

## Employing a hydrophobic-bentonite as a highly efficient and versatile catalyst for a green one-pot and rapid synthesis of 4*H*-benzo-[*b*]-pyran derivatives

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### ABSTRACT

A hydrophobic-bentonite catalyst (cetyltrimethyl ammonium bromide-bentonite) has been used as a very mild, neutral, eco-friendly, reusable, non-toxic, low-cost and easily available catalyst. It was prepared by replacing the exchangeable Na<sup>+</sup> cations of a homoionic Na-bentonite with cetyltrimethyl ammonium bromide (CTMAB) cations. The catalyst was characterized by XRD, BET and SEM. The BET data and XRD patterns showed that the surfactant ions enter the interlayer space of catalyst. In order to study the catalytic properties, we carried out a one-pot practical, efficient and green multicomponent synthesis of 4*H*-benzo-[*b*]-pyran derivatives in terms of high yield, simple experimental procedure, low reaction time and simple work-up.

**Keywords:** Hydrophobic-bentonite, Green chemistry, Multi-component reactions, One-pot synthesis, Pyran derivatives.

### 1. Introduction

The combination of clay mineral and organic cations, usually quaternary ammonium compounds, can change the hydrophilic nature of the clay minerals to hydrophobic, and this makes them suitable for adsorbing different types of organic molecules [1-11].

Ammonium surfactants used in commercially available organo-clays usually combine short aliphatic chains and benzyl groups [12-14]. Organo-clays have been widely studied in researched lots of research due to their interesting features such as large specific surface area, swelling capacity, anisotropic shape, reactive surfaces, high thermal stability and high ion exchange capacity [15,16]. They are strongly able to adsorb organic and inorganic compounds [17,18]. Organo-clays have many applications as adsorbents of enzymes, organic reactant, hazardous compounds, catalysts and nanoparticles [1-3,7,19].

As an important aspect of our ongoing research on the surface chemistry, understanding the catalytic

properties of the layered silicates such as modified bentonite is of great importance due to the widespread use of these compounds in industrial activities. We have reported the synthesis of nanocrystalline semiconductors (CdS, ZnS) on the surface of hydrophobized Na-bentonite; besides, the adsorption layer of modified bentonite at the solid/liquid interface was utilized as a nanophase reactor for preparation of nanocatalysts of Pd [6,7]. Also, our reports have demonstrated a great improvement of material properties by incorporating bentonite, a natural silicate clay, into organic molecules. In continuation of our studies on the synthesis of heterocyclic compounds [1,20-22], we tried to develop a technique focusing on the use of a medium (CTMAB-bentonite) in preparation of 4*H*-pyran derivatives from aromatic aldehydes, dimedone and malononitrile (or ethyl cyanoacetate) in excellent yield.

Development of a mild, neutral, and reusable catalyst for one-pot synthesis of benzopyrans still remains an attractive goal for researchers [23,24]. Pyrans belong to an important class of heterocyclic compounds which show a wide range of biological activities, such as spasmolytic, diuretic, anti-coagulant, anticancer and anti-anaphylactic activity. In addition to their biological importance, some 4*H*-benzo-[*b*]-pyrans have been widely used as photoactive materials.

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The conventional previous methods for the synthesis of benzopyrans are carried out by DMF, ionic liquid, microwave irradiation, ultrasound irradiations, KF-alumina, DABCO, TBAF, TBAB, HDMBAB, quaternary ammonium salt, IRA-400 (OH<sup>-</sup>), L-proline, rare earth perfluorooctanoate, molecular iodine, TFE, potassium phosphate, Thiamine Hydrochloride (VB1), glutamic acid, urea and nano particles [25-32].

Many of the previous methods for the synthesis of these compounds are associated with the use of hazardous organic solvents, long reaction time, use of toxic catalysts, low yields, long reaction time, harsh reaction conditions, tedious work-up procedures and lack of general applicability.

