Arylhydrazones derivatives containing a benzothiazole moiety, efficient ligands in the palladium-catalyzed Mizoroki-Heck and Suzuki-Miyaura cross-coupling reactions under IR irradiation

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A simple arylhydrazone-containing the benzothiazole moiety which may be used as efficient ligand in the palladium-catalyzed Mizoroki-Heck and Suzuki-Miyaura cross-coupling reactions, under infrared irradiation as an alternative source of energy, is presented. The reactions proceeded with extremely high efficiency under mild conditions and produced very good yields.

Keywords Arylhydrazones, Palladium-catalyzed, Cross-coupling reaction, IR-irradiation

Introduction

The Mizoroki-Heck reaction is one of the most general and useful method for the formation of C-C bonds. This coupling reaction has a wide variety of applications, including total synthesis of natural products,[1] fine chemical syntheses,[2] bioorganic chemistry,[3,4] material science[5] and industrial applications,[6] among others. Furthermore, the palladium-catalyzed Suzuki-Miyaura cross-coupling[7] is another very useful and convenient method especially for the synthesis of various biaryl compounds[8,9] found as important structural units in pharmaceuticals[10] and natural products.[11] Consequently, researchers have been working on developing better catalysts and increasing yields in these areas which are important for both industrial and scientific purposes.[12]

In Mizoroki–Heck and Suzuki–Miyaura reactions, phosphine compounds are active due to their excellent donor capability.[13] Nevertheless, because these compounds present some disadvantages such as natural toxicity, sensitivity to air, being expensive, exhibiting synthetic difficulties and limitations of use,[14] the development of new more robust based-on-ligands and/or phosphine-free catalytic systems, based on different ligands that contain different donor groups, has been favored. Within this scope, nitrogen-based ligands are generally advantageous because they usually are stable to air, inexpensive and easier to handle than their phosphine counterparts.[15] including NHC ligand.[16]

On the other hand, new alternative heating methodologies such as microwave,[17] ultrasound,[18] and infrared (IR) irradiation[19] have been applied in organic synthesis and catalysis with reduced reaction times, cleaner reaction mixtures and good yields. We aimed to develop an environmentally safe method, and recently reported the use of IR irradiation as the energy source in Mizoroki-Heck[20] and Suzuki-Miyaura[21] cross-coupling reactions; in addition we demonstrated an air-stable phosphine-free hydrazone containing a heterocycle moiety as an effective ligand for palladium-catalyzed Mizoroki-Heck cross-coupling under IR irradiation.[20]

For this, we are interested on the development of a simple and active catalyst system to promote Mizoroki-Heck and Suzuki-Miyaura cross-coupling reactions, and focus our attention on arylhydrazones because their structure is simple and very stable. We are also interested on extending the use of IR irradiation as an alternative energy source for coupling reactions. Because of the above, herein we report the synthesis of arylhydrazone derivatives containing the benzothiazole moiety as the effective ligand for palladium-catalyzed Mizoro-

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ki-Heck and Suzuki-Miayaura cross-coupling reactions using IR irradiation.

Experimental

Apparatus, Materials, and Measurements

All operations were carried out in open atmosphere. Column chromatography was performed using 70–230 mesh silica gel. All reagents and solvents were obtained from commercial suppliers and used without further purification. All compounds were characterized by IR spectra, recorded on a Perkin-Elmer 283B by, Perkin-Elmer 283B or 1420 spectrophotometer, by means of film and KBr techniques, and all data are expressed in wave numbers (cm^{-1}). Melting points were obtained on a Melt- Temp II apparatus and are uncorrected. NMR spectra were measured with a Varian Eclipse +300 using $CDCl_3$ as solvents. Chemical shifts are in ppm (δ), relative to TMS. The MS-EI and MS-DART spectra were obtained on a JEOL SX 102A, the values of the signals are expressed in mass/charge units (*m/z*), followed by the relative intensity with reference to a 100% base peak.

The equipment used for irradiation with IR energy was created by employing an empty cylindrical metal vessel in which an Osram lamp (bulb model Thera-Therm, 250 W, 125 V) was inserted.[20,21] This lamp is special short-wave IR lamp (IR-A) for use in body care and wellness applications, with a maximum radiation at a wavelength of about 1100 nm. The lamp instantly emits a full thermal output as soon as it is switched on. For controlling the temperature, a Digi-Sense variable-time power controller was used. This time controller turned the output load on and off and then repeated the cycle. Although all the reactions were performed in open atmosphere, this arrangement also allows the use of inert conditions.

*General synthetic procedure for de compounds **1a-c**.*

A solution of the corresponding phenylhydrazine (2.6 mmol) in methanol (5 mL) was added dropwise to a magnetically stirred solution of benzothiazol-2-carbaldehyde (2.6 mmol) in methanol (5 mL). The mixture was stirred at room temperature for 12 h, to give a yellow solid, which was recovered by filtration and recrystallized from methanol.

