

Multicomponent Synthesis of Tetrahydrobenzo[*a*]xanthene and Tetrahydrobenzo[*a*]acridine Derivatives using Sulfonated Multi-Walled Carbon Nanotubes as Heterogeneous Nanocatalysts

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ABSTRACT

This study is the first report of the application of sulfonated multi-walled carbon nanotubes (MWCNTs-SO₃H) in the synthesis of tetrahydrobenzo[*a*]xanthene and tetrahydrobenzo[*a*]acridine derivatives. The catalyst was prepared via a chemical approach and the sulfonated groups were attached to the side-wall of MWCNTs with total density of 2.58 mmol.g⁻¹. In order to prove functionalization of the MWCNTs-SO₃H, the catalyst was characterized using FE-SEM, TEM, FT-IR, and Raman spectroscopy techniques. A three-component reaction including 2-naphthol, dimedone, and aromatic aldehydes were applied in the synthesis of tetrahydrobenzo[*a*]xanthene in the presence of 15.5 mol% of MWCNTs-SO₃H under solvent-free conditions. Also, a four-component reaction including 2-naphthol, dimedone, aromatic aldehydes, and ammonium chloride was used in the synthesis of tetrahydrobenzo[*a*]acridine in the presence of 12.9 mol% of MWCNTs-SO₃H under solvent-free conditions. All the derivatives of tetrahydrobenzo[*a*]xanthene and tetrahydrobenzo[*a*]acridine were obtained in good to excellent yields. The MWCNTs-SO₃H was reused in seven consequent catalytic cycles without loss of their catalytic activity.

Keywords: Multicomponent, Carbon nanotubes, Catalyst, Heterogeneous, Xanthene, Acridine

1. Introduction

A large number of applications for carbon nanotubes (CNTs) and functionalized CNTs have developed during the last two decades since CNTs were identified by Iijima [1]. Multi-walled carbon nanotubes (MWCNTs) and single-walled carbon nanotubes (SWCNTs) could be applied as a catalyst support or as self-catalyst on their own. The pointed application has been completely discussed in several reviews [2-4]. The CNTs have been used for a long time as catalyst support in the production of different organic synthesis including CO₂ conversion [5], cross-coupling reaction [6], hydroamination [7], pyrazolopyranopyrimidines [8], 1,4-dihydropyridines [9], bisphenolic antioxidants [10, 11], 1,3,5-triarylbenzenes [12], trisphenols [13], tert-butylation of p-cresol [14], and xanthenes [15].

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In 2015, Moradi and co-workers reported a new method for the preparation of MWCNTs-SO₃H through the three steps chemical routes [16]. They prepared the MWCNTs-SO₃H in three steps including i) hydroxylation of CNTs through the radical reaction, ii) converting CNTs-OH to CNTs-ONa using NaOH at 70 °C, and iii) converting CNTs-ONa to CNTs-OSO₃H using chlorosulfonic acid in the presence of ionic liquid. Then, they applied the MWCNTs-SO₃H for the synthesis of 3,4-dihydropyrimidin-2(1H)-ones/thiones.

Acridine and xanthene derivatives are two important classes of bioactive organic compounds bearing wide range applications in the pharmaceutical industry and as antioxidant, antimicrobial, antiviral, and anticancer capabilities [17-20]. Many advanced compounds including pharmaceuticals, natural products, and industrial compounds exist which have xanthene and acridine based units (Fig. 1). It is notable that in organic

chemistry, some of the important organic molecules were synthesized using multicomponent reactions. In recent years, the different research groups have investigated the synthesis of organic molecules [21-30].

Several methodologies were applied for the synthesis of tetrahydrobenzo[a]xanthene and tetrahydrobenzo[a]acridine derivatives. For examples, toluene-sulfonic acid [31], tritylchloride [32], nano-Fe₃O₄ immobilized lewis acidic ionic liquid [33], sulfonated carbonized xylan-type hemicellulose [34], BF₃ [35], DSTMG-Cl-SO₃H ionic liquid [36], Fe₂O₃@Hap-dual acidic [37], and TiO₂-HClO₄ [38] were applied for the synthesis of tetrahydrobenzo[a]xanthene derivatives. Moreover, SnCl₂.2H₂O [39], Fe₃O₄PS-Arg[H₂SO₄] MNP [40], H₆P₂W₁₈O₆₂.18H₂O [41], L-proline [42], and DSTMG-Cl-SO₃H ionic liquid [36] were other heterogeneous

catalytic systems that are used in the synthesis of tetrahydrobenzo[a]acridine derivatives. However, many published papers have several disadvantages such as long reaction times, use of hazardous organic solvents, high amount of catalyst, and production of byproducts. Therefore, we tried to solve these problems using sulfonated multi-walled carbon nanotubes (MWCNTs-SO₃H). Up to now, there are no reports in the scientific data base for the using of MWCNTs-SO₃H in the synthesis of tetrahydrobenzo[a]xanthene and tetrahydrobenzo[a]acridine derivatives. In this study, through the chemical approach, the sulfonated groups were anchored on the side-wall of MWCNTs. Then, the prepared catalyst was characterized using different microscopic and spectroscopic techniques and subsequently used in the synthesis of tetrahydrobenzo[a]xanthene and tetrahydrobenzo[a]acridine derivatives (**Scheme 1**).

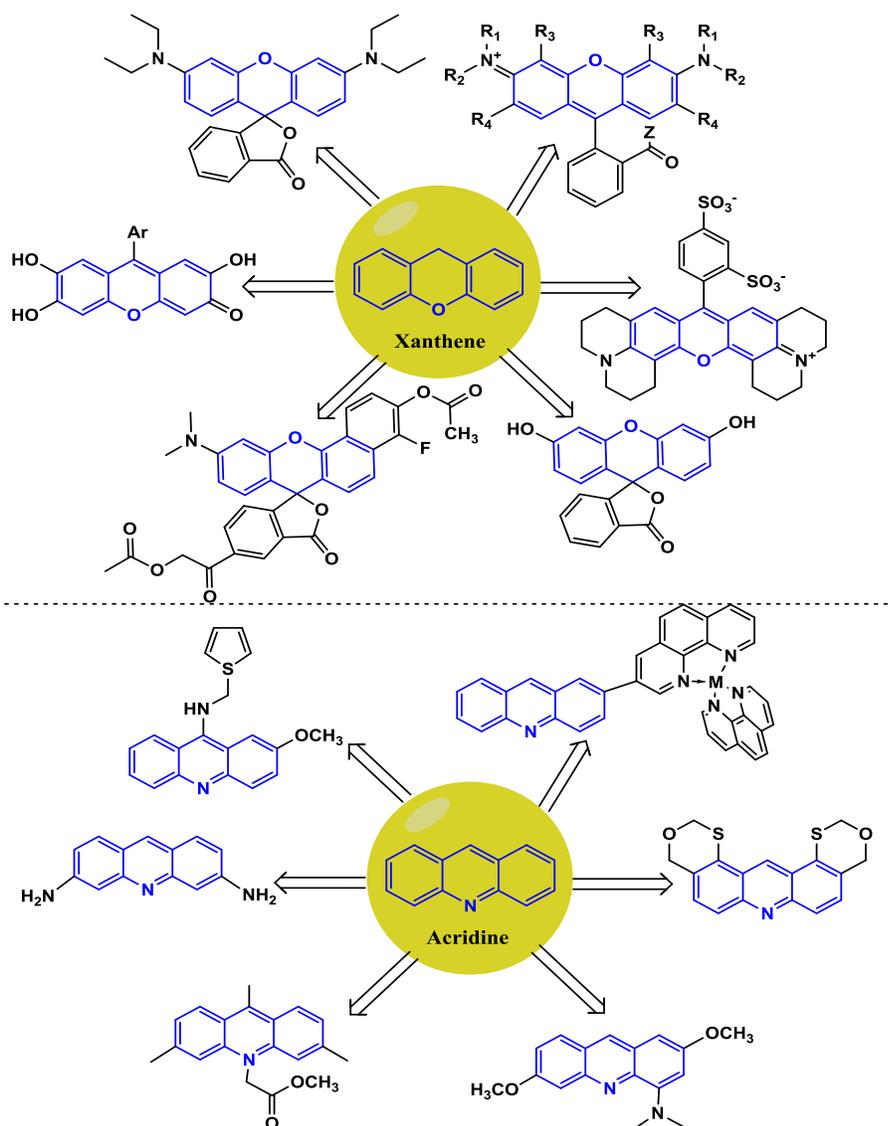
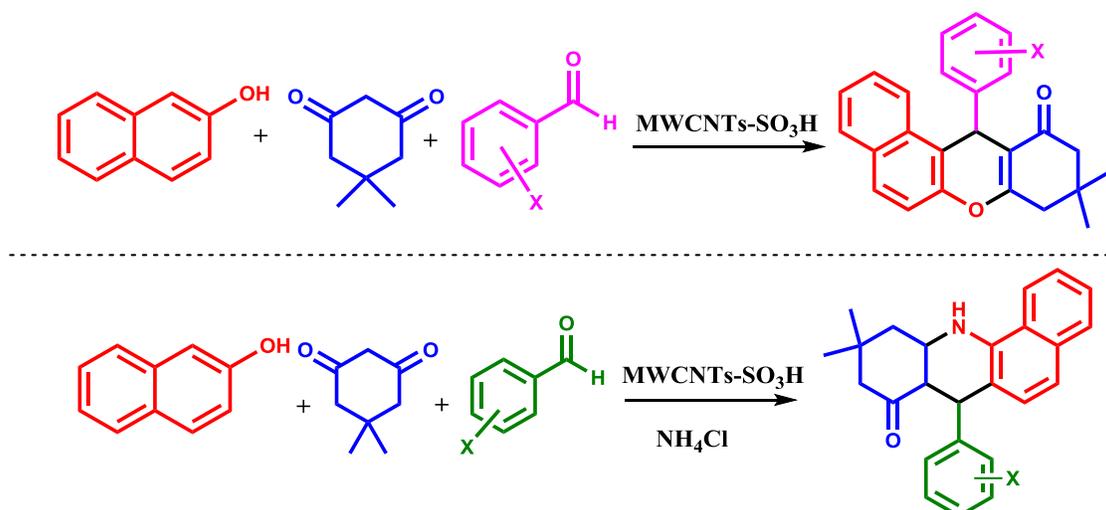


