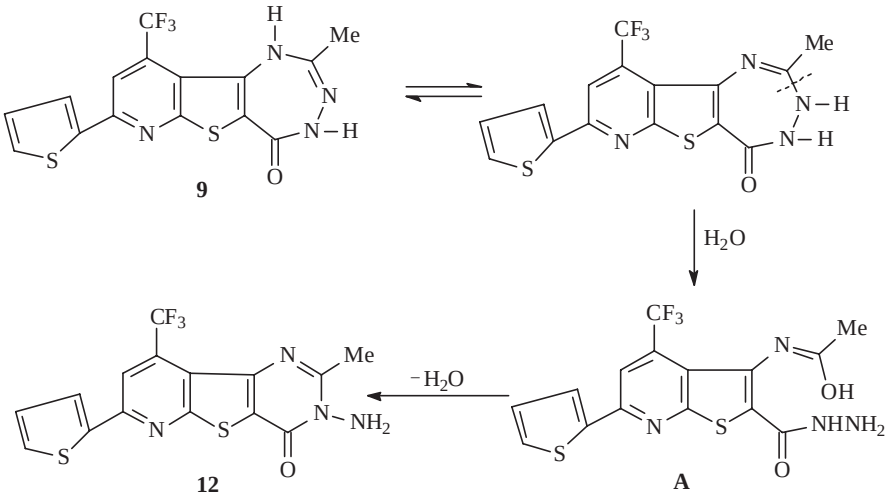


6–8	Ar
a	C_6H_5
b	C_6H_4-OCH_3(p)
c	C_6H_4-Cl(p)
d	2-Thienyl

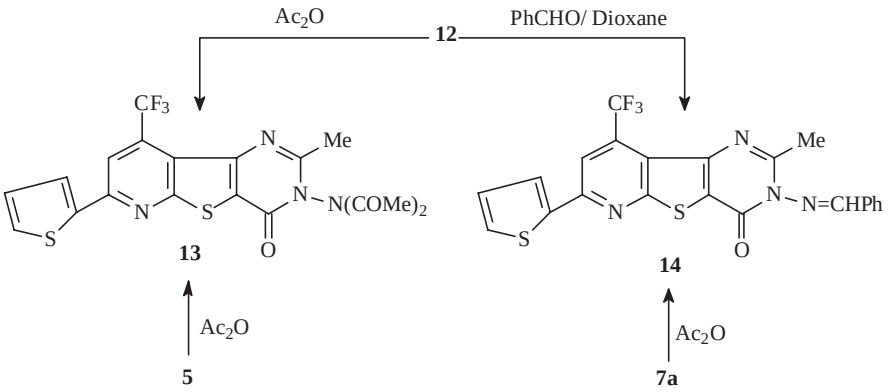
Scheme 3



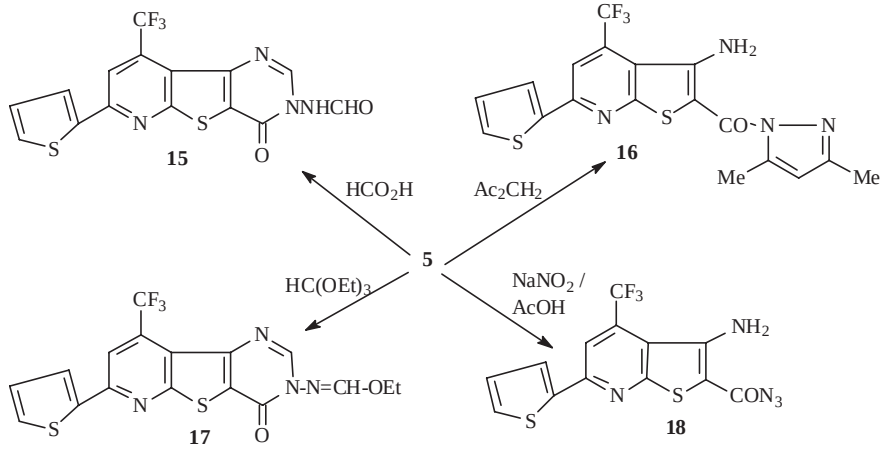
Scheme 4



Scheme 5



Scheme 6

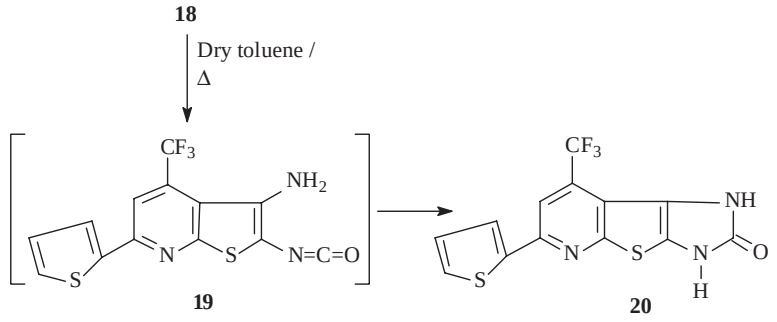


Scheme 7

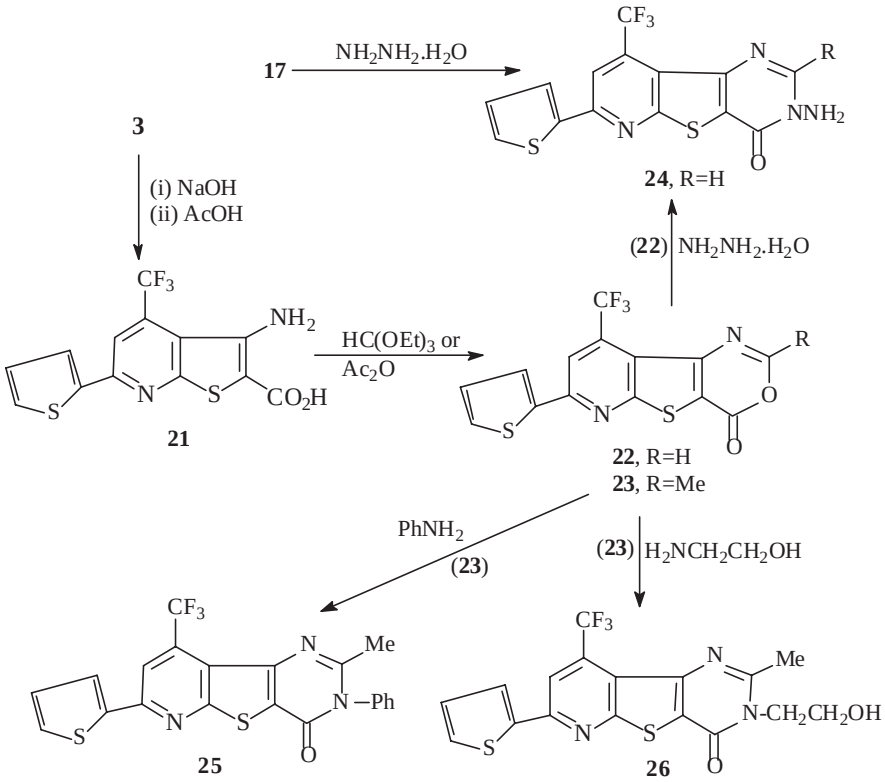
Saponification of the ester **3** with an ethanolic sodium hydroxide solution followed by acidification with acetic acid gave 3-amino-6-(2-thienyl)-4-trifluoromethyl-thieno[2,3-*b*] pyridine-2-carboxylic acid (**21**). Upon heating of the latter compound with triethyl orthoformate, the oxazinone derivative **22** was obtained. Refluxing of **21** with acetic anhydride led to the formation of 2-methyl-7-(2-thienyl)-9-trifluoro-methylpyrido[3',2':4,5]thieno[3,2-*d*]oxazin-4-one (**23**). The oxazinone derivatives **22** and **23** were recyclised into some pyrimidinone derivatives upon treatment with certain reagents. Thus, refluxing of **22** with hydrazine hydrate in ethanol gave 3-amino-7-(2-thienyl)-9-trifluoromethylpyrido[3',2':4,5]thien o[3,2-*d*]pyrimidine-4(*3H*)-one (**24**) which was also obtained upon treatment of **17** with hydrazine hydrate under neat conditions. Similarly, the reaction of **23** with aniline or with hydroxylamine gave the pyrimidinone derivatives **25** and **26** respectively (Scheme 9).

Experimental

All melting points are uncorrected and measured on a Gallen-Kamp apparatus. IR spectra were recorded on a Shimadzu 470 IR-spectrophotometer (KBr; ν max in cm^{-1}); ^1H NMR spectra on a



Scheme 8



Scheme 9

Varian EM-390, 90 MHz spectrometer with TMS as internal standard (δ in ppm); MS on a Jeol JMS-600 mass spectrometer and elemental analyses on an Elementar Analysen system GmbH VARIOEL V2.3 July 1998 CHNS Mode. The purity of all synthesised compounds was checked by TLC.

