



REGULAR ARTICLE

# Two efficient ligand-assisted systems of two different ionic Schiff base ligands for palladium chloride catalyzed in Suzuki-Miyaura reaction

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**Abstract.** The bis- methyl imidazolium chloride-salophen Schiff base ligand as cationic Schiff base ligand ( $L_1$ ) was synthesized by the reaction of methyl imidazoliumsalicylaldehyde chloride ( $S_1$ ) and phenylendiamine. The phenylendiamine was also reacted by monosodium 5-sulfonatosalicylaldehyde ( $S_2$ ) to give the bis-sodium sulfonate-salophen Schiff base ligand ( $L_2$ ) as the anionic ligand. These two ligands were characterized by the  $^1\text{H-NMR}$ ,  $^{13}\text{C-NMR}$ , IR, UV-visible and mass spectroscopy, as well as elemental analysis. The ligand assisted  $\text{PdCl}_2$  catalyst was investigated in the Suzuki-Miyaura reaction by using the  $L_1$  and  $L_2$  as cationic and anionic Schiff base ligands and different reaction conditions such as temperature, solvent and mol% of  $\text{PdCl}_2$  were optimized. The results revealed that the anionic ligand assistance had a better activity for the catalytic system of  $\text{PdCl}_2$  in Suzuki-Miyaura reaction.

**Keywords.** Schiff base ligands; ligand assisted system; Suzuki-Miyaura reaction.

## 1. Introduction

In organic chemistry, one of the most important and useful conversion is the construction of the carbon-carbon bonds. In 1979, Miyaura, Yamada and Suzuki<sup>1</sup> published a coupling reaction between boronic acid and an organo-halide catalyzed by a palladium complex. The importance of this coupling is obvious in different areas, from the synthesis of natural product to industrial material.<sup>2</sup> Although there are many research groups that have introduced many systems for this synthesis by different catalysis in water, there are many drawbacks in their procedure such as evaluated temperature, the addition of tetra butyl ammonium bromide (TBAB) as phase transfer catalyst and complicated work-up procedure.<sup>3-12</sup> In general, activation of aryl chloride needs hard reaction conditions and high amount of palladium as a catalyst. The development of benign methods for the synthesis of the Suzuki-Miyaura reaction that use the small amount of catalyst is a subject of continuous interest for synthetic chemists.<sup>13-22</sup> Especially, for the catalyst which is precious and exhaustive as palladium. There are some reports that have introduced ligand-free Suzuki-

Miyaura reactions catalyzed by simple palladium salts such as  $[\text{Pd}(\text{OAc})_2]$ ,  $[\text{Pd}(\text{dba})_2]$ , and  $\text{PdCl}_2$ . There are some drawbacks in their systems, for example, they are inappropriate for low-cost systems and in competition with the ligand assisted-systems, their selectivity is less.

For many years, phosphine-based ligands were the superior ligands for Suzuki-Miyaura reaction, because by changing the attached groups to the phosphorus atom, the properties in steric and electronic features were tuned. But, because of their environmental problems, high costs and sensitivity to air, chemists were encouraged to think about other ligands such as nitrogen-containing ligands, that in contrast to phosphines, have many advantages. In modern inorganic chemistry, Schiff bases are a class of organic-inorganic compounds that are synthesized by the condensation of the carbonyl compound with amino compounds and are used as ligands due to their versatility.<sup>23-28</sup> Among many potential organic ligands, Schiff bases are widely employed as ligands in coordination chemistry, in addition, their functionalities are tuned depending on the nature of starting materials. Recently, many researchers recognized the Schiff base ligands as excellent alternatives to phosphines in Suzuki-Miyaura reactions.<sup>29-31</sup> In this research, it is described the

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synthesis and characterization of two different ionic Schiff base ligands: imidazolium and sulfonium salophen type Schiff base ligands as cationic and anionic Schiff base ligands, respectively, (Scheme 1). In addition, the effect of ligands in ligand assisted PdCl<sub>2</sub> catalyst in Suzuki-Miyaura reaction is investigated.

## 2. Experimental

### 2.1 Materials and methods

Reagents and starting material were purchased from Merck. 5-Chloromethyl salicylaldehyde and sodium 5-sulfonatosalicylaldehydes were prepared by a method described in refs <sup>33</sup> and <sup>32</sup>, respectively. All solvents were used without purification. Infrared (IR) spectra were recorded in the range 400–4000 cm<sup>-1</sup> with a Perkin Elmer FT-IR spectrophotometer using KBr pellets. UV–visible spectra were recorded with a PerkinElmer Lambda 25 spectrometer. C, H and N determinations were achieved on a Heraeus CHN-O rapid analyzer, NMR spectra were recorded with a Bruker Avance II-400 and Mass spectra was recorded by 5975C VL MSD with Tripe-Axis Detector spectrometer.

### 2.2 Synthesis of sodium sulfoniumsalophen Schiff base ligand

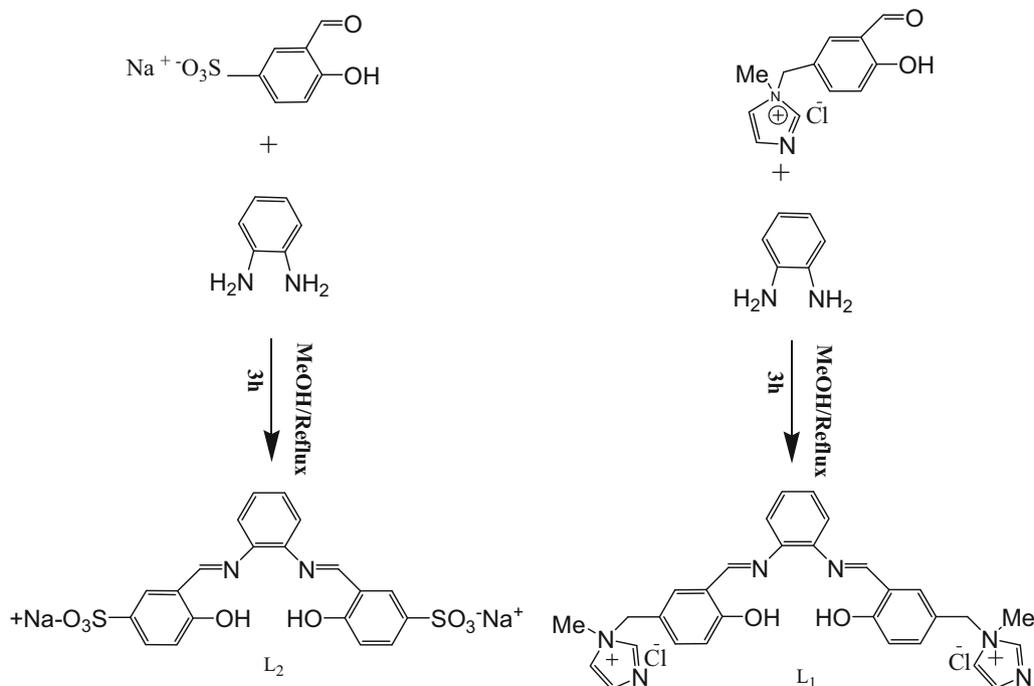
In a round bottom flask containing 20 mL of methanol, (0.5 g, 1 mmol) of phenyldiamine and (2.07 g, 2 mmol) of

sodium 5-sulfonatosalicylaldehyde was added and then the content was refluxed for 3 h. Then the solvent was evaporated and the yellow-orange product was obtained and dried in air. Anal. Calcd. for C<sub>20</sub>H<sub>14</sub>S<sub>2</sub>O<sub>8</sub>N<sub>2</sub>Na<sub>2</sub>: C, 46.15; H, 2.69; S, 12.30, N, 5.38%. Found: C, 45.60; H,3.07; S,11.50; N,4.97. <sup>1</sup>H NMR (δ, ppm, DMSO-d<sub>6</sub>) 8.42 (s, 2H, OH), 6.86–7.94 (m, 10H, Ar–H), 5.31 (s, 2H, N=CH). ESI-MS: m/z calc. for (520), found 522.

