



Aqueous Suzuki coupling reaction catalyzed by water-soluble diimine/Pd(II) systems

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ABSTRACT

A series of water-soluble diimine ligands were applied for the Suzuki reaction of arylbromide in different media. Low loading of catalyst (0.01 mol%) were necessary for the coupling reaction to proceed in water or water/ethanol. The catalytic system was found to tolerate a broad range of functional groups.

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1. Introduction

In the past two decades, the palladium-catalyzed Suzuki coupling reaction of aryl halides with arylboronic acids has evolved into one of the most important and powerful methods to form biaryls [1–3] and has been extensively used in the synthesis of pharmaceuticals [4,5], ligands [6], polymers [7], and advanced materials [8,9].

Lots of highly active supporting ligands have been developed for Suzuki coupling reaction, such as phosphine ligands [10,11], *N*-heterocyclic carbene ligands [12–14], palladacycle [15–18]. Recently, Suzuki reaction in aqueous phase including neat water and water/organic co-solvent has also received much more attention. Casalnuovo initially reported the palladium-catalyzed cross-coupling reactions in aqueous solvents catalyzed by TPPMS/Pd(OAc)₂ [19]. Several water-soluble analogues of phosphines have been developed for the Suzuki coupling reactions [20–22]. Di-2-pyridylmethylamine-based palladium complexes [23,24] have been shown to be versatile catalysts for Heck, Suzuki and Sonogashira reactions in organic and aqueous solvents. Nájera and co-workers [25,26] reported a new oxime-carbapalladacycle with hydroxy substituents on the aromatic ring as a highly active catalyst for arylchloride Suzuki coupling reaction in water with TBAB (tetrabutylammonium bromide) as an additive. Another water-soluble palladacycle [27] supported by a water-soluble phosphine ligand (*t*-Bu-Amphos) has been prepared and applied for the aqueous

Suzuki coupling, and this catalytic system could be efficiently reused in 12 reaction cycles.

As a well-known family of ligands, diimines have been applied in many catalytic processes, such as in the notable olefin polymerization [28,29]. Nolan and his co-workers [30,31] have reported the use of Pd(OAc)₂/DAB-Cy (*N,N'*-dicyclohexyl-1,4-diazabutadiene) system for the Suzuki reaction and Heck reaction. Herein, we reported a series of disulfonated water-soluble α -diimine ligands as supporting ligands for the Suzuki cross-coupling reaction in organic solvents and in aqueous phase.

2. Results and discussion

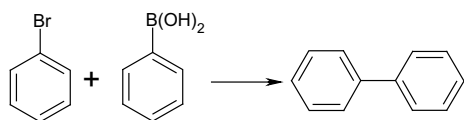
2.1. Synthesis of ligands and Pd(II) complex

2,6-Di(alkyl)aniline was first sulfonated with concentrated sulphuric acid at 200 °C, followed by neutralization with NaOH or NaOCH₃ to form the sodium salts. The ionic sulfonated α -diimine ligands (Table 1) were prepared by condensing an α -dione (2,3-butanedione, acenaphthenequinone, or 40% aqueous glyoxal) with the corresponding sulfonated anilines in methanol with a catalytic amount of formic acid. The sulfonated ligands are easily diffuent and stable in neat water and water-organic co-solvents. Ligands **9**, **10** and **11** were synthesized as yellow powders by an ion exchange reaction between the ligand **4** (or **5**) and excess 1-butyl-3-methylimidazolium chloride (BmimCl) or tetrabutylammonium chloride (TBAC) in *iso*-propanol.

Single crystals of ligand **11** suitable for X-ray diffraction were obtained from *iso*-propanol solution. The molecular structure of

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Table 1
Influence of diimine ligands.^a



Ligand	Structure	Yield ^{b,c}
1		40
2		60
3		58
4		71
5		74
6		25
7		22
8		27
9		85
10		82
11		81

Table 1 continued

Ligand	Structure	Yield ^{b,c}
9 ^d		>99

^a Reaction condition: 1.0 mmol bromobenzene, 1.3 mmol phenylboronic acid, 2 mmol K₂CO₃, 3 mol% Pd(OAc)₂, 3.3 mol% ligand, 2 ml DMA, 80 °C, 1 h.

