



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.

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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 Csp²–Br and Csp²–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

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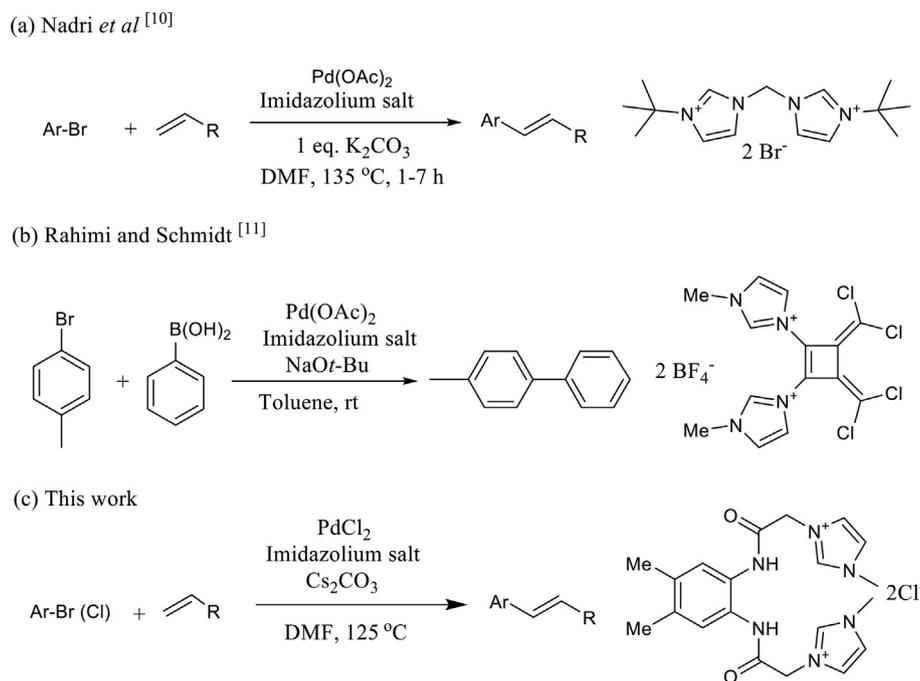
complexes are applied extensively for Mizoroki-Heck reaction. Deprotonation of NHC salts with a base in the presence of a Pd precursor can furnish the corresponding palladium complexes *in situ* suitable for cross-coupling reactions. In this regard, recently, Nadri et al. reported the application of 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).

2. Results and discussion

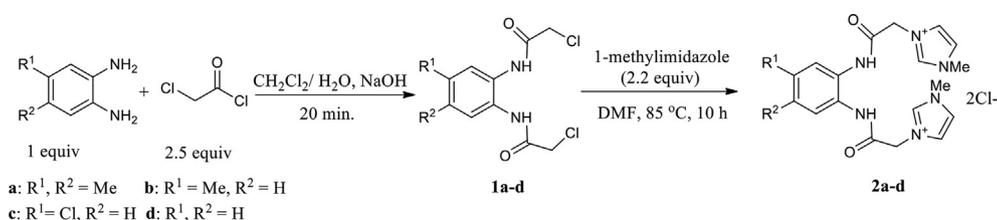
Four *bis*-imidazolium salts based on *o*-phenylenediamine as ligand precursor suitable for Pd-catalyzed Mizoroki-Heck cross-coupling reactions were prepared. As shown in Scheme 2, the reactions of chloroacetyl chloride with *o*-phenylenediamine and its derivatives were carried out to prepare the corresponding *N,N'*-(1,2-phenylene)bis(2-chloroacetamide) derivatives **1a-d** (yields (%): **1a**: 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, ¹H and ¹³C NMR, mass and elemental analysis.

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 Cs₂CO₃ (1.1 equiv) in various solvents such as water, toluene, DMSO, dioxane, and DMF by using 1.1 mol % of PdCl₂ 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 Et₃N, DIPEA (*N,N*-diisopropylethylamine), *t*-BuOK, NaOH, and K₂CO₃ instead of Cs₂CO₃ 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

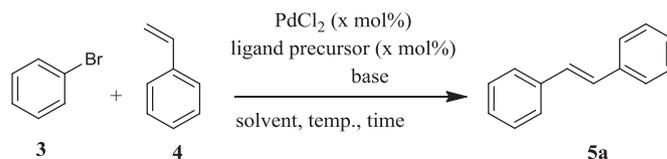


Scheme 1. Reported and proposed *bis*(imidazolium) salts as ligand precursor for C–C cross-coupling reactions.



