

Index

a

absolute asymmetric synthesis 67, 88
 acetaldehyde 48, 203, 223, 292, 321
 acetic acid moiety 207, 321
 acetic anhydride 51, 93, 209
 acetooacetic ether 129
 acetonitrile 51, 100, 103, 227, 236, 360
 acetoxyl-elimination 58
 (R)-O-acetylserine complex 294
 (S)-O-acetylserine complex 204, 293
 acrylic acid 113, 120
 alanine alkylation 215, 220
 alanopine 4, 7, 11
 aldol condensation 111, 188, 222, 223
 aldol reaction 159, 224
 alkylhalides 115, 152, 216
 allyl chloride 218
 aluminum nitrate 39
 amino acid moiety 47, 110, 186
 α -amino aldehydes 173
 2-amino-2'-carboxyindan 95
 2-aminoacetophenone 190, 201, 285
 2-aminoacrylic acid 99
 aminobinaphthols 104, 106, 112, 114, 125
 3-aminobutanoic acid 179
 γ -aminobutyric acid (GABA) 2
 1-aminocyclopropanecarboxylic acid (ACC) 85
 1-amino-2,2-dideuteriocyclopropanecarboxylic acid 85
 4-aminoglutamic acid 240, 289
 6-aminohexanoic acid (ϵ -aminocaproic acid) 2
 β -aminopropionitrile 8
 α -aminosulfone 188
 anthranilic acid 92, 287
 apoenzyme function 30
 arenechromiumtricarbonyl complexes 265

aromatic 1,2-diphosphines 84
 aspergillomarasmine 10
 asymmetric synthesis (AS)
 – absolute asymmetric synthesis 67
 – classification 51, 67
 – diastereoselective asymmetric synthesis 67
 – effectiveness of 67
 – enantiomeric asymmetric synthesis 68
 – partial asymmetric synthesis 67
 atropoisomer 296
 azetidine-2-carboxylic acid 8

b
Bacillus brevis 2
 Balz–Schiemann reaction 264
 benzaldehyde 147, 148–151, 162
 benzophenone moiety 96, 97
 benzylamine 100, 102, 176
 benzylation reaction 82, 111
 benzylbromide 82, 111, 140, 143, 145, 184,
 218, 290, 318
 benzylcinchonidine 75
 benzylcinchonine 81
 (S)-2-N-(N'-benzylprolyl)aminobenzophenone
 (BPB) 200
 (S)-BINOLAM 81
 biomimetic chemical approach 25
 biomimetic enzyme systems 25
 Δ -bis[*N*-3-methylsalicylideneglycinate]sodium
 cobaltate (III) 40
 Λ -bis[*N*-3-methylsalicylidene-(S)-threoninate]sodium
 cobaltate (III) 45
 bis-[*N*-7-methylsalicylidene-(S)-threonine]sodium
 cobaltate (III) complex 47
 bis-[*N*-salicylideneaminoacetate]sodium
 cobaltate (III) 43
 bisalkylation product 96

