Chapter 1

Studies on N-Arylation of NH-Heterocycles and Diphenylamine
1.1 Introduction

In recent years, there has been sustained interest on the development of transition metal catalyzed coupling reactions. Well-known cross coupling reactions in the literature are Wurtz-Fittig,\textsuperscript{1} Ullmann,\textsuperscript{2} Goldberg,\textsuperscript{3} Suzuki,\textsuperscript{4} Stille,\textsuperscript{5} Sonogashira,\textsuperscript{6} Heck,\textsuperscript{7} Negishi,\textsuperscript{8} Hiyama,\textsuperscript{9} Kumada,\textsuperscript{10} Buchwald-Hartwig,\textsuperscript{11} and Chan-Lam\textsuperscript{12} coupling reactions. Various cross coupling reactions C-C, C-N, C-O, C-S, and C-P have been reported. We have undertaken studies on the C-N cross coupling reaction. A brief review on this topic will be helpful for the discussion.

1.1.1 N-Arylation of amines

The C-N bond formation is one of the most important transformations useful for the synthesis of compounds of interest to pharmaceutical and material science applications. In recent years, transition-metal-mediated N-aryl bond formation has become a standard procedure for the introduction of amines into aromatic systems.\textsuperscript{13} The reports on this topic are reviewed in this section.

1.1.1.1 Palladium catalyzed N-arylations of amines

Reports on the palladium complexes with various ligands like \textit{rac}-BINAP 3 or xantpos 7 or PPF-OMe 9 are useful in N-arylation of both aliphatic and aromatic amines (chart 1).\textsuperscript{14-16}
In recent years, there have been immense interest on the development of robust methodology to obtain triarylamines. Various triarylamines 14, 18 and 21 are readily prepared by palladium complexes catalyzed cross coupling reactions of arylhalides and diarylamines in excellent yields (Chart 2).

Chart 1

**Chart 1**

\[
\begin{align*}
\text{Step-I:} & \quad R-NH_2 + Ar-Br & \rightarrow & \quad R-NH Ar \\
& \quad 5 + 2 & \rightarrow & \quad 6 \\
& \quad \text{R = Alkyl or Aryl} \\
\text{Ref. 16} & \\
\end{align*}
\]

**Chart 2**

\[
\begin{align*}
\text{Step-II:} & \quad R-NAr + Ar'-Br & \rightarrow & \quad R-NAr Ar' \\
& \quad 6 + 2 & \rightarrow & \quad 10 \\
& \quad \text{R = Alkyl or Aryl} \\
& \quad \text{R' = Alkyl or Aryl} \\
\text{Ref. 16} & \\
\end{align*}
\]
Chart 2 continued

15

16

17

18, 69-96% y

Ref. 27

19

2

20

21, 71-98% y

Ref. 28

19

2

20

21, 89-90% y

Ref. 29

19

2

1-Pd: (5 mol% Pd): 92% y
1-Pd: After 5th reuses: 92% y
2-Pd: (5 mol% Pd): < 2% y
1 (Without Pd): < 2% y
K₂PdCl₄ (Without 1): messy mixture
none (without Pd or 1): < 2% y

Ref. 30
1.1.1.2 Nickel catalyzed N-arylation of amines

A methodology using the NiCl\(_2\)(PPh\(_3\))\(_2\)-PPh\(_3\) was reported for the synthesis of triarylamines from bromomagnesium intermediates, generated \textit{in situ} from diarylamines (Scheme 1).\(^{31}\)

Scheme 1

\[
\begin{align*}
\text{Ar}^\prime & \quad \text{NH} \quad \text{Ar} \quad \text{Ar}' \quad \text{Ar}'' \\
\text{Ar} & \quad \rightarrow \\
\text{Ar} & \quad \text{N} \quad \text{Ar}'' \\
\text{Ar} & \quad \rightarrow \\
\text{Ar} & \quad \text{N} \quad \text{Ar}''
\end{align*}
\]

1.1.1.3 Copper catalyzed N-arylations of amines

Recently, copper catalyzed N-arylation reactions have gained importance over palladium catalyzed N-arylations. Some of the important reports on N-arylation of amines with various copper catalyzed catalysts are outlined in the chart 3.\(^{32-36}\)

Chart 3

\[
\begin{align*}
\text{R}^\prime & \quad \text{NH} + \text{Ar-I} \quad \text{2 equiv. HO(CH}_2\text{)}_2\text{OH} \quad \text{K}_2\text{PO}_4/i\text{-PrOH} \quad 80 \degree \text{C} / 6-24 \text{ h} \quad \text{Ref. 32} \\
1 & \quad 2 & \quad 4 & \quad 70-91\% \ y
\end{align*}
\]

\[
\begin{align*}
\text{R}^\prime & \quad \text{NH} + \text{Ar-X} \quad \text{K}_2\text{CO}_3/\text{DMSO} \quad 40-80^\circ\text{C} / 11-40 \text{ h} \quad \text{Ref. 33} \\
1 & \quad 2 & \quad 4 & \quad 64-93\% \ y
\end{align*}
\]
Chart 3 continued

\[
\begin{align*}
\text{H}_2\text{N–R} + \text{Ar-I} & \xrightarrow{5 \text{ mol% CuO}_2, 20 \text{ mol% Ligand 28}} \text{R}^\cdot \text{N–H} \quad \text{Cs}_2\text{CO}_3/\text{MeCN}/80^\circ\text{C}/18 \text{ h} \quad \text{Ref. 34} \\
5 & 2 & 6, 65-91\% y
\end{align*}
\]

\[
\begin{align*}
\text{H}_2\text{N–R} + \text{Ar-I} & \xrightarrow{20 \text{ mol% Cu(II)TMHD}} \text{R}^\cdot \text{N–H} \\
\text{t-BuOK}/\text{Toluene}/120^\circ\text{C}/12 \text{ h} & \quad \text{Ref. 35} \\
5 & 2 & 6, 70-95\% y
\end{align*}
\]

\[
\begin{align*}
\text{R}^\cdot \text{NH} + \text{Ar-I} & \xrightarrow{20 \text{ mol% (±)-BINOL 29, 20 mol% CuBr}} \text{R}^\cdot \text{N–Ar} \\
\text{K}_3\text{PO}_4/\text{DMF}/25^\circ\text{C}/4-11 \text{ h} & \quad \text{Ref. 36} \\
1 & 2 & 4, 51-85\% y
\end{align*}
\]

The air-stable and soluble Cu(PPh₃)₃Br catalyst system is useful for the synthesis of functionalized diaryl and triarylamines under mild conditions (Scheme 2).³⁷

Scheme 2

\[
\begin{align*}
\text{R}^\cdot \text{N–H} + \text{Ar-I} & \xrightarrow{20 \text{ mol% Cu(PPh₃)₃Br}} \text{R}^\cdot \text{N–Ar} \\
\text{Cs}_2\text{CO}_3/\text{Toluene} & \quad \text{110-120}^\circ\text{C}/24 \text{ h} \\
19 & 2 & 21, 10-78\% y
\end{align*}
\]
Synthesis of triarylamines in a single step has been demonstrated using a ligand-free CuI catalyst and t-BuOK.\textsuperscript{38} Optimum results were obtained using 2,6-diphenylpyridine as a ligand (Scheme 3).

