

Cross Coupling and Heck-Type Reactions 3

Metal-Catalyzed Heck-Type Reactions and C—C Cross Coupling via C—H Activation

Preface	V
Volume Editor's Preface	VII
Abstracts	XI
Table of Contents	XXI
Introduction	
L. R. Odell and M. Larhed	1
3.1 Heck Reactions	7
3.1.1 Intermolecular Reactions	7
3.1.1.1 Electron-Poor Alkenes as Reaction Components	7
3.1.1.1.1 Reaction with Aryl or Hetaryl Halides or Pseudohalides	
C.-M. Andersson and M. Andersson	7
3.1.1.1.2 Reaction with (Het)Arylmetals or (Het)Arenes	
E. W. Werner and M. S. Sigman	75
3.1.1.1.3 Reaction with Arene- or Hetarene-carboxylic Acids or Derivatives, or Related Compounds	
M. Zhang and W. Su	103
3.1.1.1.4 Reaction with Nonaromatic Halides, Sulfonates, or Related Compounds	
M. Weimar and M. J. Fuchter	137
3.1.1.2 Alkenes with Allylic Substitution and Homologues as Reaction Components	
J. Le Bras and J. Muzart	169
3.1.1.3 Electron-Rich Alkenes as Reaction Components	211
3.1.1.3.1 Reaction with Aryl or Hetaryl Halides or Pseudohalides	
S. Liu and J. Xiao	211
3.1.1.3.2 Reaction with Arylboronic Acids or Derivatives or Aryl Halides	
J. Lindh and M. Larhed	265
3.1.1.3.3 Reaction with Nonaromatic Alkenyl Halides or Alkenyl Sulfonates	
P. Nilsson	285

3.1.1.4	Cyclic Alkenes as Reaction Components V. Coeffard and P. J. Guiry	303
3.1.1.5	Alkenes with Metal-Directing Groups as Reaction Components A. Trejos and L. R. Odell	345
3.1.2	Intramolecular Reactions	391
3.1.2.1	Formation of Carbocycles K. Geoghegan and P. Evans	391
3.1.2.2	Formation of Heterocycles S. G. Stewart	441
3.1.2.3	Stereoselective Formation of Tertiary and Quaternary Centers G. Broggini, E. Borsini, and U. Piarulli	521
3.2	C—C Cross Coupling via Single C—H Activation	585
3.2.1	Intermolecular Coupling via C(sp²)—H Activation A. Kantak and B. DeBoef	585
3.2.2	Intramolecular Coupling via C(sp²)—H Activation E. Suna and K. Shubin	643
3.2.3	Coupling via C(sp³)—H Activation under Palladium Catalysis D. Kalyani and L. V. Desai	725
3.3	C—C Cross Coupling via Double C—H Activation C. S. Yeung, N. Borduas, and V. M. Dong	785
	Keyword Index	813
	Author Index	861
	Abbreviations	885

Table of Contents

Introduction

L. R. Odell and M. Larhed

Introduction	1
---------------------------	---

3.1 Heck Reactions

3.1.1 Intermolecular Reactions

3.1.1.1 Electron-Poor Alkenes as Reaction Components

3.1.1.1.1 Reaction with Aryl or Hetaryl Halides or Pseudohalides

C.-M. Andersson and M. Andersson

3.1.1.1.1	Reaction with Aryl or Hetaryl Halides or Pseudohalides	7
3.1.1.1.1	Arylation of Alkenes Carrying at Least One Keto, Ester, Nitrile, or Amide Group	7
3.1.1.1.1.1	Arylations with Aryl Halides	8
3.1.1.1.1.1.1	With Iodoarenes or Bromoarenes	8
3.1.1.1.1.1.1.1	With Resin-Bound Aryl Halides	32
3.1.1.1.1.1.1.2	Arylations in Ionic Liquids	34
3.1.1.1.1.1.1.3	Continuous-Flow Heck Arylation	37
3.1.1.1.1.1.1.4	Substrates Carrying More than One Keto, Ester, Nitrile, or Amide Group	38
3.1.1.1.1.1.2	With Chloroarenes	39
3.1.1.1.1.2	Hetarylations with Hetaryl Halides	42
3.1.1.1.1.3	Arylations with Other Electrophiles	50
3.1.1.1.1.3.1	With Diazonium Salts	50
3.1.1.1.1.3.2	With Iodonium Salts	58
3.1.1.1.1.3.3	With Aryl Trifluoromethanesulfonates	60
3.1.1.1.2	Arylation of Alkenes Carrying at Least One Sulfoxide, Sulfone, Sulfonate, or Sulfinat Group	61
3.1.1.1.2.1	Arylations with Aryl Halides	61
3.1.1.1.2.2	Arylations with Arenediazonium Salts	62
3.1.1.1.3	Arylation of Alkenes Carrying at Least One Phosphonic, Phosphinic, Nitro, or Nitroso Group	64
3.1.1.1.3.1	Arylations with Aryl Halides	64

