

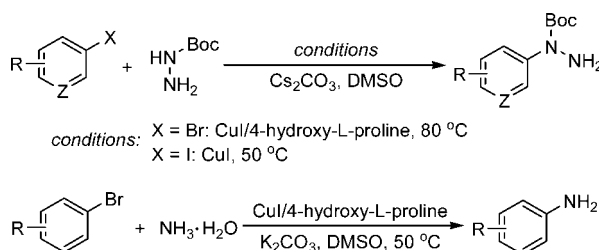
CuI/4-Hydro-L-proline as a More Effective Catalytic System for Coupling of Aryl Bromides with *N*-Boc Hydrazine and Aqueous Ammonia

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CuI/4-hydroxy-L-proline-catalyzed coupling of aryl bromides and *N*-Boc hydrazine takes place in DMSO at 80 °C to give *N*-aryl hydrazides. When aryl iodides are employed, this reaction completes at 50 °C and no ligand is required. Under the catalysis of CuI/4-hydroxy-L-proline, the coupling reaction of aqueous ammonia with aryl bromides proceeds smoothly at 50 °C to afford primary arylamines. In this case K₂CO₃ is found as a better base than Cs₂CO₃. These processes allow assembly of *N*-aryl hydrazides and primary arylamines that bear a wide range of functional groups including hydroxyl, amine, trifluoromethyl, ester, nitro, and ketone.

Introduction

Recently, great progress has been made in copper-catalyzed C–N bond formation between aryl halides and N-containing nucleophiles.¹ The use of special ligands makes this transformation work under significantly milder conditions compared with those for the traditional Ullmann reaction.² This progress has greatly expanded the reaction scope because more N-containing nucleophiles could be employed as coupling partners. For example, Buchwald³ and Kwong⁴ subsequently reported that coupling of hydrazides with aryl iodides took place under the catalysis of CuI/1,10-phenanthroline or CuI/picolinic acid to afford *N*-aryl hydrazides, while Chang⁵ described that ammonium salts and aqueous NH₃ could be used for coupling with aryl halides to deliver primary arylamines. However, in their reports, aryl bromides were not examined^{3,4} or were found to

give poor yields in cases of electron-rich substrates.^{5,6} As a continuing effort on exploring amino acid-promoted Ullmann-type reactions,^{1e,7} we found that using 4-hydroxy-L-proline as a ligand could solve the above problems, leading to coupling

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(3) Wolter, M.; Klapars, A.; Buchwald, S. L. *Org. Lett.* **2001**, *3*, 3803.

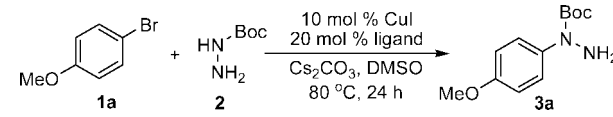
(4) Lam, M. S.; Lee, H. W.; Chen, A. S. C.; Kwong, F. Y. *Tetrahedron Lett.* **2008**, *49*, 6192.

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[‡] Shanghai University.

(1) For reviews, see: (a) Ley, S. V.; Thomas, A. W. *Angew. Chem., Int. Ed.* **2003**, *42*, 5400. (b) Beletskaya, I. P.; Cheprakov, A. V. *Coord. Chem. Rev.* **2004**, *248*, 2337. (c) Monnier, F.; Taillefer, M. *Angew. Chem., Int. Ed.* **2008**, *47*, 3096. (d) Evano, G.; Blanchard, N.; Toumi, M. *Chem. Rev.* **2008**, *108*, 3054. (e) Ma, D.; Cai, Q. *Acc. Chem. Res.* **2008**, *41*, 1450.

TABLE 1. CuI-Catalyzed Coupling of 4-Bromoanisole with *N*-Boc Hydrazine in the Presence of Different Ligands^a


entry	ligand	yield (%)
1	1,10-phenanthroline	49
2	picolinic acid	67
3	L-proline	80
4	<i>N,N</i> -dimethylglycine	71
5	4-hydroxy-L-proline	88

^a Reaction conditions: **1a** (1 mmol), **2a** (2 mmol), CuI (0.1 mmol), ligand (0.2 mmol), Cs₂CO₃ (2 mmol), DMSO (1 mL), 80 °C, 24 h.

