Iminophosphorane-mediated efficient synthesis of new tricyclic 3,5-dihydro-1,2,3-triazolo[4,5-*d*]-1,2,4-triazolo[1,5-*a*]pyrimidin-9-ones

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Received 27th September 2005, Accepted 8th November 2005
First published as an Advance Article on the web 28th November 2005
DOI: 10.1039/b513715b

The carbodiimides **2**, obtained from aza-Wittig reactions of iminophosphorane **1** with aromatic isocyanates, reacted with hydrazine to give selectively 6-amino-7*H*-1,2,3-triazolo[4,5-*d*]pyrimidin-7-ones **5**. Compounds **5** were further transformed to iminophosphoranes **6** by reaction with triphenylphosphine, hexachloroethane and triethylamine. A tandem aza-Wittig reaction of iminophosphorane **6** with isocyanate or acyl chloride generated previously unreported 3,5-dihydro-1,2,3-triazolo[4,5-*d*]-1,2,4-triazolo[1,5-*a*]pyrimidin-9-ones **10** or **12** in satisfactory yield. X-ray structure analysis of **10g** verified the proposed structure and the reaction selectivity.

Introduction

7*H*-1,2,3-Triazolo[4,5-*d*]pyrimidin-7-ones (azaguanines) are of great importance because of their structural similarity with guanines. Some derivatives of them have shown remarkable biological (antiguanine) properties such as antitumor, antiviral, and anti-HIV activities,[1–5] whereas others exhibited good fungicidal activities.[6] 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.[7–13] The introduction of a triazole ring to the triazolo[4,5-*d*]pyrimidin-7-one system is expected to influence the biological activities significantly. However, this tricyclic system has been much less investigated and there is no report on synthesis of 3,5-dihydro-1,2,3-triazolo[4,5-*d*]-1,2,4-triazolo[1,5-*a*]pyrimidin-9-ones.

Recently we have been interested in the synthesis of quinazolinones, thienopyrimidinones and imidazolinones *via* aza-Wittig reaction of α or β ethoxycarbonyl iminophosphorane with aromatic isocyanate and subsequent reaction with various nucleophiles under mild conditions.[14–18] Here we wish to report an efficient approach to the synthesis of previously unreported 3,5-dihydro-1,2,3-triazolo[4,5-*d*]-1,2,4-triazolo[1,5-*a*]pyrimidin-9-ones by tandem iminophosphorane-mediated annulation of easily accessible *N*-(5-arylamino-7*H*-1,2,3-triazolo[4,5-*d*]pyrimidin-7-on-6-yl)iminotriphenylphosphorane with isocyanates or acyl chloride.

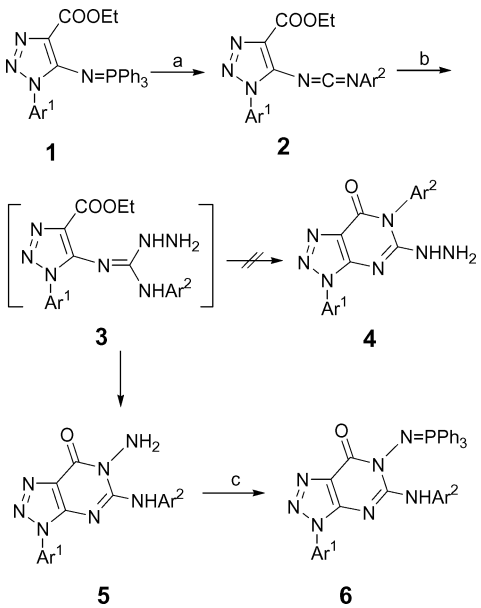
Results and discussion

Iminophosphorane **1**[19] reacted with aromatic isocyanates to give carbodiimides **2**, which were allowed to react with hydrazine to give selectively 6-amino-7*H*-1,2,3-triazolo[4,5-*d*]pyrimidin-7-ones **5** in 72–81% yields (Scheme 1, Table 1). No formation of the potential regioisomer **4** was observed. It is worth noting that the reaction of β ethoxycarbonyl carbodiimide with hydrazine seems to be controversial. Our recent result on reaction of β-ethoxycarbonyl phenylcarbodiimide with hydrazine gave selectively 3-aminoquinazolin-4(3*H*)-one,[20] consistent with formation of **5**. However, an early report on a similar reaction using carbodiimide **7** resulted in the formation of 2-hydrazinopyrimidinone **8**, another possible regioisomer (Scheme 2).[19] The selective formation

Table 1 Preparation of compounds **5** or **6**

	Ar^1	Ar^2	Yield (%)[a]
5a	Ph	Ph	91
5b	Ph	4-ClC_6H_4	86
5c	Ph	4-MeC_6H_4	84
6a	Ph	Ph	88
6b	Ph	4-ClC_6H_4	90
6c	Ph	4-MeC_6H_4	90

[a] Isolated yields based on iminophosphorane **1**.



