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FULL PAPER

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# Synthesis, structure, and characterization of picolyl- and benzyl-linked biphenyl palladium N-heterocyclic carbene complexes and their catalytic activity in acylative cross-coupling reactions

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**Abstract**

N-heterocyclic carbene ligands with picolyl ($L^1H_2Br_2$, $L^3H_2Br_2$) and benzyl ($L^2H_2Br_2$, $L^4H_2Br_2$) linked biphenyl backbone were synthesized and characterized. Their palladium(II) complexes $[PdL^1]Br_2$ (**1**), $[PdL^2Br_2]$ (**2**), $[PdL^3]Br_2$ (**3**), and $[PdL^4Br_2]$ (**4**) were synthesized by direct method using $Pd(OAc)_2$. All complexes (**1**–**4**) were characterized by CHN analysis, electrospray ionization-MS, nuclear magnetic resonance, and single-crystal X-ray diffraction. Molecular structures confirm the distorted square planar geometry around the Pd(II) center. All of them showed good catalytic activity in acylative Suzuki cross coupling of phenyl boronic acid with benzoyl chloride to afford benzophenone in good yields.

**KEYWORDS**

acylative Suzuki coupling, biaryl ketones, biphenyl NHC ligand, palladium NHC

## 1 | INTRODUCTION

In the past few decades, N-heterocyclic carbenes (NHCs) have gained immense attention in organometallic chemistry because of their inherent sigma-donating and poor pi-accepting abilities.[1–3] NHCs can bind with metals to form stable metal carbene complexes which are used as catalysts in olefin metathesis,[4] cross-coupling reactions,[5] transfer hydrogenation of ketones,[6] biological activity,[7] etc. Based on the literature reports, we found that biaryl-appended NHC–metal complexes were less explored including biphenyl analogs in terms of synthesis, structure, and catalysis.[8–10] Inspired by the coordination chemistry of our own work on biphenyl copper(II) complexes[11] and our previous experience on NHC,[12] we became interested in biphenyl NHCs and their metal complexes. The coordination and catalytic aspect of these NHC complexes especially with palladium are desirable, particularly for cross-coupling reactions. Recently, we have reported the monoacetonitrile- and diacetonitrile-coordinated Pd–NHC biphenyl complexes and their catalytic efficiency in Suzuki–Miyaura cross-coupling reaction between aryl halides and boronic acids to afford biaryls in water.[13] In this paper, we describe the synthesis, structure, and catalytic efficiency of palladium NHC–linked picolyl and benzyl biphenyl backbone in acylative Suzuki cross-coupling reaction of aryl boronic acids with benzoyl chlorides to afford biaryl ketones.

## 2 | EXPERIMENTAL

### 2.1 | General information

Unless otherwise stated all the reactions were carried out under the atmosphere of nitrogen using an oven-dried glassware and standard Schlenk line techniques. All the solvents were distilled prior to use using standard

methods. Toluene was distilled from sodium/benzophenone and all other solvents were distilled from $CaH_2$ and used. Commercially available chemicals were obtained from Sigma-Aldrich,Bangalore, India, Alfa Aesar, Hyderabad, India, and Loba Chemie, Mumbai, India and were used without further purification. Thin-layer chromatography (TLC) was performed on precoated silica gel 60 $F_{254}$ on aluminum plates and UV light (254 nm). Column chromatography was performed on silica gel 100–200-mesh size. $^1$H and $^{13}$C nuclear magnetic resonance (NMR) spectra were recorded on Bruker Avance II 400 MHz ($^1$H) and 100 MHz ($^{13}$C), and chemical shifts (δ) were given in parts per million. The residual solvent signals were used as references for $^1$H and $^{13}$C NMR spectra with tetramethylsilane as an internal standard. Electrospray ionization-MS (ESI-MS) was recorded on Agilent 6540 UHD quadrupole time-of-flight mass spectrometer. Elemental analyses were carried out using FLASH 2000 organic elemental analyzer. Single-crystal X-ray data were collected on a Rigaku-Oxford Xcalibur Eos single-crystal X-ray diffractometer with Mo-Kα radiation (λ = 0.71073 Å). Structure solution and refinement were performed using SHELXS-97,[14] SHELXL,[15] respectively, in the Olex 2.1–2 package.[16] In all the structures, all nonhydrogen atoms were refined anisotropically. The hydrogen atoms were omitted for clarity.

## 2.2 | Synthesis of ligands

### 2.2.1 | Ligand $L^1H_2Br_2$

2,2′-Bis(bromomethyl)-1,1′-biphenyl (0.1 g, 0.29 mmol) and 1-picolylimidazole (0.093 g, 0.58 mmol) were stirred in acetonitrile (5 mL) at room temperature for 4 hr. After the completion of the reaction, solvent was removed under reduced pressure, the crude solid was washed with $Et_2O$ (3 × 5 mL), and dried *in vacuo* to give ligand $L^1H_2Br_2$ as a white powder. Yield (0.185 g, 97%); melting point (MP): 176 °C. $^1$H NMR (400 MHz, dimethyl sulfoxide [DMSO]) δ 8.98 (s, 1H), 8.54 (d, $J$ = 4.1 Hz, 1H), 7.90–7.89 (td, $J$ = 7.7, 1.7 Hz, 1H), 7.76–7.75 (m, 1H), 7.50–7.48 (m, 2H), 7.47 (s, 1H), 7.41–7.39 (m, 2H), 7.32 (t, $J$ = 7.9 Hz, 1H), 7.04 (d, $J$ = 7.5 Hz, 1H), 5.53 (d, $J$ = 2.1 Hz, 2H), 5.28 (d, $J$ = 15.3 Hz, 1H), 5.16 (d, $J$ = 15.3 Hz, 1H). $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ 153.32, 149.40, 138.40, 137.88, 137.10, 132.04, 129.85, 129.27, 128.96, 123.89, 123.87, 123.43, 122.80, 122.73, 52.89, 50.67, 39.52. ESI-MS *m/z* calcd. for $C_{32}H_{30}Br_2N_6$, $[M + Na]^+$, 679.0899; found 679.0798. Anal. Calcd. for $C_{32}H_{30}Br_2N_6$ (molecular weight [MW] 658.4420 g/mol): C, 58.37; H, 4.59; N, 12.76. Found: C, 58.60; H, 4.87; N, 12.40.

### 2.2.2 | Ligand $L^2H_2Br_2$

Ligand $L^2H_2Br_2$ was synthesized by following the aforementioned procedure. Reaction of 2,2′-bis(bromomethyl)-1,1′-biphenyl (0.1 g, 0.29 mmol) and 1-benzylimidazole (0.092 g, 0.58 mmol) afforded a white solid. Yield (0.186 g, 98%). MP: 139 °C. $^1$H NMR (400 MHz, DMSO-$d_6$) δ 9.13 (s, 1H), 7.84 (s, 1H), 7.51 (s, 1H), 7.48–7.39 (m, 6H), 7.36 (d, $J$ = 7.7 Hz, 1H), 7.27 (t, $J$ = 7.5 Hz, 1H), 6.97 (d, $J$ = 7.5 Hz, 1H), 5.42 (s, 2H), 5.30 (d, $J$ = 15.3 Hz, 1H), 5.17 (d, $J$ = 15.3 Hz, 1H). $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ 138.40, 136.27, 134.79, 131.89, 129.71, 129. 42, 129.03,128.97, 128.85, 123.00, 122.63, 118.21, 51.86, 50.71. ESI-MS *m/z* calcd. for $[C_{34}H_{32}Br_2N_4]$, 677.0994 $[M + Na]^+$; found 677.1180. Anal. Calcd. for $C_{34}H_{32}Br_2N_4$ (MW 656.4660 g/mol): C, 62.21; H, 4.91; N, 8.53. Found: C, 62.25; H, 4.92, N, 8.52.

