FULL PAPER

Synthesis, characterization and catalytic performance of palladium supported on pyridine-based covalent organic polymer for Suzuki-Miyaura reaction

Yi Han¹ | Jia-Qi Di¹ | Ai-Dong Zhao² | Zhan-Hui Zhang¹

¹Hebei Key Laboratory of Organic Functional Molecules, National Demonstration Center for Experimental Chemistry Education, College of Chemistry and Material Science, Hebei Normal University, Shijiazhuang 050024, P. R. China

²Analysis and Testing Center, Hebei Normal University, Shijiazhuang 050024,
P. R. China

Correspondence

Ai-Dong Zhao, Analysis and Testing Center, Hebei Normal University, Shijiazhuang 050024, P. R. China. Email: aidongzhao@163.com

Zhan-Hui Zhang, College of Chemistry and Material Science, Hebei Normal University, Shijiazhuang 050024, P. R. China.

Email: zhanhui@126.com

Funding information

National Natural Science Foundation of China, Grant/Award Number: 21272053; Science Technology Research Foundation of Hebei Normal University, Grant/Award Number: L2018Z06

1 | INTRODUCTION

In the past few years, covalent organic polymers (COPs) have emerged as a new class of materials because of their unique physical, chemical, mechanical and electrical properties, which are completely different from traditional linear or branched polymers.^[1] COPs exhibit wonderful applications in storage and separation,^[2] drug delivery,^[3] water treatment and CO₂ capture,^[4] energy conversion and storage,^[5] adsorption,^[6] as well as catalysis.^[7] In addition, COPs have better stability against various organic solvents, water, and even strong acidity or

A bipyridine-based covalent organic polymer (COP) was successfully synthesized by condensation of trimesoyl chloride (TMC) and 2,2'-bipyridine-5,5'diamine (Bpy) under ambient conditions. This material was modified by coordination of $PdCl_2$ to COP framework, affording a hybrid material, Pd@TMC-Bpy COP, which was applied as a highly efficient heterogeneous catalyst for Suzuki-Miyaura reaction under ligand-free conditions in ethyl lactate. The catalyst could be reused for five times without obvious loss of its activity.

KEYWORDS

covalent organic polymer, ethyl lactate, heterogeneous catalyst, Suzuki-Miyaura reaction

alkalinity. These unique advantages of COPs would make them more beneficial than other supports for uploading active catalytic species (e.g. metals) for catalysis, especially those catalytic reactions that are carried out under relatively stringent conditions. According to reports in the literature, some COPs have been used as supports for immobilized metals in various organic reactions, such as nitroarene reduction,^[8] Sonogashira cross-coupling,^[9] C-Se coupling reaction,^[10] and C-C coupling reactions.^[11]

Amide bonds are common and important in some functional polymers and materials. Aromatic polyamides are a class of high performance organic materials due to their excellent thermal, chemical and mechanical resistance.^[12] Bipyridine as a COP component has proven to be a useful building block for these backbones because of its excellent chemical stability and its ability to be used in potentially metal-compatible coordination sites.^[13] In addition, biomass-derived ethyl lactate (EL) has good properties such as stability, non-corrosiveness and good solubility in water and organic compounds. It has attracted wide attention as a new green medium and is applied in some useful organic conversions.^[14]

Among the catalytic reactions discovered in the last century, the palladium-catalyzed Suzuki-Miyaura crosscoupling reaction constitutes the most well-known and the widely used method for carbon-carbon bond construction method on a laboratory and industrial scale.^[15] Despite many successes have been achieved, unfortunately, many of these reactions use phosphine ligands or toxic organic solvents in a homogeneous process. Heterogeneous catalysis has many advantages over homogeneous catalysis, such as easy recovery, recyclability, enhanced stability and lower degree of Pd contamination in the final products. Immobilization of Pd-based catalysts to some supported solid materials such as carbon nanotubes,^[16] graphene,^[17] cellulose,^[18] chitosan/starch,^[19] agar/pectin composite,^[20] chitosancellulose micro beads,^[21] agar,^[22] sporopollenin microcapsule,^[23] poly(4-((pyridine-2ylimino)methyl)benzene-1,3-diol),^[24] TiO₂,^[25] montmorillonite K 10,^[26] zeolite Y,^[27] hydrotalcites,^[28] metal oxides,^[29] porous glass,^[30] carbon nanodiamond,^[31] metal-organic frameworks,^[32] and magnetic nanoparticles^[33] by physical adsorption or chemical bonding is a good method for solving the above problems. Although the rapid development of immobilization of Pd-based catalysts has been achieved, in some cases, the catalytic activities are lower than those in their homogeneous counterparts, low recycle performance due to leaching of Pd from the support, the catalyst synthesis method is complicated, and high reaction temperature is always required. Therefore, a highly active, easily separable, reusable catalytic system is still highly desirable for Suzuki-Miyaura reaction.

