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# A novel tridentate NHC–Pd(II) complex and its application in the Suzuki and Heck-type cross-coupling reactions

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**Abstract**—A novel tridentate NHC–Pd(II) complex derived from binaphthyl-2,2'-diamine (BINAM) has been synthesized and its structure has been characterized by single crystal X-ray diffraction. This NHC–Pd(II) complex was fairly effective in Suzuki and Heck-type cross-coupling reactions to give the products in good to excellent yields in most cases.

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## 1. Introduction

Since the isolation and characterization of the stable free *N*-heterocyclic carbene (NHC) by Arduengo and co-workers in 1991,<sup>1</sup> much attention had been paid toward their properties and applications. During the past decade, numerous publications related to their metal complexes and catalytic reactions have been reported in a broad range of reactions.<sup>2</sup> Significantly, a number of Pd–NHC complexes have emerged as effective catalysts for a variety of coupling reactions.<sup>3</sup>

Previously, we reported the synthesis of a novel cis-chelated Pd(II)–NHC complex derived from binaphthyl-2,2'-diamine (BINAM) and a new dimeric bidentate NHC–Pd(II) complex from *trans*-cyclohexane-1,2-diamine and their applications in the Suzuki reaction and Heck reaction.<sup>4</sup> In this paper, we wish to report the synthesis of a novel tridentate NHC–Pd(II) complex derived from BINAM and its application in the Suzuki and Heck-type cross-coupling reactions.

## 2. Results and discussion

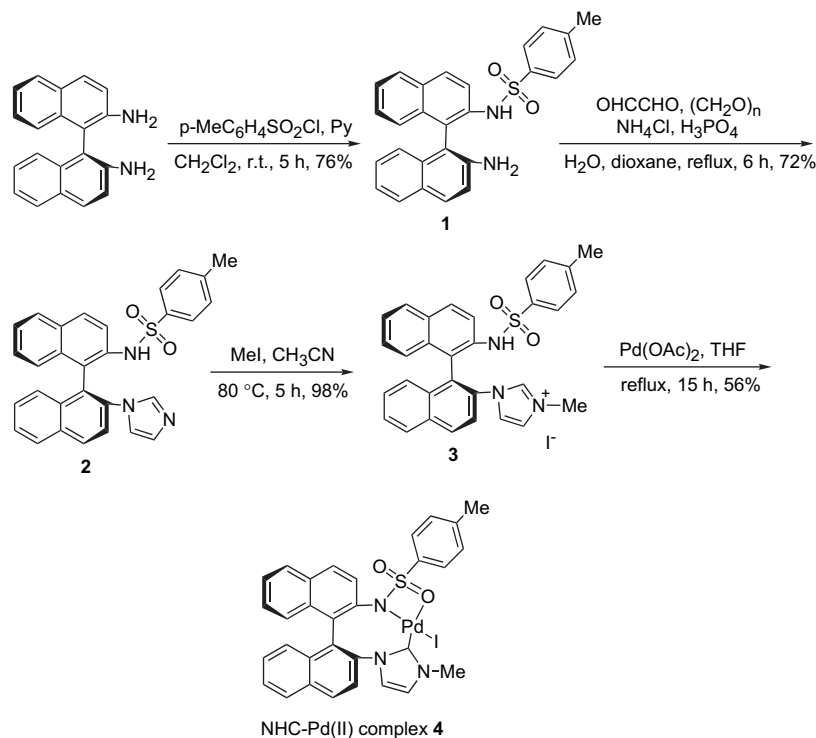
The synthesis of tridentate NHC–Pd(II) complex **4** is shown in Scheme 1. Using BINAM (1.0 equiv) as starting materials to react with *p*-toluenesulfonyl chloride (1.1 equiv) in dichloromethane, 2-(tosylamino)-2'-amino-1,1'-binaphthyl **1** was obtained in 76% yield at room temperature in the

presence of pyridine as the base for 5 h. The reaction of **1** with each 2.5 equiv of glyoxal, paraformaldehyde, and ammonium chloride under these conditions reported by Crabtree<sup>5</sup> afforded 2-(tosylamino)-2'-(imidazol-1-yl)-1,1'-binaphthyl **2** in 72% yield. The corresponding imidazolium iodide **3** was obtained in 98% yield by stirring compound **2** with excess of iodomethane in acetonitrile at 80 °C for 5 h. Reaction of the NHC precursor **3** with Pd(OAc)<sub>2</sub> under reflux in THF for 6 h afforded the desired NHC–Pd(II) complex **4** in 56% yield. The metal complex was confirmed by elemental analysis, <sup>1</sup>H NMR spectroscopy and EIMS. Its crystal structure was also determined by X-ray diffraction (Fig. 1).<sup>6</sup> The complex is air and moisture stable in the solid state and it is also stable for several days in solution.

