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An Efficient Palladium Catalyzed Mizoroki-Heck Cross-Coupling in Water

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The homogeneous Pd-catalysed Mizoroki-Heck coupling reaction has been successfully conducted in water in the absence of any additives under aerobic condition. The various key reaction parameters that affect the yield of desired cross coupling product were optimized. $Pd(PPh_3)_4/Et_3N/H_2O$/98 °C catalyst system was found to be highly active (TOF= 12 to14 h^{-1}) towards achieving the excellent yield of the Mizoroki-Heck coupling products for a wide range of electron withdrawing as well as electron donating aryl bromide and chlorides in shortest reaction time. The $Pd(PPh_3)_4$ catalyst deactivation during Mizoroki-Heck coupling reaction has been identified, which evolved a strategy for Pd-metal recyclability over ten times without appreciable loss of its activity. Thus, it provides access to variety of olefins in aqueous medium, making this protocol eco-friendly.

Introduction

In the 21st century, an organic chemist faces intimidating challenges to design a 'green' protocol which is able to make the organic transformations sustainable and economically beneficial.[1] Among various challenges, the use of greener reaction solvent is one of the most important constituents in any chemical processes. The reaction solvent is a key driver in deciding toxicity, hazards, cost, and waste generation of a particular process.[2] Water a 'nature's choice of solvent' having several unique characteristic for organic synthesis is very attractive from both economic and environmental perspectives. It is a sustainable alternative because of its comparatively high vapour pressure with respect to organic solvents. Importantly, 'water' is the primary and the only solvent in various chemical reactions of life. These properties of the water encourage researchers to explore the use water as a solvent for the chemical processes in various challenging reactions such as, Pd catalysed C-C cross coupling reactions.[3]

The transition metals, especially Pd-catalysts have revolutionized the art and practice of organic synthesis for the construction of various pharmaceuticals, agrochemical and compounds of theoretical interests by carbon-carbon and carbon-heteroatom bonds.[4] Among several different protocols that have been reported till date, special interest has been devoted to the Mizoroki-Heck cross-couplings of aryl and vinyl halides with terminal olefins for the facile synthesis of cinammates and stilbene.[5] This coupling reaction has been extensively studied and widely used in both academia and industry due to the mild conditions applied to activation of olefins.[7] The Mizoroki-Heck reaction if carried out in water under ambient conditions, would bring the radical improvement in the development of chemical industrial processes.[7]

The use of neat water in palladium catalysed Mizoroki-Heck cross coupling reaction has been attempted recently.[8] Although the Mizoroki-Heck reaction was strongly benefited from aqueous chemistry, water has not been considered to be an appropriate solvent for the synthesis because most of the chloro or bromo aryl halides are insoluble in water, making the reaction mixture heterogeneous and thereby retarding rate of reaction with low yield of the desired product. To overcome such drawbacks, alternate attempts like designing water-soluble ligands,[9] using inorganic salt promoters,[10] adding phase-transfer agents,[11] using alternative energy sources like microwave or ultrasound,[12] and co-solvents were reported.[13]

Considering the importance of water as an environmentally benign reaction media for Pd catalysed reactions[14] we report here, $Pd(PPh_3)_4/Et_3N/H_2O$ as a simple and efficient catalyst system for coupling of aryl bromides and chlorides with olefins as well as trimethylsillyl acrylate without any additive.

Results and Discussion

Initially, screening of several organic and inorganic bases for the Mizoroki-Heck cross coupling reaction of 4-bromoanisole with *t*-butyl acrylate using $Pd(PPh_3)_4$ (2 mol %) was carried out in water at reflux condition, and the results are summarized in Table 1. It was observed that water soluble inorganic bases such as K_3PO_4, NaOH and K_2CO_3 showed poor activity (Table 1, entries 1-3). Then, a series of organic bases were tested for the same protocol (Table 1, entries 4-15) among which triethylamine was the most efficient base that gave 90% yield of the desired product in 3h (Table 1, entry 4). Interestingly, under the same reaction conditions, sterically hindered tripropylamine and tributyl amines gave product yield of only 45 and 20%, respectively (Table 1, entries 6 and 7). Cyclic amines such as morpholine, DBU and DABCO were also examined (Table 1, entries 10, 11, 15) and only morpholene gave a moderate yield (38 %). Thus triethylamine showing the highest efficiency plays a dual role. It acts as a base[15] as well as a ligand in Heck reaction[16] because, it has much higher tendency to coordinate Pd to form the active Pd-complex. As a consequence, also triethylamine forming

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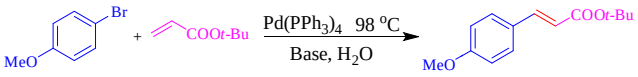
Electronic Supplementary Information (ESI) available: ^1H and ^{13}C NMR spectrum for all the synthesized products see DOI: 10.1039/x0xx00000x

ammonium salts which is able to stabilize Pd-active species in water.[16c]

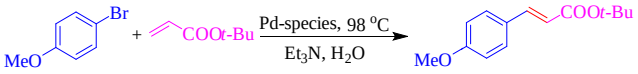
Table 1. The effect of base on the cross-coupling of 4-bromoanisole with *t*-butyl acrylate[a]



Entry	Base	Time (h)	Yield[b] (%)
1	K_3PO_4	12	30
2	NaOH	12	40
3	K_2CO_3	12	70
4	Et_3N	3	90
5	$(i\text{-Pr})_2NH$	12	40
6	$(n\text{-Pr})_2NH$	12	45
7	$(n\text{-Bu})_3N$	12	20
8	$n\text{-PrNH}_2$	12	14
9	$i\text{-PrNH}_2$	12	Trace
10	DABCO	12	10
11	DBU	12	Trace
12	Me_2NH	12	Trace
13	Pipyridine	12	Trace
14	Pyrrolidine	12	Trace
15	Morpholine	12	38

[a]Reaction conditions: 4-bromoanisole (1 mmol), *t*-butyl acrylate (1 mmol), $Pd(PPh_3)_4$ (2 mol %), bases (2 mmol), H_2O (5 mL), 98 °C, air, 3h. [b]Isolated yields after column chromatography.

Table 2. The effect of catalyst precursors on cross-coupling of 4-bromoanisole with *t*-butyl acrylate[a].



Entry	[Pd]	Mol (%)	Time (h)	Conversion (%)	Yield[b] (%)
1	$Pd(OAc)_2$	2	12	60	56
2	$PdCl_2$	2	12	61	60
3	$Pd_2(dba)_3$	2	12	70	67
4	Pd/C (10 %)	2	12	70	63
5	$PdCl_2(CH_3CN)_2$	2	12	73	69
6	$PdCl_2(PPh_3)_2$	2	12	82	73
7	$Pd(dppf)Cl_2$	2	12	86	80
8	$Pd(PPh_3)_4$	2	3	97	90
9	$Pd(PPh_3)_4$	2.5	3	98	90
10	$Pd(PPh_3)_4$	3	3	97	91
11	$Pd(PPh_3)_4$	1.5	3	89	80
12	$Pd(PPh_3)_4$	1	3	66	60

[a]Reaction conditions: 4-bromoanisole (1 mmol), *t*-butyl acrylate (1 mmol), Pd precursors (mol %), Et_3N (2 mmol), H_2O (5 mL), 98 °C, air, 3h. [b]Isolated yields after column chromatography.

The efficiency of various palladium precursors was also examined in the model reaction of coupling (Table 2). The results indicated that all the precursors containing Pd(II) species exhibited moderate catalytic activity both in the absence and in the presence of a ligand (Table 2, entries 1, 2, and 5-7). However, zerovalent Pd sources such as $Pd_2(dba)_3$ and $Pd(PPh_3)_4$ when used, as expected the product yields increased significantly (Table 2, entries 3 and 8). In this comparative investigation, if a heterogeneous catalyst like Pd/C was used, even after long reaction time of 12h (TOF=8 h^{-1}), the product yield (Table 2, entry 4) was much less than that of $Pd(PPh_3)_4$ within the 3 h (TOF=12 h^{-1}). In order to evaluate the effect of catalyst loading, model reaction was carried out using different concentrations of $Pd(PPh_3)_4$. It was observed that among different loadings, 2 mol % $Pd(PPh_3)_4$ offered quantitative yields (90%) of product in a shortest time of 3 h at 98 °C (Table 2, entry 8). No significant improvement was observed by using increased amount of 3 mol % catalyst (Table 2, entry 10).

The presence of O_2 in the reaction media played a crucial role in the catalytic activity. To investigate the influence of the O_2 present in air, we performed the model reaction under air, O_2 and N_2 atmosphere and results are illustrated in Figure 1. When the Heck reaction was carried out under N_2 atmosphere catalytic efficiency of catalytic system was comparatively less as compared to the reactions carried out in air and O_2. The kinetic study clearly indicated that the higher yields were obtained under air and O_2, than those obtained under N_2 atmosphere in the same reaction time. This was due to the continuous reoxidation of Pd(0) species under air or O_2 preventing agglomeration of Pd^{+2} to inactive Pd^0 black.[16, 17] When the model reaction was performed with I_2 as a re-oxidant under N_2 (Fig.1), the re-activation of the palladium black with I_2 was also successful giving the same performance as compared with the reaction performed under air or O_2. This fact clearly indicates that the oxygen helps re-oxidation of Pd atoms on the surface.[17b]

To investigate the effect of temperature on the catalytic system, the model reaction was carried out at different temperatures (40-98 °C) and the results are shown in Figure 2. When the temperature was increased from 40 to 80 °C, the product yield increased substantially from 8 to 65%, but a very significant enhancement to 90% was observed for a rise in temperature in the range of 90-98°C.

Figure 1. Yield *vs*. Time curves of the reactions of 4-bromoanisole with *t*-butyl acrylate under air, O_2, N_2 and I_2 in N_2 atmosphere .

