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Synthesis of Pyrimido[4′,5′:4,5]thieno[2,3-*c*]-pyridazine Derivatives

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Summary. Convenient syntheses of 3,4-diphenyl-8-oxo-6-substituted-5,6,7,8-tetrahydropyrimido[4′,5′:4,5]thieno[2,3-*c*]pyridazines (**4a–g**), 3,4-diphenyl-8-oxo-6-substituted-7,8-dihydropyrimido[4′,5′:4,5]thieno[2,3-*c*]pyridazines (**5a–g**), 8-chloro-3,4-diphenyl-6-substituted-pyrimido[4′,5′:4,5]thieno[2,3-*c*]pyridazines (**6a–g**), and 3,4,6-triphenyl-8-substituted-pyrimido[4′,5′:4,5]thieno[2,3-*c*]pyridazines (**7a–f**) from 4-cyano-5,6-diphenylpyridazine-3(2H)-thione (**1**) *via* 5-amino-3,4-diphenylthieno[2,3-*c*]pyridazine-6-carboxamide (**3**) are reported.

Keywords. Thieno[2,3-*c*]pyridazine-6-carboxamide; 5,6,7,8-Tetrahydropyrimido[4′,5′:4,5]-thieno[2,3-*c*]pyridazines; 7,8-Dihydropyrimido[4′,5′:4,5]thieno[2,3-*c*]pyridazines; Pyrimido[4′,5′:4,5]thieno-[2,3-*c*]pyridazines.

Synthese von Pyrimido[4′,5′:4,5]thieno[2,3-*c*]pyridazinderivaten

Zusammenfassung. Einfache Synthesen von 3,4-Diphenyl-8-oxo-6-substituierten-5,6,7,8-tetrahydropyrimido[4′,5′:4,5]thieno[2,3-*c*]pyridazinen (**4a–g**), 3,4-Diphenyl-8-oxo-6-substituierten-7,8-dihydropyrimido[4′,5′:4,5]thieno[2,3-*c*]pyridazinen (**5a–g**), 8-Chlor-3,4-diphenyl-6-substituierten Pyrimido[4′,5′:4,5]thieno[2,3-*c*]pyridazinen (**6a–g**) und 3,4,6-Triphenyl-8-substituierten-pyrimido[4′,5′:4,5]thieno[2,3-*c*]pyridazinen (**7a–f**) aus 4-Cyano-5,6-diphenylpyridazin-3(2*H*)-thion (**1**) *via* 5-Amino-3,4-diphenylthieno[2,3-*c*]pyridazin-6-carboxamid (**3**) werden beschrieben.

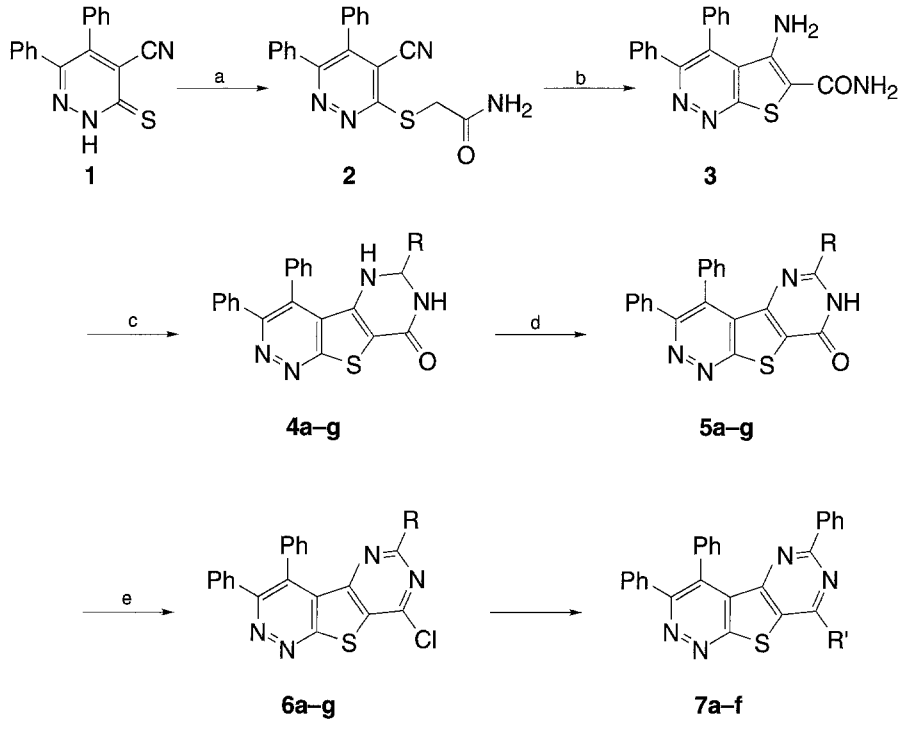
Introduction

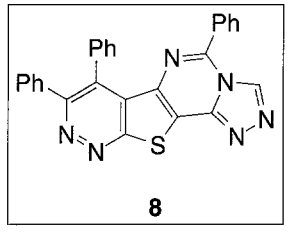
Heterocyclic annelated pyridazines continue to attract considerable attention which mainly arises from the large variety of interesting pharmacological activities observed with pyridazine derivatives [1]. The recent discovery [2] of a natural antifungal antibiotic containing this heteroarene system (Pyridazomycin) most probably will stimulate even broader interest in 1,2-diazine chemistry. Recently, our researches have been devoted to the synthesis of condensed tricyclic systems of potential biological activity with a thiophene ring as the central nucleus [3]. Whereas pyridine-annelated sulfur-containing heterocycles have been studied extensively [4], comparatively little is known about aza-analogous systems in which an S-heterocycle is fused to a pyridazine nucleus. This assessment prompted us to prepare some derivatives of the pyrimidothienopyridazine system as aza-isosters

with potential biological activity of pharmaceutically relevant pyridothienoderivatives [5].

Results and Discussion

To our knowledge, there are only two reports [6, 7] on the pyrimido [4′,5′:4,5]thieno[2,3-*c*]pyridazine system. In these reports, the approach to the heterocyclic system was achieved by the reaction of 5-amino-3,4-diphenylthieno[2,3-*c*]pyridazine-6-carboxamide (**3**) with triethyl orthoformate, formamide,





4,5,6	R	**4,5,6**	R
a	C_6H_5	**d**	2-OCH_3-C_6H_4
b	4-NO_2-C_6H_4	**e**	3,4-Methylenedioxyphenyl
c	4-Cl-C_6H_4	**f**	2,6-Cl_2-C_6H_4
		g	4-CH_3-C_6H_5

Reagents:
a: $ClCH_2CONH_2$, KI, K_2CO_3, acetone, room temperature, 1h
b: K_2CO_3, ethanol, reflux, 30 min
c: RCHO, PTSA, toluene, reflux
d: DDQ, THF, reflux
e: $POCl_3$, PCl_5, reflux

7	R'	**7**	R'
a	$NHNH_2$	**d**	Piperidino
b	OEt	**e**	Morpholino
c	$NHCH_2CH_2CH_3$	**f**	*N*-(4'-Acetylphenyl)-piperazino

Scheme 1

acetic anhydride, and carbon disulfide. We developed a straightforward, convenient synthetic method for the target compounds **5** and **6** and their substituted derivatives by a reaction between 5-amino-3,4-diphenylthieno[2,3-*c*]pyridazine-6-carboxamide (**3**) and aromatic aldehydes. The reaction sequence involved is outlined in Scheme 1.

