

## Asymmetric Synthesis The Chiral Carbon Pool And

Asymmetric Synthesis, Volume 4: The Chiral Carbon Pool and Chiral Sulfur, Nitrogen, Phosphorus, and Silicon Centers describes the practical methods of obtaining chiral fragments. Divided into five chapters, this book specifically examines initial chiral transmission and extension. The opening chapter describes the so-called chiral carbon pool, the readily available chiral carbon fragments used as building blocks in synthesis. This chapter also provides a list of 375 chiral building blocks, along with their commercial sources, approximate prices, and methods of synthesis. Schemes involving almost 1,300 structures and the use of chiral building blocks to prepare alkaloids, arachidonic acid metabolites, compounds with chemotherapeutic and pharmacological activity, insect pheromones, sugars, vitamins, terpenoids, and miscellaneous compounds are also included in this text. The remaining chapters provide a similar overview of the chemistry of compounds chiral at sulfur, phosphorus, nitrogen, and silicon. Synthetic chemists and researchers, especially those engaged in pharmaceutical research and specialty chemicals production, will find this book invaluable.

Q1-1 Jiang Han and Jian-Hua Xie: Chiral Spiro Catalysts: Fuk, Lai Lam, Fuk Yee Kwong and Albert S. C. Chan: Chiral Phosphorus Ligands with Ferrocene Properties and Practical Applications... Jiang Han, Hai-Lai Yu, Jian-He Xu, Guo-Qiang Lin: Advances in Biocatalysis: Enzymatic Reactions and Their Applications... Mei-Xiang Wang: Enantioselective Biotransformations of Nitriles... Man Kin Wong, Yiu Chung Yip and Dan Yang: Asymmetric Epoxidation Catalyzed by Chiral Ketones... W. J. Liu, N. Li and L. Z. Gong: Asymmetric Organocatalysis: Qing-Hua Fan and Kailing Ding: Enantioselective Catalysis with Structurally Tunable Immobilized Catalysts... Chang-Hua Ding, Xue-Long Hou: Transition Metal-Catalyzed Asymmetric Alkylation... Jian Zhou and Yong Tang: Enantioselective Reactions with Trioxazolones... Xiang-Ping Hu, Duo-Sheng Wang, Chang-Bin Yu, Yong-Gui Zhou, and Zhao-Zheng: Adventure in Asymmetric Hydrogenation: Synthesis of Chiral Phosphorus Ligands and Asymmetric Hydrogenation of Heteroarenes.

Asymmetric synthesis remains a challenge to practicing scientists in the need for enantiomerically pure or enriched compounds/continues to increase. Over the last decade, a large amount of literature has been published in this field. Principles and Applications of Asymmetric Synthesis consolidates and evaluates themost useful methodologies into a one-volume resource for convenience of practicing scientists and students. Authored by internationally renowned scientists in the field, this reliable reference covers more than 450 reactions and includes important stoichiometric as well as catalytic asymmetric reactions. The first chapter reviews the basic principles, common nomenclature, and analytical methods, and the remainder of the book is organized according to reaction type. The text examines such topics as: Carbon-carbon bond formations involving carbanions, enamines, imines, and Enolates Asymmetric C-C bond formations including epoxidation, dihydroxylation, and aminohydroxylation Asymmetric synthesis using the Diels-Alder reaction and other cycloadditions Applications to the total synthesis of natural products Use of enzymes in asymmetric synthesis Practicing chemists in the pharmaceutical, fine chemical, and agricultural professions as well as graduate students will find this Principles and Applications of Asymmetric Synthesis a comprehensive and current coverage.

Asymmetric Synthesis of Natural Products Fully updated learning resource covering the concept of using natural product chemistry for strategies in asymmetric synthesis The third edition of Asymmetric Synthesis of Natural Products introduces students to the rapidly growing field of natural products in organic chemistry, discussing the practical, mainly pharmacological, importance of selected compounds and emphasizing the target-oriented approach of organic synthesis which is key in industrial strategies. To aid in reader comprehension, the text includes key references and an Index of Compounds. The textbook is based on two lecture courses (Asymmetric Synthesis & Asymmetric Synthesis of Natural Products), which the author has delivered more than 50 times over the past 20 years in Finland, the UK, Italy, and Greece. This third edition is fully updated from the earlier versions (published by Wiley in 1993 and 2012). The importance of natural products as truly renewable raw materials in sustainable chemistry and circular economy is illustrated through applications of e.g. organocatalysis, organometallic catalysis, and biocatalysis. The contents consist of traditional text supplemented with illustrations (such as 3D representations and ball-and-stick models). Three-dimensional aspects are also discussed with the use of 3D renderings of structures for both reaction mechanisms (molecular modeling) and crystallographic data. Sample topics covered in the textbook include: The foundations of asymmetric synthesis, including the theory and applications of individual asymmetric reactions Sustainable development, the circular economy, and use of renewable raw materials that have become prominent in many fields of science and technology Various natural product classes, including carbohydrates, amino acids, peptides, proteins, nucleosides, nucleotides, nucleic acids, and polyketides The properties of these natural product classes, including their structures, biosynthesis, and interrelationships, as well as examples of asymmetric syntheses and the practical value of these compounds Asymmetric Synthesis of Natural Products is a comprehensive, authoritative, and up-to-date learning resource on the subject for advanced level undergraduate or early-stage graduate students. It is also useful for specialists already working in synthesis who wish to learn about asymmetric synthesis.

