Efficient Synthesis of Benzothieno[3,2-*d*]-1,2,4-triazolo [1,5-*a*]pyrimidin-5(1*H*)-ones *via* a Tandem aza-Wittig/ Heterocumulene-Mediated Annulation

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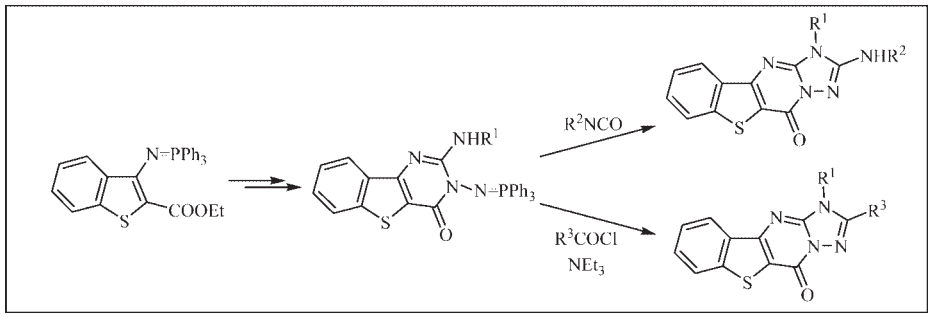

The carbodiimides **2**, obtained from reactions of iminophosphorane **1** with isocyanates, reacted with hydrazine to give selectively 3-amino-2-arylaminobenzothieno[3,2-*d*]pyrimidin-4(3*H*)-ones **4**. Reactions of **4** with triphenylphosphine, hexachloroethane, and Et_3N produced iminophosphoranes **5**. A tandem aza-Wittig reaction of iminophosphorane **5** with isocyanate, acyl chloride generated benzothieno[3,2-*d*]-1,2,4-triazolo[1,5-*a*]pyrimidin-5(1*H*)-ones **7** and **9** in satisfactory yields. The effects of the nucleophiles on cyclization have been investigated.

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INTRODUCTION

Thienopyrimidines are very important heterocycles because of their significant antifungal and antibacterial activities [1–4] as well as their good anticonvulsant and angiotensin or H_1 receptor antagonistic activities [5–7]. The chemistry of thienopyrimidinones have also received attention because of their starting materials, 2-amino-3-carboxythiophenes, which can be conveniently synthesized. On the other hand, heterocycles containing 1,2,4-triazole nucleus also exhibit various biological activities; several of them have been used as fungicidal, bactericidal, insecticidal, antitumor, and anti-inflammatory agents [8–13]. The introduction of a triazole ring into the thienopyrimidine system is expected to influence the biological activities significantly.

The aza-Wittig reactions of iminophosphoranes have received increasing attention in view of their useful utilities in the synthesis of nitrogen heterocyclic compounds under mild conditions [14,15]. Recently, we have been interested in the synthesis of triazolo-quinazolinones, thienopyrimidinones, and imidazolinones *via* aza-Wittig reaction, with the aim of evaluating their fungicidal activities [16–20]. Reported herein is a new efficient synthesis of 2-substituted benzothieno[3,2-*d*]-1,2,4-triazolo[1,5-*a*] pyrimidin-5(1*H*)-one **7** and **9** from easily accessible iminophosphorane **1** [21].

RESULTS AND DISCUSSION

Carbodiimides **2**, obtained from aza-Wittig reactions of iminophosphorane **1** with aromatic or alkyl isocyanates, reacted with hydrazine to give selectively 2-arylamino-3-aminobenzothieno[3,2-*d*]pyrimidin-4(3*H*)-ones **4** in 80–87% yields at room temperature (Table 1, Scheme 1).

The formation of **4** can be rationalized in terms of an initial nucleophilic addition of hydrazine to give intermediate **3** which directly cyclized across the strong nucleophilic hydrazine group rather than the aryl(alkyl)-amine one. Compounds **4** were further converted to functionalized iminophosphoranes **5** *via* reaction with triphenylphosphine, hexachloroethane, and Et_3N in 72–78% yields (Table 1, Scheme 1).

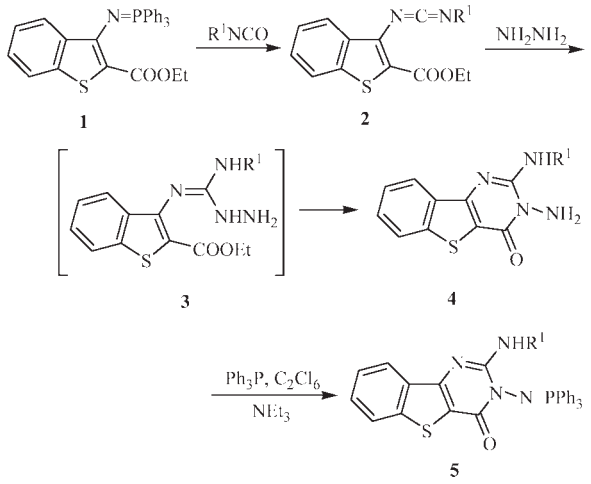
Table 1

Physical and analytical data of compounds **7**.

