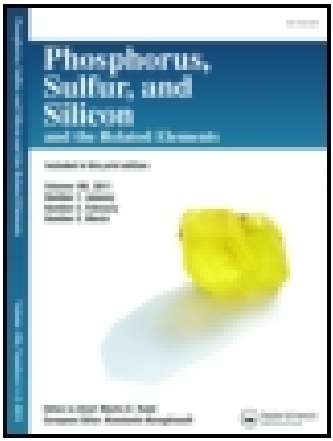

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A CONVENIENT SYNTHESIS OF DITHIENO[2,3-b] [2,3-h]QUINOLINES AND PYRIMIDO [4′,5′:4,5]THIENO [2,3-b]THIENO[2,3-h]QUINOLINES

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A CONVENIENT SYNTHESIS OF DITHIENO[2,3-b] [2,3-h]QUINOLINES AND PYRIMIDO [4′,5′:4,5]THIENO [2,3-b]THIENO[2,3-h]QUINOLINES

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6,7-Dihydrobenz[b]thiophen-4(5H)one (**1**) was condensed with 4- chlorobenzaldehyde to yield the benzylidene derivative **2** which underwent Michael addition reacting with cyanothioacetamide in methanolic sodium methoxide solution to give the thienoquinoline **3.** Compound **3** was reacted with α- halo compounds to obtain the substituted thio intermediates **4a-f,** which upon treatment with sodium ethoxide produce the dithienoquinoline derivatives **5a-f.** Thienopyrimidothienoquinoline e.g. **9** was obtained from the reaction of o- aminocarboxamide derivative **5d** with triethyl orthoformate.

Keywords: Thienoquinolines; dithienoquinolines; thienopyrimidothienoquinolines

INTRODUCTION

6,7-Dihydrobenz[b]thiophen-4(5H)one (**1**) has been the object of attention on many research groups for used as a starting material for the synthesis of various ring systems e.g thienobenzothiazole[1], thienobenzopyrane[2], thienobenzopyrazole[3] and thienocinnoline[4]. As part of our program dealing with the synthesis of poly fused heterocyclic systems containing the thiophene moiety[5–8] the synthesis of some thienoquinoline and dithienoquinoline derivatives is reported.

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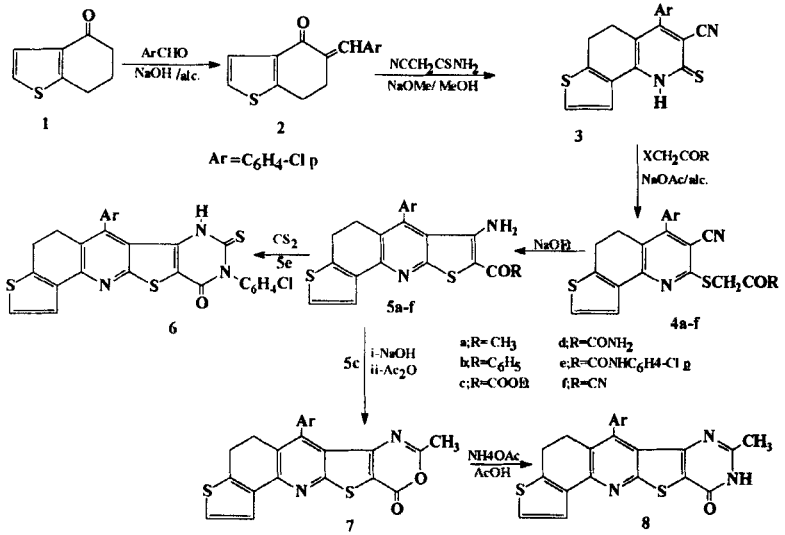
RESULTS AND DISCUSSION

