

Index

a

Abramov reaction 102, 119, 122, 224
 absolute configuration, determination 2,
 4, 5, 8, 11, 24
 CDA 12, 23
 chemical correlation method 19
 circular dichroism 24
 Cotton effect 24
 derivatising reagent 12, 13
 derivatization 21
 mandelic acid 23
 Mosher–Kusumi method 20
 MPA 20
 naproxene 12
 X-ray crystal analysis 17
 (+)-acetoxycrenulide, marine toxin 107,
 108, 116
 α -acyloxyphosphonates
 enzymatic hydrolysis 319, 320
 β -acyloxyphosphonates 316, 320
 alkene-bis-phosphonates 281
 addition of aldehydes 278
 cyclic β -ketoesters 278, 281
 cyclic ketones 108, 272
 ethyl 2-(diethoxyphosphoryl) acrylates
 278
 alkyl-methyl(phenyl)phosphine oxides 56
 alkylation
 chiral Ru complexes 214
 Friedel–Crafts 217–219
 β -ketophosphonates 217
 Pt(II) complexes 213
 aluminium-salalen complexes 225, 226
 aminocarnitine 139
 2-amino-1-hydroxyethylphosphinic acid

α -aminophosphonic acid 136, 137, 332,
 334
aspergillus oryzae 322
Carica papaya 333
penicillin acylase 333
Subtilisin Carlsberg 333
 β -amino- α -hydroxyphosphonates 151
 α -aminophosphonates 150, 156, 166, 189,
 191, 208, 228, 230, 231, 267, 334
Aspergillus niger 348
Aspergillus oryzae 333
 fluorinated 139
 kinetic resolution with CALB 334
 Papain 348
 resolution of aminoacids 333
Subtilisin Carlsberg 333
 β -aminophosphonates 142, 269, 281, 315
 aminophosphines 54, 270, 273
 mechanism of asymmetric induction 55
 as PNP and PNS ligands 56
 reactions of chlorophosphines 53
 secondary amines as chiral auxiliaries
 53
 α -aminophosphonic acids 263, 265
 β -aminophosphonic acids 253
 α -aminopropargylphosphonates 231
 anthoplalone 108
 arylation 211, 213
 $Pd(Et-FerroTANE)Cl_2]$ 216
 $Pd(S,S)-Chiraphos$ complex 215
 asymmetric addition 1, 4, 108, 109, 144
 conjugate 107, 117
 asymmetric aminohydroxylation 210
 AD-mix- α in 153, 211
 AD-mix- β in 153
 asymmetric aza-Wittig reaction 116

