CHAPTER III

Section A

Three component coupling reactions catalyzed by Liclo₄:
Synthesis of homoallylic amines
INTRODUCTION

Since last few decades Lewis acid promoted carbon-carbon bond forming reactions have been of great importance in organic synthesis because of their unique reactivity, selectivity and for the mild conditions used. While various kinds of Lewis acid catalyzed reactions are developed and many have been applied in industry. These reactions must be carried out under strictly anhydrous conditions and the presence of even a small amount of water inhibits the reaction, because most of the Lewis acids immediately react with water rather than the substrates and gets deactivated or decomposes. This fact has constrained the utility of Lewis acids.

The stereoselective addition of allylmetal reagents to aldehydes and imines is one of the most significant carbon carbon bond forming reactions in organic synthesis. Many organometallic reagents have been developed for this purpose, of these reagents allylstannanes are known as useful reagents because of their stability and solubility in the reaction. Generally homoallylic amines are prepared either addition of organometallic reagents to imines or by nucleophilic addition of allylsilane, allyltin, allylboron or allylgermane reagents to imines in the presence of acid catalysts. Lewis acids catalysts such as TiCl₄, BF₃.OEt₂, PdCl₂(PPh₃)₂ and PtCl₂(PPh₃)₂ have been employed for this transformation. However, these reactions cannot be carried out in a one-pot operation with a carbonyl compound, amine and allyl metal reagent, because the amines and water that exist during imine formation can decompose or deactivate the Lewis acids.

Therefore, it would be more efficient if one could end in a one-pot formation of homoallylic amines directly from the carbonyl compounds and amines. In order to circumvent these problems one-pot procedures have been developed for this conversion, one-pot reactions are characterized by their great elegance, frequently high stereoselectivity by the simple manner and also aid in the reduction of undesired by products. Recently lanthanide triflates are used as catalysts. Infact, these procedures do not require the isolation of the unstable imines prior to the reactions. Metal triflates are strongly acidic and highly expensive, so the development of a neutral alternative like lithium perchlorate would extend the scope of this transformation.
PRESENT WORK

Lithium perchlorate in diethyl ether (LPDE) has emerged as a mild Lewis acid imparting high regio, chemo and stereoselectivity to various organic transformations.\(^7\) The LPDE medium provides a convenient procedure to carry out reactions under neutral reaction and work-up conditions, furthermore LPDE is found to retain its activity even in the presence of amines and has also been found to activate effectively nitrogen containing compounds such as imines and nitrones.\(^8\)

In continuation of our interest on the catalytic applications of lithium perchlorate for various organic transformations,\(^9\) we herein describe a simple and efficient protocol for the synthesis of homoallylic amines using a catalytic amount of lithium perchlorate under neutral reaction conditions (Scheme 1).

The reaction of benzaldehyde, aniline and allyltributylstannane in the presence of 10-mol\% lithium perchlorate\(^10\) in acetonitrile at ambient temperature resulted in the formation of the homoallylic amine in 90% yield. Similarly various imines (formed in situ from aldehydes and amines) reacted smoothly with the allylstannane to afford the corresponding homoallylic amines in high yields.\(^11\)

\[
\text{R-CHO} + \text{R'-NH}_2 + \text{Bu}_3\text{Sn} \xrightarrow{\text{LiClO}_4, \text{CH}_3\text{CN}, \text{r.t.}} \text{HN-R} \quad \text{4b}
\]

Scheme 1

Compound 4b in its \(^1\text{H} \) NMR spectrum showed the chemical shifts for methyl protons at 2.34 ppm as a singlet, at 5.87-5.62 and 5.25-5.06 ppm as multiplets corresponding to olefinic protons, at 4.38 ppm as a triplet for benzylic proton and at 2.68-2.40 ppm as a multiplet for allylic protons. The compound 4b was also characterized by IR and mass analysis, which in its EIMS showed \(M^+\) peak at \(m/z\) 237. Similarly 2-Naphthaldehyde 1c was treated with allyl trimethyl silane and aniline 2c in the presence of lithium perchlorate (10 mol\%) to afford the expected homoallylic amine \(N-\left[1-(1-(2-naphthyl)-3-butenyl)-N-phenylamime 4c.\right.\) The compound 4c was characterized by its PMR spectrum, which showed the chemical shifts for olefinic protons at 5.96-5.73 ppm and 5.34-5.16 ppm as multiplets and broad singlet at 4.23
ppm for -NH moiety. The compound 4\(c\) was also characterized by mass spectrum (EIMS), which showed a M\(^+\) peak at m/z 273.

The reactions proceeded smoothly at ambient temperature and were completed within 2.5-5.5 h. Both aromatic and aliphatic aldehydes afforded excellent yields of products (75-90\%) in short period whereas ketones did not yield any product even after long reaction times (10-15 h). This method is effective even with aldehydes bearing electron-withdrawing substituents in the aromatic ring.

Furthermore, acid-sensitive aldehydes, such as furfuraldehyde and cinnamaldehyde, worked well without any decomposition or polymerization under the reaction conditions. Enolizable aldehydes, such as cyclohexanecarboxaldehyde and decanal also produced the corresponding homoallylic amines in good yields. In all cases, no homoallylic alcohol (an adduct between the aldehyde and allyltributylostanane) was obtained under these reaction conditions. This is because of the rapid formation and activation of imines in the presence of lithium perchlorate. There are several advantages in the use of LiClO\(_4\) as catalyst for this transformation, which include mild reaction conditions, cleaner reaction profiles, high yields of products, greater selectivity and compatibility with acid labile substrates. The scope and generality of this process is illustrated with respect to various amines and aldehydes including aromatic, \(\alpha\), \(\beta\)-unsaturated, heterocyclic, and aliphatic aldehydes and the results are presented in Table 1.

In conclusion, lithium perchlorate is found to be a mild and efficient Lewis acid in promoting three-component coupling reactions of aldehydes, amines and allyltributylostanane under neutral conditions. In addition to its simplicity, efficiency and mild reaction conditions, this method provides high yields of products in a short period, which makes it a useful and attractive process for the synthesis of homoallylic amines of synthetic importance.
# Table 1. Lithium perchlorate-catalyzed synthesis of homoallylic amines

<table>
<thead>
<tr>
<th>Entry</th>
<th>Aldehyde</th>
<th>Amine</th>
<th>Time (h)</th>
<th>Yield (%)</th>
</tr>
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<td>b)</td>
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<td>c)</td>
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<td>d)</td>
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<tr>
<td>e)</td>
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<td>83</td>
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<td>f)</td>
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<td>h)</td>
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<td><img src="image26" alt="Amine Image" /></td>
<td>4.0</td>
<td>88</td>
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</table>

* All products were characterized by 1H NMR, IR and mass spectrometry

b Isolated and unoptimized yields
EXPERIMENTAL
**EXPERIMENTAL**

**General procedure for the preparation of Homo allylic amines**

A mixture of aldehyde (5 mmol), amine (5 mmol), allyltributylstannane (5 mmol) and anhydrous LiClO₄ (10 mol%) in acetonitrile (10 mL) was stirred at ambient temperature for the appropriate time (Table 1). After completion of the reaction as indicated by TLC, the reaction mixture was quenched with water (10 mL) and extracted with ethyl acetate (2 x 15 mL). The combined organic layers were washed with water (3 x 15 mL) and dried over anhydrous Na₂SO₄, concentrated in vacuo and purified by column chromatography on silica gel (Merck, 100-200 mesh, ethyl acetate–hexane, 1:9) to afford pure homoallyl amine. The aqueous layer was quenched with saturated sodium bicarbonate solution to destroy lithium perchlorate.

*N-phenyl-N-(1-phenyl-3-butenyl)amine (4a)*

![Chemical structure of N-phenyl-N-(1-phenyl-3-butenyl)amine](image)

**¹H NMR (200 MHz, CDCl₃)**

δ 7.47-7.05 (m, 5H, Aromatic-H), 7.03 (t, 2H, J = 7.9 Hz, Aromatic-H), 6.60 (t, 1H, J = 7.9 Hz, Aromatic-H), 6.40 (d, 2H, J = 8.1 Hz, Aromatic-H), 5.84-5.60 (m, 1H, olefinic-H), 5.23-5.03 (m, 2H, olefinic-H), 4.37 (dd, 1H, J = 7.8, 5.3 Hz, \(-\text{CHNHPh}\)), 4.05 (br s, 1H, \(-\text{NH}\)), 2.66-2.38 (m, 2H, \(-\text{CH₂CH=CH₂}\)).

**¹³C NMR (75 MHz, CDCl₃)**

δ 147.5, 143.6, 134.5, 129.1, 126.0, 125.2, 118.2, 117.5, 57.3, 43.4

**IR (Neat)**

3413, 3056, 3024, 2910, 1640, 1601, 1495, 1316, 994, 919, 753 cm⁻¹

**MASS (EI/MS)**

m/z 223 (M⁺), 182, 141, 104, 77
**Chapter III**

**Section A**

*N-[1-(4-methylphenyl)-3-butenyl]-N-phenylamine (4b)*

![](image)

$^1$H NMR (200 MHz, CDCl$_3$) : δ 7.25 (d, 2H, $J = 8.1$ Hz, Aromatic-H), 7.18-7.00 (m, 4H, Aromatic-H), 6.60 (t, 1H, $J = 7.9$ Hz, Aromatic-H), 6.45 (d, 2H, $J = 8.1$ Hz, Aromatic-H), 5.87-5.62 (m, 1H, olefinic-H), 5.25-5.06 (m, 2H, olefinic-H), 4.38 (t, 1H, $J = 6.5$ Hz, -CHNHPh), 4.03 (br s, 1H, -NH), 2.68-2.40 (m, 2H, -CH$_2$CH=CH$_2$), 2.34 (s, 3H, -CHCH$_3$).

IR (Neat) : 3415, 3077, 2930, 1639, 1600, 993, 755 cm$^{-1}$

MASS (EI MS) : m/z 237 (M$^+$) 196, 128, 115, 104, 91, 77, 65, 51

*N-[1-(1-(2-naphthyl)-3-butenyl]-N-phenylamine (4c)*

![](image)

$^1$H NMR (200 MHz, CDCl$_3$) : δ 8.00-7.80 (m, 4H, Aromatic-H), 7.60-7.50 (m, 3H, Aromatic-H), 7.10 (t, 2H, $J = 7.8$ Hz, Aromatic-H), 6.60 (t, 1H, $J = 7.8$ Hz, Aromatic-H), 6.50 (d, 2H, $J = 8.0$ Hz, Aromatic-H), 5.96-5.73 (m, 1H, olefinic-H), 5.34-5.16 (m, 2H, olefinic-H), 4.57 (t, 1H, $J = 6.4$ Hz, -CHNHPh), 4.23 (br s, 1H, -NH), 2.82-2.48 (m, 2H, -CH$_2$CH=CH$_2$).

