General and Efficient Catalytic Amination of Aryl Chlorides Using a Palladium/Bulky Nucleophilic Carbene System

Jinkun Huang, Gabriella Grasa and Steven P. Nolan*

Department of Chemistry, University of New Orleans
New Orleans, Louisiana 70148

Supporting Information

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Mailing Address:	Department of Chemistry, University of New Orleans New Orleans, LA, 70148
Telephone:	(504) 280-6445
FAX:	(504) 280-6860
Email:	snolan@uno.edu

General Information

- All aryl halides (Aldrich), amines (Aldrich), 1,4-Dioxane (anhydrous, Aldrich), KO^{t}Bu (Aldrich) and $Pd_2(dba)_3$ (Strem) were used as received. Flash chromatography was performed on silica gel 60 (230-400 mesh) (Natland International corporation).
- ITolHCl (**1**, 1,3-Bis(tolyl)imidazolium chloride), IXyHCl (**2**, 1,3-Bis(2, 6-dimethylphenyl)imidazolium chloride, IMesHCl (**3**, 1,3-Bis(2,4,6-trimethylphenyl)imidazolium chloride and IPrHCl (**4**, 1,3-bis(2,6-diisopropyllphenyl)imidazolium Chlorides were prepared according to reported procedures: (a) Arduengo, A. J. III. US patent **5 077 414**, 1991; (b) Jafarpour, L.; Stevens, E. D.; Nolan, S. P. manuscript in preparation.
- ^1H and ^{13}C nuclear magnetic resonance spectra were recorded on a Varian-400 MHz spectrometer at ambient temperature in $CDCl_3$ (Cambridge Isotope Laboratories, Inc.).
- All reactions were carried out under an atmosphere of argon in oven-dried-glassware with magnetic stirring, unless otherwise indicated.
- All yields reported in Table 1 and Table 2 are isolated yields and are the average of two runs.

Aminations of Aryl Halides with Amines. *General procedure:* Under an atmosphere of argon 1,4,-dioxane (3 mL), KO^{t}Bu (168 mg, 1.5 mmol), aryl halide (1.0 mmol), amine (1.2 mmol) were added in turn to a Schlenk tube charged with $Pd_2(dba)_3$ (10 mg, 0.01 mmol), **4** (17 mg, 0.04 mmol), and a magnetic stirring bar. The Schlenk tube was placed in a 100 ˚C oil bath and stirred for 3-30 h. The mixture was then allowed to cool to room temperature. The mixture was diluted with water then extracted with diethyl ether. The extracts were combined, washed with saturated saline solution, and then dried over $MgSO_4$. The solvent was removed under vacuum and residue was purified by flash chromatography (hexane or hexane/ethyl acetate). All coupling products were found to be identical by ^1H NMR with literature data.

All coupling products have been reported previously : N-Methyl-N-phenyl-*p*-toluilidine,[1] 1-(4-methylphenyl)piperidine,[2] 1-(4-methylphenyl)morpholine,[3] N,N-Dibutyl-*p*-toluilidine,[4] N-Hexyl-*p*toluilidine,[2] N-Phenyl-*p*-toluilidine,[2] 2,4,6-trimethyl-N-(4-Methylphenyl)-benzenamine,[5] N-Phenyl-N-methyl--*p*-anisidine,[4] N-Phenyl-*p*-anisidine,[6] 4-Methoxyphenylmorpholine[7], N,N-Dibutyl-*p*-anisidine,[7] N-Methyl-N-phenyl-2,5-dimethylbenzenamine,[7] and 1-(4-Chlorophenyl)piperidine.[3]

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