

Table of Contents

Volume 3: Compounds of Groups 12 and 11 (Zn, Cd, Hg, Cu, Ag, Au)

3.6 Product Class 6: Organometallic Complexes of Gold

3.6.16 Gold-Catalyzed Cycloaddition Reactions

D. Qian and J. Zhang

New

3.6.16	Gold-Catalyzed Cycloaddition Reactions	1
3.6.16.1	Cycloadditions via Gold-Containing 1,n-Dipolar Intermediates	1
3.6.16.1.1	Method 1: Gold-Containing Benzopyrylium Intermediates	2
3.6.16.1.1.1	Variation 1: Gold-Containing Benzopyrylium Azomethine Ylides	8
3.6.16.1.1.2	Variation 2: Gold-Containing 2-Oxoalkyl Oxonium Species	11
3.6.16.1.2	Method 2: Furyl-Gold 1,n-Dipole Intermediates	12
3.6.16.1.2.1	Variation 1: Furyl-Gold 1,3-Dipole Intermediates	12
3.6.16.1.2.2	Variation 2: Furyl-Gold 1,4-Dipole Intermediates	15
3.6.16.1.2.3	Variation 3: Furan-Based <i>ortho</i> -Quinodimethane Intermediates	18
3.6.16.1.3	Method 3: Gold-Containing All-Carbon 1,3-Dipoles	19
3.6.16.2	Cycloadditions via Gold-Coordinated Allene Intermediates	21
3.6.16.2.1	Method 1: Cycloadditions Initiated by Gold Activation of Allenes	21
3.6.16.2.2	Method 2: Cycloadditions Initiated by Gold Activation of Propargylic Carboxylates	33
3.6.16.3	Cycloadditions via <i>trans</i> -Alkenylgold Intermediates	35
3.6.16.3.1	Method 1: <i>trans</i> -Alkenylgold Intermediates Generated by Alkyne Activation	35
3.6.16.3.1.1	Variation 1: Alkynes as Latent Alkenes in Gold-Catalyzed Cycloadditions	38
3.6.16.4	Cycloadditions via Gold Carbene Intermediates	40
3.6.16.4.1	Method 1: Gold Carbenes Generated by Cycloisomerization of Alkynes and Alkenes	40
3.6.16.4.2	Method 2: Gold Carbene Generated by 1,2-Acyloxy Migration of Propargyl Carboxylates	45
3.6.16.4.3	Method 3: Gold Carbene Generated by Alkyne Oxidation	48
3.6.16.4.3.1	Variation 1: Gold-Catalyzed Cycloaddition Reactions by Nitrene Transfer	51
3.6.16.4.3.2	Variation 2: Gold-Catalyzed Cycloaddition Reactions by Carbene Transfer	52
3.6.16.4.4	Method 4: Gold Carbene Generated by Diazo Decomposition	53
3.6.16.5	Cycloadditions via Gold-Coordinated Heteroatom Intermediates	55

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

4.4	Product Class 4: Silicon Compounds	
4.4.7	Product Subclass 7: Silylboron Reagents	2017
	L. B. Delvos and M. Oestreich	
4.4.7	Product Subclass 7: Silylboron Reagents	65
4.4.7.1	Synthesis of Product Subclass 7	68
4.4.7.1.1	Preparation by Si—B Bond Formation	68
4.4.7.1.1.1	Method 1: Nucleophilic Substitution at Boron with Silyllithium Reagents	68
4.4.7.1.1.1.1	Variation 1: Substitution of Amino-Substituted Chloroboranes	68
4.4.7.1.1.1.2	Variation 2: Substitution of a Diaryl-Substituted Fluoroborane	69
4.4.7.1.1.1.3	Variation 3: Nucleophilic Substitution of Diol-Substituted Hydro- or Alkoxyboranes	70
4.4.7.1.1.2	Method 2: Iridium-Catalyzed Borylation of Trialkylsilanes	71
4.4.7.1.1.3	Method 3: Reductive Coupling of Chlorosilanes and Chloroboranes	72
4.4.7.1.2	Modification of Si—B Substitution Pattern	73
4.4.7.1.2.1	Method 1: Ligand Exchange at the Boron Atom	73
4.4.7.1.2.2	Method 2: Manipulation at the Silicon Atom	75
4.4.7.2	Applications of Product Subclass 7 in Organic Synthesis	77
4.4.7.2.1	Method 1: Reactions with Alkynes	77
4.4.7.2.1.1	Variation 1: Transition-Metal-Catalyzed Silaboration	77
4.4.7.2.1.2	Variation 2: Palladium-Catalyzed Silaborative Cyclization	83
4.4.7.2.1.3	Variation 3: Nickel-Catalyzed Silaborative Dimerization	84
4.4.7.2.1.4	Variation 4: Palladium-Catalyzed (2 + 2 + 1) Cycloaddition with Silylenes ..	85
4.4.7.2.1.5	Variation 5: Copper-Catalyzed Silylation	86
4.4.7.2.2	Method 2: Reactions with Alkenes	91
4.4.7.2.2.1	Variation 1: Platinum-Catalyzed Silaboration	91
4.4.7.2.2.2	Variation 2: Base-Catalyzed Silaboration	95
4.4.7.2.2.3	Variation 3: Photochemical Radical Silylation	96
4.4.7.2.3	Method 3: Reactions with Conjugated Dienes and Enynes	97
4.4.7.2.3.1	Variation 1: Transition-Metal-Catalyzed 1,4-Silaboration	97
4.4.7.2.3.2	Variation 2: Platinum-Catalyzed Silaborative Coupling of 1,3-Dienes and Aldehydes	100
4.4.7.2.3.3	Variation 3: Nickel-Catalyzed Silylative Coupling of 1,3-Dienes and Aldehydes	101
4.4.7.2.3.4	Variation 4: Palladium-Catalyzed (4 + 1) Cycloaddition with Silylenes ..	102

