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FULL PAPER

Fe_3O_4@L-lysine-Pd(0) organic–inorganic hybrid: As a novel heterogeneous magnetic nanocatalyst for chemo and homoselective [2 + 3] cycloaddition synthesis of 5-substituted 1H-tetrazoles

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An efficient and sustainable synthetic protocol has been presented to synthesis and 5-substituted 1H-tetrazole privileged heterocyclic substructures. The synthetic protocol involves two-component reaction between aryl nitriles and NaN_3 in water using complex of L-lysine-palladium nanoparticles (NPs) modified Fe_3O_4 nanoparticles as magnetically separable, recyclable, and reusable heterogeneous catalyst. Magnetically retrievable L-lysine-Pd(0) modified Fe_3O_4 nanoparticles were applied in [2 + 3] cycloaddition synthesis of 5-substituted 1H-tetrazoles. The advantages of this strategy include easy recovery and efficient reusability of the expensive Pd NPs, obtaining high yields of [2 + 3] cycloaddition, short reaction times, and all of the reported synthetic strategies are being performed in water as green solvent for a wide range of substrates.

KEYWORDS

[2 + 3] cycloaddition, 5-substituted 1H-tetrazoles, Fe_3O_4@L-lysine-Pd(0), green nanocatalyst, water solvent

1 | INTRODUCTION

The use of nanostructured heterogeneous catalysts in organic transformations has recently been very exciting in view of their catalytic efficiency and selectivity.[1–4] The ease of isolation and separation of the heterogeneous catalysts from the desired organic product and the recyclability and reusability further enhanced the sustainability of the catalysts.[5–7] Moreover, the heterogeneous catalysts not only catalyze the reactions on their own but also serve as effective support for immobilization of active catalyst and facilitate efficient magnetic separation of catalysts for their recovery and reusability.[8,9] The functionalization and modification of iron oxide nanoparticles with various biocompatible and biodegradable materials in many different ways have been demonstrated with efficient and effective catalysis.[10] L-lysine can be considered as excellent candidate for functionalization of iron oxide nanoparticles as the presence of an α-carboxylic, an α-amino group, and a side-chain primary amine for coordination to transition metals.[11] Generally speaking, the presence of amino group beside carboxylic acid can accelerate the immobilization process, which may be aided by the N–H group of L-lysine, which is capable of forming a hydrogen bond with the O–H groups on support surface.[12] Also, the final complex can be synthesized using stable interaction between the amine group of L-lysine and the Pd atom and catalyze the chemical reactions efficiently and with high selectivity.[12]

The combination of two or more nitrogen atoms in heterocyclic structures in one molecule with the use of combinatorial synthesis avoiding multistep synthesis and hazardous organic solvents has been used as an effective molecular hybridization strategy for designing novel drug-like molecules with structural diversity and molecular complexity for drug discovery research.[13–15] The close correlations between the specificity of biological activity and the structure of complex molecule have provided the impetus to develop a molecular hybridization strategy to access challenging target molecules with privileged substructures inherent in bioactive molecules.[12,16,17] N-containing heterocycles are very interesting and elegant synthetic targets and incorporated in a number of medicinally important natural products and syntheticz pharmaceuticals.[18,19] Moreover, the synthetic pharmaceuticals with interesting biological activities such as antimicrobial and antitumor inhibitors include N-containing tetrazole structural system in their structures.[14,20–23] The [2 + 3] cycloaddition synthesis of tetrazoles with medicinally privileged fused substituent at C5 provides an opportunity for the synthesis of a library of N-heterocycles with drug-like structural diversity and complexity.[24,25] Five-substituted 1H-tetrazole heterocycles, in particular, represent a class of medicinally important and structurally diverse complex molecules and incorporated as core units in a number of natural and synthetic pharmaceuticals with a wide ranging potential bioactivities.[26–28] In most of the cases, tetrazole heterocycles have been synthesized by [3 + 2] cycloaddition of aryl nitriles with sodium azide in the presence of homogeneous metal catalysts.[27,29–31] But in the present work, we are concerned with the synthesis of 5-substituted 1H-tetrazole derivatives using L-lysine-Pd(0) catalytic complex functionalized magnetically separable nanocomposite as recyclable and reusable catalyst. The present work is probably the first report on the synthesis of 5-substituted 1H-tetrazole in the water as green solvent.

