Stereoselective Synthesis of Axially Chiral (Hetero)Biaryls, Bridged Isochromans and Amino Indanones

Abstract: The thesis entitled "*Stereoselective Synthesis of Axially Chiral (Hetero)Biaryls, Bridged Isochromans and Amino Indanones*" presents a comprehensive exploration of modern asymmetric catalysis with a particular focus on organocatalysis and silver-mediated transformations. Chapter 1 introduces the fundamentals of general organic chemistry, chirality, and its significance in everyday life, followed by a detailed discussion on asymmetric catalysis. Special emphasis is laid on organocatalysis, its diverse activation modes, cooperative catalysis, and the emerging relevance of atropoisomerism, culminating in the activation of alkynes via silver catalysis. Chapter 2 describes the development of a chiral silver phosphate-catalyzed 5-*endo*-*dig* nucleophilic cyclization of alkynyl naphthalene-substituted hydrazones, yielding C–C axially chiral pyrazoles with excellent enantioselectivity and yield. Mechanistic studies revealed the synergistic roles of silver salts and chiral phosphoric acids in facilitating and steering the reaction. In Chapter 3, an enantioselective synthesis of axially chiral 3-haloquinolines was achieved through a tandem 6π-electrocyclization of alkynyl imines mediated by NBS. This methodology is the first to exploit vinylidene ortho-quinone methide intermediates for the direct formation of 3-halogenated axially chiral quinolines. Chapter 4 details a stereoselective, silver-catalyzed one-pot vinylogous aldol addition followed by a cascade [4+2] cycloaddition, providing access to novel bridged pentacyclic isochromans with high yields and diastereoselectivity under mild conditions. Finally, Chapter 5 outlines a silver- and phosphoric acid-catalyzed stereoselective synthesis of 3-amino indanones from 2-alkynyl acetophenones and anilines. The developed method affords products with high diastereoselectivity and broad substrate scope, alongside showcasing synthetic applications of the resulting scaffolds. Together, these studies offer innovative catalytic strategies for the construction of axially and bioactive molecules with potential relevance in medicinal chemistry and material science.