The precursor 5-amino-3,4-diphenylthieno[2,3-*c*]pyridazine-6-carboxamide (**3**) was synthesized following a modified literature procedure [8]. The reaction of 4-cyano-5,6-diphenylpyridazine-3(2*H*)-thione (**1**) with 2-chloroacetamide in the presence of an equimolar amount of potassium carbonate in acetone gave 3-carbamoylmethylthio-4-cyano-5,6-diphenylpyridazine (**2**), which, on refluxing with ethanol in the presence of an excess of anhydrous potassium carbonate, underwent intramolecular ring formation to yield the 5-aminothieno[2,3-*c*]-pyridazine (**3**). **3** was also obtained directly from **1** and 2-chloroacetamide using an excess of potassium carbonate in refluxing ethanol.

The pyrimidine ring was attached to the thiophene ring by condensing **3** with an appropriate aromatic aldehyde in refluxing toluene containing a catalytic amount of *p*-toluenesulfonic acid (*PTSA*) to afford the 3,4-diphenyl-8-oxo-6-substituted-5,6,7,8-tetrahydropyrimido[4′,5′:4,5]thieno[2,3-*c*]pyridazines **4a–g** in 50–80% yields. Compounds **4a–g** were characterized by microanalyses and spectroscopic data. The mass spectra of **4a–g** showed the expected molecular ion peaks, and the IR spectra exhibited the characteristic bands of the amide group. Moreover, compounds **4a–g** showed a characteristic peak between $\delta = 5.73$ ppm and $\delta = 6.55$ ppm for the H-6 proton in the ^{1}H NMR spectra, and two signals at $\delta = 4.08$–5.16 ppm and $\delta = 5.75$–8.77 ppm, exchangeable with deuterium, which can be attributed to the *N*-bound protons at positions 5 and 7, respectively. The formation of the desired compounds **4** was also confirmed by the ^{13}C NMR spectra which showed a signal at $\delta = 63.9$–69.2 ppm corresponding to the carbon atom at position 6 of the newly formed pyrimidine ring.

By reacting compounds **4a–g** with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (*DDQ*) in tetrahydrofuran, we succeeded in the preparation of pyrazinothieno-pyrimidones **5a–g** which in turn reacted with phosphorus oxychloride to yield the expected 8-chloro derivatives **6a–g**. Nucleophilic substitution reactions of the halogen atom with appropriate agents furnished compounds **7a–f**. On heating derivative **7a**, obtained by the reaction of **6a** with hydrazine hydrate, with formic acid, it cyclized to the desired annelated triazole ring. Compound **8** showed a signal at $\delta = 9.79$ ppm in the ^{1}H NMR spectrum that was assigned to the H-3 proton. Its mass spectrum showed an intense peak at $m/z = 456$ corresponding to the molecular ion.

Experimental

All reagents used were commercial grade chemicals from freshly opened containers. Melting points were determined on a Büchi 510 apparatus and are reported uncorrected. IR spectra were recorded as potassium bromide disks on a Perkin-Elmer 383 spectrophotometer. ^{1}H an d^{13}C NMR spectra were obtained on a Bruker AC 200F instrument at room temperature. Mass spectra were obtained at 70 eV by using a VG QUATTRO spectrometer. The Silica gel 60 $HF_{254+366}$ sheets used for analytical thin layer chromatography and the Silica gel 60(230–400 mesh) employed for medium-pressure liquid

chromatography (MPLC) were purchased from Merck. Microanalyses for C, H, and N were performed by the Elemental Analyses General Service of the University of La Coruña.

4-Cyano-5,6-diphenylpyridazine-3(2H)-thione (**1**, [8])

A mixture of 3-chloro-4-cyano-5,6-diphenylpyridazine ([8]; 0.2 g, 0.68 mmol) and $NaHS \cdot H_2O$ (0.15 g) in ethanol (10 ml) was stirred at room temperature for 30 min. The solvent was removed under reduced pressure and water (30 ml) was added. Neutralization of the solution with 2*N* HCl deposited a solid which was recrystallized from acetone to yield 0.19 g (92%) of **1**. M.p.: 250 °C (dec.) (Ref. [8]: m.p.: 234 °C); $C_{17}H_{11}N_3S$ (289.35); calc.: C: 70.57, H: 3.83, N: 14.52; found: C: 70.38, H: 3.67, N: 14.68; ^{1}H NMR ($CDCl_3$): $\delta = 7.08–7.50$ (m, 10 H, C_6H_5), 12.44 (br s, 1 H, NH) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 113.5$ (CN), 128.4, 128.9, 129.0, 129.8, 130.9, 132.0, 133.1 (C_6H_5), 146.1, 151.2 (C-5, C-6), 177.1 (CS) ppm; MS (EI): *m/z* (%) = 289 (M^+, 57), 256 (17), 189 (2), 178 (46); IR (KBr): $\nu = 3200$ (NH), 2220 (CN), 1550, 1440 cm^{-1}.

3-Carbamoylmethylthio-4-cyano-5,6-diphenylpyridazine (**2**)

A mixture of **1** (0.45 g, 1.54 mmol), chloroacetamide (0.15 g, 1.54 mmol), potassium carbonate (0.23 g, 1.70 mmol), and a catalytic amount of KI in acetone (50 ml) was stirred at room temperature for 1 h. The insoluble solid was removed by filtration and washed with acetone. The filtrate and the washings were combined and evaporated. The residual solid was recrystallized from acetone to yield 0.35 g (66%) of **2**. M.p.: 150–152 °C; $C_{19}H_{14}N_4OS$ (346.41); calc.: C: 65.88, H: 4.07, N: 16.17; found: C: 65.68, H: 4.13, N: 16.23; ^{1}H NMR ($CDCl_3$): $\delta = 4.13$ (s, 2 H, CH_2), 5.80 (br s, 1 H, NH), 6.88 (br s, 1 H, NH), 7.21–7.47 (m, 10 H, C_6H_5) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 30.9$ (CH_2), 112.0 (C-4), 112.6 (CN), 128.4, 129.0, 129.2, 129.5, 129.6, 130.4, 132.3, 134.7 (C_6H_5), 141.8, 157.5 (C-5, C-6), 160.1 (C-3), 169.9 (CO) ppm; MS (EI): *m/z* (%) = 346 (M^+, 27), 345 (39), 302 (100), 277 (10); IR (KBr): $\nu = 3400$, 3190 (NH), 2220 (CN), 1670 (CO), 1620, 1380 cm^{-1}.

