One-Pot Synthesis of Dihydro-1H-Indeno[1,2-b] Pyridines and Tetrahydrobenzo[b] Pyran Derivatives using a New and Efficient Nanocomposite Catalyst Based on *N*-Butylsulfonate-Functionalized MMWCNTs-D-NH<sub>2</sub>

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- **One-Pot Synthesis** of Dihydro-1H-Indeno[1,2-b] **Pyridines** and 1 Tetrahydrobenzo[b] Pyran Derivatives using a New and Efficient 2 Nanocomposite Catalyst Based on N-Butylsulfonate-Functionalized 3 MMWCNTs-D-NH<sub>2</sub> 4 5 Fatemeh Adibian,<sup>1</sup> Ali Reza Pourali,<sup>\*1</sup> Behrooz Maleki,<sup>\*2</sup> Mehdi Baghayeri,<sup>2</sup> Amirhassan 6 7 Amiri<sup>2</sup> <sup>1</sup>School of Chemistry, Damghan University, 36715-364, Damghan, Iran 8 9 pourali@du.ac.ir <sup>2</sup>Department of Chemistry, Hakim Sabzevari University, Sabzevar, 96179-76487, Iran 10 b.maleki@hsu.ac.ir 11 12 ABSTRACT 13 In this study, magnetic multi-walled carbon nanotubes were functionalized with 14 polyamidoamine (PAMAM) dendrimers and modified with butylsulfonate to afford 15 MMWCNTs-D-(CH<sub>2</sub>)<sub>4</sub>-SO<sub>3</sub>H. The synthesized nanocomposite (MMWCNTs-D-(CH<sub>2</sub>)<sub>4</sub>-16 SO<sub>3</sub>H) was characterized by various techniques such as Fourier transform infrared 17 spectroscopy (FT-IR), transmission electron microscopy (TEM), scanning electron 18
- microscopy (SEM), X-ray diffraction (XRD) and thermo-gravimetric analysis (TGA). This 19 nanocomposite catalyst effectively catalyzed four and three component reactions for the 20 synthesis of dihydro-1H-Indeno[1,2-b] pyridines and tetrahydrobenzo[b] pyrans (85-98%) 21 yield in 15-20 min and 80-98% yield in 12-30 min, respectively). In addition, the 22 magnetically recoverable catalyst could be easily recycled at least five times without 23 24 significant loss of catalytic activity. In the first step of synthesis of nanocomposite the  $Fe_3O_4$ nanoparticles were deposited on oxidized MWCNTs, then a modified PAMAM dendrimer 25 was used to bond to the carbonyl groups. Finally MMWCNTs-D-NH<sub>2</sub> functionalized with 26 1,4-butanesultone. 27
- 28

# 29 KEYWORDS

30 Dendrimer, Dihydro-1H-Indeno[1,2-b] pyridines, Magnetic Catalyst, MMWCNTs-D-(CH<sub>2</sub>)<sub>4</sub>-

- 31 SO<sub>3</sub>H nanocomposite, tetrahydrobenzo[b] pyrans.
- 32

# 1 **1. INTRODUCTION**

Acid catalysts play an important role in organic reactions. Sulfuric, hydrochloric, nitric and 2 phosphoric acids are the most commonly used acidic catalysts. However, these catalysts are 3 of homogeneous catalysts that have disadvantages such as corrosive properties and difficult 4 separation, also they are not reusable. This is while heterogeneous catalysts have several 5 advantages such as easy separation, recyclability, minimization of waste product and 6 toleration of a wide range of temperatures and pressures [1-3]. Therefore, the design and 7 application of novel heterogeneous catalysts has been well investigated in the last few 8 9 decades [4–5].

A very used method to preparation of heterogeneous catalysts is the stabilize of organic molecules containing active catalytic sites on the surface of insoluble solids such as inorganic materials, hybrid materials or synthetic organic polymers [6]. Over the past decade carbon nanotubes (CNTs) have been used in heterogeneous catalyst systems due to their uniform nano-structure, high mechanical strength, electrical properties, thermal stability and most importantly because of their high surface area which enhance significantly the contact between reactants and catalyst [7–11].

