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Graphical Abstract

Palladium(II)-*N*-heterocyclic carbene-catalyzed direct C2- or C5-arylation of thiazoles with aryl bromides

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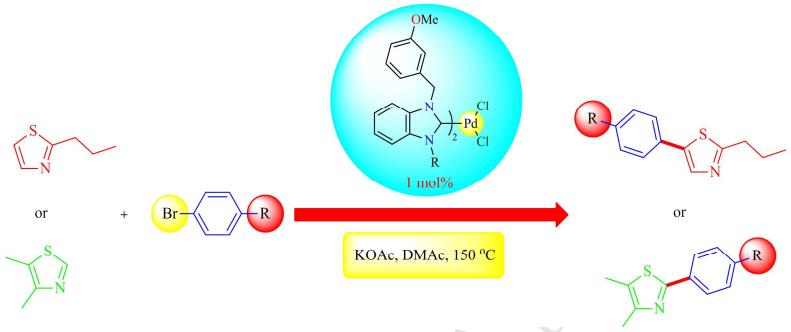

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ABSTRACT

Herein we report, a series of new benzimidazolium chlorides as *N*-heterocyclic carbene (NHC) ligand and their corresponding palladium(II)-NHC complexes with the general formula $[PdCl_2(NHC)_2]$ were synthesized. All new compounds were characterized by ^1H NMR, ^{13}C NMR, IR spectroscopy and elemental analysis techniques. The catalytic activity of palladium(II)-NHC complexes was investigated in the direct C2- or C5-arylation of thiazoles with aryl bromides in presence of palladium(II)-NHC at 150 °C for 1 h. These complexes exhibited the good catalytic performance for the direct arylation of thiazoles. The arylation of thiazoles regioselectively produced C2- or C5-arylated thiazoles in moderate to high yields.

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1. Introduction

Heteroaryls attached with aryl or heteroaryl groups represent privileged structural motifs that are utilized in both natural and synthetic compounds, as well as in bioactive compounds and pharmaceuticals.[1-5] Due to their essentiality, heteroaryl motifs have attracted synthetic chemists for more than a century, and numerous protocols have since been developed for the construction of (hetero)aryl-(hetero)aryl bonds by employing transition-metal catalysts.[6-16] Among them, the Suzuki-Miyaura,[17] Negishi[18] and Kumada[19] reactions are so successful that they have already become routine practices in synthetic laboratories. However these methods have still some fundamental drawbacks, as they required an additional synthetic operations for access to organometallic substrates, and produce a stoichiometric amount of metal waste from the arene-activating groups upon completion of the cross-coupling reaction.[20] Therefore, environmentally benign and atom economical strategies for heteroaryls synthesis, in terms of overall minimization of the formation of by-products and the simplification of overall synthesis processes, are required. The transition-metal-catalyzed direct arylation of aromatic C-H bonds is an ideal alternative. In the direct C-H bond activation, one of the preactivated reaction partners is replaced by a simple C-H containing compound, which is not only just of academic interest but also attractive for industrial applications, since only one preactivated reaction partner is needed.[21]

Thiazoles have vast application, being prominent components of biologically active natural products,[22] as well as pharmaceuticals,[23] agrochemicals,[24] and novel optical materials.[25] As selected examples, Meloxicam is a non-steroidal anti-inflammatory compound used to treat arthritis, dysmenorrhea and fever,[26] and Cefotaxime is a third generation cephalosporin antibiotic with broad spectrum activity against both gram positive and gram negative bacteria.[27] Also, Thiamin (Vitamin B1) is a vital vitamin for neural function and the metabolism of carbohydrate,[22] Ethaboxam is a fungicide used to treat mould and blight,[24] and Thiamethoxam is a neonicitinoid insecticide used as seed treatments[28] (Figure 1). Considering the importance of thiazoles in pharmaceutical and agrochemical industry, it is clear that, how popular these substrates are for the direct arylation studies.[29]

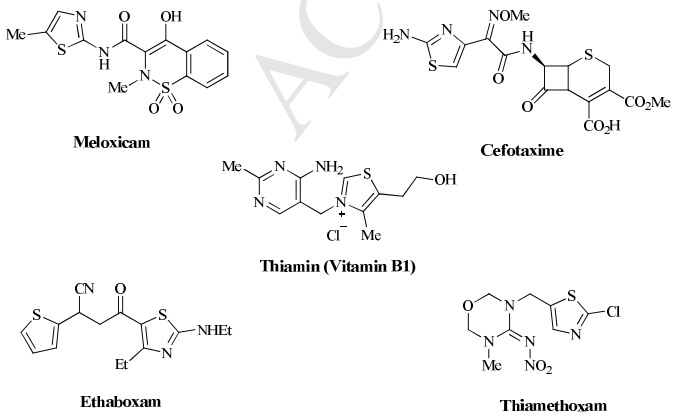
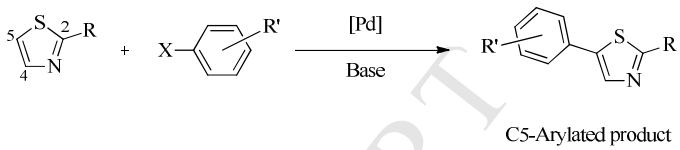


Figure 1. Examples of biologically active thiazole derivatives.

The direct arylation of thiazoles generally gives the C2- and C5-arylated products with high regioselectivity. The C2-position of thiazole is electron poor and acidic (p*K*a ~ 29.5) due to the proximity of the two heteroatoms, and the C5-position is the most electron-rich as a consequence of the resonance. The C4-position of thiazole is neither electron-rich nor electron poor and as such will only react under forcing conditions when the C2- and C5-positions are blocked[30-32] (Scheme 1).



Scheme 1. Generalized palladium-catalyzed direct C5-arylation of C2-position blocked thiazole with aryl halides.

