Chapter 3

Studies on dual role of water extract of agro-waste ash in Pd-catalyzed C_{sp2}-C_{sp2} and C_{sp2}-C_{sp} bond forming reaction

This chapter is composed of two sections, illustrated the dual characteristics of water extract of agro waste ash in palladium catalyzed Suzuki-Miyaura and Sonogashira cross-coupling reaction.

3.0. Introduction

Over the past two decades, scientific community has paid attention towards "Green Chemistry" or "Sustainable Technology", which can protect environment and human health in an economically safer way [1]. It focuses on the design, manufacture and use of chemicals and processes that have little (or no) environmental or economical threat [2]. In this quest the use of solvents remains a constant source of concern, as it give rise to toxicity, pollution and waste treatment issues. Solvents play a significant role in chemical reactions as it provides flexible communication between the reactants, intermediates and often prevents degradation of thermally sensitive reactants and products [3]. Moreover, its appropriate choice allows controlling the reaction rates, selectivity and position of equilibrium in a large number of reactions. Thus, solvents provide greatest opportunity to lower the environmental pollution and to substitute the classical VOCs based methodologies with novel green and cleaner non-conventional alternatives. Biomass derived solvents such as glycerol, 2-methyltetrahydrofuran, cyrene etc. as discussed earlier in first chapter, serves to be an attractive alternative compared to traditional solvents. They provide superior performance in terms of catalytic activity, selectivity, stability and reusability. Recently, a novel type of solvent developed from agro-waste had demonstrated their potential as green solvent for the design of sustainable processes in catalysis and organic synthesis. Sarma *et al.* established a green solvent system using ash water extract of banana peel and rice straw (WEB and WERSA) and its potential was investigated in Suzuki-Miyaura cross-coupling reaction. Moreover, these solvent system (WEB and WERSA) provides an *in situ* basic medium in the cross-coupling reaction [4,5]. Since base plays a crucial role during the transmetalation step of the cross-coupling reactions, the use of natural base is elegant for the C-C cross-coupling reaction. Again this methodology excludes the use of ligand assisting catalytic systems generally used for C-C coupling reactions. Thus, in pursuance to the principle of green chemistry, and with the aim to minimize the chemical waste, in this chapter, we decided to study in detail the use of water extract of agro-waste ash in Suzuki-Miyaura and Sonogashira cross-coupling reaction. Considering the economic view point and accessibility of the natural sources, different agro-waste sources were utilized as a reaction medium without using external basic source.

Section 3.1

Analysis of water extract of papaya bark ash and its application as in situ base in ligand-free Suzuki-Miyaura and Sonogashira cross-coupling reaction

Abstract: In this section, we have reported an efficient Suzuki-Miyaura and Sonogashira cross-coupling reaction using water extract of papaya bark ash (WEPBA) as base as well as reaction medium. The system develops an environmentally friendly *in situ* basic condition which in presence of Pd(OAc)$_2$ provides excellent cross-coupling under mild reaction condition.

3.1.1. Outline

C-C bonds are important structural framework for synthesis of complex organic moieties. From the literature studies it is seen that, exercise of "ligand-free" catalytic system with moderate basicity and wide compatibility has become a prime necessity for the current manufacturing processes [6-9]. Consequently, in this section, we have developed a green agro-waste based reaction medium from water extract of dead papaya bark ash (WEPBA) that is thrown to rot/deteriorate and its significance was studied in ligand-free palladium catalyzed Suzuki-Miyaura and Sonogashira coupling reaction. In Suzuki-Miyaura coupling reactions, base plays a crucial role in activating the organoboron reagents. However, in some cases, added base causes protodeboronation of electron-deficient aryl boronic acids [10,11]. So, the use of mild and naturally developed base in this respect serves to be an excellent alternative for the said coupling reaction. In Sonogashira coupling, base assists in deprotonation by activating the C-H bond of the terminal alkyne. In absence of copper co-catalyst, the choice of a highly active suitable base is important for the efficient C_{sp2}-C_{sp} cross-coupling reaction.

The use of pure water as reaction medium often fails to furnish maximum efficiency due to non-polarity and hydrophobic nature of most of the reaction substrates [12]. The use of aqueous system helps in dissolution of organic substrates and assists in the stabilization of the metal catalytic system. As such in this work we have used WEPBA/EtOH as reaction medium in presence of $Pd(OAc)_2$ for the coupling of aryl halide and aryl boronic acid/terminal acetylene without using conventional base. Since the reaction was performed under ligand-free catalytic system, we have studied the effect of reduction of Pd(II) salt to Pd(0) and detailed characteristics of WEPBA were studied by various characterization techniques such as Energy-dispersive X-ray spectroscopy (EDX), Ion chromatography (IC) and Flame photometry analysis. The isolated coupling products were confirmed by ^{1}H and ^{13}C NMR spectroscopy.

3.1.2. Experimental

3.1.2.1. Procedure for preparation of WEPBA

At the onset, a dead papaya bark was collected and chopped into few pieces. It was then dried in oven and burnt into its ashes. Thereafter, 10 g of the papaya bark ash was suspended in 100 mL distilled water in a beaker and stirred well for half hour at room temperature. The suspension was then filtered through a sintered glass crucible and a light yellow coloured extract was obtained which was used as WEPBA (Figure. 3.1.1)
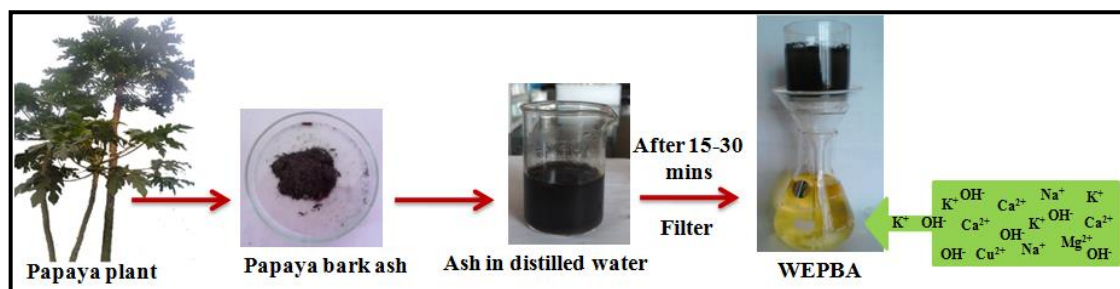
Figure 3.1.1: Preparation of WEPBA.

3.1.2.2. General procedure for Suzuki-Miyaura cross-coupling reaction

A mixture of aryl bromide (0.5 mmol), aryl boronic acid (0.6 mmol), Pd(OAc)$_2$ (0.5 mol%), WEPBA (2 mL) and EtOH (2 mL) was stirred at room temperature in a 50 mL round bottom flask. After completion (vide TLC); the reaction mixture was extracted with ethyl acetate (3×10 mL) and the combined organic layer was washed with brine (2×10 mL), dried over Na$_2$SO$_4$ and concentrated in vacuo. The residue was purified by column chromatography on silica gel [Eluent: EtOAc-Hexane (1:9)] to give the corresponding biaryl compound. The desired products are characterized by comparing ^{1}H and ^{13}C NMR with authentic samples.

For recycling experiment, the reaction mixture after the first cycle, was extracted with ethyl acetate (2×10 mL) and the separated organic fraction has been removed from the system and evaporated to get the crude product. The remaining aqueous portion was centrifuged and the residue was washed with EtOH and then directly used for the next reaction cycle followed by addition of fresh reactants, WEPBA and EtOH.

### 3.1.2.3. General procedure for Sonogashira cross-coupling reaction

A mixture of aryl halide (1 mmol), terminal acetylene (1.5 mmol) and Pd(OAc)$_2$ (1 mol%) was mixed in WEPBA/EtOH (1:1) (8 mL) and stirred for the required time at room temperature. After completion of the reaction (vide TLC), the mixture was extracted with ethyl acetate (3×10 mL). The products were purified by column chromatography over silica gel using n-hexane as eluent to obtain the desired pure products. The products were characterized by ^{1}H and ^{13}C NMR spectroscopy.

3.1.3. Results and Discussion

3.1.3.1. Analysis of water-extract (WEPBA)

The alkaline nature (pH) of WEPBA was first investigated by performing litmus test and using pH meter, it was found to be around 12. In order to reveal this basicity of

WEPBA, at first EDX analysis of the papaya bark ash was performed (Figure 3.1.2 a). The report reveals a very high distribution of the O, Na, Mg, K and Ca. It is believed that oxides of sodium, potassium, magnesium and calcium on reaction with water produce its corresponding hydroxides. From this, we can assume that these alkali or alkaline earth metals present in papaya bark ash might form its hydroxides in water and act as internal bases which participate in the cross coupling reactions.
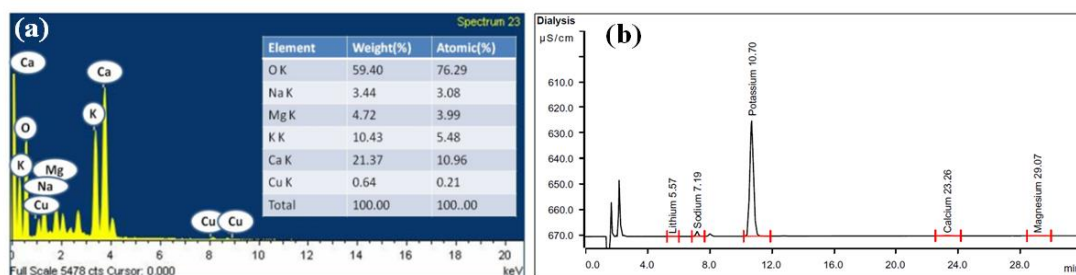
Figure 3.1.2: **(a)** EDX spectrum of papaya bark ash **(b)** IEC analysis of WEPBA.

For further confirmation of the presence of these metals in the water extract, we have performed Ion Exchange Chromatography (IEC) Figure 3.1.2 b, and Flame Photometry (FP). The metal ion concentration obtained from both the analysis (IEC and FP) were summarized in Table 3.1.1. A high distribution of K^+ and Na^+ ion with a moderate concentration of Ca^{2+} ion was observed from both the analysis. Thus, the presence of these alkali and alkaline metal ions validates the basic nature of the WEPBA system.

