Cellulose nanocrystals -palladium, a novel recyclable catalyst for coupling reaction

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Abstract
A new Schiff base catalyst (Pd (II) chemically mounted on the cellulose nanocrystals surface (CNC-APTES-IS-Pd) was developed for Ulmann and Suzuki cross-coupling reactions. The catalyst was applied for Ulmann reaction using s series of aryl halide and phenol derivatives in DMSO and preparation of biaryls via Suzuki C-C reactions between aryl halides and phenyl boronic acid. The Catalyst was characterized by FT-IR, XRD, SEM, ICP-AES and TGA techniques. The catalyst demonstrated high reaction efficiency with more than 90% reaction yield. The catalyst indicated good performance after several times recovery and reuse.

Keywords: Ullmann reaction; Suzuki reaction; coupling reaction; palladium nanoparticles; cellulose nanocrystals; Schiff base.

Introduction
Preparation of C-C, C-H, and C-heteroatom bonds in organic chemistry have been previously investigated relying on different special and expensive metal coordinated catalysts [1]. These reactions become cheaper and more popular after introducing palladium-based catalysts [2,3]. As such, Ullmann coupling reaction was introduced in 1901 for the synthesis of symmetrical biaryls using aryl iodides and copper as catalyst at high temperatures [4,5]. New Ullmann coupling reaction using aryl bromides/chlorides as reactants in presence of Zn powder and Pd as catalysts was developed later [6]. Ullmann reaction using Pd as catalyst indicated good performance for the synthesis of complicated organic molecules such as pharmaceuticals [7], medicine [8], polymers [9], alkaloids [10], and other advanced materials [11]. High performance and selectivity of Ullmann reaction on aryl halides have reported using specific design of Pd

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metal−ligand complex (Pd in the N, O, S, and P donor ligands) [12].

Suzuki cross-coupling reaction is another important and efficient method for biaryl synthesis. It is effective on the materials with broad functional groups with lower toxicity [13-15]. Suzuki reaction has become popular for the synthesis of natural products, herbicides, pharmaceuticals, and other organic products [16,17]. Palladium–phosphine catalysts are the main complex for Suzuki reaction due to their activity and selectivity [18,19].

The immobilization of metal catalysts on the surface of solid substrates has been developed to make cheaper material with better performance. Polystyrene [20], polysilylethers [21] and mesoporous silica [22] were reported as the main substrate for N-heterocyclic carbenes (NHCs) and their metal complex catalyst. However, these substrates can create major environmental concern and high cost [20,21].

Cellulose was introduced as a renewable and biodegradable substrate for catalysts [22]. Nano cellulose with high degree of crystallinity is stable in most organic solvents, having high thermal stability with high surface area. Due to presence of hydroxyl groups on the surface of nano-cellulose, it can modify and functionalize to improve its application [23].

This effort is a part of our previous published work [24,25] on the formation of C-O bonds between activated aryl halides and phenol derivatives. We tried to anchor 3-aminopropyl tri-ethoxysilane (APTES) onto the surface of cellulose nanocrystals followed by coordination with Na_2PdCl_4. The goal was preparing a novel cellulose nanocrystals -APTES-Isatine-palladium catalyst (CNC-APTES-IS-Pd). Cellulose nanocrystals (CNC) particle was first silylated using APTES followed by condensation reaction of CNC-APTES with isatine. Finally, the Pd(II) catalyst was synthesized in water with adding Na_2PdCl_4 to reaction mixture. The prepared Pd(II) catalyst was characterized by FT-IR, XRD, SEM, ICP-AES and TGA techniques. Catalytic activity and recycling performance of the prepared catalyst in Ullmann and Suzuki cross coupling reactions for synthesis of different biaryl compounds in the DMSO solvent (Scheme 1) were performed.
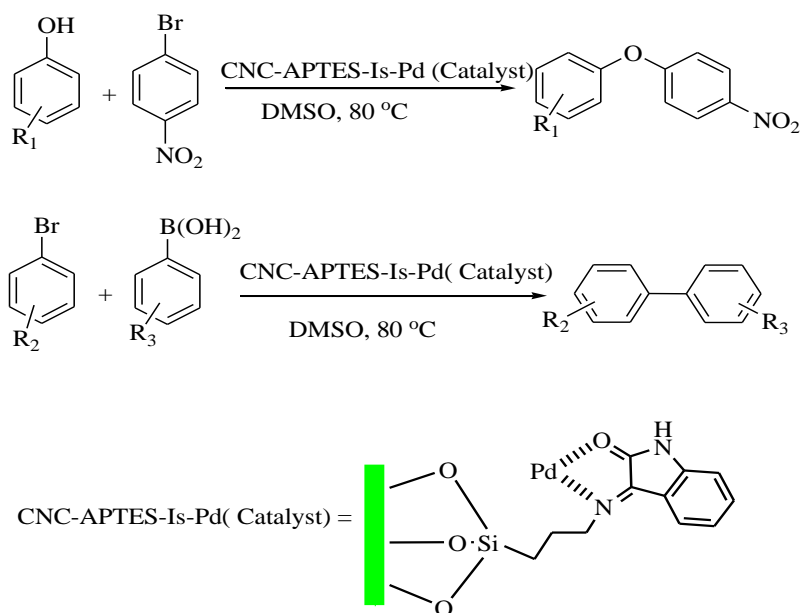
Scheme 1. General procedure for the Ullmann and 444d