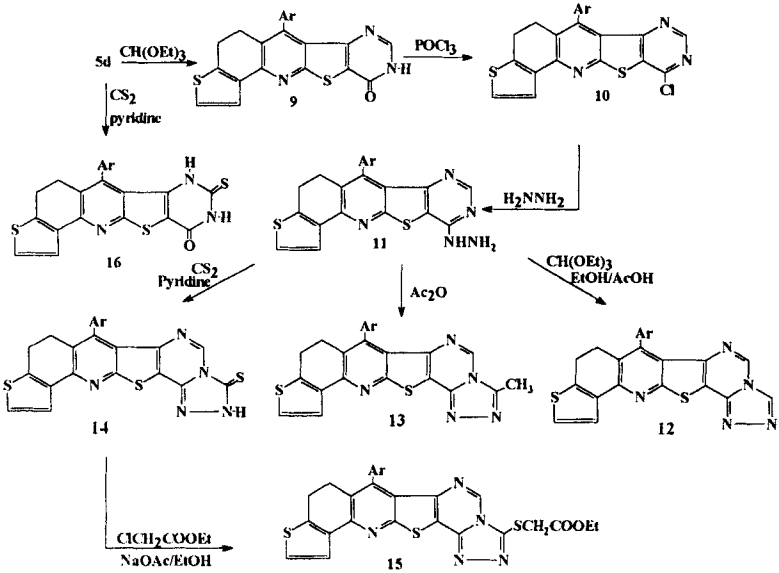
The target compound **3** was prepared through condensation of **1** with 4-chlorobenzaldehyde in alcoholic sodium hydroxide to give the benzylidene derivative **2** which underwent Michael addition via the reaction with cyanothioacetamide in methanolic sodium methoxide solution to give the thienoquinolinthione **3.** Compound **3** was easily S- alkylated through the reaction with α-halo compounds in ethanol in the presence of anhydrous sodium acetate to afford the substitutedthio intermediates **4a-f**. These upon treatment with sodium ethoxide produce the dithienoquinoline derivatives **5a-f**. Some of the latter derivatives were chosen and subjected to additional reaction to build up pentacyclic heterocycles e.g. the reaction of **5e** with carbon disulfide in pyridine led to the formation of the pyrimidinthione derivative **6.** Also, the alkaline hydrolysis of **5c** with sodium hydroxide gave the sodium salt. This on refluxing in acetic anhydride afforded the oxazinone compound **7,** which in turn was reacted with ammonium acetate in acetic acid to give the pyrimidinone derivative **8.**



SCHEME 1

The reaction of **5d** with triethyl orthoformate in ethanol in the presence of catalytic amount of acetic acid led to the formation of thieno[2,3-h]pyrimido[4′,5′:4,5] thieno[2,3-b]quinoline derivative **9.** The

chloro compound **10** was synthesized by refluxing the pyrimidinone **9** in phosphorous oxychloride. The chlorine atom in **10** underwent displacement reaction when reacted with hydrazine hydrate to afford the hydrazino derivative **11** in good yield. The hydrazino compound **11** was used as key intermediate to synthesize a new ring system, namely triazolothienopyrimidothienoquinoline, through the reaction with reagents such as triethyl orthoformate, acetic anhydride or carbon disulfide to give compounds **12–14** respectively. The triazolthione **14** was reacted with ethyl chloroacetate in ethanol in the presence of anhydrous sodium acetate to give the thioester derivative **15.** Another pyrimidine derivative **16** was obtained through the reaction of the o- amino amide derivative **5d** with carbon disulfide in pyridine.



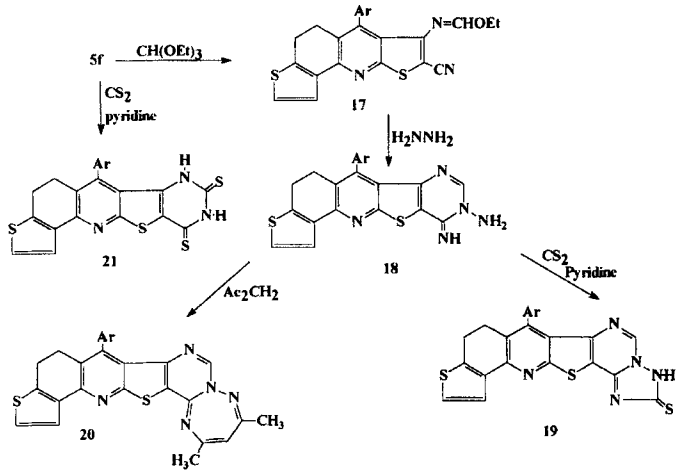
SCHEME 2

The reaction of compound **5f** with triethyl orthoformate in acetic anhydride afforded the ether derivative **17** which in turn was reacted with hydrazine hydrate in dioxan on cold to afford the o- amino imino derivative **18.** The latter compound was reacted with carbon disulfide and with acetyl acetone to give the triazolo and the triazipino derivatives **19** and **20** respectively. The pyrimidindithione derivative **21** was obtained from the reaction of **5f** with carbon disulfide in pyridine.

