Heck and Suzuki cross-couplings of aryl and heteroaryl bromides in water using a new palladium(II)-complex

Kamal M. Dawood,[a,*] Mohamed S. Fayed,[b] and Mohamed M. Elkhalea[c]

[a] *Department of Chemistry, Faculty of Science, Cairo University, Giza 12613, Egypt*
[b] *Department of Chemical Engineering, Military Technical College, Cairo, Egypt*
[c] *Excellence Center of Science and Technology, Elsalam-2, Cairo 3066, Egypt*
E-mail: dr_dawood@yahoo.com

Abstract
A new benzimidazole-based Pd(II)-complex was prepared and its catalytic activity was evaluated in Heck and Suzuki C-C cross-coupling reactions of aryl and heteroaryl bromides with olefins and arylboronic acids, respectively, under thermal heating using water as a reaction solvent. The factors affecting the optimization of such reactions are studied.

Keywords: Palladium, catalysis, C-C cross-coupling, water solvent, aryl halides, olefins

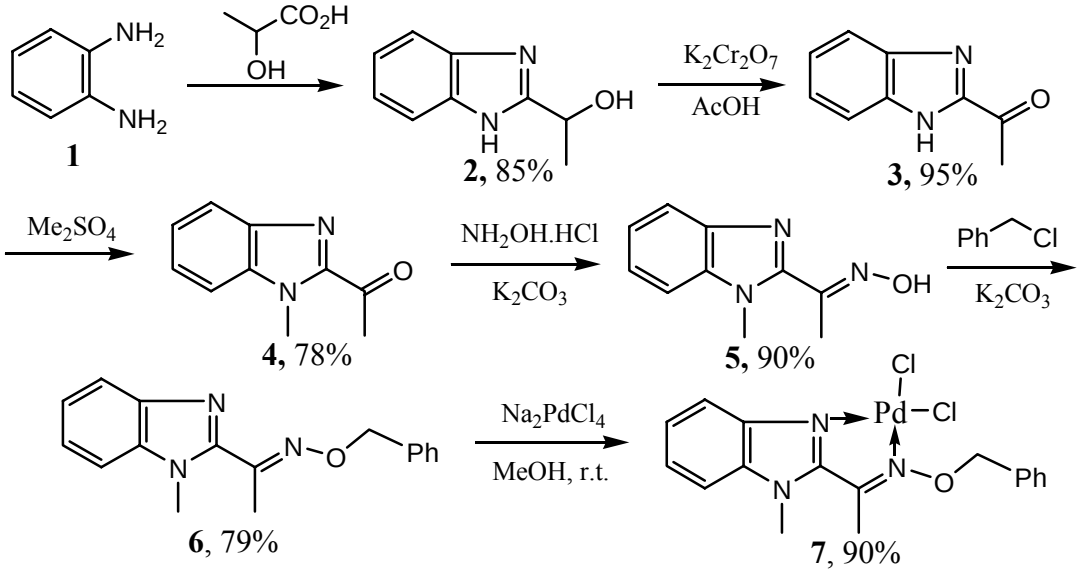
Introduction

Palladium catalyzed Suzuki–Miyaura cross-coupling reaction represents one of the most widely used processes for the synthesis of biaryls.[1-4] In addition, palladium-catalyzed Heck reactions of aryl halides with alkenes have also become one of the most powerful tools in organic synthesis for the construction of carbon–carbon bond.[5,6] From a viewpoint of green sustainable chemistry, organic reactions that can proceed well in aqueous media offer advantages over those occurring in organic solvents.[7] Recently, our interests are concerned with the use of Pd-catalysts in Suzuki-Miyaura and Heck-Mizoroki cross-coupling reactions in aqueous media.[8-10]
Therefore, developing new catalytic systems as catalysts for Suzuki-Miyaura and Heck-Mizoroki cross-coupling reactions for the synthesis of biaryls and disubstituted olefins will be of great importance. To date, various 1-alkylbenzimidazole-based Pd-catalysts have been developed and widely utilized for the Heck and Suzuki cross-coupling reactions.[11,12] In this work, we synthesized a new benzimidazole-oxime-based Pd(II)-complex and its catalytic activity in the phosphine ligand-free C-C cross-coupling reactions was evaluated. The factors affecting the optimization of the reaction conditions were also studied.

Results and Discussion

Preparation of the Pd (II)-complex 7

2-Acetyl-1-methylbenzimidazole-oxime **5** was prepared from 1,2-phenylene diamine as described in Scheme 1 following the reported literature procedures.[13] Reaction of 2-acetyl-1-methylbenzimidazole-oxime **5** with benzyl chloride in the presence of potassium carbonata in ethanol at room temperature gave *O*-benzyl 2-acetyl-1-methylbenzimidazole-oxime **6** in 79% yield. The structure of oxime **6** was established based on its elemental analysis and spectral data (MS, ^{1}H and ^{13}C NMR). Treatment of the oxime **6** with an equimolar amount of sodium tetrachloropalladate, dissolved in methanol, with stirring at room temperature for 2 h afforded a yellow precipitate of the Pd(II)-complex **7** in 90% yield as outlined in Scheme 1. The structure of the Pd(II)-complex **7** was elucidation based on the elemental analyses and spectroscopic data as well as related analogous reported examples.[9,14]

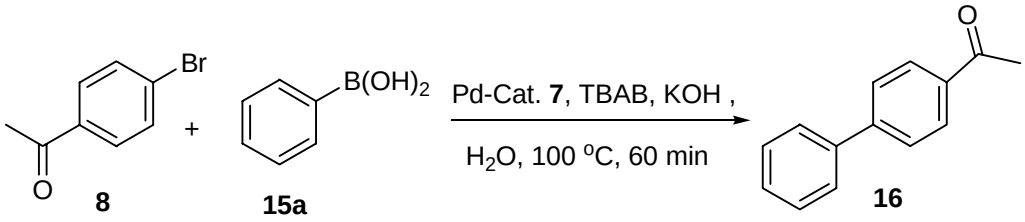


Scheme 1. Preparation of the Pd(II)-complex **7.**

The effect of concentration of the Pd(II) complex **7** on the cross-coupling reaction between 4-bromoacetophenone **8** and phenylboronic acid **15a** in water at 100 °C was examined as shown in Table 1. At first, the reaction was conducted in water (3 mL) using 1 mol% of the Pd(II) complex **7** with 1 mmol 4-bromoacetophenone **8**, 1.2 mmol phenylboronic acid, 0.6 mmol tetrabutylammonium bromide (TBAB) and 2 mmoles of potassium hydroxide at boiling temperature. TLC and ^{1}H NMR of crude reaction product showed that 4-bromoacetophenone **8** was completely consumed after one hour of heating and the product 4-acetylbiphenyl **16** was isolated in 94% yield. Next, the same experiment was repeated using 0.5 mol% of the catalyst under the same reaction conditions where complete consumption of the bromide **8** was observed

after one hour at reflux. Again, the same reaction was repeated with 0.25, 0.15, 0.1 and 0.05 mol% of the Pd(II) complex **7** to give full conversion, in each case, after one hour as illustrated in Table 1. When the same reaction was carried out without the Pd(II) complex **7** under the same reaction conditions, the starting material was completely recovered unchanged.

Table 1. Effect of concentration of the Pd(II)-complex **7** on the Suzuki coupling of 4-bromoacetophenone **8** with phenylboronic acid in water.



Entry	Cat. Conc. mol%	Yield %[a,b]	TON
1	1	100 (94)	100
2	0.5	100	200
3	0.25	100	400
4	0.15	100 (93)	666
5	0.1	100	1000
6	0.05	100	2000
7	0	0	0

[a]*Conditions:* Bromide/ boronic acid/ KOH/ TBAB /water (3 mL): 1/1.2/2/0.6, at 100 °C for one hour. [b]Conversions were based on ^{1}H NMR of crude product and the values between parenthesis refer to the isolated yields.

