

Science of Synthesis

Knowledge Updates 2023/1

	Preface	V
	Abstracts	VII
	Table of Contents	XV
47.1.1.4.12	Synthesis of Alkenes by Palladium-Catalyzed Cross-Coupling Reactions with Carbene Precursors K. Wang ^{1b} and J. Wang ^{1b}	1
47.1.2.1.5	Synthesis of Alkenes by Cross-Coupling and Heck Reactions C.-Y. Ho and D. Raja	41
47.1.2.1.6	Alkyl-Mizoroki–Heck-Type Reactions A. Lei ^{1b} and S. Tang ^{1b}	103
47.1.2.3.3	Asymmetric π-Allyl Substitution Reactions R. Jiang ^{1b} , P. Yang ^{1b} , and S.-L. You ^{1b}	137
47.1.2.5	Allylic C–H Functionalization P.-S. Wang ^{1b} , M. Sayed ^{1b} , and L.-Z. Gong ^{1b}	175
47.1.4.11	Synthesis of Alkenes by α,β-Dehydrogenation X. Jie ^{1b} and W. Su ^{1b}	223
47.1.5.2.3	Synthesis of Alkenes via Hydrogenation of Alkynes and Allenes X. Liu ^{1b} , B. Liu ^{1b} , and Q. Liu ^{1b}	271
47.1.5.5	Synthesis of Alkenes via Metal-Catalyzed Hydrofunctionalizations Z. Cheng ^{1b} , Y. Zheng ^{1b} , and Z. Lu ^{1b}	321
47.1.5.6	Synthesis of Functionalized Alkenes by Metal-Catalyzed Coupling of Carbonyls with Alkynes/Allenenes Z. Lin ^{1b} , R. Tao ^{1b} , and Y. Zhao ^{1b}	381
47.1.5.7	Synthesis of Alkenes via Radical Addition Reactions P. Chen ^{1b} and G. Liu ^{1b}	427
	Author Index	469
	Abbreviations	489

Table of Contents

Volume 47: Alkenes

47.1.1.4.12	Synthesis of Alkenes by Palladium-Catalyzed Cross-Coupling Reactions with Carbene Precursors	New
	K. Wang and J. Wang	
<hr/>		
47.1.1.4.12	Synthesis of Alkenes by Palladium-Catalyzed Cross-Coupling Reactions with Carbene Precursors	1
47.1.1.4.12.1	Method 1: Palladium-Catalyzed Cross Coupling of α -Diazocarbonyl Compounds with Arylboronic Acids	2
47.1.1.4.12.2	Method 2: Palladium-Catalyzed Cross Coupling of α -Diazocarbonyl Compounds with Organic Halides	4
47.1.1.4.12.3	Method 3: Palladium-Catalyzed Cross Coupling of <i>N</i> -Tosylhydrazones with Aryl Halides	7
47.1.1.4.12.4	Method 4: Palladium-Catalyzed Cross Coupling of <i>N</i> -Tosylhydrazones with Benzyl Halides	11
47.1.1.4.12.5	Method 5: Palladium-Catalyzed Cross Coupling of <i>N</i> -Tosylhydrazones with Arylboronic Acids	12
47.1.1.4.12.6	Method 6: Palladium-Catalyzed Cross Coupling of <i>N</i> -Tosylhydrazones with Terminal Alkynes	13
47.1.1.4.12.7	Method 7: Synthesis of Alkenes Bearing Functional Substituents through Palladium-Catalyzed Carbene Coupling Reactions	15
47.1.1.4.12.8	Method 8: Diene Synthesis via Palladium-Catalyzed Carbene Coupling Reactions	30
47.1.2.1.5	Synthesis of Alkenes by Cross-Coupling and Heck Reactions	2023
	C.-Y. Ho and D. Raja	
<hr/>		
47.1.2.1.5	Synthesis of Alkenes by Cross-Coupling and Heck Reactions	41
47.1.2.1.5.1	Mizoroki–Heck Coupling	42
47.1.2.1.5.1.1	Method 1: Palladium-Catalyzed Mizoroki–Heck Coupling	43
47.1.2.1.5.1.1.1	Variation 1: Heck Reactions Involving Organohalide Electrophiles	43
47.1.2.1.5.1.1.2	Variation 2: Boryl-Heck Couplings	47
47.1.2.1.5.1.1.3	Variation 3: Silyl-Heck Coupling	50
47.1.2.1.5.1.1.4	Variation 4: Intermolecular Oxidative Heck Reaction	52
47.1.2.1.5.1.1.5	Variation 5: Asymmetric Heck Reaction with Cyclic Alkenes	53
47.1.2.1.5.1.2	Method 2: Nickel-Catalyzed Mizoroki–Heck Coupling	55
47.1.2.1.5.1.2.1	Variation 1: Enantiospecific Intramolecular Heck Reactions of Secondary Benzylic Ethers	59

