Reactions of 6-Acetyl-4-methyl-5-(1-pyrrolyl)-2-phenylthieno-[2,3-*d*]pyrimidine in Heterocyclic Synthesis: Convenient Route to Some Schiff's Bases, Chalcones, Pyridines, Pyridin-2(1H)-ones and 2H-Pyran-2-one Derivatives Incorporating a 5-(1-Pyrrolyl)-2-phenylthieno[2,3-*d*]pyrimidine Moiety

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Treatment of 6-acetyl-5-amino-4-methyl-2-phenylthieno[2,3-*d*]pyrimidine **3** with 2,5-dimethoxytetrahydrofuran afforded the 6-acetyl-5-(1-pyrrolyl)-4-methyl-2-phenylthieno[2,3-*d*]pyrimidine **4**, which can react with appropriate primary amines **5a-f** to yield the corresponding Schiff's base derivatives **6a-f**. The reaction of acetyl compound **4** with appropriate arylaldehydes **14a-k** and arylmethylidenemalononitriles **18a-f** afforded the corresponding 6-(3-substituted-acryloyl)-5-(1-pyrrolyl)-4-methyl-2-phenylthieno[2,3-*d*]pyrimidines **15a-k** and 6-[3-cyano-2-ethoxy-4-(4-substituted-phenyl)-pyridin-6-yl]-5-(1-pyrrolyl)-4-methyl-2-phenyl-thieno[2,3-*d*]pyrimidines **21a-f** under basic conditions, respectively. On the other hand, the 6-(3-cyano-1,2-dihydro-4-substituted-2-oxopyridin-6-yl)-5-(1-pyrrolyl)-4-methyl-2-phenylthieno[2,3-*d*]pyrimidines **26a,b** and 6-(3-substituted-amido-4-substituted-pyran-2-on-6-yl)-5-(1-pyrrolyl)-4-methyl-2-phenyl-thieno[2,3-*d*]pyrimidines **30a-c** were obtained by intramolecular cyclization of 6-(3-dimethylamino-3-substituted-acryloyl)-5-(1-pyrrolyl)-4-methyl-2-phenylthieno[2,3-*d*]pyrimidines **23a,b** with cyanoacetamide **24** and N-acylglycines **27a,b**, respectively.

Keywords: 6-Acetyl-5-(1-pyrrolyl)-4-methyl-2-phenylthieno[2,3-*d*]pyrimidine; Schiff's bases; Chalcones; Pyridines; Pyridin-2(1H)-ones; 2H-Pyran-2-one derivatives.

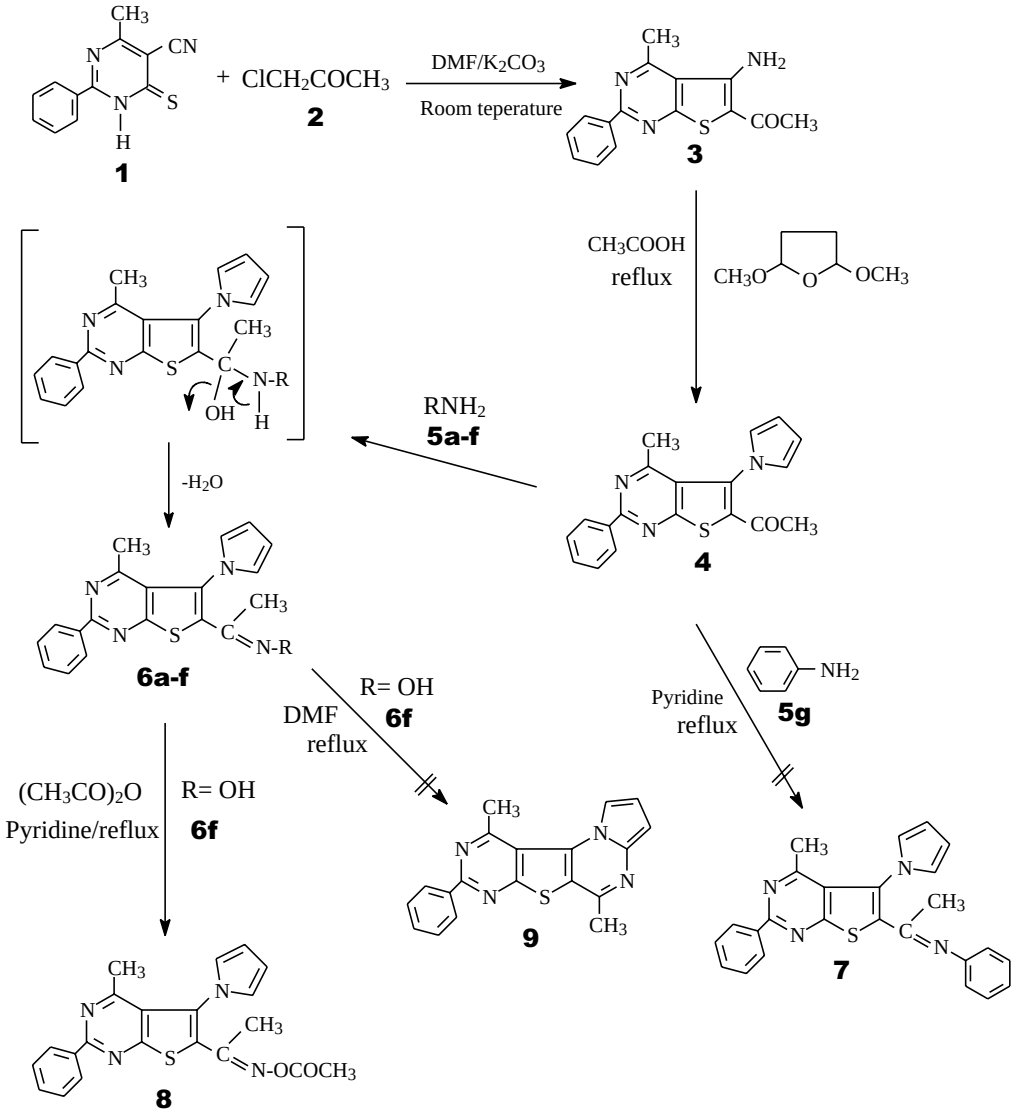
INTRODUCTION

Thienopyrimidines have been the subject of many chemical and biological studies on account of their interesting pharmacological properties.[1-8] A number of syntheses for substituted derivatives of this thienopyrimidine ring system, featuring a variety of pharmacological effects, have been developed. On the other hand, several series of heterocyclic compounds possessing a bridgehead pyrrolic moiety play a vital role in many biological activities.[9-13] Likewise, the pyrrolothione derivatives also possess a variety of pharmacological activities.[14-16] In view of these it was considered of interest to synthesize some new heterocycles containing the pyrrolothienopyrimidine moiety in the hope that they may be biologically active. In a preceding paper[17] we have described the synthesis of some new pyrimido[2,3:4,3]pyrazolo[1,5-a]pyrimidines from 5-cyano-1,6-dihydro-4-methyl-2-phenyl-6-thioxopyrimidine **1**. In continuation of our studies, we report herein the use of 6-acetyl-5-(1-pyrrolyl)-4-methyl-2-phenylthieno[2,3-*d*]pyrimidine **4** for the synthesis of various Schiff's bases, chalcones, pyridines, pyridin-2(1H)-ones and 2H-pyran-2-one derivatives incorporating a 5-(1-pyrrolyl)-4-methyl-2-phenylthieno[2,3-*d*]pyrimidine moiety.

