Section 3.1

Biogenic synthesis of cellulose supported Pd (0) nanoparticles using hearth wood extract of Artocarpus lakoocha Roxb and their characterization

3.1.1. General overview of Artocarpus lakoocha Roxb

Artocarpus lakoocha is a tropical evergreen tree species of the family Moraceae. It is distributed throughout the Indian Subcontinent and Southeast Asia. Artocarpus lakoocha Roxb is a large deciduous tree reaching 15-18 m in height with a spreading head (Fig.3.1). The tree is valued for its wood; its fruit is edible and is believed to have medicinal value. The bark is grey and the slash is deep red with milky latex. The root is an astringent and is used as a purgative; when macerated it was used as a poultice for skin ailments. The bark is used to treat headache. This tree is mentioned in the Arthashastra. The various compounds have been isolated from the plant such as cycloartenone, cycloartenol α-amyrin and leupeol acetate. One of the most important stilbenoid compounds, oxyresveratrol can be isolated from the heartwood of A. Lakoocha which acts as a bioreductant in the synthesis of metal nanoparticles and has tremendous medicinal impact.

Fig.3.1: Artocarpus lakoocha Tree
3.1.2. Preparation of hearth wood extract of *Artocarpus lakoocha* Roxb

The hearth wood extract of *Artocarpus lakoocha* Roxb was prepared by grinding the dry heart wood of *Artocarpus lakoocha* Roxb and extracted with de-ionised water.

3.1.3. Biogenic synthesis of cellulose supported Pd (0) nanoparticles using hearth wood extract of *Artocarpus lakoocha* Roxb

200 mg nanoporous cellulose and 10 mg Palladium (II) chloride added to a 250 mL round bottom flask containing 100 mL hearth wood extract of *Artocarpus lakoocha* Roxb. The mixture was stirred for 30 minutes at room temperature and then warmed (50 °C) for 15 minutes until the light brown solution turned into black colour. No further colour change was observed after 15 minutes. The black precipitate was filtered, washed, vacuum dried, and finally stored under N$_2$ atmosphere in a dessicator. The synthesized Pd NPs were characterized by UV-visible spectroscopy, FT-IR spectroscopy, XRD and TEM analysis.

3.1.4. Characterization of cellulose supported Pd (0) nanoparticles

3.1.4.1. Colour study

Synthesis of Pd(0) NPs@cellulose using hearth wood extract of *Artocarpus lakoocha* Roxb was initially assumed from the colour changes. A light brown colour of aqueous solution of oxyresveratrol, PdCl$_2$ and cellulose, C gradually changed to black colour, D. The black solid deposited on the bottom of the test tube E is solid Pd(0) NPs@cellulose(Fig.3.2).
3.1.4.2. UV-Visible study

UV-visible study of the synthesized nanoparticles revealed the formation of Pd(0) NPs (Fig.3.3). The UV-visible spectrum of PdCl$_2$ exhibits an absorption maximum in the range 400-430 nm, due to the absorption of Pd (II) ions. As this peak is completely disappeared and replaced by a broad and continuous absorption band in the UV-visible spectrum of black solid Pd/cellulose matrix, this indicates the formation of Pd(0) NPs@cellulose [1].

Fig.3.3: A comparative UV-visible spectra of PdCl$_2$, cellulose, oxyresveratrol and Pd(0) NPs@cellulose.
3.1.4.3. FT-IR study

Comparative FTIR spectra of cellulose and cellulose supported Pd is shown in Fig. 3.4. The red line indicates the FTIR of cellulose supported Pd and the blue line indicate the FT-IR of pure cellulose. Strong absorption peak at 3349.6 cm\(^{-1}\) correspond to the O-H stretching intramolecular hydrogen bonds for cellulose. Peak at 2903 cm\(^{-1}\) is due to the C-H stretching vibration. Peak at 1650 cm\(^{-1}\) is because of O-H bending vibration, 1430 cm\(^{-1}\) (CH\(_2\) scissoring motion), 1384 cm\(^{-1}\) (C-H bending), 1336 cm\(^{-1}\) (O-H in plane bending), 1317 cm\(^{-1}\) (CH\(_2\) wagging), 1053 cm\(^{-1}\) (C-O-C pyranose ring stretching vibration) and peak at 897 cm\(^{-1}\)is associated with the cellulosic β-glycosidic linkages [2]. A decrease in intensity at 3346 cm\(^{-1}\) of the cellulose supported Pd as compared to 3349.6 cm\(^{-1}\) indicates the formation of Pd(0)-Oxygen linkage, i.e. palladium metals are stabilized by the -OH groups of the cellulose moiety by metal-ligand interactions. Due to these interactions weaker absorption peaks were observed in the FT-IR spectra of cellulose supported Pd. This results demonstrate that the -OH groups on microcrystalline cellulose acts as a stabilizing agent of metal nanoparticles, i.e formation of Pd(0) NPs inside the cavities. Shifting of peaks in FT-IR of cellulose supported Pd as
compared to FT-IR of pure cellulose is also an indication of the formation of Pd(0) NPs inside the cavities of cellulose template [3].

