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2-Aminophenyl diphenylphosphinite as a new ligand for heterogeneous palladium-catalyzed Heck–Mizoroki reactions in water in the absence of any organic co-solvent

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In this article, 2-aminophenyl diphenylphosphinite has been introduced as a new ligand for the Heck–Mizoroki reactions of aryl halides with styrene and *n*-butylacrylate in water in the presence of palladium acetate. This ligand is easily prepared from the reaction of chlorodiphenyl phosphine with 2-aminophenol in high yield. Pre-catalyst $[Pd(OAc)_2]$ in the presence of the ligand produces a black solid mass. The solid catalyst has been recycled for the reaction of bromobenzene with styrene for six runs without appreciable loss of its catalytic activity.

1. Introduction

Nowadays, environmental consciousness encourages more environmentally benign chemical processes. Along this line, industries have started implementing green chemistry practices such as waste prevention, using new heterogeneous catalysts and the use of less toxic solvents and reagents.[1] However, disposal of organic solvents is the major problem in chemical industries which accounts around 80% of their waste.[2,3]

Water is considered as an alternative to expensive, flammable and toxic organic solvents.[4,5] Conducting the reactions in aqueous media is usually accompanied with selectivity that cannot be attained using organic solvents.[5] Furthermore, separation of water insoluble organic compounds from the aqueous phase could easily be achieved.[6–11]

Transition-metal-catalyzed reactions are established as important protocols in organic synthesis.[12] Among transition metals, palladium catalysis is an essential tool for C–C bond formation reactions. Among basic types of palladium-catalyzed transformations, the Heck–Mizoroki reaction which is the reaction between aryl halides and olefins occupy a special place.[13,14] Like any other established method, the Heck–Mizoroki reaction is also accompanied with some drawbacks such as the requirement of elevated temperatures, employing hazardous organic solvents and using expensive phosphine ligands. Challenging subjects for investigation in Heck–Mizoroki reactions include shortening of the reaction times, applying recyclable catalysts that can be isolated easily from the reaction mixture and improving the low reactivity of aryl bromides and chlorides.

The Heck–Mizoroki reaction is usually achieved using palladium complexes with phosphine ligands; however, phosphine-free systems have also appeared in the literature.[15–18] There are some reports on the Heck–Mizoroki reactions conducted in neat water or in aqueous media using organic co-solvents.[19–23] Other reports regarding the Heck–Mizoroki reactions include using palladium nanoparticles,[24] microwave-assisted conditions,[25] amberlite,[26] polymer supported palladium,[27] oxime-derived palladacycle,[28] C–N-palladacyclic catalyst,[29] palladium on carbon,[30] and supercritical conditions[31] in aqueous media.

Palladium in the presence of phosphinite ligands $[PPh_2(OR)]$ and related compounds have also been reported for carbon–carbon bond formation reactions.[33,34] We have also reported an imidazolium-based phosphinite ionic liquid as a medium and a ligand in the Heck–Mizoroki reaction, dehalogenation and homocoupling of aryl halides in the presence of $PdCl_2$.[32]

Now, we report efficient Heck–Mizoroki reaction of various aryl halides in the presence of an easily prepared 2-aminophenyl diphenylphosphinite as a ligand in water in the absence of any organic co-solvent.

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2. Results and discussion

Phosphinites are potential ligands for the formation of complexes with metal ions that can be used as catalysts in organic synthesis. They are prepared easily from the reaction of commercially available compounds such as PPh_2Cl with alcohols or phenols.[34–38]

In this study, 2-aminophenyl diphenylphosphinite (L) was obtained from the reaction of chlorodiphenyl phosphine with 2-aminophenol in 87% yield (Fig. 1).

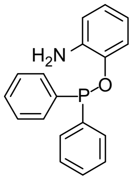


Figure 1. 2-Aminophenyl diphenylphosphinite (L).

