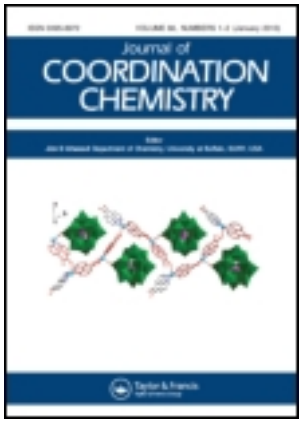


Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gcoo20

Palladium catalyzed Mizoroki-Heck and Suzuki-Miyaura reactions using naphthalenomethyl-substituted imidazolidin-2-ylidene ligands in aqueous media

Aydin Aktaş [a] , Senem Akkoç [b] & Yetkin Gök [a]

[a] Faculty of Science and Arts, Department of Chemistry , Inönü University , Malatya , Turkey

[b] Faculty of Science, Department of Chemistry , Erciyes University , Kayseri , Turkey

Accepted author version posted online: 25 Jun 2013.Published online: 24 Jul 2013.

To cite this article: Aydin Aktaş , Senem Akkoç & Yetkin Gök (2013) Palladium catalyzed Mizoroki-Heck and Suzuki-Miyaura reactions using naphthalenomethyl-substituted imidazolidin-2-ylidene ligands in aqueous media, Journal of Coordination Chemistry, 66:16, 2901-2909, DOI: 10.1080/00958972.2013.819092

To link to this article: http://dx.doi.org/10.1080/00958972.2013.819092

Journal of Coordination Chemistry, 2013
Vol. 66, No. 16, 2901–2909, http://dx.doi.org/10.1080/00958972.2013.819092

Palladium catalyzed Mizoroki–Heck and Suzuki–Miyaura reactions using naphthalenomethyl-substituted imidazolidin-2-ylidene ligands in aqueous media

AYDIN AKTAŞ†, SENEM AKKOÇ*‡ and YETKİN GÖK†

†Faculty of Science and Arts, Department of Chemistry, Inönü University, Malatya, Turkey; ‡Faculty of Science, Department of Chemistry, Erciyes University, Kayseri, Turkey

(*Received 11 April 2013; in final form 29 May 2013*)

Naphthalenomethyl-substituted imidazolidinium salts (**1a-g**) were prepared and characterized by conventional spectroscopic methods, ^{1}H NMR, ^{13}C NMR, FTIR, and elemental analysis techniques. The *in situ* prepared three component systems naphthalenomethyl-substituted imidazolidinium salts, $Pd(OAc)_2$, and K_2CO_3 catalyzed quantitatively the Mizoroki–Heck and Suzuki–Miyaura coupling of aryl halides under mild conditions in aqueous media.

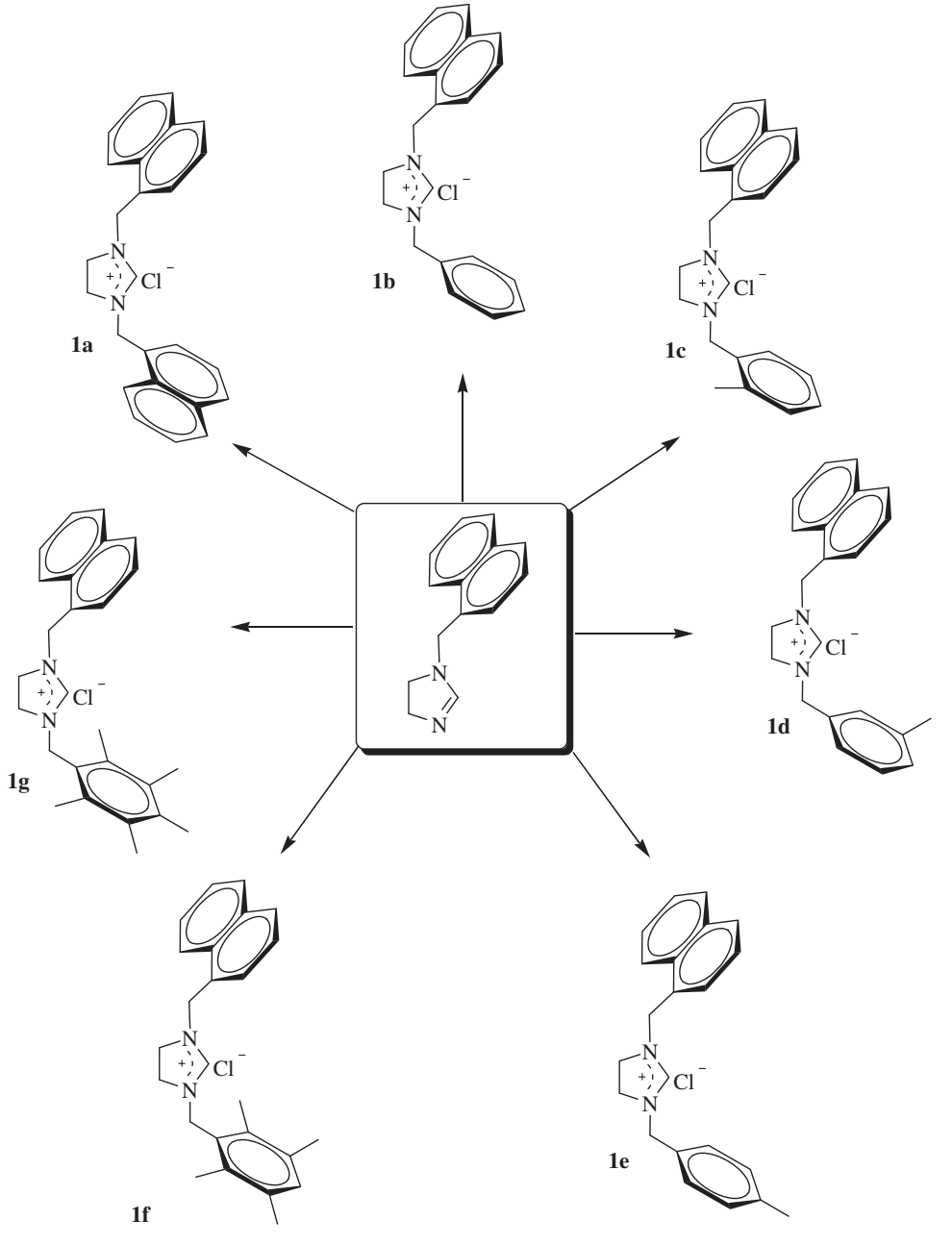
Keywords: Imidazolidinium salt; Mizoroki–Heck reaction; Suzuki–Miyaura reaction; Catalyst; N-Heterocyclic carbene

