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Palladium-NHC-PEPPSI Complexes: Synthesis, Characterization and Catalytic Activity in the Direct C5-Arylation of 2-Substituted Thiophene Derivatives with Aryl Halides

Murat Kaloğlu,[a,b] İsmail Özdemir*[a,b] Vincent Dorcet,[c] Christian Bruneau,[c] and Henri Doucet[c]

Abstract: Benzimidazolium salts (**2a-f**) having their two nitrogen atoms substituted by different alkyl groups have been synthesized in high yields. The benzimidazolium salts were readily converted into the corresponding PEPPSI-type palladium-NHC complexes (**3a-f**) (PEPPSI= pyridine-enhanced precatalyst preparation, stabilisation, and initiation). The structures of all compounds were characterized by ^{1}H NMR, ^{13}C NMR, IR and elemental analysis techniques, which supported the proposed structures. The molecular structure of the complex **3f** was determined by single-crystal *X*-ray diffraction. The catalytic activity of PEPPSI-type palladium-NHC complexes was evaluated in the direct C5-arylation of 2-substituted thiophene derivatives with various aryl halides. This arylation occured efficiently and selectively at the C5-position of 2-substituted thiophene derivatives.

Introduction

The use of *N*-heterocyclic carbenes (NHCs) as ligands for transition metals was first described in 1968 by Öfele[1] and Wanzlick.[2] The development of metal-NHC complexes by Lappert[3] in the early 1970s and the isolation of the first stable free NHC by Arduengo and co-workers[4] in 1991 set the scene for an ever-growing interest and advancement in the field of NHC chemistry. Shortly thereafter, NHCs have been utilized extensively as ligands of transition metal complexes in organometallic chemistry and homogeneous catalysis.[5-17]

Since the initial work by Ohta and co-workers, [18] transition metal-catalyzed direct arylation reactions have been rapidly developing for the synthesis of a wide range of heteroarenes and it still receives much interest from academic and industrial research groups.[19-28]

The direct arylation of heteroarenes with aryl halides has become the most valuable method for the formation of C(sp^2)-C(sp^2) bonds in contemporary organic synthesis because of the numerous applications of heteroaromatic compounds as biologically active compounds and functional materials.[29,30] Thiophene derivatives show valuable biological activities and present considerable interest in pharmaceutical chemistry. As selected examples, Canagliflozin[31a] is a drug for treatment of type-2 diabetes, Evista[31b] is used for the prevention and treatment of osteoporosis, Saviprazole[31c] is a gastric proton pump inhibitor, Tiflucarbine[31d] displays antidepressant properties and Motapizone[31e] is used against platelet aggregation. Because of these properties, the discovery of simple and direct accesses to thiophene derivatives remains an important challenge for organic chemists.

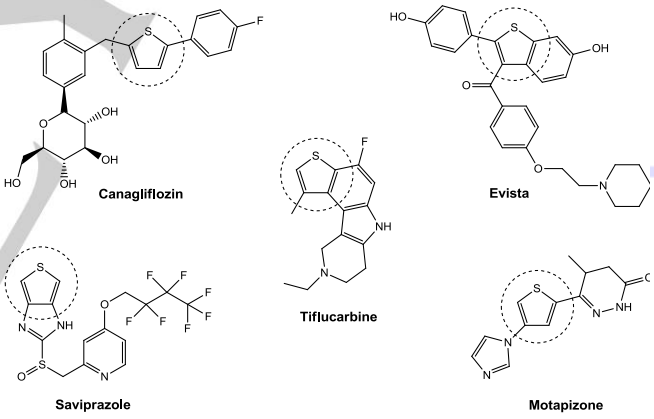
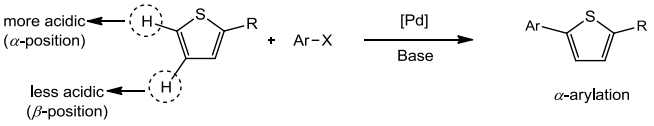


Figure 1. Examples of biologically active thiophene derivatives.

Palladium-catalyzed direct arylation of C-H bonds of thiophenes with aryl halides is known to occur preferentially at the *α*-positions to the sulfur atom (C2 and/or C5) following the typical reactivity profiles of the thiophene ring (Scheme 1). [32]



Scheme 1. Pd-catalyzed direct C5-arylation of 2-substituted thiophenes with aryl halides.

A number of palladium complexes with a single NHC ligand have proven to be useful catalysts in cross-coupling reactions of aryl halides.[33,34] Among the most popular catalysts for such reactions are PEPPSI-type palladium-NHC complexes

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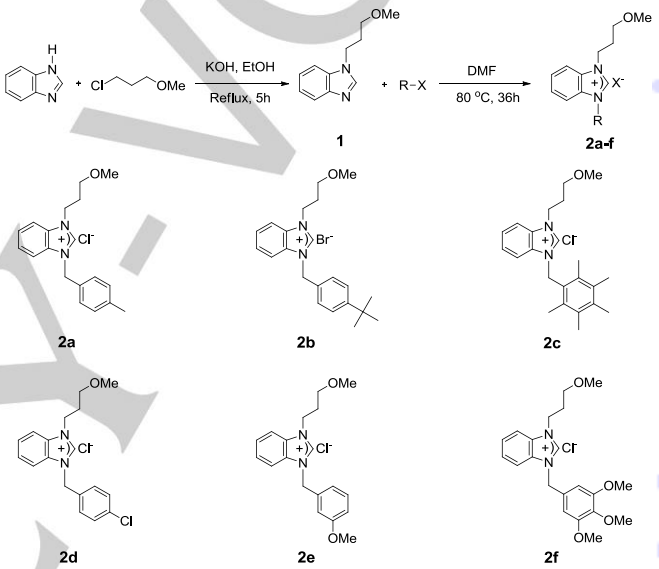
of the type [PdX_2(NHC)(pyridine)], (X= halide, PEPPSI= Pyridine-Enhanced Precatalyst Preparation, Stabilization and Initiation), which have gained real practical importance in numerous catalytic processes.[35] In 2006, Organ *et al.* reported[36] easily-handled, air and moisture-stable Pd-NHC complexes through the PEPPSI method that featured Pd(II) species bearing an NHC ligand, two halides, and a labile ligand such as 3-chloropyridine. A lot of work has been done by many groups since 2006 on this type of complexes,[37] but only a few examples deal with the direct arylation of heteroarenes.[38] In view of the above information and the growing interest of PEPPSI-type palladium-NHC complexes in catalysis we decided to investigate the catalytic activity of new members of this family in the direct C5-arylation of 2-substitued thiophenes.

We now describe the synthesis and characterization of the benzimidazolium salts (**2a-f**) as NHC species, and their corresponding PEPPSI-type palladium-NHC complexes (**3a-f**). These compounds were characterized by ^{1}H and ^{13}C NMR, IR and elemental analysis. The structure of the *trans*-dibromo[1-(3-methoxypropyl)-3-(3,4,5-trimethoxybenzyl)benzimidazol-2-ylide-ne](pyridine)palladium(II) complex (**3f**) was determined by single-crystal X-ray diffraction. We then examined the activity of the PEPPSI-type palladium-NHC complexes in the direct C5-arylation of 2-substituted thiophene derivatives with various aryl bromides and aryl chlorides as coupling partners.

