Effective Binuclear Pd(II) Complexes for Suzuki Reactions in Water

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Effective Binuclear Pd(II) Complexes for Suzuki Reactions in Water

Murat Emre HANHAN, Cemil CETINKAYA Michael P. SHAVER

A series of very effective ionic dinuclear Pd(II) complexes were synthesized and their catalytic activity for Suzuki reaction in aqueous media was investigated. Effect of TBAB on reaction determined. As a result it was found that dinuclear nature of Pd(II) complexes, accelerates the reaction rate.
Effective Binuclear Pd(II) Complexes for Suzuki Reactions in Water
Murat Emre HANHAN1*, Cemil CETINKAYA1 and Michael P. SHAVER2

Abstract
A series of new ionic binuclear Pd(II) complexes supported by water soluble bis(α-diimine) ligands were prepared and employed as catalysts for the palladium–catalyzed Suzuki reaction in aqueous media. The binuclear nature of the complexes increased the reaction rate while electronic and steric modification of the ligand frameworks had remarkable influences upon the catalytic activity of the palladium complexes. The catalysts were shown to be homogeneous through mercury poisoning experiments and complexes could be recycled over 10 times without loss of catalytic activity.

Introduction
The palladium catalyzed Suzuki coupling reaction is the most powerful synthetic method to form biaryls. This cross coupling reactions of aryl halides with organoboron compounds is an essential tool of almost every synthetic chemist, being used in the synthesis of pharmaceuticals, ligands, natural products, polymers and specialty molecules.[1-7] Broad tolerance to different functional groups, mild reaction conditions and low inherent toxicity materials makes Suzuki reactions unique for coupling

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Recently, Suzuki reactions in aqueous media have sparked research interest. Water is an inexpensive, readily available, non-toxic and environmentally friendly alternative solvent in organic synthesis but is especially important in facilitating catalyst-product separation. Casalnuovo and co-workers developed Suzuki reaction in aqueous solvents catalyzed by TPPMS/Pd(OAc)$_2$ (TPPMS = PPh$_2$(m-C$_6$H$_4$SO$_3$K))$^9$ while several water-soluble phosphine analogues have also been developed.$^{[10-18]}$ Buchwald’s group synthesized very effective sulfonated phosphine ligand for Suzuki reaction in aqueous media.$^{[19]}$ Najera and co-workers have used an oxime-carbapalladacycle$^{[8, 20]}$ an dinitrogenated ligands with tetrabutylammonium bromide salts (TBAB) as a catalyst for aqueous phase Suzuki reactions, with activity for the TBAB system high even for coupling unreactive arylchlorides.$^{[21, 22]}$ Wang and co-workers used microwaves to promote the Suzuki reaction in water, accessing shortened reaction times and high yields.$^{[23]}$

Little comparative effort has been made in the use of water-soluble diimine frameworks in cross-coupling reactions. Very good $\pi$ acceptor and $\alpha$ donor property of $\alpha$-diimine ligands can stabilize low and high oxidation state transition metals. Thus transition metals with $\alpha$-diimines can adapt to a catalytic cycle containing an oxidative addition/reduction elimination sequence. Another advantage of these types of ligands is the facile tunability of their electronic and steric properties.$^{[24]}$ There are several effective palladium catalysts which have $\alpha$ and $\beta$-diimine skeleton used in Suzuki reaction.$^{[7, 25-27]}$ On the other hand, binuclear Pd(II) complexes has attracted considerable interest recently.$^{[28]}$ Binuclear organometallic complexes have some advantages from that of analogous mononuclear complexes.$^{[29]}$ Binuclear complexes may have additional oxidation states these extra oxidation state gives the complex extra stability$^{[30]}$, interaction between nearby metal centers could potentially cause...
increased reaction yield or yield transformation rates not possible with mononuclear analogues\cite{31} and the distance between two metal centers also plays important role for the catalytic performance.\cite{32} In this paper, we report a series of novel, water-soluble binuclear palladium(II) diimine complexes as catalysts for Suzuki reaction in aqueous media. The seven ligands and complexes used in this study are shown in Figure 1.

**Figure 1**: Schematic display of ligands and complexes.

### Experimental

#### Materials

All solvents were purchased and purified according to standard procedures. Other reagents were used as received from Sigma-Aldrich Company without further purification. Gas chromatographic analyses were performed on an Agilent 6890N instrument equipped with HP-1 fused silica capillary column. FT-IR spectra were recorded on a Perkin Elmer Spectrum 100 with using ATR between the 400 – 4000 cm\(^{-1}\) range. NMR spectra were performed on a Bruker 300 MHz Ultrasound TM using DMSO as solvent and Me\(_4\)Si as internal standard. Elemental analyses were performed on a LECO CHSN 932.

#### Synthesis of diimine ligands

2,5-Diaminobenzenesulfonic acid – sodium salt,\(^{(1)}\) and 2-Aminobenzenesulfonic acid – sodium salt \(^{(2)}\)

The sodium salt of 2,5-diaminobenzenesulfonic acid or 2-aminobenzenesulfonic was prepared from the reaction of sulfonic acids and 1M sodium hydroxide solution
followed by removal of the water under reduced pressure, following a reported literature procedure.\[33\]

**General Procedure For the Synthesis of Ligands L1 – L5**

2 mmol aldehyde or ketone (2-pyridinecarboxyaldehyde (L1), 6-methylpyridine-2-carboxaldehyde (L2), 2-acetylpyridine (L3), 2-acetyl-4-methylpyridine (L4), 2-quinolinecarboxaldehyde (L5)) and 1 mmol 1 was added to a solution of dry ethanol (50 mL) and xylene (10 mL). The resulting mixture was heated to reflux overnight then cooled to ambient temperature and stored at 4°C overnight to initiate product crystallization. The resulting solid was isolated by filtration and washed with diethyl ether (3 × 10 mL) and dried under vacuum.

**L1**

Yield: 76 %. Yellow solid. FT-IR (ATR, \(\nu\), cm\(^{-1}\)) 1639 (C=N), 1196 (S=O). \(^1\)H-NMR (300 MHz, DMSO) \(\delta\): 8.86 (d, 2H, \(J = 7.8\) Hz, C(2)-H; C(2')-H), 8.52 (s, 2H, H-C(7)=N; H-C(7')=N), 8.11 – 7.92 (m, 3H, H\(_{\text{arom}}\)), 7.84 – 7.32 (m, 3H, H\(_{\text{arom}}\)), 7.21 – 7.09 (m, 3H, H\(_{\text{arom}}\)). \(^{13}\)C-NMR (75 MHz, DMSO) \(\delta\): 166.8(C\(_2\), C\(_2'\)), 156.2(C\(_7\), C\(_7'\)), 147.7(C\(_9\)), 147.5(C\(_4\), C\(_4'\)), 144.3(C\(_{12}\)), 136.9(C\(_5\), C\(_5'\)), 136.6(C\(_6\), C\(_6'\)), 132.9(C\(_{13}\)), 128.6(C\(_{10}\)), 126.8(C\(_{11}\)), 126.2(C\(_{14}\)), 124.2(C\(_{11}\)). Anal. Calcd for C\(_{18}\)H\(_{13}\)N\(_4\)NaO\(_3\)S: C, 55.67; H, 3.37; N, 14.43. Found: C, 55.22; H, 3.42; N, 14.03. LC/MS: (ESI) m/z 389 [M+1H].