### 2.2.3 | Ligand $L^3H_2Br_2$

The synthesis of ligand $L^3H_2Br_2$ was carried out similar to that of $L^1H_2Br_2$. Reaction of 2,2′-bis (bromomethyl)-1,1′-biphenyl (0.150 g, 0.44 mmol) and 1-picolylbenzimidazole (0.184 g, 0.88 mmol) afforded a white powder. Yield (0.330 g, 99%). MP: 241–243 °C. $^1$H NMR (400 MHz, DMSO-$d_6$) δ 9.70 (s, 1H), 8.46 (d, $J$ = 4.8 Hz, 1H), 7.93–7.90 (ddd, $J$ = 12.3, 6.5, 2.6 Hz, 2H), 7.70 (d, $J$ = 7.8 Hz, 1H), 7.61–7.57 (ddd, $J$ = 8.3, 6.0, 2.3 Hz, 1H), 7.55–7.48 (dd, $J$ = 15.3, 6.9 Hz, 3H), 7.42–7.36 (ddd, $J$ = 11.7, 7.1, 3.0 Hz, 2H), 7.19–7.15 (m, $J$ = 7.5, 0.9 Hz, 1H), 6.97 (d, $J$ 6.7 Hz, 1H), 5.95 (d, $J$ = 15.8 Hz, 1H), 5.86 (d, $J$ = 15.9 Hz, 1H), 5.74 (d, $J$ = 15.7 Hz, 1H), 5.60 (d, $J$ = 15.6 Hz, 1H). $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ 152.89, 149.61, 143.25, 138.61, 137.71, 131.37, 131.17, 129.91, 129.71, 129.04, 128.91, 126.79, 123.90, 122.96, 114.05, 113.66, 50.89, 48.90. ESI-MS *m/z* calcd. for $[C_{40}H_{34}Br_2N_6]$, 779.1212 $[M + Na]^+$; found 779.1105. Anal. Calcd. for $C_{40}H_{34}Br_2N_6$ (MW 758.5620 g/mol): C, 63.34; H, 4.52; N, 11.08. Found: C, 66.06; H, 5.068, N, 11.914.

### 2.2.4 | Ligand $L^4H_2Br_2$

The synthesis of ligand $L^4H_2Br_2$ was performed similar to that of $L^1H_2Br_2$. Reaction of 2,2′-bis(bromomethyl)-1,1′-biphenyl (0.200 g, 0.58 mmol) and 1-benzylbenzimidazole (0.204 g, 1.17 mmol) afforded a white powder. Yield (0.437 g, 98%). MP: 169–173 °C. $^1$H NMR (400 MHz, DMSO-$d_6$) δ 9.83 (d, J = 6.2 Hz, 1H), 7.97 (d, J = 8.3 Hz, 1H), 7.61–7.49 (m, 6H), 7.43–7.37 (ddd, J = 12.0, 7.0, 2.2 Hz, 4H), 7.20 (t, J = 7.5 Hz, 1H),

6.93 (d, J = 7.5 Hz, 1H), 5.80 (d, J = 15.0 Hz, 1H), 5.75 (d, J = 7.0 Hz, 1H), 5.71 (d, J = 6.5 Hz, 1H), 5.62 (d, J = 15.8 Hz, 1H). $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ 142.56, 138.47, 133.88, 131.29, 131.17, 130.65, 129.70, 129.57, 128.93, 128.86, 128.79, 128.33, 126.74, 113.98, 113.71, 49. 89, 48.93. ESI-MS *m/z* calcd. for $[C_{42}H_{36}Br_2N_4]$, 777.1307 $[M + Na]^+$; found 777.1180. Anal. Calcd. for $C_{42}H_{36}Br_2N_4$ (MW 756.5860 g/mol): C, 66.68; H, 4.80; N, 7.41. Found: C, 66.48; H, 4.80, N, 7.03.

## 2.3 | Synthesis of complexes

### 2.3.1 | $[PdL^1]Br_2$, 1

Ligand $L^1H_2Br_2$ (0.200 g, 0.3 mmol) and palladium(II) acetate (0.068 g, 0.3 mmol) were added to 10 mL freshly distilled acetonitrile and stirred under reflux for 24 hr in $N_2$. Solvent was removed under vacuum and re-dissolved in dichloromethane (DCM; 10 mL) and then concentrated to 1 mL. Addition of 5 mL diethyl ether resulted in the precipitation of pale yellow powder. Yield: (0.175 g, 76%). MP: 253.5 °C. $^1$H NMR (400 MHz, DMSO-$d_6$) δ 8.48 (d, J = 4.9 Hz, 1H), 8.25 (d, J = 7.3 Hz, 2H), 8.15 (t, J = 7.2 Hz, 1H), 8.01 (s, 1H), 7.80 (d, J = 7.5 Hz, 1H), 7.65–7.53 (m, 6H), 7.38–7.31 (m*, 3H), 7.19–7.15 (m, 3H), 6.95 (d, J = 7.7 Hz, 1H), 6.84 (t, J = 7.5 Hz, 1H), 5.95 (d, J = 16.8 Hz, 1H), 5.78 (d, J = 15.3 Hz, 1H), 5.63 (d, 1H), 5.39 (d, J = 16.9 Hz, 1H), 5.26 (d, J = 7.7 Hz, 1H), 5.17 (d, J = 14.1 Hz, 1H), 5.01 (d, J = 16.6 Hz, 1H), 4.19 (d, J = 16.4 Hz, 1H). $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ 154.78, 153.38, 152.97, 148.93, 140.60, 136.76, 132.56, 131.66, 130.23, 129.10, 128.83, 127.90, 127.39, 125.46, 125.00, 122.31, 121.47, 120.10, 54.65, 54.32, 51.55, 50.67. ESI-MS *m/z* calcd. for $[C_{32}H_{28}BrN_6Pd]^+$ 681.0583[M-Br]$^+$; found 681.0596. Anal. Calcd. for $C_{32}H_{28}Br_2N_6Pd$ (MW 762.8449 g/mol): C, 50.38; H, 3.70; N, 11.05. Found: 50.56; H, 3.76, N, 11.09.

### 2.3.2 | $[PdL^2Br_2]$, 2

Ligand $L^2H_2Br_2$ (0.200 g, 0.3 mmol) and palladium(II) acetate (0.0683 g, 0.3 mmol) were heated under reflux in acetonitrile (10 mL) for 24 hr. The solvent was removed under reduced pressure and the crude solid was re-dissolved in DCM. After passing through the short pad of silica gel and washing with diethyl ether, a pale yellow color powder was obtained. Yield (0.180 g, 78%). MP: 293–295 °C. $^1$H NMR (400 MHz, DMSO-$d_6$) δ 7.69 (d, J = 1.7 Hz, 1H), 7.47 (dd, J = 6.5, 2.8 Hz, 2H), 7.35–7.29 (m, 2H), 7.23–7.22(m, 3H), 7.19–7.16 (m, 2H), 7.12–7.10 (m, 1H), 5.94 (d, J = 15.0 Hz, 1H), 5.61 (d, J = 14.7 Hz, 1H), 5.12 (dd, J = 20.1, 15.0 Hz, 2H). $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ 170.70, 138.56, 136.83, 136.38, 130.66, 128.66, 128.49, 128.26, 127.82, 127.69, 126.34, 124.14, 120.20, 53.17, 50.48. ESI-MS *m/z* calcd. for $[C_{34}H_{30}BrN_4Pd]^+$, 679.0678 $[M-Br]^+$; found 679.0705. Anal. Calcd. for $C_{34}H_{30}Br_2N_4Pd$ (MW 760.8689 g/mol): C, 53.67; H, 3.97; N, 7.36. Found: C, 53.067; H, 3.97, N, 7.35.

### 2.3.3 | $[PdL^3]Br_2$, 3

Complex **3** was synthesized by adopting the procedure similar to complex **1**. Reaction of ligand $L^3H_2Br_2$ (0.200 g, 0.26 mmol) and palladium(II) acetate (0.059 g, 0.26 mmol) yielded a pale yellow powder. Yield (0.153 g, 68%). ESI-MS *m/z* calcd. for $[C_{40}H_{32}BrN_4Pd]^+$, 781.0895 $[M-Br]^+$; found 781.0907 Anal. Calcd. for $C_{40}H_{32}Br_2N_6Pd$ (MW 862.9649 g/mol): C, 55.67; H, 3.74; N, 9.74. Found: C, 55.43; H, 3.73; N, 9.75.