47.1.2.1.5.1.2.2	Variation 2:	Construction of Quaternary Centers by Intramolecular Mizoroki–Heck Cyclization	60
47.1.2.1.5.1.3	Method 3:	Cobalt-Catalyzed Mizoroki–Heck Coupling	62
47.1.2.1.5.1.4	Method 4:	Copper-Catalyzed Mizoroki–Heck Coupling	63
47.1.2.1.5.2	Suzuki–Miyaura Coupling		65
47.1.2.1.5.2.1	Method 1:	Palladium-Catalyzed Suzuki–Miyaura Coupling	65
47.1.2.1.5.2.1.1	Variation 1:	Coupling of Primary Alkylboronic Acids with Alkenyl Electrophiles	66
47.1.2.1.5.2.1.2	Variation 2:	Coupling of Alkenylboronates with Alkyl Electrophiles	68
47.1.2.1.5.2.2	Method 2:	Nickel-Catalyzed Suzuki–Miyaura Coupling	69
47.1.2.1.5.2.3	Method 3:	Iron-Catalyzed Suzuki–Miyaura Coupling	73
47.1.2.1.5.3	Negishi Coupling		74
47.1.2.1.5.3.1	Method 1:	Palladium-Catalyzed Negishi Coupling	74
47.1.2.1.5.3.2	Method 2:	Nickel-Catalyzed Negishi Coupling	80
47.1.2.1.5.3.2.1	Variation 1:	Nickel-Catalyzed Cross Coupling with Alkenylzirconium Reagents	80
47.1.2.1.5.3.3	Method 3:	Iron-Catalyzed Negishi Coupling	82
47.1.2.1.5.3.4	Method 4:	Titanium-Catalyzed Negishi-Type Coupling	82
47.1.2.1.5.4	Corriu–Kumada–Tamao Coupling		83
47.1.2.1.5.4.1	Method 1:	Palladium-Catalyzed Corriu–Kumada–Tamao Coupling	84
47.1.2.1.5.4.2	Method 2:	Nickel-Catalyzed Corriu–Kumada–Tamao Coupling	85
47.1.2.1.5.4.3	Method 3:	Iron-Catalyzed Corriu–Kumada–Tamao Coupling	86
47.1.2.1.5.4.4	Method 4:	Cobalt-Catalyzed Corriu–Kumada–Tamao Coupling	88
47.1.2.1.5.5	Hiyama Coupling		90
47.1.2.1.5.5.1	Method 1:	Palladium-Catalyzed Hiyama Coupling	90
47.1.2.1.5.5.2	Method 2:	Nickel-Catalyzed Hiyama Coupling	91
47.1.2.1.5.6	Stille Coupling		92
47.1.2.1.6	Alkyl-Mizoroki–Heck-Type Reactions		2023
	A. Lei and S. Tang		
47.1.2.1.6	Alkyl-Mizoroki–Heck-Type Reactions		103
47.1.2.1.6.1	Palladium-Catalyzed Alkyl-Mizoroki–Heck-Type Reactions		103
47.1.2.1.6.1.1	Method 1:	Alkene Synthesis from Unactivated Alkyl Halides	104
47.1.2.1.6.1.1.1	Variation 1:	Thermal Conditions	104
47.1.2.1.6.1.1.2	Variation 2:	Light-Induced Conditions	106
47.1.2.1.6.1.2	Method 2:	Alkene Synthesis from Epoxides	110
47.1.2.1.6.1.3	Method 3:	Alkene Synthesis from <i>N</i> -Hydroxyphthalimide Esters	111
47.1.2.1.6.2	Cobalt-Catalyzed Alkyl-Mizoroki–Heck-Type Reactions		112
47.1.2.1.6.2.1	Method 1:	Alkene Synthesis from Alkyl Halides	112
47.1.2.1.6.2.1.1	Variation 1:	Thermal Conditions	112