2-Benzothiazolecarboxaldehyde *N,N*-diphenylhydrazone **1a**. (820 mg, 90 %) as yellow crystals, mp 142-144 °C; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ: 7.21-7.25 (m, 4H, H-14), 7.26 (s, 1H, H-10), 7.33-7.38 (m, 2H, H-16), 7.40-7.46 (m, 6H, H-15, H-4, H-5), 7.83-7.88 (m, 2H, H-6, H-3); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ: 121.5 (C-3), 122.3 (C-6), 122.6 (C-14), 125.5 (C-10), 125.9 (C-4), 129.6 (C-5), 129.9 (C-15, C-16), 134.2 (C-7), 142.2 (C-13), 153.6 (C-2), 167.3 (C9); IR (KBr) ν: 3060, 3027, 2994, 1711, 1711, 1632 cm^{-1}; MS (70 eV) *m/z* (%):329 (M^+, 98), 168 (100).

2-Benzothiazolecarboxaldehyde *N*-methyl-*N*-phenylhydrazone **1b**. (600 mg, 85 %) as yellow crystals, mp 150-152 °C; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ: 3.45 (s, 3H, C*H*$_3$-N), 7.02-7.08 (m, 1H, H-16), 7.33-7.43 (m, 6H, H-14, H-15, H4, H-5), 7.76 (s, 1H, H-10), 7.83 (d, *J* = 9.0 Hz, 1H, H-6), 7.93 (d, *J* = 9.0 Hz, 1H, H-3,); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ: 34.2 (*C*H$_3$N), 116.3 (C-14), 121.7 (C-16), 122.7 (C-3), 125.4 (C-6), 126.2 (C-4), 126.3 (C-5), 129.4 (C-15), 129.5 (C-10), 134.3 (C-7), 146.7 (C-13), 153.8 (C-2), 168.3 (C-9); IR (KBr) ν: 3034, 2967, 2933, 1608, 1711, 1458, 1435 cm^{-1}; MS (DART) *m/z* (%): 268 (98, M^+ + H).

2-Benzothiazolecarboxaldehyde *N*-phenylhydrazone **1c**. (560 mg, 85 %) as yellow crystals, mp 202-204 °C (lit [22] 204-205 °C). ^{1}H-NMR ($CDCl_3$, 300 MHz) δ: 3.21 (s, 1H, N-*H*), 7.00-7.06 (m, 1H, H-16), 7.28-7.37 (m, 5H, H-10, H-14, H-15), 7.43 (t, *J* = 14.7 Hz, H-4,), 7.52 (t, *J* = 14.7 Hz, 1H, H-5), 7.82 (d, *J* 8.1, 1H, H-6), 8.07 (d, *J* = 8.1 Hz, 1H, H-3,); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ: 113.8 (C-14), 120.1 (C-3), 120.9 (C-6), 122.9 (C-16), 125.8 (C-4), 126.3 (C-5), 126.6 (C-10), 129.4 (C-15), 134.2 (C-7), 142.2 (C-13), 153.6 (C-9), 167.3 (C2); IR (KBr) ν: 3060, 3027, 2994 (H-Csp^2), 1711 (C=N), 1711 (C=NHet), 1632 (C=C$_{Ar}$) cm^{-1}; MS (DART) *m/z* (%): 254 (98, M^+ + H).

*General synthetic procedure for de compounds **2a-f**.*

A solution of the corresponding substituted benzaldehyde (2.6 mmol) in methanol (5 mL) was added dropwise to a magnetically stirred solution of 2-hydrazinobenzothiazole (2.6 mmol) in methanol (5 mL). The mixture was stirred at room temperature for 30 min, to give a solid, which was recovered by filtration and recrystallized from methanol.

Benzaldehyde 2-(2-benzothiazolyl)hydrazone **2a**. (630 mg, 96 %) as white crystals, mp 226-228 °C (lit [23a] 225-226 °C). ^{1}H-NMR ($CDCl_3$, 300 MHz) δ: 6.8 (s, 1H, N-*H*), 7.29-7.35 (m, 2H, H-14), 7.42-7.49 (m, 3H, H-15, H-16), 7.64-7.74 (m, 4H, H-3, H-5, H-6), 8.40 (s, 1H, H-12); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ: 116.0 (C-3), 122.0 (C-6), 124.5 (C-5), 127.8 (C-15), 128.9 (C-14), 131.3 (C-16), 132.5 (C-13), 140.2 (C-12), 150.8 (C-2), 160.3 (C-9); IR (KBr) ν: 3056, 2964, 1921, 1881, 1805, 1625, 1632, 1575 cm^{-1}; MS (DART) *m/z* (%): 254 (98, M^+ + H).