Figure 2. Temperature effects on the reaction of 4-bromoanisole with t-butyl acrylate at different temperatures.

Reaction conditions: 4-bromoanisole (1 mmol), *t*-butyl acrylate (1 mmol), $Pd(PPh_3)_4$ (2 mol %), Et_3N (2 mmol), H_2O (5 mL), 40-98 °C, air, 3h. GC yields.

Figure 3 shows the effect of the reaction time on the yield of the final product. The model reaction carried out in a time range of 20 to 200 minutes. The percentage yield of the final product line linearly increased with the increase in the reaction time from 20 to 180 min and after that it remained constant giving 90 % yield.
The effect of concentration of substrate in moles/L was also studied. When the concentration of 4-bromoanisole decreased, the product yield increased from 73% to 90% (Table 3, entries 1-4). Very interestingly, if the substrate concentration was decreased further, the product yield again dropped down to 69 % (Table 3, entries 5-6). These results revealed that the ratio of moles of 4-bromoanisole to solvent (water in liters) plays important role in present catalytic system.
The results for effect of concentration of aryl bromide on the $Pd(PPh_3)_4$ catalyzed Mizoroki-Heck reaction of 4-bromoanisol and *t*-butyl acrylate was indicated in Fig. 4. As the mmols of 4-bromoanisol increases from 1 to 1.5 the initially yield increases steadily and showed 90 % yield in the same period of time. It is interesting to note that, when the amount of 4-bromoanisol was increased from 2.0 to 3.0 mmols, the resulting yield of the desired product dropped from 90 % to 80 % in 3h. By adding an additional mmols of 4-bromoanisol, the detrimental effect on the yield of desired product, which clearly indicates the excess use of 4-bromoanisol is not attractive for present protocol.
The scope and generality of the optimized protocol was explored for Mizoroki-Heck arylation of a variety of aryl bromides and olefins.The reactions were conducted with 2 mol % of $Pd(PPh_3)_4$ catalyst and 2.0 mmol of Et_3N at 98 °C in water for 3 h, and the results are presented in Table 4. It was observed that various 4-substituted aryl bromides bearing both electron withdrawing and electron donating groups with different olefins such as $–NO_2$, -Me, -Cl, -OMe, -F, Ph, PhCO- and $-COCH_3$ afforded the desired arylation products in good to excellent yields.This catalytic system could tolerate aryl halides with bulky and sterically hindered acrylates to achieve high yields as compared with other simple acrylates under the same reaction conditions. As sulphur containing compounds are the most common units in pharmaceutically active compounds, we further investigated the Mizoroki-Heck reaction of 3-bromothiophene with acrylates. It was observed that the present catalytic system was applicable for the cross-coupling of 3-bromothiophene and acrylates with 88 to 93 % yield in 3 h (Table 4, entries 21-24). It was found that the present protocol was efficient to achieve good to excellent yields of cinnamate derivatives in 3h. From the ^1H NMR spectrums confirmed the *E*- and *Z*-isomers from the *J* coupling values. It was observed that the ratio of *E/Z* isomers was dramatically affected by the nature of the substituent present on the aryl halides. The compounds containing electron withdrawing and donating groups showed 100% *E*-isomers. 1-Naphthyl bromide reacted with different acrylates to give a 50:50 mixture of (*E/Z*) isomer ratio (Table 4, entries 33-36) due to the steric hindrance of 1-Naphthyl bromide. The excellent tolerance of the catalyst system to various functional groups was evident in terms of TOF values which were in the range of 12 to 14 h^{-1}.
These excellent results obtained with aryl bromides, encouraged us to employing the developed protocol for several aryl chlorides with various acrylates. From a practical point of view, the utilization of the easily available and inexpensive aryl chlorides is highly desirable.[19] The activation of the aryl chlorides is much more difficult than aryliodides and bromides.[20]

Therefore, one of the challenges in developing of high-performance catalytic protocol for the coupling of inactive aryl chlorides and acrylates is of great interest. The efficiency of the present catalytic protocol was found to be moderate for the variety of aryl chlorides as demonstrated by the results in Table 5. Various 4-substituted aryl chlorides containing either electron-

Figure 3. The effect of reaction time on the yield of the desired product.

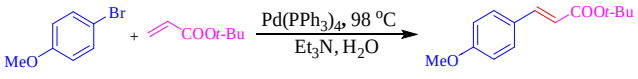
Reaction conditions: 4-bromoanisole (1 mmol), *t*-butyl acrylate (1 mmol), $Pd(PPh_3)_4$ (2 mol %), Et_3N (2 mmol), H_2O (5 mL), 98 °C, air, 20-200 min. GC yields.

Figure 4. The effect of concentration of aryl bromides on the $Pd(PPh_3)_4$ catalyzed Mizoroki-Heck reaction of 4-bromoanisol and *t*-butyl acrylate.

Reaction conditions: 4-bromoanisole (1-3 mmol), *t*-butyl acrylate (1 mmol), $Pd(PPh_3)_4$ (2 mol %), Et_3N (2 mmol), H_2O (5 mL), 98 °C, air, 3h. GC yields.

donating 4-methoxy-chlorobenzene or electron-withdrawing 4-nitro-chlorobenzene groups gave the analogous products in moderate yields in 12 h (Table 5, entries 1–8). Sterically hindered *t*-butyl acrylate and butyl acrylate were also successfully coupled with 4-nitro-chlorobenzene and 4-methoxy-chlorobenzene giving moderate yield in 12h at 98 °C (Table 5, entries 1, 2, 5, 6).

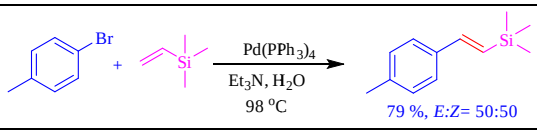
Table 3. Effect of substrate concentration in Mizoroki-Heck coupling of *t*-butyl acrylate and 4-bromoanisole [a].



Entry	4-Bromoanisole (mmol)	4-Bromoanisole/H_2O mol/L	Yield[b] (%)
1	40	0.4	73
2	30	0.3	85
3	20	0.2	90
4	10	0.1	90
5	5	0.05	81
6	1	0.01	69

[a]Reaction conditions: 4-bromoanisole (1 mmol), *t*-butyl acrylate (1 mmol), $Pd(PPh_3)_4$ (2 mol %), Et_3N (2 mmol), H_2O (100 mL), 98 °C, air, 3h. [b]Isolated yields after column chromatography.

In addition, the scope of regioselective Mizoroki-Heck reaction was explored for the arylation of allyltrimethylsilanes. Branched vinylsilanes were employed with great efficacy in intermediates in organic synthesis and their utility is mainly attributed to the high regioselectivity obtained in reactions with electrophiles such as Pd-catalyzed C-C bond formation reactions,[21] also as substrates for Tamao-Fleming oxidations[22] and in Hiyama cross-coupling reactions.[23] To understand the regioselectivity of this Mizoroki-Heck reaction, we studied the reaction between aryl bromide with allyltrimethylsilane (Scheme 1). It was observed that the reaction proceeded with moderate to good yield in 3h with *E/Z* isomers. As per the *J* coupling values of the ^1H NMR spectrum it was found that desired product having 50:50 mixture of the *E*-and *Z*-isomers. Further detailed study is in progress in our laboratory to investigate the various reaction parameters such as selectivity and substrate scope of various aryl bromides and chlorides with allyltrimethylsilane in aqueous medium.



Scheme 1. Regioselective Mizoroki-Heck reaction of allyltrimethylsilane with aryl bromide in water.

Catalyst Reusability Study

As it was a homogeneous $Pd(PPh_3)_4$ catalyst, it could be retained in the reaction flask after extracting the desired product by (ethyl acetate 3X10 mL) in the first run and the reaction was continued by charging new substrates to the flask containing the used catalyst. However, the catalyst did not show the activity after 3h. The catalyst stability was studied with the help of ^{31}P-NMR (Fig. 5). ^{31}P-NMR of the fresh $Pd(PPh_3)_4$ catalyst, the phosphorus chemical shift was at 23.3 ppm.

Figure 5. ^{31}P-NMR spectra for the (A) TPP ligand, (B) fresh $Pd(PPh_3)_4$ catalyst (C) $O=PPh_3$ and (D) recovered catalyst.

For the recovered catalyst, there was only one peak observed at 29.30 ppm corresponding to $O=PPh_3$, which clearly matched with the standard ^{31}P spectrum of the $O=PPh_3$ while the initial peak totally disappeared. The results confirmed the dissociation of the PPh_3 ligand from the precursor leading to the oxidation of the ligand to $O=PPh_3$. The dissociated Pd was deactivated due to the agglomerization which was evident by the presence of black particles in the reaction crude.

The dissociated Pd atoms from the $Pd(PPh_3)_4$ was confirmed with ICP-AES and EDS analysis. After the fresh catalytic cycle, the black particles was recovered by centrifuge method and washed with water, ethanol and acetone and dried under vacuum. ICP-AES analysis of the recovered black particles showed that 95.21 % Pd species were present in the recovered black material.

The EDS spectrum (Fig. 6) of the recovered black material taken at random points on the surface confirmed the presence of Pd species. From this observation, it was clear that Pd metal present in the inactive form needed activation for the subsequent recycle runs.

