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Palladium nanoparticles supported on modified single-walled carbon nanotubes: a heterogeneous and reusable catalyst in the Ullmann-type *N*-arylation of imidazoles and indoles†

Hojat Veisi*[a] and Nekoo Morakabati[b]

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Air- and moisture-stable and recyclable palladium nanoparticles supported on modified single-walled carbon nanotubes (SWCNT-Met/Pd) behave as very efficient heterogeneous catalysts in the Ullmann coupling of imidazoles and indoles with aryl iodides to afford the corresponding C–N coupling reactions under aerobic conditions. These cross coupled products were produced in excellent yields at low palladium loading (∼0.2 mol%) and the heterogeneous catalyst can be readily recovered by simple filtration and reused five times without a noticeable loss in its catalytic activity.

Introduction

The formation of aryl-nitrogen bonds *via* cross-coupling reactions represents a powerful technique for the preparation of various compounds (*e.g.*, arylpyrroles, arylpyrazoles, arylimidazoles, aryltriazoles, arylindoles, arylcarbazoles, *etc.*) that are of biological, biochemical, pharmaceutical and materials interest.[1–3] Traditionally, these compounds have been synthesized *via* nucleophilic aromatic substitution of N–H containing π-electron-rich nitrogen heterocycles with electron-deficient aryl halides, which limits its scope,[4] or by coupling with organometallic reagents. They have also been prepared by the classical Ullmann-type coupling with aryl halides, which sometimes suffers from limitations such as high reaction temperatures (often 150 °C or as high as 200 °C), the use of stoichiometric amounts of copper reagents, insolubility of copper(I) salts in organic solvents, moderate yields, sensitivity of the substituted aryl halide to the harsh reaction conditions, and poor substrate generality. Therefore a mild, economic, and efficient catalytic system is still desirable for this process.

Today, catalysts play a significant role in the production of chemicals and nanomaterials have the potential for improving efficiency, selectivity, and yield of the catalytic process. The higher surface to volume ratio means that much more catalyst actively participates in the reaction. The potential for cost saving is tremendous from a material, equipment, labour, and time standpoint. Higher selectivity means less waste and fewer impurities, which could lead to safer and reduced environmental impact. The study of application of metal nanoparticles in catalysis, particularly, on organic transformations, has become a frontier area of research in nanocatalysis.[5] Among the different metal nanocatalysts, immobilized Pd(II) complexes have gained a notable reputation, because palladium is a versatile catalyst in modern organic synthesis and is widely used for a significant number of synthetic transformations[6] such as, Heck, Suzuki, Stille, Sonogashira cross coupling reactions and *N*-arylation of heterocycles.[7–17]

Studies on the isolation, characterization and catalytic activities of functionalized carbon nanotubes (CNTs) have received particular attention during the last decade owing to their specific catalytic applications compared to homogeneous complexes. Metal nanoparticles as well as various transition metal complexes such as polymers and porphyrins have been used for carbon nanotubes' functionalization.[18–20] Schiff bases, which are an important class of ligands with extensive applications in different fields,[21] also showed excellent catalytic activity when grafted onto CNTs.[22–24]

We have already reported the preparation of a Pd catalyst supported on biguanide(metformin)-functionalized single-walled carbon nanotubes (SWCNT-Met/Pd) and its catalytic application in the Suzuki–Miyaura coupling reactions.[25] In order to further establish other heterogeneous palladium-catalyzed C–N cross-coupling reactions using our catalyst, we herein report the application of this catalyst in Ullmann coupling of imidazoles and indoles with aryl iodides under aerobic conditions (Scheme 1).

