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### FULL PAPER



# The capable Pd complex immobilized on the functionalized polymeric scaffold for the green benzylation reaction

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The Pd complex immobilized on the functionalized polymeric support was prepared by the functionalization of the 4-(benzyloxy)benzyl chloride polymer with 5-phenyl-1-H-tetrazole and the subsequent complexation with PdCl<sub>2</sub>. Then, it was characterized with different methods and used as catalyst in the green benzylation reaction of various aryl cyanamides with benzyl bromide and K<sub>2</sub>CO<sub>3</sub> in EtOH at 60°C for the appropriate times. Also, the antibacterial properties of the Pd polymer-supported complex were studied against a number of gram-positive and gram-negative bacteria, and in some cases, it has the same effect as a tetracycline standard antibiotic against Bacillus thuringiensis (a gram-positive bacterium) and Serratia marcescens (a gram-negative bacterium).

#### K E Y W O R D S

benzyl bromide, cyanamides, heterogeneous catalyst, the 5-phenyl-1-*H*-tetrazole ligand, the palladium polymer-supported complex

# **1** | INTRODUCTION

An effective way to encounter the challenges of energy and sustainability is the Catalysis field in microscales and nanoscales.<sup>[1]</sup> Simple recovery and efficient reusability of these compounds are the dominant characteristics in most of the processes of synthesis of novel catalysts in accordance of economic and environmental issues.<sup>[2,3]</sup> Recently, heterogeneous palladium catalysts have been obtained considerable attraction and utilized in various transformations.<sup>[4–6]</sup> organic Immobilization of nanoparticles on solid supported substances such as graphene oxide,<sup>[7]</sup> permeable silica,<sup>[8]</sup> and polymers<sup>[9]</sup> will construct suitable heterogeneous catalyst systems. Also, employing different type of heterogeneous catalysts including organic functional groups bounding to the active metals on the surfaces of organic polymers have been shown variety of special properties.[10-12] Particularly, several methods, like as polyol method, photochemical and chemical reduction, thermal decomposition, ion

exchange, and vapor deposition have been applied in the preparation of Pd nanoparticles. For stabilization, they usually require a limiting agent.<sup>[13]</sup> According to the difficulties of isolation following standard processes for prepared nanoparticles, the immobilization on heterogeneous support was utilized to facilitate their dispersion and stabilization.<sup>[14,15]</sup>

The reactions of molecules with a nitrile functional group are among the most class of significant chemicals laboratory and industrial applications because of their special structure and reactivity.<sup>[16–18]</sup> The history of calcium cyanamide (CaNCN) as a fertilizer is related to 19th century when later used as source of nitric acid and ammonia to apply in production of metal cyanamides.<sup>[19]</sup> However, in recent years, synthesis of organic cyanamides (RNHCN or RR'NCN) have been noticeable for chemists.<sup>[20]</sup> Cyanamides (RR'NCN) not only are useful intermediates for the synthesis of heterocyclic compounds but also indicate inhibition activity for tumor growth.<sup>[21]</sup> The most straightforward method for

synthesis of monosubstituted and disubstituted cyanamide derivatives is the direct alkylation of metal cyanamides.<sup>[22]</sup> N-Cyanation of a variety of secondary amines via in situ generation cyanogen chloride was investigated by Zhu et al. in 2014.<sup>[23]</sup> Establishing of active agents like [CN]<sup>+</sup> via halogenation of thiourea and in the following reaction with TMSCN, in presence of alkyl and aryl secamines, gives expectable cyanamides in good yield.<sup>[24]</sup> Another approach is the one-pot deselenization of arylisoselenocyanates through recyclable iodine mediated is utilized to access cvanamides.<sup>[25]</sup> Cvanamides participate in cycloaddition reactions with dipoles to construct different heterocyclic compounds such as synthesis of 2-aminopyridines via cocyclization of substituted cyanamides using  $Ni(cod)_2$  in presence of IMes ligand as a catalyst.<sup>[26]</sup> Aryl cyanamide complexes that play a special role in metal-metal coupling as a bridging ligand which directly impacts the magnetic properties have been progressed in medicinal activity.<sup>[27]</sup> Synthesis of Ni(II) and Cd(II) complexes with 4-nitrophenylcyanamido ligands was an approach in this field.<sup>[28,29]</sup> Teng et al. reported cyanation of sec-amines for formation of N-CN bond through transition metal that catalyzed under copper catalysis condition.<sup>[30]</sup> Heterocyclization of variety of terminal alkynes with substituted cyanamides in the presence of Ph<sub>3</sub>PAuNTf<sub>2</sub> and 2-picoline proceed through via gold catalyst leads to synthesis of 2-Amino-1,3-oxazoles.<sup>[31]</sup>