47.1.2.1.6.2.1.2	Variation 2: Light-Induced Conditions	114
47.1.2.1.6.2.2	Method 2: Alkene Synthesis from Epoxides	116
47.1.2.1.6.2.3	Method 3: Alkene Synthesis from Aliphatic Carboxylic Acids	116
47.1.2.1.6.3	Nickel-Catalyzed Alkyl-Mizoroki–Heck-Type Reactions	118
47.1.2.1.6.3.1	Method 1: Alkene Synthesis from Alkyl Halides	119
47.1.2.1.6.4	Copper-Catalyzed Alkyl-Mizoroki–Heck-Type Reactions	120
47.1.2.1.6.4.1	Method 1: Alkene Synthesis from Alkyl Halides	121
47.1.2.1.6.4.2	Method 2: Alkene Synthesis from Alkyl Nucleophiles	122
47.1.2.1.6.5	Ruthenium- or Iridium-Catalyzed Alkyl-Mizoroki–Heck-Type Reaction	124
47.1.2.1.6.5.1	Method 1: Alkene Synthesis from Alkyl Halides	124
47.1.2.1.6.5.2	Method 2: Alkene Synthesis from <i>N</i> -Alkylpyridinium Salts	126
47.1.2.1.6.6	Iron-Catalyzed Alkyl-Mizoroki–Heck-Type Reaction	128
47.1.2.1.6.6.1	Method 1: Alkene Synthesis from Alkyl Halides	128
47.1.2.1.6.6.2	Method 2: Alkene Synthesis from Alkyl Peroxides or Peroxy Esters	129
47.1.2.1.6.7	Transition-Metal-Free Alkyl-Mizoroki–Heck-Type Reaction	132
47.1.2.1.6.7.1	Method 1: Alkene Synthesis from Alkyl Halides	132
47.1.2.1.6.7.2	Method 2: Alkene Synthesis from Alkyl Peroxy Esters or Diacyl Peroxides	133
47.1.2.3.3	Asymmetric π-Allyl Substitution Reactions R. Jiang, P. Yang, and S.-L. You	137
47.1.2.3.3	Asymmetric π-Allyl Substitution Reactions	137
47.1.2.3.3.1	Palladium-Catalyzed Intermolecular Asymmetric Allylic Substitution Reactions	138
47.1.2.3.3.1.1	Resonance-Stabilized Enolates as Nucleophiles	138
47.1.2.3.3.1.2	Unstabilized Lactam Enolates as Nucleophiles	139
47.1.2.3.3.1.3	Radical Intermediates as Coupling Partners	141
47.1.2.3.3.1.4	Aromatic Compounds as Nucleophiles	144
47.1.2.3.3.2	Iridium-Catalyzed Asymmetric Allylic Substitution Reactions	146
47.1.2.3.3.2.1	Iridium-Catalyzed Allylic Substitution Reactions Using (P,Alkene)-Ligands	147
47.1.2.3.3.2.1.1	Heteroatoms as Nucleophiles	147
47.1.2.3.3.2.1.2	Nonstabilized Carbon Nucleophiles	151
47.1.2.3.3.2.1.3	Stereodivergent Dual Catalysis	153
47.1.2.3.3.2.2	Iridium-Catalyzed Allylic Substitution Reactions Using Feringa-Type Ligands	154
47.1.2.3.3.2.2.1	Stabilized Enolates as Nucleophiles	154
47.1.2.3.3.2.2.2	Nonstabilized Carbon Nucleophiles: Silyl Enol Ethers	156
47.1.2.3.3.2.2.3	Stereodivergent Dual Catalysis	157
47.1.2.3.3.2.3	Iridium-Catalyzed Allylic Substitution Reactions Using Me-THQphos	159
47.1.2.3.3.2.3.1	Stabilized Enolates as Nucleophiles	159
47.1.2.3.3.2.3.2	Dearomatization Reactions	161
47.1.2.3.3.3	Rhodium-Catalyzed Intermolecular Allylic Substitution Reactions	162