RESULTS AND DISCUSSION

All relevant reactions are depicted in Schemes I-III. The reaction of 5-cyano-1,6-dihydro-4-methyl-2-phenyl-6-thioxopyrimidine **1** with chloroacetone **2** in DMF in the presence of excess anhydrous potassium carbonate at room temperature gave the 6-acetyl-5-amino-4-methyl-2-phenylthieno[2,3-*d*]pyrimidine **3**[18] (Scheme I). Treatment of compound **3** with 2,5-dimethoxytetrahydrofuran in glacial acetic acid produced the 6-acetyl-5-(1-pyrrolyl)-4-methyl-2-phenylthieno[2,3-*d*]pyrimidine **4**,[19] which reaction with appropriate primary amines **5a-d**, **5f** in pyridine and hydrazine hydrate **5e** to afford the corresponding Schiff's bases **6a-e** and/or oxime derivatives **6f**, respectively (Scheme I). The IR spectra of compound **4** indicated the absence of the NH_2

Scheme I

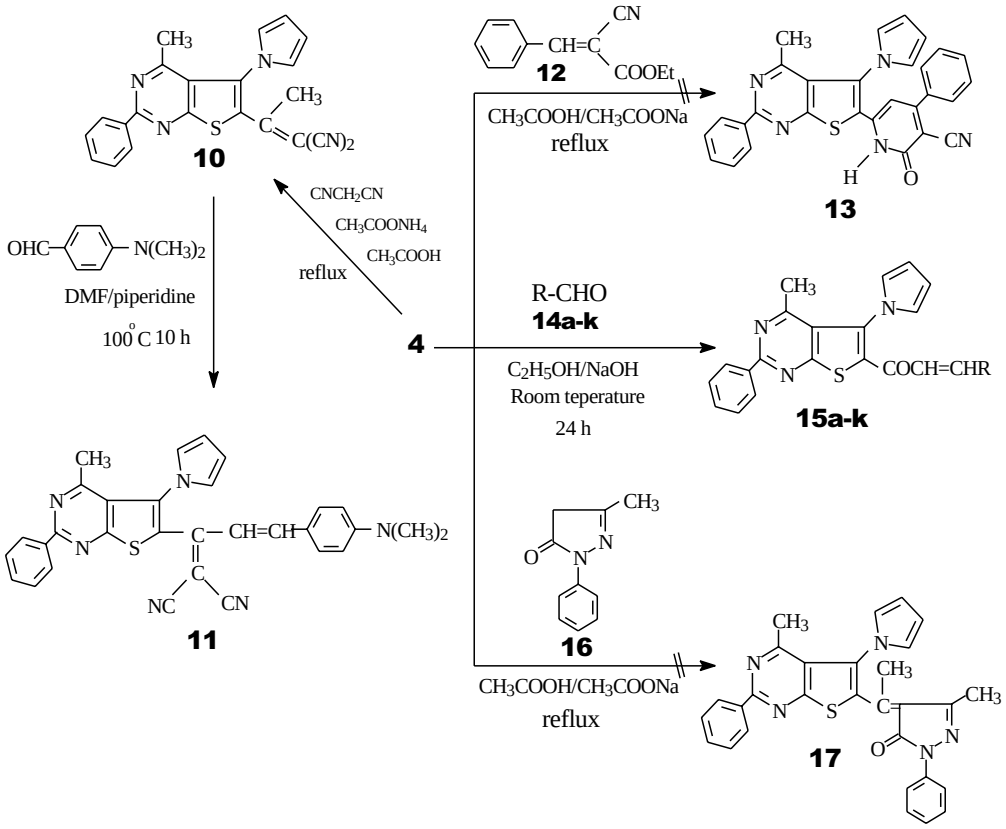


5, 6	a	b	c	d	e	f
R	CH_3	C_2H_5	C_3H_7	C_4H_9	NH_2	OH

group. The ^{1}H NMR spectra ($CDCl_3$) of compound **4** revealed two triplets at δ 6.50 (2H, t) and 6.87 (2H, t), which were readily assigned to the hydrogen attached at C_3, C_4 and C_2, C_5 of the pyrrolyl ring,[20-21] respectively. The structures of **6a-f** were established on the basis of their elemental analysis and spectral data. The IR spectra of **6a-f** indicated the absence of the C=O group absorption band, indicating the formation Schiff's base derivatives **6a-f**. Under similar reaction conditions, reaction of compound **4** with aniline **5g** did not produce the desired compound **7**, but led only to the recovery of starting material. Moreover, acetylation of oxime derivative **6f** with acetic anhydride in the presence of pyridine afforded acetoxy derivative **8**. Our attempts to cyclize **6f** in DMF to the compound **9** was unsuccessful.

Furthermore, condensation of compound **4** with malononitrile in glacial acetic acid containing ammonium acetate afforded the 6-(2,2-dicyano-1-methylvinyl)-5-(1-pyrrolyl)-4-methyl-2-phenylthieno[2,3-*d*]pyrimidine **10**, which