2-Aminophenyl diphenylphosphinite is water and air stable, and the handling of its palladium complex does not need special precautions. The formation of active Pd(0) catalyst as a black insoluble mass was achieved by reacting $Pd(OAc)_2$ with 2-aminophenyl diphenylphosphinite (L) in water at 80 °C. At the start, the colour of the heterogeneous mixture was beige, which was changed to a dark brown colour and finally, a black heterogeneous mass was produced after a few minutes.

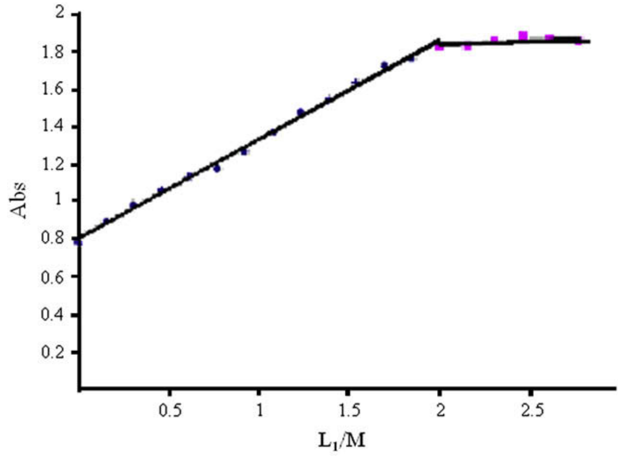


Figure 2. Mole ratio plot for complex formation between $Pd(OAc)_2$ and 2-aminophenyl diphenylphosphinite (L) at 271 nm in relation to λ_{max} of the ligand.

The molar ratio of ligand (L) with respect to Pd has been determined by employing the mole ratio method.[32] The complex formation between the ligand and $Pd(OAc)_2$ in DMF was in good harmony with the formation of ML_2 complex as presented by Figure 2.

Some information about the shape and the size of the catalyst particles was obtained by SEM images as presented in Figure 3. The images show that in the presence of $Pd(OAc)_2$ the shape of the particles have been verified from needle (A) to highly dispersed spherical form, uniformly sized particles (B) which is characteristic of Pd(0) complex formation.[39]

The formation of the Pd(0) catalyst was also supported by the XRD of the powder obtained by drying of the aqueous mixture of $Pd(OAc)_2$ and the ligand at (111),(200),(220) and (311) crystallographic planes as illustrated in Figure 4.[40]

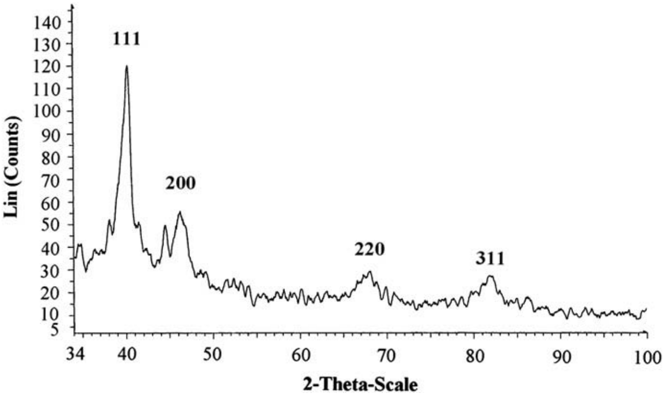


Figure 4. Powder XRD patterns resulted from the evaporation of the aqueous solution of $Pd(OAc)_2$ and the ligand.

The stability of the ligand towards basic conditions was also studied. For this purpose, a mixture of 2-aminophenyl diphenylphosphinite (2 mmol) with of NaOH (3 mmol) in H_2O (5 mL) was refluxed for 3 h. After workup of the reaction mixture, the intact aminophosphinite was isolated over 97% yield.

In order to find a suitable base for the reactions, the reaction of bromobenzene (1 mmol) as a model compound with styrene (1.5 mmol), in the presence of $Pd(OAc)_2$ (3 mol %), L (9 mol %) and different bases was studied. The results indicate that NaOH was the best base for this reaction (Table 1).

