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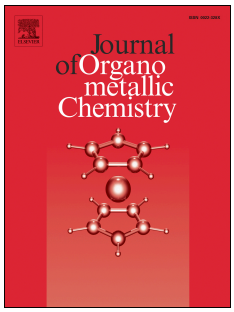

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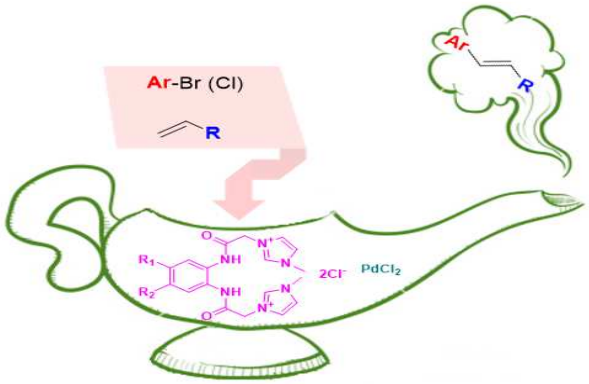

Bis(imidazolium) chloride based on 1,2-phenylenediamine as efficient ligand precursor for palladium-catalyzed Mizoroki-Heck cross-coupling reaction

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ABSTRACT

Bis(imidazolium) chlorides based on 1,2-phenylenediamine were introduced as efficient ligand precursors in the Pd-catalyzed Mizoroki-Heck cross-coupling reactions of substituted aryl halides with activated alkenes to afford the corresponding functionalized alkenes. While high to excellent yields (78-96%) were obtained with aryl bromides, moderate yields (51-59%) were achieved for aryl chlorides in this protocol.

Keywords: *N*-Heterocyclic carbene ligands, Mizoroki-Heck reaction, Aryl bromides, Terminal alkenes, Palladium

