

# Amination of Aryl Halides With Aqueous Ammonia Catalyzed by Green Recyclable Poly(4-vinylpyridine)-supported Copper Iodide Nanoparticles Catalyst

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## Abstract

In this research efficient procedure for the amination of aryl halides with aqueous ammonia in the presence of poly(4-vinylpyridine)-supported copper iodide nanoparticles catalyst is reported. A wide range of aryl halides including aryl iodides and aryl bromides are converted into the corresponding aniline derivatives. The experimental procedure with poly(4-vinylpyridine)-supported copper iodide nanoparticles catalyst is quite straightforward and it is recycled up to 3 consecutive runs by simple filtration.

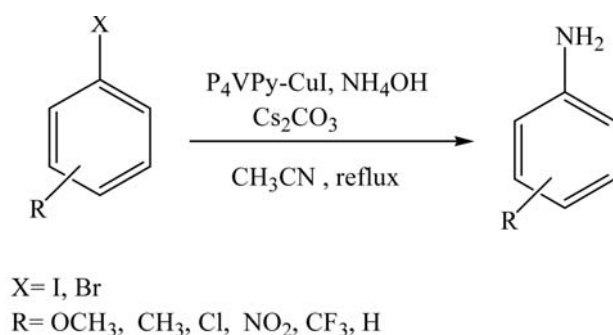
**Keywords:** Poly(4-vinylpyridine)-Supported, Copper catalysis, Nanoparticles, Amination, Aryl halide.

## 1. Introduction

The catalytic amination of aryl halides has been the subject of significant attention from many pharmaceutical and organic chemists. This procedure involves production of aryl amines by coupling of aryl halides and amines with stoichiometric amount of transition metal ions.<sup>1</sup> Aryl amines are attractive compounds for chemical synthesis because of their wide utility in fine chemicals, dyes and polymers.<sup>2</sup> These are important components in many biologically active natural products, medicinally important compounds as well as in materials with useful electrical and mechanical properties.<sup>3–4</sup> For economical and practical reasons, amination of aryl halides with ammonia is the most convenient and efficient approach. Ammonia is one of the most abundant and least expensive synthetic inorganic chemicals. It is also the most common nitrogen source for the industrial production of fertilizers and organic amino compounds.<sup>5</sup> Although many useful methods have been used for the direct amination of aryl halides with ammonia,<sup>6–12</sup> introduction of new methods and catalysts in terms of potential simplicity, high activity, low cost, high

yields and short reaction times is still in demand. Copper-catalyzed reactions are one of the most widely used methodologies for creating C-C, C-N, C-O, or C-P bonds, and they have been used in the C-N coupling of amines and aryl halides.<sup>13</sup> These reactions received significant attention from many organic chemists over the past five years. The main approach in these methods is the use of Ullmann reaction. These copper-catalyzed reactions suffer from reduced scope because of the harsh reaction conditions, long reaction times, non-recyclability, toxicity and difficulty in separation of the products from the reaction mixture. Such drawbacks could be obviated by using the copper-supported catalysts. The best supports or ligands are those which have nitrogen or oxygen binding sites and are chelated with copper catalysts. Nitrogen-based polymers have shown to protect the metal center from oxidation and disproportionation, while enhancing their catalytic activity.<sup>14</sup> Therefore, it has been observed that very efficient copper ligands permit the use of catalytic amounts of metal under very mild conditions.<sup>15–25</sup> For example, poly(4-vinylpyridine) has been used as the support for the numerous reagents and catalysts in many or-

ganic reaction transformations. It undergoes facile functionalization and has a large proportion of functional groups which show good accessibility. Moreover, it is non-hygroscopic, prepared readily and is commercially available. Also, it is easy to filter and swells in many organic solvents.<sup>26</sup> In particular, the immobilization of copper(I) salts nanoparticles on poly(4-vinylpyridine) allows a higher stability and dispersity of the particles as well as a further exploitation of the special activity and recycling properties of the catalyst. Recently, we have reported the preparation of copper iodide nanoparticles supported on poly(4-vinylpyridine) (P<sub>4</sub>VPy-CuI) and its application in the organic reactions.<sup>27–31</sup> In continuation of these studies, herein, we wish to report the applicability of this reagent for the amination of aryl halides using aqueous ammonia under mild conditions (Scheme 1).