## 2. Experimental

### 2.1. General

Bentonite was obtained from the Salafchegan mine (Salafchegan, Iran). All other chemicals and solvents were purchased from Merck, Fluka and Aldrich with high-grade quality, and used without any purification. The reactions were monitored by TLC. Visualization of the developed chromatogram was performed by UV light (254 nm). All yields refer to isolated products after purification. Products were characterized by comparing them with authentic samples and by spectroscopy data (IR, <sup>1</sup>H NMR spectra). The NMR spectra were recorded on a Bruker Avance 250 MHz instruments. The spectra were measured in DMSO-*d*<sub>6</sub> relative to TMS. IR spectra were recorded from KBr disk on the FT-IR Bruker Tensor 27. Melting points were measured by using the capillary tube method with IA 9000 series thermal analyzer. X-ray powder diffraction was performed on a Phillips diffractometer (Netherlands) with CuK $\alpha$  radiation (40kV, 30mA) over a 2 $\theta$  range 3–80°.

### 2.2. Catalyst preparation

Synthesis and characterization of CTMAB-bentonite were described in the previous work [8]. Bentonite, was dispersed in water under continuous stirring. After a period of time, NaCl solution was added and the dispersion was stirred overnight. Then, the resulting solid was washed and dried. Cetyltrimethyl ammonium bromide (CTMAB) was loaded on the Na-bentonite to obtain surfactant modified bentonite (CTMAB-bentonite) for this purpose. Na-bentonite was dispersed in CTMAB solution and the dispersion was stirred for the appropriate time and the solid was washed with water to remove excess surfactant. Finally, CTMAB-bentonite was dried at room temperature. The interlayer spacing of the original bentonite (Na-bentonite) was 12.3 Å, which changed to 13.8 Å after adsorption of

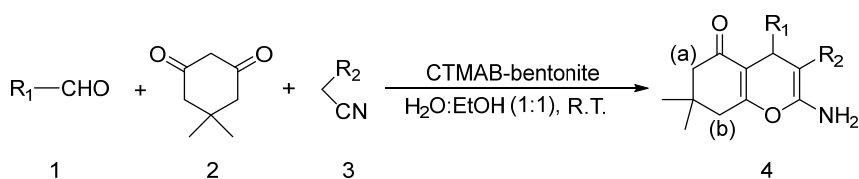
cationic surfactant. The maximum loading of CTMAB on the bentonite reached 50  $\mu$ mol/g.

### 2.3. Typical procedure

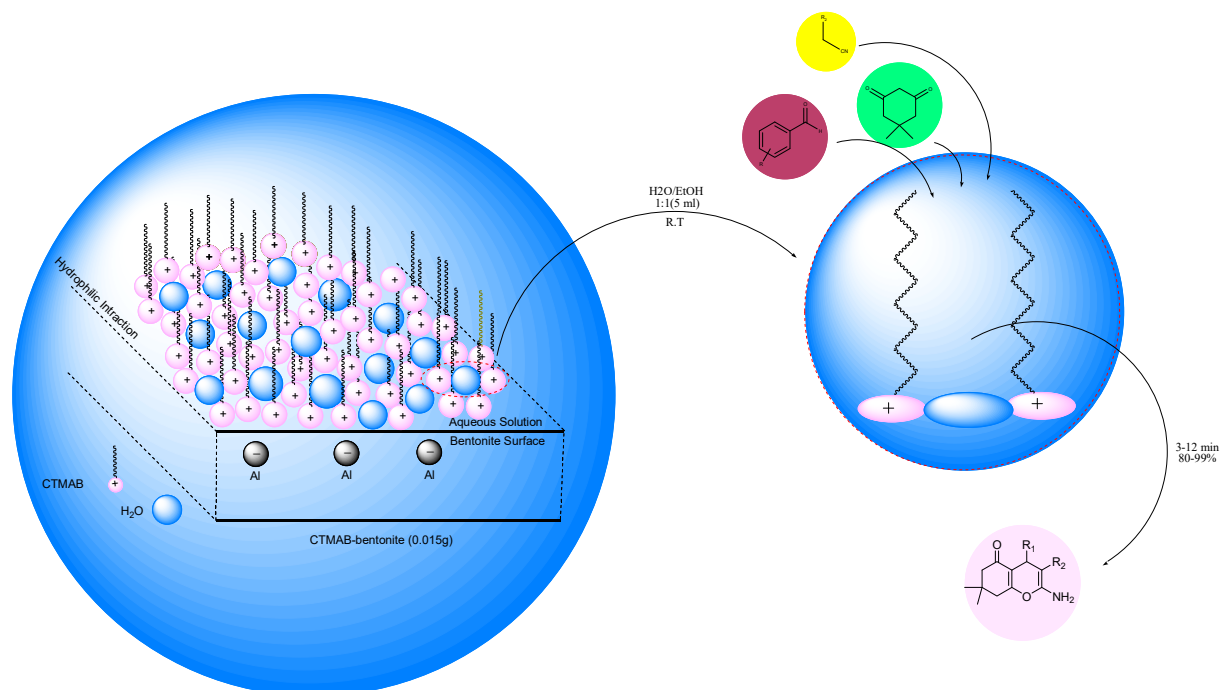
A mixture of dimedone (1 mmol), aromatic aldehyde (1 mmol), malononitrile (or ethyl cyanoacetate) (1.2 mmol) and CTMAB-bentonite (0.015 g) in 5 mL aqueous ethanol (1:1, H<sub>2</sub>O–EtOH) was rapidly stirred at room temperature for the appropriate time. The progress of the reaction was monitored by TLC. The resulting product was separated via centrifugation and washed with *n*-hexane (2  $\times$  5 mL) to obtain the appropriate compound in pure form. The solid was dissolved in acetone and the catalyst was separated by filtration. The recycled catalyst was washed with acetone, dried and reused. The purity of the product was determined by its comparison to melting points. The product was identified based on its physical and spectral characteristics.

