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# Diamine bis(phenolate) and pendant amine bis (phenolate) ligands: catalytic activity for the room temperature palladium-catalyzed Suzuki– Miyaura coupling reaction

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A series of amine bis(phenolate) ligands bearing aryl substituents of varying steric bulk are reported and characterized using single-crystal X-ray diffraction, NMR spectroscopy and high-resolution mass spectrometry experiments. Palladium complexes derived *in situ* from these ligands are evaluated as catalysts for the Suzuki–Miyaura coupling of phenylboronic acid and aryl bromides. High conversions are observed for these reactions in methanol solvent at low catalyst loadings (0.01 mol%), short reaction times (30 min) and mild temperatures (30°C). Conversion is observed for a range of substrates, and is found to depend on the nature of the external base and solvent employed. These findings demonstrate the utility of catalysts derived from late transition metal complexes of amine bis(phenolate) ligands, particularly those bearing bulky cumyl substituents. Copyright © 2015 John Wiley & Sons, Ltd.

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Keywords: palladium; cross-coupling reactions; Mannich; Suzuki; amine bis(phenolate)

## Introduction

The Suzuki coupling of aryl halides and arylboronic acids/esters has become an increasingly important catalytic transformation, allowing the facile preparation of species containing biaryl or substituted aromatic systems.<sup>[1-7]</sup> Palladium complexes have long been employed as the pre-catalyst of choice, in part due to their increased oxygen tolerance and robust reactivity when compared to other late transition metals.<sup>[5–7]</sup> Many of the palladium complexes known to serve as efficient catalysts to date have employed mono- or bidentate phosphine ligands, sometimes employing a mixed-donor set. In general, increasing the steric bulk about the palladium center has led to improved catalyst performance for these phosphine complexes.<sup>[8–12]</sup> However, these complexes may be oxidized under aerobic conditions to the corresponding phosphine oxides, leading to decomposition and hindering catalyst performance. In addition, the cost of these phosphine ligands may be significant, especially for chiral variants.

In an effort to circumvent these problems, the development of new ligand architectures bearing more oxygen-tolerant functionality is desirable. The inclusion of a mixed-donor set is also targeted, as it may afford longer-lived complexes, resulting in more productive catalysis or unexpected reactivity.<sup>[13–23]</sup> A variety of nitrogenand oxygen-based ligands have shown exceptional activity for the Suzuki coupling reaction, including amines,<sup>[3,24]</sup> imines,<sup>[25–28]</sup> substituted bipyridines<sup>[29]</sup> and amino alcohols.<sup>[30]</sup> Group 4 isopropoxide complexes of diamine bis(phenolate) or pendant amine bis(phenolate) ligands (Fig. 1) have exhibited excellent air and moisture sensitivity, and the ligand framework incorporates both amine and phenolate donors. A number of variants of these ligands have been reported,<sup>[31–50]</sup> with most employed as support for group 4 metal complexes in the polymerization of 1-hexene or cyclic ethers. Many of these reports have focused on phenolate substituents that are sterically unencumbered and electron withdrawing, as these features have been shown to promote exceptionally active or long-lived 1-hexene polymerization catalysts.<sup>[35,50–52]</sup>

Fewer studies have explored the utility of late transition metal complexes bearing bulky amine bis(phenolate) ligands. Kol and co-workers have employed bipyrrolidine bis(phenolate) complexes as a scaffold for helically chiral zinc complexes,<sup>[53]</sup> while Periana and co-workers have reported that rhodium complexes of pendant amine bis(phenolate) ligands are active for the C–H activation of benzene.<sup>[54]</sup> Bimetallic complexes of cobalt<sup>[38,55,56]</sup> and nickel<sup>[57]</sup> ligated by both diamine bis(phenolate) and pendant amine bis(phenolate) ligands have exhibited interesting magnetic properties. Iron complexes of both diamine bis(phenolate) and pendant amine bis (phenolate) ligands serve as interesting model compounds for a variety of iron-oxo species implicated in non-heme metalloenzymes such as catechol dioxygenases, as well as exhibiting intriguing reactivity with molecular oxygen.<sup>[46,58–62]</sup> Recent reports from Kozak

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**Figure 1.** (a) Diamine bis(phenolate) and (b) pendant amine bis(phenolate) ligand architectures reported in this study ( $R = CH_3$ ,  $C(CH_3)_3$ ,  $C(CH_3)_2Ph$ ; n = 1, 2).

and co-workers have described the Kumada coupling of alkyl halides with aryl grignards mediated by iron complexes bearing a variety of amine bis(phenolate) ligands.<sup>[36,37,39–43,63]</sup>

