

	Preface	V
	Abstracts	VII
	Table of Contents	XIII
15.1.4	Pyridines (Update 2016)	
	D. Spitzner	1
34.1.2.6	Synthesis by Substitution of Metals (Update 2016)	
	M. Shevchuk and G.-V. Röscenthaler	363
34.1.3.4	Synthesis by Substitution of Carbon Functionalities (Update 2016)	
	J. Desroches and J.-F. Paquin	375
34.1.4.2.9	Synthesis by Substitution of Hydroxy Groups in Alcohols (Update 2016)	
	M. Vandamme and J.-F. Paquin	395
34.5.2	Propargylic Fluorides (Update 2016)	
	J.-D. Hamel and J.-F. Paquin	409
34.6.2	Benzylic Fluorides (Update 2016)	
	P. A. Champagne, M. Drouin, and J.-F. Paquin	419
	Author Index	451
	Abbreviations	475

Table of Contents

Volume 15: Six-Membered Hetarenes with One Nitrogen or Phosphorus Atom

15.1	Product Class 1: Pyridines		
15.1.4	Pyridines D. Spitzner		
15.1.4	Pyridines		1
15.1.4.1	Pyridines		1
15.1.4.1.1	Synthesis by Ring-Closure Reactions		7
15.1.4.1.1.1	By Formation of Two N—C and Two C—C Bonds		7
15.1.4.1.1.1.1	Fragments C—C, C—C, N, and C		7
15.1.4.1.1.1.1.1	Method 1: Synthesis from 1,3-Diketones or 3-Oxo Esters, Aldehydes, and Ammonia or Amines, with Subsequent Oxidation (Hantzsch Pyridine Synthesis)		7
15.1.4.1.1.1.1.1.1	Variation 1: Polymer-Assisted Hantzsch Cyclocondensation and Enantioselective Organocatalytic Hantzsch Synthesis		8
15.1.4.1.1.1.1.1.2	Variation 2: From Oxonitriles, Aldehydes, and Ammonium Acetate		9
15.1.4.1.1.1.1.1.3	Variation 3: From Ketones, <i>N</i> -Phenacylpyridinium Compounds, Aldehydes, and Ammonium Acetate (Modified Kröhnke Method) ..		11
15.1.4.1.1.1.1.1.4	Variation 4: From Aromatic Ketones and Ammonium Acetate by Metal-Free Condensation		12
15.1.4.1.1.1.1.1.5	Variation 5: 4-Unsubstituted Pyridines from Enaminones and Ammonium Chloride		13
15.1.4.1.1.1.1.2	Method 2: Synthesis from Acryloyl Azides by Curtius Rearrangement ...		13
15.1.4.1.1.1.1.3	Method 3: Synthesis from an Arylaldehyde, Acetoacetates, and Ammonium Acetate		14
15.1.4.1.1.1.1.4	Method 4: Synthesis from Acetaldehydes and a Nitrogen Donor		14
15.1.4.1.1.1.2	Fragments N, C—C—C, C, and C		15
15.1.4.1.1.1.2.1	Method 1: Three-Component Coupling of an Allyl Alcohol, an Aldehyde, and Lithium Hexamethyldisilazanide, Followed by Metallacycle-Mediated Cyclization		15
15.1.4.1.1.1.2.2	Method 2: Synthesis from Ketones and the Vilsmeier–Haack Reagent ..		16
15.1.4.1.1.2	By Formation of One N—C and Three C—C Bonds		17
15.1.4.1.1.2.1	Fragments C—C, N—C, C, and C		17
15.1.4.1.1.2.1.1	Method 1: Synthesis from Ketenimines, Aldehydes, Nitriles, and Diethyl Methylphosphonate		17

15.1.4.1.1.3	By Formation of Two N—C Bonds and One C—C Bond	19
15.1.4.1.1.3.1	Fragments C—C—C, C—C, and N	19
15.1.4.1.1.3.1.1	Method 1: Synthesis from Acyl Enamines, β -Dicarbonyl Compounds, and Hydroxylamine or Ammonium Salts	19
15.1.4.1.1.3.1.1.1	Variation 1: From Ketene Dithioacetals, Ketones, and an Ammonium Salt ..	20
15.1.4.1.1.3.1.1.2	Variation 2: From Ketones, α,β -Unsaturated Aldehydes or Ketones, and Ammonium Salts	20
15.1.4.1.1.3.1.1.3	Variation 3: From 2-Pyrrolidinoacetophenones with Chalcones	22
15.1.4.1.1.3.1.1.4	Variation 4: From Nitroalkenes, Amines, and Enones by Condensation ...	23
15.1.4.1.1.3.1.2	Method 2: Synthesis from Acylpyridinium Compounds (Kröhnke Compounds), α,β -Unsaturated Ketones, and an Ammonium Salt ..	23
15.1.4.1.1.3.1.3	Method 3: Synthesis from α,β -Unsaturated Ketones and Ammonium Acetate	24
15.1.4.1.1.3.1.4	Method 4: 2-Arylpyridines Using One-Pot 6π -Azoelectrocyclization	25
15.1.4.1.1.3.1.5	Method 5: Synthesis from Ynones, Ketones, and Ammonium Salts (Bohlmann–Rahtz-Type Pyridine Synthesis and Bagley Variation) ..	26
15.1.4.1.1.3.1.6	Method 6: Synthesis from Propargyl Enol Ethers and <i>O</i> -Methylhydroxylamine Hydrochloride	29
15.1.4.1.1.3.1.7	Method 7: Palladium-Catalyzed Sequential Coupling/Imination/Annulation of 3-Bromoarene-2-carbaldehydes with Terminal Acetylenes and Ammonium Acetate	29
15.1.4.1.1.3.1.8	Method 8: Synthesis from 1-Methyl-3,5-dinitropyridin-2-one as C—C—C Unit	30
15.1.4.1.1.3.1.9	Method 9: Synthesis from a Dialdehyde and Hydroxylamine	31
15.1.4.1.1.3.1.10	Method 10: Synthesis from a Terminal Propargyl Alcohol, an Enamine, and Ammonium Chloride	31
15.1.4.1.1.3.1.11	Method 11: Synthesis from 3-Aryl-3-oxohydrazonopropanals, 3-Oxo-3-phenylpropanenitrile, and Ammonium Acetate	32
15.1.4.1.1.3.1.12	Method 12: Synthesis of Tetrasubstituted Pyridines from 3-Haloacrylaldehydes, Ketones, and <i>tert</i> -Butylamine	33
15.1.4.1.1.4	By Formation of One N—C Bond and Two C—C Bonds	34
15.1.4.1.1.4.1	Fragments N—C, C—C, and C—C	34
15.1.4.1.1.4.1.1	Method 1: Synthesis from Nitriles and Alkynes via an Azametallacyclopentadiene	34
15.1.4.1.1.4.1.2	Method 2: Rhodium-Catalyzed [2 + 2 + 2] Cycloaddition	35
15.1.4.1.1.4.1.2.1	Variation 1: Rhodium-Catalyzed [2 + 2 + 2] Cycloaddition of Oximes and Dienes	36
15.1.4.1.1.4.1.3	Method 3: Cobalt-, Iron-, Nickel-, or Iridium-Catalyzed [2 + 2 + 2] Cycloaddition	36
15.1.4.1.1.4.1.3.1	Variation 1: Metalated Pyridines from Two Alkynes, a Nitrile, and Titanium(IV) Alkoxides	41
15.1.4.1.1.4.1.3.2	Variation 2: Pyridines via Solid-Supported [2 + 2 + 2] Cyclotrimerization ..	43
15.1.4.1.1.4.1.4	Method 4: Synthesis from α -Amino Acids and Aldehydes by Decarboxylative Cyclization	43
15.1.4.1.1.4.1.5	Method 5: Synthesis from Imines and Haloalkenes by One-Pot Cross Coupling	44

