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Journal Name

COMMUNICATION

Chelation-Assisted C–N Cross-Coupling of Phosphinamides and Aryl Bronic Acids with Copper Powder at Room Temperature

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A protocol for chelation-assisted C–N cross-coupling of phosphinamides and aryl boronic acids with copper powder under oxygen atmosphere is reported. The reaction proceeds efficiently to afford fully substituted unsymmetrical *N*-arylation phosphinamides at room temperature in excellent yields. A diverse of unstable functional groups on the benzene ring of aryl boronic acid such as vinyl, formyl, acetyl, sulfonyl, acetylamino, cyano, nitro, and trifluoromethyl can be accommodated.

The high prevalence of fully substituted tertiary phosphinamides in pharmaceuticals, functional materials and synthetic intermediates[1] has motivated synthetic chemists to develop convenient and mild amination processes.[2] Over the past decades, comprehensive studies were conducted on transition-metal assisted C–N bond formation. [3] Traditional methods such as the reaction of amines with carboxylic acid derivatives,[4] aldehydes[5] or alcohols,[6] hydroamination of alkynes,[7] and hydrogenation of nitriles[8] are commonly limited by poor amide scope and poor reaction efficiency. The ones that are based on Buchwald-Hartwig reactions[9] using halides as coupling partners for direct C–N bond formation together with the cleavage of C–X (X = halides) bonds provide straightforward routes for direct *N*-substituent of amides. However, the use of precious palladium catalysts or ligands somewhat restricted their applications. Nonetheless, a cost-effective strategy based on the Chan-Lam-Evans reactions,[10] has been developed to obtain *N*-substituted amides *via* copper-mediated oxidative amination of aryl boronic acids. In contrast with the use of organic halides, the use of organoboron reagents has the advantages of ready availability of reagents, broad functional group tolerance, low toxicity,

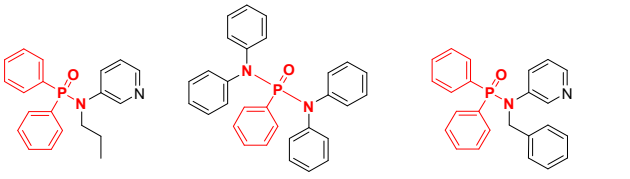

Figure 1. Selected examples of functionalized compounds having fully substituted phosphinamides motif.

and ease of separating boron-containing by-products.[11] However, this protocol is also limited because of poor product yield.

Significant achievements in this direction have been realized through the development of innovative chelation-assisted transition-metal catalysis.[12] By using naturally more abundant and inexpensive first-row transition metals as catalysts, the introduction of a coordinating functional group in the form of amide framework to promote the formation of a cyclometalated intermediate could enable the generation of unsymmetrical fully substituted amides. Unlike the well-established intramolecular amidation strategy,[13] the approach of chelation-assisted C–N cross-coupling has been rarely reported,[14] mainly due to the competing C–H functionalization of amides that are connected to the directing group. Therefore, a decisive choice to realize C(sp^2)–N cross-coupling is necessary to nullify the competing C–H functionalization of amides. Toward this end, Nicholls *et al.* developed the Cu(II)-catalyzed amidation of aryl bromides using 8-amidoquinolines at elevated temperature (Scheme 1a).[14a] More recently, Baidya *et al.* successfully realized Cu(II)-catalyzed picolinamide-assisted C(sp^2)–N cross-coupling with boronic acids to obtain unsymmetrical tertiary amides at room temperature under open-flask conditions (Scheme 1b).[14b] Both of these methods rely on Cu(II) catalysts with the assistance of a base or other additive. Relatively few papers describe the use of copper powder for these reactions.[15] More to the point, the generation of potentially useful *N,N*-disubstituted phosphinamides are still inaccessible through the described

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Electronic Supplementary Information (ESI) available: General information, experimental procedures, copies of ^{1}H, ^{31}P, ^{19}F and ^{13}C NMR spectra for products. See DOI: 10.1039/x0xx00000x

