Chapter V

Triazine Based Mesoporous Covalent Imine Polymers as Novel Solid Supports for Copper Mediated Chan-Lam Cross Coupling of $N$-Arylation Reaction

Synthesis of a novel mesoporous covalent imine polymeric (MCIPs) material involving simple schiff base chemistry is reported. This highly functionalised nitrogen rich material acts as a good support for immobilising Cu(II) ion exhibiting excellent catalytic activity in promoting the Chan-Lam cross coupling reaction between biologically active amines and arylboronic acids. The superior performance of this catalyst is also evident from broad substrate scope, high stability, real heterogeneity, milder reaction conditions and reusability without loss of its activity. The observed results will provide additional scope on design and catalytic applications of this emerging class of materials.
The creation of pores of desired dimensions in the form of frameworks is a challenging task in materials chemistry. As a new type of novel porous materials metal-organic frameworks (MOFs) and porous organic frameworks (POFs) are considered to be of more interest in the field of gas storage and catalysis. In particular, covalently linked POFs have attracted considerable attention as unique and emerging materials. A number of different type of POFs such as covalent organic frameworks (COFs), conjugated microporous polymers (CMPs), polymers of intrinsic microporosity (PIM), element organic frameworks (EOFs), triazine based organic frameworks (CTFs), porous polymer networks (PPN), covalent organic polymers (COP) and porous aromatic frameworks (PAFs), etc., have been reported. These materials have advantages, such as relatively high thermal stability, high specific surface area, low density, ease of synthesis from simple compounds and retains similar porosity even after boiling in water for a week. In addition to that, one of the most attractive aspects of POFs is the promise of tuning structures and properties through rational chemical design and synthesis. These properties allow potential applications in gas storage, explosive detection, drug release and catalysis. Consequently, the development of multifaceted functionality into porous networks is one of the frontline areas of research, which could lead to synthesis of new materials with diverse applications. For example, incorporation of catalytically active sites like metals, on a nitrogen rich porous organic framework may be beneficial to enhance the catalytic performance as well as the stability of the supported materials.

The synthesis of porous carbon based materials catalytic has immense potential in the development of sustainable substitutes over existing MOFs, zeolite and metal oxides. Jiang et al. have extensively reported that nitrogen doped CNTs are used to stabilize palladium nanoparticles which can be used
as a catalyst for the Heck reaction and hydrogenation reactions. Thomas et al. have demonstrated that nitrogen-rich covalent triazine framework can function as a good catalytic support for glycerol oxidation.\textsuperscript{15} Recently, Wang et al. have reported the palladium loaded covalent organic frameworks (Pd/COF-LZU 1) as a catalyst for Suzuki coupling reaction.\textsuperscript{11c} Bhaumik et al. have extensively reported the triazine functionalised mesoporous polymer\textsuperscript{12,16a} and nitrogen rich porous covalent imine frameworks (CIN)\textsuperscript{16b} supported palladium as catalysts for C-C cross coupling and acid group containing porous organic polymer as a catalyst for the synthesis of 3-benzhydrylindole.\textsuperscript{16c} More recently, Zhang et al. have demonstrated the utility of mesoporous poly-melamine-formaldehyde materials as efficient catalysts for chemoselective acetalization of aldehydes.\textsuperscript{17} Encouraged by these results, herein we have developed two new imine functionalised mesoporous covalent imine polymers (MCIPs) from relatively cheap starting materials and industrially important building blocks by Schiff base chemistry.

Transition metal catalysed carbon-nitrogen cross-coupling reactions have immense utility in organic synthesis to develop several pharmacophores and drug analogues.\textsuperscript{18} In addition, functionalised aromatic and heteroaromatic amines are key building blocks for the synthesis of biologically active molecules, ranging from natural products to medicinal agents, polymers and materials. In recognition of the widespread importance of these bonds, several synthetic methods of forming C-N bonds have emerged over the years in an attempt to overcome the shortcomings of the original Ullmann and Goldberg procedures.\textsuperscript{19} Meanwhile, the discovery of efficient palladium-catalyzed amination reactions by Buchwald\textsuperscript{20} and Hartwig\textsuperscript{21} has been a major breakthrough in this field, opening up access to a large number of aromatic amines that could only previously be obtained with difficulty using mild and tunable reaction conditions. Despite these significant improvements, limitations such as air and moisture sensitivity, functional-group tolerance and high cost of
palladium and ligands still exist. Thus, chemists have been forced to reconsider other metal catalysts and the Ullmann\textsuperscript{22} and Goldberg\textsuperscript{23} coupling reactions using stoichiometric amounts of metal at high temperature. Consequently the developments of milder, environmentally friendly conditions, a cheap and efficient catalyst are desirable. In this context, independent publications by Chan\textsuperscript{24} and Lam\textsuperscript{25} revolutionized the copper-mediated arylation of \(N\)-nucleophiles. They reported a generally applicable protocol for the arylation of amines using stoichiometric copper(II) acetate and boronic acids at room temperature with an impressive range of nucleophiles. Furthermore, this reaction tolerates a wide variety of functional groups, thus avoiding protecting group chemistry.

Copper salt promoted Chan-Lam coupling reactions for the synthesis of heterocyclic compounds have been extensively studied over the past few years (Table 5.1).\textsuperscript{26-43}

**Table 5.1 Copper catalysed Chan-Lam coupling reactions**

<table>
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<th>Copper catalysed Chan-Lam coupling reactions</th>
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<tr>
<td><img src="image1" alt="Reaction 1" /></td>
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<td><img src="image4" alt="Reaction 4" /></td>
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</table>
**Chapter V**

- Reaction 1: 
  - $\text{CH}_2\text{CH}_{\text{2}}\text{OH} + \text{Ar-B(OH)}_2 \xrightarrow{\text{Cu(OAc)}_2, \text{DCM, TEA, RT}} \text{ArCH}_2\text{CH}_{\text{2}}\text{OH}$

- Reaction 2: 
  - $\text{NH}_2\text{N} + \text{Ar-B(OH)}_2 \xrightarrow{[\text{Cu(OH)}_2\text{Cl}_2, \text{DCM, TEA, RT}} \text{N}-\text{Ar}$

- Reaction 3: 
  - $\text{NH}_2\text{N} + \text{Ar-B(OH)}_2 \xrightarrow{\text{Cu(OAc)}_2, \text{Myristic acid, RT, DCM, 2,6-tutidine}} \text{NHAr}$

- Reaction 4: 
  - $\text{NH}_2\text{N} + \text{Ar-B(OH)}_2 \xrightarrow{\text{CuFAP, MeOH, RT}} \text{FAP = Fluorapatite}$

- Reaction 5: 
  - $\text{NH}_2\text{N} + \text{Ar-B(OH)}_2 \xrightarrow{\text{Cu-Mn mixed oxide, K}_2\text{CO}_3, \text{water, RT}} \text{NHAr}$

- Reaction 6: 
  - $\text{NH}_2\text{N} + \text{Ar-B(OH)}_2 \xrightarrow{\text{Cu(OAc)}_2, \text{DCE, RT}} \text{NHAr}$

- Reaction 7: 
  - $\text{NH}_2\text{N} + \text{Ar-B(OH)}_2 \xrightarrow{\text{L1, K}_2\text{CO}_3, \text{water, RT}} \text{NHAr}$

- Reaction 8: 
  - $\text{NH}_2\text{N} + \text{Me-B(OH)}_2 \xrightarrow{\text{Cu(OAc)}_2, \text{Pyridine, dioxane, Reflux}} \text{NHMe}$

- Reaction 9: 
  - $\text{NH}_2\text{N} + \text{Ar-B(OH)}_2 \xrightarrow{\text{Cu(OAc)}_2, \text{F-PEG, water, RT}} \text{F-PEG}$

