

Table of Contents

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

4.4	Product Class 4: Silicon Compounds		
4.4.43	Product Subclass 43: Silylium Ions and Stabilized Silylium Ions		(New)
	T. Müller		
4.4.43	Product Subclass 43: Silylium Ions and Stabilized Silylium Ions	1
	Synthesis of Product Subclass 43	5
4.4.43.1	Method 1:	Heterolytic Cleavage of Si—Hal Bonds	5
4.4.43.2	Method 2:	Heterolytic Cleavage of Si—H Bonds	6
4.4.43.2.1	Variation 1:	By Hydride Transfer in Aromatic Hydrocarbons	7
4.4.43.2.2	Variation 2:	By Hydride Transfer in Silanes	10
4.4.43.2.3	Variation 3:	By Hydride Transfer in Halogenated Hydrocarbons	10
4.4.43.2.4	Variation 4:	By Hydride Transfer with Subsequent Intermolecular Sub- stituent Exchange	12
4.4.43.3	Method 3:	Heterolytic Cleavage of Si—C Bonds	13
4.4.43.4	Method 4:	Heterolytic Cleavage of Si—Si Bonds	14
4.4.43.5	Method 5:	Oxidation of Disilanes and Silyl Radicals	15
4.4.43.6	Method 6:	Addition of Electrophiles to Silylenes	15
	Applications of Product Subclass 43 in Organic Synthesis	16
4.4.43.7	Method 7:	Addition Reactions	16
4.4.43.7.1	Variation 1:	Addition to Lewis Bases with Formation of Onium Ions	16
4.4.43.7.2	Variation 2:	Addition to Lewis Bases with Formation of Brønsted Super- acids and Strong Alkylating Reagents	18
4.4.43.7.3	Variation 3:	Addition to C—C Unsaturated Compounds	19
4.4.43.8	Method 8:	Hydrosilylation Reactions	21
4.4.43.9	Method 9:	C—F Bond Activation Reactions	27
4.4.43.10	Method 10:	Lewis Acid Catalysis	36
4.4.44	Product Subclass 44: Silyl Radicals		(New)
	Y. Landais		
4.4.44	Product Subclass 44: Silyl Radicals	43
	Synthesis of Product Subclass 44	45
4.4.44.1	Method 1:	Synthesis from Silanes	45
4.4.44.1.1	Variation 1:	Hydrogen Abstraction Using Carbon-Centered Radicals	45
4.4.44.1.2	Variation 2:	Hydrogen Abstraction through [1,5]-Hydrogen Transfer	48
4.4.44.1.3	Variation 3:	Hydrogen Abstraction Using Oxygen-Centered Radicals	51

(2013) Updated Section · (2013) Completely Revised Contributions · (New) New Contributions

4.4.44.1.4	Variation 4:	Polarity-Reversal Catalysis	54
4.4.44.2	Method 2:	Synthesis from Disilanes	56
4.4.44.2.1	Variation 1:	Photolysis of the Silicon—Silicon Bond	56
4.4.44.2.2	Variation 2:	Thermal Cleavage of the Silicon—Silicon Bond	57
4.4.44.3	Method 3:	Synthesis from Silyl Metal Compounds	58
4.4.44.3.1	Variation 1:	From Silyllithiums and Silylsodium Reagents	58
4.4.44.3.2	Variation 2:	From Silylaluminum Reagents	60
4.4.44.3.3	Variation 3:	From Silylmercury Reagents	60
4.4.44.4	Method 4:	Synthesis from Carbosilanes	61
4.4.44.4.1	Variation 1:	From Allylsilanes	61
4.4.44.4.2	Variation 2:	From 1-Silylcyclohexa-2,5-dienes	63
4.4.44.4.3	Variation 3:	From Benzylsilanes	63
4.4.44.5	Method 5:	Synthesis through Cleavage of Silicon—Heteroatom Bonds	64
4.4.44.5.1	Variation 1:	Homolytic Cleavage of the Silicon—Boron Bond	64
4.4.44.5.2	Variation 2:	Homolytic Cleavage of the Silicon—Phosphorus Bond	65
4.4.44.5.3	Variation 3:	Homolytic Cleavage of the Silicon—Selenium Bond	66
4.4.44.6	Method 6:	Single-Electron Reduction of Silyl Halides	68
4.4.44.7	Method 7:	Reduction of Silylium Ions	69
4.4.44.8	Method 8:	Addition of Radicals to Silylenes	69
4.4.44.9	Method 9:	Reduction of Disilenes	71
4.4.44.10	Method 10:	Rearrangements	72
4.4.44.10.1	Variation 1:	1,4- and 1,5-Aryl Migration from Silicon to Carbon	72
4.4.44.10.2	Variation 2:	1,2-Aryl Migration from Silicon to Oxygen	74
4.4.44.10.3	Variation 3:	1,2-Silicon Group Migration from Silicon to Carbon	76
4.4.44.10.4	Variation 4:	1,2- and 1,3-Silicon Group Migration from Silicon to Oxygen	76
4.4.44.10.5	Variation 5:	1,2- and 1,3-Silicon Group Migration from Silicon to Sulfur	77
4.4.44.10.6	Variation 6:	Intramolecular Homolytic Substitution	79
		Applications of Product Subclass 44 in Organic Synthesis	81
4.4.44.11	Method 11:	Silyl Radicals in Reduction Processes	81
4.4.44.12	Method 12:	Addition of Silyl Radicals to Unsaturated Systems	83
4.4.44.13	Method 13:	Formation of Carbon—Carbon Bonds	84
4.4.44.14	Method 14:	Formation of Carbon—Heteroatom Bonds	86
4.4.44.15	Method 15:	Radical Cascades Mediated by Silyl Radicals	86
4.4.44.16	Method 16:	Rearrangement Processes	88
4.4.45	Product Subclass 45: Silanecarboxylic Acids and Esters		New
	K. Igawa and K. Tomooka		
4.4.45	Product Subclass 45: Silanecarboxylic Acids and Esters		93
	Synthesis of Product Subclass 45		94
4.4.45.1	Method 1:	Carboxylation of Silyl Anions	94
4.4.45.1.1	Variation 1:	Reduction of Chlorosilanes with Lithium Metal and Subsequent Carboxylation	95
4.4.45.1.2	Variation 2:	Reduction of Chlorosilanes with Lithium Arenides and Subsequent Carboxylation	95
	Applications of Product Subclass 45 in Organic Synthesis		96

