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Highly efficient and practical phosphoramidite–copper catalysts for amination of aryl iodides and heteroaryl bromides with alkylamines and N(H)-heterocycles

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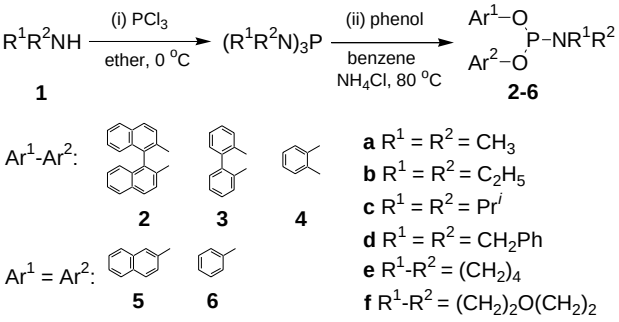
Abstract—A highly efficient copper-catalyzed system using phosphoramidite as ligands was applied to N-arylation of alkylamines and N(H)-heterocycles with aryl iodides and heteroaryl bromides. The reactions were carried out in relative mild conditions and good to excellent yields were obtained.

1. Introduction

N-Arylamines, *N*-arylpyrazoles, *N*-arylimidazoles, *N*-arylpyridine and *N*-arylpyrimidine have attracted a great deal of interest recently due to their importance in fields such as natural products, photograph and materials.[1–3] Palladium-catalyzed C–N bond formation reactions have been extensively explored in the past several years.[4–7] However, the copper-promoted *N*-arylation in mild conditions has become a focus of research for large and industrial-scale production from the practical point of view.[8–11] Recently, many ligands, such as 1,10-phenanthroline,[12–16] *trans*-1,2-cyclohexanediamine,[17–21] ethylene glycol,[22,23] amino acid,[1b,24,25] and other nitrogen, oxygen-containing ligands[26–29] have been developed and applied in copper-catalyzed aminations under mild conditions. However, only several papers have been contributed to *N*-arylation of alkylamines and just a few ligands were found to be effective in this transformation.[30–32] Furthermore, two major factors that hamper the application are the cost and the availability of the catalysts, in particular of the ligands that are often prepared in a tedious multi-step synthesis. Therefore, to find more cost-effective and highly efficient ligands is still desirable. Our group has embarked on a program aimed at the ligands that are low-cost and easily prepared in short pathway from readily available starting materials.[33,34] Very recently, the application of phosphoramidite to amination of aryl iodide has been reported in our communication (Scheme 1).[35] In this paper, we further explored the scope of substrates and applied this catalytic system to copper-catalyzed *N*-arylation of alkylamines and N(H)-heterocycles with aryl iodides and heteroaryl bromides and found the ligand was highly effective for the coupling reactions for a broader range of substrates.



Scheme 1. Phosphoramidite ligands.

2. Results and discussion

Initially, the CuBr/**2d**/DMF/Cs_2CO_3 was screened as the best catalytic system for the coupling of aliphatic primary and secondary amines with aryl iodides. The results were summarized in Table 1. It was found that phosphramidite **2d** was a powerful promoter for coupling reaction in DMF at 90 °C. When primary alkylamines were employed as substrates, excellent yields were obtained (Table 1, entries

Keywords: Amination; Phosphoramidite; Heteroaryl bromide; Copper; Catalysis.
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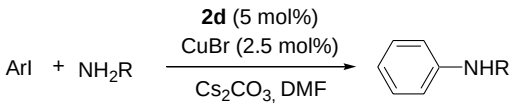
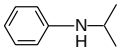
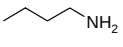
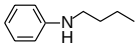
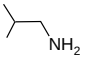
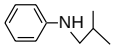
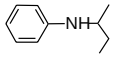
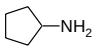
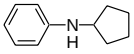
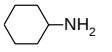
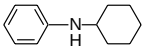
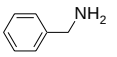
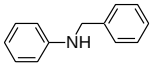
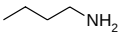
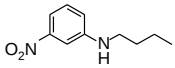
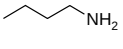
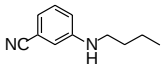
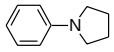
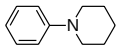
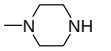
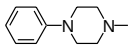
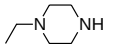
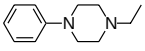
Table 1. Coupling of aryl iodides with primary and secondary amines[a]



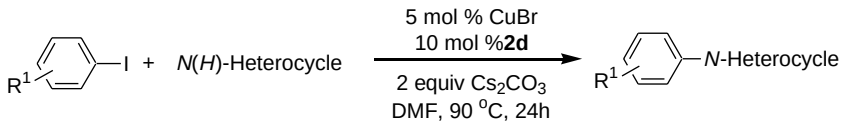
Entry	ArI	NH_2R	Product	Yield (%)[b]
1				96
2				96
3				96
4				98
5				97
6				98
7				98
8				99
9				98
10				90
11				87
12				86
13				92
14				83
15				90
16				87
17				99
18				78
19				80

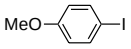
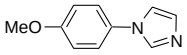
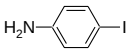
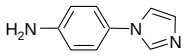
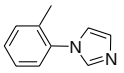
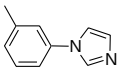
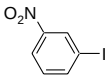
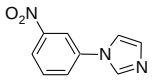
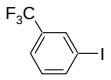
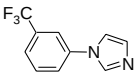
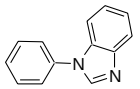
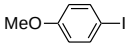
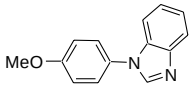
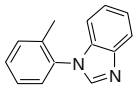
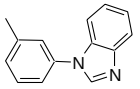
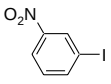
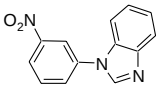
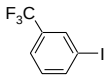
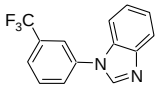
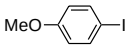
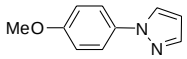
[a] Reaction conditions: CuBr (0.025 mmol), **2d** (0.5 mmol), ArI (1.0 mmol), amine (1.5 mmol), and Cs_2CO_3 (3 mmol) in DMF (1 mL), 90 °C, 24 h.
[b] Isolated yields (average of two runs).

