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Magnetic Nanoparticles Supported Palladium Complex for C-C and C-X Coupling Reactions

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ABSTRACT

The Pd-catalysed cross-coupling of thiols with aromatic electrophiles is an effective strategy for the synthesis of aryl thioethers, which are crucial compounds for pharmaceutical and agricultural activities. Because metal or metal oxide nanoparticles (NPs) have a high surface-to-volume ratio, which results in unique quantum properties, and different shapes and sizes from the corresponding bulk materials, they frequently exhibit high catalytic activity among catalysts or heterogeneous supports. However, the development of a more secure, nontoxic, environmentally benign, and recyclable support is still needed for coupling reactions in heterogeneous conditions in order to prevent the agglomeration of the NPs or the reusability of metallic complexes. Magnetic supports are famous among researchers due to their chemical stability and high specific areas. The use of insoluble, inorganic bases in the majority of C-S coupling protocols makes it difficult to achieve miniaturization and continuous flow applications. First and foremost, the reaction conditions are incompatible with numerous functional groups and therapeutically. First and foremost, the reaction conditions are incompatible with numerous functional groups due to the requirement of high temperatures. The difficulty of substituting nucleophilicity at a sp2 carbon atom using standard organic methods is overcome by using complexes of transition metals. The reported C-C and C-S coupling method exhibits remarkable functional groups tolerance, and the reactions can be carried out in neat water at low ambient temperature. The reaction was carried out in the absence of solvent, an inert atmosphere, and bases.

***Keywords**: C-C Coupling, C-S Coupling, Heterogeneous Support, Magnetic Support.*

Introduction

Effective, useful, and reliable synthetic techniques have been made possible by the ability to investigate and comprehend organometallic transformations through mechanistic analysis.[1]. Specifically, research on carbon-nitrogen (C-N), Carbon-carbon C-C, Carbon-Sulphur (C-S), and carbon-oxygen (C-O) bond-forming processes catalysed by palladium has produced more active catalysts and reliable protocols that have wide applications in industrial and academic settings [2,3]. Palladium (Pd)-catalysts hold a special place among TM catalysts because of the special properties of Pd, such as its moderate atomic size and partially filled d orbitals, which enable it to donate and accept electrons and enhance the stability and catalytic activity of Pd nano catalysts. In addition to C–C coupling reactions like Heck, Suzuki, Sonogashira, Hiyama, Kumada, Stille, and Negishi, the Pd-catalyst is also utilised for C–S, C–N, and C–O coupling reactions, among others. [4,5,6,7]. The development of moderate and universal alkyl aryl ether syntheses has received a lot of attention. Conventional methods, such as Williamson ether synthesis [8], the Nucleophilic aromatic substitution, and the Mitsunobu reaction, frequently offer

