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# Synthesis of nanomagnetic supported thiourea-copper(I) catalyst and its application in the synthesis of triazoles and benzamides

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# A novel nanomagnetic supported thiourea–copper(I) complex and inorganic– organic Takemoto-like hybrid nanomagnetic catalyst was designed, and synthesized. The prepared naomagnetic catalyst was characterized using Fourier transform infrared spectroscopy, X-ray diffraction, energy-dispersive X-ray analysis, transmission and scanning electron microscopies, thermogravimetry, nitrogen adsorption/desorption, zeta potential and vibrating sample magnetometry. Furthermore, the fabricated dual-role inorganic–organic hybrid catalyst shows a striking and robust catalytic activity for the synthesis of triazoles and benzamides through click and coupling reactions, respectively, under mild and eco-friendly reaction conditions.

#### **KEYWORDS**

benzamides, eco-friendly reaction conditions, nanomagnetic catalyst, thiourea-copper(I) complex, triazoles

# **1 | INTRODUCTION**

Nowadays, nanosized chemistry has manifested itself as an evolving and developing area in modern research fields and includes the preparation and applications of nanoparticles as catalysts or appropriate supports.<sup>[1]</sup> Also, nanochemistry has found a key role in the improvement of materials via adjusting the size, shape, porosity and surface modification.<sup>[2]</sup> A disadvantage of unsupported nanosized materials is their aggregation during a catalytic process. Therefore, surface stabilization is unavoidable. One of the most common methods for stabilizing nanomaterials is their immobilization onto appropriate magnetic supports in order to enhance stabilization and recycling possibility.<sup>[3]</sup>

Due to many benefits such as environmentally mild nature, excellent thermal and mechanical stability, insolubility in most common solvents, easy handling and mass production, much attention has been paid to magnetic nanoparticles as a superior alternative for support materials in the field of green chemistry.<sup>[4]</sup> Also, heterogeneous nanomagnetic-based catalysts exhibit outstanding catalytic reliability with high recovery and reusability potential that make them more impressive than their homogeneous analogues.  $^{\left[ 5\right] }$ 

Over the last decade, hybrid inorganic–organic skeleton architectures have emerged as an influential branch in solidstate chemistry. As a definition, hybrid inorganic–organic compounds are considered as materials that have both inorganic and organic parts in their structures.<sup>[6]</sup> In addition, hybrid frameworks have also been applied in gas storage, as heterogeneous catalysts, in photoluminescence and as porous magnets.<sup>[6–8]</sup> Therefore, reporting a new inorganic–organic heterogeneous hybrid nanomagnetic catalyst which has all the merits of both heterogeneous nanomagnetic systems and hybrid materials is valuable.

In recent years, the use of thiourea (urea) organocatalysis (Takemoto-type catalysis) in order to accelerate and alter the stereochemical features of organic transformations has been well considered. A striking dimension of Takemoto-type catalysis is the ability of thiourea (urea) moiety to form hydrogen-bonding interactions in mechanistic pathways of reactions. In addition to the importance of hydrogen-bonding interactions in chemical reactions, it is worth mentioning that they play a key role in biological processes which occur in

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living organisms and the chemistry of life.<sup>[9–29]</sup> Therefore, heterogenization of Takemoto-type catalysts by grafting onto the surface of suitable nanomagnetic supports can add merits to them and is of importance.

Due to the multidimensional capabilities of 1,2,3-triazoles in the field of medicinal and industrial chemistry, much attention has been focused on these versatile heterocyclic drug candidate materials. Triazoles have been used as bioactive compounds, agrochemicals, dyes, photographic active compounds, energetic materials and corrosion inhibitors.<sup>[30]</sup>



**SCHEME 1** Some examples of high-value molecules bearing triazole moieties<sup>[33]</sup>

Production of triazole derivatives through the common Huisgen cycloaddition reaction by the reaction of azides and terminal alkynes suffers from some disadvantages like



SCHEME 4 Preparation of amides in the presence of novel catalyst C



FIGURE 1 FT-IR spectra of different stepwise produced materials for the synthesis of desired catalyst C



SCHEME 3 Preparation of 1,2,3-triazoles in the presence of constructed catalyst C



FIGURE 2 EDX elemental analysis of the novel inorganic–organic hybrid nanomagnetic catalyst C



FIGURE 3 XRD patterns of catalyst in comparison with different stepwise prepared materials

needing a strong electron-withdrawing group on starting materials, elevated temperatures and long reaction times with moderate product yields. Therefore, because of the aforementioned biological significance and also in order to overcome the abovementioned drawbacks, the synthesis and chemistry of 1,2,3-triazoles are well investigated in the literature.<sup>[31,32]</sup> Scheme 1 presents some active compounds with triazole moieties.