4.4.45.2	Method 2:	Decomposition of Silanecarboxylic Acids as a Source of Carbon Monoxide	96
4.4.45.3	Method 3:	Esterification of Silanecarboxylic Acids	96
4.4.45.3.1	Variation 1:	Esterification of Silanecarboxylic Acids with Diazoalkanes	97
4.4.45.3.2	Variation 2:	Esterification of Silanecarboxylic Acids by Mitsunobu Reaction	97

Volume 6: Boron Compounds

6.1	Product Class 1: Boron Compounds		
6.1.6	Product Subclass 6: Haloborates		2013
	G. A. Molander and F. Beaumard		
6.1.6	Product Subclass 6: Haloborates		101
	Synthesis of Product Subclass 6		102
6.1.6.1	Aryl- and Hetaryltrifluoroborates		102
6.1.6.1.1	Method 1:	Transmetalation	102
6.1.6.1.1.1	Variation 1:	Metalation/Electrophilic Borylation	102
6.1.6.1.1.2	Variation 2:	Directed Metalation/Electrophilic Borylation	104
6.1.6.1.2	Method 2:	Miyaura Borylation	105
6.1.6.1.2.1	Variation 1:	Using Dialkoxyboranes	105
6.1.6.1.2.2	Variation 2:	Using Bisboronates	106
6.1.6.1.2.3	Variation 3:	Using Tetrahydroxydiboron	108
6.1.6.1.2.4	Variation 4:	Using Tetrakis(dimethylamino)diboron	111
6.1.6.1.3	Method 3:	C—H Activation/Electrophilic Borylation	113
6.1.6.2	Alkenyltrifluoroborates		114
6.1.6.2.1	Method 1:	Metalation/Electrophilic Borylation	114
6.1.6.2.2	Method 2:	Hydroboration	115
6.1.6.2.2.1	Variation 1:	Using Diorganoboranes	115
6.1.6.2.2.2	Variation 2:	Using Diorganooxyboranes	115
6.1.6.2.2.3	Variation 3:	Using Dihaloboranes	116
6.1.6.3	Alkynyltrifluoroborates		117
6.1.6.3.1	Method 1:	Deprotonation of Terminal Alkynes/Borylation of Alkynylmetals	117
6.1.6.3.2	Method 2:	Dehydrohalogenation of Alkenes	118
6.1.6.3.3	Method 3:	Dehydrohalogenation of Alkanes	119
6.1.6.4	Alkyltrifluoroborates		119
6.1.6.4.1	Method 1:	Metalation/Electrophilic Borylation	119
6.1.6.4.2	Method 2:	Hydroboration	122
6.1.6.4.3	Method 3:	C—H Activation/Borylation	124
6.1.6.4.4	Method 4:	1,4-Addition	125
6.1.6.4.5	Method 5:	C-Alkylation of Enolates	127
6.1.6.4.6	Method 6:	α -Halo Transfer of Nitrogen-Based Nucleophiles	128