4-Methylbenzaldehyde 2-(2-benzothiazolyl)hydrazone **2b**. (620 mg, 90 %) as yellow crystals, mp 232-234 °C (lit [23a] 231-233 °C). ^{1}H-NMR ($CDCl_3$, 300 MHz) δ: 2.39 (s, 3H, C*H*$_3$), 7.23 (d, *J* = 8.1 Hz, 2H, H-15), 7.40 (t, *J* =14.4 Hz, 2H, H-4, H-5), 7.61 (d, *J* = 8.1 Hz, 2H, H-14), 7.67, (d, *J* = 7.5 Hz, 2H, H-6), 8.31 (s, 1H, H-12) 9.36 (s, 1H, N-*H*); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ: 21.6 (*C*H$_3$), 116.3 (C-3), 121.8 (C-6), 123.95 (C-5), 125.7 (C-4), 127.4 (C-7), 127.6 (C-14), 129.5 (C-15), 130.1 (C-13), 141.5 (C-16), 142.1 (C-12), 149.6 (C-2), 168.2 (C-9); IR (KBr) ν: 3202, 3076, 2886, 2814, 1916, 1878, 1624, 1577 cm^{-1}; MS (DART) *m/z* (%): 268 (98, M^+ + H).

4-Methoxylbenzaldehyde 2-(2-benzothiazolyl)hydrazone **2c**. (710 mg, 97 %) as white crystals, mp 196-198 °C (lit [23a] 194-195 °C). ^{1}H-NMR ($CDCl_3$, 300 MHz) δ: 3.85 (s, 3H, OC*H*$_3$), 6.97 (s, 1H, N-*H*), 6.93 (d, *J* = 8.7 Hz, 2H, H-15), 7.20 (t, *J* = 14.1 Hz, 1H, H-4), 7.36 (t, *J* = 14.1 Hz, 1H, H-5), 7.55 (d, *J* = 7.5 Hz, 2H, H-6), 7.64 (d, *J* = 8.7 Hz, 2H, H-14), 8.18 (s, 1H, H-12).

^{13}C-NMR ($CDCl_3$, 75 MHz) δ: 55.3 (OCH_3), 114.2 (C-15), 116.6 (C-3), 121.7 (C-6), 123.1 (C-5), 126.0 (C-4), 126.9 (C-7), 127.2 (C-13), 129.0 (C-14), 144.7 (C-12), 147.5 (C-2), 161.6 (C-16), 168.2 (C-9); IR (KBr) ν: 3063, 3000, 2931, 2832, 1603, 1574, 1557 cm^{-1}; MS (DART) *m/z* (%): 284 (98, M^+ + H).

4-Dimethylaminolbenzaldehyde 2-(2-benzothiazolyl)hydrazone **2d**. (745 mg, 97 %) as white crystals, mp 238-240 °C (lit [23a] 236-238 °C). ^{1}H-NMR ($CDCl_3$, 300 MHz) δ: 3.01 (s, 6H, N*Me*$_2$), 6.72 (d, *J* = 8.7 Hz, 2H, H-15), 7.13 (t, *J* = 14.1 Hz, 1H, H-4), 7.33 (t, *J* = 14.1 Hz, 1H, H-5), 7.51 (d, *J* = 7.8 Hz, 2H, H-6), 7.54 (d, *J* = 8.7 Hz, 2H, H-14), 7.68 (d, *J* = 7.8 Hz, 1H, H-3), 7.91 (s, 1H, H-12). ^{13}C-NMR ($CDCl_3$, 75 MHz) δ: 40.2 (N*Me*$_2$), 111.5 (C-15), 117.8 (C-3), 121.3 (C-6), 121.6 (C-5), 121.9 (C-13), 125.9 (C-4), 128.3 (C-14), 130.2 (C-7), 144.9 (C-12), 150.0 (C-2), 151.5 (C-16), 168.3 (C-9); IR (KBr) ν: 3074, 3040, 2883, 2799, 1920, 1877, 1624, 1576, 1556 cm^{-1};. MS (DART) *m/z* (%): 297 (98, M^+ + H).

4-Cholorobenzaldehyde 2-(2-benzothiazolyl)hydrazone **2e**. (720 mg, 97 %) as white crystals, mp 143-145 °C (lit [23b] 140-142 °C). ^{1}H-NMR ($CDCl_3$, 300 MHz) δ: 7.20 (t, *J* 14.1, 2H, H-4, H-5), 7.35 (d, *J* = 7.2 Hz, 1H, H-3), 7.40 (d, *J* = 8.4 Hz, 2H, H-15), 7.55 (d, *J* = 7.8 Hz, 1H, H-6), 7.65 (d, *J* = 8.4 Hz, 2H, H-14), 7.8 (s, 1H, H-12). ^{13}C-NMR ($CDCl_3$, 75 MHz) δ: 118.3 (C-3), 121.8 (C-6), 124.5 (C-5), 125.3 (C-4), 128.9 (C-15), 130.6 (C-14), 130.8 (C-7), 134.9 (C-13), 136.6 (C-16), 143.3 (C-12), 150.1 (C-2), 169.8 (C-9); IR (KBr) ν: 3078, 2965, 1931, 1884, 1626, 1575, 1489 cm^{-1}; MS (DART) *m/z* (%): 288 (98, M^+ + H).

