# An efficient and reusable polymer-supported palladium catalyst for the Suzuki cross-coupling reactions of aryl halides

**S.M. Islam[a]*, P. Mondal[a], A. Singha Roy[a], S. Mondal[a] and M. Mobarak[a]**

*[a]Department of Chemistry, University of Kalyani, Kalyani, Nadia, 741235, W.B., India*

A reusable, air-stable polymer-anchored palladium (II) Schiff base complex catalyst, P-[{(NCH)$C_6H_4$}Pd(OAc)]$_2$ was prepared and was found to be highly active in Suzuki cross-coupling reactions of aryl halides with phenyl boronic acid in an aqueous medium to give biaryl products in high yields.

**Keywords:** palladium complex, Suzuki cross-coupling reaction, biaryls, aryl halides

The palladium catalysed Suzuki cross-coupling reaction has become a versatile tool in modern organic synthesis for the formation of symmetrical and unsymmetrical biaryl compounds.[1-4] Compounds containing the biaryl linkage are an important class of organic compounds and have widespread applications in many areas of organic synthesis, natural product synthesis, polymer science and in material science as precursors to molecular wires and rigid liquid crystals.

Usually in Suzuki cross-coupling reactions, aryl halides react with aryl boronic acids in the presence of a Pd catalyst and a suitable base in a single step under mild conditions. Many active catalytic systems have been developed for the Suzuki cross-coupling reactions. Homogeneous phosphine ligands can be used to complex the palladium species, resulting in excellent results.[5-8] However, this type of catalyst is sensitive to moisture and air oxidation and therefore requires air-free handling to minimise ligand oxidation. Moreover, homogeneous catalysis presents problems in separation and waste inorganic materials are difficult to reuse. Deactivation of soluble palladium catalysts by formation of inactive particles is also often encountered at high reaction temperatures. To overcome these problems, the development of solid-supported and insoluble transition metal catalysts has attracted a great deal of attention in organic chemistry.[9,10] Due to their versatile processing capabilities and ease of separation, long term stability in air and moisture and recycling, supported catalysts offer many advantages for industrial applications. Various supports including silica,[11] nanoporous carbon,[12] hydrotalcites,[13] zeolites and zeolites materials,[14] and polymers[15] are used to heterogenise the homogeneous catalyst.

The most readily available form of supported catalyst is palladium on charcoal, which is widely used as a heterogeneous catalyst for the Suzuki coupling reaction. It is seen that Pd/C catalyses the cross-coupling of activated haloarenes with phenylboronic acid in a DMA–$H_2O$ (20 : 1) mixture.[16] However, reusability of the catalyst was not tested for these reactions and a long reaction time is required. Palladium complex impregnated onto an MCM-41 matrix is found to be active towards the Suzuki coupling reaction.[17] In this case also, low turnover numbers and leaching of the palladium complex are the major problems. Leaching of the metal into solution and reuse of the catalyst are the important issues in coupling reactions especially when the reactions occur under heterogeneous conditions. Metal contamination is of great concern for food and pharmaceutical industries. It is therefore necessary to design a truly heterogeneous catalyst that can be easily recovered and reused with minimal palladium leaching into solution and therefore very effective in terms of practical application and operational safety.

It seems that palladium complexes anchored with in polymer matrix exhibit excellent catalytic activity for Suzuki coupling reactions of various substituted and non-substituted aryl halides.[18-27] These complexes are insoluble, reusable and stable in air and moisture. Recently, aqueous phase reactions have been one of the major interests in organic synthesis, because water is a readily available, safe, and environment-friendly solvent.[28] We now describe a truly heterogeneous palladium catalyst that is very effective for the Suzuki cross-coupling reaction between aryl halides and phenyl boronic acid in a $H_2O$–DMF (1 : 1) medium. The polymer-supported catalyst was more active than the homogeneous analogue. The catalyst is air-stable and can be reused several times without noticeable loss of catalytic activity.

