

Index

a

- δ -acetoxy allenates 63, 65
- achiral *N,N'*-binaphthyl hydrazines 67
- N*-acyl piperidines 55
- alkylation reaction 133, 220, 281, 282, 287
- 2-alkylindoles 94
- ortho*-alkynylanilines 95, 96
- alkynylation 39, 80, 90, 91, 104, 199, 265–267
- allene molecule 226
- amides
 - atropisomeric amides 118
 - atropisomeric benzamides
 - asymmetric dihydroxylation 121
 - atropisomerically stable amides 120
 - atroposelective aldol reactions 121–122
 - atroposelective [2+2+2] cycloaddition 123
 - atroposelective halogenation 122–123
 - enantioselective *O*-alkylation 123–124
 - stereochemical stability of 118
- anilides
 - kinetic resolution 129–130
 - metal-catalyzed synthesis 131
 - organocatalytic synthesis 131–133
 - stereochemical stability 129
- anionic chiral phase-transfer catalysis 286
- aromatic amines 31, 58, 97, 257, 261, 279, 280
- aromatic polyketide 61
- N*-arylindoles 91, 92, 95, 97
- aryl-naphthaquinones 64
- N*-arylpyrroles 91, 92, 97
- 4-aryl 2-quinolinones 85
- asymmetric acylation 50–53
- asymmetric alkylation 48–50
- asymmetric allylic substitution 249–250, 262
- asymmetric chemistry 3
- asymmetric electrophilic bromination 54–56
- asymmetric functionalization of olefins 248
- asymmetric hydrogenation reactions 246
- asymmetric Mannich reactions 4
- asymmetric nucleophilic addition 56
- asymmetric Suzuki–Miyaura coupling 16, 17, 20–24, 195, 251
- asymmetric transformation
 - axially chiral backbone 212–213
 - of axially chiral biaryls and heterobiaryls 211
 - of axially chiral non-biaryl compounds 214
 - with axial-to-central chirality transfer 213
 - carbanionic cyclization 217–218
 - chiral allenes 226
 - cyclization 226–232
 - cycloaddition 233–236
 - [3+2]-cycloaddition 214
 - [4+2]-cycloaddition 214
 - electrophiles
 - lithiation 221–222
 - reactivity as enolates 220–221
 - rearrangements 222–223
- Heck cyclization 217
- nucleophiles 218–220
 - carbon nucleophiles 236–238
 - chiral allenes 240–242
 - heteroatom nucleophiles 238–239
- photoreactions
 - hydrogen atom abstraction 226
 - photocyclization 225
 - photocycloaddition 224
 - radical cyclization 215–217
- atropisomeric amides 118–122
- atropisomeric biaryls 6, 9, 16, 23, 41, 50, 87, 308, 309
- atropisomeric isoquinolines 77

