

Contents

List of Contributors XV

1	Introduction	1
	<i>Li-Xin Dai and Xue-Long Hou</i>	
1.1	Foreword	1
1.2	Planar Chirality of Ferrocenyl Ligands	4
1.3	Derivatization of the Ferrocene Scaffold	6
1.4	Stability, Rigidity and Bulkiness of the Ferrocene Scaffold	9
1.5	Outlook	10
	References	11
2	Stereoselective Synthesis of Planar Chiral Ferrocenes	15
	<i>Wei-Ping Deng, Victor Snieckus, and Costa Metallinos</i>	
2.1	Introduction	15
2.2	Diastereoselective Directed ortho-Metalation of Ferrocenes with Chiral Auxiliaries	19
2.2.1	Ugi's Amine and Other Chiral α -Substituted Ferrocenylmethylamines	20
2.2.2	Chiral Sulfoxides	23
2.2.3	Chiral Acetals	26
2.2.4	Chiral Oxazolines	29
2.2.5	Other Chiral Auxiliaries	31
2.3	Enantioselective Directed ortho-Metalation of Ferrocenes with Chiral Bases	36
2.4	Enzymatic and Nonenzymatic Kinetic Resolutions	40
2.4.1	Enzymatic Kinetic Resolutions	40
2.4.2	Nonenzymatic Kinetic Resolutions	41
2.5	Summary and Perspectives	42
2.6	Selected Experimental Procedures	44

- 2.6.1 Synthesis of (*R,S_p*)-*N,N*-dimethyl-1-(2-diphenylphosphino-ferrocenyl)ethylamine (PPFA) 44
- 2.6.1.1 Synthesis of Racemic α -Ferrocenylethyldimethylamine 44
- 2.6.1.2 Resolution of α -Ferrocenylethyldimethylamine 45
- 2.6.1.3 Synthesis of (*R,S_p*)-*N,N*-dimethyl-1-(2-diphenylphosphinoferrocenyl)ethylamine (PPFA) 45
- 2.6.2 Synthesis of (*R,R_p*)-1-(tert-butylsulfinyl)-2-(diphenylphosphino)-ferrocene 45
- 2.6.2.1 Synthesis of (*R*)-tert-butylsulfinylferrocene (*R*) 45
- 2.6.2.2 Synthesis of (*R,R_p*)-1-(tert-Butylsulfinyl)-2-(diphenylphosphino)ferrocene 46
- 2.6.3 Synthesis of FcPHOX 46
- 2.6.3.1 Synthesis of (*S*)-2-ferrocenyl-4-(1-methylethyl)oxazoline 46
- 2.6.3.2 Synthesis of (*S,S_p*)-2-[2-(diphenylphosphino)ferrocenyl]-4-(1-methylethyl) oxazoline 47
- 2.6.4 Synthesis of (*S_p*)-*N,N*-diisopropyl-2-(diphenylphosphino)ferrocenecarboxamide 48
- 2.6.4.1 (*S_p*)-*N,N*-diisopropyl-2-(diphenylphosphino)ferrocenecarboxamide 48
- References 49

3 Monodentate Chiral Ferrocenyl Ligands 55

Ji-Bao Xia, Timothy F. Jamison, and Shu-Li You

- 3.1 Introduction 55
- 3.2 Nickel-Catalyzed Asymmetric Reductive Coupling Reactions 55
- 3.2.1 Synthesis of P-Chiral, Monodentate Ferrocenyl Phosphines 56
- 3.2.2 Nickel-Catalyzed Asymmetric Reductive Coupling of Alkynes and Aldehydes 56
- 3.2.3 Nickel-Catalyzed Asymmetric Reductive Coupling of Alkynes and Ketones 60
- 3.2.4 Nickel-Catalyzed Asymmetric Three-Component Coupling of Alkynes, Imines, and Organoboron Reagents 61
- 3.3 Copper(I)-Catalyzed Asymmetric Allylic Alkylation Reactions 62
- 3.4 Asymmetric Suzuki–Miyaura Reactions 64
- 3.5 Addition of Organoaluminum to Aldehydes and Enones 65
- 3.6 Asymmetric Nucleophilic Catalysis 66
- 3.7 Conclusion and Perspectives 70
- References 70