Similarly, the effect of concentration of the Pd(II) complex **7** on the cross-coupling reaction between 4-bromoacetophenone **8** (1 mmol) and other arylboronic acids (4-methoxyphenylboronic acid **15b** and 4-chlorophenylboronic acid **15c**) (1.2 mmol), in water at 100 °C was also examined. The reaction was conducted in water (3 mL) with TBAB and potassium hydroxide at boiling temperature using 1, 0.5 and 0.25 mol% of the Pd(II) complex **7**, respectively. TLC and ^{1}H NMR spectrum of crude reaction product showed in all cases that 4-bromoacetophenone **8** was completely consumed after one hour heating.

The efficiencies of different bases and solvents in the coupling reaction between 4-bromoacetophenone **8** and phenylboronic acid **15a** were also examined. As shown in Table 2, with 0.5 mol% of Pd complex **7**, the reaction was carried out in different solvents *e.g.* water, DMF, dioxane and toluene using potassium hydroxide as a base. Full conversion was obtained when water or DMF were used as solvents in the presence of TBAB after one hour at reflux condition (runs 1 and 2, Table 4), where the starting bromide **8** was completely consumed (as

examined by TLC and ^{1}H-NMR of the crude reaction mixture) and the cross coupled product 4-acetylbiphenyl **16** was obtained in 94 and 78% isolated yields, respectively. When water was replaced with dioxane and with toluene, for the same reaction time, the conversion of the starting material was decreased to 60 and 90%, respectively (runs 3 and 4, Table 2). Next, the effect of K_2CO_3 as a base instead of KOH was examined using different solvents (water, toluene and dioxane). Again, water proved itself as the efficient solvent in comparison to toluene or dioxane. When cesium carbonate was used as a base in water solvent, it resulted also in full conversion of the bromide **8** into 4-acetylbiphenyl **16** as shown in Table 2.

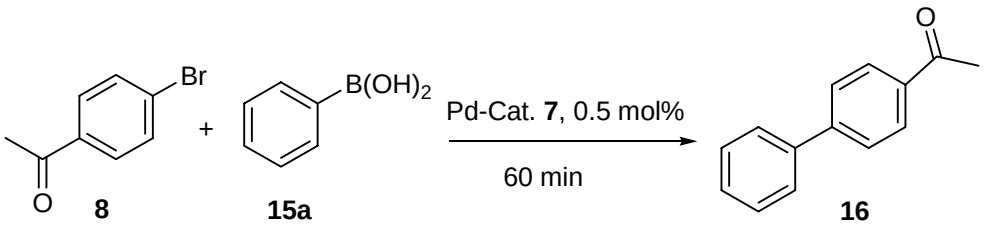


Table 2. Effect of solvent and base on Suzuki coupling 4-bromoacetophenone with phenylboronic acid

Run	Base	Solvent	Yield%[a,b]
1	KOH	H_2O	100 (94)
2	KOH	DMF	100 (78)
3	KOH	Dioxane	60
4	KOH	Toluene	90
5	K_2CO_3	H_2O	100 (83)
6	K_2CO_3	Toluene	90
7	K_2CO_3	Dioxane	40
8	Cs_2CO_3	H_2O	100 (93)

[a]*Conditions:* Bromide/ boronic acid/ base/ TBAB/ solvent: 1/1.2/2/0.6/ 3 mL at refluxing temperature. In case of water as solvent, TBAB was used as phase transfer agent [b]Conversions were based on ^{1}H NMR of the crude products and the values in parentheses refer to the isolated yields.

Therefore, water as an eco-friendly and a green solvent and KOH as a cheap and common base are chosen for carrying out all the Suzuki-Miyaura cross-coupling reactions that are performed in this work.

From the above results it is clear that our Pd complex **7** has high thermal stability in water under open air condition. In addition, it has high activity towards C-C cross coupling reactions as

the reaction could be finished after one hour with very low concentration, where $5x10^{-5}$ mmol of the catalyst are enough to convert 1 mmol of the arylbromide into the corresponding biaryl. This finding may be of interest for industrial mass applications.

Pd-complex 7 in Suzuki coupling of 4-chloroacetophenone with arylboronic acids

We next turned our attention on the cross-coupling reaction of 4-chloroacetophenone with various arylboronic acids, where chlorides are of particular importance for highly active catalysts.[15] At first, 4-chloroacetophenone **14** (1 mmol) was coupled with phenylboronic acid **15a** (1.2 mmol) in water (3 ml) in the presence of TBAB (0.6 mmol) using cesium carbonate (2 mmol) as base. Under these conditions, 88% conversion based on ^{1}H NMR spectrum of the crude reaction product were obtained after 6 h of heating at reflux using 0.5 mol% of the palladium complex **7**. The use of Pd-complex **7** for similar coupling reaction of 4-chloroacetophenone **14** with 4-methoxyphenylboronic acid **15b** and with 4-chlorophenylboronic acid **15c** in 0.5 mol% resulted in 75% and 80% conversions, respectively, after 6 h heating at reflux.

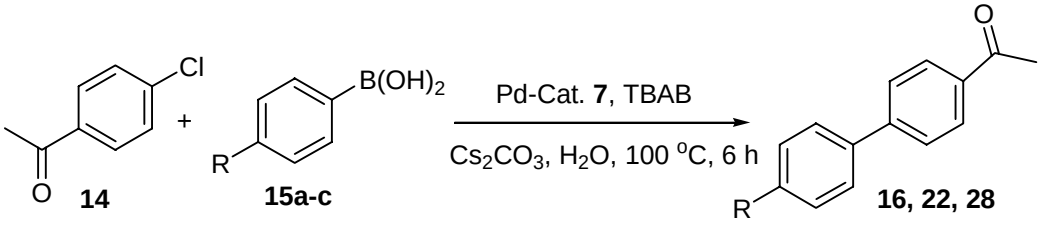
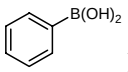
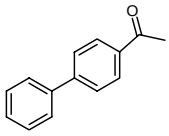
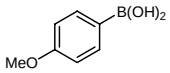
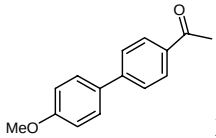
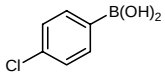
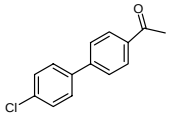


Table 3. Suzuki coupling of 4-chloroacetophenone **14** with arylboronic acids in water

Entry	Boronic acids	Product	Yield%[a]
1	 **15a**	 **16**	88
2	 **15b**	 **22**	75
3	 **15c**	 **28**	80 (64)

[a]*Reaction Conditions*: Chloride/ boronic acid/ base/ TBAB/ water (3 mL): 1/1.2/2/0.6, at 100 °C for 6 hours. Conversion yields were based on ^{1}H NMR spectrum of the crude products and the value in parentheses refer to the isolated yield.

Suzuki cross-coupling of aryl (Hetaryl) bromides with arylboronic acids

We next generalized the utility of Pd-complex **7** in Suzuki-Miyaura cross-coupling reactions under the above optimized conditions. Thus, Suzuki coupling of activated and deactivated aryl(heteroaryl) bromides **8-13** with arylboronic acids **15a-c** were carried out at 100 °C using water as solvent and KOH as base resulting in the formation of a library of the corresponding cross-coupled products **16-33** in good to excellent isolated yields as shown in Table 4. The reaction components molar ratios were typically; 1 mmol aryl(heteroaryl) bromides **8-13**, 1.2 mmol phenylboronic acid **15a-c**, 0.6 mmol TBAB, 2 mmoles of KOH using 0.5 mol% of the Pd-complex **7** in water (3 mL). Interestingly, the Pd-complex **7** was found to efficiently catalyze the coupling of a wide range of aryl bromides in excellent yields regardless their activating or deactivating substituents and the reactions could be finished mostly within one hour as can be seen in Table 4. Comparing to analogous oxime-based Pd-complexes,[8-11] our complex proved superior activity where both activated and deactivated aryl bromides as well as heterocyclic bromides could be completely consumed after 1 h giving the corresponding products in very good to excellent isolated yields as can be seen from Table 4. The identity of the coupling products was confirmed by ^{1}H and ^{13}C NMR, MS spectra and compared with the reported examples in literature whenever possible (see experimental section).