6.1.6.4.6.1	Variation 1: (Carboxamidomethyl)trifluoroborates	128
6.1.6.4.6.2	Variation 2: (Sulfonamidomethyl)trifluoroborates	129
6.1.6.4.6.3	Variation 3: (Carbamatomethyl)trifluoroborates	130
6.1.6.4.7	Method 7: Borylation of Alkyl Halides	131
6.1.6.4.8	Method 8: Borylation of Aldehydes	132
6.1.6.5	Allyltrifluoroborates	134
6.1.6.5.1	Method 1: Metalation/Electrophilic Borylation	134
6.1.6.5.2	Method 2: Palladium-Catalyzed Reactions	135
6.1.6.5.2.1	Variation 1: Using Baylis-Hillman Adducts	135
6.1.6.5.2.2	Variation 2: Using Allylic Alcohols	136
6.1.6.6	Benzyltrifluoroborates	137
6.1.6.6.1	Method 1: Transmetalation and Metalation/Electrophilic Borylation	137
6.1.6.7	Propargyltrifluoroborates	138
6.1.6.7.1	Method 1: Metalation/Transmetalation	138
6.1.6.8	Acyltrifluoroborates	138
6.1.6.8.1	Method 1: Transmetalation from Metalated Alkenyl Ethers and Hydrolysis	138
6.1.6.8.2	Method 2: Alkylation of Functionalized Carbanions	139
	Applications of Product Subclass 6 in Organic Synthesis	140
6.1.6.9	Modification of Potassium Trifluoroborates	140

Volume 14: Six-Membered Heteroarenes with One Chalcogen

14.1	Product Class 1: Pirylium Salts	
14.1.5	Pirylium Salts	2013
	A. T. Balaban and T. S. Balaban	
14.1.5	Pirylium Salts	145
14.1.5.1	Synthesis by Ring-Closure Reactions	148
14.1.5.1.1	By Formation of One O—C and Two C—C Bonds	148
14.1.5.1.1.1	Method 1: [C ₁ + C ₃ + C ₁] Diacylation of Acyclic Propene Derivatives	148
14.1.5.1.1.2	Method 2: [C ₂ + C ₁ + C ₂] Condensation of Methyl(ene) Ketones with Aldehydes	150
14.1.5.1.1.3	Method 3: Formation of Metalated Pirylium Salts from Metalated Ortho Esters and Enol Ethers of Methyl(ene) Ketones	172
14.1.5.1.2	By Formation of Two O—C Bonds	173
14.1.5.1.2.1	Method 1: Formation of Pirylium Rings from Substituted Cyclopentadienes	173
14.1.5.1.3	By Formation of One O—C and One C—C Bond	175

14.1.5.1.3.1	Method 1:	[C ₃ + C ₂] Synthesis from Methyl(ene) Ketones and α,β -Unsaturated Ketones Followed by Dehydrocyclization	175
14.1.5.1.3.2	Method 2:	From Ketones or Their Synthetic Equivalents and β -Chloro α,β -Unsaturated Ketones or Aldehydes	179
14.1.5.1.3.3	Method 3:	Formation of Metalated Pirylium Salts from Alkynes and Propargylic Esters	180
14.1.5.1.3.4	Method 4:	Formation of Pirylium Pseudobases by Alkene Cross Metathesis	182
14.1.5.1.4	[C ₄ + C ₁]:	Formation of a C ₅ Chain from Two Synthons	183
14.1.5.1.4.1	Method 1:	From α,β - or β,γ -Unsaturated Ketones and Carboxylic Acid Derivatives	183
14.1.5.1.4.2	Method 2:	2,4,6-Triarylpyrylium Salts from Acetophenone Derivatives by Cleavage of an Aroyl Group from an Initially Formed 1,3-Diarylbut-2-en-1-one Derivative	184
14.1.5.1.5	By Formation of One O—C Bond		184
14.1.5.1.5.1	Formation of Pirylium Rings by Closure of a Preformed Acyclic C ₅ Chain		184
14.1.5.1.5.1.1	Method 1:	Formation of Pirylium Salts from Pent-2-ene-1,5-diones (Pirylium Pseudobases) and 1,5-Dioates	185
14.1.5.1.5.1.2	Method 2:	Formation of Pirylium Salts by Dehydrocyclization of Penta-2,4-dienals	185
14.1.5.1.5.1.3	Method 3:	Formation of Pirylium Salts by Dehydrocyclizations of Pentane-1,5-diones	186
14.1.5.2	Aromatization		195
14.1.5.2.1	By Hydride Abstraction from a Preformed Pyran System		195
14.1.5.2.1.1	Method 1:	Formation of Pirylium Salts by Hydride Abstraction from a 4 <i>H</i> -Pyran	195
14.1.5.2.1.2	Method 2:	Formation of Pirylium Salts by Addition to 2,6-Disubstituted Pirylium Cations	197
14.1.5.2.1.3	Method 3:	Benzotriazole-Mediated Derivatization of 2,6-Disubstituted Pirylium Salts in the 4-Position by Electrophiles	200
14.1.5.2.1.4	Method 4:	Formation of Pirylium Salts by Wittig Reaction between 2,6-Disubstituted Pirylium Cations and Aldehydes	202
14.1.5.3	Synthesis by Substituent Modification		204
14.1.5.3.1	Method 1:	Modification of 2- or 4-(Arylviny)pyrylium Salts	204
14.1.5.3.2	Method 2:	Modification of Pirylium Salts by Metalation of 2- or 4-Methyl Groups	210
14.1.5.3.3	Method 3:	Formation of 4- or 2-(Azulen-1-yl)pyrylium Salts	210
14.1.5.3.4	Method 4:	Suzuki–Miyaura Reactions	211