4 Bidentate 1,2-Ferrocenyl Diphosphine Ligands 73

Hans-Ulrich Blaser and Matthias Lotz

- 4.1 Introduction 73
- 4.2 Type A Both PR_2 Groups Attached to the Cp Ring 74
- 4.3 Type B One PR_2 Group Attached to the Cp Ring, one PR_2 Group Attached to the α -Position of the Side Chain 75

4.3.1	Josiphos	76
4.3.2	Immobilized Josiphos	80
4.3.3	Josiphos Analogs	82
4.4	Type C One PR ₂ Group Attached to the Cp Ring, one PR ₂ Group Attached to the β -Position of the Side Chain	83
4.4.1	BoPhoz and Analogs	83
4.5	Type D, One PR ₂ Group Attached to the Cp Ring, One PR ₂ Group Attached to Other Positions of the Side Chain	85
4.5.1	Taniaphos	86
4.6	Type E, Both PR ₂ Groups Attached to Side Chains	87
4.6.1	Walphos	88
4.6.2	TRAP	90
	References	91
5	1,2-P,N-Bidentate Ferrocenyl Ligands	97
	<i>Yong Gui Zhou and Xue Long Hou</i>	
5.1	Introduction	97
5.2	Asymmetric Hydrogenation and Asymmetric Transfer Hydrogenation	97
5.2.1	Asymmetric Hydrogenation	97
5.2.1.1	Asymmetric Hydrogenation of Alkenes	98
5.2.1.2	Asymmetric Hydrogenation of Ketones	101
5.2.1.3	Asymmetric Hydrogenation of Heteroaromatic Compounds	103
5.2.1.4	Asymmetric Hydrogenation of Imines	104
5.2.2	Asymmetric Transfer Hydrogenation	106
5.2.3	Asymmetric Hydrosilylation Reaction	109
5.2.3.1	Palladium-Catalyzed Asymmetric Hydrosilylation of C=C Bond	110
5.2.3.2	Asymmetric Hydrosilylation of a C=O Bond	112
5.2.3.3	Asymmetric Hydrosilylation of the C=N Bond	117
5.2.4	Asymmetric Hydroboration	118
5.3	Formation of a C-C Bond	121
5.3.1	Pd-Catalyzed Asymmetric Allylic Substitution Reaction	121
5.3.2	Asymmetric Heck Reaction and Cross-Coupling Reactions	126
5.3.3	Addition of Organometallic Reagents to a C=X Bond	129
5.4	Cycloaddition Reactions	132
5.4.1	[3 + 2] Cycloaddition Reactions	132
5.4.2	Asymmetric Cyclopropanation Reactions	136
5.4.3	Asymmetric Diels-Alder Reactions	136
5.5	Miscellaneous Reactions	137
5.6	Conclusion and Perspectives	140
5.7	Experimental: Selected Procedures	140
5.7.1	Ugi's Amine Synthesis	140
5.7.1.1	Synthesis of α -Ferrocenylethyl dimethylamine (2)	141
5.7.1.2	Resolution of 2	141

- 5.7.1.3 Synthesis of (*S*)-*N*, *N*-Dimethyl-1-[(*R*)-2-(diphenylphosphino)ferrocenyl]ethylamine 141
- 5.7.2 (*S*, *S_p*)-2-[(*S*)-2-(diphenylphosphino)ferrocenyl]-4-(1-methylethyl)oxazoline 142
 - 5.7.2.1 Synthesis of (2*S*)-*N*-(1-hydroxy-3-methylbutyl)ferrocenamide 142
 - 5.7.2.2 Synthesis of Ferrocenyloxazoline 142
 - 5.7.2.3 Synthesis of (*S*, *S_p*)-2-[(*S*)-2-(diphenylphosphino)ferrocenyl]-4-(1-methylethyl)oxazoline 143
- References 144