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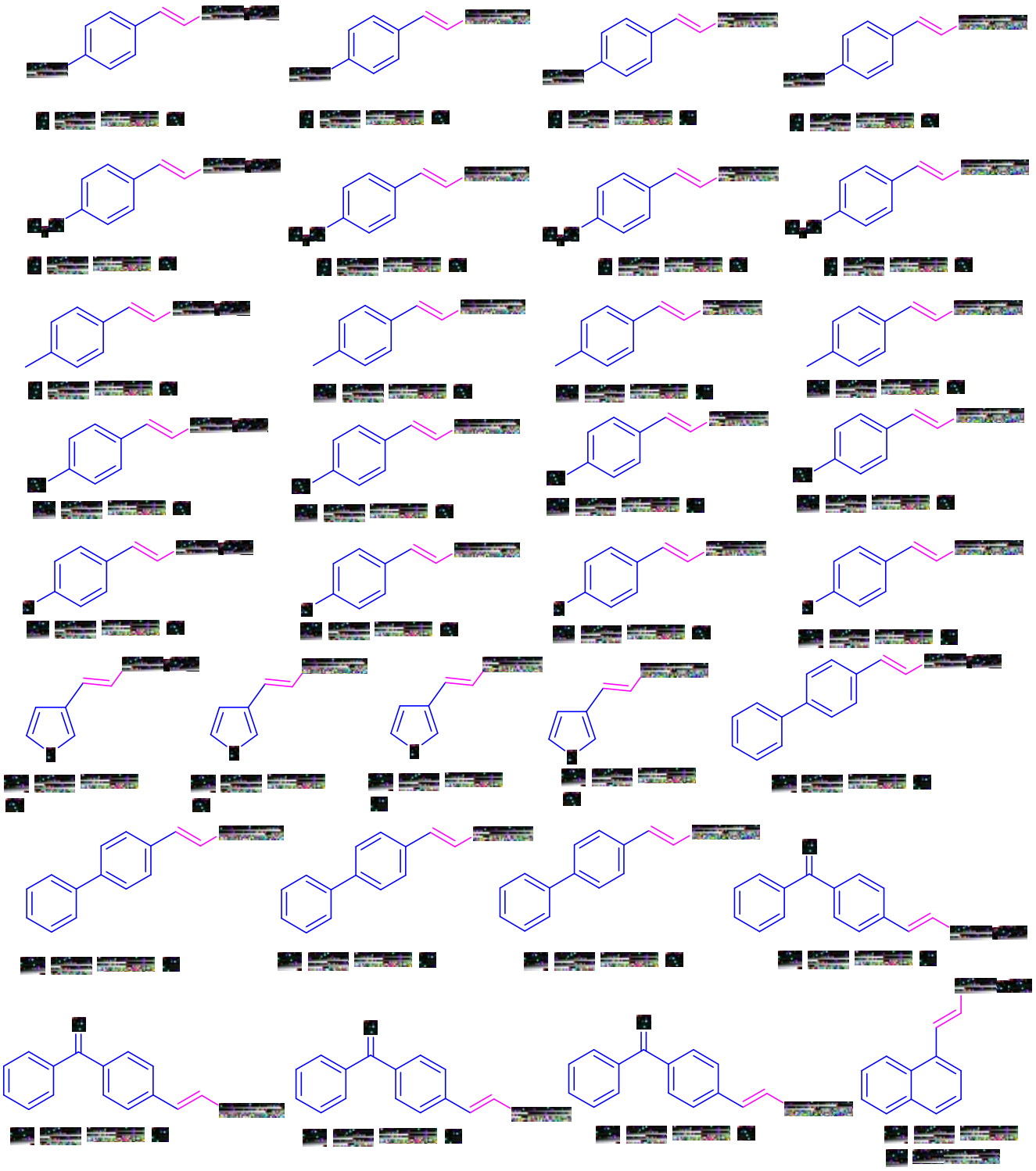
Table 4. The scope of Mizoroki-Heck cross-coupling of aryl bromides with olefins[a].



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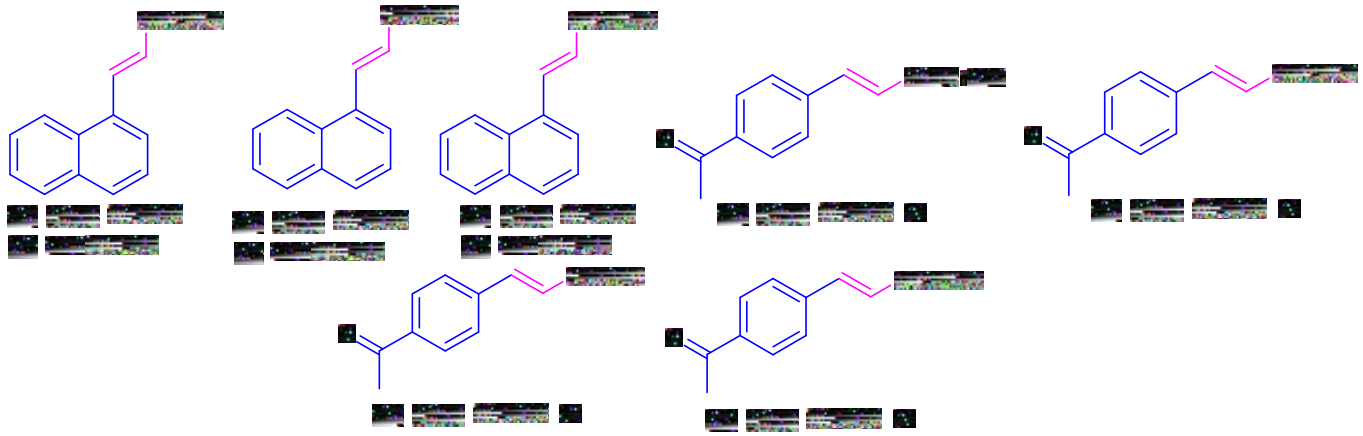
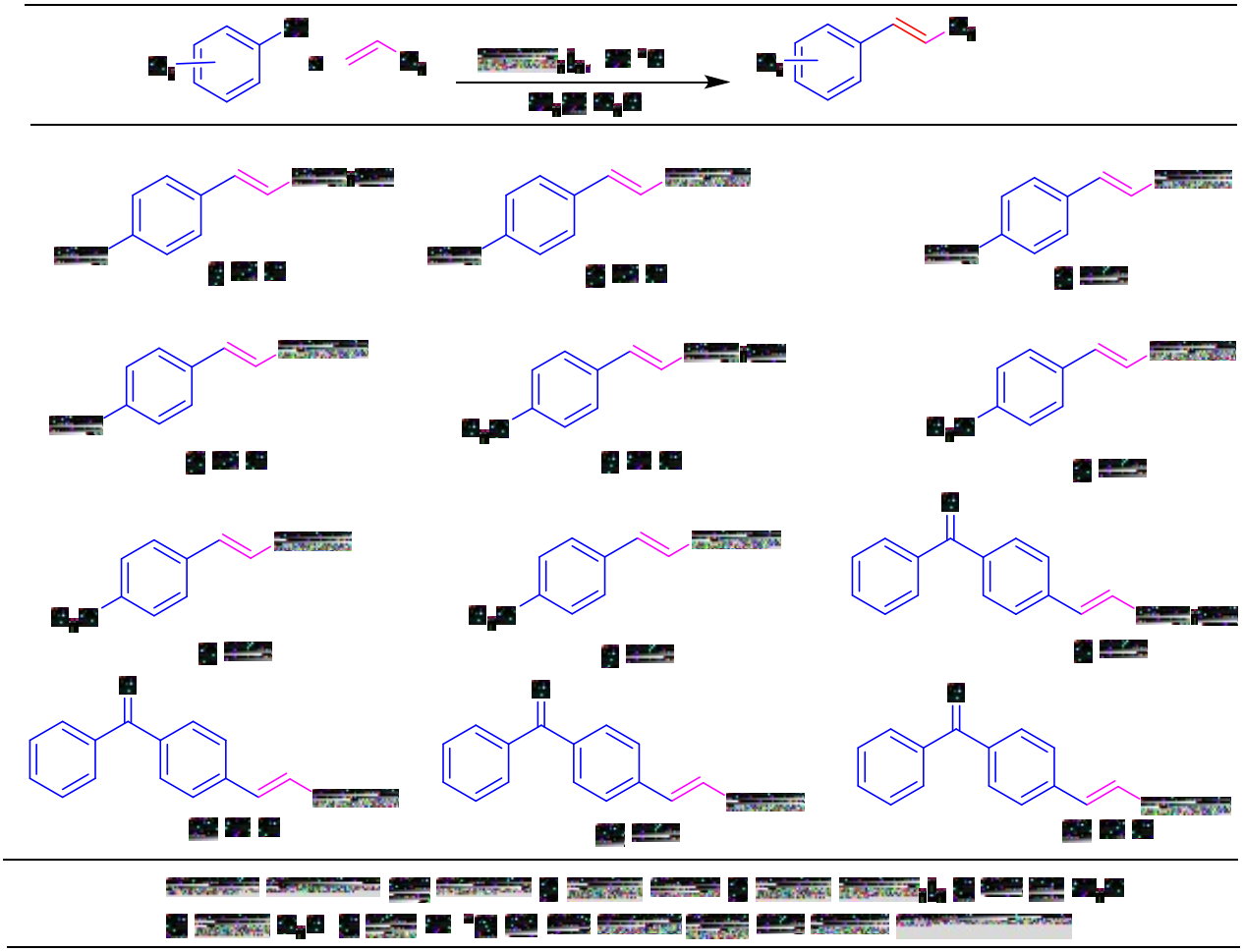


[a]Reaction conditions: aryl halides (1 mmol), olefins (1 mmol), $Pd(PPh_3)_4$ (2 mol %), Et_3N (2 mmol), H_2O (5 mL), 98 °C, air, 3h. [b]Isolated yields after column chromatography.

Table 5. The scope of Mizoroki-Heck cross-coupling of aryl chlorides with olefins.



