Computational chemistry has matured as an independent discipline where chemistry is learnt through computations. It deals with the use of computers and computational procedures to understand and explore the chemistry of the systems of interest. The recent advancement of computer technology and its easy access and affordability have greatly accelerated the growth of computer applications to chemistry and other areas of sciences. Such a growth of computational power has also complemented the growth of new concepts. As a result, today we have efficient computational tools to practice chemistry. The available quantum mechanical tools such as ab initio and density functional methods have efficiently complemented the experimental processes and even compensate the areas that are inaccessible to experiments. They have been useful to probe atomic and molecular properties, spectral properties, mechanism of reactions, thermochemical properties etc. In the analyses of imaginary/transient or short-lived species molecular modeling has an edge over experiment. As such short-lived species could not be isolated, determining their properties is a difficult task to be performed in a chemical laboratory, but it is easy to "observe" them in computers. Also, enhanced insights about certain experimental observations could be gained through orbital level analysis. Now-a-days, computational chemistry, the state-of-the-art is being extensively used in the field of mechanistic organic chemistry. Modeling reactions has become an efficient tool for comprehending the mechanism of these reactions by exploring the potential energy surfaces. Reaction path following has become a vital tool for understanding reactions and the role of catalysts. A task of such a kind is quite unimaginable for a chemist at an ordinary working laboratory. The present investigation is modeling reactions mainly focusing on the mechanism of the insertion reactions of carbenes into single bond of X-H (X=C, N, O, S).

Insertion reactions of singlet carbene and halocarbenes into non-polar C-H bonds of alkanes and into polar N-H, O-H and S-H bonds of amines, alcohols and thioalcohols have been chosen for the reason that these reactions have not been well documented. Most of the reactions chosen for modeling here have not been experimentally accomplished and
those papers do not report the barriers. They mention only the reaction conditions and product ratios (and they have been used for calibrations). During this study, we have tried to answer some queries that are mechanistically interesting. Especially, the occurrence of TSs either in the electrophilic or nucleophilic phase has been identified through NBO charge analysis in addition to the net charge flow from alkane to the carbene moiety for the singlet chlorocarbenes insertions into C-H bond by simulating these reactions using the *ab initio* and density functional theory.

The investigations presented in the thesis are mostly done on a Pentium IV computer using Gaussian98 and Gaussian03 programs. The calculations are restricted to gas phase and solvent effects have not been done for two reasons. One, the existing solvent models mimic only the bulk effect and therefore are poor in describing solvent interactions. Secondly, explicit inclusion of solvent molecules needs high computing power. Generally, B3LYP/6-31g (d, p) and MP2/6-31g (d, p) level has been chosen for computation and for comparison higher level and higher basis sets are employed wherever needed. For singlet chlorocarbenes insertion reactions with methane, CCSD, CCSD (T) and G3MP2 calculations have been done to calibrate the B3LYP results. All computations have been performed within the affordable limit.

Out of this work, five papers have been published and three more are in a ready to submit form. These materials have been adapted in the thesis with minor modifications as thesis chapters II-VI. Chapter I describes the theoretical background of the methods used, a brief introduction of carbenes, halocarbenes, their reactivity and the scope of the thesis. Since, all the chapters are independent units, repetition of certain references and computational details could not be avoided. Summary of the thesis is appended at the end of the thesis.