1–9). We then extended the scope of the substrates to secondary amines. Good yields were observed in coupling reaction (entries 10–19), but they were lower than that of primary alkylamines. A wide variety of functional groups such as cyano, nitro, methoxy could be tolerated on the aryl iodide component under the reaction conditions. Significant electronic effects were observed for substituted aryl iodides. Excellent yields for the aryl iodides containing electron-withdrawing groups were achieved (entries 14–18).

As can be seen from Table 2, several *N*-heterocycles could be converted to the desired products effectively when the amounts of CuBr and the ligand were doubled. The *N*-arylation of imidazole could be smoothly carried out using various aryl iodides (Table 2, entries 1–6). Benzimidazole could be successfully coupled with good yields (entries 7–12). The arylation of pyrazole could also be carried out smoothly under mild reaction conditions (entry 13). Noticeably, electronic and steric factors played important roles in the coupling reactions, high yields were obtained for substrates possessing electron-withdrawing groups (entries 5, 6, 11 and 12). A sterically hindered aryl iodide gave lower yields (entries 3 and 9). Aryl iodides containing a nitro, methoxy group, free NH_2 were efficiently transformed to products.

Table 2. Coupling of aryl iodides with various *N*-heterocycles[a]



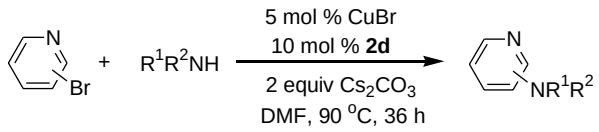
Entry	ArI	N(H)-heterocycle	Product	Yield (%)[b]
1				78
2				69
3				65
4				75
5				87
6				85
7				82
8				80
9				67
10				76
11				90
12				86
13				76

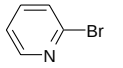
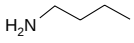
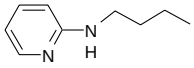
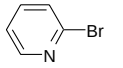
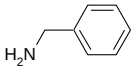
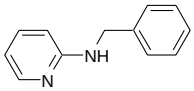
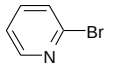
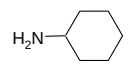
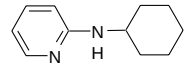
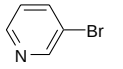
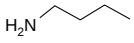
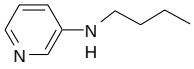
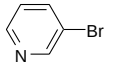
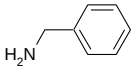
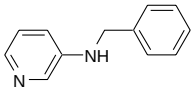
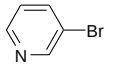
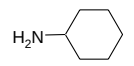
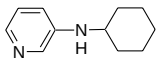
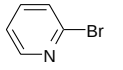
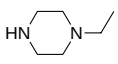
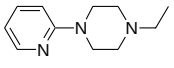
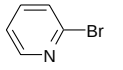
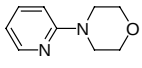
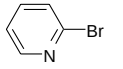
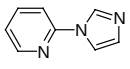
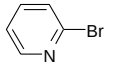
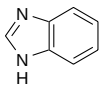
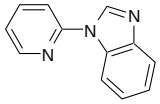
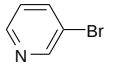
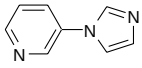
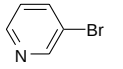
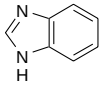
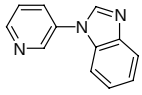
[a] Reaction conditions: 1.0 mmol ArI, 1.5 mmol amine, 0.05 mmol CuBr, 0.1 mmol **2d**, 2 mmol Cs_2CO_3, in DMF (1 mL), at 90 °C for 24 h.
[b] Isolated yields (average of two runs).

Although chloro- and bromopyridine have been used as effective coupling partners in Pd-catalyzed amination reaction,[7f,36] to the best of our knowledge, except one paper,[1b] it was rarely reported that bromopyridines were employed as coupling substrates in Cu-catalyzed amination. When reaction time was prolonged to 36 h under above reaction conditions, 2-bromopyridine and 3-bromopyridine could be efficiently coupled with aliphatic primary, secondary cyclic amines and N(H)-heterocycles (Table 3). As seen in Table 3, in general, aliphatic primary amines were excellent substrates for the coupling with bromopyridine (Table 3, entries 1–6). Good results were observed for coupling of aliphatic secondary cyclic amines and N(H)-heterocycles (entries 7–12).

Although 5-bromopyrimidine has been utilized as effective coupling substrates in Pd-catalyzed amination reactions, it was less used in Cu-catalyzed amination.[7d,28] Fortunately, when phosphoramidite was used as the ligand in Cu-catalyzed *N*-arylpyrimidine, a number of amines could be coupled with 5-bromopyrimidine in good to excellent yields in 36 h at 90 °C (Table 4). 5-bromopyrimidine could be successfully reacted with aliphatic primary, secondary cyclic amines and N(H)-heterocycles. Aliphatic primary amines were excellent substrates for the coupling with 5-bromopyrimidine (Table 4, entries 1–8). Furthermore, good results were also obtained for coupling of aliphatic secondary cyclic amines and N(H)-heterocycles (entries 9–14).

Table 3. Coupling of bromopyridines with various amines[a]



Entry	Bromopyridine	R^1R^2NH	Product	Yield (%)[b]
1				95
2				97
3				92
4				94
5				96
6				90
7				85
8				82
9				76
10				78
11				74
12				77

[a] Reaction conditions: 1.0 mmol bromopyridine, 1.5 mmol amine, 0.05 mmol CuBr, 0.1 mmol **2d**, 2 mmol Cs_2CO_3, in DMF (1 mL) at 90 °C for 36 h.
[b] Isolated yield.

3. Conclusion

In conclusion, we developed a mild and practical copper-catalyzed *N*-arylation of alkylamines and N(H)-heterocycles with aryl iodides and heteroaryl bromides using phosphoramidite ligand. It demonstrated that all reactions could be smoothly carried out at relatively low temperature in good to excellent yields. The ligands were stable, cost-effective, and easily synthesized from inexpensive, commercially available starting materials using a simple, efficient method.

