

Palladium catalyzed Suzuki cross-coupling reactions using *N,O*-bidentate ligands

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Abstract—Palladium-catalyzed Suzuki cross-coupling reactions employing Schiff-bases as ligands toward a series of substituted arylbromides and boronic acids were pursued. In the presence of a *N,O*-bidentate ligand, 2-[1-(2,4,6-trimethyl-phenylimino)-ethyl]-phenol **5**, the catalytic reactions could be carried out efficiently at room temperature with a wide array of arylbromides, even with electronically deactivated arenes. A deprotonated **5**, **5'**, chelated palladium acetate complex, [5'*Pd*(II)(OAc)(solv)] **8**, was proposed as a precursor of a genuine catalytically active species.

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1. Introduction

For the past few decades, transition metal-mediated catalytic cross-coupling reactions are among the most powerful and convenient tools of modern organic synthesis.¹ Recently, the palladium-catalyzed Suzuki reactions, involving cross-coupling of aryl halides with aryl boronic acids, have emerged as the most important synthetic methods for the preparation of biaryl compounds.^{2–7} As a result, many efforts have been devoted to the finding of even more efficient and selective methods in the synthesis of biaryls. For many years, phosphines have been the most commonly employed ligands for the reaction. Lately, *N*-heterocyclic carbenes (NHC) have been introduced as potentially effective ligands for Suzuki reactions.⁸ Nevertheless, these types of ligands are normally either air/moisture sensitive or expensive, which places significant limits on their synthetic applications. Besides, these types of compounds are not ecological friendly. On the contrary, most of the *N,O*- or *N,N*-bidentate ligands are inexpensive, easy to access and stable.⁹ Moreover, the process of the complexation of ligand with palladium is straightforward and their palladium complexes are found to be quite suitable for Suzuki cross-coupling reactions. Thereby, the practices of employing phosphine-free palladium catalysts in Suzuki cross-coupling reactions are of interest to many.¹⁰ To our knowledge, only few work using Schiff base as ligand in Suzuki reaction has been reported.¹¹ In this work, we report

some remarkable results of using several new types of *N,O*- or *N,N*-bidentate ligands in palladium-catalyzed Suzuki coupling reactions. The efficiency of these ligands are compared and discussed subsequently.

2. Results and discussion

Several *N,O*- or *N,N*-bidentate ligands, **1–6**, were prepared and screened for the Pd(OAc)₂ catalyzed Suzuki cross-coupling reactions (Fig. 1).

Table 1 summarizes the reaction conditions and results of the Suzuki coupling reactions for 4-bromo-benzaldehyde and phenylboronic acid. As shown, the best result (90% in yield) was obtained for employing **5** as the ligand while the reaction was carried out at 25 °C for 50 min in K₃PO₄/THF system (entry 5). Judging from these data alone, **5** is a quite efficient ligand in this reaction condition. Obviously, the lower yield obtained by employing **6** as ligand is mainly due to its more sterically demanding isopropyl groups on arene (entry 6). It is interesting to see that there is no catalytic efficiency being observed by using (2,4,6-trimethyl-phenyl)-(1-pyridin-2-yl-ethylidene)-amine **1** as ligand at 25 °C in KF/THF system (entry 1). For comparison, the **1**-chelated palladium complex, **1-PdCl₂**, was synthesized from the reaction of **1** with another palladium source, PdCl₂. The same results were obtained. There is not detectable catalytic ability being observed for **1-PdCl₂** in Suzuki–Miyaura coupling reaction. By contrast, in similar catalytic reactions a wide range of activities (from 0 to 99%) were reported for employing various

Keywords: Suzuki reaction; Palladium complex; Schiff-base; Bidentate ligand.

