Res Chem Intermed (2012) 38:2065–2073
DOI 10.1007/s11164-012-0526-9

An efficient and facile synthesis of polydentate ligand: pyridylpyrimidine-2-amine under solvent-free conditions

Shimin Tao · Sheng Xia · Liangce Rong · Changsheng Cao · Shujiang Tu

Received: 19 January 2012 / Accepted: 29 February 2012 / Published online: 15 March 2012

Abstract An efficient and facile synthesis of polydentate ligand pyridylpyrimidine-2-amine via a one-pot reaction of different aromatic aldehydes, 2-acetylpyridine and guanidine carbonate, in the presence of NaOH under solvent-free conditions, is reported. These compounds have four *N*-donors and they are classic polydentate ligands of many metal ions. Due to employing a one-pot, multicomponent reaction, this method offers several advantages including easy experimental work-up procedure, and lower cost, short reaction time, and especially high yields of products. This paper therefore develops a practical and convenient process for the synthesis of these ligands.

Keywords Polydentate ligand · Pyridylpyrimidine-2-amine · Multicomponent reaction · Solvent-free synthesis · Green chemistry

Introduction

The rational design and construction of novel metal–organic complexes (coordination compounds) has been the subject of a great many studies in recent years, not only due to their structural and topological novelty [1–3] but also for their potential applications as functional materials such as catalysts, molecular recognition, separation, and nonlinear optics [4–7]. The structure of metal–organic complexes is greatly influenced by many factors such as the coordination geometry of metal ions, the structure of organic ligands, the solvent system, the counteranion, and the ratio of ligands to metal ions [8–15]. Among these factors, synthesis of new organic

S. Tao · S. Xia · L. Rong (✉) · C. Cao · S. Tu
Jiangsu Key Laboratory of Green Synthetic Chemistry For Functional Materials, College of Chemistry and Chemical Engineering, Xuzhou Normal University, Xuzhou, Jiangsu 221116, People's Republic of China
e-mail: lcrong2005@yahoo.com

ligands is one of the most important topics. From the stability of the coordination compounds, polydentate ligand is much better than monodentate ligand. In this regard, a large number of polydentate ligands were designed and utilized. Among them, there is an increasing interest in the *N*,*N*'-chelating ligands, especially the *N*,*N*'-chelating oligopyridine ligands[16–19], for instance 2,2′-bipyridine and its derivatives [20–22].

Green chemistry has become a powerful strategy in organic chemistry in the last decade [23–25], and current areas of interest are the generation of complex molecular systems via multicomponent reactions under solvent-free conditions [26–28]. The avoidance solvents in chemical processes, or the replacement of hazardous solvents with more benign solvents, have become major concerns in academia and industry, and the need for green reactions is now globally accepted. Solvent-free multicomponent syntheses are particularly attractive, because they incorporate many green chemistry principles.

Pyridylpyrimidine, as *N*,*N*'-chelating ligands, has four *N*-donors and can act as a neutral mono- or bidentate ligand and an anionic tridentate ligand. This compound has tunable coordination modes and supramolecular interactions because it is the multidentate ligand and includes hydrogen-bonding donor and acceptors (aromatic *N* atoms) (Fig. 1), so chelate complexes or polymers can be obtained from pyridylpyrimidines. Thus, this type of *N*-heterocyclic ligand is a good choice in constructing metal–organic frameworks with interesting structures and properties. As we have synthesized some organic compounds under solvent-free conditions [29–31], we report here a simple and efficient method for the synthesis of *N*,*N*'-chelating polydentate ligands, i.e., pyridylpyrimidine-2-amine under solvent-free conditions.

Results and discussion

We have carefully investigated synthetic methods that have been reported of these compounds. We found that only a few papers have reported preparing similar compounds. For example, Rajendra [32] used condensation products of 2-acetyl-pyridine with different aldehydes, then reacted them with guanidine hydrochloride to give several 2-amino-4-(substituted phenyl/anthryl)-6-(2′-pyridyl)pyrimidines under EtOH condition, which were in fact two step reactions. Raymond [33] has also reported the synthesis of some substituted pyrimidines by condensing the β-diketone or β-keto ester with guanidine carbonate. In the reported methods, organic solvents were necessary. As a solvent-free condition, organic synthesis is a

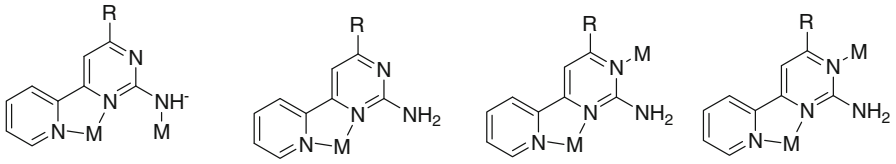


Fig. 1 The coordination modes of pyridylpyrimidine-2-amine ligands

powerful tool of current organic reactions, and we want to try to synthesize these compounds under solvent-free conditions.