1. Introduction

Palladium catalyzed cross-coupling reactions for C–C bond formation have been recognized as versatile and efficient methods. The Mizoroki–Heck cross-coupling reaction, which consists of coupling of an alkene with a halo compound, has been developed from synthetic and mechanistic points of view [1–3]. The Mizoroki–Heck reaction has been applied to many areas, such as in bioactive compounds, drug intermediates, natural products, fine chemical syntheses, antioxidants, UV absorbers, and industrial applications [4–9]. The importance of this reaction has transcended its applications in the laboratory and it has become the subject of interest in industry [10–16]. However, industrial applications of Mizoroki–Heck reactions are rare, mainly due to two problems. First, palladium is expensive and contamination of product by palladium has to be strictly controlled. Second, many phosphine ligands are even more expensive and are air sensitive, poisonous, and subject to P–C bond degradation at elevated temperatures [17].

The use of *in situ* formed bisbenzimidazole-benzimidazole–pyrimidine-imidazolidine-2-ylidene-palladium(II) systems displayed high activities in various coupling reactions of aryl bromides and aryl chlorides in studies conducted by our research groups [16–23]. To find more stable, efficient, and active ligand precursors, we prepared a series of seven new

*Corresponding author. Email: senemakkoc@erciyes.edu.tr



Scheme 1. Synthesis of the naphthalenomethyl-substituted imidazolidinium salts, **1a-g**.

1-naphthalenomethyl-3-alkylimidazolidinium salts (scheme 1) and now report the use of the *in situ* generated catalytic system consisting of $Pd(OAc)_2$ as palladium source, **1a-g** salts as carbene precursors, and K_2CO_3 as a base for cross-coupling of aryl halides with styrene (Mizoroki–Heck) or phenylboronic acid (Suzuki–Miyaura) in aqueous media.

2. Experimental

2.1. *Materials and methods*

All reactions for the preparation of 1-naphthalenomethyl-3-alkylimidazolidinium salts were carried out under argon in flame dried glassware using standard Schlenk flasks. Test reactions for the catalytic activity of carbene ancillary ligands in the Mizoroki–Heck and Suzuki–Miyaura coupling reactions were carried out in air. ^{1}H NMR and ^{13}C NMR spectra were recorded using a Bruker AC300P FT spectrometer operating at 300.13 MHz (^{1}H) and 75.47 MHz (^{13}C). Chemical shifts (δ) are given in ppm relative to TMS, and coupling constant (J) in Hz. With the use of an Electrothermal 9200 m.p. apparatus, melting points were measured in open capillary tubes. Elemental analyses were performed by the TUBITAK Microlab Center (Turkey).