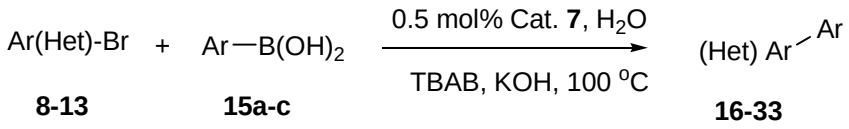
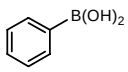
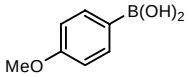
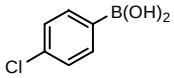
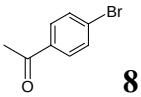
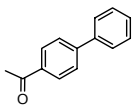
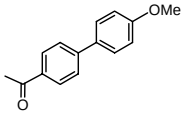
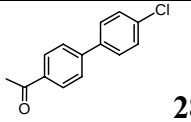
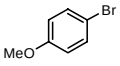
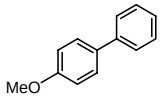
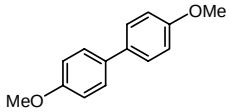
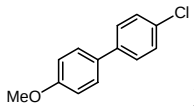
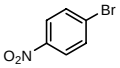
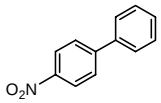
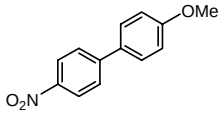
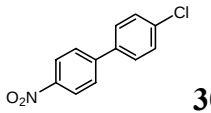
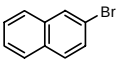
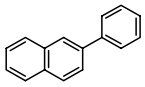
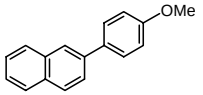
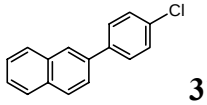
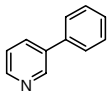
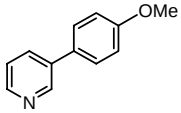
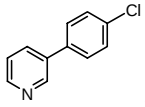
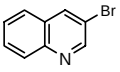
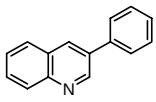
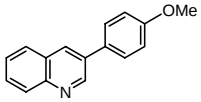
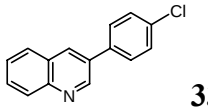


Table 4. Suzuki coupling of aryl bromides **8-13** with arylboronic acids **15a-c** in water

Ar-B(OH)$_2$	 **15a**		 **15b**		 **15c**	
Ar (Het)-Br	**Time (hr)**	**Yield%**[a]	**Time (hr)**	**Yield%**[a]	**Time (hr)**	**Yield%**[a]
 **8**	 **16**	1 96	 **22**	1 91	 **28**	1 92
 **9**	 **17**	1 93	 **23**	1 93	 **29**	1 93
 **10**	 **18**	1 90	 **24**	1 95	 **30**	1 90
 **11**		1 97	 **25**	1 93	 **31**	3 97
 **12**	 **20**	1 87	 **26**	2 93	 **32**	2 87
 **13**	 **21**	1 85	 **27**	1 90	 **33**	3 80

[a]*Reaction Conditions:* Bromide/ boronic acid/ KOH/ TBAB/ water: 1/1.2/2/0.6/ 3 mL at 100 °C temperature. All values refer to the isolated yields.

Mizoroki-Heck cross-coupling of aryl (heteroaryl) bromides with styrene

The reactivity of the Pd (II)-complex **7** towards Heck cross-coupling reaction was also investigated. At first, the Heck reaction was performed using 0.5 mol% of the Pd(II)-complex **7** with 1 mmol 4-bromoacetophenone **8**, 1.5 mmol styrene, 0.6 mmol TBAB, 2 mmol sodium hydroxide in water (3 mL) as solvent at 100 °C as outlined in Table 5. The starting bromide **8** was completely consumed after 3 h based on TLC analysis and ^{1}H NMR spectrum of the crude reaction product. 4-Acetylstilbene **35** was isolated in 92% yield (entry 1, Table 5). The same

reaction was repeated using DMF/NaOH instead of water/NaOH at 140 °C under open air, where complete consumption of the starting bromide was noticed after only one hour (entry 2, Table 5). Using triethylamine as base and water as solvent resulted in full conversion after 4 h (entry 3, Table 5).

The Heck reaction was repeated for a deactivated bromide (4-bromoanisole **9)** with styrene in DMF/NaOH in the presence of TBAB using 0.5 mol% of the Pd complex **7** at 140 °C for 2 h (based on TLC) to give 4-methyl-4'-nitrobiphenyl **36** in 87% yield (entry 4, Table 5). 4-Nitrobromobenzene **10** and 2-bromonaphthalene **11** were similarly cross-coupled with styrene in DMF or water in the presence of sodium hydroxide or triethylamine and the best results were obtained when DMF/NaOH/TBAB catalytic system was used (entries 6 and 8, Table 5).

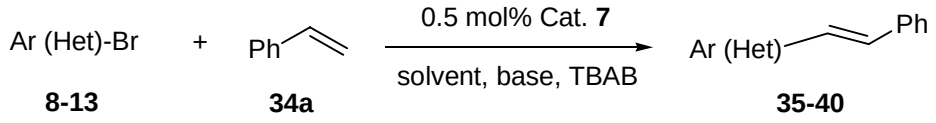
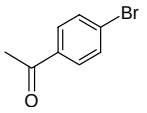
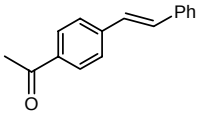
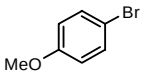
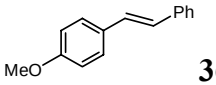
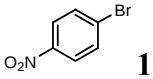
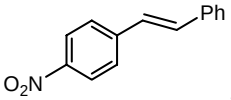
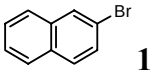
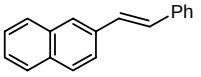
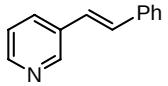
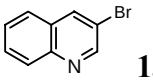
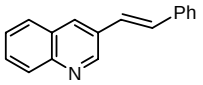


Table 5. Heck cross coupling of aryl (heteroaryl) bromides with styrene

Entry	Ar(Het)-Br	Product	Base/solvent	Time(h)	Yield%[a,b]
1	 **8**	 **35**	$NaOH/H_2O$	3	100 (92)
2			NaOH/DMF	1	100
3			Et_3N/H_2O	4	100
4	 **9**	 **36**	NaOH/DMF	2	100 (87)
5	 **10**	 **37**	$NaOH/H_2O$	5	80
6			NaOH/DMF	2	100 (95)
7	 **11**	 **38**	$NaOH/H_2O$ NaOH/DMF	3	80
8				2	100 (90)
9			Et_3N /H_2O	6	70
10	 **12**	 **39**	NaOH/DMF	5	70
11			$NaOH/H_2O$	6	100 (88)
12	 **13**	 **40**	NaOH/DMF	5	100 (90)

[a]*Conditions:* Bromide/ styrene/ base/ TBAB/ solvent: 1/1.5/2/0.6/3 mL at 100 °C for water and at 140 °C for DMF. [b]Values in parenthesis refer to the isolated yields

3-Bromopyridine **12** and 3-bromoquinoline **13**, as heterocyclic bromides, were similarly cross coupled with styrene to give the corresponding styryl derivatives **39** and **40**, respectively.