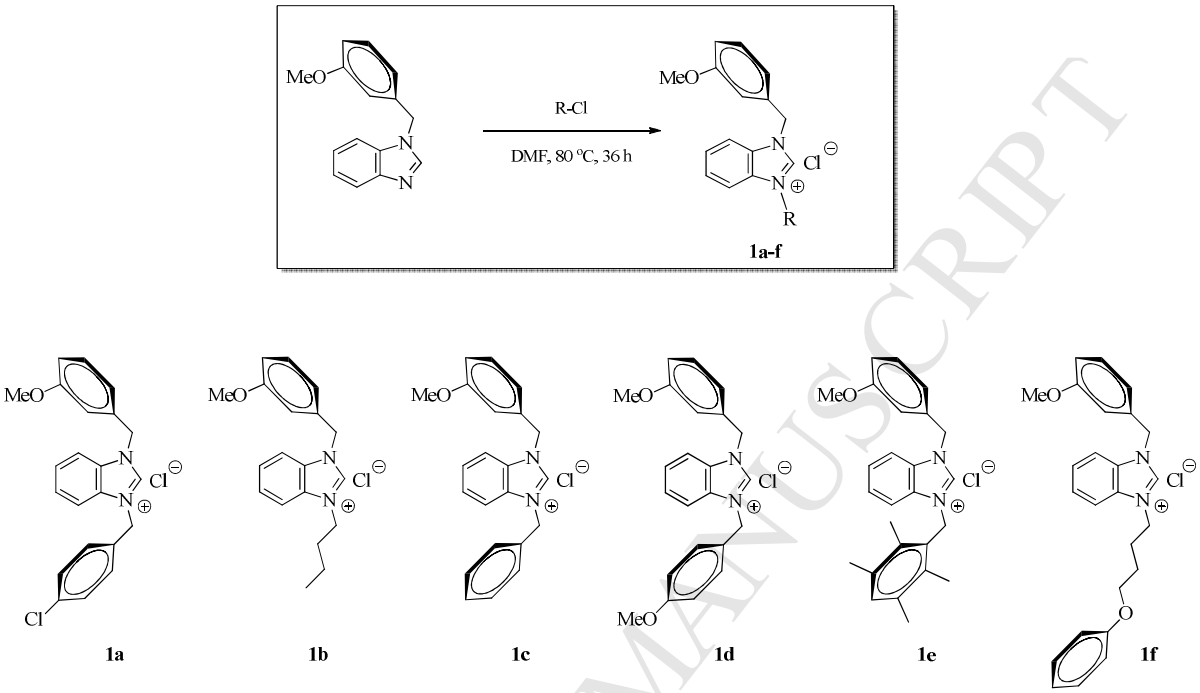
The palladium-catalyzed direct arylation of an azole ring was first accomplished in 1989 by Ohta et al.[33] The impressive foray into the direct arylation of thiazole, oxazole and imidazole yielded astounding results, both in terms of conversion and selectivity. Taking thiazole and oxazole in dimethylacetamide, together with tetrakistriphenylphosphino palladium(II) and potassium acetate, a heterocyclic chloride could be coupled at the C5-position of the azole ring in yields of up to 83%. Since these exciting results, the palladium-catalyzed direct arylation of various heteroaromatics with aryl halides has proved to be a powerful method for the synthesis of a wide variety of arylated heterocycles.[34] In this connection, recently we have also reported direct arylation of different heteroaromatic compounds with aryl halides catalyzed by palladium(II) complexes containing *N*-heterocyclic carbene (NHC) ligands.[35] The strong σ-donating but poor π-accepting ability of NHC ligands lead to the formation of many stable palladium complexes. Due to activity, stability and selectivity of palladium(II)-NHC complexes, they have been widely used as highly reactive and rather selective catalysts for numerous direct arylation reactions. But, only a few examples of palladium(II)-NHC-catalyzed direct arylation of thiazoles were found in the literature to date.[36] For this reason, we synthesized a series of new benzimidazolium chlorides as NHC ligands, (**1a-f**), and their corresponding palladium(II)-NHC complexes, (**2a-f**), with the general formula $[PdCl_2(NHC)_2]$, in this study. All new compounds were characterized by ^{1}H NMR, ^{13}C NMR, IR spectroscopy and elemental analysis techniques. Next, palladium(II)-NHC complexes were tested as catalyst in the direct C2-arylation of 4,5-dimethylthiazole and C5-arylation of 2-*n*-propylthiazole with aryl bromides in moderate to high yields.

2. Results and discussion

2.1. Synthesis of benzimidazolium chlorides

The benzimidazolium chlorides **1a-f** were synthesized by the reaction of *N*-(3-methoxybenzyl)benzimidazole with different alkyl chlorides in anhydrous dimethylformamide (DMF) at 80 °C for 36 h. All compounds were isolated as air- and moisture-stable crystalline solids in high yields (65-93%). The structures of the **1a-f** were determined by their characteristic spectroscopic data

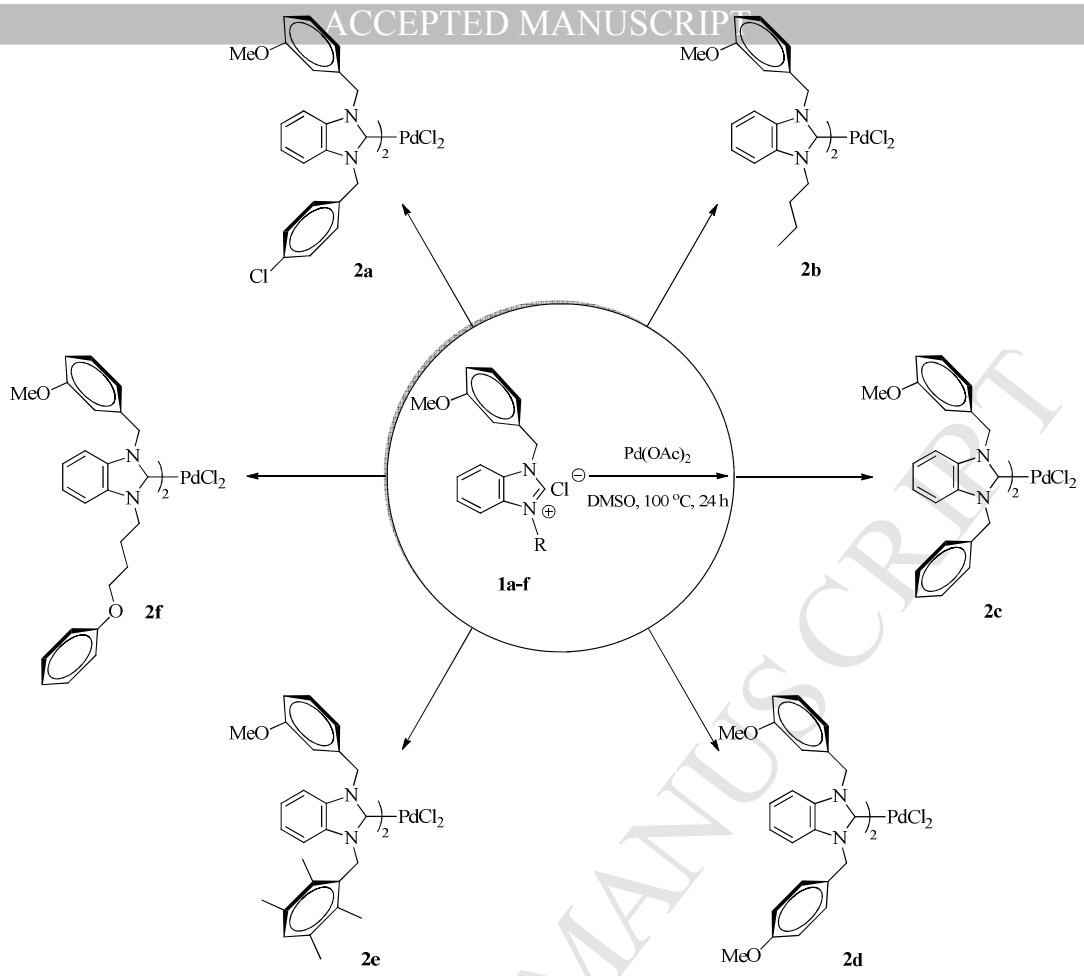
and elemental analyses. In the ^{13}C NMR spectra of **1a-f**, the characteristic peak of the imino carbon, (NCHN), resonance were detected as typical singlets at between 142.9-144.1 ppm. The ^{1}H NMR spectra of the **1a-f** further supported the assigned structures, the resonances for C(2)-*H* were observed as sharp singlets at between 11.42-12.10 ppm (see SI, pp. S1-S12). The NMR values are similar to those found for other benzimidazolium salts in the literature.[35d,e] The formation of the **1a-f** were also evident through their IR spectra, which showed peaks $\nu_{(C=N)}$ at between 1557-1563 cm^{-1} for the -C=N- bond vibration of **1a-f**. The benzimidazolium chlorides were prepared according to general reaction pathway depicted in Scheme 2.



Scheme 2. Synthesis of benzimidazolium chlorides (**1a-f**).