In order to regain the activity of the spent catalyst, black Pd particles were washed several times with water, methanol and acetone and dried under vacuum. This was followed by calcination at 600 °C for 6h. To evaluate the chemical oxidation

Figure 6. EDS of recovered black particles, Inset: centrifuged black particles.

state of recovered Pd black material (Fig. 7a) and after calcined Pd material (Fig. 7b), XPS was performed. The XPS analysis provided useful information about the oxidation state of Pd. The characteristic binding energy peak observed at 341.5, 340.7 eV for electron transitions of Pd $3d_{3/2}$ of Pd0, and 335.4, 336.6 eV for electron transitions of Pd $3d_{5/2}$ of Pd metal which clearly indicates that the mixture of Pd(0) and Pd(II) present in recovered Pd black material. The XPS analysis of calcinened Pd material showed the binding energy peaks due to PdO, suggesting that the calcined material existed in the Pd oxide state and also that PdO catalyst was showed excellent catalytic activity with PPh_3 as a ligand.
The calcined PdO metal examined for the next catalytic cycle for the model reaction of 4-bromoanisole with *t*-butyl acrylate and in presence of PPh_3. As can be seen from the recycle results in Figure 8, Pd catalyst showed excellent activity for ten runs with no appreciable change in the product yield. These results proved that the spent Pd catalyst could be revived by a simple protocol making the process sustainable.

Conclusion

In conclusion, we developed efficient and environmentally sound Mizoroki-Heck reaction in water under atmospheric conditions without any additive. Initially, we used model reaction for screening of various reaction parameters and then optimized reaction conditions are extended for the wide range of functional groups could be tolerated. This $Pd(PPh_3)_4/Et_3N/H_2O$ catalytic system showed high catalytic activity (TOF= 12 to 14 h^{-1}) and offers promising green development in terms of reaction time, wide scope of applicability, good to excellent yields of the desired products such as acrylate derivatives, operational simplicity and with excellent recyclability of Pd-metal. We also coupled unreactive aryl chlorides successfully under optimized reaction conditions with moderate yield. The deactivation of $Pd(PPh_3)_4$ catalyst during Mizoroki-Heck coupling reaction was identified for the evolving a strategy to reuse the precious Pd-metal for ten times without appreciable loss in its activity. This water-compatible and air-stable catalytic protocol described here provides a stepping stone towards a greener synthesis in pharmaceutical and agrochemical industries.

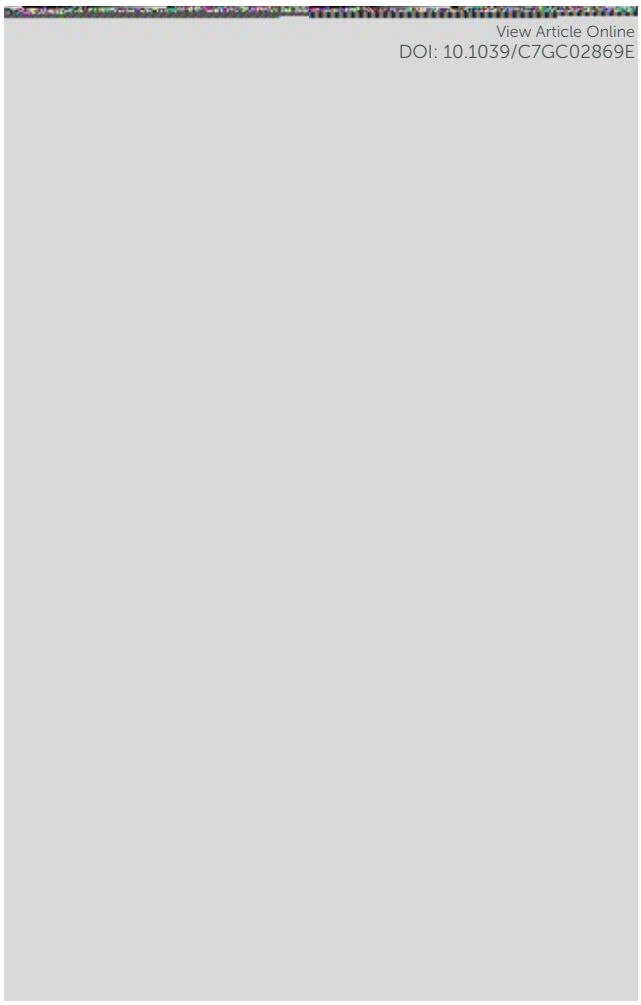


Figure 7. XPS analysis of (a) recovered Pd black material and (b) calcined Pd material.

Figure 8. Recyclability of Pd-metal in Mizoroki-Heck coupling reaction.

Experimental section
Materials and General Methods. All the reagents were commercially sourced from Sigma Aldrich and Spectrochem

chemical companies and used as received. Solvents were dried and purified by standard methods. $Pd(PPh_3)_4$, was obtained from Sigma Aldrich and used without any pretreatment. ^1H NMR and ^{13}C NMR spectra were recorded on Bruker Avon 200 MHz or 500 MHz spectrometer using $CDCl_3$ as solvent and TMS as internal reference. Mass spectra were recorded on a Shimadzu QP2010 GCMS instrument.

Typical experimental procedure for the Mizoroki-Heck cross-coupling reaction in water

In a Schlenk flask, equipped with a magnetic stir bar, septum and condenser, aryl halide (1.0mmol), olefin compound (1.0 mmol), Et_3N (2 mmol), $Pd(PPh_3)_4$ (2 mol%) and water (5mL) were added. The flask was immersed in heating oil bath and reaction mixture was stirred at 100 °C. Upon complete consumption of starting materials as analysed by TLC (hexane:ethyl acetate, 8:2). The resulting reaction mixture was extracted with diethyl ether (3×10 mL). The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated to afford crude product which was purified using column chromatography.

tert-butyl(E)-3-(4-methoxyphenyl)acrylate (Table 4, entry 1): The product was purified with column chromatography on silica gel 60-120 mesh (hexane/ethyl acetate= 9:1) as a colorless oil: yield 90% (168 mg); ^1H NMR (200 MHz, $CDCl_3$) δ 7.47 (d, 1 H, *J* = 15.9 Hz), 7.30 (d, 2H, *J* = 8.2 Hz), 7.07 (d, 2H, *J* = 7.8 Hz), 6.23 (d, 1H, *J* = 16.0 Hz), 2.30 (s, 3 H), 1.44 (s, 9 H); ^{13}C NMR (50 MHz , $CDCl_3$) δ 166.5, 143.6, 140.3, 131.9, 129.6, 129.3, 129.0, 128.5, 128.3, 128.0, 119.1, 80.3, 28.2, 21.4 ppm; MS (ESI) $C_{14}H_{18}O_3$: m/z 234.

butyl(E)-3-(4-methoxyphenyl)acrylate (Table 4, entry 2): The product was purified with column chromatography on silica gel 60-120 mesh (hexane/ethyl acetate= 9:1) as a colourless oil; yield 91 % (171 mg); ^1H NMR (200 MHz , $CDCl_3$) δ 7.55 (d, 1H, *J* = 15.9 Hz), 7.45-7.40 (m, 2 H), 6.86- 6.80 (m, 2 H), 6.30 (d, 1H, *J* = 15.9 Hz), 4.11 (t, 2H, *J* = 6.6 Hz), 3.73 (s, 3 H), 1.70-1.52 (m, 2 H), 1.46-1.30 (m, 2 H), 0.90 (t, 3H, *J* = 6.6 Hz); ^{13}C NMR (50MHz, $CDCl_3$) δ 167.4, 161.3, 144.2, 129.7, 127.2, 115.8, 114.3, 64.2, 55.3, 30.8, 19.2, 13.8 ppm; MS (ESI) $C_{14}H_{18}O_3$: m/z 234.

ethyl(E)-3-(4-methoxyphenyl)acrylate (Table 4, entry 3): The product was purified with column chromatography on silica gel 60-120 mesh (hexane/ethyl acetate= 9:1) as a white solid; yield 88 % (165 mg); mp 74-76°C; ^1H NMR ($CDCl_3$, 200 MHz): δ 7.55 (d, 1H, *J*=15.9 Hz), 7.40-7.43 (d, 2H, *J*=6 Hz), 6.81-6.84 (d, 2H, *J*=6 Hz), 6.21 (d, 1H, *J*=15.9 Hz), 4.16 (q, 2H, *J*=7.1 Hz), 3.73 (s, 3 H), 1.24 (t, 3H, *J*=7.1 Hz); ^{13}C NMR ($CDCl_3$, 50 MHz): δ 167.3, 161.3, 144.2, 129.7, 127.7, 127.2, 115.8, 114.3, 60.3, 55.3, 14.4 ppm; MS (ESI) $C_{12}H_{14}O_3$: m/z 206.

methyl(E)-3-(4-methoxyphenyl)acrylate (Table 4, entry 4): The product was purified with column chromatography on silica gel 60-120 mesh (hexane/ethyl acetate= 9:1) as a white solid; yield 85 % (160 mg); mp 90-92°C; ^1H NMR ($CDCl_3$, 200 MHz): δ 7.65 (d, 1H, *J*=16.0 Hz), 7.47 (d, 2H, *J*=8.0 Hz), 6.90 (d, 2H, *J*=8.1 Hz), 6.31 (d,1H, *J*=16.0 Hz), 3.83 (s, 3 H), 3.79 (s, 3 H); ^{13}C NMR ($CDCl_3$, 50 MHz): δ 167.7, 161.4, 144.5, 129.7, 127.1, 118.2, 114.3, 55.3, 51.5 ppm. MS (ESI) $C_{11}H_{12}O_3$: m/z 192.

tert-butyl(E)-3-(4-nitrophenyl)acrylate (Table 4, entry 5): The product was purified with column chromatography on silica gel 60-120 mesh (hexane/ethyl acetate= 9:1) as a yellow solid; yield 92 % (184 mg); mp 146-148 °C; ^1H NMR ($CDCl_3$, 200 MHz): δ 8.34 (d, 2H, *J*=8.1 Hz), 7.60-7.71 (m, 3 H), 6.49 (d, 1H, *J*=16.0 Hz), 1.55 (s, 9 H); ^{13}C NMR ($CDCl_3$, 50MHz): δ 165.3, 148.3, 140.9, 140.6, 128.5, 124.6, 124.1, 81.4, 28.1 ppm; MS (ESI) $C_{13}H_{15}NO_4$: m/z 249.

