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Air-stable imidazole-imine palladium complexes for Suzuki–Miyaura coupling: Toward an efficient, green synthesis of biaryl compounds

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ABSTRACT

New imidazole-imine ligands have been developed for the air and moisture stable Pd-catalyzed Suzuki–Miyaura cross-coupling reaction. Under optimized reaction conditions, coupling products from a wide range of aryl halides and aryl boronic acids were obtained in excellent yields.

1. Introduction

Many important reactions for carbon–carbon bond formation have been continuously developed over the past four decades. Among these, Suzuki–Miyaura cross-coupling reaction is one of the most effective methods for constructing biaryl structures which are wide-spread in many naturally occurring bioactive products [1–4]. This reaction has two significant advantages over other cross-coupling processes. Aryl boronic acid reactants are readily available and react under mild conditions. In addition, the inorganic by-products are usually easy to remove. However, several existing Suzuki–Miyaura cross-coupling methods generally employ palladium complexes supported by phosphine ligands [5–7], which are often sensitive to air oxidation and require air-sensitive handling. This oxygen sensitivity of catalyst is one of the crucial limitations that hamper the development of practical biaryl synthesis. Therefore, air- and moisture-stable ligands, which are easily prepared from inexpensive, commercially available starting materials, are needed for the improvement of Pd-catalyzed cross coupling reaction.

Our effort to develop an improved Suzuki reaction protocol has centered on the search for a catalytic system consisting of rigid phosphine-free ligands. The ligands with nitrogen-based frameworks such as, N-heterocyclic carbenes [8–12], nitrogen-acyclic carbenes [13], cyclometalated imine [14], diazabutadiene [15], and guanidines [16] have been reported. Despite the achievements of modest to high yields of products, the systems require high reaction temperatures under an inert atmosphere. In our studies, we selected the new imidazole-imine backbone due to its structural rigidity, strong σ-donating property and low-cost. In addition, compared to phosphine ligands, the imidazole-imine ligands are easier to prepare and more resistant to air. Substituents on the nitrogen atom of the imine moiety also play important roles in tuning steric and electronic properties of the molecule. Furthermore, no catalytic study of transition metal complexes supported by the bidentate, imidazole-imine based ligands has previously been investigated. Only structural, spectroscopic and water relaxivity properties of manganese(II) complexed with tetradentate imidazole-imine ligands have been reported [17].

Herein, we wish to report the synthesis of a series of new, air- and moisture-stable palladium complexes with imine ligands based on *N*-arylated imidazoles (Scheme 1) and their application in Suzuki–Miyaura cross-coupling reactions.

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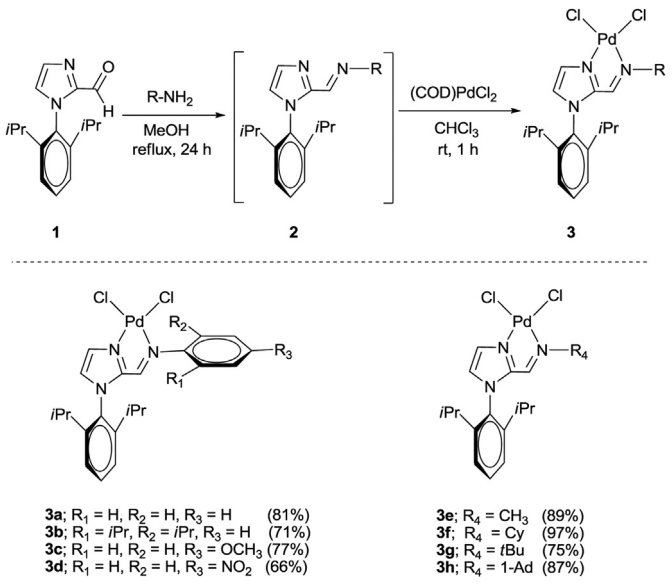
2. Results and discussion

2.1. Synthesis and X-ray crystal structure

As an access to imidazole-imine Pd complexes **3**, compound **1** was first prepared from a four-component condensation of the corresponding amine with formaldehyde, ammonium chloride, and glyoxal [18]. The 1-(2,6-diisopropylphenyl)-1*H*-imidazole compound was deprotonated by *n*-butyl lithium at −30 °C, and reacted with *N*,*N*-dimethylformamide to afford **1** in a quantitative yield. Compound **2** was obtained via the condensation of **1** with corresponding primary amines and used, without further purifications, to react with (COD)$PdCl_2$ to afford complexes **3a**–**3h** in good yields (Scheme 1).

The structural characterization of the ligands and complexes was carried out by ^1H, ^{13}C NMR spectroscopy, elemental analysis and HRMS. The ^1H NMR spectrum of the starting material **1** showed a signal of the aldehyde proton at 9.80 ppm and two singlet signals of imidazole protons at 7.51 ppm and 7.11 ppm which can be ascribed to H-4 and H-5, respectively. The NMR data are consistent with those of similar compounds described in the literature [18,19]. These imidazole protons also gave ^3J cross peaks with C-2 on the basis of HMBC correlation. In addition, only H-5 exhibited HMBC cross peaks with C-7, leaving the position of this proton at C-5. This result was confirmed by the signal enhancement of H-5 that was observed upon irradiation of methyl protons (H-12 and H-13) in an NOEDIFF experiment. According to the ^1H-COSY NMR spectral data, H-4 and H-5 appeared as distinct singlet signals and no cross-peak signal was found, suggesting no correlation between these two protons. However, the NOE enhancement of H-4 was detected upon irradiation of H-5 as shown in Fig. 1. Based on the HMBC and NOEDIFF results, H-4 and H-5 were attached on the neighboring carbon atoms and could thus be assigned as vicinal protons.

The structures of the imidazole-imine palladium complexes **3a**–**h** which were readily prepared from the reaction of ligands with (COD)$PdCl_2$ in chloroform also exhibited some characteristic ^1H NMR data and multiplicity of the two protons on the imidazole ring. Interestingly, their equivalent resonances were observed as doublet signals with low coupling constants ranging from 1.2 Hz to 1.6 Hz. For instance, the protons, H-4 and H-5, of complex **3h** appeared at 7.79 ppm and 7.07 ppm (J = 1.6 Hz), respectively, as shown in Fig. 2. Similarly, in case of the free imine ligand **2h**, the protons also resonated as the doublet signals at 7.33 ppm and 6.94 ppm (J = 0.8 Hz) (see Supporting information for the NMR data of the isolated ligand **2h**). The appearance of a cross-peak signal of complex **3h** in a ^1H-COSY spectrum indicated the correlation between these imidazole protons. The outcome of this study was also supported by the NOEDIFF results. Inspection of the NOEDIFF spectrum revealed the presence of NOE contacts which allow us to define the spatial relationship between the ligand protons, H-4 and H-5, as well as between the imine and H-16 methylene protons (Fig. 1). Moreover, the ^1H NMR data was also used to confirm the coordination of complex **3h**. The upfield shift of the characteristic singlet signal of the imine proton, H-6, with respect to the free ligand ($\delta_{coord} - \delta_{free} = -0.8$ ppm) was observed.



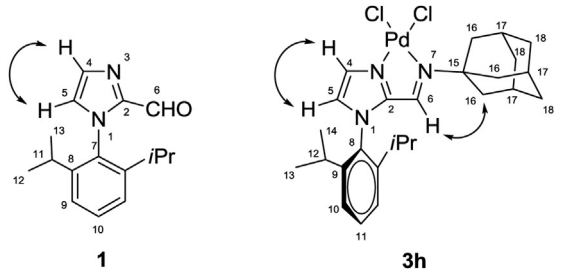
Scheme 1. Synthesis of imidazole-imine Pd complexes.