IR (Neat) : 3412, 3053, 2923, 1689, 1601, 1504, 1429, 993, 919, 866, 777, 692 cm$^{-1}$
Chapter III

Section A

MASS (EIMS) : m/z 273 (M⁺), 232, 165, 127, 104, 77.

\[ N-[1-(1,3-benzodioxol-5-yl)-3-butenyl]-N-(4-fluorophenyl)amine (4d) \]

\[ \text{\includegraphics{image}} \]

\[ \text{^1H NMR (200 MHz, CDCl}_3\text{)} : \delta 7.24-7.12 (m, 2H, Aromatic-H), 6.88-6.80 (m, 2H, Aromatic-H), 6.78-6.75 (m, 1H, Aromatic-H), 6.46-6.34 (m, 2H, Aromatic-H), 5.98 (s, 2H, -OCH}_2\text{O-), 5.94-5.66 (m, 1H, olefinic-H), 5.32-5.14 (m, 2H, olefinic-H), 5.03 (br s, 1H, -NH), 4.18 (t, 1H, } J = 6.4 \text{ Hz, -CHNHPh), 2.86-2.68 (m, 2H, -CH}_2\text{CH=CH}_2\text{).} \]

MASS (EIMS) : m/z 284 (M⁺)

IR (Neat) : 3413, 3066, 2921, 1627, 1508, 1450, 1311, 1219, 1098, 996, 920, 823, 761 cm\(^{-1}\)

\[ N-(3-methoxybenzyl)-N-[1-(4-methylphenyl)-3-butenyl]amine (4e) \]

\[ \text{\includegraphics{image}} \]

\[ \text{^1H NMR (200 MHz, CDCl}_3\text{)} : \delta 7.18-7.08 (m, 4H, Aromatic-H), 7.04-6.96 (m, 2H, Aromatic-H), 6.73-6.64 (m, 2H, Aromatic-H), 5.80-5.60 (m, 1H, olefinic-H), 5.21-5.00 (m, 2H, olefinic-H), 4.26 (t, 1H, } J = 6.4 \text{ Hz, -CHNHPh), 4.13 (br s, 1H, } -\text{NH), 4.02-3.87 (m, 2H, -CH}_2\text{NH}_3\text{Bn), 3.76 (s, 3H, -OCH}_3\text{), 2.60-2.37 (m, 2H, -CH}_2\text{CH=CH}_2\text{), 2.32 (s, 3H, -CHCH}_3\text{).} \]

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MASS (EIMS) : m/z 281 (M⁺)

\(N\)-(4-chlorophenyl)-\(N\)-[1-(4-methoxyphenyl)-3-butenyl]amine (4f)

\(1^H\) NMR (200 MHz, CDCl₃) : δ 7.20 (d, 2H, \(J = 7.6\) Hz, Aromatic-H), 6.82-6.60 (m, 4H, Aromatic-H), 6.37 (d, 2H, \(J = 7.6\) Hz, Aromatic-H), 5.80-5.58 (m, 1H, olefinic-H), 5.20-5.02 (m, 2H, olefinic-H), 4.22 (t, 1H, \(J = 6.4\) Hz, -CHNHPh), 3.76 (s, 3H, -OCH₃), 2.60-2.26 (m, 2H, -CH₂CH≡CH₂).

IR (Neat) : 3414, 3027, 2913, 1675, 1587, 1506, 1418, 1336, 1184, 985, 917, 846, 762 cm⁻¹

MASS (EIMS) : m/z 287 (M⁺)

\(N\)-[1-(4-methoxyphenyl)-3-butenyl]-\(N\)-(4-methylphenyl)amine (4g)

\(1^H\) NMR (200 MHz, CDCl₃) : δ 7.22 (d, 2H, \(J = 7.8\) Hz, Aromatic-H), 6.86-6.75 (m, 4H, Aromatic-H), 6.33 (d, 2H, \(J = 7.8\) Hz, Aromatic-H), 5.82-5.64 (m, 1H, olefinic-H), 5.20-5.04 (m, 2H, olefinic-H), 4.30-4.21 (m, 1H, -CHNHPh), 3.88 (br s, 1H, -NH), 3.76 (s, 3H, -OCH₃), 2.60-2.32 (m, 2H, -CH₂CH≡CH₂), 2.12 (s, 3H, -CHCH₃).

MASS (EIMS) : m/z 267 (M⁺)
Chapter III

Section A

\[ \text{A'-(4-bromophenyl)-Ar-[1-(3,4-dimethoxyphenyl)-3-butenyl]amine (4i)} \]

\[ \text{\textsuperscript{1}H NMR (200 MHz, CDCl}_3) \quad \delta \ 7.08-6.96 \ (m, \ 2H, \text{ Aromatic-H}), \quad 6.92-6.68 \ (m, \ 3H, \text{ Aromatic-H}), \quad 6.63-6.52 \ (m, \ 1H, \text{ Aromatic-H}), \quad 6.48-6.38 \ (m, \ 1H, \text{ Aromatic-H}), \quad 5.80-5.58 \ (m, \ 1H, \text{ olefinic-H}), \quad 5.20-5.00 \ (m, \ 2H, \text{ olefinic-H}), \quad 4.23 \ (t, \quad 1H, \ J = 6.2 \ Hz, \text{ -CHNPhH}), \quad 4.06 \ (br \ s, \ 1H, \text{-NH}), \]

\[ \text{IR (Neat)} \quad : 3427, \ 3016, \ 1686, \ 1623, \ 1531, \ 1427, \ 1333, \ 1258, \ 1079, \ 972, \ 914, \ 843, \ 761 \ cm}^{-1} \]

\[ \text{MASS (EIMS)} \quad : m/z \ 282 \ (M^+) \]

\[ \text{N-(4-methylphenyl)-N-[1-(3-nitrophenyl)-3-butenyl]amine (4h)} \]

\[ \text{1H NMR (200 MHz, CDCl}_3) \quad : 8 \ 8.27-8.23 \ (m, \ 1H, \text{ Aromatic-H}), \quad 7.78-7.66 \ (m, \ 1H, \text{ Aromatic-H}), \quad 7.56-7.40 \ (m, \ 1H, \text{ Aromatic-H}), \quad 7.18-7.02 \ (m, \ 1H, \text{ Aromatic-H}), \quad 6.76-6.62 \ (m, \ 1H, \text{ Aromatic-H}), \quad 6.53-6.40 \ (m, \ 2H, \text{ Aromatic-H}), \quad 5.82-5.62 \ (m, \ 1H, \text{ olefinic-H}), \quad 5.30-5.12 \ (m, \ 2H, \text{ olefinic-H}), \quad 4.48 \ (t, \quad 1H, \ J = 6.4 \ Hz, \text{ -CHNHPhH}), \quad 2.76-2.40 \ (m, \ 2H, \text{-CH}_2\text{CH=CH}_2), \quad 2.14 \ (s, \ 3H, \text{-CHCH}_3) \]

\[ \text{IR (Neat)} \quad : 3427, \ 3041, \ 2916, \ 1686, \ 1623, \ 1531, \ 1427, \ 1333, \ 1258, \ 1079, \ 972, \ 914, \ 843, \ 761 \ cm}^{-1} \]

\[ \text{MASS (EIMS)} \quad : m/z \ 282 \ (M^+) \]
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MASS (EIMS)  
3.80 (s, 6H, 2 x -OCH₃), 2.60-2.30 (m, 1H, -CH₂CH=CH₂).

MASS (EIMS)  
: m/z 363 (M⁺)

**N-(4-chlorophenyl)-N-[1-(4-methylphenyl)-3-butenyl]amine (4j)**

1H NMR (200 MHz, CDCl₃)  
: δ 7.21 (d, 2H, J = 7.4 Hz, Aromatic-H); 6.84-6.72 (m, 4H, Aromatic-H), 6.38 (d, 2H, J = 7.4 Hz, Aromatic-H), 5.90-5.73 (m, 1H, olefinic-H), 5.25-5.06 (m, 2H, olefinic-H), 4.38 (t, 1H, J = 6.4 Hz, -CHNHPh), 4.25 (br s, 1H, -NH), 2.78-2.50 (m, 2H, -CH₂CH=CH₂), 2.12 (s, 3H, -CHCH₃).

IR (Neat)  
: 3411, 3034, 2981, 2922, 1701, 1627, 1518, 1452, 996, 921, 787 cm⁻¹

MASS (EIMS)  

**N-(1-cyclohexyl-3-butenyl)-N-phenylamine (4k)**

1H NMR (200 MHz, CDCl₃)  
: δ 7.29-7.20 (m, 2H, Aromatic-H), 6.82-6.71 (m, 3H, Aromatic-H), 5.86-5.62 (m, 1H, olefinic-H), 5.24-5.06 (m, 2H, olefinic-H), 4.02 (t, 1H, -NH), 3.36-3.28 (m, 1H, -CHNHPh), 2.16-2.05 (m, 2H, -CH₂CH=CH₂), 1.90-1.60 (m, 4H, 2 x -CH₂'s), 1.46-0.98 (m, 7H, 3 x -CH₂'s and one -CH-).