47.1.2.3.3.3.1	Anilines as Nucleophiles	162
47.1.2.3.3.3.2	Aldehyde Enolates as Nucleophiles	164
47.1.2.3.3.3.3	Diketones as Nucleophiles	165
47.1.2.3.3.4	Miscellaneous Transition-Metal-Catalyzed Asymmetric Allylic Substitution Reactions	166
47.1.2.3.3.4.1	Copper-Catalyzed Asymmetric Allylic Substitution Reactions	166
47.1.2.3.3.4.2	Nickel-Catalyzed Asymmetric Allylic Substitution Reactions	168
47.1.2.3.3.4.3	Cobalt-Catalyzed Asymmetric Allylic Substitution Reactions	170
47.1.2.5	Allylic C—H Functionalization New P.-S. Wang, M. Sayed, and L.-Z. Gong	
47.1.2.5	Allylic C—H Functionalization	175
47.1.2.5.1	C—C Bond Formation by Allylic C—H Activation	176
47.1.2.5.1.1	Functionalization by C—H Insertion	176
47.1.2.5.1.2	Functionalization by Hydrogen-Atom-Transfer C—H Activation	179
47.1.2.5.1.3	Functionalization by Concerted Metalation/Deprotonation C—H Activation ..	185
47.1.2.5.1.4	Functionalization by Concerted Proton and Two-Electron-Transfer C—H Activation	189
47.1.2.5.1.5	Functionalization by Base-Mediated C—H Activation	199
47.1.2.5.1.6	Functionalization by Oxidative Addition of C—H Bonds	200
47.1.2.5.2	C—N Bond Formation by Allylic C—H Activation	201
47.1.2.5.2.1	Functionalization by C—H Insertion	201
47.1.2.5.2.2	Functionalization by Hydrogen-Atom-Transfer C—H Activation	202
47.1.2.5.2.3	Functionalization by Concerted Metalation/Deprotonation C—H Activation ..	204
47.1.2.5.2.4	Functionalization by Concerted Proton and Two-Electron-Transfer C—H Activation	209
47.1.2.5.3	C—O Bond Formation by Allylic C—H Activation	210
47.1.2.5.3.1	Functionalization by Hydrogen-Atom-Transfer C—H Activation	210
47.1.2.5.3.2	Functionalization by Concerted Metalation/Deprotonation C—H Activation ..	211
47.1.2.5.3.3	Functionalization by Concerted Proton and Two-Electron-Transfer C—H Activation	215
47.1.2.5.4	Formation of Other C—X Bonds by Allylic C—H Activation	216
47.1.2.5.4.1	Functionalization by Hydrogen-Atom-Transfer C—H Activation	216
47.1.2.5.4.2	Functionalization by Concerted Metalation/Deprotonation C—H Activation ..	217

47.1.4.11	Synthesis of Alkenes by α,β-Dehydrogenation	New
	X. Jie and W. Su	
<hr/>		
47.1.4.11	Synthesis of Alkenes by α,β-Dehydrogenation	223
47.1.4.11.1	Method 1: Palladium-/Iridium-Catalyzed Aerobic α,β -Dehydrogenation of Carbonyl Compounds	223
47.1.4.11.1.1	Variation 1: Aerobic Dehydrogenation of Cyclohexanones to Cyclohexenones with a Palladium(II)/2,2'-Bipyridine Catalytic System	223
47.1.4.11.1.2	Variation 2: Aerobic Dehydrogenation of Cyclic Ketones to Cyclic Enones with Bis(dimethyl sulfoxide)palladium(II) Trifluoroacetate ...	224
47.1.4.11.1.3	Variation 3: Aerobic Dehydrogenation of β -Aryl-Substituted Aldehydes to Cinnamaldehydes with a Palladium/Enamine Catalytic System	227
47.1.4.11.1.4	Variation 4: Aerobic Dehydrogenation of Ketones and β -Aryl-Substituted Aldehydes to Enones and Cinnamaldehydes with a Palladium(II)/4,5-Diazafluorenone Catalytic System	228
47.1.4.11.1.5	Variation 5: Aerobic Dehydrogenation of Aldehydes to Enals with a Palladium(II)/ <i>tert</i> -Butyl Nitrite Catalytic System	232
47.1.4.11.1.6	Variation 6: Aerobic Dehydrogenation of Ketones and Aldehydes to Enones and Enals with a Palladium(II)/Trifluoroacetic Acid System	234
47.1.4.11.1.7	Variation 7: Aerobic Dehydrogenation of Ketones with a Cerium(IV) Oxide Supported Palladium(II) on Gold Nanoparticle Catalyst	236
47.1.4.11.1.8	Variation 8: Iridium-Catalyzed Aerobic α,β -Dehydrogenation of γ,δ -Unsaturated Amides and Acids	239
47.1.4.11.2	Method 2: Palladium-Catalyzed α,β -Dehydrogenation of Carbonyl Compounds with Organic Oxidants	241
47.1.4.11.2.1	Variation 1: Allylpalladium-Catalyzed α,β -Dehydrogenation of Esters and Nitriles	241
47.1.4.11.2.2	Variation 2: Allylpalladium-Catalyzed α,β -Dehydrogenation of Amides ..	246
47.1.4.11.2.3	Variation 3: Allylpalladium-Catalyzed α,β -Dehydrogenation of Carboxylic Acids	249
47.1.4.11.2.4	Variation 4: Allylpalladium-Catalyzed α,β -Dehydrogenation of Cyclic Ketones	252
47.1.4.11.2.5	Variation 5: Palladium-Catalyzed α,β -Dehydrogenation of Lactams by Soft Enolization	254
47.1.4.11.2.6	Variation 6: Palladium-Catalyzed Wacker Oxidation/Dehydrogenation for the Synthesis of α,β -Unsaturated Ketones	256
47.1.4.11.3	Method 3: Copper-Catalyzed α,β -Dehydrogenation of Carbonyl Compounds via Radical Processes	258
47.1.4.11.3.1	Variation 1: Copper-Catalyzed Dehydrogenation of Ketones and Aldehydes Using 2,2,6,6-Tetramethylpiperidin-1-oxyl (TEMPO) as Oxidant	258
47.1.4.11.3.2	Variation 2: Copper-Catalyzed α,β -Dehydrogenation of Lactones, Lactams, and Ketones Using Di- <i>tert</i> -butyl Peroxide as Oxidant	260
47.1.4.11.4	Method 4: Miscellaneous α,β -Dehydrogenation Methods	263

