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聚合物氮化碳负载铜克级制备一种无需额外配体即可催化二级嘧啶-2-胺的碳–氮乌尔曼偶联反应的实用催化剂

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摘要 通过在 550 ℃下煅烧硝酸铜与三聚氰胺前体, 可实现聚合物氮化碳负载铜(Cu/PCN)材料的克级制备. X 射线光电子能谱(XPS)分析表明, 该材料中铜元素呈一价, 可在无需额外配体的条件下催化二级嘧啶-2-胺与芳卤代烃的碳–氮乌尔曼偶联反应, 以实现其氮官能团的修饰. 作为非均相催化剂, 该材料易于回收, 并可被重复使用至少五次而不失活. 该材料比传统的一价铜与钯催化剂更加活泼, 从而为制药工业合成含有嘧啶-2-胺结构的药物提供了一种高效而实用的催化剂.

关键词 聚合物氮化碳; 铜; 催化; 碳–氮乌尔曼偶联反应; 嘧啶-2-胺

Gram-Scale Synthesis of Polymeric Carbon Nitride-Supported Copper: A Practical Catalyst for Ullmann-Type C—N Coupling Modifying Secondary Pyrimidin-2-amines without Additional Ligand

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Abstract Cu/polymeric carbon nitride (PCN) can be prepared in 10 g scale by calcining $Cu(NO_3)_2$ with the melamine precursor at 550 ℃. X-ray photoelectron spectroscopy (XPS) analysis demonstrated that copper in the material was in Cu(I) form and it could catalyze the Ullmann-type C—N coupling reactions of pyrimidin-2-amine derivatives with aryl halides without additional ligand. As a heterogeneous catalyst, the material was recoverable and could be reused for at least five times without deactivation. This material was found to be even more active than traditional Cu(I) catalysts and Pd catalysts, affording an opportunity to develop the efficient and practical novel catalyst reagent for the synthesis of medicines containing pyrimidin-2-amine moieties in pharmaceutical industry.

Keywords polymeric carbon nitride (PCN); copper; catalysis; Ullmann-type C—N coupling reaction; pyrimidin-2-amine

1 Introduction

C—N coupling reactions[1] can construct C—N bond directly to produce the related nitrogen-containing compounds, which widely exist in natural products and medicines, and have been comprehensively applied as the reactants in organic synthesis and as the functional components in materials sciences.[2] In the field, the C—N couplings of pyrimidin-2-amine derivatives are especially important because the pyrimidin-2-amine moieties are common structures in many antitumor medicines, such as *Imatinib*,[3] *Lapatinib*,[4] *Gefitinib*,[5] *etc*. The reactions lead to facile methods to introduce pyrimidin-2-amine moieties into organic molecules and they also facilitate the modifications of pyrimidin-2-amines, affording efficient synthetic tools for the preparation of the related medicines. However, the present catalysis techniques for this reaction suffer a series of issues, such as the use of noble metals and high-loading ligands or additives, unrecoverable catalysts leading to wastes, and the low efficiency of catalysts being reflected by their poor turnover numbers (TONs). In our project, we urgently need the technique to modify secondary pyrimidin-

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2-amines under mild and relatively green conditions for pharmaceutical synthesis. It is a great challenge because the reactivities of secondary pyrimidin-2-amines are relatively low. Thus, developing recoverable and highly efficient catalysts for the reactions free of additional ligand is a meaningful research topic from the practical viewpoint.

Yet, the supported metal catalysts are novel materials attracting very broad attentions for the past twenty years.[6] In comparison with traditional metal catalysts, they are even more active and can catalyze the reactions at very high TONs.[7] In many cases, the cost of the supported metal catalysts can be reduced for their recyclable features,[8] and this also avoids the generation of wastes in large-scale production. Support is the key factor for catalyst design, and a variety of materials, such as the carbon,[9] silica,[10] alumina[11], transition metal oxides,[12] and even the small molecule stabilizers[13] have been utilized as supports of the metals. Polymeric carbon nitrides (PCNs) are a new type of carbon materials. Being prepared from easily accessible and abundant nitrogen-containing precursors such as urea and melamine, the cost of PCNs is relatively low, allowing the use of these materials for industrial purposes.[14] Moreover, Cu-catalyzed reactions have been widely employed and are very practical for the low cost of the catalytic metal.[15] Recently, we found that the PCNs could well coordinate with transition metals,[16a] and the Cu-anchored PCN mesoporous nanotubes (Cu/PCN MNT) was found to be an efficient catalyst for the coupling of 1-iodo-4-methoxybenzene with pyrimidin-2-amine, affording *N*-(4-methoxyphenyl)pyrimidin-2-amine in 62% yield.[16b] On the basis of these works, a practical method for preparing the PCN-supported copper catalyst (Cu/PCN) in 10 g scale was developed, affording an even more active and potentially applicable catalyst reagent for the Ullmann-type C—N coupling modifying of secondary pyrimidin-2-amines comprehensively for pharmaceutical development. Herein, we wish to report our findings.