MASS (EIMS)  
: m/z 229 (M⁺)
**N-[1-(2-furyl)-3-butenyl]-N-phenylamine (4l)**

\[ \text{Chemical Structure Image} \]

\[ ^1H \text{ NMR (200 MHz, CDCl}_3) : \delta 7.30 \text{ (d, 1H, } J = 1.9 \text{ Hz, Aromatic-H), 7.10 (t, 2H, } J = 7.9 \text{ Hz, Aromatic-H), 6.67 (t, 1H, } J = 7.9 \text{ Hz, Aromatic-H), 6.55 (d, 2H, } J = 8.0 \text{ Hz, Aromatic-H), 6.26 (dt, 1H, } J = 2.1, 1.9 \text{ Hz, Aromatic-H), 6.12 (d, 1H, } J = 2.1 \text{ Hz, Aromatic-H), 5.80-5.65 (m, 1H, olefinic-H), 5.20-5.08 (m, 2H, olefinic-H), 4.54 (t, 1H, } J = 5.7 \text{ Hz, -CHNHPPh), 3.90 (br s, 1H, -NH), 2.70-2.60 (m, 2H, -CH<sub>2</sub>CH=CH<sub>2</sub>).} \]

\[ ^13C \text{ NMR (75 MHz, CDCl}_3) : \delta 155.3, 146.3, 141.6, 134.1, 129.2, 118.5, 117.8, 113.4, 110.1, 106.1, 51.3, 39.1 \]

\[ \text{IR (Neat): 3411, 3077, 3052, 2918, 1640, 1603, 994, 921, 748, 691 \text{ cm}^{-1} \]

\[ \text{MASS (EIIMS): } m/z 213 (M^+), 172, 104, 91, 77 \]

**N-phenyl-N-{1-[(E)-2-phenyl-1-ethenyl]-3-butenyl]amine (4m)**

\[ \text{Chemical Structure Image} \]

\[ ^1H \text{ NMR (200 MHz, CDCl}_3) : \delta 7.38-7.08 \text{ (m, 7H, Aromatic-H), 6.69-6.56 (m, 4H, three protons from Aromatic-H, one from olefinic-H), 6.24-6.16 (m, 1H, olefinic-H), 5.95-5.80 (m, 1H, olefinic-H), 5.25-5.16 (m, 2H, olefinic-H), 4.10-4.02 (m, 1H, -CHNPH), 3.80} \]

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(br s, 1H, -NH), 2.57-2.40 (m, 2H, -CH\textsubscript{2}CH=CH\textsubscript{2}).

IR (Neat) : 3448, 2925, 2364, 1637, 1503, 749, 693 cm\textsuperscript{-1}

MASS (EIMS) : m/z 249 (M\textsuperscript{+}), 209, 200, 182, 155, 141, 91, 77
REFERENCES


12. Caution: Although, solid lithium perchlorate is stable up to its melting point, solutions in organic solvents should be prepared and handled with the utmost care.
Date run: 12-02-2002(17:27:59) Instr.: VG7070H Operator: NCMS
Scan 8 RT= 0:32 No. ions= 518 Base=100.0% F TIC=371244

EIMS SPECTRUM OF COMPOUND 4a
"H NMR SPECTRUM OF COMPOUND 4b"
Date run: 11-28-2002 (17:33:00)  Instr. : VG7070H  Operator : NCMS

Scan 19  RT = 1:36  No. ions = 612  Base = 100.0%F  TIC = 155239

EIMS SPECTRUM OF COMPOUND 4c
$^1$H NMR SPECTRUM OF COMPOUND 4f
$^1$H NMR SPECTRUM OF COMPOUND 4g
$^1$H NMR SPECTRUM OF COMPOUND 41
NCMS
12-03-2002

JSY-CAA
Date run: 12-02-2002(11:02:06) Instr.: VG7070H Operator: NCMS
Scan 6 RT= 0:26 No.ions= 397 Base=100.0% TIC=446454

EIMS SPECTRUM OF COMPOUND 4m
CHAPTER III

Section B

Sulphamic acid Catalyzed Chemoselective Allylation of Aldehydes
INTRODUCTION

Homoallylic alcohols are valuable intermediates in the synthesis of many complex molecules\(^1\) and which can be easily converted to many important building blocks for the synthesis of natural products.\(^2\) In the total synthesis of natural products having the homoallyl alcohols, as the intermediate requires an additional step for protection of the free secondary alcohol to proceed further. In general homoallylic alcohols can be prepared by the allylation of carbonyl compounds with organometallic compounds, such as alkyltrialkyl and allyltriarylstannanes.

The addition of alkyl metal compounds to carbonyl compounds or their equivalents is one of the most useful synthetic reactions. Consequently, several methods have been developed for the allylation of aldehydes with allyl metals including Lewis, Bronsted acid\(^3\)\(^-\)\(^6\) and organometallic reagent\(^7\) catalyzed allylation reactions in organic, as well as in a mixture of organic and aqueous media, ionic liquids\(^8\) and polyethylene glycol\(^9\). Very recently β-Cyclodextrin\(^14\) promoted allylation of aldehydes with allyltributyltin in acidic aqueous medium has been reported. Generally tight binding of the product homoallylic alcohol to the Lewis acid catalyst results in poor turnover, thereby necessitating the use of stoichiometric (or greater) amounts of Lewis acid.

However, most of the synthetic protocols reported so far suffer from high temperatures, prolonged reaction times, drastic reaction conditions and low yields of the products and the use of hazardous and often expensive acid catalysts and also the main disadvantage of most of the existing methods is that the catalysts are destroyed in the workup conditions and cannot be recovered or reused. Therefore, the development of simple, convenient and environmentally benign approaches for the synthesis of homoallylic alcohols is still desirable.

In recent years, the use of solid acids as heterogeneous catalysts has received tremendous interest in different areas of organic synthesis.\(^15\) Heterogeneous solid acids are advantageous over conventional homogeneous acid catalysts as they can be easily recovered from the reaction mixture by simple filtration and can be reused after activation or without activation, thereby making the process economically more viable.
Various literature methods reported for the synthesis of homoallylic alcohols using allyltributyltin:

Sonoda and co-workers,\(^7\) reported the Rhenium metal complex ReBr(CO)\(_5\) for the synthesis of homoallylic alcohols in benzene or toluene at 80 °C. Highly poisonous CO is released by the dissociation of ReBr(CO)\(_5\) under toluene reflux conditions in this reaction pathway.

\[
\begin{align*}
\text{O} & \quad \text{R}^\cdot \text{H} \quad + \quad \text{SnBu}_3 \quad \text{ReBr(CO)}_5 \\
\text{Benzene / Toluene} & \quad 80 \degree \text{C}
\end{align*}
\]

\textbf{Scheme 2}

Marcantoni and co-workers\(^8\) revealed cerium (III) chloride-Nal catalyst for the allylation of aldehydes in acetonitrile. Inorganic iodide salts were used as co-catalysts or promoters in these reactions and the catalyst (1.0 equiv) was used in more than stoichiometric amount.

\[
\begin{align*}
\text{R - CHO} & \quad + \quad \text{SnBu}_3 \quad \text{1. CeCl}_3 \cdot 7\text{H}_2\text{O} / \text{Nal} \\
\text{CH}_3\text{CN} & \quad 2. 0.1\text{N} \text{HCl}
\end{align*}
\]

\textbf{Scheme 3}

Yamamoto \textit{et al}^9 carried out the allylation reaction of aldehydes with allyltributyltin using Sn metal and HCl in aqueous THF.

\[
\begin{align*}
\text{R - H} & \quad + \quad \text{SnBu}_3 \quad \text{Sn Catalyst} \\
aq. \text{HCl / THF, 20 \degree C} & \quad \text{aq. HCl / THF, 20 \degree C}
\end{align*}
\]

\textbf{Scheme 4}

Kobayashi \textit{et al}^{10a} synthesized homoallylic alcohols from aldehydes using tetraallyltin with scandium triflate as a catalyst in micellar medium (Scheme 5). Sodium dodecylsulfate (SDS) or Triton X-100 was used as a surfactant in these reactions. They have also reported\(^{10b}\) yet another procedure for the allylation using Lewis acid scandium trifluoromethane sulfonate (Sc(OTf)\(_3\)) in H\(_2\)O/CH\(_3CN\) (1:9) in (Scheme 5).
Disadvantage of this method is the retardation of acidity of Sc(OTf)$_3$ in the presence of water retarding the allylation reaction.

\[
\text{R - CHO} + \left\{\begin{array}{c}
\text{SnBu}_3 \\
\end{array}\right\} \xrightarrow{\text{Sc(OTf)$_3$}} \text{Surfactant H$_2$O, r.t.} \xrightarrow{\text{H$_2$O / CH$_3$CN}} \text{R - CHO SnBu}_3 \\
\]

**Scheme 5**

Choudary *et al*\textsuperscript{11} Poly Ethylene Glycol (PEG) was used as solvent for the allylation of aldehydes with allyltributyltin using scandium triflate as a catalyst. One equivalent of benzoic acid was added as an additive in this reaction.

\[
R\text{-acid} + \left\{\begin{array}{c}
\text{SnBu}_3 \\
\end{array}\right\} \xrightarrow{\text{Sc(OTf)$_3$ (5 mol%)}} \text{PEG Solvent PhCOOH, r.t.} \xrightarrow{\text{PEG Solvent PhCOOH, r.t.}} \text{R - CHO SnBu}_3 \\
\]

**Scheme 6**

Loh *et al*\textsuperscript{12} reported the addition of allyltributylstannane to carbonyl compounds utilizes Indium trichloride as catalyst in ionic liquid hexylmethylimidazolium chloride ([hmin$^+$][Cl]) resulted in homoallylic alcohols.

\[
R\text{-acid} + \left\{\begin{array}{c}
\text{SnBu}_3 \\
\end{array}\right\} \xrightarrow{\text{InCl$_3$}} \text{R - CHO + \text{SnBu}_3} \\
\]

**Scheme 7**

Recently our group\textsuperscript{13a} developed the method consists of reacting aldehydes with allyltributylstannane with ceric ammonium nitrate as a Lewis acid in acetonitrile (Scheme-8). There is also another report\textsuperscript{13b} describing the synthesis of homoallylic alcohols in the presence of Lewis acid cerium (III) chloride in acetonitrile.

\[
R\text{-CHO} + \left\{\begin{array}{c}
\text{SnBu}_3 \\
\end{array}\right\} \xrightarrow{\text{CAN}} \text{CH$_3$CN, r.t.} \xrightarrow{\text{CAN}} \text{R - CHO SnBu}_3 \\
\]

**Scheme 8**
PRESENT WORK

Sulphamic acid (NH$_2$SO$_3$H, SA) has emerged as a substitute for conventional acidic catalysts. Sulphamic acid is a common inorganic acid with mild acidity, in volatility and incorrositivity, is insoluble in common organic solvents. SA is comprised not of the amino sulfonic acid, but rather of $^+$H$_3$N$^-$SO$_3$ zwitterionic units by both X-ray neutron diffraction techniques. In recent years SA has been used as an efficient heterogeneous acid catalyst for acid catalyzed reactions.$^{17a-b}$ Moreover, some important organic transformations$^{17h-k}$ have also been carried out in the presence of SA.

The usual catalytic feature and intrinsic zwitterionic property of SA is very different from the conventional acidic catalyst, which encouraged us to investigate further applications of SA as an acidic catalyst in the other carbon-carbon and carbon-heteroatom bond forming reactions. However, there are no reports for the synthesis of homoallylic alcohols using sulphamic acid. The use of SA as a recyclable catalyst makes the process convenient, economic and environmentally benign.

