Synthesis of new tetracyclic benzo[4,5]furo[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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Abstract
The carbodiimides **3**, obtained from aza-Wittig reactions of iminophosphorane **2** with aromatic isocyanates, reacted with hydrazine to give selectively 3-amino-2-arylaminobenzofuro[3,2-*d*]pyrimidin-4(3*H*)-ones **5**. Reactions of **5** with triphenylphosphine, hexachloroethane and triethylamine produced iminophosphoranes **6**. A tandem aza-Wittig reaction of iminophosphorane **6** with isocyanate or acyl chloride generated previously unreported tetracyclic benzo[4,5]furo[3,2-*d*]-1,2,4-triazolo[1,5-*a*]pyrimidin-5(1*H*)-ones **8** or **10** in high yields.

Keywords: Benzo[4,5]furo[3,2-*d*]-1,2,4-triazolo[1,5-*a*]pyrimidin-5(1*H*)-one, iminophosphorane, aza-Wittig reaction, isocyanate

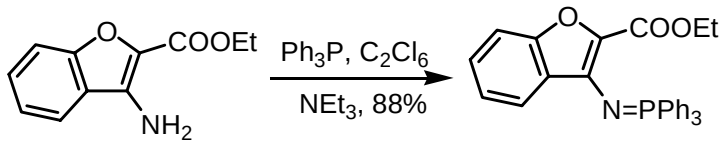
Introduction

The derivatives of heterocycles containing the benzofuropyrimidinone system are of great importance because of their remarkable biological properties. For example, some derivatives of benzofuropyrimidinones have shown good analgesic, anti-inflammatory and antimicrobial activities,[1,2] whereas others exhibited good anticoccidial and blood sugar-lowering activities.[3,4] On the other hand, heterocycles containing the 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.[5-9] The introduction of a triazole ring to the benzofuro[3,2-*d*]pyrimidin-4(3*H*)-one system is expected to influence the biological activities significantly. However, this tetracyclic system has been much less investigated and there is no report on synthesis of benzo[4,5]furo[3,2-*d*]-1,2,4-triazolo[1,5-*a*]pyrimidin-5(1*H*)-ones, probably due to the fact that the tetracyclic system is not easily accessible by routine synthetic methods.

The aza-Wittig reactions of iminophosphoranes have received increased attention in view of their utility in the synthesis of nitrogen heterocyclic compounds.[10-15] Annelation of ring systems with *N*-heterocycles by means an aza-Wittig reaction has been widely utilized because of the availability of functionalized iminophosphoranes. Recently we have been interested in the synthesis of quinazolinones, thienopyrimidinones and imidazolinones via aza-Wittig reaction, with the aim of evaluating their fungicidal activities.[16-20] Here we wish to report an efficient approach to the synthesis of previously unreported tetracyclic benzo[4,5]furo[3,2-*d*]-1,2,4-triazolo[1,5-*a*]pyrimidin-5(1*H*)-ones by tandem aza-Wittig/ heterocumulene-mediated annulation of *N*-(2-arylamino-benzofuro[3,2-*d*]pyrimidin-4(3*H*)-on-3-yl)iminotriphenylphosphorane with isocyanates or acyl chloride.

