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Synthesis of Sterically Hindered *N*-Benzyladamantyl Substituted Benzimidazol-2-ylidene Palladium Complexes and Investigation of Their Catalytic Activities in Aqueous Medium

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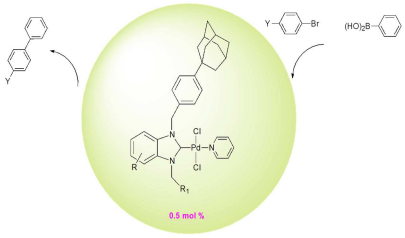

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ABSTRACT

NHC-Pd-PEPPSI complexes with bulky benzyladamantyl substituted N-heterocyclic carbenes (NHC) were synthesised and characterised by NMR, HRMS, and micro analysis. These complexes were then used for Suzuki-Miyaura coupling reactions between aryl bromides and phenylboronic acid. With low catalyst loading, all synthesised complexes rapidly catalysed the Suzuki-Miyaura cross-coupling reaction in *i*-PrOH/water (1:3 v/v) at room temperature in air. All palladium compounds were stable and had high catalytic activity for the Suzuki-Miyaura coupling reaction.

1. Introduction

N-heterocyclic carbene (NHC) complexes have been attracting considerable attention for the last 30 years due to their unique performance in homogeneous catalysis.[1-3] NHC complexes owe this unique performance both to the strong σ-donor ability of NHC ligands and the stability of the M-C_2 bond in extreme reaction conditions. Also, steric hindrance of NHCs contributes to metal complex stability. Modification of the NHC moiety has attracted great interest as a strategy to obtain better catalytic performance under different catalytic conditions.

Among the various chemical transformations catalyzed by platinum group metals, palladium catalyzed reactions are widely used. For example, the palladium catalyzed Suzuki-Miyaura reaction is one of the most important and prized[4] coupling reaction used to produce various bio-active and fine chemicals.[5-7]

Green chemical reactions extensively use water.[8] The use of water has changed the opinion that has existed for many years that many organic reactions occur only in organic solvents. The Suzuki reaction is a prototypical example of the benefits of reactions in water.[9] Many strategies have been reported for the Suzuki reaction in aqueous media that addressed water-soluble catalysts,[10] addition of organic solvents[11] and ligand-free methodology.[12] However, the Suzuki reaction has some problems, such as low substrate solubility and catalyst stability in water. To overcome these problems, several additives have already been successfully utilised.[13-16]

Another way to improve the efficiency of Suzuki catalysis in water is the employment of hydrophilic ligands, such as *N*-heterocyclic carbenes (NHCs) or phosphine ligands. Despite the wide application and success of phosphine ligands, they suffer in the Suzuki reaction due to toxicity, sensitivity to air and moisture, and difficult separation from organic products. As a result, NHCs have emerged as alternatives to phosphine ligands due to superior features such as non-toxicity and stability in air and moisture.[17-23] The most well-known palladium catalyst series for coupling reactions is PEPPSI-Pd (pyridine enhanced precatalyst preparation stabilization and initiation) type complexes.[24,25] Since 2006, when Organ and co-workers reported PEPPSI-Pd complexes that demonstrated high activity towards C-C cross-coupling reactions,[26] extensive studies on the structure and activities of PEPPSI-Pd complexes have been published.[27-29]

In this study, a series of sterically hindered PEPPSI-Pd-NHC complexes and their catalytic applications to Suzuki-Miyaura cross-coupling reactions in *i*-PrOH/water were studied.

2. Results and discussion

Our strategy was based on the construction of sterically hindered benzyladamantyl substituted *N*-heterocyclic carbene precursors from 4-adamantylbenzyl bromide (Scheme 1). This

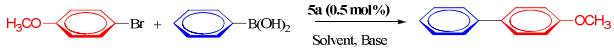
new compound was fully characterized by NMR and micro analyses. The benzylic CH_2 protons had a resonance at 4.50 ppm. To obtain the desired 1-(4-adamantylbenzyl)-3-aryl-substituted NHC precursors, the N-benzyl substituted benzimidazols were prepared according to our previous studies.[25] The reaction of N-benzyl substituted benzimidazol with 4-adamanthylbenzyl bromide in *N*,*N*-dimethylformamide (DMF) resulted in 1-benzyladmantyl-3-aryl substituted benzimiadole salts (**4a–f**) in good yields (70–90%). The formation of benzyladamantyl substituted *N*-heterocyclic carbene (**4a–f**) was clearly explicated in the ^{1}H and ^{13}C spectra, where the characteristic peaks due to N-CH-N moieties were observed at 11.75 (**4a**), 10.82 (**4b**), 11.56 (**4c**), 10.68 (**4d**), 11.44 (**4e**), and 10.41 (**4f**) ppm and at 152.7 (**4a**), 152.4 (**4b**), 152.5 (**4c**), 152.4 (**4d**), 152.5 (**4e**), and 152.2 (**4f**) ppm in the ^{1}H and ^{13}C NMR spectra, respectively, similar to those previously reported[25] in the formation of N-benzyl NHC salts.

The reaction of N-benzyladamantyl substituted NHC ligand precursors with $PdCl_2$ in neat pyridine under air conditions afforded (**5a–f**) 70 to 90% yields according to a modified literature procedure (Scheme 1).[26] The PEPPSI-Pd(II)-NHC complexes were obtained as air- and moisture-stable yellow crystals. The complexes (**5a–f**) were characterized by NMR, HRMS spectroscopy and microanalyses. The ^{13}C NMR spectra displayed resonance due to the ***C*$_2$** carbene carbon atoms at δ = 164.1, 163.7, 161.9, 161.6, 161.8, and 161.4 ppm for the complexes **5a–f**, respectively. From these results, we can say that the metal center of the **5a** complex was electronically richer than the others. This difference contributed positively to the catalytic activity of the **5a** complex in the Suzuki-Miyaura reaction.

The electrochemical properties of **5a–f** were investigated on bare platinum electrodes at a scan rate of 100mV/s in acetonitrile containing 0.1 mM TBAPC as the supporting electrolyte. The cyclic voltammograms of 0.5 mM **5a–f** complexes are shown in Figure 11S (see supporting information). The electrochemical responses of **5a–f** were similar: The **5a** complex showed a reversible reduction peak at Epc= -0.846 V with an associated oxidation peak at Epa= -1.114 V and irreversible oxidation peak at Epa= +0.712 V. The cathodic peak potential of the **5b** complex occurred at Epc= -0.941 V, while the complex was oxidized at anodic potentials of Epa= -1.265 V and Epa= +0.649 V. The **5c** complex was only reduced at Epc= -0. 939 V and oxidized at Epa= -1.277 V and Epa= +0.583 V. The reduction peak of the **5d** complex appeared at one potential, Epc= -0, 950 V, while the oxidation peak of the complex appeared at two potentials, Epa= -1.214 V and Epa= +0.625 V. The cyclic voltammogram of the **5e** complex showed a reversible reduction peak at Epc= -0.876 V with an associated oxidation peak at Epa= -1.214 V and irreversible oxidation peak at Epa= +0.650 V. The cathodic peak potentials of the **5f** complex occurred at Epc= -1.288 V and Epc= -1.025 V, while the complex was oxidized at anodic peak potentials of Epa= -1.304 V and Epa= +0.655 V. According to these cyclic voltammetry (CV) results, the **5a** complex had the lowest reduction and lowest oxidation potentials.

In order to reveal the catalytic activity of the benzyladamantyl substituted PEPPSI-Pd-NHC complexes, **5a** was subjected to a Suzuki-Miyaura coupling reaction. We optimized the reaction condition by investigating base- and solvent-dependent conversions of the reaction between 4-bromoanisol substrate (1 mmol) with **5a** (0.5 mol %) at room temperature. It is well-known that the base has a critical importance in determining the efficiency of the Suzuki reaction when water is used as solvent. Therefore, firstly, the effect of different bases was investigated for the **5a** catalyzed Suzuki coupling reaction of 4-bromoanisole with phenylboronic acid in different solvents. The results showed that K_2CO_3 was the most efficient base in *i*-PrOH/H_2O when compared to other inorganic bases. Also, the reaction could tolerate other inorganic bases, which gave moderate yields of the coupled product (Table 1, entries 2–5).