The cross-coupling of 3-bromopyridine **12** proceeded well in water/NaOH system but for 3-bromoquinoline **13** DMF/NaOH system was more suitable (entries 11 and 12, Table 5, respectively). The structures of the Heck coupled products were confirmed by spectral data and were in complete agreement with literature. The ^{1}H NMR spectra of the series prepared revealed, in each case, two characteristic doublets in the aromatic region having coupling constant *J* value about 16 Hz which supports the *trans*-configuration of the resulting disubstituted olefins.

Mizoroki-Heck cross-coupling of aryl (heteroaryl) bromides with *t*-butyl acrylate

The Heck cross-coupling reactions of the aryl (heteroaryl) bromides **8-13** with *t*-butylacrylate **34b** in 1 : 1.5 molar ratios were also studied. These reactions we conducted mainly in DMF as solvent using Et_3N as base in the presence of 0.5 mol% of the Pd-complex **7** and the reaction mixture was heated at 140 °C of under open air. The mixture was heated till the staring bromides were almost consumed after 3~9 h, based on TLC and/or ^{1}H NMR of the crude reaction products, to give the corresponding *t*-butyl esters **41-46** in high yields as illustrated in Table 6. The structures of the ester products were confirmed from their spectral data (MS, ^{1}H and ^{13}C NMR) and were consistent with the reported data. The ^{1}H NMR spectra of the obtained esters revealed two characteristic doublets having *J* value about 16 Hz giving an evidence for the *E*-configuration of the isolated products.

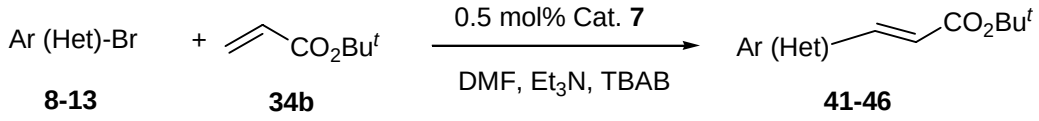
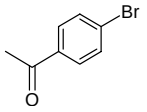
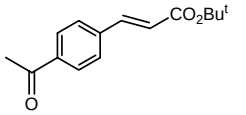
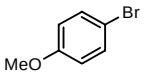
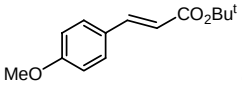
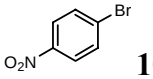
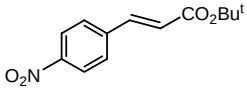
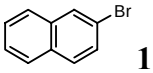
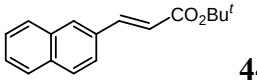
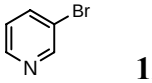
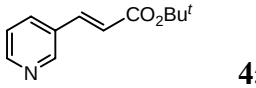
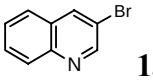
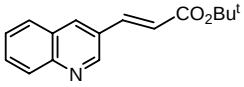


Table 6. Heck cross coupling of aryl (heteroaryl) bromides with *t*-butyl acrylate

Entry	Ar(Het)-Br	Product	Time(h)	Yield%[a,b]
1	 **8**	 **41**	4	100[c] (90)
2	 **9**	 **42**	8	90[c] (75)
3	 **10**	 **43**	3	(83)
4	 **11**	 **44**	8	(80)
5	 **12**	 **45**	5	(75)
6	 **13**	 **46**	9	(83)

[a]*Reaction Conditions:* Bromide/ styrene/ Et_3N/ TBAB/ DMF: 1/1.5/2/0.6/3 mL at 140 °C. [b]Values in parenthesis refer to the isolated yields.
[c]Conversions are based on the ^1H NMR spectra of the crude product.

Mizoroki-Heck coupling of 4-chloroacetophenone with *t*-butyl acrylate and styrene

To evaluate the catalytic activity of the Pd complex 7 towards the Heck cross coupling of aryl chlorides with olefins, we carried out the cross-coupling reaction of 4-chloroacetophenone **14** with styrene and with *t*-butyl acrylate. 4-Chloroacetophenone **14** (1 mmol) was coupled with styrene (1.5 mmol) in DMF (3 ml) in the presence of TBAB (0.6 mmol) and NaOH (2 mmol) as base using 0.5 mol% of the palladium complex **7**. Under these conditions, 63% conversion, based on ^1H NMR spectrum of the crude reaction product **35,** were obtained after 4 h of heating at 140 °C. Similar coupling of 4-choloroacetophenone **14** (1 mmol) with *t*-butyl acrylate (1.5 mmol) in DMF (3 ml) in the presence of TBAB (0.6 mmol) and triethylamine (2 mmol) as base using 0.5 mol% of Pd-complex **7** was also performed. Unfortunately, under this condition the ester **39** could not be detected at all and the starting bromide **14** was completely recovered unchanged.

In conclusion, the benzimidiazole-oxime-based palladium(II) complex **7** was found to be a very efficient and highly active precatalyst for Suzuki-Miyaura and Heck-Mizoroki cross-coupling reactions of activated and deactivated aryl bromides as well as heteroaryl bromides in water as a green solvent. The reactions were completed mostly within one hour using 0.5 mol% of the Pd-complex **7**.

Experimental Section

General. Melting points were determined in open glass capillaries with a Gallenkamp apparatus. The infrared spectra were recorded in potassium bromide disks on a Pye Unicam SP 3-300 and Shimaduz FTIR 8101 PC infrared spectrophotometer. NMR spectra were recorded with a Varian Mercury VXR-300 NMR spectrometer at 300 MHz (^{1}H NMR) and at 75 MHz (^{13}C NMR) using $CDCl_3$ as solvent and internal standard (δ 7.27 and 77.36 ppm, for ^{1}H NMR and ^{13}C NMR, respectively). Mass spectra (EI) were obtained at 70 eV with a type Shimadzu GCMQP 1000 EX spectrometer. Analytical thin-layer chromatography was performed using pre-coated silica gel 60778 plates (Fluka), and the spots were visualized with UV light at 254 nm. Fluka silica gel 60741 (70-230 mesh) was used for flash column chromatography. 2-(α-Hydroxyethyl)benzimidazole **2**,[16] 2-acetylbenzimidazole **3**,[13a] 2-acetyl-1-methylbenzimidazole **4**,[13a] 2-acetyl-1-methylbenzimidazole-oxime **5**[13b] were prepared following the reported literature.

***O*-Benzyl 2-acetyl-1-methylbenzimidazole-oxime 6.** To a solution of 2-acetyl-1-methylbenzimidazole-oxime **5** (1.89 g, 10 mmol) in anhydrous ethanol (30 ml), potassium hydroxide (0.79 g, 14 mmol) was added followed by benzyl chloride (1.77 g, 14 mmol). The reaction mixture was stirred for a few minutes at room temperature and then heated at 100 °C for further 30 minutes. The reaction mixture was diluted with water (30 mL) and then extracted with ethyl acetate (3x20 mL). The extracts were dried over $MgSO_4$ then evaporated under reduced pressure. The solid product that formed was then recrystallyzed from petroleum ether (60-80) to afford 2.2 g (79 % yield) of *O*-benzyl 2-acetyl-1-methylbenzimidazole-oxime **6** as white crystals, mp. 55 °C; IR (KBr) ν_{max} 3058, 3020, 2915, 1454, 1359, 1001, 882, 740 cm^{-1}; ^{1}H NMR (CDCl3) δ 2.54 (s, 3H, CH_3), 3.90 (s, 3H, NCH_3), 5.31 (s, 2H, OCH_2), 7.26-7.31 (m, 1H), 7.32-7.35 (m, 4H), 7.39-7.43 (m, 3H), 7.80-7.83 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 13.3, 32.8, 76.7, 109.5, 120.0, 122.2, 123.6, 127.9, 128.1, 128.3, 136.9, 137.7, 142.1, 147.9, 150.6; MS *m/z* (%) 279 (6.9, M^+), 262 (14.1), 157 (9.7), 132 (7.4), 91 (100), 77 (16.6), 65 (11.2), 51 (16.7). Anal**.** Calcd. For $C_{17}H_{17}N_3O$: C, 73.11; H, 6.09; N, 15.05. Found: C, 73.39; H, 5.94; N, 15.02.