One of the most efficient and powerful routes for the synthesis of new C-N linkages is N-arylation reaction which proceeds through the coupling reaction of nitrogen nucleophiles and aryl iodides, bromides and chlorides. In recent years, due to the industrial and medicinal importance of resulting N-aryl heterocyclic molecules, synthesis of these valuable compounds using metal-catalysed processes has received great attention. Among the metal-catalysed systems used for C-N bond formation, utilizing copper-based catalysts, due to the lower catalyst cost and toxicity, high efficiency and compatibility with large-scale goals is highly appealing.<sup>[34,35]</sup> Despite the abovementioned merits, N-arylation of amides

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**TABLE 1** XRD extracted data for the novel hybrid catalyst

Entry	<b>2</b> θ (°)	Peak width (FWHM) (°)	Size (nm)	Interplaner distance (nm)
1	25.5	0.22	37	0.35
2	28.4	0.16	51	0.31
3	42.2	0.30	28	0.21
4	49.9	0.40	21	0.18

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using copper-catalysed protocols (Goldberg-type amidation) is limited due to some disadvantages such as needing strong bases like NaH, necessity of high operational reaction temperature, poor scope of generality, requirement for highly polar solvents and large amount of copper reagent or nucleophile. Scientific research has disclosed that using certain organic ligands can impressively enhance the amidation reactions. This issue leads to a resurgence in interest in exploring



FIGURE 4 SEM micrographs of (a, b) hybrid catalyst C and (c, d) related intermediate B. (e, f) TEM images of prepared catalyst C

and developing novel and greener methods including coppercatalysed systems as an alternative for high-cost palladiumbased catalytic systems for N-arylation reactions.<sup>[36–38]</sup>

In this report, we follow our previous efforts for presenting greener and more productive procedures for the synthesis of potential bioactive species and extend our approach towards design, synthesis and application of screening knowledge-based developed task-specific nanomagnetic reusable catalytic systems as promoters.<sup>[39]</sup> In the work reported herein, we investigated the design and synthesis of а novel inorganic-organic Takemoto-like hybrid nanomagnetic catalyst C (Scheme 2) and probed the applicability of the resulting nanomagnetic core-shell catalyst for the preparation of 1,2,3-triazoles through a click reaction



FIGURE 5 (a) BET surface area analysis and (b) pore size distribution calculated based on BJH method



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FIGURE 6 TGA curve of novel core-shell catalyst



FIGURE 7 Magnetization curves of the catalyst in comparison with Fe<sub>3</sub>O<sub>4</sub> nanoparticles and compounds **a** and **B** 



FIGURE 8 Zeta potential analysis for the prepared catalyst

**TABLE 2** Screening reaction conditions for synthesis of triazoles

Entry	Catalyst load (g)	Solvent	Time (h)	Yield (%)
1	0.01	—	5	40
2	0.05	_	5	60
3	0.02	Water	1	90
4	0.05	Water	0.75	92
5	0.01	EtOH	8	50
6	0.01	MeOH	8	50
7	0.02	MeCN	1.5	90

<sup>a</sup>Reaction conditions: bromomethylbenzene (1 mmol, 0.170 g), ethynylbenzene (1 mmol, 0.102 g) and sodium azide (1 mmol, 0.065 g), r.t. <sup>b</sup>Isolated yields.