Based on the above analysis and continue our research interest in the development of new catalytic systems for organic conversions,^[34,35] herein, we describe a facile method for the synthesis of bipyridine-containing covalent organic polymer stabilized Pd as a catalyst for Suzuki-Miyaura reaction under ligand-free conditions in ethyl lactate.

2 | RESULTS AND DISCUSSION

2.1 | Preparation and characterization of covalent organic polymer supported palladium catalyst

To carry out this study, we prepared a bipyridinecontaining COP by the condensation of trimesoyl chloride (TMC) and 2,2'-bipyridine-5,5'-diamine (Bpy) by mechanochemical method. The polymerization was carried out in the presence of triethylamine under solvent-free grinding conditions at room temperature. The resulting dark yellow solid was collected and washed with acetone in a Soxhlet extractor to remove residual starting materials and by-products to give the designated TMC-Bpy COP (Scheme 1). This synthetic process is fairly



simple, cost effective and environmentally friendly. Subsequently, the obtained TMC-Bpy COP was treated with $PbCl_2$ solution of toluene under reflux conditions to afford a hybrid material, Pd@TMC-Bpy COP.

FT-IR spectra and XPS analysis were performed to confirm the structure and chemical composition of the COPs. As shown in the FT-IR spectra (Figure 1), the absorption band for TMC-Bpy COP at 3350 cm^{-1} was assigned to the N–H stretching vibration of amide



FIGURE 1 IR spectra of Bpy, TMC, TMC-Bpy COP and Pd@TMC-Bpy COP



linkage. The peak at 3025 cm⁻¹ was attributed to the stretching vibrations of the aromatic C–H bond. The C=O stretching vibration of TMC-Bpy COP occurred at 1674 cm⁻¹, and has obvious difference to TMC (C=O stretching vibration at 1760 cm⁻¹), which indicated the formation of amide bond between acyl chloride and the amine. In addition, the analysis of elementary content of the TMC-Bpy COP was as follows: C, 50.18, N, 11.39 and H, 11.36. Notably, FTIR spectra of Pd@TMC-Bpy



FIGURE 3 TGA profiles of TMC-Bpy COP and Pd@TMC-Bpy COP



FIGURE 2 XPS spectra of TMC-Bpy COP and Pd@TMC-Bpy COP: wide scan (a), high-resolution spectrum for the Pd 3d of Pd@TMC-Bpy COP (b), N 1 s of TMC-Bpy COP (c) and N 1 s of Pd@TMC-Bpy COP (d)

COP has not any apparent change to TMC-Bpy COP, which indicated the presence of $PdCl_2$ did not affect the structure of TMC-Bpy COP.

The XPS patterns of the TMC-Bpy COP and Pd@TMC-Bpy COP displayed chemical compositions of the materials (Figure 2). The XPS spectra of O1s, N1 s, and C1s corresponded to 532, 400 and 285 eV, respectively. XPS of Pd@TMC-Bpy COP showed two strong peaks at 337.9 eV and 343.2 eV, which were assigned to $3d_{5/2}$ and $3d_{3/2}$ states of Pd²⁺, respectively, indicating the Pd species is present in +2 oxidation states.^[36] In addition,

compared with the previously reported literature at 338.4 for free PdCl₂, the binding energy of 337.9 eV for Pd²⁺ species in Pd@TMC-Bpy COP shifted negatively by 0.5 eV, which indicated the palladium is coordinatively boned to the nitrogen atom of TMC-Bpy COP. The N1 s showed two peaks: 399.4 eV corresponding to the second-ary nitrogen and 400.7 eV associated with the pyridinic nitrogen in the TMC-Bpy COP matrix. As is konwn to us, a strong Pd-N interaction can lead to differences in the binding energy of nitrogen. Comparative N1 s of the parent TMC-Bpy COP and Pd@TMC-Bpy COP before



FIGURE 4 SEM images of TMC-Bpy COP (a), Pd@TMC-Bpy COP (b), and TEM images of TMC-Bpy COP (c) and Pd@TMC-Bpy COP (d)



FIGURE 5 EDX spectra of Pd@TMC-Bpy COP

WILEY Chemistry

and after the Pd²⁺ modification, only pyridinic N shifted positively 0.8 eV from 400.7 eV to 401.5 eV, which indicated that strong interaction exist between the Pd species and bipyridine moieties in the Pd@TMC-Bpy COP framework.

The thermal stability of the cross-linked COPs was evaluated by Thermogravimetric analysis (TGA) under nitrogen atmosphere at a heating rate of 10 °C min⁻¹ (Figure 3). It was clear from this figures that there was a little mass loss before 100 °C due to removal of the adsorbed water, and further heating showed a slight weight loss up to 331 °C for TMC-Bpy COP and 301 °C for Pd@TMC-Bpy COP. The chemical stability of Pd@TMC-Bpy COP was also investigated by dispersing

the samples in different organic solvents such as H_2O , MeOH, EtOH, CH₃CN, DMSO, DMF, CH₂Cl₂, THF, ethyl acetate, ethyl lactate (EL) and toluene for two days at room temperature. The sample was then collected by filtration, washed with acetone and dried under vacuum. To our delight, all samples also showed similar skeletal connections in the FT-IR spectra. The results clearly show that Pd@TMC-Bpy COP has excellent thermal and chemical stabilities.

