

Table of Contents

2.1	Alkene Metathesis	
2.1.1	Historical Overview of N-Heterocyclic Carbenes in Alkene Metathesis	
	C. Slugovc	
2.1.1	Historical Overview of N-Heterocyclic Carbenes in Alkene Metathesis	1
2.1.2	Ring-Closing Metathesis	
	J. Broggi and H. Clavier	
2.1.2	Ring-Closing Metathesis	11
2.1.2.1	Preparation of Common Rings	12
2.1.2.2	Preparation of Medium Rings	24
2.1.2.3	Preparation of Large Rings (Macrocyclization)	29
2.1.2.4	Asymmetric Ring-Closing Metathesis	36
2.1.3	Cross Metathesis	
	A. Jana, P. Małecki, and K. Grela	
2.1.3	Cross Metathesis	47
2.1.3.1	Principles of Alkene Cross Metathesis	47
2.1.3.2	Cross-Metathesis Catalysts Based on N-Heterocyclic Carbene Ligands	49
2.1.3.3	Categorization of Cross Metathesis According to Functional Groups on the Alkenes	52
2.1.3.3.1	Ethenolysis: Hydrogen as a Functional Group	52
2.1.3.3.2	Boron-Substituted Alkenes	53
2.1.3.3.3	Alkenes Bearing Carbon-Based Functional Groups	54
2.1.3.3.4	Alkenes Bearing Nitrogen-Based Substituents	58
2.1.3.3.5	Alkenes Bearing Oxygen-Based Substituents	60
2.1.3.3.6	Haloalkenes	62
2.1.3.3.7	Alkenes Bearing Silicon-Based Substituents	63
2.1.3.3.8	Alkenes Bearing Phosphorus-Based Substituents	63
2.1.3.3.9	Alkenes Bearing Sulfur-Based Substituents	64
2.1.3.4	Asymmetric Cross Metathesis	66
2.1.3.5	Z Selectivity in Cross Metathesis	66

2.1.3.6	Ethenolysis (Cross Metathesis with Ethene)	68
2.1.3.6.1	Limitations of Ethenolysis	68
2.1.3.6.2	Application of Ethenolysis in Oleochemistry	69
2.1.3.6.3	Application of Ethenolysis in Polyalkene Scission	73
2.1.3.7	Conclusions	74
 2.1.4	Enyne Metathesis	
	C. E. Diesendruck	
<hr/>		
2.1.4	Enyne Metathesis	79
2.1.4.1	Mechanism of Enyne Metathesis	79
2.1.4.2	Ring-Closing Enyne Metathesis	81
2.1.4.3	Cross Enyne Metathesis	83
2.1.4.4	The Role of Ethene	86
2.1.4.5	Introduction of N-Heterocyclic Carbene Ligands in Enyne Metathesis	87
2.1.4.6	Tandem and Cascade Enyne Metathesis	88
2.1.4.7	Challenging Enyne Substrates and Relay Metathesis	94
2.1.4.8	Conclusions	97
 2.1.5	Alkene Metathesis Based Polymerization	
	J. Liu and J. A. Johnson	
<hr/>		
2.1.5	Alkene Metathesis Based Polymerization	99
2.1.5.1	Ring-Opening Metathesis Polymerization	99
2.1.5.1.1	General Procedure and Experimental Considerations for Ring-Opening Metathesis Polymerization	102
2.1.5.1.2	Living Ring-Opening Metathesis Polymerization of Copolymers	104
2.1.5.1.3	Ring-Opening Metathesis Polymerization for Synthesis of Branched Polymer Architectures	107
2.1.5.1.4	Ring-Opening Metathesis Polymerization with Modified N-Heterocyclic Carbenes	113
2.1.5.1.4.1	Modified N-Heterocyclic Carbenes for Stereoselective, Aqueous, or Solid-Supported Ring-Opening Metathesis Polymerization with Ruthenium Catalysts	113
2.1.5.1.4.2	Modified N-Heterocyclic Carbenes for Cyclic Polymers: Ring-Expansion Metathesis Polymerization	115
2.1.5.2	Alternative Methods of Alkene Metathesis Polymerization	117
2.1.5.2.1	Acyclic Diene Metathesis Polymerization	117
2.1.5.2.2	Cyclopolymerization with N-Heterocyclic Carbene–Ruthenium Complexes ...	119