4.4.7.2.4	Method 4:	Reactions with Allenes	104
4.4.7.2.4.1	Variation 1:	Palladium-Catalyzed Silaboration	104
4.4.7.2.4.2	Variation 2:	Copper-Catalyzed Silylation	109
4.4.7.2.5	Method 5:	Reactions with C=X Bonds	115
4.4.7.2.5.1	Variation 1:	1,2-Silylation of Aldehydes	115
4.4.7.2.5.2	Variation 2:	1,2-Silylation of Imines	117
4.4.7.2.5.3	Variation 3:	Reaction with Anhydrides	121
4.4.7.2.6	Method 6:	Reactions with α,β -Unsaturated Carbonyl and Carboxy Compounds and Derivatives Thereof	122
4.4.7.2.6.1	Variation 1:	Transition-Metal-Catalyzed 1,4-Silylation of Enones and α,β -Unsaturated Esters	122
4.4.7.2.6.2	Variation 2:	N-Heterocyclic Carbene Catalyzed 1,4-Silylation of Enones, Enals, or Unsaturated Esters	135
4.4.7.2.6.3	Variation 3:	Copper-Catalyzed 1,4-Silylation of Ynones and Derivatives Thereof	137
4.4.7.2.6.4	Variation 4:	Metal-Free Phosphine-Catalyzed Silaboration of Ynoates	142
4.4.7.2.7	Method 7:	Reactions with Allylic and Propargylic Electrophiles	143
4.4.7.2.7.1	Variation 1:	Copper-Catalyzed Allylic Substitution	143
4.4.7.2.7.2	Variation 2:	Silylative Cyclopropanation	148
4.4.7.2.7.3	Variation 3:	Transition-Metal-Catalyzed Propargylic Substitution	149
4.4.7.2.8	Method 8:	Reactions with (Het)arenes	151
4.4.7.2.8.1	Variation 1:	Silaborative Dearomatization of Nitrogen Heterocycles	151
4.4.7.2.8.2	Variation 2:	Nickel/Copper-Catalyzed Silylation	153
4.4.7.2.8.3	Variation 3:	Base-Catalyzed Borylation	155
4.4.7.2.8.4	Variation 4:	Iridium-Catalyzed Borylation	158
4.4.7.2.9	Method 9:	Reactions with Strained Ring Compounds	159
4.4.7.2.9.1	Variation 1:	Silaboration of Methylenecyclopropanes	159
4.4.7.2.9.2	Variation 2:	Silaboration of Vinylcyclopropanes, Vinylcyclobutanes, and Related Compounds	163
4.4.7.2.10	Method 10:	Reactions with Carbenoids and Related Compounds	165
4.4.7.2.10.1	Variation 1:	Insertion of Alkylidene-Type Carbenoids into the Si—B Bond	165
4.4.7.2.10.2	Variation 2:	Insertion of sp^3 -Carbon-Centered Carbenoids into the Si—B Bond	168
4.4.7.2.10.3	Variation 3:	Insertion of Isocyanides into the Si—B Bond	170
4.4.7.2.11	Method 11:	Miscellaneous Reactions	172
4.4.7.2.11.1	Variation 1:	Stereoselective Deoxygenation of <i>trans</i> -Stilbene Oxides	172
4.4.7.2.11.2	Variation 2:	B—N Bond Formation by Desilacoupling Catalyzed by a Strontium Bisamide Base	173

4.4.11	Product Subclass 11: Silyllithium and Related Silyl Alkali Metal Reagents	2017
	C. Kleeberg	
4.4.11	Product Subclass 11: Silyllithium and Related Silyl Alkali Metal Reagents	177
4.4.11.1	Method 1: Reductive Cleavage of Disilanes with Alkali Metals	178
4.4.11.2	Method 2: Reduction of Halotriorganosilanes with Alkali Metals	179
4.4.11.3	Method 3: Nucleophilic Cleavage of Si—M Bonds (M = Si, Sn, etc.)	180
4.4.11.3.1	Variation 1: Si—Si Bond Cleavage	181
4.4.11.3.2	Variation 2: Si—Sn Bond Cleavage	183
4.4.11.4	Method 4: Si—H Bond Cleavage	183
4.4.11.4.1	Variation 1: Si—H Bond Cleavage by Alkali Metals	183
4.4.11.4.2	Variation 2: Si—H Bond Cleavage by Alkali Metal Hydrides	185
4.4.11.5	Method 5: Preparation via Disilylmercury Compounds	186
4.4.19.4	Silyl Sulfides and Selenides	2017
	A. Baker and T. Wirth	
4.4.19.4	Silyl Sulfides and Selenides	189
4.4.19.4.1	Synthesis of Silyl Sulfides and Selenides	189
4.4.19.4.1.1	Method 1: Synthesis by Reaction of Alkali Metals, Chalcogens, and Halosilanes or Alkali Metal Chalcogenides and Halosilanes	189
4.4.19.4.1.1.1	Variation 1: From Lithium, Sulfur, and Halosilanes	189
4.4.19.4.1.1.2	Variation 2: From Sodium, Sulfur, and Halosilanes	190
4.4.19.4.1.1.3	Variation 3: From Lithium Sulfide and Halosilanes	191
4.4.19.4.1.1.4	Variation 4: From Lithium Selenide and Halosilanes	192
4.4.19.4.1.1.5	Variation 5: From Lithium Chalcogenides, Generated from Lithium Triethylborohydride and Chalcogens, and Halosilanes	193
4.4.19.4.1.2	Method 2: Synthesis from Diselenides and Halosilanes	193
4.4.19.4.1.2.1	Variation 1: From Dimethyl Diselenide, Lithium Aluminum Hydride, and Halosilanes	193
4.4.19.4.1.2.2	Variation 2: From Diphenyl Diselenide, Sodium, and Halosilanes	194
4.4.19.4.1.2.3	Variation 3: From Diphenyl Diselenide, Lithium in Liquid Ammonia, and Halosilanes	194
4.4.19.4.1.3	Method 3: Synthesis from Selanols	195
4.4.19.4.1.4	Method 4: Synthesis from Alkynes, Butyllithium, Sulfur, and Halosilanes	196
4.4.19.4.1.5	Method 5: Synthesis Using Phosphorus-Based Reagents	197
4.4.19.4.1.5.1	Variation 1: From Silylphosphines and Sulfur	197
4.4.19.4.1.5.2	Variation 2: From Phosphine Sulfides and (Dimethylamino)trimethylsilane	197
4.4.19.4.1.5.3	Variation 3: From Phosphorus Pentasulfide and Alkoxytrimethylsilanes or (Alkylsulfanyl)trimethylsilanes	198
4.4.19.4.1.6	Method 6: Synthesis from Grignard Reagents, Selenium, and Halosilanes	198

