Benzothiazole-based Palladium Complexes as Efficient Nano-sized Catalysts for Microwave Hydrothermal Suzuki –Miyaura Cross-Couplings

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Abstract

The paper describes the synthesis of a novel nano-sized phosphine-free benzothiazole-based palladium(II) complexes from easily accessible starting materials and studies their efficiency as catalysts for Suzuki Miyaura cross coupling reaction using water as a solvent under microwaves irradiations. Structural elucidation of the novel nano-sized benzthiazole-based complexes was achieved by analytical and physical characterization tools. The catalytic activity of the novel nanocatalysts was invetigated for SMC of aryl halides with arylboronic acids using water as a solvent and under microwaves irradiation conditions as green mild reaction conditions.

Introduction

Suzuki Miyaura cross coupling reactions SMC [1] are extensively used to access a wide variety of key precursors in pharmaceuticals and material chemistry. In the last decade, palladium catalysts have attracted much attention from research teams as common catalysts in SMC [2–4]. For several years great effort has been devoted to developing stabilized catalytic species of palladium, phosphine ligands, have been widely used for such purpose. The major drawback of the use of phosphine ligands includes their sensitivity to air and humidity of which may decrease their uses in many of organic synthesis applications [5]. On the other hand, the environmental issues suppress the use of phosphorous containing compounds specially when we consider the eco-friendly conditions. On the other hand, phosphine-free catalysts are preferred due to their high catalytic activity under milder reaction conditions such as high sustainability to air and high stability to various thermal conditions [6,7]. In this consequence, many researchers have proposed various methods of developing phosphine-free ligands and has been increasingly inspected nowadays [8–11]. In the same context, nitrogen containing ligands and their complexes were predominate as catalysts in performing Suzuki Miyaura cross couplings with high efficiency [12–17]. Experimentally, using microwaves as a power source for performing organic transformations was received a great interest due to its attainments in green methodologies especially that use water as a reaction medium [18–21]. In extension to our efforts in the field of developing a new nitrogen containing heterocyclic ligands and using their palladium (II) complexes in many carbon-carbon cross coupling reactions [22–26], we explore in this work the synthesis of novel nano-sized benzothiazole-based Pd (II) complexes **4a,b** (Scheme 2) and studying their catalytic efficiency in carbon-carbon cross coupling reactions aryl halides with aryl boronic acids under microwaves irradiations in aqueous medium.

Results And Discussion

2.1 Synthesis of the benzothiazole-based Pd(II) complexes 4a,b

Treatment of benzothiazole-2-amine derivatives (1a,b) with *N*,*N*-dimethylformamide dimethylacetal (DMF DMA) (2) afforded the corresponding benzothiazole-based formamidine ligands (3a,b) as depicted in Scheme 1. The structural proof of ligands 3a,b was established based on their spectroscopic data. For

example, the proton NMR spectrum of the 3a showed the resonance of protons of the two methyl groups of $N(Me)_2$ group as two singlet signals at δ 3.00 and 3.14ppm and two sets of triplets at δ 7.13 and 7.28 ppm with coupling constant J = 8.5 Hz due to the two-aromatic ring (CH) protons. Also, two sets of doublets at δ 7.55 and 7.75 ppm with coupling constant J = 8.5 Hz due to the other two aromatic ring (CH) protons. The proton of -N=CH- of the formamidinyl group resonates as a singlet at δ 8.46 ppm (Fig.1). ^{13}C NMR spectra of the same ligand 3a showed the characteristic 9 carbon atoms resonance at their expected chemical shifts as shown in Fig 2. The other derivatives 3b reveled both ^{1}H and ^{13}C NMR spectra and the interpretation is showed in Fig. 3 and Fig. 4, respectively. Considering the IR spectrum of ligands 3a,b, the C=N group frequency showed the expected absorption band near 1636 cm^{-1} (see experimental part).

The targeted palladium complexes could be easily accessed by addition of sodium tetrachloropalladate in methanol as a solvent to equimolar amount of methanolic solution of benzothiazole-based formamidine ligands 3a,b at room with constant continuous stirring at temperature. After complete addition of the palladate salt, the corresponding 1:2 benzothiazole-based palladium(II) complex 4a,b in a moderate yield (Scheme 2). The structural elucidation of synthesized Pd complexes 4a,b has been achieved by their spectroscopic analysis and physical characteristics. ^{1}H NMR investigation of recorded spectrum of the coordination products revealed the formation of mainly 1:2 complexes and traces of 1:1 complex which was also confirmed by analytical investigation and thermogravimetric analysis that will be discussed latter. The ^{1}H NMR spectrum (Fig. 5) for complex 4a (taken as example) showed a sets of singlet signals at δ 3.03, 3.17, 3.18 ppm due to the protons of $N(Me)_2$ group. In addition to four triplets' signals at δ 7.16, 7.32, 7.33 and 7.50 ppm with J = 8.5 Hz assigned to the two aromatic rings (CH) protons at position 5 and 6 in each benzothiazole moiety and three doublet signals at δ 7.57, 7.78 and 7.83 ppm due the other aromatic positions at position 4 and 7 in each benzothiazole moiety. The last aromatic proton in position 7 in the benzothiazole moiety which is directly coordinated to the palladium atom showed a unique splitting pattern because of palladium field, where it appears as a doublet of doublet at δ 8.29 and 8.35 ppm with large value of coupling constant J = 59.5 Hz. The protons of (CH) group in formamidine moieties in 3a was found to resonates a singlet at δ 8.49 ppm for the formamidine group that is far from the coordination center and a doublet at δ 8.44 and 8.51 ppm for the formamidine group that is involved in the coordination center. The latter splitting of the formamidine proton signal is due to influence of the nitrogen atom coordination of the formamidinyl moiety with the Pd metal with coupling constant J = 59.5 Hz (Fig. 5a). Moreover, the ^{13}C NMR spectrum of complex 4a showed the characteristic carbon atoms resonance at the expected chemical shifts as shown in Fig.6. ^{1}H NMR spectral elucidation of the structure of complex 4b could be accounted in similar manner and was shown in Fig. 7. The recorded IR spectrum of complex 4a,b revealed the expected absorption band at 1627-1632 cm^{-1} assigned to the C=N bond vibration.

