

1,8-Diazabicyclo [5.4.0] undec-7-ene functionalized cellulose nanofibers as an efficient and reusable nanocatalyst for the synthesis of tetraketones in aqueous medium

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Abstract

1,8-Diazabicyclo [5.4.0] undec-7-ene functionalized cellulose nanofibers (CNF@ DBU[Cl]) were simply prepared and characterized by analytical techniques. Scanning electron microscope confirmed that CNF@DBU[Cl] was formed with average size of 30-60 nm. X-ray diffraction of CNF@DBU[Cl] showed that the crystalline structure of the cellulose nanofibers was remained unchanged after functionalization. According to elemental analyses and thermal gravimetric analysis, the loading amount of organic group on cellulose nanofibers was found to be 1.46 mmol/g. The catalytic activity of DBU functionalized cellulose nanofibers was studied for the synthesis of biologically important tetraketone derivatives in the reaction of aldehydes with 1,3-dicarbonyl compounds. In the presence of CNF@DBU[Cl], the corresponding tetraketones were obtained in 80-96% yields under very mild reaction conditions. The catalyst was recovered and reused four successive runs without significant loss of catalytic activity. This method showed several significant advantages including short reaction times, high yields of products, use of various substrates, convenient work-up, no necessity of extraction or chromatographic purification steps, environmentally friendly conditions and lack of use of any harmful solvent.

Graphic abstract



Keywords 1,8-Diazabicyclo [5.4.0] undec-7-ene functionalized cellulose nanofibers \cdot Tetraketone \cdot 1,3-dicarbonyl compounds \cdot Aldehydes \cdot Reusable heterogeneous catalyst

Introduction

Recently, the investigations of supported heterogeneous catalysts became one of the main focuses of modern worldwide research in catalysis. Many researches have been directed toward finding of sustainable and ecological resources, in other words green chemistry. To attain an environmentally friendly and sustainable chemical process, the use of renewable materials as solid supports has found many attention. In this regard, biopolymer is an attractive candidate as a solid support material in preparation of heterogeneous catalysts. Biopolymers such as cellulose [1-6], chitosan [7-10] and chitin [11-13] have attracted remarkable attention as support materials for catalytic systems owing to their unique properties, renewability, non-toxicity, low cost and abundance in nature.

Today, nanotechnology has become a top research field in the world due to different applications of nanomaterials in diverse sectors including nanomedicine, catalysis, sensors, environment, water treatment and energy storage [14–28]. In recent years, the application of nanomaterials has been attracted as catalysts supports.

The development of nano-sized systems as supported heterogeneous catalysis makes it possible to improve the reactivity and the selectivity of the catalysts [29–31] compared to the solid materials.

Cellulose nanofibers (CNFs) have received much attention because of their unbeatable properties such as large surface area-to-volume ratio, biocompatibility, simple surface functionalization, easy handling and outstanding mechanical properties [32–34]. The CNFs and their composites have been utilized for various potential applications such as sensors, energy production, catalysis, biomedical, separators and filters [35–38]. It is well known that cellulose is widely used and easily modified by functionalization, which makes it a suitable polymeric support for heterogeneous catalysts. The presence of hydroxyl groups on the surface of cellulose fibers provides a stable matrix for anchoring a variety of adsorbed compounds to prepare the biomaterials for targeted applications [39, 40]. These interesting properties make this green material an attractive alternative for conventional synthetic organic or inorganic supports in catalytic applications [41, 42].

