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Ferrocenylimidazoline palladacycles: efficient phosphine-free catalysts for Suzuki–Miyaura cross-coupling reaction

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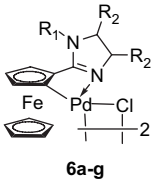
Abstract—A series of new ferrocenylimidazoline ligands **5** with different substituents in the imidazoline ring and their corresponding cyclopalladated complexes **6** were synthesized. Chloride-bridged palladacycle dimers **6**, which are thermally stable and insensitive to air and moisture, have been evaluated as effective phosphine-free catalysts for the Suzuki reaction of aryl bromides with arylboronic acid. The catalyst **6b** presents the highest efficiency in the coupling processes for less reactive 2-bromothiophene. Moreover, the reactions can be carried out at room temperature under aerobic conditions to give the corresponding biaryls in high yields. Additionally, the triphenylphosphine adduct of cyclopalladated ferrocenylimidazoline **7a** was structurally characterized by single-crystal X-ray diffraction.

1. Introduction

Palladium-catalyzed Suzuki–Miyaura reaction is one of the most efficient methods for the syntheses of biaryls and heterobiaryls,[1,2] which are widely used in pharmaceuticals, herbicides, and light-emitting materials. Considerable efforts have been dedicated to develop new and effective palladium complexes for this coupling reaction.[3–5] The utilization of palladium–phosphine complexes as catalysts has been prevalent in the past decade, and many successful examples are known.[6–14] However, most of these catalysts containing phosphines are generally sensitive to moisture and air, and required air free handling to minimize oxidation of ligand or stabilize oxidative addition products. Moreover, its large-scale application is limited in industry due to the expensive cost and toxic property.[15] Hence, the exploring of phosphine-free and more efficient catalysts is of current interest. Recently, many significant advances have been made in this area, including hydrazone–Pd complexes,[16,17] *N*-heterocyclic carbenes (NHC)–Pd complexes,[18–21] oxime palladacycles,[22–26] and sulfur-containing palladacycles.[27]

In our lab, we have developed some cyclopalladated ferrocenylimines as efficient catalysts for Suzuki–Miyaura coupling reactions.[28–31] In addition, the development of imidazoline systems has emerged as an attractive research area owing to their application in a range of transition metal (Cu, Ir, Pd, or Ru) catalyzed reactions, such as epoxidation,[32] 1,4-addition reaction,[33] copolymerization of carbon monoxide and styrene,[34–36] hydrogenation of aromatic ketones,[37] Heck reaction,[38] as well as aza-Claisen rearrangement reaction.[39] To further search more efficient catalysts and mild reaction condition for C–C bond formation, we screened a series of cyclopalladated ferrocenylimidazoline (shown in Fig. 1) as catalysts for the Suzuki–Miyaura cross-coupling reaction of aryl bromides with arylboronic acid under mild reaction conditions. To the best of our knowledge, this is the first time that ferrocenylimidazoline palladacycles as phosphine-free catalysts have been used in the Suzuki reaction.



6a: R_1=H R_2=Ph
6b: R_1=Benzyl R_2=H
6c: R_1=n-C_5H_{11} R_2=H
6d: R_1=n-C_8H_{17} R_2=H
6e: R_1=n-$C_{14}H_{29}$ R_2=H
6f: R_1=Acetyl R_2=Ph
6g: R_1=Acetyl R_2=H

Figure 1. Ferrocenylimidazoline palladacycles.

2. Results and discussion

2.1. Synthesis and characterization

Ferrocenylimidazolines **5** were synthesized in three steps starting from ferrocenylcarboxyaldehyde **1**, as shown in Scheme 1, which is different from Peters' method.[39a] Condensation reaction of ferrocenylcarboxyaldehyde with hydroxylamine hydrochloride in NMP produced ferrocenylcyanide **2** in 76% yield. Methyl ferrocenylimidoate hydrochloride **3** was obtained in nearly quantitative yield by treatment of ferrocenylcyanide **2** with HCl (gas) and

Keywords: Palladacycles; Ferrocenylimidazoline; Suzuki–Miyaura reaction; Phosphine-free catalysts; Crystal structure.
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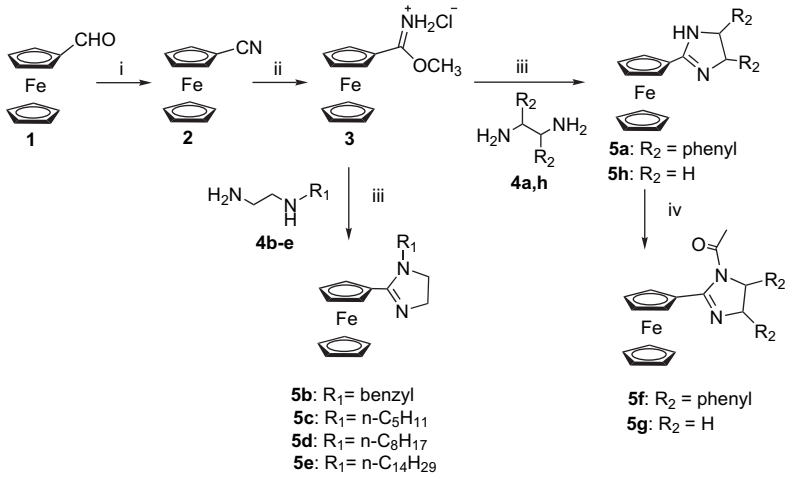


Scheme 1. Reagents: (i) $NH_2OH \cdot HCl$, NMP; (ii) CH_3OH, HCl, Et_2O; (iii) CH_3OH; (iv) CH_3COCl, NEt_3, CH_2Cl_2.

methanol in ethyl ether at 0 °C. The target ligands **5a–e** were prepared by condensation of compound **3** with the corresponding **4a–e**. Compounds **5f** and **5g** were obtained conveniently via **5a** and **5h** with acetyl chloride in dry dichloromethane, respectively. It should be noted that compounds **5c–e** were not stable in the air. They were used immediately for next reaction after purification without being characterized by NMR spectra. However, **5a**, **5f**, and **5g** with acetyl group at the N-1 position or phenyl group at C-4 and C-5 in the imidazoline ring are more stable and able to keep under air. It is proposed that the alkyl group at the N-1 position of imidazoline ring may increase the electric density of imidazoline ring, which results in the less stability of **5c–e**.