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TABLE 3 Synthesis of desired triazole products 2a-j in presence of nanomagnetic catalyst C

Entry	Halide	Product	Structure	Time (h)	Yield (%)	<b>M.p.</b> (°C)
1	Br	2a		0.5	92	129–130
2	Br	2b	OMe N.N.N	1	90	144–145
3	Br	2c	Me O N.N.N	1.5	85	98–101
4	Br	2d	Me	1	90	70–73
5	O <sub>2</sub> N Br	2e	O <sub>2</sub> N N N	0.5	90	150–153
6	O <sub>2</sub> N	2f	O <sub>2</sub> N N N N	0.5	85	90–92
7	O <sub>2</sub> N Br	2 g	O <sub>2</sub> N N-N	1.5	89	85–87
8	O <sub>2</sub> N	2 h	O <sub>2</sub> N N_Ń	1.5	90	60–63
9	o=√_Me	2i	Me	1.5	88	90–92
10	O <del>− Br</del> Me	2j	OMe N.N.N Me	1	90	106–109

(Continues)



<sup>a</sup>Reaction condition: halides (1 mmol), alkynes (1 mmol) and sodium azide (1 mmol, 0.065 g), r.t. <sup>b</sup>Isolated yields.

and benzamide derivatives through a C–N coupling reaction (Schemes 3 and 4).

# 2 | RESULTS AND DISCUSSION

The structure of the prepared nanomagnetic inorganicorganic Takemoto-like hybrid catalyst was investigated using suitable techniques such as Fourier transform infrared (FT-IR) spectroscopy, X-ray diffraction (XRD), transmission electron microscopy (TEM) and scanning electron microscopy (SEM). All these methods confirmed the formation of knowledge-based designed catalyst and the obtained data are discussed henceforth in detail.

In a comparative mode, as shown in Figure 1, the FT-IR spectra of different stepwise produced materials for the synthesis of desired catalyst **C** were investigated in the range 400–4000 cm<sup>-1</sup>. The overall changes in the FT-IR spectra from Fe<sub>3</sub>O<sub>4</sub> to the prepared catalyst can be considered as proof for the successful construction of the desired catalyst C.<sup>[39i]</sup> Also, the S=O stretching mode is confirmed by observing a signal at 1650 cm – 1, and an absorption band at 1286 cm<sup>-1</sup> can be ascribed to the vibration of CF<sub>3</sub> stretching mode.<sup>[40]</sup> The existence of uncoated hydroxyl and amino groups can be verified by the broad absorption at 2800–3600 cm<sup>-1</sup>.

For elemental characterization of the prepared inorganic– organic hybrid nanomagnetic catalyst **C**, energy dispersive X-ray (EDX) analysis was applied (Figure 2). The result from elemental analysis verifies the existence of all expected elements comprising iron, oxygen, phosphorus, carbon, nitrogen, sulfur, fluorine, copper and iodine.

The obtained XRD patterns of the prepared catalyst and its precursors are presented in Figure 3. The XRD pattern shows that the prepared hybrid catalyst has a crystalline nature and the related diffraction lines appear at  $2\theta = 25.5^{\circ}$ ,  $28.4^{\circ}$ ,  $42.2^{\circ}$  and  $49.9^{\circ}$ . Furthermore, using the Scherrer equation,  $D = K\lambda/(\beta \cos \theta)$ , where  $\lambda$  is the X-ray wavelength, *K* is the Scherrer constant,  $\beta$  is the peak width at half maximum and  $\theta$  is the Bragg diffraction angle, the crystal size and interplanar distance were calculated and are listed in Table 1. Based on SEM images, the size and morphology of the prepared hybrid catalyst were investigated. From Figure 4(a,b), it is revealed that the size of the catalyst particles is less than 70 nm. Also, in order to study the structure of the catalyst in more detail, TEM was used. The images (Figure 4e,f) show that the catalyst nanoparticles have a uniform spherical shape with nanometric scales.

Based on the absorption/desorption of nitrogen, some of the structural properties of the prepared catalyst were obtained. The obtained BET surface area, total pore volume and mean pore diameter of the prepared catalyst are  $22.8 \text{ m}^2 \text{ g}^{-1}$ , 0.096 cm<sup>3</sup> g<sup>-1</sup> and 16.8 nm, respectively (Figure 5a). The pore size distribution calculated based on the BJH method is shown in Figure 5(b). This figure shows the pore radius is mainly between 2 and 20 nm, which indicates the catalyst is mesoporous.