Scheme II

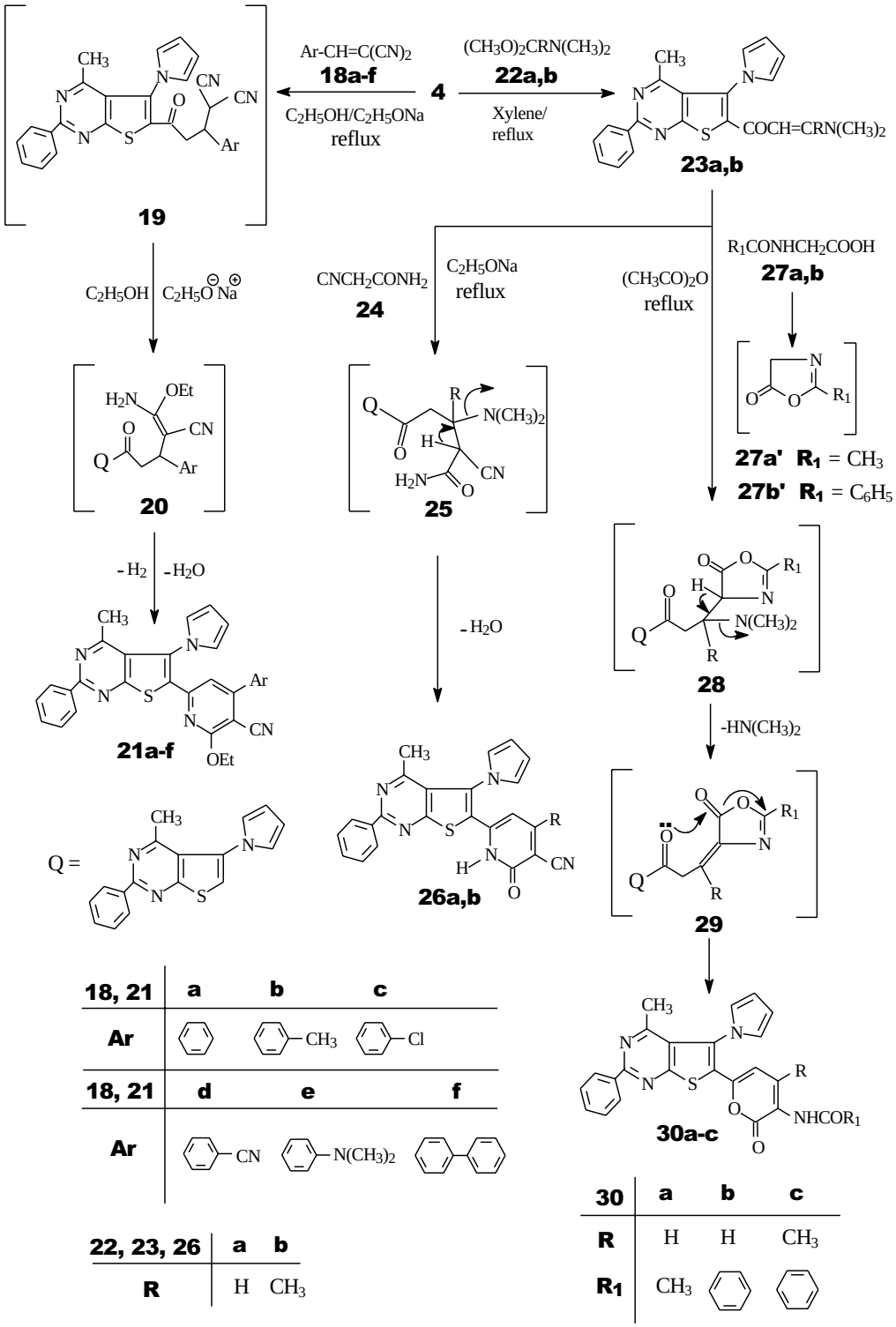


14, 15	a	b	c	d	e	f
R		CH_3	OCH_3	$N(CH_3)_2$	$N(C_2H_5)_2$	

14, 15	g	h	i	j	k
R					

then reacted with N,N-dimethylaminobenzaldehyde in DMF in the presence of a catalytic amount of piperidine at 100 °C for 10 h yielded the 6-(2-cyano-5-(4-dimethylaminophenyl)-2,4-pentadienenitrile)-5-(1-pyrrolyl)-4-methyl-2-phenylthieno[2,3-*d*]pyrimidine **11** (Scheme II). The IR spectra of compounds **10** and **11** indicated the absence of the C=O group absorption band and showed the characteristic absorption bands at 2220-2202 cm^{-1} for the C≡N group. The ^1H NMR spectra ($CDCl_3$) of compound **11** revealed a sharp singlet at δ 3.09 (6H, s) assigned to the $N(CH_3)_2$ protons and at δ 6.70 (1H, d) and 7.74 (1H, d) assigned to the -CH=CH- of pentadienonitrile moiety, and a multiplet at δ 8.57-7.51 (9H, m) assigned to the phenyl protons. Attempted cyclization of **4** with ethyl benzylidinecyanoacetate **12** in glacial acetic acid to the compound **13** was unsuccessful and the starting material was recovered.[22-23] In addition, the 6-(3-substituted-acryloyl)-5-(1-pyrrolyl)-4-methyl-2-phenylthieno[2,3-*d*]pyrimidines **15a-k**[24] were obtained in good yields by condensation of compound **4** with appropriate aldehydes **14a-k**. The structures of chalcones **15a-k** were established by examining

Scheme III



spectral data and elemental analysis. The IR spectrum of compounds **15a-k** indicated the characteristic absorption bands at 1688-1628 cm^{-1} for the CO group. The ^1H NMR spectrum ($CDCl_3$) of compounds **15a-k** showed signals at δ 5.88-5.47 (1H, d) and 8.15-7.74 (1H, d), which were assigned to the protons -CH=CH- of propenyl moiety, respectively.

Moreover, attempted preparation of compound **17** via condensation of compound **4** with pyrazole **16** also failed.[25-26]

On the other hand, the reaction of compound **4** with arylmethylidene-malononitriles **18a-f** were also investigated. Thus, the reaction of compound **4** with benzylidine-malononitrile **18a** in refluxing ethanol in the presence of an equimolar amount of sodium ethoxide afforded a product of molecular formula $C_{31}H_{23}N_5OS$ (86% yield, mp 149 °C). Spectroscopic analyses revealed that 6-(3-cyano-2-ethoxy-4-phenyl-pyridyl-6-yl)-5-(1-pyrrolyl)-4-methyl-2-phenylthieno[2,3-*d*]pyrimidine **21a** was obtained (Scheme III). The IR spectrum of the reaction product showed the characteristic absorption band at 2225 cm^{-1} for the C≡N group. The ^1H NMR spectrum ($CDCl_3$) of the reaction product, which showed a triplet at δ 1.56 (3H, t) and a quartet at δ 4.64 (2H, q) assigned to the ethoxy group (OCH_2CH_3), a single at δ 7.41 (1H, s) assigned to the proton at the 5-position of the pyridine ring and a multiplet at δ 8.63-7.47 (10H, m) assigned to the phenyl protons, was also confirmed by the mass spectrum *m/z* 513 (M^+ 100). The mass fragmentation pattern of compound **21a** showed the presence of the ion peaks $[M\text{-}CH_3]^+$ at *m/z* 498, $[M\text{-}CH_2CH_3]^+$ at *m/z* 484 and $[M\text{-}OCH_2CH_3]^+$ at *m/z* 468. The formation of **21a** from the reaction of **4** with **18a** is assumed to proceed via initial addition of the methyl anionic center of the acetyl group in **4** to the activated double bond in **18a** to yield the non-isolable intermediate Michael adduct **19** then reacts with ethoxide to form the intermediate **20**,[27-28] which then undergoes intramolecular cyclization via loss of water afforded the final product **21a**. Under similar reaction conditions, treatment of compound **4** with arylmethylidene-malononitriles **18b-f** afforded the corresponding 6-(3-cyano-2-ethoxy-4-(4-substituted-phenyl)-pyridin-6-yl)-5-(1-pyrrolyl)-4-methyl-2-phenylthieno[2,3-*d*]pyrimidines **21b-f**, respectively in good yields (Scheme III).

Next, reaction of compound **4** with dimethylformamide dimethylacetal **22a** and N,N-dimethylacetamide dimethylacetal **22b** in refluxing xylene afforded the corresponding 6-(3-substituted-3-dimethylamino-acryloyl)-5-(1-pyrrolyl)-4-methyl-2-phenylthienenylthieno[2,3-*d*]pyrimidines **23a,b**, respectively. (Scheme III). The IR spectrum of compounds **23a,b** indicated the characteristic absorption bands at 1628-1626 cm^{-1} for the CO group. The ^1H NMR spectra ($CDCl_3$) of compounds **23a,b** revealed two sharp singlets at δ 2.58 (3H, s) and 3.08-2.71 (3H, s), which were assigned to the $N(CH_3)_2$ protons. In addition, the ^1H NMR spectra ($CDCl_3$) of compound **23a** revealed signals at δ 4.41 (1H, d) and 7.15 (1H, d), which were assigned to the protons -CH=CH- of acryloyl moiety, respectively. Moreover, the ^1H NMR spectrum of compound **23b** showed signals at δ 2.07 (3H, s) and 4.77 (1H, s), which were readily assigned to the 3-CH_3 protons and 2-H of acryloyl moiety, respectively. The study was extended to investigate the behavior of enaminone derivatives **23a,b**. Intramolecular cyclization of enaminone derivatives **23a,b** gave different products depending on reaction conditions. Thus, treatment of enaminone derivatives **23a,b** with cyanoacteamide **24** in sodium ethoxide solution afforded the corresponding 6-(3-cyano-1,2-dihydro-4-substituted-2-oxopyridyl-6-yl)-5-(1-pyrrol-yl)-4-methyl-2-phenylthieno[2,3-*d*]-pyrimidines **26a,b**,[29] respectively (Scheme III). We propose that the first step of the mechanism involves via initial addition of the active methylene in **24** to the activated double bond in **23a,b** to yield the non-isolable intermediate **25**, followed by deamination, and subsequent cyclization with loss of water to afford the final products **26a,b**. The structures of compounds **26a,b** were confirmed on the basis of their elemental analysis and spectral data. The IR spectra of compounds **26a,b** showed the characteristic absorption band at 3234-3122 cm^{-1} for the NH group, at 2217-2193 cm^{-1} for the C≡N group and at 1720-1711 cm^{-1} for the C=O group. Moreover, the ^1H NMR spectrum (DMSO-d_6) of compound **26a** revealed signals at δ 7.06 (1H, d) and 8.02 (1H, d), which were assigned to the 5-H and 4-H of the pyridone ring, respectively, was also confirmed by the mass spectrum *m/z* 409 (M^+ 100). The mass fragmentation pattern of compound **26a** showed the presence of a prominent ion peak $[M\text{-}CN]^+$ at *m/z* 383. Also, the ^1H NMR spectrum of compound **26b** showed signals at δ 2.13 (3H, s) and 7.87 (1H, s), which were readily assigned to the 4-CH_3 protons and 5-H of the pyridone ring, respectively.