2.2. The Job's of continuous variation method

The stochiometric ratio and the molecular structure of the complex formed between Pd(II) and benzothiazole-based ligand was determined spectrophotometrically using a continuous variation method [27]. Within this method, $1.0x10^{-3}$ M solutions from both Pd(II) and ligand were prepared, then nine complex mixtures were prepared using various concentrations of both Pd(II) and ligand keeping the total concentration at constant value. The obtained results were represented by drawing the relation between the obtained absorbance at λ_{max} = 330 nm and the mole fraction for each mixture Fig. 8. As seen from the Fig. 8, two clear intersections at about 0.3 and 0.7 giving an evidence for a formation two stable complexes between the reaction species of stoichiometric ratios mainly (1:2) and traces of (1:1) (Pd(II):ligand). However the 1:1 complexes was not detected by NMR analysis which may atributed to their unstability in the NMR solvent DMSO-*d6*. Based on these obtained results, two solid complexes with the previous stoichiometries were prepared and a thermogravimetric analysis (TGA) was performed to confirm the structure. Figs. 9 and10 illustrated TGA for (1:2) and (1:1) complexes. From these figures, the calculated and the found weight losses for each thermo degradation step were determined and were listed in Table 1. Based on this date the proposed structures for the prepared complexes are constructed in Scheme 2,

2.3 Thermogravimetric analysis

TG (thermogravimetric) and DTA (differential thermal analysis) were performed for the palladium complexes of ligands **3a** and **3b** to investigate their thermal stability. TG and DTA analysis were investigated in range of temperature varies from ambient temperature up to 800 °C with a heating rate of 10 °C/min and under N_2 flow. The obtained TG/DTA thermograms for the complexes **4a** and **4b** are shown in Figures 9 and 10, respectively. Both complexes showed similar thermal decomposition, with a high thermal stability up to 278 °C. The weight loss observed below ≅ 250 °C in TGA curve of sample **4a** is attributed to the physically adsorbed water and solvent, as shown in differential thermal analysis by an exothermic the peak with a maximum at around ≅ 180 °C. However, this loss of weight was not noticed for **4b** because this sample was dry and crystalized. The degradation of the ligand started at around 279 °C for both complexes and was presented in the TGA curve by an obvious endothermic peak with a minimum at around 307 °C and 313 °C for samples **4a** and **4b**, respectively. This degradation corresponded to the weight loss of .66% (calculated 68%) for sample **4a** and 70% (calculated 69%) for sample **4b**.

Table 1: Results for thermogravimetric analysis (TGA) of selected two complexes formed between benzothiazole-based ligand and Pd(II).

Complex	Complex (M.Wt) Chemical formula	Temperature range (^{0}C)	Process	Weight loss %	
				Calcd.	found
4a	[RPd2Cl2] 585	70-250	Loss of 2Cl	12	10.5
	[RPd2Cl2]	250-800	Loss of organic part and $PdCO_3$ formation	71.5	69.7
4b	[RPdCl2] 399	300-800	Loss of 2Cl and organic part then PdO formation	69.3	71.2

2.3 The scanning electron microscopy (SEM)

The morphology of ligands **3a** and **3b**, and their palladium complexes **4a** and **ab**, respectively, was studied by scanning electron microscopy. The resulted micrographs of SEM are shown in Figures 11 and 12. The SEM images of ligand **3a** (Fig. 11a-c) depicted highly agglomerated particles with irregular shape, and with sizes in the micrometer range. After the complexation reaction of ligand **3a** with palladium, the SEM images of the obtained complex **4a** (Fig. 11d-f) revealed the formation of thin micro platelets with irregular shape and low aggregation compared to ligand **3a**.

SEM micrographs of ligand **3b** (Fig. 12a-c) showed creme-like surface morphology with high degree of agglomeration compared to ligand **3a**. However, after the complexation reaction of ligand **3b** with palladium, the SEM micrographs of the obtained complex **4b** (Fig. 12d-f) revealed the formation of rectangular microcrystals **3a,** with sharp edges, and a size ranging from few µm to 20 µm.

2.5 X-ray diffraction Analysis

The XRD pattern of complex **4a** recorded eight principal reflections observed at 2θ = 11.2, 16.0, 19.4, 24.9, 28.6, 35.1, 41.2 and 43.6, assigned to the (001), (111), (1-11), (022), (-122) (0-22) (114) and (0-32) planes, respectively, (Fig. 13). The calculations were performed for the crystal system *Anorthic* from all important peaks. For the complex **4b** the XRD pattern recorded twelve main reflections at 2θ = 10.5, 13.1, 16.0, 19.3, 21.9, 23.6, 24.5, 25.9, 31.4, 39.3 and 44.6, attributed to the (200), (11-1), (020), (220), (221) (202) (130), (022), (13-2), (62-1) , (133) and (730) planes, respectively, (Fig. 14). The crystal system for this sample, which was determined from all important peaks, was *Monoclinic*. The particle size for both complexes was calculated via Deby–Scherrer equation [28]. It was found that the obtained size present outstandingly in the nanometer range, which is around 10 nm, and 16 nm for complex **4a** and **4b**, respectively.

2.6. Catalytic Study

2.6.1. The catalytic efficiency of complex 4a,b in Suzuki –Miyaura Cross-Couplings

2.6.1.1. Effect of concentration of the complex 4a,b in catalysis of Suzuki –Miyaura Cross-Couplings

To investigate the catalytic performance of the synthesized palladium complexes for the Suzuki Miyaura C-C cross coupling we have intially studied of the effect of concentration of the palladium complexes **4a,b** on the formation of 4-acetyl-1,1´-biphenyl (**7a**) by the cross-coupling of phenylboronic acid (**5a**) and 4´-bromoacetophenone (**6**) in water as a solvent and using K_2CO_3 as a base. The latter reaction was considered as the model reaction of the investigation of the catalytic efficiency using the developed catalysts. Also, a co-catalyst tetrabutylammonium bromide (TBAB) was used a phase transfere reagent in such aqueous reaction. Thus, refluxing the reaction mixture in the presence of the complex **4a** with different concentrations furnshed the desired cross couplined product, 4-acetyl-1,1´-biphenyl (**7a**) after thermal heating for three hours as iullstrated in Scheme 3 and Table 2. When the cross coupling was carried out in the presence of 1 mol% of the complex **4a** and the other molar ratio of **6**: **5a**: K_2CO_3: TBAB was .01:1.2:1.0:0.6, it resulted in 100% conversion (mesured by GC-analysis) and the cross coupling product **7a** was obtained with complete disappearence of the starting materials (entry 1, Table 2). By gradual increase of the complex **4a** concentration from 0.75 to 0.125 mol%, we also obtained a full GC-conversion under the same reaction conditions (entries 2-5, Table 2). Thus, from the data in Table 2, it can be decided that the palladium complex **4** exhibited outstanding catalytic efficiency in the Suzuki Miyaura C-C cross coupling even when using very low mol%. On the other hand, the starting 4´-bromoacetophenone (**6**) was completely recovered when the cross coupling was carried out without addition of the palladium complex **4a** as expected (entry 6, Table 2). The obtained product, 4-acetyl-1,1´-biphenyl (**7a**) was analysed and its structure was confirmed by spectroscopic tools.

Table 2: Effect of concentration of complex **4a,b** on the coupling of 4´-bromoacetophenone (**6**) with phenylboronic acid (**5a**) in water.

