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Note

Highly efficient cyclopalladated ferrocenylimine catalyst for Suzuki cross-coupling reaction of 3-pyridylboronic pinacol ester with aryl halides

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Abstract

The Suzuki cross-coupling reaction of 3-pyridylboronic pinacol ester with aryl iodides, bromides and chlorides was carried out in DMF/H_2O (3/1, v/v) at 110 °C in the presence of cyclopalladated ferrocenylimine **I** and K_2CO_3 or $CsCO_3$ (1.0 equiv.) without the protection of inert gas. By using this method the synthesis of 3-pyridyl biaryl compounds could be readily achieved.

Keywords: Cyclopalladated ferrocenylimine; Suzuki reaction; 3-Pyridylboronic pinacol ester; 3-Pyridyl biaryl system

1. Introduction

As one of the most powerful methods for the formation of biaryl Compounds [1], palladium-catalyzed Suzuki reaction has attracted a lot research interest. A large number of palladium catalysts derived from phosphines, phosphites, phosphinites, amines, imines, oximes and thioethers were employed in Suzuki reaction. Among them, palladium–phosphine complexes are the most commonly employed catalysts [2,3]. This type of catalyst is sensitive to moisture and air. Therefore it requires air-free condition to minimize the ligand oxidation [4–6]. Recently, some papers on the Miyaura–Suzuki coupling under aerobic conditions have appeared [7–9]. They reported their research results by using $Pd(OAc)_2$/phosphine-free ligands such as DAPCy, Dabco or Bis(*N*-methyl-*N*-phenyl-hydrazone) as efficient air-stable catalytic system for mild Suzuki reaction.

Palladacycles are now emerging as a new family of palladium catalysts for hosting the cross-coupling reactions [10]. Usually, they are prepared in high yields through a C–H activation process, and most of them are air and moisture stable. When they become catalytically active (usually above 100 °C), high turnover numbers (TONs) could be obtained. A recent review on palladacycles has reported that the palladacycles can be also used in the fields of photoluminescent, liquid crystal, supramolecules and dendrimers [11]. Therefore, an increasing research interests are focusing on the palladacycles.

Some progresses have been made in palladacycle-catalyzed Suzuki reaction. Beller et al. [12] and Bedford [13] reported that phosphorus-based palladacycles could be used to catalyze the cross-coupling of a large range of substrates with aryl boronic acid under an inert atmosphere. Gibson et al. [14] reported the use of orthopalladated benzylphosphine complex in Suzuki reaction. However, inert atmosphere was also required. Phosphine-free *N*-heterocyclic carbenes (NHC) [15], oxime, imine, and sulphur-based palladacycles are also found to be good candidates for Suzuki reaction [15e,16]. But the disadvantage of them are being either air sensitive or catalytically inactive towards aryl chlorides [15e,17].

Ten years ago, we found that cyclopalladated ferrocenylimine [18] is a kind of phosphine-free compounds and

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almost behaves all the properties of palladacycles catalysts. The synthetic convenience, facile modification and air, moisture stability made them easily to be handled. Subsequently, we discovered their wide applications such as the resolution of racemates, the determination of amino acids [19], the homogeneous catalysis in Heck reaction [20] both in organic solvent and in neat water, the dimerization of ArHgCl [21] and recently the catalyst in Suzuki reaction of arylboronic acid with aryl halides [22].

Herein, we reported the extension of our work in cyclopalladated ferrocenylimine catalyzed Suzuki cross-coupling reaction by using 3-pyridyl boronic pinacol ester with aryl iodides, bromides and even aryl chlorides to synthesize the hetero-biaryls compounds.

Compared with boronic acids, the boronic esters are more stable in the presence of a wide variety of functional groups, non-hygroscopic and easy to be handled [23].

2. Results and discussion

The catalyst **I** was prepared in high yield from the cyclopalladation of the corresponding ferrocenylimine with Li_2PdCl_4 in MeOH in the presence of NaOAc at room temperature [18].

At the very beginning, to develop our methodology, we ran our first Suzuki cross-coupling reaction of 3-pyridyl boronic pinacol ester with iodobenzene catalyzed by **I**. Based on our previous results, we chose DMF as the solvent and potassium carbonate as the base [22]. However, we did not obtain the desired product. After a quick search of the literature, we found that O'Shea [24] and Cioffi [25] had reported the hydrolysis of boroxins or boronic esters to form boronic acid in situ. The formation of active boronate species does not readily occur under anhydrous conditions.

