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Nazan Kaloğlu, İsmail Özdemir

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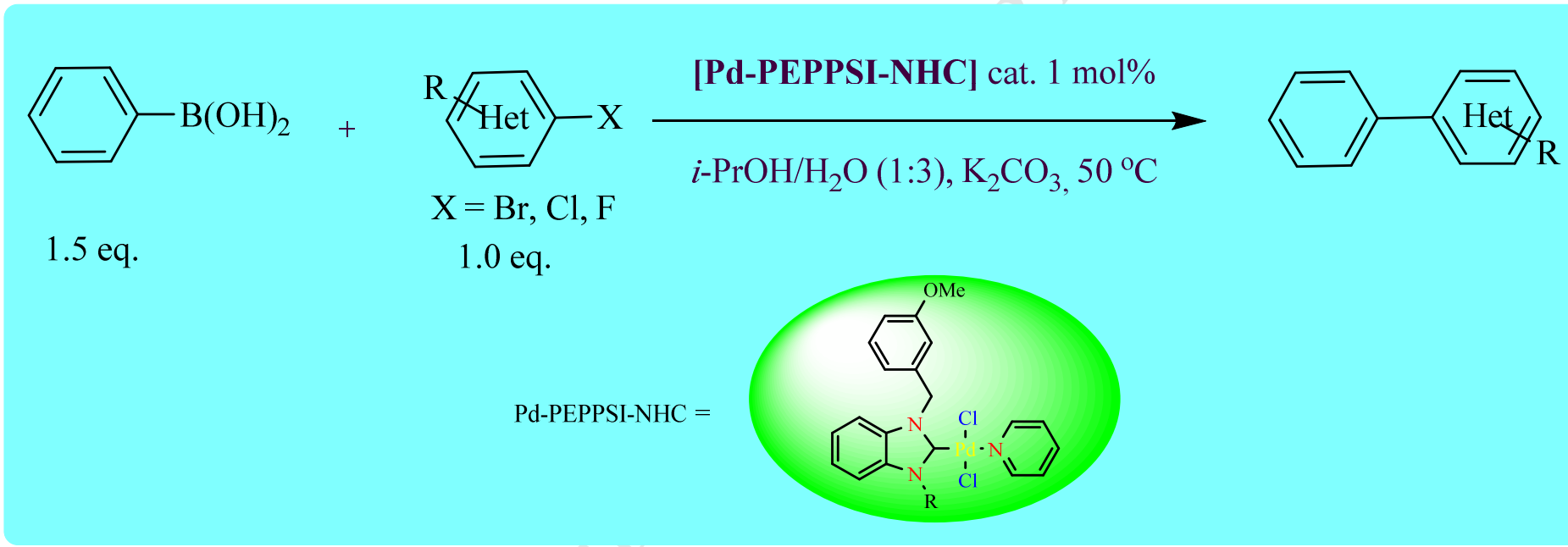
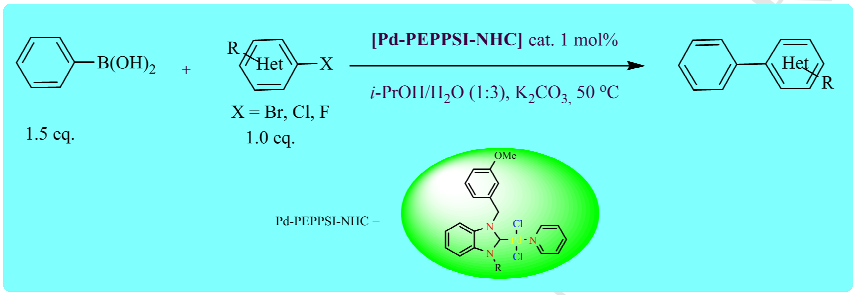


Graphical Abstract

PEPPSI-Pd-NHC Catalyzed Suzuki-Miyaura Cross-Coupling Reactions in Aqueous Media

Nazan Kaloğlu[a,b] and İsmail Özdemir*[a,b]
[a] *İnönü University, Faculty of Science and Arts, Department of Chemistry, 44280 Malatya, Turkey*
[b] *İnönü University, Catalysis Research and Application Center, 44280 Malatya, Turkey*



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Nazan Kaloğlu[a,b] and İsmail Özdemir*[a,b]

[a]*İnönü University, Faculty of Science and Arts, Department of Chemistry, 44280 Malatya, Turkey*
[b]*İnönü University, Catalysis Research and Application Center, 44280 Malatya, Turkey*

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ABSTRACT

A series of unsymmetrical 1,3-disubstituted benzimidazolium chlorides were synthesized as *N*-heterocyclic carbene (NHC) precursors. These compounds were used to synthesize of the PEPPSI-type palladium NHC complexes. The structures of all compounds were characterized by ^{1}H NMR, ^{13}C NMR, FT-IR spectroscopy and elemental analyses. The catalytic activity of the PEPPSI-type palladium–NHC complexes has been evaluated with respect to the Suzuki-Miyaura cross-coupling reactions of phenyl boronic acid with various aryl halides in aqueous media.

1. Introduction

Biaril motifs are important building blocks for commercially important compounds such as various natural products, pharmaceuticals, agrochemicals and functional materials.[1-6] Therefore, the preparation of such compounds is very important for modern organic synthesis. Transition metal-catalyzed cross-coupling reactions have becomes one of the most conventional methods among C-C bond forming processes for biaryls.[7-10] The development of this methodology has revolutionised synthetic chemistry and was acknowledged with the award of a Nobel Prize in Chemistry in 2010 for palladium-catalysed cross-couplings in organic synthesis.[11] Nowadays, the Suzuki-Miyaura reaction is probably the most commonly used cross-coupling process for synthesis of biaryls because of its mild reaction conditions and high functional group tolerance.[12] Moreover, boronic acids are environmentally safer and much less toxic than other metaloorganic compounds for example organostannanes, and the inorganic by-products are easily removed from the reaction mixture, making the reaction suitable for industrial processes.[13]

Most of the early work on Suzuki-Miyaura cross-coupling reactions focused on using tertiary phosphine as ligands and so phosphine ligands have become an indispensable class of ligands for the coupling of aryl chlorides.[14,15] Since the discovery of *N*-heterocyclic carbenes (NHCs) by Arduengo in 1991, NHCs have become one of the most versatile class of ligands for a wide range of transition metals[16,17] and begun to replace phosphine ligands[18] due to their unique properieties.[19] The easy preparation and handling of their precursors, their high modularity, and their strong σ-donor properties, which allow them to form strong metal-NHC bonds that prevent ligand dissociation, have rendered them extremely popular as supporting ligands in transition metal catalysis.[20] The σ-donor properties of NHC ligands are crucial in controlling their interaction with transition metals, and as a consequence, to determine the selectivity and reactivity of NHCs in transition-metal catalysis. Recently, Szostak and co-workers have reported a simple NMR method for estimating σ-donor properties of NHC ligands based on a straightforward ^{1}H NMR measurement of NHC ligand precursors.[21] Due to this and similar unique features, various NHC complexes have been synthesised with different transition-metals to date and have demonstrated excellent activities as catalysts in different organic transformations.[22-26]