- atropisomeric lactams
 - asymmetric tandem isomerization–Michael reaction 136
 - atroposelective [2+2+2] cycloaddition strategy 135
 - chiral auxiliary approach 136
 - diastereoselective cyclization 134
 - stereochemical stability of 134
 - atropisomerism 4, 10, 109, 118, 121, 124, 125, 127, 129, 133, 211, 220, 297, 298, 299, 302, 311
 - atropisomers 3, 6, 9, 35, 60, 62, 65, 67, 102, 105, 109, 110, 118, 119, 121, 125, 173, 181, 183, 191, 194, 197, 200, 220, 224, 242, 297–301, 303, 305
 - atroposelective aromatization 200–201, 204
 - atroposelective coupling protocol 16
 - atroposelective oxidative aryl coupling 178
 - axial chirality 3–7, 9, 18, 28, 40, 58, 61, 63, 65, 68, 79, 83, 84, 86, 91, 96, 98–104, 110, 114, 116, 117, 119, 122, 123, 124, 130–131, 151, 159, 168, 173–176, 179, 183, 185–187, 191, 192, 194, 196, 197, 200, 201, 203, 204, 214, 215, 218, 220, 224, 225, 226, 233
 - axially chiral alkaloids 186–188
 - axially chiral allenes 9, 141–143, 152, 226, 242
 - axially chiral anilides 127, 129–132, 214
 - axially chiral ligands 245
 - biaryl thermal racemization reaction 246
 - with diverse skeletons 245
 - monodentate phosphines 246
 - asymmetric allylic substitution 249–250
 - asymmetric hydrogenation 246–248
 - asymmetric hydrosilylation 248–249
 - catalytic asymmetric transformations 250–251
 - axially chiral natural products
 - asymmetric synthesis 175
 - atroposelective aromatization 200–201
 - axial aryl–aryl coupling method 174
 - biaryls asymmetric transformation 196
 - catalytic atroposelective C–H functionalization 199
 - desymmetrization 197–199
 - diastereoselective synthesis 199–200
 - lactone method 196–197
 - chiral catalyst
 - catalytic oxidative aryl coupling 191–193
 - transition-metal catalyzed atroposelective aryl coupling 194–196
 - diastereoselective coupling-point
 - intermolecular diastereoselective aryl coupling 183–191
 - intramolecular diastereoselective coupling 176–183
 - diastereoselective macrocyclization 202–204
 - diversity 174
 - enantio- or diastereoselective macrocyclization 175
 - point-to-axial chirality transfer 175–191
 - structure features 173
- axially chiral phosphines 212
- b**
- Barton–Zard reaction 99
 - benzothiadiazine-1,1-dioxide-type catalyst 152
 - 1,2,3-benzotriazinones 85
 - N*-benzylquininium chloride 80
 - biaryl amination products 32
 - biaryl atropisomers 13–42, 47–72, 75, 137, 212, 214, 242
 - biaryl coupling
 - asymmetric Hiyama–Denmark cross-coupling aryl bromides 24
 - C–H bond functionalization
 - atroposelective C–H arylation 40
 - chiral auxiliary-induced 40
 - chiral catalyst-controlled 38–40
 - cobalt-catalyzed enantioselective [2+2+2] cycloadditions 35–36
 - desymmetrization
 - prochiral biaryls 29–30
 - racemic axially chiral biaryls 30–31
 - ring-opening reactions 32–35
 - iridium-catalyzed enantioselective [2+2+2] cycloadditions 36–37
 - Kumada–Tamao–Corriu
 - cross-coupling 14–15
 - Negishi cross-coupling 15
 - oxidative coupling
 - Cu-catalyzed oxidative coupling 25–27
 - oxidative coupling reactions 27–29
 - rhodium-catalyzed enantioselective [2+2+2] cycloadditions 36
 - Suzuki–Miyaura cross-coupling 15–24
 - P,N*-bidentate 80
 - bifunctional thiourea organocatalyst 96, 99
 - 1,1'-binaphthalene-2-carbaldehyde 61
 - 1,1'-bi-2-naphthol (BINOL) 4, 24, 28, 84, 245, 276, 303
 - biocatalytic DKR 78