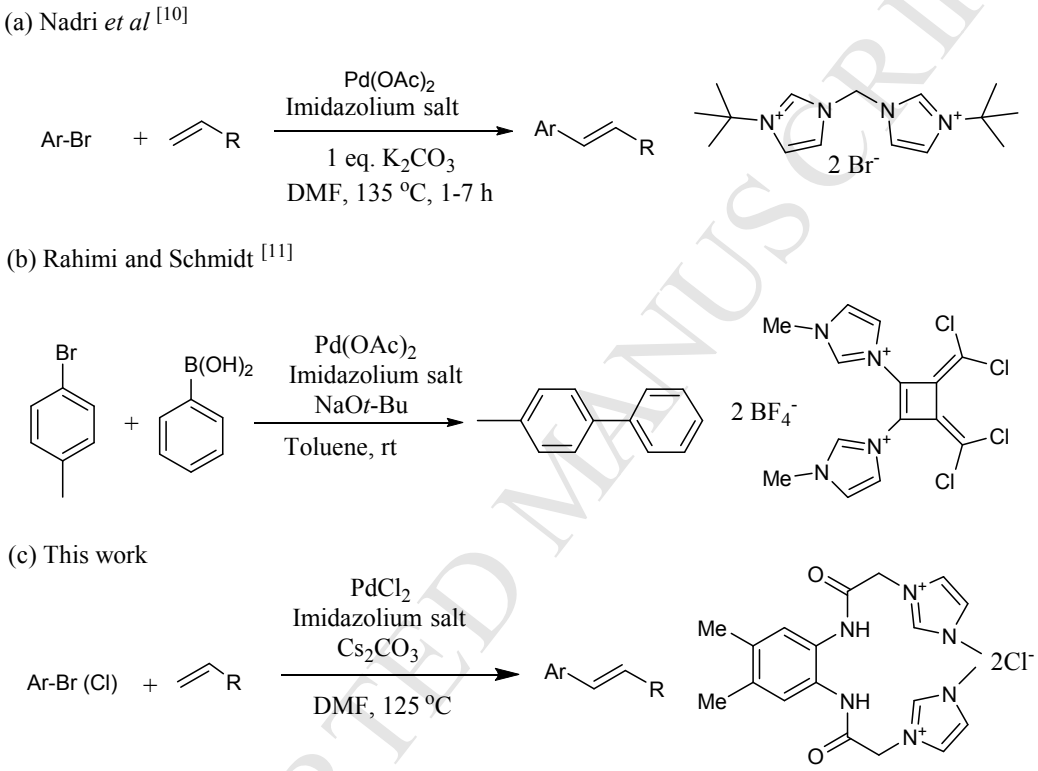
1. Introduction

Over the past few decades, palladium-catalyzed cross-coupling reactions have surprisingly advanced a wide range of organic reactions [1]. Among them, the coupling reaction of aryl halides with activated alkenes (Mizoroki-Heck coupling reaction) is one of the best synthetic routes toward C-C bond formation [2]. Application of aryl iodides as highly efficient substrates in the Mizoroki-Heck reaction has been limited due to their low availability and high cost. On the other hand, strong bond between Csp^2-Br and Csp^2-Cl needs highly active catalysts for activation to be applicable in coupling reactions [3]. The enormous applications of Mizoroki-Heck reaction in the synthesis of novel materials, pharmaceuticals and natural products have encouraged organic chemists to develop highly active catalysts and efficient synthetic methods for this transformation [4].

A wide range of palladium catalysts and ligands have been developed for Mizoroki-Heck reaction. Among them, phosphine-containing ligands have been extensively utilized in the Mizoroki-Heck reaction to improve the catalytic activity of complexes via stabilization and generation of Pd(0) species from Pd(II) complexes [5]. Unfortunately, phosphine ligands are toxic, air and moisture sensitive, and highly expensive [6]. To overcome these limitations, various catalytic systems have been introduced. Recently, various phosphine-free ligands including oxazolines, *N*-heterocyclic carbenes (NHCs), diazacrown ethers, Schiff bases, hydrazines, amino alcohols, amino acids and porphyrins have been established for Pd-catalyzed

C-C cross-coupling reactions [7]. Between these ligands, *in situ* prepared *N*-heterocyclic carbenes have been proven to be significant ligands for Pd-mediated cross-coupling reactions [8]. Lately, NHCs have attracted more efforts for introducing more efficient ligands in this area. Their advantages are easy preparation of NHCs on the large scale, their air-stability, and generally similar or higher performance in comparison to phosphane-based systems. Also, the stronger σ-donor and weaker π-acceptor properties of NHCs compared to phosphane ligands cause higher electron density on the Pd (or any NHC-metal complexes) which increase their stability to moisture, air, and heat [9]. Among NHC ligands, *bis*-NHC ligands containing an alkyl, aryl, pyridyl, lutidinyl, cyclohexyl, polyether and a solid support as bridging linkers have been well investigated for the synthesis of NHC-metal complexes with potential applications as catalyst in synthetic organic chemistry [10]. Both pre-prepared and *in situ* prepared imidazolium based NHC-Pd complexes are applied extensively for Mizoroki-Heck reaction. Deprotonation of NHC salts with a base in the presence of a Pd precursor can furnish the corresponding palladium complexes *in situ* suitable for cross-coupling reactions. In this regard, recently, Nadri *et al*. reported the application of 1,1'-Methylene-3,3'-bis[(*N*-(*tert*-butyl)imidazol-2-ylidene] as efficient ligand precursor for Pd-catalyzed C-C cross-coupling reaction of aryl bromides and activated alkenes (Scheme **1a**) [11]. In addition, *bis*-imidazolium ligand precursor in conjunction with $Pd(OAc)_2$ as catalyst for Suzuki-Miyaura reaction is developed by Rahimi and Schmidt (Scheme **1b**) [12]. In this regard, here we are interested to report the preparation of four *bis*-imidazolium

salts and their applications as ligand precursor for Pd-catalyzed Mizoroki-Heck cross-coupling reaction of aryl bromides and chlorides with activated alkenes (Scheme **1c**).

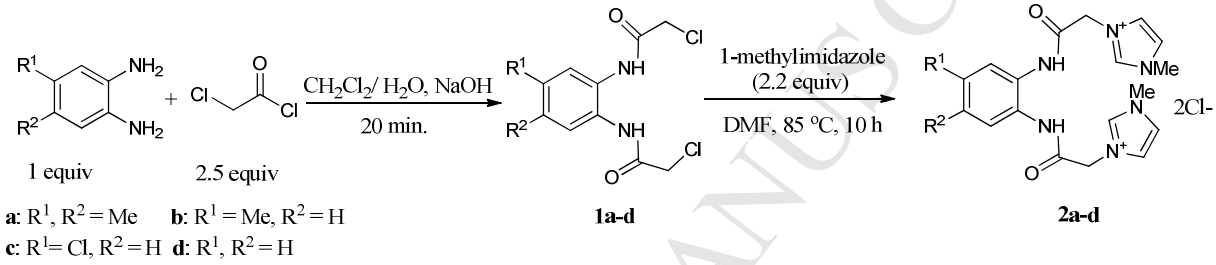


Scheme 1. Reported and proposed *bis*(imidazolium) salts as ligand precursor for C-C cross-coupling reactions.