2-Fluorobenzaldehyde **1a**, 2-acetylpyridine **2**, and guanidine carbonate **3** were chosen as the starting material for the model reaction, and three reagents were reacted under solvent-free conditions using different catalysts. In our research, we found that, when an organic base (such as Et_3N, $C_5H_{11}N$, DBU, etc.) and lewis acid (such as $ZnCl_2$, $FeCl_3$, $MgCl_2$, $SnCl_2$, etc.) were used as catalysts, the reaction could did not occur. When we used an inorganic base, K_2CO_3, Na_2CO_3, and Cs_2CO_3, the product could be generated, but with very low yield. When a strong base such as NaOH was used, the reaction could be carried out smoothly with high yield. We also found that higher loading of the NaOH did not improve the yields of the reaction, and, conversely, the yield was depressed, perhaps because large amounts of NaOH could turn the reagents into solids very quickly, and that hindered the reaction from continuing. Another strong base, KOH, is also an efficient catalyst of this reaction; however, compared with NaOH, the yield of the product is not obviously improved. Taking into account all the conditions, we chose NaOH as the ideal catalyst to accomplish these syntheses. The optimized reaction conditions are summarized in Table 1.

Under this optimized condition, the different aromatic aldehydes were allowed to undergo a one-pot reaction with 2-acetylpyridine and guanidine carbonate, affording a series of 4-aryl-6-(pyridin-2-yl) pyrimidin-2-amine with high yields in only about 45 min. (Scheme 1). The results of the reactions are listed in Table 2. As shown in Table 2, 14 compounds have been synthesized. No matter whether it was electron-withdrawing (such as F, Cl, and Br) or electron-donating substitute groups (CH_3- and CH_3O-) on aromatic aldehydes, the products could be obtained with ideal results.

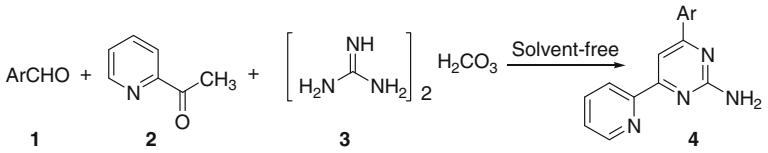
Table 1 Synthesis of **4a** under solvent-free conditions in the presence of different catalysts

Entry	Amount (mmol)	Catalyst	Yield[a]/%
1	0.2–0.4	Et_3N	0
2	0.2–0.4	$C_5H_{11}N$	0
3	0.2–0.4	DBU	0
4	0.2–0.4	$ZnCl_2$	0
5	0.2–0.4	$FeCl_3$	0
6	0.2–0.4	$MgCl_2$	0
7	0.2–0.4	$SnCl_2$	0
8	0.4	Na_2CO_3	23
9	0.4	K_2CO_3	26
10	0.4	Cs_2CO_3	21
11	0.4	NaOH	85
12	0.3	NaOH	90
13	**0.2**	**NaOH**	**95**
14	0.4	KOH	81
15	0.2	KOH	91

Reagents and conditions: 2-Fluorobenzaldehyde **1a** (1 mmol), 2-acetylpyridine **2** (1 mmol), and guanidine carbonate **3** (1.5 mmol), reaction temperature 70 °C

Bold indicates the best yield, for NaOH

[a] Isolated yields



Scheme 1 Synthesis of 4-aryl-6-(pyridin-2-yl)pyrimidin-2-amine

Table 2 Synthetic results of compounds **4**

Entry	Ar	Product	Yields (%)
1	2-FC_6H_4	**4a**	95
2	3-FC_6H_4	**4b**	91
3	4-FC_6H_4	**4c**	94
4	4-ClC_6H_4	**4d**	90
5	2,4-$Cl_2C_6H_3$	**4e**	92
6	3,4-$Cl_2C_6H_3$	**4f**	91
7	2-BrC_6H_4	**4g**	89
8	4-BrC_6H_4	**4h**	92
9	4-$CH_3C_6H_4$	**4i**	90
10	3,4-$(CH_3)_2C_6H_3$	**4j**	93
11	3-$CH_3OC_6H_4$	**4k**	94
12	4-$CH_3OC_6H_4$	**4l**	95
13	3,4-$(CH_3O)_2C_6H_3$	**4m**	91
14	3,4,5-$(CH_3O)_3C_6H_2$	**4n**	96

