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# Towards Selective Small Cation Chelation

A thesis presented  
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## Abstract

This thesis sought to identify ligands which could be used in sensing or sequestering applications for the toxic element beryllium. The overall aim was to search for ligands with tight binding cavities and those capable of fully encapsulating the small Be(II) cation. Please refer to the foldout at the end of this book for ligand descriptions.

Proton sponge ligands **L1** – **L13** were synthesised and evaluated for their use as simple bidentate small cation chelators. An efficient modified route to **L1** was developed. The derivatisation and properties of these unexplored ligands were investigated. X-ray crystallography gave insight into the structures of these unique molecules. Ligands of type **L1** had an ideal size-fit for the small cation B(III), used as a structural analogue for Be(II), as indicated by the crystal structure of the boron complex. Due to their high basicity they were unsuitable for coordination to Be(II) in aqueous systems due to competition for protonation. The larger Cu(II) cation was a poor fit for these ligands and a rare crystal structure showed large distortions of the metal ion from the ligand plane. The Cu(II) complexes were unstable and hydrolysed readily.

A fundamentally new type of tetra-coordinate ligand, **L14**, was synthesised and while untested in this thesis offers promise as an ideal Be(II) chelator.

The ligands **L15** – **L21** were evaluated for use as fully encapsulating Be(II) chelators and those containing three oxygen donors were found to be most suitable. The rigidity imparted by the locking of certain conformations of the ligands **L18** and **L19** upon Be(II) coordination gave rise to fluorescence. The ligands containing carboxylic acid groups (**L17** and **L18**) enabled good water solubility and **L18** in particular showed the most promise as a ligand for beryllium sensing or sequestering applications.



# Contents

<b>Chapter 1: Literature Review .....</b>	<b>1</b>
<b>1.1 Introduction to Beryllium.....</b>	<b>1</b>
1.1.1 Properties, Production and Uses .....	1
1.1.2 Health Hazards and Safety Precautions .....	3
<b>1.2 Beryllium Coordination Chemistry.....</b>	<b>5</b>
1.2.1 Beryllium Complexes with Oxygen Donors .....	5
1.2.2 Beryllium Complexes with Mixed Oxygen and Nitrogen Donors.....	10
1.2.3 Beryllium Complexes with Nitrogen Donors .....	13
1.2.4 Summary of Existing Beryllium Complexes .....	14
<b>1.3 The Search for a Beryllium Selective Ligand.....</b>	<b>16</b>
1.3.1 Introduction .....	16
1.3.2 Aryl Amine Proton Sponges .....	19
1.3.3 Heterocyclic Imine Proton Sponges.....	20
1.3.4 Aryl Imine Proton Sponges.....	21
1.3.5 Proton Sponge Metal Coordination Complexes.....	21
<b>1.4 Encapsulation of Beryllium.....</b>	<b>27</b>
1.4.1 Existing Ligands which Encapsulate Beryllium .....	27
1.4.2 Design of New Ligands which Fully Encapsulate Beryllium.....	28
<b>1.5 Boron as a Small Cation Analogue for Beryllium.....</b>	<b>31</b>
<b>1.6 Proposed Aims.....</b>	<b>32</b>
<b>Chapter 2: Synthesis of Proton Sponges .....</b>	<b>33</b>



<b>2.1 Assessment of Proton Sponges</b> .....	<b>33</b>
2.1.1 Introduction .....	33
2.1.2 Results / Discussion .....	33
2.1.3 Summary .....	39
<b>2.2 Zirnstein and Staab Synthesis</b> .....	<b>40</b>
2.2.1 Introduction .....	40
2.2.2 Results / Discussion .....	41
<b>2.3 Ila et al. Synthesis</b> .....	<b>52</b>
2.3.1 Introduction .....	52
2.3.2 Results / Discussion .....	52
<b>2.4 Summary</b> .....	<b>57</b>
<b>Chapter 3: Synthesis of Proton Sponge Derivatives</b> .....	<b>58</b>
<b>3.1 Introduction</b> .....	<b>58</b>
<b>3.2 Modification of 4,9 Substitution of Quino[7,8-<i>h</i>]quinoline</b> .....	<b>60</b>
3.2.1 Results / Discussion .....	60
<b>3.3 Modification of 2,11 Substitution of Quino[7,8-<i>h</i>]quinoline</b> .....	<b>79</b>
3.3.1 Results / Discussion .....	79
<b>3.4 Summary</b> .....	<b>86</b>
<b>Chapter 4: Coordination Chemistry of Proton Sponges</b> .....	<b>88</b>
<b>4.1 Complexation of Proton Sponges to Boron</b> .....	<b>88</b>
4.1.1 Introduction .....	88

4.1.2 Results / Discussion .....	90
<b>4.2 Spectroscopy of Boron Proton Sponge Complexes .....</b>	<b>98</b>
4.2.1 Introduction .....	98
4.2.2 UV-Vis Spectroscopy.....	98
4.2.3 Fluorescence Spectroscopy .....	106
4.2.4 Surface Enhanced Raman Spectroscopy .....	111
<b>4.3 Complexation of Proton Sponges to Beryllium .....</b>	<b>112</b>
4.3.1 Introduction .....	112
4.3.2 Aqueous Coordination Chemistry of Beryllium to Proton Sponges.....	113
4.3.3 Non-Aqueous Coordination Chemistry of Beryllium to Proton Sponges.....	116
<b>4.4 Complexation of Proton Sponges to Transition Metals.....</b>	<b>124</b>
4.4.1 Introduction .....	124
4.4.2 Results / Discussion .....	124
<b>4.5 Summary .....</b>	<b>135</b>
<b>Chapter 5: Synthesis of Tetra-Coordinate Ligands.....</b>	<b>138</b>
<b>5.1 Assessment of Tetra-Coordinate Ligands.....</b>	<b>138</b>
<b>5.2 Synthesis of a Phenol-Capped Tetra-Coordinate Ligand .....</b>	<b>142</b>
5.2.1 Introduction .....	142
5.2.2 Results / Discussion .....	143
<b>5.3 Synthesis of a Carboxylic Acid-Capped Tetra-Coordinate Ligand .....</b>	<b>152</b>
5.3.1 Introduction .....	152
5.3.2 Results / Discussion .....	154

<b>5.4 Synthesis of Amine-Capped Tetra-Coordinate Ligands .....</b>	<b>163</b>
5.4.1 Introduction.....	163
5.4.2 Results / Discussion .....	164
<b>5.5 Summary .....</b>	<b>169</b>
<b>Chapter 6: Coordination Chemistry of Encapsulating Compounds .....</b>	<b>171</b>
<b>6.1 Complexation of Encapsulating Compounds to Beryllium.....</b>	<b>171</b>
6.1.1 Introduction.....	171
6.1.2 <sup>9</sup> Be NMR Analysis.....	174
6.1.3 UV-Vis Spectroscopy in Organic Solvents.....	179
6.1.4 Fluorescence Spectroscopy in Organic Solvents .....	182
6.1.5 UV-Vis and Fluorescence Spectroscopy in Water.....	193
<b>6.2 Complexation of Encapsulating Compounds to Transition Metals .....</b>	<b>196</b>
<b>6.3 Summary .....</b>	<b>203</b>
<b>Chapter 7: Conclusions .....</b>	<b>204</b>
<b>Appendix A: Experimental .....</b>	<b>209</b>
<b>A.1 General Experimental.....</b>	<b>209</b>
A.1.1 Reagents and Solvents.....	209
A.1.2 Synthetic Methods.....	209
A.1.3 Chromatography.....	210
A.1.4 Characterisation.....	210
A.1.5 Computational .....	211
<b>A.2 Beryllium Coordination Chemistry Safety Considerations .....</b>	<b>213</b>