Table 3.1.1: Metal contents (in ppm) in WEPBA through Flame Photometry (FP) and Ion-Exchange Chromatography (IEC)

Entry	Metal	Metal Concentration (FP)	Metal Concentrationc(IEC)
1	K	1876.24	2042.95
2	Ca	6.812	6.76
3	Na	21.98	27.24
4	Li	Trace	Trace
5	Mg	Trace	Trace

3.1.3.2. Optimization of catalytic system for Suzuki-Miyaura coupling reaction

The effectiveness of WEPBA in Suzuki-Miyaura cross-coupling was investigated using 4-bromonitrobenzene (0.5 mmol) and phenylboronic acid (0.6 mmol) as model substrate with Pd(OAc)$_2$ (1 mol%). The results are summarized in Table 3.1.2. Initially, the reaction was performed using Pd(OAc)$_2$ (1 mol%) with WEPBA (3 mL) at room

temperature. We were able to isolate 80 % of the cross-coupling product (Table 3.1.2, entry 1). The formation of biaryl product was confirmed by its ^{1}H and ^{13}C NMR data. In ^{1}H NMR, a doublet peak at δ 8.29 ppm corresponds to 2H, is due to the presence of adjacent –NO$_2$ group and peak in the range 7.73 (d, 2H), 7.62-7.60 (m, 2H), 7.50-7.43 (m, 3H) ppm corresponds to other aromatic ring protons. The structure was further supported by its ^{13}C NMR spectra with peaks in the range δ 147.7, 138.8, 129.2, 129.0, 128.9, 127.9, 127.4, 124.2 ppm.

Table 3.1.2: Screening of Pd(OAc)$_2$/WEPBA for Suzuki-Miyaura cross-coupling [a]

Entry	Pd(OAc)$_2$ (mol%)	WEPBA (mL)	EtOH (mL)	Time(min)	Yield(%)[b]
1	1	3	-	60	80
2	1	5	-	60	80
3	1	-	3	360	nr [c]
4	1	2	2	5	98
5	1	3	1	30	85
6	1	3	2	7	94
7	0.5	2	2	7	97
8	0.25	2	2	30	30
9	0.5	2	2	360	30 [d]

[a] Reaction conditions: 4-bromonitrobenzene (0.5 mmol), phenylboronic acid (0.6 mmol), [b] Isolated yields; [c] Without extract; [d] Water extract after diluted

In view of this result, we opted for further optimization of reaction condition for Suzuki-Miyaura coupling reaction. On increasing the amount of WEPBA, no further increase in yield was noticed (Table 3.1.2, entry 2). Since Suzuki-Miyaura coupling is highly dependent on base and to reveal the role of the WEPBA in this reaction, we have performed the reaction in pure water without using the extract, but no reaction was observed even after 6 h (Table 3.1.2, entry 3). Considering the effect of co-solvent as reported in literature [13,14], the reaction was done using EtOH and WEPBA in 1:1 ratio. We were able to isolate 98 % coupling product within 5 minutes (Table 3.1.2, entry 4). The improved result on using alcoholic co-solvent may be due to the enhanced solubility of the substrates. Upon revising the ratio of ethanol and WEPBA, no appreciable improvement in the yield and reaction time was noticed (Table 3.1.2, entries 5 and 6).The reaction was optimized for different amount of Pd(OAc)$_2$ and it was found that the cross-coupling proceeds efficiently with 0.5 mol% Pd(OAc)$_2$. On further

lowering the amount of catalyst, the reaction does not provide appreciable conversion (Table 3.1.2, entries 7 and 8). To verify the basic strength of WEPBA, we performed the reaction by diluting it with equal volume of water (i.e. 2 mL pure WEPBA was diluted with 2 mL water and then 2 mL of diluted mixture was used for the reaction), but no satisfactory result was observed. This may be due the decrease in basic strength of the WEPBA on further dilution (Table 3.1.2, entry 9).

Han and co-workers have presented a strong evidence for the existence of interactions between the salt particle with palladium and aryl halide [15]. These interactions were found significant for the synergistic effect between the salts and the catalyst which enhance the rate of reaction. Thus, as an additional effect, the alkali and alkaline earth metal ions present in WEPBA contribute a synergistic interaction with the catalyst and reactant which as a result enhance the rate of reaction. We have also seen some earlier report where various salt additives such as sodium sulfate, sodium chloride and sodium acetate were used in Pd-catalyzed ligand free Suzuki-Miyaura reaction [16]. Literature reports reveal that in many Pd(II) salt catalyzed reactions, Pd(II) species decomposes to Pd nanoparticles (NPs) at the end of reaction cycle [17,18]. Considering this, we further investigated the role of the WEPBA-EtOH system during the reaction. TEM analysis of the reaction mixture after the completion indicated the formation of homogeneous palladium nanoparticles (Pd NPs) with spherical aggregate structures having average particle size of 10-20 nm (Figure 3.1.3).
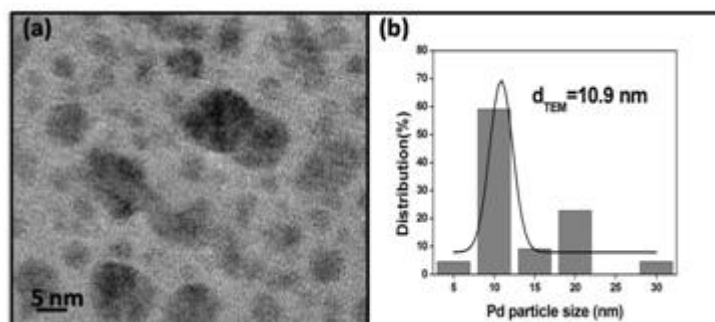
Figure 3.1.3: **(a)** TEM image of Pd NPs and **(b)** Pd NPs distribution.

3.1.3.3. Substrate scope for Suzuki-Miyaura coupling reaction

With this optimized conditions, we further studied the scope and limitation of the WEPBA/Pd(OAc)$_2$ system for Suzuki-Miyaura coupling of diverse range of aryl bromides and aryl boronic acids (Table 3.1.3).

**Table 3.1.3**: Suzuki-Miyaura coupling of aryl bromides and aryl boronic acids using WEPBA/Pd(OAc)$_2$ [a]

$$R^1 \text{—Br} + (HO)_2B\text{—} R^2 \xrightarrow[\text{WEPBA: EtOH, rt}]{\text{Pd(OAc)}_2} R^1 \text{—} R^2$$

Entry	R^1	R^2	Time (min)	Yield (%)[b]
1	4-NO$_2$	H	7	97
2	4-NO$_2$	4-Cl	20	95
3	4-NO$_2$	4-OMe	10	95
4	4-NO$_2$	4-t-Bu	10	98
5	4-OMe	H	5	97
6	2-OMe	H	30	96
7	4-OMe	3-Me	5	97
8	4-OMe	4-Cl	30	92
9	4-OCH$_3$	4-t-Bu	5	98
10	4-CHO	H	7	96
11	4-CHO	Cl	30	96
12	2-Me	H	5	99
13	2-Me	4-OMe	5	96
14	4-COMe	H	5	97
15	4-COMe	4-Cl	40	95
16	4-Me	H	5	99
17	4-OH	H	20	90
18	4-NH$_2$	H	60	85
19	4-COOH	H	24 h	30
20	3-Bromopyridine	H	2 h	85
21	4-Chloro-nitrobenzene	H	24 h	5

[a] Reaction conditions: aryl bromide (0.5 mmol), aryl boronic acid (0.6 mmol), Pd(OAc)$_2$ (0.5 mol%), WEPBA (2 mL), EtOH (2 mL) [b] Isolated yields.

The catalytic system delivers excellent and rapid cross-coupling with both electron-rich and electron-deficient aryl bromides at room temperature (Table 3.1.3, entries 1-17). However, using amines and acid substituted aryl bromides, moderate and low conversion was achieved (Table 3.1.3, entries 18 and 19). The catalytic system delivers high reactivity for coupling of electronically diverse aryl boronic acids (Table 3.1.3, entries 2-15). Noticeable catalytic efficiency was observed with 3-bromopyridine and phenylboronic acid (Table 3.1.3, entry 20). The catalytic activity of WEPBA/Pd(OAc)$_2$ system was investigated for aryl chlorides, but almost negligible conversion of cross-coupled product was observed (Table 3.1.3, entry 21).

3.1.3.4. Reusability for Suzuki-Miyaura coupling reaction

Since the major challenge of a catalytic system is its ability to reuse, we next investigated the recyclability of WEPBA/Pd(OAc)$_2$ system using 4-bromonitrobenzene (1 mmol) and phenylboronic acid (1.2 mmol) as coupling partners using the standard optimized conditions (Table 3.1.2, entry 7) (Figure 3.1.4). It was seen that the efficiency of WEPBA/Pd(OAc)$_2$ system for Suzuki-Miyaura coupling reactions was retained for five consecutive cycles and only minor loss of its catalytic activity was observed.
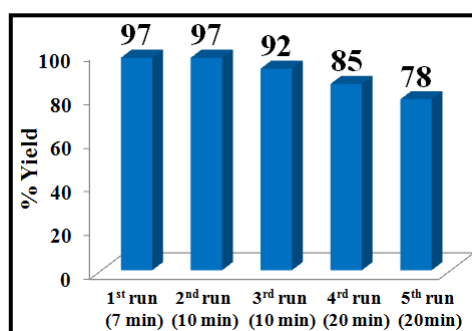
Figure 3.1.4: Reusability of WEPBA/Pd(OAc)$_2$ in Suzuki-Miyaura coupling.

The activity of WEPBA/Pd(OAc)$_2$ system was further examined in Sonogashira coupling reaction. For the purpose, 4-iodonitrobenzene and phenylacetylene was taken as the model substrates for catalytic optimization without using additional base, ligand or any other additives.

3.1.3.5. Optimization of the catalytic system for Sonogashira coupling reaction

In the initial experiment for coupling of 4-iodonitrobenzene (0.5 mmol) and phenylacetylene (1 mmol), we were able to isolate about 50% of cross-coupling product at room temperature using WEPBA as the only reaction medium (Table 3.1.4, entry 1). Since the insolubility of most of the reactants in water restricts their reaction potential. We then carried out the reaction by using WEPBA and EtOH as co-solvent. Under this reaction conditions, significant improvement was observed with 75% yield of the desired product (Table 3.1.4, entry 2). The formation of the desired product was confirmed by its NMR spectra. ^{1}H NMR spectra corresponds to δ value at 8.22 (d, 2H), 7.68-7.66 (m, 2H,), 7.57-7.55 (m, 2H), 7.40-7.38 (m, 3H) ppm due to aromatic ring proton. Further confirmation was achieved by its ^{13}C NMR data with peaks at δ 94.8 and 87.6 for two acetylene carbon and peaks at δ ppm 147.0, 132.3, 131.9, 130.3, 129.3, 128.6, 123.7, 122.1 due to aromatic ring carbon.
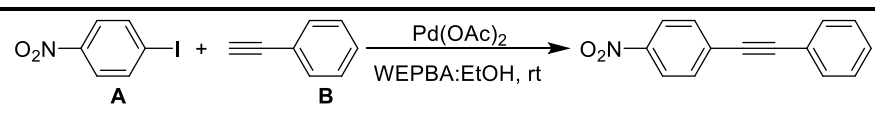
With this view, the reaction was optimized using different ratio of WEPBA/EtOH to obtain greater reaction efficiency (Table 3.1.4, entries 2-5). It has been observed that the ratio of WEPBA/EtOH is very important for the said reaction, since 98% cross-coupling product was obtained with 8 mL of WEPBA and EtOH (1:1) (Table 3.1.4, entry 3). Other alcoholic solvent, *i*-PrOH affords comparable yields of the cross-coupling product (Table 3.1.4, entry 6). In absence of WEPBA, the coupling reaction did not proceeded (Table 3.1.4, entry 7), which signifies its importance in the coupling reaction. It can be seen from Table 3.1.4, entry 8; the WEPBA/EtOH system provides high catalytic activity with other palladium(II) salts such as $PdCl_2$ for the Sonogashira cross-coupling reaction. The effect of the amount of $Pd(OAc)_2$ on the coupling reaction was also studied. Decreasing the catalyst loading to 0.5 mol% gave moderate conversion with 70% isolated yield of the product (Table 3.1.4, entry 9).