15.1.4.1.1.4.1.6	Method 6:	Synthesis from Nitriles and Alkynes under Metal-Free Conditions	45
15.1.4.1.1.4.1.7	Method 7:	Synthesis from a Nitrile, an Alkyne, and Allyl 4-Tolyl Sulfoxide	45
15.1.4.1.1.4.1.8	Method 8:	Synthesis from a Vinyl Ether and a Cyano Alkynamide	46
15.1.4.1.1.4.1.9	Method 9:	Tetrasubstituted Pyridines from Acylmethyl Azides and Acetylenedicarboxylates	47
15.1.4.1.1.4.1.10	Method 10:	Copper-Catalyzed Domino Synthesis of Pentasubstituted Pyridines from Malononitrile and Alkynes	48
15.1.4.1.1.4.2	Fragments N—C—C, C—C, and C		49
15.1.4.1.1.4.2.1	Method 1:	Chlorotrimethylsilane-Promoted Three-Component Coupling Reaction of a Functionalized Enamine, an Acetal, and an Alkyne	49
15.1.4.1.1.4.2.2	Method 2:	Synthesis from Enamines and Triethyl Orthoformate by Hafnium(IV) Trifluoromethanesulfonate Catalyzed Annulation ..	50
15.1.4.1.1.4.2.2.1	Variation 1:	From Oxime Esters, Aldehydes, and Activated Methylene Compounds	51
15.1.4.1.1.4.2.3	Method 3:	Synthesis from a Lithiated Alkylsilane, a Nitrile, and a Fluoroalkene	51
15.1.4.1.1.4.2.4	Method 4:	Synthesis from Malononitrile, Aldehydes, and Nucleophiles ..	52
15.1.4.1.1.4.2.5	Method 5:	Synthesis from Malononitrile, Dimethylformamide, and Ketones (Vilsmeier–Haack Reaction)	53
15.1.4.1.1.4.2.6	Method 6:	Copper-Catalyzed Coupling of Oxime Acetates with Aldehydes	54
15.1.4.1.1.4.2.6.1	Variation 1:	Synthesis from an Oxime Ester, Malononitrile, and Aldehydes	55
15.1.4.1.1.4.2.7	Method 7:	Synthesis from <i>N</i> -Vinyl Phosphazenes, α,β -Unsaturated Aldehydes, and Enamines by [4 + 2] Cycloaddition	55
15.1.4.1.1.4.2.8	Method 8:	Ruthenium-Catalyzed Cyclization of Ketoxime Acetates with <i>N,N</i> -Dimethylformamide	56
15.1.4.1.1.4.3	Fragments C—C—C, N—C, and C		57
15.1.4.1.1.4.3.1	Method 1:	Synthesis from Nitriles, Fluorinated Acids, and Lithiated Methoxyallene	57
15.1.4.1.1.4.3.2	Method 2:	Synthesis from Nitriles, a 1,3-Enyne, and Carbanions in a One-Pot Reaction	58
15.1.4.1.1.4.3.3	Method 3:	Pyridin-4-amines from α -Azido Vinyl Ketones, Aldehydes, and Methylamines by a One-Pot Procedure	59
15.1.4.1.1.4.3.3.1	Variation 1:	<i>N</i> -Tosylpiperidinones by a Four-Component One-Pot Synthesis	60
15.1.4.1.1.5	By Formation of Three C—C Bonds		60
15.1.4.1.1.5.1	Fragments C—N—C, C—C, and C		60
15.1.4.1.1.5.1.1	Method 1:	Synthesis from Arynes, Isocyanides, and Terminal Alkynes ..	60
15.1.4.1.1.6	By Formation of Two N—C Bonds		61
15.1.4.1.1.6.1	Fragments C—C—C—C—C and N		61
15.1.4.1.1.6.1.1	Method 1:	Synthesis from 2-Alkyl-5-amino-1- <i>tert</i> -butyliminopentadienes and Ammonium Salts	61
15.1.4.1.1.6.1.2	Method 2:	Synthesis from 1,5-Dicarbonyl Compounds and Ammonia or Ammonium Salts	62

15.1.4.1.1.6.1.2.1	Variation 1:	Synthesis from 1,1-Bis(alkylsulfanyl)penta-1,4-dienes and Ammonium Acetate	64
15.1.4.1.1.6.1.2.2	Variation 2:	From α,β -Unsaturated 1,5-Dicarbonyl Compounds (or Partially Protected Derivatives) and Ammonia or Ammonium Salts	65
15.1.4.1.1.6.1.2.3	Variation 3:	From $\alpha,\beta,\gamma,\delta$ -Unsaturated Aldehydes and Ammonium Chloride	69
15.1.4.1.1.6.1.3	Method 3:	Synthesis from Dienones, Dienals, or Related Compounds ...	70
15.1.4.1.1.6.1.3.1	Variation 1:	From α -Alkenoyl- α -aryl Ketene <i>S,S</i> -Acetals and Ammonium Acetate	71
15.1.4.1.1.6.1.3.2	Variation 2:	Cyclization of 3-Hydroxypent-4-yn-1-ones with Urea	71
15.1.4.1.1.6.1.4	Method 4:	One-Pot Synthesis of 1,2-Dihydropyridines from Propargyl Vinyl Ethers	72
15.1.4.1.1.6.1.5	Method 5:	Synthesis from 2-(Alk-2-enylidene)malononitriles and Hydroxylamine	73
15.1.4.1.1.7	By Formation of One N—C and Two C—C Bonds		73
15.1.4.1.1.7.1	Fragments N—C—C—C, C, and C		73
15.1.4.1.1.7.1.1	Method 1:	Synthesis from Benzyl 2-(Triphenylphosphoranylidene)acetate, Acetyl Chloride, and an <i>N</i> -Sulfonyl-1-aza-1,3-diene	73
15.1.4.1.1.8	By Formation of One N—C and One C—C Bond		74
15.1.4.1.1.8.1	Fragments N—C—C—C and C—C		74
15.1.4.1.1.8.1.1	Method 1:	Synthesis from Alkylketoximes and Alkynes via Transition-Metal-Catalyzed C—H Bond Activation	74
15.1.4.1.1.8.1.1.1	Variation 1:	From α,β -Unsaturated <i>N</i> -Benzyl Aldimines and Alkynes	75
15.1.4.1.1.8.1.1.2	Variation 2:	Rhodium(III)-Catalyzed Regioselective Synthesis of Pyridines from Alkenes and α,β -Unsaturated Oxime Esters	76
15.1.4.1.1.8.1.2	Method 2:	Synthesis from <i>N</i> -Acetyl β -Enamino Ketones and Alkynes ...	76
15.1.4.1.1.8.1.3	Method 3:	Aza-Diels–Alder Reaction	77
15.1.4.1.1.8.1.3.1	Variation 1:	From Azoenamines and Acetylenedicarboxylates	79
15.1.4.1.1.8.1.3.2	Variation 2:	From α,β -Unsaturated <i>N</i> -Sulfinylimines and Electron-Rich Dienophiles	79
15.1.4.1.1.8.1.3.3	Variation 3:	From Functionalized 3-Phosphoryl-1-azabuta-1,3-dienes and Electron-Poor Dienophiles	80
15.1.4.1.1.8.1.4	Method 4:	Synthesis from Alkenylboronic Acids and α,β -Unsaturated <i>O</i> -Acyl Ketoximes	81
15.1.4.1.1.8.1.5	Method 5:	Gold-Catalyzed Reaction of Ketones or β -Oxo Esters with Propargylamines	81
15.1.4.1.1.8.1.6	Method 6:	Synthesis from Ketene <i>S,S</i> -Acetals and Ketones	82
15.1.4.1.1.8.1.6.1	Variation 1:	From an <i>N</i> -Propargyl Toluenesulfonamide and Ketene <i>N,S</i> -Acetals by a Coupling–Isomerization Reaction	83
15.1.4.1.1.8.1.7	Method 7:	Synthesis from Acetylenephosphonates and 2-Amino-3-formylbenzopyran-4-ones	84
15.1.4.1.1.8.1.8	Method 8:	Synthesis from α,β -Unsaturated Ketoximes and Alkynes	84
15.1.4.1.1.8.1.9	Method 9:	Synthesis from 5-Acyl-4-aminothiazol-2-yl-Functionalized Resins and Ketones	86
15.1.4.1.1.8.1.10	Method 10:	Synthesis from Formyl-Substituted (Vinylimino)phosphoranes and Methyl Propynoate	86