^b GC conversion based on bromobenzene.

^c All reactions were monitored by GC, yields are average of two runs.

^d 95 °C 1 h or 80 °C 2.5 h.

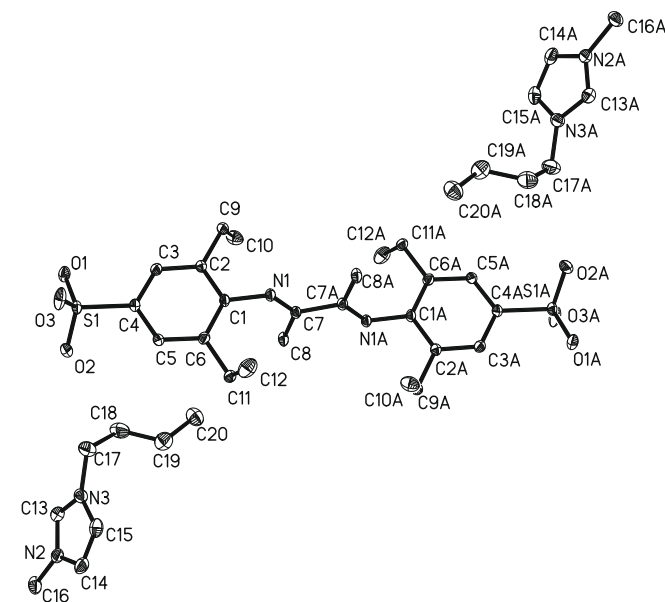


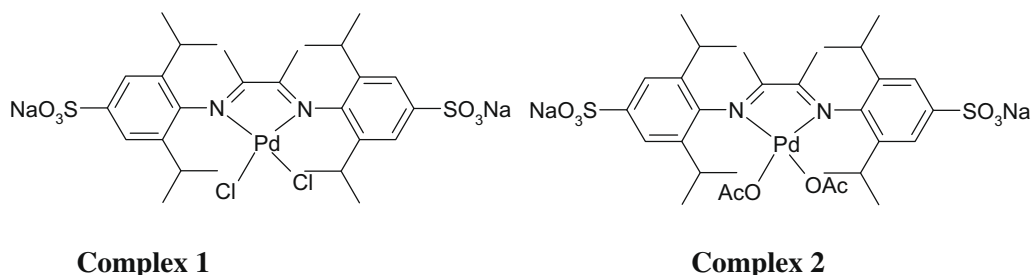
Fig. 1. ORTEP Drawing of Ligand **11**. Ellipsoids are given at the 30% probability level.

ligand **11** is depicted in Fig. 1. The C1–N1=C7–C7A=N1A–C1A moiety is planar, and has transoid arrangement with respect to the centre C7–C7A. The molecule has an inversion centre. Both imine groups assume an (*E*)-configuration to avoid repulsion between the substituted phenyl groups. The four ethyl groups are oriented toward the two different sides of the phenyl planes, respectively.

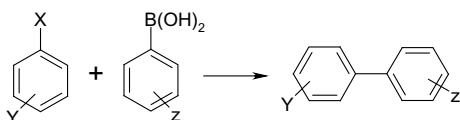
Furthermore, two new diimine palladium complexes **1** and **2** were synthesized from the reaction between the ligand **5** and suitable palladium precursor in anhydrous methanol (Scheme 1). These two complexes were also both easily diffuent and stable in neat water and water/organic co-solvents. Solutions of these complexes could be stored for several weeks without decomposition (¹H NMR) and decrease of the catalytic activity.