### 2.3.4 | $[PdL_4Br_2]$, 4

The synthesis of complex **4** followed the procedure of complex **2**. Reaction of ligand $L^4H_2Br_2$ (0.250 g, 0.3 mmol) and palladium(II) acetate (0.074 g, 0.3 mmol) yielded a pale yellow powder. Yield (0.205 g, 79%). MP 272 °C. $^1$H NMR (400 MHz, DMSO-$d_6$) δ 8.07 (d, *J* = 8.0 Hz, 1H), 7.58 (dd, *J* = 6.7, 2.8 Hz, 2H), 7.45 (dd, *J* = 10.8, 4.4 Hz, 2H), 7.39–7.36 (m, 2H), 7.32–7.27 (m, 2H), 7.24–7.20 (m, 3H), 6.93 (d, J = 7.8 Hz, 1H), 6.16 (d, *J* = 15.7 Hz, 1H), 6.03 (d, J = 15.4 Hz, 1H), 5.86 (d, *J* = 15.8 Hz, 1H), 5.55 (d, *J* = 15.4 Hz, 1H). $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ 183.50, 138.70, 136.51, 135.91, 135.84, 132.97, 130.79, 128.40, 128.15, 128.05, 127.85, 126.67, 123.73, 123.05, 111.50, 110.69, 51.42, 47.50. ESI-MS *m/z* calcd. for $[C_{42}H_{34}BrN_4Pd]^+$, 779.0991 $[M-Br]^+$; found 779.1014. Anal. Calcd. for $C_{42}H_{34}Br_2N_4Pd$ (MW 860.9889 g/mol): C, 58.59; H, 3.98; N, 6.51. Found: C, 58.011; H, 3.80, N, 6.50.

## 2.4 | General procedure for Pd–NHC-catalyzed acylative Suzuki coupling reaction of benzoyl chlorides with arylboronic acids

A mixture of arylboronic acids (1 mmol), benzoyl chlorides (1.2 mmol), and $K_2CO_3$ (2 mmol) was dissolved in toluene (4 mL). Then, catalyst (0.5 mol%) was added and the reaction mixture was stirred at 60 °C for 6 hr. Progress of the reaction was monitored by TLC. After completion of the reaction, the mixture was diluted with DCM and extracted with water, the organic layer

was dried over anhydrous $Na_2SO_4$, filtered, and concentrated under vacuum. The crude product was further purified by column chromatography using hexane and ethyl acetate as eluent. All products were well-known compounds and were confirmed by comparing their $^1H$ NMR and $^{13}C$ NMR spectra with those found in the literature.[17]

## 2.5 | Hg poisoning test

A reaction tube was charged with the catalyst (0.5 mol%), a drop of Hg (>300 equiv.) and toluene (5 mL). The reaction mixture was stirred for 10 min at room temperature before the addition of phenylboronic acid (1.0 mmol), $K_2CO_3$ (2 mmol), and benzoyl chloride (1.2 mmol). The reaction mixture was heated in an oil bath at 60 °C for 6 hr. The work-up was done in the same way according to the procedure given for carrying out acylative Suzuki cross-coupling reactions. The Hg was recovered by filtration and stored safely. Suppression of the coupling reaction was not observed which further indicated that the reaction was homogeneous.[18]

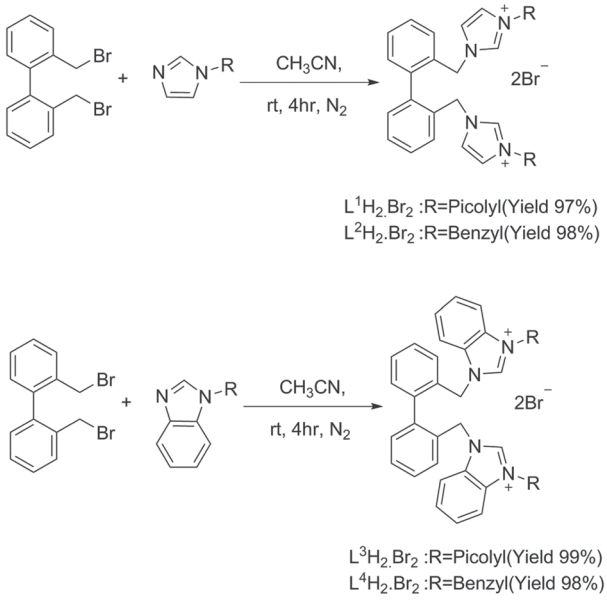
# 3 | RESULTS AND DISCUSSION

## 3.1 | Synthesis of ligands

The ligand precursors 1-picolylimidazole and 1-benzylimidazole were synthesized using the literature procedures.[19] The imidazolium ligands $L^1H_2Br_2$ and $L^2H_2Br_2$ were prepared by the reaction between 2,2′-bis (bromomethyl)-1,1′-biphenyl and 1-picolylimidazole or 1-benzylimidazole in acetonitrile at room temperature. The bis benzimidazolium salts ($L^3H_2Br_2$ and $L^4H_2Br_2$) were prepared similar to that of $L^1H_2Br_2$ and $L^2H_2Br_2$. All these reactions gave the expected NHC ligands in excellent yields (Scheme 1).

## 3.2 | Synthesis of palladium NHC complexes 1–4

Palladium NHCs (**1**, **2**, **3**, and **4**) were prepared by treating the imidazolium (or) benzimidazolium salts $L^1H_2Br_2$, $L^2H_2Br_2$, $L^3H_2Br_2$, and $L^4H_2Br_2$ with palladium(II) acetate in acetonitrile (Scheme 2). The reaction with the picolyl-substituted salts ($L^1H_2Br_2$ and $L^3H_2Br_2$) yielded the complexes **1** and **3** in 76% and 68%, respectively, as bright yellow-orange solids and the reaction with the benzyl-substituted salts $L^2H_2Br_2$ and



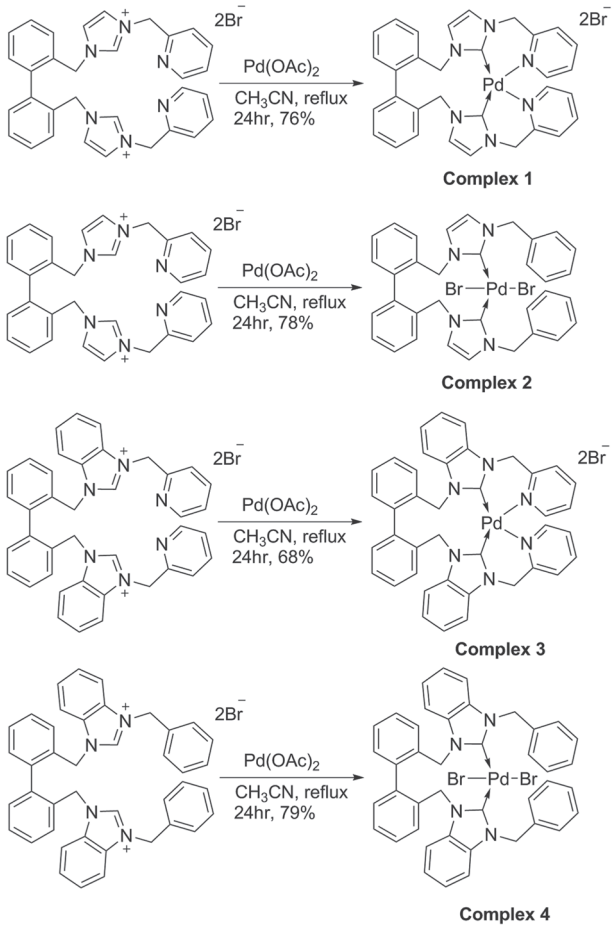

**SCHEME 1** Synthesis of ligands. rt, room temperature

$L^4H_2Br_2$ yielded the complexes **2** and **4** in 78% and 79%, respectively, as pale yellow solids.