3-Cyano-6-(2-thienyl)-4-trifluoromethylpyridine-2(1H)-thione **(1)**: This compound was prepared according to the reported method.[6]

Ethyl [3-cyano-6-(2-thienyl)-4-trifluoromethylpyridin-2-ylthio] acetate **(2)**: A mixture of **1** (5.72 g, 20 mmol), ethyl chloroacetate (2.2 ml, 20 mmol) and sodium acetate trihydrate (3.0 g, 22 mmol) in ethanol (60 ml) was heated under reflux for 10 min. The precipitate that formed on cooling was collected and recrystallised from ethanol as fine white needles of **2**. Yield: 6.0 g (80 %); m. p. 156–157 °C. IR: ν = 2210 (C≡N), 1730 (C=O) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 7.9 (s, 1H, CH pyridine), 7.7(d, 1H, CH thienyl), 7.4 (d, 1H, CH thienyl), 7.2 (t, 1H, CH thienyl), 4.2 (s, 2H, SCH_2), 3.8–4.1 (q, 2H, OCH_2), 1.0–1.3 (t, 3H, CH_3 of ester) ppm. Anal. Calcd. For $C_{15}H_{11}F_3N_2O_2S_2$ (372.39): C, 48.38; H, 2.98; N, 7.52; S, 17.22 %. Found: C, 48.27; H, 2.99; N, 7.40; S, 17.70 %.

Ethyl 3-amino-6-(2-thienyl)-4-trifluoromethylthieno[2,3-b]pyridine-2-carboxylate **(3),** *Method A*: A mixture of **1** (5.72 g, 20 mmol), ethyl chloroacetate (2.2 ml, 20 mmol) and sodium acetate trihydrate (3.0 g, 22 mmol) in ethanol (60 ml) was heated under reflux for 4 h. The precipitate that formed on cooling was collected and recrystallised from ethanol to give canary yellow needles of **3**. Yield: 6.3 g (83 %); m. p. 187–188 °C. IR: ν = 3500, 3300 (NH_2), 1660 (C=O) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 7.85 (s, 1H, CH pyridine), 7.8 (d, 1H, CH thienyl), 7.5 (d, 1H, CH thienyl), 7.2 (t, 1H, CH thienyl), 6.2 (s, 2H, NH_2), 4.2 (q, 2H, OCH_2), 1.2 (t, 3H, CH_3 of ester) ppm. MS: *m/z* = 372 (M^+, 100%), 343 (M^+–C_2H_5, 68 %), 327 (M^+–OC_2H_5, 24 %), 326 (M^+–OC_2H_5–H, 56 %), 325 (M^+–OC_2H_5–2H, 98 %), 299 (M^+–$CO_2C_2H_5$, 62 %). Anal. Calcd. For $C_{15}H_{11}F_3N_2O_2S_2$ (372.39): C, 48.38; H, 2.98; N, 7.52; S, 17.22 %. Found: C, 48.15; H, 2.74; N, 7.32; S, 17.50 %.