A.2.1 Safe Handling .....	213
A.2.2 Testing for Contamination .....	214
<b>A.3 Chapter 2 Experimental .....</b>	<b>215</b>
A.3.1 Tetramethyl 2,2'-(naphthalene-1,8-diylbis(azanediyl))difumarate (205).....	215
A.3.2 Dimethyl 4,9-dioxo-1,4,9,12-tetrahydroquinolino[7,8-h]quinoline-2,11-dicarboxylate (206) .....	215
A.3.3 Quinolino[7,8-h]quinoline-4-9-(1H,12H)-dione (208) .....	216
A.3.4 4,9-Dichloroquino[7,8-h]quinoline (L1) .....	217
A.3.5 Quino[7,8-h]quinoline (L2).....	218
A.3.6 [H(L1)]BF <sub>4</sub> .....	218
A.3.7 [H(L2)]BF <sub>4</sub> .....	222
A.3.8 3,3-bis(Methylthio)acrylaldehyde (217) .....	225
A.3.9 N-(2-(Methylthio)benzo[h]quinolin-10-yl)acetamide (214) .....	225
<b>A.4 Chapter 3 Experimental .....</b>	<b>229</b>
A.4.1 9-(4-tert-Butylphenoxy)quinolino[7,8-h]quinolin-4(1H)-one (L4) .....	229
A.4.2 4-(4-tert-Butylphenoxy)-9-chloroquinolino[7,8-h]quinoline (L5) .....	233
A.4.3 (E)-N-(9-Chloroquinolino[7,8-h]quinolin-4(1H)-ylidene)-4-methylaniline (L6) .....	236
A.4.4 (E)-N-p-tolyl-9-(p-tolylimino)-9,12-dihydroquinolino[7,8-h]quinolin-4-amine (L7).....	239
A.4.5 [H(L7)]BF <sub>4</sub> .....	243
A.4.6 (E)-Methyl 2-(9-(o-tolylamino)quinolino[7,8-h]quinolin-4(1H)-ylideneamino)benzoate (L8) .....	246
A.4.7 4,9-Dichloro-6,7-dinitroquinolino[7,8-h]quinoline (L9) .....	249
A.4.8 9-Oxo-9,12-dihydroquinolino[7,8-h]quinoline-4-sulfonic acid (L10).....	252
A.4.9 4,9-Dimethoxyquino[7,8-h]quinoline (L11) .....	255
A.4.10 4,9-Dibromoquino[7,8-h]quinoline (L12).....	258
A.4.11 Dimethyl 4,9-Dichloroquinolino[7,8-h]quinoline-2,11-dicarboxylate (L13).....	261
A.4.12 [H(L13)]BF <sub>4</sub> .....	264

<b>A.5 Chapter 4 Experimental .....</b>	<b>267</b>
A.5.1 [BF <sub>2</sub> (L1)]BF <sub>4</sub> .....	267
A.5.2 [BF <sub>2</sub> (L2)]BF <sub>4</sub> .....	271
A.5.3 Attempted beryllium complex with L1 .....	275
A.5.4 Attempted beryllium complex with L5 .....	275
A.5.5 [Cu(L1)(CH <sub>3</sub> CN) <sub>3</sub> ](ClO <sub>4</sub> ) <sub>2</sub> .....	275
A.5.6 [Cu(L2)(CH <sub>3</sub> CN) <sub>3</sub> ](ClO <sub>4</sub> ) <sub>2</sub> .....	276
A.5.7 Fluorescence Experimental .....	277
A.5.8 Surface Enhanced Raman Spectroscopy Experimental .....	279
<b>A.6 Chapter 5 Experimental .....</b>	<b>281</b>
A.6.1 2-(2-Pyridylmethyl)pyridine (504).....	281
A.6.2 2-(2-Methoxyphenyl)pyridine (508) .....	281
A.6.3 2-Chloro-6-(2-methoxyphenyl)pyridine (509).....	282
A.6.4 2-Bromo-6-(2-methoxyphenyl)pyridine (513).....	283
A.6.5 2,2'-(Bromomethylene)dipyridine (514) .....	286
A.6.6 6-(2-Methoxyphenyl)-N,N-di(pyridin-2-yl)pyridin-2-amine (518).....	286
A.6.7 2-(6-(Dipyridin-2-ylamino)pyridin-2-yl)phenol (L14) .....	290
A.6.8 N-(2-Bromophenyl)cinnamamide (533) .....	293
A.6.9 8-Bromo-2(1H)-quinolinone (523) .....	293
A.6.10 8-Bromo-2-chloroquinoline (524).....	294
A.6.11 2-Chloroquinoline-8-carboxylic acid (519) .....	294
A.6.12 Methyl 2-chloroquinoline-8-carboxylate (535).....	298
A.6.13 Methyl 2-cinnamidobenzoate (536) .....	301
A.6.14 2-Chloroquinoline-8-carbonitrile (538) .....	304
A.6.15 8-Bromo-2-(dipyridin-2-ylmethyl)quinoline (537).....	307
A.6.16 2-(Dipyridin-2-ylmethyl)quinoline-8-carbonitrile (539) .....	310
A.6.17 2-((2-(Pyridin-2-yl)ethylamino)methyl)phenol (545) .....	313
A.6.18 2-(((2-Hydroxybenzyl)(pyridin-2-ylethyl)amino)methyl)-4-nitrophenol (L15) .....	313

A.6.19 2-((2-(Pyridin-2-yl)methylamino)methyl)phenol (560) .....	317
A.6.20 2-(((2-Hydroxybenzyl)(pyridin-2-ylmethyl)amino)methyl)-4-nitrophenol (L16) .....	317
A.6.21 Methyl 3-(2-hydroxybenzylamino)propanoate (562).....	321
A.6.22 Methyl 3-((2-hydroxy-5-nitrobenzyl)(2-hydroxybenzyl)amino)propanoate (549) .....	324
A.6.23 3-((2-Hydroxy-5-nitrobenzyl)(2-hydroxybenzyl)amino)propanoic acid (L17) .....	327
A.6.24 2-(bis(2-Hydroxy-3,5-dimethylbenzyl)amino)acetic acid (L18) .....	330
A.6.25 2-(2-Hydroxybenzylamino)phenol (567) .....	330
A.6.26 2-(((2-Hydroxybenzyl)(2-hydroxyphenyl)amino)methyl)-4-nitrophenol (L19) .....	331
A.6.27 2-((Quinolin-8-ylamino)methyl)phenol (569).....	334
A.6.28 2-(((2-Hydroxybenzyl)(quinolin-8-yl)amino)methyl)-4-nitrophenol (L20)	334
A.6.29 2-((2-Phenylquinolin-8-ylamino)methyl)phenol (571) .....	338
A.6.30 2-(((2-Hydroxybenzyl)(2-phenylquinolin-8-yl)amino)methyl)-4-nitrophenol (L21).....	341
<b>A.7 Chapter 6 Experimental .....</b>	<b>344</b>
A.7.1 Be complex with L15 .....	344
A.7.2 Be complex with L16 .....	345
A.7.3 Be complex with L17 .....	346
A.7.4 Be complex with L18 .....	347
A.7.5 Be complex with L19 .....	348
A.7.6 Be complex with L20 .....	350
A.7.7 Be complex with L21 .....	351
A.7.8 Cu complex with L16.....	353
A.7.9 Zn complex with L16 .....	354
<b>Appendix B: Abandoned Proton Sponge Syntheses .....</b>	<b>356</b>