## SN2 Reactions of Chiral Allylic Carhamates with Organocopper Reagents

## Applications in Asymmetric and Stereoselective Synthesis

## Asymmetric Catalysis from a Chinese Perspective

## Copper-Catalyzed Asymmetric Synthesis

## New Systems for Catalytic Asymmetric Epoxidation

The world is chiral. Most of the molecules in it are chiral, and asymmetric synthesis is an important means by which enantiopure chiral molecules may be obtained for study and sale. Using examples from the literature of asymmetric synthesis (more than 1300 references), the aim of this book is to present a detailed analysis of the factors that govern stereoselectivity in organic reactions. It is important to note that the references were each individually checked by the authors to verify relevance to the topics under discussion. The study of stereoselectivity has evolved from issues of diastereoselectivity, through auxiliary-based methods for the synthesis of enantiomerically pure compounds (diastereoselectivity followed by separation and auxiliary cleavage), to asymmetric catalysis. In the latter instance, enantiomers (not diastereomers) are the products, and highly selective reactions and modern purification techniques allow preparation - in a single step - of chiral substances in 99% ee for many reaction types. After an explanation of the basic physical-organic principles of stereoselectivity, the authors provide a detailed, annotated glossary of stereochemical terms. A chapter on "Analytical Methods" provides a critical overview of the most common methods for analysis of stereoisomers. The authors then follow the 'tried-and-true' format of grouping the material by reaction type. Thus, there are four chapters on carbon-carbon bond forming reactions (enolate alkylations, organometal additions to carbonyls, aldol and Michael reactions, and cycloadditions and rearrangements), one chapter on reductions and hydroborations (carbon-hydrogen bond forming reactions), and one on oxidations (carbon-oxygen and carbon-nitrogen bond forming reactions). Leading references are provided to natural product synthesis that have been accomplished using a given reaction as a key step. In addition to tables of examples that show high selectivity, a transition state analysis is presented to explain - to the current level of understanding - the stereoselectivity of each reaction. In one case (Cram's rule) the evolution of the current theory is detailed from its first tentative (1952) postulate to the current Felkin-Anh-Heathcock formalism. For other reactions, only the currently accepted rationale is presented. Examination of these rationales also exposes the weaknesses of current theories, in that they cannot always explain the experimental observations. These shortcomings provide a challenge for future mechanistic investigations. Authoritative glossary to aid understanding of stereochemical terminology Explanations of the key factors influencing stereoselectivity with numerous examples, organized by reaction type A handy reference guide to the literature of asymmetric synthesis for practitioners in the field

This book reflects the increasing interest among the chemical synthetic community in the area of asymmetric copper-catalyzed reactions, and introduces readers to the latest, most significant developments in the field. The contents are organized according to reaction type and cover mechanistic and spectroscopic aspects of asymmetric synthesis of natural products. A whole chapter is devoted to understanding how primary organometallics interact with copper to provide selective catalysts for allylic substitution and conjugate addition, both of which are treated in separate chapters. Another is devoted to the variety of substrates and experimental protocols, while an entire chapter covers the use of not-carbon nucleophiles. Other chapters deal with less-known reactions, such as carbometallation or the additions to imines and related systems, while the more established reactions cyclopropanation and azidination as well as the use of copper (II) Lewis acids are warranted their own special chapters. Two further chapters concern the processes involved, as determined by mechanistic studies. Finally, a whole chapter is devoted to the synthetic applications. This is essential reading for researchers at academic institutions and professionals at pharmaceutical or agrochemical companies.