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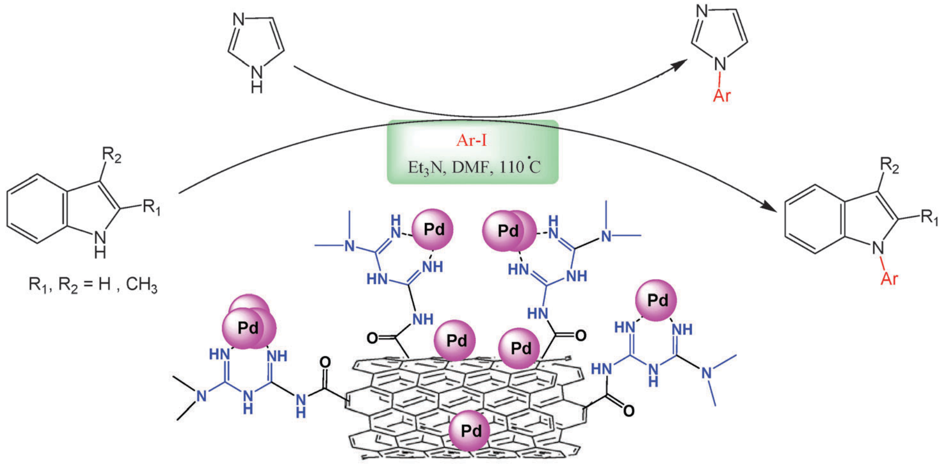
[a] *Department of Chemistry, Payame Noor University (PNU), Tehran, Iran. E-mail: hojatveisi@yahoo.com; Fax: +98 833 8380709*
[b] *Department of Chemistry, Tonekabon branch, Islamic Azad University, Tonekabon, Iran*

† Electronic supplementary information (ESI) available. See DOI: 10.1039/c4nj02108h



Scheme 1 SWCNT-Met/Pd catalyzed *N*-arylation of indoles and imidazoles.

Results and discussion

First of all, after successful fabrication of the catalyst,[25] we have investigated again the surface morphology by FESEM, EDS and TEM images (Fig. 1 and 2). FESEM and EDS images of the SWCNT-Met/Pd (Fig. 1) show that the attachment of organic components to the SWCNT materials has no distinct influence on the morphology of composition and also indicated that metformin and Pd were present in the catalyst. The concentration of palladium in SWCNT-Met/Pd was 19 wt%, which was determined by ICP-AES.

Transmission electron microscopy (TEM) investigations are carried out to observe the morphology and distribution of palladium nanoparticles supported on SWCNTs after their reduction with hydrazine (Fig. 2). It can be seen that although Pd-NPs are distributed on SWCNTs, they do not aggregate with each other because the imine groups of metformin effectively isolate adjacent Pd-NPs. The average size of Pd-NPs is ~10 nm.

In our initial screening experiments, the *N*-arylation reaction of indoles with iodobenzene was investigated to optimize the reaction conditions including Pd concentration, solvent, bases and temperature without protection by an inert gas, and the results are summarized in Table 1.

Initially, various solvents such as DMF, EtOH, CH_3CN, toluene, CH_2Cl_2, DMSO and H_2O were studied in the presence of 0.3 mol% Pd catalyst and 2 equiv. of Et_3N at 110 °C (Table 1, entries 1–7). As could be seen in Table 1, the best result was obtained in DMF (Table 1, entry 7). Next, the bases, including Et_3N, KOH, K_3PO_4, Na_2CO_3, $NaHCO_3$ and K_2CO_3 were explored, and Et_3N gave the best yields (Table 1, entries 1 and 12–16). However, a low yield was obtained without any base (Table 1, entry 10). It was also found that the reaction temperature has a great influence on this transformation (Table 1, entries 9, 17, and 18). The obvious improvement in the conversion (98%) was achieved for the reaction at 110 °C (Table 1, entry 9).

