

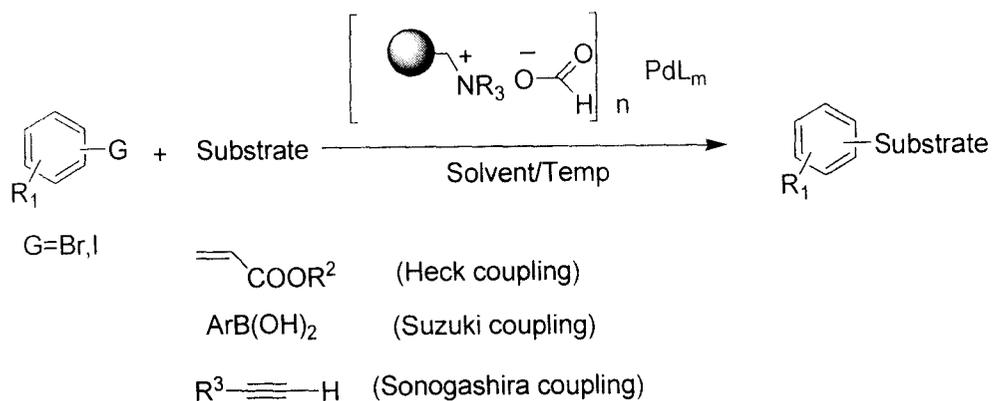
SUMMARY

The research work embodied in this thesis entitled “*Development of Polymer-Supported Reagents and Catalysts in Organic Transformations*” was initiated on February, 2005 in the Department of Chemistry, North Bengal University, Darjeeling – 734 013, under the supervision of Prof. B. Basu, Department of Chemistry, North Bengal University.

The studies described in this thesis are primarily directed towards development of immobilized reagents and catalysts and their manifold applications in various organic transformations. The thesis has been divided into three parts.

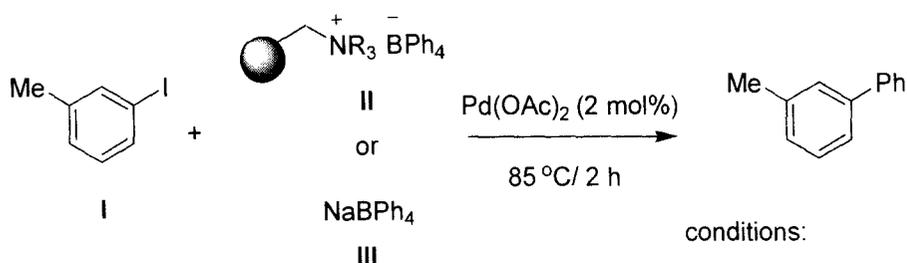
Part I begins with a preface with a general introduction to solid phase organic chemistry, where the present status of solid phase organic synthesis has been outlined in a brief and relevant review. The use of various polymeric supports to immobilize reagents/catalysts and their applications have been presented in a concise manner highlighting the nature of immobilization, applications, recovery and lifetime of the polymer-bound species. This part has been sub-divided into two sections.

Part I: Section A describes a novel methodology entitled “*Palladium Immobilized on Poly-ionic Resins as Efficient, Ligand-free & Recyclable Catalyst for Heck, Suzuki-Miyaura and Sonogashira Reactions*”. Poly-ionic Amberlite resin formate (ARF) derived from commercially available Amberlite[®] resin chloride by simple rinsing with aqueous formic acid, could be soaked with Pd(0) from palladium salts – the formate counter anion being the reducing source. The resulting Amberlite resin formate – supported with Pd(0), ARF-Pd, showed excellent catalytic activity in Heck, Suzuki-Miyaura, and Sonogashira couplings with a range of substrates. The catalyst may be recovered easily and quantitatively without leaching and recycled for five runs tested without any significant loss of activity. Notable features of this resin-soaked heterogeneous palladium catalyst are: high catalytic activity without any phosphane ligands, minimum concentration of palladium, easy quantitative recovery, and longer lifetime.



This work has been published in *Synthesis*, **2009**, 1137-1146.

Part I: Section B is entitled as **“Poly-ionic Heterogeneous Phenylating Agent for Base-Free Suzuki–Miyaura Coupling Reaction”**. This section deals with a new poly-ionic resin-bound tetraphenylborate that has been prepared and can serve as efficient phenylating agent in Pd-catalyzed Suzuki–Miyaura (SM) coupling with aryl halides in absence of any base. The conditions are mild, operationally simple and the poly-ionic resins can be recharged and reused for several runs.