Since the discovery of transition-metal-catalyzed reactions, there is a continuous effort to develop new catalyst systems which will be effective for a wide range of products. In most of these reactions are generally used organic solvents, most of which are toxic, flammable, and explosive. However, due to the environmental concerns necessity for the use of the benign solvent water as the medium for chemical reactions is continuously growing. The use of water as a solvent in Suzuki-Miyaura cross-coupling reactions helps with the solvation of

these organic-insoluble materials and inorganic bases. Also, organoboron compounds are often quite stable to protolytic decomposition by water. In addition to being cheap and safe solvent,[27] water has the additional advantage that the Suzuki-Miyaura cross-coupling reactions products are often poorly soluble in water. Thus, they can be easily separated from the reaction mixture. This advantage, though, also turns out to be a drawback, as the aryl halides are poorly soluble in water.[28] To overcome this problem, addition of a minumum volume of a protic co-solvent such as alcohol should led to even faster Suzuki coupling reactions. Thus, in recent times, there is a particular emphasis on the development of catalyst systems that will be effective for Suzuki-Miyaura cross-coupling reactions in aqueous media.[29]

Palladium-NHC complexes such as bis(NHC)-type (**a**), pincer-type (**b**), allyl-type (**c**) and PEPPSI-type, (PEPPSI = **P**yridine **E**nhanced **P**recatalyst **P**reparation **S**tabilization and **I**nitiation), (**d**) are the well-known and the most active ones for cross-coupling catalysis (Figure 1).[30] Among them, PEPPSI-type palladium-NHC complexes can be easily obtained and are easy to handle in contrast to other type palladium-NHC complexes.[31-35] The high activity of PEPPSI complexes in catalysis has been based on to the presence of a loosely bound throwaway pyridine ligand that makes way for the incoming substrate.[36]

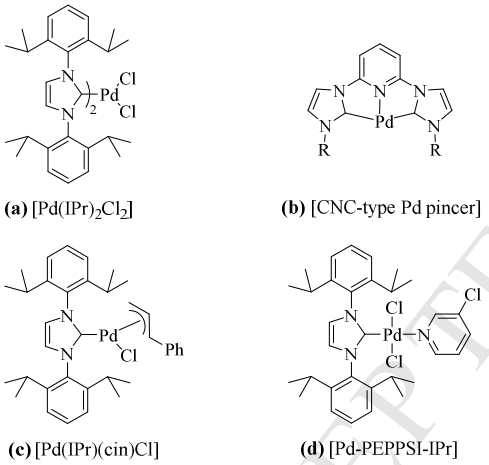
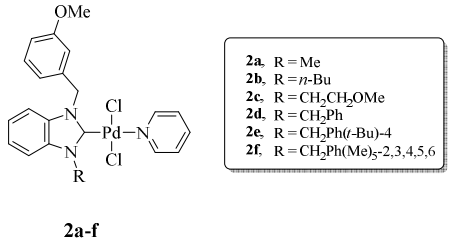


Fig. 1. Well-known different type palladium-NHC complexes.

There are many examples of the application of PEPPSI-type complexes in the Suzuki-Miyaura reaction in aqueous medium, in which their excellent catalytic activity and versatility are clearly evidenced.[37] In this context, recently we have also reported to synthesis of PEPPSI-type palladium-NHC complexes and their catalytic activity in the Suzuki-Miyaura reactions in aqueous media.[38] Here in this contribution, we report the synthesis and structural characterizations of a series of new bulky NHC precursors (**1a-f**), and their air-stable, convenient to handle and easily accessible new PEPPSI-type palladium-NHC complexes of the general formula [$PdCl_2$(NHC)(pyridine)], (**2a-f**) (Figure 2). These complexes stabilized over 3-methoxybenzyl - functionalized NHC ligands and containing a "throwaway" pyridine ligand. These precatalysts are effective for the Suzuki-Miyaura cross-coupling reactions of phenylboronic acid and aryl halides at mild conditions in aqueous media.



2a-f

Fig. 2. PEPPSI-type palladium-NHC complexes **2a-f**.

2. Results and discussion

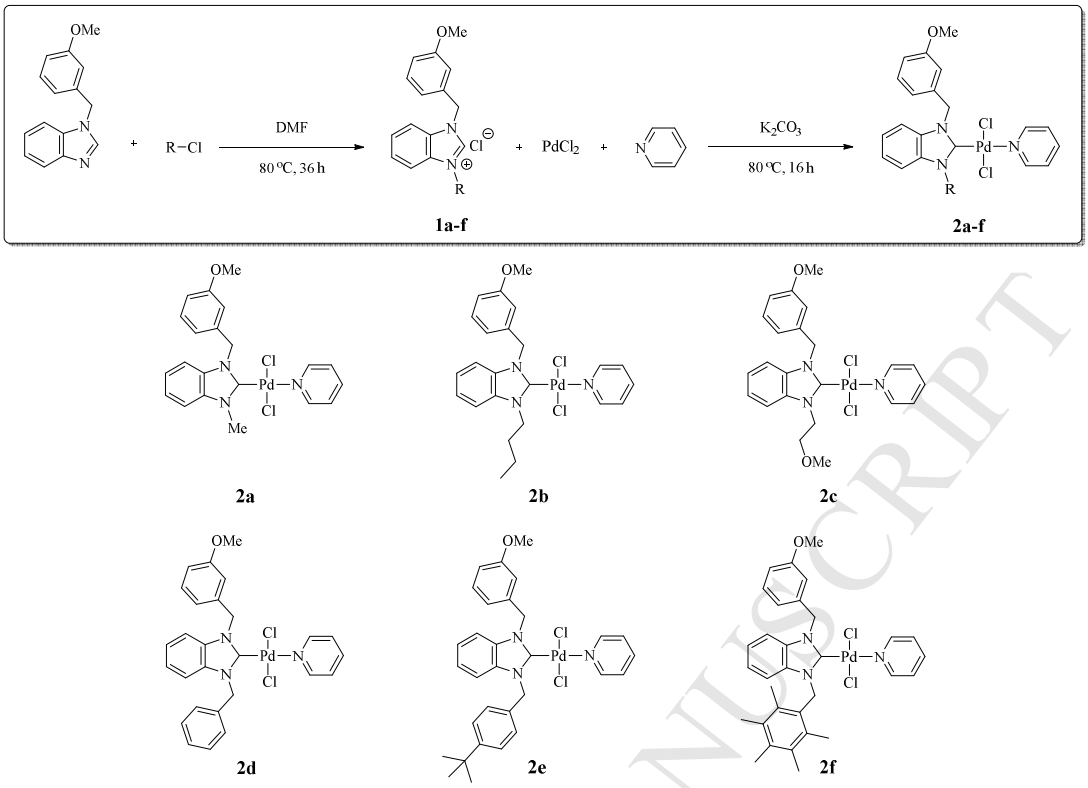
2.1. Preparation of Benzimidazolium Chlorides

