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PAPER

A general and mild Cu-catalytic N-arylation of iminodibenzyls and iminostilbenes using unactivated aryl halides†‡

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A ligand-free, highly efficient Cu-catalytic N-arylation of iminodibenzyl and iminostilbene derivatives with a broad scope of unactivated aryl halides under mild conditions has been developed for the first time. Moreover, the first Ni-based catalytic system was also applied to the N-arylation of pre-existing derivatives. These novel protocols provide facile and convenient access to the construction of dibenzazepines and offer promising alternatives to the widely used palladium catalysts.

Iminodibenzyl and iminostilbene analogues are value-adding building blocks for the construction of drug molecules[1] and notably the synthesis of organic functional materials, including organic light emitting diodes (OLEDs) (Scheme 1).[2] The applications have generated tremendous attention and demands to develop efficient, practical and general processes for the preparation of these functionalized ring derivatives.

In recent years, a series of synthetic methods, mainly catalyzed by noble-metal catalytic systems, for the construction of iminodibenzyls and iminostilbenes have been reported, such as the cyclization of amines[3] and anilines,[4] or multi-step

Scheme 1 The represented dibenzazepines.

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† Dedicated to Professor Qizhong Zhou on the occasion of his 45th birthday.

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syntheses.[5] Recently, classic copper-catalysed Friedel–Crafts cycliacylations have also been applied to the synthesis of these functionalized rings.[6] However, the above approaches still have obvious limitations: (1) the cyclization reactions are often limited by the availability of manufacturable substrates; (2) the multi-step processes always suffer from drawbacks such as narrow functional group compatibility and low catalytic efficiency; and (3) the Friedel–Crafts cycliacylations typically require harsh reaction conditions (excessive reagents and super-lewis acid catalysts).[6a]

An alternative, but less developed synthetic strategy for iminodibenzyl and iminostilbene analogues is to use aryl halides as the arylating agents. Industrially, aryl halides are the preferred reagents because they are widely available and really low-cost. However, the N-arylation of these dibenzazepines with aryl halides is still rare, and mainly occupied by the precious metal Pd.[2a,e,i,7–10] Very recently, Buchwald reported that a Ruphos-based palladacycle complex catalyses the N-arylation of iminodibenzyls and iminostilbenes with aryl halides.[11] The reaction occurred at 80–100 °C in 1,4-dioxane with 0.1–1 mol% Pd in the presence of 1.1–2.2 equivalents of Li(NSiMe3)2. This work represents a breakthrough in the catalytic N-arylation of iminodibenzyls and iminostilbenes. However, to the best of our knowledge, the earth-abundant, environmentally benign, and low-cost base-metal catalyzed N-arylation of these functionalized rings has remained undisclosed, although a stoichiometric arylating process with copper under high temperature (180–200 °C) has been reported.[2a] So, for dibenzazepine derivatives, it is still necessary to develop more efficient and practical methods.

Herein, we firstly demonstrate that copper oxide is remarkably active for the N-arylation of iminodibenzyls and iminostilbenes with unactivated aryl iodides, bromides and even aryl chlorides under mild conditions, providing the desired products in moderate to excellent yields. Furthermore, the first Ni-catalyzed arylation of dibenzazepines was also developed.

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Our initial studies focused on the direct *N*-arylation of iminodibenzyl (**1a**) with bromobenzene (**2a**) as a coupling partner by testing the catalytic activities of commercially available copper catalysts (Table 1, entries 1–5). Gratifyingly, the reaction with copper oxide showed the topmost efficiency and gave the desired product **3a** in 71% yield (entry 1). More importantly, after evaluating a variety of bases, the catalytic efficiency was improved by the substitution of the base from KOH to KO*t*Bu (95%, entry 9), while the processes using KOMe, KOAc and K$_2$CO$_3$ showed unsatisfactory yields (entries 6–8). Further optimization revealed that the solvents also have enormous impact on this arylation reaction. DMSO proved to be the best medium among the solvents studied, giving 95% of **3a** in the presence of 5 mol% CuO at 100 °C (entry 9). However, when using other solvents, including toluene (PhMe), THF, DMF, 1,4-dioxane, CH$_3$CN or CH$_3$OH, the reactions were not suitable for arylation (entries 10–15). To our delight, the high activity of CuO allowed this transformation to proceed at 80 °C, furnishing **3a** in 95% yield (entry 16). On the other hand, it should be noted that this process will not proceed at 25 °C or in the absence of copper catalysts (entries 17–18).