2.1.5.3	Alkene Metathesis Based Polymerization Using Non-ruthenium Initiators with N-Heterocyclic Carbene Ligands	121
2.1.5.3.1	Molybdenum and Tungsten Complexes	121
2.2	Polymerization, Oligomerization, and Telomerization Involving N-Heterocyclic Carbenes as Ligands or Initiators	
	C. Costabile	
2.2	Polymerization, Oligomerization, and Telomerization Involving N-Heterocyclic Carbenes as Ligands or Initiators	127
2.2.1	Polymerization Promoted by N-Heterocyclic Carbene–Metal Complexes	127
2.2.1.1	Alkene Polymerization in the Presence of Main Group and Early Transition Metals	127
2.2.1.2	Alkene Polymerization in the Presence of Late Transition Metals	130
2.2.1.3	Alkene Polymerization in the Presence of Rare Earth Metals	134
2.2.1.4	Ring-Opening Polymerization of Cyclic Esters in the Presence of Early Transition Metals	136
2.2.1.5	Ring-Opening Polymerization of Cyclic Esters in the Presence of Late Transition Metals	138
2.2.1.6	Ring-Opening Polymerization of Cyclic Esters in the Presence of Lanthanides	140
2.2.2	Polymerization Promoted by Metal-Free N-Heterocyclic Carbene Initiators ..	141
2.2.2.1	Ring-Opening Polymerization of Cyclic Esters To Give Linear Polymers ..	141
2.2.2.2	Ring-Opening Polymerization of Cyclic Esters To Give Cyclic Polymers ..	143
2.2.3	Oligomerization of Alkenes Promoted by N-Heterocyclic Carbene–Metal Complexes	144
2.2.4	Telomerization Reactions Catalyzed by N-Heterocyclic Carbene–Palladium Complexes	145
2.3	Cyclization Reactions	
	Y. Zhong, S. Felten, and J. Louie	
2.3	Cyclization Reactions	151
2.3.1	Cyclizations Catalyzed by N-Heterocyclic Carbene–Gold Complexes	151
2.3.1.1	Cycloisomerization of 1,6-Enynes	151
2.3.1.1.1	Cycloisomerization of 1,6-Enynes with Trapping by Methanol To Form exo-Methylene Cyclopentanes	152
2.3.1.1.2	Cycloisomerization of 1,6-Enynes with Trapping by External Alkenes To Form Bicyclopropane Derivatives	154
2.3.1.1.3	Cycloisomerization of Dienyl Alkynes	154
2.3.1.1.4	Cycloisomerization of 1,6-Enynes with Trapping by an External Oxidant To Form Bicyclic Aldehyde Derivatives	156

