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Unsymmetrical, oxazolinyl-containing achiral and chiral NCN pincer ligand precursors and their complexes with palladium(II)

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ABSTRACT

The unsymmetrical, achiral and chiral NCN pincer ligand precursors (**3a-3d**) with oxazoline and pyrazole as N donors as well as (**3e**) which has oxazolinyl and amino group have been synthesized in a facile manner in four steps starting from commercially available isophthalaldehyde. Direct C2 metallation of the precursors (**3a–3e**) with $Pd(OAc)_2$ in refluxing HOAc, followed by treatment with LiCl at room temperature provided convenient access to the corresponding pincer palladium(II) complexes (**4a–4e**). The molecular structure of complex **4e** has been determined by X-ray single-crystal diffraction. The obtained Pd complexes exhibited good activities in the Suzuki reactions of aryl bromides and activated aryl chlorides with phenylboronic acid.

1. Introduction

Palladium complexes with NCN pincer ligands have been extensively studied in recent years due to their high stability, feasible structural modifications, and remarkable catalytic activities in organometallic catalysis [1–4]. Much of the research has focused on symmetrical NCN pincer palladium complexes, which are symmetrical with two identical N donors such as amines [5–7], imines [8,9], pyridines [10–12], oxazolines [13–20] or other N-containing heterocycles [21,22] and 2 equiv. five-membered palladacycles (Scheme 1). Some of the complexes have been successfully applied as catalysts for stannylation of allyl [5] or propargylic substrates [6], Diels–Alder reaction [15], Heck [8,10,21,22], Suzuki and Sonogashira [22] coupling reactions. And the chiral complexes proved to be effective in asymmetric Michael reaction between α-cyanocarboxylates and methyl vinyl ketone (up to 83% ee) [8,17]. Following our interest in the metal pincer complexes and their applications, we recently reported the symmetrical chiral NCN pincer Pt(II) and Pd(II) complexes with 1,3-bis(2′-imidazolinyl)benzenes [23,24] and particularly unsymmetrical PCN pincer Pd(II) complexes containing phosphinito group by one-pot phosphorylation/palladation reaction [25,26]. We reasoned that different donors such as "hard" N and "soft" P in PCN pincers might provide a better tuning of the catalytic properties or give unique reactivity of the corresponding metal pincer complexes. In fact, some unsymmetrical pincer Pd complexes have been found to be much more active than the related symmetrical ones under certain circumstances [26,27]. Herein, we would like to report a simple protocol for the synthesis of the unsymmetrical, oxazolinyl-containing achiral and chiral NCN pincer ligand precursors (**3a–3e**) and their corresponding Pd (II) derivatives (**4a–4e**) (Scheme 2). To the best of our knowledge, there are no reports concerning the preparation and use of unsymmetrical NCN pincer Pd(II) complexes. The Pd complexes (**4a–4d**) were unusual in that they not only had different N-heterocyclic donors, but also contained both five- and six-membered metallacycles in the molecules. The obtained Pd complexes were applied to the Suzuki reactions of aryl halides with phenylboronic acid.

2. Results and discussion

2.1. Synthesis and characterization

The unsymmetrical NCN pincer ligand precursors **3a–3e** were prepared from commercially available isophthalaldehyde in four steps as shown in Scheme 2. First, selective reduction of one aldehyde group in isophthalaldehyde by $NaBH_4$ at 0 °C in MeOH readily afforded 3-(hydroxymethyl) benzaldehyde, which after bromination with PBr_3 led to 3-(bromomethyl)benzaldehyde (**1**). Then nucleophilic substitution of **1** with 3,5-dimethylpyrazole, pyrazole or diethylamine in the presence of K_2CO_3 in DMF or dioxane gave

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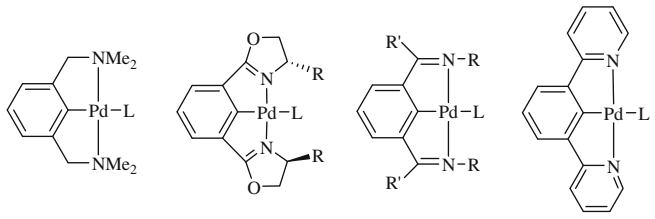


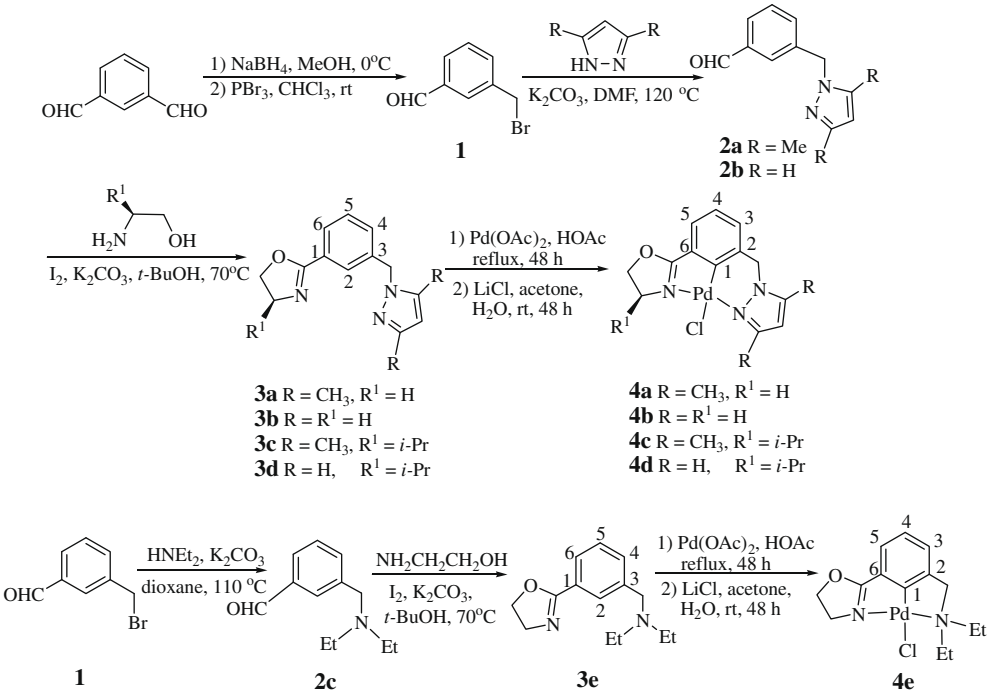
Scheme 1. Structure of the most common types of NCN pincer palladium complexes.

pyrazolyl- or amino-containing *m*-benzaldehyde derivatives **2a–2c**. Finally, the aldehyde group in **2** was directly converted to 2-oxazoline to yield achiral and chiral NCN ligand precursors **3a–3e** by the reaction of aldehyde **2** with 2-aminoethanol or (*S*)-valinol using molecular iodine and potassium carbonate in *tert*-butyl alcohol according to the published procedure [28]. With the expected ligand precursors in hand, the synthesis of the corresponding pincer Pd(II) complexes was attempted. The direct cyclopalladation reaction was carried out with **3a–3e** and 1.2 equiv. of $Pd(OAc)_2$ in refluxing acetic acid for 48 h, followed by treatment with LiCl at room temperature in acetone/water for another 48 h. The complexes **4a–4e** were successfully isolated as air- and moisture-stable yellow solids in 16–70% yields after purification.