2 Results and discussion

10.52 g of Cu/PCN was prepared by calcining $Cu(NO_3)_2$ with the melamine precursor at 550 ℃ and the detailed procedures were given in the experimental section (*vide infra*). In the Fourier transform infrared (FT-IR) spectrum of the material (Figure 1a), the peaks at 1200～1650 cm^{-1} attributed to the characteristic peaks of PCN and they were caused by the aromatic C-N heterocycles. The peaks at 3138 and 3401 cm^{-1} reflected the symmetric and asymmetric stretching of the amino. Such strong peaks showed that the material contained large amount of amino groups, affording sufficient capability of coordination after Cu doping. The peaks at 13.0° and 27.4° in the X-ray diffraction (XRD) pattern (Figure 1b) of the material reflected the in-plane repeat unit (100) of tri-*s*-triazine and interlayer reflection (002) of PCN, respectively. There was no change of the diffraction peaks of PCN, showing that the Cu doping did not affect the crystal configuration of the support. No signal of Cu could be observed in XRD pattern, attesting that the metal particles were in very small size and were highly dispersed on PCN support. Energy dispersive spectroscopy (EDS) analysis further attested the existences of Cu, O, C and N elements in the material. Thermogravimetric analysis (TGA) curves showed that the material was very stable at the temperature below 550 ℃ (Figure 1c). The weight losing started with elevated temperature and this was attributed to the decomposition of the contained tri-*s*-triazine structures, resulting in the decomposition of PCN, which completely decomposed at the temperature over 700 ℃. High resolution transmission electron microscope (HR-TEM) image of the Cu/PCN material showed that its inner

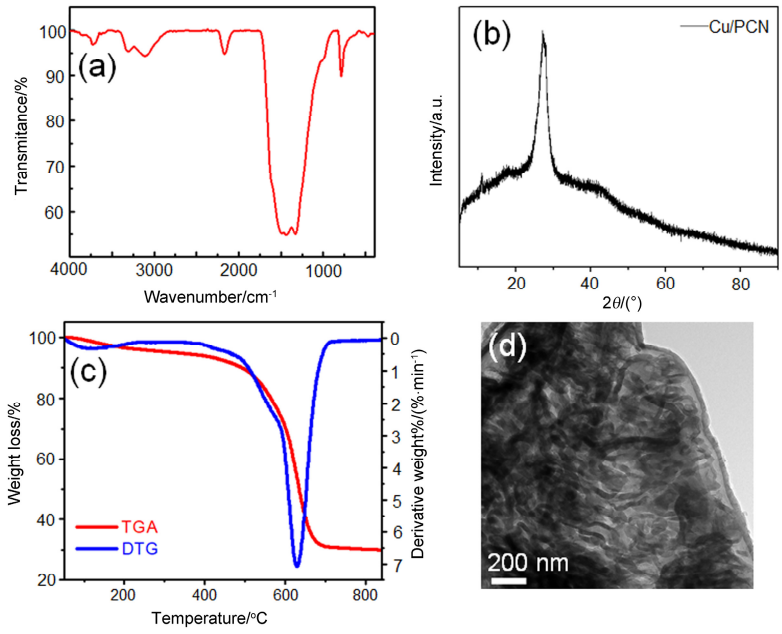


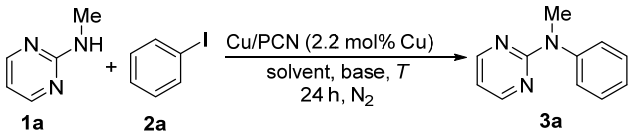
Figure 1 (a) FT-IR spectrum, (b) XRD pattern, (c) TGA-DTG curves and (d) HRTEM image (scale bar, 200 nm) of Cu/PCN

structure was formed by the flocculent fillers (Figure 1d), which was quite different to the Cu/PCN MNT possessing the nano hallows.[16b]

