New Diimine−Copper Complexes: An Efficient and Simple Catalyst System for Buchwald *N*-Arylation of Indole

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Summary: A new method of N-arylation of indole with (±)-trans-2,3-diarylpiperazines/copper(I) halide and aryl halides is described. Whereas electron-donating substituents in the phenyl group enhance the reactivity, the yields are lower with electron-withdrawing substituents. Oxidative cleavage of piperazines in the presence of oxygen to diimines has been observed under these reaction conditions. On the basis of this observation, a new catalyst system using diimines and CuI was also developed for the N-arylation of indole.

Introduction

The *N*-aryl nitrogen heterocycle motif is present in a multitude of bioactive natural products and pharmaceutically interesting compounds.[1] Various strategies have been developed for the *N*-arylation of heterocycles. The century old copper-catalyzed Ullmann reaction[2a,2b] has limitations because of the harsh reaction conditions such as high temperatures, requirement of stoichiometric amounts of copper reagents, long reaction times, and low yields.[2c] The palladium-catalyzed *N*-arylation is an alternative method under mild reaction conditions.[3] The copper-catalyzed Ullmann reactions have seen a gradual expansion in the past few years and by the correct choice of copper sources, bases, ligands, and other additives, several mild and efficient methods have been reported for the *N*-arylation of indoles.[4,5] Ligands based on diamines,[6] oxime-phosphine oxide,[7] aminoacids,[8] phosphoramidite,[9] and proline (pyrrolidinylmethylimidazole)[10] have been introduced to promote copper-catalyzed *N*-arylation of indoles and other heterocycles. In this paper, we report a simple reagent system consisting of the easily accessible (±)-*trans*-2,3-diarylpiperazines and copper(I) halides, which catalyzes the *N*-arylation of indoles in the presence of base. Also, *N*-arylation catalyzed by a diimine copper complex prepared in situ is also described.

Chart 1

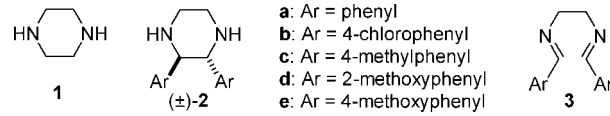
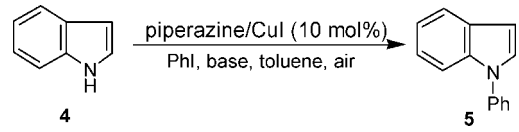


Table 1. (±)-2,3-Diarylpiperazines/CuI-Catalyzed *N*-Phenylation of Indole with Iodobenzene and Base[a]



			yield (%)[b]	
entry	piperazine	condition	K_2CO_3[c]	K_3PO_4[d]
1	**1**	reflux, 24 h	70	75
2	**2a**	reflux, 24 h	44	52
3	**2b**	reflux, 24 h	39	45
4	**2c**	reflux, 24 h	63	74
5	**2d**	reflux, 24 h	90	94
6	**2e**	reflux, 24 h	93	96
7	**2e**	rt, 48 h		<5

[a] Unless noted otherwise, all the reactions were carried out with 0.1 mmol of piperazine, 0.1 mmol of CuI, 1.0 mmol of indole, and 1.5 mmol of PhI in toluene (2 mL). [b] Yields are of the isolated product and the product was identified by using spectroscopic data (IR, ^{1}H, ^{13}C NMR) and comparison with reported data.[12] [c] With 5.0 mmol of K_2CO_3. [d] With 2.0 mmol of K_3PO_4.

Results and Discussion

The (±)-2,3-diarylpiperazines **2** (Chart 1) have been readily synthesized in good yields by the intramolecular reductive coupling of the corresponding diimines **3** in the presence of Zn and $Ti(O^iPr)_2Cl_2$ reagent system developed in this laboratory.[11]

These piperazines **2** as well as simple piperazine **1** have been examined for use in the *N*-phenylation studies. The product was obtained by using the catalyst in 10 mol % (Table 1). Simple piperazine **1** gave the product *N*-phenylindole in 75% yield (Table 1, entry 1). When the *N*-phenylation of indole was carried out with (±)-2,3-diphenylpiperazine and CuI in the presence

