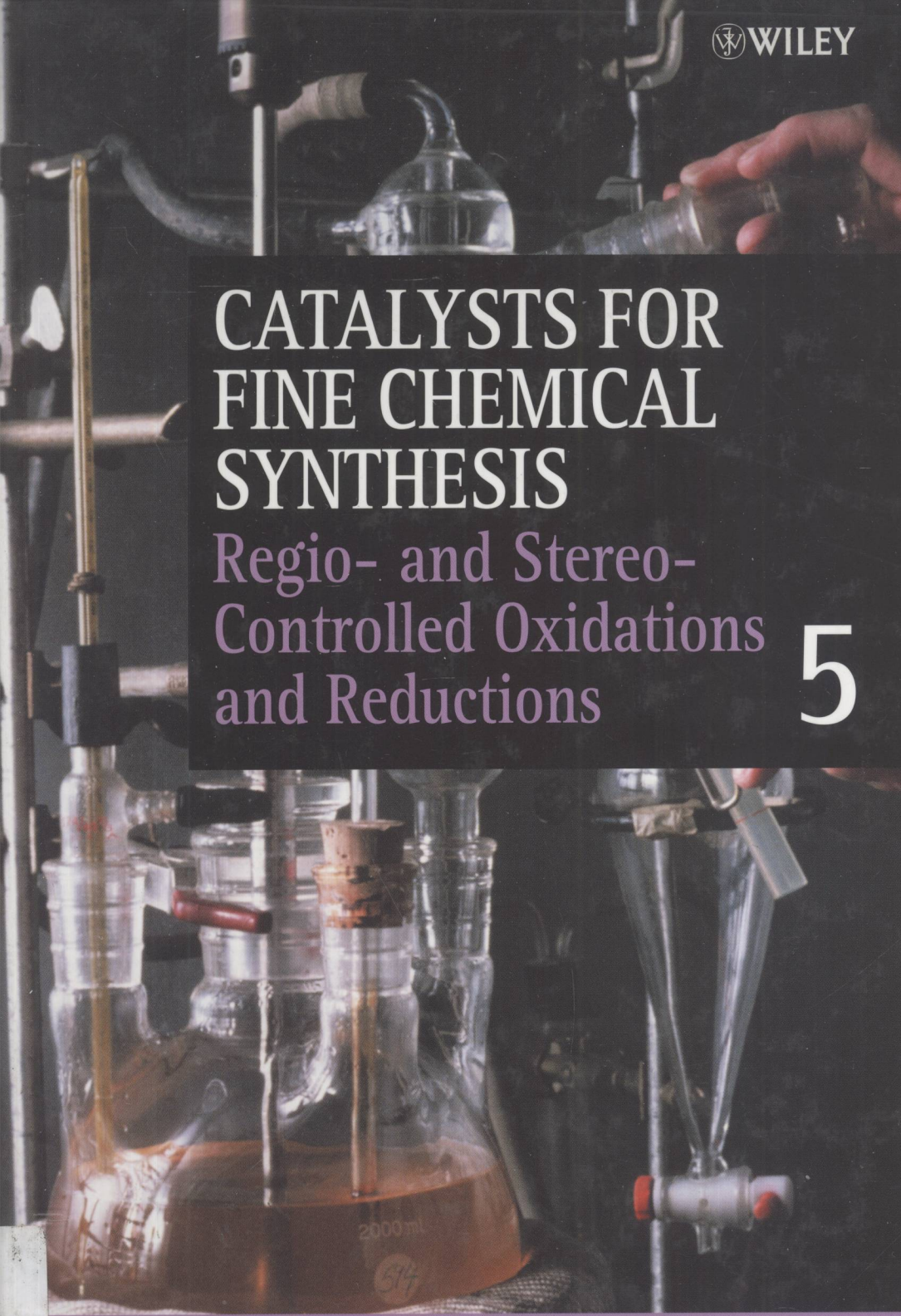

CATALYSTS FOR FINE CHEMICAL SYNTHESIS

Regio- and Stereo-Controlled Oxidations and Reductions

5

Editors: Stanley M. Roberts and John Whittall

Catalysts for Fine Chemical Synthesis

Volume 5

Regio- and Stereo-Controlled Oxidations and Reductions

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Volume 5

Catalysts for Fine Chemical Synthesis

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Catalysts for Fine Chemical Synthesis Series Preface

During the early-to-mid 1990s we published a wide range of protocols, detailing the use of biotransformations in synthetic organic chemistry. The procedures were first published in the form of a loose-leaf laboratory manual and all the protocols have been collected together and published in book form (Preparative Biotransformations, Wiley, Chichester, 1999).

Over the past few years the employment of enzymes and whole cells to carry out selected organic reactions has become much more commonplace. Very few research groups would now have any reservations about using commercially available biocatalysts such as lipases. Biotransformations have become accepted as powerful methodologies in synthetic organic chemistry.

Perhaps less clear to a newcomer to a particular area of chemistry is when to use biocatalysis as a key step in a synthesis, and when it is better to use one of the alternative non-natural catalysts that may be available. Therefore we set out to extend the objective of Preparative Biotransformations, so as to cover the whole panoply of catalytic methods available to the synthetic chemist, incorporating biocatalytic procedures where appropriate.

In keeping with the earlier format we aim to provide the readership with sufficient practical details for the preparation and successful use of the relevant catalyst. Coupled with these specific examples, a selection of the products that may be obtained by a particular technology will be reviewed. In the different volumes of this new series we will feature catalysts for oxidation and reduction reactions, hydrolysis protocols and catalytic systems for carbon–carbon bond formation inter alia. Many of the catalysts featured will be chiral, given the present day interest in the preparation of single-enantiomer fine chemicals. When appropriate, a catalyst type that is capable of a wide range of transformations will be featured. In these volumes the amount of practical data that is described will be proportionately less, and attention will be focused on the past uses of the system and its future potential.