5-Amino-3,4-diphenylthieno[2,3-c]pyridazine-6-carboxamide (**3**)

Method A: A mixture of **2** (0.30 g, 0.87 mmol) and potassium carbonate (0.15 g, 1.12 mmol) was refluxed in ethanol (20 ml) for 30 min. The insoluble solid was removed by filtration and wash with ethanol. The filtrate and the washings were combined and evaporated under reduced pressure. The solid was recrystallized from ethanol/acetone to yield 0.23 g (75%) of **3**. M.p.: 296–298 °C; $C_{19}H_{14}N_4OS$ (346.41); calc.: C: 65.88, H: 4.07, N: 16.17; found: C: 65.72, H: 4.26, N: 16.04; ^{1}H NMR (*DMSO*-d_6): $\delta = 5.69$ (br s, 2 H, NH_2), 7.26–7.42 (m, 10 H, C_6H_5), 7.59 (br s, 2 H, NH_2) ppm; ^{13}C NMR (*DMSO*-d_6): $\delta = 102.8$ (C-6), 124.7 (C-4a), 127.7, 128.0, 128.5, 129.2, 129.5, 130.1, 132.6, 134.0 (C_6H_5), 136.8 (C-5), 144.4, 155.1, 160.6, 166.3 ppm; MS (EI): *m/z* (%) = 346 (M^+, 80), 328 (27), 300 (31); IR (KBr): $\nu = 3460$, 3340, 3120 (NH), 1680 (CO), 1620, 1580, 1500 cm^{-1}.

Method B (from compound **6**): A mixture of **1** (0.45 g, 1.54 mmol), chloroacetamide (0.15 g, 1.54 mmol), potassium carbonate (0.23 g, 1.70 mmol), and a catalytic amount of KI in acetone (50 ml) was stirred at room temperature for 1 h. The solvent was removed under reduced pressure. A solution of the crude solid in ethanol (50 ml) and potassium carbonate (0.23 g, 1.70 mmol) was refluxed for 30 min. The insoluble solid was removed by filtration and washed with ethanol. The filtrate and the washings were combined and evaporated. The solid was recrystallized from ethanol/acetone to yield 0.50 g (95%) of **3**.

8-Oxo-3,4-diphenyl-6-substituted-5,6,7,8-tetrahydropyrimido[4',5':4,5]thieno[2,3-c]-pyridazines (**4a–g**); *General Procedure*

A catalytic amount of *PTSA* was added to a solution of **3** (0.87 mmol) and the appropriate aldehyde (0.95 mmol) in toluene (30 ml). The solution was refluxed for 2–10 h; the water formed was continuously

removed by means of a *Dean-Stark* trap. The desired product was isolated by suction and recrystallized from $EtOH/CH_2Cl_2$.

8-Oxo-3,4,6-triphenyl-5,6,7,8-tetrahydropyrimido[4',5':4,5]thieno[2,3-c]pyridazine (**4a**)

81%; m.p.: 285–287 °C; $C_{26}H_{18}N_4OS$ (434.51); calc.: C: 71.87, H: 4.17, N: 12.89; found: C: 71.76, H: 4.26, N: 12.64; ^{1}H NMR ($CDCl_3$): $\delta = 4.11$ (s, 1 H, NH), 5.77 (s, 1 H, H-6), 6.08 (s, 1 H, NH), 7.15–7.41 (m, 15 H, C_6H_5) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 69.2$ (C-6), 112.6 (C-8a), 123.9 (C-4a), 126.4, 128.0, 128.4, 128.6, 129.1, 129.5, 129.7, 130.0, 130.3, 132.9, 133.2, 136.0 (C_6H_5), 137.1 (C-4b), 143.2, 154.7, 162.0, 163.7 ppm; MS (EI): *m/z* = (%) 434 (M^+, 58), 357 (100), 330 (28), 300 (12); IR (KBr): $\nu = 3400$, 3190, 3050 (NH), 1650 (CO), 1550, 1480 cm^{-1}.

6-(4-Nitrophenyl)-8-oxo-3,4-diphenyl-5,6,7,8-tetrahydropyrimido[4',5':4,5]thieno[2,3-c]-pyridazine (**4b**)

Yield: 65%; m.p.: > 300 °C; $C_{26}H_{17}N_5O_3S$ (479.51); calc.: C: 65.13, H: 3.57, N: 14.60; found: C: 65.25, H: 3.43, N: 14.71; ^{1}H NMR ($CDCl_3$): $\delta = 4.20$ (s, 1 H, NH), 5.90 (s, 1 H, H-6), 6.25 (s, 1 H, NH), 7.30–7.41 (m, 10 H, C_6H_5), 7.49, 8.23 (AA'XX' system, 4 H, $J = 8.3$ Hz, C_6H_4) ppm; MS (EI): *m/z*(%) = 479 (M^+, 5), 331 (7), 327 (16), 258 (45); IR (KBr): $\nu = 3400$, 3200, 3150 (NH), 1670 (CO), 1510, 1475 cm^{-1}.

6-(4-Chlorophenyl)-8-oxo-3,4-diphenyl-5,6,7,8-tetrahydropyrimido[4',5':4,5]thieno[2,3-c]-pyridazine (**4c**)

Yield: 50%; m.p.: > 300 °C; $C_{26}H_{17}N_4OClS$ (468.96); calc.: C: 66.59, H: 3.65, N: 11.95; found C: 66.66, H: 3.72, N: 11.83; ^{1}H NMR (*DMSO*-d_6): $\delta = 5.16$ (d, 1 H, $J = 4.7$ Hz, NH), 5.79 (t, 1 H, $J = 4.0$ Hz, H-6), 7.20–7.49 (m, 14 H, C_6H_5, C_6H_4), 8.77 (d, 1 H, $J = 3.5$ Hz, NH) ppm; ^{13}C NMR (*DMSO*-d_6): $\delta = 65.1$ (C-6), 112.7 (C-8a), 124.9 (C-4a), 127.7, 127.9, 128.1, 128.3, 129.2, 129.6, 130.1, 132.5, 132.8, 134.2 (C_6H_5, C_6H_4), 136.6 (C-4b), 140.0 (C-Cl), 142.1, 155.3, 160.5, 162.5 ppm; MS (EI): *m/z* (%) = 470 ($M^+ + 2$, 22), 468 (M^+, 56), 357 (100), 330 (44), 328 (33); IR (KBr): $\nu = 3400$, 3180, 3050 (NH), 1650 (CO), 1530, 1480 cm^{-1}.

