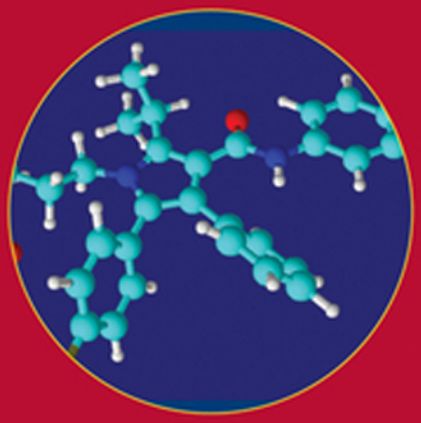

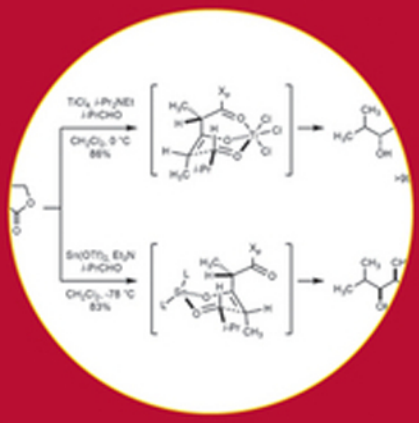

Stereoselective Synthesis of Drugs And Natural Products

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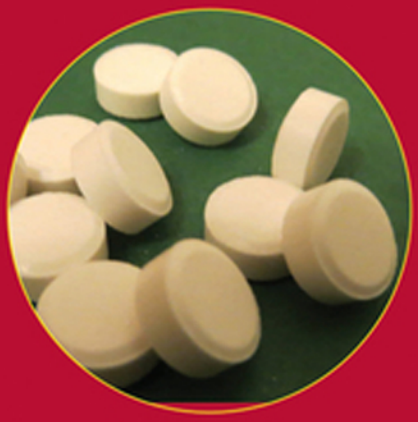

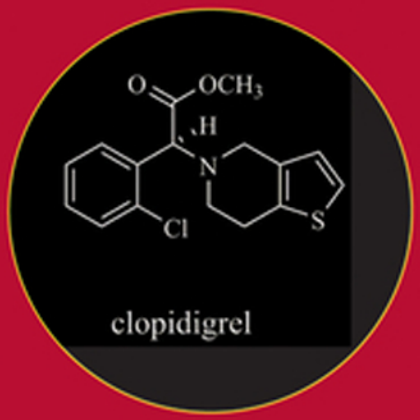

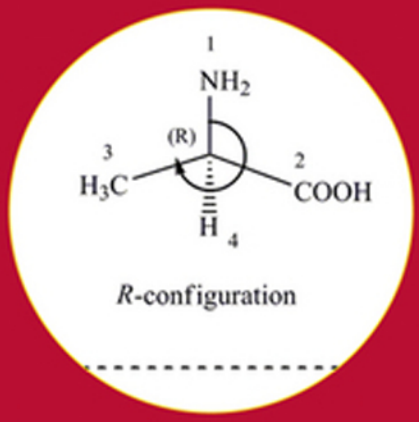

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VASYL ANDRUSHKO

NATALIA ANDRUSHKO

WILEY

STEREOSELECTIVE SYNTHESIS OF DRUGS AND NATURAL PRODUCTS

Volume 1

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To our son Daniel

CONTENTS

PREFACE

The world around us is chiral, and chiral phenomena play a significant role in nature. One phenomenon is homochirality—a property of naturally occurring chiral compounds that consist of only one enantiomer (in either left- or right-handed form). All contemporary life-forms involve unique molecular building blocks with three-dimensional (3D) stereochemistry such as amino acids, sugars, active terpenes, and alkaloids. These naturally occurring architectural masterpieces play a prominent role in living systems constituting the basic units in biopolymers and nanostructures. Enantiomerically pure monomeric L-amino acids and D-carbohydrates, for example, construct biopolymers (proteins, nucleic acids, or polysaccharides), and they are linked together in such a way that all subunits have the same chirality.

The biological activity of many pharmaceuticals, flavors and fragrances, food additives, and agrochemicals is associated with absolute configuration. Because two optical isomers of the chiral compounds can exhibit different biological activities and pharmacological profiles in living systems, the development of stereoselective synthetic methods and strategies for the generation of these precious entities (from simple chiral target molecules to complex natural products) in an efficient manner and with specific and more varied 3D structures has become recently of great interest to both the chemical and pharmaceutical industries. On the other hand, systematic investigations of biological activities, including pharmacology and toxicology, of individual stereoisomers also has become recently commonplace for all new chiral pharmaceuticals and other compounds with potential bioactivity. Concomitantly, these trends have created a rapid increase in the demand for stereoselective analysis techniques that are capable of determining precisely the stereoisomeric composition of chiral biologically active compounds from syntheses, biological assays, or pharmacological studies.

This book comprises 57 chapters. It is an attempt to review the main preparative stereoselective methods for the synthesis of chiral drugs and natural products as well as the application of modern analytical methods and separation techniques for analysis, isolation, and chiral separation with emphasis on recent advances. After the general introductory chapters covering general principles and methodologies, nomenclature, general concepts, and strategies for stereoselective synthesis, the chapters on individual stereoselective synthetic methods are organized by the type of bond formation.