Fig. 1. The Chemical structure of important compounds based on xanthene and acridine units



Scheme 1. Synthesis of tetrahydrobenzo[a]xanthene and tetrahydrobenzo[a]acridine derivatives using MWCNTs-SO₃H

2. Experimental

2.1. General

The MWCNTs applied in the current study [MWCNTs: (L= 56-78 μm , D= 35-60 nm)] have been purchased from Beijing Chemical Company Ltd. From P. R. China. The material and chemicals used in the current work were purchased from Sigma and Merck chemical companies. All organic reactions were performed under magnetic stirring in a 50 mL glass reactor. The Raman spectra were obtained with Nicolet Dispersive Almega Raman spectrometer excited at 532 nm. FT-IR spectra were recorded with potassium bromide pellets in the range of 400-4000 cm^{-1} with a Shimadzu-A20 spectrometer. FE-SEM images of MWCNTs and MWCNTs-SO₃H were obtained on a Zeiss-5625 SEM instrument. TEM image was recorded using a Zeiss-EM10C with an acceleration voltage of 80 kV. The melting points of synthesized tetrahydrobenzo[a]xanthene and tetrahydrobenzo[a]acridine derivatives were measured with a Yanagimoto micro melting point apparatus and are uncorrected. The purity determination of the starting materials and products were monitored by thin layer chromatography (TLC) on silica-gel polygram SILG/UV 254 nm plates.

2.2. Preparation of sulfonated multi-walled carbon nanotubes (MWCNTs-SO₃H)

At first for activation and purification of MWCNTs, 3.5 g of MWCNTs and 200 mL water were added in an appropriate dish and sonicated for 0.5 h using a sonicator instrument probe with power 56 KHz. After that, the MWCNTs were moved to another appropriate dish including HCl 37% and HNO₃ 69% (2:1) and stirred for 4 h at 80 $^{\circ}\text{C}$ under N₂ atmosphere. Then,

obtained MWCNTs-COOH were washed completely with water and dried at 70 $^{\circ}\text{C}$ for 12 h. After preparation of MWCNTs-COOH, the MWCNTs-SO₃H was prepared according to the following approach. 3.0 g of MWCNTs-COOH and 100 mL water was sonicated for 0.25 h. Then, the water was filtered and 50 mL H₂SO₄ (Con. 98%) was added at 180 $^{\circ}\text{C}$ for 14 h under N₂ atmosphere. After cooling to room temperature, the solution was filtered and washed completely with water for several times. The MWCNTs-SO₃H dried at 70 $^{\circ}\text{C}$ for 8 h.

2.3. General procedure for the synthesis of tetrahydrobenzo[a]xanthene using MWCNTs-SO₃H

In a 25 mL round bottom flask, 1 mmol of 2-naphthol, 1 mmol of aromatic aldehyde, and 1 mmol of dimesedone was treated with 60 mg of MWCNTs-SO₃H at 90 $^{\circ}\text{C}$ under solvent-free conditions, for the appropriate time. The progress of the reaction was controlled using TLC in the presence of EtOAc: n-hexane (2:8) as eluting. After completion of the reaction, the reaction mixtures were extracted from the MWCNTs-SO₃H using EtOAc (3 \times 5 mL). Then, the solution was slowly heated to obtain crude products. For the purification of crude products, the crude products were recrystallized from aqueous solution 15% EtOH to get pure products.

2.4. General procedure for the synthesis of tetrahydrobenzo[a]acridinone using MWCNTs-SO₃H

In a 25 mL round bottom flask, 1 mmol of 2-naphthol, 1 mmol of aromatic aldehyde, 1 mmol of ammonium chloride, and 1 mmol of dimesedone was treated in the presence of 50 mg of MWCNTs-SO₃H at 80 $^{\circ}\text{C}$ under solvent-free conditions; for the appropriate time. The progress of the reaction was controlled using TLC in the

presence of EtOAc: n-hexane (2:8) as eluting. After completion of the reaction, the reaction mixtures were extracted from the MWCNTs-SO₃H using EtOAc (3×5 mL) and dichloromethane (2×5 mL). Then, the solution was slowly heated to obtain crude products. For the purification of crude products, the crude products were recrystallized from aqueous solution 15% EtOH to get pure products.

2.5. Reusability of MWCNTs-SO₃H

The reusability and recovery of MWCNTs-SO₃H were investigated in the synthesis of tetrahydrobenzo[*a*]xanthene and tetrahydrobenzo[*a*]acridine derivatives. In this regard, after each run, the MWCNTs-SO₃H was filtered and washed exhaustively with ethanol and water, then dried at 70 °C for 10 h.

2.6. Acidity of MWCNTs-SO₃H

The total density of sulfonic acid groups anchored on MWCNTs was calculated using back acid-base titration. At the beginning, 75 mg of MWCNTs-SO₃H was accurately weighed. Then, 50 mL of water was added and sonicated for 0.25 h under N₂ atmosphere. Next, 15 mL of NaOH 0.0991 N was added, and the reaction mixture was stirred for 2 h at room temperature. After that, the reaction mixture was filtered and completely

