



Note

Bis(imino)pyridine palladium(II) complexes: Synthesis, structure and catalytic activity

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ABSTRACT

Bis(imino)pyridine palladium(II) complexes **3–6** were synthesized by two different methods. The structure of complexes **3** and **4** has been confirmed by X-ray structure analysis. The catalytic studies show that bis(imino)pyridine palladium(II) complexes are highly efficient catalysts in the Suzuki–Miyaura reaction and the complex **4** was used to catalyze the synthesis of fluorinated liquid crystalline compounds via Suzuki coupling reaction.

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1. Introduction

2,6-Diiminopyridines are versatile ligands that have found wide applications in coordination chemistry and catalysis. Despite being known for more than 30 years, these 6-electron donors have received considerable attention over the past decade, mainly due to the discovery of the high catalytic activity of their Fe and Co complexes in olefin polymerization catalysis [1–4]. Moreover, these ligands have found use in many other catalytic processes, such as olefin epoxidation [5], hydrogenation and hydrosilylation [6], and aerobic oxidation reactions [7–9]. To the best of our knowledge, few investigations have been carried out on the syntheses and catalytic properties of bis(imino)pyridine palladium(II) complexes [10]. Herein we report their syntheses, crystal structures, and catalytic activity and application.

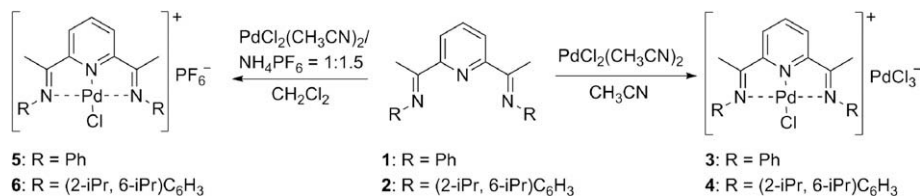
2. Result and discussion

2.1. Synthesis of complexes

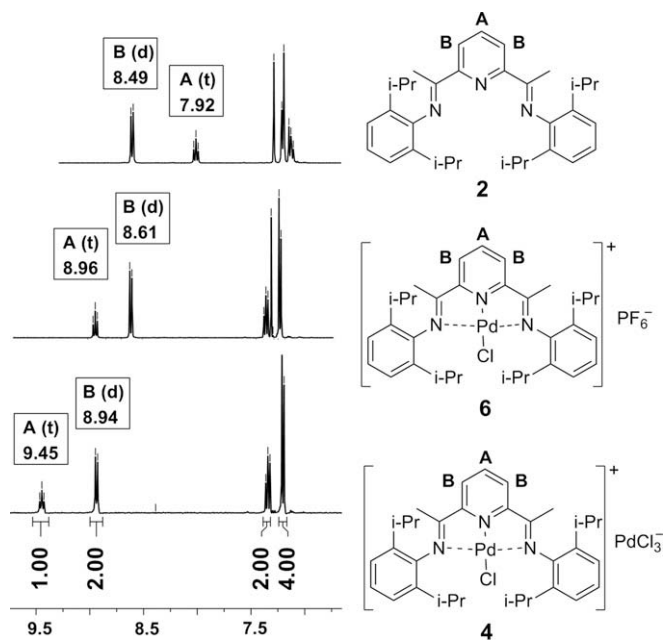
Bis(imino)pyridine palladium(II) complexes **3** and **4** were prepared by reaction of $\text{PdCl}_2(\text{CH}_3\text{CN})_2$ with 1.0 equiv. of ligands (**1** and **2**) in acetonitrile at room temperature for 2 h (Scheme 1). Their structures contained one $[\text{PdLCl}]^+$ and one $[\text{PdCl}_3]^-$ were confirmed by X-ray crystallography. Noteworthy is that the complexes **5** and **6** could be obtained by reaction of the mixture of $\text{PdCl}_2(\text{CH}_3\text{CN})_2$ and 1.5 equiv. of NH_4PF_6 with 1.0 equiv. of ligands (**1** and **2**) in