- biphenyl sesquiterpenes 188, 197
 bisoxazoline (BOX) ligand 26, 33, 105, 106, 155
 BoPhoz-type phosphineaminophosphine ligand 18
 bridged biaryl atropisomers 33, 212
 Bringmann's lactones 34, 57, 175
 1-bromo-2-methoxynaphthalene 18
 1-bromo-2-methylnaphthalene 17, 23
 1-bromonaphthalene 15, 251
 Brønsted acid-catalyzed cyclodehydration reaction 97
 Brønsted base catalyst 275, 288–289
 Bruton's Tyrosine Kinase (BTK) inhibitors 301
 Buchwald–Hartwig amination 80, 85, 188
- C**
- Cahn–Ingold–Prelog priority rules 9–10
 central chirality 3, 4, 28, 100, 116, 141, 173–176, 183, 200, 204, 213–214, 216, 225, 228, 230, 231, 237, 297, 311
 carbanionic cyclization 217–218
 chiral allenes
 catalytic asymmetric synthesis
 addition 1,3-diyne 1, 154–160
 desymmetrization 162–163
 diazo compounds 161–162
 enantioselective proton migration of alkyne 152–154
 chirality transfer
 functionalized allylic derivatives 149–150
 Isomerization of propargyl metals 148
 Pd-catalyzed stereospecific reaction 146–148
 propargyl alcohol and derivatives 142–143
 S_N2' reaction 145–146
 stereospecific rearrangements of propargyl amine 143–145
 Wittig olefination 150–151
 enantioselective allene synthesis
 dynamic kinetic processes 164–167
 kinetic resolution 163–164
 gold-catalyzed cyclization 231
 intermolecular cycloaddition 233–234
 intramolecular cycloaddition 234–236
 organic reagent-mediated cyclization 232
 palladium-catalyzed cyclization 226–228
 rhodium-catalyzed cyclization 228–231
 silver-catalyzed cyclization 231–232
 stoichiometric chiral reagents 151
 structure and properties 142
- chiral Brønsted acids 4, 31, 49, 117, 275, 276–285
 chiral catalyst 191
 catalytic oxidative aryl coupling 191–193
 transition-metal catalyzed atroposelective aryl coupling 194–196
 chiral cationic guanidinium salt 161
 chiral chromatography 303
 chiral oxazolines 189–191
 chiral recognition 6, 8, 48, 211, 302–306
 chiral stationary phases (CSPs) 6, 8, 303
 cholesteric liquid crystals (CLCs) 6, 307
 chromanones 184
 circular dichroism (CD) 303
 circularly polarized light (CPL) 307
 conventional kinetic resolution 47
 cross-coupling reactions, Negishi 15
 C₂-symmetric chiral phosphoric acid 282
 C₂-symmetric diols 267
 arrangement reaction 269
 Diels–Alder reaction 268–269
 Mukaiyama aldol condensation reactions 267–268
 reductive reactions 269–270
 Curtin–Hammett principle 101
 1-cyano-2-methoxynaphthalenes 81
 cyclic diaryliodoniums 32–34
 [4+2]-cycloaddition 214
 1,3-cyclohexanediones 97
 cyclophanes 111, 112, 173, 203
- d**
- desymmetrization, prochiral biaryls 29–30, 80, 81, 197
 di-alkynyl 2-methoxynaphthalene 81
 diaryl amines
 atroposelective approaches 138
 stereochemical stability 137
 2,3-diarylbenzoindoles 101
 diaryl ethers
 Csp²-H activation 127
 enantioselective synthesis 125–126
 enzyme-catalyzed synthesis of 126–127
 resolution studies 124–125
 diastereoselective approach 83
 diastereoselective
 macrocyclization 175, 202–204
 diazamide A 179, 180
 1,3-dibenzyloxy-2-propanol 57
 3,3'-diformyl-2,2'-dihydroxy-1,1'-bi-2-naphthol 28

dichlorodicyanobenzene (DDQ) 63, 101, 111, 177
 Diels–Alder reaction 129, 201, 203, 214, 215, 233, 234, 267–269, 280–283
 1,4-dihydropyridines (1,4-DHPs) 83
 2,3-dihydroxynaphthalenes 70
 diisopropyl azodicarboxylate (DIAD) 71
 dimeric quinones 184
 dinaphthaleneiodonium salts 32
 dinaphthothiophene 32
 diphosphine ligands 252
 C–C bond formation 255–257
 C–X bond formation 257–258
 hydrogenation reactions 252–255
P-(+)-dispegatine 186
o,o-disubstituted phenyl ring 99
 dynamic kinetic resolutions (DKR) 76, 79
 asymmetric electrophilic bromination 54–56
 asymmetric nucleophilic addition 56
 asymmetric ring-opening/expansion transformation 57–59

e

electrophiles reactivity as enolates 220–221
 electrophilic carbothiolation 66, 117, 118
 enantioenriched 3-arylpyridines 83
 enantioenriched allenylsilanes 240
 enantioselective allenation of terminal alkynes (EATA) 144
 enantioselective catalysis method 6
 enantioselective O-alkylation 123–124
 enantioselective synthesis 23, 59, 63, 75–106, 109, 111, 118, 125–126, 141, 145, 146, 148, 152, 157, 161, 162, 166, 167, 196, 259, 268, 280
 enzyme-catalyzed synthesis 126–127

f

Friedländer quinoline synthesis 84

g

glycopeptides 178, 188, 303
 gold-catalyzed cyclization 231
 gonytolide A 184, 185