This compilation embraces a wide variety of subjects, such as solid-phase and microwave stereoselective synthesis; asymmetric phase-transfer asymmetric catalysis and application of chiral auxiliaries and microreactor technology; stereoselective reduction and oxidation methods; stereoselective additions; cyclizations; metatheses and different types of rearrangements; asymmetric transition-metal–catalyzed, organocatalyzed, and biocatalytic reactions; methods for the formation of carbon–heteroatom and heteroatom–heteroatom bonds like asymmetric hydroamination and reductive amination, carboamination and alkylative cyclization, cycloadditions with carbon–heteroatom bond formation, and stereoselective halogenations; and methods for the formation of carbon–sulfur and carbon–phosphorus bonds, asymmetric sulfoxidation, and so on.

The different methodologies developed for the precise determination of the stereoisomeric composition of chiral compounds and chiral separation, such as gas and liquid chromatography on chiral stationary phases, capillary electrophoresis, and nuclear magnetic resonance (NMR) spectroscopy; the methodologies for the determination of

absolute configuration such as X-ray analysis, NMR, and chiroptical methods; as well as the methodologies for the resolution of racemates, e.g., crystallization, preparative chromatography, and (dynamic) kinetic resolution have attracted recently considerable attention. The state-of-the-art for these analytical methods and techniques are also discussed in this book.

Stereoselective Synthesis of Drugs and Natural Products is meant to serve as a reference book for scientists interested in the chirality-related aspects of organic chemistry and analysis, and it definitely will find a welcome audience with researchers, lecturers, postdoctorates, and advanced students of chemical and pharmaceutical departments, as well as with researchers and R&D managers of chemical and pharmaceutical companies working on the stereoselective organic synthesis, asymmetric catalysis, biocatalysis and organocatalysis, and stereoselective synthesis of drugs, drug precursors, biologically active compounds and natural products, medicinal and pharmaceutical chemistry, biochemical and biomolecular science, drug discovery, drug design and drug development, as well as chemical engineering and biomedicine. With this book, every chemist working on or interested in topics related to the stereoselective synthesis of drugs and natural products will find in one source gathered overviews they need and a full list of references for further readings.

Although many good reviews and books are available dealing with one or two of the above-mentioned methods, reactions, or methodologies, they are provided in a different scientific context and without experimental details. Usually, their perspective is in accord with that of readers operating in theoretical stereoselective synthesis or asymmetric catalysis, but not with that of readers in experimental work and application stereoselective methods for the synthesis of biologically active and pharmacologically important chiral compounds. This book is intended as a contribution to fill this gap. Therefore, some typical experimental procedures and general experimental details for some key-step reactions of the total syntheses of biologically active compounds have been provided.

Indeed, it was an extremely difficult task to summarize and discuss in a single book limited by a certain number of pages an almost endless number of existing examples and stereoselective methods available in the scientific literature. The enormous increasing activity of the researchers from both academia and industry in the field of stereoselective synthesis precludes a comprehensive treatment of even the literature of the last 20–25 years. Therefore, nonefficient methods with a low stereoselective outcome or pure yields generally will be omitted.

Finally, we wish to thank all the authors, who graciously accepted our invitations and contributed excellent chapters to this book. Without them this book would not have been possible. We would like to express our gratitude to Jonathan T. Rose from Wiley for his invaluable support in this project.

We hope you enjoy this book and welcome your feedback (vasyl.andrushko@gmx.de, natalia_andrushko@yahoo.com).

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Karlsruhe, Germany
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LIST OF ABBREVIATIONS AND ACRONYMS

A

AA	amino acid
AAA	asymmetric allylic alkylation
AAT	atomic axial tensor
Abu	2-aminobutyric acid
Ac	acetyl (acetate)
AC	absolute configuration
acac	acetylacetonate
ACAT	cholesterol acyltransferase
ACC	amino cyclic carbamate
ACCN	*N*,*N*′-1,1′-azobis(cylohexane-1-carbonitrile)
Accufluor	1-fluoro-4-hydroxy-1,4-diazoniabicyclo[2,2,2]octane bis(tetrafluoroborate) (Sigma-Aldrich, St. Louis, MO)
ACDC	asymmetric counteranion-directed catalysis
ACE	angiotensin converting enzyme
ACN	acetonitrile
AcOH	acetic acid
ACP	acyl-carrier protein
AD	asymmetric dihydroxylation
ADH	alcohol dehydrogenase
ADMB	4-allyl-1,2-dimethoxybenzene
ADME	absorption, distribution, metabolism, and excretion (of drugs)
AD-mix-α	asymmetric dihydroxilation mix α
AD-mix-β	asymmetric dihydroxilation mix β
AEA	1-(9-anthryl)ethylamine
Ag(coll)$_2$ClO$_4$	silver bis(*sym*-collidine) perchlorate
AGP	α1-acid glycoprotein
AHA	aminohexanoic acid
AHA	asymmetric hydroamination
AHAS	acetohydroxy acid synthase
AHL	*N*-acyl-homoserine lactone
AIBN	2,2′-azobis(*iso*-butyronitrile)
AIDS	acquired immune deficiency syndrome
ALB	aluminium-lithium-binaphthol-complex
Aliph	aliphatic group
Alloc	allyloxycarbonyl
AMA (or 9-AMA)	α-(9-anthryl)-α-methoxyacetic acid
ANF	atrial natriuretic factor
Ang I	angiotensin I
ANTS	8-aminonaphthalene-1,3,6-trisulfonate
API	active pharmaceutical ingredient
APT	atomic polar tensor
Aq	aqueous
Ar	aryl
ARA	asymmetric reductive amination
ARCM	asymmetric ring-closing metathesis
AROM	asymmetric ring-opening metathesis
AT	analysis time
ATH	asymmetric transfer hydrogenation
***At*HNL**	*Arabidopsis thaliana* hydroxynitrile lyase
Atm	atmosphere
ATP	adenosine triphosphate
ATRA	atom-transfer radical addition
ATRC	atom-transfer radical cyclization