Volume 18:
**Four Carbon—Heteroatom Bonds: $X-C\equiv X$, $X=C=X$,
 $X_2C=X$, CX_4**

18.8	Product Class 8: Acyclic and Cyclic Ureas	
18.8.22	Acyclic and Cyclic Ureas	2013
	S. Kubik	
18.8.22	Acyclic and Cyclic Ureas	217
18.8.22.1	Acyclic Unfunctionalized Ureas	218
18.8.22.1.1	Synthesis of Acyclic Unfunctionalized Ureas	218
18.8.22.1.1.1	Method 1: From Isocyanates or Isothiocyanates	218
18.8.22.1.1.1.1	Variation 1: From Isocyanates and Amines	218
18.8.22.1.1.1.2	Variation 2: From Isothiocyanates, Amines, and Hydrogen Peroxide	219
18.8.22.1.1.1.3	Variation 3: From Isocyanates via Carbodiimides	220
18.8.22.1.1.2	Method 2: From Cyanate Salts	221
18.8.22.1.1.3	Method 3: From Carboxylic Acids	223
18.8.22.1.1.3.1	Variation 1: Without Trapping of the Isocyanate	223
18.8.22.1.1.3.2	Variation 2: With Trapping of the Isocyanate	224
18.8.22.1.1.4	Method 4: From Amides	226
18.8.22.1.1.5	Method 5: From Hydroxamic Acids	227
18.8.22.1.1.6	Method 6: From Phosgene or Bis(trichloromethyl) Carbonate	228
18.8.22.1.1.7	Method 7: From Chloroformates	230
18.8.22.1.1.8	Method 8: From Carbamoylimidazoles or Carbamoylimidazolium Salts ..	231
18.8.22.1.1.9	Method 9: From Carbonates or Dithiocarbonates	233
18.8.22.1.1.9.1	Variation 1: From 1,3-Dioxolan-2-one	233
18.8.22.1.1.9.2	Variation 2: From S,S-Dimethyl Dithiocarbonate	233
18.8.22.1.1.10	Method 10: From Carbamates	235
18.8.22.1.1.11	Method 11: From Ureas or Thioureas	236
18.8.22.1.1.11.1	Variation 1: By Alkylation of Ureas	236
18.8.22.1.1.11.2	Variation 2: By Arylation of Ureas	237
18.8.22.1.1.11.3	Variation 3: By Transamidation of Ureas	240
18.8.22.1.1.11.4	Variation 4: By Desulfurization of Thioureas	241
18.8.22.1.1.12	Method 12: From Carbon Monoxide	241
18.8.22.1.1.12.1	Variation 1: With Catalysis by Transition Metals	241
18.8.22.1.1.12.2	Variation 2: With Catalysis by Main Group Elements	244
18.8.22.1.1.13	Method 13: From Carbon Dioxide	246
18.8.22.1.1.14	Method 14: Miscellaneous Methods	248
18.8.22.2	Imidazolidin-2-ones and Other Unfunctionalized Five-Membered Cyclic Ureas ..	249
18.8.22.2.1	Synthesis of Imidazolidin-2-ones and Other Unfunctionalized Five-Membered Cyclic Ureas	250
18.8.22.2.1.1	Method 1: From Alkenes	252
18.8.22.2.1.2	Method 2: Miscellaneous Methods	255