Results and Discussion

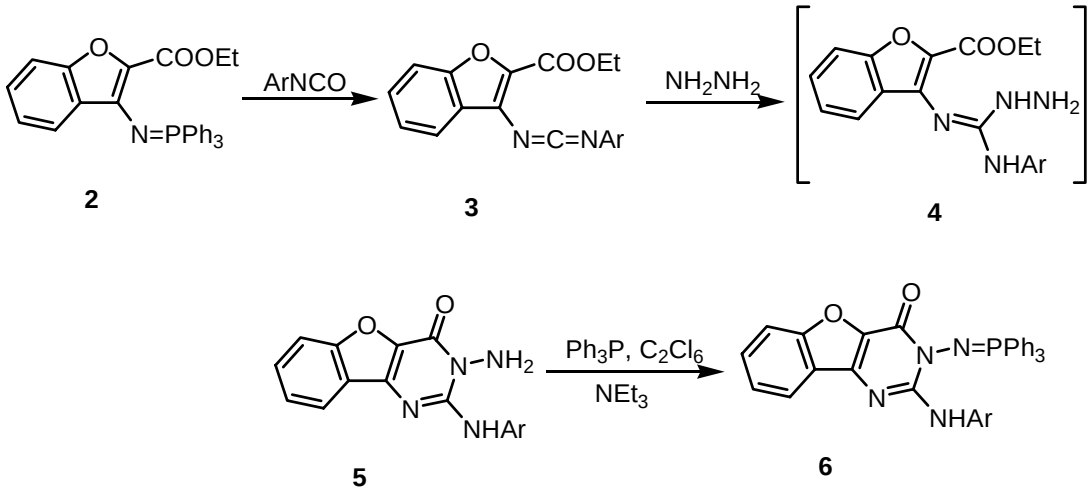
The 3-amino-2-(ethoxycarbonyl)benzofuran **1**, obtained by cyclization of 2-cyanophenol with ethyl bromoacetate under basic conditions[21,22], was converted to iminophosphorane **2** via reaction with triphenylphosphine, hexachloroethane and triethylamine (Scheme 1).



1 **2**

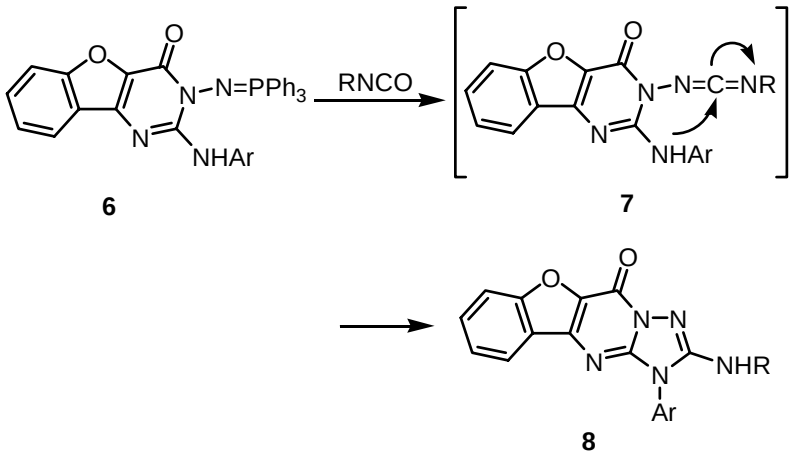
Scheme 1

Iminophosphorane **2** reacted with aromatic isocyanates to give carbodiimides **3**, which were allowed to react with hydrazine to give selectively 3-amino-2-arylaminobenzofuro[3,2-*d*]pyrimidin-4(3*H*)-ones **5** in 86-95% yields at room temperature (Scheme 2). The formation of **5** can be rationalized in terms of an initial nucleophilic addition of hydrazine to give the guanidine intermediate **4**, which cyclizes to give **5** via reaction of a nitrogen atom of the hydrazine group rather than via the less nucleophilic arylamino nitrogen atom. Compounds **5** were further converted to novel functionalized iminophosphoranes **6** via reaction with triphenylphosphine, hexachloroethane and triethylamine in good yields (78-88%, Scheme 2)



Scheme 2

When solutions of iminophosphoranes **6** in dry methylene dichloride were treated with aromatic isocyanates at room temperature, the color of the reaction mixture quickly turned red, disappearing after a few minutes, and 2-arylamino-benzo[4,5]furo[3,2-*d*]-1,2,4-triazolo[1,5-*a*]pyrimidin-5(1*H*)-ones **8** were isolated as crystalline solids in excellent yields (84-93%, Table 1, Scheme 3). Presumably, the conversion of **6** into **8** involves initial aza-Wittig reaction between the iminophosphorane **6** and the isocyanate to give a carbodiimide **7** as a highly reactive intermediate, which easily undergoes ring closure via nucleophilic attack of the arylamino group to give the previously unreported tetracyclic 2-arylamino substituted benzo[4,5]furo[3,2-*d*]-1,2,4-triazolo[1,5-*a*]pyrimidin-5(1*H*)-ones **8**. It is noteworthy that the reaction can be easily carried out at room temperature under mild neutral conditions. Moreover the separation of **8** from the reaction mixture can be easily carried out by simple filtration.