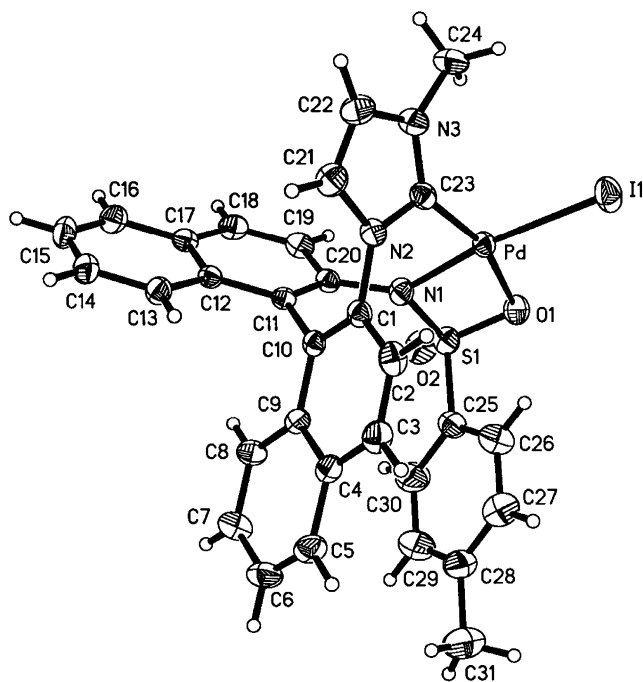
Structural features of NHC–Pd(II) complex **4**: The single crystals of this complex suitable for X-ray crystal structure analysis were grown from a saturated solution of PE/EtOAc=3/1. The structure of the compound, C<sub>31</sub>H<sub>24</sub>IN<sub>3</sub>O<sub>2</sub> PdS, is refined in space group *P*-1. The bite angle of C–Pd–N is slightly larger than 90° (95.2°). The bond lengths of Pd–C and Pd–N are 1.939(4) and 2.017(3) Å, respectively. The crystal structure shows that the O atom of sulfonyl group participates in chelating with Pd center. This is a tridentate NHC–Pd(II) complex. The bond distance of Pd–O is 2.219(3) Å. The angle of N–Pd–I is slightly less than 180° (170.6°), indicating that these three atoms extending as far as possible, which are almost on the same line. While the coordinated atoms of C (carbene), N, O, and I with Pd are effectively planar, with the maximum deviation from the best-squares plane of 0.0200 Å for atom Pd, and the mean deviation is 0.0080 Å.

**Keywords:** Tridentate NHC–Pd(II) complex; Binaphthyl-2,2'-diamine; Cross-coupling reactions; Suzuki–Miyaura cross-coupling reaction; Heck reaction.

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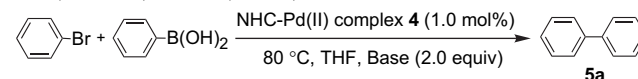
**Scheme 1.** Synthesis of the NHC-Pd(II) complex 4.



**Figure 1.** ORTEP drawing of NHC-Pd(II) complex 4.

The application of NHC-Pd(II) complex 4 as a catalyst for the Suzuki–Miyaura cross-coupling reaction was examined where both base and solvent effects were carefully examined in the reaction of phenylboronic acid with bromobenzene under argon atmosphere. The results are summarized in Tables 1 and 2, respectively. We found that using  $\text{Cs}_2\text{CO}_3$  as the base in tetrahydrofuran (THF) at 80 °C gave the coupled product biphenyl 5a in 98% yield after 12 h (Table 1,

**Table 1.** Screening for bases in the NHC-Pd(II) complex 4 catalyzed Suzuki cross-coupling reaction of bromobenzene (1.0 mmol) with phenylboronic acid (1.2 mmol) in THF (2.0 mL)



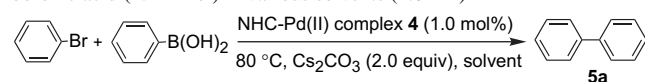
Entry	Base	Time (h)	Yield (%) <sup>a</sup>	
			5a	
1	$\text{Na}_2\text{CO}_3$	12	6	
2	$\text{K}_2\text{CO}_3$	12	24	
3	$\text{Cs}_2\text{CO}_3$	12	98	
4	$\text{KF} \cdot 2\text{H}_2\text{O}$	12	N.R. <sup>b</sup>	
5	$\text{K}_3\text{PO}_4 \cdot 3\text{H}_2\text{O}$	12	53	
6	$\text{KO}^t\text{Bu}$	12	13	
7	$\text{NaOAc}$	12	N.R. <sup>b</sup>	
8	$\text{DMAP}$	12	N.R. <sup>b</sup>	

<sup>a</sup> Isolated yields.