The four new benzimidazolium chlorides **1a**, **1c**, **1e** and **1f** were synthesized by reacting *N*-(3-methoxybenzyl)benzimidazole with alkyl chlorides in dimethylformamide (DMF) at 80 ^{o}C for 36 h (Scheme 1). These benzimidazolium chlorides **1b** and **1d** were obtained as we previously described.[16c] Benzimidazolium chlorides were characterized using ^{1}H NMR, ^{13}C NMR and FT-IR spectroscopy and gave satisfactory elemental analysis. As shown in Table 1, The FT-IR data clearly indicated that the ben zimidazolium chlorides **1a–f** exhibit a characteristic $\nu_{(NCN)}$ band typically between 1557-1567 cm^{-1}. The resonances for C(2)-*H* were observed as sharp singlets at δ 11.48-12.00 ppm. The^{13}C NMR values of N*C*HN resonances in **1a-f** appear at the range 143.7-143.9 ppm as single signal. These NMR values are in line with those found for other benzimidazolium chlorides of the literature.[12i, 16c, 17d, 20c, 26]

2.2. Preparation of PEPPSI-type palladium–NHC complexes

The general procedure for the preparation of the PEPPSI-type palladium–NHC complexes **2a-f**, according to the method reported by Organ,[40] is shown in Scheme 1. The six new palladium complexes **2a-f** were synthesized by the reaction of the corresponding benzimidazolium chlorides (**1a-f**) obtained from $PdCl_2$ and pyridine in the presence of K_2CO_3 as a base. The air and moisture-stable PEPPSI-type palladium-NHC complexes are yellow in colour and soluble in common organic solvents such as acetone, dichloromethane, chloroform, DMF, ethanol and acetonitrile. They were fully characterised by elemental analysis, ^{1}H NMR and ^{13}C NMR and FT-IR spectroscopy and gave satisfactory elemental analysis. The absence, in the ^{13}C NMR and ^{1}H NMR spectra, of the characteristic signals of the iminocarbon (143.7-143.9 ppm) and the acidic imino proton (11.48-12.00 ppm), which are present in the salts **1a-f**, suggests the formation of NHC-carbenes and their coordination to form PEPPSI-type palladium-NHC complexes. In addition, the characteristic carbene carbons in compounds **2a-f** appear in the ^{13}C NMR spectra as deshielded singlets at between 162.8-164.5 ppm. The FT-IR data clearly indicated that the PEPPSI-type palladium–NHC complexes **2a-f** exhibit a characteristic $\nu_{(NCN)}$ band typically between 1396–1410 cm^{-1}. These NMR values are in line with those found for other PEPPSI-type palladium-NHC complexes of

the literature. [20c, 26a, 39] The analytical data are in good agreement with the compositions proposed for all the new compounds we prepared, and are summarized in Table 1.



Scheme 1. Synthesis of the benzimidazolium chlorides (**1a-f**) and the PEPPSI-type palladium-NHC complexes (**2a-f**).

Table 1
Physical and spectroscopic properties of new compounds.

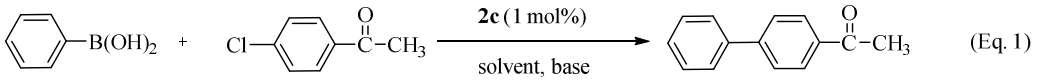
Compound	Molecular formula	Isolated yield (%)	M.p. (°C)	$\nu_{(CN)}$ (cm^{-1})	H(2) ^{1}H NMR (ppm)	C(2) ^{13}C NMR (ppm)
1a	$C_{16}H_{17}ClN_2O$	85	137-138	1567	11.73	143.9
1c	$C_{18}H_{21}ClN_2O_2$	78	93-94	1557	11.60	143.8
1e	$C_{26}H_{29}ClN_2O$	89	128-129	1558	12.00	143.8
1f	$C_{27}H_{31}ClN_2O$	82	139-140	1558	11.48	143.7
2a	$C_{21}H_{22}Cl_2N_3OPd$	60	107-108	1407	-	163.3
2b	$C_{24}H_{28}Cl_2N_3OPd$	63	143-144	1410	-	162.8
2c	$C_{23}H_{26}Cl_2N_3O_2Pd$	53	173-174	1405	-	163.2
2d	$C_{27}H_{26}Cl_2N_3OPd$	55	238-239	1410	-	164.3
2e	$C_{31}H_{34}Cl_2N_3OPd$	51	184-185	1410	-	164.5
2f	$C_{32}H_{36}Cl_2N_3OPd$	45	224-225	1396	-	164.1

2.3. Optimization of the Reaction Conditions for Suzuki-Miyaura Coupling

To study the efficiency of the PEPPSI-type palladium-NHC complexes **2a-f** in Suzuki-Miyaura coupling reactions, we first selected the complex **2c** as the model catalyst, the phenylboronic acid as model substrate and the 4-chloroacetophenone as model coupling partner (Table 2, Eq. 1). To find the best base, different bases (Na_2CO_3, K_2CO_3, Cs_2CO_3, NaOH, KOH) were tested in the present of *i*-PrOH as solvent at 50 °C for 3 h in air (Table 2, entries 1-5). When a base of K_2CO_3 was used, a good yield of coupling product was obtained (Table 2, entry 2). Then, to find the best solvent medium, different solvents such as DMF, water, EtOH or solvent mixtures such as *i*-PrOH/H_2O (1:1; *v*/*v*), *i*-PrOH/H_2O (1:3; *v*/*v*), *i*-PrOH/H_2O (3:1; *v*/*v*) were tested in the present of K_2CO_3 as base at 50 °C for 3 h (Table 2, entries 6-11). When a mixed solvent of *i*-PrOH/H_2O (1:3; *v*/*v*) was used, a good yield was observed (Table 2, entry 10). When the reaction time was reduced from 3 h to 2 h at 50 °C, no noticeable effect on the yield was observed (Table 2, entry 12), but when the reaction time was reduced from 2 h to 1 h, the conversion decreased to 63%. (Table 2, entry 13). As a result of the optimisation experiments, a very good yield (95%) was obtained with K_2CO_3 base and *i*-PrOH/H_2O (1:3; *v*/*v*) solvent system, at 50 °C for 2 h in air (Table 2, entry 12).

Table 2

Optimization of the Suzuki-Miyaura coupling reactions of phenylboronic acid with 4-chloroacetophenone by complex **2c**.[a]



Entry	Solvent	Base	Yield (%)[b,c]
1	*i*-PrOH	Na_2CO_3	50
2	*i*-PrOH	K_2CO_3	70
3	*i*-PrOH	Cs_2CO_3	40
4	*i*-PrOH	NaOH	64
5	*i*-PrOH	KOH	52
6	DMF	K_2CO_3	12
7	H_2O	K_2CO_3	8
8	EtOH	K_2CO_3	10
9	*i*-PrOH / H_2O (1:1; *v*/*v*)	K_2CO_3	70
10	*i*-PrOH / H_2O (1:3; *v*/*v*)	K_2CO_3	98
11	*i*-PrOH / H_2O (3:1; *v*/*v*)	K_2CO_3	65
12[d]	***i*-PrOH / H_2O (1:3; *v*/*v*)**	**K_2CO_3**	**95**
13[e]	*i*-PrOH / H_2O (1:3; *v*/*v*)	K_2CO_3	63

[a] Reaction conditions: complex **2c** (0.01 mmol, 1 mol %), 4-chloroacetophenone (1.0 mmol), phenylboronic acid (1.5 mmol), base (2.0 mmol), solvent (4 mL), 50 °C, 3 h.
[b] Yields (%) were calculated according to 4-chloroacetophenone by GC analysis using decane as an internal standard.
[c] Yields are average of two runs.
[d] Reaction time is 2 h.
[e] Reaction time is 1 h.

