



Science of
Synthesis

Knowledge Updates 2026/1

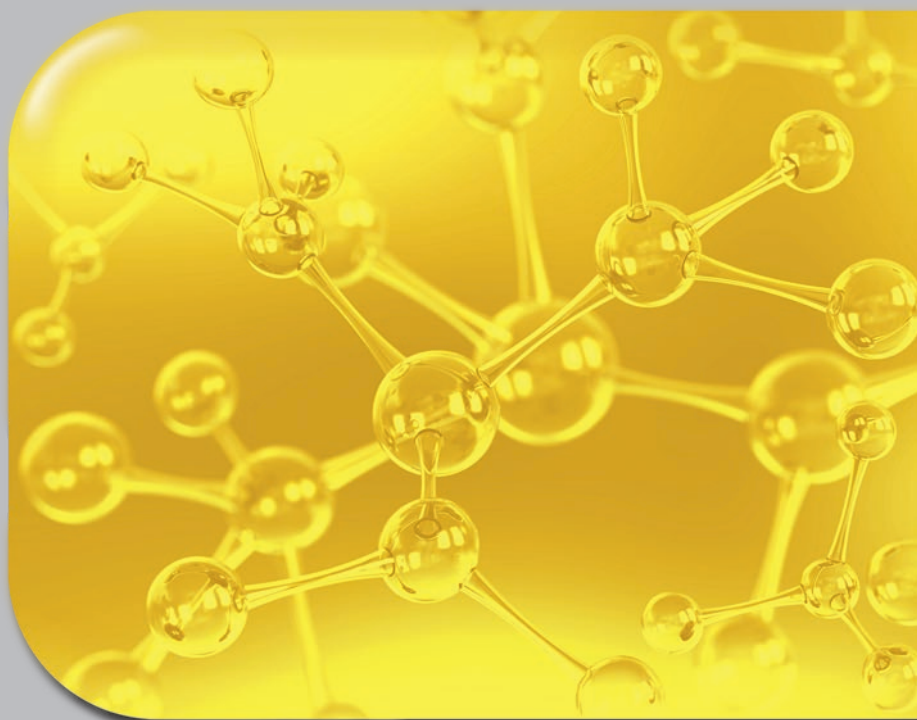
Volume Editors

J.-M. Campagne

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Science of Synthesis

Science of Synthesis is the authoritative and comprehensive reference work for the entire field of organic and organometallic synthesis.

Science of Synthesis presents the important synthetic methods for all classes of compounds and includes:

- Methods critically evaluated by leading scientists
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Preface

As the pace and breadth of research intensifies, organic synthesis is playing an increasingly central role in the discovery process within all imaginable areas of science: from pharmaceuticals, agrochemicals, and materials science to areas of biology and physics, the most impactful investigations are becoming more and more molecular. As an enabling science, synthetic organic chemistry is uniquely poised to provide access to compounds with exciting and valuable new properties. Organic molecules of extreme complexity can, given expert knowledge, be prepared with exquisite efficiency and selectivity, allowing virtually any phenomenon to be probed at levels never before imagined. With ready access to materials of remarkable structural diversity, critical studies can be conducted that reveal the intimate workings of chemical, biological, or physical processes with stunning detail.

The sheer variety of chemical structural space required for these investigations and the design elements necessary to assemble molecular targets of increasing intricacy place extraordinary demands on the individual synthetic methods used. They must be robust and provide reliably high yields on both small and large scales, have broad applicability, and exhibit high selectivity. Increasingly, synthetic approaches to organic molecules must take into account environmental sustainability. Thus, atom economy and the overall environmental impact of the transformations are taking on increased importance.

The need to provide a dependable source of information on evaluated synthetic methods in organic chemistry embracing these characteristics was first acknowledged over 100 years ago, when the highly regarded reference source **Houben–Weyl Methoden der Organischen Chemie** was first introduced. Recognizing the necessity to provide a modernized, comprehensive, and critical assessment of synthetic organic chemistry, in 2000 Thieme launched **Science of Synthesis, Houben–Weyl Methods of Molecular Transformations**. This effort, assembled by almost 1000 leading experts from both industry and academia, provides a balanced and critical analysis of the entire literature from the early 1800s until the year of publication. The accompanying online version of **Science of Synthesis** provides text, structure, substructure, and reaction searching capabilities by a powerful, yet easy-to-use, intuitive interface.

From 2010 onward, **Science of Synthesis** is being updated quarterly with high-quality content via **Science of Synthesis Knowledge Updates**. The goal of the **Science of Synthesis Knowledge Updates** is to provide a continuous review of the field of synthetic organic chemistry, with an eye toward evaluating and analyzing significant new developments in synthetic methods. A list of stringent criteria for inclusion of each synthetic transformation ensures that only the best and most reliable synthetic methods are incorporated. These efforts guarantee that **Science of Synthesis** will continue to be the most up-to-date electronic database available for the documentation of validated synthetic methods.

Also from 2010, **Science of Synthesis** includes the **Science of Synthesis Reference Library**, comprising volumes covering special topics of organic chemistry in a modular fashion, with six main classifications: (1) Classical, (2) Advances, (3) Transformations, (4) Applications, (5) Structures, and (6) Techniques. Titles will include *Stereoselective Synthesis*, *Water in Organic Synthesis*, and *Asymmetric Organocatalysis*, among others. With expert-evaluated content focusing on subjects of particular current interest, the **Science of Synthesis Reference Library** complements the **Science of Synthesis Knowledge Updates**, to make **Science of Synthesis** the complete information source for the modern synthetic chemist.

The overarching goal of the **Science of Synthesis** Editorial Board is to make the suite of **Science of Synthesis** resources the first and foremost focal point for critically evaluated information on chemical transformations for those individuals involved in the design and construction of organic molecules.

Throughout the years, the chemical community has benefited tremendously from the outstanding contribution of hundreds of highly dedicated expert authors who have devoted their energies and intellectual capital to these projects. We thank all of these individuals for the heroic efforts they have made throughout the entire publication process to make **Science of Synthesis** a reference work of the highest integrity and quality.

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Abstracts

2026

p 1

4.4.17.7 Catalytic Silylation of Alcohols toward Silyl Ethers

Yang Ding and Chuan He^{1b}

This is an update to the 2022 *Science of Synthesis* review on silyl ethers (Section 4.4.17). Unlike the original review, this update focuses primarily on catalytic methods for the synthesis of silyl ethers via the silylation of alcohols.