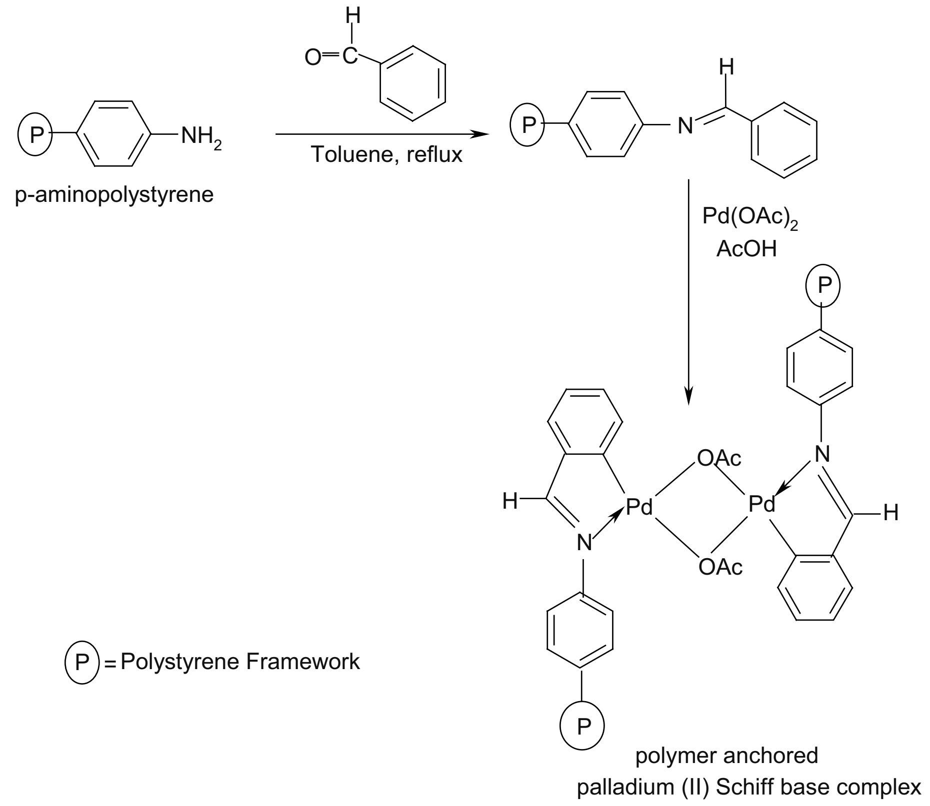
The preparation procedure followed to obtain the catalyst is given in Scheme 1. It was readily prepared in two steps. First, the amino polystyrene was treated with PhCHO to produce the corresponding Schiff base which was then reacted with Pd(II) acetate in acetic acid to yield the catalyst as dark brown solid.

The characterisation of the catalyst was done on the basis of IR spectroscopy, the diffuse reflectance spectra of the solid, thermogravimetric analysis and by using a scanning electron microscope. The metal content in the catalyst determined by atomic absorption spectroscopy suggests 2.23% Pd in the immobilised metal complex. The polymer-anchored Schiff base Pd(II) complex exhibited important IR peaks at 1615 $cm^{-1}$ (ν –C=N- coordinated), 1585 $cm^{-1}$, 1430 $cm^{-1}$ (ν COO bridged),[29] 720 $cm^{-1}$ (orthometallation)[30] and 455 $cm^{-1}$ (ν Pd–N).[31] The UV-Vis spectra provided further evidence for the presence of palladium on the polymer support. The absorption maxima around 280–320 nm may be attributed to $\pi\rightarrow\pi^*$ transition in polymer and phenyl moieties and the absorption at higher range (370–440 nm) is due to $\pi\rightarrow\pi^*$ and $n\rightarrow\pi^*$ transitions of the imine system in conjugation with the aromatic nuclei. Comparable IR and UV signals were also observed for the used catalyst. The scanning electron micrographs of amino polystyrene and the supported catalyst clearly show the morphological change which occurred on the surface of polystyrene after loading of the metal. The catalyst is insoluble in all common solvents and thermally stable up to 250 °C.

The Suzuki cross-coupling reaction is a convenient method for the C–C bond formation between aryl halides with arylboronic acids yielding biaryl derivatives. To test the applicability of the polymer anchored palladium (II) Schiff base complex catalyst, we examined the Suzuki reaction between various aryl halides and phenyl boronic acid in the presence of various solvents and bases. In order to optimise the reaction conditions, the Suzuki reaction of 4-bromoanisole (1.0 mmol) and phenylboronic acid (1.2 mmol) with 0.1 mol% of Pd catalyst at 80 °C was studied as the model reaction. The effects of different solvents and bases on the catalytic activity of the palladium complex are summarised in Table 1. It was found that the reactions performed in a mixture of water and a polar organic solvent (1 : 1) medium with $K_2CO_3$

