A simple and efficient copper-catalyzed amination of aryl halides by aqueous ammonia in water

Yefeng Zhu and Yunyang Wei

Abstract: The copper(I) iodide/1,4-bis(2-hydroxy-3,5-di-*tert*-butylbenzyl)piperazine (CuI–L2) system catalyzed the cross-coupling reactions between aryl halides and aqueous ammonia in water to produce primary aromatic amines in good yields. The protocol was simple and efficient, avoiding the need for inert atmosphere, additional base, or other additives.

Key words: copper, catalysis, cross coupling, water chemistry, aqueous ammonia, primary arylamine.

Résumé : Le système iodure de cuivre(I)/1,4-bis(2-hydroxy-3,5-di-*tert*-butylbenzyl)pipérazine (CuI–L2) catalyse les réactions de couplages croisées entre les halogénures d'aryles et une solution aqueuse d'ammoniaque pour conduire à la formation d'amines aromatiques primaires avec de bons rendements. Le protocole est simple et efficace, il ne nécessite pas d'atmosphère inerte, de base additionnelle ou d'autres additifs.

Mots-clés : cuivre, catalyse, couplage croisé, chimie dans l'eau, solution aqueuse d'ammoniaque, arylamine primaire.

[Traduit par la Rédaction]

Introduction

Ammonia is an attractive source of nitrogen in organic synthesis owing to its great abundance and low cost.[1] In recent years, the palladium- or copper-catalyzed coupling of aryl halides with ammonia has attracted increasing attention because of the value of primary aromatic amines in the preparation of natural products, agrochemicals, dyes, polymers, and medicinal compounds.[2] While palladium catalysts developed by Buchwald and Hartwig[3] proved most useful for this reaction, less progress has been achieved with copper catalysts. Recently, Kim and Chang[4] reported a proline-derived copper complex catalyzed arylation of ammonium chloride or aqueous ammonia with aryl iodides. Following these pioneering works, a lot of catalytic systems have been reported,[5] such as CuI/diketone ligands,[5a] CuI/2-pyridinyl-β-ketone ligands,[5b] CuI/4-hydroxy-L-proline,[5c] etc. Furthermore, Rao et al.[6a] also introduced a ligand-free copper-catalyzed arylation of aqueous ammonia with aromatic boronic acids at room temperature. These reactions are generally performed in organic solvents, which lead to environmental problems.[7] It is highly desirable to find a procedure to carry out these coupling reactions in cheap, nontoxic, and nonflammable "green" solvents. Obviously, water is the most cheap and environmentally benign solvent.[8] However, to the best of our knowledge, there are only a few well-established methods to effectively synthesize anilines from aryl halides and aqueous ammonia in water.[9] More recently, Wu et al.[9b] reported the coupling reactions of aryl halides with aqueous ammonia by a sulfonato–Cu(salen) complex in water, but an additional base was essential.

We have identified Mannich bases[10] (Fig. 1) as efficient ligands for the Cu-catalyzed N-arylation of imidazoles in water.[11] We now report a ligand-assisted copper(I)-catalyzed method for the coupling of aryl halides with aqueous ammonia in water. This method utilizes inexpensive CuI as the catalyst and simple synthesized Mannich bases as ligands and tolerates a wide range of functional groups. Inert atmosphere and additional base were not needed. The use of aqueous ammonia makes the reaction easier to handle than the cases where gaseous ammonia or ammonia in organic solvent was used.

Results and discussion

We initially selected iodobenzene as a model substrate for optimization of the reaction conditions. The standardized protocol was carried out by using iodobenzene (1 equiv.), CuI (10 mol%), L2 (10 mol%), and aqueous ammonia (2 mL) in water at 120 °C for 12 h. The results are summarized in Table 1.