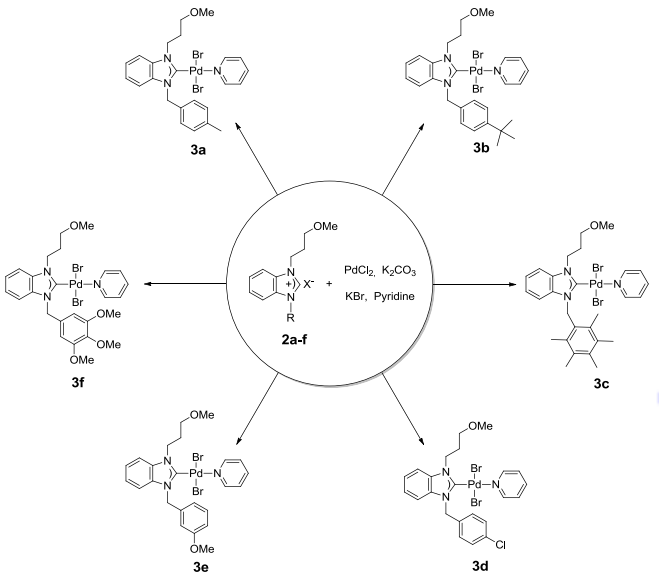
Results and Discussion

Preparation of benzimidazolium salts: The benzimidazolium salts (**2a-f**) were prepared by reacting *N*-(3-methoxypropyl)-benzimidazole (**1**) with various alkyl halides in DMF at 80 °C for 36 h (Scheme 2). The benzimidazolium salts (**2a-f**) were air- and moisture-stable both in the solid state and in solution. The structures of the salts were determined by their characteristic spectroscopic data and elemental analyses. In the ^{13}C NMR spectra of **2a-f**, the characteristic signals of the imino carbon, (N*C*HN) were detected as typical singlets at 143.8, 143.8, 143.2, 143.8, 143.7 and 143.8 ppm, respectively. The ^{1}H NMR signals of the C(2)-*H* protons were observed as sharp singlets at chemical shifts of 11.82, 11.49, 10.86, 11.83, 11.55 and 11.68 ppm, respectively for **2a-f**, and further supported the assigned structures. These NMR values were in line with those found for other benzimidazolium salts of the literature.[39] The formation of the benzimidazolium salts were also evidenced by their IR spectra, which showed (CN) bond absorption at 1560, 1557, 1556, 1557, 1558 and 1594 cm^{-1} for the respective CN bond vibration of **2a-f**.

Preparation of the PEPPSI-type palladium-NHC complexes: The general procedure for the preparation of PEPPSI-type palladium-NHC complexes (**3a-f**) according to the method reported by Organ[36] is shown in Scheme 3. Benzimidazolium salts (**2a-f**) were incorporated into the PEPPSI-type palladium-NHC complexes (**3a-f**) by reaction with $PdCl_2$ in refluxing pyridine in the presence of K_2CO_3 as a base and a large excess of KBr for 16 h. These complexes, which were stable both in solution and in solid state against air, light and moisture, were soluble in different solvents such as dimethylsulfoxide, chloroform, dichloromethane and diethylether. The absence of the characteristic signals of the imino carbon (143-144 ppm) and the acidic imino proton (10-12 ppm) in ^{13}C NMR and ^{1}H NMR, which were present in the salts (**2a-f**) suggested the formation of the NHC-carbenes and their coordination to form the PEPPSI-type palladium-NHC complexes. In addition, the characteristic carbenic carbons in compounds **3a-f** appeared in the ^{13}C NMR spectra as deshielded singlets at 163.6, 162.2, 163.1, 163.1, 163.1 and 162.0 ppm, respectively. The IR data also clearly indicated the presence of (CN) vibration at 1408, 1408, 1425, 1405, 1412 and 1410 cm^{-1} for **3a-f**. The formation of carbenes is correlated by a shift of the (CN) vibration from 1556-1594 cm^{-1} in the benzimidazolium salts to 1408-1425 cm^{-1} in the coordinated carbenes.



Scheme 2. Synthesis of the benzimidazolium salts (**2a-f**).



Scheme 3. Synthesis of the PEPPSI-type palladium-NHC complexes (**3a-f**).

Structural characterization of complex 3f: Single crystals of complex **3f** suitable for diffraction study were obtained by slow diffusion of *n*-pentane into a dichloromethane solution of complex **3f**. The molecular structure of complex **3f** has been confirmed by X-ray single-crystal analyses. This complex crystallizes in a centrosymmetric monoclinic $P\ 1\ 2_1/c\ 1$ system, and adopts a square planar geometry. The carbene and the pyridine ligands are in *trans*-position with respective distances to the palladium centre of 1.963(7) Å and 2.109(6) Å. The molecular structure of complex **3f** is shown in Figure 1, and selected bond lengths and angles are summarized in Table 1.

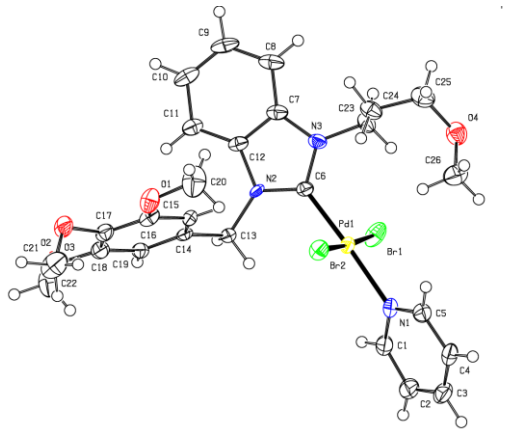
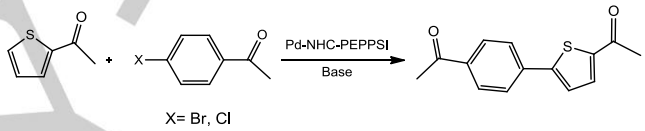


Figure 2. Perspective view of the molecular structure of **3f**.

Table 1. Selected bond lengths [Å] and angles [°] for complex **3f**.

Pd1-C6	1.963(7)	N1-Pd1-Br1	92.03(16)
Pd1-N1	2.109(6)	N1-Pd1-Br2	91.21(16)
Pd1-Br1	2.4180(9)	Br1-Pd1-Br2	176.27(4)
Pd1-Br2	2.4265(9)	C5-N1-Pd1	123.0(5)
C6-Pd1-N1	177.0(3)	C1-N1-Pd1	118.9(5)
C6-Pd1-Br1	87.70(19)	N2-C6-Pd1	125.7(5)
C6-Pd1-Br2	89.17(19)	N3-C6-Pd1	127.4(5)

Direct C5-arylation of 2-substituted thiophene derivatives: In order to screen the experimental conditions, we selected the complex **3f** as the catalyst. In all of complexes, methoxypropyl group linked to the nitrogen atom of the benzimidazole ring has an oxygen atom oriented toward the metal center. This orientation has also been proven for complex **3f** by X-ray analysis (see Figure 2). For this reason, we think that this group could be hamilable effect throughout the catalytic cycle. We also selected the 2-acetylthiophene as model heteroaromatic substrate with a blocked C2-position (Scheme 4). The results of the reaction parameters including solvent, base, temperature and catalyst loading are gathered in Table 2.



Scheme 4. Pd-NHC-PEPPSI-catalyzed direct C5-arylation of 2-acetylthiophene with 4-chloroacetophenone and 4-bromoacetophenone.