We have only identified five reports of palladium complexes of amine bis(phenolate) ligands to date, all of which employ diamine bis(phenolates) (Fig. 1(a)) rather than pendant amines (Fig. 1(b)). Balakrishna and co-workers reported the preparation of a pyrazine bis(phenolate) ligand (Fig. 2(a)) and corresponding activity of in situ generated palladium complexes for the Suzuki-Miyaura and Mizoroki-Heck cross-coupling reactions.<sup>[44,64]</sup> Related work by Zhou and co-workers describes the catalytic efficiency of a system derived from cyclic diamine bis(phenolates) (Fig. 2(b)) with comparable findings.<sup>[65]</sup> Lü and co-workers have reported the formation of a distorted square-planar palladium complex featuring a ligand derived from o-phenylenediamine and 2-methoxyphenol (Fig. 2(c)), and accompanying activity as a styrene polymerization catalyst.<sup>[66]</sup> Chaudhary and Bedekar have reported a series of bidentate ligands derived from a 1-( $\alpha$ -aminobenzyl)-2-naphthol framework, as well as the related piperazine bis(naphtholate) ligand (Fig. 2(d)).<sup>[67]</sup> Palladium complexes of these ligands have been employed as catalysts for a multicomponent Wittig-Suzuki reaction to generate styryl biphenyl compounds. All five of these reports focus on ligands with a diamine core, rather than a pendant amine; this may be due to the structural similarities between diamine bis(phenolate) ligands and the ubiquitous salen ligands.

The ligands used in this study are obtained from a double Mannich reaction (Scheme 1) utilizing two equivalents of a substituted phenol, two equivalents of formaldehyde and a single equivalent of a primary amine or a secondary diamine. The synthesis of amine bis(phenols) was originally reported by Weatherbee and co-workers in 1952,<sup>[68–70]</sup> although it was not until much later that amine bis(phenolates) were employed as ligands for a variety



Figure 2. Previously reported amine bis(phenolate) ligands to support palladium.



**Scheme 1.** Synthesis of diamine bis(phenolate) (1–3) and pendant amine bis(phenolate) (4–9) ligands used in this study. 1:  $R = CH_3$ ; 2:  $R = C(CH_3)_3$ ; 3:  $R = C(CH_3)_2Ph$ ; 4:  $R = CH_3$ , n = 1; 5:  $R = C(CH_3)_3$ , n = 1; 6:  $R = C(CH_3)_2Ph$ , n = 1; 7:  $R = CH_3$ , n = 2; 8:  $R = C(CH_3)_3$ , n = 2; 9:  $R = C(CH_3)_2Ph$ , n = 2.

of different metal centers. The first reports utilized the ligands to produce model molybdenum,<sup>[71]</sup> copper<sup>[72,73]</sup> and iron<sup>[74]</sup> complexes for the enzymes molybdenum hydroxylase, galactose oxidase and catechol 1,2-dioxygenase, respectively. Early work on this ligand class also included reports of copper,<sup>[75]</sup> tungsten,<sup>[47]</sup> molybdenum<sup>[47]</sup> and titanium<sup>[31]</sup> complexes. Particular success was seen with the group 4 metal complexes used in the polymerization of olefins and cyclic esters. We have recently reported that these amine bis(phenols) and their corresponding titanium complexes may be easily prepared in high yield and purity by undergraduate students in the teaching laboratory.<sup>[76]</sup>

As part of our interest in expanding the range of available phosphine-free, low-cost and robust ligand frameworks for the palladium-catalyzed Suzuki–Miyaura coupling reaction, we sought to prepare new variants of these ligands. We report herein the synthesis and characterization of several new amine bis(phenolate) ligands bearing bulky cumyl substituents obtained via a Mannichtype coupling reaction in poly(ethylene glycol) (PEG) solvent. The *in situ* activity of the palladium complexes of these ligands was assessed using the coupling of 4'-bromoacetophenone and phenylboronic acid as a model reaction.

## **Experimental**

## **General considerations**

Palladium precursors were purchased from Strem Chemicals Inc., 2,4-di-*tert*-butylphenol and 2,4-dimethylphenol were purchased from Alfa Aesar, 1-bromo-4-nitrobenzene and potassium carbonate were purchased from Acros Organics, and all other reagents were purchased from Sigma-Aldrich Ltd. All reagents were of high purity, and were used without further purification unless otherwise noted. Ligands were prepared using reported literature procedures.<sup>[76,77]</sup> All products were characterized using <sup>1</sup>H NMR and <sup>13</sup>C{<sup>1</sup>H} NMR, with peak assignments assisted by the use of DEPT-135, <sup>1</sup>H–<sup>13</sup>C HSQC and <sup>1</sup>H–<sup>13</sup>C HMBC experiments. NMR spectra were recorded with a Bruker Avance 400 spectrometer using a BBO probe operating at 400.1325 MHz (<sup>1</sup>H) or 100.6208 MHz (<sup>13</sup>C). Chemical shifts are reported in ppm downfield of SiMe<sub>4</sub>, and referenced using the

solvent residual peak. Fourier transform infrared (FT-IR) spectra were recorded with a Thermo Nicolet 6700 FT-IR spectrometer as KBr pellets. GC-MS was conducted using a Varian 3900 GC/Saturn 2100 T MS with a fused silica capillary (Phenomenex Zebron ZB-5MSi, 30 m × 0.25 mm × 0.25  $\mu$ m). Accurate mass determination was conducted by the Ohio State University Mass Spectrometry and Proteomics Facility in Columbus, OH using a Bruker Maxis electrospray ionization quadrupole TOF mass spectrometer. Elemental analyses were performed by Midwest Microlab LLC, Indianapolis, IN.