4.4.19.4.1.7	Method 7: Synthesis from Existing Silyl Selenides by Substitution of a Group on Selenium	199
4.4.19.4.2	Applications of Silyl Sulfides and Selenides	199
4.4.24.3	Silyl Cyanides	2017
	Y. Nishimoto, M. Yasuda, and A. Baba	
4.4.24.3	Silyl Cyanides	203
4.4.24.3.1	Tetracoordinate Silyl Cyanides	203
4.4.24.3.1.1	Method 1: Transmetalation of Silyl Chlorides	203
4.4.24.3.1.2	Method 2: Metathesis between Si—H and X—CN Bonds (X = C, N, O, Si) ..	204
4.4.24.3.1.3	Method 3: Insertion of Silylenes into Isocyanides	205
4.4.24.3.1.4	Method 4: Transformation of Si=C=N—Si Units	206
4.4.24.3.2	Extracoordinate Silyl Cyanides	208
4.4.24.3.2.1	Method 1: Reaction of Pentacoordinate Silyl Chlorides with Cyanotrimethylsilane	208
4.4.24.3.2.2	Method 2: Reaction of Hexacoordinate Silyl Chlorides with Cyanotrimethylsilane	210
4.4.47	Product Subclass 47: Silanols	New
	A. M. Hardman-Baldwin and A. E. Mattson	
4.4.47	Product Subclass 47: Silanols	213
4.4.47.1	Synthesis of Silanols	213
4.4.47.1.1	Method 1: Hydrolysis of Chlorosilanes	213
4.4.47.1.1.1	Variation 1: Biphasic Hydrolysis of Chlorosilanes	214
4.4.47.1.1.2	Variation 2: Biphasic Hydrolysis of Chlorosilanes with Triethylamine	214
4.4.47.1.1.3	Variation 3: Synthesis of Bulky Silanediols from Chlorosilanes	215
4.4.47.1.2	Method 2: Stoichiometric Oxidation of Silanes	216
4.4.47.1.2.1	Variation 1: Oxidation of Silanes with Ozone	216
4.4.47.1.2.2	Variation 2: Oxidation of Silanes with Peroxy Acids	217
4.4.47.1.2.3	Variation 3: Oxidation of Silanes with Dioxiranes or Oxaziridines	218
4.4.47.1.2.4	Variation 4: Oxidation of Silanes with Potassium Permanganate and Sonication	219
4.4.47.1.2.5	Variation 5: Oxidation of Silanes with Osmium(VIII) Oxide	219
4.4.47.1.3	Method 3: Catalytic Oxidation of Silanes	220
4.4.47.1.3.1	Variation 1: Heterogeneous Catalytic Oxidation of Silanes with Water ..	221
4.4.47.1.3.2	Variation 2: Catalytic Oxidation of Silanes with Nanoparticles	221
4.4.47.1.3.3	Variation 3: Homogeneous Catalytic Oxidation of Silanes with Water ..	223
4.4.47.1.3.4	Variation 4: Catalytic Oxidation of Silanes with Peroxides or Oxygen ..	228
4.4.47.1.3.5	Variation 5: Organocatalytic Oxidation of Silanes	230
4.4.47.1.4	Method 4: Hydrolysis of Aromatic C(sp ²)—Si Bonds	230
4.4.47.1.5	Method 5: Cleavage of Siloxy- and Alkoxy silanes	233

4.4.47.2	Catalytic Activity of Silanols	235
4.4.47.2.1	Method 1: Hydrogen-Bond-Donor Catalysis Involving Silanediols	235
4.4.47.2.2	Method 2: Silanediols in Anion-Binding Catalysis	237
4.4.47.2.3	Method 3: Catalytic Activity of Bissilanols	239
4.4.47.2.4	Method 4: Catalytic Activity of Monosilanols	239
4.4.47.3	Silanols as Directing Groups	241

