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# FULL PAPER



# Ce(IV) immobilized on halloysite nanotube–functionalized dendrimer (Ce(IV)–G2): A novel and efficient dendritic catalyst for the synthesis of pyrido[3,2-c] coumarin derivatives

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**Funding information** Research Council of the University of Isfahan In this study, a new and stable Ce(IV) immobilized on halloysite nanotubefunctionalized dendrimer was designed, synthesized, and characterized using Fourier-transform infrared, elemental analysis, thermogravimetric analysis, field emission scanning electron microscopy, scanning electron microscopyenergy dispersive X-ray spectroscopy, transmission electron microscopy, dynamic light scattering, Brunauer-Emmett-Teller, and inductively coupled plasma optical emission spectroscopy techniques. This catalyst was efficiently used for the one-pot, single-step multicomponent synthesis of pyrido[3,2-c]coumarins from 4-aminocoumarin, aldehydes, and aryl ketones. The efficiency and selectivity of this catalytic system were also evaluated for the synthesis of pyrido[3,2-*c*]coumarins from terminal/internal alkynes instead of aryl ketones. In this respect, the regioselectivity of the products was successfully assigned by X-ray crystallographic analysis. All these reactions were best performed under solvent-free conditions in the presence of only 0.28 mol% of the catalyst, and such a one-pot multicomponent synthesis of pyrido[3,2-c]coumarins is reported for the first time. It is also worth noting that single-step and short reaction path for the synthesis of a variety of pyrido[3,2-c]coumarins along with excellent reusability of this dendritic catalyst makes this method economically and environmentally attractive.

#### KEYWORDS

Ce(IV)-supported catalyst, dendrimer, HNT-functionalized dendrimer, pyrido[3,2-*c*]coumarin, reusable catalyst

# **1** | INTRODUCTION

In recent years, application of transition metal complexes, mainly lanthanides, in the field of catalysis has been of great interest due to their ability to catalyze a wide range of chemical reactions.<sup>[1,2]</sup> Among them, Ce(IV) compounds, which are commercially available, eco-friendly, strong Lewis acids, and one-electron

oxidizing agents, have been used as effective catalysts in a variety of organic reactions.<sup>[3-10]</sup> However, because of the homogeneity of these transition metal catalysts, their recyclability and reusability are restricted. One way to overcome this problem, which is important both environmentally and economically, is the use of proper supports or stabilizers to fixate metallic particles.<sup>[11-15]</sup> In the past decades, dendrimers, which are well-defined, hyperbranched, and three-dimensional synthetic macromolecules with internal cavities and chemical functionalities, have been used in various fields.<sup>[16-18]</sup> Recently, the application of dendrimers for stabilizing metal ions by encapsulation has been established.<sup>[19]</sup> In addition, dendrimer-encapsulated metallic particles (DEMs) improve the catalytic activities compared to the other ligand-stabilized particles by increasing the active sites.<sup>[20,21]</sup> Due to the improvement of the catalytic activity as well as the simplified recyclability of DEMs. heterogenization of DEMs by immobilizing on insoluble supports has gained much interest.<sup>[22-25]</sup> During the past years, using organic or inorganic nanotubular materials as support has attracted attention because of their exceptionally large surface area and specific tube-shaped structure with an empty cavity.<sup>[26]</sup> Halloysite nanotube (HNT), a kind of naturally occurring aluminosilicate nanoclav (Al<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub>·2H<sub>2</sub>O with 1:1 ratio of Al/Si),<sup>[27]</sup> has gained great attention because of its widespread applications<sup>[28-35]</sup> and advantages such as high mechanical and thermal stability, low price, environmental friendliness, biocompatibility, large surface area, resistibility against organic solvents, and ease of reusability. Owing to these outstanding properties, using HNTs as support is of practical importance and highly attractive in chemistry as well as in industry.<sup>[36–43]</sup>

Coumarins (2H-chromen-2-ones) and their fused derivatives are important cores in many natural and synthetic biologically active molecules with different applications.<sup>[44–47]</sup> Among coumarin-fused heterocycles, pyridocoumarins are fundamental parts of natural compounds with an extensive range of pharmacological properties such as antibacterial, anticoagulant, anti-inflammatory, antimicrobial, antitumor, and antidiabetic activities.<sup>[48-52]</sup> Because of the significance of pyridocoumarins, several synthetic methods of pyrido[3,2-c]coumarin derivatives have been developed over the past years.<sup>[49,50,53-57]</sup> Nevertheless, multistep sequences, low diversity of pyrido[3,2-c]coumarins, long reaction times, and the use of detrimental organic solvent as well as non-reusable catalyst are limitations of some of the previously reported methods. Furthermore, to the best of our knowledge, there have been no reports on the synthesis of pyrido [3,2-c] coumarin derivatives via the one-pot, multicomponent reaction of 4-aminocoumarin, aldehydes, and aryl ketones or terminal/internal alkynes. Therefore, the development of an efficient one-pot, multicomponent synthesis of pyrido[3,2-*c*]coumarin derivatives is an active ongoing research area and is still highly desirable.