- bromoacetonitrile 165
 5-bromosalicylic aldehyde 193
- c**
- C-alkylation 213, 215, 317
 - $C_\alpha-C_\beta$ and $C_\alpha-H$ bonds
 - α, β - elimination 45
 - carbonate buffer in D₂O 49
 - deuterium exchange 45, 48, 55
 - diastereomeric complex 47, 51, 63
 - epimerization 45, 54
 - solvation of carbanion 50
 - threonine moiety 47, 49, 54
 - transition state of 48, 57, 105
 - camphorsultam 159
 - canavanine 9, 11
 - carboxylic acids 4, 142, 165
 - catalytic asymmetric synthesis
 - O(9)-allyl-N-(9-anthracenylmethyl) cinchonidine 77
 - 1-amino-2,2-dideuterocyclopropane-carboxylic acid 85
 - 1-aminocyclopropanecarboxylic acid 85
 - alkylation reactions 78, 90, 133
 - carbanion-catalyst ion pair 78
 - chiral phosphine ligands 86
 - cinchonidine 74, 75, 79
 - cinchonine 74, 75
 - cyanomethylation reaction 74
 - dimeric structure 74, 91, 123
 - monoalkylation reaction 79, 95
 - (S)-NOBIN 84
 - PTC, *see* phase transfer catalysis (PTC)
 - racemization process 76
 - Schiff bases, achiral Ni^{II} complexes of, *see* Ni^{II} complexes
 - (R, R)-TADDOL 84
 - zwitterionic catalyst 76
 - catalytic hydrogenation 179, 184, 298
 - cephalosporins 11
 - chemoselectivity 189
 - chiroptic characteristics 217, 222, 230
 - 2-chloro-1,1,2-trifluorotriethylamine (CTT) 277
 - β -chloroalanine 35
 - chloromycetin* 15
 - chorismate 5, 7
 - Cinchona alkaloid family 72, 77, 81, 82
 - cinchonidine 72, 79, 82, 125
 - cinchonine 72–75
 - circular dichroism (CD) 43, 110, 146, 206, 242
 - Co^{III} ion complexes 43, 61
- Cotton effects 110, 205, 235, 243, 248
 cyclic aromatic amino acids 4
 cystathionine 2, 5, 8
- d**
- D-allo-isoleucine 12
 - D-allo-threonine 12
 - Danatan's hypothesis 39, 47, 207
 - deacetoxylation reaction 205, 209
 - α -decarboxylases 38
 - dehydroalanine 92, 93, 204, 224
 - dehydroamino acids 43, 203, 245
 - dehydroamino esters 36
 - dehydroaminobutyric acid 51, 208, 234, 253, 254, 258, 291, 322, 323, 326, 327, 330
 - acetic acid, elimination of 55
 - β -hydrogen signals of 52
 - nucleophiles to Co^{III} complexes 61
 - - electrochemical reduction 63, 64
 - - electrophilicity 63, 239
 - - ¹H NMR investigation 63
 - - pyridoxal systems 61
 - - salicylidene complexes of 64, 203, 208
 - Schiff base of 32, 35, 43, 58
 - dehydrochlorination 35
 - deuterium exchange 39, 45, 48, 55
 - α, α -dialkylamino acids 165, 169
 - (R)-2,2'-diamino-1,1'-binaphthyl 144
 - 2,4-diamino-3-methylbutyric acid 3
 - diammonium catalysts 84
 - 1,4-diazabicyclooctane 205
 - diazobicycloundecene (DBU) 273, 274, 277
 - α -alkyl- β -dibenzylamino-propionic acid 176
 - α, α' -dibromo-*o*-xylene 95
 - 3,4-dichlorobenzyl bromide 218
 - 3,4-dichlorobenzyl chloride 219, 220
 - dichloroethane 122
 - 1,2-dichloroethane 118, 120, 121
 - diethylaminosulfotrifluoride (DAST) 277
 - α, α -diethylglycine 96
 - 3,4-dihydroxyphenylalanine 9
 - dilithium enolate 177, 179, 181
 - dimethoxy imidazolidinone 173
 - dimethylformamide (DMF) 94, 173, 209, 210, 213, 215, 218, 227, 290
 - (R,R)-(1,2-di-*tert*-butyl)ethylenediamine 144
- e**
- electrochemical reduction 45, 51, 63
 - electrophilicity 36, 63
 - electrostatic stabilization 59
 - α, β -elimination processes 52
 - acetic acid 51–55
 - carbanion 58, 73, 100

