

## Chapter 3

# Synthesis and Application of Pd-Graphene Nano-Composite

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### I. INTRODUCTION

Nanoparticles (NPs) display better catalytic competence than bulk metal catalysts, mainly because of their higher surface-to-volume ratio [1-5]. The application of metal nanoparticles (MNPs) in catalysis has driven strong attention in the improvement of nano-catalyst over the earlier epoch [2-8]. In evaluation, with the widespread study of transition metal nanoparticles, particularly palladium (Pd) metal was found as a smart transition metal due to their rare physiochemical properties. In catalysis, palladium metal offers the most favorable combinations of activity and selectivity throughout the reaction [5-15]. Palladium catalyzed C-C bond forming coupling reactions has contributed remarkable impact of synthetic organic chemistry. Various approaches have been made to make palladium catalyst more reactive and recyclable for coupling reactions by using different types of organic/inorganic bases, ligands, solvent systems, different organic/inorganic supports (polymers, ionic liquids, Montmorillonite clay, silica, zeolite etc.) to anchor the palladium catalysts as well as substrates [15-18].

Moreover, new carbon materials have been developed to improve the catalyst utilization and catalytic performance as support. For example, mesoporous carbons, carbon nanotubes (CNTs), nanofibers (CNFs), nanohorns (CNHs), nanocoils (CNCs) and graphene (G) have been studied extensively, due to their unique structural, electronic, adsorption, mechanical and thermal properties [19-24]. CNTs with one-dimensional (1D) structure exhibit superior electronic conductivity and high electrochemical stability. Therefore, CNTs have been exploited as the catalyst support to enhance catalytic activity in fuel cells [24, 25-27].

On the other hand, Graphene is the  $sp^2$  hybridized carbon allotrope, having unique physiochemical properties such as high specific surface area (theoretical value of  $2620 \text{ m}^2 \text{ g}^{-1}$ ), superior electronic conductivity and excellent mechanical strength and elasticity [28-30]. The specific surface area (SSA) of graphene has attracted the great interest of chemical researchers for the development of a new kind of composite materials, especially as a host to carry metal nanoparticles like palladium, gold, platinum, titanium, tin, zinc etc. [29-31]. So, Graphene not only possesses all the advantages of CNTs as catalysts support, for example high electrical conductivity, and SSA, but also avoids the drawback of catalyst particles existing inside the nanotube. Furthermore, the large size of graphene (layer  $>1 \mu\text{m}$ ) can also eliminate the possible health problems caused by CNT pollution. Thus, various groups reported graphene supported metal nanocomposites to catalyze different organic transformations like oxidation, Friedel craft addition, dehydrogenation, hydration, Pechmann condensation, Aza-Michael addition, Knoevenagel condensation, esterification, hydrogenation, coupling reaction etc. in a facile, recyclable and sustainable manner [30-33]. It is well documented that immobilization/stabilization of metal nanoparticles on a carbon substance is most favorable condition for improving their catalytic activity. The presence of functional groups and the high specific surface area of chemically modified graphenes (CMGs) offer the high capability of loading metal nanoparticles (MNPs) on to it, through hydrophobic and electrostatic interactions [30-35]. These CMGs based MNPs also offers stability against air and moisture as well as easy handling during the reaction. In various reports, palladium nanoparticles were immobilized with graphene oxide (GO) or reduced graphene oxide (rGO) and further tested as catalyst for different coupling reactions such as Heck and Suzuki reaction [32-36].

The Suzuki cross-coupling reaction of aryl or vinyl boronic acid with aryl or vinyl halides is one of the important reactions in the area of the chemical science [37-41]. Initially GO immobilized as well as intercalated palladium nanoparticles were investigated for Suzuki-Miyaura coupling reaction in aqueous solution and surprisingly the catalytic system was found highly active in term yield and selectivity [42-43]. In another parallel report, Pd-graphene (Pd/G) hybrids were synthesized by reducing  $\text{Pd}(\text{OAc})_2$  using sodium dodecyl sulphate [44]. These Pd/G catalysts were further tested in aqueous as well as aerobic conditions, to increase the reaction rate of Suzuki reaction. Gao *et al* [45] also synthesized Au/GO nano composites for Suzuki-Miyaura coupling and yielded the corresponding reaction products in high yield. Although, Pd/GO and Pd/rGO found active with respect to other commercially available palladium catalysts (e.g. Pd on

charcoal) but collectively Pd/Go and Pd/rGO suffers with various drawbacks like high catalyst loading, catalyst leaching (*via* agglomeration of Pd metals into the clusters) during the recycling test, limited substrate scope, requirement of polar solvents etc. [42-45].