Experimental

Chemicals and apparatus

All chemicals were purchased from Merck and Fluka and used as received. FTIR Spectra was carried out using a Vector 22- Bruker in the range of 400–4000 cm^{-1} at room temperature. The X-ray powder diffraction (XRD) of the catalyst was carried out on a Philips PW 1830 X-ray diffractometer with CuKα source (λ=1.5418 Å) in a range of Bragg's angle (10-80°) at room temperature. Transmission electron microscopy (TEM) experiments were conducted on a Philips EM 208 electron microscope. Thermo gravimetric analysis (TGA) was carried out on a Stanton Red craft STA-780 (London, UK) using N_2 as carrier gas with temperature ramp of 10 °C/min and from room temperature to 700 °C. The content of palladium was determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) (Perkin Elmer Optima 2000 DV ICP-AES). NMR spectra related to prepared catalyst were recorded with a Bruker DRX-400 AVANCE instrument (400.1 MHz for ^{1}HNMR, 100.6 MHz for ^{13}CNMR). All of the spectra were done in DMSO-d_6 as solvent.

Preparations of cellulose nanocrystals (CNC)

Preparations of cellulose nanocrystals (CNC) (1)

The CNCs were formed by acidic hydrolysis of Whatman filter paper #1 as reported in the literature [26]. The fiber was hydrolyzed by 100mL of 2.5 M HBr at 100 °C for 3. The hydrolyzed cellulose fiber was washed and centrifuged with D.I water around 5 times to remove excess acid and water soluble impurities. After reaching pH value close to 5, the fine cellulose nano particles started to disperse into the aqueous supernatant. The suspended fiber was then collected using centrifugation at 12,000 rpm for 60 min. To have ultra-pure product, the collected cellulose nanocrystals was dialyzed against DI water for 24 h using a cellulose membrane film. Main part of the product was kept as non-dried (wet) in fridge for later process and the frozen part of that was dried for other analysis.

### Preparation of cellulose nanocrystals - APTES (CNC-APTES)

2 g of prepared cellulose nanocrystals (12.3 mmol) was washed 5 times with anhydrous toluene to remove and exchange water. 10 mL of APTES was then added in CNC mixture with anhydrous toluene (50 mL). The mixture was refluxed for 48 h to prepare cellulose nanocrystals-APTES (CNC-APTES). The prepared product was filtered and washed with ethanol 5 times and used for next step reaction [27] (Scheme 2).

Preparation of CNC-APTES bearing isatin (CNC-APTES-IS)

CNC-APTES (1 g) and isatine (0.2 mg, 0.0013 mmol) were refluxed in 50 mL of ethanol for 72 h. Light yellow color Schiff base product was filtered and washed several times with ethanol (Scheme 2).

Preparation of CNC-APTES-IS-Pd catalyst

CNC-APTES-IS-Pd catalyst was synthesized using reaction of CNC-APTES-IS suspension with Na_2PdCl_4 (0.4 g, 1.35 mmol) in water at room after being stirred for 6 h. Finally, brown colored product was filtered and washed several times with hot water to dissolve remove unreacted palladium salts residue. The prepared product was dried at room temperature (Scheme 2).
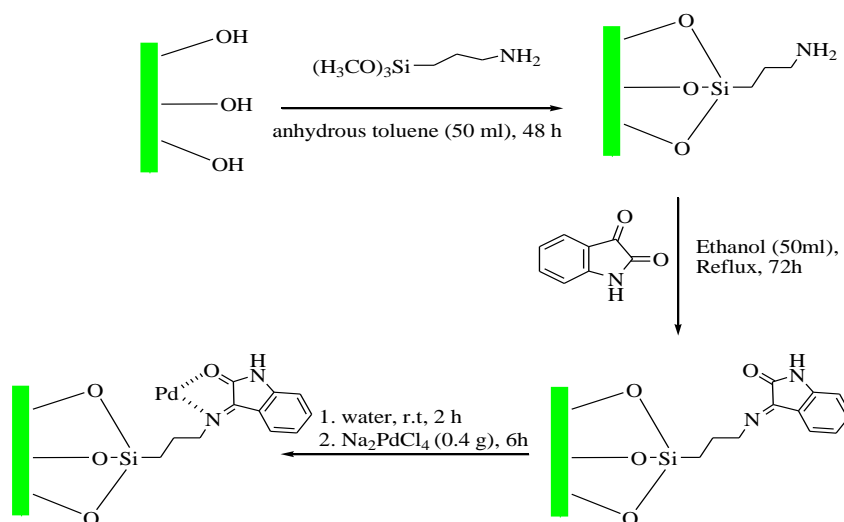
Scheme 2. General procedure for the preparation of CNC-APTES-IS-Pd

