## Journal Pre-proofs

### Short communication

Synthesis and characterization of Pd based on [2,2'- bipyridin]-4-amine functionalized nano cellulose as a novel and recyclable nano catalyst for Suzuki reaction

### Yuqi Sun, Majid Mohammadnia

PII: DOI: Reference:	S1387-7003(20)30583-9 https://doi.org/10.1016/j.inoche.2020.107993 INOCHE 107993
To appear in:	Inorganic Chemistry Communications
Received Date:	25 March 2020

Received Date:25 Match 202Revised Date:30 May 2020Accepted Date:31 May 2020



Please cite this article as: Y. Sun, M. Mohammadnia, Synthesis and characterization of Pd based on [2,2'bipyridin]-4-amine functionalized nano cellulose as a novel and recyclable nano catalyst for Suzuki reaction, *Inorganic Chemistry Communications* (2020), doi: https://doi.org/10.1016/j.inoche.2020.107993

This is a PDF file of an article that has undergone enhancements after acceptance, such as the addition of a cover page and metadata, and formatting for readability, but it is not yet the definitive version of record. This version will undergo additional copyediting, typesetting and review before it is published in its final form, but we are providing this version to give early visibility of the article. Please note that, during the production process, errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

© 2020 Elsevier B.V. All rights reserved.

# Synthesis and characterization of Pd based on [2,2'- bipyridin]-4-amine

# functionalized nano cellulose as a novel and recyclable nano catalyst for

### Suzuki reaction

Yuqi Sun,<sup>a,\*</sup>Majid Mohammadnia<sup>b</sup>

<sup>a</sup>Department of Portuguese, Faculty of Arts and Humanities, University of Macau, Macau, China <sup>b</sup>Young researcher and elite club, Department of Chemistry, Bojnord Branch, Islamic Azad University, Bojnourd, Iran.

Email: viviann534@126.com

### Abstract

In this work, it was designed and prepared an efficient nanocatalyst Pd based on [2,2'- bipyridin]-4-amine functionalized nano cellulose (Pd@BPA@CNC) and then characterized by FT-IR, XRD, ICP-AES, EDX, SEM, TEM and TGA techniques. The catalytic activity of the nanocatalyst was investigated through one-pot synthesis of biaryl derivatives from the reaction of aryl halides with arylboronic acids in DMSO solvent conditions. This Simple and mild procedure displayed excellent recyclability and provided cleaner conversion in a short reaction time. All of these advantages make the protocol feasible and economical attractive for researchers.

**Keywords:** Suzuki reaction, Nanocatalyst, biaryl derivatives, nanocellulose, palladium, [2,2'-bipyridin]-4-amine

### Introduction:

In recent years, the worthiness of nanoparticles (NPs) is one of the most important discoveries that has been advanced to an scope that researchers could have never guess a century ago, and these particles are present time ascending steadily in significance in the field of catalysis [1].

In fact, the nano catalysts is definited as the result of an fascinating and spreading out field of catalysts that are intended at the nanoscalelevel, particularly for heterogeneous catalysis [2-3].

### Journal Pre-proofs

nanocatalysts show excellent catalytic activity due to their vast surface-to-volume ratio that they increas contacting between the reactant molecules and catalyst considerably. Also, heterogeneous nanocatalysts have good thermal stabilities with substantial recoverability and reusability [4-6].

recently, the trend of scientists is more using biopolymer supports from renewable, endurable and abundant resources as efficient and interesting materials to reactions catalysis. Cellulose is the most worth and ordinary biopolymer, which is obtained from plants, bacteria and algae known with qualities such as hydrophobicity, chirality, biodegradability, economically, biocompability, and wide chemicalfunctionalizing capacity. These abilities of the cellulose make it an attractive and efficient support [7, 8]. Supported nano-maerials are emerging as a charming protocol to confirmed some transition metal complexes which are used for the synthesis of organic compounds [9-10]. The immobilization of metal catalysts on solid supports has been considered an efficient approach. Nano cellulose supported with palladium, platinum, zirconium, copper and nickel nano-particles have been advanced [8, 9, 11]. Recently, N-heterocyclic carbenes (NHCs) have attracted many researcher's attention as transition metal ligands. Nowadays, a extensive range of NHC ligands are commercially existent which show high activities in different main organic transformations when connected to metallic pre-catalysts [12]. The employ of immobilized Pd complexes has not been entirely applied. Based on the literature, there are the fewer cases for such support materials have been synthesized including nano cellulose-tagged diphenylphosphinate [9, 13, 14], triphenylphosphine [12] and ethylenediamine [15]. NHCs bind through stronger bonds with most of the metals, hindering the urgency of excess ligand in catalytic reaction [16].

