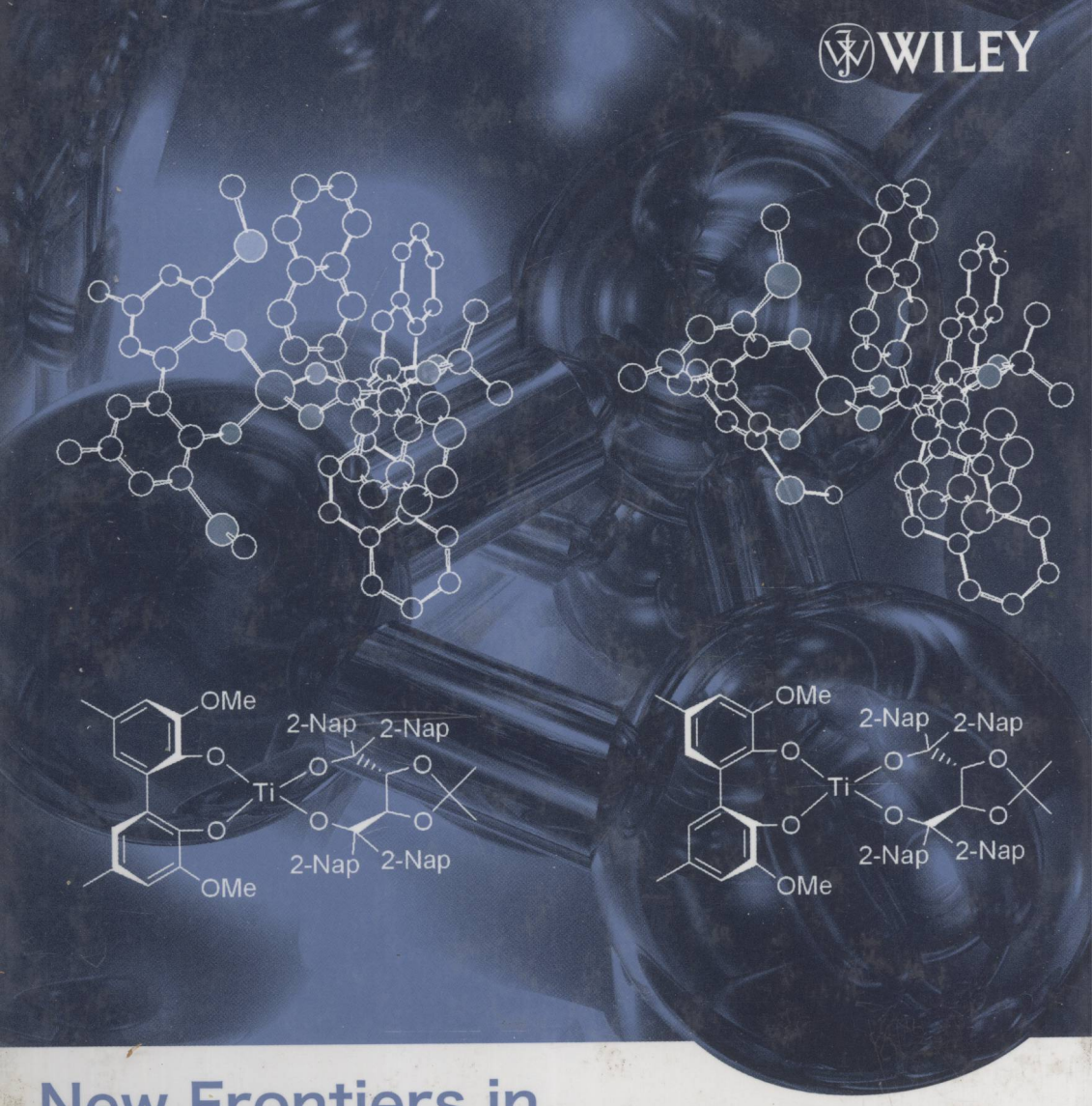

New Frontiers in

ASYMMETRIC CATALYSIS

Edited by

Koichi Mikami · Mark Lautens

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PREFACE

New Frontiers in Asymmetric Catalysis provides readers with a comprehensive perspective on understanding the concepts and applications of asymmetric catalysis reactions. Despite the availability of excellent comprehensive multivolume treatises in this field, we felt that researchers in pharmaceutical and chemical companies as well as university faculty and graduate students would benefit from a selection of some of the most important recent advances in this ever-growing area.

The key to efficient asymmetric catalysis lies in the creation of robust chiral catalysts by a suitable combination of chiral organic compounds and metal centers to which they are ligated. Many chiral organic ligands are *atropisomeric* (a + *tropos* in Greek) compounds with C_2 symmetry, such as BINOL and BINAP. The use of C_2 symmetric ligands originally introduced by Kagan had a strong impact on subsequent ligands design for asymmetric catalysis. In recent years new nonsymmetric ligands that are more effective than their C_2 counterparts have been reported. The first chapters of this book are dedicated to "rational" ligand design, which is critically dependent on the reaction type (reduction, oxidation, and C–C bond formation). The concept of C_2 symmetry for bidentate ligands can be extended to the design of C_n symmetric multidentate ligands bearing phosphorous, nitrogen, and other coordinating elements.