**L2**

Yield: 69 %. Pale yellow solid. FT-IR (ATR, \(\nu\), cm\(^{-1}\)) 1648 (C=N), 1223 (S=O). \(^1\)H-NMR (300 MHz, DMSO) \(\delta\): 8.36 (s, 2H, C(7)-H=N; C(7')-H=N), 7.89 (m, 4H, H\(_{\text{arom}}\)), 7.71 – 7.59 (m, 2H, H\(_{\text{arom}}\)), 7.32 - 7.19 (m, 3H, H\(_{\text{arom}}\)), 2.55 (s, 6H, C(2)-CH\(_3\); C(2')-CH\(_3\)). \(^{13}\)C-NMR (75 MHz, DMSO) \(\delta\): 165.3(C\(_2\), C\(_2'\)), 158.2(C\(_7\), C\(_7'\)), 149.6(C\(_9\)),...
148.2(C4, C4'), 146.1(C12), 139.5(C5, C5'), 138.7(C6, C6'), 135.4(C13), 130.9(C10), 128.4(C1, C1'), 127.4(C14), 126.8(C11), 24.2(C16, C16'). Anal. Calcld for C20H17N4NaO3S: C, 57.68; H, 4.11; N, 13.45. Found: C, 58.24; H, 3.77; N, 14.22.

LC/MS: (ESI) m/z 417 [M+1H].

L3
Yield: 77%. Yellow solid. FT-IR (ATR, v, cm⁻¹) 1657 (C=N), 1219 (S=O). ¹H-NMR (300 MHz, DMSO) δ: 8.66 (d, 2H, J = 7.6 Hz, C(2)-H; C(2')-H), 8.06 (d, 2H, J = 8.3 Hz, C(5)-H; C(5')-H), 7.84 – 7.73 (m, 4H (H arom)), 7.63 – 7.59 (m, 3H, H arom), 1.96 (s, 6H, C(7)-CH3; C(7')-CH3). ¹³C-NMR (75 MHz, DMSO) δ: 163.8 (C2, C2'), 155.1 (C5, C5'), 151.7 (C9), 148.9 (C4, C4'), 147.2 (C12), 140.7 (C5, C5'), 139.1 (C6, C6'), 137.2 (C13), 132.7 (C10), 129.2 (C1, C1'), 128.6 (C14), 127.2 (C11), 18.7 (C15, C15'). Anal. Calcld for C20H17N4NaO3S: C, 57.68; H, 4.11; N, 13.45. Found: C, 58.24; H, 3.77; N, 14.22.

LC/MS: (ESI) m/z 417 [M+1H].

L4
Yield: 59%. Yellow solid. FT-IR (ATR, v, cm⁻¹) 1232 (C=N), 1196 (S=O). ¹H-NMR (300 MHz, DMSO) δ: 8.58 (d, 2H, J = 7.8 Hz, C(2)-H; C(2')-H), 7.94 (s, 2H, C(5)-H; C(5')-H), 7.63 (d, 2H, J = 7.8 Hz, C(1)-H; C(1')-H), 7.61 – 7.54 (m, 3H, Ar-H), 2.39 (s, 6H, C(6)-CH3; C(6')-CH3), 1.96 (s, 6H, C(7)-CH3; C(7')-CH3). ¹³C-NMR (75 MHz, DMSO) δ: 179.2 (C2, C2'), 167.4 (C5, C5'), 150.6 (C9), 147.4 (C4, C4'), 146.9 (C12), 142.8 (C5, C5'), 141.7 (C6, C6') 138.4 (C13), 133.6 (C10), 130.9 (C1, C1'), 129.1 (C14), 129.7 (C11), 22.3, (C17, C17'), 19.1 (C15, C15'). Anal. Calcld for C22H21N4NaO3S: C, 59.45; H, 4.76; N, 12.60. Found: C, 59.02; H, 4.98; N, 13.14. LC/MS: (ESI) m/z 445 [M+1H].
L5

Yield: 36%. Dark yellow solid. FT-IR (ATR, ν, cm\(^{-1}\)) 1633 (C=N), 1229 (S=O). \(^1\)H-NMR (300 MHz, DMSO) δ: 9.03 (s, 2H, C(2)-H; C(2')-H), 8.66 (s, 2H C(7)-H=N; C(7')-H=N), 8.14 (s, 2H, C(5)-H; C(5')-H), 7.92-7.88 (m, 3H, Ar-H), 7.63 – 7.58 (m, 3H, Ar-H), 7.49 – 7.42 (m, 5H, Ar-H). \(^{13}\)C-NMR (75 MHz, DMSO) δ: 163.4 (C\(_2\), C\(_2'\)), 161.6(C\(_7\), C\(_7'\)), 152.7(C\(_9\)), 147.9(C\(_12\)), 146.4(C\(_4\), C\(_4'\)), 137.2(C\(_13\)), 136.3 (C\(_6\), C\(_6'\)), 132.8(C\(_1\), C\(_1'\)), 130.8(C\(_17\), C\(_17'\)), 129.9(C\(_15\), C\(_15'\)), 128.7(C\(_10\)), 127.5(C\(_16\), C\(_16'\)), 127.2(C\(_18\), C\(_18'\)), 125.4(C\(_11\)), 125.2(C\(_14\)),124.7(C\(_5\), C\(_5'\)). Anal. Calcd. for C\(_{26}\)H\(_{17}\)N\(_4\)NaO\(_3\)S: C, 63.93; H, 3.51; N, 11.47. Found: C, 64.11; H, 3.87; N, 10.23

Synthesis of L6

L4 (1 mmol) and tributylammonium chloride (TBAC) (2.5 mmol) were added to 50 mL of isopropanol. The mixture was stirred at 60°C for 24 h resulting in the formation of a white precipitate, NaCl. Removal of this precipitation by filtration, followed by removal of volatiles from the supernatant gave an oily yellow residue. Recrystallization of this residue from iso-propanol afforded the desired L6.