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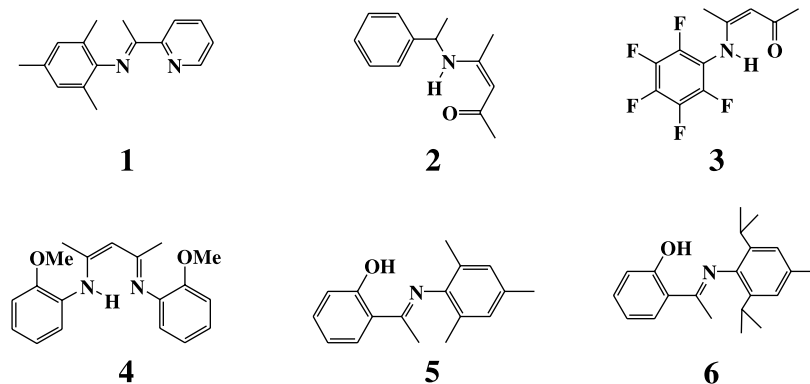
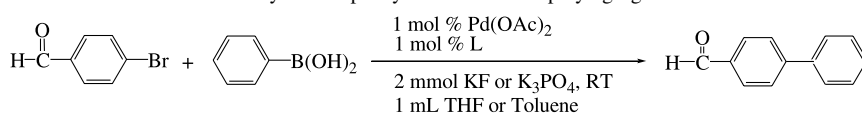


Figure 1. Some selected *N,N*- and *N,O*-bidentate ligands **1–6**.

Table 1. Suzuki coupling reactions of 4-bromo-benzaldehyde with phenylboronic acid employing ligands **1–6**



Entry ^a	Ligand	Base	Solvent	Time (min)	Conv. (%) ^b	Yield (%) ^c
1	1	K ₃ PO ₄	Toluene	50	NR	NR
		K ₃ PO ₄	THF	50	NR	NR
		KF	Toluene	50	NR	NR
		KF	THF	50	NR	NR
2	2	K ₃ PO ₄	Toluene	50	57	50
		K ₃ PO ₄	THF	50	73	65
		KF	Toluene	20	20	13
		KF	THF	50	86	85
3	3	K ₃ PO ₄	Toluene	50	68	68
		K ₃ PO ₄	THF	50	63	61
		KF	Toluene	190	16	6
		KF	THF	50	46	45
4	4	K ₃ PO ₄	Toluene	20	33	25
		K ₃ PO ₄	THF	20	0	0
		KF	Toluene	20	17	17
		KF	THF	350	87	86
5	5	K ₃ PO ₄	Toluene	90	80	77
		K ₃ PO ₄	THF	60	92	90
		KF	Toluene	20	22	10
		KF	THF	50	90	81
6	6	K ₃ PO ₄	Toluene	50	44	39
		K ₃ PO ₄	THF	50	65	63 ^d
		KF	Toluene	50	77	— ^d
		KF	THF	150	85	81
		KF	THF	50	72	70

^a Reaction conditions: 1.0 equiv of ArBr, 1.5 equiv of Ar'B(OH)₂.

^b NMR yield.

^c Isolated yield.

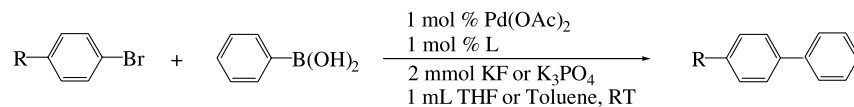
^d Not isolated.

diazabutadienes at reaction temperature around 80 °C.¹² Lower efficiency were observed for reactions employing **2**, **3** or **4** as ligand than that of **5**. In summary, the catalytic efficiencies of these types of ligands are in the sequence of imine–phenol > ketimine > imine–pyridine. It implies that the catalytic efficiency is better while the ligand–metal bonding mode is a grouping of chelated oxide- and imine–palladium bonds.

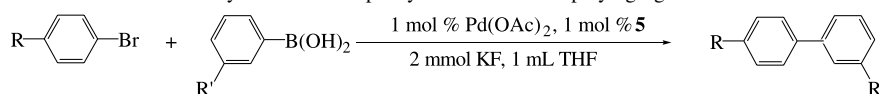
In palladium-catalyzed cross-coupling reactions, it is generally accepted that better conversions are assured for aryl halides with electron-withdrawing rather than donating substituent.¹³ The Suzuki coupling reactions were carried out and the reaction conditions and results were summarized

in Table 2. Here, two bromobenzaldehydes having electron-donating substituents, –OMe and –Me were used as the bromide sources. As expected, low conversion rates were observed for all the L/Pd(OAc)₂ combinations.