Various reports and reviews have been published on exploring the application of ionic liquids as a reaction medium for different organic transformations [46-48]. Recently [MTBD][bmsi] ionic liquid immobilized graphene-supported Pt nanoparticles were tested as to study the oxygen reduction reaction. Surprisingly, [MTBD][bmsi] immobilized graphene-supported Pt nanoparticles were found highly active for electro-catalytic reaction in terms of yield and selectivity [49].

In this work, we synthesized the Pd/rGO composite, and tested them as catalyst for phosphine ligand-free Suzuki reaction [bmim] NTf<sub>2</sub> in the ionic liquid reaction medium. We used [bmim] NTf<sub>2</sub> ionic liquid as reaction medium due to its air and moisture stable, easy availability and their higher utility in several organic reactions with respect to other reported ionic liquids. The reaction conditions were studied and optimized.

## II. EXPERIMENTAL SECTION

All the chemicals were purchased from Sigma Aldrich, Acros or Fluka. The Pd-graphene hybrids were characterized by high-resolution transmission electron microscopy (HRTEM) (Philips Tecnai G2 F20) and energy dispersive X-ray spectroscopy (EDX) (Philips Tecnai G2 F20). NMR spectra were recorded on standard Bruker 300WB spectrometer with an Avance console at 300 and 75 MHz for <sup>1</sup>H and <sup>13</sup>C NMR respectively. Mass spectra (EI) were obtained at 70 eV with Shimadzu GCMQP 100 EX spectrometer. The residue was purified by flash chromatography (FC) with hexane/ethyl acetate. 1-butyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide ([bmim] NTf<sub>2</sub>) was synthesized as per reported procedure [50].

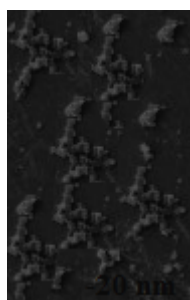
In the typical run for the Suzuki reaction, a reaction tube was charged with aryl/hetroaryl halide (0.5 mmol), aryl boronic acid (1 mmol), Pd/rGO (0.25 mol%) and [bmim]NTf<sub>2</sub> (2 mL) or other solvent system, base (1.5 mmol)/ phosphine ligand (0.05 mmol). The reaction mass was allowed to stir for 60 min at 100°C. Thin layer chromatography was used to monitor the progress of the reaction. Volatile impurities along organic solvent were removed under high vacuum pressure. The reaction product was further extracted with diethyl ether (5x2mL) by vigorous stirring followed by decantation of the upper diethyl ether layer. Evaporation of the combined organic layer and the subsequent medium pressure-FC purification of residue (eluent: AcOEt:*n*-hexane=1:3) offered pure Suzuki reaction product. A new portion of reactants was added to recycle the catalytic system.

## III. RESULTS AND DISCUSSION

Typically, Pd/rGO was prepared by reducing the mixture of Graphene suspension (2.5mg/mL) and palladium nitrate (10 mg) in water where sodium dodecyl sulphate (SDS, 0.1 mol/L) was used as a surfactant as well as reducing agent. Size distribution of Pd nanoparticles was further analyzed by TEM and the mean size of Pd nanoparticles dispersed on the graphene sheets were recorded (4 nm, ±2) (Fig. 1a-b). The presence of Pd nanoparticles on graphene is confirmed by EDX (Fig. 2). The oxygen and sulfur signal appears due the presence of residual dodecanoate and sulfonate groups while due to presence of Copper grid the Copper peaks found in EDX data.



a. Pd/rGO (*before catalysis*)



b. Pd/rGO (*after catalysis*)

