# Organic Synthesis

MICHAELB. SMITH

Second Edition

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### ORGANIC SYNTHESIS, SECOND EDITION International Edition 2004

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Cover image: The image shows the first disconnection for a synthesis of *ent*-gelsedine, taken from work by Henk Heimstra. See *First Total Synthesis of ent-Gelsedine via a Novel Iodide-Promoted Allene N-Acyliminium Ion Cyclization*, van Henegouwen, W.G.B.; Fieseler, R.M., Rutijes, F.P.J.T., Hiemstra, H., *J. Org. Chem.*, **2000**, 65, 8317

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# **Organic Synthesis**

### **About the Author**

Professor Michael B. Smith was born in Detroit, Michigan in 1946 and moved to Madison Heights, Virginia in 1957, where he attended high school. He received an A.A from Ferrum College in 1967 and a B.S in chemistry from Virginia Polytechnic Institute in 1969. After working for three years at the Newport News Shipbuilding and Dry Dock Co. in Newport News VA as an analytical chemist, he entered graduate school at Purdue University. He received a Ph.D. in Organic chemistry in 1977, under the auspices of Professor Joe Wolinsky. Professor Smith spent one year as a faculty research associate at the Arizona State University with Professor G. Robert Pettit, working on the isolation of cytotoxic principles from plants and sponges. He spent a second year of postdoctoral work with Professor Sidney M. Hecht at the Massachusetts Institute of Technology, working on the synthesis of bleomycin A<sub>2</sub>. Professor Smith moved to the University of Connecticut in 1979, where he is currently professor of chemistry. In 1986 he spent a sabbatical leave in the laboratories of Professor Leon Ghosez, at the Universite Catholique de Louvain in Louvain-la-Neuve, Belgium, as a visiting professor.

Professor Smith's research interests focus on the development of new synthetic methods, primarily based on manipulation of alkenyl lactams with a particular interest in chiral lactams. He developed asymmetric synthetic routes to fused-ring alkaloids based on radical cyclization and Diels-Alder procedures, all using pyroglutamate (derived from glutamic acid) as a chiral, non-racemic precursor. He has developed a new chiral reagent for the determination of enantiomeric composition of alcohols by <sup>1</sup>H NMR, also based on lactam chemistry. Current work is focused on developing a new lactam-based anti-AIDS drug and the synthesis and characterization of compounds isolated from dental plaque, that may be tied to heart disease. Regioselective halogenation of aromatic amines and organotin coupling reactions is another prominent area of research. In addition, there is an active program to synthesize anticancer phenanthridone alkaloids and anti-AIDS indolizidine alkaloids.

In addition to this research, Professor Smith is the author of the 5th edition of March's Advanced Organic Chemistry and editor of the Compendium of Organic Synthetic Methods, Volumes 6-10. He is also the author of Organic Chemistry: Two Semesters, an outline of undergraduate organic chemistry to be used as a study guide for the first organic course. He also authored a research monograph entitled Synthesis of Non-alpha Amino Acids.

### Preface to the 2nd Edition

The new edition of Organic Synthesis has been revised and rewritten from front to back. I want to thank all who used the book in its first edition, and thank you for your patience with its many errors. Every effort has been made to correct those problems. Every chapter in this book was revised before any new material was added. Not only were updated examples used when possible, but new material was added that make this edition reflect current synthetic methodology. In addition to correcting errors and deficiencies, the text has been modified in countless places to improve readability and pedagogy. This new edition contains references taken from more than 5600 journal articles, books, and monographs. Of these references, more than 1200 are new to this edition, and most of them were taken from the literature after 1992. About 50% of all new references were taken from literature published in 1999 or 2000. Many new reactions and topics have been added. New topics include combinatorial chemistry, directed ortho metalation, and metathesis reactions. New reactions include Jacobsen-Katsuki epoxidation, the Baylis-Hillman reaction, the Pauson-Khand reaction, Suzuki coupling, Sonogashira coupling, Tamao-Fleming oxidation, Julia-Colonna epoxidation, Ley oxidation, Danheiser annulation, and others. This edition contains references to over 650 natural products, synthetic targets, or other important molecules. It also contains reference to over 270 named reactions, reagents, or processes. Homework in each chapter has been extensively revised. Most of the homework problems are new, although many from the first edition were retained. New homework problems for the new sections and new reactions are also included. Unlike the first edition, most of the homework problems do not contain leading references for the answers. Therefore, they are true homework and thought problems. The answers to all problems from chapters 1-9, and 11-13 are found in the new and updated Student Solutions Manual for this book. As in the first edition, a few leading references are provided for the synthesis problems in chapter 10, but most problems do not have answers. The student is encouraged to discuss any synthetic problem with their instructor.

