

## Index

### **a**

- acrylamides
  - decarboxylative acylation of 218, 219
  - oxidative alkylarylation of 215, 216
  - oxidative cyclization 214, 215
- acyl radicals 188, 189
- 1,2-addition reaction 47, 48
- aerobic oxidative *ortho*-aryloxylation 143
- aerobic oxidative allylic amination 166
- $\text{AgNO}_3/\text{Na}_2\text{S}_2\text{O}_8$  catalyzed radical oxidative coupling 172
- 2-alkenylquinolines 119
- alkyl–Pd–alkynyl species 28
- alkyne–alkyne oxidative coupling 9–11
- alkyne–cyano oxidative coupling 22
- alkynyl lithium 15, 23
- alkynylboron reagents 14–17
- alkynylmagnesium reagents 17–19
- alkynylsilanes 11–14
- alkynyltrifluoroborates 16, 17
- alkynyltrimethyltin reagent 12, 14
- allylic C–H bonds 127, 163
- amine-catalyzed enantioselective  $\alpha$ -arylation reaction 68–70
- annulated eight-membered rings 113, 115
- annulated seven-membered rings 113, 114
- aryl and alkynyl Grignard reagents 24–26
- $\alpha$ -aryl- $\beta$ -oxyalkylated carbonyl ketones 192
- aryl C–H olefination reaction 128
- aryl magnesium reagents 23
- arylalkoxycarbonylation
  - imidazoheterocycles 221, 222
  - 2-isocyanobiphenyl 218, 221
  - *N*-aryl acrylamides 218, 221
- 2-arylation products 82
- aryltrimethylsilanes 88
- N*-arylsulfoximines 157

### **b**

- base-promoted homolytic aromatic substitution (BHAS) 192
- benzamides, oxidative *ortho*-phosphorylation of 172
- benzene acetoxylation 144
- benzylic C–H bonds, oxidative amination of 163
- $\beta$ -H elimination effect 40
- biomimetic C–H oxidation reactions 47, 55
- biphenols 204, 205
- Buchwald–Hartwig cross-coupling 112

### **c**

- C-2 alkenylation products 118
- C-3 alkenylation products 118
- carbenoid/nitrenoid C–H insertion reactions 47, 56–57
- carbocations 64, 105
- carbon–heteroatom bonds 56, 58, 72, 139
- catalytic cycle
  - direct arylation 54
  - metal-catalyzed carbenoid insertion 56
- celecoxib 59, 60
- Chan–Evans–Lam coupling reactions 139
- C–H bond functionalization 45
  - activation 46
  - borylation, disubstituted arenes 63, 64
  - cleavage mechanisms 47–48
  - via ionic intermediates 58, 63
  - via radical intermediates 58, 67
- chelation-assisted *ortho*-palladation reaction 53
- chemoselective C–H functionalization 4
- cobalt (Co)-catalyzed oxidative cross-couplings
  - between arylpyridines and Grignard reagents 91, 92