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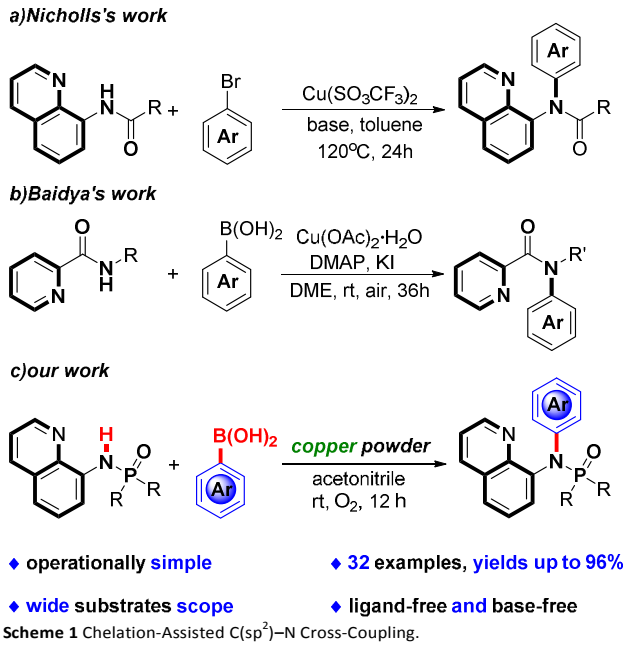


Scheme 1 Chelation-Assisted C(sp^2)–N Cross-Coupling.

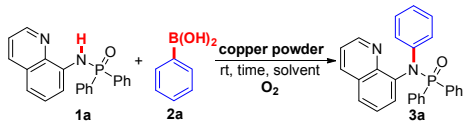
Cu(II)-catalysis methods[14a,b] (Scheme 2c, vide infra).

Herein, we disclose a facile strategy for C(sp^2)–N cross-coupling to produce *N,N*-disubstituted phosphinamides in high yields under mild conditions using copper powder (Scheme 1c). Aryl boronic acids are raw chemical materials that are abundantly available. Oxygen, which is one of the simplest oxidant, is the only additive in this system. To the best of our acknowledge, the synthesis of *N,N*-disubstituted tertiary amides mediated by copper powder has never been reported.

We initiated our study by using *P,P*-diphenyl-*N*-(quinolin-8-yl) phosphinamides **1a** as representative substrate for condition optimization (Table 1). A proper amount of copper powder is critical in this reaction. When the reaction proceeded with catalytic amount of copper powder, only trace amount of desired product was obtained (entries 1 and 2). If 50 mol% of copper powder was used instead, **3a** was obtained in 71% yield (Table 1, entry 3). When equivalent amount of copper powder was used, the reaction proceeded efficiently to obtain the coupling product **3a** in 95% yield (Table 1, entry 4). If copper powder was omitted, **3a** was not formed (Table 1, entry 5). The reaction time could be reduced from 24 h to 12 h to afford **3a** in 92% yield (Table 1, entry 6). Shortening the reaction time to 6 h, 3 h, 2 h or 1 h are also capable of obtaining **3a**, albeit in relatively lower yields (Table 1, entries 7–10). Of significant relevance was the atmosphere. The yield was depressed under nitrogen atmosphere (Table 1, entry 11), indicating that oxygen has a significant effect on reaction efficiency. Further studies showed that the use of alternate solvents resulted in lower yields of 3a, indicating the suitability of acetonitrile as a solvent (Table 1, entries 13–18).

With the optimal condition in hand, we explored the applicability of the protocol and investigated the scope of

Table 1. Optimization of reaction conditionsa.



entry	copper powder	time (h)	solvent	yield of **3a** [b]	recovery of **1a** [b]
1	10 mol%	24	MeCN	13%	78%
2	20 mol%	24	MeCN	22%	64%
3	50 mol%	24	MeCN	71%	14%
4	1 equiv	24	MeCN	95%	0%
5	none	24	MeCN	0	100%
6	1 equiv	12	MeCN	92%	0%
7	1 equiv	6	MeCN	66%	32%
8	1 equiv	3	MeCN	53%	40%
9	1 equiv	2	MeCN	44%	54%
10	1 equiv	1	MeCN	32%	63%
11[c]	1 equiv	12	MeCN	48%	49%
12[d]	1 equiv	12	MeCN	74%	22%
13	1 equiv	12	DMF	60%	39%
14	1 equiv	12	DMAC	none	99%
15	1 equiv	12	MeOH	43%	54%
16	1 equiv	12	toluene	none	99%
17	1 equiv	12	CH_2Cl_2	59%	38%
18	1 equiv	12	*o*-xylene	none	99%

