

TABLE OF CONTENTS

DECLARATION.....	i
ACKNOWLEDGEMENTS.....	ii
LIST OF ABBREVIATIONS.....	iii
ABSTRACT.....	v
CHAPTER 1: INTRODUCTION.....	1
1.1. Olefin metathesis.....	1
1.1.1. The different types of olefin metathesis.....	3
1.1.2. Some applications of ring closing metathesis.....	7
1.2. Catalysts for olefin metathesis.....	8
1.2.2. Non-metathetic behaviour of ruthenium-based catalysts.....	12
1.3. Metal-mediated olefin isomerisation.....	14
1.4. Selected synthesis of benzo-fused heterocyclic compounds.....	20
1.4.1. Some reported syntheses of 6- and 7-membered benzo-fused heterocyclic compounds.....	20
1.4.2. Some reported syntheses of 8- and 9-membered benzo-fused heterocyclic compounds by RCM.....	24
1.5. Specific aims of this project.....	34
CHAPTER 2: RESULTS AND DISCUSSION.....	36
2.1. Synthesis of 6-membered benzo-fused heterocyclic compounds.....	36
2.1.1. Attempted synthesis of <i>tert</i> -butyl 4 <i>H</i> benzoxazine-4-carboxylate 91	37
2.1.2. Attempted synthesis of di- <i>tert</i> -butyl quinoxaline-1,4-dicarboxylate 96	39

2.1.3. Attempted synthesis of 1,4-dibenzoyl-1,4-dihydroquinoxaline 100	41
2.2. Synthesis of 7-membered benzo-fused heterocyclic compounds.....	43
2.2.1. Synthesis of <i>tert</i> -butyl 1,5-benzoxazepine-5(4 <i>H</i>)-carboxylate 103	43
2.2.2. Attempted synthesis of 1-[(4-methylphenyl)sulfonyl]-1,5-dihydro-4,1-benzoxazepine 109	45
2.2.3. Attempted synthesis of 1,4- <i>bis</i> [(4-methylphenyl)sulfonyl]-4,5-dihydro-1 <i>H</i> -1,4-benzodiazepine 114	47
2.2.4. Attempted synthesis of 5 <i>H</i> -1,4-benzodioxepine 118	49
2.2.5. Attempted synthesis of 5-methyl-5 <i>H</i> -1,4-benzodioxepine 123	50
2.2.6. Attempted synthesis of 5-Phenyl-5 <i>H</i> -1,4-benzodioxepine 127	52
2.3. Synthesis of 8-membered benzo-fused heterocyclic compounds	53
2.3.1. Synthesis of <i>tert</i> -butyl 2,5-dihydro-6 <i>H</i> -1,6-benzoxazocine-6-carboxylate 128	54
2.3.2. Synthesis Of di(<i>tert</i> -butyl) 2,5-dihydro-1,6-benzodiazocine-1,6-dicarboxylate 129	55
2.3.3. Synthesis of 1,6-dibenzoyl-1,2,5,6-tetrahydro-1,6-benzodiazocine 132	59
2.3.4. Attempted synthesis of 2,5-dihydro-1,6-benzodioxacine 133	62
2.3.5. Synthesis of 7-methoxy-2,5-dihydro-1,6-benzodioxocine 137	64
2.3.6. Attempted synthesis of 13-phenyl-1,8-diazatricyclo[6.4.1.0 ^{2,7}]trideca-2,4,6,10-tetraen-13-ol 139	66
2.3.7. Attempted synthesis of <i>tert</i> -butyl 1,4-dihydro-6 <i>H</i> -5,1-benzodiazocine-1-(6 <i>H</i>)-carboxylate 149	68
2.4. Attempted synthesis of 9-membered benzo-fused heterocyclic compounds.....	70
2.4.1. Attempted synthesis of 7-methyl-2,5-dihydro-7 <i>H</i> -1,6-benzodioxonine 150	70
2.4.2. Attempted synthesis of 7-phenyl-2,5-dihydro-7 <i>H</i> -1,6-benzodioxonine 151	71
2.4.3. Attempted synthesis of 7,7-diphenyl-2,5-dihydro-7 <i>H</i> -1,6-benzodioxonine 156	72
2.4.4. Attempted synthesis of 2,5-dihydro-7 <i>H</i> -1,6-benzodioxonine 157	75
2.4.5. Attempted synthesis of 1[(4-methylphenyl)sulfonyl]-1,2,5,7-tetrahydro-6,1-	