The catalytic activity of the Cu/PCN was higher than Cu/PCN MNT. Catalyzed by Cu/PCN, the reaction of pyrimidin-2-amine with 1-iodo-4-methoxybenzene could even generate the double amination byproducts [*i.e. N*,*N*-bis(4-methoxyphenyl)pyrimidin-2-amine] and the reaction selectivity was not controllable. Similar issue existed in the reaction of aniline. Thus, it was then used as catalyst for the coupling reactions of the less reactive secondary pyrimidin-2-amines with aryl halides and the reaction of *N*-methylpyrimidin-2-amine (**1a**) with iodobenzene (**2a**) was chosen as the model reaction for condition optimizations (Table 1). Heating equimolar of **1a** with **2a** in *t*-BuOH in the presence of Cu/PCN and *t*-BuOK, the desired product *N*-methyl-*N*-phenylpyrimidin-2-amine (**3a**) could be synthesized in 23% yield (Table 1, Entry 1). A series of solvents of the reaction were then tested and 1,4-dioxane was screened out to be a better solvent, affording **3a** in elevated yield (Table 1, Entries 4 vs. 1～5). It was found that strong alkaline condition was essential for the transformation, while weaker bases, whether inorganic or organic, led to decreased product yields (Table 1, Entries 6～8 vs. 4). Thin layer chromatography indicated that the reaction was not completed at 80 ℃ and raising the reaction temperature to 90 ℃ obviously enhanced the product yield (Table 1, Entries 9 vs. 4). Further screenings demonstrated that the reaction at 110 ℃ was preferable, affording **3a** in good yield (Table 1, Entries 11 vs. 4, 9～12). The product yield did not increase at elevated reaction temperature (Table 1, Entries 12 vs. 11). The blank reaction under the conditions described in Table 1, Entry 12 but without the metal catalyst led to the generation of **3a** in only 8% yield, showing that most of the product was generated via the Cu/PCN-catalyzed coupling reaction. Notably, the catalyst prepared via the direct 50 times-scale up protocol of Ref. [16b] showed poor activity for the coupling of **1a** with **2a**, affording **3a** in only 44% yield (Table 1, Entry 13). This was probably due to the uneven heating caused by the elevated reaction scale and the improvement of the catalyst preparation protocol that extended the preheating temperature (from 60 ℃ to 80 ℃) and time (from 6 h to 24 h) was necessary (for details, please see experimental section of this work and the Ref. [16b]). Moreover, in comparison with literature,[16b] the reaction did not require excess **1a**, and this is much more economic and environment friendly from the practical viewpoint.

Under the optimized reaction conditions, a series of pyrimidin-2-amine derivatives **1** and aryl halides **2** were employed as substrates to prepare the related products **3** via the Cu/PCN-catalyzed Ullmann-type C—N coupling reactions (Table 2). For the iodoaryls bearing halide substituents, 1-chloro-4-iodobenzene was the most preferable one, affording the generation of **3c** in 90% yield (Table 2, Entry 3 vs. Entries 1, 2, 4), while the use of both 1-fluoro-4-iodobenzene and 1-bromo-4-iodobenzene resulted in decreased

Table 1 Condition optimizations[a]



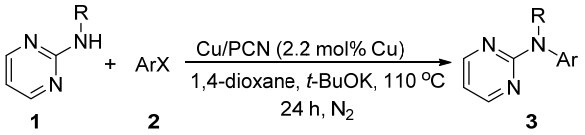
Entry	Solvent	Base	*T*/℃	Yield[b]/%
1	*t*-BuOH	*t*-BuOK	80	23
2	EtOH	*t*-BuOK	80[c]	20
3	THF	*t*-BuOK	80[c]	22
4	1,4-Dioxane	*t*-BuOK	80	28
5	Toluene	*t*-BuOK	80	16
6	1,4-Dioxane	KOH	80	20
7	1,4-Dioxane	NaOH	80	16
8	1,4-Dioxane	Pyridine	80	18
9	1,4-Dioxane	*t*-BuOK	90	45
10	1,4-Dioxane	*t*-BuOK	100	67
11	1,4-Dioxane	*t*-BuOK	110[c]	82
12	1,4-Dioxane	*t*-BuOK	120[c]	80
13[d]	1,4-Dioxane	*t*-BuOK	110[c]	44

[a] 1 mmol of **1a**, 1 mmol of **2a**, 2 mmol of base, 10 mg of Cu/PCN and 2 mL of solvent were employed. [b] Isolated yields based on **1a**. [c] Reaction performed in sealed pressure tube. [d] The catalyst was prepared by the direct 50 times-scale up protocol of Ref. [16b], *i.e.* using 250 mmol of melamine with 50 mmol of $Cu(NO_3)_2•3H_2O$.

product yield (Table 2, Entries 2, 4 vs. Entry 1). The fluoro-substituent could activate the related aryl halides and lead to the generation of a series of unknown by-products, which could be observed in the thin-layer chromatography plate. Introducing methyl as electron-donation substituent, the reaction of **1a** with 1-iodo-4-methylbenzene produced **3e** in 88% yield (Table 2, Entry 5), but for the reaction with 4-iodo-1,2- dimethylbenzene, the product yield decreased to 65% (Table 2, Entry 6). Iodoaryls bearing MeO as a strong electron-donation group produced the desired **3g**～**3i** in good yields (Table 2, Entries 7～9). For bulky substrate, the reaction of 4-iodo-1,1'-biphenyl with **1a** produced **3j** in moderate yield (Table 2, Entry 10), but for the reaction with 2-iodonaphthalene, the product **3k** could be obtained in an unexpectedly high yield (Table 2, Entry 11). Notably, although sulfur might cause catalyst poisoning, Cu/PCN was tolerant to sulfur-containing substrate, and the reaction of 3-iodothiophene with **1a** produced **3l** in excellent yield (Table 2, Entry 12). It was interesting that in the reaction of **1a** with 4,4'-diiodo-1,1'-biphenyl, the reaction occurred at one of the iodo-substituents, while another one was retained in product (Table 2, Entry 13). Replacing methyl with bulky benzyl, the substrate *N*-benzyl-*N*-(4-methoxyphenyl)-pyridin-2-amine was less reactive and afforded the coupling product in decreased yield (Table 2, Entry 14 vs. Entry 7). The C(sp^2)—Br was even more stable, and higher reaction temperature was required (Table 2, Entry 15). Introducing electron-withdrawing group into the substrate could activate the C(sp^2)—Br bond (Table 2, Entry 16), while the electron-donating group reduced the aryl bromide substrate activity on the contrary (Table 2, Entry 17). Aryl chloride was even more stable for the high C(sp^2)—Cl energy, leading to the