2. Results and discussion

Four *bis*-imidazolium salts based on *o*-phenylenediamine as ligand precursor suitable for Pd-catalyzed Mizoroki-Heck cross-coupling reactions were prepared. As shown in Scheme 2, the reactions of chloroacetyl chloride with *o*-phenylenediamine and its derivatives were carried out

to prepare the corresponding *N*,*N*'-(1,2-phenylene)bis(2-chloroacetamide) derivatives **1a-d** (yields (%): 1**a**; 96, **1b**:93, **1c**: 89, 1d: 91). Next, **1a-d** reacted with an excess amount of 1-methylimidazole to afford the corresponding *bis*-imidazolium salts **2a-d** (yields (%): **2a**; 74, **2b**:79, **2c**: 76, **2d**: 75). The structures of **2a-d** were characterized by IR, ^{1}H and ^{13}C NMR, mass and elemental analysis.



Scheme 2. Synthetic route for preparation of bis-imidazole ligand precursor

After successful preparation of *bis*-imidazolium salts **2a-d**, their applications as ligand precursor in the Mizoroki-Heck reaction were investigated. At first, the model reaction between styrene and bromobenzene was screened in the presence of Cs_2CO_3 (1.1 equiv) in various solvents such as water, toluene, DMSO, dioxane, and DMF by using 1.1 mol % of $PdCl_2$ at 120 °C (Table 1, entries 1-5). The best yield was obtained in DMF. Next, the effect of catalyst loading was examined. While by decreasing the amount of the catalyst loading to 0.8 mol %, the yield was decreased to 85%, no improvement in reaction yield was observed using 1.7 mol% of the catalyst (Table 1, entries 6-7). In addition, by decreasing of the reaction temperature to 80 °C, the yield was significantly dropped to 38% (Table 1, entry 8). The best yield (96%) was obtained at 125

°C (Table 1, entry 10). By performing the model reaction in the presence of various bases such as Et_3N, DIPEA (*N*,*N*-diisopropylethylamine), *t*-BuOK, NaOH, and K_2CO_3 instead of Cs_2CO_3 under optimized reaction conditions, lower yields were obtained (Table 1, entries 11-15). By using *bis*-imidazolium salts **2b-d** as ligand precursor, the reaction yields were slightly decreased (about 1-3%) under optimized reaction conditions (Table 1, entries 16-18]. It may be attributed to the higher electron density on the nitrogens of the amide groups in **2a** and improvement of the catalyst activity toward the Mizoroki-Heck coupling reaction. In addition, to confirm the efficiency of the *bis*(imidazolium) salts as ligand precursor in the proposed typical reaction, we performed the reaction under ligand- free condition and low yield of the product **5a** was resulted (Table 1, entry 19). Furthermore, when **1a-d** was used as ligand precursor instead of **2a-d**, the yields were significantly decreased even by prolonging the reaction time to 24 h (Table 1, entries 20-23]. Finally, stirring a solution of styrene (1.2 equiv) and bromobenzene (1 equiv) in the presence of Cs_2CO_3 (1.1 equiv), $PdCl_2$ (1.1 mol %), and **2a** (1.1 mol %) in DMF at 125 °C was considered as optimal reaction conditions for further derivatization.