## 3. Results and Discussion

The sorption of cationic surfactants on clay minerals, based on the cation exchange capacity (CEC) of the clay and the potential applications of this modified clay as organophilic, flexible and soft environmental remediation materials have been studied in our previous studies [1-3,6-11]. These studies have shown that, surfactant modified clays display higher organophilic character and uptake ability toward organic substances in comparison of unmodified clay. Not only is the immobilization of lipases frequently performed via adsorption through hydrophobic interactions between the HBC and the lid of lipases [8], but also we have successfully developed a simple, green, assisted one-pot multicomponent synthesis of 3,4-dihydropyrano[*c*] chromene derivatives from accessible starting materials using CTMAB-bentonite as a catalyst [1]. The cationic and green surfactant (CTMAB) has been widely used in several fields for a variety of applications, such as extraction procedures [33], kinetic studies [34], biotechnological and biomedical applications [35], complex reactions [36,37] and improvement of the analytical sensitivity in spectrophotometric determinations [37-40]. The TGA analysis indicated that the modified montmorillonite (bentonite is kind of montmorillonite) with CTAB, sodium dodecyl benzene sulfonate and 1,3-dihexadecyl-3H-benzimidazolium bromide exhibited high thermal stability [41]. In this work we introduced CTMAB-bentonite as a hydrophobic medium for the successfully generation of 4*H*-benzo-[*b*]-pyran derivatives (Scheme 1). As shown in Scheme 2, the catalyst can be finely interacted with tree reactant compounds and adsorbed all of them at the



Scheme 1. CTMAB-bentonite catalyzed synthesis of 4H-benzo-[b]-pyrans.