Table 3.1.4: Optimization of WEPBA/$Pd(OAc)_2$ for Sonogashira cross-coupling reaction [a]

Entry	Catalyst (mol%)	Co-solvent (mL)	WEPBA (mL)	Time (h)	Yield (%) [b]
1	$Pd(OAc)_2$ (1)	-	4	24	50
2	$Pd(OAc)_2$ (1)	EtOH (2)	4	24	75
3	$Pd(OAc)_2$ (1)	EtOH (4)	4	10	98
4	$Pd(OAc)_2$ (1)	EtOH (2)	2	10	50
5	$Pd(OAc)_2$ (1)	EtOH (3)	3	10	85
6	$Pd(OAc)_2$ (1)	*i*-PrOH (4)	4	10	95
7	$Pd(OAc)_2$ (1)	EtOH (4)	-	24	0
8	$PdCl_2$ (1)	EtOH (4)	4	10	95
9	$Pd(OAc)_2$ (0.5)	EtOH (4)	4	12	70

[a] Reaction conditions: 4-iodonitrobenzene (0.5 mmol), phenylacetylene (1 mmol), [b] Isolated yield

Considering this optimized conditions, we further investigated the substrate ratio, and the favorable condition was observed with 1:1.5 equivalent of 4-iodonitrobenzene to phenylacetylene (Table 3.1.5, entries 1-3). On using 1:1 equivalent of substrate ratio the reaction does not undergo complete conversion as a result of which lower yield of product was observed (Table 3.1.5, entry 1).

Table 3.1.5: Optimization of substrate ratio for Sonogashira cross-coupling reaction [a]

Entry	A:B (mmol)	Time(h)	Yield (%) [b]
1	1:1	12	70
2	1:1.5	10	98
3	1:2	10	98

[a] Reaction conditions: 4-iodonitrobenzene (A mmol), phenylacetylene (B mmol), WEPBA (4 mL), EtOH (4 mL), Pd(OAc)$_2$ (1 mol%).[b] Isolated yields.

3.1.3.6. Substrate scope for Sonogashira coupling reaction

The generality of the Sonogashira coupling was studied for electronically diverse aryl halides and terminal acetylene using the optimized reaction condition. The results are summarized in Table 3.1.6.

The reaction proceeds efficiently for *para-* and *meta-* substituted electron withdrawing aryl halides (Table 3.1.6, entries 2 and 3). However, steric effect results in low conversion as we have seen in case of *o*-nitroiodobenzene (Table 3.1.6, entry 4). Electron-donating aryl iodides such as 4-iodotoluene and 3-iodotoluene provides excellent yield of cross-coupling product (Table 3.1.6, entries 5 and 6). However, 4-iodotoluene gave superior product formation within shorter reaction time. Again, aryl halides bearing methoxy and amine groups gave the coupling products with slightly lower yields (Table 3.1.6, entries 7 and 8). Excellent catalytic activity was observed in case of *p*-tolylphenyl acetylene (Table 3.1.6, entry 9). The reaction also proceeds well with aliphatic alkynes (Table 3.1.6, entries 10-14). However, iodobenzene gave superior product formation with aliphatic alkynes (Table 3.1.6, entries 10, 12 and 14).

We also tried to extend the scope of this WEPBA/Pd(OAc)$_2$ system for coupling of aryl bromides and acetylene. But at room temperature we have observed lower conversion of cross-coupling product. Hence, we perform the reaction at 80°C and we were able to isolate excellent yield of diarylalkyne (Table 3.1.6, entries 15-18). In case of aryl bromide having electron donating substituent *viz.* 4-CH$_3$, good yields of isolated cross coupling products was achieved (Table 3.1.6, entries 16 and 17). However, coupling of *p*-nitrobromobenzene with phenylacetylene renders only 60% product yield (Table 3.1.6, entry 18).

Table 3.1.6: Sonogashira coupling of aryl halides with different terminal acetylenes [a]

Entry	R^1	R^2	X	Time (h)	Yield (%) [b]
1	H	C_6H_5	I	8	98
2	4-NO_2	C_6H_5	I	10	98
3	3-NO_2	C_6H_5	I	12	80
4	2-NO_2	C_6H_5	I	12	30
5	4-CH_3	C_6H_5	I	4	98
6	3-CH_3	C_6H_5	I	12	80
7	4-OCH_3	C_6H_5	I	12	70
8	4-NH_2	C_6H_5	I	12	40
9	4-CH_3	4-CH_3 C_6H_4	I	5	98
10	H	Hexyne	I	10	95
11	4-CH_3	Hexyne	I	12	90
12	H	Cyclohexyl	I	10	85
13	4-CH_3	Cyclohexyl	I	12	65
14	H	Dodecyne	I	12	75
15	H	C_6H_5	Br	8	90 [c]
16	4-CH_3	C_6H_5	Br	8	90 [c]
17	4-CH_3	4-CH_3 C_6H_4	Br	8	80 [c]
18	4-NO_2	C_6H_5	Br	8	60 [c]

[a] Reaction conditions: Aryl halide (1 mmol), phenylacetylene (1.5 mmol), Pd(OAc)$_2$ (1 mol%), WEPBA (4 mL), EtOH (4 mL). [b] Isolated yields. [c] Reaction carried out at 80°C

3.1.4. Conclusions

In summary, we have developed a simple and greener catalytic system for C_{sp2}-C_{sp2} and C_{sp2}-C_{sp} bond forming reaction using an easily accessible and economically viable natural feedstock. The significant features of the present catalytic system are, firstly the C-C cross-coupling proceeds in absence of any ligand assisting system or other co-catalyst or additives. Secondly, the system provides an *in situ* basic character which in addition fulfills the need of solvent for catalysis.

3.1.5. Analytical data of the synthesized biaryl and alkynyl derivatives
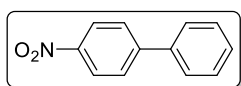
4-Nitrobiphenyl (Table 3.1.3, entry 1): Yellow Solid, m.p. 113-115 °C, **^{1}H NMR (400 MHz, CDCl$_3$):** δ 8.29 (d, 2H, *J* = 8.7 Hz), 7.73 (d, 2H, *J* = 8.7 Hz), 7.63-7.61 (m, 2H), 7.51-7.44 (m, 3H) ppm. **^{13}C NMR (100 MHz, CDCl$_3$):** δ 147.7, 138.8, 129.2, 129.0, 128.9, 127.9, 127.4, 124.2 ppm.
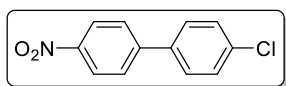
4-Chloro-4′-nitrobiphenyl (Table 3.1.3, entry 2): Pale Yellow Solid, m.p. 142-145 °C, **^{1}H NMR (400 MHz, CDCl$_3$):** δ 8.29 (d, 2H, *J* = 8.7 Hz), 7.70-7.68 (m, 2H), 7.54 (d, 2H, 8.2 Hz), 7.47-7.44 (m, 2H) ppm. **^{13}C NMR (100 MHz, CDCl$_3$):** δ 146.4, 137.2, 135.3, 129.4, 129.0, 128.7, 127.7, 124.3 ppm.
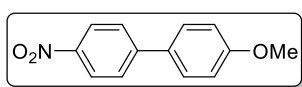
4-Methoxy-4′-nitrobiphenyl (Table 3.1.3, entry 3): Yellow Solid, m.p. 92-94 °C, **^{1}H NMR (400 MHz, CDCl$_3$):** δ 8.26 (d, 2H, *J* = 8.7 Hz), 7.68 (d, 2H, *J* = 8.7 Hz), 7.58-7.55 (m, 2H), 7.00 (d, 2H, *J* = 8.7 Hz), 3.86 (s, 3H) ppm. **^{13}C NMR (100 MHz, CDCl$_3$):** δ 160.5, 147.3, 135.8, 131.1, 128.6, 127.1, 124.2, 114.6, 55.5 ppm.
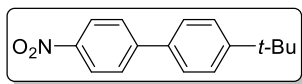
4-Nitro-4′-t-butylbiphenyl (Table 3.1.3, entry 4): Pale yellow Solid, m.p. 110-112 °C, **^{1}H NMR (400 MHz, CDCl$_3$):** 8.27 (d, 2H, *J* = 8.7 Hz), 7.72 (d, 2H, *J* = 8.7 Hz), 7.58-7.49 (m, 4H), 1.36 (s, 9H) ppm. **^{13}C NMR (100 MHz, CDCl$_3$):** δ 152.3, 147.5, 135.8, 132.5, 127.6, 127.1, 126.2, 124.2, 34.8, 31.3 ppm.
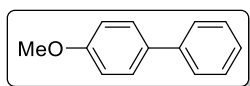
4-Methoxybiphenyl (Table 3.1.3, entry 5): White Solid, m.p. 81-83 °C, **^{1}H NMR (400 MHz, CDCl$_3$):** 7.55-7.51 (m, 3H), 7.42-7.38 (m, 2H), 7.31-7.27 (m, 2H), 6.97 (d, 2H, *J* = 8.7Hz), 3.84 (s, 3H) ppm. **^{13}C NMR (100 MHz, CDCl$_3$):** δ 159.2, 140.9, 133.8, 128.8, 128.2, 126.8, 126.7, 114.2, 55.4 ppm.
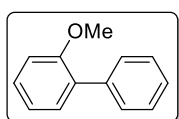
2-Methoxybiphenyl (Table 3.1.3, entry 6): Colourless liquid, **^{1}H NMR (400 MHz, CDCl$_3$):** 7.54 (d, 2H, *J* = 7.3 Hz), 7.43-7.40 (m, 2H), 7.35-7.31 (m, 3H), 7.06-6.98 (m, 2H), 3.81 (s, 3H) ppm. **^{13}C NMR (100 MHz, CDCl$_3$):** δ 156.5, 140.9, 138.6, 131.0, 129.6, 128.7, 128.0, 127.0, 120.9, 111.3, 55.6 ppm.
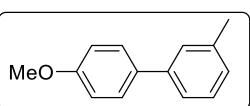
4-Methoxy-3′-methylbiphenyl (Table 3.1.3, entry 7): White Solid, m.p. 48-49 °C, **^{1}H NMR (400 MHz, CDCl$_3$):** 7.50 (d, 2H, *J* = 8.7 Hz), 7.35-7.24 (m, 3H), 7.11 (d, 1H, 7.3 Hz), 6.95 (d, 2H, *J* = 8.7 Hz), 3.84 (s, 3H), 2.39 (s, 3H) ppm. **^{13}C NMR (100 MHz, CDCl$_3$):** δ 159.1, 140.9, 138.3, 133.9, 128.7, 128.2, 127.6, 127.5, 123.9, 114.2, 55.4, 21.6 ppm.
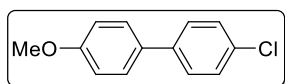
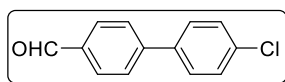**4-Chloro-4′-methoxybiphenyl (Table 3.1.3, entry 8):** White Solid, m.p. 114-116 °C, **¹H NMR (400 MHz, CDCl₃):** δ 7.48-7.44 (m, 4H), 7.36 (d, 2H, *J* = 8.7 Hz), 6.96 (d, 2H, *J* = 8.2 Hz), 3.83 (s, 3H) ppm. **¹³C NMR (100 MHz, CDCl₃):** δ 159.4, 149.7, 139.3, 132.7, 132.5, 128.9, 128.1, 114.3, 55.4 ppm.
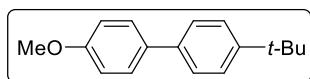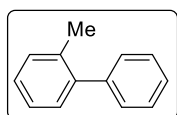
4-Methoxy-4′-t-butylbiphenyl (Table 3.1.3, entry 9): White Solid, m.p. 110-114 °C, **¹H NMR (400 MHz, CDCl₃):** 7.53-7.48 (m, 4H), 7.44 (d, 2H, *J* = 8.7 Hz), 6.98-6.95 (m, 2H), 3.84 (s, 3H), 1.36 (s, 9H) ppm. **¹³C NMR (100 MHz, CDCl₃):** δ 159.0, 149.7, 138.0, 133.7, 128.1, 126.4, 125.7, 114.2, 55.4, 34.5, 31.4 ppm.
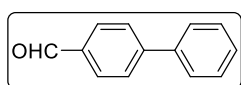
4-Formylbiphenyl (Table 3.1.3, entry 10): White Solid, m.p. 57-59 °C, **¹H NMR (400 MHz, CDCl₃):** δ 10.05 (s, 1H), 7.95 (d, 2H, *J* = 8.2 Hz), 7.74 (d, 2H, *J* = 8.2 Hz), 7.64-7.62 (m, 2H), 7.49-7.39 (m, 3H) ppm. **¹³C NMR (100 MHz, CDCl₃):** δ 192.0, 147.3, 139.8, 135.2, 130.3, 129.1, 128.5, 127.7, 127.4 ppm.