These types of nanocatalysts (Pd based NHC functionalized nano cellulose) play a key role in formation of carbon-carbon bonding reactions and have a long history in synthesis of organic compounds [17]. Suzuki cross-coupling reactions, founded by Nobel laureate Akira Suzuki, [18] are the most important extensively employed methodology for the formation of carbon–carbon bonds [19, 20]. This reaction has become one of the most affectional synthetic methods for the synthesis of biaryl compounds which

3

include a extensive range of natural products and pharmaceuticals [21-24]. Palladium-catalyzed Suzuki cross-coupling reactions of arylhalides with arylboronic acids are the most impressive and attractive protocoles to selectively form biaryl compounds in organic synthesis [25-27].

Also, suzuki cross-coupling reactions can synthesize a kinds of compounds, such as heterocycles, naproxen anti-inflammatory drugs, montelukast asthma, chips and herbicides. In addition, they can be employed in engineering materials such as conductive polymers, molecular wires and liquid crystal [28, 29].

we present the anchoring of [2,2'-bipyridin]-4-amine (BPA) onto a nano cellulose backbone as a precursor, followed by coordination with Pd(OAc)<sub>2</sub> to prepare a novel, efficient and fascinating nano catalyst (Pd@BPA@CNC). Then it investigated Pd@BPA@CNC catalytic application for the Suzuki reaction of aryl halides with arylboronic acids at 70 °C in DMSO (Scheme1).



Scheme. 1. Procedure for the Suzuki reaction of arylhalides and arylboronic acids in the presence of

Pd@BPA@CNC as nanocatalyst

### Experimental

### **Chemicals and instruments**

All reagents were purchased from Merck and Aldrich and used without further purification. The surface morphology of samples was carried out by scanning electron microscopy (SEM, EM-3200). Transmission electron microscopy (TEM) experiments were conducted on a Philips EM 208 electron microscope. Melting points were measured with an Electrothermal 9100 apparatus. Thermo gravimetric analysis

(TGA) was performed on a Stanton Red craft STA-780 (London, UK) using N<sub>2</sub> as carrier gas with temperature ramp of 10 °C/min and from room temperature to 800 °C. The content of palladium was estimated by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) (Perkin Elmer Optima 2000 DV ICP-AES).

#### Nano catalyst preparation

### Preparations of Cellulose Nanocrystals (CNC) (1)

Acidic hydrolysis of Whatman filter paper was used to obtain the cellulose nanocrystals as reported in the literature with slight modification [30]. Hydrolysis of the cellulose was achieved after 3 h at 100 °C using 100 mL of 2.5 M HBr and alternative ultra-sonication. After dilution with twice-distilled water, the mixture was subjected to five washing/centrifugation cycles to remove excess acid and water-soluble residues. After neutralization up to around pH = 5, the fine cellulose nanoparticles started to disperse into the aqueous supernatant which were collected and centrifuged at 12,000 rpm for 60 min to remove ultrafine particles.

### Tosylation of nanocellulose to synthesize Tos@CNC (2)

Tos@CNC was prepared according to the reported method [30, 31]. 0.5 g of Nanocallulose was suspended in 10 mL of pyridine and the mixture was cooled to 10 °C. Afterwards, the Tosyl chloride (0.9 g, 5 mmol) was added to the mixture and stirred for 2 days at room temperature. After completion of the reaction, 100 mL of ethanol was added to the reaction mixture and the precipitation was collected by filtration process. The obtained product was washed with more ethanol (50 mL) for five times and kept in refrigerator with no drying (Scheme 2).