- 6 *N,O*-Bidentate Ferrocenyl Ligands 149**
Anne Nijs, Olga García Mancheño, and Carsten Bolm
 - 6.1 Introduction 149
 - 6.2 Addition of Organozinc Reagents to Aldehydes 149
 - 6.2.1 Addition of Dialkylzinc 150
 - 6.2.1.1 With Ferrocenyl Amino Alcohols 150
 - 6.2.1.2 With Ferrocenyl Oxazolanyl Alcohols 158
 - 6.2.1.3 With Azaferrocenes 160
 - 6.2.2 Addition of Arylzinc 161
 - 6.2.3 Addition of Phenylacetylene 165
 - 6.3 Addition to Aldehydes with Boron Reagents 165
 - 6.3.1 Aryl Transfers with Boronic Esters 165
 - 6.3.2 Aryl Transfer with Triphenylborane [Ph₃B] 166
 - 6.3.3 Boronic Acids as Aryl Source 167
 - 6.3.4 Alkenylboronic Acids in Alkenyl Transfer Reactions 168
 - 6.4 Other Transformations: Asymmetric Epoxidation 168
 - 6.5 Conclusion and Perspectives 169
 - 6.6 Experimental: Selected Procedures 170
 - 6.6.1 Addition of Diethylzinc to Benzaldehyde with Ferrocene 13 170
 - 6.6.2 Phenylacetylene Addition to Aldehydes with Ferrocene 24 170
 - 6.6.3 Phenyl Transfer (ZnEt₂ + ZnPh₂) to Aldehydes with Ferrocene 13 171
 - 6.6.4 Phenyl Transfer to Aldehydes with Triphenylborane on a Gram Scale 171
 - 6.6.5 Aryl Transfer to Aldehydes with Boronic Acids on a Multigram Scale 171
 - References 173

- 7 Symmetrical 1,1'-Bidentate Ferrocenyl Ligands 175**
Wanbin Zhang and Delong Liu
 - 7.1 Introduction 175
 - 7.2 Symmetrical 1,1'-Disubstituted Ferrocenyl Ligands 177
 - 7.2.1 P-Centered Chiral Diphosphine Ligands 177
 - 7.2.2 C-Centered Chiral Diphosphine Ligands 180
 - 7.2.3 Chiral Nitrogen-Containing Ligands 188
 - 7.3 Symmetrical 1,1',2,2'-Tetrasubstituted Ferrocenyl Ligands 193

- 7.3.1 Tetrasubstituted Ferrocenyl Diphosphine Ligands with Multi-Chiralities 193
- 7.3.2 Tetrasubstituted Ferrocenyl Ligands with Only Planar Chirality 198
- 7.3.3 Other Tetrasubstituted Ferrocenyl Ligands 201
- 7.4 Analogs of Ferrocenes: Symmetrical 1,1'-Bidentate Ruthenocenyl Ligands 203
- 7.5 Conclusion and Perspectives 208
- 7.6 Experimental: Selected Procedures 208
 - 7.6.1 Typical Procedure for the Preparation of Ferrocenyldiphosphines L-2 208
 - 7.6.2 Typical Procedure for the Preparation of the (*R,R*)-ferrocenyl Diol 14 208
 - 7.6.3 Typical Procedure for the Preparation of ($\alpha R, \alpha' R$)-2,2'-Bis(α -*N,N*-dimethylaminopropyl)-(*S,S*)-1,1'-bis(diphenylphosphino)ferrocene L-17c 209
 - 7.6.4 Typical Procedure for the Preparation of C₂-Symmetric 1,1',2,2'-tetrasubstituted Ferrocene Derivatives L-18 209
 - 7.6.5 Typical Procedure for the Preparation of the Ferrocene-Based Ester Amide 59 209
 - 7.6.6 Typical Procedure for the Preparation of (–)-(*S*)-(*S*)-1,1'-Bis(diphenylphosphino)-2,2'-bis-(methoxycarbonyl)ferrocene L-21 210
 - 7.6.7 Typical Procedure for the Preparation of 1,1'-Bis[(*S*)-4-isopropylloxazolin-2-yl]-ruthenocene 82 210
- References 211

- 8 Unsymmetrical 1,1'-Bidentate Ferrocenyl Ligands 215**
Shu-Li You
 - 8.1 Introduction 215
 - 8.2 Palladium-Catalyzed Asymmetric Allylic Substitution Reaction 215
 - 8.2.1 A Model Reaction of Symmetrical 1,3-Disubstituted 2-Propenyl Acetates 216
 - 8.2.2 Substrate Variants of Palladium-Catalyzed Asymmetric Allylic Substitution Reaction 221
 - 8.2.3 Regioselective Control for Unsymmetrical Allylic Acetates 224
 - 8.2.4 Applications of Palladium-Catalyzed Asymmetric Allylic Substitution Reaction 228
 - 8.3 Gold or Silver-Catalyzed Asymmetric Aldol Reactions 229
 - 8.3.1 Gold-Catalyzed Asymmetric Aldol Reactions 229
 - 8.3.2 Silver-Catalyzed Asymmetric Aldol Reactions 232
 - 8.3.3 Applications of Gold or Silver-Catalyzed Asymmetric Aldol Reactions 232
 - 8.4 Asymmetric Hydrogenation 234
 - 8.4.1 Rh-Catalyzed Hydrosilylation 234
 - 8.4.2 Rh, Ir, Ru-Catalyzed Hydrogenation 235
 - 8.4.3 Rh-Catalyzed Hydroboration 238