2.2. Synthesis of palladium(II)-NHC complexes

The palladium(II)-NHC complexes **2a-f** were synthesized by the reaction of benzimidazolium chlorides, (**1a-f**), with $Pd(OAc)_2$ in degassed dimethyl sulfoxide (DMSO) at 100 °C for 24 h. All palladium(II)-NHC complexes were obtained as light yellow solids in 40-59% yields. The air- and moisture-stable palladium(II)-NHC complexes were soluble in organic solvents such as acetone, dichloromethane, chloroform, DMF, ethanol and acetonitrile. The structures of the **2a-f** complexes were also determined by their characteristic spectroscopic data and elemental analyses. In the ^{1}H NMR and ^{13}C NMR spectra of the all palladium(II)-NHC complexes, loss of the benzimidazolium proton (NC*H*N) and benzimidazolium C2-carbon (NC*C*HN) signal suggests the formation of the palladium complexes. The characteristic peak of the Pd-$C_{carbene}$ resonance for all palladium(II)-NHC complexes were detected at between 181.7-182.4 ppm, however, NMR studies showed that all palladium(II)-NHC complexes except **2d** were a mixture of *cis/trans* isomers in an approximate 40:60 ratio (see SI, pp. S13-S24). The results of the elemental analysis were in good agreement with the theoretical values. Palladium(II)-NHC complexes exhibit a characteristic $\nu_{(NCN)}$ band typically at between 1402-1408 cm^{-1}. The spectroscopic data are similar to those found for other palladium(II)-NHC complexes in the literature.[35b,c] The **2a-f** complexes were prepared according to general reaction pathway depicted in Scheme 3. The analytical data are in good agreement with the compositions proposed for all the new compounds we prepared, and are summarized in the Table 1.



Scheme 3. Synthesis of palladium(II)-NHC complexes (**2a-f**).

Table 1. Physical and spectroscopic properties of new compounds.

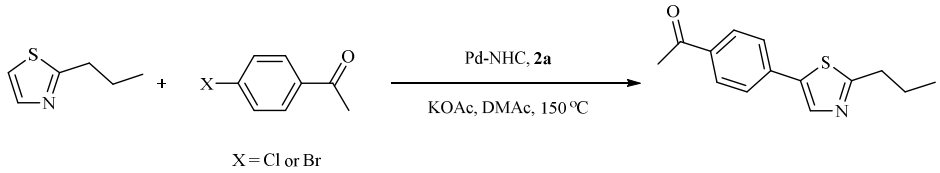
Compound	Molecular formula	Isolated yield (%)	M.p. (°C)	$\nu_{(CN)}$ (cm^{-1})	H(2) ^{1}H NMR (ppm)	C(2) ^{13}C NMR (ppm)[a]
1a	$C_{22}H_{20}Cl_2N_2O$	65	126-127	1558	12.10	144.1
1b	$C_{19}H_{23}ClN_2O$	79	102-103	1560	11.86	143.6
1c	$C_{22}H_{21}ClN_2O$	85	131-132	1557	11.85	143.7
1d	$C_{23}H_{23}ClN_2O_2$	75	190-191	1557	12.09	142.9
1e	$C_{26}H_{29}ClN_2O$	93	195-196	1558	11.42	143.9
1f	$C_{25}H_{27}ClN_2O_2$	82	141-142	1563	11.78	143.5
2a	$C_{44}H_{38}Cl_4N_4O_2Pd$	52	201-203	1408	-	182.3 and 182.5
2b	$C_{38}H_{44}Cl_2N_4O_2Pd$	53	148-150	1403	-	181.7 and 181.8
2c	$C_{44}H_{40}Cl_2N_4O_2Pd$	59	150-152	1406	-	182.3 and 182.4
2d	$C_{46}H_{44}Cl_2N_4O_4Pd$	59	296-298	1406	-	181.9
2e	$C_{52}H_{56}Cl_2N_4O_2Pd$	40	263-265	1402	-	182.2 and 182.3
2f	$C_{50}H_{52}Cl_2N_4O_4Pd$	45	198-200	1408	-	181.7 and 181.8

[a]As previously reported by several groups,[37] NMR data showed that all palladium(II)-NHC complexes except **2d** were *cis*/*trans* mixtures.

2.3. Direct arylation of thiazole derivatives

To determine the optimal catalytic conditions, we selected the complex **2a** as the model catalyst, and the 2-*n*-propylthiazole as the model heteroaromatic substrate with a blocked C2-position. We used the 4-bromoacetophenone or 4-chloroacetophenone as the model coupling partner. Also, we selected DMAc as the solvent, and KOAc as the base, because the DMAc/KOAc combination has been commonly used for the direct arylation of 5-membered heterocycles.[38] We focused on the direct arylation at the C5-position of 2-*n*-propylthiazole. The coupling reactions were regioselective, and in almost all cases, only the C5-arylated products were formed. The results of varying the other reaction conditions, including catalyst loading, chlorinated acetophenone, reaction time and reaction temperature are given in Table 2. The chemical characterizations of the products were made by NMR. The conversions were based on the aryl halide by GC and GC-MS.

Table 2. Influence of the reaction conditions for palladium(II)-NHC-catalyzed direct C5-arylation of 2-*n*-propylthiazole with 4-chloroacetophenone and 4-bromoacetophenone[a]



X = Cl or Br

Entry	**2a** (mol-%)	X	Time (h)	Temperature (°C)	Conversion(Yield)[b,c] (%)
1	No	Br	2	150	-
2	2	Br	2	150	100(91)
3	1	Br	2	150	100(91)
4	1	Br	2	120	78(64)
5	1	Br	2	90	67(53)
6	**1**	**Br**	**1**	**150**	**94(85)**
7	1	Br	0,5	150	64(47)
8	0.5	Br	1	150	57(36)
9	1	Cl	1	150	-
10	1	Cl	2	150	-
11	1	Cl	4	150	4(<2)
12	1	Cl	8	150	12(<5)
13	1	Cl	16	150	22(10)
14	1	Cl	20	150	25(15)

[a]Conditions: 2-*n*-propylthiazole (2.0 mmol), aryl halide (1.0 mmol), KOAc (2.0 mmol), DMAc (2 mL), 150 °C.
[b]Conversions were calculated with respect to aryl halide from the results of GC and GC-MS spectrometry.
[c]Isolated yields were shown in parentheses.

The arylation of 2-*n*-propylthiazole with 4-bromo-acetophenone was first carried out at 150 °C for 2 h without the addition of palladium complex in order to examine the effect of catalyst on the reaction. As attempt, no products were formed without the addition of palladium complex (Table 2, entry 1). In the presence of 2 mol% of **2a** as the catalyst, KOAc as the base, DMAc as the solvent and 4-bromoacetophenone as the coupling partner at 150 °C for 2 h, the C5-arylated product was obtained full conversion with 91% isolated yield (Table 2, entry 2). An decrease of the catalyst loading from 2 mol% to 1 mol% when the reaction was performed at similar conditions had no significant effect on the reaction, because of the full conversion were obtained (Table 2, entry 3). Decreasing the reaction temperature from 150 °C to 120 °C or 90 °C had a detrimental effect on the conversion (Table 2, entries 4 and 5). When the reaction time was reduced from 2 h to 1 h no noticeable effect on the conversion (94%) was observed (Table 2, entry 6), but when the reaction time was reduced to 0.5 h, the conversion dropped to 64% (Table 2, entry 7). Reducing the catalyst loading from 1 mol% to 0.5 mol% at 150 °C for 1 h decreased the isolated yield (36%) (Table 2, entry 8). Finally, the best conditions leading to 94% conversion with 85% isolated yield of 4-bromoacetophenone with high selectivity in favor of the C5-arylated product were obtained, when the reaction was carried out in DMAc/KOAc combination in the presence of 1 mol% **2a** catalyst at 150 °C for 1 h (Table 2, entry 6). The conditions are commonly used for the direct arylation of 5-membered heterocycles. For this reason, the conditions are also consistent with the literature.[36,38] When the less reactive 4-chloroacetophenone was used as substrate in the presence of 1 mol% of **2a** catalyst at similar conditions, no conversion was observed after lower reaction time such as 1 or 2 h (Table 2, entries 9 and 10). Although the reaction time was gradually increased from 4 h to 20 h, no significant increase in the conversion rate was observed (4-25%) (Table 2, entries 11-14). Therefore, no direct arylation of aryl chloride compounds with thiazole derivatives has been performed.