Nevertheless the use of CNTs as supports is restricted in industry due to difficulty in 17 18 separation and manipulation which increases the environmental pollution, as well as cost requirements. In addition, in many applications, external control on materials is also an 19 important point. That's why magnetic nanoparticles have been loaded on CNTs which leads 20 to the formation of magnetic CNTs [12]. Among them, magnetic nanoparticles containing 21 Fe<sub>3</sub>O<sub>4</sub> has attracted intense attention because of their high recycling capability, low 22 cytotoxicity, high commercially availability, easy handling, unique magnetic response and 23 chemically modifiable surface [13, 14]. 24

The poor solubility of CNTs in aqueous [15] and organic solutions makes them hard to 25 disperse. Dendrimers are a new category of artificial macromolecules, which have highly 26 branched, highly ordered and three-dimensional, architectures with very high degrees of 27 surface functionality and versatility. Their particular 3-D structure and unique single 28 dispersity make specific quality, so that they are usable in a wide range of applications such 29 as chemistry, nanomaterials, molecular diagnostics, and contaminated water purifiers. In 30 recent years studies on dendrimers have been considered in biochemical, catalytic, and 31 nanomaterial branches [16, 17]. 32

Sultone is cyclic ester of sulfonic acid -mostly with 5 or 6 members in the ring - that have SO<sub>2</sub>-O- group in the ring. A wide variety of nucleophiles can attack to the sulfone group of
the aryl sultone till sultone acts as a sulfoalkylating agent. Sultons are also effective acidic
catalysts in many organic reactions [18, 19].

Multi-component reactions (MCRs) involve three or more component reacting in a single 5 flask to make a new product. One example of an MCRs is synthesis of tetrahydrobenzo[b]-6 pyrans. These compounds are significant groups of heterocyclic compounds which have 7 noted pharmacological and biological properties such as antibacterial [20], antihypertensive, 8 9 hepatoprotective, cardiotonic [21], and antitumor [22]. These compounds generally synthesized via a three-component one-pot reaction in the presence various catalyst such as 10 amines [23], ionic liquids [24], hexadecyltrimethyl ammonium bromide (Fe<sub>3</sub>O<sub>4</sub>@D-NH-11 (CH<sub>2</sub>)<sub>4</sub>-SO<sub>3</sub>H) [25], [PVPH]HSO<sub>4</sub> [26], [Ch][OH] [27], Ru immobilized in zeolite beta [28], 12 ZnO-beta zeolite [29], hydroxy sodalite zeolite [30] and Zeolite Y [31]. 13

MCRs used for the synthesis of dihydro-1H-indeno[1,2-b] pyridines have also gained 14 remarkable notice in organic synthesis because dihydropyridines have a diversity of 15 biological activities and generate some drugs to treatment of hypertension such as 16 amlodipine, nicardipine and nifedipine. Generally, these compounds have been prepared 17 18 through the four-component cyclo-condensation of a 1,3-indanedione with an aldehyde, alkyl acetoacetate and ammonium acetate catalyzed by L-proline [32], Yb(OTf)<sub>3</sub> or Sc(OTf)<sub>3</sub> [33] 19 and 2,2,2-trifluoroethanol [34], But these methods have limitations such as low product 20 yields, several side products, long reaction times and tedious work-up. 21

Many applications of multifunctional nanomaterials in many fields such as biomedicine [35], 22 separation [36] and catalysis [37] have paid much attention to them. To production of 23 multifunctional nanomaterials, the integration of two or more functional components into a 24 single entity is used. A multitude of reactions have been catalyzed by CNTs or their 25 composites. For example hydrogenation of nitrobenzene and some substituted nitroarenes 26 was carried out in the presence of H<sub>2</sub>O<sub>2</sub> functionalized CNTs as catalyst [38]. Also the CNT-27 supported iridium-N-heterocyclic carbene materials were utilized in the heterogeneous 28 cyclohexanone hydrogen-transfer reduction reaction as catalyst [39]. 29

In continuation of our studies of organic reactions in the presence of catalysts [40-43] and the design of nanomagnetic heterogeneous catalysts for organic transformations [44-46]. In this work, we successfully synthesized and characterized a novel nano-magnetic carbon nanotubes based PAMAM composite as a recoverable heterogeneous catalyst and its

- 1 application for one-pot synthesis of tetrahydrobenzo[b] pyrans and dihydro-1H-indeno[1,2-b]
- 2 pyridines (Scheme 1).
- 3



SCHEME 1 Schematic shape for the synthesis of tetrahydrobenzo[b] pyrans (4) and
 dihydro-1H-Indeno[1,2-b] pyridines (7) in the presence of MMWCNTs-D-(CH<sub>2</sub>)<sub>4</sub>-SO<sub>3</sub>H
 nanocomposite as catalyst