Keywords: silyl ethers · catalysis · hydrosilanes · alcohols · dehydrogenative coupling · silylation

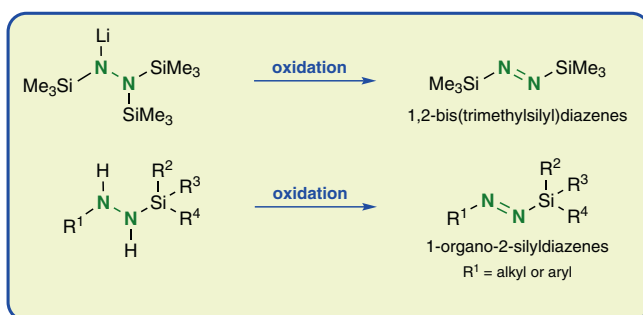
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p 45

4.4.48 Silyldiazenes

Baptiste Neil and Clément Chauvier^{1b}

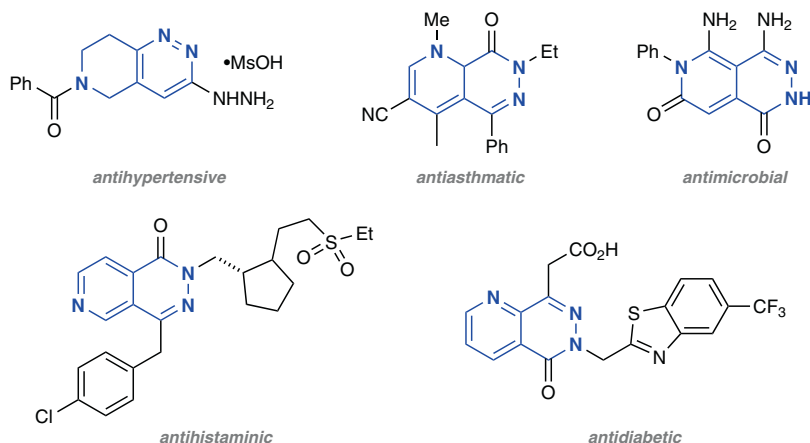
This review describes the synthesis of silyldiazenes, a class of azo compounds derived from diazene (diimide, H–N=N–H), wherein at least one of the two hydrogen atoms is substituted by a silyl group. The discussion covers the two primary subclasses of isolable silyldiazenes, 1,2-bis(silyl)diazenes and 1-organo-2-silyldiazenes, which are both invariably prepared by oxidation of silylated hydrazine or hydrazide precursors. The discussion also details the main synthetic applications of 1-organyl-2-silyldiazenes in organic synthesis. These include their use as precursors for the generation of carbanions in nucleophilic arylation and deprotonative silylation reactions, as well as their application in palladium-catalyzed C(sp²)–N(sp²) cross-couplings for the synthesis of azobenzenes.



Keywords: silyldiazenes · azo compounds · hydrazines · silylhydrazines · oxidation · nucleophilic arylation · C–H silylation · carbanions · cross coupling · palladium catalysis · azobenzenes

16.18.8 **Pyridopyridazines**Manjeet Kumar and Narendra B. Ambhakar 

Pyridopyridazines are bicyclic heterocycles composed of a pyridine ring fused to a pyridazine core and exist as six distinct regioisomeric frameworks with multiple functionalization sites. Despite this structural diversity, pyridopyridazine scaffolds remain underexplored, with limited synthetic methodologies often derived from phthalazine chemistry. Most approaches rely on preassembled heteroaromatic units followed by construction of the second ring. Notably, recent years have introduced milder and more efficient strategies, including photocatalytic and metal-catalyzed C–N bond-forming reactions. These advances have improved access to diverse pyridopyridazine frameworks. Recent biological studies are also summarized in this review, highlighting their emerging potential in drug discovery.



Keywords: pyridopyridazines · fused heterocycles · N-heterocycle synthesis · C–N bond formation · bicyclic compounds · medicinal chemistry

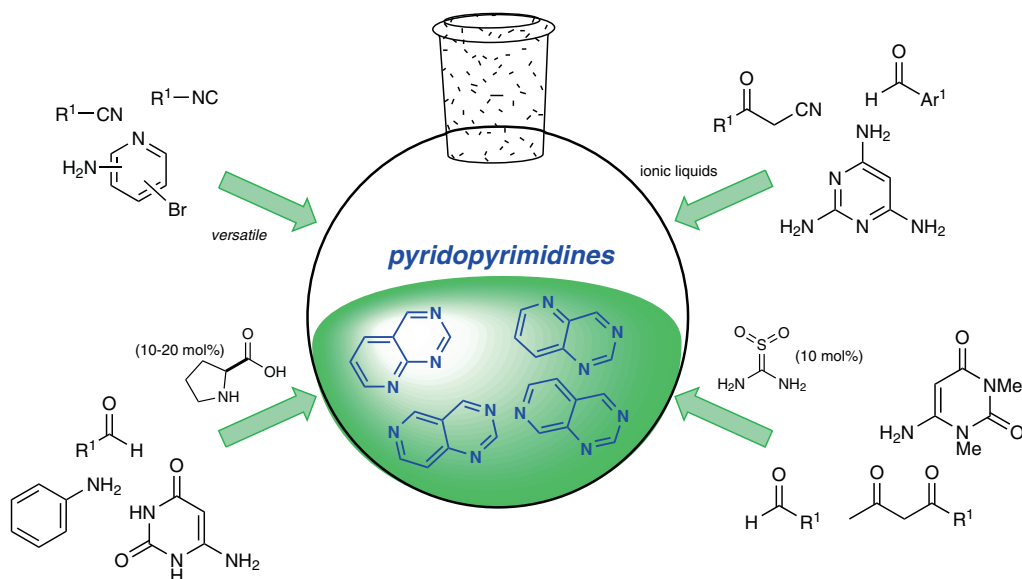
2026

p 95

16.19.6 **Pyridopyrimidines**

Charles L. Lail, III and Timothy J. Hagen

Pyridopyrimidines are a class of fused biaryl heterocycles where one ring is a pyridine ring, and the other is a pyrimidine ring. Pyridopyrimidines have found use extensively in medicinal chemistry, specifically in the antibacterial and anticancer spaces. The synthesis of pyridopyrimidines has greatly advanced in the last few years. Multicomponent reactions have allowed for increased control over substitution patterns. New catalysts have been developed. The use of ionic liquids and microwave reactors has facilitated sub-one-hour reaction times. This review covers the key advances in methods for the synthesis of pyridopyrimidines reported between 2012 and 2024.



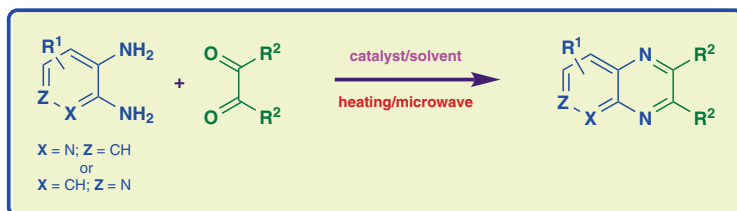
Keywords: pyridopyrimidines · pyrido[2,3-*d*]pyrimidines · pyrido[3,2-*d*]pyrimidines · pyrido[3,4-*d*]pyrimidines · pyrido[4,3-*d*]pyrimidines · heterocycles · heterocyclic chemistry · multicomponent reactions · organic synthesis · pyridines · pyrimidines · ionic liquids

2026

p 135

16.20.4 **Pyridopyrazines**Faridoon^{ORCID} and Guiping Zhang^{ORCID}

This review reports synthetic methods for the preparation of pyridopyrazines published between 2010 and 2024, providing an updated account of the earlier *Science of Synthesis* contributions on this ring system (Sections 16.20 and 16.20.3). Pyridopyrazines are an important class of heterocyclic compounds with diverse applications in medicinal chemistry, including as antidiabetic, anticancer, antifungal, and anti-inflammatory agents. The most common approach to synthesizing pyrido[2,3-*b*]pyrazines and pyrido[3,4-*b*]pyrazines remains the reactions of pyridinediamines with carbonyl compounds. Herein, we describe recent advancements in reported reaction conditions, with a focus on greener catalysts and solvent systems.