2,2'-Arylmethylene bis(3-hydroxy-5,5-dimethyl-2-cyclohexene-1-one (tetraketone) derivatives are an important class of organic compounds containing oxygen that have attracted a lot of interest due to their various uses in pharmacy, biology and material sciences. Tetraketone derivatives show biological and therapeutic properties such as lipoxygenase inhibitory [43], tyrosinase inhibitory in dermatological disorders including hyperpigmentation and skin melanoma [44], antibacterial and antiviral activities [43]. Moreover, they are important synthetic intermediates that can act as useful precursors in the synthesis of xanthene and polyhydroacridine derivatives [45, 46] that display biological and therapeutic activities. The conventional method for the preparation of tetraktones is the condensation of aromatic aldehydes with cyclic 1,3-diketones in the presence of various catalysts such as natural phosphate [47], KF/Al₂O₃ [48], alumina–sulfuric acid [49], Yb(OTf)₃–SiO₂ [50], HClO₄–SiO₂ [51], mesoporous silica nanoparticles (MSN)adsorbed HBF₄ [52], copper nanoparticles supported onto silica [53], SmCl₃ [54], Fe³⁺-montmorillonite [55], HY zeolite [56], nano-Fe/NaY [57], cerium-impregnated-MCM-41 [58] and CoFe₂O₄ [59]. Although most of these methods for synthesis of tetraketones are effective, some of them suffer from drawbacks such as low yield and long reaction times [46], leaving harmful waste on work-up [45], tedious work-up procedure [49], expensive reagents, use of organic solvents, hazardous and harsh reaction conditions [48] and using unrecyclable catalysts. The development of simple, efficient and environmentally friendly methods for the synthesis of tetraketones in the presence of novel catalysts is still in great demand.

In continuation of our work on the development of new methods for synthesis of heterocyclic compounds [60–64], herein, we report the preparation and characterization of DBU functionalized cellulose nanofibers (CNF@DBU[Cl]) and its application as a recyclable heterogeneous green catalyst for the synthesis of tetraketone derivatives in aqueous medium (Scheme 1).

Experimental

Chemicals and materials

Chemicals (except CNF) were purchased from Merck and Sigma Chemical Companies. CNF was procured from Nano Novin Polymer Company. The known products were identified by comparison of their melting points and spectral data with those reported in the literature. ¹H and ¹³C NMR spectra were recorded on a Bruker DRX-400 AVANCE spectrometer in CDCl₃ as solvent. Fourier transform infrared (FT-IR)



Scheme 1 Synthesis of tetraketone derivatives using CNF@DBU[Cl]

spectra were recorded on a Bruker Vector 22 spectrometer in KBr matrix. Scanning electron microscopy (SEM) images were observed using a VEGA/TESCAN-XMU instrument. X-ray diffraction (XRD) was performed using a Philips PW 1830 diffractometer with Cu K_a radiation ($\lambda = 1.54$ Å) in the Bragg angle range of 5-80° at room temperature. Thermogravimetric analysis was performed using TGA 951 Dupont. Elemental analyses were carried out on an Elemental Analyzer CHNLECO 600. Melting points were determined with an Electrothermal 9100 apparatus.

Preparation of modified cellulose nanofiber (CNF@[Cl])

CNF (1.0 g) was suspended in 30 mL of dry toluene for 40 min, and then, 3-chloropropyltrimethoxysilane (1.5 mL) was added to it. The suspension was stirred under reflux for 48 h. Then, the reaction was stopped and cooled to room temperature. The reaction mixture filtered and washed with toluene, ethanol and finally diethyl ether. The modified cellulose nanofiber (CNF@[Cl]) was dried in an oven at 70 °C for 6 h.

Preparation of of CNF@DBU[CI]

To 1 g of CNF@[Cl] was added acetone (50 mL) and DBU (0.7 mL). The mixture was refluxed with stirring under argon for 36 h. Then the reaction mixture was cooled to room temperature and filtered to separate the white powder. The solid was washed with acetone and dichloromethane respectively and dried in an oven at 70 °C for 6 h.

General procedure for the synthesis of tetraketone derivatives (3)

A mixture of aldehyde (1 mmol), 1,3-dicarbonyl compound (2 mmol) and CNF@ DBU[Cl] (0.08 g) in water (5 mL) was stirred at room temperature. After completion of the reaction (as monitored by TLC), acetone was added to the reaction mixture. Then, the catalyst was separated by centrifugation. Pure products were afforded by evaporation of the filtrate. The obtained products were characterized by their melting points as well as ¹H and ¹³C NMR spectral data.