**Scheme 3**

![Scheme 3 Diagram](image)

The CuI/diazabutadienes (DABs) catalyst system has been developed for the synthesis of triarylamines by N-arylation of diarylamines 19 and anilines with aryl iodides (Scheme 4).\textsuperscript{39}

**Scheme 4**

![Scheme 4 Diagram](image)

A ligand free CuI catalysed methodology for the synthesis of triarylamines using anilines and aryl iodides has been reported (Scheme 5).\textsuperscript{40}
1.1.1.4 Iron catalyzed method for the synthesis of diarylamines

Diarylamines were synthesized from N-acylamides and aryl iodides using the FeCl₃ and DMEDA catalyst system (Scheme 6).⁴¹

Scheme 6

1.1.2 N-Arylation of NH-heterocycles

Heterocyclic skeletons are widely found in nature, particularly in nucleic acids, plant alkaloids, anthocyanins, flavones, haem, chlorophyll and some vitamins, proteins and hormones. Synthetically produced heterocycles are widely used as agrochemicals, pharmaceuticals and play an important role in biological processes. Heterocycles have enormous potential as promising molecules as lead structures for the design of new drugs.⁴² A brief review of reports on the N-arylation of heterocyclics will facilitate the discussion.
1.1.2.1 Palladium catalyzed N-arylations of NH-heterocyles

Reports on some typical palladium catalyzed N-arylation of NH-Heterocycles methods are outlined in chart 4.43-44

**Chart 4**

![Diagram of palladium catalyzed N-arylations](image)

1.1.2.2 Copper catalyzed N-arylations of NH-heterocyles

Reports on the inexpensive copper catalyzed N-arylation of NH-heterocycles (pyrroles, pyrazoles, indazoles, imidazoles, and triazoles) with various aryl halide coupling partners are outlined in chart 5.45-50

**Chart 5**

![Diagram of copper catalyzed N-arylations](image)
Chart 5 continued

Ar-X + \[\text{N-Heterocycle}\] \[\text{47}\] → \[\text{Ar-NH-Heterocycle}\] \[\text{49}\]

1. 0.05-20 mol% \(\text{Cu}_2\text{O}\)
2. 0.075-3 mol% Ligand
3. 1.4 equiv. \(\text{Cs}_2\text{CO}_3\)
4. PEG/PrCN/110 °C/3-48 h
5. Ref. 46

Ar-I + \[\text{N-Heterocycle}\] \[\text{47}\] → \[\text{Ar-NH-Heterocycle}\] \[\text{49}\]

1. 10 mol% \(\text{CuBr}\)
2. 10 mol% Ligand
3. \(\text{K}_2\text{CO}_3/\text{DMF}/110 ^\circ\text{C}/24-36\) h
4. Ref. 47

\[\text{N-Heterocycle}\] + \(\text{Ar-I}\) → \[\text{Ar-NH-Heterocycle}\] \[\text{49}\]

1. 10 mol% \(\text{Cu}_2\text{O}\)
2. 20 mol% Ninhydrin
3. \(\text{K}_2\text{CO}_3/\text{KOH}/\text{DMSO}/100-150 ^\circ\text{C}/24-48\) h
4. Ref. 48

\[\text{N-Heterocycle}\] + \(\text{Ar-I}\) → \[\text{Ar-NH-Heterocycle}\] \[\text{49}\]

1. 5 mol% \(\text{CuI}\)
2. 5 mol% Ligand
3. 1.1 equiv. \(\text{K}_3\text{PO}_4/\text{DMF}/110 ^\circ\text{C}/24\) h
4. Ref. 49
1.1.2.3 Iron/Copper catalyzed N-arylation of NH-heterocycles

Besides palladium,\textsuperscript{51} nickel,\textsuperscript{52} copper,\textsuperscript{53} and iron complexes\textsuperscript{54} have been also reported for the arylation of amines,\textsuperscript{55-57} pyrroles,\textsuperscript{58} imidazoles,\textsuperscript{54b,56,59} benzimidazoles\textsuperscript{59,60} triazoles, pyrazoles, indazoles, and indoles.\textsuperscript{61} Iron, being an abundant, inexpensive, environmentally benign transition metal is widely used in various organic transformations. Some N-arylation methods using Cu/Fe reagents are described in chart 6.

\textbf{Chart 6}

\begin{center}
\begin{tikzpicture}
  \node (a) {\ce{\text{H-N=C=N-}}};
  \node (b) [right of=a] {\ce{Ar-H}};
  \node (c) [right of=b] {\ce{Ar-N=C=N-}};
  \node (d) [below of=a] {\ce{\text{R-N=C=N-}}};
  \node (e) [right of=d] {\ce{Ar-N=C=N-}};
  \node (f) [below of=b] {\ce{\text{R-N=C=N-}}};
  \node (g) [below of=c] {\ce{\text{R-N=C=N-}}};

  \draw [->] (a) -- (b) node [midway, above] {0.1 equiv. \text{CuO}};
  \draw [->] (b) -- (c) node [midway, above] {2 equiv. \text{Cs}_2\text{CO}_3/\text{DMF}};
  \draw [->] (c) -- (d) node [midway, above] {90 °C/30 h};
  \draw [->] (d) -- (e) node [midway, above] {3 mol% of \text{Cu and FeCl}_3};
  \draw [->] (e) -- (f) node [midway, above] {\text{TBAF}.3H_2O};
  \draw [->] (f) -- (g) node [midway, above] {Air/50 °C/40 h};

  \node at (3,1) {\textbf{Ref. 62}};
  \node at (3,-1) {\textbf{Ref. 63}};
\end{tikzpicture}
\end{center}
The FeCl₃/DMEDA catalyst system has been reported for the N-arylation of NH-heterocycles with different aryl halides to obtain N-aryl heterocycles (Scheme 7).⁶⁴

**Scheme 7**

![Chemical structure](image)

The Fe₂O₃/L-proline 32 catalyst system was useful for the N-arylation of NH-heterocycles with various aryl halides (Scheme 8).⁶⁵

**Scheme 8**

![Chemical structure](image)

A ligand free environmentally benign iron catalyzed method for the cascade synthesis of 1,2,4-benzothiadiazine 1,1-dioxide 62 and quinazolinone 63 derivatives has been reported (Scheme 9).⁶⁶

**Scheme 9**

![Chemical structure](image)
An alternative protocol to Cu- and Pd-catalyzed N-arylation reactions was reported using commercially available FeCl\textsubscript{3}.6H\textsubscript{2}O with conformationally rigid diamine ligand 67 for N-arylation of NH-heterocycles using aryl and heteroaryl iodides in aqueous medium (Scheme 10).\textsuperscript{67}