ATR-IR attenuated total reflectance infrared spectroscopy
Aux auxiliary
AZT azidothymidine

B

12-BrTFP 2-bromo-3,3,3-trifluoropropene
BAL benzaldehyde lyase
BBE berberine bridge enzyme
BBN (or 9-BBN) 9-borabicyclo[3.3.1]nonane
BCL *Burkholderia cepiaca* lipase
bdpp 2,4-bis(diphenylphosphino)pentane
BDPPTS 2,4-bis[di(*m*-sodiumsulfonatophenyl)phosphino]pentane
BFD benzoyl formate decarboxylase
BGE background electrolyte
BHA bis-hydroxamic acid
BHT 2,6-di-*tert*-butyl-*p*-cresol (butylated hydroxytoluene)
BIA biochemical induction assay
BIPHEMP (6,6'-dimethylbiphenyl-2,2'-diyl)bis(diphenylphosphine)
BIPHEP 2,2'-bis(diphenylphosphino) biphenyl
BINAP (1,1′-binaphthalene-2,2′-diyl)bis(diphenylphosphine) or 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl
BINAPHOS 2-(diphenylphosphino)-1,1'-binaphthalen-2'-yl-1,1'-binaphthalene-2,2'-diyl phosphite
BINOL 1,1′-binaphthyl-2,2′-diol (or 1,1′-binaphthalene-2,2′-diol or 1,1′-bi-2-naphthol)
BINPHAT 1,1′-(1,1′-binaphthal-2,2′-diolate)bis(tetrachlorobenzene-1,2-benzenediolato)phosphate(V)
bipy 2,2′-bipyridyl
BMBA-pMe bis-1,3-methylbenzylamine-2-methylpropane
Bn benzyl
Bn-BOXAX 2,2′-bis[4-(benzyl)oxazolyl]-1,1′-binaphthyl
Boc *tert*-butoxycarbonyl
BOM benzyloxymethyl
BOMCl benzyl chloromethyl ether
BPG *N*-boc-phenylglycine
BPO bromoperoxidase
BPPM *tert*-butyl 4-(diphenylphosphino)-2-((diphenylphosphino)methyl)pyrrolidine-1-carboxylate
BPS *tert*-butyldiphenylsilyl
BrBBN 9-bromo-9-borabicyclo[3.3.1.]nonane
BSA *N,O*-bis(trimethylsilylacetamide)
BSA bovine serum albumin
BSM benzenesulfinyl morpholine
BT benzothiazol-2-yl
BTFP 3,5-di(trifluoromethyl)phenyl
BtH benzotriazole
Bu butyl
BuLi *n*-butyl lithium
Burgess reagent *N*-(triethylammoniumsulfonyl) carbamate
BV (or BVO) Baeyer-Villiger oxidation
BVA bovine serum albumin
BVMO Baeyer-Villiger monooxygenase
Bz (Bzl) benzoyl

C

18-C-6 18-crown-6
CAB chiral acyloxyborane
CAL *Candida antartica* lipase
CAL-A lipase A from *Candida antarctica*
CAL-B lipase B from *Candida antarctica*
CAMP cyclohexyl(2-methoxyphenyl)(methyl)phosphine
CAN cerium(IV) ammonium nitrate (or ammonium hexanitratocerate(IV))
CAR chiral ^{1}H NMR anisotropy reagent
CASTEP (Cambridge serial total energy package) is a package for performing *ab initio* quantum-mechanical atomistic simulations
Cat. catalyst (or catalytic)
CB (2′-carboxyl)benzyl
CBD 1,2-bis((diphenylphosphino)methyl) cyclobutane
CBH I cellobiohydrolase I
Cbz (or CBz) benzyloxycarbonyl (carboxybenzyl)
CCC countercurrent chromatography
CCD multi-channel charge coupled device detector
CCK-A cholecystokinin A
CD cinchonidine
CD circular dichroism

CD cyclodextrine
CDA chiral derivatizing agent
CE capillary electrophoresis
CE cotton effect
CEC capillary electrochromatography
CF cyclofructan
CFTA α-cyano-α-fluoro-*p*-tolylacetic acid
CGE capillary gel electrophoresis
CGRP Calcitonin gene-related peptide
CHF congestive heart failure
CHMO cyclohexanone monooxygenase
CHP cumene hydroperoxide
CIEF capillary isoelectic focusing
CITP capillary isotachophoresis
ClAc chloroacetyl
CLEA cross-linked enzymes aggregates
CLSR chiral lanthanide shift reagent
CM cross-metathesis
CMC critical micelle concentration
CN cinchonine
CO_2 carbon dioxide
CoA coenzyme A
cod (or COD) 1,5-cyclooctadiene
coe cyclooctatetraene
COSMO conductor-like screening model
COSY correlation spectroscopy
COX-2 cyclooxygenase-2
Cp cyclopentadienyl
CP cross-polarization
Cp^* pentamethylcyclopentadienyl
CPD cyclopentanedione
CPL circularly polarized light
$cPLA_2$ phospholipase A_2
CP-MAS cross-polarization magic-angle spinning
CPME cyclopentyl methyl ether
CPO chloroperoxidase
CPR cytochrome P450 reductase
Crabtree catalyst tris(cyclohexyl)phosphane [(1–2-η:5–6-η)-cycloocta-1,5-diene]pyridine iridium hexafluoridophosphate
CS chiral selector
CSA camphorsulfonic acid
CSA chiral solvating agent
CSA canine serum albumin
CSDP acid camphorsultam-dichlorophthalic acid
CSP chiral stationary phase
CSP acid camphorsultam-phthalic acid
CTZ cetirizine
CuTC copper(I) thiophene-2-carboxylate
CXR chiral X-ray internal reference or chiral X-ray internal reference reagent
Cy (c-Hex) cyclohexyl (cyclohexane)
CYP cytochrome P450 monooxygenase
CZE capillary zone electrophoresis