CH_2Cl_2 at room temperature for 24 h (Scheme 1) and the anion is one PF_6^- , not one $[\text{PdCl}_3]^-$. Which is identified by elemental analysis, ^1H NMR and IR spectroscopies. Complexes **3** and **4** are poorly soluble in acetonitrile and chloroform, slightly soluble in dichloromethane and ethanol and soluble in dimethylsulfoxide. Compared with them, the complexes **5** and **6** are soluble in above any solvent. The proposed coordination pattern is different from those complexes containing 2, 6-bis(imino)pyridine as bidentate chelate ligands have been reported, [11–14] Which was testified by their ^1H NMR spectra (Fig. 1). For example, complexes **4** and **6** exhibited downfield shifts of the proton signals relative to those for ligand **2**, change of the pyridine proton chemical shift values is obvious, For complexes **4**, **6** and ligand **2**, the para proton **A** of pyridine appear as a triplet at δ 9.65, 8.96 and 7.92 ppm, respectively, and the meta protons **B** of pyridine protons appear as a doublet at δ 9.11, 8.61 and 8.48 ppm. IR spectra of complex **4** and **6** show $\nu(\text{C}=\text{N})$ around 1624 and 1635 cm^{-1} , ligand **2** show $\nu(\text{C}=\text{N})$ around 1644 cm^{-1} . Which indicate the three nitrogen atoms of bis(imino)pyridine ligand coordinate with Pd(II). To confirm the solid-state structure of the complexes **3** and **4**, X-ray crystallography of **3** and **4** was studied. Suitable crystal for X-ray analysis was obtained by slow diffusion of hexane into saturated dichloromethane solution of the complex. The crystal structure plot is shown in Fig. 2. Crystal data and other details of the structure analysis are presented in Table 1. Important bond lengths and angles are summarized in Table 2. The coordination geometry of **3** and **4** is a distorted square planar, The Pd–N_{py} bond lengths (Pd(1)–N(1): 1.925(3) Å) of **4** are slightly longer than that of **3** (1.921(4) Å), but the Pd–N_{imine} and Pd–Cl bond lengths (Pd(1)–N(3): 2.043(3) Å, Pd(1)–N(2): 2.050(3) Å, Pd(1)–Cl(1): 2.2782(10) Å) of **4** are slightly shorter

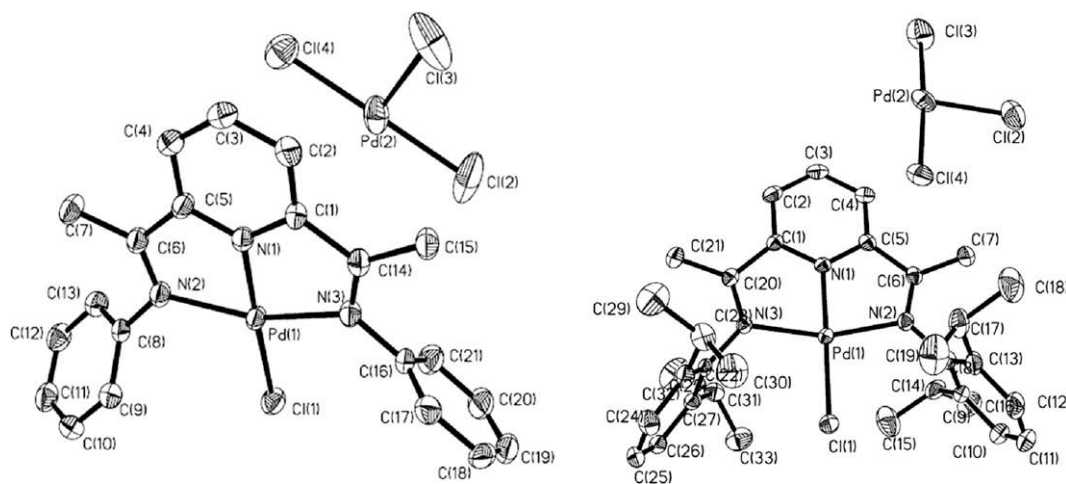
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Scheme 1. Synthesis of bis(imino)pyridine palladium(II) complexes.