Comp.	R^1	R^2 or R^3	Time (hours)	Mp (°C)	Yield %[a]	Molecular Formula	Analysis % (Calcd./Found) C	H	N
4a	Ph		2	246–247	80	$C_{16}H_{14}N_4OS$	62.32	3.92	18.17
							62.08	3.74	18.37
4b	4-ClC_6H_4		2	>300	82	$C_{16}H_{11}ClN_4OS$	56.07	3.23	16.34
							56.29	3.12	16.57
4c	4-$CH_3C_6H_4$		2	>300	83	$C_{17}H_{14}N_4OS$	63.33	4.38	17.38
							63.12	4.16	17.25
4d	i-Pr		2	207–208	79	$C_{13}H_{14}N_4OS$	56.91	5.14	20.42
							56.79	5.43	20.11
4e	n-Bu		2	199–201	77	$C_{14}H_{16}N_4OS$	58.31	5.59	11.12
							58.19	5.33	11.22
5a	Ph		6	258–260	74	$C_{34}H_{25}N_4OPS$	71.82	4.43	9.85
							71.78	4.54	9.77
5b	4-ClC_6H_4		6	260–261	72	$C_{34}H_{24}ClN_4OPS$	67.71	4.01	9.29
							67.58	4.24	9.17
5c	4-$CH_3C_6H_4$		6	259–261	78	$C_{35}H_{27}N_4OPS$	72.15	4.67	9.62
							72.02	4.84	9.52
5d	i-Pr		6	207–208	77	$C_{31}H_{27}N_4OPS$	69.65	5.09	10.48
							69.82	5.24	10.42
5e	n-Bu		6	202–204	75	$C_{32}H_{29}N_4OPS$	70.05	5.33	10.21
							70.22	5.45	10.05
7a	4-$CH_3C_6H_4$	Ph	4	>300	84	$C_{24}H_{17}N_5OS$	68.07	4.05	16.54
							68.19	4.11	16.37
7b	Ph	Ph	4	>300	82	$C_{23}H_{15}N_5OS$	67.47	3.69	17.10
							67.60	3.73	17.00
7c	4-$CH_3C_6H_4$	4-ClC_6H_4	4	>300	86	$C_{24}H_{16}ClN_5OS$	62.95	3.52	15.29
							63.08	5.57	15.14
7d	4-ClC_6H_4	4-ClC_6H_4	4	>300	85	$C_{23}H_{13}ClN_5OS$	57.75	2.74	14.64
							57.88	2.67	14.69
7e	Ph	4-ClC_6H_4	4	>300	84	$C_{23}H_{14}ClN_5OS$	62.23	3.18	15.78
							62.38	3.23	15.69
7f	4-$CH_3C_6H_4$	4-$CH_3C_6H_4$	4	>300	85	$C_{25}H_{19}N_5OS$	68.63	4.38	16.01
							68.75	4.44	15.86
7g	4-ClC_6H_4	4-$CH_3C_6H_4$	4	298–299	83	$C_{24}H_{16}ClN_5OS$	62.05	3.52	15.29
							62.18	3.54	15.16
7h	Ph	4-$CH_3C_6H_4$	4	290–291	86	$C_{24}H_{17}N_5OS$	68.07	4.05	16.54
							68.18	3.96	16.65
7i	4-ClC_6H_4	i-Pr	8	>300	76	$C_{20}H_{16}ClN_5OS$	58.60	3.93	17.09
							58.48	4.05	16.98
7j	4-ClC_6H_4	n-Bu	8	282–284	74	$C_{21}H_{18}ClN_5OS$	59.50	4.28	16.52
							59.58	4.45	16.35
7k	i-Pr	i-Pr	8	>300	77	$C_{17}H_{19}N_5OS$	59.80	5.61	20.51
							59.88	5.85	20.39
7l	i-Pr	Ph	8	>300	80	$C_{20}H_{17}N_5OS$	63.98	4.56	18.65
							64.05	4.75	18.50
7m	Ph	4-$CH_3C_6H_4$	4	>300	83	$C_{21}H_{19}N_5OS$	64.76	4.92	17.98
							64.68	5.15	17.89
7n	n-Bu	4-$CH_3C_6H_4$	8	>300	67	$C_{22}H_{21}N_5OS$	65.49	5.25	17.36
							65.54	5.45	17.19
7o	n-Bu	i-Pr	8	>300	72	$C_{18}H_{21}N_5OS$	60.82	5.95	19.70
							60.92	6.25	19.57
7p	n-Bu	Ph	8	294–296	82	$C_{21}H_{19}N_5OS$	64.76	4.92	17.98
							64.85	5.13	17.79
9a	n-Bu	CH_3	24	187–189	72	$C_{16}H_{19}N_4OS$	61.52	5.16	17.93
							61.59	5.03	17.97
9b	n-Bu	Ph	24	212–214	65	$C_{21}H_{18}N_4OS$	67.36	4.85	14.96
							67.39	4.67	14.98
9c	Ph	CH_3	24	>300	74	$C_{18}H_{12}N_4OS$	65.04	3.64	14.86
							65.29	3.77	14.65
9d	Ph	Ph	24	277–279	62	$C_{23}H_{14}N_4OS$	70.03	3.58	14.20
							70.22	3.67	14.01