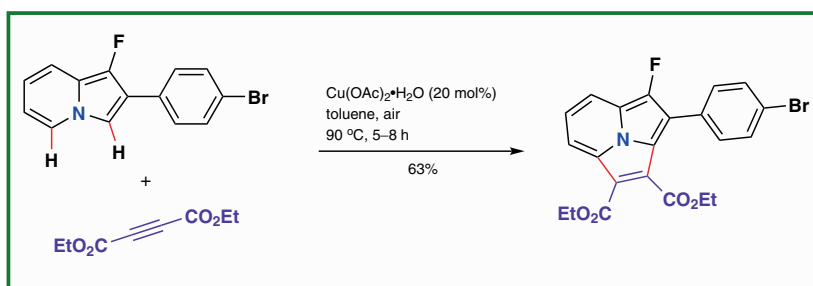
Keywords: pyridopyrazines · pyridinediamines · 1,2-diketones · condensations · metal catalysts · boron compounds · cyclizations · heterocycles

2026

p 165

17.7.8 **Cyclazines**Jie Jack Li^{ORCID}

This review is an update to Section 17.7 and covers synthetic methods for the preparation of cyclazines published since 2004. Cyclazines are frequently prepared by cycloadditions. For instance, [2.2.3]cyclazines can be assembled via the [8 + 2]-cycloaddition reaction of indolizines with alkyne derivatives. In the same vein, cyclazines can be also prepared by cycloaddition of indolizines with alkene derivatives followed by aromatization via oxidation. Similarly, azacyclazines have been produced by the cycloaddition of imidazo[1,2-*a*]pyridines with alkyne derivatives. Ullazines are often synthesized by annulation of *N*-arylpyrroles with alkynes. Finally, azaullazines may be assembled by annulation of *N*-arylimidazoles with alkynes.



Keywords: annulenes · acetylenedicarboxylate · azacyclazines · azatriquinacenes · azaullazines · cyclazines · cyclazinones · cycloaddition · diazacyclazines · diazaullazines · Groebke–Blackburn–Bienaymé (GBB) reaction · indolizines · triazaullazines · ullazines

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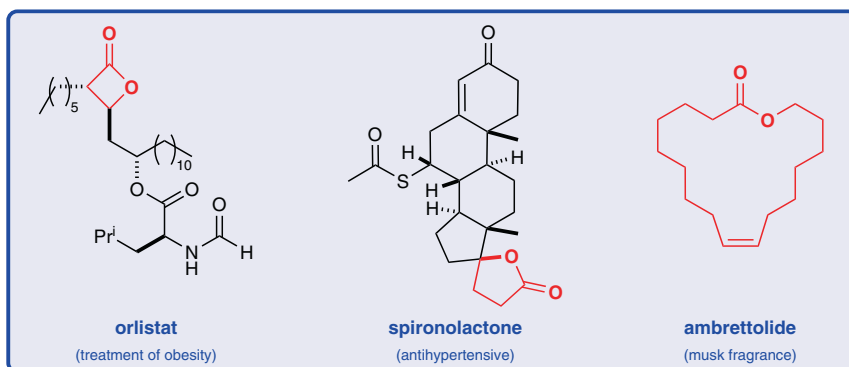
p 233

20.6.2

Lactones

Vincent Coeffard and Xavier Moreau

Lactones are an important class of oxygen-containing heterocycles found in a myriad of natural products and synthetic compounds with diverse biological activities. Owing to their great structural diversity and complexity, the development of selective strategies for the preparation of lactones of all ring sizes, from small ring lactones to macrolactones, has become a popular topic in organic chemistry. This update to the original 2007 *Science of Synthesis* contribution highlights major developments in lactone synthesis that have emerged in recent years.



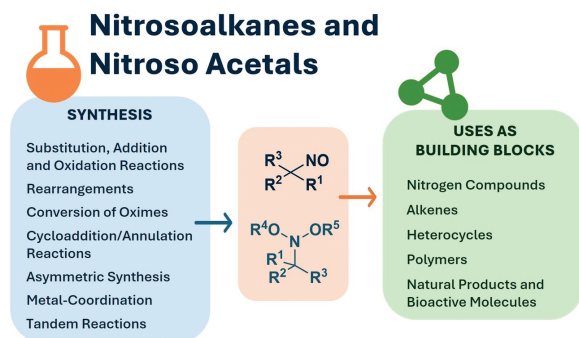
Keywords: lactones · lactonization · macrolactones · esters · carboxylic acids · spirolactones · transition-metal catalysis · C–H functionalization · asymmetric synthesis ·

41.2.3

Nitrosoalkanes and Nitroso Acetals (*N,N*-Dialkoxyamines)

Maria I. L. Soares,¹⁵ Susana M. M. Lopes,¹⁵ Ana Lúcia Cardoso,¹⁵ Marta Pineiro,¹⁵ and Teresa M. V. D. Pinho e Melo¹⁵

Nitrosoalkanes and nitroso acetals (*N,N*-dialkoxyamines) have emerged as highly versatile intermediates in modern organic synthesis, despite their intrinsic instability and tendency toward tautomerization and dimerization. This review provides an updated and comprehensive overview of their synthesis, reactivity, and applications. Recent advances include continuous-flow methodologies that enhance safety and efficiency, as well as innovative strategies for in situ generation to overcome instability issues. Synthetic approaches encompass substitution, addition, oxidation, and rearrangement reactions, enabling access to geminal chloronitroso compounds, metal-coordinated nitrosoalkanes, and structurally diverse nitroso acetals. Tandem and cascade processes have gained prominence for rapidly increasing molecular complexity with excellent regio- and stereocontrol, including catalytic asymmetric variants. Applications extend beyond classical transformations, such as oxidation to nitroalkanes, reduction to amines, and heterocycle formation via cycloaddition reactions, to cutting-edge uses in polymer synthesis, radical-mediated processes, and the functionalization of nitrosoalkane-metal complexes for C–H activation and alkene exchange. These developments underscore the growing role of nitroso compounds as strategic building blocks for complex architectures, biologically active molecules, and advanced materials, reinforcing their importance in contemporary synthetic chemistry.



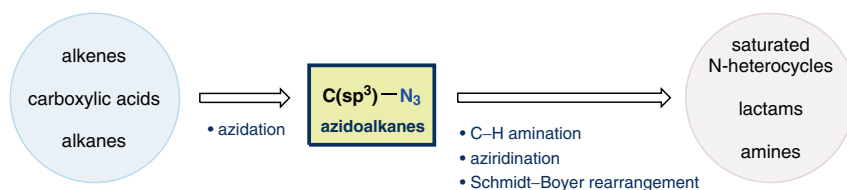
Keywords: nitrosoalkanes · nitroso acetals · cycloaddition reactions · annulation reactions · tandem reactions · rearrangements · C–H activation · radical processes · continuous-flow synthesis · geminal chloronitroso compounds · alkenes · nitrogen compounds · heterocycles · polymer synthesis · metal complexes

2026

p 413

41.8.3 **Azidoalkanes***Minh Hai Hoang, Bendik Grømer, and Shunsuke Chiba*

This review highlights the recent developments in the synthesis of azidoalkanes and their synthetic applications. The new synthetic methodologies through azidation of readily available feedstocks such as alkenes, carboxylic acids, and alkanes have led to significant diversification in the accessibility and structural complexity of azidoalkanes. Various approaches for the efficient conversion of azidoalkanes into diverse nitrogen-containing compounds, such as saturated N-heterocycles, lactams, and amines, have also been developed, enabling the expansion of chemical spaces, especially valuable in drug discovery programs.



