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Convenient and efficient Suzuki–Miyaura cross-coupling reactions catalyzed by palladium complexes containing *N*,*N*,*O*-tridentate ligands

Siddappa A. Patil, Chia-Ming Weng, Po-Cheng Huang, Fung-E Hong *

Department of Chemistry, National Chung Hsing University, Taichung 40227, Taiwan

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ABSTRACT

N,*N*,*O*-Tridentate ligands **1**–**9** were prepared from the condensation of amines with nine aromatic aldehydes or ketones. These ligands are thermally stable and neither air- nor moisture-sensitive. Combination of either 2-methoxy-6-[(pyridine-2-ylmethylimino)-methyl]-phenol, **1** or 2-(benzothiazol-2-yl-hydrazonomethyl)-4,6-di-*tert*-butyl-phenol, **6** with $Pd(OAc)_2$ furnished an excellent catalyst precursor for the Suzuki–Miyaura cross-coupling of various aryl bromides with arylboronic acids. The effects of varying solvents, bases, and ligand/palladium ratios on the performance of the coupling reaction were investigated. The molecular structures of both free ligand **1** and its palladium acetate complex **10** were determined by single-crystal X-ray diffraction methods. The DFT studies revealed that the catalytic performance of palladium complexes involving this type of a ligand may differ greatly upon a small variation in its structure.

1. Introduction

The ligand assisted palladium-catalyzed cross-coupling reactions are probably among the most frequently employed methods of carbon–carbon bond formation in organic synthesis. They have been applied to the synthesis of many organic compounds, especially those of complex natural products, supramolecular chemistry, and engineering materials such as conducting polymers, molecular wires, and liquid crystals.[1] The ligand choice is known to be crucial to the success of a catalytic reaction.[2] Therefore, tremendous efforts have been dedicated to the search for more efficient and affordable ligands. As a result, the design of novel ligands and transition metal catalysts capable of carrying out desired transformations with both high efficiency and high selectivity has become a fertile area of research.[3] Until now, phosphine-based ligands have remained to be the most popular selection in the palladium-catalyzed cross-coupling reactions.[4,1b] However, these ligands usually need to be handled under inert atmosphere or dry conditions. In addition, they sometimes suffer from significant P–C bond degradation at elevated temperatures, which leads to palladium aggregation and eventually affects the overall catalytic performance.[5] Recent application of phosphine-free ligands, such as *N*-heterocyclic carbenes, imines, oxime palladacycles, and diazabutadienes to metal-catalyzed synthetic transformations has opened new opportunities in catalysis.[6]

The object of this study was finding a versatile, robust, and easy-to-prepare catalyst system suitable for a wide range of C–C bond-forming processes. Therefore, the initial step was the selection of a potential catalyst class of ligands amenable to systematic structural and electronic variation. One of the appealing features of imine ligands is that both their steric and electronic properties may be tuned in a synthetically straightforward manner by variation of the corresponding aldehyde/ketone precursors.[7] The extraordinary thermal stability, insensitivity to both oxygen and moisture as well as ready availability and low cost of aromatic imines prompted us to study their effectiveness as ligands in palladium-catalyzed C–C bond-forming reactions and in Suzuki–Miyaura cross-coupling reaction, in particular.

2. Results and discussion

2.1. Preparations of *N*,*N*,*O*-tridentate ligands 1–9 and 1-chelated palladium complex 10

All the nine *N*,*N*,*O*-tridentate ligands, **1**–**9**, were prepared from the condensation of amines with corresponding aldehydes/ketones in methanol/ethanol as solvent.[8] They were characterized by spectroscopic methods such as ^1H, ^{13}C NMR as well as mass spectrometry (Fig. 1). Furthermore, the structure of ligand **1** was also verified by single-crystal X-ray diffraction method (Fig. 2).[9]

The preparation of **1**-chelated palladium complex **10** was achieved via the reaction of ligand **1** with one molar equivalent of $Pd(OAc)_2$ in THF. The formation of this palladium complex was confirmed by spectroscopic methods as well as single-crystal X-ray

* Corresponding author. Fax: +886 4 22862547.
E-mail address: fehong@dragon.nchu.edu.tw (F. Hong).

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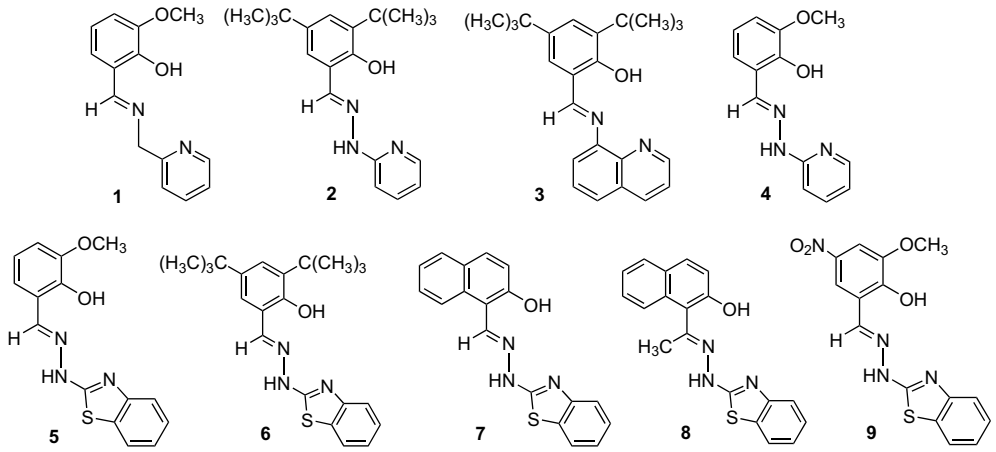


Figure 1. Some selected *N*,*N*,*O*-tridentate ligands **1**–**9**.

diffraction analysis.[10] The ORTEP diagram of **10** is depicted in Figure 2. As revealed, it is indeed an *N*,*N*,*O*-chelated palladium complex. The ∠N(1)–Pd(1)–N(2), ∠N(2)–Pd(1)–O(3), ∠O(3)–Pd(1)–O(2) and ∠O(2)–Pd(1)–N(1) bond angles are 82.7(2)°, 96.49(18)°, 86.51(15)°, and 94.29(18)°, respectively. Thereby, the Pd(II) atom is almost coplanar with all four coordinating atoms: N(1), N(2), O(3) and O(2). The metal is in a square planar environment with four coordinating sites comprised of an *N*,*N*,*O*-tridentate and an acetate ligands. The acetate coordinates to the palladium atom in a monodentate rather than bidentate mode.[11] The N(1)–Pd(1), N(2)–Pd(1), ∠O(3)–Pd(1), ∠O(2)–Pd(1) bond lengths are 1.932(5) Å, 2.005(5) Å, 2.038(4) Å, and 1.932(5) Å, respectively.