#### **Ligand syntheses**

Amine (6 mmol), phenol (12 mmol), 37 wt% aqueous formaldehyde (12 mmol) and 2.0 g of PEG-400 were combined in a 20 ml scintillation vial with a Teflon cap and stirred at 75°C for 24 h in a heated block reactor. The mixture was cooled to room temperature, 2 ml of  $CH_2Cl_2$  was added to the vial to loosen the solid, the mixture was filtered and washed with methanol. The solid was ground with a mortar and pestle, dissolved in a minimal amount of hot  $CH_2Cl_2$ , precipitated in 200 ml of rapidly stirring methanol and filtered. Ligands requiring further purification were recrystallized from ethyl acetate. Full experimental details for the preparation and characterization of **3**, **6**, **7** and **9** are provided in the supporting information.

#### General conditions for Suzuki coupling reactions

To a 20 ml scintillation vial equipped with a magnetic stir bar, 4bromoacetophenone (0.102 g, 0.50 mmol, 1 eq.), phenylboronic acid (0.091 g, 0.75 mmol, 1.5 eq.), potassium carbonate (0.142 g, 1.00 mmol, 2 eq.) and methanol (5 ml) were added. Amounts of 0.10 ml of a 0.00050 M palladium precursor stock solution in CH<sub>2</sub>Cl<sub>2</sub> and 0.10 ml of a 0.00050 M ligand stock solution in CH<sub>2</sub>Cl<sub>2</sub> were added via a syringe. The vial was placed in an aluminium block heater regulated at 30°C, and stirring was initiated. After 30 min, the vial was removed from the heat and partitioned between diethyl ether (8 ml) and water (8 ml). The aqueous layer was extracted with diethyl ether  $(2 \times 6 \text{ ml})$ , and the combined organic layers were dried over magnesium sulfate and filtered. An aliquot of the sample was diluted with CH<sub>2</sub>Cl<sub>2</sub> and analyzed using GC-MS (50°C, hold 2 min; 20°C min<sup>-1</sup> to 250°C, hold 10 min; 2.0 ml min<sup>-1</sup> flow rate, 50:1 split ratio) to determine percent conversion. Identity of products was determined using GC-MS and confirmed using <sup>1</sup>H NMR spectroscopy.

#### Crystallographic solution and refinement details

Crystallographic data were obtained at 200 (±2) K with a Bruker SMART X2S benchtop diffractometer using graphitemonochromated Mo K $\alpha$  ( $\lambda = 0.71073$  Å) radiation, employing samples that were mounted in inert oil and transferred to a cold gas stream on the diffractometer. Using Olex2,<sup>[78]</sup> the structure was solved with the ShelXT<sup>[79]</sup> structure solution program using direct methods and refined with the ShelXL<sup>[80]</sup> refinement package using least squares minimization (on  $F^2$ ) with R based on  $F_o^2 \ge 2\sigma(F_o^2)$  and  $wR^2$  based on  $F_o^2 \ge -3\sigma(F_o^2)$ . Anisotropic displacement parameters were employed throughout for the non-hydrogen atoms, and hydrogen atoms attached to carbon atoms were added at calculated positions and refined by use of a riding model employing isotropic displacement parameters based on the isotropic displacement parameter of the attached atom. Phenol hydrogen atom positions were located in the difference map, but were restrained to an

effective distance of 0.84(0.02) Å to best fit the data at 200 K. ORTEP diagrams were generated using CrystalMaker<sup>®</sup>, a crystal and molecular structures modeling program for Mac and Windows (CrystalMaker Software Ltd, Oxford, UK, www.crystalmaker.com). The structural reports described in this work have been deposited at the Cambridge Crystallographic Data Centre (numbers CCDC 1408668–1408670) and may be obtained at http://www.ccdc.cam. ac.uk/.

## **Results and discussion**

#### **Characterization of ligands**

Ligands **1–9** were prepared in moderate to good yield (Scheme 1) using a procedure modified from that reported by Kerton and coworkers.<sup>[77]</sup> The use of PEG-400 as a solvent allowed for slightly higher reaction temperatures and reduced solvent volume when compared to literature procedures employing alcohols or water as the solvent. As an additional benefit, a large number of ligand variants can be prepared simultaneously using an aluminium reactor block without the need for a typical reflux condenser setup. All ligands were purified by precipitation from a dichloromethane– methanol mixture, and recrystallized from ethyl acetate to yield a colorless crystalline solid.