8.5	Asymmetric Cross-Coupling Reaction	239
8.5.1	Nickel-Catalyzed Kumada Coupling Reaction	239
8.5.2	Palladium-Catalyzed Cross-Coupling Reaction	240
8.5.3	Palladium-Catalyzed Suzuki–Miyaura Reaction and α -Arylation of Amides	241
8.6	Asymmetric Heck Reaction	242
8.6.1	Intramolecular Heck Reaction	242
8.6.2	Intermolecular Heck Reaction	243
8.7	Miscellaneous	244
8.7.1	Addition of Zinc Reagent to Aldehydes	244
8.7.2	Conjugate Addition	247
8.7.3	Rh-Catalyzed Ring Opening Reaction of Oxabenzonorbornadiene	247
8.7.4	Asymmetric Cyclopropanation of Alkenes with Diazo Esters	248
8.7.5	Asymmetric Palladium-Catalyzed Hydroesterification of Styrene	249
8.8	Conclusion and Perspectives	250
8.9	Experimental: Selected Procedures	250
8.9.1	Synthesis of Compound (<i>S,S</i>)-L4d from (<i>S</i>)-5a	250
8.9.2	Synthesis of Compound (<i>S,R_{phos}</i>)-L8d and (<i>S,S_{phos}</i>)-L8d from (<i>S</i>)-5d	251
	References	253
9	Sulfur- and Selenium-Containing Ferrocenyl Ligands	257
	<i>Juan C. Carretero, Javier Adrio, and Marta Rodríguez Rivero</i>	
9.1	Introduction	257
9.2	Asymmetric Allylic Substitution	258
9.2.1	Palladium-Catalyzed Allylic Substitution	258
9.2.1.1	Bidentate N, <i>S</i> -ferrocene Ligands	259
9.2.1.2	Bidentate P, <i>S</i> -ferrocene Ligands	260
9.2.2	Copper-Catalyzed Allylic Substitution	265
9.3	Other Asymmetric Palladium-Catalyzed Reactions	266
9.3.1	Asymmetric Heck Reactions	266
9.3.2	Desymmetrization of Heterobicyclic Alkenes	267
9.4	Gold-Catalyzed Reactions	268
9.5	Asymmetric Reductions	269
9.6	Asymmetric 1,2- and 1,4-Nucleophilic Addition	270
9.6.1	Asymmetric 1,2 Addition to Aldehydes and Imines	270
9.6.2	Asymmetric 1,4-Conjugate Addition	272
9.7	Asymmetric Cycloaddition Reactions	272
9.7.1	[4 + 2] Cycloadditions	272
9.7.2	[3 + 2] Cycloadditions	274
9.8	Asymmetric Nucleophilic Catalysis	276
9.9	Conclusion and Perspectives	277
9.10	Experimental: Selected Procedures	278
9.10.1	Palladium-Catalyzed Allylic Alkylation Reaction with Ligand 3a	278

- 9.10.2 Fesulphos/Palladium-Catalyzed Asymmetric Ring Opening of Bicyclic Alkenes 278
- 9.10.3 Rhodium-Catalyzed Hydrogenation α -(*N*-acetamido)acrylate in the Presence of Ligand 20 278
- 9.10.4 Cu-Fesulphos Catalyzed Formal Aza Diels–Alder Reactions of *N*-Sulfonyl Imines 278
- References 280

10 Biferrocene Ligands 283

Ryoichi Kuwano

- 10.1 Introduction 283
- 10.2 Trans-Chelating Chiral Bisphosphines: TRAP 284
 - 10.2.1 Synthesis of TRAP 285
 - 10.2.2 Metal Complexes of TRAP 286
 - 10.2.3 Asymmetric Reactions of 2-Cyanocarboxylates 287
 - 10.2.4 Asymmetric Hydrosilylation of Ketones 291
 - 10.2.5 Asymmetric Hydrogenation of Olefins 292
 - 10.2.6 Asymmetric Hydrogenations of Heteroaromatics 296
 - 10.2.7 Miscellaneous Reactions using TRAP 298
- 10.3 2,2-Bis(diarylphosphino)-1,1-biferrocenes: BIFEP 299
- 10.4 Miscellaneous Biferrocene-Based Chiral Ligands 302
- 10.5 Conclusion 303
- References 304

