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$Cu(OAc)_2 \cdot H_2O$-catalyzed N-arylation of nitrogen-containing heterocycles

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ABSTRACT

In the absence of any additional ligands, the efficient N-arylation of nitrogen-containing heterocycles with aryl iodides catalyzed by relative low catalyst amount of $Cu(OAc)_2 \cdot H_2O$ was developed. This simple catalytic system is involved in the C–N cross-coupling reaction and works for a variety of pyrazole, pyrrole, imidazole, triazole, indole, benzoimidazole, benzotriazole, carbazole, and anilines as well as aryl iodides with different electronic properties. Highly efficient copper(II)-catalyzed N-arylation protocol was established.

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1. Introduction

N-Arylazoles (e.g., arylpyrroles, arylpyrazoles, arylimidazoles, aryltriazoles, arylindoles, arylcarbazoles, etc.) are ubiquitous in biochemical, biological, and medicinal structures and functions.[1] For this reason, transition-metal-catalyzed arylation of nitrogen-containing heterocycles with aryl halides is one of the most efficient and powerful methods for the synthesis of *N*-arylazole derivatives and has proven useful in both academic and industrial laboratories.[2] However, current methods have some potential limitations because these transformations often use expensive transition-metal catalysts such as palladium,[3] rhodium,[4] nickel,[5] and cobalt[6] complexes. Thus screening out inexpensive and environmentally benign metal catalysts for the arylation reaction still remains a great challenge. In recent years, initiated by Buchwald and Hartwig,[7] inexpensive copper catalysts bearing various ligands have provided a highly economical and efficient method for the N-arylation of nitrogen-containing heterocycles with aryl halides. The ligands employed in the Cu-catalyzed reactions included β-diketones,[8] 1,2-diamines,[9] phenanthrolines,[10] bipyridines,[11] α-amino acids,[12] phosphines,[13] and others.[14] These chelating ligands play an important role in controlling the concentration of active catalytic species, but they may contaminate the final products.[15] Using extra ligand-free catalysts could be a good alternative to avoid the inconvenience of ligand removal from reaction mixtures. In the past years, CuI[16] and Cu_2O[17] have been successfully employed as catalysts for this cross-coupling reaction in the absence of organic ligands. However, these catalytic systems often require excess substrates[16a,b,j] or high catalyst loadings.[16c–f] It is noted that simple inorganic copper(II) salts without extra ligands for catalyzing such coupling reactions is of limited scope.[18] Although there have been some reports on the amination of aryl halides with amines promoted by copper(II) salts without using organic ligands, they often required large amounts of $Cu(OAc)_2$[18b,d] or copper oxide nanoparticles,[18c] which raised the cost of the reaction. Choudary and coworkers reported an efficient catalytic N-arylation reaction using the copper(II) apatite as the catalyst but with a relatively high catalyst loading (~8 mol %).[18a] To this end, the development of a simple copper catalyst with a low catalyst loading in the absence of any additional ligands for such coupling reactions would be necessary.

Recently, we have reported that some copper(II) pyrazolate complexes exhibit high catalytic activity in the polymerization of MMA.[19] As we all know, copper(II) could be reduced to copper(I) by nitrogen-containing ligands via heating, forming monomeric, oligomeric or polymeric copper(I) coordination complexes.[20] It is anticipated that such copper(I) coordination compounds or those active copper(I) species generated in situ from copper(II) salts may be used to catalyze N-arylation of nitrogen-containing heterocycles, which would be the main story of this paper. We herein report our results on exploring highly efficient N-arylation of nitrogen-containing heterocycles with aryl halides catalyzed by 1 mol % of $Cu(OAc)_2 \cdot H_2O$ without extra ligands.

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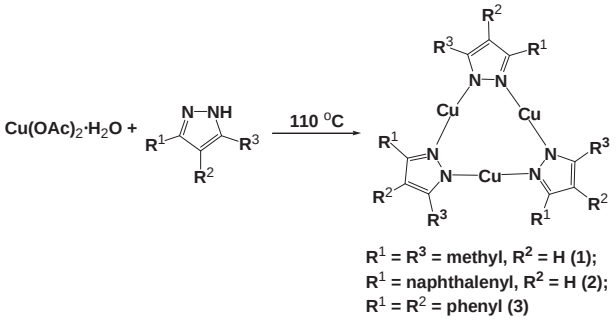
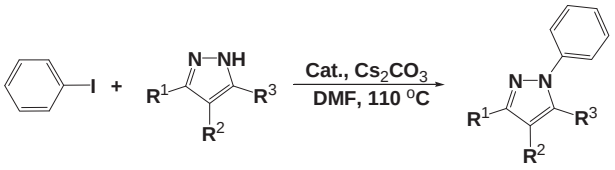
2. Results and discussion