---

* Correspondent. E-mail: manir65@rediffmail.com

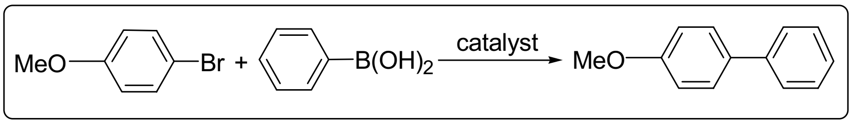


**Scheme 1** Synthesis of polymer anchored Pd (II) catalyst.

at 80 °C showed the best performance (entry 4). By contrast, the catalytic performance was not acceptable when a non polar solvent toluene was employed (entry 2). We also studied coupling reaction in sole water. The catalyst was also active in sole water medium (entry 3) but the conversion was low. Since the starting 4-bromoanisole had poor solubility in water, the addition of DMF was helpful to solve these solubility problems, and accelerated the reaction. It was seen that, high temperature was required to reach reasonable reaction speed and to obtained high yields of the coupling product and catalytic efficiency. At room temperature, no reaction takes place (entry 5). We also investigated the ability of different bases in the coupling reaction. The comparison of inorganic bases utilised showed that carbonate bases were more suitable than other bases. The reaction proceeds in high yield in the presence of $K_2CO_3$ as base. The use of sodium acetate, potassium phosphate or trialkylamine as base in the coupling reaction resulted low yields of biaryl products (entries 9–11).

The above optimised conditions could be applied to the coupling reactions between phenylboronic acid and a variety of aryl halides assisted by the polymer-anchored palladium (II) complex and the results are shown in Table 2. From the results it is seen that the electronic effect of substituents in the aryl bromides and aryl iodides had a great influence on the reaction. The electron-deficient substrates afford excellent yields of coupling products while electron-rich substrates give

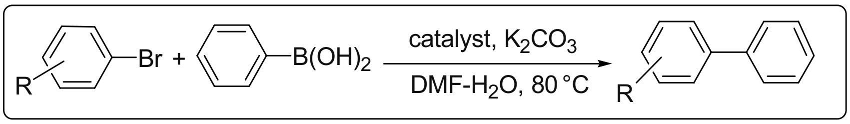
**Table 1** Suzuki cross-coupling reaction using polymer anchored Schiff base Pd (II) complex catalyst at various bases and solvents



| Entry | Base | Solvent | Temperature/°C | Time/h | Yield/% |
|---|---|---|---|---|---|
| 1 | $K_2CO_3$ | DMF | 80 | 8 | 92 |
| 2 | $K_2CO_3$ | Toluene | 100 | 8 | 45 |
| 3 | $K_2CO_3$ | Water | 90 | 8 | 72 |
| 4 | $K_2CO_3$ | DMF–$H_2O$ | 80 | 8 | 97 |
| 5 | $K_2CO_3$ | DMF–$H_2O$ | 25 | 8 | No reaction |
| 6 | $Na_2CO_3$ | DMF–$H_2O$ | 80 | 8 | 81 |
| 7 | $Cs_2CO_3$ | DMF–$H_2O$ | 80 | 8 | 74 |
| 8 | NaOH | DMF–$H_2O$ | 80 | 8 | 21 |
| 9 | NaOAc | DMF–$H_2O$ | 80 | 8 | Trace |
| 10 | $K_3PO_4$ | DMF–$H_2O$ | 80 | 8 | 17 |
| 11 | $Et_3N$ | DMF–$H_2O$ | 80 | 8 | 3 |
| 12 | $Na_2HPO_4$ | DMF–$H_2O$ | 80 | 8 | 0 |

Reaction conditions: aryl halide (1.0 mmol), phenylboronic acid (1.2 mmol), catalyst (0.1 mol% Pd), base (2.0 mmol), DMF–$H_2O$ (1:1, 6 mL), 80 °C.
Yield determined by GC and GCMS analysis.

**Table 2** Suzuki cross-coupling reaction of aryl halides with phenyl boronic acid with polymer anchored Pd (II) Schiff base complex catalyst