D

1,4-DHP 1,4-dihydro-2,6-dimethylpyridine
7DHC 7-dehydrocholesterol
DABCO 1,4-diazabicyclo[2.2.2]octane
DACH 1,2-diaminocyclohexane
DAD diode array detector
DARA direct asymmetric reductive amination
DAST diethylamino sulfur trifluoride
dba dibenzylideneacetone
DBFOX (*R*,*R*)-4,6-dibenzofurandiyl-2,2′-bis(4-phenyloxazoline)
DBT dibenzoyl-D-tartaric acid
DBU 1,8-diazabicyclo[5.4.0]undec-7-ene
DCA deoxycholic acid
DCB 2,6-dichlorobenzyl
DCC *N*,*N*′-dicyclohexylcarbodiimide
DCE 1,2-dichloroethane
DCM dichloromethane or methylene chloride
DCP dual circular polarization
D-DBTA dibenzoyl-D-tartaric acid
DD dipolar dephasing
DDH dehydrodiol dehydrogenase
DDHAIC degrading-dehydroabietylisothiocyanate
DDQ 2,3-dichloro-5,6-dicyano-1,4-benzoquinone
de diastereomeric excess
DEAD diethyl azodicarboxylate
DEIPS diethylisopropylsilyl
Deoxo-Fluor bis(2-methoxyethyl)aminosulfur trifluoride (Sigma-Aldrich, St. Louis, MO)
DEPT distortionless enhancement by polarization transfer (the experiment allows to determine multiplicity of carbon atom substitution with hydrogens)

DERA 2-deoxy-D-ribose 5-phosphate aldolase
DET diethyltartrate
DFT density functional theory
DHAP dihydroxyacetone phosphate
dHbipy 4,4′-diheptyl-2,2′-dipyridyl
DHEA dehydroepiandrosterone
DHPLC dynamic HPLC
DHQ dihydroquinine
$(DHQ)_2AQN$ hydroquinine (anthraquinone-1, 4-diyl) diether
$(DHQ)_2PHAL$ 1,4-bis-(9-*O*-dihydroquinine)phthalazine (or dihydroquinine 1,4-phthalazinediyl diether)
DHQD dihydroquinidine
$(DHQD)_2PHAL$ 1,4-bis-(9-*O*-dihydroquinidine) phthalazine (or dihydroquinidine 1,4-phthalazinediyl diether)
$(DHQD)_2PYR$ hydroquinidine 2,5-diphenyl-4,6-pyrimidinediyl diether
DIAD diisopropyl azodicarboxylate
DIBAL diisobutylaluminum
DIBAL-H (or DIBAH) diisobutylaluminum hydride
DIC *N*,*N*′-diisopropylcarbodiimide
DIEA diisopropylethylamine
DIF differentiation-inducing factor
Difluorophos 5,5′-bis(diphenylphosphino)-2,2,2′,2′-tetrafluoro-4,4′-bi-1,3-benzodioxole
DIM dimethindene
DINP diisononylphthalate
DIOP 2,2-dimethyl-4,5-bis(diphenylphosphinomethyl)-1,3-dioxolane
DIPAMP 1,2-bis((2-methoxyphenyl)(phenyl) phosphino)ethane
DIPC *N*,*N*′-diisopropylcarbodiimide
DIPE diisopropylether
DIPEA *N*,*N*-diisopropylethylamine
DIPT diisopropyltartrate
DITA diethyl azodicarboxylatediscontinuous isoperibolic thermal analysis
DKR dynamic kinetic resolution
DLP dilauroyl peroxide
DMA *N*,*N*-dimethylacetamide
DMAC dimethyl acetylenedicarboxylate
DMAP 4-*N*,*N*-dimethylaminopyridine
DMB 3,4-dimethoxybenzyl
DMBA *N*,α-dimethylbenzylamine
DME 1,2-dimethoxyethane
DMEAD diethyl azodicarboxylate
DMF *N*,*N*-dimethylformamide
DMI 1,3-dimethyl-2-imidazolidinonegive
DMM dimethoxymethane
D. M. [O] Dess-Martin oxidation
DMP Dess-Martin periodinane
DMPA 2,2-dimethoxy-2-phenylacetophenone; is a photoinitiator used to initialize radical reactions
DMPC 1,2-dimyristoyl-*sn*-glycero-3-phosphocholine
DMPM 3,4-dimethoxybenzyl
DMPS *N*,*N*-dimethyl-3-(2-methoxyphenoxy)-3-propylamine
DMPU 1,3-dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidinone (or *N*,*N*-dimethyl propylene urea)
DMS dimethylsulfide
DMSO dimethylsulfoxide
$DMSO\text{-}d_6$ hexadeuteriodimethyl sulphoxide
DMTST (dimethylthio)methylsulfonium triflate
DNA deoxyribonucleic acid
DOS diversity-oriented synthesis
DPE 1,2-bis(diphenylphosphino)ethane
DPEN diphenylethylenediamine
Dpm diphenylmethyl
DPP dipeptidylpeptidase
DPP4 selective inhibitor dipeptidyl peptidase-4 selective inhibitor
DPPA diphenylphosphoryl azide
dppb 1,2-bis(diphenylphosphino)benzene
DPPC diphenyl phosphorochloridate
dppe (or DPPE) 1,2-bis(diphenylphosphino)ethane
dppf 1,1′-bis(diphenylphosphino) ferrocene
dppp (or DPPP) 1,3-bis(diphenylphosphino)propane
DPTTA di-*p*-toluoyl-D-tartaric acid
dr diastereomeric ratio
DRA dopamine releasing agent
DS degree of substitution
DSC *O*,*O*′-di-*p*-toluoyl-D-tartaric acid
DTAF 5-(4,6-dichloro-*s*-triazin-2-ylamino) fluorescein
DTBMP 2,6-di-*tert*-butyl-4-methylpyridine