- Reaction 10: 
  - $\text{NH}_2\text{N} + \text{Ar-B(OH)}_2 \xrightarrow{\text{Cu(OAc)}_2, \text{DCE, TEA, RT}} \text{Ar}$
Eycken et al. have demonstrated that microreactor technology could be used for the copper(II)-mediated \textit{N}-arylation of pyrazinone compounds with arylboronic acids.\textsuperscript{27} Gurjar et al. have reported a general methodology for coupling aminopurines and aminopyrimidines with arylboronic acids using stoichiometric amounts of \textit{Cu}(II) acetate.\textsuperscript{28} Clark et al. have achieved \textit{N}-vinylation through the oxidative-coupling of vinylboronic acid with \textit{NH}-containing substrates in presence of stoichiometric or catalytic copper(II) acetate and TEMPO oxidant.\textsuperscript{29} Lam co-workers have reported the copper promoted C-N bond cross-coupling with phenyl and pyridylboronates.\textsuperscript{30} Combs et al. have successfully achieved the \textit{N}-arylated aminoesters with little or no racemization using copper(II) acetate and boronic acid. This reaction works under a very mild set of conditions: room temperature, mild base (triethylamine) and presence of air.\textsuperscript{31} Collman co-workers have reported the Chan-Lam coupling in the presence of a catalytic amount of [\textit{Cu}(OH).TMEDA]_2\textit{Cl}_2.\textsuperscript{32} Choudary et al. have developed a heterogeneous CuFAP catalyzed base-free \textit{N}-arylation of imidazoles and amines.\textsuperscript{33} Buchwald et al. have reported the copper catalysed C-N bond formation with myristic acid and lutidine ligands.\textsuperscript{34} Vishwakarma et al. have developed a strategy for the arylation of alkyl/aryl and heteroarylamines using bimetallic catalyst Cu-Mn bimetallic mixed oxides in aqueous media.\textsuperscript{35} Das et al. have
demonstrated a highly efficient Cu-catalyzed N-arylation of 2-amino-N-heterocycles with boronic acids under ligand and base-free conditions in presence of air. Bora et al. have developed the use of quadridentate Cu–Schiff base complex in Chan–Lam cross-coupling reactions of arylboronic acids with anilines in water and arylboronic acids with imidazoles in isopropanol at room temperature. Cruces et al. have developed a selective monomethylation of anilines by Cu(OAc)$_2$-promoted cross-coupling with MeB(OH)$_2$. Kondo et al. have described the copper-catalyzed coupling reaction of arylboronic acids with imidazoles in water containing an F-PEG fluorous amphiphilic surfactant. Pal et al. have reported the C-N bond formation of pharmacologically active of a thieno[2,3-d]pyrimidin-4(3H)-one. Campagne et al. have reported a regioselective, racemization-free and efficient functionalization of protected histidines with various aryl boronic acids in presence of 3 equiv., of NaOAc. Watson et al. have reported the selective formation of secondary amides via the copper-catalyzed cross-coupling of alkylboronic acids with primary amides. Messаoudi et al. have developed the stereoselective coupling of N-glycosylamine derivatives with functionalized arylboronic acids at room temperature to furnish aryl N-aminoglycosides.

To the best of our knowledge, there is no report describing the formation of biologically active N-arylflavones from flavones and arylboronic acids. These features promoted us to study the N-arylation of aminoflavones and heterocyclic amines using arylboronic acids to yield biologically important N-aryl derivatives using copper catalyst supported a triazine based mesoporous covalent imine polymers (MCOPs) and the observed results are discussed below.
5.2 Results and Discussion

The imine functionalized mesoporous covalent imine polymers (MCIPs) were synthesised by Schiff base chemistry involving a trialdehyde triazine derivative and diamine as given in scheme 5.1. The synthesised materials were characterized by FT-IR, $^{13}$C CP-MAS NMR spectroscopy, FE-SEM, elemental microanalysis, powder XRD, thermogravimetric analysis and nitrogen gas adsorption studies. The synthesised MCIP-1 and MCIP-2 materials are insoluble in water and also common organic solvents such as DMF, THF, DMSO, acetone, etc.

Fourier Transform Infrared (FT-IR) spectra of MCIP-1 and MCIP-2 shows a strong C=N stretching at 1560 and 1592 cm$^{-1}$ (Figures 5.1 and 5.2), indicating the formation of an imine bond. The band at 1500 cm$^{-1}$, representing the triazine ring is present in MCIP-1 and MCIP-2 materials. Meanwhile, the aldehyde (1703 cm$^{-1}$) and amine (3420 and 3358 cm$^{-1}$) bands of MCIP-1 and MCIP-2 had disappeared completely in comparison with those of the starting materials (Figures 5.1 and 5.2).

![FT-IR spectra of 2,4,6-tris(p-formylphenoxy)-1,3,5-triazine (TRIPOD), p-phenylenediamine (PPD) and MCIP-1](image)

*Figure 5.1 FT-IR spectra of 2,4,6-tris(p-formylphenoxy)-1,3,5-triazine (TRIPOD), p-phenylenediamine (PPD) and MCIP-1*
Scheme 5.1 Schematic representation of mesoporous covalent imine polymers (MCIP-1 and MCIP-2)
Figure 5.2 FT-IR spectra of 2,4,6-tris(p-formylphenoxy)-1,3,5-triazine (TRIPOD), terephthalodihydrazide (TPH) and MCIP-2

The $^{13}$C cross-polarization magic angle spinning (CP-MAS) NMR spectral data of MCIP-1 and MCIP-2 (Figures 5.3 and 5.4) clearly confirmed their chemical structure. The solid state NMR of MCIP-1 shows six peaks at 122.4, 129.0, 134.5, 148.6, 153.8, 173.5 ppm (Figure 5.3). The peak at 153.8 ppm corresponds to the carbon atom of the C=N bond obtained from the condensation reaction of trialdehyde and diamine (Table 5.2). The peak at 173.5 ppm corresponds to the triazine ring carbon. The signals at 122.4, 129.0, 134.5 and 148.6 ppm can be assigned to the carbon atoms of the phenyl rings. There was no peak around 190 ppm. These results clearly confirm the absence of unreacted aldehyde. Similarly, in the solid state NMR of MCIP-2, the main characteristic peak of C=N bond appears at 153.4 ppm (Figure 5.4). Data on solid state NMR spectra of MCIP-1 and MCIP-2 are given in tables 5.2 and 5.3.
Table 5.2 Solid State $^{13}$C NMR of MCIP-1

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<th>Signal (ppm)</th>
<th>Assignment</th>
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<tr>
<td>122.4</td>
<td>Adjacent carbon of imine attached phenyl carbon</td>
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<tr>
<td>129.0</td>
<td>Adjacent carbon of phenyl ring C-O carbon</td>
</tr>
<tr>
<td>134.5</td>
<td>Phenyl ring carbon attached to imine</td>
</tr>
<tr>
<td>148.6</td>
<td>Phenyl ring carbon attached to oxygen</td>
</tr>
<tr>
<td>153.8</td>
<td>Imine carbon</td>
</tr>
<tr>
<td>173.5</td>
<td>Triazine carbon</td>
</tr>
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</table>

Figure 5.3 $^{13}$C CP-MAS NMR spectrum of MCIP-1

Figure 5.4 $^{13}$C CP-MAS NMR spectrum of MCIP-2
Table 5.3 Solid State $^{13}$C NMR of MCIP-2

<table>
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<th>Signal (ppm)</th>
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<td>~132</td>
<td>Phenyl ring carbons (merged)</td>
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<tr>
<td>153.4</td>
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<tr>
<td>166.2</td>
<td>Amide carbon</td>
</tr>
<tr>
<td>173.3</td>
<td>Triazine carbon</td>
</tr>
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Field emission scanning electron microscopy (FE-SEM) describes the morphology of MCIP-1 and MCIP-2 materials (Figure 5.5). Images in figures 5.5a and 5.5b clearly indicate that MCIP-1 adopts an sheet-like morphology, while that of MCIP-2 (Figures 5.5c and 5.5d) images clearly indicate that MCIP-2 adopts an uniform needle-like morphology. These observations indicate that the condensation of aldehyde and amines leads to quite a uniform morphology and a certain degree of structural regularity.

![FE-SEM images](image1.png)

Figure 5.5 FE-SEM image of the synthesised MCIP-1 (a, b) and MCIP-2 (c, d)

The regularity and crystallinity of the structure of MCIP-1 and MCIP-2 materials are further confirmed by powder XRD (Figures 5.6 and 5.7). The obtained PXRD pattern of MCIP-1 indicates a partial crystallinity and the set of
peaks in the range of 9 to 40°, suggest that the framework has certain degree of order (Figure 5.6). Similarly, PXRD pattern of MCIP-2 indicates a structure with partial crystallinity and shows certain degree of order in the range 10 to 40° (Figure 5.7).

Figure 5.6 Powder XRD pattern of MCIP-1

Figure 5.7 Powder XRD pattern of MCIP-2
The thermal stability of MCIP-1 and MCIP-2 was analysed by thermogravimetry (TGA) under nitrogen atmosphere (Figure 5.8). As shown in the figure, MCIP-1 exhibits almost no weight loss around 300 °C, suggesting no loss of guest molecule. The framework decomposition of MCIP-1 was observed at about 350 °C. After that, the weight gradually decreases upto 50% at 600 °C. The TGA of Cu/MCIP-1 also represents a good thermal stability upto 200 °C. Similarly, figure 5.8 clearly shows that MCIP-2 is stable upto 250 °C.