## 3.3 | Spectral characterization of ligands and complexes

All four ligands, $L^1H_2Br_2$, $L^2H_2Br_2$, $L^3H_2Br_2$, and $L^4H_2Br_2$, were characterized by elemental analysis, NMR, and ESI–MS. $^1H$ NMR spectra of bis-imidazolium and benzimidazolium salts ($L^1H_2Br_2$–$L^4H_2Br_2$) showed characteristic downfield signal within the range of 8.98–9.83 ppm assigned to the *NCHN* proton supporting the formation of NHC ligands. Among all the ligands, $L^4H_2Br_2$ was more acidic as evident from the *NCHN* peak at 9.83 ppm. Further, these NHC ligands were characterized by $^{13}C$ spectra, where carbene carbon appeared in the range of 138.40–143.25 ppm similar to a previous report.[19] All these ligands were further confirmed by CHN and ESI-MS data. Their ESI-MS spectra showed the expected molecular ion peak as their sodium adducts (see the supplementary information).

The palladium NHC complexes **1–4** were characterized by $^1H$ NMR, $^{13}C$ NMR, ESI-MS, and elemental analyses. $^1H$ NMR spectra showed the disappearance of C-2 methine protons to support the successful formation of Pd–NHC complexes. The $^{13}C$ NMR spectra showed the carbene carbon signal at 148.93 ppm (complex **1**), 170.70 (complex **2**), and 184.50 ppm (complex **4**), which is consistent with the chemical shift values of reported palladium–NHC complexes.[20] Although the NMR spectra of complex **3** is not clean, the




**SCHEME 2** Synthesis of Pd–N-heterocyclic carbene complexes [1–4]

formation of the corresponding palladium complex was confirmed by CHN, ESI-MS, and single-crystal X-ray diffraction (XRD). ESI-MS spectra of all four complexes(**1–4**) showed a mono cationic peak corresponding to [M-Br]+ with *m/z* 681.0596, 679.0705, 781.0895, and 779.1014, respectively.

## 3.4 | X-ray structure analysis

Single crystals of complexes **1** and **2** suitable for XRD studies were obtained from chloroform and acetonitrile mixture by the slow evaporation method. Single crystals of **3** and **4** were grown from chloroform and ethyl acetate by the slow evaporation method. The ORTEP (Oak Ridge Thermal Ellipsoid Plot) diagram of all four complexes are shown in Figures 1 and 2 and their crystallographic details are given in Table 1.

Single-crystal X-ray analysis of all Pd–NHC complexes showed monomeric structure with palladium in distorted square planar geometry. The Pd–C bond lengths of complexes **1** and **3** support their *cis* configuration with congested environment.[21] The Pd–C bond distances in complexes **2** and **4** were found to be slightly longer than those in complexes **1** and **3** that was typical for *trans*-Pd complex and analogous to those of already reported palladium complexes.[22] In complexes **1** and **3** palladium was coordinated to the both pyridyl nitrogens and carbene carbons. By contrast, in complexes **2** and **4** Pd was attached with NHC carbons while two bromide anions were in a *trans* fashion. The biphenyl dihedral angles

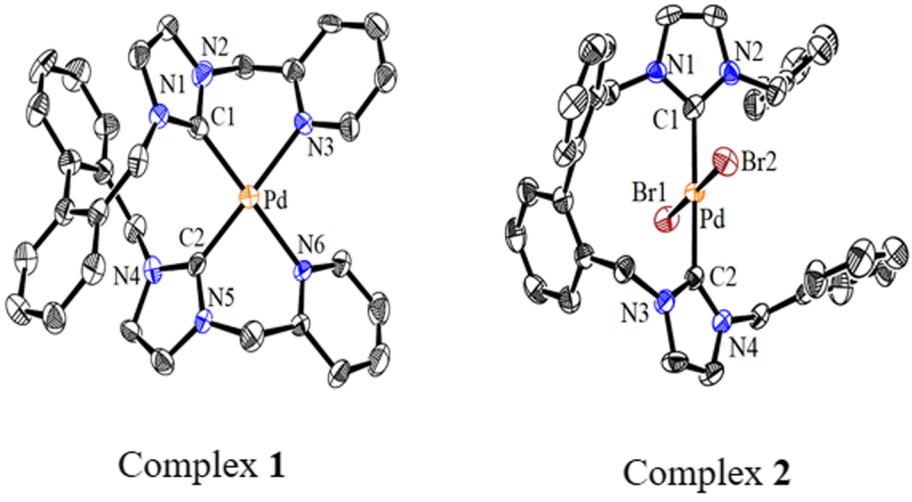



**FIGURE 1** ORTEP (Oak Ridge Thermal Ellipsoid Plot) diagram of **1** and **2** (thermal ellipsoids at 40% probability; hydrogen atoms were omitted for clarity). Selected bond parameters were shown below with distances (Å) and bond angles (degrees): (1) Pd–N3 = 2.092, Pd–C1 = 1.956, Pd–N6 = 2.088, Pd–C2 = 1.970; C1–Pd–N3 = 85.40, C1–Pd–N6 = 178.06, C1–Pd–C2 = 94.18, N3–Pd–N6 = 95.62, N3–Pd–C2 = 176.72, N6–Pd–C2 = 84.89. (**2**) Pd–Cl = 2.039, Pd–C2 = 2.020, Pd–Br1 = 2.444, Pd–Br2 = 2.438; C1–Pd–C2 = 175.34, Br1–Pd–Br2 = 178.40, C2–Pd–Br2 = 90.31, C2–Pd–Br1 = 91.17, C1–Pd–Br2 = 85.82, C1–Pd–Br1 = 92.70

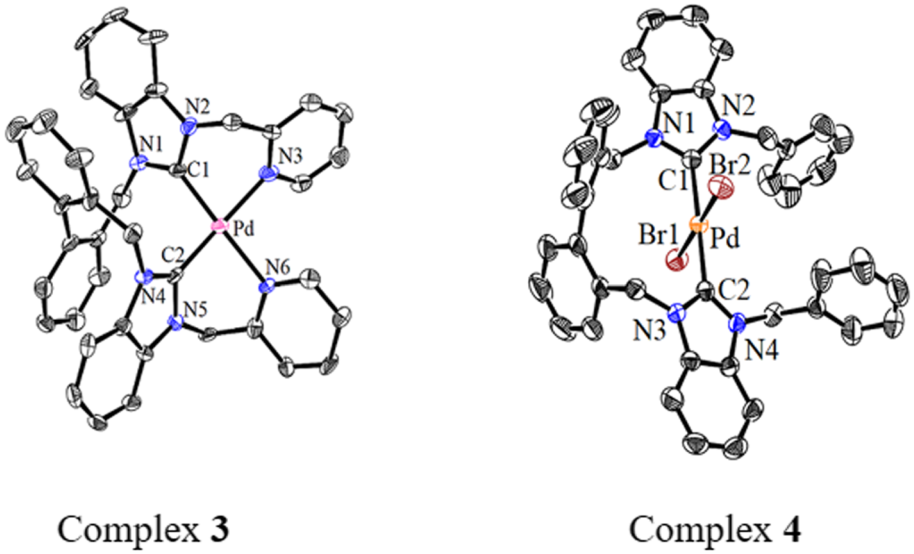



**FIGURE 2** ORTEP (Oak Ridge Thermal Ellipsoid Plot) diagram of **3** and **4** (thermal ellipsoids at 40% probability; hydrogen atoms were omitted for clarity). Selected bond parameters were shown below with distances (Å) and bond angles (degrees): (**3**) Pd–C1 = 1.970, Pd–C2 = 1.957, C1–Pd–N6 = 178.48, C2–Pd–N3 = 172.73; C1–Pd–N3 = 86.20, C2–Pd–N6 = 85.25, C1–Pd–C2 = 95.30, Pd–N3–N6 = 93.28. (**4**) Pd–Cl = 2.013, Pd–C2 = 2.013, Pd–Br1 = 2.433, Pd–Br2 = 2.433; C1–Pd–C2 = 179.14, Br1–Pd–Br2 = 179.02, C2–Pd–Br2 = 91.04, C2–Pd–Br2 = 91.04, C2–Pd–Br1 = 88.95, C1–Pd–Br2 = 88.95, C1–Pd–Br1 = 91.03