Nature has established numerous methods for synthesis of complex molecules utilizing simple and abundant resources such as the use of CO<sub>2</sub>, H<sub>2</sub>O and N<sub>2</sub> using sunlight as a source of energy. Even more impressive are the high chemo-, regio-, and stereoselectivities observed in these transformations with a wide variety of both prochiral and chiral substrates. However, methods for the enantioselective incorporation of feedstock materials such as CO, HCN, CO<sub>2</sub> or simple alkenes into prochiral molecules are limited and remain an important challenge in the field. The hydrovinylation reaction (HV), where ethylene is added across a carbon-carbon double bond, has been known for nearly fifty years, starting with the works of Hata, Alderson and Wilke. During the past few years, through an approach that relied mostly on mechanistic insights and systematic examination of ligand effects, our group discovered a number of protocols for Ni(II)- and Co(II)-catalyzed enantioselective hydrovinylation (HV) reactions of vinylarenes, 1,3-dienes and strained olefins. While the Ni(II)-catalyzed hydrovinylation (HV) reaction is one of the most selective asymmetric catalyzed carbon-carbon bond forming reactions, its use has been limited to alkenes conjugated to an aromatic ring and strained alkenes. We recently found Co(II)-bisphosphine complexes show much improved regioselectivity with broader functional group compatibility in 1,3-dienes. By utilizing finely tuned catalysts derived from Co(II)-bisphosphine complexes and Me<sub>3</sub>Al or methylaluminoxane (MAO) as cocatalyst (E) and (Z)-1,3-dienes were found to undergo efficient hydrovinylation giving mostly 1,4-hydrovinylation products in an atmosphere of ethylene. In order to expand the hydrovinylation chemistry, we turned our attention to one of the mostly widely used intermediates on organometallic synthesis, silyl enol ethers. Triallylsilyl enol ethers are exceptionally versatile intermediates often used as enolate surrogates for the synthesis of carbonyl compounds. Yet there are no reports of broadly applicable, catalytic methods for the synthesis of chiral silyl enol ethers carrying latent functionalities suitable for synthetic operations beyond the many possible reactions of the enol ether moiety itself. The work presented herein reports a general procedure for highly catalytic (substrate : catalyst ratio up to 1000:1) and enantioselective (96% to 98% major enantiomer) synthesis of silyl enol ethers bearing a vinyl group at a chiral carbon at the beta-position. The reactions, run under ambient conditions, use trialkylsiloxy-1,3-dienes and ethylene (1 atmosphere) as precursors, and readily available (bis-phosphine)-cobalt(II) complexes as catalysts. Once we have established the HV reaction conditions of the silyloxydienes, we turn our attention towards diastereoselective functionalization of the hydrovinyolated products. Under optimized conditions, we are able to successfully utilize our 1,4-hydrovinyolated products as reactive nucleophilic synthons for several electrophilic reactions keeping moderate to good diastereomeric ratios. The silyl enolates can be readily converted into novel enantipure vinyl triflates, a class of highly versatile cross-coupling reagents, enabling the syntheses of other enantiomerically pure trisubstituted alkene intermediates not easily accessible by current methods.

The world is chiral. Most of the molecules in it are chiral, and asymmetric synthesis is an important means by which enantiopure chiral molecules may be obtained for study and sale. Using examples from the literature of asymmetric synthesis (more than 1300 references), the aim of this book is to present a detailed analysis of the factors that govern stereoselectivity in organic reactions. It is important to note that the references were each individually checked by the authors to verify relevance to the topics under discussion. The study of stereoselectivity has evolved from issues of diastereoselectivity, through auxiliary-based methods for the synthesis of enantiomerically pure compounds (diastereoselectivity followed by separation and auxiliary cleavage), to asymmetric catalysis. In the latter instance, enantiomers (not diastereomers) are the products, and highly selective reactions and modern purification techniques allow preparation - in a single step - of chiral substances in 99% ee for many reaction types. After an explanation of the basic physical-organic principles of stereoselectivity, the authors provide a detailed, annotated glossary of stereochemical terms. A chapter on "Analytical Methods" provides a critical overview of the most common methods for analysis of stereoisomers. The authors then follow the 'tried-and-true' format of grouping the material by reaction type. Thus, there are four chapters on carbon-carbon bond forming reactions (enolate alkylations, organometal additions to carbonyls, aldol and Michael reactions, and cycloadditions and rearrangements), one chapter on reductions and hydroborations (carbon-hydrogen bond forming reactions), and one on oxidations (carbon-oxygen and carbon-nitrogen bond forming reactions). Leading references are provided to natural product synthesis that have been accomplished using a given reaction as a key step. In addition to tables of examples that show high selectivity, a transition state analysis is presented to explain - to the current level of understanding - the stereoselectivity of each reaction. In one case (Cram's rule) the evolution of the current theory is detailed from its first tentative (1952) postulate to the current Felkin-Anh-Heathcock formalism. For other reactions, only the currently accepted rationale is presented. Examination of these rationales also exposes the weaknesses of current theories, in that they cannot always explain the experimental observations. These shortcomings provide a challenge for future mechanistic investigations.

## Catalytic Asymmetric Synthesis

## Asymmetric Synthesis of Natural Products

## The Chiral Carbon Pool and Chiral Sulfur, Nitrogen, Phosphorus, and Silicon Centers

## Organic Synthesis - 2

## Applications of Chiral Anions in Asymmetric Catalysis

This book describes the catalytic asymmetric epoxidation of olefins mediated by chiral iminium salts. The first chapter introduces some of the most novel and effective catalytic asymmetric methods for preparing chiral oxiranes. The second chapter is divided into three sections. The first section of chapter two is dedicated to our efforts to develop new aqueous oxidative conditions using both hydrogen peroxide and sodium hypochlorite as efficient, green oxidants that remove the temperature boundaries observed with the use of Oxone® as the stoichiometric oxidant. A wide range of available temperatures was examined allowing optimization of both oxidative systems. Etheral hydrogen peroxide was observed to mediate asymmetric epoxidation within an acetonitrile monophasic co-solvent system giving enantioselectivities of up to 56%. When sodium hypochlorite was used in a biphasic solvent system in conjunction with dichloromethane; it was observed to mediate oxidation of the substrate alkenes in up to 71% ee. The second and third sections of chapter two are dedicated to our efforts to synthesize chiral iminium salts as catalysts for asymmetric epoxidation based on a biphenyl azepinium salt catalyst structure. From previous work within the Page group, the asymmetric synthesis and subsequent defined stereochemistry of a chiral carbon atom to a iminium nitrogen atom was shown to have significant effect on the enantiocontrol of epoxidation using the iminium salt catalyst. Work was completed on biphenyl azepinium salt catalysts, inserting an alkyl or aryl Grignard reagent into the iminium bond using a pre-defined dioxane unit as a chiral auxiliary. Oxidation of the subsequent azepine gave a single diastereomerically pure azepinium salt. The methyl analogue of this sub-family of azepinium catalysts has been shown to give up to 81% ee for epoxidation of 1-phenylcyclohexene, furthermore, the binaphthalene azepinium salt with an additional methyl group was also synthesized.