With the exception of scanned figures, all drawings in this book were prepared using ChemDraw or Chem3D from CambridgeSoft. I thank them for providing the software that made this project possible.

I express my gratitude to those who were kind enough to go through the first edition and supply me with lists of errors. It is not possible to list all those who contributed a brief note or an EMail, but let me thank you here for your help. Special thanks to those who assembled an extensive list of errors, which was very useful in revising this edition. They are Gabriel Tojo (Santiago de Compostella), Paul Juvvik (Kjemish Institutt, Universitetet I Bergen), Paris Georghiou (Memorial Univ. of Newfoundland), David Todd (Juniata College), Phil Hultin (Manitoba), Phil Garner (Case Western), Hugh W. Thompson (Rutgers), and Henri Bekolo.

In addition, I thank those who took the time to review chapters of the book, and made invaluable comments as well as corrections. They are Ellen Baxter (R.W. Johnson), Arthur Cammers-Goodwin (Kentucky), Phil Garner (Case Western Reserve), Bruce King (Wake Forest), Spencer Knapp (Rutgers), Frederick Luzzio (Louisville), Timo Ovaska (Connecticut College), Robin Polt (Arizona), Jon Rainier (Arizona), Victor Snieckus (Queens University) Douglass Taber (Delaware), and Frederick West (Utah).

Preface

I also thank the editors who worked to make this new edition a reality. Thanks to Spencer Cotkin, Kent Peterson, Jim Smith, Shirley Oberbrockling, and Sandy Hahn. Special thanks to Jeannette Stiefel, whose hard work and dedication vastly improved the quality of the final manuscript.

Finally, I thank my students, who have provided the inspiration over the years for this book. They have also been my best sounding board, allowing me to test new ideas and organize the text as it now appears. I thank my friends and colleagues who have provided countless suggestions and encouragement over the years, particularly Spencer Knapp (Rutgers), George Majetich (Georgia), and Phil Garner (Case Western Reserve).

A special thanks to my wife Sarah and son Steven, whose patience and understanding made the work possible.

If there are errors, corrections, and suggestions, please let me know by EMail or normal post. Any errors will be posted at

http://orgchem.chem.uconn.edu/home/books/orgsyn2.html

Other useful information that relates to organic synthesis may be found at

http://orgchem.chem.uconn.edu/colleges/orgchem.html

Thank you again. I hope this new edition is useful to you in your studies.

Michael B. Smith Storrs, Connecticut May, 2001

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### Preface to the First Edition

A reactions oriented course is a staple of most graduate organic programs, and synthesis is taught either as a part of that course or as a special topic. Ideally, the incoming student is an organic major, who has a good working knowledge of basic reactions, stereochemistry and conformational principles. In fact, however, many (often most) of the students in a first year graduate level organic course have deficiencies in their undergraduate work, are not organic majors and are not synthetically inclined. Does one simply tell the student to "go away and read about it," giving a list of references, or does one take class time to fill in the deficits? the first option works well for highly motivated students with a good background, less well for those with a modest background. In many cases, the students spend so much time catching up that it is difficult to focus them on the cutting edge material we all want to teach. If one exercises the second option of filling in all the deficits, one never gets to the cutting edge material. This is especially punishing to the outstanding students and to the organic majors. a compromise would provide the student with a reliable and readily available source for background material that could be used as needed. the instructor could then feel comfortable that the proper foundations have been laid and push on to more interesting areas of organic chemistry.