11 Applications of Aza- and Phosphaferrocenes and Related Compounds in Asymmetric Catalysis 307

Nicolas Marion and Gregory C. Fu

- 11.1 Introduction 307
- 11.2 Background on Aza- and Phosphaferrocenes 308
 - 11.2.1 Azaferrocenes 308
 - 11.2.2 Phosphaferrocenes 309
- 11.3 Azaferrocenes in Catalysis 310
 - 11.3.1 Nucleophilic Catalysis 310
 - 11.3.1.1 Acylations 310
 - 11.3.1.2 Halogenations 316
 - 11.3.1.3 Cycloadditions 317
 - 11.3.1.4 Nucleophilic Additions to Carbonyl Groups 319
 - 11.3.2 Transition-Metal Catalysis 319
 - 11.3.2.1 Copper-Catalyzed Cyclopropanations of Olefins 319
 - 11.3.2.2 Copper-Catalyzed Insertions of Diazo Compounds 320
 - 11.3.2.3 Copper-Catalyzed Cycloadditions 322
 - 11.3.2.4 Olefin Polymerizations 322
 - 11.3.2.5 Rhodium-Catalyzed Reductions of Ketones 324
- 11.4 Phosphaferrocenes in Catalysis 324
 - 11.4.1 Reduction Reactions 325

11.4.2	Palladium-Catalyzed Allylic Alkylations	326
11.4.3	Rhodium-Catalyzed Isomerizations	328
11.4.4	Copper-Catalyzed Conjugate Additions	328
11.4.5	Copper-Catalyzed Cycloadditions	329
11.4.6	Palladium-Catalyzed Cross-Couplings	331
11.5	Conclusions	333
	References	333
12	Metalloacyclic Ferrocenyl Ligands	337
	<i>Christopher J. Richards</i>	
12.1	Introduction	337
12.2	Asymmetric Synthesis of Planar Chiral Metalloacyclic Complexes	339
12.2.1	Resolution	341
12.2.2	Diastereotopic C–H Activation	342
12.2.3	Oxidative Addition of Palladium(0)	348
12.2.4	Transmetalation	350
12.2.5	Enantioselective Palladation	352
12.3	Stoichiometric Synthetic Applications of Scalemic Planar Chiral Metalloacyclic Complexes	354
12.3.1	Phosphine Recognition	354
12.3.2	Generation of Planar Chiral Ferrocene Derivatives by M–C Bond Cleavage	354
12.4	Asymmetric Catalysis with Scalemic Planar Chiral Palladoacyclic Complexes	355
12.4.1	Allylic Imidate Rearrangement	356
12.4.2	Intramolecular Aminopalladation	363
12.5	Conclusion	364
	References	364
A	Show Case of the Most Effective Chiral Ferrocene Ligands in Various Catalytic Reactions	369
A.1	Asymmetric Allylic Substitution Reactions	369
A.1.1	Copper(I)-Catalyzed Asymmetric Allylic Alkylation Reactions	369
A.1.2	Palladium-Catalyzed Asymmetric Allylic Substitution Reactions	370
A.1.2.1	Alkylation	370
A.1.2.2	Amination	371
A.1.3	Generating π -Allyl Palladium Complex Through the Reaction of Allene with Iodobenzene	372
A.1.4	Regioselective Control Concerned with Unsymmetrically 1,3-Disubstituted 2-Propenyl Acetate	372
A.1.4.1	Regio- and Enantioselective Palladium-Catalyzed Allylic Substitution	372
A.1.4.2	Allylic Substitution of 2-Cyanopropionate	373
A.1.4.3	Allylic Substitution of the Conjugated Dienyl Acetates	373

