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Palladium(II) complexes containing sterically bulky O, N donor ligands: Synthesis, characterization and catalytic activity in the Suzuki-Miyaura and Sonogashira coupling reactions

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### Palladium(II) Complexes Containing sterically bulky O, N Donor

### Ligands: Synthesis, Characterization and Catalytic activity in the Suzuki-

### **Miyaura and Sonogashira Coupling Reactions**

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### Abstract

A new class of palladium(II)1-(arylazo)naphtholate complexes of the type  $[Pd(L_{1-4})_2]$  containing sterically bulky O, N donor functionalized arylazo ligands has been synthesized. These palladium(II) complexes were characterized by elemental analysis and spectral (FT-IR, UV-Vis, <sup>1</sup>H-NMR and <sup>13</sup>C-NMR) studies. The molecular structure of the Palladium(II) complexes  $[Pd(L_1)_2]$  and  $[Pd(L_2)_2]$  were established by X-ray crystallography. These complexes were found to efficiently catalyze the Suzuki-Miyaura coupling of arylboronic acids and aryl halides, and the Sonogashira reaction of aryl halides and phenylacetylene in DMF and *i*-PrOH media to afford the corresponding C-C coupling products in high yields.

Keywords: Palladium(II) complexes; Bulkyazo ligands; X-ray structure; Suzuki-Miyaura reaction; Sonogashira reaction.

### **1. Introduction**

Arylazo ligands have important roles in coordination chemistry as they form stable complexes with most of transition metals [1-2]. Azo containing compounds are capable of stabilizing metals in formally low oxidation states [3, 4] and as redox non-innocent nature of the ligands; the metal complexes with azo-ligands have tunable redox properties [5]. Azo ligand with hard nitrogen, oxygen and soft sulphur donor atoms again have a tunable capability for coordinating with a wide range of metal ions, to give stable and intensely colored metal complexes [6]. Complexes of transition metals with azo ligands have interesting physical, chemical, photophysical, photochemical, catalytic and material properties [7,8].

Arylazo ligands provide a great platform in coordination/organometallic chemistry for development of ligand systems [9]. Most azo ligands are easily accessible using simple synthetic procedures with selection of an amine and substituted phenol. These ligands can potentially stabilize metals in different oxidation states which are particularly useful in catalytic reactions.

The palladium complexes have wide-spread application in syntheses and become one of the most powerful and convenient C–C, C-N bond forming processes in pharmaceutical chemistry, materials and synthetic chemistry [10]. Moreover, the metal complexes incorporating *ortho* substituted azo benzene ligands have versatile properties such as C-H activation [11, 12], C-C activation [13], C-C coupling [14], –N=N–bond cleavage [15], electron transfer reaction [16, 17], hydroxylation [18], isomerization [19], photoisomerization [20], cytotoxicity toward cancer cells and application in catalytic transformations [21].

Palladium-catalyzed cross-coupling reaction for the formation of carbon–carbon bonds has recently emerged as a powerful method in an organic synthesis. The palladium-catalyzed coupling [22] of an aryl halide with aryl boronic acid (Suzuki coupling) or terminal alkyne

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(Sonogashira coupling) is recognized as the most successful method for carbon–carbon bond forming reactions. Many catalytic systems have been developed for the Suzuki-Miyaura and Sonogashira cross-coupling reactions using different palladium catalysts such as Pd(PPh<sub>3</sub>)<sub>4</sub>, Pd(OAc)<sub>2</sub>, PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>, and PdCl<sub>2</sub>(CH<sub>3</sub>CN)<sub>2</sub> [23]. However, phosphine ligands used in these reactions are sensitive to air oxidation and thus require air-free conditions which pose significant inconvenience on synthetic applications [24]. Palladium(II) complexes containing nitrogen, oxygen donor ligands showed high catalytic activity in C-C coupling reaction than commercially used phosphine containing metal complexes. Further, nitrogen based ligands are popular in coordination chemistry because they are easily modified both sterically and electronically [25-27].

In the present work, we report the synthesis of Pd(II) complexes by the reaction of bulky *ortho, para* substituted 1-(arylazo)naphtholate ligands with  $[Pd(OAc)_2]$ . The molecular structure of  $[Pd(L_1)_2]$  **1** and  $[Pd(L_2)_2]$  **2** has been established using single crystal X- ray diffraction. The new complexes were fully characterized by FT-IR, UV-Vis, <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectral studies. The catalytic activity in Suzuki and Sonogashira coupling reactions of various aryl halides by these complexes has also been examined.