18.8.22.3	Tetrahydropyrimidin-2(1 <i>H</i>)-ones and Other Unfunctionalized Six-Membered Cyclic Ureas	257
18.8.22.3.1	Synthesis of Tetrahydropyrimidin-2(1 <i>H</i>)-ones and Other Unfunctionalized Six-Membered Cyclic Ureas	257
18.8.22.3.1.1	Method 1: From 1,3-Diamines	257
18.8.22.3.1.2	Method 2: From a β -Oxo Ester, an Aldehyde, and Urea (Biginelli Reaction)	257
18.8.22.3.1.3	Method 3: Miscellaneous Methods	261
18.8.22.4	1,3-Diazepan-2-one and Other Unfunctionalized Seven-Membered Cyclic Ureas	262
18.8.22.4.1	Synthesis of 1,3-Diazepan-2-one and Other Unfunctionalized Seven-Membered Cyclic Ureas	262
18.8.22.5	Acyclic <i>N</i> -Acyl-, <i>N,N</i> -Diacyl-, and <i>N,N'</i> -Diacylureas	264
18.8.22.5.1	Synthesis of Acyclic <i>N</i> -Acyl-, <i>N,N</i> -Diacyl-, and <i>N,N'</i> -Diacylureas	264
18.8.22.5.1.1	Method 1: From Acyl Isocyanates	264
18.8.22.5.1.2	Method 2: From Carboxylic Acids	265
18.8.22.5.1.3	Method 3: From Ureas or Thioureas	266
18.8.22.6	Imidazolidine-2,4-diones (Hydantoins) and Other Five-Membered Cyclic <i>N</i> -Acylureas	268
18.8.22.6.1	Synthesis of Imidazolidine-2,4-diones (Hydantoins) and Other Five-Membered Cyclic <i>N</i> -Acylureas	268
18.8.22.6.1.1	Method 1: From α -Amino Amides	268
18.8.22.6.1.2	Method 2: From 1,2-Dicarbonyl Compounds and Urea (Biltz Synthesis)	269
18.8.22.6.1.3	Method 3: From Carbonyl Compounds, Cyanide Salts, and Ammonium Carbonate (Bucherer–Bergs Synthesis)	271
18.8.22.6.1.4	Method 4: From Amino Acids and Cyanate Salts (Read Synthesis)	272
18.8.22.6.1.5	Method 5: From Amino Acid Esters and Isocyanates	272
18.8.22.6.1.6	Method 6: From Amino Acid Amides and Carbamates	272
18.8.22.6.1.7	Method 7: From Other Heterocycles	273
18.8.22.6.1.8	Method 8: Cycloadditions	277
18.8.22.6.1.9	Method 9: Multicomponent Reactions	277
18.8.22.6.1.10	Method 10: Miscellaneous Methods	281
18.8.22.7	Dihydropyrimidine-2,4(1 <i>H</i> ,3 <i>H</i>)-diones, Pyrimidine-2,4,6(1 <i>H</i> ,3 <i>H</i> ,5 <i>H</i>)-triones (Barbiturates), and Other Six-Membered Cyclic <i>N</i> -Acyl- or <i>N,N'</i> -Diacylureas ..	282
18.8.22.7.1	Synthesis of Dihydropyrimidine-2,4(1 <i>H</i> ,3 <i>H</i>)-diones, Pyrimidine-2,4,6(1 <i>H</i> ,3 <i>H</i> ,5 <i>H</i>)-triones (Barbiturates), and Other Six-Membered Cyclic <i>N</i> -Acyl- or <i>N,N'</i> -Diacylureas	282
18.8.22.7.1.1	Method 1: From Uracil Derivatives	283
18.8.22.7.1.2	Method 2: From β -Amino Acids	283
18.8.22.7.1.3	Method 3: Multicomponent Reactions	284
18.8.22.7.1.4	Method 4: From Malonic Acid Monoesters and Carbodiimides	285
18.8.22.7.1.5	Method 5: Miscellaneous Methods	286
18.8.22.8	1,3-Diazepan-2,4-diones, 1,3-Diazepan-2,4,7-triones, and Other Seven-Membered Cyclic <i>N</i> -Acyl- or <i>N,N'</i> -Diacylureas	287