Entry	Pd, mol%%	GC Conversion%	
		Cat **4a**	Cat **4b**
1	1.5	100	100
2	1	100	100
3	0.75	100	100
4	0.5	100	100
5	0.25	100	100
6	0.00	0	0

[a] Conditions: 4´-bromoacetophenone (**6**) / phenylboronic acid (**5a**)/ K_2CO_3/ TBAB / water: 1.0/1.2/1.0 / 0.6/ 10 mL, under thermal heating at 100°C for 3 h. [b] Conversions were based on GC-analysis: the conversion was monitored by Shimadzu GC-17A gas chromatography (GC), equipped with flam ionization detector and RTX-5 column, 30 m x 0.25 mm, 1 µm film thickness. Helium was used as carrier gas at flow rate 0.6 mL/min. Samples were withdrawn from the reaction mixture periodically. Injection volume was 1 µl, and total flow was 100 ml/min. Oven temperature was initiated at 100 °C for 2 min up to 130 °C at a rate of 15 °C/ min held for 2 min, then increased to 150 °C at a rate of 2 °C/ min held for 2 min. The Injector temperature was 160 °C and the detector temperature was 200 °C.

In order to explain how does the palladium complex **4** take part in the catalytic process of the reaction, it was suggested that the complex acts as “dormant species” and does not participate in the reaction catalytic cycle in an actual manner. the palladium complex **4** is considered as the main precursor for the palladium catalytically active species, thus it is considered as a precatalyst in the cross coupling reaction. Generally, the palladium(0) species was considered to be the true active catalysts as reported previouusly [29.30]. Therefore, the precatalyst **4** may serve as a reservoir that is indirectly involved in the catalytic cycle of the cross coupling and it is the main source of release of nano-sized palladium(0) which can afford catalytic role even when used with very low concentrations [31].

2.6.1.2. Effect of solvent and base on Suzuki –Miyaura Cross-Couplings using complex 4a as a catalyst

Optimization of the cross coupling conditions have been achieved by studying the effect of different parameters that may affect the cross-coupling reaction. Firstlty, solvent/base pair is one of the important factors that controls the efficiency of the catalyst in the cross coupling reactions and in consequence affects the yield optimization. However, there is no general rule for choosing the solvent/base pair for a given cross coupling, the selection of the solvent/base pair is still empirical. In the present work, we have invetigated some bases and a variety of solvents to perform the cross coupling reaction between 4´-bromoacetophenone (**6**) and phenylboronic acid (**5a**) as iullistrated in Scheme 4. Also, the heating mode for Suzuki-Miyaura cross-coupling reaction is one of the most important parameters in combination with base/solvent parameter specially in case of using the microwaves irradiation conditions. In this work we have used a solvothermal like technique under microwave irradiation in which the reaction was carried out in a special reaction vessel made from teflon and capped well to isolate it tightly which insure no

leakage of the reaction solvent (see experimental part). As Shown in Scheme 4 and Table 3, cross couplings were carried out using different solvents *e.g.* H_2O, DMF, toluene, 2-PrOH, dioxane and THF. In all entries, the catalyst concentration was 0.75 mol% of complex **4a**. Three appropriate bases were used in the cross coupling namely, KOH, K_2CO_3 and TEA under conventional heating (thermal condirions) and microwaves irradiation conditions. In case of using water as a solvent (Hydrothermal conditions) a co-catalyst tetrabutylammonium bromide (TBAB), have been used in the cross coupling reaction. From results obtained in Table 3, when H_2O was used as a solvent in the presence of K_2CO_3 as a base we got a full conversion after either 3h reflux (estimated by GC) or 7 min of microwaves irradiation and (entries 1 and 3, Table 3). Replacement of water by nonpolar solvent, toluene, we achieved less conversions and lower isolated yield of the product regardless the mode of heating as shown in Table 3 (entries 6 and 7). When less polar solvents: DMF, dioxane, or THF were used instead of water as a solvent using the same base, we obtained excellant conversions under conventional heating (entries 4,8 and 12, Table 3). When K_2CO_3 was replaced by KOH as a base we obtained the same conversions (entries 15 and 16, Table 3) however the isolated yield decreased in such case. Also, 2-propanol was found to be a suitable solvent for the reaction using either conventional heating or under microwave irradiation (entries 10, and 11, Table 3). Finally, when we used triethylamine (TEA) as an organic base using water as a solvent the cross coupling afforded 80% conversion and good isolated yield (entry 14, Table 3).

Table 3: Effect of base and solvent Suzuki cross coupling of 4´-bromoacetophenone (**6**) with phenylboronic acid (**5a**)

Entry	Base	Solvent	Heating mode	Time	Yield %[a]
1	K_2CO_3	H_2O	D	3h	100(95)
2	K_2CO_3	H_2O	mW	5 min	75(64)
3	K_2CO_3	H_2O	mW	7 min	100(100)
4	K_2CO_3	DMF	D	3h	100(90)
5	K_2CO_3	DMF	mW	7 min	80(77)
6	K_2CO_3	Toluene	D	4h	77(74)
7	K_2CO_3	Toluene	mW	7 min	84(83)
8	K_2CO_3	Dioxane	D	3h	100(73)
9	K_2CO_3	Dioxane	mW	7 min	100(92)
10	K_2CO_3	2-PrOH	D	4h	100(98)
11	K_2CO_3	2-PrOH	mW	7 min	100(98)
12	K_2CO_3	THF	D	4h	100(83)
13	K_2CO_3	THF	mW	7 min	100(87)
14	K_2CO_3	H_2O	D	4h	80(71)
15	K_2CO_3	H_2O	D	4h	100(91)
16	TEA	DMF		4h	100(81)
	KOH				
	KOH				

[a] Conversion by GC-analysis and the value between parenthesis indicates the product isolated yield%. Conditions: 4´-Bromoacetophenone/ phenylboronic acid/co-catalyst (if used)/ base/ solvents: 1/1.2/ 0.6/ 1/ 10 mL, under thermal heating at 100°C for 3 h. mW power was 300 W

H_2O as a green solvent is usually prefered in organic transformations due to the environmental advantages and K_2CO_3 is considered as a common base since it is a cheap. Thus, we recomand H_2O/ K_2CO_3 pair is the best solvent/Base combination for carrying out all the cross coupling reaction of aryl bromides in the presence of TBAB as a co catalyst. In general microwaves irradiation conditions and pressurized conditions affforded the cross coupled product in good yield and with high purity with a shorter time than the thermal conditions.

2.6.2. Suzuki–Miyaura cross-coupling reaction with arylboronic acid derivatives under conventional heating and microwaves irradiation using complex 4a

Under the optimized conditions, Suzuki–Miyaura cross-coupling of *4′*-bromoacetophenone **6** with a variety of boronic acid derivatives **5b-g** were performed under thermal and microvave assisted hydrothermal heating as iullistrated in scheme 4. Expectedly, complex **4a** was found to be an efficient catalyst for the cross-coupling reaction of boronic acid derivatives **5b-g** in excellent yield using water/K_2CO_3 as a solvent/base pair (Table 4) regardless the nature of the substituent pendant on the aromatic ring in the boronic acid.

