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5-Nitrobenzimidazole containing Pd(II) catalyzed C-C cross-coupling reactions: The effect of the N-substituent of the benzimidazole structure on catalyst activity

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ABSTRACT

A series of Pd(II) complexes (**1a-e**) were successfully synthesized by reaction of *N*-substituted 5-nitrobenzimidazole with [PdCl₂(CNCH₃)₂] in toluene under argon reflux condition. Their catalytic activity in the Suzuki-Miyaura and Mizoroki-Heck coupling reactions were investigated. All these complexes were characterized by elemental analysis, ¹H NMR, ¹³C NMR and IR spectroscopy. The catalytic activities of *N*-substituted 5-nitrobenzimidazole palladium(II) complexes were screened in Mizoroki-Heck and Suzuki-Miyaura coupling reactions. The reactions were optimized for the most suitable temperature, solvent and base system. The Pd(II) complexes exhibited good catalytic activity at the Mizoroki-Heck reaction. Additionally, the Suzuki-Miyaura showed relatively excellent activity at the coupling reaction.

Keywords: 5-Nitrobenzimidazole, Catalytic activity, Suzuki-Miyaura, Spectroscopy

1. Introduction

Palladium-catalyzed C-C cross-coupling reactions, due to its versatile features, have become very popular in recent years [1]. A wide variety of organic products composed of these reactions are important substrates which are widely used for pharmaceutical applications and various chemical industries, such as arylated olefins, asymmetric biaryls, arylalkines [2,3].

Palladium-catalyzed C-C cross-coupling reactions are also used for agricultural chemistry, natural products, herbicides, molecular organic materials and components for optical device production [4-6]. C-C bond forming reactions, particularly the intense demand for new generation products which C-C bonds are formed under mild condition, have encouraged the scientists to produce more efficient catalysts formed under mild conditions and to motivate them to explore more efficient catalysts market [7]. These reactions are most advantageous among the well-known C-C bonding reactions. This is principally because they have a wide range of functional groups including bisbenzimidazole [8], nitrogen-containing ligands [9], carbenes [10,11] and more recently Schiff bases [12]. They also possess a light reaction conditions, and their starting reagents are cheap and possess low toxicity [13].

Synthesized ligand structures and donor groups have a strong effect on the catalytic performances of transition metal complexes, and therefore the ligand design has a considerable impact on the progression of catalytic science. The ligand used to obtain these complexes has a significant degree of structural and electronic properties, catalytic performance and selectivity [14]. On the other hand, the ligands are determinative in the stability of the active species and catalyst lifetime [15]. For this reason, a new environment-friendly, stable, inexpensive and easily accessible nitrogen-based ligand class has been developed in place of toxic, expensive and sensitive phosphine ligands. Such nitrogencontaining ligands form Pd(II) complexes exhibiting high stability and high catalytic performance for C-C binding reactions [16]. Thus, the development of efficient synthetic methods that provide easy access to such heterobiarils has aroused great interest in the field of synthetic chemistry [17]. Moreover, nitrogen-based ligands are generally non-toxic, harmless to nature, air/moisture insensitive, easy-to-use and have superior properties compared to certain disadvantages of conventional phosphine ligands [18]. Thus, palladium complexes with nitrogen-ligands attract significant attention [19-22].

Furthermore, C-C coupling reactions, particularly chelating ligands containing benzimidazole groups, have been studied extensively in the last two decades because of the transition metal compounds widely used as a ligand coordination chemistry of azoles [23-28]. Herein, the synthesis and characterization of five new Pd(II) complexes having aliphatic, methyl, methoxy and only aromatic moiety bearing benzylic different types of *N*-substituted 5-nitrobenzimidazole ligands and their catalytic activity in Suzuki-Miyaura and Mizoroki-Heck reactions were reported. All synthesized compounds were characterized using ¹H NMR, ¹³C NMR and IR spectroscopy and elemental analysis. The results of the characterization were found to support the proposed structures. The catalytic activities of newly synthesized Pd(II) complexes in the Suzuki-Miyaura and Mizoroki-Heck coupling reactions were investigated.