Selected spectral data

2,2'-((2-nitrophenyl)methylene)bis(3-hydroxy-5,5-dimethylcyclohex-2-enone) (**3ia**): mp 187–189 °C (188–189 °C [65]); ¹H NMR (400 MHz, CDCl₃) δ =11.62 (br s, 1H, OH), 7.25-7.57 (m, 4H, ArH), 6.05 (s, 1H, CH), 2.21-2.53 (m, 8H, 4CH₂), 1.17 (s, 6H, 2CH₃), 1.03 (s, 6H, 2CH₃) ppm; ¹³C NMR (100 MHz, CDCl₃) δ =190.9, 189.4, 149.7, 132.1, 131.4, 129.6, 127.2, 124.3, 114.6, 46.9, 46.30, 31.9, 30.0, 28.5, 28.2 ppm.

2,2'-((3-bromophenyl)methylene)bis(3-hydroxycyclohex-2-enone) (**3fb**): mp 246–248 °C (248–249 °C [66]); ¹HNMR (400 MHz, CDCl₃) δ =12.35 (brs, 2H, OH),

7.31(d, J=7.6 Hz, 1H, ArH), 7.22 (s, 1H, ArH), 7.14 (t, J=7.6 Hz, ArH), 7.04 (d, J=8.0 Hz, 1H, ArH), 5.43 (s, 1H, CH), 2.55-2.70 (m, 4H, 2CH₂), 2.35-2.52 (m, 4H, 2CH₂), 2.00-2.09 (m, 4H, 2CH₂) ppm; ¹³CNMR (100 MHz, CDCl₃) δ =192.2, 190.9, 140.6, 129.7, 129.6, 129.0, 125.2, 122.5, 115.9, 33.5, 33.0, 32.8, 20.1 ppm.

3,3'-((4-chlorophenyl)methylene)bis(4-hydroxy-2H-chromen-2-one) (**3dc**): mp 250–252 °C (250 °C [67]); ¹H NMR (400 MHz, CDCl₃) δ =11.2 (brs, 2H, OH), 7.88 (d, *J*=12 Hz, 2H, ArH), 7.58 (t, *J*=20 Hz, 2H, ArH), 7.34 (d, *J*=8 Hz, 2H, ArH), 7.30 (t, *J*=16 Hz, 2H, ArH), 7.26 (d, *J*=8 Hz, 2H, ArH), 7.16 (d, *J*=8 Hz, 2H, ArH), 6.30 (s, 1H, CH) ppm; ¹³C NMR (100 MHz, CDCl₃) δ =166.4, 165.1, 152.8, 140.3, 132.2, 130.4, 129.1, 128.3, 124.4, 124.0, 118.8, 116.3, 103.6, 36.2 ppm.

Results and discussion

According to various research reports on composite materials and their different applications [68–77], we decided to prepare the nanocatalyst based on cellulose nanofibers as an abundant and natural material and to examine its catalytic activity for the synthesis of tetraketones.

Initially, CNF@DBU[Cl] was synthesized in two steps. In the first step, the cellulose nanofiber was reacted with 3-chloropropyltrimethoxysilane (CPTMS) in dry toluene under reflux condition, and modified cellulose nanofiber (CNF@[Cl]) was prepared. Next, CNF@[Cl] and DBU were refluxed in acetone for 36 h. The obtained catalyst (CNF@DBU[Cl]) was characterized by FT-IR, SEM, XRD, TGA and CHN analyses.

Characterization of CNF@DBU[CI]

The FT-IR transmission spectra for CNF and CNF@DBU[Cl] are shown in Fig. 1. For CNF, the strong band at 3425 cm⁻¹ is related to stretching vibration of hydroxyl group. The absorption band at 2905 cm⁻¹ is corresponding to stretching vibration of the C-H bond in the CH₂ and CH₃ groups. The appeared band at 1430 cm⁻¹ shows the bending vibrations of the CH₂ group. The characteristic vibration peak of C–O–C appears at 1090 cm⁻¹. The observed band at 1680 cm⁻¹ is attributed to the bending vibration of H–O–H, and eventually, a small sharp band at 898 cm⁻¹ refers to beta-glycoside bonds in cellulose (Fig. 1a) [78].