2 | EXPERIMENTAL

2.1 | Catalyst synthesis

The Fe_3O_4@L-lysine-Pd(0) magnetic nanoparticles (MNPs) was prepared according to the our previously reported method (Scheme 1).[32]

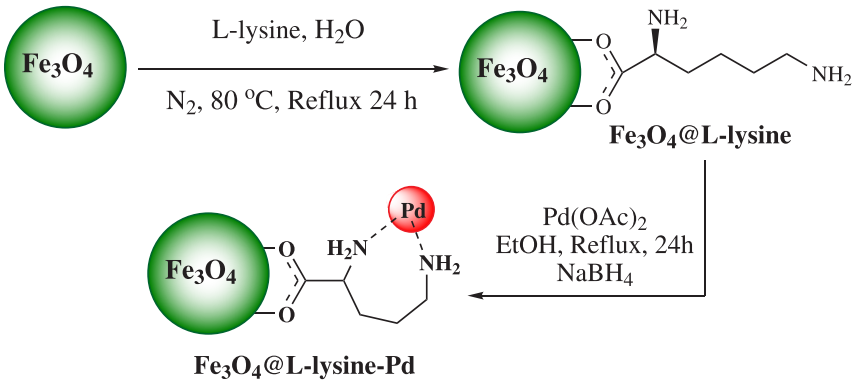
2.2 | General procedure for the synthesis of 5-substituted 1H-tetrazole derivatives catalyzed by Fe_3O_4@L-lysine-Pd(0) MNPs

A mixture of aryl nitrile (1 mmol) and sodium azide (1.3 mmol) was dissolved in water (2 mL) in the presence of Fe_3O_4@L-lysine-Pd(0) MNPs and stirred vigorously at 100°C for the required time. The progress of reaction was monitored by thin layer chromatography (TLC). After the completion of reaction, the mixture was cooled down to room temperature, then HCl (4 N, 10 mL) was added to the mixture, and after blending for 30 s, the catalyst was separated by magnetic decantation, and the product was washed with EtOAc and water, and organic layer was dried over anhydrous sodium sulfate (about 1.5 g). Then the ethyl acetate was evaporated to give the desired tetrazole derivatives.

3 | RESULTS AND DISCUSSION

3.1 | Catalytic applications

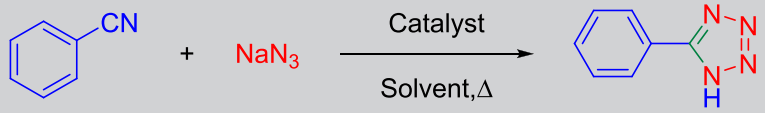
The as-prepared Fe_3O_4@L-lysine-Pd(0) was previously completely characterized as a novel magnetic nanocatalyst in our laboratory using Fourier transform infrared spectroscopy (FT-IR), X-ray diffractometer (XRD), energy-dispersive X-ray spectroscopy (EDS), inductively coupled plasma atomic emission spectroscopy (ICP), wavelength dispersive X-ray (WDX), Brunauer–



SCHEME 1 Systematic synthesis of Fe_3O_4@L-lysine-Pd(0) magnetic nanoparticles (MNPs)

Emmett–Teller (BET), thermogravimetric analysis (TGA), vibrating sample magnetometer (VSM), scanning electron microscopy (SEM), and transmission electron microscopy (TEM) techniques.[32] Our goal in this report was more completely to explore the catalytic applications of this magnetic nanocatalyst, so its catalytic applications were absolutely extended in the [3 + 2] cycloaddition synthesis of 5-substituted 1H-tetrazoles in green media.

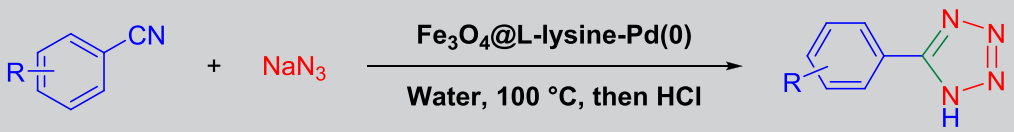
TABLE 1 Optimization of the reaction conditions for Fe_3O_4@L-lysine-Pd(0) NPs catalyzed the [3 + 2] cycloaddition reaction of sodium azide and benzonitrile