3.1.1.1.3.2	Arylations with Arenediazonium Salts	65
3.1.1.1.4	Arylation of Alkenes Carrying at Least One Halomethyl Group	66
3.1.1.1.5	Arylation of Alkenes Carrying at Least One Aryl Group	68
3.1.1.1.5.1	Arylations with Aryl Halides	68
3.1.1.1.5.2	Arylations with Other Arylating Agents	69
3.1.1.1.6	Arylation of Alkenes Carrying at Least One Hetaryl Group	70
3.1.1.1.6.1	Hetarylations with Hetaryl Halides	71
3.1.1.2	Reaction with (Het)Arylmetals or (Het)Arenes E. W. Werner and M. S. Sigman	
3.1.1.2	Reaction with (Het)Arylmetals or (Het)Arenes	75
3.1.1.2.1	Reaction with (Het)Arylmetals	77
3.1.1.2.1.1	Reaction with Arylmercury Reagents	77
3.1.1.2.1.2	Reaction with Arylstannane Reagents	79
3.1.1.2.1.3	Reaction with Arylsilane Reagents	81
3.1.1.2.1.4	Reaction with Arylboronic Acids and Derivatives	82
3.1.1.2.1.5	Reaction with Other Electrophilic Reagents	90
3.1.1.2.2	Reaction with (Het)Arenes	92
3.1.1.2.2.1	Reaction with Benzene or Electron-Rich (Het)Arenes	93
3.1.1.2.2.2	Reaction with Electron-Deficient (Het)Arenes	95
3.1.1.2.3	Non-Palladium-Catalyzed Reactions	98
3.1.1.3	Reaction with Arene- or Hetarene-carboxylic Acids or Derivatives, or Related Compounds M. Zhang and W. Su	
3.1.1.3	Reaction with Arene- or Hetarene-carboxylic Acids or Derivatives, or Related Compounds	103
3.1.1.3.1	Decarbonylative Reactions of Arene-carboxylic Acid Derivatives	103
3.1.1.3.1.1	Reaction with Aroyl Chlorides	104
3.1.1.3.1.2	Reaction with Arene-carboxylic Anhydrides	107
3.1.1.3.1.3	Reaction with Arene-carboxylates	109
3.1.1.3.2	Decarboxylative Reactions of Arene-carboxylic Acids	112
3.1.1.3.2.1	Reaction Using Palladium Catalysis	113
3.1.1.3.2.2	Reaction Using Rhodium Catalysis	125
3.1.1.3.3	Miscellaneous Reactions	127
3.1.1.3.3.1	Reaction with Arene-sulfonyl Chlorides	127

3.1.1.1.3.3.2	Reaction with Arenesulfinic Acids	131
3.1.1.1.3.3.3	Reaction with Arylphosphonic Acids	133
3.1.1.1.4	Reaction with Nonaromatic Halides, Sulfonates, or Related Compounds M. Weimar and M. J. Fuchter	
<hr/>		
3.1.1.1.4	Reaction with Nonaromatic Halides, Sulfonates, or Related Compounds	137
3.1.1.1.4.1	Reaction with Alkenyl—X Electrophiles	137
3.1.1.1.4.1.1	Reaction with Alkenyl Iodides	137
3.1.1.1.4.1.2	Reaction with Alkenyl Bromides	140
3.1.1.1.4.1.3	Reaction with Alkenyl Chlorides	144
3.1.1.1.4.1.4	Reaction with Alkenyliodonium Salts	145
3.1.1.1.4.1.5	Reaction with Alkenyl 4-Toluenesulfonates	146
3.1.1.1.4.1.6	Reaction with Alkenyl Trifluoromethanesulfonates and Nonafluorobutanesulfonates	149
3.1.1.1.4.1.7	Reaction with Alkenyl Phosphates	154
3.1.1.1.4.1.8	Reaction with Alkenylboronates	155
3.1.1.1.4.2	Reaction with Benzyl—X Electrophiles	158
3.1.1.1.4.2.1	Reaction with Benzyl Chlorides	159
3.1.1.1.4.2.2	Reaction with Benzyl Trifluoroacetates	160
3.1.1.1.4.3	Reaction with Allyl—X Electrophiles	161
3.1.1.1.4.3.1	Reaction with Allyl 4-Toluenesulfonates	161
3.1.1.1.4.4	Reaction with Other Nonaromatic Electrophiles	162
3.1.1.2	Alkenes with Allylic Substitution and Homologues as Reaction Components J. Le Bras and J. Muzart	
<hr/>		
3.1.1.2	Alkenes with Allylic Substitution and Homologues as Reaction Components	169
3.1.1.2.1	Couplings with Retention of an Allylic or Homoallylic Substituent	169
3.1.1.2.1.1	Using Allylic or Homoallylic Alcohols	169
3.1.1.2.1.1.1	With Aryl or Alkenyl Halides or Trifluoromethanesulfonates	170
3.1.1.2.1.1.2	With Arylboronic Acids	178
3.1.1.2.1.1.3	With Arenediazonium Salts	180
3.1.1.2.1.1.4	With Hypervalent Iodonium Salts	182
3.1.1.2.1.2	Using Allylic Esters or Carbonates	182
3.1.1.2.1.2.1	With Aryl or Alkenyl Halides	183
3.1.1.2.1.2.2	With Aryl- or Alkenylboronic Acids or Esters	184