3.1.4.4. PXRD study

Powder X-ray diffraction study (XRD) (Fig. 3.5) showed that in combination with three cellulose peaks at 2θ values 14.8°, 16.4°, and 22.9° corresponding to the Bragg planes (101), (101’) and (002), there were five peaks at 2θ values of 40.2°, 46.5°, 67.9°, 81.7° and 85.7° corresponding to (111), (200), (220), (311) and (222) planes representing Pd(0) NPs on cellulose [4-5]. No peaks corresponding to any other impurity were observed. The intense reflection at 40.2° (111) in comparison with four other peaks may indicate the preferred growth direction of the nanocrystals [6].

3.1.4.5. TEM study

The TEM images (Fig. 3.6, A-D) of synthesized nanocomposites showed that Pd(0) NPs were dispersed in the nanopores of cellulose matrix. The supported Pd(0) NPs were spherical in shape with sizes of in the range 10-30 nm. The HRTEM image (Fig. 3.6, C, inset) of a single Pd(0) NPs showed the reticular lattice planes inside the nanoparticles.
indicating the crystalline nature. The selected area electron diffraction (SAED) image shows the Braggs planes.

![TEM images](image)

**Fig.3.6:** TEM images of Pd(0) NPs@cellulose: (A) Dispersion of nanoparticles in cellulose; (B) & (C) Size of the Pd(0) NPs with HRTEM image (inset); (D) Selected Area Electron Diffraction (SAED) of Pd(0) NPs [7, 8].

### 3.1.5. Isolation of active bio-reductant present in hearth wood extract of *Artocarpus lakoocha* Roxb

**Method A**

10 g of dried and ground hearth wood of *Artocarpus lakoocha* Roxb was treated with 100 mL petroleum ether (40-60 °C) and kept overnight for removing fatty materials. After filtration, these wood materials were taken in 100 mL water, refluxed for six hours, filtered off at hot condition, concentrated to one fourth of the volume under reduced pressure, and
kept in a refrigerator for overnight. Separated deep brown solid materials were filtered, washed with cool water (50 mL) and vacuum dried. These solid materials are identified as oxyresveratrol (2, 3', 4, 5'-tetrahydroxy-trans-stilbene), Yield: 500 mg (5%), Mp: 200 °C, (Lit. Mp: 201 °C [9-11])

![Oxyresveratrol](image)

**Method B**

10 g of dry and powdered wood material were taken in 100 mL acidic water solution (pH = 4) and 20 mL *accelerase* enzyme [Aldrich] was added to the solution. The mixture was heated for 5 hours at 40 °C, hot filtered, extracted with ethyl acetate (3x50 mL), the organic layer washed with 5% NaHCO₃ solution and dried over anhydrous sodium sulphate for 5 hours. The solvent was distilled off under reduced pressure to give deep brown solid oxyresveratrol (2, 3', 4, 5'-tetrahydroxy-trans-stilbene), Yield: 600 mg, (6%). The compound was analyzed and found as above.

**3.1.6. Conclusion**

In summary, we have demonstrated a green biogenic approach for the synthesis of Pd(0) NPs@cellulose using the hearth wood extract of *Artocarpus lakoocha* Roxb. We have also depicted novel one step approach for the isolation of active bioreductant oxyresveratrol from the hearth wood extract of *Artocarpus lakoocha* Roxb. This novel
procedure for isolation of oxyresveratrol will be highly beneficial for industrial production of potent therapeutic agents in human health, e.g. tyrosinase inhibitor, antioxidant, antiglycation, free radical scavenger, neuroprotection etc [9-10]. This eco-friendly protocol for the synthesis of metal NPs provides thermo and air stable crystalline spherical shaped NPs without requiring harmful reducing agents, toxic nitrogenous ligands, solid waste disposals etc.

