Amino oxazolines as easily accessible water stable ligands for palladium catalysed aqueous Heck reaction

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A series of amino oxazolinyl ligands were screened for palladium catalysed Heck reaction. These ligands work well as phosphine free system in aqueous, micellar medium, can be effectively recovered and reused for subsequent cycles.

Keywords: amino oxazolines, water stable ligands, palladium, Heck reaction

Reaction of aryl halide and styrene with palladium catalyst developed by Heck and Mizoroki[1,2] remains an efficient option for the synthesis of stilbene and its derivatives. A number of different studies have been carried out to improve reaction conditions, including ligands, solvents, bases and additives.[3–5] Mostly the palladium salt is used in combination with phosphine ligand for this reaction. However, since the phosphine ligands are often costly or difficult to prepare, there is an interest to develop phosphine free conditions for this reaction. Recently, some phosphine free Mizoroki–Heck reactions to overcome some of these difficulties have been reported.[6–8] In this area mostly nitrogen based ligands are studied, some of which are difficult to synthesise or are less effective. Oxazoline based ligands are easy to prepare, are stable in basic medium and have been used in many catalytic reactions.[9–11]

Driven by environmental concerns, many efforts are being made to develop this important reaction in aqueous medium. Such reactions are generally carried out by using some additives. Generally surfactants, such as quaternary ammonium salts, and cyclodextrins are used as additives.[12–14] We now report the synthesis and applications of amino oxazoline, bis-oxazoline ligands and their use in Mizorok–Heck reaction in aqueous medium.

Results and discussion

The ligands **1**, **2** are prepared from isatoic anhydride while **3** from 1,2-dicyanobenzene and amino alcohol in presence of suitable Lewis acid[15] such as $ZnCl_2$ or clay (Scheme 1).

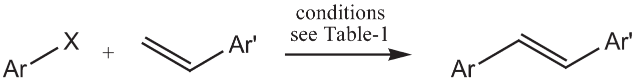
The ligands were tested for the standard reaction of iodobenzene **6** and styrene **7** (1.5 equiv.) with $Pd(OAc)_2$ (0.1%), ligand **1** to **5** (0.25%), K_2CO_3 (2 eq.) in DMF at 140 °C for 40 h. The product, *trans*-stilbene **7** was isolated respectively for ligand **1** (88%), **2** (95%), **3** (92%), **4** (28%) and **5** (92%). The oxazolinyl *N,N*-ligands **1** to **3** are comparable to bis-phosphine ligand dppp, **5**. The solvents DMF, DMA or NMP worked almost equally while further optimization showed that ligand **1** or **2** (0.025%) with $Pd(OAc)_2$ (0.01%) for the same reaction with TBAB (25%) in DMA gave *trans*-stilbene in excellent yield with respectable TON of 9300. [Turn Over Number (TON) = moles of product formed/moles of catalyst used]. The catalytic cycle of the Heck reaction starts with reduction of Pd(II) to Pd(0), often referred as preactivation, followed by oxidative addition of arylhalide, insertion of olefin and finally reductive elimination.[17–19] In the case of phosphine free reaction conditions, the initial reduction of palladium during preactivation is assisted by nucleophilic amines of the ligands (see Scheme 2 and Table 1).

In this research we have also developed reaction conditions for phosphine free ligand mediated Pd catalysed Mizorok–Heck reaction in water as part of solvent system. Initially the reaction was carried out in aqueous mixture of DMA in different proportions in order to solubilise the substrates. The presence of surfactants can help to dissolve water insoluble molecules in aqueous systems *via* their stabilisation in micellar system. We investigated the use of cetyltrimethylammonium bromide (CTAB) at concentrations higher than CMC for our catalytic Heck reaction in pure water. This reduces the use of DMA as a co-solvent in the reaction and may offer a green method for this conversion.