**Scheme 1.** Amination of aryl halides catalyzed by P<sub>4</sub>VPy-CuI

## 2. Results and Discussion

The copper iodide nanoparticles immobilized on poly(4-vinylpyridine) (P<sub>4</sub>VPy-CuI) was readily prepared in a one-step procedure. Poly(4-vinylpyridine) was refluxed with a solution of CuI under an N<sub>2</sub> atmosphere in EtOH for the synthesis of polymer-supported CuI nanoparticles. This method was developed for the effective synthesis of copper nanoparticles incorporated heterogeneously as catalyst in some organic reactions.<sup>27</sup> In order to optimize the reaction conditions, the reaction of iodobenzene and aqueous ammonia was chosen as a model and its behavior was studied under a variety of conditions. The influence of various solvents on the yield and time of the reaction was examined and CH<sub>3</sub>CN was chosen as the most efficient solvent. Amongst different bases, Cs<sub>2</sub>CO<sub>3</sub> revealed the best efficiency (Table 1).

Finally, after optimization of reaction condition, it was observed that the best results were achieved in the presence of 0.1 g of P<sub>4</sub>VPy-CuI, 2 mmol of NH<sub>4</sub>OH and 1 mmol of Cs<sub>2</sub>CO<sub>3</sub> in CH<sub>3</sub>CN (10 ml), under reflux conditions (Table 2).

The reaction was checked in the absence of the catalyst and it was observed that no product was achieved which proves that catalyst is essential for this reaction.

**Table 1.** Amination of aryl halides catalyzed by P<sub>4</sub>VPy-CuI in the presence of different bases <sup>a</sup>

Entry	Base	Time (h)	Yield (%) <sup>b</sup>
1	KOH	10	50
2	NaOH	10	50
3	NEt <sub>3</sub>	10	—
4	K <sub>2</sub> CO <sub>3</sub>	7	70
5	Na <sub>2</sub> CO <sub>3</sub>	7	75
6	Cs <sub>2</sub> CO <sub>3</sub>	5	90

<sup>a</sup> Reaction conditions: Iodobenzene (1 mmol), NH<sub>4</sub>OH (2 mmol), catalyst amount (0.1 g) in CH<sub>3</sub>CN (10 ml), at reflux conditions.

<sup>b</sup> Isolated pure products.

**Table 2.** Optimization of reaction conditions <sup>a</sup>

Entry	Condition	Catalyst amounts (g)	NH <sub>4</sub> OH (mmol)	Time (h)	Yield (%)
1	H <sub>2</sub> O/r.t.	—	2	10	—
2	H <sub>2</sub> O/reflux	—	2	10	—
3	H <sub>2</sub> O/reflux	0.075	2	10	—
4	H <sub>2</sub> O/reflux	0.1	2	10	—
5	EtOH/r.t.	0.1	2	10	—
6	EtOH/reflux	0.1	2	10	—
7	MeOH/r.t.	0.1	2	10	—
8	MeOH/reflux	0.1	2	10	—
9	CH <sub>2</sub> Cl <sub>2</sub> /r.t.	0.1	2	10	—
10	CH <sub>2</sub> Cl <sub>2</sub> /reflux	0.1	2	10	Trace
11	CH <sub>3</sub> CN/r.t.	—	2	10	—
12	CH <sub>3</sub> CN/reflux	—	2	10	—
13	CH <sub>3</sub> CN/r.t.	0.05	2	10	—
14	CH <sub>3</sub> CN/reflux	0.05	1	10	Trace
15	CH <sub>3</sub> CN/reflux	0.05	2	10	50
16	CH <sub>3</sub> CN/reflux	0.75	1	10	35
17	CH <sub>3</sub> CN/reflux	0.75	2	10	70
18	CH <sub>3</sub> CN/reflux	0.1	1	10	50
19	CH <sub>3</sub> CN/reflux	0.1	2	5	90

<sup>a</sup> Reaction conditions: Iodobenzene (1 mmol), Cs<sub>2</sub>CO<sub>3</sub> (1 mmol), CH<sub>3</sub>CN (10 mL), reflux. <sup>b</sup> Isolated pure products.