- between benzo[h]quinoline and Grignard reagents 91, 92
  - electron-rich arenes and arylboronic acids 80, 81
  - concerted metallation deprotonation (CMD) 47, 52–55, 58, 62
  - Copper (Cu)-catalyzed oxidative cross-coupling
    - aerobic oxidative coupling 176
    - aerobic trifluoromethylation 73, 74
    - benzylic and allylic C–H amination 163
    - CDC  $\alpha$ -alkynylation 66, 67
    - hypervalent iodine-mediated C–H arylation 60
    - intramolecular oxidative C–C bond formation 194, 196
    - *ortho*-alkoxylation 141
    - oxidative acetylenic coupling 96
    - oxidative *ortho*-amination 154
    - tandem oxidative  $C(sp^2)$ –H/ $C(sp)$ –H alkynylation 104
    - terminal alkynes 98
  - coumarins 176, 217
  - cross-dehydrogenative coupling (CDC) reactions 66, 67
  - $Csp$ – $Csp$  coupling 8
  - $C(sp)$ – $C(sp^2)$  bond 99
  - $C(sp)$ – $C(sp^3)$  oxidative coupling reactions 28, 72, 105
  - $Csp^2$ – $Csp$  bonds 22
  - $Csp^2$ – $Csp^2$  coupling 30
  - $Csp^2$ – $Csp^3$  bonds 34
  - $Csp^3$ – $Csp^3$  coupling 37
  - $C(sp)$ –H bonds 71
  - $Csp^2$ –H and  $Csp^2$ –H coupling 106
  - $Csp^2$ –H and  $Csp^3$ –H oxidative coupling 123
  - $Csp^3$ –H bonds
    - arylation 93, 94
    - cyanation 93
  - $C(sp^3)$ –H oxidative coupling 128, 145
  - $Csp$ –M carbon 8
  - $Csp^2$ –M carbon 8
  - $Csp^3$ –M carbon 8
  - $Cu(II)$ -catalyzed aerobic oxidative *ortho*-selective C–H chlorination 167
  - $Cu(II)$ – $Cu(I)$  synergistic cooperation 96, 97
  - $Cu(OAc)_2$ -mediated oxidative thiolation 170
  - $CuBr$ -catalyzed aerobic thiolation 171
  - $CuCl$ -catalyzed aerobic oxidative C–H thiolation 171
  - $\alpha$ -cyanoamine products 64, 65
  - cyclometalation reaction 53, 58
- d**
- decarbonylative coupling reaction 220
  - 4,5-diazafluorenone 150
  - dimeric copper acetylide mechanism 96, 97
- e**
- electron-donating groups 113, 167, 190
  - electron-poor arenes 121, 122
  - electron-rich arenes, oxidative halogenation of 166
  - electron-withdrawing *N*-protecting groups 118, 128
  - electrophilic substitution 47, 49–52
  - enantioselective  $\alpha$ -arylation reaction 68–70
  - extended PAHs 84, 85
- f**
- free-radical addition/cyclization cascade reaction 209–211
  - Friedel–Craft type reaction 50, 207
  - Fujiwara–Moritani reaction 51
  - 2-functionalized pyridines 119
- g**
- general classic synthetic route of cross coupling 2
  - Glaser coupling 9, 11, 95, 96
  - Glaser–Eglinton–Hay coupling reaction 11
  - Glaser–Hay coupling reaction 96
  - gold (Au)-catalyzed oxidative cross-coupling
    - between arenes with terminal alkynes 99, 100
    - direct  $C(sp^3)$ –H alkynylation 106
    - gold(I)–acetylide species 101
    - terminal alkynes 98, 99
  - Grignard reagents 7, 17–19, 24–26, 89, 91, 92
- h**
- Heck-type cross-coupling reaction 74, 91, 114, 116
  - Hiyama cross-coupling reactions 11, 86
  - Hoffmann–Löffler–Freytag reaction 67

*i*

- imidazoheterocycles 221, 222
- indolizine 197, 198
- inner-sphere transition metal-mediated C–H bond cleavage 47, 48
- intramolecular allylic alkylation product 125
- intramolecular kinetic isotope effect 201
- intramolecular radical reactions 58, 67, 197, 209, 211, 213, 214
- Iridium (Ir)-catalyzed *meta*-selective C–H borylation 60, 63
- iron-catalyzed oxidative coupling reaction
  - alkynyl Grignard reagents, homocoupling reaction of 18, 19
  - arylboronic acids with benzene derivatives 82, 83
  - between alkenes and Grignard reagents 89, 91
  - between alkenes and organozinc reagents 89, 90
  - between aryl imines and organozinc reagents 90
  - between  $Csp^2$ -H and organozinc reagents 88, 89
  - biaryl products 32, 33
  - *N*-heterocyclics with arylboronic acid 82
  - unactivated arenes with arylboronic acids 80, 81
- 2-isocyano biphenyl 218, 221

*k*

- Knochel's protocol 19, 20, 23
- Kumada-C cross-coupling reactions 7

*l*

- ligand-controlled strategy 58
- linear *E*-allylic esters 149–151
- linear (*E*)-allylimides 165, 166
- lithium aryl(alkynyl) cuprates 23