On the other hand, the reactivity of thienopyrimidines **23a,b** towards N-acylglycines **27a,b** was also investigated. Thus, treatment of compound **23a** with N-acetylglycine **27a** in refluxing acetic anhydride afforded a product of molecular formula $C_{24}H_{18}N_4O_3S$ (43% yield, mp 243 °C). Spectroscopic analyses revealed that the corresponding 6-(3-acetamido-pyran-2-on-6-yl)-5-(1-pyrrolyl)-4-methyl-2-phenyl-thieno-[2,3-*d*]pyrimidine **30a** was obtained (Scheme III). The IR spectra of compound **30a** revealed characteristic absorption bands at 3266 cm^{-1} and 1728 cm^{-1} due to NH group and carbonyl group, respectively. In addition, the structure of compound **30a** was supported by the ^1H NMR spectra, which revealed two doublets at δ 6.87 (1H, d) and 8.10 (1H, d) assigned to the 5-H and 4-H of oxopyran ring, respectively, a singlet at 2.21 (3H, s) assigned to the CH_3 protons of the acetamido group and a broad singlet at δ 8.02 (1H, br) assigned to the NH proton, was also confirmed by the mass

spectra *m/z* 442 (M^+). The mass fragmentation pattern of compound **30a** showed the presence of the ion peaks [M-CH_3]$^+$ at *m/z* 427, [M-$COCH_3$]$^+$ at *m/z* 399 and [M-$NHCOCH_3$]$^+$ at *m/z* 384. The formation of compound **30a** from the reaction of **23a** with **27a** is assumed that N-acetylglycine generated *in situ* is cyclised into oxazolone **27a'**[29] which then reacts with thienopyrimidine **23a** via initial addition of the active methylene in **27a'** to the activated double bond in **23a** to yield the intermediate **29**. The latter can then rearrange into an insoluble product **30a** via an attack of carbonyl on the oxazolone ring[29] (Scheme III). Under similar reaction conditions, treatment of compound **23a,b** with hippuric acid **27b** affords the corresponding 6-(3-benzoylamino-4-substituted-pyran-2-on-6-yl)-5-(1-pyrrolyl)-4-methyl-2-phenyl-thieno[2,3-*d*]pyrimidines **30b,c**, respectively. The formation of compounds **30a-c** from thienopyrimidines **23a,b** with either N-acetyl glycine or hippuric acid can thus be considered as an extension of the Kepe pyranone synthesis.[30-32]

In conclusion, 6-acetyl-5-(1-pyrrolyl)-4-methyl-2-phenylthieno[2,3-*d*]pyrimidine **4** has been shown to be a useful building block for the synthesis of some new Schiff's bases **6a-f**, chalcones **15a-k**, pyridines **21a-f**, pyridin-2(1H)-ones **26a,b** and 2H-pyran-2-one derivatives **30a-c**.

EXPERIMENTAL SECTION

All melting points were determined in a capillary tube and are uncorrected. The IR spectra were recorded on potassium bromide pellets on a JASCO FTIR-3 spectrometer. The ^{1}H NMR spectra were obtained on a Bruker AM-300WB FT-NMR spectrometer and chemical shifts are expressed in δ ppm using TMS as an internal standard. Electron impact mass spectra were obtained at 70 eV by using a Finnigan Mat TSQ-46C spectrometer. Microanalyses for C, H, and N were performed on a Perkin-Elmer 240 elemental analyzer. 6-Acetyl-5-amino-4-methyl-2-phenylthieno[2,3-*d*]pyrimidine **3**, 6-acetyl-5-(1-pyrrolyl)-4-methyl-2-phenylthieno[2,3-*d*]-pyrimidine **4** and 6-(3-substituted-acryloyl)-5-(1-pyrrolyl)-4-methyl-2-phenyl-thieno[2,3-*d*]pyrimidines **15a-k** were prepared following the methods in the literature,[18-19,24] respectively.

6-Acetyl-5-amino-4-methyl-2-phenylthieno[2,3-*d*]pyrimidine (3)

To a solution of 5-cyano-1,6-dihydro-4-methyl-2-phenyl-6-thioxopyrimidine **1** (2.27 g, 0.01 mol) in DMF (50 mL), potassium carbonate anhydrous (2.76 g, 0.02 mol) and chloroacetone **2** (0.93 g, 0.01 mol) were added. The reaction mixture was stirred at room temperature for 4 h and then diluted with cold water (50 mL). The resulting solid product was collected by filtration, washed with water and recrystallized from ethyl acetate/ethanol to give 2.66 g of yellow needles (94% yield), mp 210 °C; IR: ν 3424, 3295 (NH_2), 1663 (CO) cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 2.47 (3H, s, $COCH_3$), 3.07 (3H, s, CH_3), 3.76 (2H, br, NH_2), 8.58-8.55, 7.60-7.55 (5H, m, phenyl-H); MS: 283 (M^+, 100), 268 (95), 240 (20), 212 (2), 165 (5), 160 (10), 137 (34), 110 (18), 77 (9). Anal. Calcd. for $C_{15}H_{13}N_3OS$: C, 63.60; H, 4.59; N, 14.84. Found: C, 63.63; H, 4.50; N, 14.77%.

6-Acetyl-5-(1-pyrrolyl)-4-methyl-2-phenylthieno[2,3-*d*]-pyrimidine (4)

A mixture of 6-acetyl-5-amino-4-methyl-2-phenylthieno[2,3-*d*]pyrimidine **3** (2.83 g, 0.01 mol), 2,5-dimethoxytetrahydrofuran (1.26 g, 0.01 mol), in glacial acetic acid (20 mL) was refluxed for 12 h. After cooling, the resulting solid product was collected by filtration, washed with water, and the crude product recrystallized from ethanol/glacial acetic acid to give 2.96 g of gray white needles (89% yield), mp 204 °C; IR: ν 1660 (CO) cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 2.09 (3H, s, $COCH_3$), 2.20 (3H, s, CH_3), 6.50 (2H, t, 3,4-H of pyrrolyl), 6.87 (2H, t, 2,5-H of pyrrolyl), 8.56-8.54, 7.51-7.49 (5H, m, phenyl-H); MS: 333 (M^+, 100), 318 (35), 290 (36), 277 (4), 223 (4), 185 (8), 166 (10), 160 (14), 116 (10), 103 (20), 77 (19), 51 (5). Anal. Calcd. for $C_{19}H_{15}N_3OS$: C, 68.46; H, 4.50; N, 12.61. Found: C, 68.33; H, 4.52; N, 12.59%.

Reactions of 6-acetyl-5-(1-pyrrolyl)-4-methyl-2-phenylthieno[2,3-*d*]pyrimidine 4 with the primary amines 5a-d, 5f

General Procedure: A mixture of acetyl compound **4** (0.33 g, 1 mmol) and the primary amines **5a-d**, **5f** (1.1 mmol), namely, methylamine, ethylamine, propylamine butylamine and hydroxylamine hydrochloride, in pyridine (5 mL), was refluxed for 10 h, and cooled. The separated solid was filtered and recrystallized from an appropriate solvent into the corresponding Schiff's bases **6a-d**, **6f** respectively. The physical constants and spectral data of compounds **6a-d**, **6f** are recorded in Tables 1, 2.

Reactions of 6-acetyl-5-(1-pyrrolyl)-4-methyl-2-phenylthieno[2,3-*d*]pyrimidine 4 with the hydrazine hydrate 5e

A mixture of acetyl compound **4** (0.33 g, 1 mmol) and an excess of hydrazine hydrate **5e** (4 mL, 85% solution 0.04 mol) was refluxed in absolute ethanol (10 mL) for 24 h. After

Table 1. Physical and analytical data of compounds **6a-f**

Compound	R	Yield % (recrystallization solvent)	Mp °C	Molecular Formula	Element Analysis (%) Calcd/Found		
					C	H	N
6a	CH_3	97 pyridine/DMF	179	$C_{20}H_{18}N_4S$	69.36 69.46	5.20 5.55	16.18 16.22
6b	C_2H_5	93 pyridine/DMF	220	$C_{21}H_{20}N_4S$	70.00 70.16	5.55 5.58	15.55 15.32
6c	C_3H_7	64 pyridine/DMF	192	$C_{22}H_{22}N_4S$	70.58 70.56	5.88 5.78	14.97 15.01
6d	C_4H_9	77 pyridine/DMF	198	$C_{23}H_{24}N_4S$	71.13 71.12	6.18 6.36	14.43 14.44
6e	NH_2	78 DMF/ethanol	164	$C_{19}H_{17}N_5S$	65.70 65.52	4.89 4.91	20.17 20.30
6f	OH	98 DMF/H_2O	264	$C_{19}H_{16}N_4OS$	65.51 65.48	4.59 4.52	16.09 16.22