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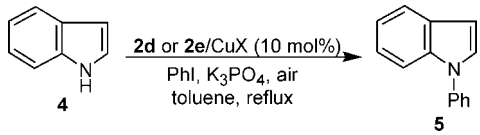
Table 2. (±)-2,3-Diarylpiperazines/CuX-Catalyzed *N*-Phenylation of Indole with PhI and K_3PO_4[a]



entry	piperazine	CuX	condition	yield (%)[b]
1	**2d**	CuI	reflux, 24 h	94
2	**2d**	CuBr	reflux, 48 h	62
3	**2d**	CuCl	reflux, 48 h	58
4	**2e**	CuI	reflux, 24 h	96
5	**2e**	CuBr	reflux, 48 h	67
6	**2e**	CuCl	reflux, 48 h	55

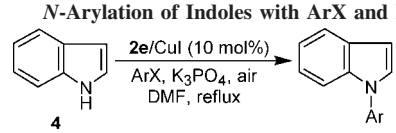
[a] Unless noted otherwise, all the reactions were carried out with 0.1 mmol of piperazine **2d** or **2e**, 0.1 mmol of CuX, 1.0 mmol of indole, K_3PO_4 (2.0 mmol), and 1.5 mmol of PhI in toluene (2 mL). [b] Yields are of the isolated product and the product was identified by using spectroscopic data (IR, ^1H, ^{13}C NMR) and comparison with reported data.[12]

of PhI and K_2CO_3, the product was obtained in 44% yield (Table 1, entry 2). The yield was improved up to 52% by using K_3PO_4 as a base (Table 1, entry 2). The yields were still low when (±)-*trans*-2,3-bis(4-chlorophenyl)piperazine and CuI were used (Table 1, entry 3). By using K_3PO_4 as a base, better yields (up to 74%) were realized in (±)-*trans*-2,3-bis(4-methylphenyl)piperazine- and CuI-catalyzed reactions (Table 1, entry 4). Piperazines with methoxy substitution in the aryl group gave the *N*-phenylindole in very good yields (Table 1, entries 5 and 6). The (±)-*trans*-2,3-bis(4-methoxyphenyl)piperazine/CuI/K_2CO_3 system gave the *N*-phenyl product in up to 93% yield. Quantitative yield was obtained by using K_3PO_4 in place of K_2CO_3 (Table 1, entry 6). When the reaction was carried out at 25 °C, only a trace (<5%) of product was obtained (Table 1, entry 7). Ultrasonication of the reaction mixture for 1 h in a Sonorex washing bath (BANDELIN electronic, type RK31H, 120 W, 35 kHz) did not give the product and the starting materials were recovered.

The enhanced reactivity of the complex with use of the ligands **2d** and **2e** may be due to the presence of the methoxy group in the phenyl ring. Though the substituent in the phenyl ring is far away from the reaction center, still it seems to exercise electronic control over the reactivity through the aryl group. Such systems and their effect on reactivity have also been noted by others.[13] For example, in a recent study with sulfonylated diarylethylenediamines−ruthenium complex in asymmetric transfer hydrogenation of α-tetralone, greater reactivity was obtained for methoxyphenyl derivatives compared to phenyl-substituted diamine complex, even though enantioselectivities were the same.

The *N*-phenylation was further examined with other copper halides (Table 2) by using ligands **2d** and **2e**. In the presence of CuCl or CuBr, *N*-phenylindole was obtained in up to 67% yield with use of ligand **2d** or **2e**. In these cases the reaction required 48 h reflux in toluene.

Table 3. (±)-2,3-Bis(4-methoxyphenyl)piperazine (2e)-Catalyzed *N*-Arylation of Indoles with ArX and K_3PO_4[a]



6: Ar = 1-naphthyl,
7: Ar = 4-methylphenyl,
8: Ar = 4-methoxyphenyl

entry	ArX	solvent	yield (%)[b]
1	1-bromonaphthalene	toluene	
2	1-bromonaphthalene	toluene + DMF (1:1)	20
3	1-bromonaphthalene	DMF	82
4	4-bromotoluene	DMF	95
5	4-chloroanisole	DMF	<5

[a] Unless noted otherwise, all the reactions were carried out with 0.05 mmol of piperazine **2e**, 0.05 mmol of CuI, 0.5 mmol of indole, K_3PO_4 (1.0 mmol), and 1.0 mmol of ArX in solvent (2 mL), reflux 24 h. [b] Yields are of the isolated product and the product was identified by using physical constant and spectroscopic data (mp, IR, ^1H, ^{13}C NMR) and comparison with reported data.[14]

The reaction was also examined by using other aryl halides and the ligand **2e** (Table 3). In the arylation with 1-bromonaphthalene, no product was obtained by using toluene as a solvent (Table 3, entry 1). When a toluene/DMF solvent mixture (1:1 v/v) was used, arylated product was obtained, but in lower yields (20%). By using DMF alone as solvent, the products were obtained in good yields. Whereas 1-bromonaphthalene yielded the *N*-aryl product in 82% yield, with 4-bromotoluene, an electron-rich aryl bromide, the product was obtained in 95% yield. Only a trace amount of product was obtained in the reaction of 4-chloroanisole in the presence of (±)-2,3-bis(4-methoxyphenyl)piperazine/CuI/K_3PO_4.