<sup>b</sup> No reaction occurred.

entry 3). The other inorganic bases such as  $\text{Na}_2\text{CO}_3$ ,  $\text{K}_2\text{CO}_3$ ,  $\text{K}_3\text{PO}_4 \cdot 3\text{H}_2\text{O}$ , and  $\text{KO}^t\text{Bu}$  were not as effective as  $\text{Cs}_2\text{CO}_3$ , only afforded moderate to low yields of coupling products (Table 1, entries 1, 2, 5, and 6). When  $\text{KF} \cdot 2\text{H}_2\text{O}$ ,  $\text{NaOAc}$ , and  $\text{DMAP}$  were employed as the bases, no reaction occurred (Table 1, entries 4, 7, and 8). Then, we examined a variety of solvents at 80 °C with  $\text{Cs}_2\text{CO}_3$  as the base. We found that using THF as the solvent gave the highest yield in 98% (Table 2, entries 1–8). Thus,  $\text{Cs}_2\text{CO}_3$  was the base of choice and THF was the preferred solvent for this reaction.

Using these optimized reaction conditions, the Suzuki–Miyaura reaction of a variety of aryl halides, including aryl bromides and phenyl iodide, with phenylboronic acid

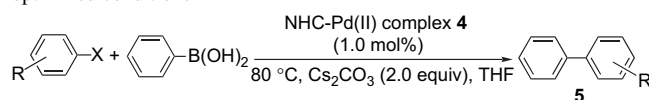
**Table 2.** Screening for solvents in the NHC–Pd(II) complex **4** catalyzed Suzuki cross-coupling reaction of bromobenzene (1.0 mmol) with phenylboronic acid (1.2 mmol) in various solvents (2.0 mL)

Entry	Solvent	Time (h)	Yield (%) <sup>a</sup>
			<b>5a</b>
1	THF	12	98
2	DMSO	12	24
3	DMF	12	55
4	DMA	12	67
5	Dioxane	12	96
6	ClCH <sub>2</sub> CH <sub>2</sub> Cl	12	21
7	CH <sub>3</sub> CN	12	19
8	PhCH <sub>3</sub>	12	54

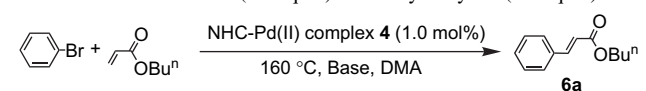
<sup>a</sup> Isolated yields.

was examined. The results are summarized in Table 3. As can be seen, aryl bromides and phenyl iodide afforded coupling products **5** in 71–90% yields within 12 h (Table 3, entries 1–6).

Heck reaction was examined in *N,N*-dimethylacetamide (DMA) by the reaction of bromobenzene with butyl acrylate in the presence of various bases (Table 4, entries 1–6). We found that Na<sub>2</sub>CO<sub>3</sub> afforded the best results for this reaction and allowed the coupling product **6a** to be obtained in 62% under argon atmosphere at 160 °C after 18 h (Table 4, entry 1). In other organic solvents, the reactions were sluggish. Adding 1.0 and 20 mol % Bu<sub>4</sub>NBr to the reaction system,

**Table 3.** NHC–Pd(II) complex **4** catalyzed Suzuki cross-coupling reaction between aryl halides (1.0 mmol) and phenylboronic acid (1.2 mmol) under optimized conditions

Entry	Ar-X	Time (h)	Yield (%) <sup>a</sup>
			<b>5</b>
1		12	<b>5b</b> , 74
2		12	<b>5c</b> , 71
3		12	<b>5d</b> , 90
4		12	<b>5e</b> , 81
5		12	<b>5f</b> , 72
6		12	<b>5a</b> , 88

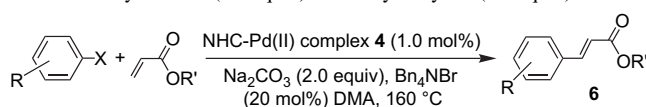
<sup>a</sup> Isolated yields.**Table 4.** NHC–Pd(II) complex **4** (1.0 mol %) catalyzed Heck coupling reaction of bromobenzene (1.0 equiv) with butyl acrylate (1.5 equiv)