3.1.7. Characterization data of isolated Oxyresveratrol

Oxyresveratrol (2, 3´, 4, 5´-tetrahydroxy-trans-stilbene): \(^1\)H NMR (500 MHz, CD\(_3\)OD, TMS): \(\delta\) 7.35 (d, \(J = 10\) Hz, 1H), 7.28 (d, \(J = 15\) Hz, 1H), 6.83 (d, \(J = 15\) Hz,1H), 6.45 (s, 2H), 6.32 (d, \(J = 5\) Hz,2H), 6.15 (dd, \(J = 5\) Hz,1H), 4.91 (s, 4H), ppm; \(^{13}\)C NMR(125 MHz, CD\(_3\)OD): \(\delta\) 158.1, 157.8, 155.9, 140.6, 127.4, 127, 125, 123.4, 116.2, 107, 104, 102.1, 100.1; MS (El) \(m/z\) 244 (M+, 100%);244, 195, 187, 185, 140, 130, 81, 61; IR (KBr): 3406, 3218, 1614, 1591, 1518, 1480, 1384, 1312, 1278, 1156, 1116, 978, 824 cm\(^{-1}\) Mp: 200 °C, (Lit. Mp: 201 °C)

3.1.8. References


3.1.9. NMR ($^1$H & $^{13}$C) spectra of isolated Oxyresveratrol
Section 3.2

Microwave assisted Suzuki and Heck coupling in water using cellulose supported Pd (0) nanoparticles as a green, efficient and versatile catalyst

3.2.1. Introduction

Palladium nanoparticles (Pd-NPs) have diverse applications in the field of both homogeneous and heterogeneous catalysis [1]. Suzuki and Heck reactions using Pd-NPs are the most important coupling reactions in the synthesis of great variety of simple to complex molecules which have tremendous application in the field of drugs, pharmaceuticals, agrochemicals and advanced materials [2]. These coupling reactions are most reliable and versatile methods for the construction of carbon–carbon bonds. Traditionally, homogeneous palladium complexes in the presence of various ligands have been used to perform these coupling reactions. Homogeneous Pd catalysts always exhibit better reaction rate, activity and selectivity but heterogeneous catalysts have many advantages over their homogeneous counterparts such as recycling, cost effectiveness and ease of catalyst/product separation [1-2]. However, the most commonly used phosphine ligands are toxic, expensive, and in large-scale applications it may become a more serious economical burden than even the metal itself [3]. Additionally, a trace amount of such ligand may act as inhibitor in some metal-catalyzed asymmetric reactions [4-5]. Therefore, the development of phosphine-free Suzuki cross-coupling reaction is of immense interest. Efforts have been focused on immobilization of homogeneous Pd complexes onto different solid supports to facilitate their separation from the products. Now a days, much attention have been paid to
investigate biocompatible solid support to provide thermo and air stable metal NPs as the synthetic solid support (carbon [6], zeolites [7], metal oxides [8], sol-gel [9], clays [10], dendrimers [11], polymers [12]) or the stabilizing ligands (phosphine etc. [13]) are expensive, toxic, and in large-scale applications it may become a more tedious for solid waste disposals.

Biogenic synthesis of cellulose supported Pd(0) NPs using hearth wood extract of *Artocarpus lakoocha* Roxb and their application as a versatile, efficient and green catalyst in Suzuki and Heck coupling is the first protocol that we depicted herein (Scheme 3.1). This protocol eliminates the use of toxic chemicals/ligands like phosphine and meets the entire shortcomings for the development of a greener methodology for Suzuki and Heck cross coupling reactions. We performed all the reactions under microwave heating. As being energy efficient, microwaves can enhance the rate of reactions and improve product yields [14].
Scheme 3.1: Schematic diagram of fabrication of Pd(0) NPs on cellulose by biogenic method and its catalytic activity towards Suzuki and Heck coupling reaction.