Under these conditions, it was observed that iodobenzene remained intact (Table 3).

Using these optimized conditions, various aryl iodides reacted with aqueous ammonia to give the corresponding amines (Table 3). The evaluation showed that the electron-withdrawing groups such as nitro on iodobenzene enhanced the yield of reactions, whereas electron-releasing groups such as methoxy and methyl decreased, and increased the time of reactions. Next, we explored the scope of this method, and amination of bromobenzenes was investigated. Various bromobenzenes were converted to their corresponding aryl amines. It was found that the rate of reactions was slower than before, but products were obtained in high yields. It is also noteworthy that the catalyst did not suffer from extensive mechanical degradation after running. For a true heterogeneous ca-

**Table 3.** Amination of aryl halides catalyzed by P<sub>4</sub>VPy-CuI

Entry	Aryl halide	Product (h)	Time (%) <sup>a</sup>	Yield
1	C <sub>6</sub> H <sub>5</sub> I	C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub>	5	90
2	2-OMeC <sub>6</sub> H <sub>4</sub> I	2-OMeC <sub>6</sub> H <sub>4</sub> NH <sub>2</sub>	7	91
3	4-OMeC <sub>6</sub> H <sub>4</sub> I	4-OMeC <sub>6</sub> H <sub>4</sub> NH <sub>2</sub>	8	89
4	4-MeC <sub>6</sub> H <sub>4</sub> I	4-MeC <sub>6</sub> H <sub>4</sub> NH <sub>2</sub>	7	91
5	3-MeC <sub>6</sub> H <sub>4</sub> I	3-MeC <sub>6</sub> H <sub>4</sub> NH <sub>2</sub>	7	90
6	2-MeC <sub>6</sub> H <sub>4</sub> I	2-MeC <sub>6</sub> H <sub>4</sub> NH <sub>2</sub>	8	90
7	4-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> I	4-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> NH <sub>2</sub>	3	91
8	4-ClC <sub>6</sub> H <sub>4</sub> I	4-ClC <sub>6</sub> H <sub>4</sub> NH <sub>2</sub>	3.5	89
9	4-CF <sub>3</sub> C <sub>6</sub> H <sub>4</sub> I	4-CF <sub>3</sub> C <sub>6</sub> H <sub>4</sub> NH <sub>2</sub>	1	91
10	3-CF <sub>3</sub> C <sub>6</sub> H <sub>4</sub> I	3-CF <sub>3</sub> C <sub>6</sub> H <sub>4</sub> NH <sub>2</sub>	2	90
11	C <sub>6</sub> H <sub>5</sub> Br	C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub>	9	88
12	4-OMeC <sub>6</sub> H <sub>4</sub> Br	4-OMeC <sub>6</sub> H <sub>4</sub> NH <sub>2</sub>	9	87
13	4-MeC <sub>6</sub> H <sub>4</sub> Br	4-MeC <sub>6</sub> H <sub>4</sub> NH <sub>2</sub>	7	87
14	3-MeC <sub>6</sub> H <sub>4</sub> Br	3-MeC <sub>6</sub> H <sub>4</sub> NH <sub>2</sub>	7	89
15	4-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> Br	4-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> NH <sub>2</sub>	4	90

<sup>a</sup> Isolated pure products. Reaction conditions: Aryl halide (1 mmol), NH<sub>4</sub>OH (2 mmol), catalyst amount (0.1 g) in CH<sub>3</sub>CN (10 ml), at reflux conditions.

talyst, supported catalyst shouldn't leach to the reaction mixture.