<b>B.1 Introduction .....</b>	<b>356</b>
<b>B.2 Muthusubramanian and Misra Synthesis<sup>199</sup> .....</b>	<b>357</b>
B.2.1 Introduction .....	357
B.2.2 Results / Discussion.....	357
B.2.3 Experimental .....	358
B.2.3.1 3-(8-Aminonaphthalen-1-ylamino)propanenitrile (B10) .....	359
<b>B.3 Schmittel and Ammon Synthesis<sup>111</sup> .....</b>	<b>360</b>
B.3.1 Introduction .....	360
B.3.2 Results / Discussion.....	360
B.3.3 Experimental .....	361
B.3.3.1 Ethyl-2-phenylacetate (B16) .....	361
B.3.3.2 Ethyl-3-hydroxy-2-phenylacetate (B18) .....	362
B.3.3.3 1H-Perimidine (B21).....	363
<b>B.4 Molock and Boykin Synthesis<sup>202</sup> .....</b>	<b>364</b>
B.4.1 Introduction .....	364
B.4.2 Results / Discussion.....	364
B.4.3 Experimental .....	365
B.4.3.1 Tetraethyl 2,2'-(naphthalene-1,8-diylbis(azanediyl))bis(methan-1-yl-1-ylidene)dimalonate (B27) .....	365
<b>B.5 Montalban et al. Synthesis<sup>203</sup> .....</b>	<b>367</b>
B.5.1 Introduction .....	367
B.5.2 Results / Discussion.....	367
<b>B.6 Summary .....</b>	<b>368</b>
<b>References .....</b>	<b>370</b>

## List of Abbreviations

Acac	Acetylacetonate
BODIPY	Boron dipyrromethene
- <sup>n</sup> Bu	Normal butyl group
- <sup>t</sup> Bu	Tertiary butyl group
CBD	Chronic beryllium disease
CCSD	Cambridge crystal structure database
C <sub>g</sub>	Centroid
COSY	Correlation spectroscopy
DFT	Density functional theory
DMAD	Dimethylacetylene dicarboxylate
DMAE	Dimethylaminoethanol
DMAN	1,8-Bis(dimethylamino)naphthalene
DMF	Dimethylformamide
DMSO	Dimethylsulfoxide
Dppe	1,2-Bis(diphenylphosphino)ethane
EDTA	Ethylenediaminetetraacetic acid
EPA	Environmental Protection Agency
ESR	Electron spin resonance
-Et	Ethyl group
GIAO	Gauge including atomic orbital
HEPA	High efficiency particulate air
H <sub>fac</sub>	Hexafluoroacetylacetonate
HMQC	Heteronuclear multiple quantum coherence
HOMO	Highest occupied molecular orbital
LUMO	Lowest unoccupied molecular orbital
-Me	Methyl group
MS	Mass spectroscopy
NBS	N-Bromosuccinimide
NMR	Nuclear magnetic resonance



-OAc	Acetoxy group
-Ph	Phenyl group
RT	Room temperature
SERS	Surface enhanced Raman spectroscopy
TLC	Thin layer chromatography
TMS	Tetramethylsilane
TOF	Time of flight
UV-Vis	Ultraviolet-Visible spectroscopy

## List of Figures, Tables and Reaction Schemes

<b>Chapter 1</b>	<b>1</b>
Table 1.1: Relative selectivity of proton sponge ligands for metal cations	<b>18</b>
Table 1.2: Similarities between B(III) and Be(II)	<b>31</b>
Figure 1.1: Structure of beryllium acetate	<b>6</b>
Figure 1.2: Selection of dicarboxylic acids and a representative complex of K <sub>2</sub> [Be( <b>102</b> ) <sub>2</sub> ]	<b>7</b>
Figure 1.3: Crystal structure of beryllium bound to dicarboxyimidazole, <b>105</b>	<b>7</b>
Figure 1.4: Resonance structure of hydroxy-keto-heterocycles	<b>8</b>
Figure 1.5: Selection of hydroxy-keto-heterocycles and a representative complex of [Be( <b>106</b> ) <sub>2</sub> ]	<b>8</b>
Figure 1.6: Salicylic acid, <b>108</b> , and its sulfonated analogue, <b>109</b> , and the complex of K <sub>2</sub> [Be( <b>108</b> )]	<b>9</b>
Figure 1.7: Catechol, <b>110</b> , and related polyols, and the complex of Na <sub>2</sub> [Be( <b>110</b> ) <sub>2</sub> ]	<b>9</b>
Figure 1.8: Crystal structure of beryllium bound to nitrilotripropionic acid, <b>114</b>	<b>10</b>
Figure 1.9: Salicylaldimines which formed bis-ligand chelates with beryllium	<b>11</b>
Figure 1.10: 2-(Pyridin-2-yl)phenol, <b>117</b> , and the bis-ligand beryllium chelate	<b>11</b>
Figure 1.11: Hydroxyphenyl indole ligand, <b>118</b>	<b>12</b>
Figure 1.12: Benzo[h]quinolin-10-ol, <b>119</b>	<b>12</b>
Figure 1.13: A colourmetric beryllium test kit utilising a sulfonated analogue of <b>119</b>	<b>13</b>
Figure 1.14: 8-Hydroxyquinoline, <b>120</b>	<b>13</b>
Figure 1.15: Crystal structure of beryllium bound to 2-(pyridin-2-yl)-1H-indole, <b>121</b>	<b>14</b>
Figure 1.16: 1-Methyl-1H-imidazole-4,5-dicarboxylic acid with Be(II) bound	<b>16</b>
Figure 1.17: Benzo[h]quinolin-10-ol, <b>119</b> showing the internal hydrogen bonding interaction	<b>17</b>
Figure 1.18: Mode of proton binding in 1,8-bis(dimethylamino)naphthalene	<b>17</b>
Figure 1.19: Naphthalene-1,8-diol, <b>122</b>	<b>18</b>
Figure 1.20: Benzo[h]quinolin-10-ol, <b>121</b>	<b>19</b>
Figure 1.21: Benzo[h]quinolin-10-amine, <b>123</b>	<b>19</b>

Figure 1.22: Alkylated proton sponge; 1,8-bis(dimethylamino)naphthalene, <b>125</b>	<b>20</b>
Figure 1.23: Fluorenediamine, <b>126</b> , and related derivatives based on <b>127</b>	<b>20</b>
Figure 1.24: Quino[7,8-h]quinoline, <b>124</b>	<b>21</b>
Figure 1.25: Aryl imine type proton sponges	<b>21</b>
Figure 1.26: Metal complexes with 4,9-dichloroquino[7,8-h]quinoline, <b>131</b>	<b>22</b>
Figure 1.27: Perspective view of the crystal structure of [Pt( <b>131</b> )Cl <sub>2</sub> ]	<b>22</b>
Figure 1.28: Perspective view of the crystal structure of [Re( <b>131</b> )(CO) <sub>3</sub> Br]	<b>23</b>
Figure 1.29: Crystal structure of [Pd(β-dik-O,O')( <b>125</b> )](hfac)	<b>24</b>
Figure 1.30: Perspective view of the crystal structure of [Pt( <b>128</b> )Cl <sub>2</sub> ]	<b>25</b>
Figure 1.31: Nitrilotripropionic acid, <b>114</b>	<b>27</b>
Figure 1.32: 2,2'-(1E,1'E)-(1,1'-Binaphthyl-2,2'-diylbis(azan-1-yl-1-ylidene))- bis(methan-1-yl-1-ylidene)diphenol, <b>132</b>	<b>28</b>
Figure 1.33: Beryllium complex of 2,6-bis(2-hydroxyphenyl)pyridine, <b>133</b>	<b>28</b>
Figure 1.34: Creation of a tetra-coordinate ligand, <b>134</b>	<b>29</b>
Figure 1.35: Conversion of a proton sponge into the third dimension	<b>29</b>
Figure 1.36: Location of an oxygen atom required to make tetrahedral binding cavity	<b>29</b>
Figure 1.37: Possible compounds containing tetrahedral binding cavities for beryllium	<b>30</b>
 <b>Chapter 2</b>	 <b>33</b>
 Table 2.1: Important parameters from the optimised proton sponge beryllium complexes	 <b>34</b>
Table 2.2: Estimated mean and standard deviation for bond lengths of neutral N-donors to beryllium	<b>35</b>
Table 2.3: Important bond lengths and angles associated with hydrogen bonding in quino[7,8-h]quinolines	<b>50</b>
Table 2.4: Proton sponge torsion angles in the solid state	<b>50</b>
Figure 2.1: Proton sponges analysed by computational methods	<b>33</b>
Figure 2.2: Highlighted structural parameters for the optimised models	<b>34</b>
Figure 2.3: 1,8-bis(Dimethylamino)naphthalene, <b>L3</b>	<b>35</b>
Figure 2.4: Computer model of the beryllium bis-ligand chelate of <b>L3</b>	<b>36</b>