Entry	Base	Time (h)	Yield (%) <sup>a</sup>
			<b>6a</b>
1	Na <sub>2</sub> CO <sub>3</sub>	18	62
2	K <sub>2</sub> CO <sub>3</sub>	18	26
3	Cs <sub>2</sub> CO <sub>3</sub>	18	36
4	KF·2H <sub>2</sub> O	18	21
5	K <sub>3</sub> PO <sub>4</sub> ·3H <sub>2</sub> O	18	33
6	NaOAc	18	24
7	Na <sub>2</sub> CO <sub>3</sub> <sup>b</sup>	18	84
8	Na <sub>2</sub> CO <sub>3</sub> <sup>c</sup>	18	97

<sup>a</sup> Isolated yields.<sup>b</sup> Bn<sub>4</sub>NBr (1.0 mol %) was added.<sup>c</sup> Bn<sub>4</sub>NBr (20 mol %) was added.

the yields of **6a** were improved to 84 and 97%, respectively (Table 4, entries 7 and 8).

Using these reaction conditions, we next examined the Heck cross-coupling reaction of a variety of aryl halides with butyl and methyl acrylate. The results are summarized in Table 5. We found that the Heck reaction products **6** were obtained in good to high yields in most cases under argon atmosphere (Table 5, entries 1–3, 6, and 7). For electron-rich 4-bromoanisole, the reaction was sluggish and product **6e** was obtained in only 19% yield under the same conditions

**Table 5.** NHC–Pd(II) complex **4** (1.0 mol %) catalyzed Heck coupling reaction of aryl halides (1.0 equiv) with butyl acrylate (1.5 equiv)

Entry	Ar-X	R'	Time (h)	Yield (%) <sup>a</sup>
				<b>6</b>
1		Bu <sup>n</sup>	18	<b>6b</b> , 81
2		Bu <sup>n</sup>	18	<b>6c</b> , 91
3		Bu <sup>n</sup>	18	<b>6d</b> , 87
4		Bu <sup>n</sup>	18	<b>6e</b> , 19
5		Me	18	<b>6f</b> , 48
6		Bu <sup>n</sup>	18	<b>6g</b> , 86
7		Bu <sup>n</sup>	18	<b>6a</b> , 99

<sup>a</sup> Isolated yields.

(Table 5, entry 4). For methyl acrylate, the coupled product **6f** was obtained in moderate yield of 48% (Table 5, entry 5). Product conformations were determined by  $^1\text{H}$  NMR spectroscopy (see Supplementary data).

In conclusion, we disclosed a novel tridentate NHC–Pd(II) complex **4** as an effective catalyst for Suzuki–Miyaura reaction and Heck cross-coupling reaction. The corresponding coupled products were obtained in good to high yields in most cases by this novel Pd(II)-catalyst under normal conditions. Efforts are underway to elucidate the mechanistic details of this C–C bond forming reaction catalyzed by Pd(II)–NHC complex and the use of **4** to catalyze other C–C bond forming transformations.

### 3. Experimental

#### 3.1. General

The synthesis of ligands was performed in untreated solvents under ambient atmosphere. The preparation of Pd complex was performed under argon atmosphere. THF and toluene were distilled from sodium (Na) under argon (Ar) atmosphere;  $\text{CH}_3\text{CN}$  and 1,2-dichloroethane were distilled from  $\text{CaH}_2$  under argon (Ar) atmosphere.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker AM-300 spectrometer for solution in  $\text{CDCl}_3$  with tetramethylsilane (TMS) as internal standard;  $J$ -values are in hertz. Mass spectra were recorded by EI, and HRMS was measured on a Finnigan  $\text{MA}^+$  mass spectrometer. All of the solid compounds reported in this paper gave satisfactory carbon, hydrogen, and nitrogen microanalyses with a Carlo-Erba 1106 analyzer [**3** was characterized by high-resolution mass spectrometry (HRMS)]. Commercially obtained reagents were used without further purification. All reactions were monitored by thin layer chromatography with silica gel coated plates. Flash column chromatography was carried out using 300–400 mesh silica gel at increased pressure.