Yield: 36 %. White-yellow solid. FT-IR (ATR, ν, cm\(^{-1}\)) 1654 (C=N), 1201 (S=O). \(^1\)H-NMR (300 MHz, DMSO) δ: 8.59 (d, 2H, J = 7.9 Hz, C(2)-H; C(2')-H), 8.01 (s, 2H, C(5)-H; C(5')-H), 7.59 (d, 2H, J=7.9 Hz, C(1)-H; C(1')-H), 7.54 – 7.49 (m, 3H, Ar-H), 3.19 (t, 8H, J = 7.1 Hz, N\(^+\)-[CH\(_2\)-CH\(_2\)-CH\(_2\)-CH\(_3\)]\(_4\) “TBA salt”), 2.59 (s, 6H, C(6)-CH\(_3\); C(6')-CH\(_3\)), 2.24 – 2.32 (m, 8H, N\(^+\)-[CH\(_2\)-CH\(_2\)-CH\(_2\)-CH\(_3\)]\(_4\) (“TBA salt”), 1.99 (s, 6H, C(7)-CH\(_3\); C(7')-CH\(_3\)), 1.39 – 1.42 (m, 8H, N\(^+\)-[CH\(_2\)-CH\(_2\)-CH\(_2\)-CH\(_3\)]\(_4\) “TBA salt”), 0.86 (t, 12H, J = 7.5 Hz, N\(^+\)-[CH\(_2\)-CH\(_2\)-CH\(_2\)-CH\(_3\)]\(_3\) “TBA salt”). \(^{13}\)C-NMR (75 MHz, DMSO) δ: 177.3 (C\(_2\), C\(_2'\)), 165.4(C\(_5\), C\(_5'\)), 149.4 (C\(_9\)), 148.6(C\(_4\), C\(_4'\)), 145.2(C\(_12\)), 141.9(C\(_5\), C\(_5'\)), 140.7(C\(_6\), C\(_6'\)), 137.1(C\(_13\)), 132.6(C\(_10\)), 129.8(C\(_1\), C\(_1'\)), 128.6(C\(_14\)), 128.1(C\(_11\)), 58.1
(N\textsuperscript{+}-[\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3]_4), 23.2 (N\textsuperscript{+}-[\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3]_4), 22.6 (C\textsubscript{17}, C\textsubscript{17}'), 20.4 (C\textsubscript{15}, C\textsubscript{15'}), 18.2 (N\textsuperscript{+}-[\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3]_4), 12.9 (N\textsuperscript{+}-[\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3]_4).

**Syntheses of L7**

1 mmol 2-acetyl-4-methylpyridine and 1 mmol 2 were added to a solution of dry ethanol (50 mL) and xylene (10 mL). The resulting mixture was heated to reflux overnight then cooled to ambient temperature and stored at 4\textdegree C overnight to initiate product crystallization. The resulting solid was isolated by filtration and washed with diethyl ether (3 × 10 mL) and dried under vacuum.

Yield: 97 %. Yellow solid. FT-IR (ATR, ν, cm\textsuperscript{-1}) 1623 (C=N), 1188 (S=O). \textsuperscript{1}H-NMR (300 MHz, DMSO) δ: 8.77 (d, 1H, J = 7.9 Hz, C(2)\textsubscript{2}H), 8.03 – 7.82 (m, 3H, H\textsubscript{arom}), 7.58 – 7.51 (m, 2H, H\textsubscript{arom}), 2.17 (s, 3H, C(6)\textsubscript{2}CH\textsubscript{3}), 2.26 (s, 6H, C(7)\textsubscript{2}CH\textsubscript{3}). Anal. Calcd for C\textsubscript{14}H\textsubscript{13}N\textsubscript{2}NaO\textsubscript{3}S: C, 53.84; H, 4.20; N, 8.97. Found: C, 54.07; H, 3.96; N, 9.17. LC/MS: (ESI) m/z 313 [M+1H].

**Synthesis of Complex C1 – C6**

All complexes were prepared via a modified literature procedure.\textsuperscript{[25]} 1 mmol ligand (L1 – L6) and 2 mmol Pd(CH\textsubscript{3}CN)\textsubscript{2}Cl\textsubscript{2} was refluxed 12 h in acetonitrile under nitrogen (Figure 1). C7 was prepared using same procedure with using 1 mmol L7 and 1 mmol Pd(CH\textsubscript{3}CN)\textsubscript{2}Cl\textsubscript{2}. Removal of solvent in vacuo afforded a crude solvent which was washed with diethyl ether (3 x 10 mL) and dried under vacuum.

**C1**

Yield: 54 %, pale yellow. FT-IR (ATR, ν, cm\textsuperscript{-1}) 1582 (C=N), 1189 (S=O). \textsuperscript{1}H-NMR (300 MHz, DMSO) δ: 9.24 (d, 2H, J = 8.0 Hz, C(2)\textsubscript{2}H; C(2')\textsubscript{2}H), 9.11 (s, 2H, H-
C(7)=N; H-C(7')=N), 8.46 (m, 2H, H_{arom}), 8.32 – 8.17 (m, 2H, H_{arom}), 8.05 – 7.96 (m, 3H, H_{arom}), 7.34 (m, 2H, H_{arom}). ^{13}C-NMR (75 MHz, DMSO) δ: 173.1(C_2, C_2'), 167.5(C_7, C_7'), 153.5(C_9), 152.6(C_4, C_4'), 149.2(C_{12}), 139.0(C_5, C_5'), 137.9(C_6, C_6'), 134.1(C_{13}), 130.4(C_{10}), 129.7(C_1, C_1'), 128.6(C_{14}), 123.9(C_{11}). Anal. Calcd. for C_{18}H_{13}Cl_4N_4NaO_3Pd_2S: C, 29.10; H, 1.76; N, 7.54. Found C, 29.77; H, 1.22; N, 7.53.

C2
Yield: 69 %, pale yellow - white. FT-IR (ATR, ν, cm\(^{-1}\)) 1592 (C=N), 1213 (S=O). ^1H-NMR (300 MHz, DMSO) δ: 9.12 (s, 2H, C(7)-H=N; C(7')-H=N), 8.06 – 7.91 (m, 4H, H_{arom}), 7.82 - 7.79 (m, 3H, H_{arom}), 7.72 – 7.63 (m, 2H, H_{arom}), 2.73 (s, 6H, C(2)-CH_3; C(2')-CH_3). ^{13}C-NMR (75 MHz, DMSO) δ: 173.4 (C_2, C_2'), 166.4(C_7, C_7'), 152.7(C_9), 151.2(C_4, C_4'), 149.7(C_{12}), 146.4(C_5, C_5'), 145.9(C_6, C_6'), 140.4(C_{13}), 135.2(C_{10}), 134.4(C_1, C_1'), 129.9(C_{14}), 128.5(C_{11}), 27.4 (C_{16}, C_{16'}) Anal. Calcd. for C_{20}H_{17}Cl_4N_4NaO_3Pd_2S: C, 31.15; H, 2.22; N, 7.27. Found C, 31.97; H, 2.21; N, 7.14.