For CNF@DBU[Cl] (Fig. 1b), the absorption bands of Si–O functional group and stretching vibration of Si–O–C group are appeared at regions of $575-750 \text{ cm}^{-1}$ and $1100-1200 \text{ cm}^{-1}$. The observed band at $1000-1350 \text{ cm}^{-1}$ is related to the stretching vibration of the C–N bond, and absorption band at 1665 cm⁻¹ is in accordance with the stretching vibration of the C=N bond [79]. This demonstrates that the compound containing silicon has been successfully attached to the oxygen of the cellulose's hydroxyl groups.

The thermal gravimetric analysis (TGA) of CNF and CNF@DBU[Cl] is shown in Fig. 2. In TGA of CNF, it was observed that weight loss occurred in two stages. The



Fig. 1 FT-IR spectrum of a CNF and b CNF@DBU[Cl]



Fig. 2 TGA curves of a CNF and b CNF@DBU[Cl]

first weight decrease was assigned to the catalyst surface moisture (at below 100 °C, 8% weight loss), while the second decrease at 250–380 °C showed the decomposition of hemicellulose polymeric chains of cellulose (Fig. 2a) [80]. According to TGA diagram, weight loss was also seen in two steps for the CNF@DBU[CI]. At the first step, there is a weight loss about 2% below 100 °C which is related to surface moisture. The second weight loss occurred at 250–350 °C, which is less than that for CNF (Fig. 1b). By comparing thermal gravimetric analysis of CNF and CNF@DBU[CI] together, it is determined that the presence of the created functional

Table 1 CHN analysis of CNF and CNF@DBU[Cl]	Catalyst	C (%)	H (%)	N (%)
	CNF	38.01	5.87	0.2
	CNF@DBU [Cl]	39.81	6.15	0.49



Fig. 3 SEM micrograph of a CNF@DBU[Cl]) and b CNF

group in the CNF@DBU[Cl] catalyst led to increase in the thermal stability of catalyst than CNF. It is necessary to mention that this catalyst is stable between 100 and 250 °C.

Elemental analyses (CHN) were carried out on CNF and CNF@DBU[Cl]. According to the obtained results from CHN (Table 1), it is observed that the percentage of carbon, hydrogen and nitrogen elements is increased in CNF@DBU[Cl], which can confirm the loading of organic group on cellulose nanofibers. The organic group loading of CNF@DBU[Cl] was found to be 1.46 mmol/g.

The morphology and particle size of CNF and CNF@DBU[Cl] were studied by scanning electron microscope (SEM) images (Fig. 3). According to SEM images of CNF, the average diameter of the cellulose nanofiber is 20–50 nm [81]. As shown in Fig. 3a, in CNF@DBU[Cl] catalyst, spherical particles were appeared on cellulosic nanofibers with average size of 30–60 nm, which led to the increase in the diameter of cellulosic fibers.

CNF@DBU[Cl] was analyzed by X-ray diffraction to compare its crystalline state with CNF. In XRD analyses of cellulose nanofiber, the presence of characteristic peaks at 2θ values of 14.9°, 16.7°, 20.36°, 52.22° and 34.7° shows the crystalline nature of the cellulose nanofibers structure [82]. In XRD of CNF@DBU[Cl], no sharp peak was observed, other than those related to CNF, and this shows that the crystalline structure of the cellulose nanofiber was retained after functionalization (Fig. 4). With respect to the XRD analyses of CNF@DBU[Cl] and using the Sherer equation, cellulose nanofiber's diameter is about 25 nm.



Scheme 2 Synthesis of CNF@DBU[Cl]

Catalytic activity of CNF@DBU[CI]

After synthesis and characterization of the catalyst, we investigated the catalytic activity of nano-solid catalyst for synthesis of tetraketones, by the condensation of various aldehydes and 1,3-dicarbonyl compounds (Scheme 2).