These recent advances in the field of cyanamide chemistry will motivate further research. In this study, we report the synthesis of diverse *N*-benzylated arylcyanamides that catalyzed via capable heterogeneous polymer-supported palladium complex. So 4-(benzyloxy) benzyl chloride polymer bound (BBCP) was functionalized with 5-phenyl-1-*H*-tetrazole (PhenTet), immobilized with PdCl<sub>2</sub> (BBCP@PhenTet@Pd) and characterized with different methods (Scheme 1).

Then, the Pd polymer-supported complex was used as a capable heterogeneous catalyst for the green synthesis of diverse *N*-benzylated aryl cyanamides from the reaction of cyanamides with benzyl bromide and  $K_2CO_3$  in EtOH at 60°C for the appropriate times (Scheme 2).

#### 2 | EXPERIMENTAL

#### 2.1 | Materials and methods

The high-grade starting materials (4-(benzyloxy)benzyl chloride polymer, 5-phenyl-1-*H*-tetrazole, PdCl<sub>2</sub>, various aryl cyanamides, and benzyl bromide), reagents, and solvents were purchased from the Aldrich and Merck chemical suppliers and used without further purification. The Pd polymer-supported complex and the benzylated products were characterized by different methods (Fourier-transform infrared [FT-IR], X-ray diffraction analysis [XRD], energy-dispersive X-ray spectroscopy [EDX], inductively coupled plasma [ICP], scanning electron microscopy [SEM], transmission electron microscopy [TEM], Brunauer–Emmett–Teller [BET], and thermogravimetric analysis/differential thermal analysis [TGA-DTA]) (Supporting Information).







**SCHEME 2** Preparation of diverse *N*-benzylated aryl cyanamides

# 2.2 | Preparation of the polymerimmobilized palladium complex

Preparation of the Pd polymer-supported complex was carried out as bellow:

• Preparation of BBCP@PhenTet: The mixture of BBCP (0.58 g, 2.5 mmol), PhenTet (0.730 g, 5.0 mmol), and  $K_2CO_3$  (0.691 g, 5.0 mmol) was stirred in DMF (50 ml) and heated for 24 h at 100°C. After cooling the mixture

to room temperature, BBCP@PhenTet was separated by filtration, washed with DMF, and dried under vacuum overnight.

• Preparation of BBCP@PhenTet@Pd: The mixture of BBCP@PhenTet (0.85 g, 5.82 mmol) and PdCl<sub>2</sub> (0.88 g, 5.0 mmol) was stirred in EtOH (40 ml) and refluxed for 24 h. After cooling the mixture to room temperature, the solid (BBCP@PhenTet@Pd) was separated, washed with EtOH, and dried under vacuum overnight.