Scheme 1 Synthesis of compounds **5** and **6**. (a) Ar^2NCO, CH_2Cl_2, 0–5 °C, 24–30 h; (b) $NH_2NH_2{\cdot}H_2O$, CH_3CN, rt, 10–20 min; (c) PPh_3, C_2Cl_6, NEt_3, CH_2Cl_2, rt, 4–6 h.

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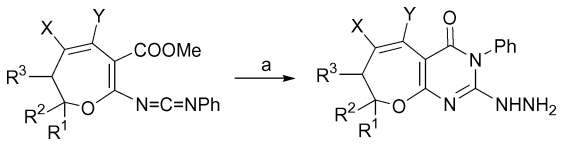
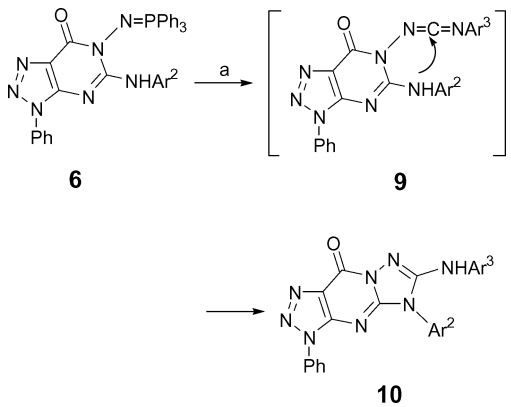


Scheme 2 Literature synthesis of compounds **8** from carbodiimide **7**. (a) $NH_2NH_2{\cdot}H_2O$, EtOH, rt, 3 h.

of **5** can be rationalized in terms of an initial nucleophilic addition of hydrazine to give the guanidine intermediate **3** which directly cyclizes to give **5** across the strong nucleophilic hydrazine group rather than the arylamine one.[21]

Compounds **5** were easily converted to novel functionalized iminophosphoranes **6** *via* reaction with triphenylphosphine, hexachloroethane and triethylamine in good yields (88–90%, Scheme 1, Table 1). When solutions of iminophosphoranes **6** in dry methylene chloride were treated with aromatic isocyanate at refluxing temperature, the previously unreported 6-arylamino-1,2,3-triazolo[4,5-*d*]-1,2,4-triazolo[1,5-*a*]pyrimidin-9-ones **10** were isolated as crystalline solids in good yields (78–91%, Table 2, Scheme 3). Presumably, the conversion of **6** into **10** involves initial aza-Wittig reaction between the iminophosphorane **6** and the isocyanate to give a carbodiimide **9** as highly reactive intermediate,



Scheme 3 Preparation of tricyclic compound **10**. (a) Ar^3NCO, CH_2Cl_2, 40 °C, 1–2 h.

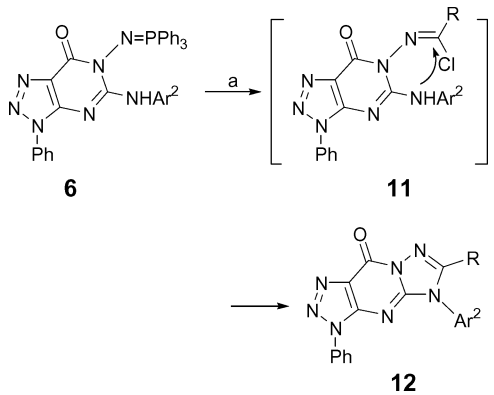
Table 2 Preparation of compounds **10a–h** or **12a–f**

	Ar^2	Ar^3	R	Yield (%)[a]
10a	Ph	Ph		91
10b	Ph	4-ClC_6H_4		84
10c	4-ClC_6H_4	Ph		78
10d	4-ClC_6H_4	4-ClC_6H_4		90
10e	4-ClC_6H_4	4-MeC_6H_4		83
10f	4-ClC_6H_4	3-MeC_6H_4		84
10g	4-MeC_6H_4	Ph		82
10h	4-MeC_6H_4	4-MeC_6H_4		87
12a	Ph		Ph	78
12b	Ph		Me	84
12c	4-ClC_6H_4		Ph	86
12d	4-ClC_6H_4		Me	73
12e	4-MeC_6H_4		Ph	75
12f	4-MeC_6H_4		Me	85

[a] Isolated yields based on iminophosphorane **6**.

which easily undergoes ring closure across the arylamino group to give the otherwise not readily available 6-arylamino substituted 1,2,3-triazolo[4,5-*d*]-1,2,4-triazolo[1,5-*a*]pyrimidin-9-ones **10**. It is noteworthy that the reaction can be easily carried out at refluxing temperature (CH_2Cl_2 as solvent) under mild neutral condition and the separation of **10** from the reaction mixture was also easily carried out by simple filtration.