The procedure for the ullmann reaction of arylhalides with phenols derivatives

0.2 mol% (0.0034 g) of CNC-APTES-IS-Pd catalyst was added to a mixture of arylhalide (0.5 mmol) and phenol derivatives (0.6 mmol) in DMSO solvent (2.5 mL). The mixture was stirred vigorously at 80 ℃ for different times using various substrates. The solid catalyst was filtered out and washed with deionized water followed by pure ether. The recovered catalyst was used for reusability test. The filtrate was extracted with ethyl acetate (3x5 mL), washed with distilled water and then dried by anhydrous MgSO4. After separation of MgSO4, the solvent was evaporated to collect the product. The final product was purified using TLC (eluent: petroleum ether/ethyl acetate, 20/1) and the yield was estimated.

^{1}H NMR and ^{13}C NMR data of two main compounds

4-(4-cyanophenoxy)nitrobenzene

^{1}H NMR (400.13 MHz, DMSO-d_6): δ =7.20-7.28 (m, 4H, 4CH$_{aromatic}$), 7.59 (d, 2H, $^3J_{HH}$ = 4.9 Hz, 2CH$_{aromatic}$), 7.99 (d, 2H, $^3J_{HH}$ = 9.4 Hz, 2CH$_{aromatic}$)ppm.;^{13}C NMR (100.6 MHz, DMSO-d_6): δ = 110.7, 122.0, 125.2, 126.0, 127.2, 135.1, 138.6, 145.3, 146.5 ppm.

4-(4-Fluorophenoxy) nitrobenzene

^{1}H NMR (400.13 MHz, DMSO): δ = 7.59 (d, 2H, J= 7.7 Hz, 2CH$_{aromatic}$), 7.70 (d, 2H, $^3J_{HH}$ = 10.09 Hz, 2CH$_{aromatic}$), 7.88 (d, 2H, $^3J_{HH}$ = 10.08 Hz, 2CH$_{aromatic}$), 8.01 (d, 2H, $^3J_{HH}$ = 7.7 Hz, 2CH$_{aromatic}$) ppm.; ^{13}C NMR (100.6 MHz, DMSO): δ = 128.1, 129.3, 129.9, 131.6, 143.0, 144.1, 145.7, 148.1 ppm.

General procedure for the synthesis of biaryls via Suzuki C- C reactions

To synthesis biaryls *via* Suzuki C-C reactions, arylhalides (1 mmol), phenyl boronic acid (1 mmol) were mixed with each other in DMSO (5 mL) in the presence of CNC-APTES-IS-Pd (0.2 mol%) as the catalyst, using 2.5 mmol of K$_2$CO$_3$ as base. The reaction mixture was stirred vigorously at 80 ℃ for different time according to each various substrate. At the end of reaction, the solid catalyst was filtered and washed several times with deionized water followed by absolute ether and saved for catalyst reusability test. The filtrate was extracted with ethyl acetate (3x5 mL), washed with distilled water and dried by anhydrous MgSO4. MgSO4 was filtered and the solvent was vaporized. The final product purified and prepared by preparative TLC (eluent: petroleum ether/ethyl

acetate, 20/1) and the desired product yield was evaluated.

^{1}HNMR and ^{13}CNMR data of two main synthesized compounds
4-methoxybiphenyl
^{1}H NMR (400 MHz, DMSO-d_6): δ = 3.88(s, 3H, OCH$_3$), 7.00 (d, $^3J_{HH}$ = 8.1 Hz, 2H Ar), 7.34 (d, $^3J_{HH}$ = 8.1 Hz, 2H Ar), 7.60-7.68 (m, 4H Ar)ppm.;^{13}C NMR (100 MHz, DMSO-d_6): δ = 53.5, 117.8, 124.6, 125.1, 128.0, 128.3, 133.2, 141.0, 159.2 ppm.

4-Methoxy-4'-ethylbiphenyl
^{1}H NMR (400 MHz, DMSO-d_6): δ = 1.28 (t, $^3J_{HH}$ = 6.2 Hz, 3H CH$_3$), 2.68 (q, $^3J_{HH}$ = 6.2 Hz, 2H CH$_2$), 3.82 (s, 3H, OCH$_3$), 7.01 (d, $^3J_{HH}$ = 9.2 Hz, 2H Ar), 7.13 (d, $^3J_{HH}$ = 9.2 Hz, 2H Ar), 7.41 (d, $^3J_{HH}$ = 7.2 Hz, 2H Ar), 7.57 (d,$^3J_{HH}$ = 7.2 Hz, 2H Ar) ppm.; ^{13}C NMR (100 MHz, DMSO-d_6): δ = 16.1, 28.7, 53.2, 118.0, 126.3, 128.2, 129.5, 134.8, 138.8, 143.5, 155.2 ppm.