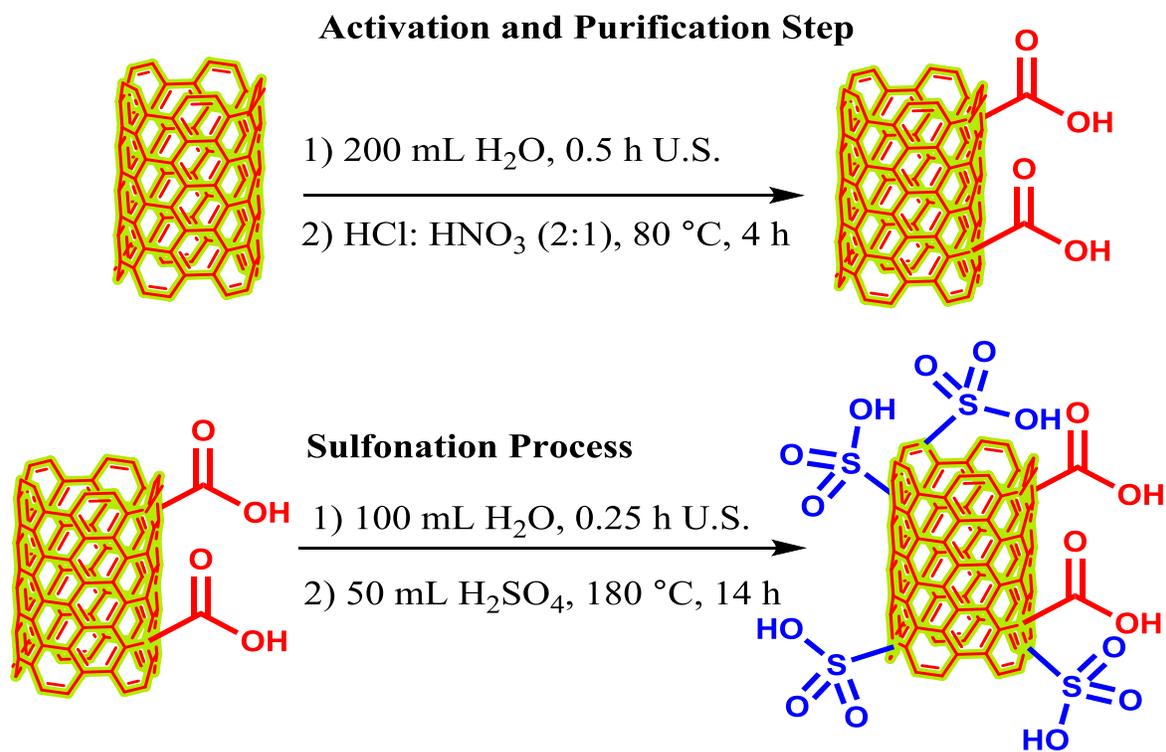
washed with water. The filtrated solution was titrated with HCl 0.1 N (titrisol) until reaching the neutral point in the presence of phenolphthalein as an indicator. The volume required to reach the neutral point was subtracted from the initial volume of NaOH used to obtain the volume of NaOH which has reacted with sulfonated group on MWCNTs.

3. Results and Discussion

3.1. Characterization of MWCNTs-SO₃H

As can be seen, the MWCNTs-SO₃H was prepared according to the reported literature (**Scheme 2**) [14]. Then, after successful preparation of MWCNTs-SO₃H the catalyst was identified using FE-SEM, TEM, FT-IR, Raman Spectroscopy, and back acid-base titration.

To investigate the morphology of pristine MWCNTs and MWCNTs-SO₃H; FE-SEM of MWCNTs and MWCNTs-SO₃H were obtained (**Fig. 2**). As can be seen, the tube and long length of pristine MWCNTs were seen (**Fig. 2a**). After sulfonation process, the tubes were covered by foreign layers and it may be covered the sulfonic acid groups on the sidewall of MWCNTs (**Fig. 2b**). In addition, TEM image of MWCNTs-SO₃H was recorded and the tube and functional groups were observed on the sidewall of MWCNTs, after sulfonation process (**Fig. 3**).