*m*

- manganese (Mn)-catalyzed oxidative cross coupling
  - alkynyl Grignard reagents 17, 18
  - arenes with arylboronic acid 79, 80
  - aryl and alkynyl Grignard reagents 25, 26
  - direct phosphonation 173
- Markovnikov amination products 161
- meta*-selective C–H functionalization 60
- methane addition reaction 55

*methylation reaction* 187

- mono-*N*-protected amino acid ligands (MPAA) 62

*n*

- native directing groups 62
- Negishi cross coupling reactions 88
- Ni-catalyzed alkenylation 91, 93
- nickel (Ni)-catalyzed oxidative cross-coupling
  - between heteroarenes and arylboronic acids 84
  - between heteroarenes with arylsilanes/alkenylsilane 87
  - heteroarenes with arylsilanes/alkenylsilane 86
  - regioselective coupling 195
  - terminal alkynes 98
- norbornene insertion 60

*o*

- O–H bonds 140
- one-pot carbazole synthesis 112
- organocatalysis 68
- organomagnesium reagents 17, 25
- organometallic reagents 2, 7, 17, 40, 47, 72, 93, 94
  - classification and applications 7–8
- organosilanes 11–12
- organotellurium compounds 19–21
- organotin reagents 7, 12–14
- ortho*-C–H acylation 205, 206
- ortho*-acylacetonitrile 187–189
- ortho*-selective C–H functionalization reaction 59

- outer-sphere transition metal-mediated C–H bond cleavage 47, 48
- oxidative addition 47, 49
  - alkyl halides 28
- oxidative alkenyl C–H amination 164
- oxidative alkenylation 119
- oxidative alkoxylation
  - azoles 144
  - ketene dithioacetals 144
- oxidative C–B bond formation 177
- oxidative C–C couplings 89, 185, 186
- oxidative C–H coupling reactions 89
- oxidative cross coupling
  - alkyl zinc and alkynyl tin 28, 29
  - alkyl zinc reagents and terminal alkynes 31
  - alkynyl magnesium reagents 17, 19
  - between unactivated arenes and pyridine *N*-oxides 108
  - bond formation 1, 2

- catalytic cycle of palladium 3
- vs. classic cross coupling 2
- directing group 76
- oxidative Heck-type cross-coupling reaction 74, 91, 114, 116
- oxidative homocoupling
- alkynylsilanes 13
- alkynyltin reagents 15
- alkynyltrifluoroborates 16, 17
- oxidative N-carbazolation 157
- oxidative olefination 119
- bromoarenes 123
- oxidative Pd-catalyzed *ortho*-arylation 187, 188
- oxidative radical C–C couplings
- alkynylation reaction
- activated methylenes, alkylation of 202
- alkenes 208
- alkynylation reaction
  - diphenylmethane derivatives 185
  - tertiary amines 185
- arenes 187, 208
- benzylic C–H bonds 200, 201
- C–C bond cleavage 218
- cascade process 208
- enones and toluenes 200
- $\beta$ -keto esters 197, 199
- methylation reaction 187
- *para*-selective coupling 188
- phenols 205
- pyridine N-oxide derivatives 190
- 2-(pyridin-2-yl) acetate 197
- quinoline N-oxides 190
- substituted olefins 204
- types 185, 186
- vinylarenes 202
- oxindoles 195–197, 211, 212
  
