



New Frontiers in

ASYMMETRIC CATALYSIS

Edited by

Koichi Mikami · Mark Lautens

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Edited by

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**NEW FRONTIERS
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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 + tropo* 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 tandem (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 Brønsted acids and Lewis acidic metals bearing the conjugate base of the Brønsted 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

PREFACE	xi
CONTRIBUTORS	xv
1 Ligand Design for Catalytic Asymmetric Reduction	1
<i>Takeshi Ohkuma, Masato Kitamura, and Ryoji Noyori</i>	
1.1 Introduction	1
1.2 Hydrogenation of Olefins	2
1.2.1 Enamide Hydrogenation with Rhodium Catalysts	2
1.2.2 Hydrogenation of Functionalized Olefins with Ruthenium Catalysts	9
1.2.3 Hydrogenation of Simple Olefins with Iridium Catalysts	11
1.3 Reduction of Ketones	12
1.3.1 Hydrogenation of Functionalized Ketones	12
1.3.2 Hydrogenation of Simple Ketones	15
1.3.3 Transfer Hydrogenation of Ketones	20
1.3.4 Hydroboration of Ketones	22
1.4 Reduction of Imines	25
References	28
2 Ligand Design for Oxidation	33
<i>Tohru Yamada</i>	
2.1 Introduction	33
2.2 Catalytic Enantioselective Epoxidation of Unfunctionalized Olefins	35

2.3	Enantioselective Metal-Catalyzed Baeyer–Villiger Oxidation	44
2.4	Optical Resolution during Oxidation of Alcohols	48
2.5	Catalytic Enantioselective Oxidative Coupling of 2-Naphthols	50
2.6	Concluding Remarks	55
	References	55
3	Ligand Design for C–C Bond Formation	59
	<i>Ryo Shintani and Tamio Hayashi</i>	
3.1	Introduction	59
3.2	1,4-Addition and Related Reactions	59
3.2.1	Copper Catalysis	60
3.2.2	Rhodium Catalysis	69
3.3	Cross-Coupling Reactions	89
3.3.1	Kumada-Type Cross-Couplings	90
3.3.2	Suzuki-Type Cross-Couplings	96
	References	97
4	Activation of Small Molecules (C=O, HCN, RN=C, and CO₂)	101
	<i>Kyoko Nozaki</i>	
4.1	Introduction	101
4.2	Asymmetric Hydroformylation of Olefins	102
4.2.1	The Mechanism of Hydroformylation	103
4.2.2	Scope and Limitation of Asymmetric Hydroformylation	104
4.2.3	“Greener” Catalysts in Asymmetric Hydroformylation	111
4.3	Asymmetric Hydrocarbohydroxylation and Related Reactions	112
4.3.1	Asymmetric Hydrocarbalkoxylation of Alkenes	112
4.3.2	Asymmetric Oxidative Hydrocarbalkoxylation of Alkenes	112
4.3.3	Asymmetric Carbonylation of Carbon–Heteroatom Bonds	115
4.4	Asymmetric Ketone Formation from Carbon–Carbon Multiple Bonds and CO	115
4.4.1	Asymmetric Pauson–Khand Reaction	115
4.4.2	Asymmetric Alternating Copolymerization of Olefins with CO	118
4.4.3	Asymmetric Polymerization of Isocyanide	118
4.5	Asymmetric Hydrocyanation of Olefins	119
4.6	Asymmetric Addition of Cyanide and Isocyanide to Aldehydes or Imines	120
4.7	Asymmetric Addition of Carbon Dioxide	123
4.8	Conclusion and Outlook	124
	References	124
5	Asymmetric Synthesis Based on Catalytic Activation of C–H Bonds and C–C Bonds	129
	<i>Zhiping Li and Chao-Jun Li</i>	
5.1	Introduction	129

5.2	Asymmetric Synthesis via Activation of C–H Bonds	130
5.2.1	Formation of C–C Bonds	130
5.2.2	Formation of C–O Bonds	142
5.2.3	Formation of C–N Bonds	144
5.3	Asymmetric Synthesis via Activation of C–C Bonds	145
5.3.1	Enantioselective C–C Bond Cleavage	146
5.3.2	Formation of C–C Bonds	146
5.3.3	Formation of C–O Bonds	149
5.4	Conclusions and Outlook	149
	Acknowledgments	150
	References	150
6	Recent Progress in the Metathesis Reaction	153
	<i>Miwako Mori</i>	
6.1	Introduction	153
6.2	Olefin Metathesis	155
6.2.1	Ring-Closing Olefin Metathesis	155
6.2.2	Cross-Metathesis (CM) of Diene	165
6.2.3	Ring-Opening Metathesis (ROM)–Ring-Closing Metathesis (RCM) of Alkene	167
6.2.4	Catalytic Asymmetric Olefin Metathesis	173
6.3	Enyne Metathesis	182
6.3.1	Ring-Closing Enyne Metathesis	182
6.3.2	Ring-Opening Metathesis (ROM)–Ring-Closing Metathesis (RCM) of Cycloalkene-Yne	186
6.3.3	Dienyne Metathesis	190
6.3.4	Cross-Metathesis of Enyne	193
6.4	Alkyne Metathesis	196
6.5	Conclusions	202
	References	203
7	Nonlinear Effects in Asymmetric Catalysis	207
	<i>Henri B. Kagan</i>	
7.1	Introduction	207
7.2	Properties of Enantiomer Mixtures	208
7.2.1	Physical Properties	208
7.2.2	Chemical Properties	208
7.3	Nonlinear Effect in Asymmetric Catalysis	209
7.3.1	The First Evidences	209
7.3.2	Origin of Nonlinear Effects: Some Models	210
7.4	Main Classes of Reactions	212
7.4.1	Organometallic Catalysts	213
7.4.2	Organocatalysts	213
7.5	Asymmetric Amplification	213