Table 1 The optimization of solvent and base for the Suzuki-Miyaura reaction of 4-bromoanisole[a]



[a]Entry	Solvent	Base	Yield(%)[b]
1	*i*-PrOH	K_2CO_3	65
2	*i*-PrOH	Na_2CO_3	52
3	*i*-PrOH	Cs_2CO_3	44
4	*i*-PrOH	K_3PO_4	51
5	*i*-PrOH	KOH	40
6	H_2O	K_2CO_3	35
7	DMF	K_2CO_3	45
8	EtOH	K_2CO_3	60
9	MeOH	K_2CO_3	58
10	Acetone	K_2CO_3	39
11	*i*-PrOH/H_2O (1:3)	K_2CO_3	96
12	*i*-PrOH/H_2O (1:1)	K_2CO_3	90
13	DMF/H_2O (1:3)	K_2CO_3	74
14	EtOH/H_2O (1:3)	K_2CO_3	81
15	*i*-PrOH/H_2O (1:3)	-	-

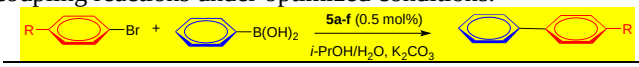
[a] Reaction Condition:1 mmol of 4-bromoanisole, 1.2 mmol of phenylboronic acid, 1 mmol of base, 0,5 mol% **5a**, 4 mL solvent, room temperature, 1 hour
[b] Isolated yield.

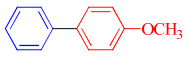
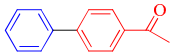
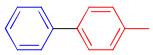
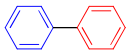
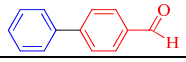
Secondly, the reaction was tested in different solvents. According to the literature, water is a very important solvent for the Suzuki reaction as it increases the reactivity.[30] Thus, we tried combinations of solvents such as *i*-PrOH/H_2O, DMF/H_2O, and EtOH/H_2O. We found *i*-PrOH/H_2O to be the most useful combination of solvents, and it gave excellent results (Table 1, entries 11–12). This difference in reactivity may be attributed to the good solubility of the carbonate base in water and palladium-PEPPSI complexes in *i*-PrOH. These helped to increase the amount of the cross-coupled product in our catalytic system. On the other hand, water, *i*-PrOH, DMF, and DMF:H_2O solutions were not as effective solvents or solvent combinations as the *i*-PrOH/H_2O (1:3) solvent combination (Table 1, entries 1–10). However, the reaction in this solvent combination did not produce product in the absence of base (Table 1, entry 15).

Then, to evaluate the scope of the limitations of the protocol we had developed, different aryl bromides were examined in our catalytic system. As shown in Table 2, either electron-donating or electron-withdrawing groups bearing aryl bromides and phenylboronic acid effectively afforded the corresponding coupled products in good yields (61–99 %) in isopropanol:water mixture in a very short time at room temperature (Table 2, entries 1–5). For example, 4-bromoacetophenone afforded a quantitative yield in 10 min, resulting in a TOF of 800 h^{-1} (Table 2, entry 3). However, electron-donating aryl bromides showed slightly lower activity than electron-withdrawing aryl bromides due to the effect of the electron-donating substituents on the nucleophilicity of the aryl bromides (Table 2, entries 1,3). A trace amount of homo-coupling by-product was observed, although cross-coupling reactions were carried out in air. The complex **5a** had higher catalytic activity when compared to other complexes. We attribute this higher performance to the electronically richer

palladium center of the **5a** complex, which in turn is due to the lower field resonance of C_2. Also, this catalytic system is almost equally effective for electronically rich and poor aryl bromides. Thus, our system shows a significant improvement in the production of coupled product when compared to related literature,[32] as it can be done at room temperature, in a very short time, using green solvents, with low catalyst loading (0.5 mol%), and without using any additives.

Table 2 Catalytic activities of **5a-f** complexes in the Suzuki coupling reactions under optimized conditions.[a]



Entry	Product	[catalyst]/yield (%)[b]					
		5a	5b	5c	5d	5e	5f
1		96, 33[c], 77[d]	61	95, 33[c]	66	78	68
2		60[c], 97[d], 99[e]	97[e]	96[e], 63[c]	97[e]	95[e]	97[e]
3		97, 50[d]	57	80	84	75	69
4		96[d,e]	88	87	80	74	81
5		96[e]	95[e]	96[e]	93[e]	93[e]	95[e]

[a] reaction condition: 0.5 mol% **5a-f**, 1 mmol *p*-R-C_6H_4Br, 1.1 mmol phenylboronic acid, 1.0 mmol K_2CO_3, rt, 1h.
[b] Isolated product
[c] use 2 mmol of substrate.
[d] use 0.25 mol% of Pd-NHC.
[e] 10 min.

3. Conclusion

We successfully synthesized six novel benzyladamantyl-subtituted benzimidazol salts and six of their palladium complexes. The electrochemical properties of the PEPPSI-Pd complexes were investigated by using CV technique. From the voltammetry results, it was found that these complexes exhibited similar electrochemical responses and were electroactive in the range of -1.214 to +0.583 V. For the PEPPSI-Pd-NHC complexes, an appropriate catalytic system has been developed for the palladium catalyzed Suzuki-Miyaura reaction in isopropanol/water. The complex **5a** has shown better catalytic activity than other complexes on Suzuki coupling reaction of various aryl bromides in room temperature due to lower reduction and oxidation potentials value. To compare the catalytic activity of our system with recently published data, there are a few reports in the literature on Suzuki-Miyaura cross-coupling of aryl bromides in aqueous media at room temperature catalysed by Pd complexes.[32-40] Here, the yield is better than the literature[40] when considering the amount of catalyst, time, temperature and solvent system. This catalytic system offers a mild and efficient alternative to existing methods, since it proceeds at room temperature, under air, in green solvents, and with low catalyst loading.

4. Experimental section

4.1. General remarks

The ^1H and ^{13}C NMR spectra were recorded with a Bruker Avance III 400 MHz NMR spectrometer with sample solutions prepared in $CDCl_3$. The chemical shifts were reported in δ units downfield from the internal reference (Me_4Si). IR spectra were recorded with a PerkinElmer Spectrum 100 GladiATR FT/IR spectrometer. Cyclic voltammetry of **5a–f** complexes was performed with a BAS (Bioanalytical Systems, Inc.) 100 BW electrochemical analyzer. A three-electrode electrochemical cell system was employed, consisting of an Ag/AgCl (CHI) electrode as the reference, a platinum disk (CHI, 2 mm diameter) as the working electrode, and a platinum wire in the form of a spiral as the counter electrode, with acetonitrile that contained tetrabutyl-ammoniumperchlorate (TBAP) as the supporting electrolyte. Electrochemical grade TBAP and acetonitrile were purchased from Sigma-Aldrich. CV of **5a–f** complexes were studied in the potential range of +1.0 to -2.0 V at a scan rate of 100mV/s. The HRMS analyses were carried out with a Shimadzu LCMS-IT-TOFF instrument. All commercial compounds were used as obtained. All coupling products of the Suzuki-Miyaura reactions were previously reported compounds.