[a] Reaction conditions: **1a** (0.1 mmol), copper powder, and **2a** (0.2 mmol) in solvent (1.0 mL) under oxygen atmosphere at room temperature. [b] Yield was determined by ^{31}P NMR analysis, using triphenylphosphine oxide (0.1 mmol) as internal standard. [c] Under nitrogen atmosphere. [d]Under air atmosphere.

substrates as shown in Table 2. It was found that both electron-donating and electron-withdrawing groups on the phenyl ring of aryl boronic acid are well tolerated. Aryl boronic acid derivatives with alkyl groups at the *para*- or *mata*-positionof phenyl ring could effectively couple with **1**, producing the desired product in up to 95% yields (**3b–3g**). As a result of steric hindrance, the reaction of substituent at the ortho-position of phenyl ring results in significantly lower amount of desired product (**3h**). The reactions proceed effectively in the presence of the C–X (X = F, Cl, Br, I) bonds (**3i–3m**), albeit at elevated temperature. The results imply that the electron-withdrawing ability of X hinders the coupling reaction. Remarkably, various labile functional groups such as vinyl (**3o**), formyl (**3p**, **3q**), acetyl (**3r**, **3s**), sulfonyl (**3t**), acetylamino (**3u**), cyano (**3v**), nitro (**3z**), and trifluoromethyl (**3w**, **3x**) can be accommodated. It is noted that the reaction proceeds smoothly with strong electron-withdrawing (3,5-bis(trifluoromethyl)phenyl)boronic acid to afford the corresponding amidation product (**3y**) in moderate yield (24%). The generality of this coupling reaction was further demonstrated by using other phosphinamides as substrates. As shown in Table 2, phosphinamides substituted with CH_3 (**3ba** and **3ca**), F (**3da** and **3ea**), Cl (**3fa**) and OCH_3 (**3ga**) work well to give the corresponding products in 73–91% yields, regardless of steric hindrance.

Having extensively investigated the substrate scope and limitation of the protocol, control experiments were performed to gain insight into the reaction mechanism. With the addition of radical scavengers such as TEMPO and BHT, a significant amount of product **3a** could still be obtained (Scheme 2a). The results confirm that the reaction does not

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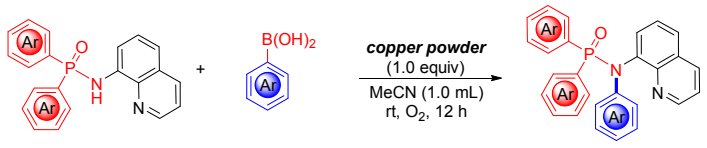
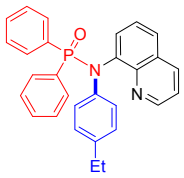
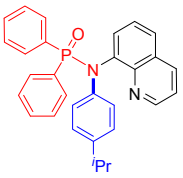
Table 2. Scope of substrate[a].



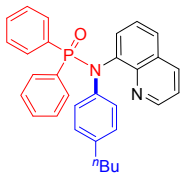
1 2 3



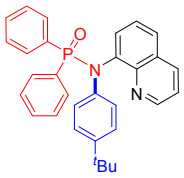
3b, 92%



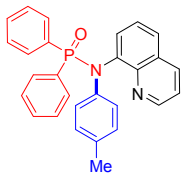
3c, 95%



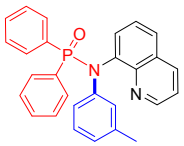
3d, 92%



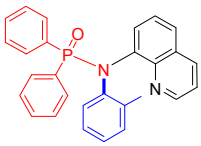
3e, 90 %



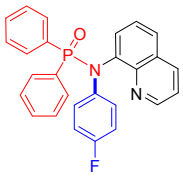
3f, 94%



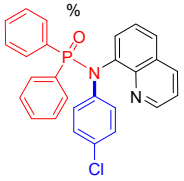
3g, 90%



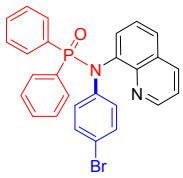
3h, 22%, 31%[d]