4. Experimental

4.1. Materials and methods

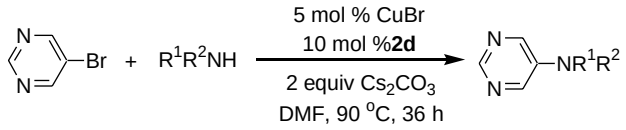
Melting points were measured on a YAZAWA micro melting point apparatus (uncorrected). ^1H, ^{31}P and ^{13}C NMR spectra were measured on a Bruker DRX-400 NMR spectrometer (400 MHz) with TMS as an internal reference. $CDCl_3$ was used as the solvent for all NMR spectra. High resolution mass spectra (HRMS) were recorded on a Mariner 5303 (Applied Biosystems, USA). All products were characterized by ^1H NMR and HRMS and compared with the previously reported data.[19,20,24,28,30,37,38]

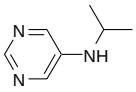
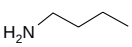
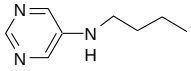
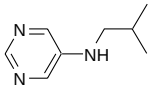
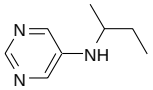
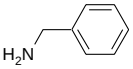
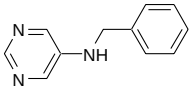
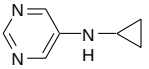
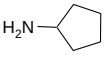
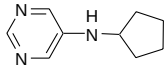
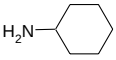
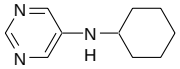
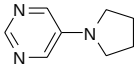
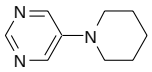
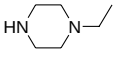
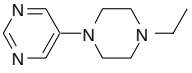
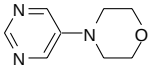
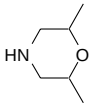
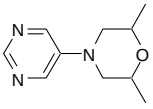
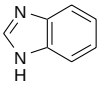
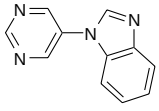
All reactions were carried out under an argon atmosphere. Column chromatography purifications were performed using silica gel. All solvents were dried and degassed by standard methods and all starting materials were commercially available. Petroleum ether refers to the boiling range of 60–90 °C. When solvent gradient was used, the increase of polarity was made gradually from petroleum ether to mixtures of petroleum ether/ethyl acetate until the isolation of the products.

4.2. Typical experimental procedure of *N*-arylation

CuBr (3.6 mg, 0.025 mmol), Cs_2CO_3 (977.5 mg, 3 mmol) and ligand **2d** (25.6 mg, 0.05 mmol) were added to

Table 4. Coupling of 5-bromopyrimidine with various amines[a]



Entry	R^1R^2NH	Product	Yield (%)[b]
1			90
2			97
3			94
4			89
5			96
6			92
7			94
8			95
9			83
10			85
11			80
12			86
13			78
14			73

[a] Reaction conditions: 1.0 mmol bromopyrimidine, 1.5 mmol amine, 0.05 mmol CuBr, 0.1 mmol **2d**, 2 mmol Cs_2CO_3, in DMF (1 mL) at 90 °C for 36 h.
[b] Isolated yield.

a Schlenk tube. The Schlenk tube was then evacuated and backfilled with argon (5 cycles). DMF (1 mL), amine (1.5 mmol) (if liquid), and aryl iodide (1 mmol) were added by syringe at room temperature. The Schlenk tube was then charged with argon and sealed. The reaction mixture was heated at 90 °C under stirring for 24 h. After cooling to ambient temperature, the resulting mixture was added with 4 mL of ethyl acetate and 10 mL of water. The organic layer was separated and the aqueous layer was further extracted with ethyl acetate (4×10 mL). The combined organic phase was washed with brine and dried over Na_2SO_4. Solvent was removed in vacuo and the residue was further purified by flash column chromatography on silica gel to afford the desired product.

4.3. Cross-coupling data of aryl iodides with primary and secondary amines

4.3.1. *N*-(*iso*-Propyl)aniline (Table 1, entry 1). Colorless liquid (0.1298 g, 96%). ^{1}H NMR: δ 1.17 (d, J=8.0 Hz, 6H), 3.35 (br, 1H), 3.56–3.62 (m, 1H), 6.54–6.56 (m, 2H),

6.63–6.67 (m, 1H), 7.12–7.16 (m, 2H). HRMS (APCI) calcd for $C_9H_{14}N$ ($M+H^+$): 136.1121, found: 136.1120.

4.3.2. *N*-(Butyl)aniline (Table 1, entry 2). Colorless liquid (0.1433 g, 96%). ^1H NMR: δ 0.94 (t, $J=8.0$ Hz, 3H), 1.36–1.45 (m, 2H), 1.53–1.61 (m, 2H), 3.07 (t, $J=8.0$ Hz, 2H), 3.54 (br, 1H), 6.56–6.58 (m, 1H), 6.65–6.69 (m, 2H), 7.13–7.33 (m, 2H). HRMS (APCI) calcd for $C_{10}H_{16}N$ ($M+H^+$): 150.1277, found: 150.1268.

4.3.3. *N*-(*iso*-Butyl)aniline (Table 1, entry 3). Colorless liquid (0.1433 g, 96%). ^1H NMR: δ 0.95 (d, $J=4.0$ Hz, 6H), 1.82–1.88 (m, 1H), 2.89 (d, $J=8.0$ Hz, 2H), 3.61 (br, 1H), 6.56 (d, $J=8.0$ Hz, 2H), 6.64–6.68 (m, 1H), 7.13–7.16 (m, 2H). HRMS (APCI) calcd for $C_{10}H_{16}N$ ($M+H^+$): 150.1277, found: 150.1288.

4.3.4. *N*-(*sec*-Butyl)aniline (Table 1, entry 4). Colorless liquid (0.1462 g, 98%). ^1H NMR: δ 0.91–0.97 (m, 3H), 1.14 (d, $J=4.0$ Hz, 3H), 1.41–1.48 (m, 1H), 1.54–1.61 (m, 1H), 3.35–3.40 (m, 2H), 6.56 (d, $J=8.0$ Hz, 2H), 6.63–6.66 (m, 1H), 7.12–7.16 (m, 2H). HRMS (APCI) calcd for $C_{10}H_{16}N$ ($M+H^+$): 150.1277, found: 150.1265.