**3.1.1. Synthesis of 2-(tosylamino)-2'-amino-1,1'-binaphthyl **1**.** To a mixture of 2,2'-diamino-1,1'-binaphthalene (a racemic compound, 569 mg, 2.0 mmol) and pyridine (2.0 mL, 24 mmol) in  $\text{CH}_2\text{Cl}_2$  (15 mL) was added dropwise *p*-toluenesulfonyl chloride solution (420 mg, 2.2 mmol in 5.0 mL of  $\text{CH}_2\text{Cl}_2$ ). The mixture was stirred at room temperature for 5 h. The reaction mixture was washed with 5% HCl and dried over anhydrous  $\text{MgSO}_4$ . The solvent was removed under reduced pressure and the residue was purified by a silica gel flash column chromatography (eluent: PE/EtOAc=6/1) to give compound **1** as a white solid (667 mg, 76%). Mp 169–170 °C; IR ( $\text{CH}_2\text{Cl}_2$ ):  $\nu$  3365, 3051, 1621, 1595, 1403, 1316, 1164, 1091, 977, 814, 666  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , TMS):  $\delta$  2.31 (3H, s,  $\text{CH}_3$ ), 3.30 (2H, br,  $\text{NH}_2$ ), 6.41 (1H, d,  $J=8.1$  Hz, ArH), 6.70 (1H, s, NH), 6.93–7.10 (5H, m, ArH), 7.19–7.24 (2H, m, ArH), 7.36–7.42 (3H, m, ArH), 7.77 (1H, d,  $J=8.1$  Hz, ArH), 7.85 (2H, t,  $J=9.0$  Hz, ArH), 8.03 (2H, dd,  $J_1=9.0$  Hz,  $J_2=49.2$  Hz, ArH);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ , TMS):  $\delta$  21.4, 117.9, 119.4, 121.5, 122.4, 123.2, 125.3, 125.6, 127.0, 127.1, 128.0, 128.1, 129.4, 129.7, 130.1, 131.2, 132.6, 136.0, 133.4, 133.5, 142.5, 143.6; EIMS  $m/z$  (%): 438 (75.20) [ $\text{M}^+$ ], 283 (100), 267 (96.03), 91 (16.90);

Anal. Calcd for  $\text{C}_{27}\text{H}_{22}\text{N}_2\text{O}_2\text{S}$  requires: C, 73.95, H, 5.06, N, 6.39%. Found: C, 73.84, H, 5.00, N, 6.25%.

**3.1.2. Synthesis of 2-(tosylamino)-2'-(imidazol-1-yl)-1,1'-binaphthyl **2**.** Compound **1** (876 mg, 2.0 mmol) and one drop of concentrated  $\text{H}_3\text{PO}_4$  was added to 10 mL of de-ionized water. Then 40% aqueous glyoxal (726 mg, 5 mmol) and paraformaldehyde (150 mg, 5 mmol) as well as 10 mL of dioxane were added. The mixture was heated with stirring to 80 °C, ammonium chloride (267 mg, 5 mmol) was added and then the temperature of oil bath was elevated to 100 °C. After 6 h, the reaction mixture was cooled and a saturated aqueous solution of  $\text{K}_2\text{CO}_3$  (20 mL) was added, and the mixture was extracted with  $\text{CH}_2\text{Cl}_2$  ( $3 \times 20$  mL). The combined organic layers were dried over anhydrous  $\text{MgSO}_4$ , filtered, and concentrated in vacuo. The residue was purified by a silica gel flash column chromatography (eluent: PE/EtOAc=1/1–0/1) to give compound **2** as a white solid (704 mg, 72%). Mp 244–245 °C; IR ( $\text{CH}_2\text{Cl}_2$ ):  $\nu$  3259, 3059, 2733, 1911, 1621, 1510, 1158, 1092, 981, 869, 523  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , TMS):  $\delta$  2.35 (3H, s,  $\text{CH}_3$ ), 6.35 (1H, br, CH), 6.70 (1H, s, NH), 6.75–6.76 (2H, m, CH), 6.88 (1H, d,  $J=8.7$  Hz, ArH), 7.11–7.27 (5H, m, ArH), 7.33–7.40 (3H, m, ArH), 7.53–7.62 (2H, m, ArH), 7.80 (1H, d,  $J=7.5$  Hz, ArH), 7.85–7.93 (2H, m, ArH), 8.00 (1H, d,  $J=8.4$  Hz, ArH), 8.15 (1H, d,  $J=9.0$  Hz, ArH);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ , TMS):  $\delta$  21.5, 117.6, 119.5, 119.7, 124.0, 124.6, 125.2, 125.7, 125.8, 127.0, 127.1, 127.5, 128.0, 128.3, 128.4, 128.0, 127.7, 130.3, 130.4, 131.3, 132.5, 132.9, 133.0, 133.3, 135.0, 136.0, 136.9, 144.0; EIMS  $m/z$  (%): 489 (30.77) [ $\text{M}^+$ ], 421 (13.21), 334 (100), 266 (36.91), 91 (11.86); Anal. Calcd for  $\text{C}_{30}\text{H}_{23}\text{N}_3\text{O}_2\text{S}$  requires: C, 73.60, H, 4.74, N, 8.58%. Found: C, 73.41, H, 4.60, N, 8.56%.