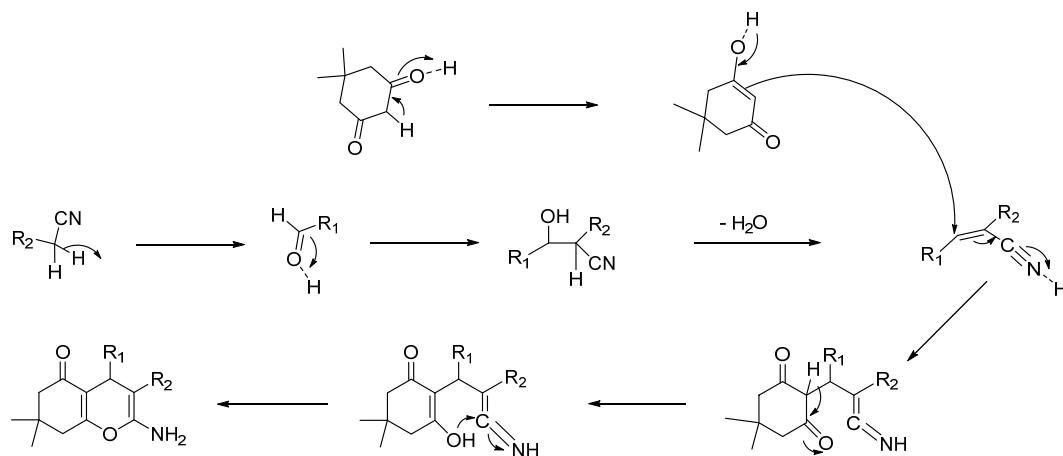
Scheme 2. synthesis of 4h-benzo-[b]-pyrans in water pools on surface of modification bentonite.

same time for one pot multiple synthesis. We proposed a plausible mechanism for the synthesis of 4H-benzo[b]pyrans in Scheme 3.

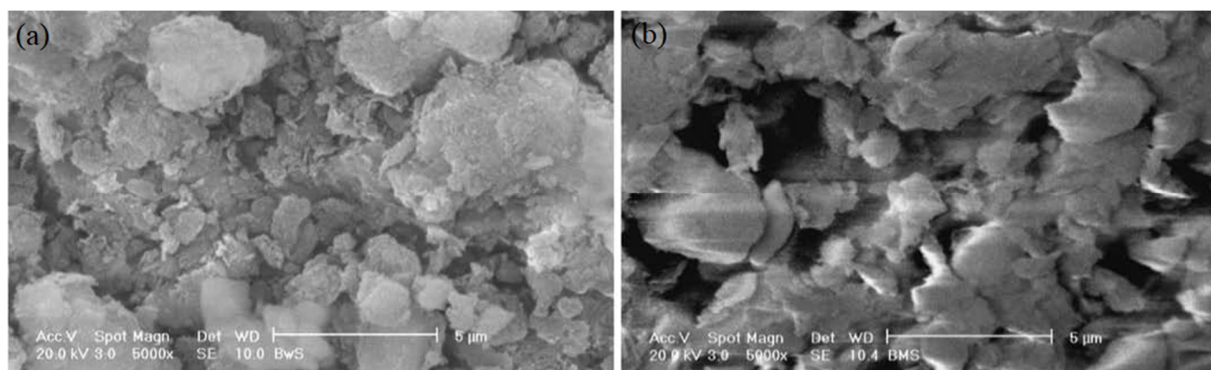
### 3.1. Structural characterization of CTMAB-bentonite

CTMAB-bentonite was prepared and characterized by XRD, BET and SEM. Considering the SEM images,

unmodified bentonite showed that a card-house type aggregation of the particles is completely different from the SEM images of modified bentonite (Fig. 1). The BET data were shown by modifying the bentonite with a surfactant monolayer, the number of pores has been increased to a large extent and the surfactant ions enter the interlayer space (Table 1).



Scheme 3. Plausible mechanism for the synthesis of 4H-benzo-[b]-pyrans catalyzed by CTMAB-bentonite.



**Fig. 1.** SEM photographs: (a) bentonite, (b) CTMAB-bentonite.

**Table 1.** Specific surface area, pore volume and pore size for bentonite and CTMAB-bentonite.

Entry	Spec. surface area ( $\text{m}^2\text{g}^{-1}$ )	Pore volume ( $\text{cc g}^{-1}$ )	Pore size (nm)
Na-bentonite	124	0.051	2.26
STMAB- bentonite	93	0.052	1.24

According to the XRD patterns, parent bentonite showed a reflection corresponding to  $d_{001}=1.23$  nm (Fig. 2). After modification of bentonite with a monolayer coverage (about CEC value), the d-value shifts to  $13.8 \text{ \AA}$ , indicating that the surfactant ions enter the interlayer space [8,9]. All the above results revealed the surfactant had a strong influence on the particle structure of the bentonite and the hydrophilic surface of the bentonite partly became hydrophobic due to the presence of the surfactant molecules.