### 2. Results and Discussion

Treatment of 2:1 molar ratio of sterically bulky 1–(arylazo)naphthol ligands with  $[Pd(OAc)_2]$  in acetonitrile at room temperature for 4h afforded the new palladium(II) complexes of the general composition  $[Pd(L_{1-4})_2]$  (Scheme 1) in good yields. All the palladium complexes are air stable in both the solid and the liquid states at room temperature and are non–hygroscopic. The synthesized complexes are readily soluble in highly polar solvents such as dichloromethane

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and chloroform etc., producing intense red colored solutions. The analytical data of all the palladium(II) complexes are in good agreement with the proposed molecular structure.



Scheme 1. Synthesis of Palladium(II) 1-(arylazo)naphtholate complexes 1-4.

#### 2.1. Characterization of the complexes

The FT–IR spectra of the free ligands displayed v(N=N) strong absorptions in the region  $1443-1446 \text{ cm}^{-1}$  (Supporting information Fig S1-S4). The stretching frequency of v(N=N) was observed at a lower frequency in the complexes around the region  $1357-1390 \text{ cm}^{-1}$ , indicating the coordination of azo nitrogen to Pd(II) ion, due to reduction of electron density in the naphthol-azo link. The stretching vibration of phenolic oxygen is confirmed by the increase in v(C–O) at higher frequencies appear at  $1300-1313 \text{ cm}^{-1}$  in all the complexes [28–31].

The electronic spectra of all the palladium(II) complexes were recorded in chloroform and exhibited three bands with absorption maxima in the region 200–800 nm (Supporting information Fig S5). The absorption spectra of palladium(II) complexes exhibited very intense bands below 250–270 nm and 320–360 nm are assigned to ligand–centre transitions. The intense bands with absorption maxima in the region 430–455nm are assigned to metal to ligand chargetransfer (MLCT) transitions. A square planar geometry around palladium(II) centre has been proposed based on the pattern of electronic spectra of other square planar palladium(II) complexes [32–37].

The <sup>1</sup>H–NMR spectra of all the complexes were recorded in CDCl<sub>3</sub> to confirm the binding of 1–(arylazo)naphthol to palladium ion. All complexes showed multiplets in the respective region at  $\delta = 7.0 - 7.9$  ppm for the presence of all the aromatic protons of the ligands. The methyl protons of the complex **1** observed as singlet at  $\delta = 2.3$  ppm. Additionally, the isopropyl proton appears as doublet at  $\delta = 1.29$  ppm and methyl proton appear as septet at  $\delta = 3.12$  ppm respectively for complex **3**. The <sup>1</sup>H and <sup>13</sup>C NMR spectra are shown in Figs. S6 –S12 (Supporting information).

#### 2.2. X-ray structure

The solid-state structure of the palladium(II) complexes (1) and (2) was performed by single crystal X-ray diffraction method and the partial atom numbering scheme shown in **Fig. 1** & 2. X-ray data collection and structure refinement parameters for complexes were shown in **Table 1** and the selected bond lengths and bond angles were given in **Table 2**. Complexes 1 and 2 crystallized with monoclinic with space group P21/c, P21/n respectively. Subsequently, two compartments of azo monodentate ligands coordinated with Pd(II) ion *via* phenolate oxygen and azo nitrogen donor atoms forming six membered chelate rings. The selected bond lengths and bond angles (Table 2) of the palladium complexes exhibited perfect square planar geometry with N<sub>2</sub>O<sub>2</sub> coordination environment. Nevertheless, the perfect square planar geometry identified with the bite angles 180° for O(1)-Pd(1)-O(1) (complex 1) and N(2)-Pd(1)-N(2) (complex 2). In both

complexes, Pd(1)-O(1) bond length (1.981-1.967 Å) is shorter than Pd(1)-N(2) (2.000-2.003 Å) bond length, which were in the expected range for the previously reported [38].





Figure 2. The ORTEP diagram of the complex (2).