![Figure 5.8 TGA of MCIP-1 (black), Cu/MCIP-1 (blue) and MCIP-2 (red)](image)

The porosity and surface area of the above materials were measured by nitrogen adsorption-desorption analysis at 77 K (Figures 5.9 and 5.10). These isotherms are closely related to a type IV isotherm, which is indicative of characteristic mesoporous materials. From the BET isotherms, the surface areas are found to be 174 m²g⁻¹ and 187 m²g⁻¹ for MCIP-1 and MCIP-2 respectively. These values are very close to that of mesoporous materials, but still well within the values of other materials. Pore size distribution plots of both MCIP-1 and MCIP-2 (Insets of figure 5.9 and 5.10) display a pore width of 32.4 Å and 44.3 Å units respectively.
As the synthesised MCIP-1 material has large amount of nitrogen atoms from triazine and imine groups, it can be used as metal ion stabilizers. MCIP-1 was stirred with copper(II) acetate in DCM solvent at room temperature for 48 h to prepare the copper loaded MCIP-1 (Cu/MCIP-1) catalyst, which was characterized by powder XRD (Figure 5.11), EDX, atomic absorption spectroscopy (AAS) and TGA. A comparison of the powder XRD patterns of MCIP-1 (Figure 5.6) and Cu/MCIP-1 shows that the crystal structure of MCIP-1 was well-kept-up after the treatment with copper acetate. Elemental analysis by AAS indicates a 2.58 mmol/g of copper loading in Cu/MCIP-1. The SEM-
EDX results suggest ~2.53 wt% of copper in Cu/MCIP-1 (Figure 5.12 and Table 5.4).

**Figure 5.11** Powder XRD pattern of Cu/MCIP-1

**Figure 5.12** EDX for fresh Cu/MCIP-1

**Table 5.4** Details of atom weight percentage in fresh Cu/MCIP-1

<table>
<thead>
<tr>
<th>Element, Atomic number</th>
<th>Series</th>
<th>Atom (wt%)</th>
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<td>C, 6</td>
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<td>N, 7</td>
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<td>O, 8</td>
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<td>Cu, 29</td>
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The catalytic activity of this heterogeneous Cu/MCIP-1 material was established in the Chan-Lam cross coupling reaction of biologically relevant amines with boronic acids. It is relevant to note here that the potential industrial applications of this reaction using other homogeneous copper catalysts to
produce pharmacologically relevant derivatives is quiet limited due to the difficulty in separating and recycling the catalyst from the reaction mixture. Catalytic studies are restricted to only Cu/MCIP-1 and are not extended to Cu/MCIP-2, since amides are known to undergo Chan-Lam N-arylation.

Table 5.5 Optimization studies for N-arylation of 7-aminoflavone

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<tr>
<th>Entry</th>
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<td>91, 69, 26</td>
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</table>

*Reaction conditions: 7-Aminoflavone (0.5 mmol), phenylboronic acid (0.6 mmol), catalyst (50 mg), solvent (2 mL), base (100 mol%) O₂ balloon, room temperature (RT); *Isolated yield based on 7-aminoflavone; *10 mol% of catalyst; *Atmospheric oxygen; *N₂ atmosphere; *Yield of the reaction carried out with 50, 40, 30, 20 mg of Cu/MCIP-1 respectively; *Yield of the reaction carried out with 100, 50, 0 mol% of base respectively.
Preliminary studies to screen the catalytic system were carried out in the reaction of phenylboronic acid with 7-aminoflavone (Table 5.5). All the reactions were conducted in oxygen atmosphere (kept in a balloon) and room temperature. In the absence of catalyst, with alone MCIP-1 and in inert atmosphere (absence of oxygen), no product was obtained (Table 5.5, entries 1, 2 and 24) and these results clearly highlight the specific role of copper catalyst in the Chan-Lam cross coupling of N-arylation reaction. When the reactions were conducted in other common Cu(II) sources such as Cu(OAc)$_2$, CuSO$_4$.5H$_2$O and CuCl$_2$, the desired product was obtained in 68, 17 and 32% yields respectively (Table 5.5, entries 3-5). When Cu(I) sources such as CuCl and CuI were used as catalyst, only trace amount of coupled product was observed (Table 5.5, entries 6-7). Our interest in heterogeneous solid catalysts to increase reactivity and reusability promoted us to use Cu/MCIP-1 in DCM at K$_2$CO$_3$ base and the desired product was formed in 70% yield (Table 5.5, entry 8). When we used other inorganic bases, almost similar results were observed (Table 5.5, entries 9-10). Interestingly, when we switched to organic bases like, NEt$_3$ and pyridine, higher yields were obtained (Table 5.5, entries 11-12). From the toxicity point of view, NEt$_3$ is a better base than pyridine for this cross coupling reaction. Other solvents such as methanol, ACN, DMF, DMSO and toluene were also employed, and there was no improvement in yield (Table 5.5, entries 13-17). When conducted in DCE as solvent, excellent yield was obtained (Table 5.5, entries 18 and 21). Water was found to be not effective in bringing out this cross coupling (Table 5.5, entry 20). When the reaction was carried out in Cu(OAc)$_2$ and organic bases (NEt$_3$ and Pyridine), the desired product was obtained in 75 and 80% yield respectively (Table 5.5, entries 19 and 22). When the reaction was conducted in atmospheric oxygen (in an open flask chemistry), 78% yield was observed (Table 5.5, entry 23).

The influence of other experimental parameters such as reaction time, amount of catalyst and base were also optimized. Increase in reaction time
from 8 h to 12 h had increased the overall yield from 67 to 91\% (Table 5.5, entry 25). The yield of the desired product had increased rapidly with an increase in the amount of the catalyst. As the amount of catalyst was increased to 40 mg, the product was obtained in excellent yield and further addition of catalyst had no positive effect on the overall yield of product (Table 5.5, entry 26). As a result shown in table 5.5, entry 27, base concentration plays an important role in this heterogeneous copper catalysed Chan-Lam cross coupling reaction. In the absence of base, only 26\% yield was obtained after 12 h and only 69\% yield was observed when 50 mol\% of base was added. These observations show that optimum conditions for this copper catalysed Chan-Lam cross-coupling reaction are use of Cu/MCIP-1 as catalyst in DCE under O\textsubscript{2} (balloon) atmosphere at room temperature for 12 h.

Table 5.6 N-Arylation of 7-aminoflavone with various substituted arylboronic acids\textsuperscript{a}

<table>
<thead>
<tr>
<th>Entry</th>
<th>7-Aminoflavone (1a)</th>
<th>Arylboronic acid (2a-2g)</th>
<th>Products (3)</th>
<th>Yield (%)\textsuperscript{b}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1a</td>
<td>C\textsubscript{6}H\textsubscript{5}B(OH)\textsubscript{2} (2a)</td>
<td>3a</td>
<td>91</td>
</tr>
<tr>
<td>2</td>
<td>1a</td>
<td>4-C\textsubscript{6}H\textsubscript{5}-C\textsubscript{6}H\textsubscript{4}B(OH)\textsubscript{2} (2b)</td>
<td>3b</td>
<td>93</td>
</tr>
<tr>
<td>3</td>
<td>1a</td>
<td>4-OCH\textsubscript{3}-C\textsubscript{6}H\textsubscript{4}B(OH)\textsubscript{2} (2c)</td>
<td>3c</td>
<td>90</td>
</tr>
<tr>
<td>4</td>
<td>1a</td>
<td>3-OCH\textsubscript{3}-C\textsubscript{6}H\textsubscript{4}B(OH)\textsubscript{2} (2d)</td>
<td>3d</td>
<td>87</td>
</tr>
<tr>
<td>5</td>
<td>1a</td>
<td>3-CH\textsubscript{3}-C\textsubscript{6}H\textsubscript{4}B(OH)\textsubscript{2} (2e)</td>
<td>3e</td>
<td>89</td>
</tr>
<tr>
<td>6</td>
<td>1a</td>
<td>4-Cl-C\textsubscript{6}H\textsubscript{4}B(OH)\textsubscript{2} (2f)</td>
<td>3f</td>
<td>80</td>
</tr>
<tr>
<td>7</td>
<td>1a</td>
<td>4-F-C\textsubscript{6}H\textsubscript{4}B(OH)\textsubscript{2} (2g)</td>
<td>3g</td>
<td>78</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Reaction conditions: 7-Aminoflavone (0.5 mmol), boronic acids (0.6 mmol), Cu/MCIP-1 (40 mg), NE\textsubscript{t}\textsubscript{3} (100 mol\%), DCE (2 mL), O\textsubscript{2} balloon, RT; \textsuperscript{b}Isolated yield based on 7-aminoflavone.

Motivated by these results, we explored the scope of this cross coupling reaction of 7-aminoflavone (1a) with various arylboronic acids (2a-g) and all
the arylations proceeded cleanly in excellent yields. As depicted in table 5.6, 1a was coupled easily with arylboronic acids having electron withdrawing and electron donating p- and m- substituents to give the corresponding N-arylated flavones in good to excellent yields. Interestingly, halogen substituted arylboronic acids were tolerated in the N-arylated reaction affording compounds 3f and 3g in 80 and 78% yields.

In a further set of experiments, we have investigated the scope and generality of the method with respect to 6-aminoflavone (1b). As depicted in table 5.7, 1b was easily coupled with arylboronic acids having both electron-donating and electron withdrawing substituents. Arylboronic acids with electron-withdrawing substituents gave somewhat lesser amount of products than those with electron-donating groups. It is pertinent to note that the presence of halogen substituents as in 3f, 3g, 4f and 4g provides a handle for further structural diversifications using this metal catalysed cross-coupling reaction.