poor product yield in regardless of the elevated reaction temperature (Table 2, Entry 18). The reaction of diphenylamine with iodobenzene was tested but failed, probably due to the too large steric hindrance of the substrate unfavorable for the supported catalyst.

Table 2 Cu/PCN-catalyzed coupling reaction of pyrimidin-2-amine derivatives (**1**) with aryl halides (**2**)[a]



Entry	Ar	X	R	3	Yield[b]/%
1	Ph	I	Me	**3a**	82
2	4-FC_6H_4	I	Me	**3b**	60
3	4-ClC_6H_4	I	Me	**3c**	90
4	4-BrC_6H_4	I	Me	**3d**	72
5	4-MeC_6H_4	I	Me	**3e**	88
6	3,4-$(Me)_2C_6H_3$	I	Me	**3f**	65
7	4-MeOC_6H_4	I	Me	**3g**	80
8	3-MeOC_6H_4	I	Me	**3h**	80
9	2-MeOC_6H_4	I	Me	**3i**	75
10	4-PhC_6H_3	I	Me	**3j**	65
11	2-$C_{10}H_7$	I	Me	**3k**	98
12		I	Me	**3l**	92
13	4-(4-IC_6H_4)C_6H_4	I	Me	**3m**	60
14	4-MeOC_6H_4	I	$PhCH_2$[c]	**3n**	53
15	Ph	Br	Me	**3a**	56, 60[d]
16	4-ClC_6H_4	Br	Me	**3c**	68[d]
17	4-MeC_6H_4	Br	Me	**3e**	52[d]
18	Ph	Cl	Me	**3a**	26, 30[d]

[a] 1 mmol of **1**, 1 mmol of **2**, 2 mmol of *t*-BuOK, 10 mg of Cu/PCN and 2 mL of 1,4-dioxane were employed to react in a sealed reaction tube. [b] Isolated yields based on **1**. [c] *N*-Benzyl-*N*-(4-methoxyphenyl)pyridin-2-amine was employed. [d] Reaction performed at 120 ℃.

As a heterogeneous catalyst, Cu/PCN could be recovered by centrifugal separation or filtration after reaction and was reusable for the next run of reaction.[17] In the 10 mmol reactions of **1a** with **2a**, the catalyst could be reused for at least five times with the product yield over 60% (Table 3, Entry 1). In the further magnified reactions at 50 mmol scale, the product yield of the reactions using recovered catalyst was obviously retained, probably due to the reduced loss ratio of the catalyst during the separation process (Table 3, Entry 2). Inspired by the phenomena, we weighted the recovered catalysts and supplied their lost weight before reusing, and found that the product yield of the reaction did not obviously decrease even after five times of catalyst recycling (Table 3, Entry 3). Therefore, it might be deduced the catalytic activity of the material did not reduce if the lost weight of catalyst was supplied before the next turn of reaction. In addition, the scanning transmission electron microscopy (STEM) images of Cu/PCN before and after the reaction showed that the inner structure of the material was not changed.

Table 3 Catalyst recycle & reuse[a]

Entry	Yield[a]/% of **3a**				
	1st run	2nd run	3rd run	4th run	5th run
1[b]	83	80	78	74	69
2[c]	84	82	80	77	76
3[c,d]	83	85	84	82	83

[a] Isolated yields based on **1a**. [b] 10 mmol of **1**, 10 mmol of **2**, 20 mmol of *t*-BuOK, 0.1 g of Cu/PCN and 2 mL of 1,4-dioxane were employed. [c] 50 mmol of **1**, 50 mmol of **2**, 100 mmol of *t*-BuOK, 0.5 g of Cu/PCN and 40 mL of 1,4-dioxane were employed. [d] Lost catalyst was supplied before each turn of reaction.

