



Research Article

An Efficient Synthesis of 1,8-Dioxo-Octahydroxanthenes Derivatives Using Heterogeneous Ce-ZSM-11 Zeolite Catalyst

Rameshwar R. Magar, Ganesh T. Pawar, Sachin P. Gadekar, Machhindra K. Lande*

Department of Chemistry, Dr. Babasaheb Ambedkar Marathwada University, Aurangabad (M.S.), 431004, India

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Abstract

The Ce-ZSM-11 zeolite has been used as an efficient catalyst for the one pot synthesis of 1,8-dioxo-octahydroxanthene derivatives from aromatic aldehyde and 5,5-dimethyl-cyclohexane-1,3-dione under reflux condition. The catalyst was characterized by Powder X-ray diffraction (XRD), Scanning Electron Microscopy (SEM), Energy Dispersive Spectroscopy (EDS), Fourier Transform Infrared Spectroscopy (FTIR), Brunauer-Emmer-Teller (BET) surface area analysis, and Temperature Programmed Desorption (TPD) techniques. This method provides several advantageous such as use of inexpensive catalyst, simple work-up procedure, high yield of desired product and reusability of catalyst. Copyright © 2018 BCREC Group. All rights reserved

Keywords: Ce-ZSM-11 Zeolite; 1,8-Dioxo-octahydroxanthene; Aromatic Aldehyde; 5,5-Dimethyl-cyclohexane-1,3-dione

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1. Introduction

The significant challenge in the synthetic chemistry is to develop environmentally benign, efficient and economical methods for the synthesis of biologically active compounds [1]. Multi-component reactions (MCRs) have become one of the best tools for modern synthesis of chemically and biologically important compounds because of their high atom economy, simple procedure and excellent yields [2-4]. Xanthene and its derivatives have received con-

siderable attention in the field of pharmaceutical and medicinal chemistry because of their wide range of biological and pharmacological properties such as antibacterial [5], analgesic [6], anti-inflammatory [7], and anti-cancer properties [8]. In addition, these heterocyclic compounds can be used as pH-sensitive fluorescent materials [9], in laser technology [10], and as luminescent dyes [11]. In view of this wide applicability of xanthene derivatives, the development of synthetic procedure is important. Several methods that have been reported for the synthesis of xanthene derivatives catalyzed by Fe₃O₄ nanoparticle [12], SiCl₄ [13], CaCl₂ [14], Imidazol-1-yl-acetic acid [15], CAN

* Corresponding Author.

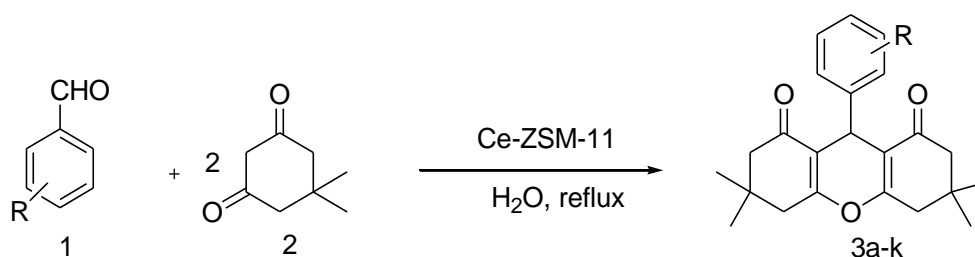
E-mail: mkl_chem@yahoo.com (M.K. Lande)

Telp: +91 0240 2403311, Fax: +91 0240 2403335

[16], DSIMHS ionic liquid [17], ZnO nanoparticle [18], Ru@SH-MWCNT [19], and Fe-Cu/ZSM-5 [20] catalyst. However, some of these protocols suffer from one or more drawbacks, such as: use of hazardous solvent, high temperature, long reaction time, tedious work-up procedure and use of expensive catalyst. Therefore, the development of alternative route for the synthesis of 1,8-dioxo-octahydroxanthene derivatives is highly desirable.

Zeolites are microporous, crystalline, aluminosilicate compounds composed of staggered framework of $[AlO_4]^{5-}$ and $[SiO_4]^{4-}$ tetrahedra which generates a network of pores and cavities having molecular dimensions. They finds extensive applications in heterogeneous catalysis due to their tunable pore sizes, high surface area, framework acid/base properties and provides greener alternatives to homogeneous catalysts [21]. ZSM-11 belongs to pentasil family of zeolites which has straight micropore with MEL framework topology [22]. ZSM-11 possesses unique properties, such as high-surface area, acidity and shape selectivity characters [23] hence it has been utilized as heterogeneous catalyst for conversion of methanol to hydrocarbon, aromatization and isomerization of 1-hexene, cracking of pentene to C_2 - C_4 olefins and conversion of methanol into light olefins [24-27]. The transition metal doped ZSM-11 possesses greater Lewis acidity compared to parent ZSM-11 and showed better catalytic performance in some reaction such as degradation of Dichlorvos, decomposition of N_2O , conversion of methane (C_1) into higher hydrocarbons, dehydrogenation-aromatization of alkane and decomposition of low-density polyethylene [28-32].

