

Synthesis and catalytic activity of ionic palladium *N*-heterocyclic carbene complexes

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Abstract: The synthesis of 3 benzimidazole-based ionic Pd(II)-NHC complexes (NHC: *N*-heterocyclic carbene) is presented. The structures of the complexes are as follows: $[\text{NHC-PdBr}_3]^- [\text{NHC}]^+$. The ionic palladium(II)-NHC complexes were synthesized in high yields and were fully characterized by nuclear magnetic resonance spectroscopy, X-ray diffraction, LC-MS/MS, and elemental analysis. These complexes have been identified as active catalysts in Suzuki–Miyaura reactions in a solution of 2-propanol and water at room temperature for different aryl bromides.

Key words: Ionic palladium complex, *N*-heterocyclic carbene, C-C bond formation, anionic palladium species, Suzuki–Miyaura cross-coupling reactions

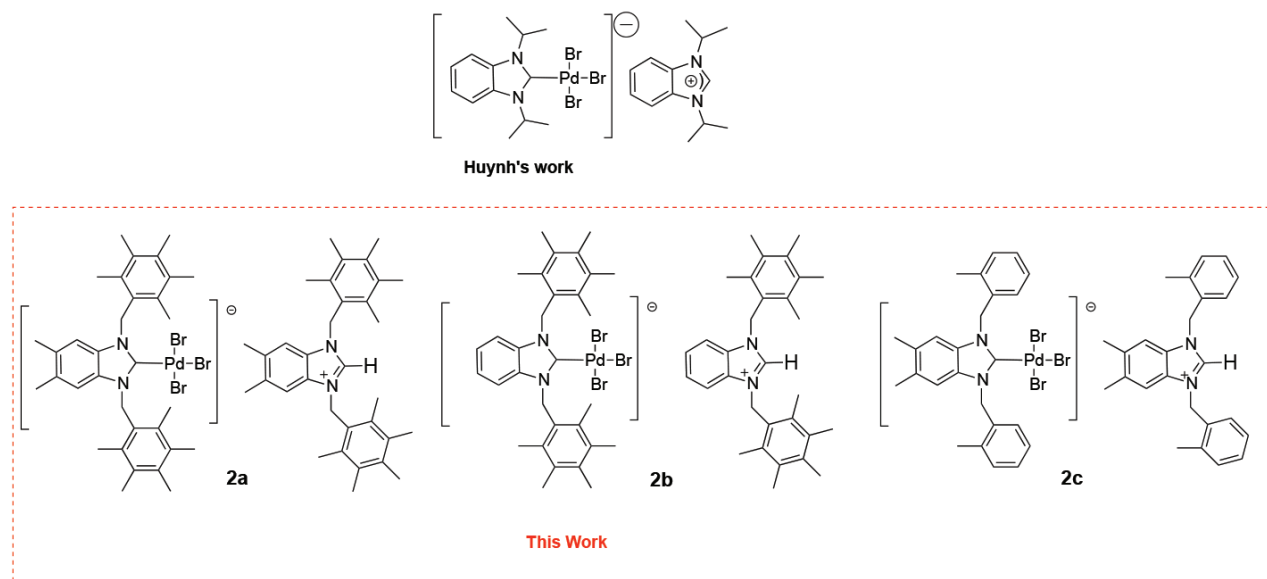
1. Introduction

C-C bond formation reactions are the most useful reactions for the synthesis of very important unsymmetrical biaryls in academic and industrial applications [1–4]. To achieve maximum benefit in C-C bond formation reactions, many different types of ligands [5–11], as well as ligand-free catalytic systems [12], have been investigated. When the history of the Suzuki–Miyaura [13] coupling reaction was examined in detail, it was seen that phosphine-based ligands were commonly used [14]. Recently, the disadvantages of phosphine-based ligands, such as toxicity and sensitivity to air and moisture, have led to the development of phosphine-free catalytic systems in Suzuki–Miyaura cross-coupling reactions [15]. Since Arduengo isolated the first free NHC, imidazole, imidazolidine, and benzimidazole-based Pd-NHC complexes have been reported and applied successfully as a catalyst in Suzuki–Miyaura cross-coupling reactions [16,17].

In 2006, Huynh et al. reported the first example of a benzimidazole-based NHC-stabilized tribromo palladium complex, containing an NHC-Pd(II)Br₃ as an anion and a corresponding benzimidazolium as a cation [18] (Scheme 1). A similar triiodo complex was reported by Herrmann et al. [19].

As additive, quaternary ammonium salts are often used in Heck-type C-C bond formation reactions [20,21]. It is believed that these salts help to stabilize or maintain stable active species via the coordination or formation of ion pairs [18,21]. Thus, the synthesis and investigation of catalytic activity of ionic type Pd(II)-NHC complexes may be interesting and nice to compare with the catalytic activity of Pd(II)-NHC on Suzuki–Miyaura reactions [22–24]. Our earlier investigations showed that neutral PdX₂(NHC)₂, PdX₂(NHC)pyridine

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Scheme 1. Our new ionic palladium complexes and those of Huynh.

complexes, which bear the same NHC ligands as the ionic Pd(II)-NHC complexes, are very active catalysts for Suzuki–Miyaura reactions.

Taking these studies into account, we present the synthesis and catalytic activity of ionic palladium(II) complexes in Suzuki–Miyaura reactions of aryl bromides.