<<Table 1>>

In order to explore the scope of the reaction, various activated and non-activated aryl halides and terminal olefins were applied in this protocol (Table 2). It is conceivable that the reaction of **2a** with Cs_2CO_3 produces the corresponding NHC ligand *in situ* for generation of the active

catalyst with $PdCl_2$ suitable for activation of the starting materials toward cross-coupling reaction. Several aryl bromides bearing electron-withdrawing and electron-donating groups were applied successfully in cross-coupling reaction to afford the corresponding *trans* isomer **5**. Lower yields were obtained for aryl bromides containing a substituent on the *ortho* position compare to *meta* and *para* positions. The results showed that aryl bromides are more reactive than aryl chlorides in the reaction with styrene, methyl acrylate and ethyl acrylate. For this purpose, the chemoselectivity of the catalytic system was examined using 4-chloro-1-bromobenzene and 4-fluoro-1-bromobenzene (Table 2, entries 9-10 and 12-14). This study showed that, -Br is a better leaving group than –Cl and –F, and the cross-coupling reaction was preferably occurred in the bromide position. Although chlorobenzene gave 51% and 55% yield in the reaction with styrene and methyl acrylate respectively. Using an electron-withdrawing group on the phenyl ring such as 4-nitro-1-chlorobenzene improved the yield up to 59% [Table 2, entry 17].

<<Table 2>>

The catalytic efficiency of our catalyst in Mizoroki–Heck cross-coupling reaction of bromobenzene and styrene is compared with those reported in the literatures and summarized in Table 3. As revealed from Table 3, our catalyst shows good activity in comparison to some of the reported methods in literatures.

<<Table 3>>

3. Conclusions

In conclusion, a new catalytic system for the Mirozoki-Heck cross coupling reactions of aryl bromides and chlorides with activated olefins is reported using a new category of *bis*(imidazolium) chlorides based on 1,2-phenylenediamine as ligand precursor, Cs_2CO_3 and $PdCl_2$. The advantages of this method include moderate to excellent yields, simple synthesis of ligand precursor, excellent regioselectivity for aryl bromides in the presence of aryl chlorides and fluorides.

4. Experimental

4.1. ***General*****:** All materials were purchased from Merck, Aldrich, and Fluka, and used as received. Melting points were measured by an Electrothermal 9100 apparatus and are uncorrected. FT-IR spectra was recorded on a Perkin-Elmer 843 spectrophotometer using KBr disc. NMR spectra were recorded on a Bruker Avance 300 MHz using DMSO-d_6 as solvent and Me_4Si (TMS) as internal standard at 298 K. The chemical shifts (δ) are reported in parts per million (ppm) and coupling constants (J) are given in Hz. Low resolution mass spectra was collected on a Hewlett-Packard 5973 mass spectrometer operating at 70 eV. Elemental analyses were carried out on a Perkin-Elmer 2004 series [II] CHN elemental analyzer.

4.2. ***General Procedure for the Preparation of*** **2a-d:**

To a solution of 1,2-phenylenediamine (or its derivatives) (10.0 mmol) in CH_2Cl_2 (30 mL), aqueous NaOH (20.0 mmol in 8 mL water) was added. Then, chloroacetyl chloride solution (2.8 g, 25.0 mmol in 25 mL CH_2Cl_2) was added to the reaction mixture *via* dropping funnel with stirring. The mixture was further stirred for 20 min to afford a precipitate. The solid was filtered off, washed with ether (10 mL), and dried under vacuum to afford **1a-d** [yields (%): **1a**; 96, **1b**:93, **1c**: 89, **1d**: 91]. The solids were used in the next step without further purification. Then, 1-methylimidazole (1.8 g, 22 mmol) was added to a solution of **1a-d** (in 40 mL DMF). The reaction mixture was stirred for 10 h at 85 °C. Then, the mixture was cooled to room temperature and the solvent was removed under vacuum and the resulting solid was suspended in 30 mL acetone with stirring for 15 min. Finally, the suspension was filtered and dried in vacuum to give the pure product. **(**Yields (%): **2a**; 74, **2b**:79, **2c**: 76, **2d**: 75**).**

4.3. ***Characterization data for*** **2a-2d:**

3,3'-(((4,5-dimethyl-1,2-phenylene)bis(azanediyl))bis(2-oxoethane-2,1-diyl))bis(1-methyl-1H-imidazol-3-ium) Chloride (2a):

Yield: 3.35 g (74%); yellow solid; ^{1}H NMR (300 MHz, DMSO-d_6) δ 10.53 (s, 2H), 9.31 (s, 2H), 7.86 (m, 2H), 7.72 (m, 2H), 7.37 (s, 2H), 5.42 (s, 4H), 3.91 (s, 6H), 2.16 (s, 6H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6) δ 163.8, 137.5, 132.8, 126.9, 125.1, 123.4, 122.7, 51.0, 35.5, 18.7 ppm. Anal. calcd for $C_{20}H_{26}Cl_2N_6O_2$ (%): C, 52.99; H, 5.78; N, 18.54. Found (%): 51.83; H, 5.48; N, 18.17; IR (cm^{-1}): 3082, 2974, 1688, 1597, 1552, 1496, 1441, 1342, 1301, 1250, 1179, 1107, 750, 692, 619, 501; LRMS (EI) $[M - Cl]^+$ *m/z* 382.