4.2. Synthesis

*Synthesis of 4-adamantanetoluene (**1**)*

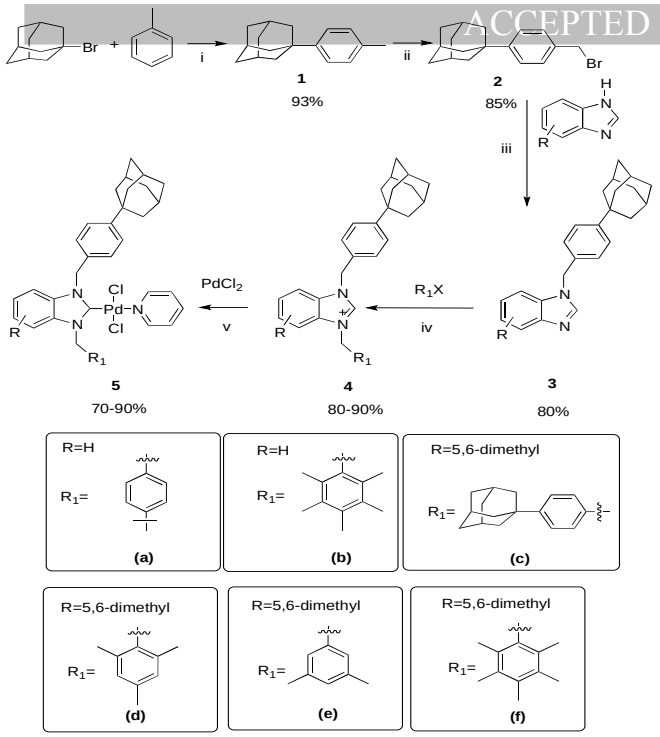
Compound **1** was synthesized according to literature.[31a] Under argon atmosphere 1-bromoadamantane (0.215g. 1.0mmol), toluene (3.5ml) and a catalytic amount of $InCl_3$ (5 mol%) were added to a round bottom flask. After stirring for 24 h at room temperature, the mixture was washed by water (3×10 mL) until the pH will be neutral then the mixture extracted with ether spirit (3×25ml). The organic layer was dried over anhydrous $MgSO_4$ and concentrated under vacuum. The solid residue was filtered in a small column with hexane give the title compound **1** (210 mg, 93%) gave as white crystals; [Found: C, 90.32; H, 9.80. $C_{17}H_{22}$ requires C, 90.20; H, 9.80%]. ^1H NMR (400 MHz, $CDCl_3$): δ=7.23–7.16 (2H, m, $CH_3C_6\mathbf{H_4}Ad$), 7.06 (2H, d, J = 8.0 Hz, $CH_3C_6\mathbf{H_4}Ad$), 2.25 (3H, s, $C\mathbf{H_3}C_6H_4Ad$), 2.01 (3H, s, $\mathbf{H_{Ad}}$), 1.83 (6H, d, J = 2.9 Hz, $\mathbf{H_{Ad}}$), 1.76 –1.62 (6H, m, $\mathbf{H_{Ad}}$); ^{13}C NMR (100 MHz, $CDCl_3$) δ=148.5, 134.9, 128.8, 124.7, 43.3, 36.8, 35.8, 29.0, 20.9.

*4.2.1. Synthesis of 4-benzyladamantyl bromide (**2**)*

Compound **2** was synthesized according to literature.[31b] Coumpond (**1**) (1g, 4.42 mmol), N-bromosuccinimide (NBS, 0.866g, 4.86 mmol), 2.2'-azobisisobutyronitrile (AIBN, 0.018 g, 0.11 mmol) and cyclohexane (7 mL) were added to a round bottom flask at room temperature. The mixture was stirred and refluxed for 2h. The reaction was monitored by TLC. Then the mixture was allowed to cool to room temperature and water (30 ml) was added and reside was extracted with ethyl acetate (3×10 ml), dried over anhydrous $MgSO_4$ and concentrated under vacuum. The residue was filtered in a small silica column and to give the title compound **2** (85%) as white solid; [Found: C, 84.30; H, 7.85; N, 8.32. $C_{24}H_{26}N_2$ requires C, 84.17; H, 7.65; N, 8.18]. $_1H$ NMR (400 MHz, $CDCl_3$): δ=7.34 (4H, s, $CH_2C_6\mathbf{H_4}Ad$), 4.50 (2H, s, $C\mathbf{H_2}C_6H_4Ad$), 2.09 (3H, s, $\mathbf{H_{Ad}}$), 1.90 (6H, t, J = 4.7 Hz, $\mathbf{H_{Ad}}$), 1.77 (6H, q, J = 12.2 Hz, $\mathbf{H_{Ad}}$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.8, 134.8, 128.8, 125.4, 43.0, 36.7, 36.2, 33.7, 28.8.

*4.2.2. Synthesis of N-substituted benzyladamantyl benzimidazole (**3**)*

Compound **3** was synthesized according to literature.[25][Found: C, 66.98; H, 7.02. $C_{17}H_{21}Br$ requires C, 66.89; H, 6.93%].
^1H NMR (400 MHz, $CDCl_3$): δ= 7.82 (s, 1H, NC$\underline{H}$N), 7.57 (s, 1H, $C_6\underline{H_2}(CH_3)_2$), 7.32 (s, 1H, $C_6\underline{H_2}(CH_3)_2$), 7.30 (s, 1H, $CH_2C_6\underline{H_4}Ad$), 7.14 – 7.07 (m, 3H, $CH_2C_6\underline{H_4}Ad$), 5.27 (s, 2H, $C\underline{H_2}C_6H_4Ad$), 2.35 (d, J = 8.7 Hz, 6H, $C_6H_2(C\underline{H_3})_2$), 2.08 (s, 3H, $\underline{H_{Ad}}$), 1.88 (t, J = 6.6 Hz, 6H, $\underline{H_{Ad}}$), 1.75 (q, J = 12.2 Hz, 6H, $\underline{H_{Ad}}$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.4, 142.5, 132.8, 132.5, 132.1, 131.1, 126.8, 125.5, 120.3, 110.1, 48.3, 43.1, 36.7, 36.1, 28.8, 20.5, 20.2. [Found: C, 66.98; H, 7.02. $C_{17}H_{21}Br$ requires C, 66.89; H, 6.93%].



Scheme 1. Synthesis of benzyladamanthyl substituted NHC and their PEPPSI-Pd complexes. i)[33a] $InCl_3$ (5 mol%). ii)[33b] (NBS, 1.1 mmol), 2.2'-azobisisobutyronitrile (AIBN, 0.025mmol) and cyclohexane (7ml). iii)[25] Benzimidazole or 5,6-dimethylbenzimidazole (1 mmol), KOH (1 mmol), ethanol (30 mL), reflux, 24 h. ıv)[25] R_1X (1.2 mmol), DMF (5 mL), 80 °C, 24h. v) [26] $PdCl_2$ (1 mmol), pyridine, 80 °C, 24h.

*4.2.3. 1-(4-Adamantylbenzyl)-3-(4-ter-butylbenzyl)benzimidazolium bromide (**4a**),*

A mixture of 1-(4-adamantylbenzyl)benzimidazole (1 mmol) and 4-alkylbenzylbromide (1.1 mmol) in dimethyl formamide (DMF; 3 mL) was stirred and heated for 2 days at 70 °C. Diethyl ether (15 mL) was added to obtain a white crystalline solid which was filtered off. The solid was washed with diethyl ether (3×15 mL), and dried under a vacuum to give the title compound **4a** (500 mg, 88٪) as white crystals; m.p= 309.5 °C. [Found: C, 73.87; H, 7.35; N, 5.03. $C_{35}H_{41}N_2Br$ requires C, 73.80; H, 7.25; N, 4.92 %]. ^{1}H NMR (400 MHz, $CDCl_3$): δ= 11.75 (1H, s, NC<u>H</u>N), 7.54 (2H, dt, *J* = 7.0, 3.5 Hz, $C_6\underline{H}_4$), 7.47–7.39 (6H, m, $C_6\underline{H}_4$ and $CH_2C_6\underline{H}_4$Ad and $CH_2C_6\underline{H}_4(CH_3)_3$-4), 7.30 (4H, dd, *J*=11.8, 8.3 Hz, $CH_2C_6\underline{H}_4$Ad and $CH_2C_6\underline{H}_4(CH_3)_3$-4), 5.75 (2H, s, $C\underline{H}_2C_6H_4(CH_3)_3$-4), 5.23 (2H, s, $C\underline{H}_2C_6H_4$Ad), 2.00 (3H, s, $\underline{H}_{Ad}$), 1.84–1.61 (12H, m, $\underline{H}_{Ad}$), 1.20 (9H, s, $CH_2C_6H_4(C\underline{H}_3)_3$-4) ; ^{13}C NMR (100 MHz, $CDCl_3$): δ=152.7, 152.5, 143.0, 131.4, 129.5, 128.2, 128.2, 127.1, 126.4, 125.9, 113.8, 113.7, 51.4, 51.3, 43.0, 36.6, 36.2, 34.7, 31.2, 28.8.

