Developing environmentally friendly catalytic synthetic methodologies that reduce or eliminate the use and generation of hazardous substances, volatile organic solvents in reaction and post-reaction stage is a major thrust area of contemporary green chemistry research. The basis and guidelines of pursuing green chemistry have been clearly defined in the Twelve Principles of Green Chemistry enunciated by P. T. Anastas and J. C Warner. The research work described in the present dissertation “Studies on Some Methods of Organic Synthesis” is primarily aimed at addressing green chemistry issues and endeavours to develop some useful synthetic protocols with focus on better environmental compliance.

Protection of functional groups and their deprotection at some appropriate stages in a multistep organic synthesis often holds key to the success of entry into multifunctional structural targets. Although protection-deprotection sequences prolong synthetic tour that should be avoided from green chemistry standpoint, mild, catalytic and nontoxic reagents should be preferably utilized during installation and cleavage of reactive protecting groups under unavoidable situations. The thesis consists of four Parts of which Part I is based upon our efforts to utilize catalytic amount of iodine and ammonium heptamolybdate tetrahydrate as activators of environment friendly and safe terminal oxidizer, 30 % aqueous hydrogen peroxide and develop iodine-hydrogen peroxide and ammonium heptamolybdate-hydrogen peroxide combinations as cleaving reagents for useful carbonyl protecting oxime group. The results have been described in Section B and C of Chapter I of this Part. A dethioacetalization protocol employing a catalytic amount of 2,4,4,6-tetrabromo-2,5-cyclohexadienone (TBCHD) and aqueous hydrogen peroxide has been disclosed in the next Chapter II of this Part. Each Chapter begins with Section A overviewing some selected recent procedures pertaining to methods described in Section B or C.

The Part 2 deals with regioselective bromination of activated coumarins with TBCHD as a surrogate of bromonium ion. It was revealed that the reagent could be successfully utilized for this highly selective synthetically relevant transformation by nucleophile-driven bromonium ion release.
The Part 3 is concerned with synthesis of secondary as well as primary amides by way of Beckmann rearrangement (BR) of ketoximes and dehydration-hydratation sequence of aldoximes. Projected as one of key thrust areas of green chemistry research due to ubiquity of amide functionality in a host of drugs, pharmaceuticals and potential drug candidates, their step- and atom-economic synthesis is of major current interest. The Beckmann rearrangement of ketoximes provides an atom- and step-economic approach to this end. We utilized tetra-n-butylammonium iodide to bolster Lewis acidity of stannous ion of stannous chloride dihydrate by way of generation of SnCl₂I species. An efficient and expeditious BR rearrangement procedure of ketoximes was accomplished with SnCl₂-TBAI combination. Aldoximes were transformed into primary amides as well with SnCl₂.2H₂O and a strong amidine base, DBU.

The three-component copper triflate-catalyzed variant of Povarov reaction (inverse electron demand Diels-Alder reaction) employing 6-aminocoumarins, aromatic aldehydes and activated dienophiles (mainly cyclic enol ethers) as reaction partners selectively generated biologically relevant trans-1,2,3,4-tetrahydropyridocoumarins (Part 4, Section B) and a complementary protocol of cis-selective imino Diels-Alder reaction catalyzed by benzoic acid under aqueous micellar conditions is reported in Section C of this last Part. The experimental details, characterization of products and mechanistic interpretation of reactions have been adequately provided.

It is a great pleasure for me to express my sincere gratitude and respect to Prof. Nemai C. Ganguly, Department of Chemistry, University of Kalyani, for introducing me to the fascinating field of “Synthetic Organic Chemistry” and allowing me to work under his active supervision and guidance.

I wish to express my sincere gratitude to Prof. Debasish Chatterjee (Head, Department of Chemistry, University of Kalyani), Prof. Shital K Chattopadhyay (Dean, Faculty of Science, University of Kalyani), Prof. K. C. Majumder, Dr. K. Ghosh, Prof. A. P. Chattopadhyay, Prof. S. P. Das, Prof. S. Dey. Prof. S. Chattopadhyay, Prof. N. Nandi of our department. I am also very grateful to Dr. A. D. Bond, University of Southern Denmark, Prof. Sibdas Ray, University of Calcutta for their prompt assistance and generous supports.
I wish to express my thankfulness to Prof. Ranjan Mukherjee (IICB, Calcutta), Mr. Debasish Maity for recording NMR spectra and Mr. Prabuddha Sur for recording FTIR spectra and all the non-teaching staffs of this department for their valuable assistance in various forms.

I express my heartiest appreciation to all my lab-mates, including Sri Sujoy Kumar Barik for their support and valuable assistance from the very first day of my research career. I owe to my juniors Mr. Pallab Mondal, Mr. Sumanta Chandra and Ms. Sushmita Ray for rendering valuable suggestions, cooperation and help.

I have a great obligation to thank Late. Debabrata Das (ex HM of my school) for his whole-hearted cooperation to start my research career.

I also thankfully acknowledge the assistance of my colleagues of Akipur Nabagopal High School, specially, Sri. Prabir Kumar Mondal (Headmaster) for their constant encouragement and help in various ways.

I am also thankful to the University of Kalyani for providing me laboratory facility throughout my Ph.D research work.

The author takes this opportunity to express his profound regards to his parents, who have shared the joys and sorrows of research and constantly encouraged in the pursuit of science. The author is also thankful to all his family members for their constant encouragement and inspiration to carry out and continue the research work.

Finally, my special thanks go to my wife Anjana for her support, encouragement, and understanding.

Date: 6.2.2012

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