All the products were characterized by IR, ^{1}H-NMR, ^{13}C-NMR, and HRMS. For example, in ^{1}H-NMR, **4i** shows a singlet at delta 2.36 due to the CH_3 protons and a singlet at delta 5.24 due to the NH_2 protons, as well as doublets at delta 7.23 ($J = 8.0$ Hz), 8.00 ($J = 8.0$ Hz), 8.32 ($J = 7.6$ Hz), 8.68 ($J = 8.8$ Hz), and a multiplet at delta 7.30–7.33, a singlet at delta 8.06, and a triplet at delta 7.77 ($J = 8.0$ Hz) due to the nine aryl protons. In ^{13}C-NMR, the chemical shifts of 16 carbon atoms show at 21.43, 104.03, 121.56, 124.90, 127.16, 129.39, 134.64, 136.91, 140.81, 149.33, 154.78, 163.50, 164.50, and 166.56, respectively. In the HRMS spectrum, the calculated m/z for $C_{16}H_{14}N_4$ $[M + Na]^+$ is 285.1116, and we found m/z to be 285.1105.

Conclusions

In conclusion, we have expanded an easy and highly efficient one-pot reaction for the synthesis of 4-aryl-6-(pyridin-2-yl)pyrimidin-2-amine via the reaction of different aromatic aldehydes, 2-acetylpyridine and guanidine carbonate, under solvent-free conditions with high yields. These compounds have four *N*-donors and they are classic polydentate ligands of many metal ions. Due to employing a one-pot multicomponent reaction, this method offers several advantages, including easy

experimental work-up procedure, procedure, and lower cost, short reaction time, and especially high yields of products. This paper develops a practical and convenient process for the synthesis of these ligands.

Experimental

Melting points were determined on XT-5 microscopic melting-point apparatus and were uncorrected. IR spectra were recorded on a FT Bruker Tensor 27 spectrometer. ^{1}H NMR spectra were obtained from solution in $CDCl_3$ with Me_4Si as internal standard using a Bruker-400 or Bruker-300 spectrometer. HRMS spectra were obtained with a Bruker microTOF-Q 134 instrument.

General procedure for the synthesis of 4-aryl-6-(pyridin-2-yl)pyrimidin-2-amine derivatives

The mixture of aromatic aldehydes 1 (1 mmol), 2-acetylpyridine 2 (1 mmol), guanidine carbonate 3 (1.5 mmol), and NaOH (0.2 mmol) was put in a reaction flask at under 70 °C for about 45 min. After completing the reaction, the reaction mixture was poured into water (0.5 % HCl), and then thoroughly washed with water. The product was filtered, dried, and recrystallized from 95% ethanol.

*4-(2-fluorophenyl)-6-(pyridin-2-yl)pyrimidin-2-amine (**4a**)*

Melting point 118–119 °C; IR (KBr) *v*: 3,328, 3,232, 2,360, 2,341, 1,698, 1,684, 1,635, 1,575, 1,558, 1,541, 1,508, 1,490, 1,474, 1,457, 1,425, 1,362, 1,207, 1,203, 764, 740, 669 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 5.24 (2H, s, NH_2), 7.11–7.16 (1H, m, ArH), 7.20–7.24 (1H, m, ArH), 7.31–7.41 (2H, m, ArH), 7.78 (1H, t, $J = 8.0$ Hz, ArH), 7.97 (1H, t, $J = 8.0$ Hz, ArH), 8.09 (1H, d, $J = 2.4$ Hz, ArH), 8.30-8.32 (1H, m, ArH), 8.68–8.70 (1H, m, ArH); ^{13}C NMR (400 MHz, $CDCl_3$) δ: 108.49 (d, $J = 38.4$ Hz), 116.38 (d, $J = 90.4$ Hz), 121.64, 124.39 (d, $J = 14.4$ Hz), 124.96, 125.93 (d, $J = 43.6$ Hz), 130.53 (d, $J = 10.4$ Hz), 131.65 (d, $J = 34.4$ Hz), 136.87, 149.51, 154.57, 159.78, 162.29, 162.93 (d, $J = 8.8$ Hz), 163.32, 164.66.

HRMS m/z calculated for $C_{15}H_{11}FN_4$ $[M + Na]^+$: 289.0865, found: 289.0879.