*4.2.4. 1-(4-Adamantylbenzyl)-3-(2,3,4,5,6-pentamethylbenzyl)benzimidazolium chloride (**4b**),*

The synthesis of **4b** was performed following the same procedure employed for the preparation of **4a**, starting from 1 mmol of 1-benzyladamanthyl benzimidazole and 1.2 mmol of 2,3,4,5,6-penthamethylbenzyl chloride to give the title compound **4b** (485 mg, 90٪) as white solide; m.p= 300.7 °C. [Found: C, 80.25; H, 8.09; N, 5.29. $C_{36}H_{43}N_2Cl$ requires C, 80.19; H, 8.04; N, 5.20 %].^{1}H NMR (400 MHz, $CDCl_3$): δ=10.82 (1H, s, NC<u>H</u>N), 7.56–7.23 (8H, m, $C_6\underline{H}_4$ and $CH_2C_6\underline{H}_4$Ad), 5.84 (2H, s, $C\underline{H}_2C_6(CH_3)_5$), 5.76 (2H, s, $\underline{CH}_2C_6H_4$Ad), 2.23 (6H, s, $CH_2C_6(C\underline{H}_3)_5$), 2.21 (3H, s, $CH_2C_6(C\underline{H}_3)_5$), 2.18 (6H, s, $CH_2C_6(C\underline{H}_3)_5$), 2.00 (3H, s, $\underline{H}_{Ad}$), 1.79–1.61 (12H, m, $\underline{H}_{Ad}$). ^{13}C NMR (100 MHz, $CDCl_3$): δ=152.4, 142.6, 137.4, 134.1, 133.6, 131.7, 131.6, 129.9, 127.9, 127.1, 127.0, 125.8, 124.7, 113.9, 113.5, 51.3, 48.2, 43.0, 36.6, 36.2, 28.8.

*4.2.5. 1,3-Bis-(4-adamantylbenzyl)-5,6-dimethylbenzimidazolium bromide (**4c**),*

The synthesis of **4c** was performed following the same procedure employed for the preparation of **4a**, starting from 1 mmol of 1-benzyladamanthyl-5,6-dimethylbenzimidazole and 1.2 mmol of 4-adamanthylbenzyl bromide to give the title compound **4c** (540 mg, 80٪) as white solid; m.p= decompose at 344.3 °C. [Found: C, 76.42; H, 7.61; N, 4.15. $C_{43}H_{51}N_2Br$ requires C, 76.42; H, 7.61; N, 4.15 %]. ^{1}H NMR (400 MHz, $CDCl_3$): δ=11.56 (1H, s, NC<u>H</u>N), 7.41 – 7.22 (10H, m, $C_6\underline{H}_2(CH_3)_2$-5,6 and $CH_2C_6\underline{H}_4$Ad), 5.67 (4H, s, $C\underline{H}_2C_6H_4$Ad), 2.28 (6H, s, $C_6H_2(C\underline{H}_3)_2$), 2.00 (6H, s, $\underline{H}_{Ad}$), 1.83 – 1.59 (24H, m, $\underline{H}_{Ad}$) ; ^{13}C NMR (100 MHz, $CDCl_3$): δ=152.5, 141.7, 137.3, 129.9, 129.8, 128.0, 125.9, 113.3, 51.0, 43.0, 36.6, 36.2, 28.8.

*4.2.6. 1-(4-Adamantylbenzyl)-3-(2,4,6-trimethylbenzyl)-5,6-dimethylbenzimidazolium chloride (**4d**),*

The synthesis of **4d** was performed following the same procedure employed for the preparation of **4a**, starting from 1 mmol of 1-benzyladamanthyl-5,6-dimethylbenzimidazole and 1.2 mmol of 2,4,6-trimethylbenzyl chloride to give the title compound **4d** (447 mg, 83٪) as white solid; m.p= decompose at 330.2 °C. [Found: C, 80.23; H, 8.06; N, 5.26. $C_{36}H_{43}N_2Cl$ requires C, 80.19; H, 8.04; N, 5.20 %]. ^{1}H NMR (400 MHz, $CDCl_3$): δ=10.68 (1H, s, NC<u>H</u>N), 7.26 (5H, d, *J* =5.8 Hz, $C_6\underline{H}_2(CH_3)_2$-5,6 and $CH_2C_6\underline{H}_4$Ad), 6.97 (1H, d, *J* = 16.3 Hz, $C_6\underline{H}_2(CH_3)_2$-5,6), 6.86 (2H, d, *J*=8.7 Hz, $CH_2C_6\underline{H}_2(CH_3)_3$-2,4,6), 5.71 (2H, s, $C\underline{H}_2C_6H_2(CH_3)_3$-2,4,6), 5.68 (2H, s, $C\underline{H}_2C_6H_4$Ad), 2.26 (3H, s, $CH_2C_6H_2(C\underline{H}_3)_3$-2,4,6), 2.25 (6H, s, $CH_2C_6H_2(C\underline{H}_3)_3$-2,4,6), 2.23 (3H, s, $C_6H_2(C\underline{H}_3)_2$-5,6), 2.21 (3H, s, $C_6H_2(C\underline{H}_3)_2$-5,6), 2.00 (3H, s, $\underline{H}_{Ad}$), 1.79 – 1.60 (12H, m, $\underline{H}_{Ad}$) ; ^{13}C NMR (100 MHz, $CDCl_3$): δ= 152.4, 141.1, 139.8, 138.0, 137.9, 137.3, 137.3, 130.2, 130.0, 127.6, 125.8, 125.0, 113.4, 113.2, 51.1, 46.9, 43.0, 36.6, 36.2, 28.8.

*4.2.7. 1-(4-Adamantylbenzyl)-3-(3,5-dimethylbenzyl)-5,6-dimethylbenzimidazolium bromide (**4e**),*

The synthesis of **4e** was performed following the same procedure employed for the preparation of **4a**, starting from 1 mmol of 1-benzyladamanthyl-5,6-dimethylbenzimidazole and 1.2 mmol of 3,5-dimethylbenzyl bromide to give the title compound **4e** (507 mg, 89٪) as white solid; m.p= 281.3 °C. [Found: C, 80.10; H, 7.94; N, 5.41. $C_{35}H_{41}N_2Cl$ requires C, 80.05; H, 7.87; N, 5.33 %]. ^{1}H NMR (400 MHz, $CDCl_3$): δ=11.44 (1H, s, NC<u>H</u>N), 7.36 (2H, d, *J* = 8.3, $CH_2C_6\underline{H}_4$Ad), 7.28 (2H, d, *J* = 8.3 Hz, $CH_2C_6\underline{H}_4$Ad), 7.21 (2H, d, *J* = 2.3 Hz, $C_6\underline{H}_2(CH_3)_2$), 6.95 (2H, s, $CH_2C_6\underline{H}_3(CH_3)_2$-3,5), 6.89 (1H, d, *J* = 16.5 Hz, $CH_2C_6\underline{H}_3(CH_3)_2$-3,5), 5.71 (2H, s, $C\underline{H}_2C_6H_3(CH_3)_2$-3,5), 5.62 (2H, s, $C\underline{H}_2C_6H_4$Ad), 2.28 (3H, s, $CH_2C_6H_3(C\underline{H}_3)_2$-3,5), 2.27 (3H, s, $CH_2C_6H_3(C\underline{H}_3)_2$-3,5), 2.21 (6H, s, $C_6H_2(C\underline{H}_3)_2$), 2.00 (3H, s, $\underline{H}_{Ad}$), 1.72 (12H, m, *J* = 48.0 Hz, $\underline{H}_{Ad}$); ^{13}C NMR (100 MHz, $CDCl_3$): δ=152.5, 141.8, 139.1, 137.3, 132.6, 130.8, 130.0, 129.9, 129.9, 128.1, 125.9, 125.7, 113.3, 113.3, 51.3, 51.0, 43.0, 36.6, 36.2, 28.8.

