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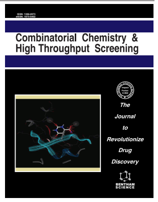
RESEARCH ARTICLE



A Clean, Mild, and Efficient Preparation of Aryl 14H-benzo[a,j]xanthene leuco-dye Derivatives *via* Nanocatalytic MCM-41-SO$_3$H under Ultrasonic Irradiation in Aqueous Media

Mostafa Fathollahi, Shahnaz Rostamizadeh* and Ali M. Amani

Department of Chemistry, K. N. Toosi University of Technology, P.O. Box 15875-4416, Tehran, Iran

Abstract: ***Aim and Objective***: The present study has developed an efficient and eco-friendly protocol for the synthesis of aryl-14-H-dibenzo[a,j] xanthenes through a one-pot condensation reaction of 2-naphthol and arylaldehydes in aqueous media using the nanocatalytic MCM-41-SO$_3$H under ultrasonic illumination.

Material and Methods: Using SEM and XRD analyses, MCM-41-SO$_3$H nanoparticles were characterized. Therefore, for high magnification, taking the SEM image, the mesoporous surface of MCM-41-SO$_3$H nanoparticles coated with gold for 2 minutes was characterized. Moreover, at a scan rate of 0.02° (2θ)/sec, XRD analysis from 1.5° (2θ) to 10.0° (2θ) was performed.

Result: For our considered sample, some well-ordered XRD patterns with one main peak as well as three minor peaks equal to those of MCM-41 materials were observed.

Conclusion: The suggested route demonstrates very promising properties like higher yields, decrease in the time of reaction (5-10 min), mild and straightforward conditions, low level of toxicity, and inclusion of a cost-efficient and ecofriendly catalyst having considerable reusability.

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1. INTRODUCTION

Much attention has recently been paid to the use of Xanthenes and benzoxanthene derivatives for pharmaceutical applications, which can be explained by their vast biological and therapeutic advantages like antibacterial [1], antiviral [2], and anti-inflammatory characteristics [3], as well as their applicability in the photodynamic therapy [4].

Furthermore, Xanthene-based materials have been investigated in terms of agricultural bactericide activities. Besides, some benzoxanthene derivatives have found industrial uses for example, dye in laser technology [5] and fluorescent radiation for bio-molecular visualization [6]. Based on the natural sources, a number of polycyclic compounds (*e.g.*, xanthene skeleton and polyimides with xanthenes pendent) have also been obtained [7]. Thus, great importance has recently been given to the preparation of benzoxanthene derivatives. In this context, different preparation routes for these derivatives such as 2-naphthol and aldehydes reaction using numerous catalytic materials like CuO nanoparticles [8], Glucose-containing Bronsted acid [9], Bronsted acid [10], Anion- binding catalysis [11], N-sulfonic acid poly (4-vinylpyridinium)chloride [12], New iodine [13], P-dodecylbenzenesulfonic (DBSA) [14], Poly(4-vinylpyridinium)hydrogen sulfate [15], Mg(BF$_4$)$_2$doped in [BMIm][BF$_4$] [16], p-tert-Butylcalix[8]arene [17], Fe^{+3}-montmorillonite K10 [18], ionic liquids [19], and P-DBSA [20] have been reported. Nevertheless, the reported protocols suffer from various demerits like high levels of solvent toxicity, severe conditions, insufficient yields, long time of reaction and excess reagents.

Recently, the direction of science and technology has increasingly been inclined toward the use of green, nature-based, and reusable catalysts such as the mesoporous and well-structured MCM-41 nanoparticles, which demonstrate a narrow distribution of pore sizes of approximately 1.5-10 nm based on the surfactant cation and a large surface area (up to 1500 $m^2 g^{-1}$) [21]. MCM-41-SO$_3$H has already been prepared and used as a Brønsted acid, by our research group for some acid catalyzed reactions [22, 23]. This reagent is nonhazardous, manageable, and can quite easily be disposed. Furthermore, as an ecofriendly preparation route, the ultrasonic-assisted organic synthesis (UAOS) can be considered as a viable technique for speeding up the organic reactions [24, 25]. As an advantage, UAOS improves the rate of the reactions, gives a high yield of pure products, and can easily be manipulated. Moreover, it has been found that ultrasound can positively contribute to the conservation of energy and minimization of waste.