Fig. 1 TEM image of Pd/rGO

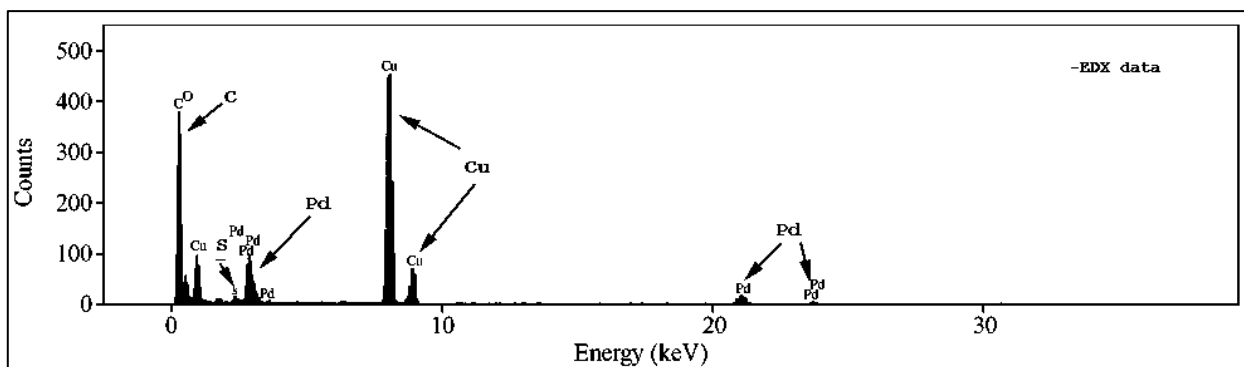


Fig. 2 EDX data for Pd/rGO

The catalyst effect of Pd/rGO on the Suzuki cross-coupling reaction (Fig. 3) between phenyl boronic acid with 4-bromo anisole was studied under different reaction parameters like reaction time, catalyst loading, solvent systems etc. (Table 1 and Fig. 3). The results from Table 1 suggested that the bases have dramatic effects on the yield of cross-coupling product in the ligand free Suzuki reaction. Among the bases, potassium carbonate gave the best result (Table 1, Entry 5). In addition, the profound solvent effect on the reaction was observed and [bmim]NTf<sub>2</sub> was found more effective over other organic solvents for Pd/rGO catalyzed Suzuki reaction.

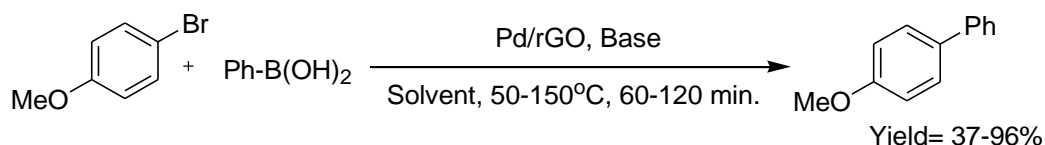


Fig. 3 Suzuki Model reaction for catalyst optimization

As summarized in Table 1 (Entry 1-33), [bmim] NTf<sub>2</sub> mediated Pd/rGO was found highly active in terms of yield and selectivity for Suzuki reaction. After the reaction, the product was easily recovered by simple extraction with diethyl ether followed by decantation of the upper organic layer. No aqueous work-up was required during the reaction.

TABLE 1 CATALYST OPTIMIZATION FOR SUZUKI REACTION

Entry <sup>a</sup>	Catalyst (0.25 mol%)	Solvent <sup>b</sup> (2 L)	Base/Ligands	Temperature (°C)	Reaction Time (Minutes)	Yield <sup>c</sup> (%)
1	Pd/rGO	DMSO	K <sub>2</sub> CO <sub>3</sub>	100	60	52
2	Pd/rGO	DMF	K <sub>2</sub> CO <sub>3</sub>	100	60	50
3	Pd/rGO	THF	K <sub>2</sub> CO <sub>3</sub>	100	60	52
4	Pd/rGO	NMP	K <sub>2</sub> CO <sub>3</sub>	100	60	55
5	Pd/rGO	[bmim]NTf <sub>2</sub>	K <sub>2</sub> CO <sub>3</sub>	100	60	<b>96</b>
6	Pd/rGO	Water:prOH	K <sub>2</sub> CO <sub>3</sub>	100	60	64
7	Pd/rGO	Water:EtOH	K <sub>2</sub> CO <sub>3</sub>	100	60	60
8	Pd/rGO	Water:MeOH	K <sub>2</sub> CO <sub>3</sub>	100	60	63
18	Pd/rGO	[bmim]NTf <sub>2</sub> (3mL)	K <sub>2</sub> CO <sub>3</sub>	100	60	95
19	Pd/rGO	[bmim]NTf <sub>2</sub> (1mL)	K <sub>2</sub> CO <sub>3</sub>	100	60	91
20	Pd/rGO	[bmim]NTf <sub>2</sub>	K <sub>2</sub> CO <sub>3</sub>	50	60	72
21	Pd/rGO	[bmim]NTf <sub>2</sub>	K <sub>2</sub> CO <sub>3</sub>	150	60	96
22	Pd/rGO	[bmim]NTf <sub>2</sub>	K <sub>2</sub> CO <sub>3</sub>	120	60	96
23	Pd/rGO	[bmim]NTf <sub>2</sub> + DMSO	K <sub>2</sub> CO <sub>3</sub>	100	60	95
24	Pd/rGO	[bmim]NTf <sub>2</sub>	K <sub>2</sub> CO <sub>3</sub>	100	30	37
25	Pd/rGO	[bmim]NTf <sub>2</sub>	K <sub>2</sub> CO <sub>3</sub>	100	90	96
26	Pd/rGO	[bmim]NTf <sub>2</sub>	K <sub>2</sub> CO <sub>3</sub>	100	120	95
27	Pd/rGO	[bmim]NTf <sub>2</sub>	Pyridine	100	60	75
28	Pd/rGO	[bmim]NTf <sub>2</sub>	ET <sub>3</sub> N	100	60	70
29	Pd/rGO	[bmim]NTf <sub>2</sub>	Na <sub>2</sub> CO <sub>3</sub>	100	60	78