All the new compounds were well characterized by HRMS, ^{1}H NMR, ^{13}C NMR, IR and ESI-MS. Comparison of the ^{1}H NMR spectra of the NCHN ligands **3** with those of their corresponding Pd pincer complexes **4**, the formation of **4** was clearly indicated by the disappearance of the singlet at δ 7.76–7.90 ppm corresponding to the central aryl proton located ortho to both N donors in **3**. Additionally, it was found that the signals of central aryl protons in **4** were shifted upfield. While those of the N-heterocycles including oxazoline and pyrazole rings as well as the CH_2 protons in NEt_2 were shifted downfield due to the N–Pd coordinations and C–Pd bond formation in the Pd complexes (selected ^{1}H NMR data of ligands **3** and Pd complexes **4** are given in Table 1). Among them, of particular note is that the significant upfield shifts of 5-aryl protons ($\Delta\delta \approx -0.6$ ppm) and large downfield shifts of the 3-pyrazolyl protons ($\Delta\delta \approx 1.0$ ppm) in complexes **4** compared to those in the ligands **3**. In fact, the downfield shift was also observed for certain protons of substituent in the oxazoline or pyrazole ring. For example, the CH proton of *i*-Pr in the oxazoline ring ($\Delta\delta \approx 1.0$ ppm) and CH_3 protons in the 3-position of pyrazole ring ($\Delta\delta \approx 0.5$ ppm). In the ^{13}C NMR spectra of the ligands **3**, the resonances due to the carbon atom of C=N appeared around 164 ppm for oxazoline ring, and 148 or 140 ppm for pyrazole ring. The resonances due to C-2 atom of central aryl appeared around 130 ppm. For the pincer Pd complexes **4**, the corresponding resonances obviously shifted downfield. They were observed around 175 ppm, 153 or 145 ppm and 150 ppm, respectively, again indicative of N–Pd coordinations and C–Pd bond formation in the complexes. Finally, it should be pointed out that in the ^{13}C NMR spectra of **4b** and **4d**, the signal for one of the quaternary carbons on the central aryl ring overlapped with the signal at δ 132.7 ppm.

2.2. Crystal structure

The molecular structure of **4e** was confirmed by a single-crystal X-ray analysis. The molecular is shown in Fig. 1. Crystallographic and data collection parameters are summarized in Table 2. Selected bond lengths (Å) and angles (°) are given in Table 3. Fig. 1 shows clearly that the ligand is coordinated to the Pd(II) centre *via* oxazolinyl-N, diethylamino-N and one aryl-C in a tridentate manner and a tetracyclic system is thus formed by the central aryl ring, the oxazoline ring and the two five-membered matallacycles. The palladium atom adopts a typical distorted-square-planar configuration defined by C (central aryl), N, N and Cl atoms. The Pd–C bond distance is 1.915(7) Å (or 1.910(8) Å) and the bond distances between Pd(II) and the two nitrogen atoms are 2.058(7) (or 2.072(7) Å) and 2.119(6) Å (or 2.126(6) Å) for N(1) and N(2), respectively. The angle of C–Pd–Cl (179.0° or 177.6°) is almost linear, while the N–Pd–N angle (around 161°) is small, which are in accordance with a pincer consisting two five-membered-ring



Scheme 2.

Table 1
Selected ^{1}H NMR data of NCHN ligands **3** and Pd complexes **4** (in $CDCl_3$, δ: ppm).

Ligand or complex	Ar^2 (1H) or Ar^1	Ar^6 or Ar^5 (1H)	Ar^5 or Ar^4 (1H)	Ar^4 or Ar^3 (1H)	PzH or N(CH_2CH_3)$_2$	OxH
3a	7.76 (s)	7.83 (d)	7.34 (t)	7.11 (d)	5.85 (s, 1H)	4.42 (t, 2H), 4.05 (t, 2H)
4a	–	7.21 (dd)	7.10–7.05 (m)		5.92 (s, 1H)	4.76 (t, 2H), 4.18 (t, 2H)
3b	7.84 (s)	7.87 (d)	7.38 (t)	7.29 (d)	7.55 (d, 1H), 7.40 (d, 1H), 6.28 (t, 1H)	4.42 (t, 2H), 4.04 (t, 2H)
4b	–	7.26–7.25 (m)	7.14–7.07 (m)		8.57 (d, 1H), 7.66 (d, 1H), 6.38 (t, 1H)	4.78 (t, 2H), 4.15 (t, 2H)
3c	7.78 (s)	7.84 (d)	7.32 (t)	7.08 (d)	5.85 (s, 1H)	4.40–4.36 (m, 1H), 4.14–4.07 (m, 2H)
4c	–	7.19 (dd)	7.09–7.05 (m)		5.92 (s, 1H)	4.63 (dd, 1H), 4.57 (t, 1H), 4.46–4.41 (m, 1H)
3d	7.87 (s)	7.88 (d)	7.37 (t)	7.28 (d)	7.55 (d, 1H), 7.39 (d, 1H), 6.28 (t, 1H)	4.42–4.38 (m, 1H), 4.15–4.07 (m, 2H)
4d	–	7.20–7.17 (m)	7.07–7.01 (m)		8.55 (d, 1H), 7.60 (d, 1H), 6.30 (t, 1H)	4.57–4.49 (m, 2H), 4.34–4.29 (m, 1H)
3e	7.90 (s)	7.82 (d)	7.36 (t)	7.49 (d)	2.52 (q, 4H)	4.43 (t, 2H), 4.06 (t, 2H)
4e	–	7.07 (d)	7.01 (t)	6.94 (d)	3.44–3.37 (m, 2H) 2.79–2.72 (m, 2H)	4.71 (t, 2H), 4.01 (t, 2H)

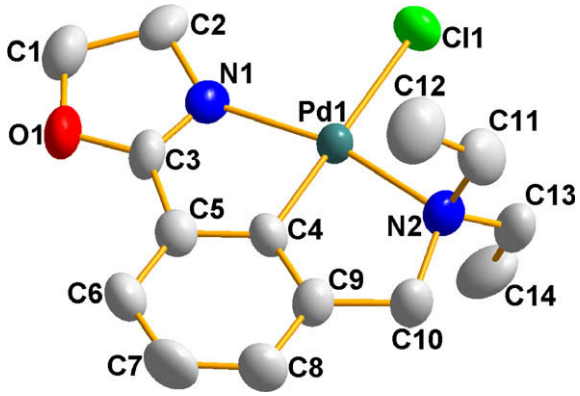


Fig. 1. Molecular structure of complex **4e** (representation of one of the two independent crystal structures). Hydrogen atoms are omitted for clarity.