2.4. Suzuki-Miyaura coupling of Phenylboronic Acid with Various Aryl Halides

The optimized conditions were applied to the Suzuki-Miyaura coupling reactions of different aryl chlorides with phenylboronic acid using the PEPPSI-type palladium-NHC complexes (**2a-f**) at 50 °C for 2 h (Table 3, Eq. 2). As shown in Table 3, both electron-rich, electron-poor and sterically hindered aryl chlorides effectively afford the corresponding products (55–95%) in 2-3 h at 50 °C (Table 3, entries 1-42). When the reaction of 4-chlorobenzene was investigated, yields at between 81–90% (Table 3, entries 1-6). The palladium-PEPPSI-NHC complex **2a-f** were further assessed in the cross-coupling of phenylboronic acid with two electron-rich aryl chlorides; namely, *p*-chlorotoluene and *p*-chloroanisole. This aryl chlorides were both rapidly converted into biaryls at 50 °C for 2 h (yields of 83-92% and 75-85%, respectively) (Table 3, entries 7-12 and 13-18). As anticipated, somewhat lower activities were found with the two *ortho*-substituted aryl chlorides; namely, *o*-chlorotoluene and *o*-chloroanisole (yields of 65-78% and 55-65%, respectively) (Table 3, entries 19-24 and 25-30). When these aryl chlorides were used, the reaction time was increased from 2 h to 3 h. The coupling of phenylboronic acid with electron-poor aryl chlorides such as *p*-chloroacetophenone and *p*-chloronitrobenzene also proceeds nicely. *p*-Chloroacetophenone and *p*-chloronitrobenzene gave the phenylboronic acid with 86%-95% and 85-93% yields, respectively at 50 °C for 2 h (Table 3, entries 31-36 and 37-42).

Although small differences in reactivities were observed for **2a-f** catalyst due to the similar nature of the NHC moieties, it can say that the most effective catalyst in this study is **2c**. We attributed these performance differences to well-accordance electronic and steric properties of the NHC ligand. It is known that oxidative additions of electron-withdrawing substrates to electron rich palladium-complexes and reductive elimination of the product from large, sterically hindered palladium-complexes proceed more readily. Therefore, the presence of an NHC ligand, (eg. **1c**), bearing a different second donating group such as ether side chains on the metal may radically increase the catalytic performance of the catalyst (eg. **2c**). The chelating nature of these ligands promotes production of highly stable complexes. The hemilabile part of such ligands is capable of reversible dissociation to produce vacant coordination sites, allowing complexation of substrates during the catalytic cycle. At the same time the strong donor carbene moiety remains connected to the metal centre. Based on these observations, the following tests were carried out different (hetero)aryl halides (X = Br, Cl, F) in presence of **2c** catalyst (Table 4, Eq. 3).

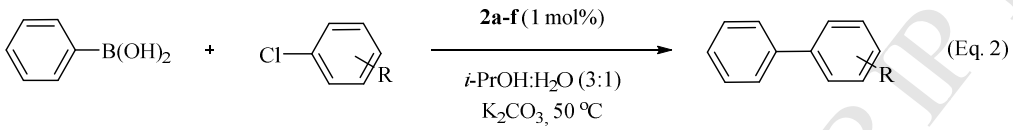
The palladium complex **2c** was further assessed in the cross-coupling of phenylboronic acid with two electron-deficient aryl chlorides; namely, 4-cyano chlorobenzene and 4-chlorobenzotrifluoride. These aryl chlorides were both rapidly converted into biaryls (yields of 94% and 78% after 2 h, respectively) (Table 4, entries 1 and 3). But, when the reaction time was reduced from 2 h to 1 h at 50 °C, the yields decreased to 70% and 54%, respectively (Table 4, entries 2 and 4). When 4-bromobenzaldehyde was used as the substrate, 97% yield was observed after 1 h (Table 4, entry 6), but when the reaction time was reduced from 1 h to 0.5 h at 50 °C, no noticeable effect on the yield was observed (yield of %94) (Table 4, entry 6).

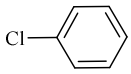
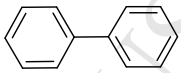
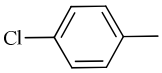
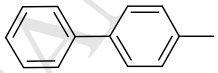
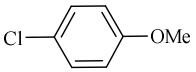
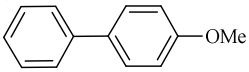
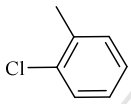
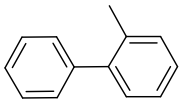
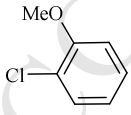
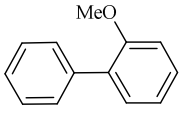
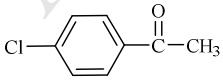
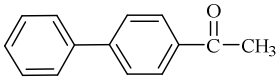
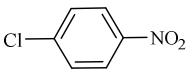
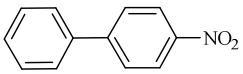
When the reactions of sterically hindered aryl bromides such as *o*-bromotoluene and *o*-cyano bromobenzene were investigated, the yield was 98% in both cases (Table 4, entries 7 and 9). As anticipated, somewhat lower activities were found

with the two *ortho*-substituted bromobenzenes *o*-cyano bromobenzene (77% yield in 0.5 h) and 4-cyano bromobenzene (72% yield in 0.5 h) (Table 4, entries 8 and 10). With phenylboronic acid, even the sterically hindered 3-bromoquinoline led to the expected coupling product with 98% yield in 1h. (Table 4, entry 11). But, when the reaction time was reduced from 1 h to 0.5 h, the yield decreased to 78% (Table 4, entry 12). A similar trend was observed when phenylboronic acid was reacted with the an unreactive substrate such as 3,4-dimethoxy fluorobenzene. For example, 3,4-dimethoxy fluorobenzene gave yield of 43% after 2 h. (Table 4, entry 13). But, when the reaction time was increased from 2 h to 5 h, the yield increased to 67% (Table 4, entry 14). When the reaction time was increased from 5 h to 10 h, 98% yield was observed in the reaction.

