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Nano-SiO_2/DBN: an efficacious and reusable catalyst for one-pot synthesis of tetrahydrobenzo[*b*]pyran derivatives

Maryam Mehravar[1], Bi Bi Fatemeh Mirjalili[1*], Elaheh Babaei[1] and Abdolhamid Bamoniri[2]

Abstract

Background: The nano-sized particles enhance the exposed surface area of the active part of the catalyst, thereby increasing the contact between precursors and catalyst considerably. In this study, nano-SiO_2/1,5-diazabicyclo[4.3.0]non-5-en was synthesized, characterized and used as a heterogeneous nanocatalyst for the synthesis of tetrahydrobenzo[*b*]pyran derivatives. Fourier Transform Infrared Spectroscopy, Field Emission Scanning Electron Microscopy, Brunauer–Emmett–Teller plot, Energy Dispersive X-ray Spectroscopy and Thermo Gravimetric Analysis were used to discern nano-SiO_2/1,5-diazabicyclo[4.3.0]non-5-en.

Results: Tetrahydrobenzo[*b*]pyrans were synthesized by using nano-SiO_2/1,5-diazabicyclo[4.3.0]non-5-en via one-pot three-component condensation of malononitrile, aldehydes and dimedone in H_2O/EtOH at 60 °C. The results indicate that tetrahydrobenzo[*b*]pyrans were synthesized in good to high yields and short reaction times.

Conclusions: The fundamental privileges of this method are short reaction time, plain procedure, recyclability of catalyst and high yields of products.

Keywords: Nano-SiO_2/DBN, Benzopyrans, Heterogeneous catalyst, Multicomponent reaction, Nano-silica

Introduction

Multi-component reactions (MCRs) have significant role in organic chemistry, because of some merits like selectivity, synthetic convergence, high atom economy, simplicity, short reaction time, facility of workup, synthetic efficiency and high yield of products [1, 2]. An efficient way for the synthesis of heterocyclic compounds is using multi-component reactions, which have great value in design of biologically new active compounds [1, 3–5].

Tetrahydrobenzo[*b*]pyrans as one of the significant group of oxygen-containing heterocycle compounds are highly considered due to their medicinal and biological properties such as spasmolytic [6], antitumor [7], antibacterial [8], anti HIV [9], insulin-sensitizing activity [10] and hypotensive antiviral [11]. Some pharmacologically and biologically active benzopyrans are shown in Fig. 1.

A suitable method for synthesis of benzopyrans is three-component condensation of malononitrile and dimedone with various aldehydes. This reaction has been investigated in the presence of various catalysts such a Fe_3O_4@SiO_2@NiSB [12], oxyammonium-based ionic liquid [13], WEMFSA [14], [Bmim]Sac [15], MNPs–$PhSO_3H$ [16], NH_2@SiO_2@Fe_3O_4 MNPs [17], choline chloride-oxalic acid [18], SCMNPs@PC/VB1-Zn [19], MMWCNTs-D-(CH_2)4-SO_3H [20] and Chlorophyll [21]. In this research a practical, simple and inexpensive procedure for the synthesis of tetrahydrobenzo[*b*]pyran derivatives is reported by the reaction of aldehydes, malononitrile and dimedone in the presence of catalytic amount of nano-silica supported 1,5-diazabicyclo[4.3.0]non-5-en (Nano-SiO_2/DBN). Moreover, the amount of catalyst used in the reaction and its effect on the product

*Correspondence: fmirjalili@yazd.ac.ir
[1] Department of Chemistry, College of Science, Yazd University, Yazd, Iran
Full list of author information is available at the end of the article