Figure 2.5: N1,N8-bis(1,3-Dimethyl-1H-imidazol-2(3H)-ylidene)naphthalene-1,8-diamine, <b>201</b>	<b>36</b>
Figure 2.6: Computer model of the beryllium bis-ligand chelate of <b>201</b>	<b>37</b>
Figure 2.7: Quino[7,8-h]quinoline, <b>L2</b>	<b>37</b>
Figure 2.8: Computer model of the beryllium bis-chelate of <b>L2</b>	<b>38</b>
Figure 2.9: Quino[7,8-h]quinoline, <b>L2</b>	<b>39</b>
Figure 2.10: Quino[7,8-h]quinoline, <b>L2</b> , and misreported products formed, <b>202</b> and <b>203</b>	<b>40</b>
Figure 2.11 IR spectrum for the tautomer of <b>208</b>	<b>44</b>
Figure 2.12: Crystal structure showing twisting of the heterocyclic ring system in <b>L1</b>	<b>45</b>
Figure 2.13: Parameters describing $\pi - \pi$ stacking interactions	<b>46</b>
Figure 2.14: Example of stacking $\pi - \pi$ stacking interactions between two molecules of <b>L1</b>	<b>47</b>
Figure 2.15: Crystal structure of Zirnstein and Staab showing flattened heterocyclic ring system of <b>L2</b>	<b>47</b>
Figure 2.16: Face view of the crystal structure of [H( <b>L1</b> )] [BF <sub>4</sub> ] showing hydrogen bonding	<b>48</b>
Figure 2.17: Example of stacking $\pi - \pi$ stacking interactions between two molecules of [H( <b>L1</b> )] [BF <sub>4</sub> ]	<b>49</b>
Figure 2.18: Classification of important bond lengths and angles associated with hydrogen bonding	<b>49</b>
Figure 2.19: Selection of proton sponges with recorded crystal structures	<b>50</b>
Figure 2.20: N-(2-(Methylthio)benzo[h]quinolin-10-yl)acetamide, <b>214</b>	<b>53</b>
Figure 2.21: N-(Benzo[h]quinolin-10-yl)benzamide, <b>215</b>	<b>54</b>
Figure 2.22: Crystal structure of <b>214</b> , grown by D. Parr	<b>54</b>
Figure 2.23: Crystal packing of <b>214</b>	<b>55</b>
Figure 2.24: Computer model of the beryllium bis-ligand chelate of <b>214</b>	<b>56</b>
Figure 2.25: Successfully synthesised proton sponge ligands	<b>57</b>
Figure 2.26: 2,11-bis(Methylthio)quinolino[7,8-h]quinoline, <b>213</b>	<b>57</b>
Scheme 2.1: Synthesis of quino[7,8-h]quinoline, <b>L2</b>	<b>40</b>
Scheme 2.2: Synthesis of tetramethyl 2,2'-(naphthalene-1,8-diylbis(azanediyl))-	

difumarate, <b>205</b>	<b>41</b>
Scheme 2.3: Synthesis of dimethyl 4,9-dioxo-1,4,9,12-tetrahydroquinolino- [7,8-h]quinoline-2,11-dicarboxylate, <b>206</b>	<b>41</b>
Scheme 2.4: Synthesis of quinolino[7,8-h]quinoline-4,9(1H,12H)-dione, <b>208</b>	<b>42</b>
Scheme 2.5: Microwave assisted ester cleavage of ethyl indole-2-carboxylate, <b>210</b>	<b>42</b>
Scheme 2.6: Microwave assisted ester cleavage of dimethyl 4,9-dioxo- 1,4,9,12-tetrahydroquinolino[7,8-h]quinoline-2,11-dicarboxylate, <b>206</b>	<b>42</b>
Scheme 2.7: Synthesis of dimethyl 4,9-dichloroquinolino[7,8-h]quinoline- 2,11-dicarboxylate, <b>L13</b>	<b>43</b>
Scheme 2.8: Synthesis of 4,9-dichloroquino[7,8-h]quinoline, <b>L1</b>	<b>43</b>
Scheme 2.9: Synthesis of quino[7,8-h]quinoline, <b>L2</b>	<b>45</b>
Scheme 2.10: Synthesis of 2,11-bis(methylthio)quino[7,8-h]quinoline, <b>213</b>	<b>52</b>
 <b>Chapter 3</b>	 <b>58</b>
Table 3.1: Lack of relationship between <sup>1</sup> H NMR NH shift and pK <sub>BH+</sub>	<b>77</b>
Table 3.2: Relative basicity of quino[7,8-h]quinolines	<b>78</b>
Table 3.3: Important bond lengths and angles associated with the hydrogen bonding of H2 and H2B in [H( <b>323</b> )] [BF <sub>4</sub> ]	<b>80</b>
Figure 3.1: Potential sites for modification of on quino[7,8-h]quinoline	<b>58</b>
Figure 3.2: Computer model showing potential encapsulation of beryllium through 2,11 substitution of acetic acid moieties on quino[7,8-h]quinoline	<b>59</b>
Figure 3.3: Tautomerism of quinolin-4-ol, <b>302</b>	<b>61</b>
Figure 3.4: Crystal structure of <b>L4</b> showing the bridging proton, H9AA	<b>62</b>
Figure 3.5: Expanded crystal structure of <b>L4</b> showing the bonds with single and double bond character	<b>63</b>
Figure 3.6: Crystal packing in <b>L4</b>	<b>64</b>
Figure 3.7: Crystal structure of <b>L7</b>	<b>66</b>
Figure 3.8: Hydrogen bonding and edge to face $\pi$ packing interactions in <b>L7</b>	<b>67</b>
Figure 3.9: Crystal structure of [H( <b>L7</b> )] [BF <sub>4</sub> ]	<b>68</b>
Figure 3.10: Crystal packing of [H( <b>L7</b> )] [BF <sub>4</sub> ]	<b>68</b>