*4-(3-fluorophenyl)-6-(pyridin-2-yl)pyrimidin-2-amine (**4b**)*

Melting point 155–156 °C; IR (KBr) *v*: 3,330, 2,360, 2,341, 1,698, 1,684, 1,647, 1,558, 1,541, 1,522, 1,508, 1,474, 1,458, 669 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 5.21 (2H, s, NH_2), 7.10–7.15 (1H, m, ArH), 7.33–7.37 (1H, m, ArH), 7.39–7.43 (1H, m, ArH), 7.78–7.85 (2H, m, ArH), 7.87 (1H, d, $J = 8.0$ Hz, ArH), 8.08 (1H, s, ArH), 8.34 (1H, d, $J = 8.0$ Hz, ArH), 8.68 (1H, d, $J = 4.4$ Hz, ArH); ^{13}C NMR (400 MHz, $CDCl_3$) δ: 104.36, 114.14 (d, $J = 91.2$ Hz), 117.35 (d, $J = 84.8$ Hz), 121.58, 122.84 (d, $J = 11.2$ Hz), 125.11, 130.14 (d, $J = 32.0$ Hz), 136.96, 139.80 (d, $J = 30$ Hz), 149.37, 154.44, 161.91, 163.41, 164.36, 165.01.

HRMS m/z calculated for $C_{15}H_{11}FN_4$ $[M + Na]^+$: 289.0865, found: 289.0884.

*4-(4-fluorophenyl)-6-(pyridin-2-yl)pyrimidin-2-amine (**4c**)*

Melting point 169–170 °C; IR (KBr) *v*: 3,343, 2,360, 2,341, 1,716, 1,690, 1,683, 1,652, 1,558, 1,541, 1,508, 1,473, 1,456, 1,361, 1,229, 842, 788, 669 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ: 5.33 (2H, s, NH_2), 7.10 (2H, t, $J = 6.6$ Hz, ArH), 7.31–7.34 (1H, m, ArH), 7.77 (1H, t, $J = 5.7$ Hz, ArH), 8.05 (1H, s, ArH), 8.09 (2H, dd, $J = 5.2$ Hz, $J = 6.0$ Hz, ArH), 8.33 (1H, d, $J = 5.7$ Hz, ArH), 8.67 (1H, d, $J = 6.6$ Hz, ArH); ^{13}C NMR (300 MHz, $CDCl_3$) δ: 103.94, 115.63 (d, $J = 86$ Hz), 121.56, 125.03, 129.25 (d, $J = 34.4$ Hz), 133.59 (d, $J = 9.3$ Hz), 136.94, 149.33, 154.54, 163.29 (d, $J = 101.4$ Hz), 164.75, 165.51 (d, $J = 56.1$ Hz).

HRMS m/z calculated for $C_{15}H_{11}FN_4$ $[M + Na]^+$: 289.0865, found: 289.0882.

*4-(4-chlorophenyl)-6-(pyridin-2-yl)pyrimidin-2-amine (**4d**)*

Melting point 184–185 °C (lit [32], 188 °C); IR (KBr) *v*: 3,185, 2,360, 2,341, 1,749, 1,717, 1,698, 1,684, 1,647, 1,558, 1,541, 1,508, 1,490, 1,474, 1,457, 1,361, 1,090, 829, 786, 669 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ: 5.29 (2H, br, NH_2), 7.31–7.41 (3H, m, ArH), 7.74–7.80 (1H, m, ArH), 8.00–8.06 (3H, m, ArH), 8.32 (1H, t, $J = 8.8$ Hz, ArH), 8.65–8.68 (1H, m, ArH); ^{13}C NMR (400 MHz, $CDCl_3$) δ: 104.00, 121.56, 125.07, 128.51, 128.85, 135.86, 136.61, 136.95, 149.32, 154.45, 163.44, 164.87, 165.24.

HRMS m/z calculated for $C_{15}H_{11}ClN_4$ $[M + H]^+$: 283.0750, found: 283.0792.