Scheme 2. Synthetic approach for preparation of MWCNTs-SO₃H

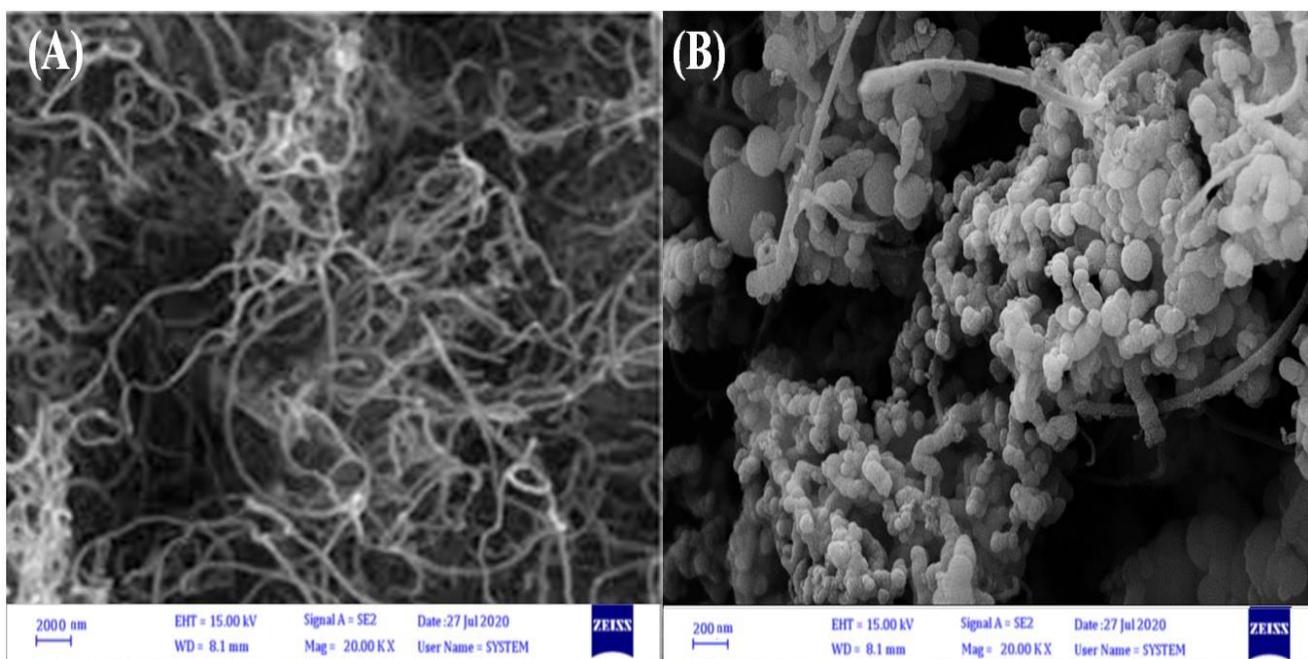


Fig. 2. FE-SEM images of a) MWCNTs and b) MWCNTs-SO₃H

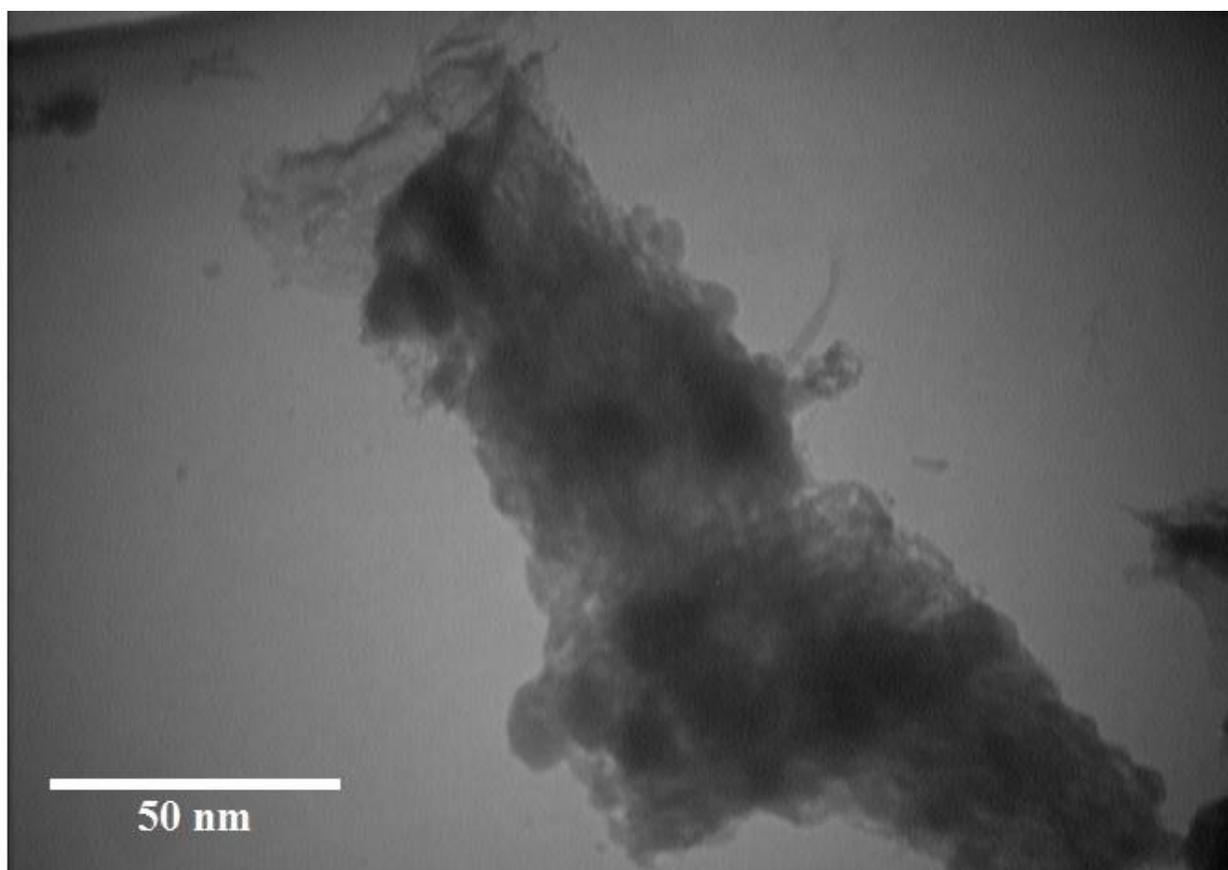


Fig. 3. TEM image of MWCNTs-SO₃H

Fig. 4 shows the FT-IR spectra of raw MWCNTs, MWCNTs-COOH, and MWCNTs-SO₃H. The FT-IR spectra of raw MWCNTs have very weak signals due to the symmetry of CNTs. However, we observed a weak

signal in 1530 cm⁻¹ due to the carbon-carbon double bond (**Fig. 4a**) [43]. After purification and activation of MWCNTs, the signals 3245, 2986, 1716, 1059 cm⁻¹ were related to O-H, C-H, C=O, and C-O stretching

mode, respectively (**Fig. 4b**) [43]. Finally, after sulfation process, the signals 3289, 1245, 1209, 590 cm^{-1} appeared on spectra due to the O-H, symmetry and asymmetry SO_2 , and C-S stretching mode, respectively (**Fig. 4c**) [43].

Raman spectra of MWCNTs, MWCNTs-COOH, and MWCNTs-SO₃H were recorded for characterization of pristine MWCNTs, and functionalized CNTs (**Fig. 5**). As we know, the Raman spectroscopy is a unique technique for investigation of process functionalization of CNTs. As can be seen, two signals are observed in the region spectrum of 1300-1600 cm^{-1} . The band at about 1300 cm^{-1} is called D-band and the band at approximately 1500 is named G-band. The ratio of intensity of D-band to G-band is corresponded to functionalization of CNTs [44]. The $I_{D/G}$ s in MWCNTs, MWCNTs-COOH, and MWCNTs-SO₃H were calculated as 0.244, 0.373, and 0.844, respectively.

These numbers show that the number of carbons with hybridization of sp^3 are increased due to the functionalization of CNTs. Finally, we determined the density of sulfonated groups on the sidewall of CNTs using back acid-base titration. Our tests showed that the amount of SO₃H groups anchored on the side-wall of MWCNTs is 2.58 mmol.g^{-1} .

3.2. Optimization study

After preparation and characterization of MWCNTs-SO₃H, the pointed catalyst was applied in the synthesis of tetrahydrobenzo[*a*]xanthene and tetrahydrobenzo[*a*]acridine derivatives. Hence, in order to optimize the reaction parameters, two model reactions were selected for the optimization of amount of MWCNTs-SO₃H, type of solvent, and temperature (**Tables 1 and 2**).

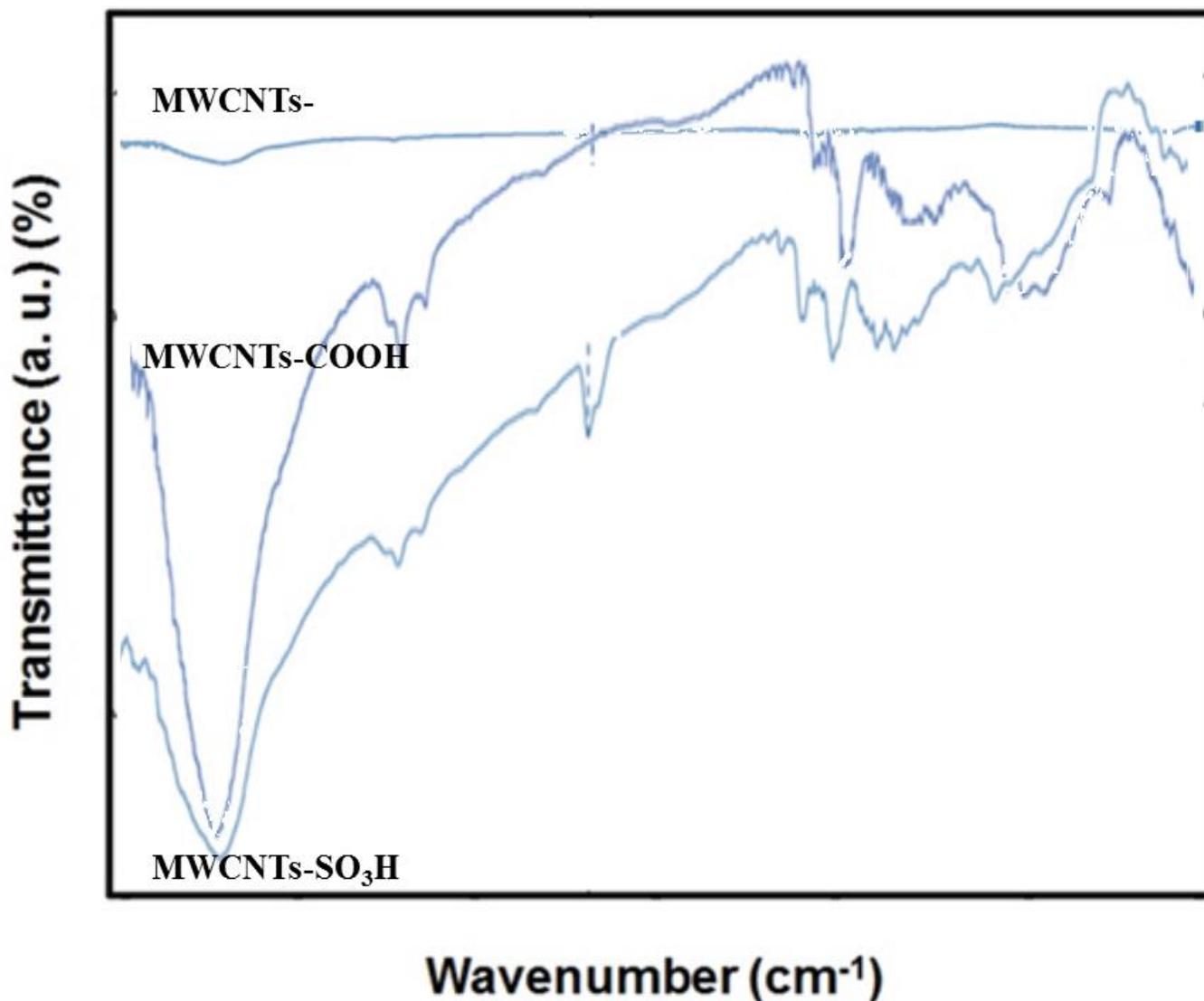
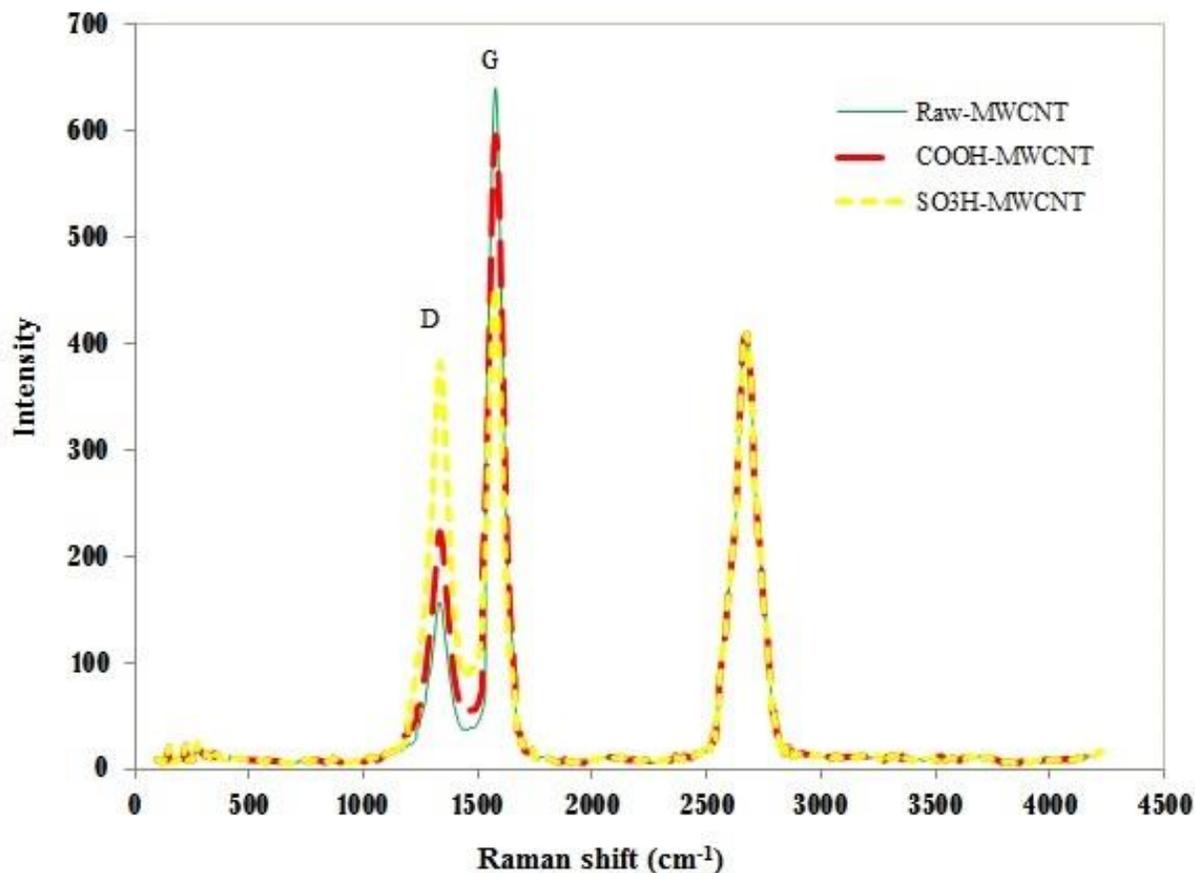