Scheme 10

![Scheme 10](image)

Recently, a ligand free Fe/Cg air sensitive catalyst system was reported for the N-arylation of NH-heterocycles with various aryl halides (Scheme 11).\textsuperscript{68}

Scheme 11

1.1.3 Ligand and transition metal free N-arylation of NH-nucleophiles

Aliphatic and aromatic amines react with chlorobenzenes in the presence of \textit{t}-BuOK to give the N-aryl amines 71 (Scheme 12).\textsuperscript{69}
Scheme 12

Transition metal free procedure for the N-arylation of amines, sulfonamides, and carbamates and O-arylation of phenols and carboxylic acids using a variety of O-silylaryl triflates in the presence of CsF has been reported (Scheme 13).70

Scheme 13

Transition metal free KN(Si(CH₃)₃)₂/dioxane methodology has been reported for the synthesis of various N-aryl amines (Scheme 14).71

Scheme 14

Transition metal free KOH(excess)/DMSO promoted N-arylation has been reported (Scheme 15).71 The reaction involves, the corresponding aryne intermediates.

Scheme 15
1.1.4 Previous work from this laboratory

The copper iodide and diimine complexes are useful for the Buchwald N-arylation of heterocycles, particularly indoles that are very important structural moieties present in various biologically active molecules and natural products (Scheme 16).\textsuperscript{72}

Scheme 16

We have undertaken efforts on the development of new methodologies for the N-arylation of various NH-heterocyles and diphenylamine. The results are described in the next section.
1.2 Results and Discussion

1.2.1 N-Phenylation of imidazole

Pursue of literature reports indicates that the most simple and straightforward method for N-arylation involves the use of t-BuOK/DMSO under ligand free and transition metal

Scheme 17: Optimization condition for the N-phenylation of imidazole

![Scheme 17](image)

Table 1: Optimization of N-Phenylation of imidazole

<table>
<thead>
<tr>
<th>Entry</th>
<th>Additive</th>
<th>Base</th>
<th>Solvent</th>
<th>Temp(°C)</th>
<th>Yield(%)b</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-</td>
<td>t-BuOK</td>
<td>DMSO</td>
<td>120</td>
<td>76</td>
</tr>
<tr>
<td>2</td>
<td>-</td>
<td>t-BuOK</td>
<td>DMSO</td>
<td>25</td>
<td>0c</td>
</tr>
<tr>
<td>3</td>
<td>-</td>
<td>t-BuOK</td>
<td>DMSO</td>
<td>80</td>
<td>50c</td>
</tr>
<tr>
<td>4</td>
<td>-</td>
<td>K3PO4</td>
<td>DMSO</td>
<td>120</td>
<td>Trace</td>
</tr>
<tr>
<td>5</td>
<td>-</td>
<td>KOH</td>
<td>DMSO</td>
<td>120</td>
<td>72</td>
</tr>
<tr>
<td>6</td>
<td>-</td>
<td>t-BuOK</td>
<td>DMF</td>
<td>120</td>
<td>Trace</td>
</tr>
<tr>
<td>7</td>
<td>-</td>
<td>t-BuOK</td>
<td>Toluene</td>
<td>120</td>
<td>Trace</td>
</tr>
<tr>
<td>8</td>
<td>-</td>
<td>t-BuOK</td>
<td>H2O</td>
<td>120</td>
<td>5</td>
</tr>
<tr>
<td>9</td>
<td>Fe2O3</td>
<td>t-BuOK</td>
<td>DMSO</td>
<td>120</td>
<td>90</td>
</tr>
<tr>
<td>10</td>
<td>FeCl3</td>
<td>t-BuOK</td>
<td>DMSO</td>
<td>120</td>
<td>76</td>
</tr>
<tr>
<td>11</td>
<td>FeSO4</td>
<td>t-BuOK</td>
<td>DMSO</td>
<td>120</td>
<td>37</td>
</tr>
<tr>
<td>12</td>
<td>ZnCl2</td>
<td>t-BuOK</td>
<td>DMSO</td>
<td>120</td>
<td>19</td>
</tr>
<tr>
<td>13</td>
<td>NiCl2</td>
<td>t-BuOK</td>
<td>DMSO</td>
<td>120</td>
<td>50</td>
</tr>
<tr>
<td>14</td>
<td>Fe2O3</td>
<td>-</td>
<td>DMSO</td>
<td>120</td>
<td>0</td>
</tr>
<tr>
<td>15</td>
<td>Fe2O3</td>
<td>t-BuOK</td>
<td>DMSO</td>
<td>120</td>
<td>81d</td>
</tr>
</tbody>
</table>

*a*Unless noted otherwise, all the reactions were carried out with an additive (10 mol %), imidazole 47a (1 mmol), iodobenzene 2a (2 mmol), base (2 mmol) and solvent (3 mL) for 24 h. *b*Isolated yields and product was identified by IR, 1H-NMR, 13C-NMR and mass spectral data. *c*Reaction was carried out for 48 h. *d*Reaction was carried out using bromobenzene.
Results and Discussion

free conditions. Accordingly, we decided to examine the N-arylation of imidazole 47a under these conditions. The reaction of imidazole 47a with phenyl halide gave N-phenyl imidazole 49a in 76% yield (Table 1, Entry 1).73 The reaction does not take place at 25 °C (Table 1, Entry 2) and the N-phenyl product 49a is obtained only in 50% yield at 80 °C (Table 1, Entry 3). The use of t-BuOK and KOH bases gave better yields over K3PO4 (Table 1, Entries 1, 4 and 5). Among the solvents screened, toluene, DMF and water were less effective compared to DMSO (Scheme 17, Table 1, Entries 1 and 6-8).

Experiments using various additives revealed that the products are obtained in higher yields when the transformation is carried out using Fe2O3 as an additive (Table 1, Entries 9-13). There is no reaction without t-BuOK (Table 1, Entry 14). As expected, iodobenzene is more reactive than bromobenzene and gave the N-phenyl imidazole 49a in higher yields (Table 1, Entries 9 and 15). The results revealed that the t-BuOK/DMSO reagent system is essential for this transformation (Table 1, Entry 14). Whereas the recently reported Fe/graphite system requires dry N2 atmosphere,68 the present t-BuOK/DMSO/Fe2O3 reagent system does not require inert conditions.

1.2.2 N-Arylation of imidazoles

We have then examined the reaction using various substituted aryl halides with imidazole 47 (Scheme 18, Compounds 49a-g). This methodology is equally effective for both electron donating and withdrawing substituents containing aryl halides (Compounds 49d and 49e). In the case of 2-bromopyridine as coupling partner, the corresponding N-aryl product is obtained in 90% yield (Compound 49g). Two regioisomers are obtained when 1-
bromonaphthalene and 4-bromoanisole are used as aryl halide coupling partners (Compounds 49b and 49d).