C3
Yield: 54 %, pale yellow. FT-IR (ATR, ν, cm\(^{-1}\)) 1583 (C=N), 1223 (S=O). ^1H-NMR (300 MHz, DMSO) δ: 8.96 (d, 2H, J = 8.1 Hz, C(2)-H; C(2')-H), 8.32 (d, 2H, J = 8.1 Hz, C(5)-H; C(5')-H), 7.91 – 7.84 (m, 3H, H_{arom}), 7.69 – 7.61 (m, 4H, H_{arom}), 2.39 (s, 6H, C(7)-CH_3; C(7')-CH_3). ^{13}C-NMR (75 MHz, DMSO) δ: 170.4 (C_2, C_2'), 159.7 (C_5, C_5'), 158.1 (C_9), 153.4(C_4, C_4'), 152.4 (C_{12}), 142.4 (C_5, C_5'), 139.7 (C_6, C_6'), 139.2 (C_{13}), 134.6 (C_{10}), 132.9 (C_1, C_1'), 129.5 (C_{14}), 128.9 (C_{11}), 20.3 (C_{15}, C_{15'}). Anal. Calcd. for C_{20}H_{17}Cl_4N_4NaO_3Pd_2S: C, 31.15; H, 2.22; N, 7.27. Found C, 31.23; H, 2.29; N, 7.79.
C4
Yield: 63 %, pale yellow. FT-IR (ATR, ν, cm\(^{-1}\)) 1589 (C=N), 1227 (S=O). \(^1\)H-NMR (300 MHz, DMSO) δ: 8.89 (d, 2H, J = 7.9, C(2)-H; C(2')-H), 8.02 (s, 2H, C(5)-H; C(5')-H), 7.79 (d, 2H, J= 8.0 Hz, C(1)-H; C(1')-H), 7.82 – 7.76 (m, 3H, H\(_\text{arom}\)), 2.45 (s, 6H, C(6)-CH\(_3\); C(6')-CH\(_3\)). \(^13\)C-NMR (75 MHz, DMSO) δ: 179.5 (C\(_2\), C\(_2\)'), 172.6 (C\(_5\), C\(_5\)'), 158.1 (C\(_9\)), 152.4 (C\(_4\), C\(_4\)'), 151.8 (C\(_12\)), 148.6 (C\(_5\), C\(_5\)'), 147.9 (C\(_6\), C\(_6\)'), 145.2 (C\(_13\)), 143.4 (C\(_10\)), 136.5 (C\(_1\), C\(_1\)'), 135.2 (C\(_14\)), 134.8 (C\(_11\)), 25.2 (C\(_17\), C\(_17\)'), 21.4 (C\(_15\), C\(_15\')). Anal. Calcld. for C\(_{22}\)H\(_{21}\)Cl\(_4\)N\(_4\)NaO\(_3\)Pd\(_2\)S: C, 33.07; H, 2.65; N, 7.01. Found C, 32.76; H, 2.34; N, 7.61.

C5
Yield: 59 %, yellow. FT-IR (ATR, ν, cm\(^{-1}\)) 1592 (C=N), 1215 (S=O). \(^1\)H-NMR (300 MHz, DMSO) δ: 9.25 (s, 2H, C(2)-H; C(2')-H), 8.79 ( s, 2H, C(7)-H=N; C(7')-H=N), 8.33 (s, 2H, C(5)-H; C(5')-H), 7.83 – 7.78 (m, 3H, H\(_\text{arom}\)), 7.66 – 7.61 (m, 3H, H\(_\text{arom}\)), 7.44 – 7.40 (m, 5H, H\(_\text{arom}\)). \(^13\)C-NMR (75 MHz, DMSO) δ: 173.7 (C\(_2\), C\(_2\)'), 171.2 (C\(_7\), C\(_7\)'), 166.5 (C\(_9\)), 153.4 (C\(_12\)), 151.7 (C\(_4\), C\(_4\)'), 142.9 (C\(_13\)), 141.3 (C\(_6\), C\(_6\)'), 140.8 (C\(_1\), C\(_1\)'), 136.3 (C\(_17\), C\(_17\)'), 135.4 (C\(_15\), C\(_15\')), 133.6 (C\(_10\)), 132.2 (C\(_16\), C\(_16\)'), 132.0 (C\(_18\), C\(_18\)'), 130.4 (C\(_11\)), 129.2 (C\(_14\)), 125.3 (C\(_5\), C\(_5\')). Anal. Calcld. for C\(_{26}\)H\(_{17}\)N\(_4\)NaO\(_3\)S: C, 63.93; H, 3.51; N, 11.47. Found C, 64.59; H, 3.28; N, 11.51.

C6
Yield: 34 %, white-yellow. FT-IR (ATR, ν, cm\(^{-1}\)) 1581 (C=N), 1192 (S=O). \(^1\)H-NMR (300 MHz, DMSO) δ: 8.91 (d, 2H, J = 8.1 Hz, C(2)-H; C(2')-H), 8.26 (s, 2H, C(5)-H; C(5')-H), 7.92 (d, 2H, J=8.0 Hz, C(1)-H; C(1')-H), 7.83 – 7.79 (m, 3H, H\(_\text{arom}\)), 3.25 (t, 8H, J = 7.4 Hz, N\(^+\)-[CH\(_2\)-CH\(_2\)-CH\(_2\)-CH\(_3\)]\(_4\) “TBA Salt”), 2.43 (s, 6H, C(6)-CH\(_3\); C(6')-CH\(_3\)), 2.36 – 2.32 (m, 8H, N\(^+\)-[CH\(_2\)-CH\(_2\)-CH\(_2\)-CH\(_3\)]\(_4\) “TBA Salt”), 2.18 (s, 6H, C(7)-CH\(_3\); C(7')-CH\(_3\)), 1.59 – 1.51 (m, 8H, N\(^+\)-[CH\(_2\)-CH\(_2\)-CH\(_2\)-CH\(_3\)]\(_4\) “TBA Salt”), 0.92 (t, 12H, J =
7.7 Hz, N$^+$-[CH$_2$-CH$_2$-CH$_2$-CH$_3$]$_4$ “TBA Salt”.$^{13}$C-NMR (75 MHz, DMSO) δ: 184.5(C$_2$, C$_2'$), 172.3(C$_5$, C$_5'$), 157.1(C$_9$), 155.9(C$_{12}$), 152.4(C$_5$, C$_5'$), 148.2(C$_6$, C$_6'$), 146.3(C$_{13}$), 142.9 (C$_{10}$), 126.9 (C$_1$, C$_1'$), 125.1 (C$_{14}$), 59.7 (N$^+$-[CH$_2$-CH$_2$-CH$_2$-CH$_3$]$_4$), 25.4 (C$_{17}$, C$_{17'}$), 23.2 (N$^+$-[CH$_2$-CH$_2$-CH$_2$-CH$_3$]$_4$), 22.8 (C$_{15}$, C$_{15'}$), 18.9 (N$^+$-[CH$_2$-CH$_2$-CH$_2$-CH$_3$]$_4$), 13.6 (N$^+$-[CH$_2$-CH$_2$-CH$_2$-CH$_3$]$_4$).