In continuation of our study, relating to the expansion of effective and valuable catalytic systems for use in important synthetic protocols,<sup>[58–61]</sup> for the first time, we described the synthesis of pyrido[3,2-*c*]coumarin derivatives via a one-pot, single-step, multicomponent reaction of 4-aminocoumarin, aldehydes, and aryl ketones or terminal/internal alkynes in the presence of only catalytic amount of a thermally, air- and moisturestable Ce(IV) immobilized on HNT-functionalized dendrimer under solvent-free conditions (Scheme 1).

## 2 | EXPERIMENTAL

## 2.1 | General

The chemicals were purchased from Fluka (Switzerland) and Merck (Germany) chemical companies. 4-Aminocoumarin and cerium(IV) triflate were synthesized as mentioned in the literature.<sup>[62,63]</sup> HNTs were purchased from Sigma-Aldrich (Germany) chemical company. According to the supplier, the properties of HNTs are as follows: diameter = 30-70 nm, length =  $1-3 \mu$ m, cation exchange capacity = 8.0 meg/g, and density =  $2.53 \text{ g/cm}^3$ . Melting points were determined using a Stuart Scientific SMP2 apparatus (UK). Fouriertransform infrared (FT-IR) spectra were recorded on a Jasco 6300 (Japan) instrument in the range of 400-4000 cm<sup>-1</sup>. <sup>1</sup>H and <sup>13</sup>C NMR (400 and 100 MHz) spectra were recorded on a Bruker-Avance 400 spectrometer (Germany) using dimethyl sulfoxide (DMSO)- $d_6$  as a solvent. Elemental analysis was done on a LECO, CHNS-932 analyzer (USA). Thermogravimetric analysis (TGA) was carried out on a Mettler TG50 (USA) instrument under argon flow at a uniform heating rate of 20°C min<sup>-1</sup> in the range of 30–700°C. The cerium content of the catalyst was measured using an inductively coupled plasma optical emission spectrometry, using a Jarrell-Ash 1100 ICP analyzer (USA). Field emission scanning electron microscopy (FE-SEM) measurements and energy dispersive X-ray spectroscopy (EDS) were performed on a Zeiss Sigma VP (Germany). Transmission electron microscopy (TEM) measurements were carried out on a Zeiss-EM10C-100kV (Germany). X-ray crystallographic analysis was performed using an STOE-IPDS 2T single crystal diffractometer (Germany). Dynamic light scattering (DLS) measurements were performed using a Nano Particle Analyzer SZ-100 (Japan) in a distilled



SCHEME 1 Synthesis of pyrido[3,2-c]coumarins catalyzed by Ce(IV)-G2

water medium. The Brunauer–Emmett–Teller (BET) measurements were taken by a BELSORP-mini 2 (Japan).

# 2.2 | Preparation of HNT-functionalized dendrimer (G2)

For the preparation of CP@HNT, HNT was first activated by heating at 100°C for 2 h. Then, a mixture of activated HNT (4 g) and 3-chloropropyltrimethoxysilane (CPTS, 8 ml) was exposed to microwave irradiation (MW) (100°C, 25 W) under constant stirring for 1 h. The mixture was filtered, washed with EtOH, and dried at 80°C under vacuum to yield CP@HNT. Then, a mixture of CP@HNT (3 g), K<sub>2</sub>CO<sub>3</sub> (4.14 g), and 3,5-bis(bromomethyl)phenol (BMP, 1 g) in dimethylformamide (DMF) (20 ml) was stirred at 80°C under N<sub>2</sub> atmosphere for 24 h. The solid material (BMP1@HNT) was separated by simple filtration, washed with distilled water and EtOH, and dried in a vacuum oven at 70°C for 1 h. Subsequently, a mixture of BMP1@HNT (3 g), bis(2-bromoethyl)amine hydrobromide (BEA, 4 g), diisopropylethylamine (DIPEA, 5.2 ml), and dry toluene (40 ml) was stirred under reflux conditions for 24 h. After cooling, the solid material was separated by filtration, washed with toluene and EtOH, and then dried in a vacuum oven at 70°C for 1 h to yield G1. For the synthesis of second generation, G2, a mixture of G1 (2.6 g), K<sub>2</sub>CO<sub>3</sub> (8.28 g), and BMP (2.9 g) in 40 ml of DMF was stirred at  $80^{\circ}$ C under N<sub>2</sub> atmosphere for 24 h. The solid material (BMP2@HNT) was separated by

filtration, washed with distilled water and EtOH, and dried in a vacuum oven at 70°C for 1 h. Then, a mixture of BMP2@HNT (2 g), diethanolamine (DEA, 20 ml), and DIPEA (20.8 ml) in 50 ml DMF was stirred under reflux conditions for 24 h under  $N_2$  atmosphere. The synthesized G2 with periphery OH groups was filtrated and washed with EtOH and dried in a vacuum oven at 70°C for 1 h.