**Scheme 18:** N-Arylation of imidazole using various aryl halides.

![Scheme 18](image)

**Table 2:** Synthesis of various N-aryl heterocycles 49a-g

<table>
<thead>
<tr>
<th>Entry</th>
<th>Aryl bromide (Ar-Br)</th>
<th>Product</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ph-Br</td>
<td><img src="image" alt="49a" /></td>
<td>81</td>
</tr>
<tr>
<td>2</td>
<td><img src="image" alt="47" /></td>
<td><img src="image" alt="49b" /></td>
<td>1-39</td>
</tr>
<tr>
<td></td>
<td></td>
<td><img src="image" alt="1 and 2%" /></td>
<td>2-37</td>
</tr>
<tr>
<td>3</td>
<td><img src="image" alt="47" /></td>
<td><img src="image" alt="49c" /></td>
<td>70</td>
</tr>
<tr>
<td>4</td>
<td><img src="image" alt="47" /></td>
<td><img src="image" alt="49d" /></td>
<td>71</td>
</tr>
<tr>
<td>5</td>
<td><img src="image" alt="47" /></td>
<td><img src="image" alt="49e" /></td>
<td>76</td>
</tr>
</tbody>
</table>
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<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td><img src="image" alt="Structural formula of 49f" /></td>
<td>49f 82</td>
</tr>
<tr>
<td>7</td>
<td><img src="image" alt="Structural formula of 49g" /></td>
<td>49g 90</td>
</tr>
</tbody>
</table>

\[ \text{All the reactions were carried out with Fe}_2\text{O}_3 (10 \text{ mol \%}), \text{imidazole 47 (1 mmol), aryl bromide 2a (2 mmol), t-BuOK (2 mmol) and DMSO (3 mL) at 120 °C for 24 h.} \]

\[ \text{Isolated yields and the products were identified by IR, } \]

\[ \text{^1H-NMR, } \]

\[ \text{^13C-NMR and mass spectral data.} \]

1.2.3 Plausible mechanistic pathways for N-arylation of imidazole

Formation of regioisomeric products 49b suggests the involvement of aryne intermediates in this reaction (Scheme 20). The reaction of para-substituted arylbromide and t-BuOK would give the aryne intermediate which could in turn react with the deprotonated imidazole intermediate to give the mixture of regioisomers (Scheme 19, Mechanism-1). However, the pathway involving electron transfer mechanism cannot be ruled out (Scheme 20) considering some recent reports in this area, especially when mild bases are used. In the electron transfer mechanism (Scheme 19, Mechanism-2), the alkoxide would transfer an electron to the aryl halide to give the corresponding radical anion which could then react with the deprotonated imidazole followed by electron transfer to give the corresponding N-aryl product 49d as a single regioisomer.
Scheme 19: Plausible mechanistic pathways for N-arylation of imidazole

**Mechanism-1: Aryne intermediate:**

In these transformations, the aryne intermediates are formed due to the highly basic nature of the t-BuOK/DMSO reagent system. In order to reduce the basic nature of t-BuOK, we have carried out a set of experiments using FeCl₃ and 3 equivalents of t-BuOK under the conditions in which iron alkoxides are expected to form (Scheme 20, Table 3). In all these experiments, only one regioisomer 49b was obtained albeit in low yields (Table 3, Entries 1-3). The N-aryl products are obtained in slightly higher yields using 4-iodoanisole 2d as coupling partner (Table 3, Entries 4 and 5). Presumably, the reaction goes through the electron transfer mechanism under these conditions (Scheme 19, Mechanism-2).
Scheme 20: N-Arylation using the FeCl₃/t-BuOK reagent system

\[
\begin{align*}
\text{FeCl}_3/t\text{-BuOK/DMSO} & \quad 120 \degree \text{C/36 h} \\
\text{47} & \quad \text{2b} \\
\end{align*}
\]

Table 3: Effect of FeCl₃/t-BuOK combination

<table>
<thead>
<tr>
<th>Entry</th>
<th>Ar-X (mmol)</th>
<th>FeCl₃ (mmol)</th>
<th>t-BuOK (mmol)</th>
<th>K₃PO₄ (mmol)</th>
<th>Product</th>
<th>Yield(%)b</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2b</td>
<td>1</td>
<td>3</td>
<td>-</td>
<td>49b</td>
<td>4</td>
</tr>
<tr>
<td>2</td>
<td>2b</td>
<td>0.1</td>
<td>0.3</td>
<td>1.5</td>
<td>49b</td>
<td>10</td>
</tr>
<tr>
<td>3</td>
<td>2b</td>
<td>1</td>
<td>3</td>
<td>1.5</td>
<td>49b</td>
<td>11</td>
</tr>
<tr>
<td>4</td>
<td>2d</td>
<td>0.1</td>
<td>0.3</td>
<td>1.5</td>
<td>49d</td>
<td>37</td>
</tr>
<tr>
<td>5</td>
<td>2d</td>
<td>1</td>
<td>3</td>
<td>1.5</td>
<td>49d</td>
<td>35</td>
</tr>
</tbody>
</table>

aUnless noted otherwise, all the reactions were carried out with imidazole 47a (1 mmol), aryl halide 2 (2 mmol), K₃PO₄ (1.5 mmol) and DMSO (5 mL) at 120 °C for 36 h. bIsolated yields.

1.2.4 N-Arylation of NH-heterocycles

We have then examined this methodology (Scheme 18) for the N-phenylation of various NH-heterocycles such as benzimidazole, pyrrole, indole and 1,2,3-benzotriazole. The corresponding N-phenyl products are obtained in moderate to excellent yields (Scheme 21, Table 4).
**Scheme 21**: N-Phenylation of various NH-heterocycles

\[
\text{NH-Heterocycle} + \stackrel{X}{Y} + \stackrel{Fe_2O_3 (10 \text{ mol} \%) \text{\quad } t\text{-BuOK/DMSO/120 °C/24 h}}{\text{NH-Heterocycle}} \rightarrow \stackrel{Y}{N-\text{Heterocycle}}
\]

2a \(X=I, Y=\text{CH}\)
2bc \(X=\text{Br}, Y=\text{N}\)

49ab-49ae \(Y=\text{CH}\)
49abc \(Y=\text{N}\)

