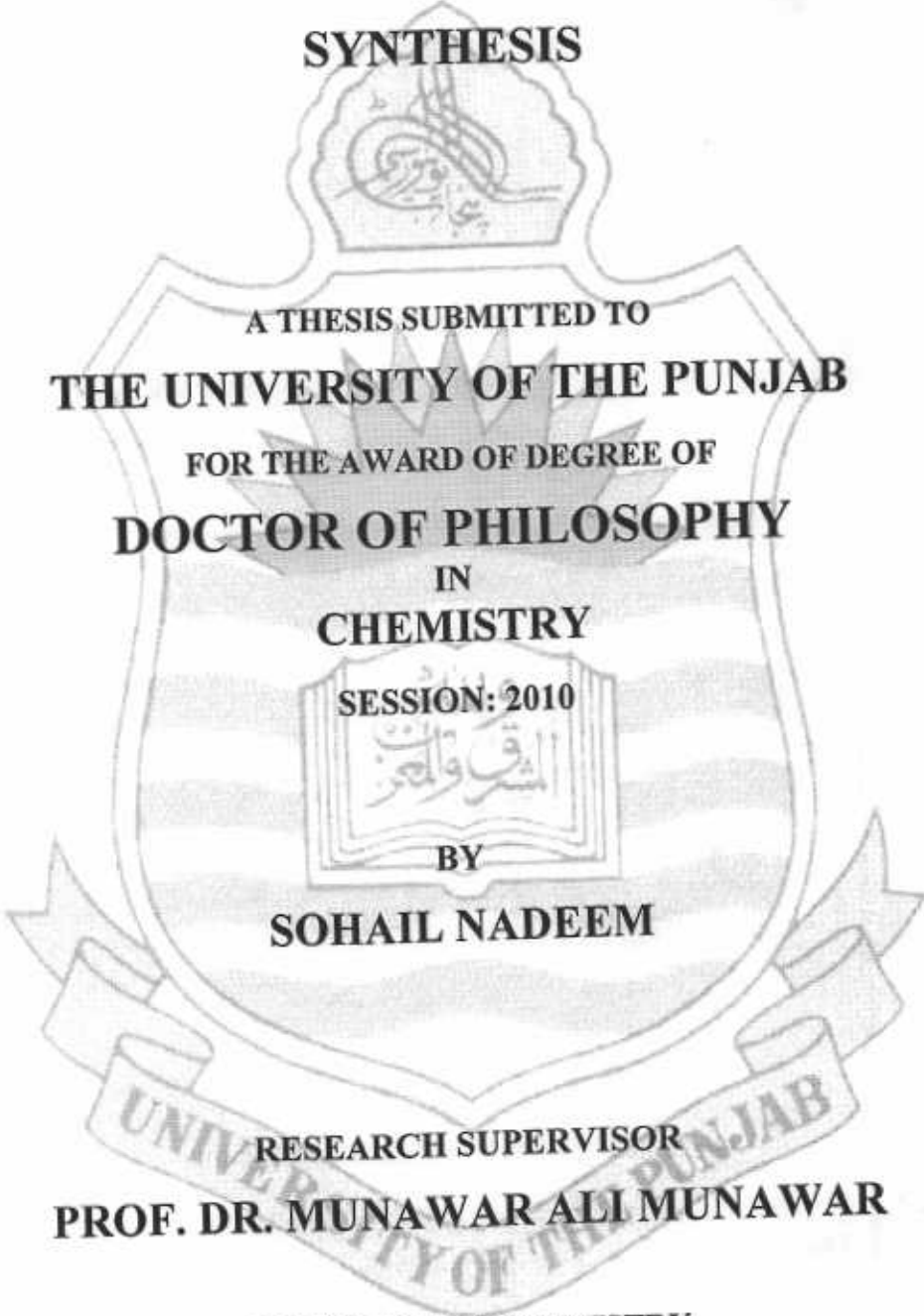


**SYNTHESIS OF IONIC LIQUIDS AND THEIR  
APPLICATIONS IN ORGANIC  
SYNTHESIS**



A THESIS SUBMITTED TO  
**THE UNIVERSITY OF THE PUNJAB**  
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BY

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*to my beloved mom...  
for supporting me throughout my life  
especially during this study  
and to someone special...  
thank you for waiting all this while.*

## DECLARATION

I declare that this thesis entitled "*SYNTHESIS OF IONIC LIQUIDS AND THEIR APPLICATIONS IN ORGANIC REACTIONS*" is the result of my own research work except as cited in references. The thesis has not been accepted for any degree and is not currently submitted in the candidature of any other degree.

Signature

.....

Name

: SOHAIL NADEEM


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: 27-12-2010

## CERTIFICATE

This is to certify that research work described in this thesis entitled "SYNTHESIS OF IONIC LIQUIDS AND THEIR APPLICATIONS IN ORGANIC SYNTHESIS" is the original work of Sohail Nadeem. We have personally gone through all the data/results/materials reported in this manuscript and certify to their correctness/authenticity. We further certify that the material included in this thesis has not been used in part or full for any manuscript already submitted or in process of submission in partial/complete fulfillment of the award of any other degree from any other institution. We also certify that Mr. Sohail Nadeem has fulfilled all the conditions and is qualified to submit the thesis in regard to the degree of philosophy in chemistry.