Table 2. Influence of the reaction conditions for Pd-NHC-PEPPSI catalyzed direct C5-arylation of 2-acetylthiophene with 4-chloro- and 4-bromoacetophenone.[a]

Entry	Pd-NHC-PEPPSI (mol %)	X	Solvent	Base	Time (h)	Temp. (°C)	Conversion[b] (%)	Yield[c] (%)
1	**3f** (1)	Br	DMAc	NaOAc	2	120	61	54
2	**3f** (1)	Br	DMF	NaOAc	2	120	34	30
3	**3f** (1)	Br	Toluene	NaOAc	2	120	47	41
4	**3f** (1)	Br	DMAc	K_2CO_3	2	120	31	22
5	**3f** (1)	Br	DMF	K_2CO_3	2	120	19	11
6	**3f** (1)	Br	Toluene	K_2CO_3	2	120	24	18
7	**3f** (1)	Br	DMAc	KOAc	2	120	86	71
8	**3f** (1)	Br	DMF	KOAc	2	120	46	37
9	**3f** (1)	Br	Toluene	KOAc	2	120	58	49
10	**3f** (1)	Br	DMAc	KOAc	2	130	91	84
11	**3f** (1)	Br	DMAc	KOAc	2	150	100	91
12	**3f** (0.5)	Br	DMAc	KOAc	2	150	81	78
13	**3f** (1)	Br	DMAc	KOAc	1	150	84	78
14	**3f** (1)	Cl	DMAc	KOAc	2	150	14	8
15	**3f** (1)	Cl	DMAc	KOAc	5	150	24	12
16	**3f** (1)	Cl	DMAc	KOAc	10	150	43	34
17	**3f** (1)	Cl	DMAc	KOAc	15	150	68	58
18	**3f** (1)	Cl	DMAc	KOAc	20	150	87	79
19	**3f** (1)	Cl	DMAc	KOAc	20	120	64	36
20	**3f** (1)	Cl	DMAc	KOAc	20	130	71	51
21	**3f** (1)	Cl	DMAc	KOAc	25	150	90	81

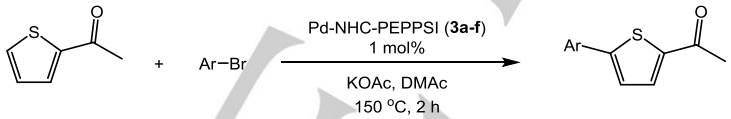
[a] Conditions: 2-acetylthiophene (2 mmol), aryl halide (1 mmol), base (2 mmol), solvent (2 mL). [b] Conversions were calculated according to aryl halide by GC and GC-MS. [c] Isolated yields.

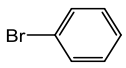
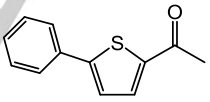
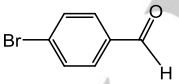
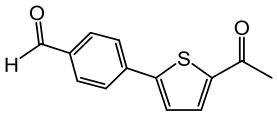
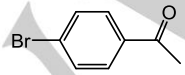
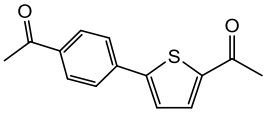
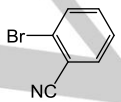
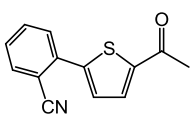
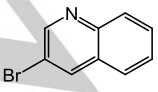
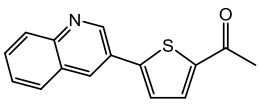
When DMF or toluene were used as solvent, the reaction gave low conversion of only 19-58% with NaOAc, K_2CO_3 or KOAc as base after 2 h at 120 °C (Table 2, entries 2, 3, 5, 6, 8, 9). DMAc proved to be the best tested solvent after 2 h at 120 °C. In this solvent decreasing the reaction temperature from 150 °C to 120 °C had a detrimental effect on the conversion (Table 2, entries 1, 4, 7, 10, 11). In the presence of 0.5 mol% of **3f** 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 in 78% isolated yield (Table 2, entry 12). When the reaction time was reduced to 1 h, the reaction gave low conversion of only 84% (Table 2, entry 13). Finally, the best conditions leading to full conversion of 4-bromoacetophenone with high selectivity in favor of the C5-arylated product were obtained when the reaction was carried out in DMAc in the presence of 2 equiv. of KOAc at 150 °C for 2 h (Table 2, entry 11).

When the less reactive 4-chloroacetophenone was used as substrate in the presence of 1 mol% of catalyst **3f** and KOAc as the base at 150 °C, the conversions increased depending on the reaction time (Table 2, entries 14, 15, 16, 17). Interestingly, up to 87% conversion with 79% isolated yield were obtained, but for this the reaction required a longer reation time of 20 h (Table 2, entry 18). The reaction temperature decreasing from 150 °C to 120 °C had a detrimental effect on the conversion (Table 2, entries 19 and 20). When the reaction time was increased from 20 h to 25 h at 150 °C, the very close conversion of 4-chloroacetophenone was obtained (Table 2, entry 21).

Finally, the scope of the direct C5-arylation of two 2-substituted thiophene substrates was investigated with various aryl halides, including five (hetero)aryl bromides (Tables 3 and 5) and four aryl chlorides (Tables 4 and 6) applying our best experimental conditions. Only a minor effect of the carbene ligand on the Pd-PEPPSI complex was observed for the coupling of aryl bromides with thiophene derivatives. In all cases, except in a few cases with complex **3f**, high conversions of the aryl bromide were observed, and the coupling products were isolated in high yields. At elevated temperature, the oxidative addition of the aryl bromide to palladium is generally easy and does not require the use of very specific ligands. A more important effect of the nature of the ligand was expected for the coupling of aryl chlorides with the thiophenes derivatives (Tables 4 and 6).[32j] Indeed, again in all cases the coupling products were produced in good yields. Surprisingly, similar yields were obtained for the coupling of electron-deficient aryl chlorides (Tables 4 and 6, entries 13-24) as with chlorobenzene (Table 4 and 6, entries 1-6). In this case, the presence of the NHC-ligands on palladium likely favors the oxidative addition step.

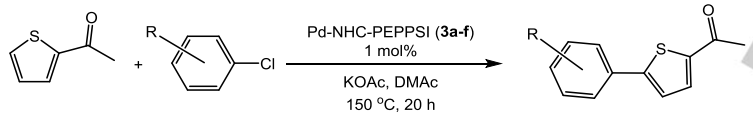
Table 3. Pd-NHC-PEPPSI-catalyzed direct C5-arylation of 2-acetylthiophene with aryl bromides.[a]

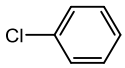
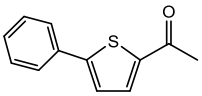
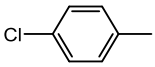
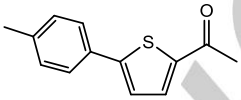
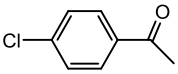
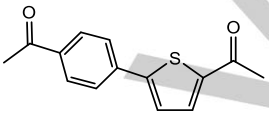
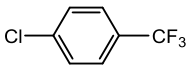
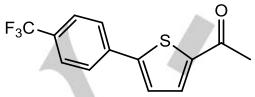


Entry	Aryl bromide	Catalyst	Product	Conversion[b] (%)	Yield[c] (%)
1		**3a**		79	71
2		**3b**		83	75
3		**3c**		90	88
4		**3d**		96	85
5		**3e**		85	80
6		**3f**		90	87
7		**3a**		91	82
8		**3b**		83	79
9		**3c**		100	92
10		**3d**		97	90
11		**3e**		96	84
12		**3f**		100	90
13		**3a**		76	70
14		**3b**		98	88
15		**3c**		93	87
16		**3d**		87	84
17		**3e**		86	81
18		**3f**		100	91
19		**3a**		86	82
20		**3b**		83	74
21		**3c**		100	93
22		**3d**		94	91
23		**3e**		91	83
24		**3f**		100	85
25		**3a**		91	84
26		**3b**		87	81
27		**3c**		98	87
28		**3d**		100	92
29		**3e**		93	88
30		**3f**		98	87

[a] Conditions: Pd-NHC-PEPPSI (0.01 mmol), 2-acetylthiophene (2 mmol), aryl bromide (1 mmol), KOAc (2 mmol), DMAc (2 mL), 150 °C, 2 h.
[b] Conversions were calculated according to aryl bromide by GC. [c] Isolated yields.