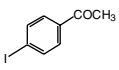
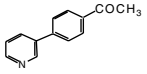
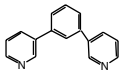
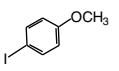
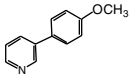
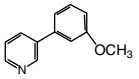
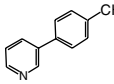
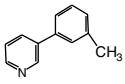
We then re-examined the coupling of iodobenzene with 1.0 equiv. of 3-pyridyl boronic pinacol ester at the similar condition in DMF/H_2O (3:1) other than anhydrous DMF. The reaction took place smoothly in the presence of 1 mol% palladium catalyst **I** and potassium carbonate as the base at 110 °C to give the desired product 3-phenyl pyridine in 97% yield after 4 h (Table 1, Entry 1).

Under the similar condition, we studied the activity of catalyst **I** towards different aryl halides. As expected, cyclopalladated ferrocenylimine **I** was found to efficiently catalyze the coupling of 3-pyridylboronic pinacol ester with a wide range of aryl iodides, bromides (Scheme 1). Good to excellent yields were obtained regardless of the substituents of aryl halides. The experiment result is listed in Tables.

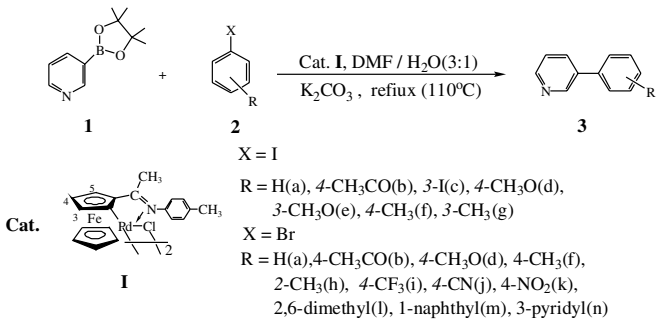
2.1. Reaction with aryl iodides

In the palladium-catalyzed Suzuki coupling with aryl halides, the order of reactivity is usually I > Br ≫ Cl. The results of Suzuki cross-coupling of 3-pyridyl-boronic pinacol ester with some aryliodides are listed in Table 1.

Table 1
Suzuki cross-coupling of 3-pyridyl boronic pinacol ester with aryl iodides catalyzed by **I**

Entry[a]	ArI	mol% of Pd	T(h)	Coupling product	No. of products, yield %
1		1	4		**3a**, 97[c]
2		1	10		**3b**, 99[b]
3		1	4		**3c**, 96[c]
4		1	10		**3d**, 88[b]
5		1	6		**3e**, 89[c]
6		1	6		**3f**, 87[c]
7		1	10		**3g**, 84[c]

[a] Reaction conditions: ArI 0.5 mmol, 3-pyridylboronic pinacol ester 0.5 mmol, K_2CO_3 0.5 mmol (Entry 3, 1.0 mmol), solvent DMF/H_2O (2.1 mL/0.7 mL), catalyst **I**, reaction temperature 110 °C.
[b] Average results of two runs determined by HPLC based on ArI.
[c] Isolated yields based on ArI. The compounds were purified by preparative TLC on silica gel.

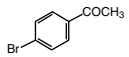
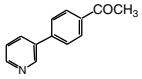
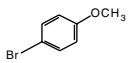
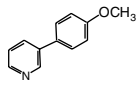
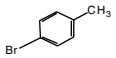
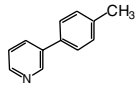
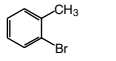
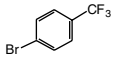
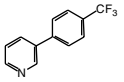
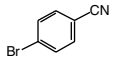
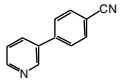
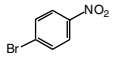
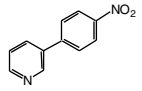


Scheme 1. Suzuki cross-coupling reaction of 3-pyridyl boronic pinacol ester with aryl halides (I, Br) catalyzed by **I**.