A.1.4.4	Allylic Substitution with Acyclic Ketone Enolate as Nucleophile	374
A.1.4.5	Allylic Alkylation with N,N-Disubstituted Amides as Nucleophile	374
A.1.4.6	Allylic Alkylation with Activated Cyclic Ketone as Nucleophile	374
A.1.5	Applications of Palladium-Catalyzed Asymmetric Allylic Substitution Reaction	375
A.2	Asymmetric Aldol Reactions	375
A.2.1	Gold-Catalyzed Asymmetric Aldol Reactions	375
A.2.1.1	Aldehyde with Isocyanoacetate	375
A.2.1.2	Imines with Isocyanoacetate	376
A.2.2	Silver-Catalyzed Asymmetric Aldol Reactions	376
A.2.3	Applications of Gold or Silver-Catalyzed Asymmetric Aldol Reactions	376
A.3	Asymmetric Cycloaddition Reactions	377
A.3.1	[3 + 2] Cycloaddition Reactions	377
A.3.2	[4 + 2] Cycloaddition Reactions	377
A.3.3	[3+2] Cycloaddition Reactions	378
A.3.4	Asymmetric 1,3-Dipolar Cycloaddition of Azomethine Ylides with N-Phenyl Maleimide	378
A.3.5	[3 + 2] Cycloaddition of Alkynes with Azomethine Imines	378
A.4	Asymmetric Hydrogenation	379
A.4.1	Asymmetric Hydrogenation of Alkenes (C=C)	379
A.4.1.1	Asymmetric Hydrogenation of Unfunctionalized Alkenes	379
A.4.1.2	Asymmetric Hydrogenation of α,β -Unsaturated Esters	379
A.4.1.3	Hydrogenation of Dehydro α -Amino Acid	380
A.4.1.4	Asymmetric Hydrogenation of Activated Imine C=N Bond	380
A.4.1.5	Applications: Hydrogenation of α,β -Unsaturated Acid	381
A.4.1.6	Asymmetric Hydrogenation of Alkyl α -Acetamido Acrylates	381
A.4.1.7	Industrial Applications	382
A.4.2	Asymmetric Hydrogenation of Alkenes (or C=N)	383
A.4.2.1	Ir-Catalyzed Asymmetric Hydrogenation of Quinolines	383
A.4.2.2	Industrial Applications	384
A.4.3	Asymmetric Hydrogenation of Ketones (C=O)	384
A.4.3.1	Asymmetric Hydrogenation of Acetophenone	384
A.4.3.2	Asymmetric Hydrogenation of β -Aminoketone	385
A.4.4	Asymmetric Hydroboration	385
A.4.5	Asymmetric Hydrosilylation Reaction	385
A.4.6	Asymmetric Transfer Hydrogenation	386
A.5	Pd-Catalyzed Asymmetric Heck Reaction	386
A.6	Addition of Organozinc Reagents	387
A.6.1	Addition of Dialkylzinc to Aldehydes	387
A.6.2	Addition of Diarylzinc to Aldehydes	388
A.6.3	Addition of Dialkylzinc to C=N Bond	388
A.6.4	Addition of Phenylacetylene to Aldehydes	389
A.6.5	Addition to Aldehydes with Boron Reagents	389
A.6.5.1	Aryl Transfer with Boronic Ester	389

- A.6.5.2 Aryl Transfer with Triphenylborane 389
- A.6.5.3 Aryl Transfer with Boronic Acids 390
- A.7 Asymmetric Rearrangement of Allylic Imidates 390
 - A.7.1 Rearrangement of N-Arylbenzimidates 390
 - A.7.2 Rearrangement of N-Aryl-trifluoroacetimidate 390
 - A.7.3 Rearrangement with Added Nucleophiles 391
- A.8 Cu-Catalyzed Cyclopropanation 391
 - A.8.1 With Diphenylethene 391
 - A.8.2 With Aryl, Alkyl or Silylethene 391
- A.9 Coupling Reaction of Vinyl Bromide and 1-Phenylethylzinc Chloride 392
- A.10 Enantioselective Intramolecular Aminopalladation 392
- A.11 Nickel-Catalyzed Asymmetric Three-Component Coupling of Alkynes, Imines, and Organoboron Reagents 392
- A.12 Reactions with Ketenes 393
 - A.12.1 O-Acylation with Ketenes 393
 - A.12.2 Kinetic Resolution by O-Acylation 393
 - A.12.3 N-Acylation with Ketenes 394
 - A.12.4 Kinetic Resolution by N-Acylation 394
 - A.12.5 C-Acylation via Rearrangement 394
 - A.12.6 Cycloadditions 395
 - A.12.7 Copper-Catalyzed Insertions of Diazo Compounds 395
 - A.12.8 Copper-Catalyzed Cycloadditions 395
- A.13 Ring Opening Reaction 396
 - A.13.1 Desymmetrization by Halogenations 396
 - A.13.2 Ring Opening of Bicyclic Alkenes 396

Index 397