Iminophosphoranes **6** reacted with acyl chlorides in the presence of triethylamine in methylene chloride at refluxing temperature to give 6-substituted 1,2,3-triazolo[4,5-*d*]-1,2,4-triazolo[1,5-*a*]pyrimidin-9-ones **12** in good yields (73–86%, Table 2, Scheme 4). The formation of **12** can be viewed as an initial aza-Wittig reaction between the iminophosphorane **6** and acyl chloride in presence of triethylamine affording the intermediate imidoyl chloride **11** which undergoes cyclization to give **12**.



Scheme 4 Synthesis of compounds **12** (a) RCOCl, CH_2Cl_2, NEt_3, 40 °C, 2–4 h.

The structure of 3,5-dihydro-1,2,3-triazolo[4,5-*d*]-1,2,4-triazolo[1,5-*a*]pyrimidin-9-ones **10** and **12** was confirmed by their spectral data. Furthermore a single crystal of **10g** was obtained from a DMF solution of **10g**. X-ray structure analysis verified again the proposed structure, and showed that all ring atoms in the tricyclic moiety are essentially planar, with the maxim deviation of 0.0392 Å for N(2) from the heterocyclic plane (Fig. 1). The bond lengths of C(4)=N(4), C(5)=N(6), and C(1)=C(2) are 1.307(3) Å, 1.311(3) Å and 1.386(3) Å, are longer than that of the typical C=N (1.28 Å) and C=C (1.34 Å) bonds respectively, while the single bond lengths of C(1)–N(1), C(2)–N(3), C(1)–N(4), C(4)–N(5), C(4)–N(7), N(7)–C(5) and C(2)–C(3) are 1.354(3) Å, 1.371(3) Å, 1.361(3) Å, 1.370(3) Å, 1.368(3) Å, 1.389(3) Å and 1.435(3) Å respectively, are significantly shorter than the typical $C(sp^2)$–N(1.426 Å) and C–C(1.53 Å), showing a degree of delocalization.

In conclusion, we have developed an efficient iminophosphorane-mediated synthesis of previously unreported 3,5-dihydro-1,2,3-triazolo[4,5-*d*]-1,2,4-triazolo[1,5-*a*]pyrimidin-9-ones *via* aza-Wittig reactions. The spectral and X-ray analysis of the product verified the proposed structure and the reaction selectivity.

Experimental

General materials and methods

Reagents and chemicals were obtained from Acros, Aldrich, Shanghai or Beijing chemicals and were used without further