The reason for the need of DMF as a solvent for ArBr could be explained considering the polarizing nature of the solvent. Whereas the reaction using the highly polarized C−I bond takes place in toluene, the solvent DMF is needed in the case of ArBr.

The *N*-arylation reaction can be explained by two types of mechanisms: (a) the oxidative addition/reductive elimination mechanism proposed by Cohen[15a] in 1974 and (b) the π-complex mechanism proposed by Paine[15b] in 1987.

Initially, a piperazine−copper complex of the type **9** or a similar binuclear complex could be formed and catalyzed the *N*-arylation. It is expected that the diarylpiperazines with electron-donating substituents favor the formation of the complex **10** and higher yields were observed (Table 1). The oxidative addition and formation of complex **10** is more feasible in the more polar solvents by the polarization of the C−X bond of aryl halides (Table 3). Thus, the results obtained in our studies support the oxidative addition/reductive elimination mechanism (Scheme 1a). When the piperazine and CuX are heated under reflux in the presence of base, the complex **9** or a similar derivative could be formed. Then, the ArX oxidatively adds to the complex **9** across the C−X bond to form the complex **10**. The replacement of X with nucleophile followed by reductive elimination affords the *N*-arylated product and the piperazine/Cu complex **9** enters into the catalyst cycle again.

To further understand the nature of the complex formed during the reaction, CuI, (±)-2,3-bis(4-methoxyphenyl)piperazine **2e**, and K_3PO_4 were heated under reflux for 12 h in toluene solvent. We could not isolate any piperazine copper complex but instead observed that the *N*,*N*′-bis(4-methoxybenzylidene)-ethylenediamine is produced via a C−C bond cleavage of the (±)-2,3-bis(4-methoxyphenyl)piperazine. The C−C bond cleav-

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Scheme 1. Plausible Mechanisms for the *N*-Arylation Catalyzed by Piperazine/CuX

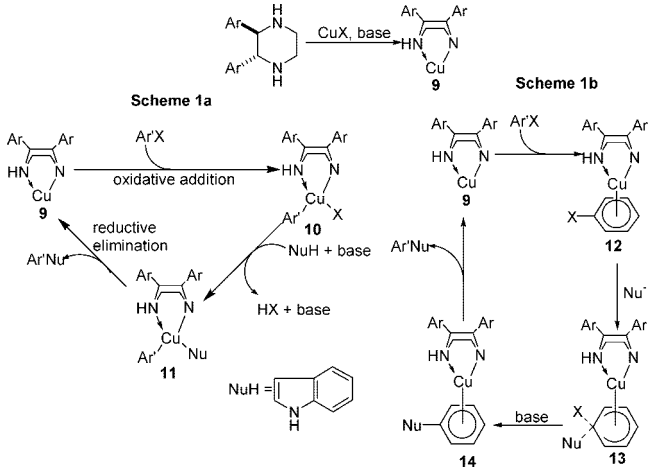
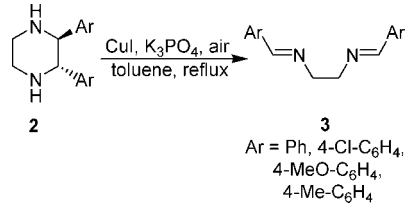


Table 4. Conversion of Piperazine to Diimine[a]



entry	2,3-diarylpiperazine	diimine	conversion (%)[b]
1	**2a**	**3a**	85
2	**2b**	**3b**	25
3	**2c**	**2c**	87
4	**2e**	**3e**	>99
5[c]	**2c**	**2c**	<20
6[d]	**2c**	**2c**	85

[a] All the experiments were carried out with 2,3-diarylpiperazine (0.5 mmol), CuI (0.5 mmol), K_3PO_4 (1.0 mmol), and toluene (2 mL). [b] The percent of conversion was obtained by comparing the integration values of the corresponding ^{1}H NMR peaks of piperazine and diimine. [c] The experiment was carried out under nitrogen. [d] 10 mol % of CuI with respect to piperazine was used.

age and the conversion to diimine were also observed with other piperazines (Table 4). In the case of (±)-2,3-bis(4-methoxyphenyl)piperazine, complete conversion was observed (Table 4, entry 4). For (±)-2,3-diphenylpiperazine, the conversion is 85% (Table 4, entry 1), and for (±)-2,3-bis(4-chlorophenyl)piperazine, the conversion to diimine is 25% (Table 4, entry 2). In the reaction of (±)-2,3-bis(4-methylphenyl)piperazine with 10 mol % of CuI, 85% conversion to diimine was observed (Table 4, entry 6).