– in soda buffer solution 56
 enantiomers 15
 enzymatic synthesis 65
 epichlorohydrin 169
 epimerization 45, 51, 54
 α -ethylphenylalanine 96

f

2-[18F]fluoro-2-deoxy-D-glucose ([18F]FDG) 18
 (S)-4-[18F]fluoroglutamic acid
 – catalytic synthesis method 271
 – stoichiometric approach 273
 18F isotope 17, 18, 261
 18F-labeled amino acids (18F-AA) 18
 4-fluoroglutamic acid
 – asymmetric synthesis of 277–279
 – stoichiometric approach 273
 3-fluoro-substituted pyroglutaminol 281

g

gel-filtration chromatography 294
 glutamic acid 2, 4
 glutamyl- γ -semialdehyde 5
 glycine 2, 7, 93
 gomarin 11
 gramicidins 11

h

1H NMR 101, 191, 202, 205, 207, 209, 219, 223, 224, 228, 234, 235, 241, 244, 245, 255–257, 262, 273, 277, 282, 283, 288, 291, 295, 300, 311, 314
 halogenated aromatic compounds 4
 heterocyclic imino acids 4
 heterocyclic-substituted α -amino acids 245
 – (2S,3S)- α -aminobutyric acid 253
 – nucleophiles to dehydroalanine chiral complexes 245
 hexamethylphosphoramide (HMPA) 160
 hippuric acid 173
 homocysteine 5, 8, 10
 hydrolysis 3, 27, 51, 85
 hydroxyacetophenone complexes 48
 o-hydroxyacetophenone 48, 58
 β -hydroxyamino acids 32
 β -hydroxy- α -amino acids 12, 188, 190
 – aldol condensation 222, 223
 – carbonyl compounds, aldol reaction 224
 2-hydroxybenzophenone 142
 β -hydroxyleucine 190
 β -hydroxy-L-ornithine 172
 β -hydroxy- γ -methylglutamate 9
 γ -hydroxy- γ -methylglutamic acid 11

hydroxyisoleucine 10
 3-hydroxysalicylaldehyde 138
 5-hydroxytryptamine 9
 5-hydroxytryptophan 9
 (S)-hydroxyvaline 230
 hypoglycines A 9

i

ibotenic acid 10
 imidazole 30, 102, 227
 α -iminoethers 171
 α -iminoglycine 170
 indole 102
 Institute of Human Brain (IHB) 269, 283, 285
 intermolecular hydrogen bonding 73
 International Science and Technology Center (ISTC) 342
 isobutyraldehyde 112, 113
 isomerization 55
 isopropyl ester 146, 150
 isopropylaldehyde 321

j

α -keto acid 38, 69
 β -ketoesters 82

l

L-2-amino-4-(4'-amino-2',5'-cyclohexadienyl)butyric acid 11
 L-asparagyl-L-phenylalanine dipeptide 2
 L-capreomycinide 172
 L-capromycinide 172
 L-erythro-4-fluoroglutamic acid 280, 281
 β -lactamacetate 184
 β -lactam synthon method 182
leucinostatin A 12
 lithium diisopropylamide (LDA) 160, 184
 lithium hexamethyldisilazide (LHMDS) 163, 164, 184
 lithium hydroxide 165
 lithium salt 159
 lycomarasmine 10

m

magnetic anisotropy 211, 324
 magnetic shielding 283, 323
 malonic ester 100, 130, 131
 malononitrile 100
 Mannich reaction 178, 188
 Merrifield's resin 82
 methacrylate 115–117, 119, 120
 methionine 2, 5, 11
 methionine sulfone 39
 α -methoxycarbamate 177
 3-methoxy-salicyl aldehyde 142

- α -methyl- α -aryl glycine derivatives 88
- (S)-O-methyl-3-bromotyrosine 261, 262, 265, 266, 273
- methyl chloride 73
- methyl groups 48, 58, 165, 294, 301
- methyl iodide 164, 290
- α -methyl-L-dihydroxyphenylalanine 12
- methyl methacrylate 188
- α -methyl-substituted α -amino acids 12
- methylene chloride 92, 100, 102, 120
- methylene moiety 96
- 3,4-methylenedioxy-6-nitrobenzaldehyde 267
- 3,4-methylenedioxy-6-nitrobenzyl bromide 267
- (S)- α -methylphenylalanine 81
- 3-methylsalicylic aldehyde complex 49
- α -methylserine 164
- α -methyltryptophan 12, 163
- α -methyltyrosine 12
- microbiological synthesis 191
- mimosine 9
- monodentate phosphites 84
- monodentate phosphoramidites 84
- monolactim esters 182
- muscazone 10
- mycosporine-like multilins 7