DTT	*O*,*O*′-di-*p*-toluoyl-D-tartaric acid
DVB	divinylbenzene
DYKAT	dynamic kinetic asymmetric transformation
DYRKR	dynamic reductive kinetic resolution

E

EC	endothelial cell
EC_{50}	half maximal effective concentration
ECD	electronic circular dichroism
ED_{50}	effective dose 50
EDC	1-ethyl-3-(3-dimethylaminopropyl) carbodiimide
EDCI	1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride
EDTA	ethylenediaminetetraacetic acid
ee	enantiomeric excess
***ee*p**	enantiomeric excess of the product
***ee*s**	enantiomeric excess of the substrate
EL	erythromycin lactobionate
EMA	european medicines agency
ent	enantiomeric
er	enantiomeric ratio
EOF	electroosmotic flow
EOTH	enantioselective organocatalytic transfer hydrogenation
equiv	equivalent(s)
ER	endoplasmic reticulum
Ery4P	erythrulose 4-phosphate
ESI	enantiomeric similarity index
ESPHOS	1,2-bis(2-phenylhexahydro-1H-pyrrolo[1,2-c][1,3,2]diazaphosphol-1-yl)benzene
Et	ethyl
EtOAc	ethyl acetate
EWG	electron withdrawing group

F

5′-FDA	5′-fluoro, 5′-deoxyadenosine
F_8BNP	5,5′,6,6′,7,7′,8,8′-octafluoro-1,1′-binaphthyl-2,2′-diyl phosphate
FAD	flavine adenine dinucleotide
FBP	D-fructose 1,6-bis-phosphate
FBRM	Focused Beam Reflectance Measurement
Fc	ferrocenyl
FDA	U.S. Food and Drug Administration
FDH	formate dehydrogenase
FEP	fluorinated ethylene-propylene
FGF	fibroblast growth factor
FID	free induction decay
FITC	fluorescein isothiocyanate
FLC	flash liquid chromatography
Fluolead	4-*tert*-butyl-2,6-dimethylphenylsulfur trifluoride
FMN	flavine mononucleotide
Fmoc	9-fluorenylmethyloxycarbonyl
FP	β-fructopyranose
FPP	farnesyl diphosphate
FruA	D-fructose 1,6-bis-phosphate aldolase
FSA	D-fructose 6-phosphate aldolase
FT	Fourier transform
F-TEDA	1-fluoro-1,4-diazoniabicyclo[2.2.2] octane

G

G6P	glucose 6-phosphate
G6PDH	glucose 6-phosphate dehydrogenase
Ga3P	D-glyceraldehyde-3-phosphate
GABA	γ-aminobutyric acid
GAG	glycosaminoglycan
GC	gas chromatography
GC-MS	gas chromatography coupled to mass spectrometry
GDH	glucose dehydrogenase
GFP	green fluorescent protein
GIAO	gauge-invariant atomic orbital
GIPAW	gauge including projector augmented wave
GLC	gas-liquid chromatography
Gln	glutamine
Gly	glycine
glygly	glycylglycine
GO	glycolaldehyde
GPC	gel permeation chromatography
GST	glutathione S-transferase

H

HA	gydroxyacetone
HA	hemagglutinin
HAART	highly active antiretroviral therapy

HATU *O*-(7-azabenzotriazol-1-yl)-*N,N,N′,N′*-tetramethyluronium hexafluorophosphate

***Hb*HNL** *Hevea brasiliensis* hydroxynitrile lyase

HCN hydrogen cyanide

HDA hetero-Diels-Alder reaction

H(dcm) *d,d*-dicampholylmethane

HDL high-density lipoprotein

HEH Hantzsch ester

HEP-G2 human liver hepatocellular carcinoma cell line

HEPES 2-[4-(2-hydroxyethyl)piperazin-1-yl] ethanesulfonic acid

HETCOR heteronuclear correlation spectroscopy

HETE (or 12-HETE) hydroxyeicosatetraenoic acid (or 12 (*S*)-hydroxyeicosatetraenoic acid)

Hex hexane

HF Hartree-Fock

HFIP 1,1,1,3,3,3-hexafluoro-2-propanol (or hexafluoroisopropanol)

