

Index

a

acetals 249–266
 acetonitrile 25
 acetylenes 8, 29, 65–74
 active volume–passive volume principle
 16, 23
 alcohols and phenols 285–303
 aldehydes 55
 aldol additions 188
 aldolcyclization 49
 alkenes
 – allyl substitution 89–109
 – cycloaddition 110–120
 – ene reaction 125–128
 – Heck cyclization 128–129
 – hydroformylation 81–84
 – hydrogenation and reduction 74–81
 – metathesis cyclization 131–133
 – oxidation and allyl oxidation 84–89
 – Pauson-Khand reaction 130–131
 – radical - and nucleophilic cyclization
 133–134
 – sigmatropic rearrangement 120–125
 alkylamine 318
 allylamines 332
 allylic acetate 89, 95
 allylic alcohols 39
 allylic anions 9, 55
 allyl oxidation and oxidation 84–89
 allylstannanes 163–165, 167
 allyl substitution 89–109
 allylsulfone 314
 allyltitanium reagents 175
 aluminum hydrides 10
 amides 30
 amines 318–334
 aminoalcohols 281
 anhydride 25

anthracynones 302
 anthraquinones 148
 Appel reaction 237
 aromatic amines 319
 aspartic acid 54
 ATPH 181
 aza-Claisen process 40
 9-azabicyclo[3.3.1]nonenes 171
 azo-dicarboxylates 325

b

Bayer–Villiger oxidations 207–208
 Baylis–Hillman reaction 324
 Beckmann fragmentation 195, 197
 benzleukodienes 7
 benzoxazepine 154
 betaine 102
 bisallylether 267
 bis-benzenesulfonylethylene 317
 bromoacrylates 205

c

carbacyclins 149
 carbenium ion 173
 carbinols 280
 carbonyl derivatives
 – conjugate addition 178
 – – cuprate additions 178–181
 – – enolate additions 181–182
 – – free radical addition to enoates 182–183
 – – olefin formation by organometal addition
 to alkynes 183–184
 – as electrophiles 141
 – – 1,2-nucleophiles addition 141–151
 – – allylation/crotylation reactions 163–177
 – – carbonyl compounds reduction 151–163
 – enolate derivatives 185–194
 – Lewis acid-mediated carbonyl ene reactions
 199–201