Over the last two decades, more than 40 different classes of chiral (mirror-image) sulfur compounds have been described, and a number of useful procedures and applications have been developed for their use. Emphasizing modern methodologies, Chiral Sulfur Reagents demonstrates the great potential of enantiomerically pure sulfur reagents in transmitting chirality to other centers. Each chapter highlights the synthesis and synthetic uses of a particular class of chiral sulfur reagent, followed by examples of the most important experimental procedures.

The synthesis of molecules with control over their three-dimensional configuration, known as absolute stereochemistry, is one of the highest goals of synthetic organic chemists. As is so often the case, we strive to reach the facility and efficiency with which Nature achieves this goal. Fortunately, the chemist's imagination allows us to envision nearly unlimited possibilities for new modes of catalysis. In this dissertation, I discuss one branch of asymmetric catalysis that has in a short time progressed from relative obscurity to the forefront of the ever-expanding set of reactions that can be achieved stereoselectively. The basis of this strategy is ion pairing between chiral anionic species and cationic catalysts or intermediates. Chapter 1 discusses the background of the field. In particular, I examine what factors and precedent led the chemical community to recognize the potential of chiral anions to influence reaction stereoselectivity. Many different contributions skirted around the issue before people began to realize that this type of catalysis represents a distinct area that can be uniquely applicable to certain classes of transformations. The suddenness of this recognition is all the more fascinating because chiral cationic species have used in catalysis for some time. Our laboratory's first endeavor in the arena of chiral anions in documented in Chapter 2. This study dovetailed from the group's work in the area of homogeneous gold catalysis. Because many gold catalysts bear a positive charge, we questioned whether a chiral counteranion could be used to induce asymmetry. We were interested in pursuing this strategy because the traditional approach of using chiral ligands bound to the metal was not always sufficient to obtain high enantioselectivity in gold catalyzed reactions. In fact, a chiral phosphate counteranion was found to mediate certain gold-catalyzed reactions with vastly superior degrees of stereoselectivity. Additionally, chiral ligands could work cooperatively with the chiral counteranion to enable particularly challenging asymmetric reactions. After this, we moved from metal-catalyzed reactions to transformations where the chiral anion could form an ion pair with a cationic reaction intermediate. Based on some precedent, we investigated an asymmetric ring opening of meso-aziridinium ions. This transformation is ideal for testing out the ability of chiral anions because the mechanism essentially dictates that any observed asymmetric induction is a result of an ion pair interaction. Furthermore, it is a type of reaction that is not readily amenable to other forms of asymmetric catalysis because the prochiral intermediate does not possess any basic sites. Here again, a chiral phosphate performed well as a chiral counteranion, promoting the ring opening with alcohol nucleophiles in very high enantioselectivity. The method was also modified to enable an asymmetric opening of epoxides and sulfonates. The third section of this dissertation concerns a number of different types of chiral anions and their applications to all-carbon electrophiles. By this time chiral anions were well established as catalysts for additions to several classes of heteroatom-stabilized cationic electrophiles. However, additions to carbocations or their functional equivalents were largely out of reach. Our hypothesis was that catalysts capable of interacting covalently with carbon electrophiles could facilitate the asymmetric substitution process. Thus we examined a variety of polarizable anionic and neutral catalyst structures. While our ideas for substitutions of carbon-centered leaving groups were generally unsuccessful in producing a highly enantioselective reaction, the same concepts did lead to an asymmetric addition of amine nucleophiles to dienes. Studies of the mechanism suggested that the catalyst did in fact add covalently to the electrophile before being displaced, thereby validating our original thinking on the subject.

Organic Synthesis — 2 consists of plenary lectures presented at the Second International Symposium on Organic Synthesis, held in Jerusalem-Haifa, Israel, on September 10-15, 1978. The papers explore advances that have been made in organic synthesis and cover topics ranging from methods in peptide synthesis based on super-nucleophiles to the use of palladium catalysts in natural products synthesis; asymmetric carbon-carbon bond forming reactions; asymmetric synthesis of chiral dimers and polymers with quantitative enantiomeric yield; and reactions based on the onium salts of azaromatics. This volume is comprised of 10 chapters and begins with a discussion on some protecting group techniques and synthetic methods for peptides based on super-nucleophiles. The reader is then introduced to the use of palladium catalyzed reactions in the synthesis of natural products; synthesis of 3aH-indenes and their heterocyclic analogues; alternatives to oxidative phenolic coupling in natural products total synthesis; and the occurrence of steric and electronic effects during reactions of propenes. The final chapter deals with alpha-alkali-metalated isocyanides in organic synthesis. This book will be a useful resource for organic chemists.