TABLE I Physical and spectral data of compounds **4a-f** and **5a-f**

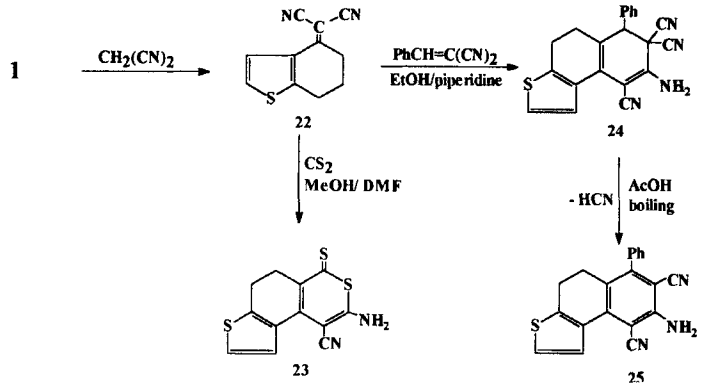
compound no.	*M.P°C yield %*	*Molecular formula*	*IR γ*	*^{1}HNMR δ*
4a	259	$C_{21}H_{15}ClN_2OS_2$	2200(CN)	(CDCl3):2.3(s,3H,CH_3),2.5–2.9(m,4H,2CH_2), 4.1 (s,2H,CH2),7.1–7.9(m,6H,Ar-Hand
	68	410.94	1700(C=O	4.2 2CH thiophene)
4b	225	$C_{26}H_{17}ClN_2OS_2$	2200(CN)	(CDCl3):2.5–2.9(m,4H,2CH_2) ,4.1(s,2H,CH_2), 7.2–7.9(m, 1 1H, Ar-H and 2CH thi
	74	472.05	1690(C=O	ophene)
4c	190	$C_{22}H_{17}ClN_2O_2S_2$	2200(CN),	(CDCl3):1.1–1.3(t,3H,CH3),2.6–2.9(m,4H,2CH_2),4.0(s,2H,CH_2),4.2–4.4 (q,2H,CH_2)
	81	440.04	1730 (C=O)	7.1-7.9(m,6H,Ar-H and 2CH thiophene)
4d	203	$C_{20}H_{14}ClN_3OS_2$	3300,3240(NH_2),	(DMSO):2.6–2.9(m,4H,2CH_2),4.2(s,2H,CH_2),5.6
	77	411.24	2200(CN),1690 (C=O)	(s,2H,NH_2),7.2–7.8(m,6H,Ar-Hand 2CH thiophene)
4e	209	$C_{26}H_{17}Cl_2N_3OS_2$	3320(NH),2200	(DMSO):2.5–2.9(m,4H,2CH_2),4.2(s,2H,CH_2),7.2-8.1(m,10H,Ar-Hand 2CH thi
	78	521.01	(CN), 1680(C=O)	ophene),8.9(s, 1H,NH)
4f	205	$C_{20}H_{12}ClN_3S_2$	2200(br.2CN)	(CDCl3):2.6–2.9(m,4H,2CH_2),4.2 (s,2H,CH_2),7.2-7.8(m,6H,Ar-Hand 2CH thiophene)
	711	393.01		
5a	290	$C_{21}H_{15}ClN_2OS_2$	3460,3360	(CDCl3):2.4(s,3H,CH_3),2.5–2.9(m,4H,2CH_2).6.1
	76	410.94	(NH_2), 1650 (C=O)	(s, 2H,NH_2).7.1–7.9(m,6H,Ar-Hand 2CH thiophene)