The morphologies of TMC-Bpy COP and Pd@TMC-Bpy COP were investigated by SEM and TEM (Figure 4). The TMC-Bpy COP and Pd@TMC-Bpy COP materials displayed good crystallinity and a regular structure. The TEM images indicated that TMC-Bpy COP and

TABLE 1	Optimization	of the reaction	conditions for	r the synthesis	of compound 3a ^a
---------	--------------	-----------------	----------------	-----------------	------------------------------------

$B(OH)_2 + Br \xrightarrow{Pd@TMC-Bpy COF} 3a$								
Entry	Solvent	Base	Catalyst (mg)	Temperature (°C)	Time (h)	Yield (%) ^b		
1	H_2O	K ₂ CO ₃	20	Reflux	3.0	trace		
2	Ethanol	K ₂ CO ₃	20	Reflux	2.0	81		
3	THF	K ₂ CO ₃	20	Reflux	2.0	89		
4	DMF	K ₂ CO ₃	20	Reflux	2.0	91		
5	Toluene	K ₂ CO ₃	20	Reflux	2.0	92		
6	EL/H ₂ O (1:1)	K ₂ CO ₃	20	Reflux	3.0	63		
7	EL	K ₂ CO ₃	20	90	1.5	95		
8	EL	Cs ₂ CO ₃	20	90	2.0	91		
9	EL	CH ₃ COONa	20	90	2.0	47		
10	EL	Et ₃ N	20	90	2.0	trace		
11	EL	K ₂ CO ₃	20	100	1.5	95		
12	EL	K ₂ CO ₃	20	80	1.5	92		
13	EL	K ₂ CO ₃	20	60	2.0	71		
14	EL	K ₂ CO ₃	20	25	6.0	59		
15	EL	K ₂ CO ₃	0	90	8.0	0		
16	EL	K ₂ CO ₃	10	90	2.0	69		
17	EL	K ₂ CO ₃	15	90	2.0	83		
18	EL	K ₂ CO ₃	25	90	2.0	95		
19 ^c	EL	K ₂ CO ₃	1.2	90	8.0	86		
20 ^d	EL	K ₂ CO ₃	200	90	1.5	93		
21 ^e	EL	K ₂ CO ₃	20	90	1.5	92		

^aExperimental conditions: bromobenzene (1.0 mmol), phenylboronic acid (1.2 mmol), catalyst (20 mg, 6.6×10^{-6} mol of Pd), solvent (2 ml) under air, unless otherwise specified in the Table 1.

^bIsolated yields.

 $^{c}6.6\times10^{-4}$ mol% of $PdCl_{2}$ was used as catalyst.

^dThe reaction was carried out in 10 mmol scale.

^e0.05 g poly(4-vinylpyridine) was added.

6 of 11 WILEY Organometallic Chemistry

Pd@TMC-Bpy COP have a sheet-like morphology. After the incorporation of Pd, the sheet-like morphology of the original TMC-Bpy COP was observed to be maintained to some extent. The presence of Pd nanoparticles on Pd @TMC-Bpy COP can be clearly distinguished as dark spots in Figure 4(d).

TABLE 2	Substrate scope	of the c	couplings o	f aryl	bromides	with a	rylboronic	acids
	1		1 0	2			2	

$R^{1} \xrightarrow{B(OH)_{2}} + R^{2} \xrightarrow{Pd@TMC-Bpy COF} R^{1} \xrightarrow{R^{2}} R^{2}$								
Entry	R ¹	R ²	Product	Time (h)	Yield (%) ^b	TON	TOF (h^{-1})	m.p. (°C)
1	Н	Н	3a	1.5	95	143939	95959	70-71
2	Н	3-OH	3b	1.5	94	142424	94949	164-165
3	Н	4-OMe	3c	1.5	93	140909	93939	89-90
4	Н	4-Me	3d	1.5	94	142424	94949	49-50
5	Н	4-Cl	3e	2.0	91	137878	91918	78–79
6	Н	4-NO ₂	3 f	1.5	95	143939	95959	60-61
7	Н	4-CN	3g	1.5	95	143939	95959	85-86
8	Н	4-CHO	3h	1.5	93	140909	93939	60-61
9	3-OMe	Н	3i	1.5	93	140909	93939	89-90
10	4-Et	Н	3j	1.5	91	137878	91918	46-47
11	4-CMe ₃	Н	3k	1.5	93	140909	93939	53-54
12	4-F	Н	31	1.5	89	134848	89899	74–75
13	4-Cl	Н	3m	1.5	90	136364	90909	78–79
14	4-Br	Н	3n	1.5	95	143939	95959	91-92
15	3-OMe	4-OMe	30	1.5	92	139394	92929	60-61
16	3-OMe	4-Me	3p	1.5	91	137878	91918	80-81
17	3-OMe	4-CN	3q	1.5	95	143939	95959	oil
18	3-OMe	4-CHO	3r	1.5	90	136364	90909	oil
19	4-Me	4-OMe	3s	1.5	92	139394	92929	112–113
20	4-Me	4-Me	3t	1.5	92	139394	92929	125-126
21	4-Me	4-CN	3u	1.5	95	143939	95959	112-113
22	4-Me	4-NO ₂	3v	1.5	93	140909	93939	139–140
23	4-Me	4-CHO	3w	1.5	91	137878	91918	106-107
24	4-CMe ₃	4-OMe	3x	1.5	94	142424	94949	127-128
25	4-CMe ₃	4-Me	3у	1.5	93	140909	93939	75–76
26	4-CMe ₃	4-CN	3z	1.5	95	143939	95959	134–135
27	4-CMe ₃	4-CHO	3aa	1.8	93	140909	93939	103-104
28	4-Br	4-OMe	3ab	1.5	94	142424	94949	143–144
29	4-Br	4-Cl	3ac	1.5	91	137878	91918	147–148
30	4-Br	4-NO ₂	3ad	1.5	95	143939	95959	173–174
31	4-Br	4-CN	3ae	1.5	95	143939	95959	144–145
32	4-Br	4-CHO	3af	1.5	93	140909	93939	138-139