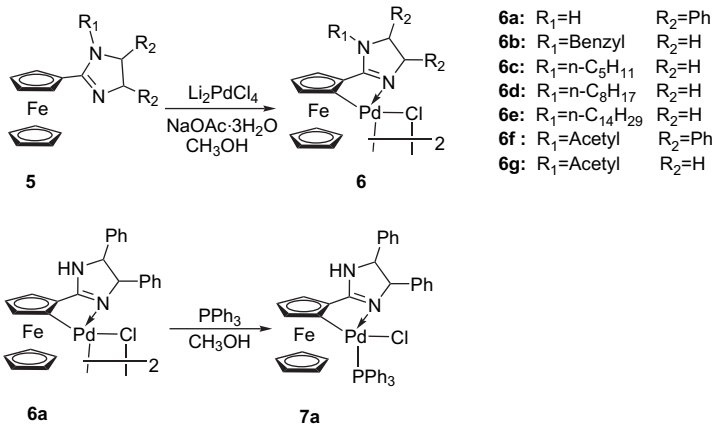
Complexes **6** were obtained successfully by cyclopalladation of compounds **5** with Li_2PdCl_4 in methanol in the presence of $NaOAc \cdot 3H_2O$ at room temperature (Scheme 2), and characterized by elemental analysis, IR, ^1H, and ^{13}C NMR spectra. The IR spectra showed strong absorption peak at ca. 1540–1560 cm^{-1} assigned to the C=N stretching of the imidazoline ring, which was shifted to lower wave number at about ca. 55 cm^{-1} by comparison with free ligands **5** due to N→Pd coordination.[40] The ^1H and ^{13}C NMR spectra are completely consistent with the expected homoannularly 1,2-disubstituted structures. The proton and carbon signals in complexes **6** were shifted to downfield in comparison with free ligands **5**. The similar shifts were also observed for the cyclopalladated ferrocenylimines reported.[41]

Complexes **6b–e** bearing alkyl groups at N-1 position of imidazoline ring are soluble in common organic solvents such as dichloromethane and acetone, while **6a**, **6f**, and **6g** with acetyl group at the N-1 position or with phenyl group in the imidazoline ring have poor solubility. Namely, the cyclopalladated ferrocenylimidazolines bearing electron-donating substituents exhibit better solubility than those with electron-withdrawing substituents in the imidazoline ring.

Furthermore, the reaction of chloride-bridged palladacycle dimer **6a** (Scheme 2) with 2 equiv of triphenylphosphine (PPh_3) in methanol at room temperature produced the corresponding triphenylphosphine (PPh_3) adduct **7a**, which was structurally characterized by single-crystal X-ray diffraction. It is air stable both in the solid state and in solution.

2.2. Crystal structure determination of the monomer complex 7a

Well-shaped crystal suitable for single-crystal X-ray analysis was obtained from methanol/dichloromethane. ORTEP drawing is shown in Figure 2. The palladium atom is located in a slightly distorted square-planar coordination geometry



Scheme 2.

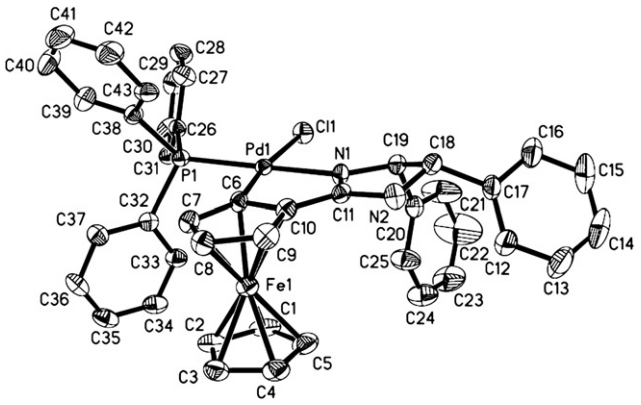


Figure 2. The molecular structure of **7a**, showing 30% probability displacement ellipsoids. H atoms have been omitted for clarity.

with one N-donor atom (N1) from the imidazoline ring, one carbon atom (C6) from the Cp, one phosphorus atom from PPh_3, and one chlorine atom (the mean deviation from plane of 0.0238 Å). The bond angles around Pd atom vary from 80.9(2) to 173.46(16)°, and the bond lengths of C–Pd and N–Pd are 2.017(6) and 2.088(5)Å, respectively. Owing to the steric hindrance of substituents on the imidazoline backbone, the imidazoline ring is twisted with the dihedral angle of 20.7° between N(1)–C(19)–C(18) and N(1)–C(11)–N(2)–C(18). In addition, there are two kinds of hydrogen bond interactions (N2–H2E···O1 and O1–H1E···Cl1) between the methanol molecule and hydrogen atom of the imidazoline ring or chlorine atom from two neighboring molecules to stabilize the corresponding crystal lattice, as shown in Figure 3 and Table 3s (see Supplementary data).

2.3. Catalytic properties

2.3.1. Palladacycles catalyzed Suzuki–Miyaura reaction under air. Initial studies were performed for 4-bromotoluene (**8a**) and phenylboronic acid (**9a**) as a model reaction in toluene at 110 °C with various bases under aerobic atmosphere using compound **6b** as the catalyst. As shown in Table 1, $K_3PO_4\cdot 7H_2O$ was found to be the best base and provided

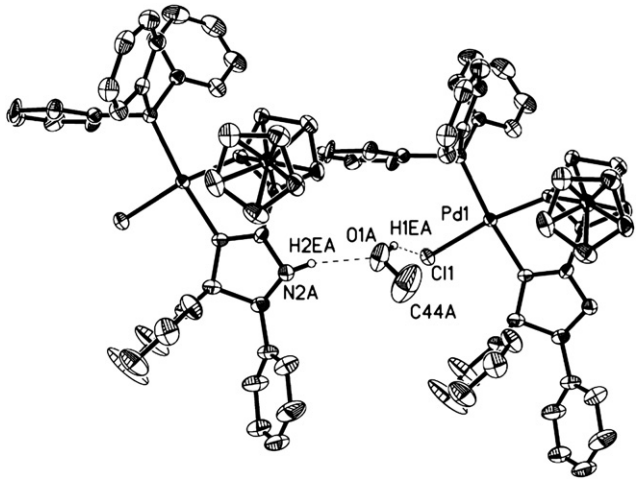
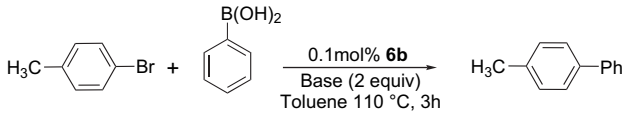


Figure 3. The intermolecular interactions of **7a**, showing 30% probability displacement ellipsoids. Thin dashed lines indicated hydrogen bonds. H atoms not involved in hydrogen bonding have been omitted.