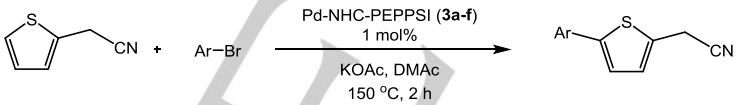
Table 4. Pd-NHC-PEPPSI catalyzed direct C5-arylation of 2-acetylthiophene by using aryl chlorides.[a]

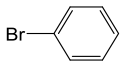
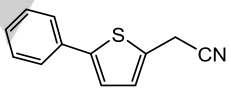
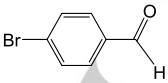
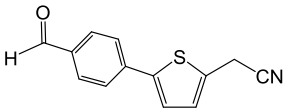
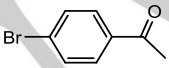
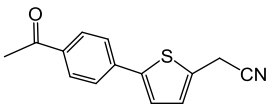
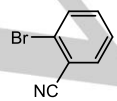
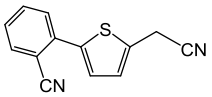
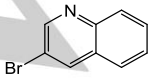
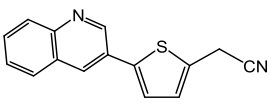


Entry	Aryl chloride	Catalyst	Product	Conversion[b] (%)	Yield[c] (%)
1		**3a**		87	78
2		**3b**		59	54
3		**3c**		51	44
4		**3d**		63	57
5		**3e**		74	71
6		**3f**		83	76
7		**3a**		71	64
8		**3b**		63	57
9		**3c**		59	51
10		**3d**		68	66
11		**3e**		78	69
12		**3f**		79	61
13		**3a**		78	76
14		**3b**		86	79
15		**3c**		50	41
16		**3d**		76	69
17		**3e**		64	60
18		**3f**		87	79
19		**3a**		80	74
20		**3b**		94	88
21		**3c**		66	61
22		**3d**		88	80
23		**3e**		73	64
24		**3f**		81	72

[a] Conditions: Pd-NHC-PEPPSI (0.01 mmol), 2-acetylthiophene (2 mmol), aryl chloride (1 mmol), KOAc (2 mmol), DMAc (2 mL), 150 °C, 20 h.
[b] Conversions were calculated according to aryl chloride by GC. [c] Isolated yields.

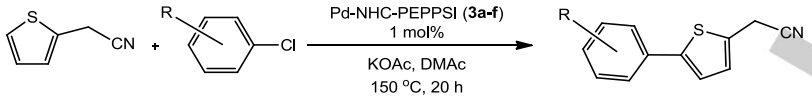
Table 5. Pd-NHC-PEPPSI catalyzed direct C5-arylation of 2-cyanomethylthiophene by using aryl bromides.[a]

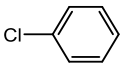
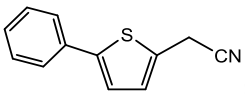
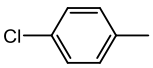
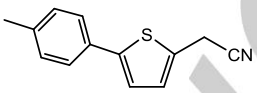
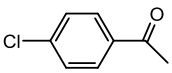
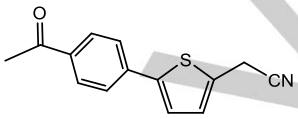
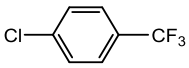
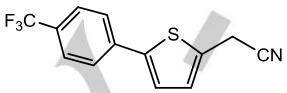


Entry	Aryl bromide	Catalyst	Product	Conversion[b] (%)	Yield[c] (%)
1		**3a**		88	84
2		**3b**		78	71
3		**3c**		85	79
4		**3d**		74	69
5		**3e**		89	85
6		**3f**		79	72
7		**3a**		100	91
8		**3b**		90	86
9		**3c**		100	88
10		**3d**		86	80
11		**3e**		90	71
12		**3f**		84	78
13		**3a**		89	81
14		**3b**		88	77
15		**3c**		84	77
16		**3d**		93	87
17		**3e**		97	89
18		**3f**		73	68
19		**3a**		94	89
20		**3b**		76	71
21		**3c**		83	78
22		**3d**		84	79
23		**3e**		81	78
24		**3f**		61	56
25		**3a**		93	86
26		**3b**		87	84
27		**3c**		77	74
28		**3d**		88	82
29		**3e**		84	77
30		**3f**		75	73

[a] Conditions: Pd-NHC-PEPPSI (0.01 mmol), 2-cyanomethylthiophene (2 mmol), aryl bromide (1 mmol), KOAc (2 mmol), DMAc (2 mL), 150 °C, 2 h.
[b] Conversions were calculated according to aryl bromide by GC. [c] Isolated yields.

Table 6. Pd-NHC-PEPPSI catalyzed direct C5-arylation of 2-cyanomethylthiophene by using aryl chlorides.[a]



Entry	Aryl chloride	Catalyst	Product	Conversion[b] (%)	Yield[c] (%)
1		**3a**		73	64
2		**3b**		71	65
3		**3c**		78	74
4		**3d**		71	68
5		**3e**		83	77
6		**3f**		70	68
7		**3a**		62	58
8		**3b**		57	54
9		**3c**		49	44
10		**3d**		67	64
11		**3e**		71	63
12		**3f**		64	59
13		**3a**		85	79
14		**3b**		78	76
15		**3c**		74	70
16		**3d**		88	84
17		**3e**		74	60
18		**3f**		70	61
19		**3a**		69	65
20		**3b**		63	58
21		**3c**		76	72
22		**3d**		75	70
23		**3e**		75	73
24		**3f**		78	74

[a] Conditions: Pd-NHC-PEPPSI (0.01 mmol), 2-cyanomethylthiophene (2 mmol), aryl chloride (1 mmol), KOAc (2 mmol), DMAc (2 mL), 150 °C, 20 h.
[b] Conversions were calculated according to aryl chloride by GC. [c] Isolated yields.

Conclusions

In summary, we have prepared a series of new benzimidazolium salts from *N*-substituted benzimidazole. These benzimidazolium salts were metallated with $PdCl_2$ in pyridine to give easily-handled, air and moisture stable new PEPPSI-type palladium-NHC complexes. Then, all benzimidazolium salts and PEPPSI-type palladium-NHC complexes were characterized using different spectroscopic and analytical techniques. The structure of complex **3f** was determined by single-crystal X-ray diffraction. The PEPPSI-type palladium-NHC complexes were used in the direct C5-arylation of 2-substituted thiophenes.

The catalytic systems generated from these PEPPSI-type palladium-NHC complexes in the presence of KOAc as the base and DMAc as the solvent at 150 °C were very efficient at 1 mol% catalyst loading for the selective C-C bond formation from aryl halides. When the catalytic studies were evaluated, it was found that all of the complexes were suitable for the direct C5-arylation of 2-substituted thiophene derivatives with aryl bromides. With these catalysts, even non-activated aryl chlorides such as chlorobenzene or 4-chlorotoluene were coupled with thiophenes derivatives in good yields.