Results and discussion
Characterization of CNC-APTES-IS-Pd
Figure 1 indicates the FTIR spectrum of cellulose nanocrystals (CNC) and final CNC-APTES-IS-pd catalyst product. The wide peak around 3300 cm^{-1} indicates free OH group in cellulose nanocrystals and NH group in pyrrole part of ligand. The stretching peaks at 2900 cm^{-1} is attributed to the C-H group [28]. The peak of 1645 cm^{-1} is related to cellulose backbone structure. The signal of 1627 cm^{-1} which is merged with cellulose structure backbone peak is an evidence for C-C double bond stretching signals in aromatic rings groups of isatine attached to cellulose nanocrystals substrate. The strong peak at 1710 cm^{-1} and 1222 cm^{-1} are belong to carbonyl group of five membered cycle of amide group and =C-N bond respectively [29].
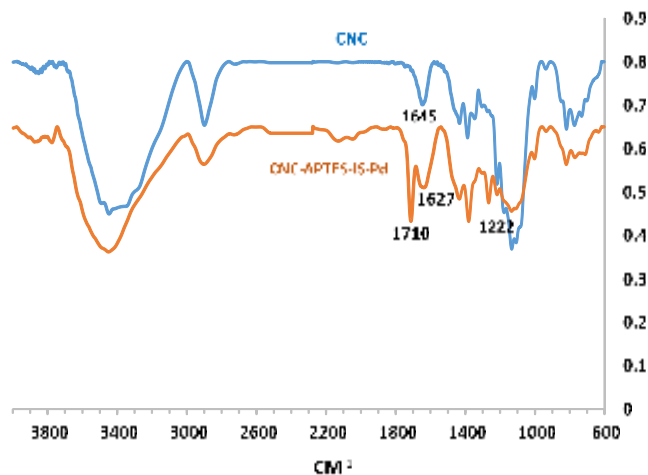

Figure 1. The FTIR spectrum of CNC and CNC-APTES-IS-Pd

X-ray diffraction (XRD) analysis
The main reason for using cellulose nanocrystals as a substrate for catalyst was its chemical and physical stability and preserves its crystalline form after surface modification (peak at 22.5 and 35 degree). The XRD spectra of CNC before and after modification (Figure 2) indicates same pattern of crystalline structure and proof its stability during modification. The modified cellulose nanocrystals also indicate crystalline structure of Palladium presence in the catalyst. Peaks at 2θ of 40.0°, 46° and 68° are assigned to diffractions from various lattice planes present in the cubic Palladium [30].
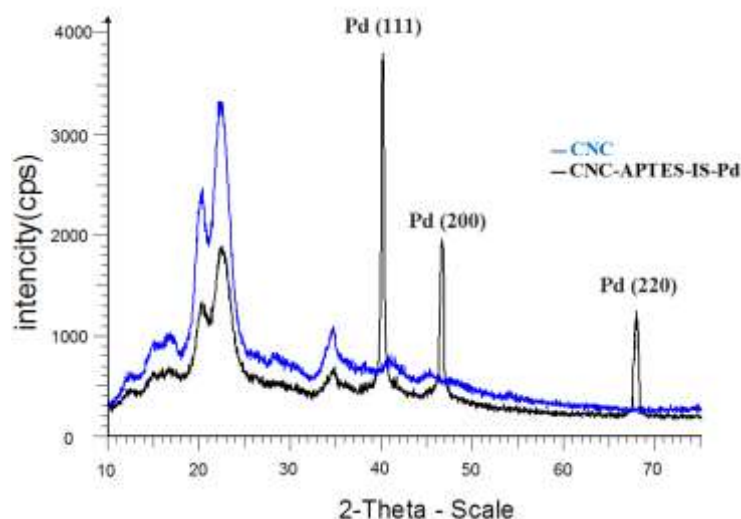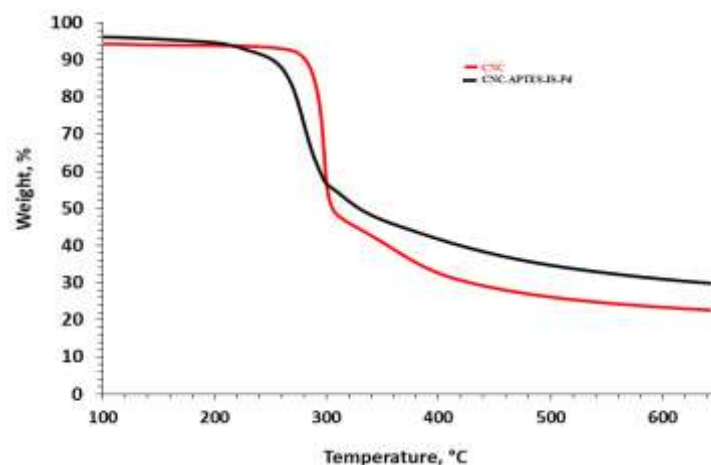
Figure 2. XRD spectra of CNC and CNC-APTES-IS-Pd