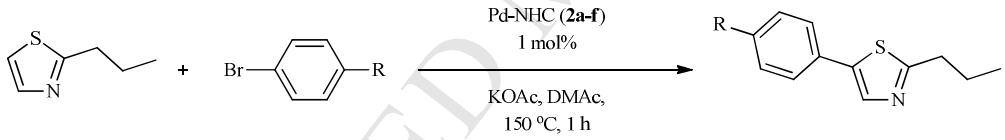
Under the determined optimal conditions, KOAc as the base in DMAc at 150 °C for 1 h, the palladium(II)-NHC complexes **2a-f** (1 mol%) were further examined in the direct C5-arylation of 2-*n*-propylthiazole with a blocked C2-position and the direct C2-arylation of 4,5-dimethylthiazole with a blocked C4- and C5-positions with five aryl bromides, namely, bromobenzene, 4-bromotoluene, 4-bromoanisole, 4-bromobenzaldehyde and 4-bromoacetophenone (Table 3 and Table 4). Initially, we performed the palladium-catalyzed direct arylation of 2-*n*-propylthiazole with aryl bromides. Regioselective arylation on only the C5-position of 2-*n*-propylthiazole was observed using different aryl bromides, because the hydrogen at the C5-position of 2-*n*-propylthiazole is more reactive than that of C4-position. When the reaction of 2-*n*-propylthiazole with bromobenzene, 4-bromotoluene, 4-bromoanisole, 4-bromobenzaldehyde and 4-bromoacetophenone using complexes **2a-f** as catalysts was investigated, conversions at between 67-93%, 64-92%, 66-85%, 82-97% and 76-94% were observed, respectively (Table 3). The reaction of 2-*n*-propylthiazole with bromobenzene generated the 5-phenyl-2-*n*-propylthiazole in 93% conversion in the presence of **2a** and **2f** (Table 3, entries 1 and 6). The reaction of 2-*n*-propylthiazole with 4-bromotoluene gave the expected product in 80% isolated yield in the presence of **2a** (Table 3, entry 7). The reaction of the electron-rich 4-bromoanisole with 2-*n*-propylthiazole gave the 5-(4-methoxyphenyl)-2-*n*-propylthiazole in 85% conversion and 73% isolated yield in the presence of 1

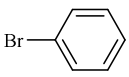
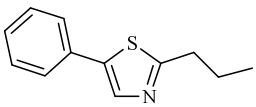
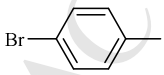
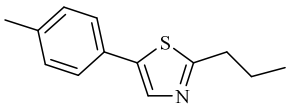
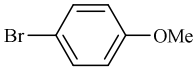
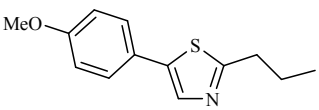
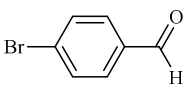
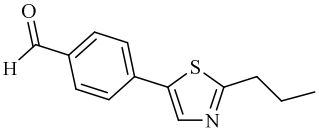
mol% of palladium complex **2f** (Table 3, entry 18). 4-Bromoanisole was also successfully coupled with 2-*n*-propylthiazole in the presence of **2a** to give desired product in 68% isolated yield (Table 3, entry 13). 2-*n*-Propylthiazole also reacts with 4-bromobenzaldehyde to give in 97% conversion and 80% isolated yield with **2f** (Table 3, entry 24). High yields of 5-(4-acetylphenyl)-2-*n*-propylthiazole were obtained for the coupling with 4-bromoacetophenone using catalyst **2a** (Table 3, entry 25).

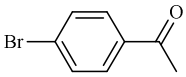
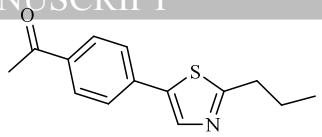
Finally, the scope of the direct arylation reaction was extended to 4,5-dimethylthiazole. Regioselective arylation on only the C2-position of 4,5-dimethylthiazole was observed. Because the C4- and C5-positions of 4,5-dimethylthiazole is blocked with methyl group, only the C2-position was arylated. When the reaction of 4,5-dimethylthiazole with bromobenzene, 4-bromotoluene, 4-bromoanisole, 4-bromobenzaldehyde and 4-bromoacetophenone using complexes **2a-f** as catalysts was also investigated, conversions at between 71-97%, 74-90%, 59-87%, 76-91% and 80-93% were observed, respectively (Table 4). Bromobenzene gave to high isolated yields of C2-arylation products in the presence of 1 mol% **2f** (Table 4, entry 6). The reaction of 4,5-dimethylthiazole with 4-bromotoluene generated the 2-(4-methylphenyl)-4,5-dimethylthiazole in 90% conversion and 74% isolated yield in the presence of **2a** (Table 4, entry 7). Moderate yields of 2-(4-methoxyphenyl)-4,5-dimethylthiazole were obtained for the coupling with 4-bromoanisole using catalysts **2a-f** (Table 4, entries 13-18) with little variance between the complexes. 4-Bromobenzaldehyde and 4-bromoacetophenone gave moderate to high yields of C2-arylation products in the presence of 1 mol% **2a-f** (Table 4, entries 19-30). Generally, the reactivity of 4,5-dimethylthiazole was similar to 2-*n*-propylthiazole, and the conversions for substrates containing electron-withdrawing groups were higher than those for substituents containing electron-donating groups.

The palladium-catalyzed direct arylation of thiazoles with aryl bromides has also been previously described by various groups.[36,39] In the previous works, similar substrates have been employed with higher catalyst loading (2-5 mol%),[36b,39a-d] and higher reaction time has been chosen (4-48 h)[36a,c,39] for arylation of thiazoles with aryl bromides. But, in the present work the catalyst loading was reduced to 1 mol%, and the reaction time was shortened to 1 h. Moreover, in the present study satisfactory results were obtained as compared to previous results.[36,39]

Table 3. Pd-NHC-catalyzed direct C5-arylation of 2-*n*-propylthiazole by using aryl bromides[a]