The oxidative cleaving of the C−C bond can be explained by considering the mechanism shown in Scheme 2. The reactivity of Cu(I) complexes with O_2 and the subsequent reactivity of the Cu–O_2 species have been well studied.[16] We have observed that when the reaction was carried out in the absence of O_2, the conversion of piperazine to diimine is very low (Table 4, entry 5). Presumably, the cleavage of piperazine is mediated by O_2 as outlined in Scheme 2. Formation of the complex **15** would be less favored with chloro substituents in the phenyl ring. Consequently, the conversion to the diimine is less favored. Hence, in the oxidative C−C bond cleavage reaction of piperazine **2b**, the conversion to diimine **3b** is very low (Table 4, entry 2) compared to that of piperazine **2e**.

We have also carried out the *N*-arylation of indole using the diimine and CuI. With this system, the *N*-phenylindole was obtained in similar or even higher yields in some cases (Table 5).

Scheme 2. Plausible Mechanisms for the Oxidative Cleavage of the C−C Bond

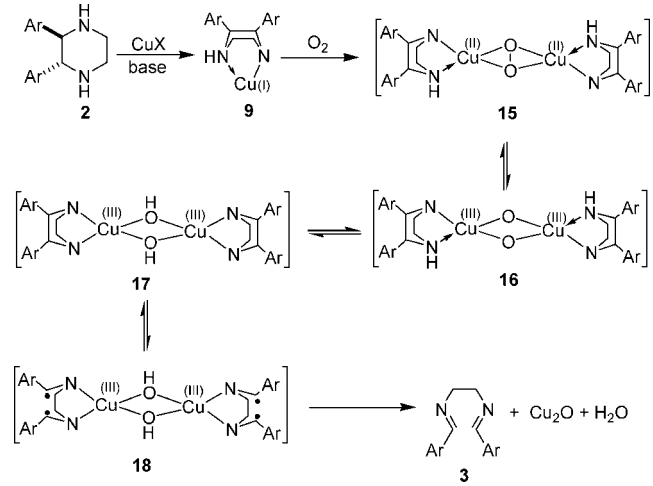
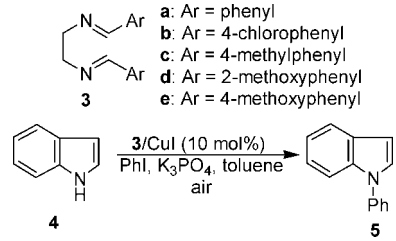


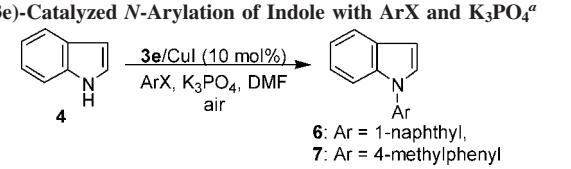
Table 5. Diimine/CuI-Catalyzed *N*-Phenylation of Indole with PhI and K_3PO_4[a]



entry	ligand	condition	yield (%)[b]
1	**3a**	reflux, 24 h	85
2	**3a**	rt, 48 h	
3	**3b**	reflux, 24 h	78
4	**3c**	reflux, 24 h	90
5	**3d**	reflux, 24 h	93
6	**3e**	reflux, 24 h	95

[a] Unless noted otherwise, all the reactions were carried out with 0.05 mmol of diimine **3**, 0.05 mmol of CuI, 0.5 mmol of indole, and 0.75 mmol of PhI in toluene (2 mL). [b] Yields are of the isolated product and the product was identified using spectroscopic data (IR, ^{1}H, ^{13}C NMR) and comparison with reported data.[12]

