# An efficient and reusable palladium nanocatalyst in C-C bond forming cross-coupling reactions

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*Palladium nanocatalyst, Pd-C covalent bond, Cross-coupling reactions*

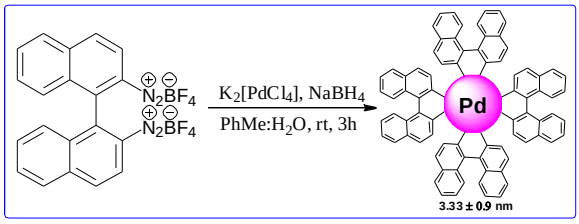
## INTRODUCTION

Palladium catalysts have been extensively studied in the synthetic organic chemistry particularly in C-C bond forming cross-coupling reactions.[1] Alternatively, palladium nanoparticles (Pd NPs) have attracted a remarkable interest in organic synthesis owing to the enhanced catalytic reactivity and lower catalytic loading.[2] Traditional stabilizers such as phosphines, amines and dendrimers are used for the preparation of NPs which often leads to agglomerization of NPs during the catalytic reaction. The Pd NPs stabilized by Pd-C covalent bond are much more stable than the traditional stabilizers.[3]

## RESULTS AND DISCUSSION

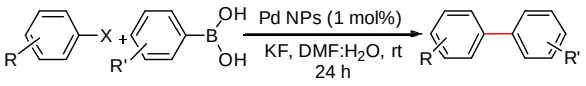
Palladium NPs were prepared by simple reduction of potassium tetrachloropalladate and 1,1′-binaphthyl,-2,2′-bis(diazonium tetrafluoroborate) with sodium borohydride (Scheme 1). The palladium NPs are well characterized with FTIR, NMR, SEM, TEM, ICP-OES and XPS analysis.[4]

**Scheme 1.** Synthesis of Pd NPs stabilized by Pd-C covalent bonds




This new class of Pd nanoparticles was efficiently used as reusable catalysts for C-C bond forming cross coupling reactions such as Heck, Suzuki–Miyaura and Sonogashira coupling reactions (Scheme 2).

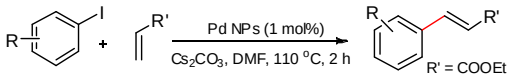
**Scheme 2.** Pd NPs catalyzed cross-coupling reactions




X= I, Br — Yield upto 97%

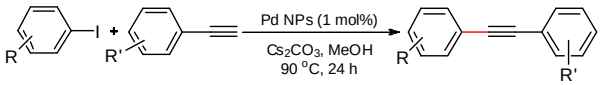
| Substrate | cycles | recovery of Pd NPs | yield (%) |
|---|---|---|---|
| R= $CH_3$; R'= H; X=I | 1 | 95% | 94 |
| | 2 | 93% | 93 |
| | 3 | 90% | 91 |

a) Suzuki-Miyaura cross-coupling reaction




Yield upto 95%

b) Heck cross-coupling reaction

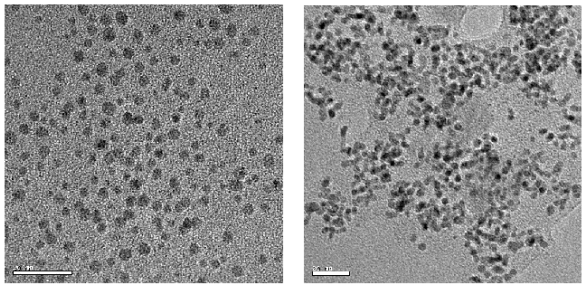



Yield upto 98%

c) Sonogashira cross-coupling reation

The Pd NPs are quantitatively recovered and reused for these reactions. After the catalytic reactions the NPs had same size and reactivity without any apparent agglomerization which was confirmed with SEM, TEM and ICP-OES analysis (Figure 1).

**Figure 1**. HRTEM images of Pd NPs before and after catalytic reactions.



**Before catalytic reaction** 3.33±0.9 nm — **After three catalytic cycle** 3.25±0.85

## CONCLUSION

In conclusion, we have synthesized a new class of stable Pd NPs stabilized by stable Pd-$C_{(binaphthyl)}$ covalent bond and were successfully utilized as recoverable and reusable catalysts for Suzuki, Heck and Sonogashira cross-coupling reactions.

## ACKNOWLEDGEMENTS

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