Using the highly active copper catalyst and optimal reaction conditions (Table 1, entry 16), the substrate scope of the reaction was explored by altering the dibenzazepines and aryl halides (Table 2). Importantly, the aryl bromides, iodides, or

even aryl chlorides containing electron-deficient groups (**2b** and **2c**) or electron-rich groups (**2d–2h**) were all well-tolerated in this transformation, offering the products in moderate to excellent yields. Furthermore, the amine- or phenyl-substituted

Table 2 The Cu-catalyzed *N*-arylation of dibenzazepines[a]
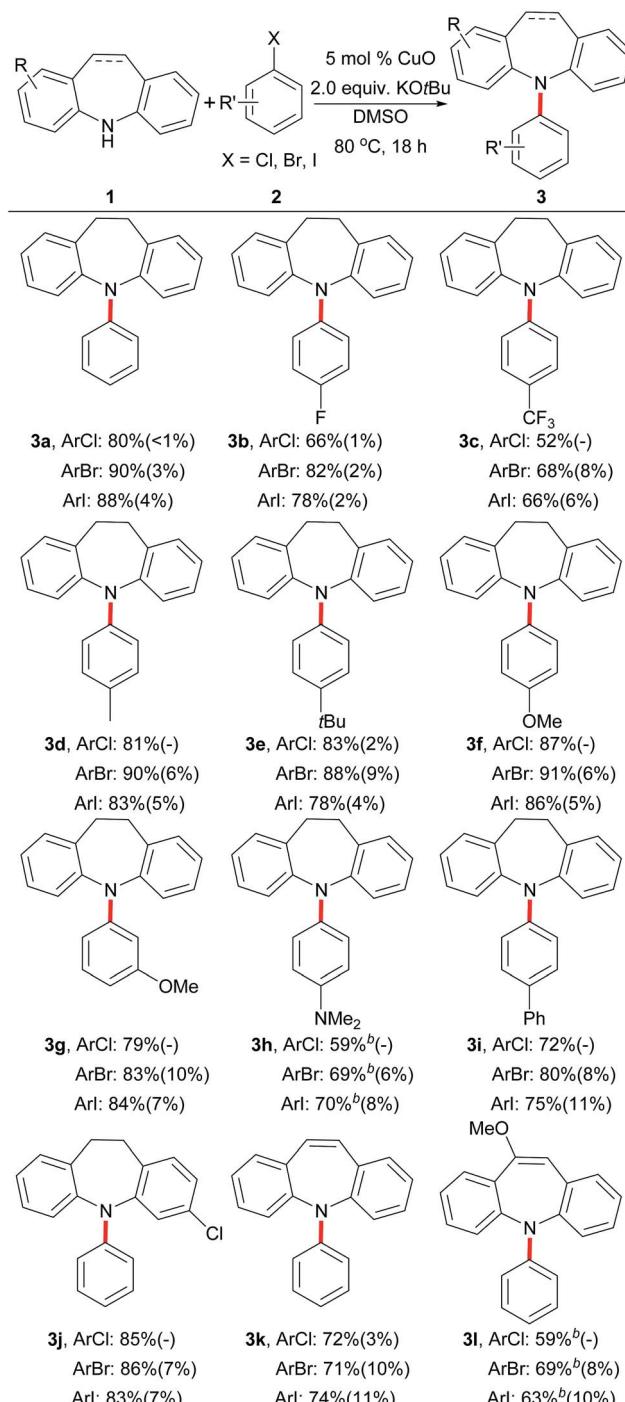
Table 1 The optimization of the reaction conditions[a]

Entry	[Cu]	Solvent	Base	T (°C)	Yield[b] (%)
1	CuO	DMSO	KOH	100	71
2	CuCl	DMSO	KOH	100	42
3	CuCN	DMSO	KOH	100	35
4	Cu(OAc)$_2$	DMSO	KOH	100	47
5	CuI	DMSO	KOH	100	42
6	CuO	DMSO	KOMe	100	40
7	CuO	DMSO	KOAc	100	0
8	CuO	DMSO	K$_2$CO$_3$	100	0
9	CuO	DMSO	KO*t*Bu	100	95
10	CuO	PhMe	KO*t*Bu	100	7
11	CuO	THF	KO*t*Bu	100	16
12	CuO	DMF	KO*t*Bu	100	77
13	CuO	1,4-Dioxane	KO*t*Bu	100	19
14	CuO	CH$_3$CN	KO*t*Bu	100	0
15	CuO	CH$_3$OH	KO*t*Bu	100	0
16	CuO	DMSO	KO*t*Bu	80	95(90)
17	CuO	DMSO	KO*t*Bu	25	0
18	—	DMSO	KO*t*Bu	25	0

[a] Reaction conditions: iminodibenzyl (1.0 mmol), bromobenzene (2.0 mmol), [Cu] (50 μmol), base (2.0 mmol) and solvent (2.0 mL) under Ar atmosphere at 80–100 °C for 18 h. [b] The GC yield based on iminodibenzyl (**1a**) with mesitylene as an internal standard, and the isolated yield is in parentheses.