An overview of the importance and consequences of asymmetry from molecules to the macroscopic world As scientists have become more capable of probing the structure of three-dimensional objects at the molecular level, the need to understand the concept and the consequences of mirror-image asymmetry—chirality—has increased enormously. Written at an introductory level, Mirror-Image Asymmetry provides an overview of the importance and effects of asymmetry from the atomic and molecular world of physics and chemistry to the organisms and structures that we see and use in our everyday life. The reader will develop a broad appreciation of three-dimensional asymmetry from the microscopic molecular world to the macroscopic world of medicines, automobiles, driving, windmills, sports, and other familiar objects. An introduction to basic definitions and nomenclature of asymmetric and dissymmetric molecules Up-to-date examples of the importance and consequences of asymmetry in modern drug applications, current theories of the origin of asymmetry in nature, and examples of molecular asymmetry in small, large, and living systems are included. Many illustrations of chiral structures, and physical and chemical phenomena that enable the actual asymmetric structures to be different phenomena that depend on structural asymmetry in the 150 years since Louis Pasteur discovered asymmetry in molecular structures, scientists have made great progress in understanding how interactions between chiral molecules influence biochemical processes. This knowledge is leading to very sophisticated asymmetric synthetic techniques that have greatly benefited many research groups especially those in the pharmaceutical industry. This guide to the role of molecular and macroscopic chirality will inspire students and scientists in chemistry, biology, physics, and drug discovery.

## Organic Synthesis

## Graphical Abstracts and Experimental Methods

## Catalytic Asymmetric Carbon-carbon Bond Forming Methodologies for Synthesis of Chiral N-containing Heterocycles and Chiral Carboxamides

## State-of-the-art and future trends in future technology

## Asymmetric Synthesis and Applications

Asymmetric synthesis is widely used in the academic and industrial sectors for the synthesis of chiral molecules of biological importance. Although catalytic asymmetric synthesis is an alternative, the use of equimolar amounts of chirality provides high selectivities over a wider range of substrates, without extensive modification of reaction conditions. This volume provides, at postgraduate student level, an accessible introduction to stoichiometric asymmetric synthesis. The authors focus on stereoselective C-C bond formation in acyclic systems, with an emphasis on the use of chiral auxiliaries and reagents. The book is extensively referenced and so provides a convenient point of entry to the research literature.

Asymmetric Synthesis, Volume 3: Stereodifferentiating Addition Reactions, Part B presents intensive investigations in leading academic and industrial laboratories on stereodifferentiating addition reactions. This book is divided into eight chapters and begins with a comprehensive review of the formation of chiral metal enolates and their stereoselective alkylation reactions. These topics are followed by discussions on chiral Aldol addition reactions and the many variations of asymmetric synthesis that may be carried out using chiral oxazolones. A chapter describes the alkylation of chiral hydrate ... This volume provides a comprehensive overview of the rapidly developing field of asymmetric synthesis. Using easy to understand graphical abstracts it presents 348 important catalytic and stoichiometric reactions leading to the synthesis of optically active chiral compounds. The first part of the book covers reactions related to reductions, oxidations, carbon-carbon bond formation and carbon-heteroatom bond formation. Each graphical abstract is accompanied by a list of important catalysts and references to assist the reader. The second part concentrates on experimental aspects, describing synthetic procedures for selected chiral reagents and chiral auxiliaries, and provides an invaluable reference tool for laboratory work. Written with both the graduate student and professional organic chemist in mind, this book will serve as an important resource for the synthetic organic chemist.

Catalytic asymmetric synthesis has been one of the most active research areas in chemistry (Nobel Prize in 2001). The development of efficient chiral catalysts plays a crucial role in asymmetric catalysis. Although many chiral ligands/catalysts have been developed in the past decades, the most efficient catalysts are derived from a few core structures, called "privileged chiral catalysts". This ultimate "must have" and long awaited reference for every chemist working in the field of asymmetric catalysis starts with the core structure of the catalysts, explaining why a certain ligand or catalyst is so successful. It describes in detail the history, the basic structural characteristics, and the applications of these "privileged catalysts". This novel presentation provides readers with a much deeper insight into the topic and makes it a must-have for organic chemists, catalytic chemists, chemists working with/on organometallics, chemists in industry, and libraries. From the contents: \* BINAP \* Bisphosphacycles - From DuPhos and BPE to a Diverse Set of Broadly Applied Ligands \* Josephos Ligands: From Discovery to Technical Applications \* Chiral Spiro Ligands \* Chiral Bisoxazolone Ligands \* PBOX Ligands \* Chiral Salen Complexes \* BINOL \* TADDOLate Ligands \* Cinchona Alkaloids \* Proline Derivatives

## Privileged Chiral Ligands and Catalysts

## Principles and Applications of Asymmetric Synthesis

## Dynamic Stereochemistry of Chiral Compounds

## Asymmetric Synthesis Using Redox-Active Diazo Compounds as Chiral Carbon Atom Precursors

## Comprehensive Chirality

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Table of Contents Preface Abbreviations Introduction 1 1 Enantioselective Pure Chiral Auxiliaries 43 2 Chiral Catalysts and Catalysts Bearing Chiral Ligands 114 4 Asymmetric Deprotonations and Protonations 143 5 Alkylations and Related Reactions 157 6 Additions to C=O and C=N Double Bonds 209 7 Additions to Carbon-Carbon Double Bonds 367 8 Additions to Double Bonds Bearing Heteroatoms. Oxidations of Sulfides and Selenides 503 9 Cycloadditions 513 10 Sigmatropic Rearrangements 593 11 Transition Metal Catalyzed Reactions 619 References 637 Index 707.