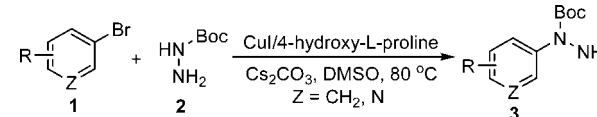
of aryl bromides with *N*-Boc hydrazine, and aqueous ammonia proceeded smoothly to afford *N*-arylation products in good yields. Herein, we wish to report our results.

Results and Discussion

As indicated in Table 1, we began our studies by conducting a CuI-catalyzed coupling reaction of 4-bromoanisole with *N*-Boc hydrazine in the presence of different ligands. It was found that at 80 °C after 24 h 1,10-phenanthroline gave the coupling product **3a** in 49% yield (entry 1). Improved yields were observed by changing the ligand to picolinic acid, L-proline, and *N,N*-dimethylglycine (entries 2–4), while the best result was obtained when 4-hydroxy-L-proline was employed (entry 5).

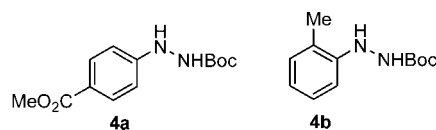
The combination of CuI and 4-hydroxy-L-proline was then examined with different aryl bromides to explore the reaction scope (Table 2). Generally, both electron-rich and electron-deficient aryl bromides worked well, providing the corresponding coupling products in good to excellent yields. Several functional groups including hydroxyl, amine, trifluoromethyl, ester, and aromatic heterocycles were found to tolerate our conditions, thereby giving *N*-aryl hydrazides in good diversity. The yields for formation of **3n–p** (entries 13–15) are superior to those reported by Buchwald³ and Kwong⁴ with aryl iodides. In the case of methyl 4-bromobenzoate as substrate, the reaction completed at 50 °C and two *N*-arylation regioisomers **3g** and **4a** (Figure 1) were isolated in a ratio of about 1:1 (entry 6). The poor selectivity might result from the two nitrogen species of *N*-Boc hydrazine having similar reactivity toward the coupling with more reactive aryl bromide. This result is inconsistent to that observed in CuI/1,10-phenanthroline-catalyzed *N*-arylation,³ indicating that this copper-catalyzed coupling process could dramatically change under different reaction conditions.

The encouraging results from aryl bromides prompted us to check if the coupling of aryl iodides with *N*-Boc hydrazine could work at relatively low reaction temperatures under the action of the CuI/amino acid catalytic system. We were pleased to find that the CuI/4-hydroxy-L-proline catalyzed coupling reaction

TABLE 2. CuI/4-Hydroxy-L-proline-Catalyzed Coupling of Aryl Bromides with *N*-Boc Hydrazine^a


entry	time (h)	product	yield (%)
1	15	3b : R = Me	80
2	20	3c : R = OH	70
3	24	3d : R = NH ₂	64
4	15	3e : R = Ph	80
5	15	3f : R = F	66
6	24	3g : R = CO ₂ Me	75 ^b
7	15	3h : R = OMe	78
8	16	3i : R = Me	90
9	16	3j : R = NH ₂	73
10	24	3k : R = CH ₂ OH	89
11	15	3l : R = CF ₃	79
12	24	3m : R = F	91
13	16	3n	56
14	15	3o	82
15	15	3p	43

^a Reaction conditions: **1a** (1 mmol), **2a** (2 mmol), CuI (0.1 mmol), ligand (0.2 mmol), Cs₂CO₃ (2 mmol), DMSO (1 mL), 80 °C, 24 h. ^b **3g** and **4a** were isolated in a ratio of about 9:11.