### 3.2. Optimization of Reaction

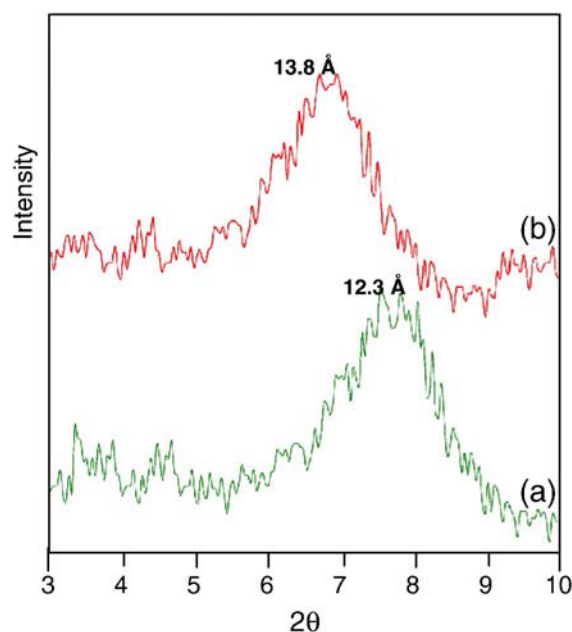
To find the optimal conditions, we studied synthesis of 2-amino-7,7-dimethyl-4-(3-nitrophenyl)-5-oxo-5,6,7,8-tetrahydro-benzo[b]pyran from the condensation of (1 mmol) 3- nitrobenzaldehyde, (1 mmol) dimedone and (1.2 mmol) malononitrile under various reaction conditions.

### 3.3. The activity of the catalyst

To optimize the catalyst loading, 0.010 g, 0.015 g, 0.020 g and 0.025 g of the catalyst were tested. The results are summarized in Table 2 which showed that the reaction was catalyzed by about 0.015 g CTMAB-bentonite giving the highest yield (Table 2, entry 4). However, in the presence of less than this amount, the yield was decreased (Table 2, entry 3). In fact, when the amount of the catalyst was increased over 0.015 g, neither the yield nor the reaction time were improved (Table 2, entry 5). The results showed that such organic modification altered the nature of clay from hydrophilic to hydrophobic so that it increased the affinity and accessibility of organic reactant.

### 3.4. Effect of temperature on the synthesis of 4H-benzo[b]-pyrans

To study the effect of temperature on this synthesis, we also performed four experiments in aqueous ethanol at room temperature,  $50$ ,  $70$  °C and under reflux conditions (Table 3). It was observed that the yield of the product was maximized at room temperature (Table 3, entry 1). By modification of bentonite with organic surfactants, the surface energy and the activation energy of it decreased so the reaction easily occurred at room temperature.



**Fig. 2.** XRD patterns: (a) bentonite, (b) CTMAB-bentonite.

**Table 2.** Optimization of the catalyzed model reaction for synthesis of 2-amino-7,7-dimethyl-4-(3-nitrophenyl)-5-oxo-5,6,7,8-tetrahydro-benzo[b]pyran in aqueous ethanol at room temperature.

Entry	Catalyst	Amount of catalyst (g)	Time (min)	Yield (%) <sup>a</sup>
1	CTMAB	0.015	8	70
2	Bentonite	0.015	6	76
3	CTMAB-bentonite	0.010	5	88
4	CTMAB-bentonite	0.015	4	97
5	CTMAB-bentonite	0.020	4	97
6	CTMAB-bentonite	0.025	4	97
7	Catalyst free	-	2 h	Trace

<sup>a</sup>Isolated yields.

### 3.5. Solvent effect

During the optimization of the reaction condition, various solvents were also screened to test their efficiency and the results are summarized in Table 4. The highest reaction activity was achieved in the system using aqueous ethanol (1:1, H<sub>2</sub>O–EtOH) as a solvent in comparison to other solvents under similar reaction conditions (Table 4, entry 5). The modification of bentonite created the water pools on its surface (Scheme 2) thereby increased the affinity and accessibility of molecules for reaction in an aqueous ethanol system.