It can be seen from Table 1 that the CuI–L combination successfully promoted the coupling reaction with yields from 75% to 90% (Table 1, entries 1–4), whereas no product was detected without the ligand under similar conditions (Table 1, entry 5). Among the ligands used, 1,4-bis(2-hydroxy-3,5-di-*tert*-butylbenzyl)piperazine (L2) displayed the best catalytic activity (Table 1, entry 2). Thus, L2 was chosen as the ligand for further optimization of the reaction conditions. Different copper sources have also been examined, the catalysis by CuI, CuCl, and $CuSO_4$ with L2 afforded the aniline product in good yields of 90%, 85%, and 87%, respectively (Table 1, entries 2, 7, and 8, respectively). However, the use of the $CuCl_2$–L2 combination resulted in a moderate yield of 51% (Table 1, entry 9). It must be pointed out that in the absence of copper catalysis, no aniline derivative was obtained

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Fig. 1. Structures of Mannich bases **L1**–**L4**.

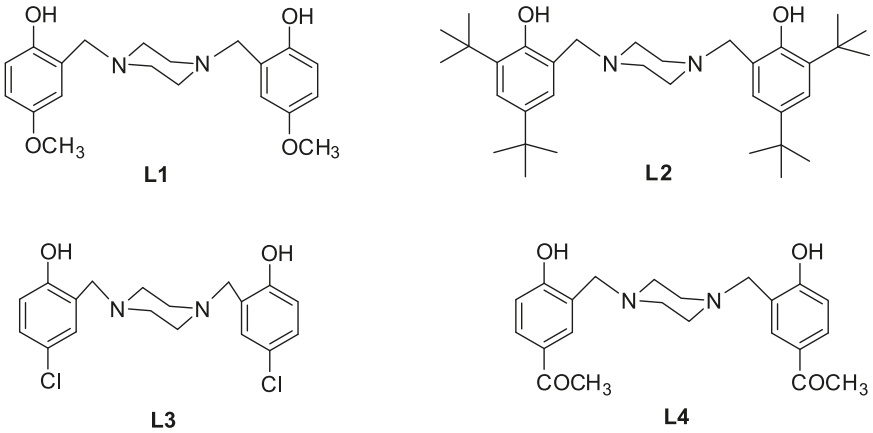
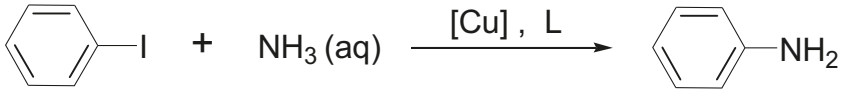


Table 1. Results of amination of iodobenzene with aqueous ammonia in water.



Entry	Cu	Ligand	NH_3(aq) (mL)	Yield (%)[a]
1	CuI	L1	2	75
2	CuI	L2	2	90
3	CuI	L3	2	80
4	CuI	L4	2	78
5	CuI		2	0
6		L2	2	0
7	CuCl	L2	2	85
8	$CuSO_4$	L2	2	87
9	$CuCl_2$	L2	2	51
10	CuI	L2	1	57
11	CuI	L2	3	91
12	CuI	L2	1	32[b]
13	CuI	L2	2	70[c]
14	CuI	L2	2	<5[d]

Note: Unless otherwise noted, the reactions were carried out with iodobenzene (1 mmol), 25%–28% aqueous ammonia (2 mL) at 120 °C for 12 h.

[a]Isolated yields.

[b]H_2O (1 mL) was added.

[c]Reaction time was 8 h.

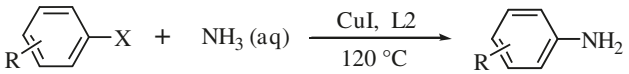
[d]Reaction temperature was 100 °C.

