

# Multi-walled carbon nanotubes functionalized with a palladium(II)-Schiff base complex: A recyclable and heterogeneous catalyst for the copper-, phosphorous- and solvent-free synthesis of ynones

Mozhgan Navidi, Barahman Movassagh\* and Saeed Rayati\*

Department of Chemistry, K.N. Toosi University of Technology, P.O. Box 16315-1618, Tehran, Iran  
Fax: (+98)-21-2285-3650; Phone: (+98)-21-88025459; e-mail: [bmovass1178@yahoo.com](mailto:bmovass1178@yahoo.com), [rayati@kntu.ac.ir](mailto:rayati@kntu.ac.ir)

## Abstract:

The Multi-walled carbon nanotubes (MWCNTs) palladium(II)-Schiff base complex was efficiently catalyzed the coupling reactions of acid chlorides with terminal alkynes under copper-, phosphorous- and solvent-free conditions in air. This moisture and air stable heterogeneous catalyst could be simply recovered and used in four successive runs.

## Keywords:

Ynones; MWCNTs-Pd(II)-Schiff base; C-C Coupling; Terminal alkynes; Acyl chlorides.

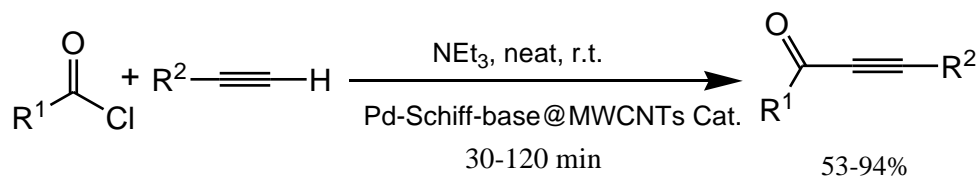
## 1. Introduction

Studies on the isolation, characterization and catalytic activity of functionalized carbon nanotubes (CNTs) received particular attention during the last decade because of their specific catalytic applications compared to homogeneous complexes. Metal nanoparticles as well as various transition metal complexes such as polymers and porphyrins were used for carbon nanotubes' functionalization [1-3]. Schiff bases, which are an important class of ligands with extensive applications in different fields [4], also showed excellent catalytic activity when grafted on CNTs [5, 6].

In recent years,  $\alpha,\beta$ -acetylenic ketones (ynones) have received considerable synthetic interest owing to their occurrence in a wide variety of bioactive molecules and natural products [7]. Moreover, they have been extensively utilized as synthetic intermediates for the synthesis of important biologically active heterocyclic compounds [8-11].

Various protocols have been reported for the synthesis of ynones which include: (a) oxidation of alkynes [12-14], (b) oxidation of propargylic alcohols [15], which are usually obtained by nucleophilic addition of acetylides to aldehydes, (c) reaction of terminal alkynes with nitriles [16], (d) cross-coupling reaction of terminal alkynes with organic halides in the presence of carbon-monoxide gas [17-19], and (e) the reaction between terminal alkynes and carboxylic acid derivatives such as acid chlorides, acid anhydrides, esters, and acyl cyanides [20]. Strong bases such as *n*-BuLi [21, 22] and elements such as silver [23], silicon [24], zinc [25], gallium [26], tin [27], lithium [28], indium [29], boron [30], palladium [31] and copper [32] could be used in these reactions. However, the above synthetic methods suffer from

serious disadvantages namely high temperatures [33, 34], long reaction times [35], use of air and moisture sensitive catalysts such as phosphorous containing catalysts [36-39], use of copper catalysts which are very much prone to form diyne side products, use of hazardous organic solvents [40], use of toxic carbon-monoxide gas and need of special instruments [41]. Taking these constraints into account, the development of new, mild, simple and efficient copper- and phosphorous-free synthetic procedures would have significant value. In this paper, MWCNTs-Pd-Schiff base complex was used as a reusable and heterogeneous catalyst for the synthesis of  $\alpha,\beta$ -acetylenic ketones under aerobic conditions (Scheme 1).