Method B: Compound **2** (3.72 g, 10 mmol) was suspended in ethanol (40 ml) containing sodium acetate trihydrate (1.5 g, 11 mmol) and then heated under reflux for 4 h. The solid that formed after cooling was collected and recrystallised from ethanol to give **3 (**Yield: 3.65 g; 98 %) which was identical to that described in method A in all aspects.

Reaction of ethyl [3-cyano-6-(2-thienyl)-4-trifluoromethylpyridin-2-ylthio]acetate **(2)** *with hydrazine hydrate, Method A*: A mixture of ester **2** (3.72, 10 mmol) and hydrazine hydrate 99 % (0.5 ml, 10 mmol) in ethanol (40 ml) was heated under reflux for 10 min. The precipitate thus formed while hot was filtered off and recrystallised from dioxane as white needles. This product was assigned as [3-cyano-6-(2-thienyl)-4-trifluoromethyl-2-pyridinylthio]acetohydrazide (**4**). Yield: 1.7 g (47 %); m.p. 240–241°C. IR: ν = 3420–3300, 3200–3100 ($NHNH_2$), 2200 (C≡N), 1650 (C=O) cm^{-1}. ^1H NMR (DMSO-d_6): δ = 9.4 (s, 1H, NH), 7.9 (s, 1H, CH pyridine), 7.7(d, 1H, CH thienyl), 7.5 (d, 1H, CH thienyl), 7.2 (t, 1H, CH thienyl), 4.3 (s, 2H, NH_2), 4.0 (s, 2H, SCH_2) ppm. Anal. Calcd. For $C_{13}H_9F_3N_4OS_2$

(358.36): C, 43.57; H, 2.53; N, 15.63; S, 17.89 %. Found: C, 43.81; H, 2.64; N, 15.44; S, 18.10 %.

The mother liquor of the above crude product was allowed to cool whereby a yellow fine needles precipitated. It was collected and recrystallised from ethanol. This compound was identified as ethyl 3-amino-6-(2-thienyl)-4-trifluoromethylthieno[2,3-b]pyridine-2-carboxylate (**3**). Yield: 1.45 g (39 %); m.p. 187–188 °C; m.p. 187–188 °C.

Method B: A mixture of ester **2** (3.72 g, 10 mmol) and hydrazine hydrate 99 % (0.5 ml, 10 mmol) in ethanol (40 ml) was heated under reflux for 3 h. The precipitate thus formed while hot was collected and recrystallised from dioxane as orange needles. This product was assigned as 3-amino-6-(2-thienyl)-4-trifluoromethyl-thieno[2,3-*b*]pyridine-2-carbohy-drazide (**5**). Yield: 1.58 g (44 %); m.p. 258–260 °C. IR: ν = 3500, 3300, 3200 (NH_2, $NHNH_2$),1620 (C=O) cm^{-1}. ^1H NMR (DMSO-d_6): δ = 9.2 (br, 1H, NH), 7.9 (s, 1H, CH pyridine), 7.8 (d, 1H, CH thienyl), 7.4 (d, 1H, CH thienyl), 7.2 (t, 1H, CH thienyl), 6.0 (s, 2H, NH_2 at C-3), 4.6 (br, 2H, NH_2 of hydrazide) ppm. MS: *m/z* = 358 (M^+, 61%), 327 (M^+–$NHNH_2$, 100 %), 299(M^+–$CONHNH_2$, 17 %). Anal. Calcd. For $C_{13}H_9F_3N_4OS_2$ (358.36): C, 43.57; H, 2.53; N, 15.63; S, 17.89 %. Found: C, 43.71; H, 2.89; N, 15.28; S, 18.00 %.

The mother liquor of the above crude product was allowed to cool whereby a yellow fine needles precipitated. It was collected and recrystallised from ethanol. This compound was identified as ethyl 3-amino-6-(2-thienyl)-4-trifluoromethylthieno[2,3-*b*]pyridine-2-carboxylate (**3**). Yield: 1.38 g (37 %); m.p. 187–188 °C; m.p. 187–188 °C.

Method C: Compound **2** (3.72 g, 10 mmol) and hydrazine hydrate 99 % (4.0 ml, 80 mmol) was heated under reflux for 2 h. The reaction mixture was cooled to room temperature and then triturated with ethanol (10 ml). The precipitated product was collected and recrystallised from dioxane as orange needles of 3-amino-6-(2-thienyl)-4-trifluoromethylthieno[2,3-*b*]pyridine-2-carbohydrazide (**5**). Yield: 3.0 g (83 %); m.p. 258–266 °C; m.p. 258–260 °C.

Reaction of ethyl 3-amino-6-(2-thienyl)-4-trifluoromethyl-thieno[2,3-b]pyridine-2-carboxylate **(3)** *with hydrazine hydrate, Method A*: Compound **3** (3.72 g, 10 mmol) and hydrazine hydrate 99 % (2.5 ml, 50 mmol) was heated under reflux for 2 h. The reaction mixture was cooled to room temperature and then triturated with ethanol (10 ml). The precipitated product was collected and recrystallised from dioxane as orange needles of 3-amino-6-(2-thienyl)-4-trifluoromethylthieno[2,3-*b*]pyridine-2-carbohydrazide (**5**). Yield: 3.1 g (86 %); m.p. 258–266 °C; m.p. 258–260 °C.

Method B: A mixture of ester **3** (3.72 g, 10 mmol) and hydrazine hydrate 99% (2.5 ml, 50 mmol) in ethanol (40 ml) was heated under reflux for 4 h. The precipitate thus formed on cooling was collected and recrystallised from ethanol to give the unchanged starting compound **3** in a very pure state.

Cyclisation of acetohydrazide **4** *into carbohyrazide* **5**: A mixture of acetohydrazide **4** (3.58g, 10 mmol) and hydrazine hydrate 99% (1.0 ml, 20 mmol) in ethanol (50 ml) was heated under reflux for 3 h. The precipitate thus formed on cooling was collected and recrystallised from dioxane to give the carbohydrazide **5** in the form of orange needles. Yield: 3.36 g (94 %); m.p. 258–266 °C; m.p. 258–260 °C.