Fig. 1. 1H NMR spectra (aromatic region) of ligand **2** (in $CDCl_3$), complexes **4** (in CD_2Cl_2) and **6** (in $CDCl_3$).

than that of **3** (Pd(1)–N(3): 2.059(4) Å, Pd(1)–N(2): 2.065(4) Å, Pd(1)–Cl(1): 2.2817(13) Å). The average angles of N(1)–Pd(1)–N(3) (79.36(16)° and 80.15(12)°) and N(1)–Pd(1)–N(2) (79.72(15)° and 79.76(12)°) in **3** and **4** are nearly 80° and the angles of N(3)–Pd(1)–Cl(1) (100.27(12)° and 99.15(9)°) and N(2)–Pd(1)–Cl(1) (100.70(12)° and 100.94(9)°) in **3** and **4** are 100° approximately.

Fig. 2. Structure of complexes **3** and **4** at 30% probability level. Hydrogen atoms are omitted for clarity.

2.2. Catalytic activity

The catalytic activity of complexes **3–6** in the Suzuki–Miyaura coupling reaction of 4-bromoanisole with phenylboronic acid was investigated in water at 80 °C (Scheme 2) and representative results are summarized in Table 3, it was found the employ of complexes **3** and **4** as a precatalyst provided good yields of biaryls (93% and 94%, respectively, Table 3, entries 1, 2), the use of complexes **5** and **6** also gave good yield (90% and 92%, respectively, Table 3, entries 3, 4). The $[PdCl_3]^-$ had no effect obviously for the catalytic activity of these complexes.

The cross-coupling reactions of various aryl bromides and arylboronic acids have been investigated. The electron-poor aryl bromide, such as 4-bromoacetophenone, reacted with phenylboronic acids to give high yield (97%, Table 4, entries 2, 3). The electron-rich aryl bromide, such as 4-bromoanisole, also gave good yield at the same condition (90%, Table 4, entry 1). When the 3-bromopyridine was treated with phenylboronic acid, 4-methylphenylboronic acid, and 4-fluorophenylboronic acid, respectively, the moderate yields were obtained (67–90%, Table 4, entries 4, 6, 7), but the reaction of 2-bromopyridine with phenylboronic acid resulted in a low yield of the product, which may be due to the coordination of the pyridine nitrogen with palladium metal (Table 4, entry 5). The cross-coupling reactions of various aryl chlorides and arylboronic acids have been also investigated in DMA at 100 °C. The coupling reaction of aryl chlorides bearing an electron-withdrawing group, such as 4-CN, 4-COCH₃, and 4-NO₂, with phenylboronic acid gave biaryls in good yields ranging from 82% to 96% for 10 h (Table 4, entries 8–11). The electron-rich aryl chlorides reaction with aryl boronic acid, such as 4-Me, also gave moderate yields at the same condition (71%, Table 4, entry 12).

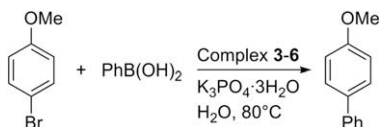
In addition, the liquid crystalline materials containing monofluoro-, difluoro- or trifluoro-substituted phenyls [15–20] are the most prominent for application in thin-film transistor liquid crys-

Table 1
Crystal data and structure refinement for complexes **3** and **4**.

	Complex 3	Complex 4
Empirical formula	C ₄ H _{3.62} Cl _{0.76} N _{0.57} Pd _{0.38}	C ₆₆ H ₈₆ Cl ₈ N ₆ Pd ₄
Formula weight	127.24	1672.61
Temperature (K)	27 273(2)	273(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> (Å)	10.9479(4)	8.8274(9)
<i>b</i> (Å)	16.3875(5)	26.711(3)
<i>c</i> (Å)	16.3875(5)	15.2801(16)
α (°)	90.00	90.00
β (°)	97.223	103.847
γ (°)	90.00	90.00
<i>V</i> (Å ³)	2283.17(13)	3498.10(6)
<i>Z</i>	4	2
<i>D_c</i> (mg m ⁻³)	1.943	1.588
μ (mm ⁻¹)	1.101	1.360
Reflections collected/unique	13 283/4009 [0.0672]	15 632/7952
R_{int}		[0.0327]
<i>F</i> (000)	1304	1688
Crystal size (mm ³)	0.60 × 0.41 × 0.25	0.39 × 0.38 × 0.17
θ range for data collection (°)	2.25–25.00	2.44–25.87
Data/restraints/parameters	4009/0/271	7952/0/379
<i>R</i> ₁ [<i>I</i> > 2 σ (<i>I</i>)]	0.0578	0.0679
<i>wR</i> ₂ [<i>I</i> > 2 σ (<i>I</i>)]	0.1904	0.1026
Goodness-of-fit on <i>F</i> ²	1.101	1.018

Table 2
Selected bond lengths (Å) and angles (°) for complexes **3** and **4**.