| Entry | Substrate | Product | Time/h | Isolated yield/% |
|---|---|---|---|---|
| 1 | Bromobenzene | Biphenyl | 4.5 | 96 |
| 2 | Iodobenzene | Biphenyl | 4.5 | 99 |
| 3 | Chlorobenzene | Biphenyl | 8 | 78 |
| 4 | 4-Bromoanisole | 4-Methoxybiphenyl | 5 | 97 |
| 5 | 3-Nitrobrobenzene | 3-Nitrobiphenyl | 5 | 99 |
| 6 | 4-Bromotoluene | 4-Methylbiphenyl | 6 | 90 |
| 7 | 4-Bromobenzaldehyde | 4-Formylbiphenyl | 6 | 97 |
| 8 | 4-Cyanobromobenzene | 4-Cyanobiphenyl | 5 | 98 |
| 9 | 4-Bromophenol | 4-Hydroxybiphenyl | 6 | 91 |
| 10 | 4-Bromoacetophenone | 4-Acetylbiphenyl | 5 | 99 |
| 11 | 2-Nitrobromobenzene | 2-Nitrobiphenyl | 8 | 86 |
| 12 | 2-Bromopyridine | 2-Phenylpyridine | 8 | 84 |
| 13 | 4-Iodoanisole | 4-Methoxybiphenyl | 5 | 98 |
| 14 | 3-Nitroiodobenzene | 3-Nitrobiphenyl | 4.5 | 98 |
| 15 | 4-Iodotoluene | 4-Methylbiphenyl | 4.5 | 92 |
| 16 | 4-Iodoacetophenone | 4-Acetylbiphenyl | 4 | 99 |
| 17 | 4-Cyanoiodobenzene | 4-Cyanobiphenyl | 4 | 99 |
| 18 | 4-Iodophenol | 4-Hydroxybiphenyl | 5 | 91 |
| 19 | 4-Chloroacetophenone | 4-Acetylbiphenyl | 8 | 81 |

Reaction conditions: aryl halide (1.0 mmol), phenylboronic acid (1.2 mmol), catalyst (0.1 mol% Pd), $K_2CO_3$ (2.0 mmol), DMF–$H_2O$ (1:1, 6 mL), 80 °C.

Isolated yields were calculated from the mass of the product after separation by column chromatography. All the isolated products showed more than 99% of GC purity.

moderate yields of coupled product under the same reaction conditions. Non-activated neutral substrates also give good yields coupled products. This is consistent with the general behaviour observed for the palladium-catalysed Suzuki reactions.[32] Sterically hindered *ortho*-substituted substrate, 2-bromonitro benzene, was also found to react smoothly under the condition giving a good yield of the desired coupling products (entry 11). An heteroaryl bromide, such as 2-bromopyridine, coupled effectively with phenylboronic acid providing 84% of the biaryl products (entry 12). The catalyst is capable of activating chlorobenzene (entry 3) which normally remains unreactive in Suzuki cross-coupling reactions. However, less reactive chlorobenzene gave poorer conversion compared to aryl bromides or iodides.

In order to see the effect of anchoring, the activity of the present polymer-anchored catalyst was compared to that of the corresponding homogeneous analogue in the Suzuki coupling reaction. The results showed that the homogeneous catalyst is less reactive than heterogeneous catalyst. The reaction using homogeneous catalyst with iodo benzene and phenylboronic acid in DMF–$H_2O$ medium at 80 °C for 8 h results in 43% conversion, while the analogous heterogeneous reaction was performed successfully with 99% conversion by GC. The activity of the catalyst was also compared with some other heterogeneous catalyst such as $Pd^{2+}$ sepiolite.[33] The results show that our catalyst is superior to the reported catalyst in terms of reaction time, reaction temperature and product yield.

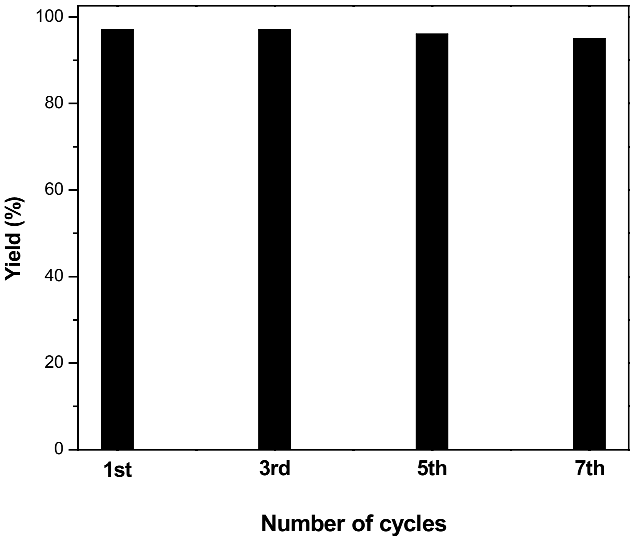


**Fig. 1** Recycling efficiency for the coupling reaction of 4-bromoanisole

For the recycling study the Suzuki cross-coupling reaction was performed with 4-bromoanisole and phenylboronic acid maintaining the same reaction conditions using the recovered catalyst. Each time after completion of the reaction, the catalyst was recovered by simple filtration, washed thoroughly with DMF and $H_2O$ to remove any excess reagents, dried under vacuum and reused under the same reaction conditions as for the initial run without any regeneration. The recycling efficiency of the catalyst up to seven successive runs is shown in Fig. 1. From the results, it is seen that the catalyst retained its high catalytic activity in these seven repeated cycles. Moreover atomic absorption spectroscopy analysis of the filtrate confirms that there was no leaching of the metal from the polymer anchored catalyst (<0.2 ppm Pd concentration).