**3.1.3. Synthesis of 2-(tosylamino)-2'-(3-methylimidazolium-1-yl)-1,1'-binaphthyl iodide **3**.** A mixture of **2** (98 mg, 0.2 mmol) and iodomethane (0.2 mL) were stirred in acetonitrile (5.0 mL) at 80 °C for 5 h. The volatiles were removed to give the crude product **3** as a yellow solid (124 mg, 98%). Mp 151–153 °C; IR ( $\text{CH}_2\text{Cl}_2$ ):  $\nu$  3045, 2956, 2855, 1655, 1595, 1508, 1321, 1161, 1092, 816, 733, 550  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , TMS):  $\delta$  2.38 (3H, s,  $\text{CH}_3$ ), 3.97 (3H, s,  $\text{CH}_3$ ), 6.47 (1H, s, NH), 6.93 (1H, d,  $J=8.4$  Hz, ArH), 7.01–7.06 (2H, m, CH), 7.15 (2H, d,  $J=8.1$  Hz, ArH), 7.27–7.32 (2H, m, ArH), 7.38–7.45 (3H, m, ArH), 7.52 (2H, d,  $J=8.1$  Hz, ArH), 7.59 (1H, t,  $J=7.8$  Hz, ArH), 7.80–7.84 (2H, m, ArH), 7.97 (1H, d,  $J=8.4$  Hz, ArH), 8.09 (2H, q,  $J=8.7$  Hz, ArH), 9.48 (1H, s, CH);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ , TMS):  $\delta$  21.3, 37.5, 121.3, 121.8, 122.7, 122.9, 123.2, 124.5, 125.9, 126.6, 126.7, 127.7, 127.8, 127.9, 128.2, 128.3, 128.4, 129.4, 130.5, 130.6, 131.3, 131.4, 132.3, 132.4, 133.3, 133.4, 136.1, 136.6, 143.6; HRMS (ESI) Calcd for  $\text{C}_{31}\text{H}_{26}\text{N}_3\text{O}_2\text{S}$  ( $\text{M}^+ - \text{I}$ ) requires: 504.1746, Found: 504.1746.

**3.1.4. Synthesis of NHC–Pd(II) complex **4**.** The compound **3** (126 mg, 0.2 mmol) and  $\text{Pd}(\text{OAc})_2$  (44.8 mg, 0.2 mmol) was refluxed in THF (10 mL) for 12 h. The volatiles were then removed under reduced pressure and the residue was purified by a silica gel flash column chromatography (eluent: PE/EtOAc=2/1) to give **4** as a red solid (82 mg, 56%). A single crystal suitable for X-ray crystal analysis was obtained by recrystallization from a saturated solution of PE/EtOAc=3/1. Mp >250 °C; IR ( $\text{CH}_2\text{Cl}_2$ ):  $\nu$  3057,



2923, 1592, 1460, 1381, 1109, 1030, 878, 680, 553  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , TMS):  $\delta$  2.12 (3H, s, Me), 3.94 (3H, s, Me), 6.21 (1H, d,  $J=8.7$  Hz, ArH), 6.46 (2H, d,  $J=8.4$  Hz, CH), 6.68–6.76 (3H, m, ArH), 6.84 (1H, d,  $J=2.1$  Hz, ArH), 7.07–7.09 (1H, m, ArH), 7.16 (2H, d,  $J=8.1$  Hz, ArH), 7.30 (1H, d,  $J=7.2$  Hz), 7.43 (1H, t,  $J=7.8$  Hz, ArH), 7.68 (1H, d,  $J=8.4$  Hz, ArH), 7.75 (2H, d,  $J=8.7$  Hz, ArH), 7.86 (1H, d,  $J=8.7$  Hz, ArH), 7.96 (1H, d,  $J=8.1$  Hz, ArH), 8.19 (1H, d,  $J=8.7$  Hz, ArH); EIMS  $m/z$  (%): 735 (1.66) [ $\text{M}^+$ ], 579 (6.51), 502 (8.28), 438 (15.37), 422 (17.26), 347 (41.10), 332 (100), 278 (58.45), 91 (22.04); Anal. Calcd for  $\text{C}_{31}\text{H}_{24}\text{IN}_3\text{O}_2\text{PdS}$  requires: C, 50.59, H, 3.29, N, 5.71%. Found: C, 50.76, H, 3.10, N, 5.52%.