![Scheme 9](image_url)

In continuation of our effort in the development of new methods for synthesis of homoallylic alcohols$^{5c, 6c}$ herein, we wish to describe a mild and efficient protocol for the allylation of aldehydes with allyltributylstannane using catalytic amount of sulphamic acid under solvent free condition at ambient temperature. Accordingly, treatment of benzaldehyde with allyltributylstannane in the presence of 5 mol% SA afforded 1-phenyl-3-buten-1-ol in 95% yield. In order to optimize the reaction conditions we have carried out this reaction in different solvents. The results show that the efficiency and the yield of the reaction in solutions were much less than that observed under solvent free conditions.

The best result was obtained with 5 mol% of SA under solvent-free condition. The catalyst was easily separated by simple filtration and reused after activation with gradual decrease in its activity. Furthermore, this method is clean and free from side
reactions such as bis-allylation of aldehydes, which are normally observed in the allylation of methoxy-benzaldehydes with allyltrimethylstannane.

Various substrates including aromatic, aliphatic, heterocyclic and \( \alpha,\beta \)-unsaturated aldehydes reacted efficiently with allyltin under similar reaction conditions to afford the corresponding homoallylic alcohols in excellent yields. Interestingly, acid sensitive aldehydes such as 2-phenyl acetaldehyde, furfural, and thiophene-2-carboxaldehyde were also efficiently converted into their corresponding homoallylic alcohols in high yields.

This protocol was found to be highly chemoselective for aldehydes. Ketones such as acetophenone, tetralone and cyclohexanone did not react with allyltributylstannane under similar reaction conditions even after a longer reaction time, and thus provides a chemoselective allylation of aldehydes without effecting the keto functionality. For example, benzaldehyde was exclusively allylated in the presence of acetophenone (Scheme 10).

Compound 6d in its \(^1\)H NMR spectrum showed the chemical shifts for the methoxy protons at 3.82 ppm as a singlet, at 5.85-5.72 and 5.18-5.06 ppm as multiplets for olefinic protons, at 4.60 ppm as a triplet \((J = 6.5 \text{ Hz})\) for benzylic proton and at 2.50-2.42 ppm as a multiplet for allylic protons. The compound 6d was also characterized by IR and mass analysis, which in its EIMS showed \((M^+)\) peak at \(m/z\) 291. Similarly 6-Bromo-1,3-benzodioxole-5-carbaldehyde 5i was treated with allyl trimethyl silane in the presence of \(\text{NH}_2\text{SO}_3\text{H} (5 \text{ mol%})\) to afford the expected homoallylic alcohol 1-(6-Bromo-benzo[1,3]dioxol-5-yl)-but-3-en-1-ol 6i. The compound 6i was characterized by its PMR spectrum, which showed the chemical shifts for olefinic protons at 5.95-5.80 ppm and 5.25-5.15 ppm as multiplets, at 5.00 ppm as a triplet \((J = 6.5 \text{ Hz})\) for benzylic proton. Allylic protons resonated as multiplets at 2.60-2.50 and 2.30-2.20 ppm.
respectively, and broad singlet at 1.90 ppm for -OH moiety. The compound 6i was also characterized by its mass spectrum (EI MS), which showed a (M⁺) peak at m/z 272.

In summary, we have described a mild and efficient protocol for the synthesis of homoallylic alcohols from aldehydes and allyltributylstannane using a cheap and readily available Sulphamic acid as a recyclable heterogeneous catalyst makes this method quite simple, more convenient and environmentally benign for the synthesis of homoallylic alcohols.
### Table 2: Sulphamic acid Catalyzed Synthesis of Homoallylic alcohols*

<table>
<thead>
<tr>
<th>Entry</th>
<th>Aldehyde</th>
<th>Homoallylic alcohol*</th>
<th>Time (min)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a)</td>
<td>CHO</td>
<td>OH</td>
<td>15</td>
<td>95</td>
</tr>
<tr>
<td>b)</td>
<td>CHO</td>
<td>OH</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>c)</td>
<td>CHO</td>
<td>OH</td>
<td>30</td>
<td>92</td>
</tr>
<tr>
<td>d)</td>
<td>TBDMSO</td>
<td>OH</td>
<td>60</td>
<td>83</td>
</tr>
<tr>
<td>e)</td>
<td>CHO</td>
<td>OH</td>
<td>45</td>
<td>99</td>
</tr>
<tr>
<td>f)</td>
<td>CHO</td>
<td>OH</td>
<td>30</td>
<td>95</td>
</tr>
<tr>
<td>g)</td>
<td>CHO</td>
<td>OH</td>
<td>60</td>
<td>89</td>
</tr>
<tr>
<td>h)</td>
<td>CHO</td>
<td>OH</td>
<td>90</td>
<td>87</td>
</tr>
<tr>
<td>i)</td>
<td>CHO</td>
<td>OH</td>
<td>75</td>
<td>90</td>
</tr>
<tr>
<td>j)</td>
<td>CHO</td>
<td>OH</td>
<td>15</td>
<td>95</td>
</tr>
<tr>
<td>k)</td>
<td>CHO</td>
<td>OH</td>
<td>75</td>
<td>90</td>
</tr>
<tr>
<td>l)</td>
<td>CHO</td>
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<td>89</td>
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<td>m)</td>
<td>CHO</td>
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<td>95</td>
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<td>n)</td>
<td>CHO</td>
<td>OH</td>
<td>60</td>
<td>90</td>
</tr>
<tr>
<td>o)</td>
<td>CHO</td>
<td>OH</td>
<td>90</td>
<td>87</td>
</tr>
</tbody>
</table>

*Reaction Conditions: Aldehyde (1 mmol), Allyltin (1.1 mmol), Sulphamic acid (5 mol%), Solvent-free

**All Products were characterized by 1H NMR, IR and mass spectrometry

* Isolated and unoptimized yield.
EXPERIMENTAL
EXPERIMENTAL

General procedure for the preparation of Homo allylic alcohols

Solvent-free (Method A): A mixture of aldehyde (1 mmol), allyltri-n-butylstannane (1.1 mmol), and sulphamic acid (5 mol%) was stirred at room temperature under solvent-free condition for an appropriate time (Table 2). After completion of the reaction as indicated by TLC, the reaction mixture was extracted with diethylether (3 x 10 mL). The combined organic layers were concentrated in vacuo and purified by column chromatography on silicagel (Merk, 100-200 mesh, EtOAc-hexane) to afford pure homoallylic alcohol. The recovered catalyst was washed with diethylether and reused for subsequent runs.

Solvent condition (Method B): A mixture of aldehyde (1 mmol), allyltri-n-butylstannane (1.1 mmol), and sulphamic acid (5 mol%) was stirred at room temperature under solvent (5 mL) condition for an appropriate time. After completion of the reaction as indicated by TLC, the reaction mixture was extracted with diethylether (3 x 10 mL). The combined organic layers were concentrated in vacuo and purified by column chromatography on silicagel (Merk, 100-200 mesh, EtOAc-hexane) to afford pure homoallylic alcohol.

1-Phenyl-3-butene-1-ol (6a)

\[
\text{HO} \hspace{1cm} \text{CH=CHCH}_2
\]\n
$^1$H NMR (200 MHz, CDCl$_3$) \(\delta 7.40-7.20 \text{ (m, 5H, Aromatic-H), 5.88-5.66 \text{ (m, 1H, olefinic-H),} \)
\(5.12-5.03 \text{ (m, 2H, olefinic-H),} \)
\(4.67 \text{ (t, 1H, } J = 6.7 \text{ Hz, } -\text{CH}_2\text{CH(OH)-},) \)
\(2.50 \text{ (t, 2H, } J = 6.7 \text{ Hz, } -\text{CH}_2\text{CH=CH}_2, \)
\(2.08 \text{ (br s, 1H, } -\text{OH).} \)

IR (Neat) \ : 3448, 2933, 1636, 1567, 1503, 1416, 1322, 1228, 914 \text{ cm}^{-1}

MASS (EIMS) \ : m/z 148 (M$^+$)
2-(1-hydroxy-3-butenyl)-6-methoxy phenol (6b)

\[
\begin{align*}
\text{IR (Neat)} & : 3414, 2938, 2842, 1641, 1593, 1481, 1401, 1355, 1272, 1076, 917 \text{ cm}^{-1} \\
\text{MASS (EI/MS)} & : m/z 194 (M+ )
\end{align*}
\]

1-(3,4,5-trimethoxyphenyl)-3-buten-1-ol (6c)

\[
\begin{align*}
\text{IR (Neat)} & : 3461, 2937, 2836, 1640, 1593, 1506, 1460, 1421, 1327, 1126, 1234, 917, 779 \text{ cm}^{-1} \\
\text{MASS (EI/MS)} & : m/z 238 (M+ ), 197, 169, 154, 138, 43
\end{align*}
\]

1-(4-t-Butyldimethoxy-3-methoxyphenyl)-3-buten-1-ol (6d)

### Chapter III

#### Section B

<table>
<thead>
<tr>
<th>Compound</th>
<th>NMR (200 MHz, CDCl\textsubscript{3})</th>
<th>IR (KBr)</th>
<th>MASS (EIMS)</th>
<th>HRMS (EIMS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-(4-methoxyphenyl)-3-buten-1-ol (6e)</td>
<td>(\delta 6.85) (s, 1H, Aromatic-H), 6.73 (s, 2H, Aromatic-H), 5.85-5.72 (m, 1H, olefinic-H), 5.18-5.06 (m, 2H, olefinic-H), 4.60 (t, 1H, (J = 6.5) Hz, -CH\textsubscript{2}CH(OH)-), 3.82 (s, 3H, -OCH\textsubscript{3}), 2.50-2.42 (m, 2H, -CH\textsubscript{2}CH=CH\textsubscript{2}), 1.80 (br s, 1H, -OH), 0.98 (s, 9H, -SiC(CH\textsubscript{3})\textsubscript{3}), 0.12 (s, 6H, -Si(CH\textsubscript{3})\textsubscript{2})</td>
<td>: 150.9, 144.5, 137.5, 134.6, 120.6, 118.2, 109.9, 107.9, 73.3, 55.5, 43.7, 25.7, 18.4, -4.6</td>
<td>: m/z 308 (M\textsuperscript{+}) 291, 267, 251, 195, 167, 136, 73.</td>
<td>: Calcd for C\textsubscript{12}H\textsubscript{26}SiO\textsubscript{3}: 308.1807. Found: 308.1836.</td>
</tr>
</tbody>
</table>

| 1-(3-nitrophenyl)-3-buten-1-ol (6f) | \(\delta 7.18\) (t, 1H, \(J = 6.4\) Hz, Aromatic-H), 6.87-6.80 (m, 2H, Aromatic-H), 6.77-6.68 (m, 1H, Aromatic-H), 5.83-5.66 (m, 1H, olefinic-H), 5.16-5.02 (m, 2H, olefinic-H), 4.60 (t, 1H, \(J = 6.7\) Hz, -CH\textsubscript{2}CH(OH)-), 3.78 (s, 3H, -OCH\textsubscript{3}), 2.44 (t, 2H, \(J = 6.7\) Hz, -CH\textsubscript{2}CH=CH\textsubscript{2}), 2.33 (br s, 1H, -OH). | : 3417, 2933, 2858, 1641, 1589, 1513, 1467, 1432, 1354, 1280, 1219, 1038, 840, 771 cm\textsuperscript{-1} | : m/z 178 (M\textsuperscript{+}) | |

\[ \text{1-(4-methoxyphenyl)-3-buten-1-ol (6e)} \]

\[ \text{1-(3-nitrophenyl)-3-buten-1-ol (6f)} \]
Chapter III

Section B

\[ ^1H \text{NMR (200 MHz, CDCl}_3 \]\n
: \( \delta \ 8.26-8.03 \) (m, 2H, Aromatic-H), 7.72-7.41 (m, 2H, Aromatic-H), 5.90-5.62 (m, 1H, olefinic-H), 5.24-5.04 (m, 2H, olefinic-H), 4.82 (t, 1H, \( J = 6.7 \) Hz, \(-\text{CH}_2\text{CH(OH)-}\)), 2.63-2.32 (m, 2H, \(-\text{CH}_2=\text{CH}_2\)), 2.18 (br s, 1H, -OH).