Unfortunately, such a source of background material either is lacking altogether or consists of several books and dozens of review articles. I believe my teaching experience at UConn as just described is rather typical, with a mix of non-organic majors, outstanding and well-motivated students, and many students with weak backgrounds who have the potential to go on to useful and productive careers if time is taken to help them. Over the years I have assigned what books were available in an attempt to address these problems, but found that "graduate level textbooks" left much to be desired. I assembled a large reading list and mountains of handouts and spent half of my life making up problems that would give my students a reasonable chance at practicing the principles we were discussing. I came to the conclusion that a single textbook was needed that would give me the flexibility I craved to present the course I wanted to teach, but yet would give the students the background they needed to succeed. As I tried different things in the classroom, I solicited the opinions of the graduate students who took the course and tried to develop an approach that worked for them and allowed me to present the information I wanted. the result is this book. I hope that it is readable, provides background information, and also provides the research oriented information that is important for graduate organic students. I also hope it will be of benefit to instructors who face the same challenges I do. I hope this book will be a useful tool to the synthetic community and to graduate level education.

From talks with many people I know that courses for which this book is targeted can be for either one or two semesters. the course can focus only on functional groups, only on making carbon-carbon bonds, on some combination of both (like my course), or only on synthesis. I have tried to organize the book in such a way that one is not a slave to its organization. Every chapter is internally cross referenced. If the course is to focus upon making carbon-carbon bonds, for example, there are unavoidable references to oxidation reagents, reducing agents, stereochemical principles, etc. When such a reaction or principle appears, the section and chapter where it is discussed elsewhere in the book is given "in line" so the student can easily find it. It is impossible to write each

chapter so it will stand alone, but the chapters are reasonably independent in their presentations. I have organized the book so that functional groups are discussed in the first few chapters and carbon-carbon bond formation reactions are discussed in later chapters, making it easier to use the one book for two different courses or for a combination course. the middle chapters are used for review and to help the student make the transitions from functional group manipulations to applying reactions and principles and thence to actually building molecules. I believe that a course devoted to making carbon-carbon bonds could begin with chap. 8, knowing that all pertinent peripheral material is in the book and readily available to the student. the ultimate goal of the book is to cut down on the mountains of handouts, provide homework to give the student proper practice, give many literature citations to tell the student exactly where to find more information, and allow the instructor to devote time to their particular focus

This book obviously encompasses a wide range of organic chemistry. Is there a theme? Should there be? the beautiful and elegant total syntheses of interesting and important molecules published by synthetic organic chemists inspired me to become an organic chemist and I believe that synthesis focuses attention on the problems of organic chemistry in a unique way. To solve a synthetic problem, all elements of organic chemistry must be brought to bear: reactions, mechanism, stereochemistry, conformational control, and strategy. Synthesis therefore brings a perspective on all aspects of organic chemistry and provides a theme for understanding it. the theme of this book is therefore the presentation of reactions in the context of organic synthesis. Wherever possible, examples of a given reaction, process, or strategy are taken from a published total synthesis. the disconnection approach is presented in the first chapter, and as each new functional group transform and carbon-carbon bond forming reaction is discussed, the retrosynthetic analysis (the disconnect products for that reaction) is given. An entire chapter (chap. 10) is devoted to synthetic strategies, and chap. 14 provides examples of first year students' first syntheses. I believe that this theme is a reasonable and

useful device for presenting advanced organic chemistry.

The text is fully referenced to facilitate further study, and (where feasible) the principal researcher who did the work is mentioned by name, so the student can follow that person's work in the literature and gain even more insight into a given area. As far as it is known to me, the pioneering work of the great chemists of the past has been referenced. Many of the "named reactions" are no longer referenced in journals, but when they are first mentioned in this book, the original references are given. I believe the early work should not be lost to a new generation of students.

In many cases I have used 3-D drawings to help illustrate stereochemical arguments for a given process. I give the structure of each reagent cited in the text, where that reagent is mentioned, so a beginning student does not have to stop and figure it out. This is probably unnecessary for many students, but it is there if needed.

This is a reaction oriented book, but an attempt is made to give brief mechanistic discussions when appropriate. In addition, some physical organic chemistry is included to try to answer the obvious if unasked questions: why does that alkyl group move, why does that bond break, why is that steric interaction greater than the other one, or why is that reaction diastereoselective?

Most of all, a student needs to practice. Chapters 1-13 have end-of chapter problems that range from those

requiring simple answers based on statements within the text to complex problems taken from research literature. In a large number of cases literature citations are provided so answers can be found.