In addition, when the loading of Pd was reduced from 0.3 mol% to 0.2 mol%, an excellent yield was also afforded. However, when 0.1 mol% of Pd was employed, the reaction yield decreased to 60% (Table 1, entries 7–9). It is important to mention that *N*-arylation of indoles did not take place in the

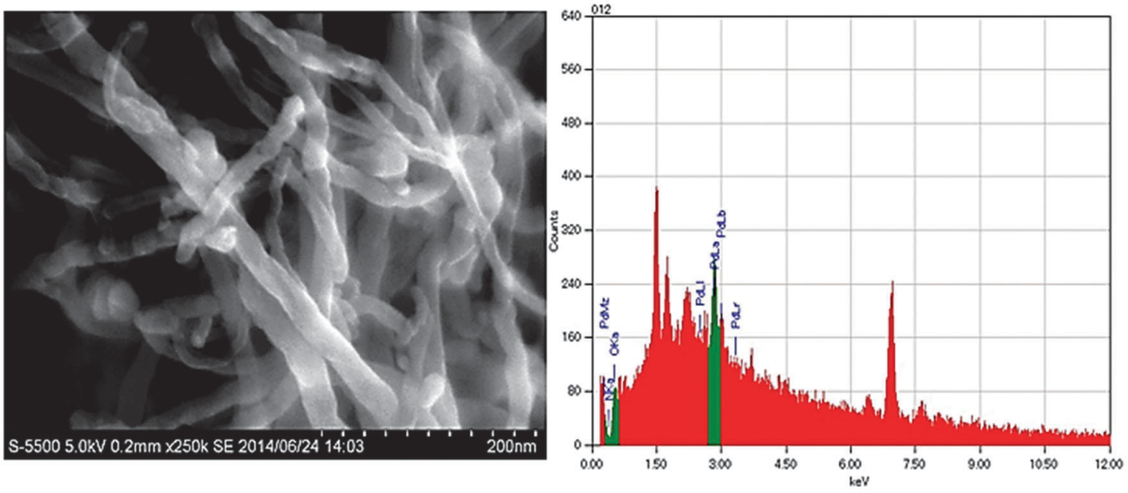


Fig. 1 FESEM and EDS images of SWCNT-Met/Pd.

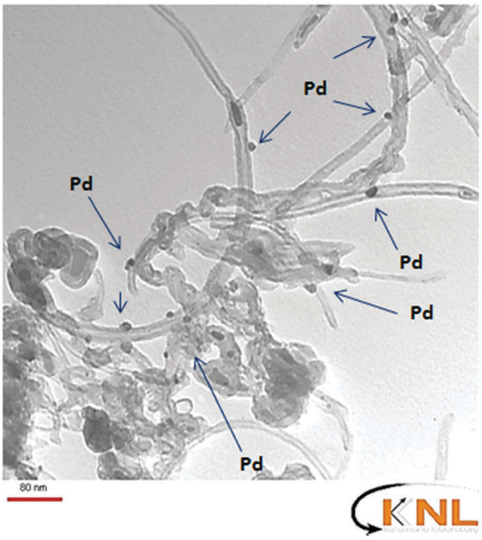


Fig. 2 TEM image of SWCNT-Met/Pd.

Table 1 Optimization of reaction conditions for the *N*-arylation of indoles with iodobenzene[a]

Entry	Pd (mol%)	Base	Solvent	*T* (°C)	*t* (h)	Yield[b] (%)
1	0.3	Et_3N	CH_3CN	82	10	50
2	0.3	Et_3N	EtOH	78	10	45
3	0.3	Et_3N	Toluene	110	10	75
4	0.3	Et_3N	H_2O	100	10	30
5	0.3	Et_3N	CH_2Cl_2	40	10	35
6	0.3	Et_3N	DMSO	110	10	90
7	0.3	Et_3N	DMF	110	6	95
8	0.1	Et_3N	DMF	110	10	60
9	0.2	Et_3N	DMF	110	6	98
10	0.2	—	DMF	110	24	Trace
11	0.0	Et_3N	DMF	110	24	0
12	0.2	K_2CO_3	DMF	110	10	75
13	0.2	Na_2CO_3	DMF	110	10	50
14	0.2	K_3PO_4	DMF	110	10	55
15	0.2	KOH	DMF	110	10	75
16	0.2	$NaHCO_3$	DMF	110	10	55
17	0.2	Et_3N	DMF	25	10	Trace
18	0.2	Et_3N	DMF	70	10	45