Table 4: Conventional and microwaves assisted SMC reaction of 4´-bromoacetophenone (**6**) with arylboronic acid derivatives **5b-g** using complex **4**

Compd. No.	Ar	D heating		mW heating	
		Time[a] (h)	Yield%[b]	Time[a] (min)	Yield %[b]
7b	4-F-C_6H_4-	4	100	7	100 (99)
7c	4-CN-C_6H_4-	4	100	7	100 (98)
7d	4-Me-C_6H_4-	5	100	9	100 (93)
7e	4-MeO-C_6H_4-	4	100	7	100 (95)
7f	4-MeCO-C_6H_4-	4	99	8	100 (92)
7g	3,5-Me_2-C_6H_3-	5	98	9	100 (94)

Molar ratio of 4´-Bromoacetophenone/ arylboronic acid derivative/ TBAB /K_2CO_3 is 1:1.2:0.6/1and 0.75 mol% of the precatalsyt **4a** in 10 mL of a given solvent. Thermal reaction was carried out at 100°C with stirring and microwave heating have been done using 300 W power at 100 °C. [a] TLC or GC were used to determine the time of reaction. [b] Determined by GC and isolated yield was indicated between paranthesis.

Materials And Methods

3.1. General

All chemicals including solvents are spectroscopic grade and purchased from Sigma-Aldrich and used without further purification. Cross coupling reactions under microwaves irradiation were carried out in a Milestone microwave Labstation (MicroSYNTH, Touch Control, built-in ASM-45001 magnetic stirrer, Infra-red temperature sensor, and APC-55E automatic pressure control up to 55 bars (800 psi), Italy. Scanning electron microscopy was done using Philips EM 300 SEM, Siemens Autoscan (Germany). Powder X-ray diffraction pattern was measured by Shimadzu Lab-XRD–6000 with CuKα radiation and a secondary monochromator. STARe System thermogravimetric analyzer (TGA) was used to investigate the thermal transformation of the obtained material was investigated under air. Melting points (mp.) were recorded by using a Gallenkamp apparatus. IR (infra-red) spectra have been recorded in KBr discs using Shimadzu FT-

IR 3600 FT spectrophotometer. ^{1}H NMR spectra ligands and complexes have been recorded using Bruker Avance 850 instrument (850 MHz for ^{1}H, 125 MHz for ^{13}C) and Varian Mercury VXR-300 NMR spectrometer was used for products in DMSO-d_6 or $CDCl_3$. The recorded chemical shifts have been related to that of the used deuterated nmr solvent.

3.2. Organic Synthesis

3.2.1. Synthesis of Ligands: *N'-(benzothiazol-2-yl)-N,N-dimethylformimidamide derivatives* (3a,b)

A mixture of benzothiazole-2-amine derivatives **1a,b** with *N,N*-dimethylformamide dimethylacetal (**2**) was refluxed for 6 hours using dry benzene as a solvent. The reaction was monitored by TLC at different intervals and when the reaction was complete the reaction mixture was allowed to cool to ambient temperature. The precipitated solid products were separated by vaccum filteration then recrystallized using *n*-hexane with few drops ethyl acetate to afford an analytically pure crustals of benzothiazole-based formamidine ligands:*N'*-(benzothiazol-2-yl)-*N,N*-dimethylformimidamide **(3a)** and *N'*-(5-fluorobenzothiazol-2-yl)-*N,N*-dimethylformimidamide (**3b**). The physical and spectroscopic data of ligands **3a,b** are illustrated in Table 4

3.2.2. Synthesis of the Pd (II)-complexes 4a,b

Sodium tetrachloropalladate was dissolvec in absolute methanol and was added dropwisely to solution of the synthesized benzothiazole-based ligands **3a,b** in methanol and under constant stirring at ambient temperatrue. The orange precipitate of the complexes starts to separate within few minutes and after stirring for 1 h. Filteration of the precipitated complex and washing with distilled water to remove any excess sodium tetrachloropalladate and then thoroughly with methanol. Recrystalization of the synthesized complexes **4a-d** was achieved by using DMF as a recrystallization solvent. The physical and spectroscopic data of complexes **4a,b** are illustrated in Table 5

Table 5: Physical and spectroscopic data of ligands **3a,b** and complex **4a,b**

Compound No.	Yield	Mp. (color)	IR (KBr) Cm^{-1}	^1H NMR ($CDCl_3$)	^{13}C NMR
3a	85%	105 °C (colorless crystals)	1616 (C=N)	^1H NMR-850 Hz (DMSO-d_6) δ 3 (s, 3H, N–CH_3), 3.14 (s, 3H, N–CH_3), 7.13 (dt, *J*=8.5 Hz, 1H, Ar-H), 7.28 (dt, *J*=8.5 Hz, 1H, Ar-H), 7.55 (d, *J*=8.5 Hz, 1H, Ar-H), 7.75 (d, *J*=8.5 Hz, 1H, Ar-H), 8.46 (s, 1H, CH)	^{13}C NMR-125 Hz (DMSO-d_6) *δ* 35.1, 120.3, 121.8, 122.9, 126.1, 133.0, 152.4, 157.6, 173.3.
3b	63%	123 °C (yellow crystals)	1637 (C=N)	^1H NMR-850 Hz (DMSO-d_6) δ 3.03 (s, 3H, N–CH_3), 3.17 (s, 3H, N–CH_3), 7.15 (d, *J*=8.5 Hz, 1H, Ar-H), 7.55 (d, *J*=8.5 Hz, 1H, Ar-H), 7.71 (d, *J*=8.5 Hz, 1H, Ar-H), 8.46 (s, 1H, CH)	^{13}C NMR-125 Hz (DMSO-d_6) *δ* 34.9, 108.5, 113.0, 121.0, 134.0, 149.1, 157.6, 158.0, 173,5.
4a	58%	228 °C (orange crystals)	1632 (C=N)	^1H NMR (DMSO-d_6) *δ*3.03 (s, 3H, CH_3), 3.17 (s, 3H, CH_3)3.18 (s, 6H, 2 CH_3), 7.16-7.18 (t, *J* = 8.5 Hz, 1H), 7.32-7.33 (t, *J* = 8.5 Hz, 1H), 7.33 (t, *J* = 8.5 Hz, 1H), 7.50-7.53(t, *J* = 8.5 Hz, 1H), 7.57-7.58 (d, *J* = 8.5 Hz, 1H), 7.78-7.79 (d, *J* = 8.5 Hz, 1H), 7.83-7.85 (dd, *J* = 8.5 Hz, 1H), and 8.29-8.36 (ddd, *J* = 59.5 Hz 1H), 8.44-8.51 (d, *J* = 59.5 Hz, 1H), 8.49 (s, 1H).	^{13}C NMR (DMSO-d_6) *δ*35.1, 35.9, 115.8, 120.2, 121.8, 123.0, 126.1, 127.1, 127.6, 133.0 146.5, 146.9 152.6, 157.6, 159.8, 160.9, 172.8, 173.6.
4b	53%	238 °C (orange crystals)	1627 (C=N)	^1H NMR (DMSO-d_6) *δ*3.03 (s, 3H, CH_3), 3.17 (s, 3H, CH_3)3.18 (s, 6H, 2 CH_3), 7.15-7.18 (td, *J* = 8.5 Hz, 1H), 7.37-7.39 (td, *J* = 8.5 Hz, 1H), 7.55-7.57 (dd, *J* = 8.5 Hz, 1H), 7.71-7.73 (dd, *J* = 8.5 Hz, 1H), 7.81-7.83 (dd, *J* = 8.5 Hz, 1H), and 8.27-8.36 (ddd, *J* = 59.5 Hz 1H), 8.43-8.50 (d, *J* = 59.5 Hz, 1H), 8.46 (s, 1H).	^{13}C NMR (DMSO-d_6) *δ*35.19, 35.89, 108.4, 108.5, 113.8, 113.9, 121.0, 121.4, 134.0, 139.4, 149.1, 150.5, 157.9, 158.1, 159.8, 159.9, 173.4, 175.4.