benzoxazonine 158	75
2.4.6. The synthesis of 1,6- <i>bis</i> [(4-methylphenyl)sulfonyl]-2,5,6,7-tetrahydro-1 <i>H</i> -1,6-benzodiazonine 159	76
2.5. Internal isomerisation of the 8- and 9-membered benzo-fused heterocyclic compounds.....	78
2.5.1 Synthesis of a mixture of 6-[(4-methylphenyl)sulfonyl]-3,6-dihydro-2 <i>H</i> -1,6-benzoxazocine 161 and 6-[(4-methylphenyl)sulfonyl]-5,6-dihydro-4 <i>H</i> -1,6-benzoxazocine 162	79
2.5.2. Synthesis of a mixture Of 10-methoxy-2,3-dihydro-1,6-benzodioxocine 163 and 7-methoxy-2,3-dihydro-1,6-benzodioxocine 164	82
2.5.3. Synthesis of 1,6- <i>bis</i> [(4-methylphenyl)sulfonyl]-1,2,3,6-tetrahydro-1,6-benzodiazocine 166	83
2.5.4. Attempted synthesis of 1,6-dibenzoyl-1,2,3,6-tetrahydro-1,6-benzodiazocine 167	86
2.5.5. Attempted synthesis of 6-[(4-methylphenyl)sulfonyl]-3,6-dihydro-2 <i>H</i> -1,6-benzothiazocine 1,1-dioxide 168 or 6-[(4-methylphenyl)sulfonyl]-5,6-dihydro-4 <i>H</i> -1,6-benzothiazocine 1,1-dioxide 169	87
2.5.6. Synthesis of 1,6- <i>bis</i> [(4-methylphenyl)sulfonyl]-2,3,6,7-tetrahydro-1 <i>H</i> -1,6-benzodiazonine 170	88

CHAPTER 3: CONCLUSION AND FUTURE WORK.....92

CHAPTER 4: EXPERIMENTAL98

4.1 General information.....	98
4.2. Experimental procedure for the synthesis of 6-membered benzo-fused heterocyclic compounds	99
4.2.1 Synthesis <i>tert</i> -Butyl 4 <i>H</i> -1,4-benzoxazine-4-carboxylate 91	99

4.2.2 Experimental procedures for the attempted synthesis of di(<i>tert</i> -butyl)-2,5-dihydro-1,6-benzodiazocine-1,6-dicarboxylate 96	104
4.2.3 Experimental procedures for the attempted synthesis of 1,4-Dibenzoyl-1,4-dihydroquinoxaline 100	107
4.3 Experimental procedure for the synthesis of 7-membered benzo-fused heterocyclic compounds.....	110
4.3.1 Experimental procedures for the synthesis of <i>tert</i> -Butyl 1,5-benzoxazepine-5(4 <i>H</i>)-carboxylate 103	110
4.3.2. Experimental procedures for the attempted synthesis of 1-[(4-methylphenyl)sulfonyl]-1,5-dihydro-1,4-benzoxapine 109	113
4.3.3 Experimental procedures for the attempted synthesis of 1,4- <i>bis</i> [(4-methylphenyl)sulfonyl]-4,5-dihydro-1 <i>H</i> -1,4-benzodiazepine 114	117
4.3.4 Experimental procedures for the attempted synthesis of 5 <i>H</i> -1,4-benzodioxepine 118	121
4.3.5. Experimental procedures for the attempted synthesis of 5-methyl-5 <i>H</i> -1,4-benzodioxepine 123	123
4.3.6 Experimental procedures for the attempted synthesis of 5-phenyl-5 <i>H</i> -1,4-benzodioxepine 127	126
4.4. Experimental procedure for the synthesis of 8-membered benzo-fused heterocyclic compounds.....	129
4.4.1 Experimental procedure for the synthesis of <i>tert</i> -Butyl-2,5-dihydro-6 <i>H</i> -1,6-benzoxazocine-6-carboxylate 128	129
4.4.2 Experimental procedure for the synthesis of di(<i>tert</i> -butyl) 2,5-dihydro-1,6-benzodiazocine-1,6-dicarboxylate 129	130
4.4.3. Experimental procedure for the synthesis of di(<i>tert</i> -butyl) 2,3,4,5-tetrahydro-1,6-benzodiazocine-1,6-dicarboxylate 130	131
4.4.4. Experimental procedures for the attempted synthesis of 1,2,3,4,5,6-hexahydro-1,6-benzodiazocine 131	132
4.4.5. Experimental procedure for the synthesis of 1,6-dibenzoyl-1,2,5,6-tetrahydro-1,6-benzodiazocine 132	133
4.4.6. Experimental procedures for the synthesis of attempted 2,5-dihydro-1,6-	