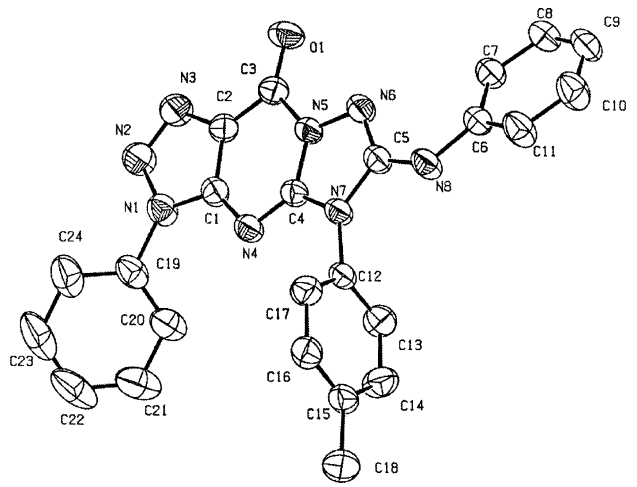


Fig. 1 ORTEP diagram of the crystal structure of tricyclic compound **10g** (50% thermal ellipsoids). For clarity, solvent molecular (DMF) and all hydrogen atoms have been omitted. Select bond lengths [Å]: C(1)–N(1) 1.354(3), N(1)–N(2) 1.377(3), N(2)–N(3) 1.304(3), C(2)–N(3) 1.371(3), C(1)–C(2) 1.386(3), C(2)–C(3) 1.435(3), C(3)–N(5) 1.420(3), C(4)–N(5) 1.370(3), C(4)–N(4) 1.307(3), C(1)–N(4) 1.361(3), N(5)–N(6) 1.403(3), C(5)–N(6) 1.311(3), C(5)–N(7) 1.389(3), C(4)–N(7) 1.368(3), C(3)–O(1) 1.211(3), C(5)–N(8) 1.347(3), C(6)–N(8) 1.414(3). Selected bond angles [deg]: N(3)–N(2)–N(1) 108.3(2), C(1)–N(1)–N(2) 109.8(2), N(1)–C(1)–C(2) 104.5(2), N(2)–N(1)–C(19) 120.9(2), C(1)–C(2)–C(3) 121.7(2), N(5)–C(3)–C(2) 107.5(2), C(4)–N(5)–C(3) 124.9(2), N(4)–C(4)–N(5) 128.5(2), C(4)–N(4)–C(1) 108.3(2), N(4)–C(1)–C(2) 129.0(2), C(4)–N(5)–N(6) 112.23(18), C(5)–N(6)–N(5) 103.03(19), N(6)–C(5)–N(7) 112.9(2), C(4)–N(7)–C(5) 107.0(2), N(7)–C(4)–N(5) 104.8(2), C(4)–N(7)–C(12) 123.9(2).†

purification. All solvents were freshly distilled. 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 $CDCl_3$ or DMSO-d_6 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.

5-Arylamino-6-amino-7*H*-1,2,3-triazolo[4,5-*d*]pyrimidin-7-ones (5)

To a solution of iminophosphorane **1**[6] (2 mmol) in dry methylene chloride (15 mL) was added aromatic isocyanate (2 mmol) under nitrogen at room temperature. After the reaction mixture was stood for 24–30 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. After filtration the solvent was removed to give carbodiimide **2**, which was used directly without further purification. To the solution of **2** prepared above in CH_3CN (15 ml) was added hydrazine hydrate (0.24 g, 4 mmol, 85%) in EtOH (5 mL). The mixture was stirred for 10 min at room temperature and filtered to give 5-arylamino-6-amino-7*H*-1,2,3-triazolo[4,5-d]pyrimidin-7-ones **5**.

6-Amino-3,6-dihydro-3-phenyl-5-phenylamino-7*H*-1,2,3-triazolo-[4,5-*d*]pyrimidin-7-one (5a). White crystals (580 mg, 91% yield), mp: 253–255 °C; IR (KBr) cm^{-1} 3329, 3262 (N–H), 1718 (C=O), 1542, 1203; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.75 (s, 2H), 7.19–8.15 (m, 10H), 8.94 (s, 1H); MS *m*/*z* (%) 319 (M^+, 9), 291 (2), 274 (2), 118 (18), 77 (100); Anal. Calcd for $C_{16}H_{13}N_7O$: C, 60.18; H, 4.10; N, 30.70. Found: C, 60.35; H, 4.03; N, 30.93%.

6-Amino-5-(4-chlorophenyl)amino-3,6-dihydro-3-phenyl-7*H*-1,2,3-triazolo[4,5-*d*]pyrimidin-7-one (5b). White crystals (607 mg, 86% yield), mp: >300 °C; IR (KBr) cm^{-1} 3309, 3263 (N–H), 1716 (C=O), 1559, 1204; ^{1}H NMR (400 MHz, DMSO-d_6) δ 5.75 (s, 2H), 7.43–8.04 (m, 9H), 10.01 (s, 1H); MS *m*/*z* (%) 355/353 (M^+, 15/45), 325 (12), 309 (5), 111 (23), 77 (100); Anal. Calcd for $C_{16}H_{12}ClN_7O$: C, 54.32; H, 3.42; N, 27.71. Found: C, 54.47; H, 3.64; N, 27.57%.

6-Amino-3,6-dihydro-5-(4-methylphenyl)amino-3-phenyl-7*H*-1,2,3-triazolo[4,5-*d*]pyrimidin-7-one (5c). White crystals (560 mg, 84% yield), mp: 253–255 °C; IR (KBr) cm^{-1} 3314, 3260 (N–H), 1701 (C=O), 1556, 1205; ^{1}H NMR (400 MHz, DMSO-d_6) δ 2.30 (s, 3H), 5.74 (s, 2H), 7.18–8.07 (m, 9H), 9.80 (s, 1H); MS *m*/*z* (%) 333 (M^+, 57), 305 (19), 289 (15), 131 (26), 77 (100); Anal. Calcd for $C_{17}H_{15}N_7O$: C, 61.25; H, 4.54; N, 29.41. Found: C, 61.08; H, 4.69; N, 29.64%.