15.1.4.1.1.8.1.11	Method 11:	Organocatalytic Synthesis of Highly Functionalized Pyridines from Allenates and <i>N</i> -Sulfonyl-1-aza-1,3-dienes	87
15.1.4.1.1.8.1.12	Method 12:	Synthesis from Alcohols and 3-Amino Alcohols Using an Iridium Catalyst	88
15.1.4.1.1.8.1.13	Method 13:	2,4,6-Trisubstituted Pyridines from (Phenylsulfanyl)acetic Acid and α,β -Unsaturated Ketimines	89
15.1.4.1.1.8.1.14	Method 14:	Synthesis from <i>N</i> -Sulfonyl Ketimines and Alkynes Using the N—S Bond as an Internal Oxidant	90
15.1.4.1.1.8.1.15	Method 15:	Synthesis of 2-Arylpyridines from Acetophenones and 1,3-Diaminopropane	91
15.1.4.1.1.8.1.16	Method 16:	Synthesis from Ethyl Cyanoacetate Derivatives and Alkynyl Imines	92
15.1.4.1.1.8.2	Fragments C—C—C and N—C		93
15.1.4.1.1.8.2.1	Method 1:	Gold-Catalyzed Hetero-Dehydro-Diels–Alder Cycloaddition of Captodative Dienynes with Nitriles	93
15.1.4.1.1.8.2.2	Method 2:	Synthesis from 1-Lithio-1,3-dienes and Nitriles	93
15.1.4.1.1.8.2.3	Method 3:	Synthesis from Fluoromethyl-Containing Alkynylimines and Primary Methylamines via C—F Bond Cleavage	94
15.1.4.1.1.8.2.4	Method 4:	Nickel-Catalyzed Dehydrogenative [4 + 2] Cycloaddition of 1,3-Dienes with Nitriles	95
15.1.4.1.1.8.2.5	Method 5:	Hetero-Diels–Alder Reaction of 1,3-Bis(trimethylsilyloxy)buta-1,3-dienes with Arenesulfonyl Cyanides	95
15.1.4.1.1.8.2.6	Method 6:	Organocatalytic [4 + 2] Cycloadditions of Allenates and Imines	96
15.1.4.1.1.8.2.7	Method 7:	[4 + 2] Cycloaddition of <i>N</i> -Phosphoryl Trihaloacetimidoyl Chlorides and Buta-1,3-dienes	97
15.1.4.1.1.8.3	Fragments N—C—C and C—C—C		97
15.1.4.1.1.8.3.1	Method 1:	Synthesis from Vinamidinium Salts with 5-Amino-2-phenyl-2,4-dihydro-3 <i>H</i> -pyrazol-3-one	97
15.1.4.1.1.8.3.1.1	Variation 1:	From Malononitrile, Vinamidinium Salts, and an Ammonium Salt	98
15.1.4.1.1.8.3.2	Method 2:	Synthesis from Enones, Cyanoacetates, and Ammonium Acetate	98
15.1.4.1.1.8.3.2.1	Variation 1:	From Malononitrile and Enones in the Presence of a Nucleophile	99
15.1.4.1.1.8.3.3	Method 3:	Synthesis from α,β -Unsaturated Aldehydes or Ketones and Primary Enamines	99
15.1.4.1.1.8.3.4	Method 4:	Cyclization of <i>N</i> -Silylenamines with In Situ Generated 2-Methylenecyclohexane-1,3-diones	101
15.1.4.1.1.8.3.5	Method 5:	Synthesis from Acylenamines and Oxoalkynes (Bohlmann–Rahtz Synthesis)	102
15.1.4.1.1.8.3.6	Method 6:	Synthesis from (Alk-1-enylimino)phosphoranes and α,β -Unsaturated Ketones (Aza-Wittig Reaction)	102
15.1.4.1.1.8.3.7	Method 7:	Synthesis from β -Sulfonyl Enamines and α,β -Unsaturated Ketones	103
15.1.4.1.1.8.3.8	Method 8:	Synthesis from Primary β -Enamino Phosphonates and Enones	104
15.1.4.1.1.8.3.9	Method 9:	Synthesis from 1,1,1,5,5,5-Hexafluoropentane-2,4-dione with (<i>R</i>)-Phenylglycinol	104

15.1.4.1.1.8.3.10	Method 10: Synthesis from Oximes and Enals through Synergistic Copper/ Iminium Catalysis	105
15.1.4.1.1.8.3.11	Method 11: Synthesis from 1-Arylethylamines and Ynones	106
15.1.4.1.1.8.4	Fragments N—C—C—C—C and C	106
15.1.4.1.1.8.4.1	Method 1: Synthesis from 2-Azido Dienoates and α -Diazo Carbonyl Compounds	106
15.1.4.1.1.8.4.2	Method 2: Formylation/Cyclization of Enamino Keto Esters	107
15.1.4.1.1.9	By Formation of Two C—C Bonds	107
15.1.4.1.1.9.1	Fragments C—N—C—C and C—C	107
15.1.4.1.1.9.1.1	Method 1: Synthesis from <i>N</i> -Vinyl and <i>N</i> -Aryl Amides and Alkynes or Enol Ethers	107
15.1.4.1.1.9.1.2	Method 2: Synthesis from 2-Azadienes and Alkenes or Alkynes	109
15.1.4.1.1.9.1.3	Method 3: Synthesis from Alk-1-ynyl Imines and Terminal Alkynes	109
15.1.4.1.1.9.1.4	Method 4: Synthesis from 2-Azadienes and Enamines by [4 + 2] Cycloaddition	110
15.1.4.1.1.9.1.5	Method 5: Synthesis by Oxidative Ugi-Type and Aza-Diels–Alder Reactions	111
15.1.4.1.1.9.2	Fragments C—C—N—C—C and C	111
15.1.4.1.1.9.2.1	Method 1: 3,5-Disubstituted 2-Chloropyridines from α,β -Unsaturated Ketoximes and the Vilsmeier Reagent under Microwave Conditions	111
15.1.4.1.1.9.2.2	Method 2: Synthesis by [1 + 5] Cycloaddition of Isonitriles with <i>N</i> -Formylmethyl-Substituted Enamides	112
15.1.4.1.1.10	By Formation of One N—C Bond	113
15.1.4.1.1.10.1	Fragment N—C—C—C—C—C	113
15.1.4.1.1.10.1.1	Method 1: Cyclization of 4-(Tosylamino)alk-1-enyl Ketones	114
15.1.4.1.1.10.1.2	Method 2: Synthesis by Electrocyclization/Aromatization	114
15.1.4.1.1.10.1.2.1	Variation 1: 6π -Electrocyclization of an <i>N</i> -Methoxy-1-aza-1,3,5-triene ..	115
15.1.4.1.1.10.1.3	Method 3: Cyclization of Alkynyl Oximes	115
15.1.4.1.1.10.1.3.1	Variation 1: Synthesis from Propargylenecarbamates by Isomerization/ Electrocyclization	116
15.1.4.1.1.10.1.4	Method 4: Synthesis by Amino–Heck Cyclization	117
15.1.4.1.1.10.1.5	Method 5: Titanium(IV) Iodide Induced Cyclization of α -(2-Cyanoalk- 1-enyl)- β -oxo Esters	118
15.1.4.1.1.10.1.5.1	Variation 1: Cyclization of Aminodienones Using Iodine or <i>N</i> -Iodosuccini- mide	118
15.1.4.1.1.10.1.5.2	Variation 2: Cyclization and Bromination	119
15.1.4.1.1.10.1.5.3	Variation 3: Cyclization of Push–Pull 2,4-Dienitriles	119
15.1.4.1.1.10.1.6	Method 6: Cyclization of Alk-2-en-4-ynal Oxime Derivatives	120
15.1.4.1.1.10.1.6.1	Variation 1: Cyclizations of Eneidyneamides	121
15.1.4.1.1.10.1.7	Method 7: Synthesis from Acyl Oximes by Visible-Light-Promoted Iminyl-Radical Formation	122
15.1.4.1.1.10.1.8	Method 8: Synthesis from α -Diazo Oxime Ethers under Rhodium(II) Catalysis	123
15.1.4.1.1.10.1.9	Method 9: Synthesis by Cyclization of Enynyl Azides	123