3.3. Catalytic Study

3.3.1. Suzuki –Miyaura cross-couplingof phenylboronic acid with 4'-bromoacetophenone

3.3.1.1. Effect of Pd-complexes 4a,b concentration on Suzuki –Miyaura cross-couplingin water under conventional heating

Refluxing a mixture of 4’-bromoacetophenone (**6**) (1 mmol), phenylboronic acid (**5a**) (1.2 mmol), TBAB (0.6 mmol), palladium complexes **4a** or **4b** (1,5 mol%), K_2CO_3 (1 mmol) and 10 mL water for 3h at 100 °C with stirring. The reaction was monitored by TLC or by GC at different intervals and when the reaction was complete the reaction mixture was allowed to cool to ambient temperature. Reaction workup was achieved by extraction the reaction product using ethyl acetate(3 x 20 mL), then drying the axtracts using unhydrous sodium sulphate. The organic layer was evporated under vaccum to give 4-acetyl-1,1'-biphenyl as a white solid. Using the same experimental conditions, different mol% of the palladium complexes **4a** or **4b** (1, 0.75, 0.5, 0.25) were used and in every run the GC yield was calculted as shown in Table 2.

3.3.1.2. Optimization of Suzuki cross-coupling of 4’-bromoacetophenone with phenylboronic acid using complex 4a in different solvent/base pairs under conventional heating and microwave irradiation

Conventional heating method

General Procedure

A reaction mixture containing 1 mmol of 4’-bromoacetophenone (**6**) (199 mg), 1.2 mmol of phenylboronic acid (**5a**) (146 mg), 0.6 mmol of TBAB (194 mg) (in case of using water as a solvent), 1 mmol of the approperiate base, 0.75 mol% of Pd-complex **4a** and 10-15 mL of the approperiate solvent was refluxed with constant stirring. The reaction was monitored by TLC or by GC at different intervals and when the reaction was complete the reaction mixture was allowed to cool to ambient temperature. Reaction workup in case of using water as a solvent was achieved by extraction the reaction product using ethyl acetate (3 x 20 mL), then drying the extracts using unhydrous sodium sulphate. The organic layer was evporated under vaccum to give 4-acetyl-1,1'-biphenyl as a white solid. In case of using organic solvents the reaction mixture was passsed through a short silica-gel column and washed thourghly with ethyl acetate. The solvent was evporated under vaccum to give also 4-acetyl-1,1'-biphenyl as a white solid. The yield % versus different solvents and bases is outlined in Table 3.

Microwaves irradiation method

General Procedure

The microwave reaction vessel was lunshed with a mixture containing 1 mmol of 4’-bromoacetophenone (**6**) (199 mg), 1.2 mmol of phenylboronic acid (**5a**) (146 mg), 0.6 mmol of TBAB (194 mg) (in case of using water as a solvent), 1 mmol of the approperiate base, 0.75 mol% of Pd-complex **4a** and 10-15 mL of the approperiate solvent. The microwaves irradiation parameters was adjusted in such away that the vessel temperature always kept near the boiling point of the approperiate solvent with low rate stirring (to avoid the pressure irregularities inside the reaction vessel). The reaction was monitored by TLC or by GC at different intervals and when the reaction was complete the reaction vessl was allowed to cool to ambient temperature. Reaction workup in case of using water as a solvent was achieved by extraction the reaction product using ethyl acetate (3 x 20 mL), then drying the organic layer using unhydrous sodium sulphate. The organic layer was evporated under vaccum to give 4-acetyl-

1,1'-biphenyl as a white solid. In case of using organic solvents the reaction mixture was passsed through a short silica-gel column and washed thourghly with ethyl acetate. The solvent was evporated under vaccum to give also 4-acetyl-1,1'-biphenyl as a white solid. The yield % versus different solvents and bases is outlined in Table 3.

Application of Suzuki cross-coupling of 4'-bromoacetophenone with aryl boronic acid derivatives using complex 4a using optimized conditions under conventional heating and microwave irradiation

Conventional heating method

General Procedure

A mixture of 1 mmol of 4'-bromoacetophenone (**6**),1.2 mmol of approperiate aryl boronic acid (**5b-g**), 0.6 mmol of TBAB (194 mg), 1 mmol of K_2CO_3, 0.75 mol% of Pd-complex **4a** and 10-15 mL of water was refluxed with constant stirring. The reaction was monitored by TLC or by GC at different intervals and when the reaction was complete the reaction mixture was allowed to cool to ambient temperature. Reaction workup was achieved by extraction the reaction product using ethyl acetate (3 x 20 mL), then drying the extracts using unhydrous sodium sulphate. The organic layer was evporated under vaccum to give biphenyl derivatives. The yield % of the isolated products is outlined in Table 4 and the physical and ^{1}H NMR data are shown in Table 6

Microwaves irradiation hydrothermal method

General Procedure

The microwave reaction vessel was lunched with a mixture containing 1 mmol of 4'-bromoacetophenone (**6**) (199 mg), 1.2 mmol of approperiate aryl boronic acid (**5b-g**) , 0.6 mmol of TBAB (194 mg), 1 mmol of K_2CO_3, 0.75 mol% of Pd-complex **4a** and 10 mL of water. The microwaves irradiation parameters was adjusted in such away that the vessel temperature always kept near the boiling point of the approperiate solvent with low rate stirring (to avoid the pressure irregularities inside the reaction vessel). The reaction was monitored by TLC or by GC at different intervals and when the reaction was complete the reaction vessel was allowed to cool to ambient temperature. Reaction workup was achieved by extraction the reaction product using ethyl acetate (3 x 20 mL), then drying the organic layer using unhydrous sodium sulphate. The organic layer was evporated under vaccum to give biphenyl derivatives **7b-g**. The yield % of the isolated products is outlined in Table 4 and the physical and ^{1}H NMR data are shown in Table 6