4-Nitrobenzaldehyde 2-(2-benzothiazolyl)hydrazone **2f**. (770 mg, 99 %) as yellow crystals, mp 118-120 °C (lit [23b] 117-119 °C). ^{1}H-NMR ($CDCl_3$, 300 MHz) δ: 7.14 (t, *J* = 14.1 Hz, 2H, H-3), 7.60-7.67 (m, 2H, H-4, H-6), 7.85 (d, *J* = 9.0 Hz, 2H, H-14), 7.95-7.96 (m, 2H, H-5, H12), 8.0 (d, *J* = 8.4 Hz, 2H, H-15). ^{13}C-NMR ($CDCl_3$, 75 MHz) δ: 116.9 (C-3), 121.7 (C-6), 123.1 (C-15), 123.2 (C-14), 126.0 (C-5), 126.9 (C-4), 127.2 (C-7), 129.0 (C-13), 144.7 (C-12), 147.5 (C-2), 161.6 (C-16), 168.2 (C-9); IR (KBr) ν: 3073, 2966, 1936, 1893, 1623, 1570, 1510 cm^{-1}; MS (DART) *m/z* (%): 299 (98, M^+ + H).

General procedure for Mizoroki–Heck coupling reactions

A mixture of aryl halide (2 mmol), methyl acrylate (3.3 mmol), and base (2.5 mmol) was placed in 5 mL of solvent in a 50-mL round-bottom flask; then, the source of palladium and the corresponding arylhydrazone, **1** or **2**, were added. The reaction mixture was irradiated with IR energy[20,21] for the time reported in Tables 1 and 2. The reaction was thereafter cooled at room temperature and the mixture was diluted with 10 mL of water and extracted with either ether or hexane (3 X 10 mL). The combined organic layers were dried over anhydrous sodium sulfate. The crude product was finally purified by flash column chromatography on silica-gel to give the isolated products.

The purified product was identified by means of mp determination and by ^{1}H and ^{13}C-NMR; the data obtained are consistent with literature.[24]

General procedure for Suzuki-Miyaura coupling reactions

Inside a 50-mL round-bottom flask, a mixture of aryl halide (0.5mmol), phenylboronic acid (0.6 mmol), and base (1 mmol) was placed in 3 mL of solvent; then, $Pd(OAc)_2$ and hydrazone **1a** were added. The reaction was irradiated with IR energy [20,21] for the time reported in Tables 3 and 4. Thereafter, the reaction was cooled at room temperature; the mixture was diluted with 10 mL of water and extracted with hexane or AcOEt (3 X 10 mL). The combined organic layers were dried over anhydrous sodium sulfate. The crude product was finally purified by column chromatography on silica-gel to give the isolated products.

The purified product was identified by means of mp determination and by ^{1}H and ^{13}C-NMR; the data obtained are consistent with literature.[25]

Results and discussion

We carried out the synthesis of two arylhydrazone derivatives containing the benzothiazole moiety, compounds **1** and **2** (Figure 1).

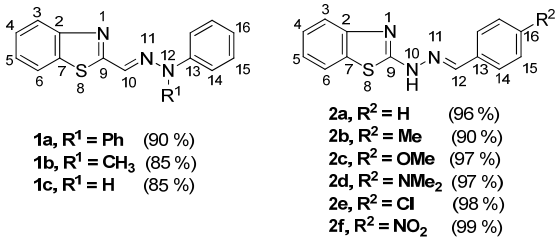


Figure 1 Structure of arylhydrazones.

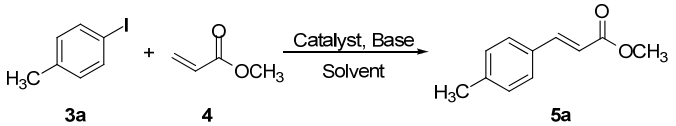
The syntheses of arylhydrazones **1a-c** were achieved by the reaction of benzothiazol-2-carbaldehyde with the corresponding arylhydrazine in methanol for 12 h obtaining good yields. Arylhydrazones **2a-f** were synthetized by the reaction of 2-hydrazinobenzothiazole with the appropriate substituted benzaldehyde in methanol for 30 min obtaining excellent yields.

Compounds **1** and **2** were fully characterized by conventional spectroscopic methods, FT-IR, ^{1}H-NMR, and ^{13}C-NMR, and the data spectra are in full accordance with previous reports.[22,23]

Compared with some previous results,[23] we observed that the syntheses of arylhydrazones **2a-f** can be performed at room temperature, with short reaction times, and without the use of reflux or acid catalysis.

Once efficiently prepared arylhydrazones **1a-c** and **2a-f** they were used as ligands in the palladium-catalyzed Mizoroki-Heck reaction under IR irradiation as a source of energy. We chose $Pd(OAc)_2$ and **1a** as model pre-catalyst and we firstly evaluated the effect of the concentration of the catalytic system [$Pd(OAc)_2$/**1a**] on the reaction between 4-iodotoluene (**3a**) and methyl acrylate (**4**) (Table 1)

Table 1 Optimization of conditions for the Mizoroki-Heck cross-coupling reaction.[a]