Table 1. Screening of bases for Suzuki–Miyaura cross-coupling reaction of 4-bromotoluene with phenylboronic acid using **6b** as catalyst[a]



8a **9a** **10a**

Entry	Base	Yield[b] (%)
1	K_2CO_3	80
2	$K_3PO_4\cdot 7H_2O$	98
3	NaOH	82
4	*t*-BuONa	19
5	$KF\cdot 2H_2O$	84
6	K_3PO_4	57
7	KF	48

[a] Reaction conditions: 1 equiv of ArBr, 1.5 equiv of $PhB(OH)_2$, 2 equiv of base, 0.1 mol % of catalyst **6b**, toluene, 110 °C, 3 h, under air.
[b] Isolated yields, based on 4-bromotoluene, average of two runs.

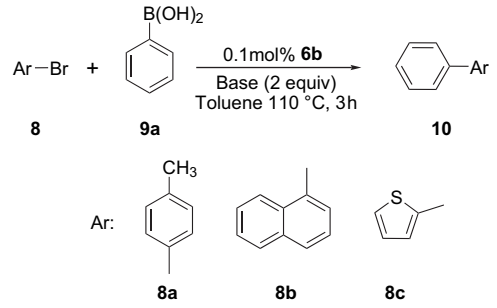
the best isolated yield of 98% (Table 1, entry 2). It can be seen obviously from the results that the aqueous bases showed higher efficiency than the anhydrous bases, indicating that a small amount of water was essential for this catalytic system.[42] It was presumed that water prevented boronic acid dimerizations and cyclic trimerizations from forming boronic acid anhydrides and boroxines, respectively.

Aryl bromides are cheaper, but more difficult to undergo the Suzuki reaction in comparison with the corresponding iodides. Therefore, it is significant to evaluate the catalytic activity of the cyclopalladed ferrocenylimidazolines in the Suzuki coupling reaction of aryl bromides with aryl boronic acids. The experimental results carried out with $K_3PO_4\cdot 7H_2O$ as base are listed in Table 2. Palladacycles **6a–g** with a loading of 0.1 mol %, exhibited advantageous catalytic activity and gave excellent yields in the reactions of phenylboronic acid coupled with 4-bromotoluene (**8a**) or 1-bromonaphthalene (**8b**) (Table 2, entries 1–14). That is to say, catalysts **6b–e** with the electron-donating groups showed similar reactivity to **6a**, **6f**, and **6g** with electron-withdrawing group. It seemed that the substituents in the imidazoline moiety did not remarkably affect the catalytic activity of the corresponding palladacycles in Suzuki reaction.

In order to screen the best catalyst, 2-bromothiophene (**8c**), which is with rich π-electron and less reactive, was selected as substrate. Surprisingly, **6b** gave an excellent yield of 96% (Table 2, entry 16), while the lower yields (Table 2, entries 15, 17–21) were obtained for others. Palladacycle **6b** is the most efficient phosphine-free palladium catalyst for the Suzuki coupling of 2-bromothiophene with phenylboronic acid reported to date.[43–46]

To expand the scope of this reaction, various aryl bromides were subjected to this coupling reaction in the presence of **6b** as catalyst with a loading of 0.1 mol %, and the results are summarized in Table 3. We were pleased to find that both electron-rich aryl bromides such as 4-bromoanisole (**8d**) and electron-deficient aryl bromides such as 4′-bromoacetophenone (**8e**), 4-bromobenzonitrile (**8f**), and 1-bromo-4-nitrobenzene (**8g**) could be efficiently coupled to give the corresponding biaryls in excellent isolated yields (>94%), which suggested that the catalytic system was applicable

Table 2. Screening of catalysts for Suzuki–Miyaura cross-coupling reaction of aryl bromides with phenylboronic acid[a]



Entry	Ar–Br (**8**)	Catalysts **6**	Products (**10**)	*T* (h)	Yields[b] (%)
1	**8a**	**6a**	**10a**	3	96
2	**8a**	**6b**	**10a**	3	98
3	**8a**	**6c**	**10a**	3	99
4	**8a**	**6d**	**10a**	3	95
5	**8a**	**6e**	**10a**	3	94
6	**8a**	**6f**	**10a**	3	89
7	**8a**	**6g**	**10a**	3	95
8	**8b**	**6a**	**10b**	3	97
9	**8b**	**6b**	**10b**	3	97
10	**8b**	**6c**	**10b**	3	99
11	**8b**	**6d**	**10b**	3	92
12	**8b**	**6e**	**10b**	3	93
13	**8b**	**6f**	**10b**	3	94
14	**8b**	**6g**	**10b**	3	96
15	**8c**	**6a**	**10c**	3	54
16	**8c**	**6b**	**10c**	3	96
17	**8c**	**6c**	**10c**	3	56
18	**8c**	**6d**	**10c**	3	49
19	**8c**	**6e**	**10c**	3	51
20	**8c**	**6f**	**10c**	3	53
21	**8c**	**6g**	**10c**	3	48

[a] Reaction conditions: 1 equiv of ArBr, 1.5 equiv of $PhB(OH)_2$, 2 equiv of $K_3PO_4\cdot 7H_2O$, 0.1 mol % of catalyst, toluene, 110 °C, under air.
[b] Isolated yields, average of two runs.

to various aryl bromides and tolerant of a broad range of functional groups (Table 3, entries 1–8). Encouraged by these results, we went ahead to determine the effect of steric bulk in the aryl bromides. It was interesting to observe from Table 3 that the nature of substituents in aryl group had minimal influence on the reaction. Using sterically hindered aryl bromides, such as 2-bromo-*m*-xylene (**8h**), 2-bromotoluene (**8i**), and 1-bromo-2-methyl-naphthalene (**8j**) as substrates, the desired products were obtained in high yield of 90%, 98%, and 97%, respectively (Table 3, entries 9–11). When the heterocyclic bromides such as 2-, 3-, 4-bromopyridine (**8k**, **8l**, **8m**) and 3-bromothiophene (**8n**) were employed, the desired products were also obtained in good to excellent yields (Table 3, entries 12–15). In addition, the catalyst **6b** could maintain its high catalytic activity for the cross-coupling of 4-bromoanisole (**8d**) with phenylboronic acid at low loading of 0.01 mol % (Table 3, entry 5). The effect of varying arylboronic acids was also investigated by using 4-bromoanisole (**8d**) as substrates. Using 4-substituted arylboronic acids, such as 4-methylphenylboronic acid (**9b**) and 4-chlorophenylboronic acid (**9c**), the corresponding coupling products were obtained in excellent yields (Table 3, entries 16 and 17).

