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## PROTECTIVE GROUPS IN ORGANIC SYNTHESIS

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### THIRD EDITION

### Theodora W. Greene

The Rowland Institute for Science

and

Peter G. M. Wuts

Pharmacia and Upjohn Company



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# PREFACE TO THE THIRD EDITION

Organic synthesis has not yet matured to the point where protective groups are not needed for the synthesis of natural and unnatural products; thus, the development of new methods for functional group protection and deprotection continues. The new methods added to this edition come from both electronic searches and a manual examination of all the primary journals through the end of 1997. We have found that electronic searches of *Chemical Abstracts* fail to find many new methods that are developed during the course of a synthesis, and issues of selectivity are often not addressed. As with the second edition, we have attempted to highlight unusual and potentially useful examples of selectivity for both protection and deprotection. In some areas the methods listed may seem rather redundant, such as the numerous methods for THP protection and deprotection, but we have included them in an effort to be exhaustive in coverage. For comparison, the first edition of this book contains about 1500 references and 500 protective groups, the second edition introduces an additional 1500 references and 206 new protective groups, and the third edition adds 2349 new citations and 348 new protective groups.

Two new sections on the protection of phosphates and the alkyne-CH are included. All other sections of the book have been expanded, some more than others. The section on the protection of alcohols has increased substantially, reflecting the trend of the nineties to synthesize acetate-and propionate-derived natural products. An effort was made to include many more enzymatic methods of protection and deprotection. Most of these are associated with the protection of alcohols as esters and the protection of carboxylic acids. Here we have not attempted to be exhaustive, but hopefully, a sufficient number of cases are provided that illustrate the true power of this technology, so that the reader will examine some of the excellent monographs and review articles cited in the references. The Reactivity Charts in Chapter 10 are identical to those in the first edition. The chart number appears beside the name of each protective group when it is first introduced. No attempt was made to update these Charts, not only because of the sheer magnitude of the task, but because it is nearly impossible in

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a two-dimensional table to address adequately the effect that electronic and steric controlling elements have on a particular instance of protection or deprotection. The concept of fuzzy sets as outlined by Lofti Zadeh would be ideally suited for such a task.

The completion of this project was aided by the contributions of a number of people. I am grateful to Rein Virkhaus and Gary Callen, who for many years forwarded me references when they found them, to Jed Fisher for the information he contributed on phosphate protection, and to Todd Nelson for providing me a preprint of his excellent review article on the deprotection of silyl ethers. I heartily thank Theo Greene for checking and rechecking the manuscript—all 15 cm of it—for spelling and consistency and for the arduous task of checking all the references for accuracy. I thank Fred Greene for reading the manuscript, for his contribution to Chapter 1 on the use of protective groups in the synthesis of himastatin, and for his contribution to the introduction to Chapter 9, on phosphates. I thank my wife, Lizzie, for encouraging me to undertake the third edition, for the hours she spent in the library looking up and photocopying hundreds of references, and for her understanding while I sat in front of the computer night after night and numerous weekends over a two-year period. She is the greatest!

Kalamazoo, Michigan June 1998 PETER G. M. WUTS

## PREFACE TO THE SECOND EDITION

Since publication of the first edition of this book in 1981, many new protective groups and many new methods of introduction or removal of known protective groups have been developed: 206 new groups and approximately 1500 new references have been added. Most of the information from the first edition has been retained. To conserve space, generic structures used to describe Formation/Cleavage reactions have been replaced by a single line of conditions, sometimes with explanatory comments, especially about selectivity. Some of the new information has been obtained from on-line searches of *Chemical Abstracts*, which have limitations. For example, *Chemical Abstracts* indexes a review article about protective groups only if that word appears in the title of the article. References are complete through 1989. Some references, from more widely circulating journals, are included for 1990.

Two new sections on the protection for indoles, imidazoles, and pyrroles and protection for the amide –NH are included. They are separated from the regular amines because their chemical properties are sufficiently different to affect the chemistry of protection and deprotection. The Reactivity Charts in Chapter 8 are identical to those in the first edition. The chart number appears beside the name of each protective group when it is first discussed.