Compared to the previous approaches, the suggested method is more useful since it involves different concepts of geen chemistry [26, 27]. As far as we know, there exists no previous study on the application of the MCM-41-SO$_3$H as a nanocatalyst in the preparation of aryl-14H-dibenzo[a,j] xanthenes under ultrasonic irradiation and in aqueous media.

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*Address correspondence to this author at the Department of Chemistry, K. N. Toosi University of Technology, P.O. Box 15875-4416, Tehran, Iran; Tel: +989354183790; E-mail: shrostamizadeh@yahoo.com

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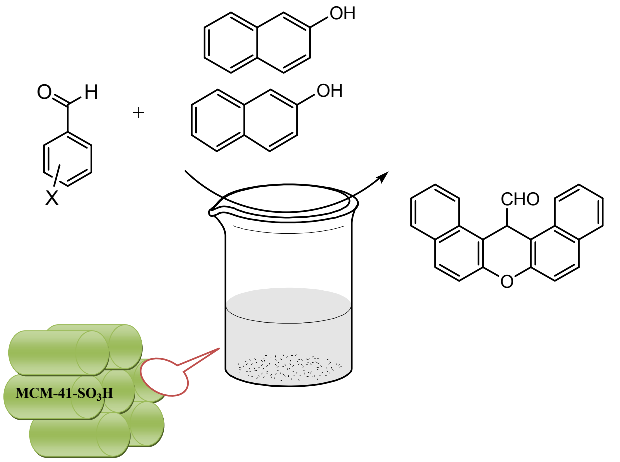
In this regard, the present study has developed an effective and ecofriendly route for the preparation of aryl-14H-dibenzo[a,j]xanthenes via our prepared nanocatalyst under ultrasound irradiation in aqueous media. Our obtained results are indicative of the favorable products in excellent yields (Scheme **1**).



Scheme 1. One-pot synthesis of aryl 14H-dibenzo[a,j]xanthenes derivatives using MCM-41-SO$_3$H as a nanocatalyst under ultrasonic irradiation.

2. MATERIALS AND METHODS

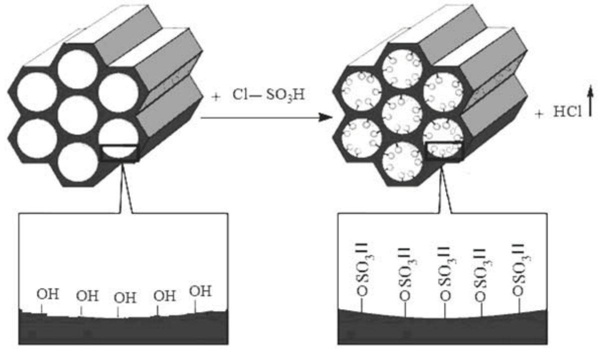
2.1. Experimental

Chemicals were purchased from Merck and Sigma-Aldrich while no additional purification was taken into account. A Büchi B-540 device was used to record the melting points, which were also uncorrected. Using an ABB Bomem Model FTLA 200-100 instrument, the record of the IR spectra was taken into account. Using a Bruker DRX-300 Avance spectrometer, ^{1}H and ^{13}C NMR spectra were calculated at 300 and 75 MHz while TMS was used as an internal standard. Chemical shifts are assumed to be (δ) with respect to TMS. Furthermore, coupling constants (J) are given in Hertz (Hz). Concerning mass spectra, a Shimadzu QP 1100 EX mass spectrometer with 70eV ionization potential was taken into account.

2.2. Synthesis and Functionalization of MCM-41

In this study, MCM-41 modification was taken into account so that the sulfonic groups can covalently be anchored on the channels' internal surface and the silica-supported substance can be supported through Bronsted acid characteristics. Besides, in order to synthesize MCM-41, the cetyltrimethylammonium bromide (CTMABr) was employed as the templating agent [28]. The template of the surfactant was then discarded from the prepared material through calcinations at 540 °C for 6 h.