2.2. Reaction with aryl bromides

To evaluate the scope and limitation of this procedure, we performed a number of coupling reactions of 3-pyridyl boronic pinacol ester with several aryl bromides (Scheme 1, Table 2). The results show that in this case the coupling reaction could be applied to aryl bromides bearing various functional groups: cyano, carbonyl, nitro, methoxyl, methyl, etc. Furthermore, 3-bromopyridine could also be

Table 2
Suzuki cross-coupling reaction of 3-pyridyl boronic pinacol ester with aryl bromides catalyzed by **I**

Entry[a]	ArBr	mol% of Pd	T(h)	Coupling product	No. of products, yield %
1		1	6		**3a**, 87[c]
2		1	6		**3b**, 83[b]
3		1	6		**3d**, 68[b]
4		1	13		**3f**, 73[c]
5		1	10		**3h**, 70[c]
6		0.5	10		**3i**, 84[c]
7		0.5	5		**3j**, 100[b]
8		1	5		**3k**, 92[c]
9		1	10		**3l**, 71[c]
10		1	10		**3m**, 83[c]
11		1	5		**3n**, 87[c]

[a] Reaction conditions: ArBr 0.5 mmol, 3-pyridylboronic pinacol ester 0.5 mmol, K_2CO_3 0.5 mmol, solvent DMF/H_2O (2.1 mL/0.7 mL), catalyst **I**, reaction temperature 110 °C.
[b] Average results of two runs determined by HPLC based on ArBr.
[c] Isolated yields based on ArBr. The compounds were purified by preparative TLC on silica gel.

coupled in good yield (Table 2, Entry 11). We also investigated the steric effect. As shown in Table 2, aryl bromides with *ortho* substituents, such as 2-bromotoluene and 2-bromo-*m*-xylene, gave the corresponding products in good yields (Table 2, Entries 5 and 9).

Table 3
Influence of base on the Suzuki coupling

Entry[a]	Base	Yield[b] (%)
1	Cs_2CO_3	69
2	K_2CO_3	58
3	K_3PO_4	22
4	KOAC	22
5	*i*-Pr_2NEt	<2

[a] Reaction conditions: 4-chloroanisole 0.2 mmol, 3-pyridylboronic pinacol ester 0.2 mmol, base 0.2 mmol, solvent DMF/H_2O (0.84 mL/0.28 mL), catalyst **I**, reaction temperature 110 °C.
[b] Average results of two runs, isolated yields based on ArCl.

2.3. Reaction with arylchlorides

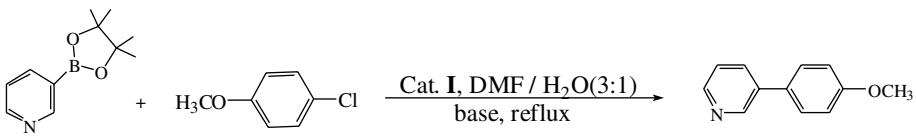
Bedford and Fu reported that the dioxane/Cs_2CO_3 system is efficient for the coupling of aryl chlorides with arylboronic acids [26]. We investigated the effect of the base in the cross-coupling reaction with 4-chloroanisole (Table 3). By alternating the base K_2CO_3, Cs_2CO_3, K_3PO_4, KOAC and *i*-Pr_2NEt. It was found that Cs_2CO_3 is much better than the others (isolated yield was 69%). Then, we examined the same reaction in dioxane by using 1% catalyst **I** and Cs_2CO_3 as the base. We found that DMF/H_2O is better than dioxane (In dioxane, the yield is only 35%) (see Schemes 2 and 3).

Under the optimized reaction conditions for aryl chlorides, we investigated the reactivity of various aryl chlorides. The electronic effect of substituent was observed but not very significant. However, the steric factor has a great influence on the reaction. The coupling with 2-chlorotoluene and 2-chloroanisole only gave isolated yields 29% and 35% in the presence of 1.5% catalyst **I**, respectively (Table 4, Entries 6 and 9).

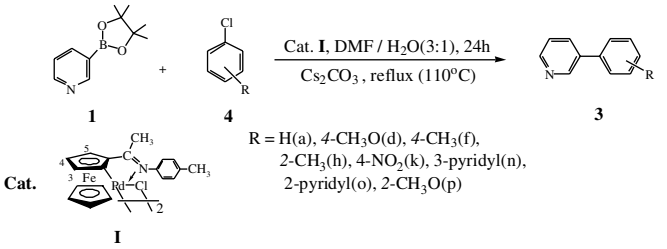
3. Experimental

3.1. General

Melting points were measured on a WC-1 microscopic apparatus and uncorrected. HPLC analyses were carried out on a Waters 600E type instrument equipped with a Nava-Pak (R) C8 60Å HPLC Cartridge column (3.9 × 150 mm, 4 μm), and UV detector for determination of the products. ^1H NMR were recorded on a Bruker DPX 400 instrument using $CDCl_3$ as the solvent and tetramethylsilane as the internal standard. API mass spectroscopic analyses were performed using atmospheric pressure chemical ionization (APCI). Elemental analyses were determined with a VARIO EL apparatus. Preparative