The first part of the book (chaps. 1-4) is a review of functional group transforms and basic principles: retrosynthesis, stereochemistry, and conformations. Basic organic reactions are covered, including substitution reactions, addition reactions, elimination reactions, acid/base chemistry, oxidation and reduction. the first two chapters are very loosely organized along the lines of an undergraduate book for presenting the functional group reactions (basic principles, substitution, elimination, addition, acyl addition, aromatic chemistry). Chapter 1 begins with the disconnection approach. I have found that this focuses the students' attention on which reactions they can actually apply and instantly shows them why it is important to have a larger arsenal of reactions to solve a synthetic problem. This has been better than any other device I have tried and that is why it is placed first. Most of the students I see come into our program deficient in their understanding of stereochemistry and conformational control, and so those topics are presented next. Some of this information is remedial material and where unneeded can be skipped, but it is there for those who need it (even if they will not admit that they do). Chapter 2 presents a mini-review of undergraduate organic chemistry reactions and also introduces some modern reactions and applications. Chapter 3 is on oxidation and chapter 4 is on reduction. Each chapter covers areas that are woefully under-emphasized in undergraduate textbooks.

Chapter 5 covers hydroboration, an area which is discussed in several books and reviews. I thought it useful to combine this material into a tightly focused presentation which (1) introduces several novel functional group transforms that appear nowhere else and (2) gives a useful review of many topics introduced in chaps. 1-4. Chapter 6 reviews the basic principles that chemists use to control a reaction rather than be controlled by it. It shows the techniques chemists use to "fix" the stereochemistry, if possible, when the reaction does not do what it is supposed to. It shows how stereochemical principles guide a synthesis. An alternative would be to separate stereochemistry into a chapter that discusses all stereochemical principles. However, the theme is synthesis, and stereochemical considerations are as important a part of a synthesis as the reagents being chosen. For that reason, stereochemistry is presented with the reactions in each chapter. Chapter 6 simply ties together the basic principles. This chapter also includes the basics of ring-forming reactions. Chapter 7 completes the first part of the book and gives a brief overview of what protecting groups are and when to use them.

The last half of the book focuses on making carbon-carbon bonds. It is organized fundamentally by the disconnection approach. In Chapter 1, breaking a carbon-carbon bond generated a disconnect product that was labeled as C<sup>d</sup> (a nucleophilic species), C<sup>a</sup> (an electrophilic species), or C<sup>radical</sup> (a radical intermediate). In some cases, multiple bonds were disconnected, and many of these disconnections involved pericyclic reactions to reassemble the target. the nucleophilic regents that are equivalent to C<sup>d</sup> disconnect products are covered in Chapters 8 and 9, with the very important enolate anion chemistry separated into Chapter 9. Chapter 10 presents various synthetic strategies that a student may apply to a given synthetic problem. This information needs to be introduced as soon as possible, but until the student "knows some chemistry", it cannot really be applied. Placement of synthetic strategies after functional group transforms and nucleophilic methods for making carbon-carbon bonds is a reasonable compromise. Chapter 11 introduces the important Diels-Alder cyclization, as well as

dipolar cycloadditions and sigmatropic rearrangements that are critically important to synthesis. Chapter 12 explores electrophilic carbons (Ca), including organometallics that generally react with nucleophilic species. Chapter 13 introduces radical and carbene chemistry. Chapter 14 is included to give the student a taste of a first time student proposal and some of the common mistakes. the point is not to reiterate the chemistry but to show how strategic shortsightedness, poor drawings, and deficiencies in overall presentation can influence how the proposal is viewed. It is mainly intended to show some common mistakes and also some good things to do in presenting a synthesis. It is not meant to supersede the detailed discussions of how and why a completed elegant synthesis is done but to assist the first-time student in preparing a proposal.

The goal of this work is to produce a graduate level textbook, and it does not assume that a student should already know the information, *before* the course. I hope that it will be useful to students and to the synthetic community. Every effort has been made to keep the manuscript error-free. Where there are errors, I take full responsibility and encourage those who find them to contact me directly, at the address given below, with corrections. Suggestions for improving the text, including additions and general comments about the book are also welcome. My goal is to incorporate such changes in future editions of this work. If anyone wishes to contribute homework problems to future editions, please send them to me and I will, of course, give full credit for any I use.