2.3.2. Palladacycle 6b catalyzed Suzuki–Miyaura reaction at room temperature under air. It is attractive that the organic synthesis can be carried out at room temperature. So we studied the Suzuki–Miyaura coupling reaction of the relatively less reactive 4-bromotoluene and phenylboronic acid in mild conditions in the presence of 0.5 mol % **6b** (Table 4). TBAB as additives was added into the catalytic system in the subsequent experiments since the ammonium salts may accelerate the coupling reaction in virtue of activating the arylboronic acid to react by the formation of $[ArB(OH)_3]^-[R_4N]^+$.[47] The results showed that K_2CO_3 was the best base (Table 4, entries 1–6). In light of the aforementioned finding that the presence of a small amount of water is necessary to accelerate this reaction, a series of water-mixed solvents (v/v=1:2), including THF/H_2O, 1,4-dioxane/H_2O, methanol/H_2O, DMF/H_2O, and toluene/H_2O, were investigated in the presence of K_2CO_3 as base at room temperature (Table 4, entries 7–11). The highest isolated yield (98%) was obtained for methanol/H_2O system.

The scope of the reaction was probed under the optimized conditions. The results are illuminated in Table 5. The various aryl bromides containing electron-rich groups (methyl, methoxyl) or electron-deficient group (acetyl) and steric bulk, such as 2-bromo-*m*-xylene (**8h**), 2-bromotoluene (**8i**), and 1-bromo-2-methyl-naphthalene (**8j**), can be coupled with phenylboronic acid in good to excellent isolated yields with a loading of 0.5 mol % of **6b** at room temperature. Moreover, the 2-, 3-, and 4-substituted pyridyl bromides gave the desired products in high yields (Table 5, entries 8–10). The reactions of the 4-substituted arylboronic acids (**9b** and **9c**) with **8d** also resulted in the corresponding coupling products in excellent yields (Table 5, entries 11 and 12).

3. Conclusion

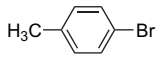
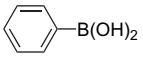
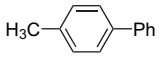
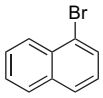
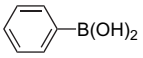
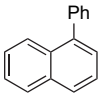
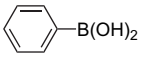
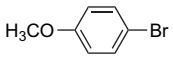
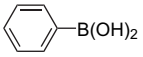
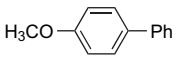
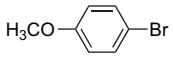
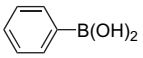
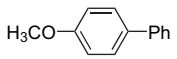
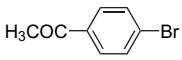
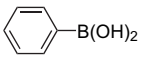
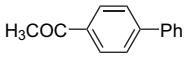
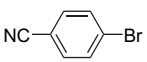
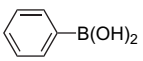
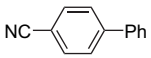
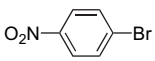
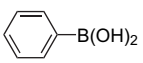
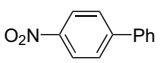
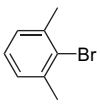
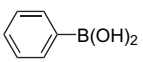
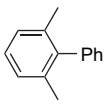
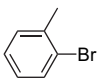
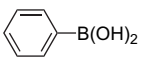
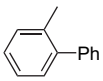
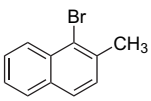
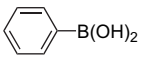
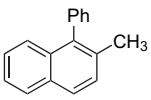
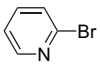
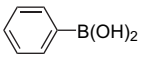
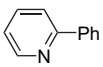
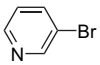
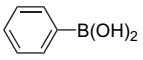
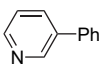
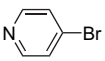
In summary, a series of new ferrocenylimidazolines **5a–g** with various substituents on the imidazoline backbone and their related chloride-bridged palladacycle dimers **6a–g** were prepared. These air- and moisture-stable ferrocenylimidazoline palladacycles are found to act as potent catalysts for a wide range of aryl bromides in Suzuki reactions at room temperature under aerobic conditions. It is well believed that they are sufficiently encouraging further investigations into the applicability of these ferrocenylimidazoline palladacycles in other catalytic reactions.

4. Experimental

4.1. General methods

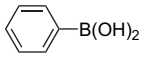
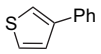
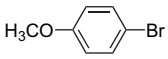
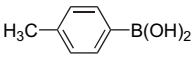
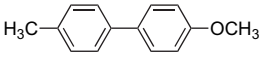
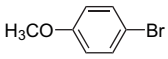
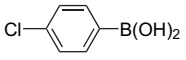
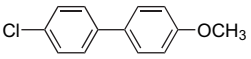
Methanol was distilled from magnesium under nitrogen. Ethyl ether was distilled from sodium and benzophenone under nitrogen. Dichloromethane was distilled from calcium hydride under nitrogen. Melting points were measured on a WC-1 microscopic apparatus and uncorrected. ^1H and ^{13}C NMR spectra were recorded on a Bruker DPX 400 instrument using $CDCl_3$ or DMSO-d_6 as the solvent and tetramethylsilane as the internal standard. Elemental analyses were determined with a PE-2400 II apparatus. IR spectra were collected on a Bruker VECTOR22 spectrophotometer in KBr pellets. *meso*-1,2-Diphenylethylenediamine **4a**,[48] *N*-benzylethylenediamine **4b**,[49] *N*-pentylethylenediamine

Table 3. Palladacycle **6b** catalyzed Suzuki coupling reaction of aryl bromides with arylboronic acid:[a] scope of substrates

Entry	Ar–Br	Arylboronic acid	Product	T (h)	Yields[b] (%)
1	 **(8a)**	 **(9a)**	 **(10a)**	3	98
2	 **(8b)**	 **(9a)**	 **(10b)**	3	97
3	 **(8c)**	 **(9a)**	 **(10c)**	3	96
4	 **(8d)**	 **(9a)**	 **(10d)**	2	94
5	 **(8d)**	 **(9a)**	 **(10d)**	8	85[c]
6	 **(8e)**	 **(9a)**	 **(10e)**	2	99
7	 **(8f)**	 **(9a)**	 **(10f)**	2	99
8	 **(8g)**	 **(9a)**	 **(10g)**	2	99
9	 **(8h)**	 **(9a)**	 **(10h)**	4	90
10	 **(8i)**	 **(9a)**	 **(10i)**	4	98
11	 **(8j)**	 **(9a)**	 **(10j)**	6	97
12	 **(8k)**	 **(9a)**	 **(10k)**	3	83
13	 **(8l)**	 **(9a)**	 **(10l)**	3	92
14	 **(8m)**	**(9a)**	**(10m)**	3	88

(*continued*)

Table 3. (*continued*)

Entry	Ar–Br	Arylboronic acid	Product	*T* (h)	Yields[b] (%)
15	 **(8n)**	 **(9a)**	 **(10n)**	6	81
16	 **(8d)**	 **(9b)**	 **(10o)**	3	95
17	 **(8d)**	 **(9c)**	 **(10p)**	3	96

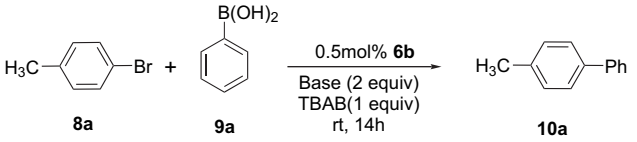
[a] Reaction conditions: 1 equiv of ArBr, 1.5 equiv of arylboronic acid, 2 equiv of $K_3PO_4 \cdot 7H_2O$, 0.1 mol % of **6b**, toluene, 110 °C, under air.
[b] Isolated yields, average of two runs.
[c] Using 0.01 mol % of **6b** as catalyst.