H(hfc) heptafluorobutylyl-*d*-camphor

HI hydriodic acid

HIV human immunodeficiency virus

HKR hydrolytic kinetic resolution

HLADH horse liver alcohol dehydrogenase

HMBA 4-hydroxymethylbenzoic acid

HMBC heteronuclear multiple bond correlation

HMDS 1,1,1,3,3,3-hexamethyldisilazane

HMG CoA 3-hydroxy-3-methyl-glutaryl-coenzyme A

[hmim][BF_4] 1-hexyl-3-methylimidazolium tetrafluoborate

HMPA hexamethylphosphoramide

HMQC heteronuclear single quantum coherence

HMTA hexamethylenetetramine

hν light

HNL hydroxynitrile lyase

HOAt 1-hydroxy-7-azabenzotriazole

HOBt 1-hydroxybenzotriazole

HOMO highest occupied molecular orbital

homochiral enantiomerically pure chiral (compound)

HOX hypohalous acid

HPA hydroxypyruvic acid

HPE heptasaccharide phytoalexin elicitor

HPLC high-performance liquid chromatography

HPP 2-hydroxy-1-phenylpropanone

HPV human papillomavirus

HRV human rhinovirus

HSA human serum albumin

HSDD hypoactive sexual desire disorder

HSQC heteronuclear single quantum coherence

HSV herpes simplex virus

H(tfc) trifluoroacetyl-*d*-camphor

HTIB [hydroxy(tosyloxy)iodo]benzene (Koser's reagent)

HTX histrionicotoxin

HUVEC human umbilical vein endothelial cell

HWE Horner-Wadsworth-Emmons reaction

HWP half-wave plate

Hypip hydroxypipecolic acid

HZ hydroxyzine

I

IBX 2-iodoxybenzoic acid

IC_{50} half maximal inhibitory concentration

I(coll)$_2$$ClO_4$ iodonium bis(*sym*-collidine) perchlorate

I(collidine)$_2$$PF_6$ bis(2,4,6-trimethylpyridine)iodonium hexafluorophosphate

ICP incident circular polarization

ICP-AES inductively coupled plasma-atomic emission spectroscopy

i.d. internal diameter

IDCP iodonium-*sym*-collidine perchlorate

IEDDA inverse-electron-demand Diels-Alder

IFNγ interferon gamma

IL interleukin

Ile isoleucine

IMDA intramolecular Diels-Alder reaction

ImP 1-methyl-2-[(diphenylphosphino) methyl]imidazole

INADEQUATE incredible natural abundance double quantum transfer experiment

Ipc isopinocampheyl

_i_-Pr *iso*-propyl

IPr 1,3-bis-(2,6-diisopropylphenyl)-imidazol-2-ylidene

IPy_2BF_4 bis(pyridine) iodonium tetrafluoroborate

IR infrared

J

K

KCN potassium cyanide

KF Karl Fischer titration

KHMDS potassium 1,1,1,3,3,3-hexamethyldisilazide [potassium bis(trimethylsilyl)amide]

KK Kramers-Kronig transform

KR kinetic resolution

L

L ligand

LA Lewis acid

LAH lithium aluminum hydride

LAR leukocyte antigen-related protein tyrosine phosphatase

LB lysogeny broth

LBA Lewis-Brønsted acid

LC liquid chromatography

LDA lithium diisopropylamide

LDBB lithium 4,4′-di(*tert*-butyl)-1,1′-biphenylide

LDEA lithium diethylamide

LDH lactate dehydrogenase

LDL low-density lipoprotein

LE ligand exchange

LEC ligand exchange chromatography

Leu leucine

Lev levulinoyl

Le^x $Lewis^x$-type oligosaccharides

LFI lethal factor inhibitor

LIA lock-in amplifier

LiDBB lithium di-*tert*-butylbiphenyl

LIF laser-induced fluorescence

LiHMDS (LHMDS) lithium 1,1,1,3,3,3-hexamethyldisilazide (or lithium bis(trimethylsilyl) amide)

LiTMP lithium 2,2,6,6-tetramethylpiperidide

LMOG low-molecular-weight organogel

LOD limit of detection

LPL linearly polarized light

LPO lactoperoxidase

L-selectride lithium tri-*sec*-butyl(hydrido)borate (or lithium tri-*sec*-butylborohydride)

LSR lanthanide shift reagent

LTB_4 leukotriene B_4

***Lu*HNL** *Linum usitatissimum* hydroxynitrile lyase

LUMO lowest unoccupied molecular orbital

LUV large unilamellar vesicle

Lys lysine

M

M metal

MαNP 2-methoxy-2-(1-naphthyl)propionic acid

MA maslinic acid

MAB metastable atom bombardment

MABR methylaluminum bis(4-bromo-2,6-di-*tert*-butylphenoxide)

MAO monoamine oxidase

MAOS microwave-assisted organic synthesis

MAPh methylaluminum bis(2,6-diphenylphenoxide)

MAS magic-angle spinning

Max. maximum

MaxiPost (3*S*)-(+)-(5-chloro-2-methoxyphenyl)-1,3-dihydro-3-fluoro-6- (trifluoromethyl)-2*H*-indol-2-one (Xi'an Unique Electronics & Chemical Co., Ltd, Xi'an, P.R. China)