Table 2
Crystallographic and data collection parameters for complex **4e**.

Formula	$C_{14}H_{19}ClN_2OPd$
M_r	373.16
Crystal size (mm)	0.20 × 0.18 × 0.18
a (Å)	20.064(4)
b (Å)	7.1728(14)
c (Å)	20.597(4)
α (°)	90
β (°)	90
γ (°)	90
V (Å^3)	2964.2(10)
Z	8
Space group	*Pca*2(1)
D_{Calcd} (g cm^{-3})	1.672
μ (mm^{-1})	1.426
θ range (°)	1.98–26.00
Number of data collected	9947
Number of unique data	5658
Observed data [$I \geq 2\sigma(I)$]	5658
R (all data)	0.0562
R_w (all data)	0.1443
R ($I > 2\sigma(I)$)	0.0508
R_w ($I > 2\sigma(I)$)	0.1336
F(0 0 0)	1504
Peak/hole (e Å^{-3})	1.256/−1.317

palladacycles [8,19,20,24,26] and reflect a relative steric strain of the almost planar tetracyclic system. All the bond distances and

Table 3
Selected bond lengths (Å) and angles (°) (corresponding values for the unshown second structure are given in brackets) for complex **4e**.

Pd(1)–C(4) [Pd(1′)–C(4′)]	1.915(7) [1.910(8)]
Pd(1)–N(1) [Pd(1′)–N(1′)]	2.058(7) [2.072(7)]
Pd(1)–N(2) [Pd(1′)–N(2′)]	2.119(6) [2.126(6)]
Pd(1)–Cl(1) [Pd(1′)–Cl(1′)]	2.4162(19) [2.426(2)]
N(1)–C(2) [N(1′)–C(2′)]	1.461(10) [1.475(10)]
N(1)–C(3) [N(1′)–C(3′)]	1.296(11) [1.277(12)]
N(2)–C(10) [N(2′)–C(10′)]	1.530(11) [1.518(10)]
N(2)–C(11) [N(2′)–C(11′)]	1.488(13) [1.504(11)]
N(2)–C(13) [N(2′)–C(13′)]	1.489(13) [1.518(11)]
O(1)–C(3) [O(1′)–C(3′)]	1.326(10) [1.360(10)]
O(1)–C(1) [O(1′)–C(1′)]	1.468(13) [1.441(13)]
C(1)–C(2) [C(1′)–C(2′)]	1.532(14) [1.549(15)]
C(3)–C(5) [C(3′)–C(5′)]	1.470(12) [1.440(13)]
C(4)–C(5) [C(4′)–C(5′)]	1.386(13) [1.400(13)]
C(4)–C(9) [C(4′)–C(9′)]	1.373(12) [1.408(11)]
C(9)–C(10) [C(9′)–C(10′)]	1.485(13) [1.476(12)]
C(4)–Pd(1)–N(1) [C(4′)–Pd(1′)–N(1′)]	79.9(3) [79.6(3)]
C(4)–Pd(1)–N(2) [C(4′)–Pd(1′)–N(2′)]	82.1(3) [82.0(3)]
N(1)–Pd(1)–N(2) [N(1′)–Pd(1′)–N(2′)]	161.7(3) [160.7(3)]
C(4)–Pd(1)–Cl(1) [C(4′)–Pd(1′)–Cl(1′)]	179.0(3) [177.6(3)]
N(1)–Pd(1)–Cl(1) [N(1′)–Pd(1′)–Cl(1′)]	99.51(19) [101.1(2)]
N(2)–Pd(1)–Cl(1) [N(2′)–Pd(1′)–Cl(1′)]	98.48(19) [97.50(18)]

angles around Pd(II) centre are similar to those observed in the related bis(oxazoline) pincer Pd(II) complexes [20,29]. In the crystal of complex **4e**, chlorine atom forms hydrogen bond with the adjacent CH_2 group of oxazoline ring [Cl(1)···H(1′B) 2.834 Å, Cl(1)···C(1′) 3.549 Å, C(1′)–H(1′B)···Cl(1) 132° and Cl(1′)···H(1A) 2.843 Å, Cl(1′)···C(1) 3.607 Å, C(1)–H(1A)···Cl(1′) 136°]. There also exist intermolecular hydrogen bonds between Pd atom and the adjacent CH_2 group of oxazoline ring [Pd(1)···H(1′A) 2.977 Å, Pd(1)···C(1′) 3.907 Å, C(1′)–H(1′A)···Pd(1) 161°]. These hydrogen bonds are attributed to construct the 1D chain structure of complex **4e** (Fig. 2).

2.3. Suzuki reaction

All the palladium complexes **4** including the chiral ones were tested as precatalysts for the Suzuki coupling reactions. The complexes are thermally stable and inert toward air and moisture both in the solid state and in solution. These properties allowed for the catalytic experiments open to air in the analytical grade solvents which were used without further purification. Initial catalytic studies were performed on the coupling of 3-bromotoluene with

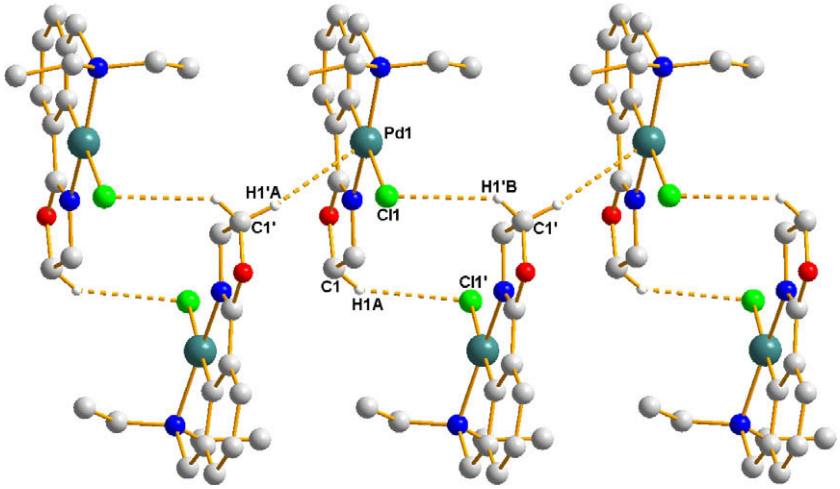
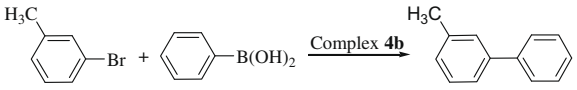


Fig. 2. 1-D chain structure of complex **4e** formed by hydrogen bonds. Non-hydrogen bonding H atoms are omitted for clarity.

phenylboronic acid as a model reaction in the presence of 0.5 mol% of complex **4b**. As shown in Table 4, when the reaction was conducted in DMF at 140 °C for 12 h, $KF{\cdot}2H_2O$, K_2CO_3 and Na_2CO_3 as a base gave excellent yields (entries 1–6). When toluene was used as solvent, excellent yields were also obtained at 110 °C after 12 h with $KF{\cdot}2H_2O$, K_2CO_3, $K_3PO_4{\cdot}3H_2O$ and NaOH as a base (entries 7–12). Several other solvents using K_2CO_3 as the base were also tested. Among them, THF was not effective (entry 13) and water produced a moderate yield (entry 14). Dioxane gave the best result after 7 h (>99% yield, entry 15). Finally, the influence of the catalytic loading on the reaction was investigated (entries 16–19). When the reaction was carried out in the presence of 0.1 mol% of complex **4b** with K_2CO_3 as the base in dioxane at 110 °C, the coupled product could be isolated in >99% yield after 7 h (entry 19).