*4.2.8. 1-(4-adamantylbenzyl)-3-(2,3,4,5,6-pentamethylbenzyl)-5,6-dimethylbenzimidazolium bromide (**4f**),*

The synthesis of **4f** was performed following the same procedure employed for the preparation of **4a**, starting from 1 mmol of 1-benzyladamanthyl-5,6-dimethylbenzimidazole and 1.2 mmol of 2,3,4,5,6-pentamethylbenzyl chloride to give the title compound **4f** (482 mg, 85٪) as white solid; m.p= 207.4 °C. [Found: C, 80.51; H, 8.43; N, 5.03. $C_{38}H_{47}N_2Cl$ requires C, 80.46; H, 8.35;

N, 4.94 %]. ^{1}H NMR (400 MHz, $CDCl_3$): δ=10.41 (1H, s, $C_6\underline{H}_2(CH_3)_2$), 7.35 (6H, dd, *J* = 25.3, 17.3 Hz, $CH_2C_6\underline{H}_4Ad$), 6.87 (2H, t, *J*=12.1 Hz, $CH_2C_6\underline{H}_4Ad$), 6.29–6.07 (4H, m, $C\underline{H}_2C_6H_4Ad$), 2.20 (6H, s, $C_6H_2(C\underline{H}_3)_2$), 2.10 (6H, s, $\underline{H}_{Ad}$), 1.92 (12H, s, $\underline{H}_{Ad}$), 1.79 (12H, s, $\underline{H}_{Ad}$). ^{13}C NMR (100 MHz, $CDCl_3$): δ=161.9, 152.6, 151.9, 151.3, 151.1, 137.9, 133.3, 132.4, 127.7, 125.3, 124.4, 111.7, 52.9, 43.1, 36.8, 36.1, 28.9. HRMS(ESI) for $C_{43}H_{50}N_2^+$ (M^++H): calcd. 595.4052, found 595.4048.

4.2.12. Dichloro[1-(4-adamantylbenzyl)-3-(2,4,6-trimethylbenzyl)-5,6-dimethylbenzimidazole-2-ylidene]pyridinepalladium(II), ***5d***

The synthesis of **5d** was performed following the same procedure employed for the preparation of **5a**, starting from **4**d to give the title compound **5d** (561 mg, 74٪) as yellow crystal; m.p= 185.4 °C. $\nu_{(CN)}$=1445.32 cm^{-1}. [Found: C, 64.89; H, 6.28; N, 5.59. $C_{41}H_{47}N_3Cl_2Pd$ requires C, 64.87; H, 6.24; N, 5.54 %]. ^{1}H NMR (400 MHz, $CDCl_3$): δ=9.01 (2H, d, *J* = 6.3 Hz, $NC_5\underline{H}_5$), 7.77 (1H, s, $NC_5\underline{H}_5$), 7.57 (2H, d, *J* = 7.9 Hz, $NC_5\underline{H}_5$), 7.37 (4H, d, *J*=7.6 Hz, $C_6\underline{H}_2(CH_3)_2$ and $CH_2C_6\underline{H}_2(CH_3)_3$-2,4,6), 7.02–6.74 (3H, m, $CH_2C_6\underline{H}_4Ad$), 6.16 (5H, dt, *J* = 36.1, 21.1 Hz, $CH_2C_6\underline{H}_4Ad$, $C\underline{H}_2C_6H_2(CH_3)_3$-2,4,6 and $C\underline{H}_2C_6H_4Ad$), 2.38 (9H, d, *J* = 6.7 Hz, $CH_2C_6H_2(C\underline{H}_3)_3$-2,4,6), 2.17 (3H, m, $C_6H_2(C\underline{H}_3)_2$), 2.10 (3H, s, $\underline{H}_{Ad}$), 2.03 (3H, m, $C_6H_2(C\underline{H}_3)_2$), 1.91 (6H, s, $\underline{H}_{Ad}$), 1.78 (6H, q, *J* = 12.3 Hz, $\underline{H}_{Ad}$). ^{13}C NMR (100 MHz, $CDCl_3$): δ=161.6, 152.6, 152.1, 151.0, 139.0, 138.9, 137.9, 132.4, 131.9, 131.7, 129.5, 127.7, 125.3, 124.4, 111.7, 53.0, 50.2, 43.1, 36.8, 36.1, 28.9. HRMS (ESI) for $C_{41}H_{47}N_3Pd^+$ (M^+-2Cl) calcd. 687.2805, found 687.1395; for $C_{36}H_{42}N_2Pd^+$ (M^++H] calcd. 609.2461 found 609.2292.

4.2.13. Dichloro[1-(4-adamantylbenzyl)-3-(3,5-dimethylbenzyl)-5,6-dimethylbenzimidazole-2-ylidene]pyridine palladium(II), ***5e***

The synthesis of **5e** was performed following the same procedure employed for the preparation of **5a**, starting from **4e** to give the title compound **5e** (603 mg, 81٪) as yellow crystal; m.p= decompose at 350 °C. $\nu_{(CN)}$=1446.30 cm^{-1}. [Found: C, 64.55; H, 6.18; N, 5.77. $C_{40}H_{45}N_3Cl_2Pd$ requires C, 64.48; H, 6.09; N, 5.64 %]. ^{1}H NMR (400 MHz, $CDCl_3$): δ=8.92 (2H, d, *J* = 4.9 Hz, $NC_5\underline{H}_5$), 7.66 (1H, s, $NC_5\underline{H}_5$), 7.50 (2H, d, *J* = 8.0 Hz, $NC_5\underline{H}_5$), 7.32 – 7.10 (6H, m, $C_6\underline{H}_2(CH_3)_2$ and $CH_2C_6\underline{H}_4Ad$), 6.91 – 6.71 (3H, m, $CH_2C_6\underline{H}_3(CH_3)_2$-3,5), 6.18 – 5.91 (4H, m, $C\underline{H}_2C_6H_3(CH_3)_2$-3,5 and $C\underline{H}_2C_6H_4Ad$), 2.23 (6H, s, $CH_2C_6H_3(C\underline{H}_3)_2$-3,5), 2.11 (6H, s, $C_6H_2(C\underline{H}_3)_2$), 2.00 (3H, s, $\underline{H}_{Ad}$), 1.82 (6H, s, $\underline{H}_{Ad}$), 1.74 – 1.62 (6H, m, $\underline{H}_{Ad}$). ^{13}C NMR (100 MHz, $CDCl_3$): δ=161.9, 152.7, 152.1, 151.3, 151.1, 138.3, 137.9, 135.2, 133.4, 133.2, 132.2, 129.6, 127.8, 127.7, 125.7, 125.3, 124.4, 111.7, 53.2, 52.9, 43.2, 36.8, 36.1, 28.9. HRMS (ESI) for $C_{35}H_{40}N_2Pd^+$ (M^+-H) calcd. 593.2148, found 593.2094; for $C_{35}H_{39}N_2Pd^+$ (M^++2H] calcd. 489.3270 found 489.3251.