- n**
- N-acyloxazolidinone 165
- N-acylsultam 165
- N-(9-anthracenylmethyl)dihydrocinchonidine 78
- N-benzyl-cinchonidine 76
- N-benzylproline 199, 201, 214, 219, 233, 245, 248, 256, 258, 285, 290, 291
- N-bromosuccinimide 166
- N-carboxyphenylprolyllysine 12
- N-fluorobenzenesulfonimide (NFSi) 281
- N-galactosyl- α -aminonitrile 167
- N-galactosyl- β -amino acid 178
- N-methoxycarbonyl imine 177
- N-nitrozoproline 192
- N-pyruvylidenglycinate 172
- N-sulfonyl imines 171
- N-tert-butoxycarbonyl-l-pyroglutamic acid 279
- N-tosylmethoxy imidazolidinone 174
- N^8 -acetyl-L- α , γ -diaminobutyric acid 10
- β -naphthol 94, 95, 97, 100, 122
- β -naphthylamine 122
- Ni^{II} complexes 135, 142, 144, 188, 189, 191, 199, 201, 223
- α -carbon atom 93
- achiral dehydroalanine substrate nucleophiles 31, 36, 43, 125
- aldol condensation 111, 112, 188, 202
- - isobutyraldehyde 112, 113
- chiral auxiliary reagents 133, 188, 190, 191, 198, 199
- crystallographic structures 91, 97
- dehydroalanine 203, 204, 292
- dehydroaminobutyric acid 206, 208
- glycine and dehydroalanine complexes, 1,4-Michael addition to 241, 242
- - acrylic acid methyl ester 97
- - alcohols 100
- - crystallographic structure of 101
- - electron-donor compounds 99
- - glutamic acid 98
- - imidazole 100, 102
- - indole 102
- - β -naphthol 97
- - nucleophiles 99, 100
- - phenol 100, 102
- Michael addition, electron-withdrawing compounds 113
- N-benzylproline moiety 214, 219, 245, 304
- - dehydroamino acid complexes, nucleophilic addition reactions 321
- phase-transfer catalysis, alkylation
- - alkyl halides 95, 103
- - alkylation products, structures of 96
- - mono alkylation product 96
- - steric nonbinding interaction 219, 229
- radiographic structure of 91
- X-ray data 91
- nitromethane 100
- NMR spectrum 123

- o**
- O-acetylated complexes 204
- O-acetylation 93, 204, 209, 271, 291–293, 322
- O-acetylthreonine 52, 53
- O-acetylthreonine complexes 51, 55
- O(9)-allyl-N-(9-anthracenylmethyl)cinchonidine 77
- O'Donnell's substrate 75–78, 81, 82, 84
- O-methyl-L-threonine 12
- onium salts 71, 82
- optical rotatory dispersion (ORD) curves 43
- in H₂O 45
- threonine and acetylthreonine complexes 51
- threonine complex 43
- Overhauser's effect 51, 294, 300, 301
- oxalidinone 189

- oxazolidinone 162, 163
- β -oxocarboxylic acid 178
- 2-oxocyclopentanecarboxylic acid 81, 82
- α -oxyacetophenone 43
- β -oxyamino acids 35
- oxyethyl group 45, 47, 48