2. Experimental

The entire reactions for the preparation of Pd(II) complexes and *N*-coordinated 5nitrobenzimidazole as the ligand were carried out using the standard Schlenk techniques to degrade the glass materials under argon gas. Chemicals were purchased from Sigma Aldrich and Fluka. Melting points were detected in glass capillaries under air with an electrothermal-9200 melting point apparatus. FTIR spectra were recorded by KBr pellets in the range of 400-4000 cm⁻¹ on a Perkin Elmer Spectrum 65 spectrophotometer at the Center Research Laboratory located in Muş Alparslan University. ¹H and ¹³C NMR spectra were recorded with a Bruker Avance DPX at 300 Merkur spectrometer operated at 300 MHz in CDCl₃ with tetramethylsilane as an internal reference. Elemental analyses were recorded at the Research Center Laboratory of Inonu University. All catalytic reactions were monitored on an Agilent 6890N GC system by GC-FID with an HP-5 column of 30 m length, 0.32 mm diameter and 0.25 mm film thickness. Column chromatography was performed using silica gel 60 (70-230 mesh). Solvent ratios are given as v/v.

2.1. General procedure to synthesis of Pd(II) complexes(1a-e)

A solution of the *N*-substituted 5-nitrobenzimidazole (12 mmol) and $PdCl_2(CH_3CN)_2$ (6 mmol) in toluene (25 mL) were heated and refluxed for 5 h. Upon cooling to room temperature, the precipitates (**1a**–e) were obtained. The obtained products were recrystallized from dichloromethane/diethyl ether (1:3) at room temperature, filtered off and dried under vacuum.

Synthesis of dichloro-*N*-(benzyl)-5-nitrobenzimidazole palladium(II) **1a**. mp.:224°C. ¹H NMR (300 MHz, CDCl₃) δ : 8.76 (s, 1H, NCHN), 8.22-7.21 (m, 8H, NC₆H₃N and NCH₂C₆H₄), 5.46 (s, 2H, NCH₂C₆H₄(CH₃)-2). ¹³C NMR (300 MHz, CDCl₃) δ : 146.6 (NCHN), 110.1, 117.2, 118.9, 127.2, 128.8, 129.3, 134.3, 137.9, 143.3, (NC₆H₃N and NCH₂C₆H₄), 49.4 (NCH₂C₆H₄(CH₃)-2). IR (KBr, cm⁻¹): 1518 v(C=N). Anal. Calc. for C₂₈H₂₂N₆O₄PdCl₂: C, 49.16; H, 3.22; N, 12.29. Found: C, 49.16; H, 3.20; N, 12.28.

Synthesis of dichloro-*N*-(2-ethylbutane)-5-nitrobenzimidazole palladium(II) **1b**. mp: >320 °C. ¹H NMR (300 MHz, CDCl₃) δ : 8.60 (s, 1H, NCHN), 8.30-7.20 (m, 3H, NC₆H₃N), 4.06 (s, 2H, NCH₂CH(CH₂CH₃)₂), 1.84 (m, 1H,NCH₂CH(CH₂CH₃)₂), 1.29 and 1.27 (m, 4H, NCH₂CH(CH₂CH₃)₂), 0.90 (m, 6H, NCH₂CH(CH₂CH₃)₂). ¹³C NMR (300 MHz, CDCl₃) δ : 147.0 (NCHN), 146.8-105.8 (NC₆H₃N), 48.0 (NCH₂CH(CH₂CH₃)₂), 40.1 (NCH₂CH(CH₂CH₃)₂), 22.3 (NCH₂CH(CH₂CH₃)₂), 9.5 (NCH₂CH(CH₂CH₃)₂). IR (KBr, cm⁻¹): 1520 v(C=N). Anal. Calc. for C₂₆H₃₄N₆O₄PdCl₂: C, 46.45; H, 5.06; N, 12.51. Found: C, 46.47; H, 5.04; N, 12.50.

Synthesis of dichloro-*N*-(2-methylcyclohexyl)-5-nitrobenzimidazole palladium(II) **1c**. mp: 236 °C. ¹H NMR (300 MHz, CDCl₃) δ : 9.23(s, 1H, NCHN), 8.52-7.84 (m, 3H, NC₆H₃N), 4.58 (d, 2H, CH₂C₆H₁₁), 2.51 and 1.18 (m, 11H, CH₂C₆H₁₁). ¹³C NMR (300 MHz, CDCl₃) δ : 144.1 (NCHN), 143.8-109.8 (NC₆H₃N), 45.3 (CH₂C₆H₁₁), 36.0-25.4 (CH₂C₆H₁₁). IR (KBr, cm⁻¹): 1514 v(C=N). Anal. Calc. for C₂₈H₃₄N₆O₄PdCl₂: C, 48.31; H, 4.88; N, 12.07. Found: C, 48.28; H, 4.86; N, 12.05.