IR (Neat)

: 3461, 2937, 2836, 1640, 1593, 1506, 1460, 1421, 1327, 1234, 1126, 1005, 917, 835, 779 cm\(^{-1}\).

MASS (EIMS)

: m/z 193 (M\(^+\))

2-hydroxy-1-phenyl-4-penten-1-one (6g)

\[ \text{\begin{center}
\begin{array}{c}
\text{O} \\
\text{OH}
\end{array}
\end{center}} \]

\[ ^1H \text{NMR (300 MHz, CDCl}_3 \]\n
: \( \delta \ 7.98-7.80 \) (m, 2H, Aromatic-H), 7.66-7.36 (m, 3H, Aromatic-H), 5.88-5.62 (m, 1H, olefinic-H), 5.20-4.82 (m, 3H, two olefinic-H & one -CHOH), 3.66 (br s, 1H, -OH), 2.75-2.48 (m, 1H, one of \(-\text{CH}_2\text{CH}=\text{CH}_2\)), 2.44-2.20 (m, 1H, one of \(-\text{CH}_2\text{CH}=\text{CH}_2\)).

\[ ^13C \text{NMR (75 MHz, CDCl}_3 \]\n
: \( \delta \ 134.0, 118.1, 109.0, 78.1, 70.5, 65.2, 37.6, 26.5, 25.2 \)

IR (KBr)

: 3468, 3078, 2888, 1656, 1352, 1201, 913 cm\(^{-1}\).

MASS (EIMS)

: m/z 177 (M\(^+\)+H), 143, 101, 83, 69, 59, 43

1-phenyl-4-penten-2-ol (6h)

\[ \text{\begin{center}
\begin{array}{c}
\text{O} \\
\text{OH}
\end{array}
\end{center}} \]

\[ ^1H \text{NMR (400 MHz, CDCl}_3 \]\n
: \( \delta \ 7.36-7.06 \) (m, 5H, Aromatic-H), 5.96-5.70 (m, 1H, olefinic-H), 5.20-5.02 (m, 2H, olefinic-H), 3.88-3.73 (m, 1H, \(-\text{CH}_2\text{CH(OH)-}\)), 2.82-2.58 (m,
Chapter III

Section B

2H, -CH$_2$Ph), 2.40-2.06 (m, 2H, -CH$_2$CH=CH$_2$)
1.60 (br s, 1H, -OH).

IR (Neat) : 3416, 2925, 2856, 1695, 1641, 1495, 1453, 1239,
1111, 1076, 915 cm$^{-1}$

MASS (EIMS) : m/z 162 (M$^+$)

1-(6-Bromo-benzo[1,3]dioxol-5-yl)-but-3-en-1-ol (6i)

IR (Neat)

MASS (EIMS)

1H NMR (200 MHz, CDCl$_3$)

3416, 2925, 2856, 1695, 1641, 1495, 1453, 1239,
1111, 1076, 915 cm$^{-1}$

m/z 162 (M$^+$)

1-(6-Bromo-benzo[1,3]dioxol-5-yl)-but-3-en-1-ol (6i)

IR (Neat) : 3416, 2925, 2856, 1695, 1641, 1495, 1453, 1239,
1111, 1076, 915 cm$^{-1}$

MASS (EIMS) : m/z 162 (M$^+$)

1-(2-naphthyl)-3-buten-1-ol (6j)

IR (Neat) : 3416, 2925, 2856, 1695, 1641, 1495, 1453, 1239,
1111, 1076, 915 cm$^{-1}$

MASS (EIMS) : m/z 272 (M$^+$+H), 229, 173, 122, 63

1-(2-naphthyl)-3-buten-1-ol (6j)

IR (Neat) : 3416, 2925, 2856, 1695, 1641, 1495, 1453, 1239,
1111, 1076, 915 cm$^{-1}$

MASS (EIMS) : m/z 272 (M$^+$+H), 229, 173, 122, 63

1-(2-naphthyl)-3-buten-1-ol (6j)

IR (Neat) : 3416, 2925, 2856, 1695, 1641, 1495, 1453, 1239,
1111, 1076, 915 cm$^{-1}$

MASS (EIMS) : m/z 272 (M$^+$+H), 229, 173, 122, 63

1-(2-naphthyl)-3-buten-1-ol (6j)
MASS (EIMS) : m/z 200, 158, 130, 39

2-Phenyl-5-hexene-3-ol (6k)

\[
\begin{align*}
\text{\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3})} & : \delta 7.32-7.16 (m, 5H, Aromatic-H), 5.85-5.72 (m, 1H, olefinic-H),
5.16-5.06 (m, 2H, olefinic-H), 3.73-3.62 (m, 1H, -CH\textsubscript{2}CH(OH)-), 2.80-2.70 (m, 1H, -CH\textsubscript{2}Ph),
2.20-1.96 (m, 2H, -CH\textsubscript{2}CH=CH\textsubscript{2}), 1.57 (br s, 1H, -OH), 1.32 (d, 3H, J = 7.2 Hz, -CH\textsubscript{2}CH\textsubscript{3}).
\end{align*}
\]

\[
\begin{align*}
\text{\textsuperscript{13}C NMR (75 MHz, CDCl\textsubscript{3})} & : \delta 144.4, 135.0, 128.4, 127.7, 126.4, 117.9, 75.0, 45.4, 39.5, 16.3
\end{align*}
\]

IR (KBr) : 3466, 2925, 2856, 1736, 1640, 1455, 1329, 1159, 1094, 814 cm\textsuperscript{-1}.

MASS (EIMS) : m/z 176 (M\textsuperscript{+}), 135, 117, 107, 106, 105, 91, 79, 65, 71, 51, 43, 41.

1-(2-thienyl)-3-buten-1-ol (6l)

\[
\begin{align*}
\text{\textsuperscript{1}H NMR (200 MHz, CDCl\textsubscript{3})} & : \delta 7.25-7.13 (m, 1H, Aromatic-H), 6.98-6.84 (m, 2H, Aromatic-H),
5.92-5.67 (m, 1H, olefinic-H), 5.23-5.04 (m, 2H, olefinic-H), 4.93 (t, 1H, J = 6.3 Hz, -CH\textsubscript{2}CH(OH)-), 2.58 (t, 2H, J = 5.8 Hz, -CH\textsubscript{2}CH=CH\textsubscript{2}), 2.02 (br s, 1H, -OH).
\end{align*}
\]

MASS (EIMS) : m/z 156 (M\textsuperscript{+})

(5E)-1,5-nonadien-4-ol (6m)
(1Z)-1-phenyl-1,5-hexadien-3-ol (6n)

\[
\begin{align*}
\text{\textbf{\textit{\textsuperscript{1}H NMR (200 MHz, CDCl\textsubscript{3})}} :} & \ \delta 5.85-5.72 (m, 1H, olefinic-H), 5.70-5.60 (m, 1H, olefinic-H), 5.50-5.40 (m, 1H, olefinic-H), 5.16-5.05 (m, 2H, olefinic-H), 4.10 (q, 1H, J = 5.4 Hz, -CH\textsubscript{2}CH(OH)-), 2.30-2.20 (m, 2H, -CH\textsubscript{2}CH=CH\textsubscript{2}), 2.05-1.95 (m, 2H, -CH\textsubscript{2}CH=CH\textsubscript{2}), 1.60 (br s, 1H, -OH), 1.45-1.34 (m, 2H, -CH\textsubscript{2}CH-), 0.90 (t, 3H, J = 7.4 Hz, -CH\textsubscript{2}CH\textsubscript{3}). \\
\text{\textbf{\textit{IR (Neat)}} :} & \ 3416, 3025, 2925, 1673, 1625, 1494, 1299, 1201, 1127, 1030, 970 cm\textsuperscript{-1}. \\
\text{\textbf{\textit{MASS (EIMS)}} :} & \ m/z 140 (M\textsuperscript{+}), 99, 71, 57
\end{align*}
\]

\[
\begin{align*}
\text{1-octen-4-ol (6o)}
\end{align*}
\]

\[
\begin{align*}
\text{\textbf{\textit{\textsuperscript{1}H NMR (200 MHz, CDCl\textsubscript{3})}} :} & \ \delta 7.38-7.14 (m, 5H, Aromatic-H), 6.58 (d, 1H, J = 7.3 Hz, olefinic-H), 6.21 (dd, 1H, J = 12.3, 5.8 Hz, olefinic-H), 5.91-5.75 (m, 1H, olefinic-H), 5.22-5.10 (m, 2H, olefinic-H), 4.31 (q, 1H, J = 6.1 Hz, -CH\textsubscript{2}CH(OH)-), 2.50-2.28 (m, 2H, -CH\textsubscript{2}CH=CH\textsubscript{2}), 1.72 (br s, 1H, -OH). \\
\text{\textbf{\textit{IR (Neat)}} :} & \ 3416, 2925, 2855, 1673, 1626, 1494, 1451, 1299, 1202, 1068, 971, 919 cm\textsuperscript{-1}. \\
\text{\textbf{\textit{MASS (EIMS)}} :} & \ m/z 174 (M\textsuperscript{+}), 134, 116, 92, 78, 55, 39
\end{align*}
\]
CH$_2$CH(OH)$^-$, 2.40-2.02 (m, 2H, -CH$_2$CH=CH$_2$),
1.60-1.20 (m, 6H), 1.02-0.80 (m, 3H).