Table 4
Optimization of reaction conditions for the coupling of 3-bromotoluene with phenylboronic acid.[a]



Entry	Solvent	Base	Temperature (°C)	Time (h)	Yield[b] (%)
1	DMF	$K_3PO_4{\cdot}3H_2O$	140	12	47.6
2	DMF	$NaOAc{\cdot}3H_2O$	140	12	14.3
3	DMF	$K_2HPO_4{\cdot}3H_2O$	140	12	45.2
4	DMF	$KF{\cdot}2H_2O$	140	12	94.0
5	DMF	K_2CO_3	140	12	>99
6	DMF	Na_2CO_3	140	12	>99
7	Toluene	$K_2HPO_4{\cdot}3H_2O$	110	12	45.2
8	Toluene	Na_2CO_3	110	12	19.0
9	Toluene	$KF{\cdot}2H_2O$	110	12	>99
10	Toluene	K_2CO_3	110	12	96.4
11	Toluene	$K_3PO_4{\cdot}3H_2O$	110	12	>99
12	Toluene	NaOH	110	12	>99
13	THF	K_2CO_3	65	12	8.3
14	H_2O	K_2CO_3	100	12	78.6
15	Dioxane	K_2CO_3	110	7	>99
16[c]	DMF	K_2CO_3	140	12	>99
17[c]	Dioxane	K_2CO_3	110	12	>99
18[d]	DMF	K_2CO_3	110	7	39.3
19[d]	Dioxane	K_2CO_3	110	7	>99

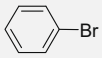
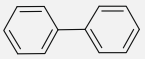
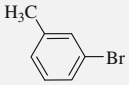
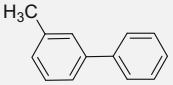
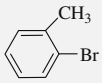
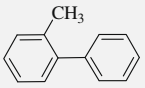
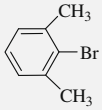
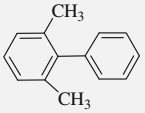
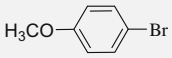
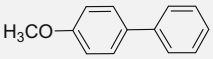
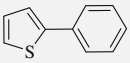
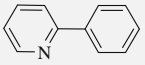
[a] *Reaction conditions*: complex **4b** (0.5 mol%), 3-bromotoluene (0.5 mmol), $PhB(OH)_2$ (0.75 mmol), base (1.0 mmol), solvent (3 mL), under air.
[b] Isolated yield.
[c] 0.25 mol% of complex **4b**.
[d] 0.1 mol% of complex **4b**.

Under these optimized reaction conditions, several electron-neutral aryl bromides such as boromobenzene, 3-bromotoluene and even the sterically hindered 2-bromo-*m*-xylene could be coupled efficiently with phenylboronic acid, giving the corresponding biaryls in excellent yields. And it was found that complex **4a** with 3,5-dimethyl pyrazolyl group and **4b** with pyrazolyl group displayed comparable activity in these reactions (Table 5, entries 1–8). While in the case of electron-rich aryl bromides such as 4-bromoanisole, complex **4a** exhibited higher activity than complex **4b** (entries 9–10). Similarly, **4c** was more active than **4d** (entries 11–12). Among the five Pd complexes, **4c** with 4-*i*-Pr-oxazolinyl and 3,5-dimethyl pyrazolyl group was the most active, providing the 4-methoxybiphenyl in an excellent yield (entries 9–13). While for heteroaryl bromides such as 2-bromothiophene and 2-bromopyridine, complex **4a** and **4c** were found to be inferior to **4b** and excellent yields could also be achieved in the presence of **4b** (entries 14–19).

In the following experiments, the catalytic activities of unsymmetrical NCN Pd complex **4c** and the symmetrical NCN complex **5** [24] as well as the related unsymmetrical PCN complexes **6–7** [25,26] were compared under two different reaction conditions. It was found that the symmetrical Pd complex **5** exhibited an obviously lower activity than the other unsymmetrical ones, especially at reduced temperature giving only trace amount of the coupled product (Table 6). The three unsymmetrical Pd complexes showed comparable activities at 110 °C, giving the product in almost quantitative yield (entries 1, 3 and 4). While at 50 °C, complexes **4c** and **6a** were inferior to **6b** and **7**, indicating that the activity was influenced by the substituent on the N- or P-donors (entries 5, 7–9). Since palladium black formation was observed under the investigated reaction conditions, the Suzuki reaction catalyzed by these systems was believed to proceed via a Pd(0)–Pd(II) catalytic cycle. Consequently, the lower activity of complex **5** was possibly due to its higher stability that would lead to a slower release of the true catalytic active Pd(0) species. In contrast, the relatively lower stability of the unsymmetrical complexes resulted from the hemilabile coordination of the ligands made it easier for these complexes to generate active Pd(0).

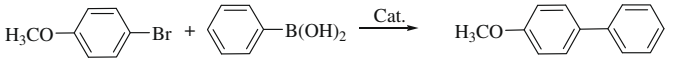
The Suzuki reaction of aryl chlorides with phenylboronic acid catalyzed by complex **4** was also investigated since aryl chlorides are more readily available, less expensive but less reactive than aryl bromides (Scheme 3). It turned out that for an activated chloride such as 4-chloroacetophenone, high yields could be obtained in DMF with $K_3PO_4{\cdot}7H_2O$ as the base at 120 °C after 12 h in the presence of 1 mol% of complex **4a** (>99%) or **4b** (86.7%).

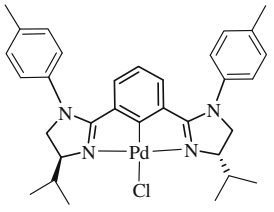
Table 5
Suzuki reactions of aryl bromides with phenylboronic acid catalyzed by complex **4**.[a]

Entry	Aryl bromide	Cat. (mol%)	Product	Yield [b](%)
1		**4a** (0.1)		>99
2		**4b** (0.1)		>99
3		**4a** (0.1)		>99
4		**4b** (0.1)		>99
5		**4a** (0.1)		>99
6		**4b** (0.1)		91.7
7		**4a** (0.1)		>99
8		**4b** (0.1)		>99
9		**4a** (0.1)		85.9
10		**4b** (0.1)		67.3
11		**4c** (0.1)		>99
12		**4d** (0.1)		83.4
13		**4e** (0.1)		70.0
14		**4a** (0.1)		88.8
15		**4b** (0.1)		97.5
16		**4c** (0.1)		89.8
17		**4a** (0.1)		65.8
18		**4b** (0.1)		92.9
19		**4c** (0.1)		39.5

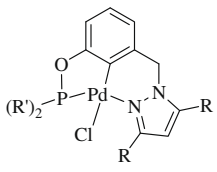
[a] *Reaction conditions*: aryl bromide (0.5 mmol), $PhB(OH)_2$ (0.75 mmol), K_2CO_3 (1.0 mmol), dioxane (3 mL), 110 °C, 7 h, under air.
[b] Isolated yield.