4c,[50] *N*-octylethylenediamine **4d**,[51] and *N*-tetradecylethylenediamine **4e**[51] were prepared according to the literature procedure. All other chemicals were used as purchased.

4.1.1. Ferrocenylcyanide (2). A solution of ferrocenecarboxyaldehyde **1** (2.14 g, 10 mmol) in NMP (25 mL) and hydroxylamine hydrochloride (0.966 g 12 mmol) was stirred at 110 °C under nitrogen. Progress of the reaction was monitored by TLC. After the reaction was completed, the mixture was poured into water (50 mL) and extracted with AcOEt (2×10 mL). The combined organic phase was washed with brine (2×10 mL), dried (Na_2SO_4), and the solvent was evaporated in vacuo. The crude product was purified by column chromatography on silica gel (eluant: petroleum ether (60–90 °C)/dichloromethane=1:1) to give compound **2** (1.60 g, 76%) as golden-yellow solid. Mp 105–106 °C (lit.[52] 107–108 °C). IR (KBr): 3092, 2232, 1450, 870 cm^{-1}.

4.1.2. Ferrocenylimidic acid methyl ester hydrochloride (3). To an ice-cooled solution of ferrocenylcyanide **2** (1.055 g, 5 mmol) in the mixture of absolute anhydrous Et_2O (15 mL) and methanol (3 mL), dry hydrogen chloride (gas) was bubbled through till the solution was saturated. Then the resulting solution was stirred for 2 h at 0 °C and kept overnight at room temperature. After evaporating the solvent in vacuo, the crude product was washed with dry ethyl ether (2×3 mL) under nitrogen, then the red solid 3 (1.37 g, 98%) was obtained. Mp 155–157 °C (lit.[53] 155–156 °C). IR (KBr): 3079, 2921, 1625, 1502, 1389, 1227, 1072, 1006 cm^{-1}.

Table 4. Suzuki–Miyaura coupling of $PhB(OH)_2$ and 4-$BrC_6H_4CH_3$ at room temperature: study on reaction conditions for base and solvent[a]



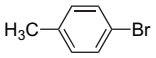
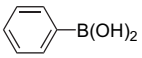
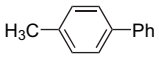
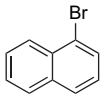
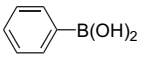
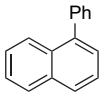
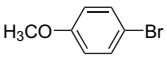
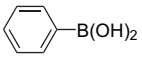
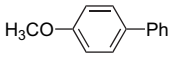
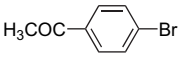
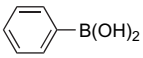
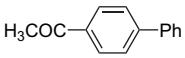
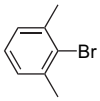
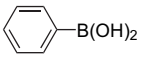
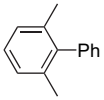
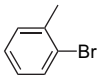
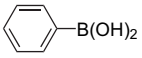
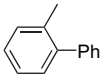
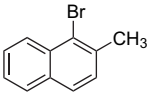
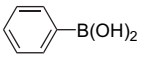
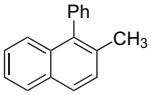
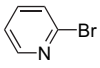
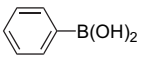
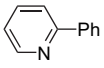
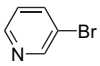
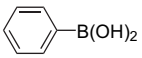
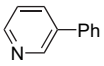
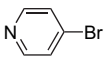
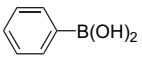
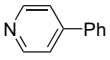
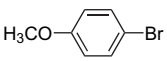
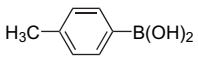
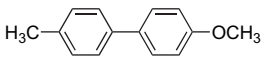
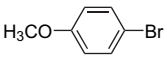
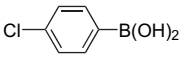
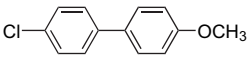
Entry	Base[b]	Yield[d] (%)	Entry	Solvent[c]	Yield[d] (%)
1	Na_2CO_3	53	7	THF/H_2O	83
2	K_2CO_3	83	8	1,4-Dioxane/H_2O	37
3	NaOH	22	9	DMF/H_2O	90
4	KOH	27	10	Methanol/H_2O	98
5	K_3PO_4	61	11	Toluene/H_2O	32
6	KF	44			

[a] Reaction conditions: 4-bromotoluene (0.5 mmol), $PhB(OH)_2$ (0.75 mmol), base (1 mmol), solvent (3 mL) (v/v=2:1, 3 mL), NBu_4Br (0.5 mmol), 0.5 mol % catalyst **6b**, at room temperature under air for 14 h.
[b] THF/H_2O (v/v=2:1, 3 mL) as solvent.
[c] v/v=2:1; K_2CO_3 as base.
[d] Isolated yields, average of two runs.

4.1.3. [*cis*-4,5-Diphenyl-4,5-dihydro-1*H*-2-imidazolyl]-ferrocene (5a). Compound **4a** (212 mg, 1 mmol) was added into the solution of compound **3** (280 mg, 1 mmol) in dry methanol (20 mL) under nitrogen. The solution was stirred at room temperature for 1 h, and then refluxed for 6 h. After the reaction was completed, methanol was removed in vacuo. The residue was dissolved into 20 mL of dichloromethane, washed with a saturated aqueous solution of Na_2CO_3 (2×10 mL) and NaCl (2×10 mL), and dried over anhydrous Na_2SO_4. Evaporation of the solvent in vacuo gave a crude residue, which was further purified by column chromatography on silica gel (eluant: methanol/dichloromethane=1:10) to give **5a** (332 mg, 82%) as orange solid. Mp 146–147 °C (dec). IR (KBr): 3273, 3083, 3027, 2921, 1602, 1494, 1451, 1105, 1001, 760, 699 cm^{-1}. ^1H NMR ($CDCl_3$, ppm): δ=7.05–6.99 (m, 6H, ArH), 6.71–6.75 (m, 4H, ArH), 5.58 (s, 2H, CHPh), 5.08 (s, 2H, C_5H_4), 4.53 (s, 2H, C_5H_4), 4.32 (s, 5H, C_5H_5). ^{13}C NMR ($CDCl_3$, ppm): δ=169.9, 134.9, 128.3, 127.9, 127.7, 127.6, 127.3, 72.9, 70.9, 70.7, 69.6, 69.3, 65.7, 64.1, 62.7. Anal. Calcd for $C_{25}H_{22}FeN_2$: C, 73.90; H, 5.46; N, 6.89. Found: C, 73.76; H, 5.63; N, 6.97%.