47.1.4.11.4.1	Variation 1:	Iridium-Catalyzed Acceptorless Dehydrogenation of C—C Single Bonds Adjacent to Functional Groups	263
47.1.4.11.4.2	Variation 2:	Platinum-Catalyzed Dehydrogenation of Lactams, Ketones, and Lactones	264
47.1.4.11.4.3	Variation 3:	Nickel-Catalyzed Benzylic Dehydrogenation of Electron-Deficient Hetarenes	266
47.1.4.11.4.4	Variation 4:	Benzeneseleninic Acid Mediated α,β -Dehydrogenation of Amides	267
47.1.5.2.3	Synthesis of Alkenes via Hydrogenation of Alkynes and Allenes		2023
	X. Liu, B. Liu, and Q. Liu ^{id}		
47.1.5.2.3	Synthesis of Alkenes via Hydrogenation of Alkynes and Allenes		271
47.1.5.2.3.1	Hydrogenation of Alkynes for Alkene Synthesis		271
47.1.5.2.3.1.1	(Transfer) Hydrogenation of Terminal Alkynes to Terminal Alkenes		272
47.1.5.2.3.1.1.1	Method 1:	Heterogeneous Catalysis for (Transfer) Semihydrogenation of Terminal Alkynes to Terminal Alkenes	272
47.1.5.2.3.1.1.1.1	Variation 1:	Hydrogenation of Terminal Alkynes to Terminal Alkenes via Heterogeneous Catalysis	272
47.1.5.2.3.1.1.1.2	Variation 2:	Transfer Hydrogenation of Terminal Alkynes to Terminal Alkenes via Heterogeneous Catalysis	275
47.1.5.2.3.1.1.2	Method 2:	Homogeneous Catalysis for (Transfer) Semihydrogenation of Terminal Alkynes to Terminal Alkenes	277
47.1.5.2.3.1.1.2.1	Variation 1:	Hydrogenation of Terminal Alkynes to Terminal Alkenes via Homogeneous Catalysis	277
47.1.5.2.3.1.1.2.2	Variation 2:	Transfer Hydrogenation of Terminal Alkynes to Terminal Alkenes via Homogeneous Catalysis	278
47.1.5.2.3.1.2	Stereoselective (Transfer) Hydrogenation of Internal Alkynes to Z-Alkenes		280
47.1.5.2.3.1.2.1	Method 1:	Heterogeneous Catalysis for (Transfer) Semihydrogenation of Internal Alkynes to Z-Alkenes	280
47.1.5.2.3.1.2.1.1	Variation 1:	Hydrogenation of Internal Alkynes to Z-Alkenes via Heterogeneous Catalysis	280
47.1.5.2.3.1.2.1.2	Variation 2:	Transfer Hydrogenation of Internal Alkynes to Z-Alkenes via Heterogeneous Catalysis	284
47.1.5.2.3.1.2.2	Method 2:	Homogeneous Catalysis for (Transfer) Semihydrogenation of Internal Alkynes to Z-Alkenes	285
47.1.5.2.3.1.2.2.1	Variation 1:	Hydrogenation of Internal Alkynes to Z-Alkenes via Homogeneous Catalysis	285
47.1.5.2.3.1.2.2.2	Variation 2:	Transfer Hydrogenation of Internal Alkynes to Z-Alkenes via Homogeneous Catalysis	289
47.1.5.2.3.1.3	Stereoselective (Transfer) Hydrogenation of Internal Alkynes to E-Alkenes		292
47.1.5.2.3.1.3.1	Method 1:	Heterogeneous Catalysis for (Transfer) Semihydrogenation of Internal Alkynes to E-Alkenes	292
47.1.5.2.3.1.3.1.1	Variation 1:	Hydrogenation of Internal Alkynes to E-Alkenes via Heterogeneous Catalysis	292