Table 6
Relative catalytic activities of unsymmetrical and symmetrical pincer Pd(II) complexes **4**–**7** in the Suzuki coupling of 4-bromoanisole with phenylboronic acid.[a]

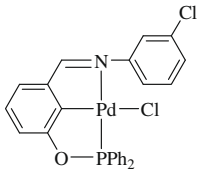




5



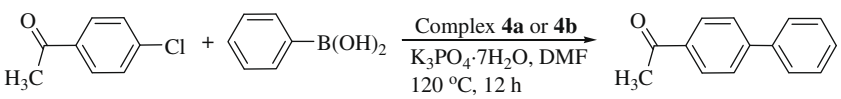
6a R = CH_3; R' = Cy
6b R = H; R' = Ph



7

Entry	Cat. (mol%)	Solvent	Base	Temperature (°C)	Time (h)	Yield[b] (%)
1	**4c** (0.1)	Dioxane	K_2CO_3	110	7	>99
2	**5** (0.1)	Dioxane	K_2CO_3	110	7	11.9
3	**6a** (0.1)	Dioxane	K_2CO_3	110	7	>99
4	**7** (0.1)	Dioxane	K_2CO_3	110	7	>99
5[c]	**4c** (0.3)	EtOH	$K_3PO_4{\cdot}7H_2O$	50	10	82.0
6[c]	**5** (0.3)	EtOH	$K_3PO_4{\cdot}7H_2O$	50	10	trace
7[c]	**6a** (0.3)	EtOH	$K_3PO_4{\cdot}7H_2O$	50	10	80.9
8[c]	**6b** (0.3)	EtOH	$K_3PO_4{\cdot}7H_2O$	50	10	95.0
9[c,d]	**7** (0.3)	EtOH	$K_3PO_4{\cdot}7H_2O$	50	10	91.0

[a] *Reaction conditions*: 4-bromoanisole (0.5 mmol), $PhB(OH)_2$ (0.75 mmol), base (1.0 mmol), solvent (3 mL), under air.
[b] Isolated yield.
[c] $PhB(OH)_2$ (0.6 mmol).
[d] From Ref. [26].



Scheme 3.

However, for methyl-substituted chlorobenzenes only poor yields (<40%) were obtained under similar reaction conditions.

In conclusion, we have synthesized a series of unsymmetrical, oxazolinyl-containing achiral and chiral NCN pincer ligand precursors starting from easily available isophthalaldehyde. The corresponding pincer Pd complexes were prepared via direct C2 palladation of the ligand precursors and used as efficient catalysts for Suzuki reactions of aryl bromides and activated aryl chlorides with phenylboronic acid. Further studies will focus on the synthesis of chiral pincer Pt complexes with the ligands and their applications in asymmetric catalysis.

3. Experimental

3.1. General

Compounds **1** [30,31], 3,5-dimethylpyrazole [32], **2** [25,33] and (*S*)-valinol [34] were prepared according to the literature methods. All the other reagents were used as commercial sources. Melting points were measured using a WC-1 microscopic apparatus and were uncorrected. IR spectra were collected on a Bruker VECTOR22 spectrophotometer in KBr pellets. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX-400 spectrometer. Mass spectra were performed on the Agilent LC/MSD Trap XCT instrument. HRMS were measured on a Micromass Q-TOF mass spectrometry (Waters, Manchester, UK) with an ESI source. Elemental analyses were measured on a Thermo Flash EA 1112 elemental analyzer. Optical rotations of chiral compounds were recorded on a Perkin–Elmer 341 polarimeter.

3.2. Synthesis of 3-(bromomethyl)benzaldehyde (*1*)

To a solution of isophthalaldehyde (4.75 g, 35.5 mmol) in ethanol (105 mL) was added sodium borohydride (0.33 g, 8.85 mmol) at 0 °C and the mixture was stirred overnight at 0 °C. After the solvent was removed, CH_2Cl_2 were added to the residue. The combined extracts were washed with brine, dried, and then concentrated in vacuo. The crude product was purified by SiO_2 column chromatography (eluent: 1/1 *n*-hexane/ethyl acetate) to furnish the desired 3-(hydroxymethyl)benzaldehyde (3.94 g, 81.7%) as a colorless oil. To a solution of 3-(hydroxymethyl)benzaldehyde (1.36 g, 10.0 mmol) in $CHCl_3$ (20 mL), PBr_3 (1.12 mL, 12.0 mmol) was added at room temperature and stirred for 3 h. Then a spot of water was added to end the reaction, the organic phase was separated and the aqueous layer was extracted twice with CH_2Cl_2 (2×20 mL). The organic phase was dried over $MgSO_4$, filtered, and evaporated. The residue was purified by SiO_2 column chromatography (eluent: CH_2Cl_2) to afford the desired 3-(bromomethyl)benzaldehyde (**1**) (1.42 g, 71.6%) as a colorless oil which solidified at 0 °C.

3.3. Synthesis of pyrazolyl- or amino-containing m-benzaldehyde derivatives *2*

Method A: Under nitrogen atmosphere, a mixture of 3-(bromomethyl)benzaldehyde (**1**) (396.0 mg, 2.0 mmol), 3,5-dimethylpyrazole (2.0 mmol), and NaH (144.0 mg, 6.0 mmol) in 30 mL of dioxane was refluxed with stirring for 3 days. After being cooled, the reaction was quenched with water. The aqueous layer was then extracted with dichloromethane, and the organic layers were dried over $MgSO_4$, filtered, and evaporated. The crude was purified by preparative TLC on silica gel plates eluting with acetone/petroleum ether (1:2) to afford **2a** (101.8 mg, 23.8%) as a colorless oil.

Method B: A mixture of 3-(bromomethyl)benzaldehyde (**1**) (396.0 mg, 2.0 mmol), 3,5-dimethylpyrazole, pyrazole (2.5 mmol) or diethylamine (2.0 mmol), and potassium carbonate (552.0 mg, 4.0 mmol) was heated at 120 °C in DMF (5 mL) for 24 h (or 110 °C in 30 mL of dioxane for 5 h for the reaction of **1** with $HNEt_2$). Then solvent was removed in vacuo and water (15 mL) was added. The aqueous layer was extracted with chloroform. The organic layers were dried over $MgSO_4$, filtered, and evaporated. The crude was purified by preparative TLC on silica gel plates eluting with acetone/petroleum ether (1/2) for **2a** and **2b** or ethyl acetate for **2c**. Compound **2c** is a known compound.