Figure 3.11: Hydrogen bonding in methyl 2-aminobenzoate, <b>304</b>	<b>69</b>
Figure 3.12: Compounds; (a) <b>L7</b> , (b) [H( <b>L7</b> )] $[\text{BF}_4]$ , (c) <b>L8</b> , (d) [H( <b>L8</b> )] $[\text{BF}_4]$ , viewed in the dark under a long wave 385 nm UV lamp	<b>70</b>
Figure 3.13: Molecular orbitals associated with the $\pi - \pi^*$ transition for [H( <b>L7</b> )] $[\text{BF}_4]$	<b>71</b>
Figure 3.14: Molecular orbitals associated with the $\pi - \pi^*$ transition for [H( <b>L8</b> )] $[\text{BF}_4]$	<b>71</b>
Figure 3.15: $^1\text{H}$ NMR of the nitrated quinolino[7,8-h]quinoline, <b>L9</b>	<b>72</b>
Figure 3.16: Crystal structure of <b>L11</b>	<b>74</b>
Figure 3.17: Crystal packing of <b>L11</b>	<b>75</b>
Figure 3.18: Proton sponges with different chemical environments	<b>77</b>
Figure 3.19: Crystal structure of [H( <b>L13</b> )] $[\text{BF}_4]$ showing H2 close contacts	<b>80</b>
Figure 3.20: Crystal packing of [H( <b>L13</b> )] $[\text{BF}_4]$	<b>81</b>
Figure 3.21: Crystal structure of [H( <b>L3</b> )] $[\text{BF}_4]$ with a long range contact to a $\text{BF}_4^-$ anion	<b>82</b>
Figure 3.22: 4-(4-tert-Butylphenoxy)-9-chloroquinolino[7,8-h]quinoline, <b>L5</b>	<b>86</b>
Scheme 3.1: General scheme for the synthesis of substituted <b>301</b>	<b>60</b>
Scheme 3.2: Synthesis of 9-(4-tert-butylphenoxy)quinolino[7,8-h]quinolin- 4(1H)-one, <b>L4</b>	<b>60</b>
Scheme 3.3: Synthesis of 4-(4-tert-butylphenoxy)-9- chloroquinolino[7,8-h]quinoline, <b>L5</b>	<b>64</b>
Scheme 3.4: Synthesis of (E)-N-(9-chloroquinolino[7,8-h]quinolin-4(1H)-ylidene)- 4-methylaniline, <b>L6</b>	<b>65</b>
Scheme 3.5: Synthesis of (E)-N-p-tolyl-9-(p-tolylimino)-9,12-dihydroquinolino- [7,8-h]quinolin-4-amine, <b>L7</b>	<b>65</b>
Scheme 3.6: Synthesis of (E)-methyl 2-(9-(o-tolylamino)quinolino[7,8-h]quinolin- 4(1H)-ylideneamino)benzoate, <b>L8</b>	<b>69</b>
Scheme 3.7: Attempted synthesis of the asymmetrically substituted <b>305</b>	<b>72</b>
Scheme 3.8: Synthesis of 4,9-dichloro-6,7-dinitroquinolino[7,8-h]quinoline, <b>L9</b>	<b>72</b>
Scheme 3.9: Synthesis of 9-oxo-9,12-dihydroquinolino[7,8-h]quinoline-4- sulfonic acid, <b>L10</b>	<b>73</b>
Scheme 3.10: Synthesis of 4,9-dimethoxyquino[7,8-h]quinoline, <b>L11</b>	<b>74</b>
Scheme 3.11: General scheme for the synthesis of alkyl-substituted <b>307</b>	<b>75</b>

Scheme 3.12: Proposed generalised Suzuki coupling reaction with <b>L12</b>	<b>76</b>
Scheme 3.13: Synthesis of dimethyl 4,9-dichloroquinolino[7,8-h]quinoline-2,11-dicarboxylate, <b>L13</b>	<b>79</b>
Scheme 3.14: Proposed ester hydrolysis of <b>L13</b>	<b>82</b>
Scheme 3.15: Proposed synthesis of 2,2'-(4,9-dichloroquinolino[7,8-h]quinoline-2,11-diyl)diacetonitrile, <b>315</b>	<b>83</b>
Scheme 3.16: Proposed synthesis of 2,2'-(4,9-dichloroquinolino[7,8-h]quinoline-2,11-diyl)diacetic acid, <b>316</b>	<b>83</b>
Scheme 3.17: Proposed limitation of side reactions through substitution of the chlorides on <b>317</b>	<b>84</b>
Scheme 3.18: Generalised tautomerised product when oxygen-containing groups were substituted	<b>86</b>
Scheme 3.19: Generalised tautomerised product when anilines were substituted	<b>87</b>
<b>Chapter 4</b>	<b>88</b>
Table 4.1: Comparison of the $\pi - \pi^*$ transitions and charge transfer peaks for quino[7,8-h]quinolines	<b>101</b>
Table 4.2: Comparison of bond parameters for the B(III) ion between the crystal structure and calculated models	<b>101</b>
Table 4.3: Calculation of relative quantum yields, $\Phi_{F(X)}$	<b>109</b>
Table 4.4: Related bands for the SERS and calculated Raman spectra of $[\text{BF}_2(\mathbf{L1})][\text{BF}_4]$	<b>110</b>
Table 4.5: NMR analysis of beryllium complexes with <b>L1</b>	<b>118</b>
Table 4.6: Major structural parameters for the geometry of the Cu(II) ion in $[\text{Cu}(\mathbf{L1})(\text{CH}_3\text{CN})_3][(\text{ClO}_4)_2]$	<b>126</b>
Table 4.7: Major structural parameters for the geometry of the Cu(II) ion in $[\text{Cu}(\mathbf{L2})(\text{CH}_3\text{CN})_3][(\text{ClO}_4)_2]$	<b>129</b>
Table 4.8: ESR data for the copper complexes of <b>L1</b> and <b>L2</b>	<b>131</b>
Table 4.9: Atom distances to relate the size-fit of various cations for <b>L1</b>	<b>130</b>
Figure 4.1: Example of a boron-dipyrromethene complex with a high quantum yield	<b>88</b>

Figure 4.2: Neutral nitrogen donor ligands with boron complexes; 2,2'-bipyridine, 1,10-phenanthroline, and 1,8-bis(dimethylamino)naphthalene respectively	<b>89</b>
Figure 4.3: Perspective view of the crystal structure of [Pt(L1)Cl <sub>2</sub> ]	<b>89</b>
Figure 4.4: 4,9-Dichloroquino[7,8-h]quinoline, L1	<b>90</b>
Figure 4.5: Side view of the crystal structure of [BF <sub>2</sub> (L1)][BF <sub>4</sub> ]	<b>91</b>
Figure 4.6: Top view of the crystal structure of [BF <sub>2</sub> (L1)][BF <sub>4</sub> ]	<b>91</b>
Figure 4.7: Packing within the structure of [BF <sub>2</sub> (L1)][BF <sub>4</sub> ]	<b>92</b>
Figure 4.8: Quino[7,8-h]quinoline, L2	<b>93</b>
Figure 4.9: Side view of the crystal structure of [BF <sub>2</sub> (L2)][BF <sub>4</sub> ]	<b>93</b>
Figure 4.10: Top view of the crystal structure of [BF <sub>2</sub> (L2)][BF <sub>4</sub> ]	<b>94</b>
Figure 4.11: Packing within the structure of [BF <sub>2</sub> (L2)][BF <sub>4</sub> ]	<b>95</b>
Figure 4.12: Ligands which did not show good coordination to B(III)	<b>96</b>
Figure 4.13: UV-Vis spectra of [BF <sub>2</sub> (L2)][BF <sub>4</sub> ] and [BF <sub>2</sub> (L1)][BF <sub>4</sub> ] showing the $\pi - \pi^*$ transitions at 10 <sup>-4</sup> M	<b>99</b>
Figure 4.14: UV-Vis spectra of [BF <sub>2</sub> (L2)][BF <sub>4</sub> ] and [BF <sub>2</sub> (L1)][BF <sub>4</sub> ] showing the charge transfer peak for [BF <sub>2</sub> (L1)][BF <sub>4</sub> ] at 10 <sup>-6</sup> M	<b>100</b>
Figure 4.15: UV-Vis spectra of L1 and [H(L1)][BF <sub>4</sub> ] showing the $\pi - \pi^*$ transitions	<b>100</b>
Figure 4.16: Comparison between the IR spectra of [BF <sub>2</sub> (L1)][BF <sub>4</sub> ]; measured as KBr disc, OLYP and B3LYP	<b>102</b>
Figure 4.17: Comparison between the IR spectra of L1; measured as KBr disc, OLYP and B3LYP	<b>103</b>
Figure 4.18: Comparison between the UV-Vis spectra of [BF <sub>2</sub> (L1)][BF <sub>4</sub> ]; measured in MeCN at 10 <sup>-6</sup> M, OLYP and B3LYP	<b>104</b>
Figure 4.19: Comparison between the UV-Vis spectra of L1; measured in MeCN, OLYP and B3LYP	<b>104</b>
Figure 4.20: Normalised absorption and emission spectra of [BF <sub>2</sub> (L1)][BF <sub>4</sub> ]	<b>105</b>
Figure 4.21: Molecular orbitals associated with the fluorescence for [BF <sub>2</sub> (L1)][BF <sub>4</sub> ]	<b>106</b>
Figure 4.22: Normalised absorption and emission spectra of [H(L1)][BF <sub>4</sub> ]	<b>107</b>
Figure 4.23: Molecular orbitals associated with the fluorescence for [H(L1)][BF <sub>4</sub> ]	<b>108</b>
Figure 4.24: Raman spectra of [BF <sub>2</sub> (L1)][BF <sub>4</sub> ]; calculated and SERS	<b>110</b>
Figure 4.25: Coordination of beryllium to 2,2'-bipyridine	<b>111</b>