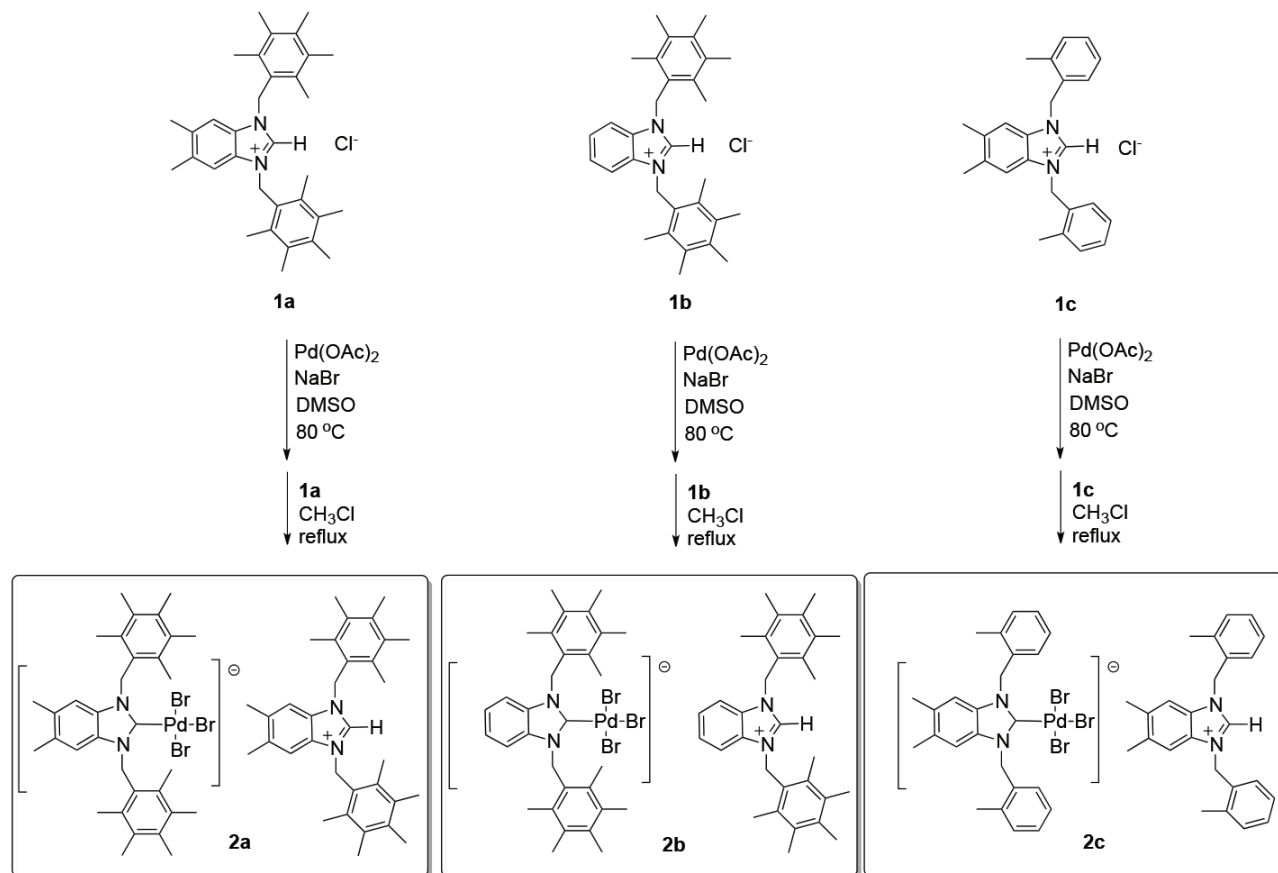
2. Materials and methods

All reactions were carried out under normal atmospheric conditions. Pd(OAc)₂ was purchased from Alfa-Easer (Tewksbury, MA, USA) and used without any purification. Elemental analyses were performed using the ElementarVario EL III Carlo Erba 1108 (Elemental Microanalysis Ltd., Okehampton Devon, UK). The ¹H and ¹³C nuclear magnetic resonance (NMR) spectra were recorded in CDCl₃ or DMSO-d₆ solutions operating on a Bruker Avance III HD 300 and 400 MHz NMR spectrometer (Billerica, MA, USA); chemical shifts were reported relative to tetramethylsilane for ¹H and ¹³C NMR spectra as the standard. Signals were quoted in parts per million as δ downfield from tetramethylsilane (δ 0.00) as an internal standard. Coupling constants (*J* values) were given in Hertz. NMR multiplicities were abbreviated as follows: singlet (s), doublet (d), doublet of doublet (dd), triplet (t), and multiplet (m) signals. The LC-MS/MS (ESI) electrospray ionization mass spectra were recorded on an Agilent LC-MS/MS spectrometer (Santa Clara, CA, USA) in CH₃OH. The solvent ratio was given as v/v.

3. Results

In homogeneous catalysis systems, the solubility of catalysts and reagents in aqueous media is an important parameter for the efficiency of the reaction. In this manner, to increase the solubility of catalyst precursors in aqueous media, our strategy was based on the synthesis of ionic Pd(II)-NHC complexes (Scheme 1). With this aim, we chose symmetrical 1,3-bisalkylbenzimidazolium precursors (**1a–1c**), which were previously used in the synthesis of neutral Pd-NHC complexes [22–24]. These results may provide knowledge about the catalytic activities of neutral and ionic Pd-NHC complexes, which bear the same NHC ligands.

A general method for the synthesis of ionic Pd(II)-NHC includes the reaction of 1 equiv. of Pd(OAc)₂ with 1 equiv. of NHC salts and 5 equiv. of NaBr in DMSO; this produces the corresponding ionic Pd(II)-N-heterocyclic carbene complex. A similar synthetic method for the synthesis of ionic palladium(II)-NHC complexes was reported by Huynh [18]. With this method, the ionic palladium(II)-NHC complexes were obtained in high yields of 80%–90% (Scheme 2).



Scheme 2. Synthesis method for the NHC-stabilized ionic palladium(II)-NHC complexes **2a–2c**.

Due to the formation of black palladium, the quantity of Pd(OAc)₂ decreases in reaction media and the excess amounts of NHC ligands in the reaction medium cause cleavage of the dimeric palladium complex, forming the ionic palladium complex. In our case, this reaction was carried out in normal DMSO under aerobic reaction conditions without a significant loss of yield. Ionic Pd(II)-NHC complexes were isolated as an orange-yellow solid that was soluble in the polar solvent. The formation of ionic Pd(II)-NHC complexes was confirmed by ¹H NMR spectroscopy, which showed the existence of the NCHN proton on the benzimidazolium cation. Furthermore, a significant downfield shift signal of the coordinated NCN carbon of NHC ligands to palladium metal and a slight downfield shift signal of NCHN emerging in one ¹³C NMR spectrum confirmed the formation of ionic palladium complexes. The formation of 3 ionic Pd(II)-NHC complexes (**2a–2c**) was supported by LC-MSMS (ESI) spectroscopy in negative mode, which showed an isotopic envelope centered at $m/z = 813.8$, $m/z = 1226.0$, and $m/z = 902.9$, respectively, corresponding to the ionic complexes.

The ORTEP-3 view of **2a** with the atom-labelling scheme is shown in Figure, while important bond lengths and angles are listed in Table 1. The compound crystallized as salt and its asymmetric unit contained a discrete complex anion and a benzimidazolium cation. The ionic complex consisted of a 5,6-dimethyl-1,3-bis(2,3,4,5,6-pentamethylbenzyl)-2,3-dihydro-1*H*-benzo[*d*]imidazole with a Pd metal center and 3 bromide ligands. The coordination around the Pd was a distorted square-planar with angles between adjacent ligands ranging from 86.32(15)° to 95.00(3)°. The 2 *trans* angles also deviated from the ideal value of 180°, being 171.34(3)° for Br1|Pd1|Br3 and 176.22(15)° for Br2|Pd1|C1. The 4-coordinate geometry index for the complex, τ_4 [25], was 0.09 (where 0 would be perfectly square-planar, and 1 was perfectly tetrahedral).