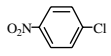
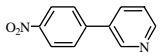
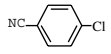
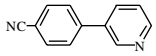
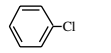
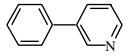
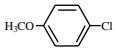
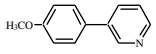
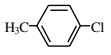
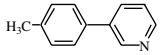
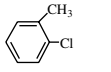
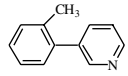
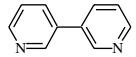
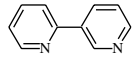
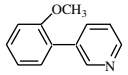


Scheme 2. Effect of base on the Suzuki cross-coupling of 3-pyridyl boronic pinacol ester with 4-chloroanisole catalyzed by **I**.



Scheme 3. Suzuki cross-coupling of 3-pyridyl boronic pinacol ester with aryl chlorides.

Table 4
Suzuki cross-coupling reaction of 3-pyridyl boronic pinacol ester with aryl chlorides catalyzed by **I**

Entry[a]	Aryl halides	mol% of Pd	Coupling product	No. of products, yield[b] %
1		1		**3k,** 77
2		1		**3j,** 80
3		1		**3a**, 66
4		1		**3d**, 69
5		1		**3f**, 76
6		1.5		**3h**, 29
7		1		**3n**, 64
8		1		**3o**, 74
9		1.5		**3p**, 35

[a] Reaction conditions: arylchlorides 0.2 mmol, 3-pyridylboronic pinacol ester 0.2 mmol, Cs_2CO_3 0.2 mmol, solvent DMF/H_2O (0.84 mL/0.28 mL), catalyst **I**.

[b] Isolated yields based on ArCl. The compounds were purified by preparative TLC on silica gel.

TLC was performed on dry silica gel plates developed with acetic ether/petroleum ether.

Cyclopalladated ferrocenylimine **I** was synthesized according to the literature procedures [18]. All solvents were dried according to the standard methods. The aryl halides were obtained from commercial sources and were generally used without further purification. The biaryls for HPLC external standard were prepared via Suzuki reaction and characterized by comparison of the melting points to the literatures, by elemental analysis or by ^{1}H NMR.

3.2. Preparation of 3-pyridylboronic pinacol ester [27]

A 0.5 L three-necked flask equipped with a stir bar, a nitrogen inlet adapter, and a Dean-Stark trap with a condenser was charged with 3-pyridylboroxin · 0.5H_2O (10.0 g, 30.8 mmol), pinacol (13.5 g, 114 mmol), and toluene (400 mL). The solution was heated to reflux in a 120 °C oil bath using a Dean–Stark apparatus for 2.5 h. The reaction was completed when the reaction solution changed from cloudy white to clear. The solution was then concentrated in vacuo to provide a solid. This crude solid was transferred to cyclohexane (50 mL) and crystallized by holding the suspension at 85 °C for 30 min and then allowing the temperature to slowly return to room temperature. The slurry was filtered, and the solid was washed with cyclohexane (10 mL) and dried under vacuum to afford 15.39 g of 3-pyridylboronic pinacol ester as a white solid. Yield: 72%. M.p.: 104–105 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.95 (br, 1H), 8.67 (dd, 1H, $J = 1.8$, 4.9 Hz), 8.06 (dt, 1H, $J = 1.8$, 7.5 Hz), 7.29–7.26 (m, 1H), 1.36 (s, 12H).

3.3. General procedure of Suzuki coupling reaction of 3-pyridylboronic pinacol ester with aryl halides

A 5 mL round-bottom flask was charged with aryl halides (0.5 mmol), 3-pyridylboronic pinacol ester (0.5 mmol, 0.1024 g), potassium carbonate (0.5 mmol, 0.079 g) and catalyst **I** in DMF/H_2O (2.1 mL/0.7 mL) at room temperature. The reaction mixture was stirred at reflux temperature (110 °C) in air and the reaction progress was monitored by TLC. After the completion of the reaction, the mixture was quenched by 5 mL water and then extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layer was dried over Na_2SO_4. After removal of the solvent in vacuo, the product was obtained by preparative TLC, eluting with acetic ether/petroleum ether (1:1–1: 5) and the yield was calculated based on ArX or determined by HPLC. Final products were characterized by ^{1}H NMR, LC/MS/MS and elemental analysis.