47.1.5.2.3.1.3.1.2	Variation 2:	Transfer Hydrogenation of Internal Alkynes to <i>E</i> -Alkenes via Heterogeneous Catalysis	294
47.1.5.2.3.1.3.2	Method 2:	Homogeneous Catalysis for (Transfer) Semihydrogenation of Internal Alkynes to <i>E</i> -Alkenes	295
47.1.5.2.3.1.3.2.1	Variation 1:	Hydrogenation of Internal Alkynes to <i>E</i> -Alkenes via Homogeneous Catalysis	296
47.1.5.2.3.1.3.2.2	Variation 2:	Transfer Hydrogenation of Internal Alkynes to <i>E</i> -Alkenes via Homogeneous Catalysis	299
47.1.5.2.3.1.4		Stereodivergent Synthesis of <i>E</i> - and <i>Z</i> -Alkenes	301
47.1.5.2.3.1.4.1	Method 1:	Catalytic Hydrogenation	302
47.1.5.2.3.1.4.1.1	Variation 1:	Catalysis by Frustrated Lewis Pairs	302
47.1.5.2.3.1.4.1.2	Variation 2:	Transition-Metal Catalysis	303
47.1.5.2.3.1.4.2	Method 2:	Transfer Hydrogenation	305
47.1.5.2.3.2		Hydrogenation of Allenes for Alkene Synthesis	308
47.1.5.2.3.2.1		Selective Hydrogenation of Allenes to Terminal Alkenes	309
47.1.5.2.3.2.1.1	Method 1:	Homogeneous Catalysis	309
47.1.5.2.3.2.2		Selective Hydrogenation of Allenes to Internal Alkenes	310
47.1.5.2.3.2.2.1	Method 1:	Catalysis by Frustrated Lewis Pairs	310
47.1.5.2.3.2.2.2	Method 2:	Transition-Metal Catalysis	311
47.1.5.2.3.2.2.2.1	Variation 1:	Heterogeneous Catalysis	311
47.1.5.2.3.2.2.2.2	Variation 2:	Homogeneous Catalysis	312
47.1.5.2.3.2.2.3	Method 3:	Electrochemical Reduction	314

47.1.5.5 **Synthesis of Alkenes via Metal-Catalyzed Hydrofunctionalizations**

2023

Z. Cheng, Y. Zheng, and Z. Lu¹⁵

47.1.5.5		Synthesis of Alkenes via Metal-Catalyzed Hydrofunctionalizations	321
47.1.5.5.1	Method 1:	Hydrosilylation of Alkynes	323
47.1.5.5.1.1	Variation 1:	Using Cobalt Catalysts	323
47.1.5.5.1.2	Variation 2:	Using Iron Catalysts	327
47.1.5.5.1.3	Variation 3:	Using Ruthenium Catalysts	329
47.1.5.5.2	Method 2:	Hydrosilylation of Allenes	332
47.1.5.5.2.1	Variation 1:	Using Cobalt Catalysts	333
47.1.5.5.2.2	Variation 2:	Using Nickel Catalysts	335
47.1.5.5.2.3	Variation 3:	Using Copper Catalysts	336
47.1.5.5.3	Method 3:	Hydroboration of Alkynes	337
47.1.5.5.3.1	Variation 1:	Using Copper Catalysts	338
47.1.5.5.3.2	Variation 2:	Using Cobalt Catalysts	344
47.1.5.5.4	Method 4:	Hydroboration of Allenes	348
47.1.5.5.4.1	Variation 1:	Using Cobalt Catalysts	348
47.1.5.5.4.2	Variation 2:	Using Copper Catalysts	350