Axially Chiral Compounds Explore this comprehensive and current volume summarizing the characteristics, synthesis, and applications of axial chirality. Appearing widely in natural products, biologically active molecules, asymmetric chemistry, and material science, axially chiral motifs constitute the core backbones of the majority of chiral ligands and organocatalysts in asymmetric catalysis. In a new work of particular relevance to synthetic chemists, Axially Chiral Compounds: Asymmetric Synthesis and Applications delivers a clearly structured and authoritative volume covering the classification, characteristics, synthesis, and applications of axial chirality. A must read for every synthetic chemist practicing today, the book follows the development history, research status, and applications of axial chirality. An introductory chapter familiarizes the reader with foundational material before the distinguished authors describe the different classes and the synthesis of axial chiral compounds used in asymmetric synthesis. The book concludes with a focus on the applications of chiral ligands, chiral catalysts, and materials. Readers will also benefit from the inclusion of: A thorough introduction to asymmetric synthesis, including biaryls atropisomers, heterobiaryls atropisomers, and non-biaryls atropisomers Explorations of chiral allene, spiro skeletons, and natural products Practical discussions of asymmetric transformation, chiral ligands, and chiral catalysts An examination of miscellaneous applications of axially chiral compounds Perfect for organic chemists, chemists working with or on organometallics, catalytic chemists, and materials scientists, Axially Chiral Compounds: Asymmetric Synthesis and Applications will also earn a place in the libraries of natural products chemists who seek a one-stop reference for compounds exhibiting axial chirality.

"Organic Synthesis: Strategy and Control" is a sequel to Stuart Warren's bestseller "Organic Synthesis: The Disconnection Approach." The "Disconnection" book concentrated on the planning behind the synthesis of compounds. The two themes of this new book are "strategy" and "control." Solving problems either by finding an alternative strategy or by controlling any established strategy to make it work. The book is divided into five sections that deal with selectivity, carbon-carbon single bonds, carbon-carbon double bonds, stereochemistry and functional group strategy. Interpenetrating this structure, the 36 chapters start with classic methods and progress to modern methods and modern strategic considerations. Heterocyclic chemistry is treated throughout the book with full mechanistic explanations as part of organic chemistry rather than a separate mystery. A comprehensive, practical account of the key concepts involved in synthesising compounds. Takes a mechanistic approach, which explains reactions and gives guidelines on how reactions might behave in different situations. Focuses on reactions that really work rather than those with limited application. Extensive, up-to-date references in each chapter. Students and professional chemists familiar with "Organic Synthesis: The Disconnection Approach" will enjoy the leap into a book designed for chemists at the coalface of organic synthesis.

## Stereocenters of Organic Compounds

## Plenary Lectures Presented at the Second International Symposium on Organic Synthesis

## Asymmetric Synthesis of Tertiary and Quaternary Carbon Centers

## A Study of Chiral Base Catalysts

## Mirror-Image Asymmetry

Asymmetric Synthesis, Volume 2: Stereodifferentiating Addition Reactions, Part A is concerned with asymmetric addition reactions. This volume contains chapters that cover B-H additions across carbon-carbon and carbon-oxygen double bonds; carbonyl reductions using chiral modifications of lithium aluminum hydride and chiral dihydroxypridines; additions of achiral and chiral nucleophiles to chiral and achiral aldehydes and ketones; organometal additions to chiral vinyl siloxanes; and description of imine and enamine alkylations. Chemists will find the book interesting.