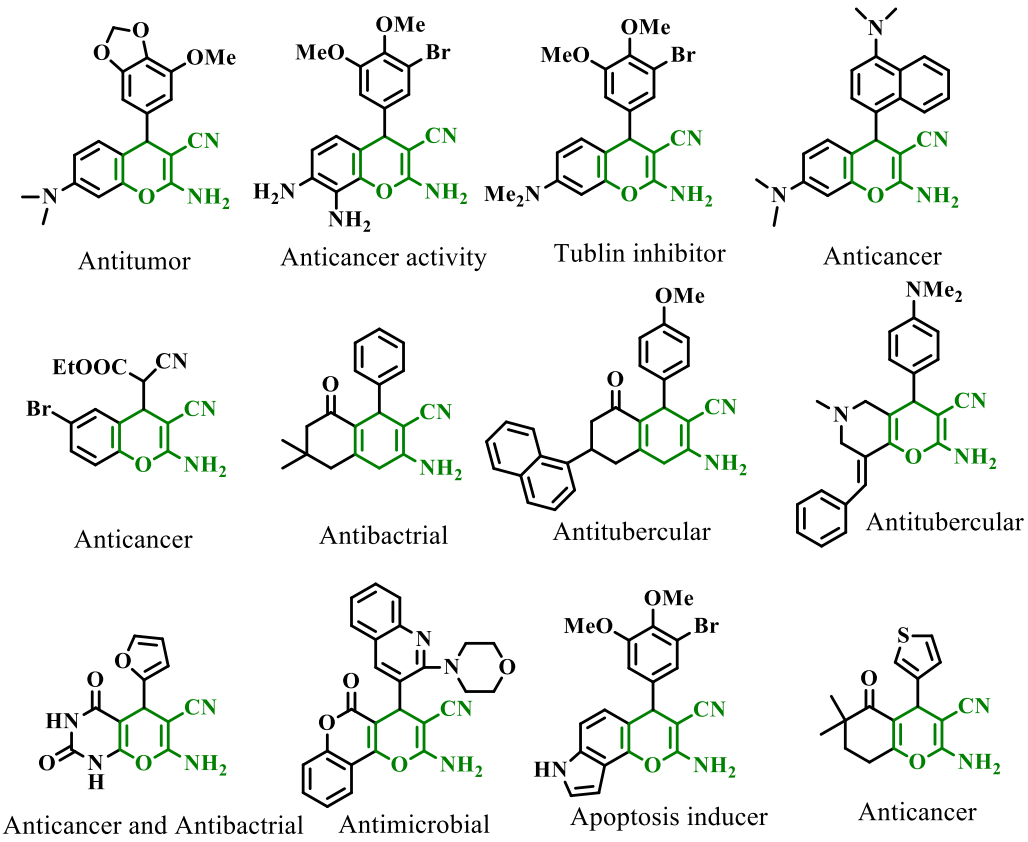


Fig. 1 Selected examples of pharmacologically and biologically active benzopyrans

yields, as well as the ability to recovery have been studied. Inexpensive and readily available catalyst, easy work-up and high yield of the products, usage of environmentally benign solvents, short reaction times and simplicity of experimental procedure are some advantages of this procedure.

Experimental

Materials and methods

General

Whole reagents and solvent were procured from Merck, Aldrich and fluka chemical companies. Fourier transform infrared spectroscopy (FT-IR) (ATR or KBr pellets) was run on a Bruker, Eqinox 55 spectrometer. The nanoparticles size and catalyst morphology were ascertained at Field emission scanning electron microscope (FE-SEM) using a Mira 3-XMU. Proton nuclear magnetic resonance (^{1}H NMR) and carbon nuclear magnetic resonance (^{13}C NMR) spectra were record at Bruker (DRX-400 Avance) in DMSO-d_6 as the solvent. The crystallographic characteristics of the sample were obtained by X-ray diffractometer (XRD, Philips Xpert) using Ni-filtered CuKα (kCuK = 0.1542 nm, radiation at 40 kV and 30 Ma) in the 2θ range from 10° to 80°. Thermo gravimetric analysis (TGA) was accomplished using a STA 505 instrument under argon atomosphere. The BET surface area, pore size and pore volume were measured by using Tristar II 3020 analyzer. Melting points were recorded on a Buchi B-540 B. V. CHI apparatus. Energy Dispersive X-ray Spectroscopy (EDS) was measured by Phenom pro X.

Chemistry

General procedure for synthesis of tetrahydrobenzo[b] pyran derivatives Nano-SiO_2/DBN (0.03 g) as a nanocatalyst was combined with a mixture of dimedone (1 mmol), aromatic and aliphatic aldehyde (1 mmol), malononitrile (1 mmol) in a round bottom flask and then the mixture was stirred magnetically in H_2O/EtOH (1:1) at 60 °C. The advancement of the reaction was controlled by TLC (*n*-hexane–ethyl acetate, 3:1). When the reaction was over, the catalyst was separated and recovered for the next run. Then, the crude products were recrystallized in EtOH.

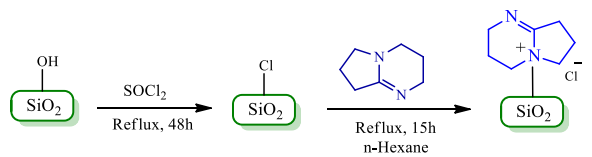
Procedure for synthesis of silica chloride Thionyl chloride (40 mL) (toxic and should be used under ventilator)

and nano-silicagel (10 g) were added to a round bottomed flask (250 mL) provided with a condenser under reflux condition for 48 h. Then it was cooled to room temperature, the mixture of reaction was filtrated via a Buchner funnel, then the remainder was rinsed several times with dichloromethane. Finally, obtained sillica chloride was dried at ambient temperature.

Procedure for synthesis of nano-SiO_2/DBN Silica chloride (1 g), DBN (1.5 mL) and *n*-hexane (10 mL) were added to a round bottomed flask (100 mL) furnished with a condenser, under reflux conditions for 15 h. When reaction was completed, it was cooled, filtrated and rinsed three times with *n*-hexane. Finally, the nano-SiO_2/DBN catalyst was dehydrated at ambient temperature in open air.