In order to investigate the thermal stability and determine the mass loss during decomposition process of the novel hybrid core-shell catalyst  $\mathbf{C}$ , thermogravimetric

TABLE 4 Reaction conditions for synthesis of secondary amides 3a-f

Entry	Catalyst load (g)	Solvent	Base	Temperature (°C)	Yield (%)
1	0.01	DMSO	КОН	80	50
2	0.05	DMSO	KOH	80	90
3	0.02	DMSO	KOH	80	85
4	0.015	DMSO	KOH	80	85
5	0.015	DMSO	KOH	r.t.	_
6	0.015	DMSO	KOH	50	30
7	0.015	DMSO	KOH	120	20
8	0.015	DMSO	$K_2CO_3$	80	5
9	0.015	DMF	KOH	80	20
10	0.015	Toluene	$K_2CO_3$	80	10
11	0.015	Toluene	CsCO <sub>3</sub>	80	40
12	0.015	MeCN	CsCO <sub>3</sub>	80	75
13	0.015	$H_2O$	КОН	80	-

<sup>a</sup>Reaction conditions: benzamide (1 mmol, 0.121 g), iodobenzene (1 mmol, 0.204 g), base (1 mmol).

<sup>b</sup>Isolated yields.

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TABLE 5 Synthesis of desired banzamide products 3a-h in presence of nanomagnetic catalyst C

Entry	Arykalide	Product	Structure	Time (h)	Yield (%)	<b>M.p.</b> (°C)
1		3a	O T	12	85	150–153
2		3b	O N N N	12	85	130–132
3		3с	O H H H	24	60	250–255
4	F <sub>3</sub> C	3d	O H H CF <sub>3</sub>	12	80	220–221
5	O <sub>2</sub> N	3e	O NO <sub>2</sub>	12	73	159–160
6	F <sub>3</sub> C	3f	CF <sub>3</sub>	12	75	176–178
7	O <sub>2</sub> N	3 g	O N N N N N N N N N N N N N N 2	12	75	123–125
8	F F F F F	3 h		24	85	193–196
9	Br	3a		24	70	150–153
10	CI	3a	O H H	24	60	150–153

<sup>&</sup>lt;sup>a</sup>Reaction condition: aryl halides (1 mmol), amides (1 mmol), 80 °C. <sup>b</sup>Isolated yields.

analysis (TGA) was conducted. The TGA plot is shown in Figure 6. The TGA plot shows insignificant weight loss from room temperature to about 200°C which can be attributed to evaporation of water or trapped organic solvents during the synthesis of the catalyst. Also, a mass loss between 280 and 350°C (about 35%) can be attributed to the decomposition and separation of the organic–inorganic

complex anchored to the surface of  $Fe_3O_4$  nanoparticles. Therefore, the prepared hybrid catalyst preserves its catalytic performance at elevated temperatures as can be inferred from the TGA curve.

The magnetic properties of the materials used in the prepared from  $Fe_3O_4$  nanoparticles to desired catalyst **C** were investigated using vibrating sample magnetometry.

The obtained results are presented in Figure 7. During the preparation route, by anchoring different layers, the saturation magnetization diminished. In the case of catalyst **C**, the related profile indicates a saturation magnetization of 25.5 emu g<sup>-1</sup> which guarantees the facile separation of the magnetic hybrid catalyst from a reaction mixture by applying a simple magnet.

The data obtained from inductively coupled plasma analysis confirmed the stability of the catalyst and did not show any meaningful leaching of Cu from the surface of the catalyst (in the case of synthesis, the release of Cu from the surface of the catalyst after five reuse runs is  $10^{-6}$  mol% (0.015 g of catalyst consisting of 5 mol% Cu), and in the case of triazole synthesis the leaching of Cu from the surface of the catalyst after five reuse runs is  $2 \times 10^{-7}$  mol% (0.02 g of catalyst consisting of 6.5 mol% Cu)).

To determine the surface charge of the catalyst, the zeta potential was measured. The resulting data show that the zeta potential for the prepared catalyst is -2.09 mV indicating the surface charge of catalyst in nearly neutral (Figure 8).

After completion of investigation and confirmation of the structure of the presented nanomagnetic core–shell catalyst **C**, its catalytic activity was screened in the synthesis of triazoles and benzamides through click and coupling reactions, respectively, under mild and eco-friendly reaction conditions.