Keywords: azides · azidation · alkenes · alkanes · carboxylic acids · amination · saturated N-heterocycles · lactams · amines

Science of Synthesis Knowledge Updates 2026/1

	Preface	V
	Abstracts	VII
	Table of Contents	XV
4.4.17.7	Catalytic Silylation of Alcohols toward Silyl Ethers (Update 2026) Yang Ding and Chuan He ^{id}	1
4.4.48	Silyldiazenes Baptiste Neil and Clément Chauvier ^{id}	45
16.18.8	Pyridopyridazines (Update 2026) Manjeet Kumar and Narendra B. Ambhaikar ^{id}	59
16.19.6	Pyridopyrimidines (Update 2026) Charles L. Lail, III and Timothy J. Hagen ^{id}	95
16.20.4	Pyridopyrazines (Update 2026) Faridoon and Guiping Zhang ^{id}	135
17.7.8	Cyclazines (Update 2026) Jie Jack Li ^{id}	165
20.6.2	Lactones (Update 2026) Vincent Coeffard ^{id} and Xavier Moreau ^{id}	233
41.2.3	Nitrosoalkanes and Nitroso Acetals (N,N-Dialkoxyamines) (Update 2026) Maria I. L. Soares ^{id} , Susana M. M. Lopes ^{id} , Ana Lúcia Cardoso ^{id} , Marta Pineiro ^{id} , and Teresa M. V. D. Pinho e Melo ^{id}	295
41.8.3	Azidoalkanes (Update 2026) Minh Hai Hoang, Bendik Grømer, and Shunsuke Chiba ^{id}	413
	Author Index	467
	Abbreviations	485

Table of Contents

Volume 4: Compounds of Group 15 (As, Sb, Bi) and Silicon Compounds

4.4	Product Class 4: Silicon Compounds	
4.4.17.7	Catalytic Silylation of Alcohols toward Silyl Ethers	2026
	Yang Ding and Chuan He ¹⁰	
4.4.17.7	Catalytic Silylation of Alcohols toward Silyl Ethers	1
4.4.17.7.1	Metal Catalysis toward Silyl Ethers	1
4.4.17.7.1.1	Rhodium Catalysis	1
4.4.17.7.1.1.1	Dirhodium(II) Tetrakis(perfluorobutanoate) Catalyzed Alcoholysis of Triethylsilane	1
4.4.17.7.1.1.2	[Au]-SMAP-Rhodium-Catalyzed Alcoholysis of Dimethyl(phenyl)silane	3
4.4.17.7.1.1.3	Hydroxy(cyclooctene)rhodium(I) Dimer Catalyzed Asymmetric Synthesis of Dibenzooxasilines	3
4.4.17.7.1.1.4	Chloro(cycloocta-1,5-diene)rhodium(I) Dimer Catalyzed Enantioselective Dehydrogenative Si—O Coupling	5
4.4.17.7.1.2	Copper Catalysis	7
4.4.17.7.1.2.1	Copper(I) Chloride Catalyzed Asymmetric Silane Alcoholysis	7
4.4.17.7.1.2.2	Copper(I) Chloride Catalyzed Kinetic Resolution of Chiral Secondary Alcohols ·	7
4.4.17.7.1.2.3	Mesitylcopper(I)-Catalyzed Kinetic Resolution of Tertiary Propargylic Alcohols	13
4.4.17.7.1.2.4	Tetrakis(acetonitrile)copper(I) Hexafluorophosphate Catalyzed Desymmetrization of Prochiral Silanediols	14
4.4.17.7.1.3	Platinum Catalysis	15
4.4.17.7.1.3.1	Cationic Platinum(II)-Catalyzed Silylation of Alcohols Using Allyl(<i>tert</i> -butyl)dimethylsilane	15
4.4.17.7.1.3.2	Tris(dibenzylideneacetone)diplatinum(0)-Catalyzed One-Pot Multicomponent Alcoholysis/Silylation	15
4.4.17.7.1.3.3	Tris(dibenzylideneacetone)diplatinum(0)-Catalyzed Tandem Hydrosilylation and Cyclization with Dihydrosilanes Using the RuPhos Ligand	16
4.4.17.7.1.3.4	Chloroplatinic Acid Hexahydrate Catalyzed O-Silylation of Oximes by Trisubstituted Organosilanes	17
4.4.17.7.1.4	Gold Catalysis	18
4.4.17.7.1.4.1	Chloro(triphenylphosphine)gold(I)-Catalyzed Intramolecular Allylation of Silylalkynes Induced by Silane Alcoholysis	18
4.4.17.7.1.4.2	Etherification of Silanes Catalyzed by Nanohydroxyapatite-Supported Gold Nanoparticles	20
4.4.17.7.1.4.3	Dehydrogenative Coupling of Organosilanes with Alcohols Catalyzed by a Cyanographene-Supported Gold Catalyst	20

4.4.17.7.1.5	Cobalt Catalysis	21
4.4.17.7.1.5.1	Cobalt(II)–N,N,N-Pincer Complex-Catalyzed Synthesis of Disiloxanes, Hydrodisiloxanes, and Hydrotrisiloxanes	21
4.4.17.7.1.5.2	Dehydrogenative Cross-Coupling Reaction Catalyzed by a Cobalt(II)–P,N,P-Pincer Complex	23
4.4.17.7.1.6	Ruthenium Catalysis	25
4.4.17.7.1.6.1	Dichloro(<i>p</i> -cymene)ruthenium(II) Dimer Catalyzed Dehydrosilylation of Various Alcohols with Silanes	25
4.4.17.7.1.6.2	Ru/Al(O)(OH)-Catalyzed Dehydrosilylation of Primary Alcohols	25
4.4.17.7.1.6.3	Ruthenium–Triphos Acetate Complex Catalyzed Silylation of Alcohols	26
4.4.17.7.1.7	Nickel Catalysis	27
4.4.17.7.1.7.1	Nickel(II) Complex Catalyzed Dehydrosilylation of Various Alcohols with Hydrosilanes	27
4.4.17.7.2	Organocatalysis toward Silyl Ethers	28
4.4.17.7.2.1	Lewis and Brønsted Base Organocatalysis	28
4.4.17.7.2.1.1	Organocatalytic Enantioselective Silyl Protection of Alcohols	28
4.4.17.7.2.1.2	Kinetic Resolution of 1,2-Diols	30
4.4.17.7.2.1.3	Enantioselective Silylation of Acyclic and Cyclic Triols	31
4.4.17.7.2.1.4	Scaffolding-Catalyst-Enabled Silylation of Alcohols	36
4.4.17.7.2.2	Lewis and Brønsted Acid Organocatalysis	38
4.4.17.7.2.2.1	Asymmetric Silylation of Alcohols Catalyzed by a Spirocyclic Phosphoric Acid	38
4.4.17.7.2.2.2	One-Pot Desymmetrization/Peterson Alkenation of Silacyclopentene Oxides	39
4.4.17.7.2.2.3	Imidodiphosphorimidate-Catalyzed Enantioselective Desymmetrizing Aryloxylation of Bis(methallyl)silanes	40
4.4.17.7.2.2.4	Imidodiphosphorimidate-Catalyzed Desymmetrization of Silanediols	41
4.4.17.7.2.2.5	Tris(pentafluorophenyl)borane-Catalyzed Silylation of Alcohols	42
4.4.48	Silyldiazenes New	
	Baptiste Neil and Clément Chauvier ^{1b}	
4.4.48	Silyldiazenes	45
4.4.48.1	Synthesis of 1,2-Bis(silyl)diazenes	47
4.4.48.1.1	Oxidation of Lithium Silylhydrazides	47
4.4.48.1.1.1	From Monolithiated Tris(silyl)hydrazines	47
4.4.48.1.1.2	From Dilithiated Bis(silyl)hydrazines	47
4.4.48.1.2	Thermolysis of Lithium 1-Tosyl-2,2-bis(silyl)hydrazides	48
4.4.48.2	Synthesis of 1-Organo-2-silyldiazenes	48
4.4.48.2.1	Oxidative Dehydrogenation of 1-Organo-2-silylhydrazines	49
4.4.48.2.2	Oxidation of Lithium 1-Organo-2-silylhydrazides	51
4.4.48.2.3	Oxidation of 1-Organo-2-silyl-1,2-bis(stannyll)hydrazines	51