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# 2.3 | Preparation of Ce(IV) immobilized on HNT-functionalized dendrimer (Ce(IV)-G2)

A solution of  $Ce(OTf)_4$  (2 mmol) in dry tetrahydrofuran (THF) (15 ml) was added slowly to a mixture of HNT-functionalized dendrimer (G2, 1 g) in dry THF (10 ml), and the mixture was stirred at room temperature for 24 h. The solid material was filtered, washed with THF, and then dried in a vacuum oven at 80°C for 1 h to synthesize Ce(IV)–G2 catalyst.

## 2.4 | Preparation of Ce(OTf)<sub>4</sub>@HNT

A solution of Ce (OTf)<sub>4</sub> (1 g, 0.7 mmol) in 10 ml of dry THF was added slowly to a mixture of HNT (0.5 g) in dry THF (10 ml), and the mixture was stirred at room temperature for 24 h. The solid material was filtered, washed with THF, and then dried in a vacuum oven at 80°C for 1 h. The cerium content of Ce(OTf)<sub>4</sub>@HNT, measured by ICP, exhibited a value of 0.014 mmol per gram of Ce(OTf)<sub>4</sub>@HNT.

# 2.5 | General procedure for the synthesis of pyrido[3,2-c]coumarins in the presence of Ce(IV)-G2 catalyst

In a screw-cap glass tube with a magnetic stirrer, a mixture of 4-aminocoumarin (1 mmol), aryl ketone or alkyne (1 mmol), aldehyde (1 mmol), and Ce(IV)–G2 (80 mg, containing 0.0028 mmol Ce(IV)) was stirred at 130°C under solvent-free conditions. The reaction progress was checked by thin layer chromatography(eluent: *n*hexane/EtOAc, 10:1). At the end of the reaction, the mixture was cooled to room temperature, and EtOAc (15 ml) was added. The catalyst was separated by filtration and washed with EtOAc (10 ml). The filtrate was evaporated, and the crude product was purified by chromatography on silica gel (*n*-hexane/ethyl acetate, 10:1) to afford the pure product in 70-80% yields.

#### **3** | **RESULTS AND DISCUSSION**

# 3.1 | Preparation of Ce(IV) immobilized on HNT-functionalized dendrimer (Ce(IV)-G2)

So far, by combining different dendrons and functionalized surfaces, several types of dendrimers such as poly(amidoamine) dendrimer,<sup>[64,65]</sup> poly(propyleneimine)



SCHEME 2 Preparation of halloysite nanotube-functionalized dendrimer (G2)

dendrimer,<sup>[66]</sup> triazine dendrimer,<sup>[67,68]</sup> poly(propyletherimine) dendrimer<sup>[69,70]</sup> and carbosilane dendrimer<sup>[71,72]</sup> have been synthesized. In this study, we tried to design a new second generation of dendrimer using BMP and BEA. The synthetic pathway of this HNT-functionalized dendrimer (G2) is illustrated in Scheme 2.

At first, the activated HNT was treated with CPTS according to the reported procedure,<sup>[73]</sup> to yield CP@HNT which is essential for growing dendritic molecules. The reaction between CP@HNT and BMP produced BMP1@HNT, which upon reaction with BEA provided the first generation of dendrimer, G1. In the following, G1 was transformed to BMP2@HNT by the reaction with BMP. Finally, BMP2@HNT reacted with DEA to form HNT-functionalized hydroxyl groups on the molecular surface (G2) (Scheme 2). The synthesized G2 with OH groups on its periphery was applied for the immobilization of Ce(IV) via the reaction of G2 with cerium(IV) trifluoromethanesulfonate to produce Ce(IV)–G2 (Scheme 3).

The stepwise preparation of Ce(IV)–G2 was determined by FT-IR, TGA, and elemental analysis.