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# 2.3 | General procedure for the green *N*benzylation of aryl cyanamides by the Pd polymer-supported complex

The mixture of the cyanamide (1.0 mmol), benzyl bromide (171 mg, 1.0 mmol),  $K_2CO_3$  (171 mg, 1.0 mmol), and the Pd polymer-supported complex (10 mg) was stirred in EtOH (5 ml) at 60°C for the appropriate time, and the end of the reaction was controlled by TLC. After cooling to room temperature, the mixture was filtered, the filtrate evaporated, and the solid (**2a–j**, 1–10) recrystallized in the EtOH/H<sub>2</sub>O (1:1) mixture and characterized by comparison of their spectroscopic data with authentic samples. In the IR spectra of the following compounds (Supporting Information), the disappearance of the characteristic N—H peak at about 3300 cm<sup>-1</sup> and the appearance of the new —CN peak at about 2300 cm<sup>-1</sup>, clearly confirm formation of the products (**2a–j**).

- 1. N-Benzyl-N-p-tolyl cyanamide 2a
- 2. N-Benzyl-N-(4-methoxyphenyl)cyanamide 2b
- 3. N-Benzyl-N-(2-chlorophenyl)cyanamide 2c
- 4. *N*-Benzyl-*N*-(4-chlorophenyl)cyanamide **2d**
- 5. *N*-Benzyl-*N*-(2,5-dichlorophenyl)cyanamide **2e**
- 6. *N*-Benzyl-*N*-(2,4-dichlorophenyl)cyanamide **2f**
- 7. N-Benzyl-N-(4-nitrophenyl)cyanamide 2g
- 8. N-Benzyl-N-(4-iodophenyl)cyanamide 2h
- 9. N-Benzyl-N-(3-bromophenyl)cyanamide 2i
- 10. N-Benzyl-N-(4-bromophenyl)cyanamide 2j

### 3 | RESULTS AND DISCUSSION

The Pd polymer-supported complex was prepared, characterized, and used as a heterogeneous catalyst in the green benzylation reaction. The 4-(benzyloxy)benzyl chloride polymer was chosen as a support to heterogenize the catalyst for better separation.

Also, it is necessary to say that the advantage of the selected polymer as a support compared with magnetic iron oxide is that all the catalytic properties observed in reactions is directly related to the Pd complex immobilized on the polymer. While if the magnetic iron oxide is chosen instead of polymer, a percentage of the observed catalytic properties may be related to iron oxide because it itself has catalytic properties.

# 3.1 | Characterization of the Pd polymersupported complex

# 3.1.1 | Characterization of the Pd polymer-supported complex by FT-IR

Figure 1 shows the four IR spectra: (a) BBCP, (b) the PhenTet ligand, (c) BBCP@PhenTet, and (d) BBCP@PhenTet@Pd. Comparison of (a) and (b) with (c) indicates deletion of the two peaks (the N—H bond at about 3129 cm<sup>-1</sup> and the C—Cl bond at about 751 cm<sup>-1</sup>) which clearly confirms formation of (c). Also, comparison of (c) and (d) will show the shift of the C=N



**FIGURE 2** The X-ray diffraction analysis (XRD) pattern of the Pd polymer-supported complex

bonds of the tetrazole rings from  $1654 \text{ cm}^{-1}$  in (c) to  $1600 \text{ cm}^{-1}$  in (d), representing the coordination between the free lone pair of the two nitrogen atoms of the tetrazole rings with the Pd atom (Supporting Information).

# 3.1.2 | Characterization of the Pd polymer-supported complex by XRD

Figure 2 shows the XRD powder pattern of the complex. As can be seen, the peaks at  $2\theta$  about 40, 47, 52, 58, and 68 confirmed the synthesis of the Pd complex. The presence of peaks in  $2\theta$  at about 12, 21, 25, 28, 33, and 35 are related to the 5-phenyl-1-*H*-tetrazole.<sup>[32]</sup> Also, because the 4-(benzyl- oxy)benzyl chloride polymer is amorphous, the XRD analysis is not able to show the presence of this polymer.<sup>[33]</sup>

# 3.1.3 | Characterization of the Pd polymer-supported complex by EDX

Figure 3 shows the EDX analysis indicating the elemental composition of the Pd polymer-supported complex. As we expected, the carbon, nitrogen, oxygen, and palladium elements can be seen in the EDX spectrum of the complex. Also, the relatively high value of the palladium content (EDX: about 37.4%, ICP: 23.6%) indicates the successful immobilization of Pd on the surface of polymer. The EDX analysis is more qualitative rather than the ICP measurement which is more quantitative and more reliable.