18.8.22.8.1	Synthesis of 1,3-Diazepane-2,4-diones, 1,3-Diazepane-2,4,7-triones, and Other Seven-Membered Cyclic <i>N</i> -Acyl- or <i>N,N'</i> -Diacylureas	288
18.8.22.8.1.1	Method 1: From Pyroglutamates	288
18.8.22.9	Biurets and Triurets	289
18.8.22.9.1	Synthesis of Biurets and Triurets	289
18.8.22.10	<i>N</i> -(Iminomethyl)ureas	289
18.8.22.10.1	Synthesis of <i>N</i> -(Iminomethyl)ureas	289
18.8.22.10.1.1	Method 1: From Isocyanides and Ureas	290
18.8.22.11	<i>N</i> -Carbamimidoylureas	291
18.8.22.11.1	Synthesis of <i>N</i> -Carbamimidoylureas	291
18.8.22.11.1.1	Method 1: From Guanidines	291
18.8.22.12	Semicarbazides and Carbonohydrazides	293
18.8.22.12.1	Synthesis of Semicarbazides and Carbonohydrazides	293
18.8.22.13	<i>N</i> -Nitroso- and <i>N</i> -Nitroureas	294
18.8.22.13.1	Synthesis of <i>N</i> -Nitroso- and <i>N</i> -Nitroureas	295
18.8.22.14	<i>N</i> -Chloroureas	296
18.8.22.14.1	Synthesis of <i>N</i> -Chloroureas	296
18.8.22.14.1.1	Method 1: From Hydantoins	296
18.8.22.15	<i>N</i> -Hydroxyureas	297
18.8.22.15.1	Synthesis of <i>N</i> -Hydroxyureas	297
18.8.22.16	<i>N</i> -Alkoxy- <i>N</i> -chloro-, <i>N</i> -Acyloxy- <i>N</i> -alkoxy-, and <i>N,N</i> -Dialkoxyureas	298
18.8.22.16.1	Synthesis of <i>N</i> -Alkoxy- <i>N</i> -chloro-, <i>N</i> -Acyloxy- <i>N</i> -alkoxy-, and <i>N,N</i> -Dialkoxyureas	298
18.8.22.17	<i>N</i> -Sulfonylureas	298
18.8.22.17.1	Synthesis of <i>N</i> -Sulfonylureas	298
18.8.22.18	<i>N</i> -Phosphorylureas	299
18.8.22.18.1	Synthesis of <i>N</i> -Phosphorylureas	299

Volume 19: Three Carbon—Heteroatom Bonds: Nitriles, Isocyanides, and Derivatives

19.5	Product Class 5: Nitriles	
19.5.14.15	Synthesis from Nitriles with Retention of the Cyano Group N. Mase	2013
19.5.14.15	Synthesis from Nitriles with Retention of the Cyano Group	311
19.5.14.15.1	Organocatalytic Reactions of Nucleophiles Containing a Cyano Group with Electrophiles	312

19.5.14.15.1.1	Nucleophilic Additions of Cyanide to Double Bonds	312
19.5.14.15.1.1.1	Method 1: Nucleophilic Additions of Cyanide to Carbonyl and Imino Groups	312
19.5.14.15.1.1.2	Method 2: Michael Addition of Cyanide to Electron-Deficient Alkenes	313
19.5.14.15.1.1.2.1	Variation 1: Michael Addition of Cyanide to Enones	313
19.5.14.15.1.1.2.2	Variation 2: Michael Addition of Cyanide to Nitroalkenes	315
19.5.14.15.1.2	Addition of Carbon Nucleophiles to Various Electrophiles	317
19.5.14.15.1.2.1	Method 1: Cyanomethylations	317
19.5.14.15.1.2.1.1	Variation 1: Cyanomethylation of Aldehydes and Ketones	317
19.5.14.15.1.2.1.2	Variation 2: Cyanomethylation of Imines	319
19.5.14.15.1.2.2	Method 2: Knoevenagel Condensations	319
19.5.14.15.1.2.2.1	Variation 1: Knoevenagel Condensation of an α -Cyano Ester with Aldehydes and Ketones	320
19.5.14.15.1.2.2.2	Variation 2: Knoevenagel Condensation of α -Cyanoamides with Aldehydes	322
19.5.14.15.1.2.2.3	Variation 3: Knoevenagel Condensation of Malononitrile with Aldehydes and Ketones	322
19.5.14.15.1.2.2.4	Variation 4: Knoevenagel Condensation Using a Heterogeneous Organocatalyst	323
19.5.14.15.1.2.3	Method 3: Mannich Reaction	327
19.5.14.15.1.2.3.1	Variation 1: Mannich Reactions with Imines	327
19.5.14.15.1.2.3.2	Variation 2: Mannich Reactions with Imines Generated In Situ	329
19.5.14.15.1.2.3.3	Variation 3: Vinylogous Mannich Reactions	330
19.5.14.15.1.2.3.4	Variation 4: One-Pot Mannich/Cyclization/Tautomerization Reactions of Malononitrile with Imines Generated In Situ	332
19.5.14.15.1.2.4	Method 4: Amination Reactions	334
19.5.14.15.1.2.4.1	Variation 1: Amination Reactions of α -Cyano Carbonyl Compounds	334
19.5.14.15.1.2.4.2	Variation 2: Vinylogous Amination Reactions	337
19.5.14.15.1.2.5	Method 5: Nitroso-Aldol Reactions	338
19.5.14.15.1.2.6	Method 6: Michael Reactions between Nucleophiles Containing a Cyano Group and Enals or Enones	339
19.5.14.15.1.2.6.1	Variation 1: Michael Reactions of α -Cyano Esters with Enals	339
19.5.14.15.1.2.6.2	Variation 2: Michael/Hemiaminal Reactions of N-Protected α -Cyano Esters with Enals	341
19.5.14.15.1.2.6.3	Variation 3: Michael Reactions of α -Cyano Esters with Enones	342
19.5.14.15.1.2.6.4	Variation 4: Michael Reactions of α -Cyano Sulfones with Enones	344
19.5.14.15.1.2.6.5	Variation 5: Michael Reactions of α -Cyanophosphonates with Enones	344
19.5.14.15.1.2.6.6	Variation 6: Michael Reactions of Malononitriles with Enones	345
19.5.14.15.1.2.6.7	Variation 7: Michael/Hemiacetal Reactions of α -Cyano Ketones with Enones	348
19.5.14.15.1.2.6.8	Variation 8: Michael/Cyclization/Tautomerization Reactions of Malononitrile with Enones	350
19.5.14.15.1.2.7	Method 7: Michael Reactions between Nucleophiles Containing a Cyano Group and α,β -Unsaturated Carboxylic Acid Derivatives	353
19.5.14.15.1.2.7.1	Variation 1: Michael Reactions with α,β -Unsaturated Esters	353
19.5.14.15.1.2.7.2	Variation 2: Michael Reactions with Acyclic Imides	355
19.5.14.15.1.2.7.3	Variation 3: Michael Reactions with Cyclic Imides	357