Firstly, in the case of triazole derivatives, in order to find the best operational reaction conditions, the reaction of bromomethylbenzene, ethynylbenzene and sodium azide was selected as a model reaction. The reaction was carried out at ambient temperature in various solvents including water, ethanol, methanol and acetonitrile and in the presence of various amounts of catalyst. The obtained data are collected in Table 2. From the results, it can be inferred that the optimal reaction conditions are room temperature using 0.02 g of the novel Takemoto-like catalyst in water as solvent (Table 2, entry 3). Also, the reaction was tested using CuI salt as the catalyst, but, in comparison with the prepared catalyst, the obtained data were not satisfactory and catalyst C shows better performance than CuI salt (20 h, 90%).

Subsequently, in order to evaluate the generality and the versatility of the presented protocol for the preparation of target triazoles 2a-j, three halides 1a-c were reacted with various alkynes and NaN<sub>3</sub> under optimized reaction conditions. The data obtained are presented in Table 3. The obtained information verifies that all desired target triazole derivatives 2a-j are produced in relatively short reaction times with good to excellent yields. It is worth mentioning that the target molecules derived from phenylacetylene derivatives show better experimental data.

As in the case of triazole preparation, the synthesis of secondary amide derivatives 3a-f was screened in the presence of the described catalyst C. For this goal, initially, we determined the optimal reaction conditions. Therefore, for the reaction of benzamide and iodobenzene

 TABLE 6
 Reusability for synthesis of triazole 2a

Entry	Recycling run	Reaction time (min)	Isolated yield (%)
1	1	90	95
2	2	90	90
3	3	90	90
4	4	90	90
5	5	105	87
6	6	120	85
7	7	120	80
8	8	120	80
9	9	120	80

<sup>a</sup>Reaction conditions: bromomethylbenzene (1 mmol, 0.170 g), ethynylbenzene (1 mmol, 0.102 g) and sodium azide (1 mmol, 0.065 g), r.t.



FIGURE 9 Reusability of catalyst C for synthesis of desired product 3a



FIGURE 10 Mechanistic pathway for the synthesis of target compounds 3a-h

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TABLE 7         Comparison of novel nanomagnetic catalyst and other systems for synthesis of con	pound 2a
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Entry	Reaction conditions	Time (min)	Yield (%)	Ref.
1	Thiourea supported copper(I) chloride complex (2 mol%), water, r.t.	180	93	[32a]
2	[CuBr(PPh <sub>3</sub> ) <sub>3</sub> ] (0.5 mol%), neat, r.t.	180	99	[32b]
3	Copper(I) isonitrile complex (2 mol%), water, r.t.	120	95	[32c]
4	LCO NPs/water, sonication	15	99	[32d]
5	FMNPs@TD-cu(II), EtOH-H2O/Na2CO3, 25 °C	15	99	[32e]
6	CuNPs@agarose (0.05 mol% cu), water, 40 °C	480	96	[32f]
7	Cu <sub>2</sub> S-PANI (5 mol% cu), MeOH, UV	120	88	[32g]
8	CuSO <sub>4</sub> .5H <sub>2</sub> O (5 mol%), Na ascorbate (5 mol%), MonoPhos (1.1 mol%), DMSO/H <sub>2</sub> O (1:3)	60	91	[32h]
9	Copper(I)-tren ([Cu <sup>I</sup> ] 0.05 mol%), toluene, 60 °C	1440	86	[32i]
10	Novel nanomagnetic catalyst C (0.02 g), water, r.t.	30	92	This work

in 12 h, the operational temperature, solvents, bases and amount of catalyst were investigated. The resulting data are presented in Table 4. It can be deduced that the new catalyst exhibited good performance for the preparation of target compounds 3a-f in DMSO as reaction medium at  $80^{\circ}C$ .

In the next step, with optimal reaction conditions in hand, we investigated the efficiency and capability of the procedure for the synthesis of secondary amide derivatives. A good range of target molecules were obtained by the reaction of various aryl halides and benzamide derivatives under optimized reaction conditions with good to high yields. The resulting data are collected in Table 5. The obtained experimental data indicate that the coupling reactions using aryl iodide as precursor present better results compared with other aryl halides. Also, this method is applicable for chlorobenzene precursor (Table 5, entry 10).