In summary, we have described a simple heterogeneous palladium catalytic system for the Suzuki cross-coupling reaction of aryl halides. This polymer anchored catalyst, P-[{(NCH)$C_6H_4$}Pd(OAc)]$_2$ is easy to make, air-stable, inexpensive and non-polluting solid. The remarkable advantages with the use of the catalyst are its ready accessibility, its reusability and storage. Furthermore, the used catalyst is free from fire hazards or explosions. The catalyst has shown a notable activity towards a wide variety of substrates and excellent yields of products are obtained in aqueous media. The subsequent reuse of the catalyst without any loss of catalytic activity makes it an ideal protocol and a useful and attractive alternative for the synthesis of biaryls. Further studies of other coupling reactions catalysed by this system are currently in progress.

## Experimental

*Materials and instrument*

Analytical grade reagents and freshly distilled solvents were used throughout the investigation. Poly(styrene-co-divinyl benzene) 2% crosslinked, (Art.No. 434442-50G) was supplied by Aldrich, USA and palladium acetate was purchased from Arora Matthey. Other organic reagents were purchased from Merck and were used as such without further purification.

The FTIR spectra of the samples were recorded from 400 to 4000 cm$^{-1}$ on a Perkin-Elmer FTIR 783 spectrophotometer using KBr pellets. UV-Vis spectra were taken using a Shimadzu UV-2401PC doubled beam spectrophotometer having an integrating sphere attachment for solid samples. Thermogravimetric analysis (TGA) was carried out using a Mettler Toledo TGA/DTA 851e. Surface morphology of the samples was measured using a scanning electron microscope (SEM) (ZEISS EVO40, England) equipped with EDX facility. Palladium content in the catalyst was determined using a Varian AA240 atomic absorption spectrophotometer (AAS).

*Synthesis of the metal complex*

*Preparation of* p-*aminopolystyrene*

**CAUTION:** Mixtures of fuming nitric acid and acetic anhydride are known to be dangerously unstable and can detonate,[34] see also refs 35 and 36. Although in the present case, the acid used in not fuming but caution is advised.

The suspension of macroporous polystyrene beads (5.0 g) in a mixture of acetic anhydride (20 mL), nitric acid (~70%, 2 mL) and glacial acetic acid (4 mL) was constantly stirred for 30 min at 5 °C and for 5 h at 50 °C.[37] The corresponding p-nitro polystyrene was washed successively with acetic acid, water and methanol and finally dried under vacuum. Chemical analysis of P–NO$_2$ (P = polymer moiety) suggests that 56% nitration of the polystyrene ring.

A mixture of acetic acid (20 mL), stannous chloride (5 g), concentrated hydrochloric acid (6 mL) and the suspension of *p*-nitropolystyrene (5.0 g) were stirred for 72 h at room temperature to reduce the nitro-compound to the corresponding amine hydrochloride [34]. The residue was washed several times with hydrochloric acid (12 M) and glacial acetic acid (1:4) mixture and then with methanol. The estimation of chloride and nitrogen in the polymer amine hydrochloride suggests approximately 90% reduction of nitropolystyrene. The product on repeated treatment with dilute alcoholic NaOH (5%) produced the corresponding free amine. This was washed with alcohol and dried under vacuum.

*Preparation of polymer anchored Schiff base ligand and palladium (II) complex*

The suspension of macroporous *p* aminopolystyrene (2 g) in dry toluene (30 mL) was taken in a round bottom flask. Benzaldehyde (5 mL) was added dropwise to the stirring suspension. The reaction mixture was refluxed for 72 h until the colour of the suspension changed to yellow. After cooling to room temperature, the light yellow polymer-anchored Schiff base ligand was filtered off, washed successively with toluene, tetrahydrofuran and methanol and finally dried at reduced pressure. The chemical analysis suggests that nearly 80% of the polymer amine groups react with the carbonyl compound to produce the corresponding Schiff base ligand.