3.1.1.2.1.2.3	With Arenecarboxylates	185
3.1.1.2.1.2.4	With Arenes	185
3.1.1.2.1.3	Using Allylic Ethers	186
3.1.1.2.1.3.1	With Aryl Halides	186
3.1.1.2.1.3.2	With Arylboronic Acids or Alkenylboronic Esters	187
3.1.1.2.1.3.3	With Arenecarboxylates	189
3.1.1.2.1.4	Using Allyltrimethylsilane with Aryl Iodides or Trifluoromethanesulfonates ...	189
3.1.1.2.1.5	Using Allylic or Homoallylic Amine Derivatives	190
3.1.1.2.1.5.1	With Aryl or Alkenyl Halides or Trifluoromethanesulfonates	191
3.1.1.2.1.5.2	With Arylboronic Esters	195
3.1.1.2.1.5.3	With Arenediazonium Salts	196
3.1.1.2.2	Couplings with Cleavage of an Allylic or Homoallylic Substituent	197
3.1.1.2.2.1	Using Tertiary Homoallylic Alcohols with Aryl or Alkenyl Halides or Trifluoromethanesulfonates	197
3.1.1.2.2.2	Using Allylic Esters or Carbonates	199
3.1.1.2.2.2.1	With Aryl Halides	199
3.1.1.2.2.2.2	With Arylboronic Acids	201
3.1.1.2.2.3	Using Allylic Silanes with Aryl or Alkenyl Halides or Trifluoromethanesulfonates	203
3.1.1.2.2.4	Using Allylic Halides with Arenecarboxylates	206
3.1.1.3	Electron-Rich Alkenes as Reaction Components	
3.1.1.3.1	Reaction with Aryl or Hetaryl Halides or Pseudohalides S. Liu and J. Xiao	
3.1.1.3.1	Reaction with Aryl or Hetaryl Halides or Pseudohalides	211
3.1.1.3	Electron-Rich Alkenes as Reaction Components	211
3.1.1.3.1	Reaction with Aryl or Hetaryl Halides or Pseudohalides	211
3.1.1.3.1.1	Regioselective α -Arylation and Vinylation of Vinyl Ethers	212
3.1.1.3.1.1.1	With Aryl Halides in the Presence of a Halide Scavenger	213
3.1.1.3.1.1.2	With Aryl Halides in Ionic Liquids	217
3.1.1.3.1.1.3	With Aryl Halides in Aqueous Media	223
3.1.1.3.1.1.4	With Aryl Halides in Alcohols	226
3.1.1.3.1.1.5	With Hetaryl Halides in Ionic Liquids	232
3.1.1.3.1.1.6	With Hetaryl Halides in Aqueous Media	233
3.1.1.3.1.1.7	With Hetaryl Halides in Alcohols	233
3.1.1.3.1.1.8	With Aryl Trifluoromethanesulfonates	237

3.1.1.3.1.1.9	With Hetaryl 4-Toluenesulfonates	238
3.1.1.3.1.1.10	With Vinyl Halides	239
3.1.1.3.1.1.11	With Vinyl Trifluoromethanesulfonates	241
3.1.1.3.1.1.12	With Vinyl 4-Toluenesulfonates	242
3.1.1.3.1.1.13	With Vinyl Methanesulfonates	242
3.1.1.3.1.2	Regioselective α -Arylation and Vinylation of Enamides	243
3.1.1.3.1.2.1	With Aryl Trifluoromethanesulfonates	243
3.1.1.3.1.2.2	With Aryl Halides in Ionic Liquids	244
3.1.1.3.1.2.3	With Aryl Halides in Alcohols	245
3.1.1.3.1.2.4	With Hetaryl 4-Toluenesulfonates	247
3.1.1.3.1.2.5	With Vinyl Trifluoromethanesulfonates	248
3.1.1.3.1.2.6	With Vinyl 4-Toluenesulfonates	250
3.1.1.3.1.2.7	With Vinyl Methanesulfonates	251
3.1.1.3.1.3	Regioselective α -Arylation of In Situ Generated Enamines	251
3.1.1.3.1.4	Regioselective α -Arylation of Styrenes	254
3.1.1.3.1.5	Regioselective β -Arylation and Vinylation of Vinyl Ethers	255
3.1.1.3.1.5.1	With Aroyl and Hetaroyl Chlorides	255
3.1.1.3.1.5.2	With Aryl Trifluoromethanesulfonates	256
3.1.1.3.1.5.3	With Aryl Halides	257
3.1.1.3.1.5.4	With Vinyl Trifluoromethanesulfonates	259
3.1.1.3.1.6	Effect of Ligands	261
3.1.1.3.2	Reaction with Arylboronic Acids or Derivatives or Aroyl Halides J. Lindh and M. Larhed	
3.1.1.3.2	Reaction with Arylboronic Acids or Derivatives or Aroyl Halides	265
3.1.1.3.2.1	Oxidative Heck Reactions	265
3.1.1.3.2.1.1	Regioselectivity	266
3.1.1.3.2.2	Reactions Using Enamides	269
3.1.1.3.2.2.1	With Arylboronic Acids Employing Conventional Heating	269
3.1.1.3.2.2.2	With Arylboronic Acids Using Microwave Heating	272
3.1.1.3.2.3	Reactions Using Vinyl Ethers	273
3.1.1.3.2.3.1	With Arylboronic Acids Employing Conventional Heating	273
3.1.1.3.2.3.2	With Arylboronic Acids Using Microwave Heating	275
3.1.1.3.2.3.3	With Arylboronic Acids under Continuous-Flow Conditions	276
3.1.1.3.2.3.4	With Aroyl Chlorides	277