2.2. Influence of the diimine ligands on Suzuki reaction

We initiated the research of Suzuki reaction in the organic solvents in order to study the influence of the diimine ligands (Table 1). Coupling reaction of bromobenzene and phenylboronic acid was selected as a model reaction. DMA (dimethyl acetamide) was used as the solvent, and K₂CO₃ as the base. The similar reactivity trend with Nolan's report [30] is in agreement with the stronger donating ability of alkyl substituents, making the donor atoms more electron-rich. In the series of ligands (**1–8**), ligand **5** gave the highest yield while the acenaphthenequinone and glyoxal diimines gave low or moderate yields. Using [Bmim]⁺ or [NBu₄]⁺ instead of [Na]⁺ the yields improved. But the mechanisms leading



Scheme 1.

Table 2Suzuki coupling of aryl halides and various arylboronic acid.^a

Entry	X	Y	Z	t (h)	GC conv. (isolated yield) ^b
1	Br	H	H	1.5	100 (99)
2	Br	4-COMe	H	1	100 (98)
3	Br	2-CHO	H	2	100 (98)
4	Br	3-NO ₂	H	1	100 (97)
5	Br	4-Cl	H	1	100 (93)
6	Br	4-NH ₂	H	2	100 (97)
7	Br	4-Me	H	1.5	100 (99)
8	Br	4-OMe	H	5	95 (92)
9	Br	2-Me	H	5	95 (93)
10	Br	4-Ph	H	3.5	98 (95)
11	Br	1-Naph	H	5	96 (95)
12	Br	H	4-Me	1.5	100 (97)
13	Br	H	4-OMe	2	96 (94)
14	Br	H	4-Cl	3	99 (90)
15	Br	4-Me	4-Me	3	98 (96)
16	Br	4-OMe	4-Me	4.5	99 (97)
17 ^c	Cl	H	H	24	20
18 ^c	Cl	4-NO ₂	H	24	78 (76)

^a Reaction condition: 1.0 mmol aryl halide, 1.3 mmol arylboronic acid, 2 mmol K₂CO₃, 3 mol% Pd(OAc)₂, 3.3 mol% ligand **9**, 2 ml DMA, 95 °C.

^b All reactions were monitored by GC, yields are average of two runs.

^c 120 °C.

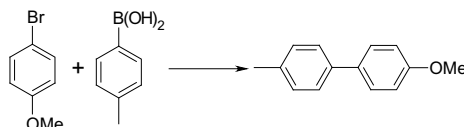
to improved yields were different. The ionic liquid ligand **11** (ligand **11** could be considered as a special ionic liquid) could be deprotonated at the 2-position of [Bmim]⁺ by the base to form a carbene catalytic precursor [14,32] while the [NBu₄]⁺ of ligand **9** stabilizes the active Pd(0) species. The ligand **9** was selected for Suzuki coupling of aryl halide and aryl boronic acid.

2.3. Suzuki coupling of aryl halides and various arylboronic acid

The catalytic system was applicable to a wide range of aryl bromides and chloride (Table 2). The electron-deficient aryl bromides showed an excellent reactivity and gave nearly quantitative yields in short reaction times (Table 2, entries 2–6). A prolongation of reaction time was required for the electron-rich and sterically hindered aryl bromides (Table 2, entries 7–10). The coupling reaction of active aryl chloride gave moderate yields at higher reaction temperature (Table 2, entries 18, 19) while the coupling reaction of chlorobenzene and the unactivated chloride showed much lower reactivity and yields (Table 3, entries 17, 20). The coupling of 4-bromochlorobenzene with the phenylboronic acid gave 4-chlorobiphenyl in 93% isolated yield with a little other coupling by-product which was not identified (Table 2, entries 5). It was also shown that the coupling of arylboronic acid and bromobenzene gave high yields (Table 2, entries 12–16).