# 9 2. EXPERIMENTAL

# 10 2.1. Materials and Method

Oxidized multi-walled carbon nanotubes (MWCNTs-COOH) with specific surface area of 25 11 m<sup>2</sup>.g<sup>-1</sup> and average tube inner diameter of 10 to 50 nm were purchased from Sigma-Aldrich. 12 Other chemicals of high purity were purchased from Merck as analytical reagent (AR) grade 13 and were used straight without extra purification. For the recording of TEM and SEM images 14 a Philips CM200 instrument and a S-4300, Hitachi, Japan scanning electron microscope were 15 respectively used and energy dispersive X-ray analysis (EDAX) attached to the SEM. 16 Thermal analysis was carried out by thermo gravimetric analysis (TGA) (Q50, TA 17 Instruments, USA). The Powder X-ray diffraction (XRD) measurements were carried out 18 19 using DMAX-2500, Rigaku X-ray diffractometer. IR spectra were recorded with potassium bromide pellets from 4000 to 400 cm<sup>-1</sup> at room temperature using a VERTEX 80V 20 21 spectrometer. A Bruker AVANCE 300 MHZ spectrometer was used for recording <sup>1</sup>H &<sup>13</sup>C NMR spectra at 400 MHz and 100 MHz in DMSO-d<sub>6</sub> using tetramethylsilane as internal 22 23 standard. A vibrating sample magnetometer (VSM) (JDM-13D magnetometer) was used to characterize the magnetic properties of nanocomposite. 24

25

# 26 **2.2. Preparation of catalyst**

27 2.2.1. Synthesis of MWCNTs-COOH/Fe<sub>3</sub>O<sub>4</sub> (MMWCNTs)

Magnetic MWCNTs-COOH (MWCNTs-COOH/Fe<sub>3</sub>O<sub>4</sub> or MMWCNTs) was synthesized via 1 modifying the method proposed by Chan et al [47]. 1.5 g FeCl<sub>3</sub>.6H<sub>2</sub>O and 0.8 g FeCl<sub>2</sub>.4H<sub>2</sub>O 2 were added to the mixture of 0.05 g MWCNTs-COOH in 200 mL distilled water which was 3 stirred at 50 °C. After one hour, about 20 mL NH<sub>3</sub> was drop wise added to the mixture to 4 obtain an alkaline environment that was monitored by litmus paper. The mixture was allowed 5 to cool. After precipitation of nanocomposites, an external magnet was used to separate 6 product. At the end, nanocomposite was washed several times with ethanol and acetone to get 7 8 pure product.

9

# 10 2.2.2. Functionalization of MWCNTs-COOH/Fe<sub>3</sub>O<sub>4</sub> with a modified PAMAM 11 dendrimer (MMWCNTs-D-NH<sub>2</sub>)

MMWCNTs-D-NH<sub>2</sub> were synthesized according to the reported procedure [4]. 0.5 g of 12 MMWCNTs was sonicated in 300 ml of deionized water for 30 min. In order to activate the 13 carbonyl group of MMWCNTs, 0.052 g of 1-ethyl-3- (3-dimethy lamino propyl) 14 carbodiimide hydrochloride (EDC.HCl) and 0.015 g of N-hydroxysuccinimide (NHS) were 15 added to the solution and stirred for 10 min. After this time, the dendrimer (5 ml) was added 16 dropwise and the reaction continued for 24 h at room temperature. The resulting sediment 17 18 was separated by an external magnetic field and dried in the oven vacuum at 70 °C after being washed several times with deionized water and ethanol. Scheme 3 schematically shows 19 the dendrimer connection to MMWCNTs. 20

21

# 22 2.2.3. Synthesis of *N*-butylsulfonate-functionalized MMWCNTs-D-NH<sub>2</sub>

1 g of MMWCNTs-D-NH<sub>2</sub> in 25 ml of toluene was dispersed by sonication. After 30 minutes, 0.7 g of 1,4-butanesultone was added to the reaction mixture and the reaction continued for 48 h at 100 °C under stirring. The product were collected via an external magnetic field and washed several times with toluene and acetone to eliminate the unreacted compounds and finally was dried in oven vacuum at 70 °C for 24 h [4].

28

# 29 2.3. General procedure for one-pot synthesis of tetrahydrobenzo[b] pyrans

A mixture of MMWCNTs-D-( $CH_2$ )<sub>4</sub>-SO<sub>3</sub>H nanocomposite (0.04 g), the aldehyde (1 mmol), 1,3-dicarbonyl compounds (1 mmol) and malononitrile (2 mmol) in EtOH (azeotropic composition of 96% ethanol containing 4% water, 3 ml) was stirred under reflux condition for the appropriate time (Table 2). After recognition of the end of the reaction by TLC

(hexane-ethyl acetate, 3:1), the catalyst was separated using an external magnet. The resulting
mixture was poured into crushed ice and the final product was obtained through filtration and
pure product was obtained by recrystallization from ethanol (96%). The products were
characterized by <sup>1</sup>H and <sup>13</sup>C NMR and IR spectroscopic data.