The functionalization of HNT surface was recognized by FT-IR spectroscopy (Figure 1). In the FT-IR spectrum of HNT, the characteristic bands were observed at 3694, 3623, and 910 cm<sup>-1</sup> (inner surface –OH groups), 1029 and 466 cm<sup>-1</sup> (Si–O–Si), and 531 cm<sup>-1</sup> (Al–O–Si).<sup>[37]</sup> In the spectra of CP@HNT, BMP2@HNT, and G2, the specific bands at 3050, 2921, 2857, and 1453 cm<sup>-1</sup> are related to the C–H stretching and bending vibrations of aryl and alkyl groups. Moreover, the bands that appeared at 1595 (C=C) and 1313 cm<sup>-1</sup> (C–O) are good evidence for the functionalization of HNT with the desired organic moieties. It is noteworthy that the frequency of stretching bands of inner-surface OH groups of HNT does not alter upon functionalization, indicating that grafting has occurred on the outer surface of HNT.<sup>[74,75]</sup>

The amount of organic moieties of different steps of functionalization of HNT surface was determined by elemental analysis. First, the CP@HNT was investigated and revealed only hydrogen and carbon on the surface. The amount of organic moieties was found to be 0.42 mmol  $g^{-1}$  of HNT, based on the carbon result of the elemental analysis. In the next step, the amount of organic moieties in BMP1@HNT was evaluated to be 8.74 mmol  $g^{-1}$  based on the carbon result of the elemental analysis. The higher carbon content in BMP1@HNT (8.74 mmol  $g^{-1}$ ) compared to CP@HNT (0.42 mmol  $g^{-1}$ ) is due to the presence of BMP fragment on the surface of HNT. The nitrogen content of G1, BMP2@HNT, G2, and Ce(IV)–G2 was also measured by the elemental analysis. The results were found to be 0.67, 0.49, 1.01, and 0.74%, respectively. According to these results, the amount of organic layers coated on HNT was about 0.239, 0.175, 0.072, and 0.053 mmol g<sup>-1</sup> in G1, BMP2@HNT, G2, and Ce(IV)-G2, respectively. Consequently, the conversion of G1  $\rightarrow$  BMP2@HNT, BMP2@HNT  $\rightarrow$  G2, and  $G2 \rightarrow Ce(IV)$ -G2 was achieved with 73.18, 41.17, and 73.33% yields. The elemental analysis results are presented in Table 1.

Figures 2 and 3 show the thermogravimetric and derivative thermogravimetric (TG/DTG) analysis curves for HNT, CP@HNT, BMP1@HNT, G1, and Ce(IV)–G2. The weight loss in each step was studied as a function of temperature between 30 and 700°C. As shown in Figure 2, HNT experienced two weight losses, at 103.1



SCHEME 3 Preparation of Ce(IV) immobilized on halloysite nanotube-functionalized dendrimer (Ce(IV)-G2)



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**FIGURE 1** Fourier-transform infrared spectra of halloysite nanotube (HNT), CP@HNT, BMP2@HNT, and G2

and 553.6°C, corresponding to the loss of adsorbed water and structural dehydroxylation, respectively.<sup>[76]</sup> According to the weight loss at 553.6°C, the quantity of total hydroxyl groups of HNT was calculated to be 6.3 mmol g<sup>-1</sup>. The amount of inner hydroxyl groups in HNT was determined by their substitution with fluoride of ammonium fluoride and subsequent titration with H<sub>2</sub>SO<sub>4</sub>. Based on the obtained results, the amount of these hydroxyl groups was found to be about 2.8 mmol g<sup>-1</sup>.<sup>[77,78]</sup> Consequently, the amount of outer hydroxyl groups in HNT was estimated to be about 3.5 mmol g<sup>-1</sup>. To further approve this aim, the pristine HNT was first functionalized by CPTS (which occurred on the outer surface of HNT)<sup>[79]</sup> and then treated with ammonium fluoride and finally titrated. Under these

conditions, the amount of OH groups found in HNT, which correspond to inner ones, was also obtained (about 2.8 mmol  $g^{-1}$ ). These results were completely comparable with those obtained by the aforementioned direct determination of the amount of hydroxyl groups in HNT.<sup>[78]</sup>

As shown in Figure 3a–d, CP@HNT experienced two weight losses, one at 162.67°C and one at 502.17°C. BMP1@HNT experienced two weight losses at 75.25 and 502.15°C. G1 experienced three weight losses at 66.95, 330.90, and 508.76°C, and Ce(IV)–G2 also experienced three weight losses at 49.50, 352.83, and 520.83°C. Weight losses up to 200°C correspond to the removal of physically adsorbed water molecules, whereas, the weight losses at 300°C and higher are due to the removal of organic moieties from the surface. This shows that the catalyst has high