Table 6: Physical and ^{1}H NMR data of cross coupling products **7a-g**

Compound No.	Name	Mp. (Lit mp. [ref]) (color)	^{1}H NMR ($CDCl_3$)
7a	**4-Acetyl-1,1'-biphenyl**	118–120 °C (121 °C [32]) (colorless crystals)	^{1}H NMR-300 Hz ($CDCl_3$) δ 2.65 (s, 3H, $COCH_3$), 7.41-7.51 (m, 3H, Ar–H), 7.63–7.65 (d, 2H, *J* =7.2 Hz, Ar–H), 7.68–7.71 (d, 2H, *J* =8.1 Hz, Ar–H), 8.03–8.06 (d, 2H, *J* = 8.4 Hz, Ar–H).
7b	**1-(4'-Fluoro-[1,1'-biphenyl]-4-yl)ethanone**	102 °C (102–103 °C [33]) (white crystals)	^{1}H NMR-300 Hz ($CDCl_3$) δ 2.65 (s, 3H, $COCH_3$), 7.14–7.62 (m, 4H, Ar–H), 7.64 (d, *J* =8.4 Hz, 2H, Ar–H), 8.03 (d, *J* =8.4 Hz, 2H, Ar–H).
7c	**4'-acetyl-[1,1'-biphenyl]-4-carbonitrile**	115 °C (115–116 °C [34]) (colorless crystals)	^{1}H NMR-300 Hz ($CDCl_3$) δ 2.58 (s, 3H, $COCH_3$), 7.61–7.62 (d, 2H, Ar–H), 7.6-7.66 (d, *J* = 8.1 Hz, 2H, Ar–H), 7.68-7.69 (d, *J* = 8.1 Hz, 2H, Ar–H), 7.99-8.00 (d, *J* = 8.1 Hz, 2H, Ar–H).
7d	**1-(4'-Methyl-[1,1'-biphenyl]-4-yl)ethanone**	118-120 °C (121–122 °C [32]) (white crystals)	^{1}H NMR-300 Hz ($CDCl_3$) δ 2.42 (s, 3H, CH_3), 2.64 (s, 3H, $COCH_3$), 7.28 (d, *J* = 8.1 Hz, 2H, Ar–H), 7.54 (d, *J* = 8.1 Hz, 2H, Ar–H), 7.67 (d, *J* = 8.1 Hz, 2H, Ar–H), 8.02 (d, *J* = 8.1 Hz, 2H, Ar–H).
7e	**1-(4'-methoxy-[1,1'-biphenyl]-4-yl)ethan-1-one**	152-153 °C (153–154 °C [35]) (white crystals)	^{1}H NMR-300 Hz ($CDCl_3$) δ 2.55 (s, 3H, CH_3), 3.78 (s, 3H, $COCH_3$), 6.91-6.93 (d, *J* = 8.1 Hz, 2H, Ar–H), 7.49-7.51 (d, *J* = 8.1 Hz, 2H, Ar–H), 7.56-7.57 (d, *J* = 8.1 Hz, 2H, Ar–H), 7.92-7.93 (d, *J* = 8.1 Hz, 2H, Ar–H).
7f	**1,1'-([1,1'-biphenyl]-4,4'-diyl)bis(ethan-1-one) (7f)**	190-192 °C	^{1}H NMR-300 Hz ($CDCl_3$) δ 2.50 (s, 6H, $2COCH_3$), 7.64-7.66 (d, 4H, *J* = 7.2 Hz, Ar–H), 7.98–7.99 (d, 4H, *J* = 7.2 Hz, Ar–H).

		(190-191 °C [36]) (white crystals)	
7g	**1-(3',5'-dimethyl-[1,1'-biphenyl]-4-yl)ethan-1-one**	82-83 °C (83 °C [37]) (white crystals)	^{1}H NMR-300 Hz ($CDCl_3$) δ 2.30 (s, 6H, $2CH_3$), 2.54 (s, 3H, $COCH_3$), 6.96 (s, 1H, Ar–H), 7.16 (2, 2H, Ar–H), 7.57-7.58 (d, *J* = 8.1 Hz, 2H, Ar–H), 7.91-7.93 (d, *J* = 8.1 Hz, 2H, Ar–H).

Conclusions

From the outcome of our investigation it is possible to conclude that the novel phosphine-free benzothiazole-based palladium(II) complexes are efficient in catalysis of Suzuki-Miyaura Cross-coupling reactions using water as a solvent under conventional heating conditions and microwaves irradiations. The novel benzothiazole-based palladium(II) complexes could be easily accessed from simple starting materials and showed their applicability as catalysts for SMC of aryl halides with arylboronic acids using green mild conditions.

Declarations

Conflicts of Interest:

All authors declare no conflict of interest

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Scheme

Scheme 1-5 are available in Supplementary Files section.