Preparation of Pd-complex 7. A solution of sodium tetrachloropalladate (294 mg, 1 mmol) in methanol (2 mL) was added dropwise to a stirred solution of *O*-benzyl 2-acetyl-1-methylbenzimidazole-oxime **6** (279 mg, 1 mmol) in dioxane / methanol (4 mL, 1:1, v/v). After stirring for 2 h, the yellow precipitate that formed was filtered off, washed with water then with methanol and dried. The complex **7** was obtained as a yellow powder (411 mg, 90% yield). Mp. > 300 °C; IR (KBr) ν_{max} 3027, 2948, 1463, 1368, 1035, 946, 739 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 2.99 (s, 3H, CH_3), 3.81 (s, 3H, NCH_3), 5.39 (s, 2H, OCH_2), 7.34-7.51 (m, 7H), 7.68-7.72 (m, 1H), 8.27-8.30 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 16.3, 32.8, 76.5, 111.8, 119.5, 123.9, 124.8, 127.9, 128.1, 128.4, 134.0, 137.2, 138.4, 146.9, 147.8. Anal**.** Calcd. for $C_{17}H_{17}Cl_2N_3OPd$: C, 44.73; H, 3.72; N, 9.21. Found: C, 44.80; H, 3.91; N, 9.42.

Effect of concentration of palladium complex 7 on the Suzuki-Miyaura cross-coupling of 4-bromoacetophenone with phenylboronic acid in water. In a 10 mL round-bottom flask, a mixture of 4-bromoacetophenone **8** (199 mg, 1 mmol) and phenylboronic acid **15a** (146 mg, 1.2 mmol), TBAB (TBAB) (194 mg, 0.6 mmol), palladium(II)-catalyst **7** (4.5 mg, 1 mol%), KOH (112 mg, 2 mmol) and water (3 mL) was heated at 100 °C for one hour (monitored by TLC). The product was then extracted with EtOAc (3 x 20 mL) and the combined organic extracts were dried over anhydrous Na_2SO_4 then filtered and the solvent was evaporated under reduced pressure. The residue was then subjected to separation via flash column chromatography with hexane/EtOAc (10:1) as an eluent to give 4-acetylbiphenyl **16** in (96%) isolated yield. The same experiment was repeated using of palladium complex **7** in different mol% *e.g.* 0.5, 0.25 0.15, 0.1 and 0.05 mol% with respect to 4-bromoacetophenone **8**. The molar ratios of the reaction components were in all cases as follows; 4-bromoacetophenone/ phenylboronic acid/ TBAB/ KOH: 1 / 1.2 / 0.6 / 2, in water 3 mL. The yield% versus concentration of Pd-complex **7** is outlined in Table 1.

Effect of base and solvent on Suzuki-Miyaura cross-coupling of 4-bromoacetophenone with phenylboronic acid. In a 10 mL round-bottom flask, a mixture of 4-bromoacetophenone **8** (199 mg, 1 mmol) and phenylboronic acid **15a** (146 mg, 1.2 mmol), TBAB (TBAB) (194 mg, 0.6 mmol), palladium(II)-catalyst **7** (2.3 mg, 0.5 mol%), KOH (112 mg, 2 mmol) and water (3 mL) was heated at 100 °C for one hour (monitored by TLC). The same experiment was repeated using different solvents and bases. The molar ratio of the reaction components were in all cases as follows; 4-bromoacetophenone/ phenylboronic acid/ TBAB (in case of water)/ base/ solvent: 1 / 1.2 / 0.6 / 2 / 3 mL. The yield % versus different solvents and bases is outlined in Table 2.

Reactivity of Pd complex 7 in Suzuki coupling of 4-chloroacetophenone 14 with arylboronic acids in water. In a 10 mL round-bottom flask, a mixture of 4-chloroacetophenone **14** (154.5 mg, 1 mmol) and the appropriate arylboronic acids **15a-c** (1.2 mmol), TBAB (TBAB) (194 mg, 0.6 mmol), palladium (II)-complex **7** (2.3 mg, 0.5 mol%), cesium carbonate (650 mg, 2 mmol) and water (3 mL) were heated at 100 °C for the appropriate reaction time (monitored by TLC). The product, in each case, was then extracted with EtOAc and purified with flash column chromatography as shown above to give the biaryl derivatives **16, 22** and **28**, respectively, as outlined in Table 3.

Suzuki-Miyaura cross-coupling of aryl(heteroaryl) bromides 8-13 with arylboronic acids 15a-c in water. General procedure

A mixture of the appropriate aryl (heteroaryl) bromides **8-13** (1 mmol), and the appropriate arylboronic acid **15a-c** (1.2 mmol), TBAB (194 mg, 0.6 mmol), palladium complex **7** (2.3 mg, 0.5 mol%), KOH (2 mmol), and distilled water (3 mL) was heated with stirring at 100 °C under open air for the appropriate reaction time listed in Table 4. After the reaction was completed (TLC-monitored), the product was then extracted with EtOAc (3x20 mL). The combined organic extracts were dried over anhydrous Na_2SO_4 then filtered and the solvent was evaporated under

reduced pressure. The residue was then subjected to separation via flash column chromatography with hexane/EtOAc (10:1) as an eluent to give the corresponding pure cross-coupled products **16-33**.

4-Acetylbiphenyl 16. Colorless crystals, mp. 117-119 °C (Ref.[17] mp. 118-120 °C); ^{1}H NMR ($CDCl_3$) δ 2.65 (s, 3H, CH_3CO), 7.35-7.49 (m, 3H), 7.62-7.65 (m, 2H), 7.70 (d, 2H *J* = 8.4 Hz), 8.04 (d, 2H, *J* = 8.4 Hz).

4-Methoxybiphenyl 17. Colorless solid; mp. 85-86 °C (Ref.[18] mp. 87-88 °C); ^{1}H NMR ($CDCl_3$) δ 3.87 (s, 3H, OCH_3), 6.99 (d, 2H, *J* = 9 Hz), 7.29-7.35 (m, 1H), 7.40-7.46 (m, 2H), 7.53-7.59 (m, 4H); MS *m/z* (%) 184 (M^+, 92.5), 169 (77.5), 150 (45.0), 141 (70), 139 (40), 131 (30), 115 (55), 99 (32.5), 91 (52.5), 76 (100), 63 (55.0), 50 (42.5).

4-Nitrobiphenyl 18. Pale yellow powder, mp. 115-116 °C (Ref.[18] mp. 113-114 °C); ^{1}H NMR ($CDCl_3$) δ 7.46-7.54 (m, 3H), 7.62-7.66 (m, 2H), 7.75 (d, 2H, *J* = 6.9 Hz), 8.31 (d, 2H, *J* = 6.9 Hz); MS *m/z* (%) 199 (M^+, 35.6), 169 (28.9), 153 (19.3), 152 (100), 127 (20.7), 102 (13.3), 76 (49.6), 50 (40).

2-Phenylnaphthalene 19. White crystals, mp. 99-100 °C (Ref.[17] mp. 100-101 °C); ^{1}H NMR ($CDCl_3$) δ 7.37-7.43 (m, 1H), 7.47-7.56 (m, 4H), 7.73-7.79 (m, 3H), 7.87-7.95 (m, 3H), 8.06 (s, 1H); MS *m/z* (%) 204 (M^+, 73.7), 173 (47.4), 131 (52.6), 109 (47.4), 96 (52.6), 75 (100), 65 (78.9), 51 (84.2).