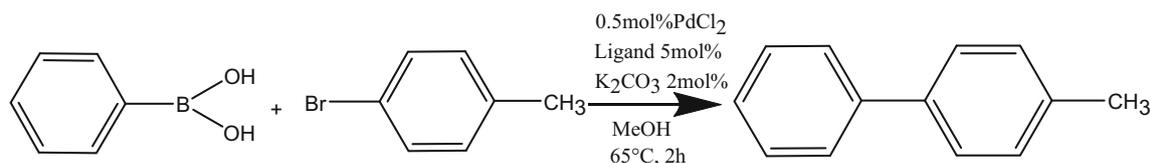
### 2.3 Synthesis of imidazolium salophen chloride Schiff base

**a)** Preparation of methyl-imidazolium-salicylaldehyde chloride: In a round bottom flask, 5-chloromethyl salicylaldehyde (0.907 g, 0.0074 mol) and 1-methyl-imidazole (0.61 g, 0.0074 mol) were stirred in 25 mL of acetonitrile for 3 h at room temperature. After filtration, the product was dried under vacuum. M.p.: 64 °C, Anal. Calcd. for C<sub>12</sub>H<sub>13</sub>O<sub>2</sub>N<sub>2</sub>Cl: C, 57.02; H, 5.18; N,11.08% Found: C, 55.92; H, 4.89; N, 10.92. <sup>1</sup>HNMR (δ, ppm, MeOD): (8.47, 1H, CHO), (7.50, 1H, CH), (6.25, 6.07, 6.03, 3H, aromatic), (5.40, CH<sub>2</sub>, methylene), (5.38, 5.33, 2H, ethylene), (3.37, CH<sub>3</sub>, methyl).

**b)** Synthesis of the imidazoliumsalophen chloride Schiff base ligand: In a round bottom flask, methyl-imidazole-salicylaldehyde (1.5 g, 0.0059 mol) and phenyldiamine (0.178 g, 0.0029 mol) were refluxed in methanol for 3 h. Then the solvent was removed under reduced pressure. The product was purified by diethyl ether and n-hexane. Anal. Calcd. for C<sub>30</sub>H<sub>30</sub>Cl<sub>2</sub>N<sub>6</sub>O<sub>2</sub>: C,62; H, 5.23; N,14.54%,



**Scheme 1.** Synthetic procedures of cationic L1 and anionic L2 Schiff base ligands.



**Scheme 2.** Suzuki-Miyaura reaction.

Found: C,59.90; H,4.93; N,13.90.  $^1\text{H}$  NMR ( $\delta$ , ppm, DMSO- $d_6$ ): 9.45 (s, 2H, OH), 6.81–7.72 (m, 16H, aromatic), 5.43 (s, 4H, methylene), 5.16 (s, 2H, ethylene), 3.89 (s, 6H). ESI-MS:  $m/z$  calcd. for (577), found 577.6.

#### 2.4 General protocol for Suzuki-Miyaura reaction

A mixture of phenylboronic acid (1 mol, 0.12 g), 4-bromotoluene (1 mol, 0.17 g),  $\text{PdCl}_2$  (0.5 mol%) and ligand (5 mol%) and  $\text{K}_2\text{CO}_3$  (2 mol%) was refluxed in 20 mL of MeOH for 2 h. Then the reaction was diluted with distilled water (20 mL) and extracted with diethyl ether ( $3 \times 20$  mL). The organic phase was separated and evaporated. The product was purified by column chromatography, authenticated by  $^1\text{H}$ -NMR and by comparison of their melting point with those reported in the literature.

#### 2.5 Catalytic reaction

The water-soluble ligands  $L_1$  and ligand  $L_2$  were synthesized as described previously. Then their effect was investigated in the catalytic Suzuki-Miyaura condensation reaction in the presence of  $\text{PdCl}_2$ . In order to optimize the reaction conditions, the phenylboronic acid and 4-bromotoluene was chosen as a model substrate and different reaction conditions such as temperature, solvent, and mol% of  $\text{PdCl}_2$  in assistance of ligands  $L_1$  and ligand  $L_2$  were investigated. For determination of the efficient solvent, the effect of different organic solvents was investigated in the Suzuki-Miyaura reaction (Scheme 2) and the data was shown that the methanol was efficient solvent. The effect of temperature was considered and optimized on  $65^\circ\text{C}$ . The amount of 5 mol% of ligand  $L_2$  is employed in the presence of the minimum amount of  $\text{PdCl}_2$ . The results showed that in the absence of the ligand the yield of the reaction decreased significantly.

**2.5a Effect of the mol% of Palladium chloride on the reaction:** In order to gauge the performance of our ligand system, we decided to employ the minimum amount of palladium chloride in the presence of ligands system. Three mol% of palladium chloride were employed and the results were showed that by using the 0.5 mol% of palladium chloride, high yield was achieved (Table 1). The Suzuki-Miyaura coupling of aryl halides has been reported by many research groups that employed different mol% of Pd-catalyzed systems from the minimum amount of 0.1

**Table 1.** Suzuki-Miyaura condensation of phenylboronic acid and 4-bromotoluene in methanol, at reflux conditions by using 5 mol% of ligand  $L_2$ .

Entry	Catalyst	Catalyst (mol%)	Time (min)	Yield (%)
1	$\text{PdCl}_2$	0.1	120	60
2	$\text{PdCl}_2$	0.3	120	68
3	$\text{PdCl}_2$	0.5	120	80

mol% to a large amount of Pd complexes. For example, Buchwald and co-workers had reported high quantities of catalyst (2–3 mol%).<sup>34</sup> Rao, Gyandshwar Kumar and co-workers proposed 2 mol% of Pd-catalyst for this coupling.<sup>35</sup> Pankaj Nehra and co-workers used the ionic Schiff base complexes in Suzuki-Miyaura coupling, by using 0.1% mol catalyst in the presence of  $\text{K}_2\text{CO}_3$  in coupling of I, Br aryls with the yields 70–89%.<sup>36</sup> Whaghmode and Borhade investigated the Pd-Salen complexes as catalysts in Suzuki reaction of aryl iodides and aryl bromides in 1:1 DMF: water ratio,  $\text{Na}_2\text{CO}_3$  as base 0.5 mol% Pd-Salen complex at  $90^\circ\text{C}$ .<sup>37, 38</sup> They found that the Suzuki reaction of aryl iodides and bromides give excellent yields (37–100%) of products in short reaction times (10–60 min). Anindita Dewan and co-workers introduced some catalytic system based on Pd complex of tetradentate Schiff base ligands that efficiently converts the aryl bromides up to 95%.<sup>39</sup> Some other research work have been provided in the reference section in which they used Schiff base Pd-complexes to convert aryl iodides or aryl bromides with moderate to high yields.<sup>40–42</sup> In comparison to these reports, the efficiency of our system is appreciable and this system showed medium to high efficiency with respect to catalyst amount usage and reaction conditions.

**2.5b Effect of solvent:** Despite the fact that literature presented a protocol for the Suzuki-Miyaura reaction in different media, the preparation of the ligand as pre-catalyst for complexation with Palladium is not a simple and benign reaction.<sup>43–45</sup> The effect of different solvents such as methanol, ethanol, acetonitrile, acetone, THF/ $\text{H}_2\text{O}$  and carbon tetrachloride were studied on the model reaction at room temperature. The results are given in Table 2.

Among these solvents, methanol was found to have better results than the aprotic or non-polar solvents.

**2.5c Effect of the ligands on the reaction:** The model reaction of phenylboronic acid and 4-bromotoluene was selected for the Suzuki-Miyaura reaction in this

**Table 2.** Effect of the solvent on the model reaction of the Suzuki-Miyaura condensation in the presence of ligand L<sub>2</sub>.