It should also be noted that, to determine the elemental composition of a compound based on existing standard, the sample will be usually coated with a very thin layer of gold; hence, the Au peak will be appeared in the EDX graph analysis, as well.



**FIGURE 3** The energy-dispersive X-ray spectroscopy (EDX) pattern elemental analysis of the Pd polymer-supported complex



FIGURE 4 The scanning electron microscopy (SEM) images of BBCP

# 3.1.4 | Characterization of BBCP by the SEM images

Figure 4 shows the SEM images of a polymer support, which indicate that the morphologies of the polymer particles are regular and their sizes are about 116.7, 117.5, and 130.3  $\mu$ M.

# 3.1.5 | Characterization of the BBCPsupported PhenTet ligand by the SEM images

Figure 5 shows the SEM images of the BBCP-supported PhenTet ligand, which indicate that the morphologies of the polymer-supported particles are relatively regular and the average particle size is about  $145 \mu$ M.

# 3.1.6 | Characterization of the Pd polymer-supported complex by the SEM images (before its application as a catalyst)

Figure 6 shows the SEM images of the Pd polymersupported complex before its application as a catalyst. These images indicate that the morphologies of the catalyst particles are relatively regular and the average particle sizes are about 169–175  $\mu$ M.

# 3.1.7 | Characterization of the Pd polymer-supported complex by the SEM image after its application as a catalyst in the five consecutive runs

Figure 7 shows the SEM image of the Pd polymersupported complex after its application as a catalyst in



FIGURE 5 The scanning electron microscopy (SEM) images of the BBCP-supported PhenTet ligand



FIGURE 6 The scanning electron microscopy (SEM) images of the Pd polymer-supported complex before its application as a catalyst

five consecutive runs. Similar to the previous images, these images also indicate that the morphologies of the catalyst particles are relatively regular.

# 3.1.8 | Characterization of the Pd polymer-supported complex by the SEM mapping images (after its application as a catalyst in five consecutive runs)

Figure 8 shows the SEM mapping images of the Pd polymer-supported catalyst after its application as a catalyst in the five consecutive runs. These images show the uniform dispersed characters of the C, N, O, and Pd elements.

As well as the IR spectral data that confirm the synthesis of the polymer-supported complex, a nice increase in the size of the polymer support (116.7, 117.5, and 130.3  $\mu$ M), the polymer-supported ligand (145  $\mu$ M), and the polymer-supported complex (170–175  $\mu$ M) clearly show the synthesis of the polymer-supported complex.

# 3.1.9 | Characterization of the Pd polymer-supported complex by the TEM images (before its application as a catalyst)

Figure 9 shows the TEM images of the Pd polymersupported complex before its application as a catalyst. On the basis of these images, it should be noted that



**FIGURE 7** The scanning electron microscopy (SEM) image of the Pd polymersupported complex after its application as a catalyst in the five consecutive runs



**FIGURE 8** The four scanning electron microscopy (SEM) mapping images of the Pd polymer-supported complex after its application as a catalyst in the five consecutive runs (C: red, N: green, O: blue, and Pd: violet)





#### FIGURE 9 The transmission electron microscopy (TEM) images of the Pd polymer-supported complex (before its application as a catalyst)





**FIGURE 10** The transmission electron microscopy (TEM) images of the Pd polymersupported complex after its application as a catalyst in the consecutive five runs



FIGURE 11 The thermogravimetric analysis/differential thermal analysis (TGA-DTA) pattern of the Pd polymer-supported complex

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the morphologies and the particle sizes are relatively regular.

# 3.1.10 | Characterization of the Pd polymer-supported complex by the TEM images (after its application as a catalyst in consecutive five runs)

Figure 10 shows the TEM images of the Pd polymersupported complex after its application as a catalyst. It should also be noted that the morphologies and the particle sizes are relatively regular.