^aExperimental conditions: aryl halides (1.0 mmol), aryl boronic acid (1.2 mmol), potassium carbonate (1.5 mmol), Pd@TMC-Bpy (20 mg, 6.6×10^{-4} mol% of Pd), ethyl lactate (2 ml) under air at 90 °C. TON: (turnover number, yield of product/per mol of Pd). TOF: (turn over frequency, TON/time of reaction).18a ^bIsolated yield.

Additionally, The EDS spectrum of Pd @TMC-Bpy COP clearly exhibited the existence of C, N, O, Pd and Cl elements (Figure 5). This result also revealed that Pd (II) catalyst was obtained. Inductively coupled plasmaatomic emission spectroscopy (ICP-AES) confirmed the amount of Pd in Pd@TMC-Bpy COP as 3.54 wt%.

2.2 | Evaluation of the catalytic activity of Pd@TMC-Bpy COP for Suzuki-Miyaura reaction

Thereafter the successful synthesis and characterization of Pd@TMC-Bpy COP, its catalytic activity was then evaluated in Suzuki-Miyaura coupling reaction, one of the representative Pd-catalyzed reactions. Some control experiments were conducted using bromobenzene and phenylboronic acid as model substrates to optimize the reaction conditions by varying different parameters such as solvent, base, temperature as well as the loading of the catalyst. Some representative results were shown in Table 1. At first, the solvent effect was examined (Table 1, entries 1-7). It was found that ethyl lactate (EL) was the most suitable solvent for the reaction in terms of yield and the reaction rate. Subsequently, a brief screening of bases revealed that K₂CO₃ was the most effective one. Furthermore, by monitoring the reaction at various temperatures, it was found that the reaction temperature of 90 °C was the best choice. Finally, optimization of the loadings of the catalyst showed that 20 mg catalyst gave the optimal yield of 3a. Increasing the amount of catalyst had no significant effect on the reaction yield (Table 1, entry 18). When the reaction was conducted with a lower catalyst loading, the product **3a** was furnished in lower yields. Control experiment revealed that the formation of the desired product was not observed in the absence of a catalyst. The homogenous catalyst PdCl₂ was tested and it gave lower yield in comparison with Pd@TMC-Bpy COP (entry 19). Therefore, we inferred that the optimum reaction conditions were achieved with K₂CO₃ as the base in EL at 90 °C in the presence of 20 mg of catalyst (Table 1, entry 7).

To explore the practical utility of this method, a gramscale experiment was performed with bromobenzene (10.0 mmol), phenylboronic acid (12.0 mmol) and catalyst (200 mg) in EL (20 ml). As anticipated, the desired **3a** was formed with minimal loss of yield (93%), which suggested that the methodology is an economic and practical process for the preparation of various biphenyl products.

After the reaction conditions were established, the generality of this new protocol was evaluated in Suzuki-Miyaura reactions against a variety of substituted arylboronic acids with aryl halides. As illustrated in Table 2, the current reaction system was suitable for a wide range of aryl bromides with phenyl boronic acid under the optimized conditions. No matter whether the benzene ring of aryl bromides was substituted with either an electron-donating or electron-withdrawing group, all of them delivered the desired products in good to excellent yields (Table 2, entries 1-8). Importantly, a variety of functional groups, such as free OH, methoxy, methyl, nitrile, and aldehyde functionalities were all compatible with the reaction conditions. We were pleased to find that the current method is also applicable for aryl bromides bearing chloro substituent to afford the corresponding products 3e and 3ac in high yields. Subsequently, a series of arylboronic acids were investigated under the optimal conditions. Phenyl boronic acid or the substituted arylboronic acids with either an electron-donating-group (such as -OMe, -Me and -CMe₃, entries 9-11) or an electron-withdrawing group (such as -F, -Cl, -Br, entries 12-14) were well tolerated in this transformation, delivering the biphenyl product in excellent yields, indicating that the electronic effect on arylboronic acids was insensitive in current system. In addition, TON and TOF values are the key parameters for industrial applications,^[19] they were calculated for very reaction and are presented in Table 2.