Ligands **3**, **6**, **7** and **9** are reported here for the first time, and exhibit spectral and structural features similar to those expected based on comparisons to related species. Single crystals of **3**, **6** and **7** suitable for X-ray diffraction studies were obtained by slow evaporation of a saturated solution in ethyl acetate at room temperature (**3** and **6**) or 0°C (**7**). ORTEP<sup>[81]</sup> diagrams of **3** (Fig. 3), **6** (Fig. 4) and **7** (Fig. 5) are shown with selected bond lengths and angles collected in the corresponding figure caption, and relevant experimental parameters for all three compounds are presented in Table 1. All three ligands exhibit intramolecular hydrogen bonding between phenol and amine functional groups, as has been observed for related amine bis(phenols).<sup>[36,37,40–42,44,66,82]</sup> Heavy atom (O...N) interatomic distances are consistent with the presence of hydrogen bonds, and are within the range of those reported for similar amine bis(phenolate) ligands.

The structure of  $\mathbf{3}$  exhibits a crystallographically imposed inversion center, such that half of the molecule lies within the



**Figure 3.** ORTEP diagram for **3** shown with 50% displacement ellipsoids and the numbering scheme for non-hydrogen atoms shown. Hydrogen atoms are draw arbitrarily small for clarity. Selected bond distances (Å) and angles (°) for **3**: N1–C7 1.471(2); N1–C8 1.464(2); N1–C9 1.465(2); O1–C1 1.3664(18); O1–H1 0.902(16); O1...N1 2.601; C7–N1–C8 109.93(12); C7–N1–C9 111.21(12); C8–N1–C9 111.48(13); O1–C1–C2 120.57(14); O1–C1–C6 118.64(13).



**Figure 4.** ORTEP diagram for **6** shown with 50% displacement ellipsoids and the numbering scheme for selected non-hydrogen atoms shown. Disordered phenyl ring left intact. Hydrogen atoms are draw arbitrarily small for clarity. Selected bond distances (Å) and angles (°) for **6**: N1–C1 1.465(2); N1–C5 1.471(2); N1–C30 1.479(2); N2–C2 1.457(2); N2–C3 1.462(2); N2–C4 1.469(2); O1–C11 1.3666(19); O2–C36 1.360(2); O1–H1 0.877; O1… N1 2.824; O2–H2 0.878; O2…N2 2.764; C1–N1–C5 111.36(13); C1–N1–C30 111.87(12); C5–N1–C30 110.49(12); C2–N2–C3 110.94(15); C2–N2–C4 10.19(15); C3–N2–C4 108.54(14); O1–C11–C10 118.48(14); O1–C11–C16 120.01(14); O2–C36–C31 122.60(15); O2–C36–C35 117.13(15).



**Figure 5.** ORTEP diagram for **7** shown with 50% displacement ellipsoids and the numbering scheme for non-hydrogen atoms shown. Disordered methyl groups C8 and C17 left intact. Hydrogen atoms are draw arbitrarily small for clarity. Selected bond distances (Å) and angles (°) for **7**: N1–C1 1.474(2); N1–C19 1.4727(19); N1–C10 1.4759(19); N2–C21 1.475(2); N2–C22 1.461(2); N2–C23 1.468(2); O1–C7 1.3732(19); O2–C16 1.3640(18); O1...N1 2.730; O2...N2 2.706; C1–N1–C10 109.98(12); C1–N1–C19 108.99(13); C10–N1–C19 111.15(12); C21–N2–C22 111.25(13); C21–N2–C23 107.71(13); C22–N2–C23 108.30(14); O2–C16–C15 115.43(14); O2–C16–C11 123.97(13); O1–C7–C6 117.58(14); O1–C7–C2 121.09(14).

asymmetric unit. In the molecular depiction of **3**, the nitrogen atom adopts a distorted pyramidal geometry, with the sum of angles about N1 equal to 332.62°. Hydrogen bonding is observed between the phenol OH and neighboring nitrogen atom, with an O...N interatomic distance of 2.601 Å. This distance is notably shorter than those observed for **6** and **7**, and is similar to the value of 2.633 Å observed for a pyrazine-bridged diamine bis(phenolate) ligand.<sup>[44]</sup> A cursory examination of the structure for **3** reveals less steric congestion than is observed for pendant amine bis(phenolates) (i.e. **4–9**), facilitating a stronger hydrogen bonding interaction. In the molecular depiction of **6**, the nitrogen atoms adopt a distorted pyramidal geometry, with the sum of angles about N1 and N2 equal to 330.12°

and 327.10°, respectively. Weak hydrogen bonding is observed between the phenol OH and neighboring nitrogen atoms, with O...N interatomic distances of 2.764 and 2.824 Å. The steric bulk of **6** is similar to that observed for **5**, as evidenced by the sum of the angles around the quaternary carbon of the cumyl (325.29° and 325.57°) or *t*-butyl (324.11° and 324.92°) group in the 2-position.<sup>[82]</sup> In the molecular depiction of **7**, the nitrogen atoms adopt a distorted pyramidal geometry, with the sum of angles about N1 and N2 equal to 330.10° and 327.27°, respectively. Weak hydrogen bonding is observed between the phenol OH and neighboring nitrogen atoms, with O...N interatomic distances of 2.706 and 2.730 Å. Though the lengths of the methylene chain in **6** and **7** differ, the solid-state structure of these two ligands are quite similar to one another, as well as to related amine bis(phenolate) ligands bearing pendant donors.<sup>[37,40,42]</sup>