4-Chloro-4′-formylbiphenyl (Table 3.1.3, entry 11): White Solid, m.p. 114-118 °C, **¹H NMR (400 MHz, CDCl₃):** δ 10.05 (s, 1H), 7.94(d, 2H, *J* = 8.2 Hz), 7.70 (d, 2H, *J* = 8.2 Hz), 7.564-7.54 (m, 2H), 7.44 (d, 2H, *J* = 8.7 Hz) ppm. **¹³C NMR (100 MHz, CDCl₃):** δ 191.9, 145.9, 138.2, 135.4, 134.8, 130.4, 128.7, 127.6, 127.4 ppm.

2-Methylbiphenyl (Table 3.1.3, entry 12): Colourless liquid, **¹H NMR (400 MHz, CDCl₃):** 7.61 (d, 2H, *J* = 7.7 Hz), 7.45-7.41 (m, 3H), 7.35-7.24 (m, 4H), 2.29 (s, 3H) ppm. **¹³C NMR (100 MHz, CDCl₃):** δ 142.0, 135.4, 130.4, 129.9, 129.3, 128.8, 128.1, 127.3, 126.8, 125.8, 20.5 ppm.
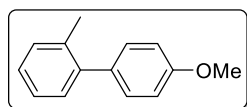
4-Methoxy-2′-methylbiphenyl (Table 3.1.3, entry 13): Colourless liquid, **¹H NMR (400 MHz, CDCl₃):** 7.25-7.21 (m, 6H), 6.94 (d, 2H, *J* = 8.7 Hz), 3.84 (s, 3H), 2.27 (s, 3H) ppm. **¹³C NMR (100 MHz, CDCl₃):** δ 159.1, 140.9, 138.3, 133.9, 128.7, 128.2, 127.6, 127.5, 123.9, 114.2, 55.4, 21.6 ppm.
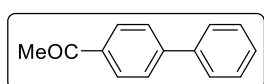
4-Acetylbiphenyl (Table 3.1.3, entry 14): White Solid, m.p. 118-120 °C, **¹H NMR (400 MHz, CDCl₃):** 8.02 (d, 2H, *J* = 8.2 Hz), 7.67 (d, 2H, *J* = 8.2 Hz), 7.62 (d, 2H, *J* = 7.3 Hz), 7.48-7.39 (m, 3H), 2.63 (s, 3H) ppm. **¹³C NMR (100 MHz, CDCl₃):** δ 197.9, 145.8, 139.9, 135.9, 129.0, 128.8, 128.3, 127.3, 127.1, 26.7 ppm.
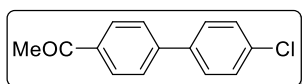
4-Acetyl-4′-chlorobiphenyl (Table 3.1.3, entry 15): White Solid, m.p. 104-106 °C, **^{1}H NMR (400 MHz, CDCl$_3$):** δ 8.01 (d, 2H, *J* = 8.2 Hz), 7.63 (d, 2H, *J* = 8.2 Hz), 7.54 (d, 2H, *J* = 8.7 Hz), 7.42 (d, 2H, *J* = 8.7 Hz), 2.63 (s, 3H) ppm. **^{13}C NMR (100 MHz, CDCl$_3$):** δ 197.7, 144.5, 138.3, 136.1, 134.5, 129.2, 129.0, 128.5, 127.1, 26.7 ppm.
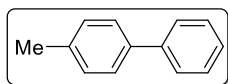
**4-Methylbiphenyl (Table 3.1.3, entry 16):** White Solid, m.p. 46-48 °C, **^{1}H NMR (400 MHz, CDCl$_3$):** 7.58 (d, 2H, *J* = 7.7 Hz), 7.50 (d, 2H, *J* = 7.7 Hz), 7.45-7.41 (m, 2H), 7.35-7.33 (m, 1H) 7.26 (d, 2H, *J* = 8.7 Hz), 2.41 (s, 3H) ppm. **^{13}C NMR (100 MHz, CDCl$_3$):** δ 141.2, 138.4, 137.1, 129.5, 128.8, 127.4, 127.2, 127.0, 21.1 ppm.
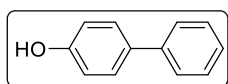
4-Hydroxybiphenyl (Table 3.1.3, entry 17): Light brown Solid, m.p. 164-168 °C, **^{1}H NMR (400 MHz, CDCl$_3$):** 7.54-7.21 (m, 7H), 6.91-6.70 (m, 2H), 5.08 (s, 3H) ppm. **^{13}C NMR (100 MHz, CDCl$_3$):** δ 155.1, 140.8, 132.7, 128.8, 128.5, 126.8, 117.3, 115.7 ppm.
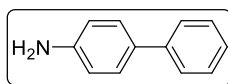
4-Aminobiphenyl (Table 3.1.3, entry 18): Light brown Solid, m.p. 52-54 °C, **^{1}H NMR (400 MHz, CDCl$_3$):** 7.54-7.52 (m, 2H), 7.42-7.37 (m, 3H), 7.24-7.21 (m, 2H), 6.76-6.74 (m, 1H) 6.56-6.54 (m, 1H), 3.67 (s, 3H) ppm. **^{13}C NMR (100 MHz, CDCl$_3$):** δ 145.9, 145.5, 141.2, 132.1, 131.6, 128.7, 128.1, 126.4, 116.8, 115.4 ppm.
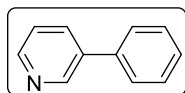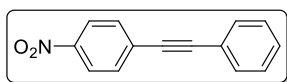
3-Phenylpyridine (Table 3.1.3, entry 20): Colourless liquid, **^{1}H NMR (400 MHz, CDCl$_3$):** δ 8.68 (s, 1H), 8.53-8.51 (m, 3H), 7.86-7.83 (m, 2H), 7.24-7.18 (m, 3H) ppm. **^{13}C NMR (100 MHz, CDCl$_3$):** δ 156.6, 150.6, 147.4, 139.3, 129.6, 125.1, 121.2, 120.1, 115.5 ppm.
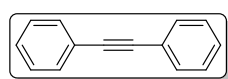
Diphenylacetylene (Table 3.1.6, entry 1): White Solid, m.p. 54-56 °C, **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.56-7.54 (m, 4H), 7.38-7.34 (m, 6H) ppm. **^{13}C NMR (100 MHz, CDCl$_3$):** δ 131.7, 128.4, 128.3, 123.3, 89.4 ppm.

1-Nitro-4-(2-phenylethynyl)benzene (Table 3.1.6, entry 2): Yellow Solid, m.p. 119-121 °C, **^{1}H NMR (400 MHz, CDCl$_3$):** δ 8.22 (d, 2H, *J* = 8.8 Hz), 7.68-7.66 (m, 2H,), 7.57-7.55 (m, 2H), 7.40-7.38 (m, 3H) ppm. **^{13}C NMR (100 MHz, CDCl$_3$):** δ 147.0, 132.3, 131.9, 130.3, 129.3, 128.6, 123.7, 122.1, 94.8, 87.6 ppm.
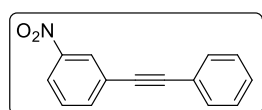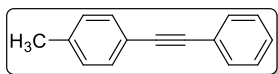
1-Nitro-3-(2-phenylethynyl)benzene (Table 3.1.6, entry 3): Yellow gum, **^{1}H NMR (400 MHz, CDCl$_3$):** δ 8.35 (s, 1H), 8.15

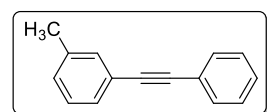(d, 1H, J = 8.2 Hz), 7.80 (d, 1H, J = 7.7 Hz), 7.56-7.48 (m, 3H), 7.38-7.34 (m,3H) ppm. **^{13}C NMR (100 MHz, CDCl$_3$):** δ 148.2, 137.3, 131.8, 129.4, 129.1, 128.6, 126.4, 125.2, 122.9, 122.2, 92.0, 86.9 ppm.