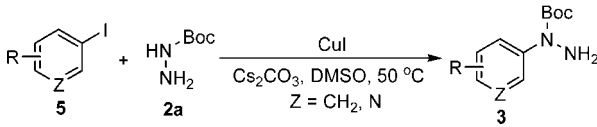
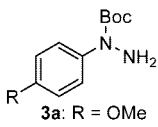
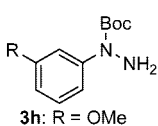
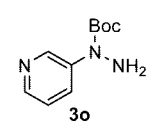
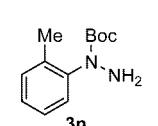
**FIGURE 1.** Structures of compounds **4a** and **4b**.

of 4-iodoanisole with *N*-Boc hydrazine proceeded smoothly to give **3a** in 92% yield after 2.5 h (Table 3, entry 1). Further evaluation indicated that 4-hydroxy-L-proline was useless for this transformation (compare entries 1 and 2). With CuI alone as a catalyst, a number of para- and meta-substituted aryl iodides

(6) During the preparation of this paper, an efficient procedure for coupling of aryl bromides with aqueous ammonia (catalyzed by Cu(acac)₂ and CH₃COCH₂COCH₃) was reported, see: Xia, N.; Taillefer, M. *Angew. Chem., Int. Ed.* **2009**, *48*, 337.

(7) For recent progress, see: (a) Liu, F.; Ma, D. *J. Org. Chem.* **2007**, *72*, 4844. (b) Chen, Y.; Xie, X.; Ma, D. *J. Org. Chem.* **2007**, *72*, 9329. (c) Chen, Y.; Wang, Y.; Sun, Z.; Ma, D. *Org. Lett.* **2008**, *10*, 625. (d) Wang, B.; Lu, B.; Jiang, Y.; Zhang, Y.; Ma, D. *Org. Lett.* **2008**, *10*, 2761. (e) Yuan, Q.; Ma, D. *J. Org. Chem.* **2008**, *73*, 5159. (f) Li, L.; Wang, M.; Zhang, X.; Jiang, Y.; Ma, D. *Org. Lett.* **2009**, *11*, 1309.

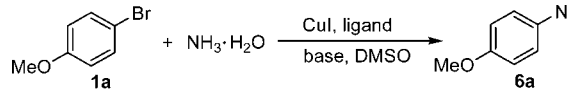
TABLE 3. CuI-Catalyzed Coupling of Aryl Iodides with *N*-Boc Hydrazine^a

			
entry	time (h)	product	yield (%)
1	2.5	 3a : R = OMe	92
2	2.5	3a	92
3	2.5	3b : R = Me	85
4	4	3c : R = OH	65
5	4	3d : R = NH ₂	76
6	4	3f : R = F	88
7	3	3g : R = CO ₂ Me	90
8	4	3q : R = CF ₃	86
9	2.5	3r : R = COCH ₃	60
10	4	3s : R = Br	76
11	4	3t : R = NO ₂	43
12	3	 3h : R = OMe	92
13	4	3i : R = Me	92
14	4	3u : R = CO ₂ Me	88
15	4	3v : R = NO ₂	75
16	4	3m : R = F	80
17	5	 3o	91
18	5	 3n	43 ^b

^a Reaction conditions: **5** (1 mmol), **2** (1.2 mmol), CuI (0.05 mmol), Cs₂CO₃ (1.5 mmol), DMSO (1 mL), 50 °C, 2.5–4 h. ^b **3n** and **4b** were isolated in a ratio of about 3:1.

were examined and they generally worked well to afford coupling products with a great diversity. When methyl 4-iodobenzoate was used, **3g** was obtained as a single product in 90% yield (entry 7), in contrast to the case of the corresponding bromide as a substrate. Regioselectivity could be reached for 4-bromiodobenzene, as is evident from **3s** being isolated in 76% yield (entry 10). Poor yield was observed in the case of 4-iodonitrobenzene because some unidentified side products were detected (entry 11). However, 3-iodonitrobenzene gave the desired product in good yield (entry 15). When 2-iodotoluene was used, a mixture of **3n** and **4b** (Figure 1) was obtained (entry