[a] Yields based on iminophosphorane **1** or **5**.

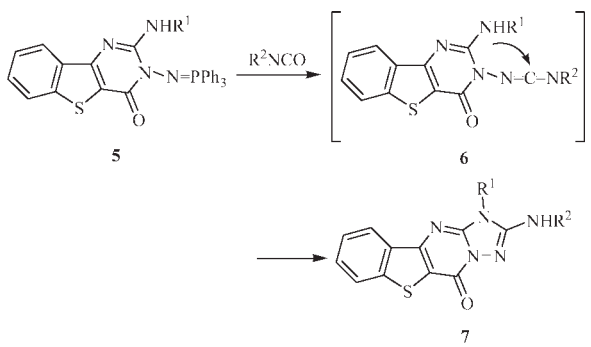
Scheme 1



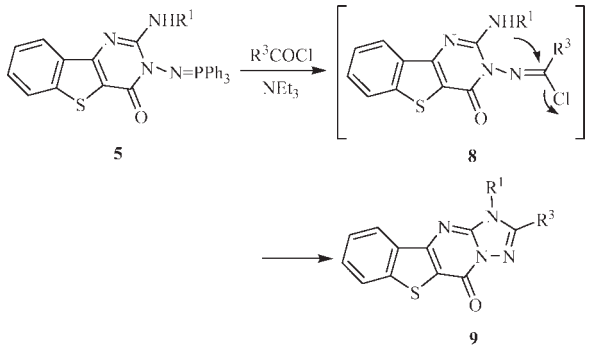
When iminophosphoranes **5** in anhydrous CH_2Cl_2 were treated with isocyanate at room temperature, the color of the reaction mixture quickly turned red, disappearing after few minutes, and 2-aminobenzothieno[3,2-*d*]-1,2,4-triazolo-[1,5-*a*]pyrimdin-5(1*H*)-ones **7** were isolated as crystalline solids in good yields (67–86%, Table 1, Scheme 2). Presumably, the conversion of **5** into **7** involves initial aza-Wittig reaction between the iminophosphorane **5** and the isocyanate to give a carbodiimide **6** as highly reactive intermediate, which easily undergoes ring closure across the amino group to give the otherwise not readily available 2-amino substituted benzothieno[3,2-*d*]-1,2,4-triazolo[1,5-*a*] pyrimidin-5(1*H*)-ones **7**. It is noteworthy that the reaction can be easily carried out at room temperature under mild, neutral condition, and the separation of **7** from the reaction mixture was also easily carried out by simple filtration.

Iminophosphorane **5** reacted with acyl chlorides in the presence of Et_3N in CH_2Cl_2 at room temperature to give 2-substituted benzothieno[3,2-*d*]-1,2,4-triazolo[1,5-*a*] pyrimidin-5(1*H*)-ones **9** in good yields (62–74%, Table 1, Scheme 3). The formation of **9** can be viewed as an initial aza-Wittig reaction between the

Scheme 2



Scheme 3



iminophosphorane **5** and acyl chloride in the presence of Et_3N affording the intermediate imidoyl chloride **8**, which undergoes cyclization to give **9**.

The structure of the synthesized compound **5**, **7**, **9** were confirmed by their spectral data. For example, the IR spectra of **7k** revealed C=O absorption bands at 1672 cm^{-1}. The ^1H NMR spectral data of **7k** show the signals of —NH at 9.89 ppm as singlet. The Ar—H signals appeared at 7.50–8.34 (m, 4H, Ar—H). The MS spectrum of **7k** shows an obvious molecule ion peak at m/z 341 with 34% abundance.

