

Contents

List of Abbreviations *IX*

Introduction *XI*

- 1 **Non-Proteinogenic α -Amino Acids, Natural Origin, Biological Functions** *1*
References *20*

 Part I Natural Synthesis of Amino Acids, Mechanisms, and Modeling *25*
 References *25*
- 2 **Some Regularities of Mechanisms for the Natural Synthesis of Amino Acids** *27*
 References *33*
- 3 **Systems for Modeling Some Aspects of Pyridoxal Enzyme Action** *35*
 References *40*
- 4 **Modeling of Processes Associated with Cleavage of $C\alpha-H$ and $C\alpha-C\beta$ Bonds** *43*
 References *50*
- 5 **Modeling of α,β -Elimination Processes of PP-Catalysis, Kinetics, and Stereochemistry** *51*
 References *60*
- 6 **Biomimetic Addition Reaction of Nucleophiles to Co^{III} Complexes of Dehydroaminobutyric Acid** *61*
 References *64*

Part II Asymmetric Synthesis of Nonprotein α -Amino Acids 65

7	The Main Rules of Asymmetric Synthesis 67
	References 70
8	Catalytic Asymmetric Synthesis 71
8.1	Achiral Ni ^{II} Complexes of Schiff Bases of Amino Acids 90
8.1.1	The Alkylation of Achiral Ni ^{II} Complexes Under Phase-Transfer Catalysis 94
8.1.2	Reactions of 1,4-Michael Addition to Achiral Glycine and Dehydroalanine Complexes 97
8.1.3	Synthesis of Enantiomerically Enriched α -Amino Acids 103
8.1.3.1	The Asymmetric Alkylation of Substrate 65a by Alkyl Halides Under Phase-Transfer Catalysis 103
8.1.3.2	Asymmetric Aldol Condensation of Achiral Ni ^{II} Complexes of Amino Acids 111
8.1.3.3	The Asymmetric Michael Addition of Achiral Ni ^{II} Substrates to Electron-Withdrawing Compounds 113
8.1.3.4	Catalytic Asymmetric Addition of Nucleophiles to an Achiral Dehydroalanine Substrate 125
8.2	Salen Complexes as Chiral Catalysts for PTC Alkylation 132
8.2.1	Structural Features of Salen Complexes 134
8.2.1.1	The Influence of the Structure of Salen Ligand 137
8.2.1.2	Chiral Diamine-Based Complexes 144
	References 154
9	Stoichiometric Asymmetric Synthesis of α-Amino Acids 159
9.1	Synthesis of Chiral Auxiliary Reagents and Complexes Based on (<i>S</i>)- and (<i>R</i>)-Prolines 191
9.1.1	Effective Low-Waste Technology for Producing (<i>S</i>)-Proline 192
9.1.2	Preparation of (<i>R</i>)-Proline from (<i>S</i>)-Proline 198
9.1.3	Synthesis of Chiral Auxiliary Reagents and Ni ^{II} Complexes of their Schiff Bases with Amino Acids 199
9.1.4	Preparation of Ni ^{II} Complexes of Schiff Bases of Dehydroamino Acids 203
9.1.4.1	Synthesis of Chiral Ni ^{II} Complexes of Dehydroalanine 204
9.1.4.2	Synthesis of Chiral Ni ^{II} Complexes of Dehydroaminobutyric Acid 208
9.2	Stoichiometric Asymmetric Synthesis of α -Amino Acids 213
9.2.1	Synthesis of α -Substituted (<i>S</i>)- α -Amino Acids 213
9.2.2	Synthesis of α -Substituted (<i>R</i>)- α -Amino Acids 218
9.2.3	Diastereoselective Synthesis of β -Hydroxy- α -Amino Acids 220

9.2.4	The Asymmetric Synthesis of β -Substituted- α -Amino Acids	223
9.2.4.1	Asymmetric Addition of Nucleophiles to Chiral Dehydroalanine Complexes	224
9.2.4.2	Asymmetric Nucleophilic Addition to Chiral Complexes of Dehydroaminobutyric Acid	233
9.2.5	Asymmetric Synthesis of All Possible Stereoisomers of 4-Aminoglutamic Acid	239
9.2.6	Asymmetric Synthesis of Heterocyclic-Substituted α -Amino Acids	245
9.2.6.1	Addition of Heterocyclic Nucleophiles to Dehydroalanine Chiral Complexes	245
9.2.6.2	Asymmetric Synthesis of β -Heterocyclic-Substituted Derivatives of (2 <i>S</i> ,3 <i>S</i>)- α -Aminobutyric Acid	253
9.3	Asymmetric Synthesis of Precursors for PET Radiopharmaceuticals	260
9.3.1	Preparation of Active Tyrosine Derivatives	261
9.3.1.1	Catalytic Methods of Substitution	261
9.3.1.2	Nucleophilic Substitution in Activated Arenechromiumtricarbonyl Complexes	265
9.3.1.3	A New Method for Synthesis of Precursors for Known Radiotracer (S)-O-2-([¹⁸ F]Fluoroethyl) Tyrosine	269
9.3.2	Synthesis of Precursors for Producing a New Radiotracer (S)-4-[¹⁸ F]Fluoroglutamic Acid	269
9.3.2.1	Catalytic Synthesis Method	271
9.3.2.2	Stoichiometric Approach to the Synthesis of 4-Fluoroglutamic Acid Precursors	273
9.3.3	Asymmetric Synthesis of 4-Fluoroglutamic Acid	277
9.4	Modified Chiral Auxiliary Reagents for Efficient Asymmetric Synthesis of Amino Acids	285
9.4.1	Chiral Ni ^{II} Complexes of Amino Acids with Modified Aldimine Fragments	286
9.4.1.1	Synthesis and Research of Dehydroalanine Complexes with Modified Aldimine Fragment	292
9.4.1.2	Asymmetric Addition of Nucleophiles to Dehydroalanine Complex Modified by Aldimine Fragment	296
9.4.2	Chiral Ni ^{II} Complexes of Schiff Bases of Amino Acids Modified by <i>N</i> -Benzylproline Moiety	304
9.4.2.1	New Modified Chiral Reagents and Ni ^{II} Complexes of their Schiff Base with Amino Acids	306
9.4.2.2	Amino Acid Complexes with Modified <i>N</i> -Benzylproline Moiety in C-Alkylation Reactions	317
9.4.2.3	Dehydroamino Acid Complexes with Modified <i>N</i> -Benzylproline Moiety in Nucleophilic Addition Reactions	321

VIII | Contents

9.5	Stoichiometric Asymmetric Synthesis of Unsaturated α -Amino Acids	332
9.6	Universal Technology for Small-Scale Production of Optically Active Non-Proteinogenic α -Amino Acids	339
	References	342
	Index	353