Furthermore, this catalytic system allowed for the coupling with heteroatom-containing arylboronic acids such as pyridin-4-ylboronic acid and thiophen-3-ylboronic acid under the optimal conditions, known as a less efficient reagent, to provide 72% and 63% isolated yields for the corresponding cross-coupling products **4a** and **4b**, respectively (Scheme 2).

In addition, the optimized conditions were used to synthesize polyaromatic compounds via dual Suzuki-Miyaura couplings formation of two C-C bonds in a



SCHEME 2 Synthesis of biaryls using heteroaryl boronic acids



SCHEME 3 Synthesis of terphenyl via dual Suzuki-Miyaura couplings

8 of 11 WILEY-Organometallic

single operation (Scheme 3). Indeed, the dual Suzuki-Miyaura couplings between dibromoaryl (5) and two molecules of arylboric acids have been performed to produce terphenyl and its derivatives with excellent yields. The reaction was exhaustive dual couplings, no monocoupling product was observed.

3 | RECYCLABILITY OF SUPPORTED CATALYST

The reusability and durability of the catalyst were investigated by performing model reaction under the optimal conditions. After completion of the reaction, the catalyst was recovered by filtration, washed with ethyl acetate and then dried at 60 °C under reduced pressure. The recovered catalyst was reused for the subsequent catalytic runs without further activation (Figure 6). It was found that the stability and efficiency of Pd/COP are constant even after five cycles of testing. The TEM and SEM images showed that no obvious change was observed in morphology and size of the Pd@TMC-Bpy COP after five runs (Figure 7). The FT-IR spectrum of the recovered Pd@TMC-Bpy COP also showed no significant change in functionality. Leaching of Pd from the solid catalyst in the filtrate was also analyzed by ICP-MS. It was found that the Pd content in the solution was less than 1.0 ppm even after five reaction cycles. This indicates that the Pd catalyst is heterogeneous and remains on the support under the reaction conditions. Further check of the heterogeneous



FIGURE 6 The recycle test of Pd@TMC-Bpy COF



Applied Organometallic 9 of 11

nature of the catalyst, poisoning test was also performed on the model reaction.^{19e} When commercially available poly(4-vinylpyridine) was added to the reaction mixture before starting the reaction, no significant inhibition reaction was observed (Table 1, entry 21), which clearly demonstrates that our novel catalyst is heterogeneous in nature.^[37]

4 | CONCLUSION

In summary, a bipyridine functionalized COP has been successfully prepared by a simple and environmentally friendly mechanochemical grinding method by condensation of trimesoyl chloride and 2,2'-bipyridine-5,5'diamine under solvent-free and room temperature conditions. The prepared COP stabilized Pd catalyst show high catalytic activity for Suzuki-Miyaura reaction in ethyl lactate under ligand-free conditions. The catalysts could be conveniently separated from the products and reused without significant loss of catalytic activity.

5 | EXPERIMENTAL

5.1 | Instruments and reagents

All solvents and chemicals were obtained commercially and were used without further purification unless otherwise stated. 2,2'-Bipyridine-5,5'-diamine (Bpy) was prepared according to the method reported in the literature.^[38] Surface morphology and particle size were investigated using a Hitachi S-4800 SEM instrument. Transmission electron microscope (TEM) observation was performed at 80 KV using Hitachi H-7650 microscope. Melting points were determined on X-5 apparatus and were uncorrected. The IR spectra were obtained with KBr pellets in the range of 400-4000 cm⁻¹ using a Thermo Fisher is50 spectrometer. The ¹H NMR and ¹³C NMR spectra were recorded on a Bruker AV III-500 or Zhongke Niujin AS 400 spectrometer using TMS as internal standard. The ICP-MS analyses were carried out with a X Series 2 spectometer.

5.2 | Synthesis of TMC-Bpy COP

Trimesoyl chloride (2.64 g, 10 mol) and 2,2'-bipyridine-5,5'-diamine (1.86 g, 15 mmol) were placed in an agate mortar to ground with pestle at room temperature. After 15 minutes, a dark yellow color solid was formed. After that time, 30 drops of triethylamine were added and the mixture was ground for further 30 minutes. The resulting dark yellowish solid was washed with acetone in a Soxhlet extractor for 24 hr and dried in vacuo at 80 °C overnight to afford a brown COP in 85% isolated yield.

5.3 | Synthesis of Pd@TMC-Bpy COP

In a round bottom flask, 600 mg TMC-Bpy COP was treated with palladium chloride (177 mg, 1 mmol) in 100 ml of toluene under N₂ atmosphere and the reaction mixture allowed to stir at 110 °C for about 12 hr until the color of solid from yellow to gray. The solid was isolated from reaction mixture and washed with acetone in a Soxhlet extractor for 24 hrs and dried in vacuo at 80 °C.