7.6	Current Trends	216
7.7	Conclusion	216
	Acknowledgment	216
	References and Notes	217
8	Asymmetric Activation and Deactivation of Racemic Catalysts	221
	<i>Koichi Mikami and Kohsuke Aikawa</i>	
8.1	Introduction	221
8.2	Racemic Catalysis	222
8.2.1	Asymmetric Deactivation	223
8.2.2	Asymmetric Activation of Chirally Rigid (Atropos) Catalysts	228
8.2.3	Asymmetric Activation/Deactivation of Chirally Rigid (Atropos) Catalysts	238
8.2.4	Self-Assembly into the Most Enantioselective Catalyst	239
8.2.5	Asymmetric Activation of Chirally Flexible (Tropos) Catalysts	243
8.3	Future Perspectives	254
	References and Notes	255
9	Asymmetric Autocatalysis with Amplification of Chirality and Origin of Chiral Homogeneity of Biomolecules	259
	<i>Kenso Soai, Tsuneomi Kawasaki, and Itaru Sato</i>	
9.1	Introduction	259
9.2	Asymmetric Autocatalysis	260
9.3	Amplification of Chirality by Asymmetric Autocatalysis	262
9.4	Asymmetric Autocatalysis and Its Role in the Origin and Amplification of Chirality	263
9.4.1	Asymmetric Autocatalysis Triggered by Organic Compounds Induced by Circularly Polarized Light	263
9.4.2	Asymmetric Autocatalysis Triggered Directly by Circularly Polarized Light	265
9.4.3	Asymmetric Autocatalysis Triggered by Chiral Inorganic Crystals	265
9.4.4	Asymmetric Autocatalysis Triggered by Chiral Organic Crystals Composed of Achiral Organic Compounds	267
9.4.5	Spontaneous Absolute Asymmetric Synthesis	268
9.5	Conclusions	270
	Acknowledgment	271
	References	271
10	Recent Advances in Catalytic Asymmetric Desymmetrization Reactions	275
	<i>Tomislav Rovis</i>	
10.1	Introduction	275

10.2	Allylic Alkylation	276
10.3	Ring Opening of Epoxides and Aziridines	279
10.4	Ring Opening of Bridged Systems	284
10.5	Olefin Metathesis	289
10.6	Acylation	291
10.7	Asymmetric Deprotonation	294
10.8	Oxidations	296
10.9	Cyclic Anhydride Desymmetrization	300
10.10	Miscellaneous	303
10.11	Concluding Remarks	307
	Acknowledgments	308
	References	308
11	History and Perspective of Chiral Organic Catalysts	313
	<i>Gérald Lelais and David W. C. MacMillan</i>	
11.1	Introduction	313
11.2	Historical Background	315
11.3	Iminium Catalysis: A New Concept in Organocatalysis	319
11.4	Enamine Catalysis: Birth, Rebirth, and Rapid Growth	326
11.5	Brønsted Acid Catalysis: Hydrogen-Bonding Activation	331
11.6	Phase Transfer Catalysis (PTC)	335
11.7	Future Perspective	339
	Acknowledgments	340
	References and Notes	341
12	Chiral Brønsted/Lewis Acid Catalysts	359
	<i>Kazuaki Ishihara and Hisashi Yamamoto</i>	
12.1	Introduction	359
12.2	Chiral Brønsted Acid Catalysts	359
12.3	Chiral Lewis Acid Catalysts	363
12.3.1	B(III)	363
12.3.2	Al(III)	366
12.3.3	Ti(IV)	368
12.4	Lewis Acid-Assisted Chiral Brønsted Acid Catalysts	373
12.5	Conclusions and Outlook	379
	References	380
13	Chiral Bifunctional Acid/Base Catalysts	383
	<i>Masakatsu Shibasaki and Motomu Kanai</i>	
13.1	Introduction	383
13.2	Chiral Brønsted Base Catalysis	384
13.3	Chiral Brønsted Base–Lewis Acid Bifunctional Catalysis	386

13.4	Chiral Brönsted Base–Brönsted Acid Bifunctional Catalysis	392
13.5	Chiral Lewis Base Catalysis	394
13.6	Chiral Lewis Base–Lewis Acid Bifunctional Catalysis	397
13.7	Conclusion	404
	References and Notes	405
Index		411

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 synthesize 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