C7
Yield: 83 %, orange. FT-IR (ATR, ν, cm$^{-1}$) 1588 (C=N), 1229 (S=O). $^1$H-NMR (300 MHz, DMSO) δ: 8.93 (d, 1H, J = 7.7, C(2)), 8.22 – 8.06 (m, 3H, H$_{arom}$), 7.91 – 7.78 (m, 2H, H$_{arom}$), 2.19 (s, 3H, C(6)-CH$_3$), 2.02 (s, 6H, C(7)-CH$_3$). Anal. Calcd. for C$_{14}$H$_{13}$Cl$_2$N$_2$NaO$_3$PdS: C, 34.34; H, 2.68; N, 5.72. Found C, 34.96; H, 2.41; N, 5.16.

General Procedure of Suzuki Coupling Reactions
A 50 mL Schlenk tube was equipped with a magnetic stir bar. Complex C1 - C6 and 5 mL of H$_2$O were added into the flask. Then 1 mmol of aryl bromide, 1.3 mmol of arylboronic acid and 2 mmol powder K$_2$CO$_3$ were added into the flask. The reaction mixture was stirred at the pre-arranged temperature for appropriate reaction time. It was then cooled to room temperature, diluted with water, and extracted with CH$_2$Cl$_2$ for three times. The organic phase was dried with Na$_2$SO$_4$ and concentrated to yield a solid.

Mercury Poisoning Experiments
Mercury is an established poison for heterogeneous Pd-coupling reactions. For the test, the coupling reaction of 4-methylphenylboronic acid and 4-bromoanisole using C6 as a catalyst under the conditions listed in Table 3 were used. The reaction was allowed to proceed for 25 min (63% yield, determined by GC) and then 300 molar
equivalents of mercury, relative to the Pd catalyst, were added. The reaction was
allowed to continue for another 25 min, giving 96% product as a final yield.

**Catalyst Recycling for the Suzuki Reaction**

Catalyst recycling experiments were performed via a modified literature procedure.\[34\] When the reaction of Table 4 entry 9 with the catalysts C4 and C6 were completed, the reaction mixtures were cooled to room temperature and extracted with 5 mL ethyl ether. Aqueous phase was separated and used for next cycle. Time difference between cycles did not pass more than 5 min. To separated aqueous phase, 4-bromoanisole (1 mmol), 4-methylphenylboronic acid (1.3 mmol), K$_2$CO$_3$ (2 mmol) were reacted again at 70°C for 2h. This procedure repeated for 15 times.

**Results and Discussion**

**Synthesis and Characterization of ligands and Pd(II) complexes**

Ligands were prepared via condensation reactions of the sodium salt of 2,5-diaminobenzene sulfonylic acid. The diamine precursor was first dissolved in 1M NaOH and converted to 2,5-diaminobenzene sulfonylic acid’s sodium salt. Sodium salts of α-diamine ligands were prepared by condensing the corresponding aldehyde or ketone with sulfonated aniline in toluene using a Dean-Stark apparatus. L6 was prepared with using L5 and excess tetrabuhylammonium chloride in iso–propanol in a modified literature procedure.\[35\] Palladium complexes C1 – C6 were prepared with using ligands L1 – L6 and two fold Pd(CH$_3$CN)$_2$Cl$_2$ precursor in anhydrous THF (Figure 1). Characterization of ligands and complexes were accomplished by a combination of elemental analysis, FT-IR, $^1$H–NMR and $^{13}$C–NMR spectroscopy. Ligands and complexes elemental analysis and mass results are compatible with experimental results. After complexation, decreasing ν(C=N) values between 41 – 74
cm\(^{-1}\) is an important clue which point out that nitrogen atoms of ligands coordinate to Pd(II) center\[^{36}\]. Other important information about ligands coordination to metal was collected by \(^1\)H-NMR spectra. The characteristic imine proton resonance of L\(_1\), L\(_2\) and L\(_5\) shows between δ 8.36 – 8.52 ppm as a sharp singlet. Similar resonance shifts have been observed in related divalent compounds before\[^{37-39}\]. Compared to those of the free ligands L\(_1\), L\(_2\) and L\(_5\), the imine proton resonances for C\(_1\), C\(_2\) and C\(_5\) are shifted downfield about 0.6 – 0.8 ppm. Similar trends were observed with our and Buffin’s studies before\[^{25, 33, 40, 41}\]. Protons in the 6-position of the pyridine ring (L\(_1\) and L\(_5\)) are observed as doublets slightly downfield from the imine signal (δ 8.86 ppm for L\(_1\) and δ 8.48 ppm for L\(_5\)). L\(_3\) is a derivative of L\(_1\) which imine proton in L\(_1\) exchange with CH\(_3\) group. Disappearing of imine proton resonance and sharp singlets at δ 1.96 ppm are characteristic for L\(_3\). In L\(_6\), sharp singlets at δ 1.99 and δ 2.59 ppm are CH\(_3\) resonances. Other resonances different form L\(_4\) derivative are NBu\(_4\) resonances and these resonances determinded between δ 3.19 – 0.86 ppm as multiplets and triplets. \(^{13}\)C-NMR can be very useful to prove the generation of diimines. Singlet resonances between 163.4 – 168.8 ppm attributed to the imine carbons L\(_1\), L\(_2\) and L\(_5\)\[^{42}\]. All complexes are stable in air and readily soluble in polar organic compounds such as methanol, DMSO and DMF.

**Influence of the Diimine Ligands on Suzuki Reaction**

To examine the effect of ligands on Suzuki reaction, coupling reaction of bromobenzene and phenylboronic acid was as a model reaction. DMA (dimethyl acetamide) was used as a solvent, and K\(_2\)CO\(_3\) as the base. Reactivity of ligands are increased with alkyl groups because stronger donating ability of alkyl substituents, making the donor atoms more electron-rich (Table 1). Using [TBA]\(^+\)instead of [Na]\(^+\) increased the yields (Table 1, entry 4 and 6). According to our previous report, this
improvement on yields was investigated by using $^1$H-NMR spectroscopy and stability of complexes in water was compared. Decomposition process was tracked with occurring of aldehyde proton. As a result, catalyst C4 was started to decompose after 4h. On the other hand, catalyst C6 was started to decompose very slowly after a day\textsuperscript{[43]}. Imine ligands which had two binding sites found more active than analogues which had one binding sites (Table 1, Entry 4 and 7).