Table 3

Catalytic activities of complexes (**2a-f**) in the Suzuki-Miyaura coupling reactions of phenylboronic acid with aryl chlorides.[a]

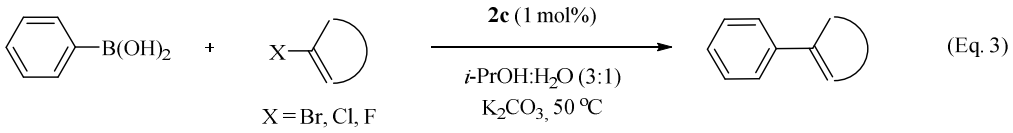


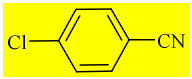
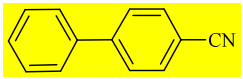
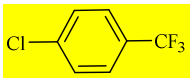
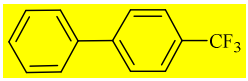
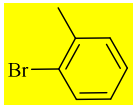
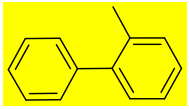
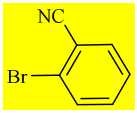
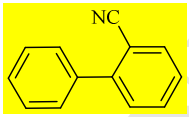
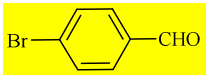
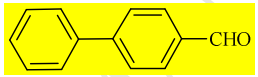
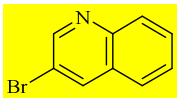
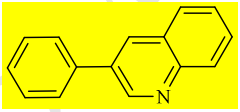
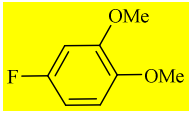
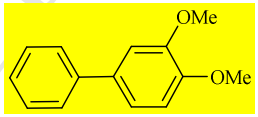
Entry	Aryl chloride	[Pd]	Biaryl product	Time (h)	Yield (%)[b]
1		**2a**		2	87
2		**2b**		2	86
3		**2c**		2	90
4		**2d**		2	83
5		**2e**		2	81
6		**2f**		2	88
7		**2a**		2	86
8		**2b**		2	83
9		**2c**		2	92
10		**2d**		2	88
11		**2e**		2	85
12		**2f**		2	90
13		**2a**		2	78
14		**2b**		2	75
15		**2c**		2	85
16		**2d**		2	79
17		**2e**		2	77
18		**2f**		2	81
19		**2a**		3	69
20		**2b**		3	65
21		**2c**		3	78
22		**2d**		3	71
23		**2e**		3	73
24		**2f**		3	75
25		**2a**		3	59
26		**2b**		3	55
27		**2c**		3	65
28		**2d**		3	57
29		**2e**		3	58
30		**2f**		3	60
31		**2a**		2	89
32		**2b**		2	86
33		**2c**		2	95
34		**2d**		2	92
35		**2e**		2	90
36		**2f**		2	94
37		**2a**		2	91
38		**2b**		2	89
39		**2c**		2	93
40		**2d**		2	87
41		**2e**		2	85
42		**2f**		2	92

[a] Reaction conditions: palladium **2a-f**, (0.01 mmol, 1 mol%), aryl chloride (1.0 mmol), phenylboronic acid (1.5 mmol), K_2CO_3 (2.0 mmol), *i*-PrOH/H_2O (1:3; *v/v*) (4 mL), 50 °C.

[b] Yields (%) were calculated according to aryl chloride by GC analysis using decane as an internal standard.

Table 4
Suzuki-Miyaura cross-coupling of different aryl halides catalyzed by palladium complex **2c**.[a]



Entry	Aryl halide	Biaryl product	Time (h)	Yield (%)[b]
1			2	94
2			1	70
3			2	78
4			1	54
5			1	98
6			0.5	77
7			1	98
8			0.5	72
9			1	97
10			0.5	94
11			1	98
12			0.5	78
13			2	43
14			5	67
15			10	98

[a] Reaction conditions: palladium **2c** (0.01 mmol, 1 mol%), aryl halide (1.0 mmol), phenylboronic acid (1.5 mmol), K_2CO_3 (2.0 mmol), *i*-PrOH/H_2O (1:3; *v/v*) (4 mL), 50 °C.
[b] Yields (%) were calculated according to aryl halide by GC analysis using decane as an internal standard.

In previous works, similar substrates have been employed with higher reaction time (3 h), and higher reaction temperature (80 °C) has been chosen for Suzuki-Miyaura cross-coupling reaction in presence of palladium-PEPPSI catalysts. However, in the present work the reaction temperature was reduced to 50 °C, and the reaction time was shortened to 2 h for aryl chlorides. When compared with our previous work, here, the reaction time was shortened to 2 h and higher yields were obtained, whereas in previous work, the reaction was carried out in presence of 1.0 mol% palladium-PEPPSI-NHC catalyst and K_2CO_3 as the base in DMF/water mixture at 80 °C.[41]

3. Conclusion

In conclusion, six new PEPPSI-type palladium-NHC complexes were successfully synthesized and characterized by ^{1}H NMR, ^{13}C NMR and FT-IR spectroscopy. These palladium complexes were used as the catalysts in the synthesis of biaryls using Suzuki-Miyaura cross-coupling reaction between the phenylboronic acid and aryl halides. When the catalytic studies were evaluated, it was found that all of the complexes were suitable for the Suzuki-Miyaura cross-coupling reaction. Surprisingly, similar yields were obtained for the coupling of each aryl halides. We can say that there is no significant difference between these complexes on the catalytic activity. The only significant difference between **2a-f** complexes indicates that electronic and steric properties are also playing some role in these processes. As a result of this catalytic reactions provides many advantages such as low catalyst loading, very good yields, green solvent system, simple and efficient procedure, short reaction times under an air atmosphere.

4. Experimental

4.1. General Methods

The synthesis of NHC salts and PEPPSI-type palladium-NHC complexes were carried out under argon using standard Schlenk

line techniques. Elemental analyses were performed by İnönü University Scientific and Technological Research Center (Malatya, Turkey). Melting points were measures in open capillary tubes with an Electrothermal-9200 melting points apparatus. IR spectra were recorded on ATR unit in the range of 400-4000 cm^{-1} with Perkin Elmer Spectrum 100 Spectrofotometer. ^{1}H NMR and ^{13}C NMR spectra were recorded using Bruker Avance AMX and Bruker Avance III spectrometer operating at 300, 400 and 500 MHz (^{1}H NMR) and at 75, 100 and 125 MHz (^{13}C NMR) in $CDCl_3$. The NMR studies were carried out in high-quality 5 mm NMR tubes. The chemical shifts (δ) are reported in ppm relative to $CDCl_3$. Coupling constants (J values) are given in hertz. NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, pent = pentet, hext = hextet, m = multiplet. ^{1}H NMR spectra are solvents (δ = 77.16 ppm for $CDCl_3$). All catalytic reactions were monitored on an Agilent 6890N GC and Schimadzu 2010 Plus GC-MS system by GC-FID with an HP-5 column of 30 m length, 0.32 mm diameter, and 0.25 μm film thickness.referenced to residual protiated solvents (δ = 7.26 ppm for $CDCl_3$), ^{13}C chemical shifts are reported relative to deuteriated.