3,3'-(((4-methyl-1,2-phenylene)bis(azanediyl))bis(2-oxoethane-2,1-diyl))bis(1-methyl-1H-imidazol-3-ium) Chloride (2b):

Yield: 3.46 g (79%); pale yellow solid; mp 225-227 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 10.67 (s, 1H), 10.62 (s, 1H), 9.35 (s, 2H), 7.88 (m, 2H), 7.74 (m, 2H), 7.49 – 7.35 (m, 2H), 6.97 (m, 1H), 5.46 (s, 2H), 5.44 (s, 2H), 3.91 (s, 6H), 2.24 (s, 3H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6) δ 164.2, 137.8, 134.4, 129.6, 127.1, 124.6, 123.7, 123.0, 51.3, 35.8, 20.6 ppm; Anal. calcd for $C_{19}H_{24}Cl_2N_6O_2$ (%): C, 51.94; H, 5.51; N, 19.13. Found (%): C, 51.76; H, 5.62; N, 19.16; IR (cm^{-1}): 2977, 1687, 1606, 1549, 1511, 1309, 1251, 1179, 1107, 821, 748; LRMS (EI) [M – Cl]+ m/z 368.

3,3'-(((4-chloro-1,2-phenylene)bis(azanediyl))bis(2-oxoethane-2,1-diyl))bis(1-methyl-1H-imidazol-3-ium) Chloride (2c):

Yield: 3.48 g (76%); pale yellow, ^{1}H NMR (300 MHz, DMSO-d_6) δ 10.97 (s, 1H), 10.88 (s, 1H), 9.36 (s, 1H), 9.35 (s, 1H), 7.89 (m, 2H), 7.74 (m, 3H), 7.64 – 7.52 (m, 1H), 7.23 (dd, J = 8.7, 2.5 Hz, 1H), 5.49 (s, 2H), 5.48 (s, 2H), 3.91 (s, 6H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6) δ 164.7, 164.5, 137.8, 131.2, 128.7, 128.2, 123.8, 123.1, 120.5, 51.4, 35.8 ppm; Anal. calcd for $C_{18}H_{21}Cl_3N_6O_2$ (%): C, 47.02; H, 4.60; N, 18.28. Found (%): C, 47.21; H, 4.44; N, 18.61; IR (cm^{-1}): 2952, 1694, 1612, 1546, 1487, 1396, 1306, 1250, 1180, 830; LRMS (EI) $[M – Cl]^+$ *m/z* 388.

3,3'-((1,2-phenylenebis(azanediyl))bis(2-oxoethane-2,1-diyl))bis(1-methyl-1H-imidazol-3-ium) Chloride (**2d**):

Yield: 3.18 g (75%); pink solid; ^{1}H NMR (300 MHz, DMSO-d_6) δ 10.74 (s, 1H), 9.36 (s, 1H), 7.89 (d, J = 1.7 Hz, 1H), 7.74 (d, J = 1.7 Hz, 1H), 7.59 (dd, J = 6.0, 3.6 Hz, 1H), 7.16 (dd, J = 6.1, 3.5 Hz, 1H), 5.48 (s, 2H), 3.91 (s, 3H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6) δ 164.3, 137.8,

129.7, 125.2, 124.7, 123.7, 123.0, 51.4, 35.8 ppm; Anal. calcd for $C_{18}H_{22}Cl_2N_6O_2$ (%): C, 50.83; H, 5.21; N, 19.76. Found (%): C, 51.03; H, 5.33; N, 19.14. IR (cm^{-1}): 2955, 1688, 1597, 1551, 1496, 1442, 1341, 1310, 1250, 1179, 1107, 751, 693, 618, 502; LRMS (EI) $[M - Cl]^+$ *m/z* 354.