47.1.5.5.5	Method 5:	Hydroarylation of Alkynes	352
47.1.5.5.1	Variation 1:	Using Copper Catalysts	353
47.1.5.5.2	Variation 2:	Using Manganese Catalysts	356
47.1.5.5.6	Method 6:	Hydroalkylation of Alkynes and Allenes	360
47.1.5.5.7	Method 7:	Addition of S—H Bonds to Alkynes	366
47.1.5.5.8	Method 8:	Addition of P—H Bonds to Alkynes	370
47.1.5.5.8.1	Variation 1:	Hydrophosphination	371
47.1.5.5.8.2	Variation 2:	Hydrophosphinylation and Hydrophosponylation	373
47.1.5.6	Synthesis of Functionalized Alkenes by Metal-Catalyzed Coupling of Carbonyls with Alkynes/Allenes		381
	Z. Lin, R. Tao, and Y. Zhao		
47.1.5.6	Synthesis of Functionalized Alkenes by Metal-Catalyzed Coupling of Carbonyls with Alkynes/Allenes		381
47.1.5.6.1	Synthesis with a Reductant via Metallocycle Intermediates		382
47.1.5.6.1.1	Triethylborane as Reductant		382
47.1.5.6.1.1.1	Method 1:	Nonenantioselective Synthesis from Alkynes and Aldehydes	382
47.1.5.6.1.1.2	Method 2:	Enantioselective Synthesis from Alkynes and Aldehydes	383
47.1.5.6.1.1.3	Method 3:	Nonenantioselective Synthesis from Enynes and Aldehydes	384
47.1.5.6.1.1.4	Method 4:	Synthesis of (+)-Acutiphycin from an Alkyne and an Aldehyde	384
47.1.5.6.1.2	Silanes as Reductant		385
47.1.5.6.1.2.1	Method 1:	Nonenantioselective Synthesis from Aldehydes, Alkynes, and Triethylsilane	385
47.1.5.6.1.2.2	Method 2:	Enantioselective Synthesis from Aldehydes, Alkynes, and Triethylsilane	386
47.1.5.6.1.2.3	Method 3:	Synthesis from α,β -Unsaturated Aldehydes, Alkynes, and Silanes	387
47.1.5.6.1.2.4	Method 4:	Synthesis from α,β -Unsaturated Ketones, Allenes, and Triethylsilane	388
47.1.5.6.1.2.5	Method 5:	Synthesis from Ynals, Alkyl Bromides, and Chlorotriethylsilane	389
47.1.5.6.1.3	Molecular Hydrogen as Reductant		390
47.1.5.6.1.3.1	Method 1:	Synthesis from Diynes and α -Oxo Aldehydes	390
47.1.5.6.1.3.2	Method 2:	Synthesis from Diynes and Ethyl Glyoxalate	391
47.1.5.6.1.3.3	Method 3:	Synthesis from Enynes and α -Oxo Aldehydes	392
47.1.5.6.1.3.4	Method 4:	Synthesis from Enynes and Aldehydes	393
47.1.5.6.1.3.5	Method 5:	Synthesis from Enynes and α -Oxo Esters	394
47.1.5.6.1.4	Alcohol as Reductant		395
47.1.5.6.1.4.1	Method 1:	Synthesis from Alkynes and Aldehydes	395
47.1.5.6.2	Synthesis with Nucleophilic π -Allyl Intermediates		396
47.1.5.6.2.1	Method 1:	Synthesis from Allenes and Aldehydes or Alcohols	396
47.1.5.6.2.2	Method 2:	Synthesis from Aminoallenenes and Aldehydes	399

47.1.5.6.2.3	Method 3:	Synthesis from Trifluoromethyl-Substituted Allenes and Paraformaldehyde	400
47.1.5.6.2.4	Method 4:	Enantioselective Synthesis from 1,1-Dimethylallene and Aldehydes	401
47.1.5.6.3		Synthesis with Electrophilic π -Allyl Intermediates	402
47.1.5.6.3.1		Synthesis Involving C—O Bond Formation	402
47.1.5.6.3.1.1		Synthesis from Alkynes and Carboxylic Acids	402
47.1.5.6.3.1.1.1	Method 1:	anti-Markovnikov Addition of Carboxylic Acids to Terminal Alkynes	402
47.1.5.6.3.1.1.2	Method 2:	Intermolecular C(sp ³)—O Bond Formation between Terminal Alkynes and Carboxylic Acids	403
47.1.5.6.3.1.2		Synthesis from Allenes and Carboxylic Acids	404
47.1.5.6.3.1.2.1	Method 1:	Enantioselective Intermolecular Coupling of Terminal Allenes and Carboxylic Acids	404
47.1.5.6.3.2		Synthesis Involving C—N Bond Formation	405
47.1.5.6.3.2.1		Addition of Heterocycles to Allenes	405
47.1.5.6.3.2.1.1	Method 1:	Enantioselective Addition of Pyridin-2(1 <i>H</i>)-ones to Terminal Allenes	405
47.1.5.6.3.2.1.2	Method 2:	Enantioselective N—H Functionalization of Quinazolinones with Terminal Allenes	407
47.1.5.6.3.2.1.3	Method 3:	Enantioselective N ² -Allylation of Pyridazin-3(2 <i>H</i>)-ones with Terminal Allenes	408
47.1.5.6.3.2.2		Intramolecular Addition to Allenes	409
47.1.5.6.3.2.2.1	Method 1:	Diastereoselective Intramolecular Addition of Tosylcarbamates to Terminal Allenes	409
47.1.5.6.3.3		Synthesis Involving C—C Bond Formation	411
47.1.5.6.3.3.1		Synthesis from 1,3-Dicarbonyl Substrates	411
47.1.5.6.3.3.1.1	Method 1:	Decarboxylative Synthesis of Alkenyl Ketones from Allenes and β -Oxo Carboxylic Acids	411
47.1.5.6.3.3.1.2	Method 2:	Decarboxylative Synthesis of Alkenyl Ketones from Alkynes and β -Oxo Carboxylic Acids	412
47.1.5.6.3.3.1.3	Method 3:	Addition of Dicarbonyl Compounds to Internal Alkynes	413
47.1.5.6.3.3.1.4	Method 4:	Addition of 1,3-Diketones to Terminal Alkynes	414
47.1.5.6.3.3.1.5	Method 5:	Enantioselective Addition of 1,3-Diketones to 1,1-Disubstituted Terminal Allenes	416
47.1.5.6.3.3.1.6	Method 6:	Enantioselective Synthesis of Allylic 1,3-Diketones from Internal Allenes and 1,3-Diketones by Parallel Kinetic Resolution	417
47.1.5.6.3.3.2		Synthesis from Alkynyl Carboxylic Acids	418
47.1.5.6.3.3.2.1		Enantioselective Synthesis of 3-Substituted 1,4-Enynes from Arylpropynoic Acids and Allenes	418