Table 3 summarizes the results of the palladium-catalyzed Suzuki reactions for various substituted arylbromides and phenylboronic acids by employing **5** as ligand. Excellent yields were obtained for the reactions of arylbromides with electron-withdrawing groups at 25 °C for 50–120 min (entries 1, 2, 7, and 8). On the contrary, rather low yield was observed for arylbromide with electron-donating group at that temperature (entry 6). Yields might be improved while the reaction temperature was raised to 100 °C for

Table 2. Suzuki coupling reactions of 4-bromo-benzene derivatives with phenylboronic acid employing ligands **1–6**

Entry ^a	Ligand	R	Base	Solvent	Time (min)	Conv. (%) ^b	Yield (%) ^c
1	2	CH ₃	KF	THF	20	13	— ^d
2		CH ₃	KF	THF	50	13	11
3		OCH ₃	K ₃ PO ₄	Toluene	50	7	— ^d
4	3	OCH ₃	K ₃ PO ₄	Toluene	50	22	— ^d
5		CH ₃	KF	THF	1210	50	48
6		CH ₃	KF	THF	20	11	— ^d
7	4	CH ₃	KF	THF	50	20	— ^d
8		CH ₃	KF	THF	120	23	20
9		OCH ₃	KF	Toluene	50	24	17

^a Reaction conditions: 1.0 equiv of ArBr, 1.5 equiv of Ar'B(OH)₂.^b NMR yield.^c Isolated yield.^d Not isolated.**Table 3.** Suzuki coupling reactions of substituted arylbromides and phenylboronic acids employing ligand **5**

Entry ^a	R	R'	Base/solvent	Time (min)	Conv. (%) ^b	Yield (%) ^c
1 ^d	CHO	H	KF/THF	50	90	81
2 ^d	COCH ₃	H	KF/THF	50	92	90
3 ^e	CH ₃	H	KF/THF	120	23	20
4 ^e	CH ₃	H	KF/EtOH	120	77	68
5 ^e	MeO	H	KF/CH ₃ CN	240	34	30
6 ^d	MeO	H	KF/THF	720	10	— ^f
7 ^d	CHO	NO ₂	KF/THF	120	82	75
8 ^d	COCH ₃	NO ₂	KF/THF	120	71	70
9 ^e	CH ₃	NO ₂	KF/EtOH	120	87	83
10 ^e	MeO	NO ₂	KF/CH ₃ CN	360	40	33
11 ^e	CHO	H	KF/EtOH	1440	10	— ^f

^a Reaction conditions: 1.0 equiv of ArBr, 1.5 equiv of Ar'B(OH)₂.^b NMR yield.^c Isolated yield.^d The reaction was conducted at 25 °C.^e At 100 °C.^f Not isolated.

aryl bromides with electron-donating group (entries 3, 5, and 10). Recently, a reductive process of Pd(II) to Pd(0) through the β-H elimination of the coordinated alkoxide ligand was proposed by Nolan et al.^{8a} Nevertheless, there was no formation of acetaldehyde being observed by ¹H NMR while the reaction was performed in ethanol, Pd(OAc)₂, and **5** at 100 °C for 24 h (entries 4 and 9). Even though the β-H elimination process did not take place in this case, it indeed increases the solubility of the reactants and eventually speed up the reaction (entry 3 vs 4). Accidentally, the **5**/Pd(OAc)₂ catalytic system worked for aryl chlorides. About 10% conversion was observed for the reaction of 4-chlorobenzaldehyde with phenylboronic acid at 100 °C for 24 h employing **5**/Pd(OAc)₂ as catalyst.

A bis-**5'**-chelated palladium complex, **7**, was obtained while in an attempt to isolate the active species in the reaction. The orange crystals of **7** were grown in toluene at room temperature, then suitable crystals were sampled and subjected for X-ray crystal structural determination (Table 4). The ORTEP drawing of **7** are depicted in Figure 2. The bond angles for O(1)–Pd(1)–N(1),

Table 4. Crystal data of **7**

Formula	C ₃₄ H ₃₆ N ₂ O ₂ Pd
<i>F</i> _w	611.05
Crystal system	Monoclinic
Space group	<i>P</i> 2(1)
<i>a</i> (Å)	15.987(3)
<i>b</i> (Å)	20.699(3)
<i>c</i> (Å)	8.9941(15)
β (°)	95.428(3)
<i>V</i> (Å ³)	2963.1(8)
<i>Z</i>	4
Density (calcd) (Mg/m ³)	1.370
λ (Mo Kα) (Å)	0.71073
Absorption coefficient (mm ^{−1})	0.658
<i>F</i> (000)	1264
Crystal size	0.60 × 0.35 × 0.21 mm ³
2θ Range (°)	2.35–26.03°
Reflections collected	16,492
Independent reflections	5790 [R(int)=0.0753]
Data/restraints/parameters	5790/0/355
<i>R</i> 1 for significant reflections ^a	0.0578
<i>wR</i> 2 for significant reflections ^b	0.1484
GoF ^c	0.962

^a *R*1 = Σ(|*F*_o| − |*F*_c|)/Σ|*F*_o|.^b *wR*2 = {Σ[w(*F*_o² − *F*_c²)²]/Σ[w(*F*_o²)²]}^{1/2}; *w* = 0.0993 for **7**.^c GoF = [Σw(*F*_o² − *F*_c²)²/(*N*_{refl} − *N*_{params})]^{1/2}.