Volume 10: Fused Five-Membered Hetarenes with One Heteroatom

10.22	Product Class 22: Azaindoles and Their Derivatives	
10.22.2	Product Subclass 2: Azaindol-1-ols	
	J.-Y. Mérour and B. Joseph	
10.22.2	Product Subclass 2: Azaindol-1-ols	247
10.22.2.1	Synthesis by Ring-Closure Reactions	247
10.22.2.1.1	By Annulation to a Pyridine	247
10.22.2.1.1.1	With Formation of One N—C Bond	247
10.22.2.1.1.1.1	With Formation of the 1—2 Bond	247
10.22.2.1.1.1.1.1	Method 1: From 2-(<i>o</i> -Nitropyridyl)acetates	247
10.22.2.1.1.1.1.2	Method 2: From an (Alkenylpyridyl)hydroxylamine	249
10.22.2.1.1.1.1.3	Method 3: From a 2-(3-Nitropyridin-2-yl)ethanone	250
10.22.2.1.1.1.1.4	Method 4: From 2-(3-Nitropyridin-2-yl)pent-4-enenitrile	250
10.22.2.1.1.2	With Formation of the 1—7a Bond	251
10.22.2.1.1.2.1	Method 1: From 1-(3-Pyridyl)-2-nitropropene and an Isocyanide	251
10.22.2.2	Synthesis by Substituent Modification	252
10.22.2.2.1	Substitution of Existing Substituents	252
10.22.2.2.1.1	Pyrrole Ring Substituents	252
10.22.2.2.1.1.1	Method 1: Modification of C-Nitrogen at C2	252
10.22.2.2.1.1.2	Method 2: Modification of N-Oxygen at N1	253
10.22.3	Product Subclass 3: 1,3-Dihydroazaindol-2-ones	
	J.-Y. Mérour and B. Joseph	
10.22.3	Product Subclass 3: 1,3-Dihydroazaindol-2-ones	257
10.22.3.1	Synthesis by Ring-Closure Reactions	257
10.22.3.1.1	By Annulation to a Pyridine	257
10.22.3.1.1.1	By Formation of Two N—C Bonds	257
10.22.3.1.1.1.1	With Formation of the 1—7a and 1—2 Bonds	257

10.22.3.1.1.1.1	Method 1: From 2-(2-Chloropyridin-3-yl)acetic Acid	257
10.22.3.1.1.2	By Formation of One N—C Bond and One C—C Bond	258
10.22.3.1.1.2.1	With Formation of the 1—2 and 2—3 Bonds	258
10.22.3.1.1.2.1.1	Method 1: From Lithiated <i>ortho</i> -Methylpyridinamines	258
10.22.3.1.1.2.2	With Formation of the 1—2 and 3—3a Bonds	259
10.22.3.1.1.2.2.1	Method 1: From a 2-Pyridylhydrazide	259
10.22.3.1.1.3	By Formation of Two C—C Bonds	260
10.22.3.1.1.3.1	With Formation of 2—3 and 3—3a Bonds	260
10.22.3.1.1.3.1.1	Method 1: From <i>N</i> -Pivaloylpyridinamines	260
10.22.3.1.1.4	By Formation of One N—C Bond	261
10.22.3.1.1.4.1	With Formation of the 1—7a Bond	261
10.22.3.1.1.4.1.1	Method 1: From 2-(2-Chloropyridin-3-yl)acetamide	261
10.22.3.1.1.4.1.2	Method 2: From 2-(2-Bromopyridin-3-yl)acetonitrile	262
10.22.3.1.1.4.1.3	Method 3: From 2-Hydroxy- <i>N</i> -morpholino-2-(3-pyridyl)acetamide	262
10.22.3.1.1.4.2	With Formation of the 1—2 Bond	264
10.22.3.1.1.4.2.1	Method 1: From a 2-(Nitropyridyl)malonate	264
10.22.3.1.1.4.2.2	Method 2: From a 2-Cyano-2-(3-nitropyridyl)acetate	267
10.22.3.1.1.4.2.3	Method 3: From (3-Nitropyridyl)acetonitriles	271
10.22.3.1.1.4.2.4	Method 4: From (3-Nitropyridyl)acetates	272
10.22.3.1.1.4.2.5	Method 5: From (2-Aminopyridin-3-yl)acetic Acid	275
10.22.3.1.1.5	By Formation of One C—C Bond	276
10.22.3.1.1.5.1	With Formation of the 3—3a Bond	276
10.22.3.1.1.5.1.1	Method 1: From <i>N</i> -(3-Bromopyridin-2-yl)alk-2-enamides	276
10.22.3.1.1.5.1.2	Method 2: From <i>N</i> -Pyridylpropanamides	276
10.22.3.1.1.5.1.3	Method 3: From <i>N</i> -(Halopyridyl) Amides	278
10.22.3.1.1.5.1.4	Method 4: From <i>N</i> -(2-Chloropyridin-3-yl)acetamides	280
10.22.3.1.1.5.1.5	Method 5: From a 2-Bromo- <i>N</i> -pyridylacetamide	280
10.22.3.1.1.5.1.6	Method 6: From a Pyridylcarbamoylmethyl Xanthate	281
10.22.3.1.1.5.1.7	Method 7: From Diethyl [2-[(2-Bromopyridin-3-yl)amino]-2-oxoethyl]phosphonate and an Aldehyde	284
10.22.3.2	Synthesis by Ring Transformation	285
10.22.3.2.1	From Other Heterocyclic Systems	285
10.22.3.2.1.1	Method 1: 1 <i>H</i> -Pyrrolopyridines by 3,3-Dibromination	285
10.22.3.2.1.2	Method 2: From a 1 <i>H</i> -Pyrrolo[2,3- <i>b</i>]pyridine by Enzymatic Oxidation	290
10.22.3.2.1.3	Method 3: From a 1 <i>H</i> -Pyrrolopyridine-2,3-dione	290
10.22.3.3	Synthesis by Substituent Modification	294
10.22.3.3.1	Substitution of Existing Substituents	294
10.22.3.3.1.1	Pyridine Ring Substituents	294
10.22.3.3.1.1.1	Modification of C-Halogen at C5	294