2.3.1.1.5	Cycloisomerization of 1,6-Enynes with Trapping by External Aldehydes To Form Bicyclic Dihydropyran Derivatives	157
2.3.1.2	Cycloisomerization of 1,5-Enynes	159
2.3.1.2.1	Tandem Nucleophilic Substitution/Cycloisomerization of Propargyl Alcohols To Form Bicyclo[3.1.0]hex-2-enes	159
2.3.1.2.2	Sequential Claisen Rearrangement/Heterocyclization of N-Tethered 1,5-Enynes To Form Pyrrole Derivatives	161
2.3.1.2.3	Sequential Claisen Rearrangement/Heterocyclization of O-Tethered 1,5-Enynes To Form Furan Derivatives	162
2.3.1.2.4	Cycloisomerization of 1,5-Enynes with Trapping by External Aldehydes To Form Bicyclic Tetrahydrofurans	162
2.3.1.3	Cycloaddition Reactions	165
2.3.1.3.1	[2 + 2] Cycloaddition of N-Tethered 1,5-Bisallenes To Give 6,7-Dimethylene-3-azabicyclo[3.1.1]heptanes	165
2.3.1.3.2	Intramolecular [4 + 3] Cycloaddition of Allenedienes To Form Bicyclic Cycloheptadienes	167
2.3.1.3.3	Asymmetric Intermolecular [4 + 2] Cycloaddition of Allenyl Amides and Dienes To Form Cyclohexenes	168
2.3.1.3.4	Dipolar [4 + 2] Cycloaddition of 1-Alkynylcyclopropyl Ketones with Indoles To Form Tetracyclic Furocarbazoles	169
2.3.1.3.5	Dipolar [4 + 2] Cycloaddition of 1-Alkynylcyclopropyl Ketones with Carbonyl Compounds To Form Dihydrofuropyrans	171
2.3.1.4	Rearrangement of Propargylic Esters	171
2.3.1.4.1	Intramolecular Rearrangement of 1-Arylpropargylic Acetates To Form Indene Derivatives	172
2.3.1.4.2	Cycloisomerization of 1,7-Enyne Esters To Form <i>cis</i> -1,2,3,6-Tetrahydropyridin-4-yl Ketones	173
2.3.1.4.3	Cycloisomerization of 1,6-Diyne Esters To Form 1 <i>H</i> -Cyclopenta[<i>b</i>]-naphthalenes	174
2.3.1.4.4	Cyclization of 1,6-Diyne Carbonates and Esters with Aldehydes To Form 4-(Cyclohexa-1,3-dienyl)-1,3-dioxolanes	175
2.3.1.4.5	Intermolecular Cyclization of Propargyl 4-Toluenesulfonates and Imines To Form Cyclopent-2-en-1-imines	177
2.3.1.5	Nucleophilic Addition to Activated Alkynes	178
2.3.1.5.1	Intramolecular Cyclization of γ -Alkynoic Acids To Give Enol Lactones	179
2.3.1.5.2	Carboxylative Cyclization of Propargylamines with Carbon Dioxide To Form Cyclic Carbamates	180
2.3.1.5.3	Domino Aminocyclization/1,3-Sulfonyl Migration of N-Substituted N-Sulfonyl-1-aminobut-3-yn-2-ols To Form 1-Substituted 3-Sulfonyl-1 <i>H</i> -pyrroles	181