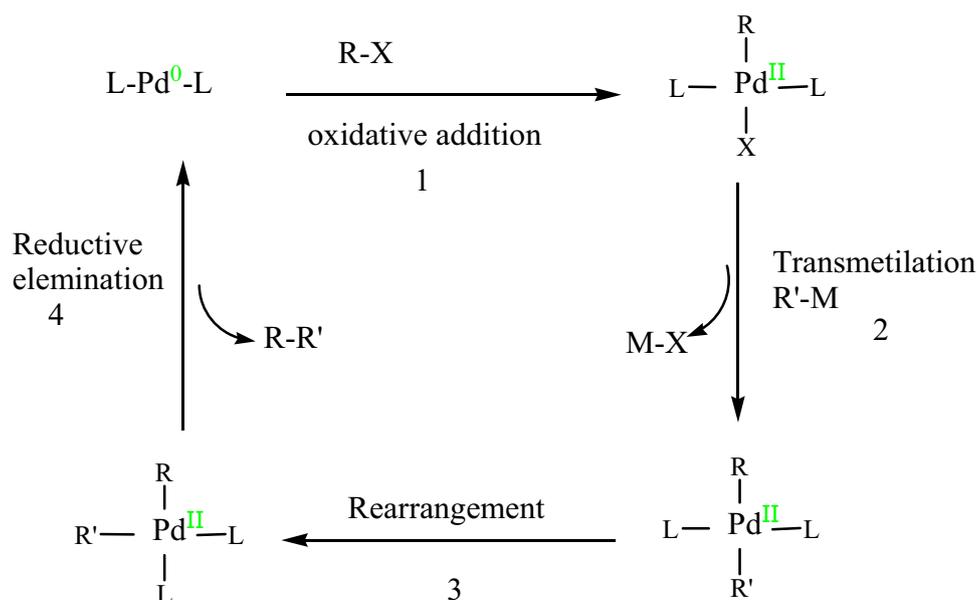
Entry	Solvent	Temperature (°C)	Time (min)	Yield%
1	H <sub>2</sub> O	r.t	120	30
2	H <sub>2</sub> O/THF	r.t	120	50
3	MeOH	r.t	120	80
6	EtOH	r.t	120	65
7	CH <sub>3</sub> CN	r.t	120	55
8	CCl <sub>4</sub>	r.t	120	No reaction
9	(CH <sub>3</sub> ) <sub>2</sub> CO	r.t	120	No reaction

**Table 3.** Suzuki-Miyaura condensation of phenylboronic acid and 4-bromotoluene in methanol, at reflux conditions.

Entry	Additive	Time (min)	Yield (%)
1	Ligand L <sub>2</sub>	120	80
2	Ligand L <sub>1</sub>	120	60
3	Non-ligand	120	40

presented catalyst system. By using the L<sub>1</sub> and L<sub>2</sub> ligands in the present methodology, the applied mol% of PdCl<sub>2</sub> and reaction time were reduced in high yield of the reaction. As it is observed in Table 3, although L<sub>1</sub> and L<sub>2</sub> ligands enhanced the yield of the reaction, the ligand L<sub>2</sub> was more effective than the ligand L<sub>1</sub>. The mechanism of the ligand-assisted Suzuki-Miyaura reaction was given in ref<sup>30</sup> in a similar to many other pieces of research (Scheme 3). It has been mentioned that the role of the ligand in the ligand

assisted Suzuki-Miyaura reaction is not straightforward and this mechanism has been given on the computational studies. The catalytic cycles involve the steps of: *in situ* generation of the L-Pd(0), transmetalation involving the exchange of halide for an aryl group and, reductive elimination of diaryl from Pd(II) species. By considering this mechanism, it could be suggested that additives which accelerate these steps can improve the performance of the catalytic system. The effect of the ligands could be remarkable in step 1 of the catalytic cycle. The ionic character of the catalysts providing an efficient media for oxidative addition of R-X on ligand assisted Pd-catalyst system. At this step, the ligand L<sub>2</sub> could accelerate this step by the counter ion Na<sup>+</sup>. It could be proposed that the separation of the X<sup>-</sup> (halide) from the substrate could be easier by interaction of Na<sup>+</sup> by using ligand L<sub>2</sub> while, the Cl<sup>-</sup> (counter ion of the imidazolium moiety) of the ligand L<sub>1</sub> competes with the R-X in coordinating to PdCl<sub>2</sub> in step 1, thus decreases the activity of the PdCl<sub>2</sub>. So the ligand L<sub>2</sub> should be more effective than ligand L<sub>1</sub>.

**Scheme 3.** Pd catalysis mechanism in Suzuki-Miyaura coupling.

**Table 4.** Effect of temperature on the model reaction of the Suzuki-Miyaura condensation in the presence of ligand L<sub>2</sub> in methanol.

Entry	Time (min)	Yield (%)	Temperature (°C)
1	120	69	40
2	120	72	60
3	120	80	65

**2.5d Effect of temperature:** The effect of temperature on the Suzuki-Miyaura was considered on the methanol in the presence of ligands L<sub>1</sub> and L<sub>2</sub> (Table 4). Results showed that yield% was enhanced by increasing the temperature to 65 °C. Considering technical limitations, the lower temperature for the reaction is one of the main concerns of synthesis in chemistry. The number of literature that reports the Suzuki-Miyaura condensation in high temperature and even long reaction time is enormous.<sup>46-52</sup> The refluxed temperature of methanol is 65 °C, so the optimized reaction temperature in the mixture of Methanol/H<sub>2</sub>O was set at 65 °C and the obtained results were acceptable.

**2.5e Effect of aryl halides on the condensation with boronic acid:** In this protocol, a series of aryl

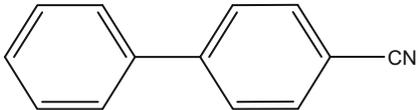
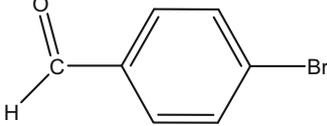
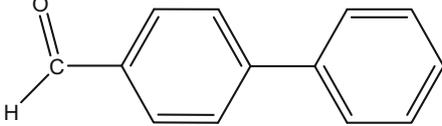
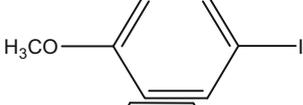
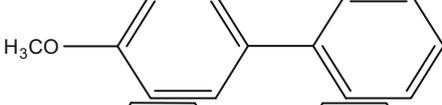
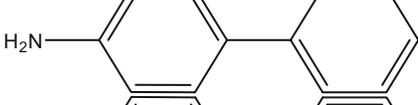
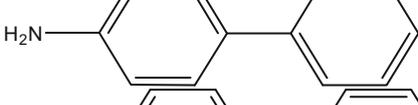
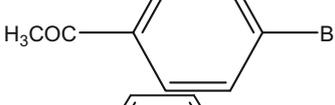
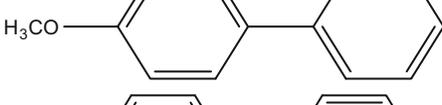
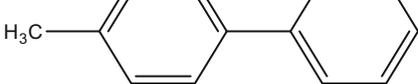
halides bearing electron-donating or withdrawing substituents are applied that provided substituted biphenyls. Although this method is effective for both aryl halides with donating or withdrawing electron, the yields in the reaction of aryl halides containing electron-donating substituents were comparatively better than the yields by the reaction of aryl halides bearing electron-withdrawing groups. Moreover, the nature of halides on aryl halides was the important factor for the reactivity and the yield of the Suzuki-Miyaura condensation. Aryl halides containing I and Br atoms showed good to excellent yield than aryl halides with F<sup>-</sup> and Cl<sup>-</sup>, because those are better-leaving groups (Table 5).

Although calculated turnover numbers are not very good in comparison with other turnover numbers reported in the Suzuki-Miyaurareactions<sup>53</sup> considering the benign reaction conditions, easy workup and short reaction time proposed in this paper, and introducing a new Schiff base compound as a capable promoter catalyst for Suzuki-Miyaura reaction is outstanding (Table 6).

## 2.6 Characterization of the reaction products

After completion of the reaction, the reaction was diluted with distilled water. The extraction of the organic phase was

**Table 5.** Suzuki Coupling of different Aryl Bromides.

Entry	Aryl halide	Product	Time (min)	Yield	TON	M.p. (°C)
1			120	88	176	>250
2			120	75	150	182
3			120	78	156	145
4			120	80	160	139
5			120	75	150	190
6			120	70	140	165
7			120	80	160	185

**Table 6.** Reported turnover frequencies for Suzuki-Miyaura reaction.

Entry	Solvent	mol% Catalyst	Time	Yield	TON	Ref.
1	H <sub>2</sub> O	0.1	20 h	70	70	54
2	PEG 300	5	24 h	83	83	55
3	EtOH	5	24 h	85	17	55
4	Methanol	0.5	2 h	80	160	This study

done with diethyl ether. The extracted phase was evaporated and purified by column chromatography. The melting point of the products was compared with the melting points that were reported in the literature and the <sup>1</sup>H NMR confirmed the products.