Thermo-gravimetric analysis (TGA)

The thermal stability of cellulose nanocrystals and its modified catalyst (CNC-APTES-IS-Pd) is investigated through thermo-gravimetric analysis (TGA) using nitrogen gas flow (Figure 3). The CNC-APTES-IS-Pd catalyst indicated stability up to 200 °C which is a good sign for its application in higher temperature reaction. Nanocellulose itself illustrated higher thermal stability (start to degradation around 300 °C). Presence of metal (Pd) and silica in the catalyst which can increase heat transfer and lower stability of attached ligand can account for the lower thermal stability of modified cellulose nanocrystals compared with un-modified one [23,27]. In general, the profiles of two samples in starting degradation temperature are different. Following the full decomposition of the samples, the remaining char for cellulose nanocrystals was around 24% while this number was around 31% for modified sample. The presence of Pd and silica along with more carbon content from ligand are the reasons for these results and can proof the presence of the catalyst on the surface of Nano-cellulose. The determination of exact Pd in the remaining char after sample decomposition is not possible due to presence of Si and extra carbon from ligand in the char.

Figure 3. Thermogravimetric analysis of CNC and CNC-APTES-IS-Pd

Electron microscopy

The morphology of the catalyst is investigated by electron microscope (SEM) (Figure 4). Palladium catalyst visible as dark points on the modified cellulose nanocrystals (CNC-APTES-IS-Pd) reveals presence of Pd on the nano-cellulose surface. Also, the morphological feature and particle size of the catalysts on the synthesized CNC-APTES-IS-Pd was studied by SEM. The SEM indicates structure in CNC and presence of Pd particles on the surface of CNC-APTES-IS-Pd. The average particle size of the catalyst on the surface of cellulose nanocrystals was around 47-58 nm.
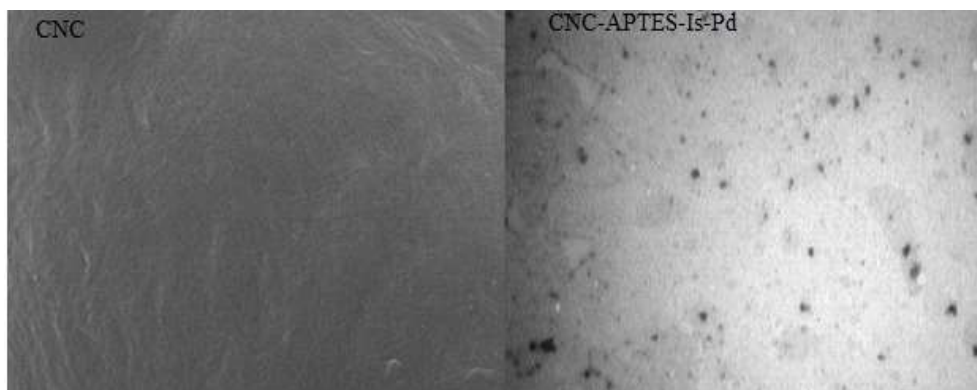
Figure 4. SEM of CNC and CNC-APTES-IS-Pd

Pd content in the catalyst and elemental analysis

To have an estimation of Pd content in synthesized catalyst, The ICP-AES analysis was carried out. The results indicated presence of 62406 mg/kg of Pd(II) the CNC-APTES-IS-Pd catalyst which was equal to 6.2%. Due to the presence of one Pd atom in the catalyst structure, the loading of APTES-IS coated on the surface of the cellulose nanocrystals was calculated to be around 0.58 mmol/g of prepared catalyst.

The CHN/O analysis was carried out to determine the elemental contents of the CNC-APTES-IS-Pd. The CHN results indicated the 2.18% N, 38% C and 6% H in the catalyst. The total nitrogen in the catalyst was calculated to be around 1.45 mmol/g ((2.18/100)/15) x1000. Due to the presence of two nitrogen atoms in the catalyst structure, the amounts of catalyst on the surface of prepared catalyst could be calculated around 0.72 mmol/g which was close to the number calculated with Pd content (0.58 mmol/g). Therefore, the data obtained from Elemental analysis (CHN) could confirm the existence of almost the same amounts of APTES-IS on the surface of the CNC.

Catalytic application of CNC-APTES-IS-Pd

To evaluate catalytic performance of developed catalyst, a range of standard Ullmann and Suzuki reaction were carried out. Initially, a series of optimization reaction were done using one-pot reactions to find the optimum condition. The following optimum conditions were found for each reaction along with the details of results in supplementary file:

• Cross coupling of 4-cyanophenol and1-bromo-4-nitrobenzene as model substrates with various solvents and bases were employed in the initial study to optimize reaction conditions and the experiments were performed. The details of these experiments are reported in Table 1.