2.3.1.5.4	Tandem Hydroamination/Hydroarylation of Aromatic Amines and Alkynes To Form 1,2-Dihydroquinolines	182
2.3.1.5.5	Cyclization of 2-Aminophenyl Ketones and Alkynes To Form 2,4-Disubstituted Quinolines	184
2.3.1.5.6	Intermolecular Cyclization of N-Substituted o-Phenylenediamines and Terminal Alkynes To Form 1-Substituted 2,3-Dihydro-1 <i>H</i> -benzo[<i>b</i>][1,4]-diazepines	184
2.3.1.5.7	Domino Cycloisomerization/Pictet–Spengler Reaction of 2-(4-Aminobut-1-ynyl)anilines with Aldehydes To Form Tetrahydropyrido[4,3- <i>b</i>]indoles	185
2.3.1.5.8	Relay N-Heterocyclic Carbene–Gold/Lewis Acid Catalyzed Cascade Hydroamination/Aza-Diels–Alder Reaction of <i>N</i> -(2-Ethynylbenzyl)-4-toluene-sulfonamides and Unsaturated Oxo Esters To Form Spiroaminals	187
2.3.1.5.9	Intramolecular Hydroamination of 3-Substituted 1-(2-Ethynylaryl)ureas To Form 4-Methylene-3,4-dihydroquinazolin-2-ones	188
2.3.1.5.10	Intramolecular 5-exo Oxygen-Transfer Redox Cyclization of Homopropargyl Hydroxylamines To Form Pyrrolidin-3-ones	189
2.3.1.5.11	Inter-/Intramolecular Addition Cascade of Diynes for the Synthesis of Substituted Naphthalenes	189
2.3.2	Cyclizations Catalyzed by N-Heterocyclic Carbene–Copper Complexes	191
2.3.2.1	N-Heterocyclic Carbene–Copper-Catalyzed 1,3-Dipolar [3+2] Cycloaddition ..	191
2.3.2.1.1	Regioselective 1,3-Dipolar [3+2] Cycloaddition of Azides and Alkynes To Form 1,4-Disubstituted 1,2,3-Triazoles under Neat Conditions	191
2.3.3	Cyclizations Catalyzed by N-Heterocyclic Carbene–Palladium Complexes	194
2.3.3.1	Intramolecular Wacker-Type Cyclizations	194
2.3.3.1.1	Aerobic Intramolecular Wacker-Type Cyclization of 2-Allylphenols To Form Benzofurans	194
2.3.3.1.2	Aerobic Intramolecular Aza-Wacker-Type Cyclization of 2-Allylanilines To Form Dihydroindoles	195
2.3.3.2	Intramolecular α -Arylation of Amides	196
2.3.3.2.1	Asymmetric Intramolecular α -Arylation of <i>N</i> -(2-Bromophenyl) Amides To Form Oxindoles Using Imidazolium Catalysts Bearing Chiral Centers on the Side Branches	197
2.3.3.2.2	Asymmetric Intramolecular α -Arylation of <i>N</i> -(2-Bromophenyl) Amides To Form Oxindoles Using Imidazolium Catalysts Bearing Chiral Centers on the Backbone	198
2.3.4	Cyclizations Catalyzed by N-Heterocyclic Carbene–Nickel Complexes	200
2.3.4.1	Cycloaddition Reactions	200
2.3.4.1.1	[2+2+2] Cycloaddition of Diynes and Carbon Dioxide To Afford Pyranones ..	201
2.3.4.1.2	[2+2+2] Cycloaddition of Diynes and Isocyanates To Afford Pyridin-2-ones ..	202
2.3.4.1.3	[2+2+2] Cycloaddition of Alkynes and Isocyanates To Afford Pyrimidinediones	203

2.3.4.1.4	[2 + 2 + 2] Cycloaddition of Diynes and Nitriles To Afford Pyridines	204
2.3.4.1.5	[2 + 2 + 2] Cycloaddition of Diynes and Cyanamides To Afford Pyridin-2-amines	205
2.3.4.1.6	[4 + 2 + 2] Cycloaddition of Diynes and Cyclobutanones To Afford Cyclooctadienones	206
2.3.4.1.7	[4 + 2 + 2] Cycloaddition of Diynes and Azetidin-3-ones To Afford Dihydroazocinones	208
2.3.4.1.8	Cycloaddition of Diynes and Tropone To Afford Tricyclic Dihydrobenzo[7]annulenones	209
2.3.4.1.9	[3 + 2] Cycloaddition of Cyclopropyl Ketones and Enones To Afford Cyclopentanes	211
2.3.4.1.10	[3 + 2] Cycloaddition of Cyclopropyl Aldimines and Enones To Afford Cyclopentanes	213
2.3.4.1.11	[2 + 2] Cycloaddition of Enynes and Electron-Deficient Alkenes To Afford Cyclobutenes	214
2.3.4.2	Cycloisomerization Reactions	215
2.3.4.2.1	Cycloisomerization of Vinylcyclopropanes To Give Cyclopentenes	215
2.3.4.2.2	Cycloisomerization of Enynes To Give Exocyclic 1,3-Dienes	216
2.3.4.2.3	7-exo-trig Cycloisomerization of 1,7-Dienes	217
2.3.5	Cyclizations Catalyzed by N-Heterocyclic Carbene–Rhodium Complexes	218
2.3.5.1	Cycloaddition Reactions	218
2.3.5.1.1	Diastereoselective [4 + 2 + 2] Cycloaddition of 1,6-Enynes and Buta-1,3-diene To Form Bicyclic Cyclooctadienes	219
2.3.5.1.2	Intramolecular [4 + 2] Cycloaddition of 1,6-Dienynes To Form Bicyclic Cyclohexadienes	220
2.3.5.1.3	Intermolecular [4 + 2] Cycloaddition of Alkynes and 2,3-Dimethylbuta-1,3-diene To Form Cyclohexadienes	221
2.3.5.1.4	Intramolecular [5 + 2] Cycloaddition of Cyclopropylvinyl-Tethered Alkynes To Form Bicyclic Cycloheptadienes	221
2.3.6	Cyclizations Catalyzed by N-Heterocyclic Carbene–Cobalt Complexes	222
2.3.6.1	Cycloaddition Reactions	222
2.3.6.1.1	Intramolecular [2 + 2 + 2] Cycloaddition of Triynes To Form Annulated Benzenes	222
2.3.6.1.2	Intramolecular [2 + 2 + 2] Cycloaddition of Enediynes To Form Annulated Cyclohexadienes	223
2.3.7	Cyclizations Catalyzed by N-Heterocyclic Carbene–Iron Complexes	224
2.3.7.1	Cycloaddition Reactions	224
2.3.7.1.1	Intramolecular [2 + 2 + 2] Cycloaddition of Triynes To Form Annulated Benzenes	224
2.3.7.1.2	Formal Intermolecular [3 + 2] Cycloaddition of Vinylcyclopropanes and Alkenes To Form Cyclopentanes	225