IR (Neat) : 3424, 2913, 1638, 1462, 1279, 1215, 1127, 1030 cm$^{-1}$. 

Chapter III

Section B
REFERENCES
REFERENCES


1309.
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Hecheng Huaxue 2000, 8, 364. (d) Tong-shou, J. Synth. Commun. 1998, 28,
3173. (e) Daohua, L.; Bi, W. Huaxue Shijie 2000, 41, 373. (f) Wang, B.; Yang,
L.; Suo, J. Synth. Commun. 2003, 33, 3929. (g) Bo, W.; Ming, Y. L.; Shuan, S.
SPECTRA
EIMS SPECTRUM OF COMPOUND 6b
$^1$H NMR SPECTRUM OF COMPOUND 6d
$^1\text{H} \text{NMR SPECTRUM OF COMPOUND 6g}$
NCMS IICT
07-30-2002

PH.LRP P S R REDDY PH-GLY-OH

Scan 4 RT= 0:16 No.ions= 417 Base= 87.5%F TIC=185016

EIMS SPECTRUM OF COMPOUND 6g
$^1$H NMR SPECTRUM OF COMPOUND 6j
Indian Institute of Chemical Technology, Hyderabad

FT-IR Analysis Report

IR SPECTRUM OF COMPOUND 6j

Sample: NPA [NEAT]
Collection time: Fri Feb 11 26:24 2005 (GMT+05:30)
Bench: Thermo Nicolet Nexus 670 Spectrometer
Resolution: 4 cm⁻¹

Detector: DTGS KBr
Beamsplitter: KBr
Source: IR

Sample: NPA [NEAT]
Collection time: Fri Feb 11 26:24 2005 (GMT+05:30)
Bench: Thermo Nicolet Nexus 670 Spectrometer
Resolution: 4 cm⁻¹

Detector: DTGS KBr
Beamsplitter: KBr
Source: IR
Indian Institute of Chemical Technology, Hyderabad

IR Analysis Report

IR SPECTRUM OF COMPOUND 6m

Sample: CAA [NEAT]
Collection time: Fri Feb 11 11:33:24 2005 (GMT+05:30)
Bench: Thermo Nicolet Nexus 6/0 Spectrometer
Resolution: 4 cm⁻¹

Detector: DTGS KBr
Beamsplitter: KBr
Source: IR
CAA.LRP
Date run: 02-10-2005(17:10:03) Instr.: VG 7070H Operator: NCMS
Scan 6 RT= 0:28 No. ions= 487 Base= 59.1%F TIC=159694

EIMS Spectrum of Compound 6a
CHAPTER III

Section C
Efficient Halogenation of Aromatic Systems Using N-Halo succinimides in Ionic Liquids
INTRODUCTION

Environment protection laws and corporate pressure to minimize the amount of toxic waste arising from chemical processes have led to the development of innovative and eco-friendly chemical technologies. In this context, ionic liquids have recently gained recognition as possible environmentally benign alternative solvents in various chemical processes. They provide an eco-friendly reaction medium for a variety of organic transformations, as they are non-volatile, recyclable, non-explosive, easy to handle, thermally robust and in addition they are compatible with various organic compounds and organometallic reagents. Because of the great potential of room temperature ionic liquids as environmentally benign media for catalytic processes, much attention has been currently focused on organic reactions catalyzed by ionic liquids.

Historical development:

What are ionic liquids? Quite simply, they are liquids that are composed entirely of ions. Molten sodium chloride, for example, is an ionic liquid but a solution of sodium chloride in water is an ionic solution. The term ‘Molten salts’, which was previously used to describe such materials, evokes an image of high temperature, viscous and highly corrosive media. The term ionic liquid, in contrast, implies a material that is fluid at (or close to) ambient temperature, is colourless, has a low viscosity and is easily handled, that is a material with attractive properties for a solvent. Room temperature ionic liquids are generally salts of organic cations, e.g. tetraalkylammonium, tetraalkylphosphonium, N-alkylpyridinium, 1,3-dialkylimidazolium and trialkylsulfonium cations.

In order to be liquid at room temperature, the cation should preferably be unsymmetrical, e.g., R₁ and R₂ should be different alkyl groups in the dialkyl imidazolium cation. The first examples of ionic liquids based on dialkylimidazolium cations were reported in the early 1980’s by Wilkes and co-workers. They contained chloro aluminate anions (AlCl₄⁻ or Al₂Cl₇⁻) and proved to be useful catalysts/solvents for Friedel-Crafts acylations.
The first example of the new ionic liquids, that are receiving much attention as novel reaction media for homogeneous catalysis, ethylmethylimidazolium tetrafluoroborate (emim)BF$_4$ was reported by Wilkes et al., in 1992. The synthesis of corresponding hexafluorophosphate followed shortly thereafter. In contrast to the chloroaluminate salts the fluoroaluminates and hexafluorophosphates are stable towards hydrolysis. Subsequently, 1,3-dialkylimidazolium salts containing a wide variety of anions, e.g., CF$_3$SO$_3^-$, [CF$_3$SO$_2$]$_2$N$^-$, CF$_3$CO$_2^-$, PhSO$_3^-$ and many more have been prepared. Room temperature ionic liquids, especially those based on the 1-n-alkyl-3-methylimidazolium cation, have shown great promise as an alternative to conventional solvents.

The hydrophilicity/lipophilicity of an ionic liquid can be modified by a suitable choice of anions, e.g., (bmim)BF$_4$ is completely miscible with water while the PF$_6$ salt is largely immiscible with water. The lipophilicity of dialkylimidazolium salts, or other ionic liquids, can also be increased by increasing the chain length of the alkyl groups.

Another question, which arises in any discussion of ionic liquids as reaction media pertains to the isolation of soluble reaction products. Volatile products, on the other hand, can be separated by solvent extraction. Although this seems paradoxical–using an ionic liquid to avoid atmospheric emissions and subsequently using a volatile organic solvent to extract the product it could have environmental benefits. For example, substituting an environmentally unacceptable solvent by an ionic liquid as the reaction medium, followed by extraction with a more benign organic solvent would constitute an environmental benefit. In this context it is worth noting the use of supercritical CO$_2$ to extract product from ionic liquids, which is currently the focus of attention.
PRESENT WORK

Halogenation of aromatic systems is an important industrial process for the synthesis of drugs, pharmaceuticals, agrochemicals, pigments and photographic materials.\textsuperscript{11} The direct method for the bromination of aromatic systems using Br$_2$ generates toxic and corrosive HBr, which causes serious environmental pollution.\textsuperscript{12} Subsequently, several methods have been developed for the bromination of aromatic systems using a variety of brominating agents under various reaction conditions.\textsuperscript{13,14}

Among these reagents, NBS is one of the most popular and inexpensive brominating agents for allylic, benzylic and aromatic nuclear brominations under mild conditions.\textsuperscript{15} The major advantage of the use of NBS as brominating agent is that the by-product succinimide can be easily recovered and reconverted to NBS and can be reused in subsequent reactions. Allylic and benzylic bromination with NBS takes place in the presence of a radical initiator in CCl$_4$.\textsuperscript{16} The bromination of unactivated aromatics with NBS proceeds only in the presence of stoichiometric amounts of strong Lewis acids or protic acids.\textsuperscript{17} The nuclear bromination of activated aromatic systems with NBS is generally favoured in polar solvents such as propylene carbonate, DMF and CH$_3$CN.\textsuperscript{18} However, the use of solvents like water, supercritical fluids and ionic liquids has received a great deal of attention in different areas of organic chemistry.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{chemical_structures.png}
\caption{Chemical structures of ionic liquids (ILs)}
\end{figure}

Ionic liquids are being used as ‘green solvents’ with unique properties such as good solvating ability, wide liquid range, tunable polarity, high thermal stability, immiscibility with a number of organic solvents, negligible vapor pressure and ease of recyclability.\textsuperscript{19} Due to the stabilization of charged intermediates by ionic liquids, the latter can promote unprecedented selectivities and reaction rates in comparison with conventional solvents. Because of their distinct advantages, ionic liquids can make a greater contribution to green chemistry.\textsuperscript{20} More recently, ionic liquids have also been used for the bromination of aromatic systems.\textsuperscript{21} We herein report the use of ionic
liquids as novel and recyclable polar reaction media for the halogenation of aromatic systems using N-halosuccinimides (Scheme 11).

Accordingly, treatment of anisole with NBS and NIS in 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim]PF₆) ionic liquid afforded p-bromo- and p-iodoanisoles in 92% and 95% yields, respectively. In a similar manner, various substituted aromatic systems were converted to their corresponding bromo and iodo derivatives in high to quantitative yields by using this procedure.

Methyl substituted aromatic compounds also reacted smoothly with N-halosuccinimides in ionic liquids to produce the corresponding halo benzenes without halogenation of the alkyl side-chain. The substrates show significant enhancement in reaction rates and yields in ionic liquids compared to molecular organic solvents. Treatment of o-methoxy phenol with NBS in [bmim]PF₆ ionic liquid for 15 min afforded the corresponding 4-bromo-2-methoxyphenol in 90% yield with para-selectivity whereas the same reaction in acetonitrile after 2 h gave the product in 79% yield as a mixture of para- (major) and ortho-isomers (minor).

The rate enhancement in ionic liquids is probably due to the enhanced reactivity of N-halosuccinimides as a result of increased polarization of the N-X bond in polar ionic media and also to the stabilization of the charged ionic intermediates by ionic liquids. This type of ionic environment might not be achieved in molecular organic solvents. It is also known that the polar solvents can enhance the polarization of NBS thereby ring bromination is possible even in the case of polyalkylbenzenes. Since the products were weakly soluble in the hydrophobic [bmim]PF₆ ionic liquid, they could be easily separated by simple extraction with toluene or ether. Then the rest of the ionic liquid was thoroughly washed with water to recover the water-soluble succinimide. The recovered succinimide was reconverted to the corresponding N-halosuccinimide and
then reused in subsequent reactions. The rest of the ionic liquid was activated at 80 °C under reduced pressure and recycled in further runs without any loss of activity and also, the products were obtained of the same purity as in the first run, in runs carried out using recycled activated ionic liquid.