[a] Reaction conditions: indole (1.0 mmol), iodobenzene (1.1 mmol), Pd catalyst, base (2.0 mmol), solvent (5.0 mL). [b] Isolated yield.

absence of a Pd catalyst (Table 1, entry 11). In summary, the optimal conditions for the *N*-arylation of indoles with iodobenzene were 0.2 mol% of Pd catalyst and 2 equiv. of Et_3N in DMF at 110 °C for 6 h (Table 1, entry 9).

With these optimum reaction conditions in hand, the scope and generality of the *N*-arylation method were investigated by the variations of aryl iodides and indoles with different substituents and the results are summarized in Table 2.

We examined the reaction of indoles with substituted aryl iodides (Table 3, entries 1–14). All the substituted aryl iodides reacted with indoles to afford the coupling products in good to high yield. We did not observe any limitation as for aryl iodide derivatives. The reactivity of 2-methylindole was slightly lower than that of indoles and 3-methyl-indole due to the steric effect (Table 2, entries 1, 10, and 12).

Table 2 Synthesis of *N*-aryl-indoles catalyzed by SWCNT-Met/Pd[a]

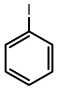
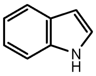
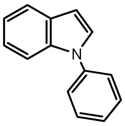
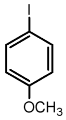
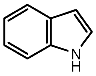
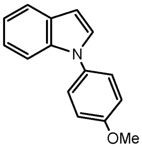
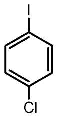
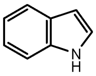
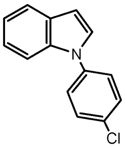
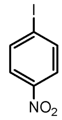
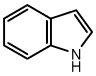
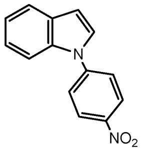
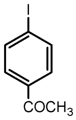
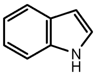
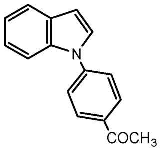
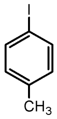
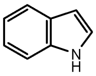
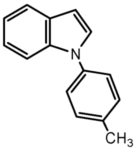
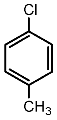
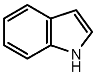
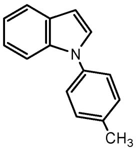
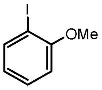
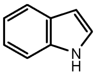
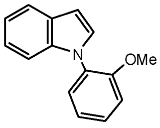
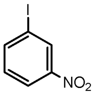
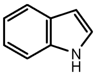
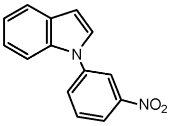
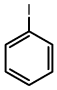
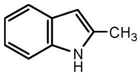
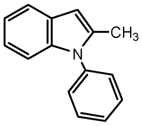
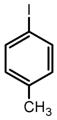
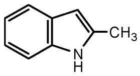
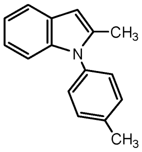
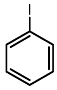
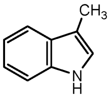
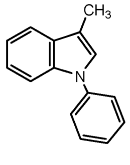
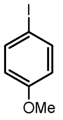
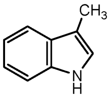
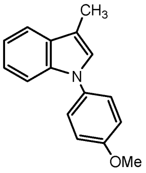
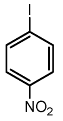
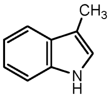
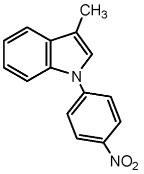
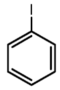
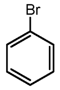
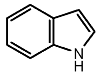
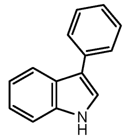
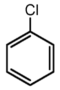
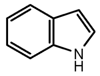
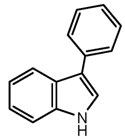
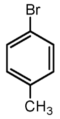
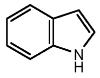
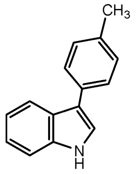
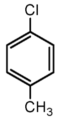
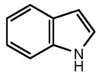
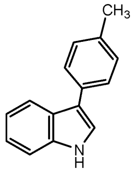
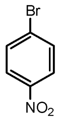
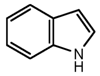
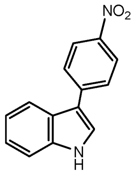
Entry	Aryl halide	Indole	Product	Yield[b] (%)	Ref.
1				98	26*a*
2				98	26*a*
3				96	26*a*
4				95	26*a*
5				90	26*a*
6				95	26*a*
7				60	26*a*
8				90	26*a*
9				85	26*c*
10				90	26*b*
11				92	27