10.22.3.3.1.1.1.1	Method 1: Formation of C-Carbon	294
10.22.3.3.1.1.2	Modification of Nitrogen at N4	297
10.22.3.3.1.2.1	Method 1: Formation of N-Carbon	297
10.22.3.3.1.2	Pyrrole Ring Substituents	298
10.22.3.3.1.2.1.1	Substitution of C-Hydrogen at C3	298
10.22.3.3.1.2.1.1.1	Method 1: Formation of C-Carbon (Alkylation)	298
10.22.3.3.1.2.1.2	Method 2: Formation of C-Carbon (Alkenylation)	303
10.22.4	Product Subclass 4: 1,2-Dihydroazaindol-3-ones	New
	J.-Y. Mérour and B. Joseph	
10.22.4	Product Subclass 4: 1,2-Dihydroazaindol-3-ones	313
10.22.4.1	Synthesis by Ring-Closure Reactions	314
10.22.4.1.1	By Annulation to a Pyridine	314
10.22.4.1.1.1	By Formation of One N—C and One C—C Bond	314
10.22.4.1.1.1.1	With Formation of the 1—7a and 2—3 Bonds	314
10.22.4.1.1.1.1.1	Method 1: From a Pyridine Ester with an <i>ortho</i> -Amino Group	314
10.22.4.1.1.1.2	With Formation of the 3—3a and 1—2 Bonds	315
10.22.4.1.1.1.2.1	Method 1: From 3-Iodopyridin-2-amines and 1-Methoxyallene	315
10.22.4.1.1.2	By Formation of One N—C Bond	316
10.22.4.1.1.2.1	With Formation of the 1—7a Bond	316
10.22.4.1.1.2.1.1	Method 1: From (2-Chloropyridin-3-yl)(1 <i>H</i> -pyrrol-2-yl)methanone	316
10.22.4.1.1.3	By Formation of One C—C Bond	316
10.22.4.1.1.3.1	With Formation of the 2—3 Bond	316
10.22.4.1.1.3.1.1	Method 1: From an <i>N</i> -Pyridylglycine	316
10.22.4.1.2	By Annulation to a Pyrrole	318
10.22.4.1.2.1	By Formation of Two C—C Bonds	318
10.22.4.1.2.1.1	With Formation of the 4—5 and 6—7 Bonds	318
10.22.4.1.2.1.1.1	Method 1: From a Masked 2-Amino-4-oxo-1 <i>H</i> -pyrrole-3-carbaldehyde ..	318
10.22.4.2	Synthesis by Ring Transformation	319
10.22.4.2.1	From Other Heterocyclic Systems	319
10.22.4.2.1.1	Method 1: From a Tetrazolo[1,5- <i>a</i>]pyridine	319
10.22.4.2.1.2	Method 2: From a 1 <i>H</i> -Pyrrolo[2,3- <i>b</i>]pyridine-3-carbaldehyde	319
10.22.4.3	Synthesis by Substituent Modification	320
10.22.4.3.1	Substitution of Existing Substituents	320
10.22.4.3.1.1	Pyrrole Ring Substituents	320
10.22.4.3.1.1.1	Modification of C-Oxygen at C3	320
10.22.4.3.1.1.1.1	Method 1: Formation of O-Carbon	320
10.22.4.3.1.1.2	Substitution of C-Hydrogen at C2	321

10.22.4.3.1.1.2.1	Method 1: Formation of C-Carbon	321
10.22.4.3.1.1.3	Modification of Nitrogen at N1	323
10.22.4.3.1.1.3.1	Method 1: Formation of N-Carbon	323
10.22.5	Product Subclass 5: 1<i>H</i>-Azaindole-2,3-diones	New
	J.-Y. Mérour and B. Joseph	
10.22.5	Product Subclass 5: 1<i>H</i>-Azaindole-2,3-diones	325
10.22.5.1	Synthesis by Ring-Closure Reactions	326
10.22.5.1.1	By Annulation to a Pyridine	326
10.22.5.1.1.1	By Formation of One N—C Bond	326
10.22.5.1.1.1.1	With Formation of the 1—2 Bond	326
10.22.5.1.1.1.1.1	Method 1: From [4-[(<i>tert</i> -Butoxycarbonyl)amino]pyridin-3-yl]glyoxylate	326
10.22.5.2	Synthesis by Ring Transformation	326
10.22.5.2.1	From Other Heterocyclic Systems	326
10.22.5.2.1.1	Method 1: From a 1,3-Dihydro-2 <i>H</i> -pyrrolopyridin-2-one	326
10.22.5.2.1.2	Method 2: From a Pyrrolopyridine	329
10.22.5.3	Synthesis by Substituent Modification	335
10.22.5.3.1	Substitution of Existing Substituents	335
10.22.5.3.1.1	Pyridine Ring Substituents	335
10.22.5.3.1.1.1	Substitution of C-Hydrogen at C5	335
10.22.5.3.1.1.1.1	Method 1: Giving C-Halogen	335
10.22.5.3.1.2	Pyrrole Ring Substituents	336
10.22.5.3.1.2.1	Substitution of N-Hydrogen at N1	336
10.22.5.3.1.2.1.1	Method 1: Formation of N-Carbon	336
10.22.6	Product Subclass 6: Azaindol-2- and Azaindol-3-amines	New
	J.-Y. Mérour and B. Joseph	
10.22.6	Product Subclass 6: Azaindol-2- and Azaindol-3-amines	339
10.22.6.1	Synthesis by Ring-Closure Reactions	339
10.22.6.1.1	By Annulation to a Pyridine	339
10.22.6.1.1.1	By Formation of One N—C and One C—C Bond	339
10.22.6.1.1.1.1	With Formation of the 1—2 and 3—3a Bonds	339
10.22.6.1.1.1.1.1	Method 1: From a 2-Halo-3-nitropyridine and a 2-Cyanoacetamide	339
10.22.6.1.1.1.2	With Formation of the 1—2 and 2—3 Bonds	340
10.22.6.1.1.1.2.1	Method 1: From Aminopyridine-3-carbonitriles	340
10.22.6.1.1.2	By Formation of One N—C Bond	341
10.22.6.1.1.2.1	With Formation of the 1—2 Bond	341
10.22.6.1.1.2.1.1	Method 1: From an Ethyl 2-Cyano-2-(3-nitropyridyl)acetate	341