• To test the activity of the catalyst, the Suzuki cross coupling reaction of

phenylboronic acid (0.048 g, 0.4 mmol) with 4-bromoanisole (0.187 g, 1 mmol) was used as a model. Various reaction conditions such as solvent, temperature, the amount of catalyst and the base were optimized. The results were summarized in Table 2. The optimized reaction conditions were as follows: the ratio of phenylboronic acid to 4-bromoanisole, 1:0.4; the catalyst, 0.2 mol %; K_2CO_3 as a base; DMSO as a solvent; and 80 °C in air (Table 2).

Table 1. [a]Optimization of the reaction condition for the Ullmann coupling of *O*-arylation

Entry	Base	Solvent	Temperature (°C)	Yield(%)[b]
1	Cs_2CO_3	DMSO	80	65
2	Na_2CO_3	DMSO	80	62
3	K_2CO_3	Dioxane	80	10
4	K_2CO_3	Toluene	80	21
5	K_2CO_3	DMAc	80	71
6	K_2CO_3	DMF	80	70
7	-	DMSO	80	0
8	K_2CO_3	DMSO	50	80
9	K_2CO_3	DMSO	60	81
10	K_2CO_3	DMSO	80	94,94[c],78[d]
11	K_2CO_3	DMSO	100	90

[a]Reaction Conditions: 1-bromo-4-nitrobenzene (0.5 mmol),4-cyano phenol (0.6 mmol), base (1 mmol), solvent (2.5 mL), CNC-APTES-IS-Pd (0.2 mol%), 0.33 h.
[b] Yields refer to isolated pure product
[c]0.3 mol% of catalyst,[d]0.1 mol% of catalyst.

Table2. Optimization of the Suzuki cross-coupling reaction using CNC- APTES-Is-Pd as a catalyst[a]

Entry	Solvent	Temperature (°C)	Base	Amount of catalyst (mol%)	Yield(%)[b]
1	EtOH	80	K_2CO_3	0.2	69
2	H_2O	80	K_2CO_3	0.2	38
3	DMF	80	K_2CO_3	0.2	67
4	DMSO	80	K_2CO_3	0.2	95
5	DMSO	70	K_2CO_3	0.2	94
6	DMSO	110	K_2CO_3	0.2	90
7	DMSO	50	K_2CO_3	0.2	72
8	DMSO	50	K_2CO_3	0.1	62
9	DMSO	80	K_2CO_3	0.05	51
10	DMSO	80	K_2CO_3	0.3	90
11	DMSO	80	Cs_2CO_3	0.2	88
12	DMSO	80	Et_3N	0.2	52

a) Reaction Conditions: phenylboronic acid (0.4 mmol), 4-methoxybromohalide (1 mmol), base (2.5 mmol), solvent (5 mL), CNC-APTES-IS-Pd (0.2 mol%), 2 hours
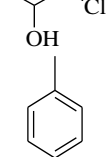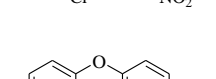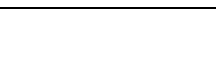b) Isolated yield by TLC
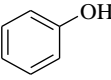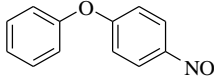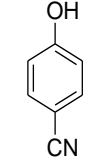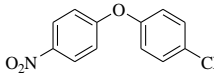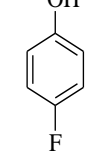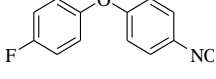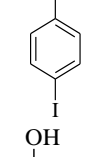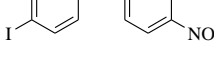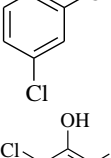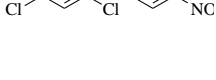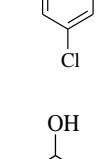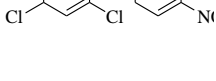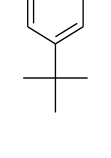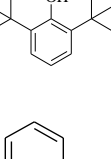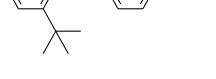
Using optimum condition, a series of Ullmann reactions between 1-bromo-4-nitrobenzene with various phenol derivatives were performed in the presence of CNC-APTES-Is-Pd at 80 °C in DMSO solvent for 20 min. As it can be observed in Table 3, every phenol derivative obtained the corresponding products from good to excellent yields (Table 3).
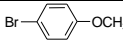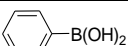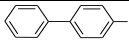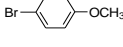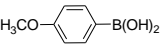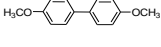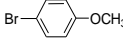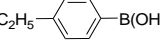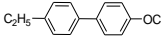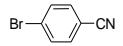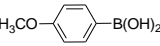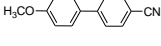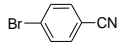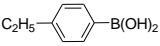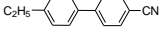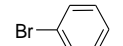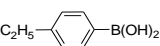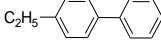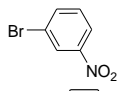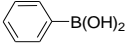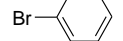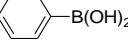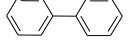
Table 3. one-pot reactions of di-aryl ether derivative using 1-bromo-4-nitrobenzene and phenol derivative in DMSO in the presence of CNC-APTES-IS-Pd