In order to show the benefit of using water as solvent, we compared the coupling reaction of 4-bromotoluene with styrene in toluene and water. For this aim, 4-bromotoluene was treated with styrene in the presence of $Pd(OAc)_2$ (3 mol %) and L (9 mol %) in toluene and water at 95 °C for 3 h. The reaction which was conducted in water resulted in the isolation of 81% of the product

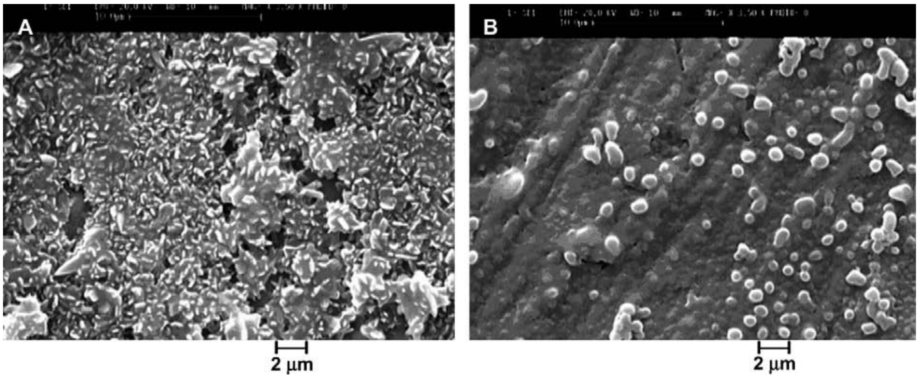
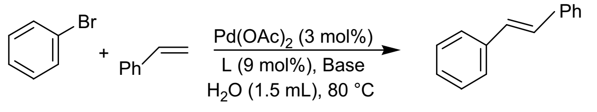


Figure 3. SEM image of L in the absence of $Pd(OAc)_2$ (A) and after addition of $Pd(OAc)_2$ to L (B) (magnification of 5000).

Table 1
The results of the reaction of bromobenzene with styrene in the presence of different bases using Pd(OAc)$_2$ and the ligand

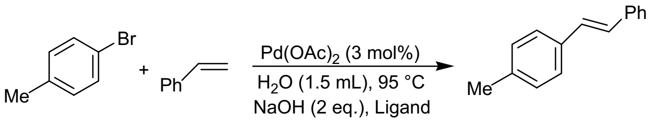


Entry	Base	Time (h)	Isolated yield%
1	0	24	0
2	NaOH	0.75	83
3	K_2CO_3	18	70
4	K_3PO_4	18	60
5	CS_2CO_3	7	78
6	Et_3N	14	54
7	DBU	14	45

while, for the similar reaction in toluene, only 20% of the desired product was isolated.

The benefit of using 2-aminophenyl diphenylphosphinite ligand in comparison with Ph_3P and under ligand-free conditions has also been disclosed upon the reaction of 4-bromotoluene with styrene in water. The results are presented in Table 2.

Table 2
Comparison of the reaction of 4-bromotoulene with styrene in the presence of 2-aminophenyl diphenylphosphinite, Ph_3P and ligand-free conditions in water



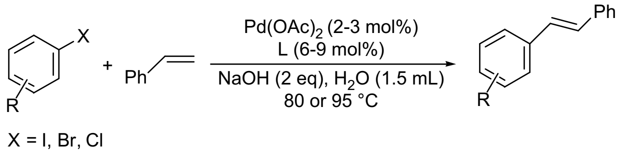
Entry	Ligand	Time (h)	Yield%
1	Ligand-free	5	Trace
2	PPh_3	4	30
3	L	3	81

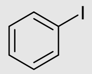
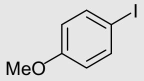
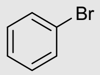
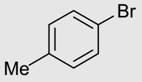
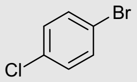
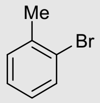
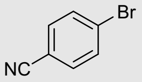
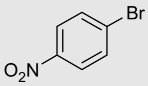
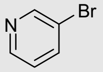
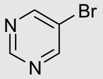
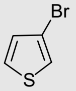
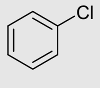
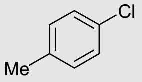
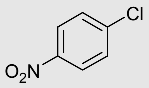
Then, the optimized conditions were applied in Heck–Mizoroki reactions of structurally different aryl halides. The amount of the Pd(OAc)$_2$ varies from 2 to 3 mol % and the nature of the aryl halides determines the temperature requirement for the reaction.