3.1.1.3.2.4	Reactions Using Vinyl Acetate	279
3.1.1.3.2.4.1	With Arylboronic Acids Using Microwave Heating	279
3.1.1.3.2.4.2	With Arylboronic Acids under Continuous-Flow Conditions	280
3.1.1.3.3	Reaction with Nonaromatic Alkenyl Halides or Alkenyl Sulfonates P. Nilsson	
3.1.1.3.3	Reaction with Nonaromatic Alkenyl Halides or Alkenyl Sulfonates	285
3.1.1.3.3.1	Using Vinyl Ethers	286
3.1.1.3.3.1.1	With Alkenyl Trifluoromethanesulfonates	286
3.1.1.3.3.1.2	With Alkenyl Halides	289
3.1.1.3.3.1.3	With Alkenyl 4-Toluenesulfonates and Methanesulfonates	292
3.1.1.3.3.2	Using Enamides	295
3.1.1.3.3.2.1	With Alkenyl Trifluoromethanesulfonates	295
3.1.1.3.3.2.2	With Alkenyl 4-Toluenesulfonates and Methanesulfonates	296
3.1.1.3.3.3	Using Linear Alkenes	298
3.1.1.3.3.3.1	With Alkenyl Halides	298
3.1.1.3.3.4	Using Trimethyl(vinyl)silane	299
3.1.1.3.3.4.1	With Alkenyl Trifluoromethanesulfonates	299
3.1.1.3.3.4.2	With Alkenyl Halides	300
3.1.1.4	Cyclic Alkenes as Reaction Components V. Coeffard and P. J. Guiry	
3.1.1.4	Cyclic Alkenes as Reaction Components	303
3.1.1.4.1	Non-enantioselective Intermolecular Heck Reactions	304
3.1.1.4.1.1	Reactions of Cycloalkenes	304
3.1.1.4.1.2	Reactions of Oxygen-Containing Cyclic Alkenes	307
3.1.1.4.1.3	Reactions of Nitrogen-Containing Cyclic Alkenes	312
3.1.1.4.1.4	Reactions of Other Types of Cyclic Alkenes	315
3.1.1.4.2	Asymmetric Intermolecular Heck Reactions	317
3.1.1.4.2.1	Mechanism Overview	317
3.1.1.4.2.2	Reactions of Cycloalkenes	318
3.1.1.4.2.3	Reactions of Oxygen-Containing Cyclic Alkenes	320
3.1.1.4.2.3.1	Reactions of 2,3-Dihydrofuran and 2,2-Dialkyl-2,3-dihydrofurans	321
3.1.1.4.2.3.2	Reactions of 2,5-Dihydrofuran	337
3.1.1.4.2.3.3	Reactions of 3,4-Dihydro-2H-pyran	338

3.1.1.4.2.3.4	Reactions of 4,7-Dihydro-1,3-dioxepin	338
3.1.1.4.2.4	Reactions of Nitrogen-Containing Cyclic Alkenes	340
3.1.1.4.3	Conclusions	342
3.1.1.5	Alkenes with Metal-Directing Groups as Reaction Components A. Trejos and L. R. Odell	
3.1.1.5	Alkenes with Metal-Directing Groups as Reaction Components	345
3.1.1.5.1	Using Vinyl Ethers	347
3.1.1.5.1.1	Regioselective β -Arylation/ β -Vinylation	347
3.1.1.5.1.1.1	With Aryl Iodides	348
3.1.1.5.1.1.2	With Aryl Bromides	348
3.1.1.5.1.1.3	With Aryl or Vinyl Trifluoromethanesulfonates	350
3.1.1.5.1.1.4	With Arylboronic Acids	353
3.1.1.5.1.2	Regioselective Sequential β,β -Diarylation	354
3.1.1.5.1.2.1	With Aryl Iodides	354
3.1.1.5.1.2.2	With Aryl Bromides	356
3.1.1.5.1.2.3	With Aryl Chlorides	357
3.1.1.5.1.3	Asymmetric Arylation/Vinylation	357
3.1.1.5.1.3.1	With Aryl Iodides	358
3.1.1.5.1.3.2	With Aryl Bromides	359
3.1.1.5.1.3.3	With Aryl or Vinyl Chlorides	360
3.1.1.5.1.3.4	With Vinyl Trifluoromethanesulfonates	362
3.1.1.5.2	Using Vinylsilanes	362
3.1.1.5.2.1	Regioselective β -Arylation/ β -Vinylation	363
3.1.1.5.2.1.1	With Aryl or Vinyl Iodides	363
3.1.1.5.2.1.2	With Organozinc and Grignard Reagents	365
3.1.1.5.2.2	Regioselective Sequential β,β -Diarylation	366
3.1.1.5.2.2.1	With Aryl Iodides	366
3.1.1.5.3	Using Vinyl Sulfides	367
3.1.1.5.3.1	Regioselective Sequential β,β -Diarylation	368
3.1.1.5.3.1.1	With Aryl Iodides	368
3.1.1.5.4	Using Vinyl Sulfoxides	369
3.1.1.5.4.1	Regioselective β -Arylation	369
3.1.1.5.4.1.1	With Aryl Iodides	369
3.1.1.5.4.2	Asymmetric Arylation	370