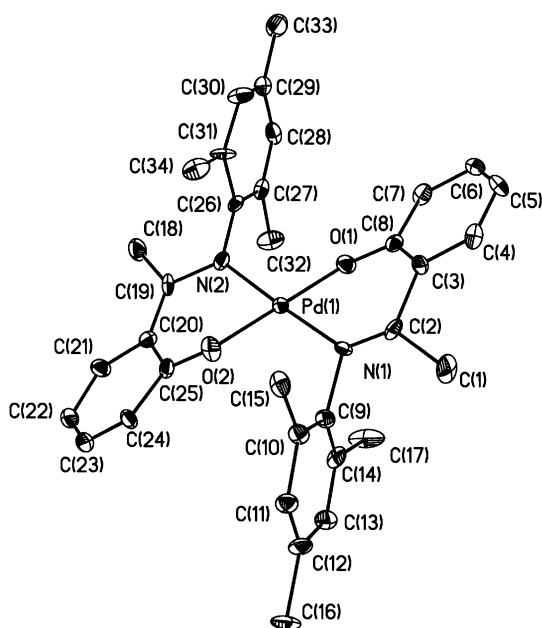


Figure 2. ORTEP drawing of **7** with the numbering. Some carbon and hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Pd(1)–O(1) 1.974(11); Pd(1)–O(2) 1.989(10); Pd(1)–N(1) 1.980(14); Pd(1)–N(2) 2.051(15); O(1)–C(8) 1.32(2); O(1)–C(25) 1.29(2); N(1)–C(2) 1.19(2); N(1)–C(9) 1.54(2); N(2)–C(26) 1.38(2); N(2)–C(19) 1.39(2); O(1)–Pd(1)–N(1) 88.1(5); O(1)–Pd(1)–O(2) 179.0(8); N(1)–Pd(1)–O(2) 92.6(6); O(1)–Pd(1)–N(2) 89.8(5); N(1)–Pd(1)–N(2) 177.8(7); O(2)–Pd(1)–N(2) 89.5(6); C(8)–O(1)–Pd(1) 121.3(11); O(25)–O(2)–Pd(1) 120.3(10).

N(1)–Pd(1)–O(2), O(1)–Pd(1)–N(2) and O(2)–Pd(1)–N(2) are 88.1(5)°, 92.6(6)°, 89.8(5)° and 89.5(6)°, respectively. Obviously, the Pd(II) metal center is a typical square planar environment with d^8 electron configuration. The bond lengths of Pd(1)–O(1), Pd(1)–O(2), Pd(1)–N(1) and Pd(1)–N(2) are 1.974(11), 1.989(10), 1.980(14), and 2.051(15), respectively. Interestingly, two oxides and two nitrogen atoms are trans to each other. This arrangement is believed due to the steric demand from two tri-methyl-phenyl rings rather than the reflection of the electronic effect.

Rather low efficiency was observed by employing **7** as the catalyst in Suzuki reaction than that of using the mixed **5**/Pd(OAc)₂ in situ. Apparently, **7** is not the genuine catalytically active species. It might be, at most, a precursor of a more reactive compound. Nevertheless, the catalytic process could be greatly improved while 1 equiv of Pd(OAc)₂ was added to **7**. It is believed that certain amount of **8**, **5'**Pd(OAc)(solv), was formed through the process of disproportionation and most of the catalytic reactivity was caused by this newly formed complex (**Scheme 1**). The

efficiency is further improved by adding in additional amount of Pd(OAc)₂. By that, presumably more species **8** was formed via equilibrium. Nonetheless, the proposed complex **8** is still regarded as a precursor of the genuine catalytically active species, which might be a Pd(0) complex.