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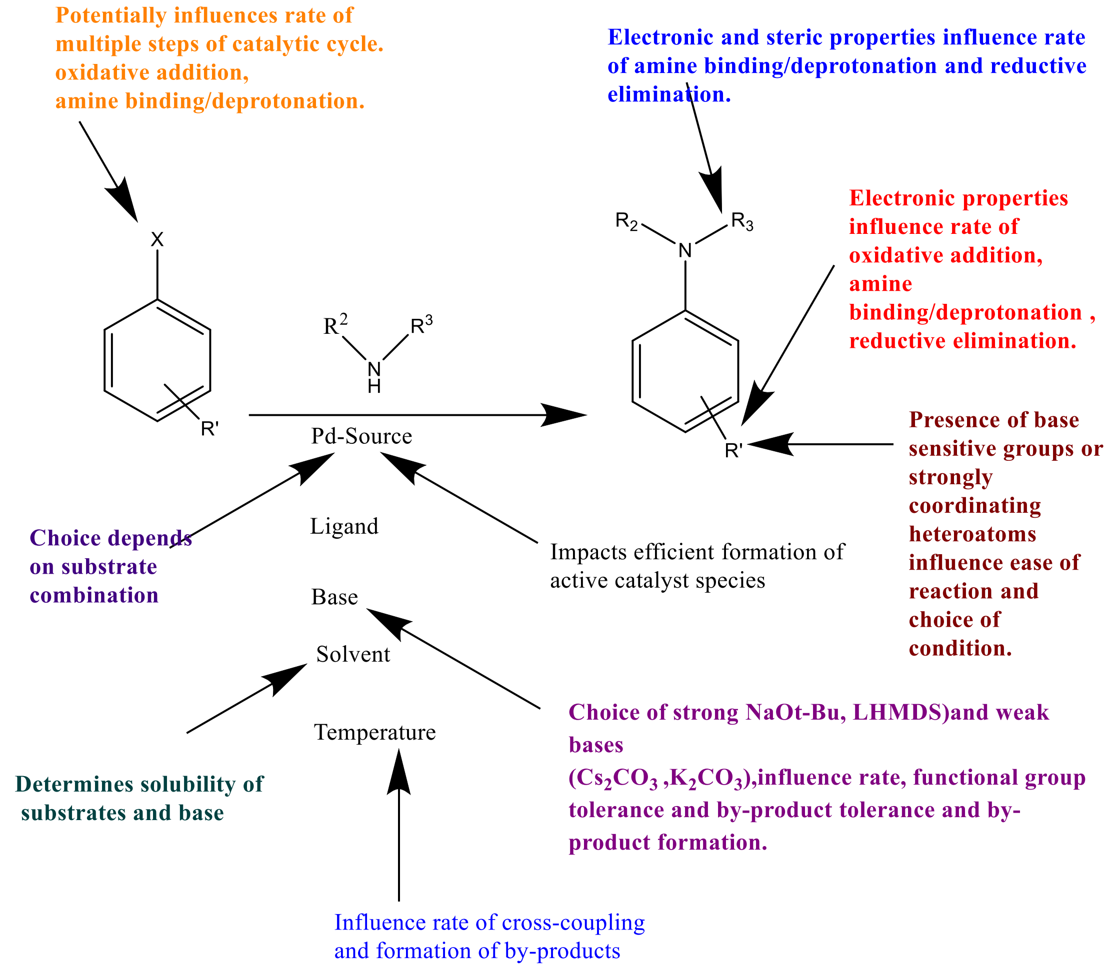
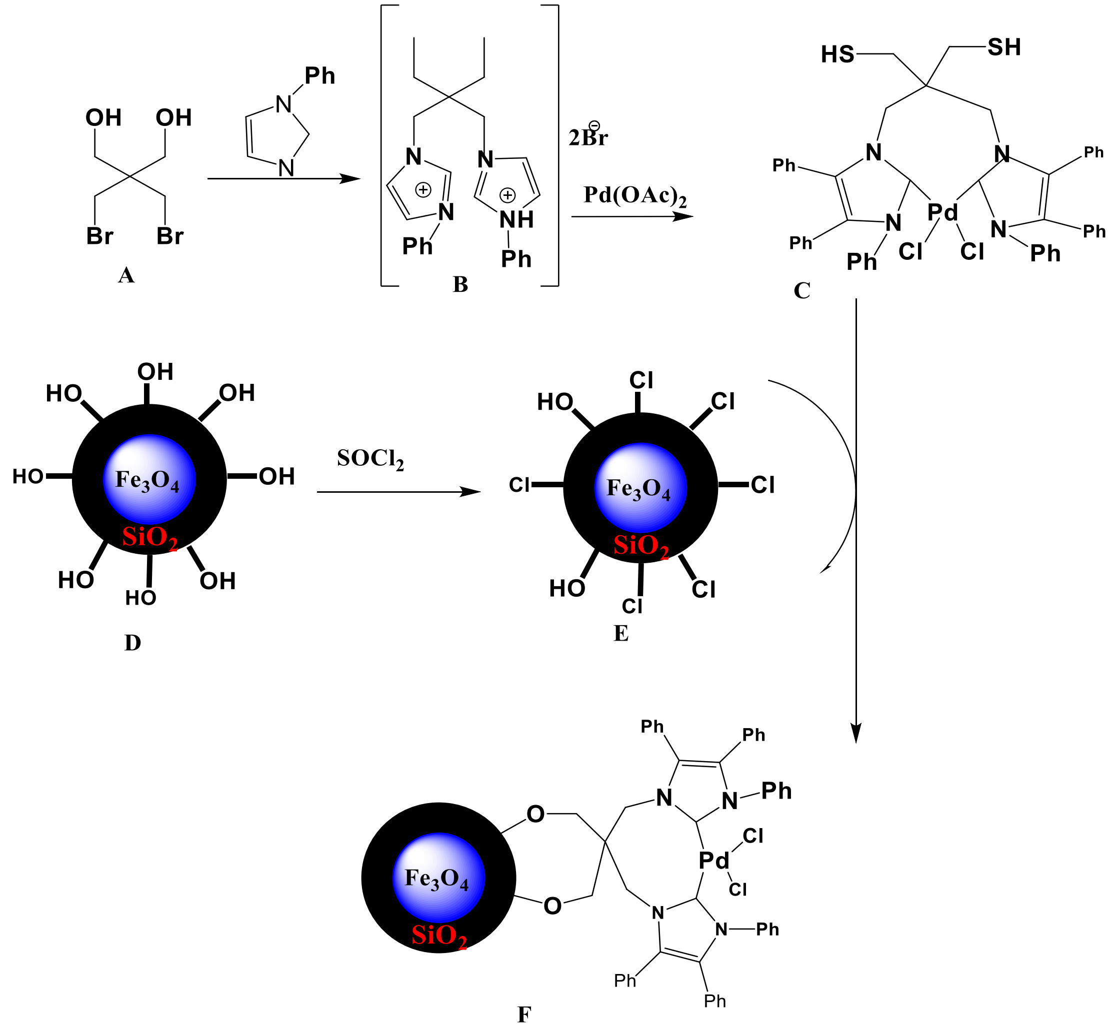
limited substrate scope and functional group compatibilities. To overcome these constraints, transition-metal catalysed [9,10] or metal-free10 reactions have been developed recently. Pd-catalysed O-arylation of aliphatic alcohols, in particular, has drawn a lot of attention from researchers.