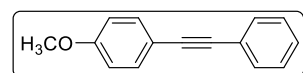**1-Methyl-4-(2-phenylethynyl)benzene (Table 3.1.6, entry 5):** White solid, m.p. 68-70 °C, **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.53-7.50 (m, 2H), 7.42 (d, 2H, J = 7.7 Hz), 7.34-7.31 (m, 3H), 7.15(d, 2H, J = 7.7 Hz), 2.36 (s, 3H) ppm. **^{13}C NMR (100 MHz, CDCl$_3$):** δ 138.5, 132.4, 131.6, 131.2, 129.2, 128.1, 123.5, 120.2, 89.6, 88.8, 21.6 ppm.
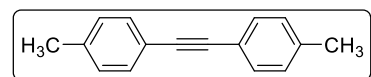
1-Methyl-3-(2-phenylethynyl)benzene (Table 3.1.6, entry 6): Colourless liquid, **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.53-7.51 (m, 2H), 7.36-7.33 (m, 4H), 7.25-7.21(m, 2H), 7.14 (d, 1H, J = 7.3 Hz), 2.35 (s, 3H) ppm. **^{13}C NMR (100 MHz, CDCl$_3$):** δ 138.1, 134.5, 132.6, 131.7, 129.2, 128.8, 128.4, 128.3, 128.2, 123.4, 89.6, 89.1, 21.3 ppm

**1-Methoxy-4-(2-phenylethynyl)benzene (Table 3.1.6, entry 7):** White solid, m.p. 79-81 °C, **^{1}H NMR (400 MHz, CDCl$_3$)**, δ 7.51-7.45 (m, 4H), 7.32-7.30 (m, 3H), 6.86 (d, 2H, J = 8.7 Hz), 3.82 (s, 3H) ppm **^{13}C NMR (100 MHz, CDCl$_3$):** δ 159.7, 133.1, 131.5, 128.4, 128.0, 123.7, 115.4, 114.1, 89.9, 89.4, 55.4 ppm.
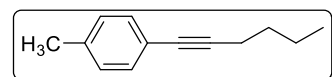
1-Methyl-4-[2-(p-tolyl)ethynyl]benzene (Table 3.1.6, entry 9), White solid, m.p. 126-128 °C, **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.41-7.39 (m, 4H), 7.14-7.12 (m, 4H), 2.35 (s, 6H) ppm. **^{13}C NMR (100 MHz, CDCl$_3$):** δ 138.2, 131.5, 129.3, 120.4, 88.9, 87.2, 21.5 ppm.
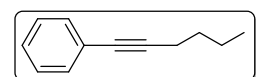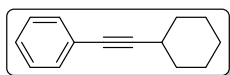
1-(Hex-1-yn-1-yl)-benzene (Table 3.1.6, entry 10): yellow liquid; 1H NMR (400 MHz, CDCl$_3$): δ 7.40-7.38 (m, 2H), 7.27-7.25 (m, 3H), 2.41 (t, 2H, J = 6.8 Hz), 1.59-1.47 (m, 4H), 0.94 (t, 3H, J = 7.3 Hz) ppm. **^{13}C NMR (100 MHz, CDCl$_3$):** δ 131.6, 128.2, 127.5, 124.1, 90.5, 80.6, 29.7, 22.1, 19.1, 13.7 ppm.
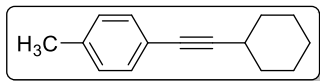
1-(Hex-1-yn-1-yl)-4-methylbenzene (Table 3.1.6, entry 11), Yellow liquid, **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.29-7.25 (m, 2H), 7.08-7.06 (m, 2H), 2.41-2.37 (m, 2H), 2.32 (s, 3H), 1.60-1.46 (m, 4H), 0.96-0.92 (m, 3H) ppm.**^{13}C NMR (100 MHz, CDCl$_3$):** δ 137.4, 131.4, 129.3, 128.8, 89.6, 87.2, 30.9, 22.1, 21.4, 19.2. 13.7 ppm
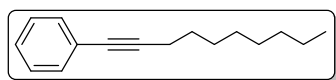
1-(Cyclohexylethynyl)benzene (Table 3.1.6, entry 12): Yellow liquid, **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.40-7.38 (m, 2H),, 7.29-7.25

(m, 3H), 2.59-2.57 (m, 1H), 1.89-1.34 (m, 10H) ppm.**^{13}C NMR (100 MHz, CDCl$_3$):** δ 131.9, 131.6, 128.3, 128.2, 127.4, 94.5, 80.5, 32.7, 26.0, 23.4, 22.8 ppm.
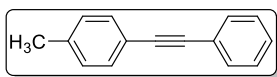

1-(Cyclohexylethynyl)-4-methylbenzene (Table 3.1.6, entry 13): Yellow liquid, **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.29-7.10 (m, 4H), 2.58-2.56 (m, 1H), 2.37-2.32 (m, 3H), 1.73-1.26 (m, 10H) ppm.**^{13}C NMR (100 MHz, CDCl$_3$):** δ 137.4, 131.8, 129.1, 128.8, 93.7, 80.6, 40.5, 32.8, 29.7, 26.0, 21.5 ppm.


1-(Dodec-1-yn-1-yl)-benzene (Table 3.1.6, entry 14): yellow liquid; 1H NMR (400 MHz, CDCl$_3$): δ 7.40-7.37 (m, 2H), 7.27-7.25 (m, 3H), 2.39 (t, 2H, J = 6.8 Hz), 1.62-1.27 (m, 12H), 0.88 (t, 3H, J = 6.8 Hz) ppm. **^{13}C NMR (100 MHz, CDCl$_3$):** δ 131.6, 128.2, 127.5, 124.1, 90.5, 80.6, 31.9, 29.7, 29.4, 29.2, 28.8, 22.7, 19.4, 14.2 ppm.

1-Methyl-4-(2-phenylethynyl)benzene (Table 3.1.6, entry 16): White solid, m.p. 68-70 °C, **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.56-7.50 (m, 2H), 7.42 (d, 2H, J = 7.7 Hz), 7.36-7.31 (m, 3H), 7.15 (d, 2H, J = 7.7 Hz), 2.36 (s, 3H) ppm.**^{13}C NMR (100 MHz, CDCl$_3$):** δ 138.4, 132.4, 131.6, 129.2, 128.5, 128.1, 123.5, 120.2, 89.6, 88.8, 21.6 ppm.

^{1}H and ^{13}C NMR spectra of 4-Nitrobiphenyl
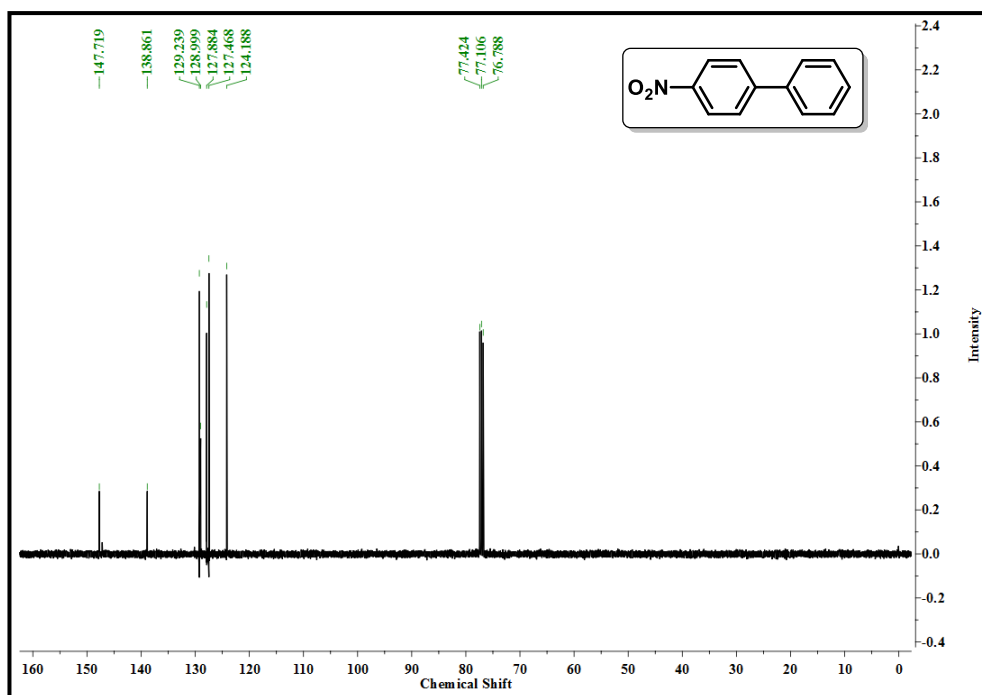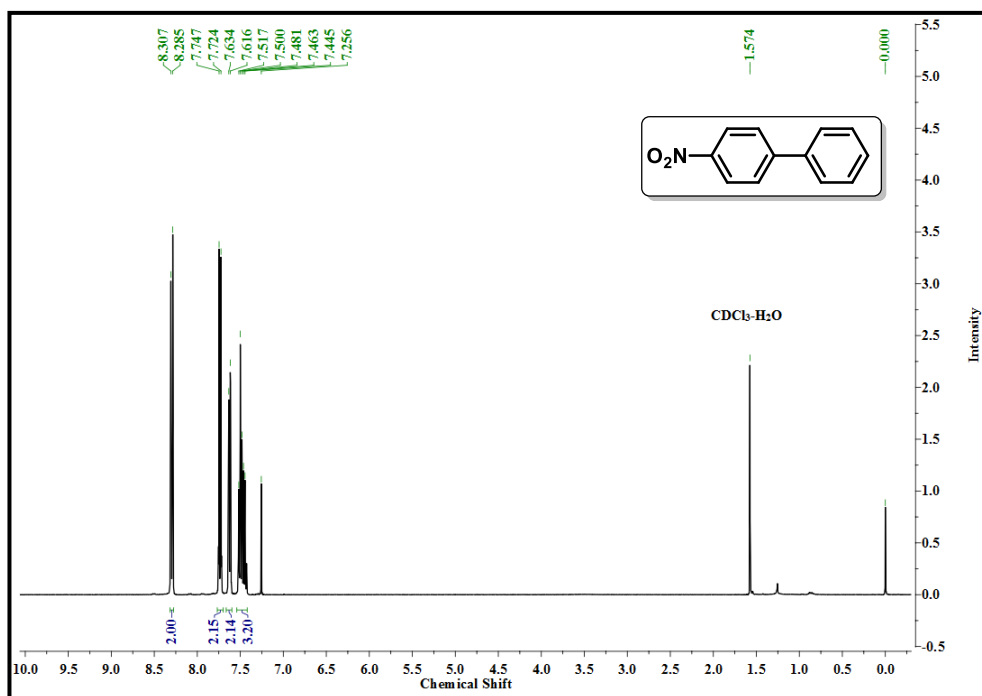
^{1}H and ^{13}C NMR spectra of 1-Methyl-4-(2-phenylethynyl)benzene
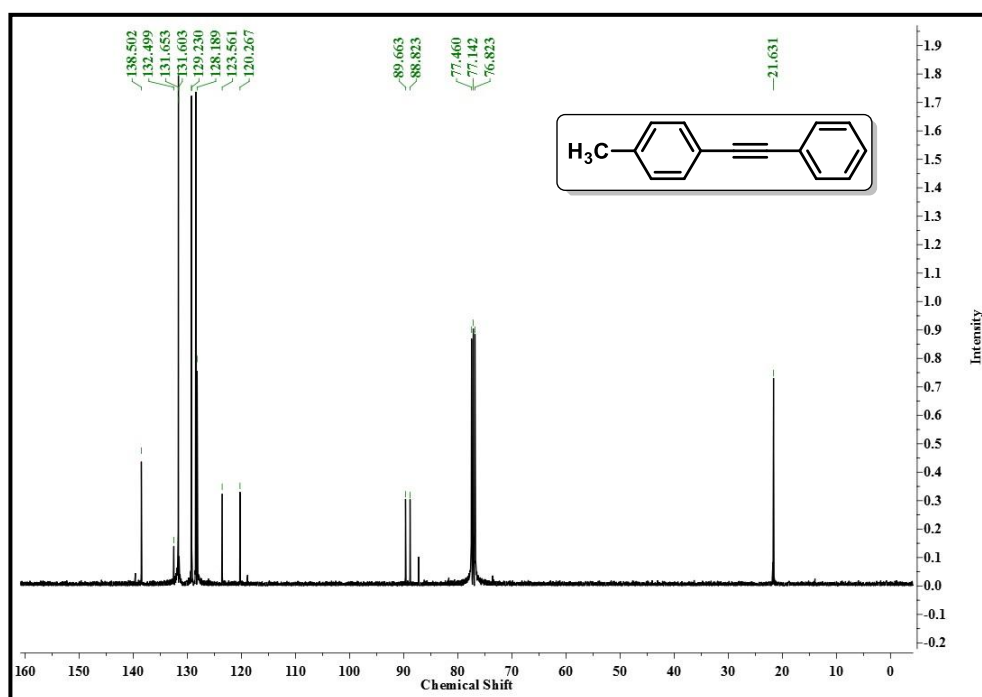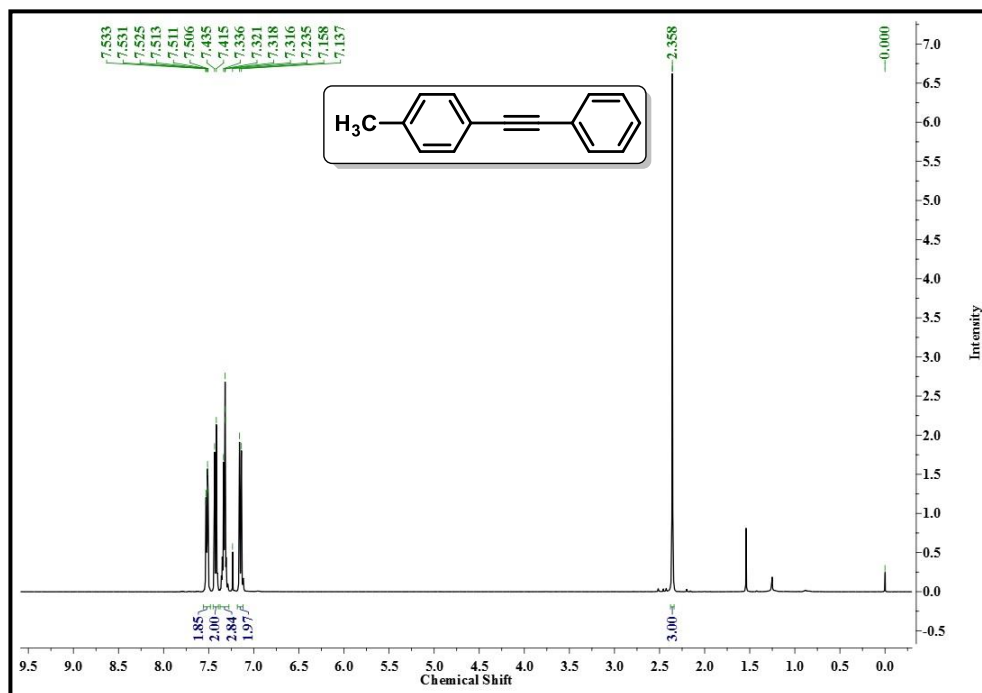
Section 3.2