TABLE 1 CHNS results for the preparation of Ce(IV)-G2

	Elemental analysis (%)					
Product	С	Н	Ν	S	HNT (mmol g <sup>-1</sup> )	Yield (%)
CP@HNT	1.53	2.32	-	-	0.42	-
BMP1@HNT	11.55	2.22	-	-	8.74	-
G1	12.21	2.32	0.67	-	0.239	2.73
BMP2@HNT	15.30	2.43	0.49	-	0.175	73.18
G2	15.28	2.50	1.01	-	0.072	41.17
Ce(IV)–G2	15.48	3.19	0.74	1.43	0.053	73.33
	Product CP@HNT BMP1@HNT G1 BMP2@HNT G2 Ce(IV)–G2	El        Product      C        CP@HNT      1.53        BMP1@HNT      11.55        G1      12.21        BMP2@HNT      15.30        G2      15.28        Ce(IV)-G2      15.48	Elemental anal        Product      C      H        CP@HNT      1.53      2.32        BMP1@HNT      11.55      2.22        G1      12.21      2.32        BMP2@HNT      15.30      2.43        G2      15.28      2.50        Ce(IV)-G2      15.48      3.19	Elemental analysis (%)        Product      C      H      N        CP@HNT      1.53      2.32      -        BMP1@HNT      11.55      2.22      -        G1      12.21      2.32      0.67        BMP2@HNT      15.30      2.43      0.49        G2      15.28      2.50      1.01        Ce(IV)-G2      15.48      3.19      0.74	Elemental analysis (%)        Product      C      H      N      S        CP@HNT      1.53      2.32      -      -        BMP1@HNT      11.55      2.22      -      -        G1      12.21      2.32      0.67      -        BMP2@HNT      15.30      2.43      0.49      -        G2      15.28      2.50      1.01      -        Ce(IV)-G2      15.48      3.19      0.74      1.43	Elemental analysis (%)        Product      C      H      N      S      HNT (mmol g <sup>-1</sup> )        CP@HNT      1.53      2.32      -      -      0.42        BMP1@HNT      11.55      2.22      -      -      8.74        G1      12.21      2.32      0.67      -      0.239        BMP2@HNT      15.30      2.43      0.49      -      0.175        G2      15.28      2.50      1.01      -      0.072        Ce(IV)-G2      15.48      3.19      0.74      1.43      0.053





thermal stability. Consequently, the total weight losses of CP@HNT, BMP1@HNT, G1, and Ce(IV)–G2 are 9.43, 20.26, 21.17, and 23.30%, respectively.

The morphology of the surface of HNT and Ce(IV)–G2 was determined by FE-SEM (Figure 4a,b). Both HNT and Ce(IV)–G2 particles are tubular. The SEM–EDS analysis for HNT shows only the presence of O, Al, and Si, whereas the SEM–EDS of Ce(IV)–G2 clearly demonstrates the presence of C, N, F, O, Al, Si, S, and Ce elements in the construction of the prepared catalyst (Figure 4c,d). These results indicate the successful functionalization of HNT by covalent attachment of designed dendrimer along with immobilization of cerium(IV) trifluoromethanesulfonate.

HNT and Ce(IV)–G2 were also characterized using TEM (Figure 5a,b). The tubular morphology of HNT is also displayed in the TEM image of Ce(IV)–G2, indicating that the surface morphology of HNT does not alter extremely in the presence of organic unit (Figure 5b). The histogram of size distribution verified that the matrix has an average diameter of about 30–60 nm (Figure 5c). The cerium content of the catalyst, measured by ICP, exhibited a value of 0.035 mmol Ce(IV) per gram of Ce(IV)–G2 catalyst.

The average hydrodynamic diameter of HNT and Ce(IV)–G2 was evaluated using DLS (Figure 6). As shown, the average hydrodynamic diameter of Ce(IV)–G2 (426.9 nm) is larger than that of HNT (399.7 nm)<sup>[80]</sup>



FIGURE 3 Thermogravimetric and derivative thermogravimetric curves of (a) CP@HNT, (b) BMP1@HNT, (c) G1, and (d) Ce(IV)-G2



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FIGURE 4 Field emission scanning electron microscopy images of (a) halloysite nanotube (HNT) and (b) Ce(IV)-G2. Scanning electron microscopy-energy dispersive X-ray spectroscopy spectra of (c) HNT and (d) Ce(IV)-G2



FIGURE 5 Transmission electron microscopy image of (a) halloysite nanotube and (b) Ce(IV)-G2. (c) Histogram of size distribution for Ce(IV)-G2



FIGURE 6 Dynamic light scattering plots of halloysite nanotube and Ce(IV)-G2



FIGURE 7 (a) Barrett–Joyner–Halenda plots and (b) N<sub>2</sub> adsorption–desorption isotherms of hallovsite nanotube and Ce(IV)–G2

which indicates that dendrimer had been attached to the surface of HNT.