2.2. Application of $Pd(OAc)_2$/L (L=1–9) in Suzuki reactions

A variety of diimines containing *N*,*N*,*O*-tridentate ligands, **1**–**9**, have been designed and prepared (Fig. 1). The combination of these ligands with various palladium salts was expected to form excellent catalytic systems for the Suzuki–Miyaura cross-coupling reactions. The performance of a palladium-catalyzed Suzuki–Miyaura cross-coupling reaction is known to be governed by a number of factors such as the kind of palladium salt or ligand employed, the presence/absence of base, solvent, reaction temperature, etc.[12] Furthermore, the ligand/palladium salt ratio is also crucial since various bonding modes are possible for different types of ligands. In this study, the Suzuki coupling reactions were carried out in situ by employing the synthesized *N*,*N*,*O*-ligands **1**–**9** in the presence of a palladium salt. In most cases the reactions were carried out with 1.0 mmol of 4-bromo-benzaldehyde, 1.5-fold excess of phenylboronic acid, 2.0-fold excess of a base in 1.0 mL solvent, and 1.0 mol % of $Pd(OAc)_2$/**L** (**L**=**1**–**9**) (Scheme 1). K_3PO_4 was chosen as the base because previously it has shown a good performance in our related studies on Suzuki reactions.

The impact of variation of solvent and temperature on the performance of the coupling reaction was evaluated by employing $Pd(OAc)_2$/**1** as the catalytic precursor (Table 1). Two of the most commonly used solvents, THF and toluene, having been shown to perform well in our previous studies, were chosen. The best yield was observed with toluene at 85 °C (Entry 8). As shown, high temperature was required to reach reasonable reaction speed. By contrast, the catalytic performance was not acceptable when a more polar solvent THF was employed (Entries 1–3).

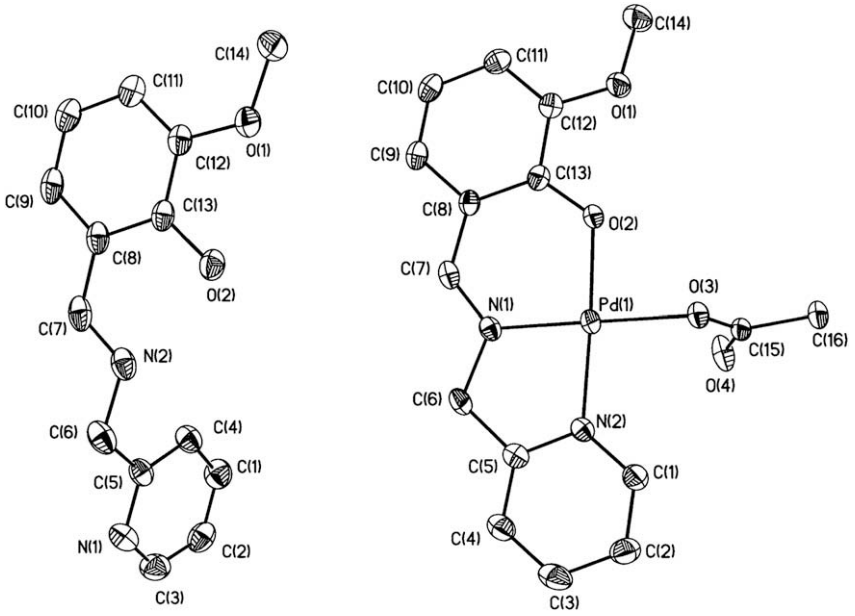
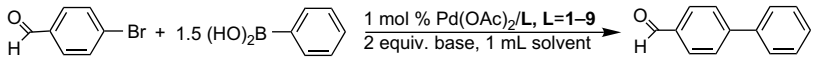


Figure 2. ORTEP drawings of **1** and **10**.



Scheme 1. Suzuki–Miyaura cross-coupling reaction of 4-bromo-benzaldehyde with phenylboronic acid in the presence of $Pd(OAc)_2$/**L**.

Table 1
Suzuki–Miyaura coupling reactions using $Pd(OAc)_2$/**1** at various solvents and temperatures[a]

Entry[a]	Solvent	Temp (°C)	Time (h)	Conv.[b] (%)
1	THF	25	1	NR
2	THF	25	2	NR
3	THF	25	4	1.2
4	Toluene	25	1	3.1
5	Toluene	25	2	3.2
6	Toluene	25	4	3.9
7	Toluene	85	1	65.5
8	Toluene	85	2	100.0

[a] Reaction conditions: 1.0 mmol of 4-bromo-benzaldehyde, 1.5 mmol of phenylboronic acid, $Pd(OAc)_2$/**1**=1:1 mol %, 2.0 mmol of K_3PO_4, 1 mL solvent.
[b] Average of two runs; measured by ^{1}H NMR.

Table 2
Suzuki–Miyaura coupling reactions using $Pd(OAc)_2$/**6** at various solvents and temperatures[a]

Entry[a]	Solvent	Temp (°C)	Time (h)	Conv.[b] (%)
1	THF	25	2	11.9
2	THF	25	4	12.7
3	THF	25	24	21.4
4	Toluene	25	2	61.6
5	Toluene	25	4	63.9
6	Toluene	25	24	68.4
7	Toluene	85	2	100.0

[a] Reaction conditions same as in the footnote of Table 1 except for the usage of **6** as the ligand.
[b] Average of two runs; measured by ^{1}H NMR.

Similar procedures for the Suzuki reactions were carried out for the rest of *N*,*N*,*O*-ligands, **2**–**9**. Among all the ligands involved, only **6** showed promising results (Table 2). Other ligands did not exhibit competitive efficiencies. The catalytic performance of **6** was about as good as that of ligand **1**. Again, toluene was superior to THF as a solvent.

For polydentate ligands such as **1**–**9**, various bonding modes and conformations are possible depending on the ligand to palladium salt ratio. The Suzuki coupling reactions were carried out in situ by employing ligands **1** and **6** in the presence of palladium acetate. As shown in Table 3, excellent yields were obtained when the ratio of $Pd(OAc)_2$:**L** (**L**=**1** or **6**) was close to 1:1 (Entries 2–3, 7–8). The yield decreased rapidly when the ratio approached 1:2 (Entries 5, 10). The fact that unsatisfactory results were detected in those entries can be explained by the formation of an exceedingly stable bis-L-chelated palladium complex, **11**, as shown in Scheme 2.[6a] The robust structure of **11** makes the reduction process, from Pd(II) to Pd(0), rather difficult thus leading to a sharp decrease of the overall catalytic performance.