2.2. *General procedure for the preparation of imidazolidinium salts (1a-g)*

Alkyl halide (1.0 mM) was added slowly to a solution of 1-naphthalenomethylimidazolidine (1.0 mM) in DMF (4 mL) at 25 °C and the resulting mixture was heated to 80 °C for 12 h. 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 EtOH-Et_2O (1 : 2) at room temperature.

2.2.1. 1-3-Di(naphthalenomethyl)imidazolidinium chloride (1a). To a solution of 1-naphthalenomethylimidazolidine (1.0 mM) in DMF (4 mL), 1-(chloromethyl)naphthalene (1.0 mM) was added slowly at 25 °C. The resulting mixture was stirred at room temperature for 2 h and then heated at 80 °C for 12 h. Diethyl ether (10 mL) was added to gain a white crystalline solid, which was filtered off. The solid was washed with diethyl ether (3 × 10 mL), dried under vacuum, and recrystallized from EtOH/Et_2O (1 : 2) at room temperature. Yield: 82%, m.p.: 217–218 °C, υ(C=N): 1651.6 cm^{-1}. ^{1}H NMR (300.13 MHz, $CDCl_3$), δ 3.60 (s, 4H, NCH_2CH_2N); 5.37 (s, 4H, NCH_2C$_{10}$H$_7$); 7.37–8.21 (m, 14H, Ar–*H*); 11.12 (s, 1H, 2-C*H*). ^{13}C NMR (75.47 MHz, $CDCl_3$), δ 47.8 (NCH_2CH_2N); 50.1 (NCH_2C$_{10}$H$_7$); 123.1, 125.5, 126.6, 127.8, 128.1, 128.7, 129.2, 130.2, 131.3, and 134.4 (Ar–*C*); 159.2 (2-*C*H). Anal. Calcd for $C_{25}H_{23}N_2Cl$ (%): C, 77.61; H, 5.99; N, 7.24. Found: C, 77.59; H, 6.00; N, 7.21.

2.2.2. 1-Naphthalenomethyl-3-benzylimidazolidinium chloride (1b). Compound **1b** was prepared in the same way as **1a** from 1-naphthalenomethylimidazolidine (1.0 mM) and benzyl chloride (1.0 mM). Yield: 75%, m.p.: 97–99 °C, υ(C=N): 1658.6 cm^{-1}. ^{1}H NMR (300.13 MHz, $CDCl_3$), δ 3.61–3.70 (m, 4H, NCH_2CH_2N); 4.84 (s, 2H, NCH_2C$_6$H$_5$); 5.35 (s, 2H, NCH_2C$_{10}$H$_7$); 7.34–8.21 (m, 12H, Ar–*H*); 10.70 (s, 1H, 2-C*H*). ^{13}C NMR (75.47 MHz, $CDCl_3$), δ 47.5 and 48.1 (NCH_2CH_2N); 50.0 (NCH_2C$_6$H$_5$); 52.3 (NCH_2C$_{10}$H$_7$); 122.9, 125.3, 126.5, 127.6, 128.1, 128.3, 128.4, 128.6, 129.2, 130.1, 131.2, 132.5, and 133.9 (Ar–*C*); 159.0 (2-*C*H). Anal. Calcd for $C_{21}H_{21}N_2Cl$ (%): C, 74.88; H, 6.28; N, 8.32. Found: C, 74.76; H, 6.25; N, 8.33.

2.2.3. 1-Naphthalenomethyl-3-(2-methylbenzyl)imidazolidinium chloride (1c). Compound **1c** was prepared in the same way as **1a** from 1-naphthalenomethylimidazolidine (1.0 mM) and 2-methylbenzyl chloride (1.0 mM). Yield: 70%, m.p.: 99–101 °C, υ(C=N): 1638.3 cm^{-1}. ^{1}H NMR (300.13 MHz, $CDCl_3$), δ 2.34 (s, 3H, $C_6H_4CH_3$-2); 3.61 and 3.68 (m, 4H, NCH_2CH_2N); 4.87 (s, 2H, $NCH_2C_6H_4CH_3$-2); 5.41 (s, 2H, $NCH_2C_{10}H_7$); 7.23 and 8.23 (m, 11H, Ar–*H*); 10.48 (s, 1H, 2-C*H*). ^{13}C NMR (75.47 MHz, $CDCl_3$), δ 19.3 ($C_6H_4CH_3$-2); 38.0, and 44.9 (NCH_2CH_2N); 47.9 ($NCH_2C_6H_4CH_3$-2); 50.0 ($NCH_2C_{10}H_7$); 122.7, 125.3, 126.5, 127.6, 128.1, 128.2, 128.4, 128.7, 129.1, 129.3, 130.1, 131.2, and 133.9 (Ar–*C*); 158.8 (2-*C*H). Anal. Calcd for $C_{22}H_{23}N_2Cl$ (%): C, 75.31; H, 6.61; N, 7.98. Found: C, 75.28; H, 6.71; N, 7.97.