6-(2-Methoxyphenyl)-8-oxo-3,4-diphenyl-5,6,7,8-tetrahydropyrimido[4',5':4,5]thieno[2,3-c]-pyridazine (**4d**)

Yield: 72%; m.p.: 279–281 °C; $C_{27}H_{20}N_4O_2S$ (464.54); calc.: C: 69.81, H: 4.34, N: 12.06; found: C: 69.93, H: 4.26, N: 12.18; ^{1}H NMR ($CDCl_3$): $\delta = 3.61$ (s, 3 H, CH_3O), 4.71 (br s, 1 H, NH), 6.05 (t, 1 H, $J = 2.3$ Hz, H-6), 6.50 (br s, 1 H, NH), 6.77–7.53 (m, 14 H, C_6H_5, C_6H_4) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 55.3$ (OCH_3), 63.9 (C-6), 110.7 (C-8a), 124.1 (C-4a), 110.3, 120.6, 126.0, 126.5, 127.9, 128.3, 128.6, 128.8, 129.2, 129.7, 130.2, 132.8, 133.3 (C_6H_5, C_6H_4), 135.9 (C-4b), 142.9, 154.7, 155.7, 162.4, 163.6 ppm; MS (EI): *m/z* (%) = 464 (M^+, 6), 357 (9), 330 (4), 328 (10), 272 (8); IR (KBr): $\nu = 3400$, 3190, 3050 (NH), 1640 (CO), 1480, 1460 cm^{-1}.

6-(3,4-Methylenedioxyphenyl)-8-oxo-3,4-diphenyl-5,6,7,8-tetrahydropyrimido[4',5':4,5]thieno-[2,3-c]pyridazine (**4e**)

Yield: 80%; m.p.: 290–292 °C; $C_{27}H_{18}N_4O_3S$ (478.52); calc.: C: 67.77, H: 3.79, N: 11.71; found: C: 67.89, H: 3.65, N: 11.90; ^{1}H NMR (*DMSO*-d_6): $\delta = 4.96$ (d, 1 H, $J = 4.1$ Hz, NH), 5.71 (t, 1 H, $J = 3.9$ Hz, H-6), 5.98 (s, 2 H, OCH_2O), 6.68–6.85 (m, 3 H, C_6H_3), 7.27–7.39 (m, 10 H, C_6H_5), 8.65 (d, 1 H, $J = 2.9$ Hz, NH) ppm; ^{13}C NMR (*DMSO*-d_6): $\delta = 65.8$ (C-6), 101.2 (OCH_2O), 112.4 (C-8a), 124.8 (C-4a), 106.4, 107.8, 119.5, 127.7, 128.1, 129.2, 129.6, 130.1, 132.6, 134.1, 134.5 (C_6H_5, C_6H_3), 136.6 (C-4b), 142.2, 147.2, 155.2, 160.7, 162.5 ppm; MS (EI): *m/z* (%) = 478 (M^+, 38), 357 (45), 330 (24), 300 (17), 272 (17); IR (KBr): $\nu = 3400$, 3350 (NH), 1650 (CO), 1480 cm^{-1}.

6-(2,6-Dichlorophenyl)-8-oxo-3,4-diphenyl-5,6,7,8-tetrahydropyrimido[4',5':4,5]thieno[2,3-c]-pyridazine (**4f**)

Yield: 70%; m.p.: >300 °C; $C_{26}H_{16}N_4OCl_2S$ (503.40); calc.: C: 62.03, H: 3.20, N: 11.13; found: C: 61.91, H: 3.33, N: 11.27; ^{1}H NMR (*DMSO*-d_6): $\delta = 4.45$ (d, 1 H, $J = 2.8$ Hz, NH), 6.55 (d, 1 H, $J = 1.9$ Hz, H-6), 7.26–7.50 (m, 13 H, C_6H_3, C_6H_5), 8.40 (br s, 1 H, NH) ppm; ^{13}C NMR (*DMSO*-d_6): $\delta = 65.7$ (C-6), 111.0 (C-8a), 124.6 (C-4a), 127.8, 128.1, 129.1, 129.8, 130.1, 131.5, 132.3, 133.7, 134.9 (C_6H_5, C_6H_3), 136.5 (C-4b), 143.0, 155.1, 160.8, 162.5 ppm; MS (EI): *m/z* (%) = 506 ($M^+ + 4$, 3), 504 ($M^+ + 2$, 13), 502 (M^+, 18), 357 (100), 330 (24), 328 (11), 300 (6), 272 (5); IR (KBr): $\nu = 3400$, 3380, 3180, 3050 (NH), 1650 (CO), 1560, 1480 cm^{-1}.

6-(4-Methylphenyl)-8-oxo-3,4-diphenyl-5,6,7,8-tetrahydropyrimido[4',5':4,5]thieno[2,3-c]-pyridazine (**4g**)

Yield: 80%; m.p.: >300 °C; $C_{27}H_{20}N_4OS$ (448.54); calc.: C: 72.30 H, 4.49, N: 12.49; found: C: 72.18, H: 4.41, N: 12.36; ^{1}H NMR ($CDCl_3$): $\delta = 2.36$ (s, 3 H, CH_3), 4.08 (br s, 1 H, NH), 5.73 (s, 1 H, H-6), 5.75 (br s, 1 H, NH), 7.14–7.38 (m, 14 H, C_6H_5, C_6H_4) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 21.2$ (CH_3), 69.2 (C-6), 112.3 (C-8a), 123.9 (C-4a), 126.3, 128.0, 128.4, 128.6, 128.8, 129.2, 129.5, 129.7, 130.3, 133.0, 133.2, 134.0 (C_6H_5, C_6H_4), 136.0 (C-4b), 140.1, 143.3, 154.8, 162.1, 163.7 ppm; MS (EI): *m/z* (%) = 448 (M^+, 70), 357 (100), 330 (30), 328 (15), 272 (9); IR (KBr): $\nu = 3400$, 3200, 3050 (NH), 1700 (CO), 1480 cm^{-1}.

8-Oxo-3,4-diphenyl-6-substituted-7,8-dihydropyrimido[4',5':4,5]thieno[2,3-c]pyridazines (**5a–g**); *General Procedure*

A solution of the appropriate pyrimidone **4** (0.45 mmol) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (*DDQ*) (0.67 mmol) in tetrahydrofuran (10 ml) was refluxed for 3 h. After cooling, the precipitate obtained was filtered off. The crude solid was used in the next step without further purification.