**Suzuki Reaction in Aqueous Phase**

Palladium catalyzed Suzuki coupling reaction depends on several variables like reaction temperature, base system, catalyst type and amount. To regulate the reaction, coupling reaction between 4-bromoanisole and 4-methylphenylboronic acid was chosen as a model reaction. But before optimization reactions the best catalyst was determined with using model reaction and results were compared with literature results (Table 2). The primary objection was determining the most active catalyst according to side groups of diimine ligands. In the series of complexes (C1 – C5), complex C4 gave the highest yield while the quinoline derivative of C5 gave low yields (Table 2, Entry 7). It was clear from Table 2 that increasing the alkyl group on ligand structure increased the activity of catalyst. Nolan and co-workers explained that activity increasing because of the stronger donating ability of alkyl substituents\textsuperscript{[44]}. To make a clear comparison between dinuclear and mononuclear complexes C7, which is mononuclear analogue of C4, was synthesized, characterized and applied as a catalyst in Suzuki reaction (Figure 2). According to Table 2, when C7 was used catalytic reaction ended in 4h. Otherwise when C4 was used as a catalyst reaction ended in 2h. These results proved that, in dinuclear complex both Pd centre works as an independent catalyst so substrates turns to products faster than mononuclear analogue. Also we compared our catalysts with Zhou’s complexes which is one cored
but very similar complexes to our complexes at the same conditions and complex C4 was found more active than Zhou’s complexes [35] (Figure 2).

**Figure 2** Schematic displays of C4 and C7

To improve the activity of C4, sodium group was exchanged with [NBu4]⁺ group. [NBu4]⁺ derivative of C4 is entitled as C6. The addition of 0.5 equiv. of TBAB to the reaction mixture accelerated the reaction (Table 2, Entry 6 and 8). The role of the ammonium salt is thought to be twofold. Firstly, it facilitates solvation of the aryl halide in neat water. Secondly, it accelerates the coupling reaction by formation of a boronate complex [ArB(OH)₃][R₄N]⁺ [45, 46]. A comparison between the additives which binds to metal center (C6) and free in the reaction medium (C4 + TBAB) was made. As a result, there were no significant differences between (C4 + TBAB) and C6 observed on catalytic reaction at the same conditions (Table 2, Entry 8 and 9). Also it was found that the position of the R groups effects the reaction and R groups which bind to imine carbon, increases the reaction yield (Table 2, Entry 4-5). To understand the effects between mononuclear and binuclear catalyst structures, C7 was synthesized and model reaction with C7 was tried with different catalyst loadings (Table 2, Entry 10-11). According to the results, we prove that difference in reaction rates between mononuclear and binuclear structures directly related to the Pd concentration.

**Table 2** Effect of Complexes on Suzuki Coupling Reaction

As a result C4 with TBAB and C6 was chosen as the active catalysts and focused on them for further studies. In order to determine the reaction temperature, series of
reactions were performed with using C4 and C6. Reaction results are summarized in Figure 3. Figure 3 is a complete temperature screening of reaction and according to the figure maximum yield was obtained at 70 °C for both catalysts. As a result the reaction temperature was identified as 70°C.

**Figure 3**: The effect of temperature on the Suzuki reaction. Reaction conditions: 1 mmol of 4-bromoanisole, 1.3 mmol of 4-methylphenylboronic acid, 2 mmol of K$_2$CO$_3$, 0.01 mol % catalyst, 4h, 5 mL of H$_2$O, 0.5 mmol TBAB used for the reactions with C4. To determine the reaction time and base system, model reaction was screened and results were summarized in Table 3. According to Table 3, reaction almost completes after 2h and no significant difference was observed between selected bases so K$_2$CO$_3$ which gave highest yield and cheaper (Table 3, entry 1), was chosen as the suitable base. NEt$_3$ as an organic base was not efficient for the reaction (Table 3 entry 5).[47]

**Table 3** Time dependent optimization of base for Suzuki reaction using C4$^9$

**Mercury Poisoning**

According to Whitesides and Finke’s studies, mercury forms amalgam with the catalytically active NP’s and if the catalytic reaction stops after mercury was added this means the reaction mechanism follows heterogeneous pathway or follows homogeneous pathway if mercury does not suppress the pathway $^{[48-50]}$. The coupling of 4-bromoanisole and 4-methylphenylboronic acid under optimized conditions with using C6 as a catalyst in the presence or absence of mercury was investigated. The
reaction was allowed to proceed for 60 min (54% yield) before the mercury was added in a molar ratio of 300 equivalents to the palladium complex. Then the reaction was continued to proceed another 60 min, a 92% product yield was obtained. The result verifies that the palladium complex is the real catalyst in the reaction.

**Effect of Catalyst on Suzuki coupling reactions**

As illustrated in Table 3, various aryl bromides containing an electron-withdrawing groups (Table 4, entries 1-6) and electron-donating groups (Table 4, entries 7-12) were tried for the cross-coupling reaction with using catalysts C4 and C6. The electron deficient aryl bromides and electron-rich aryl bromides showed an excellent reactivity and gave nearly quantitative yields. Interestingly sterically hindered aryl bromide didn’t prevent the reaction and reaction completed with very high yields almost quantitatively with C6. (Table 4, entry 12). Coupling of aryl chlorides with phenylboronic acid were tried and all reactions were completed with moderate yields (Table 4, entries 14 - 16).

**Table 4** Suzuki Coupling of various aryl halides with arylboronic acids.  

**Catalyst Recycling**

We knew that Pd-diimine complexes are very sensitive to aqueous media and most of Pd-diimine complexes can stay stable in water only couple of hours. On the other hand, there are some examples which can stay stable in water more than a week [33, 41]. To investigate the relation between recyclability potential of complexes and their
stability in water, complexes was screened with using \(^1\)H-NMR spectroscopy. All 
prepared samples stayed in solution during the test. As a result, it was observed that 
\(\text{\textit{C1}}\) decomposed in 4 hours and \(\text{\textit{C5}}\) decomposed in 6 hours. Other catalysts except 
\(\text{\textit{C6}}\) decomposed between 4 and 6 hours. However \(\text{\textit{C6}}\) stayed stable in water more 
than a day. After 28 h \(\text{\textit{C6}}\) decomposed to untraceable products. This additional 
stability of \(\text{\textit{C6}}\) can be explained by the effect of bulky \([\text{NBu}_4]^+\) group\(^{[43]}\). To test the 
reusability of \(\text{\textit{C4}}\) and \(\text{\textit{C6}}\) model reaction was used at optimized conditions. Table 5 
summarizes the reusability properties of \(\text{\textit{C4}}\) and \(\text{\textit{C6}}\). According to the Table 5, 
catalyst \(\text{\textit{C4}}\) can be reused for three times and the yield and conversion decreases 
sharply after second cycle. On the other hand, \(\text{\textit{C6}}\) was used for 10 cycles without any 
decrease on the yield or conversion. After 10\(^{th}\) cycle, yield and conversion begins to 
decrease and both was reached zero after 14\(^{th}\) cycle. According to the results, 
reusability properties of complexes are directly related with the stability complexes in 
water. To further ascertain whether the recovered catalyst is a palladium complex or 
palladium particles, a mercury poisoning test was designed for the reuse of the 
catalysts in the second runs of the coupling of model reaction under the optimized 
conditions. Reactions were allowed to proceed for 1h before the mercury was added 
in a molar ration of 300 equivalents to the palladium. Both coupling reaction was 
quantitatively completed after another hour. These results indicate that the recovered 
catalysts for both run are palladium complexes.