Results and discussion

A new catalyst was prepared as nano-SiO_2/DBN in two steps. At first, a mixture of thionyl chloride and commercial nano-silica gel was stirred for 48 h under reflux condition to carry out nano-silica chloride. In this reaction, OH functional groups of silica gel were replaced by Cl atoms of thionyl chloride. Then, nano-silica chloride, which is dried, reacted with DBN in *n-hexane* under reflux condition. The chlorine atoms in nano-silica chloride were replaced with N-nucleophiles in DBN (Scheme1).



Scheme 1 The preparation protocol for nano-SiO_2/DBN

Figure 2a–c shows the FT-IR spectra of the synthesized materials. Figure 2d shows absorption band at 3397 cm^{-1} which is due to the SiO–H stretching vibration, 1652 cm^{-1} for the C=N stretching vibration and 1056 cm^{-1} for Si–O stretching vibration and 796 cm^{-1} due to the Si–O–Si bending vibrational mode.

Energy-dispersive X-ray spectroscopy (EDS) was used to determine the percentage of elements in nano-SiO_2/DBN (Fig. 3). The percentage of C, N, O, Si and Cl in nano-SiO_2/DBN was 10.75, 4.88, 47.38, 36.48 and 0.25 respectively.

The EDX-map of elements in the structure of nano-SiO_2/DBN (Fig. 4) displays homogenous distribution of elements in catalyst.

The particle size of nano-SiO_2/DBN was studied using field emission scanning electron microscopy (FESEM) and found to be less than 50 nm (Fig. 5).

TGA analysis is shown in Fig. 6A, which exhibits the stability of the nano-SiO_2/DBN as nano-catalyst which can be used up to 120 °C. The weight loss (4.2%) below 100 °C is likely due to the loss of catalyst moisture. However, the main decomposition occurs at 165–450 °C (20.7%). Nano-SiO_2/DBN has noticeably high thermal stability with char yield 68.72% at 800 °C.

Figure 6B display the XRD Patterns of nano-SiO_2, nano-SiO_2/DBN in the range of 10–80°. A broad peak (Fig. 6B (a)) is observed at $2\theta = 23°$, showing the SiO_2 is

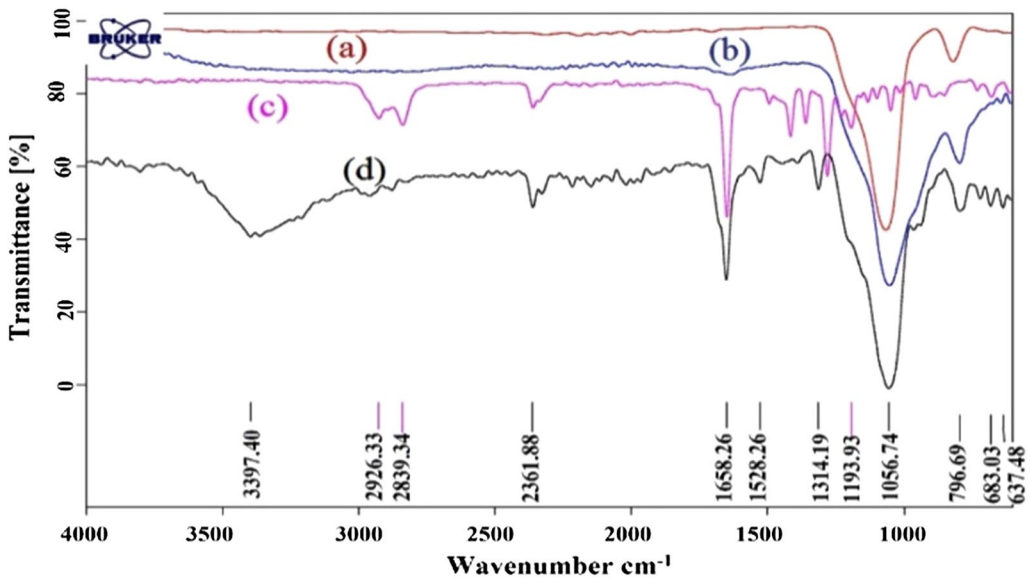


Fig. 2 FT-IR spectra of **a** Nano-SiO_2, **b** nano-silica chloride, **c** DBN, **d** nano-SiO_2/DBN