2.4	N-Heterocyclic Carbenes in Asymmetric Transition-Metal Catalysis	
	S. K. Collins and M. Holtz-Mulholland	
<hr/>		
2.4	N-Heterocyclic Carbenes in Asymmetric Transition-Metal Catalysis	229
2.4.1	Hydrosilylation of Ketones	232
2.4.2	Allylic Substitution	235
2.4.3	Conjugate Addition	240
2.4.4	Alkene Metathesis	244
2.4.5	Hydrogenation of Alkenes	249
2.4.6	Cyclization Reactions	251
2.4.7	Addition to Imines	253
2.4.8	Hydroboration of Alkenes	255
2.4.9	Nickel-Catalyzed Reductive Coupling	257
2.4.10	Conclusions	257
<hr/>		
2.5	Transition-Metal-Catalyzed Oxidations	
	D. Munz	
<hr/>		
2.5	Transition-Metal-Catalyzed Oxidations	265
2.5.1	Stoichiometric Reactions with Dioxygen	266
2.5.2	Alcohol Oxidation	268
2.5.3	Oxidation of Alkenes	270
2.5.3.1	Wacker-Type Cyclizations	270
2.5.3.2	Wacker Oxidation to Ketones	272
2.5.3.3	Epoxidation	272
2.5.3.4	Aziridination	273
2.5.3.5	Alkene Scission to Aldehydes	274
2.5.4	Oxidation of Hydrocarbons	276
2.5.4.1	Oxidation of Alkanes and Arenes with Palladium Complexes	276
2.5.4.2	Oxidation of Cycloalkanes with Iridium Catalysts	278
<hr/>		
2.6	Carboxylation, Carbonylation, and Dehalogenation	
	D. J. Nelson	
<hr/>		
2.6	Carboxylation, Carbonylation, and Dehalogenation	281
2.6.1	Carboxylation	281
2.6.1.1	Carboxylation of C—H Bonds Catalyzed by Gold(I) Hydroxide Complexes	281
2.6.1.2	Carboxylation of C—H and N—H Bonds Catalyzed by Copper(I) Hydroxide Complexes	283