3-Phenylpyridine 20. Colorless oil;[19] ^{1}H NMR ($CDCl_3$) δ 7.43-7.61 (m, 6H), 7.98 (d, 1H, *J* = 7.8 Hz), 8.62 (d, 1H, *J* = 3.9 Hz), 8.88 (s, 1H); MS *m/z* (%) 155 (M^+, 100), 127 (20.4), 111 (16.29), 97 (26.73), 85 (25.29), 71 (39.31), 57 (69.58).

3-Phenylquinoline 21. Pale yellow powder, mp. 50 °C (Ref.[20] mp. 52 °C); ^{1}H NMR ($CDCl_3$) δ 7.43-7.61 (m, 4H), 7.71-7.74 (m, 3H), 7.89 (d, 1H, *J* = 8.1 Hz), 8.16 (d, 1H, *J* = 8.7 Hz), 8.31 (s, 1H), 9.20 (s, 1H); MS *m/z* (%) 205 (M^+, 100), 176 (11.4), 151 (5.3), 102 (13), 88 (14.9), 76 (37.2), 61 (14.2).

4-Acetyl-4'-methoxybiphenyl 22. White crystals; mp. 153-154 °C (Ref.[21] mp. 154 °C); ^{1}H NMR ($CDCl_3$) δ 2.63 (s, 3H, $COCH_3$), 3.88 (s, 3H, OCH_3), 7.01 (d, 2H, *J* = 8.7 Hz), 7.58 (d, 2H, *J* = 8.7 Hz), 7.65 (d, 2H, *J* = 8.4 Hz), 8.01 (d, 2H, *J* = 8.4 Hz); MS *m/z* (%) 226 (M^+, 44), 211 (100), 183 (30.4), 168 (28), 152 (33.6), 139 (65.6), 89 (21.6), 77 (20), 63 (40.8), 55 (27.2).

4,4′-Dimethoxybiphenyl 23. Colorless crystals, mp. 175-176 °C (Ref.[18] mp. 174-175 °C); ^{1}H NMR ($CDCl_3$) δ 3.86 (s, 6H, OCH_3), 6.97 (d, 4H, *J* = 8.7 Hz), 7.50 (d, 4H, *J* = 8.7 Hz); MS *m/z* (%) 214 (M^+, 93.4), 199 (100), 171 (36.8), 156 (25), 128 (48.7), 115 (17.1), 102 (28.9), 91 (39.5), 74 (32.9), 63 (47.4), 51 (38.2).

4-Methoxy-4'-nitrobiphenyl 24. Yellow powder, mp. 105-106 °C (Ref.[18] mp. 107-108 °C); ^{1}H NMR ($CDCl_3$) δ 3.88 (s, 3H, OCH_3), 7.02 (d, 2H, *J* = 8.7 Hz), 7.58 (d, 2H, *J* = 8.7 Hz), 7.70 (d, 2H, *J* = 8.7 Hz), 8.27 (d, 2H, *J* = 8.7 Hz); ^{13}C NMR ($CDCl_3$) δ 55.4, 114.6, 124.1, 127.0, 128.5, 131.1, 147.2, 160.4; MS *m/z* (%) 229 (M^+, 100), 199 (25.4), 183 (13.9), 168 (23), 139 (49.8), 63 (23.2).

2-(4-Methoxyphenyl)naphthalene 25. White crystals, mp. 133-135 °C (Ref.[22] mp. 135-137 ◦C); ^{1}H NMR ($CDCl_3$) δ 3.89 (s, 3H, OCH_3), 7.04 (d, 2H, *J* = 8.7 Hz), 7.46-7.51 (m, 2H), 7.68 (d, 2H,

J = 9 Hz), 7.72-7.75 (m, 1H), 7.85-7.92 (m, 3H), 8.0 (s, 1H); MS *m/z* (%) 234 (M^+, 32.5), 189 (25.3), 165 (22.9), 97 (25.3), 69 (39.1), 57 (100).

3-(4-Methoxyphenyl)pyridine 26. Colorless crystals, mp 58-60 °C (Ref.[23] mp. 59-60 °C); ^{1}H NMR ($CDCl_3$) δ 3.87 (s, 3H, OCH_3), 7.02 (d, 2H, *J* = 8.4 Hz), 7.31-7.35 (m, 1H), 7.53 (d, 2H, *J* = 8.4 Hz), 7.83 (d, 1H, *J* = 7.8 Hz), 8.55 (d, 1H, *J* = 4.2 Hz), 8.82 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 55.4, 114.5, 123.4, 128.2, 130.2, 133.8, 136.2, 147.8, 147.9, 159.7; MS *m/z* (%) 185 (M^+, 18.8), 170 (14.8), 139 (14.8), 115 (17.2), 85 (23.4), 55 (100).

3-(4-Methoxyphenyl)quinoline 27. Yellow crystals, mp. 81-83 °C; (Ref.[24] mp. 83-85 °C); ^{1}H NMR ($CDCl_3$) δ 3.88 (s, 3H, OCH_3), 7.05 (d, 2H, *J* = 8.7 Hz), 7.55 (m, 1H), 7.65 (d, 2H, *J* = 8.7 Hz), 7.67-7.73 (m, 1H), 7.85 (d, 1H, *J* = 8.1 Hz), 8.13 (d, 1H, *J* = 8.4 Hz), 8.23 (d, 1H, *J* = 2.1 Hz), 9.17 (d, 1H, *J* = 2.1 Hz); ^{13}C NMR ($CDCl_3$) δ 29.7, 55.4, 114.6, 126.9, 127.8, 128.1, 128.4, 128.9, 129.1, 130.2, 132.3, 133.4, 147, 149.8, 159.8.; MS *m/z* (%) 235 (M^+, 96.4), 220 (63.3), 192 (43.4), 165 (26.5), 139 (13.3), 118 (10.7), 86 (100), 58 (43.9).

4-Acetyl-4'-chlorobiphenyl 28. White crystals, mp. 101-102 °C (Ref. [21] mp. 101-103 °C); ^{1}H NMR ($CDCl_3$) δ 2.64 (s, 3H, $COCH_3$), 7.44 (d, 2H, *J* = 8.4 Hz), 7.55 (d, 2H, *J* = 8.4 Hz), 7.65 (d, 2H, *J* = 8.4 Hz), 8.04 (d, 2H, *J* = 8.4 Hz); ^{13}C NMR ($CDCl_3$) δ 26.6, 127, 128.4, 128.9, 129.1, 134.4, 136.1, 138.3, 144.4, 197.5; MS *m/z* (%) 230 (M^+, 52), 217 (68), 204 (100), 150 (72), 108 (88), 88 (68), 74 (100), 67 (40).

4-Chloro-4'-methoxybiphenyl 29. White crystals, mp. 112-114 °C (Ref. [25] mp. 110-112 °C); ^{1}H NMR ($CDCl_3$) δ 3.86 (s, 3H, OCH_3), 6.98 (d, 2H, *J* = 8.7 Hz), 7.38 (d, 2H, *J* = 8.4 Hz), 7.47-7.51 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 55.3, 114.3, 125.9, 127.9, 128, 128.8, 132.5, 139.2, 159.3; MS *m/z* (%) 220 (M^++2, 37.7), 218 (M^+, 88.7), 203 (66), 175 (62.3), 152 (47.2), 139 (56.6), 111 (24.5), 101 (30.2), 87 (49.1), 75 (67.9), 63 (79.2), 57 (100).