2.4. Suzuki reaction in aqueous phase

The use of neat water as solvent is attractive because of the complete elimination of organic solvent. It is shown that the

Table 3Pd source screening of aqueous Suzuki coupling.^a

Entry	Catalyst	Catalyst (mol%)	Solvent	TBAB	T (°C)	t (h)	Yield ^b
1	Complex 1	0.01	H ₂ O	0	75	4	70 ^c
2	Complex 2	0.01	H ₂ O	0	75	4	57 ^c
3	PdCl ₂	0.01	H ₂ O	0.5	75	1.5	56
4	Li ₂ PdCl ₄	0.01	H ₂ O	0.5	75	1.5	47
5	Complex 1	0.01	H ₂ O	0.5	75	1.5	92
6	Complex 2	0.01	H ₂ O	0.5	75	1.5	67
7	Complex 1	0.01	H ₂ O	0.5	75	1.5	85 ^e
8	Complex 1	0.01	H ₂ O	0	100	45 min	98
9	Complex 1	0.01	H ₂ O/EtOH ^d	0	70	1.5	99
10	Complex 1	0.1	H ₂ O/EtOH ^d	0	50	3	99
11	Complex 1	0.1	H ₂ O/EtOH ^d	0	18	12	93
12	Complex 1	0.0001	H ₂ O/EtOH ^d	0	70	10	98

^a Reaction conditions: 1 mmol of 4-bromoanisole, 1.3 mmol of 4-methylphenylboronic acid, 2 mmol of K₂CO₃, 5 ml of H₂O, N₂.

^b Isolated yields.

^c Toluene produced.

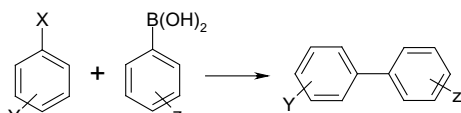
^d EtOH:H₂O = 1 ml:1 ml, under air.

^e Reacted under air.

reaction yields are moderate in neat water without any additive at 75 °C (Table 3, entry 1). The addition of 0.5 equiv. of TBAB to the reaction mixture greatly accelerated the reaction and decreased the yields of arene formed from protodeboronation of the boronic acid. The role of the ammonium salt is thought to be twofold. Firstly, it facilitates solvation of the arylhalide in neat water. Secondly, it accelerates the coupling reaction by formation of a boronate complex $[\text{ArB}(\text{OH})_3]^- [\text{R}_4\text{N}]^+$ [33,34]. The complete conversion and 99% isolated yield were obtained when the reaction was carried out at 100 °C with no toluene and only a trace of 4,4'-dimethylbiphenyl (Table 3, entries 8) as by-products. The reaction in water under air showed a bit lower conversions than the reaction under nitrogen (Table 3, entries 5, 7). When the Suzuki coupling of 4-bromoanisole and 4-methylboronic acid was run in EtOH/H₂O under air, shorter reaction times were necessary compared to the water system with TBAB as an additive. High yields were also obtained at lower reaction temperature (room temperature or 50 °C) with 0.1 mol% loading of complex **1** for the EtOH/H₂O co-solvent system (Table 3, entries 10, 11). Complex **1** is a more active species compared to the complex **2** and other palladium precursors for the aqueous Suzuki coupling.

The Suzuki coupling of arylhalide and arylboronic acid in water (Method A) or water/ethanol (Methods B and C) system (Table 4) was studied. The reaction times were not optimized because all

Table 4
Aqueous Suzuki coupling of aryl halides and various arylboronic acid.^a



Entry	X	Y	Z	Method	Isolated yield (%) ^b
1	Br	H	H	A	99
				B	99
2	Br	4-Me	H	A	98
				B	99
				C	95
3	Br	4-Cl	H	A	99
				B	99
				C	90
4	Br	4-OMe	H	A	99
				B	99
				C	90
5	Br	4-OMe	4-Me	A	97
				B	98
6	Br	4-OMe	4-Me	C ^c	25
				C	93
7	Br	4-OMe	4-OMe	A	97
				B	98
8	Br	4-OMe	4-Cl	A	96
				B	99
9	Br	2-Me	H	A	80
				B	92
10	Br	3-NO ₂	H	B ^d	98
				A	98
11	Br	4-OH	H	A ^e	95
				C	98
12	Cl	4-NO ₂	H	A	98
13 ^f	Cl	H	H	A	20 ^g
14 ^f	Cl	4-CH ₃	H	A	<5 ^g