MBA α-methylbenzylamine

MBHA 4-methylbenzhydrylamine

MBz 4-methylbenzoyl

***m*CPBA (or MCPBA)** *meta*-chloroperoxybenzoic acid

MDM2 mouse double minute 2

MDPS methyldiphenylsilyl

MDR multidrug resistance

Me methyl

MEA 2-methyl-5-ethylaniline

MeCN acetonitrile

MED male erectile dysfunction

MEEKC microemulsion micellar electrokinetic chromatography

***Me*HNL**	*Manihot esculenta* hydroxinitrile lyase
MEKC	micellar electrokinetic chromatography
MEM	β-methoxyethoxymethyl
MenD	2-succinyl-5-enolpyruvyl-6-hydroxy-3-cyclohexene-1-carboxylate synthase
MeO-BIPHEP	(6,6'-dimethoxybiphenyl-2,2'-diyl) bis(diphenylphosphine)
MeOH	methanol
Mes	2,4,6-trimethylphenyl
MES	2-(*N*-morpholino)ethanesulfonic acid
MeSOTf	methylsulfenyl triflate
MG	methylglucuronide
MGAM	human maltase-glucoamylase
MIBK	methyl isobutyl ketone
ML	mother liquor
MLV	multilamellar vesicle
MO	migration order
MOA	methoxyacetone
MOC	memory of chirality
MOM	methoxymethyl
MOMCl	chloromethyl methyl ether
MOP	(2'-methoxy-1,1'-binaphthyl-2-yl) diphenylphosphine
MP	4-methoxyphenyl
MPA	α-methylphenylacetic acid
MPPP	methyl(phenyl)(*n*-propyl)phosphine
MRSA	methicillin-resistant *Staphylococcus aureus*
MRT	micro reaction technology
Ms	methanesulfonyl (or mesyl) functional group
MS	molecular sieves
MS	mass spectrometer
MSNT	1-(2-mesitylenesulfonyl)-3-nitro-1*H*-1,2,4- triazole
Mtase	methyltransferase
MTBE	methyl *tert*-butyl ether
MTNA	α-methoxy-α-trifluoromethyl-1-naphthylacetyl
MTPA	α-methoxy-α-trifluoromethylphenylacetic acid
MVK	methyl vinyl ketone
MW	molecular weight
MW (or μW)	microwave

N

Na_2EDTA	disodium edetate
NA	nonaqueous
NACE	nonaqueous capillary electrochromatography
nAChR	neuronal nicotinic acetylcholine receptor
NAD^+	nicotinamide adenine dinucleotide, oxidized form
NADH	nicotinamide adenine dinucleotide–hydride (reduced NAD)
$NADP^+$	nicotinamide adenine dinucleotide phosphate, oxidized form
NADPH	nicotinamide adenine dinucleotide phosphate, reduced form
NaHMDS	sodium 1,1,1,3,3,3-hexamethyldisilazide
NAP	2-naphthylmethyl
Naph	naphtyl
nbd	norbornadiene
NBS	*N*-bromosuccinimide
NBSH	2-nitrobenzenesulfonylhydrazide
***n*-Bu**	*n*-butyl
NCE	new chemical entity
NCS	*N*-chlorosuccinimide
NCS	neocarzinostatin
NDF	neutral detergent fiber
NDO	naphthalene dioxygenase
NEA	1-(1-naphthyl)ethylamine
NEM	*N*-ethylmorpholine
NEP	neutral endopeptidase
NeuAc	*N*-acetylneuraminic acid
NFOBS	*N*-fluoro-*o*-benzenedisulfonimide
NFSI	*N*-fluorobenzenesulfonimide
NHC	*N*-heterocyclic carbene
NHK	Nozaki-Hiyama-Kishi reaction
NIS	*N*-iodosuccinimide
NK	neurokinin
NMDA	*N*-methyl-*d*-aspartate
NMDPP	((1*S*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl)diphenylphosphine
NMM	*N*-methylmorpholine
NMO	*N*-methylmorpholine *N*-oxide
NMP	*N*-methyl-2-pyrrolidone
$NMQPF_6$	*N*-methylquinolinium hexafluorophosphate
NMR	nuclear magnetic resonance

NNRTI non-nucleoside reverse transcriptase inhibitor
NOE nuclear Overhauser effect
NOESY nuclear Overhauser effect spectroscopy
NOM natural organic matter
NPA nicotinamide/palmitic acid
Npes 2-(4-nitrophenyl)ethylsulfonyl
Nphth *N*-phthaloyl
NRA norepinephrine releasing agent
NRTI nucleotide reverse transcriptase inhibitor
Ns 4-nitrobenzenesulfonyl
NS 2-nitrobenzenesulfonyl
NSAID non-steroidal anti-inflammatory drugs
NTD nitrendipine
Nu nucleophile

O

OAMA acetoxyphenylacetic acid
o.d. outer diameter
***o*-DPPB** *ortho*-diphenylphosphanylbenzoate
OPA orthophthaldialdehyde
OR optical rotation
ORD optical rotatory dispersion
ORF open reading frame
OTf trifluoromethanesulfonate (or triflate)
OVM ovomucoid