### 3.6. Reusability of the catalyst

In green chemistry, the reuse of the catalyst is one of the most important benefits. Thus the recovery and reusability of the catalyst has been studied for the synthesis of 4H-benzo-[b]-pyran derivatives. As the catalyst is insoluble in acetone, it was collected by simple filtration, while the product is completely soluble in acetone. So, after completion of reaction, it became very easy to isolate the catalyst from the product. The catalyst was washed with acetone, dried and stored for another subsequent run. The recovered catalyst was used five times

to obtain 4H-benzo-[b]-pyran derivatives without any appreciable decrease in the reaction yield (The yields were 97, 97, 96, 95, 95 and 93%, respectively). Almost all existing methods have one essential disadvantage in common. In their work-up procedure, the catalysts are destroyed and cannot be recovered or reused.

To show the merit of the present work in comparison with the reported results in the literature, we summarized some of the results for the preparation of 2-amino-7,7-dimethyl-4-(3-nitrophenyl)-5-oxo-5,6,7,8-tetrahydro-benzo[b]pyran in Table 5. The results showed that CTMAB-bentonite is a more efficient catalyst than reported ones in the literature with respect to the reaction temperature, catalyst load, reaction time and yield (Table 6, entry 10). To ascertain the scope and limitation of the present system, several aldehydes were examined and the results of their reaction with dimedone and malononitrile (or ethyl cyanoacetate) were summarized in Table 6. Aromatic aldehydes with both activating and deactivating groups underwent smooth transformation to the corresponding 4H-benzo-[b]-pyran derivatives, with no side products formation, at high to excellent yields and in very short reaction times.

**Table 3.** Optimization of reaction temperature using CTMAB-bentonite (0.015 g) as catalyst in aqueous ethanol.

Entry	Catalyst	Temp. (°C)	Time (min)	Yields (%) <sup>a</sup>
1	CTMAB-bentonite	Room temperature	4	97
2	CTMAB-bentonite	Reflux	4	95
3	CTMAB-bentonite	70	4	95
4	CTMAB-bentonite	50	4	96

<sup>a</sup>Isolated yield.

**Table 4.** Effect of solvents in reaction of 3-nitrobenzaldehyde, dimedone and malononitrile catalyzed by CTMAB-bentonite at room temperature.

Entry	Catalyst	Solvent	Time (min)	Yields (%) <sup>a</sup>
1	CTMAB-bentonite	EtOH	5	90
2	CTMAB-bentonite	H <sub>2</sub> O	4	92
3	CTMAB-bentonite	H <sub>2</sub> O–EtOH (1:2)	4	94
4	CTMAB-bentonite	H <sub>2</sub> O–EtOH (2:1)	5	92
5	CTMAB-bentonite	H <sub>2</sub> O–EtOH (1:1)	4	97
6	CTMAB-bentonite	Solvent free	2 h	Trace

<sup>a</sup>Isolated yields.

#### 4. Conclusions

Results indicate that surfactant have been supported on the bentonite layers and a hydrophobic and flexible structure is formed (CTMAB-bentonite). Then the CTMAB-bentonite as a hydrophobic, flexible, mild, eco-friendly, very economical, non-toxic and efficient heterogeneous catalyst have been used for one pot synthesis of wide variety of 4H-benzo-[b]-pyran derivatives obtained from the three-component condensation reaction of aromatic aldehyde, malononitrile (or ethyl cyanoacetate), and dimedone under solvent free conditions in good to excellent yield and short reaction times. After modification, bentonite clay can be compatibilized by organic molecules so the surfactant functionalization enhances the dispersion stability in aqueous ethanol media. The significant advantages of this protocol are a green procedure, high yields, simple workup, and reusability of the catalyst.

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**Table 5.** Synthesis of 2-amino-7,7-dimethyl-4-(3-nitrophenyl)-5-oxo-5,6,7,8-tetrahydro-benzo[b]pyran using different reagents and reaction conditions.