^a Reaction condition: 1.0 mmol aryl halide, 1.3 mmol arylboronic acid, 2 mmol K₂CO₃, reaction time not optimized, Method A: 0.01 mol% Complex **1**, 5 ml deionized water, 75 °C, 0.5 equiv. TBAB, under N₂, 3–5 h. Method B: 0.01 mol% Complex **1**, EtOH/H₂O = 1 ml:1 ml, 70 °C, under air, 1.5–2 h. Method C: same to method B, but 0.1 mol% catalyst, r.t. (about 18–20 °C), 10 h.

^b All isolated yields, average of two runs.

^c 0.01 mol% catalyst, 24 h.

^d 0.02 mol% catalyst.

^e No additive.

^f 1 mol% catalyst, 120 °C, 1 equiv. TBAB.

^g GC yield.

Table 5
Recycling of catalyst.^a

Entry	Catalyst (mol%)	Reaction yield by cycle ^b			
		1	2	3	4
1	0.01	97	61	0	
2	0.1	99	90	60	10

^a Reaction condition: 1.0 mmol 4-bromoanisole, 1.3 mmol phenylboronic acid, 2 mol K₂CO₃, 100 °C, 5 ml H₂O.

^b GC yield.

the coupling reaction could be accomplished in short time in nearly quantitative yields. It is worth noticing that the catalytic system was found to tolerate a wide range of functional group, such as NO₂, OMe, OH, Cl, NH₂ (Table 4). The coupling of 4-bromochlorobenzene with the phenylboronic acid showed good selectivity and gave exclusively 4-chlorobiphenyl in 99% yield (Table 4, entry 3). Due to the steric hindrance and solubility of substrates, reactions in neat water appear to be more sensitive to steric bulk on the aryl boronide than in the water/ethanol system, as 2-bromotoluene gave 80% of the coupling product with phenylboronic acid in neat water, while the yield in water/ethanol was up to 98% (Table 4, entry 9A and B). The ammonium salt additive were not necessary for the coupling reaction of 4-bromophenol with Method A because of its water-solubility in basic aqueous phase (Table 4, entry 11). The coupling reactions of aryl chloride and phenylboronic acid were carried out at 120 °C with 1 mol% catalyst and 1.0 equiv. TBAB except for 4-nitrochlorobenzene. It was shown that the conversion of activated aryl chloride was up to 98%. But the conversion of unactivated aryl chloride was very low.

2.5. Catalyst recycling

The potential recyclability of the catalysts derived from diimine/Pd system was also explored in the model cross-coupling of 4-bromoanisole and phenylboronic acid (Table 5). The reaction was carried out in water at 100 °C. After cooling to room temperature, the organic products were extracted by ethyl ether and the yields were determined by GC. The aqueous phase was then transferred to a new reaction flask for the next cycle. It was shown that the coupling reaction using 0.1 mol% catalyst could be reused by two cycles and the yield significantly dropped for the third cycle. Employing lower amounts of catalyst (0.01 mol%), the yield of the second cycle dropped to 60%, and little product for the third cycle.

3. Conclusion

A series of new ionic diimine ligands were applied for the high yield Suzuki coupling reaction of arylbromide and arylboronic acid in organic solvent, neat water and water/ethanol co-solvent system. Very low loading of catalyst (0.01 mol%) were necessary for the coupling reaction in water or EtOH/water co-solvent system. An addition of TBAB greatly accelerated the rate of coupling reaction and decreased the formation of by-products in neat water at lower temperatures. The coupling reactions could be smoothly carried out at room temperature with low loading of catalyst (0.1 mol%). The catalytic system tolerates a broad range of functional groups on the phenyl ring.