5.4 | General procedure for Suzuki-Miyaura coupling reaction

Aryl halides (1.0 mmol), aryl boronic acid (1.2 mmol), potassium carbonate (1.5 mmol) and Pd@TMC-Bpy (20 mg) were added to 2 ml ethyl lactate in a round bottom flask. Then the reaction mixture was allowed to stir at 90 °C and the progress of the reaction was monitored by TLC. After completion of the reaction, the catalyst was separated by filtration. The mixture was diluted with H_2O and the product was extracted with EtOAc. The combined organic layer was washed with brine and dried over Na₂SO₄. The crude product was purified by column chromatography to give the desired pure product. The characterization data and copies of ¹H NMR and ¹³C NMR spectra of all products have been provided in the Supporting Information.

5.5 | Selected spectra data of some products

4-Fluoro-1,1'-biphenyl (3l)

White solid; m.p. 74–75 °C; IR (KBr): 2934, 1207, 1053, 758, 588; ¹H NMR (400 MHz, CDCl₃) δ 7.62–7.59 (m, 4H), 7.49 (t, 2H, J = 7.6 Hz), 7.40 (t, 1H, J = 7.4 Hz), 7.20–7.15 (m, 2H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 162.5 (d, J_{C-F} = 245.0 Hz), 140.3, 137.3, 128.8, 128.7 (d, J_{C-F} = 8.0 Hz), 127.3, 127.1, 115.6 (d, J_{C-F} = 21.0 Hz) ppm.

3-Phenylthiophene (4b)

Yellow solid; m.p. 91–92 °C; IR (KBr): 2996, 1611, 1522,1429, 903; ¹H NMR (400 MHz, CDCl₃) δ 7.67 (d, 2H, J = 8.4 Hz), 7.52 (s, 1H), 7.49–7.43 (m, 4H), 7.40–7.34 (m, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 142.4, 135.9, 128.8, 127.2, 126.4, 126.3, 126.2, 120.4 ppm.

4,4"-Diethyl-1,1':4',1"-terphenyl (6b)

White solid; m.p. 278–279 °C; IR (KBr): 3027, 2897, 1601, 1511, 841; ¹H NMR (400 MHz, CDCl₃) δ 7.72–7.68 (m,

10 of 11 WILEY Organometallic Chemistry

4H), 7.62 (d, 4H, J = 8.4 Hz), 7.35 (d, 4H, J = 8.4 Hz), 2.76 (q, 4H, J = 7.6 Hz), 1.34 (t, 6H, J = 7.6 Hz) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 143.4, 139.8, 138.2, 128.4, 127.3, 126.9, 28.5, 15.6 ppm.

[1,1':4',1"-Terphenyl]-4,4"-dicarbonitrile (6c)

White solid; m.p. 296–297 °C; IR (KBr): 3033, 2215, 1625, 1500, 832; ¹H NMR (400 MHz, CDCl₃) δ 7.77 (t, 4H, J = 7.6 Hz), 7.70–7.64 (m, 6H), 7.49 (d, 2H, J = 8.8 Hz) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 144.5, 138.1, 132.7, 132.3, 128.8, 127.6, 111.4 ppm.

ACKNOWLEDGEMENTS

Financial support from the National Natural Science Foundation of China (No. 21272053) and the Science Technology Research Foundation of Hebei Normal University (No. L2018Z06) is gratefully acknowledged.

AUTHOR CONTRIBUTIONS

Yi Han and Jia-Qi Di contributed equally to this work.

ORCID

Zhan-Hui Zhang D https://orcid.org/0000-0002-1082-5773

REFERENCES

- [1] Z. H. Xiang, D. P. Cao, L. M. Dai, Polym. Chem. 2015, 6, 1896.
- [2] W. Chen, L. Huang, X. F. Yi, A. M. Zheng, Phys. Chem. Chem. Phys. 2018, 20, 6487.
- [3] H. R. Wang, W. W. Zhu, J. J. Liu, Z. L. Dong, Z. Liu, ACS Appl. Mater. Interfaces 2018, 10, 14475.
- [4] S. Bhowmik, R. G. Jadhav, A. K. Das, J. Phys. Chem. C 2018, 122, 274.
- [5] Z. H. Xiang, Q. B. Dai, J. F. Chen, L. M. Dai, Adv. Mater. 2016, 28, 6253.
- [6] R. Gomes, P. Bhanja, A. Bhaumik, *Chem. Commun.* 2015, 51, 10050.
- [7] R. Khatioda, D. Talukdar, B. Saikia, K. K. Bania, B. Sarma, *Cat. Sci. Technol.* 2017, *7*, 3143.
- [8] R. Khatioda, D. Pathak, B. Sarma, ChemistrySelect 2018, 3, 6309.
- [9] V. Sadhasivam, M. Mariyappan, A. Siva, *ChemistrySelect* 2018, 3, 13442.
- [10] V. Sadhasivam, R. Balasaravanan, C. Chithiraikumar, A. Siva, *ChemCatChem* 2018, 10, 3833.
- [11] P. Y. Ju, S. J. Wu, Q. Su, X. D. Li, Z. Q. Liu, G. H. Li, Q. L. Wu, J. Mater. Chem. A 2019, 7, 2660.
- [12] Y. Sim, Y. X. Shi, R. Ganguly, Y. X. Li, F. Garcia, *Chem. Eur. J.* 2017, 23, 11279.
- [13] a)E. M. Johnson, R. Haiges, S. C. Marinescu, ACS Appl. Mater. Interfaces 2018, 10, 37919. b)H. B. Aiyappa, J. Thote, D. B.