To further confirm the structure of the Pd complexes, crystals suitable for X-ray diffraction studies of **3b** and **3h** were obtained by slow diffusion of hexane into a chloroform solution. As shown in Figs. 3 and 4, the solid state of both palladium complexes revealed a distorted square planar geometry around Pd(II) center with the angle sum of approximately 360°. The imidazole-imine ligand coordinates to Pd(II) in a bidentate binding mode through imidazole and imine nitrogen atoms as expected. The closest C···C distances between isopropyl aryl substituents on imidazole and imine substituents (2,6-$^iPrC_6H_3$ and 1-adamantyl) are 3.993(13) Å (for **3b**) and 5.117(8) Å (for **3h**). The Pd–N1(imine) bond distances are slightly more than the expected range [20–22] and about 0.1 Å longer than those of Pd–N2(imidazole) [23]. All Pd–Cl bond lengths are similar and in the range of 2.26–2.27 Å, indicating comparable *trans* influence of imidazole and imine ligands. The N1–Pd–N2 bite angles of **3b** and **3h** are 80.00(13)° and 80.04(9)°, respectively (Table 1). Based on crystal data, 1-adamantyl substituent appears to be more sterically hindered than 2,6-$^iPrC_6H_3$, as evidenced by the unusually long Pd–N1 bond, larger N1–Pd–Cl2 angle of 101.33(7)° for **3h** [*cf.* 95.04(10)° for **3b**], and smaller Cl1–Pd–Cl2 angle of 88.45(3)° [*cf.* to 92.26(5)° for **3b**].

2.2. Suzuki–Miyaura cross-coupling catalyzed by imidazole-imine Pd complexes

To evaluate the catalytic activity of **3a**–**3h** for the palladium-catalyzed Suzuki–Miyaura cross-coupling, a reaction between phenyl boronic acid and *p*-bromoanisole was used as the model reaction at room temperature under aerobic conditions (Table 2). Interestingly, quantitative yields of the coupling product were obtained when catalysts **3b** and **3d** were used. However, compared to **3b**, palladium complexes of the more sterically hindered imine ligands **3g** and **3h** afforded only moderate product yields (entries 7 and 8). We also found that ligands **3e**–**h** which were prepared with the alkyl substituents tend to result in lower yields than those with the aromatic ones. Moreover, appropriated steric bulks at the imine moiety are crucial to achieve good catalytic activities, as very large substituents such as *tert*-butyl and 1-adamantyl only showed low activities. In comparison, the catalytic activity of palladium complexes containing our imidazole-imine ligands are superior to those with commercially available ligands including pyridine, phenanthroline, BINAP, and in the absence of ligand (Supporting information; Table S1).

Despite the fact that both catalysts **3b** and **3d** exhibited similar catalytic properties, we chose **3b** as the control catalyst for determining optimal conditions for palladium-catalyzed cross-coupling reaction of *p*-bromoanisole with phenyl boronic acid due to the more complicated preparation of **3d**. We then began to optimize reaction conditions by examining the catalyst loading and found that highly efficient catalysis could still be maintained even at



Complex **3h**	δ (ppm)
H-4	7.79
H-5	7.07
H-6	7.20
H-16	2.09

Fig. 1. Double arrows show the NOE contacts in aldehyde **1** and complex **3h**.

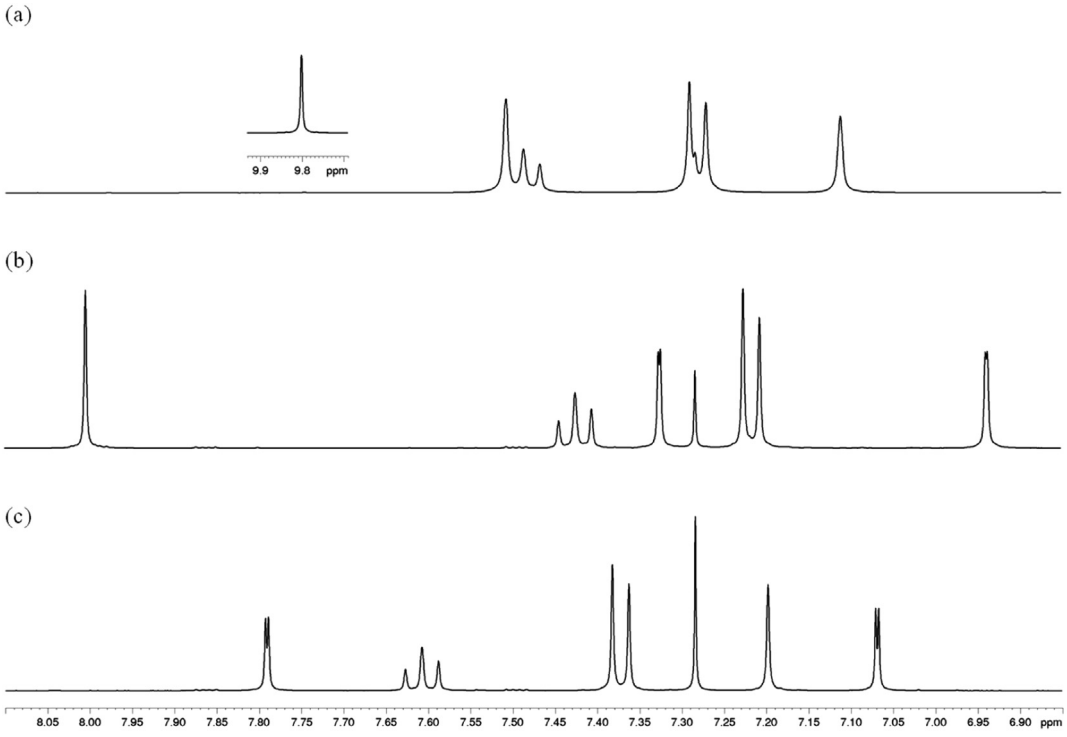


Fig. 2. ^{1}H NMR spectra of (a) aldehyde **1**; (b) ligand **2h** and; (c) complex **3h**.

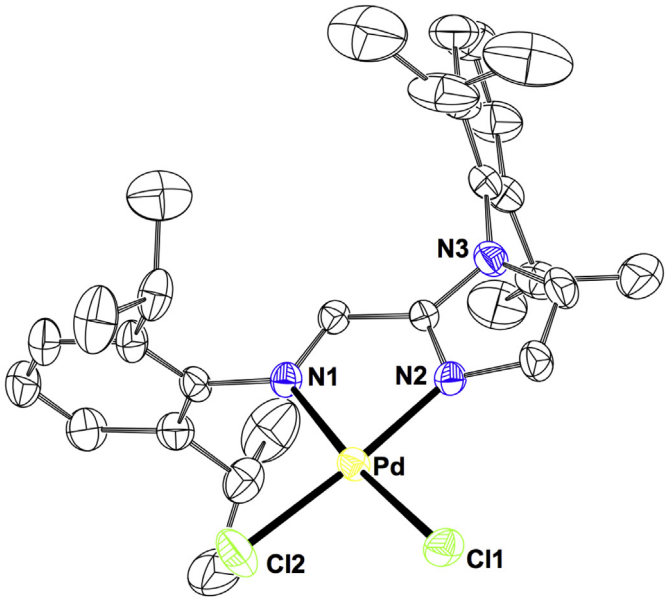


Fig. 3. ORTEP diagram of **3b** with 30% probability ellipsoids and partial labeling scheme. Hydrogen atoms and a molecule of $CHCl_3$ are omitted for clarity.

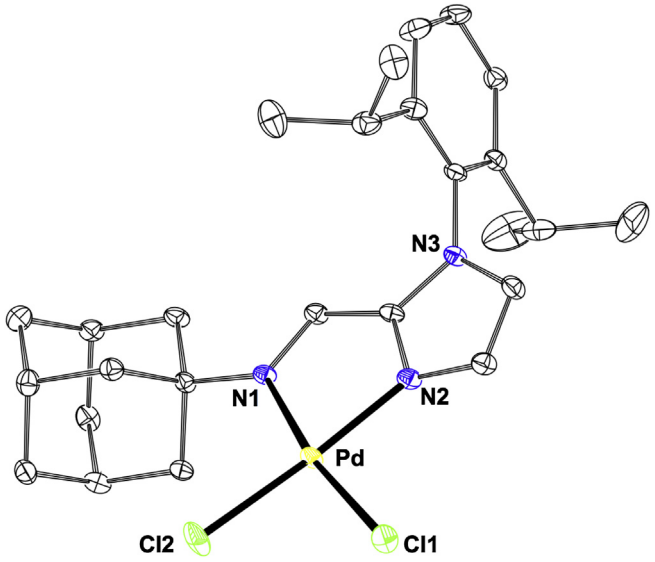


Fig. 4. ORTEP diagram of **3h** with 30% probability ellipsoids and partial labeling scheme. Hydrogen atoms are omitted for clarity.

Table 1
Selected bond lengths (Å) and bond angles (°) for **3b** and **3h**.

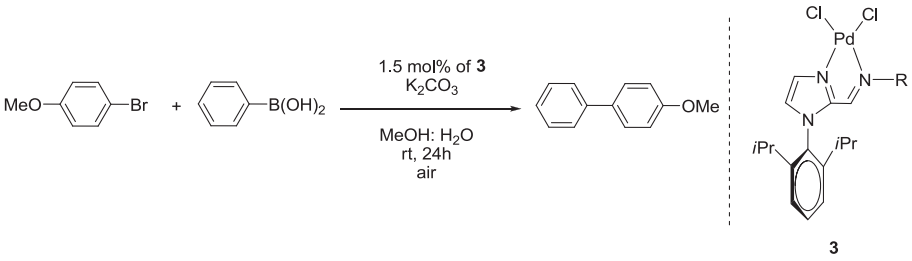
	Bond length (Å)			Bond angle (°)	
	3b	**3h**		**3b**	**3h**
Pd–N1	2.073(3)	2.120(2)	N1–Pd–N2	80.00(13)	80.04(9)
Pd–N2	2.007(3)	2.002(2)	Cl1–Pd–Cl2	92.26(5)	88.45(3)
Pd–Cl1	2.273(1)	2.270(1)	N1–Pd–Cl2	95.04(10)	101.33(7)
Pd–Cl2	2.258(1)	2.272(1)	N2–Pd–Cl1	92.71(9)	90.60(7)

catalyst loading as low as 0.15 mol% with a TON up to 666 (highest TON up to 12,000 with 0.001 mol % catalyst loading) (Table 3). Complex **3b** also exhibited higher efficiencies in terms of yields/TONs than the majority of those reported for the similar *N*,*N*-bidentate palladium catalysts with 4-MeOC$_6$H$_4$Br as substrate. For example, the catalytic systems consisting of Pd(OAc)$_2$/hydrazone [24] and Pd(OAc)$_2$/guadinine [16] were reported to have TONs up to 44.5 and 180, respectively. Also, the procedure using pyridyltriazole ligands resulted in a TON up to 180 [25]. Another pyridyltriazole based catalytic system recently reported by some of us exhibited a comparable activity (yields up to 85% with 0.1 mol % catalyst loading and a TON up to 850) [26]. An additional experiment under ambient conditions was carried out by varying the reaction time. The quantitative yield of 4-methoxybiphenyl could be achieved with the shortest reaction time of 4 h (Supporting information; Table S2).

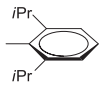
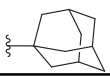
We also probed the effect of solvent and observed that aprotic solvents such as THF, DMF, acetonitrile, toluene, chloroform, acetone, and DMSO afforded low product yields in the range of 2–27%. On contrary, higher coupling product yields were obtained in methanol. Interestingly, although the coupling reaction in H_2O resulted in a low product yield, a small percentage of water in methanol has a beneficial effect on the reaction rate as found with other catalytic systems [27–29] (Supporting information; Tables S3 and S4). It was found that a 4:1 mixture of CH_3OH:H_2O at the *p*-bromoanisole concentration of 0.2 M provided the biaryl product in a quantitative yield. Next, we sought to determine which base offered the best result of the coupling reaction under the optimized conditions: 0.15 mol% of **3b** in the 4:1 CH_3OH:H_2O solvent. As a result, *p*-bromoanisole was successfully coupled with phenyl boronic acid in the highest product yield when K_2CO_3 was used as a base (Supporting information; Table S5).

Under the optimized reaction conditions, a wide variety of aryl halide substrates were highly reactive, generally giving the desired coupling products in good to quantitative yields (Table 4). The substrate scope was found to be remarkably broad, as the reaction tolerated both electron-donating and electron-withdrawing substituents. For example, with the exception of *ortho*-methoxy substituent, the electron-donating methoxy groups at *meta* and *para* positions gave the corresponding coupling products in quantitative yields (entries 2–5). Most aryl halides with an electron-withdrawing substituent resulted in excellent product yields *i.e.*,

Table 2
Ligand screening for Suzuki–Miyaura cross-coupling reaction between *p*-bromoanisole and phenyl boronic acid.[a]

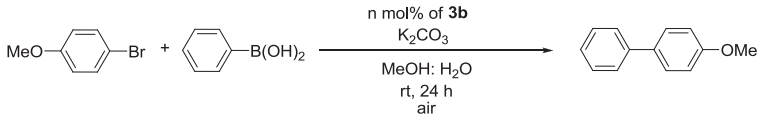


3

Entry	Complexes	R	Yield (%)[b]
1	**3a**		91
2	**3b**		>99
3	**3c**		82
4	**3d**		>99
5	**3e**		88
6	**3f**		83
7	**3g**		73
8	**3h**		69

[a] Reaction condition: 1.5 mol% of Pd catalyst, 0.5 mmol of *p*-bromoanisole, 0.6 mmol of phenyl boronic acid, 1.1 mmol of K_2CO_3, 2 mL of MeOH, 0.5 mL of H_2O, rt, 24 h. All reactions were carried out in air.
[b] The yield was determined by GC analysis using hexamethylbenzene as a calibrated internal standard.

Table 3
Catalytic activity of complex **3b** on the Suzuki–Miyaura cross-coupling reaction of *p*-bromoanisole with phenyl boronic acid.[a]



Entry	*n* mol%	Yield (%)[b]	TON
1	0.0001	0	0
2	0.001	12	12,000
3	0.01	85	8500
4	0.1	99	990
5	0.15	>99	666
6	0.2	>99	500
7	0.3	>99	333
8	0.4	>99	250
9	0.75	>99	133
10	1.5	>99	66
11	3	>99	33

[a] Reaction condition: 0.5 mmol of *p*-bromoanisole 0.6 mmol of phenyl boronic acid, 1.1 mmol of K_2CO_3, 2 mL of MeOH, 0.5 mL of H_2O, rt, 24 h.
[b] The yield was determined by GC analysis using hexamethylbenzene as a calibrated internal standard.

more than 90% (entries 6–11), except for *para*-fluoro (65%), hydroxyl (84%), and phenyl (86%) groups (entries 12–14). When heterocyclic halides were used as substrates, moderate yields of the coupling products were obtained (entries 15–17), presumably due to nitrogen coordination and subsequent inactivation of the palladium catalyst. Based on the results thus far, no significant effect on product yields was observed from varying aryl bromide substrates, suggesting relatively fast oxidative addition. Moreover, no reaction was observed when *p*-chloroanisole was used as a substrate (Data not shown).

In Table 5, C–C coupling between the electron-rich 4-methoxyphenyl boronic acid and bromobenzene gave products in high yields (entries 1–3). However, the yields decreased with the electron-withdrawing 4-acetylphenyl boronic acid substrate (entries 4 and 5). Furthermore, an electron-deficient acetyl substituent on aryl bromide afforded an increase in product yields, from 80% to 90% (entries 1 and 6). It seems that although electronic properties of aryl halides do not significantly affect the reaction rates, the presence of electron-withdrawing substituent on phenyl boronic acid apparently decreases product yields.

It should be noted that, formation of palladium black was not observed with catalyst **3b** during the course of the reactions. In order to elucidate whether Pd(0) nanoparticles are involved in the reaction, we have also carried out a mercury poisoning test with **3b**. A coupling reaction between *p*-bromoanisole and $PhB(OH)_2$ in the presence of excess Hg (Hg:Pd = 400:1) under the reaction conditions described for entry 2 (Table 4) showed a decrease of product yield (down to 33%). The drop in the coupling product yield implies that the cross-coupling reactions were catalyzed, to some extent, by heterogeneous Pd(0) nanoparticles [30,31]. Furthermore, a previous study on the catalytic activity of Pd(0) species in the Suzuki–Miyaura cross-coupling reaction has shown that O_2 can prevent Pd(0) nanoparticle aggregation [32], probably by inhibiting the formation of Pd–Pd bonds through the adsorption of O_2 [33,34]. This could be a reason why our catalytic system can operate in air.

3. Conclusion

In summary, an efficient, air-stable protocol for the palladium-catalyzed Suzuki–Miyaura cross-coupling reaction has been developed. The use of imidazole-imine supporting ligands offers substantial catalyst improvements with regard to air-stability and catalytic efficiency. The catalytic studies have also shown that our catalyst system is wide in substrate scope, uses low catalyst loading, and generates water-soluble by-products. These are consistent with characteristics of green chemistry.

4. Experimental

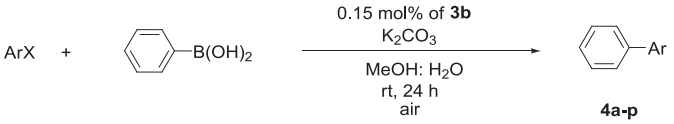
4.1. General information

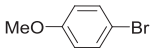
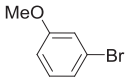
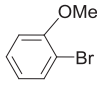
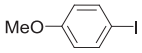
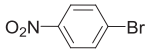
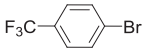
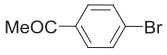
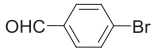
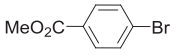
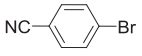
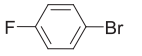
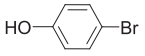
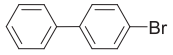
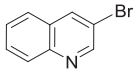
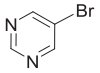
All reagents were purchased from commercial sources and used without further purification. *n*-BuLi was titrated with diphenylacetic acid to confirm the correct concentration. The $(COD)PdCl_2$ was prepared following the literature procedure [35]. DMF was distilled from CaH_2, stored over 4 Å molecular sieves, and handled under argon atmosphere. Thin layer chromatography (TLC) was purchased on Merck silica gel 60 F_{254} aluminum sheets. Column chromatography was performed using Merck silica gel 60 (70–230 mesh.). NMR spectra were recorded on Bruker DPX-300 (300 MHz) and Bruker Ascend™ 400 (400 MHz) spectrometers. The chemical shifts (δ) for ^1H are given in ppm and referenced to the residual proton signal of the deuterated solvent. The chemical shifts (δ) for ^{13}C are referenced relative to the signal from the carbon of the deuterated solvent. The high resolution mass spectra were recorded on HR-TOF-MS Micromass model VQ-TOF2 spectrometer. The elemental analyses were performed by Perkin Elmer Elemental Analyzer 2400 CHN. Gas chromatography analysis was performed on Agilent Technologies 6890N with FID detector and HP-1 capillary column (polymethylsiloxane, 25 m, 0.32 mm, 0.17 μm film thickness). Gas chromatography-mass analysis was performed on Agilent Technologies 7890A with 5975C inert XL MSD with Triple-Axis detector and HP-5 capillary column (polydimethylsiloxane with 5% phenyl group, 20 m, 0.25 mm, 0.25 μm film thickness) using helium as a carrier gas.

4.2. X-ray crystallography

Crystallographic analyses of complexes **3b** and **3h** were carried out at the Mahidol crystallographic facility. Diffraction measurements were made on a 4 K Bruker SMART [36] CCD area detector diffractometer using graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å). Crystals were mounted in paratone oil and held at room temperature during data collection. Cell constants and an orientation matrix for data collection were obtained from a least-square refinement using the measured positions of reflections in

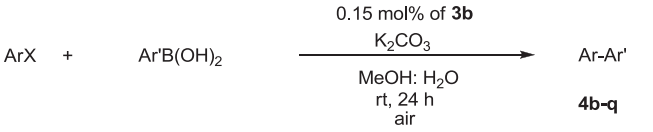
Table 4
Study of substrate scopes for Suzuki–Miyaura cross-coupling reaction between aryl halides and phenyl boronic acid.[a]

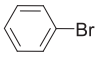
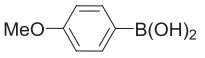
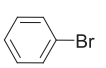
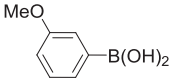
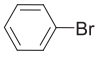
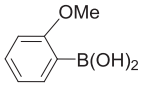
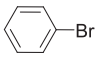
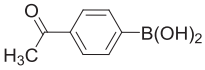
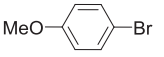
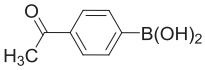
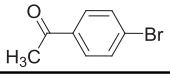
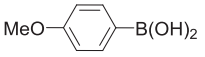


Entry	ArX	Product	Yield[b] (%)
1		**4a**	95
2		**4b**	>99[c]
3		**4c**	>99
4		**4d**	68
5		**4b**	95[c]
6		**4e**	92
7		**4f**	>99
8		**4g**	>99
9		**4h**	91
10		**4i**	97
11		**4j**	98
12		**4k**	65
13		**4l**	84
14		**4m**	86
15		**4n**	60[d]
16		**4o**	41[d]
17		**4p**	45[d]

[a] Reaction condition: 0.15 mol% of Pd catalysts, 0.5 mmol of aryl halide, 0.6 mmol of phenyl boronic acid, 1.1 mmol of K_2CO_3, 2 mL of MeOH, 0.5 mL of H_2O, rt, 24 h. All reactions were carried out in air.
[b] Isolated yield.
[c] GC yield.
[d] 1.5 mol% catalyst loading.

Table 5
Study of substrate scopes for Suzuki–Miyaura cross-coupling reaction between aryl halides and aryl boronic acids.[a]



Entry	ArX	Ar′B(OH)$_2$	Product	Yield[b] (%)
1			**4b**	80
2			**4c**	75
3			**4d**	85[c]
4			**4g**	64[c]
5			**4q**	68[c]
6			**4q**	90[c]

[a] Reaction condition: 0.15 mol% of Pd catalysts, 0.5 mmol of aryl halide, 0.6 mmol of phenyl boronic acid, 1.1 mmol of K_2CO_3, 2 mL of MeOH, 0.5 mL of H_2O, rt, 24 h. All reactions were carried out in air.
[b] Isolated yield.
[c] 1.5 mol% catalyst loading.

the range $0.998° < \theta < 28.4°$ (for **3b**) and $0.998° < \theta < 29.1°$ (for **3h**). The frame data were integrated by the program SAINT [37] and corrected for Lorentz and polarization effects. The structure was solved by the maXus crystallographic software package [38], using

Table 6
Crystal data for **3b** and **3h**.

	3b•$CHCl_3$	**3h**
Empirical formula	$C_{29}H_{37}Cl_5N_3Pd$	$C_{26}H_{35}Cl_2N_3Pd$
FW	711.27	566.87
Cryst color, habit	Orange, cube	Orange, cube
Cryst size (mm)	0.35 × 0.25 × 0.20	0.30 × 0.25 × 0.20
Cryst system	Orthorhombic	Monoclinic
Space group	*Pbca* (#61)	$P2_1/c$ (#14)
a (Å)	13.6508(2)	14.2165(6)
b (Å)	21.1682(4)	11.9991(3)
c (Å)	23.4645(4)	18.7543(7)
α (deg)	90.00	90.00
β (deg)	90.00	125.0801(14)
γ (deg)	90.00	90.00
Volume (Å^3)	6780.50(2)	2618.09(16)
θ range (deg)	0.998–26.4	0.998–29.1
Z	8	4
T/K	298	298
D_{calc} (g/cm^3)	1.392	1.438
μ (mm^{-1})	0.963	0.931
No. of reflns	6914	7035
No. of params refined	353	289
Refln/param ratio	19.6	24.3
Final residuals R_1[a]; wR_2[b]	0.0557; 0.1852	0.0478; 0.1126
Goodness of fit indicator[c]	1.331	0.987
Max. shift/error in final LS cycle	0.001	0.001

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.
[b] $wR_2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$, where $w = [\sigma^2(F_o^2) + (aP)^2 + bP]^{-1}$.
[c] GOF $= [\Sigma w(|F_o| - |F_c|)^2/(N_{obs} - N_{param})]^{1/2}$.

direct methods (SIR97) [39] and refined by full-matrix least-squares method on $(F_{obs})^2$ using the SHELXTL-PC V 6.12 software package [40] (Table 6).

X-ray quality crystals of **3b** and **3h** were grown by layer diffusion of hexane onto the $CHCl_3$ solution of the palladium complexes at room temperature.

Complex **3b** crystallizes in the orthorhombic *Pbca* space group with each asymmetric unit cell containing one molecules of **3b** and one distorted $CHCl_3$ molecule. The $CHCl_3$ molecule was modeled with Cl5 and Cl6 atoms each occupying a half-occupancy with no hydrogen. Large thermal ellipsoids were observed for isopropyl groups. All non-hydrogen atoms were refined anisotropically while the hydrogen atoms were placed in calculated positions and not refined.

Complex **3h** crystallized in the monoclinic $P2_1/c$ space group with each asymmetric unit containing one molecule of **3h**. Large thermal ellipsoids were observed for isopropyl groups. All non-hydrogen atoms were refined anisotropically while the hydrogen atoms were placed in calculated positions and not refined.

4.3. Synthesis of 1-(2,6-diisopropylphenyl)-1H-imidazole

The 1-(2,6-diisopropylphenyl)-1*H*-imidazole was prepared according to the literature procedure [18]. The crude product was purified by column chromatography (SiO_2, EtOAc). The NMR spectra agree with published data [18]. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.48 (s, 1H), 7.46 (t, J = 7.9 Hz, 1H), 7.28 (s, 1H), 7.27 (d, J = 7.4 Hz, 2H), 6.96 (s, 1H), 2.41 (sept, J = 6.9 Hz, 2H), 1.15 (d, J = 6.9 Hz, 12H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 146.5, 138.5, 132.8, 129.8, 129.3, 123.7, 121.5, 28.1, 24.4, 24.3. HRMS (ESI): calcd. for $C_{15}H_{20}N_2$ $[M + H]^+$ 229.1705; Found: 229.1727.

4.4. Synthesis of 1-(2,6-diisopropylphenyl)-1H-imidazole-2-carboxaldehyde (*1*)

In a 100 mL round-bottomed flask equipped with a magnetic stir bar was charged with 1-(2,6-diisopropylphenyl)-1*H*-imidazole (855 mg, 3.74 mmol, 1.0 equiv), closed with three-way, evacuated and backfilled with argon (this procedure was repeated three times). The dried THF (20 mL) was added by syringe then *n*-BuLi (1.17 M in hexane, 3.9 mL, 4.48 mmol, 1.2 equiv) was slowly added at −30 °C. The reaction mixture was allowed to warm to room temperature and stirred for 3 h. Dried DMF (0.45 mL, 5.61 mmol, 1.5 equiv) was added under argon atmosphere and continually stirred for 16 h. The saturated NH_4Cl solution was added to reaction flask and poured into the separatory funnel. The aqueous phase was extracted with CH_2Cl_2 (3 × 10 mL), washed with brine (1 × 10 mL) and dried with Na_2SO_4. The combined organic phase was concentrated under vacuum. The crude product was purified by column chromatography (SiO_2, CH_2Cl_2) to afford the pure product **1** (955 mg, 99%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.80 (s, 1H), 7.51 (s, 1H), 7.49 (t, J = 7.7 Hz, 1H), 7.28 (d, J = 7.7 Hz, 2H), 7.11 (br s, 1H), 2.21 (sept, J = 6.8 Hz, 2H), 1.12 (d, J = 6.8 Hz, 6H), 1.08 (d, J = 6.8 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 180.2, 145.1, 144.6, 132.5, 132.0, 130.0, 127.4, 123.9, 28.3, 24.6, 23.3. HRMS (ESI): calcd. for $C_{16}H_{20}N_2O$ $[M + H]^+$ 257.1654, Found: 257.1631.

4.5. General procedure for the preparation of palladium complexes (*3a–h*)

In a 50 mL round-bottomed flask equipped with a magnetic stir bar and a reflux condenser was charged with 1-(2,6-diisopropylphenyl)-1*H*-imidazole-2-carboxaldehyde (1.0 equiv) and the corresponding primary amine (1.0 equiv). Then, MeOH (6 mL) was added into the reaction vial. The reaction mixture was refluxed for 16 h and concentrated under reduced pressure to afford the target imine ligand (the imine ligand was used in the next step without further purification) (**Note**: If the starting material is *p*-nitroaniline, a Dean–Stark trap will be used and the reaction mixture will be refluxed for 48 h). In a 10 mL vial equipped with magnetic stir bar was charged with (COD)$PdCl_2$ (1.0 equiv) and the corresponding imine ligand (1.0 equiv) under air condition. Chloroform (0.05 M) was added as solvent into the reaction vial. The reaction mixture was stirred at room temperature for 1 h. The solvent was evaporated. The crude product was recrystallized three times by using chloroform and hexane to give pure palladium complexes.

4.5.1. Synthesis of palladium complex (*3a*)

((1-(2,6-Diisopropylphenyl)-1*H*-imidazol-2-yl)methylene)aniline ligand was prepared from **1** (76.9 mg, 0.3 mmol, 1.0 equiv) and aniline (27.4 μL, 0.3 mmol, 1.0 equiv) in MeOH (6 mL, 0.05 M). The crude imine ligand was reacted with (COD)$PdCl_2$ (86.2 mg, 0.3 mmol, 1.0 equiv) in chloroform (6 mL, 0.05 M) following the general procedure for the preparation of palladium complexes to afford complex **3a** as a red crystalline (124 mg, 81%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (d, J = 1.4 Hz, 1H), 7.59 (t, J = 8.0 Hz, 1H), 7.49 (s, 1H), 7.40–7.36 (m, 5H), 7.30–7.27 (m, 2H), 7.25 (d, J = 1.4 Hz, 1H), 2.35 (sept, J = 6.9 Hz, 2H), 1.21 (d, J = 6.9 Hz, 6H), 1.19 (d, J = 6.9 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 151.5, 147.5, 146.7, 145.8, 132.2, 130.3, 129.6, 129.5, 128.7, 126.0, 124.9, 123.7, 28.6, 24.6, 24.2. HRMS (ESI): calcd. for $C_{22}H_{25}Cl_2N_3Pd$ $[M + Na]^+$ 532.0351, Found: 532.0352.

4.5.2. Synthesis of palladium complex (*3b*)

((1-(2,6-Diisopropylphenyl)-1*H*-imidazol-2-yl)methylene)-2,6-diisopropylaniline ligand was prepared from **1** (76.9 mg, 0.3 mmol, 1.0 equiv) and 2,6-diisopropylamine (56.6 μL, 0.3 mmol, 1.0 equiv) in MeOH (6 mL, 0.05 M). The crude imine ligand was reacted with (COD)$PdCl_2$ (86.2 mg, 0.3 mmol, 1.0 equiv) in chloroform (6 mL, 0.05 M) following the general procedure for the preparation of palladium complexes to afford complex **3b** as a red crystalline (127 mg, 71%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.88 (d, J = 1.2 Hz, 1H), 7.57 (t, J = 7.9 Hz, 1H), 7.47 (s, 1H), 7.35–7.26 (m, 3H), 7.14 (d, J = 7.9 Hz, 2H), 3.27 (sept, J = 6.9 Hz, 2H), 2.34 (sept, J = 6.7 Hz, 2H), 1.42 (d, J = 6.9 Hz, 6H), 1.21 (d, J = 6.7 Hz, 6H), 1.18 (d, J = 6.7 Hz, 6H), 1.06 (d, J = 6.9 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 207.0, 153.8, 146.8, 145.7, 142.6, 140.6, 132.3, 130.3, 129.6, 128.9, 126.3, 124.8, 123.3, 28.7, 24.7, 24.2, 23.8, 23.2. HRMS (ESI): calcd. for $C_{28}H_{37}Cl_2N_3Pd$ $[M + Na]^+$ 616.1291; Found: 616.1291. Anal. Calcd. for $C_{28}H_{37}Cl_2N_3Pd$: C, 56.72; H, 6.29; N, 7.09. Found: C, 56.85; H, 6.74; N, 7.15.

4.5.3. Synthesis of palladium complex (*3c*)

((1-(2,6-Diisopropylphenyl)-1*H*-imidazol-2-yl)methylene)-4-methoxyaniline ligand was prepared from **1** (76.9 mg, 0.3 mmol, 1.0 equiv) and *p*-anisidine (36.9 mg, 0.3 mmol, 1.0 equiv) in MeOH (6 mL, 0.05 M). The crude imine ligand was reacted with (COD)$PdCl_2$ (86.2 mg, 0.3 mmol, 1.0 equiv) in chloroform (6 mL, 0.05 M) following the general procedure for the preparation of palladium complexes to afford complex **3c** as a red crystalline (124 mg, 77%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.82 (d, J = 1.3 Hz, 1H), 7.60 (t, J = 7.8 Hz, 1H), 7.41 (s, 1H), 7.37 (d, J = 7.8 Hz, 2H), 7.29–7.26 (m, 2H), 7.22 (d, J = 1.3 Hz, 1H), 6.87 (d, J = 9.0 Hz, 2H), 3.81 (s, 3H), 2.35 (sept, J = 6.9 Hz, 2H), 1.21 (d, J = 6.9 Hz, 6H), 1.18 (d, J = 6.9 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 160.7, 149.7, 147.7, 145.8, 140.0, 132.1, 130.0, 129.7, 125.5, 125.3, 124.9, 113.8, 55.6, 28.6, 24.5, 24.2. HRMS (ESI): calcd. for $C_{23}H_{27}Cl_2N_3OPd$ $[M + Na]^+$ 562.0457; Found: 562.0457.

4.5.4. Synthesis of palladium complex (**3d**)

((1-(2,6-Diisopropylphenyl)-1*H*-imidazol-2-yl)methylene)-4-nitroaniline ligand was prepared from **1** (76.9 mg, 0.3 mmol, 1.0 equiv) and *p*-nitroaniline (41.4 mg, 0.3 mmol, 1.0 equiv) in MeOH (6 mL, 0.05 M). The crude imine ligand was reacted with (COD)$PdCl_2$ (86.2 mg, 0.3 mmol, 1.0 equiv) in chloroform (6 mL, 0.05 M) following the general procedure for the preparation of palladium complexes to afford complex **3d** as an orange solid (110 mg, 66%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.21 (d, J = 9.0 Hz, 2H), 7.85 (d, J = 1.2 Hz, 1H), 7.62–7.57 (m, 2H), 7.49 (d, J = 9.0 Hz, 2H), 7.37 (d, J = 7.8 Hz, 2H), 2.41 (sept, J = 6.8 Hz, 2H), 1.22–1.18 (m, 12H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 153.1, 150.9, 147.6, 147.3, 146.0, 132.3, 130.9, 129.9, 129.6, 126.9, 125.1, 125.0, 124.1, 28.6, 24.8, 24.3. HRMS (ESI): calcd. for $C_{22}H_{24}Cl_2N_4O_2Pd$ $[M + Na]^+$ 577.0202, Found: 577.0202.

4.5.5. Synthesis of palladium complex (**3e**)

((1-(2,6-Diisopropylphenyl)-1*H*-imidazol-2-yl)methylene) methylamine ligand was prepared from **1** (64 mg, 0.25 mmol, 1.0 equiv) and 40 %w/w methylamine solution (22 μL, 0.25 mmol, 1.0 equiv) in MeOH (4 mL, 0.05 M). The crude imine ligand was reacted with (COD)$PdCl_2$ (71.8 mg, 0.25 mmol, 1.0 equiv) in chloroform (5 mL, 0.05 M) following the general procedure for the preparation of palladium complexes to afford complex **3e** as a yellow solid (99.3 mg, 89%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.68 (d, J = 1.4 Hz, 1H), 7.59 (t, J = 7.8 Hz, 1H), 7.45 (m, 1H), 7.37 (d, J = 7.8 Hz, 2H), 7.14 (d, J = 1.4 Hz, 1H), 3.70 (s, 3H), 2.31 (sept, J = 6.8 Hz, 2H), 1.20–1.16 (m, 12H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 152.8, 147.2, 145.8, 132.1, 129.7, 129.6, 124.8, 49.1, 28.5, 24.7, 24.1. Anal. Calcd. for $C_{17}H_{23}Cl_2N_3Pd$: C, 45.71; H, 5.19; N, 9.41. Found: C, 45.77; H, 5.21; N, 9.22.

4.5.6. Synthesis of palladium complex (**3f**)

((1-(2,6-Diisopropylphenyl)-1*H*-imidazol-2-yl)methylene) cyclohexylamine ligand was prepared from **1** (128 mg, 0.3 mmol, 1.0 equiv) and cyclohexylamine (34.4 μL, 0.3 mmol, 1.0 equiv) in MeOH (6 mL, 0.05 M). The crude imine ligand was reacted with (COD)$PdCl_2$ (86.2 mg, 0.3 mmol, 1.0 equiv) in chloroform (5 mL, 0.05 M) following the general procedure for the preparation of palladium complexes to afford complex **3f** as a red crystalline (149.9 mg, 97%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.69 (d, J = 1.4 Hz, 1H), 7.60 (t, J = 7.8 Hz, 1H), 7.36 (d, J = 7.8 Hz, 2H), 7.28 (m, 1H), 7.14 (d, J = 1.4 Hz, 1H), 4.29 (m, 1H), 2.30–2.20 (m, 4H), 1.81–1.65 (m, 4H), 1.41 (m, 2H), 1.19–1.10 (m, 12H), 1.04–0.99 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 148.7, 147.9, 145.6, 132.1, 129.6, 129.4, 124.9, 124.6, 65.5, 33.8, 28.4, 25.1, 25.0, 24.2. HRMS (ESI): calcd. for $C_{22}H_{31}Cl_2N_3Pd$ $[M + Na]^+$ 538.0820, Found: 538.0820.

4.5.7. Synthesis of palladium complex (**3g**)

((1-(2,6-Diisopropylphenyl)-1*H*-imidazol-2-yl)methylene)-*tert*-butylamine ligand was prepared from **1** (64 mg, 0.25 mmol, 1.0 equiv) and *tert*-butylamine (26.4 μL, 0.25 mmol, 1.0 equiv) in MeOH (4 mL, 0.05 M). The crude imine ligand was reacted with (COD)$PdCl_2$ (71.8 mg, 0.25 mmol, 1.0 equiv) in chloroform (5 mL, 0.05 M) following the general procedure for the preparation of palladium complexes to afford complex **3g** as a red crystalline (93.9 mg, 75%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.78 (d, J = 1.4 Hz, 1H), 7.61 (t, J = 7.8 Hz, 1H), 7.37 (d, J = 7.8 Hz, 2H), 7.26 (m, 1H), 7.11 (d, J = 1.4 Hz, 1H), 2.26 (sept, J = 6.7 Hz, 2H), 1.54 (s, 9H), 1.19 (d, J = 6.7 Hz, 6H), 1.12 (d, J = 6.7 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 147.7, 147.6, 145.6, 132.2, 129.6, 129.5, 124.9, 124.4, 66.7, 29.6, 28.4, 24.3, 24.2. Anal. Calcd. for $C_{20}H_{29}Cl_2N_3Pd$: C, 49.14; H, 5.98; N, 8.60. Found: C, 49.28; H, 6.03; N, 8.48.

4.5.8. Synthesis of palladium complex (**3h**)

((1-(2,6-Diisopropylphenyl)-1*H*-imidazol-2-yl)methylene) adamantylamine ligand was prepared from **1** (89.7 mg, 0.35 mmol, 1.0 equiv) and 1-adamantylamine (52.9 mg, 0.35 mmol, 1.0 equiv) in MeOH (7 mL, 0.05 M). The crude imine ligand was reacted with (COD)$PdCl_2$ (100 mg, 0.35 mmol, 1.0 equiv) in chloroform (7 mL, 0.05 M) following the general procedure for the preparation of palladium complexes to afford complex **3h** as a red microcrystalline (86.7 mg, 87%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.79 (d, J = 1.6 Hz, 1H), 7.61 (t, J = 7.7 Hz, 1H), 7.37 (d, J = 7.7 Hz, 2H), 7.20 (s, 1H), 7.07 (d, J = 1.6 Hz, 1H), 2.27 (sept, J = 7.0 Hz, 2H), 2.18 (m, 3H), 2.09 (m, 6H), 1.70 (m, 6H), 1.20 (d, J = 7.0 Hz, 6H), 1.14 (d, J = 7.0 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 147.9, 147.7, 145.8, 132.1, 129.7, 129.5, 124.9, 124.1, 67.0, 42.1, 35.5, 29.5, 28.5, 24.31, 24.30. Anal. Calcd. for $C_{26}H_{35}Cl_2N_3Pd$; C, 55.09; H, 6.22; N, 7.41. Found: C, 55.16; H, 6.59; N, 7.31.

4.6. General procedure for screening of palladium complexes for Suzuki–Miyaura cross coupling reaction (Table 1)

In the air condition, a 10 mL vial equipped with a magnetic stir bar was charged with Pd complexes (1.5 mol%), hexamethylbenzene (0.05 mmol, 0.0081 g, 0.1 equiv) phenyl boronic acid (0.6 mmol, 0.073 g, 1.2 equiv), K_2CO_3 (1.1 mmol, 0.153 g, 2.2 equiv) and *p*-bromoanisole (0.5 mmol, 0.062 mL, 1.0 equiv). MeOH (2 mL) and water (0.5 mL) were mixed and added to the reaction mixture. The reaction vial was capped and vigorously stirred at room temperature for 24 h. The reaction mixture was extracted with CH_2Cl_2 (3 × 10 mL), washed with water (2 × 10 mL), brine (1 × 10 mL) and dried over Na_2SO_4. Solvent was then evaporated. The reaction was monitored by GC-FID to determine the yield of the product based on integration relative to hexamethylbenzene as an internal standard.

4.7. General procedure for the investigation of the effect of catalyst loading, base, solvent, time and substrate scopes on Suzuki–Miyaura cross coupling reaction (Tables S1–S5, Tables 4 and 5)

In the air condition, hexamethylbenzene (0.05 mmol, 0.0081 g, 0.1 equiv), aryl halide (0.5 mmol, 1 equiv), aryl boronic acid (0.6 mmol, 1.2 equiv), base (1.1 mmol, 2.2 equiv) and solvent was subsequently added into a 10 mL vial equipped with a magnetic stir bar. The 5 mM Pd catalyst solution in MeOH was added as indicated in the table. The reaction vial was capped and vigorously stirred at room temperature for desired time as indicated. The reaction mixture was extracted with CH_2Cl_2 (3 × 10 mL), washed with water (2 × 10 mL), brine (1 × 10 mL) and dried over Na_2SO_4. The combined organic phase was then concentrated to afford the crude coupling product. The reaction was monitored by GC-FID based on integration relative to hexamethylbenzene as an internal standard. The crude product was finally isolated by column chromatography (0–10%: EtOAc/hexane) to afford the desired product.

4.8. Analytical data of coupling products (**4a**–**q**)

4.8.1. Biphenyl (**4a**, Table 4, entry 1)

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.65 (d, J = 7.7 Hz, 4H), 7.49 (t, J = 7.7 Hz, 4H), 7.37 (m, 2H). EI-MS (*m*/*z*, relative intensity): 155 (14), 154 (M^+, 100), 153 (42), 152 (29). CAS Number: 92-52-4.

4.8.2. 4-Methoxybiphenyl (**4b**, Table 4, entries 2 and 5; Table 5, entry 1)

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.57 (t, J = 8.7 Hz, 4H), 7.44 (t, J = 7.5 Hz, 2H), 7.35–7.28 (m, 1H), 7.00 (d, J = 8.7 Hz, 2H), 3.88 (s,

3H). EI-MS (*m/z*, relative intensity): 185 (14), 184 (M^+, 100), 169 (46), 141 (45), 115 (33). CAS Number: 613-37-6.

*4.8.3. 3-Methoxybiphenyl (**4c**, Table 4, entry 3; Table 5, entry 2)*

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.62 (d, J = 7.5 Hz, 2H), 7.47 (t, J = 7.5 Hz, 2H), 7.42–7.36 (m, 2H), 7.22 (d, J = 8.1 Hz, 1H), 7.16 (m, 1H), 6.94 (d, J = 8.1 Hz, 1H), 3.90 (s, 3H). EI-MS (*m/z*, relative intensity): 185 (15), 184 (M^+, 100), 154 (23), 153 (20), 141 (32), 115 (30). CAS Number: 2113-56-6.

*4.8.4. 2-Methoxybiphenyl (**4d**, Table 4, entry 4; Table 5, entry 3)*

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.64 (d, J = 7.2 Hz, 2H), 7.51 (t, J = 7.4 Hz, 2H), 7.42 (t, J = 7.3 Hz, 3H), 7.15–7.06 (m, 2H), 3.89 (s, 3H). EI-MS (*m/z*, relative intensity): 185 (14), 184 (M^+, 100), 183 (21), 169 (54), 168 (15), 141 (37), 139 (17), 115 (37). CAS Number: 86-26-0.

*4.8.5. 4-Nitrobiphenyl (**4e**, Table 4, entry 6): ^{1}H NMR (300 MHz, $CDCl_3$)*

δ = 8.33 (d, J = 9.0 Hz, 2H), 7.76 (d, J = 9.0 Hz, 2H), 7.67–7.64 (m, 2H), 7.56–7.47 (m, 3H). EI-MS (*m/z*, relative intensity): 200 (13), 199 (M^+, 97), 169 (35), 153 (28), 152 (100), 151 (30), 141 (28). CAS Number: 92-93-3.

*4.8.6. 4-(Trifluoromethyl)biphenyl (**4f**, Table 4, entry 7)*

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.61–7.55 (m, 4H), 7.49 (m, 2H), 7.39–7.27 (m, 3H). EI-MS (*m/z*, relative intensity): 223 (13), 222 (M^+, 100), 201 (10), 151 (20). CAS Number: 398-36-7.

*4.8.7. 4-Acetylbiphenyl (**4g**, Table 4, entry 8; Table 5, entry 4)*

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.06 (d, J = 8.6 Hz, 2H.), 7.71 (d, J = 8.6 Hz, 2H), 7.66 (d, J = 8.1 Hz, 2H), 7.50 (t, J = 7.2 Hz, 2H), 7.43 (t, J = 7.2 Hz, 1H), 2.66 (s, 3H). EI-MS (*m/z*, relative intensity): 196 (M^+, 50), 181 (100), 153 (35), 152 (58), 151 (16). CAS Number: 92-91-1.

*4.8.8. 4-Biphenylcarboxaldehyde (**4h**, Table 4, entry 9)*

^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.09 (s, 1H), 7.98 (d, J = 8.2 Hz, 2H), 7.77 (d, J = 8.2 Hz, 2H), 7.66 (d, J = 6.8 Hz, 2H), 7.54–7.44 (m, 3H). EI-MS (*m/z*, relative intensity): 183 (13), 182 (M^+, 96), 181 (100), 153 (38), 152 (63), 151 (18). CAS Number: 3218-36-8.

*4.8.9. Methyl biphenyl-4-carboxylate (**4i**, Table 4, entry 10)*

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.14 (d, J = 8.2 Hz, 2H), 7.69 (d, J = 8.4 Hz, 2H), 7.65 (d, J = 7.5 Hz, 2H), 7.50 (t, J = 7.3 Hz, 2H), 7.42 (t, J = 7.1 Hz, 1H), 3.97 (s, 3H). EI-MS (*m/z*, relative intensity): 212 (M^+, 65), 182 (13), 181 (100), 153 (28), 152 (60), 151 (17). CAS Number: 720-75-2.

*4.8.10. 4-Cyanobiphenyl (**4j**, Table 4, entry 11)*

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.76 (d, J = 8.6 Hz, 2H), 7.71 (d, J = 8.6 Hz, 2H), 7.62 (d, J = 6.9 Hz, 2H), 7.54–7.45 (m, 3H). EI-MS (*m/z*, relative intensity): 179 (M^+, 100), 178 (24), 151 (12). CAS Number: 2920-38-9.

*4.8.11. 4-Fluorobiphenyl (**4k**, Table 4, entry 12)*

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.62–7.58 (m, 4H), 7.50 (t, J = 7.4 Hz, 2H), 7.40 (t, J = 7.4 Hz, 1H), 7.18 (t, J = 8.7 Hz, 2H). EI-MS (*m/z*, relative intensity): 173 (13), 172 (M^+, 100), 171 (36), 170 (25). CAS Number: 324-74-3.

*4.8.12. 4-Hydroxybiphenyl (**4l**, Table 4, entry 13)*

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.58 (d, J = 8.5 Hz, 2H), 7.52 (d, J = 8.5 Hz, 2H), 7.45 (t, J = 7.5 Hz, 2H), 7.34 (t, J = 7.5 Hz, 1H), 6.94 (d, J = 8.5 Hz, 2H), 5.08 (br s, 1H). EI-MS (*m/z*, relative intensity): 171 (13), 170 (M^+, 100), 141 (22), 115 (28). CAS Number: 92-69-3.

*4.8.13. p-Terphenyl (**4m**, Table 4, entry 14)*

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.73–7.71 (m, 4H), 7.69 (d, J = 7.4 Hz, 4H), 7.51 (t, J = 7.4 Hz, 4H), 7.41 (t, J = 7.4 Hz, 2H). EI-MS (*m/z*, relative intensity): 231 (19), 230 (M^+, 100), 228 (13). CAS Number: 92-94-4.

*4.8.14. 3-Phenylpyridine (**4n**, Table 4, entry 15)*

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.88 (s, 1H), 8.62 (d, J = 4.4 Hz, 1H), 7.91 (d, J = 8.0 Hz, 1H), 7.61 (d, J = 7.4 Hz, 2H), 7.51 (t, J = 7.4 Hz, 2H), 7.46–7.37 (m, 2H). EI-MS (*m/z*, relative intensity): 155 (M^+, 100), 154 (50), 127 (14), 102 (11). CAS Number: 1008-88-4.

*4.8.15. 3-Phenylquinoline (**4o**, Table 4, entry 16)*

^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.21 (s, 1H), 8.32 (s, 1H), 8.18 (d, J = 8.3 Hz, 1H), 7.90 (d, J = 8.3 Hz, 1H), 7.77–7.22 (m, 3H), 7.62–7.52 (m, 3H), 7.46 (t, J = 7.2 Hz, 1H). EI-MS (*m/z*, relative intensity): 206 (16), 205 (M^+, 100), 204 (53), 176 (14). CAS Number: 1666-96-2.

*4.8.16. 5-Phenylpyrimidine (**4p**, Table 4, entry 17)*

^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.23 (s, 1H), 8.98 (s, 2H), 7.62–7.49 (m, 5H). EI-MS (*m/z*, relative intensity): 157 (12), 156 (M^+, 100), 155 (17), 102 (64). CAS Number: 34771-45-4.

*4.8.17. 1-(4′-Methoxybiphenyl-4-yl)ethanone (**4q**, Table 5, entries 5 and 6)*

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.02 (d, J = 8.2 Hz, 2H), 7.66 (d, J = 8.2 Hz, 2H), 7.60 (d, J = 8.9 Hz, 2H), 7.02 (d, J = 8.4 Hz, 2H), 3.87 (s, 3H), 2.64 (s, 3H). EI-MS (*m/z*, relative intensity): 226 (M^+, 66), 212 (18), 211 (100), 183 (11), 168 (19), 139 (25). CAS Number: 13021-18-6.

4.9. Hg poisoning test

The reaction vial charged with an excess of Hg (Hg:Pd = 400:1) was added hexamethylbenzene (0.05 mmol, 0.0081 g, 0.1 equiv), phenyl boronic acid (0.6 mmol, 0.073 g, 1.2 equiv), K_2CO_3 (1.1 mmol, 0.153 g, 2.2 equiv), *p*-bromoanisole (0.5 mmol, 0.062 μL, 1.0 equiv), MeOH (2 mL) and water (0.5 mL), followed by 0.00075 mmol of Pd catalyst **3b** (0.15 mol%). After 24 h, the mixture was extracted by CH_2Cl_2 (3 × 10 mL), washed with water (2 × 10 mL), brine (1 × 10 mL), dried over Na_2SO_4, and solvent was concentrated to afford the crude 4-methoxybiphenyl product. The yield was determined by GC method. A 33% yield was obtained in the presence of excess of Hg.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem.2013.12.015.

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