3.2.2. Results and Discussion

3.2.2.1. Catalytic activity of Pd(0) NPs@cellulose under microwave heating

Cellulose supported Pd(0) NPs were tested as a catalyst in the Suzuki cross/homo coupling and Heck reactions under microwave heating. Initially, we have chosen the coupling reaction of 2-bromobenzaldehyde (0.5 mmol) and phenylboronic acid (0.75 mmol) as model substrates for the development of optimized conditions under microwave heating taking water as a solvent. Several bases such as Et₃N, NaOH, NaOAc, Cs₂CO₃, K₂CO₃ etc were used in order to find the optimized reaction condition (table 3.1). Study with different bases indicates that they have remarkable effect on the yields of the product. Among the tested bases, K₂CO₃ (entry 3, table 3.1) gave the highest yield of 1a, (94%) as compared to all other bases (entries 7-10, table 3.1). These results imply that K₂CO₃, among the bases under study, was the most effective for activating this catalytic system in the Suzuki cross coupling reaction. Next we studied the catalytic behaviour of Pd(0) NPs@cellulose as well as loading of the catalyst in this coupling reaction. Control experiments showed that no product formation took place in the absence of Pd(0) NPs@cellulose in aqueous medium under microwave irradiation (entry 1, table 3.1). However, addition of the catalyst to this mixture has rapidly increased the formation of product in high yields. Taking PdCl₂ salt as a catalyst for this coupling reaction under the same reaction condition gave disappointing result (entry 2, yield 30%, table 3.1) as
compared to Pd(0)NPs@cellulose which showed more than 90% product yield. A decrease in the catalyst loading from 0.5 mol% to 0.3 mol% lowered the product yield (entry 4, table 3.1). On the other hand, increasing the catalyst loading did not improve the yield of the product significantly (entry 5, table 3.1). 0.5 mol% of the catalyst was found to be optimal for the coupling reaction (entry 3, table 3.1). The optimum temperature for the reaction is 80 °C and only 5-10 minutes time is required to complete the reaction under microwave heating. The best result was obtained with 0.5 mmol of 2-bromobenzaldehyde, 0.75 mmol of phenylboronic acid, 0.5 mol% (0.028 g) of catalyst, 1.5 mmol of K₂CO₃ and 5 mL of H₂O at 80 °C, which gave the product in an excellent yield. Furthermore two comparative cross coupling reactions were performed using the same substrates, one in microwave heating and the other in conventional heating using oil bath at 100 °C to find the best reaction condition. It was observed that reactions performed under microwave heating require shorter time and afforded maximum yield as compared to the conventional heating. Taking water as a solvent we got very high yield of products, therefore, studies of the reactions in other solvents was excluded.

**Table 3.1:** Optimization of the reaction conditions for the Suzuki cross-coupling reaction of 2-bromobenzaldehyde with phenylboronic acid

\[
\text{BrCHO} + \text{B(OH)₂} \xrightarrow{\text{Pd(0)NPs@cellulose, H₂O, Base, MW}} \text{OHC}
\]

\(\text{1a}\)
Entry | Catalyst | catalyst Loading | Base (1.5mmol) | Temp(°C)/Time(min) | Yield (%)
--- | --- | --- | --- | --- | ---
1 | ........... | ........... | K₂CO₃ | 100/10 | 0
2 | PdCl₂ | 0.05 mmol | K₂CO₃ | 100/15 | 25
3 | Pd(0)NPs | 0.5 mol% | K₂CO₃ | 80/5 | 94
4 | Pd(0)NPs | 0.3 mol% | K₂CO₃ | 100/5 | 82
5 | Pd(0)NPs | 1.0 mol% | K₂CO₃ | 100/15 | 94
6 | Pd(0)NPs | 0.5 mol% | K₂CO₃ | 140/15 | 94
7 | Pd(0)NPs | 0.5 mol% | NaOH | 100/5 | 20
8 | Pd(0)NPs | 0.5 mol% | Et₃N | 100/5 | 40
9 | Pd(0)NPs | 0.5 mol% | NaOAc | 100/5 | 20
10 | Pd(0)NPs | 0.5 mol% | Cs₂CO₃ | 100/5 | 68

*Reaction conditions: 2-bromobenzaldehyde (0.5 mmol), phenylboronic acid (0.75 mmol), Pd(0) NPs@cellulose (0.5 mol%), K₂CO₃ (1.5 mmol), H₂O (5 mL), 80 °C, microwave. The reaction was monitored by TLC. *Isolated yield.