15.1.4.1.1.11	By Formation of One C—C Bond	124
15.1.4.1.1.11.1	Fragment C—N—C—C—C	124
15.1.4.1.1.11.1.1	Method 1: Synthesis from (Alkoxycarbonyl)enamides	124
15.1.4.1.1.11.1.2	Method 2: Synthesis by Electrocyclization/Aromatization of 2-Azatrienes	126
15.1.4.1.1.11.1.3	Method 3: Palladium-Catalyzed Cyclization of Allenylimines	127
15.1.4.1.1.11.2	Fragment C—C—N—C—C—C	127
15.1.4.1.1.11.2.1	Method 1: Ruthenium-Catalyzed Ring-Closing Alkene Metathesis and Aromatization	127
15.1.4.1.1.11.2.2	Method 2: Synthesis from <i>N</i> -Propargylaminoquinones by 6- <i>endo-dig</i> Chlorocyclization and Oxidative Aromatization	128
15.1.4.1.1.11.2.3	Method 3: Synthesis from <i>N</i> -Propargylic Enaminones	129
15.1.4.1.1.11.2.3.1	Variation 1: Synthesis from <i>N</i> -Propargylic Enaminones via Iodine-Mediated Cyclization	129
15.1.4.1.1.11.2.4	Method 4: Synthesis from (Trimethylsilyl)alkynyl Imines	130
15.1.4.1.1.11.2.5	Method 5: Synthesis from Amino Acid Derivatives by Dieckmann Condensation Followed by Aromatization	131
15.1.4.1.1.11.2.6	Method 6: Synthesis from <i>N</i> -Allyl Ynamides	131
15.1.4.1.1.11.2.6.1	Variation 1: Synthesis from 3-Aza-1,5-enynes	132
15.1.4.1.1.11.2.7	Method 7: Palladium-Catalyzed Cyclization of Vinyl Iodide Tethered Allenesulfonamides	133
15.1.4.1.2	Synthesis by Ring Transformation	134
15.1.4.1.2.1	Ring Enlargement	134
15.1.4.1.2.1.1	From Three-Membered Carbocyclic or Heterocyclic Compounds	134
15.1.4.1.2.1.1.1	Method 1: Synthesis from Cyclopropanols with Vinyl Azides	134
15.1.4.1.2.1.1.2	Method 2: Synthesis from Aziridiny Propargylic Esters	135
15.1.4.1.2.1.1.3	Method 3: Synthesis by Carbenoid-Mediated Ring Opening of 2 <i>H</i> -Azirines	136
15.1.4.1.2.1.2	From Five-Membered Carbocyclic or Heterocyclic Compounds	137
15.1.4.1.2.1.2.1	Method 1: Synthesis from Furans	137
15.1.4.1.2.1.2.2	Method 2: Synthesis from a Thiophene 1-Oxide and a Nitrile	137
15.1.4.1.2.1.2.3	Method 3: Palladium(II)-Catalyzed Ring Expansion of Cyclic 2-Azido Alcohol Derivatives	138
15.1.4.1.2.1.2.4	Method 4: Synthesis from Isotellurazoles, Isoselenazoles, or Isotellurazole <i>Te</i> -Oxides and Acetylenic Dienophiles	139
15.1.4.1.2.1.2.5	Method 5: Synthesis from Azabicyclo[3.2.0]hept-2-en-4-ones	140
15.1.4.1.2.1.2.6	Method 6: Synthesis from 2,5-Dihydropyrroles	140
15.1.4.1.2.1.2.7	Method 7: Synthesis from Isoxazoles by Rhodium Carbenoid Induced Ring Expansion	141
15.1.4.1.2.1.2.8	Method 8: Synthesis from Oxazoles by Cycloaddition (Kondrat'eva Pyridine Synthesis)	142
15.1.4.1.2.1.2.9	Method 9: Heterocycle Formation from Zirconacycles	143
15.1.4.1.2.2	Formal Exchange of Ring Members with Retention of Ring Size	143
15.1.4.1.2.2.1	Synthesis from Oxygen Heterocycles and Nitrogen Sources	143
15.1.4.1.2.2.1.1	Method 1: Synthesis from Pirylium Salts and Ammonium Salts	144

15.1.4.1.2.2.1.2	Method 2:	Synthesis from Benzopyranones and Ketimines	144
15.1.4.1.2.2.1.3	Method 3:	Synthesis from 2 <i>H</i> -Pyran-2-ones or 4 <i>H</i> -Pyran-4-ones and Ammonium Salts	145
15.1.4.1.2.2.1.3.1	Variation 1:	From 2,3,12 <i>a</i> ,12 <i>b</i> -Tetrahydro-1 <i>H</i> -pyrano[3',2':5,6]pyrano[4,3- <i>b</i>]benzopyran-7(4 <i>aH</i>)-ones	146
15.1.4.1.2.2.2		Synthesis from Pyridinium Compounds, Pyridines, or Pyridinones	146
15.1.4.1.2.2.2.1	Method 1:	Synthesis from Pyridinium Compounds by an ANRORC Substitution	146
15.1.4.1.2.2.2.1.1	Variation 1:	From Pyridinium Compounds by an Addition–Elimination Reaction	146
15.1.4.1.2.2.2.1.2	Variation 2:	From Pyridinium Compounds by Retro-Michael Reaction	148
15.1.4.1.2.2.2.1.3	Variation 3:	By Cope Rearrangement	148
15.1.4.1.2.2.2.2	Method 2:	Alkylation (Methylation, Benzylation)	148
15.1.4.1.2.2.2.2.1	Variation 1:	Triplet-Sensitized Photolysis of 1-[1-(1-Naphthyl)ethoxy]pyridin-2-one	149
15.1.4.1.2.2.2.3	Method 3:	Aminoalkylation	150
15.1.4.1.2.2.2.4	Method 4:	Elimination	150
15.1.4.1.2.2.2.5	Method 5:	Acylation/Trifluoromethylsulfonylation	151
15.1.4.1.2.2.2.5.1	Variation 1:	Trifluoromethylsulfonylation of 5-Azaspiro[2.5]oct-7-ene-4,6-dione	151
15.1.4.1.2.2.3		Synthesis from 1, <i>n</i> -Oxazines	152
15.1.4.1.2.2.3.1	Method 1:	Cycloaddition of 6 <i>H</i> -1,2-Oxazines and Alkynes	152
15.1.4.1.2.2.3.2	Method 2:	Benzofuro[3,2- <i>b</i>]pyridines from Benzofuro[3,2- <i>d</i>][1,3]oxazines	153
15.1.4.1.2.2.3.3	Method 3:	Synthesis from 1,4-Oxazin-2-ones by [4 + 2] Cycloaddition ..	153
15.1.4.1.2.2.4		Synthesis from 1, <i>n</i> -Diazines	154
15.1.4.1.2.2.4.1	Method 1:	Synthesis from Pyrimidines or Pyrimidinium Salts	154
15.1.4.1.2.2.5		Synthesis from 1, <i>n,m</i> -Triazines	155
15.1.4.1.2.2.5.1	Method 1:	Synthesis from 1,2,3-Triazines	155
15.1.4.1.2.2.5.2	Method 2:	Synthesis from 1,2,4-Triazines	155
15.1.4.1.2.2.6		Ring Opening of Fused Pyridine Derivatives	157
15.1.4.1.2.2.6.1	Method 1:	Synthesis from Imidazo[1,5- <i>a</i>]pyridine-Type Compounds	157
15.1.4.1.2.2.6.2	Method 2:	Pyridine-Substituted 1,2,3-Triazoles by Copper(I)-Catalyzed Click Reaction with Alkynes	158
15.1.4.1.2.2.6.3	Method 3:	Synthesis from [1,2,3]Triazolopyridines	159
15.1.4.1.2.3		Ring Contraction	159
15.1.4.1.2.3.1		From Seven-Membered Heterocycles	159
15.1.4.1.2.3.1.1	Method 1:	Synthesis from 1,4-Oxazepines	159
15.1.4.1.3		Aromatization	160
15.1.4.1.3.1		By Dehydrogenation	160
15.1.4.1.3.1.1	Method 1:	Oxidation (Dehydrogenation) of Dihydropyridines	160
15.1.4.1.3.2		Elimination from Dihydropyridines or Tetrahydropyridines	161

15.1.4.1.3.2.1	Method 1:	Synthesis from 1,2,3,6-Tetrahydropyridines	161
15.1.4.1.3.2.2	Method 2:	Synthesis from 2,3,4,5-Tetrahydropyridines	163
15.1.4.1.3.2.3	Method 3:	Synthesis from 2,6-Dioxopiperidines by Deoxygenation– Halogenation and Elimination	164
15.1.4.1.4		Synthesis by Substituent Modification	164
15.1.4.1.4.1		Substitution of Existing Substituents	164
15.1.4.1.4.1.1		Of Hydrogen	164
15.1.4.1.4.1.1.1	By Metals		164
15.1.4.1.4.1.1.1.1	Method 1:	By Alkali Metals	165
15.1.4.1.4.1.1.1.2	Method 2:	Mixed Metalation	165
15.1.4.1.4.1.1.1.3	Method 3:	By Silicon	167
15.1.4.1.4.1.1.1.3.1	Variation 1:	Intramolecular Iridium-Catalyzed Dehydrogenative Coupling ·	167
15.1.4.1.4.1.1.1.4	Method 4:	By Boron	168
15.1.4.1.4.1.1.2	By a Carbon Functionality		168
15.1.4.1.4.1.1.2.1	Method 1:	Direct Intermolecular Arylation Catalyzed by Transition-Metal Catalysts	169
15.1.4.1.4.1.1.2.2	Method 2:	Dimerization of Pyridine Derivatives	171
15.1.4.1.4.1.1.2.3	Method 3:	Direct Alkylation or Alkenylation	172
15.1.4.1.4.1.1.2.3.1	Variation 1:	Intramolecular Alkylation	176
15.1.4.1.4.1.1.2.4	Method 4:	C—H Arylation with Arylboronic Acids	177
15.1.4.1.4.1.1.2.5	Method 5:	Arylation/Alkylation Using Nickel or Iron Catalysts	177
15.1.4.1.4.1.1.2.6	Method 6:	Direct Arylation with Diaryliodonium Salts	178
15.1.4.1.4.1.1.2.7	Method 7:	Potassium <i>tert</i> -Butoxide Promoted Direct Arylation	179
15.1.4.1.4.1.1.2.8	Method 8:	Chichibabin-Type Direct Alkylation of Pyridylmethanols with Alkylolithium Reagents	179
15.1.4.1.4.1.1.2.9	Method 9:	Acylation via a Carbene Species	179
15.1.4.1.4.1.1.2.10	Method 10:	Carboxylation, Acylation, Hydroxyalkylation, and Related Reactions	180
15.1.4.1.4.1.1.2.10.1	Variation 1:	Direct Difluoromethylation	181
15.1.4.1.4.1.1.2.10.2	Variation 2:	Dihalomethylation of Nitropyridines (Vicarious Nucleophilic Substitution)	181
15.1.4.1.4.1.1.2.11	Method 11:	Activation and Copper(I)-Catalyzed Annulation	182
15.1.4.1.4.1.1.2.12	Method 12:	4-Alkylation of Pyridines via a Dipole-Reversal Process of 1,4-Dihydropyridine-4-phosphonates	182
15.1.4.1.4.1.1.2.13	Method 13:	Boron Trifluoride Mediated Regioselective Direct Alkylation and Arylation	183
15.1.4.1.4.1.1.3	By a Halogen		184
15.1.4.1.4.1.1.3.1	Method 1:	Directed Lithiation and Halogenation	184
15.1.4.1.4.1.1.3.2	Method 2:	C—H Fluorination	186
15.1.4.1.4.1.1.4	By Oxygen or Sulfur		186
15.1.4.1.4.1.1.4.1	Method 1:	Anionic Thia-Fries Rearrangement	186
15.1.4.1.4.1.1.4.2	Method 2:	C—H Activation/Oxidation	187
15.1.4.1.4.1.1.5	By Nitrogen		188
15.1.4.1.4.1.1.5.1	Method 1:	Nitration of Pyridines	188