Condensation of acetohydrazide **4** *with aromatic aldehydes or thiophene-2-carboxaldehyde; formation of hydrazone derivatives* **6a–d**; *general procedure*: A mixture of acethydrazide **4** (3.58 g, 10 mmol) and the respective aldehyde (10 mmol) in ethanol (40 ml) was heated under reflux for 2 h. The precipitate that formed while hot was collected and recrystallised from an ethanol-chloroform mixture to give white crystals of **6a–d**.

N^1-Benzylidene-[3-cyano-6-(2-thienyl)-4-trifluoromethylpyridin-2-ylthio]acetohydrazide (**6a**): It was obtained from **4** and benzaldehyde. Yield: 3.8 g (89 %); m.p. 254–256 °C. IR: ν = 3390–3300 (NH), 2210 (C≡N), 1670 (C=O) cm^{-1}. Anal. Calcd. For $C_{20}H_{13}F_3N_4OS_2$ (446.47): C, 53.80; H, 2.93; N, 12.55; S, 14.36 %. Found: C, 53.92; H, 2.84; N, 12.79; S, 14.58 %.

N^1-(4-Methoxybenzylidene)-[3-cyano-6-(2-thienyl)-4-trifluoro-methylpyridin-2-ylthio]acethydrazide (**6b**): It was obtained from **4** and 4-methoxybenzaldehyde. Yield: 4.1 g (86 %); m.p. 228–229 °C. IR: ν = 3390–3300 (NH), 2210 (C≡N), 1670 (C=O) cm^{-1}. ^1H NMR (DMSO-d_6): δ = 9.2 (s, 1H, NH), 8.4 (s, 1H, N=CH), 7.8 (s, 1H, CH pyridine), 7.6–7.0 (m, 7H: ArH's and 3 CH thienyl), 4.8 (s, 2H, SCH_2), 3.8 (s, 3H, OCH_3) ppm. Anal. Calcd. For $C_{21}H_{15}F_3N_4O_2S_2$ (476.50): C, 52.93; H, 3.17; N, 11.76; S, 13.46 %. Found: C, 53.17; H, 2.99; N, 12.56; S, 13.25 %.

N^1-(4-Chlorobenzylidene)-[3-cyano-6-(2-thienyl)-4-trifluoro-methylpyridin-2-ylthio]acethydrazide (**6c**): It was obtained from **4** and 4-chlorobenzaldehyde. Yield: 4.33 g (90 %); m.p. 260–262 °C. IR: ν = 3390-3300 (NH), 2210 (C≡N), 1670 (C=O) cm^{-1}. Anal. Calcd. For $C_{20}H_{12}F_3ClN_4OS_2$ (480.92): C, 49.95; H, 2.51; N, 11.65; S, 13.33 %. Found: C, 50.12; H, 2.55; N, 12.87; S, 13.00 %.

N^1-(2-Thienylmethylene)-[3-cyano-6-(2-thienyl)-4-trifluoro-methylpyridin-2-ylthio]acetohydrazide (**6d**): It was obtained from **4** and thiophene-2-carboxaldehyde. Yield: 4.0 g (88 %); m.p. 251–252 °C. IR: ν = 3390–3300 (NH), 2210 (C≡N), 1670 (C=O) cm^{-1}. Anal. Calcd. For $C_{18}H_{11}F_3N_4OS_3$ (452.50): C, 47.78; H, 2.45; N, 12.38; S, 21.26 %. Found: C, 47.82; H, 2.71; N, 12.36; S, 21.00 %.

Condensation of carbohydrazide **5** *with aromatic aldehydes; formation of hydrazone derivatives* **7a–d**; *general procedures, Method A*: Compound **6a–d** (5 mmol) was suspended in ethanol (40 ml) containing sodium acetate trihydrate (1.5 g, 11 mmol) and then heated under reflux for 4 h. The precipitate thus formed while hot was collected and recrystallised from dioxane to give orange crystals of **7a–d**.

3-Amino-N^1-benzylidene-6-(2-thienyl)-4-trifluoromethylthieno [2,3-b]pyridine-2-carbohydrazide (**7a**): It was obtained from **6a**. Yield: 2.05 g (92 %); m.p. 338–339 °C. IR: ν = 3500, 3270 (NH_2), 3130 (NH), 1630 (C=O) cm^{-1}. Anal. Calcd. For $C_{20}H_{13}F_3N_4OS_2$ (446.47): C, 53.80; H, 2.93; N, 12.55; S, 14.36 %. Found: C, 53.73; H, 2.82; N, 12.73; S, 14.00 %.

3-Amino-N^1-(4-methoxybenzylidene)-6-(2-thienyl)-4-trifluoro-methylthieno[2,3-b]pyridine-2-carbohydrazide (**7b**): It was obtained from **6b**. Yield: 2.1 g (88 %); m.p. 310–312 °C. IR: ν = 3500, 3270 (NH_2), 3130 (NH), 1630 (C=O) cm^{-1}. Anal. Calcd. For $C_{21}H_{15}F_3N_4O_2S_2$ (476.50): C, 52.93; H, 3.17; N, 11.76; S, 13.46 %. Found: C, 52.77; H, 3.43; N, 11.66; S, 13.86 %.

3-Amino-N^1-(4-chlorobenzylidene)-6-(2-thienyl)-4-trifluoromethyl-thieno[2,3-b]pyridine-2-carbohydrazide (**7c**): It was obtained from **6c**. Yield: 2.09 g (87 %); m.p. 330–332 °C. IR: ν = 3500, 3270 (NH_2), 3130 (NH), 1630 (C=O) cm^{-1}. Anal. Calcd. For $C_{20}H_{12}F_3ClN_4OS_2$ (480.92): C, 49.95; H, 2.51; N, 11.65; S, 13.33 %. Found: C, 49.80.12; H, 2.16; N, 11.73; S, 13.50 %.