It is clear that, the use of PEPPSI-type palladium-NHC complexes as catalysts in the direct arylation of thiophenes was very limited in the literature. Also, this study has some advantages such as low catalyst loading and less reaction time when compered with the previously reported studies on the arylation of thiophene derivatives.[29f,30j,32c,38c]

Experimental Section

General Methods: All manipulations were performed in Schlenk type flasks under argon. All chemical reactants were obtained from commercial sources. The solvents used were purified by distillation over the drying agents indicated and were transferred under argon. Pd-NHC-PEPPSI complexes were prepared according to known methods in the literature.[37] DMAc analytical grade (99%) was not distilled before use. KOAc (99%) was employed. ^{1}H NMR (used 300 and 500 MHz) and ^{13}C NMR (used 75 and 125 MHz) spectra were recorded in $CDCl_3$. Chemical shifts (δ) are reported in ppm relative to $CDCl_3$. ^{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 $CDCl_3$). IR spectra were recorded on ATR unit in the range of 400-4000 cm^{-1} with Perkin Elmer Spectrum 100 Spectrofotometer. Melting points were determined in glass capillaries under air with an Electrothermal-9200 melting point apparatus. Elemental analyses were performed by İnönü University Scientific and Technological Research Center (İBTAM). 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.

General procedure for the preparation of benzimidazolium salts: For the preparation of *N*-(3-methoxypropyl)benzimidazole (**1**), benzimidazole (1.0 mmol) and potassium hydroxide (1.0 mmol) were dissolved in ethyl alcohol (50 mL). 3-Methoxypropyl chloride (1.0 mmol) was slowly added and the reaction mixture was stirred at room temperature for 1 h. The solution was refluxed for 5 h, then cooled to room temperature and the precipitated potassium chloride was removed by filtration. The solvent was removed by distillation. The crude product was then distilled under vacuum. For the preparation of the benzimidazolium salts (**2a-f**), *N*-(3-methoxypropyl)benzimidazole (**1**), (1.0 mmol) was dissolved in dried dimethylformamide (3 mL) and the alkyl halide (1.0 mmol) was added

slowly. The reaction mixture was stirred at 80 °C for 36 h under argon. After completion of the reaction, all dimethylformamide was removed by vacuum and diethylether (15 mL) was added to obtain a white crystalline solid, which was filtered off. The solid was washed with diethylether (3 × 10 mL) and dried under vacuum. The crude product was recrystallized from an ethanol/diethylether mixture (1:2, *v/v*).

1-(3-Methoxypropyl)-3-(4-methylbenzyl)benzimidazolium chloride (2a): Yield: 1.76 g, 91%; mp: 130-131 °C; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): *δ* 2.30 (s, 3H, $NCH_2C_6H_4(CH_3)$-4); 2.36 (p, *J*= 5.6 Hz, 2H, $NCH_2CH_2CH_2OCH_3$); 3.27 (s, 3H, $NCH_2CH_2CH_2OCH_3$); 3.49 (t, *J*= 5.4 Hz, 2H, $NCH_2CH_2CH_2OCH_3$); 4.74 (t, *J*= 7.0 Hz, 2H, $NCH_2CH_2CH_2OCH_3$); 5.84 (s, 2H, $NCH_2C_6H_4(CH_3)$-4); 7.15-7.76 (m, 8H, NC_6H_4N, $NCH_2C_6H_4(CH_3)$-4); 11.82 (s, 1H, NCHN). ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): *δ* 21.2 ($NCH_2C_6H_4(CH_3)$-4); 29.7 ($NCH_2CH_2CH_2OCH_3$); 45.0 ($NCH_2CH_2CH_2OCH_3$); 51.3 ($NCH_2C_6H_4(CH_3)$-4); 58.8 ($NCH_2CH_2CH_2OCH_3$); 68.9 ($NCH_2CH_2CH_2OCH_3$); 113.0, 113.7, 126.9, 128.3, 129.9, 130.0, 130.1, 131.0, 131.8, 139.1 (NC_6H_4N, $NCH_2C_6H_4(CH_3)$-4); 143.8 (NCHN). IR (cm^{-1}) $\nu_{(CN)}$: 1560; Anal. Calcd. for $C_{19}H_{23}ClN_2O$: C, 68.97; H, 7.01; N, 8.47. Found: C, 68.78; H, 7.02; N, 8.49.

1-(3-Methoxypropyl)-3-(4-*tert*-butylbenzyl)benzimidazolium bromide (2b): Yield: 2.12 g, 87%; mp: 161-162 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): *δ* 1.19 (s, 9H, $NCH_2C_6H_4(C(CH_3)_3)$-4); 2.29 (p, *J*= 5.6 Hz, 2H, $NCH_2CH_2CH_2OCH_3$); 3.18 (s, 3H, $NCH_2CH_2CH_2OCH_3$); 3.42 (t, *J*= 5.4 Hz, 2H, $NCH_2CH_2CH_2OCH_3$); 4.67 (t, *J*= 7.0 Hz, 2H, $NCH_2CH_2CH_2OCH_3$); 5.76 (s, 2H, $NCH_2C_6H_4(C(CH_3)_3)$-4); 7.32-7.70 (m, 8H, NC_6H_4N, $NCH_2C_6H_4(C(CH_3)_3)$-4); 11.49 (s, 1H, NCHN). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): *δ* 29.6 ($NCH_2CH_2CH_2OCH_3$); 31.2 ($NCH_2C_6H_4(C(CH_3)_3)$-4); 34.6 ($NCH_2C_6H_4(C(CH_3)_3)$-4); 45.0 ($NCH_2CH_2CH_2OCH_3$); 51.0 ($NCH_2C_6H_4(C(CH_3)_3)$-4); 58.7 ($NCH_2CH_2CH_2OCH_3$); 68.9 ($NCH_2CH_2CH_2OCH_3$); 113.0, 113.7, 126.2, 126.3, 127.0, 127.1, 128.1, 129.8, 131.1, 131.7, 152.4 (NC_6H_4N, $NCH_2C_6H_4(CH_3)$-4); 143.8 (NCHN). IR (cm^{-1}) $\nu_{(CN)}$: 1557; Anal. Calcd. for $C_{22}H_{29}BrN_2O$: C, 63.31; H, 7.00; N, 6.71. Found: C, 63.38; H, 7.12; N, 6.79.

1-(3-Methoxypropyl)-3-(2,3,4,5,6-pentamethylbenzyl)benzimidazolium chloride (2c): Yield: 1.55 g, 84%; mp: 143-144 °C; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): *δ* 2.20 (p, *J*= 5.3 Hz, 2H, $NCH_2CH_2CH_2OCH_3$); 2.23, 2.26 and 2.28 (s, 15H, $NCH_2C_6(CH_3)_5$-2,3,4,5,6); 3.20 (s, 3H, $NCH_2CH_2CH_2OCH_3$); 3.44 (t, *J*= 5.5 Hz, 2H, $NCH_2CH_2CH_2OCH_3$); 4.82 (t, *J*= 6.9 Hz, 2H, $NCH_2CH_2CH_2OCH_3$); 5.84 (s, 2H, $NCH_2C_6(CH_3)_5$-2,3,4,5,6); 7.33-7.79 (m, 4H, NC_6H_4N); 10.86 (s, 1H, NCHN). ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): *δ* 17.0, 17.1 and 17.3 ($NCH_2C_6(CH_3)_5$-2,3,4,5,6); 29.7 ($NCH_2CH_2CH_2OCH_3$); 45.1 ($NCH_2CH_2CH_2OCH_3$); 48.1 ($NCH_2C_6(CH_3)_5$-2,3,4,5,6); 58.7 ($NCH_2CH_2CH_2OCH_3$); 69.0 ($NCH_2CH_2CH_2OCH_3$); 113.1, 113.6, 125.1, 127.0, 131.3, 131.9, 133.6, 133.9, 137.3 (NC_6H_4N, $NCH_2C_6(CH_3)_5$-2,3,4,5,6); 143.2 (NCHN). IR (cm^{-1}) $\nu_{(CN)}$: 1556; Anal. Calcd. for $C_{23}H_{31}ClN_2O$: C, 71.39; H, 8.07; N, 7.24. Found: C, 71.78; H, 8.12; N, 7.29.