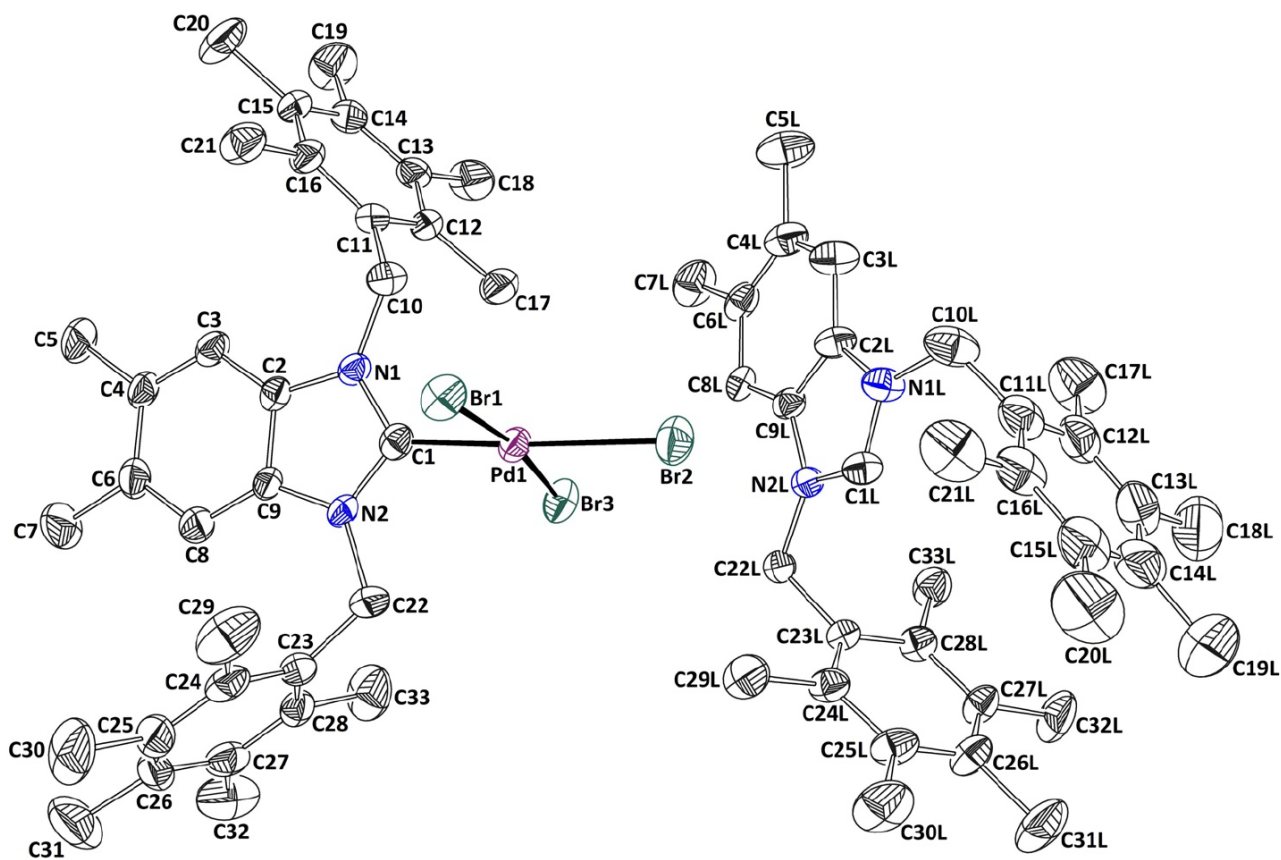


Figure 1. View of **2a** showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms have been omitted for clarity.

The Pd|C bond length amounted to 1.943(5) Å; this length is characteristic for Pd-NHC complexes [18,26]. Among the 3 Pd|Br bonds in the complex, the Pd|Br bond *trans* to the carbene ligand was notably longer than the others due to the *trans* influence of the carbene, which had strong σ -donating and weak π -acceptor ability; these data were consistent with those in the literature [18]. The carbene ring plane was oriented almost perpendicular to the PdBr₃ coordination plane with a dihedral angle of 79.23(13)°, which is typical for NHC complexes to minimize steric hindrance [27]. Compared to the benzimidazolium cation, the $C_{\text{carbene}}|N1/N2$ bond lengths had increased, which was accompanied by a decrease in the N|C|N angle at 4.8°. Furthermore, the C1|N1|C10 and C1|N2|C22 angles contracted, while the C1|N1|C2 and C1|N2|C9 angles

Table 1. Selected geometric parameters for **2a**.

Parameters	[NHCPdBr ₃] ⁻	X ⁺	Parameters	[NHCPdBr ₃] ⁻	X ⁺
Bond lengths (Å)					
<i>Pd1 Br1</i>	2.4410(8)	–	<i>N1 C2</i>	1.392(6)	1.394(6)
<i>Pd1 Br2</i>	2.4975(8)	–	<i>N1 C10</i>	1.482(6)	1.474(7)
<i>Pd1 Br3</i>	2.4429(8)	–	<i>N2 C1</i>	1.341(6)	1.317(7)
<i>Pd1 C1</i>	1.943(5)	–	<i>N2 C9</i>	1.409(6)	1.390(6)
<i>N1 C1</i>	1.363(6)	1.320(6)	<i>N2 C22</i>	1.483(6)	1.464(6)
Bond angles (°)					
<i>Br1 Pd1 Br2</i>	95.00(3)	–	<i>C1 N1 C2</i>	109.7(4)	107.0(5)
<i>Br1 Pd1 Br3</i>	171.34(3)	–	<i>C1 N1 C10</i>	122.2(4)	124.9(5)
<i>Br2 Pd1 Br3</i>	92.19(3)	–	<i>C2 N1 C10</i>	127.4(4)	128.0(5)
<i>Br1 Pd1 C1</i>	86.79(15)	–	<i>C1 N2 C9</i>	110.6(4)	107.2(4)
<i>Br2 Pd1 C1</i>	176.22(15)	–	<i>C1 N2 C22</i>	120.7(4)	123.7(4)
<i>Br3 Pd1 C1</i>	86.32(15)	–	<i>C9 N2 C22</i>	128.7(5)	129.0(4)
<i>N1 C1 N2</i>	107.0(4)	111.8(5)			

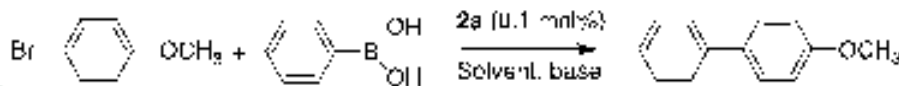
X: Corresponding benzimidazolium cation

expanded. Other parameters remained almost unchanged. In the ionic complex, the NHC ring made dihedral angles of 79.24(17) and 87.52(16)° with the pentamethyl benzene rings. In the case of the benzimidazolium cation, the corresponding dihedral angles were 81.0(2) and 85.94(17)°, respectively. In order to perform a better comparison, we presented the crystallographic data obtained in Tables 1 and S2.

3.1. Catalysis

In preliminary studies [17,24], the Pd-PEPPSI complexes of NHC ligands used in this study were tested for the Suzuki–Miyaura reaction of aryl halides. The reaction of 4-bromoanisole with phenylboronic acid was chosen as a model reaction with which to compare our preliminary study with the published works on the Suzuki–Miyaura reaction of aryl bromides [17,24]. The reaction conditions were optimized using complex **2a**. The results summarized in Table 2 indicated good catalytic activity of **2a** in 2-propanol and water (1:2 v/v), in the presence of K₂CO₃ under aerobic conditions at room temperature with low catalyst loading (0.1 mol%), giving virtually quantitative asymmetric-symmetric biaryl products. This catalysis system was especially important, since coupling reactions in aqueous media usually require harsh reaction conditions, such as a higher temperature, strong base, or higher catalyst loading [28–30]. This catalysis system was free of such harsh reaction conditions. On the other hand, low yield with different types of bases, such as Na₂CO₃, KO^tBu, KOH, K₃PO₄, and Cs₂CO₃, were also observed (Table 2, entries 1–5). Furthermore, the use of pure *i*-PrOH, H₂O, DMF, and EtOH with K₂CO₃ resulted in poor yields (Table 2, entries 12–17).

With the optimized reaction conditions in hand, the substrate scope was investigated. We focused on the coupling of electronically and sterically different types of aryl bromides with different phenylboronic acids. Different types of aryl bromides, such as electron-withdrawing and electron-donating functional groups, and phenylboronic acids, were tolerated very well by this catalysis system (Table 3, entries 2, 5, and 6). Electron-

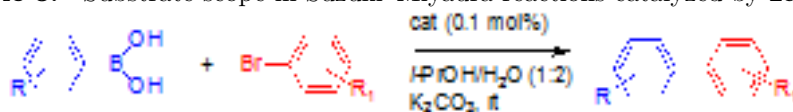
Table 2. Optimization of the reaction conditions ^a.

^a Entry	Solvent	Base	Yield (%) ^b
1	<i>i</i> -PrOH/H ₂ O(1:2, v/v)	K ₂ CO ₃	74
2	<i>i</i> -PrOH/H ₂ O(1:2, v/v)	Na ₂ CO ₃	49
3	<i>i</i> -PrOH/H ₂ O(1:2, v/v)	CS ₂ CO ₃	28
4	<i>i</i> -PrOH/H ₂ O(1:2, v/v)	K ₃ PO ₄	53
5	<i>i</i> -PrOH/H ₂ O(1:2, v/v)	KOH	39
6	<i>i</i> -PrOH/H ₂ O(1:1, v/v)	K ₂ CO ₃	68
7	DMF/H ₂ O(1:2, v/v)	K ₂ CO ₃	36
8	EtOH/H ₂ O(1:2, v/v)	K ₂ CO ₃	60
9	MeOH/H ₂ O(1:2, v/v)	K ₂ CO ₃	49
10	<i>i</i> -PrOH/H ₂ O(1:3, v/v)	K ₂ CO ₃	70
11	<i>i</i> -PrOH/H ₂ O(1:4, v/v)	K ₂ CO ₃	58
12	<i>i</i> -PrOH	K ₂ CO ₃	50
13	H ₂ O	K ₂ CO ₃	5
14	DMF	K ₂ CO ₃	23
15	EtOH	K ₂ CO ₃	53
16	MeOH	K ₂ CO ₃	42
17	Acetone	K ₂ CO ₃	45

^aReaction condition: 1 mmol of 4-bromoanisole, 1.0 mmol of phenylboronic acid, 1 mmol of base, 0.1 mol% **2a**, 3 mL of solvent, room temperature, 0.5 h. GC yields are the average of the 2 runs.