In the <sup>1</sup>H NMR spectra (CDCl<sub>3</sub>) for these ligands, **3** exhibits a broad singlet at 10.25 ppm attributed to the phenol OH, while 6, 7 and 9 exhibit similar broad signals between 9.40 and 9.44 ppm. The difference in chemical shift may be attributed to the structural differences between the ligands, namely the diamine bis(phenolate) (3) and pendant amine bis(phenolate) (6, 7 and 9). These chemical shifts lie well within the reported range for similar ligands.<sup>[37,40,43,44,63]</sup> Other spectral features in the <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra support the proposed structural formulation depicted in Scheme 1, and are consistent with the solid-state structures of 3, 6 and 7 (see above). The equivalence of the proton signals corresponding to the methylene adjacent to the phenol residue suggests that the hydrogen bonding observed in the solid state is not present in CDCl<sub>3</sub> solution. Were this not the case, hydrogen bonding would lead to restricted rotation of the phenol ring, and cause these methylene signals to be split into two diasterotopic resonances. While the <sup>1</sup>H NMR spectra for ligands **3**, 6 and 9 feature a large number of overlapping aromatic signals, these correlate with well-separated peaks in the <sup>13</sup>C{<sup>1</sup>H} spectrum, and complete assignments may be made with the assistance of data from HSQC and HMBC experiments. Bands between 3414 and  $3453 \text{ cm}^{-1}$  in the FT-IR spectra are observed for ligands **3**, **6**, 7 and 9, and are assigned as the phenolic OH stretch. These values are consistent with those reported in the literature for related ligands.[36,37,43,44,63,66]

#### **Catalytic studies**

In order to assess the properties of these ligands relative to other reported amine bis(phenols), catalytic studies were undertaken using palladium complexes generated in situ from a 1:1 mixture of the chosen ligand (1-9) and palladium(II) acetate. For ease of characterization, the initial survey of catalyst activity (Table 2) was conducted at 30°C in methanol, using 4'-bromoacetophenone and phenylboronic acid as the coupling partners, and potassium carbonate as an external base. Using ligand 1 in conjunction with palladium(II) acetate at a catalyst loading of 1 mol% (Table 2, entry 1) or 0.1 mol% (entry 2), no unreacted 4'-bromoacetophenone is observed in the 'H NMR spectrum after 30 min, indicating >99% conversion to the coupled product; these findings were confirmed using GC-MS. Further reducing the catalyst loading to 0.01 mol% (entry 3) generates a reaction mixture with 56.3% of the available 4'-bromoacetophenone converted to the coupled product, as determined by comparing the integrated area for each species in the GC-MS chromatogram.

With these conditions established, the remaining ligands (**2–9**) were evaluated using 0.01 mol% Pd(OAc)<sub>2</sub> (Table 2, entries 4–11).