The suspension of the polymer-anchored Schiff base ligand (2 g) in acetic acid solution (15 mL) of palladium acetate (0.75 g) was refluxed on an oil bath for 8 h when the colour of the suspension changed completely from yellow to deep brown. After cooling the reaction mixture to room temperature, the separated polymer complex was filtered out, washed thoroughly with tetrahydrofuran and methanol and dried in room temperature under vacuum. Chemical analysis suggests the coordination of nearly 50% of the Schiff base to form palladium complex.

*General procedure for the synthesis of biaryls*

A mixture of aryl halide (1.0 mmol), phenylboronic acid (1.2 mmol), K$_2$CO$_3$ (2.0 mmol), DMF–H$_2$O (3 mL-3 mL) and catalyst containing 0.1 mol% palladium was stirred at 80 °C under air. To study the progress of the reaction samples of the reaction mixtures were collected at different time interval and quantified by GC analysis. At the end of the reaction, the catalyst was separated by simple filtration. The filtrate was extracted with Et$_2$O and passed through a pad of silica gel. The organic phase thus collected was dried over Na$_2$SO$_4$, filtered, concentrated and the residue was purified by flash chromatography on silica gel. The product was analysed by GC-MS.

*Biphenyl*:[38] White solid, m.p. 69 °C (lit.[39] 69–70 °C). $^1$H NMR (300 MHz, CDCl$_3$) δ: 7.58–7.28 (m, 10H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ: 141.2, 128.7, 127.2, 127.1; IR (cm$^{-1}$, KBr) ν: 2682, 1630, 1600, 1474, 1350. GC-MS: *m/z* 154.

*4-Methoxybiphenyl*:[38] White solid**,** m.p. 85 °C (lit.[40] 86 °C). $^1$H NMR (300 MHz,CDCl$_3$) δ: 7.52–7.24 (m, 7H), 6.96–6.90 (m, 2H), 3.77 (s, 3H); $^{13}$C NMR(75 MHz, CDCl$_3$) δ: 159.1, 140.7, 133.7, 128.7, 128.1, 126.6, 126.6, 114.2, 55.2; IR (cm$^{-1}$, KBr) ν: 2832, 1632, 1523, 1486, 1350. GC-MS: *m/z* 184.

*3-Nitrobiphenyl*:[38] Yellow solid, m.p. 60 °C (lit.[41] 59 °C). $^1$H NMR (300 MHz, CDCl$_3$) δ: 8.42 (dd, 1H, *J* = 2.4, 1.8 Hz), 8.14 (dd, 1H, *J* = 8.1, 2.4 Hz),7.86 (d, 1H, *J* = 7.8 Hz), 7.54 (dd, 3H, *J* = 8.7, 8.1 Hz), 7.49–7.34(m, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ: 148.7, 142.9, 138.6, 133.0, 129.7,129.1, 128.5, 127.1, 122.0, 121.9; IR (cm$^{-1}$, KBr) ν: 2675, 1601, 1523,1457, 1345, 1106. GC-MS: *m/z* 199.

**CAUTION:** The isomer 4-nitrobiphenyl is a known carcinogen.

*4-Methylbiphenyl*:[38] White solid, m.p. 46–47 °C (lit.[42] 44–46 °C). $^1$H NMR (300 MHz, CDCl$_3$) δ: 7.58–7.23 (m, 9H), 2.37 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ: 141.2, 138.4, 137.0, 129.5, 128.7, 127.0, 20.1; IR (cm$^{-1}$, KBr) ν: 2793, 2662, 1631, 1351. GC-MS: *m/z* 168.

*4-Formylbiphenyl*:[43] Colourless liquid, $^1$H NMR (300 MHz, CDCl$_3$): δ: 7.41–7.53 (m, 3H), 7.62–7.67 (m, 2H), 7.74–7.77 (m, 2H), 7.94–7.97 (m, 2H), 10.06 (s, 1H); $^{13}$C NMR (75 MHz, CDCl$_3$)δ: 127.3, 127.6, 128.4, 129.0, 130.2, 135.2, 139.7, 147.2, 191.9; GC-MS: *m/z* 182.

*4-Cyanobiphenyl*:[38] White solid, m.p. 83–85 °C (lit.[41] 84–86 °C). $^1$H NMR (300 MHz,CDCl$_3$) δ: 7.75–7.64 (m, 4H), 7.60–7.55 (m, 2H), 7.50–7.41 (m, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ: 145.6, 139.1, 132.5, 129.0, 128.6, 127.6, 127.4,118.9, 110.8; IR (cm$^{-1}$, KBr) ν: 2661, 2227, 1605, 1485, 768. GC-MS: *m/z* 179.