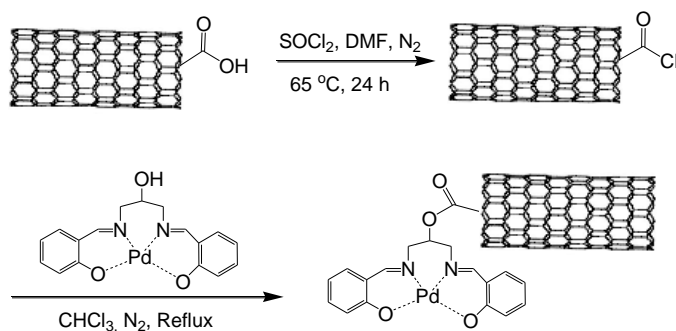


**Scheme 1.**

## 2. Results and discussion

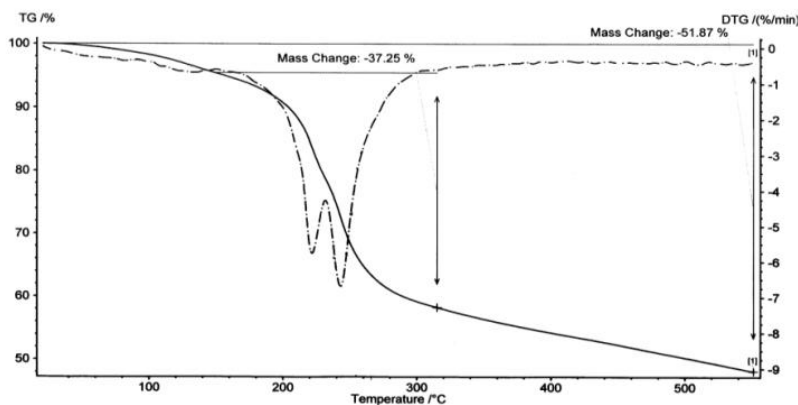
### 2.1 Synthesis and characterization of MWCNTs-Pd-Schiff base catalyst

Carboxylic acid multi-walled carbon nanotubes (CO<sub>2</sub>H-MWCNTs) used in this study was purchased from Times company (China) with outer diameters ranging from 10-20 nm, internal diameters varying from 5-10 nm, lengths about 30  $\mu\text{m}$  and purity of >95%. It was then chlorinated using SOCl<sub>2</sub> in DMF at 65 °C for 24 h. Pd(II)-Schiff base complex which was previously prepared was then anchored to the MWCNTs-COCl after 20 hours of heating under N<sub>2</sub> (Fig. 1).