A number of people must be thanked for their contributions and help in completing this project. I am grateful to Gordon Bundy, who loaned me his card file, which provided many references that the computer failed to find, and to Bob Williams, Spencer Knapp, and Tohru Fukuyama for many references on amine and amide protection. I thank Theo Greene who checked and rechecked the manuscript for spelling and consistency and for the herculean task of checking all the references to make sure that my 3's and 8's and 7's and 9's were not interchanged—all done without a single complaint. I thank Fred Greene who read the manuscript and provided valuable suggestions for its improvement. My wife Lizzie was a major contributor to getting this project finished, by looking up and photocopying references, by turning on the computer in an evening ritual, and by

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typing many sections of the original book, which made the changes and additions much easier. Without her understanding and encouragement, the volume probably would never have been completed.

Kalamazoo, Michigan May 1990 PETER G. M. WUTS

## PREFACE TO THE FIRST EDITION

The selection of a protective group is an important step in synthetic methodology, and reports of new protective groups appear regularly. This book presents information on the synthetically useful protective groups (~500) for five major functional groups: –OH, –NH,–SH,–COOH, and >C=O. References through 1979, the best method(s) of formation and cleavage, and some information on the scope and limitations of each protective group are given. The protective groups that are used most frequently and that should be considered first are listed in Reactivity Charts, which give an indication of the reactivity of a protected functionality to 108 prototype reagents.

The first chapter discusses some aspects of protective group chemistry: the properties of a protective group, the development of new protective groups, how to select a protective group from those described in this book, and an illustrative example of the use of protective groups in a synthesis of brefeldin. The book is organized by functional group to be protected. At the beginning of each chapter are listed the possible protective groups. Within each chapter protective groups are arranged in order of increasing complexity of structure (e.g., methyl, ethyl, t-butyl, ..., benzyl). The most efficient methods of formation or cleavage are described first. Emphasis has been placed on providing recent references, since the original method may have been improved. Consequently, the original reference may not be cited; my apologies to those whose contributions are not acknowledged. Chapter 8 explains the relationship between reactivities, reagents, and the Reactivity Charts that have been prepared for each class of protective groups.

This work has been carried out in association with Professor Elias J. Corey, who suggested the study of protective groups for use in computer-assisted synthetic analysis. I appreciate his continued help and encouragement. I am grateful to Dr. J. F. W. McOmie (Ed., *Protective Groups in Organic Chemistry*, Plenum Press, New York and London, 1973) for his interest in the project and for several exchanges of correspondence, and to Mrs. Mary Fieser, Professor Frederick D. Greene, and

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Professor James A. Moore for reading the manuscript. Special thanks are also due to Halina and Piotr Starewicz for drawing the structures, and to Kim Chen, Ruth Emery, Janice Smith, and Ann Wicker for typing the manuscript.

Harvard University September 1980 THEODORA W. GREENE

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### **ABBREVIATIONS**

### PROTECTIVE GROUPS

In some cases, several abbreviations are used for the same protective group. We have listed the abbreviations as used by an author in his or her original paper, including capital and lowercase letters. Occasionally, the same abbreviation has been used for two different protective groups. This information is also included.

ABO 2,7,8-trioxabicyclo[3.2.1]octyl

Ac acetyl

ACBZ 4-azidobenzyloxycarbonyl AcHmb 2-acetoxy-4-methoxybenzyl

Acm acetamidomethyl Ad 1-adamantyl

Adoc 1-adamantyloxycarbonyl

Adpoc 1-(1-adamantyl)-1-methylethoxycarbonyl

Alloc or AOC allyloxycarbonyl allylsulfonyl

AMB 2-(acetoxymethyl)benzoyl
AN 4-methoxyphenyl or anisyl
Anpe 2-(4-acetyl-2-nitrophenyl)ethyl

AOC or Alloc allyloxycarbonyl

*p*-AOM *p*-anisyloxymethyl or (4-methoxyphenoxy)methyl

Azb p-azidobenzyl
Bam benzamidomethyl
BBA butane-2,3-bisacetal
BDMS biphenyldimethylsilyl
Bdt 1,3-benzodithiolan-2-yl
Betsyl or Bts benzothiazole-2-sulfonyl