The facile separation of a catalyst from a reaction mixture is an outstanding merit connected with constructed catalysts using magnetic nanoparticles as support. In the case of the novel nanomagnetic core-shell catalyst C, in addition to its easy separation from a reaction mixture by applying a simple external magnet, the study of the reusability potential of the catalyst for both the presented procedures was successful. In the case of triazole synthesis, the reusability test was performed for the reaction of bromomethylbenzene, ethynylbenzene and sodium azide to yield desired product **2a** for nine cycles. The obtained results confirm the versatility of catalyst C in reusability test after nine runs as summarized in Table 6.

The reusability of catalyst C was also examined via the reaction of benzamide and iodobenzene for the synthesis of desired product 3a in 12 h. After six recycles and reuses, catalyst C acts as a robust catalyst for the synthesis of target molecule 3a, and the reuse capability of the prepared catalyst was verified (Figure 9).

As a mechanistic route for the synthesis of target molecules 3a-h, at first in the nucleophilic coordination step, the amide used throughout the reaction with base generates the deprotonated nucleophile species which coordinate to copper(I) to yield complex intermediate I. The reaction of this intermediate with any halide leads to intermediate II. In another mechanistic pathway, the intermediate III through an oxidative addition of aryl halide and Cu-based catalyst is generated, and the second coordination process gives the Cu(III)-based complex II. Finally, reductive elimination process of intermediate II yields the desired products 3a-h and regenerates the catalyst C. It is worth mentioning that compared with cross-coupling reactions catalysed by Pd(0), the oxidative addition step occurs before the trans-metalation step. But in the copper-catalysed cyclic system both of the routes of Figure 2 are acceptable (due to unpredictability of the relative order of these two steps). A schematic representation of the abovementioned mechanistic aspect is portrayed in Figure 10.<sup>[41]</sup>

In order to explore the utility of the new protocol for triazole synthesis in comparison with other procedures reported in the literature, the case of target molecule **2a** was used and a comparison of data is provided in Table 7. The collected data indicate that our presented method provides results that compare favourably with other reported protocols.

# **3 | CONCLUSION**

In summary, the design and synthesis of a novel inorganic– organic Takemoto-like hybrid nanomagnetic catalyst were reported. Also, the application of the prepared catalyst Cwas successful in the synthesis of triazoles and benzamides through click and coupling reactions, respectively, under mild and eco-friendly reaction conditions. Moreover, the catalyst shows high potential for recycling and reuse for both mentioned reactions.

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## 4 | EXPERIMENTAL

# 4.1 | General procedure for construction of inorganic–organic Takemoto-like hybrid Nanomagnetic catalyst C (Scheme 2)

Fe<sub>3</sub>O<sub>4</sub> nanoparticles and intermediate A were produced according to previously reported methods.<sup>[42,43]</sup> Afterwards, a mixture of isothiocyanate (1.84 mmol, 0.5 g) and DBU (0.27 g, 1.84 mmol) in dry dichloromethane was added to a dispersed solution of 0.5 g of nanomagnetic coated intermediate A in dry dichloromethane (2 ml) at 0°C during 20 min. In the next step, the generated mixture was shaken for 24 h at ambient temperature to afford the desired intermediate **B**. The prepared intermediate **B** was washed with dry dichloromethane and dried. Then, CuI (1 mmol, 0.19 g) was added to intermediate **B** dispersed in dry dichloromethane solution. The resulting mixture was shaken for 48 h under argon atmosphere. Finally, the resulting desired catalyst C was collected using an external magnet and washed with absolute ethanol (5  $\times$  5 ml) and dried under vacuum. All obtained spectral data confirmed the structural formation of catalyst C.

## **4.2** | General method for synthesis of desired Triazole products 2a–j in presence of Nanomagnetic catalyst C (Scheme 3)

A solution of aryl halide (1 mmol) and NaN<sub>3</sub> (1 mmol, 0.065 g) in water (1.5 ml) was placed in a vial, then catalyst **C** (0.02 g) and alkynes (1 mmol) were added to the resulting mixture. The reaction mixture was stirred at ambient temperature for 1 h. After completion of the reactions as monitored by TLC, the nonomagnetic catalyst **C** was collected from the reaction mixture using an external magnet and washed with methanol and water successively and preserved. Then, for extraction of the products, ethyl acetate was added to the reaction mixture. Finally, the solvent was removed and the crude solids obtained were purified using  $CH_2Cl_2$  and *n*-hexane. The desired products were obtained in good to excellent isolated yields as presented in Table 4.