compound no.	*M.P°C yield %*	*Molecular formula*	*IR γ*	*^{1}HNMR δ*
5b	255	$C_{26}H_{17}ClN_2OS_2$	3480,3360	(CDC13):2.5–2.9(m,4H,2CH2) ,6.4(s,2H,NH_2),7.0-7.8(m,11H,Ar-H and 2CH thiophene)
	83	472.05	(NH_2), 1650 (C=O)	
5c	220	$C_{22}H_{17}ClN_2O_2S_2$	3460,3340	(CDCl3):1.1-1.3(t,3H,CH_3),2.6-2.9(m,4H,2CH_2)
		440.04	(NH_2),1660 (C=0)	,4.2-4.4(q,2H,CH_2)6.1(s,2H,NH_2),7.1-7.9(m,6H,Ar-H and 2 CH thiophene)
5d	265	$C_{20}H_{14}ClN_3OS_2$	3400,3300,3220	(DMSO):2.6–2.9(m,4H,2CH_2),5.6(s,2H,NH2)6.0
	74	411.24	(2NH_2), 1640 (C=O)	(s,2H,NH2),7.2–7.8(m,6H,Ar-Hand 2CH thiophene)
5e	240	$C_{26}H_{17}Cl_2N_3OS_2$	3460,3380,3300	(DMSO):2.5–3.0(m,4H,2CH_2),6.7(s,2H,NH_2),7.3-
	77	521.01	(NH_2,NH),1650 (C=O)	8.2(m, 10H, Ar-H and 2CH thiophene), 9. 1(s, 1H,NH)
5f	242	$C_{20}H_{12}ClN_3S_2$	3450,3350(NH_2),	(CDCl3):2.5–2.9(m,4H,2CH2),6.3 (s,2H,NH_2),7.2-7.8(m, 6H, Ar-Hand 2CH thiophene)
	76	393.01	2220(CN)	.



SCHEME 3

Compound **1** was condensed with malononitrile in ethanol in the presence of catalytic amount of triethyl amine to afford the dicyanomethylene derivative **22**[9] compound **22** was reacted with carbon disulfide in methanol / DMF mixture to give the thiopyrane [10] derivative **23** in very low yield. Compound **22** was subjected to Michael reaction when reacted with bezylidene malononitrile in ethanol in the presence of a few drops of piperidine to give the dicyano naphthothiophene derivative **24,** which in turn loses an HCN molecule when refluxed in acetic acid to give compound **25** [11].



SCHEME 4

EXPERIMENTAL

Melting points are uncorrected and were determined on Gallen Kamp melting point apparatus. IR spectra were recorded on Pye- Unicam sp3 – 100 spectrophotometer using KBr wafer technique. ^{1}HNMR spectra were recorded on a Varian 390 90MHz NMR spectrometer in the suitable deu-treated solvent, using TMS as internal standard. Mass spectra were determined on JEOL JMS600 mass spectrometer. Elemental analyses were determined on Perkin-Elmer 240C microanalyzer and all compounds gave results in acceptable range.

6, 7-Dihydrobenz[b]thiophen-4(5H)one (1)

This compound was synthesized according to literature procedure, m.p. 35 °C, [4] 35–37 °C.

5-(4-chlorobenzylidene)-6,7-Dihydrobenz[b]thiophen-4one (2)

General procedure

A mixture of **(1)** (0.01 mol) and 4-chlorobenzaldehyde (0.01mol) in ethanolic sodium hydroxide solution (50 ml, 10%) was stirred for 2 h. The solid product separated was filtered off and recrystallized from ethanol into buff crystals m.p.157 °C, yield 54 %; $C_{15}H_{11}ClOS$(274.02); IRυ:2950 (aliph.CH), 1660 (C=O); ^{1}HNMR(DMSO)δ= 2.1–2.3(t, 2H, CH_2), 2.9–3.1(t, 2H, CH_2), 7.3–8.1(m, 7H, Ar-H, 2CH thiophene and =CH).

3-Cyano-4-(4-chlorophenyl)-5,6-dihydrothieno[2,3-h] quinolin-2(1H)-thione (3)

A mixture of the benzylidene derivative 2 (0.01 mol) and cyanothioacetamide (0.01mol) in methanolic sodium methoxide solution (0.0lmol Na in 50 ml methanol) was heated on water bath at 50 °C for 6h. The solvent was removed under reduced pressure, the residue was dissolved in 100 ml water and acidified with dil. hydrochloric acid. The solid product was filtered off and recrystallized from dioxan into orange crystals of 3 m.p. 265 °C, yield 42 %; $C_{18}H_{11}ClN_2S_2$(354.0); IRυ: 3200 (NH), 2200(CN),

1620(C=N); ^{1}HNMR(DMSO)δ = 2.5–2.9(m, 4H, 2CH2), 7.3–7.9(m, 6H, Ar-H and 2CH thiophene),10.8(s, 1H, NH); MS: m/z 354.

3-Cyano-4-(4-chlorophenyl)-5,6-dihydro-2-substitutedthiothieno [2,3-h] quinolines (4a-f)

General procedure

A mixture of **3** (0.01mol) and α-halo carbonyl compound (0.01mol) in ethanol (30 ml) in the presence of anhydrous sodium acetate was refluxed for 2 h. The solid product separated from the hot mixture was filtered off, washed with water and recrystallized from ethanol. The physical constants and spectra data of compounds 4a-f were summarized in table I.