2.6.1.3	Carboxylation of Organoboron Reagents Catalyzed by N-Heterocyclic Carbene–Copper Complexes	284
2.6.1.4	Carboxylation of Organoboron Reagents Catalyzed by N-Heterocyclic Carbene–Nickel Complexes	285
2.6.1.5	Hydrocarboxylation of Alkynes Catalyzed by N-Heterocyclic Carbene–Copper Complexes	286
2.6.1.6	Carboxylative Coupling of Alkynes with Alkyl Chlorides Catalyzed by N-Heterocyclic Carbene–Copper Complexes	288
2.6.1.7	Carboxylative Cyclization Reactions: Synthesis of Pyrones from Diynes	288
2.6.2	Carbonylation	289
2.6.2.1	Synthesis of Glyoxamides Catalyzed by N-Heterocyclic Carbene–Copper Complexes	289
2.6.2.2	Synthesis of <i>N</i> -Acylpyrroles Catalyzed by N-Heterocyclic Carbene–Palladium Complexes	290
2.6.2.3	Synthesis of Ketones Catalyzed by N-Heterocyclic Carbene–Rhodium Complexes	291
2.6.2.4	Synthesis of Ketones Catalyzed by N-Heterocyclic Carbene–Palladium Complexes	292
2.6.3	Dehalogenation	294
2.6.3.1	Dechlorination of Arenes Catalyzed by N-Heterocyclic Carbene–Palladium Complexes	294

2.7 Recyclable Systems

2.7.1	Biphasic Systems C. Claver, C. Godard, and A. Martínez Lombardía	
2.7.1	Biphasic Systems	297
2.7.1.1	Alkene Metathesis	298
2.7.1.2	Other Reactions	303
2.7.2	Covalently Immobilized N-Heterocyclic Carbene Complexes C. Thieuleux and D. Crozet	
2.7.2	Covalently Immobilized N-Heterocyclic Carbene Complexes	309
2.7.2.1	Covalent Immobilization on Oxide Supports	310
2.7.2.1.1	Post-Grafting Functionalization	310
2.7.2.1.1.1	General Description, Advantages, and Drawbacks	310
2.7.2.1.1.2	Catalytic Applications	311

2.7.2.1.1.2.1	Palladium Complexes	312
2.7.2.1.1.2.2	Rhodium Complexes	316
2.7.2.1.1.2.3	Gold Complexes	319
2.7.2.1.1.2.4	Ruthenium Complexes	320
2.7.2.1.1.2.5	Iridium Complexes	325
2.7.2.1.1.2.6	Non-noble Metal Complexes	327
2.7.2.1.2	Direct Incorporation by Sol-Gel Processes	330
2.7.2.1.2.1	General Description, Advantages, and Drawbacks	330
2.7.2.1.2.2	Catalytic Applications	331
2.7.2.1.2.2.1	Palladium Complexes	332
2.7.2.1.2.2.2	Ruthenium Complexes	336
2.7.2.1.2.2.3	Iridium Complexes	343
2.7.3	Catalytic Systems Featuring Ionically Tagged N-Heterocyclic Carbene Ligands	
	T. E. Schmid, C. Crévisy, O. Baslé, and M. Mauduit	
2.7.3	Catalytic Systems Featuring Ionically Tagged N-Heterocyclic Carbene Ligands	351
2.7.3.1	Palladium Complexes for Cross-Coupling Reactions	351
2.7.3.1.1	Mizoroki–Heck Reaction	351
2.7.3.1.2	Suzuki–Miyaura Reaction	352
2.7.3.2	Ruthenium-Catalyzed Alkene Metathesis	354
2.7.3.3	Copper-Catalyzed Azide–Alkyne Cycloaddition	356
2.7.3.4	Hydrosilylation	359
2.7.3.5	Hydrogenation	360
2.7.3.6	Alcohol Isomerization	361
2.7.3.7	Gold-Catalyzed Cycloisomerization	362
2.7.3.8	Intramolecular Cyclization of Enynols	364
2.7.3.9	Copper-Catalyzed Carboxylation of Arylboronic Esters	365
2.7.4	Flow Systems for N-Heterocyclic Carbene Catalysis	
	I. Peñafiel and A. Lapkin	
2.7.4	Flow Systems for N-Heterocyclic Carbene Catalysis	369
2.7.4.1	Continuous Synthesis of N-Heterocyclic Carbenes and N-Heterocyclic Carbene Based Transition-Metal Catalysts	373
2.7.4.1.1	N-Heterocyclic Carbene Precursor Preparation under Continuous-Flow Conditions	373