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

Table 1
Optimization of the reaction conditions^a.



Yield ^b	Ligand precursor (x mol%)	PdCl ₂ (x mol %)	T (°C)/Time (h)	Base	Solvent	Entry
15	2a (1.1%)	1.1	120/6	Cs ₂ CO ₃	H ₂ O	1
38	2a (1.1%)	1.1	120/5	Cs ₂ CO ₃	Toluene	2
66	2a (1.1%)	1.1	120/3	Cs ₂ CO ₃	DMSO	3
52	2a (1.1%)	1.1	120/5	Cs ₂ CO ₃	Dioxane	4
93	2a (1.1%)	1.1	120/3	Cs ₂ CO ₃	DMF	5
85	2a (0.8%)	0.8	120/5	Cs ₂ CO ₃	DMF	6
93	2a (1.7%)	1.7	120/3	Cs ₂ CO ₃	DMF	7
38	2a (1.1%)	1.1	80/10	Cs ₂ CO ₃	DMF	8
72	2a (1.1%)	1.1	115/5	Cs ₂ CO ₃	DMF	9
96	2a (1.1%)	1.1	125/3	Cs₂CO₃	DMF	10
77	2a (1.1%)	1.1	125/3	Et ₃ N	DMF	11
71	2a (1.1%)	1.1	125/3	DIPEA	DMF	12
78	2a (1.1%)	1.1	125/3	<i>t</i> -BuOK	DMF	13
75	2a (1.1%)	1.1	125/3	NaOH	DMF	14
80	2a (1.1%)	1.1	125/3	K ₂ CO ₃	DMF	15
92	2b (1.1%)	1.1	125/3	Cs ₂ CO ₃	DMF	16
90	2c (1.1%)	1.1	125/3	Cs ₂ CO ₃	DMF	17
90	2d (1.1%)	1.1	125/3	Cs ₂ CO ₃	DMF	18
25	–	1	125/10	Cs ₂ CO ₃	DMF	19
18	1a (1.1%)	1.1	125/24	Cs ₂ CO ₃	DMF	20 ^h
22	1b (1.1%)	1.1	125/24	Cs ₂ CO ₃	DMF	21 ⁱ
17	1c (1.1%)	1.1	125/24	Cs ₂ CO ₃	DMF	22 ^j
19	1d (1.1%)	1.1	125/24	Cs ₂ CO ₃	DMF	23 ^k

^a Reaction conditions: Bromobenzene (1 mmol), Styrene (1.2 mmol), base (1.1 mmol), solvent (1.5 mL).

^b Isolated yields.

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 Cs₂CO₃ (1.1 equiv), PdCl₂ (1.1 mol %), and **2a** (1.1 mol %) in DMF at 125 °C was considered as optimal reaction conditions for further derivatization.

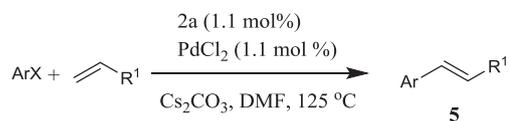
In order to explore the scope of the reaction, various activated and non-activated aryl halides and terminal olefins were applied in this protocol (Table 2). It is conceivable that the reaction of **2a** with Cs₂CO₃ produces the corresponding NHC ligand *in situ* for generation of the active catalyst with PdCl₂ 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].

The catalytic efficiency of our catalyst in Mizoroki–Heck cross-coupling reaction of bromobenzene and styrene is compared with those reported in the literature and summarized in Table 3. As

Table 2

^aDiversity of Mizoroki–Heck reaction of Aryl halides and olefins^a.