Bic 5-benzisoxazolylmethoxycarbonyl

Bim 5-benzisoazolylmethylene

Bimoc benz[f]inden-3-ylmethoxycarbonyl BIPSOP N-2,5-bis(triisopropylsiloxy)pyrrolyl

#### xiv **ABBREVIATIONS**

o-(benzoyloxymethyl)benzoyl **BMB** 2,4-dimethylthiophenoxycarbonyl Bmpc

bis(4-methoxyphenyl)-1'-pyrenylmethyl Bmpm

benzyl Bn

2,2-bis(4'-nitrophenyl)ethoxycarbonyl Bnpeoc

t-butoxycarbonyl BOC benzyloxymethyl **BOM** 

1-methyl-1-(4-biphenyl)ethoxycarbonyl **Bpoc** 

**BSB** benzoSTABASE

1,1-dioxobenzo[b]thiophene-2-ylmethoxycarbonyl Bsmoc

benzothiazole-2-sulfonyl Bts or Betsyl B<sup>t</sup>SE 2-t-butylsulfonylethyl

t-butoxymethyl Bum

1-(3,5-di-t-butylphenyl)-1-methylethoxycarbonyl t-Bumeoc

t-butylsulfonyl Bus Bzbenzoyl

2-[(2-chloroacetoxy)ethyl]benzoyl **CAEB** 

carboxamidomethyl Cam

2-(chloroacetoxymethyl)benzoyl **CAMB** 

benzyloxycarbonyl Cbz or Z cyclohexane-1,2-diacetal CDA 2-cyano-1,1-dimethylethyl **CDM** 

2-cyanoethyl CE or Cne

Cee 1-(2-chloroethoxy)ethyl

cyclohexyl cHex

2-chloro-3-indenylmethoxycarbonyl Climoc

carboxymethylsulfenyl Cms

2-cyanoethyl Cne or CE

cinnamyloxycarbonyl Coc

2-(cyano-1-phenyl)ethoxycarbonyl Cpeoc

4,4',4"-tris(4,5-dichlorophthalimido)triphenylmethyl **CPTr** 1-[(2-chloro-4-methyl)phenyl]-4-methoxypiperidin-4-yl **CTMP** 

Cys cysteine

**DAM** di-p-anisylmethyl or bis(4-methoxyphenyl)methyl

1,1-di-p-anisyl-2,2,2-trichloroethyl DATE 1,1-dimethyl-2,2-dibromoethoxycarbonyl DB-t-BOC

2,7-di-*t*-butyl[9-(10,10-dioxo-10,10,10,10-tetra= DBD-Tmoc

hydrothioxanthyl)]methoxycarbonyl

**DBS** dibenzosuberyl

2-(4,4-dimethyl-2,6-dioxocyclohexylidene)ethyl Dde 1-methyl-1-(3,5-dimethoxyphenyl)ethoxycarbonyl Ddz

diethoxymethyl **DEM** diethylisopropylsilyl **DEIPS** 2-oxo-1,2-diphenylethyl Desyl 1,3-dithianyl-2-methyl Dim

Dmab 4-{*N*-[1-(4,4-dimethyl-2,6-dioxocyclohexylidene)-3-

methylbutyl]amino}benzyl

DMB "3',5'-dimethoxybenzoin"

Dmb 2,4-dimethoxybenzyl

DMIPS dimethylisopropylsilyl

Dmoc dithianylmethoxycarbonyl

Dmp 2,4-dimethyl-3-pentyl

Dmp dimethylphosphinyl

DMPM 3,4-dimethoxybenzyl

DMT or DMTr di(*p*-methoxyphenyl)phenylmethyl or dimethoxytrityl di(*p*-methoxyphenyl)phenylmethyl or dimethoxytrityl