2.2.4. 1-Naphthalenomethyl-3-(3-methylbenzyl)imidazolidinium chloride (1d). Compound **1d** was prepared in the same way as **1a** from 1-naphthalenomethylimidazolidine (1.0 mM) and 3-methylbenzyl chloride (1.0 mM). Yield: 81%, m.p.: 157-159 °C, υ(C=N): 1658.7 cm^{-1}. ^{1}H NMR (300.13 MHz, $CDCl_3$), δ 2.63 (s, 3H, $C_6H_4CH_3$-3); 3.23–3.38 (m, 4H, NCH_2CH_2N); 4.79 (s, 2H, $NCH_2C_6H_4CH_3$-3); 5.35 (s, 2H, $NCH_2C_{10}H_7$); 7.37–8.33 (m, 11H, Ar–*H*); 10.63 (s, 1H, 2-C*H*). ^{13}C NMR (75.47 MHz, $CDCl_3$), δ 22.9 ($C_6H_4CH_3$-3); 33.9 and 39.4 (NCH_2CH_2N); 50.9 ($NCH_2C_6H_4CH_3$-3); 53.8 ($NCH_2C_{10}H_7$); 124.9, 127.9, 128.2, 129.0, 129.9, 130.6, 131.3, 131.9, 132.5, 133.2, 135.5, and 136.1 (Ar–*C*); 167.4 (2-*C*H). Anal. Calcd for $C_{22}H_{23}N_2Cl$ (%): C, 75.31; H, 6.61; N, 7.98. Found: C, 75.42; H, 6.63; N, 7.95.

2.2.5. 1-Naphthalenomethyl-3-(4-methylbenzyl)imidazolidinium chloride (1e). Compound **1e** was prepared in the same way as **1a** from 1-naphthalenomethylimidazolidine (1.0 mM) and 4-methylbenzyl chloride (1.0 mM). Yield: 74%, m.p.: 186–187 °C, υ(C=N): 1657.1 cm^{-1}. ^{1}H NMR (300.13 MHz, $CDCl_3$), δ 2.27 (s, 3H, $C_6H_4CH_3$-4); 3.58–3.70 (m, 4H, NCH_2CH_2N); 4.75 (s, 2H, $NCH_2C_6H_4CH_3$-4); 5.36 (s, 2H, $NCH_2C_{10}H_7$); 7.16–8.21 (m, 11H, Ar–*H*); 10.74 (s, 1H, 2-C*H*). ^{13}C NMR (75.47 MHz, $CDCl_3$), δ 21.1 ($C_6H_4CH_3$-4); 47.3 and 47.9 (NCH_2CH_2N); 49.9 ($NCH_2C_6H_4CH_3$-4); 52.0 ($NCH_2C_{10}H_7$); 123.0, 125.4, 127.6, 128.2, 128.6, 128.7, 129.4, 130.0, 131.2, and 133.9 (Ar–*C*); 158.8 (2-*C*H). Anal. Calcd for $C_{22}H_{23}N_2Cl$ (%): C, 75.31; H, 6.61; N, 7.98. Found: C, 75.39; H, 6.58; N, 7.93.

2.2.6. 1-Naphthalenomethyl-3-(2,3,5,6-tetramethylbenzyl)imidazolidinium chloride (1f). Compound **1f** was prepared in the same way as **1a** from 1-naphthalenomethylimidazolidine (1.0 mM) and 2,3,5,6-tetramethylbenzyl chloride (1.0 mM). Yield 85%, m.p.: 245–247 °C, υ(C=N): 1655.2 cm^{-1}. ^{1}H NMR (300.13 MHz, $CDCl_3$), δ 2.15 and 2.17 [s, 12H, $C_6H(CH_3)_4$-2,3,5,6]; 3.54–3.75 (m, 4H, NCH_2CH_2N); 4.89 [s, 2H, $NCH_2C_6H(CH_3)_4$-2,3,5,6]; 5.40 (s, 2H, $NCH_2C_{10}H_7$); 7.38–8.22 (m, 8H, Ar–*H*); 10.41 (s, 1H, 2-C*H*). ^{13}C NMR (75.47 MHz, $CDCl_3$), δ 15.9, and 20.4 [$C_6H(CH_3)_4$-2,3,5,6]; 46.8, and 47.4 (NCH_2CH_2N); 47.8 [$NCH_2C_6H(CH_3)_4$-2,3,5,6]; 49.9 ($NCH_2C_{10}H_7$); 123.1, 125.4, 126.4, 127.5, 128.0, 128.3, 128.7, 128.9, 130.0, 131.2, 132.7, 133.8, and 134.7 (Ar–*C*); 158.4 (2-*C*H). Anal. Calcd for $C_{25}H_{29}N_2Cl$ (%): C, 76.41; H, 7.44; N, 7.13. Found: C, 76.46; H, 7.38; N, 7.10.