# 3.1.11 | Characterization of the Pd polymer-supported complex by TGA-DTA

Figure 11 shows the TGA-DTA curves of the Pd polymersupported complex to investigate its thermal stability and

**TABLE 1** Results of the Brunauer–Emmett–Teller (BET)

 measurements of the Pd-supported complex

Parameter	Value
$a_{\rm s}({\rm m}^2/{\rm g})$	9.35
$V_{\rm m}~({\rm cm}^3/{\rm g})$	2.14
Total pore volume	0.022
Mean pore diameter	9.5

to verify the existence of the immobilized complex on the surface of the polymer.

According to the TGA pattern, weight losses have roughly been exhibited in three consecutive steps in thermal range of  $100^{\circ}$ C to  $400^{\circ}$ C. The first weight loss at about  $100^{\circ}$ C is probably related to the removal of the water, the second weight loss occurs at about  $265^{\circ}$ C to  $300^{\circ}$ C, which is probably related to the thermal decomposition of the complex and ligand, and the third weigh loss at about  $400^{\circ}$ C is probably related to decomposition of polymer bound. These results confirm the successful immobilization of the Pd complex on the surface of the polymer support.

# 3.1.12 | Characterization of the Pd polymer-supported complex by the BET measurements

To obtain the specific surface area, the total volume of the pores, and the mean pore diameter of the Pd polymer-supported complex, the nitrogen adsorption (uptake) and desorption analysis was performed at 77 K, and Table 1 shows the results of the BET measurements.

Figure 12 is a type III curve and indicates the absence of the hysteresis.

Figure 13 is the BJH adsorption curve of the Pd-supported complex indicating that there is almost no pore with a radius higher than 10 nm in a sample, and the most abundant pores are those with an approximate radius of 1.8 nm which are micropores.



**FIGURE 12** The nitrogen adsorption and desorption curve (Brunauer–Emmett–Teller [BET]) of the Pd polymer-supported complex





**FIGURE 13** The BJH adsorption curve of the Pd polymer-supported complex

$R \xrightarrow{H} + PhCH_2Br \xrightarrow{BBCP@PhenTet@Pd}_{K_2CO_3, EtOH, 60 °C} \xrightarrow{R} \xrightarrow{CH_2Ph}_{2(a-j)} CN$							
Entry	Solvent	Catalyst (mg)	Temperature (°C)	Time (min)	Yield (%)		
1	MeCN	15	60	120	65		
2	MeCN	10	60	120	71		
3	MeCN	5	60	120	33		
4	DMSO	10	60	120	82		
5	EtOH	10	60	100	89		
6	<i>n</i> -Hexane	10	60	180	-		
7	EtOH	10	Reflux	120	71		
8	EtOH	10	r.t.	180	Trace		

**TABLE 2**Optimization of thegreen N-benzylation reaction

# 3.2 | Optimization of the green *N*-benzylation reaction

Table 2 shows the *N*-benzylation reaction of 2,5-dichlorophenyl cyanamide under different situations to optimize the reaction conditions. The best result (a model reaction) was obtained with 1.0 mmol of 1:1:1 of 2,5-dichlorophenyl cyanamide:benzyl bromide: $K_2CO_3$  with 10 mg of the Pd polymer-supported complex in EtOH at 60°C in 100 min (Entry 5). We expected the

reaction to be better under reflux conditions, but performing the reaction at  $60^{\circ}$ C had a higher yield. Production of by-products and the speed of the reverse reaction will probably be increased if the reaction performs at higher temperature than  $60^{\circ}$ C.