19.5.14.15.1.2.8	Method 8:	Michael Reactions between Nucleophiles Containing a Cyano Group and Various Other Electrophiles	358
19.5.14.15.1.2.8.1	Variation 1:	Michael Reactions with Alkynyl Electrophiles	358
19.5.14.15.1.2.8.2	Variation 2:	Michael Reactions of Malononitrile with Dienones	359
19.5.14.15.1.2.8.3	Variation 3:	Michael/Cyclization/Tautomerization Reactions with Dienones	360
19.5.14.15.1.2.8.4	Variation 4:	Michael Reactions with a Vinylogous Imine	361
19.5.14.15.1.2.8.5	Variation 5:	Michael Reactions of Cyano Compounds with Nitroalkenes ..	362
19.5.14.15.1.2.8.6	Variation 6:	Michael/Cyclization/Tautomerization Reactions of Malononitrile with Nitroalkenes	364
19.5.14.15.1.2.8.7	Variation 7:	Michael Reactions with Vinyl Sulfones	366
19.5.14.15.1.2.8.8	Variation 8:	Michael Reactions with Vinyl Selenones	368
19.5.14.15.1.2.9	Method 9:	Vinylogous Michael Reactions of Nucleophiles Containing a Cyano Group	369
19.5.14.15.1.2.9.1	Variation 1:	Vinylogous Michael Reactions with Enals	369
19.5.14.15.1.2.9.2	Variation 2:	Vinylogous Michael Reactions with Enones	371
19.5.14.15.1.2.9.3	Variation 3:	Vinylogous Michael Reactions with Quinones	373
19.5.14.15.1.2.9.4	Variation 4:	Vinylogous Michael Reactions with Dienones	375
19.5.14.15.1.2.9.5	Variation 5:	Vinylogous Michael Reactions with Imides	376
19.5.14.15.1.2.9.6	Variation 6:	Vinylogous Michael Reactions with Nitroalkenes	377
19.5.14.15.1.2.10	Method 10:	Michael Reactions of Isocyanide Derivatives with Imides	378
19.5.14.15.1.2.11	Method 11:	[3 + 2] Cycloadditions of Cyano Derivatives with Enals	379
19.5.14.15.1.3	Substitutions of Carbon Nucleophiles by Various Electrophiles	381	
19.5.14.15.1.3.1	Method 1:	Alkylation	381
19.5.14.15.1.3.2	Method 2:	Allylation	384
19.5.14.15.1.3.2.1	Variation 1:	Allylation of α -Cyano Esters	384
19.5.14.15.1.3.2.2	Variation 2:	Allylation of α -Hydroxy Nitrile Derivatives	385
19.5.14.15.1.3.2.3	Variation 3:	Allylation of Aminonitriles	386
19.5.14.15.1.3.2.4	Variation 4:	Allylation of Vinylogous Nucleophiles	387
19.5.14.15.1.3.3	Method 3:	Vinylic Substitutions	389
19.5.14.15.2	Organocatalytic Reactions of Nucleophiles with Electrophiles Containing Cyano Groups	391	
19.5.14.15.2.1	Michael Reactions with Electrophiles Containing Cyano Groups	391	
19.5.14.15.2.1.1	Method 1:	Michael Reactions of Carbon Nucleophiles	392
19.5.14.15.2.1.1.1	Variation 1:	Michael Reactions of Carbonyl Compounds with Monocyano Electrophiles	392
19.5.14.15.2.1.1.2	Variation 2:	Michael Reactions of Carbonyl Compounds with Dicyano Electrophiles	394
19.5.14.15.2.1.1.3	Variation 3:	Michael/Cyclization Reactions of Nucleophiles Containing a Carbonyl Group with Cyano Electrophiles	396
19.5.14.15.2.1.1.4	Variation 4:	Michael/Cyclization/Tautomerization Reactions of Carbonyl Compounds with Dicyano Electrophiles	400
19.5.14.15.2.1.1.5	Variation 5:	Michael Reactions of Phosphonates with Cyano Electrophiles ..	404
19.5.14.15.2.1.1.6	Variation 6:	Michael Reactions of Nitroalkanes with Cyano Electrophiles ..	405
19.5.14.15.2.1.2	Method 2:	Aza-Michael Reactions	407
19.5.14.15.2.1.3	Method 3:	Oxa-Michael Reactions	408

