

CONTENTS

CERTIFICATE

DECLARATION

ACKNOWLEDGEMENTS

CONTENTS

LIST ABBREVIATIONS

CHAPTER 1 SYNTHESIS AND STEREO-CHEMICAL STUDIES ON 8-AZASTEROID FRAGMENTS

1.1	Synthesis and stereochemistry of 2-arylperhydrocyclopenta[<i>b</i>]pyridines	
1.1.1	Introduction	2
1.1.2	Methods for synthesis of <i>N</i> -hydroxylamines	3
1.1.3	Result and discussion	5
1.1.4	Synthesis of 8-azaestrone fragments	10
1.1.5	Synthesis of 2-arylperhydrocyclopenta[<i>b</i>]pyridines	11
1.2	Synthesis and stereochemistry of 2,4-diarylperhydro cyclopenta[<i>b</i>]pyridines	15
1.2.1	Leuckart Wallach (LW) reductive amination cyclization (RAC) of 1,5-diketones generated from chalcone and cyclopentanone	15
1.2.2	Reductive cyclization of mono-oximes derived from 1,5-diketones	19
1.2.3	Synthesis of 2,4-diarylperhydrocyclopenta[<i>b</i>]pyridine from <i>N</i> -hydroxylamines	24
1.3	Synthesis and stereo chemical studies on 2-arylperhydroquinolin-1-ols	25
1.3.1	Introduction	25
1.3.2	Result and discussion	27
1.4	Synthesis of 2-aryl-perhydroquinolines from 2-arylperhydroquinolin-1-ols	32
1.5	Synthesis and stereochemistry of 2,4-diphenylperhydroquinolines	33
1.5.1	Reductive cyclization of mono-keto oximes generated from 2-(3-oxo-1,3-diphenylpropyl)-1-cyclohexanone	33

1.5.2	Synthesis of 2,4-dipheyl perhydroquinoline from 2,4-diphenylperhydro-1-quinolinol	38
1.6.	Synthetic efforts towards 12-phenyl-D-homo-8-azasteroids	40
1.6.1	Introduction	40
1.6.2	Results and discussion	42
1.6.2.1	Synthesis of <i>N</i> -(2-hydroxyethyl)-2,4-diphenylperhydroquinoline	44
1.6.2.2	Cyclization reactions on 2-(2,4-diarylperhydro-1-quinolinyl)-1-ethanols	46
1.6.2.3	Synthesis of 1-(2-chloroethyl)-2,4-diarylperhydroquinoline	46
1.7	Synthetic efforts towards B-nor-8-azasteroids	50
1.7.1	Introduction	50
1.7.2	Results and discussion	53
1.7.2.1	Synthesis of 2-[(<i>E</i>)-3-phenyl-2-propenoyl]benzotrile	53
1.7.2.2	Synthesis of 3-(2-oxocyclohexyl)-3-[(<i>E</i>)-2-aryl-1-ethenyl] -1-isindolinones	54
1.8	Experimental section	54
1.9	References	94

CHAPTER 2 STEREOCHEMISTRY OF QUINOLIZINES BY DYNAMIC NMR SPECTRAL STUDIES

2.1	Synthesis and stereochemistry of cyclopentaquinolizines	100
2.1.1	Synthesis and characterizations of quinolizines	103
2.1.2	Chair to boat interconversion and face to face interactions in isomeric aryl substituted perhydrocyclopentaquinolizines	114
2.1.3	Stereochemistry of quinolizine salts 1-H ⁺ and 2-H ⁺	126
2.1.4	Synthetic efforts towards quinolizine based crown ethers	143
2.2	Synthesis and stereochemistry of cyclohexaquinolizines	145
2.3	Experimental Section	149
2.4	References	165

**CHAPTER 3 SYNTHESIS AND STEREOCHEMISTRY OF MANZAMINE
FRAGMENTS VIA OLEFIN METATHESIS REACTION**

3.1	Introduction	166
3.2	Mechanism of olefin metathesis	168
3.3	Catalysts	169
3.4	Recent application of RCM for the synthesis of 13-membered crown ethers	173
3.5	Results and discussion	176
3.5.1	Synthesis of substrates required for RCM	177
3.5.1.1	Synthesis and characterization of substituted 6,9,16,17-tetrahydro-15 <i>H</i> -dibenzo[<i>g,l</i>][1,6]dioxacyclotridecines	177
3.5.1.2	Synthesis and characterization of 6,9,16,17-tetrahydro-15 <i>H</i> -dibenzo[<i>b,g</i>] [1,9,5]dioxazacyclotridecine-16-carbaldehyde	179
3.5.1.3	Synthesis and characterization of 6,9-dihydro-15 <i>H</i> ,17 <i>H</i> -dibenzo[<i>b,g</i>] [1,5,9]trioxacyclotridecine	180
3.5.1.4	Synthesis and characterization of 6,9-dihydro-15 <i>H</i> ,17 <i>H</i> -dibenzo[<i>b,g</i>] [1,9,5]dioxathiacyclotridecine	181
3.6	RCM Reaction	181
3.7	Synthesis of 13-membered crown ethers	185
3.8	Summary	188
3.9	Experimental Section	188
3.10	References	199

**APPENDIX APPLICATION OF BLAISE REACTION FOR THE
SYNTHESIS OF β -KETO ESTERS: A FACILE SYNTHESIS
OF THE PRECURSOR FOR NAZAROV REAGENT**

1.	Introduction	203
2.	Results and Discussion	206
3.	Experimental Section	207
4.	References	208
	<i>SUMMARY</i>	210
	<i>LIST OF PUBLICATIONS</i>	220