3-Amino-4-(4-chlorophenyl)-5,6-dihydro-2-substituteddithieno[2,3-b] [2,3-h] quinolines (5a-f)

General procedure

A sample of compounds **4a-f** (0.5 g) in 20 ml ethanolic ethoxide solution was refluxed for 1 h. The solid product separated from the hot mixture was filtered off and recrystallized from the proper solvent. The physical constants and spectral data of compounds **5a-f** were summarized in table I.

3,12di(4-chlorophenyl)-10,11-dihydro-4-oxo dihydropyrimido [4′, 5′:4, 5]thieno[2,3-b] thieno[2,3-h]quinolin-2(1H)thione (6)

A sample of **5e** (0.5 g) and carbon disulfide (3 ml) in pyridine (10 ml) was heated on water bath until the hydrogen sulfide was ceased (6 h). The solid product separated from the hot mixture was filtered off and recrystallized from dioxan into golden yellow crystals m.p. 328 °C, yield 61 %; $C_{27}H_{15}Cl_2N_3OS_3$(564.52); IRυ: 3300 (NH), 1680(C=O) Cm^{-1}; ^{1}HNMR(DMSO)δ = 2.5–2.9(m, 4H, $2CH_2$), 7.1–8.1 (m, 10H, Ar-H and 2CH thiophene), 12. 1(s, 1H, NH).

12-(4-Chlorophenyl)-10,11-dihydro-2-methyloxazino [4′,5′:4, 5]thieno[2,3-b] thieno[2,3-h]quinolin-4-one (7)

a- Synthesis of sodium salt of 5c

A sample of 5c (1 g) was refluxed in alcoholic sodium hydroxide 10 % for 3h. During this period of time the sodium salt of 5c was separated as lustrous yellow crystals which was filtered off, washed several times with ethanol and air dried.

b- Reaction of the sodium salt of 5c with acetic anhydride

The sodium salt of 5c was refluxed in acetic anhydride (20 ml) for 2 h, then cool. The solid product was filtered off and recrystallized from dioxan into yellow crystals m.p. 280°C, yield 67 %; $C_{22}H_{13}ClN_2O_2S_2$(436.01); IRυ: 1750(C=O), 1620(C=N) Cm^{-1}; ^{1}HNMR (DMSO)δ = 2.5–2.9(m, 4H, $2CH_2$),3.0(s, 3H, CH_3), 7.3–7.8(m, 6H, Ar-H and 2CH thiophene).

12-(4-Chlorophenyl)-10,11-dihydro-2-methylpyrimido [4′, 5′:4, 5]thieno[2,3-b] thieno[2,3-h]quinolin-4(3H)-one (8)

A mixture of the oxazino compound (0.5 g) and ammonium acetate (2 g) in acetic acid (10 ml) was refluxed for 2h. The solid product separated from the hot mixture was filtered off, washed several times with water and recrystallized from acetic acid into yellow crystals m.p.>360 °C, yield 73 %; $C_{22}H_{14}ClN_3OS_2$ (435.02); IRυ: 3220(NH), 1680(C=O), 1620(C=N) Cm^{-1}; ^{1}HNMR(CF_3COOD)δ=2.6–3. (m, 4H, $2CH_2$), 3.1(s, 3H, CH_3), 7.3–7.8(m, 6H, Ar-H and 2CH thiophene).

12-(4-Chlorophenyl)-10,11-dihydropyrimido [4′,5′:4, 5]thieno[2,3-b]thieno[2,3-h] quinolin-4(3H)-one (9)

A mixture of the o-aminocarboxamide derivative 5d (0.01 mol) and triethyl orthoformate (3 ml) was refluxed for 3h in ethanol in the presence of few drops of acetic acid. The solid product separated from the hot mixture was filtered off and recrystallized from acetic acid into pale yellow crystals m.p. >360°C, yield 78 %; $C_{21}H_{12}ClN_3OS_2$ (421.01); IRυ: 3220(NH), 1670(C=O) Cm^{-1}; ^{1}HNMR(DMSO)δ = 2.4–2.9(m, 4H, $2CH_2$), 7.3–8.0(m, 6H, Ar-H and 2CH thiophene), 8.9(s, 1H, CH pyrimidine), 11.3(s, 1H, NH).