4.1.4. [1-Benzyl-4,5-dihydro-1*H*-2-imidazolyl]-ferrocene (5b). Red solid. Yield: 65%. Mp 179–180 °C (dec). IR (KBr): 3066, 2997, 2923, 2864, 1592, 1495, 1449, 1416, 1385, 1359, 1289, 1105, 1002, 738, 699 cm^{-1}. ^1H NMR ($CDCl_3$, ppm): δ=7.49–7.43 (m, 3H, ArH), 7.27–7.26 (m, 2H, ArH), 5.18 (s, 2H, CH_2Ph), 4.85 (s, 2H, C_5H_4), 4.64 (s, 2H, C_5H_4), 4.42 (s, 5H, C_5H_5), 4.06 (s, 2H, C=NCH_2), 3.85 (s, 2H, NCH_2). ^{13}C NMR ($CDCl_3$, ppm): δ=169.3, 133.4, 129.6, 128.8, 126.4, 74.6, 73.3, 72.4, 71.2, 69.4, 62.8, 52.3, 51.5, 50.8. Anal. Calcd for $C_{20}H_{20}FeN_2$: C, 69.78; H, 5.86; N, 8.14. Found: C, 69.43; H, 5.59; N, 7.89%.

Table 5. Palladacycle **6b** catalyzed coupling of aryl bromides with arylboronic acid at room temperature:[a] scope of substrates

Entry	Ar–Br	Catalyst	Products	*T* (h)	Yield[b] (%)
1	 **(8a)**	 **(9a)**	 **(10a)**	14	98
2	 **(8b)**	 **(9a)**	 **(10b)**	14	99
3	 **(8d)**	 **(9a)**	 **(10d)**	14	97
4	 **(8e)**	 **(9a)**	 **(10e)**	14	84
5	 **(8h)**	 **(9a)**	 **(10h)**	20	82
6	 **(8i)**	 **(9a)**	 **(10i)**	14	92
7	 **(8j)**	 **(9a)**	 **(10j)**	14	95
8	 **(8k)**	 **(9a)**	 **(10k)**	20	93
9	 **(8l)**	 **(9a)**	 **(10l)**	20	90
10	 **(8m)**	 **(9a)**	 **(10m)**	20	89
11	 **(8d)**	 **(9b)**	 **(10o)**	20	96
12	 **(8d)**	 **(9c)**	 **(10p)**	20	95

[a] Reaction conditions: aryl bromide (0.5 mmol), arylboronic acid (0.75 mmol), K_2CO_3 (1 mmol), methanol/H_2O (v/v=2:1, 3 mL), NBu_4Br (0.5 mmol), 0.5 mol % **6b**, under air.

[b] Isolated yields, average of two runs.

4.1.5. [4,5-Dihydro-1*H*-2-imidazolyl]-ferrocene (5h). Orange solid. Yield: 81%. Mp 161–162 °C (dec). IR (KBr): 3137, 3100, 3025, 2923, 2873, 2740, 1601, 1511, 1447, 1412, 1380, 1267, 1150, 1107, 1001 cm^{-1}. ^1H NMR ($CDCl_3$, ppm): δ=4.71 (s, 2H, C_5H_4), 4.34 (s, 2H, C_5H_4), 4.19 (s, 5H, C_5H_5), 3.69 (s, 4H, C=NCH_2CH_2NH). ^{13}C NMR ($CDCl_3$, ppm): δ=166.1, 72.9, 70.6, 69.9, 69.7, 69.5, 67.9, 50.1. Anal. Calcd for $C_{13}H_{14}FeN_2$: C, 61.45; H, 5.55; N, 11.02. Found: C, 61.63; H, 5.35; N, 11.25%.

4.1.6. [*cis*-1-Acetyl-4,5-diphenyl-4,5-dihydro-1*H*-2-imidazolyl]-ferrocene (5f). Acetyl chloride (1.2 mmol) was added into the solution of **5a** (406 mg, 1 mmol) and 2.5 mmol of Et_3N in dry dichloromethane and kept at 0 °C under nitrogen for 1 h. Then the reaction mixture was stirred for 20 h at room temperature. Evaporation of the solvent in vacuo gave a crude product, which was purified by column chromatography on silica gel (eluant: methanol/dichloromethane=1:15) to give **5f** (389 mg, 87%) as a red solid. Mp 135–136 °C. IR (KBr): 3328, 3067, 3032, 2934, 1682, 1622, 1378, 1260, 1034, 721, 698 cm^{-1}. ^1H NMR ($CDCl_3$, ppm): δ=7.20–7.13 (m, 6H, ArH), 7.09–7.08 (m, 2H, ArH), 7.02–7.01 (m, 2H, ArH), 5.61 (s, 1H, C=NCHPh), 5.50 (s, 1H, NCHPh), 5.11 (s, 1H, C_5H_4), 4.82 (s, 1H, C_5H_4), 4.55 (s, 1H, C_5H_4), 4.43 (s, 1H, C_5H_4), 4.38 (s, 5H, C_5H_5), 2.0 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$, ppm): δ=168.0, 162.0, 137.2, 136.5, 128.0, 127.8, 127.5, 127.1, 126.6, 75.5, 73.6, 72.8, 70.5, 69.7, 69.4, 69.2, 68.5, 25.0. Anal. Calcd for $C_{27}H_{24}FeN_2O$: C, 72.33; H, 5.40; N, 6.25. Found: C, 72.02; H, 5.67; N, 6.16%.

4.1.7. [1-Acetyl-4,5-dihydro-1*H*-2-imidazolyl]-ferrocene (5g). A procedure similar to the preparation of **5f** was followed to synthesize **5g**. Red solid. Yield: 83%. Mp 101–102 °C. IR (KBr): 3094, 2926, 1670, 1628, 1553, 1381, 1290, 1101, 1021 cm^{-1}. ^1H NMR ($CDCl_3$, ppm): δ=4.72 (s, 2H, C_5H_4), 4.39 (s, 2H, C_5H_4), 4.24 (s, 5H, C_5H_5), 3.99–3.97 (m, 2H, C=NCH_2), 3.84–3.82 (m, 2H, NCH_2), 1.92 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$, ppm): δ=168.5, 159.2, 71.3, 71.0, 70.6, 70.1, 68.9, 68.3, 52.8, 48.5, 25.1. Anal. Calcd for $C_{15}H_{16}FeN_2O$: C, 60.84; H, 5.45; N, 9.46. Found: C, 60.69; H, 5.37; N, 9.27%.