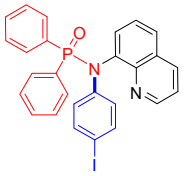
3i, 61%, 93%[b]



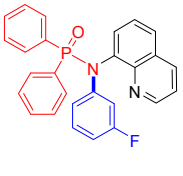
3j, 58%, 96%[b]



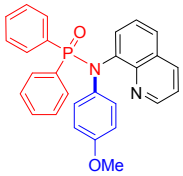
3k, 75%



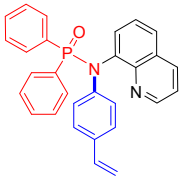
3l, 56%, 90%[b]



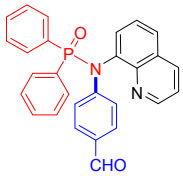
3m, 51%, 94%[b]



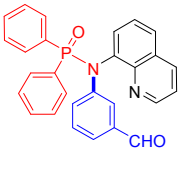
3n, 95%



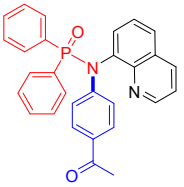
3o, 60%, 92%[b]



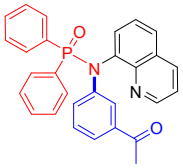
3p, 39%



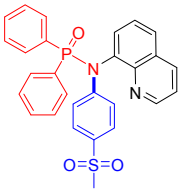
3q, 37%, 82%[b]



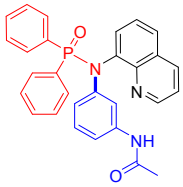
3r, 48%, 57%[b]



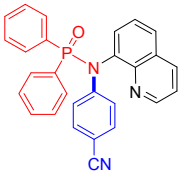
3s, 45%, 70%[c]



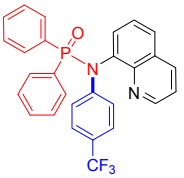
3t, 25%, 55%[d]



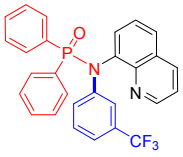
3u, 27%, 89%[b]



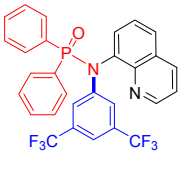
3v, 20%, 49%[d]



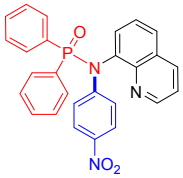
3w, 25%, 68%[d]



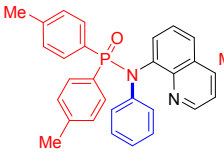
3x, 22%, 79%[d]



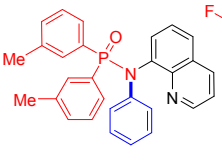
3y, 0%, 24%[d]



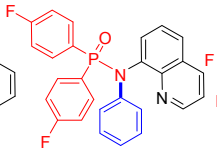
3z, 19%, 27%[b]



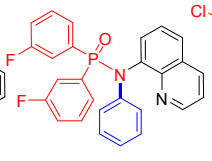
3ba, 78%



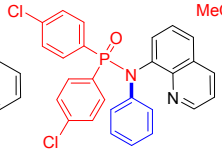
3ca, 73%



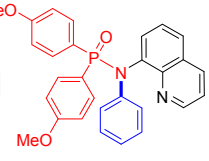
3da, 91%



3ea, 85%



3fa, 91%



3ga, 84%

[a] Reaction conditions: **1** (0.1 mmol), copper powder, and **2** (0.2 mmol) in acetonitrile (1.0 mL) under oxygen atmosphere for 12 h at 25 °C. ^{31}P NMR yield, using triphenylphosphine oxide (0.1 mmol) as internal standard. [b] Performed at 60 °C. [c] Performed for 24 h. [d] Performed at 100 °C.