The hydrothermal reaction of $Cu(NO_3)_2\cdot 3H_2O$ with 2-methylimidazole (Hmim)[20c] in the presence of NH_3 at 160 °C was reported to afford a polymeric complex $[Cu(mim)]_n$, while an analogous reaction of $Cu(NO_3)_2\cdot 3H_2O$ with 3,5-dimethylpyrazole (Hdmpz) afforded a trimeric complex $[Cu(dmpz)]_3$.[20b] In our cases, solvothermal reactions of $Cu(OAc)_2\cdot H_2O$ with 2 equiv of Hdmpz, 3-naphthalen-2-yl-1*H*-pyrazole (Hnapz) and 3,4-diphenyl-1*H*-pyrazole (Hdphpz) in MeCN, DMF and EtOH at 110 °C for 12 h gave rise to the trimeric complexes, $[Cu(dmpz)]_3$ (**1**), $[Cu(napz)]_3$ (**2**), and $[Cu(dphpz)]_3$ (**3**), respectively, in which Cu(II) was reduced to Cu(I) by Hdmpz, Hnapz, and Hdphpz (Scheme 1). The results clearly indicated that amine or *N*-containing heterocycle compounds could reduce Cu(II) into Cu(I) under solvothermal reactions. The molecular structures of **2** and **3** were shown in Fig. 1. In **2** and **3**, three Cu(I) atoms are interconnected by three napz or dphpz ligands to form a triangular structure with a three-fold axis running through the center of the molecule. Their structures resemble that of **1**.[20b] Being linearly coordinated by two N atoms from two pyrazolate ligands, each Cu atom in **2** or **3** is coordinatively unsaturated and could be bound by the reactive functional groups of substrates. Thus, these Cu(I) complexes might be employed as catalysts for the cross-coupling reactions of pyrazoles with aryl halides.



Scheme 1. Synthesis of **1**–**3**.



pyrazole	cat.	yield
R^2 = H, R^1 = R^3 = Me	1	23%
R^2 = R^3 = H, R^1 = naphthalenyl	2	75%
R^3 = H, R^1 = R^2 = phenyl	3	71%

Scheme 2. N-Arylation catalyzed by **1**–**3**.

efficiently catalyzed by the Cu(I) pyrazolate complexes. We postulated that the pyrazole substrates themselves might work as labile ligands to accelerate Cu-catalyzed N-arylation reactions without using any additional ligands.

When the reaction of phenyl iodide with equimolar Hnapz was carried out in the presence of $CuBr_2\cdot 2H_2O$ (5 mol %) and Cs_2CO_3 in DMF at 110 °C, the color of the mixture was changed from blue to colorless in several minutes, implying that Cu(II) was reduced to certain Cu(I) species. After 24 h, 3-naphthalen-2-yl-1-phenyl-1*H*-pyrazole could be isolated in 98% yield (Table 1, entry 1). This result showed that the in situ formed Cu(I) species in solution may possess higher catalytic activity than the trimeric Cu(I) pyrazolate complexes such as **1**–**3**. To find the most active ligand-free catalyst system, several Cu(II) salts were used for the N-arylation of Hnapz with phenyl halide. It was found that $Cu(OAc)_2\cdot H_2O$ was the best one (Table 1, entry 3) among those listed in Table 1. For the solvents used, DMF was the best one for such a reaction (Table 1, entry 15), while others such as H_2O, toluene, and MeCN gave relatively low yields. For a variety of bases (e.g., K_2CO_3, K_3PO_4, and Cs_2CO_3), Cs_2CO_3 is the best one for this reaction in DMF (Table 1, entry 15). A blank experiment confirmed that no arylated product was observed in the absence of the metal catalyst (Table 1, entry 11). Furthermore, the reaction temperature exerted great impact on this reaction. At lower temperature (70–90 °C), the reaction did not work (Table 1, entry 19) or gave the product in a low yield (Table 1, entry 18). It is noted that the catalyst loading for this reaction could be reduced from 5 to 1 mol % without affecting the product yields (Table 1, entries 3, 15, and 16). Thus the optimized reaction conditions were found to be 1 mol % of $Cu(OAc)_2\cdot H_2O$ and Cs_2CO_3 (as the base) and DMF (as a solvent) at 110 °C.

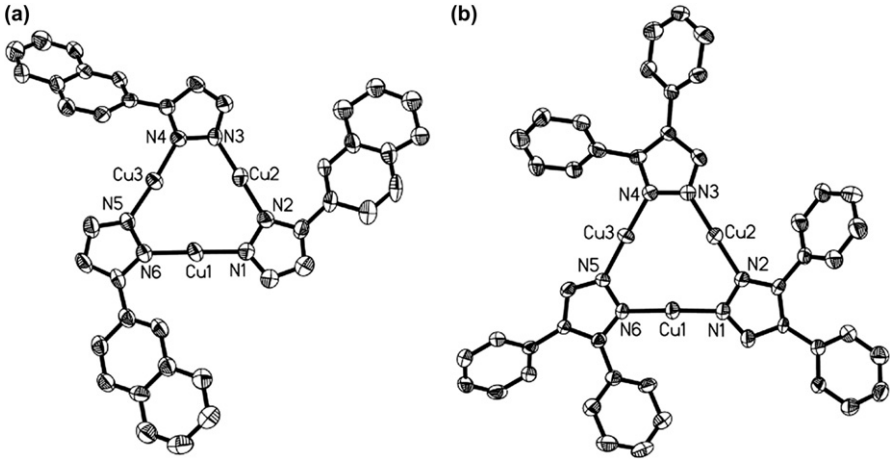
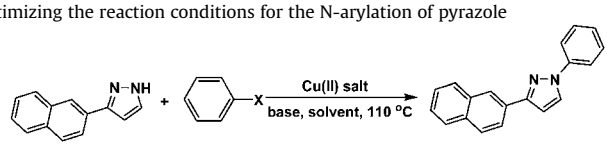


Fig. 1. (a) View of the molecular structure of $[Cu(napz)]_3$. (b) View of the molecular structure of $[Cu(dphpz)]_3$.

