Abstract

The five-membered carbocycles are recognized as essential class of substructures widely present in natural products and pharmaceutically active molecules. They are often utilized as a key building block for the synthesis of complex targets. On the other hand, arene and heteroarene-fused cyclopentanes consisting of indole, thiophene, benzothiophene, benzofuran, and furans are abundant in a diverse range of bioactive natural products, pharmaceutically relevant molecules. They also found broad application in material science, especially in organic semiconducting materials and optoelectronics. Numerous synthetic strategies have been developed to access cyclopentanoids by utilizing precious metals and organocatalysts. The commonly employed strategies include [3+2], [4+1], [2+2+1] cycloaddition reactions, Pauson- Khand reaction, Rauhut-Currier (RC) reaction, and Morita-Baylis-Hillman (MBH) reaction. However, the development of general, efficient and atom-economic organocatalytic methods starting from the readily accessible materials remain an emerging research area. This thesis mainly focused on the design and development of phosphine-mediated strategies to cyclopentanoids. In this regard, the substrates were designed amenable to an intramolecular MBH reaction. The first section of the seminar will highlight an efficient enantioselective intramolecular MBH reaction of □-mono and □□□-disubstituted enones to access enantioenriched cyclopenta[b]annulated arenes and heteroarenes. While the enones are well explored in a MBH reaction, only a handful of reports are successfully developed with activated dienes. Towards this, the second section will give an account of an enantioselective intramolecular MBH reaction of previously unexplored dienones to fused-cyclopentanes and their subsequent synthetic utility towards the one-pot telescopic synthesis of fluorenones. In an alternative approach, the third section describes a phosphine and water-mediated intramolecular reductive cyclization reaction of □-substituted dienone-aldehydes to afford the highly functionalized cyclopenta-fused arenes and heteroarenes bearing two contiguous stereogenic centers, one of them being an all-carbon quaternary center, in good yields and diastereoselectivities. A series of serendipitous one-step elaborations of reductive aldol products were established to access indeno-[1,2-b]furanones, indeno[1,2-b]pyrans, and dibenzo[a,h]- azulen-8-ones.