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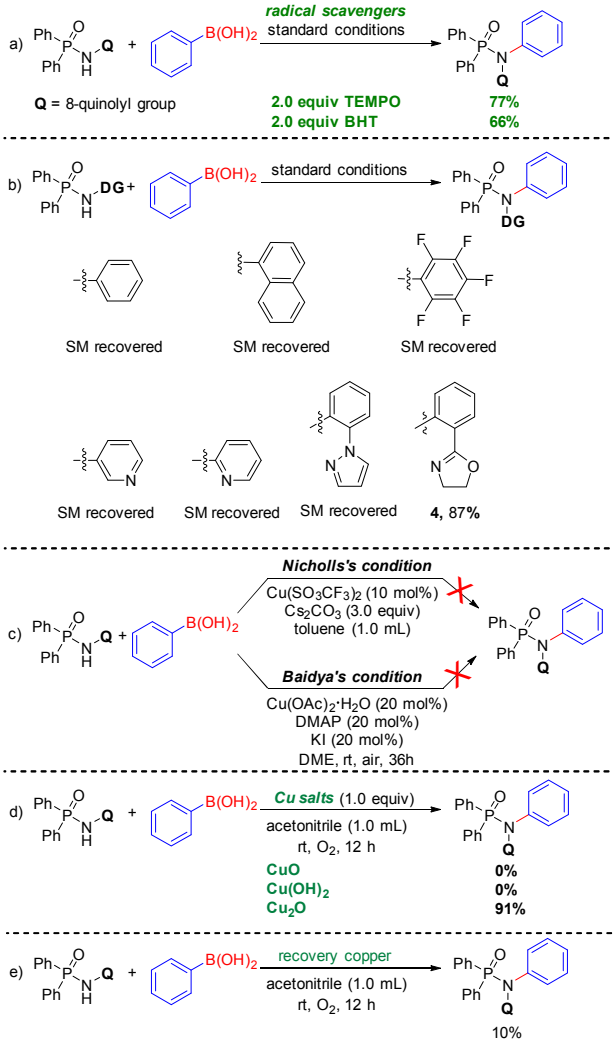


Scheme 2 Control experiments.

involve a free radical pathway. Systematic tuning of the auxiliary groups was carried out under the optimal conditions. Starting materials were fully recovered when phenyl, naphthyl, perfluorophenyl, 3-pyridyl, 2-pyridyl, and 2-(1*H*-pyrazol-1-yl)phenyl were used as auxiliary groups, suggesting that the chelation with the 8-amidoquinoline is critical (Scheme 2b). It was found that when *N*-(2-(4,5-dihydrooxazol-2-yl)phenyl)-P,P-diphenylphosphinamide was used as substrate [16], the corresponding product was also obtained in 87% ^{31}P NMR yield (**4**). With such notation, it is envisioned that the scope of chelating group can be further enlarged. To further demonstrate the advantage of this method, we attempted the C–N cross-coupling using the Cu(II)-catalyzed amidation approach of phenyl boronic acid at the conditions recently reported by the groups of Nicholls[14a] and Baidya[14b]. It was found that neither of these catalytic systems could generate the desired product **3a**, and the results demonstrate the specificity of the methodology explored in the present study (Scheme 2c). To identify the catalytically active metal species, we performed three parallel experiments using CuO, $Cu(OH)_2$ and Cu_2O as catalysts under the optimized conditions (Scheme 2d). We observed that there was no reaction over CuO or $Cu(OH)_2$. In contrast, when Cu_2O was used instead,