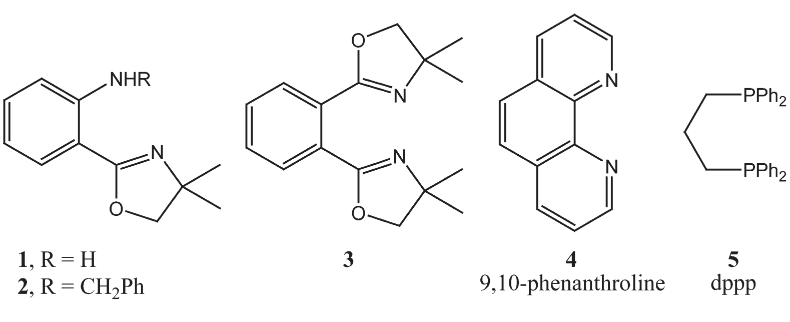
Conditions were optimised for the use of amino oxazoline ligands **1** and **2** in DMA for the Heck reaction with excellent conversions and high TON; several examples are shown in Table 2.

At the same time we also developed same reaction in mixture of DMA–water and then in pure water with CTAB and results are presented in Tables 3 and 4.

Generally, the disadvantage of homogeneous system is its inability to reuse the catalyst, usually this is overcome for the Mizoroki-–Heckby using heterogeneous palladium catalysts.[16] Alternatively, this deficiency may be addressed if the catalyst



Scheme 2 Standard Heck reaction.



1, R = H
2, R = CH_2Ph
3
4
9,10-phenanthroline
5
dppp

Scheme 1 Ligands screened for Heck reaction.

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Table 1 Optimisation of reaction conditions for Mizoroki–Heck reaction

No.	Aryl halide 1 equiv.	$Pd(OAc)_2$/mol %	Ligand **1** /mol %	Solvent (DMA:H_2O)	Yield^a/% [TON]	Additive
1	Iodobenzene	0.01	0.025	1:0	93 [9300]	TBAB (0.25 equiv.)
2	Iodobenzene	1	2.5	1:2	98 [98]	--
3	Iodobenzene	0.1	0.25	1:2	86 [863]	--
4	Iodobenzene	0.005	0.0125	1:2	91 [18163]	--
5	Iodobenzene	0.1 ($PdCl_2$)	0.25	1:2	98 [977]	--
6	Iodobenzene	0.5	1.25	1:2	90 [180]	--
7	Iodobenzene	0.5	1.25	1:2	86 [172]	CTAB (0.1 equiv.)
8	Iodobenzene	0.5	1.25	1:2	87 [174]	CTAB (0.1 equiv.)
9	Bromobenzene	0.5	1.25	1:2	34 [68]	--
11	Bromobenzene	0.5	1.25	1:2	66 [132]	TBAB (0.1 equiv.)
12	Iodobenzene	0.5	1.25	0:1	86 [172]	CTAB (0.1 equiv.)
13	Iodobenzene	0.5	1.25	0:1	52 [104]	--

All reactions with styrene (1.5 equiv.), K_2CO_3 (2 equiv.), at 140 °C for 40 h.
^{a}Isolated.

Table 2 Screening the present catalyst system for Mizoroki-Heck reaction for various examples in DMA

No	Aryl halide	Product	Yield/%^{a}
1	4-Iodoanisole (**9**)	4-Methoxystilbene (**10**)	79
2	4-Bromonitrobenzene (**11**)	4-Nitrostilbene (**12**)	82
3	3-Bromophenanthrene (**13**)	3-Styrylphenanthrene (**14**)	95
4	2-Bromobenzo[c]phenanthrene (**15**)	2-Styrylbenzo[c]phenanthrene(**16**)	95
5	2-Bromonaphthalene (**17**)	2-Styrylnaphthalene (**18**)	88
6	Iodobenzene (**19**)	*tert*-Butylcinnamate (**20**)	80

Entry 1–5 with styrene (1.5 equiv.) and 6 with *tert*-butyl acrylate (1.5 equiv.), K_2CO_3 (2 equiv.), $Pd(OAc)_2$ (1.0%), **1** or **2** (1.25%) in DMA at 140 °C for 40 h.
^{a}Isolated.