	Complex 3	Complex 4
Bond lengths		
Pd(1)–N(1)	1.921(4)	1.925(3)
Pd(1)–N(3)	2.059(4)	2.043(3)
Pd(1)–N(2)	2.065(4)	2.050(3)
Pd(1)–Cl(1)	2.2817(13)	2.2782(10)
Bond angles		
N(1)–Pd(1)–N(3)	79.36(16)	80.15(12)
N(1)–Pd(1)–N(2)	79.72(15)	79.76(12)
N(3)–Pd(1)–Cl(1)	100.27(12)	99.15(9)
N(2)–Pd(1)–Cl(1)	100.70(12)	100.94(9)

**Scheme 2.****Table 3**
Effect of complexes **3–6** on Suzuki cross-coupling reaction.^a

Entry	Complexes	Yield (%) ^b
1	3	93
2	4	94
3	5	90
4	6	92

^a Reaction conditions: 4-bromoanisole 0.50 mmol, phenylboronic acid 0.75 mmol, K₃PO₄ · 3H₂O 1.2 mmol, **3–6** 0.50 mmol%, H₂O 2.0 mL, 80 °C, reaction time 3 h.

^b Isolated yields.

tal displays (TFT-LCDS). The long, lath-like molecular structure of most fluorinated liquid crystalline compounds demanded by thin-film transistor liquid crystal displays makes Suzuki cross-cou-

pling reactions very important in synthesis. We can use this new protocol to synthesize liquid crystal compounds, but consider solubility of arylbromides, we select ethanol as solvent. The products **8m–8q** can be synthesized by this reaction to give excellent yield (≥92%) for 3 h (Table 5, entries 1–4). However, **8q** is obtained with only 75% yield because the aryl bromide is not soluble in ethanol at 80 °C. Thus, this method provides an efficient way to prepare biphenyl derivatives used as liquid crystal compounds.

3. Conclusion

In conclusion, we have synthesized air- and moisture-stable bis(imino)pyridine palladium(II) complexes **3–6** and have investigated their catalytic activity in the Suzuki cross-coupling reaction. The complex **4** are found to be excellent catalysts for Suzuki cross-coupling reactions of arylboronic acids and aryl bromides or chlorides and the synthesis of various fluorinated biphenyl derivatives was readily achieved via complex **4** catalyzed Suzuki cross-coupling reaction.

4. Experimental

4.1. General

Infrared spectra were obtained as KBr pellets on a Perkin-Elmer FT-IR 430 spectrometer. ¹H NMR spectral data were recorded on a Bruker DPX-400 spectrometers using TMS as internal standard and CDCl₃, CD₂Cl₂ as solvent. EI-Mass spectra were measured on a LC/Q-TOF MS (Micromass, England). Acetonitrile was dried over CaH₂, distilled and stored under nitrogen. Methanol were dried and distilled from Mg. All other reagents were of analytical grade quality purchased commercially and used as received unless noted otherwise.

4.2. Synthesis of ligands **1** and **2**

Bis(imino)pyridine ligands **1** and **2** were synthesized according to literature methods [21].

1: Yellow solid, yield 85%. ¹H NMR (400 MHz, CDCl₃): δ 8.36 (d, *J* = 7.60 Hz, 2H, Py-Hm), 7.89 (t, *J* = 7.60 Hz, 1H, Py-Hp), 7.41–6.84 (m, 10H, Ar-H), 2.42 (s, 6H, N=CMe). IR (KBr, cm⁻¹): 1637 (C=N).

2: Yellow solid, yield 84%. ¹H NMR (400 MHz, CDCl₃): δ 8.49 (d, *J* = 7.60 Hz, 2H, Py-Ho), 7.92 (t, *J* = 7.60 Hz, 1H, Py-Hp), 7.19–7.13 (m, 6H, Ar-H), 2.78 (t, *J* = 8.40 Hz, 4H, CH), 2.74 (s, 6H, N=CMe), 1.17 (d, *J* = 8.40 Hz, 24H, ⁱPr-H). IR (KBr, cm⁻¹): 1644 (C=N).