Table 2 (*continued*)

Entry	Aryl halide	Indole	Product	Yield[b] (%)	Ref.
12				98	26*a*
13				95	26*a*
14				90	26*a*
15			No reaction	0	—

[a] Reactions were carried out under aerobic conditions in 5 mL of DMF, 1.1 mmol aryliodides, 1.0 mmol indoles and 2 mmol Et_3N in the presence of a Pd catalyst (0.020 g, 0.2 mol% Pd) and 110 °C for 6 h. [b] Isolated yield.

Table 3 Palladium-catalyzed *C*3 arylation of indoles[a]

Entry	Aryl halide	Indole	Product	Yield[b] (%)	Ref.
1				90	28
2				70	28
3				82	28
4				65	28
5				75	28

[a] Reactions were carried out under aerobic conditions in 5 mL of DMF, 1.1 mmol arylhalide, 1.0 mmol indoles and 3 mmol K_2CO_3 in the presence of a Pd catalyst (0.020 g, 0.2 mol% Pd) and 110 °C for 10 h. [b] Isolated yield.

To ensure that no *C*-arylation took place in the reaction, the reaction was carried out with 1-methyl indole and it was found that there was no product formed (Table 2, entry 17). This shows the high selectivity of SWCNT-Met/Pd as a catalyst in the *N*-arylation of indoles using aryl iodides.

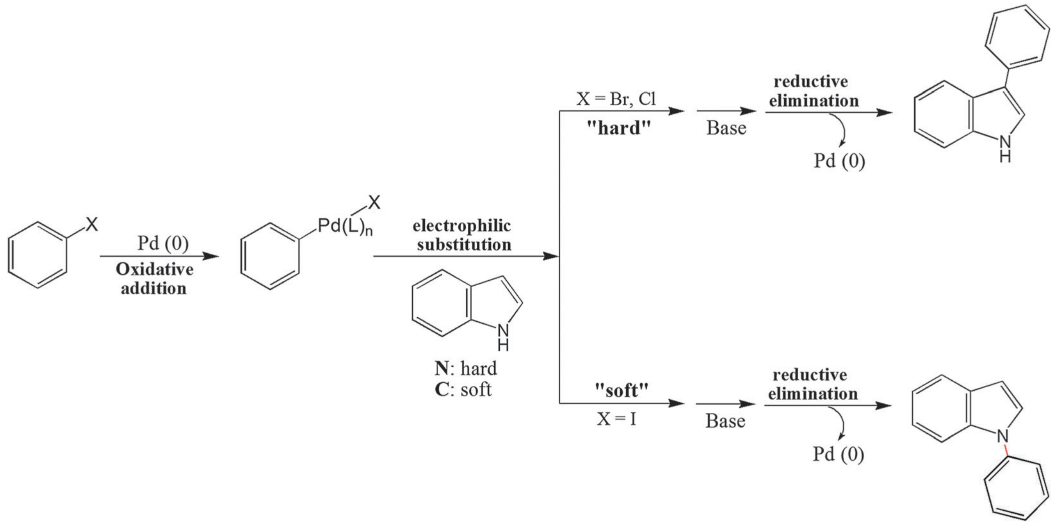
Interestingly, less reactive aryl halides such as bromobenzenes and chlorobenzenes also couple with indoles furnishing *C*3-aryl indole in good to appreciable yields at longer reaction times (Table 3).