With the optimized reaction conditions in hand, a variety of substituted pyrazole derivatives were chosen as the substrates in

Table 1
Optimizing the reaction conditions for the N-arylation of pyrazole



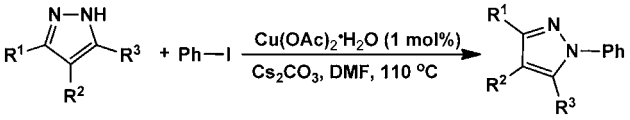
Entry[a]	Salt	Base	Solvent	Yield[b] %
1	$CuBr_2 \cdot 2H_2O$	Cs_2CO_3	DMF	98
2	$CuCl_2 \cdot 2H_2O$	Cs_2CO_3	DMF	96
3	$Cu(OAc)_2 \cdot H_2O$	Cs_2CO_3	DMF	99
4	CuO	Cs_2CO_3	DMF	50
5	$Cu(NO_3)_2 \cdot 3H_2O$	Cs_2CO_3	DMF	97
6	$CuSO_4 \cdot 5H_2O$	Cs_2CO_3	DMF	94
7	$Cu(OAc)_2 \cdot H_2O$	Cs_2CO_3	Toluene	0
8	$Cu(OAc)_2 \cdot H_2O$	Cs_2CO_3	MeCN	45
9	$Cu(OAc)_2 \cdot H_2O$	Cs_2CO_3	DMSO	90
10	$Cu(OAc)_2 \cdot H_2O$	Cs_2CO_3	H_2O	0
11		Cs_2CO_3	DMF	0
12	$Cu(OAc)_2 \cdot H_2O$	Na_2CO_3	DMF	50
13	$Cu(OAc)_2 \cdot H_2O$	K_2CO_3	DMF	52
14	$Cu(OAc)_2 \cdot H_2O$	K_3PO_4	DMF	60
15[c]	$Cu(OAc)_2 \cdot H_2O$	Cs_2CO_3	DMF	99
16[d]	$Cu(OAc)_2 \cdot H_2O$	Cs_2CO_3	DMF	99
17[e]	$Cu(OAc)_2 \cdot H_2O$	Cs_2CO_3	DMF	90
18[f]	$Cu(OAc)_2 \cdot H_2O$	Cs_2CO_3	DMF	27
19[g]	$Cu(OAc)_2 \cdot H_2O$	Cs_2CO_3	DMF	0

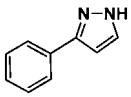
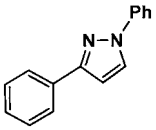
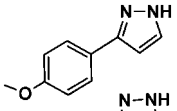
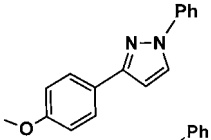
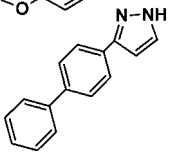
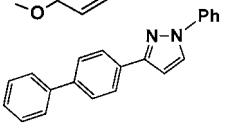
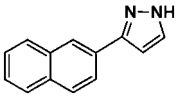
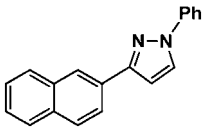
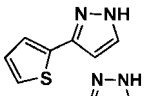
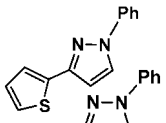
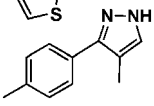
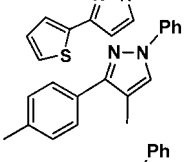
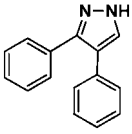
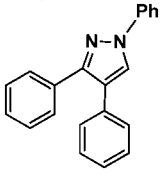
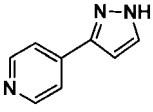
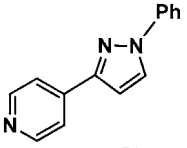
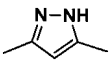
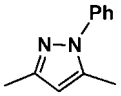
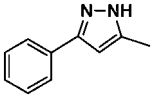
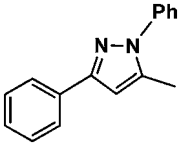
[a] Reaction conditions: phenyl halide (1.2 mmol), Hnapz (1.0 mmol), base (2.0 mmol), solvent (2.0 mL), and salt (5 mol %) at 110 °C for 24 h.
[b] Isolated yield.
[c] Catalyst loading: 3 mol %.
[d] Catalyst loading: 1 mol %.
[e] Catalyst loading: 0.5 mol %.
[f] The reaction was carried out at 90 °C.
[g] The reaction was carried out at 70 °C.