2.6a *NMR spectra of the products:* <sup>1</sup>H NMR spectra of the products were exactly according to the reports in the literature.

4-methyl-biphenyl. <sup>1</sup>H NMR (CDCl<sub>3</sub>), 7.68–7.65 (m, 2H), 7.59–7.57 (m, 2H), 7.52–7.48 (m, 2H), 7.42–7.38 (m, 1H), 7.34–7.32 (m, 2H), 2.47 (s, 3H).

4-methoxybiphenyl. <sup>1</sup>H NMR (CDCl<sub>3</sub>), 7.68–7.65 (m, 2H), 7.59–7.57 (m, 2H), 7.52–7.48 (m, 2H), 7.42–7.38 (m, 1H), 7.34–7.32 (m, 2H), 2.47 (s, 3H).

4-phenylbenzotrile. <sup>1</sup>H NMR (DMSO), 7.22–7.20 (m, 2H), 7.07–7.10 (m, 2H), 7.22 (s, 1H), 6.95–6.98 (m, 2H).

4-aminobiphenyl. <sup>1</sup>H NMR (CDCl<sub>3</sub>), 6.46 (s, 2H), 6.50–6.52 (m, 2H), 7.39–7.42 (m, 2H), 7.48–7.53 (m, 2H), 7.59–7.63 (m, 2H), 7.25 (s, 1H).

4-Phenylacetophenone. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.85 (d, 2 H), 7.63 (d, 2 H), 7.58 (d, 2 H), 7.40–7.37 (m, 3 H), 2.63 (s, 3 H).

### 3. Results and Discussion

#### 3.1 Synthesis of ligands

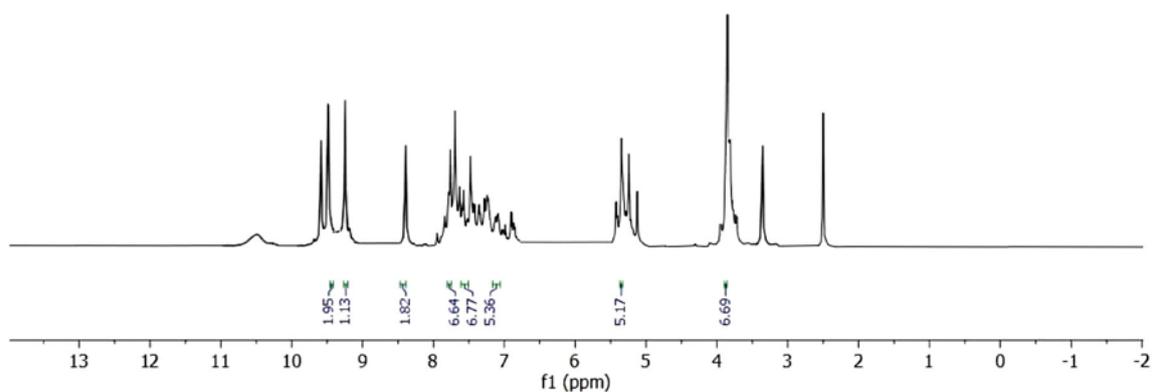
S<sub>1</sub> and S<sub>2</sub> were prepared as described elsewhere.<sup>32,56</sup> The synthesis of ionic Schiff base ligands of the L<sub>1</sub> and ligand L<sub>2</sub> were carried out by condensation reaction of the prepared (cationic and/or anionic) salicylaldehyde and phenylendiamine in methanol in refluxed condition (Scheme 1). The synthesized compounds were characterized *via* different spectral and analytical methods.

3.1a *IR spectra:* In the FT-IR Spectra of S<sub>1</sub> and S<sub>2</sub>, a characteristic band was seen at 1650 and 1660 cm<sup>-1</sup> for C=O bonds of aldehydic group, respectively. The absorption of the O-H bond for these aldehydes was exhibited at the region 3500–3600 cm<sup>-1</sup>. In the FT-IR spectra of the L<sub>1</sub> and L<sub>2</sub> these aldehydic carbonyl bands disappeared and a new band appeared in each

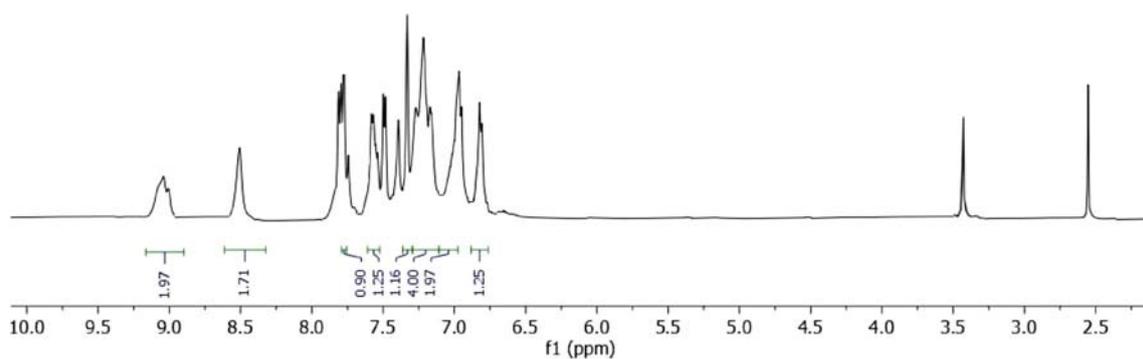
spectrum of the L<sub>1</sub> and L<sub>2</sub>, at 1630 and 1620 cm<sup>-1</sup>, respectively, due to new imine (C=N) bond formation during the condensation reaction of aldehydes and phenylendiamine. The absorptions of the O-H bonds for Schiff base ligands appeared at 3430–3455 cm<sup>-1</sup>

3.1b *NMR spectra:* The <sup>1</sup>H-NMR spectrum of ligand L<sub>1</sub> and ligand L<sub>2</sub> gives useful information for approval of the structures. For the L<sub>1</sub>, the peaks in the region of the 9.5–11.0 ppm are related to imine-amine tautomerization due to the interaction of the proton of phenol with the imine nitrogen. The resonances of the iminic protons were also observed in the region of 8.3–9.4 ppm. L<sub>1</sub> has three phenyl groups and two imidazole rings and is expected to have multiple signals in the aromatic region. In the <sup>1</sup>H-NMR spectrum, in region 6.81–7.72 ppm multiple resonances are observed. The resonances at 5.43 and 5.39 ppm are related to the 4H of the methylene groups. The resonance at 3.89 ppm is related to the 6H of the two methyl groups of the imidazole rings.