Table 1. Crystallographic data for ligands 3, 6 and 7					
Compound	3	6	7		
Empirical formula	$C_{54}H_{64}N_2O_2$	$C_{54}H_{64}N_2O_2$	C <sub>23</sub> H <sub>34</sub> N <sub>2</sub> O <sub>2</sub>		
Formula weight	773.07	773.07	370.52		
Crystal size	0.62 × 0.31 × 0.16	0.48 × 0.4 × 0.32	$0.55 \times 0.48 \times 0.24$		
Crystal system	Triclinic	Triclinic	Monoclinic		
Space group	P-1	P-1	P21/c		
a (Å)	8.7770(14)	8.2644(9)	17.951(2)		
b (Å)	9.5027(18)	10.9137(14)	8.4276(10)		
<i>c</i> (Å)	14.581(3)	25.659(3)	14.5978(18)		
α (°)	107.320(6)	94.108(4)	90		
β (°)	102.688(6)	97.725(4)	107.074(4)		
γ (°)	99.219(6)	98.263(4)	90		
V (Å <sup>3</sup> )	1098.9(3)	2259.8(5)	2111.1(4)		
Ζ	1	2	4		
$ ho_{ m cacld} ({ m gcm}^{-3})$	1.168	1.136	1.166		
$\mu$ (mm <sup>-1</sup> )	0.070	0.068	0.074		
F(000)	418.0	836.0	808.0		
Radiation	Mo K <sub><math>\alpha</math></sub> ( $\lambda$ = 0.71073)	Mo K <sub><math>\alpha</math></sub> ( $\lambda$ = 0.71073)	Mo $K_{\alpha}$ ( $\lambda = 0.71073$ )		
$2\theta$ limit (°)	4.578 to 50.164	4.25 to 50.13	4.748 to 50.124		
	$-10 \le h \le 10$	$-9 \le h \le 9$	-21 < <i>h</i> < 21		
	$-11 \le k \le 11$	$-12 \le k \le 12$	-10 < k < 10		
	−17 <i>≤l≤</i> 17	-30 <i>≤I≤</i> 30	-17 < <i>l</i> < 17		
Total data collected	10 789	22 177	19 889		
No. of independent reflections	3861	7901	3734		
No. of observed reflections	2836	5453	2880		
R <sub>int</sub>	0.0385	0.0350	0.0400		
Abs correction	Multiscan (SADABS)	Multiscan (SADABS)	Multiscan (SADABS)		
Range of transmission	0.6286–0.7452	0.6982–0.7452	0.6936-0.7452		
Data/restraints/parameters	3861/1/270	7901/84/572	3734/2/258		
$R_1 \left[ F_{\rm o}^2 \ge 2\sigma (F_{\rm o}^2) \right]$	0.0461	0.0477	0.0420		
$wR_2 \left[F_o^2 \ge -3\sigma(F_o^2)\right]$	0.1149	0.1140	0.1014		
GOF	1.035	1.042	1.049		
Largest peak/hole (e Å <sup>-3</sup> )	0.19/-0.23	0.16/-0.23	0.17/-0.20		

In general, percent conversion increases as the steric bulk and electron-donating ability of the ligand increase, within a set of similar ligands. For example, the smaller ligand 4 bearing methyl substituents generates a conversion of 51.5% (entry 6), while the more electron-donating ligand bearing t-butyl groups (5) results in a notable increase to 65.9% (entry 7). Having similar sterics and electronics to 5, the cumyl ligand (6) demonstrates a comparable conversion of 65.0% (entry 8). A parallel trend has been observed for catalyst systems employing phosphine ligands, where increased steric bulk and electron-rich ligands lead to improved catalyst performance.<sup>[8-12]</sup> It is notable that previous reports of palladium systems featuring similar ligand sets have focused on the diamine bis(phenolates), rather than pendant amine bis (phenolates).<sup>[44,64–67]</sup> In our hands, the corresponding pendant amine bis(phenolate) ligands exhibit slightly enhanced catalyst performance when compared with the corresponding diamine bis(phenolates). As an example, when paired with Pd(OAc)<sub>2</sub>, the cumyl substituted diamine ligand 3 (entry 5) exhibits 47.3% conversion, while the corresponding cumyl-substituted pendant amine ligands 6 and 9 (entries 8 and 11, respectively) exhibit higher conversions of 65.0% and 63.8% under the same conditions. Given the relatively high percent conversion for systems containing the newly reported cumyl-substituted ligands (3, 6 and 9), further studies were conducted using ligand 9. The electronic and steric properties of these cumyl-substituted ligands appear at first glance to be similar to those of related *t*-butyl-substituted ligands, allowing for a clear assessment of ligand performance.

Employing bis(benzonitrile) palladium(II) chloride as the metal precursor in conjunction with **9** results in a decrease in catalytic performance (Table 2, entry 12; 38.7%) when compared to palladium(II) acetate. No cross-coupling activity is observed when palladium(II) chloride is employed as a precursor (entry 13), though this may be attributed in part to the reduced solubility of the salt. Palladium(0) precursors (entries 14 and 15) are also found to be effective at forming catalytically active species, albeit with reduced efficiency compared with palladium(II) acetate.

Using the conditions established by this survey, the effects of solvent and external base on catalyst performance were evaluated (Table 3). The reaction is found to proceed in ethanol (entry 2, 33.3%), 2-propanol (entry 3, 26.4%) and PEG (entry 4, 17.4%) solvents. It is notable that increasing alkyl or ether chain length corresponds to a decrease in catalyst performance. Negligible or no catalytic activity is observed for the polar aprotic solvents diethyl ether (entry 5) and acetonitrile (entry 6), as well as for toluene (entry 7), a relatively non-polar solvent. The identity of the external base is found to play a significant role in catalyst performance. Catalyst performance comparable to that observed with potassium carbonate is noted when potassium hydroxide (entry 8) or sodium phosphate (entry 11) is employed. The relatively weak bases sodium bicarbonate (entry 9) and sodium acetate (entry 10) support moderate



<sup>a</sup>Catalyst loading relative to 4-bromoacetophenone. Reaction conditions: 4-bromoacetophenone (0.50 mmol, 1 eq.), phenylboronic acid (0.75 mmol, 1.5 eq.),  $K_2CO_3$  (1.0 mmol, 2 eq.), ligand (0.10 ml of a 0.0005 M stock solution in  $CH_2CI_2$ ), palladium(II) acetate (0.10 ml of a 0.0005 M stock solution in  $CH_2CI_2$ ), methanol (5.0 ml).