4-Chloro-12-(4-chlorophenyl)-10,11-dihydropyrimido[4′,5′:4,5] thieno[2,3-b] thieno[2,3-h]quinoline (10)

A sample of the pyrimidinone derivative **9** (3g) in phosphorous oxychloride (15 ml) was refluxed for 4 h, then cool. The reaction mixture was poured into ice/ water mixture and the solid product was collected by filtration. Recrystallisation from dioxan gave pale yellow crystals m.p. 235 °C, yield 66 %; $C_{21}H_{11}Cl_2N_3S_2$(438.97); IRυ : 1620(C=N); ^{1}HNMR(DMSO)δ = 2.4–2.9(m, 4H, $2CH_2$), 7.3–8. 1(m, 6H, Ar-H and 2CH thiophene), 8.9(s, 1H, CH pyrimidine).

12-(4-Chlorophenyl)-4-hydrazino-10,11-dihydropyrimido[4′,5′:4,5] thieno[2,3-b] thieno[2,3-h]quinoline (11)

A mixture of the chloro compound **10** (0.01 mol) and hydrazine hydrate (0.012 mol) in ethanol (50 ml) was refluxed for 30 min. The solid product separated from the hot mixture was filtered off and recrystallized from dioxan into yellow crystals m.p. 286 °C, yield 74 %; $C_{21}H_{14}ClN_5S_2$(435.03); IRυ: 3380, 3200($NHNH_2$), 1620(C=N); ^{1}HNMR(DMSO)δ = 2.5–2.9(m, 4H, $2CH_2$),4.0(s, 2H, NH_2), 7.3–8.0(m, 6H, Ar-H and 2CH thiophene), 8.8(s, 1H, CH pyrimidine), 9.2(s, 1H, NH).

14-(4-Chlorophenyl)-12,13-dihydro-[1,2,4]triazolo[4″,3″: 1′,6′] pyrimido [4′,5′:4,5] thieno[2,3-b] thieno[2,3-h]quinoline (12)

A mixture of **11** (0.01mol) and triethyl orthoformate (2 ml) in ethanol (30 ml) in the presence of a few drops of acetic acid was refluxed for 3 h. The solid crystals separated from the hot mixture was filtered off and recrystallized from acetic acid as yellow crystals m.p. >360 °C, yield 74 %; $C_{22}H_{12}ClN_5S_2$(445.02);

IRυ: 2950(CH aliph.) 1620(C=N); ^{1}HNMR(CF_3COOD)δ = 2.5–2.9(m, 4H, $2CH_2$) 7.3–7.9(m, 6H, Ar-H and 2CH thiophene), 8.7, 9.1(2s, 2H. 2CH triazole and pyrimidine).

14-(4-Chlorophenyl)-12,13-dihydro-2-methyl-[1,2,4]triazolo[4″,3″:1′, 6′] pyrimido [4′,5′:4,5]thieno[2,3-b] thieno[2,3-h]quinoline (13)

A mixture of the hydrazino derivative **11** (0.01 mol) and acetic anhydride (20 ml) was refluxed for 4h. The solid crystals separated from the hot mixture were filtered off and recrystallized from DMF into yellow crystals m.p.>360 °C, yield 55 %; $C_{23}H_{14}ClN_5S_2$(459.03); IRυ; 1600(C=N); ^{1}HNMR(CF_3 COOD)δ=2.5–2.9(m, 4H, $2CH_2$),3.1(s, 3H, CH_3), 7.3–7.8(m, 6H, Ar-H and 2CH thiophene), 9.0(s, 1H, CH pyrimidine).

14-(4-Chlorophenyl)-12,13-dihydro-[1,2,4]triazolo[4″,3″:1′,6′] pyrimido [4′,5′:4,5] thieno[2,3-b] thieno[2,3-h]quinolin-4(5H) thione (14)

A mixture of the hydrazino derivative **11** (0.01 mol) and carbon disulfide (3 ml) in pyridine (15 ml) was heated on water bath for 3h. The solid product separated from the hot mixture was filtered off and recrystallized from DMF into orange crystals m.p.>360°C, yield 69 %; $C_{22}H_{12}ClN_5S_3$(478.0); IRυ : 3200(NH), 1620(C=N); ^{1}HNMR(CF_3COOD) δ = 2.5–2.9 (m, 4H, $2CH_2$), 7.3–7.8(m, 6H, Ar-H and 2CH thiophene), 9.0(s, 1H, CH pyrimidine).