TABLE 4. CuI-Catalyzed Coupling of 4-Bromoanisole with Aqueous Ammonia under Different Conditions^a

		
entry	reaction conditions	yield (%)
1	Cs ₂ CO ₃ /50 °C/24 h	48
2	Cs ₂ CO ₃ /70 °C/24 h	71 ^b
3	K ₂ CO ₃ /50 °C/24 h	81
4	K ₂ CO ₃ /50 °C/36 h	85
5	K ₂ CO ₃ /50 °C/36 h	74 ^c

^a Reaction conditions: **1a** (1 mmol), aqueous ammonia (28%, 1 mL), CuI (0.2 mmol), 4-hydroxy-L-proline (0.4 mmol), base (3 mmol), DMSO (2 mL). ^b 0.1 mmol CuI and 0.2 mmol 4-hydroxy-L-proline were used. ^c L-Proline was used as a ligand.

18), indicating that steric hindrance plays an important role for this coupling reaction. Noteworthy is that Buchwald and co-workers have mentioned that without addition of the 1,10-phenanthroline ligand, the coupling reaction of aryl iodides with *N*-Boc hydrazine occurred in some cases but slightly low yields were observed.³ Our results demonstrated that DMSO is a better solvent than DMF for this *N*-arylation.

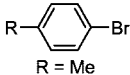
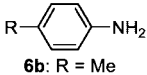
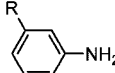
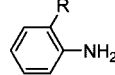
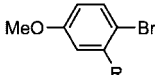
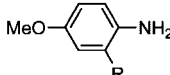
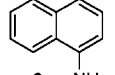
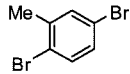
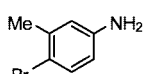
Since 4-hydroxy-L-proline performed better than L-proline for promoting CuI-catalyzed *N*-arylation,⁸ we next tried its application in the coupling of aryl bromides with aqueous ammonia. Accordingly, we chose the coupling of 4-bromoanisole and aqueous ammonia as a model reaction to explore the optimized reaction conditions. We were pleased to find that this reaction proceeded at 50 °C to give 4-methoxybenzenamine in 48% yield (Table 4, entry 1). Raising the reaction temperature to 70 °C while reducing catalytic loading gave a better yield (entry 2). Surprisingly, switching base to K₂CO₃ also improved the reaction conversion dramatically (entry 3). Further improvement could be achieved by prolonging the reaction time (entry 4). Under the same conditions L-proline gave only 74% yield (entry 5), indicating that 4-hydroxy-L-proline is a more suitable ligand for this transformation.

The established optimized reaction conditions were then tested by varying aryl bromides and the results were summarized in Table 5. It was found that both electron-donating and electron-withdrawing substituents, no matter at the para-, meta- or ortho-positions, are tolerated under these conditions. Remarkably, several sterically hindered aryl bromides also afforded the coupling products in good yields although the reaction temperature should be increased to 70 °C to ensure the satisfactory conversion (entries 9–14). When 1,4-dibromo-2-methylbenzene was used, regioselective monoamination could be achieved as is evident from **6p** being isolated in 63% yield (entry 15).

In conclusion, we have revealed that 4-hydroxy-L-proline is a powerful promoter for CuI-catalyzed *N*-arylation of aryl bromides with *N*-Boc hydrazine and aqueous ammonia, leading to reactions complete at 50–80 °C. A wide range of aryl bromides bearing both electron-donating and electron-withdrawing substituents were found applicable to these two coupling reactions. In addition, coupling of aryl iodides with *N*-Boc hydrazine was found to proceed well at 50 °C in DMSO in the absence of any ligands. These new reaction conditions provide more general procedures for assembly of *N*-aryl hydrazides and primary arylamines from aryl halides. Considering that the

(8) This ligand has showed some advantages in our previous studies, see: Xie, X.; Chen, Y.; Ma, D. *J. Am. Chem. Soc.* **2006**, *128*, 16050, and ref 20.