Fig. 4. FT-IR spectra of a) MWCNTs b) MWCNTs-COOH, c) MWCNTs-SO₃H



	Max _D line	Max _G line	I _{DC}
MWCNTs	156.491244	639.0532	0.244879838
MWCNTs-COOH	222.699078	596.0981	0.373594678
MWCNTs-SO ₃ H	382.199769	452.5743	0.844501707

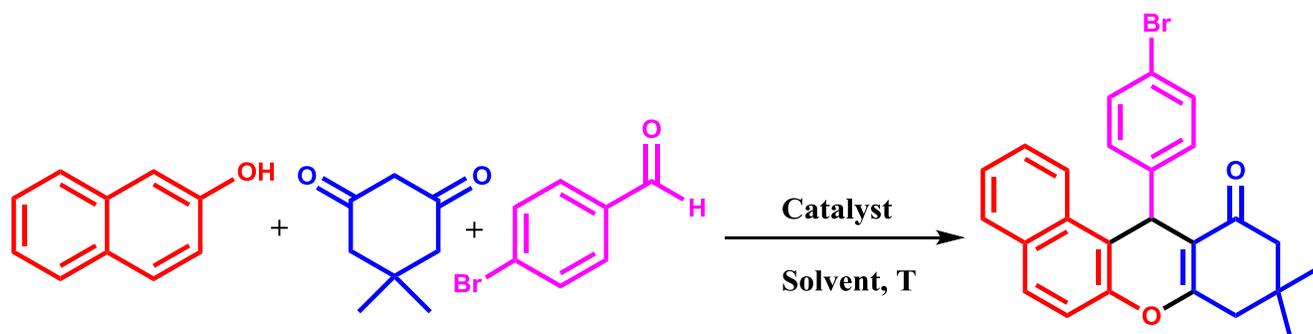
Fig. 5. Raman spectra of MWCNTs-, MWCNTs-COOH, and MWCNTs-SO₃H

We used 2-naphthol, dimedone, and 4-bromobenzaldehyde as a model reaction for the synthesis of tetrahydrobenzo[*a*]xanthene (**Table 1**). In order to select the optimum medium of the reaction, we performed the model reaction under different mediums including water, ethanol, acetonitrile, and solvent-free conditions. Our tests show that the model reaction was the best yield under solvent-free conditions (**Table 1**, entry 4). Moreover, the best temperature was 90 °C (**Table 1**, entry 4). Finally, the model reaction was performed in the presence of different amounts of MWCNTs-SO₃H (**Table 1**, entries 6-8). The best result was obtained in 60 mg or 15.5 mol% of MWCNTs-SO₃H. Also, we optimized the reaction parameters for the synthesis of tetrahydrobenzo[*a*]acridine derivatives using the following model reaction including 2-naphthol, dimedone, 4-chlorobenzaldehyde, and ammonium chloride (**Table 2**). Entry 4 in **Table 2**

shows the best conditions for the synthesis of tetrahydrobenzo[*a*]acridine derivatives.

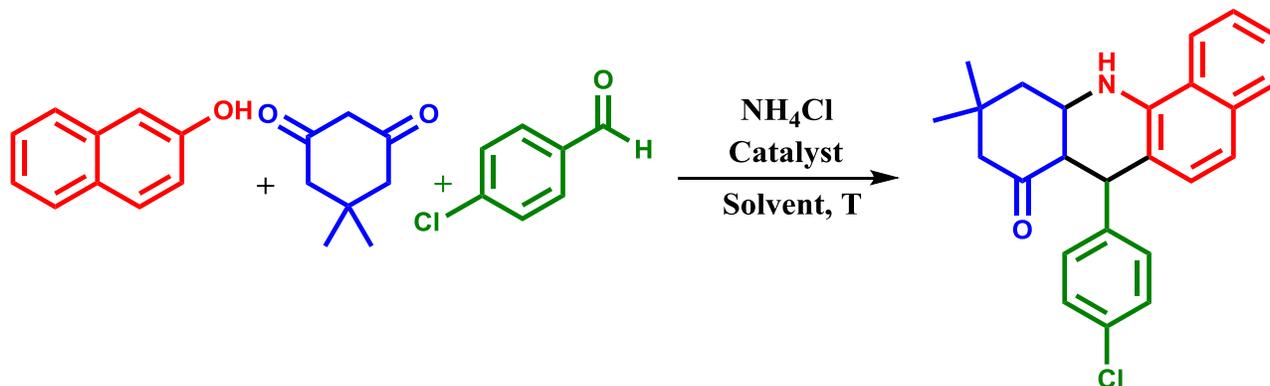
3.3. Catalytic study

After optimization of reaction parameters for the synthesis of tetrahydrobenzo[*a*]xanthene and tetrahydrobenzo[*a*]acridine derivatives, we generalize these methodologies for synthesis of other types of derivatives (**Tables 3** and **4**). The optimum amounts of MWCNTs-SO₃H were 60 mg (15.5 mol%) and 50 mg (12.9 mol%) for the synthesis of tetrahydrobenzo[*a*]xanthene and tetrahydrobenzo[*a*]acridine derivatives, respectively. Our tests show that the aromatic aldehydes with electron-withdrawing groups accelerate the reaction time and increase the yield of the reaction.