30	Pd/rGO	[bmim]NTf <sub>2</sub>	K <sub>2</sub> CO <sub>3</sub> :PPh <sub>3</sub>	100	60	85
31	PdCl <sub>2</sub>	[bmim]NTf <sub>2</sub>	K <sub>2</sub> CO <sub>3</sub>	100	60	92
32	Pd(OAc) <sub>2</sub>	[bmim]NTf <sub>2</sub>	K <sub>2</sub> CO <sub>3</sub>	100	60	93
31	Pd/rGO (4 mol%)	[bmim]NTf <sub>2</sub>	K <sub>2</sub> CO <sub>3</sub>	100	60	96
33	Pd/rGO (1 mol%)	[bmim]NTf <sub>2</sub>	K <sub>2</sub> CO <sub>3</sub>	100	60	68

a.) The reaction was carried out with Pd/rGO (0.25 mol%), 4-bromo anisole (0.50 mmol), phenyl boronic acid (1 mmol), base (1.5 mmol), PPh<sub>3</sub> as ligand (0.05 mmol), solvent (2 mL). b.) The water: organic solvent ratio 1:1. c.) Isolated yield after column chromatography.

For the recycling of Pd/rGO/[bmim]NTf<sub>2</sub> catalytic system, no significant loss in yield was found up to 8 runs (Fig. 4 and 5) though the catalyst activity dropped mainly because of agglomeration of Pd nanoparticles. It was confirmed by TEM image of Pd/rGO after catalysis (Fig. 1b).