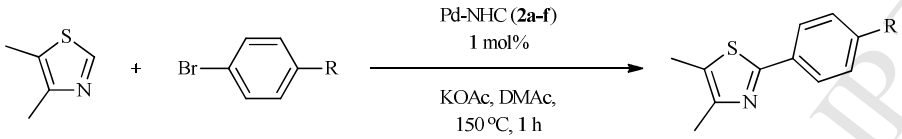


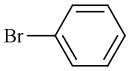
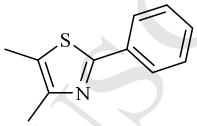
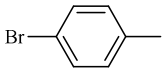
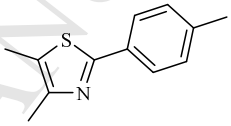
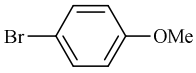
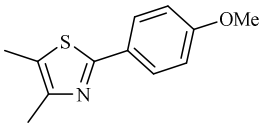
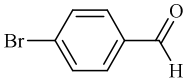
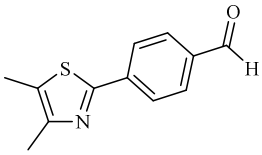
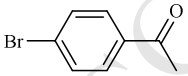
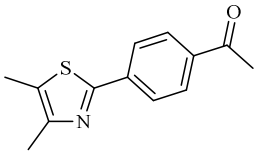
Entry	Aryl bromide	Catalyst	Product	Conversion(Yield)[b,c] (%)
1		**2a**		93(83)
2		**2b**		73(61)
3		**2c**		67(54)
4		**2d**		89(75)
5		**2e**		84(70)
6		**2f**		93(80)
7		**2a**		92(80)
8		**2b**		75(62)
9		**2c**		82(68)
10		**2d**		64(50)
11		**2e**		85(70)
12		**2f**		90(77)
13		**2a**		81(68)
14		**2b**		66(54)
15		**2c**		71(58)
16		**2d**		76(63)
17		**2e**		68(57)
18		**2f**		85(73)
19		**2a**		85(70)
20		**2b**		82(70)
21		**2c**		89(74)
22		**2d**		90(76)
23		**2e**		92(79)
24		**2f**		97(80)

25		**2a**		94(85)
26		**2b**		76(62)
27		**2c**		84(70)
28		**2d**		79(66)
29		**2e**		89(74)
30		**2f**		92(78)

[a]Conditions: Pd-NHC **2a-f** (0.01 mmol), 2-*n*-propylthiazole (2.0 mmol), aryl bromide (1.0 mmol), KOAc (2.0 mmol), DMAc (2 mL), 150 °C, 1 h.
[b]Conversions were calculated with respect to aryl bromide from the results of GC spectrometry.
[c]Isolated yields were shown in parentheses.

Table 4. Pd-NHC-catalyzed direct C2-arylation of 4,5-dimethylthiazole by using aryl bromides[a]



Entry	Aryl bromide	Catalyst	Product	Conversion(Yield)[b,c] (%)
1		**2a**		90(76)
2		**2b**		78(65)
3		**2c**		71(57)
4		**2d**		83(70)
5		**2e**		93(80)
6		**2f**		97(84)
7		**2a**		90(74)
9		**2b**		81(67)
9		**2c**		88(75)
10		**2d**		74(60)
11		**2e**		86(73)
12		**2f**		84(70)
13		**2a**		83(68)
14		**2b**		59(45)
15		**2c**		68(53)
16		**2d**		75(60)
17		**2e**		68(55)
18		**2f**		87(73)
19		**2a**		90(76)
20		**2b**		76(63)
21		**2c**		89(74)
22		**2d**		79(66)
23		**2e**		91(76)
24		**2f**		79(66)
25		**2a**		93(80)
26		**2b**		80(65)
27		**2c**		85(66)
28		**2d**		81(61)
29		**2e**		89(76)
30		**2f**		90(75)

[a]Conditions: Pd-NHC **2a-f** (0.01 mmol), 4,5-dimethylthiazole (2.0 mmol), aryl bromide (1.0 mmol), KOAc (2.0 mmol), DMAc (2 mL), 150 °C, 1 h.
[b]Conversions were calculated with respect to aryl bromide from the results of GC spectrometry.
[c]Isolated yields were shown in parentheses.

3. Conclusion

In summary, six new benzimidazolium halides and their corresponding palladium(II)-NHC complexes were successfully synthesized and characterized by NMR and IR spectroscopy, and microanalysis techniques. The catalytic activities of the new palladium(II)-NHC complexes were investigated in the direct C2- or C5-arylation of thiazole derivatives. In all cases, except in a few cases with complex **2a**, high conversions of the aryl bromides were observed. Only a minor effect of the NHC ligand on the palladium complex was observed for the coupling of aryl bromide with thiazole derivatives. Surprisingly, similar conversions were obtained for the coupling of each aryl bromides. We can say that there is no significant difference between these complexes on the catalytic activity of direct arylation of thiazole derivatives by aryl bromides. The only significant difference between **2a-f** complexes indicates that electronic effects are also playing some role in these processes. The performances and stabilities of these processes may be attributed to the ability of the possibility of flexible substituents

on **2a-f** complexes, which would rotate away from the axial site of the palladium center. Also, Glorius has recently reported that the possibility of *in situ* generated of palladium nanoparticle when used less bulky substituents, and this process would be rapid occurred.[40] Finally, when compared to previous reports,[36,39] satisfactory results were obtained with aryl bromides in presence of low catalyst loading in this study. This low catalyst loading procedure is economically and environmentally attractive. Also, the only byproducts are AcOH/KBr instead of metallic salts with classical coupling procedures such as Suzuki, Stille, or Negishi reactions. Moreover, no preparation of an organometallic derivative is required, reducing the number of steps and consequently the amount of waste to prepare these compounds. It has to be emphasized that this procedure is environmentally more attractive than these classical coupling procedures.

4. Experimental

4.1. General methods

All manipulations were carried out under argon using standard Schlenk line techniques. Chemicals and solvents were purchased from Sigma-Aldrich Co. (Poole, Dorset, UK). The solvents used were purified by distillation over the drying agents indicated and were transferred under argon. DMAc analytical grade (99%) was not distilled before use. KOAc (99%) was employed. 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 referenced to residual protiated solvents (δ = 7.26 ppm for $CDCl_3$), ^{13}C chemical shifts are reported relative to deuteriated 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.

*4.2. General procedure for the preparation of benzimidazolium chloride (**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 (1:2, *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 65-93% yields.

*4.2.1. 1-(3-Methoxybenzyl)-3-(4-chlorobenzyl)benzimidazolium Chloride (**1a**)*

(1.10 g, yield 65%) ^{1}H NMR (300 MHz, $CDCl_3$, 25 ^{o}C): δ = 3.72 (s, 3H, $CH_2C_6H_4(OCH_3)$-3); 5.74 (s, 2H, $CH_2C_6H_4(Cl)$-4); 5.86 (s, 2H, $CH_2C_6H_4(OCH_3)$-3); 6.76-7.53 (m, 12H, arom. C*H*s, NC_6H_4N, $CH_2C_6H_4(OCH_3)$-3 and $CH_2C_6H_4(Cl)$-4); 12.10 (s, 1H, NC*H*N) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 ^{o}C): δ = 50.7 ($CH_2C_6H_4(Cl)$-4); 51.6 ($CH_2C_6H_4(OCH_3)$-3); 55.6 ($CH_2C_6H_4(OCH_3)$-3); 113.7, 113.8, 114.9, 120.2, 127.1, 129.5, 129.9, 130.4, 131.2, 131.3, 131.4, 134.0, 135.2, 160.3 (arom. *C*s, NC_6H_4N, $CH_2C_6H_4(OCH_3)$-3 and $CH_2C_6H_4(Cl)$-4); 144.1 (N*C*HN) ppm. Elemental analysis calcd (%) for $C_{22}H_{20}Cl_2N_2O$ (Mr = 399.30): C 66.17, H 5.05, N 7.02; found (%): C 66.19, H 5.08, N 7.05.