10.22.6.1.2.1.2	Method 2: From a 2-[3-(Alkylamino)pyridin-2-yl]acetonitrile	342
10.22.6.1.2.1.3	Method 3: From 3-Ethynyl-N-methylpyridin-2-amine	343
10.22.6.1.1.3	By Formation of One C—C Bond	344
10.22.6.1.1.3.1	With Formation of the 2—3 Bond	344
10.22.6.1.1.3.1.1	Method 1: From Substituted 2-Aminopyridine-3-carbonitriles	344
10.22.6.2	Synthesis by Ring Transformation	345
10.22.6.2.1	From Other Heterocyclic Systems	345
10.22.6.2.1.1	Method 1: From a Pyrrolopyridine	345
10.22.6.2.1.1.1	Variation 1: From a Halopyrrolopyridine	345
10.22.6.2.1.1.2	Variation 2: Via Nitrosation	346
10.22.6.2.1.1.3	Variation 3: Via Diazonium Coupling	348
10.22.6.2.1.1.4	Variation 4: By Reduction of Nitro Groups	349
10.22.6.2.1.1.5	Variation 5: Via Azidation	352
10.22.6.2.1.2	Method 2: From a 1,2,3-Dithiazole	354

Volume 21:

Three Carbon—Heteroatom Bonds: Amides and Derivatives; Peptides; Lactams

21.17	Synthesis of Amides (Including Peptides) in Continuous-Flow Reactors	New
	S. Ramesh, P. Cherkupally, T. Govender, H. G. Kruger, B. G. de la Torre, and F. Albericio	
21.17	Synthesis of Amides (Including Peptides) in Continuous-Flow Reactors	357
21.17.1	Microreactors: A Faster Tool for Synthesis Laboratories	358
21.17.2	Amide Formation in Microflow Reactors: Exploring Different Possibilities	359
21.17.2.1	Peptide Synthesis	359
21.17.2.1.1	Method 1: Synthesis of Di- and Tripeptides in Solution	359
21.17.2.1.2	Method 2: Synthesis of Di- and Tripeptides Using Immobilized Reagents	362
21.17.2.1.3	Method 3: β -Peptide Synthesis Using Fluorine-Activated Amino Acids	364
21.17.2.1.4	Method 4: Peptide Synthesis Using Triphosgene as the Activating Agent	366
21.17.2.1.5	Method 5: Cyclization of Peptides Driven by Microfluidics	369
21.17.2.1.6	Method 6: Analysis of Racemization During Peptide Formation	371
21.17.2.2	Synthesis of Drugs	371
21.17.2.3	Carbonylation Reactions	373
21.17.2.4	Lactam Synthesis	375
21.17.2.5	Dendrimer Synthesis	375
21.17.2.6	Miscellaneous Syntheses of Amides	377

Volume 27:

Heteroatom Analogues of Aldehydes and Ketones

27.19	Product Class 19: Azomethine Imines	
<hr/>		
27.19.5	Azomethine Imines	2017
I. Atodiresei and M. Rueping		
<hr/>		
27.19.5	Azomethine Imines	381
27.19.5.1	Acyclic Azomethine Imines	381
27.19.5.1.1	Synthesis and Applications of Acyclic Azomethine Imines	381
27.19.5.1.1.1	Method 1: In Situ Generation from Hydrazones Followed by [3 + 2] Cycloaddition	382
27.19.5.1.1.1.1	Variation 1: In Situ Generation from Hydrazones with Boron Trifluoride-Diethyl Ether Complex and Subsequent Intramolecular [3 + 2] Cycloaddition	382
27.19.5.1.1.1.2	Variation 2: In Situ Generation from Hydrazones with Iodosylbenzene and Subsequent [3 + 2] Cycloaddition with Imines	384
27.19.5.1.1.2	Method 2: In Situ Generation from Aldehydes and Hydrazides	385
27.19.5.1.1.2.1	Variation 1: In Situ Generation from Aldehydes and Hydrazides and Reaction with Nucleophiles	385
27.19.5.1.1.2.2	Variation 2: In Situ Generation from Aldehydes and Hydrazides and Intermolecular [3 + 2] Cycloaddition with Alkynes	387
27.19.5.2	Azomethine Imines with C—N Incorporated in a Ring	388
27.19.5.2.1	Synthesis and Applications of Azomethine Imines with C—N Incorporated in a Ring	388
27.19.5.2.1.1	Method 1: Synthesis of Cyclic Azomethine Imines from 2-(2-Bromoethyl)benzaldehydes and Benzoylhydrazine	388
27.19.5.2.1.2	Method 2: Synthesis of Cyclic Azomethine Imines by Intramolecular Cyclization	390
27.19.5.2.1.2.1	Variation 1: Synthesis of Cyclic Azomethine Imines from Alkynyl Hydrazides	390
27.19.5.2.1.2.2	Variation 2: Synthesis of Cyclic Azomethine Imines from γ,δ -Unsaturated N-Trichloroacetyl and N-Trifluoroacetyl Hydrazones	391
27.19.5.2.1.3	Method 3: Synthesis of Cyclic Azomethine Imines from Pyridine Derivatives	392
27.19.5.2.1.3.1	Variation 1: Synthesis of N-Benzoyl- and N-Tosyliminopyridinium Ylides from Pyridines by Amination and Acylation	392
27.19.5.2.1.3.2	Variation 2: Synthesis of N-Tosyliminopyridinium Ylides from Pyridines by Metal-Catalyzed Imination with [N-(4-Toluenesulfonyl)imino]-phenyliodinane	394
27.19.5.2.1.4	Method 4: Metal-Catalyzed Synthesis of Cyclic Azomethine Imines from N'-(2-Alkynylbenzylidene) Hydrazides	395