Extraction of base from naturally abundant aquatic biomass and its implication in palladium catalyzed Suzuki-Miyaura cross-coupling reaction

Abstract: This section describes the development of non-conventional base using a naturally abundant waste aquatic biomass, *Eichhornia crassipes* (Common name: Water Hyacinth). The system serves as an excellent alternative base and green solvent system for palladium catalyzed Suzuki-Miyaura cross-coupling reaction of aryl halides and aryl boronic acids at room temperature.

3.2.1. Outlines

In recent years, development of environmentally and economically green methodologies is a key driving force of synthetic organic chemistry in industry as well as in academia [1, 4 & 5]. There is a need to design very simple reaction methodologies in aqueous media under mild reaction conditions using nontoxic reagents preferably using natural feedstock. Among various natural sources, plant materials are the most readily available resources which offer eco-friendliness, cost-effectiveness, safety and easy handling [19,20]. In this section, we have reported an aqueous system using a worldwide abundant waterborne biomass species, *Eichhornia crassipes* (commonly known as water hyacinth) via low temperature combustion of its dried mass and corresponding utilization of its ash water extract as *in situ* basic medium in synthetic application.

Water hyacinth is composed with host of organic and inorganic constituents and it has high potential for bio-gas production, used as detergents, in wastewater treatment and various industrial applications [21-24]. Moreover, huge mass of water hyacinth sometimes cause trouble in transportation, oxygen quantity for aquatic inhabitants and as such becomes necessary to clean up, which in turn can be utilized in industrial application instead of wasteful dumping. Thus with an aim of waste minimization, we opt to study the detailed characteristic of ash water extract of water hyacinth, and its significance was investigated in palladium catalyzed Suzuki-Miyaura cross-coupling reaction.

3.2.2. Experimental

3.2.2.1. Procedure for preparation of Ash water Extract of Water hyacinth (AWEH)

At the onset, *Eichhornia crassipes* was collected from nearby water body and then sun dried. The dried mass was burnt into its ashes and thereafter, 20 g of ash was suspended in 100 mL distilled water in a 250 mL beaker. The mixture was allowed to stir for half an hour at room temperature. The aqueous mixture was then filtered and a clear solution was obtained which was used as solvent cum basic medium in Suzuki-Miyaura coupling reaction. (Figure. 3.2.1)
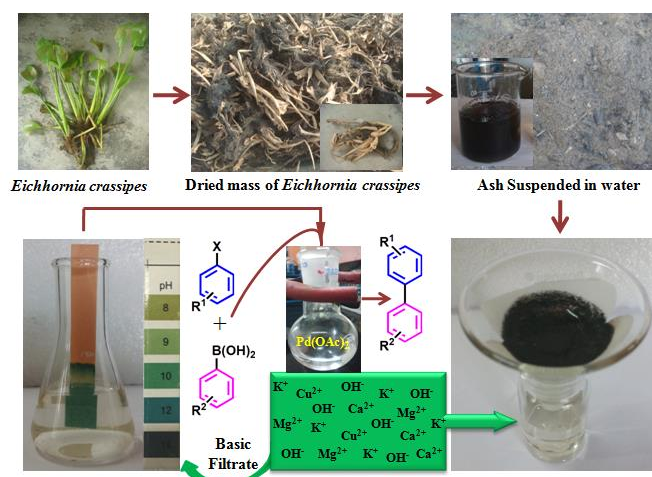
Figure 3.2.1: Preparation of AWEH and their application in Suzuki-Miyaura coupling.

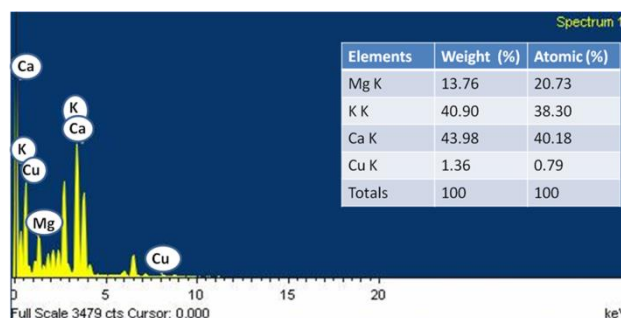### 3.2.2.2 General procedure for Suzuki-Miyaura cross-coupling reaction

The Suzuki-Miyaura reaction was performed by stirring aryl halide (0.5 mmol), aryl boronic acid (0.6 mmol), $Pd(OAc)_2$ (1 mol%) with AWEH (6 mL) in a 50 mL round bottomed flask. The resulting mixture was stirred at room temperature which was monitored vide TLC. After completion, the reaction mixture was extracted with ethyl acetate (3×10 mL) and washed with water, dried over anhydrous Na_2SO_4 and concentrated in *vacuo*. The residue was purified by column chromatography on silica gel using n-hexane as eluent. The desired product was characterized by comparing ^{1}H and ^{13}C spectral data with authentic samples.

3.2.3. Results and Discussion

3.2.3.1. Analysis of water-extract (AWEH)

Initially, the characteristic of AWEH was investigated using a pH meter and it was found to be alkaline in nature with pH about 10.29. In order to reveal the basicity of AWEH, Energy Dispersive X-ray spectroscopy (EDX) analysis of the ash was performed. The distribution of metal contents based on EDX analysis is shown in Figure 3.2.2. It was observed that, the ash contains a high distribution of Mg, K and Ca along with small amount of Cu. As already mentioned in the literature, the roots, bulbs, and leaves of *Eichhornia crassipes* contains large distribution of K, Na, Mg, Ca, and P [23,24]. The exceptional basic property of this AWEH may be due to the formation of metal oxides or hydroxides in their ash water extract which as a result directs the coupling reaction to an external base free condition. As such the water extract (AWEH)

contributes a dual role in the synthesis of biaryl derivative, *i.e in situ* base cum reaction media (solvent system).

Elements	Weight (%)	Atomic (%)
Mg K	13.76	20.73
K K	40.90	38.30
Ca K	43.98	40.18
Cu K	1.36	0.79
Totals	100	100

Figure 3.2.2: EDX Spectrum of ash of *Eichhornia crassipes*.

