CONTENTS

PREFACE xi

CONTRIBUTORS xv

1 Ligand Design for Catalytic Asymmetric Reduction 1
Takeshi Ohkuma, Masato Kitamura, and Ryoji Noyori

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
Tohru Yamada

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**
Ryo Shintani and Tamio Hayashi

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 CO_2) **101**
Kyoko Nozaki

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**
Zhiping Li and Chao-Jun Li

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
Miwako Mori

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
Henri B. Kagan

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
Koichi Mikami and Kohsuke Aikawa

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
Kenso Soai, Tsuneomi Kawasaki, and Itaru Sato

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
Tomislav Rovis

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
Gérald Lelais and David W. C. MacMillan

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
Kazuaki Ishihara and Hisashi Yamamoto

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
Masakatsu Shibasaki and Motomu Kanai

13.1 Introduction 383
13.2 Chiral Brönsted Base Catalysis 384
13.3 Chiral Brönsted 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**