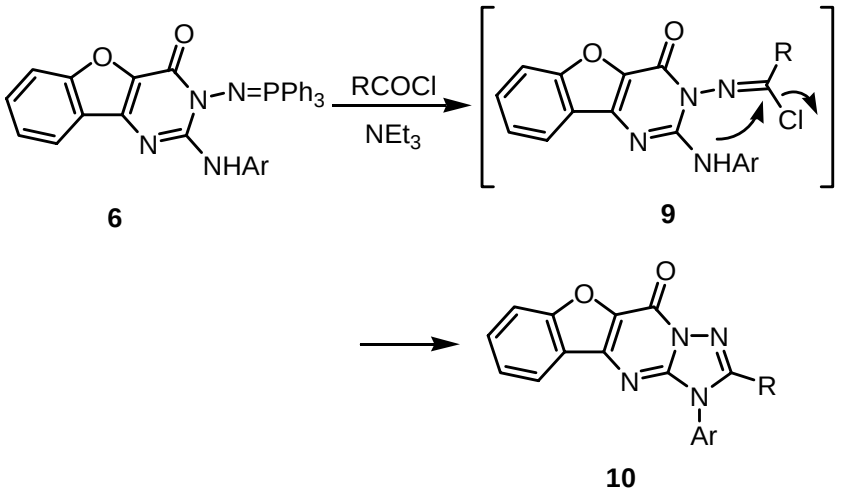
Scheme 3

Table 1. Preparation of Compounds **5, 6, 8** and **10**

	Ar	R	Conditions	Yield (%)[a]
5a	Ph		r.t./30 min	92
5b	4-Me-C_6H_4		r.t./20 min	95
5c	3-Me-C_6H_4		r.t./30 min	91
5d	4-Cl-C_6H_4		r.t./30 min	86
6a	Ph		r.t./4 h	85
6b	4-Me-C_6H_4		r.t./6 h	88
6c	3-Me-C_6H_4		r.t./5 h	78
6d	4-Cl-C_6H_4		r.t./5 h	81
8a	Ph	4-Me-C_6H_4	r.t./2 h	93
8b	Ph	3-Me-C_6H_4	r.t./2 h	90
8c	Ph	Ph	r.t./1 h	87
8d	Ph	*n*-Bu	r.t./3 h	84
8e	3-Me-C_6H_4	4-Me-C_6H_4	r.t./2 h	91
8f	3-Me-C_6H_4	Ph	r.t./2 h	86
8g	3-Me-C_6H_4	*i*-Pr	r.t./4 h	85
8h	4-Me-C_6H_4	4-Me-C_6H_4	r.t./2 h	87
8i	4-Me-C_6H_4	Ph	r.t./2 h	91
8j	4-Cl-C_6H_4	4-Me-C_6H_4	r.t./1 h	86
10a	Ph	Ph	r.t./4 h	80
10b	Ph	Me	r.t./6 h	73

[a]Isolated yields.

Iminophosphoranes **6** reacted with acyl chlorides in the presence of triethylamine in methylene dichloride at room temperature to give 2-substituted benzo[4,5]furo[3,2-*d*]-1,2,4-triazolo[1,5-*a*]pyrimidin-5(1*H*)-ones **10** in good yields (73-80%, Table 1, Scheme 4). The formation of **10** can be viewed as an initial aza-Wittig reaction between the iminophosphorane **6** and acyl chloride in the presence of triethylamine affording the intermediate imidoyl chloride **9** which undergoes cyclization via addition-elimination to give **10**.



Scheme 4

The structure of the benzo[4,5]furo[3,2-*d*]-1,2,4-triazolo[1,5-*a*]pyrimidin-5(1*H*)-ones **8** and **10** was confirmed by their spectral data[19]. For example, the IR spectra of **8b** revealed N-H and C=O absorption bands at 3274 and 1701 cm^{-1} respectively. The ^1H NMR spectrum of **7a** shows two singlets at 6.50 and 2.08 ppm due to the NH and CH_3 respectively. The signals attributable to the Ar-Hs are found at 6.88-7.80 ppm as mutiplet. The ^{13}C NMR spectrum data in **8b** showed the signals of C=O and CH_3 at 163.8 and 19.0 ppm respectively. The MS spectrum of **8b** shows a strong molecular ion peak at m/z 407.