	1	2
Empirical formula	$C_{36} H_{30} N_4 O_2 Pd$	$C_{38} H_{34} N_4 O_2 Pd$
Formula weight	657.04	685.09
Temperature	296(2)	296(2)
Wavelength/ Å	0.71073 Å	0.71073 Å
Crystal system	monoclinic	monoclinic
Space group	P 21/c	P 21/n
a/ Å	11.4362(9) Å	11.3334(5) Å
b/ Å	17.4698(13) Å	12.3600(6) Å
c/ Å	16.6423(13) Å	12.2210(5) Å
α/°	90	90
β/°	107.094(2)	107.5880 (10)
$\gamma^{\prime \circ}$	90	90
Volume/ Å <sup>3</sup>	3178.1(4)	1631.90(13)
Z	4	2
Density (calculated)/ Mg/m <sup>3</sup>	1.373	1.394
Absorption coefficient/ mm <sup>-1</sup>	0.621	0.608
F(000)	1344	704
Crystal size/mm <sup>3</sup>	0.22 x 0.17 x 0.11	0.24 x 0.17 x 0.09
Theta range of data collection/°	1.166 to 29.213°	2.708 to 29.218
Reflections collected	40759	35090
Independent reflections	17251 [R(int) = 0.0301]	4424 [R(int) = 0.0462]
Data / restraints / parameters	14068 / 2 / 775	4410 / 0 / 205
Goodness-of-fit on F <sup>2</sup>	0.848	0.806
Final R indices [I>2sigma(I)]	R1 = 0.0381, $wR2 = 0.1172$	R1 = 0.0466, wR2 = 0.1655
R indices (all data)	R1 = 0.0766, wR2 = 0.1704	R1 = 0.0621, wR2 = 0.1967
Largest diff. peak / hole/ e.Å <sup>-3</sup>	0.282 and -0.359	1.213 and -0.489

 Table 1. Selected crystal data and structure refinement summary of complexes 1 and 2.

Distances/ angles	1	2
Pd(1)-O(1)	1.981(3)	1.967(2)
Pd(1)-N(2)	2.000(3)	2.003(2)
O(1)-C(1)	1.288(4)	1.283(3)
N(2)-N(1)	1.275(4)	1.281(3)
N(2)-C(11)	1.456(5)	1.452(4)
N(1)-C(10)	1.366(4)	1.369(3)
C(11)-C(12)	1.396(6)	1.387(4)
O(1)-Pd(1)-O(1)	180.0	180.0
O(1)-Pd(1)-N(2)	90.29(11)	88.52(9)
N(2)-Pd(1)-N(2)	180.0	180.00(5)
C(1)-O(1)-Pd(1)	124.1(2)	125.21(18)
N(1)-N(2)-C(11)	111.7(3)	111.6(2)
N(1)-N(2)-Pd(1)	128.1(2)	127.71(17)
C(11)-N(2)-Pd(1)	120.2(2)	120.49(19)
N(2)-N(1)-C(10)	123.1(3)	122.8(2)

Table 2. Selected bond lengths (Å) and angles (°) in complexes 1 and 2.

### 2.3. Catalytic Suzuki-Miyaura coupling reaction

Table 3. Optimization of the reaction condition<sup>a</sup>

I	$Br \longrightarrow NO_2 + \longrightarrow B(C)$	OH) <sub>2</sub> Catalyst 1 base/ reflux/ 5	$\rightarrow \qquad \qquad$		
Entry	Catalyst (mol%)	Solvent	Base	Yield <sup>b</sup> (%)	
1	1.0	DMF	K <sub>2</sub> CO <sub>3</sub>	99	
2	0.5	DMF	K <sub>2</sub> CO <sub>3</sub>	90	
3	0.2	DMF	K <sub>2</sub> CO <sub>3</sub>	88	
4	0.1	DMF	K <sub>2</sub> CO <sub>3</sub>	65	
5	0.01	DMF	K <sub>2</sub> CO <sub>3</sub>	50	
6	0.001	DMF	$K_2CO_3$	43	
7	0.0001	DMF	K <sub>2</sub> CO <sub>3</sub>	32	
8	1.0	Methanol	$K_2CO_3$	84	
9	1.0	Toluene	K <sub>2</sub> CO <sub>3</sub>	68	
10	1.0	THF	K <sub>2</sub> CO <sub>3</sub>	40	
11	1.0	DCM	K <sub>2</sub> CO <sub>3</sub>	36	
12	1.0	H <sub>2</sub> O	$K_2CO_3$	NR <sup>c</sup>	
13	1.0	DMF	NaOH	80	
14	1.0	DMF	КОН	88	
15	1.0	DMF	Na <sub>2</sub> CO <sub>3</sub>	90	
16	1.0	DMF	Et <sub>3</sub> N	60	

<sup>a</sup>Reaction conditions: 4-bromonitrobenzene (1mmol), phenylboronic acid (1.2mmol), base (1mmol), catalyst, solvent (5mL). <sup>b</sup>Isolated yields. <sup>c</sup>No reaction.