2a: 270.5 mg. Yield: 63.2%. Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.96 (d, J = 1.0 Hz, 1H, CHO), 7.77 (d, J = 7.6 Hz, 1H, ArH), 7.59 (s, 1H, ArH), 7.48 (t, J = 7.6 Hz, 1H, ArH), 7.33 (d, J = 7.6 Hz, 1H, ArH), 5.88 (s, 1H, PzH), 5.28 (s, 2H, CH_2), 2.25 (s, 3H, CH_3), 2.16 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.0, 148.0, 139.2, 138.7, 136.7, 132.6, 129.5, 128.9, 127.6, 105.8, 51.9, 13.5, 11.1. IR (KBr, cm^{-1}): ν 2923, 2821, 1699, 1589, 1554, 1458, 1424, 1285, 1349, 1308, 1280, 1240, 1142, 1084, 1030, 973, 783, 708. MS (*m/z*, ESI$^+$): 215 (M+H). HRMS (*m/z*, ESI$^+$): found for M+H = 215.1185, $C_{13}H_{15}N_2O$ requires 215.1184.

2b: 178.9 mg. Yield: 48.1%. Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.97 (s, 1H, CHO), 7.80 (d, J = 7.6 Hz, 1H, ArH), 7.69 (s, 1H, ArH), 7.57 (d, J = 1.6 Hz, 1H, PzH), 7.50 (t, J = 7.6 Hz, 1H, ArH), 7.46 (d, J = 2.0 Hz, 2H, PzH), 7.46–7.44 (m, 1H, ArH), 6.31 (t, J = 2.0 Hz, 1H, PzH), 5.40 (s, 2H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.8, 139.8, 137.9, 136.6, 133.2, 129.4, 129.3, 129.2, 128.2, 106.2, 55.0. IR (KBr, cm^{-1}): ν 2935, 2840, 2734, 1699, 1592, 1513, 1446, 1394, 1353, 1285, 1243, 1145, 1089, 1050, 967, 919, 754. MS (*m/z*, ESI$^+$): 187 (M+H). HRMS (*m/z*, ESI$^+$): found for M+H = 187.0877, $C_{11}H_{11}N_2O$ requires 187.0871.

3.4. Synthesis of the unsymmetrical NCN ligand precursors *3a–3e* by direct oxidative conversion of aldehyde in *2a-2c* to 2-oxazoline

To a solution of **2a** (214.0 mg, 1 mmol) [or **2b** (186.0 mg, 1 mmol) or **2c** (191.0 mg, 1 mmol)] in *t*-BuOH (10 mL) was added 2-aminoethanol (67.2 mg, 1.1 mmol) [or (*S*)-valinol (113.3 mg, 1.1 mmol)]. The mixture was stirred at room temperature under N_2 atmosphere for 30 min, and K_2CO_3 (414.6 mg, 3 mmol) and I_2 (507.6 mg, 2 mmol) were added to the mixture and stirred at 70 °C. After 18 h, the mixture was quenched with satd. aq. Na_2SO_3 until the color of iodine almost disappeared and was extracted with Et_2O. The organic layer was washed with brine and dried over Na_2SO_4, filtered, and evaporated. The crude was purified by preparative TLC on silica gel plates eluting with AcOEt/petroleum ether (1/1) to afford **3a–3e**.

3a: 103.5 mg. Yield: 40.6%. Colorless solid. M.p. 65–66 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 (d, J = 7.7 Hz, 1H, ArH), 7.76 (s, 1H, ArH), 7.34 (t, J = 7.7 Hz, 1H, ArH), 7.11 (d, J = 7.7 Hz, 1H, ArH), 5.85 (s, 1H, PzH), 5.24 (s, 2H, CH_2), 4.42 (t, J = 9.5 Hz, 2H, OxH), 4.05 (t, J = 9.5 Hz, 2H, OxH), 2.25 (s, 3H, CH_3), 2.14 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.3, 147.7, 139.1, 137.7, 129.4, 128.8, 128.0, 127.2, 126.3, 105.6, 67.6, 54.8, 52.2, 13.5, 11.1. IR (KBr, cm^{-1}): ν 3275, 2925, 2874, 1721, 1646, 1583, 1551, 1482, 1456, 1425, 1367, 1327, 1256, 1177, 1086, 1029, 980, 956, 914, 800, 777, 709. MS (*m/z*, ESI$^+$): 256 (M+H). HRMS (*m/z*, ESI$^+$): found for M+H = 256.1451 and M+Na = 278.1259, $C_{15}H_{18}N_3O$ and $C_{15}H_{17}N_3NaO$ require 256.1450 and 278.1269, respectively.

3b: 81.5 mg. Yield: 35.9%. Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (d, J = 7.6 Hz, 1H, ArH), 7.84 (s, 1H, ArH), 7.55 (d, J = 1.3 Hz, 1H, PzH), 7.40 (d, J = 2.0 Hz, 1H, PzH), 7.38 (t, J = 7.6 Hz, 1H, ArH), 7.29 (d, J = 8.9 Hz, 1H, ArH), 6.28 (t, J = 2.0 Hz, 1H, PzH), 5.34 (s, 2H, CH_2), 4.42 (t, J = 9.6 Hz, 2H, OxH), 4.04 (t, J = 9.6 Hz, 2H, OxH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.2, 139.6, 136.9, 130.4, 129.2, 128.9, 128.1, 127.7, 127.3, 106.1, 67.6,

55.4, 54.8. IR (KBr, cm^{-1}): ν 3106, 2935, 2877, 1719, 1650, 1606, 1586, 1513, 1483, 1450, 1434, 1395, 1362, 1269, 1189, 1088, 1067, 980, 954, 916, 805, 756, 709. MS (*m/z*, ESI^+): 228 (M+H). HRMS (*m/z*, ESI^+): found for M+H = 228.1132 and M+Na = 250.0975, $C_{13}H_{14}N_3O$ and $C_{13}H_{13}N_3NaO$ require 228.1137 and 250.0956, respectively.

3c: 150.9 mg. Yield: 50.8%. Colorless oil. $[\alpha]_D^{20} = +1^\circ$ (*c* 0.15, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ 7.84 (d, *J* = 7.6 Hz, 1H, ArH), 7.78 (s, 1H, ArH), 7.32 (t, *J* = 7.8 Hz, 1H, ArH), 7.08 (d, *J* = 8.0 Hz, 1H, ArH), 5.85 (s, 1H, PzH), 5.25 (s, 2H, CH_2), 4.40–4.36 (m, 1H, OxH), 4.14–4.07 (m, 2H, OxH), 2.24 (s, 3H, CH_3), 2.13 (s, 3H, CH_3), 1.89–1.82 (m, 1H, C*H*$(CH_3)_2$), 1.02 (d, *J* = 6.8 Hz, 3H, CH(C*H*$_3)_2$), 0.92 (d, *J* = 6.8 Hz, 3H, CH(C*H*$_3)_2$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.1, 147.7, 139.2, 137.6, 129.4, 128.8, 128.2, 127.4, 126.4, 105.7, 72.5, 70.1, 52.2, 32.8, 18.9, 18.0, 13.5, 11.1. IR (KBr, cm^{-1}): ν 3198, 2960, 2921, 2872, 1717, 1649, 1605, 1588, 1555, 1461, 1430, 1383, 1356, 1307, 1279, 1188, 1110, 1079, 1030, 975, 923, 784, 710. MS (*m/z*, ESI^+): 298 (M+H). HRMS (*m/z*, ESI^+): found for M+H = 298.1912, $C_{18}H_{24}N_3O$ requires 298.1919.