Thus, in continuation to our research work [33,34], we report the synthesis, characterization, and catalytic application of Ce-ZSM-11 zeolite catalyst for one pot synthesis of 1,8-dioxo-octahydroxanthene derivatives via cyclocondensation of aromatic aldehyde, 5,5 dimethyl-cyclohexane-1,3-dione using catalytic amount of Ce-ZSM-11 under reflux condition in water as solvent (Scheme 1).



Scheme 1. Synthesis of 1,8-dioxo-octahydroxanthene derivatives

2. Materials and Method

2.1 Chemicals and Instrument

All the chemicals were purchased from Merck, Avra, and Spectrochem and were used without purification. Thin layer chromatography was performed on Merck pre-coated silica gel 60F₂₅₄ aluminum sheets as adsorbent. Melting points were taken in an open capillary and are uncorrected. FT-IR spectra were recorded on Thermo Nicolet; Avatar 370. ¹H NMR spectra were recorded on a 400 MHz using DMSO-*d*₆ as solvent and tetramethylsilane (TMS) as an internal standard. The X-ray diffraction (XRD) patterns were recorded on Bruker AXS D8 Advance X-ray diffractometer using monochromatic Cu-K α radiation having wavelength $\lambda = 1.5406 \text{ \AA}$. Scanning Electron Microscope image (SEM) was obtained on JS-6390 LV operated at 30.0 KV. Surface area and porosity (BET) of catalyst was measured on micromeritics, ASAP 2010 instrument. Temperature Programmed Desorption (TPD) ammonia was measured on Micromeritics instrument.

2.2 Synthesis of ZSM-11 Zeolite Catalyst

The ZSM-11 zeolite was synthesized by hydrothermal method. Tetraethyl orthosilicate and sodium aluminate were used as silicon and aluminum source respectively and tetra propyl ammonium bromide was used as structure directing agent. In a typical synthesis, tetraethyl orthosilicate (20.8 g) was mixed with 50 mL deionized water and stirred at room temperature for 2 h to obtain silica sol. Sodium aluminate (0.246 g) and 2 g NaOH were dissolved in 50 mL deionized water and added drop-wise to stirred solution of silica sol. Tetra propyl ammonium bromide (2 g) was dissolved in 20 mL of deionized water and added drop wise to above solution. The resulting mixture was stirred at room temperature for 12 h. The viscous homogeneous gel was transferred into Teflon lined stainless steel autoclave and treated hydrothermally under static condition and autogenous pressure at 150 °C for 24 h. The solid

product was collected, filtered and washed with deionized water. Finally, it was dried in an oven and calcined at 550 °C for 4 h in muffle furnace.

For the enhancement of acidic strength in the catalyst, the cerium ion containing ZSM-11 was prepared by ion exchange method. In this procedure 2 g ZSM-11 zeolite and 20 mL 0.1 M ceric ammonium nitrate solution were stirred at 50 °C for 12 h. The resulting product (Ce-ZSM-11) was filtered, washed with deionized water and dried in oven at 100 °C for 5 h.

2.3 General Procedure for the Synthesis 1,8-dioxo-octahydroxanthene Derivatives:

To a mixture of aromatic aldehyde (1 mmol), 5,5 dimethyl-cyclohexane-1,3-dione (2 mmol) and Ce-ZSM-11 catalyst (0.1 g) in water (10 mL) as solvent were added and refluxed for the time shown in (Table 4). The progress of the reaction was monitored by TLC (petroleum ether: ethyl acetate = 7:3 as eluent). After completion of the reaction, the reaction mixture was filtered, the catalyst was separated and the crude product obtained was recrystallized from ethanol to afford pure product (3a-k) and representative compound characterized by FT-IR, ¹H, and ¹³C NMR spectroscopy.