1-(3-Methoxypropyl)-3-(4-chlorobenzyl)benzimidazolium chloride (2d): Yield: 1.89 g, 90%; mp: 125-126 °C; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): *δ* 2.35 (p, *J*= 5.4 Hz, 2H, $NCH_2CH_2CH_2OCH_3$); 3.26 (s, 3H, $NCH_2CH_2CH_2OCH_3$); 3.47 (t, *J*= 5.4 Hz, 2H, $NCH_2CH_2CH_2OCH_3$); 4.71 (t, *J*= 7.0 Hz, 2H, $NCH_2CH_2CH_2OCH_3$); 5.96 (s, 2H, $NCH_2C_6H_4(Cl)$-4); 7.29-7.76 (m, 8H, NC_6H_4N, $NCH_2C_6H_4(Cl)$-4); 11.83 (s, 1H, NCHN). ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): *δ* 29.6 ($NCH_2CH_2CH_2OCH_3$); 45.1 ($NCH_2CH_2CH_2OCH_3$); 50.6 ($NCH_2C_6H_4(Cl)$-4); 58.8 ($NCH_2CH_2CH_2OCH_3$); 68.8 ($NCH_2CH_2CH_2OCH_3$); 113.1, 113.6, 127.1, 129.5, 129.6, 129.9, 130.9, 131.6, 131.7, 135.2 (NC_6H_4N, $NCH_2C_6H_4(Cl)$-4); 143.8 (NCHN). IR (cm^{-1}) $\nu_{(CN)}$: 1557; Anal. Calcd. for $C_{18}H_{20}Cl_2N_2O$: C, 61.55; H, 5.74; N, 7.97. Found: C, 61.78; H, 5.82; N, 7.99.

1-(3-Methoxypropyl)-3-(3-methoxylbenzyl)benzimidazolium chloride (2e): Yield: 1.46 g, 74%; mp: 95-96 °C; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): *δ* 2.31 (p, *J*= 5.5 Hz, 2H, $NCH_2CH_2CH_2OCH_3$); 3.22 (s, 3H, $NCH_2CH_2CH_2OCH_3$); 3.44 (t, *J*= 5.4 Hz, 2H, $NCH_2CH_2CH_2OCH_3$); 3.75 (s, 3H, $NCH_2C_6H_4(OCH_3)$-3); 4.72 (t, *J*= 6.8 Hz, 2H, $NCH_2CH_2CH_2OCH_3$); 5.83 (s, 2H, $NCH_2C_6H_4(OCH_3)$-3); 6.79-7.74 (m, 8H, NC_6H_4N, $NCH_2C_6H_4(OCH_3)$-3); 11.55 (s, 1H, NCHN). ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): *δ* 29.6 ($NCH_2CH_2CH_2OCH_3$); 45.0 ($NCH_2CH_2CH_2OCH_3$); 51.2 ($NCH_2C_6H_4(OCH_3)$-3); 55.5 ($NCH_2C_6H_4(OCH_3)$-3); 58.7 ($NCH_2CH_2CH_2OCH_3$); 68.9 ($NCH_2CH_2CH_2OCH_3$); 113.0, 113.7, 113.9, 114.6, 120.3, 127.0, 130.3, 131.1, 131.7, 134.5, 160.2 (NC_6H_4N, $NCH_2C_6H_4(OCH_3)$-3); 143.7 (NCHN). IR (cm^{-1}) $\nu_{(CN)}$: 1558; Anal. Calcd. for $C_{19}H_{23}ClN_2O_2$: C, 65.79; H, 6.68; N, 8.08. Found: C, 65.78; H, 6.62; N, 8.01.

1-(3-Methoxypropyl)-3-(3,4,5-trimethoxylbenzyl)benzimidazolium chloride (2f): Yield: 2.15 g, 91%; mp: 121-122 °C; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): *δ* 2.34 (p, *J*= 5.4 Hz, 2H, $NCH_2CH_2CH_2OCH_3$); 3.24 (s, 3H $NCH_2CH_2CH_2OCH_3$); 3.46 (t, *J*= 5.3 Hz, 2H, $NCH_2CH_2CH_2OCH_3$); 3.79 and 3.85 (s, 9H, $NCH_2C_6H_2(OCH_3)_3$-3,4,5); 4.72 (t, *J*= 6.4 Hz, 2H, $NCH_2CH_2CH_2OCH_3$); 5.80 (s, 2H, $NCH_2C_6H_2(OCH_3)_3$-3,4,5); 7.57-7.75 (m, 6H, NC_6H_4N, $NCH_2C_6H_2(OCH_3)_3$-3,4,5); 11.68 (s, 1H, NCHN). ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): *δ* 29.6 ($NCH_2CH_2CH_2OCH_3$); 44.9 ($NCH_2CH_2CH_2OCH_3$); 51.7 ($NCH_2C_6H_2(OCH_3)_3$-3,4,5); 56.6 and 60.8 ($NCH_2C_6H_2(OCH_3)_3$-3,4,5); 58.7 ($NCH_2CH_2CH_2OCH_3$); 68.8 ($NCH_2CH_2CH_2OCH_3$); 106.1, 113.1, 113.6, 127.0, 128.6, 131.1, 131.7, 138.5, 153.8 (NC_6H_4N, $NCH_2C_6H_2(OCH_3)_3$-3,4,5); 143.8 (NCHN). IR (cm^{-1}) $\nu_{(CN)}$: 1594; Anal. Calcd. for $C_{21}H_{27}ClN_2O_4$: C, 61.99; H, 6.69; N, 6.88. Found: C, 62.03; H, 6.72; N, 6.92.

General procedure for the preparation of the PEPPSI-type palladium-NHC complexes: The PEPPSI-type palladium-NHC complexes (**3a-f**) were obtained in moderate to good yields using the standard procedure initially developed by Organ.[37] A mixture of K_2CO_3 (5.0 mmol), pyridine (3 mL), $PdCl_2$ (1.1 mmol), benzimidazolium salt (1.0 mmol), and KBr (10.0 mmol) was heated at 80 °C for 16 h. The reaction mixture was then filtered through a pad of celite and silica gel to remove the unreacted $PdCl_2$ and benzimidazolium salt. The solvent in the reaction medium was then removed. The resulting complexes were washed with *n*-pentane (3 × 5 mL) and dried under vacuum. The crude products were recrystallized from dichloromethane/*n*-pentane (1:2, *v/v*).