### Preparation of BPA@CNC (3)

A suspension containing 400 mg of Tos@CNC in methoanol was mixed with 20 mL of DMF (N, Ndimethyl formamide) and centrifuged 3 times to exchange methanol with DMF. Then, 400 mg of [2,2'bipyridin]-4-amine (BPA) was added to the above mixture and stirred for 24h at 100 °C. Afterwards, 50

### Journal Pre-proofs

mL deionized water was added to reaction mixture and obtained precipitate was centrifuged and separated. The product was washed more than 5 times with ethanol and water. The resulting product was dialyzed against deionized water for 3 days using a cellulose membrane which led to the water replacing (exchanging) with DMF and eventually the attained product was kept in refrigerator (Scheme 2).

### Preparation of Pd@BPA@CNC catalyst

0.50 g of BPA@CNC in DMF was added to a solution of  $Pd(CL)_2$  (0.10 g, 0.45 mmol) in 10 mL DMF under N<sub>2</sub> atmosphere and the obtained mixture was stirred for 24 h at 60 °C. After the reaction was completed, the mixture was cooled to room temperature and resulted product was collected by filtration process. The resulting black solid product was washed carefully with deionized water (3×25 mL), absolute ether (2×25 mL) and absolute ethyl alcohol (2×25 mL) and dried under vacuum oven at room temperature (Scheme 2).



Scheme. 2. General procedure for preparation of Pd@BPA@CNC catalyst

# General procedure of Suzuki reaction of arylhalides with arylboronic acids by Pd@BPA@CNC nanocatalysts

To synthesize biaryl derivatives using Suzuki reaction via C-C arylation reactions, aryl halide (1 mmol), arylboronic acid (1.6 mmol) and K<sub>2</sub>CO<sub>3</sub> (3 mmol) in DMSO (10 mL) were placed into a round bottom flask containing 10 mg of the Pd@BPA@CNC as nanocatalyst. The above obtained mixture was stirred at 70 °C for a definite time which is required for each substrate. After completion of the reaction, the solid catalyst was filtered and washed 5 times with deionized water and absolute ether and kept for reusability

study of the catalyst under resembling reaction conditions. The filtrate was extracted with ethyl acetate ( $3 \times 5 \ mL$ ), washed with deionized water and dried by anhydrous MgSO<sub>4</sub>. After that, MgSO<sub>4</sub> was filtered, the solvent was evaporated and the resulting product was purified by preparative TLC (eluent: petroleum ether/ethyl acetate, 20/1) (scheme 1).

### Selected spectra for two known products are given below:

4-Cyano-2'-methoxybiphenyl

<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  = 3.86(s, 3H, OCH<sub>3</sub>), 7.11 (d, J= 7.0 Hz, 1H Ar), 7.17-7.21 (m, 3H Ar), 7.32 (d, J= 7.8 Hz, 2H Ar), 7.50 (d, J= 7.8 Hz, 2H Ar) ppm.; <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  = 56.8, 111.0, 116.5, 117.2, 120.6, 125.1, 127.6, 129.2, 131.6, 132.4, 146.6, 159.7 ppm.

4-Cyano-3'-methoxybiphenyl

<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>): δ = 3.79(s, 3H, OCH<sub>3</sub>), 7.07-7.20 (m, 4H Ar), 7.56 (d, J= 7.3 Hz, 2H Ar), 7.70 (d, J= 7.3 Hz, 2H Ar) ppm.; <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>): δ = 57.6, 110.9, 112.2, 113.8, 119.5, 120.6, 129.9, 131.7, 134.6, 140.1, 140.0, 159.9 ppm.

### **Results and discussion**

### Characterization of prepared nanocell-AMPD-Pd

### Energy dispersive x-ray (EDX)

The EDX analysis of Pd@BPA@CNC is shown in Fig 1. As can be seen, Pd@BPA@CNC is composed of C, O and Pd, indicating Pd has been inserted in desired catalyst. In other words, there is a Pd peak, which is consistent with the ICP-AES results.

7



Fig. 1. EDX spectra of Pd@BPA@CNC

### **ICP-AES** analysis

The ICP-AES analysis was performed to determine the amount of Pd (82517 mg /L) in Pd@BPA@CNC

as catalyst.

### CHNS/O total elemental analysis

The CHNS/O analysis was employed to identify the elemental contents of the BPA@CNC. The results of

the elemental analysis are reported in Table 1.