Entry	Catalyst	Catalyst (mol %)	Solvent	Temperature (°C)	Time (h)	Yield (%)[a]	TON	TOF (min^{-1})
1	-	-	H_2O	Reflux	24	NR	-	-
2	-	-	Solvent-free	100	24	NR	-	-
3	Fe_3O_4	0.30	H_2O	Reflux	1	Trace	-	-
4	Fe_3O_4@L-lysine	0.30	H_2O	Reflux	1	NR	-	-
5	Pd $(OAc)_2$	0.30	H_2O	Reflux	1	67	223.33	3.88
6	Fe_3O_4@L-lysine-Pd(0)	0.02	H_2O	Reflux	1	Trace	-	-
7	Fe_3O_4@L-lysine-Pd(0)	0.05	H_2O	Reflux	1	41	820	13.66
8	Fe_3O_4@L-lysine-Pd(0)	0.10	H_2O	Reflux	1	63	630	10.50
9	Fe_3O_4@L-lysine-Pd(0)	0.20	H_2O	Reflux	1	83	415	6.91
10	Fe_3O_4@L-lysine-Pd(0)	0.25	H_2O	Reflux	1	90	360	6.00
11	Fe_3O_4@L-lysine-Pd(0)	0.30	H_2O	Reflux	1	99	330	5.50
12	Fe_3O_4@L-lysine-Pd(0)	0.35	EtOH	Reflux	1	83	376	4.61
13	Fe_3O_4@L-lysine-Pd(0)	0.30	H_2O:EtOH (1:1)	Reflux	1	90	300	5.00
14	Fe_3O_4@L-lysine-Pd(0)	0.30	H_2O	R.T	1	N.R	-	-
15	Fe_3O_4@L-lysine-Pd(0)	0.30	H_2O	45	1	37	123	2.05
16	Fe_3O_4@L-lysine-Pd(0)	0.30	H_2O	75	1	68	226	3.77
17	Fe_3O_4@L-lysine-Pd(0)	0.30	H_2O	80	1	73	243	4.05
18	Fe_3O_4@L-lysine-Pd(0)	0.30	H_2O	90	1	88	293	4.88
19	Fe_3O_4@L-lysine-Pd(0)	0.30	H_2O	95	1	96	320	5.33

Abbreviations: NPs, nanoparticles; TOF, turnover frequency; TON, turnover number.
[a]Isolated yield.

TABLE 2 The synthesis of 5-substituted 1H-tetrazole derivatives from the reaction of various aryl nitriles with NaN_3 catalyzed by Fe_3O_4@L-lysine-Pd(0) in water at reflux conditions



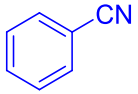
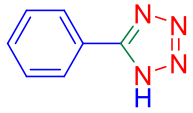
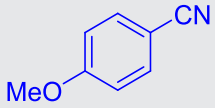
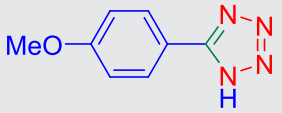
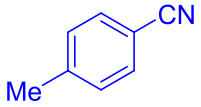
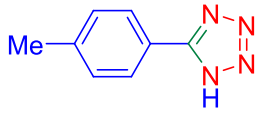
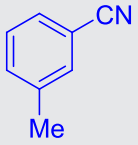
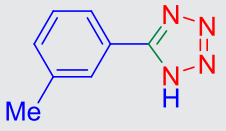
Entry	Aryl nitrile	Product	Time (min)	Yield (%)[a],[b]	TON	TOF (min^{-1})	Melting point (°C)	
							Measured	Literature
			60	99	330	5.5	214–216	214–216[33]
			110	88	293	2.66	153–154	150–153[34]
			85	93	310	3.64	249–250	249–251[35]
			75	95	316	4.22	149–150	149–150[33]

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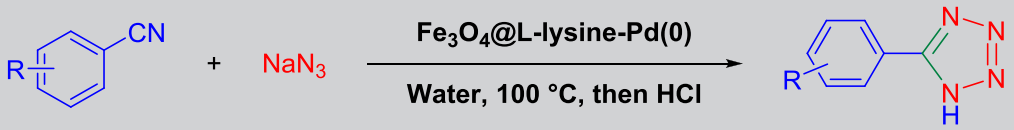
TABLE 2 (Continued)