5-Arylamino-6-(triphenylphosphoranylidene)amino-7*H*-1,2,3-triazolo[4,5-*d*]pyrimidin-7-ones (6)

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_2Cl_2 (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 being stirred for 4–6 h, the solvent was removed under reduced pressure and the residue was recrystallized from EtOH to give iminophosphorane **6**.

3,6-Dihydro-3-phenyl-5-phenylamino-6-(triphenylphosphoranylidene)amino-7*H*-1,2,3-triazolo[4,5-*d*]pyrimidin-7-one (6a). White crystals (4.07 g, yield 88%), mp: 278–280 °C; IR (KBr) cm^{-1}: 3264 (N–H), 1699 (C=O), 1550, 1110; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.12–8.18 (m, 25H), 9.90 (s, 1H); MS *m*/*z* (%) 579 (M^+, 62), 551 (8), 262 (74), 183 (83), 77 (100); Anal. Calcd for $C_{34}H_{26}N_7OP$: C, 70.46; H, 4.52; N, 16.92. Found: C, 70.68; H, 4.37; N, 16.75%.

5-(4-Chlorophenyl)amino-3,6-dihydro-3-phenyl-6-(triphenylphosphoranylidene)amino-7*H*-1,2,3-triazolo[4,5-*d*]pyrimidin-7-one (6b). White crystals (4.42 g, yield 90%), mp: 287–288 °C; IR (KBr) cm^{-1}: 3305 (N–H), 1701 (C=O), 1549, 1107; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.26–8.14 (m, 24H), 9.93 (s, 1H); MS *m*/*z* (%) 615/613 (M^+, 3/9), 276 (16), 262 (24), 183 (78), 77 (100); Anal. Calcd for $C_{34}H_{25}ClN_7OP$: C, 66.51; H, 4.10; N, 15.97. Found: C, 66.35; H, 4.35; N, 15.84%.

3,6-Dihydro-5-(4-methylphenyl)amino-3-phenyl-6-(triphenylphosphoranylidene)amino-7*H*-1,2,3-triazolo[4,5-*d*]pyrimidin-7-one (6c). White crystals (4.26 g, yield 90%), mp: >300 °C; IR (KBr) cm^{-1}: 3276 (N–H), 1699 (C=O), 1557, 1107; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 2.36 (s, 3H), 7.17–8.19 (m, 24H), 9.79 (s, 1H); MS *m*/*z* (%) 593 (M^+, 28), 304 (40), 262 (60), 183 (100), 77 (95); Anal. Calcd for $C_{35}H_{28}N_7OP$: C, 70.82; H, 4.75; N, 16.52. Found: C, 70.75; H, 4.76; N, 16.68%.

† CCDC reference number 279775. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b513715b

6-Arylamino-1,2,3-triazolo[4,5-*d*]-1,2,4-triazolo[1,5-*a*]pyrimidin-9-one (10)

To a solution of iminophosphorane **6** (1 mmol) in dry methylene chloride (10 mL) was added aromatic isocyanate (1 mmol) under nitrogen at room temperature. After the solution is stirred at refluxing temperature for 1–2 h, the white precipitated solid is collected by filtration and recrystallized from CH_2Cl_2–ethanol to give **10** as crystalline solids.

3,5-Dihydro-3,5-diphenyl-6-phenylamino-1,2,3-triazolo[4,5-*d*]-1,2,4-triazolo[1,5-*a*]pyrimidin-9-one (10a). White crystals (384 mg, yield 91%), mp: >300 °C; IR (KBr) cm^{-1}: 3413 (N–H), 1720 (C=O), 1544, 1399; ^1H NMR (DMSO-d_6, 400 MHz) δ: 7.08–7.95 (m, 15H), 9.16 (s, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 119.8, 123.5 (2), 124.6, 125.7 (2), 127.8 (2), 129.5 (2), 129.8 (2), 130.2, 130.4, 132.3 (2), 134.1, 134.9, 135.8, 147.7, 148.3, 150.2, 150.4; MS *m*/*z* (%) 420 (M^+, 26), 392 (10), 260 (14), 245 (16), 77 (100); Anal. Calcd for $C_{23}H_{16}N_8O$: C, 65.71; H, 3.84; N, 26.65. Found: C, 65.94; H, 3.97; N, 26.58%.