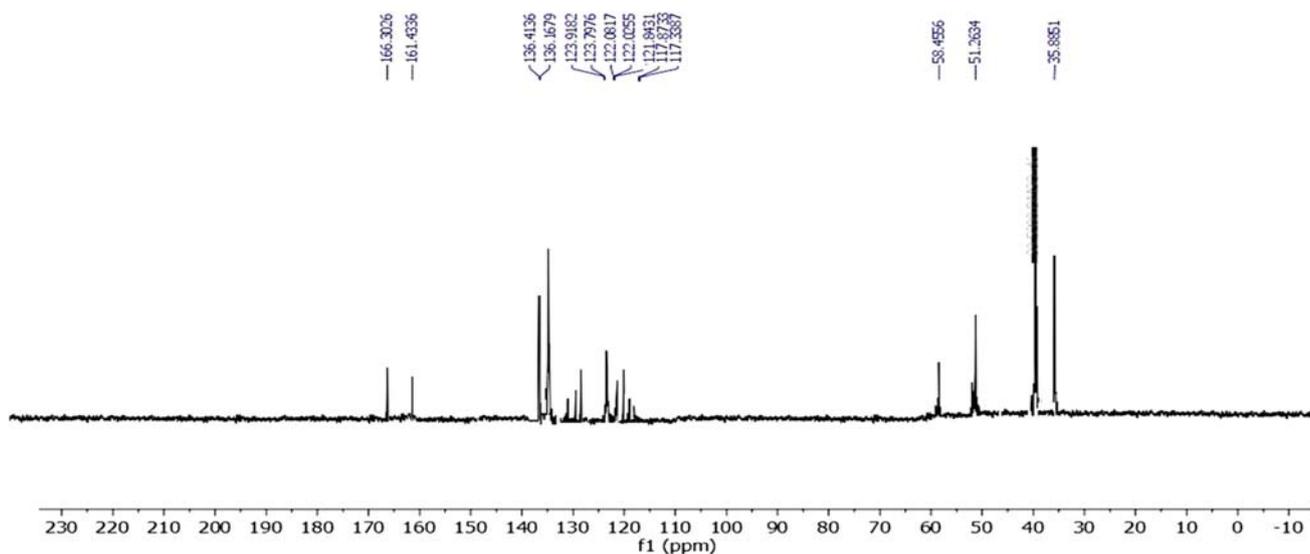
The broad resonance at 9.12 ppm is related to the OH protons. The resonance at 8.50 ppm is related to the 2H from the two imine groups. In similar to the ligand L<sub>1</sub>, the ligand L<sub>2</sub> has multiple signals in the aromatic region because of the three phenyl groups, so the resonances at region 6.86–8.00 ppm are related to the protons of the aromatic rings. The observed sharp resonance at 8.55 ppm and the broad resonance at 9.00–9.25 ppm are attributed to the iminic and phenolic protons of L<sub>2</sub>, respectively. The <sup>1</sup>H-NMR spectra of ligand L<sub>1</sub> and ligand L<sub>2</sub> are shown in Figure 1 and Figure 2, respectively. The <sup>13</sup>C-NMR of the ligand L<sub>1</sub> and ligand L<sub>2</sub> are given in Figure 3 and Figure 4, respectively. For Ligand L<sub>1</sub> the 14 resonances of 35.88, 51.26, 58.45, 117.33, 117.87, 121.84, 122.02, 122.08, 123.79, 123.91, 136.16, 136.41, 161.43 and 166.30 ppm were observed. These resonances are completely consistent with the 14 kind carbons in the ligand L<sub>1</sub> that confirm the structure of the L<sub>1</sub> ligand. The low resonances of 35.81 ppm, 51.26 ppm are related to the carbon of methyl on



**Figure 1.**  $^1\text{H-NMR}$  of ligand  $L_1$ .



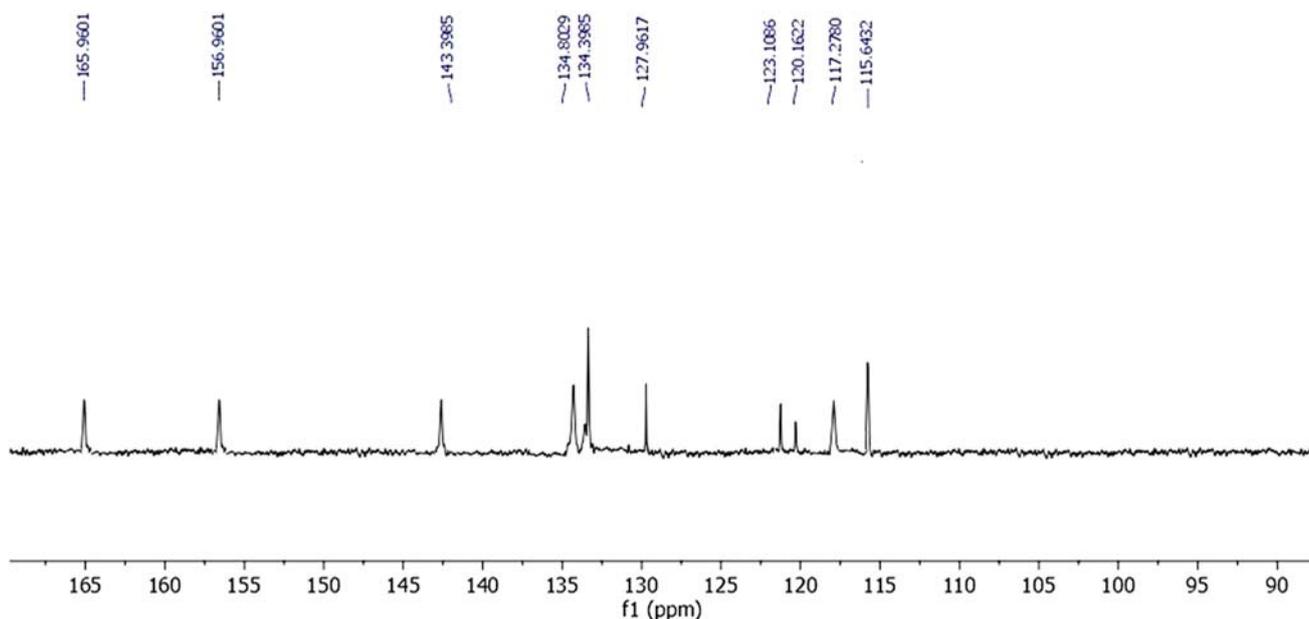
**Figure 2.**  $^1\text{H-NMR}$  of ligand  $L_2$ .



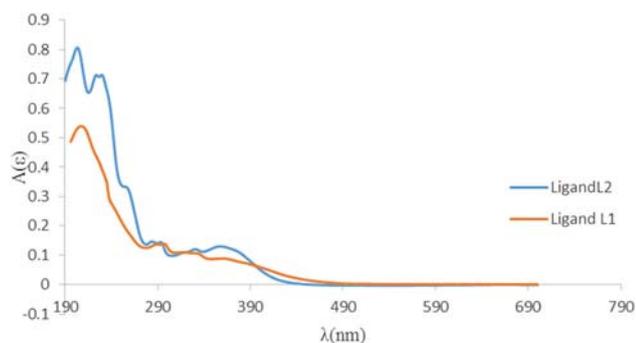
**Figure 3.**  $^{13}\text{C-NMR}$  of ligand  $L_1$ .

imidazole and methylene of benzylic carbon. Whereas, the resonance in 161.43 ppm and 166.30 ppm are attributed to the Carbon-Nitrogen bond (C=N) and

phenolic carbon (C-OH), respectively. The other resonances are for aromatic carbons in phenyl and imidazole rings. For  $L_2$  ligand the resonances of 115.64,



**Figure 4.**  $^{13}\text{C}$ -NMR of ligand  $\text{L}_2$ .



**Figure 5.** UV-visible spectra of Ligand  $\text{L}_1$  and ligand  $\text{L}_2$ .

117.27, 120.16, 123.10, 127.96, 134.39, 134.80, 143.39, 156.96 and 165.96 ppm that finally attributed to the 10 kind carbons in the  $\text{L}_2$  ligand are observed. In this ligand, the last two resonances (156.96 and 165.96 ppm) are with respect to the carbon of imin ( $-\text{C}=\text{N}$ ) and carbon of phenol ( $\text{C}-\text{OH}$ ), respectively, and the other resonances are related to the aromatic carbons.

**3.1c UV-visible spectra:** Since ligand  $\text{L}_1$  and ligand  $\text{L}_2$  are water-soluble, the UV-visible of them were recorded in  $\text{H}_2\text{O}$ . The UV-visible spectrum of the  $\text{L}_2$  showed two bands at 200 and 225 for  $\pi \rightarrow \pi^*$  and 385 nm and  $n \rightarrow \pi^*$  transitions, respectively, while for  $\text{L}_1$  these two bands are seen at 220 and 364 nm, respectively. The UV-visible spectra are shown in (Figure 5).