DNB p,p'-dinitrobenzhydryl

DNMBS 4-(4',8'-dimethoxynaphthylmethyl)benzenesulfonyl

DNP 2,4-dinitrophenyl

Dnpe 2-(2,4-dinitrophenyl)ethyl

Dnpeoc 2-(2,4-dinitrophenyl)ethoxycarbonyl

DNs 2,4-dinitrobenzenesulfonyl Dnseoc 2-dansylethoxycarbonyl

Dobz p-(dihydroxyboryl)benzyloxycarbonyl
Doc 2,4-dimethylpent-3-yloxycarbonyl
DOPS dimethyl[1,1-dimethyl-3-(tetrahydro-2*H*-

pyran-2-yloxy)propyl]silyl

DPA diphenylacetyl

DPIPS diphenylisopropylsilyl
DPM or Dpm diphenylmethyl
DPMS diphenylmethylsilyl
Dpp diphenylphosphinyl

Dppe 2-(diphenylphosphino)ethyl
Dppm (diphenyl-4-pyridyl)methyl
DPSE 2-(methyldiphenylsilyl)ethyl
Dpt diphenylphosphinothioyl
DPTBS diphenyl-t-butoxysilyl or

diphenyl-t-butylsilyl

DTBMS di-t-butylmethylsilyl DTBS di-t-butylsilylene

DTE 2-(hydroxyethyl)dithioethyl or "dithiodiethanol"

Dts dithiasuccinimidyl
EE 1-ethoxyethyl
EOM ethoxymethyl
Fcm ferrocenylmethyl
Fm 9-fluorenylmethyl

Fmoc 9-fluorenylmethoxycarbonyl

GUM guaiacolmethyl HBn 2-hydroxybenzyl

HIP 1,1,1,3,3,3-hexafluoro-2-phenylisopropyl

### **XVI** ABBREVIATIONS

Hoc cyclohexyloxycarbonyl

HSDIS (hydroxystyryl)diisopropylsilyl HSDMS (hydroxystyryl)dimethylsilyl hZ or homo Z homobenzyloxycarbonyl

IDTr 3-(imidazol-1-ylmethyl)-4',4"-

dimethoxytriphenylmethyl

IETr 4,4'-dimethoxy-3"-[N-(imidazolylethyl)carbamoyl]trityl

iMds 2,6-dimethoxy-4-methylbenzenesulfonyl

Ipaoc 1-isopropylallyloxycarbonyl

Ipc isopinocamphenyl IPDMS isopropyldimethylsilyl

Lev levulinoyl

LevS 4,4-(ethylenedithio)pentanoyl LevS levulinoyldithioacetal ester

MAQ 2-(9,10-anthraquinonyl)methyl or 2-methylene-

anthraquinone

MBE 1-methyl-1-benzyloxyethyl

MBF 2,3,3a,4,5,6,7,7a-octahydro-7,8,8-trimethyl-4,7-

methanobenzofuran-2-yl

MBS or Mbs *p*-methoxybenzenesulfonyl

Mds 2,6-dimethyl-4-methoxybenzenesulfonyl

MEC α-methylcinnamyl
MEM 2-methoxyethoxymethyl

Menpoc $\alpha$ -methylnitropiperonyloxycarbonylMeOZ or Mozp-methoxybenzyloxycarbonylMesmesityl or 2,4,6-trimethylphenyl

MIP methoxyisopropyl or 1-methyl-1-methoxyethyl

MM menthoxymethyl

MMT or MMT p-methoxyphenyldiphenylmethyl MMTr or MMT p-methoxyphenyldiphenylmethyl

MOM methoxymethyl moMO methoxymethoxy

Moz or MeOZ p-methoxybenzyloxycarbonyl

MP *p*-methoxyphenyl

MPM or PMB *p*-methoxyphenylmethyl or *p*-methoxybenzyl

Mpsp-methoxyphenylsulfonylMptdimethylphosphinothioylMsmethanesulfonyl or mesylMsib4-(methylsulfinyl)benzyl

Msz 4-methylsulfinylbenzyloxycarbonyl Mtb 2,4,6-trimethoxybenzenesulfonyl

Mte 2,3,5,6-tetramethyl-4-methoxybenzenesulfonyl

MTHP 4-methoxytetrahydropyranyl

MTM methylthiomethyl

MTMB 4-(methylthiomethoxy)butyryl

**MTMECO** 2-(methylthiomethoxy)ethoxycarbonyl **MTMT** 2-(methylthiomethoxymethyl)benzoyl Mtpc 4-(methylthio)phenoxycarbonyl