Entry	Aryl nitrile	Product	Time (min)	Yield (%)[a],[b]	TON	TOF (min^{-1})	Melting point (°C)	
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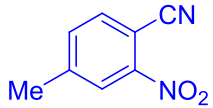
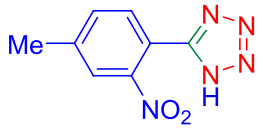
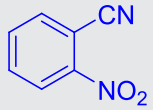
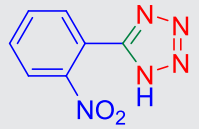
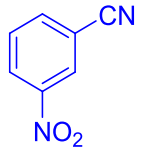
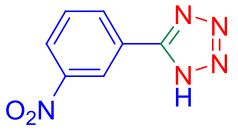
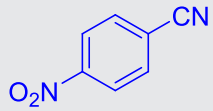
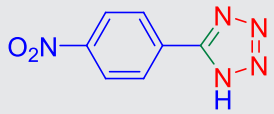
			140	83	276	1.97	180–182	180–182[27,36]
			30	95	316	10.55	159–160	157–159[36]
			80	95	316	3.95	184	183–185[34]
			30	100	333	11.11	217–219	219[35]

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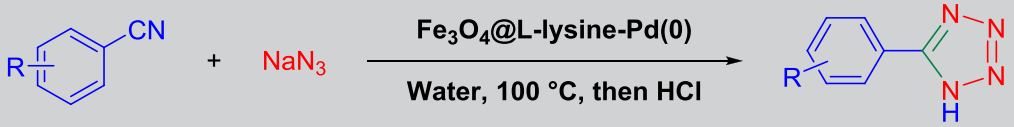
TABLE 2 (Continued)



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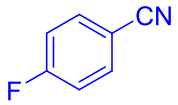
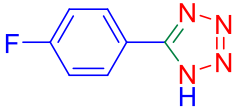
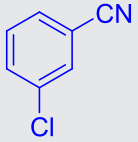
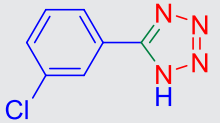
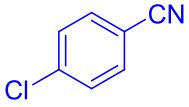
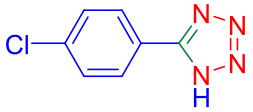
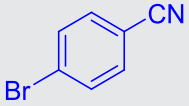
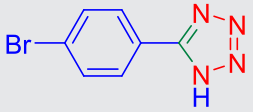
			60	86	286	4.77	204–207	205–207[37]
			40	95	316	7.91	141–142	141–142[38]
			45	91	303	6.74	257–259	257–259[34]
			45	94	313	6.96	266–267	268–270[34]

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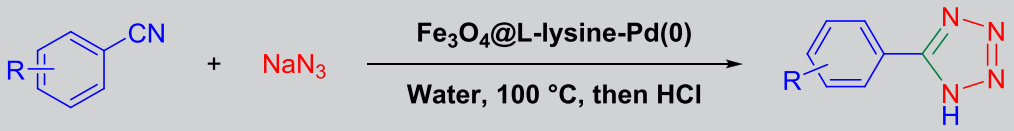

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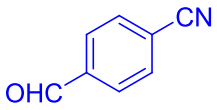
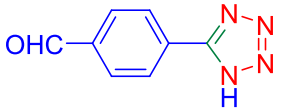
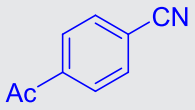
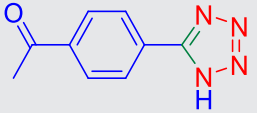
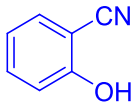
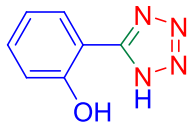
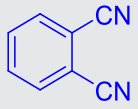
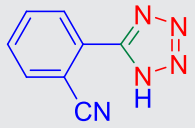
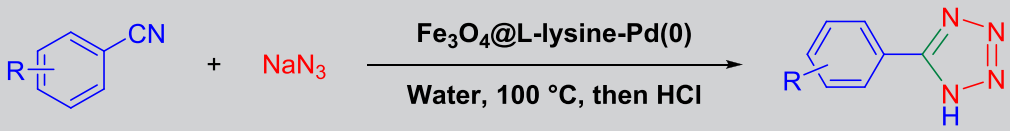
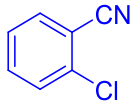
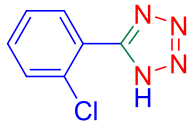
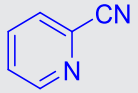
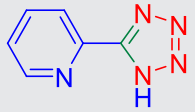
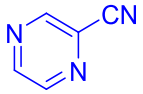
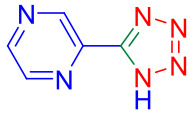
			75	93	310	4.13	185–187	185–187[39]
			80	93	310	3.87	173–176	173–176[40]
			60	96	320	5.33	224–227	223–225[41]
			120	83	276	2.30	209–211	208–210[42]