^bYield was determined by GC with use of undecane as the internal standard.

withdrawing substrates were converted into the product in 1 min with high TOF values of 59,400 mol h⁻¹, 57,831 mol h⁻¹, and 56,024 mol h⁻¹, respectively, for **2a–2c**. On the other hand, 4-phenoxyboronic acid was converted to the coupled product in very high yields, regardless of their electronic and steric situation (Table 3, entries 7–11). Aryl bromides with steric hindrance required long reaction times to produce high yields (Table 3, entries 12 and 14).

Table 3. ^aSubstrate scope in Suzuki–Miyaura reactions catalyzed by **2a–2c**.

Entry	Product	Cat/ %Yield ^b						
		2a	2b	2c	Time	2a	2b	2c TOF (mol h ⁻¹)
1		94	87	96	1 h	940	870	960

Table 3. continued


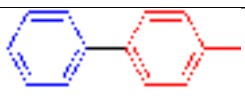
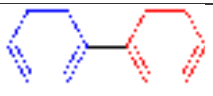

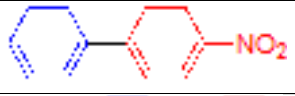
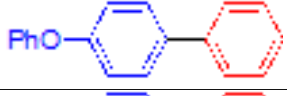
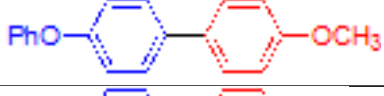
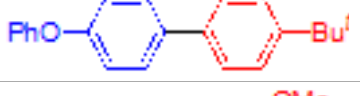
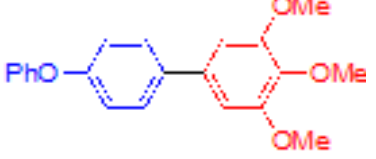
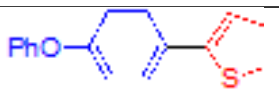
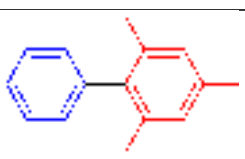
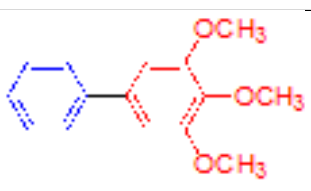
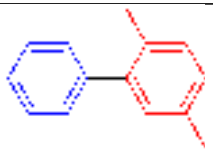

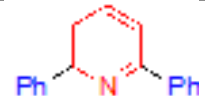
2		99	99	99	1 min	59400	59400	59400
3		77	67	73	1 h	770	670	730
4		80	81	89	1 h	800	810	890
5		94	96	95	1 min	56626	57831	57022
6		90	91	93	1 min	54021	54819	56024
7		98	95	96	2 min	29402	28528	28802
8		94	93	94	2 min	28228	27902	28202
9		30	45	23	12 h	25	37	19
10		95	88	85	6 h	158	146	141
11		37	30	35	6 h	61	50	58
12		15	11	12	12 h	12	9	10
13		86	88	84	12 h	71	73	70
14		55	45	52	12 h	45	37	43
15 ^c		99	99	99	10 min	5940	5940	5940

Table 3. continued

16 ^c		95	90	99	4 h	237	225	247
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^aReaction condition: 0.1 mol% [Cat.], 1 mmol substrate, 1.0 mmol phenylboronic acid, 1.0 mmol K₂CO₃, at room temperature.

Yields are based on aryl bromides after the average of 2 runs.

^bYield was determined by GC with use of undecane as the internal standard.

^c 2.0 mmol K₂CO₃.

When we compared the preliminary studies [17,18,24] with the current results, it can be seen that the present study was more effective than the preliminary studies in many respects. However, it remains unclear why the reaction times for the couplings of some aryl bromides were so different (Table 3, entries 9–14).

3.2. Synthesis

3.2.1. Synthesis of NHC precursors 1a–1c.

NHC precursors **1a–1c** were synthesized according to the published procedure [22–24].

3.2.2. Synthesis of ionic Pd(II)-NHC complexes 2a–2c.

Ionic Pd(II)-NHC complexes **2a–2c** were synthesized according to the published procedure [18].

3.2.3. 1,3-Bis-(2,3,4,5,6-pentamethylbenzyl)-5,6-dimethylbenzimidazolium tribromo-(1,3-bis-(2,3,4,5,6-pentamethylbenzyl)-5,6-dimethylbenzimidazole-2-ylidene)palladate(II), (2a):

¹H NMR (400 MHz, CDCl₃, signals from the counter-cation are marked with an asterisk*): δ 9.23 (s, 1H, NCH*N), 7.06 (s, 2H, ArH*), 6.17, 6.09, 5.96, 5.89, 5.49 (bs, 10H, ArH, CH₂*-Ar, CH₂-Ar), 2.24–2.10 (m, 72H, Ar-CH₃*, Ar-CH₃). ¹³C{¹H} NMR (100 MHz, CDCl₃): 166.7 (s, NCN), 140.6 (s, NC*HN), 136.8, 135.3, 134.8, 134.6, 134.5, 133.9, 133.7, 133.6, 133.5, 132.9, 132.4, 130.4, 129.8, 128.3, 125.6, 113.5, 111.5, 111.4 (Ar-C*, Ar-C), 52.4, 52.3, 52.1 (CH₂-Ar), 48.5 (CH₂*-Ar), 20.7, 20.2, 20.1, 17.9, 17.6, 17.4, 17.2, 17.1, 16.8 (Ar-CH₃*, Ar-CH₃). Anal. Calc for C₆₆H₈₅Br₃N₄Pd: C, 61.90; H, 6.69; N, 4.38. Found: C, 61.74; H, 6.73; N, 4.34. LC-MSMS (ESI): for C₃₃H₄₂Br₃N₂Pd found *m/z* = 813.8 (100%) [M+H], Calcd. 814.0

3.2.4. 1,3-Bis-(2,3,4,5,6-pentamethylbenzyl)benzimidazolium tribromo(1,3-bis-(2,3,4,5,6-pentamethylbenzyl)benzimidazole-2-ylidene)palladate(II), (2b):

¹H NMR (400 MHz, CDCl₃, signals from the counter-cation are marked with an asterisk*): δ 9.62 (s, 1H, NCH*N), 7.29 (dd, 2H, Ar-H*), 7.23 (dd, 2H, Ar-H*), 6.70, 6.48, 5.86 (m, 4H, Ar-H), 6.20 (m, 4H, CH₂*-Ar), 5.94 (bs, 4H, CH₂-Ar), 2.23–2.10 (m, 60H, Ar-CH₃*, Ar-CH₃). ¹³C{¹H} NMR (100 MHz, CDCl₃): 167.6 (s, NCN), 135.9 (s, NC*HN), 134.4, 134.2, 133.7, 132.7, 132.5, 131.5, 130.9, 126.9, 125.8, 124.4, 120.5, 113.0, 109.9 (Ar-C*, Ar-C), 54.4, 51.7, (CH₂-Ar), 48.5 (CH₂*-Ar), 16.6, 16.2, 15.9, 15.8 (Ar-CH₃*, Ar-CH₃). Anal. Calc for C₆₂H₇₇Br₃N₄Pd: C, 60.82; H, 6.34; N, 4.58. Found: C, 60.88; H, 6.38; N, 4.30. LC-MSMS (ESI) for C₆₂H₇₇Br₃N₄Pd found *m/z* = 1226.0 [M+2H], Calcd. 1226.3; LC-MSMS (ESI) for C₃₁H₃₈Br₃N₂Pd found *m/z* = 785.6 (100%) [M], Calcd. 785.0