3d: 97.5 mg. Yield: 36.1%. Colorless oil. $[\alpha]_D^{20} = -25^\circ$ (*c* 0.05, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ 7.88 (d, *J* = 8.8 Hz, 1H, ArH), 7.87 (s, 1H, ArH), 7.55 (d, *J* = 1.5 Hz, 1H, PzH), 7.39 (d, *J* = 2.4 Hz, 1H, PzH), 7.37 (t, *J* = 7.6 Hz, 1H, ArH), 7.28 (d, *J* = 7.7 Hz, 1H, ArH), 6.28 (t, *J* = 2.0 Hz, 1H, PzH), 5.34 (s, 2H, CH_2), 4.42–4.38 (m, 1H, OxH), 4.15–4.07 (m, 2H, OxH), 1.88–1.83 (m, 1H, C*H*$(CH_3)_2$), 1.02 (d, *J* = 6.8 Hz, 3H, CH(C*H*$_3)_2$), 0.92 (d, *J* = 6.8 Hz, 3H, CH(C*H*$_3)_2$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.0, 139.7, 136.9, 130.5, 129.3, 128.9, 128.4, 127.9, 127.5, 106.1, 72.6, 70.2, 55.6, 32.8, 19.0, 18.1. IR (KBr, cm^{-1}): ν 3101, 2961, 2929, 2872, 1721, 1651, 1606, 1585, 1515, 1451, 1393, 1359, 1284, 1189, 1088, 1049, 975, 921, 803, 753, 711. MS (*m/z*, ESI^+): 270 (M+H). HRMS (*m/z*, ESI^+): found for M+H = 270.1606 and M+Na = 292.1433, $C_{16}H_{20}N_3O$ and $C_{16}H_{19}N_3NaO$ require 270.1606 and 292.1426, respectively.

3e: 31.3 mg. Yield: 13.5%. Colorless oil. ^1H NMR (400 MHz, $CDCl_3$): δ 7.90 (s, 1H, ArH), 7.82 (d, *J* = 7.7 Hz, 1H, ArH), 7.49 (d, *J* = 7.7 Hz, 1H, ArH), 7.36 (t, *J* = 7.7 Hz, 1H, ArH), 4.43 (t, *J* = 9.5 Hz, 2H, OxH), 4.06 (t, *J* = 9.5 Hz, 2H, OxH), 3.59 (s, 2H, CH_2), 2.52 (q, *J* = 7.2 Hz, 4H, C*H*$_2$CH$_3$), 1.04 (t, *J* = 7.2 Hz, 6H, CH$_2$C*H*$_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.2, 140.6, 132.4, 129.1, 128.7, 127.9, 127.1, 68.0, 57.6, 55.3, 47.1, 12.1. IR (KBr, cm^{-1}): ν 3421, 3128, 2969, 2925, 2804, 1720, 1650, 1595, 1451, 1393, 1361, 1270, 1193, 1071, 986, 952, 914, 803, 709. MS (*m/z*, ESI^+): 233 (M+H). HRMS (*m/z*, ESI^+): found for M+H = 233.1652, $C_{14}H_{21}N_2O$ requires 233.1654.

3.5. Synthesis of pincer palladium complexes **4a–4e**

A mixture of unsymmetrical NCN pincer ligand precursors **3a–3e** (0.2 mmol) and $Pd(OAc)_2$ (54.0 mg, 0.24 mmol) in dry HOAc (60 mL) were refluxed for 48 h under nitrogen atmosphere. The solvent was removed under reduced pressure and a solution of lithium chloride (102.0 mg, 2.4 mmol) in acetone/water (3/2, 35 mL) was added. The resulting solution was stirred at room temperature for 48 h. The solution was extracted with dichloromethane and the organic layer was washed with brine, dried over $MgSO_4$ and evaporated. The crude was purified by preparative TLC on silica gel plates eluting with AcOEt/CH_2Cl_2 (1:10–1:20) to afford the corresponding pincer palladium complexes **4a–4e**.

4a: Yield: 20.3%. Yellow solid. M.p. >250 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 7.21 (dd, *J* = 1.7, 7.0 Hz, 1H, ArH), 7.10–7.05 (m, 2H, ArH), 5.92 (s, 1H, PzH), 5.03 (s, 2H, CH_2), 4.76 (t, *J* = 9.5 Hz, 2H, OxH), 4.18 (t, *J* = 9.5 Hz, 2H, OxH), 2.72 (s, 3H, CH_3), 2.37 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 175.0, 153.4, 151.6, 140.7, 134.4, 131.7, 128.3, 124.9, 124.5, 107.8, 70.9, 52.0, 50.5, 16.2, 12.1. IR (KBr, cm^{-1}): ν 3134, 2921, 2885, 2853, 1729, 1633, 1575, 1554, 1468, 1440, 1398, 1358, 1277, 1179, 1152, 1123, 1049, 989, 945, 913, 861, 791, 729. MS (*m/z*, ESI^+): 360 (M−Cl). HRMS (*m/z*, ESI^+): found for M−Cl = 360.0314, $C_{15}H_{16}N_3OPd$ requires 360.0328. Anal. Calc. for $C_{15}H_{16}ClN_3OPd$: C, 45.47; H, 4.07; N, 10.61. Found: C, 46.09; H, 4.45; N 10.04%.

4b: Yield: 43.5%. Yellow solid. M.p. >250 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 8.57 (d, *J* = 1.6 Hz, 1H, PzH), 7.66 (d, *J* = 1.8 Hz, 1H, PzH), 7.26–7.25 (m, 1H, ArH), 7.14–7.07 (m, 2H, ArH), 6.38 (t, *J* = 2.2 Hz, 1H, PzH), 5.28 (s, 2H, CH_2), 4.78 (t, *J* = 9.5 Hz, 2H, OxH), 4.15 (t, *J* = 9.5 Hz, 2H, OxH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 175.4, 149.1, 145.0, 132.7, 131.9, 128.8, 125.4, 124.6, 106.6, 71.0, 56.3, 50.8. IR (KBr, cm^{-1}): ν 3117, 2923, 2853, 1739, 1639, 1573, 1515, 1476, 1436, 1406, 1370, 1268, 1173, 1148, 1103, 1078, 1057, 997, 959, 919, 862, 779, 725. MS (*m/z*, ESI^+): 332 (M−Cl). HRMS (*m/z*, ESI^+): found for M−Cl = 332.0016, $C_{13}H_{12}N_3OPd$ requires 332.0015. Anal. Calc. for $C_{13}H_{12}ClN_3OPd$: C, 42.41; H, 3.29; N, 11.41. Found: C, 42.65; H, 3.39; N 11.21%.