**Table 5.7 N-Arylation of 6-aminoflavone with various substituted arylboronic acids**

<table>
<thead>
<tr>
<th>Entry</th>
<th>6-Aminoflavone (1b)</th>
<th>Arylboronic acid (2a-g)</th>
<th>Products (4)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1b</td>
<td>2a</td>
<td>4a</td>
<td>93</td>
</tr>
<tr>
<td>2</td>
<td>1b</td>
<td>2b</td>
<td>4b</td>
<td>90</td>
</tr>
<tr>
<td>3</td>
<td>1b</td>
<td>2c</td>
<td>4c</td>
<td>91</td>
</tr>
<tr>
<td>4</td>
<td>1b</td>
<td>2d</td>
<td>4d</td>
<td>89</td>
</tr>
<tr>
<td>5</td>
<td>1b</td>
<td>2e</td>
<td>4e</td>
<td>90</td>
</tr>
<tr>
<td>6</td>
<td>1b</td>
<td>2f</td>
<td>4f</td>
<td>81</td>
</tr>
<tr>
<td>7</td>
<td>1b</td>
<td>2g</td>
<td>4g</td>
<td>77</td>
</tr>
</tbody>
</table>

*aReaction conditions: 6-Aminoflavone (0.5 mmol), boronic acids (0.6 mmol) Cu/MCIP-1 (40 mg), NEt₃ (100 mol%), DCE (2 mL), O₂ balloon, RT; bIsolated yield based on 6-aminoflavone.*
The scope of the protocol was extended further, to the coupling of substituted arylboronic acids with 8-aminoquinoline (1c) to give the corresponding products in good to excellent yield and the results are summarized in table 5.8. 1c was coupled readily with electronically diverse boronic acids. Interestingly, all the examined substrates underwent clean conversion to the desired \( N \)-arylated aminoquinolines and the only noticeable difference in the reaction time. Substituting both electron-donating and electron withdrawing groups at \( p \)- and \( m \)-positions gave very good yield. However, \( o \)-substituted arylboronic acid gave lower yield, might be due to steric hindrance.

**Table 5.8** \( N \)-Arylation of 8-aminoquinoline with various substituted arylboronic acids

<table>
<thead>
<tr>
<th>Entry</th>
<th>8-Aminoquinoline (1c)</th>
<th>Arylboronic acid (2a-2j)</th>
<th>Products (5)</th>
<th>Yield (%)(^{b})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1c</td>
<td>2a</td>
<td>5a</td>
<td>94</td>
</tr>
<tr>
<td>2</td>
<td>1c</td>
<td>2b</td>
<td>5b</td>
<td>93</td>
</tr>
<tr>
<td>3</td>
<td>1c</td>
<td>2c</td>
<td>5c</td>
<td>90</td>
</tr>
<tr>
<td>4</td>
<td>1c</td>
<td>2d</td>
<td>5d</td>
<td>88</td>
</tr>
<tr>
<td>5</td>
<td>1c</td>
<td>2e</td>
<td>5e</td>
<td>90</td>
</tr>
<tr>
<td>6</td>
<td>1c</td>
<td>2f</td>
<td>5f</td>
<td>84</td>
</tr>
<tr>
<td>7</td>
<td>1c</td>
<td>2g</td>
<td>5g</td>
<td>80</td>
</tr>
<tr>
<td>8</td>
<td>1c</td>
<td>3-CN-C(_6)H(_4)B(OH)(_2) (2h)</td>
<td>5h</td>
<td>78</td>
</tr>
<tr>
<td>9</td>
<td>1c</td>
<td>3-NO(_2)-C(_6)H(_4)B(OH)(_2) (2i)</td>
<td>5i</td>
<td>76</td>
</tr>
<tr>
<td>10</td>
<td>1c</td>
<td>2-Cl-5-OCH(_3)-C(_6)H(_4)B(OH)(_2) (2j)</td>
<td>5j</td>
<td>58</td>
</tr>
</tbody>
</table>

\(^{a}\)Reaction conditions: 8-Aminoquinoline (0.5 mmol), boronic acids (0.6 mmol), Cu/MCIP-1 (40 mg), NE\(_3\) (100 mol\%), DCE (2 mL), O\(_2\) balloon, RT; \(^{b}\)Isolated yield based on 8-aminoquinoline.

As recyclability is important for industrial applications of a good catalyst, reuse performance of Cu/MCIP-1 was also investigated. In this context, the reusability of Cu/MCIP-1 was checked in the Chan Lam cross-coupling under the optimized conditions, as given in figure 5.13. After
completion of the reaction, products were extracted with dichloromethane, dried with anhydrous sodium sulfate, and concentrated under reduced pressure. The recovered Cu/MCIP-1 was washed three times with dichloromethane and activated under vacuum at room temperature for 1 h. Even after the fourth consecutive reaction, the recovered Cu/MCIP-1 catalyst retained its activity, resulting in 91-87% yield.

![Figure 5.13 Reusability of Cu/MCIP-1 catalysed experiments](image)

In order to verify whether real heterogeneity of catalyst or due to some metal leached copper species present in the filtrate, Sheldon’s test was performed. The reaction was carried out under the optimized conditions and the Cu/MCIP-1 catalyst was filtered from the reaction mixture at 67% yield of desired N-arylation product formation (Table 5.9). After removal of Cu/MCIP-1 catalyst, the filtrate was further stirred for an additional four hours and no further increase in yield was observed. The absence of metal leaching was also confirmed from atomic absorption spectroscopy analyses of the filtrate from the reaction mixture and also of the filtrate from a stirred solution of Cu/MCIP-1 in DCE under the same reaction conditions which was also further confirmed from SEM-EDX analysis. The SEM-EDX results suggested ~2.50% of copper in reused Cu/MCIP-1 (Figure 5.14 and Table 5.10). These results demonstrate clearly that Cu/MCIP-1 is truly heterogeneous in nature.
Table 5.9 Sheldon Test

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Yield (%)&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu/MCIP-1</td>
<td>67  67  91</td>
</tr>
</tbody>
</table>

<sup>a</sup>Reaction conditions: 7-Aminoflavone (0.5 mmol), phenylboronic acids (0.6 mmol), Cu/MCIP-1 (40 mg), NEt<sub>3</sub> (100 mol%), DCE (2 mL), O<sub>2</sub> balloon, RT;

<sup>b</sup>Isolated yield based on 7-aminoflavone.

Figure 5.14 EDX for after fourth run Cu/MCIP-1

Table 5.10 Details of Atom weight percentage after fourth run with Cu/MCIP-1

<table>
<thead>
<tr>
<th>Element, Atomic number</th>
<th>Series</th>
<th>Atom (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C, 6</td>
<td>K-series</td>
<td>63.91</td>
</tr>
<tr>
<td>N, 7</td>
<td>K-series</td>
<td>18.53</td>
</tr>
<tr>
<td>O, 8</td>
<td>K-series</td>
<td>15.06</td>
</tr>
<tr>
<td>Cu, 29</td>
<td>K-series</td>
<td>2.49</td>
</tr>
</tbody>
</table>

To find out any metal leaching, the following control experiment was also performed. Cu/MCIP-1 (0.040 g) was added to a mixture of 7-aminoflavone (0.5 mmol), phenylboronic acid (0.6 mmol) and NEt<sub>3</sub> (100 mol%) in DCE (2 mL) and stirred at room temperature for 12 h. After completion of reaction, the reaction mixture was filtered. The filtrate and reused Cu/MCIP-1 (dissolved in H<sub>2</sub>SO<sub>4</sub>) were analysed by AAS. The copper concentration in filtrate is found to be BDL (BELOW DETECTABLE LIMIT).
In the reused Cu-MCIP-1 (dissolved in H$_2$SO$_4$), the copper concentration is found to be 2.54 mmol/g. This result shows that no leaching of copper has taken place from the solid to the liquid phase. These results further prove that catalyst is heterogeneous in nature.

Based on the above results and previous reports, a plausible mechanistic pathway for the present cross coupling $N$-arylation reaction involving a Cu(I)/Cu(III) cycle is depicted in scheme 5.2. The first step involves the coordination of Cu/MCIP-1 to the amine (1) to form a Cu(II) complex A. The second step involves transmetallation of the arylboronic acid (2) with complex A which results in an arylated Cu(II) complex B. Complex B then undergoes oxidation to form a Cu(III) species C, which undergoes reductive elimination to form the Cu(I) complex D and $N$-arylated products. Subsequently oxidative addition of 1 and 2 to the Cu(I) complex D, generates the Cu(III) species C, thereby propagating the Cu(I)/Cu(III) cycle.
Scheme 5.2 Plausible mechanistic pathway of Chan-Lam N-arylations
5.3 Conclusions

We have developed two new imine functionalised MCIPs from relatively cheap starting materials and industrially important building blocks by simple Schiff base chemistry. In the view of catalytic applications, this copper loaded MCIP-1 material showed excellent catalytic activity in Chan-Lam cross-coupling of N-arylation under mild reaction conditions. In all the reactions, removal of catalyst consists of simple filtration. The catalyst is highly stable, shows no metal leaching and can be reused without loss of its catalytic activity. To the best of our knowledge, the C-N bond of biologically active flavones was reported for the first time in solid catalyst system. The observed results will provide further stimulus on design and catalytic applications of this novel class of materials.