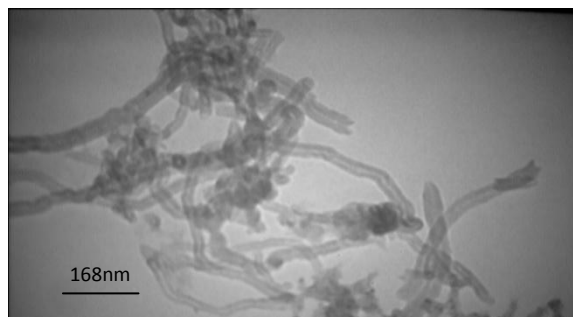


**Fig. 1.** Preparation of Pd-Schiff base@MWCNTs

The Pd(II)-Schiff base complex covalently anchored on modified MWCNTs was characterized by different techniques. Attenuated total reflection infrared spectroscopy (ATR) was used to assure the esterification step, with disappearance of the characteristic peak of the acid chloride at  $1750\text{ cm}^{-1}$ . Metal content of the complex was measured using inductive coupled plasma (ICP) as 16.20 ppm and analytical calculated for the catalyst Pd/N obtained to be 1.82%. The X-ray diffraction (XRD) pattern of the catalyst confirmed the presence of graphite at around  $26^\circ$  [42] and also the palladium metal at  $39.9^\circ$ ,  $47.4^\circ$  and  $82.0^\circ$ . Raman spectroscopy also showed four bands which are characteristic of CNTs including tangential stretching G-band ( $1567\text{ cm}^{-1}$ ), D-band ( $1331\text{ cm}^{-1}$ ), second harmonic D\*- band ( $2678\text{ cm}^{-1}$ ) and radial breathing band (RBM) ( $288\text{ cm}^{-1}$ ) [43, 44]. Further evidence for the modification of MWCNTs came from the X-ray photoelectron spectroscopy (XPS) of the complex. The peaks at 290.8, 344.6 and 539.2 eV are attributed to C, N and O atoms, respectively. Palladium  $3d_{3/2}$  and  $3d_{5/2}$  peaks appear at 349.8 and 344.4 eV, respectively [42, 45, 46]. Thermogravimetric-differential thermal analysis (TG-DTA) showed that the significant mass loss happened at 200-320  $^\circ\text{C}$  within two steps (Fig. 2). The surface grown Pd-Salen groups were lost at this temperature range [42]. Transmission electron microscopic (TEM) image was also taken (Fig. 3). MWCNTs-Pd-Schiff base complex exhibited stretched or folded feature with Schiff base complex. Besides, it was obvious that the layered structure of the MWCNTs remained largely intact, which indicated that there was no real damage to the MWCNTs during the functionalization process [42].



**Fig. 2.** TG-DTA Curve of the Pd-Schiff base@MWCNTs



**Fig. 3.** TEM Image of Pd-Schiff base@MWCNTs

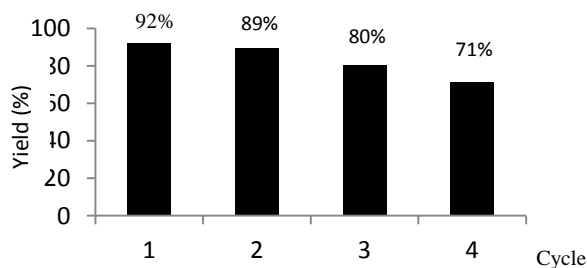
## 2.2 Catalytic performance of MWCNTs-Pd-Schiff base catalyst for the synthesis of ynones

The coupling between phenyl acetylene (1.5 mmol) and benzoyl chloride (1 mmol) in the presence of  $\text{NEt}_3$  (2 mmol) in air and at ambient temperature was chosen as a model reaction to find out the optimum reaction conditions (Scheme 1). The effect of different reaction parameters such as solvents, the molar ratio of the reactants and catalyst concentration was evaluated. The influence of solvents such as  $\text{CH}_3\text{CN}$  (52%) and DMF (21%) on ynone synthesis was investigated and the best result was achieved when solvent-free condition (92%) was used. Different molar ratios of the reactants were used for this C-C coupling reaction. It was observed that the coupling reaction required 1:1:1.2 molar ratios of benzoyl chloride, phenyl acetylene and  $\text{NEt}_3$  respectively. 0.006 Mmol of the Pd-Schiff base@MWCNTs catalyst was used in this work. Higher (8 mg, 73%) and lower (2 mg, 83%) amounts of the catalyst did not improve the yield.

To examine the scope of this coupling reaction, a variety of terminal alkynes (aliphatic and aromatic) with different acid chlorides (aliphatic, aromatic and heteroaromatic) were used (Table 1). As shown in Table 1, both aryl and alkyl acid chlorides coupled with alkynes under solvent-free and aerial condition, at ambient temperature. Aromatic terminal alkynes gave better yields and proceeded at relatively higher rates than the aliphatic ones. Moreover, no particular difference was noticed when aliphatic or aromatic acid chlorides were used. In addition, no significant steric effect was observed owing to the presence of the methyl group at the ortho position of 2-methylbenzoyl chloride, and the reaction was utilized successfully with both electron-donating and electron-withdrawing substituents on the aroyl chlorides. Also, heteroaryl acid chlorides such as 2-thiophene- and 2-furane carbonyl chlorides reacted smoothly with terminal alkynes to give the corresponding ynones in excellent yields.