In summary, we have developed an efficient synthesis of 2-substituted benzothieno[3,2-*d*]-1,2,4-triazolo[1,5-*a*] pyrimidin-5(1*H*)-one. Due to the easily accessible and versatile starting material, this method has the potential in the synthesis of many biologically and pharmaceutically active thienopyrimidinones derivatives.

EXPERIMENTAL

Melting points were determined using a X-4 model apparatus and were uncorrected. MS were measured on a Finnigan Trace MS spectrometer. NMR spectra were recorded in $CDCl_3$ on a Varian Mercury Plus 400 (400 Hz) spectrometer and chemical shifts (δ) were given in ppm using $(CH_3)_4Si$ as an internal reference (δ = 0). IR were recorded on a PE-983 infrared spectrometer as KBr pellets with absorption in cm^{-1}. Elementary analyses were taken on a Vario EL III elementary analysis instrument.

Preparation of compounds 4. To a solution of imino-phosphorane 1 (1.44 g, 3 mmol) in anhyd. CH_2Cl_2 (10 mL) was added isocyanate (3 mmol) under N_2 at r.t. After the reaction mixture was left unstirred for 8–12 h at 0–5°C, the solvent was removed off under reduced pressure and Et_2O/petroleum ether (1:2, 12 mL) was added to precipitate triphenylphosphine oxide. Removal of the solvent gave carbodiimides 2, which were used directly without further purification. To the solution of 2 prepared above in CH_2Cl_2 (10 mL) was added hydrazine (0.18 g, 3 mmol). The mixture was stirred for 2 h at r. t. and filtered to give 4.

3-Amino-2-phenylamino-benzo[4,5]thieno[3,2-*d*]pyrimidin-4(3*H*)-one (4a). ^1H NMR (400 MHz, $CDCl_3$): δ (ppm): 4.65 (s, 1H, NH), 4.72 (s, 2H, NH_2), 7.15–8.06 (m, 9H, Ar—H). IR

(KBr): 3412 (NH), 1674 (C=O), 1530, 1380, 698 cm^{-1}. MS: *m/z* (%) 308 (47, M^+), 292 (33), 200 (19), 145 (28), 77 (87).

3-Amino-2-(4-chlorophenylamino)-benzo[4,5]thieno[3,2-d] pyrimidin-4(3*H*)-one (4b). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm): 4.71 (s, 1H, NH), 4.86 (s, 2H, NH_2), 7.43–7.68 (m, 6H, Ar—H), 7.87 (d, J = 8.0 Hz, 1H, Ar—H), 8.25 (d, J = 7.6 Hz, 1H, Ar—H). IR (KBr): 3428 (NH), 1676 (C=O), 1531, 1385, 693 cm^{-1}. MS: *m/z* (%) 342 (35, M^+), 327 (24), 200 (34), 146 (43), 77 (26).

3-Amino-2-(4-methylphenylamino)-benzo[4,5]thieno[3,2-*d*] pyrimidin-4(3*H*)-one (4c). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm): 2.66 (s, 3H, CH_3), 4.73 (s, 1H, NH), 4.77 (s, 2H, NH_2), 7.23–8.46 (m, 8H, Ar—H). IR (KBr): 3420 (NH), 1678 (C=O), 1531, 1377, 693 cm^{-1}. MS: *m/z* (%) 322 (52, M^+), 306 (47), 200 (34), 146 (52), 77 (47).

3-Amino-2-isopropylamino-benzo[4,5]thieno[3,2-d]pyrimidin-4(3*H*)-one (4d). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 1.16 (d, J = 6.4 Hz, 6H, $2CH_3$), 3.40–3.60 (m, 1H, NCH), 4.66 (d, J = 6.8 Hz, 1H, NH), 4.74 (s, 2H, NH_2), 7.40–7.61 (m, 2H, Ar—H), 7.83 (d, J = 8.4 Hz, 1H, Ar—H), 8.15 (d, J = 7.6 Hz, 1H, Ar—H). IR (KBr): 3417 (NH), 1676 (C=O), 1535, 1371, 694 cm^{-1}. MS: *m/z* (%) 274 (47, M^+), 258 (17), 200 (47), 146 (44), 77 (45).

3-Amino-2-butylamino-benzo[4,5]thieno[3,2-*d*]pyrimidin-4-(3*H*)-one (4e). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm): 0.92 (t, J = 7.0 Hz, 3H, CH_3), 1.20–1.37 (m, 4H, CH_2), 3.55 (m, 2H, NCH_2), 4.61 (s, 1H, NH), 4.75 (s, 2H, NH_2), 7.43–7.58 (m, 2H, Ar—H), 7.85 (d, J = 8.0 Hz, 1H, Ar—H), 8.26 (d, J = 7.6 Hz, 1H, Ar—H). IR (KBr): 3411 (NH), 1676 (C=O), 1533, 1372, 694 cm^{-1}. MS: *m/z* (%) 288 (58, M^+), 272 (31), 200 (55), 146 (37), 77 (58).