h

Heck cyclization 212, 213, 217
 Heck reaction 80, 161, 203, 217, 218, 255
 helical chirality 3, 4
 helical twisting power (HTP) 6, 307
 heterobiaryl atropisomers 102

aminopyrrolopyrimidine 93
N-arylindole and pyrrole atropisomers 91
 atroposelective ring formations 81–87, 105–106
 azodicarboxylate and 3-aryl indoles 90
 enantioselective cross-coupling reactions 87
 functionalization of 75–81, 103–104
 heterobiaryl axis 93–95
 bis-heterocycle 104–105
 hindered indole heterocycles 89
 preformed cyclic systems 89
 prochiral arene–chromium complexes 92
 TADDOL-phosphoramidite ligand 89
 heterobiaryl carbinols 78
 homo-coupling reaction 29
 bis-hydrazone ligands 22, 24
 hydroamination reaction 257
 hydrogen atom abstraction 226
 hydrogen-bonding catalysis 9
 hydroxycarboxylic acids 6, 305
 4-hydroxyindole synthesis 97
 5-hydroxyindoles 71
 2-hydroxyquinones 64, 65

i

indole-quinoline atropisomers 102, 103
 intermolecular annulation 63–67
 intramolecular cycloaddition 204, 234–236
 intramolecular diastereoselective aryl–aryl coupling 176, 183
 intramolecular [4+2] hetero-Diels–Alder cycloaddition 86
 intramolecular oxidative aryl coupling 176, 178, 181, 184
 intramolecular Suzuki–Miyaura coupling 179
 isocyanacetates 98
 isoquinoline *N*-oxides carbaldehyde 78
 isoquinolines 76, 77, 79, 82, 188, 254
 isoquinolone 85

k

2,3-ketodiester 97, 98
 ketoreductase enzymes (KREDs) 78
 kinetic resolution strategy
 asymmetric acylation 50–53
 asymmetric alkylation 48–50
 asymmetric transfer hydrogenation and Michael addition 53–54
 conventional kinetic resolution 47–48
 Kumada–Tamao–Corriu cross-coupling 14–15

l

lactone method 34, 175, 196–198, 204
 Lewis bases promote reactions 289
 lignan natural products 176, 177, 199
 limonoids 184, 185
 liquid crystals 6, 8, 307–313
 lithiation/borylation method 148, 221

m

macrolactone natural products 180–182
 macropeptide natural products 178–180
 metal-catalyzed enantioselective synthesis 111–113, 259
 2-methoxy-1-naphthalenylmagnesium bromide 15
 2-methyl-1-naphthylboronic acid 17
 monodentate phosphines 246
 asymmetric allylic substitution 249–250
 asymmetric hydrogenation 246–248
 asymmetric hydrosilylation 248–249
 catalytic asymmetric transformations 250–251
 mono *N*-protected amino acid (MPAA) ligands 78
 Morita–Baylis–Hillman reaction 290

n

2-naphthols 24–29, 68, 84, 94, 100, 117, 131, 245, 276, 303
 1,2-naphthylene oligomers 62
 naphthylpyridines 76
N-bromoacetamide (NBA) 55, 77
 Negishi cross-coupling 15
N-heterocyclic carbene (NHC) 14, 52, 86, 145
 non-biaryl atropisomers
 amides stereochemical stability of 118
 styrenes
 metal-catalyzed enantioselective synthesis 111–113
 organocatalytic synthesis 114–118
 point-to-axial chirality transfer 110–111
 non-functionalized 1,3-enynes 156
 nonsteroidal anti-inflammatory drug (NSAID) 69
N-*P* ligands 264–267
 nucleophiles
 carbon nucleophiles 236–238
 chiral allenes 240–242
 heteroatom nucleophiles 238–239