Figure 4.26: Proton sponge ligands tested for beryllium coordination	<b>112</b>
Figure 4.27: 4,9-Dichloroquino[7,8-h]quinoline, <b>L1</b>	<b>113</b>
Figure 4.28: Normalised absorption and emission spectra at $10^{-5}$ M of neutral <b>L1</b> and after BeSO <sub>4</sub> or H <sub>2</sub> SO <sub>4</sub> addition	<b>113</b>
Figure 4.29: Change in UV-Vis spectrum at $10^{-5}$ M of neutral <b>L1</b> and after BeSO <sub>4</sub> or H <sub>2</sub> SO <sub>4</sub> addition	<b>114</b>
Figure 4.30: Calculated distribution of beryllium hydroxo species at C <sub>Be</sub> = 0.002 M	<b>115</b>
Figure 4.31: Normalised absorption and emission spectra at $10^{-5}$ M of neutral <b>L1</b> and after BeSO <sub>4</sub> addition in DMF and NEt <sub>3</sub>	<b>116</b>
Figure 4.32: Shift in UV-Vis spectrum at $10^{-5}$ M of neutral <b>L1</b> and after BeSO <sub>4</sub> addition or simply heating <b>L1</b> in DMF and NEt <sub>3</sub>	<b>117</b>
Figure 4.33: <sup>9</sup> Be NMR shift of <b>L1</b> coordinated to beryllium and BeSO <sub>4</sub> in DMF / NEt <sub>3</sub>	<b>118</b>
Figure 4.34: Quino[7,8-h]quinoline, <b>L2</b>	<b>119</b>
Figure 4.35: 1,8-bis(Dimethylamino)naphthalene, <b>L3</b>	<b>119</b>
Figure 4.36: 9-(4-tert-Butylphenoxy)quinolino[7,8-h]quinolin-4(1H)-one, <b>L4</b>	<b>120</b>
Figure 4.37: 4-(4-tert-butylphenoxy)-9-chloroquinolino[7,8-h]quinoline, <b>L5</b>	<b>120</b>
Figure 4.38: The broad <sup>9</sup> Be NMR shift for the reaction mixture of beryllium and <b>L5</b> in DMF / NEt <sub>3</sub>	<b>120</b>
Figure 4.39: Shift in UV-Vis spectrum at $10^{-5}$ M of neutral <b>L5</b> and after BeSO <sub>4</sub> addition in DMF and NEt <sub>3</sub>	<b>121</b>
Figure 4.40: Normalised absorption and emission spectras at $10^{-5}$ M of neutral <b>L5</b> and after BeSO <sub>4</sub> addition in DMF and NEt <sub>3</sub>	<b>121</b>
Figure 4.41: Proton sponges with tautomers incapable of coordinating to Be(II)	<b>122</b>
Figure 4.42: Metal complexes with <b>L1</b>	<b>123</b>
Figure 4.43: Perspective view of the crystal structure of [Cu( <b>L1</b> )(CH <sub>3</sub> CN) <sub>3</sub> ][(ClO <sub>4</sub> ) <sub>2</sub> ]	<b>125</b>
Figure 4.44: Space-filling diagram showing a perchlorate stabilising the acetonitriles	<b>126</b>
Figure 4.45: Crystal packing of [Cu( <b>L1</b> )(CH <sub>3</sub> CN) <sub>3</sub> ][(ClO <sub>4</sub> ) <sub>2</sub> ]	<b>127</b>
Figure 4.46: UV-Vis of [Cu( <b>L1</b> )(CH <sub>3</sub> CN) <sub>3</sub> ][(ClO <sub>4</sub> ) <sub>2</sub> ] and copper perchlorate in acetonitrile	<b>127</b>
Figure 4.47: Summary of energy ranges for closely related CuN <sub>x</sub> chromophores	

with different stereochemistries	<b>128</b>
Figure 4.48: Perspective view of the crystal structure of [Cu( <b>L2</b> )(CH <sub>3</sub> CN) <sub>3</sub> ][(ClO <sub>4</sub> ) <sub>2</sub> ]	<b>129</b>
Figure 4.49: Crystal packing of [Cu( <b>L2</b> )(CH <sub>3</sub> CN) <sub>3</sub> ][(ClO <sub>4</sub> ) <sub>2</sub> ]	<b>130</b>
Figure 4.50: UV-Vis of [Cu( <b>L2</b> )(CH <sub>3</sub> CN) <sub>3</sub> ][(ClO <sub>4</sub> ) <sub>2</sub> ] and copper perchlorate in acetonitrile	<b>131</b>
Figure 4.51: Atoms used to relate the size-fit of various cations for quino[7,8-h]quinolines	<b>132</b>
Figure 4.52: Atomic motion relative to cation size	<b>132</b>
Figure 4.53: Coordination of boron trifluoride to quino[7,8-h]quinoline	<b>134</b>
Figure 4.54: Coordination of beryllium hydrate to benzo[h]quinolin-10-ol	<b>135</b>
Figure 4.55: Inactivation of quino[7,8-h]quinoline by protonation	<b>135</b>
 <b>Chapter 5</b>	 <b>137</b>
Figure 5.1: 2-(6-(Dipyridin-2-ylmethyl)pyridin-2-yl)phenol, <b>501</b>	<b>137</b>
Figure 5.2: A related four-coordinate ligand to <b>501</b>	<b>138</b>
Figure 5.3: Computer model of beryllium coordinated to <b>501</b>	<b>138</b>
Figure 5.4: 2-(Dipyridin-2-ylmethyl)quinoline-8-carboxylic acid, <b>502</b>	<b>139</b>
Figure 5.5: Computer model of beryllium coordinated to <b>502</b>	<b>139</b>
Figure 5.6: Range of tetra-coordinate amine-capped ligands	<b>140</b>
Figure 5.7: Computer model of beryllium coordinated to <b>L17</b>	<b>140</b>
Figure 5.8: Disconnection of 2-(6-(dipyridin-2-ylmethyl)pyridin-2-yl)phenol, <b>501</b>	<b>141</b>
Figure 5.9: Proposed model for external chelations in substituted phenylpyridines leading to chloride substitution at the 2-position	<b>142</b>
Figure 5.10: Dipyridin-2-ylamine, <b>517</b>	<b>145</b>
Figure 5.11: COSY of 6-(2-methoxyphenyl)-N,N-di(pyridin-2-yl)pyridin- 2-amine, <b>518</b>	<b>147</b>
Figure 5.12: HMQC of 6-(2-methoxyphenyl)-N,N-di(pyridin-2-yl)pyridin- 2-amine, <b>518</b>	<b>148</b>
Figure 5.13: <sup>1</sup> H NMR of 2-(6-(dipyridin-2-ylamino)pyridin-2-yl)phenol, <b>L14</b> showing the deshielded proton at 12.55 ppm.	<b>150</b>