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The synthesis of molecules with control over their three-dimensional configuration, known as absolute stereochemistry, is one of the highest goals of synthetic organic chemists. As is so often the case, we strive to reach the facility and efficiency with which Nature achieves this goal. Fortunately, the chemist's imagination allows us to envision nearly unlimited possibilities for new modes of catalysis. In this dissertation, I discuss one branch of asymmetric catalysis that has in a short time progressed from relative obscurity to the forefront of the ever-expanding set of reactions that can be achieved stereoselectively. The basis of this strategy is ion pairing between chiral anionic species and cationic catalysts or intermediates. Chapter 1 discusses the background of the field. In particular, I examine what factors and precedent led the chemical community to recognize the potential of chiral anions to influence reaction stereoselectivity. Many different contributions skirted around the issue before people began to realize that this type of catalysis represents a distinct area that can be uniquely applicable to certain classes of transformations. The suddenness of this recognition is all the more fascinating because chiral cationic species have used in catalysis for some time. Our laboratory's first endeavor in the arena of chiral anions in documented in Chapter 2. This study dovetailed from the group's work in the area of homogeneous gold catalysis. Because many gold catalysts bear a positive charge, we questioned whether a chiral counteranion could be used to induce asymmetry. We were interested in pursuing this strategy because the traditional approach of using chiral ligands bound to the metal was not always sufficient to obtain high enantioselectivity in gold catalyzed reactions. In fact, a chiral phosphate counteranion was found to mediate certain gold-catalyzed reactions with vastly superior degrees of stereoselectivity. Additionally, chiral ligands could work cooperatively with the chiral counteranion to enable particularly challenging asymmetric reactions. After this, we moved from metal-catalyzed reactions to transformations where the chiral anion could form an ion pair with a cationic reaction intermediate. Based on some precedent, we investigated an asymmetric ring opening of meso-aziridinium ions. This transformation is ideal for testing out the ability of chiral anions because the mechanism essentially dictates that any observed asymmetric induction is a result of an ion pair interaction. Furthermore, it is a type of reaction that is not readily amenable to other forms of asymmetric catalysis because the prochiral intermediate does not possess any basic sites. Here again, a chiral phosphate performed well as a chiral counteranion, promoting the ring opening with alcohol nucleophiles in very high enantioselectivity. The method was also modified to enable an asymmetric opening of epoxides and sulfonates. The third section of this dissertation concerns a number of different types of chiral anions and their applications to all-carbon electrophiles. By this time chiral anions were well established as catalysts for additions to several classes of heteroatom-stabilized cationic electrophiles. However, additions to carbocations or their functional equivalents were largely out of reach. Our hypothesis was that catalysts capable of interacting covalently with carbon electrophiles could facilitate the asymmetric substitution process. Thus we examined a variety of polarizable anionic and neutral catalyst structures. While our ideas for substitutions of carbon-centered leaving groups were generally unsuccessful in producing a highly enantioselective reaction, the same concepts did lead to an asymmetric addition of amine nucleophiles to dienes. Studies of the mechanism suggested that the catalyst did in fact add covalently to the electrophile before being displaced, thereby validating our original thinking on the subject.

Organic Synthesis — 2 consists of plenary lectures presented at the Second International Symposium on Organic Synthesis, held in Jerusalem-Haifa, Israel, on September 10-15, 1978. The papers explore advances that have been made in organic synthesis and cover topics ranging from methods in peptide synthesis based on super-nucleophiles to the use of palladium catalysts in natural products synthesis; asymmetric carbon-carbon bond forming reactions; asymmetric synthesis of chiral dimers and polymers with quantitative enantiomeric yield; and reactions based on the onium salts of azaromatics. This volume is comprised of 10 chapters and begins with a discussion on some protecting group techniques and synthetic methods for peptides based on super-nucleophiles. The reader is then introduced to the use of palladium catalyzed reactions in the synthesis of natural products; synthesis of 3aH-indenes and their heterocyclic analogues; alternatives to oxidative phenolic coupling in natural products total synthesis; and the occurrence of steric and electronic effects during reactions of propenes. The final chapter deals with alpha-alkali-metalated isocyanides in organic synthesis. This book will be a useful resource for organic chemists.

An overview of the importance and consequences of asymmetry from molecules to the macroscopic world As scientists have become more capable of probing the structure of three-dimensional objects at the molecular level, the need to understand the concept and the consequences of mirror-image asymmetry—chirality—has increased enormously. Written at an introductory level, Mirror-Image Asymmetry provides an overview of the importance and effects of asymmetry from the atomic and molecular world of physics and chemistry to the organisms and structures that we see and use in our everyday life. The reader will develop a broad appreciation of three-dimensional asymmetry from the microscopic molecular world to the macroscopic world of medicines, automobiles, driving, windmills, sports, and other familiar objects. An introduction to basic definitions and nomenclature of asymmetric and dissymmetric molecules Up-to-date examples of the importance and consequences of asymmetry in modern drug applications, current theories of the origin of asymmetry in nature, and examples of molecular asymmetry in small, large, and living systems are included. Many illustrations of chiral structures, and physical and chemical phenomena that enable the actual asymmetric structures to be different phenomena that depend on structural asymmetry in the 150 years since Louis Pasteur discovered asymmetry in molecular structures, scientists have made great progress in understanding how interactions between chiral molecules influence biochemical processes. This knowledge is leading to very sophisticated asymmetric synthetic techniques that have greatly benefited many research groups especially those in the pharmaceutical industry. This guide to the role of molecular and macroscopic chirality will inspire students and scientists in chemistry, biology, physics, and drug discovery.

## Organic Synthesis

## Graphical Abstracts and Experimental Methods

## Catalytic Asymmetric Carbon-carbon Bond Forming Methodologies for Synthesis of Chiral N-containing Heterocycles and Chiral Carboxamides

## State-of-the-art and future trends in future technology

## Asymmetric Synthesis and Applications

Asymmetric synthesis is widely used in the academic and industrial sectors for the synthesis of chiral molecules of biological importance. Although catalytic asymmetric synthesis is an alternative, the use of equimolar amounts of chirality provides high selectivities over a wider range of substrates, without extensive modification of reaction conditions. This volume provides, at postgraduate student level, an accessible introduction to stoichiometric asymmetric synthesis. The authors focus on stereoselective C-C bond formation in acyclic systems, with an emphasis on the use of chiral auxiliaries and reagents. The book is extensively referenced and so provides a convenient point of entry to the research literature.