47.1.5.6.4	Miscellaneous Methods	419
47.1.5.6.4.1	α -Allylation of Cyclic Ketones Using Allenes	419
47.1.5.6.4.1.1	Method 1: Enantioselective Synthesis from Cyclohexanones and Allenamides	419
47.1.5.6.4.2	α -Allylation of Cyclic Ketones Using Alkynes	420
47.1.5.6.4.2.1	Method 1: α -Allylic Alkylation of Cyclohexanone with Internal Alkynes	420
47.1.5.6.4.2.2	Method 2: Enantioselective α -Allylation of Cyclohexanone by Internal Alkynes	421
47.1.5.6.4.3	Alkyne Hydroacylation	422
47.1.5.6.4.3.1	Method 1: Synthesis of β,γ -Unsaturated Ketones from Aldehydes and Internal Alkynes	422
47.1.5.6.4.4	Decarboxylative Coupling	424
47.1.5.6.4.4.1	Method 1: Decarboxylative Cross Coupling between β -Oxo Carboxylic Acids and Internal Alkynes	424
47.1.5.7	Synthesis of Alkenes via Radical Addition Reactions	New
	P. Chen and G. Liu	
47.1.5.7	Synthesis of Alkenes via Radical Addition Reactions	427
47.1.5.7.1	Radical Addition to Alkynes	427
47.1.5.7.1.1	Method 1: Metal-Free Radical Addition to Alkynes	428
47.1.5.7.1.1.1	Variation 1: Carbon Radical Addition to Alkynes	428
47.1.5.7.1.1.2	Variation 2: Germanium Radical Addition to Alkynes	431
47.1.5.7.1.1.3	Variation 3: Sulfur Radical Addition to Alkynes	432
47.1.5.7.1.1.4	Variation 4: Boryl Radical Addition to Alkynes	433
47.1.5.7.1.2	Method 2: Photoredox-Catalyzed Radical Addition to Alkynes	435
47.1.5.7.1.2.1	Variation 1: Carbon Radical Addition to Alkynes	436
47.1.5.7.1.2.2	Variation 2: Silyl Radical Addition to Alkynes	441
47.1.5.7.1.2.3	Variation 3: Sulfur Radical Addition to Alkynes	442
47.1.5.7.1.2.4	Variation 4: Phosphine Radical Addition to Alkynes	446
47.1.5.7.1.3	Method 3: Transition-Metal-Catalyzed Radical Addition to Alkynes	447
47.1.5.7.1.3.1	Variation 1: Carbon Radical Addition to Alkynes	448
47.1.5.7.1.3.2	Variation 2: Sulfur Radical Addition to Alkynes	454
47.1.5.7.2	Radical Addition to Allenes	456
47.1.5.7.2.1	Method 1: Metal-Free Radical Addition to Allenes	457
47.1.5.7.2.1.1	Variation 1: Carbon Radical Addition to Allenes	457
47.1.5.7.2.1.2	Variation 2: Sulfur Radical Addition to Allenes	458
47.1.5.7.2.1.3	Variation 3: Nitrogen Radical Addition to Allenes	459
47.1.5.7.2.1.4	Variation 4: Halogen Radical Addition to Allenes	460
47.1.5.7.2.2	Method 2: Photoredox-Catalyzed Radical Addition to Allenes	461
47.1.5.7.2.2.1	Variation 1: Carbon Radical Addition to Allenes	461
47.1.5.7.2.2.2	Variation 2: Silyl Radical Addition to Allenes	462

47.1.5.7.2.3	Method 3: Metal-Catalyzed Radical Addition to Allenes	463
47.1.5.7.2.3.1	Variation 1: Carbon Radical Addition to Allenes	463
47.1.5.7.2.3.2	Variation 2: Nitrogen Radical Addition to Allenes	465
	Author Index	469
	Abbreviations	489