6-(4-Chlorophenyl)amino-3,5-dihydro-3,5-diphenyl-1,2,3-triazolo-[4,5-*d*]-1,2,4-triazolo[1,5-*a*]pyrimidin-9-one (10b). White crystals (381 mg, yield 84%), mp: >300 °C; IR (KBr) cm^{-1}: 3403 (N–H), 1721 (C=O), 1544, 1493; ^1H NMR (DMSO-d_6, 400 MHz) δ: 7.42–7.94 (m, 14H), 9.30 (s, 1H); MS *m*/*z* (%) 456/454 (M^+, 3/9), 426 (6), 274 (13), 258 (10), 77 (100); Anal. Calcd for $C_{23}H_{15}ClN_8O$: C, 60.73; H, 3.32; N, 24.63. Found: C, 60.65; H, 3.35; N, 24.52%.

5-(4-Chlorophenyl)-3,5-dihydro-3-phenyl-6-phenylamino-1,2,3-triazolo[4,5-*d*]-1,2,4-triazolo[1,5-*a*]pyrimidin-9-one (10c). White crystals (355 mg, yield 78%), mp: >300 °C; IR (KBr) cm^{-1}: 3402 (N–H), 1721 (C=O), 1540, 1492; ^1H NMR (DMSO-d_6, 400 MHz) δ: 7.08–7.94 (m, 14H), 9.16 (s, 1H); MS *m*/*z* (%) 456/454 (M^+, 15/44), 426 (17), 294 (15), 273 (38), 77 (100); Anal. Calcd for $C_{23}H_{15}ClN_8O$: C, 60.73; H, 3.32; N, 24.63. Found: C, 60.87; H, 3.41; N, 24.47%.

5-(4-Chlorophenyl)-6-(4-chlorophenyl)amino-3,5-dihydro-3-phenyl-1,2,3-triazolo[4,5-*d*]-1,2,4-triazolo[1,5-*a*]pyrimidin-9-one (10d). White crystals (440 mg, yield 90%), mp: >300 °C; IR (KBr) cm^{-1}: 3407 (N–H), 1729 (C=O), 1544, 1492; ^1H NMR (DMSO-d_6, 400 MHz) δ: 7.44–7.93 (m, 13H), 9.30 (s, 1H); MS *m*/*z* (%) 492/490/488 (M^+, 3/16/25), 460 (12), 308 (15), 273 (43), 77 (100); Anal. Calcd for $C_{23}H_{14}Cl_2N_8O$: C, 56.46; H, 2.88; N, 22.90. Found: C, 56.31; H, 2.90; N, 22.81%.

5-(4-Chlorophenyl)-3,5-dihydro-6-(4-methylphenyl)amino-3-phenyl-1,2,3-triazolo[4,5-*d*]-1,2,4-triazolo[1,5-*a*]pyrimidin-9-one (10e). White crystals (388 mg, yield 83%), mp: >300 °C; IR (KBr) cm^{-1}: 3364 (N–H), 1731 (C=O), 1541, 1493; ^1H NMR (DMSO-d_6, 400 MHz) δ: 2.27 (s, 3H), 7.16–7.93 (m, 13H), 9.04 (s, 1H); MS *m*/*z* (%) 470/468 (M^+, 11/35), 440 (14), 308 (28), 273 (42), 77 (100); Anal. Calcd for $C_{24}H_{17}ClN_8O$: C, 61.48; H, 3.65; N, 23.90. Found: C, 61.35; H, 3.52; N, 23.97%.

5-(4-Chlorophenyl)-3,5-dihydro-6-(3-methylphenyl)amino-3-phenyl-1,2,3-triazolo[4,5-*d*]-1,2,4-triazolo[1,5-*a*]pyrimidin-9-one (10f). White crystals (393 mg, yield 84%), mp: >300 °C; IR (KBr) cm^{-1}: 3359 (N–H), 1733 (C=O), 1543, 1493; ^1H NMR (DMSO-d_6, 400 MHz) δ: 2.29 (s, 3H), 6.87–7.94 (m, 13H), 9.07 (s, 1H); MS *m*/*z* (%) 470/468 (M^+, 9/28), 440 (10), 308 (17), 273 (26), 77 (100); Anal. Calcd for $C_{24}H_{17}ClN_8O$: C, 61.48; H, 3.65; N, 23.90. Found: C, 61.41; H, 3.78; N, 23.84%.