Catalyst systems can be described as biomimetic assemblies of multifunctional or bimetallic catalysts. Ideally, their design can be based on quantitative analysis of the transition state for a given reaction. Alternatively, a combinatorial screening of metal centers and chiral ligands can also lead to new catalyst systems. The development of efficient high-throughput screening methods for finding a good lead or an optimized catalytic system is still in its infancy.

In asymmetric catalysis, Sharpless emphasized the importance of "ligand-accelerated catalysis" through the construction of an asymmetric catalyst from an achiral precatalyst via ligand exchange with a chiral ligand. By contrast, a dynamic combinatorial approach, where an achiral precatalyst combined with several multicomponent chiral ligands (L^1*, — —) and several chiral activator ligands (A^1*, — —) may selectively assemble into the most active and highest enantioselective activated catalyst (ML^m* A^n*).

In Chapters 4–6, recent findings on activation of C–H bonds, C–C bonds and small molecules (C=O, HCN, RN=C, and CO_2) are covered. The latest developments on C–C bond reorganization such as metathesis (which earned the Nobel prize in chemistry, 2005) are also described.

Studies on the origin of chirality generated from achiral or racemic "primitive earth" provide the basis for asymmetric catalysis starting from racemic or achiral catalysts. Asymmetric catalysis through enantiomeric fluctuation or discrimination by an external chiral bias and subsequent amplification of chirality can be developed through autocatalysis with nonlinear effects. One strategy for achieving this enantiomeric discrimination is the addition of a chiral source, which selectively transforms one catalyst enantiomer into a highly activated or deactivated catalyst enantiomer. Recent progress on "chirally economical" nonlinear phenomena, racemic catalysis, and autocatalysis are highlighted in Chapters 7–9.

Asymmetric catalysis in target- or diversity-oriented synthesis becomes an increasingly important tool. Desymmetrization of symmetric intermediates (asymmetric or enantioselective desymmetrization) is one important synthetic strategy reviewed in Chapter 10. Use of naturally occurring enzymes is one of the oldest and most important approaches employed in asymmetric desymmetrization, the so-called classic mesotrick process. Generally effective methods for highly enantioselective aziridination of olefins, reduction and C–C bond formation of aliphatic ketones, are also expected to become practical (often via a pseudodesymmetrization process) in the very near future. Asymmetric catalytic tendem (domino) reaction sequences are likely to remain at the forefront of future research efforts.

Finally in Chapters 11–13, some of the more recent discoveries that have led to a renaissance in the field of organocatalysis are described. Included in this section are the development of chiral Brönsted acids and Lewis acidic metals bearing the conjugate base of the Brönsted acids as the ligands and the chiral bifunctional acid–base catalysts.

Although tremendous progress has been made in the field of asymmetric catalysis, very few systems have become widely applicable on an industrial scale because of challenges of catalyst efficiency (turnover number (TON) and frequency (TOF), catalyst loading, applicability to a wide range of systems and with feedstocks of varying purity and the levels of enantioselectivity). The best known are the Takasago menthol process, the Novartis imine hydrogenation for metolachlor, the Sumitomo cyclopropanation for cilastatine, and the Firmenich process of fragrant paradisone. For many asymmetric reactions, the recovery and recycling of the catalysts are a serious concern for both industry and society in order to limit the amount of waste, and impurities, that affect the overall costs of the processes.

Thus, the use of catalysts in new "green" reaction media such as ionic liquids, fluorous solvents, and supercritical carbon dioxide has become a viable alternative to those discussed within the chapters.

We hope that readers will find helpful and thought-provoking information in this book written by frontrunners in their respective fields, including the areas recognized by recent Nobel prizes in chemistry.

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December 25, 2006

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CONTENTS

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LIGAND DESIGN FOR CATALYTIC ASYMMETRIC REDUCTION

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1.1 INTRODUCTION

Molecular catalysts consisting of a metal or metal ion and a chiral organic ligand are widely used for asymmetric synthesis. Figure 1.1 illustrates a typical (but not general) scheme of asymmetric catalytic reaction.[1] The initially used chiral precatalyst **1A** is converted to the real catalyst **1B** through an induction process. An achiral reactant A and substrate B are activated by **1B** to form reversibly an intermediate **1C**. The chiral environment of **1C** induces asymmetric transformation of A and B to the chiral product A–B (*R* or *S*) through an intermediate **1D** with reproduction of catalyst **1B**. The absolute configuration of A–B is kinetically determined at the first irreversible step, **1C→1D**. The efficiency of catalysis depends on several kinetic and thermodynamic parameters, because most catalytic reactions proceed through such multistep transformation.

Catalytic asymmetric reduction of unsaturated compounds is one of the most reliable methods used to synthsize the corresponding chiral saturated products.[2–4] Chiral transition metal complexes repeatedly activate an organic or inorganic hydride source, and transfer the hydride to olefins, ketones, or imines from one

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