14-(4-Chlorophenyl)-4-ethoxycarbonylmethylthio-12,13-dihydro-[1,2,4]triazolo [4″,3″:1′,6 ′]pyrimido[4′,5′:4, 5]thieno[2,3-b]thieno [2,3-h] quinoline (15)

A mixture of the triazolthione 14 (0.005 mol) and ethyl chloroacetate (0.005 mol) in ethanol (30 ml) in presence of anhydrous sodium acetate (3 g) was refluxed for 1h, then cool. The solid product was filtered off, washed several times with water and recrystallized from ethanol into yellow crystals m.p.276°C, yield 81 %; $C_{26}H_{18}ClN_5O_2S_3$(563.03); IRυ: 1730(C=O), 1620(C=N). ^{1}HNMR(DMSO)δ=1.1–1.3(t, 3H, CH_3), 2.6–2.9(m, 4H, $2CH_2$), 4.0(s, 2H, CH_2), 4.2–4.4(q, 2H, CH_2), 7.3–7.8(m, 6H, Ar-H and 2CH thiophene), 9.1(s, 1H, CH pyrimidine); MS :m/z 563.

12-(4-Chlorophenyl)-1,2,3,4,10,11-hexahydro-4-oxopyrimido[4′,5′:4,5] thieno[2,3-b] thieno[2,3-h]quinolin-2-thione (16)

A sample of 5d (0,5 g) and carbon disulfide (3 ml) in pyridine (10 ml) was heated on water bath until the hydrogen sulfide ceased, then cool. The solid product was filtered off, washed several times with ethanol and recrystallized from dioxan into yellow crystals m.p.>360°C, yield 72 %; $C_{21}H_{12}ClN_3OS_3$(453.98); IRυ: 3380, 3200(2NH), 1670(C=O), 1620(C=N); ^{1}HNMR(CF_3COOD)δ=2.5–2.9(m, 4H, $2CH_2$), 7.3–7.9 (m, 6H, Ar-H and 2CH thiophene).

4-(4-Chlorophenyl)-2-cyano-3-ethoxymethyleneamino-5, 6-dihydrodithieno [2,3-b][2,3-h]quinoline (17)

A mixture of 5f (0.01 mol) and triethyl orthoformate (0.02 mol) in acetic anhydride (10 ml) was refluxed for 3h, then cool. The solid product was filtered off, washed several times with cold ethanol and recrystallized from ethanol into yellow crystals m.p. 202°C, yield 74 %; $C_{23}H_{16}ClN_3OS_2$(449.04); IRυ: 29509aliph.CH), 2200(CN), 1620(C=N); ^{1}HNMR($CDCl_3$)δ = 1.1–1.3(t, 3H, CH_3), 2.6–2.9(m, 4H, $2CH_2$), 3.8–4.0(q, 2H, CH_2), 7.3–7.9(m, 6H, Ar-H and 2CH thiophene), 8.2(s, 1H, N=CH)

3-Amino-12-(4-chlorophenyl)-4-imino-10,11-dihydropyrimido [4′,5′:4,5]thieno [2,3-b]thieno[2,3-h]quinoline (18)

A sample of compound 17 (0.01 mol) was dissolved in dioxan (50 ml) and then hydrazine hydrate (0.01 mol) was added drop wise while stirring. Stirring was continued for 2h, during this period of time, solid crystals were separated. The mixture was heated on water bath for 1h, cool and the solid product was collected by filtration. Recrystallisation from dioxan gave yellow crystals of 18 m.p.296°C, yield 65 %; $C_{21}H_{14}ClN_5S_2$(435.03); IRυ: 3400, 3300, 3200(NH2,NH), 1620(C=N); ^{1}HNMR (DMSO)δ = 2.6–2.9(m, 4H, $2CH_2$), 4.2(s, 2H, NH_2), 7.3–7.9(m, 6H, Ar-H and 2CH thiophene), 8.9(s, 1H, CH pyrimidine), 10,8(s, 1H, NH); MS : m/z 435.

14-(4-Chlorophenyl)-12,13-dihydrotriazolo[1″,5″:1′,6′]pyrimido [4′, 5′:4, 5]thieno [2,3-b]thieno[2,3-h]quinolin-5(4H)thione (19)

This compound was synthesized according an procedure as following compound 16. 19 was separated from dioxan as orange crystals m.p. 335°C, yield 71%; $C_{22}H_{12}ClN_5S_3$(476.99); IRυ: 3200(NH), 1620(C=N), 1130(C=S); ^{1}HNMR(CF_3COOD)δ = 2.6–2.9(m, 4H, $2CH_2$),7.3–7.9(m, 6H, Ar-H and 2CH thiophene), 9.1(s, 1H, CH pyrimidine).