this cross-coupling reaction. As shown in Table 2, the coupling reactions were performed well for all the substrates examined, and the desired products were isolated in moderate to excellent yields. It seemed that 3- or 4-substituent of pyrazole ring did not hamper the N-arylation reaction (entries 2, 7, and 8). However, this reaction was sensitive to the 5-substituent of pyrazole ring and moderate yields were obtained for 3,5-dimethylpyrazole (31% yield; entry 10) and 5-methyl-3-phenyl-1*H*-pyrazole (36% yield; entry 11), which may be ascribed to the large steric hindrance during the course of the crossing-coupling reaction. It is noted that the N-arylation reaction of the asymmetric pyrazoles such as 3-phenyl-1*H*-pyrazole, 3-(4-methoxyphenyl)-1*H*-pyrazole, 3-([1,1′-biphenyl]-4-yl)-1*H*-pyrazole, 3-(naphthalen-2-yl)-1*H*-pyrazole, 3-(thiophen-2-yl)-1*H*-pyrazole, 4-methyl-3-(*p*-tolyl)-1*H*-pyrazole, 4-(1*H*-pyrazol-3-yl) pyridine, and 5-methyl-3-phenyl-1*H*-pyrazole with aryl iodide gave only one regioisomeric product. However, the cross-coupling reaction of 3,4-diphenyl-1*H*-pyrazole with phenyl iodide resulted in the formation 1,3,4-triphenyl-1*H*-pyrazole as the major product (97% yield) along with a byproduct 1,4,5-triphenyl-1*H*-pyrazole (ca. 1% yield). Thus the protocol provided a highly efficient and regioselective synthesis of unsymmetrically substituted 1-arylpyrazoles.

Encouraged by the high efficiency for the reaction of pyrazole described above, we also examined the substrate scope of other *N*-containing heterocycles and different aryl iodides. As shown in Table 3, the method was applicable to a broad substrate scope on both aryl iodides and nitrogen-containing heterocycles including pyrazole, pyrrole, imidazole, triazole, indole, benzoimidazole, benzotriazole, and carbazole under the standard reaction conditions. The arylation of pyrazole, pyrrole, imidazole, triazole, or indole with aryl iodide in the presence of 1 mol % $Cu(OAc)_2 \cdot H_2O$ afforded the corresponding products in excellent yields (Table 3, entries 1–20). Other *N*-containing heterocycles such as benzoimidazole, benzotriazole or carbazole (Table 3, entries 21–28) were also coupled with aryl iodide to give the corresponding products

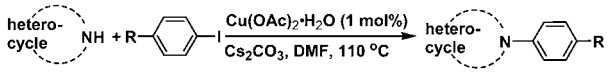
Table 2
Reaction of different pyrazole derivatives with benzene iodide

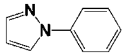
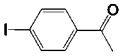
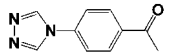
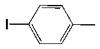
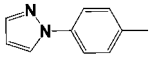
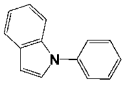
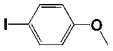
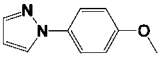
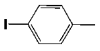
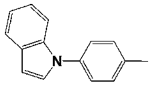
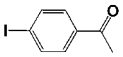
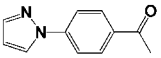
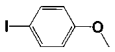
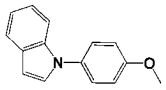
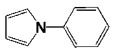
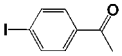
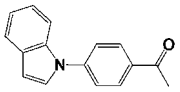
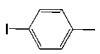
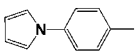
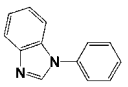
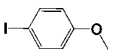
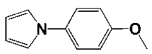


Entry[a]	Pyrazole	Product	Yield[b] %
1			99
2			98
3			95
4			95
5			99
6			97
7			95
8[c]			97
9			99
10			31
11			36

[a] Reaction conditions: phenyl iodide (1.2 mmol), pyrazole (1.0 mmol), Cs_2CO_3 (2.0 mmol), DMF (2.0 mL), and $Cu(OAc)_2 \cdot H_2O$ (1 mol %) at 110 °C for 24 h.
[b] Isolated yield.
[c] A byproduct 1,4,5-triphenyl-1*H*-pyrazole was isolated in ca. 1% yield.

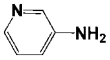
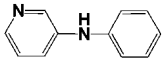
Table 3
Ligand-free N-arylation reaction of aryl iodide with pyrrole, triazole, indole, benzimidazole, benzotriazole, carbazole, aniline or aniline derivatives



Entry[a]	Amine	ArI	Product	Yield[b] %	Entry	Amine	ArI	Product	Yield %
1				99	16				99
2				96	17				99
3				95	18				99
4				99	19				89
5				98	20				95
6				96	21				70
7				94	22				25
8				99	23				22
9				98	24				80
10				98	25				50
11				95	26				61
12				99	27				58
13				99	28				50
14				89	29				50
15				84	30				58

(*continued on next page*)