5.4 Experimental Section

5.4.1 Synthesis of MCIP-1

2,4,6-Tris(p-formylphenoxy)-1,3,5-triazine (TRIPOD) was prepared according to the published procedure. A round-bottom flask fitted with a condenser was charged with TRIPOD (2 mmol) and p-phenylenediamine (3 mmol) in THF and mesitylene (1:1, 30 mL) at 120 °C for 72 h. When solid was appeared, it was then filtered and washed with methanol, acetone and DCM (each solvent 100 mL) to remove unreacted aldehyde and diamine. Finally, the product was dried in vacuum to obtain the desired solvent free material with 85% yield.

5.4.2 Synthesis of MCIP-2

The synthesis of MCIP-2 was similar to that of MCIP-1 except that terephthalic dihydrazide was used instead of p-phenylenediamine. Pale yellow powder was obtained in a 82% yield.
5.4.3 Synthesis of catalyst (Cu/MCIP-1)

In a typical experiment, a mixture of copper acetate (40 mg) in DCM and MCIP-1 material (500 mg) was stirred at room temperature for 48 h. When a greenish brown solid was appeared, it was filtered and washed with methanol, acetone and DCM to remove any unreacted copper acetate. It was dried in vacuum to obtain the designed solvent free catalyst. Powder XRD, EDX and atomic adsorption spectroscopy analyses of the catalyst suggested the presence of copper metal. The stability of the catalyst was confirmed by TGA. The Cu/MCIP-1 is dissolved in \( \text{H}_2\text{SO}_4 \), diluted and analysed with AAS and the results show that copper concentration in Cu/MCIP-1 is loaded to be 2.58 mmol/g. In the after fourth used Cu-MCIP-1 (dissolved in H\( \text{SO}_4 \)), the copper concentration is found to be 2.54 mmol/g.

5.4.4 Cu/MCIP-1 catalysed Chan-Lam cross coupling reaction

In a typical reaction, a mixture of Cu/MCIP-1 (40 mg), amines (0.5 mmol) and arylboronic acids (0.6 mmol) was taken in 2 mL of DCE under oxygen balloon atmosphere at room temperature for 16 h. The progress of the reaction was monitored by TLC. After completion of the reaction, the reaction mixture was extracted with dichloromethane (10 mL), the catalyst was filtered and the filtrate was extracted with distilled water, and organic layer was dried over anhydrous sodium sulfate. After the organic solvent was evaporated in vacuum, the residues were purified by column chromatography silica gel (60-120 mesh) afforded the corresponding pure \( N \)-arylated products. The recovered catalyst was thoroughly washed with dichloromethane and activated under vacuum at room temperature for 1 h, which was subsequently reused.
5.4.5 Spectral data of Chan-Lam cross coupling products

**7-(Phenylamino)-2-phenyl-4H-chromen-4-one (Table 5.6, 3a):** Compound 3a was prepared according to the general procedure and purified by column chromatography to give a yellow solid; mp. 195-196 °C.

$^1$H-NMR (300 MHz, 25 °C, CDCl$_3$, δ ppm): 8.08 (d, J=8.7 Hz, 1H), 7.91-7.85 (m, 2H), 7.50 (dd, J=5.1, 1.9 Hz, 3H), 7.44-7.37 (m, 2H), 7.28 (s, 1H), 7.25 (s, 1H), 7.16 (t, J=7.3 Hz, 1H), 7.06 (d, J=2.2 Hz, 1H), 6.94 (dd, J=8.7, 2.2 Hz, 1H), 6.74 (s, 1H), 6.27 (s, 1H); $^{13}$C-NMR (75 MHz, 25 °C, CDCl$_3$, δ ppm): 177.6, 162.6, 158.3, 149.5, 140.1, 131.9, 131.2, 129.6, 128.9, 127.1, 126.1, 124.1, 121.5, 116.6, 114.6, 107.4, 100.1; ESI-MS: m/z calcd. for C$_{21}$H$_{15}$NO$_2$: 313.11; found, 314.23 (M+H).

**7-((4-Ethylphenyl)amino)-2-phenyl-4H-chromen-4-one (Table 5.6, 3b):** Compound 3b was prepared according to the general procedure and purified by column chromatography to give a yellow solid; mp. 137-138 °C.

$^1$H-NMR (300 MHz, 25 °C, CDCl$_3$, δ ppm): 8.08-8.05 (d, J=8.7 Hz, 1H), 7.90-7.73 (m, 2H), 7.52-7.50 (m, 3H), 7.27-7.21 (m, 4H), 7.00-6.92 (m, 2H), 6.74 (s, 1H), 6.24 (s, 1H), 2.73-2.65 (q, 2H), 1.30-1.26 (t, 3H); $^{13}$C-NMR (75 MHz, 25 °C, CDCl$_3$, δ ppm): 177.6, 162.4, 158.2, 150.1, 140.3, 137.3, 131.7, 131.0, 128.8, 128.7 126.8, 125.9, 122.1, 115.9, 114.1, 107.1, 99.2, 28.1, 15.4; ESI-MS: m/z calcd. for C$_{23}$H$_{19}$NO$_2$: 341.14; found, 342.28 (M+H).

**7-((4-Methoxyphenyl)amino)-2-phenyl-4H-chromen-4-one (Table 5.6, 3c):** Compound 3c was prepared according to the general procedure and purified by column chromatography to give a yellow solid; mp. 194-195 °C.

$^1$H-NMR (400 MHz, 25 °C, CDCl$_3$, δ ppm): 8.04-8.02 (d, J=8.4 Hz, 1H), 7.87-7.84 (dd, J=7.4, 2.2 Hz, 2H), 7.50-7.47 (dt, J=5.6, 2.6 Hz, 3H), 7.22-7.20 (d, 2H), 6.97-6.95 (m, 2H), 6.84-6.81 (m, 2H), 6.71 (s, 1H), 6.18 (s, 1H), 3.84 (s, 3H); $^{13}$C-NMR (100 MHz, 25 °C, CDCl$_3$, δ ppm): 177.7, 162.5, 158.5, 157.2, 151.4, 132.6, 132.0, 131.2, 128.9, 127.1, 126.1, 125.4, 115.9, 114.9, 113.7, 107.4, 98.8, 55.6; ESI-MS: m/z calcd. for C$_{22}$H$_{17}$NO$_3$: 343.12; found, 344.20 (M+H).
7-((3-Methoxyphenyl)amino)-2-phenyl-4H-chromen-4-one (Table 5.6, 3d): Compound 3d was prepared according to the general procedure and purified by column chromatography to give a yellow solid;

\[
{^1}H-NMR (400 MHz, 25 ^\circ C, CDCl_3, \delta ppm): 8.02-8.00 (d, J=8.7 Hz, 2H), 7.82-7.80 (m, 2H), 7.44-7.42 (m, 3H), 7.25-7.19 (m, 2H), 7.03-7.02 (d, 1H), 6.89-6.87 (dd, J = 8.7, 2.0 Hz, 1H), 6.79-6.77 (d, J = 7.9 Hz, 1H), 6.73-6.68 (d, 2H), 6.64-6.62 (dd, J = 8.2, 1.9 Hz, 1H), 6.16 (s, 1H), 3.76 (s, 2H); {^{13}}C-NMR (100 MHz, 25 ^\circ C, CDCl_3, \delta ppm): 177.9, 162.9, 161.0, 149.5, 141.6, 132.3, 131.5, 130.7, 129.2, 127.4, 126.4, 117.1, 115.0, 114.5, 113.9, 109.5, 107.7, 107.5, 100.9, 55.6. ESI-MS: m/z calcd. for C_{22}H_{17}NO_3: 343.12; found, 344.25 (M+H).
\]