Synthesis of dichloro-*N*-(3,5-dimethylbenzyl)-5-nitrobenzimidazole palladium(II) **1d**. mp: 279 °C. ¹H NMR (300 MHz, CDCl₃) δ : 8.81 (s, 1H, NCHN), 8.67-7.20 (m, 6H, NC₆H₃N and NCH₂C₆H₃(CH₃)₂-3,5), 5.65 (s, 2H, NCH₂C₆H₃(CH₃)₃-3,5), 2.28 and 2.22 (s, 6H, NCH₂C₆H₃(CH₃)₂-3,5). ¹³C NMR (300 MHz, CDCl₃) δ : 149.7 (NCHN), 144.5-110.0 (NC₆H₃N and NCH₂C₆H₃(CH₃)₂-3,5), 49.01 (NCH₂C₆H₃(CH₃)₃-3,5), 20.81 (NCH₂C₆H₃(CH₃)₂-3,5). IR (KBr, cm⁻¹): 1520 v(C=N). Anal. Calc. for C₃₂H₃₀N₆O₄PdCl₂: C, 51.93; H, 4.05; N, 11.36. Found: C, 51.93; H, 4.05; N, 11.36.

Synthesis of dichloro-*N*-(3,4,5-trimethoxybenzyl)-5-nitrobenzimidazole palladium(II) **1e**. mp: 296 °C. ¹H NMR (300 MHz, CDCl₃) δ: 9.15 (s, 1H, NCHN), 8.71-6.70 (m, 5H, NC₆H₃N and NCH₂C₆H₂(OCH₃)-3,4,5), 5.55 (s, 2H, NCH₂C₆H₂(OCH₃)-3,4,5), 3.62 and 3.52 (s, 9H, NCH₂C₆H₂(OCH₃)-3,4,5). ¹³C NMR (300 MHz, CDCl₃) δ :153.1 (NCHN), 149.1-105.8 (NC₆H₃N and NCH₂C₆H₂(OCH₃)-3,4,5), 49.3 (NCH₂C₆H₂(OCH₃)-3,4,5), 60.02 and 56.1 (NCH₂C₆H₂(OCH₃)-3,4,5). IR (KBr, cm⁻¹): 1510 v(C=N). Anal. Calc. for C₃₄H₃₄N₆O₁₀PdCl₂: C, 47.25; H, 3.93; N,9.72. Found: C, 47.23; H, 3.91; N, 9.71.

2.2. General procedure for the Mizoroki-Heck type coupling reactions

After preliminary tests at different temperatures and different bases, the optimum condition for the reaction of aryl bromide and styrene was achieved with the use of ethanol (solvent), K_2CO_3 (base), 80 °C (temperature) and 3 h (duration). Palladium complexes (1.0 mmol%), aryl bromide (1.0 mmol), styrene (1.5 mmol), K_2CO_3 (2.0 mmol) and ethanol (3 mL) were added into a small Schlenk tube under atmosphere air, and the mixture was heated at 80 °C for 3 h. Isolated yield was determined by GC.

2.3. General procedure for the Suzuki-Miyaura type coupling reactions

After preliminary testing of various bases at different temperatures, the use of ethanol (solvent), K_2CO_3 (base), 80 °C (temperature) and 3 h (duration) provided the optimum condition for the reaction of aryl bromide and phenylboronic acid. Palladium complexes (1.0 mmol%), aryl bromide (0.2 mmol), phenylboronic acid (0.3 mmol), K_2CO_3 (1.2 mmol) and ethanol (3 mL) were added in to a small Schlenk tubes under atmosphere air, and the mixture was heated at 80 °C for 3 h. Isolated yield was determined by GC.