Also, three extra reactions were performed under the optimum conditions as below:

1. The *N*-benzylation reaction in the absence of BBCP@PhenTet@Pd: The reaction efficiency was very

#### TABLE 3 The green N-benzylation reactions

$R \xrightarrow{H} PhCH_2Br \xrightarrow{BBCP@PhenTet@pd}{K_2CO_3, EtOH, 60 °C} R \xrightarrow{CH_2Ph} CN$						
Entry	Aryl cyanamide (1a–j)	Product (2a–j)	Time (min)	Yield (%)	TON <sup>[a]</sup>	TOF <sup>[b]</sup>
1	Me NH 1a	Me N CH <sub>2</sub> Ph 2a	60	75	120	2
2	MeO-NH 1b	MeO-V-CH <sub>2</sub> Ph CN 2b	60	71	126.88	3.014
3		$ \underbrace{ \left( \begin{array}{c} C \\ N \end{array} \right) }^{C I} \underbrace{ \left( \begin{array}{c} C \\ C \\ N \end{array} \right) }^{C H_2 P h} 2 c \\ C \\ C \\ N \end{array} \right) $	110	75	120	1.09
4	CI-NH 1d	CI-CH <sub>2</sub> Ph CN 2d	95	85	106	1.11
5		$Cl = Cl + CH_2Ph CN + CN $	100	89	101.2	1.01
6		$CI \rightarrow CI \rightarrow CH_2Ph 2f$ $CI \rightarrow CN 2f$	110	74	121.74	1.1
7	O <sub>2</sub> N-NH 1g	0 <sub>2</sub> N-N-CH <sub>2</sub> Ph CN 2g	90	81	111.6	1.24
8	NH 1h	$I \rightarrow N \sim CN = 2h$	90	77	117	1.3
9	Br NH CN 1i	Br N CN 2i	100	70	128.7	1.287
10	Br - NH 1j	Br N CH <sub>2</sub> Ph 2j	100	75	120	1.2

<sup>a</sup>Turnover number (TON): moles of aryl cyanamide (2 mmol) converted per mole of catalyst (10 mg). According to the ICP measurement, the content of Pd in the catalyst is about 23.6%, so the mmol of Pd in 10 mg of the catalyst is  $23.6 \div 10 = 2.36 \div 106.42 = 0.0222$ . For Entry 1, because the yield is about 75%, the effective mmol of Pd is about  $0.0222 \times 0.75 = 0.01665$  and so the TON is  $2 \div 0.01665 = 120$ .

<sup>b</sup>Turnover frequency (TOF): TOF = TON  $\div$  time. For Entry 1, because the time is about 60 min, the TOF is 120  $\div$  60 = 2.

low (about 2%). This observation was expectable because the reaction does not take place in the absence of the Pd polymer-supported complex, or alternatively, the rate of the reaction is very low.

- 2. The *N*-benzylation reaction in the presence of the polymer-supported ligand (BBCP@ PhenTet): No product was observed. This observation was also expectable, because the supported ligand alone cannot act as a catalyst, so the reaction did not take place.
- 3. The *N*-benzylation reaction in the presence of PdCl<sub>2</sub>: The product yield was reduced to about 40% compared with when the Pd polymer-supported complex was used. This observation was also expectable, because the polymer-supported complex system is more efficient than the noncomplex system due to the more

available surface area of the polymer-supported complex system.

Incidentally, in the absence of  $K_2CO_3$ , the yield of the product was very low or negligible because there is no base to abstract the hydrogen atom of the N—H of cyanamide, which is discussed mechanistically in the proposed mechanism section.

### 3.3 | The green *N*-benzylation reaction

Using the model reaction conditions (Table 2, Entry 5), the green benzylation of various aryl cyanamides were carried out with 1.0 mmol of 1:1:1 of phenyl cyanamide:



**SCHEME 3** The plausible *N*-benzylation reaction mechanism

benzyl bromide: $K_2CO_3$  with 10 mg of the palladium polymer-supported complex in ethanol at 60°C in appropriate times (Table 3).

According to Table 3, the reaction with aryl cyanamides having electron donor groups (Entries 1 and 2) requires less reaction times, which is probably related to the better nucleophilicity of the nitrogen atom. The *N*-benzylated aryl cyanamides (**2a**-**j**) were characterized by comparing their IR, NMR, and MP/BP with those reported in the literature (Supporting Information).