**3.1d Mass spectrometry:** For further characterization of the ligands ( $\text{L}_1$  and  $\text{L}_2$ ), the mass

spectrometry was also used. Mass spectrometric data of  $\text{L}_1$  approved the structure of the ligand. In mass spectrometry, in some cases, the ion-molecule shows very low intensity or in rare cases it is not seen.<sup>57</sup> In addition, the molecular ion is seen in lower or higher  $m/z$  than the original molecule with losing or abstracting of one or more protons.<sup>58</sup> The molecular weight of ligand  $\text{L}_1$  ( $\text{C}_{30}\text{H}_{30}\text{Cl}_2\text{N}_6\text{O}_2$ ) is 577, and the molecular ion of the  $\text{L}_1$  with  $M/z^+ = 577.6$  is observed in the spectrum at (Figure 6). There are some main signals with the  $m/z$  of 480, 300, 284, 224, 183, 132 and 82. Although there are many picks with low abundance, it is focused on the indicator picks that confirm the structure. The pick at  $m/z$  480 is related to the molecular ion by losing of one methyl imidazole ring ( $\text{C}_{25}\text{H}_{23}\text{Cl}_2\text{N}_4\text{O}_2$ ). As a consequence, the signal at  $m/z$  300 is related to the residual molecular ion without another methyl imidazole ring with the other chlorine counter ion plus one hydroxyl group ( $\text{C}_{20}\text{H}_{16}\text{N}_2\text{O}$ ) and, the loss of another hydroxyl group gives the signal at  $m/z$  284. The signal at  $m/z = 132$  is related to the phenyldiamine and a signal at  $m/z = 82$  is related to methyl imidazole group. For ligand  $\text{L}_2$ , mass spectrometric data shows the molecular weight of ligand  $\text{L}_2$  ( $\text{C}_{20}\text{H}_{14}\text{N}_2\text{Na}_2\text{O}_8\text{S}_2$ ) at  $M+2(522)$ , and the exact mass of the ligand  $\text{L}_2$  is 520. The spectrum is shown in (Figure 7). There are some main signals at  $m/z$  of 497, 474, 397, 313, 299, 285, 194, 119, 108, 77 and 43 that determine the structure of the ligand. Signals at  $m/z$  497 and 474 are related to the molecular ions by losing one and two

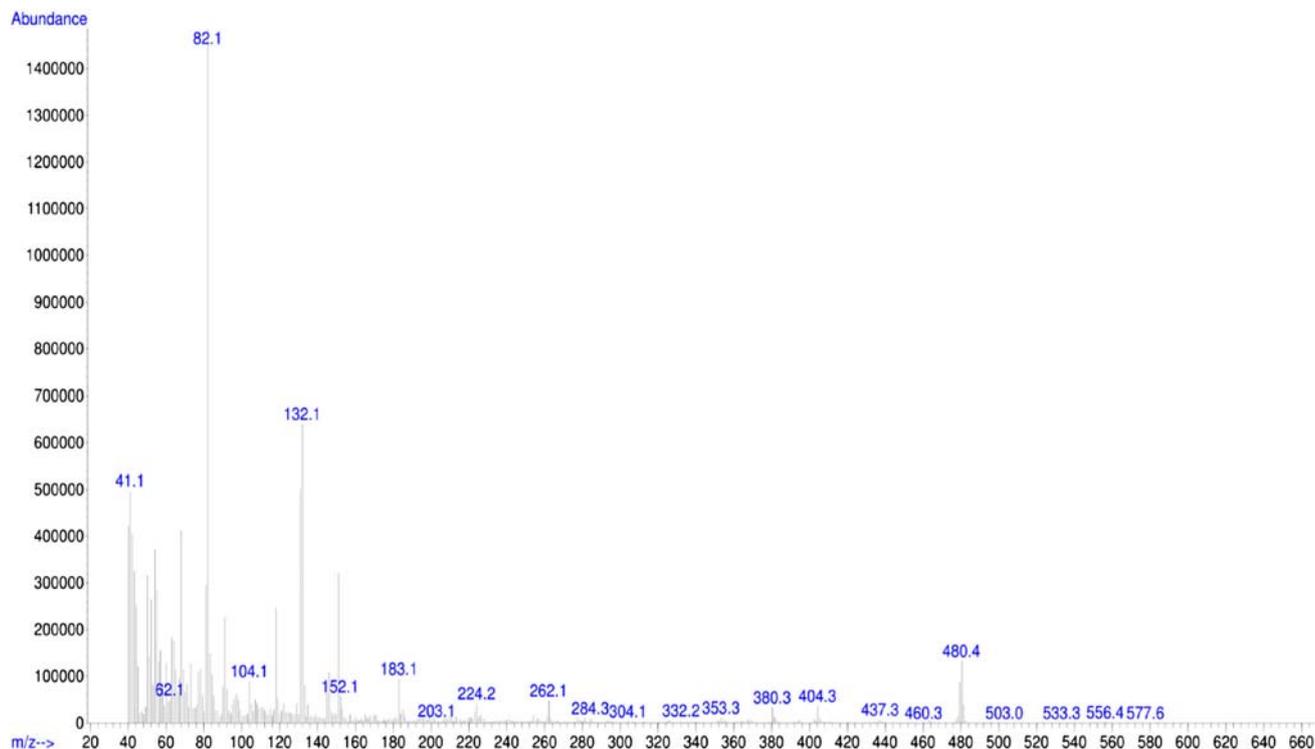


Figure 6. Mass spectra of ligand L<sub>1</sub>.

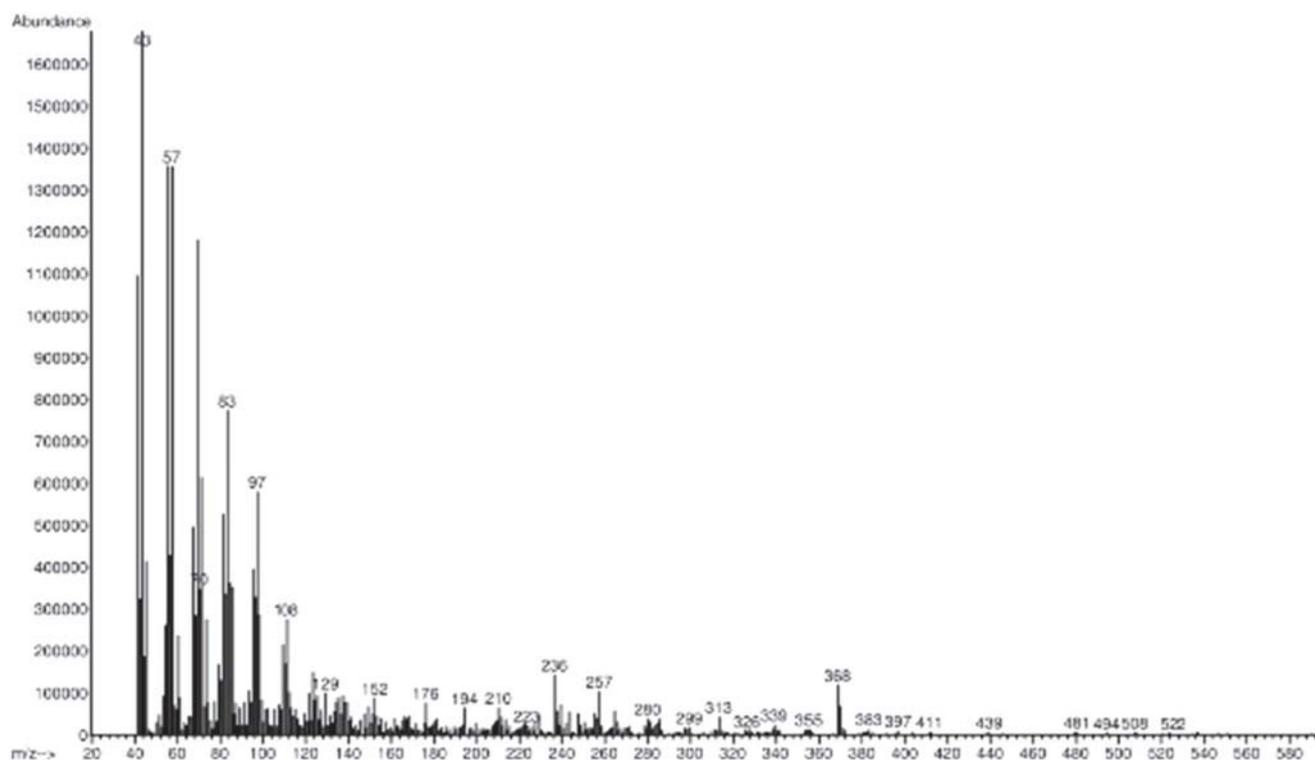


Figure 7. Mass spectra of ligand L<sub>2</sub>.