3a **4** **5a**

Entry	Ligand (% mol)	Source of Pd (% mol)	Base	Solvent	Time (min)[b]	Yield (%)[c]	TON[d]	TOF (h^{-1})[e]
1	1a (0.5)	$Pd(OAc)_2$ (0.5)	K_3PO_4	DMF	90	70	200	133
2	1a (0.1)	$Pd(OAc)_2$ (0.1)	K_3PO_4	DMF	90	65	650	433
3	1a (0.05)	$Pd(OAc)_2$ (0.05)	K_3PO_4	DMF	60	85	1700	1700
4	1a (0.01)	$Pd(OAc)_2$ (0.01)	K_3PO_4	DMF	300	83	8300	1660
5	**1a (0.05)**	**$Pd(OAc)_2$ (0.05)**	**K_3PO_4**	**DMA**	**60**	**90**	**1800**	**1800**
6	1a (0.05)	$Pd(OAc)_2$ (0.05)	K_3PO_4	NMP	60	85	1700	1700
7	1a (0.05)	$Pd(OAc)_2$ (0.05)	Na_3PO_4	DMA	60	60	1200	1200
8	1a (0.05)	$Pd(OAc)_2$ (0.05)	Li_3PO_4	DMA	240	50	1000	250
9	1a (0.05)	$Pd(OAc)_2$ (0.05)	K_2CO_3	DMA	90	75	1500	1000
10	1a (0.05)	$Pd(OAc)_2$ (0.05)	KOAc	DMA	90	76	1520	1013
11	1b (0.05)	$Pd(OAc)_2$ (0.05)	K_3PO_4	DMA	60	80	1600	1600
12	1c (0.05)	$Pd(OAc)_2$ (0.05)	K_3PO_4	DMA	60	70	1400	1400
13	2a (0.05)	$Pd(OAc)_2$ (0.05)	K_3PO_4	DMA	60	87	1740	1740
14	2b (0.05)	$Pd(OAc)_2$ (0.05)	K_3PO_4	DMA	120	85	1700	850
15	2c (0.05)	$Pd(OAc)_2$ (0.05)	K_3PO_4	DMA	60	80	1600	1600
16	2d (0.05)	$Pd(OAc)_2$ (0.05)	K_3PO_4	DMA	60	84	1680	1680
17	2e (0.05)	$Pd(OAc)_2$ (0.05)	K_3PO_4	DMA	90	80	1600	1066
18	2f (0.05)	$Pd(OAc)_2$ (0.05)	K_3PO_4	DMA	120	85	1700	850
19	1a (0.05)	$PdCl_2$ (0.05)	K_3PO_4	DMA	90	87	1740	1160
20	1a (0.05)	$Pd(PhCN)_2Cl_2$ (0.05)	K_3PO_4	DMA	60	86	1720	1720
21	1a (0.05)	$Pd(PPh_3)_2Cl_2$ (0.05)	K_3PO_4	DMA	60	85	1700	1700
22	None	$Pd(OAc)_2$ (0.05)	K_3PO_4	DMA	60	10	200	200
23	1a (0.05)	None	K_3PO_4	DMA	0	0	0	0
24[f]	1a (0.05)	$Pd(OAc)_2$ (0.05)	K_3PO_4	DMA	360	90	1800	300

[a] Reaction conditions: 4-iodotoulene (1 mmol), methyl acrylate (2 mmol), base (2 mmol), 5 mL solvent, reflux. [b] Based on total consumption of aryl iodide determined by TLC. [c] Isolated yields. [d] TON = ratio of moles of product formed to moles of catalyst used. [e] TOF = TON/t (h). [f] Employing heating blanket.

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The coupling reaction was stirred under reflux, using different concentrations of the [$Pd(AcO)_2$/**1a**] system and different solvents (DMF, DMA and NMP); also, different bases, such as K_3PO_4, Na_3PO_4, Li_3PO_4, K_2CO_3, and KOAc, were evaluated (entries 1-10, Table 1). The best yield was obtained when DMA, K_3PO_4, and 0.05 % mol of the [$Pd(OAc)_2$/**1a]** system were used (entry 5, Table 1). Under similar conditions, the cross-coupling reaction was carried out using ligands **1b-c** (entries 11 and 12, Table 1) and **2a-f**, that afforded **5a** (entries 13-18, Table 1) though yielded less. Thus, hydrazone **1a** provides better performance in comparison to others compounds, with turn over numbers (TON) around ~10^3.

Once the best catalyst and the appropriate solvent were identified, different palladium sources (entries

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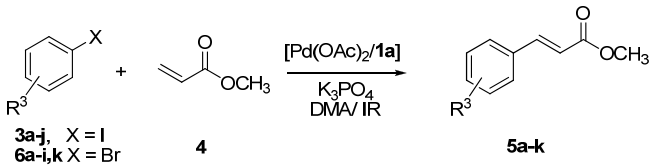
19-21, Table 1) were tested and **5a** was obtained with good yields; however, these yields did not exceed the efficiency of entry 5. Furthermore, we conducted two additional experiments; the first one was performed in absence of ligand and the second experiment was performed in absence of $Pd(OAc)_2$ (entries 22 and 23, Table 1). As expected, we only observed the formation of the coupling product in absence of ligand but in a low yield (entry 22, Table 1). Afterwards, in order to compare the energy sources, conventional heating (entry 24, Table 1) was used, which increased the reaction time in comparison with the use of IR heating.