Most of the reactions proceeded at two different temperatures, 80 and 95 °C and in some cases, in a sealed tube at 130 °C. The amount of the aminophosphinite ligand (L) varies from 6 to 9 mol % (Table 3). However, iodobenzene, 4-iodoanisole, bromobenzene and 3-bromothiophene reacted with styrene at 80 °C to give the desired *trans*-alkenes in 85%, 86%, 84% and 85% isolated yields respectively (Table 3, entries 1, 2, 3, 11). Homo-coupled products were also obtained in 5–8% isolated yields. The reaction of the other aryl bromides with styrene were performed at 95 °C to give their corresponding *trans*-stilbenes in the appropriate reaction times in high to excellent yields (Table 3). In these reactions, the corresponding homo-coupled products were also isolated in 5–8% yields.

The reaction of aryl chlorides with styrene is usually sluggish with low yields. We have also studied this reaction in the presence of 2-aminophenyl diphenylphosphinite (L, 9 mol %) with Pd(OAc)$_2$ (3 mol %) in water at 95 °C using aryl chlorides and styrene. The desired *trans*-stilbenes were isolated in 40–45% yields after 10–24 h (Table 3, entries 12–14). These low yielding reactions forced us to study similar reactions in a sealed-tube at higher temperatures in water. For this purpose, chlorobenzene, 4-chlorotoluene and 4-chloronitrobenzene were reacted with styrene in the presence of Pd(OAc)$_2$ (3 mol %) and L (9 mol %) in water in a sealed tube at 130 °C for about 20 h (Table 3). Reaction of chlorobenzene and 4-chlorotoluene was successful and the corresponding products

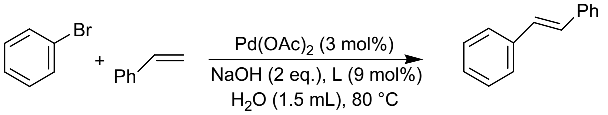
Table 3
Heck–Mizoroki coupling of different aryl halides with styrene in water in the presence of the ligand and NaOH as base



Entry	Ar–X	Pd(OAc)$_2$ (mol %), [T °C]	Time (h)	Isolated yield%	Product[Ref.]
1		2, [80]	0.4	85	**1a**[41]
2		2, [80]	2	86 (15)[a]	**1b**[42]
3		3, [80]	0.75	84 (10)[a]	**1a**[41]
4		3, [95]	3	81 (trace)[a]	**1c**[43]
5		3, [95]	5	79	**1d**[44]
6		3, [95]	9	84[b]	**1e**[41]
7		3, [95]	3.5	90 (38)[a,c]	**1f**[41]
8		3, [95]	5	90[c]	**1g**[42]
9		3, [95]	16	85 (35)[a]	**1h**[42]
10		3, [95]	15	85[c]	**1k**[d]
11		3, [80]	1	85	**1l**[45]
12		3, [95]	10	45 (85)[e]	**1a**[41]
13		3, [95]	20	42 (80)[e]	**1c**[43]
14		3, [95]	24	40[c] (68)[c,e]	**1g**[42]

[a] Yields in parenthesis show the reactions conducted in the absence of ligand.
[b] GC yields, *n*-octane was used as an internal standard.
[c] The reaction of high melting point substrates was preformed in the presence of TBAB (15 mol %) in order to facilitate the solubility of the substrate.
[d] Spectroscopic data are given in Experimental section.
[e] Yields in the parenthesis show the reactions conducted in sealed tubes at 130 °C.