3.2.5. 1,3-Bis-(2-methylbenzyl)-5,6-dimethylbenzimidazolium tribromo(1,3-bis-(2-methylbenzyl)-5,6-dimethylbenzimidazole-2-ylidene)palladate(II), (2c):

^1H NMR (400 MHz, CDCl_3 , signals from the counter-cation are marked with an asterisk*): δ 10.85 (s, 1H, $\text{NC}^*\text{H}^*\text{N}$), 7.17–6.94 and 6.45 (m, 20H, $\text{Ar}-\text{H}^*$ and $\text{Ar}-\text{H}$), 6.16–6.0 (m, 4H, $\text{CH}_2^*\text{-Ar}$), 5.71 (bs, 4H, $\text{CH}_2\text{-Ar}$), 2.34, 2.32, 2.26, 2.19, 2.02 (bs, 24H, $\text{Ar}-\text{CH}_3^*$, $\text{Ar}-\text{CH}_3$). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): 165.6 (s, NCN), 143.4 (s, NC^*HN), 137.0, 136.5, 135.1, 133.4, 133.3, 133.2, 131.9, 131.8, 131.1, 130.1, 130.0, 128.9, 128.0, 127.9, 127.8, 127.3, 126.6, 126.3, 126.2, 113.4, 111.4 ($\text{Ar}-\text{C}^*$ and $\text{Ar}-\text{C}$), 50.6, 50.4 ($\text{CH}_2\text{-Ar}$), 49.9 ($\text{CH}_2^*\text{-Ar}$), 20.6, 20.1, 19.7, 19.6, 19.5 ($\text{Ar}-\text{CH}_3^*$, $\text{Ar}-\text{CH}_3$). Anal. Calc for $\text{C}_{50}\text{H}_{53}\text{Br}_3\text{N}_4\text{Pd}$: C, 56.86; H, 5.06; N, 5.30. Found: C, 56.91; H, 5.09; N, 5.23; LC-MSMS (ESI) for $\text{C}_{25}\text{H}_{26}\text{Br}_2\text{N}_2\text{Pd}$ found $m/z = 616.6$ (100%) [$\text{M}-\text{H}$], Calcd. 616.9

3.3. X-ray diffraction analysis

The intensity data of **2a** were collected on an STOE IPDS II diffractometer at room temperature using graphite-monochromated Mo $\text{K}\alpha$ radiation by applying the ω -scan method. Data collection and cell refinement were carried out using X-AREA [31], while data reduction was applied using X-RED32 [31]. The structure was solved by a dual-space algorithm using SHELXT-2014 [32] and refined with full-matrix least-squares calculations on F^2 using SHELXL-2018 [32] implemented in the WinGX [33] program suit. All carbon-bound H atoms were located in different electron-density maps. Next, they were treated as riding atoms in geometrically idealized positions, with $\text{C}|\text{H} = 0.93$ (aromatic), 0.97 (CH_2), and 0.96 Å (CH_3), and with $U_{iso}(\text{H}) = kU_{eq}(\text{C})$, where $k = 1.5$ for the methyl groups and 1.2 for all other H atoms. The molecular graphic was drawn using ORTEP-3 [33]. Crystal data, data collection, and structure refinement details are summarized in Table S1 in the Supplemental Information.

3.4. Suzuki–Miyaura cross-coupling reaction

In a typical run, in the air atmosphere, a reaction tube was charged with aryl halide (1.0 mmol), phenylboronic acid (1.0 mmol), ionic Pd-NHC complex (0.001 mmol), and K_2CO_3 (1 mmol). Solvent (2-propanol/ H_2O , 1:2 v/v) (3 mL) was added to tube and the mixture was vigorously stirred at room temperature for a specific time. After the desired reaction time, 5 mL of diethyl ether was added to the reaction mixture, and the organic phase was extracted with the appropriate volume of water and dried over MgSO_4 . Next, the organic phase (1 μL) was injected to GC. The reactions were monitored with a Shimadzu GC-2010 Plus (FID) (Kyoto, Japan). The results were the average of the 2 runs. The yields were determined by GC with use of undecane as the internal standard. All of the coupling products were previously reported. The turn over frequency (TOF) was calculated using the following equations: $\text{TOF} = \text{TON}/\text{time of reaction}$ and $\text{TON} = \text{moles of desired product formed}/\text{moles of the catalyst}$.

4. Discussion

This study showed that ionic palladium-*N*-heterocyclic carbene complexes **2a–2c** had high catalytic activity in the Suzuki–Miyaura cross-coupling reactions of various aryl bromides and boronic acids, which was characterized by a TOF of up to 10^5 h^{-1} in aqueous media at room temperature, in a very short time with low catalyst loading. We believe that the benzimidazolium cation on the ionic palladium complex contributed extra stability to the active palladium catalyst and led to better solubility in aqueous media. This structural difference resulted

in better activity than neutral Pd-NHC complexes [17,24]. Wide substrate tolerance, short reaction times, and moderate yields with easy reactions and work-up procedures rendered this catalytic system more attractive and economically viable.

Appendix A. Supplementary data

CCDC 1816638 contains the supplementary crystallographic data for **2a** (see Supplementary data). These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/data_request/cif, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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Supplemental Information

Table S1. Crystal data and structure refinement parameters for **2a**.

CCDC depository	1816638
Color/shape	Orange/prism
Chemical formula	$[\text{PdBr}_3(\text{C}_{33}\text{H}_{42}\text{N}_2)] \cdot (\text{C}_{33}\text{H}_{43}\text{N}_2)^+$
Formula weight	1280.51
Temperature (K)	296
Wavelength (Å)	0.71073 Mo $K\alpha$
Crystal system	Monoclinic
Space group	$P2_1/n$ (No. 14)
Unit cell parameters	
a, b, c (Å)	13.0856(7), 24.9258(9), 19.6128(10)
α, β, γ (°)	90, 103.349(4), 90
Volume (Å ³)	6224.2(5)
Z	4
$D_{calc.}$ (g/cm ³)	1.366
μ (mm ⁻¹)	2.265
Absorption correction	Integration
$T_{min.}, T_{max.}$	0.4015, 0.7976
F_{000}	2640
Crystal size (mm ³)	0.66 × 0.22 × 0.11
Diffractometer/measurement method	STOE IPDS II/rotation (ω scan)
Index ranges	$-15 \leq h \leq 16, -32 \leq k \leq 31, -25 \leq l \leq 25$
θ range for data collection (°)	$1.634 \leq \theta \leq 27.171$
Reflections collected	40895
Independent/observed reflections	13725/5770
$R_{int.}$	0.0998
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	13725/0/688
Goodness-of-fit on F^2	0.834
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0558, wR_2 = 0.0763$
R indices (all data)	$R_1 = 0.1666, wR_2 = 0.0983$
$\Delta\rho_{max.}, \Delta\rho_{min.}$ (e/Å ³)	0.42, -0.42,

Table S2. Comparison of the selected geometric parameters for **2a** and published reference.