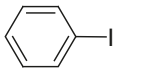
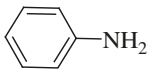
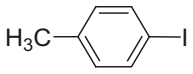
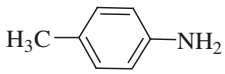
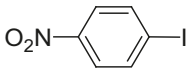
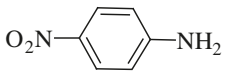
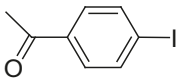
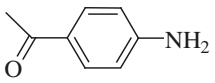
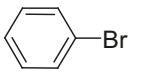
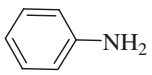
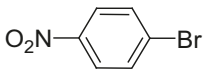
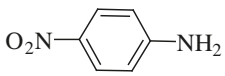
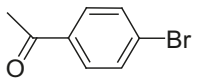
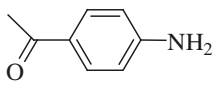
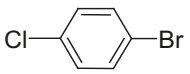
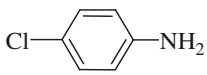
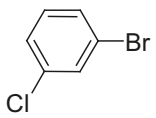
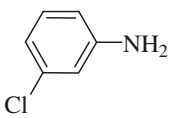
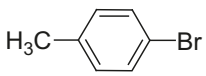
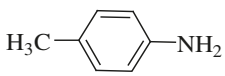
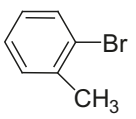
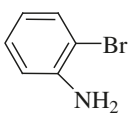
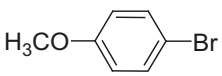
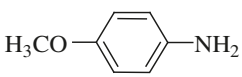
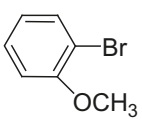
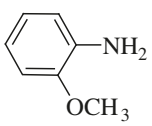
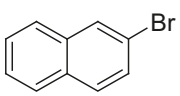
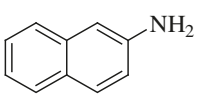
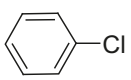
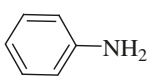
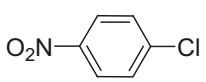
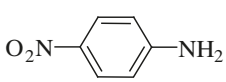
(Table 1, entry 6). Further investigation revealed that 2 mL aqueous ammonia was needed for the reaction to take place. When we decreased the amount or the concentration of aqueous ammonia, the reaction rate decreased (Table 1, entries 10–12). In addition, a lower temperature decelerated the reaction rate and led to a lower yield (Table 1, entry 14). In summary, the proper conditions for amination of aryl halides by aqueous ammonia in water consist of the combination of CuI (10 mol %), L2 (10 mol %), and aqueous ammonia (2 mL) at 120 °C for 12 h in air.

With this practical procedure in hand, we explored the scope of this reaction and screened a wide range of aryl iodides and bromides. As shown in Table 2, most of the aryl iodides with either electron-donating or electron-withdrawing substituents afforded aniline derivatives in water in excellent yields, and the highest yield was obtained by using 4-iodoacetophenone. However, when the highly activated 4-nitroiodobeneze was used, a slightly lower yield (61%; Table 2, entry 3) was obtained because of the formation of a small amount of unidentified byproduct.

Next, we were intrigued by the possibility of using aryl bromides as coupling partners, which are less reactive substrates but of much greater interest for industrial applications. It can be seen from Table 2 that all the electron-deficient aryl bromides afforded the aniline products with excellent yields ranging from 72% to 92% under the optimized conditions (Table 2, entries 5–9). The reactions with the electron-rich aryl bromides were slower, but the products could be isolated in good yields by extending the reaction time to 24 h (Table 2, entries 10–14). It is noteworthy that the catalytic system displayed a great tolerance for multiple groups including the nitro, acetyl, and ether groups. However, the steric hin-

Table 2. CuI–L2 catalyzed amination of aryl halides with aqueous ammonia in water.



Entry	ArX	ArNH2	Yield (%)[a]
1			90
2			85
3			61
4			95
5			85
6			90
7			92
8			72
9			85
10			85[b]
11			27[b]
12			83[b]
13			85[b]
14			88[b]
15			0
16			<5[b]

Note: Reaction conditions: aryl halides (1 mmol), 25%–28% aqueous ammonia (2 mL), CuI (10 mmol%), L2 (10 mmol%), 120 °C, 12 h.

[a]Isolated yield.

[b]Reaction time was 24 h.

drance has a huge influence on the coupling reaction. When 2-methylbromobenzene was aminated with this catalytic system, only a 27% isolated yield was obtained (Table 2, entry 11). Fortunately, when the reaction was performed with *o*-methoxybromobenzene, the corresponding *o*-methoxyaniline was obtained in an 85% isolated yield (Table 2, entry 13). Furthermore, attempts to use chlorobenzene as an aryl source failed (Table 2, entry 15). When 4-nitrochlorobenzene, an activated aryl chloride, was used as the arylating agent, only a 5% yield of the corresponding coupling product was detected (Table 2, entry 16).

