

## Table of Contents

|   | <i>Page No.</i> |
|---|-----------------|
| Abstract.....   | i-vi            |
| Declaration.....  | vii             |
| Certificate of the Supervisor.....                                    | viii            |
| Certificate of the Co-Supervisor.....                                 | ix              |
| Certificate of the External Examiner and ODEC.....                    | ixa             |
| Acknowledgements.....   | x-xi            |
| Abbreviations and Symbols.....  | xii-xiv         |
| List of Schemes.....  | xv-xvi          |
| List of Figures.....  | xvii-xix        |
| List of Tables.....   | xx-xxi          |
| <br>  |                 |
| <b>Chapter 1. General Introduction</b>                                | <b>1-56</b>     |
| <b>1.1 Cu as a base–metal</b>   | 1-3             |
| <b>1.2 Cyanation reaction</b>   |                 |
| <b>1.2.1 Importance of cyanation</b>                                  | 3-4             |
| <b>1.2.2 The pioneers of cyanation reaction</b>                       | 4-6             |
| <b>1.2.3 Cyanating sources</b>  | 6-7             |
| <b>1.2.4 Cu-catalysis in cyanation reactions</b>                      | 8-22            |
| <b>1.3 The Chan–Lam cross–coupling reaction</b>                       | 23              |
| <b>1.3.1 The history of Chan-Lam cross-coupling</b>                   | 23-25           |
| <b>1.3.2 The arylating partner</b>                                    | 25-29           |
| <b>1.3.3 The nucleophile</b>  | 29-34           |
| <b>1.3.4 Important applications of Chan–Lam cross–coupling</b>        | 34-35           |
| <b>1.3.5 General mechanism of Chan–Lam cross–coupling</b>             | 35-37           |
| <b>1.4 Thesis overview and objectives</b>                             | 37              |
| <b>1.5 Bibliography</b>   | 38-56           |
| <br>  |                 |
| <b>Chapter 2. Nitromethane: An Alternative Organic Nitrile Source</b> | <b>57-84</b>    |
| <b>2.1 Introduction</b>   | 57              |
| <b>2.2 Background</b>   | 58-60           |
| <b>2.3 Results and Discussion</b>                                     | 60              |

|  |   |                |
|--|---|----------------|
| <b>2.3.1</b>   | Optimization of reaction conditions   | 60-62          |
| <b>2.3.2</b>   | Substrate scope study   | 62-63          |
| <b>2.3.3</b>   | Mechanistic study   | 63-65          |
| <b>2.3.4</b>   | Plausible mechanism   | 65-66          |
| <b>2.3.5</b>   | Computational study   | 66-70          |
| <b>2.3.6</b>   | Conclusion  | 71             |
| <b>2.3.7</b>   | Experimental section  | 71-73          |
| <b>2.3.8</b>   | Characterization data for aryl nitrile derivatives ( <b>13a-k</b> )                     | 73-76          |
| <b>2.3.9</b>   | Representative $^1\text{H}$ and $^{13}\text{C}$ NMR spectra of aryl nitrile derivatives | 77-78          |
| <b>2.4</b>   | Bibliography  | 79-84          |
| <b>Chapter 3. Dual Role of Ceric Ammonium Nitrate in cyanation reaction</b>                    |   | <b>85-111</b>  |
| <b>3.1</b>   | Introduction  | 89-90          |
| <b>3.2</b>   | Background  | 86-90          |
| <b>3.3</b>   | Results and Discussion  |                |
| <b>3.3.1</b>   | Optimization of reaction conditions   | 91-93          |
| <b>3.3.2</b>   | Substrate scope study   | 93-94          |
| <b>3.3.3</b>   | Mechanistic study   | 94-95          |
| <b>3.3.4</b>   | Plausible mechanism   | 96-97          |
| <b>3.3.5</b>   | Conclusion  | 97             |
| <b>3.3.6</b>   | Experimental section  | 98-101         |
| <b>3.3.7</b>   | NMR spectral analysis of aryl nitrile derivatives ( <b>23a-r</b> )                      | 101-105        |
| <b>3.3.8</b>   | Representative $^1\text{H}$ and $^{13}\text{C}$ NMR spectra of aryl nitrile derivatives | 106-107        |
| <b>3.4</b>   | Bibliography  | 108-111        |
| <b>Chapter 4. <i>N,N'</i>-dimethylurea as an auxiliary in Chan-Lam cross-coupling reaction</b> |   | <b>112-159</b> |
| <b>4.1</b>   | Introduction  | 112-113        |
| <b>4.2</b>   | Homogeneous catalysis in Chan-Lam cross-couplings                                       | 113-115        |
| <b>4.3</b>   | Urea as auxiliaries in homogeneous catalysis  | 115-117        |
| <b>4.4</b>   | Results and Discussion  | 117            |
| <b>4.4.1</b>   | Optimization of reaction conditions   | 118-120        |
| <b>4.4.2</b>   | Catalyst study  | 120-121        |
| <b>4.4.3</b>   | Substrate scope study   | 121-122        |