4.3.5. *N*-Cyclopentylaniline (Table 1, entry 5). Colorless liquid (0.1564 g, 97%). ^1H NMR: δ 1.18–1.26 (m, 8H), 3.41 (br, 1H), 3.58–3.62 (m, 1H), 6.57 (d, $J=8.0$ Hz, 2H), 6.64–6.68 (m, 1H), 7.13–7.17 (m, 2H). HRMS (APCI) calcd for $C_{11}H_{16}N$ ($M+H^+$): 162.1277, found: 162.1265.

4.3.6. *N*-Cyclohexylaniline (Table 1, entry 6). Colorless liquid (0.1717 g, 98%). ^1H NMR: δ 1.09–1.21 (m, 3H), 1.32 (t, $J=16.0$ Hz, 2H), 1.62 (t, $J=8.0$ Hz, 1H), 1.71–1.76 (m, 2H), 2.02 (d, $J=12.0$ Hz, 2H), 3.18–3.24 (m, 1H), 3.44 (br, 1H), 6.55 (d, $J=8.0$ Hz, 2H), 6.63 (t, $J=4.0$ Hz, 1H), 7.13 (t, $J=8.0$ Hz, 2H). HRMS (APCI) calcd for $C_{12}H_{18}N$ ($M+H^+$): 176.1434, found: 176.1430.

4.3.7. *N*-(Phenyl)benzylamine (Table 1, entry 7). White solid (0.1796 g, 98%); mp 33–34 °C. ^1H NMR: δ 3.99 (br, 1H), 4.29 (s, 2H), 6.61 (d, $J=8.0$ Hz, 2H), 6.68–6.72 (m, 1H), 7.14–7.18 (m, 2H), 7.24–7.27 (m, 1H), 7.30–7.36 (m, 4H). HRMS (APCI) calcd for $C_{13}H_{14}N$ ($M+H^+$): 184.1121, found: 184.1129.

4.3.8. *N*-(Butyl)-3-nitroaniline (Table 1, entry 8). Yellow liquid (0.1923 g, 99%). ^1H NMR: δ 0.96 (t, $J=8.0$ Hz, 3H), 1.39–1.48 (m, 2H), 1.58–1.66 (m, 2H), 3.14 (t, $J=8.0$ Hz, 2H), 4.05 (br, 1H), 6.84–6.86 (m, 1H), 7.24 (t, $J=8.0$ Hz, 1H), 7.36 (s, 1H), 7.47 (d, $J=8.0$ Hz, 1H). HRMS (APCI) calcd for $C_{10}H_{15}N_2O_2$ ($M+H^+$): 195.1128, found: 195.1113.

4.3.9. *N*-(Butyl)-3-nitrylaniline (Table 1, entry 9). Greenish liquid (0.1708 g, 98%). ^1H NMR: δ 0.96 (t, $J=8.0$ Hz, 3H), 1.38–1.48 (m, 2H), 1.57–1.64 (m, 2H), 3.09 (t, $J=8.0$ Hz, 2H), 3.93 (br, 1H), 6.76 (t, $J=8.0$ Hz, 2H), 6.92 (d, $J=8.0$ Hz, 1H), 7.18–7.27 (m, 1H), 7.47 (d, $J=8.0$ Hz, 1H). HRMS (APCI) calcd for $C_{11}H_{15}N_2$ ($M+H^+$): 175.1230, found: 175.1218.

4.3.10. *N*-(Phenyl)pyrrolidine (Table 1, entry 10). Colorless liquid (0.1325 g, 90%). ^1H NMR: δ 1.93–1.97 (m, 4H), 3.23 (t, $J=8.0$ Hz, 4H), 6.53 (d, $J=8.0$ Hz, 2H), 6.62–6.65 (m, 1H), 7.18–7.22 (m, 2H). HRMS (APCI) calcd for $C_{10}H_{14}N$ ($M+H^+$): 148.1121, found: 148.1131.

4.3.11. *N*-(Phenyl)piperidine (Table 1, entry 11). Colorless liquid (0.1403 g, 87%). ^1H NMR: δ 1.52–1.58 (m, 2H), 1.66–1.72 (m, 4H), 3.13 (t, $J=8.0$ Hz, 4H), 6.79–6.82 (m, 1H), 6.93 (d, $J=8.0$ Hz, 2H), 7.18–7.25 (m, 2H). HRMS (APCI) calcd for $C_{11}H_{16}N$ ($M+H^+$): 162.1277, found: 162.1271.

4.3.12. *N*-Phenyl-*N*-(methyl)piperazine (Table 1, entry 12). Colorless liquid (0.1516 g, 86%). ^1H NMR: δ 2.33 (s, 3H), 2.55 (t, $J=4.0$ Hz, 4H), 3.19 (t, $J=4.0$ Hz, 4H), 6.83–6.91 (m, 3H), 7.24–7.27 (m, 2H). HRMS (APCI) calcd for $C_{11}H_{17}N_2$ ($M+H^+$): 177.1386, found: 177.1376.

4.3.13. *N*-Phenyl-*N*-(ethyl)piperazine (Table 1, entry 13). White solid (0.1750 g, 92%); mp 38–39 °C. ^1H NMR: δ 1.11–1.15 (m, 3H), 2.45–2.50 (m, 2H), 2.61 (t, $J=8.0$ Hz, 4H), 3.22 (t, $J=8.0$ Hz, 4H), 6.83–6.87 (m, 1H), 6.93 (d, $J=12.0$ Hz, 2H), 7.24–7.34 (m, 2H). HRMS (APCI) calcd for $C_{12}H_{19}N_2$ ($M+H^+$): 191.1543, found: 191.1528.