<sup>b</sup>Conversion of 4-bromoacetophenone to coupled product by comparison of integrated area in the GC-MS chromatogram. <sup>c</sup>No coupled product detected.

<sup>d</sup>dba = dibenzylideneacetone,  $C_{17}H_{14}O$ .

<b>Table 3.</b> Dependence of observed catalytic activity on external base and solvent <sup>a</sup>					
	B(OH) <sub>2</sub>	0.01 mol% [Pd(OAc) <sub>2</sub> ] 0.01 mol% Ligand <b>9</b> 2 eq. base			
Br	1.5	solvent, 30°C 30 minutes			
Entry	Solvent	Base	Conversion (%) <sup>b</sup>		
1	MeOH	K <sub>2</sub> CO <sub>3</sub>	62.8		
2	EtOH	K <sub>2</sub> CO <sub>3</sub>	33.3		
3	i-PrOH	K <sub>2</sub> CO <sub>3</sub>	26.4		
4	PEG-400	K <sub>2</sub> CO <sub>3</sub>	17.4		
5	Et <sub>2</sub> O	K <sub>2</sub> CO <sub>3</sub>	2.8		
6	MeCN	K <sub>2</sub> CO <sub>3</sub>	nd <sup>c</sup>		
7	Toluene	K <sub>2</sub> CO <sub>3</sub>	0.9		
8	MeOH	КОН	57.8		
9	MeOH	NaHCO <sub>3</sub>	27.7		
10	MeOH	NaOAc	32.6		
11	MeOH	Na <sub>3</sub> PO <sub>4</sub>	65.6		

<sup>a</sup>Reaction conditions: 4-bromoacetophenone (0.50 mmol, 1 eq.), phenylboronic acid (0.75 mmol, 1.5 eq.), base (1.0 mmol, 2 eq.), ligand **9** (0.10 ml of a 0.0005 M stock solution in  $CH_2Cl_2$ ), palladium(II) acetate (0.10 ml of a 0.0005 M stock solution in  $CH_2Cl_2$ ), solvent (5.0 ml). <sup>b</sup>Conversion of 4-bromoacetophenone to coupled product by comparison of integrated area in the GC-MS chromatogram. <sup>c</sup>No coupled product detected.

conversions under these conditions. In general, percent conversion increases as a function of basicity, as assessed by a comparison of  $pK_a$  values for the conjugate acids.<sup>[83]</sup>

To further probe the utility of this catalyst system, a series of cross-coupling reactions were conducted in which the identity of the aryl halide was varied (Table 4). While moderate conversion to the coupled product is noted for bromobenzene (entry 1, 32.4%), 4-bromotoluene (entry 2, 33.4%) and 4-bromoanisole (entry 4, 40.1%), catalytic activity is notably decreased when the bulky methyl substituent is moved closer to the aryl bromide (entries 4 and 5). Increased conversion is observed when both the reaction time (2h) and temperature (60°C) are increased (entries 3 and 6). Using substrates featuring electron-donating groups para to the aryl-bromine bond such as 4-bromoaniline (entry 8) results in a marked decrease in coupling efficiency (4.7%), while the strongly electron-withdrawing groups in 1bromo-4-nitrobenzene (entry 10, 94.1%) and 4-bromobenzonitrile (entry 11, >99%) facilitate near quantitative conversion to the coupled products. Moderate conversion (entry 9, 73.6%) is noted when 4-bromoaniline is coupled at elevated temperatures for 2 h. Bromoaryl ketones such as 4-bromoacetophenone (entry 12, 84.5%) are well tolerated, as is the aldehyde functional group in 4-bromobenzaldehyde (entry 13, >99%). Moving these substituents to the meta position results in a marked decrease in catalytic

Table 4.         Survey of substrate scope <sup>a</sup>						
Br R	+ 1.5 B(OH) <sub>2</sub>	0.01 mol% [Pd(OAc) <sub>2</sub> ] 0.01 mol% Ligand <b>9</b> 2 eq. K <sub>2</sub> CO <sub>3</sub> MeOH, 30°C	+			
Entry	R	Time (h)	Conversion (%) <sup>b</sup>			
1	н	0.5	32.4			
2	<i>p</i> -Me	0.5	33.4			
3	<i>p</i> -Me	2 <sup>d</sup>	86.0			
4	<i>p</i> -OMe	0.5	40.1			
5	o-Me-p-Me	0.5	3.4			
6	o-Me-p-Me	2 <sup>d</sup>	36.7			
7	<i>m</i> -Me- <i>p</i> -Me	0.5	6.9			
8	$p-NH_2$	0.5	4.7			
9	$p-NH_2$	2 <sup>d</sup>	73.6			
10	p-NO <sub>2</sub>	0.5	94.1			
11	<i>p</i> -CN	0.5	>99			
12	<i>p</i> -C(O)Ph	0.5	84.5			
13	<i>p</i> -C(O)H	0.5	>99			
14	<i>m</i> -C(O)H	24	23.2			
15	<i>o</i> -C(O)Me	96 <sup>d</sup>	nd <sup>c</sup>			
16	p-C(O)Me-PhCl	96 <sup>d</sup>	3.9			
17	<i>o</i> -F	0.5	12.2			
18	<i>o</i> -F	2 <sup>d</sup>	73.6			
19	o-F-Phl	0.5	36.4			
20	o-F-PhI	2 <sup>d</sup>	99.1			