Na. The  $m/z = 397$  is related to the molecular ion by loss of one of the sulfonyl group. The pick at  $m/z = 299$  is related to the residual molecular ion without

another sulfonyl group and one of the hydroxyl group. This fragment would be a radical cation with one oxygen atom ( $C_{20}H_{15}N_2O^+$ ). Signals at  $m/z = 285$  are

related to ( $C_{20}H_{16}N_2$ ) and the  $m/z = 194$  is related to the residual molecular ion by losing of ( $C_6H_5CH^{+2}$ ) group. At the  $m/z = 108$ , there is a signal which is related to the phenylendiamine ( $C_6H_8N_2$ ). The peaks at  $m/z = 77$  and  $43$  are related to the phenyl group and allyl group of the aromatic ring.

#### 4. Conclusions

In this study, two active catalyst system for Suzuki-Miyaura coupling of aryl halides based on ionic Schiff base ligands, which are easily prepared have been developed. A comparison of catalytic activity of  $PdCl_2$  in the presence of these two ligands have been made and was found that the catalyst in the presence of anionic Schiff base ligand was more effective. The effect of different parameters on the rate and yield of the reaction has been considered and the optimized system has been introduced. The Suzuki-Miyaura reaction can be carried out by the Palladium Chloride lonely, but because of the value and costliness of the Palladium, a way to save the precious catalyst by introducing the Schiff base ligand have been presented. Thus, the simplicity in synthetic route for preparation of the ionic Schiff base ligands in this research, using low amount of catalyst (0.5 mol%) as well as medial to high yields and moderate reaction conditions for the Suzuki-Miyaura coupling of aryl bromides and iodides can be introduced as the advantages of the titled catalytic system in this research.

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#### References

- Miyaura N, Yamada K and Suzuki A 1979 A new stereospecific cross-coupling by the palladium-catalyzed reaction of 1-alkenylboranes with 1-alkenyl or 1-alkynyl halides *Tetrahedron Lett.* **20** 3437
- Miyaura N 2002 Cross-coupling reaction of organoboron compounds via base-assisted transmetalation to palladium(II) complexes *J. Organomet. Chem.* **653** 54
- Leadbeater N E and Marco M 2003 Rapid and amenable Suzuki coupling reaction in water using microwave and conventional heating *J. Org. Chem.* **68** 888
- Leadbeater N E and Smith R 2006 Real-time monitoring of microwave-promoted Suzuki coupling reactions using in situ Raman spectroscopy *Org. Lett.* **8** 4589
- Huang R and Shaughnessy K H 2006 Water-soluble palladacycles as precursors to highly recyclable

- catalysts for the Suzuki coupling of aryl bromides in aqueous solvents *Organometallics* **25** 4105
- Marziale A N, Jantke D, Faul S H, Reiner T, Herdtweck E and Eppinger J 2011 An efficient protocol for the palladium-catalysed Suzuki-Miyaura cross-coupling *Green Chem.* **13** 169
- Li S, Lin Y, Cao J and Zhang S 2007 Guanidine/Pd(OAc)<sub>2</sub>-catalyzed room temperature Suzuki cross-coupling reaction in aqueous media under aerobic conditions *J. Org. Chem.* **72** 4067
- Cohen A, Crozet M D, Rathelot P and Vanelle P 2009 An efficient aqueous microwave-assisted Suzuki-Miyaura cross-coupling reaction in the thiazole series *Green Chem.* **11** 1736
- Blakemore J D, Chalkley M J, Farnaby J H, Guard L M, Hazari N, Incarvito C D, Luzik Jr E D and Suh H W 2011 New bidentate trans-chelating N-heterocyclic carbene ligands for palladium *Organometallics* **30** 1818
- Türkmen H, Pelit L and Cetinkaya B J 2011 Synthesis And Exploration Of Catalytic Potentials Of Palladium Complexes With Symmetrical and Unsymmetrical Schiff Base Ligands *J. Mol. Catal. A: Chem.* **348** 88
- Ogo S, Takebe Y, Uehara K, Yamazaki T, Nakai H, Watanabe Y and Fukuzumi S 2006 pH-Dependent C-C Coupling Reactions Catalyzed by Water-Soluble Palladacyclic Aqua Catalysts in Water *Organometallics* **25** 331
- Ines B, San Martin R, Churrua F, Dominguez E, Urtiaga M K and Arriortua M I 2008 A nonsymmetric pincer-type palladium catalyst in Suzuki, Sonogashira, and Miyama couplings in neat water *Organometallics* **27** 2833
- Dewan A, Buragohain Z, Mondal M, Sarmah G, Borah G and Bora U 2014 Acetanilide palladacycle: an efficient catalyst for room-temperature Suzuki-Miyaura cross-coupling reaction *Appl. Organomet. Chem.* **28** 230
- Mondal M, Dewan A, Begum T, Gogoi P K, Thakur A J and Bora U 2016 Suzuki-Miyaura Cross-Coupling in Aqueous Medium Using Recyclable Palladium/Amide-Silica Catalyst *Catal. Lett.* **146** 1718
- Dewan A 2014 A Highly Efficient and Inexpensive Palladium-Salen Complex for Room Temperature Suzuki-Miyaura Reaction *Bull. Korean. Chem. Soc.* **35** 1855
- Begum T, Mondal M, Borpuzari M P, Kar R, Kalita G, Gogoi P K and Bora U 2017 An immobilized symmetrical bis-(NHC) palladium complex as a highly efficient and recyclable Suzuki-Miyaura catalyst in aerobic aqueous media *Dalton Trans.* **46** 539
- Mondal M and Bora U 2016 Eco-friendly Suzuki-Miyaura coupling of arylboronic acids to aromatic ketones catalyzed by the oxime-palladacycle in bio solvent 2-Me THF *New J. Chem.* **40** 3119
- Sarmah G and Bora U 2015 Simple aminobenzoic acid promoted palladium catalyzed room temperature Suzuki-Miyaura cross-coupling reaction in aqueous media *Tetrahedron Lett.* **56** 2906
- Begum T, Mondal M, Gogoi P K and Bora U 2015 Palladium-Schiff-base-silica framework as a robust and recyclable catalyst for Suzuki-Miyaura cross-coupling in aqueous media *RSC Adv.* **5** 38085
- Mondal M and Bora U 2014 O-Aryloxime ether analogues as novel and efficient ligands for palladium-