4.2.14. Dichloro[1-(4-adamantylbenzyl)-3-(2,3,4,5,6-pentamethylbenzyl)-5,6-dimethylbenzimidazole-2-ylidene]pyridinepalladium(II), ***5f***

The synthesis of **5f** was performed following the same procedure employed for the preparation of **5a**, starting from **4**f to give the title compound **5**f (710 mg, 90٪) as yellow crystal; m.p= 236.3 °C. $\nu_{(CN)}$=1444.74 cm^{-1}. [Found: C, 65.66; H, 6.61; N, 5.43. $C_{43}H_{51}N_3Cl_2Pd$ requires C, 65.61; H, 6.53; N, 5.34 %]. ^{1}H NMR (400 MHz, $CDCl_3$): δ=8.92–8.80 (2H, m, $NC_5\underline{H}_5$), 7.66 (1H, s, $NC_5\underline{H}_5$), 7.47 (2H, d, *J* = 8.1 Hz, $NC_5\underline{H}_5$), 7.25 (4H, dd, *J* = 15.3, 7.3 Hz, $C_6\underline{H}_2(CH_3)_2$ and $CH_2C_6\underline{H}_4Ad$), 6.71 (1H, t, *J* = 13.3 Hz, $CH_2C_6\underline{H}_4Ad$), 6.17 – 5.91 (5H, m, $CH_2C_6\underline{H}_4Ad$, $C\underline{H}_2C_6(CH_3)_5$ and $C\underline{H}_2C_6H_4Ad$), 2.25-2.18 (15H, m, $CH_2C_6(C\underline{H}_3)_5$), 2.05 (3H, m, $C_6H_2(C\underline{H}_3)_2$), 2.00 (3H, s, $\underline{H}_{Ad}$), 1.93 (3H, m, $C_6H_2(C\underline{H}_3)_2$), 1.81 (6H, s, $\underline{H}_{Ad}$), 1.68 (6H, q, *J* = 12.3 Hz, $\underline{H}_{Ad}$). ^{13}C NMR (100 MHz,

4.2.9. Dichloro[1-(4-adamantylbenzyl)-3-(4-ter-butylbenzyl)benzimidazole-2-ylidene]pyridinepalladium(II), ***5a***

In air, a pressure tube was charged with PdCl2 (180 mg, 1 mmol), 4a (1.1 mmol), K2CO3 (700 mg, 5 mmol) and 3 mL of pyridine. The reaction mixture was heated with vigorous stirring for 7 h at 80 oC then cooled to room temperature and diluted with dichloromethane (DCM). A short silica column was used for filtration. All volatiles were evaporated. Residue yellow solid was washed with hexane (2x10 mL) and diethyl ether (2x10 mL). Yellow solid was crystallized by DCM/Hexane (1:3) at room temperature to give the title compound 5a (603 mg, 81٪) as yellow crystal; m.p= 214.6 °C. $\nu_{(CN)}$= 1446.93 cm^{-1}. [Found: C, 64.54; H, 6.17; N, 5.74. $C_{40}H_{45}N_3Cl_2Pd$ requires C, 64.68; H, 6.09; N, 5.64 %]. ^{1}H NMR (400 MHz, $CDCl_3$): δ= 9.05 (2H, d, *J* = 5.1 Hz, $NC_5\underline{H}_5$), 7.78 (1H, d, $NC_5\underline{H}_5$) 7.66 – 7.52 (4H, m, $NC_5\underline{H}_5$ and $C_6\underline{H}_4$), 7.45 – 7.32 (6H, m, $CH_2C_6\underline{H}_4(CH_3)_3$-4, $C_6\underline{H}_4$ and $CH_2C_6\underline{H}_4Ad$), 7.17 – 7.05 (4H, m, $CH_2C_6\underline{H}_4(CH_3)_3$-4 and $CH_2C_6\underline{H}_4Ad$), 6.31 – 6.17 (4H, m, $C\underline{H}_2C_6H_4(CH_3)_3$-4 and $C\underline{H}_2C_6H_4Ad$), 2.10 (3H, s, $\underline{H}_{Ad}$), 1.92 (6H, s, $\underline{H}_{Ad}$), 1.78 (6H, q, *J* = 12.3 Hz, $\underline{H}_{Ad}$), 1.32 (9H, s, $CH_2C_6H_4(C\underline{H}_3)_3$-4). ^{13}C NMR (100 MHz, $CDCl_3$): δ=164.1, 164.0, 152.7, 152.1, 151.3, 151.1, 138.0, 134.7, 132.0, 127.8, 125.8, 125.2, 124.5, 123.1, 111.5, 53.5, 53.2, 43.1, 36.8, 36.1, 34.6, 31.3, 28.9. HRMS(ESI) for $C_{35}H_{40}N_2PdCl_2$ (M-H): calcd. 663.1525, found 663.2485; $C_{35}H_{40}N_2Pd^+$ (M^+-H): calcd. 593.2148, found 593.2130.

4.2.10. Dichloro[1-(4-adamantylbenzyl)-3-(2,3,4,5,6-pentamethylbenzyl)benzimidazole-2-ylidene]pyridinepalladium(II), ***5b***

The synthesis of **5b** was performed following the same procedure employed for the preparation of **5a**, starting from **4b** to give the title compound **5b** (637 mg, 84٪) as yellow crystal; m.p= 204.7 °C. $\nu_{(CN)}$=1442.18 cm^{-1}. [Found: C, 64.96; H, 6.31; N, 5.67. $C_{41}H_{47}N_3Cl_2Pd$ requires C, 64.87; H, 6.24; N, 5.54 %]. ^{1}H NMR (400 MHz, $CDCl_3$): δ=8.99 – 8.85 (2H, m, $NC_5\underline{H}_5$), 7.69 (1H, m, $NC_5\underline{H}_5$), 7.48 (2H, t, *J* = 11.0 Hz, $NC_5\underline{H}_5$), 7.32 – 7.22 (4H, m, $C_6\underline{H}_4$), 7.07 – 6.71 (3H, m, $CH_2C_6\underline{H}_4Ad$), 6.34 – 6.02 (5H, m, $CH_2C_6\underline{H}_4Ad$, $C\underline{H}_2C_6(CH_3)_5$ and $C\underline{H}_2C_6H_4Ad$), 2.28 – 2.24 (9H, s, $CH_2C_6(C\underline{H}_3)_5$), 2.18 (6H, s, $CH_2C_6(C\underline{H}_3)_5$), 2.00 (3H, s, $\underline{H}_{Ad}$), 1.81 (6H, s, $\underline{H}_{Ad}$), 1.67 (6H, q, *J* = 12.2 Hz, $\underline{H}_{Ad}$). ^{13}C NMR (100 MHz, $CDCl_3$): δ=163.7, 152.6, 152.0, 151.3, 151.2, 138.0, 136.0, 135.3, 134.7, 133.1, 132.1, 127.8, 125.3, 124.5, 122.9, 122.5, 111.5, 53.4, 51.9, 43.1, 36.8, 36.1, 28.9. HRMS(ESI) for $C_{36}H_{42}N_2Pd^+$ (M^+-H): calcd. 607.2305, found 607.2271; $C_{36}H_{42}N_2^+$ (M^++H): calcd. 503.3426, found 503.3361. [Found: C, 64.96; H, 6.31; N, 5.67. $C_{41}H_{47}N_3Cl_2Pd$ requires C, 64.87; H, 6.24; N, 5.54 %].