Compound 9c in its $^{1}$H NMR spectrum showed the chemical shifts for the phenolic proton at 10.9 ppm as a broad singlet, at 9.95 ppm as singlet for aldehyde proton and aromatic protons resonated at 7.70 ppm as a singlet, at 7.60 ppm as a doublet of doublet ($J = 8.0, 2.0$ Hz) and at 6.90 ppm as a doublet ($J = 8.0$ Hz). The compound 9c was also characterized by its mass analysis, which in its EIMS showed (M$^{+}$) peak at m/z 201. IR spectrum showed the absorption band at 1673 cm$^{-1}$ indicated for the aldehyde stretching and the absorption band at 3226 cm$^{-1}$ corresponding to $\text{-OH}$ moiety.

Similarly compound 9n was also characterized by its PMR spectrum, which showed the chemical shifts for aromatic protons at 7.48 ppm as multiplet, at 7.08 ppm as a double doublet ($J = 8.0, 2.0$ Hz) and at 6.88 ppm as doublet ($J = 7.0$ Hz). Isopropyl protons resonated as quartet at 2.80 ppm and at 1.22 ppm, 1.20 ppm as singlets respectively. The compound 9n was also characterized by its mass spectrum (EIMS), which showed a (M$^{+}$) peak at m/z 262.

Treatment of anisole with NIS in hydrophobic [bmim]PF$_{6}$ gave 95%, 93% and 94% yields over three cycles. Even though similar results were also obtained in hydrophilic [bmim]BF$_{4}$ ionic liquid, the recovery of succinimide is especially simple in [bmim]PF$_{6}$ ionic liquid due to its hydrophobic nature.

To compare the efficiency of ionic liquids, the reactions were also carried out in various quaternary ammonium salts such as 1-butyl-3-methylimidazolium chloride [bmim]Cl and tetra-$n$-butylammonium chloride. The scope and generality of this process is illustrated with respect to various aromatic substrates and N-halosuccinimides. Furthermore, NCS also reacted similar to NBS and NIS, with aromatic systems to give the corresponding chloroaromatics in 79-92% yields within 0.5-1.5 h in [bmim]PF$_{6}$ ionic liquid and the results are presented in the Table 3.

In conclusion, [bmim]PF$_{6}$ ionic liquid has proved to be a useful and polar alternative reaction media for the regioselective halogenation of aromatic compounds
using $N$-halosuccinimides avoiding the use of environmentally unfavorable organic solvents by playing a dual role of solvent as well as promoter. The simple experimental and product isolation procedures combined with ease of recovery and reuse of this novel reaction media are expected to contribute to the development of a green strategy for the halogenation of aromatic systems. The recoverability of succinimide and recyclability of [bmim]PF$_6$ is facilitated by its hydrophobic nature.
### Table 3. Halogenation of arenes using N-Halosuccinimides in [bmim]PF₆ ionic liquid

<table>
<thead>
<tr>
<th>Entry</th>
<th>Arene</th>
<th>N-Halosuccinimides</th>
<th>Product[^a^]</th>
<th>Time (min)</th>
<th>Yield (%)[^b^]</th>
</tr>
</thead>
<tbody>
<tr>
<td>a)</td>
<td><img src="image" alt="Chemical Structure" /></td>
<td>NBS</td>
<td><img src="image" alt="Chemical Structure" /></td>
<td>55</td>
<td>84</td>
</tr>
<tr>
<td>b)</td>
<td><img src="image" alt="Chemical Structure" /></td>
<td>NBS</td>
<td><img src="image" alt="Chemical Structure" /></td>
<td>35</td>
<td>85</td>
</tr>
<tr>
<td>c)</td>
<td><img src="image" alt="Chemical Structure" /></td>
<td>NBS</td>
<td><img src="image" alt="Chemical Structure" /></td>
<td>35</td>
<td>87</td>
</tr>
<tr>
<td>d)</td>
<td><img src="image" alt="Chemical Structure" /></td>
<td>NBS</td>
<td><img src="image" alt="Chemical Structure" /></td>
<td>50</td>
<td>82</td>
</tr>
<tr>
<td>e)</td>
<td><img src="image" alt="Chemical Structure" /></td>
<td>NBS</td>
<td><img src="image" alt="Chemical Structure" /></td>
<td>25</td>
<td>92</td>
</tr>
<tr>
<td>f)</td>
<td><img src="image" alt="Chemical Structure" /></td>
<td>NCS</td>
<td><img src="image" alt="Chemical Structure" /></td>
<td>45</td>
<td>87</td>
</tr>
<tr>
<td>g)</td>
<td><img src="image" alt="Chemical Structure" /></td>
<td>NCS</td>
<td><img src="image" alt="Chemical Structure" /></td>
<td>30</td>
<td>90</td>
</tr>
<tr>
<td>h)</td>
<td><img src="image" alt="Chemical Structure" /></td>
<td>NCS</td>
<td><img src="image" alt="Chemical Structure" /></td>
<td>40</td>
<td>90</td>
</tr>
<tr>
<td>i)</td>
<td><img src="image" alt="Chemical Structure" /></td>
<td>NCS</td>
<td><img src="image" alt="Chemical Structure" /></td>
<td>45</td>
<td>87</td>
</tr>
<tr>
<td>j)</td>
<td><img src="image" alt="Chemical Structure" /></td>
<td>NCS</td>
<td><img src="image" alt="Chemical Structure" /></td>
<td>75</td>
<td>78</td>
</tr>
<tr>
<td>k)</td>
<td><img src="image" alt="Chemical Structure" /></td>
<td>NIS</td>
<td><img src="image" alt="Chemical Structure" /></td>
<td>15</td>
<td>95</td>
</tr>
<tr>
<td>l)</td>
<td><img src="image" alt="Chemical Structure" /></td>
<td>NIS</td>
<td><img src="image" alt="Chemical Structure" /></td>
<td>25</td>
<td>94</td>
</tr>
<tr>
<td>m)</td>
<td><img src="image" alt="Chemical Structure" /></td>
<td>NIS</td>
<td><img src="image" alt="Chemical Structure" /></td>
<td>20</td>
<td>92</td>
</tr>
<tr>
<td>n)</td>
<td><img src="image" alt="Chemical Structure" /></td>
<td>NIS</td>
<td><img src="image" alt="Chemical Structure" /></td>
<td>40</td>
<td>89</td>
</tr>
<tr>
<td>o)</td>
<td><img src="image" alt="Chemical Structure" /></td>
<td>NIS</td>
<td><img src="image" alt="Chemical Structure" /></td>
<td>35</td>
<td>92</td>
</tr>
</tbody>
</table>

[^a^] Product structure with X = Br, Cl and I

[^b^] All products were characterised by 1H NMR, IR and mass spectrometry

[^b^] Yield refers to pure products after column chromatography
EXPERIMENTAL
EXPERIMENTAL

General Procedure

A mixture of aromatic substrate (1 mmol) and N-halosuccinimide (1.2 mmol) in [bmim]PF₆ or [bmim]BF₄ (2 mL) was stirred at 27 °C for the appropriate time (Table 3). After completion of the reaction, as indicated by TLC, the reaction mixture was washed with toluene or diethyl ether (3 x 10 mL). The combined organic extracts were concentrated under vacuum and the resulting product was directly charged onto a small silica gel column and eluted with a mixture of ethylacetate:n-hexane (1 : 9) to afford the pure halogenated arene. The rest of the [bmim]PF₆ ionic liquid was washed with water to remove the succinimide, the ionic liquid was reactivated at 80 °C under reduced pressure and recycled in subsequent runs without any loss of activity. In the case of liquids, the products were easily be separated by distillation. The spectral data of all the products were identical with those of authentic samples.  

2-Bromo-4,5-dimethoxy-acetophenone (9a)

\[
\begin{align*}
\text{H NMR (200 MHz, CDCl₃)} & : \delta 7.52-7.40 (m, 1H, Aromatic-H), 6.80 (d, 1H, J = 8.1 Hz, Aromatic-H), 3.90 (s, 3H, -OCH₃ ), 3.89 (s, 3H, -OCH₃ ), 2.50 (s, 3H, -COCH₃ ). \\
\text{IR (Neat)} & : 2921, 2851, 1683, 1591, 1502, 1371, 1258, 1216, 1171, 1011, 773 \text{ cm}^{-1} \\
\text{MASS (EIMS)} & : m/z 259 (M⁺), 228, 213, 133, 90, 74, 50
\end{align*}
\]

2-Bromo-4-isopropylphenol (9b)

\[
\begin{align*}
\text{H NMR (200 MHz, CDCl₃)} & : \delta 7.52-7.40 (m, 1H, Aromatic-H), 6.80 (d, 1H, J = 8.1 Hz, Aromatic-H), 3.90 (s, 3H, -OCH₃ ), 3.89 (s, 3H, -OCH₃ ), 2.50 (s, 3H, -COCH₃ ). \\
\text{IR (Neat)} & : 2921, 2851, 1683, 1591, 1502, 1371, 1258, 1216, 1171, 1011, 773 \text{ cm}^{-1} \\
\text{MASS (EIMS)} & : m/z 259 (M⁺), 228, 213, 133, 90, 74, 50
\end{align*}
\]
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\[ ^1H \text{NMR (200 MHz, CDCl}_3 \]: \delta 7.28 (s, 1H, Aromatic-H), 7.12-7.05 (dd, 1H, \( J = 8.1, 2.0 \text{ Hz, Aromatic-H} \)), 6.93 (d, 1H, \( J = 8.1 \text{ Hz, Aromatic-H} \)), 2.90-2.75 (m, 1H, \(-\text{CH(}\text{CH}_3\)_2-}), 1.28 (s, 3H, \(-\text{CHCH}_3\)), 1.22 (s, 3H, \(-\text{CHCH}_3\)). \\

IR (Neat) : 3507, 2962, 2872, 2361, 1711, 1606, 1559, 1496, 1476, 1414, 1364, 1324, 1276, 1184, 1039, 873, 848, 823, 735, 670 cm\(^{-1}\) \\

MASS (EIMS) : \text{m/z} 215 (M\(^+\)), 172, 91, 74, 43. \\

\(5\)-Bromo-2-hydroxybenzaldehyde (9c) \\

\begin{center}
\begin{tikzpicture}
  \node at (0,0) {\text{Br}};
  \node at (0.5,0) {\text{CHO}};
  \node at (-0.5,0) {\text{OH}};
\end{tikzpicture}
\end{center}

Solid, M.P : 104-105 °C \\
\[ ^1H \text{NMR (200 MHz, CDCl}_3 \]: \delta 10.9 (br s, 1H, \(-\text{OH phenolic} \)), 9.95 (s, 1H, \(-\text{CHO} \)), 7.70 (s, 1H, Aromatic-H), 7.60 (dd, 1H, \( J = 8.0, 2.0 \text{ Hz, Aromatic-H} \)), 6.90 (d, 1H, \( J = 8.0 \text{ Hz, Aromatic-H} \)). \\