4.1.8. Bis-μ-chloro-{2-[*cis*-4,5-diphenyl-4,5-dihydro-1*H*-imidazolyl]-ferrocenyl} dipalladium (6a). A mixture of **5a** (203 mg, 0.5 mmol), $LiPdCl_4$ (0.5 mmol), and $NaOAc\cdot 3H_2O$ (68 mg, 0.5 mmol) in 10 mL of methanol was stirred for 24 h at room temperature. The precipitate obtained was filtered, washed with methanol, and dried in vacuo. The red solid **6a** (185 mg, 68% yield) was obtained. Mp 250–251 °C (dec). IR (KBr): 3380, 3084, 2925, 1540, 1455, 1104, 1003 cm^{-1}. ^1H NMR (DMSO-d_6, ppm): δ=8.78 (s, 2H, NH), 7.20–7.03 (m, 20H, ArH), 5.58 (s, 2H, C=NCHPh), 5.24 (s, 2H, NCHPh), 4.89 (s, 2H, C_5H_3), 4.70 (s, 2H, C_5H_3), 4.41 (s, 10H, C_5H_5), 4.13 (s, 2H, C_5H_3). ^{13}C NMR (DMSO-d_6, ppm): δ=176.9, 139.0, 136.8, 127.4, 127.2, 126.7, 125.9, 99.4, 76.5, 72.5, 69.9, 69.7, 69.3, 67.4, 67.2, 64.6. Anal. Calcd for $C_{50}H_{42}Cl_2Fe_2N_4Pd_2$: C, 54.88; H, 3.87; N, 5.12. Found: C, 54.67; H, 3.96; N, 4.93%.

4.1.9. Bis-μ-chloro-{2-[1-benzyl-4,5-dihydro-1*H*-imidazolyl]-ferrocenyl} dipalladium (6b). Dark red solid. Yield: 57%. Mp 202–203 °C (dec). IR (KBr): 3086, 2933, 2878, 1555, 1476, 1454, 1401, 1357, 1281, 1180, 1156, 1105, 1000 cm^{-1}. ^1H NMR (DMSO-d_6, ppm): δ=7.40–7.30 (m, 10H, ArH), 4.87 (s, 2H, C_5H_3), 4.68–4.53 (m, 4H, NCH_2Ph), 4.61 (s, 2H, C_5H_3), 4.37 (s, 2H, C_5H_3), 4.19 (s, 10H, C_5H_5), 3.71–3.49 (m, 8H, C=NCH_2CH_2N). ^{13}C NMR (DMSO-d_6, ppm): δ=174.9, 128.9, 127.8, 127.5, 99.4, 74.9, 73.0, 70.8, 70.2, 68.1, 66.1, 51.6, 50.3. Anal. Calcd for $C_{40}H_{38}Cl_2Fe_2N_4Pd_2$: C, 49.52; H, 3.95; N, 5.77. Found: C, 49.29; H, 4.19 N, 5.63%.

4.1.10. Bis-μ-chloro-{2-[1-(*n*-pentyl)-4,5-dihydro-1*H*-imidazolyl]-ferrocenyl} dipalladium (6c). Yellow solid. Yield: 77%. Mp 220–221 °C (dec). IR (KBr): 3089, 2955, 2929, 2866, 1558, 1460, 1373, 1279, 1182, 1105, 1051, 1000 cm^{-1}. ^1H NMR ($CDCl_3$, ppm): δ=4.62 (s, 2H, C_5H_3), 4.38 (s, 5H, C_5H_5), 4.37 (s, 5H, C_5H_5), 4.35 (s, 2H, C_5H_3), 4.20 (s, 2H, C_5H_3), 3.73–3.56 (m, 8H, C=NCH_2 and $NCH_2C_4H_9$), 3.32–3.28 (m, 4H, CH_2N), 1.65–1.62 (m, 4H, $CH_2C_3H_7$), 1.45–1.38 (m, 8H, CH_2CH_2), 0.96–0.93 (m, 6H, CH_3). ^{13}C NMR ($CDCl_3$, ppm): δ=175.1, 97.8, 72.5, 70.5, 67.1, 64.0, 51.3, 47.5, 29.0, 28.2, 22.5, 14.1. Anal. Calcd for $C_{36}H_{46}Cl_2Fe_2N_4Pd_2$: C, 46.48; H, 4.98; N, 6.02. Found: C, 46.25; H, 4.71; N, 5.87%.

4.1.11. Bis-μ-chloro-{2-[1-(*n*-octyl)-4,5-dihydro-1*H*-imidazolyl]-ferrocenyl} dipalladium (6d). Yellow solid. Yield: 75%. Mp 186–187 °C (dec). IR (KBr): 3090, 2925, 2853, 1561, 1461, 1372, 1281, 1177, 1104, 1046, 1000 cm^{-1}. ^1H NMR ($CDCl_3$, ppm): δ=4.62 (s, 2H, C_5H_3), 4.39 (s, 5H, C_5H_5), 4.35 (s, 5H, C_5H_5), 4.30 (s, 2H, C_5H_3), 4.20 (s, 2H, C_5H_3), 3.68–3.57 (m, 8H, C=NCH_2 and $NCH_2C_7H_{15}$), 3.31–3.28 (m, 4H, CH_2N), 1.64–1.63 (m, 4H, $CH_2C_6H_{13}$), 1.36–1.25 (m, 20H, C_5H_{10}), 0.91–0.87 (m, 6H, CH_3). ^{13}C NMR ($CDCl_3$, ppm): δ=175.6, 94.7, 75.2, 72.9, 72.6, 70.9, 67.5, 64.4, 51.8, 50.2, 47.9, 32.2, 29.8, 29.6, 28.9, 23.0, 14.5. Anal. Calcd for $C_{42}H_{58}Cl_2Fe_2N_4Pd_2$: C, 49.73; H, 5.76; N, 5.52. Found: C, 49.58; H, 5.61; N, 5.74%.