Entry	Phenol	Product	Time, min	Yeild, %	TON	TOF, 1/h	Found	Ref.
1			20	94	470	1410	60	57-60[31]
2			20	94	470	1410	160	159[31]
3			25	93	465	1116	59-60	58–60[31]
4			24	93	465	1162	50-51	51[31]
5			24	94	470	1175	73-75	73[31]
6			21	92	470	1342	92-93	94[31]
7			24	93	465	1162	63-66	63–64[32]
8			28	90	450	964	107	107[31]
9			24	91	455	1137	77-78	77[31]
10			27	90	450	1000	60-71	69[31]

To prepare diaryls, Suzuki cross coupling reactions of bromohalides and phenylboronic acids under optimum condition was carried out. A broad range of substituted and structurally diverse bromohalides and phenylboronic acids were applied and the corresponding products were synthesized from good to excellent yields (Table 4).

Table 4. one-pot reactions of diaryl derivative using in the presence of CNC-APTES-IS-Pd

Entry	Aryl halide	Phenyl boronic acid	Product	Time (h)	Yield, %	TON	TOF (1/h)	Melting point, (ºC)	Ref.
1	Br—⟨⟩—OCH₃	⟨⟩—B(OH)₂	⟨⟩—⟨⟩—OCH₃	2	95	475	237.5	89-90	[33]
2	Br—⟨⟩—OCH₃	H₃CO—⟨⟩—B(OH)₂	H₃CO—⟨⟩—⟨⟩—OCH₃	1.7	84	420	247	173	[34]
3	Br—⟨⟩—OCH₃	C₂H₅—⟨⟩—B(OH)₂	C₂H₅—⟨⟩—⟨⟩—OCH₃	5	91	455	91	222	[35]
4	Br—⟨⟩—CN	H₃CO—⟨⟩—B(OH)₂	H₃CO—⟨⟩—⟨⟩—CN	4	95	475	118.75	100	[36]
5	Br—⟨⟩—CN	C₂H₅—⟨⟩—B(OH)₂	C₂H₅—⟨⟩—⟨⟩—CN	2.5	97	485	194	189-190	[37]
6	Br—⟨⟩	C₂H₅—⟨⟩—B(OH)₂	C₂H₅—⟨⟩—⟨⟩	4	90	450	112.5	210-211	[38]
7	Br—⟨⟩ NO₂	⟨⟩—B(OH)₂	⟨⟩—⟨⟩ NO₂	3.5	90	450	128.5	59-60	[39]
8	Br—⟨⟩	⟨⟩—B(OH)₂	⟨⟩—⟨⟩	3.5	92	460	131.4	71-72	[38]

Turn over number (TON) and turn over frequency (TOF) values were estimated for all Carbon–Oxygen Ullmann reactions. The obtained results are inserted in Table 3. These results demonstrated that CNC-APTES-IS-Pd catalyst had notable TON and TOF values with trivial loading of the catalyst in a short time and it was therefore efficient for various Ullmann coupling reactions. Also, the catalytic efficiency of CNC-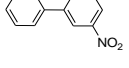APTES-IS-Pd catalyst was appraised against different commercial palladium salts with the model reaction under optimum conditions (Table 3). These experiments demonstrated that the CNC-APTES-IS-Pd catalyst had excellent catalytic activity as well as TON and TOF values compared with the commercial palladium catalysts.

Another main parameter concerning the application of a heterogeneous catalyst was its reusability and stability under reaction conditions.

To achieve this, catalyst recycling experiments were performed using the Ullmann reaction of 1-bromo-4-nitrobenzene and 4-cyanophenol over CNC-APTES-IS-Pd. The results are indicated in Table 5.

After each cycle, the catalyst was filtered off, washed with water, diethyl ether and acetone. After wards it needed to be dried in an oven at 60 ˚C and reused in the Ullmann reaction. The results displayed that CNC-APTES-IS-Pd catalyst had a good stability in reaction media and could be reused four times with no considerable loss of catalytic activity.

We also studied recyclability of the CNC-APTES-IS-Pd in Suzuki reaction using the model reaction of 4-bromoanisole and phenylboronic acid under DMSO solvent at 80 ºC conditions (Table 5). The recovered Catalyst could be reused four runs with no loss of its activities.

The results demonstrated that CNC-APTES-IS-Pd catalyst could be reused without losing its efficiency after four times. It should be said that there was low Pd leaching (about 7%) during the reaction and the catalyst showed high stability even after four cycles (Table 5).