Yields ^b	Time (h)	Product	R ¹	ArX	Entry
96	3	5a	Ph	PhBr	1
95	3.5	5b	CO ₂ Me	PhBr	2
95	3	5c	Ph	1-NaphBr	3
93	4	5d	CO ₂ Et	1-NaphBr	4
94	3	5e	Ph	4-BrC ₆ H ₄ Br	5
95	3.5	5f	CO ₂ Me	4-BrC ₆ H ₄ Br	6
92	3.5	5g	Ph	3-MeC ₆ H ₄ Br	7
93	3.5	5h	CO ₂ Me	3-MeC ₆ H ₄ Br	8
84	5	5i	CO ₂ Me	2-ClC ₆ H ₄ Br	9
85	5	5j	CO ₂ Et	2-ClC ₆ H ₄ Br	10
78	5.5	5k	CO ₂ Me	2-EtC ₆ H ₄ Br	11
87	5	5l	CO ₂ Me	2-FC ₆ H ₄ Br	12
94	4.5	5m	CO ₂ Me	4-FC ₆ H ₄ Br	13
91	4.5	5n	CO ₂ Et	4-FC ₆ H ₄ Br	14
51	15	5a	Ph	PhCl	15
55	15	5b	CO ₂ Me	PhCl	16
59	15	5o	CO ₂ Me	4-NO ₂ C ₆ H ₄ Cl	17

^a Reaction conditions: Aryl halide (1 mmol), olefin (1.2 mmol), Cs₂CO₃ (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.

Yield (%) ^a	Time (h)/T (°C)	Base	Solvent	Catalyst/(mol% Pd)	Entry
96 [This work]	3/125	Cs ₂ CO ₃ (1.1 mmol)	DMF	2a , PdCl ₂ (1.1 mol%)	1
74 [13a]	0.17/130	Et ₃ N (1.1 mmol)	DMF	PdCl ₂ -Kryptofix (1.5 mol%)	^b 2
57 [10b]	16/130	K ₃ PO ₄ (2 mmol)	[HEmim][BF ₄]	Pd(OAc) ₂ (2 mol%)	3
91 [13b]	4/70	basic-IL (4 mmol)	[BMIM][PF ₆]	[BMIM][X]-Pd(OAc) ₂ (6 mol%)	4
89 [13c]	24/130	Cs ₂ CO ₃ (1.5 mmol)	DMF	CNT@Fe ₃ O ₄ @SiO ₂ -Pd (1.5 mol%)	^c 5
85 [13d]	5/130	Et ₃ N (1.1 mmol)	DMF	Pd-Salen@MWCNTs	^d 6

^a Isolated yield.^b 1 mmol TBAB was used as additive.^c 0.5 mmol TBAB was used as additive.^d 1 mmol TBAB was used as additive.

revealed from Table 3, our catalyst shows good activity in comparison to some of the reported methods in literature.

3. Conclusions

In conclusion, a new catalytic system for the Mizoroki-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, Cs₂CO₃ and PdCl₂. 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 were 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 Me₄Si (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 [III] 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 CH₂Cl₂ (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 CH₂Cl₂) 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

4.3.1. 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; ¹H 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; ¹³C 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 C₂₀H₂₆Cl₂N₆O₂ (%): 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.

4.3.2. 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; ¹H 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; ¹³C 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 C₁₉H₂₄Cl₂N₆O₂ (%): 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.

4.3.3. 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, ¹H 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; ¹³C 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 C₁₈H₂₁Cl₃N₆O₂ (%): 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.

4.3.4. 3,3'-(((1,2-phenylene)bis(azanediyl))bis(2-oxoethane-2,1-diyl))bis(1-methyl-1H-imidazol-3-ium) chloride (**2d**)

Yield: 3.18 g (75%); pink solid; ¹H 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; ¹³C 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 C₁₈H₂₂Cl₂N₆O₂ (%): 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 N₂ atmosphere, **2a** (5 mg, 0.011 mmol), PdCl₂ (2 mg, 0.011 mmol), Cs₂CO₃ (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 Na₂SO₄ and was evaporated under vacuum to give the crude product which was further purified by column chromatography using EtOAc/hexane, 1:9.

4.5. ¹H NMR data of Mizoroki–Heck products (**5a–5o**)

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

Methyl cinnamate (5b): ¹H 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): ¹H 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): ¹H 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): ¹H 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): ¹H 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): ¹H 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): ¹H 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): ¹H NMR (300 MHz, Chloroform-*d*) δ 8.07 (d, *J* = 16.0 Hz, 1H), 7.63–7.54 (m, 1H), 7.38 (m, 1H), 7.31–7.20 (m, 2H), 6.41 (d, *J* = 16.0 Hz, 1H), 3.80 (s, 3H).

Ethyl (E)-3-(2-chlorophenyl)acrylate (5j): ¹H 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): ¹H 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): ¹H 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): ¹H 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): ¹H 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): ¹H NMR (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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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jorganchem.2019.02.025>.

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