

Contents

1 Abstract.....	1
2 Introduction.....	3
2.1 Synthesis of α-Diazocarbonyl Compounds	3
2.1.1 Acylation of Diazoalkanes.....	4
2.1.2 Diazo Transfer Reactions.....	5
2.1.3 Diazo Cross-Coupling Reaction	7
2.2 Application of α-Diazocarbonyl Compounds in Metal-Catalyzed X–H (X = N, O) Insertion Reactions	9
2.2.1 Early Achievements in X–H Insertion Reactions	10
2.2.2 Mechanistic Studies of Copper-Catalyzed X–H Insertion Reactions	12
2.2.3 Mechanistic Studies of Rhodium (II)-catalyzed X–H Insertion Reactions ^[39]	14
2.2.4 Ruthenium-catalyzed X–H Insertion Reactions.....	15
2.3 Development of Enantioselective X–H Insertion Reactions.....	16
2.3.1 Enantioselective N–H Insertion Reactions	16
2.3.2 Enantioselective O–H Insertion Reactions	18
2.4 Paracyclophane Derivatives in Asymmetric Catalysis	20
2.4.1 [2.2]Paracyclophane.....	20
2.4.2 Chirality of [2.2]Paracyclophane Derivatives.....	20
2.4.3 Functionalization of [2.2]Paracyclophane Derivatives.....	21
2.4.4 Application of [2.2]Paracyclophane Derivatives in Asymmetric Catalysis	24
2.5 Enzymes as Efficient Biocatalysts in the Asymmetric Reduction of Ketones ..	27
2.5.1 General Remarks and Potential of Enzymes as Catalysts in Organic Synthesis .	27
2.5.2 Type of Enzymatic Reactions Commonly Used in Organic Synthesis.....	28
2.5.3 Enzyme-Catalyzed Asymmetric Reduction of Ketones	29

3	Aim of the Work.....	33
4	Results and Discussion.....	35
4.1	Synthesis of α-Diazocarbonyl Compounds	35
4.1.1	α -Diazocarbonyl Compounds for Model System Tests.....	35
4.1.2	α -Diazocarbonyl Compounds for Enzyme-Catalyzed Reduction.....	37
4.1.3	Unsaturated α -Diazocarbonyl Compounds for the Synthesis of Hexahydroindole: Key Intermediate towards the Total Synthesis of Rostratin B-D	38
4.2	[2.2]Paracyclophane-based Ligands in Metal-Catalyzed N–H Insertion Reactions.....	47
4.2.1	Synthesis of Enantiopure pseudo- <i>ortho</i> [2.2]Paracyclophane-based Bisoxazoline Ligands.....	48
4.2.2	Synthesis of Ruthenium Complexes with [2.2]Paracyclophane Oxazoline Ligands.....	51
4.2.3	Synthesis of Amino-substituted [2.2]Paracyclophane Derivatives.....	55
4.3	Metal-catalyzed N–H Insertion with [2.2]Paracyclophane Ligands	58
4.3.1	Copper-Catalyzed N–H Insertion of Saturated α -Diazocarbonyl Compounds with [2.2]Paracyclophane Ligands.....	58
4.3.2	Copper-Catalyzed N–H Insertion of Unsaturated α -Diazocarbonyl Compounds with [2.2]Paracyclophane Ligands.....	62
4.3.3	Application of the Copper-catalyzed N–H insertion in the Synthesis of Hexahydroindole Motif.....	73
4.4	Chemoenzymatic Synthesis of O-Containing Heterocycles via Ketoreductase- catalyzed Highly Enantioselective Reduction.....	75
4.4.1	Enzyme-catalyzed Reduction from Keto α -Diazocarbonyl Compounds.....	77
4.4.2	Characterization of the Enzyme Activity via NADPH Consumption	78
4.4.3	Characterization of the Enzyme Activity via Chiral HPLC.....	81
4.4.4	Transition Metal-Catalyzed Intramolecular O–H Insertion.....	84
5	Summary and Outlook	87

5.1	Synthesis of α-Diazocarbonyl Compounds	87
5.2	[2.2]Paracyclophane-based Catalysts and Metal-catalyzed N–H Insertion Reactions	88
5.3	Chemoenzymatic Synthesis of <i>O</i>-Containing Heterocycles <i>via</i> Ketoreductase-catalyzed Highly Enantioselective Reduction.....	91
6	Experimental Part.....	93
6.1	General Information on [2.2]Paracyclophane.....	93
6.1.1	Nomenclature of [2.2]Paracyclophane.....	93
6.1.2	Analytics and Equipment.....	94
6.1.3	Preparative work	97
6.2	Synthesis and Characterization	98
6.2.1	General Procedures	98
6.2.2	Synthesis and Characterization of Paracyclophane Derivatives	102
6.2.3	Synthesis and Characterization of the Saturated α -Diazocarbonyl Compounds	118
6.2.4	Synthesis and Characterization of the N–H Insertion Products from the Unsaturated α -Diazocarbonyl Substrates.....	122
6.2.5	Synthesis and Characterization of the Substituted Buta-2,3-Dienoates.....	127
6.2.6	Synthesis and Characterization of the Unsaturated α -Diazocarbonyl Compound.....	129
6.2.7	Synthesis and Characterization of N–H Insertion Products from the Unsaturated α -Diazocarbonyl Substrates	136
6.2.8	Synthesis and Characterization of Iodo-substituted Ketones.....	156
6.2.9	Synthesis and Characterization of the Hydroxyl-substituted α -Diazocarbonyl Compounds	157
7	List of Abbreviations	169
8	Literature.....	173
9	Appendix.....	192
9.1	X-ray Crystallographic data	192

9.2	Curriculum Vitae	197
9.3	Publications and Conference Contributions	198
9.4	Acknowledgement.....	199