In conclusion, we have developed an efficient synthesis of previously unreported tetracyclic benzo[4,5]furo[3,2-*d*]-1,2,4-triazolo[1,5-*a*]pyrimidin-5(1*H*)-ones via aza-Wittig reactions. This method utilizes easily accessible starting materials and allows mild reaction conditions, straightforward product isolation and good yields.

Experimental Section

General Procedures. Melting points are uncorrected. MS were measured on a Finnigan Trace MS spectrometer. IR were recorded on a PE-983 infrared spectrometer as KBr pellets with absorption in cm^{-1}. NMR were recorded in $CDCl_3$ on a Varian Mercury 400 spectrometer and resonances are given in ppm (δ) relative to TMS. Elementary analyses were taken on a Vario EL III elementary analysis instrument.

Preparation of *N*-(2-ethoxycarbonylbenzofuran-3-yl)iminotriphenylphosphorane (2). To a mixture of ethyl 3-amino-2-benzofurancarboxylate **1**[21,22] (1.64 g, 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 colour of the reaction mixture quickly turned yellow. After

stirred for 4 h, the solvent was removed under reduced pressure and the residue was recrystallized from EtOH to give iminophosphorane **2**. White solid (yield 3.27 g, 88%), mp: 172-173 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.23 (t, *J* = 7.2 Hz, 3H, CH_3), 4.18 (q, *J* = 7.2 Hz, 2H, CH_2), 6.93-7.80 (m, 19H, Ar-H). IR (KBr, cm^{-1}): 1755 (C=O), 1599, 1212. MS *m/z*: 465 (M^+, 99), 436 (31), 392 (100), 262 (37), 183 (80). Anal. Calcd for $C_{29}H_{24}NO_3P$ (465.5): C, 74.83; H, 5.20; N, 3.01. Found: C, 74.96; H, 5.25; N, 2.79.

Preparation of 3-amino-2-arylaminobenzofuro[3,2-*d*]pyrimidin-4(3*H*)-ones 5a-5d

To a solution of iminophosphorane **2** (4.65 g, 10 mmol) in dry methylene dichloride (20 mL) was added aromatic isocyanate (10 mmol) under nitrogen at room temperature. After the reaction mixture was stood for 8-12 hours at 0-5 °C, the solvent was removed off under reduced pressure and ether/petroleum ether (1:2, 20 mL) was added to precipitate triphenylphosphine oxide. Filtered, the solvent was removed to give carbodiimide **3**, which was directly used without further purification. To the solution of hydrazine hydrate (2.40 g, 40 mmol, 85%) in CH_3CN (10 mL) was added **3** prepared above in CH_3CN (30 mL). The mixture was stirred for 20-30 min at room temperature and filtered to give 3-amino-2-arylamino benzofuro[3,2-*d*]pyrimidin-4(3*H*)-one **5a-5d**.

3-Amino-2-phenylamino-benzofuro[3,2-*d*]pyrimidin-4(3*H*)-one (5a). White crystals recrystallized from ethanol (yield 2.69 g, 92%), mp: 263-265 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 5.85 (s, 2H, NH_2), 7.09-8.00 (m, 9H, Ar-H), 9.45 (s, 1H, NH). IR (KBr, cm^{-1}): 3320, 1701 (C=O), 1542, 1402, 1199. MS *m/z*: 292 (M^+, 21), 184 (23), 130 (31), 102 (48), 76 (100). Anal. Calcd for $C_{16}H_{12}N_4O_2$ (292.3): C, 65.75; H, 4.14; N, 19.17. Found: C, 65.58; H, 4.24; N, 19.15.

3-Amino-2-(4-methylphenylamino)-benzofuro[3,2-*d*]pyrimidin-4(3*H*)-one (5b). White crystals recrystallized from ethanol (yield 2.91 g, 95%), mp: 292-294 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 2.31 (s, 3H, CH_3), 5.82 (s, 2H, NH_2), 7.18-7.98 (m, 8H, Ar-H), 9.35 (s, 1H, NH). IR (KBr, cm^{-1}): 3327, 1702 (C=O), 1544, 1401, 1200, 742. MS *m/z*: 306 (M^+, 100), 288 (76), 201 (35), 130 (29). Anal. Calcd for $C_{17}H_{14}N_4O_2$ (306.3): C, 66.66; H, 4.61; N, 18.29. Found: C, 66.47; H, 4.75; N, 18.16.