2.2.7. 1-Naphthalenomethyl-3-(2,3,4,5,6-pentamethylbenzyl)imidazolidinium chloride (1g). Compound **1g** was prepared in the same way as **1a** from 1-naphthalenomethylimidazolidine (1.0 mM) and 2,3,4,5,6-pentamethylbenzyl chloride (1.0 mM). Yield: 69%, m.p.: 116–118 °C, υ(C=N): 1641.2 cm^{-1}. ^{1}H NMR (300.13 MHz, $CDCl_3$), δ 2.19, 2.20, and 2.24 [s, 15H, $C_6(CH_3)_5$-2,3,4,5,6]; 3.61-3.98 (m, 4H, NCH_2CH_2N); 4.92 [s, 2H, $NCH_2C_6(CH_3)_5$-2,3,4,5,6]; 5.39 (s, 2H, $NCH_2C_{10}H_7$); 7.29-8.22 (m, 7H, Ar–*H*); 10.05 (s, 1H, 2-C*H*). ^{13}C NMR (75.47 MHz, $CDCl_3$), δ 15.7, 15.9, and 20.5 [$C_6(CH_3)_5$-2,3,4,5,6]; 46.7, and 47.8 (NCH_2CH_2N); 48.8 [$NCH_2C_6(CH_3)_5$-2,3,4,5,6]; 50.1 ($NCH_2C_{10}H_7$); 122.7, 122.9, 125.4, 126.5, 127.5, 128.0, 128.3, 128.7, 129.1, 130.1, 131.2, 132.8, 133.2, 133.5, 133.8, 134.7, 156.4, and 157.9 (Ar–*C*); 158.1 (2-*C*H). Anal. Calcd for $C_{26}H_{31}N_2Cl$ (%): C, 76.73; H, 7.68; N, 6.88. Found: C, 76.78; H, 7.66; N, 6.89.

2.3. *General procedure for the Mizoroki–Heck cross-coupling reactions*

1-Naphthalenomethyl-3-alkylimidazolidinium salts (**1a-g**) (2.0 mM %), $Pd(OAc)_2$ (1.0 mM %), styrene (1.5 mM), aryl bromide (1.0 mM), K_2CO_3 (2.0 mM), DMF (3 mL), and water (3 mL) were added to a small Schlenk tube for the Mizoroki–Heck reaction and the mixture was heated to 80 °C for 2 h. The Mizoroki–Heck cross-coupling reactions for catalytic activities of the carbene ancillary ligands were carried out in the presence of air. At the end of the Mizoroki–Heck cross-coupling reactions, the mixture was cooled, extracted with hexane/ethylacetate (5 : 1), filtered through a pad of silica gel with copious washings, concentrated, and purified by flash chromatography on silica gel. The purity of the compounds was checked by GC and NMR. Yields are based on arylbromide. All reactions were monitored by GC-FID with an HP-5 column of 30 m length, 0.32 mm diameter, and 0.25 μm film thickness.

2.4. *General procedure for the Suzuki–Miyaura coupling reaction*

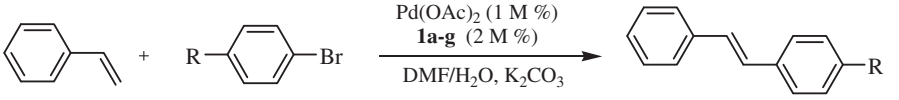
$Pd(OAc)_2$ (1.0 mM %), 1-naphthalenomethyl-3-alkylimidazolidinium salts (**1a-g**) (2.0 mM %), aryl chloride (1.0 mM), phenylboronic acid (1.5 mM), K_2CO_3 (2.0 mM), and water (2 mL) were added to a small Schlenk tube and the mixture was heated to 80 °C for 2 h. At the end of the reaction, the mixture was cooled, extracted with ethylacetate/hexane (1 : 5), filtered through a pad of silica gel with copious washings, concentrated, and purified by flash chromatography on silica gel. The purity of the compounds was checked by NMR and GC; yields were based on arylchloride.