**TABLE 1** Crystallographic data of complexes **1–4**

| Parameters | Complex 1 | Complex 2 | Complex 3 | Complex 4 |
|---|---|---|---|---|
| Empirical formula | $C_{32}H_{28}N_6Br_2Pd$ | $C_{34}H_{30}Br_2N_4Pd$ | $C_{40}H_{32}N_6Br_2Pd$ | $C_{42}H_{34}\ Br_2N_4Pd$ |
| CCDC number | 1958397 | 1958566 | 1959259 | 1958565 |
| Formula weight | 762.8449 | 760.8689 | 862.9649 | 860.9889 |
| Temperature/K | 293(2) | 293(2) | 293(2) | 296(2) |
| Crystal system | Triclinic | Monoclinic | Triclinic | Monoclinic |
| Space group | P1 | $P2_1/c$ | P-1 | C2/c |
| a/Å | 8.3584(5) | 13.7586(13) | a = 11.027(4) | 17.3187(6) |
| b/Å | 9.8504(5) | 17.5508(14) | b = 12.353(3) | 11.9757(4) |
| c/Å | 10.0593(7) | 14.0314(11) | c = 16.739(4) | 18.5094(6) |
| α/degrees | 98.793(5) | 90.00 | a = 68.83(2) | 90 |
| β/degrees | 105.065(6) | 116.032(11) | b = 83.87(3) | 108.1030(10) |
| γ/degrees | 104.716(5) | 90.00 | g = 69.54(3) | 90 |
| Volume/$Å^3$ | 751.98(8) | 3044.5(4) | 1991.6(11) | 3648.9(2) |
| Z | 1 | 4 | 2 | 4 |
| $\rho_{calc}/mg/mm^3$ | 1.602 | 1.664 | 1.567 | 1.567 |
| $\mu/mm^{-1}$ | 2.547 | 3.266 | 2.248 | 2.734 |
| F(000) | 357 | 1516 | 951 | 1720 |
| Reflections collected | 8285 | 15,562 | 9311 | 28,112 |
| Independent reflections | 5359[R (int) = 0.0334] | 6985[R (int) = 0.0834] | 6140 [R (int) = 0.0571] | 3211 [R (int) = 0.0867] |
| Data/restraints/parameters | 5359/3/379 | 6985/0/370 | 6140/20/515 | 3211/0/222 |
| Goodness-of-Fit on $F^2$ | 1.086 | 1.005 | 1.027 | 1.046 |
| Final R indexes [$I >= 2\sigma$ (I)] | $R_1$ = 0.0672, $wR_2$ = 0.1741 | $R_1$ = 0.0703, $wR_2$ = 0.1478 | R1 = 0.0787, wR2 = 0.1928 | R1 = 0.0406, wR2 = 0.0635 |
| Final R indexes [all data] | $R_1$ = 0.0820, $wR_2$ = 0.1927 | $R_1$ = 0.1381, $wR_2$ = 0.1880 | R1 = 0.1136, wR2 = 0.2339 | R1 = 0.0939, wR2 = 0.0769 |
| Largest diffraction peak/hole/e $Å^{-3}$ | 1.25/−1.17 | 1.88/−1.04 | 1.434/−1.469 | 0.383/−0.399 |

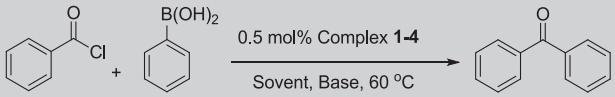
between the two benzene rings for complexes **1**, **2**, **3,** and **4** were observed as 83.78°, 64.24°, 86.20°, and 62.74°, respectively. These values indicated that the two phenyl rings of biphenyl in picolyl-substituted complexes were closer to perpendicular direction when compared with benzyl-substituted analogs.

## 3.5 | Catalytic activity of Pd–NHC complexes in acylative Suzuki cross-coupling reaction

Cross-coupling reaction of aryl boronic acids with carboxylic acid derivatives over palladium catalysts has emerged as a powerful tool for the synthesis of biaryl ketones.[23] Reports by Yamamoto *et al*. and Goossen *et al*. described the palladium-catalyzed C(O)–O bond cleavage of carboxylic anhydrides to obtain biaryl ketones under mild reaction conditions.[24,25] This protocol is superior to the earlier methods in terms of reaction conditions; functional group tolerance; thermal, air, and moisture stability; and commercially available organoboron reagents as starting materials. However, the aforementioned two reports showed that the phosphine ligands were essential to execute the reaction and in absence of the phosphine ligand the reaction was unsuccessful and no product was obtained.

Acylative Suzuki cross coupling of benzoyl chlorides and arylboronic acids is an interesting and promising reaction to obtain biarylketones. Palladium–NHC-catalyzed acylative Suzuki cross-coupling reaction was less explored when compared with the traditional

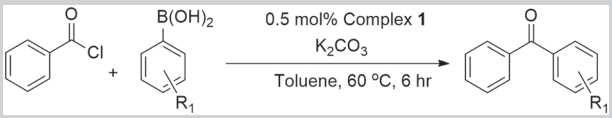
**TABLE 2** Optimization of reaction conditions for acylative Suzuki cross-coupling reaction[a]

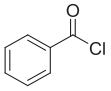
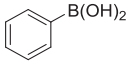
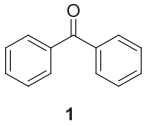
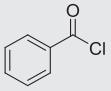
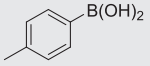
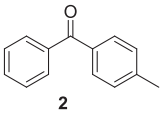
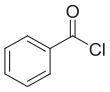
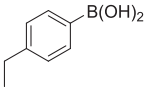
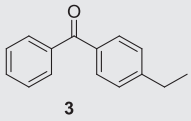
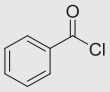
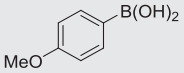
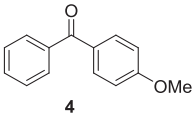
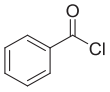
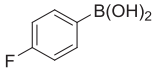
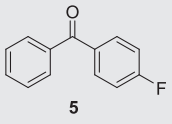
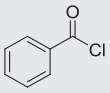
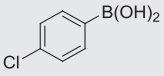
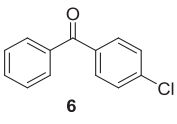
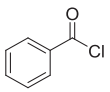
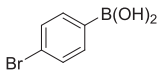



| S. No | Solvent | Complex | Base | Time | Yield (%)[b] |
|---|---|---|---|---|---|
| 1. | Acetone | 1 | $K_2CO_3$ | 6 | 79 |
| 2. | Dimethylformamide | 1 | $K_2CO_3$ | 6 | 77 |
| 3. | Dichloromethane | 1 | $K_2CO_3$ | 6 | 86 |
| 4. | Ethanol | 1 | $K_2CO_3$ | 6 | 62 |
| **5.** | **Toluene** | **1** | **$K_2CO_3$** | **6** | **93** |
| 6. | Dichloroethane | 1 | $K_2CO_3$ | 6 | 75 |
| 7. | Acetonitrile | 1 | $K_2CO_3$ | 6 | 86 |
| 8. | $CHCl_3$ | 1 | $K_2CO_3$ | 6 | 90 |
| 9 | Methanol | 1 | $K_2CO_3$ | 6 | 67 |
| 10. | Water | 1 | $K_2CO_3$ | 6 | ND |
| 11. | Toluene | 1 | $Et_3N$ | 6 | 55 |
| 12. | Toluene | 1 | $NaHCO_3$ | 6 | 64 |
| 13. | Toluene | 1 | $K_3PO_4$ | 6 | 72 |
| 14. | Toluene | 1 | KOH | 6 | 60 |
| 15. | Toluene | 1 | NaOAc | 6 | 40 |
| 16 | Toluene | **2** | $K_2CO_3$ | 6 | 79 |
| 17 | Toluene | **3** | $K_2CO_3$ | 6 | 81 |
| 18 | Toluene | **4** | $K_2CO_3$ | 6 | 73 |
| 19[c] | Toluene | **1** | $K_2CO_3$ | 12 | 87 |
| 20[d] | Toluene | **1** | $K_2CO_3$ | 4 | 93 |

[a]Reaction conditions: boronic acid (1 mmol), benzoyl chloride (1.2 mmol), and base (2 mmol) were used.
[b]Isolated yield.
[c]0.25 mol% catalyst was used.
[d]1.0 mol% catalyst was used.

