ABSTRACT

The thesis titled ***"Stereoselective Cascade Approaches Involving [1,2]-Phospha Brook Rearrangement/Conjugate Addition and Cycloaddition Reactions"*** is structured into four chapters that primarily focus on the development of stereoselective C-C and C-X bond-forming methodologies involving [1,2]-phospha Brook rearrangement, conjugate addition, and cycloaddition reactions. Chapters 2 and 3 detail the role of the [1,2]-phospha Brook rearrangement in stereoselective addition reactions, while Chapter 4 focuses on (5+2) cycloaddition reactions for constructing complex cyclic molecules.

Chapter 1: This chapter provides a concise overview of general organic chemistry, chirality, and its significance in everyday life, along with a discussion on asymmetric catalysis, with a particular focus on organocatalysis and its various activation modes. The chapter further elaborates on the concepts of aminocatalysis, the [1,2]-Phospha Brook Rearrangement, and cycloaddition reactions.

Chapter 2: This chapter introduces an aminocatalytic enantioselective conjugate addition reaction involving [1,2]-phospha-Brook rearrangement. Here, a simple aminocatalyst featuring both primary/secondary amine and tertiary amine functionalities, enabling the simultaneous activation of *α,β*-unsaturated enones and the generation of anionic nucleophiles *via* the Pudovik addition/[1,2]-phospha-Brook rearrangement. The approach provides a simple one-pot process employing a stable, additive-free catalytic system, yielding a variety of oxindole derivatives with two adjacent stereocenters, achieved in high yields and exceptional stereoselectivities.

Chapter 3: This work describes a highly regio- and diastereoselective approach for synthesizing phosphate-substituted dihydrocoumarins through the [1,2]-phospha-Brook rearrangement catalyzed by a Brønsted base. The method employs a two-step, one-pot process involving the Michael addition of *α*-phosphonyloxy enolates formed through the coupling of dialkyl phosphite with *α*-ketoesters to *o*-quinone methides, followed by intramolecular cyclization. This strategy efficiently produces 3,4-dihydrocoumarin frameworks in high yields with excellent diastereoselectivity.

Chapter 4: This section presents a base-catalyzed intermolecular (5+2) cycloaddition/oxa-Michael addition between α-arylidene pyrazolones and acylated pyranone acetals. The reaction proceeds through a sequential vinylogous aldol-Michael addition of alkylidene pyrazolones to oxidopyrylium ylides, generated in situ from the acylated pyranone acetals. This process yields

bridged cycloaddition products, which subsequently undergo oxa-Michael addition. The method offers a highly regioselective and stereoselective route to synthesize 8-oxobicyclo[3.2.1]octane cores, achieving moderate to good yields with excellent diastereoselectivity.