Preparation of iminophosphorane 5. To a mixture of **4** (8 mmol), PPh_3 (3.14 g, 12 mmol) and C_2Cl_6 (2.84 g, 12 mmol) in dry CH_3CN (40 mL), was added dropwise NEt_3 (2.42 g, 24 mmol) at room temperature. The color of the reaction mixture quickly turned yellow and the mixture was stirred 4–6 h at room temperature. After completion of the reaction (monitored with TLC), the solvent was removed under reduced pressure and the residue was recrystallized from EtOH to give iminophosphoranes **5**.

2-Phenylamino-3-(triphenylphosphoranylidene)aminobenzo[4,5]thieno[3,2-d]pyrimidin-4(3*H*)-one (5a). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 4.66 (s, 1H, NH), 7.09–8.25 (m, 24H, Ar—H). IR (KBr): 3420 (NH), 1670 (C=O), 1533, 1381, 696 cm^{-1}. MS: *m/z* (%) 568 (52, M^+), 292 (20), 276 (57), 200 (13), 145 (24), 77 (50).

2-(4-Chlorophenyl)amino-3-(triphenylphosphoranylidene) amino-benzo[4,5]thieno[3,2-*d*]pyrimidin-4(3*H*)-one (5b). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 4.73 (s, 1H, NH), 7.20–8.30 (m, 23H, Ar—H). IR (KBr): 3428 (NH), 1676 (C=O), 1531, 1385, 693 cm^{-1}. MS: *m/z* (%) 602 (32, M^+), 327 (9), 276 (26), 200 (12), 146 (51), 77 (22).

2-(4-Methylphenyl)amino-3-(triphenylphosphoranylidene) amino-benzo[4,5]thieno[3,2-*d*]pyrimidin-4(3*H*)-one (5c). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 2.55 (s, 3H, CH_3), 4.78 (s, 1H, NH), 7.23–8.46 (m, 23H, Ar—H). IR (KBr): 3434 (NH), 1668 (C=O), 1529, 1378, 690 cm^{-1}. MS: *m/z* (%) 582 (56, M^+), 306 (31), 200 (14), 146 (55), 77 (83).

2-(Isopropylamino)-3-(triphenylphosphoranylidene) aminobenzo[4,5]thieno[3,2-*d*]pyrimidin-4(3*H*)-one (5d). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 1.17 (d, J = 6.4 Hz, 6H, $2CH_3$), 3.94 (m, 1H, NCH), 4.60 (s, 1H, NH), 7.23–8.20 (m, 19H, Ar—H). IR (KBr): 3430 (NH), 1673 (C=O), 1531, 1377, 696 cm^{-1}. MS: *m/z* (%) 534 (47, M^+), 272 (37), 200 (37), 146 (68), 77 (79).

2-(Butylamino)-3-(triphenylphosphoranylidene)aminobenzo [4,5]thieno[3,2-*d*]pyrimidin-4(3*H*)-one (5e). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 0.90 (t, J = 7.0 Hz, 3H, CH_3), 1.22–1.37 (m, J = 7.0 Hz, 4H, $2CH_2$), 3.50(m, 2H, NCH_2), 4.61 (s, 1H, NH), 7.27–8.22 (m, 19H, Ar—H). IR (KBr): 3431 (NH), 1671 (C=O), 1529, 1376, 697 cm^{-1}. MS: *m/z* (%) 548 (58, M^+), 286 (25), 200 (56), 146 (52), 77 (71).

General procedure for the preparation of 2-arylamino benzothieno[3,2-*d*]-1,2,4-triazolo[1,5-*a*]pyrimidin-5(1*H*)-ones 7a–7p. To a solution of iminophosphorane 5 (1 mmol) in anhyd. CH_2Cl_2 (15 mL) was added aromatic isocyanate (1 mmol) under N_2 at r.t. The color of the reaction mixture became red, then decolorized after few minutes. The colorless solution was stirred at r.t for 4–8 h. The white precipitated solid was collected by filtration and recrystallized from CH_2Cl_2—EtOH to give 7a–7p.

1-(4-Methylphenyl)-2-phenylamino-benzo[4,5]thieno[3,2-*d*] [1,2,4]triazolo[1,5-a]pyrimidin-5(1*H*)-one (7a). ^{1}H NMR (400 MHz, $CDCl_3$/TFA) δ (ppm): 2.54 (s, 3H, CH_3), 6.72–8.07 (m, 13H, Ar—H). IR (KBr): 3409 (NH), 1671 (C=O), 1575, 1487, 737 cm^{-1}. MS: *m/z* (%) 422 (43, M^+), 277 (62), 201 (28), 146 (86), 91 (77), 77 (58).