The surface properties of HNT and Ce(IV)-G2 were studied by nitrogen adsorption-desorption measurements at -196°C (Figure 7). According to the International Union of Pure and Applied Chemistry classification, the isotherms of HNT and Ce(IV)-G2 are of type IV with H3 hysteresis loops.<sup>[81]</sup> The Brunauer-Emmett–Teller (BET) and Barrett-Joyner-Halenda (BJH) methods were used for the calculation of specific surface areas and pore size distributions, respectively. As shown in Table 2, the specific surface area,  $a_{\rm SBET}$ , and the total pore volume of Ce(IV)-G2

 $(a_{\rm s BET} = 27.788 \text{ m}^2 \text{ g}^{-1}, \text{ total pore volume} = 0.189 \text{ cm}^3 \text{ g}^{-1})$ are considerably lower than those of pristine HNT ( $a_{s,-}$  $_{\text{BET}} = 39.156 \text{ m}^2 \text{ g}^{-1}$ , total pore volume = 0.214 cm<sup>3</sup> g<sup>-1</sup>). These results show that dendrimer due to its huge structure covers the surface of HNT.<sup>[37,82]</sup> In addition, the higher amount of pore diameter of Ce(IV)-G2) compared to that of HNT can be related to the porous structure of dendrimer.<sup>[36]</sup>

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To summarize, the data obtained indicate that the Ce(IV)-G2 catalyst has been successfully prepared. As far as we know, the synthesis of Ce(IV) immobilized on HNT-functionalized dendrimer is reported for the first time.

TABLE 2 BET analysis results of HNT and Ce(IV)-G2

Sample	$a_{s,BET} (m^2 g^{-1})$	Total pore volume ( $p/p_0 = 0.990$ ) (cm <sup>3</sup> g <sup>-1</sup> )	Mean pore diameter (nm)
HNT	39.156	0.214	21.904
Ce(IV)-G2	27.788	0.189	27.143

# 3.2 | Synthesis of pyrido[3,2-*c*]coumarin derivatives catalyzed by Ce(IV)–G2

Because of the aforesaid disadvantages of the reported synthetic methodologies of pyrido[3,2-c]coumarin, the introduction of a one-pot, single-step, multicomponent reaction for the synthesis of these heterocyclic compounds is of practical importance. Accordingly, we initially tested the reaction between 4-aminocoumarin (1, 1 mmol), 4-methylacetophenone (**2b**, 1 mmol), and 3-methoxybenzaldehyde (**3e**, 1 mmol) in the absence of the catalyst (Table 3). No respective product was observed even at a high temperature (150°C) (entry 1).

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Due to the novelty of this method, several reactions were performed to determine the optimal conditions for the synthesis of pyrido[3,2-*c*]coumarins in the presence of various potential catalysts (entries 2–15). The results surprisingly showed that the prepared dendritic catalyst (Ce(IV)–G2) was the most effective catalyst for this reaction, and the respective pyrido[3,2-*c*]coumarin **4be** was obtained in higher yield than those of pure Ce (OTf)<sub>4</sub>, HNT, or even Ce(OTf)<sub>4</sub> coated on HNT (Ce(OTf)<sub>4</sub>@HNT). The three variables, solvent, temperature, and the amount of catalyst were investigated (entries 16–27). The best yield of the product was obtained using 80 mg Ce(IV)–G2 catalyst (containing

**TABLE 3** Optimization of reaction conditions for the synthesis of **4**<sup>[a]</sup>

Entry	Catalyst (mol%)	Solvent (3 ml)	<i>T</i> (°C)	Yield (%) <sup>c</sup>
1	-	-	150	-
2	$BiCl_3(2)$	-	140	5
3	$\operatorname{ZnCl}_{2}(2)$	-	140	10
4	$AlCl_3(2)$	-	140	5
5	$CeCl_3 \cdot 7H_2O(2)$	-	140	5
6	$Bi(OTf)_3(2)$	-	140	20
7	Triflic acid (3 ml)	-	140	25
8	Diethanolamine (2)	-	140	-
9	CAN (2) <sup>c</sup>	-	140	5
10	Ce(OTf) <sub>4</sub> (0.28)	-	140	28
11	$Ce(OTf)_4(2)$	-	140	40
12	HNT(80 mg)	-	140	-
13	Ce(OTf) <sub>4</sub> @HNT (2)	-	140	45
14	G2 (80 mg)	-	140	-
15	Ce(IV)-G2 (0.28)	-	140	70
16	Ce(IV)-G2 (0.28)	DMF	140	5
17	Ce(IV)-G2 (0.28)	Ethylene glycol	140	20
18	Ce(IV)-G2 (0.28)	H <sub>2</sub> O	Reflux	-
19	Ce(IV)-G2 (0.28)	EtOH	Reflux	-
20	Ce(IV)-G2 (0.28)	CH <sub>3</sub> CN	Reflux	-
21	Ce(IV)-G2 (0.28)	Toluene	Reflux	5
22	Ce(IV)-G2 (0.28)	DMSO	140	5
23	Ce(IV)-G2 (0.14)	-	140	45
24	Ce(IV)-G2 (0.50)	-	140	70
25	Ce(IV)-G2 (0.28)	-	130	70
26	Ce(IV)-G2 (0.28)	-	120	30
27	Ce(IV)-G2 (0.28)	_	80	5

Abbreviations: DMF, dimethylformamide; DMSO, dimethyl sulfoxide; HNT, halloysite nanotube.