4.4.48.3	Applications of Silyldiazenes in Organic Synthesis	52
4.4.48.3.1	Generation of Carbanions from 1-Organo-2-silyldiazenes	52
4.4.48.3.1.1	Nucleophilic Arylation Reactions Using 1-Aryl-2-silyldiazenes	53
4.4.48.3.1.2	Catalytic Synthesis of Organosilicon Compounds Using 1- <i>tert</i> -Butyl-2-silyldiazenes	54
4.4.48.3.2	Synthesis of Azobenzenes	55

Volume 16: Six-Membered Heteroarenes with Two Identical Heteroatoms

16.18 Product Class 18: Pyridopyridazines

16.18.8	Pyridopyridazines	2026
	Manjeet Kumar and Narendra B. Ambhaikar	
16.18.8	Pyridopyridazines	59
16.18.8.1	Pyrido[2,3- <i>c</i>]pyridazines	62
16.18.8.1.1	Synthesis by Ring-Closure Reactions	62
16.18.8.1.1.1	By Formation of One N—C and One C—C Bond	62
16.18.8.1.1.1.1	Method 1: Cyclization of a Pyridazinone with Malononitrile	62
16.18.8.1.1.1.2	Method 2: Stille Coupling Followed by Ring Cyclization	63
16.18.8.1.1.1.3	Method 3: Palladium-Mediated Cross Coupling for the Synthesis of a Pyridopyridazine Scaffold	64
16.18.8.1.1.2	By Formation of Two N—C Bonds	66
16.18.8.1.1.2.1	Method 1: Copper-Catalyzed Tandem C—N Bond Formation	66
16.18.8.2	Pyrido[2,3- <i>d</i>]pyridazines	68
16.18.8.2.1	Synthesis by Ring-Closure Reactions	68
16.18.8.2.1.1	By Formation of Two N—C Bonds	68
16.18.8.2.1.1.1	Method 1: Directed <i>ortho</i> -Lithiation of Aromatic Aldehydes	68
16.18.8.2.1.1.2	Method 2: Visible-Light-Mediated Intramolecular Cyclization of Alkynyl-Substituted Phosphonohydrazone	69
16.18.8.2.1.1.3	Method 3: Visible-Light-Mediated Photoredox Cascade Hydroamination Reaction Followed by Smiles Rearrangement	70
16.18.8.2.1.1.4	Method 4: Reaction of 5,7-Dinitroquinolin-8-ol with Hydrazine Hydrate	71
16.18.8.2.1.1.5	Method 5: Cyclization of a Geminal Dihalo Ester Derivative with Hydrazine	71
16.18.8.2.1.1.6	Method 6: Iodine-Promoted One-Pot Multicomponent Reaction to 2,3-Diaroylquinolines and Pyridazino[4,5- <i>b</i>]quinolines	73
16.18.8.2.1.1.7	Method 7: Regioselective Intramolecular Annulations of Ambident β -Enamino Esters	75

16.18.8.2.1.1.8	Method 8: Pyridopyridazinone Analogues as Toll-like Receptor 8 Specific Antagonists	76
16.18.8.2.1.2	By Formation of One N—C Bond	77
16.18.8.2.1.2.1	Method 1: 5-Oxopyrido[2,3- <i>d</i>]pyridazin-6(5 <i>H</i>)-yl Acetamides as Inhibitors of NLRP3 Inflammasome Production	77
16.18.8.3	Pyrido[3,2- <i>c</i>]pyridazines	80
16.18.8.3.1	Synthesis by Ring-Closure Reactions	80
16.18.8.3.1.1	By Formation of One N—N and One N—C Bond	80
16.18.8.3.1.1.1	Method 1: Oxidative Cyclization of Diamine	80
16.18.8.4	Pyrido[3,4- <i>c</i>]pyridazines	83
16.18.8.4.1	Synthesis by Ring-Closure Reactions	83
16.18.8.4.1.1	By Formation of One N—C and One C—C Bond	83
16.18.8.4.1.1.1	Method 1: Diazotization Followed by Aromatic Cyclization	83
16.18.8.4.1.1.2	Method 2: Diazotization Followed by Acetyl Cyclization	84
16.18.8.4.1.2	By Formation of One C—C Bond	87
16.18.8.4.1.2.1	Method 1: Cyclization of 2,6-Diaryl-5-(phenyldiazenyl)pyridine-3-carbonitriles	87
16.18.8.5	Pyrido[4,3- <i>c</i>]pyridazines	88
16.18.8.5.1	Synthesis by Ring-Closure Reactions	88
16.18.8.5.1.1	By Formation of One N—C and One C—C Bond	88
16.18.8.5.1.1.1	Method 1: Autooxidation of a Quinolinyldiazine	88
16.18.8.5.1.2	By Formation of Two N—C and Two C—C Bonds	90
16.18.8.5.1.2.1	Method 1: Cyclization of 6-Aryl-3-methylpyridazine-4-carboxamides with the Vilsmeier–Haack Reagent	90
16.18.8.5.1.3	By Formation of Two N—C Bonds and One C—C Bond	91
16.18.8.5.1.3.1	Method 1: Regioselective Synthesis of 3-Arylpyridazino[4,3- <i>c</i>]quinolin-5(6 <i>H</i>)ones	91

16.19 Product Class 19: Pyridopyrimidines

16.19.6	Pyridopyrimidines 2026 Charles L. Lail, III ^B and Timothy J. Hagen ^B	
16.19.6	Pyridopyrimidines	95
16.19.6.1	Pyrido[2,3- <i>d</i>]pyrimidines	96
16.19.6.1.1	By Formation of One N—C Bond and One C—C Bond	96
16.19.6.1.1.1	Method 1: Cyclization of 3-Bromopyridin-2-amine with Nitriles and Isocyanides	96
16.19.6.1.1.2	Method 2: Aldol Reaction Followed by Amide Formation	98
16.19.6.1.1.3	Method 3: Condensation of Enamines with 1,3-Diketones	98
16.19.6.1.1.4	Method 4: Knoevenagel Condensation Followed by Michael Addition	99