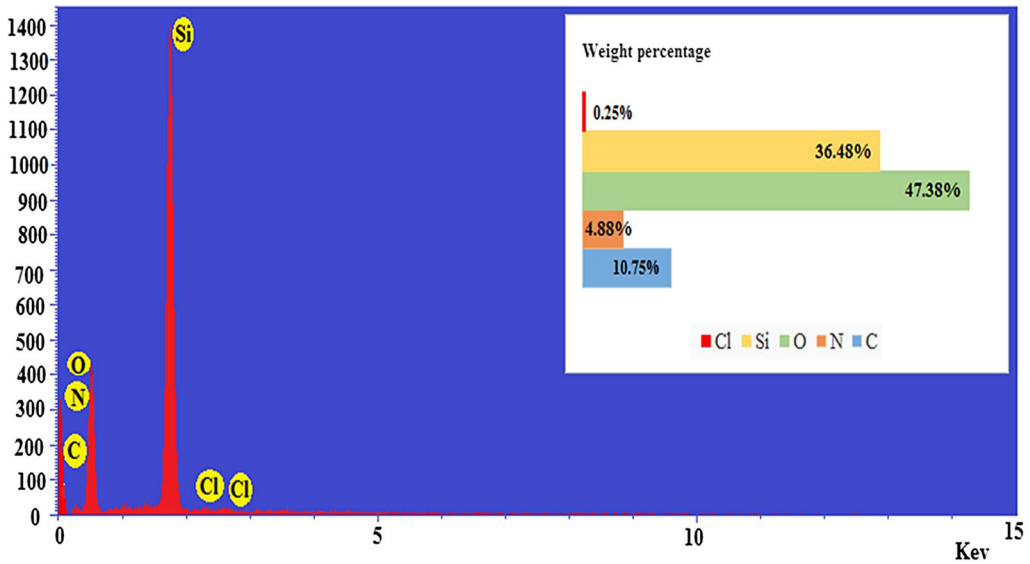


Fig. 3 The EDX spectra of nano-SiO_2/DBN

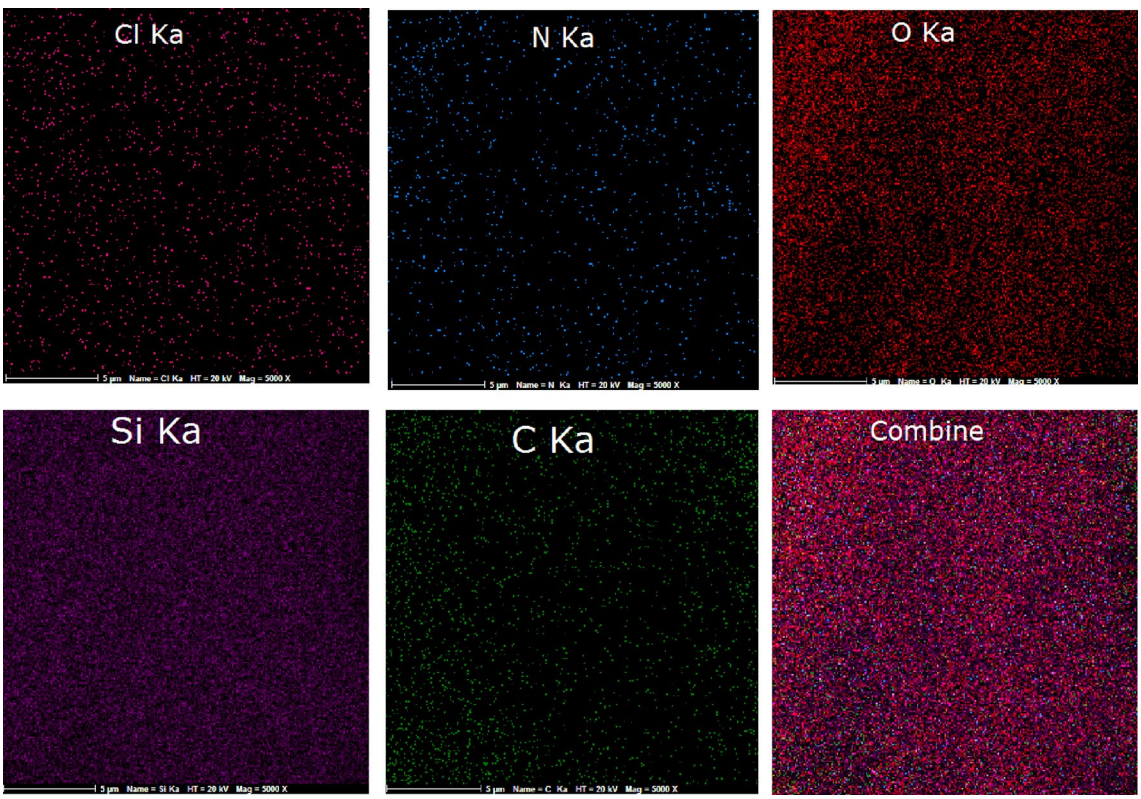


Fig. 4 EDX-map of elements in the structure of nano-SiO_2/DBN

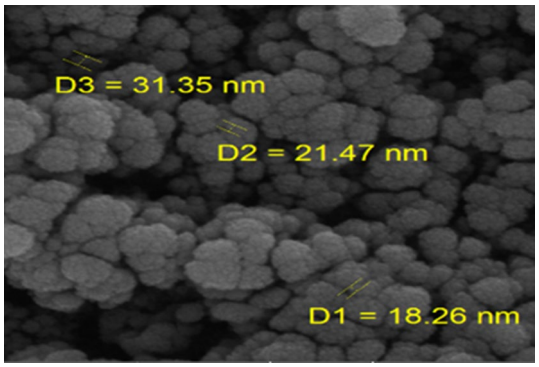


Fig. 5 FESEM images of nano-SiO_2/DBN

amorphous. While, the diffraction pattern of the nano-SiO_2/DBN (Fig. 6B (b)) indicated peak at $2\theta = 23.525°$ with FWHM = 2.3616. According to Scherrer equation, the particle size of catalyst is 3.4 nm.