4.1.12. Bis-μ-chloro-{2-[1-(*n*-tetradecyl)-4,5-dihydro-1*H*-imidazolyl]-ferrocenyl} dipalladium (6e). Yellow solid. Yield: 64%. Mp 140–141 °C. IR (KBr): 3091, 2923, 2852, 1560, 1464, 1372, 1282, 1104, 1051, 1000 cm^{-1}. ^1H NMR ($CDCl_3$, ppm): δ=4.62 (s, 2H, C_5H_3), 4.38 (s, 5H, C_5H_5), 4.35 (s, 5H, C_5H_5), 4.30 (s, 2H, C_5H_3), 4.20 (s, 2H, C_5H_3), 3.71–3.58 (m, 8H, C=NCH_2 and $NCH_2C_{13}H_{27}$), 3.31–3.28 (m, 4H, CH_2N), 1.66–1.63 (m, 4H, $CH_2C_{12}H_{25}$), 1.36–1.26 (m, 44H, $C_{11}H_{22}$), 0.89–0.82 (m, 6H, CH_3). ^{13}C NMR ($CDCl_3$, ppm): δ=175.1, 94.2, 74.9, 72.4, 70.5, 67.0, 64.0, 51.3, 50.5, 49.8, 47.5, 31.9, 29.7, 29.6, 29.4, 29.3, 28.4, 26.9, 22.6, 14.1. Anal. Calcd for $C_{54}H_{82}Cl_2Fe_2N_4Pd_2$: C, 54.84; H, 6.99; N, 4.74. Found: C, 54.68; H, 6.84; N, 4.52%.

4.1.13. Bis-μ-chloro-{2-[*cis*-1-acetyl-4,5-diphenyl-4,5-dihydro-1*H*-imidazolyl]-ferrocenyl} dipalladium (6f). Red solid. Yield: 71%. Mp 273–275 °C (dec). IR (KBr): 3067, 3032, 2925, 1715, 1628, 1551, 1376, 1003 cm^{-1}. ^1H NMR (DMSO-d_6, ppm): δ=7.03–6.92 (m, 12H, ArH), 6.82–6.73 (m, 8H, ArH), 6.28 (s, 2H, C=NCHPh), 5.65 (s, 2H, NCHPh), 5.29 (s, 2H, C_5H_3), 5.22 (s, 2H, C_5H_3), 4.54 (s, 2H, C_5H_3), 4.39 (s, 10H, C_5H_5), 1.92 (s, 6H, CH_3). ^{13}C NMR (DMSO-d_6, ppm): δ=173.7, 168.9, 137.8, 136.8, 128.2, 127.6, 127.2, 126.5, 104.2, 75.2, 74.8, 72.1, 70.5, 70.3, 69.4, 68.7, 24.6. Anal. Calcd for $C_{54}H_{46}Cl_2Fe_2N_4O_2Pd_2$: C, 55.04; H, 3.93; N, 4.75. Found: C, 55.23; H, 3.71; N, 4.67%.

4.1.14. Bis-μ-chloro-{2-[1-acetyl-4,5-dihydro-1*H*-imidazolyl]-ferrocenyl} dipalladium (6g). Red solid. Yield: 67%. Mp 233–235 °C (dec). IR (KBr): 3090, 2943, 2887, 1708, 1563, 1470, 1391, 1359, 1306, 1185, 1104, 1073, 1030, 1000 cm^{-1}. ^1H NMR (DMSO-d_6, ppm): δ=5.20

(s, 2H, C_5H_3), 5.06 (s, 2H, C_5H_3), 4.40–4.26 (m, 6H, C=NCH_2 and C_5H_3), 4.26 (s, 10H, C_5H_5), 3.71–3.73 (m, 4H, CH_2N), 1.81 (s, 6H, CH_3). ^{13}C NMR (DMSO-d_6, ppm): δ=171.7, 168.0, 101.8, 75.7, 74.3, 71.4, 70.3, 68.9, 50.9, 49.0, 24.5. Anal. Calcd for $C_{30}H_{30}Cl_2Fe_2N_4O_2Pd_2$: C, 41.23; H, 3.46; N, 6.41. Found: C, 41.47; H, 3.68; N, 6.29%.

4.1.15. Triphenylphosphine-{2-[*cis*-4,5-diphenyl-1*H*-imidazolyl]-ferrocenyl-*C*,*N*} palladium(II) chloride (7a). The complex **6a** (150 mg, 0.137 mmol) was treated with PPh_3 (71 mg, 0.27 mmol) in methanol (15 mL) at room temperature for 1 h and the mixture was concentrated in vacuo. The residue was purified by column chromatography on silica gel (eluant: dichloromethane) to give the monomer orange-yellow solid **7a** (192 mg, 88%). Mp 208–209 °C (dec). IR (KBr): 3254, 3056, 2923, 1581, 1438, 1435, 1285, 1097, 1029, 1001 cm^{-1}. ^1H NMR ($CDCl_3$, ppm): δ=7.71–7.67 (m, 9H, ArH), 7.39–7.33 (m, 12H, ArH), 7.08–7.06 (m, 4H, ArH), 5.60 (s, 1H, C=NCHPh), 5.51 (s, 1H, NCHPh), 5.39 (s, 1H, C_5H_3), 4.48 (s, 1H, C_5H_3), 4.12 (s, 5H, C_5H_5), 3.25 (s, 1H, C_5H_3). ^{13}C NMR ($CDCl_3$, ppm): δ=176.8, 138.6, 137.7, 136.8, 136.6, 135.2, 135.0, 134.9, 134.8, 128.1, 127.9, 127.8, 127.4, 127.3, 127.2, 126.4, 97.4, 76.3, 75.7, 70.6, 70.2, 69.2, 68.5, 63.6. Anal. Calcd for $C_{43}H_{36}ClFeN_2PPd$: C, 63.80; H, 4.48; N, 3.46. Found: C, 63.53; H, 4.63; N, 3.17%.

4.2. General procedure for the coupling reactions

4.2.1. General procedure A. A mixture of aryl bromide (1 mmol), palladacycle dimer (0.1 mol %), arylboronic acids (1.5 mmol), $K_3PO_4\cdot 7H_2O$ (2 mmol), and toluene (3 mL) was stirred and refluxed under air. Then, the reaction mixture was cooled and evaporated under reduced pressure to dryness. CH_2Cl_2 (15 mL) and water (5 mL) were added. The organic layer was separated and the aqueous layer was extracted with dichloromethane, then the combined organic phases were washed with water, dried over $MgSO_4$, filtered, and the solvent was evaporated under reduced pressure to dryness. The residue was purified by flash column chromatography on silica gel.

4.2.2. General procedure B. A mixture of aryl bromide (0.5 mmol), catalyst **6b** (0.5 mol %), arylboronic acids (0.75 mmol), K_2CO_3 (1 mmol), TBAB (0.5 mmol), and methanol/H_2O (2 mL/1 mL) was stirred at room temperature under air. The mixture was diluted with ethyl ether and water. The aqueous layer was extracted with ethyl ether, then the combined organic phase was washed with water, dried over $MgSO_4$, filtered, and the solvent was evaporated under reduced pressure to dryness. The residue was purified by flash column chromatography on silica gel.

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Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2007.04.022.

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