16.19.6.1.1.5	Method 5:	Addition of Vilsmeier–Haack Reagent to 6-Aminouracils and Annulation with Methylene Nitriles	100
16.19.6.1.1.6	Method 6:	Cyclocondensation with Vinamidinium Salts	101
16.19.6.1.2		By Formation of One N—C Bond and Two C—C Bonds	102
16.19.6.1.2.1	Method 1:	Three-Component Reactions with Catalysis	102
16.19.6.1.2.2	Method 2:	Three-Component Reactions Using Ionic Liquids	110
16.19.6.1.2.3	Method 3:	Three-Component Reactions with Magnetized Deionized Water	112
16.19.6.1.3		By Formation of One N—C Bond	114
16.19.6.1.3.1	Method 1:	Silver-Catalyzed Cyclization	114
16.19.6.1.4		By Formation of Two N—C Bonds	116
16.19.6.1.4.1	Method 1:	Cyclization of 3-[Aryl(imino)methyl]pyridin-2-amines	116
16.19.6.1.4.2	Method 2:	Condensation of 2-Aminopyridine-3-carbonitriles with Acid Chlorides	117
16.19.6.1.5		By Formation of Three N—C Bonds	118
16.19.6.1.5.1	Method 1:	Condensation of 6-Amino-2-thioxo-1,2-dihydropyridine-3,5-dicarbonitrile with Aryl Isothiocyanates	118
16.19.6.2		Pyrido[3,2- <i>d</i>]pyrimidines	119
16.19.6.2.1		By Formation of One N—C Bond and One C—C Bond	119
16.19.6.2.1.1	Method 1:	Cyclization of 2-Bromopyridin-3-amine with Nitriles and Isocyanides	119
16.19.6.2.1.2	Method 2:	Intramolecular Electrocyclization of 6-Allyl-5-aminopyrimidine-2,4(1 <i>H</i> ,3 <i>H</i>)-diones with Arylaldehydes ...	120
16.19.6.2.2		By Formation of One N—C Bond	121
16.19.6.2.2.1	Method 1:	Ultraviolet-Light-Induced Intramolecular Amide Formation ..	121
16.19.6.2.3		By Formation of One C—C Bond	122
16.19.6.2.3.1	Method 1:	Cyclization of Carboxylate Enamines	122
16.19.6.3		Pyrido[3,4- <i>d</i>]pyrimidines	124
16.19.6.3.1		By Formation of One N—C Bond	124
16.19.6.3.1.1	Method 1:	Intramolecular Imine/Isocyanide Cyclization	124
16.19.6.3.2		By Formation of Two N—C Bonds	125
16.19.6.3.2.1	Method 1:	Cycloamidation of an <i>N'</i> -(4-Carboxypyridin-3-yl) Amidine with Alkylamines	125
16.19.6.3.1.2	Method 2:	Cyclization of Ethyl 3-Amino-2-chloropyridine-4-carboxylate with Chloroformamidine	126
16.19.6.3.1.3	Method 3:	Cyclization of a Pyrimidine Oxo Acid	126
16.19.6.3.1.4	Method 4:	Cyclization of a 5-(2-Ethoxyvinyl)pyrimidine-4-carboxamide ..	127
16.19.6.4		Pyrido[4,3- <i>d</i>]pyrimidines	128
16.19.6.4.1		By Formation of One N—C Bond and One C—C Bond	128
16.19.6.4.1.1	Method 1:	Condensation of Aromatic Dielectrophiles with Enediamines ..	128
16.19.6.4.1.2	Method 2:	Aza-Diels–Alder Reaction	129

16.19.6.4.2	By Formation of Two N—C Bonds and Two C—C Bonds	131
16.19.6.4.2.1	Method 1: Condensation of Ketones with Aldehydes and Thiourea	131
16.19.6.4.3	By Formation of Two N—C Bonds	132
16.19.6.4.3.1	Method 1: Cycloamidation of an <i>N'</i> -(3-Carboxypyridin-4-yl) Amidine with Alkylamines	132
16.20	Product Class 20: Pyridopyrazines	
<hr/>		
16.20.4	Pyridopyrazines 2026	
	Faridooon ^{ip} and Guiping Zhang ^{ip}	
<hr/>		
16.20.4	Pyridopyrazines	135
16.20.4.1	Pyrido[2,3- <i>b</i>]pyrazines	136
16.20.4.1.1	Synthesis by Ring-Closure Reactions	136
16.20.4.1.1.1	By Formation of Two N—C Bonds	136
16.20.4.1.1.1.1	Method 1: Condensation of Pyridine-2,3-diamines with Dicarboxyl Compounds	136
16.20.4.1.1.1.2	Method 2: Condensation of Pyridine-2,3-diamines with α -Hydroxy Ketones	149
16.20.4.1.1.1.3	Method 3: Condensation of Pyridine-2,3-diamines with α -Oxo Acetals ..	150
16.20.4.1.1.1.4	Method 4: Condensation of Pyridine-2,3-diamines with Vicinal Diols	152
16.20.4.1.2	Multicomponent Syntheses	153
16.20.4.1.2.1	Method 1: Multicomponent Synthesis of Pyrido[2,3- <i>b</i>]pyrazine Derivatives	153
16.20.4.1.2.2	Method 2: Multicomponent Synthesis of Phenylpyrido[2,3- <i>b</i>]pyrazines ..	154
16.20.4.1.2.3	Method 3: Multicomponent Microwave-Assisted Green Synthesis of Arylpyrido[2,3- <i>b</i>]pyrazines	155
16.20.4.1.3	Miscellaneous Syntheses	156
16.20.4.2	Pyrido[3,4- <i>b</i>]pyrazines	158
16.20.4.2.1	Synthesis by Ring-Closure Reactions	158
16.20.4.2.1.1	By Formation of Two N—C Bonds	158
16.20.4.2.1.1.1	Method 1: Condensation of Pyridine-3,4-diamines with Dicarboxyl Compounds	158
16.20.4.2.1.1.2	Method 2: Condensation of Pyridine-3,4-diamines with α -Oxo Acetals ..	162

Volume 17: Six-Membered Hetarenes with Two Unlike or More Than Two Heteroatoms and Larger Hetero-Rings