Table 6. *N,N′*-Bis(4-methoxybenzylidene)ethylenediamine (3e)-Catalyzed *N*-Arylation of Indole with ArX and K_3PO_4[a]



entry	ArX	condition	yield (%)[b]
1	1-bromonaphthalene	reflux, 24 h	82
2	4-bromotoluene	reflux, 24 h	95
3	4-chloroanisole	reflux, 24 h	<5

[a] Unless noted otherwise, all the reactions were carried out with 0.05 mmol of diimine **3e**, 0.05 mmol of CuI, 0.5 mmol of indole, and 1.0 mmol of ArX in DMF (2 mL). [b] Yields are of the isolated product and the products were identified by using physical constant and spectroscopic data (mp, IR, ^{1}H, ^{13}C NMR) and comparison with reported data.[14]

The *N*-arylation with the diimine−copper complex was studied by using different aryl halides and the diimine **3e** (Table 6). The yields of the product obtained were quite similar to the yields obtained by using (±)-2,3-bis(4-methoxyphenyl)piperazine **2e** (Table 3). The *N*-arylindoles were obtained in very good yields by using DMF solvent. With this catalyst also, 4-chloroanisole did not react. No product was obtained when the reaction was carried out at room temperature even under ultrasonication.

Chart 2

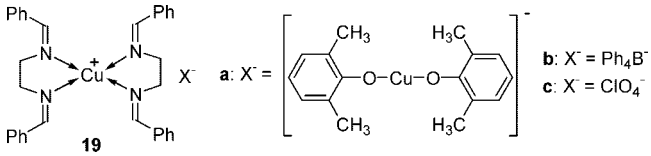
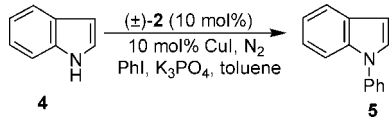


Table 7. *N*-Phenylation of Indole under N_2[a]



entry	2,3-diarylpiperazine	condition	yield (%)[b]	% conversion of piperazine to diimine[c]
1	(±)-**2a**	reflux, 24 h	62	3
2	(±)-**2b**	reflux, 24 h	47	
3	(±)-**2c**	reflux, 24 h	85	5

[a] All the reactions were carried out with 0.05 mmol of piperazine **2**, 0.05 mmol of CuI, 0.5 mmol of indole, and 0.75 mmol of PhI in toluene (2 mL) under nitrogen. [b] Yields are of the isolated product and the product was identified by using spectroscopic data (IR, ^{1}H, ^{13}C NMR) and comparison with reported data.[12] [c] The percent of conversion of piperazine to diimine was obtained by comparing the integration values of the corresponding ^{1}H NMR peaks of piperazine and diimine.

A plausible mechanism for the diimine−copper complex-catalyzed *N*-arylation of indole is given in Scheme 3. Formation of the diimine−copper(I) complexes **19** was reported with other anions (Chart 2).[17] Accordingly, the formation of a similar complex **20** is not entirely unexpected.

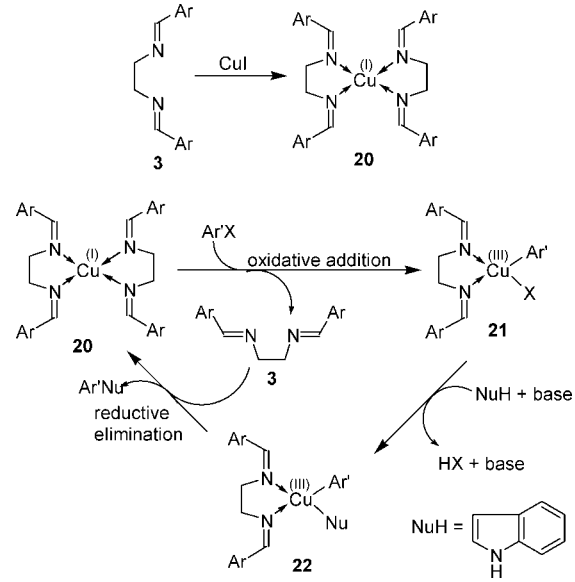
N-Phenylation of indole with 2,3-diarylpiperazines **2** was also examined under N_2. In these runs, the *N*-phenyl product was obtained in up to 85% yield (Table 7). Also, in these cases, it was found that piperazines were cleaved to only a small extent, 0–5% (Table 7). Clearly, both the piperazine ligand (Scheme 1) and the diimine ligand (Scheme 3) are involved in the formation of active catalysts in the *N*-arylation reaction.