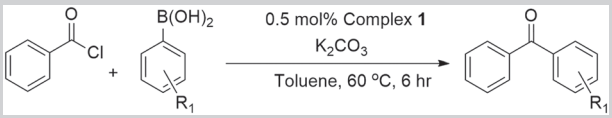
**TABLE 3** Palladium–NHC-catalyzed acylative cross-coupling reactions of acyl chlorides with aryl boronic acids[a]




| S. No | Acyl chloride | Aryl boronic acid | Product | Yield (%)[b] |
|---|---|---|---|---|
| 1 |  |  |  **1** | 93 |
| 2 |  | |  | 90 |
| 3 |  **2** |  |  | 88 |
| 4 |  **3** |  |  | 72 |
| 5 |  **4** |  |  | 91 |
| 6 |  **5** |  |  | 89 |
| 7 |  **6** |  |  | 87 |

(Continues)

**TABLE 3** (Continued)



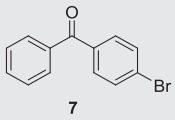
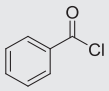
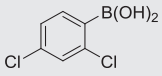
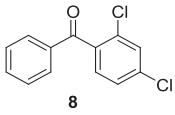
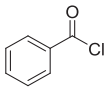
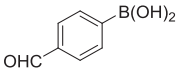
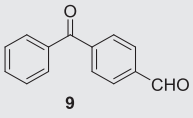
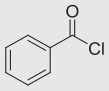
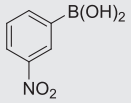
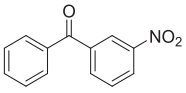
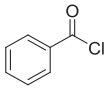
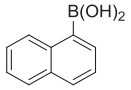
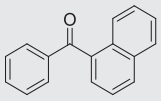
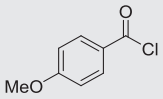
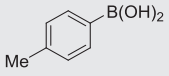
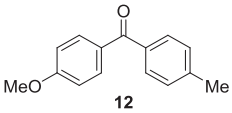
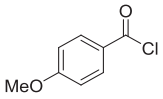
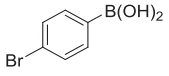
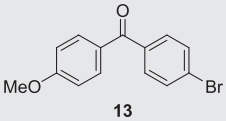
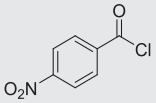
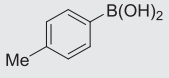

| S. No | Acyl chloride | Aryl boronic acid | Product | Yield (%)[b] |
|---|---|---|---|---|
| 8 |  **7** |  |  | 91 |
| 9 |  **8** |  |  | 61 |
| 10 |  **9** |  |  | 67 |
| 11 |  **10** |  |  | 74 |
| 12 |  **11** |  |  | 73 |
| 13 |  **12** |  |  | 76 |
| 14 |  **13** |  |  | 66 |

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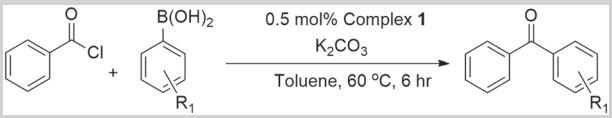
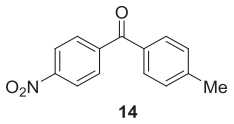
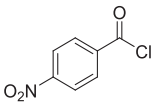
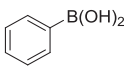
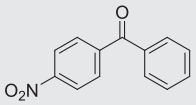
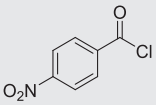
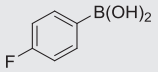
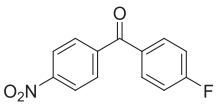
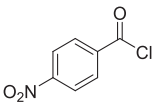
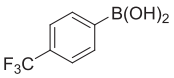
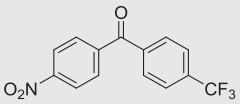
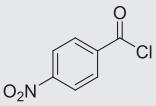
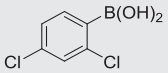
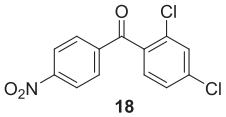
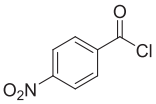
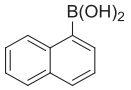
**TABLE 3** (Continued)




| S. No | Acyl chloride | Aryl boronic acid | Product | Yield (%)[b] |
|---|---|---|---|---|
| 15 |  14 |  |  | 79 |
| 16 |  15 |  |  | 63 |
| 17 |  16 |  |  | 69 |
| 18 |  17 |  |  | 73 |
| 19 |  18 |  |  | 62 |

[a]Reaction conditions: boronic acid (1 mmol), benzoyl chloride (1.2 mmol), $K_2CO_3$ (2 mmol), and 0.5 mol% palladium–NHC complex (**1**) were refluxed in toluene at 60 °C for 6 hr.
[b]Isolated yield.
NHC, N-heterocyclic carbene.

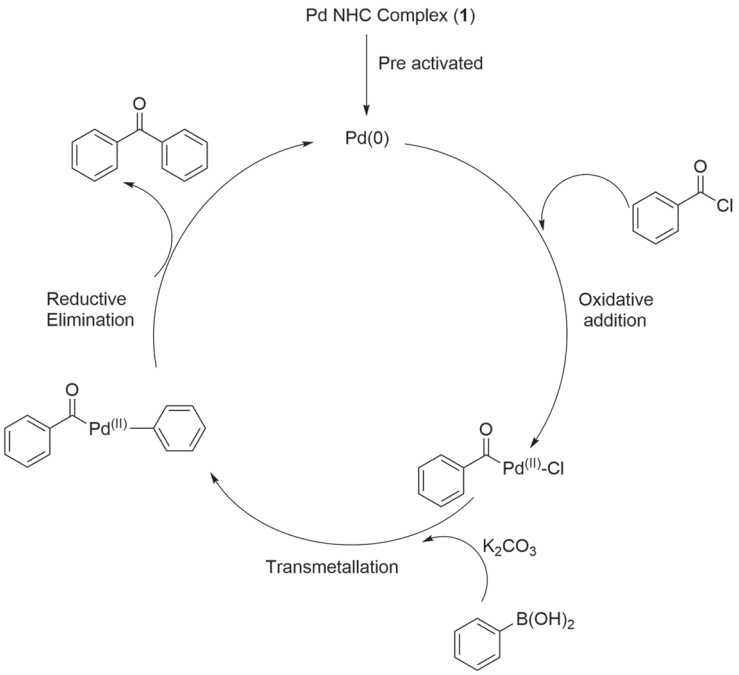
Suzuki–Miyaura coupling reaction.[26] Recently, heterogeneous and recyclable Pd(II)–NHC complex as a catalyst was reported by Movassagh *et al*. for cross coupling of acyl chlorides with arylboronic acids.[27] To the best of our knowledge, Pd-biphenyl NHCs are not reported for the acylative coupling between acid chlorides and aryl boronic acids. Hence, the synthesized Pd–NHC complexes **1–4** were tested in the acylative Suzuki cross-coupling reaction.