17.7 Product Class 7: Cyclazines

17.7.8	Cyclazines	2026
	Jie Jack Li ^{1b}	
17.7.8	Cyclazines	165
17.7.8.1	[2.2.2]Cyclazines (Pyrrolo[2,1,5- <i>cd</i>]pyrrolizines)	166
17.7.8.1.1	Method 1: Azatriquinacene from Fully Reduced [2.2.2]Cyclazine	166
17.7.8.1.2	Method 2: Zwitterionic [2.2.2]Cyclazine from Azatriquinacene	167
17.7.8.1.3	Method 3: Functionalization of a Zwitterionic [2.2.2]Cyclazine	169
17.7.8.1.4	Method 4: Synthesis of Anionic [2.2.2]Cyclazine	169
17.7.8.1.5	Method 5: Functionalization of Anionic [2.2.2]Cyclazine	170
17.7.8.2	[2.2.3]Cyclazines (Pyrrolo[2,1,5- <i>cd</i>]indolizines) and Related Compounds	170
17.7.8.2.1	[2.2.3]Cyclazines (Pyrrolo[2,1,5- <i>cd</i>]indolizines)	170
17.7.8.2.1.1	Synthesis by Ring Closure	170
17.7.8.2.1.1.1	Method 1: [8 + 2] Cycloaddition Reactions of Indolizines with Alkynes ..	170
17.7.8.2.1.1.1.1	Variation 1: Palladium-Catalyzed Dehydrogenative Heck Annulation of Indolizines with Diarylacetylenes	171
17.7.8.2.1.1.1.2	Variation 2: [8 + 2] Cyclization of Indolizines and a Terminal Acetylene ...	172
17.7.8.2.1.1.1.3	Variation 3: Visible-Light-Induced Intermolecular [3 + 2] Cycloaddition ...	172
17.7.8.2.1.1.1.4	Variation 4: Dimesitylboron-Functionalized [2.2.3]Cyclazines	174
17.7.8.2.1.1.1.5	Variation 5: [8 + 2] Cycloaddition of Indolizidines and Dimethyl Acetylenedicarboxylate Using a Palladium Catalyst	175
17.7.8.2.1.1.1.6	Variation 6: [8 + 2] Cycloaddition of Indolizidines and Diethyl Acetylenedicarboxylate Using a Copper Catalyst	177
17.7.8.2.1.1.1.7	Variation 7: Catalyst-Free [8 + 2] Cycloaddition of a 5-Bromoindolizidine and Dimethyl Acetylenedicarboxylate	178
17.7.8.2.1.1.2	Method 2: Cycloaddition of Indolizines with Alkenes	178
17.7.8.2.1.1.2.1	Variation 1: Annulation of Indolizines with α,β -Unsaturated Carboxylic Acids	178
17.7.8.2.1.1.2.2	Variation 2: Visible-Light-Induced [8 + 2] Cyclization	179
17.7.8.2.1.1.2.3	Variation 3: Stereoselective [8 + 2] Cycloaddition of 3 <i>H</i> -Pyrrolizines with Alkenes	180
17.7.8.2.1.1.2.4	Variation 4: [12 + 2] Cycloaddition Reactions of Indolizines with Alkenes ..	182
17.7.8.2.1.1.2.5	Variation 5: One-Pot, Two-Step Procedure To Prepare Fully Unsaturated Benzo[2.2.3]cyclazines	183
17.7.8.2.1.1.3	Method 3: Mechanochemically Induced Dehydrogenative Coupling and [8 + 2] Cycloaddition Reactions of Indolizines with Allenes ...	184

17.7.8.2.1.1.4	Method 4:	Microwave-Promoted Three-Component Cycloaddition in Water	185
17.7.8.2.1.1.5	Method 5:	Gold-Catalyzed Cycloisomerization To Access Luminescent [3.2.2]Cyclazines	186
17.7.8.2.1.1.6	Method 6:	Strong-Base-Promoted Intramolecular Condensation	187
17.7.8.2.1.2	Synthesis by Substituent Modification		188
17.7.8.2.1.2.1	Method 1:	Hydrolysis of [2.2.3]Cyclazine Esters to the Corresponding Carboxylic Acids	188
17.7.8.2.1.2.2	Method 2:	Conversion of a [2.2.3]Cyclazine Dicarboxylic Acid into a [2.2.3]Cyclazine Dinitrile	189
17.7.8.2.1.2.3	Method 3:	Chlorination of a [2.2.3]Cyclazine Diester at Position 4	190
17.7.8.2.1.2.4	Method 4:	Conversion of a [2.2.3]Cyclazine Dicarboxylic Acid into [2.2.3]Cyclazine Monoamides	190
17.7.8.2.1.2.5	Method 5:	Conversion of a [2.2.3]Cyclazine Acid into the Corresponding Acylurea	191
17.7.8.2.2	Aza- and Diaza[2.2.3]cyclazines		192
17.7.8.2.2.1	Method 1:	Palladium-Catalyzed Oxidative [3 + 2] Cycloaddition To Prepare Aza[2.2.3]cyclazines	193
17.7.8.2.2.2	Method 2:	Palladium-Catalyzed Oxidative [3 + 2] Cycloaddition To Prepare Diaza[2.2.3]cyclazines	194
17.7.8.2.2.3	Method 3:	Diaza[2.2.3]cyclazines from the Groebke–Blackburn–Bienaymé Reaction	195
17.7.8.2.2.3.1	Variation 1:	Diaza[2.2.3]cyclazines from Intramolecular Aminolysis	196
17.7.8.2.2.4	Method 4:	Manganese-Catalyzed Cascade Reaction To Produce Aza[2.2.3]cyclazines	197
17.7.8.3	[2.3.3]Cyclazines (Pyrrolo[2,1,5- <i>de</i>]quinolizines) and Related Compounds ...		198
17.7.8.3.1	[2.3.3]Cyclazinones		198
17.7.8.3.1.1	Method 1:	[3 + 2] Cycloaddition of 1-Oxoquinolizinium Ylides with Cyclic Alkenes	198
17.7.8.3.1.2	Method 2:	[3 + 2] Cycloadditions of 2-Alkylquinolizinium-1-olates with Alkynes	200
17.7.8.3.1.3	Method 3:	Condensation of Indolizidine with Dimethylformamide Dimethyl Acetal	202
17.7.8.3.1.4	Method 4:	Alkenation of [2.3.3]Cyclazinone	202
17.7.8.3.2	Benzo-Fused [2.3.3]Cyclazines (Ullazines)		203
17.7.8.3.2.1	Method 1:	Ullazines from <i>N</i> -Arylpyrroles and Alkynes	204
17.7.8.3.2.1.1	Variation 1:	Rhodium(III)-Catalyzed Double Annulation of <i>N</i> -Arylpyrroles with Diarylacetylenes	204
17.7.8.3.2.1.2	Variation 2:	Rhodium(III)-Catalyzed Single Annulation of <i>N</i> -Arylpyrroles with Diphenylacetylene	205
17.7.8.3.2.1.3	Variation 3:	π -Extended Dibenzo[<i>d,k</i>]ullazines by a Palladium-Catalyzed Double Annulation Using Arynes	205
17.7.8.3.2.1.4	Variation 4:	Chromium-Mediated Coupling between Pyrroloquinolines and Alkynes	206

Chemical (cont.)