After optimization of reaction conditions, we explored the scope and limitations of this protocol towards the coupling reactions. As illustrated in table 3.2, it was subsequently extended to a wide range of substituted aryl bromides and phenylboronic acids as substrates for Suzuki cross coupling reaction. In general, all the reactions gave excellent yields of
coupling product under microwave heating. However, arylbromides containing electron withdrawing groups as substrates gave slightly more yields (1a, 1c; table 3.2) as compared to the electron donating counterparts. This protocol was found to be well tolerated toward the hetero aryl bromides (1e, 1i) and ortho substituted aryl bromide (1a, 1g, 1h, 1j, 1k; table 3.2) as substrates. Overall, steric and electronic factors of the substrates do not affect significantly on the yield of the products because of the high catalytic activity of Pd(0) NPs@cellulose system.

Table 3.2: Suzuki cross-coupling reaction between phenylboronic acid and substituted arylbromides under microwave heating

\[ \text{B(OH)}_2 + \text{Br} \rightarrow \text{0.5 mol\% Pd(0)Nps@ cellulose} \rightarrow \text{H}_2\text{O, K}_2\text{CO}_3, \text{MW, 80 °C, 5-10 min} \]

<table>
<thead>
<tr>
<th>R¹</th>
<th>R²</th>
<th>Yield (%)</th>
</tr>
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<tbody>
<tr>
<td>H</td>
<td>R²</td>
<td>1a, 94⁺b</td>
</tr>
<tr>
<td>OHC</td>
<td>R²</td>
<td>1b, 92⁺b</td>
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<tr>
<td>R²</td>
<td>NO₂</td>
<td>1c, 93⁺b</td>
</tr>
<tr>
<td>R²</td>
<td></td>
<td>1d, 84⁺b</td>
</tr>
<tr>
<td>R²</td>
<td>N</td>
<td>1e, 88⁺b</td>
</tr>
<tr>
<td>R²</td>
<td>Br</td>
<td>1f, 82⁺b</td>
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<tr>
<td>R²</td>
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<td>1g, 85⁺b</td>
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<tr>
<td>R²</td>
<td>OMe</td>
<td>1h, 84⁺b</td>
</tr>
</tbody>
</table>
Next, we tried to study the homocoupling reactions of arylboronic acids, table 3.3. It was observed that Pd(0) NPs@cellulose system efficiently catalyzes the homocoupling reaction with high yield percentage of desired product regardless of the nature of boronic acids under microwave heating (2a-2d; table 3.3). In homocoupling reaction the requirement of time as well as temperature is somewhat less than the cross coupling reactions. All the products were well characterized by the comparison of their physical characteristics (TLC Rf value and melting point) and spectral data (\(^{1}\text{H} \& \^{13}\text{C} \text{NMR}) with those of the authentic samples.

Table 3.3: Pd(0) mediated Suzuki homocoupling reaction of phenyl boronic acids\(^{a}\)
Synthesis, characterization and application of cellulose supported Pd (0)-nanoparticles

Reactions conditions: arylbromide (1.0 mmol), Pd(0) NPs@cellulose (0.5 mol%), K$_2$CO$_3$ (1.5 mmol), H$_2$O (5 mL), 60 °C, microwave. The reactions were monitored by TLC. *Isolated yield.

We investigated the catalytic activity of Pd(0)NPs@cellulose towards the Heck reaction (Table 3.4). 15-20 minutes time is required for successful completion of all Heck reactions under study. To find the optimized reaction condition we used iodobenzene (0.5 mmol) and methyl acrylate (1.0 mmol) as substrates. Regardless of the substituents present in arylbenzenes and alkenes (3a-3d, Table 3.4), the catalyst effectively catalyzed the Heck coupling reactions with excellent yields in aqueous media under microwave heating.

**Table 3.4:** Heck reaction of aryl halides and olefins under microwave heating catalyzed by Pd(0)NPs@cellulose
aReaction conditions: arylhalides (0.5 mmol), alkene (0.75 mmol), Pd(0) NPs@cellulose (0.5 mol%), K₂CO₃ (1.5 mmol), H₂O (5 mL), 80 °C, microwave. The reactions were monitored by TLC.

bIsolated yield. cReaction time is 15 minutes. dReaction time is 20 minutes. eIodobenzene as a substrate. fSubstituted bromobenzene as a substrate.

3.2.2.2. Reusability study of Pd(0) NPs@cellulose

The reusability of Pd(0) NPs@cellulose catalyst was investigated by using the Suzuki cross-coupling reaction between phenyl boronic acid and 2-bromobenzaldehyde under the above mentioned optimized conditions in microwave heating. After completion of the reaction the catalyst was separated from the mixture by simple filtration, washing it with H₂O and acetone alternatively and finally vacuum dried. Then it was reused directly for the next cycle without any further treatment. This experiment showed that our catalyst can be recycled up to ten times without major loss of yield of product. At the end of the 5th and 10th run we were able to collect 89% and 71% yield of the product respectively (table 3.5).