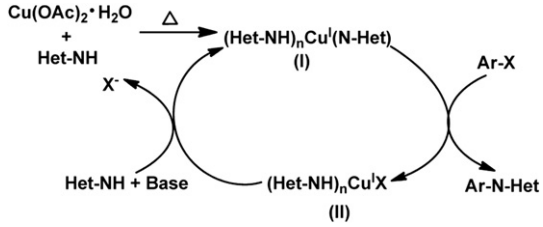
Table 3 (*continued*)

Entry[a]	Amine	ArI	Product	Yield[b] %	Entry	Amine	ArI	Product	Yield %
31				24					

[a] Reaction conditions: ArI (1.2 mmol), nitrogen-containing heterocycle compounds (1.0 mmol), Cs_2CO_3 (2 mmol), DMF (2.0 mL), and $Cu(OAc)_2 \cdot H_2O$ (1 mol %) at 110 °C for 24 h.
[b] Isolated yield.

in good to moderate yields. As shown in entries 4, 8, 12, 16, 20, 24, and 26, electron-deficient *p*-substituted aryl iodides were found to proceed in higher yields than those with electron-donating substituent groups. For example, lower yields (entries 23 and 25) were obtained for aryl iodides bearing electron-donating substituent groups relative to those of electron-withdrawing ones (entries 24 and 26). These results are comparable with those reported in the literature using CuI with chelating ligands as catalysts.[7–14] It is noted that readily available $Cu(OAc)_2 \cdot H_2O$ could also catalyze N-arylation of anilines (entries 29–31). This methodology presents the advantage of avoiding the separation of other ligands in the reaction system with high economy and efficiency.

The catalytic reaction mechanism for the above reactions is proposed as follows (Scheme 3). Firstly, heating the mixture of $Cu(OAc)_2 \cdot H_2O$ and *N*-containing heterocycle (Het-NH) may lead to the formation of the intermediate I, $(Het\text{-}NH)_nCu^I(N\text{-}Het)$. Secondly, the intermediate I may react with aryl iodide to give the N-arylation product and the intermediate II, $(Het\text{-}NH)_nCu^IX$. Thirdly, reaction of the intermediate II with Het-NH in the presence of base may yield the intermediate I again, thereby furnishing the catalytic cycle.



Scheme 3. Proposed catalytic mechanism.

3. Conclusions

In summary, the association of amine or *N*-containing heterocycle compounds from Cu(II) complexes via heating produced certain Cu(I) active species, which could efficiently catalyze the cross-coupling reactions of *N*-containing heterocycles with aryl iodides, affording the corresponding products in good yields. Simple $Cu(OAc)_2 \cdot H_2O$ salt was found to be an efficient catalyst with low catalyst loadings for such a reaction without extra organic ligands. This methodology can be applicable to many other substrates with *N*-containing heterocycles and aryl iodides bearing different steric and electronic groups.

4. Experimental

4.1. General

All reactions and manipulations were carried out under an oxygen-free nitrogen atmosphere with standard Schlenk techniques. Solvents were dried and degassed before use. Pyrazole, 3,5-dimethylpyrazole, 3-phenyl-1*H*-pyrazole, pyrrole, imidazole, triazole, indole, benzoimidazole, benzotriazole, carbazole, *p*-tolylamine, 4-nitro-phenylamine, pyridin-3-ylamine, iodo-benzene, 1-iodo-4-methyl-benzene, 1-iodo-4-methoxy-benzene, and 1-(4-iodo-phenyl)-ethanone were purchased from Aldrich. 5-Methyl-3-phenyl-1*H*-pyrazole, 5-(4-methoxyphenyl)-1*H*-pyrazole, 3-naphthalen-2-yl-1*H*-pyrazole, 4-(1*H*-pyrazol-3-yl)-pyridine, 3-thiophen-2-yl-1*H*-pyrazole, and 4,5-diphenyl-1*H*-pyrazole[21] were prepared according to literature procedures. ^1H NMR spectra were recorded at ambient temperature on a Varian UNITYplus-300 or 400 spectrometer. ^1H NMR chemical shifts were referenced to the solvent signal in DMSO-d_6 or $CDCl_3$. Elemental analyses for C, H, and N were performed on a Carlo-Erbo CHNO-S microanalyzer. The IR spectra (KBr disc) were recorded on a Nicolet MagNa-IR550 FT-IR spectrometer (4000–400 cm^{-1}). High-resolution mass spectra were obtained by using a Micromа GCT-TOF instrument. The uncorrected melting points were measured on a Mel-Temo II apparatus. Elemental analyses were performed on a Carlo-Erbo CHNO-S microanalyzer.