**Table 4**: N-Arylation of various NH-heterocycles 49ab-ae<sup>a</sup>

<table>
<thead>
<tr>
<th>Entry</th>
<th>Aryl bromide</th>
<th>Product</th>
<th>Yield (%)&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td><img src="image1.png" alt="Image" /></td>
<td><img src="image2.png" alt="Image" /></td>
<td>49ab</td>
</tr>
<tr>
<td>2</td>
<td><img src="image3.png" alt="Image" /></td>
<td><img src="image4.png" alt="Image" /></td>
<td>49abc</td>
</tr>
<tr>
<td>3</td>
<td><img src="image5.png" alt="Image" /></td>
<td><img src="image6.png" alt="Image" /></td>
<td>49ac</td>
</tr>
<tr>
<td>4</td>
<td><img src="image7.png" alt="Image" /></td>
<td><img src="image8.png" alt="Image" /></td>
<td>49ad</td>
</tr>
<tr>
<td>5</td>
<td><img src="image9.png" alt="Image" /></td>
<td><img src="image10.png" alt="Image" /></td>
<td>49ae</td>
</tr>
</tbody>
</table>

<sup>a</sup>All the reactions were carried out with \(\text{Fe}_2\text{O}_3\) (10 mol %), NH-heterocycle (1 mmol), aryl halide 2 (2 mmol), \(t\text{-BuOK}\) (2 mmol) and DMSO (3 mL) for 24 h at 120 °C. <sup>b</sup>Isolated yields and the products were identified by IR, \(^1\text{H}-\text{NMR}, \text{\ }^{13}\text{C}-\text{NMR}\) and mass spectral data.
1.2.5 Applications of N-aryl imidazoles 49

The N-phenyl imidazole 49a is readily converted to the corresponding N-butyl,N'-phenyl ionic liquid 81 following a procedure reported for the preparation of ionic liquids containing N,N'-dialkyl moieties (Scheme 22). This observation illustrates the synthetic potential of the N-arylation methodology to access a series of ionic liquids that have proven applications in electrochemical devices.

Scheme 22: Synthesis of N-butyl,N'-phenyl imidazolium bromide salt 80

![Scheme 22: Synthesis of N-butyl,N'-phenyl imidazolium bromide salt 80](image)

**Scheme 23:** Synthesis of N-butyl,N'-phenyl imidazolium tetrafluoroborate 81

```
49a + Br-C₄H₉ → MeCN
0 - 25 °C/24h → 80, 70% y
```

1.2.6 N-Arylation of diphenylamine

We have then turned our attention towards examining the use of the t-BuOK/DMSO/Fe₂O₃ reagent system for N-arylation of diphenylamine 82 to obtain the corresponding triarylamine derivatives 83a-e since such a methodology has potential for use in the synthesis of optoelectronic materials. We have carried out the N-arylation of diphenylamine 82 with various aryl bromides 2a-e at 130 °C (Scheme 24). It was observed
**Scheme 24:** N-Arylation of diphenylamine with various aryl bromides$^a$

$$\text{Ph} \quad \text{NH} \quad \text{Ph} \quad + \quad \text{Ph}\text{Br} \quad \xrightarrow{\text{Fe}_2\text{O}_3 \ (10 \text{ mol } \%) / t-\text{BuOK}/\text{DMSO}/130 ^\circ \text{C}/36 \text{ h}} \quad \text{Ph} \quad \text{N} \quad \text{Ph} \quad \text{R}$$

| Table 5: Synthesis of various triarylamines 83a-e$^a$ |
|---|---|---|
| **Entry** | **Aryl bromide (2)** | **Triarylmine** | **Yield (%)$^b$** |
| 1 | Ph-Br | ![83a](image) | 83a | 83 |
| 2 | ![1&2 ratio:60:40](image) | ![83b](image) | 83b | 76 |
| 3 | ![p&m ratio:56:44](image) | ![83c](image) | 83c | 84 |
| 4 | ![p&m ratio:61:39](image) | ![83d](image) | 83d | 72 |
| 5 | ![83e](image) | ![83e](image) | 83e | 47 |

$^a$All the reactions were carried out with Fe$_2$O$_3$ (10 mol %), diphenylamine 82 (1 mmol), aryl bromide 2 (2 mmol), $t$-BuOK (2 mmol) and DMSO (3 mL) at 130 °C for 36. $^b$Isolated yields and all the products were identified by IR, $^1$H-NMR, $^{13}$C-NMR.
that the aryl halides containing electron donating substituents gave the products in higher yields (Compounds 83c and 83d) compared to the derivatives containing electron withdrawing groups (Compound 83e). Again, two regioisomers are obtained in reactions using some substituted aryl halides (Compounds 83b, 83c and 83d) indicating the involvement of arylene intermediates in this transformation (Scheme 19, Table 3).

Previously, N-arylation methods using palladium\textsuperscript{77} and copper\textsuperscript{78} catalyst systems have been employed in the synthesis of bioactive and energy harvesting molecules (Fig. 1).
The Fe$_2$O$_3$ promoted method for N-arylation described here involves a simple and inexpensive ligand free $t$-BuOK/DMSO reagent system which does not require dry N$_2$ atmosphere. Accordingly, the methods described here are expected to be useful in accessing compounds which have potential for applications in the synthesis of bioactive molecules, organic optoelectronics and electricity storage materials.
1.3 Conclusions

In summary, we have developed a simple and inexpensive ligand free $t$-BuOK/DMSO reagent system promoted by Fe$_2$O$_3$ for the successful synthesis of different N-aryl substituted imidazoles 49a-g and various other N-aryl substituted NH-heterocyles 49ab-ae. We have also synthesized various triarylamines 83a-e starting from diphenyl amines using this reagent system. We have also demonstrated the synthesis of N-alkyl,N'-aryl ionic liquids 81 starting from N-phenyl imidazole.

The methods described here are expected to be useful in the synthesis of N-aryl heterocyclic derivatives, with potential applications for the synthesis of a variety of biologically active compounds and for the synthesis of organic optoelectronics and electrochemically active materials.
1.4 Experimental Section

1.4.1 General Information

The information given in the section 1.4 are also applicable for experiments outlined in this section. t-BuOK (Spectrum, India), all aryl halides and metal catalysts were supplied from Aldrich chemicals Ltd., used as purchased. Fe$_2$O$_3$ (J. T. Baker Chemicals Co. assay Fe$_2$O$_3$ by iodometry) 100% and all solvents (Merck) were used as such without any further purification. Melting points were determined using a Superfit capillary point apparatus and are uncorrected. IR (KBr) spectra were recorded on JASCO-FT-IR model 5300 spectrometer with polystyrene as reference. $^1$H NMR (400 MHz) and $^{13}$C (100 MHz) spectra were recorded in CDCl$_3$ on Bruker Avance 400 spectrometer using TMS as internal standard ($\delta = 0$ ppm). For TLC analysis, plates coated with silica gel were run in hexane/EtOAc mixture and spots were developed in an I$_2$ chamber.