3. Results and discussion

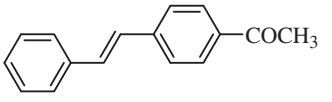
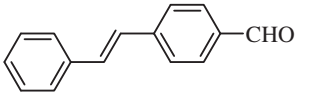
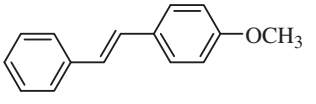
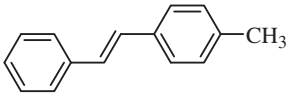
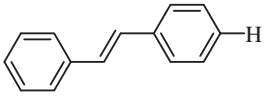
3.1. *Synthesis and characterization of naphthalenomethyl-substituted imidazolidinium salts (1a-g)*

Naphthalenomethyl-substituted imidazolidinium salts (**1a-g**) are conventional NHC precursors. These salts were obtained in almost quantitative yield by quaternization of 1-naphthalenomethylimidazolidine with various alkyl halides in DMF [24, 25] (scheme 1). The structures of **1a-g** were determined by their characteristic spectroscopic data and elemental analysis. The ^{1}H NMR spectra of the imidazolidinium salts further supported the assigned structures; the resonances for C(2)–H were observed as sharp singlets at 11.12, 10.70,

Table 1. Mizoroki–Heck coupling of various aryl bromides with styrene in the presence of *in situ* generated catalysts from different imidazolium salts[a].



A **B** **C**

Entry	R	LHX	Product	Yield b–d (%)
1	$COCH_3$	**1a**		89
2	$COCH_3$	**1b**		91
3	$COCH_3$	**1c**		97
4	$COCH_3$	**1d**		99
5	$COCH_3$	**1e**		98
6	$COCH_3$	**1f**		99
7	$COCH_3$	**1g**		94
8	CHO	**1a**		90
9	CHO	**1b**		96
10	CHO	**1c**		94
11	CHO	**1d**		98
12	CHO	**1e**		94
13	CHO	**1f**		96
14	CHO	**1g**		87
15	OCH_3	**1a**		95
16	OCH_3	**1b**		100
17	OCH_3	**1c**		91
18	OCH_3	**1d**		100
19	OCH_3	**1e**		91
20	OCH_3	**1f**		99
21	OCH_3	**1g**		91
22	CH_3	**1a**		87
23	CH_3	**1b**		89
24	CH_3	**1c**		92
25	CH_3	**1d**		92
26	CH_3	**1e**		94
27	CH_3	**1f**		94
28	CH_3	**1g**		93
29	H	**1a**		91
30	H	**1b**		99
31	H	**1c**		97
32	H	**1d**		97
33	H	**1e**		94
34	H	**1f**		99
35	H	**1g**		100

Notes: [a]Reaction conditions: styrene (1.5 mM), p-R-C_6H_4Br (1.0 mM), $Pd(OAc)_2$ (1.0 mM %), K_2CO_3 (2.0 mM), **1** (2.0 mM %), water (3 mL)-DMF (3 mL), 80 °C, 2 h.
[b]The purity of the compounds was checked by NMR and GC spectroscopy.
[c]Yields are based on aryl bromide.
[d]Isolated yields.

10.48, 10.63, 10.74, 10.41, and 10.05 ppm for **1a-g**, respectively. The ^{13}C NMR chemical shifts were consistent with the proposed structure; the imino carbon appeared as a typical singlet in the ^{1}H-decoupled mode at 159.2, 159.0, 158.8, 167.4, 158.8, 158.4, and 158.1 ppm for **1a-g**, respectively.

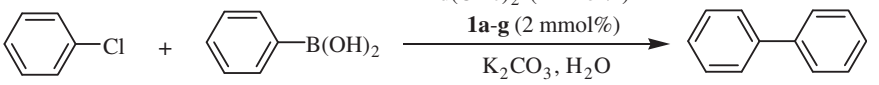
3.2. *Mizoroki–Heck cross-coupling reaction*

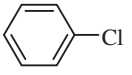
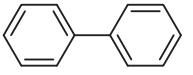
The palladium catalyzed coupling of styrene with various aryl bromides has been observed to proceed under a variety of conditions. Diverse bases (K_2CO_3, Cs_2CO_3, and KOBu^t) and solvents (DMF, H_2O, and dioxane), as well as ligand precursors, have been employed with varying degrees of success according to the substrates. A series of experiments was performed with styrene and 4-bromoacetophenone as model compounds to find optimum conditions. K_2CO_3 as a base was the best choice in DMF/water systems. Water was used as solvent in the Mizoroki–Heck cross-coupling reactions because it is inexpensive, nonflammable, nontoxic, abundant, and readily separable from organic compounds. The reactions were performed in air and without degassing water prior to use. Under the reaction conditions using **1a-g** as ligands, $Pd(OAc)_2$ as the catalyst, DMF-water mixture as the solvent, and K_2CO_3 as the base at 80 °C, various aryl bromides and styrene were examined (table 1). After establishing the optimized coupling reaction conditions, the scope of the reaction and efficiencies of the salts were evaluated by investigating the coupling of various p-substituted aryl bromides with styrene. The corresponding products, **C,** were obtained in good yields. The results are given in table 1.