The results indicate that the selectivity of the reaction is mainly controlled by the "*electronic character*" of the Pd(II)-intermediate.[29] Using an aryl bromide or aryl chloride under the same conditions would generate an electron deficient Pd(II)-species ("*hard electrophile*") more able to perform *C*3-arylation, while using aryl iodide would generate electron rich Pd(II)-species ("*soft electrophile*") due to orbital overlapping between the Pd(II)-centre and the iodide ligand, species involved in the *N*1-arylation (Scheme 2).

We were pleased to find that the arylation reactions also proceed with imidazoles in good yields under the same conditions (Table 4, entries 1–9). We found that aryl iodides containing electron-donating groups as well as those with electron-withdrawing groups reacted with imidazoles to give the corresponding *N*-arylated imidazoles.

To probe the leaching of the catalyst, a hot filtration test was performed. The reaction between indoles and iodobenzene was stopped after 2 hours (40% yields) and the resin filtered off while the solution was still hot. The filtrate was heated further and the reaction mixture was analyzed by GC after 4 hours. The results indicated that the reaction stops after the catalyst is filtered off. Additionally the reaction mixture was extracted with ether and the aqueous layer was analyzed for palladium by ICP-AAS. The total palladium concentration was found to be 150 ± 10 ppb. The negative results of the hot filtration test indicate that the leaching of palladium is negligible and most probably the reaction is heterogeneous in nature. Based on these results, it appears that the reaction studied has the same mechanism as that reported in other Pd-catalyzed *N*-arylations (Scheme 3).[32] According to the general mechanism depicted in Scheme 3, the reaction of Het-NH with the oxidative addition product **I** in the presence of base leads to a novel **II** complex. When the latter complex undergoes a reductive elimination, the coupled product *N*-aryl-Het is produced, and the catalyst is released to complete the catalytic cycle.

Another important point concerning heterogeneous catalysis is the deactivation and recyclability of the catalyst. In order to investigate this, a series of 5 consecutive runs of the coupling between indoles and iodobenzene (*N*-arylation) in the presence of SWCNT-Met/Pd was carried out (Fig. 3). These results demonstrate that nanocatalysts could be reused five times without a noticeable loss of their catalytic activity. The stability and good



Scheme 2 Selectivity study for *N*1-/*C*3-arylation of indoles in the presence of various aryl halides.

reusability of the catalyst should result from the chelating action of bidentate metformin groups on palladium and the mesoporous structure of the SWCNT support.

The XPS spectroscopic analysis of the heterogeneous catalyst is a quantitative technique to indicate the electron properties of the species immobilized on the surface, such as the oxidation state, the electron environment and the binding of the core electron (E binding) of the metal. Fig. 4 displays the Pd binding energy of SWCNT-Met/Pd. The study of the SWCNT-Met/Pd at the Pd 3p level shows peaks at 531.4 and 553.7 eV for Pd $3p_{3/2}$, which clearly indicates that the Pd nanoparticles are stable as metallic states in the nanocomposite structure. In comparison to the standard binding energy of Pd^0, with Pd $3p_{3/2}$ of about 532.4 eV and Pd $3p_{1/2}$ of about 560.2 eV, it can be concluded that the Pd peaks for SWCNT-Met/Pd shifted to lower binding energy than Pd^0 standard binding energy. The previous studies[33,34] indicated that the position of the Pd 3p peak is usually influenced by the local chemical/physical environment around Pd species besides the formal oxidation state, and shifts to lower binding energy when the charge density around it increases. Therefore, the peaks at 553.7 and 531.4 could be due to Pd^0 species bound directly to metformin groups in SWCNT-Met/Pd.