8-Oxo-3,4,6-triphenyl-7,8-dihydropyrimido[4',5':4,5]thieno[2,3-c]pyridazine (**5a**)

Yield: 77%; m.p.: >300 °C; $C_{26}H_{16}N_4OS$ (432.50); calc.: C: 72.21, H: 3.73, N: 12.95; found: C: 72.09, H: 3.95, N: 13.03; ^{1}H NMR ($CDCl_3$): $\delta = 7.29$–7.78 (m, 15 H, C_6H_5), 11.88 (br s, 1 H, NH) ppm; MS (EI): *m/z* (%) = 432 (M^+, 78), 328 (4), 300 (4); IR (KBr): $\nu = 1650$ (CO), 1550, 1490, 1300 cm^{-1}.

6-(4-Nitrophenyl)-8-oxo-3,4-diphenyl-7,8-dihydropyrimido[4',5':4,5]thieno[2,3-c]pyridazine (**5b**)

Yield: 84%; m.p.: >300 °C; $C_{26}H_{15}N_5O_3S$ (477.50); calc.: C: 65.40, H: 3.17, N: 14.67; found: C: 65.31, H: 3.12, N: 14.52; ^{1}H NMR (*DMSO*-d_6): $\delta = 7.27$–7.54 (m, 10 H, C_6H_5), 7.92, 8.22 (AA'XX' system, 4 H, $J = 8.9$ Hz, C_6H_4), 13.25 (br s, 1 H, NH) ppm; MS (EI): *m/z* (%) = 477 (M^+, 17), 299 (16), 272 (13); IR (KBr): $\nu = 1650$ (CO), 1550, 1510 cm^{-1}.

6-(4-Chlorophenyl)-8-oxo-3,4-diphenyl-7,8-dihydropyrimido[4',5':4,5]thieno[2,3-c]pyridazine (**5c**)

Yield: 94%; m.p.: >300 °C; $C_{26}H_{15}N_4OClS$ (466.94); calc.: C: 66.88, H: 3.24, N: 12.00; found: C: 66.75, H: 3.15, N: 11.94; ^{1}H NMR (*DMSO*-d_6): $\delta = 7.27$–7.54 (m, 10 H, C_6H_5), 7.46, 7.70 (AA'XX' system, 4 H, $J = 8.6$ Hz, C_6H_4), 13.30 (br s, 1 H, NH) ppm; MS (EI): *m/z* (%) = 468 ($M^+ + 2$, 6), 466 (M^+, 14), 432 (14), 328 (6), 300 (5), 272 (22); IR (KBr): $\nu = 1650$ (CO), 1595, 1580, 1540 cm^{-1}.

6-(2-Methoxyphenyl)-8-oxo-3,4-diphenyl-7,8-dihydropyrimido[4',5':4,5]thieno[2,3-c]pyridazine (**5d**)

Yield: 85%; m.p.: >300 °C; $C_{27}H_{18}N_4O_2S$ (462.52); calc.: C: 70.12, H: 3.92, N: 12.11; found: C: 69.97, H: 4.00, N: 11.99; ^{1}H NMR ($CDCl_3$): $\delta = 4.07$ (s, 3 H, CH_3O), 6.89 (t, 1 H, $J = 7.6$ Hz), 7.00 (d, 1 H,

$J = 7.6$ Hz), 7.00 (d, 1 H, $J = 8.7$ Hz), 7.30–7.50 (m, 12 H, C_6H_5, C_6H_4) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 56.3$ (OCH_3), 118.2 (C-8a), 125.5 (C-4a), 111.7, 121.5, 128.0, 128.3, 130.2, 130.5, 131.7, 133.6, 133.9, 135.9, 136.4 (C_6H_5, C_6H_4), 151.0, 152.7, 156.5, 157.8, 158.1, 164.2 ppm; MS (EI): m/z (%) = 462 (M^+, 81), 328 (16), 299 (34), 272 (35); IR (KBr): $\nu = 3290$ (NH), 1680 (CO), 1580, 1540, 1490 cm^{-1}.

6-(3,4-Methylenedioxyphenyl)-8-oxo-3,4-diphenyl-7,8-dihydropyrimido[4',5':4,5]thieno[2,3-c]-pyridazine (**5e**)

Yield: 85%; m.p.: > 300 °C; $C_{27}H_{16}N_4O_3S$ (476.51); calc.: C: 68.06, H: 3.38, N: 11.76; found: C: 67.95, H: 3.27, N: 11.90; ^1H NMR (*DMSO*-d_6): $\delta = 6.10$ (s, 2 H, OCH_2O), 6.90–7.44 (m, 13 H, C_6H_5, C_6H_3), 13.16 (br s, 1 H, NH) ppm; MS (FAB): m/z (%) = 477 [$(MH)^+$, 54], 401 (5), 357 (7), 327 (11), 311 (11), 272 (6); IR (KBr): $\nu = 1650$ (CO), 1550, 1500, 1475 cm^{-1}.

6-(2,6-Dichlorophenyl)-8-oxo-3,4-diphenyl-7,8-dihydropyrimido[4',5':4,5]thieno[2,3-c]pyridazine (**5f**)

Yield: 55%; m.p.: > 300 °C; $C_{26}H_{14}N_4OCl_2S$ (501.39); calc: C: 62.28, H: 2.81, N: 11.17; found: C: 62.15, H: 2.99, N: 11.26; ^1H NMR (*DMSO*-d_6): $\delta = 7.14$–7.60 (m, 13 H, C_6H_3, C_6H_5), 13.69 (br s, 1 H, NH) ppm; MS (FAB): m/z (%) = 505 [$(MH)^+ + 4$,15], 503 [$(MH)^+ + 2$, 64], 501 [$(MH)^+$, 68], 300 (21), 298 (27); IR (KBr): $\nu = 1650$ (CO), 1590, 1540, 1480 cm^{-1}.

6-(4-Methylphenyl)-8-oxo-3,4-diphenyl-7,8-dihydropyrimido[4',5':4,5]thieno[2,3-c]pyridazine (**5g**)

Yield: 91%; m.p.: > 300 °C; $C_{27}H_{18}N_4OS$ (446.52); calc.: C: 72.63, H: 4.06, N: 12.55; found: C: 72.70, H: 3.91, N: 12.46; ^1H NMR (*DMSO*-d_6): $\delta = 2.72$ (s, 3 H, CH_3), 7.16, 7.60 (AA'XX' system, 4 H, $J = 8.1$ Hz, C_6H_4), 7.29–7.47 (m, 10 H, C_6H_5), 13.15 (br s, 1 H, NH) ppm; ^{13}C NMR (*DMSO*-d_6): $\delta = 21.0$ (CH_3), 124.8, 127.6; 127.8, 128.1, 128.2, 128.6, 129.0, 130.2, 130.3, 133.1, 135.9, 136.6 (C_6H_5, C_6H_4), 142.1, 146.5, 150.6, 154.2, 156.4, 159.0, 163.4 ppm; MS (EI): m/z (%) = 446 (M^+, 79), 445 (66), 368 (4), 313 (10), 272 (14); IR (KBr): $\nu = 1660$ (CO), 1580, 1550, 1500 cm^{-1}.