The results of the Suzuki cross-coupling reactions between phenylboronic acid and various substituted aryl bromides assisted by ligands **1** and **6** are shown in Tables 4 and 5, respectively. The catalytic performance varied from good to excellent for the substrates with electron-withdrawing groups (Table 4, Entries 1–6; Table 5, Entries 1–4). By contrast, it was unsatisfactory for the substrates with electron-donating groups (Table 4, Entries 8–9; Table 5, Entries 6–10). It is consistent with the general behavior observed for the palladium-catalyzed Suzuki reactions.[13]

Table 3
Suzuki–Miyaura coupling reactions using various $Pd(OAc)_2$/**1** or $Pd(OAc)_2$/**6** ratios[a]

Entry[a]	Ligand	Ratio	Conv.[b] (%)
1	**1**	1.0/0.0	NR
2	**1**	1.0/0.5	100.0
3	**1**	1.0/1.0	100.0
4	**1**	1.0/1.5	57.4
5	**1**	1.0/2.0	NR
6	**6**	1.0/0.0	NR
7	**6**	1.0/0.5	100.0
8	**6**	1.0/1.0	100.0
9	**6**	1.0/1.5	NR
10	**6**	1.0/2.0	NR

[a] Reaction conditions: 1.0 mmol of 4-bromo-benzaldehyde, 1.5 mmol of phenylboronic acid, $Pd(OAc)_2$/**1** (or **6**)=1:1 mol %, 2.0 mmol of K_3PO_4, 1 mL toluene, 85 °C, 2 h.
[b] Average of two runs; measured by ^{1}H NMR.

Nevertheless, the effect is more pronounced in the *N*,*N*,*O*-tridentate ligand case compared with that of a phosphine ligand.

2.3. Effect of palladium salt on coupling reaction

To evaluate the effect of a palladium source, the coupling reaction between 4-bromo-benzaldehyde and phenylboronic acid was performed with a series of palladium compounds. The most commonly used ones, such as $Pd(OAc)_2$ and $[(\eta^3\text{-}C_3H_5)ClPd]_2$ were found to be the most effective. Unexpectedly, $(COD)PdCl_2$ combined with ligand **1** led to mediocre conversion while that with ligand **6** yielded no conversion at all. The rest of palladium sources, namely $PdCl_2$ and $PdCl_2[MeCN]_2$, performed poorly as shown in Table 6.

2.4. Effect of solvent on coupling reaction

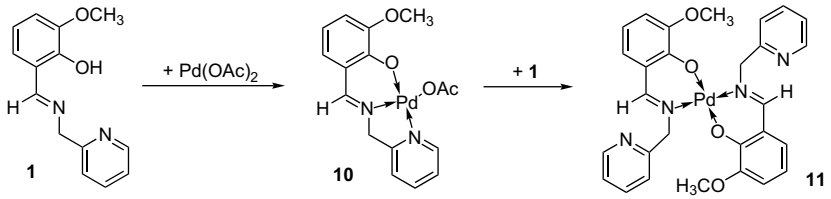
The solvent effect on the rate of the coupling reaction between 4-bromo-benzaldehyde and phenylboronic acid was probed using a variety of solvents. As shown in Table 7, quantitative yields were observed within 2 h with high-boiling solvents such as toluene, DMF, DMSO, and 1,4-dioxane. On the contrary, unsatisfactory yields were obtained with low-boiling solvents. In part, this may be due to a better solubility of a palladium complex at higher temperatures. Again, running the reaction at lower temperatures sharply decreases the catalytic performance in this system.

2.5. Effect of base on coupling reaction

The effect of a base on the catalytic performance of this system was investigated by employing various bases (Table 8). The commonly used inexpensive bases such as K_3PO_4 and KOH were found to be rather effective. However, using bases like K_2CO_3, Cs_2CO_3, and KF led to low or zero conversion. No conversion was observed with either NaO^tBu or KO^tBu.

2.6. DFT studies on the geometries of compound 10 reduced species

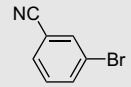
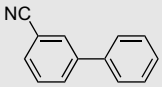
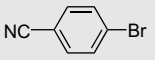
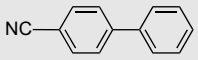
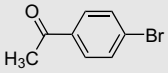
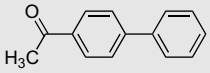
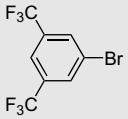
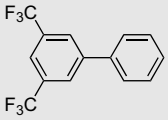
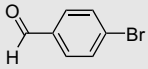
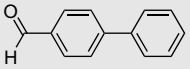
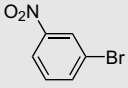
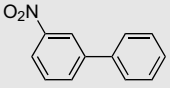
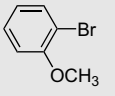
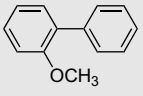
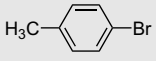
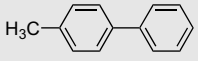
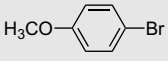
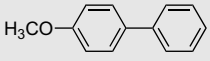
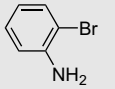
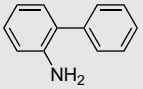
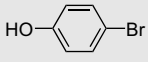
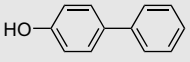
As shown above, the catalytic performance of the Suzuki reactions employing ligands **1**–**9** differs significantly with a small change in ligand structure. It is of interest to us to examine the reasons behind the obvious differences in reactivities observed. The



Scheme 2. The formation of **1**-chelated palladium complexes **10** and **11**.