Table 3 Investigating the present system for Mizoroki-Heck reaction with DMA-water (1:2)

No	Aryl halide	Product	Yield/%^{a} [TON]^b
1	4-Iodoanisole (**9**)	4-Methoxystilbene (**10**)	89 [179]
2	4-Bromonitrobenzene (**11**)	4-Nitrostilbene (**12**)	64 [127]
3	3-Bromonitrobenzene (**21**)	3-Nitrostilbene (**22**)	90 [180]
4	1,2-Dibromobenzene(**23**)	1,2-Distyrylbenzene (**24**)	58 [58]

Entry 1–3 with styrene (1.5 equiv.), K_2CO_3 (2 equiv.), $Pd(OAc)_2$ (0.5%), **1** (1.25%) and entry 4 with styrene (3.0 equiv.), K_2CO_3 (4 equiv.), $Pd(OAc)_2$ (1.0%), **1** (2.5%). All reactions with DMA–water (1:2), 120 °C, for 40 h, TBAB (10% for entries 1–3 and 20% for entry 4).
^{a}Isolated, ^{b}TON= Turn Over Number = moles of product formed/moles of catalyst used.

Table 4 Examples of Mizoroki–Heck reaction in water–CTAB system

No.	Ar–X	Olefin (1.5 equiv.)	Product	Yield^a/% [TON]^b
1	Iodobenzene	Styrene	**8**	87 [174]
2	Iodobenzene	4-Methylstyrene	**25**	88 [176]
3	Iodobenzene	4-Vinylpyridine (1.2 equiv.)	**26**	94 [186]
4	4-Iodoanisole	Styrene	**10**	82 [172]
5	4-Iodoanisole	4-Methylstyrene	**27**	95 [190]
6	4-Bromochlorobenzene	Styrene	**28**	71 [141]

All reactions with ligand $Pd(OAc)_2$ (0.5%), **1** (1.25%), K_2CO_3 (2.0 equiv.), at 140 °C for 40 h.
^{a}Isolated. ^{b}TON= Turn Over Number = moles of product formed/moles of catalyst used.

can be recovered and reused for the next set of reactions. Since the product of the standard Heck reaction is stilbene, which can be extracted in non polar solvent such as petroleum ether, the catalyst/ligand may remain in the aqueous portion and may be recycled. Accordingly, a separate set of experiment was run, the product stilbene extracted and aqueous system used as such for the second cycle. The yields of first and second cycles were comparable (88 and 84%); however, there was a drop in the third cycle (60%) probably due to slight solubility of CTAB in petroleum ether. In order to check this, half of the original quantity of CTAB was added in the fourth cycle. The yield was increased substantially (73%).

Thus we have demonstrated that the present phosphine free catalyst system not only works well in water–CTAB or water–DMA solvent but it can be recovered and reused effectively for subsequent reactions.

Experimental

2-(4,4-Dimethyl-4,5-dihydrooxazol-2-yl)phenylamine (**1**): In a 100-mL two-necked flask, anhydrous zinc chloride (0.042 g, 0.306 mmol, 10 mol %) was prepared by melting it under high vacuum. After cooling to room temperature under nitrogen, dry chlorobenzene (10 mL), isatoic anhydride (0.50 g, 3.06 mmol) and 2-amino-2-methylpropan-1-ol (0.41 g, 4.60 mmol) were charged to this flask under nitrogen. The mixture was refluxed for 24 h. The solvent was removed under reduced pressure and the oily residue was dissolved in dichloromethane (25–30 mL). The solution was washed three times with water (3 × 20 mL) and the aqueous phase was extracted again with dichloromethane (2 × 20 mL). The combined organic phase was dried with anhydrous sodium sulfate and the solvent was removed in a vacuum. The resulting oil was purified by column chromatography on neutral alumina using light petroleum ether as eluent to afford **1** (0.455 g; 78%) as a white solid; m.p.103–106 °C (lit.[15]104–106 °C). ^{1}H NMR (CDCl$_3$, 400 MHz) δ 1.37 (s, 6 H), 4.00 (s, 2 H), 5.81 (s, 2 H), 6.63–6.69 (m, 2 H), 7.17–7.21 (m, 1 H), 7.67–7.70 (dd, *J* = 8.0 and 1.6 Hz, 1 H). IR (KBr) υ 3445, 3284, 3032, 2962, 1381, 1331, 1186, 754 cm^{-1}.