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

(1.10 g, yield 79%) ^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C): δ = 0.97 (t, ^3J = 7.4 Hz, 3H, $CH_2CH_2CH_2CH_3$); 1.45 (hext, ^3J = 7.4 Hz, 2H, $CH_2CH_2CH_2CH_3$); 2.04 (pent, ^3J = 7.4 Hz, 2H, $CH_2CH_2CH_2CH_3$); 3.77 (s, 3H, $CH_2C_6H_4(OCH_3)$-3); 4.61 (t, ^3J = 7.5 Hz, 2H, $CH_2CH_2CH_2CH_3$); 5.88 (s, 2H, $CH_2C_6H_4(OCH_3)$-3); 6.82-7.70 (m, 8H, arom. C*H*s, NC_6H_4N and $CH_2C_6H_4(OCH_3)$-3); 11.86 (s, 1H, NC*H*N) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 25 ^{o}C): δ = 13.5 ($CH_2CH_2CH_2CH_3$); 19.8 ($CH_2CH_2CH_2CH_3$); 31.3 ($CH_2CH_2CH_2CH_3$); 47.6 ($CH_2CH_2CH_2CH_3$); 51.3 ($CH_2C_6H_4(OCH_3)$-3); 55.6 ($CH_2C_6H_4(OCH_3)$-3); 113.0, 113.8, 113.9, 114.7, 120.4, 127.0, 127.1, 130.3, 131.2, 131.4, 134.4, 160.2 (arom. *C*s, NC_6H_4N and $CH_2C_6H_4(OCH_3)$-3); 143.6 (N*C*HN) ppm. Elemental analysis calcd (%) for $C_{19}H_{23}ClN_2O$ (Mr = 330.90): C 68.97, H 7.01, N 8.47; found (%): C 68.96, H 7.03, N 8.49.

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

(1.30 g, yield 85%) ^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C): δ = 3.76 (s, 3H, $CH_2C_6H_4(OCH_3)$-3); 5.87 (s, 2H, $CH_2C_6H_5$); 5.90 (s, 2H, $CH_2C_6H_4(OCH_3)$-3); 6.81-7.60 (m, 13H, arom. C*H*s, NC_6H_4N, $CH_2C_6H_4(OCH_3)$-3 and $CH_2C_6H_5$); 11.85 (s, 1H, NC*H*N) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 25 ^{o}C): δ = 51.6 ($CH_2C_6H_5$); 51.7 ($CH_2C_6H_4(OCH_3)$-3); 55.6 ($CH_2C_6H_4(OCH_3)$-3); 113.7, 113.8, 113.9, 114.7, 114.8, 120.3, 127.0, 127.1, 127.9, 128.3, 129.2, 129.4, 130.4, 131.3, 131.4, 132.8, 134.2, 160.2 (arom. *C*s, NC_6H_4N, $CH_2C_6H_4(OCH_3)$-3 and $CH_2C_6H_5$); 143.7 (N*C*HN) ppm. Elemental analysis calcd (%) for $C_{22}H_{21}ClN_2O$ (Mr = 364.90): C 72.42, H 5.80, N 7.68; found (%): C 72.45, H 5.83, N 7.70.

*4.2.4. 1-(3-Methoxybenzyl)-3-(4-methoxybenzyl)benzimidazolium Chloride (**1d**)*

(1.20 g, yield 75%) ^{1}H NMR (300 MHz, $CDCl_3$, 25 ^{o}C): δ = 3.69 (s, 3H, $CH_2C_6H_4(OCH_3)$-4); 3.73 (s, 3H, $CH_2C_6H_4(OCH_3)$-3); 5.73 (s, 2H, $CH_2C_6H_4(OCH_3)$-4); 5.76 (s, 2H, $CH_2C_6H_4(OCH_3)$-3); 6.78-7.54 (m, 12H, arom. C*H*s, NC_6H_4N, $CH_2C_6H_4(OCH_3)$-3 and $CH_2C_6H_4(OCH_3)$-4); 12.09 (s, 1H, NC*H*N) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 ^{o}C): δ = 50.2 ($CH_2C_6H_4(OCH_3)$-4); 50.5 ($CH_2C_6H_4(OCH_3)$-3); 54.3 ($CH_2C_6H_4(OCH_3)$-4); 54.6 ($CH_2C_6H_4(OCH_3)$-3); 112.7, 112.8, 113.7, 119.3, 123.7, 126.0, 126.1, 129.0, 129.4, 130.2, 130.4, 133.1, 159.2, 159.3 (arom. *C*s, NC_6H_4N, $CH_2C_6H_4(OCH_3)$-3 and $CH_2C_6H_4(OCH_3)$-4); 142.9 (N*C*HN) ppm. Elemental analysis calcd (%) for $C_{23}H_{23}ClN_2O_2$ (Mr = 394.90): C 69.95, H 5.87, N 7.09; found (%): C 69.97, H 5.88, N 7.11.

*4.2.5. 1-(3-Methoxybenzyl)-3-(2,3,5,6-tetramethylbenzyl)benzimidazolium Chloride (**1e**)*

(1.64 g, yield 93%) ^{1}H NMR (300 MHz, $CDCl_3$, 25 ^{o}C): δ = 2.18 and 2.19 (s, 12H, $CH_2C_6H(CH_3)_4$-2,3,5,6); 3.72 (s, 3H, $CH_2C_6H_4(OCH_3)$-3); 5.83 (s, 2H, $CH_2C_6H(CH_3)_4$-2,3,5,6); 5.84 (s, 2H, $CH_2C_6H_4(OCH_3)$-3); 6.76-7.51 (m, 9H, arom. C*H*s, NC_6H_4N, $CH_2C_6H_4(OCH_3)$-3 and $CH_2C_6H(CH_3)_4$-2,3,5,6); 11.42 (s, 1H, NC*H*N) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 ^{o}C): δ = 16.2 and 20.6 ($CH_2C_6H(CH_3)_4$-2,3,5,6); 47.9 ($CH_2C_6H(CH_3)_4$-2,3,5,6); 51.5 ($CH_2C_6H_4(OCH_3)$-3); 55.6 ($CH_2C_6H_4(OCH_3)$-3); 113.6, 113.8, 114.7, 120.1, 127.0, 127.6, 130.3, 131.6, 133.4, 133.6, 134.1, 134.5, 135.0, 135.1, 160.2 (arom. *C*s, NC_6H_4N, $CH_2C_6H_4(OCH_3)$-3 and $CH_2C_6H(CH_3)_4$-2,3,5,6); 143.9 (N*C*HN) ppm. Elemental analysis calcd (%) for $C_{26}H_{29}ClN_2O$ (Mr = 421.00): 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-(4-phenoxybutyl)benzimidazolium Chloride (**1f**)*

(1.46 g, yield 82%) ^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C): δ = 1.97 (pent, ^3J = 5.8 Hz, 2H, $CH_2CH_2CH_2CH_2OC_6H_5$); 2.32 (pent, ^3J = 7.3 Hz, 2H, $CH_2CH_2CH_2CH_2OC_6H_5$); 3.78 (s, 3H, $CH_2C_6H_4(OCH_3)$-3); 4.04 (t, ^3J = 5.8 Hz, 2H, $CH_2CH_2CH_2CH_2OC_6H_5$); 4.75 (t, ^3J = 7.3 Hz, 2H, $CH_2CH_2CH_2CH_2OC_6H_5$); 5.84 (s, 2H, $CH_2C_6H_4(OCH_3)$-3); 6.82-7.71 (m, 13H, arom. C*H*s, NC_6H_4N, $CH_2C_6H_4(OCH_3)$-3 and $CH_2CH_2CH_2CH_2OC_6H_5$); 11.78 (s, 1H, NC*H*N) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 25 ^{o}C): δ = 26.1 ($CH_2CH_2CH_2CH_2OC_6H_5$); 26.4 ($CH_2CH_2CH_2CH_2OC_6H_5$); 47.4 ($CH_2CH_2CH_2CH_2OC_6H_5$); 51.3 ($CH_2C_6H_4(OCH_3)$-3); 55.6 ($CH_2C_6H_4(OCH_3)$-3); 66.7 ($CH_2CH_2CH_2CH_2OC_6H_5$); 113.1, 113.8, 114.4, 114.8, 120.4, 120.8, 127.2, 129.5, 130.4, 131.2, 131.5, 134.3, 158.5, 160.2 (arom. *C*s, NC_6H_4N, $CH_2C_6H_4(OCH_3)$-3 and $CH_2CH_2CH_2CH_2OC_6H_5$); 143.5 (N*C*HN) ppm. Elemental analysis calcd (%) for $C_{25}H_{27}ClN_2O_2$ (Mr = 422.90): C 70.99, H 6.43, N 6.62; found (%): C 71.02, H 6.44, N 6.63.