4c: Yield: 37.8%. Yellow solid. M.p. >250 °C. $[\alpha]_D^{20} = +58^\circ$ (*c* 0.06, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ 7.19 (dd, *J* = 2.3, 6.5 Hz, 1H, ArH), 7.09–7.05 (m, 2H, ArH), 5.92 (s, 1H, PzH), 5.07 (d, *J* = 14.9 Hz, 1H, C*H*H), 5.02 (d, *J* = 14.9 Hz, 1H, CH*H*), 4.63 (dd, *J* = 5.1, 8.8 Hz, 1H, OxH), 4.57 (t, *J* = 9.1 Hz, 1H, OxH), 4.46–4.41 (m, 1H, OxH), 2.97–2.93 (m, 1H, C*H*$(CH_3)_2$), 2.72 (s, 3H, CH_3), 2.37 (s, 3H, CH_3), 0.94 (d, *J* = 7.0 Hz, 3H, CH(C*H*$_3)_2$), 0.84 (d, *J* = 7.0 Hz, 3H, CH(C*H*$_3)_2$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.9, 153.3, 151.5, 140.6, 134.5, 131.6, 128.4, 125.0, 124.5, 107.8, 70.6, 66.7, 52.0, 29.1, 18.9, 16.4, 14.0, 12.2. IR (KBr, cm^{-1}): ν 2953, 2925, 2864, 1618, 1558, 1484, 1463, 1433, 1395, 1347, 1276, 1181, 1149, 1054, 997, 972, 936, 815. MS (*m/z*, ESI^+): 402 (M−Cl). HRMS (*m/z*, ESI^+): found for M−Cl = 402.0798, $C_{18}H_{22}N_3OPd$ requires 402.0798. Anal. Calc. for $C_{18}H_{22}ClN_3OPd$: C, 49.33; H, 5.06; N, 9.59. Found: C, 49.17; H, 5.12; N 9.41%.

4d: Yield: 69.5%. Yellow solid. M.p. >250 °C. $[\alpha]_D^{20} = +137^\circ$ (*c* 0.13, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ 8.55 (d, *J* = 2.0 Hz, 1H, PzH), 7.60 (d, *J* = 2.2 Hz, 1H, PzH), 7.20–7.17 (m, 1H, ArH), 7.07–7.01 (m, 2H, ArH), 6.30 (t, *J* = 2.3 Hz, 1H, PzH), 5.26 (d, *J* = 15.3 Hz, 1H, C*H*H), 5.17 (d, *J* = 15.3 Hz, 1H, CH*H*), 4.57–4.49 (m, 2H, OxH), 4.34–4.29 (m, 1H, OxH), 2.80–2.76 (m, 1H, C*H*$(CH_3)_2$), 0.87 (d, *J* = 7.0 Hz, 3H, CH(C*H*$_3)_2$), 0.75 (d, *J* = 7.0 Hz, 3H, CH(C*H*$_3)_2$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 174.1, 149.0, 145.0, 132.7, 131.8, 128.7, 125.5, 124.6, 106.5, 70.6, 66.9, 56.3, 29.1, 18.8, 14.2. IR (KBr, cm^{-1}): ν 3123, 2958, 2926, 2869, 1712, 1674, 1626, 1575, 1516, 1483, 1438, 1402, 1371, 1277, 1182, 1152, 1105, 1075, 995, 935, 866, 755, 727. MS (*m/z*, ESI^+): 374 (M−Cl). HRMS (*m/z*, ESI^+): found for M−Cl = 374.0485, $C_{16}H_{18}N_3OPd$ requires 374.0485. Anal. Calc. for $C_{16}H_{18}ClN_3OPd$: C, 46.85; H, 4.42; N, 10.24. Found: C, 47.12; H, 4.84; N 10.04%.

4e: Yield: 16.3%. Yellow solid. M.p. 196 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 7.07 (d, *J* = 7.3 Hz, 1H, ArH), 7.01 (t, *J* = 7.6 Hz, 1H, ArH), 6.94 (d, *J* = 7.6 Hz, 1H, ArH), 4.71 (t, *J* = 9.5 Hz, 2H, OxH), 4.07 (s, 2H, CH_2), 4.01 (t, *J* = 9.5 Hz, 2H, OxH), 3.44–3.37 (m, 2H, C*H*$_2$CH$_3$), 2.79–2.72 (m, 2H, C*H*$_2$CH$_3$), 1.57 (t, *J* = 7.0 Hz, 6H, CH$_2$C*H*$_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 175.1, 160.4, 147.9, 128.8, 124.3, 123.9, 123.3, 70.7, 66.7, 58.0, 50.5, 14.1. IR (KBr, cm^{-1}): ν 3432, 3131, 2968, 2925, 2868, 1609, 1565, 1473, 1433, 1396, 1269, 1183, 1143, 1091, 1045, 976, 923, 802, 729. MS (*m/z*, ESI^+): 337 (M−Cl). HRMS (*m/z*, ESI^+): found for M−Cl = 337.0529, $C_{14}H_{19}N_2OPd$ requires 337.0532. Anal. Calc. for $C_{14}H_{19}ClN_2OPd$: C, 45.06; H, 5.13; N, 7.51. Found: C, 45.37; H, 5.24; N 7.48%.

3.6. X-ray crystallography

The crystals of **4e** were obtained by recrystallization from CH_2Cl_2/petroleum ether at room temperature. Crystallographic data for **4e** were measured on a Rigaku-Raxis-IV X-ray diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at 291(2) K. The hydrogen atoms were included but not refined.

The full-matrix least-squares calculations on F^2 were applied on the final refinement. The structure was solved by direct methods. All non-hydrogen atoms were described anisotropically. Its raw data were corrected and the structure was solved using the SHELXL-97 program.

3.7. General procedure for the Suzuki reaction

The palladium complex **4** was dissolved in dioxane or DMF (3 mL). To this solution was added aryl halide (0.5 mmol), phenylboronic acid (0.75 mmol) and base (1.0 mmol). The reaction mixture was then placed in an oil bath with stirring and heated for a certain time. After the reaction mixture was cooled to ambient temperature, 15 mL of diethyl ether and 15 mL of water were added. The organic layer was separated, and the aqueous phase was extracted with 10 mL of diethyl ether. The combined organic phase was dried over $MgSO_4$, filtered and evaporated. The products were isolated by flash chromatography on silica gel (the purified products were identified by comparison of melting points with the literature values or by ^1H NMR spectra).

4. Supplementary material

CCDC 748266 contains the supplementary crystallographic data for **4e**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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