Table 2 Scope of Mizoroki-Heck cross-coupling of aryl halides and methyl acrylate under IR irradiation.[a]



3a-j, X = I
6a-i,k X = Br

4

5a-k

Entry	X	R_3	Product	Time (min)[b]	Yield (%)[c]	TON[d]	TOF (h^{-1})[e]
1	I	4-CH_3	5a	60	90	1800	1800
2	I	2-CH_3	5b	70	90	1800	1551
3	I	4-OCH_3	5c	30	94	1880	3760
4	I	4-NH_2	5d	30	90	1800	3600
5	I	H	5e	60	85	1700	1700
6	I	4-Ac	5f	300	80	1000	200
7	I	4-Br	5g	60	85	1400	1400
8	I	4-AcO	5h	30	80	1600	3200
9	I	4-NO_2	5i	360	75	900	150
10	I	4-CF_3	5j	420	80	1600	228
11	Br	4-CH_3	5a	120	10	200	100
12[f]	Br	4-CH_3	5a	60	85	1800	1800
13	Br	2-CH_3	5b	180	80	1600	533
14[f]	Br	4-OCH_3	5c	60	90	1880	3760
15[f]	Br	4-NH_2	5d	60	85	1800	3600
16[f]	Br	H	5e	90	90	1700	1700
17[f]	Br	4-Ac	5f	150	65	1000	200
18[f]	Br	4-AcO	5h	120	80	1600	3200
19[f]	Br	4-NO_2	5i	300	50	900	150
20[f]	Br	4-Cl	5k	90	70	1400	1400

[a] Aryl halide (2 mmol), methyl acrylate (**4**) (3.3 mmol), DMA (5 mL), K_3PO_4 (2.5 mmol), [$Pd(AcO)_2$/**1a**] = 0.05 % mol. [b] Based on total consumption of aryl iodide determined by TLC. [c] Isolated yields after SiO_2 column chromatography. [d] TON = ratio of moles of product formed to moles of catalyst used. [e] TOF = TON/t (h). [f] Used TBAB (40%) as additive and 1 % mol of [$Pd(OAc)_2$/**1a**] system.

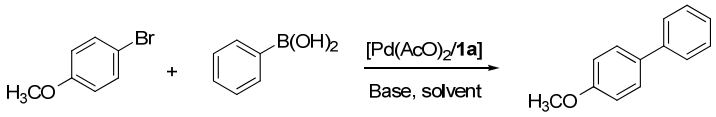
The next step was to explore the scope for the Mizoroki-Heck reaction in order to afford methyl *trans*-cinnamates **5a-k**. In this context, we carried out the reaction with a variety of activated and deactivated aryl iodides (**3a-j**) and aryl bromides (**6a-i,k**) with methyl acrylate (**4**), using the [$Pd(OAc)_2$/**1a**] system as the catalyst (Table 2). However, the coupling reaction of 4-bromotoluene (**6a**) and methyl acrylate (**3**), produced methyl *trans*-cinnamate **5a** in a very low yield in 120 min (entry 11, Table 2). As a result, we had to improve the reaction condition and, thus, used TBAB as additive, and 1 % mol of the [$Pd(OAc)_2$/**1a**] system (entries 12-20, Table 2).

This study shows that the Mizoroki-Heck reaction can be carried out using IR irradiation as a heating source to reduce reaction times and increase the efficiency of the reaction.

To extend the study of the catalytic properties of the [$Pd(AcO)_2$/**1a**] system, we performed a series of experiments using the Suzuki-Miyuara cross-coupling re-

action (Table 3). The coupling reaction between 4-bromoanisole and phenylboronic acid was selected as a model reaction. The approach used for the proposed Mizoroki–Heck reaction was also followed for the Suzuki–Miyaura reaction. In a first attempt, we used 0.05 % mol of the [$Pd(AcO)_2$/**1a**] system in methanol/water 3 mL (1:1) (entry 1, Table 3) using IR as the energy source for the optimization of conditions.

Table 3 Optimization of the conditions for the Suzuki-Miyaura cross-coupling reaction using the [$Pd(OAc)_2$/**1a**] system.[a]



6c **7** **8c**

Entry	Catalyst [$Pd(AcO)_2$/**1a**] (%)	Base	Solvent	Time (min)[j]	Yield (%)[k]	TON[l]	TOF (h^{-1})[m]
1	0.05	K_3PO_4	MeOH/H_2O (1:1)[b]	15	99	1980	7920
2	0.01	K_3PO_4	MeOH/H_2O (1:1)[b]	15	99	9900	39600
3	0.001	K_3PO_4	MeOH/H_2O (1:1)[b]	30	80	80000	160000
4	0.01	K_2CO_3	MeOH/H_2O (1:1)[b]	60	99	9900	9900
5	0.01	KOH	MeOH/H_2O (1:1)[b]	30	99	9900	19800
6	0.01	KOAc	MeOH/H_2O (1:1)[b]	40	60	6000	9090
7	0.01	K_3PO_4	MeOH/H_2O (1:1)[c]	15	99	9900	39000
8	0.01	K_3PO_4	MeOH[d]	15	99	9900	39600
10	**0.01**	**K_3PO_4**	**H_2O[e]**	**15**	**99**	**9900**	**39600**
11	0.01	K_3PO_4	EtOH[f]	25	99	9900	24146
12	0.01	K_3PO_4	EtOH/H_2O (1:1)[g]	20	99	9900	30000
13	0.01	K_3PO_4	H_2O[h]	60	99	9900	9900
14	0.01	K_3PO_4	H_2O[i]	1020	80	9900	582
15	0.01	K_3PO_4	H_2O[n]	120	45	4500	2250
16	0.01	K_3PO_4	H_2O[o]	120	0	0	0