Elemental name	Weight (%)	Weight (mg)	Response	Reten time (min)
N	N/A	N/A	75.623	1.283
C	39.07	1.544	10298.835	2.187
Н	6.12	0.242	5436.099	8.497
S	0.28	0.011	101.895	18.477
Total	45.47	3.951		

Table 1 Elemental analysis of BPA@CNC with the CHNS/O analysis

### Catalytic application of Pd@BPA@CNC for the Suzuki reaction

In order to investigate the optimum conditions, the reaction of 4-Bromoanisole and phenylboronic acid for the synthesis of 4-Methoxy biphenyl in the presence of the catalyst was selected as a model

reaction. The reaction was carried out with various amounts of the Pd@BPA@CNC as catalyst (5, 10 and 15 mg) at different temperatures (25 and 70 °C) in various solvents. As can be seen in table 2, the yield of the product was increased upon enhancing the temperature. In addition, as expected, different results were obtained by employing various solvents and amounts of the catalyst. According to the Table 2, 10 mg of the catalyst was determined as the optimum amount of the catalyst. The obtained results in Table 2 showed that optimal condition was 10 mg of Pd@BPA@CNC and 3 mmol  $K_2CO_3$  as base at 70 °C in DMSO (Table 2, entry 7).

	alarysi					
Entry	Solvent	Temperature (°C)	Catalyst (mg)	Base	Time (min)	Yield(%) <sup>a</sup>
1	DMF	25	10	$K_2CO_3$	100	28
2	DMSO	25	10	K <sub>2</sub> CO <sub>3</sub>	45	70
3	$H_2O$	25	10	K <sub>2</sub> CO <sub>3</sub>	75	34
4	Ethanol	25	10	$K_2CO_3$	70	35
5	Ethanol/ $H_2O(1:1)$	25	10	$K_2CO_3$	73	33
6	DMSO	70	5	$K_2CO_3$	35	87
7	DMSO	70	10	$K_2CO_3$	30	98
8	DMSO	70	15	$K_2CO_3$	30	99
9	DMSO	70	10	Et <sub>3</sub> N	42	87
10	DMSO	70	10	$Cs_2CO_3$	38	82
11	DMSO	70	10	KH <sub>2</sub> PO <sub>4</sub>	40	86

 Table 2 Optimization conditions for preparation 4-Methoxy biphenyl in the presence of Pd@BPA@CNC as nanocatalyst

Next, the obtained optimal conditions were exploited to assess the efficiency and generality of our catalytic procedure in Suzuki coupling reactions. For this purpose, the reaction of several substituted aryl halides (1 mmol) with arylboronic acids (1.6 mmol) in the presence of  $K_2CO_3$  (3 mmol) by using Pd@BPA@CNC (10 mg) as nano catalyst at 70 °C in DMSO were estimated (Table 3). Based on the obtained results from the Table 3 , using 4-bromoanisole, the reaction was carried out in short time and higher yield in respect of 4-bromobenzonitrile. Also, arylboronic acids including electron-donating groups (CF<sub>3</sub>, F) showed shorter time and better yield than those electron-withdrawing groups (OCH<sub>3</sub>). By comparing the results of arylboronic acids, it can be concluded that arylboronic acids with ethyl groups have longer reaction times and lower yields than other groups. As shown in Table 3, Most of the substituted bromobenzenes, chlorobenzenes afforded the corresponding biphenyl with similar yields and reaction

10

times. Besides, evaluating the effect of substituent position (*ortho*, *meta* and *para*)-either on the aromatic ring of aryl halides or arylboronic acids- over the yields and reaction times exhibited no evident preference for any of these positions.

 Table 3 one-pot reactions of biphenyl derivative using aryl halides and arylboronic acid derivative with Pd@BPA@CNC (10 mg) as nano catalyst in DMSO (10ml) conditions