4. Experimental

4.1. Materials

Alkyl substituted sulfonated aniline sodium salts [35,36], Disulfonated diimine ligands [37,38] and [Bmim]Cl [39] were pre-

pared according to literature methods. All solvents were purchased and purified according to standard methods. Other reagents were used as received without further purification.

4.2. Apparatus

All NMR spectra were recorded at Bruker 300 or 400 MHz Spectrometer using CDCl_3 or CD_3OD . GC is Zheda Zhida 9790 with a SE-30 GC column. Elemental analyses were carried out on Elementar Vario EL III.

4.3. Synthesis of ligands and complexes

4.3.1. Synthesis of ligands

Ligands (**1–8**) were prepared in the light of our recent publication [40].

Ligand 9: Ligand **5** (0.20 g, 0.33 mmol) and TBAC (0.24 g, 0.86 mmol) were added into 30 ml of isopropanol. The mixture was stirred at 60 °C for 24 h. The yellow solid was gradually dissolved, and white NaCl precipitated. After cooling and filtration the volatiles were completely removed in vacuo. The yellow residue was recrystallized in *iso*-propanol and delivered ligand **9** as yellow power (0.31 g, 91%).

IR (KBr): 1647 cm^{-1} ($\nu_{\text{C=N}}$), 1188 cm^{-1} ($\nu_{\text{S=O}}$). ^1H NMR (300 MHz, CD_3OD): δ 7.80 (s, 4H), 3.09 (t, 4H), 2.79–2.87 (m, 4H), 2.15 (s, 6H), 1.48–1.56 (m, 4H), 1.34 (d, 12H), 1.28–1.21 (m, 16H), 0.84 (t, 6H).

Ligands **10** and **11** were synthesized by the reaction of ligand **5** or **4** with excess [Bmim]Cl in isopropanol.

Ligand 10: IR (KBr): 1647 cm^{-1} , ($\nu_{\text{C=N}}$) 1188 cm^{-1} ($\nu_{\text{S=O}}$). ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ 0.90 (t, 6H), δ 1.10 (d, 12H), 1.15 (d, 12H), 1.25 (m, 4H), 1.76 (m, 4H), 2.00 (s, 6H), 2.67 (m, 4H), 3.36 (s, 6H), 4.16 (m, 4H), 7.42 (s, 4H), 7.72 (s, 2H), 7.79 (s, 2H), 9.18 (s, 2H). Anal. Calc. for $\text{C}_{44}\text{H}_{68}\text{N}_6\text{O}_6\text{S}_2$: C, 62.83; H, 8.15; N, 9.99. Found: C, 62.41; H, 7.98; N, 10.24%.

Ligand 11: IR (KBr): 1648 cm^{-1} ($\nu_{\text{C=N}}$), 1190 cm^{-1} ($\nu_{\text{S=O}}$). ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ 0.90 (t, 6H), 1.08 (t, 12H), 1.25 (m, 4H), 1.76 (m, 4H), 1.98 (s, 6H), 2.32 (q, 8H), 3.85 (s, 6H), 4.16 (m, 4H), 7.36 (s, 4H), 7.72 (s, 2H), 7.79 (s, 2H), 9.18 (s, 2H). Anal. Calc. for $\text{C}_{40}\text{H}_{60}\text{N}_6\text{O}_6\text{S}_2$: C, 61.20; H, 7.70; N, 10.70. Found: C, 61.32; H, 7.88; N, 10.43%.

4.3.2. Synthesis of complex 1

0.50 g (0.82 mmol) of ligand **5** and 0.31 g (0.82 mmol) of $\text{PdCl}_2(\text{PhCN})_2$ was dissolved in 20 ml of absolute methanol. The mixture was stirred for 10 h at room temperature under nitrogen. All the volatiles were removed in vacuo after filtration. The residues were recrystallized from methanol/ethyl ether and delivered the complex **1** as an orange solid (0.55 g, 86%). M.p. > 250 °C.