[a]4-Bromoanisole **6b** (0.5 mmol), phenylboronic acid (**7**) (0.6 mmol), solvent (3 mL), Base (1 mmol), TBAB 0.5 mol. [b] T = 75 °C. [c] The reaction was conducted in absence of TBAB T = 75 °C. [d] T = 65 °C. [e] T = 96 °C. [f] T = 78 °C. [g] T = 82 °C. [h] Under conventional heating T = 96 °C. [i] Under room temperature. [j] Based on total consumption of 4-bromoanisole determined by TLC. [k] Isolated yields after SiO_2 column chromatography. [l] TON = ratio of moles of product formed to moles of catalyst used. [m] TOF = TON/t (h).[n] Without ligand. [o] Without Pd sourse.

We evaluated the effect of the concentration of the catalytic system on the reaction between 4-bromoanisole and phenylboronic acid (entry 1-3, Table 3). To find this optimum concentration, the reaction was carried out with different bases (entries 4-6, Table 3). We observed excellent yields using K_3PO_4 in the absence of TBAB (entry 7; Table 3); different solvent systems were tested, (entries 8-12, Table 3).

Furthermore, to compare the energy sources, the reaction at reflux conditions under conventional heating was tested (entry 13, Table 3), obtaining a quantitative yield of the coupling product of **8b**. The same reaction was performed at room temperature and produced 76% yield of **8b**, in 7 h (entry 14, Table 3). Thus, the optimized conditions for this cross-coupling reaction involve the use of 0.01% mol catalyst system [$Pd(OAc)_2$/**1a**], K_3PO_4 as the base, and H_2O as the solvent in absence of TBAB under IR-irradiation (entry 10, Table 3).

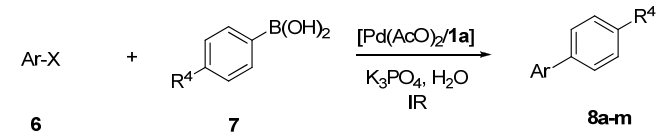
Finally, we conducted two additional experiments; the first one was performed in absence of ligand and the second experiment was performed in absence of $Pd(OAc)_2$ (entries 15 and 16, Table 3). As expected, we only observed the formation of the coupling product in absence of ligand but in a longer time and lower yield (entry 15, Table 3).

Subsequently, catalytic experiments were conducted with various aryl halide and boronic acid derivatives (entries 1-14, Table 4), including two heterocyclic substrates as a representative examples (entries 15 and 16,

Table 4). In every case, the substrates were quantitatively converted to the corresponding biphenyl, in general with good to excellent isolated yields after purification. The results showed that the catalytic system [$Pd(OAc)_2$/**1a**] is active with a wide range of substituents, and good yields of the coupling product were obtained. In spite of the reactivity of 4-chlorotoluene in the same reaction conditions (entry 5, Table 4), the catalytic system promotes the C-Cl bond activation but is moderately efficient compared to other aryl halides.

In order to compare other sources of palladium in the Mizoroki-Heck coupling, we previously reported[20a] the use of this methodology with different commercial palladium compounds in combination with triphenylphosphine due to this is the most used ligand in this reaction.

Table 4 Scope of Suzuki-Miyaura cross-coupling of aryl halides and phenyl boronic acids under IR irradiation.[a]



6 **7** **8a-m**

Entry	X	Ar	R_4	Product	Time (min)[b]	Yield (%)[c]	TON[e]	TOF (h^{-1})[f]
1	I	4-$CH_3C_6H_5$	H	8a	15	99	9900	39600
2	I	2-$CH_3C_6H_5$	H	8b	20	96	9600	2909
3	Br	4-$CH_3C_6H_5$	H	8a	15	99	9900	39600
4	Br	2-$CH_3C_6H_5$	H	8b	30	95	9500	19000
5	Cl	4-$CH_3C_6H_5$	H	8a	60	15	1500	1500
6	Br	4-$OCH_3C_6H_5$	H	8c	15	99	9900	39600
7	Br	C_6H_5	H	8d	30	90	9000	18000
8[d]	Br	$C_{10}H_8$	H	8e	30	75	7500	15000
9	Br	4-ClC_6H_5	H	8f	15	97	9700	38800
10	Br	4-AcC_6H_5	H	8g	15	99	9900	39600
11	Br	4-$NO_2C_6H_5$	H	8h	15	99	9900	39600
12	Br	4-$OCH_3C_6H_5$	CH_3	8i	15	85	8500	34000
13	Br	4-$OCH_3C_6H_5$	Cl	8j	15	99	9900	39600
14	Br	4-$OCH_3C_6H_5$	NO_2	8k	40	99	9900	15000
15	Br	2-Pyridine	H	8l	60	55	5500	5500
16	Br	2-Thiophene	H	8m	120	60	6000	3000