### 3.2. General procedure for the Suzuki cross-coupling reaction of aryl halides with boronic acids

A typical procedure is given below for the reaction expressed in entry 3 of Table 1. An oven-dried Schlenk flask was evacuated and filled with argon (3 cycles), then charged with NHC–Pd(II) complex **4** (7.3 mg, 0.01 mmol), cesium carbonate (650 mg, 2.0 mmol), benzene bromide (105  $\mu\text{L}$ , 1.0 mmol), phenylboronic acid (146 mg, 1.2 mmol), and THF (2.0 mL). The mixture was stirred at 80  $^\circ\text{C}$  for 12 h. The reaction mixture was diluted with  $\text{H}_2\text{O}$  (10 mL) and  $\text{CH}_2\text{Cl}_2$  (10 mL), followed by extraction twice with  $\text{CH}_2\text{Cl}_2$ . The combined organic layers were dried over anhydrous  $\text{Na}_2\text{SO}_4$ , filtered, and evaporated under reduced pressure to give crude product. The pure product was isolated by column chromatography on silica gel (eluent: petroleum ether) to give biphenyl (151 mg, 98%) as a white solid, which was analyzed by  $^1\text{H}$  NMR spectroscopy.

**3.2.1. Compound 5a.** A white solid;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , TMS):  $\delta$  7.37 (2H, m, ArH), 7.48 (4H, m, ArH), 7.65 (4H, m, ArH).

**3.2.2. Compound 5b.** A white solid;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , TMS):  $\delta$  2.46 (3H, s,  $\text{CH}_3$ ), 7.31–7.63 (2H, m, ArH), 7.36–7.41 (1H, m, ArH), 7.47–7.52 (2H, m, ArH), 7.56–7.58 (2H, m, ArH), 7.64–7.67 (2H, m, ArH).

**3.2.3. Compound 5c.** A colorless liquid;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , TMS):  $\delta$  2.44 (3H, s,  $\text{CH}_3$ ), 7.17–7.69 (1H, m, ArH), 7.32–7.47 (6H, m, ArH), 7.59–7.62 (2H, m, ArH).

**3.2.4. Compound 5d.** A white solid;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , TMS):  $\delta$  7.37–7.60 (9H, m, ArH).

**3.2.5. Compound 5e.** A white solid;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , TMS):  $\delta$  3.86 (3H, s,  $\text{OCH}_3$ ), 6.98–7.01 (2H, m, ArH), 7.32–7.35 (1H, m, ArH), 7.41–7.46 (2H, m, ArH), 7.53–7.59 (4H, m, ArH).

**3.2.6. Compound 5f.** A white solid;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , TMS):  $\delta$  2.39 (6H, s,  $\text{CH}_3$ ), 7.01 (1H, s, ArH), 7.22 (2H, s, ArH), 7.30–7.36 (1H, m, ArH), 7.40–7.45 (2H, m, ArH), 7.57–7.60 (2H, m, ArH).

### 3.3. Typical reaction procedure for Heck reaction

A typical procedure is given below for the reaction expressed in entry 8 of Table 4. An oven-dried Schlenk flask was

evacuated and filled with argon (3 cycles), then charged with aryl halide (1.0 mmol), butyl acrylate (1.5 mmol), sodium carbonate (212 mg, 2.0 mmol), cetyltrimethylammonium bromide (64.4 mg, 0.2 mmol), *N,N*-dimethylacetamide (DMA, 2.0 mL), and NHC–Pd(II) complex **4** (7.3 mg, 0.01 mmol). The reaction mixture was stirred at 160  $^\circ\text{C}$  for 18 h. The reaction mixture was diluted with  $\text{H}_2\text{O}$  (15 mL) and  $\text{Et}_2\text{O}$  (15 mL), followed by extraction twice with  $\text{Et}_2\text{O}$ . The combined organic layers were dried over anhydrous  $\text{Na}_2\text{SO}_4$ , filtered, and evaporated under reduced pressure to give crude product. A pure product (198 mg, 97%) was isolated by column chromatography (eluent: PE/ $\text{EtOAc}$ =30/1) on silica gel. The purified product was analyzed by  $^1\text{H}$  NMR spectroscopy.

**3.3.1. Compound 6a.** A yellow liquid;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , TMS):  $\delta$  0.97 (3H, t,  $J=7.2$  Hz,  $\text{CH}_3$ ), 1.40–1.48 (2H, m,  $\text{CH}_2$ ), 1.65–1.72 (2H, m,  $\text{CH}_2$ ), 4.21 (2H, t,  $J=6.6$  Hz,  $\text{OCH}_2$ ), 6.45 (1H, d,  $J=15.9$  Hz, =CH), 7.37–7.40 (3H, m, ArH), 7.51–7.54 (2H, m, ArH), 7.69 (1H, d,  $J=15.9$  Hz, =CH).