Factors influencing the outcomes of Pd-catalysed animation reactions.

Result and Discussion

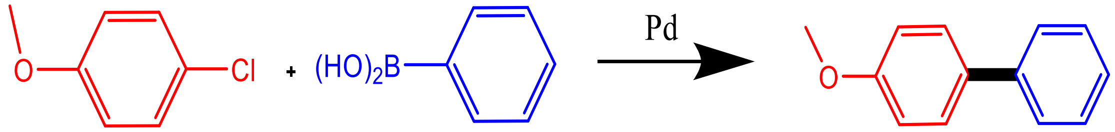
As shown in Scheme 1, the Pd-NHC-MNP catalyst has been synthesized in a four-step process. First, 2,2-bis (bromomethyl)propane-1,3-thiol (A) was reacted with 1-(3-mercapto-2-(mercaptomethyl)-2-((3-phenyl-1H-imidazol-3-ium-1-yl)methyl)propyl)-3-phenyl-1H-3λ^4-imidazol-1-ium. in order to synthesize ionic liquid 1-(3-mercaptomethyl)-2-((3phenyl-1H-imidazol-3-ium-1-yl) methyl)propyl)-3-phenyl-1H-3λ^4 -imidazol-1-ium. The ionic liquid B, in the presence of $PdCl_2$, forms a novel Pd-NHC complex (C). The reaction between chlorinated magnetic nanoparticles (E) and Pd-NHC(C)resulted in the production of a new magnetic reusable Pd-NHC catalyst (F; Pd-NHC-MNP). For the synthesis of (E), the prepared magnetic nanoparticles (D) were treated with thionyl chloride to convert the hydroxy functional groups on the surface of the magnetic nanoparticles to chlorine.



Pd-NHC-MNP

Reaction Parameters for C-C Coupling Reactions

Initially, the Pd catalysts were tested in the Suzuki-Miyaura coupling reaction of 4-chloroanisole with phenylboronic acid to optimise conditions. As shown in Table 1, H_2O was found to be the best solvent, providing 4-methoxybiphenyl in 42% yield (Table 1, entry 1). Other solvents gave lower yields than H_2O (Table 1, entries 2–11). Base optimisation was also performed; K_2CO_3 was a suitable base, although K_3PO_4 was similarly efficient for the Pd-catalysed Suzuki-Miyaura coupling reactions (Table 1, entries 12–16). When the loading of the Pd catalyst was decreased to 0.075 mol% and 0.05 mol%, 4-methoxybiphenyl was obtained in 99% and 85% yield, respectively, with TOF values of 73.3 and 94.4 h−1, respectively (Table 1, entries 17 and18). with phenylboronic acid.