(Continues)

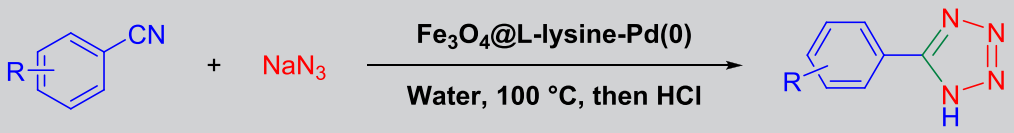
TABLE 2 (Continued)

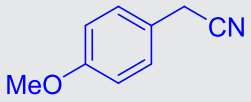
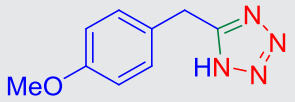
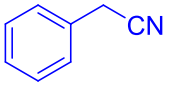
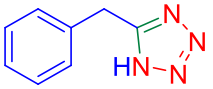
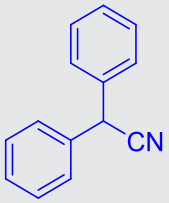
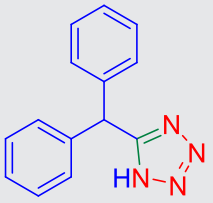


Entry	Aryl nitrile	Product	Time (min)	Yield (%)[a],[b]	TON	TOF (min^{-1})	Melting point (°C)	
							Measured	Literature
			90	88	293	3.25	179–180	177[35]
			45	92	306	6.81	211–213	213[35]
			45	88	293	6.51	191–193	193–195[43]

(Continues)

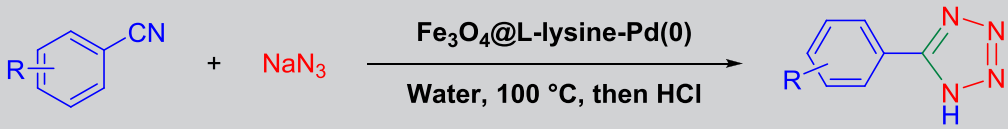
TABLE 2 (Continued)

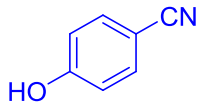
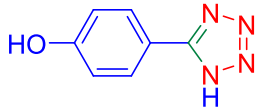
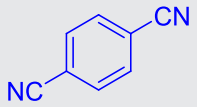
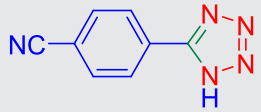


Entry	Aryl nitrile	Product	Time (min)	Yield (%)[a],[b]	TON	TOF (min^{-1})	Melting point (°C)	
							Measured	Literature
			100	70	233	2.33	151–154	150–153[34]
			90	77	256	2.85	125–126	124–125[44]
			50	95	316	6.33	165–166	164[35]

(Continues)

TABLE 2 (Continued)



Entry	Aryl nitrile	Product	Time (min)	Yield (%)[a],[b]	TON	TOF (min^{-1})	Melting point (°C)	
							Measured	Literature
			110	96	320	2.90	233–235	233–234[45]
			120	87	290	2.41	188–190	188–190[34]

Abbreviations: TOF, turnover frequency; TON, turnover number.

[a]Isolated yield.

[b]Reaction conditions: aryl nitrile (1 mmol), NaN_3 (1.3 mmol), and Fe_3O_4@L-lysine-Pd(0) MNPs (25 mg) in water at reflux conditions.

As a part of our research program on the development of environmentally benign synthetic protocol to synthesize structurally tetrazole molecules with medicinally privileged heterocyclic substructures, we wish to report an efficient and environmentally sustainable protocol to synthesize 5-substituted 1H-tetrazoles involving pseudo-tow component reaction of aryl nitriles and sodium azide in water mixture using L-lysine-Pd (0) functionalized magnetically separable Fe_3O_4 NPs as recyclable and reusable nanocatalyst. Initially, the reaction of benzonitrile and NaN_3 was selected as a model reaction to optimize the reaction conditions and to explore the feasibility of the present synthetic strategy.