7-((3-Methylphenyl)amino)-2-phenyl-4H-chromen-4-one (Table 5.6, 3e): Compound 3e was prepared according to the general procedure and purified by column chromatography to give a yellow solid; mp. 192-193 ^\circ C;

\[
{^1}H-NMR (400 MHz, 25 ^\circ C, CDCl_3, \delta ppm): 8.00-7.98 (d, J = 8.7 Hz, 1H), 7.81 - 7.79 (m, 2H), 7.43-7.41 (m, 3H), 7.21 – 7.19 (m, 1H), 7.01-6.99 (d, 2H), 6.97-6.96 (d, 1H), 6.91-6.89 (d, J = 7.5 Hz, 1H), 6.87-6.84 (dd, J = 8.7, 2.1 Hz, 1H), 6.65 (s, 1H), 6.22 (s, 1H), 2.31 (s, 3H); {^{13}}C-NMR (100 MHz, 25 ^\circ C, CDCl_3, \delta ppm): 177.7, 162.6, 158.4, 149.8, 140.1, 139.7, 132.1, 131.3, 129.5, 128.9, 127.1, 126.2, 125.0, 122.3, 118.7, 116.6, 114.6, 107.5, 100.1, 21.5. ESI-MS: m/z calcd. for C_{22}H_{17}NO_2: 327.13; found, 328.26 (M+H).
\]

7-((4-Chlorophenyl)amino)-2-phenyl-4H-chromen-4-one (Table 5.6, 3f): Compound 3f was prepared according to the general procedure and purified by column chromatography to give a yellow solid; mp. 248-249 ^\circ C;

\[
{^1}H-NMR (400 MHz, 25 ^\circ C, CDCl_3, \delta ppm): 9.08 (s, 1H), 8.01-7.99 (d, 2H), 7.82-7.80 (d, J=8.7 Hz, 1H), 7.51-7.48 (m, 3H), 7.36-7.24 (d, J = 8.7 Hz, 2H), 7.25-7.23 (d, J = 8.7 Hz, 2H), 7.12 (d, 1H), 7.02-6.99 (dd, J = 8.7, 1.7 Hz, 1H), 6.81 (s, 1H); {^{13}}C-NMR (100 MHz, 25 ^\circ C, CDCl_3, \delta ppm): 175.9, 161.6, 157.7, 149.1, 139.8, 131.4, 131.3, 129.3, 129.0, 126.2, 126.1, 125.9, 121.5, 115.6, 114.8, 106.7, 99.6; ESI-MS: m/z calcd. for C_{21}H_{14}ClNO_2: 347.07; found, 346.31 (M-H).
7-((4-Fluorophenyl)amino)-2-phenyl-4H-chromen-4-one (Table 5.6, 3g): Compound 3g was prepared according to the general procedure and purified by column chromatography to give a yellow solid; mp. 239-240 °C.

$^1$H-NMR (400 MHz, 25 °C, CDCl$_3$, δ ppm): 8.08-8.05 (d, J=8.6 Hz, 1H), 7.89-7.86 (m, 2H), 7.51-7.49 (m, 3H), 7.26-7.22 (m, 2H), 7.15-7.09 (t, 2H), 6.90 -6.86 (m, 2H), 6.73 (s, 1H), 6.14 (s, 1H); $^{13}$C-NMR (100 MHz, 25 °C, CDCl$_3$, δ ppm): 176.6, 161.6, 157.4, 149.2, 134.9, 134.9, 130.9, 130.9, 130.2, 127.9, 126.24, 125.1, 123.6, 123.5, 115.6, 115.6, 115.5, 115.4, 113.0, 106.5, 98.6; ESI-MS: m/z calcd. for C$_{21}$H$_{14}$FNO$_2$: 331.10; found, 332.20 (M+H).

6-(Phenylamino)-2-phenyl-4H-chromen-4-one (Table 5.7, 4a): Compound 4a was prepared according to the general procedure and purified by column chromatography to give a yellow solid; mp. 186-187 °C.

$^1$H-NMR (400 MHz, 25 °C, CDCl$_3$, δ ppm): 7.93-7.91 (d, 2H), 7.81 (s, 1H), 7.53-7.48 (m, 4H), 7.44-7.42 (d, J=9.4 Hz, 1H), 7.33-7.29 (t, J=7.5 Hz, 2H), 7.14-7.12 (d, J=7.9 Hz, 2H), 7.02-6.98 (t, J=7.3 Hz, 1H), 6.80 (s, 1H), 6.05 (s, 1H); $^{13}$C-NMR (100 MHz, 25 °C, CDCl$_3$, δ ppm): δ 178.4, 163.1, 151.0, 142.3, 141.2, 131.9, 131.5, 129.6, 129.0, 126.3, 124.8, 124.2, 122.0, 119.2, 118.5, 110.7, 106.8; ESI-MS: m/z calcd. for C$_{21}$H$_{15}$NO$_2$: 313.11; found, 314.23 (M+H).

6-((4-Ethylphenyl)amino)-2-phenyl-4H-chromen-4-one (Table 5.7, 4b): Compound 4b was prepared according to the general procedure and purified by column chromatography to give a yellow solid; mp. 91-92 °C.

$^1$H-NMR (400 MHz, 25 °C, CDCl$_3$, δ ppm): 7.91-7.89 (d, 2H), 7.74-7.73 (d, 1H), 7.51-7.45 (m, 4H), 7.15-7.13 (d, 2H), 7.08-7.03 (m, 3H), 6.82 (s, 2H), 2.63-2.55 (m, 2H), 1.24-1.21 (q, 3H); $^{13}$C-NMR (100 MHz, 25 °C, CDCl$_3$, δ ppm): δ 178.7, 163.3, 154.2, 150.7, 142.1, 139.6, 138.5, 135.9, 131.5, 129.0, 128.9, 128.8, 126.3, 119.6, 115.3, 109.5, 106.7, 28.2, 15.9; ESI-MS: m/z calcd. for C$_{23}$H$_{19}$NO$_2$: 341.14; found, 342.27 (M+H).
6-((4-Methoxyphenyl)amino)-2-phenyl-4H-chromen-4-one (Table 5.7, 4c): Compound 4c was prepared according to the general procedure and purified by column chromatography to give a yellow solid; mp. 159-160 °C.

^1H-NMR (400 MHz, 25 °C, CDCl3, δ ppm): 7.91-7.89 (d, 2H), 7.61 (s, 1H), 7.52-7.50 (d, 3H), 7.44-7.42 (d, J=8.9 Hz, 1H), 7.26-7.24 (d, 1H), 7.13-7.11 (d, J=8.2 Hz, 2H), 6.90-6.86 (d, 2H), 6.78 (s, 1H), 5.86 (s, 1H), 3.81 (s, 3H); ^13C-NMR (100 MHz, 25 °C, CDCl3, δ ppm): δ 178.5, 162.9, 155.9, 150.3, 143.2, 134.8, 132.0, 131.4, 129.0, 126.2, 124.8, 122.9, 122.5, 119.1, 114.9, 108.0, 106.7, 55.6; ESI-MS: m/z calcd. for C_{22}H_{17}NO_{3}: 343.12; found, 344.29 (M+H).

6-((3-Methoxyphenyl)amino)-2-phenyl-4H-chromen-4-one (Table 5.7, 4d): Compound 4d was prepared according to the general procedure and purified by column chromatography to give a yellow solid; mp. 153-154 °C.

^1H-NMR (400 MHz, 25 °C, CDCl3, δ ppm): 7.93-7.91 (d, 2H), 7.81 (s, 1H), 7.53-7.46 (m, 5H), 7.23-7.19 (t, J=8.1 Hz, 1H), 6.81 (s, 1H), 6.73-6.71 (d, J=8.0 Hz, 1H), 6.66 (s, 1H), 6.56-6.54 (d, J=8.2 Hz, 1H), 6.05 (s, 1H), 3.79 (s, 3H); ^13C-NMR (100 MHz, 25 °C, CDCl3, δ ppm): δ 178.4, 163.2, 160.8, 151.2, 143.7, 140.8, 131.9, 131.5, 130.3, 129.05, 126.2, 124.8, 124.6, 119.1, 111.4, 110.7, 107.2, 106.8, 104.1, 55.3; ESI-MS: m/z calcd. for C_{22}H_{17}NO_{3}: 343.12; found, 344.23 (M+H).

6-((3-Methylphenyl)amino)-2-phenyl-4H-chromen-4-one (Table 5.7, 4e): Compound 4e was prepared according to the general procedure and purified by column chromatography to give a yellow solid; mp. 170-171 °C.