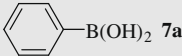
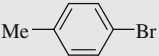
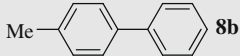
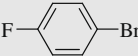
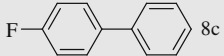
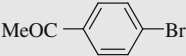
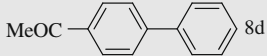
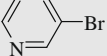
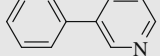
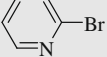
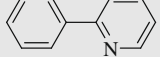
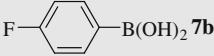
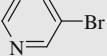
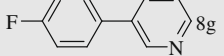
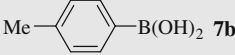
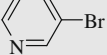
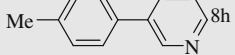
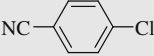
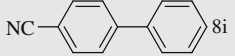
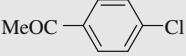
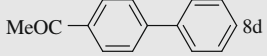
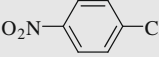
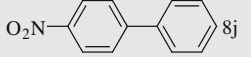
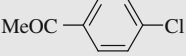
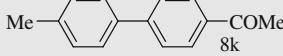
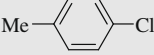
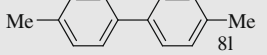
4.3. Synthesis of complexes **3** and **4**

0.20 mmol of PdCl₂(CH₃CN)₂ and 0.20 mmol of ligand were dissolved in 10 mL of acetonitrile. The solution was stirred at room temperature for 2 h. Ether (100 mL) was added to the reaction mixture, and this mixture was placed for an appropriate period of time, after which it was filtered and the solid was obtained.

3: Yellow solid, yield 84%. Elemental Anal. Calc. for C₂₁H₁₉ClN₃Pd · PdCl₃ · 1.5CH₃CN: C, 39.51; H, 3.25; N, 8.64. Found: C, 41.00; H, 3.44; N, 8.52%. ¹H NMR (400 MHz, CDCl₃): δ 8.69 (t, *J* = 8.0 Hz, 1H, Py-Hp), 8.50 (d, *J* = 8.0 Hz, 2H, Py-Hm), 7.48–7.19 (m, 10H, Ar-H), 2.46 (s, 6H, N=CMe). IR (KBr, cm⁻¹): 1636 (C=N); HRMS (EI), *m/z*: [M–PdCl₃]⁺, calculated for: 454.0302; found, 454.0222.

4: Yellow solid, yield 80%. Elemental Anal. Calc. for C₃₃H₄₃Cl₂N₃Pd · PdCl₃: C, 47.39; H, 5.18; N, 5.02. Found: C, 47.60; H, 5.50; N, 5.05%. ¹H NMR (400 MHz, CD₂Cl₂): δ 8.94 (t, *J* = 8.0 Hz, 1H, Py-Hp), 9.45 (d, *J* = 8.0 Hz, 2H, Py-Ho), 7.36–7.19 (m, 6H, Ar-H), 3.18 (t, *J* = 6.8 Hz, 4H), 2.51 (s, 6H, N=CMe), 1.31

Table 4
Suzuki cross-coupling reaction catalyzed by complex **4**.^{a,b}

Entry	ArB(OH) ₂	Ar-X	Product	Time (h)	Yield (%) ^c
1	 7a		 8b	3	90
2	7a		 8c	3	90
3	7a		 8d	3	97
4	7a		 8e	5	90
5	7a		 8f	5	trace
6	 7b		 8g	5	81
7	 7b		 8h	5	67
8	7a		 8i	10	90
9	7a		 8d	10	84
10	7a		 8j	10	96
11	7b		 8k	10	82
12	7b		 8l	10	71

^a Reaction conditions: aryl bromide 0.50 mmol, arylboronic acid 0.75 mmol, K₃PO₄ · 3H₂O 1.20 mmol, complex **4** (0.50 mmol%), H₂O 2.0 mL, 80 °C.^b Reaction conditions: aryl chloride 0.25 mmol, arylboronic acid 0.40 mmol, K₃PO₄ · 3H₂O 0.75 mmol, complex **4** (0.25 mmol%), DMA 2.0 mL, 100 °C.^c Isolated yields.