- p**
- paracyclophanes 189
- partial asymmetric synthesis 67
- penicillamine 11
- phase transfer catalysis (PTC)
 - advantages 71
 - C_2 -asymmetric chiral guanidine derivative 81
 - cinchonidine-based phase transfer catalysts 80
 - definition of 71
 - indanone derivatives 72
 - Lygo's catalyst 83
 - Maruoka's catalyst 83
 - *N*-alkyl-*O*-alkylcinchonine 76
 - Ni^{II} complexes, alkylation of
 - alkyl halides 94, 95, 103
 - alkylation products, structures of 96
 - monoalkylation product 96
 - salen complexes, *see* salen complexes
- phenylalanine 2, 5
- (R)-phenylethylenediamine 144
- phenylserines 35
- phosphorazo method 308
- phosphoserine 5
- picolinic acid 92, 188
- (S)-2-[*N*-(2-picolyloxy)amino]benzophenone 304
- polyethylene glycol matrix 82
- positron emission decay 16
- positron emission tomography (PET) 260
 - active tyrosine derivatives 261
 - activated arenechromiumtricarbonyl complexes, nucleophilic substitution in 265
 - catalytic methods of substitution 261
 - radiotracer (S)-O-2-([¹⁸F]fluoroethyl) tyrosine 269
 - α -amino acids, PET radiotracers 19
 - asymmetric synthesis of 4-fluoroglutamic acid 277
 - [¹⁸F] FDG 18
 - 2-[¹⁸F]FTYR 20
 - 6-[¹⁸F]-L-DOPA 19
 - fluorine-labeled amino acids 19
 - quantum annihilation radiation 16
 - radioisotopes, characteristics of 17
- radiotracer (S)-4-[¹⁸F]fluoroglutamic acid
 - catalytic synthesis method 271
 - stoichiometric approach 273
 - PP-catalysis, kinetics and stereochemistry, α , β -elimination processes, *see* α , β -elimination processes
- 2-propyldanone 73
- pyridoxal catalysis 27, 32, 43
- pyridoxal enzyme 35, 39
 - β -chloroalanine 35
 - dehydroalanine complex 36
 - deuterated complex 36
 - free β -oxyamino acids 35
 - tryptophan complex 36
 - tyrosine complex 36
- pyridoxal phosphate (PP) 9, 27
 - carbanion 27
 - catalysis, stereochemical aspects of 31
 - covalent interactions 30
 - imine intermediate compound 31
 - principle of 27
- pyridoxal-N-metachloride 39
- pyridoxine 9
- 2-pyridyl-carboxylic acid 90
- pyroglutamic acid 5, 189, 283
- pyrrolidine moiety 207, 293, 330, 332
- pyruvic acid 61

- q**
- quaternary ammonium salts 71, 72
- quaternary nitrogen atom 82
- quinidine 72
- quinine 72

- r**
- racemization process 76
- radiopharmaceutical drug (RPD) 16, 17, 20
- retroaldol cleavage 32, 35
- rizobiotoksin 10

- s**
- S-(2-aminoethyl)-L-cysteine 15
- S-phenyl- β -methylcysteine 63
- salen complexes
 - amino acids, C-alkylation reactions of 150
 - of asymmetric structure 141
 - benzyl bromide 132, 133
 - chiral diamines, SR-groups 145
 - salicylaldehydes 138
 - structural features of 134
 - trimethylsilylcyanation of aldehydes 147
- salicylaldehyde 47, 61, 134, 137, 138, 194, 196
- salicylaldehyde complex 48, 49, 58, 59