4-Chloro-4'-nitrobiphenyl 30. Pale yellow powder, mp. 138-139 °C (Ref. mp. 112-113 °C[26a] and. 144 °C[26b]); ^{1}H NMR ($CDCl_3$) δ 7.49 (d, 2H, *J* = 8.7 Hz), 7.57 (d, 2H, *J* = 8.7 Hz), 7.70 (d, 2H, *J* = 8.7 Hz), 8.30 (d, 2H, *J* = 9 Hz); ^{13}C NMR ($CDCl_3$) δ 124.5, 125.9, 127.6, 128.6, 129.3, 135.2, 137.2, 146.3; MS *m/z* (%) 235 (M^++2, 10.4), 233 (M^+, 17.2), 203 (31.3), 175 (26.9), 152 (100), 126 (11.2), 113 (11.2), 101 (21.6), 75 (32.8), 63 (26.9), 57 (43.3).

2-(4-Chlorophenyl)naphthalene 31. White crystals, mp. 131-132 °C (Ref.[27] mp. 133-134 °C); ^{1}H NMR ($CDCl_3$) δ 7.48 (d, 2H, *J* = 8.4 Hz), 7.52-7.57 (m, 2H), 7.67 (d, 2H, *J* = 8.4 Hz), 7.71 (dd, 1H, *J* = 8.7, 1.8 Hz), 7.88-7.95 (m, 3H), 8.02 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 125.2, 125.7, 125.9, 126.1, 126.4, 127.6, 128.2, 128.6, 128.9, 132.7, 133.5, 133.6, 137.3, 139.5; MS *m/z* (%) 240 (M^++2, 38.5), 238 (M^+, 82), 215 (20.5), 202 (64.1), 152 (92.3), 126 (23.1), 111 (17.9), 101 (76.9), 81 (84.6), 75 (64.1), 57 (100).

3-(4-Chlorophenyl)pyridine 32. Colorless oil;[28] ^{1}H NMR ($CDCl_3$) δ 7.44-7.55 (m, 5H), 7.94 (d, 1H, *J* = 8.1 Hz), 8.63 (d, 1H, *J* = 4.8 Hz), 8.85 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 124.1, 126, 126.1, 128.4, 129.4, 134.8, 135.4, 146.8, 147.4; MS *m/z* (%) 191 (M^++2, 27.6), 190 (M^++1, 12.6), 189 (M^+, 79.5), 167 (11.4), 154 (38.8), 149 (63.7), 127 (39.7), 98 (25.7), 85 (42.3), 71 (66), 57 (100).

3-(4-Chlorophenyl)quinoline 33. White crystals, mp. 135-136 °C (Ref.[29] mp. 133-134 °C); ^{1}H NMR ($CDCl_3$) δ 7.51 (d, 2H, *J* = 8.7 Hz), 7.58-7.66 (m, 3H), 7.73-7.78 (m, 1H), 7.90 (d, 1H, *J* =

8.4 Hz), 8.19 (d, 1H, *J* = 8.4 Hz), 8.31 (d, 1H, *J* = 2.1 Hz), 9.15 (d, 1H, *J* = 2.4 Hz); ^{13}C NMR ($CDCl_3$) δ 125.9, 127.4, 127.9, 128.6, 128.8, 129.4, 129.9, 132.7, 133.6, 134.5, 136.1, 146.8, 149.0; MS *m/z* (%) 241 (M^++2, 37.1), 240 (M^++1, 26.6), 239 (M^+, 100), 204 (37.3), 176 (25.3), 102 (12.2), 88 (45.7), 75 (29.6), 63 (13.8), 50 (23).

Mizoroki-Heck cross-coupling of aryl (heteroaryl) bromides 8-13 with olefins 34a,b. General procedure

In a 10-mL round bottomed flask, a mixture of the appropriate aryl (heteroaryl) bromide **8-13** (1 mmol) and the appropriate olefin **34a,b** (1.5 mmol), TBAB (194 mg, 0.6 mmol), Pd-complex **7** (2.3 mg, 0.5 mol%), and the appropriate base (potassium hydroxide, sodium hydroxide or triethylamine) (3 mmol) in water or DMF (3 mL) were heated at 100 °C for water and 140 °C for DMF with stirring under open air for the appropriate reaction time as listed in Tables 5 and 6. After the reaction was almost complete (monitored by TLC), the reaction mixture was left to cool to room temperature, then extracted three times with EtOAc (3x20 mL). The organic fractions were combined altogether, dried over $MgSO_4$, and the solvent was then removed under vacuum. The residue was subjected to purification via flash column chromatography with Hexane–EtOAc (10:1) as eluent to give the corresponding pure products **35-46**.

Mizoroki-Heck cross-coupling of 4-chloroacetophenone 14 with olefins 34a,b. In a 10-mL round bottomed flask, a mixture of 4-chloroacetophenone **14** (1 mmol) and styrene **34a** or *t*-butyl acrylate **34b** (1.5 mmol), TBAB (194 mg, 0.6 mmol), Pd-complex **7** (2.3 mg, 0.5 mol%), and the appropriate base (sodium hydroxide or triethylamine) (3 mmol) in DMF (3 mL) were heated at 140 °C with stirring under open air for the appropriate reaction time as listed in Table 7. After the reaction was almost complete (monitored by TLC), the reaction mixture was left to cool to room temperature, then extracted three times with EtOAc (3x20 mL). The organic fractions were combined altogether, dried over $MgSO_4$, and the solvent was then removed under vacuum. The residue was subjected to purification via flash column chromatography with Hexane–EtOAc (10:1).

***trans*-4-Acetylstilbene 35.** Colorless crystals, mp. 138-140 °C (Ref.[30] mp. 141-142 °C); ^{1}H NMR ($CDCl_3$) δ 2.62 (s, 3H, CH_3CO), 7.14 (d, 1H, *J* = 16.2 Hz), 7.24 (d, 1H, *J* = 16.2 Hz), 7.31-7.42 (m, 3H), 7.54-7.57 (m, 2H), 7.60 (d, 2H, *J* = 8.4 Hz), 7.97 (d, 2H, *J* = 8.4 Hz); ^{13}C NMR ($CDCl_3$) δ 26.6, 126.5, 126.8, 127.5, 128.3, 128.8, 128.9, 131.5, 136.7, 142.0, 197.6; MS *m/z* (%) 222 (M^+, 53.4), 207 (100), 178 (53), 152 (11), 104 (11.6), 89 (31), 76 (19.7), 63 (12.5), 51 (17.4).

***trans*-4-Methoxystilbene 36.** White crystals, mp. 134-135 °C (Ref.[21] mp. 136 °C); ^{1}H NMR ($CDCl_3$) δ 3.84 (s, 3H, OCH_3), 6.91 (d, 2H, *J* = 8.4 Hz), 6.98 (d, 1H, *J* = 16.5 Hz), 7.08 (d, 1H, *J* = 16.5 Hz), 7.22-7.38 (m, 3H), 7.45-7.52 (m, 4H); MS *m/z* (%) 210 (M^+, 100), 195 (23.3), 167 (34.1), 152 (26.3), 105 (10.1), 89 (20), 76 (18.9), 63 (24.4).

***trans*-4-Nitrostilbene 37.** Yellow crystals, mp. 153-154 °C (Ref.[21] mp. 154 °C); ^{1}H NMR ($CDCl_3$) δ 7.15 (d, 1H, *J* = 16.2 Hz), 7.29 (d, 1H, *J* = 16.5 Hz), 7.34-7.44 (m, 3H), 7.55-7.58 (m, 2H), 7.64 (d, 2H, *J* = 8.7 Hz), 8.23 (d, 2H, *J* = 8.7 Hz); MS *m/z* (%) 225 (M^+, 28.6), 178 (100),

152 (28), 126 (15.4), 102 (21.1), 87 (22.3), 76 (25.7), 63 (49.1), 51 (78.9).