Table 1. Optimization of the reaction conditions for tetrahydrobenzo[*a*]xanthene^a

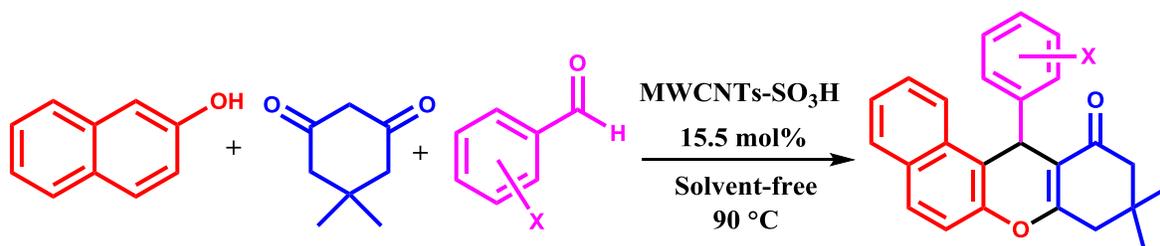
Entry	MWCNTs-SO ₃ H (mg)	T (°C)	Solvent	Yield (%) ^b	Time (min)
1	60	Reflux	H ₂ O	54	60
2	60	Reflux	EtOH	44	60
3	60	Reflux	CH ₃ CN	60	60
4	60	90	Solvent-free	94	60
5	60	100	Solvent-free	94	60
6	60	80	Solvent-free	85	60
7	70	90	Solvent-free	92	60
8	50	90	Solvent-free	79	60

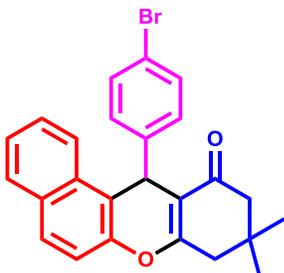
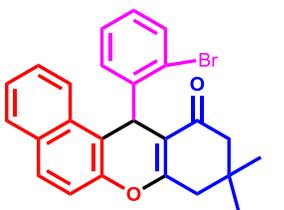
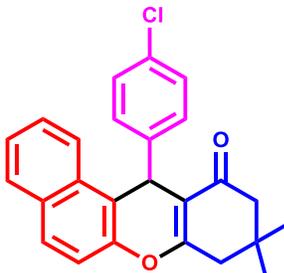
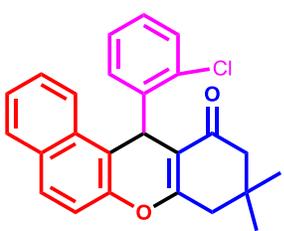
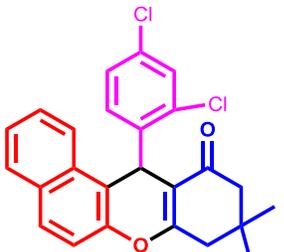
a) Reaction conditions: 2-naphthol (1 mmol), dimedone (1 mmol), 4-bromobenzaldehyde (1 mmol), Solvent: 5 mL. b) Isolated yield.

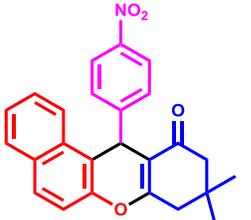
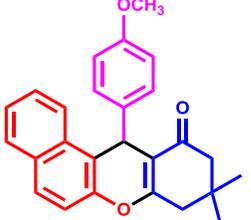
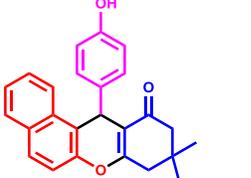
Table 2. Optimization of the reaction conditions for tetrahydrobenzo[*a*]acridine^a

Entry	MWCNTs-SO ₃ H (mg)	T (°C)	Solvent	Yield (%) ^b	Time (min)
1	50	Reflux	H ₂ O	52	60
2	50	Reflux	EtOH	43	60
3	50	Reflux	CH ₃ CN	49	60
4	50	80	Solvent-free	93	60
5	50	90	Solvent-free	93	60
6	50	70	Solvent-free	78	60
7	60	80	Solvent-free	88	60
8	40	80	Solvent-free	69	60

a) Reaction conditions: 2-naphthol (1 mmol), dimedone (1 mmol), 4-chlorobenzaldehyde (1 mmol), ammonium chloride (1 mmol), solvent: 5 mL. b) Isolated yield.

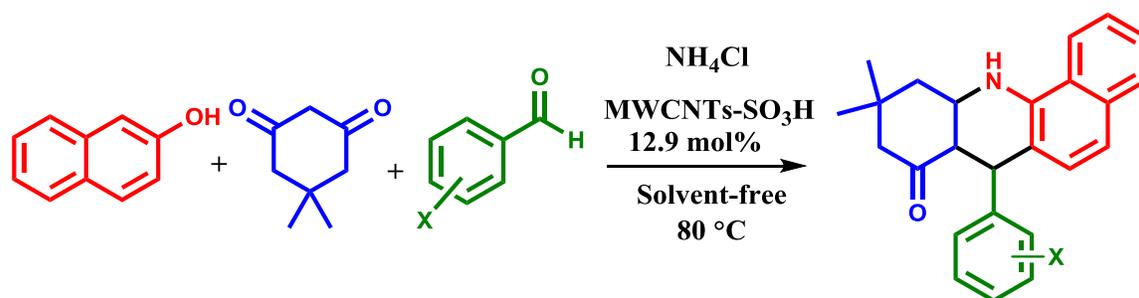
Table 3. Synthesis of tetrahydrobenzo[a]xanthene using MWCNTs-SO₃H under solvent-free conditions ^a

Entry	Aldehyde	Product	Yield (%)	Time (min)	TON	TOF (h ⁻¹)	M. P. (°C) [Ref.]
1	4-Br-C ₆ H ₄ -CHO		94	20	36.43	110.4	186-188 [185-187] [45]
2	2-Br-C ₆ H ₄ -CHO		96	18	37.21	124.0	169-171 [170-172] [45]
3	4-Cl-C ₆ H ₄ -CHO		94	21	36.43	104.09	182-183 [180-182] [46]
4	2-Cl-C ₆ H ₄ -CHO		90	23	34.88	91.32	178-180 [179-180] [46]
5	2,4-Cl ₂ -C ₆ H ₃ -CHO		98	16	37.98	142.8	181-183 [180-181] [45]

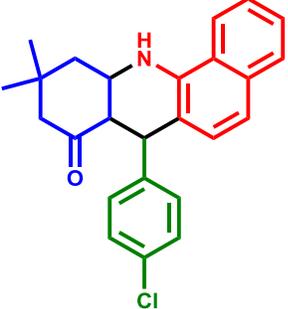
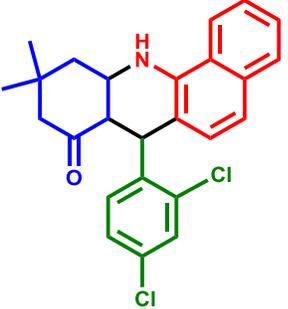
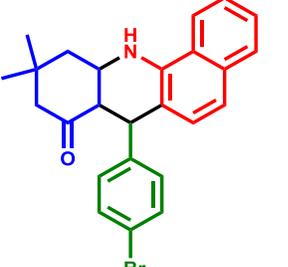
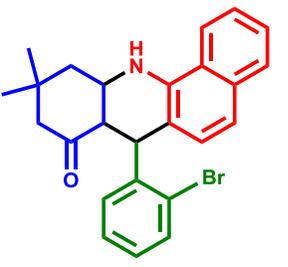
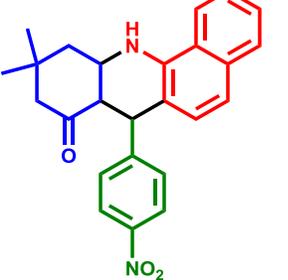
6	C ₆ H ₅ -CHO		90	25	34.88	83.9	150-152 [149-151] [46]
7	4-NO ₂ -C ₆ H ₄ -CHO		92	26	35.66	82.4	176-178 [175-178] [45]
8	4-OMe-C ₆ H ₄ -CHO		88	30	34.1	68.2	203-205 [204-205] [46]
9	4-OH-C ₆ H ₄ -CHO		83	36	32.2	53.6	224-227 [223-225] [46]