Figure 7 shows (a) BJH plot, (b) BET (Brunauer–Emmett–Teller) plot, (c) t-plot, (d) Langmuir plot and (e) Adsorption/desorption isotherm of nano-SiO_2/DBN. The obtained data of BET, Langmuir, t and BJH plots were summarized in Table 1.

To optimize the reaction conditions in the synthesis of tetrahydrobenzo[*b*]pyran, the one-pot three-component condensation reaction of 4-chlorobenzaldehyde, dimedone and malononitrile was investigated, as model reaction, for various factors such as the amount of nano-SiO_2/DBN, time, temperature and solvent (Table 2). Therefore, the best reaction condition was performed using 0.03 g of catalyst in various solvents such as H_2O, $CHCl_3$, MeOH, EtOH and H_2O/EtOH (Table 2, entries 1–5). The use of H_2O/EtOH (1:1) as solvent at 60 °C is the most efficient condition for the model reaction with high yield and short time (Table 2, entry 10). The reaction performed under solvent free conditions, gave a lower

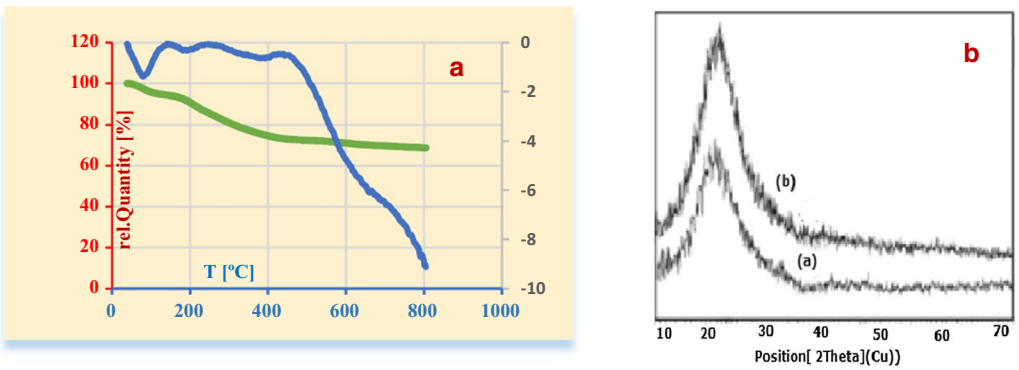


Fig. 6 (**A**) TGA patterns of nano-SiO_2/DBN and (**B**) XDR patterns of a) nano-SiO_2 and b) nano-SiO_2/DBN

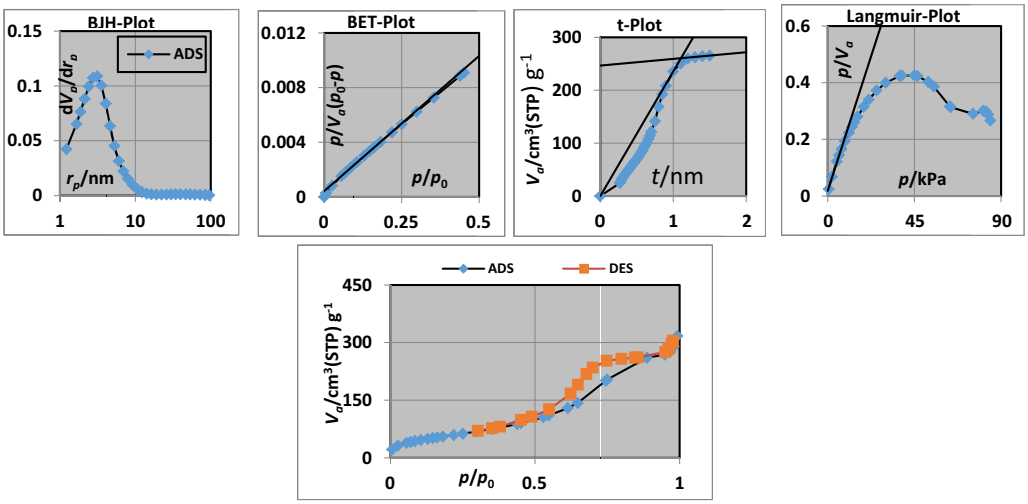
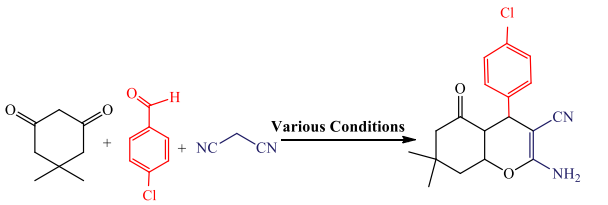