Inductively coupled plasma-mass spectrometry (ICP-MS) analysis showed that the Cu/PCN material contained *ca.* 14.1% of Cu, and on the basis of this result, the TON of the reaction in Table 2, Entry 1 was calculated to be 37.1. It was also found that *ca.* 0.7% of the metal leached into the reaction liquid, while the product contained *ca.* 0.09×10^{-6} of Cu, showing that the strong coordination of nitrogen in the material could well restrain the metal leaching and reduce the metal residue in product.[16a] X-ray photoelectron spectroscopy (XPS) analysis demonstrated that copper in Cu/PCN existed as Cu^{+}, and partial of them might be oxidized into Cu^{2+} after reaction (Figure 2). In comparison with Cu_2O, the related peaks of Cu/PCN in XPS spectrum shifted *ca.* 0.42～0.64 eV, attesting the coordination of the nitrogen in PCN with the metal.[18]

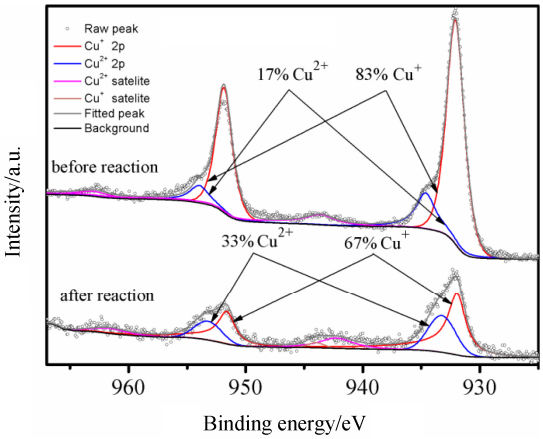


Figure 2 XPS spectra of Cu/PCN before and after the reaction

A series of Cu(I) or Cu(II) catalysts, such as Cu_2O, CuCl, CuBr, CuI and $Cu(OAc)_2$, were used in 10 mg amount in the 1 mmol-scale reaction of **1a** with **2a** to compare with Cu/PCN and all of them resulted in very poor TONs (Figure 3). The Cu/PCN catalyst was even more active than the expensive $PdCl_2$ and $Pd(OAc)_2$ catalysts. For the reactions with same molar amount of catalytic metals, Cu/PCN also afforded the highest product yield. Moreover, a control reaction was designed and performed to examine the catalytic activity of dissolved Cu from Cu/PCN. In the process, Cu/PCN catalyst was initially heated at 110 ℃ in 1,4-dioxane for 24 h. After removing Cu/PCN by centrifugal

separation, the reactants **1a** and **2a** and *t*-BuOK were added into the supernatant and heated at 110 ℃ for another 24 h and it only afforded traces of **3a**, showing that the dissolved Cu from Cu/PCN could no catalyze the reaction.

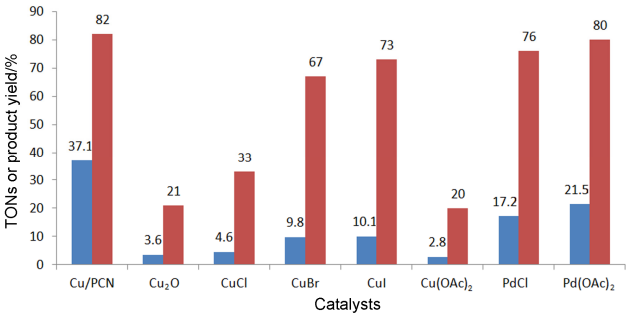


Figure 3 Comparison of Cu/PCN with other catalysts
Left bar: TONs of the catalysts of the parallel experiments using same weight catalysts; right bar: product yields/% of the parallel experiments using catalysts with same molar amount of Cu or Pd)

3 Conclusion

In conclusion, Cu/PCN can be prepared in 10 g scale by calcining $Cu(NO_3)_2$ with the melamine precursor at 550 ℃. It was found to be an efficient catalyst for the Ullmann-type C—N couplings of pyrimidin-2-amine derivatives with aryl halides. The reactions occurs without additional ligand and the catalyst TON was higher than the traditional Cu(I) catalysts. The relatively green features of the reaction are in line with the developing trend of sustainable chemistry.[19] The elevated preheating temperature and extended preheating time are the key factors to ensure the catalyst activity in large scale production. Further investigations on the applications of the novel materials as well as the mechanism insights are ongoing in our laboratory.

4 Experimental

4.1 General methods

Melting points were measured by a WRS-2A digital melting pointing instrument. NMR spectra were recorded on a Bruker Avance 400 instrument (400 MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR spectroscopy) by using $CDCl_3$ as the solvent and Me_4Si as the internal standard. Chemical shifts for ^{1}H and ^{13}C NMR were referred to internal Me_4Si. XPS were measured on a ESCALAB 250Xi X photoelectron spectrometer. SEM were measured on a Zeiss_Supra55 Field Emission Scanning Electron Microscope. ICP were measured on a Optima 7300 DV Inductively Coupled Plasma Spectrometer.

4.2 Preparation of Cu/PCN

Melamine (250 mmol) and $Cu(NO_3)_2$•$3H_2O$ (40 mmol) were mixed with 1 L of water and were stirred for 4 h at 800 r/min. The mixture was then dried in oven at 80 ℃ for 24 h. The solid was grinded into powders and calcined in pipe furnace at 550 ℃ under N_2 for 4 h (the temperature rose at the rate of 5 ℃/min). After cooling to room temperature, the obtained mass (10.52 g) was grinded into powders again, and washed with deionized water and EtOH and dried before use.