- asymmetric biocatalysis 315
 asymmetric dihydroxylation 20
 asymmetric electrophilic catalysis 211
 asymmetric hydrogenation 187, 188,
 202
 of alkene phosphonates 188
 $\text{BPE}[\text{Rh}(\text{COD})]\text{BF}_4$ 196
 catalyzed by BoPhos $[\text{Rh}(\text{COD})]\text{BF}_3$
 190
 ClickFerrophos II 197
 α -enolphosphonates 197
 Ir/phenyloxazoline ligands 198
 iridium catalysts 198
 ketophosphonates 201
 $\text{Me-CATPHOS}[\text{Rh}(\text{COD})]\text{BF}_4$ 192
 $\text{PHANEPHOS}[\text{Rh}(\text{COD})]\text{BF}_4$ 192
 $\text{Rh}(\text{P-OP})$, catalysts 190
 $\text{Rh}(+)-\text{DIOP}$ 188, 189
 $\text{Rh}(\text{R})\text{-MonoPhos}$ 197
 $\text{Rh}(\text{R,R})\text{-t-Bu-BisP}$ 190
 Rh/DpenPhos 197
 Rh/HyPhos 196
 Rh/IndolPhos 197
 Rh/JOSIPHOS 192, 193, 209, 215
 $\text{Rh}(\text{S})\text{-P-OP}$ 192
 Ru-(S)-SunPhos 201, 203
 Ru(II)-BINAP 201, 202
 $\text{SynPhos}[\text{Rh}(\text{COD})]\text{BF}_4$ complex
 $\text{TangPhos}[\text{Rh}(\text{COD})]\text{BF}_4$ complex 192
 asymmetric hydrogenation
 DuPHOS/Rh(COD) 190
 asymmetric induction at P(III) 25, 160
 1,2-asymmetric induction 105
 1,4-asymmetric induction 103
 double stereoselectivity 159, 161
 1,4-induction 107
 matched pair 161, 162
 mismatched pair 161, 167, 169
 asymmetric induction at P(IV) 161
 asymmetric organocatalysis 253
 asymmetric oxidation 152, 155, 210–212
 asymmetric reduction 147, 151, 152, 204,
 209
 α -ketiminophosphonates 150
 of ketophosphonates 147
 asymmetric synthesis
 in side chain 102, 136, 159
 asymmetric Wittig type reaction 37
 2H-azirin-2-phosphine oxides 141, 287
 carboxylic acids 287
 AZT, zidovudine 101
- b**
- bacteria
 $\text{Acinetobacter baumannii}$ 349, 357
 $\text{Arthrosphaera maxima}$ 357
 $\text{Aspergillus fumigatus}$ 356, 357
 Aspergillus niger 349
 Bacillus subtilis 328, 357
 $\text{Beauveria bassiana}$ 349
 $\text{Beauveria brongniartii}$ 349
 $\text{Cunninghamella elegans}$ 349
 $\text{Geotrichum candidum}$ 349
 gram-negative 210
 gram-positive 210
 $\text{Nodularia sphaerocarpa}$ 358
 $\text{Penicillium citrinum}$ 356, 357
 $\text{Penicillium oxalicum}$ 349
 Proteus vulgaris 357
 $\text{Pseudomonas aeruginosa}$ 349, 357
 $\text{Pseudomonas fluorescens}$ 318, 319, 324,
 325, 338, 343, 349, 356, 357
 $\text{Pseudomonas syringae}$ 337
 Rhodococcus sp 349
 $\text{Serratia liquefaciens}$ 349, 357
 $\text{Streptomyces veridochromogenes}$ 336
 Baker's yeast 203, 349, 352
 berkelic acid 107
 bialaphos 336
 herbicide 336
 bicyclo[3.3.0]octane derivatives 116
 BINAP complex 201
 BINAP-Ru 201
 binaphthol derivatives 230
 BINOL 218, 224, 229
 Al(III)-BINOL 224
 derivatives in 197, 224
 phosphonates 115, 230
 biocatalysis 5
 in supercritical carbon dioxide 339
 biocatalytic desymmetrization 340, 347
 biosynthesis of C-P compounds 315, 349
 2-amino-1-hydroxyethylphosphinic acid
 336
 bis(cyanomethyl)phenylphosphine oxide
 343