***trans*-2-Styrylnaphthalene 38.** White crystals, mp. 142-144 °C (Ref.[31] mp. 143-145 °C); ^{1}H NMR ($CDCl_3$) δ 7.28 (d, 2H, *J* = 3.3 Hz), 7.33 (d, 1H, *J* = 5.4 Hz), 7.38-7.42 (m, 2H), 7.43-7.50 (m, 2H), 7.59 (d, 2H, *J* = 7.2 Hz), 7.76 (d, 1H, *J* = 9.3 Hz), 7.84 (d, 2H, *J* = 3.0 Hz), 7.87 (d, 2H, *J* = 6.6 Hz); MS *m/z* (%) 230 (M^+, 100), 215 (21.3), 114 (36.4), 74 (16.2), 63 (13.4), 51 (33.6).

***trans*-3-Styrylpyridine 39.** Yellow crystals, mp. 79-80 °C (Ref.[32] mp. 80-81 °C); ^{1}H NMR ($CDCl_3$) δ 7.08 (d, 1H, *J* = 16.2 Hz), 7.21 (d, 1H, *J* = 16.2 Hz), 7.27-7.42 (m, 4H), 7.52-7.56 (m, 2H), 7.91 (d, 1H, *J* = 7.8 Hz), 8.5 (s, 1H), 8.76 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 123.9, 124.3, 125.9, 126, 126.7, 128.4, 128.8, 131.6, 133.6, 136.4, 147.2; MS *m/z* (%) 181 (M^+, 37.7), 152 (16.4), 121 (19.7), 115 (19.7), 105 (75.4), 83 (21.3), 77 (70.5), 65 (24.6), 51 (100).

***trans*-3-Styrylquinoline 40.** Pale yellow crystals, mp. 96-97 °C (Ref.[32] mp. 97-98 °C); ^{1}H NMR ($CDCl_3$) δ 7.24 (d, 1H, *J* = 16.2 Hz), 7.30-7.44 (m, 4H), 7.54-7.60 (m, 3H), 7.67-7.73 (m, 1H), 7.84 (d, 1H, *J* = 7.5 Hz), 8.13 (d, 1H, *J* = 8.4 Hz), 8.2 (d, 1H, *J* = 2.1 Hz), 9.14 (d, 1H, *J* = 2.1 Hz); ^{13}C NMR ($CDCl_3$) δ 125, 125.9, 126.7, 127.2, 127.8, 128.2, 128.3, 128.8, 129.4, 130.4, 131.2, 132.6, 136.6, 146.9, 149; MS *m/z* (%) 231 (M^+, 65.2), 230 (100), 202 (33.7), 149 (19.6), 127 (12.0), 115 (19.6), 101 (26.1), 84 (19.6), 76 (47.8), 63 (16.3), 55 (47.8).

***trans-tert*-Butyl 3-(4-acetylphenyl)prop-2-enoate 41.** Pale yellow crystals, mp. 97-98 °C (Ref.[19] mp. 99-100 °C); ^{1}H NMR ($CDCl_3$) δ 1.55 (s, 9H, $C(CH_3)_4$), 2.61 (s, 3H, CH_3CO), 6.46 (d, 1H, *J* = 16.2 Hz), 7.58-7.63 (m, 3H), 7.96 (d, 2H, *J* = 7.8 Hz); MS *m/z* (%) 246 (M^+ 6.5) 190 (20.1), 175 (59), 131 (9.4), 102 (25.2), 91 (13.7), 79 (11.5), 57 (100).

***trans-tert*-Butyl 3-(4-methoxphenyl)prop-2-enoate 42.** Pale yellow oil;[19] ^{1}H NMR ($CDCl_3$) δ 1.54 (s, 9H, $C(CH_3)_4$), 3.84 (s, 3H, OCH3) , 6.43 (d, 1H, *J* = 15.9 Hz), 6.89 (d, 2H, *J* = 8.7 Hz), 7.46 (d, 2H, *J* = 8.7 Hz), 7.55 (d, 1H, *J* = 15.9 Hz); ^{13}C NMR ($CDCl_3$) δ 28.2, 55.3, 80.2, 114.2, 117.7, 127.4, 129.5, 143.2, 161.1, 166.6; MS *m/z* (%) 234 (M^+, 12.6), 224 (16.73), 178 (69.84), 161 (29.86), 150 (8.83), 133 (18.15), 119 (9.24), 103 (10.82), 89 (14.67), 77 (23.2), 57 (100).

***trans-tert*-Butyl 3-(4-nitrophenyl)prop-2-enoate 43.** White crystals, mp. 143-144 °C (Ref.[19] mp. 144-146 °C); ^{1}H NMR ($CDCl_3$) δ 1.55 (s, 9H, $C(CH_3)_4$), 6.49 (d, 1H, *J* = 16.2 Hz), 7.61 (d, 1H, *J* = 16.2 Hz), 7.66 (d, 2H, *J* = 8.7 Hz), 8.24 (d, 2H, *J* = 8.7 Hz); ^{13}C NMR ($CDCl_3$) δ 28.1, 81.3, 124.1, 124.6, 128.5, 140.6, 140.9, 148.4, 165.2; MS *m/z* (%) 249 (M^+, 7.4), 194 (28.4), 176 (39.5), 147 (11.1), 130 (15.8), 102 (23.7), 90 (19.5), 75 (13.2), 57 (100).

***trans-tert*-Butyl 3-(2-naphthyl)prop-2-enoate 44.** White crystals, mp. 73-75 °C (Ref.[29] mp. 74-75 °C); ^{1}H NMR ($CDCl_3$) δ 1.57 (s, 9H, $C(CH_3)_4$), 6.50 (d, 1H, *J* = 15.9 Hz), 7.49- 7.52 (m, 2H), 7.66 (d, 1H, *J* = 8.7 Hz), 7.76 (d, 1H, *J* = 15.9 Hz), 7.81-7.87 (m, 3H), 7.92 (s, 1H); MS *m/z* (%) 254 (M^+, 13.7), 198 (100), 181 (32.9), 152 (41), 76 (17.1), 57 (41.3).

***trans-tert*-Butyl 3-(3-pyridyl)prop-2-enoate 45.** Colorless crystals, mp. 56-57 °C (Ref.[32] mp. 57-58 °C); ^{1}H NMR ($CDCl_3$) δ 1.54 (s, 9H, $C(CH_3)_4$), 6.43 (d, 1H, *J* = 15.9 Hz), 7.26-7.32 (m, 1H), 7.56 (d, 1H, *J* = 15.9 Hz), 7.79-7.82 (m, 1H), 8.58 (d, 1H, *J* = 4.2 Hz), 8.72 (d, 1H, *J* = 1.8 Hz); MS *m/z* (%) 205 (M^+, 4.6), 199 (10.2), 182 (13), 150 (36.1), 132 (17.6), 120 (18.5), 104 (32.4), 93 (13), 77 (13), 57 (100).

***trans-tert*-Butyl 3-(3-quinolyl)prop-2-enoate 46.** Light yellow crystals, mp. 131-132 °C (Ref.[32] mp. 131-132 °C); ^{1}H NMR ($CDCl_3$) δ 1.57 (s, 9H, $C(CH_3)_4$), 6.61 (d, 1H, *J* = 16.2 Hz), 7.56-7.71 (m, 2H), 7.75 (d, 1H, *J* = 15.9 Hz), 7.86 (d, 1H, *J* = 7.8 Hz), 8.16 (d, 1H, *J* = 8.1 Hz), 8.27 (s, 1H), 9.09 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 28.2, 81.0, 122.5, 127.5, 127.7, 128.2, 128.9, 130.7, 135.7, 139.7, 147.7, 148.7, 165.5; MS *m/z* (%) 255 (M^+, 17.4), 199 (92.8), 182 (45.8), 170 (25.6), 153 (20.8), 127 (24), 101 (8.8), 77 (26), 63 (13.2), 57 (100).

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