The reusability of the catalyst was also examined. The catalyst was separated from the reaction mixture by centrifugation after each experiment, washed with water (3 mL) and chloroform (5 mL) and dried in

vacuum before being used in the subsequent reaction. The catalyst was recovered and used in four successive runs (Fig. 4).



**Fig. 4.** Reusability chart of the catalyst

### 3. Conclusion

In Conclusion, we presented a solvent-, copper- and phosphorous-free cross-coupling reaction of terminal alkynes with acyl halides catalyzed by Pd-Schiff base@MWCNTs. The catalyst was reusable and showed high activity for this simple, mild and green reaction with good to excellent yields. All these make this method well-suited for ynone synthesis.

### 4. Experimental

#### 4.1. General Remarks

All the solvents were purchased from Merck and distilled or dried using molecular sieves (4 Å). XPS (X-Ray photoelectron spectroscopy) data were recorded with 8025-BesTec twin anode XR3E2 x-ray source system. Thermogravimetric-diffraction thermal analysis (TG-DTA) was carried out using a thermal gravimetric analysis instrument (NETZSCH TG 209F1 Iris) with a heating rate of 10 °C min<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz) and <sup>13</sup>C NMR (100 MHz) spectra were measured in CDCl<sub>3</sub> solutions. XRD patterns were recorded by an Xpert MPD, X-ray diffractometer using CuKα radiation. Transmission electron microscopy (TEM) image was obtained on a Zeiss-Em10c transmission electron microscope with an accelerating voltage of 80 kV. FT-IR and ATR spectra were recorded on ABB FTLA 2000 and Nicolet NEXUF 670 spectrophotometers respectively. The metal content of the complex was measured using

**Table 1**

C-C Coupling reaction of acyl chlorides and terminal alkynes.

Entry	R <sup>1</sup>	R <sup>2</sup>	product <sup>a</sup>	Time (h)	Yield (%) <sup>b</sup>
1	Ph	Ph	<b>3a</b> <sup>38</sup>	1	92
2	2-Me-C <sub>6</sub> H <sub>4</sub>	Ph	<b>3b</b> <sup>38</sup>	0.75	92
3	C <sub>4</sub> H <sub>4</sub> S	Ph	<b>3c</b> <sup>38</sup>	1	93
4	C <sub>4</sub> H <sub>4</sub> O	Ph	<b>3d</b> <sup>38</sup>	1	94
5	4-Cl-C <sub>6</sub> H <sub>4</sub>	Ph	<b>3e</b> <sup>38</sup>	0.92	88
6	4-MeO-C <sub>6</sub> H <sub>4</sub>	Ph	<b>3f</b> <sup>38</sup>	1	87
7	4-NO <sub>2</sub> -C <sub>6</sub> H <sub>4</sub>	Ph	<b>3g</b> <sup>30</sup>	0.83	89
8	<i>c</i> -C <sub>6</sub> H <sub>11</sub>	Ph	<b>3h</b> <sup>38</sup>	0.5	86
9	4-MeO-C <sub>6</sub> H <sub>4</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub>	<b>3i</b> <sup>36</sup>	1.25	60
10	2-Me-C <sub>6</sub> H <sub>4</sub>	<i>n</i> -C <sub>4</sub> H <sub>9</sub>	<b>3j</b> <sup>25</sup>	1	64
11	C <sub>4</sub> H <sub>4</sub> S	<i>n</i> -C <sub>4</sub> H <sub>9</sub>	<b>3k</b> <sup>25</sup>	1.5	70
12	4-MeO-C <sub>6</sub> H <sub>4</sub>	<i>n</i> -C <sub>6</sub> H <sub>13</sub>	<b>3l</b> <sup>31</sup>	1.17	53
13	<i>c</i> -C <sub>6</sub> H <sub>11</sub>	<i>n</i> -C <sub>6</sub> H <sub>13</sub>	<b>3m</b> <sup>36</sup>	2	57

<sup>a</sup>References provided for known compounds. <sup>b</sup> Isolated yields.

inductively coupled plasma (ICP; Varian vista-mpx), and Almega thermo nicolelet dispersive raman spectrometer was used for raman spectroscopy.