IR (KBr) : 3226, 2876, 2364, 1673, 1610, 1563, 1467, 1373, 1305, 1276, 1207, 1155, 1114, 890, 828, 766 cm\(^{-1}\) \\

MASS (EIMS) : \text{m/z} 201(M\(^+\)), 200, 157, 144, 65, 63, 43. \\

\(1\)-Bromo-2-methylnaphthalene (9d) \\

\begin{center}
\begin{tikzpicture}
  \node at (0,0) {\text{Br}};
  \node at (-1,0) {\text{Me}};
\end{tikzpicture}
\end{center}

\[ ^1H \text{NMR (200 MHz, CDCl}_3 \]: \delta 8.30 (d, 1H, \( J = 8.0 \text{ Hz, Aromatic-H} \)), 7.80 (d, 1H, \( J = 8.1 \text{ Hz, Aromatic-H} \)), 7.73-7.65 (m, 1H, Aromatic-H), 7.60 (dd, 1H, \( J = 8.1, 2.0 \text{ Hz, Aromatic-H} \)), 7.55 (d, 1H, \( J = 8.0 \text{ Hz, Aromatic-H} \)), 7.30 (d, 1H, \( J = 8.1 \text{ Hz, Aromatic-H} \)), 2.65 (s, 3H, \(-\text{CHCH}_3\)).
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IR (Neat)  
: 3052, 2979, 2867, 2361, 1595, 1556, 1440, 1326, 1259, 1138, 862, 763 cm⁻¹

MASS (EIMS)  
: m/z 221 (M⁺), 142, 126, 116, 91, 43.

2-Bromo-4,5-methylenedioxyphenol (9e)

![Structure of 2-Bromo-4,5-methylenedioxyphenol (9e)]

Solid, M.P  
: 150-152 °C

¹H NMR (200 MHz, CDCl₃)  
: δ 6.83 (s, 1H, Aromatic-H), 6.58 (s, 1H, Aromatic-H), 5.92 (s, 2H, -OCH₂O-), 5.30 (br s, 1H, -OH).

IR (KBr)  
: 3489, 2924, 2854, 1619, 1469, 1379, 1164, 1014, 963, 827, 650 cm⁻¹

MASS (EIMS)  
: m/z 217 (M⁺), 187, 106, 90, 74, 50.

2-Methoxy-4-chlorophenol (9f)

![Structure of 2-Methoxy-4-chlorophenol (9f)]

¹H NMR (200 MHz, CDCl₃)  
: δ 7.05-6.95 (m, 1H, Aromatic-H), 6.98 (d, 1H, J = 8.0 Hz, Aromatic-H), 6.81 (d, 1H, J = 8.0 Hz, Aromatic-H), 5.65 (br s, 1H, -OH), 3.88 (s, 3H, -OCH₃).

IR (Neat)  
: 3478, 2949, 2863, 1606, 1581, 1473, 1422, 1293, 1229, 1091, 932, 865 cm⁻¹

MASS (EIMS)  
: m/z 160 (M⁺²), 158, 143, 126, 91, 76, 51.

1,2,3-Trimethoxy-4-chlorobenzene (9g)

![Structure of 1,2,3-Trimethoxy-4-chlorobenzene (9g)]
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$^1$H NMR (200 MHz, CDCl$_3$) : $\delta$ 7.00 (d, 1H, $J = 8.0$ Hz, Aromatic-H), 6.58 (d, 1H, $J = 8.0$ Hz, Aromatic-H), 3.90 (s, 3H, -OCH$_3$), 3.85 (s, 3H, -OCH$_3$), 3.80 (s, 3H, -OCH$_3$).

$^{13}$C NMR (50 MHz, CDCl$_3$) : $\delta$ 152.6, 150.2, 143.5, 123.6, 107.9, 107.5, 61.6, 56.4

IR (Neat) : 2941, 2840, 1722, 1581, 1466, 1414, 1297, 1221, 1177, 1094, 1070, 1017, 936, 896, 865, 774 cm$^{-1}$

MASS (EIMS) : $m/z$ 204 (M$^+$), 202, 187, 172, 156, 141, 125

4,5-Methylenedioxy-2-chlorophenol (9h)

\[\text{Solid, M.P} : 88-90 ^\circ C\]

$^1$H NMR (200 MHz, CDCl$_3$) : $\delta$ 9.40 (br s, 1H, -OH phenolic), 6.79 (s, 1H, Aromatic-H), 6.59 (s, 1H, Aromatic-H), 5.95 (s, 2H, -OCH$_2$O-).

IR (KBr) : 3463, 2902, 1631, 1480, 1376, 1305, 1188, 1110, 1036, 934, 841, 767 cm$^{-1}$

MASS (EIMS) : $m/z$ 174 (M$^+$), 172, 157, 129, 111, 99, 93, 86, 79

1-Chloro-2-methoxynaphthalene (9i)

\[\text{Solid, M.P} : 68-69 ^\circ C\]

$^1$H NMR (200 MHz, CDCl$_3$) : $\delta$ 8.20 (d, 1H, $J = 7.9$ Hz, Aromatic-H), 7.82 (d, 1H, $J = 8.0$ Hz, Aromatic-H), 7.75 (d, 1H, $J = 7.9$ Hz, Aromatic-H), 7.60-7.32 (m, 2H, Aromatic-H), 7.19 (d, 1H, $J = 8.0$ Hz, Aromatic-H), 3.98 (s, 3H, -OCH$_3$).
Chapter III

Section C

IR (KBr) : 2983, 2847, 1608, 1471, 1267, 1227, 1183, 1096, 924, 896, 862, 810, 764 cm⁻¹

MASS (EIMS) : m/z 194 (M⁺), 192, 177, 161, 149, 126, 101, 63.

1-Chloro-2-methylnaphthalene (9j)

\[
\text{\includegraphics[width=0.2\textwidth]{9j.png}}
\]

\[1^H \text{NMR (200 MHz, CDCl}_3\] : δ 8.22 (d, 1H, \(J = 8.0\) Hz, Aromatic-H), 7.78-7.60 (m, 2H, Aromatic-H), 7.40-7.35 (m, 2H, Aromatic-H), 7.24 (d, 1H, \(J = 8.0\) Hz, Aromatic-H), 2.60 (s, 3H, -CHCH₃).

IR (Neat) : 3056, 2981, 2873, 2364, 1716, 1597, 1558, 1503, 1447, 1331, 1224, 1176, 1132, 1091, 1009, 918, 834, 794, 772 cm⁻¹

MASS (EIMS) : m/z 178 (M⁺), 176, 141, 126, 116, 91, 66

1,2,3-Trimethoxy-4-iodobenzene (9k)

\[
\text{\includegraphics[width=0.2\textwidth]{9k.png}}
\]

\[1^H \text{NMR (200 MHz, CDCl}_3\] : δ 7.42 (d, 1H, \(J = 8.0\) Hz, Aromatic-H), 6.44 (d, 1H, \(J = 8.0\) Hz, Aromatic-H), 3.85 (s, 3H, -OCH₃), 3.80 (s, 3H, -OCH₃), 3.79 (s, 3H, -OCH₃).

IR (Neat) : 2937, 2838, 1572, 1476, 1430, 1405, 1292, 1221, 1176, 1132, 1091, 1009, 918, 834, 794, 772 cm⁻¹

MASS (EIMS) : m/z 294 (M⁺), 179, 109, 77.

1-Iodo-2-hydroxynaphthalene (9l)

\[
\text{\includegraphics[width=0.2\textwidth]{9l.png}}
\]

Solid, M.P : 90-92 °C
Chapter III

Section C

$^1$H NMR (200 MHz, CDCl$_3$)

$^{13}$C NMR (50 MHz, CDCl$_3$)

IR (KBr)

MASS (EIMS)

3,4-Methylenedioxy-6-iodophenol (9m)

Solid. M.P

$^1$H NMR (200 MHz, CDCl$_3$)

IR (KBr)

MASS (EIMS)

4-Isopropyl-6-iodophenol (9n)

$^1$H NMR (200 MHz, CDCl$_3$)
Chapter III

Section C

IR (Neat): 3506, 2961, 1709, 1607, 1558, 1473, 1416, 1322, 1278, 1183, 1037, 871, 846, 823, 736, 675 cm\(^{-1}\)

MASS (EIMS): \(m/z\) 262 (M\(^+\)), 219, 92, 74, 43.

1-Iodo-2-methoxynaphthalene (9o)

\[
\text{Solid. M.P: 86-87 °C}
\]

\(^1\text{H NMR (200 MHz, CDCl}_3\)): \(\delta\) 8.13 (d, 1H, \(J = 8.3\) Hz, Aromatic-H), 7.80 (d, 1H, \(J = 8.2\) Hz, Aromatic-H), 7.74 (d, 1H, \(J = 8.3\) Hz, Aromatic-H), 7.52 (dd, 1H, \(J = 8.3, 2.1\) Hz, Aromatic-H), 7.36 (dd, 1H, \(J = 8.3, 2.0\) Hz, Aromatic-H), 7.24 (d, 1H, \(J = 8.3\) Hz, Aromatic-H), 4.02 (s, 3H, -OCH\(_3\)).

IR (KBr): 2973, 2843, 1676, 1506, 1483, 1374, 1296, 1229, 1126, 1046, 949, 848, 774 cm\(^{-1}\)

MASS (EIMS): \(m/z\) 284 (M\(^+\)), 169, 168, 128, 127, 115, 63
REFERENCES
REFERENCES


$^1$H NMR SPECTRUM OF COMPOUND 9c
SAL.LRP  a k basak, jsy-sal

Scan 6  RT= 0:20  No.ions= 598  Base= 35.2%  TIC=178537

EIMS SPECTRUM OF COMPOUND 9c
H NMR SPECTRUM OF COMPOUND 9d
MNAPH.LRP  a k basak, jsy-mnaph

Scan 6  RT= 0:22 No.ions= 443 Base= 50.6%F TIC=340306

EIMS SPECTRUM OF COMPOUND 9d
$^1$H NMR SPECTRUM OF COMPOUND 9h
\textbf{H NMR SPECTRUM OF COMPOUND 9k}
$^1$H NMR SPECTRUM OF COMPOUND 9n
$^1$H NMR SPECTRUM OF COMPOUND 9a
Scan 5  RT: 0:19  No. ions: 110  Base: 79.1%  TIC: 150424

EIMS SPECTRUM OF COMPOUND 9a