*4-(2,4-dichlorophenyl)-6-(pyridin-2-yl)pyrimidin-2-amine (**4e**)*

Melting point 160–161 °C (lit [32], 180 °C); IR (KBr) *v*: 3,327, 2,361, 2,341, 1,698, 1,684, 1,647, 1,636, 1,558, 1,541, 1,522, 1,508, 1,474, 1,458, 669 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ: 5.26 (2H, s, NH_2), 7.34–7.40 (2H, m, ArH), 7.51 (1H, d, $J = 1.2$ Hz, ArH), 7.57 (1H, d, $J = 6.2$ Hz, ArH), 7.84 (1H, t, $J = 6.2$ Hz, ArH), 7.97 (1H, s, ArH), 7.37 (1H, d, $J = 6.0$ Hz, ArH), 8.71 (1H, d, $J = 2.7$ Hz, ArH); ^{13}C NMR (300 MHz, $CDCl_3$) δ: 108.72, 121.67, 125.12, 127.32, 130.05, 131.72, 133.03, 135.61, 136.24, 136.93, 149.51, 154.29, 163.16, 164.39, 165.58.

HRMS m/z calculated for $C_{15}H_{10}Cl_2N_4$ $[M + Na]^+$: 339.0180, found: 339.0198.

*4-(3,4-dichlorophenyl)-6-(pyridin-2-yl)pyrimidin-2-amine (**4f**)*

Melting point 156–157 °C; IR (KBr) *v*: 3,327, 2,361, 2,341, 1,698, 1,684, 1,647, 1,636, 1,558, 1,541, 1,522, 1,508, 1,474, 1,458, 669 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ: 5.22 (2H, s, NH_2), 7.42 (1H, dd, $J = 5.1$ Hz, $J = 6.9$ Hz, ArH), 7.59 (1H, d, $J = 8.4$ Hz, ArH), 7.86 (1H, t, $J = 7.8$ Hz, ArH), 8.00 (1H, dd, $J = 2.1$ Hz, $J = 8.4$ Hz, ArH), 8.11 (1H, s, ArH), 8.29 (1H, d, $J = 1.8$ Hz, ArH), 8.40 (1H, d, $J = 7.8$ Hz, ArH), 8.74 (1H, d, $J = 5.2$ Hz, ArH); ^{13}C NMR (300 MHz, $CDCl_3$) δ: 103.91, 121.55, 125.17, 126.22, 129.04, 130.03, 130.54, 133.03, 136.98, 139.44, 149.29, 154.83, 162.47, 163.27, 164.39, 165.13.

HRMS m/z calculated for $C_{15}H_{10}Cl_2N_4$ $[M + Na]^+$: 339.0180, found: 339.0189.

*4-(2-bromophenyl)-6-(pyridin-2-yl)pyrimidin-2-amine (**4g**)*

Melting point 148–149 °C; IR (KBr) *v*: 3,329, 3,177, 2,360, 2,341, 1,646, 1,575, 1,558, 1,540, 1,475, 1,456, 1,432, 1,349, 1,237, 1,127, 1,073, 993, 846, 790, 773, 669, 650 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ: 5.37 (2H, s, NH_2), 7.27 (1H, t, $J = 8.0$ Hz, ArH), 7.31–7.34 (1H, m, ArH), 7.53 (1H, dd, $J = 0.8$ Hz, $J = 8.0$ Hz, ArH), 7.77 (1H, t, $J = 8.0$ Hz, ArH), 7.99 (1H, d, $J = 8.0$ Hz, ArH), 8.04 (1H, s, ArH), 8.24 (1H, t, $J = 1.6$ Hz, ArH), 8.32 (1H, d, $J = 8.0$ Hz, ArH), 8.67 (1H, dd, $J = 0.8$ Hz, $J = 8.8$ Hz, ArH); ^{13}C NMR (400 MHz, $CDCl_3$) δ: 104.23, 121.60, 122.95, 125.77, 130.14, 130.24, 133.33, 136.96, 139.51, 149.34, 154.38, 163.45, 164.93, 164.98.

HRMS m/z calculated for $C_{15}H_{11}BrN_4$ $[M + Na]^+$: 349.0065, found: 349.0016.

*4-(4-bromophenyl)-6-(pyridin-2-yl)pyrimidin-2-amine (**4h**)*

Melting point 193–194 °C; IR (KBr) *v*: 3,180, 2,361, 2,341, 1,716, 1,698, 1,683, 1,647, 1,558, 1,541, 1,522, 1,508, 1,473, 1,459, 669 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ: 5.25 (2H, s, NH_2), 7.32–7.35 (1H, m, ArH), 7.56 (2H, d, $J = 6.6$ Hz, ArH), 7.78 (1H, t, $J = 6.0$ Hz, ArH), 7.97 (2H, d, $J = 6.3$ Hz, ArH), 8.06 (1H, s, ArH), 8.33 (1H, d, $J = 6.0$ Hz, ArH), 8.68 (1H, dd, $J = 0.6$ Hz, $J = 2.7$ Hz, ArH); ^{13}C NMR (300 MHz, $CDCl_3$) δ: 103.99, 121.58, 125.10, 128.77, 131.83, 136.34, 136.96, 149.34, 154.46, 163.45, 164.93, 165.32.