4.2. Preparation of 3-biphenyl-4-yl-1*H*-pyrazole

This was prepared in two steps from 1-biphenyl-4-yl-ethanone. In the first step, a mixture of 1-biphenyl-4-yl-ethanone (1.96 g, 10 mmol) and *N*,*N*-dimethylformamide-dimethyl acetal (4 mL) was refluxed for 2 h. After concentration in vacuo, recrystallization of the orange residue from hexane afforded a pale yellow powder of 1-biphenyl-4-yl-3-dimethylamino-propenone in 67% yield. ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 2.89 (s, 3H), 3.09 (s, 3H), 5.75 (d, J=12.0 Hz, 1H), 7.35 (t, J=7.2 Hz, 1H), 7.43 (t, J=7.2 Hz, 2H), 7.62 (t, J=7.2 Hz, 4H), 7.82 (d, J=12.4 Hz, 1 Hz, 1H), 7.98 (d, J=12.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 37.3, 45.1, 92.1, 126.8, 127.2, 127.7, 128.1, 128.9, 139.3, 140.5, 143.6, 154.3, 188.0. HRMS calcd for $C_{17}H_{17}NO$ 251.1310, found 251.1309. Anal. Calcd for $C_{17}H_{17}NO$: C 81.24, H 6.82, N 5.57; found: C 81.32, H 6.84, N 5.58. IR (KBr disk, cm^{-1}): 3442(m), 3072(w), 3031(w), 2984(w), 2913(w), 2868(w), 2800(w), 1638(s), 1603(m), 1563(m), 1535(s), 1479(m), 1416(m), 1385(w), 1308(m), 1279(m), 1236(m), 1188(m), 1115(m), 1051(m), 1005(m), 983(m), 898(s), 783(m), 756(s), 697(s). Mp: 140.0–141.6 °C. A mixture of 1-biphenyl-4-yl-3-dimethylamino-propenone (1.6 g, 6.4 mmol), ethanol (10 mL) and hydrazine hydrate (2 mL) was then refluxed for 4 h. After cooling to room temperature, the volatile species were removed in vacuo. The remaining yellow oil was re-dissolved in EtOH (20 mL) and the solution was dried over $MgSO_4$. The solvent was removed in vacuo to obtain a light yellow solid, which was recrystallized from toluene at −10 °C, giving colorless crystals. Yield: 1.27 g (91%). ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 6.61 (s, 1H), 7.32 (t, J=7.2 Hz, 1H), 7.40 (t, J=7.2 Hz, 2H), 7.56–7.60 (m, 5H), 7.80 (d, J=8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 102.8, 126.4, 127.1, 127.6, 128.9, 131.2, 133.6, 133.6, 133.6, 140.7, 140.9. HRMS calcd for $C_{15}H_{12}N_2$ 220.1000, found 220.1007. Anal. Calcd for $C_{15}H_{12}N_2$: C, 81.79; H, 5.49; N, 12.72.

Found: C, 81.32; H, 5.23; N, 12.82. IR (KBr disk, cm^{-1}): 3031(w), 2971(w), 1525(m), 1488(s), 1445(m), 1409(m), 1384(m), 1337(w), 1294(m), 1192(w), 1109(m), 1046(m), 1005(m), 954(s), 933(s), 841(s), 754(s), 722(m), 688(s), 608(m). Mp: 163.9–164.2 °C.

4.3. Preparation of 4-methyl-3-*p*-tolyl-1*H*-pyrazole

This was prepared in a similar manner to 3-biphenyl-4-yl-1*H*-pyrazole, except using 1-*p*-tolyl-propan-2-one as a starting material. For 4-dimethylamino-3-*p*-tolyl-but-3-en-2-one: ^1H NMR (400 MHz, DMSO-d_6, ppm): δ 1.97 (s, 3H), 2,29 (s, 3H), 2.96 (s, 6H), 6.82 (s, 1H), 7.17 (s, 4H). ^{13}C NMR (100 MHz, DMSO-d_6, ppm): δ 10.8, 20.7, 42.7, 104.1, 127.9, 128.2, 138.2, 139.1, 155.6, 194.4. HRMS calcd for $C_{13}H_{17}NO$ 203.1310, found 203.1308. Anal. Calcd for $C_{13}H_{17}NO$: C, 76.81; H, 8.43; N, 6.89. Found: C, 76.63; H, 8.11; N, 6.69. IR (KBr disk, cm^{-1}): 3455(m), 3116(w), 3010(w), 2923(w), 2771(w), 2695(w), 1641(s), 1382(m), 1575(s), 1535(m), 1431(s), 1382(w), 1364(w), 1326(s), 1240(m), 1206(w), 1027(m), 907(w), 868(m), 825(s), 751(s), 702(m), 617(m), 569(m). Mp: 89.5–91.5 °C. For 4-methyl-3-*p*-tolyl-1*H*-pyrazole: ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 2.20 (s, 3H), 2.36 (s, 3H), 7.40 (d, J=8.0 Hz, 2H), 7.34 (s, 1H), 7.46 (d, J=8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 9.8, 21.4, 112.6, 127.4, 129.3, 135.4, 135.6, 137.4, 144.8. HRMS calcd for $C_{11}H_{12}N_2$ 172.1000, found 172.1002. Anal. Calcd for $C_{11}H_{12}N_2$: C, 76.71; H, 7.02; N, 16.27. Found: C, 77.03; H, 6.76; N, 16.11. IR (KBr disk, cm^{-1}): 3468(m), 3197(w), 3148(w), 3059(m), 2964(w), 2917(w), 2891(w), 1618(w), 1513(s), 1462(m), 1442(w), 1385(m), 1336(m), 1304(m), 1273(m), 1172(m), 1111(s), 1081(m), 1013(m), 990(s), 948(s), 867(s), 823(s), 721(m), 692(m), 636(m). Mp: 87.2–88.7 °C.