Figure 5.14: 2-Chloro-3-(trifluoromethyl)quinoline-8-carboxylic acid, <b>520</b>	<b>151</b>
Figure 5.15: <sup>1</sup> H NMR of the trace amount of <b>525</b> (A) and the side-product (B) isolated in Scheme 5.19	<b>155</b>
Figure 5.16: <sup>1</sup> H NMR of 2-chloroquinoline-8-carboxylic acid, <b>519</b>	<b>156</b>
Figure 5.17: Successfully synthesised 2-(6-(dipyridin-2-ylamino)pyridin-2-yl)phenol, <b>L14</b>	<b>160</b>
Figure 5.18: Variety of amine-capped tetra-coordinate ligands	<b>163</b>
Figure 5.19: COSY of 2-(((2-hydroxybenzyl)(quinolin-8-yl)amino)methyl)-4-nitrophenol, <b>L20</b>	<b>165</b>
Figure 5.20: HMQC of 2-(((2-hydroxybenzyl)(quinolin-8-yl)amino)methyl)-4-nitrophenol, <b>L20</b>	<b>166</b>
Figure 5.21: Successfully synthesised 2-(6-(dipyridin-2-ylamino)pyridin-2-yl)phenol, <b>L14</b>	<b>168</b>
Figure 5.22: Unsuccessfully synthesised 2-(dipyridin-2-ylmethyl)quinoline-8-carboxylic acid, <b>502</b>	<b>168</b>
Figure 5.23: Variety of amine-capped tetra-coordinate ligands	<b>169</b>
Scheme 5.1: Synthesis of 2-chloro-6-(2-methoxyphenyl)pyridine, <b>509</b>	<b>141</b>
Scheme 5.2: Synthesis of 2-(2-pyridylmethyl)pyridine, <b>504</b>	<b>142</b>
Scheme 5.3: Attempted synthesis of 2-(dipyridin-2-ylmethyl)-6-(2-methoxyphenyl)pyridine, <b>512</b>	<b>142</b>
Scheme 5.4: Synthesis of 2-bromo-6-(2-methoxyphenyl)pyridine, <b>513</b>	<b>143</b>
Scheme 5.5: Attempted synthesis of 2-(dipyridin-2-ylmethyl)-6-(2-methoxyphenyl)pyridine, <b>512</b>	<b>143</b>
Scheme 5.6: Synthesis of 2,2'-(bromomethylene)dipyridine, <b>514</b>	<b>144</b>
Scheme 5.7: Attempted synthesis of 2-(dipyridin-2-ylmethyl)-6-(2-methoxyphenyl)pyridine, <b>512</b>	<b>144</b>
Scheme 5.8: Attempted synthesis of (6-(2-methoxyphenyl)pyridin-2-yl)dipyridin-2-ylmethanol, <b>516</b>	<b>144</b>
Scheme 5.9: Proposed synthesis of 6-(2-methoxyphenyl)-N,N-di(pyridin-2-yl)pyridin-2-amine, <b>518</b>	<b>145</b>
Scheme 5.10: Synthesis of 6-(2-methoxyphenyl)-N,N-di(pyridin-2-yl)pyridin-	

2-amine, <b>518</b>	<b>146</b>
Scheme 5.11: Synthesis of 2-(6-(dipyridin-2-ylamino)pyridin-2-yl)phenol, <b>L14</b>	<b>149</b>
Scheme 5.12: Disconnection of 2-(dipyridin-2-ylmethyl)quinoline-8-carboxylic acid, <b>502</b>	<b>151</b>
Scheme 5.13: Proposed synthesis of 2-chloroquinoline-8-carboxylic acid, <b>519</b>	<b>151</b>
Scheme 5.14: Proposed synthesis of ethyl 2-chloroquinoline-8-carboxylate, <b>525</b>	<b>152</b>
Scheme 5.15: Proposed synthesis of methyl 2-chloroquinoline-8-carboxylate, <b>528</b>	<b>152</b>
Scheme 5.16: Proposed synthesis of ethyl 2-(dipyridin-2-ylmethyl)quinoline-8-carboxylate, <b>529</b>	<b>152</b>
Scheme 5.17: Synthesis of N-(dipyridin-2-yl(quinolin-2-yl)methyl)acetamide, <b>532</b>	<b>153</b>
Scheme 5.18: Synthesis of 2-(2-pyridylmethyl)pyridine, <b>504</b>	<b>153</b>
Scheme 5.19: Synthesis of 8-bromo-2-chloroquinoline, <b>524</b>	<b>154</b>
Scheme 5.20: Unsuccessful esterification of <b>525</b>	<b>154</b>
Scheme 5.21: Synthesis of 2-chloro-3-(trifluoromethyl)quinoline-8-carboxylic acid, <b>520</b>	<b>155</b>
Scheme 5.22: Synthesis of 2-chloroquinoline-8-carboxylic acid, <b>519</b>	<b>155</b>
Scheme 5.23: Synthesis of methyl 2-chloroquinoline-8-carboxylate, <b>535</b>	<b>156</b>
Scheme 5.24: Attempted synthesis of methyl 2-oxo-1,2-dihydroquinoline-8-carboxylate, <b>527</b>	<b>157</b>
Scheme 5.25: Attempted synthesis of 2-(dipyridin-2-ylmethyl)quinoline-8-carboxylic acid, <b>502</b>	<b>157</b>
Scheme 5.26: Synthesis of 8-bromo-2-(dipyridin-2-ylmethyl)quinoline, <b>537</b>	<b>158</b>
Scheme 5.27: Attempted synthesis of 2-(dipyridin-2-ylmethyl)quinoline-8-carboxylic acid, <b>502</b>	<b>158</b>
Scheme 5.28: Synthesis of 2-chloroquinoline-8-carbonitrile, <b>538</b>	<b>159</b>
Scheme 5.29: Synthesis of 2-(dipyridin-2-ylmethyl)quinoline-8-carbonitrile, <b>539</b>	<b>159</b>
Scheme 5.30: Attempted synthesis of 2-(dipyridin-2-ylmethyl)quinoline-8-carboxylic acid, <b>502</b>	<b>159</b>
Scheme 5.31: Attempted synthesis of 2-(dipyridin-2-ylamino)quinoline-8-carboxylic acid, <b>540</b>	<b>160</b>
Scheme 5.32: Proposed synthesis of 2,8-dibromoquinoline, <b>541</b>	<b>160</b>

Scheme 5.33: Synthesis of 8-bromo-2-(dipyridin-2-ylmethyl)quinoline, <b>537</b>	<b>161</b>
Scheme 5.34: Proposed synthesis of 8-bromo-N,N-di(pyridin-2-yl)quinolin-2-amine, <b>542</b>	<b>161</b>
Scheme 5.35: Synthesis of the tetra-coordinate ligand, <b>547</b>	<b>162</b>
Scheme 5.36: Generalised Schiff base condensations for ligands <b>L15, L16, L17, L19, L20</b> and <b>L21</b>	<b>163</b>
Scheme 5.37: Generalised reaction scheme for tertiary amines <b>L15, L16, L17, L19, L20</b> and <b>L21</b>	<b>164</b>
Scheme 5.38: Acid hydrolysis of <b>549</b> to achieve <b>L17</b>	<b>167</b>
Scheme 5.39: Mannich reaction to achieve <b>L18</b>	<b>167</b>
 <b>Chapter 6</b>	 <b>167</b>
Table 6.1: <sup>9</sup> Be NMR shifts and line widths of tetra-coordinate ligands in a number of different solvents	<b>175</b>
Table 6.2: Calculated <sup>9</sup> Be NMR shifts for tetra-coordinate ligands	<b>176</b>
Table 6.3: Calculated and experimental maximum absorption wavelengths	<b>181</b>
Table 6.4: Comparison of the angle of intersection between the aromatic phenol rings	<b>186</b>
Table 6.5: Major structural parameters for the geometry of the Cu(II) ion in [Cu <sub>2</sub> ( <b>L16</b> ) <sub>2</sub> ]	<b>196</b>
Table 6.6: Major structural parameters for the geometry of the Zn(II) ion in [Zn <sub>2</sub> ( <b>L16</b> ) <sub>2</sub> ]	<b>199</b>
Figure 6.1: Crystal structures of [Cu <sub>2</sub> ( ' <b>L16</b> ' ) <sub>2</sub> ] and [Cu( ' <b>L16</b> ' H)(OAc)]	<b>171</b>
Figure 6.2: 2-(((2-Hydroxybenzyl)(2-(pyridin-2-yl)ethyl)amino)methyl)-4-nitrophenol, <b>L15</b>	<b>172</b>
Figure 6.3: Crystal structure of [Fe( ' <b>L18</b> ' )(bipy)]	<b>172</b>
Figure 6.4: 2-(((2-Hydroxybenzyl)(2-hydroxyphenyl)amino)methyl)-4-nitrophenol, <b>L19</b>	<b>173</b>
Figure 6.5: Previously unreported tertiary amine ligands	<b>173</b>
Figure 6.6: 2-(((2-hydroxybenzyl)(2-phenylquinolin-8-yl)amino)methyl)-4-nitrophenol, <b>L21</b>	<b>174</b>