Liquid Chromatography (LC) and mass analysis (LC-MS) were performed on SHIMADZU-LCMS-2010A. The mass spectral analyses were carried out using Chemical Ionization (CI) or Electro Spray Ionization (ESI) techniques. Elemental analyses were carried out using a Perkin-Elmer elemental analyzer model-240C and Thermo Finnigan analyzer series Flash EA 1112. Mass spectral analyses for some of the compounds were carried out on VG 7070H mass spectrometer using EI technique at 70 eV. Analytical thin layer chromatographic tests were carried out on glass plates (3 x 10 cm) coated with 250µm acme's silica gel-G and GF$_{254}$ containing 13% calcium sulfate as binder. The spots were
visualized by short exposure to iodine vapor or UV light. Column chromatography was carried out using acme's silica gel (100-200 or 230-400 mesh) and neutral alumina.

All the glassware were pre-dried at 140 °C in an air-oven for 4 h, assembled in hot condition and cooled under a stream of dry nitrogen. Unless otherwise mentioned, all the operations and transfer of reagents were carried out using standard syringe-septum technique recommended for handling air sensitive reagents and organometallic compounds. Reagents prepared in situ in solvents were transferred using a double-ended stainless steel (Aldrich) needle under a pressure of nitrogen whenever required.

In all experiments, a round bottom flask of appropriate size with a side arm, a side septum, a magnetic stirring bar, a condenser and a connecting tube attached to a mercury bubbler were used. The outlet of the mercury bubbler was connected to the atmosphere by a long tube. All dry solvents and reagents (liquids) used were distilled from appropriate drying agents. As a routine practice, all organic extracts were washed with saturated sodium chloride solution (brine) and dried over anhydrous MgSO₄ or Na₂SO₄ or K₂CO₃ and concentrated on Heidolph-EL-rotary evaporator. All yields reported are of isolated materials judged homogeneous by TLC, IR and NMR spectroscopy.

1.4.2 Representative procedure for the N-arylation of aryl halides with NH-heterocycles 49a-g and 49a-49ae

In a 25 mL, round-bottom (RB) flask with side arm, containing magnetic stirring bar equipped with an air condenser (condenser without water circulation), were placed Fe₂O₃ (0.016 g, 10 mol %), imidazole 47 (0.068 g, 1 mmol), t-BuOK (0.22 g, 2 mmol), DMSO (3 mL) and idobenzene 2a (0.41 g, 2 mmol) in open atmosphere. The contents were stirred for
24 h at 120 °C and allowed to cool to 25 °C. The reaction mixture was diluted with ethyl acetate (5 mL) and water (5 mL) and the stirring was continued for another 10 min. The organic layer was separated and the aqueous layer was extracted with ethyl acetate (3 X 10 mL). The combined organic extracts were washed with water and brine solution and dried using anhydrous Na$_2$SO$_4$. The solvent was evaporated and the residue was purified by column chromatography (silica gel 100-200 mesh, 1:1 hexanes/ethyl acetate) to obtain the desired product $20a$ as yellow solid.

**1-Phenyl-1H-imidazole 49a**

Yield : 0.129 g (90%).

IR (neat) : (cm$^{-1}$) 3113, 1956, 1873, 1674, 1601, 1512, 1249.

$^1$H NMR : (400MHz, CDCl$_3$) δ: 7.22 (s, 1H), 7.29-7.30 (m, 1H), 7.37-7.41 (m, 3H), 7.47-7.51 (m, 2H), 7.87 (s, 1H).

$^{13}$C NMR : (100 MHz, CDCl$_3$) δ: 118.2, 121.5, 127.5, 129.9, 130.4, 135.6, 137.4

LCMS : (EI, m/z): 143 (M-1).

The same procedure was followed for N-arylation of several other NH-heterocycles. The physical constant and spectral data are listed below.

**1-Naphthalen-1-yl-1H-imidazole 49b**

Yield : 0.076 g (39%), colorless solid.

mp : 58-60 °C (lit. 62 °C).$^{79}$

IR (KBr) : (cm$^{-1}$) 3109, 3055, 1595, 1489, 1304, 802, 661.
**1H NMR** : 
(400MHz, CDCl₃) δ: 7.27-7.31 (m, 2H), 7.46-7.63 (m, 5H), 7.77 (s, 1H), 7.95-7.97 (m, 2H).

**13C NMR** : 
(100 MHz, CDCl₃) δ: 121.7, 122.3, 123.7, 125.2, 126.9, 127.6, 128.3, 129.2, 129.5, 134.1, 138.4.

**LCMS** : 
(EI, m/z): 193 (M-1).

### 1-Paphthalen-2-yl-1H-imidazole 49b

**Yield** : 0.072 g (37%), yellow solid.

**mp** : 122-124 °C (lit. 122-123 °C).<sup>80</sup>

**IR (KBr)** : (cm⁻¹) 3094, 1631, 1493, 1307, 1057, 814, 657.

**1H NMR** : 
(400MHz, CDCl₃) δ: 7.27 (s, 1H), 7.41 (s, 1H), 7.53-7.60 (m, 3H), 7.83-7.98 (m, 5H).

**13C NMR** : 
(100 MHz, CDCl₃) δ: 118.5, 119.1, 120.3, 126.5, 127.4, 127.9, 130.1, 130.6, 132.2, 133.5, 134.7, 135.8.

**LCMS** : 
(EI, m/z): 193 (M-1).

### 1-Anthracen-9-yl-1H-imidazole 49c

**Yield** : 0.086 g (70%), yellow solid.

**mp** : 154-156 °C (lit. 154-156 °C).<sup>81</sup>

**IR (KBr)** : (cm⁻¹) 3094, 1626, 1493, 1307, 1059, 733, 659.

**1H NMR** : 
(400MHz, CDCl₃) δ: 7.28 (s, 1H), 7.45-7.54 (m, 7H), 7.79 (s, 1H), 8.08-8.1 (m, 2H), 8.61 (s, 1H).
$^{13}$C NMR : (100 MHz, CDCl$_3$) δ: 122.4, 122.7, 125.9, 127.6, 128.4, 128.5, 128.8, 129.7, 131.2, 139.6.

LCMS : (EI, m/z): 245 (M+1).

1-(4-Methoxy-phenyl)-1H-imidazole 49d

Yield : 0.123 g (71%), yellow oil.

IR (neat) : (cm$^{-1}$) 3117, 2941, 2839, 1608, 15206, 1249, 831.

$^1$H NMR : (400MHz, CDCl$_3$) δ: 3.86 (s, 3H), 6.97-7.03 (m, 2H), 7.20-7.21 (m, 2H), 7.23-7.35 (m, 2H), 7.82 (s, 1H).

$^{13}$C NMR : (100 MHz, CDCl$_3$) δ: 55.6, 109.1, 112.4, 115.0, 123.3, 129.8, 130.6, 135.8, 158.9.

LCMS : (EI, m/z): 174 (M+1).

1-(4-Nitro-phenyl)-1H-imidazole 49e

Yield : 0.143 g (76%), yellow solid.

mp : 202-204 °C (lit. mp 204.4–205.2 °C).

IR (KBr) : (cm$^{-1}$) 2926, 1599, 1510, 1338, 1051, 848, 648.