3.1.1.5.4.2.1	With Aryl Iodides	370
3.1.1.5.5	Using Allylic Alcohols	371
3.1.1.5.5.1	With Aryl or Vinyl Iodides	372
3.1.1.5.5.2	With Vinyl Trifluoromethanesulfonates	374
3.1.1.5.5.3	With Iodonium Salts	375
3.1.1.5.6	Using Allylic Esters	376
3.1.1.5.6.1	With Aryl or Vinyl Halides	377
3.1.1.5.6.2	With Arylboronic Acids	378
3.1.1.5.6.3	With Arenediazonium Salts	379
3.1.1.5.6.4	With Arenes	381
3.1.1.5.7	Using Allylic Carbamates	382
3.1.1.5.7.1	With Aryl Iodides	382
3.1.1.5.8	Using Allylic Amines	383
3.1.1.5.8.1	Regioselective Arylation	383
3.1.1.5.8.1.1	With Aryl Iodides	383
3.1.1.5.8.1.2	With Aryl Trifluoromethanesulfonates	384
3.1.1.5.9	Using Allylic Sulfones	385
3.1.1.5.9.1	Regioselective Arylation	385
3.1.1.5.9.1.1	With Aryl Iodides	385
3.1.1.5.10	Using Other Alkenes	386
3.1.2	Intramolecular Reactions	
3.1.2.1	Formation of Carbocycles K. Geoghegan and P. Evans	
3.1.2.1	Formation of Carbocycles	391
3.1.2.1.1	Construction of Five- and Six-Membered Carbocycles by Intramolecular Mizoroki–Heck Reactions	393
3.1.2.1.1.1	From Halides and Pseudohalides	393
3.1.2.1.1.1.1	By 5- and 6- <i>exo-trig</i> Processes	393
3.1.2.1.1.1.2	By 5- and 6- <i>endo-trig</i> Processes	408
3.1.2.1.1.2	By Matsuda–Heck Processes	413
3.1.2.1.1.3	By C–H Activation-Based Processes	414
3.1.2.1.2	Construction of Seven-Membered and Medium-Sized Carbocyclic Rings by Intramolecular Heck Reactions	420
3.1.2.1.3	Formation of Macrocyclic Rings by Intramolecular Heck Reactions	424

3.1.2.1.4	Stereoselective Formation of Carbocycles by Intramolecular Heck Reactions	426
3.1.2.1.4.1	Diastereoselective Formation of Carbocycles	426
3.1.2.1.5	Intramolecular Heck-Type Processes Using Metals Other than Palladium	434
3.1.2.2	Formation of Heterocycles S. G. Stewart	
3.1.2.2	Formation of Heterocycles	441
3.1.2.2.1	Formation of N-Heterocycles	442
3.1.2.2.1.1	Formation of Five-Membered Rings	442
3.1.2.2.1.1.1	Formation of Indoles	442
3.1.2.2.1.1.2	Formation of Indolines	454
3.1.2.2.1.1.3	Formation of Oxindoles	458
3.1.2.2.1.1.4	Formation of Isoindolinones	461
3.1.2.2.1.1.5	Formation of Pyrrolidines	461
3.1.2.2.1.1.6	Formation of Pyrroles	469
3.1.2.2.1.1.7	Formation of Imidazoles	472
3.1.2.2.1.2	Formation of Six-Membered Rings	473
3.1.2.2.1.2.1	Formation of Isoquinolines	473
3.1.2.2.1.2.2	Formation of Isoquinolinones	479
3.1.2.2.1.2.3	Formation of Quinolines	485
3.1.2.2.1.2.4	Formation of Quinolinones	485
3.1.2.2.1.2.5	Formation of Piperidines	486
3.1.2.2.1.2.6	Formation of Pyrrolopyrimidines	488
3.1.2.2.1.2.7	Formation of Pyridines	489
3.1.2.2.1.3	Formation of Seven-Membered and Larger Rings	490
3.1.2.2.1.3.1	Formation of Azepines	490
3.1.2.2.1.3.2	Formation of Azocines and Larger N-Heterocycles	494
3.1.2.2.2	Formation of O-Heterocycles	496
3.1.2.2.2.1	Formation of Benzofurans	496
3.1.2.2.2.2	Formation of Furans	503
3.1.2.2.2.3	Formation of Lactones	504
3.1.2.2.2.4	Formation of Benzopyrans	505
3.1.2.2.2.5	Formation of Pyrans	508
3.1.2.2.2.6	Formation of Oxepins and Oxocins	510
3.1.2.2.3	Formation of S-Heterocycles	511
3.1.2.2.3.1	Formation of Benzothiophenes	511

3.1.2.2.3.2	Formation of Sultams	512
3.1.2.2.3.3	Formation of Thiocins	514
3.1.2.3	Stereoselective Formation of Tertiary and Quaternary Centers G. Broggin, E. Borsini, and U. Piarulli	
3.1.2.3	Stereoselective Formation of Tertiary and Quaternary Centers	521
3.1.2.3.1	Formation of Tertiary Centers from Acyclic Alkenes	524
3.1.2.3.1.1	Reactions of Aryl Iodides	524
3.1.2.3.1.1.1	Using Chiral Ligands	524
3.1.2.3.1.1.2	Using Chiral Substrates	525
3.1.2.3.1.2	Reactions of Aryl Bromides	527
3.1.2.3.1.2.1	Using Chiral Substrates	527
3.1.2.3.2	Formation of Tertiary Centers from Cyclic Alkenes	528
3.1.2.3.2.1	Reactions of Aryl Iodides	528
3.1.2.3.2.1.1	Using Chiral Ligands	528
3.1.2.3.2.1.2	Using Chiral Substrates	529
3.1.2.3.2.2	Reactions of Aryl Bromides	531
3.1.2.3.2.2.1	Using Chiral Ligands	531
3.1.2.3.2.2.2	Using Chiral Substrates	532
3.1.2.3.2.3	Reactions of Aryl Trifluoromethanesulfonates	535
3.1.2.3.2.3.1	Using Chiral Ligands	535
3.1.2.3.2.3.2	Using Chiral Substrates	535
3.1.2.3.2.4	Reactions of Vinyl Iodides	536
3.1.2.3.2.4.1	Using Chiral Ligands	536
3.1.2.3.2.4.2	Using Chiral Substrates	539
3.1.2.3.2.5	Reactions of Vinyl Bromides	540
3.1.2.3.2.5.1	Using Chiral Ligands	540
3.1.2.3.2.6	Reactions of Vinyl Trifluoromethanesulfonates	541
3.1.2.3.2.6.1	Using Chiral Ligands	541
3.1.2.3.2.6.2	Using Chiral Substrates	545
3.1.2.3.3	Formation of Quaternary Centers from Acyclic Alkenes	547
3.1.2.3.3.1	Reactions of Aryl Iodides	547
3.1.2.3.3.1.1	Using Chiral Ligands	547
3.1.2.3.3.1.2	Using Chiral Substrates	553
3.1.2.3.3.2	Reactions of Aryl Trifluoromethanesulfonates	555
3.1.2.3.3.2.1	Using Chiral Ligands	555

3.1.2.3.3.2.2	Using Chiral Substrates	562
3.1.2.3.3.3	Reactions of Vinyl Trifluoromethanesulfonates	563
3.1.2.3.3.3.1	Using Chiral Ligands	563
3.1.2.3.3.3.2	Using Chiral Substrates	565
3.1.2.3.4	Formation of Quaternary Centers from Cyclic Alkenes	565
3.1.2.3.4.1	Reactions of Aryl Iodides	566
3.1.2.3.4.1.1	Using Chiral Ligands	566
3.1.2.3.4.1.2	Using Chiral Substrates	568
3.1.2.3.4.2	Reactions of Aryl Bromides	569
3.1.2.3.4.2.1	Using Chiral Ligands	569
3.1.2.3.4.2.2	Using Chiral Substrates	570
3.1.2.3.4.3	Reactions of Aryl Trifluoromethanesulfonates	574
3.1.2.3.4.3.1	Using Chiral Ligands	574
3.1.2.3.4.4	Reactions of Vinyl Trifluoromethanesulfonates	580
3.1.2.3.4.4.1	Using Chiral Substrates	580