- p**
- palladium catalyzed homocoupling
- alkylsilanes 12, 13
- alkynylborates 15
- functionalized *n*-butyl alkynyltellurides 20, 21
- palladium catalyzed oxidative cross-coupling reaction
- aerobic oxidative intramolecular alkenylation 125, 126
- anilides, cyclization of 113
- arenes with olefins 51
- aryl zinc reagents and alkyl indium reagents 35, 36
- benzoic acids with aryltrifluoroborates 77, 78
- between acetamido group directing *ortho*-C–H bond and trialkoxyarylsilanes 86, 87
- between arylboronic acids and acetamido-containing arenes 77, 78
- between benzoquinoline (Bzq) and benzene 107, 108
- between phenylureas and dienes 119, 120
- between polycyclic aromatic hydrocarbons and arylboroxins 84, 85
- between simple arenes and arylstannanes 76
- between thiophenes and benzothiophenes 88
- C-2 arylation
  - benzofuran 110
  - indoles 109, 110
  - C-3 arylation, indoles 109
  - C4-arylation 84, 86
  - catalytic cycle 3
  - direct oxidative alkynylation
  - *N*-protected indoles with terminal alkynes 101, 102
  - thiophenes 101, 102
- double C(sp<sup>3</sup>)–H alkoxylation 147
- electron-deficient arenes 82, 83
- electron-rich arenes with arylboronic acid 78, 79
- enantioselective C–H functionalization 62, 63
- Heck-type alkenylation
  - aromatic C–H palladation 116, 117
  - intermolecular carbopalladation 116
  - intramolecular biaryl bond formation 113
  - intramolecular oxidative cyclization 113, 114
  - *N*-benzoylindoles 110, 111
  - diarylethers and diarylanilines 111, 112
- *meta*-selective C–H oxidative alkenylation 60
- one-pot synthesis 112
- *ortho*-alkenylation of anilides 116, 117
- *ortho* C–H amination 154
- *ortho*-selective phosphorylation 172
- phosphine ligand 33, 34
- pyridine-directed arenes 77
- regioselective amination 153
- sequential allylic acyloxylation/vinylic C–H arylation 149
- unactivated arenes with arenes 108
- Pd/polyoxometalate-catalyzed pyridine-directed aerobic olefination 128, 129

- phenylacetic acids 120, 121  
 phenylacetylene 9, 66, 99, 100  
 photoredox-catalyzed C–H arylation reaction 70, 71  
*N*-pivaloyl pyrroles, intramolecular cyclization of 123, 124  
 pyridine *N*-oxides 118  
 pyridine group directed oxidative *ortho*-acetoxylation 141  
 pyridyl benzene 89
- r**  
 radical addition/cyclization mechanism 197, 199  
 – free 209–211  
 – tandem 213–215  
 radical–radical coupling reaction 71  
 reaction rate, aryl and alkynyl Grignard reagents 25, 26  
 regioselective C–H functionalization 4  
 regioselective C–H acyloxylation 147  
 rhodium (Rh)-catalyzed oxidative coupling – between 2-phenylpyridine and aryl stannanes 75  
 – non-directed oxidative alkenylation 123  
 – – *ortho*-aryloxylation 143  
 – – *ortho*-C–H functionalization 50  
 – stereoselectivity carbенoid insertion 56–57  
 – stereoselectivity nitrenoid insertion 56–57  
 $(\pm)$ -rhazinicine 121  
 ruthenium-catalyzed *meta*-selective C–H sulfonation and alkylation reaction 60
- s**  
 selective C-2-alkenylation 117, 118  
 $\sigma$ -bond metathesis 47, 52  
 silver-mediated direct C(sp<sup>3</sup>)–H alkynylation 106
- single-electron transfer (SET) processes 4  
 Sonogashira cross coupling reactions 11, 22, 23, 99, 104  
 sterically controlled C–H functionalization 58, 63  
 Stille reagents 7, 12  
 stoichiometric reactions 49, 75, 80
- t**  
 tandem oxidative C(sp<sup>3</sup>)–H/C(sp)–H alkynylation and cyclization reaction 106  
 tandem radical addition/cyclization 213–215  
 $(-)$ -tetrodotoxin 57  
 terminal alkynes 11, 15, 17, 22, 29–31, 71–74, 95, 99–106, 153, 171, 176, 185  
 – oxidative amidation of 152  
 tert-butyldimethylsilyl (TBS)-protected diynes 11, 12  
 2,2,6,6-tetramethylpiperidine-N-oxyl radical (TEMPO) 19, 25, 80, 91, 156  
 trans-olefins 117, 118  
 transition metal-catalyzed radical oxidative cross-coupling reactions 68, 69  
 tributyl(phenylacetylenyl)tin 13–14  
 1,3,5-trimethoxybenzene 80, 207, 209
- u**  
 unactivated Csp<sup>3</sup>–H bond arylation 93–95, 123–128, 185–187, 200  
 unsymmetrical biaryls 32
- v**  
*N*-vinylcarbazoles 161, 162  
 vinyllogous arylamino ketones 159
- z**  
 Z-enamides 160  
 Z-vinyl(triethylsilanes) 151