4.3.14. *N*-(Phenyl)piperazincarboxylethylether (Table 1, entry 14). White solid (0.1812 g, 83%); mp 57–58 °C. ^1H NMR: δ 1.28 (t, $J=8.0$ Hz, 3H), 3.13 (t, $J=4.0$ Hz, 4H), 3.62 (t, $J=8.0$ Hz, 4H), 4.14–4.19 (m, 2H), 6.87–6.94 (m, 3H), 7.25–7.35 (m, 2H). HRMS (APCI) calcd for $C_{13}H_{19}N_2O$ ($M+H^+$): 235.1441, found: 235.1436.

4.3.15. *N*-(Phenyl)morpholine (Table 1, entry 15). White solid (0.1469 g, 90%); mp 53–54 °C. ^1H NMR: δ 3.14 (t, $J=8.0$ Hz, 4H), 3.85 (t, $J=8.0$ Hz, 4H), 6.86–6.92 (m, 3H), 7.23–7.30 (m, 2H). HRMS (APCI) calcd for $C_{10}H_{14}NO$ ($M+H^+$): 164.1070, found: 164.1058.

4.3.16. *N*-Phenyl-3,5-dimethylmorpholine (Table 1, entry 16). Colorless liquid (0.1664 g, 87%). ^1H NMR: δ 1.23–1.30 (m, 6H), 2.35–2.41 (m, 2H), 3.42 (d, $J=12.0$ Hz, 2H), 3.76–4.12 (m, 2H), 6.83–6.90 (m, 3H), 7.23–7.27 (m, 2H). HRMS (APCI) calcd for $C_{12}H_{18}NO$ ($M+H^+$): 192.1383, found: 192.1387.

4.3.17. *N*-(3-Nitrophenyl)pyrrolidine (Table 1, entry 17). Yellow solid (0.1903 g, 99%); mp 33–34 °C. ^1H NMR: δ 2.04–2.09 (m, 4H), 3.33 (t, $J=8.0$ Hz, 4H), 6.79 (t, $J=4.0$ Hz, 1H), 7.26–7.32 (m, 2H), 7.44–7.46 (m, 1H). HRMS (APCI) calcd for $C_{10}H_{13}N_2O_2$ ($M+H^+$): 193.0972, found: 193.0967.

4.3.18. *N*-(4-Methoxyphenyl)piperazine (Table 1, entry 18). White solid (0.1492 g, 78%); mp 64–65 °C. ^1H NMR: δ 1.51–1.57 (m, 2H), 1.69–1.75 (m, 4H), 3.02 (t, $J=4.0$ Hz, 4H), 3.75 (d, $J=8.0$ Hz, 3H), 6.83 (t, $J=8.0$ Hz, 2H), 6.92 (d, $J=8.0$ Hz, 2H). HRMS (APCI) calcd for $C_{12}H_{18}NO$ ($M+H^+$): 192.1383, found: 192.1371.

4.3.19. *N*-(4-Methoxyphenyl)morpholine (Table 1, entry 19). White solid (0.1546 g, 80%); mp 66–67 °C. ^1H NMR: δ 3.06 (d, $J=4.0$ Hz, 4H), 3.77 (s, 3H), 3.86 (s, 4H), 6.84–6.91 (m, 4H). HRMS (APCI) calcd for $C_{11}H_{16}NO_2$ ($M+H^+$): 194.1176, found: 194.1184.

4.4. Cross-coupling data of aryl iodides with various *N*-heterocycles

4.4.1. *N*-(4-Methoxyphenyl)imidazole (Table 2, entry 1). White solid (0.1359 g, 78%); mp 121–122 °C. ^{1}H NMR: δ 3.82 (s, 3H), 6.94–6.98 (m, 2H), 7.17–7.29 (m, 4H), 7.72–7.81 (s, 1H). HRMS (APCI) calcd for $C_{10}H_{11}N_2O$ ($M+H^+$): 175.0866, found: 175.0853.

4.4.2. *N*-(4-Aminophenyl)imidazole (Table 2, entry 2). White solid (0.1098 g, 69%); mp 138–139 °C. ^{1}H NMR: δ 3.53 (br, 2H), 6.74 (d, J=8.0 Hz, 2H), 7.15 (d, J=4.0 Hz, 4H), 7.81 (s, 1H). HRMS (APCI) calcd for $C_9H_{10}N_3$ ($M+H^+$): 160.0869, found: 160.0854.

4.4.3. *N*-(2-Methylphenyl)imidazole (Table 2, entry 3). Colorless liquid (0.1028 g, 65%). ^{1}H NMR: δ 2.18 (s, 3H), 7.14–7.27 (m, 4H), 7.28–7.37 (m, 2H), 8.46 (s, 1H). HRMS (APCI) calcd for $C_{10}H_{11}N_2$ ($M+H^+$): 159.0917, found: 159.0912.

4.4.4. *N*-(3-Methylphenyl)imidazole (Table 2, entry 4). Colorless liquid (0.1187 g, 75%). ^{1}H NMR: δ 2.41 (s, 3H), 7.16–7.49 (m, 6H), 7.86 (s, 1H). HRMS (APCI) calcd for $C_{10}H_{11}N_2$ ($M+H^+$): 159.0917, found: 159.0902.

4.4.5. *N*-(3-Nitrophenyl)imidazole (Table 2, entry 5). Yellowish solid (0.1646 g, 87%); mp 93–94 °C. ^{1}H NMR: δ 7.27–7.38 (m, 2H), 7.69–7.78 (m, 2H), 7.95 (s, 1H), 8.23–8.28 (m, 2H). HRMS (APCI) calcd for $C_9H_8N_3O_2$ ($M+H^+$): 190.0611, found: 190.0600.

4.4.6. *N*-(3-Trifluoromethylphenyl)imidazole (Table 2, entry 6). Colorless liquid (0.1803 g, 85%). ^{1}H NMR: δ 7.25–7.73 (m, 6H), 8.01 (s, 1H). HRMS (APCI) calcd for $C_{10}H_8F_3N_2$ ($M+H^+$): 213.0634, found: 213.0623.

4.4.7. *N*-(Phenyl)benzimidazole (Table 2, entry 8). Colorless liquid (0.1554 g, 80%). ^{1}H NMR: δ 7.24–7.30 (m, 2H), 7.34–7.38 (m, 3H), 7.44–7.48 (m, 3H), 7.86 (d, J=8.0 Hz, 1H), 8.04 (s, 1H). HRMS (APCI) calcd for $C_{13}H_{11}N_2$ ($M+H^+$): 195.0917, found: 195.0903.