3,5-Dihydro-5-(4-methylphenyl)-3-phenyl-6-phenylamino-1,2,3-triazolo[4,5-*d*]-1,2,4-triazolo[1,5-*a*]pyrimidin-9-one (10g). White crystals (355 mg, yield 82%), mp: >300 °C; IR (KBr) cm^{-1}: 3402 (N–H), 1719 (C=O), 1543, 1457; ^1H NMR ($CDCl_3$–TFA, 400 MHz) δ: 2.54 (s, 3H), 6.88–7.82 (m, 14H); ^{13}C NMR ($CDCl_3$–TFA, 100 MHz) δ 21.1, 119.4, 123.0 (2), 124.4, 125.4 (2), 127.7 (2), 129.5 (2), 129.9 (2), 130.0, 130.4, 132.1 (2), 134.3, 135.6, 143.7, 147.8, 148.4, 150.3, 150.6; MS *m*/*z* (%) 434 (M^+, 42), 406 (19), 288 (22), 274 (17), 77 (100); Anal. Calcd for $C_{24}H_{18}N_8O$: C, 66.35; H, 4.18; N, 25.79. Found: C, 66.15; H, 4.10; N, 25.88%.

3,5-Dihydro-5-(4-methylphenyl)-3-phenyl-6-(4-methylphenyl)-amino-1,2,3-triazolo[4,5-*d*]-1,2,4-triazolo[1,5-*a*]pyrimidin-9-one (10h). White crystals (390 mg, yield 87%), mp: >300 °C; IR (KBr) cm^{-1}: 3411 (N–H), 1717 (C=O), 1545, 1510; ^1H NMR ($CDCl_3$–TFA, 400 MHz) δ: 2.15 (s, 3H), 2.54 (s, 3H), 6.70–7.82 (m, 13H); ^{13}C NMR ($CDCl_3$–TFA, 100 MHz) δ 20.6, 21.1, 122.8 (2), 124.1, 125.3 (2), 127.5 (2), 128.4, 129.2 (2), 129.7 (2), 129.8, 130.2, 132.0 (2), 134.0, 135.5, 143.8, 147.7, 148.2, 150.1, 150.4; MS *m*/*z* (%) 448 (M^+, 42), 420 (19), 288 (40), 273 (16), 91 (100). Anal. Calcd for $C_{25}H_{20}N_8O$: C, 66.95; H, 4.49; N, 24.98; Found: C, 66.84; H, 4.57; N, 25.05%.

1,2,3-Triazolo[4,5-*d*]-1,2,4-triazolo[1,5-*a*]pyrimidin-9-one (12)

To a solution of iminophosphorane **6** (1 mmol) in dry CH_2Cl_2 (10 mL) was added acyl chloride (1 mmol) and triethylamine (0.10 g, 1 mmol) under nitrogen at room temperature. The solution was stirred at refluxing temperature for 2–4 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–ethanol to give **12** as crystalline solids.

3,5-Dihydro-3,5,6-triphenyl-1,2,3-triazolo[4,5-*d*]-1,2,4-triazolo-[1,5-*a*]pyrimidin-9-one (12a). White crystals (316 mg, 78% yield), mp: >300 °C; IR (KBr) cm^{-1}: 1736 (C=O), 1548, 1510; ^1H NMR (400 MHz, $CDCl_3$) δ 7.36–7.59 (m, 13H), 8.02 (d, J = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 121.4, 123.0, 124.2, 126.7 (2), 128.4 (2), 128.6 (2), 128.8 (2), 129.2, 129.5 (2), 130.7 (2), 132.0, 132.4, 134.4, 141.0, 148.6, 150.2, 150.4, 153.2; MS *m*/*z* (%) 405 (M^+, 6), 377 (5), 245 (7), 103 (30), 77 (100); Anal. Calcd for $C_{23}H_{15}N_7O$: C, 68.14; H, 3.73; N, 24.18. Found: C, 68.25; H, 3.81; N, 24.05%.