Conclusion

In summary, we have developed a ligand-assisted copper (I)-catalyzed method for coupling aryl halides with aqueous ammonia in water. This protocol avoids the use of toxic organic solvents and eliminates the need for an inert atmosphere, additional base, or other additives, which greatly facilitates operations. Excellent yields are obtained with a wide range of aryl bromides and aryl iodides as substrates in the catalytic system.

Experimental

General method

All reactions were carried out in a Teflon septum screw-capped tube under air atmosphere. All chemicals were obtained from a commercial source (Sinopharm Chemical Reagent Company, Ltd., Shanghai, China, and Aladdin Reagent, Shanghai, China) and used without further purification. Ligands L1–L4 were synthesized according to the literature.[10] Column chromatography was performed on silica 200–300 mesh. ^{1}H NMR and ^{13}C NMR spectra was recorded on a Bruker Avance 300, 400, or 500 and 125 spectrometer at ambient temperature in $CDCl_3$ or DMSO-d_6. Chemical shifts are reported in parts per million relative to TMS.

Typical procedure for the coupling

Aryl halides (1 mmol), CuI (0.1 mmol), 1,4-bis(2-hydroxy-3,5-di-*tert*-butylbenzyl)piperazine (0.1 mmol), and aqueous ammonia (2 mL) were added to a Teflon septum screw-capped tube. The reaction mixture was stirred at 120 °C for 12 h and then cooled to room temperature and extracted with ethyl acetate. The organic layer was then dried with anhydrous Na_2SO_4, and the solvent was removed under reduced pressure. The aniline product was finally obtained by column chromatography on silica gel.

1,4-Bis(2-hydroxy-5-methoxybenzyl)piperazine (L1)

White solid; mp (recrystallization in methanol) 184–186 °C (lit. value[10a] mp 184–186 °C). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.40–2.90 (m, 8H), 3.69 (s, 4H), 3.72 (s, 6H), 6.57–6.76 (m, 6H), 10.25 (br s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 151.7, 150.2, 120.4, 115.6, 113.6, 112.9, 60.2, 54.8, 51.2. MS (ESI, *m*/*z*): 359 [M$^+$].

*1,4-Bis(2-hydroxy-3,5-di-*tert*-butylbenzyl)piperazine (L2)*

White solid; mp (recrystallization in methanol) 258–260 °C (lit. value[10b] mp > 250 °C). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.31 (s, 18H), 1.43 (s, 18H), 2.39–2.90 (m, 8H), 3.72 (s, 4H), 6.84–7.27 (m, 4H), 10.75 (br s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 153.1, 139.8, 134.6, 122.6, 122.2, 119.3, 61.0, 51.2, 33.9, 33.2, 30.7, 28.6. MS (ESI, *m*/*z*): 523 [M$^+$].

1,4-Bis(2-hydroxy-5-chlorobenzyl)piperazine (L3)

White solid; mp (recrystallization in methanol) 243–246 °C (lit. value[10a] mp 243–245 °C). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.48–2.78 (m, 8H), 3.70 (s, 4H), 6.77 (d, J = 8.6 Hz, 2H), 6.98 (d, J = 2.2 Hz, 2H), 7.15 (dd, J = 8.6, 2.2 Hz, 2H). ^{13}C NMR (125 MHz, DMSO-d_6) δ: 154.9, 128.2, 127.2, 124.2, 121.7, 116.3, 56.7, 51.6. MS (ESI, *m*/*z*): 368 [M$^+$].

1,4-Bis(2-hydroxy-5-acetylbenzyl)piperazine (L4)

White solid; mp (recrystallization in methanol) 222–223 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.54 (s, 6H), 2.67–2.86 (m, 8H), 3.81 (s, 4H), 6.86 (d, J = 8.5 Hz, 2H), 7.68 (s, 2H), 7.83 (dd, J = 8.6, 2.0 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 195.7, 161.4, 129.5, 128.5, 128.3, 119.4, 115.1, 59.8, 51.1, 25.2. MS (ESI, *m*/*z*): 383 [M$^+$]. Elemental anal. calcd. (%): C 68.75, H 7.15, N 7.06; theoretical: C 69.09, H 6.85, N 7.32.