Figure 6.7: $^9\text{Be}$ NMR shift of <b>L18</b> coordinated to beryllium in DMF	175
Figure 6.8: Tetra-coordinate ligands with well correlated $^9\text{Be}$ NMR shifts	177
Figure 6.9: Tetra-coordinate ligands with poorly correlated $^9\text{Be}$ NMR shifts	177
Figure 6.10: Optimised model of $[\text{Be}(\mathbf{L16})(\text{H}_2\text{O})]$	178
Figure 6.11: Change in UV-Vis spectrum at $10^{-5}$ M of neutral <b>L15</b> and after $\text{BeSO}_4$ addition	179
Figure 6.12: Change in UV-Vis spectrum at $10^{-5}$ M of neutral <b>L17</b> and after $\text{BeSO}_4$ addition	179
Figure 6.13: Change in UV-Vis spectrum at $10^{-5}$ M of neutral <b>L19</b> and after $\text{BeSO}_4$ addition	180
Figure 6.14: Change in UV-Vis spectrum at $10^{-5}$ M of neutral <b>L18</b> and after $\text{BeSO}_4$ addition	180
Figure 6.15: Normalised absorption and emission spectras at $10^{-5}$ M of neutral <b>L18</b> and after $\text{BeSO}_4$ addition in DMF and $\text{NEt}_3$	182
Figure 6.16: Normalised absorption and emission spectras at $10^{-5}$ M of neutral <b>L19</b> and after $\text{BeSO}_4$ addition in DMF and $\text{NEt}_3$	182
Figure 6.17: Flexible tetra-coordinate ligands with a single conformer upon beryllium coordination	183
Figure 6.18: Optimised model of $[\text{Be}(\mathbf{L17})]^-$ with anti geometry	183
Figure 6.19: 3,3',3''-nitrilotripropanoic acid, <b>601</b>	184
Figure 6.20: Crystal structure of $[\text{Be}(\mathbf{601})]^-$ with anti geometry	184
Figure 6.21: Strained four-coordinate ligands with two conformers upon beryllium coordination	184
Figure 6.22: Syn conformer (left) and anti conformer (right) of $[\text{Be}(\mathbf{L18})]^-$	185
Figure 6.23: Top view of the Syn conformer (left) and anti conformer (right) of $[\text{Be}(\mathbf{L18})]^-$	185
Figure 6.24: Molecular orbitals associated with the $\pi - \pi^*$ transition for $[\text{Be}(\mathbf{L15})]$ (anti conformer)	187
Figure 6.25: Molecular orbitals associated with the $\pi - \pi^*$ transition for $[\text{Be}(\mathbf{L17})]^-$ (anti conformer)	187
Figure 6.26: Molecular orbitals associated with the $\pi - \pi^*$ transition	

for [Be( <b>L18</b> )] <sup>-</sup> (syn conformer)	<b>188</b>
Figure 6.27: Molecular orbitals associated with the $\pi - \pi^*$ transition for [Be( <b>L18</b> )] <sup>-</sup> (anti conformer)	<b>189</b>
Figure 6.28: Molecular orbitals associated with the $\pi - \pi^*$ transition for [Be( <b>604</b> )] <sup>-</sup> (syn conformer)	<b>190</b>
Figure 6.29: Second possible minimised structure of [Be( <b>L19</b> )] <sup>-</sup>	<b>190</b>
Figure 6.30: Molecular orbitals associated with the $\pi - \pi^*$ transition for [Be( <b>L19</b> )] <sup>-</sup>	<b>191</b>
Figure 6.31: Water-soluble encapsulating ligands	<b>192</b>
Figure 6.32: Change in UV-Vis spectrum at $10^{-5}$ M of neutral <b>L18</b> and after BeSO <sub>4</sub> addition in H <sub>2</sub> O	<b>192</b>
Figure 6.33: Change in UV-Vis spectrum at $10^{-5}$ M of neutral <b>L17</b> and after BeSO <sub>4</sub> addition in H <sub>2</sub> O	<b>193</b>
Figure 6.34: Normalised absorption and emission spectras at $10^{-5}$ M of neutral <b>L18</b> and after BeSO <sub>4</sub> addition in H <sub>2</sub> O	<b>193</b>
Figure 6.35: Asymmetric unit for the crystal of [Cu <sub>2</sub> ( <b>L16</b> ) <sub>2</sub> ]	<b>195</b>
Figure 6.36: The bridged dimer [Cu <sub>2</sub> ( <b>L16</b> ) <sub>2</sub> ]	<b>195</b>
Figure 6.37: UV-Vis of [Cu <sub>2</sub> ( <b>L16</b> ) <sub>2</sub> ] at $10^{-4}$ M showing metal d – d transition in MeOH	<b>197</b>
Figure 6.38: UV-Vis of [Cu <sub>2</sub> ( <b>L16</b> ) <sub>2</sub> ] at $10^{-5}$ M showing ligand $\pi - \pi^*$ transitions in MeOH	<b>197</b>
Figure 6.39: Crystal structure of [Zn <sub>2</sub> ( <b>L16</b> ) <sub>2</sub> ]	<b>198</b>
Figure 6.40: Perspective view of [Zn <sub>2</sub> ( <b>L16</b> ) <sub>2</sub> ]	<b>199</b>
Figure 6.41: UV-Vis of [Zn <sub>2</sub> ( <b>L16</b> ) <sub>2</sub> ] at $10^{-5}$ M showing ligand $\pi - \pi^*$ transitions in MeOH	<b>200</b>
Figure 6.42: Water-soluble and fluorescent encapsulating ligand, <b>L18</b>	<b>200</b>
Figure 6.43: Water-soluble and fluorescent encapsulating ligand, <b>L18</b>	<b>202</b>
<b>Chapter 7</b>	<b>203</b>
Figure 7.1: Benzo[h]quinolin-10-ol, <b>701</b>	<b>203</b>
Figure 7.2: Quinolino[7,8-h]quinoline, <b>L2</b>	<b>203</b>

Figure 7.3: 2,2'-(pyridine-2,6-diyl)diphenol, <b>702</b>	<b>204</b>
Figure 7.4: 2-(bis(2-Hydroxy-3,5-dimethylbenzyl)amino)acetic acid, <b>L18</b>	<b>205</b>
Figure 7.5: A representation of the lack of selectivity of simple bidentate ligands	<b>206</b>
Figure 7.6: Successfully synthesised 2-(6-(dipyridin-2-ylamino)pyridin-2-yl)phenol, <b>L14</b>	<b>206</b>
Figure 7.7: A representation of the potential selectivity of the encapsulating ligand <b>L14</b>	<b>207</b>