4.3 General procedure for the coupling of **1** with **2**

1 (1 mmol), **2** (1 mmol), *t*-BuOK (2 mmol), Cu/PCN (10 mg) and a piece of magnetic bar were added into a glass pressure reaction tube. 1,4-Dioxane (2 mL) was then injected by a syringe. The tube was charged with N_2 and sealed. The mixture was stirred at 110 ℃ for 24 h. After cooling to room temperature, the solvent was removed by distillation under reduced pressure with a rotary evaporator and the residue was isolated by preparative thin layer chromatography [eluent: *V*(petroleum ether)∶*V*(EtOAc)=10∶1]. As a heterogeneous catalyst, Cu/PCN could be recycled by centrifugal separation after reaction in the 50 mmol of **1a** scale reaction. It was washed by deionized water and then dried at 100 ℃ in oven. The recycled catalyst was weighted and less than 10% of the catalyst lost during the separation. After making up the lost weight of the catalyst, the recycled catalyst was reused for the next run of reaction.

N-Methyl-*N*-phenylpyrimidin-2-amine (**3a**): 151.9 mg, yield 82%. White solid, m.p. 51.4～52.8 ℃ (lit.[20a] 49～51 ℃); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.33 (d, J=4.7 Hz, 2H), 7.41 (t, J=7.1 Hz, 2H), 7.33 (d, J=7.8 Hz, 2H), 7.23 (t, J=7.3 Hz, 1H), 6.55 (t, J=4.3 Hz, 1H), 3.54 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 161.91, 157.65, 145.50, 129.18, 126.57, 125.86, 110.76, 38.70; IR (KBr) ν: 3153, 3031, 2934, 1957, 1577, 1483, 1386, 1165, 1060, 973, 780, 692, 570, 475 cm^{-1}.

N-(4-Fluorophenyl)-*N*-methylpyrimidin-2-amine (**3b**): 121.93 mg, yield 60%. White solid, m.p. 69.5～70.6 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.32 (d, J=4.1 Hz, 2H), 7.29～7.22 (m, 2H), 7.08 (t, J=8.0 Hz, 2H), 6.57 (t, J=4.3 Hz, 1H), 3.48 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 161.80 (d, $J_{C\text{-}F}$=11 Hz), 159.30, 157.67, 141.38 (d, $J_{C\text{-}F}$=3 Hz), 128.36 (d, $J_{C\text{-}F}$=8 Hz), 116.08 (d, $J_{C\text{-}F}$=23 Hz), 110.80, 38.83; ^{19}F NMR (242 MHz, $CDCl_3$) δ: −116.48; IR (KBr) ν: 3021, 2928, 1600, 1583, 1551, 1508, 1439, 1396, 1318, 1276, 1215, 1153, 1090, 1068, 982, 897, 840, 815, 723, 637, 585, 556 cm^{-1}; MS (EI, 70 eV) *m*/*z* (%): 203 (18, [M$^+$]), 108 (100). Anal. calcd for $C_{11}H_{10}FN_3$: C 65.01, H 4.96; found C 65.00, H 4.98.

N-(4-Chlorophenyl)-*N*-methylpyrimidin-2-amine (**3c**): 197.7 mg, yield 90%. White solid, m.p. 78.3～79.8 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.32 (d, J=4.7 Hz, 2H), 7.34 (d, J=7.3 Hz, 2H), 7.25 (d, J=7.3 Hz, 2H), 6.57 (t, J=4.7 Hz, 1H), 3.49 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 161.64, 157.66, 143.92, 131.03, 129.24, 127.80, 111.13, 38.54; IR (KBr) ν: 3028, 2928, 2856, 1903, 1583, 1549, 1491, 1394, 1311, 1093, 976, 832, 790, 717, 575, 479 cm^{-1}; MS (EI, 70 eV) *m*/*z* (%): 219 (12, [M$^+$]), 108 (100). Anal. calcd for $C_{11}H_{10}ClN_3$: C 60.14, H 4.59; found C 60.17, H 4.56.

N-(4-Bromophenyl)-*N*-methylpyrimidin-2-amine (**3d**): 190.2 mg, yield 72%. White solid, m.p. 93.2～94.1 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.32 (d, J=4.7 Hz, 2H), 7.48

(d, J=7.5 Hz, 2H), 7.19 (d, J=7.5 Hz, 2H), 6.58 (t, J=4.7 Hz, 1H), 3.49 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 161.59, 157.67, 144.43, 132.18, 128.13, 118.92, 111.18, 38.48; IR (KBr) ν: 3445, 3060, 3027, 2925, 2854, 1903, 1581, 1489, 1394, 1309, 1101, 1065, 1006, 976, 828, 790, 713, 632, 572, 480 cm^{-1}; MS (EI, 70 eV) m/z (%): 263 (18, [M$^+$]), 108 (100). Anal. calcd for $C_{11}H_{10}BrN_3$: C 50.02, H 3.82; found C 50.05, H 3.78.