3. Result and discussion

Nitrogen-containing ligands have been found to be more stable against air and moisture. They are also modular and less expensive. In recent years, a number of various ligand design Pd(II) complexes are reported to exhibit high activity for the C-C coupling reactions [29]. In particular, the transition metal complexes with nitrogen-donor atoms containing the benzimidazole scaffold have been successfully utilized for the catalytic conversion of organic compounds [30]. These findings have encouraged the researchers in this field to examine the design and catalytic properties of new metal complexes with *N*-coordinated ligands [31]. All complexes are isolated from the air as stable, non-hygroscopic solids and can be dissolved in dimethylformamide, dimethylsulfoxide, chloroform, dichloromethane and halogenated solvents. However, they are insoluble in diethyl ether,

petroleum ether and n-hexane solution and also did not show any decomposition symptoms when exposed to air for days.

All compounds were synthesized in a single step, and the latter products were stable in solution and in solid form, as seen in Scheme1.

Scheme 1 Synthesis of palladium-*N*-5-nitrobenzimidazole complexes

The ¹H and ¹³C NMR of palladium complexes (**1a-e**) showed that the NCHN signals occurred between 8.60-9.23 ppm and 146.0-153.1 ppm, respectively. The ¹H NMR values indicated that the NCHN signals shifted to the low area in the palladium complexes compared to the corresponding ligand because of an electron withdrawing effect of the metal center. The IR spectrums showed that palladium-*N*-5-nitrobenzimidazole complexes (**1a-e**) exhibited a characteristic v(NCN) band typically at the range of 1510-1520 cm⁻¹.

Table 1

Table 2

It is of importance to determine the appropriate proportions and amounts of base and solvent. Therefore, many different bases and solvents were examined for the Suzuki-Miyaura reaction. At the beginning, many bases and different solvents were examined, as seen in the (Table 1, 2). For ethanol, the coupling reaction was completed at approximately 3 h when the most suitable base, K_2CO_3 , was used (Table 2, entry 9). The other bases such as NaOH, KOH, KO'Bu and Cs₂CO₃ produced slightly lower yields (Table 1, entries 1-5). The use of DMF, H₂O, ethanol, methanol, toluene, dioxane, THF, DMF+H₂O as solvents were studied (Table 2, entries 1-9) at elevated temperature. The tests indicated that high yields were obtained using ethanol as solvent and K₂CO₃ as a base. The reaction was effected at 80 °C temperature.

Table 3

Initially, the optimized conditions with arylboronic acid and various aryl halides (Table 1, Table 2) were investigated. For the structures of 4-bromo aryl substrates containing both electron donating (-OCH₃, -CH₃) and electron withdrawing (-CHO) groups, the desired products were obtained in yields at 70-100% in the presence of catalysts of Pd(II) (**1a-e**) complexes. In general, the activated bromides, 4-bromoacetophenone, 4-bromotoluene, 4-bromobenzaldehyde (Table 3, entries1, 8, 9, 13) could couple efficiently with phenylboronic acid **1a,1c, 1d** to afford the desired products in >99% yields. After that, the disubstituted

substrate p-bromobenzene, which provided the biaryl product in 70% yield, was obtained under the same reaction conditions (Table 3, entry 18). The reactions of phenylboronic acid with bromobenzene exhibited good yields of up to yield 70-87% at 80 °C (Table 3, entries 16-20). On the other hand, the presence of electron-donating or electron-withdrawing groups in the para-position, particularly in the para position due to the aryl bromides substrates, significantly contributed to the increase of the reaction rates by significantly affecting the catalyst activity. Palladium complexes (1a-e) were shown to be effective compounds for C-C binding reactions of Suzuki-Miyaura, and the C-C coupling products were obtained in high yield. The palladium complexes (1a-e) also promoted the transformation of biaryl in very high yields in the condition reactions (Table 3, entries 1,8,9,13). These results showed that five novel N-coordinated palladium complexes (1a-e) could catalyzed C-C coupling reaction. Almost all complexes were obviously good catalyst for Suzuki-Miyaura reaction. Both electron withdrawing releasing (p-Ar-Br) groups with phenylboronic acid provided the corresponding products with high yields. Moreover, the results showed that both activated and deactivated aryl bromides are efficiently converted into biaryl at these conditions. In this regard, N-donor ligand-based Pd(II) complexes have been reported in many studies [30]. Overall, these results suggest that the steric and electronic properties of the ligand are highly effective on the catalytic activity of the catalyst complexes.