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

All benzimidazolium chlorides were converted, with moderated yields, into the palladium(II)-NHC complexes (**2a-f**). A suspension of the benzimidazolium chloride (1.0 mmol) and $Pd(OAc)_2$ (0.50 mmol) in degassed DMSO (3 mL) was heated with vigorous stirring at 100 ^{o}C for 24 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 to remove the unreacted $Pd(OAc)_2$ and benzimidazolium chloride. Next, the crude complex was crystallized from dichloromethane/diethyl ether mixture (1:2, *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 40-59% yields.

*4.3.1. cis/trans-Dichloro-bis[1-(3-methoxybenzyl)-3-(4-chlorobenzyl)benzimidazol-2-ylidene]palladium(II) (**2a**)*

(0.234 g, yield 52%) ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C): δ = 3.69 and 3.70 (s, 6H, $CH_2C_6H_4(OCH_3)$-3); 5.26 and 5.29 (s, 4H, $CH_2C_6H_4(Cl)$-4); 6.20 and 6.23 (s, 4H, $CH_2C_6H_4(OCH_3)$-3); 6.80-7.59 (m, 24H, arom. C*H*s, NC_6H_4N, $CH_2C_6H_4(OCH_3)$-3 and $CH_2C_6H_4(Cl)$-4) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 ^{o}C): δ = 52.7 and 52.8 ($CH_2C_6H_4(Cl)$-4); 52.9 and 53.0 ($CH_2C_6H_4(OCH_3)$-3); 55.6 and 55.7 ($CH_2C_6H_4(OCH_3)$-3); 111.3, 111.4, 112.5, 112.6, 114.5, 114.7, 120.2, 120.3, 123.0, 127.8, 127.9, 128.7, 128.8, 129.5, 134.8, 135.4, 135.5, 137.0, 137.1, 160.0, 160.1 (arom. *C*s, NC_6H_4N, $CH_2C_6H_4(OCH_3)$-3 and $CH_2C_6H_4(Cl)$-4); 182.3 and 182.5 (Pd-$C_{carbene}$) ppm. Elemental analysis calcd (%) for $C_{44}H_{38}Cl_4N_4O_2Pd$ (Mr = 903.00): C 58.52, H 4.24, N 6.20; found (%): C 58.54, H 4.26, N 6.22.

*4.3.2. cis/trans-Dichloro-bis[1-(3-methoxybenzyl)-3-(n-butyl) benzimidazol-2-ylidene]palladium(II) (**2b**)*

(0.203 g, yield 53%) ^{1}H NMR (300 MHz, $CDCl_3$, 25 ^{o}C): δ = 0.72 and 1.01 (t, ^3J = 7.4 Hz, 6H, $CH_2CH_2CH_2CH_3$); 1.22 and 1.53 (hext, ^3J = 7.6 Hz, 4H, $CH_2CH_2CH_2CH_3$); 2.06 and 2.21 (pent, ^3J = 7.6 Hz, 4H, $CH_2CH_2CH_2CH_3$); 3.56 and 3.68 (s, 6H, $CH_2C_6H_4(OCH_3)$-3); 4.68 and 4.79 (t, ^3J = 7.8 Hz, 4H, $CH_2CH_2CH_2CH_3$); 5.90 and 6.07 (s, 4H, $CH_2C_6H_4(OCH_3)$-3); 6.65-7.32 (m, 16H, arom. C*H*s, NC_6H_4N and $CH_2C_6H_4(OCH_3)$-3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 ^{o}C): δ = 13.7 and 14.0 ($CH_2CH_2CH_2CH_3$); 20.4 and 20.7 ($CH_2CH_2CH_2CH_3$); 31.8 and 31.9 ($CH_2CH_2CH_2CH_3$); 48.3 and 48.4 ($CH_2CH_2CH_2CH_3$); 52.8 and 53.2 ($CH_2C_6H_4(OCH_3)$-3); 55.6 and 55.8 ($CH_2C_6H_4(OCH_3)$-3); 110.3, 110.4, 111.4, 111.5, 112.5, 112.6, 114.4, 114.8, 120.2, 122.8, 122.9, 129.4, 129.7, 134.3, 134.6, 134.9, 135.0, 137.1, 137.2, 160.0, 160.3 (arom. *C*s, NC_6H_4N and $CH_2C_6H_4(OCH_3)$-3); 181.7 and 181.8 (Pd-$C_{carbene}$) ppm. Elemental analysis calcd (%) for $C_{38}H_{44}Cl_2N_4O_2Pd$ (Mr = 766.10): C 59.57, H 5.79, N 7.31; found (%): C 59.59, H 5.80, N 7.33.

*4.3.3. cis/trans-Dichloro-bis[1-(3-methoxybenzyl)-3-(benzyl)benz imidazol-2-ylidene]palladium(II) (**2c**)*

(0.246 g, yield 59%) ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C): δ = 3.61 and 3.62 (s, 6H, $CH_2C_6H_4(OCH_3)$-3); 5.92 and 5.94 (s, 4H, $CH_2C_6H_5$); 5.95 and 5.97 (s, 4H, $CH_2C_6H_4(OCH_3)$-3); 6.71-7.39 (m, 26H, arom. C*H*s, NC_6H_4N, $CH_2C_6H_4(OCH_3)$-3 and $CH_2C_6H_5$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 ^{o}C): δ = 52.7 and 52.8 ($CH_2C_6H_5$); 52.9 and 53.0 ($CH_2C_6H_4(OCH_3)$-3); 55.6 and 55.7 ($CH_2C_6H_4(OCH_3)$-3); 111.3, 111.4, 114.5, 114.7, 120.2, 120.3,

127.8, 127.9, 128.6, 128.7, 134.8, 135.5, 137.0, 137.1, 160.0, 160.1 (arom. *C*s, NC_6H_4N, $CH_2C_6H_4(OCH_3)$-3 and $CH_2C_6H_5$); 182.3 and 182.4 (Pd-$C_{carbene}$) ppm. Elemental analysis calcd (%) for $C_{44}H_{40}Cl_2N_4O_2Pd$ (Mr = 834.10): C 63.36, H 4.83, N 6.72; found (%): C 63.38, H 4.85, N 6.75.