butyl(E)-3-(4-nitrophenyl)acrylate (Table 4, entry 6): The product was purified with column chromatography on silica gel 60-120 mesh (hexane/ethyl acetate= 9:1) as a white solid; yield 90 % (180 mg); mp 158-160 °C; ^1H NMR (200 MHz, $CDCl_3$) δ 8.31-8.22 (m, 2 H), 7.78-7.70 (m, 3 H), 6.57 (d, 1H, *J* = 16.0 Hz,), 4.24 (*t*, 2H, *J* = 6.6 Hz), 1.81- 1.72 (m, 2 H), 1.51 - 1.40 (m, 2 H), 0.97 (t, 3H, *J* = 7.3 Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ 166.1, 148.5, 141.6, 140.6, 128.6, 128.4, 124.2, 122.6, 64.9, 30.7, 19.2, 13.7 ppm. MS (ESI) $C_{13}H_{15}NO_4$: m/z 249.

ethyl(E)-3-(4-nitrophenyl)acrylate (Table 4, entry 7): The product was purified with column chromatography on silica gel 60-120 mesh (hexane/ethyl acetate= 9:1) as a yellow solid; yield 82 % (164 mg); mp 152-154 °C; ^1H NMR (200MHz, $CDCl_3$) δ 8.35 (d, 2H, *J* = 8.7 Hz), 7.81- 7.73 (m, 3 H), 6.56 (d, 1H, *J* = 16.0 Hz), 4.30 (q, 2H, *J* = 7.1 Hz), 1.36 (*t*, 3H, *J* = 7.1 Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ 166.0, 148.5, 141.6, 140.6, 128.6, 124.2, 122.6, 61.0, 14.3 ppm. MS (ESI) $C_{11}H_{11}NO_4$: m/z 221.

methyl(E)-3-(4-nitrophenyl)acrylate (Table 4, entry 8): The product was purified with column chromatography on silica gel 60-120 mesh (hexane/ethyl acetate= 9:1) as a yellow solid; yield 84 % (168 mg); mp 180-182 °C; ^1H NMR (200MHz, $CDCl_3$) δ 8.26 (d, 2H, *J* = 8.8 Hz), 7.77- 7.65 (m, 3 H), 6.56 (d, 1H, *J* = 16.0 Hz), 3.84 (s, 3 H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 166.4, 148.5, 141.5, 141.9, 140.5, 128.6, 124.1, 122.1, 52.0 ppm; MS (ESI) $C_{10}H_9NO_4$: m/z 207.

tert-butyl(E)-3-(p-tolyl)acrylate (Table 4, entry 9): The product was purified with column chromatography on silica gel 60-120 mesh (hexane/ethyl acetate= 9:1) as a colorless oil; yield 90 % (154 mg); ^1H NMR (200 MHz, $CDCl_3$) δ 7.44 (d, 1H, *J* = 16.0 Hz), 7.23 (d, 2H, *J* = 8.0 Hz), 6.99 (d, 2H, *J* = 6.0 Hz,), 6.19 (d, 1H, *J* = 16.0 Hz), 2.19 (s, 3 H), 1.41 (s, 9H); ^{13}C NMR (50MHz, $CDCl_3$) δ 166.4, 143.5, 140.2, 131.9, 129.5, 127.9, 119.0, 80.1, 28.2, 21.3 ppm; MS (ESI) $C_{14}H_{18}O_2$: m/z 218.

butyl(E)-3-(p-tolyl)acrylate (Table 4, entry 10): The product was purified with column chromatography on silica gel 60-120 mesh (hexane/ethyl acetate= 9:1) as a colorless oil; yield 90 % (154 mg); ^1H NMR (200 MHz, $CDCl_3$) δ 7.57 (d, 1H, *J* = 16.0 Hz), 7.37-7.26 (m, 2 H), 7.12-7.03 (m, 2 H), 6.30 (d, 1H, *J* = 16.0 Hz), 4.11 (*t*, 2H, *J* = 6.5 Hz), 2.3 (s, 3H), 1.59 (*q*, 2H, *J* = 6.9 Hz), 1.42-1.27 (m, 2 H), 0.88 (*t*, 3H, *J* = 8 Hz); ^{13}C NMR (50MHz, $CDCl_3$) δ 167.3, 144.6, 140.6, 131.8, 129.6, 128.1, 117.2, 30.8, 21.4, 19.2, 13.8 ppm. MS (ESI) $C_{14}H_{18}O_2$: m/z 218.

ethyl(E)-3-(p-tolyl)acrylate (Table 4, entry 11): The product was purified with column chromatography on silica gel 60-120 mesh (hexane/ethyl acetate= 9:1) as a colorless oil; yield 86 % (147 mg); ^1H NMR (200MHz , $CDCl_3$) δ 7.59 (d, 1H, *J* = 16.0 Hz), 7.40-7.30 (m, 2 H), 7.20-7.11 (m, 2 H), 6.32 (d, 1H, *J* = 15.9 Hz), 4.18 (q, 2H, *J* = 7.2 Hz), 2.30 (s, 3 H), 1.26 (*t*, 3H, *J* = 7.1 Hz);

^{13}C NMR (50MHz, $CDCl_3$) δ 167.2, 144.6, 140.6, 131.8, 129.6, 128.1, 117.2, 60.4, 21.5, 14.4 ppm. MS (ESI) $C_{12}H_{14}O_2$: m/z 190.

methyl(E)-3-(p-tolyl)acrylate (Table 4, entry 12): The product was purified with column chromatography on silica gel 60-120 mesh (hexane/ethyl acetate= 9:1) as a colorless oil; yield 88 % (150 mg); ^{1}H NMR (200MHz , $CDCl_3$) δ 7.67 (d, 1H, *J* = 16.0 Hz), 7.42 (d, 2H, *J* 8.0 Hz), 7.18 (d, 2H, *J* = 8.0 Hz), 6.39 (d, 1H, *J* =16.0 Hz), 3.79 (s, 3 H), 2.37 (s, 3 H); ^{13}C NMR (50MHz, $CDCl_3$) δ 167.6, 144.9, 140.7, 131.6, 129.6, 128.0, 116.7, 51.6, 21.4 ppm MS (ESI) $C_{11}H_{12}O_2$: m/z 176.

tert-butyl(E)-3-(4-chlorophenyl)acrylate (Table 4, entry 13): The product was purified with column chromatography on silica gel 60-120 mesh (hexane/ethyl acetate= 9:1) as a white solid; yield 91 % (174 mg); mp 158-160 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.53 (d, 1H, *J* = 16.0 Hz), 7.57 - 7.30 (m, 4 H), 6.34 (d, 1H, *J* = 15.9 Hz), 1.53 (s, 9 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 166.0, 142.1, 135.8, 133.2, 129.1, 128.6, 120.8, 80.7, 28.2 ppm. MS (ESI) $C_{13}H_{15}ClO_2$: m/z 238.

butyl(E)-3-(4-chlorophenyl)acrylate (Table 4, entry 14): The product was purified with column chromatography on silica gel 60-120 mesh (hexane/ethyl acetate= 9:1) as a yellow oil; yield 90 % (172 mg); ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.52 (d, 1H, *J* = 15.9 Hz), 7.34 (d, 2H, *J* = 8.6 Hz), 7.23 (d, 2H, *J* = 8.6 Hz), 6.30 (d, 1H, *J* = 16.0 Hz), 4.11 (*t*, 2H, *J* = 6.6 Hz), 1.65 - 1.50 (m, 2 H), 1.41-1.33 (m, 2 H), 0.86 (*t*, 3H, *J* = 7.3 Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ 166.7, 143.0, 136.1, 133.0, 129.7, 129.2, 129.1, 128.2, 118.9, 64.5, 30.8, 19.2, 13.7 ppm. MS (ESI) $C_{13}H_{15}ClO_2$: m/z 238.

ethyl(E)-3-(4-chlorophenyl)acrylate (Table 4, entry 15): The product was purified with column chromatography on silica gel 60-120 mesh (hexane/ethyl acetate= 9:1) as a yellow oil; yield 85 % (162 mg); ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.52 (d, 1H, *J* = 16.0 Hz), 7.40-7.21 (m, 4 H), 6.30 (d, 1H, *J* = 16.0 Hz), 4.12 (*t*, 2H, *J* = 6.6 Hz), 1.24 (*t*, 3H, *J*=7.1 Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ 166.6, 143.0, 136.1, 133.0, 129.2, 128.2, 118.9, 60.6, 14.3 ppm. MS (ESI) $C_{11}H_{11}ClO_2$: m/z 210.

methyl(E)-3-(4-chlorophenyl)acrylate (Table 4, entry 16): The product was purified with column chromatography on silica gel 60-120 mesh (hexane/ethyl acetate=9:1) as a yellow solid; yield 85 % (162 mg); mp 82-84 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.74 (d, 1H, *J* = 15.9 Hz), 7.57-7.42 (m, 4 H), 6.48 (d, 1H, *J* = 16.0 Hz), 3.82 (s, 3 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 167.2, 143.4, 136.2, 132.9, 129.2, 128.1, 118.4, 51.8 ppm. MS (ESI) $C_{10}H_9ClO_2$: m/z 196.

tert-butyl(E)-3-(4-fluorophenyl)acrylate (Table 4, entry 17): The product was purified with column chromatography on silica gel 60-120 mesh (hexane/ethyl acetate= 9:1) as a yellow oil; yield 90 % (158 mg); ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.45-7.37 (m, 3 H), 6.95-6.82 (m, 2 H), 6.13 (d, 1H, *J* = 16.0 Hz), 1.40 (s, 9 H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 165.9, 161.1, 142.1, 130.9, 130.8, 129.8, 129.6, 119.9, 116.0, 115.6, 80.3, 27.7 ppm; MS (ESI) $C_{13}H_{15}FO_2$: m/z 222.