2.4 Selected Spectroscopic Data 3,3,6,6 tetramethyl-9-(3-nitro-phenyl)-3,4,5,6,7,9-hexahydro-2H-Xanthene-1,8-dione (3c)

FT-IR (KBr, cm⁻¹): 2955, 2874, 1708, 1584, 1452, 1363, ¹H NMR (400 MHz, DMSO-d₆): δ(ppm)= 8.05 (s, 1H), 7.97 (d, J= 8.1 Hz, 1H), 7.63 (d, J= 7.7 Hz, 1H), 7.48 (t, J= 7.9 Hz, 1H), 4.67 (s, 1H), 2.56 (s, 4H), 2.09 (s, 4H), 1.08 (s,

6H), 0.9 (s, 6H), ¹³C NMR (400 MHz, DMSO-d₆): 26.61, 28.61, 31.63, 39.57, 49.94, 113.48, 121.17, 122.70, 129.08, 134.55, 146.27, 147.39, 163.14, 195.74.

3. Results and Discussions

3.1 Catalyst Characterizations

3.1.1 Powder X-ray diffraction analysis

X-ray diffraction pattern of parent ZSM-11 and Ce-ZSM-11 are given in Figure 1 which shows intense peaks at 2θ = 8.17, 9.08, 14.15, 15.00, 23.30, 24.04, 26.05, 27.06, 29.45, 45.31 with corresponding planes (101), (111), (221), (301) (223), (303), (441), (413), (224), (814), respectively. The high intense peaks at 23.30 and 24.04 is the characteristic peak for the MEL type framework topology which indicates the presence of ordered tetragonal crystal structure of ZSM-11 material [35]. Figure 1 (b) shows decreased peak intensities as compared Figure 1(a) this may be due to insertion of cerium ion inside the channels of parent ZSM-11. However, crystal structure of parent ZSM-11 is retained after ion exchange.

3.1.2 Scanning electron microscopy-energy dispersive spectrometry analysis

The surface morphology and chemical composition of synthesized catalyst was analyzed by SEM-EDS spectroscopy. The Figure 2 shows uniform sphere shaped crystals which is characteristic morphology of ZSM-11. The SEM images show that prepared catalyst has uniform particle size and ordered morphology. The elemental composition Ce-ZSM-11 is shown in Figure 3 which confirms the presence of Si, Al, O and Ce with atomic wt. % 29.82, 1.11, 67.82, 1.25, respectively.

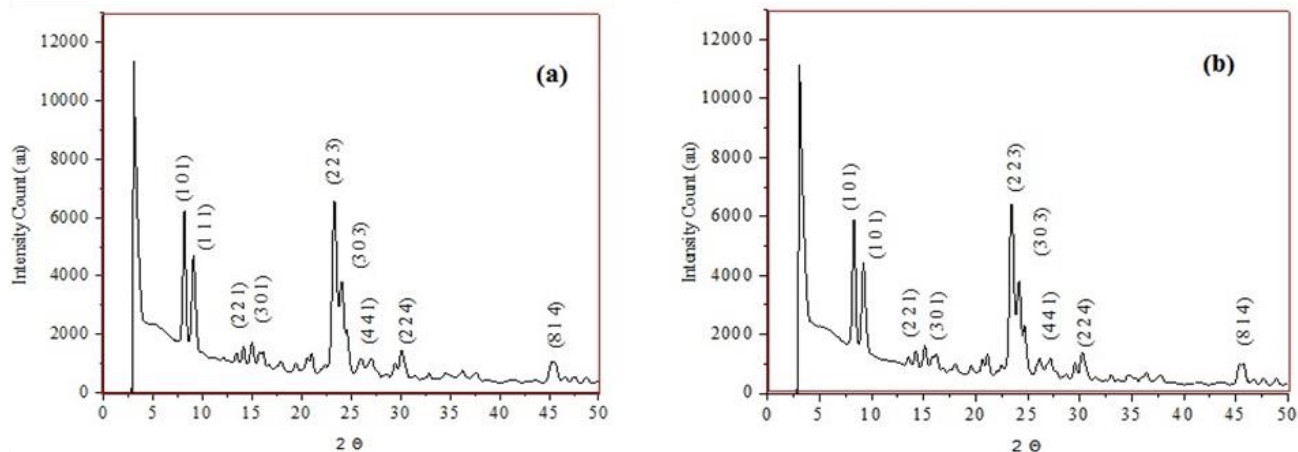


Figure 1. Powder XRD pattern of (a) ZSM-11 and (b) Ce-ZSM-11

3.1.3 Fourier Transforms Infrared Spectroscopy analysis

The FT-IR spectrum of the ZSM-11 and Ce-ZSM-11 zeolite is shown in Figure 4. The FT-IR spectrum shows sharp peak at 451, 550, 798, 1104, and 1229 cm^{-1} which are characteristic adsorption bands of ZSM-11. The band at 798, 1229 assigned for external symmetric and asymmetric stretching vibration and sharp band at 1104 cm^{-1} is assigned to internal asym-

metric stretching of T-O-T (T= Si or Al) unit in ZSM-11 framework. The band at 550 cm^{-1} confirms the presence of double five member ring which is secondary building unit of pentasil family zeolites framework (MFI or MEL) [36]. The peak at 1635 cm^{-1} is attributed to deformation mode of Si-OH bond. The band appear between 3455 cm^{-1} confirms presence of bridged hydroxyl group, i.e. Brönsted acidic center.