#### 4.2 Preparation of the Schiff base ligand

A round-bottomed flask was charged with salicylaldehyde (4 mmol), 1,3-diamino-2-propanol (2 mmol) and absolute ethanol (25 mL). The reaction mixture was then refluxed until the completion of the reaction. The yellow precipitate was separated, washed with diethyl ether (3 × 3 mL) and dried in vacuum. Mp 100.5-102 °C. IR (KBr):  $\nu_{\text{C=N}}$  1632 cm<sup>-1</sup>.

#### 4.2 Preparation of the Pd(II)-Schiff base complex

A solution of the ligand (0.336 mmol) in acetonitrile (50 mL) was magnetically stirred in a round-bottomed flask followed by addition of palladium dichloride salt (0.336 mmol). The reaction mixture was refluxed for 1 h. The product formed was filtered off, washed with diethyl ether (3 × 3 mL) and dried in vacuum as yellow solid. Mp 250 °C (dec.). IR (KBr):  $\nu_{\text{C=N}}$  1615  $\text{cm}^{-1}$ .

#### 4.3 Chlorination of MWCNTs and anchoring the Pd(II)-Schiff base complex to it

The procedure reported by Salavati et al. [42] was used for the chlorination and esterification steps. The purchased CO<sub>2</sub>H-MWCNTs (100 mg) were suspended in a solution of thionyl chloride (25 mL) and DMF (1 mL). The suspension was stirred at 65 °C for 24 h. The solid was then separated by filtration and washed with anhydrous THF (30 mL), and dried in vacuum. COCl-MWCNTs (50 mg) were added to a solution of Pd(II)-Schiff base (100 mg) in degassed CHCl<sub>3</sub> (8 mL), and the suspension was refluxed for 20 h under N<sub>2</sub> atmosphere. The solid was then filtered and washed with THF (3 × 10 mL) and CH<sub>2</sub>Cl<sub>2</sub> (2 × 10 mL) and dried in vacuum.

#### 4.4 General procedure for synthesis of ynones

A mixture of acid chloride (1.0 mmol), terminal alkyne (1.0 mmol), NEt<sub>3</sub> (1.2 mmol) and Pd-Schiff base@MWCNTs (0.006 mmol) was stirred at room temperature (25 °C) under aerial and solvent-free conditions. The progress of the reaction was monitored by TLC. After completion, chloroform (10 mL) was added to the reaction mixture, and the catalyst was recovered with centrifugation. The organic layer was washed with water (2 × 5 mL), dried over anhydrous magnesium sulfate, filtered and concentrated in vacuum. The crude product was further purified by preparative TLC (silica gel) using *n*-hexane/EtOAc (9:1) to afford the desired product. All compounds were characterized by IR, <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy. Compound (**3b**): Yellow oil; IR (neat):  $\nu = 2196, 1638 \text{ cm}^{-1}$ ; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta = 8.35$  (d,  $J = 7.6$  Hz, 1H), 7.69 (d,  $J = 6.8$  Hz, 2H), 7.38-7.52 (m, 5H), 7.29-7.32 (m, 1H), 2.72 (s, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta = 179.8, 140.5, 135.7, 133.3, 133.0, 132.9, 132.2, 130.7, 128.7, 126.0, 120.4, 91.9, 88.4, 22.0$ ; (**3d**): Dark brown oil; IR (neat):  $\nu = 2199, 1631 \text{ cm}^{-1}$ ; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta = 7.66$ -7.72 (m, 3H), 7.42-7.53(m, 4H), 6.63 (dd,  $J = 3.4, 1.2$  Hz, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta = 164.8, 153.2, 148.1, 133.1, 130.9, 128.7, 121.1, 91.9, 86.2$ .

#### Acknowledgements

We are pleased to acknowledge financial support from the K. N. Toosi University of Technology Research Council and Iranian National Science Foundation (INSF, Grant No. 90006262). We are also thankful to Professors J. Ghasemi and M. Joshaghani for their generous support.

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