butyl(E)-3-(4-fluorophenyl)acrylate (Table 4, entry 18): The product was purified with column chromatography on silica gel 60-120 mesh (hexane/ethyl acetate= 9:1) as a yellow oil; yield 90 % (158 mg); ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.48-7.32 (m, 3 H), 6.98-6.90 (m, 2 H), 6.29-6.21 (m, 1 H), 4.15-4.03 (m, 2 H), 1.61 - 1.51 (m, 2 H), 1.39 - 1.15 (m, 2 H), 0.98-0.80 (m, 3 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 166.6, 161.2, 143.0, 130.7, 129.9, 118.0, 116.0, 115.6, 64.2, 30.7, 19.1, 13.6 ppm. MS (ESI) $C_{13}H_{15}FO_2$: m/z 222.

ethyl(E)-3-(4-fluorophenyl)acrylate (Table 4, entry 19): The product was purified with column chromatography on silica gel 60-120 mesh (hexane/ethyl acetate= 9:1) as a colorless oil; yield 80 % (140 mg); ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.65-7.41 (m, 3H), 7.15-70 (m, 2 H), 6.43 - 6.29 (m, 1 H), 4.30-4.11 (m, 2 H), 1.33-1.27 (m, 3 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 166.5, 161.2, 142.9, 130.7, 129.9, 129.7, 128.7, 127.9, 117.9, 116.0, 115.6, 60.3, 14.1 ppm. MS (ESI) $C_{11}H_{11}FO_2$: m/z 194.

methyl(E)-3-(4-fluorophenyl)acrylate (Table 4, entry 20): The product was purified with column chromatography on silica gel 60-120 mesh (hexane/ethyl acetate= 9:1) as a yellow oil; yield 81 % (142 mg); ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.57 (d, *J*=16.0 Hz, 1H), 7.46-7.39 (m, 2 H), 7.03-6.95 (m, 2H), 6.28 (d, *J*=16.0, 1 H), 3.72 (s, 3 H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 167.2, 161.4, 143.5, 130.0, 129.8, 117.5, 116.2, 115.8, 51.7 ppm. MS (ESI) $C_{10}H_9FO_2$: m/z 180.

tert-butyl(E)-3-(thiophen-3-yl)acrylate (Table 4, entry 21): The product was purified with column chromatography on silica gel 60-120 mesh (hexane/ethyl acetate= 9:1) as a purple oil; yield 93 % (152 mg); ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.60 (d, 1H, *J* = 15.7 Hz), 7.23 (d, 1H, *J* = 5.1 Hz), 7.12-7.08 (m, 1 H), 6.94-6.90 (m, 1 H), 6.09 (d, 1H, *J* = 15.7 Hz), 1.43 (s, 9 H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 166.1, 139.8, 136.1, 130.5, 128.0, 124.4, 123.8, 119.1, 80.5, 28.2 ppm. MS (ESI) $C_{11}H_{14}SO_2$: m/z 210.

butyl(E)-3-(thiophen-3-yl)acrylate (Table 4, entry 22): The product was purified with column chromatography on silica gel 60-120 mesh (hexane/ethyl acetate= 9:1) as a yellow oil; yield 90 % (148 mg). ^{1}H NMR (200 MHz , $CDCl_3$) δ 7.79 (d, 1H, *J* = 15.7 Hz), 7.37 (d, 1H, *J* = 4.9 Hz), 7.26-7.03 (m., 1 H), 6.95 (dd, 1H, *J* = 3.7, 4.9 Hz), 6.15 (d, 1H, *J* = 15.7 Hz), 4.10 (t, 2H, *J* = 6.6 Hz), 1.78 - 1.60 (m, 2H), 1.41-1.38 (m, 2 H), 0.88 (*t*, 3H, *J* = 6.6 Hz). ^{13}C NMR (50 MHz, $CDCl_3$) δ 166.9, 139.6, 137.0, 130.8, 128.7, 128.3, 128.1, 117.1, 64.4, 30.8, 19.2, 13.8 ppm. MS (ESI) $C_{11}H_{14}SO_2$: m/z 210.

ethyl(E)-3-(thiophen-3-yl)acrylate (Table 4, entry 23): The product was purified with column chromatography on silica gel 60-120 mesh (hexane/ethyl acetate= 9:1) as a purple oil; yield 89 % (145 mg); ^{1}H NMR (200 MHz , $CDCl_3$) δ 7.71 (d, 1H, *J* = 15.8 Hz), 7.29 (d, 1H, *J* = 5.1 Hz), 7.17 (d, 1H, *J* = 4.0 Hz), 6.97 (dd, 1H, *J* = 3.7, 5.1 Hz), 6.16 (d, 1H, *J* = 15.7 Hz), 4.23 - 4.12 (m, 2 H), 1.27 (*t*, 3H, *J* =6.6 Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ 166.9, 139.6, 137.0, 130.8, 128.4, 128.1, 117.1, 60.5, 14.3 ppm. MS (ESI) $C_9H_{10}SO_2$: m/z 182.

methyl(E)-3-(thiophen-3-yl)acrylate (Table 4, entry 24): The product was purified with column chromatography on silica gel 60-120 mesh (hexane/ethyl acetate= 9:1) as a purple oil; yield 88 % (144 mg). ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.71 (d, 1H, *J* = 15.7 Hz), 7.29 (d, 1H, *J* = 5.1 Hz), 7.17 (d, 1H, *J* = 3.5 Hz), 7.29-6.92 (m, 1 H), 6.16 (d, 1H, *J* = 15.8 Hz), 3.71 (s, 3 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 167.3, 139.5, 137.3, 131.0, 128.5, 128.1, 127.8, 124.4, 123.8, 116.6, 51.7 ppm. MS (ESI) $C_8H_8SO_2$: m/z 168.

tert-butyl(E)-3-([1,1'-biphenyl]-4-yl)acrylate (Table 4, entry 25): The product was purified with column chromatography on silica gel 60-120 mesh (hexane/ethyl acetate= 9:1) as a white solid; yield 90 % (209 mg); mp 134-136 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.78 - 7.55 (m, 7 H), 7.49- 7.45 (m, 3 H), 6.40 (d, 1H, *J* = 15.9 Hz), 1.55 (s, 9 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 166.4, 143.1, 142.7, 140.3, 133.7, 128.9, 128.5, 127.8, 127.5, 127.1, 126.6, 120.1, 80.6, 28.3 ppm. MS (ESI) $C_{19}H_{20}O_2$: m/z 280.

butyl(E)-3-([1,1'-biphenyl]-4-yl)acrylate (Table 4, entry 26): The product was purified with column chromatography on silica gel 60-120 mesh (hexane/ethyl acetate= 9:1) as a yellow solid; yield 92 % (214 mg); mp 118-120 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.78-7.57 (s., 7 H), 7.31 (d, 3H, *J* = 7.7 Hz), 6.36 (d, 1H, *J* = 15.9 Hz), 4.11 (*t*, 2H, *J* = 5.6 Hz), 1.65 - 1.53 (m, 2 H), 1.41-1.28 (m, 2 H), 0.87 (*t*, 3H, *J* = 6.7 Hz); ^{13}C NMR (50MHz, $CDCl_3$) δ 167.0, 143.9, 142.8, 140.0, 133.3, 128.8, 128.4, 127.7, 127.4, 126.9, 126.5, 118.0, 64.3, 30.7, 19.1, 13.7 ppm. MS (ESI) $C_{19}H_{20}O_2$: m/z 280.

ethyl(E)-3-([1,1'-biphenyl]-4-yl)acrylate (Table 4, entry 27): The product was purified with column chromatography on silica gel 60-120 mesh (hexane/ethyl acetate= 9:1) as a yellow solid; yield 84 % (196 mg); mp 90-92 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.80-7.56 (m, 7 H), 7.49-7.36 (m, 3 H), 6.47 (d, 1H, *J* = 15.9 Hz), 4.28 (q, 2H, *J* = 7.1 Hz), 1.35 (*t*, 3H, *J* = 7.1 Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ 167.1, 144.1, 143.0, 140.2, 133.5, 128.9, 128.6, 127.9, 127.6, 127.1, 118.2, 60.6, 14.4 ppm. MS (ESI) $C_{17}H_{16}O_2$: m/z 252.

methyl(E)-3-([1,1'-biphenyl]-4-yl)acrylate (Table 4, entry 28): The product was purified with column chromatography on silica gel 60-120 mesh (hexane/ethyl acetate= 9:1) as a yellow solid; Yield 86 % (200 mg); mp 176-178 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.74 (d, *J* = 16.0 Hz, 1 H), 7.63-7.59 (m, 6H), 7.46-7.37 (m, 3 H), 6.48 (d, *J* = 16.0 Hz, 1 H), 3.82 (s, 3 H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 167.4, 144.4, 143.0, 140.1, 133.3, 128.9, 128.6, 128.6, 127.5, 127.0 117.6, 51.7 ppm; MS (ESI) $C_{16}H_{14}O_2$: m/z 238.

tert-butyl(E)-3-(4-benzoylphenyl)acrylate (Table 4, entry 29): The product was purified with column chromatography on silica gel 60-120 mesh (hexane/ethyl acetate= 9:1) as a white solid; yield 90 % (235 mg); mp 96-98 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.84-7.76 (m, 4 H), 7.68-7.56 (m, 4 H), 7.53 - 7.43 (m, 2 H), 6.48 (d, 1H, *J* = 15.9 Hz), 1.55 (s, 9 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 196.0, 165.9, 142.1, 138.5, 137.4, 132.6, 130.6, 130.0, 128.4, 127.7, 122.6, 81.0, 28.2 ppm; MS (ESI) $C_{20}H_{20}O_3$: m/z 308.