o

oligo-1,2-naphthylenes 62
 omeprazole 302
 organocatalysts 275
 BINOL 276
 Brønsted base catalyst 288–289
 chiral Brønsted acid catalysts 276
 chiral counteranion catalysts 285–288
 chiral phase transfer catalysts 285–288
 classification 275
 phosphoric acid 276–285
 salient features 275
 organocatalytic asymmetric synthesis, of biaryl atropisomers
 atroposelective arene formation
 intermolecular annulation 63–67
 intramolecular atroposelective arene formation 61–63
 desymmetrization strategy 59–60
 direct C–H arylation strategy
 atroposelective nucleophilic aromatic substitution 71–72
 quinone derivatives 68–71
 [3,3]-sigmatropic rearrangement 67–68
 kinetic resolution strategy
 asymmetric acylation 50–53
 asymmetric alkylation 48–50
 asymmetric transfer hydrogenation and Michael addition 53–54
 conventional kinetic resolution 47–48
 dynamic kinetic resolution (DKR) 54–59
 organocatalytic synthesis 114–118
 oxidative phenolic coupling 176, 180, 184

p

palladium-catalyzed asymmetric carbonylation 32
 palladium-catalyzed cross-coupling 14, 79
 palladium-catalyzed cyclization 212, 226–228
 palladium-chiral diene complex 23
 Paterno–Buchi reaction 224
 Pauson–Khand reaction 256
P-chiral phosphorus ligands 20, 21
 Pd-catalyzed asymmetric Kumada–Tamao–Corriu reactions 15
 Pd-catalyzed Heck reaction 161
 peptidic phosphoric acid 98
 perylenequinones 184, 191
 phase-transfer-catalysis (PTC) 80, 131, 133, 152, 165, 286–288
 phenyl alanine derivative ligand 78

- phleichrome 26, 184
 2-(phenylethynyl)phenols 96, 114
 phosphamide ligands 259
 allylic substitutions 262–263
 asymmetric hydrogenolysis 263–264
 hydroboration/hydrosilylation
 reactions 261–262
 hydrogenation 260–261
 organometallic nucleophiles 259–260
 phosphine free ligands 22
 phosphoramidite 24, 34, 41, 89, 111, 245,
 246, 259–264
 photochromic molecules 309
 photocyclization 225
 photocycloaddition 224
 photoinduced electron transfer (PET) 304
 photoreactions
 hydrogen atom abstraction 226
 photocyclization 225
 photocycloaddition 224
 photostationary states (PPSs) 310, 311
 planar chirality 3, 4, 92, 119, 120
 P–N cross-coupling reaction 80
 point-to-axial chirality transfer 110–111, 201
 polystyrene-poly(ethyleneglycol) copolymer
 (PS-PEG) resin 20
 porcine pancreatic lipase (PPL) 162, 164
 potassium thioates 33
 prochiral biaryls 29–30, 80, 81, 174, 196,
 197, 204
 (*S*)-proline 275, 292
N-protected amino acids 6, 78, 305
 proteins 3, 297, 299
Pseudomonas fluorescens (PFL) 162
 2-pyridones 82, 224, 225
 pyrrole atropisomers 91, 99
- q**
 quinolinone atropisomers 84
 quinone derivatives 68–71
- r**
 radical reaction 215
 red, green and blue (RGB) reflection 311
- rhodium-catalyzed cyclization 228–231
 ring-opening amination reaction 32
 ring-opening nucleophiles 33
 ring-opening reagents 32
 R/S stereodescriptors 9
- S**
 γ -secretase inhibitors 59
 silver-catalyzed cyclization 231–232
 spiranes 3, 4, 9, 10
 stereochemically stable nonbiaryl
 atropisomers 110
 stereoselective oxidative homo-coupling 6
 structure–activity relationship (SAR) 6, 300
 styrenes
 metal-catalyzed enantioselective
 synthesis 111–113
 organocatalytic synthesis 114–118
 point-to-axial chirality transfer 110–111
 2-substituted 3-alkynoates 153
N-sulfonyl iminoquinones 69, 70
 sulfur nucleophiles 33
 Suzuki–Miyaura coupling reaction 13, 15–24,
 78, 80, 88, 148, 179, 188, 194–196, 251
- t**
 tetrahydroxanthones 185
 tropos biaryls 312
- u**
 unsaturated ketoaldehydes 61
- v**
 vancomycin 6, 124, 173, 178, 188, 303
 vancomycin aglycon 178
 vancomycin-related glycopeptides 178, 188
 vinylidene *ortho*-quinone methides (VQM) 63
 vinylidene-quinone methide (VQM) 86
- w**
 Wang's protocol 290
- x**
 xanthones 168, 184–186