[a] Aryl halide **6** (0.5 mmol), phenylboronic acid (**7**) (0.6 mmol), H_2O (3 mL), K_3PO_4 (1 mmol),), [$Pd(AcO)_2$/**1a**] = 0.01 % mol, T = 96 °C [b] Based on total consumption of aryl halide determined by TLC. [c] Isolated yields after extraction with hexane and SiO_2 column chromatography. [d] 1-Bromonaphtalene was used as starting material. [e] TON = ratio of moles of product formed to moles of catalyst used. [f] TOF = TON/t (h).

These previously reported results show that the system formed by $Pd(AcO)_2/PPh_3/K_3PO_4$ can be considered the most efficient catalytic system, however our results herein presented are similar to these results. Moreover, compared to other ligands in the Mizoroki-Heck coupling previously reported, our protocol using the [$Pd(OAc)_2$/arylhidrazone] system shows important advantages in terms of lower reaction times,[26] lower catalytic system loading,[27] and the use of open atmosphere.[28] These advantages also exceed the results obtained by studies where the Mizoroki-Heck reaction was carried out in the absence of ligands using various palladium sources.[29,30]

Regarding the Suzuki-Miyaura coupling, many *N*-based compounds have been reported to be efficient ligands, in most cases the reactions were carried out in organic solvent at high temperature and/or under an inert atmosphere.[31,32,33-35] Suzuki-Miyaura reactions under aerobic conditions at room temperature can be accomplished by using a simple amine/$Pd(OAc)_2$ or glyoxal bis(*N*-methyl-*N*-phenylhydrazone)/$Pd(OAc)_2$ system[36, 37a] with a Pd loading as high as 2 mol % and the reaction time is longer. In addition the use of $Pd(AcO)_2$- and $PdCl_2$–free ligands to carry out such coupling is also reported, the results show good efficiency of the catalytic system, reaction at room temperature and good yields.[34] However, palladium loads are usually used above 0.5 mol% and the system only works well with electron donor groups on the arylhalide.

Furthermore, in comparison to other studies on the Suzuki-Miyaura coupling reaction available in the literature, the present reaction protocol is advantageous in

terms of arylboronic acid loading,[38] lower reaction times,[36,39] low catalyst loading,[36,37,39a,40] use of open atmosphere[28] and the absence of additives.[41]

Finally, the use of infrared irradiation as the energy source promotes the Mizoroki-Heck and Suzuki-Miyaura cross-coupling reactions in an efficient way in lower reaction times, compared to experiments performed using conductive heating.

Conclusions

Arylhydrazones **1-2** containing the benzothiazole moiety are an efficient ligand in the palladium-catalyzed Mizoroki-Heck and Suzuki-Miyaura cross-coupling reactions under infrared irradiation. The stability of the [$Pd(OAc)_2$/arylhydrazone] system to both air and moisture, avoids the use of inert conditions and facilitates all the manipulation processes in open atmosphere. Therefore, we evidence that infrared irradiation is an efficient, economical, and accessible alternative source of energy to assist Mizoroki-Heck and Suzuki-Miyaura cross-coupling reactions.

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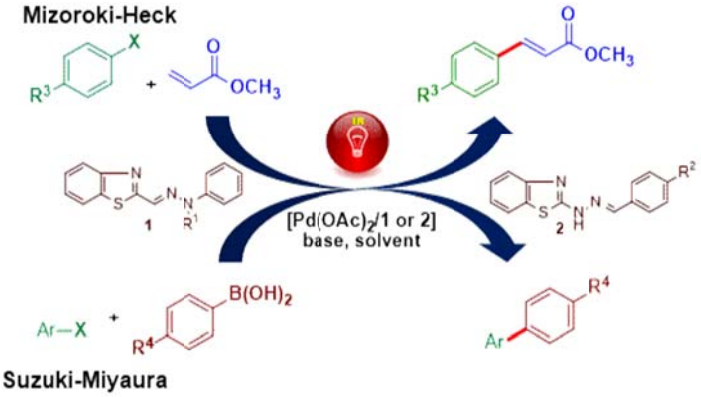
Entry for the Table of Contents

Page No.

Arylhydrazones derivatives containing the benzothiazole moiety, efficient ligands in the palladium-catalyzed Mizoro-ki-Heck and Suzuki-Miyaura cross-coupling reactions under IR irradiation.



Fernando Ortega-Jiménez* José Guillermo Penieres-Carrillo, José Guadalupe López-Cortés, M. Carmen Ortega-Alfaro and Selene Lagunas-Rivera.

A simple arylhydrazone **1** and **2** that containing a benzothiazole moiety are used as efficient ligand in the Mizoroki-Heck and Suzuki-Miyaura cross-coupling to the palladium-catalyzed under infrared irradiation as an alternative source of energy is herein reported.