3.3.1. 3-Phenyl pyridine (**3a**) [28]

Colourless oil, n_D^{20} 1.6150. APCI MS: *m/z* 156 $[C_{11}H_9N + H]^+$. ^{1}H NMR ($CDCl_3$) δ 8.86 (1H, s), 8.60 (1H, $J = 4.0$ Hz, d), 7.87 (1H, $J = 8.0$ Hz, d), 7.35–7.60 (6H, m).

3.3.2. 1-(4-Pyridin-3-ylphenyl) ethanone (**3b**) [29]

White plates, m.p. 81–83 °C. ^{1}H NMR ($CDCl_3$) δ 8.89 (1H, s), 8.64 (1H, $J = 4.0$ Hz, m), 8.09 (2H, $J = 8.4$ Hz, $J = 6.4$ Hz, dd, Ar H), 7.92 (1H, m), 7.02 (2H, $J = 8.4$ Hz, $J = 6.4$ Hz, dd, Ar H), 7.39 (1H, m), 2.65 (3H, s, CH_3).

3.3.3. 1,3-Bis(3-pyridyl) benzene (**3c**) [30]

White needles, m.p. 84–86 °C ^{1}H NMR ($CDCl_3$) δ 8.91 (2H, s), 8.65 (2H, $J = 4.0$ Hz, $J = 1.2$ Hz, dd), 7.96 (2H, $J = 8.4$ Hz, $J = 1.6$ Hz, dd, Py-H), 7.77 (1H, s), 7.65 (3H, $J = 4.8$ Hz, m), 7.44 (2H, $J = 4.8$ Hz, d, Ar H). APCI MS: *m/z* 233 $[C_{16}H_{12}N_2 + H]^+$. Anal. Calc. for $C_{16}H_{12}N_2$: C, 82.73; H, 5.21; N, 12.06. Found: C, 82.74; H, 5.22; N, 12.09%.

*3.3.4. 3-(4-Methoxyphenyl) pyridine (**3d**) [29]*

White solid, m.p. 55–57 °C. ^{1}H NMR ($CDCl_3$) δ 8.83 (1H, s), 8.60 (1H, d), 7.87 (1H, $J = 8.0$, d), 7.53 (2H, $J = 8.4$ Hz, d, Ar H), 7.38 (1H, m), 7.02 (2H, $J = 8.4$ Hz, d, Ar H), 3.87 (3H, s, CH_3).

*3.3.5. 3-(3-Methoxyphenyl) pyridine (**3e**) [31]*

White solid, m.p. 119–120 °C. APCI MS: m/z 186 $[C_{12}H_{11}NO + H]^+$.

*3.3.6. 3-(4-Tolyl) pyridine (**3f**) [32]*

White solid, m.p. 39–40 °C. ^{1}H NMR ($CDCl_3$) δ 8.84 (1H, s), 8.57 (1H, $J = 4.0$ Hz, d), 7.87 (1H, $J = 8.0$ Hz, d), 7.49 (2H, $J =$ 8.0 Hz, d, Ar H), 7.36 (1H, m), 7.32 (2H, $J = 8.0$ Hz, d, Ar H), 2.40 (3H, s, CH_3). APCI MS: m/z 170 $[C_{12}H_{11}N + H]^+$. Anal. Calc. for $C_{12}H_{11}N$: C, 85.17; H, 6.55; N, 8.28. Found C, 85.03; H, 6.56; N, 8.18%.

*3.3.7. 3-(3-Tolyl) pyridine (**3g**) [31]*

White solid, m.p. 186–187 °C. APCI MS: m/z 170 $[C_{12}H_{11}N + H]^+$.

*3.3.8. 3-(2-Tolyl) pyridine (**3h**) [25]*

Colorless oil, ^{1}H NMR ($CDCl_3$) δ 8.61 (2H, s), 7.69 (1H, $J = 7.6$ Hz, d), 7.41–7.21 (5H, m), 2.98 (3H, s, CH_3).