Newcomers to a particular area of catalysis may use these volumes to validate their techniques, and, when a choice of methods is available, use the background

information better to delineate the optimum strategy to try to accomplish a previously unknown conversion.

S. M. ROBERTS
I. KOZHEVNIKOV
E. DEROUANE
Liverpool, 2002

Preface to Volume 5: Regio- and Stereo-Controlled Oxidations and Reductions

In recent years the world has become increasingly energy conscious. For the chemistry arena, this means that old-fashioned, inefficient processes are continually being replaced by modern methods. In turn, this fuels the search for effective catalysts to promote a wide range of transformations.

Across this range there can be no doubt that reactions resulting in either the oxidation or the reduction of a starting material are of paramount importance. In this Volume, a series of new or improved redox catalysts are featured. The catalysts have been disclosed in the recent primary literature (learned Journals) and the respective authors have amplified the disclosure of their catalysts in this Volume. Thus in each report herein, the exact method of preparation of the catalyst is described, the precise method for its use is disclosed and the breadth of substrate range is considered. A description of the equipment required as well as noteworthy safety issues form part of the description of each protocol. Finally, where potentially useful, tips and hints are appended, making these detailed "recipes" often more extensive than those found in the experimental sections of most Journals.

In order to place later chapters in proper context, the first chapter offers a comprehensive overview of industrially important catalysts for oxidation and reduction reactions. Chapters 2 and 3 describe the preparation of chiral materials by way of the asymmetric reduction of alkenes and ketones respectively. These two areas have enjoyed a significant amount of attention in recent years. Optically active amines can be prepared by imine reduction using chiral catalysts, as featured in Chapter 4, which also discloses a novel reductive amination protocol.

The remaining chapters deal with a variety of catalysts for effecting oxidation reactions. Chapter 5 describes three simple protocols for the controlled oxidation of primary or secondary alcohols. The importance of stereocontrolled epoxidation and hydroxylation reactions is reflected by the fact that Chapter 6, directed at this field, is one of the most extensive sections of the book. An interesting example of an enantioselective Baeyer-Villiger reaction is featured in Chapter 7, together with an industrially important ketone to enone conversion. Oxidative carbon-carbon

coupling reactions are the focus for Chapter 8, while the controlled oxidation of sulfides and sulfoxides is the topic chosen for the final chapter.

As for the previous volumes in this Series, the Editors are most grateful to the 100+ authors, who have submitted details of their work to the prescribed format for inclusion in this book. We hope that this Volume will increase exposure of their discoveries to the industrial chemical community and so contribute to the expanded employment of their catalysts in fine chemical synthesis.

STANLEY ROBERTS
JOHN WHITTALL
Manchester, 2007

Abbreviations

Ac	Acetyl
ACS	American Chemical Society
Ala	Alanine
API	Active Pharmaceutical Ingredient
aq	Aqueous
Ar	Aryl
ATH	Asymmetric Transfer Hydrogenation
atms	Atmosphere
BARF	*tetrakis*[3,5-Bis(trifluoromethyl)phenyl]borate
Bn	Benzyl
BINAP	2,2′-(Bisdiphenylphosphino)-1,1′-binaphthol
BINOL	1,1′-Binaphthol
tBME	*tert*-Butyl Methyl Ether
Boc	Butoxycarbonyl
Bu	Butyl
BuLi	Butyl Lithium
ca	*circa approxima*
CAL-B	*Candida antarctica* lipase B
CAN	Ceric Ammonium Nitrate
CATHy™	Catalytic Asymmetric Transfer Hydrogenation
CBS	Corey-Bakshi-Shibata
COD	Cyclooctadiene
Cp	Cyclopentadienyl
DBT	Dibenzoyltartaric Acid
DCM	Dichloromethane
de	Diastereomeric Excess
DMAP	4-Dimethylaminopyridine
DMF	Dimethylformamide
DKR	Dynamic Kinetic Resolution
DPEN	1,2-Diphenylethylene1,2-diamine
DVB	Divinylbenzene
ee	Enantiomeric Excess
EtOAc	Ethyl Acetate
eq	Equivalent

FID	Flame Ionisation Detector
GC	Gas Chromatography
HIV	Human Immunodeficiency Virus
HPLC	High Performance Liquid Chromatography
IBX	o-Iodoxybenzoic Acid
IR	Infra Red
LDA	Lithium diisopropylamide
LDBB	Lithium di-*tert*-butylbiphenylide
LDH	Layered Double Hydroxide
Me	Methyl
MOM	Methoxymethyl
Ms	Methane Sulfonyl
NAD(H)	Nicotinamide Adenine Dinucleotide (reduced)
NADP(H)	Nicotine Adenine Dinucleotide Phosphate (reduced)
Nbd	Norbornadiene
NK	Neurokinin
NMDA	N-Methyl-(D)-aspartate
NMR	Nuclear Magnetic Resonance
Oxone™	Potassium Peroxymonosulfate
PDE	Phosphodiesterase
Ph	Phenyl
psi	Pounds Per Square Inch
PTC	Phase Transfer Catalyst
R_f	Retention Factor
R_t	Retention Time
SALEN	Salicylaldehyde Ethylenediamine Imine
SDS	Sodium Dodecylsulfate
TEMPO	2,2,6,6-Tetramethylpiperidin-1-oxyl
THF	Tetrahydrofuran
TLC	Thin Layer Chromatography
TMEDA	*N*,*N*,*N*′,*N*′-Tetramethylethylenediamine
TOF	Turn Over Frequency
TON	Turn Over Number
Ts	Toluene sulfonyl
UV	Ultraviolet

Contents