^1H-NMR (400 MHz, 25 °C, CDCl3, δ ppm): 7.90-7.88 (d, 2H), 7.77 (s, 1H), 7.51-7.44 (m, 5H), 7.20-7.16 (t, 1H), 6.95-6.89 (m, 2H), 6.82-6.80 (d, 2H), 6.05 (s, 1H), 2.32 (s, 3H); ^13C-NMR (100 MHz, 25 °C, CDCl3, δ ppm): δ 178.7, 163.3, 150.9, 142.2, 141.4, 139.5, 131.6, 129.1, 126.3, 124.2, 122.9, 120.9, 119.3, 119.1, 116.3, 115.6, 112.5, 110.6, 106.7, 21.6; ESI-MS: m/z calcd. for C_{22}H_{17}NO_{2}: 327.13; found, 328.24 (M+H).
6-((4-Chlorophenyl)amino)-2-phenyl-4H-chromen-4-one (Table 5.7, 4f): Compound 4f was prepared according to the general procedure and purified by column chromatography to give a yellow solid; mp. 223-224 °C.

\[^{1}\text{H-NMR (400 MHz, 25 °C, CDCl}_3, \delta \text{ ppm): 7.93-7.91 (d, 2H), 7.78 (s, 1H), 7.55-7.51 (m, 4H), 7.26-7.16 (m, 4H), 7.06-7.04 (d, 1H), 6.81-6.79 (d, 2H), 5.99 (s, 1H); \]^\[^{13}\text{C-NMR (100 MHz, 25 °C, CDCl}_3, \delta \text{ ppm): } \delta 178.6, 163.6, 154.7, 151.3, 140.8, 131.7, 129.6, 129.4, 129.1, 126.3, 125.2, 124.5, 119.6, 119.4, 116.7, 110.9, 106.7; ESI-MS: m/z calcd. for C\text{\textsubscript{21}}H\text{\textsubscript{14}}ClNO\text{\textsubscript{2}}: 347.07; found, 348.22 (M+H).\]

6-((4-Fluorophenyl)amino)-2-phenyl-4H-chromen-4-one (Table 3, 4g): Compound 4g was prepared according to the general procedure and purified by column chromatography to give a yellow solid; mp. 216-217 °C.

\[^{1}\text{H-NMR (400 MHz, 25 °C, CDCl}_3, \delta \text{ ppm): 7.93-7.91 (d, 2H), 7.70 (s, 1H), 7.54-7.47 (m, 4H), 7.33-7.31 (d, 1H), 7.13-7.11 (m, 2H), 7.05-7.01 (t, 2H), 6.80 (s, 1H), 5.89 (s, 1H); \]^\[^{13}\text{C-NMR (100 MHz, 25 °C, CDCl}_3, \delta \text{ ppm): } \delta 178.3, 163.2, 159.8, 157.4, 150.8, 141.9, 138.1, 131.9, 131.5, 129.05, 126.2, 124.8, 123.4, 121.5, 121.4, 119.3, 116.4, 116.2, 109.53, 106.8; ESI-MS: m/z calcd. for C\text{\textsubscript{21}}H\text{\textsubscript{14}}FNO\text{\textsubscript{2}}: 331.10; found, 330.24 (M-H).\]

N-Phenylquinolin-8-amine (Table 5.8, 5a): Compound 5a was prepared according to the general procedure and purified by column chromatography.

\[^{1}\text{H-NMR (300 MHz, 25 °C, CDCl}_3, \delta \text{ ppm): 8.80-8.77 (m, 1H), 8.25 (s, 1H), 8.13-8.10 (dd, J=8.3, 1.6 Hz, 1H), 7.52-7.46 (m, 1H), 7.43-7.33 (m, 6H), 7.22-7.20 (d, J=8.1 Hz, 1H), 7.06-7.01 (m, 1H); \]^\[^{13}\text{C-NMR (75 MHz, 25 °C, CDCl}_3, \delta \text{ ppm): } \delta 147.3, 141.8, 140.3, 138.6, 136.2, 129.3, 128.9, 127.3, 122.1, 121.6, 120.1, 116.5, 107.8; ESI-MS: m/z calcd. for C\text{\textsubscript{15}}H\text{\textsubscript{12}}N\text{\textsubscript{2}}: 220.10; found, 221.18 (M-H).\]

N-(4-Ethylphenyl)quinolin-8-amine (Table 5.8, 5b): Compound 5b was prepared according to the general procedure and purified by column chromatography.

\[^{1}\text{H-NMR (300 MHz, 25 °C, CDCl}_3, \delta \text{ ppm): 8.79-8.77 (d, 1H), 8.15 (s, 1H), 8.11-8.09 (d, J=8.3 Hz, 1H), 7.43-7.37 (m, 3H), 7.33-7.30 (m, 2H), 7.22-7.19 (m, 3H), 2.69-2.62 (q, 2H), 1.26-1.24 (t, 3H); \]^\[^{13}\text{C-NMR (75 MHz, 25 °C, CDCl}_3, \delta \text{ ppm): 140.7, 134.5, 132.9, 132.0, 131.9, 129.7, 122.5, 122.2, 120.9, 115.1, 114.4, 109.6, 100.9, 21.8, 9.3; ESI-MS: m/z calcd. for C\text{\textsubscript{17}}H\text{\textsubscript{16}}N\text{\textsubscript{2}}: 248.13; found, 249.21 (M+H).\]
N-(4-Methoxyphenyl)quinolin-8-amine (Table 4, 5c): Compound 5c was prepared according to the general procedure and purified by column chromatography.

$^1$H-NMR (400 MHz, 25 °C, CDCl$_3$, δ ppm): 8.75-8.73 (dd, J=4.1, 1.5 Hz, 1H), 8.07-8.04 (dd, J=8.2, 1.4 Hz, 1H), 7.98 (s, 1H), 7.38-7.29 (m, 4H), 7.21-7.19 (d, J=7.0 Hz, 1H), 7.13-7.11 (d, J=7.8 Hz, 1H), 6.93-6.91 (d, J=8.8 Hz, 2H), 3.80 (s, 3H); $^{13}$C-NMR (100 MHz, 25 °C, CDCl$_3$, δ ppm): 155.8, 147.2, 142.0, 138.3, 136.2, 134.8, 128.9, 127.5, 123.7, 121.6, 115.6, 114.7, 106.7, 55.6; ESI-MS: m/z calcd. for C$_{16}$H$_{14}$N$_2$O: 250.11; found, 251.22 (M+H).

N-(3-Methoxyphenyl)quinolin-8-amine (Table 5, 5d): Compound 5d was prepared according to the general procedure and purified by column chromatography.

$^1$H-NMR (300 MHz, 25 °C, CDCl$_3$, δ ppm): 8.79-8.77 (dd, J=4.1, 1.5 Hz, 1H), 8.27 (s, 1H), 8.12-8.09 (dd, J=8.2, 1.5 Hz, 1H), 7.55-7.52 (d, J=7.7 Hz, 1H), 7.43-7.37 (m, 2H), 7.30-7.24 (m, 2H), 7.00-6.96 (2H), 6.61-6.58 (m, 1H), 3.83 (s, 3H); $^{13}$C-NMR (75 MHz, 25 °C, CDCl$_3$, δ ppm): 160.6, 147.3, 143.2, 139.9, 138.6, 136.2, 130.0, 128.8, 127.2, 121.6, 116.7, 112.4, 108.4, 107.4, 105.5, 55.2; ESI-MS: m/z calcd. for C$_{16}$H$_{14}$N$_2$O: 250.11; found, 251.20 (M+H).

N-(3-Methylphenyl)quinolin-8-amine (Table 5, 5e): Compound 5e was prepared according to the general procedure and purified by column chromatography.

$^1$H-NMR (300 MHz, 25 °C, CDCl$_3$, δ ppm): 8.78-8.76 (dd, J=4.2, 1.6 Hz, 1H), 8.22 (s, 1H), 8.11-8.07 (dd, J=8.3, 1.6 Hz, 1H), 7.50-7.47 (m, 1H), 7.42-7.36 (m, 2H), 7.25-7.18 (m, 4H), 6.87-6.85 (d, J=6.8 Hz, 1H), 2.37 (s, 3H); $^{13}$C-NMR (75 MHz, 25 °C, CDCl$_3$, δ ppm): 147.1, 141.7, 140.2, 139.0, 138.4, 136.0, 129.0, 128.7, 127.2, 122.9, 121.4, 120.7, 116.9, 116.2, 107.7, 21.4; ESI-MS: m/z calcd. for C$_{16}$H$_{14}$N$_2$: 234.12; found, 235.17 (M+H).

N-(4-Chlorophenyl)quinolin-8-amine (Table 5, 5f): Compound 5f was prepared according to the general procedure and purified by column chromatography.

$^1$H-NMR (400 MHz, 25 °C, CDCl$_3$, δ ppm): 8.66-8.64 (dd, J=4.1, 1.4 Hz, 1H), 8.12 (s, 1H), 7.98-7.96 (dd, J=8.3, 1.3 Hz, 1H), 7.31-7.26 (m, 2H), 7.18 (s, 4H), 7.12-7.09 (dd, J=7.6, 1.5 Hz, 1H); $^{13}$C-NMR (100 MHz, 25 °C, CDCl$_3$, δ ppm): 147.5, 140.6, 139.8, 138.6, 136.3, 129.4, 128.9, 127.3, 126.7, 121.8, 121.1, 117.1, 108.1; ESI-MS: m/z calcd. for C$_{15}$H$_{11}$ClN$_2$: 254.06; found, 225.14 (M+H).
N-(4-Fluorophenyl)quinolin-8-amine (Table 5.8, 5g):
Compound 5g was prepared according to the general procedure and purified by column chromatography.