I must begin my thank-yous with the graduate students at UConn, who inspired this work and worked with me through several years to develop the pedagogy of the text. I must also thank Dr. Chris Lipinski and Dr. David Burnett of Pfizer Central Research (Groton, CT) who organized a reactions/synthesis course for their research assistants. This allowed me to test this book upon an "outside" and highly trained audience. I am indebted to them for their suggestions and their help.

There are many other people to thank. Professor Janet Carlson (Macalester College) reviewed a primeval version of this book and made many useful comments. Professors Al Sneden and Suzanne Ruder (Virginia Commonwealth University) classroom tested an early version of this text and both made many comments and suggestions that assisted me in putting together the final form of this book. of the early reviewers of this book I would particularly like to thank Professor Brad Mundy (Colby College) and Professor Marye Anne Fox (University of Texas, Austin), who made insightful and highly useful suggestions that were important for shaping the focus of the book.

Along the way, many people have helped me with portions or sections of the book. Professor Barry Sharpless (Scripps) reviewed the oxidation chapter and also provided many useful insights into his asymmetric epoxidation procedures. Dr. Peter Wuts (Upjohn) was kind enough to review the protecting group chapter (chap. 7) and helped me focus it in the proper way. Professor Ken Houk (UCLA), Professor Stephen Hanessian (Université de Montréal), Professor Larry Weiler (U. of British Columbia), Professor James Hendrickson (Brandeis), Professor Tomas Hudlicky (U. Florida), and Professor Michael Taschner (U. of Akron) reviewed portions of work that applied to their areas of research and I am grateful for their help.

Several people provided original copies of figures or useful reprints or comments. These include Professor Dieter Seebach (ETH), Professor Paul Williard (Brown), Professor E.J. Corey (Harvard), Dr. Frank Urban (Pfizer Central Research), Professor Rene Barone (Université de Marseilles), and Professor Wilhelm Meier (Essen).

### Preface

Two professors reviewed portions of the final manuscript and not only pointed out errors but made enormously helpful suggestions that were important for completing the book: Professor Fred Ziegler (Yale) and Professor Douglass Taber (U. of Delaware). I thank both of them very much.

There were many other people who reviewed portions of the book and their reviews were very important in shaping my own perception of the book, what was needed and what needed to be changed. These include: Professor Winfield M. Baldwin, Jr. (U. of Georgia), Professor Albert W. Burgstahler (U. of Kansas), Professor George B. Clemens (Bowling Green State University), Professor Ishan Erden (San Francisco State University), Professor Raymond C. Fort, Jr. (U. of Maine), Professor John F. Helling (U. of Florida), Professor R. Daniel Little (U. of California), Professor Gary W. Morrow (U. of Dayton), Professor Michael Rathke (Michigan State University), Professor Bryan W. Roberts (U. of Pennsylvania), Professor James E. Van Verth (Canisius College), Professor Frederick G. West (U. of Utah), and Professor Kang Zhao (New York University). I thank all of them.

I must also thank the many people who have indulged me at meetings, at Gordon conferences, and as visitors to UConn and who discussed their thoughts, needs, and wants in graduate level education. These discussions helped shape the way I put the book together.

Finally, but by no means last in my thoughts, I am indebted to Professors Joe Wolinsky and Jim Brewster of Purdue University. Their dedication and skill taught me how to teach. Thank you!

I want to thank those at McGraw-Hill who have brought this book to life, particularly Kathi Prancan, without whose perseverance this book would never have been accepted in the first place. I also thank Karen Misler, who was there at the beginning to get things going, and Professor Leroy Wade (Whitman College), whose review made the contract possible. I particularly want to thank Denise Schank for keeping things going over the years, and Jennifer Speer, whose initiative and drive made the manuscript finally become a book. Finally, I thank Melanie Kiel, who together with Ms. Speer, fought the day-to-day battles over all aspects of the manuscript.

I particularly want to thank my wife Sarah and son Steven. They endured the many days and nights of my being in the library and the endless hours on the computer with patience and understanding. My family provided the love, the help, and the fulfillment required for me to keep going and helped me to put this project into its proper perspective. They helped me in ways that are too numerous to mention. I thank them and I dedicate this work to them.