Shinde, R. Banerjee, S. Kurungot, *Chem. Mater.* **2016**, *28*, 4375. c)J. Q. Zhang, Y. S. Peng, W. G. Leng, Y. A. Gao, F. F. Xu, J. L. Chai, *Chin. J. Catal.* **2016**, *37*, 468.

- [14] a)J. P. Wan, S. Cao, C. F. Hu, C. P. Wen, Asian J. Org. Chem.
 2018, 7, 328. b)M. Zhang, Q. Y. Fu, G. Gao, H. Y. He, Y. Zhang, Y. S. Wu, Z. H. Zhang, ACS Sustainable Chem. Eng. 2017, 5, 6175. c)L. Wei, X. W. Chen, Y. Y. Liu, J. P. Wan, Chin. J. Org. Chem. 2016, 36, 954. d)G. Gao, Y. Han, Z. H. Zhang, ChemistrySelect 2017, 2, 11561. e)G. Gao, M.-N. Chen, L.-P. Mo, Z.-H. Zhang, Phosphorus, Sulfur Silicon Relat. Elem. 2019, 194, 528.
- [15] a)A. Biffis, P. Centomo, A. Del Zotto, M. Zeccal, Chem. Rev. 2018, 118, 2249. b)F. S. Han, Chem. Soc. Rev. 2013, 42, 5270.
- [16] M. Adib, R. Karimi-Nami, H. Veisi, New J. Chem. 2016, 40, 4945.
- [17] a)K. Bahrami, S. N. Kamrani, *Appl. Organomet. Chem.* 2018, 32, e4102. b)B. Heidari, M. M. Heravi, M. R. Nabid, R. Sedghi, S. E. Hooshmand, *Appl. Organomet. Chem.* 2019, 33, e4632.
- [18] a)N. Y. Baran, T. Baran, A. Mentes, *Appl. Catal. A: Gen.* 2017, 531, 36. b)T. Baran, I. Sargin, A. Mentes, M. Kaya, *Appl. Catal. Gen.* 2016, 523, 12.
- [19] a)T. Baran, N. Y. Baran, A. Mentes, Appl. Organomet. Chem.
 2018, 32, e4075. b)T. Baran, N. Y. Baran, A. Mentes, Appl. Organomet. Chem. 2018, 32, e4076. c)T. Baran, A. Inanan, Mentes, Carbohydr. Polym. 2016, 145, 20. d)T. Baran, J. Colloid Interface Sci. 2017, 496, 446. e)T. Baran, E. Aciksoz, A. Mentes, J. Mol. Catal. A: Chem. 2015, 407, 47. f)T. Baran, I. Sargin, M. Kaya, A. Mentes, J. Mol. Catal. A: Chem. 2016, 420, 216. g)T. Baran, J. Mol. Struct. 2017, 1141, 535. h)T. Baran, A. Mentes, J. Mol. Struct. 2016, 1122, 111. i)T. Baran, A. Mentes, J. Mol. Struct. 2017, 1134, 591.
- [20] T. Baran, Carbohydr. Polym. 2018, 195, 45.
- [21] T. Baran, I. Sargin, M. Kaya, A. Mentes, *Carbohydr. Polym.* 2016, 152, 181.
- [22] a)T. Baran, N. Y. Baran, A. Mentes, Int. J. Biol. Macromol. 2018, 115, 249. b)T. Baran, Ultrason. Sonochem. 2018, 45, 231.
- [23] T. Baran, I. Sargin, M. Kaya, A. Mentes, T. Ceter, J. Colloid Interface Sci. 2017, 486, 194.
- [24] a)T. Baran, N. Y. Baran, A. Mentes, J. Mol. Struct. 2018, 1160, 154.
 b)N. Y. Baran, T. Baran, A. Mentes, M. Karakisla, M. Sacak, J. Organomet. Chem. 2018, 866, 87.
- [25] M. Nasrollahzadeh, S. M. Sajadi, J. Colloid Interface Sci. 2016, 465, 121.
- [26] A. Mahanta, P. K. Raul, S. Saikia, U. Bora, A. J. Thakur, *Appl. Organomet. Chem.* 2018, 32, e4192.
- [27] A. Tadjarodi, M. Dehghani, M. Imani, Appl. Organomet. Chem. 2018, 32, e4594.
- [28] B. Van Vaerenbergh, K. De Vlieger, K. Claeys, G. Vanhoutte, J. De Clercq, P. Vermeir, A. Verberckmoes, *Appl. Catal. A: Gen.* 2018, 550, 236.
- [29] G. J. Lichtenegger, M. Maier, M. Hackl, J. G. Khinast, W. Gossler, T. Griesser, V. S. P. Kumar, H. Gruber-Woelfler, P. A. Deshpande, J. Mol. Catal. A: Chem. 2017, 426, 39.
- [30] C. Schmoger, T. Szuppa, A. Tied, F. Schneider, A. Stolle, B. Ondruschka, *ChemSusChem* 2008, 1, 339.