^1H NMR (400 MHz, CD_3OD): δ 7.77 (s, 4H), 3.31–3.22 (m, 4H), 2.23 (s, 6H), 1.48 (d, $J = 6.8$ Hz, 12H), 1.28 (d, 12H, $J = 6.8$ Hz). Anal. Calc. for $\text{C}_{28}\text{H}_{38}\text{N}_2\text{Na}_2\text{O}_6\text{S}_2\text{PdCl}_2$: C, 42.78; H, 4.87; N, 3.56. Found: C, 42.62; H, 5.10; N, 3.42%.

4.3.3. Synthesis of complex 2

0.70 g (1.15 mmol) of ligand **5** and 0.26 g (1.15 mmol) of $\text{Pd}(\text{OAc})_2$ were dissolved in 20 ml of absolute methanol. The mixture was stirred for 10 h at room temperature. After filtration of the palladium black, the volatiles were removed in vacuo. The residues were recrystallized from methanol/ethyl ether and delivered complex **2** as an orange solid (0.65 g, 68%). M.p. > 250 °C.

^1H NMR (300 MHz, D_2O): δ 7.42 (s, 4H), 2.89 (s, 6H), 2.74 (s, 6H), 2.60–2.55 (m, 4H), 1.07 (d, 12H), 1.01 (d, 12H). Anal. Calc. for $\text{C}_{32}\text{H}_{44}\text{N}_2\text{Na}_2\text{O}_{10}\text{S}_2\text{Pd}$: C, 46.13; H, 5.32; N, 3.36. Found: C, 45.81; H, 5.52; N, 3.60%.

4.4. General procedure of Suzuki coupling reaction in organic solvent

A 25-ml-two-necked flask was equipped with a magnetic stir bar and purged with nitrogen gas. 0.03 mmol of $\text{Pd}(\text{OAc})_2$, 0.033 mmol of ligands and 2 ml of DMA were added into the flask under N_2 . The mixture was stirred for 30 min at room temperature. Then 1 mmol of arylhalide, 1.3 mmol of arylboronic acid and 2 mmol of powdered K_2CO_3 were added into the flask under nitrogen. The reaction mixture was stirred and heated at reaction temperature for appropriate time. It was then cooled to room temperature, diluted with water, and extracted with CH_2Cl_2 for three times. The organic phase was dried with Na_2SO_4 and concentrated to yield an oil or solid. The crude material was flash chromatographed on a short silica gel column eluting with a mixture of ethyl acetate and petrol ether (the purified products were identified by ^1H NMR spectra).

4.5. General procedure of aqueous Suzuki coupling reaction

A 25-ml-two-necked flask was equipped with a magnetic stir bar. Complex **1** and 5 ml of H_2O (Method A) or $\text{EtOH}/\text{H}_2\text{O}$ (1 ml:1 ml, Methods B and C) were added into the flask. Then 1 mmol of aryl bromide, 1.3 mmol of arylboronic acid and 2 mmol of powdered K_2CO_3 were added into the flask under nitrogen if necessary. The reaction mixture was stirred at the pre-arranged temperature for appropriate reaction time. It was then cooled to room temperature, diluted with water, and extracted with CH_2Cl_2 for three times. The organic phase was dried with Na_2SO_4 and concentrated to yield an oil or a solid. The crude material was flash chromatographed on a short silica gel column.

4.6. Recycling of catalyst

A vial was charged with complex **1**, K_2CO_3 2 mmol, and phenylboronic acid 1.3 mmol. To this mixture were added water (5 ml) and 4-bromoanisole (1.0 mmol). The reactions were run at 100 °C for 1 h. After the reaction mixture was cooled to room temperature, diethyl ether (5 ml) was added and stirring was continued for 1 min. The aqueous phase was transferred to another vial for the next reaction cycle. The yields were determined by GC using *n*-dodecane as an internal standard.

4.7. ^1H NMR of the coupling product

Biphenyl ^1H NMR (CDCl_3): δ 7.59–7.57 (m, 4H), 7.45–7.40 (m, 4H), 7.35–7.30 (m, 2H).