*4.2. General procedure for the preparation of benzimidazolium chlorides (**1a-f**)*

N-(3-Methoxybenzyl)benzimidazole (1.0 g; 4.2 mmol) was dissolved in degassed DMF (3 mL) and alkyl chloride (4.2 mmol) was added at room temperature. The reaction mixture was stirred at 80 °C for 36 h under argon. After completion of the reaction, the solvent was removed by vacuum and diethyl ether (15 mL) was added to obtain a white crystalline solid, which was filtered off. The solid was washed with diethyl ether (3×10 mL) and dried under vacuum. The crude product was recrystallized from ethanol/diethyl ether mixture (1:3, *v/v*) at room temperature and, completely dried under vacuum. All benzimidazolium chlorides (**1a-f**) were isolated as air- and moisture-stable white solids and were isolated in 78-89 % yields.

*4.2.1. 1-(3-Methoxybenzyl)-3-(methyl)benzimidazolium Chloride (**1a**)*

(1.02 g, yield 85%) ^{1}H NMR (300 MHz, $CDCl_3$, 25 ^{o}C): δ = 3.71 (s, 3H, $CH_2C_6H_4(OCH_3)$-3); 4.23 (s, 3H, CH_3); 5.77 (s, 2H, $CH_2C_6H_4(OCH_3)$-3); 6.75-6.78, 6.96-7.03, 7.15-7.24 and 7.48-7.68 (m, 8H, arom. C*H*s, NC_6H_4N and $CH_2C_6H_4(OCH_3)$-3); 11.73 (s, 1H, NC*H*N) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 ^{o}C): δ = 33.8 (CH_3); 51.3 ($CH_2C_6H_4(OCH_3)$-3); 55.6 ($CH_2C_6H_4(OCH_3)$-3); 112.8, 113.7, 113.8, 114.7, 120.5, 127.1, 127.2, 130.3, 131.01, 132.15, 134.2, 160.2. (arom. *C*s, NC_6H_4N and $CH_2C_6H_4(OCH_3)$-3); 143.9 (N*C*HN) ppm. Elemental analysis calcd (%) for $C_{16}H_{17}ClN_2O$ (Mr = 288.10 g. mol^{-1}): C 66.58, H 5.93, N 9.70; found (%): C 66.60, H 5.94, N 9.72.

*4.2.2. 1-(3-Methoxybenzyl)-3-(n-butyl)benzimidazolium Chloride (**1b**)*

This benzimidazolium chloride was synthesized according to published procedure.[16c]

*4.2.3. 1-(3-Methoxybenzyl)-3-(2-methoxyethyl)benzimidazolium Chloride (**1c**)*

(1.08 g, yield 78%) ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C): δ = 3.35 (s, 3H, $CH_2CH_2OCH_3$); 3.80 (s, 3H, $CH_2C_6H_4(OCH_3)$-3); 3.96 (t, 2H, J = 4.7 Hz, $CH_2CH_2OCH_3$); 4.87 (t, 2H, J= 4.7 Hz, $CH_2CH_2OCH_3$); 5.83 (s, 2H, $CH_2C_6H_4(OCH_3)$-3); 6.85-6.87, 7.03-7.11, 7.25-7.29, 7.51-7.59 and 7.82-7.84 (m, 8H, arom. C*H*s, NC_6H_4N and $CH_2C_6H_4(OCH_3)$-3); 11.60 (s, 1H, NC*H*N) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 ^{o}C): δ = 47.8 ($CH_2CH_2OCH_3$); 51.4 ($CH_2C_6H_4(OCH_3)$-3); 55.6 ($CH_2C_6H_4(OCH_3)$-3); 59.09 ($CH_2CH_2OCH_3$); 70.44 ($CH_2CH_2OCH_3$); 113.4, 113.8, 114.1, 114.8, 120.3, 126.9, 130.3, 131.0, 132.3, 134.2, 160.2 (arom. *C*s, NC_6H_4N and $CH_2C_6H_4(OCH_3)$-3); 143.8 (N*C*HN) ppm. Elemental analysis calcd (%) for $C_{18}H_{21}ClN_2O_2$ (Mr = 332.13 g. mol^{-1}): C 64.96, H 6.36, N 8.42; found (%): C 64.98, H 6.39, N 8.43.

*4.2.4. 1-(3-Methoxybenzyl)-3-(benzyl)benzimidazolium Chloride (**1d**)*

This benzimidazolium chloride was synthesized according to published procedure.[16c]

*4.2.5.1-(3-Methoxybenzyl)-3-(4-tert-butylbenzyl)benzimidazolium Chloride (**1e**)*

(1.57 g, yield 89%) ^{1}H NMR (300 MHz, $CDCl_3$, 25 ^{o}C): δ = 1.20 (s, 9H, $CH_2C_6H_4(C(CH_3)_3)$-4); 3.74 (s, 3H, $CH_2C_6H_4(OCH_3)$-3); 5.75 (s, 2H, $CH_2C_6H_4(C(CH_3)_3)$-4); 5.78 (s, 2H, $CH_2C_6H_4(OCH_3)$-3); 6.78-6.82, 6.96-7.03 and 7.20-7.54 (m, 12H, arom. C*H*s, NC_6H_4N, $CH_2C_6H_4(OCH_3)$-3 and $CH_2C_6H_4(C(CH_3)_3)$-4); 12.00 (s, 1H, NC*H*N) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 ^{o}C): δ = 31.1 ($CH_2C_6H_4(C(CH_3)_3)$-4); 34.6 ($CH_2C_6H_4(C(CH_3)_3)$-4); 51.3 $CH_2C_6H_4(C(CH_3)_3)$-4); 51.5 ($CH_2C_6H_4(OCH_3)$-3); 55.6 ($CH_2C_6H_4(OCH_3)$-3); 113.7, 114.9, 120.3, 126.3, 127.0, 128.0, 129.6, 130.4, 131.4, 134.1, 152.4, 160.2 (arom. *C*s, NC_6H_4N, $CH_2C_6H_4(OCH_3)$-3 and $CH_2C_6H_4(C(CH_3)_3)$-4); 143.8 (N*C*HN) ppm. Elemental analysis calcd (%) for $C_{26}H_{29}ClN_2O$ (Mr = 420.20 g. mol^{-1}): C 74.18, H 6.94, N 6.65; found (%): C 74.20, H 6.95, N 6.67.

*4.2.6.1-(3-Methoxybenzyl)-3-(2,3,4,5,6-pentamethylbenzyl)-benzimidazolium Chloride (**1f**)*

(1.49 g, yield 82%) ^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C): δ = 2.25, 2.28 and 2.31 (s, 15H, $CH_2C_6(CH_3)_5$-2,3,4,5,6); 3.79 (s, 3H, $CH_2C_6H_4(OCH_3)$-3); 5.88 (s, 2H, $CH_2C_6(CH_3)_5$-2,3,4,5,6); 5.94 (s, 2H, $CH_2C_6H_4(OCH_3)$-3); 6.84-6.86, 6.96-6.98, 7.02-7.29 and 7.42-7.59 (m, 8H, arom. C*H*s, NC_6H_4N, $CH_2C_6H_4(OCH_3)$-3); 11.48 (s, 1H, NC*H*N) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 25 ^{o}C): δ = 17.0, 17.1 and 17.3 ($CH_2C_6(CH_3)_5$-2,3,4,5,6); 48.3($CH_2C_6(CH_3)_5$-2,3,4,5,6); 51.4 ($CH_2C_6H_4(OCH_3)$-3); 55.5 ($CH_2C_6H_4(OCH_3)$-3); 113.6, 113.7, 114.6, 120.1, 126.9, 127.0, 130.3, 131.5, 133.5, 133.9, 134.5, 137.3, 160.1 (arom. *C*s, NC_6H_4N, $CH_2C_6H_4(OCH_3)$-3 and $CH_2C_6(CH_3)_5$-2,3,4,5,6); 143.7 (N*C*HN) ppm. Elemental analysis calcd (%) for $C_{26}H_{29}ClN_2O$ (Mr = 421.00 g. mol^{-1}): C 74.18, H 6.94, N 6.65; found (%): C 74.20, H 6.95, N 6.67.Elemental analysis calcd (%) for

$C_{27}H_{31}ClN_2O$ (Mr = 434.21): C 74.55, H 7.18, N 6.44; found (%): C 74.57, H 7.19, N 6.45.