Asymmetric Synthesis, Volume 3: Stereodifferentiating Addition Reactions, Part B presents intensive investigations in leading academic and industrial laboratories on stereodifferentiating addition reactions. This book is divided into eight chapters and begins with a comprehensive review of the formation of chiral metal enolates and their stereoselective alkylation reactions. These topics are followed by discussions on chiral Aldol addition reactions and the many variations of asymmetric synthesis that may be carried out using chiral oxazolones. A chapter describes the alkylation of chiral hydrazones, a process that yields chiral-substituted aldehydes and ketones. Other chapters explore a variety of cyclization processes that form carbon-carbon and carbon-heteroatom bonds. The last chapters deal with the asymmetric cycloadditions and asymmetric tropic reagents. Synthetic chemists and researchers will find this book invaluable.

Table of Contents Preface Abbreviations Introduction 1 1 Enantioselective Pure Chiral Auxiliaries 43 2 Chiral Catalysts and Catalysts Bearing Chiral Ligands 114 4 Asymmetric Deprotonations and Protonations 143 5 Alkylations and Related Reactions 157 6 Additions to C=O and C=N Double Bonds 209 7 Additions to Carbon-Carbon Double Bonds 367 8 Additions to Double Bonds Bearing Heteroatoms. Oxidations of Sulfides and Selenides 503 9 Cycloadditions 513 10 Sigmatropic Rearrangements 593 11 Transition Metal Catalyzed Reactions 619 References 637 Index 707.

Axially Chiral Compounds Explore this comprehensive and current volume summarizing the characteristics, synthesis, and applications of axial chirality. Appearing widely in natural products, biologically active molecules, asymmetric chemistry, and material science, axially chiral motifs constitute the core backbones of the majority of chiral ligands and organocatalysts in asymmetric catalysis. In a new work of particular relevance to synthetic chemists, Axially Chiral Compounds: Asymmetric Synthesis and Applications delivers a clearly structured and authoritative volume covering the classification, characteristics, synthesis, and applications of axial chirality. A must read for every synthetic chemist practicing today, the book follows the development history, research status, and applications of axial chirality. An introductory chapter familiarizes the reader with foundational material before the distinguished authors describe the different classes and the synthesis of axial chiral compounds used in asymmetric synthesis. The book concludes with a focus on the applications of chiral ligands, chiral catalysts, and materials. Readers will also benefit from the inclusion of: A thorough introduction to asymmetric synthesis, including biaryls atropisomers, heterobiaryls atropisomers, and non-biaryls atropisomers Explorations of chiral allene, spiro skeletons, and natural products Practical discussions of asymmetric transformation, chiral ligands, and chiral catalysts An examination of miscellaneous applications of axially chiral compounds Perfect for organic chemists, chemists working with or on organometallics, catalytic chemists, and materials scientists, Axially Chiral Compounds: Asymmetric Synthesis and Applications will also earn a place in the libraries of natural products chemists who seek a one-stop reference for compounds exhibiting axial chirality.

"Organic Synthesis: Strategy and Control" is a sequel to Stuart Warren's bestseller "Organic Synthesis: The Disconnection Approach." The "Disconnection" book concentrated on the planning behind the synthesis of compounds. The two themes of this new book are "strategy" and "control." Solving problems either by finding an alternative strategy or by controlling any established strategy to make it work. The book is divided into five sections that deal with selectivity, carbon-carbon single bonds, carbon-carbon double bonds, stereochemistry and functional group strategy. Interpenetrating this structure, the 36 chapters start with classic methods and progress to modern methods and modern strategic considerations. Heterocyclic chemistry is treated throughout the book with full mechanistic explanations as part of organic chemistry rather than a separate mystery. A comprehensive, practical account of the key concepts involved in synthesising compounds. Takes a mechanistic approach, which explains reactions and gives guidelines on how reactions might behave in different situations. Focuses on reactions that really work rather than those with limited application. Extensive, up-to-date references in each chapter. Students and professional chemists familiar with "Organic Synthesis: The Disconnection Approach" will enjoy the leap into a book designed for chemists at the coalface of organic synthesis.

## Stereocenters of Organic Compounds

## Plenary Lectures Presented at the Second International Symposium on Organic Synthesis

## Asymmetric Synthesis of Tertiary and Quaternary Carbon Centers

## A Study of Chiral Base Catalysts

## Mirror-Image Asymmetry

Asymmetric Synthesis, Volume 2: Stereodifferentiating Addition Reactions, Part A is concerned with asymmetric addition reactions. This volume contains chapters that cover B-H additions across carbon-carbon and carbon-oxygen double bonds; carbonyl reductions using chiral modifications of lithium aluminum hydride and chiral dihydroxypridines; additions of achiral and chiral nucleophiles to chiral and achiral aldehydes and ketones; organometal additions to chiral vinyl siloxanes; and description of imine and enamine alkylations. Chemists will find the book interesting.

Over the last two decades, more than 40 different classes of chiral (mirror-image) sulfur compounds have been described, and a number of useful procedures and applications have been developed for their use. Emphasizing modern methodologies, Chiral Sulfur Reagents demonstrates the great potential of enantiomerically pure sulfur reagents in transmitting chirality to other