15.1.4.1.4.1.1.5.2	Method 2:	Direct Amination or Alkylamination with Alkali Amides (Chichibabin Amination)	189
15.1.4.1.4.1.1.6	By Phosphorus		189
15.1.4.1.4.1.1.6.1	Method 1:	Silver-Catalyzed Coupling Reaction of Pyridines with Dialkyl Phosphites	189
15.1.4.1.4.1.2	Of Metals		190
15.1.4.1.4.1.2.1	Replacement of Silicon		190
15.1.4.1.4.1.2.1.1	Method 1:	Replacement of Silicon by Carbon: Hiyama Cross Coupling ..	190
15.1.4.1.4.1.2.1.2	Method 2:	Replacement of Silicon by Halogen	191
15.1.4.1.4.1.2.2	Replacement of Boron		191
15.1.4.1.4.1.2.2.1	Method 1:	Replacement of Boron by a Nitroso Group	191
15.1.4.1.4.1.2.2.2	Method 2:	Replacement of Boron by Oxygen	192
15.1.4.1.4.1.2.2.3	Method 3:	Replacement of Boron by Halogen	192
15.1.4.1.4.1.2.3	Replacement of Metals: Cross-Coupling Reactions		193
15.1.4.1.4.1.3	Of Halogens		196
15.1.4.1.4.1.3.1	By Hydrogen		197
15.1.4.1.4.1.3.1.1	Method 1:	Reduction	197
15.1.4.1.4.1.3.1.2	Method 2:	Protodeiodination via Hetaryltriphenylphosphonium Iodides with Base	198
15.1.4.1.4.1.3.2	By Metals		198
15.1.4.1.4.1.3.2.1	Method 1:	Lithium or Magnesium	198
15.1.4.1.4.1.3.2.2	Method 2:	Other Metals	200
15.1.4.1.4.1.3.3	By Other Halogen Groups		201
15.1.4.1.4.1.3.3.1	Method 1:	Oxidation of Iodopyridines	201
15.1.4.1.4.1.3.3.2	Method 2:	Halogen–Halogen Exchange	202
15.1.4.1.4.1.3.4	By a Carbon Functionality		204
15.1.4.1.4.1.3.4.1	Method 1:	Cyanation	204
15.1.4.1.4.1.3.4.2	Method 2:	Introduction of a Carboxylic Acid Derivative	205
15.1.4.1.4.1.3.4.3	Method 3:	Alkynylation or Alkenylation	205
15.1.4.1.4.1.3.4.4	Method 4:	Difluoro- or Trifluoromethylation	206
15.1.4.1.4.1.3.4.5	Method 5:	Arylation	207
15.1.4.1.4.1.3.4.5.1	Variation 1:	Arylation or Hetarylation under Lewis Acid Catalysis	211
15.1.4.1.4.1.3.4.5.2	Variation 2:	Decarboxylative Cross Coupling	211
15.1.4.1.4.1.3.4.5.3	Variation 3:	Palladium-Catalyzed Direct Arylation	211
15.1.4.1.4.1.3.4.6	Method 6:	Alkylation	212
15.1.4.1.4.1.3.4.6.1	Variation 1:	Intramolecular Alkylation	215
15.1.4.1.4.1.3.4.7	Method 7:	Substituted Pyridines via Pyridynes	217
15.1.4.1.4.1.3.5	By Oxygen		218
15.1.4.1.4.1.3.6	By Sulfur or Selenium		219
15.1.4.1.4.1.3.7	By Nitrogen		219
15.1.4.1.4.1.3.7.1	Method 1:	N-Nucleophiles	219

15.1.4.1.4.1.3.7.1.1	Variation 1:	Uncatalyzed Amination	222
15.1.4.1.4.1.3.7.1.2	Variation 2:	Rhodium(I)/Palladium(0) Catalyzed Chlorine–Amino Exchange	223
15.1.4.1.4.1.3.8	By Phosphorus		224
15.1.4.1.4.1.3.8.1	Method 1:	Halogen–Phosphorus Exchange	224
15.1.4.1.4.1.4	Of Oxygen or Sulfur		225
15.1.4.1.4.1.4.1	By Hydrogen		225
15.1.4.1.4.1.4.1.1	Method 1:	Reductive Removal of a Trifluoromethylsulfonyl Group	225
15.1.4.1.4.1.4.2	By Carbon		226
15.1.4.1.4.1.4.2.1	Method 1:	Cross Coupling of Pyridinol Derivatives with Organoboron Compounds	226
15.1.4.1.4.1.4.2.2	Method 2:	Palladium-Catalyzed Coupling of 4-Pyridyl Nonafluorobuta- nesulfonates with Methyl Diazoacetate	227
15.1.4.1.4.1.4.2.3	Method 3:	[1,2]-Anionic Rearrangement of 2-(Benzyloxy)pyridines	227
15.1.4.1.4.1.4.2.4	Method 4:	Cross Coupling of Organozinc Reagents with (Methylsulfa- nyl)pyridines	228
15.1.4.1.4.1.4.2.5	Method 5:	Cross Coupling of Pyridyl 4-Toluenesulfonates	228
15.1.4.1.4.1.4.3	By Halogen		230
15.1.4.1.4.1.4.4	By Nitrogen		231
15.1.4.1.4.1.4.4.1	Method 1:	Buchwald–Hartwig Cross Coupling	231
15.1.4.1.4.1.4.4.1.1	Variation 1:	Nickel-Catalyzed Amination of Sulfamates and Carbamates	232
15.1.4.1.4.1.5	Of Nitrogen		233
15.1.4.1.4.1.5.1	By Halogen		233
15.1.4.1.4.1.5.1.1	Method 1:	Fluorodenitration	233
15.1.4.1.4.1.5.1.1.1	Variation 1:	Fluorodenitration with N-Heterocyclic Carbenes	234
15.1.4.1.4.1.5.1.2	Method 2:	Sandmeyer Reaction	234
15.1.4.1.4.1.5.2	By Oxygen or Sulfur		235
15.1.4.1.4.1.5.2.1	Method 1:	Reaction of 2,6-Bis(pyridinium)-Substituted 3,5-Dichloropyri- dines with O- and S-Nucleophiles	235
15.1.4.1.4.1.5.2.2	Method 2:	Hydroxydenitration/Methoxydenitration	235
15.1.4.1.4.1.5.2.3	Method 3:	Hydroxydeamination	235
15.1.4.1.4.1.5.3	By Nitrogen		236
15.1.4.1.4.1.5.4	By Carbon		237
15.1.4.1.4.1.5.4.1	Method 1:	Substitution of a Nitro Group by Malonate	237
15.1.4.1.4.1.5.4.2	Method 2:	Via Benzidine Rearrangement	237
15.1.4.1.4.1.6	Of Carbon		238
15.1.4.1.4.1.6.1	By Hydrogen		238
15.1.4.1.4.1.6.1.1	Method 1:	Decarboxylation	238