- carbonyl derivatives (*contd.*)
- metal complex formation in carbonyl and imine additions 201–205
 - organometal-mediated C–C connections 201
 - oxidation reactions 207–209
 - pericyclic reactions 197–199
 - rearrangements and fragmentations 195–197
 - Wittig-type reactions 205–207
- charge acceleration 40
- chemoselectivity 1–7, 59, 84, 151, 217
- chiral amino alcohols 153
- chiral sulfoxides 157, 158
- chloroacetate 93, 163
- Claisen process 124, 125
- Claisen rearrangement 38
- conjugate addition 178
- cuprate additions 178–181
 - enolate additions 181–182
 - free radical addition to enoates 182–183
 - olefin formation by organometal addition to alkynes 183–184
- Cope elimination 326, 328
- countercation 125
- cyanohydrin 308
- π -cyclizations 31
- cycloadditions 32–35, 37, 38, 42, 50, 197, 317
- cyclobutanones 149–150
- cyclobutene 77
- cyclohexenes 78
- cyclohexenone 294
- cyclopentadiene 325
- cyclopentane 74, 81, 99, 119
- cyclopentenone 13, 17, 19, 48, 52, 130–132, 180, 321, 343
- cyclopropanes 111, 116, 333
- d**
- desymmetrization 298–299
- diacetylenes 71
- dialkylacetylenes 72
- diaminocyclopentenes 325
- diastereoselectivity 142–144, 153, 157, 161, 163–164, 169, 171, 184, 190, 220–222, 229, 260, 261, 264, 266, 271, 274, 280, 288, 290, 294, 306, 307, 309, 313, 314, 333
- Dieckmann reaction 41
- Dieckmann cyclization 47
- Diels–Alder reactions 48, 51, 73, 112, 113, 115, 197–199, 325, 344
- diethyl ether 25
- difluoroallene 344
- dihydrofuran 12
- 1,3-diketone 41
- diketone 50
- dioxenone 119
- dipole 37, 38, 51
- Duthaler Haffner reagent 146
- e**
- electrophiles 9, 16, 20, 22, 23, 27, 30, 31, 42, 43, 105, 107, 127, 186, 275
- and carbonyls 141
 - – 1,2-nucleophiles addition 141–151
 - – allylation/crotylation reactions 163–177
 - – carbonyl compounds reduction 151–163
- enamines 331–334
- enantioselectivity 47–59, 144, 145, 153–155, 162, 165, 171, 175, 177, 201, 208
- ene reaction 125–128
- enolate derivatives 185–194
- enthioat 18
- episulfides 306
- epoxides 8–12, 15, 217–249
- ethers 266–284
- f**
- fluorohydrins 222
- Friedel–Crafts alkylation 103
- fumaric acid 33
- Fürst–Plattner rule 11, 226, 227
- g**
- Geissman–Waiss lactone 170–171
- geranyl acetate 92
- Grignard reactions 5, 22, 25, 46, 142, 148–149, 161, 227–228, 265, 282, 286, 290, 291
- h**
- haloethers 30
- halogen compounds 334–345
- halolactones 30
- hard–soft principle 17, 29, 304
- Heck cyclization 128–129
- Heck-hydroformylation 83
- hemiacetals 82, 84, 157
- heptelidic acid 219
- heteronucleophiles 101
- hexafluoroamine 341
- HMPA 161–162, 186, 207
- homoallylic alcohols 158
- homochiral epoxide 308
- hydrazones 32
- hydrindane 80, 134
- hydroazulenes 32, 110
- hydrocarboxylation 70

hydroformylation 81–84
hydrogenations 32
hydroxyalkylation 300, 301
hydroxyketones 30, 44
hydroxylamines 326–328
hydroxyolefins 280

i

iminium ion 172
indenoquinoline 320
indolizidine 56, 134
iodo compounds 275
(*Z*)-3-iodoacrylic acid 337
iodovinyl compounds 335, 336
isosphingosine 239

k

ketene acetal 39
 α -ketoester 45
 β -ketoester 29, 42, 44, 57, 95, 154, 163, 186
ketones 12–16, 29, 32, 44, 45, 48, 49, 73, 77,
82, 84, 87–89, 101, 107, 111, 115, 151, 157,
158, 160, 161, 188, 225, 288

l

γ -lactone 32, 82
lactone 33, 54, 341
lankacidin 335
L-aspartic acid 186
leucotrienes 158
Lewis acid 10–12, 18, 28, 40, 44, 46, 72, 86,
103, 113, 115, 121, 127, 142, 146, 149, 152,
155, 163, 164, 167, 168, 180–183, 188, 190,
192, 199–201, 225, 230, 231, 234, 237,
242–244, 246, 251–252, 255–257, 260, 272,
273, 281, 290, 291, 316, 319, 340

m

Macdonald–Still reagent 141
maleic acid 33
MAPH 149, 151
meta compound 148
metal-catalyzed aminations and coupling
reactions 319
metal complex formation in carbonyl and
imine additions 201–205
metathesis cyclization 131–133
methylaluminum
bis(2,6-di-*tert*-butyl-4-alkylphenoxide)
(MAD) 142–143, 149
 α -methylcyclohexanone 14
methylolithium 141, 142
Meyer–Schuster rearrangement 195, 196