P

P4-*t*-Bu phosphazene base P_4-*tert*-Bu: 3-*tertio*-butylimino-1,1,1,5,5,5-hexakis(dimethylamino)-3-{[tris(dimethylamino)phosphoranylidene]amino}-$1\lambda^5,3\lambda^5,5\lambda^5$-1,4-triphosphazadiene
PAC (*R*)-phenylacetylcarbinol
PAF platelet aggregating factor
PAT process analytical technology
***Pa*HNL** *Prunus amygdalus* hydroxynitrile lyase
PAMO phenylacetone monooxygenase
PAMP (2-methoxyphenyl)(methyl)(phenyl) phosphine
PBLG poly(γ-benzyl-L-glutamate)
PBN phosphabicyclo[3.3.1]nonane
PCA principal component analysis
PCBLL poly-ε-carbobenzyloxy-L-lysine
PCC pyridinium chlorochromate
PCM polarizable continuum model
PCP peptidyl carrier protein
PCPA *p*-chlorophenyl acetate
PDC pyridinium dichromate
PDC pyruvate decarboxylase
PDE phosphodiesterase
PDMA poly(dimethylacrylamide)
PDMS polydimethylsiloxane
pdta propylenediaminetetraacetic acid
PE propyl ether
PEA 1-phenylethylamine
PEG poly(ethylene glycol)
PEGA polyethylene glycol
PELG poly(γ-ethyl-L-glutamate)
PEM photoelastic modulator
PEP phosphoenolpyruvate
PES potential energy surface
PET position emission tomography
PFA perfluoroalkoxy-polymer
PFL *Pseudomonas fluorescens* lipase
PG protecting group
PGA phenylglycine amide
PGA penicillin G acylase
PGME phenylglycine methyl ester
Ph phenyl
PHAL phthalazine
Ph-DBFOX (*R*,*R*)-4,6-dibenzofurandiyl-2,2′-bis(4-phenyloxazoline)
Phe phenylalanine
PhEur European Pharmacopoeia
PHM pheniramine
PHOX phosphinooxazoline
PhSOTf phenylsulfenyl triflate
Phth phthalimido (phthaloyl)
Piv pivaloyl
PKC protein kinase C
PKS-NRPS polyketide synthase-nonribosomal peptide synthase
PLP pyridoxal-5′-phosphate
PMB *p*-methoxybenzyl (4-methoxybenzyl)
PMBM *p*-methoxybenzyloxymethyl
PMHS polymethylhydrosiloxane
PMP *p*-methoxyphenyl
PNA peptide nucleic acid

p-NBA *p*-nitrobenzoic acid
PNBz *p*-nitrobenzoyl
PNNP N^1,N^2-bis(diphenylphosphino)-N^1, N^2-bis((*R*)-1-phenylethyl)ethane-1,2-diamine
PP 4-pyrrolidinopyridine
PPAP polyprenylated acylphloroglucinol
PPAR peroxisome proliferator-activated receptor
PPDC phenylpyruvate decarboxylase
PPi pyrophosphate
PPI proton pump inhibitor
PPL porcine pancreas lipase
ppm parts per million
PPNO 4-phenylpyridine *N*-oxide
PPPNO 4-(3-phenylpropyl)pyridine *N*-oxide
PPTS pyridinium *p*-toluenesulfonate
Pr propyl
PR pattern recognition
PRA plasma renin activity
PRP polyvinylpyrrolidone
PS polystyrene
PS-CI *Pseudomonas cepacia* lipase
Psig pounds per square inch (gauge)
PSL-C *Burkholderia cepacia* lipase
PSP pseudo-stationary phase
PT 1-phenyl-1*H*-tetrazol-5-yl
PTC phase-transfer catalysis
PTFE polytetrafluoroethylene
PTrMA polytriphenylmethacrylate
p-TSA *p*-toluensulfonic acid
***p*TsOH** *para*-toluenesulfonic acid
Ptx pentoxifylline
PUFA polyunsaturated fatty acid
PVA polyvinyl alcohol
PVP polyvinylpyrrolidone
Py (or pyr) pyridine
PyAOP (7-azabenzotriazol-1-yloxy)tripyrrolidinophosphonium hexafluorophosphate
PyBOP (benzotriazol-1-yloxy)tripyrrolidinophosphonium hexafluorophosphate
PYR pyridin-2-yl

Q

QD quinidine
QN quinine
qNMR quantitative nuclear magnetic resonance

R

(4*R*)-MEOX methyl 2-oxazolidone-4(*R*)-carboxylate
(*R,R*)-BIPHOP-F (3*R*,4*R*)-1,1,6,6-tetrakis(perfluorophenyl)-3,4-diphenyl-2,5-dioxa-1,6-diphosphahexane
R_s resolution
Ra-Ni Raney nickel
RAMP (*R*)-1-amino-2-methoxymethylpyrrolidine
RCM ring-closing metathesis
RDC residual dipolar coupling
***R*-DOSP** *N*-[(4-dodecylphenyl)sulfonyl]-(*R*)-prolinate
Recryst. recrystallization
Red-Al sodium bis(2-methoxyethoxy)aluminium hydride
rel E. relative energy
RF radiofrequency
RI refractive index
Rib5P D-ribose 5-phosphate
ROA Raman optical activity
ROESY rotation frame nuclear Overhauser effect spectroscopy
ROM ring-opening metahteis
RRM ring rearrangement metathesis
RT room temperature

S

SA simulated annealing
SAD Sharpless asymmetric dihydroxylation
SAE Sharpless asymmetric epoxidation
salen *N,N′*-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediamine (or *N, N′*-ethylenebis(salicylimine))
SAM (*S*)-adenosyl-L-methionine
SAMP (*S*)-1-amino-2-methoxymethylpyrrolidine
SAP (*S*)-3-amino-1,2-propanediol
SAR structure–activity relationship
SARS severe acute respiratory syndrome
***Sb*HNL** *Sorghum bicolor* hydroxynitrile lyase