**3.3.2. Compound 6b.** A yellow liquid;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , TMS):  $\delta$  0.96 (3H, t,  $J=7.2$  Hz,  $\text{CH}_3$ ), 1.40–1.47 (2H, m,  $\text{CH}_2$ ), 1.63–1.71 (2H, m,  $\text{CH}_2$ ), 2.37 (3H, s,  $\text{CH}_3$ ), 4.20 (2H, t,  $J=6.9$  Hz,  $\text{OCH}_2$ ), 6.40 (1H, d,  $J=16.2$  Hz, =CH), 7.18–7.44 (4H, m, ArH), 7.66 (1H, d,  $J=16.2$  Hz, =CH).

**3.3.3. Compound 6c.** A yellow liquid;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , TMS):  $\delta$  0.93 (3H, t,  $J=7.2$  Hz,  $\text{CH}_3$ ), 1.37–1.44 (2H, m,  $\text{CH}_2$ ), 1.61–1.68 (2H, m,  $\text{CH}_2$ ), 2.33 (3H, s,  $\text{CH}_3$ ), 4.17 (2H, t,  $J=6.9$  Hz,  $\text{OCH}_2$ ), 6.40 (1H, d,  $J=16.2$  Hz, =CH), 7.14–7.17 (1H, m, ArH), 7.21–7.24 (1H, m, ArH), 7.28–7.30 (2H, m, ArH), 7.62 (1H, d,  $J=16.2$  Hz, =CH).

**3.3.4. Compound 6d.** A white solid;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , TMS):  $\delta$  0.96 (3H, t,  $J=7.5$  Hz,  $\text{CH}_3$ ), 1.35–1.51 (2H, m,  $\text{CH}_2$ ), 1.63–1.73 (2H, m,  $\text{CH}_2$ ), 4.20 (2H, t,  $J=6.3$  Hz,  $\text{OCH}_2$ ), 6.41 (1H, d,  $J=15.9$  Hz, =CH), 7.33–7.46 (4H, m, ArH), 7.62 (1H, d,  $J=15.9$  Hz, =CH).

**3.3.5. Compound 6e.** A yellow liquid;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , TMS):  $\delta$  0.96 (3H, t,  $J=7.2$  Hz,  $\text{CH}_3$ ), 1.37–1.49 (2H, m,  $\text{CH}_2$ ), 1.63–1.73 (2H, m,  $\text{CH}_2$ ), 3.83 (3H, s,  $\text{OCH}_3$ ), 4.19 (2H, t,  $J=6.6$  Hz,  $\text{OCH}_2$ ), 6.31 (1H, d,  $J=15.9$  Hz, =CH), 6.89–7.47 (4H, m, ArH), 7.64 (1H, d,  $J=15.9$  Hz, =CH).

**3.3.6. Compound 6f.** A yellow liquid;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , TMS):  $\delta$  3.81 (3H, s,  $\text{OCH}_3$ ), 6.45 (1H, d,  $J=16.2$  Hz, =CH), 7.37–7.40 (3H, m, ArH), 7.51–7.54 (2H, m, ArH), 7.70 (1H, d,  $J=16.2$  Hz, =CH).

**3.3.7. Compound 6g.** A yellow liquid;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , TMS):  $\delta$  0.96 (3H, t,  $J=7.5$  Hz,  $\text{CH}_3$ ), 1.38–1.50 (2H, m,  $\text{CH}_2$ ), 1.64–1.73 (2H, m,  $\text{CH}_2$ ), 2.33 (6H, s,  $\text{CH}_3$ ), 4.20 (2H, t,  $J=6.9$  Hz,  $\text{OCH}_2$ ), 6.41 (1H, d,  $J=15.9$  Hz, =CH), 7.02 (1H, s, ArH), 7.15 (2H, s, ArH), 7.62 (1H, d,  $J=15.9$  Hz, =CH).

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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.2006.04.034.

### References and notes

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6. The crystal data of complex **4** has been deposited in CCDC with number 290551. Empirical formula: C<sub>31</sub>H<sub>24</sub>IN<sub>3</sub>O<sub>2</sub>PdS; formula weight: 735.89; crystal color, Habit: colorless, prismatic; crystal dimensions: 0.506×0.345×0.133 mm; crystal system: triclinic; lattice type: primitive; lattice parameters:  $a=9.9182(6)$  Å,  $b=12.4974(8)$  Å,  $c=13.4366(9)$  Å,  $\alpha=114.8630(10)^\circ$ ,  $\beta=105.8190(10)^\circ$ ,  $\gamma=90.1450(10)^\circ$ ,  $V=1440.74(16)$  Å<sup>3</sup>; space group:  $P-1$ ;  $Z=2$ ;  $D_{\text{calcd}}=1.696$  g/cm<sup>3</sup>;  $F_{000}=724$ ; diffractometer: Rigaku AFC7R; residuals:  $R$ ;  $R_w$ : 0.0461, 0.1268.