Benzyl-[2(4,4-dimethyl-4,5-dihydrooxazol-2-yl)phenyl]amine (**2**): In a 100-mL two-necked flask, anhydrous zinc chloride (0.054 g, 0.395 mmol, 10 mol %) was prepared by melting it under high vacuum. After cooling to room temperature under nitrogen, dry chlorobenzene (10 mL), 1-benzyl-1*H*-benzo[*d*][1,3]oxazine-2,4-dione (1.0 g, 3.95 mmol) and 2-amino-2-methylpropan-1-ol (0.527 g, 5.92 mmol) were mixed under nitrogen. The mixture was refluxed for 24 h. The solvent was removed under reduced pressure and the oily residue was dissolved in dichloromethane (25–30 mL). The solution was washed three times with water (3 × 20 mL) and the aqueous phase was extracted again with dichloromethane (2 × 20 mL). The combined organic phase was dried with anhydrous sodium sulfate and the solvent was removed in a vacuum. The resulting oil was purified by column chromatography on neutral alumina using light petroleum ether as eluent to afford **2** (0.421 g; 72%) as a white solid. 0.792 g (72%) of a clean product**;** m.p. 80 °C. ^{1}H NMR: (CDCl$_3$, 400 MHz) δ 1.36 (s, 6 H), 4.01 (s, 2 H), 4.51 (s, 2 H), 6.59–6.62 (t, *J* = 14.2 Hz and 5.9 Hz, 2 H), 7.19–7.25 (m, 2H), 7.37–7.30 (m, 4 H), 7.74–7.76 (d, *J* = 7.4 Hz, 1 H), 8.96 (bs, 1H). IR (KBr) υ 3262, 2963, 1918, 1811, 1628, 1384, 1089, 925, 840, 766 cm.$^{-1}$ Elemental Anal. Calcd for $C_{18}H_{20}N_2O$: C, 77.11; H, 7.18; N, 9.99. Found C, 77.12; H, 7.36; N, 10.02%.

1,2-Bis(4,4-dimethyl-2-oxazolin-2-yl)benzene (**3**): A mixture of anhydrous zinc chloride (0.06 g, 0.39 mmol, 10 mol %), 1,2-dicyanobenzene (0.5 g, 3.87 mmol) and 2-amino-2-methylpropan-1-ol (1.04 g, 11.7 mmol) in chlorobenzene (5 mL) was heated under nitrogen at 120 °C for 24 h. The solvent was removed under reduced pressure and the oily residue was dissolved dichloromethane. The solution was washed with water and the aqueous phase was again extracted with dichloromethane. The combined organic phase was dried with sodium sulfate and the solvent was removed in vacuum. The resulting oil was purified by column chromatography on neutral alumina using petroleum ether as eluent to afford **3** as pale yellow oil [30] (0.638 g, 60%). ^{1}H NMR (CDCl$_3$, 400 Hz) δ 1.39 (s, 12H), 4.07 (s, 2H), 7.45–7.48 (m, 2H), 7.74–7.76 (m, 2H). IR (KBr) υ 3068, 2968, 1651, 1599, 1493, 1383, 1249, 1189, 1080, 989, 921, 864, 776, 689 cm^{-1}.

Typical procedure for the Heck reaction

Catalyst solution (entry 1, Table 1): In a typical procedure, a catalyst solution was separately prepared in an oven dry, N_2 flushed two-neck round bottomed flask. A solution of palladium acetate (1.2 mg, 0.0055 mmol, 0.5 mol %) and ligand **1** (2.6 mg, 0.0137 mmol, 1.25 mol %) was prepared in dry *N,N*-dimethylacetamide (5 mL), under N_2 atmosphere. The mixture was stirred at room temperature until homogeneous (about 15 min) and degassed several times prior to use.

A mixture of 4-iodoanisole (0.250 g, 1.1 mmol), dry K_2CO_3 (0.297 g, 2.20 mol) in dry *N,N*-dimethylacetamide (5 mL) was repeatedly degassed by purging with N_2 gas. The solution was heated to 60 °C and styrene (0.172 g, 1.65 mol) was slowly added. After the addition, the temperature was increased (100 °C) and previously prepared palladium catalyst solution was added dropwise and the reaction mixture heated to 140 ± 5 °C for 40 h. The cooled mixture was then poured in water (25 mL) containing 6N HCl (5 mL) and extracted with dichloromethane (3 × 30 mL). The organic layer was washed with water (2 × 20 mL) and dried over anhydrous sodium sulfate. The solution was concentrated under reduced pressure to obtain a viscous liquid, which was purified by column chromatography on silica gel and petroleum ether as eluent to give pure stilbene as white solid (0.178 g, 79%).

Using the general procedure following stilbenes were synthesised utilising appropriate styrene derivatives:

4-Methoxystilbene (**10**): White solid; m.p. 134–135 °C (lit.[20] 135–136 °C). ^{1}H NMR: (CDCl$_3$, 400 MHz) δ 3.83 (s, 3H), 6.89–6.91 (m, 2H), 6.95–6.99 (d, *J* = 16.3 Hz, 1H), 7.05–7.09 (d, *J* = 16.2 Hz, 1H), 7.23–7.25 (m, 1H), 7.32–7.36 (m, 2H), 7.44–7.50 (m, 4 H). IR (KBr) υ 3002, 2853, 1641, 1511, 1446, 1384, 1296, 1179 cm.$^{-1}$ MS (EI) (*m/z*): 210 (M$^+$, 100), 179 (14), 167 (27), 105 (7), 76(3).

4-Nitrostilbene (**12**): Yellow solid; m.p.159–160 °C (lit.[21] 157 °C). ^{1}H NMR (CDCl$_3$, 400 MHz) δ 7.16–7.12 (d, *J* = 16.3 Hz, 1H), 7.3–7.26 (d, *J* = 16.3 Hz, 1H), 7.31–7.33 (m, 2H), 7.36–7.42 (m, 2H), 7.58–7.60 (m, 2H), 7.60–7.90 (m, 2H), 8.73–8.75 (d, *J* = 9.2 Hz, 1H). IR (KBr) υ 2922, 1590, 1340, 1107, 970, 694 cm.$^{-1}$ MS (EI) (*m/z*): 225 (M$^+$, 100), 179 (43), 167 (8.9), 89 (12.5), 77(5.86).

tert-Butyl cinnamate (**20**): Colourless liquid.[22] ^{1}H NMR (CDCl$_3$, 400 MHz) δ 1.53 (s, 9H), 6.35–6.39 (d, *J* = 16.0 Hz, 1H), 7.35–7.37 (m, 3H), 7.49–7.52 (m, 2H), 7.56–7.60 (d, *J* = 16.0 Hz, 1H). IR (neat) υ 2978, 1711, 1635, 1578, 1496, 1475, 1450, 1392, 1367, 1328, 1257, 1207, 1150 cm^{-1}.

3-Styrylphenanthrene (**14**): White solid; m.p. 152–154 °C (lit.[23] 154 °C). ^{1}H NMR (CDCl$_3$, 400 MHz) δ 7.30–7.36 (m, 2H), 7.40–7.45 (m, 3H), 7.62–7.65 (m, 3H), 7.68–7.75 (m, 3H), 7.85–7.93 (m, 3H), 8.76 (s, 1H), 8.77–8.78 (d, *J* = 4.4 Hz, 1H). IR (KBr) υ 3023, 1595, 1487, 1109, 1034, 940, 771, 738 cm^{-1}. MS (EI) (*m/z*): 281 (M^{+1}, 22.6), 280 (M$^+$, 100), 263 (8.7), 140 (19).

2-Styrylbenzo[c]phenanthrene (**16**): White solid: m.p. 142 °C (lit.[24] 140 °C). ^{1}H NMR (CDCl$_3$, 400 MHz) δ 7.28–7.35 (m, 3H), 7.41–7.45 (m, 3H), 7.63–7.69 (m, 3H), 7.43–7.78 (m, 1H), 7.81–7.86 (m, 2H), 7.89–7.94 (m, 3H), 8.04–8.07 (m, 2H), 9.18 (s, 1H), 9.18–9.20 (d, *J* = 3.6 Hz, 1H). IR (KBr) υ 3017, 1600, 1499, 1072, 1043, 982, 902, 782, 744 cm.$^{-1}$ MS (EI) (*m/z*): 331 (M^{+1}, 28), 330 (M$^+$, 100), 226 (12.3), 164 (23.6).

2-Styrylnaphthalene (**18**): White solid; m. p. 146–147 °C (lit.[25] 147–149 °C). ^{1}H NMR (CDCl$_3$, 400 MHz) δ 7.24–7.30 (m, 3H), 7.34–7.40 (m, 2H), 7.42–7.49 (m, 2H), 7.55–7.57 (dd, *J* = 8.6 and 1.3 Hz, 2H), 7.73–7.75 (dd, *J* = 8.6 and 1.3 Hz, 1H), 7.77–7.85 (m, 4H). IR (KBr) υ 3077, 3045, 1595, 1510, 1496, 1448, 1350, 1074, 957, 794, 775 cm^{-1}. MS (EI) (*m/z*): 230 (M$^+$, 100), 215 (21), 115 (15), 107 (9.1).

Synthesis of trans-*stilbene (8) (with CTAB in water)*

Catalyst solution: A solution of palladium acetate (0.0014 g, 0.006 mmol/0.5 mol %) and **1** (0.0029 g, 0.0153 mmol/1.25 mol %) was prepared in 5 mL water. The mixture was sonicated in ultrasonic water bath for 5 min.

In another two-neck round bottom flask iodobenzene (**6**) (0.250 g, 1.2 mmol), K_2CO_3 (0.338 g, 2.45 mmol), CTAB (0.045 g, 0.123 mmol) in water 5 mL were mixed. Then the solution was heated up to 60 °C, and styrene (0.19 g, 1.838 mmol) was added. After 15 mins temperature was raised to 90 °C, and to this the previously prepared catalyst solution was added at once. The combined reaction mixture was heated to 100 °C for 40 h. The cooled mixture was poured in 6N HCl and extracted with dichloromethane (3 × 40 mL). The organic layer was washed with water and dried over Na_2SO_4, concentrated under reduced pressure. The product was purified by column chromatography using silica gel and petroleum ether as eluent. White crystals, 0.192 g (86%), m.p. 120–122 °C (lit. [29] 121–123 °C).

(E)-3-Nitrostilbene (**22**): Pale yellow crystals; m.p. 108–110 °C (lit.[26] 111–112 °C). ^{1}H NMR (DMSO, 400 MHz) δ 7.31–7.34 (m, 1H), 7.40–7.53 (m, 4H), 7.66–7.70 (m, 3H), 8.07–8.12 (m, 2H), 8.44 (s, 1H). IR (KBr) υ 2925, 1588, 1355, 1117, 980, 714 cm^{-1}. MS (EI) (*m/z*): 225 (M$^+$, 60), 178 (100), 152 (23), 76(12).

1,2-Distyrylbenzene (**24**): Pale yellow crystals; m.p.115 °C (lit.[27] 111–112 °C). ^{1}H NMR (CDCl$_3$, 400 MHz) δ 6.98–7.02 (d, *J* = 16.4 Hz, 2H), 7.24–7.30 (m, 4H), 7.34–7.38 (m, 4H), 7.44–7.48 (d, *J* = 16.4 Hz, 2H), 7.51–7.54 (m, 4H), 7.58–7.60 (m, 2H). IR (KBr) υ 3086, 3053, 3019, 1600, 1491, 1213, 1158, 1071, 956, 758, 691 cm^{-1}. MS (EI) (*m/z*): 223 (M^{+1}, 8.9), 282 (M$^+$, 38), 191 (100), 178(5.6), 91 (12.3).

(E)-4-Methylstilbene (**25**): White solid; m.p. 112–114 °C (lit.[28] 114–116 °C). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.38 (S, 3H), 7.06–7.10 (d, *J* = 16.2 Hz, 1H), 7.10–7.14 (d, *J* = 16.2 Hz, 1H), 7.19–7.21 (d, *J* = 8 Hz, 2H), 7.25–7.29 (m, 1H), 7.36–7.40 (m, 2H), 7.43–7.45 (d, *J* = 8 Hz, 2H), 7.52–7.54 (m, 2H). IR (KBr) υ 2925, 1588, 1355, 1117, 980, 714 cm^{-1}. MS (EI) (*m/z*): 195 (M^+, 93.5), 179 (100), 89 (11), 76 (5.3).

(E)-4-Styrylpyridine (**26**): Off white solid: m.p. 126–128 ^{0}C (lit.[31] 129 °C). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.02–7.06 (d, *J* = 16.2 Hz, 1H), 7.30–7.34 (d, *J* = 16.2 Hz, 1H), 7.35–7.43 (m, 4H), 7.55–7.57 (m, 2H), 8.58–8.60 (dd, *J* = 4.8 Hz and 1.6 Hz, 2H). IR (KBr) υ 3022, 1590, 1564, 1485, 1309, 1187, 1022, 962, 800, 752 cm^{-1}. MS (EI) (*m/z*): 180 (M^{-1}, 100), 181 (M^+, 80.57), 97 (29), 71 (21).

(E)-4′-Methoxy-4-methylstilbene (**27**): White solid; m.p.160 °C (lit.[28]160–162 °C). ^{1}H NMR: ($CDCl_3$, 400 MHz) δ 2.35 (s, 3H), 3.82 (s, 3H), 6.88–6.90 (m, 2H), 6.92–6.96 (d, *J* = 16.2 Hz, 1H), 6.99–7.04 (d, *J* = 16.2 Hz), 7.14–7.16 (d, *J* = 7.9 Hz, 1H), 7.37–7.39 (d, *J* = 8.0 Hz, 2H), 7.42–7.45 (m, 2H). IR (KBr) υ 3014, 2913, 2840, 1605, 1510, 1250, 1172, 1037, 967, 825 cm^{-1}.

(E)-4-Chlorostilbene (**28**): White solid; m.p. 130 °C (lit.[28] 129–130 °C). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.04–7.08 (d, *J* = 16.2 Hz, 1H), 7.09–7.13 (d, *J* = 16.2 Hz, 1H), 7.29–7.47 (m, 5H), 7.44–7.47 (m, 2H), 7.52–7.54 (m, 2H). IR (KBr) υ 2925, 1588, 1355, 1117, 980, 714 cm^{-1}. MS (EI) (*m/z*): 214 (M^+, 80), 179 (100), 89 (33), 76 (20).

Synthesis of trans-*stilbene (***8***) (recycle experiment)*

Catalyst solution: A solution of palladium acetate (0.0014 g, 0.0613 mmol/0.5 mol %) and **1** (0.0029 g, 0.0153 mmol/1.25 mol %) was prepared in water (5 mL). The mixture was sonicated in ultrasonic water bath for 5 min.

In another two-neck round bottomed flask iodobenzene (**6**) (0.250 g, 1.2 mmol), K_2CO_3 (0.338 g, 2.45 mmol), CTAB (0.045 g, 0.123 mmol) in water (5 mL) were mixed. Then the solution was heated up to 60 °C, and styrene (0.19 g, 1.84 mmol) was added. After 15 mins temperature was raised to 90 °C, and to this mixture the previously prepared catalyst solution was added at once. The combined reaction mixture was heated to 100 °C for 40 h. The cooled mixture was poured in water (10 mL), extracted with petroleum ether (40 mL) for 7 to 8 times (till complete removal of product from aqueous layer, as indicated by TLC). The combined organic layer was washed with water and dried over anhydrous Na_2SO_4, concentrated under reduced pressure. The product was purified by column chromatography using silica gel and petroleum ether as eluent. The aqueous layer was collected in another round bottomed flask quantitatively which contain catalyst solution. To this solution all the other starting materials for next cycle were added and the reaction was conducted. The same procedure was employed for the recycle study.

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