3-Amino-2-(3-methylphenylamino)-benzofuro[3,2-*d*]pyrimidin-4(3*H*)-one (5c). White crystals recrystallized from ethanol (yield 2.78 g, 91%), mp: 243-245 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 2.36 (s, 3H, CH_3), 5.83 (s, 2H, NH_2), 6.92-8.00 (m, 8H, Ar-H), 9.35 (s, 1H, NH). IR (KBr, cm^{-1}): 3364, 1700 (C=O), 1548, 1398, 1200. MS *m/z*: 306 (M^+, 100), 288 (58), 201 (25), 130 (33). Anal. Calcd for $C_{17}H_{14}N_4O_2$ (306.3): C, 66.66; H, 4.61; N, 18.29. Found: C, 66.51; H, 4.53; N, 18.49.

3-Amino-2-(4-chlorophenylamino)-benzofuro[3,2-*d*]pyrimidin-4(3*H*)-one (5d). White crystals recrystallized from ethanol (yield 2.81 g, 86%), mp: > 300 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 5.84 (s, 2H, NH_2), 7.45-8.04 (m, 8H, Ar-H), 9.60 (s, 1H, NH). IR (KBr, cm^{-1}): 3336, 1969 (C=O), 1545, 1402, 1208. MS *m/z*: 326 (M^+, 100), 288 (58), 201 (25), 130 (33). Anal. Calcd for $C_{16}H_{11}ClN_4O_2$ (326.7): C, 58.82; H, 3.39; N, 17.15. Found: C, 58.96; H, 3.33; N, 17.33.

Preparation of *N*-(benzofuro[3,2-*d*]pyrimidin-4(3*H*)-on-3-yl)iminotriphenylphosphoranes 6a-6d

To a mixture of **5** (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 **6a-6d**.

2-Phenylamino-3-(triphenylphosphoranylidene)amino-benzofuro[3,2-*d*]pyrimidin-4(3*H*)-one (6a). White crystals (yield 3.75 g, 85%), mp: 233-235 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.07-8.01 (m, 24H, Ar-H), 9.63 (s, 1H, NH). IR (KBr, cm^{-1}): 3268 (N-H), 1693 (C=O), 1548, 1108. MS *m/z*: 552 (M^+, 66), 262 (70), 183 (100), 152 (18), 108 (18), 76 (12). Anal. Calcd for $C_{34}H_{25}N_4O_2P$ (552.6): C, 73.90; H, 4.56; N, 10.14. Found: C, 73.85; H, 4.59; N, 10.09.

2-(4-Methylphenylamino)-3-(triphenylphosphoranylidene)amino-benzofuro[3,2-*d*]pyrimidin-4(3*H*)-one (6b). White crystals (yield 3.98 g, 88%), mp: 238-240 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.36 (s, 3H, CH_3), 7.19-8.00 (m, 23H, Ar-H), 9.50 (s, H, NH). IR (KBr, cm^{-1}): 3286 (N-H), 1697 (C=O), 1550, 1110. MS *m/z*: 566 (M^+, 46), 262 (49), 183 (100), 152 (26), 108 (56), 76 (44). Anal. Calcd for $C_{35}H_{27}N_4O_2P$ (566.6): C, 74.19; H, 4.80; N, 9.89. Found: C, 74.15; H, 4.59; N, 9.93.

2-(3-Methylphenylamino)-3-(triphenylphosphoranylidene)amino-benzofuro[3,2-*d*]pyrimidin-4(3*H*)-one (6c). White crystals (yield 3.53 g, 78%), mp: 221-223 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.41 (s, 3H, CH_3), 6.90-8.00 (m, 23H, Ar-H), 9.55 (s, H, NH). IR (KBr, cm^{-1}): 3305 (N-H), 1701 (C=O), 1549, 1107. MS *m/z*: 566 (M^+, 48), 262 (45), 183 (100), 152 (26), 108 (56), 76 (44). Anal. Calcd for $C_{35}H_{27}N_4O_2P$ (566.6): C, 74.19; H, 4.80; N, 9.89. Found: C, 74.03; H, 4.85; N, 9.85.