3-Amino-6-(2-thienyl)-N^1-(2-thienylmethylene)-4-trifluoromethyl-thieno[2,3-b]pyridine-2-carbohydrazide (**7d**): It was obtained from **6d**. Yield: 1.9 g (84 %); m.p. 300–302 °C. IR: ν = 3500, 3270 (NH_2), 3130 (NH), 1630 (C=O) cm^{-1}. MS: *m/z* = 452 (M^+, 30 %), 451(M^+-1, 70 %). 326 (M^+-(NHN=CHC_4H_3S), 100 %), 298 (M^+-(CONHN=CHC_4H_3S), 26 %). Anal. Calcd. For $C_{18}H_{11}F_3N_4OS_3$ (452.50): C, 47.78; H, 2.45; N, 12.38; S, 21.26 %. Found: C, 48.02; H, 2.51; N, 12.45; S, 21.44 %.

Method B: A mixture of **5** (1.79 g, 5 mmol) and the respective aldehyde (5 mmol) in ethanol (30 ml) was refluxed for 3 h. The solid thus formed was collected and recrystallised from dioxane to give **7a–d** (yield: 85–92 %) which were identical to those described above in all aspects.

3-aryl- or 3-(2-thienyl)methyleneamino-7-(2-thienyl)-9-trifluoro methylpyrido[3',2':4,5]thieno[3,2-d]pyrimidine-4(3H)-ones (**8a–d**), *Method A*: A mixture of **7a–d** (2 mmol) and triethyl orthoformate (5 ml) in acetic anhydride (10 ml) was heated under reflux for 5 h. and then allowed to cool. The solid product was collected and recrystallised from an ethanol–chloroform mixture as pale yellow crystals of **8a–d**.

3-Benzylideneamino-7-(2-thienyl)-9-trifluoromethylpyrido[3',2': 4,5]thieno[3,2-d]pyrimidine-4(3H)-one (**8a**): Obtained from **7a**. Yield: 0.83 g (91 %); m.p. 294–296 °C. IR: ν = 1670 (C=O) cm^{-1}. ^1H NMR (TFA) δ = 9.0 (s, 1H, CH pyrimidine), 8.8 (s, 1H, CH=N), 7.4–8.4 (m, 9H: ArH's, 3CH thienyl and CH pyridine) ppm. Anal. Calcd. For $C_{21}H_{11}F_3N_4OS_2$ (456.47): C, 55.26; H, 2.43; N, 12.27; S, 14.05 %. Found: C, 55.42; H, 2.32; N, 12.17; S, 13.90 %.

3-(4-Methoxybenzylideneamino)-7-(2-thienyl)-9-trifluoromethyl pyrido[3',2':4,5]thieno[3,2-d]pyrimidine-4(3H)-one (**8b**): Obtained from **7b**. Yield: 0.9 g (92 %); m.p. 275–276°C. IR: ν = 1670 (C=O) cm^{-1}. Anal. Calcd. For $C_{22}H_{13}F_3N_4O_2S_2$ (486.49): C, 54.32; H, 2.69; N, 11.52; S, 13.18 %. Found: C, 54.44; H, 2.67; N, 11.58; S, 13.34 %.

3-(4-Chlorobenzylideneamino)-7-(2-thienyl)-9-trifluoromethyl-pyrido[3',2':4,5]thieno[3,2-d]pyrimidine-4(3H)-one (**8c**): Obtained from **7c**. Yield: 0.93 g (95 %); m.p. 300–302 °C. IR: ν = 1670 (C=O) cm^{-1}. Anal. Calcd. For $C_{21}H_{10}F_3ClN_4OS_2$ (490.91): C, 51.38; H, 2.05; N, 11.41; S, 13.06 %. Found: C, 51.43; H, 2.30; N, 11.38; S, 13.10 %.

7-(2-thienyl)-3-(2-thienylmethyleneamino)-9-trifluoromethyl-pyrido[3',2':4,5]thieno[3,2-d]pyrimidine-4(3H)-one (**8d**): Obtained from **7d**. Yield: 0.82 g (89 %); m.p. 265–266 °C. IR: ν = 1670 (C=O) cm^{-1}. MS: *m/z* = 462 (M^+, 17 %), 352 (M^+–(N=CHC_4H_3S), 100 %). Anal. Calcd. For $C_{19}H_9F_3N_4OS_3$ (462.49): C, 49.34; H, 1.96; N, 12.11; S, 20.80 %. Found: C, 49.43; H, 1.88; N, 12.31; S, 20.90 %.

Method B: A mixture of **24** (0.74 g, 2 mmol) and the respective aldehyde (2 mmol) in ethanol (25 ml) was refluxed for 3 h. The solid thus formed was collected and recrystallised from an ethanol–chloroform mixture to give **8a–d** (yield: 82–91 %) which were identical to those described above in all aspects.

Reaction of carbohydrazide derivative **5** *with acetic acid; formation of 3-amino-2-methyl-7-(2-thienyl)-9-trifluoromethylpyrido [3',2':4,5]thieno[3,2-d]pyrimidine-4(3H)-one* (**12**): Compound **5** (2.15 g, 6 mmol) in glacial acetic acid (35 ml) was heated under reflux for 4 h. The solid product that formed on cooling was collected and recrystallised from ethanol in the form of pale yellow crystals. This product was identified as 3-amino-2-methyl-7-(2-thienyl)-9-trifluoromethylpyrido[3',2':4,5]thieno[3,2-d]pyrimid-ine-4(3H)-one (**12**). Yield: 1.65 g (72 %); m.p. 333–335 °C. IR: ν = 3300, 3200 (NH_2); 1660 (C=O, pyrimidinone) cm^{-1}. ^1H NMR (DMSO-d_6): δ = 8.3 (s, 1H, CH pyridine), 8.1 (s, 1H, CH thienyl), 7.8 (m, 1H, CH thienyl), 7.3 (m, 1H, CH thienyl), 6.3 (s, 2H, NH_2), 3.2 (s, 3H, CH_3) ppm. MS: *m/z* = 382 (M^+, 100 %), 366 (M^+-NH_2, 17 %). 352(M^++H-NH_2-CH_3, 41%). Anal. Calcd. For $C_{15}H_9F_3N_4OS_2$ (382.38): C, 47.12; H, 2.37; N, 14.65; S, 16.77 %. Found: C, 47.18; H, 2.19; N, 12.57; S, 16.80 %.