4.4. ***General Procedure for the Mizoroki–Heck Cross Coupling Reaction:***

In a Schlenk flask under N_2 atmosphere, **2a** (5 mg, 0.011 mmol), $PdCl_2$ (2 mg ,0.011 mmol), Cs_2CO_3 (358 mg, 1,1 mmol) and DMF (1.5 mL) were added. The reaction mixture was heated at 90 °C for 30 min. Then, an aryl halide (1.0 mmol) and an olefin (1.2 mmol) were added and the mixture was further stirred at 125 °C under air atmosphere conditions. The reaction progress was monitored by Thin Layer Chromatography (EtOAc/hexane, 1:9). After completion of the reaction, the mixture was cooled to room temperature, and water (8 mL) was added and was extracted with EtOAc (3 × 10 mL). The organic solvent was dried over Na_2SO_4 and was evaporated under vacuum to give the crude product which was further purified by column chromatography using EtOAc/hexane, 1:9.

4.5. ***^{1}HNMR data of Mizoroki-Heck products*** **(5a-5o):**

(*E*)-1,2-diphenylethene (5a): ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.54 (m, 4H), 7.38 (m, 5H), 7.32 – 7.25 (m, 3H).

Methyl cinnamate (5b): ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.70 (d, *J* = 16.0 Hz, 1H), 7.51 (m, *J* = 3.9, 1.6 Hz, 2H), 7.43 – 7.32 (m, 3H), 6.44 (d, *J* = 16.0 Hz, 1H), 3.80 (s, 3H).

(*E*)-1-styrylnaphthalene (5c): ^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.39 – 8.29 (m, 1H), 8.10 – 7.79 (m, 4H), 7.76 – 7.55 (m, 5H), 7.54 – 7.33 (m, 3H), 7.31 – 7.17 (m, 1H).

Ethyl (*E*)-3-(naphthalen-1-yl)acrylate (5d): ^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.54 (d, *J* = 15.7 Hz, 1H), 8.21 (dd, *J* = 8.4, 1.4 Hz, 1H), 7.97 – 7.82 (m, 2H), 7.76 (dd, *J* = 7.2, 1.1 Hz, 1H), 7.63 – 7.38 (m, 3H), 6.54 (d, *J* = 15.8 Hz, 1H), 4.33 (q, *J* = 7.1 Hz, 2H), 1.39 (t, *J* = 7.1 Hz, 3H).

(*E*)-1-bromo-4-styrylbenzene (5e): ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.54 – 7.48 (m, 2H), 7.45 – 7.26 (m, 5H), 7.17 (m, 1H).

Methyl (*E*)-3-(4-bromophenyl)acrylate (5f) :^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.60 (d, *J* = 16.0 Hz, 1H), 7.50 (d, *J* = 8.5 Hz, 2H), 7.36 (d, *J* = 8.5 Hz, 2H), 6.41 (d, *J* = 16.0 Hz, 1H), 3.79 (s, 3H).

(*E*)-1-methyl-3-styrylbenzene (5g): ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.54 – 7.46 (m, 3H), 7.42 – 7.27 (m, 6H), 7.14 – 6.91 (m, 2H), 2.89 (s, 3H).

Methyl (*E*)-3-(m-tolyl)acrylate (5h): ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.67 (d, *J* = 16.0 Hz, 1H), 7.39 – 7.16 (m, 4H), 6.43 (d, *J* = 16.0 Hz, 1H), 3.80 (s, 3H), 2.37 (s, 3H).

Methyl (*E*)-3-(2-chlorophenyl)acrylate (5i): ^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.07 (d, *J* = 16.0, 1H), 7.63 – 7.54 (m, 1H), 7.38 (m, 1H), 7.31 – 7.20 (m, 2H), 6.41 (d, *J* = 16.0, 1H), 3.80 (s, 3H).

Ethyl (*E*)-3-(2-chlorophenyl)acrylate(5j):^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.60 (d, *J* = 16.0 Hz, 1H), 7.53 – 7.47 (m, 2H), 7.39 – 7.33 (m, 2H), 6.41 (d, *J* = 16.0 Hz, 1H), 3.79 (s, 3H).