Entry	Base	Solvent	Time(h)	Pd(mol%)	Yield(%)	TOF g (h^{-1})
1	NaOH	i-PrOH/H_2O	10	0.15	42	28.0
2	NaOH	i-PrOH	10	0.15	5	3.4
3	NaOH	H_2O	10	0.15	28	18.7
4	NaOH	Toluene/H_2O	10	0.15	3	2.0
5	NaOH	Toluene	10	0.15	2	1.4
6	NaOH	DMF/H_2O	10	0.15	4	2.7
7	NaOH	DMF	10	0.15	5	3.4
8	NaOH	1,4-Dioxane/H_2O	10	0.15	40	26.7
9	NaOH	1,4-Dioxane	10	0.15	34	22.7
10	NaOH	Acetonitrile/H_2O	10	0.15	14	9.4
11	NaOH	Acetonitrile	10	0.15	8	5.4
12	NaOH	Water	18	0.15	65	24
13	K_2CO_3	Water	18	0.15	100	37.1
14	K_3PO_4	Water	18	0.15	97	35.9
15	Cs_2CO_3	Water	18	0.15	60	22.2
16	Na_2CO_3	Water	18	0.15	72	26.1
17	K_2CO_3	Water	18	0.075	99	73.3
18	K_2CO_3	Water	18	0.05	85	94.4
19	K_2CO_3	Water	18	0.075	88	65.2

Reaction conditions: 4-chloroanisole 1.0mmol;1.0;phenylboronic acid, 1.5mmol;catalyst Pd (Pd content 0.58 wt%, NaOH. (4.0mmol, 160.1mg), solvent volume, 2.0ml 80 °C.

Using the optimised reaction conditions, the application scope of the Pd catalysed Suzuki-Miyaura reactions of aryl chlorides was studied with phenylboronic acids; the results are listed in Table 2. The Pd catalyst showed high efficiency for the Suzuki-Miyaura reaction of aryl chlorides with phenylboronic acids, providing the corresponding products in good to excellent yields with quite low Pd catalyst loading (Table 2, entries 1–12). A range of functional groups were well tolerated under the reaction conditions. Aryl chlorides containing MeCO, CN, Me, MeO and HCO groups were converted to the corresponding biphenyl products in high yields (Table 2, entries 1–9).Additionally, the equivalent biphenyl compounds were produced in high quantities by the Suzuki-Miyaura coupling reactions of chlorobenzene with functional phenyl boric acids (Table 2, entries 10 and 11).

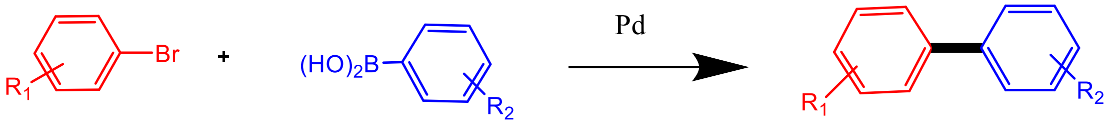
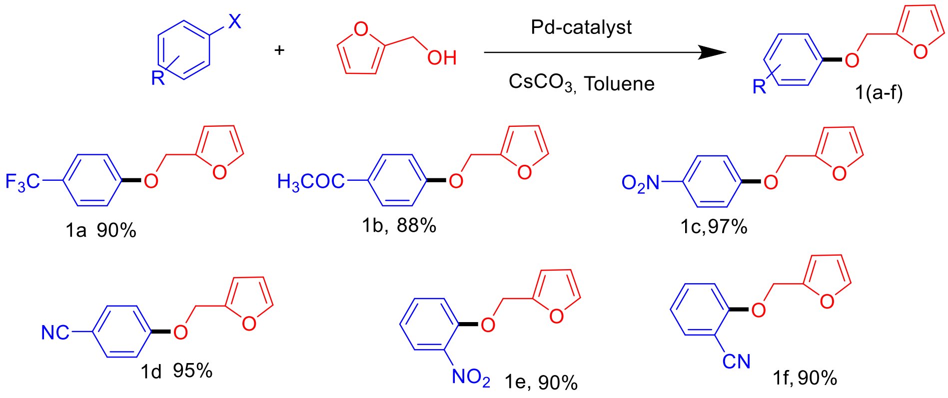


Table 1: Suzuki Miyaura coupling of aryl bromides with phenyl boronic acids

Entry	R_1	R_2	Time(h)	Yield^b(%)
1	4-MeO	H	6	100
2	4-CHO	H	3	78
3	4-MeCO	H	4	70
4	4-NO_2	H	3	80
5	4-Me	H	3	70
6	4-CN	H	3	68
7	2-CN	H	3	65
8	2-NO_2	H	3	60
9	2-Me	H	4	62
10	2-MeO	H	4	60
11	4-tert-Butyl	H	8	58