\textbf{Table 5} Reusability of the catalysts\(^a\)
Conclusion

In summary a series of new binuclear ionic sulfonated α-diimine ligands were prepared and employed as ligands for the palladium catalyzed Suzuki reactions. According to our results and recent work\cite{24}, both active sites in binuclear structure behaves as an individual catalyst (like mono-nuclear) and completed the reaction more quickly than mono-nuclear analogue. So, to increase the rate of the Suzuki reaction, increasing the active sites may be a useful alternative. On the other hand, it was proved that the activities of complexes are directly related to the decomposition time of diimine ligands. Also it was found that alkyl groups which bind to the imine carbon, increases the reaction yield. Mercury poisoning experiments demonstrate that coupling reactions were catalyzed by synthesized complexes. Using TBA salt instead of Na salt gained stability to the complex C6 so C6 was reused in the coupling reaction more than 10 times without any decrease on the yield or conversion.

Acknowledgements

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References


Figure 1: Schematic display of ligands and complexes.
**Figure 2** Schematic displays of C4, C7 and Complex 1
**Figure 3:** The effect of temperature on the Suzuki reaction. Reaction conditions: 1 mmol of 4-bromoanisole, 1.3 mmol of 4-methylphenylboronic acid, 2 mmol of K$_2$CO$_3$, 0.01 mol % catalyst, 4h, 5 mL of H$_2$O, 0.5 mmol TBAB used for the reactions with C4.
Table 1: Effect of Ligands on Suzuki Coupling Reaction

![Chemical structure diagram](image)

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<td>L7</td>
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<sup>a</sup> Reaction conditions: 1 mmol of bromobenzene, 1.3 mmol of phenylboronic acid, 2 mmol of K<sub>2</sub>CO<sub>3</sub>, 3 mol% Pd(OAc)<sub>2</sub>, 3.3 mol% ligand, 2 mL DMA, 80 °C, 1 h.

<sup>b</sup> All reactions were monitored by GC, yields are average of two runs.
Table 2 Effect of Complexes on Suzuki Coupling Reaction

![Reaction diagram]

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\(^a\) Reaction conditions: 1 mmol of 4-bromoanisole, 1.3 mmol of 4-methylphenylboronic acid, 2 mmol of K\(_2\)CO\(_3\), 0.01 mol % catalyst, 75 °C, 5 mL of H\(_2\)O, reaction time = 4h.\(^b\) 0.5 mmol TBAB. \(^c\)Catalyst loading: 0.02 mol%.\(^d\) Reaction Time: 8h, catalyst loading.
Table 3 Time dependent optimization of base for Suzuki reaction using C4 and C7

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*aReaction Conditions: 1 mmol of 4-bromoanisole, 1.3 mmol of 4-methylphenylboronic acid, 2 mmol of base, 0.01 mol % C4, 70 °C, 5 mL of H₂O, N₂, 0.5 mmol TBAB, C7 yields represented in parantheses. 

bIsolated yield.
Table 4 Suzuki Coupling of various aryl halides with arylboronic acid. \(^a\)

![Chemical Structure](image)

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\(^a\) Reaction Conditions: 1 mmol of aryl halide, 1.3 mmol of boronic acid, 2 mmol of K\(_2\)CO\(_3\), 0.01 mol % catalyst, 75 °C, 2 h, 5 mL of H\(_2\)O.

\(^b\) 0.5 mmol TBAB

\(^c\) Isolated Yield

\(^d\) All reactions were monitored by GC and results are average of 2 run.
Table 5 Reusability of the catalysts

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<tr>
<td>Yield (%)&lt;sup&gt;b&lt;/sup&gt;</td>
<td>79</td>
<td>63</td>
<td>11</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Conversion (%)&lt;sup&gt;b&lt;/sup&gt;</td>
<td>84</td>
<td>72</td>
<td>19</td>
<td>4</td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Yield (%)&lt;sup&gt;c&lt;/sup&gt;</td>
<td>98</td>
<td>98</td>
<td>97</td>
<td>96</td>
<td>95</td>
<td>93</td>
<td>94</td>
<td>92</td>
<td>90</td>
<td>43</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Conversion (%)&lt;sup&gt;c&lt;/sup&gt;</td>
<td>99</td>
<td>99</td>
<td>99</td>
<td>99</td>
<td>99</td>
<td>98</td>
<td>98</td>
<td>95</td>
<td>94</td>
<td>92</td>
<td>43</td>
<td>7</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup>Reaction Conditions: 1 mmol of 4-bromoanisole, 1.3 mmol of 4-methylphenylboronic acid, 2 mmol of base, 0.01 mol % catalyst, 2h for each run, 70 °C, 5 mL of H₂O, N₂. <sup>b</sup>Values for C4. <sup>c</sup>Values for C6.
Table 1: Effect of Ligands on Suzuki Coupling Reaction\(^a\)

\[
\begin{align*}
\ce{C6H5Br + C6H5B(OH)2 &-> C6H5C6H5} \\
\hline
\text{Entry} & \text{Catalyst} & \text{Yield}^b \\
\hline
1 & L1 & 23 \\
2 & L2 & 36 \\
3 & L3 & 42 \\
4 & L4 & 54 \\
5 & L5 & 13 \\
6 & L6 & 71 \\
7 & L7 & 63 \\
\hline
\end{align*}
\]

\(^a\) Reaction conditions: 1 mmol of bromobenzene, 1.3 mmol of phenylboronic acid, 2 mmol of \(\text{K}_2\text{CO}_3\), 3 mol % \(\text{Pd(OAc)}_2\), 3.3 mol% ligand, 2 mL DMA, 80 \(^\circ\)C, 1h.