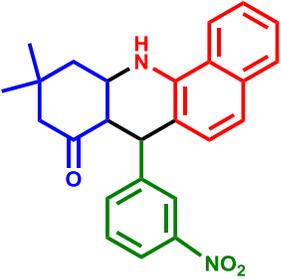
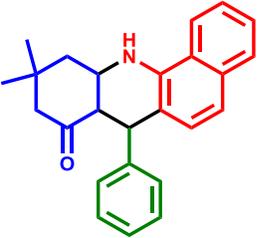
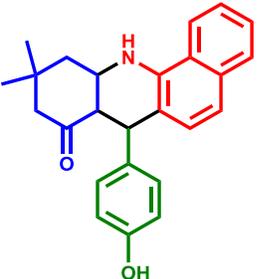
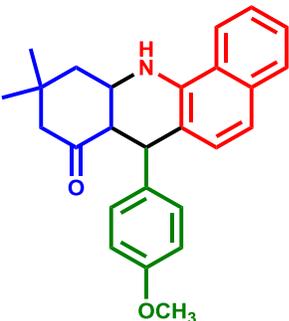
a) Reaction conditions: 2-naphthol (1 mmol), dimedone (1 mmol), aromatic aldehyde (1 mmol), T: 90 °C, MWCNTs-SO₃H (60 mg) (15.5 mol%), b) Isolated yield.

Table 4. Synthesis of tetrahydrobenzo[*a*]acridine using MWCNTs-SO₃H under solvent-free conditions ^a



Entry	Aldehyde	Product	Yield (%)	Time (min)	TON	TOF (h ⁻¹)	M. P. °C [Ref.]
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1	4-Cl-C ₆ H ₄ -CHO	 <p>The structure shows a blue six-membered ring with a carbonyl group (=O) and a nitrogen atom (NH) attached to a red naphthalene ring. A green benzene ring with a chlorine atom (Cl) at the para position is attached to the nitrogen atom.</p>	93	35	36.0	61.8	269-271 [268-270] [47]
2	2,4-Cl ₂ -C ₆ H ₃ -CHO	 <p>The structure is similar to the first one, but the green benzene ring has two chlorine atoms (Cl) at the 2 and 4 positions.</p>	96	30	37.2	74.4	286-288 [285-287] [47]
3	4-Br-C ₆ H ₄ -CHO	 <p>The structure is similar to the first one, but the green benzene ring has a bromine atom (Br) at the para position.</p>	91	38	35.3	55.7	277-279 [279-280] [47]
4	2-Br-C ₆ H ₄ -CHO	 <p>The structure is similar to the first one, but the green benzene ring has a bromine atom (Br) at the ortho position.</p>	90	40	34.9	52.1	267-269 [268-270] [47]
5	4-NO ₂ -C ₆ H ₄ -CHO	 <p>The structure is similar to the first one, but the green benzene ring has a nitro group (NO₂) at the para position.</p>	89	41	34.5	50.5	278-279 [279-280] [47]

6	3-NO ₂ -C ₆ H ₄ -CHO		87	45	33.7	45.0	272-274 [271-273] [47]
7	C ₆ H ₅ -CHO		85	50	32.9	39.5	262-264 [261-263] [47]
8	4-OH-C ₆ H ₄ -CHO		80	55	31.0	33.8	259-260 [262-264] [47]
9	4-OMe-C ₆ H ₄ -CHO		79	60	30.6	30.6	258-260 [259-261] [47]

a) Reaction conditions: 2-naphthol (1 mmol), dimedone (1 mmol), aromatic aldehyde (1 mmol), ammonium chloride (1 mmol) T: 80 °C, MWCNTs-SO₃H (50 mg) (12.9 mol%), b) Isolated yield.

In this part, the suggested mechanism for the synthesis of tetrahydrobenzo[*a*]xanthene and tetrahydrobenzo[*a*]acridine in the presence of MWCNTs-SO₃H is presented (**Scheme 3**). It is plausible that these multicomponent reactions could be started through the activation of aldehyde using MWCNTs-SO₃H followed by nucleophilic attack of dimedone molecules and then subsequent steps according to **Scheme 3**.

3.4. Reusability study

In the current study, the MWCNTs-SO₃H was evaluated in respect of recoverability and reusability. Therefore,

we selected two derivatives of tetrahydrobenzo[*a*]xanthene and tetrahydrobenzo[*a*]acridine for investigation of this item. **Fig. 6** shows that the prepared catalyst could be reused for 7 consequent runs without the significant loss of catalytic activity.

3.5. The Comparison Study

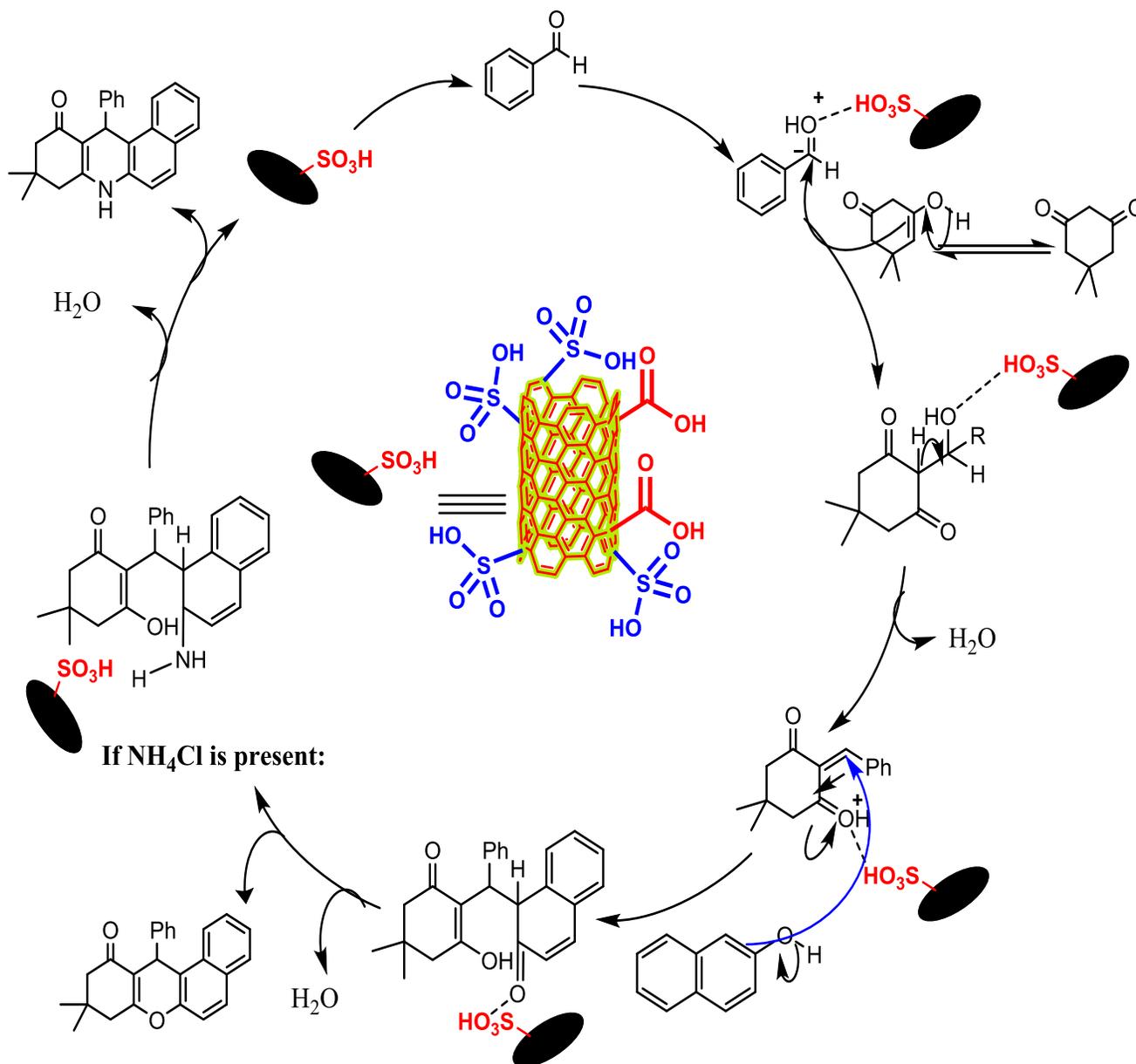
In order to show the efficiency of the MWCNTs-SO₃H for the synthesis of tetrahydrobenzo[*a*]xanthene and tetrahydrobenzo[*a*]acridine, we compared the current study with those using other catalytic cycles (**Tables 5 and 6**). The obtained result showed that the current study was fantastic in terms of catalytic amount, yield of the

reaction, time of the reaction, and sustainability chemistry compared with those other reported papers in the literatures.