[a] Reaction conditions: **1** (1.0 mmol), **2** (2.0 mmol), CuO (50 μmol, 5 mol%), KO*t*Bu (2.0 mmol) and THF (2.0 mL) under Ar atmosphere at 80 °C for 18 h; the yields of the isolated products are shown; the approximate ArH yields in the parentheses were estimated by GC analysis. [b] CuO (0.1 mmol, 10 mol%), at 100 °C.
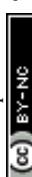
substrates (**2h** and **2i**) also proceeded smoothly with iminodibenzyl and produced chloroiminodibenzyl, which also underwent arylation smoothly using the standard conditions. Moreover, the yields of the arylating products in most cases indicate that the reaction occurred more smoothly when using

an aryl bromide as the arylating partner. However, the introduction of a stronger electron-withdrawing group (–CF₃) at the *para*-position of the aryl halides gave reduced yields of the corresponding products (**3c**). In addition, iminostilbenes are suitable substrates in the same arylation reaction, as demonstrated by the coupling with bromo-, iodo- or even chlorobenzene to form **3k** and **3l** in moderate to useful yields.

Similarly, nickel-based catalysts are also recognized in C–N bond-formation reactions, constituting an essential part of the amination methodologies.[12] Moreover, the catalytic *N*-arylation of iminodibenzyls and iminostilbenes has not been disclosed so far. Therefore, we focused our attention on developing the *N*-arylation of dibenzazepines catalyzed by the low-cost and abundant metal Ni.

After the optimization of the reaction conditions,[13] we evaluated dibenzazepines and various aryl halides (Table 3). The unactivated aryl bromides or iodides were also smoothly converted into the corresponding products in moderate to excellent yields at 100 °C after 24 h with 5 mol% NiO and 10 mol% PPh₃. Many synthetically important functional groups, including fluorine (**5b**), trifluoromethyl (**5c**), alkyl (**5d** and **5e**), methoxyl (**5f** and **5g**), *N*,*N*-dimethyl (**5h**) and phenyl (**5i**) groups, are all well tolerated with the yields of iminodibenzyl ranging from 49% to 91%. On the other hand, chlorine-containing iminodibenzyl (**4j**) also gave the desired dibenzazepine in excellent yield (90%). Furthermore, the coupling of iminostilbenes (**4k** and **4l**) with aryl halides also formed the desired products **6k**–**6l** in useful yields.

To investigate the possibility of a radical-mediated pathway, we explored the Cu-catalyzed arylation of dibenzazepines (Table 4). Consequently, the reactions of **1a** with bromobenzene in standard conditions using commonly available radical scavengers, including 9,10-dihydroanthracene (entry 2), BHT (butylated hydroxytoluene) (entry 3), or TEMPO (2,2,6,6-

Table 3 The Ni-catalyzed *N*-arylation of dibenzazepines[a]

6a, ArBr: 80%(7%)
ArI: 81%(10%)

6b, ArBr: 73%[b](10%)
ArI: 62%[b](3%)

6c, ArBr: 79%[b](9%)
ArI: 74%[b](9%)

6d, ArBr: 84%(6%)
ArI: 79%(8%)

6e, ArBr: 82%(6%)
ArI: 81%(2%)

6f, ArBr: 91%(1%)
ArI: 87%(2%)

6g, ArBr: 83%(5%)
ArI: 87%(9%)

6h, ArBr: 57%[c](12%)
ArI: 49%[c](7%)

6i, ArBr: 74%[b](10%)
ArI: 77%[b](13%)

6j, ArBr: 90%(2%)
ArI: 90%(2%)

6k, ArBr: 85%(-)
ArI: 68%(4%)

6l, ArBr: 63%[c](3%)
ArI: 57%[c](7%)

[a] Reaction conditions: **4** (1.0 mmol), **5** (2.0 mmol), NiO (50 μmol, 5 mol%), PPh₃ (0.1 mmol, 10 mol%), KO*t*Bu (2.0 mmol) and THF (2.0 mL) under Ar atmosphere at 100 °C for 24 h; the yields of the isolated products are shown; the approximate ArH yields in the parentheses were estimated by GC analysis. [b] NiO (0.1 mmol, 10 mol%) and PPh₃ (0.2 mmol, 20 mol%). [c] NiO (0.1 mmol, 10 mol%) and PPh₃ (0.2 mmol, 20 mol%) at 120 °C for 24 h.