				Timo			TOF	Melting	Point (°C)
Entry	Ar-X	arylboronic acid	Product	(min)	Yield (%)	TON	(h <sup>-1</sup> )	Found	Reported [Rf]
1	Br-OCH3	B(OH)2		30	98	980	1960	85-86	86 [32]
2		F <sub>3</sub> C-B(OH) <sub>2</sub>	F <sub>3</sub> C-	70	78	780	672	115-116	115-117 [33]
3		H <sub>3</sub> CO-B(OH) <sub>2</sub>	H <sub>3</sub> CO	25	85	850	2073	176	175-178 [34]
4	Br OCH3	B(OH) <sub>2</sub> H <sub>3</sub> CO	H <sub>3</sub> CO	25	81	810	1975	59-60	59 [34]
5	Br OCH3	B(OH) <sub>2</sub> OCH <sub>3</sub>	OCH <sub>3</sub>	25	77	770	1833	67-69	67-68 [34]
6		F B(OH) <sub>2</sub>	FOCH3	75	92	920	526	91-92	90 [34]
7	Br - OCH3	FB(OH) <sub>2</sub>	F-OCH3	75	82	820	539	46	45-47 [35]
8	Br-OCH3	FB(OH) <sub>2</sub>	F-OCH3	75	51	510	408	65-66	65-67 [36]
9	Br-OCH3	C <sub>2</sub> H <sub>5</sub> —B(OH) <sub>2</sub>		75	94	940	752	220	221 – 224 [37]
10	Br-CN	B(OH) <sub>2</sub>		30	99	990	1980	86-87	85-86 [38]
11	Br-CN	H <sub>3</sub> CO-B(OH) <sub>2</sub>	H <sub>3</sub> CO-CN	60	99	990	990	100	101-102 [38]

								3	
12	Br	B(OH) <sub>2</sub> H <sub>3</sub> CO		60	96	960	960	Colorles s oil	Colorless oil[38]
13	Br	B(OH) <sub>2</sub> OCH <sub>3</sub>		60	95	950	950	73	72-74 [38]
14	Br	C <sub>2</sub> H <sub>5</sub> —B(OH) <sub>2</sub>		35	98	980	1690	191	188-190 [39]
15		C <sub>2</sub> H <sub>5</sub> ———B(OH) <sub>2</sub>	C <sub>2</sub> H <sub>5</sub>	60	65	650	650	211-212	211-213 [40]
16	Br	C <sub>2</sub> H <sub>5</sub> ——B(OH) <sub>2</sub>	C <sub>2</sub> H <sub>5</sub> -	60	57	570	570	211-212	211-213 [40]
17	CI	C <sub>2</sub> H <sub>5</sub> ——B(OH) <sub>2</sub>	C <sub>2</sub> H <sub>5</sub>	60	42	420	420	211-212	211-213 [40]
18	Br	B(OH) <sub>2</sub>	$\bigcirc - \bigcirc$	50	92	920	1108	70	70 [32]
19	CI	B(OH)2		50	55	550	662	70	70 [32]

### Comparing superiority of Pd@BPA@CNC over some previously reported protocols

To estimate the performance and efficiency of our method, it was compared with several reported results in the literature, which were summarized in Table 4. The results displayed short times and remarkable yields in the presence of Pd@BPA@CNC nanocatalyst relative to other catalysts. Simple reaction conditions as well as, convenient work-up procedure makes it an advantageous protocol for the synthesis of the corresponding biaryl compounds in comparison with the other reported works in the literature (Table 4).

Entry	Catalyst Conditions		Time	Yield (%) <sup>a</sup>
				[Ref]
1	aminomethyldiphosphine–Pd(II) (1.2mmol)	DMF/H <sub>2</sub> O(3/3 ml), 80 °C	7 h	95[12]
2	ferrocene-tagged N-heterocyclic carbene (NHC)-Pd(II) (2 mol%)	Na <sub>2</sub> CO <sub>3</sub> (3 mmol), DMF:H <sub>2</sub> O(3:1), 80 °C	2 h	88[16]
3	Palladium N-Heterocyclic Carbene (0.02 mmol), K <sub>2</sub> CO <sub>3</sub> (1.2 eq)	i-PrOH (4 mL), r.t	6 h	98[41]
4	Pd(OAc) <sub>2</sub> /LHX (15mol%)	DMF/H <sub>2</sub> O(2 mmol), 50°C	3 h	93[42]
5	Pd (1.0 mol)	K <sub>3</sub> pO <sub>4</sub> .3H <sub>2</sub> O (1.5 mmol), H <sub>2</sub> O/Ethanol (2 ml), 80 °C	3 h	98[43]
6	CNC@BIA@Pd(10 mg), K <sub>2</sub> CO <sub>3</sub> (3 mmol)	70 °C, DMSO (10ml)	30 min	98 (Present work)