***trans*-Dibromo[1-(3-methoxypropyl)-3-(4-methylbenzyl)benzimidazole-2-ylidene](pyridine)palladium(II) (3a):** Yield: 0.12 g, 54%; mp: 79-80 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): *δ* 2.24 (s, 3H, $NCH_2C_6H_4(CH_3)$-4); 2.53 (p, *J*= 7.1 Hz, 2H, $NCH_2CH_2CH_2OCH_3$); 3.29 (s, 3H, $NCH_2CH_2CH_2OCH_3$); 3.44 (t, *J*= 5.6 Hz, 2H, $NCH_2CH_2CH_2OCH_3$); 4.95 (t, *J*= 7.1 Hz, 2H, $NCH_2CH_2CH_2OCH_3$); 6.10 (s, 2H, $NCH_2C_6H_4(CH_3)$-4); 7.04-7.73 and 8.92-8.95 (m, 13H, NC_6H_4N, $NCH_2C_6H_4(CH_3)$-4 and NC_5H_5). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): *δ* 21.2 ($NCH_2C_6H_4(CH_3)$-4); 30.1 ($NCH_2CH_2CH_2OCH_3$); 45.1 ($NCH_2CH_2CH_2OCH_3$); 53.0 ($NCH_2C_6H_4(CH_3)$-4); 58.6 ($NCH_2CH_2CH_2OCH_3$); 69.1 ($NCH_2CH_2CH_2OCH_3$); 110.5, 111.4, 123.1, 123.2, 124.5, 127.9, 129.5, 132.0, 134.0, 135.2, 137.8, 138.2, 151.2 (NC_6H_4N, $NCH_2C_6H_4(CH_3)$-4 and NC_5H_5); 163.6 (Pd-$C_{carbene}$). IR (cm^{-1}) $\nu_{(CN)}$: 1408; Anal. Calcd. for $C_{24}H_{27}Br_2N_3OPd$: C, 45.06; H, 4.25; N, 6.57. Found: C, 45.08; H, 4.27; N, 6.59.

***trans*-Dibromo[1-(3-methoxypropyl)-3-(4-*tert*-butylbenzyl)benzimidazole-2-ylidene](pyridine)palladium(II) (3b):** Yield: 0.19 g, 74%; mp: 109-110 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): *δ* 1.21 (s, 9H, $NCH_2C_6H_4(C(CH_3)_3)$-4); 2.54 (p, *J*= 5.6 Hz, 2H, $NCH_2CH_2CH_2OCH_3$); 3.30 (s, 3H, $NCH_2CH_2CH_2OCH_3$); 3.45 (t, *J*= 5.3 Hz, 2H, $NCH_2CH_2CH_2OCH_3$); 4.93 (t, *J*= 7.1 Hz, 2H, $NCH_2CH_2CH_2OCH_3$); 6.06 (s, 2H, $NCH_2C_6H_4(C(CH_3)_3)$-4); 7.00-7.70 and 8.94-8.98 (m, 13H, NC_6H_4N, $NCH_2C_6H_4(C(CH_3)_3)$-4 and NC_5H_5). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): *δ* 28.8 ($NCH_2CH_2CH_2OCH_3$); 30.3 ($NCH_2C_6H_4(C(CH_3)_3)$-4); 33.5 ($NCH_2C_6H_4(C(CH_3)_3)$-4); 44.3 ($NCH_2CH_2CH_2OCH_3$); 51.8 ($NCH_2C_6H_4(C(CH_3)_3)$-4); 57.6 ($NCH_2CH_2CH_2OCH_3$); 68.1 ($NCH_2CH_2CH_2OCH_3$); 109.4, 110.5, 122.0, 122.1, 123.4, 123.5, 124.7, 126.7, 126.8, 130.9, 133.1, 137.0, 151.0 (NC_6H_4N, $NCH_2C_6H_4(CH_3)$-4

and NC_5H_5); 162.2 (Pd-$C_{carbene}$). IR (cm^{-1}) $\nu_{(CN)}$: 1408; Anal. Calcd. for $C_{27}H_{33}Br_2N_3OPd$: C, 47.56; H, 4.88; N, 6.16. Found: C, 47.60; H, 4.92; N, 6.19.

***trans*-Dibromo[1-(3-methoxypropyl)-3-(2,3,4,5,6-pentamethylbenzyl) benzimidazole-2-ylidene](pyridine)palladium(II) (3c):** Yield: 0.21 g, 63%; mp: 204-205 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 2.25, 2.31 and 2.33 (s, 15H, $NCH_2C_6(CH_3)_5$-2,3,4,5,6); 2.61 (p, *J*= 6.1 Hz, 2H, $NCH_2CH_2CH_2OCH_3$); 3.38 (s, 3H, $NCH_2CH_2CH_2OCH_3$); 3.52 (t, *J*= 6.2 Hz, 2H, $NCH_2CH_2CH_2OCH_3$); 5.03 (t, *J*= 7.1 Hz, 2H, $NCH_2CH_2CH_2OCH_3$); 6.27 (s, 2H, $NCH_2C_6(CH_3)_5$-2,3,4,5,6); 6.40-7.83 and 8.98-9.00 (m, 9H, NC_6H_4N and NC_5H_5). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ 16.9, 17.3 and 17.4 ($NCH_2C_6(CH_3)_5$-2,3,4,5,6); 30.1 ($NCH_2CH_2CH_2OCH_3$); 45.2 ($NCH_2CH_2CH_2OCH_3$); 51.2 ($NCH_2C_6(CH_3)_5$-2,3,4,5,6); 58.6 ($NCH_2CH_2CH_2OCH_3$); 69.2 ($NCH_2CH_2CH_2OCH_3$); 110.2, 111.5, 122.6, 123.0, 124.4, 127.8, 133.1, 134.6, 135.0, 135.9, 138.0, 151.2 (NC_6H_4N, $NCH_2C_6(CH_3)_5$-2,3,4,5,6 and NC_5H_5); 163.1 (Pd-$C_{carbene}$). IR (cm^{-1}) $\nu_{(CN)}$: 1425; Anal. Calcd. for $C_{28}H_{35}Br_2N_3OPd$: C, 48.33; H, 5.07; N, 6.04. Found: C, 48.34; H, 5.07; N, 6.09.

***trans*-Dibromo[1-(3-methoxypropyl)-3-(4-chlorobenzyl)benzimidazole-2-ylidene](pyridine)palladium(II) (3d):** Yield: 0.10 g, 44%; mp: 92-93 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 2.52 (p, *J*= 7.0 Hz, 2H, $NCH_2CH_2CH_2OCH_3$); 3.30 (s, 3H, $NCH_2CH_2CH_2OCH_3$); 3.44 (t, *J*= 5.5 Hz, 2H, $NCH_2CH_2CH_2OCH_3$); 4.93 (t, *J*= 7.3 Hz, 2H, $NCH_2CH_2CH_2OCH_3$); 6.11 (s, 2H, $NCH_2C_6H_4$(Cl)-4); 7.20-7.75 and 8.92-8.94 (m, 13H, NC_6H_4N, $NCH_2C_6H_4$(Cl)-4 and NC_5H_5). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ 29.0 ($NCH_2CH_2CH_2OCH_3$); 44.2 ($NCH_2CH_2CH_2OCH_3$); 51.4 ($NCH_2C_6H_4$(Cl)-4); 57.6 ($NCH_2CH_2CH_2OCH_3$); 68.0 ($NCH_2CH_2CH_2OCH_3$); 109.7, 110.1, 122.3, 122.4, 123.6, 128.1, 128.3, 132.5, 132.8, 133.0, 134.1, 137.2, 150.2 (NC_6H_4N, $NCH_2C_6H_4$(Cl)-4 and NC_5H_5); 163.1 (Pd-$C_{carbene}$). IR (cm^{-1}) $\nu_{(CN)}$: 1405; Anal. Calcd. for $C_{23}H_{24}Br_2ClN_3OPd$: C, 41.85; H, 3.66; N, 6.37. Found: C, 41.87; H, 3.72; N, 6.39.