<sup>a</sup>Reaction conditions: aryl halide (0.50 mmol, 1 eq.), phenylboronic acid (0.75 mmol, 1.5 eq.), base (1.0 mmol, 2 eq.), ligand **9** (0.10 ml of a 0.0005 M stock solution in CH<sub>2</sub>Cl<sub>2</sub>), palladium(II) acetate (0.10 ml of a 0.0005 M stock solution in CH<sub>2</sub>Cl<sub>2</sub>), solvent (5.0 ml).

<sup>b</sup>Conversion of 4-bromoacetophenone to coupled product by comparison of integrated area in the GC-MS chromatogram. <sup>c</sup>No coupled product detected.

<sup>d</sup>Reaction conducted at 60°C.

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activity (entry 14, 23.2%), even after extended reaction times. Similarly, no coupled product is observed when 2'bromoacetophenone is employed (entry 15), despite extended reaction times and elevated temperatures. This is likely a result of increased steric bulk near the aryl-bromine bond rendering the substrate too large to interact with the metal complexes featuring the bulky cumyl substituents. Although the inductive withdrawal of electron density and donation of the lone pair of a fluoride substituent are often closely balanced, the additional steric bulk in the ortho position results in somewhat reduced conversion (entry 17, 12.2%); increasing the reaction time and temperature results in increased coupling activity (entry 18, 73.6%). Using the more facile aryl iodide, enhanced conversion at both 30°C (entry 19, 36.4%) and 60°C (entry 20, 99%) is observed. Aryl chlorides are significantly less reactive, showing only trace conversion to the coupled product (entry 16, 3.9%) after four days at 60°C.

Our data suggest that the system reported in this work is comparable, if not superior, to similar catalyst systems based on amine bis (phenolate) scaffolds reported in the literature to date. Using a sterically less demanding pyrazine-bridged bis(naphtholate) ligand (Fig. 2(d)) and Pd(OAc)<sub>2</sub> at 0.1 mol% catalyst loading in dioxanewater solvent, Bedekar and co-workers obtained biphenyl in 85% yield (turnover number of 854) after 4 h at 95°C.<sup>[67]</sup> This coupling reaction relied on iodobenzene as the aryl halide, and required longer reaction times at higher catalyst loadings than are required for the system reported in the present work. Balakrishna and co-workers have also reported using palladium complexes featuring pyrazinebridged bis(phenolate) ligands (Fig. 2(a)) for cross-coupling applications.<sup>[44,64]</sup> At catalyst loadings of 0.5 mol%, quantitative conversion of several aryl bromides to the corresponding biphenyl species was observed after 10 min at room temperature in methanol solution. The authors also report high yields (95%) at 0.0125 mol% catalyst loading, similar to those observed for the catalysts derived from 1-9 as reported here. Zhou and co-workers observed yields of 40% under conditions comparable to those described in this work, with higher yields (85-99%) observed upon refluxing the reaction mixture in acetone-water solvent for 1-3 h.<sup>[65]</sup> Collectively, these findings support the claim that palladium complexes derived from amine bis(phenolate) ligands are highly effective catalysts for the Suzuki–Miyaura coupling of aryl bromides and phenylboronic acid. Our results also suggest that pendant amine bis(phenolate) ligands represent an underexploited and highly active system for palladium-mediated cross-coupling reactions under mild conditions.

## Conclusions

A catalyst system for the Suzuki coupling of aryl halides and arylboronic acids derived from diamine bis(phenolate) and pendant amine bis(phenolate) liagnds has been developed. This system shows exceptional activity at low catalyst loadings under mild temperatures in air, and requires short reaction times. The most effective catalyst systems incorporate oxoanion bases and short-chain polar protic solvents, and a wide range of substrates are tolerated. While both ligand scaffolds show activity, the highest conversions were observed for pendant amine bis(phenolate) ligands featuring large substituents. These findings suggest that pendant amine bis(phenolate) ligands represent an underexploited class of ligands for late transition metal-catalyzed transformations. Further studies directed towards elucidating the structure of the palladium complexes and probing the effect of ligand donor identity on catalyst performance are underway in our laboratory, and will be reported in due course.

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