Parameters	2a	Huynh's Comp. ^{[1] <i>makale</i>}
Bond lengths (Å)		
<i>Pd1 Br1</i>	2.4410(8)	2.4441(7)
<i>Pd1 Br2</i>	2.4975(8)	2.5042(7)
<i>Pd1 Br3</i>	2.4429(8)	2.4284(7)
<i>Pd1 C1</i>	1.943(5)	1.951(5)
<i>N1 C1</i>	1.363(6)	1.340(7)
Bond angles (°)		
<i>Br1 Pd1 Br2</i>	95.00(3)	94.01(2)
<i>Br1 Pd1 Br3</i>	171.34(3)	172.92(3)
<i>Br2 Pd1 Br3</i>	92.19(3)	93.06(3)
<i>Br1 Pd1 C1</i>	86.79(15)	87.83(14)
<i>Br2 Pd1 C1</i>	176.22(15)	178.02(15)
<i>Br3 Pd1 C1</i>	86.32(15)	85.11(14)
<i>N1 C1 N2</i>	107.0(4)	109.2(4)

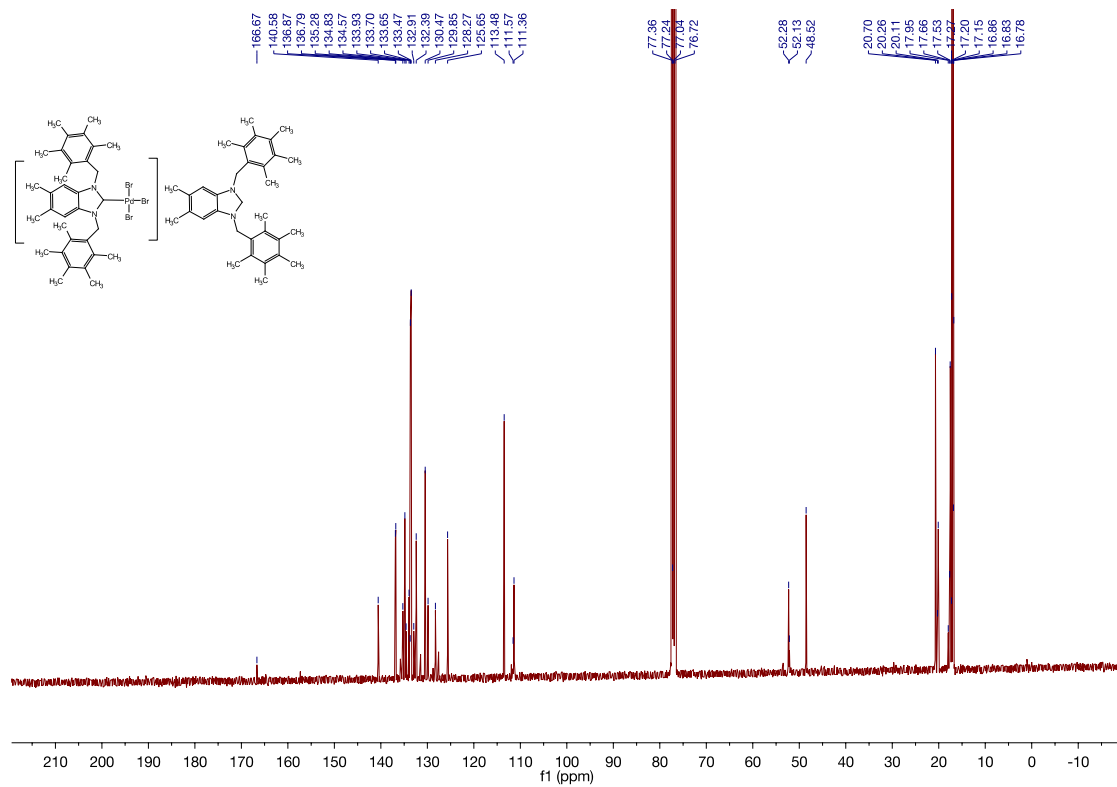
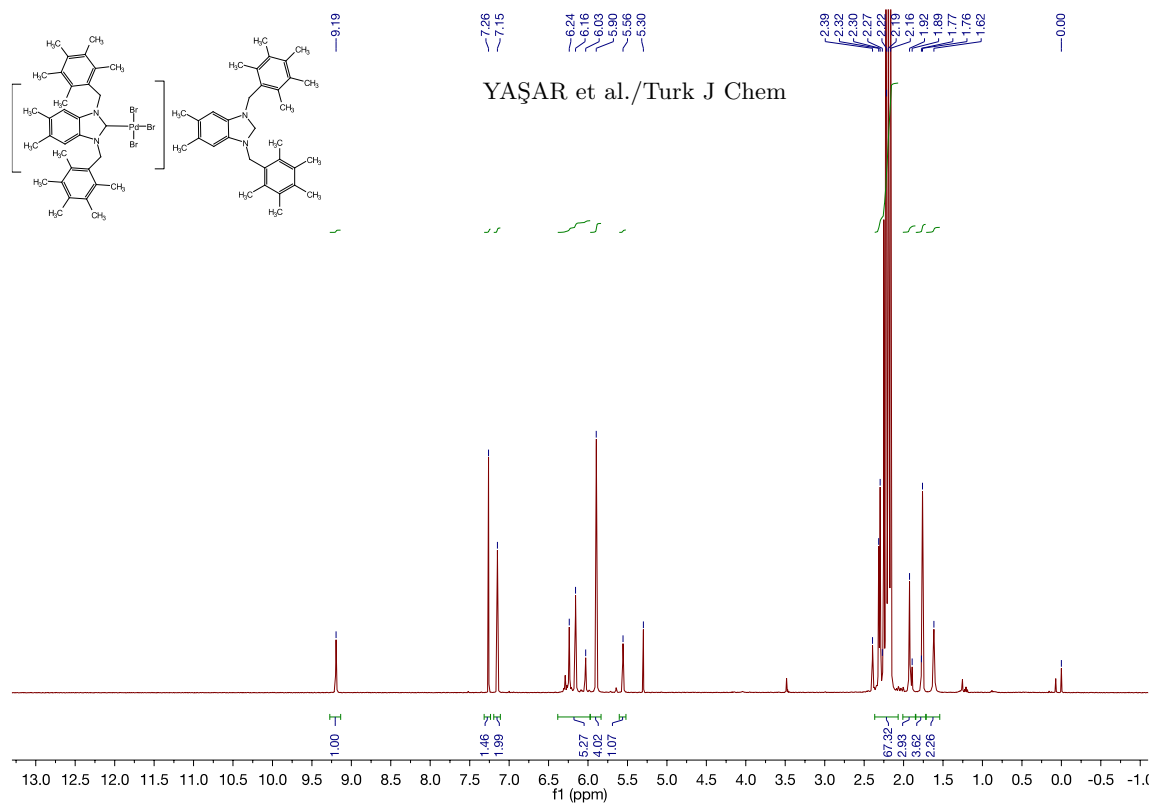