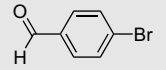
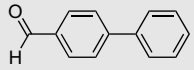
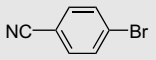
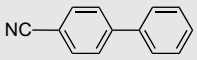
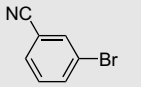
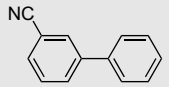
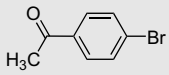
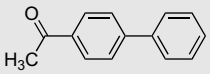
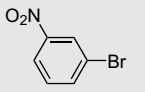
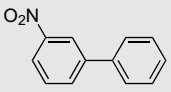
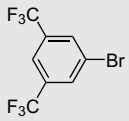
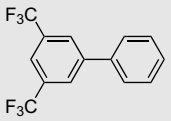
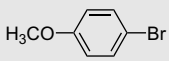
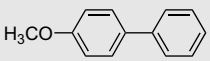
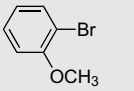
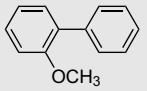
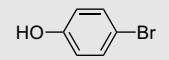
catalytic cycle for the palladium-catalyzed Suzuki reaction is generally believed to begin with a Pd(0) species. Thereby, at first the starting Pd(II) complex **10** must be reduced to an active Pd(0) species. There are several possible routes for the reduction to proceed.[14] In the absence of a phosphine ligand, one and the most probable reduction pathway involves the initial attack of the borate, $BPh(OH)_3^-$, on the Pd(II) metal center. The boronic acid $PhB(OH)_2$ is known to play a dual role in Suzuki reactions. In the first role, it acts as the reducing agent via the formation of borate, $BPh(OH)_3^-$, by combining with base; in the second, it behaves as a reactant. The mechanisms proposed for the reduction of Pd(II) of **10** to an active Pd(0) species **TS4** and the subsequent catalytic cycle are shown in Scheme 3. The *N,N*-chelated Pd(0) intermediate, **TS4**, resulting from the reduction via a series of sequential steps, might indeed be the

Table 4
Suzuki–Miyaura coupling reactions using $Pd(OAc)_2$/**1** and substituted bromobenzenes[a]

Entry	Aryl bromide	Product	Conv.[b] (%)	Yield[c] (%)
1			—	95.6
2			—	98.3
3			100	95.0
4			—	95.0
5			100	94.5
6			—	90.8
7			77.9	71.8
8			40.0	38.8
9			29.0	—[d]
10			24.6	—[d]
11			Trace	—[d]

[a] Reaction conditions same as in the footnote of Table 1 except keeping the reaction at 85 °C for 2 h.
[b] Average of two runs; measured by ^{1}H NMR.
[c] Isolated yield.
[d] Not isolated.

Table 5
Suzuki–Miyaura coupling reactions using $Pd(OAc)_2$/**6** and substituted bromobenzenes[a]

Entry	Aryl bromide	Product	Conv.[b] (%)	Yield[c] (%)
1			100	95.0
2			—	95.3
3			—	94.9
4			100	94.8
5			—	89.3
6			—	59.1
7			5.0	—[d]
8			4.4	—[d]
9			Trace	—[d]
10			Trace	—[d]
11			Trace	—[d]

[a] Reaction conditions same as in the footnote of Table 4 except for the usage of **6** as the ligand.
[b] Average of two runs; measured by ^{1}H NMR.
[c] Isolated yield.
[d] Not isolated.

Table 6
Suzuki–Miyaura coupling reactions using various palladium salt/**1** or **6**[a]

Entry	Ligand	Pd Source	Conv.[b] (%)
1	**1**	$Pd(OAc)_2$	100
2	**1**	$[(\eta^3\text{-}C_3H_5)ClPd]_2$	100
3	**1**	$(COD)PdCl_2$	55.7
4	**1**	$PdCl_2$	NR
5	**1**	$PdCl_2[MeCN]_2$	NR
6	**6**	$Pd(OAc)_2$	100
7	**6**	$[(\eta^3\text{-}C_3H_5)ClPd]_2$	100
8	**6**	$(COD)PdCl_2$	NR
9	**6**	$PdCl_2$	NR
10	**6**	$PdCl_2[MeCN]_2$	NR

[a] Reaction conditions same as in the footnote of Table 1 except using various palladium salts.
[b] Average of two runs; measured by ^1H NMR.

catalytically active species that carries the catalytic cycle further. The intermediate, **TS5**, is formed as a result of oxidative addition of ArX to the Pd(0) intermediate, **TS4**. Subsequently, the transmetallation processes, from **TS6** to **TS8**, take place by the attack of borate, $BPh(OH)_3^-$ on **TS6**. Eventually, the reductive elimination process brings about the desired coupling product and regeneration of the catalytically active species **TS4**. Recently, some theoretical investigations on the stability of low coordinated Pd(0) based on DFT methods have been reported by Buchwald and Norrby.[15] The performance of a catalytic reaction is known to be affected greatly by the structure of intermediate. At first glance, the reactivity does not seems to be changed substantially upon variation of R substituent on the phenyl ring of **TS4** since it is far away from the inner coordination sphere of Pd(0) metal center. Nevertheless, a closer examination of the intermediate **TS4** by DFT methods shows otherwise.

As a versatile tool in the studies of reaction mechanism, the density functional theory (DFT) at the B3LYP level has proven repeatedly to be a reliable method in providing insightful information about the transition metal-mediated catalytic reactions.[16] It has been employed in the current study to account for the effect caused by a substituent on the phenyl ring of **TS4**. To make the computations affordable, only the intermediates **TS4a** and **TS4b** (**a**: R=OMe; **b**: R=^{t}Bu), derived from **10**, were considered. The optimized structures of **TS4a** and **TS4b** from the calculations carried out at B3LYP level of theory are shown in Figure 3. A closer look at the conformation of the intermediate **TS4** provides some useful information concerning the effect caused by the substituent on the phenyl ring. As shown from the stereo view of **TS4a** and **TS4b** created by Gauss View, the bulky ^{t}Bu group in **TS4b** exerts a greater steric effect on the phenoxide moiety than –OMe group does in **TS4a**, subsequently forcing the phenoxide ring to get even closer to the Pd(0) metal center (Fig. 3). Thereby, less space is available for the upcoming reaction substrate, arylhalide, to attack the activated Pd(0) center of **TS4b**.

Table 7
Suzuki–Miyaura coupling reactions using $Pd(OAc)_2$/**1** or **6** with various solvents[a]

Entry	Ligand	Solvent	Temp (°C)	Conv.[b] (%)
1	**1**	Toluene	85	100
2	**1**	DMF	85	100
3	**1**	DMSO	85	100
4	**1**	Dioxane	85	100
5	**6**	Toluene	85	100
6	**6**	DMF	85	100
7	**6**	DMSO	85	25.9
8	**6**	Dioxane	85	17.9

[a] Reaction conditions same as in the footnote of Table 1 except using various solvents.
[b] Average of two runs; measured by ^1H NMR.