Table 2. Spectral data of compounds **6a-f**

Compound	MS (M^+)	^{1}H NMR ($CDCl_3$) δ (ppm)
6a	346 (36), 333 (100), 318 (35), 290 (44), 277 (4), 228 (30), 187 (14), 160 (14), 116 (8), 103 (20), 77 (18), 56 (29).	1.66 (3H, s, CH_3), 2.07 (3H, s, CH_3), 2.20 (3H, s, CH_3), 6.50 (2H, t, 3,4-H of pyrrolyl), 6.87 (2H, t, 2,5-H of pyrrolyl), 8.56-8.53, 7.52-7.48 (5H, m, phenyl-H).
6b	360 (52), 333 (100), 318 (41), 301 (50), 290 (8), 277 (4), 228 (20), 199 (14), 160 (8), 116 (8), 103 (18), 77 (19), 68 (22).	1.31 (3H, t, *J* = 1.5 Hz, CH_3), 1.65 (3H, s, CH_3), 2.06 (3H, s, CH_3), 3.49 (2H, q, *J* = 1.5 Hz, CH_2), 6.50 (2H, t, 3,4-H of pyrrolyl), 6.88 (2H, t, 2,5-H of pyrrolyl), 8.56-8.53, 7.51-7.48 (5H, m, phenyl-H).
6c	374 (100), 359 (38), 345 (52), 332 (85), 318 (82), 302 (98), 290 (22), 275 (25), 251 (39), 213 (38), 172 (28), 116 (22), 103 (54), 77 (50), 68 (36), 52 (20).	1.02 (3H, t, *J* = 1.5 Hz, CH_3), 1.65 (3H, s, CH_3), 1.78-1.71 (2H, m, CH_2), 2.15 (3H, s, CH_3), 3.40 (2H, t, *J* = 1.4 Hz, CH_2), 6.42 (2H, t, 3,4-H of pyrrolyl), 6.83 (2H, t, 2,5-H of pyrrolyl), 8.54-8.52, 7.52-7.47 (5H, m, phenyl-H).
6d	388 (98), 373 (60), 359 (24), 345 (48), 332 (78), 318 (74), 302 (100), 290 (18), 275 (24), 251 (36), 213 (34), 172 (24), 128 (16), 116 (18), 103 (50), 77 (44), 56 (43).	0.98 (3H, t, *J* = 2.1 Hz, CH_3), 1.50-1.42 (2H, m, CH_2), 1.65 (3H, s, CH_3), 1.73-1.68 (2H, m, CH_2), 2.14 (3H, s, CH_3), 3.44 (2H, t, *J* = 1.4 Hz, CH_2), 6.42 (2H, t, 3,4-H of pyrrolyl), 6.83 (2H, t, 2,5-H of pyrrolyl), 8.54-8.51, 7.48-7.47 (5H, m, phenyl-H).
6e	347 (28), 331 (100), 316 (10), 290 (18), 282 (30), 253 (8), 228 (16), 213 (6), 165 (4), 122 (3), 103 (21), 77 (16), 56 (6).	1.76 (3H, s, CH_3), 2.09 (3H, s, CH_3), 6.53 (2H, t, 3,4-H of pyrrolyl), 6.84 (2H, t, 2,5-H of pyrrolyl), 8.27-8.14, 7.72-7.58 (5H, m, phenyl-H).[a]
6f	348 (6), 331 (100), 317 (4), 290 (4), 239 (4), 228 (16), 213 (8), 165 (4), 103 (21), 77 (16), 56 (3).	1.65 (3H, s, CH_3), 2.08 (3H, s, CH_3), 6.35 (2H, t, 3,4-H of pyrrolyl), 7.09 (2H, t, 2,5-H of pyrrolyl), 8.46-8.44, 7.55-7.52 (5H, m, phenyl-H), 12.12 (1H, s, OH).[b]

[a] ^{1}H NMR in CF_3COOD

[b] ^{1}H NMR in DMSO-d_6

cooling, the resulting solid product was collected by filtration and washed with water. The physical constants and spectral data of compound **6e** is recorded in Tables 1, 2.

Reaction of oxime derivative 6f with acetic anhydride

A mixture of oxime derivative **6f** (0.35 g, 1 mmol), pyridine (10 mL) and acetic anhydride (10 mL) was refluxed for 4 h. After cooling, the resulting solid product was collected by filtration, washed with water. and recrystallized from acetic acid/ethanol to give 0.25 g of gray white needles **8** (64% yield), mp 225 °C; IR: ν 1701 (CO) cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.84 (3H, s, CH_3), 2.22 (3H, s, $COCH_3$), 2.27 (3H, s, CH_3), 6.44 (2H, br, 3,4-H of pyrrolyl), 6.82 (2H, br, 2,5-H of pyrrolyl), 8.55, 7.51-7.50 (5H, m, phenyl-H); MS: 390 (M^+, 23), 347 (2), 331 (80), 317 (9), 302 (10), 290 (4), 264 (3), 225 (40), 185 (8), 213 (45), 199 (38), 165 (31), 116 (38), 104 (70), 77 (100), 51 (38). Anal. Calcd. for $C_{21}H_{18}N_4O_2S$: C, 64.61; H, 4.61; N, 14.35. Found: C, 64.56; H, 4.72; N, 14.32%.

6-(2,2-Dicyano-1-methylvinyl)-5-(1-pyrrolyl)-4-methyl-2-phenylthieno[2,3-*d*]pyrimidine (10)

A mixture of compound **4** (0.33 g, 1 mmol), malononitrile (0.07 g, 1 mmol) and ammonium acetate (0.82 g, 1.1 mmol) was refluxed in glacial acid (8 mL) for 5-6 h. After cooling, the resulting solid product was collected by filtration, washed with water, and the crude product recrystallized from ethanol/acetic acid to give 0.25 g (66% yield), mp 173 °C; IR: ν 2220, 2200 (CN) cm^{-1}; ^1H NMR ($CDCl_3$): δ 2.08 (3H, s, CH_3), 2.21 (3H, s, CH_3), 6.50 (2H, t, 3,4-H of pyrrolyl), 6.87 (2H, t, 2,5-H of pyrrolyl), 8.57-8.55, 7.52-7.50 (5H, m, phenyl-H); MS: 381 (M^+, 15), 355 (20), 333 (100), 317 (26), 302 (2), 290 (19), 264 (4), 237 (4), 229 (7), 186 (10), 160 (14), 116 (8), 103 (44), 77 (38), 51 (9). Anal. Calcd. for $C_{22}H_{15}N_5S$: C, 69.29; H, 3.93; N, 18.37. Found: C, 69.33; H, 3.72; N, 18.32%.

6-[2-Cyano-5-(4-dimethylaminophenyl)-2,4-pentadienenitrile)]-5-(1-pyrrolyl)-4-methyl-2-phenylthieno[2,3-*d*]-pyrimidine (11)

To a mixture of compound **10** (0.25 g, 0.65 mmol) and 4-(dimethylamino)benzaldehyde (0.10 g, 0.65 mmol) in dry DMF (5 mL), a few drops of piperidine was added. The reaction mixture was heated at 100 °C for 10 h. After cooling, the mixture was poured into water, acidified with hydrochloric acid, and the precipitated product was collected by filtration, washed with water, and the crude product recrystallized from ethanol/THF to give 0.30 g of red violet needles **11** (90% yield), mp 138 °C; IR: ν 2202 (CN) cm^{-1}; ^1H NMR ($CDCl_3$): δ 2.08 (3H, s, CH_3), 3.09 (6H, s, $N(CH_3)_2$), 6.50 (2H, t, 3,4-H of pyrrolyl), 6.88 (2H, t, 2,5-H of pyrrolyl), 6.70 (1H, d, J = 2.0 Hz, -CH=), 7.74 (1H, d, J = 2.0 Hz, =CH-), 8.57-8.55, 7.52-7.51 (9H, m, phenyl-H); MS: 512 (M^+,10), 464 (100), 421 (8), 397 (2), 332 (52), 318 (18), 290 (14), 232 (5), 146 (10), 134 (46), 78 (17). Anal. Calcd. for $C_{31}H_{24}N_6S$: C, 72.65; H, 4.68; N, 16.40. Found: C, 72.49; H, 4.60; N, 16.48%.

General procedure of 6-(3-substituted-acryloyl)-5-(1-pyrrolyl)-4-methyl-2-phenylthieno[2,3-*d*]pyrimidines (15a-k)

A mixture of compound **4** (0.33 g, 1 mmol), appropriate aldehydes **14a-k** (1.0 mmol) and NaOH (2.2 mmol) in absolute ethanol (10 mL) was stirred at room temperature for 24 h. The mixture was acidified with dilute acetic acid and the precipitated product was collected by filtration, washed with water, and the crude product recrystallized from THF/ethanol. The physical constants and spectral data of compounds **15a-k** are recorded in Tables 3, 4.