Fig. 7 **a** BJH plot, **b** BET (Brunauer–Emmett–Teller) plot, **c** t-plot, **d** Langmuir plot and **e** adsorption/desorption isotherm of nano-SiO_2/DBN

Table 1 The summerized data of BET, Langmuir, t and BJH plots

BET plot		
V_m	49.439	[cm^3(STP) g^{-1}]
$a_{s,BET}$	215.18	[m^2 g^{-1}]
C	48.241	
Total pore volume ($p/p_0 = 0.990$)	0.4823	[cm^3 g^{-1}]
Mean pore diameter	8.966	[nm]
Langmuir plot		
Vm	47.372	[cm^3(STP) g^{-1}]
$a_{s,Lang}$	206.18	[m^2 g^{-1}]
B	1.1678	
t plot		
Plot data	**Adsorption branch**	
a_1	362.85	[m^2 g^{-1}]
V_1	0	[cm^3 g^{-1}]
a_2	19.303	[m^2 g^{-1}]
V_2	0.3824	[cm^3 g^{-1}]
2t	2.2126	[nm]
BJH plot		
Plot data	**Adsorption branch**	
V_p	0.504	[cm^3 g^{-1}]
$r_{p,peak}(Area)$	3.1	[nm]
a_p	290.06	[m^2 g^{-1}]

Table 2 The reaction of malononitrile, 4-chlorobenzaldehyde and dimedone in the presence of nano-SiO_2/DBN under various conditions



Entry	Conditions	Time (min)	Yield[a] (%)
	Solvent/temp (°C)/catalyst (g)		
1	H_2O/EtOH (1:1)/60/–	180	28
2	H_2O/60/0.03	30	70
3	EtOH/60/0.03	30	58
4	$CHCl_3$/60/0.03	60	50
5	MeOH/60/0.03	60	70
6	–/60/0.03	120	42
7	–/80/0.03	90	58
8	H_2O/EtOH (1:1)/r.t/0.03	15	10
9	H_2O/EtOH (1:1)/40/0.03	15	58
10	H_2O/EtOH (1:1)/60/0.03[b]	15	92
11	H_2O/EtOH (1:1)/60/0.01	50	76
12	H_2O/EtOH (1:1)/60/0.02	30	80
13	H_2O/EtOH (1:1)/60/0.04	20	92
14	H_2O/EtOH (1:1)/60/0.05	35	70

Reaction conditions: malononitrile (1 mmol), 4-chlorobenzaldehyde (1 mmol), dimedone (1 mmol) and nano-SiO_2/DBN as catalyst

[a] Isolated yield

[b] The modified condition

yield in comparison with those performed in the solvent (Table 2, entries 6, 7).

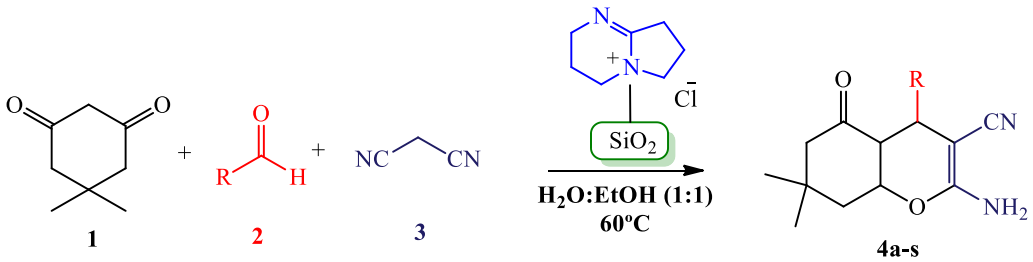
After determining the optimized condition, the reaction between different aldehydes with dimedone and malononitrile was investigated (Table 3). In result, tetrahydrobenzo[*b*]pyrans were synthesized in good to high yields and short reaction times. The progress of reaction was monitored by TLC continuously. Meanwhile, the aldehydes with electron withdrawing group in 4-position have reacted in lower time with higher yields (Table 3, entries 2, 5, 8, 9, 10). The aldehydes with a substitution group in 2-position, have steric hindrance which caused longer reaction time (Table 3, entries 3, 4, 5) (Additional file 1).

As shown in Table 4, performance of synthesized catalyst compared to nano-SiO_2, DBN and previously reported catalysts. Nano-SiO_2/DBN can be presented as an efficacious one, among others, catalyst in terms of reaction time and yields. There are many privileges in this regard simple procedure, nontoxic solvent and mild reaction conditions. DBN is a good catalyst for this reaction, but is not a heterogeneous recoverable catalyst.

A suggested mechanism for synthesis of tetrahydrobenzo[*b*]pyran derivatives by using nano-SiO_2/DBN is illustrated in Scheme 2. Initially, the nano-SiO_2/DBN catalyst activates both the methylene group **5** and the carbonyl group **1**. After, the Knoevenagal condensation reaction between the malononitrile and aldehyde in existence of basic catalyst forms the intermediate **6**. Then, the Michael addition of enol **4** and intermediate **6** is performed to produce the intermediate **7**. Finally, the product is formed by cyclization and tautomerization of the intermediate **8**.