<sup>a</sup>Reaction of 4-aminocoumarin **1** (1.0 mmol) with 4-methylacetophenone **2b** (1.0 mmol) and 3-methoxybenzaldehyde **3e** (1.0 mmol) was investigated under solvent-free conditions for 10 h at different conditions.

<sup>b</sup>Isolated yield.

<sup>c</sup>Ceric ammonium nitrate.

0.0028 mmol Ce(IV), 0.28 mol%) at 130°C under solventfree conditions (entry 25).

Then, the scope and generality of this catalytic system were investigated in the synthesis of a series of pyrido[3,2-c] coumarins under the optimized reaction

conditions. As shown in Scheme 4, acetophenone 2a reacted effectively with 4-aminocoumarin 1 and different aromatic aldehydes such as benzaldehyde 3a. 4-chlorobenzaldehyde 3b, 4-isopropylbenzaldehyde 3c, and even 2-phenylpropanal 3d as an aliphatic aldehyde







SCHEME 5 Synthesis of compound 6 using diphenylacetylene under optimized reaction conditions

6fa, R<sup>2</sup> = 4-MeC<sub>6</sub>H<sub>4</sub>, (4 h, 71%)

**6ha**,  $R^2 = 4$ -MeOC<sub>6</sub>H<sub>4</sub>, (4 h, 75%)

**6ia**,  $R^2 = 2,4$ -(Cl)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, (4 h, 70%)



FIGURE 8 Molecular structures of 8ja and 9bb

to produce the desired products **4aa–ad** in 70–80% yields. Moreover, the aryl ketones with electron-donating groups such as 4-methyl and 4-cyclohexylacetophenones (**2b** and **2c**) and electron-withdrawing groups such as halogenated acetophenones (**2d–f**) and 4-nitroacetophenone **2g**, as well as 2- and 3-acetylpyridines (**2h** and **2i**) as the heterocyclic substrates, underwent smooth reaction with 4-aminocoumarin and aromatic aldehydes bearing either electron-withdrawing or electron-donating groups to produce the corresponding pyrido[3,2-*c*]coumarins in 70–78% yields.

To further examine the efficiency and selectivity of this catalytic system, this one-pot, multicomponent reaction was also checked with diphenylacetylene **5a** instead of aryl ketones in the presence of Ce(IV)–G2. Under these conditions, the desired polysubstituted pyrido[3,2-c]

**SCHEME 7** Proposed mechanism for the synthesis of **8** from phenylacetylene



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**SCHEME 8** Proposed mechanism for the synthesis of **9** from methyl propiolate

coumarins (**6fa**, **6ha**, and **6ia**) were obtained in 70–75% yields (Scheme 5).

Finally, the applicability of this new one-pot, multicomponent reaction was examined using phenylacetylene **7a** and methyl propiolate **7b** as terminal alkynes (Scheme 6). It is worth mentioning that in the reaction of phenylacetylene **7a** with 4-aminocoumarin and different aldehydes, the respective 2,4-disubstituted pyrido[3,2-*c*]coumarins (**8ea**, **8ja**, and **8ka**) were produced with excellent selectivity and good yields. However, treatment of methyl propiolate **7b** with 4-aminocoumarin and aldehydes produced the regioisomeric 3,4-disubstituted pyrido[3,2-*c*]coumarins (**9ab**, **9bb**, and **9fb**) as sole product in 70–75% yields. The observed regioselectivity of these products was further confirmed using the X-ray crystallographic analysis



# FIGURE 9 Reusability of Ce(IV)-

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G2 and Ce(OTf)<sub>4</sub>@HNT

(Figure 8, CCDC of **8ja**: 1981325 and CCDC of **9bb**: 1981326). Disordered acetonitrile solvent molecule has been removed by Squeeze.<sup>[83]</sup>

As reported previously, Ce(IV) triflate can act as an efficient Lewis acidic catalyst.<sup>[6]</sup> Based on this observation and according to the aforementioned results, reasonable mechanisms for the selective synthesis of 2,4- and 3,4-disubstituted pyrido[3,2-c]coumarins catalyzed by Ce(IV)–G2 are suggested in Schemes 7 and 8.

