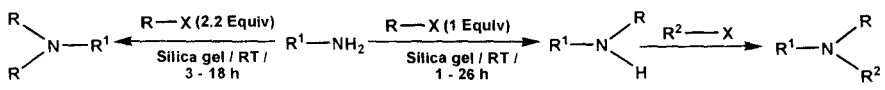
Summary

The research work embodied in this thesis entitled "***Studies on Solid Phase Organic Synthesis: Applications to C–C & C–N Bond–Forming Reactions***" was started on May, 2006 in the Department of Chemistry, University of North Bengal, Darjeeling – 734013, under the guidance and supervision of Prof. B. Basu, Department of Chemistry, University of North Bengal. The studies described in this thesis are primarily directed towards development of new methodology using greener and cleaner technology with the help of solid-phase synthesis and their manifold applications in various organic transformations. The thesis has been divided into two parts.

Part I begins with a preface presenting 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 solid supports mainly inorganic solid supports and immobilization of reagents/catalysts onto the solid supports and their applications have been delineated in a concise manner highlighting the nature of supports, immobilization, applications, recovery and lifetime of the solid supported species.

Part II of the thesis has been divided into **five Sections**, each describing the present work, primarily based on the development of solid phase organic reactions.

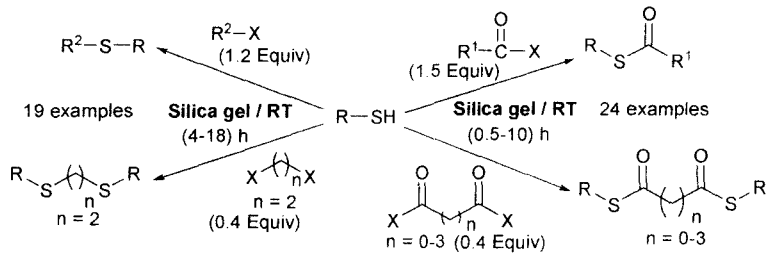
Part II: Section A describes a novel methodology entitled ***"Highly Selective N-Alkylation of Amines Promoted On Silica: An Efficient and Recyclable Surface"***. Silica gel is a rigid, insoluble material, which does not swell in organic solvents. Silica gel enables efficient and rapid transfer of solvents and reagents to its entire surface. Commercially available silica gel differs in particle size, pore size (typically 2-10 nm) and surface area (typically 200-800 m^2/g). Commercially available silica gel (source: SRL, India; particle size: -325 Mesh) showed excellent selectivity towards the *N*-alkylation of amines with electron-rich benzyl halides. The solid support may be recovered easily and quantitatively and recycled for consecutive eleven runs tested without any significant loss of activity. Notable features of this solid heterogeneous support are: high catalytic activity without any base, easy quantitative recovery, and longer lifetime.



High selectivity on silica
High recycling capability

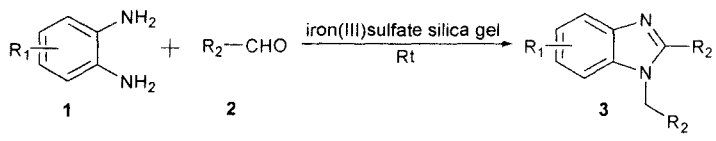
This work has been published in *Green Chem.*, **2009**, 11, 1115-1120.

Part II: Section B is entitled as ***"Silica-Promoted Facile Synthesis of Thioesters and Thioethers: Highly Efficient, Reusable and Environmentally Safe Solid Support"***. This section deals with a new synthetic methodology towards the synthesis of thioesters and thioethers on silica surface at ambient temperature using thiols and acid chloride or alkyl halide respectively under base-free conditions. The protocol allows the protection of thiols under neutral heterogeneous conditions without requiring any bases or Lewis acids, and the silica gel used as the promoter can be recycled for several runs without any loss of activity.



An account of this work has been published in *Green Chem.*, **2010**, 12, 767-771.

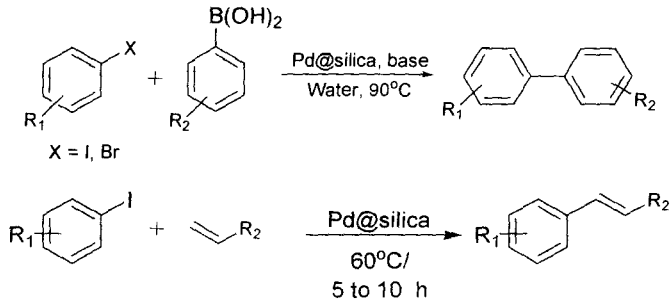
Part II: Section C of the thesis delineates a highly efficient and selective synthesis of functionalized 1,2–benzimidazoles under solvent-free conditions at room temperature using eco-friendly ferric sulphate impregnated with silica [Fe(III)–Silica]. Recycling of the solid support up to six runs was investigated with appreciable yield of the product. While most other methods in the literature involve formation of either a mixture of both 2-substituted and 1,2-disubstitute benzimidazoles or only 2-substituted benzimidazoles, our conditions resulted in the formation of only 1,2-disubstituted benzimidazoles exclusively. Such selectivity is rare and the methodology has been generalized with different substrate molecules. The section has been entitled ***"Chemoselective Synthesis of 1,2-Disubstituted Benzimidazoles on Silica Supported Iron (III) Catalyst"***.



The manuscript is ready and being submitted for publication soon.

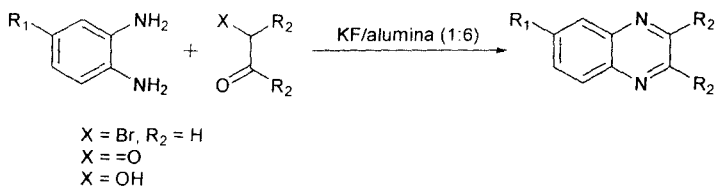
Part II: Section D entitled ***"Synthesis and Characterization of Pd Nanoparticles (NPs) Supported on Silica (Pd@Silica) and its Application to Suzuki and Heck Coupling Reactions"*** describes the development of a new and simple method to prepare silica-supported Pd NPs (Pd@Silica) and subsequent applications in C-C cross coupling reactions (Suzuki and Heck reaction). Its surface morphology was obtained by TEM, which confirmed average particle size distributions. Indeed the present study revealed an easy, green and economically more viable

procedure for immobilization of palladium on to silica surface and further high catalytic efficiency (0.06 mol%) under mild conditions are noteworthy. However, further investigations would be undertaken regarding optimization of any leaching effect (studies are underway with XPS studies), recycling ability and extension to other cross-coupling reactions.



The manuscript is under the process of preparation.

Part II: Section E is entitled as ***"KF-Alumina: A Versatile Solid Surface for the Synthesis of Quinoxalines under Solvent-free Conditions"***. We have presented here another application of KF-alumina: as a versatile heterogeneous basic surface for the synthesis of quinoxalines from a variety of precursors under mild reaction condition. All the three substrates *viz.* α-keto hydroxy, α-keto halides and 1,2-dicabonyl compounds react smoothly with 1,2-diamine to yield the corresponding quinoxaline derivatives in excellent yields. Other studies in the literature involved requirement of an oxidizing agent, particularly for the tandem oxidation-condensation-aromatization route. The present investigation showed that such process can be made effective in the presence of only KF-alumina thereby negating the presence of any strong oxidizing agent and the procedure is shown to be tolerated with wide variety of functional groups.



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