In the IR spectra of all benzylated aryl cyanamides, disappearance of the characteristic N—H peak of the starting material (about  $3300 \text{ cm}^{-1}$ ) clearly confirms formation of the products.

# 3.4 | The plausible *N*-benzylation reaction mechanism

Scheme 3 shows the probable three steps proposed mechanism for the *N*-benzylation reaction:

- The first step: the N—H proton of phenyl cyanamide will be abstracted by K<sub>2</sub>CO<sub>3</sub> as a base and the related anion stabilized by the benzene ring as well as the —CN group.
- The second step: as a Lewis acid, the Pd polymersupported complex will be attached to the bromine atom of benzyl bromide to weaken the C—Br bond.
- The third step: the nucleophilic attack of the nitrogen anion of phenyl cyanamide to the benzyl carbon of benzyl bromide will form the final product, consequently.

### 3.5 | Comparison of the catalyst activity

Table 4 shows the comparison of the previous methods (Entries 1–19) used for the synthesis of cyanamides with our proposed method (Entry 20). In general, the disadvantages of the previous methods are formation of by-products and impurities, tedious work-up, long reaction times, and low yields, whereas our proposed method does not have any mentioned disadvantages and is easy, applicable, and reusable with good to high yields.

# 3.6 | Reusability of the Pd polymersupported complex

Figure 14 shows the recyclability of the Pd polymersupported complex (BBCP@PhenTet@Pd) with the model reaction in the green *N*-benzylation reaction of aryl cyanamides. So, after completion of the reaction which monitored by TLC, the reaction mixture was cooled to room temperature and filtered, the solid (BBCP@PhenTet@Pd) was separated, washed with EtOH, dried under vacuum overnight, and reused for the next successive runs. The corresponding diagram indicates that the Pd polymer-supported complex is relatively efficient even after five successive runs without the significant loss of activity (89%, 88%, 88%, 85, and 84%).

# 3.7 | The antibacterial activity of the Pd polymer-supported complex

The antibacterial properties of the Pd polymer-supported complex were studied against a number of gram-positive

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TABLE 4	Comparison of different methods for	r the synthesis of cyanamide	es
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Entry	Catalyst	Subject	Time (h)	Yield (%)	Ref.
1	<i>trans</i> -[Mo(NCN) <sub>2</sub> (dppe) <sub>2</sub> ]	Monoalkylation of cyanoimide at a Mo(IV) diphosphinic center by alkyl halides	1–170	42–75	Alegri et al. <sup>[34]</sup>
2	-	Synthesis of pyrimido[2,1- <i>b</i> ]quinazoline via the cyanamide formation	0.5–8	27–96	Nag et al. <sup>[35]</sup>
3	Pd(0)	Allylation of cyanamide	4-24	2-88	Cerezo et al. <sup>[36]</sup>
4	-	Synthesis of <i>N</i> -cyanomonoaza crown ethers by the <i>N</i> -alkylation of cyanamide with	2–20	17–34	Maeda et al. <sup>[37]</sup>
5	-	Synthesis of quinazolinones through radical cascade reactions involving <i>N</i> -acyl cyanamides	2–24	60–90	Larraufie et al. <sup>[38]</sup>
6	-	Synthesis of N-alkyl-N-aryl cyanamides	3	0–71	Karabanovich et al. <sup>[39]</sup>
7	Zeolite	Benzylation of aryl cyanamides	2-2.5	5-84	Azarifar et al. <sup>[40]</sup>
8	CoSO <sub>4</sub>	Synthesis of aryl/alkyl cyanamides	3	42–97	Seelam et al. <sup>[41]</sup>
9	Microwave	Synthesis of 2-yliden cyanamidopyridines	4–16	50-73	Vega et al. <sup>[42]</sup>
10	-	Synthesis of N-substituted cyanamides	0.5–12	27-95	Lin et al. <sup>[43]</sup>
11	-	Synthesis of 4-aryl-2-cyanoimino-3,4-dihydro- 1 <i>H</i> -pyrimidine	4	20-68	Hulme et al. <sup>[44]</sup>
12	Metal complexes of cyanamides	Synthesis of substituted ureas, isoureas, and guanidines	1–3	62–99	Jochims et al. <sup>[45]</sup>
13	Aliquat 336	Alkylation of cyanamide	2-3	32-96	Jonczyk et al. <sup>[46]</sup>
14	Zn/FeCl <sub>2</sub>	Formation of 2-aminopyridines	3-24	35–97	Lane et al. <sup>[47]</sup>
15	-	Alkylation of cyanamide	5 min	41-92	Shestakov et al. <sup>[48]</sup>
16	-	Synthesis of azacyclophanes by alkylation of cyanamide	20-44	9–95	Wen et al. <sup>[49]</sup>
17	-	Alkylation of N-aryl cyanamide	48	38-76	Butkevich et al. <sup>[50]</sup>
18	-	<i>N,N</i> -Disubstituted cyanamides from amid- oximes	3	70–92	Bakunov et al. <sup>[51]</sup>
19	$Pd_2(dba)_3$	Novel synthetic route to allyl cyanamides	0.5-2	77–99	Kamijo et al. <sup>[52]</sup>
20		Our method	60–110 min	71-89	-