butyl(E)-3-(4-benzoylphenyl)acrylate (Table 4, entry 30): The product was purified with column chromatography on silica gel 60-120 mesh (hexane/ethyl acetate= 9:1) as a white solid; yield 90% (235 mg); mp 56-58 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.78- 7.62 (m, 5 H), 7.60 - 7.49 (m, 3 H), 7.45 - 7.34 (m, 2 H), 6.45 (d, 1H, *J* = 16.0 Hz), 4.13 (*t*, 2H, *J* = 6.6 Hz), 1.72 - 1.49 (m, 2 H), 1.43-1.35 (m, 2 H), 0.88 (*t*, 3H, *J* = 6.6 Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ 195.8, 166.6, 143.0, 138.6, 138.1, 132.6, 130.5, 129.9, 128.3, 127.7, 120.6, 64.6, 30.7, 19.1, 13.7 ppm; MS (ESI) $C_{20}H_{20}O_3$: m/z 308.

ethyl(E)-3-(4-benzoylphenyl)acrylate (Table 4, entry 31): The product was purified with column chromatography on silica gel 60-120 mesh (hexane/ethyl acetate= 9:1) as a white solid; yield 83 % (217 mg); mp 80-82 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.85- 7.79 (m, 4 H), 7.78- 7.65 (m, 4 H), 7.61 - 7.50 (m, 2 H), 6.54 (d, 1H, *J* = 16.0 Hz), 4.35-4.24 (*q*, 2 H), 1.36 (*t*, 3H, *J* = 6.6 Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ 195.8, 166.5, 143.1, 138.6, 138.2, 137.3, 132.6, 130.5, 129.9, 128.4, 127.8, 120.7, 60.7, 14.3 ppm. MS (ESI) $C_{18}H_{16}O_3$: m/z 280.

methyl(E)-3-(4-benzoylphenyl)acrylate (Table 4, entry 32): The product was purified with column chromatography on silica gel 60-120 mesh (hexane/ethyl acetate= 9:1) as a white solid; yield 84 % (219 mg); mp 150-152 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.98-7.76 (m, 5H), 7.74-7.58 (m, 4 H), 7.52 (d, 2H, *J* = 7.5 Hz), 6.56 (d, 1H, *J* = 16.0 Hz), 3.84 (s, 3 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 195.8, 166.9, 143.4, 138.1, 132.6, 130.6, 130.0, 128.4, 127.8, 120.2, 51.9 ppm. MS (ESI) $C_{17}H_{14}O_3$: m/z 266.

tert-butyl(E)-3-(naphthalen-1-yl)acrylate (Table 4, entry 33): The product was purified with column chromatography on silica gel 60-120 mesh (hexane/ethyl acetate= 9:1) as a yellow oil; yield 89 % (184 mg); ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.56-8.48 (d, 1H, *J*= 16.0 Hz), 8.11 (s, 1H), 7.85-7.68 (m, 7H), 7.50-7.39 (m, 7H), 6.57-6.47 (m, 2 H), 1.63 (s, 18 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 166.1, 143.6, 140.4, 134.1, 133.7, 133.3, 132.1, 131.8, 131.4, 129.7, 128.6, 127.8, 123.5, 120.4, 80.1, 28.3 ppm; MS (ESI) $C_{17}H_{18}O_2$: m/z 254.

butyl(E)-3-(naphthalen-1-yl)acrylate (Table 4, entry 34): The product was purified with column chromatography on silica gel 60-120 mesh (hexane/ethyl acetate= 9:1) as a yellow solid; yield 90% (186 mg); mp 52-54 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.51-8.43 (d, 1H, *J*=16.0 Hz), 8.11-8.06 (d, 1H, *J*=9.3 Hz), 7.76-7.63 (m, 7H), 7.52-7.36 (m, 7H), 6.51-6.41 (dd, 2H, *J* = 8.0, 16.0 Hz), 4.25-4.16 (m, 4 H), 1.69-1.58 (m, 4 H), 1.46-1.35 (m, 4H), 0.93 (*t*, 6H, *J* = 7.3 Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ 167.1, 144.6, 141.5, 132.0, 129.9, 128.6, 128.5, 127.8, 126.7, 123.5, 118.4, 64.4, 30.8, 19.3, 13.8 ppm; MS (ESI) $C_{17}H_{18}O_2$: m/z 254.

ethyl(E)-3-(naphthalen-1-yl)acrylate (Table 4, entry 35): The product was purified with column chromatography on silica gel 60-120 mesh (hexane/ethyl acetate= 9:1) as a yellow oil; yield 85 % (176 mg); ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.38-830 (d, 1H, *J*=16.0 Hz), 7.98 (d, 1H, *J*=8.0 Hz), 7.63-7.54 (m, 7H), 7.48-7.25 (m, 7H), 6.38-6.29 (dd, 2H, *J* = 8.0, 16.0 Hz), 4.19-4.09 (m, 4 H), 1.22-1.14 (m, 6 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 167.0, 144.6, 133.3, 129.9, 128.7, 128.5, 127.8, 127.2, 126.8, 126.6, 123.5, 118.4, 60.5, 14.4 ppm; MS (ESI) $C_{15}H_{14}O_2$: m/z 226.

methyl(E)-3-(naphthalen-1-yl)acrylate (Table 4, entry 36): The product was purified with column chromatography on silica gel 60-120 mesh (hexane/ethyl acetate= 9:1) as a yellow solid; yield 82 % (170 mg); mp 88-90 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.51 (d, 1H, *J* = 16.0 Hz), 8.16 (d, 1H, *J* = 8.0 Hz), 7.86-7.75 (m, 7H), 7.62- 7.42 (m, 7H), 6.56-6.46 (dd, 2H, *J* = 8.0, 16.0 Hz), 3.83 (s, 3 H), 3.81 (s, 3 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 167.5, 144.9, 141.9, 134.3, 130.6, 130.0, 128.7, 127.8, 127.3, 126.7, 125.0, 123.5, 118.0, 51.8 ppm; MS (ESI) $C_{14}H_{12}O_2$: m/z 212.

tert-butyl(E)-3-(4-acetylphenyl)acrylate (Table 4, entry 37): The product was purified with column chromatography on silica gel 60-120 mesh (hexane/ethyl acetate= 9:1) as a colorless solid;

yield 91 % (181 mg); mp 120-122 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.87 (d, 2H, *J* = 8.3 Hz,), 7.59 -7.54 (m, 3 H), 6.37 (d, 1H, *J* = 16.0 Hz), 2.52 (s, 3 H), 1.56 (s, 9 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 197.3, 165.7, 141.9, 139.0, 137.8, 128.8, 128.0, 122.8, 80.9, 28.2, 26.7 ppm; MS (ESI) $C_{15}H_{18}O_3$: m/z 246.

butyl(E)-3-(4-acetylphenyl)acrylate (Table 4, entry 38): The product was purified with column chromatography on silica gel 60-120 mesh (hexane/ethyl acetate= 9:1) as a colorless oil; yield 92 % (183 mg); ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.98 (d, 2H, *J* = 8.3 Hz), 7.61 (d, 1H, *J* = 16.0 Hz), 7.52 (d, 2H, *J* = 8.3 Hz), 6.44 (d, 1H, *J* = 16.0 Hz), 4.14 (*t*, 2H, *J* = 6.6 Hz), 2.53 (s, 3 H), 1.69 - 1.53 (m, 2 H), 1.49-1.36 (m, 2 H), 0.88 (*t*, 3H, *J* = 7.3 Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ 197.3, 166.6, 143.0, 138.8, 138.0, 128.9, 128.1, 120.9, 64.7, 30.7, 26.7, 19.2, 13.7 ppm; MS (ESI) $C_{15}H_{18}O_3$: m/z 246.

ethyl(E)-3-(4-acetylphenyl)acrylate (Table 4, entry 39): The product was purified with column chromatography on silica gel 60-120 mesh (hexane/ethyl acetate= 9:1) as a yellow solid; yield 86 % (171 mg); mp 46-48 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.86 (d, 2H, *J* = 8.3 Hz), 7.58 (d, 1H, *J* = 16.2 Hz), 7.49 (d, 2H, *J* = 8.3 Hz), 6.41 (d, 1H, *J* = 16.0 Hz), 4.17 (q, 2H, *J* = 7.1 Hz), 2.50 (s, 3 H), 1.24 (*t*, 3H, *J* = 7.1 Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ 197.2, 166.4, 142.9, 138.7, 137.9, 128.8, 128.1, 120.8, 60.7, 26.6, 14.3 ppm; MS (ESI) $C_{13}H_{14}O_3$: m/z 218.

methyl(E)-3-(4-acetylphenyl)acrylate (Table 4, entry 40): The product was purified with column chromatography on silica gel 60-120 mesh (hexane/ethyl acetate= 9:1) as a white solid; yield 83 % (165 mg); mp 114-116 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.0 (d, 2H, *J* = 8.2 Hz), 7.71 (d, 1H, *J* = 16.0 Hz), 7.61 (d, 2H, *J* = 8.2 HzH), 6.53 (d, 1H, *J* = 16.0 Hz), 3.83 (s, 3 H), 2.62 (s, 3 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 197.3, 166.9, 143.3, 138.7, 138.1, 128.9, 128.2, 120.4, 51.9, 26.7 ppm; MS (ESI) $C_{12}H_{12}O_3$: m/z 204.