2-(3-Chlorophenylamino)-3-(triphenylphosphoranylidene)amino-benzofuro[3,2-*d*]pyrimidin-4(3*H*)-one (6d). White crystals (yield 3.80 g, 81%), mp: 253-255 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.32-8.00 (m, 23H, Ar-H), 9.65 (s, 1H, NH). IR (KBr, cm^{-1}): 3276 (N-H), 1699 (C=O), 1557, 1107. MS *m/z*: 586/588 (M^+, 65/25), 280 (20), 262 (70), 183 (100), 152 (18), 108 (18), 77 (12). Anal. Calcd for $C_{34}H_{24}ClN_4O_2P$ (587.0): C, 69.57; H, 4.12; N, 9.54. Found: C, 69.30; H, 4.16; N, 9.47.

Preparation of 2-arylamino-benzo[4,5]furo[3,2-*d*]-1,2,4-triazolo[1,5-*a*]pyrimidin-5(1*H*)-ones 8

To a solution of iminophosphorane **6** (1 mmol) in dry methylene dichloride (10 mL) was added isocyanate (1 mmol) under nitrogen at room temperature. The colour of the reaction mixture turns red, disappearing after few minutes. The colourless solution is stirred at room temperature for 1-4 h. The white precipitated solid is collected by filtration and recrystallized from CH_2Cl_2/ethanol to give **8** as white solid.

2-(4-Methylphenylamino)-1-phenylbenzo[4,5]furo[3,2-*d*]-1,2,4-triazolo[1,5-*a*]pyrimidin-5(1*H*)-one (8a). White crystals (yield 0.38 g, 93%), mp: > 300 °C. ^{1}H NMR (400 MHz, $CDCl_3$/TFA) δ: 1.98 (s, 3H, CH_3), 6.53 (s, 1H, NH), 6.83-7.78 (m, 13H, Ar-H). IR (KBr, cm^{-1}): 3286 (NH), 1700 (C=O), 1575, 1398, 1201. MS *m/z*: 407 (M^+, 100), 391 (13), 130 (22), 103 (21), 91 (23), 77 (50). Anal. Calcd for $C_{24}H_{17}N_5O_2$ (407.4): C, 70.75; H, 4.21; N, 17.19. Found: C, 70.93; H, 4.38; N, 17.07.

2-(3-Methylphenylamino)-1-phenylbenzo[4,5]furo[3,2-*d*]-1,2,4-triazolo[1,5-*a*]pyrimidin-5(1*H*)-one (8b). White crystals (yield 0.37 g, 90%), mp: > 300 °C. ^{1}H NMR (400 MHz, $CDCl_3$/TFA) δ: 2.08 (s, 3H, CH_3), 6.50 (s, 1H, NH), 6.88-7.80 (m, 13H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 19.0, 112.7, 116.4, 116.6, 118.2, 121.7, 122.3, 129.5, 129.8, 129.9, 130.0, 130.3, 130.5, 134.2, 135.4, 137.9, 141.9, 149.7, 153.5, 157.2, 161.3, 163.8. IR (KBr, cm^{-1}): 3274 (NH), 1701 (C=O), 1572, 1398, 1202. MS *m/z*: 407 (M^+, 100), 392 (8), 103 (11), 91 (23), 76 (30). Anal. Calcd for $C_{24}H_{17}N_5O_2$ (407.4): C, 70.75; H, 4.21; N, 17.19. Found: C, 70.63; H, 4.35; N, 17.34.

1-Phenyl-2-(phenylamino)benzo[4,5]furo[3,2-*d*]-1,2,4-triazolo[1,5-*a*]pyrimidin-5(1*H*)-one (8c). White crystals (yield 0.34 g, 87%), mp: > 300 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 6.68 (s, 1H, NH), 7.05-7.81 (m, 14H, Ar-H). IR (KBr, cm^{-1}): 3293 (NH), 1701 (C=O), 1565, 1398, 1203. MS *m/z*: 393 (M^+, 26), 247 (17), 140 (59), 138 (100), 108 (18), 77 (98). Anal. Calcd for $C_{23}H_{15}N_5O_2$ (393.4): C, 70.22; H, 3.84; N, 17.80. Found: C, 70.15; H, 3.68; N, 17.94.