HRMS m/z calculated for $C_{15}H_{11}BrN_4$ $[M + Na]^+$: 349.0065, found: 349.0020.

*4-(pyridin-2-yl)-6-p-tolylpyrimidin-2-amine (**4i**)*

Melting point 144–145 °C; IR (KBr) *v*: 3,310, 3,180, 2,361, 2,341, 1,698, 1,684, 1,636, 1,559, 1,541, 1,508, 1,474, 1,457, 1,362, 785, 669 cm^{-1}; ^1H NMR (400 MHz, DMSO–d_6) δ: 2.36 (3H, s, CH_3), 5.33 (2H, s, NH_2) 7.23 (2H, d, $J = 8.0$ Hz, ArH), 7.30–7.33 (1H, m, ArH), 7.77 (1H, t, $J = 8.0$ Hz, ArH), 8.00 (2H, d, $J = 8.0$ Hz, ArH), 8.06 (1H, s, ArH), 8.32 (1H, d, $J = 7.6$ Hz, ArH), 8.68 (1H, d, $J = 8.8$ Hz, ArH); ^{13}C NMR (400 MHz, DMSO-d_6) δ: 21.43, 104.03, 121.56, 124.90, 127.16, 129.39, 134.64, 136.91, 140.81, 149.33, 154.78, 163.50, 164.50, 166.56.

HRMS m/z calculated for $C_{16}H_{14}N_4$ $[M + Na]^+$: 285.1116, found: 285.1105.

*4-(3,4-dimethylphenyl)-6-(pyridin-2-yl)pyrimidin-2-amine (**4j**)*

Melting point 173–174 °C; IR (KBr) *v*: 3,326, 3,194, 2,360, 2,341, 1,698, 1,645, 1,574, 1,558, 1,540, 1,507, 1,476, 1,456, 1,433, 1,404, 1,350, 1,225, 785, 740, 669 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ: 2.27 (3H, s, CH_3), 2.30 (3H, s, CH_3), 5.28 (2H, s, NH_2), 7.19 (1H, d, $J = 8.0$ Hz, ArH), 7.31–7.34 (1H, m, ArH), 7.77 (1H, t, $J = 8.0$ Hz, ArH), 7.84 (1H, d, $J = 8.0$ Hz, ArH), 7.89 (1H, s, ArH), 8.06 (1H, s, ArH), 8.33 (1H, dd, $J = 0.8$ Hz, $J = 8.0$ Hz, ArH), 8.69 (1H, dd,

$J = 0.8$ Hz, $J = 8.0$ Hz, ArH); ^{13}C NMR (400 MHz, $CDCl_3$) δ: 19.79, 19.85, 104.07, 121.58, 124.73, 124.88, 129.97, 135.00, 136.91, 139.53, 149.32, 154.83, 163.47, 164.39, 166.74.

HRMS m/z calculated for $C_{17}H_{16}N_4$ $[M + Na]^+$: 299.1273, found: 299.1298.

*4-(3-methoxyphenyl)-6-(pyridin-2-yl)pyrimidin-2-amine (**4k**)*

Melting point 131–132 °C; IR (KBr) *v*: 3,336, 3,196, 2,361, 2,341, 1,699, 1,637, 1,559, 1,541, 1,508, 1,474, 1,458, 1,361, 1,246, 669 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 3.91 (3H, s, OCH_3), 5.22 (2H, s, NH_2), 7.04 (1H, d, $J = 8.4$ Hz, ArH), 7.38–7.43 (2H, m, ArH), 7.72 (2H, d, $J = 6.6$ Hz, ArH), 7.85 (1H, t, $J = 7.8$ Hz, ArH), 8.13 (1H, s, ArH), 8.39 (1H, d, $J = 7.8$ Hz, ArH), 8.74 (1H, d, $J = 4.8$ Hz, ArH); ^{13}C NMR (300 MHz, $CDCl_3$) δ: 55.35, 104.50, 111,96, 116.67, 119.69, 121.52, 124.92, 129.59, 136.87, 138.89, 149.30, 154.60, 159.88, 163.32, 166.38.

HRMS m/z calculated for $C_{16}H_{14}N_4O$ $[M + Na]^+$: 301.1066, found: 301.1067.