**FIGURE 14** Reusability of the Pd polymer-supported complex

Microorganisms	Standard (10 mg/ml)		Blank	Zone of inhabitation (mm)	
	Tetracycline Tobramycin		DMSO	Pd-supported complex	
MIC (mcg/ml)	8	8	-	16	
Gram (+)					
Bacillus thuringiensis	30	33	-	30	
Bacillus cereus	36	25	-	23	
Staphylococcus aureus	30	30	-	20	
Gram (–)					
Pseudomonas aeruginosa	25	23	-	20	
Serratia marcescens	20	25	-	20	
Escherichia coli	22	13	-	10	

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**TABLE 5** Antibacterial activity of the Pd complex expressed as diameter of inhabitation zone (mm) and minimum inhibitory concentration (MIC)

and gram-negative bacterial strains (Table 5). The Pd polymer-supported complex inhibited the growth of the bacterial strains, producing a zone of inhibition of diameter 10–30 mm. In some cases, the Pd polymer-supported complex has the same effect as a tetracycline standard antibiotic against *Bacillus thuringiensis* (a gram-positive bacterium) and *Serratia marcescens* (a gram-negative bacterium). Because the comparison of the size of inhibition zones is generally not trustable, the minimum inhibitory concentration (MIC) value of the compound was also determined. The results indicated that the MIC value against the tested organisms was about 16. The standard antibiotic showed MIC value about 8 mg/ml for tetracycline; hence, the Pd complex has reasonable properties against some bacterial strains.

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# 4 | CONCLUSION

In summary, the Pd complex immobilized on the functionalized polymeric support was prepared, characterized by FT-IR, XRD, EDX, ICP, SEM, SEM mappings, TEM, TGA-DTA, and the BET measurement techniques and used as a capable heterogeneous polymer-supported palladium complex in the green benzylation reaction of various aryl cyanamides with benzyl bromide and  $K_2CO_3$  in EtOH at 60°C for the appropriate times.

Finally, the antibacterial properties of the Pd polymer-supported complex were studied against a number of gram-positive and gram-negative bacteria, and in some cases, it has the same effect as a tetracycline standard antibiotic against В. thuringiensis (a gram-positive bacterium) and S. marcescens (a gram-negative bacterium).

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#### AUTHOR CONTRIBUTIONS

**Davood Habibi:** Project administration; supervision. **Somayyeh Heydari:** Formal analysis.

#### **CONFLICT OF INTEREST**

There are no conflicts of interest to be declared.

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#### SUPPORTING INFORMATION

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

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