benzodioxazine 133	134
4.4.7. Experimental procedures for the synthesis of 7-methoxy-2,5-dihydro-1,6-benzodioxocine 137	136
4.4.8. Experimental procedures for the synthesis of 13-phenyl-1,8-diazatricyclo[6.4.1.0 ^{2,7}]trideca-2,4,6,10-tetraen-13-ol 139	137
4.4.9. Experimental procedures for the attempted synthesis of <i>tert</i> -butyl 1,4-dihydro-6 <i>H</i> -5,1-benzoxazocine-1-(6 <i>H</i>)-carboxylate 149	140
4.5. Experimental procedures for the synthesis of 9-membered benzo-fused heterocyclic compounds.....	144
4.5.1. Experimental procedure for the attempted synthesis of 7-methyl-2,5-dihydro-7 <i>H</i> -1,6-benzodioxonine 150	144
4.5.2. Experimental procedure for the synthesis of 7-phenyl-2,5-dihydro-7 <i>H</i> -1,6-benzodioxonine 151	145
4.5.3. Experimental procedures for the attempted synthesis of 7,7-diphenyl-2,5-dihydro-7 <i>H</i> -1,6-benzodioxonine 156	145
4.5.4. Experimental procedure for the attempted synthesis of 2,5-dihydro-7 <i>H</i> -1,6-benzodioxonine 157	148
4.5.5. Experimental procedure for attempted synthesis of 1[(4-methylphenyl)sulfonyl]-1,2,5,7-tetrahydro-6,1-benzoxazonine 158	149
4.5.6. Experimental procedure for the synthesis of 1,6- <i>bis</i> [(4-methylphenyl)sulfonyl]-2,5,6,7-tetrahydro-1 <i>H</i> -1,6-benzodiazonine 159	150
4.6. Experimental procedures for the internal isomerisation of 8- and 9-membered benzo-fused heterocyclic compounds.....	151
4.6.1. Experimental procedure for the synthesis of a mixture of 6-[(4-methylphenyl)sulfonyl]-3,6-dihydro-2 <i>H</i> -1,6,-benzoxazocine 161 and 6-[(4-methylphenyl)sulfonyl]-5,6-dihydro-4 <i>H</i> -1,6,-benzoxazocine 162	151
4.6.2. Experimental procedure for the synthesis of a mixture of 10-methoxy-2,3-dihydro-1,6-benzodioxocine 163 and 7-methoxy-2,3-dihydro-1,6-benzodioxocine 164	152
4.6.3. Experimental procedure for the synthesis of 1,6- <i>bis</i> [(4-methylphenyl)sulfonyl]-1,2,3,6-tetrahydro-1,6-benzodiazocine 166	153

4.6.3. Experimental procedure for the synthesis of 1,6- <i>bis</i> [(4-methylphenyl)sulfonyl]-1,2,3,6-tetrahydro-1,6-benzodiazocine 166	153
4.6.4. Experimental procedure for the attempted synthesis of 1,6-Dibenzoyl-1,2,3,6-tetrahydro-1,6-benzodiazocine 167	154
4.6.5. Experimental procedure for the attempted synthesis of a mixture 6-[(4-methylphenyl) sulfonyl]-3,6-dihydro-2 <i>H</i> -1,6-benzothiazocine 1,1-dioxide 168 and 6-[(4-Methylphenyl) sulfonyl]-5,6-dihydro-4 <i>H</i> -1,6-benzothiazocine 1,1-dioxide 169	155
4.6.6. Experimental procedure for the synthesis of 1,6- <i>bis</i> [(4-Methylphenyl)sulfonyl]-2,3,6,7-tetrahydro-1 <i>H</i> -1,6-benzodiazonine 170	156

REFERENCES.....158

APPENDIX A.....163

1. Crystal data and structure refinement for di(<i>tert</i> -butyl) 2,5-dihydro-1,6-benzodiazocine-1,6-dicarboxylate 129	163
2. Crystal data and structure refinement for di(<i>tert</i> -butyl) 2,3,4,5-tetrahydro-1,6-benzodiazocine-1,6-dicarboxylate 130	165
3. Crystal data and structure refinement for 6-[(4-methylphenyl)sulfonyl]-3,6-dihydro-2 <i>H</i> -1,6,-benzoxazocine 161	167
4. Crystal data and structure refinement for [2-(allyloxy)phenyl](diphenyl)methanol 154	169
5. Crystal data and structure refinement for 1-(alloxy)-2-[allyloxy)(diphenyl)methyl]benzene 155	171
6. Crystal data and structure refinement for 1,6- <i>bis</i> [(4-methylphenyl)sulfonyl]-2,5,6,7-tetrahydro-1 <i>H</i> -1,6-benzodiazonine 159	173
7. Crystal data and structure refinement for 1,6- <i>bis</i> [(4-methylphenyl)sulfonyl]-2,3,6,7-tetrahydro-1 <i>H</i> -1,6-benzodiazonine 170	175
8. Crystal data and structure refinement for 1,6- <i>bis</i> [(4-methylphenyl)sulfonyl]-1,2,3,6-	

tetrahydro-1,6-benzodiazocine 166	177
9. Crystal data and structure refinement for 1,6-dibenzoyl-1,2,5,6-tetrahydro-1,6-benzodiazocine 132	179
10. Crystal data and structure refinement for 6-[4-methylphenylsulfonyl]-5,6-dihydro-4 <i>H</i> -1,6,-benzodiazocine 162	181