*4-(4-methoxyphenyl)-6-(pyridin-2-yl)pyrimidin-2-amine (**4l**)*

Melting point 199–200 °C (lit [32], 142 °C); IR (KBr) *v*: 3,356, 2,361, 2,341, 1,736, 1,717, 1,698, 1,646, 1,560, 1,541, 1,474, 1,457, 1,435, 1,364, 1,259, 1,178, 1,032, 789, 669 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 3.87 (3H, s, OCH_3), 5.24 (2H, s, NH_2), 6.99 (2H, d, $J = 7.2$ Hz, ArH), 7.36–7.40 (1H, m, ArH), 7.84 (1H, t, $J = 7.8$ Hz, ArH), 8.08 (1H, d, $J = 0.9$ Hz, ArH), 8.13 (2H, d, $J = 7.2$ Hz, ArH), 8.37 (1H, d, $J = 7.8$ Hz, ArH), 8.73 (1H, t, $J = 2.7$ Hz, ArH); ^{13}C NMR (300 MHz, $CDCl_3$) δ: 55.30, 103.15, 113.90, 121.48, 128.71, 128.78, 129.79, 136.88, 149.26, 154.73, 161.60, 163.33, 164.27, 166.00.

HRMS m/z calculated for $C_{16}H_{14}N_4O$ $[M + Na]^+$: 301.1065, found: 301.1074.

*4-(3,4-dimethoxyphenyl)-6-(pyridin-2-yl)pyrimidin-2-amine (**4m**)*

Melting point 192–193 °C (lit [32], 242 °C); IR (KBr) *v*: 3,340, 3,189, 2,360, 2,341, 1,698, 1,647, 1,559, 1,541, 1,519, 1,474, 1,459, 1,434, 1,354, 1,269, 787, 669 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 3.96 (3H, s, OCH_3), 4.02 (3H, s, OCH_3), 5.26 (2H, s, NH_2), 6.96 (1H, d, $J = 8.7$ Hz, ArH), 7.38–7.42 (1H, m, ArH), 7.77 (2H, t, $J = 6.0$ Hz, ArH), 7.85 (1H, t, $J = 7.8$ Hz, ArH), 8.10 (1H, s, ArH), 8.39 (1H, d, $J = 7.8$ Hz, ArH), 8.74 (1H, d, $J = 5.2$ Hz, ArH); ^{13}C NMR (300 MHz, $CDCl_3$) δ: 55.94, 55.98, 76.58, 77.01, 77.43, 103.64, 109.69, 110.67, 120.48, 121.58, 124.94, 130.08, 136.97, 148.99, 149.29, 151.15, 154.76, 163.34, 164.34, 166.03.

HRMS m/z calculated for $C_{17}H_{16}N_4O_2$ $[M + Na]^+$: 331.1171, found: 331.1175.

*4-(pyridin-2-yl)-6-(3,4,5-trimethoxyphenyl)pyrimidin-2-amine (**4n**)*

Melting point 163–164 °C (lit [32], 208 °C); IR (KBr) *v*: 3,336, 3,198, 2,361, 2,341, 1,717, 1,698, 1,648, 1,560, 1,541, 1,507, 1,457, 1,363, 1,309, 1,221, 1,010, 846, 789, 669 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 3.88 (3H, s, OCH_3), 3.92 (6H, s, $2XOCH_3$), 5.57 (2H, s, NH_2), 7.32–7.37 (3H, m, ArH), 7.78 (1H, t, $J = 7.8$ Hz,

ArH), 8.05 (1H, s, ArH), 8.35 (1H, d, $J = 7.8$ Hz, ArH), 8.70 (1H, d, $J = 5.2$ Hz, ArH); ^{13}C NMR (300 MHz, $CDCl_3$) δ: 56.15, 60.83, 103.75, 104.27, 121.54, 124.94, 132.84, 136.90, 140.07, 149.16, 153.23, 154.54, 163.39, 164.54, 165.98.

HRMS m/z calculated for $C_{18}H_{18}N_4O_3$ $[M + Na]^+$: 361.1277, found: 361.1284.

Acknowledgments We are grateful to the National Natural Science Foundation of China (NSFC) (21172188), the Foundation of Xuzhou Normal University (10XLS02) and the Priority Academic Program Development of Jiangsu Higher Education Institutions for financial support.