# **4.3** | General method for synthesis of desired Banzamide products 3a-h in presence of Nanomagnetic catalyst C (Scheme 4)

To a round-bottom flask containing a mixture of amides (1 mmol), aryl halide (1 mmol) and KOH (1 mmol) as base in dry DMSO (2 ml), 0.02 g of catalyst C was added. The resulting mixture was refluxed at 80°C under argon atmosphere for 12 h. After completion of the reactions as monitored by TLC, the catalyst C was separated from the

reaction mixture using an external magnet and the residue was purified using chromatography with a mixture of ethyl acetate and n-hexane (50/50) as eluent system. The desired products were obtained in good to high isolated yields as listed in Table 6.

#### 4.4 | Selected spectral data

1-Benzyl-4-(4-methoxyphenyl)-1*H*-1,2,3-triazole (**2b**). White solid; yield 90% (Table 4, entry 2). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz,  $\delta$ , ppm): 3.86 (s, 3H, -OMe), 5.66 (s, 2H, triazole-N-CH<sub>2</sub>), 6.97 (d, *J* = 7.2 Hz, 2H, Ar-OMe), 7.28 (s, 1H, triazole-H), 7.46 (d, *J* = 8.0 Hz, 2H, Ar-OMe), 7.76–7.68 (m, 3H, ArH), 8.26 (d, *J* = 7.2 Hz, 2H, ArH). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 126 MHz,  $\delta$ , ppm): 54.3, 55.4, 114.3, 119.0, 123.4, 127.1, 128.1, 128.8, 129.2, 134.9, 159.7. ESI-MS *m*/*z*: 265 (M<sup>+</sup>). Anal. Calcd for C<sub>16</sub>H<sub>15</sub>N<sub>3</sub>O (%): C 72.43, H 5.89, N 15.82, O 6.03; found (%): C 72.50, H 5.82, N 15.84, O 6.10.

1-(4-Nitrobenzyl)-4-pentyl-1*H*-1,2,3-triazole (**2** h). White solid; yield 90% (Table 4, entry 8). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz,  $\delta$ , ppm): 0.80 (t, J = 6.5 Hz, 3H, -CH<sub>3</sub>), 1.30-1.18 (m, 4H, -CH<sub>2</sub>), 1.62-1.53 (m, 2H, -CH<sub>2</sub>), 5.55 (s, 2H, triazole-N-CH<sub>2</sub>), 7.28 (s, 1H, triazole-H), 7.31 (d, J = 8.5 Hz, 2H, Ar-NO<sub>2</sub>), 8.13 (d, J = 8.5 Hz, 2H, Ar-NO<sub>2</sub>), 1<sup>3</sup>C NMR (CDCl<sub>3</sub>, 126 MHz,  $\delta$ , ppm): 14.0, 22.4, 25.7, 29.1, 31.5, 53.0, 121.0, 149.5, 124.2, 128.5, 142.3, 148.0. ESI-MS *m/z*: 275 (M + 1). Anal. Calcd for C<sub>14</sub>H<sub>18</sub>N<sub>4</sub>O<sub>2</sub> (%): C 61.30, H 6.61, N 20.42, O 11.66; found (%): C 61.15, H 6.66, N 20.47, O 11.71.

Ethyl 2-(4-phenyl-1*H*-1,2,3-triazol-1-yl)acetate (**2i**). White solid; yield 88% (Table 4, entry 9). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz,  $\delta$ , ppm): 1.27 (t, *J* = 7.0 Hz, 3H, -OEt), 4.25 (q, *J* = 7.0 Hz, -OEt), 5.17 (s, 2H, triazole-N-CH<sub>2</sub>), 7.43–7.36 (m, 3H, ArH), 7.91–7.79 (m, 2H, ArH), 7.97 (s, 1H, triazole-H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 126 MHz,  $\delta$ , ppm): 14.2, 51.2, 62.6, 126.0, 128.4, 129.0, 130.6, 166.2. ESI-MS *m/z*: 231 (M<sup>+</sup>). Anal. Calcd for C<sub>12</sub>H<sub>13</sub>N<sub>3</sub>O<sub>2</sub> (%): C 62.33, H 5.67, N 18.17, O 13.84; found (%): C 62.39, H 5.61, N 18.10, O 13.82.