$^1$H NMR : (400MHz, CDCl$_3$) δ: 7.27-7.28 (m, 1H), 7.38 (s, 1H), 7.58-7.60 (m, 2H), 7.99 (s, 1H), 8.37-8.40 (m, 2H).

$^{13}$C NMR : (100 MHz, CDCl$_3$) δ: 117.6, 121.1, 125.8, 131.7, 135.4, 142.0, 146.3.

LCMS : (EI, m/z): 189 (M-1).
1-(3,5-Bis-trifluoromethyl-phenyl)-1H-imidazole 49f

Yield : 0.229 g (82%), white solid.

mp : 92-94 °C (lit. 93-95 °C). 83

IR (KBr) : (cm⁻¹) 3113, 3049, 1626, 1508, 1248, 1124, 1060, 887.

¹H NMR : (400MHz, CDCl₃) δ: 7.30-7.31 (m, 1H), 7.38-7.39 (m, 1H), 7.88-7.97 (m, 3H), 8.23 (s, 1H).

¹³C NMR : (100 MHz, CDCl₃) δ: 117.9, 120.9-121.4 (quartet) 123.9, 126.6, 133.2-134.2 (quartet), 133.8, 134.2, 135.4, 138.

LCMS : (EI, m/z): 279 (M-1).

2-Imidazol-1-yl-pyridine 49g

Yield : 0.130 g (90%), light yellow oil.

IR (neat) : (cm⁻¹) 3117, 2592, 1670, 1597, 1304, 1055, 904.

¹H NMR : (400 MHz, CDCl₃) δ: 7.21-7.29 (m, 2H), 7.36-7.38 (m, 1H), 7.65-7.66 (m, 1H), 7.81-7.86 (m, 1H).

¹³C NMR : (100 MHz, CDCl₃) δ: 112.3, 116.1, 121.9, 130.7, 134.9, 138.9, 149.1

LCMS : (EI, m/z): 290 (M+1).
1-Phenyl-1\textit{H}-benzoimidazole 49ab

Yield : 0.137 g (71\%), yellow solid.

mp : 94-96 °C (lit. 96-98 °C).\textsuperscript{83}

IR (KBr) : (cm\textsuperscript{-1}) 3117, 2592, 1670, 1597, 1304, 1055, 904.

\textsuperscript{1}H NMR : (400MHz, CDCl\textsubscript{3}) δ: 7.32-7.35 (m, 2H), 7.47-7.60 (m, 7H), 7.88-7.90 (m, 1H), 8.13 (s, 1H).

\textsuperscript{13}C NMR : (100 MHz, CDCl\textsubscript{3}) δ: 110.5, 120.6, 122.8, 123.7, 124.1, 127.8, 130.1, 133.7, 136.3, 142.3, 144.1.

LCMS : (EI, m/z): 195 (M+1).

1-Pyridin-2-yl-1\textit{H}-benzoimidazole 49abc

Yield : 0.189 g (97\%), yellow solid.

mp : 54-56 °C (lit. 59-60 °C).\textsuperscript{84}

IR (neat) : (cm\textsuperscript{-1}) 1589, 1473, 1371, 1143, 887, 744.

\textsuperscript{1}H NMR : (400MHz, CDCl\textsubscript{3}) δ: 7.24-7.27 (m, 1H), 7.32-7.38 (m, 2H), 7.52-7.54 (m, 1H), 7.84-7.87 (m, 2H), 8.03-8.05 (m, 1H), 8.56-8.58 (s, 2H).

\textsuperscript{13}C NMR : (100 MHz, CDCl\textsubscript{3}) δ: 112.6, 114.3, 120.6, 121.8, 123.7, 124.1, 127.8, 130.1, 138.9, 141.3, 144.6, 149.4, 149.8.

LCMS : (EI, m/z): 195 (M+1).
1-Phenyl-1H-benzotriazole 49ac

Yield : 0.155 g (79%), white solid.

mp : 84-86 °C (lit. 85-87 °C).

IR (KBr) : (cm⁻¹) 3055, 1595, 1500, 1275, 1057, 572.

¹H NMR : (400MHz, CDCl₃) δ: 7.29-7.47 (m, 1H), 7.48-7.57 (m, 2H), 7.59-7.62 (m, 2H), 776-7.88 (m, 3H), 8.16-8.18 (m, 1H).

¹³C NMR : (100 MHz, CDCl₃) δ: 110.4, 120.3, 122.9, 124.4, 128.3, 128.7, 129.9, 132.3, 137.0, 146.5.

LCMS : (EI, m/z): 196 (M+1).

1-Phenyl-1H-pyrrole 49ad

Yield : 0.082 g (58%), white solid.

mp : 58-60 °C (lit. 58-60 °C).

IR (KBr) : (cm⁻¹) 3138, 2928, 1510, 1253, 1022, 607.

¹H NMR : (400MHz, CDCl₃) δ: 6.38-6.39 (m, 2H), 7.12-7.13 (m, 2H), 7.25-7.31 (m, 1H), 7.36-7.47 (m, 4H).

¹³C NMR : (100 MHz, CDCl₃) δ: 110.4, 119.3, 120.5, 125.6, 129.5, 140.8

LCMS : (EI, m/z): 143 (M+1).

1-Phenyl-1H-indole 49ae

Yield : 0.124 g (64%), yellow oil.

IR (neat) : (cm⁻¹) 3055, 1888, 1597, 1331, 1014, 740.
$^1$H NMR : (400MHz, CDCl$_3$) $\delta$: 6.77 (d, 1H), 7.24-7.33 (m, 2H), 7.39-7.46 (m, 2H), 7.56-7.59 (m, 4H), 7.65-7.67 (m, 1H); 7.77-7.79 (m, 1H).

$^{13}$C NMR : (100 MHz, CDCl$_3$) $\delta$: 103.6, 110.5, 120.4, 121.2, 122.4, 126.5, 128.0, 129.4, 129.7, 135.9, 139.9.

LCMS : (EI, m/z): 194 (M+1).

1.4.3 N-Butyl,N'-phenyl imidazolium bromide salt 80

A slightly modified reported procedure was followed.$^{76a}$ To a stirred solution of N-phenyl imidazole 49a (0.14 g, 1 mmol) and acetonitrile (5 mL) in a 25 mL, round-bottom (RB) flask with side arm, was added n-butyl bromide 79 (0.41 g, 3 mmol) in drops at 0°C. The contents were slowly brought to 25 °C and stirring was continued for another 24 h. The solvent was evaporated under reduced pressure and washed with hexane and dried under high vacuum to obtain the desired product 80.

Yield : 0.196 g (70%), brown color oil.

We proceeded to next step without further purification of the product.