- catalyzed Suzuki–Miyaura coupling in water *Tetrahedron Lett.* **55** 3038
21. Kumbhar A, Jadhav S, Kamble S, Rashinkar G and Salunkhe R 2013 Palladium supported hybrid cellulose–aluminum oxide composite for Suzuki–Miyaura cross-coupling reaction *Tetrahedron Lett.* **54** 1331
  22. Jadhav S N, Kumbhar A S, Rode C V and Salunkhe R S 2016 Ligand-free Pd catalyzed cross-coupling reactions in an aqueous hydrotropic medium *Green Chem.* **18** 1898
  23. Santhosh M, Nagendra Prasad H, Nagashree S, Manukumar H, Mallesh L and Mallu P 2019 Synthesis and characterization of Schiff base analogues of fluoroaniline and their antibioid activity against MRSA *Curr. Chem. Lett.* **8** 169
  24. Shivakumara N and Krishna P 2019 5-[Substituted]-1, 3, 4-thiadiazol-2-amines: Synthesis, Spectral Characterization, and Evaluation of their DNA interactions *Curr. Chem. Lett.* **8** 157
  25. Subbaiyan S and Ponnusamy I 2019 Biological investigations of ruthenium (III) 3-(Benzothiazol-2-yliminomethyl)-phenol Schiff base complexes bearing PPh<sub>3</sub>/AsPh<sub>3</sub> coligand *Curr. Chem. Lett.* **8** 145
  26. Sinha B, Bhattacharya and Saha S 2019 Transition metal complexes obtained from an ionic liquid-supported Schiff base: synthesis, physicochemical characterization and exploration of antimicrobial activities *J. Chem. Sci.* **131** 19
  27. Barwiolek M, Szczyński R and Szyk E 2016 Copper (II) Schiff base complexes and their mixed thin layers with ZnO nanoparticles *J. Chem. Sci.* **128** 1057
  28. Saha S, Basak G and Sinha B 2018 Physico-chemical characterization and biological studies of newly synthesized metal complexes of an Ionic liquid-supported Schiff base: 1-[2-[(2-hydroxy-5-bromobenzylidene) amino] ethyl]-3-ethylimidazolium tetrafluoroborate *J. Chem. Sci.* **130** 9
  29. Dharani S, Kalaiarasi G, Sindhuja D, Lynch V M, Shankar R, Karvembu R and Prabhakaran R 2019 Tetranuclear Palladacycles of 3-Acetyl-7-methoxy-2H-chromen-2-one Derived Schiff Bases: Efficient Catalysts for Suzuki–Miyaura Coupling in an Aqueous medium *Inorg. Chem.* **58** 8045
  30. Das P and Linert W 2016 Schiff base-derived homogeneous and heterogeneous palladium catalysts for the Suzuki–Miyaura reaction *Coord. Chem. Rev.* **315** 1
  31. Kotha S, Lahiri K and Dhurke K 2002 Recent applications of the Suzuki–Miyaura cross-coupling reaction in organic synthesis *Tetrahedron* **58** 9633
  32. Hager E B, Makhubela B C and Smith G S 2012 Aqueous-phase hydroformylation of 1-octene using hydrophilic sulfonate salicylaldimine dendrimers *Dalton Trans.* **41** 13927
  33. Glaser T, Heidemeier M, Fröhlich R, Hildebrand P, Bothe E and Bill E 2005 Trinuclear nickel complexes with tripalsen ligands: simultaneous occurrence of mixed valence and valence tautomerism in the oxidized species *Inorg. Chem.* **44** 5467
  34. Wolfe J P, Singer R A, Yang B H and Buchwald S L 1999 Highly active palladium catalysts for Suzuki coupling reactions *J. Am. Chem. Soc.* **121** 9550
  35. Rao G K, Kumar A, Kumar B, Kumar D and Singh A K 2012 Palladium (II)-selenated Schiff base complex catalyzed Suzuki–Miyaura coupling: Dependence of efficiency on alkyl chain length of ligand *Dalton Trans.* **41** 1931
  36. Nehra P, Khungar B, Pericherla K, Sivasubramanian S C and Kumar A 2014 Imidazolium ionic liquid-tagged palladium complex: an efficient catalyst for the Heck and Suzuki reactions in aqueous media *Green Chem.* **16** 4266
  37. Borhade S R and Waghmode S B 2010 Studies on phosphine free Pd-salen complexes as effective catalysts for aqueous Suzuki reaction *Ind. J. Chem.* **49B** 565
  38. Borhade S R and Waghmode S B 2008 Phosphine-free Pd-salen complexes as efficient and inexpensive catalysts for Heck and Suzuki reactions under aerobic conditions. *Tetrahedron Lett.* **49** 3423
  39. Dewan A, Bora U and Borah G 2014 A simple and efficient tetradentate Schiff base derived palladium complex for Suzuki–Miyaura reaction in water *Tetrahedron Lett.* **55** 1689
  40. Lai Y C, Chen H Y, Hung W C, Lin C C and Hong F E 2005 Palladium catalyzed Suzuki cross-coupling reactions using N, O-bidentate ligands *Tetrahedron* **61** 9484
  41. Cui J, Zhang M and Zhang Y 2010 Amino-salicylaldimine–palladium (II) complexes: New and efficient catalysts for Suzuki and Heck reactions *Inorg. Chem. Commun.* **13** 81
  42. Liu F S, Huang Y T, Lu C, Shen D S and Cheng T 2012 Efficient salicylaldimine ligands for a palladium-catalyzed Suzuki–Miyaura cross-coupling reaction *Appl. Organomet. Chem.* **26** 425
  43. Huang R and Shaughnessy K H 2006 Water-soluble palladacycles as precursors to highly recyclable catalysts for the Suzuki coupling of aryl bromides in aqueous solvents *Organometallics* **25** 4105
  44. Mahamo T, Mogorosi M M, Moss J R, Mapolie S F, Slootweg J C, Lammertsma K and Smith G S 2012 Neutral palladium (II) complexes with P, N Schiff-base ligands: Synthesis, characterization and application as Suzuki–Miyaura coupling catalysts *J. Organomet. Chem.* **703** 34
  45. González-Arellano C, Corma A, Iglesias M and Sánchez F 2006 Gold (I) and (III) catalyze Suzuki cross-coupling and homocoupling, respectively *J. Catal.* **238** 497
  46. Phan N T, Brown D H and Styring P 2004 A polymer-supported salen-type palladium complex as a catalyst for the Suzuki–Miyaura cross-coupling reaction *Tetrahedron Lett.* **45** 7915
  47. Shahnaz N, Banik B and Das P 2013 A highly efficient Schiff-base derived palladium catalyst for the Suzuki–Miyaura reactions of aryl chlorides *Tetrahedron Lett.* **54** 2886
  48. Banik B, Tairai A, Shahnaz N and Das P 2012 Palladium (II) complex with a potential N4-type Schiff-base ligand as highly efficient catalyst for Suzuki–Miyaura reactions in aqueous media *Tetrahedron Lett.* **53** 5627
  49. Barder T E and Buchwald S L 2004 Efficient catalyst for the Suzuki–Miyaura coupling of potassium aryl trifluoroborates with aryl chlorides *Org. Lett.* **6** 2649
  50. Kumar A, Agarwal M, Singh A K and Butcher R J 2009 Palladium (II), platinum (II), ruthenium (II) and

- mercury (II) complexes of potentially tridentate Schiff base ligands of (E, N, O) type (E= S, Se, Te): Synthesis, crystal structures and applications in Heck and Suzuki coupling reactions *Inorg. Chim. Acta* **362** 3208
51. Baran T, Açiksöz E and Menteş A 2015 Carboxymethyl chitosan Schiff base supported heterogeneous palladium (II) catalysts for Suzuki cross-coupling reaction *J. Mol. Catal. A* **407** 47
52. Esmailpour M and Javidi J 2015 Magnetically-recoverable Schiff Base Complex of Pd (II) Immobilized on Fe<sub>3</sub>O<sub>4</sub>@ SiO<sub>2</sub> Nanoparticles: An Efficient Catalyst for Mizoroki-Heck and Suzuki-Miyaura Coupling Reactions *J. Chin. Chem. Soc.* **62** 614
53. Ishiyama T, Takagi J, Ishid K, Miyaura N, Anastasi N R and Hartwig J F 2002 Mild iridium-catalyzed borylation of arenes. High turnover numbers, room temperature reactions, and isolation of a potential intermediate *J. Am. Chem. Soc.* **124** 390
54. Diallo AK, Ornelas C, Salmon L, Ruiz Aranzaes J and Astruc D 2007 Homeopathic Catalytic Activity and Atom-Leaching Mechanism in Miyaura–Suzuki Reactions under Ambient Conditions with Precise Dendrimer-Stabilized Pd Nanoparticles *Angew. Chem. Int. Edit.* **46** 8644
55. de Souza A L F, Silva A D C and Antunes O A C 2009 Suzuki–Miyaura reactions in PEG–water solutions using Pd/BaSO<sub>4</sub> as catalytic source *Appl. Org. Chem.* **23** 5
56. Ali R, Saleh S M and Elshaarawy R F 2016 Turn-on pH nano-fluorosensor based on imidazolium salicylaldehyde ionic liquid-labeled silica nanoparticles *RSC Adv.* **6** 86965
57. Ebsworth E A V, DWH Rankin and S Cradock 1987 *Structural Methods in Inorganic Chemistry* 2<sup>nd</sup> edn. (Oxford: Blackwell Scientific Publications)
58. Talouki S A, Grivani G and Khalaji A D 2018 Six-coordinated vanadium (IV) complexes with tridentate task-specific ionic liquid Schiff base ligands: Synthesis, characterization and effect of ionic nature on catalytic activity *Appl. Org. Chem.* **32** e4078