|  |   |                |
|--|---|----------------|
| <b>4.4.4</b>   | Chemosselectivity of the catalyst   | 122-125        |
| <b>4.4.5</b>   | Extension of scope of reaction  | 125-129        |
| <b>4.4.6</b>   | Applications  | 129-130        |
| <b>4.4.7</b>   | Plausible mechanism   | 130            |
| <b>4.4.8</b>   | Conclusion  | 131            |
| <b>4.4.9</b>   | Experimental section  | 131-134        |
| <b>4.4.10</b>  | Characterization data of the <i>N</i> -aryl derivatives                                       | 134-147        |
| <b>4.4.11</b>  | Representative $^1\text{H}$ and $^{13}\text{C}$ NMR spectra of the <i>N</i> -aryl derivatives | 148-150        |
| <b>4.5</b>   | Bibliography  | 151-159        |
| <b>Chapter 5. Copper(zero) nanoparticles in Chan-Lam cross-coupling reaction</b> |   | <b>160-211</b> |
| <b>5.1</b>   | Introduction  | 160            |
| <b>5.2</b>   | Heterogeneous catalysis in Chan-Lam cross-couplings   | 161-163        |
| <b>5.3</b>   | Results and Discussion  |                |
| <b>5.3.1</b>   | Characterization of the catalyst  | 163-168        |
| <b>5.3.2</b>   | Optimization of reaction conditions   | 168-169        |
| <b>5.3.3</b>   | Substrate scope study   | 169-170        |
| <b>5.3.4</b>   | Mechanism study   | 171            |
| <b>5.3.5</b>   | Plausible mechanism   | 171-174        |
| <b>5.3.6</b>   | Extension of scope of reaction  | 174-180        |
| <b>5.3.7</b>   | Conclusion  | 180            |
| <b>5.3.8</b>   | Experimental section  | 181-185        |
| <b>5.3.9</b>   | NMR spectral analysis of <i>N</i> -aryl nitrile derivatives                                   | 185-196        |
| <b>5.3.10</b>  | Representative $^1\text{H}$ and $^{13}\text{C}$ NMR spectra of <i>N</i> -aryl derivatives     | 197-199        |
| <b>5.4</b>   | Bibliography  | 200-211        |
| <b>Chapter 6. Conclusion &amp; Future Scope</b>                                  |   | <b>212-215</b> |
| <b>6.1</b>   | General conclusion  | 212            |
| <b>6.1.1</b>   | Significant findings of the performed cyanation reactions                                     | 212            |
| <b>6.1.2</b>   | Significant findings of the performed Chan-Lam cross-coupling reactions                       | 213            |
| <b>6.2</b>   | Future scope of the work  | 213-215        |

**Annexure A & B**

|                      |     |
|----------------------|-----|
| CheckCIF report      | a-d |
| List of Publications | e   |
| List of Conferences  | f   |