The latter compound (**12**) was also obtained when an equimolar mixture of **23** (0.74 g, 2 mmol) and hydrazine hydrate in ethanol (30 ml) was heated under reflux for 3 h. Yield: 0.6 g (78 %); m.p. 333–335 °C, m.p.333–335 °C.

3-Diacetylamino-2-methyl-7-(2-thienyl)-9-trifluoromethylpyrido [3',2':4,5]thieno[3,2-d]pyrimidine-4(3H)-ones (**13**), *Method A*: A suspension of compound **12** (0.76 g, 2 mmol) in acetic anhydride (10 ml) was refluxed for 3 h. The reaction mixture was diluted with water (20 ml) and allowed to stand at room temperature for 2 h. The precipitated solid was collected and recrystallised from ethanol as fine white crystals of **13**. Yield: 0.78 g (84 %); m.p. 270–271 °C. IR: ν = 1730 (2C=O, biacetylamino), 1680 (C=O, pyrimidinone) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 8.6 (s, 1H, CH pyridine), 8.4 (m, 1H, CH thienyl), 8.2 (m, 1H, CH thienyl), 7.5 (t, 1H, CH thienyl), 2.7 (s, 3H, CH_3), 2.6 (s, 6H, 2X$COCH_3$) ppm. MS: *m/z* = 466 (M^+, 65 %), 423 (M^+–$COCH_3$, 31 %), 381 (M^++H–($COCH_3$)$_2$,100%), 366 (M^+–N($COCH_3$)$_2$, 6 %), 352 (M^++H–N($COCH_3$)$_2$-CH_3, 21 %). Anal. Calcd. For $C_{19}H_{13}F_3N_4O_3S_2$ (466.46): C, 48.92; H, 2.81; N, 12.01; S, 13.75 %. Found: C, 48.82; H, 2.86; N, 12.13; S, 14.11 %.

Method B: A suspension of compound **5** (0.71g, 2 mmol) in acetic anhydride (10 ml) was refluxed for 4 h. The reaction mixture was diluted with water (10 ml) and allowed to stand at room temperature for 2 h. The precipitate that obtained on recrystallisation was identical to that described above in all aspects. Yield: 0.83 g (89 %); m.p. 270–271 °C, m.p. 270–271 °C.

3-Benzylideneamino-2-methyl-7-(2-thienyl)-9-trifluoromethyl-pyrido[3',2':4,5]thieno[3,2-d]pyrimidine-4(3H)-one (**14**), *Method A*: A mixture of compound **12** (0.76 g, 2 mmol) and benzaldehyde (0.2 ml, 2 mmol) in dioxane (15 ml) was heated under reflux for 2 h. The precipitate that formed while hot was collected and recrystallised from an ethanol–chloroform mixture to give pale yellow crystals of **14**. Yield: 0.73 g (78%); m.p. 321–322 °C. IR: ν = 1670 (C=O) cm^{-1}. ^1H NMR (TFA): δ = 8.7 (s, 1H, N=CH), 7.5–8.4 (m, 9H: 5ArH's, 3CH thienyl and CH pyridine), 2.9 (s, 3H, CH_3) ppm. Anal. Calcd. For $C_{22}H_{13}F_3N_4OS_2$ (470.49): C, 56.16; H, 2.78; N, 11.91; S, 13.63 %. Found: C, 56.32; H, 2.82; N, 11.83; S, 13.77 %.

Method B: Compound **7a** (0.89g, 2 mmol) in acetic anhydride (10 ml) was heated under reflux for 4 h and then allowed to cool. The solid product collected and recrystallised from an ethanol-chloroform mixture to give pale yellow crystals of **14**. Yield: 0.75 g (80 %); m.p. 321–322 °C, m. m.p. 321–322 °C.

3-Formylamino-7-(2-thienyl)-9-trifluoromethylpyrido[3',2':4,5] thieno[3,2-d]pyrimidin-4(3H)-one (**15**): Compound **5** (0.72 g, 2 mmol) in formic acid 85 % (20 ml) was refluxed for 4 h. The pale yellow precipitate that formed after cooling was collected and crystallised from ethanol to give **15**. Yield: 0.62 g (78 %); m.p. 309–310 °C. IR: ν = 3200 (NH), 1710 (C=O, formyl), 1650 (C=O, pyrimidinone) cm^{-1}. ^1H NMR (DMSO-d_6): δ = 8.7 (s, 1H, CH pyrimidine), 8.4 (s, 1H, NH), 8.2 (s, 1H, CH pyridine), 8.0 (m, 1H, CH thienyl), 7.6 (m, 2H: CHO and CH thienyl), 7.3 (t, 1H, CH thienyl) ppm. MS: *m/z* = 397 (M^++1, 84 %), 396 (M^+, 35 %), 366 (M^+–HCHO, 93 %), 352 (M^+–NHCHO, 56 %), 338 (M^+–NNHCHO, 63 %), 318(100%). Anal. Calcd. For $C_{15}H_7F_3N_4O_2S_2$ (396.37): C, 45.45; H, 1.78; N, 14.14; S, 16.18 %. Found: C, 45.32; H, 1.59; N, 14.28; S, 16.12 %.

1-[3-Amino-6-(2-thienyl)-4-trifluoromethylthieno[2,3-b]pyridin-2-yl]carbonyl-3,5-dimethyl-1H-pyrazole (**16**): A mixture of **5** (0.72 g, 2 mmol) in acetylacetone (5 ml) was heated under reflux for 6 h. The reaction mixture was triturated with ethanol (5 ml) and then left to cool. The precipitated solid was collected by filtration and recrystallised from ethanol to give yellow crystals of **16**. Yield: 0.7 g (83 %); m.p. 188–190 °C. IR: ν = 3500, 3300 (NH_2), 1630 (C=O) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 7.9 (s, 1H, CH pyridine), 7.8 (d, 1H, CH thienyl), 7.5 (d, 1H, CH thienyl), 7.2 (t, 1H, CH thienyl), 6.7 (s, 2H, NH_2), 6.0 (s, 1H, CH pyrazole), 2.7 (s, 3H, CH_3 attached to pyrazole ring), 2.4 (s, 3H, CH_3 attached to pyrazole ring) ppm. MS: *m/z* = MS: *m/z* = 421 (M^+-H, 100 %), 405(M^+-H–NH_2, 34 %), 326 (M^+-H-dimethylpyrazolyl moiety, 76%), 297(M^+-2H-dimethyl-pyrazolyl–carbonyl moiety, 95 %), 69 (CF_3^+, 9 %). Anal. Calcd. For $C_{18}H_{13}F_3N_4OS_2$ (422.45): C, 51.18; H, 3.10; N, 13.26; S, 15.18 %. Found: C, 51.41; H, 3.30; N, 13.38; S, 15.20 %.