Table 8
Suzuki–Miyaura coupling reactions using $Pd(OAc)_2$/**1** or **6** with various bases[a]

Entry	Ligand	Base	Conv.[b] (%)
1	**1**	K_3PO_4	100
2	**1**	KOH	100
3	**1**	K_2CO_3	23.8
4	**1**	Cs_2CO_3	19.1
5	**1**	KF	NR
6	**1**	NaO^tBu	NR
7	**1**	KO^tBu	NR
8	**6**	K_3PO_4	100
9	**6**	KOH	100
10	**6**	K_2CO_3	89.1
11	**6**	KF	60.2
12	**6**	Cs_2CO_3	NR
13	**6**	NaO^tBu	NR
14	**6**	KO^tBu	NR

[a] Reaction conditions same as in the footnote of Table 1 except using various bases in toluene.
[b] Average of two runs; measured by ^1H NMR.

Naturally, it leads to a sharp decrease in the overall reaction rate and catalytic performance.

The optimized geometries of **TS4a** and **TS4b** also reveal that the Pd(0) atom is stabilized by imine and pyridine nitrogen atoms as well as the phenoxide oxygen. Unlike in **10**, the Pd(0) atom in **TS4** is not coplanar with the imine and pyridine rings; rather, it is located above the plane and leans toward the phenoxide ring. The methyl group bends away from the phenoxide ring in **TS4a** thus reducing the steric hindrance. By contrast, the ^{t}Bu group exhibits a strong steric effect on the phenoxide ring in **TS4b**. Interestingly, while the optimized structure of **TS4a** shows an interaction between Pd(0) and the *ipso*-carbon of the phenoxide ring; undoubtedly, there is a η^2-coordination to the Pd(0) through a double bond of the phenoxide ring in **TS4b** (Fig. 4). These results indeed show that the catalytic performance of the palladium complex with this type of *N*,*N*,*O*-ligand may indeed be significantly affected by a small variation in structure of the ligand.

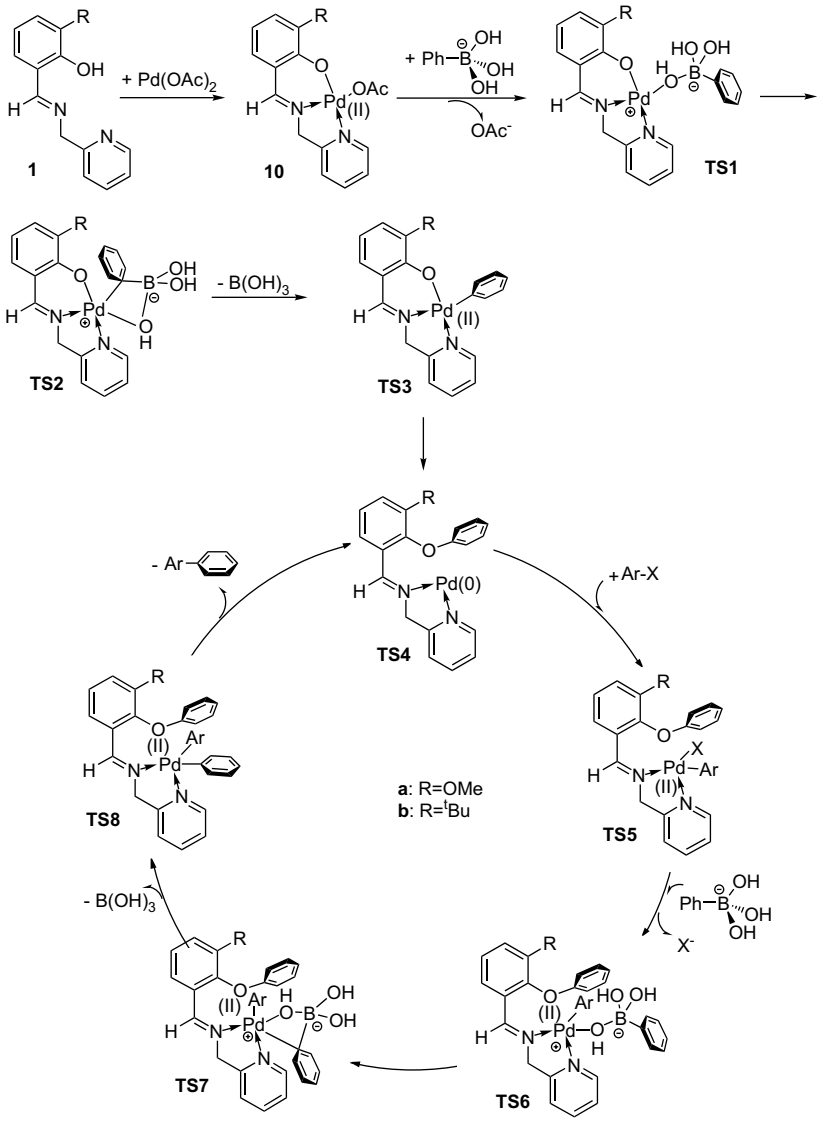
3. Conclusion

In summary, a series of versatile and inexpensive *N*,*N*,*O*-ligands have been synthesized. It has been demonstrated that combinations of $Pd(OAc)_2$ with either **1** or **6** are efficient catalyst precursors for Suzuki–Miyaura couplings of various aryl bromides with arylboronic acid. The optimized conditions for this systems are found to be the reaction in toluene with K_3PO_4 as a base at 85 °C for 2 h. Applications of this system to other catalytic transformations are currently under investigation.

4. Experimental section

4.1. Materials and methods

All the chemicals and reagents used for the synthesis of these imines were of highest purity or purified by the standard methods of purification. 2-Aminomethylpyridine, 8-aminoquinoline, 2-hydrazinopyridine, 2-hydrazinobenzothiazole, *o*-vanillin, 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde, 2-hydroxy-1-naphthaldehyde, and 2-hydroxy-1-acetonaphthone were obtained from Aldrich and were used without further purification. ^1H and ^{13}C NMR spectra were recorded on a Varian Mercury-400 (400 MHz for ^1H and 100 MHz for ^{13}C) spectrometer with chemical shifts given in parts per million from the internal TMS or center line of $CHCl_3$. Mass spectra were recorded on JEOL JMS-SX/SX 102A GC/MS/MS spectrometer.



Scheme 3. Proposed catalytic cycle for the Suzuki–Miyaura cross-coupling reaction catalyzed by palladium complex with ligand **1**.