Michael B. Smith

## THIS BOOK IS DEDICATED TO

MY WIFE SARAH

**AND** 

MY SON STEVEN

Abbreviations

### COMMON ABBREVIATIONS

Other, less common abbreviations are given in the text when the term is used.

Ac Acetyl

Acac Acetylacetonate

AIBN azo-bis-isobutyronitrile

All Allyl

Am Amyl  $-CH_2(CH_2)_3CH_3$ 

aq Aqueous Ax Axial

(B-)

9-Borabicyclo[3.3.1]nonylboryl

9-BBN 9-Borabicyclo[3.3.1]nonane

BINAP 2*R*,3*S*-2,2'-*bis*-(diphenylphosphino)-1,1'-binapthyl

Bn Benzyl -CH<sub>2</sub>Ph

S Me

Boc *t*-Butoxycarbonyl Bpy (Bipy) 2,2'-Bipyridyl

Bu n-Butyl -CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>

Bz Benzoyl

CAM Carboxamidomethyl

CAN Ceric ammonium nitrate (NH)<sub>2</sub>Ce(NO<sub>3</sub>)<sub>6</sub>

*c*- Cyclo-cat. Catalytic

Cbz Carbobenzyloxy

chap Chapter(s)

Chirald 2S,3R-(+)-4-dimethylamino-1,2-diphenyl-3-methylbutan-2-ol

CIP Cahn–Ingold-Prelog
COD 1,5-Cyclooctadienyl
COT 1,3,5-cyclooctatrienyl
Cp Cyclopentadienyl

CSA Camphorsulfonic acid

CTAB Cetyltrimethylammonium bromide C<sub>16</sub>H<sub>33</sub>NMe<sub>3</sub><sup>+</sup> Br<sup>-</sup>

xxxviii Abbreviations

Cy (c-C <sub>6</sub> H <sub>11</sub> )	Cyclohexyl	ξ- <b>(</b> _)
°C	Temperature in Degrees Centigrade	
2D	Two-dimensional	
3D	Three-dimensional	
DABCO	1,4-Diazobicyclo[2.2.2]octane	
d	Day(s)	
dba	Dibenzylidene acetone	
DBE	1,2-Dibromoethane	BrCH <sub>2</sub> CH <sub>2</sub> Br
DBN	1,8-Diazabicyclo[5.4.0]undec-7-ene	
DBU	1,5-Diazabicyclo[4.3.0}non-5-ene	
DCC	1,3-Dicyclohexylcarbodiimide	c-C <sub>6</sub> H <sub>13</sub> -N=C=N-c-C <sub>6</sub> H <sub>13</sub>
DCE	1,2-Dichloroethane	CICH2CH2CI
DDQ	2,3-Dichloro-5,6-dicyano-1,4-benzoquinone	
% de	% Diasteromeric excess	
DEA	Diethylamine	HN(CH <sub>2</sub> CH <sub>3</sub> ) <sub>2</sub>
DEAD	Diethylazodicarboxylate	EtO <sub>2</sub> C-N=NCO <sub>2</sub> Et
DET	Diethyl tartrate	
DHP	Dihydropyran	
DIBAL-H	Diisobutylaluminum hydride	(Me <sub>2</sub> CHCH <sub>2</sub> ) <sub>2</sub> AlH
Diphos (dppe)	1,2-bis-(Diphenylphosphino)ethane	Ph <sub>2</sub> PCH <sub>2</sub> CH <sub>2</sub> PPh <sub>2</sub>
Diphos-4 ( <b>dppb</b> )	1,4-bis-(Diphenylphosphino)butane	$Ph_2P(CH_2)_4PPh_2$
DIPT	Diisopropyl tartrate	
DMAP	4-Dimethylaminopyridine	
DME	Dimethoxyethane	MeOCH <sub>2</sub> CH <sub>2</sub> OMe
DMF	N,N'-Dimethylformamide	H NMe <sub>2</sub>
DMS	Dimethyl sulfide	
DMSO	Dimethyl sulfoxide	
dppb	1,4-bis-(Diphenylphosphino)butane	Ph <sub>2</sub> P(CH <sub>2</sub> ) <sub>4</sub> PPh <sub>2</sub>
dppe	1,2-bis-(Diphenylphosphino)ethane	Ph <sub>2</sub> PCH <sub>2</sub> CH <sub>2</sub> PPh <sub>2</sub>
dppf	bis-(Diphenylphosphino)ferrocene	
dppp	1,3-bis-(Diphenylphosphino)propane	$Ph_2P(CH_2)_3PPh_2$
dvb	Divinylbenzene	
e-	Electrolysis	