N-Methyl-*N*-(*p*-tolyl)pyrimidin-2-amine (**3e**): 175.3 mg, yield 88%. White solid, m.p. 81.5～82.6 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.33 (d, J=4.7 Hz, 2H), 7.25～7.17 (m, 4H), 6.54 (t, J=4.7 Hz, 1H), 3.51 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 162.03, 157.66, 142.91, 135.66, 129.93, 126.49, 110.48, 38.77, 21.12; IR (KBr) ν: 3395, 3070, 2924, 2852, 1585, 1550, 1459, 1394, 1292, 1252, 1180, 1153, 1094, 1022, 974, 791, 754, 632, 591, 524 cm^{-1}; MS (EI, 70 eV) m/z (%): 199 (26, [M$^+$]), 108 (100). Anal. calcd for $C_{12}H_{13}N_3$: C 72.33, H 6.58; found C 72.35, H 6.61.

N-(3,4-Dimethylphenyl)-*N*-methylpyrimidin-2-amine (**3f**): 138.6 mg, yield 65%, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.33 (d, J=4.3 Hz, 2H), 7.18 (d, J=7.8 Hz, 1H), 7.12～7.02 (m, 2H), 6.53 (t, J=4.2 Hz, 1H), 3.50 (s, 3H), 2.27 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 162.10, 157.69, 143.22, 137.60, 134.55, 130.48, 127.82, 124.07, 110.34, 38.88, 20.01, 19.46; IR (film) ν: 3023, 2925, 2860, 1584, 1549, 1490, 1395, 1219, 1181, 1137, 983, 944, 621, 592 cm^{-1}; MS (EI, 70 eV) m/z (%): 213 (23) [M$^+$], 106 (100). Anal. calcd for $C_{13}H_{15}N_3$: C 73.21, H 7.09; found C 73.20, H 7.12.

N-(4-Methoxyphenyl)-*N*-methylpyrimidin-2-amine (**3g**): 172.2 mg, yield 80%. White solid, m.p. 133.1～134.2 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.31 (d, J=4.1 Hz, 2H), 7.26～7.18 (m, 2H), 6.93 (d, J=8.2 Hz, 2H), 6.55～6.48 (m, 1H), 3.81 (s, 3H), 3.48 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 162.20, 157.62, 157.52, 138.47, 127.84, 114.56, 110.29, 55.37, 38.89; IR (KBr) ν: 3026, 2930, 2840, 1580, 1485, 1381, 1302, 1228, 1169, 1011, 804, 723, 563 cm^{-1}; MS (EI, 70 eV) m/z (%): 215 (28, [M$^+$]), 106 (100). Anal. calcd for $C_{12}H_{13}N_3O$: C 66.96, H 6.09; found C 66.99, H 6.12.

N-(3-Methoxyphenyl)-*N*-methylpyrimidin-2-amine (**3h**): 171.8 mg, yield 80%, white oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.33 (d, J=4.4 Hz, 2H), 7.31 (t, J=8.0 Hz, 1H), 6.93～6.84 (m, 2H), 6.78 (d, J=8.2 Hz, 1H), 6.56 (t, J=4.4 Hz, 1H), 3.79 (s, 3H), 3.51 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 161.78, 160.20, 157.66, 146.60, 129.82, 118.86, 112.55, 111.44, 110.75, 55.27, 38.74; IR (film) ν: 3447, 2996, 2934, 2837, 1583, 1490, 1396, 1318, 1266, 1214, 1176, 1042, 981, 941, 779, 697, 639, 518 cm^{-1}; MS (EI, 70 eV) m/z (%): 215 (22, [M$^+$]), 106 (100). Anal. calcd for $C_{12}H_{13}N_3O$: C 66.96, H 6.09; found C 66.92, H 6.12.

N-(2-Methoxyphenyl)-*N*-methylpyrimidin-2-amine (**3i**):[20b] Colorless oil, 161.4 mg, yield 75%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.33 (d, J=3.7 Hz, 2H), 7.25～7.17 (m, 4H), 6.54 (t, J=3.6 Hz, 1H), 3.51 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.02, 157.65, 142.89, 135.67, 129.93, 129.82, 126.47, 115.19, 110.47, 38.77, 21.12; IR (film) ν: 3453, 3028, 2927, 2858, 2371, 2288, 1890, 1584, 1486, 1393, 1313, 1108, 979, 797, 636, 588, 553 cm^{-1}.