2.7.4.1.2	N-Heterocyclic Carbene Based Transition-Metal Catalyst Preparation	375
2.7.4.2	Application of N-Heterocyclic Carbenes in Flow Systems	378
2.7.4.2.1	Alkene Metathesis Reactions	379
2.7.4.2.2	C–N Coupling and Heck Coupling Reactions	384
2.7.4.2.3	Murahashi Coupling Reaction	386
2.7.4.2.4	Suzuki–Miyaura Reaction	387
2.7.4.2.5	Other Contributions	388
 2.8	Recent Advances in N-Heterocyclic Carbene Organocatalysis	
	A. T. Davies and A. D. Smith	
 2.8	Recent Advances in N-Heterocyclic Carbene Organocatalysis	395
2.8.1	Acyl Anion Intermediates	396
2.8.1.1	Benzoin Condensation	396
2.8.1.1.1	The Enantioselective Benzoin Condensation	397
2.8.1.1.2	The Cross-Benzoin Condensation	397
2.8.1.2	Stetter Reaction	399
2.8.1.3	Miscellaneous Acyl Anion Mediated Processes	402
2.8.1.3.1	Hydroacylation	402
2.8.1.3.2	Aldehyde–Alkyl Halide Cross Coupling	403
2.8.1.3.3	Arylation of Aldehydes	404
2.8.1.3.4	Acyl Anion Combinatorial Catalysis	404
2.8.1.4	Mechanistic Investigations of Acyl Anion Mediated Processes	405
2.8.2	Homoenolate Intermediates	407
2.8.2.1	Homoenolates Reacting with Carbonyl Compounds	407
2.8.2.2	Homoenolates Reacting with Michael Acceptors	409
2.8.2.3	β-Protonation of Homoenolates	410
2.8.2.4	New Methods of Generating Homoenolates	411
2.8.3	Azolium Enolate Intermediates	412
2.8.3.1	Azolium Enolates from α-Reducible Aldehydes	413
2.8.3.2	Azolium Enolates from Ketenes	414
2.8.3.3	Azolium Enolates from Enals	414
2.8.3.4	Azolium Enolates from Esters	415
2.8.3.5	Azolium Enolates from Carboxylic Acids	416
2.8.3.6	Azolium Enolates from Unfunctionalized Aldehydes	417
2.8.3.7	Mechanistic Investigations of Azolium Enolate Processes	418

2.8.4	Dienolate Intermediates	419
2.8.4.1	Dienolate Intermediates Accessed through γ -Deprotonation	419
2.8.4.2	Dienolates Accessed through Cyclobutene Ring Opening	420
2.8.5	Acy Azolium Intermediates	421
2.8.6	α,β -Unsaturated Acyl Azolium Intermediates	423
2.8.6.1	α,β -Unsaturated Acyl Azolium Intermediates from Ynals	423
2.8.6.2	α,β -Unsaturated Acyl Azolium Intermediates from α -Bromo Enals	424
2.8.6.3	α,β -Unsaturated Acyl Azolium Intermediates from α,β -Unsaturated Acyl Species	424
2.8.6.4	α,β -Unsaturated Acyl Azolium Intermediates through Addition of External Oxidants	425
2.8.7	Allenoate Intermediates	425
2.8.8	Radical Intermediates	428
2.8.9	Miscellaneous Reactions	430
2.8.9.1	Hemiacetal Azolium Intermediates	430
2.8.9.2	Activation of Boryl, Silyl, and Stanny Groups	431
2.8.9.3	Morita–Baylis–Hillman Reactions	432
2.8.9.4	Umpolung of Michael Acceptors	433
2.8.9.5	N-Heterocyclic Carbene Catalyzed Sulfonyl Transfer	434
2.8.9.6	pK _a Studies	435
2.8.10	Conclusions	436
Keyword Index	443
Author Index	461
Abbreviations	481