We conducted control experiments (not using ligand precursors) by using p-bromoacetophenone and found that the reaction resulted in a 4% yield. This result shows that the synthesized ligand precursors are very efficient in the Mizoroki–Heck and Suzuki–Miyaura coupling reactions.

The ligand precursors used for Mizoroki–Heck reactions were stable against air and moisture. These ligands render the design of goal-oriented catalysts possible because of their steric and electronic effects that can be easily changed. Electron-poor arylbromides, such as p-bromobenzaldehyde or p-bromoacetophenone, were equally effective in the presence of catalysts generated from imidazolidinium salts and excellent yields were obtained when coupled with styrene (table 1, entries 1–14). Reactions of electron-rich arylbromides, such as p-bromoanisole or p-bromotoluene, with a number of styrenes resulted in full conversion to give the desired products after 2 h at 80 °C in excellent yields (table 1, entries 15–28). The Mizoroki–Heck coupling reaction using the synthesized ligand precursors gave yields of 87–100%.

Table 2. The Suzuki–Miyaura coupling of aryl chlorides with phenyl boronic acid[a].



Entry	Chlorobenzene	LHX	Product	Yield (%)
1		**1a**		94
2		**1b**		93
3		**1c**		89
4		**1d**		92
5		**1e**		92
6		**1f**		90
7		**1g**		91

Notes: [a]Reaction conditions: C_6H_5Cl (1.0 mM), phenylboronic acid (1.5 mM), $Pd(OAc)_2$ (1.0 mM %), K_2CO_3 (2.0 mM), **1a-g** (2.0 mM %), water (2 mL), 80 °C, 2 h.

3.3. *Suzuki–Miyaura coupling reaction*

The palladium-catalyzed Suzuki–Miyaura cross-coupling reaction of aryl halides and pseudo-halides is a common method employed for the formation of C–C bonds. The coupling of aryl halides with phenylboronic acid has been used in the synthesis of several industrially applicable compounds along with a number of natural products. The ability to use aryl chlorides as substrates in Suzuki–Miyaura coupling reactions is advantageous for two reasons. First, aryl chlorides are more commercially available than aryl bromides. Second, they are much less expensive [26]. The search for catalysts that can activate these substrates is a highly topical field of study. Development of catalysts used with aryl chlorides [27] and aryl bromides has been reported by Buchwald [28], Fu [29], Bedford [30], Beller [31], Gök [32], and others [33].

In **1a-g**/$Pd(OAc)_2$ catalyst, chlorobenzene and phenylboronic acid were examined in the Suzuki–Miyaura coupling as the model reaction with water as solvent. The yield of the Suzuki–Miyaura cross-coupling reaction is between 89 and 94% (table 2). Thus, synthesized imidazolidinium salts are effective carbene ancillary ligands in the Mizoroki–Heck and Suzuki–Miyaura cross-coupling reactions.

In our previous study, catalytic activities in the Mizoroki–Heck and Suzuki–Miyaura coupling (DMF-water) reactions of N-phenyl-substituted benzimidazolium salts were examined [18]. In this study, catalytic activity of Mizoroki–Heck (DMF-water mixture as solvent) and Suzuki–Miyaura (water as solvent) coupling of synthesized naphthalene-substituted imidazolidinium salts were analyzed. We concluded that imidazolidinium salts, like benzimidazolium salts in the Mizoroki–Heck and Suzuki–Miyaura coupling reactions show high activity. Instead of using a DMF-water as solvent in Suzuki–Miyaura coupling, the reaction occurred in high yields when water was used as solvent as well.

4. Conclusions

Seven new saturated and unsaturated carbene ancillary ligands were synthesized and characterized using FTIR, ^{1}H NMR, ^{13}C NMR, and elemental analyses. The catalytic behavior of the imidazolidinium salts (**1a-g**) was investigated in the Mizoroki–Heck and Suzuki–Miyaura reactions, processes which are environmentally benign, easy to handle, and highly effective. Use of the *in situ* formed naphthalenomethyl-substituted imidazolidin-2-ylidene palladium(II) systems exhibited high catalytic activity.

Acknowledgment

This work was financially supported by Inönü University Research Fund (I.U.B.A.P. 2011/130).

References

[1] B.M. Trost. *Science*, **234**, 1471 (1991).
[2] J. Tsuji. *Palladium Reagents and Catalysts: Innovations in Organic Synthesis*, Wiley, New York (1995).
[3] E. Negishi, A. de Meijere. *Handbook of Organopalladium Chemistry for Organic Synthesis*, John Wiley, New York (2002).
[4] S. Liu, X. Jiang, G. Zhuo. *J. Mol. Catal. A: Chem.*, **290**, 72 (2008).