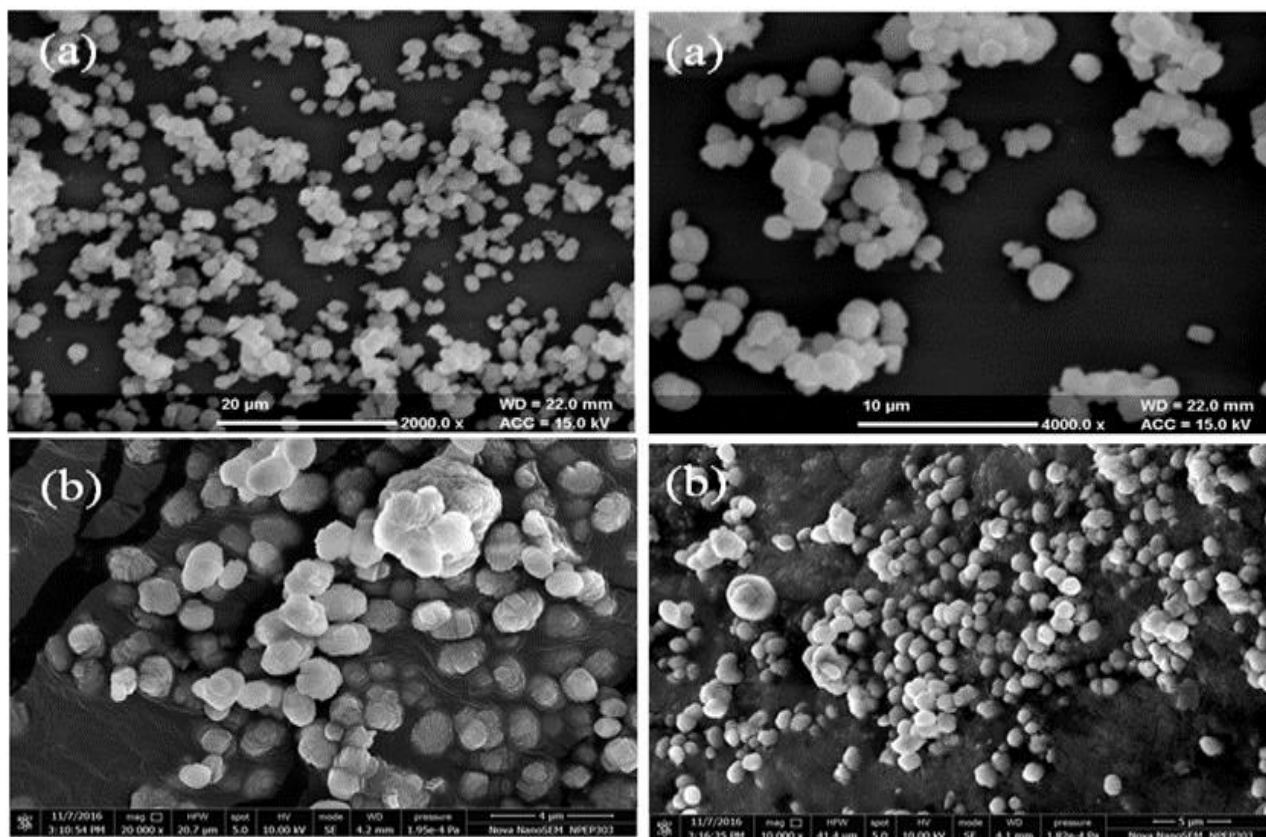


Figure 2. (a) SEM images of ZSM-11 zeolite and (b) SEM images of Ce-ZSM-11 zeolite