General procedure of 6-[3-cyano-2-ethoxy-4-(4-substituted-phenyl)-pyridin-6-yl]-5-(1-pyrrolyl)-4-methyl-2-phenylthieno[2,3-*d*]pyrimidines (21a-f)

A mixture of compound **4** (0.33 g, 1 mmol), arylmethylidenemalononitrile **18a-f** (1 mmol) and sodium ethoxide (0.07 g, 1 mmol) was refluxed in absolute ethanol (10 mL) for 10 h. After cooling, the mixture was poured into water, acidified with hydrochloric acid, and the precipitated product was collected by filtration, washed with water, and the crude product recrystallized from THF/ethanol. The physical constants and spectral data of compounds **21a-f** are recorded in Tables 5, 6.

6-(3-Dimethylamino-acryloyl)-5-(1-pyrrolyl)-4-methyl-2-phenylthieno[2,3-*d*]pyrimidine (23a)

To a solution of compound **4** (3.3 g, 0.01 mol) in dry xylene (40 mL), dimethylformamide dimethylacetal **22a** (1.20 g, 0.01 mol) was added. The reaction was heated under reflux for 6 h. The solvent was removed by evaporation under reduced pressure and the remainder was left to cool. The solid product so formed was collected by filtration, washed with petroleum ether (bp 40-60 °C), and the crude product was recrystallized from ethanol to give 3.22 g (83% yield) of **23a**, mp 212 °C; IR: ν 1628 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$): δ 2.23 (3H, s, CH_3), 2.58 (3H, s, NCH_3), 3.08 (3H, s, NCH_3), 4.41 (1H, d, J = 2.3 Hz, -COCH=), 6.50-6.43 (2H, m, 3,4-H of pyrrolyl), 6.87 (2H, t, 2,5-H of pyrrolyl), 7.75 (1H, d, J = 2.4

Table 3. Physical and analytical data of compounds **15a-k**

Compd.	R	Yield %	Mp °C	Molecular Formula	Element Analysis (%) Calcd/Found		
					C	H	N
15a	phenyl	93	169	$C_{26}H_{19}N_3OS$	74.10	4.51	9.97
					74.18	4.55	10.09
15b	4-$CH_3C_6H_4$	96	165	$C_{27}H_{21}N_3OS$	74.48	4.82	9.65
					74.16	4.58	9.66
15c	4-$CH_3OC_6H_4$	95	245	$C_{27}H_{21}N_3O_2S$	71.84	4.65	9.31
					71.56	4.78	9.33
15d	$(CH_3)_2NC_6H_4$	87	263	$C_{28}H_{24}N_4OS$	72.41	5.17	12.06
					72.12	5.36	12.14
15e	$(C_2H_5)_2NC_6H_4$	93	229	$C_{30}H_{28}N_4OS$	73.17	5.69	11.38
					73.11	5.74	11.30
15f	furyl	92	130	$C_{24}H_{17}N_3O_2S$	70.07	4.13	10.21
					70.11	4.21	10.30
15g	thienyl	98	262	$C_{24}H_{17}N_3OS_2$	67.44	3.98	9.83
					67.35	4.01	9.88
15h	2,4,6-$(CH_3)_3C_6H_2$	93	152	$C_{29}H_{25}N_3OS$	75.16	5.39	9.07
					75.22	5.45	9.08
15i	biphenyl	95	148	$C_{32}H_{23}N_3OS$	77.26	4.62	8.45
					77.22	4.65	8.56
15j	$(C_6H_5)_2NC_6H_4$	94	286	$C_{38}H_{28}N_4OS$	77.55	4.76	9.52
					77.48	4.52	9.22
15k	pyrenyl	95	278	$C_{36}H_{23}N_3OS$	79.26	4.22	7.70
					79.33	4.62	7.79

Hz, =CH-), 8.56-8.53, 7.51-7.49 (5H, m, phenyl-H); MS: 388 (M^+, 30), 371 (19), 357 (10), 344 (10), 322 (11), 289 (22), 274 (12), 239 (5), 187 (4), 160 (8), 142 (8), 116 (8), 104 (18), 98 (100), 77 (22), 55 (28). Anal. Calcd. for $C_{22}H_{20}N_4OS$: C, 68.04; H, 5.15; N, 14.43. Found: C, 68.23; H, 5.23; N, 14.49%.

6-(3-Dimethylamino-3-methyl-acryloyl)-5-(1-pyrrolyl)-4-methyl-2-phenyl-thieno[2,3-*d*]pyrimidine (23b)

This compound was synthesized from compound **4** (3.3 g, 0.01 mol) and N,N-dimethylacetamide dimethylacetal **22b** (1.34 g, 0.01 mol) in a manner similar to that described for the preparation of **23a**. It was recrystallized from ethanol/THF to give 3.09 g (77% yield), mp 260 °C; IR: ν 1626 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$): δ 2.07 (3H, s, CH_3), 2.20 (3H, s, CH_3), 2.58 (3H, s, NCH_3), 2.71 (3H, s, NCH_3), 4.77 (1H, s, -COCH=), 6.50-6.40 (2H, m, 3,4-H of pyrrolyl), 6.88-6.83 (2H, m, 2,5-H of pyrrolyl), 8.56-8.52, 7.52-7.47 (5H, m, phenyl-H); MS: 402 (M^+, 18), 369 (9), 331 (22), 304 (17), 289 (12), 239 (5), 187 (6), 160 (8), 116 (4), 111 (18), 70 (18), 56 (25). Anal. Calcd. for $C_{23}H_{22}N_4OS$: C, 68.65; H, 5.47; N, 13.93. Found: C, 68.53; H, 5.33; N, 14.01%.

6-(3-Cyano-1,2-dihydro-2-oxopyridin-6-yl)-5-(1-pyrrolyl)-4-methyl-2-phenylthieno[2,3-*d*]pyrimidine (26a)

A mixture of compound **23a** (0.39 g, 1 mmol), cyanoacetamide **24** (0.084 g, 1 mmol) and sodium ethoxide (0.14 g, 2.0 mmol) was refluxed in absolute ethanol (10 mL) for 10 h. After cooling, the mixture was poured into water, acidified with hydrochloric acid, and the precipitated product was collected by filtration, washed with water, and the crude product recrystallized from ethanol to give 0.4 g (98% yield) of **26a**, mp 245 °C; IR: ν 3243 (NH), 2193 (C≡N), 1720 (C=O) cm^{-1}; ^1H NMR (DMSO-d_6): δ 2.06 (3H, s, CH_3), 6.50-6.48 (2H, m, 3,4-H of pyrrolyl), 6.97 (2H, m, 2,5-H of pyrrolyl), 7.06 (1H, d, J = 1.0 Hz, 5-H of oxopyridyl), 8.02 (1H, d, J = 1.0 Hz, 4-H of oxopyridyl), 8.45-8.44, 7.53-7.51 (5H, m, phenyl-H); MS: 409 (M^+, 100), 383 (50), 355 (41), 333 (37), 290 (46), 250 (13), 185 (7), 116 (8), 104 (18), 77 (19), 56 (4). Anal. Calcd. for $C_{23}H_{15}N_5OS$: C, 67.48; H, 3.66; N, 17.11. Found: C, 67.23; H, 3.66; N, 17.01%.