### Table 4 Comparison the results of Pd@BPA@CNC with other catalysts in the Suzuki reaction

<sup>a</sup>Yields refer to isolated pure products

The recyclability of the Pd@BPA@CNC was investigated using the one pot reactions of 4-bromoanisole with phenylboronic acid at 70 °C in DMSO solvent for the synthesis of 4-methoxy biphenyl as model reaction (Experimental section). After completion of the reaction, the solid nanocatalyst was filtered and washed carefully with deionized water and absolute ether to checking the reusability of the catalyst under the resembling reaction conditions. The results demonstrated that Pd@BPA@CNC is stable catalyst under reaction conditions and it can be recovered and reused four times without substantial loss of its catalytic activity (Fig. 2).



Fig. 2. The recycling of Pd@BPA@CNC as nanocatalyst

In conclusion, Pd based on [2,2'-Bipyridin]-4-amine functionalized nano cellulose (Pd@BPA@CNC) has been successfully synthesized and characterized by FT-IR, XRD, ICP-AES, EDX, SEM, TEM and TGA techniques. The catalytic activity of the nanocatalyst was investigated by one-pot synthesis of biphenyl products using aryl halides and arylboronic acid derivatives. This promising and effective methodology resulted in excellent yields of the products along with short reaction times, which makes this protocol a novel, biocompatible and economically noteworthy process for the Suzuki coupling reactions.

### Acknowledgments

The author acknowledges the University of Macau for support of this work.

### **References:**

- [1] A. Fihri, M. Bouhrara, B. Nekoueishahraki, J.M., Basset, V. Polshettiwar, Chem. Soc. Rev. 40 (2011) 5181-5203.
- [2] V. Polshettiwar, J. Thivolle-Cazat, M. Taoufik, F. Stoffelbach, S. Norsic, J.M. Basset, Angew. Chem. Int. Ed. 50 (2011) 2747-2751.
- [3] V. Polshettiwar, B. Baruwati, R.S. Varma, ACS nano, 3 (2009) 728-736.
- [4] A.R. Hajipour, Z. Khorsandi, Z. Abeshtian, Inorg Chem Commun. 107 (2019) 107470-107474.
- [5] H. Zhang, Y. Song, Z. Liang, X. Zhang, B. Xu, J. Guo, Inorg Chem Commun. 96 (2018) 101-105.
- [6] Y. Shao, S. Zhang, C. Wang, Z. Nie, J. Liu, Y. Wang, Y. Lin, J. Power Sources. 195 (2010) 4600-4605.
- [7] D. Zareyee, M. Serehneh, J Mol Catal A Chem. 391 (2014) 88-91.
- [8] C.M. Cirtiu, A.F. Dunlop-Briere, A. Moores, Green Chem. 13 (2011) 288-291.
- [9] Q. Du, Y. Li, Beilstein J. Org. Chem. 7 (2011) 378-385.

- [10] Y. Xu, L. Zhang, Y. Cui, J. Appl. Polym. Sci. 110 (2008) 2996-3000.
- [11] K.R. Reddy, N.S. Kumar, B. Sreedhar, M.L. Kantam, J Mol Catal A Chem. 252 (2006) 136-141.
- [12] X. Wang, P. Hu, F. Xue, Y. Wei, Carbohydr. Polym. 114 (2014) 476-783.
- [13]Q. Du, Y. Li, Res. Chem. Intermed. 38, (2012). 1807–1817.
- [14] S. Keshipour, S. Shojaei, A.Shaabani, Cellulose, 20 (2013) 973–980.
- [15] C. Zheng, Y. Li, W. Zheng, Chin. J. Chem. 29 (2009) 1983–1987.
- [16] D.M. Pore, D.S. Gaikwad, J.D. Patil, Monatsh Chem. 144 (2013) 1355-1361.
- [17] S. Guin, S.K. Rout, A. Banerjee, S. Nandi, B.K. Patel, Org. Lett. 14 (2012) 5294-5297.
- [18] N. Miyaura, K. Yamada, A. Suzuki, Tetrahedron Lett. 20 (1979) 3437-3440.
- [19] N. Miyaura, T. Yanagi, A.J.S.C. Suzuki, Synth. Commun. 11 (1981) 513-519.
- [20] N. Miyaura, A. Suzuki, Chem. Rev. 95 (1995) 2457-2483.
- [21] V. Polshettiwar, A. Decottignies, C. Len, A. Fihri, ChemSusChem. 3 (2010) 502-522.
- [22] L. Bai, J.X. Wang, Curr Org Chem.9 (2005) 535-553.
- [23] R. Franzén, Y. Xu, Can J Chem. 83 (2005) 266-272.
- [24] A.F., Littke, G.C. Fu, Angew. Chem. Int. Ed. 41 (2002) 4176-4211.
- [25] J.X. Li, X. Li, H. Tang, Y.Y. Zhang, Z.B. Han, Inorg Chem Commun. 103 (2019) 82-86.
- [26] R. Martin, S.L. Buchwald, Acc. Chem. Res. 41 (2008) 1461–1473.