MCM-41 was modified by means of a 100 mL suction flask with a fixed pressure dropping funnel having chlorosulfonic acid (81.13g, 0.7mol) and a gas inlet tube used to conduct HCl gas over an adsorbing solution. 60.0 grams of MCM-41 was charged into the said tube and a drop-wise addition of chlorosulfonic acid in a period of 30 min at room temperature was then considered. from the reaction vessel, HCl gas immediately evolved. After the completion of the addition, the mixture was shaken for 30 minutes so that MCM-41-SO$_3$H, as a white solid, was produced (115.9 grams) (Scheme **2**).



Scheme 2. Preparation of MCM-41-SO$_3$H.

By employing the scanning electron microscopy (SEM) and X-ray diffraction (XRD), MCM-41-SO$_3$H nanoreactor has been characterized. For high magnification, taking the SEM image, the mesoporous surface of MCM-41-SO$_3$H nanoparticles coated with gold for 2 minutes was characterized, the result of which is represented in Fig. (**1**). At a scan rate of 0.02°(2θ)/sec, XRD analysis from 1.5°(2θ) to 10.0°(2θ) was carried out. Fig. (**2**) shows the XRD patterns of the prepared MCM-41-SO$_3$H sample. Some quite distinct XRD patterns were observed for the MCM-41-SO$_3$H sample, with one major peak as well as three minor ones relative to those of MCM-41.

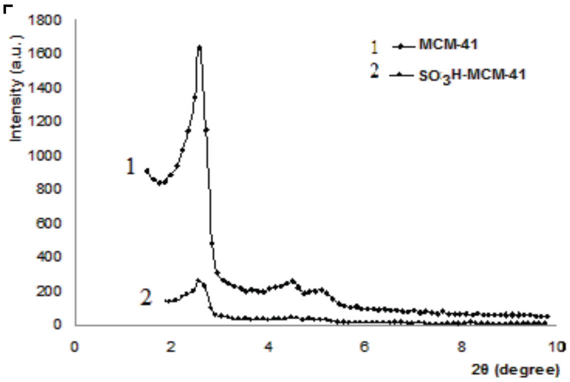


Fig. (1). XRD patterns for MCM-41 and MCM-41-SO$_3$H materials.

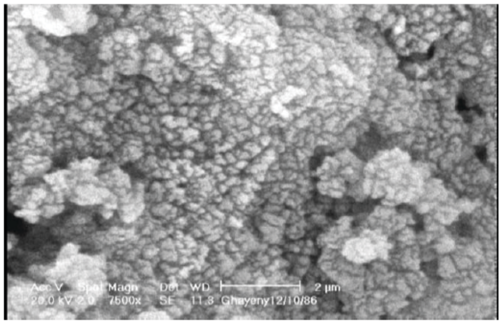


Fig. (2). SEM images for MCM-41-SO$_3$H materials.

2.3. Reusability of the Catalyst

Next, we investigated the reusability of MCM-41-SO$_3$H. With this end in view, a mixture of aldehyde (1 mmol), 2-naphthol (2 mmol) and MCM-41-SO$_3$H (0.1g) and water: EtOH (50:50) (10ml) was taken into account. The temperature rose to 30°C while the mixture was kept under ultrasonic irradiation for a proper duration of time. After the reaction was completed (managed by TLC, 2/1 petroleum ether/ethyl acetate), the evaporation and dilution of the water with CHCl$_3$/CH$_3$OH was performed, and consequently the catalyst was filtrated off. Furthermore, using simple filtration, the catalyst was separated. Besides, in the succeeding reactions, the recovered MCM-41-SO$_3$H was used again with no considerable reduction in activity even after three runs.

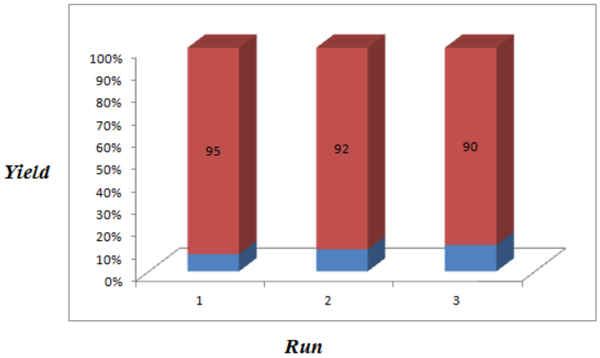


Fig. (3). Reusability of MCM-41-SO$_3$H.

2.4. Preparation of Aryl-14H-dibenzo [a,j]xanthenes

Procedure: aldehyde (1 mmol), 2-naphthol (2 mmol) and MCM-41-SO$_3$H (0.1g) and water: EtOH (50:50) (10 ml) were mixed. The temperature rose to 30°C while the mixture was kept under ultrasonic irradiation for a proper duration of time (Table **1**). After the reaction was completed (controlled by TLC, 2/1 petroleum ether/ethyl acetate), the evaporation and dilution of the water with CHCl$_3$/CH$_3$OH occurred, and subsequently the catalyst was filtrated off. Under vacuum, the solvent evaporation was taken into account. Finally, recrystallization of the resultant solid materials from ethanol was observed.

The spectral data of some representative products;

Compound 3a: IR (KBr): 3281, 3121, 3044, 1668, 1586, 1534, 1509, 1401, 1242. ^{1}H NMR (300 MHz DMSO) δ= 1.8 (s, J=1.88 HZ, 3 H), 6.63 (s, J=6.63 HZ, 1H), 7.29 (d, J=6.30 HZ, 2H), 7.45 (d, J=8.08 Hz, 2H), 7.52 (t, J=6.57 HZ, 4H), 7.59 (d,J=6.43 HZ, 2H), 7.91 (d, J=6.57, 4H), 8.63 (d, J=7.46HZ , 2H), 9.7 (s, J=9.72 Hz,1H). ^{13}C NMR (75 MHz, DMSO) δ=168, 147.85, 140.17, 137.38, 130.84, 130.62,128.91, 128.57, 128.15, 123.4, 119, 117.66, 117.36, 35.94, 23.75. MS (EI): m/e (%)=415 (44.8), 416 (30.4), 417 (3.4).

Compound 3b: IR(KBr): 3049, 3029 , 1591 , 1509, 1457, 1406, 1242, 1175, ^{1}H NMR (300 MHz, DMSO): δ= 4.8 (s, J =4.84 Hz, 2 H), 6.65 (s, J=6.65 HZ,1H),6.7 (d, J=8.64 HZ, 2H), 7.25 (m, 5H), 7.44 (t, J=7.62 HZ, 2H), 7.52 (d, J=8.62 HZ, 2H), 7.54 (d, J=8.84 HZ, 2H), 7.8 (d, J=5.17 HZ, 2H), 7.9(d, J=4.18 HZ, 2H), 8.6 (d,J=8.52 HZ, 2H).^{13}C NMR(75 MHz, DMSO): δ=156.6, 147.8, 137.9, 136.9, 130.8,130.6, 128.9, 128.8, 128.6,123.3, 127.7, 127.5, 126.9, 124.5, 123.4, 117.6, 114.4,69, 35.67 MS(EI):m/e (%)=464 (49.6), 465 (19.7).

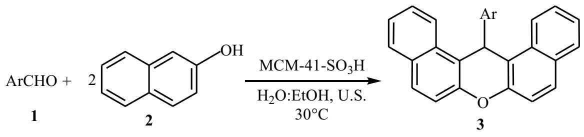
Compound 3c: IR (KBr): 3168, 1637, 1596, 1570, 1509, 1386, 1237, 1124, 738.^{1}H NMR (300 MHz, DMSO): δ= 3.54 (s, J=3.54 Hz, 1H), 7.05 (s, J=6.98 Hz, 1H) 7.09 (d, J=6 Hz, 2H), 7.24 (t, J= 9 Hz, 2H), 7.35 (t, J=9 Hz, 2H), 7.65 (d, J=9 Hz,2H), 7.73 (d, J=8.1 Hz, 2H), 9.72 (s, J= 9.72 Hz, 1H). ^{13}C NMR(75 MHz, DMSO):δ=155.3,138.52, 137, 134.6, 129.31, 127.72, 127.54, 126.12, 125.99, 124.13, 123.48, 122.64, 122.15, 120.85, 118.62, 118.18, 112.45, 108.64, 35.6. MS (EI): m/e (%) =397(40.6), 398 (15.7), 399 (5.2).

3. RESULTS AND DISCUSSION

For the first time, in the present study, MCM41-SO$_3$H has been employed as an effective nanocatalyst for the preparation of the xanthene derivatives and transformations. It is shown that the suggested catalyst is highly advantageous owing to its low level of toxicity, inexpensiveness, manageability, and considerable catalytic activity as a promising and ecofriendly material. Therefore, following our research group's previous works on the development of green synthetic routes [29-32], the present study has introduced an innovative, ecofriendly, straightforward, and viable one-pot strategy for the preparation of aryl-14-H-dibenzo[a,j]xanthenes derivatives using the catalytic amounts of MCM-41-SO$_3$H under ultrasonic irradiation (Scheme **1**).

The reactions were conducted through a highly facile route, in which the need for the use of the toxic organic solvents or inert atmospheres was removed. The reactions were performed at 30°C for 5-10 min using a 1:2 molar ratio mixture of aldehyde and 2-naphtol in the presence of 100 mg of MCM-41-SO$_3$H using H$_2$O-EtOH as a solvent at 25 kHz under ultrasonic irradiation. As far as we know, no previous studies have been conducted using ultrasonic-assisted strategies for this transformation.

In what follows, the procedures involved are discussed in detail.



Scheme 3. Synthesis of aryl 14H-dibenzo[a,j]xanthenes derivatives using MCM-41-SO$_3$H as a nanocatalyst under ultrasonic irradiation

Initially, we selected the reaction of 4-chlorobenzaldehyde and 2-naphtholes (compound 3g) as a model reaction for investigation of different reaction parameters under ultrasonic irradiation (Scheme **3**). In order to evaluate the catalytic amount in this condensation reaction, in an initial study, 4-chlorobenzaldehyde and β naphtol were reacted in water-etanol (10ml) for 8 min under ultrasonic irradiation in the presence of 0, 0. 5, 0.1, and 0.15 g of

MCM41-SO_3H separately. Using 0.1 g of MCM-41-SO_3H, the best result was obtained (yield=95%). When lower catalytic amounts were applied, the yield decreased. However, by further increases (over 0.1 g) in the amount of the catalyst, -the reaction times and yields did not change. Besides, when no catalytic amount was applied, the yield was observed to be very low (Table **1**).

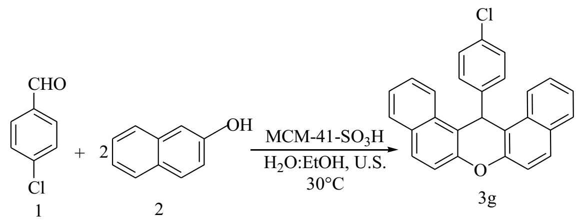
For investigation of the impact of the ultrasonic irradiation on the reactions, 14-(4-chlorophenyl)14-H-dibenzo[a,j]xanthenes were synthesized using 0, 0.5, 0.1, and 0.15 g of MCM-41-SO_3H in the presence and in the absence of ultrasonic irradiation (Table **2**).

According to the results, under sonication, shorter reaction times and higher product yields are generally observed. As the results show, using ultrasound, both the reaction times and the product yields are thus improved.

The generality of the suggested protocol can be understood by the numerous substituted aryl aldehydes used for the preparation of the related products in high to excellent yields (Table **3**).

These high yields were accordingly transformed, while the amount of unfavorable byproducts was not significant. As opposed to some previous studies, in the present study, the need for the use of the toxic or toxic organic solvents for preparation of aryl-14-H-dibenzo[a,j] xanthene derivatives is completely removed. Using NMR, IR, and melting point, the products were all characterized. Besides, our obtained results were compared with the results of the recorded literature. A large number of aromatic aldehydes were used and benzoxanthene derivatives were all produced in high-to-excellent yields (Table **4**).

The proposed route can be considered as an overall approach that allows for electron-withdrawing and electron-donating constituents. Furthermore, since the reaction was carried out under mild conditions, it did not affect such moieties as methoxy that is mostly cleaved in the strictly acidic reaction environments.



Scheme 4. Three-component one-step synthesis of 4-chloro-phenyl-14H-dibenzo[a,j]xanthenes.

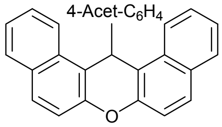
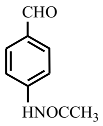
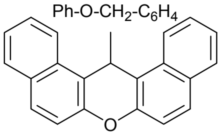
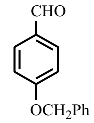
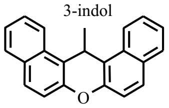
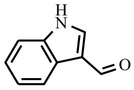
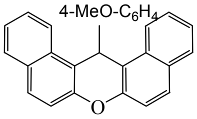
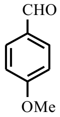
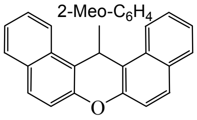
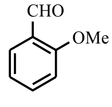
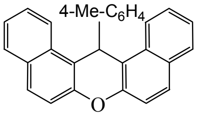
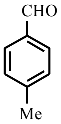
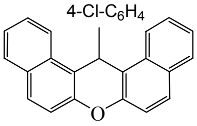
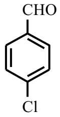
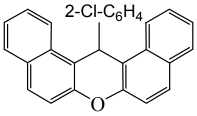
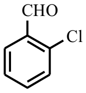
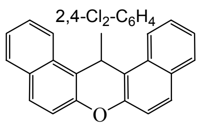
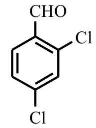
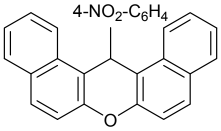
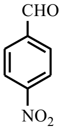
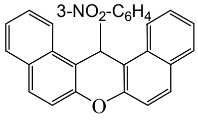
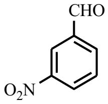
Table 1. The time and yield of reaction for 3g as a function of solvent and catalytic amount.

Entry	Conditions	Solvent	Catalyst(g)	Time	Yield (%)[a]
1	MCM-41-SO_3H, U.S., 30 ºC	C_2H_5OH	0.1	10 min	0
2	MCM-41-SO_3H, U.S., 30 ºC	H_2O	0.1	10 min	0
3	MCM-41-SO_3H, U.S., 30 ºC	H_2O: C_2H_5OH	0.1	8min	95
4	MCM-41-SO_3H, U.S., 30 ºC	H_2O: C_2H_5OH	0.05	10 min	70
5	MCM-41-SO_3H, U.S., 30 ºC	H_2O: C_2H_5OH	0.15	8 min	95
6	MCM-41-SO_3H, U.S., 30 ºC	THF	0.1	35 min	38
7	MCM-41-SO_3H, U.S., 30 ºC	DMSO	0.1	20 min	45
8	MCM-41-SO_3H, Reflux	H_2O: C_2H_5OH	0.1	6h	77
9	MCM-41-SO_3H, Reflux	THF	0.1	6 h	30
10	MCM-41-SO_3H, Reflux	DMSO	0.1	6 h	35
11	Without catalyst, U.S., 30 ºC	H_2O: C_2H_5OH	0	90min	0

Table 2. Comparison of product yields and the catalytic amount with or with no sonication for preparation of 14-(4-chlorophenyl)-14-H-dibenzo[a,j]xanthene.

Entry	Miligram of MCM-41-SO_3H	With Sonication		Without Sonication	
		Time	Yield	Time	Yield
1	0	90 min	nill	360 min	nill
2	50	60 min	45	360 min	5
3	100	8 min	95	360 min	77
4	150	8 min	95	360 min	77

Table 3. MCM-41-SO_3H-mediated preparation of Aryl-14-H-dibenzo[a,j]xanthenes under ultrasonic irradiation.

M.P.(lit.m.p)/[◦C] Found Ref	Yield (%)	Time (min)	Product	Ar	Aldehyde	Entry
182-183	80	5	3a			1
166-167	90	5	3b			2
138-139	86	6	3c			3
203-205(203-205) [29]	96	10	3d			4
258-259(260-262) [29]	85	10	3e			5
233-234(227-229) [29]	81	10	3f			6
295(289-290) [29]	95	8	3g			7
213-215(214-216) [29]	80	8	3h			8
254-255(254-255) [29]	97	6	3i			9
309-310(311-312) [29]	87	8	3j			10
215(210-211) [29]	96	8	3k			11

(Table 3) Contd….

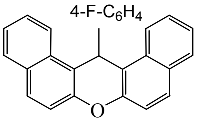
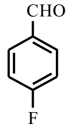
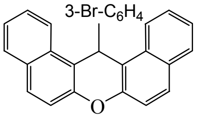
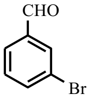
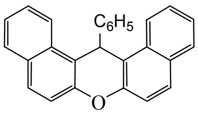
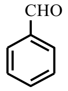
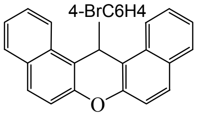
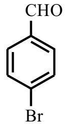
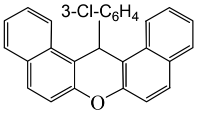
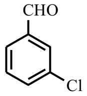
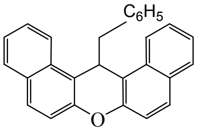
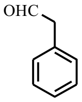
M.P.(lit.m.p)/[◦C] Found Ref	Yield (%)	Time (min)	Product	Ar	Aldehyde	Entry
237-238(239-240) [29]	81	6	3l			12
194-195(194-195) [29]	80	10	3m			13
189(184-185) [29]	92	7	3n			14
193-195(194-195) [29]	97	10	3o			15
212-214(210-213) [29]	85	10	3p			16
179-181(178-180) [29]	80	10	3q			17

Table 4. Efficiency comparison of MCM-41-SO$_3$H and other catalysts for the synthesis.

Entry	Catalyst	Temperature (◦C)	Time (h)	Yield (%)
1	Iodine	90	2.5 -5	82-95
2	*p*-TSA	125	15–24	81–93
3	Sulfamic acid	125	6-12	90-95
5	H_2SO_4/SiO_2	125	4-8	78-95
6	PTC	110	2-3	87–93
7	Selecfluor	125	6-11	74–93
8	$Fe(HSO_4)_3$	125	23 min	72–90
9	Amberlyst-15	125	0.5-2	80–94
10	$K_5CoW_{12}O_{40}.3H_2O$	125	3	64–78
11	LiBr	130	1-2	80–84
12	Dowex-50W	100	1-2	78–91

(Table 4) Contd….

Entry	Catalyst	Temperature (◦C)	Time (h)	Yield (%)
13	$NaHSO_4$	90	0.5-1	74–91
14	$CoPy_2Cl_2$	85	2-8	65–94
15	$Yb(OTf)_3$, ILs	110	3-7	78–95
16	P_2O_5 or $InCl_3$	80	0.5-1	87–97
17	P_2O_5/Al_2O_3	MW, 900 W	10-15 min	60-95
18	H_3BO_3	120	1.5-3	85-98
19	**MCM-41-SO_3H, U.S.**	**30**	**5 min**	**95**

The mixture of reagents was sonicated for 5-10 minutes. In our studies, we found that water and ethanol was the most appropriate solvent for this transformation giving the best results (Table **3**).

We have also observed that only (0.1 g) of MCM-41-SO_3H had a significant effect on the yield of compound 3h and was sufficient to push the reaction forward. It is worth mentioning that greater volumes of catalyst (0.15 g) did not increase the yield. On the other hand, reduction in the catalytic amount resulted in the reduction in the yield of the reaction.

It is important to mention that in order that the impact of ultrasonic irradiation can be verified, this work has done the above model reaction with no sonication and under reflux condition in which the reaction goes to completion in 6h and the yield of compound 3h was 77%. However, under ultrasound the yield for 3h was 95% (Table **1**, Entry 8).

The process scope and generality are shown in more detail in Table **2** (Scheme **1**) through the preparation of the 14H-dibenzo[a,j]xanthenes series.

The reactions were all performed within 5-10 min without any byproduct seen under TLC analysis. These reactions fit appropriately with both of electron-withdrawing (NO2, Cl) and electron-donating (Me, MeO) groups, offering numerous xanthenes' derivatives in 80-97% yields. As observed in Table **2**, the proposed method seems to be comprehensive and can work with different functional groups.

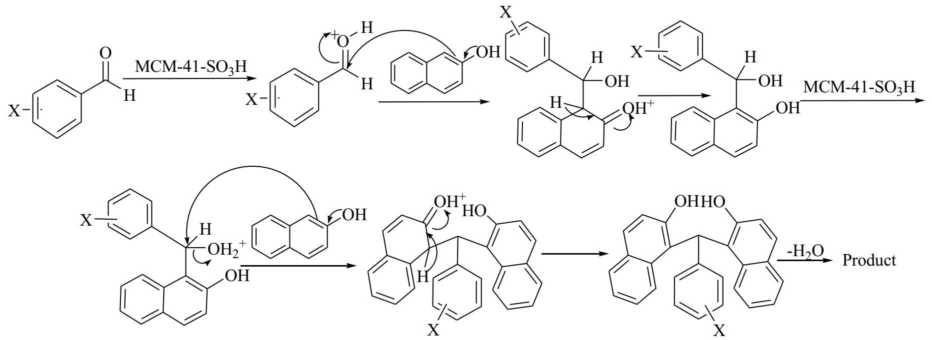
In order that the proposed approach can be further corroborated, a comparison was made between our obtained results for the synthesis of dibenzoxanthenes with the results from the recent literature (Table **4**).

Reduction in the time of reaction (5-10 min), mild reaction condition, and use of cost-effective and easy to prepare catalyst are among the merits of the proposed approach, as compared to the recorded approaches in the literature. Our suggested procedure for this transformation is shown in Scheme **4**.

After that, the MCM-41-SO_3H sample's reusability and recycling was verified. To this end, we first put p-Cholorobenzaldehyde (1 mmol), 2-naphthol (2 mmol) and 0.1 g MCM-41-SO_3H in ethanol/water (50:50) (5 ml) as solvent at 30°C under ultrasonic irradiation. By the completion of the reaction as monitored by TLC analysis, the mixture of the reaction was stirred for 10 minutes at a temperature of 80°C. The produced solid (catalyst) was separated by simple filtration and recovered. Moreover, MCM-41-SO_3H was reused in the next reactions while no significant reduction was observed the in the catalytic activity even after three runs of the reaction.

CONCLUSION

The present study has introduced a very efficient preparation route for the preparation of aryl-14-H-dibenzo [a,j]xanthenes based on the reaction between aldehydes and 2-naphtol by the catalytic activity of MCM-41-SO_3H under sonication. Furthermore, this method has made use of a straightforward, quick, easily implementable, and inexpensive mechanism for preparing these products. Besides, the considered catalyst is straightforwardly produced and



Scheme 5. A provisional mechanism for the synthesis of aryl 14H-dibenzo[a,j]xanthenes.

removed using a convenient filtration. Due to such a convenient catalytic production and elimination, this protocol can be considered as an attractive option for different chemical applications.

CONSENT FOR PUBLICATION

Not applicable.

CONFLICT OF INTEREST

The authors declare no conflict of interest, financial or otherwise.

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