4.3.4. Dichloro-bis[1-(3-methoxybenzyl)-3-(4-methoxybenzyl) benzimidazol-2-ylidene]palladium(II) ***(2d)***

(0.263 g, yield 59%) ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C): δ = 3.61 (s, 6H, $CH_2C_6H_4(OCH_3)$-4); 3.66 (s, 6H, $CH_2C_6H_4(OCH_3)$-3); 5.96 (s, 4H, $CH_2C_6H_4(OCH_3)$-4); 5.99 (s, 4H, $CH_2C_6H_4(OCH_3)$-3); 6.69-7.40 (m, 24H, arom. C*H*s, NC_6H_4N, $CH_2C_6H_4(OCH_3)$-3 and $CH_2C_6H_4(OCH_3)$-4) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 ^{o}C): δ = 51.8 ($CH_2C_6H_4(OCH_3)$-4); 52.4 ($CH_2C_6H_4(OCH_3)$-3); 55.2 ($CH_2C_6H_4(OCH_3)$-4); 55.6 ($CH_2C_6H_4(OCH_3)$-3); 111.3, 112.4, 114.0, 114.1, 114.5, 114.7, 120.1, 123.0, 127.7, 129.0, 129.1, 129.5, 134.5, 137.3, 159.2, 160.1 (arom. *C*s, NC_6H_4N, $CH_2C_6H_4(OCH_3)$-3 and $CH_2C_6H_4(OCH_3)$-4); 181.9 (Pd-$C_{carbene}$) ppm. Elemental analysis calcd (%) for $C_{46}H_{44}Cl_2N_4O_4Pd$ (Mr = 894.20): C 61.79, H 4.96, N 6.27; found (%): C 61.81, H 4.98, N 6.29.

4.3.5. cis/trans-Dichloro-bis[1-(3-methoxybenzyl)-3-(2,3,5,6-tetramethylbenzyl)benzimidazol-2-ylidene]palladium(II) ***(2e)***

(0.189 g, yield 40%) ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C): δ = 2.23, 2.24, 2.27 and 2.34 (s, 24H, $CH_2C_6H(CH_3)_4$-2,3,5,6); 3.66 and 3.68 (s, 6H, $CH_2C_6H_4(OCH_3)$-3); 6.09 and 6.20 (s, 4H, $CH_2C_6H(CH_3)_4$-2,3,5,6); 6.23 and 6.34 (s, 4H, $CH_2C_6H_4(OCH_3)$-3); 6.72-7.32 (m, 18H, arom. C*H*s, NC_6H_4N, $CH_2C_6H_4(OCH_3)$-3 and $CH_2C_6H(CH_3)_4$-2,3,5,6) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 ^{o}C): δ = 16.5, 16.7, 20.5 and 20.6 ($CH_2C_6H(CH_3)_4$-2,3,5,6); 50.7 and 50.8 ($CH_2C_6H(CH_3)_4$-2,3,5,6); 52.2 and 52.3 ($CH_2C_6H_4(OCH_3)$-3); 55.4 and 55.5 ($CH_2C_6H_4(OCH_3)$-3); 111.0, 111.1, 111.8, 111.9, 112.3, 112.6, 114.4, 114.5, 119.9, 120.2, 122.4, 122.5, 122.9, 123.1, 129.4, 129.6, 131.0, 131.1, 132.2, 132.3, 134.2, 134.3, 134.6, 134.7, 134.8, 134.9, 137.3, 137.4, 160.0, 160.1 (arom. *C*s, NC_6H_4N, $CH_2C_6H_4(OCH_3)$-3 and $CH_2C_6H(CH_3)_4$-2,3,5,6); 182.2 and 182.3 (Pd-$C_{carbene}$) ppm. Elemental analysis calcd (%) for $C_{52}H_{56}Cl_2N_4O_2Pd$ (Mr = 946.40): C 66.00, H 5.96, N 5.92; found (%): C 66.01, H 5.98, N 5.94.

4.3.6. cis/trans-Dichloro-bis[1-(3-methoxybenzyl)-3-(4-phenoxy-butyl)benzimidazol-2-ylidene]palladium(II) ***(2f)***

(0.213 g, yield 45%) ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C): δ = 1.65 and 1.95 (pent, ^3J = 6.0 Hz, 4H, $CH_2CH_2CH_2CH_2OC_6H_5$); 2.29 and 2.46 (pent, ^3J = 7.0 Hz, 4H, $CH_2CH_2CH_2CH_2OC_6H_5$); 3.36 and 3.63 (s, 6H, $CH_2C_6H_4(OCH_3)$-3); 3.69 and 3.94 (t, ^3J = 5.8 Hz, 4H, $CH_2CH_2CH_2CH_2OC_6H_5$); 4.80 and 4.90 (t, ^3J = 7.0 Hz, 4H, $CH_2CH_2CH_2CH_2OC_6H_5$); 5.93 and 6.10 (s, 4H, $CH_2C_6H_4(OCH_3)$-3); 6.70-7.34 (m, 26H, arom. C*H*s, NC_6H_4N, $CH_2C_6H_4(OCH_3)$-3 and $CH_2CH_2CH_2CH_2OC_6H_5$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 ^{o}C): δ = 26.8 and 27.0 ($CH_2CH_2CH_2CH_2OC_6H_5$); 27.1 and 27.2 ($CH_2CH_2CH_2CH_2OC_6H_5$); 47.9 and 48.0 ($CH_2CH_2CH_2CH_2OC_6H_5$); 52.3 and 52.5 ($CH_2C_6H_4(OCH_3)$-3); 55.5 and 55.7 ($CH_2C_6H_4(OCH_3)$-3); 67.1 and 67.3 ($CH_2CH_2CH_2CH_2OC_6H_5$); 110.4, 110.5, 111.3, 111.4, 112.3, 112.4, 114.4, 114.5, 114.6, 114.7, 119.9, 120.0, 120.6, 120.7, 123.1, 123.2, 129.4, 129.5, 129.6, 129.7, 134.1, 134.3, 134.6, 134.7, 137.3, 158.9, 160.0, 160.1, 160.3 (arom. *C*s, NC_6H_4N, $CH_2C_6H_4(OCH_3)$-3 and $CH_2CH_2CH_2CH_2OC_6H_5$); 181.7 and 181.8 (Pd-$C_{carbene}$) ppm. Elemental analysis calcd (%) for $C_{50}H_{52}Cl_2N_4O_4Pd$ (Mr = 950.30): C 63.19, H 5.52, N 5.90; found (%): C 63.34, H 5.58, N 5.97.

4.4. General procedure for the direct arylation of thiazole derivatives

An oven dried 10 mL Schlenk tube was charged with palladium(II)-NHC complex (0.01 mmol), thiazole derivative, (2-*n*-propylthiazole or 4,5-dimethylthiazole), (2.0 mmol), aryl bromide derivative, (bromobenzene, 4-bromotoluene, 4-bromoanisole, 4-bromobenzaldehyde or 4-bromoacetophenone), (1.0 mmol), KOAc (2.0 mmol), and DMAc (2 mL) under argon. The Schlenk tube was placed in a preheated oil bath at 150 °C, and the reaction mixture was stirred for 1 h. Completion of the reaction, the solvent was removed under vacuum and the residue was charged directly onto a micro silica gel column. The products were eluted by using *n*-pentane/diethyl ether mixture (4:1, *v/v*). The chemical characterizations of the products were made by NMR. The conversions were based on the aryl halide by GC and GC-MS.

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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**) and their corresponding palladium(II)-NHC complexes (**2a-f**) with general formula $[PdCl_2(NHC)_2]$ were synthesized, (NHC = *N*-heterocyclic carbene).

- The obtained palladium(II)-NHC complexes were characterized by NMR (^{1}H and ^{13}C), IR spectroscopy and microanalysis techniques.

- These palladium(II)-NHC complexes were used as efficient catalysts in the direct C2- or C5-arylation of thiazoles with aryl bromides.