2,3,6-trimethyl-4-methoxybenzenesulfonyl Mtr

2,4,6-trimethylbenzenesulfonyl or mesitylenesulfonyl Mts

nitrobenzyloxymethyl **NBOM** 

2-nitroethyl Ne

4-nitrocinnamyloxycarbonyl Noc 2- or 4-nitrobenzenesulfonyl Nosyl or Ns

2-(nitrophenyl)ethyl Npe or npe

2-(4-nitrophenyl)ethoxycarbonyl Npeoc 2-(4-nitrophenyl)ethylsulfonyl **Npes** 

2-nitrophenylsulfenyl NPS or Nps

2-[(2-nitrophenyl)dithio]-1-phenylethoxycarbonyl **NpSSPeoc** 

3-nitro-2-pyridinesulfenyl **Npys** Ns or Nosyl 2- or 4-nitrobenzenesulfonyl

**NVOC** or Nvoc 3,4-dimethoxy-6-nitrobenzyloxycarbonyl or

6-nitroveratryloxycarbonyl

OBO 2,6,7-trioxabicyclo[2.2.2]octyl

**ONB** o-nitrobenzyl **PAB** p-acylaminobenzyl

2-[2-(benzyloxy)ethyl]benzoyl PAC<sub>u</sub>

2-[2-(4-methoxybenzyloxy)ethyl]benzoyl PAC<sub>M</sub>

3-(3-pyridyl)allyloxycarbonyl or Paloc

3-(3-pyridyl)prop-2-enyloxycarbonyl

Pbf 2,2,4,6,7-pentamethyldihydrobenzofuran-5-sulfonyl

Peoc 2-phosphonioethoxycarbonyl

Peoc 2-(triphenylphosphonio)ethoxycarbonyl

2-(2'-pyridyl)ethyl Pet 9-phenylfluorenyl Pf phenylacetamidomethyl Phamc

Phenoc

4-methoxyphenacyloxycarbonyl phthalimidomethyl Pim 9-(9-phenyl)xanthenyl Pixyl or Px

PMB or MPM p-methoxybenzyl or p-methoxyphenylmethyl

p-methoxybenzyloxymethyl **PMBM** 

Pmc 2,2,5,7,8-pentamethylchroman-6-sulfonyl

pentamethylbenzenesulfonyl Pme

p-methoxyphenyl **PMP PMS** p-methylbenzylsulfonyl

p-nitrobenzyl **PNB** p-nitrophenyl **PNP** 

2-(4-nitrophenyl)ethyl **PNPE** POM 4-pentenyloxymethyl pivaloyloxymethyl **POM** 

### xviii ABBREVIATIONS

Pp 2-phenyl-2-propyl

Ppoc 2-triphenylphosphonioisopropoxycarbonyl

Ppt diphenylthiophosphinyl PSE 2-(phenylsulfonyl)ethyl

Psec 2-(phenylsulfonyl)ethoxycarbonyl

PTE 2-(4-nitrophenyl)thioethyl

PTM phenylthiomethyl

Pv pivaloyl

Px or pixyl 9-(9-phenyl)xanthenyl Pyet  $1-(\alpha-pyridyl)$ ethyl

Pyoc 2-(2'- or 4'-pyridyl)ethoxycarbonyl

Qm 2-quinolinylmethyl SATE S-acetylthioethyl

Scm S-carboxymethylsulfenyl

SEE 1-[2-(trimethylsilyl)ethoxy]ethyl
SEM 2-(trimethylsilyl)ethoxymethyl
SES 2-(trimethylsilyl)ethanesulfonyl

Sisyl tris(trimethylsilyl)silyl

SMOM (phenyldimethylsilyl)methoxymethyl
Snm S-(N'-methyl-N'-phenylcarbamoyl)sulfenyl
STABASE 1,1,4,4-tetramethyldisilylazacyclopentane