4-Methylbiphenyl ^1H NMR (CDCl_3): δ 7.54 (d, 2H), 7.45 (d, 2H), 7.37 (t, 2H), 7.27 (t, 1H), 7.19 (d, 2H), 2.34 (s, 3H).

4-Methoxybiphenyl ^1H NMR (CDCl_3): δ 7.57–7.52 (m, 4H), 7.42 (t, 2H), 7.30 (t, 1H), 6.98 (d, 2H), 3.85 (s, 3H).

2-Methylbiphenyl ^1H NMR (CDCl_3): δ 7.43–7.35 (m, 2H), 7.34–7.27 (m, 3H), 7.26–7.18 (m, 4H), 2.27 (s, 3H).

4-Acetylbiphenyl ^1H NMR (CDCl_3): δ 8.04 (d, 2H), 7.62 (d, 2H), 7.55–7.30 (m, 3H), 2.64 (s, 3H).

4-Chlorobiphenyl ^1H NMR (CDCl_3): δ 7.68–7.33 (m, 9H).

Biphenyl-4-carbaldehyde ^1H NMR (CDCl_3): δ 9.98 (s, 1H), 8.03 (d, 1H), 7.67–7.61 (m, 1H), 7.52–7.36 (m, 7H).

3-Nitrobiphenyl ^1H NMR (CDCl_3): δ 8.43 (s, 1H), 8.18 (d, 1H), 7.90 (d, 1H), 7.62–7.56 (m, 3H), 7.51–7.39 (m, 3H).

p-Terphenyl ^1H NMR (CDCl_3): δ 7.68–7.55 (m, 8H), 7.46 (t, 4H), 7.37 (t, 2H).

4-Aminobiphenyl ^1H NMR (CDCl_3): δ 7.52 (d, 2H), 7.48–7.35 (m, 4H), 7.25 (t, 1H), 6.71 (d, 2H), 3.66 (s, 2H).

4,4'-Dimethoxybiphenyl ^1H NMR (CDCl_3): δ 7.47 (d, 4H), 6.95 (d, 4H), 3.83 (s, 6H).

4-Methoxy-4'-methylbiphenyl ^1H NMR (CDCl_3): δ 7.50 (d, 2H), 7.45 (d, 2H), 7.22 (d, 2H), 6.96 (d, 2H), 3.83 (s, 3H), 2.38 (s, 3H).

4'-Methylbiphenyl-2-carboxaldehyde ^1H NMR (CDCl_3): δ 9.98 (s, 1H), 8.00 (d, 1H), 7.60 (t, 1H), 7.44–7.40 (m, 2H), 7.25 (s, 4H), 2.41 (s, 3H).

4-Phenylphenol ^1H NMR (CDCl_3): δ 7.56–7.25 (m, 6H), 6.91 (d, 2H), the hydrogen of hydroxy was exchanged with the D_2O of DCCl_3 .

4-Chloro-4'-Methoxybiphenyl ^1H NMR (CDCl_3): δ 7.51–7.46 (m, 4H), 7.39 (d, 2H), 6.98 (d, 2H), 3.86 (s, 3H).

4-Nitro-4-methylbiphenyl ^1H NMR (CDCl_3): δ 8.25 (d, 2H), 7.72 (d, 2H), 7.53 (d, 2H), 7.30 (d, 2H), 2.42 (s, 3H).

1-Phenylanthralene ^1H NMR (CDCl_3): δ 7.92–7.71 (m, 3H), 7.48–7.36 (m, 9H).

2-Aminobiphenyl ^1H NMR (CDCl_3): δ 7.42–7.28 (m, 5H), 7.12 (t, 1H), 6.82 (t, 1H), 6.72 (d, 1H), 3.58 (s, 2H).

4-Nitrobiphenyl ^1H NMR (CDCl_3): δ 8.27 (d, 2H), 7.71 (d, 2H), 7.70–7.34 (m, 5H).

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2008.11.060](https://doi.org/10.1016/j.jorganchem.2008.11.060).

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