Aniline[9a]

Pale yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.24–7.28 (m, 2H), 6.87–6.88 (m, 1H), 6.75–6.86 (m, 2H), 3.66 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 145.7, 128.5, 117.6, 114.3, 19.6.

4-Toluidine[9a]

Slight yellow solid; mp (recrystallization in methanol) 43–45 °C (lit. value[12a] mp 43–44 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 6.99 (d, J = 10.0 Hz, 2H), 6.63 (d, J = 10.0 Hz, 2H), 3.46 (s, 2H), 2.26 (s, 3H). ^{13}C NMR (125 MHz, DMSO-d_6) δ: 145.5, 128.7, 123.4, 113.5.

4-Nitroaniline[9b]

Yellow solid; mp (recrystallization in methanol) 148–149 °C (lit. value[12b] mp 146–149 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.09 (d, J = 10.0 Hz, 2H), 6.64 (d, J = 10.0 Hz, 2H), 4.40 (s, 2H). ^{13}C NMR (125 MHz, DMSO-d_6) δ: 155.2, 135.1, 125.6, 111.8.

4-Aminoacetophenone[9b]

Slight yellow solid; mp (recrystallization in methanol) 105–106 °C (lit. value[12c] mp 103–105 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.82 (d, J = 5.0 Hz, 2H), 6.66 (d, J = 5.0 Hz, 2H), 4.22 (s, 2H), 2.51 (s, 3H). ^{13}C NMR (125 MHz, DMSO-d_6) δ: 194.5, 153.1, 130.1, 124.4, 112.0, 25.3.

4-Chloroaniline[9b]

Pale white solid; mp (recrystallization in methanol) 69–71 °C (lit. value[12b] mp 69–72 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.12 (d, J = 10.0 Hz, 2H), 6.62 (d, J = 10.0 Hz, 2H), 3.65 (s, 2H). ^{13}C NMR (125 MHz, DMSO-d_6) δ: 147.1, 128.0, 118.2, 114.7.

3-Chloroaniline[6]

Slight yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.02–7.06 (m, 1H), 6.65–6.71 (m, 2H), 6.52–6.54 (m, 1H), 3. 63 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 146.9, 133.8, 129.5, 117.4, 114.0, 112.4.

***2-Toluidine*[9b]**

Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.09–7.12 (m, 2H), 6.72–6.80 (m, 2H), 3.59 (s, 2H), 2.23 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 143.8, 129.6, 126.2, 121.5, 117.8, 114.1, 16.5.

***4-Methoxyaniline*[9b]**

Pale white solid; mp (recrystallization in methanol) 54–56 °C (lit. value[12a] mp 57 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.72–6.74 (m, 2H), 6.62–6.65 (m, 2H), 3.73 (s, 3H), 2.92 (s, 2H). ^{13}C NMR (125 MHz, DMSO-d_6) δ: 150.2, 141.8, 114.2, 114.1, 54.7.

***2-Methoxyaniline*[9b]**

Slight yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 6.85–6.88 (m, 2H), 6.76–6.81 (m, 2H), 3.90 (s, 3H), 3.75 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 146.4, 135.4, 120.2, 117.5, 114.1, 109.6, 54.5.

***β-Aminonaphthalene*[6]**

Dark brown solid; mp (recrystallization in methanol) 109–111 °C (lit. value[12a] mp 107–109 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.51–7.63 (m, 3H), 7.27–7.31 (m, 1H), 7.13–7.19 (m,1H), 6.86–6.92 (m, 2H), 3.76 (s, 2H). ^{13}C NMR (125 MHz, DMSO-d_6) δ: 146.1, 134.5, 128.0, 127.0, 125.8, 125.3, 124.5, 120.3, 117.9, 105.3.

Supplementary data

Supplementary data for this article (^{1}H NMR and ^{13}C NMR spectra for all products) are available on the journal Web site (www.nrcresearchpress.com/cjc).

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