N-Butyl,N'-phenyl imidazolium tetrafluoroborate 81$^{74a}$

In a 25 mL RB flask, to a stirred solution of bromide salt 80 (0.28 g, 1 mmol) in acetone (10 mL) at 25 °C, was added NaBF$_4$ salt (0.13 g, 1.2 mmol). The contents were stirred for another 6 h. The reaction mixture was filtered through Buchner funnel and evaporated the solvent. The residue was diluted with dichloromethane (20 mL), followed by
filtration and concentration of solvent. The residue was washed with hexane and dried under high vacuum to obtain the desired product 81 as brown oil.

Yield : 0.277 g (96%)

IR (neat) : (cm⁻¹) 3157, 2876, 1746, 1599, 1203, 763.

¹H NMR : (400MHz, CDCl₃) δ: 0.90-0.94 (m, 3H), 1.34-1.39 (m, 2H), 1.85-1.93 (m, 2H), 4.32-4.36 (t, 2H), 7.36-7.52 (m, 4H), 7.60-7.69 (m, 3H), 9.36 (s, 1H).

¹³C NMR : (100 MHz, CDCl₃) δ: 13.3, 19.4, 32.0, 50.2, 121.3, 121.5, 123.4, 129.9, 130.3, 130.5, 134.3.

¹¹B NMR : (100 MHz, CDCl₃) δ: -0.90.

1.4.4 Representative procedure for synthesis of triarylamines 83a-e

In a 25 mL, round-bottom (RB) flask with side arm, containing magnetic stirring bar equipped with an air condenser (condenser without water circulation), Fe₂O₃ (0.016 g, 10 mol %), diphenylamine (0.17 g 1, mmol), t-BuOK (0.22 g, 2 mmol), DMSO (3 mL) and iodo benzene (0.41 g, 2 mmol) were placed. The contents were stirred for 36 h at 130 °C and allowed to cool to 25 °C. The reaction mixture was diluted with ethyl acetate (5 mL) and water (5 mL) and stirring was continued for another 10 min. The organic layer was separated and the aqueous layer was extracted with ethyl acetate (3 X 10 mL). The combined organic extracts were washed with water and brine solution and dried using anhydrous Na₂SO₄. The solvent was evaporated and the residue was purified by column chromatography (silica gel 100-200 mesh, pure hexanes) to obtain the desired product 83a as colorless solid.
Triphenylamine 83a

Yield : 0.202 g (83%) using bromobenzene and 0.220 g (90%) using iodobenzene.

mp : 124-126 °C (lit. 126-128 °C).

IR (KBr) : (cm⁻¹) 1583, 1489, 1329, 1277, 748, 692.

¹H NMR : (400MHz, CDCl₃) δ: 6.98-7.03 (m, 3H), 7.09-7.11 (m, 6H), 7.23-7.27 (m, 6H).

¹³C NMR : (100 MHz, CDCl₃) δ: 122.6, 124.2, 129.2, 147.8.

LCMS : (EI, m/z): 246 (M+1).

The same procedure was followed for the preparation of several other N-aryl diphenyl amines. The physical constant and spectral data are listed below.

Naphthalene-1 or 2-yl-diphenylamine 83b

Yield : 0.224 g (76%), colorless solid; regioisomeric ratio was calculated based on ¹H-NMR spectra. All spectral details are for a mixture of regioisomers in 60:40 ratio.

¹H-NMR : range of values 7.08-7.17 and 7.21-7.27.

IR (KBr) : (cm⁻¹) 3057, 1626, 1589, 1493, 1273, 750, 696.

¹H NMR : (400MHz, CDCl₃) δ: of 6.95-7.75.

¹³C NMR : (100 MHz, CDCl₃) δ: 120.3, 120.5, 121.3, 121.7, 121.9, 122.9, 124.4, 126.3, 126.4, 126.9, 127.3, 127.6, 128.4, 128.9, 129.1, 129.2, 129.3, 130.1, 134.5, 145.5, 147.8, 148.5, 149.1.
LCMS : (EI, m/z): 296 (M+1).

**Diphenyl-p or m-tollyl-amine 83c**

Yield : 0.217 g (84%), colorless solid; regioisomeric ratio was calculated based on $^1$H-NMR analysis of –CH$_3$ protons at 2.28 and 2.34. All spectral details are for a mixture of regioisomers in 56:44 ratio.

**IR (KBr)** : (cm$^{-1}$) 3028, 2916, 1593, 1504, 1284, 1024, 754, 694.

$^1$H NMR : (400MHz, CDCl$_3$) $\delta$: 2.28 (s, 3H), 2.34 (s, 3H), 6.85-7.04 (m, 9H), 7.09-7.18 (m, 11H), 7.22-7.28 (m, 8H).

$^{13}$C NMR : (100 MHz, CDCl$_3$) $\delta$: 20.8, 21.6, 121.6, 122.2, 122.5, 123.6, 124.1, 124.9, 132.7, 139.1, 145.3, 147.8, 147.9, 148.1.

**Diphenyl-p or m-methoxy-amine 83d**

Yield : 0.20 g (72%), colorless solid; regioisomeric ratio was calculated based on $^1$H-NMR analysis of –OCH$_3$ protons 3.78-3.8 and 3.87-3.89. All spectral details are for a mixture of regioisomers in 61:39 ratio.

**IR (KBr)** : (cm$^{-1}$) 3036, 2951, 1593, 1587, 1485, 1242, 1035, 694.

$^1$H NMR : (400MHz, CDCl$_3$) $\delta$: 3.78-3.8 (d, 3H), 3.87-3.89 (d, 3H), 6.63-7.34 (m, 28H).
\(^{13}\text{C NMR} \quad \text{(100 MHz, CDCl}_3\text{)} \, \delta: \, 55.3, \, 55.6, \, 108.1, \, 109.8, \, 114.8, \, 116.5, \, 121.9, \, 122.9, \, 124.5, \, 127.4, \, 129.2, \, 129.3, \, 129.8, \, 140.8, \, 147.8, \, 148.3, \, 149.2, \, 156.2, \, 160.5.

(4-Nitrophenyl)-diphenylamine 83e

\text{Yield} \quad : \quad 0.14 \text{ g (47\%), yellow solid.}

\text{IR (KBr)} \quad : \quad (\text{cm}^{-1}) \, 1581, \, 1491, \, 1313, \, 1109, \, 841, \, 694.

\text{\(^1\text{H NMR} \quad \text{(400MHz, CDCl}_3\text{)} \, \delta: \, 6.92-6.94 \text{ (m, } 2\text{H}), \, 7.18-7.31 \text{ (m, } 6\text{H}), \, 7.36-7.39 \text{ (m, } 4\text{H}), \, 8.03-8.05 \text{ (m, } 2\text{H}).}

\text{\(^{13}\text{C NMR} \quad \text{(100 MHz, CDCl}_3\text{)} \, \delta: \, 118.1, \, 125.5, \, 125.7, \, 126.5, \, 129.9, \, 140.1, \, 145.6, \, 153.5.}

\text{LCMS} \quad : \quad (\text{EI, m/z): 291 (M+1).}
1.5 References


References


References