3. Conclusion

We have demonstrated the exceptional catalytic reactivity of a *N,O*-bidentate ligand, 2-[1-(2,4,6-trimethyl-phenyl-imino)-ethyl]-phenol **5**, in the palladium-catalyzed Suzuki cross-coupling reaction. These types of ligands are attractive alternatives to the conventional phosphine ligands. A deprotonated **5**, **5'**, chelated palladium acetate complex, [**5'**Pd(II)(OAc)(solv)] **8**, was proposed as a precursor of a genuine catalytically active species and which has been proposed from the ligand exchange reaction of **7** with Pd(OAc)₂.

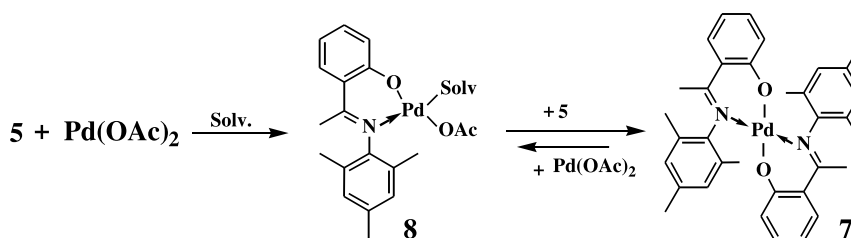
4. Experimental

4.1. General

All manipulations were carried out under a dry nitrogen atmosphere. All solvents including deuterated solvents were purified before use. ¹H and ¹³C NMR spectra were recorded on a Varian Mercury-400 (400 MHz for ¹H and 100 MHz for ¹³C) spectrometer with chemical shifts given in ppm from the internal TMS or center line of CHCl₃. Mass spectra were recorded on JOEL JMS-SX/SX 102A GC/MS/MS spectrometer. Microanalyses were performed using a Heraeus CHN-O-RAPID instrument.

4.1.1. Synthesis of (2,4,6-trimethyl-phenyl)-(1-pyridin-2-yl-ethylidene)-amine 1. 2-Acetylpyridine (12 mmol, 1.4 mL), 2,4,6-trimethylaniline (10 mmol, 1.4 mL), and benzenesulfonic acid (0.30 mL) were placed in a 100 mL round flask and was refluxed in absolute toluene (10 mL) for 36 h. After being cooled to room temperature, the orange extraction was dried over MgSO₄ and filtered. Removal of the solvent in vacuum afforded **1** as the desired light yellow oily product. Yield: 2.2 g (90%). ¹H NMR (CDCl₃, δ/ppm): 7.38–8.68 (m, 4H, Py), 6.88 (s, 2H, Ph), 2.88 (s, 3H, MeCN); 1.99 (s, 6H, Ph-*o*-Me), 2.18 (s, 3H, Ph-*p*-Me); Elemental Anal. Calcd for C₁₆H₁₈N₂: C, 80.63; H, 7.6; N, 11.75%. Found: C, 80.79; H, 7.61; N, 11.87%.

4.1.2. Synthesis of 4-(1-phenyl-ethylamino)-pent-3-en-2-one 2. DL-α-Methyl benzylamine (0.1 mol, 12.1 g),



Scheme 1. The formation of a proposed catalyst precursor **8**.

2,4-pentanedione (0.1 mol, 10.0 g), and benzenesulfonic acid (0.30 mL) were placed in a 100 mL round flask and was refluxed in absolute toluene (10 mL) for 24 h. Removal of the solvent in vacuum afforded mixture. The resulting mixture was extracted by water and toluene. The organic extraction was recrystallized from hexane at 0 °C to afford a yellow solid **2** as the desired product. Yield: 18.29 g (90%). ¹H NMR (CDCl₃, δ/ppm): 11.24 (s, 1H, COH), 7.20–7.32 (m, 5H, Ph), 4.99 (s, 1H, CCHC), 4.66, 2.26 (m, 2H, PhCH), 2.04 (s, 1H, H(CO)C), 1.78 (s, 1H, NCHCH); ¹³C NMR (CDCl₃, δ/ppm): 18.8 (PhCC), 125.2, 126.9, 128.1, 143.9 (Ph), 24.4 (NCCH₃), 28.5 (O=CCH₃), 32.7 (PhC), 95.5 (NC=CH), 162.3 (NC=C), 194.9 (O=CCH₃); MS (FAB, *m/z*): 203 (M⁺).