TABLE 5. CuI/4-Hydroxy-L-proline-Catalyzed Coupling of Aryl Bromides with Aqueous Ammonia^a

entry	aryl bromides	product	yield (%)
1	 R = Me	 6b : R = Me	55
2	R = NO ₂	6c : R = NO ₂	92
3	R = CF ₃	6d : R = CF ₃	91
4	R = CN	6e : R = CN	91
5	R = Ph	6f : R = Ph	91
6	 R = OMe	 6g : R = OMe	83
7	R = NO ₂	6h : R = NO ₂	91
8	R = CF ₃	6i : R = CF ₃	90
9	 R = OMe	 6j : R = OMe	81 ^b
10	R = Me	6k : R = Me	55 ^b
11	R = NO ₂	6l : R = NO ₂	78 ^b
12	 R = Me	 6m : R = Me	77 ^{b,c}
13	R = OMe	6n : R = OMe	82 ^b
14	 Br	 6o	76 ^c
15	 Br	 6p	63

^a Reaction conditions: aryl bromide (1 mmol), aqueous ammonia (28%, 1 mL), CuI (0.2 mmol), 4-hydroxy-L-proline (0.4 mmol), K₂CO₃ (3 mmol), DMSO (2 mL), 50 °C, 24 h. ^b Reaction was carried out at 70 °C. ^c Reaction was carried out for 36 h.

present catalytic system is inexpensive and could be easily removed by simple washing with water, our results may find applications in the synthesis of related *N*-aryl compounds.^{9,10}

Experimental Section

General Procedure for the CuI/4-Hydroxy-L-proline-Catalyzed Coupling Reaction of Aryl Bromides with *N*-Boc Hydrazide. A mixture of aryl bromide (1 mmol), *N*-Boc hydrazine (2 mmol), Cs₂CO₃ (2 mmol), CuI (0.1 mmol), and 4-hydroxy-L-proline (0.2 mmol) in 1 mL of DMSO was heated at 80 °C until the bromide was consumed as indicated by TLC. The cooled 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 Na₂SO₄, and concentrated in vacuo. The residual oil was loaded on a silica gel column and eluted with 1:8 to 1:2 ethyl acetate/petroleum ether to afford the corresponding *N*-aryl hydrazide.

***tert*-Butyl 1-(4-fluorophenyl)hydrazinecarboxylate (**3f**):** pale yellow oil; ¹H NMR (300 MHz, CDCl₃) δ 7.41–7.37 (m, 2H), 7.02–6.95 (m, 2H), 4.19 (br s, 2H), 1.48 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 160.0 (d, *J* = 242.4 Hz), 155.4, 139.4 (d, *J* = 3.0 Hz), 125.5 (d, *J* = 7.7 Hz, 2C), 115.0 (d, *J* = 22.4 Hz, 2C), 82.1, 28.4 (3C); EI-MS *m/z* 226 (M⁺), 170, 153, 126, 110, 95, 83, 77, 57; EI-HRMS for C₁₁H₁₅FN₂O₂ (M⁺) requires 226.1118, found 226.1116.

***tert*-Butyl 1-(3-methylphenyl)hydrazinecarboxylate (**3i**):** pale yellow oil; ¹H NMR (300 MHz, CDCl₃) δ 7.27–7.15 (m, 3 H), 6.92 (d, *J* = 6.9 Hz, 1H), 4.45 (br s, 2H), 2.30 (s, 3H), 1.47 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) 155.4, 143.3, 138.1, 128.2, 125.7, 124.4, 120.9, 81.8, 28.4 (3C), 21.7; EI-MS *m/z* 222 (M⁺), 166, 149, 133, 122, 106, 91, 77, 65, 57; EI-HRMS for C₁₂H₁₈N₂O₂ (M⁺) requires 222.1368, found 222.1367.