At the outset, optimization of the reaction condition was performed using benzoyl chloride and phenyl boronic acid as model substrate in the presence of 0.5 mol% of complex **1** (Table 2). Initially, the reaction was screened in various solvents such as water, ethanol,

dimethylformamide (DMF), acetone, chloroform, toluene, dichloroethane (DCE), THF, and MeCN in the presence of $K_2CO_3$ at 60 °C. Among these solvents, toluene was found to be superior, providing the benzophenone in 93% yield. The reaction did not proceed in water (Table 2, Entry 10). Moreover, moderate yield was obtained in high boiling solvent DMF (Table 2, Entry 2). Other organic solvents such as chloroform and DCE yielded 90% and 75% of the benzophenone, respectively (Table 2, Entries 6 and 8, respectively). Further, different bases including triethyl amine, $NaHCO_3$, $K_3PO_4$, KOH, and NaOAc were tested for obtaining the better optimized conditions. However, among all, $K_2CO_3$ was the best (Table 2, Entry 5). Further, the catalytic efficiency of complexes **2–4** were investigated in the acylative coupling reaction of phenyl boronic acid with benzoyl chloride in toluene in the presence of $K_2CO_3$. Complexes **2–4** gave the desired biaryl ketone in 79%, 81%, and 73%, respectively. (Table 2, Entries 16–18). Overall, complex **1** showed superior activity than other complexes in the coupling reaction. It was also observed that decreasing the catalyst loading to 0.25 mol% led to increased reaction time, whereas with 1 mol% of catalyst the reaction proceeded a bit faster, suggesting that 0.5 mol% of the catalyst would be optimum.

Having established the optimized condition, we explored the acylative cross coupling of a variety of phenyl boronic acids with benzoyl chlorides to afford diverse biaryl ketones (Table 3, Entries 1–19). Boronic acids bearing electron-donating as well as electron-withdrawing groups participated in the coupling reaction with benzoyl chloride very efficiently and provided the desired biaryl ketones in good to excellent yields (Table 3, Entries 1–10). However, aldehyde- and nitro-functionalized substrates gave the desired biaryl ketones in relatively lower yields (Table 3, Entries 9 and 10). Interestingly, sterically hindered *ortho*-substituted boronic acid gave the desired product in 91% and 73% yield, respectively (Table 3, Entries 8 and 18). Nevertheless, the bulkier naphthylboronic acids gave the desired biaryl ketone in 74% and 62% yield (Table 3, Entries 11 and 19, respectively). Having explored the scope of different boronic acids, we investigated the reactivity of electron-donating– and electron-withdrawing groups–functionalized benzoyl chlorides in the coupling reactions. To our delight, the methoxy- and nitro-substituted benzoyl chlorides participated in the coupling reaction efficiently with different arylboronic acids and gave the desired biaryl ketones in 62%–79% yields (Table 3, Entries 12–19). Palladium–NHC-catalyzed acylative cross-coupling reactions are very few. However, the activity of the present complexes were comparable with the available competent catalysts from the literature for acylative coupling reaction.[26] The proposed mechanism for acylative cross-coupling reaction is shown in Scheme 3.

Eventually the present complexes were effectively used as catalysts for cross coupling of acyl chlorides with arylboronic acids to obtain diverse biaryl ketones which will broaden up the scope of acylative coupling reaction in organometallic chemistry.




**SCHEME 3** Probable mechanism for acylative cross-coupling reaction. NHC, N-heterocyclic carbene

## 4 | CONCLUSIONS

We have successfully synthesized four NHC ligands ($L^1H_2Br_2$, $L^2H_2Br_2$, $L^3H_2Br_2$, and $L^4H_2Br_2$) with picolyl- and benzyl-linked biphenyl backbone and their corresponding palladium(II) complexes. All the NHC ligands and complexes were characterized by elemental analysis, NMR, and ESI-MS. Single-crystal XRD of Pd–NHC complexes **1–4** showed their monomeric nature with palladium in distorted square-planar geometry. All Pd–NHC complexes were examined as catalysts in acylative Suzuki cross-coupling reaction of benzoyl chloride and phenyl boronic acid. Complex **1** was found to be an efficient catalyst compared with the other Pd–NHC complexes.

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## REFERENCES

[1] a)M. G. Gardiner, C. C. Ho, *Coord. Chem. Rev.* **2018**, *375*, 373. b)E. Peris, *Chem. Rev.* **2018**, *118*, 9988. c)W. A. Herrmann, *Angew. Chem. Int. Ed.* **2002**, *41*, 1290. d)N. Marion, S. P. Nolan, *Acc. Chem. Res.* **2008**, *41*, 1440. e)F. E. Hahn, M. C. Jahnke, *Angew. Chem., Int. Ed.* **2008**, *47*, 3122. f)V. Nair, S. Bindu, V. Sreekumar, *Angew. Chem. Int. Ed.* **2004**, *116*, 5240. g)S. Kuwata, F. E. Hahn, *Chem. Rev.* **2018**, *118*, 9642. h) M. Mora, M. C. Jemeno, R. Visbal, *Chem. Soc. Rev.* **2019**, *48*, 447. i)A. A. Danopoulos, T. Simler, P. Braunstein, *Chem. Rev.* **2019**, *119*, 3730.

[2] a)S. Diez-Gonzalez, S. P. Nolan, *Coord. Chem. Rev.* **2007**, *251*, 874. b)B. Liu, D. Xu, W. Z. Chen, *Chem. Commun.* **2011**, *47*, 2883. c)Y. Xia, D. Qiu, J. B. Wang, *Chem. Rev.* **2017**, *117*, 13810. d)R. Zhong, A. C. Lindhorst, F. J. Groche, F. E. Kuhn, *Chem. Rev.* **2017**, *117*, 1970. e)N. T. Patil, *Angew. Chem. Int. Ed.* **2011**, *50*, 1759. f)E. A. B. Kantchev, C. J. O'Brien, M. G. Organ, *Angew. Chem., Int. Ed.* **2007**, *46*, 2768.

[3] a)N. Sinha, F. E. Hahn, *Acc. Chem. Res.* **2017**, *50*, 2167. b) D. M. Flanigan, F. R. Michailidis, N. A. White, T. Rovis, *Chem. Rev.* **2015**, *115*, 9307. c)Z. N. Gafurov, A. O. Kantyukov, A. A. Kagilev, A. A. Balabayev, O. G. Sinyashin, D. G. Yakhvarov, *Russ. Chem. Bull., Int. Ed.* **2017**, *66*, 1529.

[4] a)P. Malecki, K. Gajda, R. Gajda, K. Wozniak, B. Trzaskowski, A. Kajetanowicz, K. Grela, *ACS Catal.* **2018**, *9*, 587. b) V. Paradiso, C. Costabile, F. Grisi, *Beilstein J. Org. Chem.* **2018**, *14*, 3122. c)A. Poater, *Molecules* **2016**, *21*, 177.

[5] >a)S. Shi, S. P. Nolan, M. Szostak, *Acc. Chem. Res.* **2018**, *51*, 2589. b)P. P. Mpungose, Z. P. Vundla, G. E. M. Maguire, H. B. Friedrich, *Molecules* **2018**, *23*, 1676. c)T. Wang, G. Guo, X. Wang, H. Guo, D. Jia, H. Wang, L. Liu, *RSC Adv.* **2019**, *9*, 5738. dI. A. Bhat, I. Avinash, G. Anantharaman, *Organometallics* **2019**, *38*, 1699. eP. Conelly-Espinosaa, R. A. Toscanoa, D. Morales-Moraless, *Tetrahedron Lett.* **2014**, *55*, 5841.

[6] a)F. P. Malan, E. Singleton, P. H. van Rooyen, M. Landman, *New J. Chem.* **2019**, *43*, 8472. b)R. Zhong, Z. Wei, W. Zhang, S. Liu, Q. Liu, *Chem* **2019**, *5*, 1. c)S. Abubakar, H. Ibrahim, M. D. Bala, *Inorg. Chim. Acta* **2019**, *484*, 276.