N-([1,1'-Biphenyl]-4-yl)-*N*-methylpyrimidin-2-amine (**3j**): 169.9 mg, yield 65%. White solid, m.p. 116.5～117.6 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.39 (d, J=3.8 Hz, 2H), 7.70～7.57 (m, 4H), 7.45 (q, J=7.1, 6.7 Hz, 4H), 7.36 (t, J=7.3 Hz, 1H), 6.61 (d, J=4.8 Hz, 1H), 3.60 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 161.84, 157.75, 144.65, 140.70, 138.60, 128.79, 127.92, 127.10, 126.68, 115.78, 110.95, 38.75; IR (KBr) ν: 3023, 2927, 2854, 1578, 1485, 1394, 1314, 1183, 1109, 978, 840, 796, 761, 725, 691, 636, 586, 526, 481, 419 cm^{-1}; MS (EI, 70 eV) m/z (%): 261 (18, [M$^+$]), 106 (100). Anal. calcd for $C_{17}H_{15}N_3$: C 78.10, H 5.79; found C 78.06, H 5.75.

N-Methyl-*N*-(naphthalen-2-yl)pyrimidin-2-amine (**3k**): 230.6 mg, yield 98%. White solid, m.p. 81.2～82.1 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.41～8.35 (m, 2H), 7.90～7.78 (m, 3H), 7.75 (s, 1H), 7.53～7.42 (m, 3H), 6.62～6.57 (m, 1H), 3.66 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 161.94, 157.72, 143.12, 134.05, 131.65, 128.70, 127.69, 127.66, 126.19, 125.97, 125.65, 123.59, 111.00, 38.92; IR (KBr) ν: 3043, 2938, 1579, 1482, 1395, 1140, 1065, 971, 804, 748, 559, 482 cm^{-1}; MS (EI, 70 eV) m/z (%): 235 (20, [M$^+$]), 106 (100). Anal. calcd for $C_{15}H_{13}N_3$: C 76.57, H 5.57; found C 76.61, H 5.61.

N-Methyl-*N*-(thiophen-3-yl)pyrimidin-2-amine (**3l**): 176.0 mg, yield 92%. White solid, m.p. 73.5～74.4 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.37 (d, J=4.6 Hz, 2H), 7.26 (s, 2H), 7.12 (s, 1H), 6.59 (t, J=4.5 Hz, 1H), 3.55 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 161.24, 157.64, 143.55, 125.37, 123.99, 114.53, 111.14, 38.35; IR (KBr) ν: 3079, 2940, 1546, 1470, 1382, 1209, 1065, 954, 854, 786, 640, 539 cm^{-1}; MS (EI, 70 eV) m/z (%): 191 (11, [M$^+$]), 106 (100). Anal. calcd for $C_9H_9N_3S$: C 56.52, H 4.74; found C 56.53, H 4.69.

N-(4'-Iodo-[1,1'-biphenyl]-4-yl)-*N*-methylpyrimidin-2-amine (**3m**): 232.3 mg, yield 60%. White solid, m.p. 146.9～147.4 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.36 (d, J=4.5 Hz, 2H), 7.75 (d, J=7.8 Hz, 2H), 7.57 (d, J=8.0 Hz, 2H), 7.40 (d, J=7.6 Hz, 2H), 7.32 (d, J=7.6 Hz, 2H), 6.60 (t, J=4.1 Hz, 1H), 3.56 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 161.75, 157.73, 145.02, 140.14, 137.82, 137.24, 128.88, 127.60, 126.73, 111.05, 92.96, 38.65; IR (KBr) ν: 3400, 3029, 2923, 1901, 1729, 1579, 1517, 1476, 1110, 1063, 980, 808, 733, 582, 524, 483 cm^{-1}; MS (EI, 70 eV) m/z (%): 387 (14, [M$^+$]), 106 (100). Anal. calcd for $C_{17}H_{14}IN_3$: C 52.73, H 3.64; found C 52.67, H 3.66.

N-Benzyl-*N*-(4-methoxyphenyl)pyridin-2-amine (**3n**): 153.9 mg, yield 53%. White solid, m.p. 78.5～82.2 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.22 (d, J=4.8 Hz, 1H), 7.32～7.19 (m, 6H), 7.11 (d, J=7.6 Hz, 2H), 6.89 (d, J=7.7 Hz, 2H), 6.59 (t, J=5.6 Hz, 1H), 6.37 (d, J=8.6 Hz, 1H), 5.22 (s, 2H), 3.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.91, 157.73, 147.77, 139.47, 137.95, 136.78, 129.15, 128.23, 127.81, 126.69, 114.97, 112.82, 108.24, 55.40, 53.59; IR (KBr) ν: 3026, 2930, 2840, 1889, 1580, 1485, 1381, 1302, 1228, 1169, 1011, 804, 723, 563 cm^{-1}; MS (EI,

70 eV) *m*/*z* (%): 290 (10, [M^+]), 183 (100). Anal. calcd for $C_{19}H_{18}N_2O$: C 78.59, H 6.25; found C 78.64, H 6.28.

Supporting Information The EDS, STEM, XPS spectra of Cu/PCN and NMR spectra of compounds **3a**～**3n**. The Supporting Information is available free of charge via the Internet at http://sioc-journal.cn.

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