*4-Hydroxybiphenyl*:[44] Colourless solid, m.p. 165 °C (lit.[44] 166 °C). $^1$H NMR (acetone-d$_6$): $_{\mathrm{H}}$ = 8.44(s,1H,*OH*), 7.57 (d, *J* = 7.3 Hz, 2H, *ArH*), 7.50 (d, *J* = 8.6 Hz, 2H, *ArH*), 7.42-7.37 (m, 2H, *ArH*), 7.29–7.24 (m, 1H, *ArH*) and 6.93 (d, *J* = 8.6 Hz, 2H, *ArH*); $^{13}$C NMR (acetone-d6): C = 158.0, 141.8, 133.1 (ArC), 129.5, 128.8, 127.2, 127.1 and 116.5 (ArCH). IR (cm$^{-1}$, KBr) ν: 3404, 1610, 1523.GC-MS: *m/z* 170.

*4-Acetylbiphenyl*:[38] White solid, m.p. 118–119 °C (lit[45] 119–120 °C). $^1$H NMR (300 MHz, CDCl$_3$) δ: 8.05 (d, 2H, *J* = 8.4 Hz), 7.72–7.60 (m, 4H), 7.50–7.40(m, 3H), 2.64 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ: 197.5, 145.7, 139.8, 135.9, 128.9, 128.8, 128.2, 127.2, 127.1, 26.5; IR (cm$^{-1}$, KBr) ν: 2999, 2789, 2660, 1679, 1604, 1501, 1351, 764. GC-MS: *m/z* 196.

*2-Nitrobiphenyl*:[46] Pale yellow oil, $^1$H NMR (400 MHz, CDCl$_3$): δ 7.86 (d, *J* = 8 Hz, 1H), 7.62 (t, *J* = 7.2 Hz, 1H), 7.51–7.40 (m, 5H), 7.33–7.30 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ: 163.7, 140.3, 137.3, 128.8, 128.7, 128.6, 127.3, 127.0, 115.7, 115.5.

*2-Phenylpyridine*:[47] Colourless liquid. $^1$H NMR (CDCl$_3$, 200 MHz) δ 8.62 (d, 1 H), 7.98 (d, 2 H), 7.65 (d, 1 H), 7.64 (dd, 1 H), 7.44 (dd, 2 H), 7.38 (dd, 1 H), 7.14 (dd,1H). $^{13}$C NMR (CDCl$_3$,50 MHz) δ 157.3, 149.6, 139.3, 136.6, 128.9, 128.7, 126.8,122.0, 120.3. GC-MS: *m/z* 155.

We gratefully acknowledge Department of Science and Technology (DST), Council of Scientific and Industrial Research (CSIR) and University Grant Commission (UGC), New Delhi, India for funding. We also thank the DST and UGC, New Delhi, India for providing instrumental support under the FIST and SAP programmes.

*Received 27 August 2009; accepted 22 November 2009*
*Paper 09/0760 doi: 10.3184/030823409X12594170566203*

## References

1 N. Miyaura and A. Suzuki, *Chem. Rev*., 1995, **95**, 2457.
2 A. Suzuki, *J. Organomet. Chem*.,1999, **576**, 147.
3 F. Bellina, A. Carpita and R. Rossi, *Synthesis*, 2004, **15**, 2419.
4 S.A. Patil, C.M. Weng, P. Huang and F. Hong, *Tetrahrdron*, 2009, **65**, 2889.
5 T.E. Barder, *J. Am. Chem. Soc*., 2006, **128,** 898.

6 S.D. Walker, T.E. Barder, J.R. Martinelli and S.L. Buchwald, *Angew. Chem., Int. Ed*. 2004, **43**, 1871.

7 W.A. Herrmann, K. Ofele, D. von Preysing and S.K. Schneider, *J. Organomet. Chem*., 2003, **687**, 229.

8 S.-Y. Liu, M.J. Choi, G.C. Fu, *Chem. Commun*., 2001, **23**, 2408.

9 J.W. Byun and Y.S. Lee, *Tetrahedron Lett*., 2004, **45**, 1837.

10 E.B. Mubofu, J.H. Clark and D.J. Macquarrie, *Green Chem*., 2001, **1**, 23.

11 J.H. Clark, D.J. MacQuarrie and E.B. Mubofu, *Green Chem*., 2000, **2**, 53.

12 A.N. Vasiliev, L.V. Golovko, V.A. Povazhny, E. Zlotnikov, J. Chen and J.G. Khinast, *Microporous Mesoporous Mater*., 2007, **101**, 342.