4.1.3. Synthesis of 4-pentafluorophenylamino-pent-3-en-2-one 3. Pentafluoroaniline (0.02 mol, 3.6 g), 2,4-pentanedione (0.02 mol, 2.0 g), and benzenesulfonic acid (0.30 mL) were placed in a 100 mL round flask and was refluxed in absolute toluene (10 mL) for 24 h. Removal of the solvent in vacuum yielded mixture. The resulting mixture was extracted by water and toluene. The organic extraction was recrystallized from hexane at 0 °C to give a desired yellow solid **3**. Yield: 3.88 g (25%). ¹H NMR (CDCl₃, δ/ppm): 2.15 (s, 1H, H₃C(CO)CH), 5.340 (s, 1H, H₃C(CO)CH), 1.86 (s, 1H, NCHCH(CO)); ¹³C NMR (CDCl₃, δ/ppm): 136.4–144.8 (Ph), 18.6 (NCCH₃), 29.1 (O=CCH₃), 99.5 (NC=CH), 159.7 (NC=C), 197.9 (O=CCH₃); Elemental Anal. Calcd for C₁₁H₈NOF₅: C, 49.82; H, 3.04; N, 5.28%. Found: C, 49.55; H, 3.12; N, 4.98%.

4.1.4. Synthesis of 2-((2-methoxyphenyl)amino)-4-((2-methoxyphenyl)imino)-2-pentene 4. 2-Methoxyaniline (12.30 g, 100 mmol), 2,4-pentanedione (5.00 g, 50 mmol), and benzenesulfonic acid (0.30 mL) were placed in a 100 mL round flask and was refluxed in absolute toluene (30 mL) for 24 h. After being cooled to room temperature, volatile materials were removed under vacuum to give brown oil. Diethyl ether (100 mL) were then added and the resulting precipitate was extracted by CH₂Cl₂ (30 mL). The orange extraction was dried over MgSO₄, and filtered. Removal of the solvent in vacuum afforded a light yellow solid **4** as the targeted product. Yield: 3.88 g (25%). ¹H NMR (CDCl₃, δ/ppm): 12.20 (1H, s, NH), 6.99 (4H, d, *J* = 7.2 Hz, MeOArH), 6.86–6.88 (4H, m, ArH), 4.92 (1H, s, β-CH), 3.77 (6H, s, CH₃O), 1.98 (6H, s, α-CH₃) ppm; ¹³C NMR (CDCl₃, δ/ppm): 160.21 (C=N), 151.51 (MeOCCN), 135.61 (MeOCCN), 123.84, 123.29, 120.74, 111.68 (Ph), 98.16 (β-C), 55.98 (CH₃O), 21.39 (C=CHC); Elemental Anal. Calcd for C₁₉H₂₂N₂O₂: C, 73.52; H, 7.14; N, 9.03%. Found: C, 72.66; H, 7.58; N, 8.40%.

4.1.5. Synthesis of 2-[1-(2,4,6-trimethyl-phenylimino)-ethyl]-phenol 5. 2-Hydroxyacetophenone (50 mmol, 6.0 mL), 2,4,6-trimethylaniline (50 mmol, 7.0 mL), and benzenesulfonic acid (0.30 mL) were placed in a 100 mL round flask and was refluxed in 1-butanol (50 mL) for 48 h. Removal of the solvent in vacuum afforded mixture. The mixture was purified by column chromatography (silica gel, ethyl acetate/hexane = 1:23). The organic extraction was recrystallized from hexane at 0 °C to give a yellow solid **5**. Yield: 4.05 g (32%). ¹H NMR (CDCl₃, δ/ppm): 14.90 (s,

1H, OH), 7.61–7.65 (m, 1H, Ph), 7.33–7.42 (m, 1H, Ph); 7.01–7.05 (m, 1H, Ph), 6.85–6.89 (m, 3H, Ph), 2.30 (s, 3H, C=NCH₃), 2.16 (s, 6H, *o*-PhCH₃), 2.03 (s, 3H, *p*-PhCH₃); ¹³C NMR (CDCl₃, δ/ppm): 171.90 (C=N), 162.33, 142.42, 133.67, 132.85, 128.75, 128.63, 127.35, 119.18, 118.15, 117.84 (Ph), 20.64 (C=NCH₃), 17.98 (*o*-PhCH₃), 16.71 (*p*-PhCH₃); MS (EI, *m/z*): 253 (M⁺); Elemental Anal. Calcd for C₁₇H₁₉NO: C, 80.60; H, 7.56; N, 5.53%. Found: C, 80.84; H, 7.64; N, 5.90%.