- salicylaldehyde moiety 43, 45, 47
- Schöllkopf's method 159
- Schiff base 27, 30–32
 - Co^{III} complexes of 43, 49
 - dehydroalanine complex 36
 - dehydroamino acids 37
 - N-methylpyridoxal 36
 - Ni^{II} complexes, *see* Ni^{II} complexes
 - salicylaldehyde 48
- self-reproducing chirality 161, 162, 163, 177
- Shvern's method 92
- sodium hydride 105
- staking* 316
- steric hindrances 40, 324
- stoichiometric asymmetric synthesis 159
 - α-alkylsubstituted α-amino acids 190
 - β-aryl-β-amino acids 177
 - α, α-dialkylamino acids 165
 - α, β-diamino acids 171
 - (±)-2,3-diamino-3-phenylpropionic acid 170
 - α, α-disubstituted α-amino acids 167, 169
 - alkylation 163
 - 4-aminoglutamic acid 240
 - aqueous peroxide/lithium hydroxide 165
 - bis-lactim esters 159
 - bis-lactim ether 171, 181
 - bisalkylated products 169
 - camphorsultam 159
 - carboxylic acids 165
 - CH-acidity 186
 - chiral enolate 161
 - chiral glycines 170
 - cyanocuprate and cyanide 173
 - cyclic compound 161
 - deprotonation 168
 - diastereoselective synthesis 159
 - dimethoxy imidazolidinone 173
 - electrophilic bromination 166
 - enantiomeric purity 162
 - glycine complex 188, 208
 - glycine ester 165
 - heterocyclic chiral dihydropyrimidinone 177
 - heterocyclic-substituted α-amino acids 245
 - hippuric acid 173
 - β-hydroxy-α-amino acids 221
 - L-capreomycidine 172
 - L-capriomicidine 172
 - β-lactam ester 184
 - β-lactamacetate 184
 - lithium dibenzylamide 176
 - lithium enolate 163, 184
 - methyl iodide 164
 - modified aldimine fragments, Ni^{II} complexes, *see* Ni^{II} complexes
 - N-methoxycarbonyl imine 177
 - N-protected glycinate 164
 - Ni^{II} complexes, Schiff bases, *see* Ni^{II} complexes
 - β-oxocarboxylic acid 178
 - (±)-2-oxo-1,5-diphenyl-4-carboxylic acid 170
 - paracyclophanes 189
 - peptide antibiotics 170
 - PET radiopharmaceuticals, *see* positron emission tomography (PET)
 - picolinic acid 188
 - piperidine 172
 - pivaloyl aldehyde 161, 177, 181
 - preparative production, α-amino acids 341
 - (R)-proline, preparation of 198
 - (S)-proline, low-waste technology for 198
 - Schöllkopf's method 159
 - self-reproducing chirality 161–163
 - Strecker's reaction 167
 - α-substituted (R)-α-amino acids 218
 - α-substituted (S)-α-amino acids 213
 - β-substituted-α-amino acids 224
 - sulfinylimine 171
 - tetrahydropyrimidinone 181
 - thermodynamic equilibrium 187
 - strombine 7
 - α-substituted (R)-α-amino acids 218
 - α-substituted (S)-α-amino acids
 - alkylation products 216
 - chiroptic characteristics 217
 - glycine moiety, C-alkylation of 213, 215
 - β-substituted-α-amino acids
 - dehydroaminobutyric acid to chiral complexes 233
 - nucleophiles to chiral dehydroalanine complexes 224
 - sulfinylimine 171
 - 5-sulfosalicyl aldehyde 193
 - 5-sulphosalicyl aldehyde 195, 196
- t**
- TADDOL 84, 104, 114, 126–128, 130, 131, 272
- tetrabutylammonium bromide (TBA-Br) 94
- tetrahydropyrimidinone 181
- thalidomide 15
- thermodynamic stability 214, 248
- thiophenol 39
- threonine complex 43, 52

- threonine hydroxyl moiety 51
threonine moiety 49, 209
trans-4-hydroxy-L-proline 277, 279
triazoles 255, 258
tricholomic acid 10
triethylamine 171
triethylbenzylammonium bromide (TEBA-Br) 94
trifluoroacetic acid 208
trifluoroacetic anhydride 208
trifluoroacetylation 208
trinitrobenzoic acid 192
tryptophan 1, 4, 59
- tyrosinase oxidation 3
tyrosine 5, 59
- u**
- UV measurements 120
- v**
- vitamin B₃ 2
- x**
- X-ray diffraction (XRD) 48, 136, 202, 274–276, 282, 311, 312, 315, 316, 322
X-ray structural analysis 209, 211