In our opinion this thesis is sufficient in terms of scope and quality for the award of degree of Doctor of Philosophy in Chemistry.

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Date : 27.12.2010 .....

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**Sohail Nadeem**

## LIST OF SYMBOLS / ABBREVIATIONS / NOTATION / TERMINOLOGY

$^{\circ}\text{C}$	degrees Celcius
$^{13}\text{C-NMR}$	Carbon nuclear magnetic resonance
$^1\text{H-NMR}$	Proton nuclear magnetic resonance
AA	Amino Acid
AAIL	Amino Acid Ionic Liquids
$\text{BF}_4$	tetrafluoroborate
BINAP	2,2'-bis(diphenylphosphino)-1,1'-binaphthyl
BMIM	Bmim - 1-butyl-3-methylimidazolium
BTI	benzothiazolium iodide
$\text{Bu}_4\text{NCl}$	Tetrabutylammonium chloride
$\text{CDCl}_3$	Chloroform- <i>d</i>
$\text{CF}_3\text{SO}_3$	trifluoromethanesulfonate
DMF	<i>N,N</i> -dimethylformamide
DMSO	Dimethylsulfoxide- <i>d6</i>
DSC	Differential Scanning Calorimetry
emim	1-ethyl-3-methylimidazolium
$\text{Et}_3\text{N}$	Triethylamine
GC	Gas Chromatography
HRMS	High resolution mass spectrometry.
hrs	hour(s)
Hz	Hertz (Frequency)
IR	Infrared (Spectroscopy)
m.p	melting point
MHz	Mega Hertz (10 <sup>6</sup> Hertz)
mmol	milli moles (10 <sup>-3</sup> moles)
$\text{NTf}_2$	Bis(trifluoromethylsulfonyl)imide
$\text{PF}_6$	hexafluorophosphate
ppm	parts per million (NMR)
PTFE	Poly Tetrafluoroethylene
RTIL	Room temperature ionic liquid
$\text{ScCO}_2$	Supercritical carbon dioxide
TFSA	Bis(trifluoromethanesulfonyl)amide
TGA	Thermogravimetric Analysis
XRD	X-Ray Diffraction
$\delta$	Delta (NMR)
TFA	trifluoroacetate

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## ABSTRACT

A series of thirteen benzothiazolium iodide salts (311-323a) have been prepared in solvent-free conditions by reacting equimolar quantities of the benzothiazole and alkyl halide at appropriate temperature (from room temperature to 150 °C). Three benzothiazolium iodide salts (321-323a) were successfully crystallized and their structures have been confirmed through XRD analysis. An additional fiftytwo benzothiazolium salts with  $[\text{BF}_4]^-$  (311-323b),  $[\text{PF}_6]^-$  (311-323c),  $[\text{CF}_3\text{SO}_3]^-$  (311-323d) and  $[\text{NTf}_2]^-$  (311-323e) anions were prepared via simple metathesis reactions from the iodide precursors with corresponding metal salts of the anions. Out of a total of sixtyfive prepared salts, fiftytwo were identified as ionic liquids, with melting points as low as 42 °C observed for dodecylbenzothiazolium bistrifluoromethanesulfonimide ( $[\text{C}_{12}\text{BT}][\text{Tf}_2\text{N}]$ ) (323e). Thermal analyses of all the prepared compounds have been performed with help of TGA and DSC instruments. The thermal stabilities of all the prepared salts were determined through TGA analysis. The melting points of most of the prepared salts were checked on DSC and some of the salts were checked by visual method. It was found that the benzothiazolium salts with the bis(trifluoromethanesulfonylimide) ( $[\text{Tf}_2\text{N}]^-$ ) anion (311-323f) have the greater stabilities over rest of the salts. The phase behaviour study of the  $[\text{C}_{11}\text{BT}]\text{I}-\text{AlCl}_3$  (322f) mixtures were carried out with the help of DSC to find the appropriate mole ratio of the aluminum chloride to the  $[\text{C}_{11}\text{BT}]\text{I}-\text{AlCl}_3$  mixture (Figure-12), the lowest melting point for the mixture (*i.e.* 22.5 °C at 0.5 mol% of  $\text{AlCl}_3$ ) were obtained from DSC analysis as mentioned in the curve in figure-12. After finding the appropriate mole ratios of  $[\text{C}_{11}\text{BT}]\text{I}-\text{AlCl}_3$  system the benzothiazolium based lewis acidic ionic liquid was used as promoter and solvent for the Friedel-Crafts acylation reactions. A total of nine compounds (330-338) were prepared successfully by using different acylating agents and substrates. These compounds have been characterized by the  $^1\text{H}$  NMR spectroscopic technique to confirm the structural parameters. The bis (trifluoromethanesulfonimide) based prepared ionic liquids were applied to Diels-Alder coupling reactions. Fruitful results have been obtained and the reaction of cyclopentadien with three dienophiles