Table 4
Recycling of the catalyst for the reaction of bromobenzene with styrene



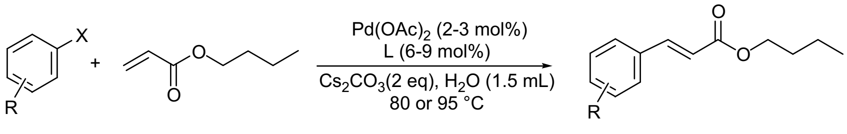
Run	Time (h)	Isolated yield%
1	1	83
2	1	83
3	1	81
4	1	80
5	1	80
6	1	79

were obtained in 85 and 80% isolated yields respectively. However, the reaction of 4-chloronitrobenzene did not proceed to completion and the desired product was isolated in 68% yield.

Isolation of the heterogeneous catalyst was easily performed by filtration or centrifugation. The isolated catalyst was washed with diethyl ether and dried in air. The resulting isolated catalyst was used for the reaction of bromobenzene with styrene for six runs to afford *trans*-stilbene in 79–83% isolated yields (Table 4).

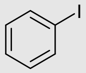
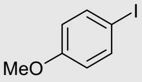
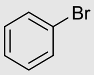
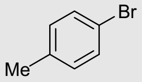
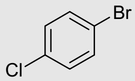
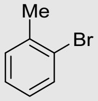
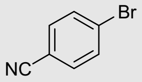
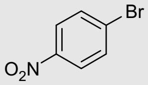
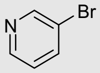
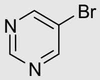
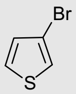
Finally, the reaction of *n*-butyl acrylate with different aryl halides was investigated. In these reactions iodobenzene and 4-iodoanisole were treated with *n*-butyl acrylate in the presence of Pd(OAc)$_2$ (2 mol %), Cs$_2$CO$_3$ as a base and the ligand L (6 mol %) at 80 °C. The reactions proceeded smoothly with the formation of trans-isomers in 85% and 89% isolated yields respectively (Table 5,

Table 5
Heck–Mizoroki reactions of different aryl halides with *n*-butyl acrylate in water



X = I, Br

2a-2l

Entry	Ar–X	Pd(OAc)$_2$ (mol %), [T °C]	Time (h)	Isolated yield%	Product$^{\text{Ref.}}$
1		2, [80]	2	85	**2a**[41]
2		2, [80]	5	89	**2b**[41]
3		3, [80]	4	86	**2a**[41]
4		3, [95]	20	80	**2c**[46]
5		3, [95]	10	72	**2d**[43]
6		3, [95]	24	76[a]	**2e**[41]
7		3, [95]	5	86[b]	**2f**[41]
8		3, [95]	6	88[b]	**2g**[42]
9		3, [95]	22	80	**2h**[41]
10		3, [95]	20	75[b]	**2k**[c]
11		3, [80]	5	73	**2l**[41]

[a] GC yield, *n*-octane has been used as an internal standard.

[b] For the solid and high melting point substrates, the reactions were preformed in TBAB (15 mol %) in order to facilitate their solubility.

[c] Spectroscopic data of these products are given in Experimental section.

entries 1, 2). The corresponding homo-coupled products were also isolated in less than 10% yields. In these reactions, *n*-butyl acrylate cannot tolerate strong basic conditions such as NaOH solutions; therefore, the reactions were performed in the presence of a weaker base such as Cs_2CO_3. Aryl bromides were also reacted with *n*-butyl acrylate with the molar ratios of aryl bromides, *n*-butyl acrylate, $Pd(OAc)_2$ (3 mol %) and the ligand L (9 mol %) in water at 80 °C and 95 °C. The reactions proceeded smoothly and the desired products were isolated in 72–88% yields (Table 5). The reaction of aryl chlorides with *n*-butyl acrylate in the presence of $Pd(OAc)_2$, L and Cs_2CO_3 at 95 °C failed completely in water and the starting materials were isolated intact after prolonged reaction times.

3. Conclusions

In this study, for the first time, we have introduced 2-aminophenyl diphenylphosphinite (L) as a ligand for Heck–Mizoroki reactions in water in the absence of an organic co-solvent.

Aryl iodides and bromides were reacted efficiently with styrene and *n*-butylacrylate at 80 and 95 °C in the presence of the catalyst in water. However, the reaction of less reactive aryl chlorides with styrene was conducted in a sealed tube at 130 °C. The procedure is easy and does not require special precautions. All the reactions were conducted in the air in water without the use of an organic co-solvent. The solid catalyst was simply isolated by filtration or centrifugation and was recycled smoothly for several runs without appreciable loss of its catalytic activity.

4. Experimental

4.1. General

IR spectra were run on a Perkin–Elmer 781 spectrophotometer. The ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance DPX 250 MHz Spectrometer in $CDCl_3$ or DMSO-d_6 solvents using TMS as an internal standard. ^{31}P NMR spectra were recorded at 90 MHz in DMSO-d_6 solvent using TMS as an internal standard. Chemical shifts were reported in ppm (δ), and coupling constants (J), in Hz. Mass spectra were obtained at 70 eV. The reaction monitoring were carried out on silica gel analytical sheets or by GC analysis using a 3-m length column packed with DC-200 stationary phase. Scanning electron micrographs were obtained by SEM (SEM, XL-30 FEG SEM, Philips, at 20 kV). X-ray diffractions were obtained using XRD, D8, Avance, Bruker, axs.

4.2. Preparation of 2-aminophenyl diphenylphosphinite (L)

To a flask (50 mL) containing of *t*-BuOH (15 mL), was added potassium (43 mg, 11 mmol) at room temperature and stirred slowly until the potassium was completely consumed. To the resulting solution, 2-aminophenol (1.1 g, 10 mmol) was added and stirred for 30 min. To the resulting black colour solution, chlorodiphenylphosphine (1.9 mL, 10 mmol) was added drop wise with steering in a period of 15 min at room temperature. Then, the reaction mixture was stirred for 10 h. To the resulting heterogeneous light brown mixture, water (30 mL) was added and filtered. The filter cake was washed with diethyl ether (15 mL) and dried under vacuum at room temperature. 2-Aminophenyl diphenylphosphinite was isolated as a beige solid compound in 87% yield, mp: 155–158 °C. ^1H NMR (250 MHz, DMSO-d_6) δ (ppm): 7.86–7.78 (m, 4H), 7.53–7.47 (m, 6H), 6.93–6.37 (m, 4H). ^{13}C NMR (62.9 MHz, $CDCl_3$) δ (ppm): 147.7, 133.5, 131.9, 131.5, 131.4, 128.7, 122.5, 120.3, 119.1, 115.5. IR (cm^{-1}): 3355, 3267, 3047, 1504, 1434, 1280, 1218, 1110, 921, 867, 817, 694, 509, 455. ^{31}P NMR (DMSO-d_6): δ (ppm)=22.400. Anal. Calcd for %C: 73.71, %H: 5.49, %N: 4.77; found: %C: 73.43, %H: 5.07, %N: 4.14. m/z (M^+): 293.

4.3. General experimental procedure for the Heck–Mizoroki reaction

In a conical flask (5 mL), a mixture of $Pd(OAc)_2$ (7 mg, 0.03 mmol) and L (26 mg, 0.09 mmol) in distilled water (1.5 mL) was prepared and heated at 80 °C for 10 min with steering to give an insoluble black material. To the resulting black material, aryl halide (1 mmol), styrene (0.17 mL, 1.5 mmol) or *n*-butyl acrylate (0.21 mL, 1.5 mmol) and NaOH (80 mg, 2 mmol) were added at 80 or 95 °C. Stirring was continued until the consumption of the starting materials (GC and TLC). The resulting heterogeneous mixture was extracted with ethyl acetate or diethyl ether (6×1 mL). The organic phase was separated and dried over anhydrous Na_2SO_4 and evaporated. The resulting crude product was purified by flash chromatography to give the desired pure coupling products in high to excellent isolated yields (Tables 3 and 5).