4.4.8. *N*-(4-Methoxyphenyl)benzimidazole (Table 2, entry 9). White solid (0.1741 g, 80%); mp 94–95 °C. ^{1}H NMR: δ 3.87 (s, 3H), 7.05–7.07 (m, 2H), 7.30–7.33 (m, 2H), 7.39–7.45 (m, 3H), 7.86–7.88 (m, 1H), 8.06 (s, 1H). HRMS (APCI) calcd for $C_{14}H_{13}N_2O$ ($M+H^+$): 225.1022, found: 225.1036.

4.4.9. *N*-(2-Methylphenyl)benzimidazole (Table 2, entry 10). Colorless liquid (0.1395 g, 67%). ^{1}H NMR: δ 2.09 (s, 3H), 7.16–7.45 (m, 6H), 7.90 (d, J=4.0 Hz, 2H), 8.00 (s, 1H). HRMS (APCI) calcd for $C_{14}H_{13}N_2$ ($M+H^+$): 209.1073, found: 209.1087.

4.4.10. *N*-(3-Methylphenyl)benzimidazole (Table 2, entry 11). Colorless liquid (0.1583 g, 76%). ^{1}H NMR: δ 2.42 (s, 3H), 7.21–7.51 (m, 6H), 7.85–7.87 (m, 2H), 8.07 (s, 1H). HRMS (APCI) calcd for $C_{14}H_{13}N_2$ ($M+H^+$): 209.1073, found: 209.1054.

4.4.11. *N*-(3-Nitrophenyl)benzimidazole (Table 2, entry 12). Yellowish solid (0.2153 g, 90%); mp 145–146 °C. ^{1}H NMR: δ 7.38–7.40 (m, 2H), 7.51–7.58 (m, 1H), 7.78–7.83 (m, 1H), 7.90 (d, J=8.0 Hz, 2H), 8.19 (s, 1H), 8.32 (d, J=12.0 Hz, 1H), 8.43 (s, 1H). HRMS (APCI) calcd for $C_{13}H_{10}N_3O_2$ ($M+H^+$): 240.0767, found: 240.0754.

4.4.12. *N*-(3-Trifluoromethylphenyl)benzimidazole (Table 2, entry 13). Colorless liquid (0.2255 g, 86%). ^{1}H NMR: δ 7.32–7.36 (m, 2H), 7.48–7.51 (m, 1H), 7.69–7.72 (m, 3H), 7.79 (1H), 7.86–7.89 (m, 1H), 8.13 (s, 1H). HRMS (APCI) calcd for $C_{14}H_{10}F_3N_2$ ($M+H^+$): 263.0791, found: 263.0805.

4.4.13. *N*-(4-Methoxyphenyl)pyrazole (Table 2, entry 7). White solid (0.1428 g, 82%); mp 32–33 °C. ^{1}H NMR: δ 3.84 (s, 3H), 6.43–6.44 (m, 1H), 6.95–6.98 (m, 2H), 7.58–7.61 (m, 2H), 7.69 (s, 1H), 7.81 (d, J=4.0 Hz, 1H). HRMS (APCI) calcd for $C_{10}H_{11}N_2O$ ($M+H^+$): 175.0866, found: 175.0872.

4.5. Cross-coupling data of bromopyridine with various amines

4.5.1. 2-(Butylamimo)pyridine (Table 3, entry 1). White solid (0.1427 g, 95%); mp 32–33 °C. ^{1}H NMR: δ 0.93 (t, J=8.0 Hz, 3H), 1.36–1.45 (m, 2H), 1.54–1.61 (m, 2H), 3.19–3.24 (m, 2H), 4.75 (br, 2H), 6.34 (d, J=8.0 Hz, 2H), 6.50–6.53 (m, 1H), 7.35–7.40 (m, 1H), 8.03 (d, J=4.0 Hz, 1H). HRMS (APCI) calcd for $C_9H_{15}N_2$ ($M+H^+$): 151.1230, found: 151.1221.

4.5.2. 2-(Benzylamimo)pyridine (Table 3, entry 2). White solid (0.1787 g, 97%); mp 79–80 °C. ^{1}H NMR: δ 4.47 (d, J=4.0 Hz, 2H), 5.06 (br, 1H), 6.34 (d, J=4.0 Hz, 1H), 6.52–6.57 (m, 1H), 7.26–7.39 (m, 1H), 8.06 (d, J=4.0 Hz, 1H). HRMS (APCI) calcd for $C_{12}H_{13}N_2$ ($M+H^+$): 192.1495, found: 192.1508.

4.5.3. 2-(Cyclohexylamimo)pyridine (Table 3, entry 3). White solid (0.1622 g, 92%); mp 103–104 °C. ^{1}H NMR: δ 1.18–1.24 (m, 3H), 1.35–1.42 (m, 2H), 1.60–1.78 (m, 3H), 2.01–2.05 (m, 2H), 3.48–3.56 (m, 1H), 4.48 (br, 1H), 6.35 (d, J=8.0 Hz, 1H), 6.49–6.54 (m, 1H), 7.91 (d, J=8.0 Hz, 1H), 8.04 (d, J=4.0 Hz, 1H). HRMS (APCI) calcd for $C_{11}H_{17}N_2$ ($M+H^+$): 177.1386, found: 177.1381.

4.5.4. 3-(Butylamimo)pyridine (Table 3, entry 4). White solid (0.1412 g, 94%); mp 35–36 °C. ^{1}H NMR: δ 0.94 (t, J=4.0 Hz, 3H), 1.39–1.44 (m, 2H), 1.57–1.62 (m, 2H), 3.02–3.16 (m, 2H), 4.07 (br, 1H), 6.84–6.86 (m, 1H), 7.04–7.07 (m, 1H), 7.90 (d, J=4.0 Hz, 1H), 8.00 (d, J=4.0 Hz, 1H). HRMS (APCI) calcd for $C_9H_{15}N_2$ ($M+H^+$): 151.1230, found: 151.1237.