*3.3.9. 3-(4-Trifluoroacetphenyl) pyridine (**3i**) [33]*

White plates, m.p. 64–66 °C. ^{1}H NMR ($CDCl_3$) δ 8.90 (1H, s), 8.67 (1H, s), 7.99 (2H, $J = 7.2$ Hz, d, Ar H), 7.78 (2H, $J = 8.0$ Hz, d, Ar H), 7.72 (2H, $J = 8.0$ Hz, d, Ar H), 7.52 (1H, m). APCI MS: m/z 224 $[C_{12}H_8NF_3 + H]^+$. Anal. Calc. for $C_{12}H_8NF_3$: C, 64.58; H, 3.61; N, 6.28. Found: C, 64.37; H, 3.53; N, 6.07%.

*3.3.10. 4-Pyridin-3-ylbenzonitrile (**3j**) [34]*

White needles, m.p. 95–96 °C. ^{1}H NMR ($CDCl_3$) δ 8.87 (1H, s), 8.68 (1H, d), 7.91 (1H, $J = 8.4$ Hz, d), 7.79 (2H, $J = 8.4$ Hz, d, Ar H),7.70 (2H, $J = 8.4$ Hz, d, Ar H), 7.45 (1H, m), 3.87 (3H, s, CH_3). Anal. Calc. for $C_{12}H_8N_2$ C, 79.98; H, 4.47; N, 15.55. Found: C, 80.05; H, 4.42; N, 15.74%.

*3.3.11. 3-(4-Nitrophenyl) pyridine (**3k**) [35]*

Yellow needles, m.p. 148–149. Anal. Calc. for $C_{11}H_8N_2O_2$: C, 66.00; H, 4.03; N, 13.99. Found: C, 65.72; H, 4.03; N, 13.92%.

*3.3.12. 3-(2,6-Dimethylphenyl) pyridine (**3l**) [36]*

Yellow oil ^{1}H NMR ($CDCl_3$) δ 8.63 (1H, s), δ 8.45 (1H, s), 7.55 (1H, $J = 7.6$ Hz, d), 7.42 (1H, m), 7.21 (1H, m), 7.14 (2H, d), 2.03 (6H, s, CH_3).

*3.3.13. 3-Naphthalen-1-ylpyridine (**3m**) [29]*

Yellow oil ^{1}H NMR ($CDCl_3$), δ 8.81 (s, 1H), 8.74 (s, 1H), 8.04 (m, 1H), 7.95 (d, 2H), 7.74 (m, 2H), 7.63–7.48 (m, 3H), 7.43 (m, 1H).

*3.3.14. 3,3′-Bipyridine (**3n**) [37]*

Yellow oil, APCI MS: m/z 157 $[C_{10}H_8N_2 + H]^+$. ^{1}H NMR ($CDCl_3$) δ 8.54 (2H, s), 8.66 (2H, $J = 4.0$ Hz, d), 7.90 (2H, $J = 8.0$ Hz, $J = 4.0$ Hz, dt), 7.43 (2H, $J = 4.8$ Hz, $J = 8.0$ Hz, m).

*3.3.15. 2,3′-Bipyridine (**3o**) [29]*

^{1}H NMR (CDCl3, 400 MHz), δ 9.21 (1H, s), 8.74 (dt, $J = 8.4$ Hz, $J = 4.0$ Hz, 1H), 8.60 (d, $J = 4.0$ Hz, 1H), 8.55 (dt, $J = 8.0$ Hz, $J = 6.0$ Hz, 1H), 7.83-7.75 (m, 2H), 7.44 (m, 1H), 7.30 (m, 1H).

*3.3.16. 3-(2-Methoxyphenyl) pyridine (**3p**) [31]*

Colorless oil ^{1}H NMR ($CDCl_3$) δ 8.81 (1H, s), 8.58 (1H, s), 7.92 (1H, $J = 8.0$ Hz, d), 7.41–7.32 (3H, m), 7.09–7.01 (2H, m), 3.12 (3H, s, CH_3).

4. Conclusion

In conclusion, cyclopalladated ferrocenylimine **I** provides a convenient catalyst for the cross-coupling of 3-pyridylboronic pinacol ester with a variety of aryl halides (even including electron-rich aryl chlorides). Moderate to excellent yields were obtained without the protection of inert gas. The tolerance towards various substrates, high stability and activity make it an excellent and practical catalyst for this Suzuki cross-coupling reaction.

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