2-(*n*-Butylamino)-1-phenylbenzo[4,5]furo[3,2-*d*]-1,2,4-triazolo[1,5-*a*]pyrimidin-5(1*H*)-one (8d). White crystals (yield 0.31 g, 84%), mp: 263-265 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.94 (t, *J* = 7.2 Hz, 3H, CH_3), 1.34-1.68 (m, 4H, $2CH_2$), 3.52-3.57 (m, 2H, NCH_2), 4.30 (t, *J* = 5.2 Hz, 1H, NH), 7.30-7.96 (m, 9H, Ar-H). MS *m/z*: 373 (100), 330 (77), 316 (34), 200 (24), 130 (29), 102 (27), 91 (69), 76 (21). Anal. Calcd for $C_{21}H_{19}N_5O_2$ (373.4): C, 67.55; H, 5.13; N, 18.76; Found: C, 67.39; H, 5.17; N, 18.58.

1-(3-Methylphenyl)-2-(4-methylphenylamino)benzo[4,5]furo[3,2-*d*]-1,2,4-triazolo[1,5-*a*]pyrimidin-5(1*H*)-one (8e). White crystals (yield 0.38 g, 91%), mp: > 300 °C. ^{1}H NMR (400 MHz, $CDCl_3$/TFA) δ: 1.89 (s, 3H, CH_3), 2.55 (s, 3H, CH_3), 6.96 (s, 1H, NH), 6.74-7.73 (m, 12H, Ar-H). MS *m/z*: 421 (M^+, 100), 291 (6), 130 (8), 113 (7), 90 (12). Anal. Calcd for $C_{25}H_{19}N_5O_2$ (421.5): C, 71.25; H, 4.54; N, 16.62. Found: C, 71.35; H, 4.73; N, 16.38.

1-(3-Methylphenyl)-2-phenylaminobenzo[4,5]furo[3,2-*d*]-1,2,4-triazolo[1,5-*a*]pyrimidin-5(1*H*)-one (8f). White crystals (yield 0.35 g, 86%), mp: > 300 °C. ^{1}H NMR (400 MHz, $CDCl_3$/TFA) δ: 2.48 (s, 3H, CH_3), 6.53 (s, H, NH), 6.99-7.95 (m, 13H, Ar-H). MS *m/z*: 407 (M^+, 100), 391 (11), 130 (10), 90 (15). Anal. Calcd for $C_{24}H_{17}N_5O_2$ (407.4): C, 70.75; H, 4.21; N, 17.19. Found: C, 70.94; H, 4.08; N, 17.24.

1-(3-Methylphenyl)-2-(*i*-propylamino)benzo[4,5]furo[3,2-*d*]-1,2,4-triazolo[1,5-*a*]pyrimidin-5(1*H*)-one (8g). White crystals (yield 0.32 g, 85%), mp: >300 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.31 (d, *J* = 6.4 Hz, 6H, $2CH_3$), 2.50 (s, 3H, CH_3), 4.09 (d, *J* = 8.0 Hz, 1H, NH), 4.27-4.33 (m, 1H, NCH), 7.30-7.94 (m, 8H, Ar-H). MS *m/z*: 373 (91), 330 (100), 288 (66), 184 (14), 130 (50),

102 (41). Anal. Calcd for $C_{21}H_{19}N_5O_2$ (373.4): C, 67.55; H, 5.13; N, 18.76. Found: C, 67.51; H, 5.15; N, 18.97.

1-(4-Methylphenyl)-2-(4-methylphenylamino)benzo[4,5]furo[3,2-*d*]-1,2,4-triazolo[1,5-*a*]pyrimidin-5(1*H*)-one (8h). White crystals (yield 0.37 g, 87%), mp: > 300 °C. ^{1}H NMR (400 MHz, $CDCl_3$/TFA) δ: 2.31 (s, 3H, CH_3), 2.36 (s, 3H, CH_3), 7.06 (s, 1H, NH), 7.13-7.69 (m, 12H, Ar-H). MS *m/z*: 421 (M^+, 16), 332 (100), 290 (34), 106 (96). Anal. Calcd for $C_{25}H_{19}N_5O_2$ (421.5): C, 71.25; H, 4.54; N, 16.62. Found: C, 71.08; H, 4.65; N, 16.90.