$^1$H-NMR (400 MHz, 25 °C, CDC$_3$, δ ppm): 8.76-8.74 (dd, J=4.2, 1.6 Hz, 1H), 8.09-8.05 (m, 2H), 7.39-7.26 (m, 5H), 7.18-7.16 (d, 1H), 7.07-7.00 (m, 2H); $^{13}$C-NMR (100 MHz, 25 °C, CDC$_3$, δ ppm): 159.8, 157.4, 147.4, 141.0, 138.4, 137.9, 137.9, 136.3, 128.9, 127.4, 122.7, 122.6, 121.7, 116.5, 116.1, 115.9, 107.2; ESI-MS: m/z calcd. for C$_{15}$H$_{11}$FN$_2$: 238.09; found, 239.18 (M+H).

N-(3-Cyanophenyl)quinolin-8-amine (Table 5.8, 5h):
Compound 5h was prepared according to the general procedure and purified by column chromatography.

$^1$H-NMR (300 MHz, 25 °C, CDC$_3$, δ ppm): 8.81-8.79 (dd, J=4.2, 1.6 Hz, 1H), 8.41 (s, 1H), 8.17-8.14 (dd, J=8.3, 1.6 Hz, 1H), 7.67 (d, J=1.5 Hz, 1H), 7.57-7.25 (m, 6H), 6.95-6.92 (d, J=7.4 Hz, 1H); $^{13}$C-NMR (75 MHz, 25 °C, CDC$_3$, δ ppm): 147.6, 142.8, 138.3, 136.2, 135.8, 130.1, 128.7, 126.9, 123.0, 121.72, 121.2, 121.1, 118.2, 113.1, 109.1; ESI-MS: m/z calcd. for C$_{16}$H$_{11}$N$_3$: 245.10; found, 246.15 (M+H).

N-(3-Nitrophenyl)quinolin-8-amine (Table 5.8, 5i):
Compound 5i was prepared according to the general procedure and purified by column chromatography. mp. 135-136 °C.

$^1$H-NMR (300 MHz, 25 °C, CDC$_3$, δ ppm): 8.82-8.80 (dd, J=4.2, 1.6 Hz, 1H), 8.55 (s, 1H), 8.27-8.25 (t, 1H), 8.18-8.15 (dd, J=8.3, 1.6 Hz, 1H), 7.83-7.80 (m, 1H), 7.65-7.57 (m, 2H), 7.50-7.45 (m, 3H), 7.36-7.34 (m, 1H); $^{13}$C-NMR (75 MHz, 25 °C, CDC$_3$, δ ppm): δ 149.1, 147.7, 143.3, 138.6, 138.2, 136.2, 129.8, 128.7, 126.9, 124.3, 121.8, 118.4, 115.7, 112.3, 109.2; ESI-MS: m/z calcd. for C$_{15}$H$_{11}$N$_3$O$_2$: 265.09; found, 266.20 (M+H).

N-(2-Chloro-5-methoxyphenyl)-quinolin-8-amine (Table 45.8, 5j):
Compound 5j was prepared according to the general procedure and purified by column chromatography. mp. 94-95°C.

$^1$H-NMR (300 MHz, 25 °C, CDC$_3$, δ ppm): 8.85-8.83 (dd, J=4.2, 1.6 Hz, 1H), 8.60 (s, 1H), 8.15-8.12 (dd, J=8.3, 1.6 Hz, 1H), 7.58-7.55 (d, J=7.7 Hz, 1H), 7.47-7.41 (m, 2H), 7.36-7.27 (m, 3H), 6.52-6.48 (dd, J=8.8, 2.8 Hz, 1H), 3.81 (s, 3H); $^{13}$C-NMR (75 MHz, 25 °C, CDC$_3$, δ ppm): δ 159.1, 147.9, 139.5, 139.2, 138.8, 136.1, 130.2, 128.9, 126.9, 121.7, 117.9, 116.4, 109.4, 107.1, 104.5, 55.5; ESI-MS: m/z calcd. for C$_{16}$H$_{13}$ClN$_2$O: 284.07; found, 285.19 (M+H).
5.5 References


**Characterization spectra of N-arylated products**

*Figure 5.15* $^1$H NMR spectrum of 7-(phenylamino)-2-phenyl-4H-chromen-4-one (3a)

*Figure 5.16* $^{13}$C NMR spectrum of 7-(phenylamino)-2-phenyl-4H-chromen-4-one (3a)
**Figure 5.17** ESI-MS spectrum of 7-(phenylamino)-2-phenyl-4H-chromen-4-one (3a)

**Figure 5.18** $^1$H NMR spectrum of 7-((3-methoxyphenyl)amino)-2-phenyl-4H-chromen-4-one (3d)
Figure 5.19 $^{13}$C NMR spectrum of 7-((3-methoxyphenyl)amino)-2-phenyl-4H-chromen-4-one (3d)

Figure 5.20 ESI-MS spectrum of 7-((3-methoxyphenyl)amino)-2-phenyl-4H-chromen-4-one (3d)
**Figure 5.21** $^1$H NMR spectrum of 7-((4-fluorophenyl)amino)-2-phenyl-4H-chromen-4-one (3g)

**Figure 5.22** $^{13}$C NMR spectrum of 7-((4-fluorophenyl)amino)-2-phenyl-4H-chromen-4-one (3g)
Figure 5.23 ESI-MS spectrum of 7-((4-fluorophenyl)amino)-2-phenyl-4H-chromen-4-one (3g)

Figure 5.24 $^1$H NMR spectrum of 6-(phenylamino)-2-phenyl-4H-chromen-4-one (4a)
Figure 5.25 $^{13}$C NMR spectrum of 6-(phenylamino)-2-phenyl-4H-chromen-4-one (4a)

Figure 5.26 ESI-MS spectrum of 6-(phenylamino)-2-phenyl-4H-chromen-4-one (4a)
Figure 5.27 $^1H$ NMR spectrum of 6-((3-methoxyphenyl)amino)-2-phenyl-4H-chromen-4-one (4d)

Figure 5.28 $^{13}C$ NMR spectrum of 6-((3-methoxyphenyl)amino)-2-phenyl-4H-chromen-4-one (4d)
**Figure 5.29** ESI-MS spectrum of 6-((3-methoxyphenyl)amino)-2-phenyl-4H-chromen-4-one (4d)

**Figure 5.30** $^1$H NMR spectrum of 6-((4-fluorophenyl)amino)-2-phenyl-4H-chromen-4-one (4g)
**Figure 5.31** $^{13}$C NMR spectrum of 6-((4-fluorophenyl)amino)-2-phenyl-4H-chromen-4-one (4g)

**Figure 5.32** ESI-MS spectrum of 6-((4-fluorophenyl)amino)-2-phenyl-4H-chromen-4-one (4g)
**Figure 5.33** $^1$H NMR spectrum of N-phenylquinolin-8-amine (5a)

**Figure 5.34** $^{13}$C NMR spectrum of N-phenylquinolin-8-amine (5a)
**Figure 5.35** ESI-MS spectrum of N-phenylquinolin-8-amine (5a)

**Figure 5.36** $^1$H NMR spectrum of N-(4-ethylphenyl)quinolin-8-amine (5b)
Figure 5.37 $^{13}$C NMR spectrum of N-(4-ethylphenyl)quinolin-8-amine (5b)

Figure 5.38 ESI-MS spectrum of N-(4-ethylphenyl)quinolin-8-amine (5b)
**Figure 5.39** $^1$H NMR spectrum of N-(3-methoxyphenyl)quinolin-8-amine (5d)

**Figure 5.40** $^{13}$C NMR spectrum of N-(3-methoxyphenyl)quinolin-8-amine (5d)
**Figure 5.41** ESI-MS spectrum of N-(3-methoxyphenyl)quinolin-8-amine (5d)

**Figure 5.42** $^1$H NMR spectrum of N-(4-fluorophenyl)quinolin-8-amine (5g)
Figure 5.43 ¹³C NMR spectrum of N-(4-fluorophenyl)quinolin-8-amine (5g)

Figure 5.44 ESI-MS spectrum of N-(4-fluorophenyl)quinolin-8-amine (5g)
Figure 5.45 $^1$H NMR spectrum of $N$-(3-nitrophenyl)quinolin-8-amine (5i)

Figure 5.46 $^{13}$C NMR spectrum of $N$-(3-nitrophenyl)quinolin-8-amine (5i)
Figure 5.47 ESI-MS spectrum of N-(3-nitrophenyl)quinolin-8-amine (5i)

Figure 5.48 $^1$H NMR spectrum of N-(2-chloro-5-methoxyphenyl)-quinolin-8-amine (5i)
Figure 5.49 $^{13}$C NMR spectrum of N-(2-chloro-5-methoxyphenyl)quinolin-8-amine (5j)

Figure 5.50 ESI-MS spectrum of N-(2-chloro-5-methoxyphenyl)quinolin-8-amine (5j)
Figure 5.51 $^1$H NMR spectrum of TRIPOD

Figure 5.52 $^{13}$C NMR spectrum of TRIPOD