3-Ethoxymethyleneamino-7-(2-thienyl)-9-trifluoromethylpyrido [3',2':4,5]thieno[3,2-d]pyrimidine-4(3H)-one (**17**): A mixture of **5** (0.72 g, 2 mmol) and triethyl orthoformate (3 ml) in DMF (10 ml) was refluxed for 6 h. The solid that formed on cooling was collected and recrystallised from DMF as yellow crystals of **17**. Yield: 0.63 g (74 %); m.p. 237–238 °C. IR: ν = 1660 (C=O) cm^{-1}. ^1H NMR (TFA): δ = 9.3 (s, 1H, CH pyrimidine), 8.5 (s, 1H, CH pyridine), 8.2 (s, 1H, N=CH), 8.0 (d, 1H, CH thienyl), 7.5 (d, 2H, 2CH thienyl), 4.3–4.6 (q, 2H, OCH_2), 1.3–1.6 (t, 3H, CH_3) ppm. MS: *m/z* = 424 (M^+, 42 %), 379 (M^+-OC_2H_5, 11 %), 353 (M^++H-(N=$CHOC_2H_5$), 100 %), 352 (M^+-(N=$CHOC_2H_5$), 56 %), 69(CF_3^+, 11 %), 29($C_2H_5^+$, 72 %). Anal. Calcd. For $C_{17}H_{11}F_3N_4O_2S_2$ (424.42): C, 48.11; H, 2.61; N, 13.20; S, 15.11 %. Found: C, 48.20; H, 2.45; N, 13.15; S, 15.44 %.

3-Amino-7-(2-thienyl)-9-trifluoromethylthieno[2,3-b]pyridine-2-carbonylazide (**18**): To a cold solution of **5** (1.8 g, 5 mmol) in glacial acetic acid (25 ml), sodium nitrite solution 100 % (7.7 ml, 11 mmol) was added dropwise with stirring during 5 mins at room temperature. The formed precipitated was collected, dried in air and utilised in the next reactions without purification. Yield: 1.6 g (87 %); m.p. 188–190 °C (dec.). IR: ν = 3500, 3300 (NH_2), 2120 (N_3), 1700 (C=O) cm^{-1}. Anal. Calcd. For $C_{13}H_6F_3N_5OS_2$ (369.34): C, 42.28; H, 1.64; N, 18.96; S, 17.36 %. Found: C, 42.71; H, 1.93; N, 19.13; S, 17.50 %.

6-(2-Thienyl)-4-trifluoromethyl-1H-imidazolo[4',5':4,5]thieno [2,3-b]pyridine-2(3H)-ones (**20**): The acid azide **18** (1.1 g, 3 mmol) was heated under reflux for 3 h in dry toluene (30 ml). The reaction mixture was cooled whereby a precipitated solid was formed. It was collected and recrystallised from dioxane as yellow crystals of **20**. Yield: 0.85 g (83 %); m.p. 343–345 °C. IR: ν = 3500, 3200 (2NH), 1680 (C=O) cm^{-1}. MS: *m/z* = 340 (M^+–H, 100 %), 339 (M^+–2H, 13 %), 285 (M^+–NHCONH, 49 %), 69 (CF_3^+, 12 %). Anal. Calcd. For $C_{13}H_6F_3N_3OS_2$ (341.33): C, 45.74; H, 1.77; N, 12.31; S, 18.79 %. Found: C, 45.32; H, 1.55; N, 12.57; S, 18.39 %.

3-Amino-6-(2-thienyl)-4-trifluoromethylthieno[2,3-b]pyridine-2-carboxylic acid (**21**): A suspension of **3** (3.72 g, 10 mmol) in ethanolic sodium hydroxide solution 10 % (50 ml) was heated under reflux for 4 h. and then allowed to cool. The reaction mixture was diluted with 50 ml water, filtered and then acidified the clear filtrate with dilute acetic acid. The precipitate was collected and crystallised from ethanol–chloroform mixture to give yellow crystals of **21**. Yield: 3.1 g (90 %); m.p. 209–210 °C. IR: ν = 3490, 3350 (NH_2), at 3200–3000 (OH), 1640 (C=O) cm^{-1}. Anal. Calcd. For $C_{13}H_7F_3N_2O_2S_2$ (344.33): C, 45.35; H, 2.05; N, 8.14; S, 18.62 %. Found: C, 44.98; H, 2.32; N, 8.13; S, 18.48 %. ^1H NMR (TFA): δ = 10.2 (s, 1H, CO_2H); 7.8 (s, 1H, CH pyridine), 7.7 (d, 1H, CH thienyl), 7.5 (d, 1H, CH thienyl), 7.2 (t, 1H, CH thienyl), 6.6 (s, 2H, NH_2) ppm.