3,5-Dihydro-3,5-diphenyl-6-methyl-1,2,3-triazolo[4,5-*d*]-1,2,4-triazolo[1,5-*a*]pyrimidin-9-one (12b). White crystals (289 mg, 84% yield), mp: >300 °C; IR (KBr) cm^{-1}: 1743 (C=O), 1557, 1498; ^1H NMR (400 MHz, $CDCl_3$–TFA) δ 2.52 (s, 3H), 7.46–7.89 (m, 10H); ^{13}C NMR ($CDCl_3$–TFA, 100 MHz) δ 11.9, 121.7 (2), 125.0, 127.0 (2), 129.0, 129.4 (2), 130.4 (2), 130.5, 131.0, 135.0, 148.4, 149.6, 150.1, 153.0; MS *m*/*z* (%) 343 (M^+, 23), 315 (16), 286 (16), 245 (9), 77 (100); Anal. Calcd for $C_{18}H_{13}N_7O$: C, 62.97; H, 3.82; N, 28.56. Found: C, 62.75; H, 3.91; N, 28.36%.

5-(4-Chlorophenyl)-3,5-dihydro-3,6-diphenyl-1,2,3-triazolo[4,5-*d*]-1,2,4-triazolo[1,5-*a*]pyrimidin-9-one (12c). White crystals (377 mg, 86% yield), mp: 287–288 °C; IR (KBr) cm^{-1} 1731 (C=O), 1535, 1494; ^1H NMR (400 MHz, $CDCl_3$–TFA) δ 7.25–7.59 (m, 12H), 7.96 (d, J = 8.4 Hz, 2H); MS *m*/*z* (%) 441/439

(M^+, 6/20), 411 (16), 279 (22), 111 (69), 77 (100); Anal. Calcd for $C_{23}H_{14}ClN_7O$: C, 62.80; H, 3.21; N, 22.29. Found: C, 62.73; H, 3.15; N, 22.33%.

5-(4-Chlorophenyl)-3,5-dihydro-6-methyl-3-phenyl-1,2,3-triazolo-[4,5-*d*]-1,2,4-triazolo[1,5-*a*]pyrimidin-9-one (12d). White crystals (275 mg, 73% yield), mp: >300 °C; IR (KBr) cm^{-1} 1740 (C=O), 1554, 1509; ^1H NMR (400 MHz, $CDCl_3$/TFA) δ 2.49 (s, 3H), 7.42–7.92 (m, 10H); MS *m*/*z* (%) 379/377 (M^+, 8/27), 349 (19), 320 (19), 273 (21), 111 (100); Anal. Calcd for $C_{18}H_{12}ClN_7O$: C, 57.23; H, 3.20; N, 25.95. Found: C, 57.47; H, 3.15; N, 25.87%.

3,5-Dihydro-3,6-diphenyl-5-(4-methylphenyl)-1,2,3-triazolo[4,5-*d*]-1,2,4-triazolo[1,5-*a*]pyrimidin-9-one (12e). White crystals (314 mg, 75% yield), mp: >300 °C; IR (KBr) cm^{-1} 1732 (C=O), 1543, 1510; ^1H NMR (400 MHz, $CDCl_3$) δ 2.48 (s, 3H), 7.26–8.09 (m, 14H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.1, 121.8, 123.2, 124.8, 127.0 (2), 128.8 (2), 128.9 (2), 129.0 (2), 129.3, 129.5 (2), 130.9 (2), 132.3, 134.9, 141.4, 148.5, 150.2, 150.5, 153.3; MS *m*/*z* (%) 419 (M^+, 90), 391 (61), 262 (24), 259 (80), 91 (100); Anal. Calcd for $C_{24}H_{17}N_7O$: C, 68.73; H, 4.09; N, 23.38. Found: C, 68.80; H, 4.16; N, 22.36%.

3,5-Dihydro-6-methyl-5-(4-methylphenyl)-3-phenyl-1,2,3-triazolo-[4,5-*d*]-1,2,4-triazolo[1,5-*a*]pyrimidin-9-one (12f). White crystals (304 mg, 85% yield), mp: >300 °C; IR (KBr) cm^{-1} 1737 (C=O), 1558, 1517; ^1H NMR (400 MHz, $CDCl_3$) δ 2.48 (s, 3H), 2.51 (s, 3H), 7.34–8.05 (m, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 11.9, 21.2, 122.2 (2), 124.7, 126.7 (2), 127.6, 129.5 (2), 129.6, 131.1 (2), 134.7, 141.9, 148.5, 149.7, 150.2, 153.6; MS *m*/*z* (%) 357 (M^+, 70), 329 (49), 288 (21), 259 (26), 91 (100). Anal. Calcd for $C_{19}H_{15}N_7O$: C, 63.86; H, 4.23; N, 27.44. Found: C, 63.73; H, 4.36; N, 27.31%.

Acknowledgements

We gratefully acknowledge financial support of this work by the National Basic Research Program of China (2004CCA00100) and the National Natural Science Foundation of China (Project No. 20102001).

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