16-(4-Chlorophenyl)-14,15-dihydro-5, 7-dimethyltriazipino[2″,3″:1′, 6′] pyrimido [4′,5′:4, 5]thieno[2,3-b]thieno[2,3-h]quinoline (20)

A mixture of compound 18 (0.005 mol) and acetyl acetone (0.005 mol) in absolute ethanol was refluxed for 5 h. The solid crystals separated from the hot mixture was filtered off and recrystallized from acetic acid into pale yellow crystals m.p. 312°C, yield 63 %; $C_{26}H_{18}ClN_5S_2$(499.06); IRυ: 2970(aliph. CH), 1620(C=N); ^{1}HNMR(DMSO)δ = 2.3(s, 3H, CH_3) 2.5(s, 3H, CH_3), 2.5–2.9(m, 4H, $2CH_2$) 6.1(s, 1H, CH), 7.3–7.9(m, 6H, Ar-H and 2CH thiophene), 8.9(s, 1H, CH pyrimidine).

12-(4-Chlorophenyl)- 10,11-dihydropyrimido[4′, 5′:4, 5]thieno [2,3-b]thieno[2,3-h] quinolin-2,4(1H,3H)dithione (21)

This compound was synthesized following an analogous procedure that for compound 16. 21 was separated from dioxan as orange crystals m.p. >360°C, yield 59 %; $C_{21}H_{12}ClN_3S_4$(470.04); IRυ:3380(NH), 2700(SH), 1620(C=N); ^{1}HNMR(CF_3COOD)δ = 2.4–2.7(m, 4H, $2CH_2$), 7.3–8.0(m, 6H, Ar-H and 2CH thiophene).

4-Dicyanomethylene-4, 5, 6, 7-tetrahydrobenz[b]thiophene (22)

This compound was prepared according to the known procedure, m.p. 133 °C, lit.[9], m.p. 131–133 °C.

2-Amino-1-cyanothieno[2,3-f]benz[c]thiopyran-4-thione (23)

A mixture 12 (0.01 mol), carbon disulfide (5 ml), DMF (2 ml) and triethyl amine (2 ml) in methanol (30 ml) was stirred for 48h. The solid product

separated was filtered off and recrystallized from acetic acid into yellow crystals m.p. 285°C, yield 18 %; $C_{12}H_8N_2S_3$ (275.98); IRυ: 3320, 3260 (NH_2), 2200(CN), 1620(C=N); ^{1}HNMR (DMSO-d_6)δ= 2.5–2.9(m, 4H, $2CH_2$)6.7(s, 2H, NH_2),7.3–8.1(2d, 2H, 2CH thiophene); MS : m/z 276.

5-Amino-8, 9-dihydro-4, 6, 6-tricyano- 7-phenyl-7[H]naphth [2,1-b]thiophene (24)

A mixture of 22 (0.01 mol) and benzylidene malononitrile (0.01 mol) in absolute ethanol (50 ml) in the presence of few drops of piperidine was stirred for 1h. The solid product was filtered off and recrystallized from ethanol into white crystals m.p.235°C, yield 82 %; $C_{21}H_{14}N_4S$(354.43); IRυ: 3420,3300 (NH_2), 2220, 2200(3CN) 1630(C=N); ^{1}HNMR($CDCl_3$)δ = 2.3, 2.8(2t, 4H, $2CH_2$),4.6(s, 1H, CH), 5.9(s, 2H, NH_2) 7.4–8.2 (m, 7H, Ar-H and 2 CH thiophene).

5-Amino-4, 6-dicyano-8, 9-dihydro-7-phenylnaphth[2,1-b]thiophene (25)

A sample of compound 24 (0.5 g) was refluxed in acetic acid for 2h, the solid product separated from the hot mixture was collected by filtration. Recrystallisation from acetic acid gave yellow crystals of 25 m.p. 266°C, yield 62 %; $C_{20}H_{13}N_3S$(327.4); IRυ: 3420, 3300 (NH_2), 2200(br.2CN), 1620(C=N). ^{1}HNMR($CDCl_3$)δ = 2.3,2.6 (2t, 4H, $2CH_2$), 6.6(s, 2H, NH_2) 7.4–8.0(m, 7H, Ar-H and 2 CH thiophene).

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