Methyl (*E*)-3-(2-ethylphenyl)acrylate (5k): ^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.04 (d, *J* = 15.8 Hz, 1H), 7.56 (d, *J* = 7.4 Hz, 1H), 7.39 – 7.28 (m, 1H), 7.25 – 7.17 (m, 2H), 6.38 (d, *J* = 15.8 Hz, 1H), 3.82 (s, 3H), 2.79 (q, *J* = 7.6 Hz, 2H), 1.23 (t, *J* = 7.6 Hz, 3H).

Methyl (*E*)-3-(2-fluorophenyl)acrylate(5l): ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.82 (d, *J* = 16.2 Hz, 1H), 7.53 (td, *J* = 7.6, 1.8 Hz, 1H), 7.41 – 7.20 (m, 1H), 7.20 – 6.97 (m, 2H), 6.54 (d, *J* = 16.3 Hz, 1H), 3.81 (s, 3H).

Methyl (*E*)-3-(4-fluorophenyl)acrylate (5m): ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.63 (d, *J* = 16.0 Hz, 1H), 7.53 – 7.42 (m, 2H), 7.05 (t, *J* = 8.6 Hz, 2H), 6.34 (d, *J* = 16.0 Hz, 1H), 3.78 (s, 3H).

Ethyl (*E*)-3-(4-fluorophenyl)acrylate (5n): ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.65 (d, *J* = 16.0 Hz, 1H), 7.56 – 7.45 (m, 2H), 7.13 – 6.97 (m, 2H), 6.36 (d, *J* = 16.0 Hz, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 1.34 (t, *J* = 7.1 Hz, 3H).

Methyl (*E*)-3-(3-nitrophenyl)acrylate (5o): ^{1}HNMR (300 MHz, Chloroform-*d*) δ 8.36 (t, *J* = 2.0 Hz, 1H), 8.22 (ddd, *J* = 8.2, 2.3, 1.1 Hz, 1H), 7.82 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.75 – 7.68 (m, 1H), 7.58 (t, *J* = 8.0 Hz, 1H), 6.56 (d, *J* = 16.0 Hz, 1H), 3.83 (s, 3H).

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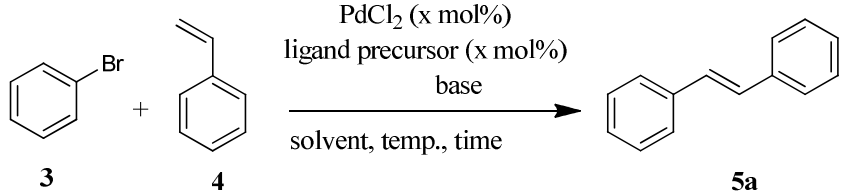
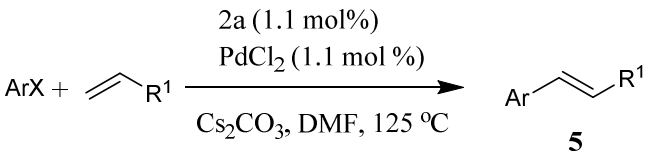
Table 1 Optimization of the reaction conditions[a]



Entry	Solvent	Base	T(°C)/Time (h)	$PdCl_2$ (x mol %)	Ligand precursor (x mol%)	Yield [b]
1	H_2O	Cs_2CO_3	120/6	1.1	**2a** (1.1%)	15
2	Toluene	Cs_2CO_3	120/5	1.1	**2a** (1.1%)	38
3	DMSO	Cs_2CO_3	120/3	1.1	**2a** (1.1%)	66
4	Dioxane	Cs_2CO_3	120/5	1.1	**2a** (1.1%)	52
5	DMF	Cs_2CO_3	120/3	1.1	**2a** (1.1%)	93
6	DMF	Cs_2CO_3	120/5	0.8	**2a** (0.8%)	85
7	DMF	Cs_2CO_3	120/3	1.7	**2a** (1.7%)	93
8	DMF	Cs_2CO_3	80/10	1.1	2a (1.1%)	38
9	DMF	Cs_2CO_3	115/5	1.1	**2a** (1.1%)	72
10	**DMF**	**Cs_2CO_3**	**125/3**	**1.1**	**2a** (1.1%)	**96**
11	DMF	Et_3N	125/3	1.1	**2a** (1.1%)	77
12	DMF	DIPEA	125/3	1.1	**2a** (1.1%)	71
13	DMF	*t*-BuOK	125/3	1.1	**2a** (1.1%)	78
14	DMF	NaOH	125/3	1.1	**2a** (1.1%)	75
15	DMF	K_2CO_3	125/3	1.1	**2a** (1.1%)	80
16	DMF	Cs_2CO_3	125/3	1.1	**2b** (1.1%)	92
17	DMF	Cs_2CO_3	125/3	1.1	**2c** (1.1%)	90
18	DMF	Cs_2CO_3	125/3	1.1	**2d** (1.1%)	90
19	DMF	Cs_2CO_3	125/10	1	-	25
20[h]	DMF	Cs_2CO_3	125/24	1.1	**1a** (1.1%)	18
21[i]	DMF	Cs_2CO_3	125/24	1.1	**1b** (1.1%)	22
22[j]	DMF	Cs_2CO_3	125/24	1.1	**1c** (1.1%)	17
23[k]	DMF	Cs_2CO_3	125/24	1.1	**1d** (1.1%)	19