Figure S1. NMR spectra of **2a**

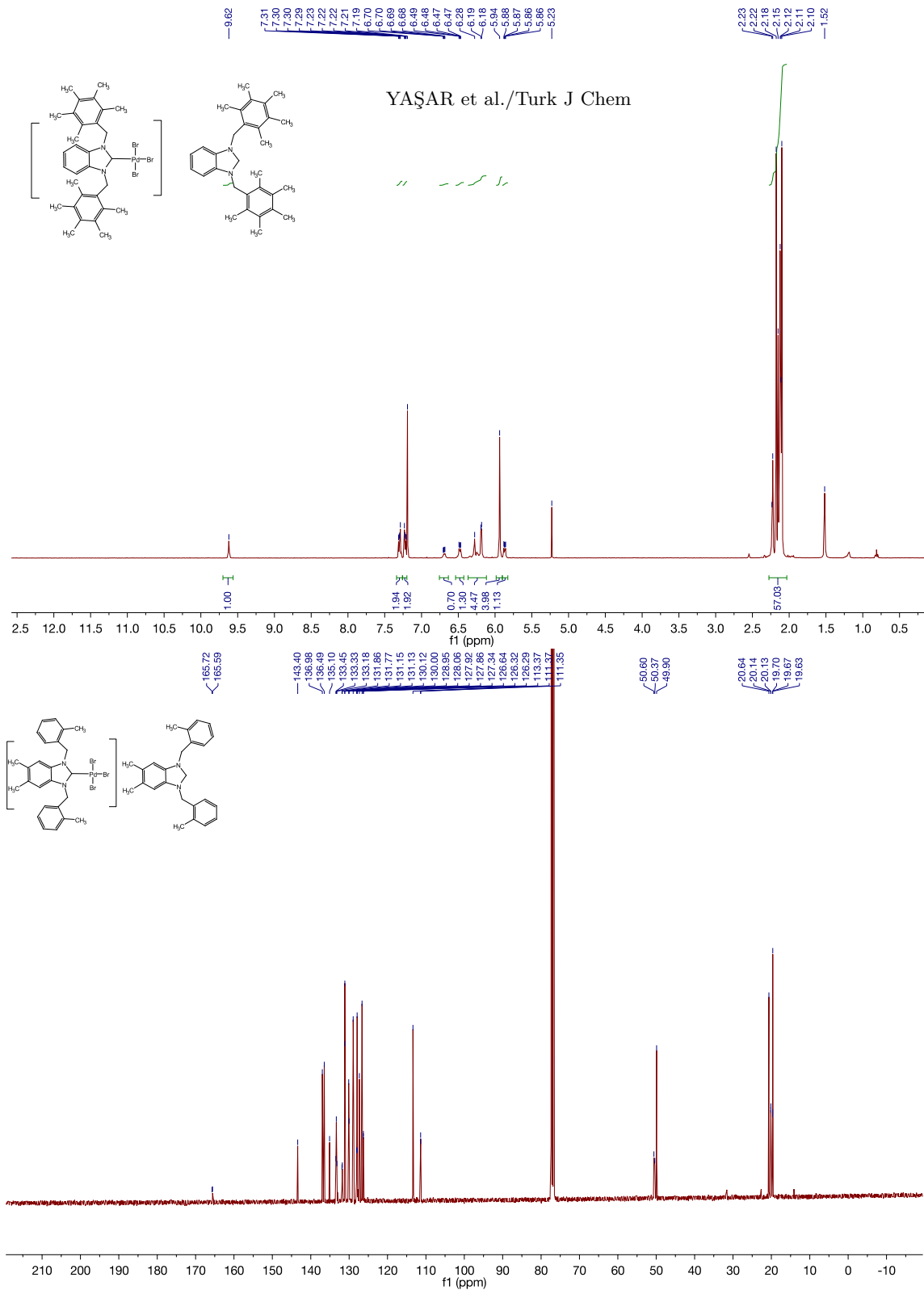
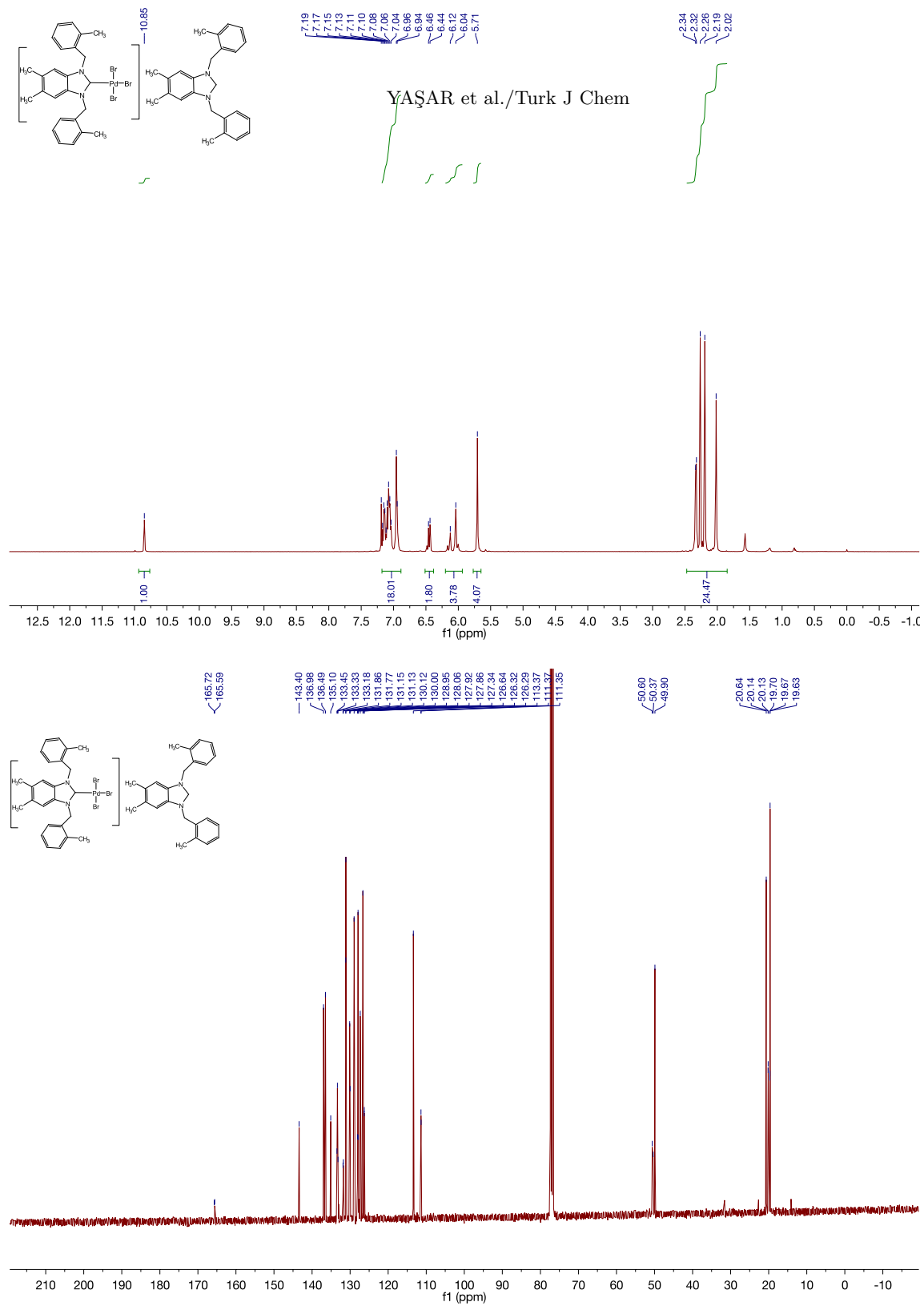
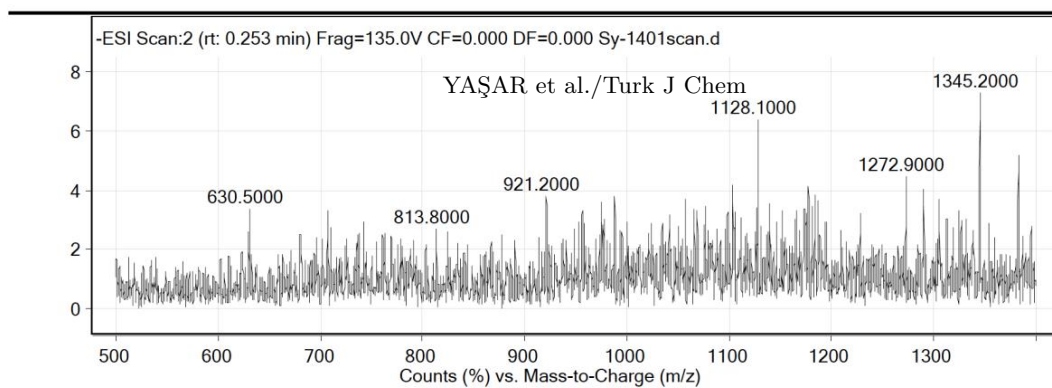