(E)-trimethyl(3-(p-tolyl)allyl)silane (Scheme 1): The product was purified with column chromatography on silica gel 60-120 mesh (hexane/ethyl acetate= 9:1) as a colorless oil; yield 79 % (135 mg); ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.29 (d, 4H, *J* = 8.1 Hz), 7.16 (d, 4H, *J* = 8.0 Hz), 6.36 - 6.25 (m, 4 H), 2.39 (s, 6 H), 1.75- 1.71 (m, 4 H), 0.13 (s, 18 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 138.1, 131.5, 130.5, 129.0, 127.8, 26.2, 23.4, 0.5 ppm; MS (ESI) $C_{13}H_{20}Si$: m/z 204.

tert-butyl(E)-3-(4-methoxyphenyl)acrylate (Table 5, entry 1): The product was purified with column chromatography on silica gel 60-120 mesh (hexane/ethyl acetate= 9:1) as a colorless oil; yield 40 % (57 mg); ^{1}H NMR (200MHz, $CDCl_3$) δ 7.48 (d, 1H, *J*=14 Hz), 7.32 (d, 2H, *J*=8.0 Hz), 7.09 (d, 2H, *J*=8.0 Hz), 6.24 (d, 1H, *J*=16.0 Hz), 2.28 (s, 3 H), 1.45 (s, 9 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 166.5, 143.5, 140.3, 132.0, 129.5, 127.9, 119.1, 80.3, 28.2, 21.4. MS (ESI) $C_{14}H_{18}O_3$: m/z 234.

butyl(*E*)-3-(4-methoxyphenyl)acrylate (Table 5, entry 2): The product was purified with column chromatography on silica gel 60-120 mesh (hexane/ethyl acetate= 9:1) as a colorless oil; yield 42 % (60 mg); ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.55 (d, 1H, *J*=16.0 Hz), 7.38 (d, 2H, *J*=8.0 Hz), 6.83 (d,2H, *J*=10 Hz), 6.31 (d, 1H, *J*=16.0 Hz), 4.11 (*t*, 3H, *J*=4.66 Hz) 3.73 (s, 3 H), 1.63-1.53 (m, 2 H), 1.40-1.29 (m, 2 H), 0.87 (*t*, 3H, *J* = 4.6 Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ 167.4, 161.3, 144.2, 129.6, 127.2, 115.8, 64.2, 55.3, 30.8, 19.2, 13.7; MS (ESI) $C_{14}H_{18}O_3$: m/z 234.

ethyl(E)-3-(4-methoxyphenyl)acrylate (Table 5, entry 3): The product was purified with column chromatography on silica gel 60-120 mesh (hexane/ethyl acetate= 9:1) as a white solid; yield 45 % (64 mg); mp 74-76 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.54 (d, 1H, *J*=16 Hz), 7.36 (d, 2H, *J*=10 Hz), 6.79 (d, 2H, *J*=8 Hz), 6.21 (d, 1H, *J*=16 Hz), 4.15 (*q*, 2H, *J*=7.0 Hz), 3.72 (s, 3 H), 1.23 ppm (t, 3H, *J*=7.0 Hz); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 167.3, 161.4, 144.2, 129.6, 127.2, 115.7, 114.3, 60.3, 55.3, 14.4 ppm; MS (ESI) $C_{12}H_{14}O_3$: m/z 206.

methyl(E)-3-(4-methoxyphenyl)acrylate (Table 5, entry 4): The product was purified with column chromatography on silica gel 60-120 mesh (hexane/ethyl acetate= 9:1) as a white solid; yield 44 % (63 mg); mp 90-92 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.64 (d, 1H, *J*=16.0 Hz), 7.48 (d, 2H, *J*=8.0 Hz), 6.90 (d, 2H, *J*=10 Hz), 6.31 (d, 1H, *J*=16.0 Hz), 3.84 (s, 3 H), 3.79 (s, 3 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 167.7, 161.4, 144.5, 129.7, 127.2, 115.3, 114.3, 55.3, 51.5 ppm; MS (ESI) $C_{13}H_{15}NO_4$: m/z 249.

tert-butyl(E)-3-(4-nitrophenyl)acrylate (Table 5, entry 5): The product was purified with column chromatography on silica gel 60-120 mesh (hexane/ethyl acetate= 9:1) as a yellow solid; yield 41 % (64 mg); mp 146-148 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.16 (d, 2 H, *J*= 8.1Hz), 7.60-7.50 (m, 3 H), 6.42 (d, 1H, *J*=16.0 Hz), 1.47 (s, 9 H); ^{13}C NMR (50MHz, $CDCl_3$) δ 165.2, 148.3, 140.8, 140.5, 128.5, 124.5, 124.1, 81.3, 28.1 ppm; MS (ESI) $C_{13}H_{15}NO_4$: m/z 249.

butyl(E)-3-(4-nitrophenyl)acrylate (Table 5, entry 6): The product was purified with column chromatography on silica gel 60-120 mesh (hexane/ethyl acetate= 9:1) as a white solid; yield 43 % (68 mg); mp 158-160 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.25 (d, 2H, *J* = 8.0 Hz), 7.75-7.66 (m, 3 H), 6.57 (d, 1H, *J* = 16.0 Hz), 4.24 (*t*, 2H, *J* = 6.6 Hz), 1.74-1.64 (m, 2 H), 1.50 - 1.39 (m, 2 H), 0.97 (*t*, 3H, *J* = 8.0 Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ 166.1, 148.4, 141.5, 140.6, 128.6, 128.4, 124.1, 122.6, 64.9, 30.7, 19.1, 13.7 ppm; MS (ESI) $C_{13}H_{15}NO_4$: m/z 249.

ethyl(E)-3-(4-nitrophenyl)acrylate (Table 5, entry 7): The product was purified with column chromatography on silica gel 60-120 mesh (hexane/ethyl acetate= 9:1) as a yellow solid; yield 46 % (72 mg); mp 152-154 °C; ^{1}H NMR (200MHz, $CDCl_3$) δ 8.25 (d, 2H, *J* = 8.0 Hz), 7.75- 7.65 (m, 3 H), 6.56 (d, 1H, *J* = 16.0 Hz), 4.30 (*q*, 2H, *J* = 7.20 Hz), 1.36 (*t*, 3H, *J* = 7.20 Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ 166.0, 148.5, 141.6, 140.6, 128.6, 124.2, 122.6, 61.0, 14.3 ppm; MS (ESI) $C_{11}H_{11}NO_4$: m/z 221.

methyl(E)-3-(4-nitrophenyl)acrylate (Table 5, entry 8): The product was purified with column chromatography on silica gel 60-120 mesh (hexane/ethyl acetate= 9:1) as a white solid; yield 40 % (63 mg); mp 180182 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.25 (d, 1H, *J*=8.0 Hz), 7.77-7.65 (m, 3 H), 6.56 (d, 1H, *J*=16.0 Hz), 3.84 (s, 3 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 166.4, 148.5, 141.9, 140.5, 128.6, 124.2, 122.1, 52.0 ppm; MS (ESI) $C_{10}H_9NO_4$: m/z 207.

tert-butyl(E)-3-(4-benzoylphenyl)acrylate (Table 5, entry 9): The product was purified with column chromatography on silica gel 60-120 mesh (hexane/ethyl acetate= 9:1) as a white solid; yield 43 % (93 mg); mp 96-98 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.84-

7.82 (m, 4 H), 7.79-7.77 (m, 4 H), 7.63- 7.49 (m, 2 H), 6.48 (d, 1H, *J* = 16.0 Hz), 1.55 (s, 9 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 195.9, 165.8, 142.1, 138.5, 137.3, 132.6, 130.5, 130.0, 128.3, 127.7, 122.6, 81.0, 28.1 ppm; MS (ESI) $C_{20}H_{20}O_3$: m/z 308.

butyl(E)-3-(4-benzoylphenyl)acrylate (Table 5, entry 10): The product was purified with column chromatography on silica gel 60-120 mesh (hexane/ethyl acetate= 9:1) as a white solid; yield 45 % (97 mg); mp 56-58 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.85-7.77 (m, 4 H), 7.69 - 7.58 (m, 4 H), 7.53 - 7.45 (m, 2 H), 6.55 (d, 1H, *J* = 16.0 Hz), 4.24 (*t*, 2H, *J* = 4.66 Hz), 1.75 - 1.64 (m, 2 H), 1.62-1.43 (m, 2H), 0.97 (*t*, 3H, *J*=4.66 Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ 195.9, 166.6, 143.1, 138.6, 138.2, 132.6, 130.5, 130.0, 128.4, 127.8, 120.7, 64.7, 30.7, 19.21, 13.7 ppm; MS (ESI) $C_{20}H_{20}O_3$: m/z 308.

ethyl(E)-3-(4-benzoylphenyl)acrylate (Table 5, entry 11): The product was purified with column chromatography on silica gel 60-120 mesh (hexane/ethyl acetate= 9:1) as a white solid; yield 40 % (86 mg); mp 80-82 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.85- 7.81 (m, 4H), 7.78 - 7.65 (m, 4H), 7.61- 7.49 (m, 2 H), 6.54 (d, 1H, *J* = 16.0 Hz), 4.29 (*q*, 2H, *J* = 7.20 Hz), 1.36 (*t*, 3H, *J* = 7.20 Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ 195.8, 166.5, 143.5, 138.7, 138.2, 137.3, 132.6, 130.5, 130.0, 128.4, 127.8, 120.7, 60.7, 14.3 ppm; MS (ESI) $C_{18}H_{16}O_3$: m/z 280.

methyl(E)-3-(4-benzoylphenyl)acrylate (Table 5, entry 12): The product was purified with column chromatography on silica gel 60-120 mesh (hexane/ethyl acetate= 9:1) as a white solid; yield 49 % (106 mg); mp 150-152 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.85-7.78 (m, 4H), 7.78-7.65 (m, 4 H), 7.61-7.51 (m, 2 H), 6.55 (d, 1H, *J* = 16.0 Hz), 3.83 (s, 3 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 195.8, 166.9, 143.4, 138.7, 138.1, 137.3, 132.6, 130.5, 130.0, 128.4, 127.8, 120.7, 51.9 ppm; MS (ESI) $C_{17}H_{14}O_3$: m/z 266.

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An Efficient Palladium Catalyzed Mizoroki-Heck Cross-Coupling in Water

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Graphical Abstract