4.3.1. *β-4-Chlorophenyl styrene*[44]

Table 3, entry 5; ^1H NMR (250 MHz, $CDCl_3$) δ (ppm): 7.5–7.23 (m, 11H). ^{13}C NMR (62.9 MHz, $CDCl_3$) δ (ppm): 136.9, 135.8, 133.1, 129.3, 128.8, 128.7, 127.8, 127.6, 127.3, 126.5.

4.3.2. *5-Styryl-pyrimidine*

Table 3, entry10; beige solid powder, mp: 68–70 °C. ^1H NMR (250 MHz, $CDCl_3$) δ (ppm): 9.01 (s, 1H), 8.79 (s, 2H), 7.45–7.48 (d, 2H, J=7.2), 7.23–7.48 (m, 3H), 7.17 (d, 1H, J=16.5), 6.92 (d, 1H, J=16.5). ^{13}C NMR (62.9 MHz, $CDCl_3$) δ (ppm): 157.1, 154.2, 135.9, 132.7, 130.9, 128.8, 128.6, 126.8, 121.0. IR (cm^{-1}): 3041.1, 1634.1, 1556.5, 1414.1, 1186.4, 961.0, 718.7, 694.2, 633.5. Anal. Calcd for %C: 79.10, %H: 5.53, %N: 15.37; found: %C: 79.04, %H: 5.51, %N: 15.45.

4.3.3. *3-p-Tolyl-butyl acrylate*[46]

Table 5, entry 4; ^1H NMR (250 MHz, $CDCl_3$) δ (ppm): 7.57 (d, 1H, J=16.0), 7.33 (d, 2H, J=8.0), 7.09 (d, 2H, J=8.0), 6.31 (d, 1H, J=16.0), 4.12 (t, 2H, J=6.7), 2.28 (s, 3H), 1.60 (m, 2H), 1.35 (m, 2H), 0.88 (t, 3H, J=7.2).

4.3.4. *3-Pyrimidin-5-yl-butyl acrylate*

Table 5, entry 10; light yellow coloured viscous oil. ^1H NMR (250 MHz, $CDCl_3$) δ (ppm): 9.14 (s, 1H), 8.79 (s, 2H), 7.54 (d, 1H, J=16.2), 6.55 (d, 1H, J=16.2), 4.15 (t, 2H, J=6.7), 1.56–1.64 (m, 2H), 1.39–1.31 (m, 2H), 0.88 (t, 3H, J=7.2). ^{13}C NMR (62.9 MHz, $CDCl_3$) δ (ppm): 165.6, 159.0, 155.5, 137.0, 128.2, 122.3, 64.8, 30.5, 19.0, 13.6. IR (cm^{-1}): 3164.5, 3002.6, 2944.2, 2627.7, 2410.1, 2292.7, 1716.3, 1175.5, 1039.2, 918.3, 749.1. Anal. Calcd for %C: 64.06, %H: 6.84, %N: 13.58; found: %C: 63.94, %H: 6.75, %N: 13.43.

4.4. Recycling of the catalyst for the reaction of bromobenzene with styrene

Bromobenzene (0.1 mL, 1 mmol) was reacted with styrene (0.17 mL, 1.5 mmol) in distilled water (1.5 mL) in the presence of $Pd(OAc)_2$ (7 mg, 0.03 mmol), L (26 mg, 0.09 mmol) and NaOH (80 mg, 2 mmol) at 80 °C. After completion of the reaction (GC), work up of the reaction mixture was continued as stated in the preceding general procedure. The black solid material (the catalyst) was isolated by centrifugation. Then, the isolated black catalyst was washed with diethyl ether and dried in air. The resulting solid catalyst was charged into another batch of the similar reaction. This was repeated for 6 runs to complete the reaction in 1 h. Isolation of the coupled product was performed as discussed in the preceding general procedure to give the desired product in 79–83% isolated yields (Table 4).

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Supplementary data

NMR spectra of products are available as a supplementary data. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2009.06.081.

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