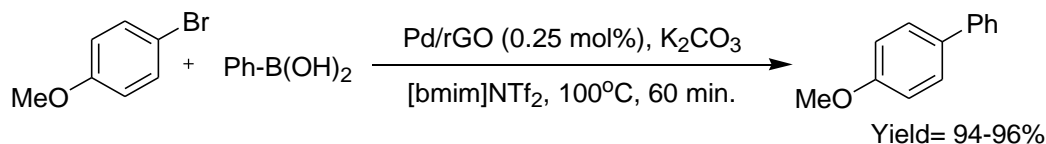


Fig. 4 Catalyst Recycling

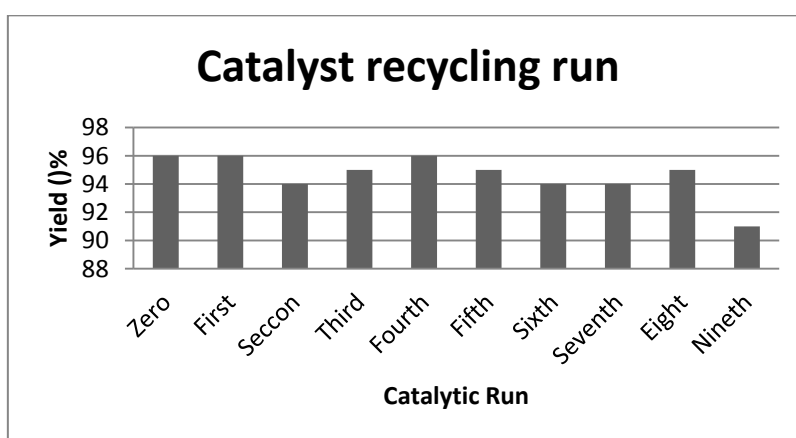


Fig. 5 Recycling Results of Pd/rGO/[bmim]NTf<sub>2</sub> for Suzuki reaction

Under the optimized reaction condition (Pd/rGO as a catalyst, K<sub>2</sub>CO<sub>3</sub> as a base and [bmim] NTf<sub>2</sub> as solvent), a series of aryl/hetero aryl halides with aryl boronic acid were tested, of which the results were summarized in (Table 2, Fig. 6, Entry 1-18). All the substrates enjoyed the proposed protocol, and easily isolated. The Pd/rGO was found efficient to catalyze the coupling of different range of aryl/ hetero aryl halides with a series of aryl boronic acids, in excellent yield, regardless their activating or deactivating substituents and the reactions could be finished in one hour. Electron rich as well as electron -deficient, aryl/ hetero aryl halides coupled efficiently with aryl boronic acids (Table 2, Fig. 6, Entry 1-18). Aryl boronic acids with electron -withdrawing substituted group, which are less nucleophilic and hence, transmetalate more slowly than electron-neutral analogues, are prone to homocoupling and protodeboronation side reactions. The identity of the coupling products was confirmed by <sup>1</sup>H and <sup>13</sup>C NMR, MS spectra [40-45].

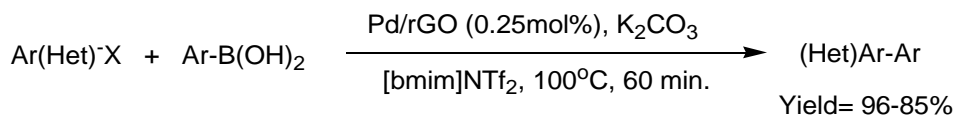
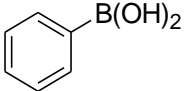
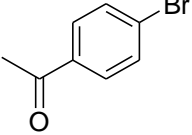
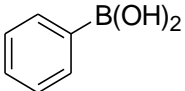
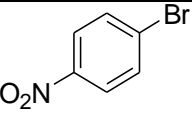
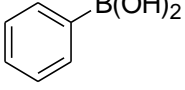
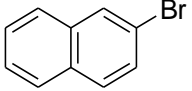
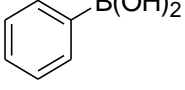
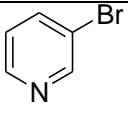
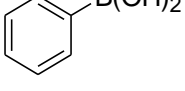
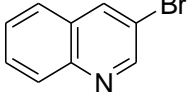
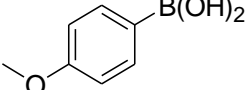
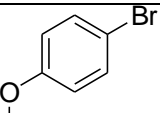
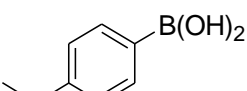
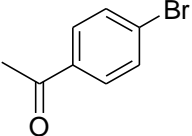
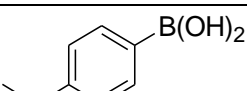
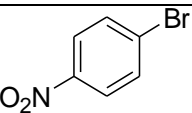
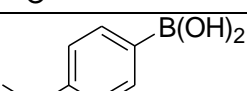
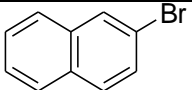
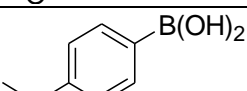
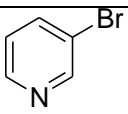
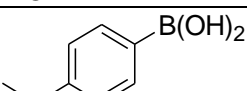
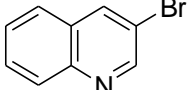
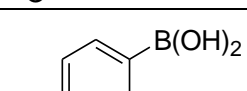
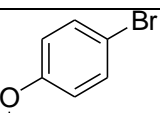
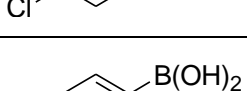
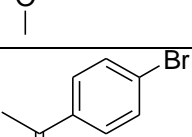
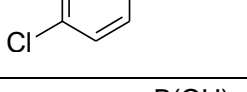
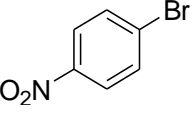


Fig. 6 Application of Pd/rGO catalyst for Suzuki cross-coupling reaction in [bmim]NTf<sub>2</sub>

TABLE 2 Pd/rGO CATALYZED SUZUKI CROSS COUPLING REACTION OF ARYL HALIDES WITH ARYL BORONIC ACIDS IN [BMIM]NTF<sub>2</sub>

Entry <sup>a</sup>	Aryl boronic acid	Aryl Halide	Yield (%) <sup>b</sup>
1			96

2			96
3			90
4			97
5			91
6			89
7			91
8			92
9			94
10			91
11			93
12			90
13			92
14			93
15			91

16			96
17			88
18			85

a.) The reaction was carried out with Pd/rGO (0.25 mol%), Aryl/hetero aryl halide (0.50 mmol), Aryl boronic acid (1 mmol),  $K_2CO_3$  (1.5 mmol), [bmim]NTf<sub>2</sub> (2 mL) at 100°C for 1h. b.) Isolated yields after column chromatography.