4.2.11. Dichloro[1,3-bis-(4-adamantylbenzyl)-5,6-dimethylbenzimidazole-2-ylidene]pyridinepalladium(II), ***5c***

The synthesis of **5c** was performed following the same procedure employed for the preparation of **5a**, starting from **4c** to give the title compound **5**c (596 mg, 70٪) as yellow crystal; m.p= decompose at 300.6 °C. $\nu_{(CN)}$=1447.42 cm^{-1}. [Found: C, 67.79; H, 6.61; N, 5.05. $C_{48}H_{55}N_3ClPd$ requires C, 67.72; H, 6.51; N, 4.94%]. ^{1}H NMR (400 MHz, $CDCl_3$): δ=9.02 (2H, s, $NC_5\underline{H}_5$), 7.76 (1H, s, $NC_5\underline{H}_5$), 7.59 (4H, d, *J* = 7.3 Hz, $NC_5\underline{H}_5$ and

$CDCl_3$): δ=161.4, 152.6, 152.0, 151.2, 151.0, 137.8, 135.2, 134.8, 133.9, 133.0, 132.3, 131.7, 128.2, 127.7, 125.2, 124.4, 111.9, 111.4, 53.1, 51.3, 43.1, 36.8, 36.1, 28.9. HRMS (ESI) for $C_{38}H_{46}N_2^+$ (M^++H) calcd. 531.3739, found 531.3678.

4.2.3. General Procedure for the Suzuki Coupling Reaction

Under air, a 10 mL tube containing a stirring bar was charged with palladium catalyst (0.5 mol %, 0.005 mmol), potassium carbonate (138 mg, 1 mmol), aryl bromide (1 mmol), phenylboronic acid (135 mg, 1 mmol), isopropanol (1.0 mL), and water (3 mL). The mixture was stirred at room temperature for an appropriate time. The reaction was quenched with water, and the mixture was extracted with ethyl acetate, dried with $MgSO_4$, and filtered on short silica. The solvent was removed under reduced pressure to give the crude product. The residue was subjected to PTLC (hexane:ethyl acetate) (9:1) to give the pure product.

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References and notes

1. (a) Vougioukalakis, G. C.; Grubbs, R. H. *Chem. Rev*. **2010**, *110*, 1746-1787; (b) Colacino, E.; Martinez, J.; Lamaty, F. *Coord. Chem. Rev.* **2007**, *251*, 726-764; (c) Samojlowicz, C.; Bieniek, M.; Grela, K. *Chem. Rev.* **2009**, *109*, 3708-3742.

2. (a) Yus, M.; Pastor, I. M. *Chem. Lett.* **2013**, *42*, 94-108; (b) Schaper, L.A.; Hock, S. J.; Herrmann, W. A.; Kuhn, F. E. *Angew. Chem. Int. Ed*. **2013**, *52*, 270-289; (c) Ingleson, M. J.; Layfield, R. A. *Chem. Commun.* **2012**, 3579-3589.

3. Fortman, G. C.; Nolan, S. P. *Chem. Soc. Rev*. **2011**, *40*, 5151-5169; (e) Marion, N.; Nolan, S. P. *Acc. Chem. Res*. **2008**, *41*, 1440-1449.

4. www.nobelprize.org

5. Littke, F. A.; Fu, G. C. *Angew. Chem. Int. Ed*. **2002**, *41*, 4176.

6. (a) Dupont, J.; Consorti, C. S.; Spencer, J. *Chem. Rev*. **2005**, *105*, 2527; (b) Gaikwad, V.; Holuigue, A.; Thathagar, M. B.; Elshof, J. E.; Rothenberg, G. *Chem. Eur. J*. **2007**, *13*,6908.

7. (a) Suzuki, A. *Angew. Chem. Int. Ed*. **2011**, *50*, 6722; (b) Suzuki, A.; Yamamoto, Y. *Chem. Lett*. **2011**, *40*, 894; (c) Fihri, A.; Bouhrara, M.; Nekoueishahraki, B.;Basset, J.-M.; Polshettiwar, V. *Chem. Soc. Rev*. **2011**, *40*, 5181; (d) Balanta, A.; Godard, C.; Claver, C. *Chem. Soc. Rev*. **2011**,*40*, 4973.

8. (a) Kappe, D.; Dallinger C. O. *Chem. Rev*. **2007**, *107*, 2563; (b) Chen, C.-J.; Li, L. *Chem. Soc. Rev*. **2006**, *35*, 68; (c) Sheldon, R. A. *Green Chem*. **2005**, *7*, 267.

9. (a) Modak, A.; Mondal, J. M.; Bhaumik, Sasidharan, A. *Green Chem*. **2011**, *13*, 1317; (b) Marziale, A. N.; Jantke, D.; Faul, S. H. ; Reiner, T.; Eppinger, E. Herdtweck and J. *Green Chem*. **2011**, *13*, 169; (c) Polshettiwar, V.; Decottignies, A.; Fihri, C. Len and A. *ChemSusChem*. **2010**, *3*, 502; (d) Carril, M.; Domínguez, R.; SanMartin, E. *Chem. Soc. Rev*. **2008**, *37*, 639; (e) Herrerías, C. I.; Yao, X.; Li, Z.;Li, C.-J. *Chem. Rev*. **2007**, *107*, 2546; (f) Li, C.-J. *Chem. Rev*. **2005**, *105*, 3095; (g) Yamada, Y. M. A.; Takeda, K.; Ikegami, H.; Takahashi, S. *J. Org. Chem*. **2003**, *68*, 7733; (h) Yamada, Y. M. A.; Takeda, K.; Ikegami, H.; Takahashi, S. *Org. Lett*. **2002**, *4*, 3371.

10. (a) Plenio, C. A.; Fleckenstein, H. *Green Chem*. **2007**, *9*, 1287; (b) Shaughnessy, R. Huang, K.; H. *Organometallics*. **2006**, *25*, 4105.

11. (a) Hor, F.; Li, T. S. A. *Adv. Synth. Catal*. **2008**, *350*, 2391; (b) Moore, L. R.; Western, E. C.; Craciun, R.; Spruell, J. M.; Dixon, D. A.; Shaughnessy, K. P.; O'Halloran, K. H. *Organometallics*. **2008**, *27*, 576; (c) Čapek, P.; Hocek, R.; Pohl, M. *Org. Biomol. Chem*. **2006**, *4*, 2278.

12. (a) Basu, B.; Biswas, K.; Ghosh, S.; Kundu, S. *Green Chem*. **2010**, *12*, 1734; (b) Zhang, S.; Shi, Y. *Green Chem*. **2008**, *10*, 868; (c) Maegawa, T.; Kitamura, Y.; Sako, S.; Udzu, T.; Sakurai, A.; Tanaka, A.; Kobayashi, Y.; Endo, K.; Bora, U.; Kurita, T.; Kozaki, A.; Sajiki, Y.; Monguchi, H. *Chem.–Eur. J*. **2007**, *13*, 5937.

13. Mu, B.; Li, J.; Han, Z.; Wu, Y. J. *Organomet. Chem.***2012**, *700*, 117-124.

14. Leadbeater, N. E.; Marco, M. *Org. Lett.***2002**, *4*, 2973-2976.

15. Saha, D.; Chattopadhyay,K.; Ranu, B. C. *Tetrahedron Lett.***2009**, *50*, 1003-1006.

16. Baur, M.; Frank, M.; Schatz, J.; Schildbach, F. *Tetrahedron*. **2001**, *57*, 6985-6991.

17. Scott, N. M.; Nolan, S. P. *Eur. J. Inorg. Chem*. **2005**, 1815-1828.

18. Wanzlick, H. W.; Schikora, E. *Angew. Chem.***1960**, *72*, 494.

19. Bourissou, D.; Guerret, O.; Gabbaï, F. P.; Bertrand, G. *Chem. Rev*.**2000**, *100*, 39-91.

20. Regitz, M. *Angew. Chem. Int. Ed.***1996**, *35*, 725-728.

21. Herrmann, W. A.; Christian, K. *Angew. Chem. Int. Ed.***1997**, *36*, 2162-2187.

22. Perry, M. C.; Burgess, K.; *Tetrahedron: Asymmetry*. **2003**, *14*, 951-961.

23. Kirmse, W. *Angew. Chem. Int. Ed*.**2010**, *49*, 8798-8801.

24. (a) Valente, C.; Pompeo, M.; Sayah, M.; Organ, M. G. *Org. Process Res. Dev*. **2014**, *18*, 180-190; (b) Valente, C.; Çalimsiz, S.; Hoi, K. H.; Mallik, D.; Sayah, M.; Organ, M. G. *Angew. Chem. Int. Ed*. **2012**, *51*, 3314-3332; (c) Kantchev, E. A. B.; O'Brien, C. J.; Organ, M. G. *Angew. Chem. Int. Ed*. **2007**, *46*, 2768-2813; (d) Pompeo, M.; Farmer, J. L.; Froese, R. D. J.; Organ, M. G. *Angew. Chem., Int. Ed*. **2014**, *53*, 3223-3226; (e) Zhang, Y.; Cesar, V.; Storch, G.; Lugan, N.; Lavigne, G. *Angew. Chem. Int. Ed*. **2014**, *53*, 6482-6486.