\(^b\) All reactions were monitored by GC, yields are average of two runs.
Table 2 Effect of Complexes on Suzuki Coupling Reaction\(^a\)

![Chemical structure]

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PdCl(_2)</td>
<td>24</td>
</tr>
<tr>
<td>2</td>
<td>Li(_2)PdCl(_4)</td>
<td>19</td>
</tr>
<tr>
<td>3</td>
<td>C1</td>
<td>52</td>
</tr>
<tr>
<td>4</td>
<td>C2</td>
<td>61</td>
</tr>
<tr>
<td>5</td>
<td>C3</td>
<td>74</td>
</tr>
<tr>
<td>6</td>
<td>C4</td>
<td>82</td>
</tr>
<tr>
<td>7</td>
<td>C5(^b)</td>
<td>24</td>
</tr>
<tr>
<td>8</td>
<td>C4(^b)</td>
<td>92</td>
</tr>
<tr>
<td>9</td>
<td>C6</td>
<td>97</td>
</tr>
<tr>
<td>10</td>
<td>C7(^c)</td>
<td>57</td>
</tr>
<tr>
<td>11</td>
<td>C7(^c)</td>
<td>89</td>
</tr>
</tbody>
</table>

\(^a\) Reaction conditions: 1 mmol of 4-bromoanisole, 1.3 mmol of 4-methylphenylboronic acid, 2 mmol of K\(_2\)CO\(_3\), 0.01 mol % catalyst, 75 \(^\circ\)C, 5 mL of H\(_2\)O, reaction time = 4h.\(^b\) 0.5 mmol TBAB. \(^c\) Catalyst loading: 0.02 mol%.\(^d\) Reaction Time: 8h, catalyst loading.
Table 3 Time dependent optimization of base for Suzuki reaction using C4 and C7

<table>
<thead>
<tr>
<th>Entry</th>
<th>Base</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>30 min</td>
</tr>
<tr>
<td>1</td>
<td>K₂CO₃</td>
<td>7(-)</td>
</tr>
<tr>
<td>2</td>
<td>Cs₂CO₃</td>
<td>11(-)</td>
</tr>
<tr>
<td>3</td>
<td>Na₂CO₃</td>
<td>8(-)</td>
</tr>
<tr>
<td>4</td>
<td>NaOH</td>
<td>(-)</td>
</tr>
<tr>
<td>5</td>
<td>NEt₃</td>
<td>(-)</td>
</tr>
</tbody>
</table>

*aReaction Conditions: 1 mmol of 4-bromoanisole, 1.3 mmol of 4-methylphenylboronic acid, 2 mmol of base, 0.01 mol % C4, 70 °C, 5 mL of H₂O, N₂, 0.5 mmol TBAB, C7 yields represented in parantheses.  
*bIsolated yield.
Table 4 Suzuki Coupling of various aryl halides with arylboronic acid.  

\[
\begin{array}{cccccc}
\text{Entry} & \text{X} & \text{Y} & \text{Z} & \text{Yield (Conversion)}\%^c & \text{Yield (Conversion)}\%^d \\
1 & \text{Br} & \text{H} & \text{H} & 99 (99) & 99 (99) \\
2 & \text{Br} & 4-\text{COMe} & \text{H} & 92 (96) & 97 (99) \\
3 & \text{Br} & 2-\text{CHO} & \text{H} & 91 (93) & 94 (97) \\
4 & \text{Br} & 4-\text{NO}_2 & \text{H} & 96 (99) & 96 (99) \\
5 & \text{Br} & 4-\text{Cl} & \text{H} & 93 (97) & 98 (99) \\
6 & \text{Br} & 4-\text{NH}_2 & \text{H} & 96 (99) & 99 (99) \\
7 & \text{Br} & 4-\text{OMe} & \text{H} & 96 (99) & 99 (99) \\
8 & \text{Br} & 4-\text{Me} & \text{H} & 91 (97) & 99 (99) \\
9 & \text{Br} & 4-\text{OMe} & \text{Me} & 94 (96) & 97 (99) \\
10 & \text{Br} & 2-\text{Me} & \text{H} & 95 (99) & 99 (99) \\
11 & \text{Br} & 4-\text{Me} & 4-\text{Me} & 84 (92) & 94 (99) \\
12 & \text{Br} & 2-\text{Me} & 4-\text{Me} & 84 (91) & 97 (99) \\
13 & \text{Br} & 2,6-\text{diMe} & \text{H} & 89 (93) & 96 (99) \\
14 & \text{Cl} & \text{H} & \text{H} & 69 (72) & 77 (82) \\
15 & \text{Cl} & 4-\text{Me} & \text{H} & 71 (68) & 79 (72) \\
15 & \text{Cl} & 4-\text{NO}_2 & \text{H} & 79 (83) & 82 (89) \\
16 & \text{Cl} & 4-\text{OMe} & \text{H} & 73 (75) & 78 (81) \\
\end{array}
\]

\(a\) Reaction Conditions: 1 mmol of aryl halide, 1.3 mmol of boronic acid, 2 mmol of K\(_2\text{CO}_3\), 0.01 mol % catalyst, 75 °C, 2 h, 5 mL of H\(_2\text{O}\).

\(b\) 0.5 mmol TBAB

\(c\) Isolated Yield

\(d\) All reactions were monitored by GC and results are average of 2 run.
Table 5 Reusability of the catalysts$^a$

<table>
<thead>
<tr>
<th>Cycle</th>
<th>1st</th>
<th>2nd</th>
<th>3rd</th>
<th>4th</th>
<th>5th</th>
<th>6th</th>
<th>7th</th>
<th>8th</th>
<th>9th</th>
<th>10th</th>
<th>14th</th>
<th>15th</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yield (%)$^b$</td>
<td>79</td>
<td>63</td>
<td>11</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Conversion (%)$^b$</td>
<td>84</td>
<td>72</td>
<td>19</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Yield (%)$^c$</td>
<td>98</td>
<td>98</td>
<td>97</td>
<td>96</td>
<td>95</td>
<td>93</td>
<td>94</td>
<td>92</td>
<td>90</td>
<td>43</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Conversion (%)$^c$</td>
<td>99</td>
<td>99</td>
<td>99</td>
<td>99</td>
<td>99</td>
<td>98</td>
<td>98</td>
<td>95</td>
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</tr>
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$^a$Reaction Conditions: 1 mmol of 4-bromoanisole, 1.3 mmol of 4-methylphenylboronic acid, 2 mmol of base, 0.01 mol % catalyst, 2h for each run, 70 °C, 5 mL of H$_2$O, N$_2$. $^b$Values for C$_4$. $^c$Values for C$_6$. 
Schematic display of ligands and complexes.

203x156mm (300 x 300 DPI)
Schematic displays of C4, C7 and Complex 1
191x61mm (300 x 300 DPI)
The effect of temperature on the Suzuki reaction.

67x38mm (300 x 300 DPI)
\[
\text{\begin{tikzpicture}
    \node (start) at (0,0) {\text{Br}};
    \node (reactant1) at (1,0) {\text{Br}};
    \node (reactant2) at (2,0) {\text{D(OH)$_2$}};
    \node (product) at (3,0) {\text{D}};
    \draw[->] (reactant1) -- (reactant2) -- (product);
\end{tikzpicture}}
\]

96x10mm (300 x 300 DPI)
\[
\text{Br} \quad \text{OMe} \\
\text{B(OH)}_2 \quad \text{OMe}
\]