Table 5. Reusability of CNC-BIA-Pd in Ullmann and Suzuki reaction

The of cycle	Yield (%)	Pd content of catalyst[C] (mmol/100)	TON	TOF
(a) Ullmann cross-coupling reactions				
Fresh	94	0.1724	470	1424
1st	94	0.1724	470	1424
2nd	91	0.1702	455	1378
3rd	90	0.1682	450	1363
4th	87	0.1652	435	1318
(b) Suzuki cross-coupling reactions				
Fresh	95	0.1724	475	237.5
1 st	95	0.1724	475	237.5
2nd	93	0.1702	465	232.5
3rd	90	0.1682	450	225
4th	88	0.1652	440	220

(a) Reaction conditions: 0.6 mmol4-cyanophenol, 0.5 mmol1-bromo-4-nitrobenzene, 1 mmol base, 0.2% mol catalyst, 80 °C, 0.33 h in DMSO
(b)Reaction conditions: 1 mmol4-methoxybromohalide, 0.4 mmolphenylboronic acid, 2. 5 mmol base, 0.2% mol catalyst, 80 °C, 2 h in DMSO
(c) Pd content was estimated by inductively coupled plasma atomic emission spectrometry (ICP-AES).

To further investigate the catalytic performance of CNC-APTES-Is-Pd, a comparison was made between the activity of different catalysts in the synthesis of 4-Nitro-diphenylether (Table 6). The obtained results exhibited that the desired reactions were carried out in the presence of CNC-APTES-Is-Pd in somewhat short times in comparison with other catalysts with the nearly similar yields.

To exhibit the availability of the present work in comparison with other reported results in the literature, a summary of the results for the preparation of 4-methoxybiphenylin is presented in Table 4. The obtained results showed that CNC-APTES-Is-Pd is the better catalyst because of the short reaction time and good yields of the product.

Table 6. Comparison of CNC-APTES-IS-Pd with reported catalysts for Ullmann and suzuki reactions

Catalyst	Conditions	Yield (%)	[Ref]
(a) Ulmann cross-coupling reactions			
Silica-supported Cu (0.05 mmol of Cu), KF (2.00 mmol)	DMSO, 130 °C,16 h	98	[40]
Copper(I)-Bipyridyl Complex (0.5-5 mol%), K_3PO_4 (2 mmol)	DMF, 90 °C,0.5 h	92	[41]
Cs_2CO_3 (2 mmol), Cu_2O(5 mol%), Chxn-Py-Al(600 mg)	MeCN, 120 °C,18 h	97	[42]
$PdCl_2$ (0.006 g), SDPP(0.009 g)	n-Bu_4NOH 20%, NaOH, 70 °C,0.5 h	92	[43]
CNC-APTES-Is-Pd (0.2 mol %)	70 °C, DMSO	94	Present work
(b) Suzuki cross-coupling reactions			
Palladium N-Heterocyclic Carbene (0.02 mmol), K_2CO_3 (1.2 eq)	i-PrOH, r.t,6 h	96	[44]
Pd (OAc)$_2$ /LHX (15 mol%)	DMF/H_2O, 50 °C ,3 h	80	[45]

Cell-NHC-Pd (0.75 mol%)	K_2CO_3, DMF:HO (1:1),80 °C,2 h	97	[46]
Pd (1.0 mol)	$K_3pO_4 .3H_2O$, H_2O/Ethanol , 80 °C,4 h	97	[47]
CNC-APTES-Is-Pd (0.2 mol %)	DMSO, 80 °C ,2 h	95	Present work

(a)one pot reactions of diaryl ether derivative using 1-bromo-4-nitrobenzene and 4-cyanophenolderivative
(b)reaction of 4-methoxybromohalide and phenylboronic acid to prepare 4-methoxybiphenyl

To investigate the recyclability of CNC-APTES-Is-Pd, the model reaction of 1-bromo-4-nitrobenzene with 4-cyanophenol at 80 ºC in DMSO solvent was performed (Experimental section). Each time after each reaction, the catalyst was separated, washed and dried to use for next step. The catalyst (CNC-APTES-IS-Pd) indicated good stability during four times reaction and reuse without substantial loss of its catalytic activity. The results indicated reaction yield decreased from 94% from fresh catalyst to 87% after four times recycling for Ullmann reaction and from 95% to 88% for Suzuki reaction.

Conclusion

A palladium catalyst based on 3-aminopropyltriethoxysilane on the cellulose nanocrystals as substrate developed (CNC-APTES-IS-Pd) and successfully synthesized and characterized by FT-IR, SEM, XRD, ICP-AES and TGA techniques. The catalytic performance was evaluated by Ullmann and Suzuki cross-coupling reactions under eco-friendly conditions. The results indicated high efficiency with more than 90% reaction yields. The catalyst also indicated good recyclability, high thermal stability, easy filtration and recovery from the reaction media. The developed catalyst illustrated good potential for Ullmann and Suzuki cross-coupling reactions.

Acknowledgements

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