1-Phenyl-2-phenylamino-benzo[4,5]thieno[3,2-*d*][1,2,4] tri-azolo[1,5-*a*]pyrimidin-5(1*H*)-one (7b). ^{1}H NMR (400 MHz, $CDCl_3$/TFA) δ (ppm): 7.10–8.13 (m, 14H, Ar—H). IR (KBr): 3412 (NH), 1671 (C=O), 1577, 1490, 744 cm^{-1}. MS: *m/z* (%) 408 (67, M^+), 277 (78), 201 (22), 146 (93), 77 (100).

2-(4-Chloro-phenylamino)-1-(4-methylphenyl)-benzo[4,5]-thieno[3,2-*d*][1,2,4]triazolo[1,5-a]pyrimidin-5(1*H*)-one (7c). ^{1}H NMR (400 MHz, $CDCl_3$/TFA) δ (ppm): 2.55 (s, 3H, CH_3), 6.88–8.03 (m, 12H, Ar—H). IR (KBr): 3421 (NH), 1672 (C=O), 1572, 1496, 743 cm^{-1}. MS: *m/z* (%) 457 (23, M^+), 277 (64), 200 (35), 146 (90), 91 (77), 77 (76).

1-(4-Chlorophenyl)-2-(4-chloro-phenylamino)-benzo[4,5]-thieno[3,2-*d*][1,2,4]triazolo[1,5-*a*]pyrimidin-5(1*H*)-one (7d). ^{1}H NMR (400 MHz, $CDCl_3$/TFA) δ (ppm): 6.82–8.09 (m, 12H, Ar—H). IR (KBr): 3420 (NH), 1673 (C=O), 1574, 1492, 742 cm^{-1}. MS: *m/z* (%) = 477 (34, M^+), 277 (75), 201 (19), 145 (89), 77 (63).

2-(4-Chloro-phenylamino)-1-phenyl-benzo[4,5]thieno[3,2-*d*] [1,2,4]triazolo[1,5-*a*]pyrimidin-5(1*H*)-one (7e). ^{1}H NMR (400 MHz, $CDCl_3$/TFA) δ (ppm): 7.19–8.08 (m, 13H, Ar—H). IR (KBr): 3421 (NH), 1673 (C=O), 1573, 1490, 743 cm^{-1}. MS: *m/z* (%) = 442 (50, M^+), 277 (67), 201 (32), 145 (87), 77 (61).

1-(4-Methylphenyl)-2-(4-methyl-phenylamino)-benzo[4,5]-thieno[3,2-*d*][1,2,4]triazolo[1,5-*a*]pyrimidin-5(1*H*)-one (7f). ^{1}H NMR (400 MHz, $CDCl_3$/TFA) δ (ppm): 1.80 (s, 3H, CH_3), 2.54 (s, 3H, CH_3), 6.72–8.02 (m, 12H, Ar—H). IR (KBr): 3419 (NH), 1671 (C=O), 1575, 1493, 742 cm^{-1}. MS: *m/z* (%) 436 (29, M^+), 277 (64), 201 (19), 146 (84), 91 (73), 77 (89).

1-(4-Chlorolphenyl)-2-(4-methyl-phenylamino)-benzo[4,5] thieno[3,2-*d*][1,2,4]triazolo[1,5-*a*]pyrimidin-5(1*H*)-one (7g). ^{1}H NMR (400 MHz, $CDCl_3$/TFA) δ (ppm): 2.41 (s, 3H, CH_3), 7.40–8.00 (m, 12H, Ar—H). IR (KBr): 3422 (NH), 1672 (C=O), 573, 1490, 744 cm^{-1}. MS: *m/z* (%) 457 (65, M^+), 277 (58), 200 (31), 146 (82), 91 (67), 77 (78).

2-(4-Methyl-phenylamino)-1-phenyl-benzo[4,5]thieno[3,2-*d*][1,2,4]triazolo[1,5-a]pyrimidin-5(1*H*)-one (7h). ^{1}H NMR (400 MHz, $CDCl_3$/TFA) δ (ppm): 2.03 (s, 3H, CH_3), 6.76–8.06 (m, 13H, Ar—H). IR (KBr): 3412 (NH), 1671 (C=O), 1577, 1491, 742 cm^{-1}. MS: *m/z* (%) 423 (54, M^+), 277 (56), 201 (25), 146 (85), 91 (66), 77 (79).