Table 3.5: Reusability of Pd(0) NPs@cellulose in the Suzuki cross-coupling reaction of 2-bromobenzaldehyde and phenyl boronic acid under microwave heating a
Chapter-3  Synthesis, characterization and application of cellulose supported Pd (0)-nanoparticles

*aReaction conditions: arylbromides (0.5 mmol), phenylboronic acid (0.75 mmol), Pd(0) NPs@cellulose (0.5 mol%), K$_2$CO$_3$ (1.5 mmol), H$_2$O (5 mL), 80 °C, microwave. bIsolated yield.

The recovered catalyst (after 5$^{th}$ run) was further investigated by powder XRD and TEM studies (Fig. 3.5). The appearance of low intensity peaks as compared to the fresh one may indicates the aggregation and leaching of Pd(0) NPs in the surface of cellulose. Due to these combined effects of aggregation and leaching reduction of catalytic activity was observed after multiple runs. The catalyst can also be reusable in Heck reactions.

![Fig. 3.5: The powder XRD pattern and TEM image of recovered catalyst.](image)

3.2.3. Conclusion

Pd(0) NPs@cellulose exhibit versatile catalytic activity towards the Suzuki and Heck reactions in water under microwave heating with very high product yield. The main advantages of this environmentally benign protocol are such as ease of catalyst preparation, ease of work up procedure, high catalytic activity, stability, reusability up-to ten times
without measurable Pd leaching etc. Pd(0) NPs@cellulose may be regarded as a phosphine free very effective alternative for Suzuki and Heck reaction considering the green chemistry point of view.

### 3.2.4. Experimental

#### 3.2.4.1. General procedure for Suzuki coupling using Pd(0) NPs@cellulose under microwave heating

In a 10 mL microwave glass vial 0.5 mol% (0.028 g) Pd(0)NPs@cellulose, 0.5 mmol arylbromides, 0.75 mmol phenylboronic acid and 1.5 mmol K$_2$CO$_3$ were mixed in 5 mL water. The mixture was stirred at 80 °C for the stipulated time in microwave. After completion of the reaction [monitored by TLC], the catalyst was filtered off and washed with acetone and stored for further reactions. The filtrate was concentrated and then extracted with ethyl acetate (2 × 20 mL). The organic layer was washed with water (2 × 10 mL) and brine (15 mL), dried over anhydrous Na$_2$SO$_4$, concentrated, and purified by column chromatography.

#### 3.2.4.2. General procedure for Heck coupling using Pd(0) NPs@cellulose under microwave heating

0.5 mol% (0.028 g) Pd(0)NPs@cellulose, 0.5 mmol arylbromides, 1.0 mmol alkene (e.g. methyl acrylate) and 1.5 mmol K$_2$CO$_3$ were mixed in 5 mL water in a 10 mL microwave glass vial and heated under microwave for stipulated time period. Progress of the reaction was monitored by TLC. After completion of the reaction, the catalyst was filtered off and washed with acetone. The filtrate was concentrated and then extracted with
ethyl acetate (2 × 20 mL). The organic layer was washed with water (2 × 10 mL) and brine (15 mL), dried over anhydrous Na₂SO₄, concentrated, and purified by column chromatography.

3.2.5. Characterization data of synthesized compounds

Biphenyl-2-carbaldehyde (1a, table 3.2): ¹H NMR (500 MHz, CDCl₃, TMS): δ 10.02 (s, 1H), 8.06 (d, J = 10 Hz, 1H), 7.69-7.52 (t, J = 10 Hz), 7.55-7.36 (m, 7H), ppm; ¹³C NMR (125 MHz, CDCl₃): δ 192.4, 145.8, 137.6, 133.6, 133.5, 130.7, 130, 128.3, 128.0, 12.7, 127.5.