General Procedure for the CuI-Catalyzed Coupling Reaction of Aryl Iodides with *N*-Boc Hydrazide. A mixture of aryl iodide (1 mmol), *N*-Boc hydrazine (1.2 mmol), Cs₂CO₃ (1.5 mmol), and CuI (0.05 mmol) in 1 mL of DMSO was heated at 50 °C until the iodide disappeared monitored by TLC. The cooled 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 Na₂SO₄, and concentrated in vacuo. The residue was purified via chromatography (eluting with 1:8 to 1:2 ethyl acetate/petroleum ether) to afford the corresponding *N*-aryl hydrazide.

***tert*-Butyl 1-(3-fluorophenyl)hydrazinecarboxylate (**3m**):** pale yellow oil; ¹H NMR (300 MHz, CDCl₃) δ 7.34–7.19 (m, 3H), 6.81–6.75 (m, 1H), 4.42 (br s, 2H), 1.52 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 162.7 (d, *J* = 242.4 Hz), 154.9, 144.9 (d, *J* = 10.5 Hz), 129.2 (d, *J* = 8.9 Hz), 118.4 (d, *J* = 3.2 Hz), 111.1 (d, *J* = 20.9 Hz), 110.3 (d, *J* = 28.6 Hz), 82.6, 28.4 (3C); EI-MS *m/z* 226 (M⁺), 170, 153, 137, 126, 111, 95, 83, 75, 57; EI-HRMS for C₁₁H₁₅FN₂O₂ (M⁺) requires 226.1118, found 226.1116.

***tert*-Butyl 1-(3-nitrophenyl)hydrazinecarboxylate (**3v**):** yellow oil; ¹H NMR (300 MHz, CDCl₃) δ 8.50 (s, 1 H), 7.98–7.89 (m, 2H), 7.44 (t, *J* = 8.1 Hz, 1H), 4.49 (br s, 2H), 1.55 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 154.6, 148.3, 144.5, 128.9, 128.1, 118.7, 117.5, 83.4, 28.5 (3C); EI-MS *m/z* 253 (M⁺), 180, 166, 153, 136, 123, 105, 90, 77, 63, 57; EI-HRMS for C₁₁H₁₅N₃O₄ (M⁺) requires 253.1063, found 253.1066.

General Procedure for CuI/4-Hydroxy-L-proline-Catalyzed Coupling of Aryl Bromides with Ammonia. A mixture of aryl bromide (1 mmol), ammonia (28%, 1 mL), CuI (38 mg, 0.2 mmol), *trans*-4-hydroxy-L-proline (52.4 mg, 0.4 mmol), and K₂CO₃ (414 mg, 3 mmol) in 2 mL of DMSO was heated at 50 °C until the bromide was consumed as monitored by TLC. The cooled 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 Na₂SO₄, and concentrated in vacuo. The residue was purified by chromatography on silicon gel to provide the corresponding primary aryl amine.

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Biphenyl-4-amine (6f): ^1H NMR (300 MHz, CDCl_3) δ 7.55 (d, $J = 7.2$ Hz, 2H), 7.43–7.37 (m, 4H), 7.29–7.24 (m, 1H), 6.78 (d, $J = 8.4$ Hz, 2H), 3.72 (br s, 2H); EI-MS m/z 169 (M^+), 152, 141, 128.

4-Methoxy-2-methylaniline (6m): ^1H NMR (300 MHz, CDCl_3) δ 6.67 (m, 1H), 6.62 (m, 2H), 3.74 (s, 3H), 3.20 (br s, 2H), 2.17 (s, 3H); ^{13}C NMR (300 MHz, CDCl_3) δ 152.6, 138.2, 124.0, 116.3, 116.0, 112.0, 55.6, 17.6; EI-MS m/z 137 (M^+), 122, 94, 77.

Naphthalen-1-amine (6o): ^1H NMR (300 MHz, CDCl_3) δ 7.84–7.79 (m, 2H), 7.49–7.43 (m, 2H), 7.34–7.25 (m, 2H), 6.79 (dd, $J = 1.5, 6.6$ Hz, 1H), 4.16 (br s, 2H). EI-MS m/z 143 (M^+), 140, 126, 115.

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Supporting Information Available: The analytical data and copies of ^1H NMR and ^{13}C NMR spectra for coupling products. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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