Reactions conditions:aryl bromide, 1.0mmol ,phenyl boronic acids 1.5mmol; catalyst (13.7mg 0.075 mol% Pd);H_20 (2ml), $K2CO_3$,(2.0mmol, 276.4mg), temperature 80°C



1a 90%

1b, 88%

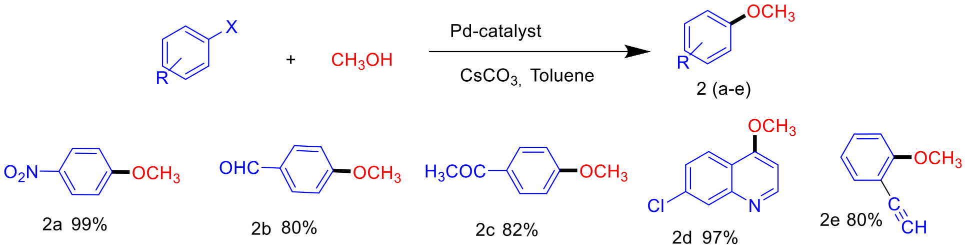
1c,97%

1d 95%

1e, 90%

1f, 90%

Reaction conditions : aryl chloride(1mmol),alcohol (1.2mmol),base(2mmol),25mg of Catalyst (0.15mol% Pd),Solvent (2ml)



2a 99%

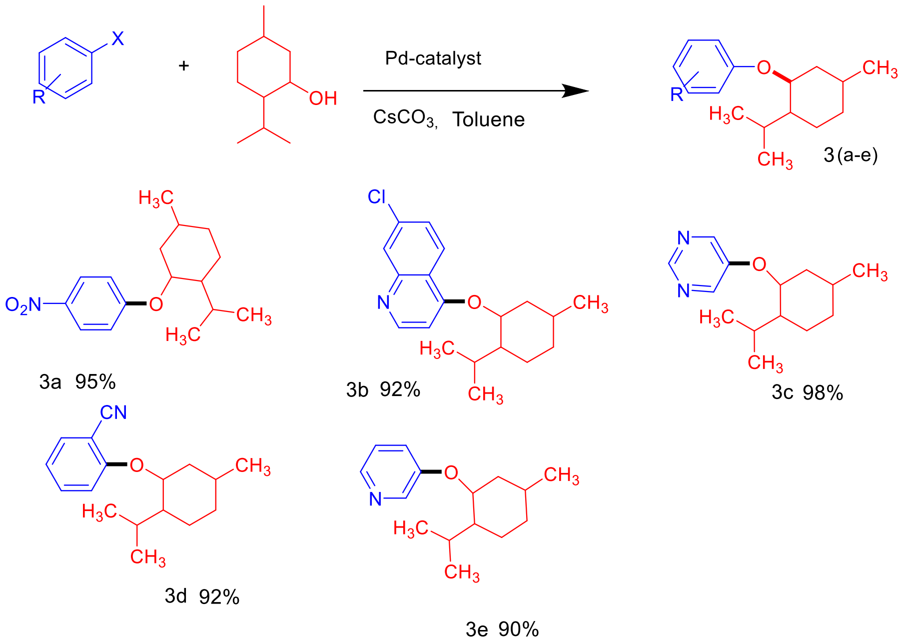
2b 80%

2c 82%

2d 97%

2e 80%

Reaction conditions : aryl chloride(1mmol),alcohol (1.2mmol),base(2mmol),acetylene(0.122g,1,2mmol),25mg of Pd(II)Catalyst (0.15mol% Pd),Solvent (2ml)



3a 95%

3b 92%

3c 98%

3d 92%

3e 90%

Reaction conditions : aryl chloride(1mmol),alcohol (1.2mmol),base(2mmol),25mg of Pd(II) Catalyst (0.15mol% Pd),Solvent (2ml)

Conclusion

In the Suzuki-Miyaura reaction of aryl chlorides and bromides with phenylboronic acids, the Pd catalysts demonstrated remarkable efficiency. Functional groups including CN, MeO, CHO, MeCO, and NO_2 were also well tolerated, and large quantities of the corresponding biphenyls were produced. The Pd catalyst also shows remarkable activity in C-N, C-O, and C-S cross-coupling reactions. At least five reuses of the Pd catalysts were possible without noticeable degradation. We think that this type of catalyst exhibits promise for the industrial and experimental synthesis of biphenyl, ethers, substituted amines, and thioether compounds.

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