To optimize quantity of CNF@DBU[Cl] and reaction conditions, a model experiment was carried out using 4-chloro benzaldehyde and dimedone. When the model reaction was examined in the absence of catalyst at room temperature, no desired product was formed even after 60 min (Table 2, entry 1), but in the presence of





Entry	Catalyst (g)	Solvent/condition	Time (min)	Yield (%) ^a
1	_	H ₂ O/25 °C	60	_
2	CNF@DBU[Cl] (0.08)	H ₂ O/25 °C	4	92
3	MCC (0.08)	H ₂ O/25 °C	85	60
4	DBU(0.08)	H ₂ O/25 °C	180	90
5	MCC@DBU[Cl] (0.08)	H ₂ O/25 °C	30	70
6	CNF (0.08)	H ₂ O/25 °C	50	65
7	CNF@DBU[Cl] (0.08)	EtOH/25 °C	8	30
8	CNF@DBU[Cl] (0.08)	CH ₂ Cl ₂ /25 °C	60	35
9	CNF@DBU[Cl] (0.08)	CH ₃ CN/25 °C	60	30
10	CNF@DBU[Cl] (0.08)	PhCH ₃ //25 °C	70	20
11	CNF@DBU[Cl] (0.04)	H ₂ O/25 °C	10	73
12	CNF@DBU[Cl] (0.06)	H ₂ O/25 °C	10	76
13	CNF@DBU[Cl] (0.1)	H ₂ O/25 °C	4	94

Reaction conditions: reactants 1d (1.0 mmol) and 2a (2.0 mmol) in 5 mL solvent

^aYields refer to isolated products

CNF@DBU[Cl] (0.08 g) after 4 min a high yield of the expected tetraketone **3da** was obtained, showing the role of the catalyst in this reaction (Table 2, entry 2). The model reaction was also studied in the presence of MCC, DBU, MCC@DBU[Cl] and CNF, which no satisfactory result was achieved under these catalytic conditions (Table 2, entries 3–6). The above reaction was also examined in various solvents such as EtOH, CH_2Cl_2 , CH_3CN and toluene at room temperature (Table 2, entries 7–10). All the solvents required a longer reaction time and gave lower yields than in water (Table 2, entry 2).

Similar reactions were then attempted using 0.04, 0.06, 0.08 and 0.1 g of CNF@ DBU[Cl] (Table 2, entries 2 and 11–13). It was found that utilizing 0.08 g CNF@ DBU[Cl] in water at 25 °C is sufficient to complete the reaction with maximum yield (Table 2, entry 2). Increasing the amount of catalyst did not change the yield, whereas reduction in it significantly decreased the product yield (Table 2, entries 11, 12). Therefore, the best result was obtained by the use of molar ratio of 1: 2 of benzaldehyde with 1,3-dicarbonyl compound and 0.08 g CNF@DBU[Cl] as catalyst in H₂O at 25 °C.

After optimization studies, the scope and generality of this method were further explored with different substrates. As shown in Table 3, we initially