8-Chloro-3,4-diphenyl-6-substituted pyrimido[4',5':4,5]thieno[2,3-c]pyridazines (**6a**–**g**); *General Procedure*

A stirred solution of the corresponding pyrimidone **5** (0.29 mmol) and phosphorous pentachloride (0.29 mmol) in phosphorous pentachloride (0.29 mmol) in phosphorous oxychloride (15 ml) was refluxed for 2–10 h. Then the reaction mixture was evaporated under reduced pressure, and ice (10 g) was added. The resulting solid was filtered off and recrystallized from a suitable solvent or purified by MPLC.

8-Chloro-3,4,6-triphenylpyrimido[4',5':4,5]thieno[2,3-c]pyridazine (**6a**)

Purified by MPLC using CH_2Cl_2 as eluent; yield: 78%; m.p.: 250–252 °C; $C_{26}H_{15}N_4ClS$ (450.94); calc.: C: 69.25, H: 3.35, N: 12.42; found C: 69.04, H: 3.41, N: 12.36; ^1H NMR ($CDCl_3$): $\delta = 7.23$–8.02 (m, 15 H, C_6H_5) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 127.2$ (C-4a), 128.1, 128.3, 128.4, 128.5, 128.6, 130.0, 130.2, 130.5, 131.4, 132.8, 135.5 (C_6H_5), 136.0, 136.8, 155.8, 156.5, 157.5, 161.1, 163.7 ppm; MS (EI): m/z (%) = 452 ($M^+ + 2$, 35), 450 (M^+, 100), 283 (28); IR (KBr): $\nu = 1560$, 1490, 1380 cm^{-1}.

8-Chloro-6-(4-nitrophenyl)-3,4-diphenylpyrimido[4',5':4,5]thieno[2,3-c]pyridazine (**6b**)

Purified by MPLC using CH_2Cl_2/hexane (3:1) as eluent; yield: 59%; m.p.: 289–291 °C; $C_{26}H_{14}N_5O_2ClS$ (495.94); calc.: C: 62.97, H: 2.85, N: 14.12; found: C: 63.03, H: 3.01, N: 14.06; ^1H NMR ($CDCl_3$): $\delta = 7.34$–7.51 (m, 10 H, C_6H_5), 8.10, 8.30 (AA'XX' system, 4 H, $J = 9.2$ Hz, C_6H_4) ppm; ^{13}C

NMR ($CDCl_3$): δ = 127.0 (C-4a), 123.6, 128.1, 128.5, 128.8, 129.3, 129.8, 130.5, 131.8, 132.8, 135.7 (C_6H_5, C_6H_4), 136.9, 141.3, 149.5, 156.2, 156.5, 157.8, 159.3, 163.6 ppm; MS (EI): *m/z* (%) = 497 (M^+ + 2, 41), 495 (M^+, 100), 449 (24), 283 (14); IR (KBr): ν = 1520, 1350 cm^{-1}.

8-Chloro-6-(4-chlorophenyl)-3,4-diphenylpyrimido[4',5':4,5]thieno[2,3-c]pyridazine (**6c**)

Recrystallized from CH_2Cl_2/acetone; yield: 58%; m.p.: 286–288 °C; $C_{26}H_{14}N_4Cl_2S$ (485.39); calc.: C: 64.34, H: 2.91, N: 11.54; found: C: 64.28, H: 3.05, N: 11.64; ^1H NMR ($CDCl_3$): δ = 7.31–7.48 (m, 10 H, C_6H_5), 7.46, 7.92 (AA'XX' system, 4 H, J = 8.0 Hz, C_6H_4) ppm; ^{13}C NMR ($CDCl_3$): δ = 127.0 (C-4a), 128.1, 128.3, 128.7, 129.8, 129.9, 130.5, 132.9, 134.1, 135.9 (C_6H_5, C_6H_4), 136.8, 137.7, 155.9, 156.5, 157.6, 160.7, 163.7 ppm; MS (EI): *m/z* (%) = 486 (M^+ + 2, 28), 484 (M^+, 39), 483 (2), 283 (24); IR (KBr): ν = 1550, 1500, 1380 cm^{-1}.

8-Chloro-6-(2-methoxyphenyl)-3,4-diphenylpyrimido[4',5':4,5]thieno[2,3-c]pyridazine (**6a**)

Purified by MPLC using CH_2Cl_2/AcOEt (19:1) as eluent; yield: 69%; m.p.: 204–206 °C; $C_{27}H_{17}N_4OClS$ (480.97); calc.: C: 67.43, H: 3.56, N: 11.65; found: C: 67.38, H: 3.67, N: 11.72; ^1H NMR ($CDCl_3$): δ = 3.77 (s, 3 H, CH_3O), 6.89–7.00 (m, 2 H, C_6H_4), 7.26, 7.44 (m, 14 H, C_6H_5, C_6H_4) ppm; ^{13}C NMR ($CDCl_3$): δ = 55.9 (CH_3O), 127.2 (C-4a), 112.0, 120.1, 125.7, 127.8, 127.9, 128.4, 128.5, 129.9, 130.1, 130.4, 131.8, 132.4, 132.5 (C_6H_5, C_6H_4), 136.1, 136.8, 154.9, 156.2, 157.5, 158.2, 162.0, 163.6 ppm; MS (EI): *m/z* (%) = 482 (M^+ + 2, 41), 480 (M^+, 100), 465 (12), 445 (52), 283 (20); IR (KBr): ν = 1600, 1550, 1500, 1480, 1380 cm^{-1}.