Figures

Figure 1

^{1}H NMR of spectra and their interpretation Ligand 3a

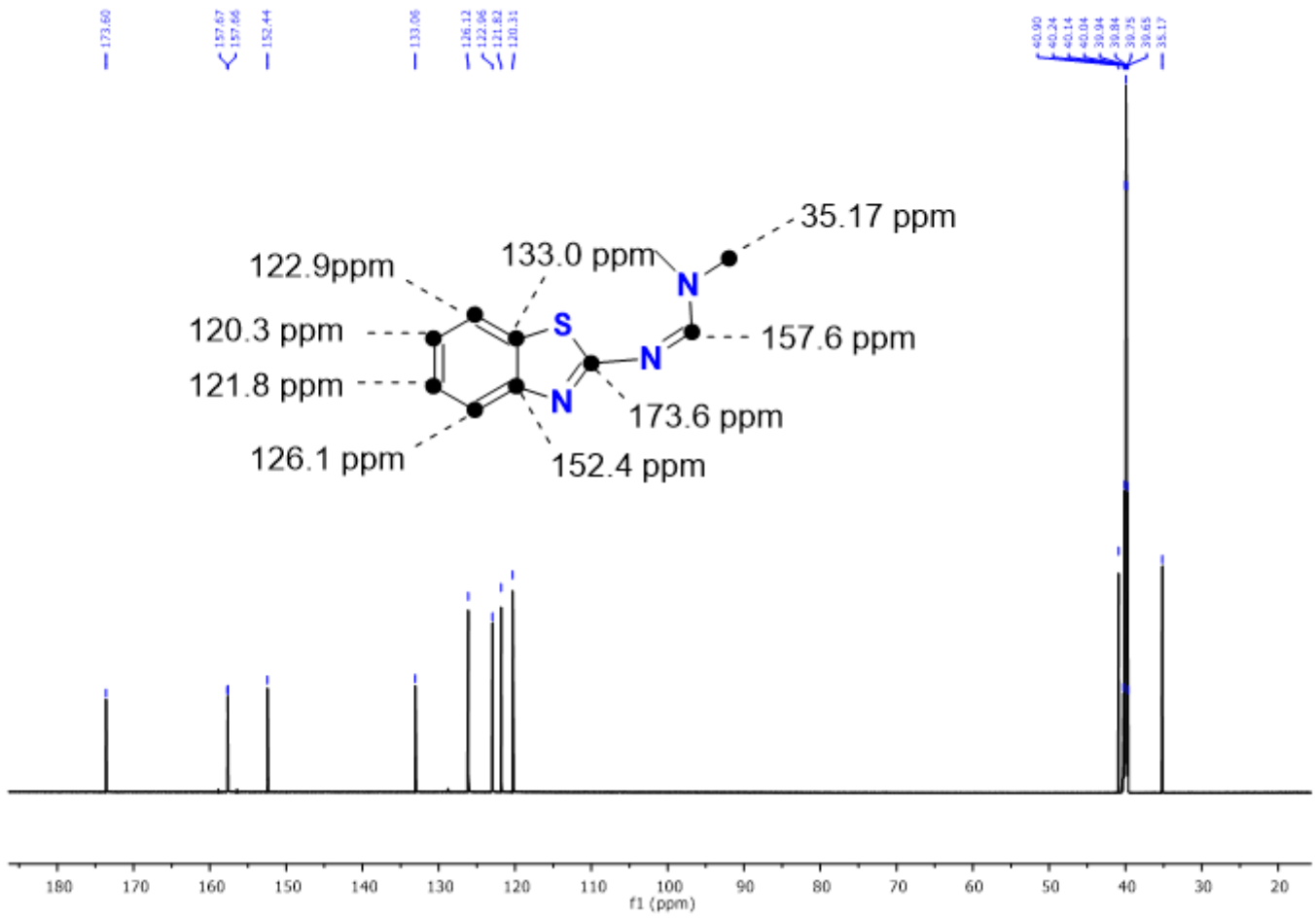

Figure 2

^{13}C NMR spectra and their interpretation of Ligand 3a

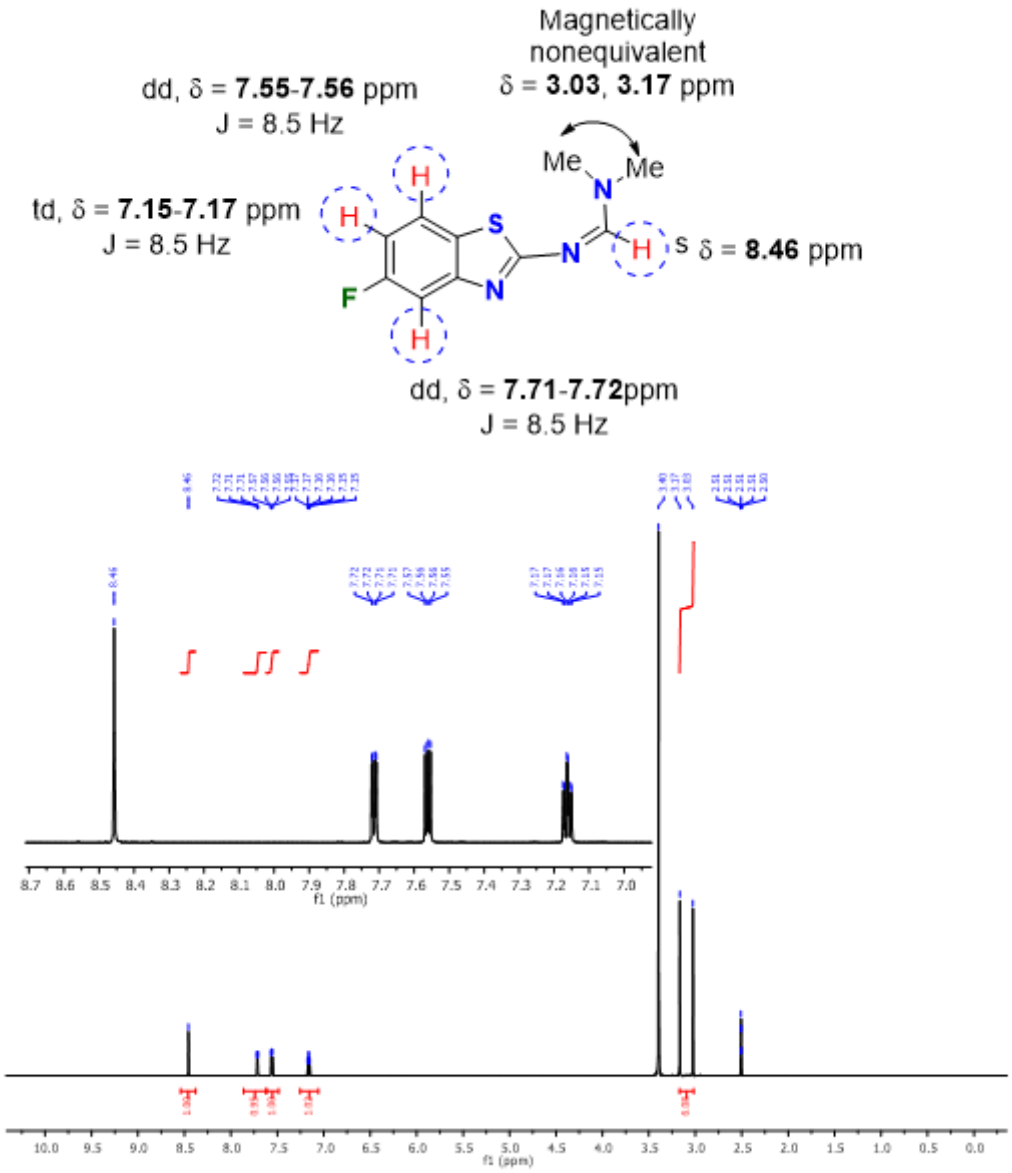

Figure 3

^{1}H NMR spectra and their interpretation of Ligand 3b

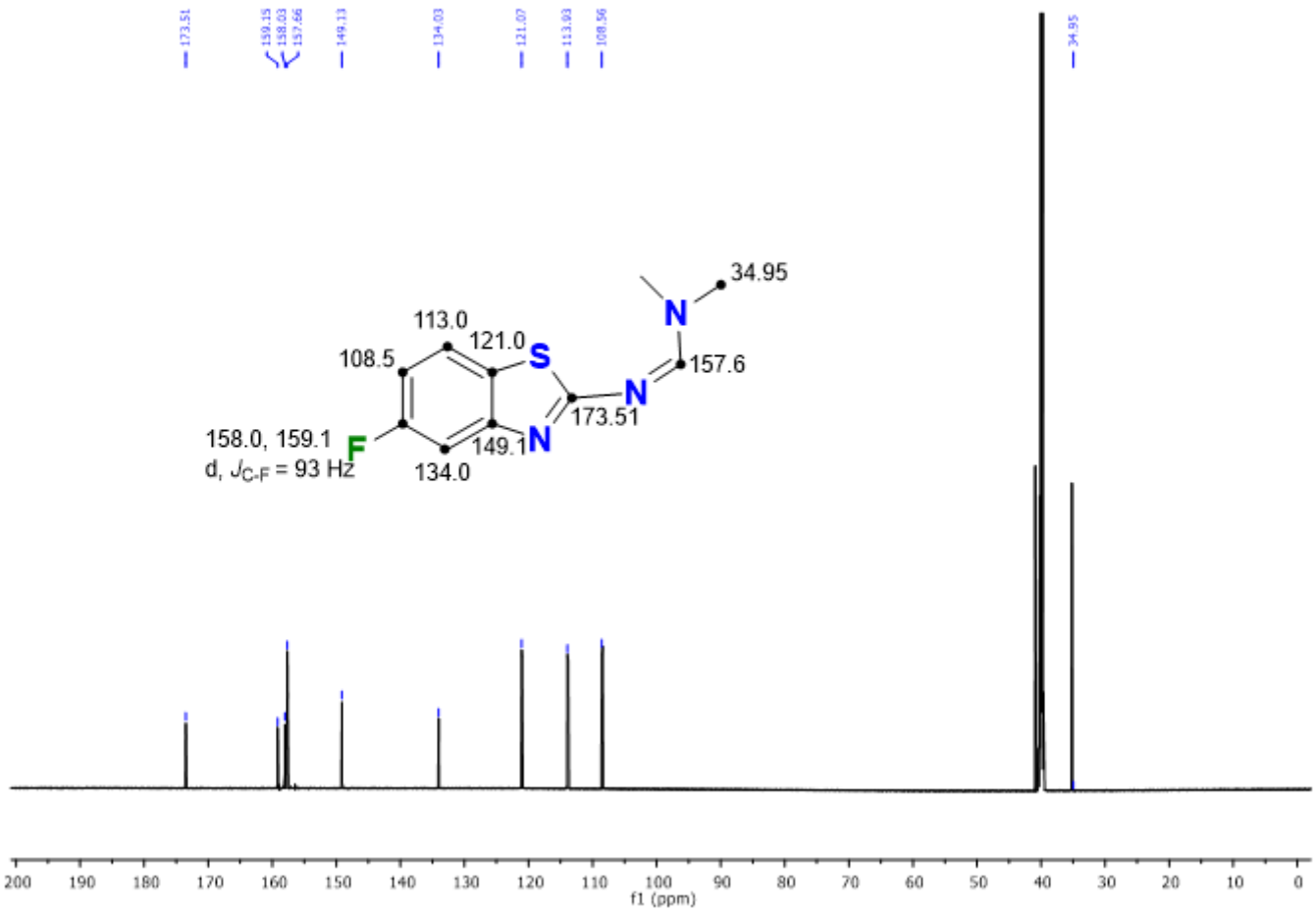

Figure 4

^{13}C NMR spectra and their interpretation of Ligand 3b

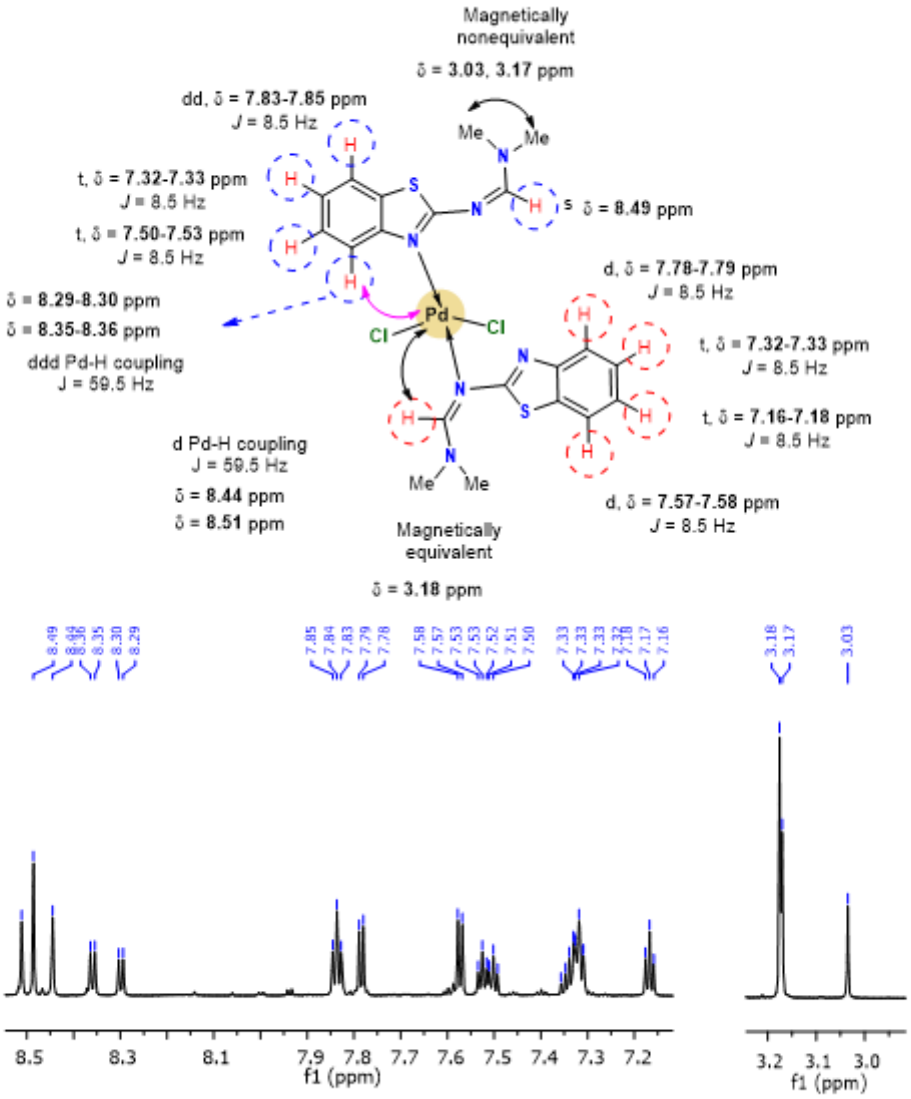

Figure 5

Effect of coordination of Pd on the ^{1}H NMR spectra and their interpretation of complex 4a

Figure 6

^{13}C NMR spectra and their interpretation of complex 4a

Figure 7

Effect of coordination of Pd on the ^{1}H NMR spectra and their interpretation of complex 4b

Figure 8

Job's method of continuous variation method for Benzothiazole-based (R) and Pd(II) complex (inset: the obtained absorption spectra and the measured absorbance at λ_{max} = 330)

Figure 9

TGA and DTA of complex **4a**

Figure 10

TGA and DTA of complex **4b**

Figure 11

The SEM micrographs of ligand **3a** (a-c) and complex **4a** (d-e) with different magnifications

Figure 12

The SEM micrographs of ligand **3b** (a-c) and complex **4b** (d-f) with different magnifications

Figure 13

X-ray diffraction (XRD) analysis of complexes **4a**

Figure 14

X-ray diffraction (XRD) analysis of complexes **4b**

Supplementary Files

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