3.2.3.2. Optimization of catalytic system for Suzuki-Miyaura coupling reaction

The sustainability of this novel aqueous extract was examined for Suzuki-Miyaura coupling of aryl halides and aryl boronic acid. The reaction was screened with different amount of AWEH and Pd(OAc)$_2$ at room temperature. The results are highlighted in Table 3.2.1. At the onset, we have performed the reaction using Pd(OAc)$_2$ (0.5 mol%) and AWEH (3 mL) considering 4-bromoanisole (0.5 mmol) and phenylboronic acid (0.6 mmol) as the model substrate. However, the reaction did not proceed well even with longer reaction time (Table 3.2.1, entry 1). Thereafter the reaction was performed by increasing the amount of Pd(OAc)$_2$ (1 mol%) and AWEH (5 mL). Interestingly, 85% of cross-coupled product was obtained within 3h (Table 3.2.1, entry 2). We have carried out the reaction in absence of both Pd(OAc)$_2$ and AWEH respectively. But as expected, the reaction did not proceed in absence of one another (Table 3.2.1, entries 3 and 4). So, the presence of both Pd(OAc)$_2$ and AWEH is the prime necessity for the coupling reaction We then examined the reaction using 1 mol% Pd(OAc)$_2$ and lowering the amount of AWEH, a comparative poor conversion of reaction was noticed (Table 3.2.1, entry. 5). Finally, on further increasing the amount of AWEH, an appreciable increase in reaction yield was observed (Table 3.2.1, entry 6). On decreasing the amount of Pd loading, the reaction yield significantly decreases even with greater amount of AWEH (Table 3.2.1, entry 7). Thus, this system delivers a novel approach towards Suzuki-Miyaura coupling, as AWEH prevail an important role providing a natural basic condition, which in addition leads to a synergistic interaction of the suspended metal ions with palladium and aryl halide [15].

Table 3.2.1: Screening of AWEH and catalyst amount for Suzuki-Miyaura cross-coupling [a]

MeO—⟨ ⟩—Br + (HO)₂B—⟨ ⟩ $\xrightarrow[\text{AWEH, rt}]{\text{Pd(OAc)}_2}$ MeO—⟨ ⟩—⟨ ⟩

Entry	Pd(OAc)$_2$ (mol%)	AWEW (mL)	Time (h)	Yield (%) [b]
1	0.5	3	24	40
2	1	5	3	85
3	1	-	24	nr [c]
4	-	6	24	nr
5	1	3	6	65
6	1	6	3	88
7	0.5	6	7	50

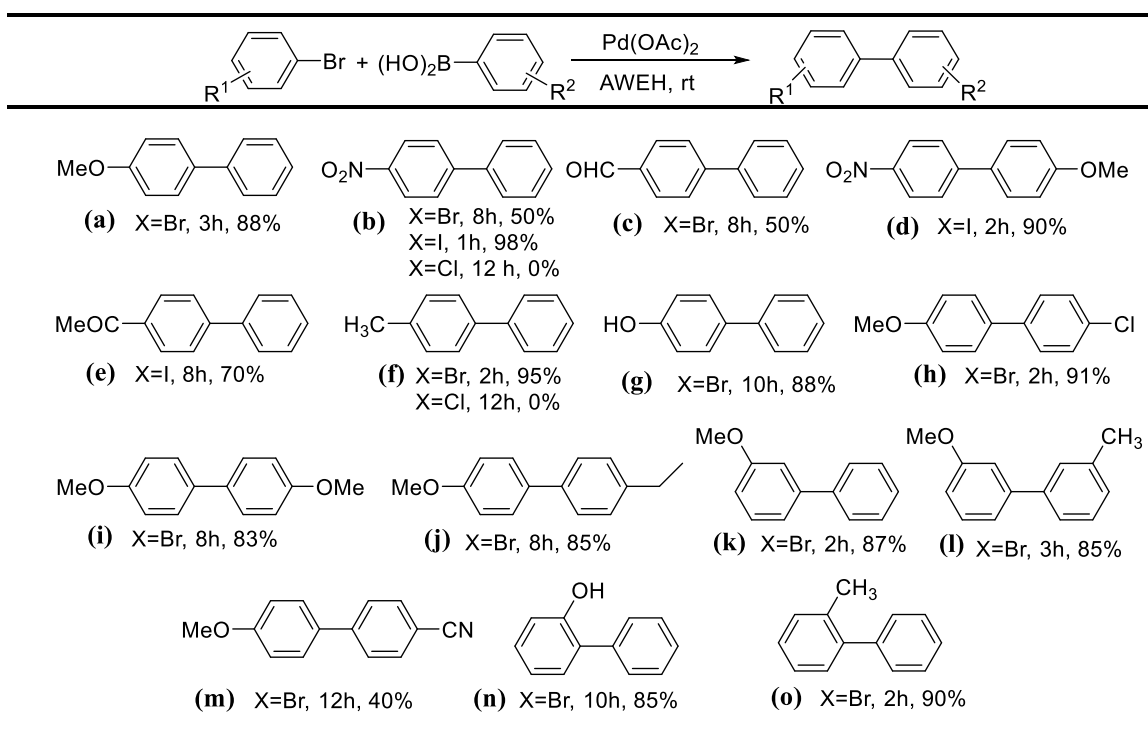[a] Reaction conditions: 4-Bromoanisole (0.5 mmol), Phenylboronic acid (0.6 mmol),
[b] Isolated yields, [c] H$_2$O is used as solvent

3.2.3.3. Substrate scope for Suzuki-Miyaura coupling reaction

The present protocol was extended to a variety of electronically diverse aryl bromides and aryl boronic acid using the above optimization condition (Table 3.2.2). The catalytic system delivers appreciable yield for electron donating substituents. But, some electron withdrawing aryl bromides suffers a comparative lower conversion. This may be due to the weaker solvent-substrate interaction leading to poorer solubility of organic halides in pure water. Nevertheless, attractive reaction outcome was achieved affording variety of biaryl derivatives. From Table 3.2.2, it is seen that aryl bromides with *p*-NO$_2$, *p*-CHO resulted in poor conversion (50% yields, Table 3.2.2, b & c) which may be due to the insolubility of the solid substrates in water resulting in weaker interaction with the solvent and catalytic system and as a result slows down the oxidative addition of the mechanistic step. Nevertheless, coupling with aryl iodides provides excellent yields of desired cross-coupled product in a shorter reaction time (Table 3.2.2, b, d & e). Greater efficiency of aryl iodides may be due to difference in electronic effect of the bromide and iodide. Again, *para-* and *meta-* bromoanisole with both its electron donating and electron withdrawing effect respectively results in excellent cross-coupled product (Table 3.2.2, a & h-l). Additionally, aryl bromides with electron donating group such as -OH, -CH$_3$ shows appreciable conversion in both *para-* and *ortho-* substituted centre (Table 2, entries f, g & n, o). Moreover, from the above results we have seen that the catalytic system is compatible with wide variety of aryl boronic acid (Table 3.2.2, d & h-l). But, a relatively lower conversion was observed with cyano substituted boronic acid (Table

3.2.2, m). The coupling of aryl chloride with the present catalyst system was also studied. Unfortunately, no cross-coupling product was obtained even with 2 mol% Pd(OAc)$_2$ and at 80 °C (Table 3.2.2, b & f), although homocoupling product of aryl boronic acid was observed under the reaction conditions. This incompatibility of the catalyst system may be due to high stability of the aromatic carbon-chlorine bond (i.e high C–Cl bond strength) which hampers the oxidative addition step [25,26]. However, we were unable to reuse the catalytic system, and the second catalytic cycle gave only trace amount of coupling product.

Table 3.2.2: Pd(OAc)$_2$/AWEH catalyzed Suzuki-Miyaura coupling of aryl halides and aryl boronic acids [a]

(a) X=Br, 3h, 88%

(b) X=Br, 8h, 50% / X=I, 1h, 98% / X=Cl, 12 h, 0%

(c) X=Br, 8h, 50%

(d) X=I, 2h, 90%

(e) X=I, 8h, 70%

(f) X=Br, 2h, 95% / X=Cl, 12h, 0%

(g) X=Br, 10h, 88%

(h) X=Br, 2h, 91%

(i) X=Br, 8h, 83%

(j) X=Br, 8h, 85%

(k) X=Br, 2h, 87%

(l) X=Br, 3h, 85%

(m) X=Br, 12h, 40%

(n) X=Br, 10h, 85%

(o) X=Br, 2h, 90%

[a] Reaction conditions: aryl Bromides (0.5 mmol), aryl boronic acid (0.6 mmol), Pd(OAc)$_2$ (1 mol%), AWEH (6 mL), [b] Isolated yields, [c] aryl iodides (0.5 mmol) [d] aryl chlorides (0.5 mmol) [e] 80 °C, Pd(OAc)$_2$ (2 mol%)

3.2.4. Conclusions

In summary, this methodology provides a remarkable advantage over many ligands assisting catalytic system for Suzuki-Miyaura cross-coupling reaction. This strategy involves the use of worldwide abundant aquatic biomass (*Eichhornia crassipes*) whose use in industrial implementation will not hamper the ecological balance or pyramid. Further, it minimizes the inclusion of additional petroleum based conventional solvent and external base to this present protocol for Suzuki-Miyaura cross-coupling reaction.

**3.2.5. Analytical data of the synthesized biaryl derivatives**
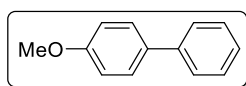
4-Methoxybiphenyl: (Table 3.2.2, a): White Solid, m.p. 81-83 °C, **¹H NMR (400 MHz, CDCl₃):** 7.55-7.51 (m, 3H), 7.42-7.38 (m, 2H), 7.31-7.27 (m, 2H), 6.97 (d, 2H, J = 8.7 Hz), 3.84 (s, 3H) ppm. **¹³C NMR (100 MHz, CDCl₃):** δ 159.2, 140.9, 133.8, 128.8, 128.2, 126.8, 126.7, 114.2, 55.4 ppm.
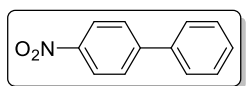

4-Nitrobiphenyl: (Table 3.2.2, b): Yellow Solid, m.p. 113-115 °C, **¹H NMR (400 MHz, CDCl₃):** δ 8.29 (d, 2H, J = 8.7 Hz), 7.73 (d, 2H, J = 8.7 Hz), 7.62-7.60 (m, 2H), 7.50-7.43 (m, 3H) ppm. **¹³C NMR (100 MHz, CDCl₃):** δ 147.7, 138.8, 129.2, 129.0, 128.9, 127.9, 127.4, 124.2 ppm.
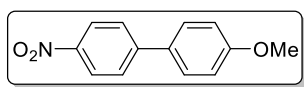

4-Methoxy-4′-nitrobiphenyl: (Table 3.2.2, d): Yellow Solid, m.p. 92-94 °C, **¹H NMR (400 MHz, CDCl₃):** δ 8.26 (d, 2H, J = 8.7 Hz), 7.68 (d, 2H, J = 8.7 Hz), 7.58-7.55 (m, 2H), 7.00 (d, 2H, J = 8.7 Hz), 3.86 (s, 3H) ppm. **¹³C NMR (100 MHz, CDCl₃):** δ 160.5, 147.3, 146.6, 131.1, 128.6, 127.1, 124.2, 114.6, 55.5 ppm.
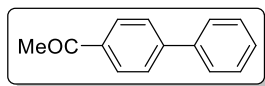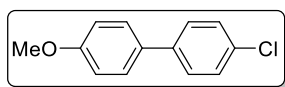

