

Executive Summary of the UGC Minor Research Project

1. Name of Principal Investigator- Dr. R. K. Sharma
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3. UGC approval Letter No. and Date –
F.No.:MS-143/302082/XII/14-15/CRO/1553dated 17.11.2015

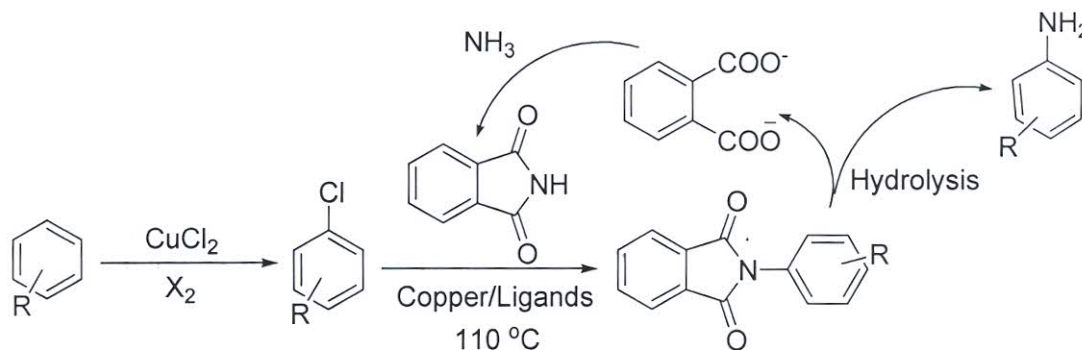
4. Title of the Research Project-

Synthesis of aniline from benzene using Green Chemistry approaches

5. Effective date of starting the project- 14.12.2015

6. Summary of research work carried out and Publications under the Project-

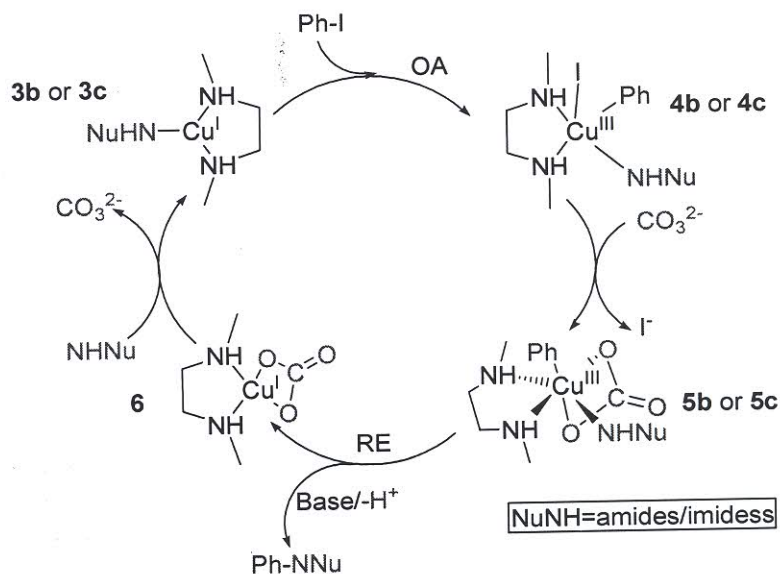
The proposed project is aimed to synthesis of aniline from benzene using Green Chemistry approaches and therefore after extensive literature survey, in the first phase of the project focus was on investigation of copper mediated arylation of ammonia surrogate (phthalimide). Dealing with ammonia is very challenging for safety purpose and hence commercially available recyclable phthalimide was used as ammonia surrogate.



Scheme 1. Copper mediated arylation of ammonia surrogate (phthalimide)

During literature survey, it was realised that there are no direct experimental evidences in favour of mechanism proposed for copper catalysed arylation of phthalimide (C-N coupling) reactions. Therefore, it was planned to investigate the mechanism of copper mediated C-N coupling reactions. A number of reactions were performed with typical substrates, aryl iodides, amide/imide and widely used bases (CO₃²⁻ and PO₄³⁻). Reactions were in situ monitored spectroscopically. DFT studies were also performed to investigate the thermodynamic possibilities of the proposed intermediate species. Specific emphasis was given to find out the role of the bases. These studies have provided direct spectroscopic evidences of actual Cu(III) species as an intermediate of the coupling reactions. Present studies have also revealed that carbonate and phosphate ions act as bidentate ligand as well as

base in the catalytic cycle and thus actual intermediate species is carbonate or phosphate ligated distorted octahedral Cu(III) complex. Present experimental and computational studies have strongly strengthened the hypothesis that these reactions follow OA-RE path. On the basis of experimental and DFT studies, mechanism has been proposed for aryl iodide and amide/imide C-N bond formation.



Scheme 2. Proposed catalytic cycle for C-N coupling of aryl iodide and amides/imides

These research findings have been published in the form of research paper entitled "Mechanistic Studies of Ullmann Type C-N Coupling Reactions: Carbonate Ligated-Cu(III) Intermediates" in an international Journal *ChemCatChem* **9(5)**, 2017, 862–869, Wiley, (DOI: 10.1002/cctc.201601174, Impact Factor: 4.72).


 (R. K. Sharma)