(d, *J* = 6.8 Hz, 12H, ⁱPr-H₁), 1.19 (d, *J* = 6.8 Hz, 12H, ⁱPr-H₂). IR (KBr, cm⁻¹): 1624 (C=N). HRMS (EI), *m/z*: [M–PdCl₃]⁺, calculated for: 622.2175; found, 622.2180.

4.4. Synthesis of complexes **5** and **6**

0.20 mmol of PdCl₂(CH₃CN)₂ and 0.30 mmol of NH₄PF₆ were dissolved in 10 mL of CH₂Cl₂. The solution was stirred at room temperature for 12 h. The ligand was added to the reaction mixture, and continue to be stirred for 24 h, after which it was filtered, ether (100 mL) was added to the filtrate and this mixture was placed for an appropriate period of time, after which it was filtered and the solid was obtained.

5: Yellow solid, yield 70%. Elemental Anal. Calc. for C₂₁H₁₉ClF₆N₃PPd: C, 42.02; H, 3.19; N, 7.00. Found: C, 41.35; H, 3.32; N, 6.96%. ¹H NMR (400 MHz, CDCl₃): δ 8.55 (t, *J* = 8.0 Hz, 1H, Py-Hp), 8.18 (d, *J* = 8.0 Hz, 2H, Py-Hm), 7.46–7.13 (m, 10H, Ar-H), 2.50 (s, 6H, N=CMe). IR (KBr, cm⁻¹): 1632 (C=N).

6: Yellow solid, yield 72%. Elemental Anal. Calc. for C₃₃H₄₃ClF₆N₃PPd: C, 51.57; H, 5.64; N, 5.47. Found: C, 50.46; H, 5.46; N, 5.54%. ¹H NMR (400 MHz, CDCl₃): δ 8.96 (t, *J* = 8.40 Hz, 1H, Py-Hp), 8.61 (d, *J* = 8.40 Hz, 2H, Py-Ho), 7.31 (t, *J* = 8.00 Hz, 2H, Ar-H), 7.18 (d, *J* = 8.00 Hz, 2H, Ar-H), 3.07 (m, 4H), 2.46 (s, 6H, N=CMe), 1.33 (d, *J* = 6.40 Hz, 12H, ⁱPr-H₁), 1.20 (d, *J* = 6.40 Hz, 12H, ⁱPr-H₂). IR (KBr, cm⁻¹): 1635 (C=N).

4.5. X-ray crystallography

Crystal data and other details of the structure analysis are presented in Table 1. Suitable crystal for X-ray diffraction was mounted on a glass fiber. Data collection was performed on a Bruker Smart APEX CCD diffractometer using graphite monochromated Mo K α radiation (λ = 0.71073 Å) at 273 K. The diffraction frames were integrated using the SAINT package. The structure was solved by direct methods using the program SHELXS97. Structure refinement by the full-matrix least-squares on *F*² was carried out with the program SHELXL97. All non-hydrogen atoms of the complex were assigned anisotropic displacement parameters. The hydrogen atoms were constrained to idealized geometries and assigned isotropic displacement parameters equal to 1.2 times the Uiso values of their respective parent atoms.

4.6. General procedure for Suzuki cross-coupling reaction

A 5 mL flask was charged with **3** or **4** (0.25 mmol%), K₃PO₄ · 3H₂O (1.20 mmol), and arylboronic acid (0.75 mmol), toluene, water or ethanol (2 mL) and aryl bromide (0.5 mmol) were added. The reaction was stirred at 80 °C for the certain time. After the reaction was allowed to cool to room temperature, the resulting mixture was extracted with ether (5 × 2 mL). The combined ether extracts were dried (MgSO₄) and the solvent was removed

Table 5
Suzuki cross-coupling reaction catalyzed by complex **4** for synthesis of TFT-LCDS.^a

Entry	ArBr Ar'B(OH) ₂	Product	Yield (%) ^b
1			95
2			93
3			94
4			92
5			75

^a Reaction conditions: aryl bromide 0.50 mmol, arylboronic acid 0.75 mmol, K₃PO₄ · 3H₂O 1.20 mmol, **4** (0.50 mmol%), EtOH 2.0 mL, 80 °C, reaction time 3 h.

^b Isolated yields.

under reduced pressure. The crude material was flash chromatographed on a short silica gel column.

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Appendix A. Supplementary material

CCDC 686605 and 635773 contain the supplementary crystallographic data for **3** and **4**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2009.03.021.

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