Table 4

Table 5

Table 6

Initially, various solvents were investigated, and it was observed that the yield of **1a** was improved with ethanol (Table 5, entries 2,9). Then, other bases were examined, and the desired coupling product **1a** was obtained in high yields by employing K_2CO_3 as bases (Table 4, entry 4). Based on the results of other bases, such as Na₂CO₃, Cs₂CO₃, KOH, KO^tBu and NaOH, they are found to be less effective in obtaining the coupling product (Table 1, entries 1-5). Overall, the catalytic protocol using Pd(II) complexes as catalyst with K_2CO_3 as base in ethanol at 80 °C was determined to be the most effective method in a high yield (Table 6, entry 16). As attempt, no products were observed without the addition of palladium complex (Table 4, entry 6). Once the reaction conditions were established (e.g., base, solvent and temperature parameters), the full conversion was obtained (in Table 5, entry 10). It was found

that the reduction of the catalyst amount used in the reaction did not have an effect on the conversion products.

A model reaction was performed by stirring styrene with various types of aryl bromides, such as 4-bromoacetophenone, 4-bromotoluene, 4-bromobenzene, 4-bromobenzaldehyde in ethanol using (0.005 mmol) Pd(II) complexes at 80 °C for 3 h. Furthermore, when reactions were performed using aryl bromides, high yields were obtained in the case of the Pd(II) catalysts (1a-e) (Table 6, entries 5, 7, 9, 16, 18, 19, 23 and 25). When Table 6 is evaluated, catalysts were observed to be active in the Mizoroki-Heck reaction in general. In order to compare the catalyst performance, Pd(II) catalysts (1a-e) were tested under the same conditions. The yield increased on the substrate having the electron-donating or electronwithdrawing groups. It was observed that the catalyst exhibited higher conversion and yield. Optimized reaction conditions were tested, and the Pd(II) catalysts (1a-e) were reacted with both the electron-donating and the electron-withdrawing styrene and the aryl bromides reaction. Aryl bromides were converted to the corresponding coupled product in high yields (Table 6). Furthermore, increasing electron donating or electron-withdrawing on the aryl bromides did not have much effect on catalytic activities (Table 6, entry 1-25). That is, high yields were obtained when styrene reacted with both aryl bromides bearing electronwithdrawing or electron-donating substituent -CHO and -COCH₃, -OCH₃ and -CH₃ (Table 6, entries 1-15).

All in all, several factors are effective in catalyst performance. The catalyst performance, the molecular structure of the substrate, the electronic effects of the ligands and complex catalyst concentration used also play an important role. On the other hand, the reaction temperature is highly effective on the efficiency of the coupling product [4,15]. Moreover, ligand is found to have a significant impact both on the catalytic activity and sustainability. It is observed that Pd(II) catalysts (**1a-e**) exhibit higher conversions and yields [32, 33].

4. Conclusions

In this work, the preparation and characterization a series of new Pd(II) catalysts (1ae) and their catalytic activities for Mizoroki-Heck and Suzuki-Miyaura reactions are presented. Catalytic experiments show that for the C-C coupling product the Pd(II) catalysts (1a-e) can be obtained for a wide range of aryl bromide with styrene for good yields. 5-

nitrobenzimidazole Pd(II) complexes containing aryl and aliphatic positions are also observed to show a better activity. The results exhibit that their catalytic efficiency depends significantly on the ligand properties. Pd(II) catalysts (**1a-e**) listed in Table 3, Table 6 are determined to be highly effective compounds in the preparation of C-C coupling products obtained by coupling phenylboronic acid and aryl bromides and styrene to aryl bromides. It is also found that the activities of the Pd(II) complexes present in the Mizoroki-Heck coupling reactions are relatively lower than those of the Suzuki-Miyaura coupling reactions. Apparently, Pd(II) catalysts show a similar effectiveness in the formation of desired C-C coupling product under optimal conditions at 80 °C in ethanol. It is expected that catalysts such as [PdCl₂(N-substituted 5-nitrobenzimidazole)₂]will have environmental industrial applications because the preparation and purification of such catalysts are extremely simple. The observed catalytic activity demonstrates that synthesized *N*-coordinated 5nitrobenzimidazole Pd(II) catalysts (**1a-e**) are significantly effective for catalytic of Suzuki-Miyaura and Mizoroki-Heck coupling reaction.