6-(3-Cyano-1,2-dihydro-4-methyl-2-oxopyridin-6-yl)-5-(1-pyrrolyl)-4-methyl-2-phenylthieno[2,3-*d*]pyrimidine (26b)

This compound was synthesized from compound **23b** (0.40 g, 1.0 mmol) cyanoacetamide **24** (0.084 g, 1 mmol) and

Table 4. Spectral data of compounds **15a-k**

Compd.	IR ν (cm^{-1})	MS (M^+)	^1H NMR ($CDCl_3$) δ (ppm)
15a	1667 (C=O)	421	2.20 (3H, s, CH_3), 5.80 (1H, d, *J* = 3.1 Hz, COCH=), 6.63-6.42 (2H, m, 3,4-H of pyrrolyl), 6.87-6.80 (2H, m, 2,5-H of pyrrolyl), 8.57-8.55, 7.55-7.21 (11H, m, =CH- and phenyl-H).
15b	1663 (C=O)	435	2.27 (3H, s, CH_3), 2.39 (3H, s, CH_3), 6.02 (1H, d, *J* = 3.0 Hz, COCH=), 6.61-6.51 (2H, m, 3,4-H of pyrrolyl), 7.09-6.87 (2H, m, 2,5-H of pyrrolyl), 7.79 (1H, d, *J* = 3.0 Hz, =CH-), 8.59-8.58, 7.81-7.33 (9H, m, phenyl-H).
15c	1688 (C=O)	451	2.33 (3H, s, CH_3), 3.84 (3H, s, OCH_3), 5.75 (1H, d, *J* = 3.1 Hz, COCH=), 6.60 (2H, t, 3,4-H of pyrrolyl), 6.87 (2H, d, *J* = 1.0 Hz, 3,5-H of phenyl), 6.99 (2H, t, 2,5-H of pyrrolyl), 7.28 (2H, d, *J* = 1.0 Hz, 2,6-H of phenyl), 7.76 (1H, d, *J* = 3.0 Hz, =CH-), 8.59-8.55, 7.52-7.51 (5H, m, phenyl-H).
15d	1628 (C=O)	464	2.27 (3H, s, CH_3), 3.06 (6H, s, $N(CH_3)_2$), 5.70 (1H, d, *J* = 3.1 Hz, COCH=), 6.59-6.50 (2H, m, 3,4-H of pyrrolyl), 6.98-6.87 (2H, m, 2,5-H of pyrrolyl), 6.70 (2H, d, *J* = 1.0 Hz, 3,5-H of phenyl), 7.25 (2H, d, *J* = 1.5 Hz, 2,6-H of phenyl l), 7.75 (1H, d, *J* = 3.1 Hz, =CH-), 8.57-8.54, 7.51-7.50 (5H, m, phenyl-H).
15e	1628 (C=O)	492	1.21 (6H, t, *J* = 1.4 Hz, CH_3), 2.27 (3H, s, CH_3), 3.41 (4H, q, *J* = 1.4 Hz, CH_2), 5.68 (1H, d, *J* = 3.1 Hz, COCH=), 6.59-6.49 (4H, m, 3,4-H of pyrrolyl and 3,5-H of phenyl), 6.98-6.87 (2H, m, 2,5-H of pyrrolyl), 7.24 (2H, d, *J* = 1.0 Hz, 2,6-H of phenyl), 7.74 (1H, d, *J* = 3.0 Hz, =CH-), 8.56-8.53, 7.50-7.49 (5H, m, phenyl-H).
15f	1667 (C=O)	411	2.28 (3H, s, CH_3), 5.88 (1H, d, *J* = 3.1 Hz, COCH=), 6.59-6.48 (3H, m, 3,4-H of pyrrolyl and 4-H of furyl), 6.87 (2H, m, 2,5-H of pyrrolyl), 7.00 (1H, d, *J* = 2.0 Hz, 3-H of furyl), 8.15 (1H, d, *J* = 3.0 Hz, =CH-), 8.63-8.54, 7.58-7.48 (6H, m, 5-H of furyl and phenyl-H).
15g	1641 (C=O)	427	2.11 (3H, s, CH_3), 5.47 (1H, d, *J* = 3.2 Hz, COCH=), 6.63-6.39 (3H, m, 3,4-H of pyrrolyl and 4-H of thienyl), 7.06-7.03 (2H, m, 2,5-H of pyrrolyl), 7.13 (1H, d, *J* = 1.0 Hz, 3-H of thienyl), 7.80 (1H, d, *J* = 3.0 Hz, =CH-), 8.48-8.45, 7.54-7.44 (6H, m, 5-H of thienyl and phenyl-H).
15h	1643 (C=O)	463	2.10 (3H, s, CH_3), 2.22 (3H, s, CH_3), 2.28 (3H, s, CH_3), 2.42 (3H, s, CH_3), 5.88 (1H, d, *J* = 4.0 Hz, COCH=), 6.51-6.45 (2H, m, 3,4-H of pyrrolyl), 6.88-6.84 (2H, m, 2,5-H of pyrrolyl), 7.39 (1H, d, *J* = 1.2 Hz, =CH-), 8.58-8.53, 7.54-7.51 (7H, m, phenyl-H).
15i	1667 (C=O)	497	2.18 (3H, s, CH_3), 5.75 (1H, d, *J* = 3.0 Hz, COCH=), 6.50 (2H, t, 3,4-H of pyrrolyl), 6.86 (2H, t, 2,5-H of pyrrolyl), 8.65-8.54, 7.63-7.38 (15H, m, =CH- and phenyl-H).
15j	1631 (C=O)	588	2.30 (3H, s, CH_3), 5.71 (1H, d, *J* = 3.0 Hz, COCH=), 6.55 (2H, t, 3,4-H of pyrrolyl), 6.98-6.94 (4H, m, 3,5-H of phenyl and 2,5-H of pyrrolyl), 7.74 (1H, d, *J* = 3.0 Hz, =CH-), 8.59-8.57, 7.53-7.13 (17H, m, phenyl-H).
15k	1679 (C=O)	545	2.06 (3H, s, CH_3), 5.79 (1H, d, *J* = 3.1 Hz, COCH=), 6.51 (2H, m, 3,4-H of pyrrolyl), 6.90 (2H, m, 2,5-H of pyrrolyl), 8.62-8.42, 8.32-8.05 (15H, m, =CH-, phenyl-H and pyrenyl-H).

sodium ethoxide (0.14 g, 2.0 mmol) in a manner similar to that described for the preparation of **26a**. It was recrystallized from ethanol/THF to give 0.18 g (43% yield), mp 146 °C; IR: ν 3122 (NH), 2217 (C≡N), 1711 (C=O) cm^{-1}; ^1H NMR (DMSO-d_6): δ 2.10 (3H, s, CH_3), 2.13 (3H, s, CH_3), 6.40-6.26 (2H, m, 3,4-H of pyrrolyl), 6.93-6.84 (2H, m, 2,5-H of pyrrolyl), 7.87 (1H, s, 5-H of oxopyridyl), 8.47-8.45, 7.47-7.41 (5H, m, phenyl-H); MS: 423 (M^+, 60), 385 (71), 356 (42), 333 (100), 290 (90), 246 (14), 228 (20), 202 (34), 187 (18), 160 (24), 104 (79), 77 (62), 56 (28). Anal. Calcd. for $C_{24}H_{17}N_5OS$: C, 68.08; H, 4.01; N, 16.54. Found: C, 68.23; H, 4.12; N, 16.55%.

6-(3-Acetamidopyran-2-on-6-yl)-5-(1-pyrrolyl)-4-methyl-2-phenylthieno[2,3-*d*]pyrimidine (30a)

A mixture of N-acetylglycine **27a** (0.12 g, 1 mmol) in

Table 5. Physical and analytical data of compounds **21a-f**

Compd.	Ar	Yield %	Mp °C	Molecular Formula	Element Analysis (%) Calcd/Found		
					C	H	N
21a	phenyl	86	149	$C_{31}H_{23}N_5OS$	72.51	4.48	13.64
					72.46	4.55	13.42
21b	4-$CH_3C_6H_4$	84	151	$C_{32}H_{25}N_5OS$	72.86	4.74	13.28
					72.99	4.58	13.32
21c	4-ClC_6H_4	71	147	$C_{31}H_{22}ClN_5OS$	67.94	4.01	12.78
					67.88	4.11	12.69
21d	4-CNC_6H_4	95	199	$C_{32}H_{22}N_6OS$	71.37	4.08	15.61
					71.12	4.36	15.44
21e	$(CH_3)_2NC_6H_4$	88	163	$C_{33}H_{28}N_6OS$	71.22	5.03	15.10
					71.52	4.91	15.30
21f	biphenyl	93	132	$C_{37}H_{27}N_5OS$	75.38	4.58	11.88
					75.48	4.52	11.97