Name Used in Text	Abbreviation Used in Tables and on Arrow in Schemes	Abbreviation Used in Experimental Procedures
1,2-dimethoxyethane	DME	DME
dimethylacetamide	DMA	DMA
dimethyl acetylenedicarboxylate	DMAD	DMAD
2-(dimethylamino)ethanol	Me ₂ N(CH ₂) ₂ OH	2-(dimethylamino)ethanol
4-(dimethylamino)pyridine	DMAP	DMAP
dimethylformamide	DMF	DMF
dimethyl sulfide	DMS	DMS
dimethyl sulfoxide	DMSO	DMSO
1,3-dimethyl-3,4,5,6-tetrahydropyrimidin-2-(1 <i>H</i>)-one	DMPU	DMPU
ethyl diazoacetate	EDA	EDA
ethylenediaminetetraacetic acid	edta	edta
hexamethylphosphoric triamide	HMPA	HMPA
hexamethylphosphorous triamide	HMPT	HMPT
iodomethane	MeI	MeI
<i>N</i> -iodosuccinimide	NIS	NIS
lithium diisopropylamide	LDA	LDA
lithium hexamethyldisilazane	LiHMDS	LiHMDS
lithium isopropylcyclohexylamide	LICA	LICA
lithium 2,2,6,6-tetramethylpiperidide	LTMP	LTMP
lutidine	lut	lut
methylaluminum bis(2,6-di- <i>tert</i> -butyl-4-methylphenoxide)	MAD	MAD
methyl ethyl ketone	MEK	methyl ethyl ketone
methylmaleimide	NMM	NMM
4-methylmorpholine <i>N</i> -oxide	NMO	NMO
1-methylpyrrolidin-2-one	NMP	NMP
methyl vinyl ketone	MVK	methyl vinyl ketone
petroleum ether	PE ^a	petroleum ether
<i>N</i> -phenylmaleimide	NPM	NPM
polyphosphoric acid	PPA	PPA
polyphosphate ester	PPE	polyphosphate ester
potassium hexamethyldisilazane	KHMDS	KHMDS
pyridine	pyridine ^b	pyridine
pyridinium chlorochromate	PCC	PCC
pyridinium dichromate	PDC	PDC
pyridinium 4-toluenesulfonate	PPTS	PPTS
sodium bis(2-methoxyethoxy)aluminum hydride	Red-Al	Red-Al

^a Used to save space; abbreviation must be defined in a footnote.^b py used on arrow in schemes.

Chemical (cont.)

Name Used in Text	Abbreviation Used in Tables and on Arrow in Schemes	Abbreviation Used in Experimental Procedures
tetrabutylammonium bromide	TBAB	TBAB
tetrabutylammonium chloride	TBACl	TBACl
tetrabutylammonium fluoride	TBAF	TBAF
tetrabutylammonium iodide	TBAI	TBAI
tetracyanoethene	TCNE	tetracyanoethene
tetrahydrofuran	THF	THF
tetrahydropyran	THP	THP
2,2,6,6-tetramethylpiperidine	TMP	TMP
trimethylamine <i>N</i> -oxide	TMANO	trimethylamine <i>N</i> -oxide
<i>N,N,N',N'</i> -tetramethylethylenediamine	TMEDA	TMEDA
tosylmethyl isocyanide	TosMIC	TosMIC
trifluoroacetic acid	TFA	TFA
trifluoroacetic anhydride	TFAA	TFAA
trimethylsilyl cyanide	TMSCN	TMSCN

Ligands

acetylacetonato	acac
2,2'-bipyridyl	bipy
1,2-bis(dimethylphosphino)ethane	DMPE
2,3-bis(diphenylphosphino)bicyclo[2.2.1]hept-5-ene	NORPHOS
2,2'-bis(diphenylphosphino)-1,1'-binaphthyl	BINAP
1,2-bis(diphenylphosphino)ethane	dppe (not diphos)
1,1'-bis(diphenylphosphino)ferrocene	dppf
bis(diphenylphosphino)methane	dppm
1,3-bis(diphenylphosphino)propane	dppp
1,4-bis(diphenylphosphino)butane	dppb
2,3-bis(diphenylphosphino)butane	Chiraphos
bis(salicylidene)ethylenediamine	salen
cyclooctadiene	cod
cyclooctatetraene	cot
cyclooctatriene	cte
η^5 -cyclopentadienyl	Cp
dibenzylideneacetone	dba
6,6-dimethylcyclohexadienyl	dmch
2,4-dimethylpentadienyl	dmpd
ethylenediaminetetraacetic acid	edta
isopinocampheyl	lpc
2,3- <i>O</i> -isopropylidene-2,3-dihydroxy-1,4-bis-(diphenylphosphino)butane	Diop
norbornadiene (bicyclo[2.2.1]hepta-2,5-diene)	nbd
η^5 -pentamethylcyclopentadienyl	Cp*

Radicals

acetyl	Ac
aryl	Ar
benzotriazol-1-yl	Bt
benzoyl	Bz
benzyl	Bn
benzyloxycarbonyl	Cbz
benzyloxymethyl	BOM
9-borabicyclo[3.3.1]nonyl	9-BBN
<i>tert</i> -butoxycarbonyl	Boc
butyl	Bu
<i>sec</i> -butyl	<i>s</i> -Bu
<i>tert</i> -butyl	<i>t</i> -Bu
<i>tert</i> -butyldimethylsilyl	TBDMS
<i>tert</i> -butyldiphenylsilyl	TBDPS
cyclohexyl	Cy
3,4-dimethoxybenzyl	DMB
ethyl	Et
ferrocenyl	Fc
9-fluorenylmethoxycarbonyl	Fmoc
isobutyl	iBu
mesityl	Mes
mesyl	Ms
4-methoxybenzyl	PMB
(2-methoxyethoxy)methyl	MEM
methoxymethyl	MOM
methyl	Me
4-nitrobenzyl	PNB
phenyl	Ph
phthaloyl	Phth
phthalimido	NPhth
propyl	Pr
isopropyl	iPr
tetrahydropyranyl	THP
tolyl	Tol
tosyl	Ts
triethylsilyl	TES
triflyl, trifluoromethanesulfonyl	Tf
triisopropylsilyl	TIPS
trimethylsilyl	TMS
2-(trimethylsilyl)ethoxymethyl	SEM
trityl [triphenylmethyl]	Tr

General

absolute	abs
anhydrous	anhyd
aqueous	aq
boiling point	bp
catalyst	no abbreviation
catalytic	cat.
chemical shift	δ
circular dichroism	CD
column chromatography	no abbreviation
concentrated	concd
configuration (in tables)	Config
coupling constant	<i>J</i>
day	d
density	<i>d</i>
decomposed	dec
degrees Celsius	$^{\circ}\text{C}$
diastereomeric ratio	dr
dilute	dil
electron-donating group	EDG
electron-withdrawing group	EWG
electrophile	E^+
enantiomeric excess	ee
enantiomeric ratio	er
equation	eq
equivalent(s)	equiv
flash-vacuum pyrolysis	FVP
gas chromatography	GC
gas chromatography-mass spectrometry	GC/MS
gas-liquid chromatography	GLC
gram	g
highest occupied molecular orbital	HOMO
high-performance liquid chromatography	HPLC
hour(s)	h
infrared	IR
in situ	in situ
in vacuo	in vacuo
lethal dosage, e. g. to 50 % of animals tested	LD_{50}
liquid	liq
liter	L
lowest unoccupied molecular orbital	LUMO
mass spectrometry	MS
medium-pressure liquid chromatography	MPLC
melting point	mp
milliliter	mL
millimole(s)	mmol
millimoles per liter	mM
minute(s)	min
mole(s)	mol
nuclear magnetic resonance	NMR
nucleophile	Nu^-
optical purity	op
phase-transfer catalysis	PTC
proton NMR	^1H NMR