- bis(oxazoline) 217, 238
Cu(II) complexes 238
1,2-bis(tert-butylmethylphosphino)
benzene (BenzP) 62
BMS-188494 318
Buchwald-type ligands 57
- c**
Caldariomyces fumago 342
calix[4]arene aminophosphane ligands 63, 64
catalysis by metal complexes
asymmetric hydrogenation of methyl 63
chiral secondary alcohols 45
 α -chloromethylphosphonamides 108
chlorophosphine boranes 60, 63
racemization 42
chiral auxiliaries 5
chiral derivatizing agents
NMR 11
chiral diamines 292
derivatives of cytosine 290
chiral epoxy aldehydes 126
chiral shift reagents 11
chiral solvating reagents 8
chirality 5
chirality transfer 103, 147, 160, 207
from phosphorus 103, 147
chloroperoxidase 342
chlorophosphine boranes, *P*-chirogenic
as chiral starting reagents 60
nucleophiles 61
organo-lithium 59
P(III)-compounds 41
preparation 62
prepared from ephedrine with
organo-lithium 59
synthesis of the DPPM ligands 61
chlorophosphines, chiral 51, 72
chromatographic methods of analysis 14, 16, 131
Cinchona alkaloids 161, 163, 254, 258, 269, 270, 287
derivatives 224
Claisen rearrangement 110
ClickFerrophos II 197
cooperative asymmetric catalysis 170
cycloaddition reactions 237
- 1,3-dipolar 158
bis(oxazoline) Cu(II) complexes 217, 238
Diels–Alder 159
of acylphosphonate to cyclopentadiene 159, 238
cyclodextrines 9
cyclopentanones, trisubstituted 109
cyclopropanation 108, 109
cyclopropane 2-aminophosphonic acids 108, 110
- d**
diarylphosphinocarbonic acids,
P-chirogene
chiral derivatizing agents 11–13
chiral solvating agent 8
 ^{13}C NMR 11
derivatizing agent 8, 13, 14
 ^{19}F NMR 12, 20
gas chromatography 14, 15
HPLC 15, 16
Mosher's acid 12
 ^{31}P NMR 21
specific rotation 19
lanthanide chemical shift reagents 8, 10
specific rotation 112, 155, 192
diastereoselective reactions 44
with alcohols 45
amines 53
2-(o-phosphono)alkylpropane-1,3-diols 347
phosphinates bifunctional 340
prochiral diol 348
diazaphospholidine, *P*-chiral 110
Diels–Alder reaction 157, 159
diethyl α -hydroxyphosphonate 318
Burkholderia cepacia 317, 318
CALB 318, 322–331, 333–335, 338, 348
O,O-diethyl
 α -iminotrifluoroethylphosphonate 286
reaction with acetone 286
diferrocene diphosphines 298
 α,α - difluoro- β -aminophosphonates 139
 α,α -difluoro- β -aminophosphonic acids 139

- dihydroxyalkylphosphonates 153
 dihydroxylation 152, 329
 1,5-dihydroxy-2-oxopyrrolidine-3-phosphonic acid 148
 dihydroxypropylphosphonates 329
 dimethylchlorophosphite 13
 dimethoxyphosphoryl-D-erythritol 129
 (R,R)-DIPT 300
 1,4-diphosphacyclohexanes 296
 diphosphine dioxides 301
 dissymmetry 1
 double asymmetric induction 160, 161, 163, 169
DYKAT 43
 transformation 43
 dynamic kinetic resolution (DKR) 201, 323, 331
- e**
 electrophilic substitution at P(III) 213
 amination 221
 chlorination 219, 220
 fluorination 219
 halogenation 219
 (R)-DM-BINAP 221
 (R)-DM-SEGPHOS 221
 in side chain 217
 electrophilic substitution at the phosphorus atom 212, 216
 enantiomer composition determination 7
 enantiomer excess (ee) 6
 enantioselective olefination 105, 113, 117
 enantioselective organocatalysis 6
 enzymatic desymmetrization 341
 enzymatic hydrolysis 320–322, 325
 enzymatic resolution 187, 321, 325–327, 330, 332, 333, 338, 344, 345
 α -hydroxyphosphonates 319, 322
 β -hydroxyphosphonates 329
 tertiary phosphines 41, 47, 50, 52, 59, 214, 232, 315, 338
 tertiary phosphines oxides 315, 358
 enzymatic transesterification 317, 320, 344
 ephedrine as chiral auxiliary 57–67
 epoxidation of allylphosphonates 126, 155
- biocatalyzed 351
 estrone 107
 ethyl (1-hydroxyalkyl)phenylphosphinates 338
- f**
 ferrocenyl, 1- and 2-adamantyl tert-butylphosphines 64
 ferrocenyl phosphine ligands 57
 Flack parameter 6, 18
 fosfadecin 210
 fosfomycin 101, 127, 201, 210, 211, 338, 354
 biocatalytic synthesis 338
 deuterated 337, 338
FR-33289 101
fungi
Beauveria bassiana 356
Cladosporium sp 355
Cunninghamella echinulata 356
Geotrichum candidum 349, 354–356
Penicillium oxalicum 356
Rhodococcus sp 349, 355
Rhodotorula glutinis 355
Rhodotorula rubra 349, 351, 355
- g**
GABOB 148, 195, 325, 330, 351
 gas chromatography 7
 geometrodynamics 1
 glucofuranosyl phosphinites 51
H-phosphinates, enantiomers 165, 285
H-phosphine oxides 265
- h**
 Haynes's conjugate addition 143, 288
 HPLC 15
 hydrindenones 110
 hydrolysis enzymatic 316
 1-hydroxy-2-aminoethylphosphonic acid (HO-AEP) 101, 155
 α -hydroxy- β -aminophosphonates 150
 α -iminophosphonates 287
 asymmetric cyanation 287
 aza-Henry reaction 290
 α -iminotrifluoroethylphosphonate, diethyl 286
 with acetone 286