References

1. F.C. Liu, Y.F. Zeng, J.R. Li, X.H. Bu, H.J. Zhang, J. Ribas, Inorg. Chem. **44**, 7298 (2005)
2. Y.F. Zhou, F.L. Jiang, D.Q. Yuan, B.L. Wu, R.H. Wang, Z.Z. Lin, M.C. Hong, Angew. Chem. Int. Ed. **43**, 5665 (2004)
3. M. Fujita, M. Tominaga, K. Suzuki, M. Kawano, T. Kusukawa, Angew. Chem. Int. Ed. **43**, 5621 (2004)
4. M. Fujita, Y.J. Kwon, S. Washizu, K. Ogura, J. Am. Chem. Soc. **116**, 1151 (1994)
5. O.R. Evans, W. Lin, Acc. Chem. Res. **35**, 511 (2002)
6. K. Kasai, M. Aoyagi, M. Fujita, J. Am. Chem. Soc. **122**, 2140 (2000)
7. S. Kitagawa, R. Kitaura, S.I. Noro, Angew. Chem. Int. Ed. **43**, 2334 (2004)
8. N.S. Oxtoby, N.R. Champness, Cryst. Eng. Comm **7**, 284 (2005)
9. E.Q. Gao, A.L. Cheng, Y.X. Xu, C.H. Yan, M.H. He, Cryst. Growth Des. **5**, 1005 (2005)
10. M. Oh, C.L. Stern, C.A. Mirkin, Inorg. Chem. **44**, 2647 (2005)
11. M.B. Zaman, K. Udachin, J.A. Ripmeester, Inorg. Chem. **44**, 5047 (2005)
12. A.N. Khlobystov, N.R. Champness, M. Schroder, J. Am. Chem. Soc. **125**, 6753 (2003)
13. X.C. Huang, J.P. Zhang, Y.Y. Lin, X.M. Chen, Chem. Commun. **2005**, 2232 (2005)
14. P. Diaz, J. Benet-Buchholz, R. Vilar, A.J.P. White, Inorg. Chem. **45**, 1617 (2006)
15. R.P. Feazell, C.E. Carson, K.K. Klausmeyer, Inorg. Chem. **45**, 2627 (2006)
16. A. Rodriguez, R. Kivekas, E. Colacio, Chem. Commun. **2005**, 5228 (2005)
17. A. Petitjean, N. Kyritsakas, J.M. Lehn, Chem. Commun. **2004**, 1168 (2004)
18. H. Grove, J. Sletten, M. Julve, F. Lloret, J. Chem. Soc., Dalton Trans. **2001**, 2487 (2001)
19. M.H. Klingele, P.D.W. Boyd, B. Moubaraki, K.S. Murray, S. Brooker, Eur. J. Inorg. Chem. **2005**, 910 (2005)
20. R. Lescouezec, F. Lloret, M. Julve, M. Verdaguer, Inorg. Chem. **41**, 818 (2002)
21. A.Q. Wu, F.K. Zheng, G.C. Guo, Inorg. Chem. **43**, 4839 (2004)
22. B.H. Ye, M.L. Tong, X.M. Chen, Coord. Chem. Rev. **249**, 545 (2005)
23. S. Rupam, P. Dipak, Green Chem. **13**, 718 (2011)
24. M.J. Percino, V.M. Chapela, O. Urzua, L.F. Montiel, C. Rodriguez-Barbarin, Res. Chem. Intermed. **33**, 623 (2007)
25. K. Tanaka, F. Toda, Chem. Rev. **100**, 1025 (2000)
26. R. Wang, M.Z. Sun, H. Jiang, Res. Chem. Intermed. **37**, 61 (2011)
27. M. Chhanda, T.K. Pradip, Tetrahedron Lett. **49**, 6237 (2008)
28. R.H. Abdol, G. Yosof, S. Nafisehsadat, E.R. Arnold, Synlett 741 (2010)
29. L.C. Rong, X.Y. Li, H.Y. Wang, D.Q. Shi, S.J. Tu, Chem. Lett. **35**, 1314 (2006)
30. L.C. Rong, L.J. Gao, H.X. Han, H. Jiang, Y.S. Dai, S.J. Tu, Synth. Commun. **40**, 289 (2010)
31. L.J. Gao, H.L. Ji, L.C. Rong, D. Tang, Y.Y. Zha, Y.H. Shi, S.J. Tu, J. Heteocyclic Chem. **48**, 957 (2011)
32. P.Y. Rajendra, K.P. Praveen, K.P. Ravi, Orien. J. Chem. **23**, 1069 (2007)
33. P.M. Raymond, J.Z. James, J. Org. Chem. **25**, 647 (1960)