The reusability of the nano-SiO_2/DBN was investigated. After completion of the reaction, the nanocatalyst was separated and washed with some EtOH, then dried at 70 °C. The catalyst was regained in good yields and catalyst was used in the synthesis of tetrahydrobenzo[*b*]pyran for five times (Fig. 8).

Table 3 Synthesis of tetrahydrobenzo[*b*]pyran in the presence of nano-SiO_2/DBN at 60 °C in H_2O/EtOH (1:1)[a]



Entry	R[a]	Product	Time (min)	Yield (%)[b]	M.P (°C) found	M.P (°C) reported (refs.)
1	C_6H_5-	**4a**	20	85	232–234	234–235 [22]
2	4-Cl-C_6H_4-	**4b**	15	92	214–216	215–216 [22]
3	2-Cl–C_6H_4-	**4c**	35	81	217–218	218–219 [23]
4	2,6-Cl_2-C_6H_3-	**4d**	50	79	245–247	250–252 [23]
5	4-NO_2-C_6H_4-	**4e**	15	89	181–183	181–182 [27]
6	3-NO_2-C_6H_4-	**4f**	20	91	215–217	217–218 [27]
7	2-NO_2-C_6H_4-	**4 g**	35	80	232–234	233–234 [22]
8	4-Br-C_6H_4-	**4 h**	30	89	199–201	197–201 [13]
9	4-F-C_6H_4-	**4i**	40	91	192–194	191–193 [15]
10	4-CN-C_6H_4-	**4j**	25	85	231–233	226–228 [24]
11	4-OCH_3-C_6H_4-	**4 k**	25	70	208–210	208–212 [23]
12	3,4-$(OCH_3)_2$-C_6H_3-	**4 l**	50	82	175–176	206–208 [25]
13	4-OH-C_6H_4-	**4 m**	40	78	217–219	214–216 [23]
14	4-$(CH_3)_2$CH-C_6H_4-	**4n**	30	90	197–199	203–207 [13]
15	4-CO_2CH_3-C_6H_4-	**4o**	15	78	257–259	259–260 [27]
16	1,4-Phenylene	**4p**	50	91	285 (d)[c]	270 (d) [26]
17	2-Furyl-	**4q**	25	84	216–218	217–219 [23]
18	Pentyl-	**4r**	20	83	162–164	164–165 [27]
19	Styryl-	**4 s**	30	90	217–219	218–218 [23]

4a-s are the synthesized tetrahydrobenzo[b]pyrans with different R

[a] Reaction conditions: malononitrile (1 mmol), aldehyde (1 mmol), dimedone (1 mmol) and nano-SiO_2/DBN (0.03 g)

[b] Isolated yield

[c] Decomposed

Table 4 Comparison of nano-SiO_2/DBN catalyst with some other catalyst for the synthesis of **4b**

Entry	Conditions Solvent/temp (°C)/catalyst	Time (min)	Yield[b] (%) (refs.)
1	CH_2Cl_2/60/SiO_2/NH_2OAc	360	90 [28]
2	H_2O/80/Fe_3O_4@SiO_2/DABCO	25	90 [29]
3	EtOH /reflux/L-Proline	360	87 [30]
4	EtOH /reflux/SO_4^{2-}/MCM-41	60	80 [31]
5	H_2O/reflux/DABCO	150	68 [32]
6	H_2O/120/SDS	120	85 [33]
7	H_2O/60/Thiourea dioxide	13	93 [34]
8	H_2O/EtOH/60/catalyst[a]	15	92 (this work)[c]
9	H_2O/EtOH/60/nano-SiO_2	15	40 (this work)
10	H_2O/EtOH/DBN	15	93 (this work)

