Development of new synthetic methodologies with focus on high selectivity, manipulative simplicity and environmental compatibility is an area of considerable contemporary interest to organic chemists. Synthetic processes based on electrophilic aromatic substitution reactions are ubiquitous, mechanistically intriguing and industrially important. Of these, nitration of aromatics and heteroaromatics is notoriously unselective of aromatic substitutions and an immensely important industrial process. The nitro compounds are widely utilized as chemical feedstocks for a great range of useful materials, such as dyes, pharmaceuticals, perfumes and plastics. Aromatic and heteroaromatic nitro compounds are easily interconverted into a host of useful functionalities and therefore these compounds are also widely used as synthetic intermediates particularly for the synthesis of heterocycles. Nitrations typically require the use of potent mixtures of concentrated or fuming nitric acid with sulphuric acid leading to excessive acid waste streams. With chemists under increasing pressure to perform atom economic processes with minimal or no environmentally unfriendly by-products, development of alternative reagents and solvent systems for regioselective nitration is being pursued actively. Ceric ammonium nitrate (CAN) is one of lanthamide reagents which has been widely employed for accomplishing many efficient and selective synthetic protocols. CAN has been employed to achieve a variety of synthetic transformations of aromatic and heteroaromatic compounds which include ring substitution, benzylic oxidation, oxidative nitration, acetoxylation and, more recently, radical coupling reactions leading to C-C and C-O bond formations. However, use of CAN as a solid equivalent of nitric acid for nitration of heteroarenes has not been adequately investigated. With control over its oxyphilicity and oxidizing ability by choice of appropriate solvent and use of solid inorganic supports such as clays, silica gel, CAN has the potential to emerge as an useful alternative reagent for nitration. The first part of the thesis entitled “Studies on Some Methods of Organic Synthesis” embodies the results of our investigations on CAN-based nitration of some coumarins with varying levels of electron availability in the benzenoid as well as α-pyrone ring. This part (Part I) of the thesis comprises an introductory review on the synthetic applications of CAN in
Use of protective groups in multistep organic synthesis of natural and unnatural products is common and search for new methods of functional group protection and deprotection continues. Protection of carbonyl group as oxime, semicarbazones and phenylhydrazones has been widely used in synthetic operations and, therefore, their deprotection to parent carbonyl compounds has received tremendous attention over the years. Cleavage of these nitrogen-containing derivatives by oxidants such as oxochromium (VI) reagents is of particular interest for acid-sensitive and oxidation-prone carbonyl compounds. The chromium (VI) reagents have undergone improvement over the years to suit the specific needs of practising chemists and pyridinium chlorochromate (PCC), pyridinium dichromate (PDC), pyridinium fluorochromate (PFC) and, recently, quinolinium fluorochromate (QFC) have figured as useful selective two-electron Cr(VI) oxidants. It was our interest to explore the potential of pyridinium fluorochromate (PFC) as a mild selective deoximating agent. Part II of the thesis deals with our efforts to develop new convenient methods of deprotection of oximes based on PFC adsorbed on wet alumina and PFC in combination with 30% hydrogen peroxide as cooxidant. This part is divided into four sections (Section A-D). Section A enumerates a list of different reagents for cleavage of oximes developed over the years. A discussion on advantages and disadvantages of some typical recent methods is also included in this Section. Section B reveals a new mild and selective method of oxidative demasking of oximes using PFC supported on wet alumina. The Section C of this part reports a more general method of deoximation using PFC along with 30% hydrogen peroxide and is
complementary to the former protocol. The Section D describes the experimental details related to Section B and C of this part.

The Part III of the present dissertation is concerned with environmental hazards associated with the oxochromium reagents and our efforts to minimize it. In view of well-known genotoxicity and mutagenic nature of Cr(VI) reagents, it was decided to address the issue of developing synthetic methods which combine efficiency of PFC with environmental compliance by reducing substantially the amount of reagent employed for deprotection purpose. We were also interested to find general conditions of regenerating carbonyl compounds from other derivatives, such as semicarbazones and phenylhydrazones with PFC. The results of these investigations embody Part III of the thesis. The Section A of this part reveals our attempt at greening the deprotection protocol by the catalytic use of PFC in combination with 70% t-butyl hydroperoxide. The following Section B describes an alternative solventless solid-state general protocol of cleavage of oximes, semicarbazones and phenylhydrazones with PFC on montmorillonite K-10 clay under microwave irradiation. The experimental aspects of these two protocols have been described in the last Section C of this Part.

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