In conclusion, we have developed a new catalyst system consisting of easily accessible (±)-*trans*-2,3-diarylpiperazines copper complex for the *N*-arylation of indole using different aryl halides. The oxidative addition/reductive elimination mechanism is proposed based on the results obtained. It was observed that the piperazines are oxidatively cleaved to diimines in the presence of oxygen under these reaction conditions. On the basis of this observation, a new catalyst system diimine/CuI was also developed for the *N*-arylation of indole.

Experimental Section

Representative Procedure for the *N*-Arylation of Indoles Catalyzed by Piperazine/CuX. In a 5 mL round-bottomed flask equipped with a reflux condenser were placed (±)-2,3-diarylpiperazine (0.1 mmol), CuI (19.0 mg, 0.1 mmol), K_3PO_4 (430 mg, 2.0 mmol), indole (117 mg, 1 mmol), and toluene (2 mL) and the solution was stirred for 10–15 min. To this was added PhI (310 mg, 1.5 mmol) then the mixture was heated under reflux for 24 h. The reaction mixture was cooled and filtered through a small silica gel column and washed with EtOAc. The filtrate was evaporated and the product was purified by column chromatography (Silica, hexane/EtOAc = 99.5/0.5). *N*-Phenylindole **5**: IR (neat) 3055, 1597, 1498 cm^{-1}; ^{1}H NMR (200 MHz, CDC1$_3$) δ 6.70 (d, 1H, J = 4.0 Hz), 7.21–7.69 (m, 10H); ^{13}C NMR (50 MHz, CDC1$_3$) δ 103.8, 110.7, 120.6, 121.4, 122.6, 124.6, 126.6, 128.1, 129.6, 129.8, 136.1,140.0. *N*-(1-Naphthyl)indole **6**: mp 74–76 °C (lit.[14] mp 76–78 °C); IR (KBr) 3048, 1593, 1578, 1508 cm^{-1}; ^{1}H NMR (200 MHz, CDC1$_3$) δ 6.78 (d, 1H, J = 2.8 Hz), 7.03–7.78 (m, 9H), 7.76 (d, 1H, J = 6.8 Hz), 7.96 (br s, 1H), 8.00 (d, 1H, J = 2.8 Hz); ^{13}C NMR (50 MHz, CDC1$_3$) δ 103.0, 110.9, 120.2, 121.0, 122.2, 123.5, 125.2, 125.6, 126.7, 127.0, 128.3, 128.5, 129.8, 130.7, 134.6, 136.2, 138.1. *N*-(4-methylphenyl)indole **7**: IR (neat) 3032, 2922, 2860, 1608, 1520, 1456 cm^{-1}; ^{1}H NMR (200 MHz, CDC1$_3$) δ 2.44 (s, 3H), 6.67 (d, 1H, J = 4.0 Hz), 7.19–7.71 (m, 9H); ^{13}C NMR (50 MHz, CDC1$_3$) δ 21.1, 103.3, 110.6, 120.3, 121.1, 122.3, 124.4, 128.1, 129.3, 130.2, 136.1, 136.4, 137.4.

Scheme 3. Plausible Mechanisms for the *N*-Arylation Catalyzed by Diimine/CuX



Representative Procedure for the Oxidative Cleavage of (±)-*trans*-2,3-Diarypiperazine 2. In a 5 mL round-bottomed flask were placed toluene (2 mL), CuI (100 mg, 0.5 mmol), K_3PO_4 (210 mg, 1.0 mmol), and 2,3-diarylpiperazine **3** (0.5 mmol) then the solution was heated under reflux for 12 h. After the reaction mixture was cooled, the inorganic solid was filtered through a small silica gel column and the filtrate was concentrated under reduced pressure. The percent of conversion of piperazine to diimine was calculated from the integration value of the corresponding ^{1}H NMR signals of diarylpiperazine and diimine.

Representative Procedure for the *N*-Arylation of Indoles Catalyzed by Diimine/CuX. In a 5 mL round-bottomed flask equipped with a reflux condenser were placed *N*,*N*′-dibenzylidene-ethylenediamine (12 mg, 0.05 mmol), CuI (10 mg, 0.05 mmol), K_3PO_4 (215 mg, 1.0 mmol), indole (60 mg, 0.5 mmol), and toluene (2 mL). To this solution was added PhI (310 mg, 1.5 mmol) then the mixture was heated under reflux for 24 h. The reaction mixture was cooled and filtered through a small silica gel column and washed with EtOAc. The filtrate was evaporated and the product was purified by column chromatography (Silica, hexane/EtOAc = 99.5/0.5).

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