Biphenyl (1b, table 3.2): ¹H NMR (500 MHz, CDCl₃, TMS): δ 7.70-7.27 (m, 10H), ppm; ¹³C NMR (125 MHz, CDCl₃): δ 141.1, 128.7, 127.2, 127.1

4-Nitro-biphenyl (1c, table 3.2): ¹H NMR (500 MHz, CDCl₃, TMS): δ 8.32 (d, J = 8.5 Hz, 2H), 7.76 (d, J = 8.6 Hz, 2H), 7.72 (d, J = 8.6 Hz, 2H), 7.53-7.40 (m, 3H), ppm; ¹³C NMR (125 MHz, CDCl₃): δ 147.5, 146.9, 138.7, 129, 128.8, 127.7, 127.3, 124.2

1-Biphenyl-4-yl-ethanone (1d, table 3.2): ¹H NMR (500 MHz, CDCl₃, TMS): δ 8.06 (d, J = 7 Hz, 2H), 7.72 (d, J = 7.5 Hz, 2H), 7.66 (d, J = 8 Hz, 2H), 7.52-7.42 (m, 3H), 2.66 (s, 3H), ppm; ¹³C NMR (125 MHz, CDCl₃): δ 197.7, 145.7, 139.8, 135.7, 128.9, 128.8, 128.1, 127.2, 127.1, 26.6

2-Phenyl-pyridine (1e, table 3.2): ¹H NMR (500 MHz, CDCl₃, TMS): δ 8.7 (d, J = 4.4Hz, 1H), 8.4 (d, J = 5 Hz, 2H), 7.86-7.81 (m, 2H), 7.35-7.25 (m, 4H), ppm.
4''-Bromo-[1, 1', 4', 1''] terphenyl (1f, table 3.2): $^1$H NMR (500 MHz, CDCl$_3$, TMS):
$\delta$ 7.71 (d, $J$ = 5 Hz, 2H), 7.66 (d, $J$ = 5 Hz, 4H), 7.61 (d, $J$ = 10 Hz, 2H), 7.53 (d, $J$ = 5 Hz, 2H), 7.49 (t, 2H), 7.41 (t, 1H), ppm; $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 141.5, 140.5, 131.8, 128.8, 128.5, 127.5, 126.9, 121

2-Methyl-1-phenyl-naphthalene (1g, table 3.2): $^1$H NMR (500 MHz, CDCl$_3$, TMS):
$\delta$ 7.87 (d, $J$ = 10 Hz, 1H), 7.82 (d, $J$ = 10 Hz, 1H), 7.55-7.48 (m, 2H), 7.46-7.41 (m, 4H), 7.37-7.30 (m, 3H), 2.28 (s, 3H), ppm; $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 139.7, 138, 133, 132.8, 130.1, 130, 128.5, 128.3, 127.9, 127.1, 126.9, 126, 125.7, 124.6, 20.7

1-(4-Methoxy-phenyl)-2-methyl-naphthalene (1h, table 3.2): $^1$H NMR (500 MHz, CDCl$_3$, TMS): $\delta$ 7.87 (d, $J$ = 8 Hz, 1H), 7.81 (d, $J$ = 8.5 Hz, 1H), 7.50-7.36 (m, 4H), 7.24 (d, $J$ = 10 Hz, 2H), 7.08 (d, $J$ = 5 Hz, 2H), 3.93 (s, 3H), 2.30 (s, 3H), ppm; $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 158.5, 137.7, 133.4, 133.2, 131.8, 131.1, 128.5, 127.6, 126.9, 126.1, 125.6, 124.6, 113.6, 55.2, 20.8

2-(4-Methoxy-phenyl)-pyridine (1i, table 3.2): $^1$H NMR (500 MHz, CDCl$_3$, TMS): $\delta$ 8.66 (s, 1H), 7.96 (d, $J$ = 5 Hz, 2H), 7.74-7.67 (m, 2H), 7.19 (t, 1H), 7.02 (d, $J$ = 5 Hz), 3.88 (s, 3H), ppm; $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 160.3, 157, 149.4, 136.6, 131.9, 128, 127.3, 119.7, 114, 55.2

1-(4-Ethyl-phenyl)-2-methyl-naphthalene (1j, table 3.2): $^1$H NMR (500 MHz, CDCl$_3$, TMS): $\delta$ 7.87 (d, $J$ = 10 Hz, 1H), 7.81 (d, $J$ = 10 Hz, 1H), 7.49-7.42 (m, 4H), 7.37 (d, $J$ = 10 Hz, 2H), 7.22 (d, $J$ = 5 Hz, 2H), 2.84-2.76 (m, 2H), 2.29 (s, 3H), 1.39 (s, 3H), ppm; $^{13}$C
NMR (125 MHz, CDCl\textsubscript{3}): δ 142.7, 138.1, 136.8, 133.1, 131.8, 130, 128.5, 128.1, 127.7, 127.0, 126.1, 125.5, 124.8, 124.4, 28.5, 20.7, 15.4