13 M. Mora, C.J. Sanchidrian and J.R. Ruiz, *J. Colloid Interface Sci*., 2006, **302**, 568.

14 L. Artok and H. Bulut, *Tetrahedron Lett*., 2004, **45**, 3881.

15 J.W. Kim, J.H. Kim, D.H. Lee and Y.S. Lee, *Tetrahedron Lett*., 2006, **47**, 4745.

16 C.R. LeBlond, A.T. Andrews, Y. Sun and R. Sowa, *Org. Lett*., 2001, **3**, 1555.

17 H. Kosslick, I. Monnich, E. Fuhrmann, R. Fricke, D. Muller and G. Oehme, *Microporous Mesoporous Mater.,* 2001, **537**, 44.

18 T.Y. Zhang and M.J. Allen, *Tetrahedron Lett.,* 1999, **40**, 5813.

19 J.H. Li, X.-C. Hu, Y.-X. Xie, *Tetrahedron Lett.,* 2006, **47**, 9239.

20 N.T.S. Phan, D.H. Brown and P. Styring, *Tetrahedron Lett*., 2004, **45**, 7915.

21 J.-H. Kim, J.-W. Kim, M. Shokouhimehr, and Y.-S. Lee, *J. Org. Chem*., 2005, **70**, 6714.

22 B. Karimi and P. F. Akhavan, *Chem. Commun*., 2009, **25**, 3750.

23 X. Zeng, T. Zhang, Y. Qin, Z. Wei and M. Luo, *Dalton Trans*., 2009, **39**, 8341.

24 N. Jamwal, M. Gupta and S. Paul, *Green Chem*., 2008, **9**, 999.

25 N.T.S. Phan, J. Khan and P. Styring, *Tetrahedron,* 2005, **61**, 12065.

26 P.G. Steel and C.W.T. Teasdale, *Tetrahedron Lett*., 2004, **45**, 8977.

27 K. Inada, N. Miyaura. *Tetrahedron,* 2000, **56**, 8661.

28 Y. Uozumi and Y. Nakai, *Org. Lett*., 2002, **4**, 2997.

29 P.A. Stephenson and G. Wilkinson, *Inorg. Nucl. Chem*.,1967, **29**, 2122.

30 H. Onue and I. Moritani, *J. Organomet. Chem*., 1972, **43**, 431.

31 J.R. Durig, R. Layton, D.W. Sink and B.R. Mitchell, *Spectrochim. Acta*, 1965, **21**, 1367.

32 R.S. Verma and K.P. Naicker, *Tetrahedron Lett*., 1999, **40**, 439.

33 K. Shimizu, T. Kan-no, T. Kodama, H. Hagiwara and Y. Kitayama, *Tetrahedron Lett*., 2002, **43**, 5653.

34 P.G. Urban (ed.) *Bretherick's Handbook of reactive chemical hazards*, 6th edn, Butterworth, Oxford, 1999, Vol.1, p 1568.

35 G.A. Olah, *Chem. Br*., 1963, **32**, 21.

36 T.A. Brown and J.A.C. Watt, *Chem. Br*., 1967, **3**, 504.

37 R.B. King, E.M. Sweet, *J. Org. Chem*., 1979, **44**, 385.

38 L. Zhang, L. Wang, H. Li and P. Li, *Synthetic Commun.,* 2008, **38**, 1498.

39 J.B. Hendrickson and W.A. Wolf, *J. Org. Chem*., 1968, **33**, 3610.

40 T.B. Patrick, R.P. Willaredt and D.J. DeGonia, *J. Org. Chem*., 1985, **50**, 2232.

41 M.L. Kantam, M. Roy, S. Roy, B. Sreedhar, S.S. Madhavendra, B.M. Choudary and R.L. Dey, *Tetrahedron*, 2007, **63**, 8002.

42 M.S. Newman and J.A. Eberwein, *J. Org. Chem*., 1964, **29**, 2516.

43 Z. Xiong, N. Wang, M. Dai, A. Li, J. Chen and Z. Yang, *Org. Lett*., 2004, **19,** 3337.

44 C. Najera, J. Gil-Molto, S. Karlstrom and L.R. Falvello, *Org. Lett*., 2003, **5,** 1451.

45 L. Zhu, J. Duquette and M. Zhang, *J. Org. Chem*., 2003, **68**, 3729.

46 J.-H. Li, W.-J. Liu, and Y.-X. Xie, *J. Org. Chem*., 2005, **70**, 5409.

47 A.F. de Souza, A.C. Silva and O. A. C. Antunes, *Appl. Organomet. Chem*., 2009, **23**, 5.