4-Acetylbiphenyl: (Table 3.2.2, e): White Solid, m.p. 118-120 °C, **¹H NMR (400 MHz, CDCl₃):** 8.02 (d, 2H, J = 8.2 Hz), 7.67 (d, 2H, J = 8.2 Hz), 7.62 (d, 2H, J = 7.3 Hz), 7.48-7.39 (m, 3H), 2.63 (s, 3H) ppm. **¹³C NMR (100 MHz, CDCl₃):** δ 197.9, 145.8, 139.9, 135.9, 129.0, 128.8, 128.3, 127.3, 127.1, 26.7 ppm.
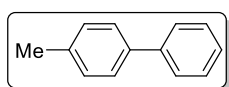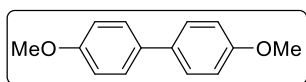

4-Methylbiphenyl: (Table 3.2.2, f): White Solid, m.p. 46-48 °C, **¹H NMR (400 MHz, CDCl₃):** 7.71-7.70 (m, 2H), 7.63-7.61 (m, 2H), 7.55-7.50 (m, 3H), 7.45 (d, 1H, J = 8.2 Hz), 7.37-7.35 (m, 1H), 2.51 (s, 3H) ppm. **¹³C NMR (100 MHz, CDCl₃):** δ 141.3, 138.5, 137.2, 131.0, 130.8, 129.7, 128.9, 127.2, 21.3 ppm.
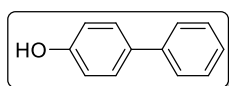

4-Hydroxybiphenyl: (Table 3.2.2, g): Light brown Solid, m.p. 164-168 °C, **¹H NMR (400 MHz, CDCl₃):** 7.53 (d, 1H, J = 7.7 Hz), 7.47 (d, 1H, J = 8.2 Hz), 7.41 (t, 2H, J = 7.7 Hz), 7.35-7.24 (m, 3H), 6.90 (d, 1H, J = 8.2 Hz), 6.71 (d, 1H, J = 8.7 Hz), 5.05 (m, 1H) ppm. **¹³C NMR (100 MHz, CDCl₃):** δ 154.7, 140.8, 132.5, 128.8, 128.5, 126.8, 117.3, 115.7 ppm.


4-Chloro-4′-methoxybiphenyl: (Table 3.2.2, h): White Solid, m.p. 114-116 °C, **¹H NMR (400 MHz, CDCl₃):** δ 7.48-7.45 (m, 4H), 7.36 (d, 2H, J = 8.2 Hz), 6.96 (d, 2H, J = 8.7 Hz), 3.84 (s, 3H) ppm. **¹³C NMR (100 MHz, CDCl₃):** δ 159.4, 149.7, 139.3, 132.7, 132.5, 128.9, 128.1, 114.3, 55.4 ppm.

4,4′-Dimethoxybiphenyl: (Table 3.2.2, i): White Solid, m.p. 179-181 °C, **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.46 (d, 4H, *J* = 8.7 Hz), 6.94 (d, 4H, *J* = 8.7 Hz), 3.83 (s, 6H) ppm. **^{13}C NMR (100 MHz, CDCl$_3$):** δ 158.7, 133.5, 127.8, 114.2, 55.4 ppm.
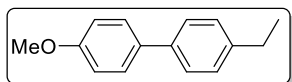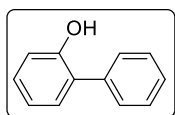
4-Ethyl-4′-methoxybiphenyl: (Table 3.2.2, j): White Solid, m.p. 110-112 °C, **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.52-7.46 (m, 4H), 7.26-7.24 (m, 2H), 6.96 (d, 2H, *J* = 8.7 Hz), 3.84 (s, 3H), 2.68 (q, 2H, *J* = 7.7, 15.11 Hz) 1.27 (t, 3H, *J* = 7.7 Hz) ppm. **^{13}C NMR (100 MHz, CDCl$_3$):** δ 158.9, 142.8, 138.3, 133.8, 128.3, 128.0, 126.7, 114.2, 55.4, 28.5, 15.7 ppm.
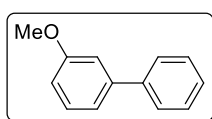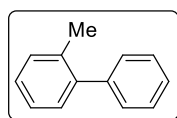
3-Methoxybiphenyl: (Table 3.2.2, k): Colourless liquid, **^{1}H NMR (400 MHz, CDCl$_3$):** 7.58 (d, 2H, *J* = 7.7Hz), 7.43 (t, 2H, *J* = 7.3 Hz), 7.37-7.32 (m, 2H), 7.18 (d, 1H, *J* = 7.7 Hz), 7.12 (s, 1H), 6.90 (d, 1H, *J* = 8.2 Hz), 3.86 (s, 3H) ppm. **^{13}C NMR (100 MHz, CDCl$_3$):** δ 160.0, 142.8, 141.1, 129.8, 128.8, 127.5, 127.3, 119.7, 112.9, 112.7, 55.4 ppm.
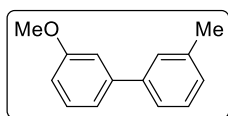
3-Methoxy-3′-methylbiphenyl: (Table 3.2.2, l): Colourless liquid, **^{1}H NMR (400 MHz, CDCl$_3$):** 7.40-7.31 (m, 4H), 7.18 (d, 2H, *J* = 7.3 Hz), 7.12 (s, 1H), 6.91-6.88 (m, 1H), 3.87 (s, 3H), 2.42 (s, 3H) ppm. **^{13}C NMR (100 MHz, CDCl$_3$):** δ 159.9, 143.0, 141.1, 138.4, 129.7, 128.7, 128.2, 128.1, 124.4, 119.8, 112.9, 112.7, 55.4, 21.6 ppm.

2-Hydroxybiphenyl: (Table 3.2.2, n): White Solid, m.p. 57-59 °C, **^{1}H NMR (400 MHz, CDCl$_3$):** 7.53-7.38 (m, 5H), 7.28-7.23 (m, 2H), 7.01-7.97 (m, 2H), 5.20 (s, 1H) ppm. **^{13}C NMR (100 MHz, CDCl$_3$):** δ 152.4, 135.7, 132.8, 130.3, 129.4, 129.2, 128.1, 127.9, 120.9, 115.8 ppm.

2-Methylbiphenyl: (Table 3.2.2, o): Colourless liquid, **^{1}H NMR (400 MHz, CDCl$_3$):** 7.68 (d, 1H, *J* = 7.7 Hz), 7.54-7.48 (m, 3H), 7.42-7.41 (m, 2H), 7.35-7.33 (m, 3H), 2.37 (s, 3H) ppm. **^{13}C NMR (100 MHz, CDCl$_3$):** δ 142.1, 141.4, 135.5, 130.5, 130.0, 129.3, 1289, 128.2, 127.4, 127.3, 126.9, 125.9, 20.6 ppm.

^{1}H and ^{13}C NMR spectra of 4-Ethyl-4′-methoxybiphenyl
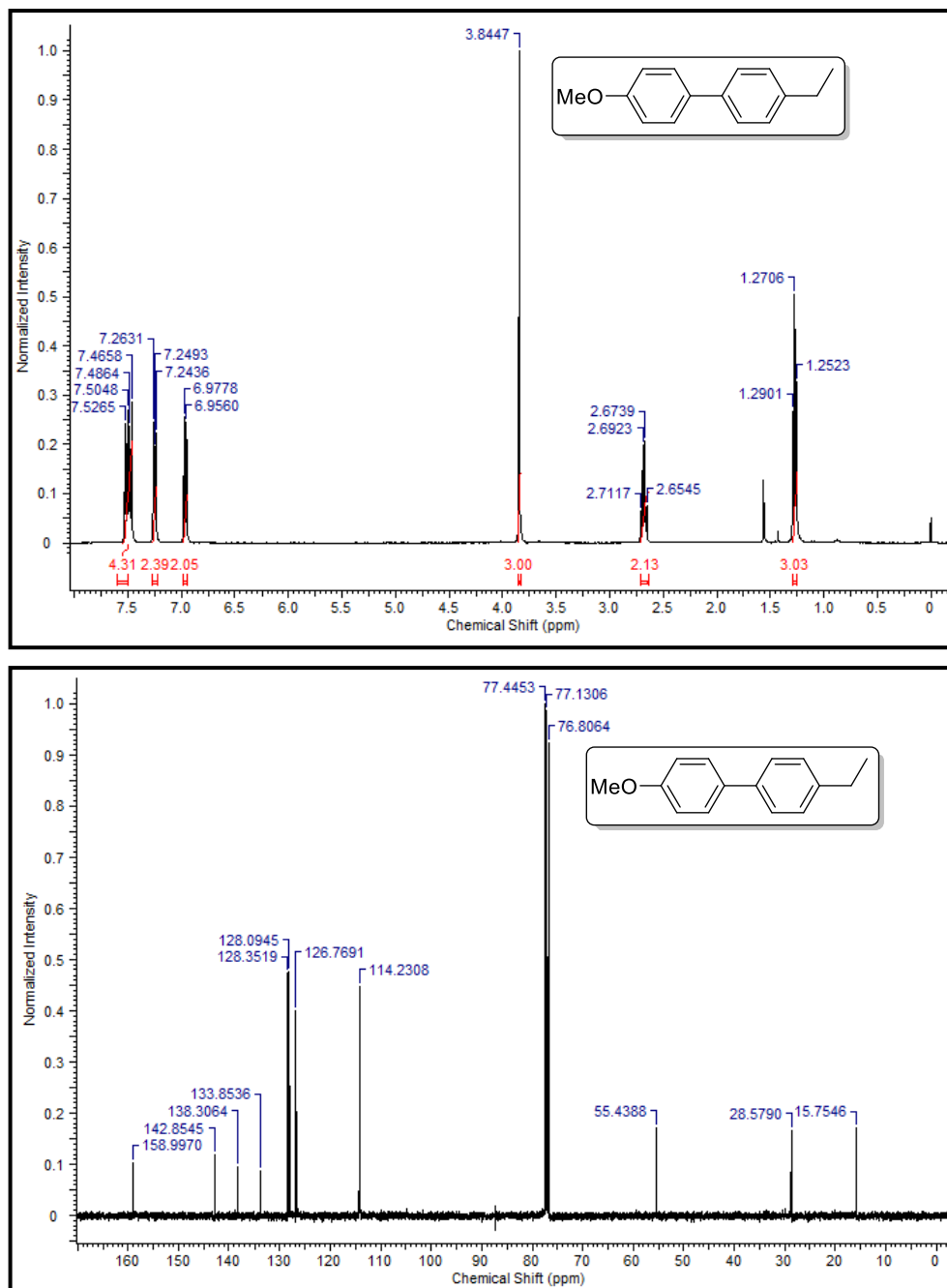
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