i

- inhibitors of HIV-protease 125
 internal rotation 39
 energy barrier 40
 intramolecular asymmetric Stetter reaction 274, 275
 inversion of configuration 45
 iridium complexes 191

j

- Josiphos 101, 187
 Jugé–Stephan method 57

k

- Kabachnik–Fields reaction 118, 130, 140
 aluminum (salen) complexes 230
 conditions 140
 with N-Boc ketimines 268
 organocatalyzed 257
 Sc(III) complex 230
 Kagan's amides 8
 Kazlauskas rule 316, 329, 334
 α -keto-bis-phosphonates 279
 ketophosphonates 331, 349, 351
 addition reactions 288
 catalyzed by
 9-amino-9-deoxyepiquinine 282
 cinchonine-based thiourea 285
 isothiourea 285, 286
 L-prolinamide 283
 ketones 279, 282
 Me₃SiCN 288
 organocatalysis 279
 proline 282
 kinetic resolution 187, 201, 211, 332, 357
 α -hydroxyphosphonates 319, 320, 326
 β -hydroxyphosphonates 319

l

- L-phosphinothrinicin 137, 315, 335
 L-prolinamid
 as organocatalyst 283
 L-prolinamide 283, 284
 lanthanide chemical shift reagents 10
 lateral C-13 chains of taxoids 123, 163,
 164
 ligands
 Al-salen 225, 230

bisphosphine (BisP*) ligands 296

(DHQ)₂PHAL 153, 210, 270

DIOP 188

DuPhos 190, 214, 216, 233

ethane boranes 299

Me-CATPHOS 192

methylene-bridged diphosphines 298

MiniPHOS 299

MT-Siliphos 297

phospholane–oxazolines 301

Ru-BINAP 201, 202

TangPhos 192, 301

lipase-catalyzed acylation 339

lipases

Aspergillus niger 320, 328, 332

Aspergillus oryzae 333

Bacillus subtilis 328

Candida antarctica lipase B (CALB) 330, 338, 341, 345

Geotrichum candidum 318, 349

liposome 325

Mucor miehei 328

Pseudomonas cepacia 322, 323

Pseudomonas fluorescens 319, 324, 325, 338

Pseudomonas syringae 101, 337

Rhizopus oryzae 320

Streptomyces fradiae 101, 337

Subtilisin Carlsberg 333

m

Mannich/Wittig tandem type reaction 291

metathioiminophosphate 40

methyl jasmonate 107

(S)-metolachlor 187

microbiological synthesis 349, 357, 358

fungi 349

yeast 349

yeast-catalyzed

 with *Saccharomyces cerevisiae* 349

 with *unicellular fungi* 354–356

Mosher's acid 2, 12, 17

MT-Siliphos 297

Mukaiyama aldol reactions 286

of ketophosphonates 218

phosphonates 286

multiple asymmetric induction 159
 chiral Al(III)-BINOL complex 161
 chiral complex (R,R)-TA/NaBH₄ 169
 double 159
 matched 160
 mismatched 160
 N(p-tolylsulfinyl)benzaldimine 166
 phosphaldol reaction 160
 Schiff bases 166
 with Ti(O*i*Pr)₄ 163
 triple 160