8-Chloro-6-(3,4-methylenedioxyphenyl)-3,4-diphenylpyrimido[4',5':4,5]thieno[2,3-c]pyridazine (**6e**)

Purified by MPLC using CH_2Cl_2 as eluent and recrystallized from CH_2Cl_2/acetone; yield: 50%; m.p.: 285–287 °C; $C_{27}H_{15}N_4O_2ClS$ (494.95); calc.: C: 65.52, H: 3.06, N: 11.32; found: C: 65.45, H: 3.18, N: 11.44; ^1H NMR ($CDCl_3$): δ = 4.78 (s, 2 H, OCH_2O), 6.77 (d, 1 H, J = 8.3 Hz, C_6H_3), 7.30–7.70 (m, 12 H, C_6H_5, C_6H_3) ppm; ^{13}C NMR ($CDCl_3$): δ = 101.4 (OCH_2O), 127.2 (C-4a), 108.1, 108.4, 123.8, 125.6; 128.1, 128.3, 128.6, 128.7, 129.4, 129.9, 130.5, 132.9 (C_6H_5, C_6H_4), 136.0, 136.8, 148.0, 150.5, 155.6, 156.5, 157.5, 161.3, 164.0 ppm; MS (EI): *m/z* (%) = 496 (M^+ + 2, 41), 494 (M^+, 100), 465 (6), 283 (19); IR (KBr): ν = 1560, 1480, 1450, 1380 cm^{-1}.

8-Chloro-6-(2,6-dichlorophenyl)-3,4-diphenylpyrimido[4',5':4,5]thieno[2,3-c]pyridazine (**6f**)

Purified by MPLC using CH_2Cl_2 as eluent; yield: 40%; m.p.: 254–256 °C; $C_{26}H_{13}N_4Cl_3S$ (519.83); calc.: C: 60.07, H: 2.52; N, 10.78; found: C: 59.98, H: 2.63, N: 10.99; ^1H NMR ($CDCl_3$): δ = 7.22–7.43 (m, 13 H, C_6H_5, C_6H_3) ppm; ^{13}C NMR ($CDCl_3$): δ = 126.9 (C-4a), 127.7, 128.0, 128.1, 128.6, 129.4, 130.4, 131.6, 131.8, 134.0, 135.8 (C_6H_5, C_6H_3), 136.2, 137.3, 155.7, 156.5, 157.9, 159.7, 163.5 ppm; MS (EI): *m/z* (%) = 520 (M^+ + 2, 100), 518 (M^+, 99), 483 (6), 283 (45); IR (KBr): ν = 1550, 1480, 1430, 1390 cm^{-1}.

8-Chloro-6-(4-methylphenyl)-3,4-diphenylpyrimido[4',5':4,5]thieno[2,3-c]pyridazine (**6g**)

Purified by MPLC using CH_2Cl_2 as eluent; yield: 86%; m.p.: 266–268 °C; $C_{27}H_{17}N_4ClS$ (464.97); calc.: C: 69.75, H: 3.69; N, 12.05; found: C: 69.98, H: 3.73, N: 11.92; ^1H NMR ($CDCl_3$): δ = 2.36 (s, 3 H, CH_3), 7.11, 7.82 (AA'XX' system, 4 H, J = 8.1 Hz, C_6H_4), 7.30–7.56 (m, 10 H, C_6H_5) ppm; ^{13}C NMR ($CDCl_3$): δ = 21.5 (CH_3), 127.2 (C-4a), 128.0, 128.3, 128.6, 129.1, 129.8, 130.1, 130.5, 132.8, 132.9, 136.1 (C_6H_5, C_6H_4), 136.8, 141.9, 155.6, 156.4, 157.5, 161.8, 163.8 ppm; (MS (EI): *m/z* (%) = 466 (M^+ + 2, 40), 464 (M^+, 100), 463 (64), 283 (29); IR (KBr): ν = 1560, 1490, 1380 cm^{-1}.

3,4,6-Triphenyl-8-substituted pyrimido[4′,5′:4,5]thieno[2,3-c]pyridazines (**7a–f**); *General Procedure for* **7a, d–f**

A solution of 8-chloro-3,4,6-triphenylpyrimido[4′,5′:4,5]thieno[2,3-*c*]pyridazine **6a** (0.22 mmol) and the appropriate amine (0.44 mmol) in ethanol (7 ml) was refluxed for 3 h. The solid was filtered off and recrystallized from ethanol/dichloromethane.

8-Hydrazino-3,4,6-triphenylpyrimido[4′,5′:4,5]thieno[2,3-c]pyridazine (**7a**)

81%; m.p.: 294–296 °C; $C_{26}H_{18}N_6S$ (446.53); calc.: C: 69.94, H: 4.06, N: 18.82; found: C: 70.05, H: 4.16, N: 18.68; ^{1}H NMR ($CDCl_3$): $\delta = 7.25–7.50$ (m, 16 H, C_6H_5 + NH), 7.90 (d, 2 H, $J = 6.6$ Hz, NH_2) ppm; MS (EI): *m/z* (%) = 446 (M^+, 19), 445 (22), 416 (28), 415 (18), 283 (11); IR (KBr): $\nu = 3320$, 3180 (NH), 1650, 1550, 1480, 1400 cm^{-1}.

3,4,6-Triphenyl-8-piperidinopyrimido[4′,5′:4,5]thieno[2,3-c]pyridazine (**7d**)

86%; Yield: m.p.: 252–254 °C; $C_{31}H_{25}N_5S$ (499.63); calc.: 74.52, H: 5.04, N: 14.02; found: C: 74.48, H: 4.96, N: 14.16; ^{1}H NMR ($CDCl_3$): $\delta = 1.81$ (s, 4 H, CH_2), 1.93 (s, 2 H, CH_2), 4.06 (s, 4 H, NCH_2), 7.26–7.95 (m, 15 H, C_6H_5) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 24.8$ (CH_2), 26.1 (CH_2), 47.8 (NCH_2), 114.7 (C-8a), 127.7 (C-4a), 127.9, 128.1, 128.2, 130.1, 130.3, 130.5, 133.9, 135.9 (C_6H_5); 136.8, 137.7, 155.5, 157.0, 158.5, 160.1, 163.3 ppm; MS (EI): *m/z* (%) = 499 (M^+, 90), 498 (100), 471 (11), 470 (31), 443 (23), 415 (16), 283 (15); IR (KBr): $\nu = 1545$, 1480, 1440, 1370 cm^{-1}.

8-Morpholino-3,4,6-triphenylpyrimido[4′,5′:4,5]thieno[2,3-c]pyridazine (**7e**)

Yield: 85%; m.p.: 220–222 °C; $C_{30}H_{23}N_5OS$ (501.60); calc: C: 71.84, H: 4.62, N: 13.97; found: C: 7.198, H: 4.76, N: 14.06; ^{1}H NMR ($CDCl_3$): $\delta = 3.93–3.96$ (m, 4 H, NCH_2), 4.06–4.09 (m, 4 H, OCH_2), 7.27–8.02 (m, 15 H, C_6H_5) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 46.4$ (NCH_2), 66.5 (OCH_2), 114.4 (C-8a), 127.0 (C-4a), 127.7, 127.8, 127.9, 128.0, 128.1, 130.1, 130.3, 130.5, 133.5, 135.8, 136.4 (C_6H_5), 137.2, 155.5, 156.9, 158.5, 159.8, 163.0 ppm; MS (EI): *m/z* (%) = 501 (M^+, 60), 500 (58), 443 (33), 415 (11), 312 (12), 283 (20); IR (KBr): $\nu = 1525$, 1440, 1380, 1300 cm^{-1}.