4.5.5. 3-(Benzylamimo)pyridine (Table 3, entry 5). White solid (0.1768 g, 96%); mp 77–78 °C. ^{1}H NMR: δ 4.28–4.36 (m, 2H), 5.23 (br, 1H), 6.84–6.87 (m, 1H), 7.03–7.06 (m, 1H), 7.93 (d, J=4.0 Hz, 1H), 8.04 (s, 1H). HRMS (APCI) calcd for $C_{12}H_{13}N_2$ ($M+H^+$): 185.1073, found: 185.1056.

4.5.6. 3-(Cyclohexylamimo)pyridine (Table 3, entry 6). White solid (0.1587 g, 90%); mp 91–92 °C. ^{1}H NMR:

δ 1.15–1.24 (m, 3H), 1.35 (t, J=16.0 Hz, 1H), 1.62–1.74 (m, 1H), 1.74–1.79 (m, 2H), 2.02–2.06 (m, 2H), 3.17–3.27 (m, 1H), 3.64 (br, 1H), 6.83–6.86 (m, 1H), 7.03–7.06 (m, 1H), 7.89 (d, J=4.0 Hz, 1H), 7.96 (d, J=20.0 Hz, 1H). HRMS (APCI) calcd for $C_{11}H_{17}N_2$ ($M+H^+$): 177.1386, found: 177.1378.

4.5.7. *N*-(2-Pyridinyl)-*N*-(ethyl)piperazine (Table 3, entry 7). Colorless liquid (0.1626 g, 85%). ^{1}H NMR: δ 1.13 (t, J=8.0 Hz, 3H), 2.44–2.49 (m, 2H), 2.55 (t, J=4.0 Hz, 4H), 3.53–3.58 (m, 4H), 6.59–6.65 (m, 2H), 7.44–7.53 (m, 1H), 8.18–8.19 (m, 1H). HRMS (APCI) calcd for $C_{11}H_{18}N_3$ ($M+H^+$): 192.1495, found: 192.1508.

4.5.8. *N*-(2-Pyridinyl)morpholine (Table 3, entry 8). Colorless liquid (0.1346 g, 82%). ^{1}H NMR: δ 3.47 (t, J=4.0 Hz, 4H), 3.79 (t, J=6.0 Hz, 4H), 6.60–6.65 (m, 2H), 7.45–7.49 (m, 1H), 8.18–8.20 (m, 1H). HRMS (APCI) calcd for $C_9H_{13}N_2O$ ($M+H^+$): 165.1022, found: 165.1015.

4.5.9. *N*-(2-Pyridinyl)imidazole (Table 3, entry 9). Colorless liquid (0.1104 g, 76%). ^{1}H NMR: δ 7.21–7.25 (m, 2H), 7.35 (t, J=4.0 Hz, 1H), 7.68 (d, J=16.0 Hz, 1H), 7.80–7.84 (m, 1H), 8.38 (s, 1H), 8.46–8.48 (m, 1H). HRMS (APCI) calcd for $C_8H_8N_3$ ($M+H^+$): 146.0713, found: 146.0707.

4.5.10. *N*-(2-Pyridinyl)benzoimidazole (Table 3, entry 10). Colorless liquid (0.1242 g, 78%). ^{1}H NMR: δ 7.23 (s, 1H), 7.33–7.36 (m, 2H), 7.48 (d, J=8.0 Hz, 1H), 7.80 (d, J=4.0 Hz, 1H), 7.85 (t, J=6.0 Hz, 1H), 8.03 (t, J=4.0 Hz, 1H), 8.56 (s, 2H). HRMS (APCI) calcd for $C_{12}H_{10}N_3$ ($M+H^+$): 196.0869, found: 196.0851.

4.5.11. *N*-(3-Pyridinyl)imidazole (Table 3, entry 11). Colorless liquid (0.1074 g, 74%). ^{1}H NMR: δ 7.30–7.36 (m, 2H), 7.44–7.47 (m, 1H), 7.74–7.76 (m, 1H), 7.94 (s, 1H), 8.62 (t, J=4.0 Hz, 1H), 8.74 (s, 1H). HRMS (APCI) calcd for $C_8H_8N_3$ ($M+H^+$): 146.0713, found: 146.0700.

4.5.12. *N*-(3-Pyridinyl)benzoimidazole (Table 3, entry 12). White solid (0.1503 g, 77%); mp 89–91 °C. ^{1}H NMR: δ 7.36–7.38 (m, 2H), 7.50–7.56 (m, 2H), 7.86–7.90 (m, 2H), 8.16 (s, 1H), 8.73 (d, J=4.0 Hz, 1H), 8.86 (s, 1H). HRMS (APCI) calcd for $C_{12}H_{10}N_3$ ($M+H^+$): 196.0869, found: 196.0860.

4.6. Cross-coupling data of 5-bromopyrimidine with various amines

4.6.1. 5-(*iso*-Propylamino)pyrimidine (Table 4, entry 1). White solid (0.1235 g, 90%); mp 49–50 °C. ^{1}H NMR: δ 1.25 (d, J=8.0 Hz, 6H), 3.64–3.65 (m, 1H), 3.85 (br, 1H), 8.10 (s, 2H), 8.55 (s, 1H). HRMS (APCI) calcd for $C_7H_{12}N_3$ ($M+H^+$): 138.1026, found: 138.1012.

4.6.2. 5-(Butylamimo)pyrimidine (Table 4, entry 2). White solid (0.1467 g, 97%); mp 73–74 °C. ^{1}H NMR: δ 0.91–0.99 (m, 3H), 1.42–1.47 (m, 2H), 1.60–1.66 (m, 2H), 3.15 (t, J=8.0 Hz, 2H), 4.05 (br, 1H), 8.06 (s, 2H), 8.55 (s, 1H). HRMS (APCI) calcd for $C_8H_{14}N_3$ ($M+H^+$): 152.1182, found: 152.1169.