[7] a)M. Mora, M. C. Gemeno, R. Visbal, *Chem. Soc. Rev.* **2019**, *48*, 447. b)M. Pellei, V. Gandin, M. Marinelli, C. Marzano, M. Yousufuddin, H. V. R. Dias, C. Santini, *Inorg. Chem.* **2012**, *51*, 9873. c)H. Valdés, D. Canseco-González, J. M. Germán-Acacio, D. Morales-Morales, *J. Organomet. Chem.* **2018**, *867*, 51. d)A. Sánchez-Moraa, H. Valdésa, M. T. Ramírez-Apana, A. Nieto-Camachoa, S. Hernández-Ortegaa, D. Canseco-González, D. Morales-Morales, *Inorg. Chim. Acta* **2019**, *496*, 119061.

[8] a) W.-L. Duan, M. Shi, G. B. Rong, *Chem. Commun.* **2003**, 2916. b)G.-N. Ma, T. Zhang, M. Shi, *Org. Lett.* **2009**, *11*, 875. c) P. Gu, Q. Xu, M. Shi, *Organometallics* **2013**, *32*, 7575. d)A. R. Chianese, R. H. Crabtree, *Organometallics* **2005**, *24*, 4432.

[9] a)D. S. Clyne, J. Jin, E. Genest, J. C. Gallucci, T. V. RajanBabu, *Org. Lett.* **2000**, *2*, 1125.

[10] a)O. Navarro, R. A. Kelly, S. P. Nolan, *J. Am. Chem. Soc.* **2003**, *125*, 16194. b)S. Guchhait, K. Ghosh, B. Sureshbabu, V. Ramkumar, S. Sankararaman, *J. Organomet. Chem.* **2014**, *768*, 68. c)L.-J. Liu, F. Wang, M. Shi, *Organometallics* **2009**, *28*, 4416.

[11] S. Sabiah, B. Varghese, N. N. Murthy, *Chem. Commun.* **2009**, 5636.

[12] a)S. Sabiah, B. Varghese, N. N. Murthy, *J. Chem. Crystallogr.* **2010**, *40*, 1195. b)S. Sabiah, C. S. Lee, W.-S. Hwang, I. J. B. Lin, *Organometallics* **2010**, *29*, 290. cC.-S. Lee, S. Sabiah, J.-C. Wang, W.-S. Hwang, I. J. B. Lin, *Organometallics* **2010**, *29*, 286. dC.-S. Lee, R. R. Zhuang, S. Sabiah, J.-C. Wang, W.-S. Hwang, I. J. B. Lin, *Organometallics* **2011**, *30*, 3897.

[13] L. Seva, W.-S. Hwang, S. Sabiah, *J. Mol. Catal. A: Chem.* **2016**, *418*, 125.

[14] G. M. Sheldrick, *SHELXS-97 and SHELXL-97, Program for Crystal Structure Solution and Refinement*, University of Gottingen, Gottingen **1997**.

[15] G. M. Sheldrick, *Acta Crystallogr. Sect. A* **2008**, *64*, 112.

[16] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Crystallogr.* **2009**, *42*, 339.

[17] a)S. Zhen, L. Xu, C. Xia, *Appl. Organometal. Chem.* **2007**, *21*, 772. b)M. Mondal, U. Bora, *Appl. Organometal. Chem.* **2014**, *28*, 354. c)B. Xin, Y. Zhang, K. Cheng, *J. Org. Chem.* **2006**, *71*(15), 5725. d)M. V. Khedkar, T. Sasaki, B. M. Bhanage, *RSC Adv.* **2013**, *3*, 7791. e)G. Meng, M. Szostak, *Org. Biomol. Chem.* **2016**, *14*, 5690.

[18] a)N. T. S. Phan, M. Van Der Sluys, C. W. Jones, *Adv. Synth. Catal.* **2006**, *348*, 609. b)M. R. Eberhard, *Org. Lett.* **2004**, *6*, 2125.

[19] aF. E. Hahn, C. M. Jahnke, T. Pape, *Organometallics* **2007**, *26*, 150. bS.-C. Chen, H.-H. Hsueh, C.-H. Chen, C.-S. Lee, F.-C. Liu, I. J. B. Lin, G.-H. Lee, S.-M. Peng, *Inorg. Chim. Acta* **2009**, *362*, 3343. cD. Tapu, D. A. Dixon, C. Roe, *Chem. Rev.* **2009**, *109*, 3385.

[20] M. C. Jahnke, T. Pape, F. E. Hahn, *Eur. J. Inorg. Chem.* **1960**, *2009*.

[21] aQ. Xu, W.-L. Duan, Z.-Y. Lei, Z.-B. Zhua, M. Shi, *Tetrahedron* **2005**, *61*, 11225. bM. R. Chapman, B. R. M. Lake, C. M. Pask, B. N. Nguyen, C. E. Willans, *Dalton Trans.* **2015**, *44*, 15938. cX. Zhang, Q. Xia, W. Chen, *Dalton Trans.* **2009**, 7045.

[22] aQ. Teng, D. Upmann, S. A. Z. N. Wijaya, H. V. Huynh, *Organometallics* **2014**, *33*, 3373. bX. Cai, S. Majumdar, G. C. Fortman, C. S. J. Cazin, A. M. Z. Slawin, C. Lhermitte, R. Prabhakar, M. E. Germain, T. Palluccio, S. P. Nolan, E. V. Rybak-Akimova, M. Temprado, B. Captain, C. D. Hof, *J. Am. Chem. Soc.* **2011**, *133*, 1290. cJ. D. Blakemore, M. J. Chalkley, J. H. Farnaby, L. M. Guard, N. Hazari, C. D. Incarvito, E. D. Luzik, H. W. Suh, *Organometallics* **2011**, *30*, 1818. dL. Ray, M. M. Shaikh, P. Ghosh, *Organometallics* **2007**, *26*, 958.

[23] aF. Rafiee, A. R. Hajipour, *Appl. Organometal. Chem.* **2015**, *29*, 181. bA. R. Hajipour, R. Pourkaveh, *Synlett* **2014**, *25*, 1101. cM. Mondal, U. Bora, *New J. Chem.* **2016**, *40*, 3119. dM. Blangetti, H. Rosso, C. Prandi, A. Deagostino, P. Venturello, *Molecules* **2013**, *18*, 1188. eC. Liu, G. Li, S. Shi, G. Meng, R. Lalancette, R. Szostak, M. Szostak, *ACS Catal.* **2018**, *8*, 9131. fH. Ma, C. Bai, Y.-S. Bao, *RSC Adv.* **2019**, *9*, 17266. gA. M. Forbes, G. P. Meier, E. Jones-Mensah, J. Magolan, *Eur. J. Org. Chem.* **2016**, *2016*, 2983.

[24] aR. Kakino, H. Narahashi, I. Shimizu, A. Yamamoto, *Chem. Lett.* **2001**, *30*, 1242. bR. Kakino, I. Shimizu, A. Yamamoto, *Bull. Chem. Soc. Jpn.* **2001**, *74*, 371. cR. Kakino, S. Yasumi, I. Shimizu, A. Yamamoto, *Bull. Chem. Soc. Jpn.* **2002**, *75*, 137. dR. Kakino, H. Narahashi, I. Shimizu, A. Yamamoto, *Bull. Chem. Soc. Jpn.* **2002**, *75*, 1333.

[25] aL. J. Goossen, K. Ghosh, *Angew. Chem., Int. Ed.* **2001**, *40*, 3458. bL. J. Goossen, K. Ghosh, *Chem. Commun.* **2001**, 2084. cL. J. Goossen, K. Ghosh, *Eur. J. Org. Chem.* **2002**, *2002*, 3254. dV. Ramakrishna, M. J. Rani, N. D. Reddy, *Eur. J. Org. Chem.* **2017**, 7238. eH. Solarova, I. Cisarova, P. Stepnicka, *Organometallics* **2014**, *33*, 4131. fA. Feiz, M. M. Amini, A. Bazgir, *Mol. Catal.* **2017**, *438*, 159.

[26] J. Buchspies, M. Szostak, *Catalysts* **2019**, *9*, 53.

[27] B. Movassagh, F. Hajizadeh, E. Mohammadi, *Appl. Organomet. Chem.* **2018**, *32*, 3982.

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