8-(N-(4′-Acetylphenyl)-piperazino)-3,4,6-triphenylpyrimido[4′,5′:4,5]thieno[2,3-c]pyridazine (**7f**)

Yield: 73%; m.p.: 294–296 °C; $C_{38}H_{30}N_6OS$ (618.75); calc.: C: 73.76, H: 4.89, N: 13.58; found: C: 73.65, H: 4.75, N: 13.47; ^{1}H NMR ($CDCl_3$): $\delta = 2.56$ (s, 3 H, $COCH_3$), 3.65 (t, 4 H, $J = 5.0$ Hz, NCH_2), 4.29 (t, 4 H, $J = 5.0$ Hz, NCH_2), 6.96 (d, 2 H, $J = 9.0$ Hz, C_6H_4), 7.28–7.99 (m, 17 H, C_6H_5 + C_6H_4) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 26.2$ (CH_3), 45.7 (NCH_2), 47.0 (NCH_2), 114.8 (C-8a), 127.5 (C-4a), 113.4, 127.9, 128.0, 128.1, 128.3, 128.4, 128.5, 130.0, 130.2, 130.4, 130.5, 132.8, 133.6, 136.1, 136.5 (C_6H_5 + C_6H_4), 137.3, 153.5, 155.8, 157.2, 158.6, 160.2, 163.2, 196.6 (CO) ppm; MS (FAB): *m/z* (%) = 619 ($(MH)^+$, 46), 453 (44), 451 (100), 417 (9), 312 (14), 283 (13); IR (KBr): $\nu = 1670$ (CO), 1600, 1520, 1440, 1380 cm^{-1}.

8-Ethoxy-3,4,6-triphenylpyrimido[4′,5′:4,5]thieno[2,3-c]pyridazine (**7b**)

To a solution of sodium ethoxide (0.05 g of sodium, 2 g Atom) in ethanol (5 ml) **6a** (0.10 g, 0.22 mmol) was added. The mixture was refluxed for 1 h. The solvent was removed under reduced pressure and the solid was recrystallized from ethanol to give 0.06 g (60%) of **7b**. M.p.: 213–215 °C; $C_{28}H_{20}N_4OS$ (460.55); calc.: C: 73.02, H: 4.38, N: 12.17; found: C: 73.18, H: 4.26, N: 12.28; ^{1}H NMR ($CDCl_3$): $\delta = 1.59$ (t, 3 H, $J = 7.1$ Hz, CH_3), 4.80 (q, 2 H, $J = 7.1$ Hz, CH_2), 7.27–8.04 (m, 15 H, C_6H_5) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 14.3$ (CH_3), 63.5 (CH_2), 118.0 (C-8a), 127.4 (C-4a), 127.9, 128.0, 128.1, 128.2, 128.3, 130.3, 130.5, 130.6, 133.3, 136.0, 136.4 (C_6H_5), 136.8, 155.5, 156.8, 160.8, 164.9 ppm; MS (EI): *m/z* (%) = 460 (M^+, 81), 459 (100), 431 (98), 300 (8), 272 (17); IR (KBr): $\nu = 1565$, 1530, 1420, 1380 cm^{-1}.

3,4,6-Triphenyl-8-propylaminopyrimido[4',5':4,5]thieno[2,3-c]pyridazine (**7c**)

A mixture of 8-chloro-3,4,6-triphenylpyrimido[4',5':4,5]thieno[2,3-*c*]pyridazine (**6a**, 0.10 g, 0.22 mmol) and propylamine (3 ml) was stirred at room temperature for 30 min. The solvent was removed under reduced pressure and the solid was then recrystallized from ethanol/hexane to give 0.1 g (95%) of **7c**. M.p.: 296–298 °C; $C_{29}H_{23}N_5S$ (473.59); calc.: C: 73.55, H: 4.90, N: 14.79; found: C: 73.67, H: 4.76, N: 14.88; ^{1}H NMR ($CDCl_3$): $\delta = 1.10$ (t, 3 H, $J = 7.4$ Hz, CH_3), 1.84 (m, 2 H, CH_3CH_2), 3.78 (q, 2 H, $J = 6.7$ Hz, NCH_2), 5.03 (br s, 1 H, NH), 7.27–8.04 (m, 15 H, C_6H_5) ppm; ^{13}C NMR (*DMSO*-d_6): $\delta = 11.6$ (CH_3), 38.2 (CH_2), 42.4 (CH_2), 115.1 (C-8a), 127.6, 127.8, 127.9, 128.0, 130.2, 130.3, 133.5, 135.6 (C_6H_5), 136.8,137.5, 152.7, 156.5, 157.3, 159.8, 163.4 (ppm; MS (EI): m/z (%) = 473 (M^+, 44), 472 (64), 430 (20) 283 (8); IR (KBr): $\nu = 3280$ (NH), 1595, 1550, 1480, 1380 cm^{-1}.

5,7,8-Triphenyl-1,2,4-triazolo[3'',4'':6',1']pyrimido[4',5':4,5]thieno[2,3-c]pyridazine (**8**)

A solution of **7a** (0.10 g, 0.24 mmol) in formic acid (5 ml) was refluxed for 12 h. The solvent was then removed under reduced pressure and water (10 ml) was added to the residue. The solid was filtered off and recrystallized from ethanol/acetone to yield 0.07 g (61%) of **8**. M.p.: 267–269 °C; $C_{27}H_{16}N_6S$ (456.52); calc.: C: 71.04, H: 3.53, N: 18.41; found: C: 70.97, H: 3.65, N: 18.52; ^{1}H NMR (*DMSO*-d_6): $\delta = 7.30$–7.72 (m, 15 H, C_6H_5), 9.79 (s, 1 H, CH) ppm; ^{13}C NMR (*DMSO*-d_6): $\delta = 120.5$ (C-8a), 126.4 (C-4a), 127.5, 127.7, 127.8, 128.2, 128.3, 128.7, 129.2, 130.3, 131.2, 132.0, 133.1, 134.8, 136.6 (C_6H_5 + NCH), 137.3, 140.0, 145.1, 156.8, 162.4, 166.0 ppm; MS (EI): m/z (%) = 456 (M^+, 100), 455 (98), 428 (5), 325 (56), 297 (12); IR (KBr): $\nu = 3150$, 1600, 1520, 1480, 1370 cm^{-1}.

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