15.1.4.1.4.1.6.2	By Another Carbon Group	239
15.1.4.1.4.1.6.2.1	Method 1: Arylation via Palladium-Catalyzed Decarboxylative Cross Coupling	239
15.1.4.1.4.2	Addition Reactions	239
15.1.4.1.4.2.1	Method 1: N-Arylation Using Arynes and Nitriles	239
15.1.4.1.4.3	Rearrangement of Substituents	239
15.1.4.1.4.3.1	Method 1: Rearrangement of Halogens: Halogen Dance	239
15.1.4.1.4.4	Modification of Substituents	240
15.1.4.1.4.4.1	Selective Degradation of Annulated Pyridines	240
15.1.4.1.4.4.1.1	Method 1: Partial Hydrogenation of Quinolines	240
15.1.4.1.4.4.2	Synthesis from Pyridine 1-Oxides	240
15.1.4.1.4.4.2.1	Method 1: Dehydrative Amidation or Amination	241
15.1.4.1.4.4.2.2	Method 2: Cyanation or Ethynylation	242
15.1.4.1.4.4.2.3	Method 3: Halogenation	243
15.1.4.1.4.4.2.3.1	Variation 1: Using Oxalyl Halides	243
15.1.4.1.4.4.2.4	Method 4: Reduction	244
15.1.4.1.4.4.2.5	Method 5: Addition of Arynes	245
15.1.4.1.4.4.2.6	Method 6: Addition of Grignard Reagents	246
15.1.4.1.4.4.2.7	Method 7: Boekelheide Reaction	247
15.1.4.1.4.4.2.8	Method 8: Catalyzed Oxidative Addition to Pyridine 1-Oxides	247
15.1.4.1.4.4.3	Addition to Existing Substituents	248
15.1.4.1.4.4.3.1	Method 1: Diels–Alder Reaction of 3-Methylenepyridin-4-one	248
15.1.4.1.4.4.3.2	Method 2: Alkylation of Pyridinethiones	248
15.1.4.1.4.4.4	Modification of Sidechains	249
15.1.4.1.4.4.4.1	Method 1: Modification of an Alkyl Substituent	249
15.1.4.1.4.4.4.1.1	Variation 1: Samarium/Scandium-Promoted Coupling Reactions	250
15.1.4.1.4.4.4.1.2	Variation 2: Lewis Acid Catalyzed Benzylic C—H Bond Functionalization ..	251
15.1.4.1.4.4.4.2	Method 2: Selective Oxidation	252
15.1.4.1.4.4.4.3	Method 3: Catalyzed <i>ortho</i> -Functionalization of 2-Arylpyridines	253
15.1.4.1.4.4.4.3.1	Variation 1: Arylation	253
15.1.4.1.4.4.4.3.2	Variation 2: Aminoalkylation and Acylation	254
15.1.4.1.4.4.4.3.3	Variation 3: Cyanation	254
15.1.4.1.4.4.4.3.4	Variation 4: Cyclopropylmethylation	255
15.1.4.1.4.4.4.3.5	Variation 5: Benzoylation, Acetoxylation, and Chlorination	255
15.1.4.1.4.4.4.3.6	Variation 6: Amidation and Nitration	256
15.1.4.1.4.4.4.4	Method 4: Catalytic Coupling of C—H and C—I Bonds Using Pyridine as a Directing Group	256
15.1.4.1.4.4.4.5	Method 5: C—H Bond Arylation of a Benzylic Amine	257
15.1.4.1.4.4.4.6	Method 6: Alkylation/Reduction of a Pyridinium <i>N</i> -Pyridylaminide	257
15.1.4.1.4.4.4.7	Method 7: Fluorination of 2-(2-Bromophenyl)pyridines	258

15.1.4.2	Pyridine 1-Oxides	258
15.1.4.2.1	Synthesis by Ring-Closure Reactions	260
15.1.4.2.1.1	By Formation of Two N—C Bonds	260
15.1.4.2.1.1.1	Fragments C—C—C—C and N	260
15.1.4.2.1.1.1.1	Method 1: Synthesis from Dimethyl 2-[(Dimethylamino)methylene]- 3-(2-oxoalkylidene)butanedioates and Hydroxylamine	260
15.1.4.2.1.2	By Formation of One N—C and One C—C Bond	262
15.1.4.2.1.2.1	Fragments N—C—C—C and C—C	262
15.1.4.2.1.2.1.1	Method 1: Synthesis from O-Propargylic α,β -Unsaturated Oximes by Copper-Catalyzed Tandem [2,3]-Rearrangement and 6π -3-Azatriene Electrocyclization	262
15.1.4.2.1.2.1.1.1	Variation 1: Thermally Induced Skeletal Rearrangement of O-Propargylic α,β -Unsaturated Z-Aldoximes	262
15.1.4.2.1.2.1.2	Method 2: Rhodium(III)-Catalyzed Cyclization of α,β -Unsaturated Oximes and Diazo Compounds	263
15.1.4.2.2	Synthesis by Substituent Modification	264
15.1.4.2.2.1	Substitution of Existing Substituents	264
15.1.4.2.2.1.1	Of Hydrogen	264
15.1.4.2.2.1.1.1	Metalation	264
15.1.4.2.2.1.1.1.1	Method 1: Intermediate Lithiation	264
15.1.4.2.2.1.1.1.2	Method 2: Cross Coupling by Addition–Elimination (Oxidation)	267
15.1.4.2.2.1.1.1.3	Method 3: Regioselective Metalation Followed by Palladium-Catalyzed Negishi Cross Coupling	267
15.1.4.2.2.1.1.2	By Carbon	268
15.1.4.2.2.1.1.2.1	Method 1: Catalytic Arylation, Hetarylation and Alkenylation, and Alkyl- ation of Pyridine 1-Oxides	268
15.1.4.2.2.1.1.2.1.1	Variation 1: Regioselective Cross-Dehydrogenative Coupling, Followed by Protodecarboxylation	273
15.1.4.2.2.1.1.2.2	Method 2: Metalation–Alkylation and –Acylation	274
15.1.4.2.2.1.1.3	By Halogen	274
15.1.4.2.2.1.1.3.1	Method 1: Iodination	274
15.1.4.2.2.1.1.4	By Nitrogen	275
15.1.4.2.2.1.1.4.1	Method 1: Nitration	275
15.1.4.2.2.1.2	Of Nitrogen	275
15.1.4.2.2.1.2.1	By Carbon	275
15.1.4.2.2.1.2.1.1	Method 1: Replacement of a Nitro Group with Grignard Reagents	275
15.1.4.2.2.1.2.2	By Halogen	276
15.1.4.2.2.1.2.2.1	Method 1: Halodenitration	276
15.1.4.2.2.1.2.3	By Oxygen	276
15.1.4.2.2.1.2.3.1	Method 1: Replacement of a Nitro Group by Oxygen Nucleophiles	276

15.1.4.2.2.1.3	Of Halogen	277
15.1.4.2.2.1.3.1	By Hydrogen	277
15.1.4.2.2.1.3.1.1	Method 1: Metalation–Protonation	277
15.1.4.2.2.1.3.2	By a Carbon Functionality	278
15.1.4.2.2.1.3.2.1	Method 1: Metal-Catalyzed Cross Coupling	278
15.1.4.2.2.1.3.2.2	Method 2: Metalation (Magnesiation) and Reaction with Electrophiles	278
15.1.4.2.2.1.3.3	By Nitrogen	279
15.1.4.2.2.1.3.3.1	Method 1: Aminodehalogenation	279
15.1.4.2.2.3	Addition Reactions	280
15.1.4.2.2.3.1	Method 1: N-Oxidation of Pyridines	280
15.1.4.2.2.3.2	Method 2: Addition of Alkyl Grignard Reagents to 2-Nitropyridine 1-Oxides	283
15.1.4.2.2.4	Modification of Alkyl Substituents	283
15.1.4.2.2.4.1	Method 1: Palladium-Catalyzed (1-Oxidopyridin-2-yl)methyl Transfer	283
15.1.4.2.2.4.2	Method 2: Palladium-Catalyzed Site-Selective Arylation	284
15.1.4.2.2.5	Modification at Oxygen	285
15.1.4.2.2.5.1	Method 1: Alkylation	285
15.1.4.3	Pyridinium Salts and N-Substituted Hydropyridines	285
15.1.4.3.1	Synthesis by Ring-Closure Reactions	291
15.1.4.3.1.1	By Formation of Two N—C Bonds and Two C—C Bonds	291
15.1.4.3.1.1.1	Fragments C—C—C, C, C, and N	291
15.1.4.3.1.1.1.1	Method 1: Aryl-Substituted Tetrahydropyridines by Multicomponent Reactions	291
15.1.4.3.1.1.2	Fragments C—C, C—C, C, and N	292
15.1.4.3.1.1.2.1	Method 1: Chichibabin-Type Synthesis	293
15.1.4.3.1.1.2.2	Method 2: Hantzsch-Type Synthesis from Primary Alkylamines, Alkyl Isocyanides, and Acetylenic Esters	296
15.1.4.3.1.1.2.2.1	Variation 1: Hantzsch-Type Synthesis from Primary Amines, Alkynes, and Aldehydes	296
15.1.4.3.1.2	By Formation of Two N—C Bonds and One C—C Bond	297
15.1.4.3.1.2.1	Fragments C—C—C, C—C, and N	297
15.1.4.3.1.2.1.1	Method 1: Synthesis from α,β -Unsaturated Ketones or Aldehydes and Primary Amines	297
15.1.4.3.1.2.1.2	Method 2: One-Pot Synthesis from Propargyl Vinyl Ethers	297
15.1.4.3.1.2.1.2.1	Variation 1: One-Pot Reaction of an Alkynoate, a Propargyl Alcohol, and a Primary Amine	298
15.1.4.3.1.2.1.3	Method 3: Rhodium(III)-Catalyzed Condensation of Vinyl Ketones or Aldehydes, Amines, and Alkynes	299
15.1.4.3.1.2.2	Fragments C—C—C—C, C, and N	299