n

N-heterocyclic carbenes 257
 nitro-Michael/Michael-Wittig cascade reaction 290, 291
 NMR 8

o

optically active amines
 amination 105, 106, 222
 DIPAMP 3
 ottelione A 108
 ottelione B 108
 organocatalysis 253, 254, 256
 binaphthol derivatives 257
 BINAPO 260
 Cinchona-thiourea 260
 commonly used 232
 dihydroquinine 269
 guanidinium salts 257, 265, 273
N-heterocyclic carbenes 234, 274
 proline derivatives 274
 thiourea 256
 tris-aminoiminophosphorane 261
 organocatalytic modification 290
 alpha, β -unsaturated ketones 292
 nitroolefins 291, 292
 of P-ylids 290
 oxazaborolidine in 150
 AD-Mix- α 211
 biocatalytic 317
 DKR oxidation 201
 NaOCl/Mn(III)(salen) complex 211
 OH-AEP 336
 oxidation 203
 potassium osmium (VI) complexes bearing (DHQ)₂ PHAL ligands 210

vanadyl(V)methoxide complex 211
 1,3,2-oxazaphospholanes 106
 (R_p)-oxazaphospholidine 58–60, 62, 66
 oxazaborolidines
 oxidation 207
P-chiral phosphorus compounds 337
 biocatalytic synthesis 337
P-chirogenic 7
P-chirogenic aldehydes 296
P-naproxen 198

p

P-OP catalyst 190, 192
P,P-diphenylamino phosphazenes 56
P-stabilized carbanions 105
 alkylations 107
 barrier to rotation 104
 NMR spectra 103
 reactions with electrophiles 106
 X-ray crystallography 103, 107
 PEP phosphomutase 335
 PHANEPHOS 192
 phospha Mannich reaction 263
 Brønsted acids 264
 cinchona alkaloids 262
 imines 260
 iminium salts 272
 phospha-Carnitine 325
 phospha-Henry reaction 288
 cinchona-thioureas 269
 cupreine 269, 289
 organocatalitic 289
 phospha-Michael reactions 142, 232, 236, 257, 269, 270, 272, 273, 275, 279
 ALB 236
 axially chiral guanidines 281
 cinchona alkaloids 269
 cinchonine-based thiourea 285
 di-nuclear zinc complexes 236
 diarylprolinol 274
 dihydroxypropylphosphonates 128
 geminal bis-phosphonates 277
 iminium salts 265
 lithio diphenylphosphine 145
N-heterocyclic carbenes 274
 [Ni (3-Pigiphos) (NCMeCCH₂)] complex 234