4.4. Preparation of [Cu(napz)]$_3$

To a Pyrex glass tube (15 cm in length, 7 mm in inner diameter) was loaded $Cu(OAc)_2\cdot H_2O$ (0.0201 g, 0.1 mmol), 3-naphthalen-2-yl-1*H*-pyrazole (0.0396 g, 0.2 mmol), and ethanol (2 mL). The tube was then sealed and heated in an oven at 110 °C for 12 h to form colorless octahedral crystals of [Cu(napz)]$_3$, which were collected by filtration, washed with acetonitrile, and dried in air. Yield: 20 mg (76% based on $Cu(OAc)_2\cdot H_2O$). Anal. Calcd for $C_{39}H_{27}N_6Cu_3$: C, 60.81; H, 3.53; N, 10.91. Found: C, 60.70; H, 3.47; N, 10.79. IR (KBr disk, cm^{-1}): 3051(w), 1629(m), 1601(m), 1497(s), 1449(s), 1333(m), 1308(w), 1268(m), 1136(m), 1078(m), 960(w), 887(w), 854(m), 814(s), 755(s), 696(w), 649(w), 593(m), 471(m).

4.5. Preparation of [Cu(dphpz)]$_3$

Colorless plates of [Cu(dphpz)]$_3$ were prepared by a similar method used in the synthesis of [Cu(napz)]$_3$. Yield: 85% (based on $Cu(OAc)_2\cdot H_2O$). ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 6.81 (s, 1H), 6.96–7.45 (m, 10H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 119.4, 126.1, 128.2, 128.4, 128.5, 128.7, 133.6, 140.5, 141.0, 149.0, 149.7. Anal. Calcd for $C_{45}H_{33}N_6Cu_3$: C 63.70, H 3.92, N 9.91; found: C 63.63, H 4.36, N 9.71. IR (KBr disk, cm^{-1}): 3055(w), 3024(w), 1637(w), 1603(s), 1508(m), 1431(m), 1342(m), 1111(m), 1018(m), 967(m), 912(m), 831(m), 761(s), 697(s), 584(w), 515(w).

4.6. General catalytic procedure for the N-arylation of nitrogen-containing heterocycles with aryl iodides

To a solution of $Cu(OAc)_2\cdot H_2O$ (0.01 mmol) in DMF (2 mL) were added aryl iodide (1.2 mmol), nitrogen-containing heterocycle (1.0 mmol), and Cs_2CO_3 (2 mmol) under nitrogen atmosphere. The mixture was stirred at 110 °C for 24 h. After cooling to ambient temperature, the mixture was partitioned between water and ethyl acetate. The organic layer was separated, and the aqueous layer was extracted with ethyl acetate. The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by flash chromatography on silica gel.

4.6.1. 3-Naphthalen-2-yl-1-phenyl-1H-pyrazole (Table 1). ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 6.90 (d, J=2.4 Hz, 1H), 7.30 (t, J=7.6 Hz, 1H), 7.45–7.51 (m, 4H), 7.80 (d, J=8 Hz, 2H), 7.84 (d, J=8.4 Hz, 1H), 7.90 (d, J=8 Hz, 2H), 7.98 (d, J=2.4, 1 Hz), 8.11 (dd, J=8.6, 1.2 Hz, 1H), 8.34 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 105.4, 119.2, 124.3, 124.6, 126.1, 126.4, 126.5, 127.9, 128.3, 128.4, 128.5, 129.6, 130.7, 133.4, 133.7, 140.4, 153.0. HRMS calcd for $C_{19}H_{14}N_2$ 270.1157, found 270.1152. Anal. Calcd for $C_{19}H_{14}N_2$: C, 84.42; H; 5.22; N, 10.36. Found: C, 84.41; H, 5.24; N, 9.95. IR (KBr disk, cm^{-1}): 3052(w), 2962(w), 2925(w), 2853(w), 1725(w), 1598(s), 1524(s), 1517(m), 1381(m), 1319(w), 1261(s), 1098(m), 1045(w), 1023(w), 948(m), 895(m), 867(m), 802(s), 755(s), 690(m), 475(m).

4.6.2. 3-Biphenyl-4-yl-1-phenyl-1H-pyrazole (Table 2, entry 4). ^1H NMR (300 MHz, $CDCl_3$, ppm): δ 6.76 (d, J=2.4 Hz, 1H), 7.20–7.76 (m, 12H), 7.90 (d, J=2.4 Hz, 1H), 7.98 (d, J=8.4 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 105.2, 119.1, 126.3, 126.4, 127.1, 127.4, 128.1, 128.9, 129.5, 131.0, 132.2, 140.3, 140.8, 140.9, 152.6. HRMS calcd for $C_{21}H_{16}N_2$ 296.1313, found 296.1313. Anal. Calcd for $C_{21}H_{16}N_2$: C, 85.11; H, 5.44; N, 9.45. Found: C, 85.43; H, 5.61; N, 9.48. IR (KBr disk, cm^{-1}): 3051(w), 1597(s), 1519(m), 1501(m), 1441(m), 1411(m), 1356(m), 1155(m), 1125(w), 1043(s), 951(m), 904(m), 841(s), 750.7(s), 690(s), 502(w).