25. Yaşar, S.; Şahin, C.; Arslan, M.; Özdemir, İ. *J. Org.Chem.* **2015**, *776*, 107.

26. (a) O'Brien, C. J.; Kantchev, E. A. B.; Valente, C.; Hadei, N.; Chass, G. A.; Lough, A.; Hopkinson, A. C.; Organ, M. G. *Chem. Eur. J*. **2006**, *12*, 4743-4748. (b) Organ, M. G.; Avola, S.; Dubovyk, I.; Hadei, N. E. A. B. O'Brien, C. J.; Valente, C. *Chem. Eur. J*. **2006**, *12*, 4749- 4755.

27. a) Valente, C.; Baglione, S.; Candito, D.; O'Brien, C. J.; Organ, M. G. *Chem. Commun*. **2008**, 735-737. (b) Organ, M. G.; Calimsiz, S.; Sayah, M.; Hou Hoi, K.; Lough, A. J. *Angew. Chem. Int. Ed*. **2009**, *48*, 2383-2387. (c) Valente, C.; Belowich, M. E.; Hadei, N.; Organ, M. G. *Eur. J. Org. Chem*. **2010**, 4343-4354. (d) Pompeo, M.; Froese, R. D. J.; Hadei, N.; Organ, M. G. *Angew. Chem. Int. Ed*. **2012**, *51*, 11354-11357. (e) Hou Hoi, K.; Organ, M. G. *Chem. Eur. J*. **2012**, *18*, 804- 807. (f) Sayah, M.; Organ, M. G. *Chem. Eur. J*.

2011, *17*, 11719- 11722. (g) Sayah, M.; Organ, M. G. *Chem. Eur. J*. **2013**, *19*, 16196- 16199.

28. Dunsford, J. J.; Cavell, K. J. *Organomettallics*. **2014**,*33*,2902-2905.

29. (a) Özdemir, İ.; Gök, Y.; Özeroğlu, Ö.; Kaloğlu, M.; Doucet, H.; Bruneau, C. *Eur. J. Inorg. Chem.* **2010**, 1798-1805. (b) Teci, M.; Brenner, E.; Matt, D.; Toupet, L. *Eur. J. Inorg. Chem*. **2013**, 2841- 2848.

30. (a) Hiroshige, M.; Zhou, J. R.; Hauske P. *Tetrahedron Lett.* **1995**, *36*, 4567; (b) Bueno, A. C.; Gusevskaya, A. O.; de Souza, E. V. *Adv. Synth. Catal*. **2009**, *351*, 2491; (c) Conlon, D. A.; Pipik, B.; Ferdinand, S.; Le Blond, C. R.; Sowa, J. R.; Izzo, B.; Collins, P.; Ho, G. J.; Williams, J. M.; Sun, Y. J.; Shi, Y. K. *Adv. Synth. Catal*. **2003**, *345*, 931; (d) Vallin, K. S. A.; Hallberg, M.; Larhed, A. *J. Org. Chem*. **2001**, *66*, 4340; (e) Miao, G.; Ye, P.; Baldino, L.; Yu, C. M. *J. Org. Chem*. **2005**, *70*, 2332.

31. (a) Mosset, P.;Gree, R. *Synlett*. **2013**, 24(9): 1142-1146; (b) Ikunaka, M.; Maruoka, K.; Okuda, Y.; Ooi, T. *Organic process Research&Development*, **2003**, *7*, 644-648.

32. (a) Saikia, B.; Ali, A. A.; Boruah, P. R.; Sarma, D.; Barua, N. C. *New J. Chem*. **2015**, *39*, 2440; (b) Borah, G.; Boruah, D.; Sarmah, G.; Bharadwaj, S.K.; Bora, U. *Appl. Organometal. Chem*. **2013**, *27*, 688; (c) Mondal, M.; Bora, U. *Green Chem*. **2012**, *14*, 1873; (d) Liu, N.; Jin, Z. *Green. Chem*. **2012**, *14*, 592; (e) Liu, C.; Zhang, Y.; Liu, N.; Qui, J. *Green Chem*., **2012**, *14*, 2999; (e) Saikia, B.; Boruah, P. R.; Ali, A. A.; Sarma, D. *Tetrahedron Lett*. **2015**, *5*6, 33; (f) Kim, Y. -J.; Lee, J. –H.; Kim, T.; Ham, J.; Zheng, Z. N.; Lee, S. W. *Eur. J. Chem.* **2012**, 6011; (g) Karimi, B.; Akhavan, P. F. *Chem. Commun*. **2011**, *47*, 7686.

33. Gu, P.; Xu, Q.; Shi, M. *Tetrahedron*, **2014**, *70*,7886.

34. Barrios, G.G.; Hiller, J.; Peris, E. *Chem. Eur. J*. **2013**, *19*, 10405.

35. Sutar, R.L.; Kumar, V.; Shingare, R.D.; Thorat, S.; Gonnade, R.; Reddy, S. *Eur. J. Org. Chem.* **2014**, 4482.

36. Ren, H.; Xu, Y.; Jeanneau, E.; Bonnamour, I.; Tu, T.; Darbost, U. *Tetrahedron*, **2014**, *70*, 2829.

37. Valds, H.; Poyatos, M.; Ujaque, G.; Peris, E. *Chem. Eur. J.* **2015**, *21*, 1578.

38. Saikia, B.; Boruah, P.R.; Ali, A.A.; Sarma, D. *Tetrahedron Lett.* **2015**, *56*, 633.

39. Kim, Y.–J.; Lee, J.–H.; Kimm,T.; Ham, J.; Zheng, Z.N.; Lee, S.W. *Eur. J. Inorg. Chem.* **2012**, 6011.

40. (a) Joucla, L.; Cusati, G.; Pinel, C.; Djakovitch, L.; *Tetrahedron. Lett.* **2008**, *49*, 4738. (b) Chatterjee, A.; Ward, T. R. *Catal Lett* **2016**, *146*, 820. (c) Soomro, S.S.; Röhlich, C.; Köhler, K. *Adv. Synth. Catal.*, **2011**, 353, 767. (d) Zhou, J.; Guo, X.; Tu, C.; Li, X.; Sun, H.; *J.Organomet. Chem.* **2009**, *694*, 697. (e) Leadbeater, N.; Marco, E. M. *J. Org. Chem.* **2003**, *68*, 888. (f) Li, Z.; Gelbaum, C.; Heaner, W. L.; Fisk, J.; Jaganathan, A.; Holden, B.; Pollet, P.; Liotta, C. L. *Org. Process Res. Dev.* **2016**, *20*, 1489. (g) Liang, Q.; Xing, P.; Huang, Z.; Dong, J.; Sharpless, K. B.; Li, X.; Jiang, B. *Org. Lett*. **2015**, *17*, 1942. (h) Boubakri, L.; Yaşar, S.; Dorcet, V.; Roisnel, T.; Bruneau,C.; Hamdi, N.; Özdemir, İ. *New J. Chem.* **2017**, *41*, 5105.