Entry	R	1,3-dicarbonyl compound	Product ^a	Time (min)	Yield (%) ^a	References
1	C ₆ H ₅ (1a)	2a	3aa	15	90	[44]
2	2-Cl–C ₆ H ₄ (1b)	2a	3ba	4	95	[59]
3	3-Cl– C_6H_4 (1c)	2a	3ca	2	96	[83]
4	4-Cl–C ₆ H ₄ (1d)	2a	3da	4	92	[59]
5	$2-Br-C_6H_4$ (1e)	2a	3ea	10	90	[67]
6	$3-Br-C_6H_4$ (1f)	2a	3fa	4	95	[84]
7	$4-Br-C_{6}H_{4}(1g)$	2a	3ga	12	93	[85]
8	$4-F-C_{6}H_{4}$ (1h)	2a	3ha	6	96	[67]
9	$2-NO_2-C_6H_4$ (1i)	2a	3ia	5	95	[65]
10	$4-NO_2-C_6H_4(1j)$	2a	3ja	7	95	[65]
11	$4-CN-C_{6}H_{4}(1k)$	2a	3ka	8	90	[85]
12	$4-CF_{3}-C_{6}H_{4}$ (11)	2a	3la	60	90	[85]
13	$4-\text{MeO}-C_6\text{H}_4$ (1m)	2a	3ma	20	87	[65]
14	4-Me– C_6H_4 (1n)	2a	3na	45	93	[65]
15	2-HO–C ₆ H ₄ (10)	2a	30a	30	92	[67]
16	4-HO– C_6H_4 (1p)	2a	3pa	35	90	[85]
17	$CH_3CH_2CH_2$ (1q)	2a	3qa	5	40	[67]
18	CH ₃ (CH ₂) ₃ CH ₂ (1r)	2a	3ra	15	30	[86]
19	C ₆ H ₅ (1a)	2b	3ab	20	90	[44]
20	$2\text{-Cl-C}_{6}\text{H}_{4}(\mathbf{1b})$	2b	3bb	8	92	[59]
21	$3-Cl-C_{6}H_{4}$ (1c)	2b	3cb	5	94	[83]
22	$4-Cl-C_{6}H_{4}(1d)$	2b	3db	4	95	[59]
23	2-Br– C_6H_4 (1e)	2b	3eb	12	90	[44]
24	$3-Br-C_6H_4$ (1f)	2b	3fb	7	92	[66]
25	$4-Br-C_{6}H_{4}(1g)$	2b	3gb	16	95	[85]
26	4-F–C ₆ H ₄ (1h)	2b	3hb	9	95	[87]
27	$2-NO_2-C_6H_4$ (1i)	2b	3ib	8	93	[84]
28	$3-NO_2-C_6H_4$ (1s)	2b	3sb	7	94	[<mark>66</mark>]
29	$4-NO_2-C_6H_4$ (1j)	2b	3jb	10	92	[44]
30	$4\text{-}CN\text{-}C_{6}H_{4}(\mathbf{1k})$	2b	3kb	10	92	[87]
31	$4-\text{MeO}-C_6\text{H}_4$ (1m)	2b	3mb	25	90	[84]
32	4-Me– C_6H_4 (1n)	2b	3nb	60	95	[84]
33	2-HO–C ₆ H ₄ (10)	2b	3ob	45	94	[66]
34	4-HO– C_6H_4 (1p)	2b	3pb	45	90	[59]
35	$CH_3CH_2CH_2$ (1q)	2b	3qb	13	35	[87]
36	$CH_{3}(CH_{2})_{3}CH_{2}$ (1r)	2b	3rb	30	40	[87]
37	$4-Cl-C_{6}H_{4}$ (1d)	2c	3dc	100	90	[67]
38	$4-Br-C_{6}H_{4}(1g)$	2c	3gc	130	92	[88]
39	$4-\text{MeO}-C_6\text{H}_4$ (1m)	2c	3mc	180	80	[89]
40	$4-Me-C_{6}H_{4}$ (1n)	2c	3nc	240	85	[90]

 Table 3
 Synthesis of tetraketone derivatives 3

All compounds are known, and their structures were established from their spectral data and melting points as compared with literature values

^aYields refer to isolated products

investigated the reaction of dimedone with benzaldehyde which afforded the corresponding tetraketone in excellent yields (Table 3, entries 1). When dimedone reacted with benzaldehydes including halogen group and electron-withdrawing group on phenyl ring, the corresponding product was formed with 90-96% yields (Table 3, entries 2-12). Aromatic aldehydes bearing electron-donating gave high yields of the corresponding products (Table 3, entries 13-16), but within longer reaction time and lower yields than benzaldehydes containing electron-withdrawing group.

1,3-cyclohexane-dione was also treated successfully with different aromatic aldehydes and gave the target tetraketones in high yields (Table 3, entries 19-34). But the reaction with dimedone was finished faster than with 1,3-cyclohexane-dione which may be owing to the difference of the activity between the two active methylene reagents.

Similarly, when dimedone and 1,3-cyclohexane-dione were treated with aliphatic aldehydes in the presence of CNF@DBU[Cl] (0.08 g) in water, a moderate yield of the corresponding products was obtained (Table 3, entries 17-18 and 35-36). The obtained results showed aromatic aldehydes afforded to desired product with higher yields in shorter reaction time than aliphatic aldehydes.

4-Hydroxy-2H-chromen-2-one (2c) was also reacted with various aromatic aldehydes, and the corresponding tetraketone products were obtained in good yields but within longer times (Table 3, entries 37-40).