15.1.4.3.1.2.2.1	Method 1: Cascade Synthesis of 1,2-Dihydropyridines from Dienamino-dioates and Imines	299
15.1.4.3.1.3	By Formation of One N—C and Two C—C Bonds	300
15.1.4.3.1.3.1	Fragments N—C, C—C—C, and C	300
15.1.4.3.1.3.1.1	Method 1: Synthesis from Imines, Enamino Esters, and Aldehydes	300
15.1.4.3.1.3.2	Fragments N—C, C—C, and C—C	301
15.1.4.3.1.3.2.1	Method 1: Synthesis from Imines and Aldehydes	301
15.1.4.3.1.3.2.1.1	Variation 1: Reaction of α,β -Unsaturated Carbonyl Compounds and N-Tosylimines	301
15.1.4.3.1.3.2.2	Method 2: Synthesis from 1,2,4-Triazines and Ketones	301
15.1.4.3.1.4	By Formation of Two N—C Bonds	302
15.1.4.3.1.4.1	Fragments C—C—C—C—C, and N	302
15.1.4.3.1.4.1.1	Method 1: Synthesis from Protected 1,5-Dioxo Compounds and Primary Amines	302
15.1.4.3.1.5	By Formation of One N—C Bond and One C—C Bond	303
15.1.4.3.1.5.1	Fragments N—C—C and C—C—C	303
15.1.4.3.1.5.1.1	Method 1: Synthesis from β -Acyl Enamines and α,β -Unsaturated Aldehydes	303
15.1.4.3.1.5.1.2	Method 2: Chemoselective Alkylation of Exocyclic Enamino Esters	303
15.1.4.3.1.5.2	Fragments N—C and C—C—C—C	304
15.1.4.3.1.5.2.1	Method 1: N-Substituted Tetrahydropyridines via a Nitro-Mannich/Hydroamination Cascade	304
15.1.4.3.1.5.3	Fragments N—C—C—C and C—C	304
15.1.4.3.1.5.3.1	Method 1: Synthesis from 1-Azadienes and Alkynes via Rhodium(I)-Catalyzed C—H Activation	304
15.1.4.3.1.5.3.2	Method 2: Synthesis from Ethyl Cyanoacetate Derivatives and Alkynyl Imines	305
15.1.4.3.1.5.4	Fragments N—C—C—C—C and C	306
15.1.4.3.1.5.4.1	Method 1: Synthesis from a β -Amino Alkene and 1,3,5-Trioxane	306
15.1.4.3.1.5.4.2	Method 2: Aza-Prins Cyclization from 2-Allylpyrrolidines and Aldehydes ..	306
15.1.4.3.1.6	By Formation of Two C—C Bonds	307
15.1.4.3.1.6.1	Fragment C—C—N—C and C—C	307
15.1.4.3.1.6.1.1	Method 1: Synthesis from an α,β -Diketone and Iminium Salts by Westphal Condensation under Microwave Conditions	307
15.1.4.3.1.7	By Formation of One N—C Bond	307
15.1.4.3.1.7.1	Fragment N—C—C—C—C—C	307
15.1.4.3.1.7.1.1	Method 1: Synthesis from 5-(Alkylamino)penta-2,4-dienals	307
15.1.4.3.1.7.1.2	Method 2: Synthesis from N,N-Diethyl-5-iminopenta-1,3-dien-1-amines ..	308
15.1.4.3.1.7.1.2.1	Variation 1: 1,6-Electrocyclization of 1-Azatriene Derivatives	309
15.1.4.3.1.8	By Formation of One C—C Bond	309

15.1.4.3.1.8.1	Fragment C—C—N—C—C—C	309
15.1.4.3.1.8.1.1	Method 1: Cyclization of a Baylis–Hillman Adduct	309
15.1.4.3.1.8.1.2	Method 2: Intramolecular Cyclization of N-Propargylic β -Enaminones ..	310
15.1.4.3.1.8.2	Fragment C—N—C—C—C—C	311
15.1.4.3.1.8.2.1	Method 1: Intramolecular Cyclization of 3-Phenyl- 7,8,9,10,12,13,14,15,15a,15b-decahydro-2 <i>H</i> -ben- zo[c][1,2,4]triazino[1,6- <i>a</i>]azecine-1,6(2 <i>H</i>)-dione	311
15.1.4.3.2	Synthesis by Ring Transformation	311
15.1.4.3.2.1	Ring Enlargement	311
15.1.4.3.2.1.1	Method 1: Ring Enlargement of Azetidin-3-ones Using Alkynes	311
15.1.4.3.2.1.2	Method 2: Ring Enlargement of 2-(Hydroxymethyl)-2,5-dihydropyrroles ..	312
15.1.4.3.2.1.3	Method 3: Ring Enlargement of 2-(Aminomethyl)furans	312
15.1.4.3.2.1.3.1	Variation 1: Aza-Achmatowicz Reaction	313
15.1.4.3.2.2	Formal Exchange of Ring Members with Retention of Ring Size	314
15.1.4.3.2.2.1	Method 1: Synthesis from Pyrylium Compounds	314
15.1.4.3.2.2.2	Method 2: Synthesis from 2-Alkoxy-3,4-dihydro-2 <i>H</i> -pyrans	314
15.1.4.3.2.2.3	Method 3: Synthesis from Other Pyridinium Compounds and Primary Amines or Hydrazines (Zincke Reaction)	315
15.1.4.3.3	Aromatization	316
15.1.4.3.3.1	Synthesis from Dihydropyridines	316
15.1.4.3.3.1.1	Method 1: Oxidation of 1-Alkyl- or 1-Aryl-1,4-dihydropyridines	316
15.1.4.3.3.1.2	Method 2: Borane Trifluoride–Diethyl Ether Complex as Aromatization Promoter	316
15.1.4.3.4	Synthesis by Substituent Modification	317
15.1.4.3.4.1	Substitution of Existing Substituents	317
15.1.4.3.4.1.1	Of Hydrogen	317
15.1.4.3.4.1.1.1	By Carbon	317
15.1.4.3.4.1.1.1.1	Method 1: Palladium-Catalyzed C-Arylation with Aryl Bromides	317
15.1.4.3.4.1.1.1.1.1	Variation 1: Silver-Catalyzed C-Arylation with Arylboronic Acids	317
15.1.4.3.4.1.1.1.2	Method 2: Copper-Catalyzed C-Alkylation	318
15.1.4.3.4.1.2	Of Oxygen	319
15.1.4.3.4.1.2.1	By Nitrogen	319
15.1.4.3.4.1.2.1.1	Method 1: Replacement by an Amino Group	319
15.1.4.3.4.1.3	Of Halogen	320
15.1.4.3.4.1.3.1	By Carbon	320
15.1.4.3.4.1.3.1.1	Method 1: Sonogashira Reaction	320
15.1.4.3.4.2	Addition Reactions	320
15.1.4.3.4.2.1	Method 1: N-Arylation, N-Alkylation, and N-Acylation	320
15.1.4.3.4.2.1.1	Variation 1: Zwitterionic Pyridinium Salts	327
15.1.4.3.4.2.1.2	Variation 2: Polymer-Supported Pyridinium Salts	328