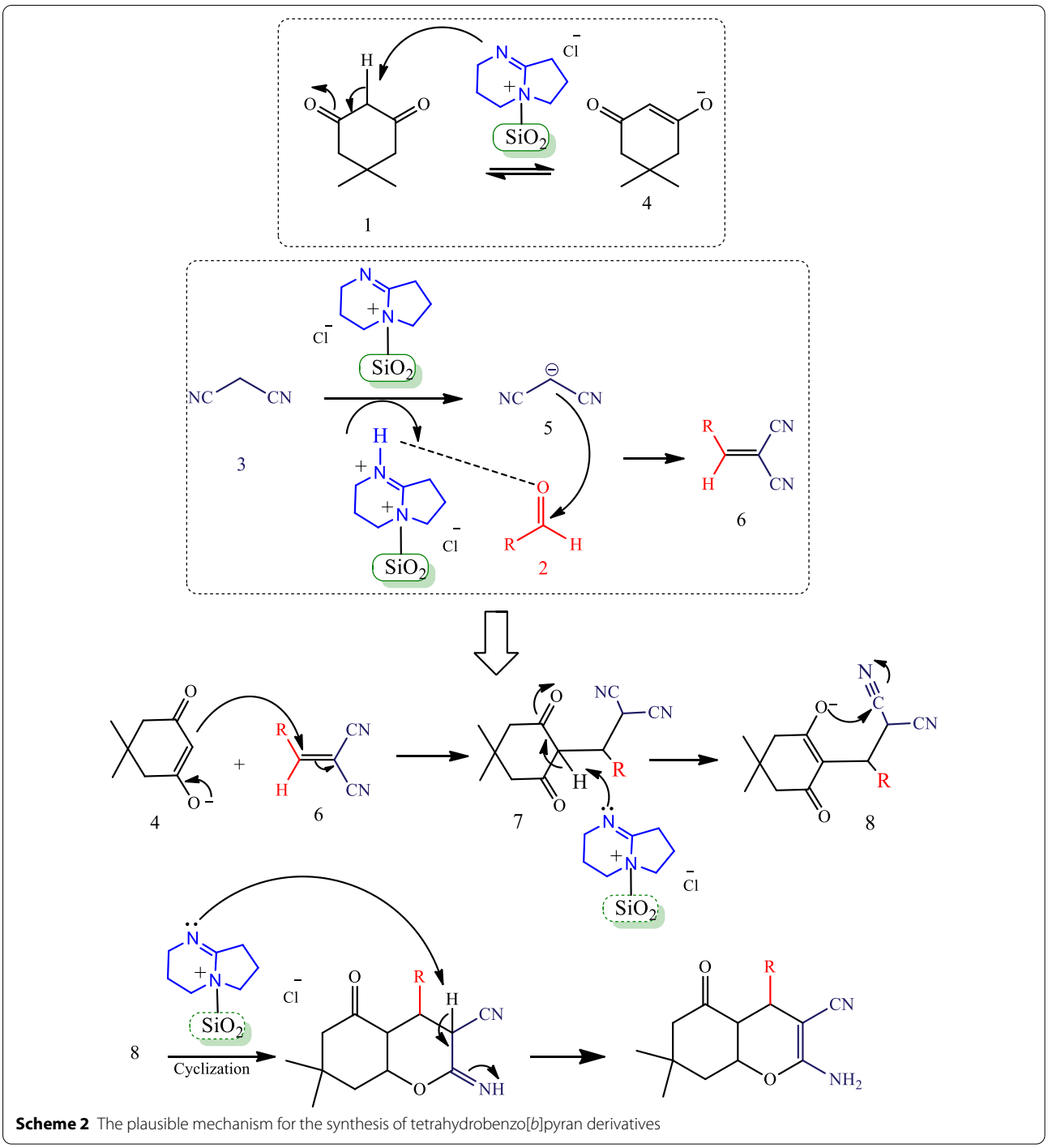
[a] Nano-SiO_2/DBN

[b] Isolated yield

[c] The modified condition

Conclusion

We have reported one-pot three component condensation reaction of various aldehydes, malononitrile and dimedone at 60 °C under mild conditions. The novel synthesis has been explored of tetrahydrobenzo[*b*] pyran derivatives in the presence nano-SiO_2/DBN as a heterogeneous nanocatalyst. The synthesized nanocatalyst was characterized by FT-IR, XRD, FESEM, TGA, EDS and BET analysers. The advantages of this method are summarized in the following orders, inexpensive, recyclability and reusability of the catalyst, easy work-up and good yield of the products, the use of relatively environmentally benign solvents, short reaction times and simplicity experimental of the procedure.



Scheme 2 The plausible mechanism for the synthesis of tetrahydrobenzo[*b*]pyran derivatives

Fig. 8 Reusability of the nano-SiO_2/DBN catalyst.

Abbreviations

DBN: 1,5-Diazabicyclo[4.3.0]non-5-en; MCRs: Multi-component reactions; EtOH: Ethanol; MeOH: Methanol; CH_3Cl: Chloroform; DMSO: Dimethyl sulfoxide; FESEM: Field emission scanning electron microscope; FT-IR: Fourier transform infrared; XRD: X-ray diffraction; EDX: Energy-dispersive X-ray; TGA : Thermo gravimetric analysis; NMR: Nuclear magnetic resonance; TLC: Thin layer chromatography; EDS: Dispersive X-ray spectroscopy.

Supplementary Information

The online version contains supplementary material available at https://doi.org/10.1186/s13065-021-00760-3.

Additional file 1. Spectroscopic data for the synthesized tetrahydrobenzo[b]pyran derivatives.

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Authors' contributions

MM and BFM designed and performed the research, analyzed the data, interpreted the results and prepared the manuscript. MM performed the assay, conducted the optimization, purification of compounds. EB and AB revised the manuscript. All authors read and approved the final manuscript.

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Availability of data and materials

All data generated or analyzed during this study are included in this published article.

Declarations

Ethics approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

Competing interests

The authors declare no competing interests.

Author details

[1]Department of Chemistry, College of Science, Yazd University, Yazd, Iran. [2]Department of Organic Chemistry, Faculty of Chemistry, University of Kashan, Kashan, Iran.

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