Electron affinity

% Enantiomeric excess

EA % ee Abbreviations

EE 1-Ethoxyethyl EtO(Me)HCOEt Ethyl -CH2CH3

EDA Ethylenediamine H2NCH2CH2NH2

EDTA Ethylenediaminetetraacetic acid

Equiv Equivalent(s)

ESR Electron Spin Resonance Spectroscopy

FMN Flavin mononucleotide FMO Frontier Molecular Orbital

fod tris-(6,6,7,7,8,8,8)-Heptafluoro-2,2-dimethyl-3,5-octanedionate

Fp Cyclopentadienyl-bis-carbonyl iron

FVP Flash Vacuum Pyrolysis
GC Gas chromatography

gl Glacial

h Hour (hours)

hv Irradiation with light 1,5-HD 1,5-Hexadienyl

HMPA Hexamethylphosphoramide (Me<sub>3</sub>N)<sub>3</sub>P=O HMPT Hexamethylphosphorus triamide (Me<sub>3</sub>N)<sub>3</sub>P

<sup>1</sup>H NMR Proton Nuclear Magnetic Resonance Spectroscopy

HOMO Highest occupied molecular orbital

HPLC High performance liquid chromatography

HSAB Hard/Soft Acid/Base
IP Ionization potential

*i*-Pr Isopropyl -CH(Me)<sub>2</sub>

IR Infrared spectroscopy

LICA (LIPCA) Lithium cyclohexylisopropylamide

LDA Lithium diisopropylamide LiN(i-Pr)<sub>2</sub>
LHMDS Lithium hexamethyl disilazide LiN(SiMe<sub>3</sub>)<sub>2</sub>

LTMP Lithium 2,2,6,6-tetramethylpiperidide
LUMO Lowest unoccupied molecular orbital

MCPBA meta-Chloroperoxybenzoic acid

MeMethyl-CH3 or MeMEMβ-MethoxyethoxymethylMeOCH2CH2OCH2-MesMesityl2,4,6-tri-Me-C6H2

min minutes

MOM Methoxymethyl MeOCH<sub>2</sub>Ms Methanesulfonyl MeSO<sub>2</sub>-

xl Abbreviations

MS Molecular Sieves (3Å or 4Å)

MTM Methylthiomethyl

MVK Methyl vinyl ketone MeSCH<sub>2</sub>-

NAD Nicotinamide adenine dinucleotide
NADP Sodium triphosphopyridine nucleotide

Napth Napthyl ( $C_{10}H_8$ )
NBD Norbornadiene

NBSN-BromosuccinimideNCSN-ChlorosuccinimideNISN-Iodosuccinimide

Ni(R) Raney nickel

NMO N-Methylmorpholine N-oxide

Nu (Nuc) Nucleophile

OBs O-Benzenesulfonate

Oxone 2 KHSO<sub>5</sub>•KHSO<sub>4</sub>•K<sub>2</sub>SO<sub>4</sub>

Polymeric backbone

PCC Pyridinium chlorochromate
PDC Pyridinium dichromate

PEG Polyethylene glycol

Ph Phenyl

PhH Benzene PhMe Toluene

Phth Phthaloyl

Pip Piperidinyl

PPA Polyphosphoric acid

PPTS para-Toluenesulfonic acid

Pr n-Propyl -CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>

Py Pyridine

Quantitative yield

Red-Al [(MeOCH<sub>2</sub>CH<sub>2</sub>O)<sub>2</sub>AlH<sub>2</sub>]Na

RT Room temperature

sBu sec-Butyl CH<sub>3</sub>CH<sub>2</sub>CH(CH<sub>3</sub>)

CH<sub>3</sub>CH<sub>2</sub>CH(Li)CH<sub>3</sub>

CH<sub>3</sub>CH<sub>2</sub>CH(Li)CH<sub>3</sub>

sBuLi sec-Butyllithium

s seconds sec section(s)

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