27.19.5.3	Azomethine Imines with N—N Incorporated in a Ring	397
27.19.5.3.1	Synthesis and Applications of Azomethine Imines with N—N Incorporated in a Ring	397
27.19.5.3.1.1	Method 1: Synthesis from Hydrazones and Alkenes	397

Volume 35: Chlorine, Bromine, and Iodine

35.1	Product Class 1: One Saturated Carbon—Chlorine Bond	
35.1.5.1.12	Synthesis of 1-Chloro-n-Heteroatom-Functionalized Alkanes ($n \geq 2$) by Addition across C=C Bonds	2017
	T. Wirth and F. V. Singh	
35.1.5.1.12	Synthesis of 1-Chloro-n-Heteroatom-Functionalized Alkanes ($n \geq 2$) by Addition across C=C Bonds	403
35.1.5.1.12.1	Method 1: Dichlorination of Alkenes	403
35.1.5.1.12.1.1	Variation 1: Using Manganese(III)/Hydrochloric Acid as the Chlorine Source	403
35.1.5.1.12.1.2	Variation 2: Using an Iodine(III) Reagent as the Chlorine Source	405
35.1.5.1.12.1.3	Variation 3: Using Organic Chlorides as the Chlorine Source	406
35.1.5.1.12.1.4	Variation 4: Using Alkali Metal Chlorides as the Chlorine Source	409
35.1.5.1.12.1.5	Variation 5: Using N-Chlorosuccinimide as the Chlorine Source	411
35.1.5.1.12.1.6	Variation 6: Using a Carbene–Palladium(IV) Chloride Complex as the Chlorine Source	412
35.1.5.1.12.1.7	Variation 7: Organocatalyzed Dichlorination of Alkenes	413
35.1.5.1.12.2	Method 2: Aminochlorination of Alkenes	415
35.1.5.1.12.2.1	Variation 1: Carbon Dioxide Promoted Aminochlorination of Alkenes Using Chloramine-T as the Source of Chlorine and Nitrogen ..	416
35.1.5.1.12.2.2	Variation 2: Transition-Metal-Catalyzed Aminochlorination of Alkenes ..	417
35.1.5.1.12.2.3	Variation 3: Asymmetric Catalytic Aminochlorination of α,β -Unsaturated γ -Oxo Esters	419
35.1.5.1.12.2.4	Variation 4: Selenium-Catalyzed Chloroamidation of Alkenes	422
35.1.5.1.12.2.5	Variation 5: Photocatalytic Aminochlorination of Alkenes	423
35.1.5.1.12.3	Method 3: Halochlorination of Alkenes	424
35.1.5.1.12.3.1	Variation 1: Iodochlorination of Styrene Using Tetramethylammonium Dichloroiodate	424
35.1.5.1.12.3.2	Variation 2: Copper-Catalyzed Bromochlorination of Styrene Using Tetrabutylammonium Dichlorobromate	425
35.1.5.1.12.3.3	Variation 3: Catalytic Enantioselective Bromochlorination of Allylic Alcohols	425
35.1.5.1.12.4	Method 4: Oxychlorination of Alkenes	427
35.1.5.1.12.4.1	Variation 1: Thiourea Catalyzed Methoxychlorination of Alkenes	427
35.1.5.1.12.4.2	Variation 2: Iodine(III)-Mediated Methoxychlorination of Alkenes	428

