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Book Review

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Enantioselective Organocatalysis: Reactions and Experimental Procedures

Wiley-VCH, 2007

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The ability of organic molecules to catalyse a multitude of chemical transformations asymmetrically has been at the forefront of much synthetic chemistry over the last decade. This compilation, edited by Peter I. Dalko, provides a concise and comprehensive overview of many topics within this ever expanding field. The book is made up of 15 chapters, covering topics that include enamine and iminium reactions, phase transfer catalysis, N-heterocyclic carbene mediated transformations and oxidation and reduction. The length and style of each of the chapters differs markedly, with each chapter comprehensive in its coverage and in this way will be a useful addition as a reference text to practicing chemists or newcomers to the area.

Chapter 1 introduces asymmetric organocatalysis and gives a brief historical review of the area before introducing a number of the privileged scaffolds that can be used to promote multiple catalytic transformations in this area. Chapter 2 covers three major areas of organocatalysis that involve enamine-based catalysis. Firstly, Barbas and Tanaka give an in-depth review of asymmetric aldol and Mannich reactions, including the use of ketone and aldehyde donors and intramolecular reactions as well as rationalizing the stereoselectivity of these transformations. Marigo and Jørgensen focus upon the α -functionalisation of enamines with heteroatoms, covering asymmetric amination, oxidation, halogenation and sulfenylation reactions. The chapter closes with Bressy and Dalko focusing upon conjugate additions via enamine activation, including the addition of ketones/aldehydes to nitroolefins, malonates and enones before finishing on intramolecular variants and application to multiple component coupling. In Chapter 3, Lelais and MacMillan focus on iminium catalysis, elegantly introducing the area and the concept behind this activation protocol and illustrating its application in a number of processes including cycloaddition reactions, 1,4 addition reactions, hydrogenation and cascade catalysis. Ooi and Maruoka then cover the use of ammonium ions as chiral templates, including both homogeneous and heterogeneous catalysis in great detail and depth. Chapter 5 focuses upon asymmetric Morita-Baylis-Hillman type reactions, covering reaction mechanism, the use of chiral amine catalysts, dual catalyst systems including the combination of thiourea and amine catalyst systems and phosphine catalysts. In chapter 6, Rawal et al. introduce the field of asymmetric proton catalysis and cover the use of hydrogen bonding based activation of a multitude of chemical transformations including the use of thioureas, cinchona alkaloids, peptides, ureas, phosphoric acids and taddols as catalysts. Kocovsky and Malkov subsequently cover the use of chiral Lewis bases as catalysts in a succinct and comprehensive fashion, giving an interesting account of the Lewis basic species capable of promoting asymmetric transformations in this area. In chapter 8, Spivey and McDaid give a definitive account of asymmetric acyl transfer reactions, classifying the types of processes available in this area and comprehensively including the range of catalysts that have been developed within this arena for both kinetic resolution and desymmetrisation processes. Enders et al. then cover the main areas of asymmetric organocatalysis employing N-heterocyclic carbenes as catalysts, including benzoin, stetter, conjugate umpolung and transesterification and polymerization processes. In chapter 10, McGarrigle and Aggarwal cover the use of ylides of sulfur, nitrogen, tellurium and selenium as organocatalysts for epoxidation, aziridination and cyclopropanation, covering the current state of the art in this field and reflecting upon possible areas where improvements in this methodology can be made. Kagan then focuses upon the organocatalytic reduction of olefins, ketones and imines before Armstrong gives an interesting introduction to asymmetric oxidation reactions, including the use of ketone, iminium salt and amine mediated oxidation processes for a plethora of transformations. In chapter 13, Bogliotti and Dalko consider shape and site-selective asymmetric transformations, including the use of peptide based catalysts for acetylation and phosphorylation, and the use of calixarenes and cyclodextrins for esterification, hydrolysis and oxidation. It is interesting and instructive that chapter 14 also includes experimental details of selected transformations of each of the preceding chapters, enabling a range of synthetic protocols to be easily accessed, while chapter 15 provides a useful summary of the catalysts structures that are typically used in each type of transformation.

In conclusion, this book is a truly excellent and important addition to the field of enantioselective organocatalysis, giving a comprehensive overview of the vast array of supporting chemistry. The focus of the treatise is on promoting understanding of the catalytic mechanisms underpinning the various areas, and on this it clearly delivers. This book will be a useful reference for both specialists and non-specialists chemists working within synthetic organic chemistry.

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