15.1.4.3.4.2.1.3	Variation 3:	Mitsunobu Reaction	329
15.1.4.3.4.2.1.4	Variation 4:	Pyridine–Aldehyde Alkylation	329
15.1.4.3.4.2.1.5	Variation 5:	Reaction with Acetals	329
15.1.4.3.4.2.1.6	Variation 6:	Reaction with Oxiranes	330
15.1.4.3.4.2.1.7	Variation 7:	Aerobic Palladium-Catalyzed Pyridine-Directed C(sp ³)–H Alkylation	330
15.1.4.3.4.2.1.8	Variation 8:	Reversible Frustrated Lewis Pair Addition of N-Heterocycles to Unsaturated C–C Bonds	331
15.1.4.3.4.2.2	Method 2:	Metal Complexes of 1-Acylpyridinium Salts	331
15.1.4.3.4.2.3	Method 3:	N-Fluorination	332
15.1.4.3.4.2.4	Method 4:	N-Silylation	333
15.1.4.3.4.2.5	Method 5:	Borylation	333
15.1.4.3.4.3	Modification of Substituents		334
15.1.4.3.4.3.1	Method 1:	O-Functionalization of Pyridine 1-Oxides	334
15.1.4.3.4.3.2	Method 2:	Alkylation/Hydrogenation of Pyridin-2-amines	334
15.1.4.3.4.3.3	Method 3:	Reduction of an Acyloxymethyl Group	335
15.1.4.3.4.3.4	Method 4:	Pyridines from Pyridinium Salts by 3-Aza-Cope Rearrangement	336
15.1.4.3.4.3.5	Method 5:	Reactions of Pyridinium Superelectrophiles	336
15.1.4.3.4.3.6	Method 6:	Regioselective C–H Activation on Stabilized Nitrogen Ylides	337
15.1.4.3.4.3.7	Method 7:	Deprotonation and Arylation/Alkylation of 1-Aminopyridinium Salts	337
15.1.4.3.4.3.8	Method 8:	Reaction of Pyridine 1-Oxides or 1-Amidates with Diaryliodonium Salts	337

Volume 34: Fluorine

34.1	Product Class 1: Fluoroalkanes	
34.1.2.6	Synthesis by Substitution of Metals M. Shevchuk and G.-V. Röschenthaler	
34.1.2.6	Synthesis by Substitution of Metals	363
34.1.2.6.1	Method 1: Synthesis from Organoboron Compounds	363
34.1.2.6.1.1	Variation 1: Silver-Catalyzed Radical Fluorination of Alkylboronic Acids and Pinacol Alkylboronates	363
34.1.2.6.1.2	Variation 2: Enantioselective Fluorination of Tetracoordinate Boronate Complexes	366
34.1.2.6.2	Method 2: Synthesis from Organosilanes	368
34.1.2.6.3	Method 3: Synthesis from Organopotassium Compounds	369
34.1.2.6.4	Method 4: Synthesis from Organometallic Complexes of Groups 10 and 11	369
34.1.2.6.4.1	Variation 1: Synthesis by Electrophilic Fluorination of Au–C(sp ³) Complexes	370

34.1.2.6.4.2	Variation 2: Synthesis by Electrophilic Fluorination of Pt—C(sp ³) and Pd—C(sp ³) Complexes	371
34.1.3.4	Synthesis by Substitution of Carbon Functionalities J. Desroches and J.-F. Paquin	
34.1.3.4	Synthesis by Substitution of Carbon Functionalities	375
34.1.3.4.1	Method 1: Decarboxylative Fluorination Using Selectfluor or <i>N</i> -Fluorobenzenesulfonimide	375
34.1.3.4.1.1	Variation 1: Metal-Free Conditions	375
34.1.3.4.1.2	Variation 2: Using Ruthenium- and Iridium-Based Photocatalysts	379
34.1.3.4.1.3	Variation 3: Using a Silver-Based Catalyst	382
34.1.3.4.2	Method 2: Decarboxylative Fluorination Using a Nucleophilic Source of Fluorine	384
34.1.3.4.3	Method 3: Ring-Opening Fluorination	386
34.1.3.4.3.1	Variation 1: Using Photocatalysis	386
34.1.3.4.3.2	Variation 2: Using Silver-Based Catalysts	387
34.1.3.4.3.3	Variation 3: Ring-Opening Fluoroselenylation	388
34.1.3.4.3.4	Variation 4: Ring-Opening Hydrofluorination	389
34.1.3.4.3.5	Variation 5: Diethylaminosulfur Trifluoride Mediated Ring-Opening Fluorination	390
34.1.4.2.9	Synthesis by Substitution of Hydroxy Groups in Alcohols M. Vandamme and J.-F. Paquin	
34.1.4.2.9	Synthesis by Substitution of Hydroxy Groups in Alcohols	395
34.1.4.2.9.1	Method 1: Reaction with <i>N,N</i> -Diethylaminosulfur Trifluoride	395
34.1.4.2.9.1.1	Variation 1: Use of Ionic Liquids as Recyclable Solvents	395
34.1.4.2.9.1.2	Variation 2: Fluorination in a Continuous-Flow Microreactor	396
34.1.4.2.9.2	Method 2: Reaction with Aminodifluorosulfonium Salts	399
34.1.4.2.9.3	Method 3: Reaction with Diethyl[difluoro(3-tolyl)methyl]amine	401
34.1.4.2.9.4	Method 4: Reaction with Perfluorobutanesulfonyl Fluoride	402
34.1.4.2.9.5	Method 5: Reaction with 4- <i>tert</i> -Butyl-2,6-dimethylphenylsulfur Trifluoride (Fluolead)	403
34.1.4.2.9.6	Method 6: Reaction with 1,3-Bis(2,6-diisopropylphenyl)-2,2-difluoro-2,3-dihydro-1 <i>H</i> -imidazole (PhenoFluor)	405
34.1.4.2.9.7	Method 7: Reaction with Pyridine-2-sulfonyl Fluoride (PyFluor)	406
34.5	Product Class 5: Propargylic Fluorides	
34.5.2	Propargylic Fluorides J.-D. Hamel and J.-F. Paquin	
34.5.2	Propargylic Fluorides	409
34.5.2.1	Method 1: Dehydroxyfluorination of Hexacarbonyldicobalt-Protected Propargylic Alcohols	409

34.5.2.1.1	Variation 1:	Using Preformed Cobalt Complexes	409
34.5.2.1.2	Variation 2:	Using In Situ Prepared Cobalt Complexes	410
34.5.2.2	Method 2:	Fluorination of Allenylsilanes	411
34.5.2.3	Method 3:	Fluorination of Allenolates	413
34.5.2.4	Method 4:	Fluorination/Homologation of Aldehydes	414
34.5.2.4.1	Variation 1:	Using Preformed Ohira–Bestmann Reagent	414
34.5.2.4.2	Variation 2:	Using In Situ Prepared Ohira–Bestmann Reagent	415
34.5.2.5	Method 5:	Alkynylation of α -Fluoro Sulfones	416

34.6 Product Class 6: Benzylic Fluorides

34.6.2 Benzylic Fluorides

P. A. Champagne, M. Drouin, and J.-F. Paquin

34.6.2	Benzylic Fluorides		419
34.6.2.1	Method 1:	Dehydrofluorination	419
34.6.2.1.1	Variation 1:	Enantioselective α -Fluorination of Arylacetic Acid Chlorides ..	419
34.6.2.1.2	Variation 2:	Enantioselective α -Fluorination of Arylacetamide Derivatives ..	421
34.6.2.1.3	Variation 3:	Fluorination of Oxindoles	422
34.6.2.1.4	Variation 4:	Fluorination of α -Cyano Esters	424
34.6.2.1.5	Variation 5:	Iron-Catalyzed Free-Radical Process	425
34.6.2.1.6	Variation 6:	By Photocatalysis	426
34.6.2.1.7	Variation 7:	Using Radical Initiators	427
34.6.2.1.8	Variation 8:	Palladium-Catalyzed Process	428
34.6.2.2	Method 2:	Monofluoroalkylation of Arenes	430
34.6.2.2.1	Variation 1:	Cross Coupling of α,α -Dihalo Ketones, Esters, and Derivatives	430
34.6.2.2.2	Variation 2:	Cross Coupling of α -Fluoro Sulfones	433
34.6.2.2.3	Variation 3:	Cross Coupling of Fluorohalomethanes	435
34.6.2.3	Method 3:	Fluorinative Addition to Styrenes	437
34.6.2.3.1	Variation 1:	Palladium-Catalyzed Fluorination of Alkenes	437
34.6.2.3.2	Variation 2:	Silver-Catalyzed Fluoroarylation of Alkenes	440
34.6.2.4	Method 4:	Hydrofluorination of Aryl <i>N</i> -Tosylhydrazones	441
34.6.2.5	Method 5:	Fluorodecarboxylation of Benzylic Acids	443
34.6.2.5.1	Variation 1:	Silver-Catalyzed Fluorodecarboxylation	443
34.6.2.5.2	Variation 2:	Manganese-Catalyzed Fluorodecarboxylation	444
34.6.2.6	Method 6:	Deoxofluorination of Benzylic Alcohols	445
34.6.2.7	Method 7:	Aryl Epoxide Opening	447
	Author Index		451
	Abbreviations		475