Michael addition 5, 16, 17, 19, 41, 42, 48, 93,
278, 317, 341
monoaminocyclopentenes 325
Mukaiyama aldol addition 190
Mukaiyama oxidative cyclization, of pentenols
279

n

Nazarov cyclization 343
neodisyherbaine 258, 281
neryl acetate 92
Nicholas complex 66, 240, 241
N-tosylhydrazones 277
nucleophiles 11, 12, 17, 18, 21, 22, 25, 27, 29,
31, 43, 46, 51, 66, 89–92, 98–99, 102–105,
107, 133–134, 141–151

o

olefins 8, 27, 29, 30, 65, 72, 74, 82, 88, 220,
284, 301, 328
– formation by organometal addition to
alkynes 183–184
Oppolzer sultam aldol reaction 192, 194
organolithium 141, 142
organometal-mediated C–C connections
201
ortho compound 148
osmylation 86
oxazolidinone 237, 239
oxidation reactions 207–209

p

Pauson–Khand reaction 130–131, 321
Payne rearrangement 235
pericyclic reactions 197–199
Peterson reaction 27
p-fluoraldehyde 23
p-fluorophenol 23
phenyllithium 142, 151
Pictet–Spengler cyclization 329
piperazinedione 96
Polonovsky elimination and fragmentation
328
prephenic acid 38
Prins cyclization 247, 261–262
proline derivatives 153, 154
prolinolamide 285
propargylic alcohols 195, 256
propargylic systems 240
prostacyclins 149
protecting groups 1, 7
pseudo-sugar chemistry 85
Pummerer reaction 44, 309–310

q

quarternized compounds 23
quinole acetate 25

r

regioselectivity 7–26, 66–69, 71, 74, 78, 79,
81–84, 89, 90, 93, 95–96, 98, 110–111, 116,
117, 120, 126, 128, 148–150, 154, 175, 177,
184, 186, 188, 203, 208. *See also* sp₃
selectivity
Roush crotylation 175

s

Sakurai reactions 101, 118, 182
sesquiterpenes 149
Sharpless reaction 5, 59, 84, 98, 229, 231, 236
sigmatropic rearrangement 120–125
silyl enol ethers 182, 185, 190, 192
 γ -silyloxy allylstannanes 165
S_N1-substitution 224, 235, 253, 259, 307
S_N2-substitution 224, 235
Sonogashira coupling 342
sp₃ selectivity
– acetals 249–266
– alcohols and phenols 285–303
– amines 318–334
– epoxides 8–12, 15, 217–249
– ethers 266–284
– halogen compounds 334–345
– sulfur compounds 303–318
sphingosine 238, 239, 264
spirodiketone 246
spiroketalization 265
spiro skeletons 201
stereocomplementary processes 53
stereoselectivity 26–47, 74, 77–79, 82, 89,
104, 109, 110, 114, 116, 117, 119, 128, 133,
141–146, 148, 152, 155, 161, 162, 164,
179–181, 188, 190, 204
stereotriads 288
Stork–Wittig olefination 335

Strecker reaction 205
sulfones 217
 α -sulfonfylcarbanions 313
sulfoxides 217
sulfoximine 98
sulfur compounds 303–318
Swern oxidation 265

t

Tamao–Fleming protocol 189
TASF 182
terpinones 209
tetrahydrofurans 237, 275, 276, 280
tetramethylethylenediamine (TMEDA) 149
thioester 54
thiophosphate 306
titanium compounds 146, 147, 156–157
tosyldiazomethane 269
transprotonation equilibrium 317
2-trimethylsilyloxyfuran 190

v

vinyl anions 8, 21
vinyl bromides 334
(Z)-vinylacetylenes 73
vinyl-nitro compound 36
vinyloxiranes 98
vinylpiperidine 84
vinylsilane 34, 171–174
vinylsulfones 307
vinylsulfoxide 309

w

Wagner–Meerwein-type 1,2-rearrangements
195
Weinreb amide 318
Wittig rearrangement 125, 266, 267, 269
Wittig-type reactions 205–207

y

ynamines 331