Tacm trimethylacetamidomethyl

TBDMS or TBS t-butyldimethylsilyl TBDPS t-butyldiphenylsilyl

Tbf-DMTr 4-(17-tetrabenzo[a,c,g,i]fluorenylmethyl-4',4''-

dimethoxytrityl

Tbfmoc 17-tetrabenzo[a,c,g,i]fluorenylmethoxycarbonyl

TBDS tetra-t-butoxydisiloxane-1,3-diylidene

TBMPS *t*-butylmethoxyphenylsilyl

TBS or TBDMS *t*-butyldimethylsilyl

TBTr 4,4',4"-tris(benzyloxy)triphenylmethyl TCB 2,2,2-trichloro-1,1-dimethylethyl

TcBOC 1,1-dimethyl-2,2,2-trichloroethoxycarbonyl

TCP *N*-tetrachlorophthalimido

Tcroc 2-(trifluoromethyl)-6-chromonylmethyleneoxycarbonyl

Tcrom 2-(trifluoromethyl)-6-chromonylmethylene

TDE (2,2,2-trifluoro-1,1-diphenyl)ethyl

TDS thexyldimethylsilyl

Teoc 2-(trimethylsilyl)ethoxycarbonyl

TES triethylsilyl

Tf trifluoromethanesulfonyl

TFA trifluoroacetyl

Tfav 4,4,4-trifluoro-3-oxo-1-butenyl

Thexyl 2,3-dimethyl-2-butyl tetrahydrofuranyl

THP tetrahydropyranyl triisobutylsilyl

TIPDS 1,3-(1,1,3,3-tetraisopropyldisiloxanylidene)

TIPS triisopropylsilyl

TLTr 4,4',4"-tris(levulinoyloxy)triphenylmethyl

Tmb 2,4,6-trimethylbenzyl
Tmob trimethoxybenzyl
TMPM trimethoxyphenylmethyl

TMS trimethylsilyl

TMSE or TSE 2-(trimethylsilyl)ethyl

TMSEC 2-(trimethylsilyl)ethoxycarbonyl
TMSP 2-trimethylsilylprop-2-enyl
TMTr tris(p-methoxyphenyl)methyl

Tos or Ts p-toluenesulfonyl
TPS triphenylsilyl

TPTE 2-(4-triphenylmethylthio)ethyl
Tr triphenylmethyl or trityl
Tritylone 9-(9-phenyl-10-oxo)anthryl
Troc 2,2,2-trichloroethoxycarbonyl

Ts or Tosp-toluenesulfonylTSE or TMSE2-(trimethylsilyl)ethylTse2-(p-toluenesulfonyl)ethyl

Voc vinyloxycarbonyl Z or Cbz benzyloxycarbonyl

### **REAGENTS**

9-BBN 9-borabicyclo[3.3.1]nonane

bipy 2,2'-bipyridine

BOP Reagent benzotriazol-1-yloxytris(dimethylamino)phosphonium

hexafluorophosphate

BOP-Cl bis(2-oxo-3-oxazolidinyl)phosphinic chloride BroP bromotris(dimethylamino)phosphonium

hexafluorophosphate

Bt benzotriazol-1-yl or 1-benzotriazolyl BTEAC benzyltriethylammonium chloride

CAL Candida antarctica lipase
CAN ceric ammonium nitrate

CMPI 2-chloro-1-methylpyridinium iodide

cod cyclooctadiene cot cyclooctatetraene CSA camphorsulfonic acid

DABCO 1,4-diazabicyclo[2.2.2]octane
DBAD di-t-butyl azodicarboxylate
DBN 1,5-diazabicyclo[4.3.0]non-5-ene

#### **XX** ABBREVIATIONS

DBU 1,8-diazabicyclo[5.4.0]undec-7-ene

DCC dicyclohexylcarbodiimide

DDQ 2,3-dichloro-5,6-dicyano-1,4-benzoquinone

DEAD diethyl azodicarboxylate
DIAD diisopropyl azodicarboxylate
DIBAL-H diisobutylaluminum hydride
DIPEA diisopropylethylamine
DMAC N,N-dimethylacetamide
DMAP 4-N,N-dimethylaminopyridine