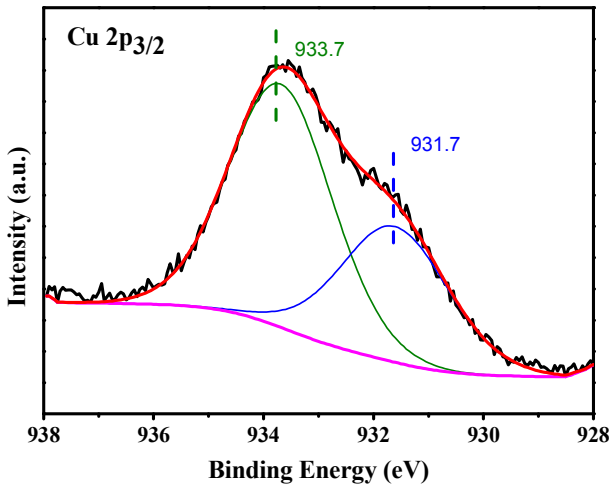
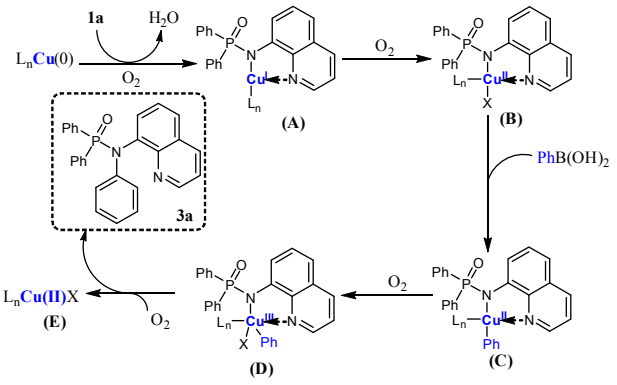


Figure 2 XPS Cu $2p_{3/2}$ spectrum of copper species collected after reaction under the optimized conditions.

the reaction proceeded smoothly to give 3a in 91% yield. It is hence reasonable to hypothesize that the C–N cross-coupling reaction was enabled by Cu(I) species of low valence but restricted by Cu(II) species.

To test this hypothesis, we collected the copper residue by centrifugation after the reaction. Compared to copper powder, the recovered copper residue showed a lower yield (only 10%) (Scheme 2e). We used X-ray photoelectron spectroscopy (XPS) analysis technique to characterize the copper species after the coupling reaction. As shown in Figure 2, the peak at 933.7 eV binding energy corresponds to Cu^{2+} valence state. The peak at 931.7 eV binding energy indicates the presence of Cu^0 or Cu^+ species.[17a,17e] With peak intensity lower than that of Cu^{2+} peak, the Cu^0 or Cu^+ species are present in lower amount. The results suggest that Cu^{2+} is the main copper species after the reaction.[17]



Scheme 3 Plausible mechanism.

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Based on the above results and those of previous reports,[18] a plausible mechanism is proposed as illustrated in Scheme 3. First, Cu(0) coordinates with the substrate to give complex **1a** that reacts with O_2 to give bidentate chelating complex (**A**) endowed with a Cu(I) centre, together with the generation of H_2O. After reacting with O_2, **A** is converted to Cu(II) species **B**, which upon transmetalation with $PhB(OH)_2$ produces complex **C**. Then, undergoing disproportionation or oxidation reaction with O_2, complex **C** yields Cu(III) complex **D** that undergoes smooth reductive elimination to deliver product **3a** with concurrent formation of low-valence Cu(I) species. The latter can be easily oxidized with O_2 to produce Cu(II) species **E**, restricting the whole reaction as a result.

Conclusions

In conclusion, we have developed an efficient method for aminoquinoline-assisted C–N cross-coupling of phosphinamides and readily available aryl boronic acids with copper powder under mild conditions. The reaction proceeds efficiently with a wide array of boronic acids and phosphinamides to afford the corresponding products in up to 96% yield. The wide substrate scopes and simple operation demonstrates that the protocol opens a practical avenue for C–N cross-coupling. Further investigations of the application of fully substituted unsymmetrical *N*-arylation phosphinamides are currently underway in our laboratory.

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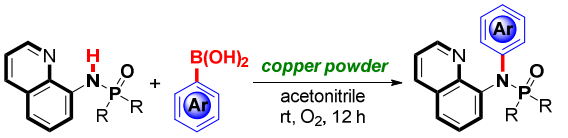

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