19.5.14.15.2.1.4	Method 4: Thia-Michael Reactions	409
19.5.14.15.2.2	Cyclopropanation	409
19.5.14.15.2.2.1	Method 1: Cyclopropanation of Acrylonitrile Derivatives	409
19.5.14.15.2.3	Epoxidation	411
19.5.14.15.2.3.1	Method 1: Epoxidation of α -Acylacrylonitriles	411
19.5.14.15.2.4	Morita-Baylis-Hillman Reactions	412
19.5.14.15.2.4.1	Method 1: Morita-Baylis-Hillman Reactions with Acrylonitrile	412
19.5.14.15.2.4.2	Method 2: Aza-Morita-Baylis-Hillman Reactions	412
19.5.14.15.2.5	Cycloaddition Reactions	413
19.5.14.15.2.5.1	Method 1: [4 + 2] Cycloadditions with Cyano Dienophiles	413
19.5.14.15.3	One-Pot Sequential Reactions	416
19.5.14.15.3.1	One-Pot Reactions via Knoevenagel Condensations	416
19.5.14.15.3.1.1	Method 1: Knoevenagel/Hydrogenation Reactions	416
19.5.14.15.3.1.2	Method 2: Knoevenagel/Hydrogenation/Alkylation Reactions	418
19.5.14.15.3.1.3	Method 3: Knoevenagel/Michael Reactions	419
19.5.14.15.3.1.4	Method 4: Knoevenagel/Michael/Cyclization Reactions	421
19.5.14.15.3.1.5	Method 5: Knoevenagel/Michael/Cyclization/Tautomerization Reactions	423
19.5.14.15.3.1.6	Method 6: Knoevenagel/Friedel-Crafts/Cyclization/Tautomerization Reactions	427
19.5.14.15.3.1.7	Method 7: Knoevenagel/Cycloaddition Reactions	428
19.5.14.15.3.1.8	Method 8: Deacetalization/Knoevenagel Reactions	428
19.5.14.15.3.1.9	Method 9: Michael/Cyclization/Tautomerization/Knoevenagel Reactions	429
19.5.14.15.3.1.10	Method 10: Multicomponent Reactions	430
19.5.14.15.3.2	One-Pot Reactions via Allylation	434
19.5.14.15.3.2.1	Method 1: Cyanation/Allylation Reactions of Aldehydes	434
19.5.14.15.3.2.2	Method 2: Cyanation/Allylation Reactions of Imines	435
19.5.14.15.3.3	One-Pot Michael/Michael/Cyclization Reactions	437
19.5.14.15.3.3.1	Method 1: Michael/Michael/Cyclization Reactions with a Brønsted Base Catalyst	437
19.5.14.15.3.3.2	Method 2: Michael/Michael/Cyclization Reactions with Nucleophilic Catalysis	441
19.5.14.15.3.4	Michael/Michael Reactions Using Enamine and/or Iminium Catalysis	442
19.5.14.15.3.4.1	Method 1: Enamine/Iminium Catalysis	442
19.5.14.15.3.4.2	Method 2: Iminium/Enamine Catalysis	443
19.5.14.15.3.4.3	Method 3: Iminium/Iminium Catalysis	445
19.5.14.15.3.4.4	Method 4: Enamine/Iminium/Enamine Catalysis	446
19.5.14.15.3.5	Singly Occupied Molecular Orbital (SOMO) Catalysis	447
19.5.14.15.3.5.1	Method 1: Polycyclization of Polyenals	447
19.5.14.15.3.6	Reaction Sequences Involving Metal Catalysts and Organocatalysts	449
19.5.14.15.3.6.1	Method 1: Hydroformylation/Knoevenagel Reaction	449
19.5.14.15.3.6.2	Method 2: Michael/Cyclization/Isomerization Reaction	451

19.5.14.15.3.6.3	Method 3: Knoevenagel/Hydrogenation/Cyclization Reaction	452
	Author Index	459
	Abbreviations	481