DMDO 2,2-dimethyldioxirane
DME 1,2-dimethoxyethane
DMF N,N-dimethylformamide

DMPU 1,3-dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidinone

DMS dimethyl sulfide DMSO dimethyl sulfoxide

dppb 1,4-bis(diphenylphosphino)butane dppe 1,2-bis(diphenylphosphino)ethane

DTE dithioerythritol DTT dithiothreitol

EDC or EDCI 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (or

1-[3-(dimethylamino)propyl]-3-ethylcarbodimide)

hydrochloride

EDCI or EDC 1-ethyl-3-(3-(dimethylaminopropyl)carbodiimide

EDTA ethylenediaminetetraacetic acid

HATU N-[(dimethylamino)(3H-1,2,3-triazolo(4,5-b)pyridin-3-

yloxy)methylene]-*N*-methylmethanaminium hexafluorophosphate, previously known as *O*-(7-azabenzotriazol-1-yl)-1,1,3,3-tetramethyluronium hexafluorophosphate

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

HMPA hexamethylphosphoramide HMPT hexamethylphosphorous triamide

HOAt 7-aza-1-hydroxybenzotriazole HOBT 1-hydroxybenzotriazole Im imidazol-1-yl or 1-imidazolyl

IPA isopropyl alcohol

**HMDS** 

IPCF (=IPCC) isopropenyl chloroformate (isopropenyl chlorocarbonate)

KHMDS potassium hexamethyldisilazide LAH lithium aluminum hydride LDBB lithium 4,4'-di-t-butylbiphenylide

MAD methylaluminumbis(2,6-di-*t*-butyl-4-methylphenoxide)

MCPBA *m*-chloroperoxybenzoic acid

MoOPH oxodiperoxymolybdenum(pyridine)hexamethylphosphor-

amide

ms molecular sieves
MSA methanesulfonic acid

MTB methylthiobenzene
MTBE t-butyl methyl ether
NBS N-bromosuccinimide
Ni(acac)<sub>2</sub> nickel acetylacetonate
NMM N-methylmorpholine

NMO *N*-methylmorpholine *N*-oxide

NMP N-methylpyrrolidinone
P polymer support
Pc phthalocyanine

PCC pyridinium chlorochromate

PdCl<sub>2</sub>(tpp)<sub>2</sub> dichlorobis[tris(2-methylphenyl)phosphine]palladium

Pd<sub>2</sub>(dba)<sub>3</sub> tris(dibenzylideneacetone)dipalladium

PG protective group

PhI(OH)OTs [hydroxy(tosyloxy)iodo]benzene

PPL porcine pancreatic lipase
PPTS pyridinium *p*-toluenesulfonate
proton sponge 1,8-bis(dimethylamino)naphthalene

Pyr pyridine

Rh<sub>2</sub>(pfb)<sub>4</sub> rhodium perfluorobutyrate

ScmCl methoxycarbonylsulfenyl chloride

SMEAH sodium bis(2-methoxyethoxy)aluminum hydride

Su succinimidyl

TAS-F tris(dimethylamino)sulfonium difluorotrimethylsilicate

TBAF tetrabutylammonium fluoride

TEA triethylamine

TEBA or TEBAC triethylbenzylammonium chloride triethylbenzylammonium chloride

TESH triethylsilane

Tf trifluoromethanesulfonyl
TFA trifluoroacetic acid
TFAA trifluoroacetic anhydride
TFMSA or TfOH trifluoromethanesulfonic acid
TfOH or TFMSA trifluoromethanesulfonic acid

THF tetrahydrofuran THP tetrahydropyran

TMEDA N, N, N', N'-tetramethylethylenediamine

TMOF trimethyl orthoformate

TPAP tetrapropylammonium perruthenate

TPP tetraphenylporphyrin

TPPTS sulfonated triphenylphosphine
TPS triisopropylbenzensulfonyl chloride
Tr<sup>+</sup>BF<sub>4</sub> or Ph<sub>3</sub>C<sup>+</sup>BF<sub>4</sub> triphenylcarbenium tetrafluoroborate

TrS<sup>-</sup>Bu<sub>4</sub>N<sup>+</sup> tetrabutylammonium triphenylmethanethiolate

Ts toluenesulfonyl

## PROTECTIVE GROUPS IN ORGANIC SYNTHESIS

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