Table 6. Spectral data of compounds **21a-f**

Compd.	IR ν (cm^{-1})	MS (M^+)	^{1}H NMR ($CDCl_3$) δ (ppm)
21a	2225 (CN)	513 (100), 498 (5), 484 (36), 468 (4), 423 (2), 357 (1), 290 (3), 242 (2), 213 (1), 140 (1), 103(1).	1.56 (3H, t, *J* = 1.8 Hz, CH_3), 2.35 (3H, s, CH_3), 4.64 (2H, q, *J* = 2.1 Hz, OCH_2), 6.53-6.49 (2H, m, 3,4-H of pyrrolyl), 6.98-6.87 (2H, m, 2,5-H of pyrrolyl), 7.41 (1H, s, 5-H of pyridyl), 8.63-8.54, 7.53-7.47 (10H, m, phenyl-H).
21b	2225 (CN)	527 (100), 512 (30), 498 (44), 487 (10), 472 (8), 393 (3), 357 (2), 335 (10), 290 (11), 249 (8), 185 (1), 105 (5), 77 (1).	1.56 (3H, t, *J* = 1.7 Hz, CH_3), 2.33 (3H, s, CH_3), 2.44 (3H, s, CH_3), 4.62 (2H, q, *J* = 2.1 Hz, OCH_2), 6.66-6.39 (4H, m, 3,4-H of pyrrolyl and 3,5-H of phenyl), 6.97-6.87 (2H, m, 2,5-H of pyrrolyl), 8.62-8.54, 7.51-7.17 (8H, m, 5-H of pyridyl and phenyl-H).
21c	2217 (CN)	547.5 (100), 532 (5), 518 (40), 507 (18), 493 (12), 477 (4), 363 (1), 335 (5), 290 (9), 242 (22), 162 (1), 104 (2), 77 (1).	1.54 (3H, t, *J* = 2.3 Hz, CH_3), 2.34 (3H, s, CH_3), 4.63 (2H, q, *J* = 2.1 Hz, OCH_2), 6.65-6.39 (4H, m, 3,4-H of pyrrolyl and 3,5-H of phenyl), 6.97-6.86 (2H, m, 2,5-H of pyrrolyl), 8.61-8.51, 7.51-7.27 (8H, m, 5-H of pyridyl and phenyl-H).
21d	2217 (CN)	538 (10), 531 (100), 516 (36), 502 (20), 484 (10), 451 (5), 422 (16), 381 (10), 316 (22), 290 (80), 263 (4), 185 (4), 160 (1), 128 (16), 104 (4).	1.46 (3H, t, *J* = 1.4 Hz, CH_3), 2.18 (3H, s, CH_3), 4.53 (2H, q, *J* = 2.0 Hz, OCH_2), 6.53-6.27 (4H, m, 3,4-H of pyrrolyl and 3,5-H of phenyl), 7.03-6.92 (2H, m, 2,5-H of pyrrolyl), 8.46-8.42, 7.47-7.39 (8H, m, 5-H of pyridyl and phenyl-H).[a]
21e	2217 (CN)	556 (100), 541 (9), 527 (16), 511 (5), 466 (5), 422 (1), 333 (3), 316 (10), 290 (2), 264 (4), 147 (1), 134 (11), 77 (1).	1.53 (3H, t, *J* = 1.4 Hz, CH_3), 2.30 (3H, s, CH_3), 3.06 (6H, s, $N(CH_3)_2$), 4.60 (2H, q, *J* = 2.0 Hz, OCH_2), 6.56-6.38 (2H, m, 3,4-H of pyrrolyl), 6.88-6.85 (2H, m, 2,5-H of pyrrolyl), 6.74 (2H, d, *J* = 2.0 Hz, 3,5-H of phenyl), 7.40 (2H, d, *J* = 1.8 Hz, 2,6-H of phenyl), 8.55-8.52, 7.50-7.46 (6H, m, 5-H of pyridyl and phenyl-H).
21f	2208 (CN)	589 (100), 574 (4), 564 (83), 560 (38), 549 (24), 535 (16), 512 (4), 423 (2), 380 (3), 330 (2), 312 (18), 290 (5), 280 (4), 178 (2), 167 (16), 152 (4), 77 (2).	1.56 (3H, t, *J* = 1.3 Hz, CH_3), 2.33 (3H, s, CH_3), 4.65 (2H, q, *J* = 2.1 Hz, OCH_2), 6.60-6.39 (4H, m, 3,4-H of pyrrolyl and 3,5-H of phenyl), 6.92-6.86 (2H, m, 2,5-H of pyrrolyl), 8.64-8.50, 7.70-7.41 (13H, m, 5-H of pyridyl and phenyl-H).

[a] ^{1}H NMR in DMSO-d_6

acetic anhydride (5 mL) was heated for ten minutes; compound **23a** (0.39 g, 1 mmol) was added. The reaction mixture was refluxed for 10 h. After cooling, the resulting solid product was collected by filtration, washed with ethanol and water, and the crude product was recrystallized from ethanol/acetic acid to give 0.19 g (43% yield), mp 243 °C; IR: ν 3266 (NH), 1728 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$): δ 2.21 (3H, s, CH_3), 2.32 (3H, s, CH_3), 6.53-6.50 (2H, m, 3,4-H of pyrrolyl), 6.78 (2H, t, 2,5-H of pyrrolyl), 6.87 (1H, d, *J* = 1.4 Hz, 5-H of pyranyl), 8.02 (1H, br, NH), 8.10 (1H, d, *J* = 1.6 Hz, 4-H of pyranyl), 8.56-8.54, 7.52-7.47 (5H, m, phenyl-H); MS: 442 (M^+, 22), 427 (5), 399 (24), 384 (71), 355 (13), 331 (32), 318 (71), 290 (22), 246 (14), 232 (18), 222 (100), 208 (54), 194 (28), 179 (21), 121 (43), 106 (88), 77 (59), 56 (19). Anal. Calcd. for $C_{24}H_{18}N_4O_3S$: C, 65.15; H, 4.07; N, 12.67. Found: C, 65.19; H, 4.12; N, 12.55%.

6-(3-Benzolyaminopyran-2-on-6-yl)-5-(1-pyrrolyl)-4-methyl-2-phenylthieno[2,3-*d*]pyrimidine (30b)

This compound was synthesized from hippuric acid **27b** (0.18 g, 1.0 mmol), acetic anhydride (5 mL) and compound **23a** (0.39 g, 1 mmol) in a manner similar to that described for the preparation of **30a**. It was recrystallized from ethanol/acetic acid to give 0.16 g (32% yield), mp 345 °C; IR: ν 3388 (NH), 1711, 1671 (C=O) cm^{-1}; ^1H NMR (CF_3COOD): δ 2.81 (3H, s, CH_3), 6.28 (1H, d, *J* = 2.0 Hz, 5-H of pyranyl), 6.89 (2H, m, 3,4-H of pyrrolyl), 7.07 (2H, m, 2,5-H of pyrrolyl), 8.75 (1H, d, *J* = 1.6 Hz, 4-H of pyranyl), 8.47, 8.06-7.73 (10H, m, phenyl-H); MS: 504 (M^+, 18), 486 (10), 371 (6), 331 (12), 253 (2), 213 (3), 105 (100), 77 (46), 51 (3). Anal. Calcd. for $C_{29}H_{20}N_4O_3S$: C, 69.04; H, 3.96; N, 11.11. Found: C, 69.31; H, 3.72; N, 11.12%.

6-(3-Benzolyamino-4-methylpyran-2-on-6-yl)-5-(1-pyrrolyl)-4-methyl-2-phenylthieno[2,3-*d*]pyrimidine (30c)

This compound was synthesized from hippuric acid **27b** (0.18 g, 1 mmol), acetic anhydride (5 mL) and compound **23b** (0.40 g, 1 mmol) in a manner similar to that described for the preparation of **30a**. It was recrystallized from ethanol/acetic acid to give 0.15 g (29% yield), mp 186 °C; IR: ν 3126 (NH), 1720 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$): δ 2.08 (3H, s, CH_3), 2.21 (3H, s, CH_3), 6.50 (2H, t, 3,4-H of pyrrolyl), 6.87 (2H, t, 2,5-H of pyrrolyl), 8.57-8.55, 7.52-7.51 (11H, m, 5-H of pyranyl and phenyl-H); MS: 518 (M^+, 10), 413 (3), 396 (2), 332 (100), 318 (23), 290 (9), 246 (14), 229 (2), 202 (34), 160 (3), 104 (8), 77 (9), 56 (3). Anal. Calcd. for $C_{30}H_{22}N_4O_3S$: C, 69.49; H, 4.24; N, 10.81. Found: C, 69.44; H, 4.12; N, 10.55%.

ACKNOWLEDGEMENT

We are grateful to the Nanya Institute of Technology for financial support.

Received June 28, 2004.

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