1-(4-Chlorophenyl)-2-isopropylamino-benzo[4,5]thieno-[3,2-*d*][1,2,4]triazolo[1,5-*a*]pyrimidin-5(1*H*)-one (7i). ^{1}H NMR (400 MHz, $CDCl_3$/TFA) δ (ppm): 1.33 (d, J = 7.0 Hz, 6H, $2CH_3$), 4.09 (d, J = 6.9 Hz, 1H, NCH), 7.37–8.14 (m, 8H, Ar—H). IR (KBr): 3414 (NH), 1672 (C=O), 1567, 1489, 743 cm^{-1}. MS: *m/z* (%) 409 (46, M^+), 277 (46), 201 (22), 145 (100), 77 (69).

2-Butylamino-1-(4-chlorophenyl)-benzo[4,5]thieno[3,2-*d*]-[1,2,4]triazolo[1,5-a]pyrimidin-5(1*H*)-one (7j). ^{1}H NMR (400 MHz, $CDCl_3$/TFA) δ (ppm): 0.93 (t, J = 7.0 Hz, 3H, CH_3), 1.31–1.38 (m, 2H, CH_2), 1.60–1.69 (m, 2H, CH_2), 3.44 (t, J = 6.9 Hz, 2H, NCH_2), 7.47–8.13 (m, 8H, Ar—H). IR (KBr): 3415 (NH), 1673 (C=O), 1566, 1488, 742 cm^{-1}. MS: *m/z* (%) 423 (59, M^+), 277 (67), 200 (24), 146 (88), 77 (75).

1-Isopropyl-2-isopropylamino-benzo[4,5]thieno[3,2-*d*]-[1,2,4]triazolo[1,5-*a*]pyrimidin-5(1*H*)-one (7k). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 1.35 (d, J = 7.0 Hz, 6H, $2CH_3$), 1.75 (d, J = 7.0 Hz, 6H, $2CH_3$), 4.05 (t, J = 6.9 Hz, 1H, NCH), 4.70 (s, 1H, NCH), 7.50–8.34 (m, 4H, Ar—H), 9.89 (s, 1H, NH). IR (KBr): 3411 (NH), 1672 (C=O), 1574, 1490, 741 cm^{-1}. MS: *m/z* (%) 341 (34, M^+), 277 (55), 201 (37), 146 (73), 77 (65).

1-Isopropyl-2-phenylamino-benzo[4,5]thieno[3,2-*d*][1,2,4]triazolo[1,5-*a*]pyrimidin-5(1*H*)-one (7l). ^{1}H NMR (400 MHz, $CDCl_3$/TFA) δ (ppm): 1.86 (d, J = 7.2 Hz, 6H, $2CH_3$), 4.80–4.91 (m, 1H, CH), 6.90–8.35 (m, 9H, Ar—H). IR (KBr): 3416 (NH), 1672 (C=O), 1577, 1493, 743 cm^{-1}. MS: *m/z* (%) 375 (42, M^+), 277 (57), 201 (18), 146 (86), 77 (67).

1-Isopropyl-2-(4-methyl-phenylamino)-benzo[4,5]thieno-[3,2-*d*][1,2,4]triazolo[1,5-*a*]pyrimidin-5(1*H*)-one (7m). ^{1}H NMR (400 MHz, $CDCl_3$/TFA) δ (ppm): 1.86 (d, J = 7.0 Hz, 6H, $2CH_3$), 2.10 (s, 3H, Ar—CH_3), 4.83 (d, J = 6.9 Hz, 1H, NCH), 6.97–8.37 (m, 8H, Ar—H). IR (KBr): 3415 (NH), 1670 (C=O), 1576, 1490, 742 cm^{-1}. MS: *m/z* (%) 389 (59, M^+), 277 (77), 201 (16), 146 (92), 91 (71), 77 (86).

1-Butyl-2-(4-methyl-phenylamino)-benzo[4,5]thieno[3,2-*d*][1,2,4]triazolo[1,5-*a*]pyrimidin-5(1*H*)-one (7n). ^{1}H NMR (400 MHz, $CDCl_3$/TFA) δ (ppm): 1.02 (t, J = 7.0 Hz, 3H, CH_3), 1.48–1.43 (m, 2H, CH_2), 1.91–1.98 (m, 2H, CH_2), 2.34 (s, 3H, Ar—CH_3), 4.47 (t, J = 6.9 Hz, 2H, NCH_2), 7.22–8.43 (m, 8H, Ar—H). IR (KBr): 3418 (NH), 1676 (C=O), 1572, 1495, 749 cm^{-1}. MS: *m/z* (%) 403 (67, M^+), 277 (69), 201 (21), 146 (80), 91 (68), 77 (79).