[a]Reaction conditions: Bromobenzene (1mmol), Styrene (1.2 mmol), base (1.1 mmol), solvent (1.5 mL). [b]Isolated yields.

Table 2 'Diversity of Mizoroki-Heck reaction of Aryl halides and olefins.[a]



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Entry	ArX	R^1	Product	Time (h)	Yields[b]
1	PhBr	Ph	**5a**	3	96
2	PhBr	CO_2Me	**5b**	3.5	95
3	1-NaphBr	Ph	**5c**	3	95
4	1-NaphBr	CO_2Et	**5d**	4	93
5	4-BrC_6H_4Br	Ph	**5e**	3	94
6	4-BrC_6H_4Br	CO_2Me	**5f**	3.5	95
7	3-MeC_6H_4Br	Ph	**5g**	3.5	92
8	3-MeC_6H_4Br	CO_2Me	**5h**	3.5	93
9	2-ClC_6H_4Br	CO_2Me	**5i**	5	84
10	2-ClC_6H_4Br	CO_2Et	**5j**	5	85
11	2-EtC_6H_4Br	CO_2Me	**5k**	5.5	78
12	2-FC_6H_4Br	CO_2Me	**5l**	5	87
13	4-FC_6H_4Br	CO_2Me	**5m**	4.5	94
14	4-FC_6H_4Br	CO_2Et	**5n**	4.5	91
15	PhCl	Ph	**5a**	15	51
16	PhCl	CO_2Me	**5b**	15	55
17	4-$NO_2C_6H_4Cl$	CO_2Me	**5o**	15	59

[a] Reaction conditions: Aryl halide (1 mmol), olefin (1.2 mmol), Cs_2CO_3 (1.1 mmol), DMF (1.5 mL), 125 °C, under air. [b] Isolated yield.

Table 3 Comparison of activity and reaction conditions for homogeneous and heterogeneous catalysts in the Mizoroki-Heck reaction of bromobenzene and styrene.

Entry	Catalyst/(mol% Pd)	Solvent	Base	Time (h)/T (°C)	Yield (%)[a]
1	**2a**, $PdCl_2$ (1.1 mol%)	DMF	Cs_2CO_3 (1.1 mmol)	3/125	96 [This work]
[b]2	$PdCl_2$-Kryptofix (1.5 mol%)	DMF	Et_3N (1.1 mmol)	0.17/130	74 [13a]
3	$Pd(OAc)_2$ (2 mol%)	[HEmim][BF_4]	K_3PO_4 (2 mmol)	16/130	57 [10b]
4	[BMIM][X]-$Pd(OAc)_2$ (6 mol%)	[BMIM][PF6]	basic-IL (4 mmol)	4/70	91 [13b]
[c]5	CNT@Fe3O4@SiO2-Pd (1.5 mol%)	DMF	Cs_2CO_3 (1.5 mmol)	24/130	89 [13c]
[d]6	Pd-Salen@MWCNTs	DMF	Et_3N (1.1 mmol)	5/130	85 [13d]

[a] Isolated yield. [b, d] 1mmol TBAB was used as additive. [c] 0.5 mmol TBAB was used as additive.

A novel bis(imidazolium) chlorides as ligand precursor synthesized

Pd-catalyzed Mizoroki-Heck cross-coupling reactions was successfully performed

Performing the reaction with aryl chlorides and bromides

Moderate to excellent yields

Excellent regioselectivity for aryl bromides