4.1.6. Synthesis of 2-[1-(2,6-diisopropyl-phenylimino)-ethyl]-phenol 6. 2-Hydroxyacetophenone (50 mmol, 6.0 mL), 2,6-diisopropylaniline (50 mmol, 9.4 mL), and benzenesulfonic acid (0.30 mL) were placed in a 100 mL round flask and was refluxed in 1-butanol (50 mL) for 48 h. Removal of the solvent in vacuum afforded **6**. The organic extraction was recrystallized from hexane at 0 °C to afford a yellow solid **6**. Yield: 4.43 g (32%). ¹H NMR (CDCl₃, δ/ppm): 7.65 (d, *J* = 4 Hz, 1H, Ph), 7.39 (t, *J* = 3 Hz, 1H, Ph), 7.19 (d, 1H, Ph), 7.07 (d, *J* = 4 Hz, 1H, Ph), 6.93 (t, *J* = 2 Hz, 1H, Ph), 2.75–2.81 (m, 2H, CH(CH₃)₂), 2.20 (s, 3H, C=NCH₃), 1.13 (d, 6H, CH(CH₃)₂); ¹³C NMR (CDCl₃, δ/ppm): 172.22 (C=N), 162.42, 142.15, 138.14, 133.17, 128.93, 125.23, 123.27, 119.08, 118.36, 118.04 (Ph), 28.36 (C=NCH₃), 23.62 (CH(CH₃)₂), 22.78 (CH(CH₃)₂), 17.60 (CH(CH₃)₂); MS (EI, *m/z*): 295 (M⁺); Elemental Anal. Calcd for C₂₀H₂₅NO: C, 81.31; H, 8.53; N, 4.74%. Found: C, 81.48; H, 8.47; N, 4.64%.

4.1.7. Synthesis of Pd(C₁₇H₁₈NO)₂ 7. 2-[1-(2,4,6-Tri-methyl-phenylimino)-ethyl]-phenol (2.0 mmol, 0.506 g) and palladium acetate (1.0 mmol, 0.224 g) were placed in a 100 mL round bottle, and removal of air in vacuum for 1 h. The mixture was then allowed to react in absolute THF (10 mL) at room temperature for 1 h. Removal of the solvent in vacuum afforded **7** as a brown solid product. Yield: 0.604 g (96%). ¹H NMR (CDCl₃, δ/ppm): 7.37 (q, *J* = 2 Hz, 1H, Ph), 7.06 (m, *J* = 8 Hz, 1H, Ph), 6.98 (s, 2H, Ph), 6.49 (m, *J* = 8 Hz, 1H, Ph), 6.32 (d, *J* = 2 Hz, 1H, Ph), 2.33 (s, 3H, *p*-PhCH₃), 2.32 (s, 6H, *o*-PhCH₃), 2.03 (s, 3H, C=NCH₃); MS (EI, *m/z*): 610 (M⁺).

4.2. Exchanging procedure for the Suzuki coupling of aryl bromide

An oven-dried flask was evacuated and charged with complex **7** (3.05 mg, 0.5 mmol%), Pd(OAc)₂ (1.10 mg, 0.5 mmol%), the boronic acid (0.183 g, 1.0 mmol), 4-bromo-benzaldehyde (0.185 g, 1.0 mmol), KF (0.116 g, 2.0 mmol). Toluene (1 mL) was added and the mixture was stirred. After 50 min, 37% conversion was observed. Then, the conversion reached 81% after 7 days in reaction.

4.3. X-ray crystallographic studies

Suitable crystals of **7** were sealed in thin-walled glass capillaries under nitrogen atmosphere and mounted on a Bruker AXS SMART 1000 diffractometer. Intensity data were collected in 1350 frames with increasing (width of 0.3° per frame). The absorption correction was based on the symmetry equivalent reflections using SADABS program. The space group determination was based on a check of the Laue symmetry and systematic absences, and was

confirmed using the structure solution. The structure was solved by direct methods using a SHELXTL package. All non-H atoms were located from successive Fourier maps and hydrogen atoms were refined using a riding model. Anisotropic thermal parameters were used for all non-H atoms, and fixed isotropic parameters were used for H atoms.

5. Supplementary information available

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC no. 253791 for compound **7**. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or www.ccdc.cam.ac.uk).

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References and notes

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