An interesting feature of this method is that the catalyst can be regenerated at the end of the reaction and used several times without losing its activity. To recover the catalyst after completion of the reaction, catalyst was separated by centrifuging followed by filtration. The solid residue was washed several times with acetone. Finally, the regenerated catalyst was dried at 60 °C. After activating the catalyst, it was used for the reaction of 4-chloro benzaldehyde with dimedone. This process was repeated for four cycles, and the yield of product 3da did not significantly change (Table 4). These results clearly show the stability of CNF@DBU[Cl] in the reaction media as well its recovery and recycling without any appreciable decrease in its activity.

The proposed mechanism for the formation of tetraketon derivatives has shown in Scheme 3. First, the catalyst basic site (DBU[Cl]) absorbs the proton from 1,3-dicarbonyl compound 2 and enolate I is formed [91]. In next step, by the Knoevenagel reaction of enolate I and the activated aldehyde 1 (activated with OH groups of CNF), intermediate II is generated. Subsequently, dehydration took place to form

Table 4 Recycling studies forthe model reaction using CNF@	Run	Cycle	Time (min)	Yield (%) ^a
DBU[Cl] under optimal reaction	1	0	4	92
conditions	2	1	4	92
	3	2	4	92
	4	3	4	90
	5	4	4	90

^aIsolated yield



Scheme 3 Suggested mechanism for synthesis of tetraketone derivatives catalyzed by CNF@DBU[Cl]

the intermediate **III**. This intermediate as a Michael accepter reacts with enolate **I**, to give **IV**. After tautomerization, the product **3** is prepared [84].

In Table 5, the efficiency of CNF@DBU[Cl] was compared with some of the previously introduced procedures to demonstrate its catalytic activity for the synthesis of different tetraketones. Obviously, CNF@DBU[Cl] shows higher catalytic activity

Entry	Catalyst	Conditions	Time (min)	Yield (%)	References
1	CNF@DBU[Cl]	H ₂ O, rt, 80 mg	4	92	[This work]
2	Fe ₃ O ₄ @SiO ₂ -SO ₃ H	H ₂ O, rt, 10 mg	80	83	[92]
3	HClO ₄ -SiO ₂	H ₂ O, 100 °C, 10 mol%	30	89	[44]
4	Natural phosphate	H ₂ O, rt, 500 mg	120	98	[47]
5	Copper nanoparticles onto silica	EtOH, 80 °C, 100 mg	60	93	[53]
6	CoFe2O4 Nanoparticles	H ₂ O: EtOH 60 °C, 11.7 mg	4	89	[59]
7	Nano-Fe/NaY zeolite	EtOH, 78 °C, 2.5 mg	70	98	[57]
8	GO/ZnO	H ₂ O, 100 °C, 10 mg	10	99	[84]

Table 5 Comparative synthesis of compounds 3da using different catalysts method

in comparison with several of the others in terms of catalyst loading, product yield, avoiding the use of toxic transition metals, toxic solvents and short reaction time. One of the most important advantages of CNF@DBU[Cl] is that it is based on cellulose as the most abundant renewable biomass.

Conclusion

In conclusion, DBU functionalized cellulose nanofiber was introduced as a heterogeneous eco-friendly nanocatalyst for the synthesis of tetraketones in aqueous medium. According to SEM image, average size of catalyst was 30-60 nm. Thermogravimetric analysis of catalyst exhibited thermal stability between 100 and 250 °C. According to the results of TGA and CHN, the loading amount of catalyst was 1.46 mmol/g. All the reactions worked easily for a variety of benzaldehydes with both electron-donating and electron-withdrawing groups to give corresponding products in high yields (80–96%). The excellent catalytic performance, easy preparation and separation of the catalyst make it to be a good heterogeneous natural-based renewable nanocatalyst for organic synthesis and transformations. In addition, operational simplicity, good yields, low cost, short reaction times, non-use of toxic solvent, increased safety, environmental friendly reaction condition, easy removal and recyclability of the catalyst are supporting this method toward the green chemistry.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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