4. Conclusions

In conclusion, an efficient heterogeneous catalyst namely MWCNTs-SO₃H was prepared through the chemical approach. The MWCNTs-SO₃H was characterized and identified using FE-SEM, TEM, FT-IR and Raman spectroscopy, and back acid-base titration. The total density of sulfonated groups on the

side wall of MWCNTs was calculated as 2.58 mmol.g⁻¹. This catalyst was suitable in the synthesis of tetrahydrobenzo[*a*]xanthene and tetrahydrobenzo[*a*]acridine derivatives using 15.5 mol% and 12.9 mol% of MWCNTs-SO₃H, respectively. Excellent yields, short reaction times, solvent-free conditions, and atomic economic are other worthwhile advantages of the present methodologies. In addition, the MWCNTs-SO₃H could be reused for seven continuous catalytic cycles without loss of its in catalytic activity.



Scheme 3. The suggested mechanism for the synthesis of tetrahydrobenzo[*a*]xanthene and tetrahydrobenzo[*a*]acridine in the presence of MWCNTs-SO₃H

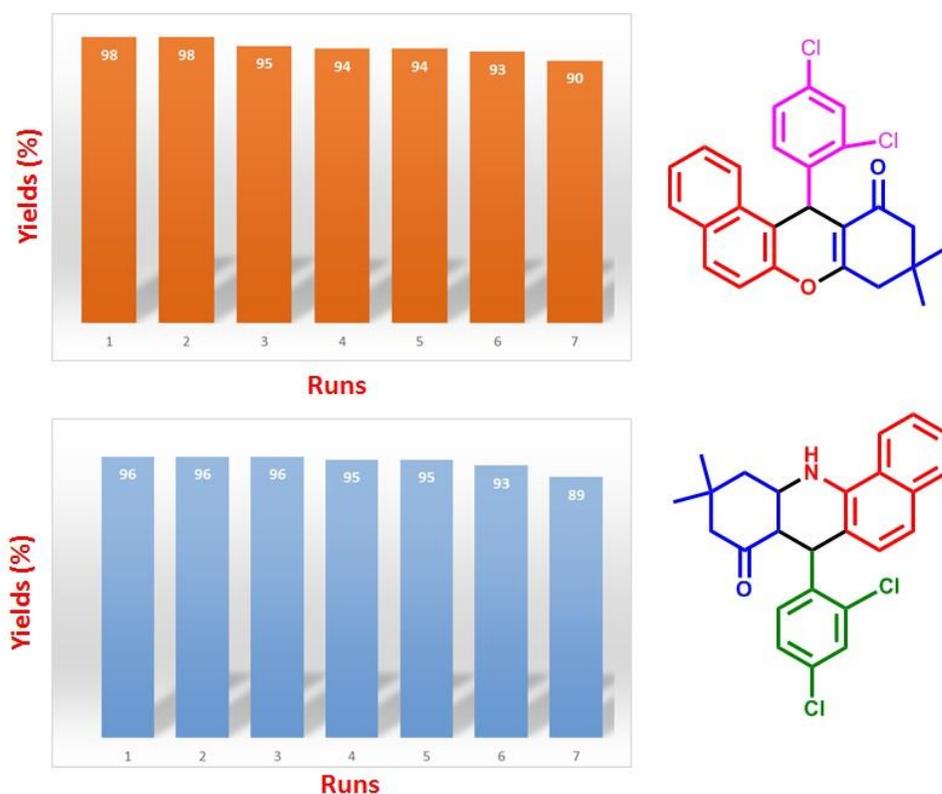
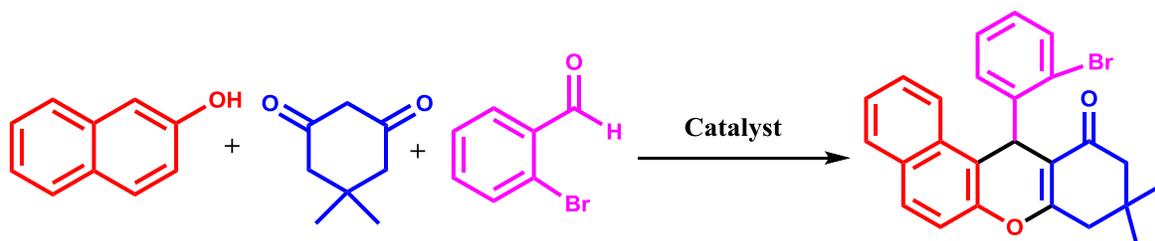
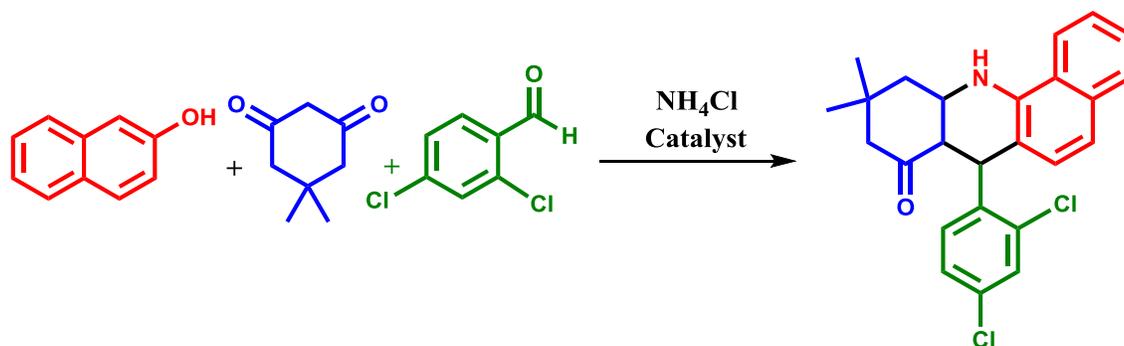


Fig. 6. The reusability and recoverability of MWCNTs-SO₃H

Table 5. The comparison study for the synthesis of tetrahydrobenzo[a]xanthene (Aldehyde: 2-bromobenzaldehyde)



Entry	Conditions	Yield (%)	Time (h)	Ref.
1	toluene-4-sulfonic acid, 120 °C	92	0.66	[31]
2	hydroxyapatite-encapsulated γ -Fe ₂ O ₃ -supported dual acidic nanocatalyst, Ethanol, 60 °C	91	0.18	[37]
3	(2,3,4,5,6-pentafluorophenyl)ammonium triflate, Toluene,	90	5	[48]
4	trityl chloride, no Solvent, 110 °C	89	0.916	[32]
5	titania-supported perchloric acid, 90 °C	89	0.45	[38]
6	MWCNTs-SO ₃ H, no Solvent, 90 °C	96	0.3	This work

Table 6. The comparison study for the synthesis of tetrahydrobenzo[*a*]acridine (Aldehyde: 2,4-dichlorobenzaldehyde)

Entry	Conditions	Yield (%)	Time (h)	Ref.
1	γ -Fe ₂ O ₃ @Si-(CH ₂) ₃ @melamine@butyl sulfonic acid nanoparticles, Ethanol	92	0.46	[49]
2	Fe ₃ O ₄ PS-Arg[HSO ₄] MNPs, Ethanol, reflux	93	0.36	[40]
3	tin(II) chloride dihydrate, Ethanol, 25 °C	89	1	[39]
4	H ₆ P ₂ W ₁₈ O ₆₂ *18H ₂ O, no Solvent, 120 °C	80	1.5	[41]
5	MWCNTs-SO ₃ H, no Solvent, 80 °C	96	0.5	This work

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