7-(2-Thienyl)-9-trifluoromethylpyrido[3',2':4,5]thieno[3,2-d] oxazine-4-one (**22**): Compound **21** (0.69 g, 2 mmol) in triethyl orthoformate (10 ml) was heated under reflux for 3 h. The solid product that formed on cooling was collected and dried in air to give white needles of **22.** Yield: 0.64 g (91 %); m.p. 275–276 °C. IR: ν = 1740 (C=O) cm^{-1}. ^1H NMR (TFA): 8.8 (s, 1H, CH oxazinone), 7.9 (s, 1H, CH pyridine), 7.8 (d, 1H, CH thienyl), 7.4 (d, 1H, CH thienyl), 7.2 (t, 1H, CH thienyl) ppm. MS: *m/z* = 354 (M^+, 100 %), 353 (M^+-H, 15 %), 326 (M^+-CO, 39 %), 69 (CF_3^+, 25 %). Anal. Calcd. For $C_{14}H_5F_3N_2O_2S_2$ (354.33): C, 47.46; H, 1.42; N, 7.91; S, 18.10 %. Found: C, 47.30; H, 1.73; N, 7.82; S, 17.90 %.

2-Methyl-7-(2-thienyl)-9-trifluoromethylpyrido[3',2':4,5]thieno [3,2-d]oxazine-4-one (**23**): Compound **21** (1.72 g, 5 mmol) in redistilled acetic anhydride (25 ml) was heated under reflux for 4 h and then left to cool. The crystalline product was collected, dried in air and applied in the next reactions without recrystallisation. Yield: 1.7 g (92 %); m.p. 256–257 °C. IR: ν = 1740 (C=O) cm^{-1}. ^1H NMR (TFA): 7.8 (s, 1H, CH pyridine), 7.7 (d, 1H, CH thienyl), 7.4 (d, 1H, CH thienyl), 7.2 (t, 1H, CH thienyl), 2.6 (s, 3H, CH_3) ppm. MS: *m/z* = 368 (M^+, 100 %), 353 (M^+–CH_3, 37 %), 324 (M^+–CO_2, 100 %), 69 (CF_3^+, 14 %). Anal. Calcd. For $C_{15}H_7F_3N_2O_2S_2$ (368.35):

C, 48.91; H, 1.92; N, 7.61; S, 17.41 %. Found: C, 49.15; H, 2.12; N, 7.87; S, 17.10 %.

3-Amino-7-(2-thienyl)-9-trifluoromethylpyrido[3',2':4,5]thieno [3,2-d]pyrimidine-4(3H)-one (**24**), *Method A*: A mixture of **22** (0.71g, 2 mmol) and hydrazine hydrate (0.2 ml, 4 mmol) in ethanol (15 ml) was heated under reflux for 3 h. The solid that formed after cooling was collected and recrystallised from ethanol as white needles of **24**. Yield: 0.65 g (88 %); m.p. 310–312°C, IR: ν = 3300–3200 (NH_2); 1660 (C=O, pyrimidinone) cm^{-1}. ^1H NMR (DMSO-d_6): δ = 9.0 (s, 1H, CH pyrimidinone), 8.3 (s, 1H, CH pyridine), 8.1 (s, 1H, CH thienyl), 7.8 (m, 1H, CH thienyl), 7.3 (m, 1H, CH thienyl), 6.3 (s, 2H, NH_2) ppm. Anal. Calcd. For $C_{14}H_7F_3N_4OS_2$ (368.36): C, 45.65; H, 1.92; N, 15.21; S, 17.41 %. Found: C, 45.56; H, 2.11; N, 15.27; S, 17.50 %.

Method B: A mixture of **17** (0.85 g, 2 mmol) and hydrazine hydrate 99 % (5 ml) was heated under reflux for 4 h. The reaction mixture was triturated with ethanol (5 ml) and then left to cool. The precipitated solid was collected and recrsyallised from ethanol to give compound **24** (Yield: 0.64 g; 87 %). This product was identical to that described in method A in all aspects.

2-Methyl-3-phenyl-7-(2-thienyl)-9-trifluoromethylpyrido[3',2':4,5] thieno[3,2-d]pyrimidine-4(3H)-one (**25**): A mixture of **23** (0.74 g, 2 mmol) and aniline (0.4 ml) in glacial acetic acid (10 ml) was heated under reflux for 3 h. The reaction mixture was cooled and diluted with water whereupon a solid precipitated. It was collected and crystallised from an ethanol-chloroform mixture to give white needles of **25.** IR: ν = 1660 (C=O) cm^{-1}. ^1H NMR (TFA): δ = 7.2–8.3 (m, 9H: 5ArH's, 3CH thienyl and CH pyridine); 2.4 (s, 3H, CH_3) ppm. MS: *m/z* = 443 (M^+, 100 %), 428 (M^+–CH_3, 20 %), 374 (M^+–CF_3, 1 %), 350 (M^+–CH_3–C_6H_5–H, 16%), 77($C_6H_5^+$, 73 %), 69 (CF_3^+, 6 %). Yield: 0.7 g (79 %); m.p. 297-298 °C. Anal. Calcd. For $C_{21}H_{12}F_3N_3OS_2$ (443.47): C, 56.88; H, 2.73; N, 9.48; S, 14.46 %. Found: C, 56.54; H, 2.62; N, 9.39; S, 14.37 %.

2-Methyl-3-(2-hydroxyethyl)-7-(2-thienyl)-9-trifluoromethylpyrido [3',2':4,5]thieno[3,2-d]pyrimidine-4(3H)-one (**26**): A mixture of **23** (0.74 g, 2 mmol) and ethanolamine (0.4 ml) in glacial acetic acid (10 ml) was heated under reflux for 3 h. The reaction mixture was cooled and diluted with water whereupon a solid precipitated. It was collected and crystallised from ethanol-chloroform mixture to give white needles of **26**. Yield: 0.71 g (86 %); m.p. 275–276 °C. IR: ν = 3400 (OH), 1660 (C=O) cm^{-1}. MS: *m/z* = 411 (M^+, 61 %), 367 (M^++H–CH_2CH_2OH, 100 %), 366 (M^+-CH_2CH_2OH, 32 %), 351(M^+-CH_2CH_2OH-CH_3, 8 %), 69 (CF_3^+, 6 %). Anal. Calcd. For $C_{17}H_{12}F_3N_3O_2S_2$ (411.42): C, 49.63; H, 2.94; N, 10.21; S, 15.59 %. Found: C, 49.42; H, 2.82; N, 10.33; S, 15.83 %.

Received 27 January 2005; accepted 11 April 2005
Paper 05/3038

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