Initially, a brief screening of the base, catalyst loading and solvent was conducted by running a carbon-carbon coupling reaction of 4-bromonitrobenzene and phenylboronic acid (Table 3). After optimization, we found that 1mol% catalyst, 1mmol K<sub>2</sub>CO<sub>3</sub>, DMF as solvent and a reaction time 5h furnished a good yield of expected product.

Upon lowering the catalyst loading, the yield of the reaction also decreased significantly. Different bases were tested and the coupling products were obtained in good yields when  $K_2CO_3$  was used. Moderate yields were obtained in the cases of  $Na_2CO_3$ , KOH and NaOH and very low yield was obtained with Et<sub>3</sub>N. Using  $K_2CO_3$  as a base, different solvent were tested and the product were obtained in DMF.

A general catalytic cycle for the cross-coupling reaction of organoboron reagents with aryl halides involves an oxidative-addition of the aryl halide, transmetalation, and reductiveelimination steps [39, 40]. Aryl bromides with various functional groups efficiently reacted with boronic acids (entries 1-9) using  $K_2CO_3$  and 5 mL of DMF at reflux temperature in presence of palladium(II) complex **1** for 5 h to yield Suzuki-Miyaura products in good to excellent conversions. The conversion of 4–bromotoluene and 4–bromoanisole (entries 3 and 4) in to their corresponding biaryls compounds are 95% and 92% respectively. Substrate with electron withdrawing substituents such as NO<sub>2</sub> and CN (entries 2 and 5) gave excellent conversions of 99% and 85% respectively. In addition, the complex efficiently catalyzes the 4-chloro phenol and 4-bromo benzaldehyde (entries 6 and 8) into corresponding C-C coupling products of 88% and 80% respectively.

	<b>Br</b> + - <b>B</b> ( <b>O</b> )	H) <sub>2</sub> $\xrightarrow{\text{Complex 1}}_{\text{(1 mol%)}}$ $\swarrow$	
Entry	Substrate	Product	Yield <sup>b</sup> (%)
1	Br		96
2	Br NO <sub>2</sub>	$\mathbf{O}_2\mathbf{N}$	99
3	Br-CH <sub>3</sub>	H <sub>3</sub> C-	95
4	Br-CH <sub>3</sub>	H <sub>3</sub> CO-	92
5			85
6	СІОН	но-	80
7	Br H <sub>3</sub> C		82
8	Br CHO	онс	88
9		$\bigcirc - \bigcirc$	68

Table 4. Suzuki-Miyaura coupling of aryl halide with phenylboronic acid using complex  $(1)^{a}$ 

<sup>a</sup>Reaction conditions: aryl halides (1 mmol), phenylboronic acid (1.2 mmol), K<sub>2</sub>CO<sub>3</sub> (1 mmol), catalyst (1 mol%), DMF solvent (5mL). <sup>b</sup>Isolated yield after column chromatography.

### 2.4. Catalytic Sonogashira coupling reactions

To extend the scope of our work, we next investigated the coupling of various aryl bromides with terminal alkynes. The results are summarised in Table 5. The electron donating groups such as –Me, –OMe, at the *para* position of aryl bromide couple smoothly with phenyl acetylene to give good to excellent yield of isolated cross coupling products (Table 5, entries 3 & 4). The *p*-chlorobenzonitrile having electron-deficient aromatic rings, also underwent the Sonogashira coupling with terminal alkynes under similar conditions to afford the corresponding products in good yields (entries 5). Bromobenzene could be smoothly coupled with phenyl acetylene resulting in a high yield of diphenyl acetylene (95%, entry 1). 2-Bromotoluene (entry 7), gave the corresponding product in a slightly lower yield (73–87%), which may be due to steric effects compare with *p*-bromotoluene (entry 3). The reaction of chlorophenol (entry 6) found to be moderate yield 85%.

ournalpre

$  Br +  Br = \frac{Pd \text{ catalyst (1-4)}}{Base/ 5 hr/ Solvent} $						
Entry	Substrate	Product		Yield <sup>b</sup> (%)		
			Complexes			
			1	2	3	4
1	Br		95	82	95	92
2		$O_2N - \langle \rangle = \langle \rangle$	92	86	89	85
3	Br-CH <sub>3</sub>	$H_3C$ – ()	90	79	92	89
4	Br-CH3	$H_3CO$	97	90	95	90
5	CI-CN		90	89	80	92
6	СІ-ОН	но-{>-=-{>	85	80	75	79
7	Br		87	83	80	73
8	Br-CHO	онс-	89	85	91	79

Table 5 Sonogashira reaction of aryl halides with phenylacetylene<sup>a</sup>.

<sup>a</sup>Reaction condition: aryl halides (1 mmol), phenyacetylene (1.5 mmol), K<sub>2</sub>CO<sub>3</sub> (2 mmol), catalyst (1 mol%), solvent 5mL.

<sup>b</sup>Isolated yield after column chromatography.

### 3. Conclusion

The present study shows that the steric bulky 1-(arylazo)naphthol ligands can readily bind to palladium(II) metal ion. The characterization of all the complexes was accomplished by analytical and spectral (IR, UV-Vis, <sup>1</sup>H NMR and <sup>13</sup>C-NMR) methods. Single crystal X-ray

diffraction studies evidenced the coordination mode of ligands to the metal through O, N donors and reveal the presence of a square-planar geometry. Our catalyst showed good catalytic activities toward Suzuki and Sonogashira cross-coupling reactions of aryl halides with phenylboronic acid and phenylacetylene.

### 4. Experimental Section

### 4.1. Materials and physical measurements

Commercial Pd(OAc)<sub>2</sub> was purchased from Himedia. All the used reagents were chemically pure or analytical reagent grade. Solvents were purified and dried according to standard procedures. The 1–(aryllazo)naphthol ligands [31] were prepared by diazotization reaction of *ortho*, *para*-substituted amines with  $\beta$ -naphthol. The substrates used in the catalytic studies, were purchased from Merck and Aldrich. The IR spectra of the complexes were recorded on an agilent resolution pro model in 4000–400 cm<sup>-1</sup> range. Electronic spectra of the complexes were recorded in CHCl<sub>3</sub> solution in a Cary 300 Bio UV–Vis Varian spectrophotometer in the range 800–200 nm. The <sup>1</sup>H-NMR spectra were recorded in CDCl<sub>3</sub> with Bruker 300MHz instrument using TMS as internal reference.

### 4.2. Synthesis of Palladium (II) 1-(arylazo)naphtholate complexes

To a solution of (1-arylazo)naphthols ( $HL_1-HL_4$ ) (2 mmol, 0.1229-0.2160 g),  $Pd(OAc)_2$  (1 mmol, 0.224 g) and triethylamine were mixed in acetonitrile with constant stirring for 4h. The precipitate of the resulting product was filtered and dried in vacuo.

[Pd(L<sub>1</sub>)<sub>2</sub>] (1): Red solid, M.p. 230 °C. Anal. Calc. for C<sub>36</sub>H<sub>30</sub>O<sub>2</sub>N<sub>4</sub>Pd: C, 65.85; H, 4.57; N, 8.53. Found: C, 65.84; H, 4.58; N, 8.52. IR (cm<sup>-1</sup>):1370 υ(N=N), 1303 υ(C-O). UV–Vis  $\lambda_{max}$  (nm): 455, 345, 250. <sup>1</sup>H–NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 7.1–7.6 (m, Ar-H), 6.4 (dd, CH), 2.3 (s, CH<sub>3</sub>). <sup>13</sup>C–NMR (CDCl<sub>3</sub>)  $\delta$  (ppm): 128-132 (m, Ar-H), 18.0 (s, CH<sub>3</sub>).

[Pd(L<sub>2</sub>)<sub>2</sub>] (**2**): Orange solid, M.p. 210 °C. Anal. Calc. for  $C_{38}H_{34}O_2N_4Pd$ : C, 66.47; H, 5.24; N, 8.16. Found: C, 66.47; H, 5.23; N, 8.17. IR (cm<sup>-1</sup>): 1367 v(N=N), 1304 v(C-O). UV–Vis  $\lambda_{max}$  (nm): 440, 360, 260. <sup>1</sup>H–NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) =7.0–7.6 (m, Ar-H), 6.4 (dd, CH), 2.4 (s, 3CH<sub>3</sub>). <sup>13</sup>C–NMR (CDCl<sub>3</sub>)  $\delta$  (ppm): 120-136 (m, Ar-H), 24.0 (2CH<sub>3</sub>), 44.0 (CH<sub>3</sub>, s).

[Pd(L<sub>3</sub>)<sub>2</sub>] (**3**): Brown solid, M.p. 200 °C. Anal. Calc. for C<sub>44</sub>H<sub>48</sub>O<sub>2</sub>N<sub>4</sub>Pd: C, 68.57; H, 6.23; N, 7.27. Found: C, 68.56; H, 6.24; N, 7.26. IR (cm<sup>-1</sup>): 1387 v(N=N), 1313v(C-O). UV–Vis  $\lambda_{max}$  (nm): 450, 350, 270. <sup>1</sup>H–NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) =7.1–7.9 (m, Ar-H), 3.12 (m, CH), 1.29 (d, 2(CH<sub>3</sub>)<sub>2</sub>C).

[Pd(L<sub>4</sub>)<sub>2</sub>] (**4**): Brown solid, M.p. 240 °C. Anal. Calc. for C<sub>32</sub>H<sub>18</sub>O<sub>2</sub>N<sub>4</sub>Br<sub>6</sub>Pd: C, 35.88; H, 1.68; N, 5.23. Found: C, 35.90; H, 1.67; N, 5.24. IR (cm<sup>-1</sup>): 1354 υ(N=N), 1313 υ(C-O). UV–Vis  $\lambda_{max}$  (nm): 450, 320, 260. <sup>1</sup>H–NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 7.0–7.7 (m, Ar-H). <sup>13</sup>C–NMR (CDCl<sub>3</sub>)  $\delta$  (ppm): 120-134 (m, Ar-H).

### 4.3. X-ray crystallography

Single crystals of the complexes  $[Pd(L_1)_2]$  (1) and  $[Pd(L_2)_2]$  (2) were grown in dichloromethane–pentane mixture at room temperature. A single crystal of suitable size was covered with Paratone oil, mounted on the top of a glass fiber, and transferred to a Bruker SMART APEX II single crystal X-ray diffractometer using monochromated Mo-K $\alpha$  radiation (kI = 0.71073 Å). Data were collected at 293 K. The structure was refined by full matrix least squares method on F2 with SHELXL-18. Non-hydrogen atoms were refined with anisotropy thermal parameters. All hydrogen atoms were geometrically fixed and allowed to refine using a riding model. Frame integration and data reduction were performed using the Bruker SAINT-Plus (Version 7.06a) software. The multi scan absorption correction was applied to the data using SADABS software.

#### 4.4. General procedure for Suzuki-Miyaura cross coupling reactions

A mixture of the appropriate aryl halide (1 mmol), phenylboronic acid (1.2 mmol), palladium catalyst (1 mmol%), K<sub>2</sub>CO<sub>3</sub> (1 mmol) was added to DMF (2 mL) in round-bottom flask equipped with condenser and placed into the oil bath. Then the reaction mixture was heated for the desired time at 110 °C. After the reaction was completed (monitored by TLC), the mixture was cooled to room temperature and the reaction mixture was poured into a separating funnel and water (30 mL) and n-hexane (30 mL) were added. The organic phase was dried over CaCl<sub>2</sub>, filtered, and the solvent was evaporated. The residue was purified by silica gel column chromatography.

### 4.5. General procedure for the Sonogashira coupling reactions

A mixture of aryl halides (1mmol), alkyne (1.5 mmol), base (2 mmol), *i*-PrOH (2 mL), and the catalyst (1 mol%) was stirred at 82 °C under aerial conditions. The progress of the reaction was monitored by TLC. After the completion of the reaction, the mixture was diluted with 20 mL of water and extracted with diethyl ether (3  $\times$ 20 mL). The combined organic layer were washed with brine and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and evaporated in a rotary evaporator under reduced pressure. The crude compound was purified by column chromatography on silica gel using hexane as eluent to afford the desired products.

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#### Appendix A. Supplementary data

FT-IR, UV-Vis, <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra of representative complexes. CCDC 1957026 and CCDC 1938588 contain the supplementary crystallographic data for complex **1** and **2**. These data can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1223 336033; email: deposit@ccdc.cam.ac.uk or <u>http://www.ccdc.cam.ac.uk</u>).

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## **Highlights**

- > The new family of Palladium(II) 1-(arylazo)naphtholate complexes have been synthesized.
- > Characterizations of the complexes were performed by spectral and SC-XRD.
- > Palladium(II) 1-(arylazo)naphtholate complexes were used as catalysts for the Suzuki-Miyaura and Sonogashira coupling reactions.

#### **Declaration of interests**

 $\Box$  The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

No conflict of interest.

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