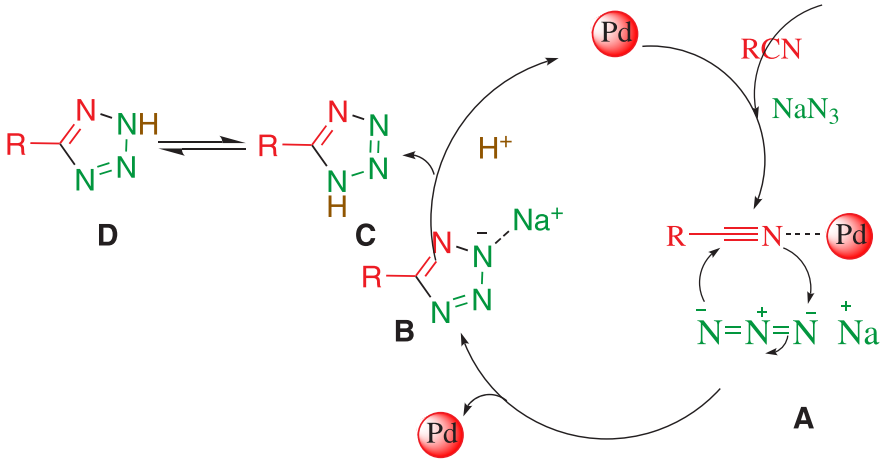
It was observed that the reaction could not provide the desired product when performed without using catalyst in the presence of solvent and without solvent even after continuous stirring the reactants at room temperature for 24 h (Table 1, Entries 1 and 2). Thus, from these observations, it was evident that the reaction required suitable catalyst to obtain the desired product. The reaction was further performed with three nanocatalysts: Fe_3O_4, Fe_3O_4@L-lysine, and Pd $(OAc)_2$ in water as solvent; the use of catalyst Fe_3O_4@L-lysine-Pd(0) MNPs provided comparatively better yield as compared with obtained by using Fe_3O_4, Fe_3O_4@L-lysine and Pd $(OAc)_2$ catalysts (Table 1, Entries 3–5 and 11). The influence of catalyst loading on the yield of the product was also examined by varying the loading amounts of the catalyst. With the observations, it was inferred that 0.30 mol % of Fe_3O_4@L-lysine-Pd(0) nanoparticles on the basis of amount of Pd in catalyst provided the maximum yield of the product in short conversion time (Table 1, Entry 11). The reaction conditions were also optimized by performing the reaction with Fe_3O_4@L-lysine-Pd(0) using ethanol, water, and water/ethanol mixture (1:1) as green and inexpensive solvents and observed that water provided better results (Table 1, Entries 11–13). The model reaction was also evaluated in the various temperatures; the observations show that the reflux conditions provided maximum yield of the product in short time. Therefore, on the basis of these observations, temperature exhibited excellent effect in terms of product yield and duration of the reaction.

Under the optimized reaction conditions, the reaction was extended with various sodium azide and various aryl nitriles possessing either electron-withdrawing or electron-donating substituents to synthesize a library of 5-substituted 1H-tetrazoles incorporating medicinally privileged heterocyclic substructures with a view to explore the feasibility and scope of the present synthetic protocol to synthesize the N-containing heterocyclic molecules. The synthesized 5-substituted 1H-tetrazoles are presented in Table 2. As presented in Table 2, this catalytic system worked very well, and various aryl nitriles bearing both electron-donating and electron-withdrawing functional groups give the corresponding 5-substituted 1H-tetrazole derivatives in good to excellent yields.

A plausible mechanism for [3 + 2] cycloaddition synthesis of 5-substituted 1H-tetrazoles is shown in Scheme 2.[46] In the first step, interaction of nitrile group with Fe_3O_4@L-lysine-Pd(0) forms intermediate A, which accelerates the [3 + 2] cycloaddition step. Really, Fe_3O_4@L-lysine-Pd(0) activates the nitrile groups via coordination to nitrogen and/or triple bond. Afterwards, it enhances the electrophilic character of cyanide group, then sodium azide reacts with this complex and produces the intermediate B. Finally, acidic work up, affords C which converted to D via 1,3 H-shift.