*4.3. General procedure for the preparation of PEPPSI-type palladium-NHC complexes (**2a-f**)*

Benzimidazolium chlorides (**1a-f**) (1.0 mmol) were converted, with moderated yields, into the PEPPSI-type palladium-NHC complexes (**2a-f**) by reaction with $PdCl_2$ (1.0 mmol) in refluxing pyridine in the presence of K_2CO_3 (5.0 mmol) as a base at 80 °C for 16 h. Volatiles were removed in vacuo, and the residue was washed with *n*-pentane (2×5 mL). The crude product was dissolved with CH_2Cl_2 then filtered through a pad of celite and silica gel (70-230 mesh) to remove the unreacted $PdCl_2$ and benzimidazolium chloride. Then, the crude complex was crystallized from CH_2Cl_2/*n*-pentane mixture (1:4, *v/v*) at room temperature and, completely dried under vacuum. All palladium complexes were isolated as air- and moisture-stable yellow solids and were isolated in 45-63 % yields.

*4.3.1. Dichloro-[1-(3-methoxybenzyl)-3-(methyl)benzimidazole-2-ylidene](pyridine)palladium(II), (**2a**)*

(0.317 g, yield 60%) ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 3.66 (s, 3H, $CH_2C_6H_4(OCH_3)$-3); 4.30 (s, 3H, CH_3); 6.04 (s, 2H, $CH_2C_6H_4(OCH_3)$-3); 7.02-7.04, 7.16-7.31 (m, 10H, arom. C*H*s, NC_6H_4N, $CH_2C_6H_4(OCH_3)$-3 and NC_5H_5); 7.67-7.71 and 8.97-9.00 (m, 3H, NC_5H_5). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 35.3 (CH_3); 53.5 ($CH_2C_6H_4(OCH_3)$-3); 55.6 ($CH_2C_6H_4(OCH_3)$-3);109.9, 111.4, 112.9, 114.8, 120.3, 129.7, 134.2, 135.5, 136.5, 138.0, 160.2. (arom. *C*s, NC_6H_4N and $CH_2C_6H_4(OCH_3)$-3); 123.2, 124.6, 152.5 (NC_5H_5)163.3 (Pd-$C_{carbene}$) ppm. Elemental analysis calcd (%) for $C_{21}H_{22}Cl_2N_3OPd$ (Mr = 508.02 g. mol^{-1}): C 49.48, H 8.24, N 4.35; found (%): C 49.50, H 8.25, N 4.36.

*4.3.2. Dichloro-[1-(3-methoxybenzyl)-3-(n-butyl)benzimidazol-2-ylidene](pyridine)palladium(II), (**2b**)*

(0.343 g, yield 63%) ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.03 (t, *J* = 7.3 Hz, 3H, $CH_2CH_2CH_2CH_3$); 1.53 (hext, *J* = 7.4 Hz, 4H, $CH_2CH_2CH_2CH_3$); 2.19 (pent, *J* = 7.4 Hz, 2H, $CH_2CH_2CH_2CH_3$); 3.67 (s, 3H, $CH_2C_6H_4(OCH_3)$-3); 4.80 (t, *J* = 7.4 Hz, 2H, $CH_2CH_2CH_2CH_3$); 6.06 (s, 2H, $CH_2C_6H_4(OCH_3)$-3); 7.03-7.31 (m, 10H, arom. C*H*s, NC_6H_4N, $CH_2C_6H_4(OCH_3)$-3 and NC_5H_5) ppm, 7.70 and 8.99 (m, 3H, C_5H_5). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 13.9 ($CH_2CH_2CH_2CH_3$); 20.4 ($CH_2CH_2CH_2CH_3$); 31.8 ($CH_2CH_2CH_2CH_3$); 48.7 ($CH_2CH_2CH_2CH_3$); 53.2 ($CH_2C_6H_4(OCH_3)$-3); 55.7 ($CH_2C_6H_4(OCH_3)$-3); 110.3, 111.6, 113.05, 114.7, 120.3, 120.4, 129.7, 134.4, 135.0, 136.6, 137.9, 160.2 (arom. *C*s, NC_6H_4N and $CH_2C_6H_4(OCH_3)$-3); 123.0, 124.6, 152.6 (NC_5H_5); 162.8 (Pd-$C_{carbene}$) ppm. Elemental analysis calcd (%) for $C_{24}H_{28}Cl_2N_3OPd$ (Mr = 550.06 g. mol^{-1}): C 52.24, H 5.11, N 7.61; found (%): C 52.25, H 5.13, N 7.62.

*4.3.3. Dichloro-[1-(3-methoxybenzyl)-3-(2-methoxyethyl)benzimidazol-2-ylidene](pyridine)palladium(II), (**2c**)*

(0.264 g, yield 53%) ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 3.40 (s, 3H, $CH_2CH_2OCH_3$); 3.77 (s, 3H, $CH_2C_6H_4(OCH_3)$-3); 4.26 (*t*, 2H, *J*= 5.4 Hz, $CH_2CH_2OCH_3$); 5.10 (t, 2H, *J*= 5.3 Hz, $CH_2CH_2OCH_3$); 6.16 (s, 2H, $CH_2C_6H_4(OCH_3)$-3); 6.88-6.90, 7.11-7.33 and 7.77-7.81(m, 8H, arom. C*H*s, NC_6H_4N and $CH_2C_6H_4(OCH_3)$-3); 7.36-7.39, 7.58-7.60 and 9.07-9.09 (m, 3H, NC_5H_5) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 47.8 ($CH_2CH_2OCH_3$); 53.7 ($CH_2C_6H_4(OCH_3)$-3); 55.6 ($CH_2C_6H_4(OCH_3)$-3); 59.1 ($CH_2CH_2OCH_3$); 71.3 ($CH_2CH_2OCH_3$); 111.2, 111.5, 113.0, 114.7, 120.3, 129.7, 134.2, 136.5, 138.0, 160.2 (arom. *C*s, NC_6H_4N and $CH_2C_6H_4(OCH_3)$-3); 123.1, 124.6, 152.6 (NC_5H_5); 163.2 (Pd-$C_{carbene}$) ppm. Elemental analysis calcd (%) for $C_{23}H_{26}Cl_2N_3O_2Pd$ (Mr = 552.04 g. mol^{-1}): C 49.88, H 4.73, N 7.59; found (%): C 49.89, H 4.75, N 7.60.