Ethyl 2-(4-(4-methoxyphenyl)-1*H*-1,2,3-triazol-1-yl)acetate (**2j**). Colourless solid; yield 90% (Table 4, entry 10). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz,  $\delta$ , ppm): 1.26 (t, J = 7.0 Hz, 2H, ArH), 3.81 (s, 3H, ArH), 4.29 (q, J = 7.0 Hz, 2H, -OEt), 5.16 (s, 2H, triazole-N-CH<sub>2</sub>), 7.04–6.82 (m, 2H, ArH), 7.71–7.90 (m, 4H, ArH and triazole-H).<sup>13</sup>C NMR (CDCl<sub>3</sub>, 126 MHz,  $\delta$ , ppm): 13.9, 51.0, 55.5, 62.6, 110.9, 114.4, 123.7, 127.2, 150.4, 159.8, 166.1. ESI-MS *m/z* 261 (M<sup>+</sup>). Anal. Calcd for C<sub>13</sub>H<sub>15</sub>N<sub>3</sub>O<sub>3</sub> (%): C 59.76, H 5.79, N 16.08, O 18.37; found (%): C 59.90, H 5.74, N 16.06, O 18.42.

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1,3-Diphenylurea (**3c**). Grey solid; yield 65% (Table 6, entry 3). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz,  $\delta$ , ppm): 6.85 (s, b, 1H, amide), 7.11–7.02 (m, 2H, ArH), 7.16 (brs, 1H, amide), 7.38–7.24 (m, 8H, ArH). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 126 MHz,  $\delta$ , ppm): 110.0, 120.9, 121.8, 124.0, 124.10, 129.23, 129.38, 138.2, 156.6. ESI-MS *m*/*z*: 212 (M<sup>+</sup>). Anal. Calcd for C<sub>13</sub>H<sub>12</sub>N<sub>2</sub>O (%): C 73.56, H 5.70, N 13.20, O 7.54; found (%): C 73.40, H 5.74, N 13.30, O 7.56.

*N*-(4-(Trifluoromethyl)phenyl)nicotinamide (**3f**). White solid; yield 75% (Table 6, entry 6). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz,  $\delta$ , ppm): 7.55–7.39 (m, 3H), 7.88 (d, *J* = 8.0 Hz, 1H, pyridine-H), 7.98 (s, 1H, Ar-CF<sub>3</sub>), 8.26 (d, *J* = 8.0 Hz, 1H, pyridine-H), 8.38 (s, 1H, pyridine-H), 8.77 (s, 1H, pyridine-H), 9.05 (s, 1H, amide). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 126 MHz,  $\delta$ , ppm): 117.2, 121.7, 123.7, 124.07, 128.9, 131.0, 131.6, 135.9, 138.1, 147.8, 152.6, 164.6. ESI-MS *m*/*z*: 266 (M<sup>+</sup>). Anal. Calcd for C<sub>13</sub>H<sub>9</sub>F<sub>3</sub>N<sub>2</sub>O (%): C 58.72, H 3.33, F 1.40, N 10.48, O 6.10; found (%): C, 58.65; H, 3.34; F, 21.46; N, 10.48; O, 6.10.

*N*-(3-Nitrophenyl)nicotinamide (**3** g). Brown solid; yield 75% (Table 6, entry 7). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz,  $\delta$ , ppm): 7.20 (t, *J* = 7.5 Hz, 1H, pyridine-H), 7.36 (d, *J*=13.0 Hz, 2H, aromatic) 7.40 (t, *J*=12.5 Hz, 1H, aromatic), 7.67 (s, 1H, Ar-NO<sub>2</sub>), 7.80 (d, 2H, pyridine-H), 8.55 (s, 1H, pyridine-H), 8.77 (brs, 1H, pyridine-H), 9.03 (s, 1H, amide), 9.56 (s, 1H, amide). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 126 MHz,  $\delta$ , ppm): 115.8, 120.1, 126.6, 129.3 × 2, 130.6, 131.4 × 2, 133.0, 136.2, 153.5, 164.3. ESI-MS *m/z*: 243 (M<sup>+</sup>). Anal. Calcd for C<sub>12</sub>H<sub>9</sub>N<sub>3</sub>O<sub>3</sub> (%): C 59.26, H 3.73, N 17.28, O 19.73; found (%): C 59.35, H 3.70, N 17.2, O 19.6.

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