Indazole, the indole bioisoster, is a highly applicable intermediate and found in various biologically active compounds such as lonidamine and Akt1 inhibitor [51-53]. Due to a series of applications in terms of biological activity, the syntheses of indazole derivatives as well as the structural modification of the indazole ring system have been recently reviewed by scientific community [39-42]. We applied the Pd/rGO catalysts for the synthesis of novel indazole derivatives followed by Suzuki reaction. We applied the optimized Pd/rGO catalyzed Suzuki reaction condition to couple 5-bromo-1-ethyl-1H-indazole with *N*-Boc-2-pyrroleboronic acid in [bmim]NTf<sub>2</sub> reaction medium and surprisingly, our Pd/rGO catalyst system offered the corresponding reaction product 2-(1-Ethyl-1H-indazol-5-yl)pyrrole-1-carboxylic acid *tert*-butyl ester in good yield (88%) (Table 3, Entry 1). We also synthesized four different indazole derivatives with *N*-Boc-2-pyrroleboronic acid and the corresponding results were summarized in Table 3, Entry 2-5.

TABLE 3 CATALYTIC APPLICATION OF PD/RGO FOR NOVEL SYNTHESIS

Entry	Indazole derivatives	<i>N</i> -Boc-2-pyrroleboronic	Reaction product	Yield <sup>a</sup> (%)
1				88
2				80
3				60
4				55
5				51

a. Isolated yield after column chromatography

#### IV. CONCLUSIONS

It has been found that the carbon nanotubes (CNTs) and graphene oxide (GO) having extended orbital, can interact strongly with substrates and metal NPs, and in this way these carbons supports can influence the catalytic activity by favoring the contact of substrates with the active sites. In addition to this, CNTs and GO offer epitaxial interaction while

maintaining the small average particle size of the metal nanoparticles. These unique factors can apply significant influence on the catalytic activity exposing the most active metal facets and tuning the electronic density of the metal atoms. Particularly, GO materials can have some advantage over CNTs due to the wide availability and their more convenient preparation and modification. In this chapter, we illustrated the potential application of that nanostructured allotropic carbon (Graphene) material as support for paid nanoparticles and tested them as a catalyst for Suzuki cross coupling reaction in ionic liquid medium. Here, the material was suspended indefinitely and the system can work similarly to a homogeneous catalyst with the added advantage of easy recovery after the completion of the reaction. The effects of various reaction parameters, such as solvent, base, time, temperature, were investigated for Suzuki reaction. The optimized protocol was applied to a wide variety of substituted aryl/hetroaryl halides along with various aryl boronic acids and afforded the corresponding products in good to excellent yield. The proposed Pd/rGO catalyzed Suzuki reaction protocol was also extended for the synthesis of novel indazole derivatives. The developed catalytic system circumvents the use of phosphine ligands, with an additional advantage of easy palladium catalyst recovery and its recycling up to eight consecutive runs.

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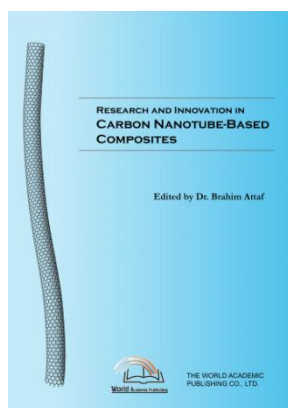
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This book of nanoscience and nanotechnology provides an overview for researchers, academicians and industrials to learn about scientific and technical advances that will shape the future evolution of composite materials reinforced with carbon nanotubes (CNTs). It involves innovation, addresses new solutions and deals with the integration of CNTs in a variety of high performance applications ranging from engineering and chemistry to medicine and biology. The presented chapters will offer readers an open access to global studies of research and innovation, technology transfer and dissemination of results and will respond effectively to challenges related to this complex and constantly growing subject area.

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