- nitroalkenes 142, 146, 236, 257, 260, 269, 271–273
 α -nitrophosphonates 270
 organonickel complex 233
 phosphinites 144
 secondary phosphine boranes 145
 thiourea 264
 derivatives of cinchona alkaloids 269
 organocatalytic 259
 unsaturated nitrosaccharides 146
 phospha-Mukaiyama aldol reactions 286
 phospha–Mannich reaction 130, 142
 phosphaaldol reaction 118, 160, 225, 261, 285
 ALB 236, 237
 aluminium-salalen complex 225, 226
 BINAPO 260
 catalyzed by cinchona alkaloids 161, 287
 cinchona-thiourea 259
 N,N-dibenzylphenylglycinal 122, 123
 double 159
 with Garner aldehyde 122
 LLB 224
 organocatalytic 257
 2,3-O-substituted-D-glyceraldehyde 122
 (2S,4S)-pentanediol acetals 128
 (S)-N-Boc-phenylglycinal 123
 silylphosphines and chiral aldehydes 129
 triple 160
 tris-aminoiminophosphorane 261
 phosphahelicenes, chiral 304
 phosphinites
 8-aluminum bis-(TBOx) complex 230, 232
 bis(8-chinolinato) (TBOx)Al complex 228
 Brønsted acids 264
 with chiral sulfinylimines 135
 cinchona alkaloids 262
 Cu/bis(oxazoline) complex 229
 desymmetrization 341
 guanidinium salts 265
 hydroquinidine 264
 hydroquinine 264
 imines 260
 iminium salts 265
 lithiated bis(diethylamino)phosphine borane 136
 mutant phosphotriesterase 342
 α -nitro phosphonates 271
 p-toluenesulfonimines 136
 photoresponsive polymers 297
 theoretical studies 230
 wild-type phosphotriesterase 342
 (S)- and (R)-phosphocarnitine 152, 205
 phosphoenol pyruvate (PEP) 335
 phospholane–oxazoline ligands 301
 phosphonamide, *P*-chiral 107, 108
 conjugate additions 107
 enones 108
 (1R,2R) 201
 phosphono-carbohydrates 128
 phosphono-emeriamine 139
 phosphono-GABOB 195, 205
 phosphono-tyrosine 126, 332
 phosphonoaspartic acid 139
 phosphonocyclopropylamino acid, DCG-IV 117
 phosphonothrixin 101, 155
 phosphonothrixine 155
 phosphopyruvate 335
 phosphothreonine 127, 201
 modelling of transition states 124
 δ -phoston 128
 photoresponsive polymers 298
 Pro-R and Pro-S 7
 prochirality 7
 proline 254
 derivatives 240
 as organocatalysts 269
 Pudovik reaction 119
- q**
- quaternary asymmetric carbon atom
 construction 105, 111, 133, 150, 216
 quinine and its derivatives 253
- r**
- racemization of chiral tertiary phosphines 41
 reduction 147, 151
 of alkenephosphonates 210

- reduction (*contd.*)
borohydrides 147, 151
catecholborane 150, 207
of chiral oxazaborolidines 207
(-)-chlorodiisopinocampheylboranes 151
of formic acid/trimethylamine/Ru complex 207
ketophosphonates 103, 148, 151
of iminophosphonates 188, 207
model of the reaction complex 204
NaBH₄-Pro 204
of NaBH₄/tartaric acid complex 205
- resolution
aminophosphonates 332
biocatalytic oxidation 342
dynamic kinetic 201, 203, 213, 290, 323, 324, 331
enzymatic resolution 333, 345
enzymatic transesterification 317, 320
 α -hydroxy-*H*-phosphinates 165, 285, 322, 339
 β -and ω -hydroxyphosphonates 323
in ionic liquids 343, 344
in supercritical CO₂ 339, 344, 345
- retro-Abramov reaction 120
- S**
SF-1293 336
(-)-sparteine 292
benzophenone 293
catalyzed reactions 286
CO₂ 294, 301
disulfides 294
DMF 296
molecular oxygen 294
sparteine-alkyllithium complex 293
spirooxyphosphoranes 81
squalene synthase inhibitor 318
stereoselective addition of phosphorous nucleophiles 117
- t**
TADDOL 13, 16, 120, 133, 134
derivatives 142, 196
phosphite 142
tartaric-acid-derived phosphonate 133, 150
- terms for stereochemistry asymmetric and dissymmetric 5
enantiomer 5
erythro/threo 6
meso compounds 6
optical activity 6
optical purity 6
prochirality 7
racemate 7
racemization 7
Re and Si 7
scalemic 7
stereoisome 7
tertiary dimethylphosphine boranes 293, 294
alkylation 304
tertiary phosphines 358
thiourea organocatalysis 256
THNAPhos 195
transesterification 316
transfer of chirality 147
trichickenfootphos 300
tricoordinate P(III) 40
tripeptidyl α - hydroxyphosphonates 125
- v**
vitamin D analogs 110
- w**
Wittig rearrangements 103, 111, 113, 114
- y**
yeast 351
Rhodotorula rubra 351
Saccharomyces cerevisiae 349, 350
ylides, phosphonium 290
chiral Brönsted acids 292
L-proline 292
Mannich/Wittig tandem type reaction 291
modification 290
nitro-Michael/Michael-Wittig 290
organocatalytic modification 290
alpha,beta-unsaturated ketones 292
- z**
zidovudine 101