**2-Methyl-1-o-tolyl naphthalene (1k, table 3.2):** \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}, TMS): δ 7.87 (d, J = 5 Hz, 1H), 7.81 (d, J = 5 Hz, 1H), 7.47-7.15 (m, 8H), 2.19 (s, 3H), 1.95 (s, 3H), ppm; \textsuperscript{13}C NMR (125 MHz, CDCl\textsubscript{3}): δ 139, 137.3, 136.7, 132.9, 132.4, 131.8, 130.2, 129.9, 129.7, 128.4, 127.9, 127.3, 126.9, 125.8, 125.4, 124.3, 20.2, 19.4

**4, 4’-Dimethoxy biphenyl (2a, table 3.3):** \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}, TMS): δ 7.50 (d, J = 4.5Hz, 4H), 6.98 (d, J = 5 Hz, 4H), 3.87 (s, 6H), ppm; \textsuperscript{13}C NMR (125 MHz, CDCl\textsubscript{3}): δ 158.5, 133.3, 127.6, 144, 55.2

**3, 3’-Dimethyl-biphenyl (2b, table 3.3):** \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}, TMS): δ 7.40 (d, J = 5 Hz, 2H), 7.31 (t, J = 7.5 Hz, 2H), 7.26 (s, 2H), 7.15 (d, J = 7.5 Hz, 2H), 2.42(s, 6H), ppm; \textsuperscript{13}C NMR (125 MHz, CDCl\textsubscript{3}): δ 141.2, 138.1, 128.4, 127.8, 124.1, 21.4

**4, 4’-Dibromo-biphenyl (2c, table 3.3):** \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}, TMS): δ 7.59 (d, J = 10 Hz, 4H), 7.43 (d, J = 5 Hz, 4H), ppm; \textsuperscript{13}C NMR (125 MHz, CDCl\textsubscript{3}): δ 138.7, 131.9, 128.4, 121.8

**4, 4’-Diethyl-biphenyl (2d, table 3.3):** \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}, TMS): δ 7.55 (d, J = 5 Hz, 4H), 7.30 (d, J = 10 Hz, 4H), 2.72 (q, 4H), 1.33-1.29 (t, 6H), ppm; \textsuperscript{13}C NMR (125 MHz, CDCl\textsubscript{3}): δ 142.9, 138.4, 128.1, 126.8, 28.3, 15.5

**3-Phenyl-acrylic acid methyl ester (3a, table 3.4):** \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}, TMS): δ 7.78 (d, J = 16 Hz, 1H), 7.50 (d, J = 5 Hz, 2H), 7.36 (t, J = 4 Hz, 3H), 6.43 (d, J = 16 Hz,
3-(4-Nitro-phenyl)-acrylic acid methyl ester (3b, table 3.4): $^1$H NMR (500 MHz, CDCl$_3$, TMS): δ 8.25 (d, $J = 8.5$ Hz, 2H), 7.74-2.65 (m, 3H), 6.56 (d, $J = 16$ Hz, 1H), 3.84 (s, 3H), ppm.

3-(2-Formyl-phenyl)-acrylic acid methyl ester (3c, table 3.4): $^1$H NMR (500 MHz, CDCl$_3$, TMS): δ 10.29 (s, 1H), 8.53 (d, $J = 15.5$ Hz, 1H), 7.88 (d, $J = 5$ Hz, 1H), 7.64-7.56 (m, 3H), 6.38 (d, $J = 16$Hz, 1H), 3.83 (s, 3H), ppm.

3-Phenyl-acrylonitrile (3d, table 3.4): $^1$H NMR (500 MHz, CDCl$_3$, TMS): δ 7.54-7.41 (m, 6H), 5.91 (d, $J = 15$ Hz, 1H), ppm.

3.2.6. References


3.2.7. NMR ($^1$H & $^{13}$C) spectra of selected products

Biphenyl-2-carbaldehyde, 1a, table 3.2
1-(4-Methoxy-phenyl)-2-methyl-naphthalene, 1h, table 3.2
Chapter 3  
Synthesis, characterization and application of cellulose supported Pd (0)-nanoparticles

4, 4'-Diethyl-biphenyl, 2d, table 3.3
3-Phenyl-acrylic acid methyl ester, 3a, table 3.4