4.6.3. 5-(*iso*-Butylamimo)pyrimidine (Table 4, entry 3). Colorless liquid (0.1421 g, 94%). ^{1}H NMR: δ 0.99–1.01 (d, J=8.0 Hz, 6H), 1.77–1.84 (m, 1H), 3.03 (d, J=8.0 Hz, 2H), 4.69 (br, 1H), 8.01 (s, 2H), 8.19 (s, 1H). HRMS (APCI) calcd for $C_8H_{14}N_3$ ($M+H^+$): 152.1182, found: 152.1174.

4.6.4. 5-(*sec*-Butylamimo)pyrimidine (Table 4, entry 4). Colorless liquid (0.1354 g, 89%). ^{1}H NMR: δ 0.95–0.99 (m, 3H), 1.21 (d, J=8.0 Hz, 3H), 1.51–1.63 (m, 2H), 3.38–3.45 (m, 1H), 3.97 (br, 1H), 8.09 (s, 2H), 8.53 (s, 1H). HRMS (APCI) calcd for $C_8H_{14}N_3$ ($M+H^+$): 152.1182, found: 152.1168.

4.6.5. 5-(Benzylamimo)pyrimidine (Table 4, entry 5). White solid (0.1778 g, 96%); mp 99–100 °C. ^{1}H NMR: δ 4.30–4.39 (m, 2H), 5.21 (br, 1H), 8.16 (s, 2H), 8.57 (s, 1H). HRMS (APCI) calcd for $C_{11}H_{12}N_3$ ($M+H^+$): 186.1026, found: 186.1031.

4.6.6. 5-(Cylcopropylamino)pyrimidine (Table 4, entry 6). White solid (0.1244 g, 92%); mp 86–87 °C. ^{1}H NMR: δ 0.54–0.58 (m, 2H), 0.76–0.84 (m, 2H), 2.44–2.49 (m, 1H), 4.60 (br, 1H), 8.27 (s, 2H), 8.60 (s, 1H). HRMS (APCI) calcd for $C_7H_{10}N_3$ ($M+H^+$): 136.0869, found: 136.0861.

4.6.7. 5-(Cylcopentylamino)pyrimidine (Table 4, entry 7). Colorless liquid (0.1534 g, 94%). ^{1}H NMR: δ 1.48–1.52 (m, 2H), 1.63–1.76 (m, 4H), 2.02–2.08 (m, 2H), 3.75–3.81 (m, 1H), 4.31 (br, 1H), 8.12 (s, 2H), 8.54 (s, 1H). HRMS (APCI) calcd for $C_9H_{14}N_3$ ($M+H^+$): 164.1182, found: 164.1171.

4.6.8. 5-(Cyclohexylamimo)pyrimidine (Table 4, entry 8). White solid (0.1683 g, 95%); mp 109–110 °C. ^{1}H NMR: δ 1.18–1.26 (m, 3H), 1.37 (t, J=8.0 Hz, 2H), 1.62–1.73 (m, 1H), 1.76–1.81 (m, 2H), 2.03–2.07 (m, 2H), 3.25–3.30 (m, 1H), 3.71 (s, 1H), 8.09 (s, 2H), 8.54 (s, 1H). HRMS (APCI) calcd for $C_{10}H_{16}N_3$ ($M+H^+$): 178.1139, found: 178.1328.

4.6.9. 5-(Pyrimidinyl)pyrrolidine (Table 4, entry 9). Colorless liquid (0.1238 g, 83%). ^{1}H NMR: δ 1.94–2.02 (m, 4H), 3.20–3.24 (m, 4H), 8.00 (s, 2H), 8.53 (s, 1H). HRMS (APCI) calcd for $C_8H_{12}N_3$ ($M+H^+$): 150.1026, found: 150.1029.

4.6.10. 5-(Pyrimidinyl)piperidine (Table 4, entry 10). Colorless liquid (0.1387 g, 85%). ^{1}H NMR: δ 1.55–1.62 (m, 2H), 1.63–1.72 (m, 4H), 3.20–3.27 (m, 4H), 8.35 (s, 1H), 8.61 (s, 1H). HRMS (APCI) calcd for $C_9H_{14}N_3$ ($M+H^+$): 164.1182, found: 164.1172.

4.6.11. *N*-(5-Pyrimidinyl)-*N*-(ethyl)piperazine (Table 4, entry 11). Colorless liquid (0.1538 g, 80%). ^{1}H NMR: δ 1.13 (t, J=8.0 Hz, 3H), 2.46–2.51 (m, 2H), 2.62 (t, J=4.0 Hz, 4H), 3.29 (t, J=4.0 Hz, 4H), 8.37 (s, 2H), 8.68 (s, 1H). HRMS (APCI) calcd for $C_{10}H_{17}N_4$ ($M+H^+$): 193.1448, found: 193.1434.

4.6.12. *N*-(5-Pyrimidinyl)morpholine (Table 4, entry 12). Colorless liquid (0.1421 g, 86%). ^{1}H NMR: δ 3.22 (t, J=4.0 Hz, 4H), 3.87 (t, J=4.0 Hz, 4H), 8.36 (s, 2H), 8.64 (s, 1H). HRMS (APCI) calcd for $C_8H_{12}N_3O$ ($M+H^+$): 166.0975, found: 166.0960.

4.6.13. *N*-(5-Pyrimidinyl)-2,6-dimethylmorpholine (Table 4, entry 13). Colorless liquid (0.1508 g, 78%). ^{1}H NMR: δ 1.29 (t, J=8.0 Hz, 6H), 2.50 (t, J=6.0 Hz, 4H), 3.79–3.83 (m, 2H), 8.36 (s, 2H), 8.69 (s, 1H). HRMS (APCI) calcd for $C_{10}H_{16}N_3O$ ($M+H^+$): 194.1288, found: 194.1279.

4.6.14. *N*-(5-Pyrimidinyl)benzoimidazole (Table 4, entry 14). White solid (0.1432 g, 73%); mp 143–144 °C. ^{1}H NMR: δ 7.40–7.44 (m, 2H), 7.52 (d, J=4.0 Hz, 4H), 7.93 (t, J=8.0 Hz, 1H), 9.03 (s, 1H), 9.34 (s, 1H). HRMS (APCI) calcd for $C_{11}H_9N_4$ ($M+H^+$): 197.0822, found: 197.0812.

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