[5] A. Kumar, M. Agarwal, A.K. Singh, R.J. Butcher. *Inorg. Chim. Acta*, **362**, 3208 (2009).
[6] C. Mazet, L.H. Gade. *Eur. J. Inorg. Chem.*, **2003**, 1161 (2003).
[7] H. Türkmen, T. Pape, F.E. Hahn, B. Çetinkaya. *Eur. J. Inorg. Chem.*, **2009**, 285 (2009).
[8] B. Yiğit, Y. Gök, İ. Özdemir, S. Günal. *J. Coord. Chem.*, **65**, 371 (2012).
[9] A. Kumar, P. Ghosh. *Eur. J. Inorg. Chem.*, 3955 (2012).
[10] M. Bagherzadeh, M. Amini, A. Ellern, L.K. Woo. *Inorg. Chim. Acta*, **383**, 46 (2012).
[11] S.T. Henriksen, P.O. Norrby, P. Kaukoranta, P.G. Andersson. *J. Am. Chem. Soc.*, **130**, 10414 (2008).
[12] R.F. Heck, J.P. Nolley. *J. Org. Chem.*, **37**, 2320 (1972).
[13] I.P. Beletskaya, A.V. Cheprakov. *Chem. Rev.*, **100**, 3009 (2000).
[14] L. Yi, J. Liebscher. *Chem. Rev.*, **107**, 133 (2007).
[15] R.T. Ruck, M.A. Huffman, M.M. Kim, M. Shevlin, W.V. Kandur, W. Daviesi. *Angew. Chem. Int. Ed.*, **47**, 4711 (2008).
[16] S. Demir, İ. Özdemir, B. Çetinkaya. *Appl. Organomet. Chem.*, **23**, 520 (2009).
[17] X. Cui, Z. Li, C.-Z. Tao, Y. Xu, J. Li, L. Liu, Q.-X. Guo. *Organic Letters*, **8**, 2467 (2006).
[18] İ. Özdemir, Y. Gök, N. Gürbüz, S. Yaşar, E. Çetinkaya, B. Çetinkaya. *Pol. J. Chem.*, **78**, 2141 (2004).
[19] S. Akkoç, Y. Gök. *J. Coord. Chem.*, **66**, 1396 (2013).
[20] H. Türkmen, S. Denizaltı, İ. Özdemir, E. Çetinkaya, B. Çetinkaya. *J. Organomet. Chem.*, **693**, 425 (2008).
[21] Y. Gök, N. Gürbüz, İ. Özdemir, B. Çetinkaya, E. Çetinkaya. *Appl. Organomet. Chem.*, **19**, 870 (2005).
[22] B. Yiğit, M. Yiğit, İ. Özdemir, E. Çetinkaya. *Turk. J. Chem.*, **34**, 327 (2010).
[23] A. Slamani, S. Demir, İ. Özdemir. *Catal. Commun.*, **29**, 141 (2012).
[24] A.C. Hillier, G.A. Grasa, M.S. Viciu, H.M. Lee, C.L. Yang, S.P. Nolan. *J. Organomet. Chem.*, **653**, 69 (2002).
[25] C.M. Zhang, M.L. Trudell. *Tetrahedron Lett.*, **41**, 595 (2000).
[26] İ. Özdemir, N. Şahin, Y. Gök, S. Demir, B. Çetinkaya. *J. Mol. Catal. A: Chem.*, **234**, 181 (2005).
[27] A.F. Littke, G.C. Fu. *Angew. Chem. Int. Ed.*, **41**, 4176 (2002).
[28] J.P. Wolfe, S.L. Buchwald. *Angew. Chem. Int. Ed.*, **38**, 2413 (1999).
[29] A.F. Littke, C. Dai, G.C. Fu. *J. Am. Chem. Soc.*, **122**, 4020 (2000).
[30] R.B. Bedford, C.S.J. Cazin, S.J. Coles, T. Gelbrich, P.N. Horton, M.B. Hursthouse, M.E. Light. *Organometallics*, **22**, 2810 (2003).
[31] A. Zapf, R. Jackstell, F. Rataboul, T. Riermeier, A. Monsees, C. Fuhrmann, N. Shaikh, U. Dingerdissen, M. Beller. *Chem. Commun.*, 38 (2004).
[32] Y. Gök, E. Çetinkaya, İ. Özdemir, B. Çetinkaya, M.F. Lappert. *Acta Chim. Slov.*, **51**, 437 (2004).
[33] R.A. Singer, S. Caron, R.E. McDermott, P. Arpin, N.M. Do. *Synlett*, **12**, 1727 (2003).