Contents

List of Abbreviations IX Introduction XI

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

Part INatural Synthesis of Amino Acids, Mechanisms, andModeling25References25

v

- 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 Cα–H and Cα–Cβ 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

VI Contents

	Part II /	Asymmetric Synthesis of Nonprotein α-Amino Acids 6	5
7	The Main Ru References	lles of Asymmetric Synthesis 67 70	
8	Catalytic Asy	ymmetric Synthesis 71	
8.1	Achiral Ni ^{II} Complexes of Schiff Bases of Amino Acids 90		
8.1.1	The Alkylati Catalysis	ion of Achiral Ni ^{II} Complexes Under Phase-Transfer 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 Asymm Electron-Wi	etric Michael Addition of Achiral Ni ^{II} Substrates to ithdrawing Compounds <i>113</i>	
8.1.3.4	Catalytic As Dehydroalai	symmetric Addition of Nucleophiles to an Achiral nine Substrate 125	
8.2	Salen Comp	lexes as Chiral Catalysts for PTC Alkylation 132	
8.2.1	Structural F	eatures of Salen Complexes 134	
8.2.1.1	The Influence	ce of the Structure of Salen Ligand 137	
8.2.1.2	Chiral Diam References	nine-Based Complexes 144 154	
9	Stoichiomet	ric Asymmetric Synthesis of α -Amino Acids 159	
9.1	Synthesis of and (<i>R</i>)-Pro	Chiral Auxiliary Reagents and Complexes Based on (Slines 191	5)-
9.1.1	Effective Lor (S)-Proline	w-Waste Technology for Producing 192	
9.1.2	Preparation	of (<i>R</i>)-Proline from (<i>S</i>)-Proline 198	
9.1.3	Synthesis of Schiff Bases	² Chiral Auxiliary Reagents and Ni ^{II} Complexes of their with Amino Acids <i>199</i>	r
9.1.4	Preparation Acids 203	of Ni^II Complexes of Schiff Bases of Dehydroamino	
9.1.4.1	Synthesis of	Chiral Ni ^{II} Complexes of Dehydroalanine 204	
9.1.4.2	Synthesis of Acid 208	Chiral Ni ^{II} Complexes of Dehydroaminobutyric	
9.2	Stoichiomet	ric Asymmetric Synthesis of α-Amino Acids 213	
9.2.1	Synthesis of	α -Substituted (S)- α -Amino Acids 213	
9.2.2	Synthesis of	α -Substituted (<i>R</i>)- α -Amino Acids 218	
9.2.3	Diastereose	lective Synthesis of β -Hydroxy- α -Amino Acids 220	

Contents VII

0.2.4	The Assume metric from the sein of Q. Such stituted on Assistan Asida 202
9.2.4	A summetric Synthesis of p-Substituted-α-Amino Acids 223
9.2.4.1	Complexed 224
0242	Complexes 224
9.2.4.2	Asymmetric Nucleophilic Addition to Chiral Complexes of
0.25	Denyaroaminobulyric Acia 233
9.2.5	A symmetric Symmetric A aid 220
0.26	4-Ammoglutamic Acid 239
9.2.0	Asymmetric symmetric symmetric substituted & Ammo
0261	Actus 245 Addition of Hotorocyclic Nucleonhiles to Debydroslaning Chiral
7.2.0.1	Complexes 245
9262	Asymmetric Synthesis of B-Heterocyclic-Substituted Derivatives of
7.2.0.2	$(2S,3S)$ - α -Aminobutyric Acid 253
9.3	Asymmetric Synthesis of Precursors for PET
210	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
	(<i>S</i>)- <i>O</i> -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 ^{ll} 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 th Complexes of Schiff Bases of Amino Acids Modified by
0.4.0.1	N-Benzylproline Moiety 304
9.4.2.1	New Modified Chiral Reagents and Ni ^a Complexes of their Schiff
0.4.0.0	Base with Amino Acids 306
9.4.2.2	Amino Acid Complexes with Modified N -Benzylproline Molety in C Alludetice Description 217
0422	C-AIKYIAUON KEACTIONS 31/ Debudyeemine Acid Complexes with Madified M. Derevised in the
7.4.2.3	Mojoty in Nucleonhilic Addition Practions 221
	Molecy in Mucleophilic Addition Reactions 521

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