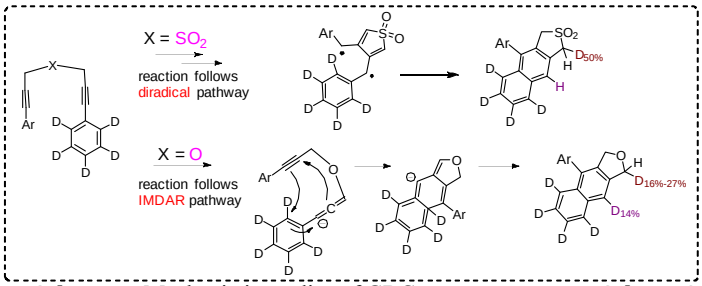
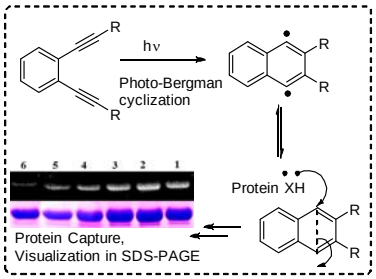
Abstract

Studies on the Synthesis and Reactivity of Diradical Generating Molecules

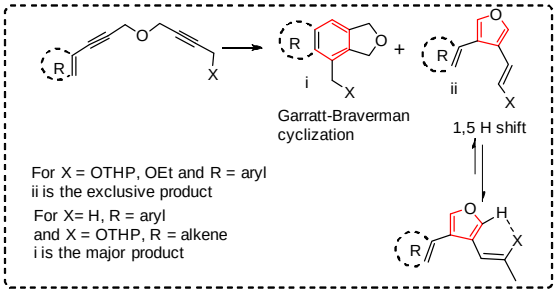
This thesis is a compilation of mechanistic studies and synthetic potential of diradical generating cycloaromatization reactions, in particular, the Garratt-Braverman cyclization (GBC) and the Bergman cyclization (BC). The first chapter contains a brief review on sequential developments on the mechanistic aspects of BC and GBC. The second chapter deals with the mechanistic investigation on GBC. By using various experimental techniques like ^{2}H NMR, LA-LDI and from the fate of deuterium labeled substrates we have been able to propose a diradical pathway for bis-propargyl sulfones and an anionic intramolecular Diels Alder (IMDAR) pathway for bis-propargyl ethers (**Scheme 1**). The third chapter comprises the validation of enediyne moiety to act as a photoaffinity label in protein capture. The probable mechanism of capture *via* a photo-Bergman cyclization of enediynes has also been described (**Scheme 2**). The fourth chapter contains differential reactivity of bis-propargyl ethers appended with aliphatic substituents. These systems may undergo either GBC to aryl (dihydro) naphthalenes or follow a 1,5-H shift pathway to yield 3,4-disubstituted furans. Strategies have been developed to shift the preference from GBC to 1,5-H shift process to yield 3,4-disubstituted furans that are otherwise difficult to obtain and also constitute an important skeleton in medicinal chemistry (**Scheme 3**). Unlike the ethers which follow a GBC pathway under base treatment, the corresponding propargyl alkenyl sulfones follow a base-mediated 6π-electrocyclizaton reaction to substituted thiopyran dioxides. The mechanistic investigations (briefly represented in **Scheme 4**) of this 6π-electrocyclization process have been discussed in the fifth chapter. In the sixth chapter, the synthetic potential of GBC was further exploited by carrying out a one pot GBC and Scholl oxidation reaction to polyaromatic compounds having low lying E_{LUMO} level without sacrificing the band gap and the aerial stability of the compounds (**Scheme 5**).



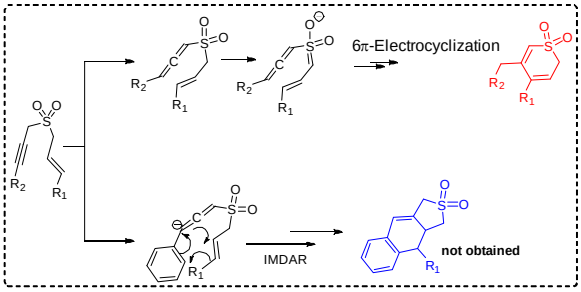
Scheme 1: Mechanistic studies of GBC



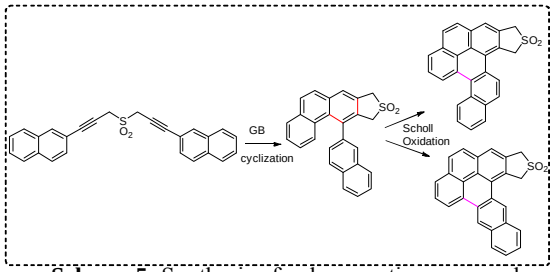
Scheme 2: Protein capture using photo-Bergman cyclization



Scheme 3: Base mediated rearrangement of bis-propargyl ethers



Scheme 4: Base mediated rearrangement of propargyl alkenyl sulfones



Scheme 5: Synthesis of polyaromatic compounds

Keywords: Radical, ionic, Garratt-Braverman cyclization, Bergman cyclization, mechanism, furans, thiopyran dioxides, protein capture.