- [31] A. Elhage, A. E. Lanterna, J. C. Scaiano, ACS Sustainable Chem. Eng. 2018, 6, 1717.
- [32] a)R. Sun, B. Liu, B. G. Li, S. Y. Jie, *ChemCatChem* 2016, *8*, 3261. b)S. Tahmasebi, J. Mokhtari, M. R. Naimi-Jamal, A. Khosravi, L. Panahi, *J. Organomet. Chem.* 2017, *853*, 35. c)A. W. Augustyniak, W. Zawartka, J. A. R. Navarro, A. M. Trzeciak, *Dalton Trans.* 2016, *45*, 13525.
- [33] a)A. K. Rathi, M. B. Gawande, J. Pechousek, J. Tucek, C. Aparicio, M. Petr, O. Tomanec, R. Krikavova, Z. Travnicek, R. S. Varma, R. Zboril, Green Chem. 2016, 18, 2363. b)R. K. Sharma, S. Dutta, S. Sharma, R. Zboril, R. S. Varma, M. B. Gawande, Green Chem. 2016, 18, 3184. c)M. Arghan, N. Koukabi, E. Kolvari, Appl. Organomet. Chem. 2018, 32, e4346. d)A. Dadras, M. R. Naimi-Jamal, F. M. Moghaddam, S. E. Ayati, Appl. Organomet. Chem. 2018, 32, e3993. e)M. Kempasiddhaiah, V. Kandathil, R. B. Dateer, B. S. Sasidhar, S. A. Patil, S. A. Patil, Appl. Organomet. Chem. 2019, 33, e4846. f)T. Baran, Catal. Lett. 2019, 149, 1496. g)T. Baran, Catal. Lett. 2019, 149, 1721. h)T. Baran, I. Sargin, M. Kaya, P. Mulercikas, S. Kazlauskaite, A. Mentes, Chem. Eng. J. 2018, 331, 102. i)A. Khazaei, M. Khazaei, M. Nasrollahzadeh, Tetrahedron 2017, 73, 5624.
- [34] a)Y. Han, M. Zhang, Y. Q. Zhang, Z. H. Zhang, Green Chem.
 2018, 20, 4891. b)M. Zhang, Y. Han, J. L. Niu, Z. H. Zhang, Adv. Synth. Catal. 2017, 359, 3618. c)M. Zhang, Y. H. Liu, Z. R. Shang, H. C. Hu, Z. H. Zhang, Catal. Commun. 2017, 88, 39. d)C. T. Ma, J. J. Wang, A. D. Zhao, Q. L. Wang, Z. H. Zhang, Appl. Organomet. Chem. 2017, 31, e3888. e)X. N. Zhao, H. C. Hu, F. J. Zhang, Z. H. Zhang, Appl. Catal. A: Gen. 2014, 482, 258.

- [35] a)W. H. Zhang, M. N. Chen, Y. Hao, X. Jiang, X. L. Zhou, Z. H. Zhang, J. Mol. Liq. 2019, 278, 124. b)G. Gao, P. Wang, P. Liu, W. H. Zhang, L. P. Mo, Z. H. Zhang, Chin. J. Org. Chem. 2018, 38, 846. c)R. Y. Guo, P. Wang, G. D. Wang, L. P. Mo, Z. H. Zhang, Tetrahedron 2013, 69, 2056; d)R. Y. Guo, Z. M. An, L. P. Mo, S. T. Yang, H. X. Liu, S. X. Wang, Z. H. Zhang, Tetrahedron 2013, 69, 9931.
- [36] H. Mahdavi, O. Rahmani, Catal. Lett. 2016, 146, 2292.
- [37] A. S. Roy, J. Mondal, B. Banerjee, P. Mondal, A. Bhaumik, S. M. Islam, *Appl. Catal. A: Gen.* 2014, 469, 320.
- [38] M. Albrecht, I. Janser, A. Lutzen, M. Hapke, R. Frohlich, P. Weis, *Chem. Eur. J.* 2005, 11, 5742.

SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of the article.

How to cite this article: Han Y, Di J-Q, Zhao A-D, Zhang Z-H. Synthesis, characterization and catalytic performance of palladium supported on pyridine-based covalent organic polymer for Suzuki-Miyaura reaction. *Appl Organometal Chem.* 2019;e5172. <u>https://doi.org/10.1002/aoc.5172</u>