4.2. 2-Methoxy-6-[(pyridine-2-ylmethylimino)-methyl]-phenol (1)

This ligand has been prepared by a literature reported method.[8a] 2-Aminomethylpyridine (1.03 g, 0.01 mol) dissolved in ethanol (10 mL) was added to a stirred ethanol (10 mL) solution of *o*-vanillin (1.52 g, 0.01 mol). The reaction mixture was stirred overnight and then the solvent was removed under reduced pressure. The resulted red residue was saturated with diethyl ether to get a red solid, which was recrystallized from hot methanol to obtain yellow crystals suitable for X-ray analysis. Yield: 1.60 g (66.04%). ^{1}H NMR ($CDCl_3$, δ/ppm): 13.75 (s, 1H, OH), 8.55–8.53 (m, 1H, Py), 8.52 (t, J=1.2 Hz, 1H, HC=N), 7.67–7.63 (m, 1H, Py), 7.36 (d, J=7.6 Hz, 1H, Py), 7.19–7.16 (m, 1H, Py), 6.94–6.90 (m, 2H, Ar), 6.82 (t, J=7.8 Hz, 1H, Ar), 4.94 (s, 2H, CH_2), 3.89 (s, 3H, OCH_3). ^{13}C NMR ($CDCl_3$, δ/ppm): 166.58, 157.59, 151.28, 149.00, 148.09, 136.53, 122.90, 122.00, 121.47, 118.34, 117.84, 114.01, 64.28, 55.75. HRMS: m/z=242.1053 (M^+). Anal. Calcd for **1**: C, 69.41; H, 5.82; N, 11.56. Found: C, 69.50; H, 5.90; N, 11.60.

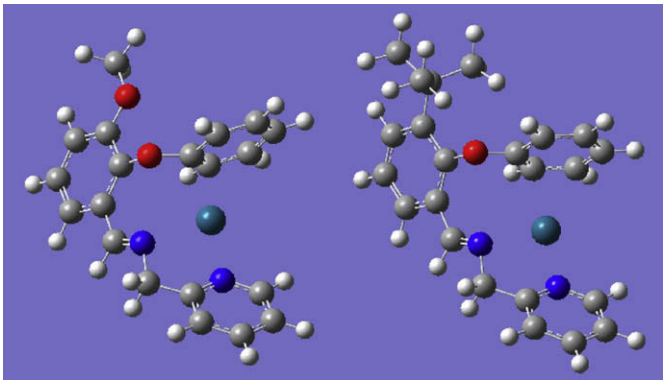


Figure 3. Optimized geometries of **TS4a** and **TS4b**. The calculations were carried out at B3LYP level of theory.

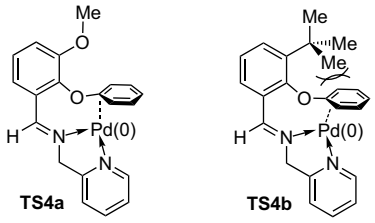


Figure 4. Sketched figures for the optimized structures of **TS4a** and **TS4b**.

4.3. 2,4-Di-*tert*-butyl-6-(pyridine-2-yl-hydrazonomethyl)-phenol (2)

3,5-Di-*tert*-butyl-2-hydroxybenzaldehyde (1.64 g, 0.007 mol) was added to a solution of 2-hydrazinopyridine (0.76 g, 0.007 mol) in ethanol (15 mL). The reaction mixture was under refluxing for 3–4 h and cooled down afterward. The light yellow precipitate of the title compound, **2**, was filtered and crystallized from methanol and dried in vacuo. Yield: 2.12 g (93.05%). ^{1}H NMR ($CDCl_3$, δ/ppm): 11.12 (s, 1H, NH), 8.18–8.16 (m, 1H, Py), 7.98 (s, 1H, HC=N), 7.64–7.60 (m, 1H, Py), 7.34 (d, J=2.0 Hz, 1H, Ar), 7.13 (d, J=8.4 Hz, 1H, Ar), 6.99 (d, J=2.4 Hz, 1H, Py), 6.81–6.78 (m, 1H, Py), 1.47 (s, 9H, *t*-Bu), 1.31 (s, 9H, *t*-Bu). ^{13}C NMR ($CDCl_3$, δ/ppm): 156.33, 154.15, 147.08, 144.60, 140.99, 138.67, 136.34, 125.32, 124.68, 117.53, 115.81, 106.84, 35.07, 34.13, 31.50, 29.50. HRMS: m/z=225.2152 (M^+). Anal. Calcd for **2**: C, 73.81; H, 8.36; N, 12.91. Found: C, 74.05; H, 8.75; N, 13.08.

4.4. 2,4-Di-*tert*-butyl-6-(quinolin-8-yliminomethyl)-phenol (3)

This ligand also has been prepared by a literature reported method.[8b] To a stirred solution of 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde (2.343 g, 0.01 mol) in methanol (30 mL) was added 8-aminoquinoline (1.442 g, 0.01 mol). Two drops of formic acid was added to the reaction mixture. After refluxing for 1 h, the resulting dark-brown colored precipitate was filtered out and was washed with methanol to yield **3** as an orange powder and dried in vacuo. Yield: 3.40 g (94.31%). ^{1}H NMR ($CDCl_3$, δ/ppm): 8.99 (d, J=4 Hz, 1H, Qu), 8.91 (s, 1H, HC=N), 8.20 (d, J=8.4 Hz, 1H, Qu), 7.70 (t, J=4.4 Hz, 1H, Qu), 7.57 (t, J=7.8 Hz, 1H, Qu), 7.48–7.44 (m, 4H, Ar and Qu), 1.50 (s, 9H, *t*-Bu), 1.33 (s, 9H, *t*-Bu). ^{13}C NMR ($CDCl_3$, δ/ppm): 166.28, 158.90, 150.08, 145.82, 142.08, 140.12, 136.93, 135.78, 128.99, 127.94, 126.84, 126.40, 125.58, 121.39, 119.26, 118.55, 35.04, 34.03, 31.40, 29.47. HRMS: m/z=360.2196 (M^+). Anal. Calcd for **3**: C, 79.96; H, 7.83; N, 7.77. Found: C, 79.88; H, 7.72; N, 7.17.

4.5. 2-Methoxy-6-(pyridine-2-yl-hydrazonomethyl)-phenol (4)

To a stirred solution of 2-hydrazinopyridine (0.764 g, 0.007 mol) in ethanol (25 mL) was added drop-wise *o*-vanillin (1.065 g, 0.007 mol) in ethanol (25 mL). After the addition was completed, the stirring was continued for 2 h at 70 °C. The reaction mixture was then allowed to cool to room temperature overnight. Then the colorless precipitate of the title compound was filtered and washed two times with ethanol and dried in vacuo. Yield: 1.60 g (93.96%). ^{1}H NMR ($CDCl_3$, δ/ppm): 10.78 (s, 1H, NH), 8.17 (t, J=3.0 Hz, 1H, Py), 7.93 (s, 1H, HC=N), 7.65–7.60 (m, 1H, Py), 7.08 (d, J=8.4 Hz, 1H, Ar), 6.92–6.82 (m, 4H, Ar and Py), 3.93 (s, 3H, OCH_3). ^{13}C NMR ($CDCl_3$, δ/ppm): 156.48, 147.94, 145.70, 138.98, 137.98, 120.80, 119.14, 119.09, 115.06, 112.27, 106.18, 55.83. HRMS: m/z=243.1005 (M^+). Anal. Calcd for **4**: C, 64.19; H, 5.39; N, 17.27. Found: C, 64.44; H, 5.97; N, 17.36.