Moreover, recyclability of the catalyst was also examined under optimized conditions. To investigate this property, the reaction of iodobenzene with aqueous ammonia was selected as the model (Table 4). After reaction completion, P<sub>4</sub>VPy-CuI was washed with ethylacetate, dried and stored for another consecutive reaction run. This process was repeated for 3 runs and no appreciable decrease in yield was observed. Next, the leaching of CuI into the reaction mixture from the poly(4-vinylpyridine)-support using ICP-AES was checked and it was observed that the difference between the copper content of the fresh and reused catalyst (3th run) was only 3% which indicated the low leaching amount of copper iodide catalyst into the reaction mixture.

**Table 4.** Recyclability study of the P<sub>4</sub>VPy-CuI

Run	1	2	3
Tim (min)	5	5.5	7
Yield (%) <sup>a</sup>	90	89	87

Reaction conditions: Iodobenzene (1 mmol), NH<sub>4</sub>OH (2 mmol), catalyst amount (0.1 g), in CH<sub>3</sub>CN (10 ml), at reflux conditions. <sup>a</sup>Pure products.

### 3. Experimental

All Products were characterized by comparison of their spectroscopic data (NMR, IR) and physical properties with those reported in the literature.<sup>10–12,25</sup> Chemicals were purchased from Fluka and Merck chemical compa-

nies. The IR spectra were recorded on a Perkin Elmer 781 Spectrophotometer. All the NMR spectra were recorded on a Bruker Advance 400 MHz. Melting points were recorded on an Bransted Electro thermal 9100BZ melting point apparatus. Yields refer to isolated pure products.

### 3. 1. Determination of the Copper Content in P<sub>4</sub>VPy-CuI

The P<sub>4</sub>VPy-CuI (100 mg) was extracted with concentrated HCl (5 × 2 mL) in a screw-capped vessel, followed by treatment with concentrated nitric acid (2 mL) to digest the metal complex. The mixture was then transferred into a volumetric flask (100 mL), diluted 1:50 for the second time and was analyzed by the ICP analysis. The copper concentration was determined from the atomic emissions (324.754 nm) by reference to a linear (R = 0.99) calibration curve of (1–4 ppm) of CuI prepared in a manner identical to the sample preparation. The loading of supported catalyst was calculated to be 1.32 mmol CuI g<sup>-1</sup> of prepared catalyst. The same procedure was used to measure the leaching accounts of supported catalyst after 3 consecutive runs.

### 3. 2. General Procedure

A mixture of the aryl halide (1 mmol), NH<sub>4</sub>OH (2 mmol), Cs<sub>2</sub>CO<sub>3</sub> (1 mmol) and P<sub>4</sub>VPy-CuI (0.1 g) in CH<sub>3</sub>CN (10 mL) was stirred at reflux temperature. After reaction completion (monitored by TLC), the catalyst was recovered by filtration and solvent was evaporated. The residue was poured into a saturated NaCl solution, extracted with ethyl acetate and dried over anhydrous MgSO<sub>4</sub>. Evaporation of the solvent was followed by column chromatography on silica gel afforded the pure products.

## 4. Conclusion

In summary, in this research we have developed an efficient procedure for the amination of aryl halides with aqueous ammonia using recyclable P<sub>4</sub>VPy-CuI at reflux temperature. This catalyst promoted the yields and reaction times over 3 runs without significant decrease in its catalytic activity. Moreover, ease of work-up and clean procedure, will make the present method an useful and important addition to the available methods. We are exploring further applications of P<sub>4</sub>VPy-CuI for other types of functional group transformations in our laboratory.

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## Povzetek

V prispevku je predstavljena učinkovita aminacija aril halidov z vodno raztopino amonijaka v prisotnosti bakrovega(I) jodida kot katalizatorja, vezanega na poli(4-vinilpiridin). Na ta način so pretvorili različne aril halide, vključujoč aril jodide in aril bromide, do ustreznih derivatov anilina. Postopek z uporabo bakrovega(I) jodida, vezanega na poli(4-vinilpiridin), je enostaven, katalizator pa lahko vsaj trikrat recikliramo z enostavno filtracijo.