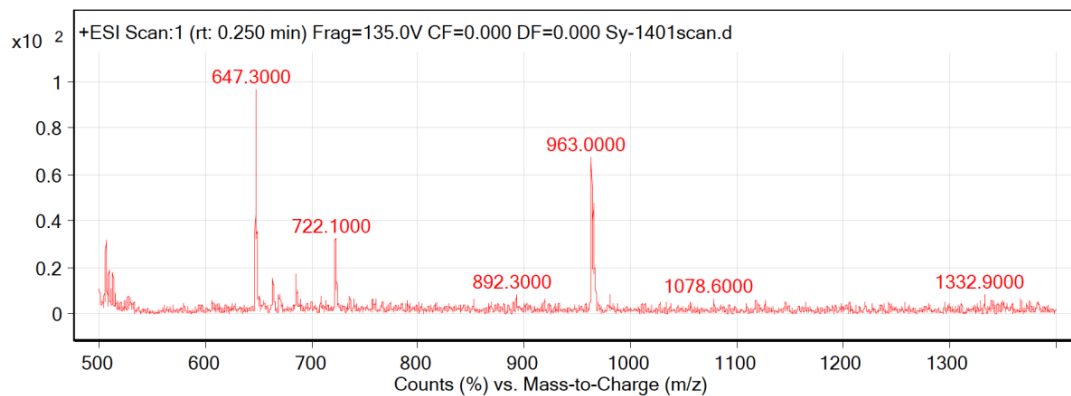
Figure S2. NMR spectra of **2b**





Peak List

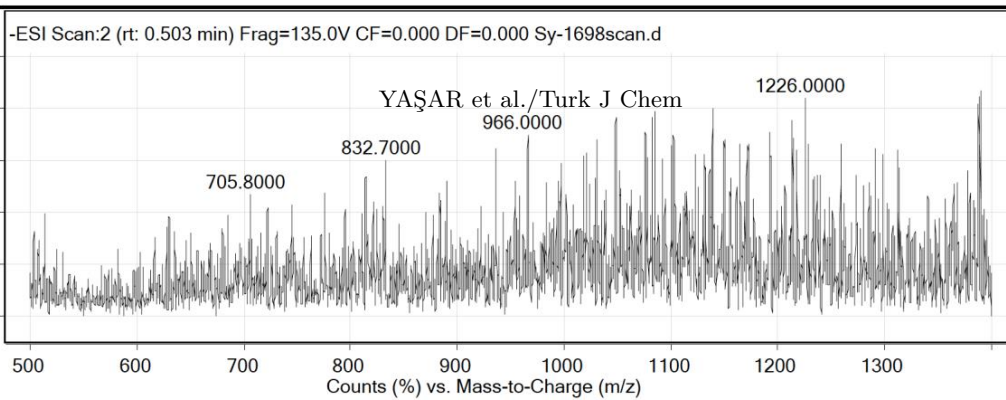
m/z	Abund
921.2	94.62
988.1	94.52
1103.8	99.74
1128.1	129.62
1177.8	99.04
1183.8	95.1
1272.9	103.44
1290.6	97.76
1345.2	142.36
1382.8	113.66



Peak List

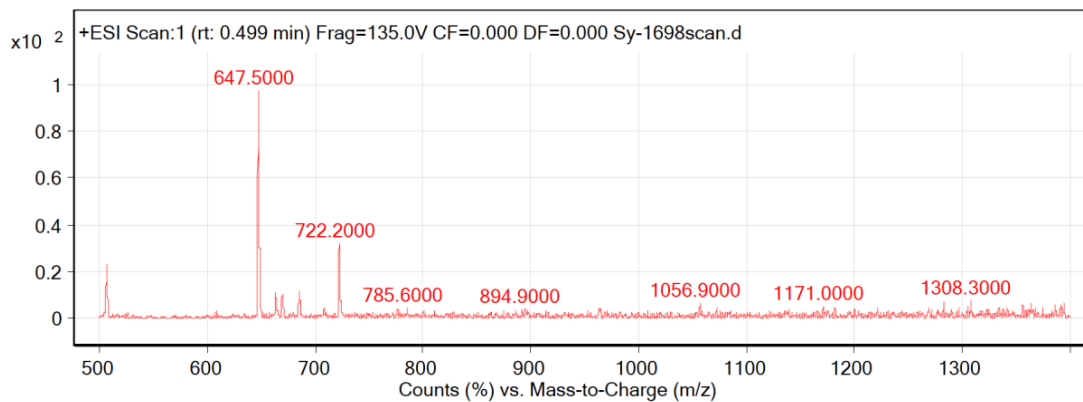
m/z	z	Abund
506.1		478.12
508.9		306.28
512.8		287.54
647.3	1	1363.92

Figure S4. LC-MS/MS spectra of **2a**



Peak List

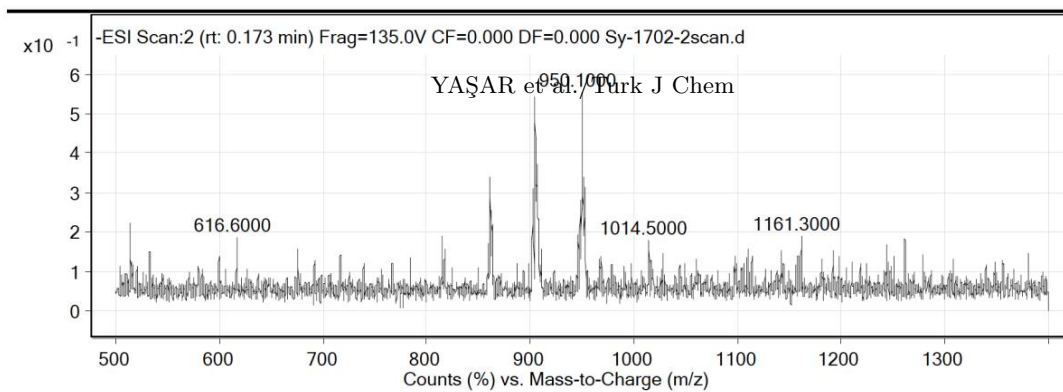
m/z	Abund
1048.2	114.36
1082.4	114.42
1085.4	116.7
1139	117.96
1192.8	109.34
1213.9	113.6
1226	121.32
1388.1	119.16
1389.4	122.02
1390.6	124.3



Peak List

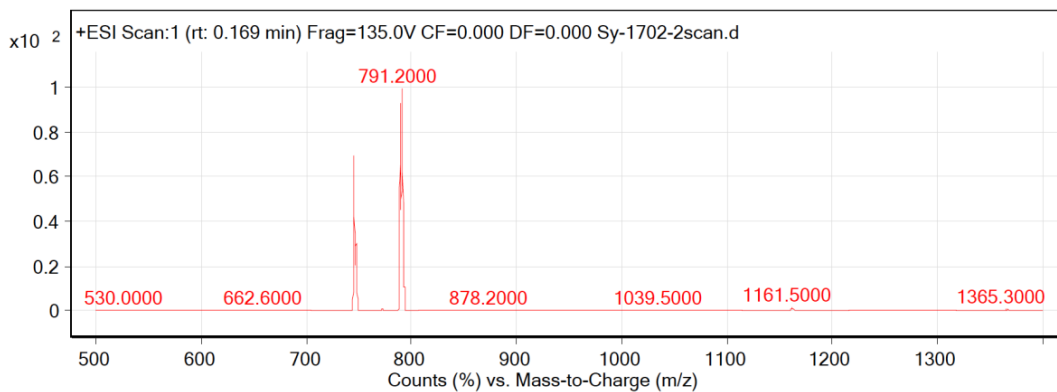
m/z	z	Abund
506.3		470.56
507		283.02
647.5		1844.04
649.1		298.42

Figure S5. LC-MS/MS spectra of **2b**



Peak List

m/z	z	Abund
860.7		87.52
861.3		84.76
902.9		83.5
904.4		115.38
906		85.04
907.1		92
948.1		79.58
950.1	1	117.06
951.1	1	87.36
952.4		83.88



Peak List

m/z	z	Abund
745.3	1	9471.24
746.3	1	4382.74
747.2	1	4126.52
748.2	1	2154.48

Figure S6. LC-MS/MS spectra of **2c**

References

[1] Huynh HV, Han Y, Ho JH, Tan GK. *Organometallics* 2006; 25: 3267-3274.