***trans*-Dibromo[1-(3-methoxypropyl)-3-(3-methoxylbenzyl)benzimidazole-2-ylidene](pyridine)palladium(II) (3e):** Yield: 0.18 g, 94%; mp: 138-139 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 2.53 (p, *J*= 6.0 Hz, 2H, $NCH_2CH_2CH_2OCH_3$); 3.30 (s, 3H, $NCH_2CH_2CH_2OCH_3$); 3.45 (t, *J*= 5.6 Hz, 2H, $NCH_2CH_2CH_2OCH_3$); 3.66 (s, 3H, $NCH_2C_6H_4(OCH_3)$-3); 4.91 (t, *J*= 7.2 Hz, 2H, $NCH_2CH_2CH_2OCH_3$); 6.06 (s, 2H, $NCH_2C_6H_4(OCH_3)$-3); 6.06-7.69 and 8.96-8.99 (m, 13H, NC_6H_4N, $NCH_2C_6H_4(OCH_3)$-3 and NC_5H_5). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ 29.6 ($NCH_2CH_2CH_2OCH_3$); 45.5 ($NCH_2CH_2CH_2OCH_3$); 53.7 ($NCH_2C_6H_4(OCH_3)$-3); 55.7 ($NCH_2C_6H_4(OCH_3)$-3); 58.6 ($NCH_2CH_2CH_2OCH_3$); 69.2 ($NCH_2CH_2CH_2OCH_3$); 110.5, 111.4, 113.0, 114.7, 120.4, 123.0, 123.1, 123.2, 124.6, 129.7, 134.2, 135.4, 136.5, 137.9, 152.6, 160.2 (NC_6H_4N, $NCH_2C_6H_4(OCH_3)$-3 and NC_5H_5); 163.1 (Pd-$C_{carbene}$). IR (cm^{-1}) $\nu_{(CN)}$: 1412; Anal. Calcd. for $C_{24}H_{27}Br_2N_3O_2Pd$: C, 43.96; H, 4.15; N, 6.41. Found: C, 43.95; H, 4.15; N, 6.40.

***trans*-Dibromo[1-(3-methoxypropyl)-3-(3,4,5-trimethoxylbenzyl)benzimidazole-2-ylidene](pyridine)palladium(II) (3f):** Yield: 0.26 g, 78%; mp: 176-177 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 2.62 (p, *J*= 7.2 Hz, 2H, $NCH_2CH_2CH_2OCH_3$); 3.39 (s, 3H, $NCH_2CH_2CH_2OCH_3$); 3.53 (t, *J*= 5.6 Hz, 2H, $NCH_2CH_2CH_2OCH_3$); 3.84 (s, 9H, $NCH_2C_6H_2(OCH_3)_3$-3,4,5); 5.00 (t, *J*= 7.2 Hz, 2H, $NCH_2CH_2CH_2OCH_3$); 6.10 (s, 2H, $NCH_2C_6H_2(OCH_3)_3$-3,4,5); 6.87-7.83 and 9.06-9.08 (m, 11H, NC_6H_4N, $NCH_2C_6H_2(OCH_3)_3$-3,4,5 and NC_5H_5). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ 29.6 ($NCH_2CH_2CH_2OCH_3$); 45.5 ($NCH_2CH_2CH_2OCH_3$); 54.0 ($NCH_2C_6H_2(OCH_3)_3$-3,4,5); 56.6 and 60.8 ($NCH_2C_6H_2(OCH_3)_3$-3,4,5); 58.6 ($NCH_2CH_2CH_2OCH_3$); 69.1 ($NCH_2CH_2CH_2OCH_3$); 105.3, 110.5, 111.4, 123.1, 123.2, 124.6, 130.6, 134.2, 135.4, 137.7, 138.0, 152.6, 153.6 (NC_6H_4N, $NCH_2C_6H_2(OCH_3)_3$-3,4,5 and NC_5H_5); 163.0 (Pd-$C_{carbene}$). IR (cm^{-1}) $\nu_{(CN)}$: 1410; Anal. Calcd. for $C_{26}H_{31}Br_2N_3O_4Pd$: C, 43.63; H, 4.37; N, 5.87. Found: C, 43.68; H, 4.42; N, 5.91.

General procedure for the arylation reaction: An oven dried Schlenk flask was charged with KOAc (1.0 mmol), aryl halide (1.0 mmol), 2-substituted thiophene derivative (2.0 mmol), Pd-NHC-PEPPSI complexes **3a-f** (1.0 mol%). Then degassed DMAc (2 mL) was added under an argon stream. The Schlenk flask was placed in a preheated oil bath at 150 °C, and the reaction mixture was stirred for different durations given in the specific tables. At the end of the reaction, the solvent was removed under vacuum, and the residue was charged directly onto a silica gel column. The products were eluted from *n*-hexane/diethylether mixture (5:1, *v/v*). The chemical characterizations of the products were made by GC and GC-MS. The convertions were based on aryl halides.

X-ray Crystallographic Data: Single crystals of complex **3f** suitable for X-ray analysis were obtained by slow diffusion of *n*-pentane into a dichloromethane solution of the complex **3f**. Empirical formula= $C_{26}H_{31}Br_2N_3O_4Pd$; *M*= 715.76 g.mol^{-1}; crystal color= yellow; crystal system= monoclinic; space group= $P\,1\,2_1/c\,1$ system; a= 7.4450(3), b= 45.231(2), c= 8.8912(5) Å, β= 111.745(2) °, *V*= 2781.0(2) Å^3. *Z*= 4, *d*= 1.710 g.cm^{-3}, μ= 3.577 mm^{-1}. *F*(000)= 1424; *T*= 150(2) K. The crystal size (0.340 × 0.200 × 0.150 mm) was studied with an D8 VENTURE Bruker AXS diffractometer. Mo-Kα radiation (λ= 0.71073 Å). The structure was solved by direct methods using the *SIR97* program,[40] and then refined with full-matrix least-square methods based on F^2 (*SHELXL-97*).[41] All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. H atoms were finally included in their calculated positions. A final refinement on F^2 with 6350 unique intensities and 329 parameters converged at $\omega R(F^2)$ = 0.1438 ($R(F)$= 0.0645) for 5558 observed reflections with $I > 2\sigma(I)$. w= 1 / [$\sigma(F_o^2)$ + aP^2 + bP] where P= [2F_c^2 + MAX(F_o^2, 0)] /3.

CCDC reference number is 1510296 (for complex **3f**) contain the supplementary crystallographic data for this paper. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

Supporting Information (see footnote on the first page of this article): for the ^{1}H NMR, ^{13}C NMR and IR spectra of benzimidazolium salts (**2a-f**) and PEPPSI-type palladium-NHC complexes (**3a-f**).

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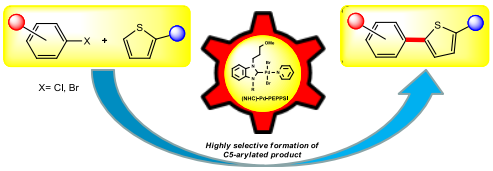

PEPPSI-type palladium-NHC complexes have been synthesized and the catalytic activity of the complexes have been evaluated in the direct C5-arylation of 2-substituted thiophene derivatives with various aryl bromides and aryl chlorides

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Palladium-NHC-PEPPSI Complexes: Synthesis, Characterization and Catalytic Activity in the Direct C5-Arylation of 2-Substituted Thiophene