First, the reaction between activated aldehyde A and phenylacetylene 7a synthesizes intermediates B and then C, which via Meyer–Schuster rearrangement is converted to intermediate D.<sup>[84]</sup> Then, 1,4-addition of 4-aminocoumarin 1 to the intermediate D results in

intermediate **E** which upon the elimination of water forms intermediate **F**. Finally, aerial oxidation of **F** forms the desired 2,4-disubstituted pyrido[3,2-c]coumarin **8** (Scheme 7).

In the case of 3,4-disubstituted pyrido[3,2-c]coumarin, the amino group of 4-aminocoumarin 1 initially attacks the terminal carbon of activated methyl propiolate **G** by Ce(IV)–G2 catalyst to yield intermediate **H**, wherein the negative charge is stabilized by the adjacent carbonyl group. Next, intermediate **H** attacks the activated aldehyde **I** to give **J**, which upon intramolecular cyclization along with elimination of water produces **K**. The Intermediate **K** is converted to **L** by hydrogen shift. Finally, aerial oxidation of **L** gives the corresponding



**FIGURE 10** Fourier-transform infrared spectra of fresh Ce(IV)–G2 and Ce(IV)–G2 after the sixth run

3,4-disubstituted pyrido[3,2-*c*]coumarin **9** (Scheme 8). To further confirm the suggested mechanism, the reaction was also performed under argon atmosphere, and the product yield was reduced considerably under these conditions. This result ruled out the anomeric-based oxidation of the intermediate **L** to the product **9**.<sup>[85,86]</sup>

As we know, this is a new synthetic method for the preparation of pyrido[3,2-c]coumarin derivatives directly from 4-aminocoumarin via such a multicomponent reaction. Therefore, such a synthesis can be anticipated as an appropriate practical method for the preparation of pyrido[3,2-c]coumarin derivatives.

All products were identified by their FT-IR, <sup>1</sup>H NMR, and <sup>13</sup>C NMR spectra and CHNS elemental analysis (Supporting Information).

The recycling and reusability of the Ce(IV)-G2 catalyst, which is economically and environmentally important, was explored in the reaction between 4-aminocoumarin, 4-methylacetophenone, and 3-methoxybenzaldehyde at 130°C under solvent-free conditions. At the end of the reaction, the mixture was cooled to ambient temperature and then ethyl acetate was added. The catalyst was separated by filtration, washed with ethyl acetate, dried, and reused in the next cycle. As shown in Figure 9, the catalyst could be reused five consecutive times without a significant loss in its catalytic activity. In addition, the leaching of Ce(IV) ion from Ce(IV)-G2 catalyst was measured by ICP technique, and it was found that the leaching grade was insignificant. Also, no considerable difference was observed between FT-IR spectra of the fresh and recycled catalyst after six runs (Figure 10). All these results signify that the Ce(IV)-G2 catalyst is stable in the reaction mixture. To show the fundamental role of dendrimer in stabilizing Ce(IV) ions, the reusability of Ce(OTf)<sub>4</sub>@HNT was compared with that of Ce(IV)-G2 under the same conditions. As shown, the corresponding product was achieved in 45, 22, and 5% yields from the first to third runs, demonstrating that substantial leaching of Ce(IV) ions from the HNT support has occurred during the reaction.

## 4 | CONCLUSIONS

In conclusion, the synthesis and characterization of a stable Ce(IV) immobilized on HNT-functionalized dendrimer (Ce(IV)–G2) is reported for the first time. This catalyst has been successfully applied for the synthesis of a series of pyrido[3,2-c]coumarins via a one-pot, single-step, three-component reaction of 4-aminocoumarin, aryl ketones, and aldehydes. Efficient regioselective synthesis of pyrido[3,2-c]coumarins from internal and terminal

alkynes has also been achieved using this catalytic system. As far as we know, this is a new synthetic method for the preparation of pyrido[3,2-c] coumarins via such a one-pot, single-step, three-component reaction directly from 4-aminocoumarin. Furthermore, good yields, avoidance of toxic organic solvents, and simple work-up procedure, as well as the stability and reusability of the catalyst, are noteworthy features of the present protocol and make it useful and attractive for the synthesis of pyrido[3,2-c]coumarins.

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#### **AUTHOR CONTRIBUTIONS**

Tahereh Ataee-Kachouei: Investigation; software. Mahboobeh Nasr-Esfahani: Investigation. Iraj Mohammadpoor-Baltork: Project administration; supervision. Valiollah Mirkhani: Funding acquisition; methodology. Majid Moghadam: Software. Shahram Tangestaninejad: Conceptualization; formal analysis. Behrooz Notash: Formal analysis; methodology.

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#### Abbreviation: HNT, halloysite nanotube.

Abbreviations: BET, Brunauer–Emmett–Teller; HNT, halloysite nanotube.

#### SUPPORTING INFORMATION

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

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