*4.3.4. Dichloro-[1-(3-methoxybenzyl)-3-(benzyl)benzimidazol-2-ylidene](pyridine)palladium(II) (**2d**)*

(0.264 g, yield 55%) ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 3.76 (s, 3H, $CH_2C_6H_4(OCH_3)$-4); 6.19 (s, 2H, $CH_2C_6H_4(OCH_3)$-3); 6.22 (s, 2H, $CH_2C_6H_5$); 6.88-7.37 (m, 10H, arom. C*H*s, NC_6H_4N, $CH_2C_6H_4(OCH_3)$-3 and $CH_2C_6H_5$); 7.60-7.62, 7.71-7.75 and 9.02-9.03 (m, 3H, NC_5H_5) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 53.7 ($CH_2C_6H_4(OCH_3)$-3 and $CH_2C_5H_5$); 55.6 ($CH_2C_6H_4(OCH_3)$-3); 111.4, 113.0, 114.7, 128.1, 128.2, 128.8, 129.7, 134.7, 134.9, 136.5, 137.9, 154.3, 160.2 (arom. *C*s, NC_6H_4N, $CH_2C_6H_4(OCH_3)$-3 and $CH_2C_6H_5$); 123.1, 124.5, 152.6 (NC_5H_5); 164.3 (Pd-$C_{carbene}$) ppm. Elemental analysis calcd (%) for $C_{27}H_{26}Cl_2N_3OPd$ (Mr = 584.05 g. mol^{-1}): C 55.36, H 4.47, N 7.17; found (%): C 55.37, H 4.48, N 7.19.

*4.3.5.Dichloro-[1-(3-methoxybenzyl)-3-(4-tert-butyl)benzimidazol-2-ylidene](pyridine)palladium(II) (**2e**)*

(0.233 g, yield 51%) ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.29 (s, 9H, $CH_2C_6H_4(C(CH_3)_3)$-4); 3.76 (s, 3H, $CH_2C_6H_4(OCH_3)$-3); 6.26 (s, 4H, $CH_2C_6H_4(C(CH_3)_3)$-4 and $CH_2C_6H_4(OCH_3)$-3); 7.06-7.39 (m, 12H, arom. C*H*s, NC_6H_4N, $CH_2C_6H_4(OCH_3)$-3 and $CH_2C_6H_4(C(CH_3)_3)$-4); 7.56-7.58, 7.73-7.75 and 9.00-9.03 (m, 5H, NC_5H_5) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 31.3 ($CH_2C_6H_4(C(CH_3)_3)$-4); 34.5 ($CH_2C_6H_4(C(CH_3)_3)$-4); 52.9 ($CH_2C_6H_4(C(CH_3)_3)$-4); 53.1 ($CH_2C_6H_4(OCH_3)$-3); 55.6 ($CH_2C_6H_4(OCH_3)$-3); 111.3, 111.5, 112.9, 114.6, 120.2, 125.8, 127.7, 129.7, 132.0, 134.5, 136.7, 138.1, 152.0, 160.2 (arom. *C*s, NC_6H_4N, $CH_2C_6H_4(OCH_3)$-3 and $CH_2C_6H_4(C(CH_3)_3)$-4); 123.2, 124.4, 151.2 (NC_5H_5); 164.5 (Pd-$C_{carbene}$) ppm. Elemental analysis calcd (%) for $C_{31}H_{34}Cl_2N_3OPd$ (Mr = 640.11 g. mol^{-1}): C 58.00, H 5.34, N 6.55; found (%): C 58.01, H 5.35, N 6.56.

*4.3.6. Dichloro-[1-(3-methoxybenzyl)-3-(2,3,4,5,6-pentamethylbenzyl)benzimidazol-2-ylidene](pyridine)palladium(II) (**2f**)*

(0.203 g, yield 45%) ^{1}H NMR (00 MHz, $CDCl_3$, 25 °C): δ = 2.33, 2.34 and 2.36 (s, 15H, $CH_2C_6(CH_3)_5$-2,3,4,5,6); 3.79 (s, 3H, $CH_2C_6H_4(OCH_3)$-3); 6.25 (s, 2H, $CH_2C_6(CH_3)_5$-2,3,4,5,6); 6.35 (s, 2H, $CH_2C_6H_4(OCH_3)$-3); 6.88-7.38 (m, 8H, arom. C*H*s, NC_6H_4N, $CH_2C_6H_4(OCH_3)$-3); 7.35-7.40, 7.76-7.82 and 8.98-9.01 (m, 5H, NC_5H_5) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ

= 16.9, 17.3 and 17.5 ($CH_2C_6(CH_3)_5$-2,3,4,5,6); 51.3 ($CH_2C_6(CH_3)_5$-2,3,4,5,6); 53.2 ($CH_2C_6H_4(OCH_3)$-3); 55.5 ($CH_2C_6H_4(OCH_3)$-3); 111.1, 111.6, 113.0, 114.5, 119.6, 120.2, 122.7, 127.8, 129.7, 133.1, 134.3, 134.5, 135.1, 135.9, 136.8, 138.0, 160.1 (arom. *C*s, NC_6H_4N, $CH_2C_6H_4(OCH_3)$-3 and $CH_2C_6(CH_3)_5$-2,3,4,5,6); 123.1, 124.4, 151.2 (NC_5H_5); 164.1 (Pd-$C_{carbene}$) ppm. Elemental analysis calcd (%) for $C_{32}H_{36}Cl_2N_3OPd$ (Mr = 654.13 g. mol^{-1}): C 58.59, H 5.53, N 6.41; found (%): C 58.60, H 5.54, N 6.43.

4.4. General procedure for Suzuki-Miyaura cross-coupling reaction

Phenylboronic acid (1.5 mmol), aryl chloride (1.0 mmol), K_2CO_3 (2.0 mmol), PEPPSI-type palladium-NHC catalyst (0.01 mmol, 1 mol%) (**2a-f**) and mixture of isopropanol/water (1:3; *v/v*) (4 mL) were added to a small raund bottom flask in air. The mixture was stirred at 50 ° C for 2 h. At the end of the reaction, the cooled solution to room temperature was extracted with a mixture of EtOAc/*n*-hexane (1:5, *v/v*). The organic phase was separated and dried over anhydrous $MgSO_4$, the solution passed through the micro silica gel column was concentrated. Product characterizations were performed by GC. The reaction yields were determined by GC based on aryl chloride.

Appendix A. Supplementary data

Supplementary data related to this article can be found at https://

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- A series of new benzimidazolium chlorides (**1a-f**) as *N*-heterocyclic carbene (NHC) ligand precursors and their corresponding new PEPPSI-type palladium-NHC complexes (**2a-f**) were synthesized.

- The all new compounds were fully characterized by analytical and spectral methods.

- PEPPSI-type palladium-NHC complexes were tested as promising catalyst in the synthesis of biaryls using Suzuki-Miyaura cross-coupling reaction between the phenylboronic acid and aryl halides.