Conclusion

In conclusion, we have applied palladium nanoparticles supported on modified single-walled carbon nanotubes (SWCNT-Met/Pd) as very efficient heterogeneous catalysts in the Ullmann coupling of imidazoles and indoles with aryl iodides to afford the corresponding C–N coupling reactions under aerobic conditions. The corresponding *N*-arylindoles and *N*-arylimidazoles were obtained in good yields and were applicable to various indoles, imidazoles and a variety of aryl iodides. Less reactive aryl halides such as bromobenzenes and chlorobenzenes also couple with indoles furnishing *C*3-aryl indoles in good yields in the presence of the catalyst. Moreover, the catalyst could be reused for four consecutive cycles without a noticeable loss of its catalytic activity. The stability of the palladium nanoparticles on the support was studied by XPS and ICP-AAS analysis and also using the hot filtration test. These advantages make the process highly valuable from the synthetic and environmental points of view. Further efforts to extend the application of this system in other reactions are currently in progress in our laboratory.

Experimental

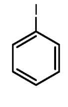
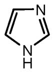
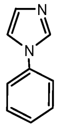
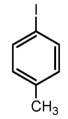
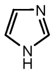
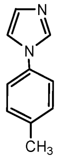
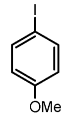
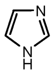
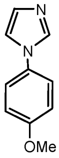
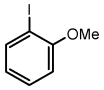
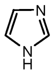
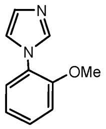
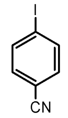
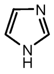
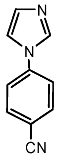
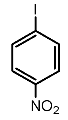
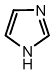
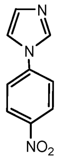
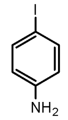
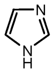
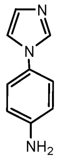
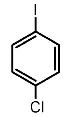
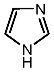
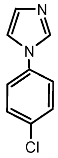
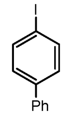
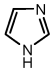
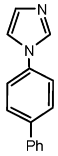
N-Arylation of indoles and imidazoles in the presence of SWCNT-Met/Pd under mild conditions

In a typical reaction, 20 mg of the catalyst (20 mg catalyst = 0.002 mmol Pd, 0.2 mol%) was placed in a 25 mL round-bottom flask, 1.1 mmol of the aryl iodides in 3 mL of DMF was added to 1 mmol of indoles or imidazoles and 2 mmol of Et_3N. The mixture was then refluxed for an appropriate amount of time at 110 °C (see Tables 2 and 4). After completion of reaction monitored by TLC (hexane/acetone, 4 : 1), the reaction mixture was cooled to room temperature (the catalyst was recovered using a centrifuge) and was extracted with diethyl ether three times (3 × 10 mL). The combined organic layers were washed with brine solution and dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The crude product was purified by column chromatography on silica gels (60–120 mesh) to provide the *N*-aryl indoles and *N*-aryl imidazoles.

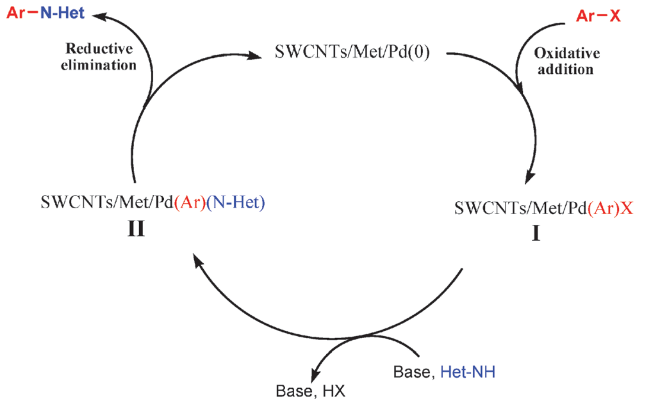
*C*3-Arylation of indoles in the presence of SWCNT-Met/Pd under mild conditions.