4.6. 2-(Benzothiazol-2-yl-hydrazonomethyl)-6-methoxy-phenol (5)

Compound **5** was prepared by stirring *o*-vanillin (0.761 g, 0.005 mol) and 2-hydrazinobenzothiazole (0.826 g, 0.005 mol) in ethanol (25 mL) for 4–5 h at 80 °C. The resulted colorless compound was filtered, washed three times with ethanol, and finally dried in vacuo. Yield: 1.40 g (93.53%). ^{1}H NMR (DMSO-d_6, δ/ppm): 12.20 (s, 1H, NH), 8.43 (s, 1H, HC=N), 7.73 (d, J=7.2 Hz, 1H, Bt), 7.35 (s, 1H, Bt), 7.28 (t, J=7.6 Hz, 1H, Bt), 7.21 (d, J=8 Hz, 1H, Bt), 7.08 (t, J=7.4 Hz, 1H, Ar), 6.99 (t, J=4.20 Hz, 1H, Ar), 6.84 (t, J=7.8 Hz, 1H, Ar), 3.81 (s, 3H, OCH_3). ^{13}C NMR ($CDCl_3$, δ/ppm): 166.48, 147.93, 146.25, 126.12, 121.70, 121.51, 120.01, 119.15, 113.11, 55.86. HRMS: m/z=299.0731 (M^+). Anal. Calcd for **5**: C, 60.14; H, 4.38; N, 14.04; S, 10.71. Found: C, 57.72; H, 5.27; N, 14.23; S, 10.98.

4.7. 2-(Benzothiazol-2-yl-hydrazonomethyl)-4,6-di-*tert*-butyl-phenol (6)

The imine ligand **6** was synthesized by the following procedures. 3,5-Di-*tert*-butyl-2-hydroxybenzaldehyde (1.172 g, 0.005 mol) dissolved in hot ethanol (20 mL) was added to 2-hydrazinobenzothiazole (0.826 g, 0.005 mol) in ethanol (20 mL). The reaction mixture was heated to reflux for 4 h. The light yellow product obtained was filtered out and washed several times with ethanol and dried in vacuo. Yield: 1.52 g (79.67%). ^{1}H NMR ($CDCl_3$, δ/ppm): 10.97 (s, 1H, NH), 8.32 (s, 1H, HC=N), 7.57 (d, J=8 Hz, 1H, Bt), 7.38 (d, J=2.4 Hz, 1H, Bt), 7.33–7.28 (m, 2H, Bt), 7.15–7.11 (m, 1H, Ar), 7.00 (s, 1H, Ar), 1.50 (s, 9H, *t*-Bu), 1.28 (s, 9H, *t*-Bu). ^{13}C NMR ($CDCl_3$/DMSO-d_6, δ/ppm): 165.67, 154.34, 152.04, 143.80, 140.23, 135.58, 125.61, 125.08, 124.86, 121.00, 116.98, 113.78, 34.42, 33.47, 30.88, 28.89. HRMS: m/z=381.1870 (M^+). Anal. Calcd for **6**: C, 69.26; H, 7.13; N, 11.01; S, 8.40. Found: C, 68.92; H, 7.46; N, 10.84; S, 8.66.

4.8. 1-(Benzothiazol-2-yl-hydrazonomethyl)-naphthalen-2-ol (7)

The preparation of compound **7** was carried out by refluxing a solution of 2-hydroxy-1-naphthaldehyde (1.033 g, 0.006 mol) in ethanol (15 mL) with a solution of 2-hydrazinobenzothiazole (0.991 g, 0.006 mol) in ethanol (15 mL) for 4 h. The reaction mixture was then allowed to cool down to room temperature overnight. The resulted dark yellow colored compound was filtered and washed with ethanol and dried in vacuo. Yield: 1.83 g (95.49%). ^{1}H NMR (DMSO-d_6, δ/ppm): 9.18 (s, 1H, NH), 8.63 (s, 1H, HC=N), 7.87 (t, J=8.2 Hz, 3H, Ar and Bt), 7.75 (d, J=7.2 Hz, 1H, Ar), 7.57 (t, J=7.2 Hz, 1H, Bt), 7.39 (t, J=7.4 Hz, 1H, Bt), 7.29 (t, J=7.4 Hz, 2H, Ar), 7.23 (d, J=8.8 Hz, 1H, Ar), 7.09 (t, J=8 Hz, 1H, Ar). ^{13}C NMR (DMSO-d_6, δ/ppm): 165.92, 157.37, 132.28, 131.41, 128.82, 128.07, 127.67, 126.48, 123.51, 122.23, 122.12, 121.66, 118.47, 109.70. HRMS: m/z=319.0777 (M^+). Anal. Calcd for **7**: C, 67.69; H, 4.10; N, 13.16; S, 10.04. Found: C, 68.01; H, 4.19; N, 13.34; S, 10.14.

4.9. 1-[1-(Benzothiazol-2-yl-hydrazono)-ethyl]-naphthalen-2-ol (8)

The imine **8** was prepared by refluxing a mixture of 2-hydrazinobenzothiazole (0.991 g, 0.006 mol) and 2-hydroxy-1-acetonaphthone (1.117 g, 0.006 mol) in ethanol (30 mL) for 8–10 h. The light yellow colored solution was concentrated to dryness on a vacuum line. The colorless compound was washed three times with hexane and crystallized with ether and dried on a vacuum line. Yield: 1.82 g (91.06%). ^{1}H NMR ($CDCl_3$, δ/ppm): 7.67–7.62 (m, 2H, Bt), 7.53–7.50 (m, 2H, Ar), 7.46–7.42 (m, 2H, Bt), 7.30–7.26 (m, 1H, Ar), 7.16–7.12 (m, 1H, Ar), 6.75 (d, J=8.8 Hz, 1H, Ar), 6.62 (d,

J=8.8 Hz, 1H, Ar), 2.38 (s, 3H, H_3C=N). ^{13}C NMR (DMSO-d_6, δ/ppm): 152.75, 151.83, 132.67, 130.53, 130.04, 128.37, 128.12, 126.95, 126.65, 125.91, 123.97, 123.40, 122.92, 121.56, 121.29, 119.92, 118.70, 118.49. HRMS: m/z=333.0935 (M^+). Anal. Calcd for **8**: C, 68.45; H, 4.53; N, 12.60; S, 9.62. Found: C, 68.47; H, 4.68; N, 12.68; S, 9.74.

4.10. 2-(Benzothiazol-2-yl-hydrazonomethyl)-6-methoxy-4-nitro-phenol (9)

The preparation of **9** was carried out by refluxing a solution of 0.005 mol of 3-methoxy-5-nitrosalicylaldehyde (0.985 g) in ethanol (10 mL) and with a solution of 0.005 mol of 2-hydrazinobenzothiazole (0.826 g) in ethanol (10 mL) for 4–5 h. The reaction mixture was then allowed to cool to room temperature at overnight. The resulting dark yellow colored precipitate was filtered and washed 2–3 times with hot ethanol and dried in vacuo. Yield: 1.68 g (97.65%). ^1H NMR (DMSO-d_6, δ/ppm): 8.47 (s, 1H, HC=N), 8.25 (d, J=2.8 Hz, 1H, Bt), 7.75 (d, J=2.8 Hz, 3H, Ar and Bt), 7.30 (t, J=7.6 Hz, 1H, Bt), 7.11 (t, J=7.6 Hz, 1H, Bt). ^{13}C NMR (DMSO-d_6, δ/ppm): 166.94, 151.82, 148.00, 139.68, 126.11, 121.73, 120.00, 106.55, 56.41. HRMS: m/z=344.0577 (M^+). Anal. Calcd for **9**: C, 52.32; H, 3.51; N, 16.27; S, 9.31. Found: C, 52.41; H, 4.25; N, 16.42; S, 9.41.

4.11. General procedure for the palladium-catalyzed Suzuki cross-coupling reactions

The five reactants, aryl bromide (1.0 mmol), boronic acid (1.0 mmol), ligand **L** (**L**=**1**–**9**) (1.0 mol %), $Pd(OAc)_2$ (1.0 mol %), and K_3PO_4 (3.0 mmol), were placed in an oven dried Schlenk flask. The flask was evacuated and backfilled with nitrogen. To the mixture then toluene/THF (1.0 mL) was added and stirred at required temperature with designated hours. The mixture was then allowed to cool to room temperature and quenched by adding ether (3.0 mL) and water (2.0 mL). Ether layer is separated from water layer through separatory funnel and dried with anhydrous magnesium sulfate. The dried ether layer was concentrated in vacuo and purified by column chromatography using hexane and ethyl acetate as eluting solvent.

4.12. Preparation of Pd complex (10)

2-Methoxy-6-[(pyridine-2-ylmethylimino)-methyl]-phenol (0.121 g, 0.005 mol) and palladium acetate (0.112 g, 0.005 mol) were placed in 100 mL round flask. The mixture was then allowed to react in dried THF (10 mL) at room temperature for overnight. Removal of the solvent in vacuum afforded complex as dark-brown solid product. Yield: 0.192 g (94.51%). ^1H NMR ($CDCl_3$, δ/ppm): 8.13 (d, J=5.6 Hz, 1H, Py), 8.06 (s, 1H, HC=N), 7.56 (t, J=7.0 Hz, 1H, Py), 7.22 (d, J=8.8 Hz, 1H, Py), 7.13 (t, J=6.4 Hz, 1H, Py), 6.70 (d, J=7.2 Hz, 2H, Ar), 6.33 (t, J=7.6 Hz, 1H, Ar), 5.60 (s, 2H, CH_2), 3.80 (s, 3H, OCH_3), 2.40 (s, 3H, CH_3).

^1H NMR (DMSO-d_6, δ/ppm): 8.12–8.06 (m, 3H, HC=N and Py), 7.71 (d, J=8.0 Hz, 1H, Py), 7.53 (t, J=6.8 Hz, 1H, Py), 7.05 (d, J=8.4 Hz, 1H, Ar), 6.89 (d, J=7.6 Hz, 1H), 6.52 (t, J=7.8 Hz, 1H, Ar), 5.50 (s, 2H, CH_2), 3.67 (s, 3H, OCH_3), 1.91 (s, 3H, CH_3). ^{13}C NMR (DMSO-d_6, δ/ppm): 167.47, 157.65, 151.50, 149.23, 148.01, 136.97, 123.23, 122.48, 122.02, 118.43, 117.81, 114.98, 63.29, 55.73. HRMS: m/z=347.006 (M−OAc^+). Anal. Calcd for **10**: C, 48.41; H, 4.54; N, 6.64. Found: C, 46.72; H, 5.82; N, 6.72.

4.13. Computational methods

All calculations were carried out using the Gaussian 03 package, in which the tight criterion (10^{-8} hartree) is the default for the SCF convergence.[17] The molecular geometries were fully optimized with the hybrid B3LYP-DFT method under C_1 symmetry, in which the Becke three parameter exchange functional[18] and the Lee–Yang–Parr correlation functional[19] were used. The LANL2DZ including the double-ζ basis sets for the valence and outermost core orbitals combined with pseudopotential were used for Pd,[20] and 6-31G(d) basis sets for the other atoms.

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Supplementary data

Tables for the Suzuki–Miyaura coupling reactions using $Pd(OAc)_2$/**L** (**L**=**2**–**5**, **7**–**9**) at various solvents and temperatures; tables for the parameters of the optimized structures **TS4a** and **TS4b**; X-ray crystallographic files (CIFs) for **1** and **10**; ORTEP drawings of **1** and **10** (Figs. S1 and S2). Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC nos. 683204 and 685915 for **1** and **10**. 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: http://www.ccdc.cam.ac.uk). Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2009.02.017.

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10. Crystal data for **10**: $C_{16}H_{16}N_2O_4Pd\cdot 1.5H_2O$, M_w=406.71, triclinic, space group P-1, a=7.4414(16) Å, b=10.971(2) Å, c=11.059(2) Å, α=80.793(4)°, β=74.361(4)°, γ=87.814(4)°, V=858.2(3) Å^3, D_c=1.678 Mg/m^3, Z=1, μ=1.112 mm^{-1}, 5009 data collected, 3365 unique data [R(int)=0.0260], R_1=0.0516, wR_2=0.1256, CCDC 685915.
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