- [27] L. Yin, J. Liebscher, Chem. Rev. 107 (2007) 133-173.
- [28] K.R. Reddy, N.S. Kumar, P.S. Reddy, B. Sreedhar, M.L. Kantam, J. Mol. Catal. Chem. 252 (2006) 12-16.
- [29] C.J. Mathews, P.J. Smith, T. Welton, ChemComm. 14 (2000) 1249-1250.
- [30] H. Sadeghifar, I. Filpponen, S.P. Clarke, D.F. Brougham, D.S. Argyropoulos, J. Mater. Sci. 46 (2011) 7344-7355.
- [31] E. Feese, H. Sadeghifar, H.S. Gracz, D.S. Argyropoulos, R.A. Ghiladi, Biomacromolecules, 12 (2011) 3528-3539.
- [32] D. Paul, S. Rudra, P. Rahman, S. Khatua, M. Pradhan, P.N. Chatterjee, J. Organomet. Chem. 871 (2018) 96-102.
- [33] D.S. Ziegler, K. Karaghiosoff, P. Knochel, Angew. Chem. Int. Ed. 57 (2018) 6701-6704.
- [34] B. Schmidt, M. Riemer, J. Org. Chem. 79 (2014) 4104-4118.
- [35] W. Erb, M. Albini, J. Rouden, J. Blanchet, J. Org. Chem. 79 (2014) 10568-10580.
- [36] A. Antoft-Finch, T. Blackburn, V. Snieckus, JACS. 131 (2009) 17750-17752.
- [37] M. Planellas, R. Pleixats, A. Shafir, Adv. Synth. Catal. 354 (2012) 651-662.
- [38] J.I. Kuroda, K. Inamoto, K. Hiroya, T. Doi, Eur. J. Org. Chem. 2009 (2009) 2251-2261.
- [39] J.M. Hammann, F.H. Lutter, D. Haas, P. Knochel, Angew. Chem. Int. Ed. 56 (2017) 1082-1086.
- [40] D. Qiu, H. Meng, L. Jin, S. Wang, S. Tang, X. Wang, F. Mo, Y. Zhang, J. Wang, Angew. Chem. Int. Ed. 52 (2013) 11581-11584.
- [41] F. Rajabi, W.R. Thiel, Adv. Synth. Catal. 356 (2014) 1873-1877.
- [42] S. Yaşar, S. Çekirdek, İ. Özdemir, Heteroat. Chem. 25 (2014) 157-162.
- [43] B. Li, Z. Guan, W. Wang, X. Yang, J. Hu, B. Tan, T. Li, Adv. Mater. 24 (2012) 3390-3395.

### **Graphical Abstract**



### Highlights

- ✓ Pd based on [2,2'-Bipyridin]-4-amine functionalized nano cellulose (Pd@BPA@CNC) as a novel nanocatalyst
- The catalytic activity of the nanocatalyst was probed through one-pot synthesis of biaryl derivatives
- ✓ This nanocatalyst can easily be separated and recycled from the products.

10

Yuqi Sun chemistry, Arts and Humanities

Majid Mohammadnia: organic chemistry, nano catalyst, magnetic catalyst, Suzuki reaction,

coupling reaction

12

### **Declaration of interests**

 $\boxtimes$  The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

□The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: