

Index

a

- alkene
 - cross-coupling routes 239, 241
 - directed C–H alkenylation
 - cobalt complexes 248, 249
 - manganese catalysis 249–250
 - ortho-C–H activations 244, 245
 - palladium catalyst 244
 - rhodium catalysis 245, 246
 - ruthenium complexes 245, 247, 248
 - hetero(arene) C–H bonds 251, 253
 - hydroacylation 208, 261–265
 - hydroarylation 257–261
 - natural and bioactive compounds 239, 240
 - nickel catalysis 252
 - non-directed C–H alkenylation 241–243
 - non-oxidative C–H alkenylation 251, 252, 265
 - oxidative C–H alkenylation process 245, 248, 251
 - pathways 240
- α -amino phenylacetic acid 183
- α -hydroxyl acid 183
- 8-aminoquinoline (AQ) 108
- anti*- β -hydroxy- α -amino acids (anti- β hAAs) 111
- atropopure biarylsulfoxides 161
- atroposelective cross-coupling
 - Pd-catalyzed C–H arylation
 - biaryl sulfoxides 169–171
 - thiophene derivatives 167–169
 - Rh-catalyzed C–H arylation 171–172
- axial chirality
 - asymmetric couplings
 - biphenols and binaphtols derivatives 155
 - copper-catalyzed reactions 153–154
 - HHDP 156, 157
 - iron-catalyzed reactions 155
 - vanadium-catalyzed reactions 154–155
- atroposelective cross-coupling 167–172
- compounds 151, 152, 172
- diastereoselective C–H functionalization
 - phosphates 162–163
 - sulfinyl 159–162
- enantioselective C–H functionalization 163–165
- proatropisomeric 151
- stereoselective C–H functionalization 158–167
 - naphthylpyridines 158–159
- transient chiral directing groupfa 165–167

b

- β -lactam ring 19
- biaryl-sulfoxide substrates 159, 169
- Binol-derived phosphoric acids (BPAs) 83, 96, 97, 140
- bisoxazolines 7–8, 11, 22, 23, 28–30, 167, 169

C

- catalysis
 - asymmetric intermolecular amination 60–64
 - asymmetric intramolecular amination 63–65
 - azides 56
 - carbamates 54
 - chiral amines 51, 52
 - chloramine-T 56
 - cyclic sulfonamides 53
 - enzymatic intramolecular amination 68–70
 - hypervalent iodine reagent 52
 - iminoiodinanes 53–55
 - intermolecular diastereoselective reactions 66–67
 - iodine(III) oxidants 55–57
 - iron-and manganese-porphyrins 52
 - Lewis acidic ruthenium(Salen) complex 56
 - mechanistic and stereochemical issues 56–59
 - metallanitrene species 53, 54
 - m*-xylene tether 54
 - nitrene precursors 53
 - nitrenes 51
 - O*-(sulfamoyl)-hydroxylamines 54
 - regiocontrolled nucleophilic additions 53
 - stereoselective intermolecular allylic 70–71
 - sulfamates 54, 55
 - sulfamides 54
 - synthesis of amines 51
 - transition metal-catalyzed reactions 67–69
 - ureas and guanidines 54
- cationic iridium complex 222, 257
- central chirality
 - desymmetrization
 - amino acids act 176
 - benzofuranones 177
 - bifunctional phosphine/carboxylate ligand 179, 180
 - C-H imidoxylation reaction, Pd-catalyst 180
 - C-stereogenic molecules 177
 - diarylacetic acids 176
 - enantiopure diarylamines 177
 - isoindoline scaffolds 179
 - meta*-selective arylation 178
 - non-ligated Pd species 177
 - nosyl-protected directing group 177
 - oxidative Heck reaction 176
 - Pd(II)/Pd(0) and Pd(II)/Pd(IV) catalytic cycles 178
 - prochiral biaryl substrate 175
 - Rh-catalyst 181
 - styrenes and acrylates 176
 - kinetic resolution 182–183
 - organosilicon compounds 187–189
 - P-chiral compounds
 - alkynylation 187
 - Cp^XRh complex 186
 - diphenylphosphine oxide 184
 - enantioselective amidation 184, 185
 - kinetic resolution 187
 - oxaphosphinine 6-oxide 185
 - Pd-catalyzed arylation 185
 - Pd(0)-catalyzed arylation 186
 - prochiral phosphoryl substrate 184
 - sulfoxides 189–190
 - C(sp²)–H bonds
 - non-stereoselective C-H activation 193
 - planar chirality 133
 - C(sp³)-H functionalizations
 - achiral phosphine L5 ligated Pd complex 83
 - aryl (pseudo)halide 80
 - chiral fused indolines **3** 80, 81
 - chiral phosphine ligands 83
 - chiral phosphine ligands display activity 83
 - chloroacetamide 88
 - C-X coupling
 - chiral organosilicon compounds 89
 - 3,3'-diaryl-binol phosphoric acid 89

ligands screening 90, 92
 secondary amines/hydrosilane 89
 tertiary carbon stereocenter 89
 cycloheptyl-fused indoline 81
 cyclopropyl-fused azacycle **19** 86
 efficiency and stereoselectivity 91
 2-ethyl substituted indoline **6a** 83
 examples 84
 expanded ring products 83–86
 follow-up study 80
 halide/carboxylate ligand exchange 80
 Ir catalysis 102–104
 membered palladacyclic intermediates 82
 ortho-substitution 82
 Pd catalysis
 APAO ligands 95, 96
 aryl halide 92
 aza-heterocycles 97
 benzoquinone 92
 benzylic C(sp³)-H arylation 101
 bis(pinacolato)diboron 94–95
 BPAs 97
 carboxamide groups 97–98
 chiral environment 92
 chiral phosphoric acid 98
 coordination and activation 101
 cyclobutane 93–95
 electron deficient aldehydes 101
 enantioenriched N-compounds 96
 ethylenediamine derived chiral ligand 100
 example of 92, 93
 isobutyric acid derivatives 99
 mechanism of 91–93
 mono-coordination site 98
 mono *N*-protected chiral amino acid 97, 98
 N-arylamide directed cyclopropane 93
 neurological disorders 100
 N-fluoro-2,4,6-trimethylpyridinium salt 101
 stereocontrol 98

stoichiometric and covalent installation 100
 tertiary carbon stereocenters 99–100
 Pd(0)/Pd(II) mechanism 79
 Pd-phosphine catalyst 86
 phenyl and benzyl substituents 85–86
 pivalic acid 80
 Rh catalysis 102, 103
 seven-membered palladacyclic intermediate 82
 taddol phosphoramidite ligand L10 85
 tertiary acetamides 88
 trifluoroacetimidoyl chloride 86–87
 unsymmetrical *N*-alkanes 81
 Concerted-metalation-deprotonation (CMD) 79, 80, 82, 83, 89, 135, 143, 165, 199
 copper 3, 7–8, 22, 23, 28, 33, 36, 42, 45, 52, 53, 55, 56, 153–156, 251, 253
 copper-catalyzed reactions 153–154
 cyclopentadienyl ligands 199, 213, 214, 218

d

DFT computational studies 5
 dialkylaminomethylferrocene 135
 diaryldiketones 137
 diastereoselective directed ortho-metalation (DoM) 133
 diastereoselective functionalization
 alkene 239
 chiral oxazoline auxiliary
 alkyl carboxamides 120
 amide derivatives 119
 asymmetric iodination 117
 chiral directing group 117–118
 cycloalkanes 119–120
 cyclopropanes 119–120
 direct arylation 120–121
 γ-methylene C(sp³)-H bonds 119
 stereoselective acetoxylation 117
 steric repulsion model 116, 118
 γ-C(sp³)-H arylation

- diastereoselective functionalization
(*contd.*)
- dipeptides/tripeptides 116
 - N*-SO₂Py-protected aliphatic amines 114
 - N*-phthaloyl- α -amino acids
 - α -amino- β -lactam motif 111–112
 - 8-aminoquinoline 108
 - anti*- β -hydroxy- α -amino acids 111
 - asymmetric synthesis 108
 - celogentin C 108, 109
 - α -haloacetates and methyl iodide 109, 110
 - monodentate directing group 114, 115
 - palladium 113, 114
 - phthaloyl and phenyl groups 108, 109
 - reductive elimination 108
 - secondary C—H bonds 111, 112
 - unactivated β -methylene C(sp³)—H bonds 110
 - preferred conformation
 - aminoquinoline directing group 123, 124
 - 1-Boc-3-aminopiperidine 126
 - CO in methanol 122
 - indole diterpenoid paspaline 125
 - picolinamide-directed arylation 122
 - 3-Pinanamine 123, 124
 - piperaborenine 123
 - proline derivatives 123, 124
 - psiguadial B 125
 - racemic 77 121
 - rimantadinyll methylenes 126
 - teleocidin B-4 core 122
 - transannular C—H bond arylation 127
 - tripeptide 126, 127
 - diazo esters 215, 216
 - diazoethane 4
 - diazomethane 4, 11
 - diazonaphthoquinones 171–172
 - Dynamic kinetic asymmetric transformation (DYKAT) 159, 161
- e**
- electron donating groups 5, 6, 41, 101
 - electrophilic metal carbenoid 3, 5
 - enantioselective hydroacylation
 - carbocyclic nucleoside 206
 - catalytic cycle 204, 206
 - chiral indanones 206
 - heteroatom 207–209
 - nonsteroidal aromatase inhibitor MR 20492 207
 - phosphoramidite–alkene ligands 206
 - rhodium complex 204, 205
 - yuremamine 207
- f**
- ferrocene
 - derivatives 140, 141, 147
 - planar chirality 134
 - ferrocenyl pyridine catalysts 142
 - Friedel-Crafts-type pathway 194
 - Fujiwara-Moritani reactions 194, 241, 242, 245
- h**
- Heck-type reaction 227
 - Hexahydroxydiphenoyl (HHDP) 156, 157
 - hydroacylation
 - alkynes 261–264
 - allenes 263–265
 - hydroarylation
 - alkynes
 - (*E*)-alkene product 256
 - catalytic system 254
 - cobalt catalysis 256
 - developments 254
 - manganese catalysis 256, 257
 - nickel catalysis 255
 - regio- and stereoselectivity 254
 - allenes
 - cobalt 260
 - iridium complex 257, 258

- manganese 260
nickel 261
rhodium 258, 259
ruthenium 258
- i**
- imidoylation 144, 180, 181
- intermolecular C–H insertion,
regioselectivity
chemoselectivity
catalyst effects 34–35
diazocompounds 32–34
substrate functional groups
35–36
components 30, 32
diastereoselectivity
catalyst effects 42–43
substrate effects 39–42
enantioselectivity 43–45
regioselectivity
catalyst effects 38–39
diazocompound effects 39, 40
substrate effects 36–38
- intramolecular C–H insertion
chemoselectivity
catalyst effects 13–15
substrate effects 14–17
diastereoselectivity 23–25
 α -diazoketone 12, 13
enantioselectivity
bisoxazoline ligands 28
copper-bisoxazoline systems 28
C₁ symmetric ligands 25, 26
C₂ symmetric ligands 26
diastereomeric catalysts 28
 α -diazocarbonyl compounds 25
 α -diazomotif 29, 30
diphenyl bisoxazoline ligand 29
Maguire group 28
O–Rh–O plane 25, 26
synthesis of molecules 30, 31
regioselectivity
entropic factors 17
3-membered rings 17
4-membered rings 18–20
5-membered rings 20
6-membered rings 20–23
- steric/electronic factors 17
- iridium 7, 11, 12, 35, 36, 43, 45, 68, 70,
102–104, 144, 200–203, 219,
221–223, 225, 226, 257, 258, 263
- iridium catalysis
intermolecular couplings
acetophenones/benzamide 222
alkylation reagents 223, 224
bicycloalkenes 222, 223
cyclopentadienyl Ir(I) complexes
220
general procedure 221
N-acyl ketimines 226
vinyl ethers 223, 225
intramolecular couplings
catalytic cycle 200
indoles 203, 204
ketone 201, 203
phenyl-substituted alkene 203
- iron-catalyzed reactions 155, 156
iron-phthalocyanine (FePc) 169
- l**
- Ligand-to-ligand H-transfer (LLHT)
230
- m**
- metal carbenoid induced C–H insertion
rhodium
rhodium(II) carboxylates 10
- metal ligated catalyst (ML_{*n*}) coordinates
5
- 4-methoxyphenyl ketone 203
Mizoroki-Heck reaction 239, 241
Mono-*N*-protected amino acid (MPAA)
93, 126, 135, 163, 165, 175–177,
182, 183, 185, 189, 190
Monoprotected aminoethyl amine
(MPAAM) 100
- n**
- N*-acyl ketimines 226
N-allylic imidazoles 198
naphthylpyridines 158–159
N-ferrocenyl amide 146

- N*-heterocyclic carbene (NHC) 80, 81, 83, 102, 169, 170, 194, 196, 230, 252
- nickel catalysis 194–196, 252, 254, 263
- nitrogen extrusion 3–5, 7
- N*-methoxyferrocenecarboxamides 146
- non-stereoselective C-H activation
- directing groups 193
 - enantioselective functionalization 193
 - enantioselective hydroacylation 203–209
- iridium catalysis 203, 219–226
- metal catalysis
- cationic Sc benzyl species 228, 230
 - Heck-type reaction 226–227
 - iron 230
 - spiroindolines and spirodihydrobenzofurans 228
 - Zr-pyridyl complexes 228
- nickel catalysis 194–196
- palladium catalysis 194–196
- rhodium catalysts 200, 208
- N*-vinylindole-2-carboxaldehydes 207
- o**
- organosilicon compounds 89, 187–189
- p**
- palladium catalysis 135, 194–196, 242, 245, 250, 251, 263
- palladium-catalyzed C–H alkenylation 242, 243
- Pd/ethyl nicotinate catalytic system 194
- phenyl-substituted alkene 203
- planar chirality
- Au/Pt-catalyzed 146–147
 - diastereoselective synthesis 134
 - Ir/Rh-catalyzed 144–146
- Pd0 catalysis
- enantioselective and diastereoselective synthesis 144
 - ferrocenes 140, 141
- hetero-Diels-Alder reaction 141
- imidoylation 144
- TADDOL-derived
- phosphoramidite 141, 144
 - transition states 143
- Pd(II) catalysis
- catalytic enantioselective 138, 139
 - cross-coupling reaction 136, 137
 - CuOTf/bis-oxazoline 134
 - diaryldiketones 137
 - dimethylaminomethylferrocene 134, 135
 - ferrocenyl ketones 139
 - Heck reaction 136, 137
 - plausible catalytic cycle 135, 136
 - sandwich-type structure 133
- prochiral 2-(arylsilyl)aryl triflates 187
- Protein kinase C (PKC) inhibitor 198
- protonolysis 215, 226, 258
- PyOx ligands 194
- 2-pyridone structural motif 194
- r**
- rhodium
- ortho*-metalated arylphosphines 11
 - rhodium(II) carboxamidates 10
 - rhodium(II) carboxylates 9–10
 - selectivity and efficiency 8
- rhodium catalysts
- intermolecular couplings
 - alkyne coordination and migratory insertion 217
 - alkynyl and monofluoroalkenyl isoindolinones 218, 220, 221
 - biaryl derivatives 218, 220
 - chiral Cp ligand 214
 - cyclopentadienyl ligands 213–215
 - diazo compounds 215–216
 - enantioselective reaction 213
 - half-sandwich complexes 217
 - imine 210
 - ketones 211, 212
 - naphthols 217
 - nitroalkenes 215
 - spirocyclic sultams 218–219
 - stereinduction 215
 - α -substituted acrylates 211, 212

- supramolecular strategy 213
 - intramolecular couplings
 - chiral phosphine ligand 196
 - cyclopentadienyl ligand 199
 - 1,5-dienes 197
 - enantioselectivity 198
 - 2-imidazolyl 196
 - ketimines 197
 - meta*-alkoxy group 200
 - monocyclopentadienyl ligand 199
 - phosphoramidite/Rh ratio 197
 - PKC inhibitor 198, 199
 - Rh(I)/Rh(III) catalytic cycle 196, 197
 - syn*-isomer products 198
 - tert*-cyclobutanols 200, 202
 - transition-metal catalyzed reactions 200
 - Wilkinson's catalyst 196
 - rhodium catalysts*
 - intermolecular couplings*
 - N*-methoxybenzamides 214
 - ruthenium 7, 11, 12, 54, 56, 57, 65, 67, 72, 242, 245, 247, 248, 250–252, 254, 258, 259, 263
- S**
- Schiff base copper complex 8
 - σ -orbital 6
 - SPINOL-derived phosphoramidite ligand 144
 - spirosilabifluorene 188, 189
- t**
- TADDOL-derived phosphoramidite 141, 144
- v**
- vanadium-catalyzed reactions 154–155
- w**
- Wilkinson's catalyst 196
 - wittig-type reactions 239
- y**
- yuremamine 207
- z**
- Zr-pyridyl complexes 228