35.1.5.1.12.4.3	Variation 3:	(Diacetoxyiodo)benzene-Mediated Ethoxychlorination of Enamides	429
35.1.5.1.12.4.4	Variation 4:	Organocatalytic Enantioselective Chlorocyclization of Unsaturated Amides	430
35.1.5.1.12.5	Method 5:	Chloroselanylation of Alkenes	432
35.1.5.1.12.5.1	Variation 1:	β -Chloroselanylation of Alkenes with <i>N,N</i> -Diethylbenzeneselenenamide in the Presence of Phosphoryl Chloride or Thionyl Chloride	432
35.1.5.1.12.5.2	Variation 2:	Chloroselanylation of Alkenes with Phenylselenenyl Chloride ..	433
35.1.5.1.12.6	Method 6:	Sulfanylchlorination of Alkenes	434
35.1.5.1.12.7	Method 7:	Trihalomethylchlorination of Alkenes	435
35.1.5.1.12.7.1	Variation 1:	Trichloromethylchlorination of Alkenes with Trichloromethanesulfonyl Chloride	435
35.1.5.1.12.7.2	Variation 2:	Trichloromethylchlorination of Alkenes in Subcritical Carbon Tetrachloride	436
35.1.5.1.12.7.3	Variation 3:	Copper/Ruthenium-Catalyzed Trifluoromethylchlorination of Alkenes	437
35.1.5.1.12.8	Method 8:	Azidochlorination of Alkenes	438
35.1.5.1.12.8.1	Variation 1:	Azidochlorination of Alkenes with Sodium Azide in the Presence of Sodium Hypochlorite and Acetic Acid	438
35.1.5.1.12.9	Method 9:	Chlorodiacetylation of Alkenes	440
35.1.5.1.12.9.1	Variation 1:	Chlorodiacetylation of Cycloalkenes with Acetylacetone and Manganese(III) Acetate in the Presence of Hydrochloric Acid ..	440

35.2 Product Class 2: One Saturated Carbon—Bromine Bond

35.2.1.5.7 Synthesis of Bromoalkanes by Substitution of Oxygen Functionalities
2017

M. Braun

35.2.1.5.7	Synthesis of Bromoalkanes by Substitution of Oxygen Functionalities ..		443
35.2.1.5.7.1	Method 1:	Substitution of Alcoholic Hydroxy Groups	443
35.2.1.5.7.1.1	Variation 1:	Reaction of Alcohols with Oxalyl Chloride and Lithium Bromide under Catalysis by Triphenylphosphine Oxide	443
35.2.1.5.7.1.2	Variation 2:	Reaction of Alcohols with Diethyl Bromomalonate and Diphenylsilane under Catalysis of 5-Phenyldibenzophosphole ..	444
35.2.1.5.7.1.3	Variation 3:	Reaction of Primary Alcohols with 7,7-Dichlorocyclohepta-1,3,5-triene and Tetrabutylammonium Bromide	445
35.2.1.5.7.1.4	Variation 4:	Reaction of Alcohols with 2,2-Dibromo-1,3-dicyclohexylimidazolidine-4,5-dione	446
35.2.1.5.7.1.5	Variation 5:	Reaction of Alcohols with <i>tert</i> -Butyl Bromide in the Ionic Liquid 3-Methyl-1-pentylimidazolium Bromide	447
35.2.1.5.7.2	Method 2:	Cleavage of Silyl- and Tetrahydropyranyl-Protected Alcohols ..	448
35.2.1.5.7.2.1	Variation 1:	Reaction of Tetrahydropyranyl Ethers with Dibromotriphenylphosphorane	448

35.2.1.5.7.2.2	Variation 2:	Reaction of Tetrahydropyranyl and Silyl Ethers with N-Bromosaccharin–Triphenylphosphine	450	
35.2.1.5.7.2.3	Variation 3:	Reaction of Tetrahydropyranyl and Silyl Ethers in Ionic Liquids	451	
35.2.1.5.7.3	Method 3:	Substitution of Sulfonyloxy Groups	452	
35.2.1.5.7.3.1	Variation 1:	Reaction of Arene- or Methanesulfonates with Lithium Bromide in Tetrahydrofuran	452	
35.2.1.5.7.3.2	Variation 2:	Reaction of Methanesulfonates with Magnesium Bromide–Diethyl Ether Complex	453	
35.2.1.5.7.3.3	Variation 3:	Reaction of Arene- or Methanesulfonates with the Ionic Liquid 1-Butyl-3-methylimidazolium Bromide	454	
35.2.2.2	Propargylic Bromides		2017	
	M. Braun			
35.2.2.2	Propargylic Bromides		457	
35.2.2.2.1	Method 1:	Synthesis by Heteroatom Substitution: Substitution of Hydroxy or Tetrahydropyranyl Ether Groups	457	
35.2.2.2.1.1	Variation 1:	Reaction of Propargylic Alcohols with Phosphorus Tribromide in Perfluorohexane	458	
35.2.3.3.3	Synthesis of Benzylic Bromides by Substitution of σ-Bonded Heteroatoms		2017	
	M. Braun			
35.2.3.3.3	Synthesis of Benzylic Bromides by Substitution of σ-Bonded Heteroatoms		461	
35.2.3.3.3.1	Method 1:	Substitution of Oxygen Functionalities	461	
35.2.3.3.3.1.1	Variation 1:	Reaction of (Hydroxymethyl)phenols with 2,4,6-Trichloro-1,3,5-triazine and Sodium Bromide	464	
35.2.3.3.3.1.2	Variation 2:	Reaction of Benzylic Alcohols with Poly(vinylpyrrolidin-2-one)–Bromine Complex and Hexamethyldisilane	465	
35.2.3.3.3.1.3	Variation 3:	Reaction of Benzylic Alcohols with Monolithic Triphenylphosphine Reagent and Carbon Tetrabromide	466	
35.2.4.2.3	Synthesis of Allylic Bromides by Substitution of σ-Bonded Heteroatoms		2017	
	M. Braun			
35.2.4.2.3	Synthesis of Allylic Bromides by Substitution of σ-Bonded Heteroatoms		469	
35.2.4.2.3.1	Method 1:	Substitution of Other Halogens	469	
35.2.4.2.3.1.1	Variation 1:	Reaction of Allylic Chlorides with 1,2-Dibromoethane under Rhodium Catalysis	469	
35.2.4.2.3.2	Method 2:	Substitution of Hydroxy Groups	469	
Author Index				473
Abbreviations				491