1-Butyl-2-(isopropylamino)-benzo[4,5]thieno[3,2-d][1,2,4]-triazolo[1,5-*a*]pyrimidin-5(1*H*)-one (7o). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 0.98 (t, J = 7.0 Hz, 3H, CH_3), 1.35 (t, J = 7.0 Hz, 6H, $2CH_3$), 1.40–1.49 (m, 2H, CH_2), 1.80–1.88 (m, 2H, CH_2),4.00–4.15 (m, 1H, NCH), 4.22 (t, J = 6.9 Hz, 2H, NCH_2), 7.55–8.33 (m, 4H, Ar—H), 9.83 (s, 1H, NH). IR (KBr): 3413 (NH), 1671 (C=O), 1571, 1493, 733 cm^{-1}. MS: *m/z* (%) 355 (55, M^+), 277 (64), 200 (26), 146 (89), 77 (67).

1-Butyl-2-phenylamino-benzo[4,5]thieno[3,2-*d*][1,2,4]triazolo[1,5-*a*]pyrimidin-5(1*H*)-one (7p). ^{1}H NMR (400 MHz, $CDCl_3$/TFA) δ (ppm): 1.01 (t, J = 7.0 Hz, 3H, CH_3), 1.40–1.47 (m, 2H, CH_2), 1.85–1.99 (m, 2H, CH_2), 4.41 (q, J = 6.9 Hz, 2H, NCH_2), 7.23–8.40 (m, 9H, Ar—H). IR (KBr): 3418 (NH), 1675 (C=O), 1576, 1492, 742 cm^{-1}. MS: *m/z* (%) 389 (63, M^+), 277 (62), 201 (26), 146 (88), 77 (74).

General procedure for the preparation of 2-substituted benzothieno[3,2-*d*]-1,2,4-triazolo[1,5-*a*]pyrimidin-5(1*H*)-ones 9a–9d. To a solution of iminophosphorane 5 (2 mmol) in anhyd. CH_2Cl_2 (10 mL) were added acyl chloride (2 mmol) and Et_3N (0.20 g, 2 mmol) under N_2 at r.t. The solution was stirred at r.t for 24 h. The white precipitated ammonium salt was separated by filtration and the filtrate was concentrated to dryness. The residue was recrystallized from CH_2Cl_2—EtOH to give 9a–9d.

1-Butyl-2-methyl-benzo[4,5]thieno[3,2-*d*][1,2,4]triazolo-[1,5-*a*]pyrimidin-5(1*H*)-one (9a). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 1.02 (t, J = 7.0 Hz, 3H, CH_3), 1.40–1.49 (m, 2H, CH_2), 1.81–1.88 (m, 2H, CH_2), 2.57 (s, 3H, CH_3), 4.13 (t, J = 6.9 Hz, 2H, NCH_2), 7.42–8.26 (m, 4H, Ar—H). IR (KBr): 1672 (C=O), 1572, 1493, 740 cm^{-1}. MS: *m/z* (%) 312 (57, M^+), 277 (69), 201 (17), 145 (60), 77 (86).

1-Butyl-2-phenyl-benzo[4,5]thieno[3,2-*d*][1,2,4]triazolo-[1,5-*a*]pyrimidin-5(1*H*)-one (9b). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 0.92 (t, J = 7.0 Hz, 3H, CH_3), 1.30–1.39 (m, 2H, CH_2), 1.80–1.88 (m, 2H, CH_2), 4.30 (t, J = 6.9 Hz, 2H, NCH_2), 7.48–8.33 (m, 9H, Ar—H). IR (KBr): 1674 (C=O), 1573, 1495, 745 cm^{-1}. MS: *m/z* (%) 374 (65, M^+), 277 (68), 200 (24), 146 (87), 77 (83).

2-Methyl-1-phenyl-benzo[4,5]thieno[3,2-*d*][1,2,4]triazolo-[1,5-*a*]pyrimidin-5(1*H*)-one (9c). ^{1}H NMR (400 MHz, $CDCl_3$/TFA) δ (ppm): 2.42 (t, J = 7.2 Hz, 3H, CH_3), 7. 44 –7. 99 (m, 9H, Ar—H). IR (KBr): 1671 (C=O), 1571, 1491, 741 cm^{-1}. MS: *m/z* (%) 332 (57, M^+), 277 (68), 201 (31), 146 (92), 77 (65).

1-Phenyl-2-phenyl-benzo[4,5]thieno[3,2-d][1,2,4]triazolo-[1,5-*a*]pyrimidin-5(1*H*)-one (9d). H NMR (400 MHz, $CDCl_3$/TFA) δ (ppm): 7.48–8.33 (m, 14H, Ar—H). IR (KBr): 1673 (C=O), 1575, 1494, 737 cm^{-1}. MS: *m/z* (%) 394 (100, M^+), 277 (64), 201 (25), 145 (73), 77 (76).

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