Table 4 The effects of radical scavengers on the *N*-arylation of **1a**[a]

Entry	Additive	Equivalent	Yield[b] (%)
1	—	—	95(90)
2	9,10-Dihydroanthracene	0.5	77
		1.0	56
3	BHT	0.5	74
		1.0	49
4	TEMPO	0.5	76
		1.0	58

[a] Reaction conditions: **1a** (1.0 mmol), ArBr (2.0 mmol), CuO (50 μmol, 5 mol%), KO*t*Bu (2.0 mmol), additive (0.5 or 1.0 equiv.), and THF (2.0 mL), under Ar atmosphere at 80 °C for 18 h. [b] The yields were determined by GC, and the isolated yield is in parentheses.

tetramethylpiperidinooxy) (entry 4), were conducted. However, these reactions indicated slightly decreased yields of **3a** compared with the reaction in the absence of radical scavengers.

Meanwhile, in order to gain insight into the reaction pathway, we also carried out a radical-clock experiment using substrate **7**, which is a radical well-known for 5-*exo*-trig cyclization to form 1-methylindane after H-atom abstraction.[14] Under the current conditions, the reaction of **7** with iminodibenzyl **1a** failed to produce the cyclization product **8** (Scheme 2). In summary, these results all indicated that this Cu-catalytic reaction might not appear to go through a radical process.

To distinguish homogeneous from heterogeneous catalysis, we conducted the reactions of iminodibenzyl with bromobenzene in the presence of the commonly used heterogeneous catalyst poisons liquid Hg[15] and PMe$_3$ (ref. 15*d*) (Table 5). The addition of Hg or PMe$_3$ resulted in a slight decrease of the yield of **3a** in comparison with that without the heterogeneous catalyst poison in the Cu-based catalytic system. However, the reactions catalysed by the metal Ni showed that the yield of the *N*-arylation process decreased significantly in the presence of

100 equivalents of Hg or 1.0 equivalent of PMe$_3$ (relative to Ni). Therefore, these results suggest that the Cu catalyst is likely to be homogeneous under the standard conditions, whereas the reactions catalyzed by nickel are possible with metal particles.

Conclusions

We have developed the first and efficient approach for the *N*-arylation of iminodibenzyl and iminostilbene derivatives with aryl bromides, iodides and even aryl chlorides, using the really simple copper reagent CuO in the absence of any ligand. Moreover, a Ni-based catalyst was also applied to the *N*-arylation of these derivatives for the first time. Featuring broad substrate scopes, low-cost metal-based catalysts, and mild conditions, these novel methods are practical and general processes for the *N*-arylation of dibenzazepines, which are useful for a variety of value-adding applications.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

Scheme 2 The radical-clock experiment.

Table 5 The homogeneity test with Hg and PMe$_3$
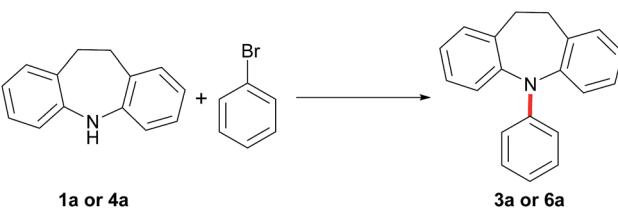
Entry	Additive	Equivalent	Yield^c (%)
[Cu]^a	—	—	95(90)
	Hg	100	88
	PMe$_3$	1.0	89
[Ni]^b	—	—	86(80)
	Hg	100	11
	PMe$_3$	1.0	16

^{a} Reaction conditions: **1a** (1.0 mmol), ArBr (2.0 mmol), CuO (50 μmol, 5 mol%), KO*t*Bu (2.0 mmol) and THF (2.0 mL) under Ar atmosphere at 80 °C for 18 h. ^{b} **4a** (1.0 mmol), ArBr (2.0 mmol), NiO (50 μmol, 5 mol%), PPh$_3$ (0.1 mmol, 10 mol%), KO*t*Bu (2.0 mmol) and THF (2.0 mL) under Ar atmosphere at 100 °C for 24 h. ^{c} The yields were determined by GC, and the isolated yields are in parentheses.

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