3.2 | Recyclability of the catalyst

Reusability of the catalyst was also examined. For confirmation of a real heterogeneous catalysis, the supported



SCHEME 2 Plausible mechanism for the [3 + 2] cycloaddition synthesis of 5-substituted 1H-tetrazoles in the presence of Fe_3O_4@L-lysine-Pd(0) magnetic nanoparticles (MNPs)

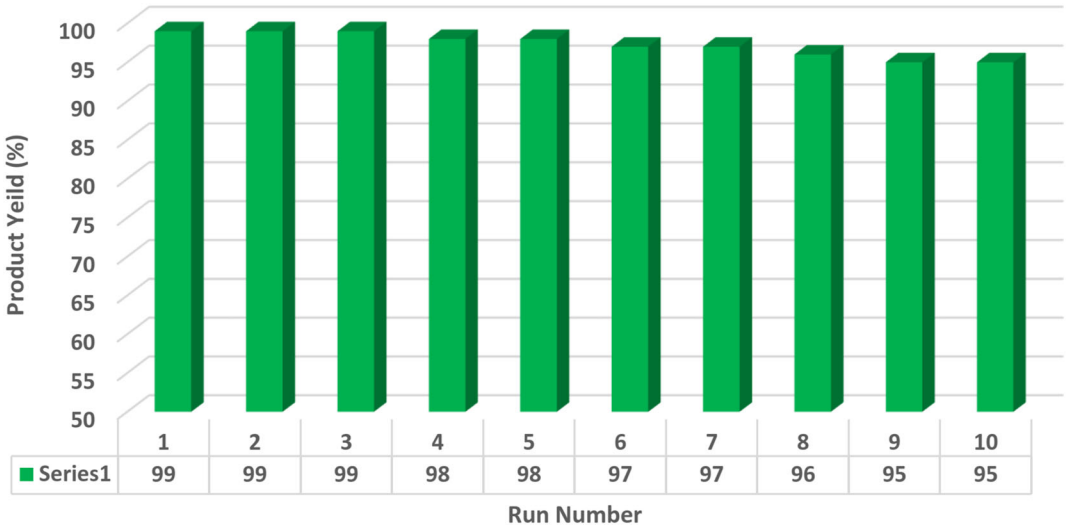


FIGURE 1 Reusability study of the Fe_3O_4@L-lysine-Pd(0) magnetic nanoparticles (MNPs) in the [3 + 2] cycloaddition of benzonitrile and NaN_3 as a model reaction in the synthesis of 5-substituted 1H-tetrazoles

catalyst is not supposed not leaching into the reaction mixture, and the recyclability of the catalyst is highly important. To confirm these properties, the reaction of benzonitrile and NaN_3 was selected again as model (Figure 1). A model reaction was preformed 10 times with recycled catalyst. The model reaction proceeded smoothly using recovered catalyst and without any need to reload the under optimal reaction conditions. After eight consecutive runs, nonappreciable loss of yields of product, thus, no considerable loss inactivity of catalyst was observed. Furthermore, only small difference in the Pd content for the fresh and reused catalyst, after the 10 runs, was only 1.26%, proving a low rate of leaching (Figure 1).

4 | CONCLUSION

In conclusion, we have developed an efficient and sustainable synthetic protocol to {3 + 2] cycloaddition synthesis of a wide library of 5-substituted 1H-tetrazole derivatives with privileged heterocyclic substructures involving pseudo-tow component reaction of sodium azide and various aryl nitriles possessing either electron-withdrawing or electron-donating substituents in water mixture using L-lysine-Pd(0) catalytic complex functionalized Fe_3O_4 nanoparticles as magnetically separable and reusable heterogeneous catalyst. The synthesis of 5-substituted 1H-tetrazoles with medicinally privileged substructures using magnetically separable Fe_3O_4@L-lysine-Pd(0) MNPs is probably the first report and not appeared in the literature. The modification of Fe_3O_4 nanoparticles with L-lysine-Pd(0) enhanced catalytic efficiency and facilitated the reaction with excellent yields of the reaction products. The sustainability of the catalyst has been demonstrated by its reuse for subsequent reaction cycles without an appreciable lose in its activity. The present synthetic protocol with its special features, synthetic efficiency, operational simplicity, atom and step economy, and environmental sustainability including easy separation of heterogeneous catalyst, is expected to provide an environmentally sustainable versatile and economically viable synthetic methodology to access a large library of drug-like small molecules with structural diversity and molecular complexity with excellent scope.

DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

AUTHOR CONTRIBUTIONS

Muhammad Aqeel Ashraf : Conceptualization; investigation; methodology; software. **Zhenling Liu:** Data curation; investigation; methodology; software.

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