1-(4-Methylphenyl)-2-phenylaminobenzo[4,5]furo[3,2-*d*]-1,2,4-triazolo[1,5-*a*]pyrimidin-5(1*H*)-one (8i). White crystals (yield 0.37 g, 91%), mp: > 300 °C. ^{1}H NMR (400 MHz, $CDCl_3$/TFA) δ: 2.55 (s, 3H, CH_3), 6.72 (s, 1H, NH), 6.87-7.74 (m, 13H, Ar-H). IR (KBr, cm^{-1}): 3305 (NH), 1687 (C=O), 1560, 1398, 1203. MS *m/z*: 407 (M^+, 20), 332 (100), 290 (43), 102 (24). Anal. Calcd for $C_{24}H_{17}N_5O_2$ (407.4): C, 70.75; H, 4.21; N, 17.19. Found: C, 70.67; H, 4.33; N, 17.08.

1-(4-Chlorophenyl)-2-(4-methylphenylamino)benzo[4,5]furo[3,2-*d*]-1,2,4-triazolo[1,5-*a*]pyrimidin-5(1*H*)-one (8j). White crystals (yield 0.38 g, 86%), mp: > 300 °C. ^{1}H NMR (400 MHz, $CDCl_3$/TFA) δ: 2.16 (s, 3H, CH_3), 6.72 (s, 1H, NH), 7.02-7.83 (m, 12H, Ar-H). IR (KBr, cm^{-1}): 3264 (NH), 1699 (C=O), 1569, 1389, 1067. MS *m/z*: 441/443 (M^+, 94/34), 245 (28), 178 (50), 129 (91), 91 (100). Anal. Calcd for $C_{24}H_{16}ClN_5O_2$ (441.9): C, 65.24; H, 3.65; N, 15.85. Found: C, 65.51; H, 3.55; N, 15.76.

Preparation of benzo[4,5]furo[3,2-*d*]-1,2,4-triazolo[1,5-*a*]pyrimidin-5(1*H*)-ones 10

To a solution of iminophosphorane **6** (2 mmol) in dry CH_2Cl_2 (15 mL) was added acyl chloride (2 mmol) and triethylamine (0.20 g, 2 mmol) under nitrogen at room temperature. The solution was stirred at room temperature for 4-6 h. The white precipitated ammonium salt was separated by filtration and the filtrate was concentrated. The residue was recrystallized from CH_2Cl_2/ethanol to give **10** as crystalline solid.

1,2-Diphenylbenzo[4,5]furo[3,2-*d*]-1,2,4-triazolo[1,5-*a*]pyrimidin-5(1*H*)-one (10a). White crystals (yield 0.60 g, 80%), mp: > 300 °C. ^{1}H NMR (400 MHz, $CDCl_3$/TFA) δ: 7.39-7.73 (m, 13H, Ar-H), 7.93 (d, *J* = 8.0 Hz, 1H, Ar-H). IR (KBr, cm^{-1}): 1721 (C=O), 1524, 1402, 740. MS *m/z*: 378 (M^+, 100), 129 (2), 76 (19). Anal. Calcd for $C_{23}H_{14}N_4O_2$ (378.4): C, 73.01; H, 3.73; N, 14.81. Found: C, 72.91; H, 3.82; N, 14.75.

2-Methyl-1-phenylbenzo[4,5]furo[3,2-*d*]-1,2,4-triazolo[1,5-*a*]pyrimidin-5(1*H*)-one (10b). White crystals (yield 0.46 g, 73%), mp: > 300 °C. ^{1}H NMR (400 MHz, $CDCl_3$/TFA) δ: 2.38 (s, 3H, CH_3), 7.39-7.91 (m, 9H, Ar-H). MS *m/z*: 316 (M^+, 100), 113 (10), 102 (13), 76 (33). Anal. Calcd for $C_{18}H_{12}N_4O_2$ (316.3): C, 68.35; H, 3.82; N, 17.71. Found: C, 68.41; H, 3.91; N, 17.63

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