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Scheme 1 Synthesis of palladium-N-5-nitrobenzimidazole complexes

Highlight

- ✓ Novel Pd(II) complexes synthesized and characterized.
- ✓ The catalytic activities of newly synthesized Pd(II) complexes in the Suzuki-Miyaura and Mizoroki-Heck coupling reactions were investigated.
- ✓ The synthesized Pd(II) complexes (1a-e) were found to exhibit good activity in Suzuki-Miyaura and Mizoroki-Heck C-C coupling reactions.

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Entry	Base	Time (h)	Conversion (%)
1	NaOH	10	40
2	Cs_2CO_3	10	51
3	Na ₂ CO ₃	10	27
4	K_2CO_3	10	100
5	KO ^t Bu	10	28
6	_	10	_

Table 1 Effect of bases for the Suzuki-Miyaura reaction

Reaction conditions: 4-Bromoacetophenone (0.2 mmol), phenylboronic acid (0.3 mmol), catalyst (0.001 mmol) and base (1.2 mmol), solvent (3 mL)

Table 2

Effect of solvents for the Suzuki-Miyaura reaction

Entry	Solvents	Time (h)	Conversion
			(%)
1	H_2O	24	-
2	Ethanol	10	100
3	Methanol	10	26
4	DMF	10	12
5	Toluene	10	21
6	Dioxane	10	80
7	THF	10	25
8	DMF+H ₂ O	10	16
9	Ethanol	3	100

Reaction conditions: 4-Bromoacetophenone (0.2 mmol), phenylboronic acid (0.3 mmol), catalyst (0.001 mmol) and base (1.2 mmol), solvent (3 mL)

Table 3

The Suzuki-Miyaura coupling reaction of aryl halides with phenylboronic acid 1a-e



Reaction conditions: 4-Bromoacetophenone (0.2 mmol), phenylboronic acid (0.3 mmol), catalyst (0.001 mmol) and base (1.2 mmol), EtOH (3 mL)

Entry	Base	Time (h)	Conversior (%)	
1	NaOH	10	42	
2	Cs_2CO_3	10	38	
3	Na ₂ CO ₃	10	30	
4	K_2CO_3	10	100	
5	KOtBu	10	31	
6	_	10	_	

Table 4Effect of bases for the Mizoroki-Heck reaction

Reaction conditions: 4-Bromobenzene (1 mmol), styrene (1.5 mmol), catalyst (% Pd(II) complexes(1a-e)) (0.005 mmol) and base (2 mmol), solvent (3 mL)

Table 5

Effect of solvents for the Mizoroki-Heck reaction

Entry	Solvents	Time (h)	Conversion
			(%)
1	H_2O	24	
2	Ethanol	10	100
3	Methanol	10	42
4	DMF	10	15
5	Toluene	10	13
6	Dioxane	10	75
7	THF	10	25
8	DMF+H ₂ O	10	16
9	Ethanol	3	100
10*	Ethanol	3	100

Reaction conditions: 4-Bromobenzene (1 mmol), styrene (1.5 mmol), catalyst (% Pd(II) complexes (1a-e)) (0.005 mmol) and base (2 mmol), solvent (3 mL),*catalyst% Pd(II) (0.001 mmol)

Table 6

The Mizoroki-Heck coupling reaction of aryl halides with styrene 1a-e



Entry	Catalyst(1a-e)	ArX	Time(h)	Yield(%)
1	1a		3	80
2	1b		3	82
3	1c	Br—COCH ₃	3	88
4	1d		3	70
5	1e		3	98
6	1a		3	93
7	1b		3	95
8	1c	Br—CH ₃	3	80
9	1d		3	99
10	1e		3	72
11	1a	$\overline{\boldsymbol{\mathcal{A}}}$	3	79
12	1b		3	68
13	1c	Br—OCH ₃	3	75
14	1d		3	60
15	1e		3	67
16	1 a		3	100
17	1b		3	73
18	1c	Br	3	95
19	1d		3	100
20	1e		3	100
21	1a		3	80
22	1b		3	90
23	1c	Br—CHO	3	100
24	1d		3	78

25	1e	 3	100

^aReaction conditions: R-C₆H₄Br-*p* (1 mmol), styrene (1.5 mmol), K₂CO₃ (2 mmol), % Pd(II) complexes (1a-e) (0.005 mmol), EtOH (3 mL), purity of compounds is checked by GC and NMR yields are based on *p*-arylbromide.

All reactions were monitored by GC. Temperature 80 °C, 3 h.