

Table of Contents

Acknowledgements	iii
Abstract	iv
Résumé	v
List of Figures	ix
List of Schemes	xi
List of Tables	xiii
Introduction	1
I. Carbon dioxide in chemical synthesis	1
II. Activation of carbon dioxide	2
III. Thesis aims and objectives	6
Chapter 1 N-Formylation of Amines with Ionic Liquid Catalysts	8
1.1 Introduction	8
1.2 Ionic liquid catalysts	10
1.3 Proposed mechanism	11
1.4 Scope and selectivity	13
1.5 Conclusions	15
Chapter 2 Mechanistic Study of the N-Formylation of Amines with CO ₂	16
2.1 Introduction	16
2.2 Pathway 1 and CO ₂ -hydrosilane chemical equilibria	18
2.3 Pathway 2 and role of the amine	23
2.4 Pathway 3 and silylcarbamate intermediate	27
2.5 Conclusions	32
Chapter 3 Critical Parameters of N-Formylation Salt Catalysts	33
3.1 Introduction	33
3.2 The ionic liquid cation	34
3.3 The ionic liquid anion	37
3.4 Conclusions	41
Chapter 4 Quinazoline-2,4(1H,3H)-dione Synthesis	42
4.1 Introduction	42
4.2 The ionic liquid cation	43
4.3 The ionic liquid anion	44
4.4 Conclusion	47
Chapter 5 Basicity of Organocatalysts in CO ₂ Reactions with Amines	48
5.1 Introduction	48
5.2 Reductive C-N bond forming reactions	49

5.2.1 N-formylation	50
5.2.2 N-methylation	55
5.2.3 Aminals	58
5.2.4 Formamides, N-methylamines or aminals	58
5.3 Reductive cyclization reactions	59
5.4 Non-reductive C-N bond forming reactions	60
5.4.1 Quinazoline-2,4-diones	61
5.4.2 Cyclic carbamates	64
5.4.3 Cyclic and non-cyclic urea derivatives	66
5.5 Concluding remarks	68
Summary and Outlook	69
Annex 1 N-Formylation of Amines with Ionic Liquid Catalysts	71
1.1. General procedures	71
1.2. NMR study of PhSiH ₃ with [TBA]F	71
1.3. N-formylation product characterization	73
Annex 2 Mechanistic Study of the N-Formylation of Amines with CO ₂	79
2.1. General catalytic procedure	79
2.2. NMR spectra and kinetic measurements	79
2.2.1. Reaction of CO ₂ with PhSiH ₃ catalysed by [TBA][OAc]	79
2.2.2. Reaction of CO ₂ with PhSiH ₃	83
2.2.3. Reaction of CO ₂ with (EtO) ₃ SiH catalysed by [TBA][OAc]	84
2.2.4. reaction of CO ₂ with (EtO) ₃ SiH catalysed by [TBA][HCO ₂]	89
2.2.5. Reaction of N-methylaniline with CO ₂ and PhSiH ₃ catalysed by [TBA][OAc]	91
2.2.6. Reaction of N-methylaniline with CO ₂ and PhSiH ₃	94
2.2.7. Reaction of N-methylaniline with CO ₂ and (EtO) ₃ SiH catalysed by [TBA][OAc]	95
2.2.8. Reactions of p-substituted anilines with CO ₂ and (EtO) ₃ SiH catalysed by [TBA][OAc]	99
2.2.9. Reactions of benzylamine with CO ₂ and (EtO) ₃ SiH catalysed by [TBA][OAc]	104
2.2.10. Reaction of benzylamine with CO ₂ and PhSiH ₃ catalysed by [TBA][OAc]	117
2.2.11. Synthesis of (EtO) ₃ SiOAc	118
Annex 3 Critical Parameters of N-Formylation Salt Catalysts	120
3.1. Standard catalyst test procedure (Chloride salts)	120
3.2. Standard catalyst test procedure (Tetra-n-butylammonium salts)	120
3.3. Electrospray ionization mass spectrometry (ESI-MS)	122
3.4. ESI-MS/MS fragmentation study of mixed IL clusters	125
3.5. Quantum chemical calculations	126
3.6. Ionic liquid synthesis and characterization	127
Annex 4 Quinazoline-2,4(1H,3H)-dione Synthesis	130

4.1. General procedures	130
4.2. Effect of water on the reaction rate	130
4.3. Ionic liquid synthesis and characterization	130
4.4. Measurement of quinazoline-2,4(1H,3H)-dione pK_a	134
References	135
Curriculum Vitae	153