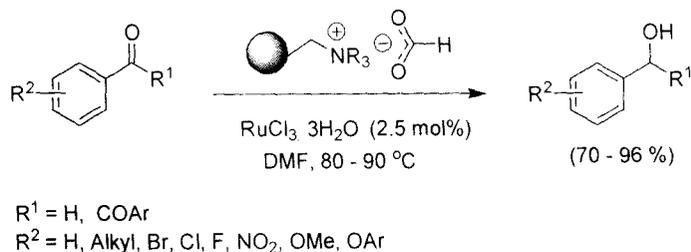


conditions:

- (a) I/II/Na₂CO₃ = 1:1 g/mmol:1; 90%
- (b) I/III/Na₂CO₃ = 1:1:1; 43%
- (c) I/III/Na₂CO₃ = 1:2.5:1; 88%
- (d) I/III = 1:2.5; 88%
- (e) I/II = 1:1 g/mmol; 96%

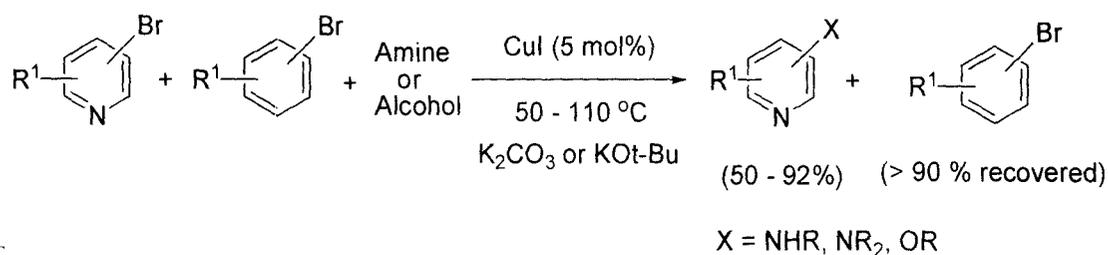
An account of this work has been published in *Synlett*, **2008**, 255-259.

Part II of the thesis describes a simple and chemoselective method for the transfer hydrogenation of aryl aldehydes with the aid of Amberlite resin formate (ARF), a stable H-donor, in the presence of catalytic ruthenium trichloride. Aromatic aldehydes and 1,2-diketones are reduced efficiently and selectively, while aryl ketones remain unchanged. Several other potentially reducible groups attached to the aromatic moiety are unaffected. The section has been entitled **“Catalytic Transfer Hydrogenation: Chemoselective Reduction of Aldehydes with Ruthenium trichloride and Resin-Bound Formates”**



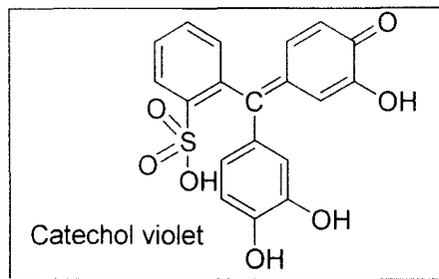
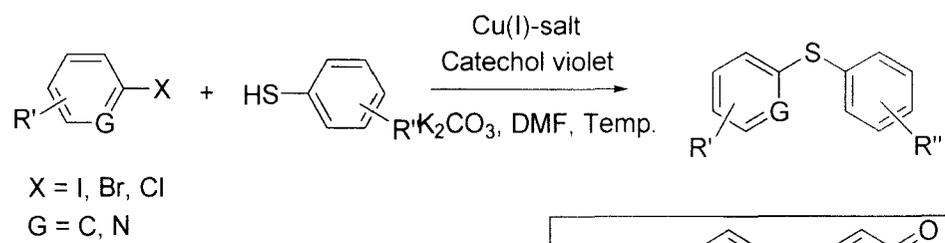
The work has been published in *Beilstein J. Org. Chem.*, **2008**, *4*, No. 53; (doi:10.3762/bjoc.4.53).

Part III is again sub-divided into two sections. **Section A** entitled “*Role of copper in catalyzing aryl and heteroaryl -Nitrogen (or -Oxygen) bond formation under ligand-free and solvent-free conditions*” shows that the formation of aryl- or heteroaryl-nitrogen (or -oxygen) bonds under ligand and solvent-free conditions are highly selective to the presence of copper. While bromoarenes undergo C-N (or -O) couplings in stoichiometric presence of copper, heteroaryl bromides require only catalytic amounts of copper(I) salts depending on the position of bromo substituents. Such selectivity coupled with ligand and solvent-free protocols appear promising from the viewpoint of ecology and economy and are more attractive as compared to the existing protocols.



The work has been published in *Indian J. Chem.* **2008**, *47B*, 1701-1706.

Part III: Section B is entitled “*Catechol Violet as Novel and Efficient Ligand for Cu(I)-Catalyzed C-S Coupling Reactions*”. We have presented here an efficient copper(I) catalyzed C-S coupling reaction protocol, where a wide variety of aromatic halides such as aryl iodides, bromo-pyridines, activated aryl chlorides and vinyl iodide undergo coupling with aromatic or aliphatic thiols to afford the corresponding thioether in good to excellent yields. Presence of catechol violet (CV) (only catalytic amount), which is stable in air, greatly accelerated the reaction. Wide variety of functional group tolerance has also been observed in this reaction methodology.



The manuscript is under the process of preparation.