Entry	Reagent	Conditions	Time	Yield (%) <sup>a</sup>	Ref.
1	-	Electrolysis (10 mA)	4-5 h	96	[42]
2	PhB(OH) <sub>2</sub> , 5 mol%	EtOH/H <sub>2</sub> O, reflux	0.5 h	85	[43]
3	RE(PFO) <sub>3</sub>	EtOH, 60 °C	4 h	83	[44]
4	Na <sub>2</sub> SeO <sub>4</sub> , 0.1 g	EtOH/H <sub>2</sub> O, reflux	2.5 h	90	[45]
5	TBAB, 10 mol%	H <sub>2</sub> O, reflux	40 min	90	[46]
6	POPINO, 7.5 mol%	H <sub>2</sub> O, reflux	10 min	92	[47]
7	Starch solution, 4mL	50 °C	35 min	94	[48]
8	(AP-SiO <sub>2</sub> ), 10 mol%	H <sub>2</sub> O, 70 °C	60 min	92	[49]
9	SiO <sub>2</sub> NPs, 5 mg	EtOH, r.t.	30 min	98	[50]
10	CTMAB-bentonite, 0.015 g	EtOH/H <sub>2</sub> O, r.t.	4 min	97	This work

<sup>a</sup>Isolated yields.

**Table 6.** CTMAB-bentonite catalyzed synthesis of 4H-benzo-[b]-pyran derivatives.<sup>a</sup>

Entry	R <sub>1</sub>	R <sub>2</sub>	Product	Time (min)	Yield (%) <sup>b</sup>	m.p. (°C)		Ref.
						Found	Reported	
1	C <sub>6</sub> H <sub>5</sub>	CN	4a	5	81	226-228	227-229	[46]
2	4-BrC <sub>6</sub> H <sub>4</sub>	CN	4b	3	99	200-203	205-207	[46]
3	3-ClC <sub>6</sub> H <sub>4</sub>	CN	4c	6	89	226-228	228-229	[43]
4	4-ClC <sub>6</sub> H <sub>4</sub>	CN	4d	6	98	212-215	212-214	[46]
5	2,4-ClC <sub>6</sub> H <sub>3</sub>	CN	4e	3	97	181-183	182-183	[46]
6	2-O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub>	CN	4f	5	95	229-231	230	[45]
7	3-O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub>	CN	4g	4	97	209-212	210-212	[46]
8	4-O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub>	CN	4h	4	98	175-177	178-180	[46]
9	4-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	CN	4i	7	80	212-215	212-215	[46]
10	4-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	CN	4j	10	94	198-201	201-203	[46]
11	4-CNC <sub>6</sub> H <sub>4</sub>	CN	4k	4	98	226-228	227-230	[51]
12	4-FC <sub>6</sub> H <sub>4</sub>	CN	4l	4	98	208-210	210-211	[52]
13	2-ClC <sub>6</sub> H <sub>4</sub>	CN	4m	3	98	189-191	191-192	[52]
14	2-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	CN	4n	12	92	193-195	194-196	[43]
15	3-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	CN	4o	10	80	185-187	188-190	[53]
16	Furan	CN	4p	5	95	221-223	222-224	[43]
17	Thiophene	CN	4q	5	97	210-212	212-214	[48]
18	C <sub>6</sub> H <sub>5</sub>	COOEt	4r	8	93	156-158	156	[45]
19	4-ClC <sub>6</sub> H <sub>4</sub>	COOEt	4s	6	98	155-157	157	[45]
20	3-O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub>	COOEt	4t	4	97	186-188	185-188	[45]
21	4-O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub>	COOEt	4u	4	98	184-186	184	[45]

<sup>a</sup>Reaction conditions: Aromatic aldehyde (1 mmol), malononitrile (or ethyl cyanoacetate) (1.2 mmol), dimedone (1 mmol), CTMAB-bentonite (0.015 g), aqueous ethanol (5 mL), r.t.

<sup>b</sup>Isolated yields.

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