3.2 C–C Cross Coupling via Single C–H Activation

3.2.1 Intermolecular Coupling via C(sp²)–H Activation

A. Kantak and B. DeBoef

3.2.1	Intermolecular Coupling via C(sp²)–H Activation	585
3.2.1.1	Nondirected Arylation of Benzene	587
3.2.1.1.1	Palladium-Catalyzed Methods	587
3.2.1.1.1.1	Nondirected Palladium-Catalyzed Arylation of Benzene with Aryl Halides	587
3.2.1.1.1.2	Nondirected Palladium-Catalyzed Arylation of Benzene Derivatives with Carboxylic Acids	589
3.2.1.1.2	Copper-Catalyzed Methods for the <i>meta</i> and <i>para</i> Arylation of Simple Arenes	591
3.2.1.2	Arylation of Benzene Derivatives Containing Directing Groups	593
3.2.1.2.1	Carbonyl Directing Groups	593
3.2.1.2.1.1	Palladium-Catalyzed Methods	594
3.2.1.2.1.2	Palladium-Catalyzed Reactions Employing Additional Oxidants	595
3.2.1.2.1.3	Ruthenium-Catalyzed Methods	597
3.2.1.2.2	Amine, Imine, and Azole-Type Directing Groups	598
3.2.1.2.2.1	Palladium-Catalyzed Methods	598
3.2.1.2.2.1.1	Amine Directing Groups	598
3.2.1.2.2.1.2	Imine and Oxime Directing Groups	599

3.2.1.2.2.1.3	Pyridine Directing Groups	601
3.2.1.2.2.2	Rhodium-Catalyzed Methods	603
3.2.1.2.2.3	Rhodium-Catalyzed Reactions Employing Additional Oxidants	604
3.2.1.2.2.4	Ruthenium-Catalyzed Methods	606
3.2.1.2.2.5	Iron-Catalyzed Methods	609
3.2.1.2.3	Alcohol Directing Groups	610
3.2.1.2.3.1	Rhodium-Catalyzed <i>ortho</i> Arylation of Phenols	610
3.2.1.2.4	Carboxylic Acid Directing Groups	612
3.2.1.2.4.1	Palladium-Catalyzed Methods	612
3.2.1.3	Arylation of Indoles	613
3.2.1.3.1	Palladium-Catalyzed Arylation of Indoles with Aryl Halides	613
3.2.1.3.2	Rhodium-Catalyzed Arylation of Indoles with Aryl Halides	615
3.2.1.3.3	Copper-Catalyzed Arylation of Indoles with Aryl Iodides	616
3.2.1.3.4	Palladium-Catalyzed Arylation of Indoles with Benzoic Acids	616
3.2.1.3.5	Palladium-Catalyzed Arylation of Indoles with Arylboronic Acids, Aryltrifluoroborates, or Trialkoxy(aryl)silanes	618
3.2.1.4	Arylation of Indolizines	619
3.2.1.4.1	Palladium-Catalyzed Methods	619
3.2.1.5	Arylation of Pyrroles	620
3.2.1.5.1	Palladium-Catalyzed Methods	620
3.2.1.5.2	Rhodium-Catalyzed Methods	621
3.2.1.6	Arylation of Furans and Benzofurans	622
3.2.1.7	Arylation of Thiophenes and Benzothiophenes	623
3.2.1.7.1	Palladium-Catalyzed Methods	623
3.2.1.7.2	Rhodium-Catalyzed Methods	625
3.2.1.7.3	Copper-Catalyzed Methods	625
3.2.1.8	Arylation of Pyridines	626
3.2.1.8.1	Palladium-Catalyzed Arylation of Pyridines	626
3.2.1.8.2	Palladium-Catalyzed Arylation of Pyridine 1-Oxides	628
3.2.1.8.3	Rhodium-Catalyzed Methods	628
3.2.1.8.4	Nickel-Catalyzed Methods	629
3.2.1.8.5	Copper-Catalyzed Arylation of Pyridine 1-Oxides	630
3.2.1.9	Arylation of Pyrazine 1-Oxides	630
3.2.1.9.1	Palladium-Catalyzed Methods	630
3.2.1.10	Arylation of Pyridazines	631
3.2.1.10.1	Copper-Catalyzed Methods	631
3.2.1.11	Arylation of Imidazoles, Oxazoles, and Thiazoles	632