4.6.3. 4-Methyl-1-phenyl-3-p-tolyl-1H-pyrazole (Table 2, entry 7). ^1H NMR (300 MHz, $CDCl_3$, ppm): δ 2.28 (s, 3H), 2.38 (s, 3H), 7.19–7.26 (m, 3H), 7.41 (t, J=8.4 Hz, 2H), 7.66–7.73 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 10.5, 21.4, 116.2, 118.7, 125.9, 127.1, 127.6, 129.3, 129.5, 131.1, 137.5, 140.3, 151.8. HRMS calcd for $C_{17}H_{16}N_2$ 248.1313, found 248.1313. Anal. Calcd for $C_{17}H_{16}N_2$: C, 82.22; H, 6.49; N, 11.28. Found: C, 81.93; H, 6.51; N, 11.18. IR (KBr disk, cm^{-1}): 3047(w), 2964(w), 2917(w), 2860(w), 1637(w), 1598(s), 1554(m), 1506(s), 1458(m), 1405(m), 1384(w), 1342(w), 1240(m), 1064(m), 954(s), 899(m), 823(s), 724(s), 757(s), 724(m), 689(s).

4.6.4. 4-(1-Phenyl-1H-pyrazol-3-yl)-pyridine (Table 2, entry 9). ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 6.81 (d, J=2.4 Hz, 1H), 7.30 (t, J=7.2 Hz, 1H), 7.45 (t, J=8 Hz, 2H), 7.73–7.77 (m, 4H), 7.94 (d, J=2.4 Hz, 1H), 8.64 (d, J=3.2 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 105.7, 119.2, 120.1, 127.0, 128.5, 129.5, 139.9, 140.4, 150.2, 150.3. HRMS calcd for $C_{14}N_{11}N_3$ 221.0953, found 221.0953. Anal. Calcd for $C_{14}H_{11}N_3$: C, 76.00; H, 5.01; N, 18.99. Found: C, 75.59; H, 4.92; N, 18.67. IR (KBr disk, cm^{-1}): 3060(w), 1598(s), 1526(m), 1503(m), 1444(m), 1416(m), 1372(m), 1309(m), 1267(m), 1174(m), 1117(m), 1072(w), 1046(s), 988(m), 909(m), 834(m), 759(s), 690(s), 512(m).

4.7. X-ray diffraction crystallography

Single crystals of **2** and **3** were obtained directly from the above preparations. The measurements were made on a Rigaku Mercury CCD X-ray diffractometer by using graphite monochromated Mo Kα (λ=0.71073 Å). Single crystals of **2** and **3** were mounted with grease at the top of a glass fiber. Compound **3** was cooled to 223 K in a liquid-nitrogen stream while **2** was kept at 293 K. A colorless block of **2** with dimensions 0.20 mm×0.22 mm×0.26 mm, and a colorless block of **3** with dimensions 0.10 mm×0.15 mm×0.20 mm were mounted at the top of a glass fiber. The collected data were reduced by the program Crystalclear (Rigaku and MSC, Ver.1.3, 2001). The reflection data were also corrected for Lorentz and polarization effects.

The structures of **2** and **3** were solved by direct method applying SHELXS-97 program and refined by full-matrix least-squares on F^2.[22] The atoms C(10), C(11), C(12), C(13), and C(16) are disordered over

two sites with an occupancy ratio of 0.50:0.50. All the non-hydrogen atoms were refined on F^2 anisotropically by full-matrix least-squares method. All hydrogen atoms were introduced at the calculated positions and included in the structure-factor calculations. All calculations were performed on a Dell workstation utilizing the crystalstructure crystallographic software package (Rigaku and MSC, Ver. 3.60, 2004). Compound **2**: $C_{39}H_{27}Cu_3N_6$, M_r=770.31, triclinic, space group $P\bar{1}$, a=10.607(5), b=10.627(5), c=15.140(7) Å, α=106.085(11)°, β=98.189(9)°, γ=100.192(9)°, V=1580.6(13) Å^3, Z=2, D_c=1.618 g/cm^3, μ=2.040 mm^{-1}, 15,216 reflections measured, 5740 unique reflections (R_{int}=0.0360), 3490 observed reflections ($I>2\sigma(I)$), 428 parameters, R_1=0.0921, wR_2=0.1858, S=1.074. Compound **3**: $C_{90}H_{66}Cu_6N_{12}$, M_r=1696.79, triclinic, space group $P\bar{1}$, a=9.7434(10), b=15.6013(11), c=25.995(3) Å, α=81.746(8)°, β=87.987(11)°, γ=75.311(9)°, V=3782.7(6) Å^3, Z=2, D_c=1.490 g/cm^3, μ=1.713 mm^{-1}, 32,570 reflections measured, 14,014 unique reflections (R_{int}=0.0700), 7453 observed reflections ($I>2\sigma(I)$), 974 parameters, R_1=0.0921, wR_2=0.1602, S=1.108.

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Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2011.05.025.

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