In a typical reaction, 20 mg of the catalyst (20 mg catalyst = 0.002 mmol Pd, 0.2 mol%) was placed in a 25 mL round-bottom flask, and 1.1 mmol of the arylbromides or arylchlorides in 3 mL of DMF was added to 1 mmol of indoles and 3 mmol of K_2CO_3. The mixture was then refluxed for 10 hours at 110 °C

Table 4 SWCNT-Met/Pd-catalyzed *N*-arylation of imidazoles with aryl iodides[a]

Entry	Aryl iodides	Imidazole	Product	Yield[b] (%)	Ref.
1				96	30
2				98	31
3				96	30
4				85	31
5				92	30
6				96	31
7				90	30
8				96	31
9				85	31

[a] Reactions were carried out under aerobic conditions in 3 mL of DMF, 1.1 mmol aryliodide, 1.0 mmol imidazole and 2 mmol Et_3N in the presence of a Pd catalyst (0.020 g, 0.2 mol% Pd) and 110 °C for 10 h. [b] Isolated yield.



Scheme 3 Plausible mechanism for the *N*-arylation.

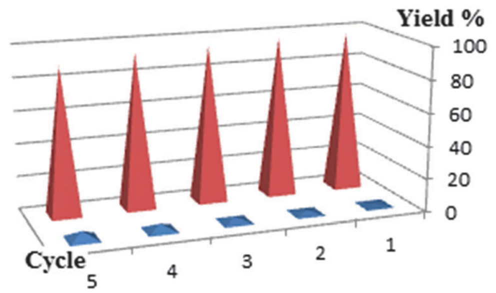


Fig. 3 Reusability of the SWCNT-Met/Pd catalyst for the *N*-arylation of indoles under similar conditions.

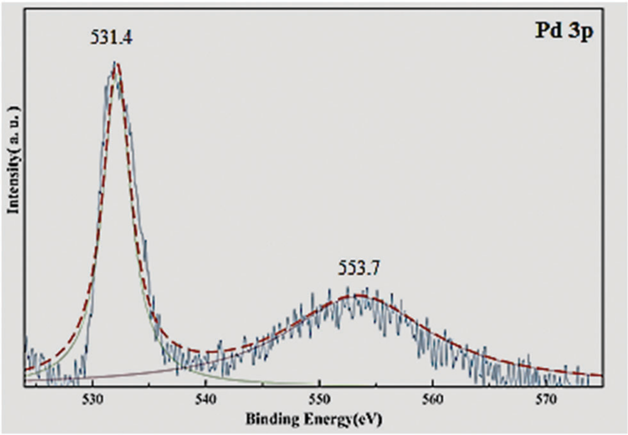


Fig. 4 XPS spectra of SWCNT-Met/Pd.

(see Table 3). After completion of reaction monitored by TLC (hexane/acetone, 5 : 1), the reaction mixture was cooled to room temperature (the catalyst was recovered using a centrifuge) and was extracted with ethyl acetate three times (3 × 10 mL). The combined organic layers were washed with brine solution and dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The crude product was purified by column chromatography on silica gels (60–120 mesh) to provide the *C*3-aryl indoles.

Analytical data for selected products

***N*-Phenylindole (Table 2, entry 1).** Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.71 (d, J = 3.0 Hz, 1H), 7.20 (t, J = 8.0 Hz, 1H), 7.23 (t, *J* = 8.0 Hz, 1H), 7.32–7.40 (m, 2H), 7.50–7.56 (m, 4H), 7.60 (d, *J* = 8.0 Hz, 1H), 7.70 (d, *J* = 8.0 Hz, 1H).

***N*-Phenylimidazole (Table 3, entry 1).** Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.28 (s, 1H), 7.76 (t, 1H), 7.67 (q, *J* = 5.8 Hz, 2H), 7.53 (t, 2H), 7.37 (t, 1H), 7.14 (s, 1H).

Acknowledgements

We are thankful to Payame Noor University (PNU) for financial support.

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