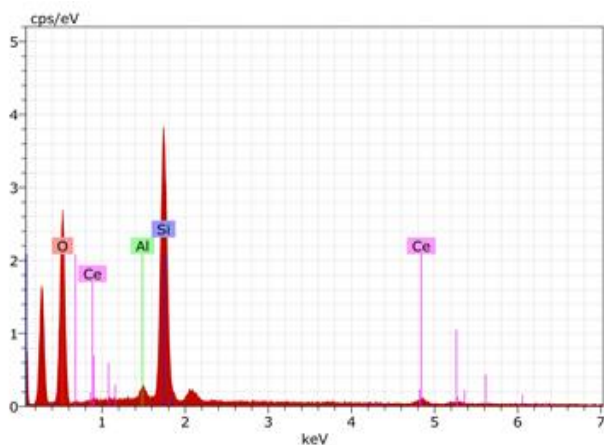


Figure 3. EDS-Spectrum of Ce-ZSM-11

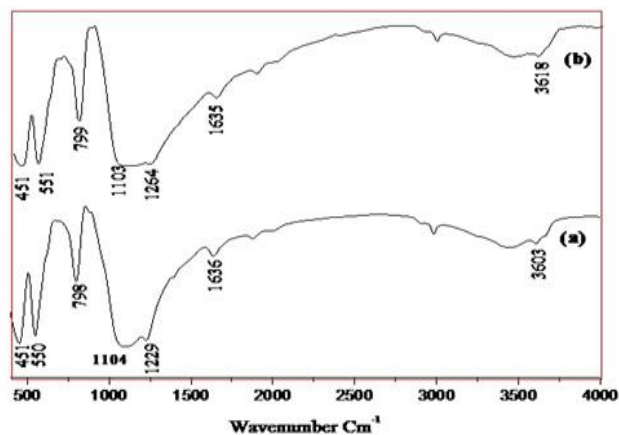


Figure 4. FT-IR Spectrum of (a) ZSM-11 and (b) Ce-ZSM-11

3.1.4 Brunauer-Emmer-Teller Surface Area analysis

The presence of intercrystalline pore was studied by N₂ adsorption-desorption isotherm. It is observed that surface area, micropore volume and average pore diameter of Ce-ZSM-11 decreased as compared to ZSM-11 zeolite which implies that cerium ions are well dispersed in framework (Table 1).

3.1.5 Temperature Programmed Desorption (Ammonia) analysis

The Figure 5a and 5b shows NH₃-TPD profile of ZSM-11 and Ce-ZSM-11 zeolite. The single broad peak at 662.5 °C for ZSM-11 and 623.4 °C for Ce-ZSM-11 is due to desorption of ammonia from strong acidic sites. The total acidity was found 1.8195 mmol.g⁻¹ and 2.6178 mmol.g⁻¹ for ZSM-11 and Ce-ZSM-11, respectively. It was observed that the acidity of ZSM-11 zeolite increases after ion exchange.

3.2 Optimization of Reaction Conditions

3.2.1 Optimization of solvent and amount of catalyst

In order to investigate suitable solvent and optimum loading of catalyst amount for the

synthesis of 1,8-dioxo-octahydroxanthene derivatives, 3-nitro benzaldehyde (1 mmol) and 5,5-dimethyl-cyclohexane-1,3-dione (2 mmol) were taken as model substrate and various solvents were screened on model reaction. Initially the model reaction was performed under solvent free condition low yield of desired product was obtained. The same reaction was performed using different solvents such as, EtOH, MeOH, THF, and H₂O under reflux condition. Among all these solvents in H₂O maximum yield was obtained, hence H₂O was selected as

Table 2. Effect of various solvent on the synthesis of synthesis of 1,8-dioxo-octahydroxanthene derivatives^a

Entry	Solvent	Time (min.)	Yield(%) ^b
1	No	120	30
2	EtOH	120	30
3	MeOH	120	20
4	THF	120	35
5	H ₂ O	120	90

^aReaction conditions: 3-Nitro benzaldehyde (1 mmol) and 5, 5 dimethyl-cyclohexane-1,3-dione (2 mmol) and catalyst with different solvents (10 ml) at reflux condition. ^bIsolated yields.

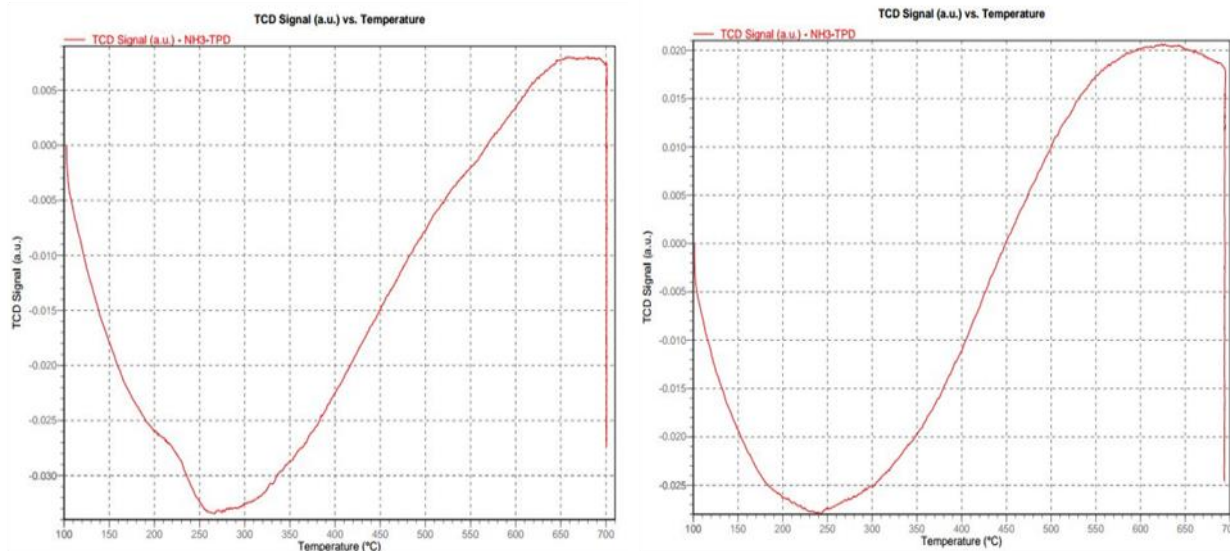


Figure 5. NH₃-TPD Spectrum of (a) ZSM-11 and (b) Ce-ZSM-11

Table 1. BET surface area, micropore volume, and average pore diameter for ZSM-11 and Ce-ZSM-11

Sr. No.	Sample	Surface area (m ² /g)	Micropore volume (cm ³ /g)	Average pore diameter (Å)
1	ZSM-11	641.37	0.52	16.37
2	Ce-ZSM-11	541.44	0.35	13.12

optimum solvent (Table 2). Therefore, further optimization of catalyst was carried out in water solvent. It was observed that 0.1 g of catalyst is sufficient for the reaction and use of excessive catalyst had no effect on either the rate of reaction or on the product yield (Table 3).

The scope and efficiency of the present method was studied by reacting various substituted aromatic aldehyde with 5,5-dimethyl-cyclohexane-1,3-dione under optimize reaction conditions and results are summarized in Table 4. In all cases, it was found that aromatic aldehydes having electron withdrawing or electron donating group reacted effectively and gave the

product in good yields. It is observed that the substituents in aromatic ring of aldehydes have little effect on the reaction time as well as yield of the product.

The main advantage of present method is reusability of Ce-ZSM-11 zeolite catalyst. The catalyst was separated after completion of reaction by diluting reaction mixture by hot ethanol and filtration. The recovered catalyst was washed with acetone and dried at 100 °C for 3 h before the next catalytic run. Reusability of the catalyst was investigated on model reaction for three times and it was found that the catalyst has retained almost consistent activity (Table 4, entry 3).

Table 3. Optimization of amount catalyst for the synthesis of of 1,8-dioxo-octahydroxanthene derivatives^a

Entry	Catalyst amount (g)	Time (min.)	Yield (%) ^b
1	0	120	-
2	0.05	120	85
3	0.10	120	90
4	0.15	120	90
5	0.20	120	90

^aReaction condition: 3-trio benzaldehyde (1 mmol) and 5,5 dimethyl-cyclohexane-1,3-dione (2 mmol) and catalyst in water (10 mL) at reflux condition. ^bIsolated yields

Table 4. Ce-ZSM-11 catalyzed synthesis for 1,8-dioxo-octahydroxanthene derivatives^a

Entry	Aldehyde (R)	Product	Time (min.)	Yield (%) ^b	M.P. (°C)	
					Observed	Literature
1	H	3a	120	85	200-202	203-204 [15]
2	4-NO ₂	3b	120	88	226-228	222-224 [15]
3	3-NO ₂	3c	120	90 (90, 85, 85) ^c	171-173	172-174 [19]
4	4-Br	3d	120	88	240-243	240-242 [19]
5	2-Br	3e	120	88	226-228	225-227 [18]
6	4-OH	3f	120	80	248-250	247-249 [18]
7	3-OH	3g	120	84	220-222	222-224 [18]
8	4-CH ₃	3h	120	80	216-218	215-217 [18]
9	2-NO ₂	3i	120	92	250-252	248-250 [18]
10	4-N(CH ₃) ₂	3j	120	80	222-224	221-223 [14]
11	4-Cl	3k	120	90	229-231	232-234 [19]

^aReaction condition: 3-NO₂ benzaldehyde (1 mmol), 5,5 dimethyl-cyclohexane-1,3-dione (2 mmol) and catalyst 0.1 g in water 10 mL. ^bIsolated yields. ^cYield after consecutive cycle.

To specify the advantages of present methods, results of different reported methods are compared with present work and summarized in Table 5. It is observed that, Ce-ZSM-11 zeolite promote reaction more effectively than other reported catalyst.

4. Conclusions

In summary, we described the synthesis, characterization of ZSM-11 and Ce-ZSM-11 zeolite catalyst. The Ce-ZSM-11 zeolite was found efficient catalyst for the synthesis of 1,8-dioxo-octahydroxanthene derivatives. The distinguished advantageous of present method are use of inexpensive catalyst, simple reaction workup, good to excellent yield, and reusability of catalyst.

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Table 5. Comparison for synthesis methods 1,8-dioxo-octahydroxanthene derivatives with various reported catalyst

Entry	Catalyst	Condition	Time	Yield (%)	Ref.
1	Magnetic nps Fe ₃ O ₄	H ₂ O, 80 °C	8 min.	86-96	[12]
2	SiCl ₄	DCE, 60-70 °C	3 h	85-95	[13]
3	CaCl ₂	DMSO, 85-90 °C	4 h	80-93	[14]
4	Imidazol-1-yl-acetic acid	Solvent free, 60 °C	8-15 min.	85-95	[15]
5	CAN/HY-Zeolite	Solvent free, 80 °C	90 min.	72-93	[16]
6	DSIMHS	Solvent free, 55 °C	4 min.	88-94	[17]
7	ZnO nps	EtOH, reflux	90 min.	78-98	[18]
8	Ru@SH-MWCNT	EtOH, reflux	30-60 min.	82-94	[19]
9	Fe-Cu/ZSM-5	H ₂ O, (((5-9 min.	90-96	[20]
10	Ce-ZSM-11	H ₂ O, reflux	120 min.	90	Present result

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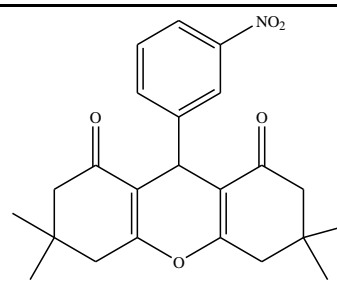
APPENDICES

3,3,6,6 Tetramethyl-9-(3-nitro-phenyl)-3,4,5,6,7,9-hexahydro-2H-Xanthene-1,8-dione (3c)

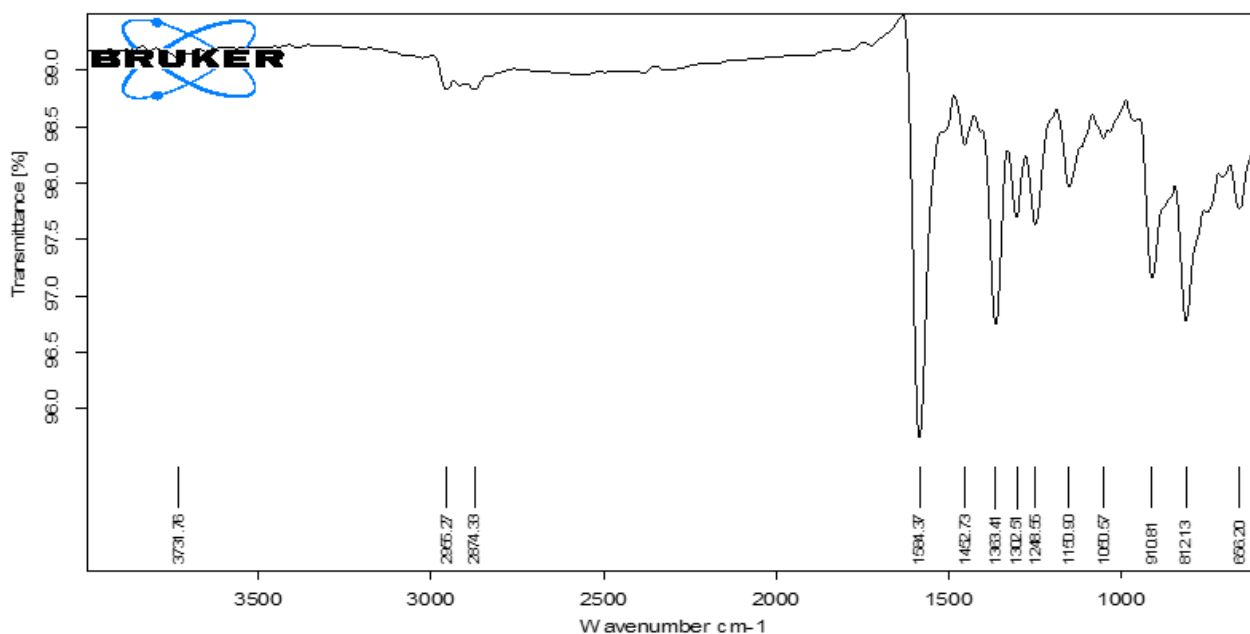
FT-IR (KBr, cm⁻¹): 2955, 2874, 1708, 1584, 1452, 1363

¹H NMR (400 MHz, DMSO-d₆): δ(ppm)= 8.05 (s, 1H), 7.97 (d, J= 8.1 Hz, 1H), 7.63 (d, J= 7.7 Hz, 1H), 7.48 (t, J= 7.9 Hz, 1H), 4.67 (s, 1H), 2.56 (s, 4H), 2.09 (s, 4H), 1.08 (s, 6H), 0.9 (s, 6H)

¹³C NMR (400 MHz, DMSO-d₆): 26.61, 28.61, 31.63, 39.57, 49.94, 113.48, 121.17, 122.70, 129.08, 134.55, 146.27, 147.39, 163.14, 195.74



FT-IR spectrum of 3,3,6,6 Tetramethyl-9-(3-nitro-phenyl)-3,4,5,6,7,9-hexahydro-2H-Xanthene-1,8-dione (3c)



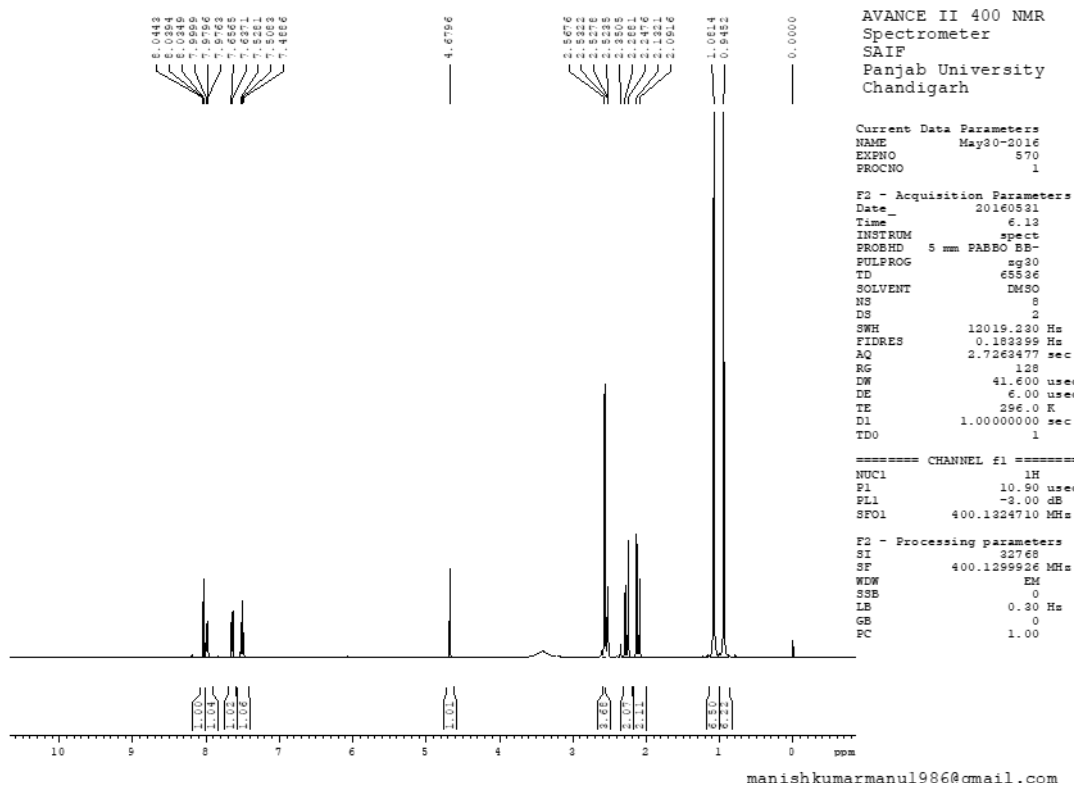
D:\FTIR DATA\Ram X2 6July 2017.0

Ram X2

Instrument type and / or accessory

7/6/2017

¹H NMR spectrum of 3,3,6,6 Tetramethyl-9-(3-nitro-phenyl)-3,4,5,6,7,9-hexahydro-2H-Xanthene-1,8-dione (3c)



¹³C NMR spectrum of 3,3,6,6 Tetramethyl-9-(3-nitro-phenyl)-3,4,5,6,7,9-hexahydro-2H-Xanthene-1,8-dione (3c)