3.2.1.11.1	Palladium-Catalyzed Methods	632
3.2.1.11.2	Rhodium-Catalyzed Methods	634
3.2.1.11.3	Copper-Catalyzed Methods	635
3.2.1.12	Arylation of Isoxazoles	636
3.2.1.12.1	Palladium-Catalyzed Methods	636
3.2.1.13	Arylation of Pyrazoles	636
3.2.1.13.1	Palladium-Catalyzed Methods	636
3.2.1.14	Arylation of Triazoles	638
3.2.1.14.1	Palladium-Catalyzed Methods	638
3.2.2	Intramolecular Coupling via C(sp²)–H Activation E. Suna and K. Shubin	
3.2.2	Intramolecular Coupling via C(sp²)–H Activation	643
3.2.2.1	Addition to Alkenes	643
3.2.2.1.1	The Fujiwara–Moritani Annulation	643
3.2.2.1.1.1	Ligand-Promoted Synthesis, Including Enantioselective Synthesis	645
3.2.2.1.1.2	Ligandless Synthesis	650
3.2.2.1.1.3	Synthesis with Stoichiometric Palladium Complexes	653
3.2.2.1.2	Hydroarylation	655
3.2.2.1.2.1	Rhodium-Catalyzed Stereoselective Hydroarylation	656
3.2.2.1.2.2	Rhodium-Catalyzed Annulation of Heterocycles	659
3.2.2.1.2.3	Ruthenium-Catalyzed Hydroarylation	663
3.2.2.2	Addition to Ketones	665
3.2.2.3	Addition to Alkynes	666
3.2.2.3.1	5- <i>exo-dig</i> Cyclization	667
3.2.2.3.2	5- <i>endo-dig</i> Cyclization	670
3.2.2.4	Coupling with C–X Groups (X = Halogen, Trifluoromethanesulfonate)	674
3.2.2.4.1	General Method for Aryl Chlorides, Bromides, Iodides, and Trifluoromethanesulfonates	677
3.2.2.4.2	General Methods for Bromides and Iodides	683
3.2.2.4.2.1	Under Ligandless Conditions	683
3.2.2.4.2.2	Using Triphenylphosphine with Acetate Base	687
3.2.2.4.2.3	Using Bidentate Arylphosphines	692
3.2.2.4.2.4	Using Herrmann’s Palladacycle	694
3.2.2.4.2.5	Using Heterogeneous Palladium Catalysts	697
3.2.2.4.3	Coupling with C–I Groups	699
3.2.2.4.4	Coupling with C–Br Groups	702

3.2.2.4.4.1	Coupling with Aryl Bromides	702
3.2.2.4.4.2	Coupling with Alkenyl Bromides	705
3.2.2.4.5	Coupling with C—Cl Groups	708
3.2.2.4.5.1	Coupling with Aryl Chlorides	708
3.2.2.4.5.2	Coupling with Alkyl Chlorides	711
3.2.2.4.6	Coupling with C—OTf Groups	715
3.2.2.4.6.1	Coupling with Aryl Trifluoromethanesulfonates	715
3.2.2.4.6.2	Coupling with Alkenyl Trifluoromethanesulfonates	717
3.2.2.5	Coupling with Arenecarboxylic Acids	720
3.2.3	Coupling via C(sp³)—H Activation under Palladium Catalysis D. Kalyani and L. V. Desai	
<hr/>		
3.2.3	Coupling via C(sp³)—H Activation under Palladium Catalysis	725
3.2.3.1	Arylation	726
3.2.3.1.1	Palladium(0)/(II)-Catalyzed Arylations	726
3.2.3.1.1.1	Arylations Using Prefunctionalized Reagents	726
3.2.3.1.1.1.1	Intramolecular Arylations	726
3.2.3.1.1.1.2	Intermolecular Arylations	739
3.2.3.1.1.2	Arylations without Prefunctionalized Arylating Reagents	746
3.2.3.1.2	Palladium(II)/(IV)-Catalyzed Arylations	748
3.2.3.2	Carbonylation and Alkenylation	752
3.2.3.3	Alkylation	758
3.2.3.4	Enantioselective Reactions	770
3.2.3.5	Applications in the Synthesis of Bioactive Molecules	777
3.2.3.6	Summary and Future Outlook	780
3.3	C—C Cross Coupling via Double C—H Activation C. S. Yeung, N. Borduas, and V. M. Dong	
<hr/>		
3.3	C—C Cross Coupling via Double C—H Activation	785
3.3.1	Intermolecular C—C Bond Formation	785
3.3.1.1	Reaction in the Absence of a Directing Group	786
3.3.1.1.1	Reaction of 1 <i>H</i> -Indoles, 1 <i>H</i> -Pyrroles, or Benzofurans with Unactivated Arenes	786
3.3.1.1.2	Reaction of Azoles with Unactivated Arenes or with Hetarenes	789
3.3.1.1.3	Reaction of Hetarene <i>N</i> -Oxides with Unactivated Arenes or with Hetarenes ..	791
3.3.1.1.4	Reaction of Fluorinated Arenes with Unactivated Arenes or with Hetarenes ..	794
3.3.1.1.5	Reaction of Two Different Hetarenes under Copper Catalysis	796

3.3.1.2	Reaction Involving a Directing Group	797
3.3.1.2.1	Ring-Nitrogen-Directed C—H Bond Activation	797
3.3.1.2.2	Amide-Directed C—H Bond Activation	799
3.3.1.2.3	Carbamate-Directed C—H Bond Activation	804
3.3.2	Intramolecular C—C Bond Formation	806
3.3.2.1	Five-Membered Ring Formation	806
3.3.2.1.1	Synthesis of Carbazoles	806
3.3.2.1.2	Synthesis of Dibenzofurans	808
3.3.2.1.3	Synthesis of Indole Derivatives	808
3.3.2.2	Six-Membered Ring Formation	808
3.3.2.2.1	Synthesis of Phenanthridinones	808
3.3.2.2.2	Synthesis of Fused 1,2,3-Triazole Derivatives	809
3.3.2.3	Seven-Membered and Larger Ring Formation	810
	Keyword Index	813
	Author Index	861
	Abbreviations	885