5

# 6 2.4. General procedure for one-pot synthesis of Dihydro-1H-Indeno[1,2-b] pyridines

A mixture of MMWCNTs-D-(CH<sub>2</sub>)<sub>4</sub>-SO<sub>3</sub>H nanocomposite (0.06 g), the aldehyde (1 mmol), 7 1,3-indandione (1 mmol), ethyl acetoacetate (1 mmol) and ammonium acetate (3 mmol) was 8 9 stirred at 120°C for the appropriate time (Table 2). The reaction progress was monitored by TLC (n-hexane:ethyl acetate, 2:1). After completion of the reaction we added 2 ml hot 10 ethanol to the reaction mixture and it was stirred for 2 minutes, then the catalyst was 11 separated using an external magnet. The resulting mixture was poured into crushed ice and 12 the final product was obtained through filtration and pure product was obtained by 13 recrystallization from ethanol (96%). The final products were identified by IR, <sup>1</sup>H and <sup>13</sup>C 14 NMR spectral data. 15

16

# 17 **3. RESULTS AND DISCUSSION**

# **3.1.** Characterizations of catalyst

Magnetic MWCNTs, that was synthesized via blending of MWCNTO with FeCl<sub>3</sub>.6H<sub>2</sub>O and FeCl<sub>2</sub>.4H<sub>2</sub>O in the presence of distilled water and NH<sub>3</sub>, functionalized with a modified PAMAM dendrimer in the presence of EDC and NHS (scheme 2). The MMWCNTs-D-(CH<sub>2</sub>)<sub>4</sub>-SO<sub>3</sub>H nanocomposite was synthesized by the heating of MWCNTs-D-NH<sub>2</sub> and 1,4-butanesultone at 100 °C under stirring (Scheme 3). The resulting product was characterized by various techniques including FT-IR, TEM, SEM, XRD and TGA.



- SCHEME 2 Preparation of MWCNTs-COOH/Fe $_3O_4$  and functionalization of it with a modified PAMAM dendrimer



2 SCHEME 3 Reaction of the terminal NH<sub>2</sub> of the MMWCNTs-D-NH<sub>2</sub> with 1,4-butanesultone

1

FT-IR spectra was used to assessment of the successful attachment of functional groups onto 4 5 the surface of the MWCNTs-COOH at each step of the catalyst synthesis (Fig. 1, 2). As shown in Fig. 1a, a broad peak between 3000 and 3600 cm<sup>-1</sup> corresponding to the vibration 6 of O-H groups and the sharp peak in the region 1635 cm<sup>-1</sup> is attributed to the stretching 7 vibrations of C=O of -COOH groups. Moreover, the peak at 1095 cm<sup>-1</sup> correspond to the C-8 9 OH of COOH, confirming the presence of carboxyl group within the structure of the MWCNTs-COOH. The FT-IR spectrum of MMWCNTs which is illustrated in Figure 1b 10 11 shows a specific peak at 582 cm<sup>-1</sup> relating to the stretching vibration of the Fe-O bond. In the FT-IR spectrum of MWCNTs-D-NH<sub>2</sub> (Figure 1c), C-H stretching of the alkyl group in the 12 modified PAMAM component are detected by the peak at 2925 and 2847 cm<sup>-1</sup>. The 13 characteristic peaks of MWCNTs-D-NH<sub>2</sub> at 1637, 1565 and 1425 cm<sup>-1</sup> are attributed to NH 14

- 1 deformation vibration of primary amine, the coupling of N-H bending and C-N stretching of
- 2 amide, respectively. The symmetric and asymmetric stretching vibrations of S=O assigned by
- 3 two significant peaks at 1052 and 1223  $cm^{-1}$ , respectively, confirm the reaction of
- 4 MWCNTs-D-NH<sub>2</sub> with 1,4-butanesultone (Fig. 2a). The FT-IR spectrum of MMWCNTs-D-
- 5 (CH<sub>2</sub>)<sub>4</sub>-SO<sub>3</sub>H nanocomposite after five runs of recyclability (Fig. 2b) revealed that recycling
- 6 process has not changed the locations of IR absorptions of the nanoparticles.









**FIGURE 2** FT-IR spectra of MMWCNTs-D-(CH<sub>2</sub>)<sub>4</sub>-SO<sub>3</sub>H (a) and MMWCNTs-D-(CH<sub>2</sub>)<sub>4</sub>-

 $3 \quad SO_3H$  nanocomposite after five runs of recyclability (b)

1 TEM analysis was used to evaluation the nanoparticles size distribution more accurately and the results have been shown in Fig. 2a,b with their size distribution histograms. All of the 2 samples have the size range of 5-21 nm with average diameter of about 10 nm. High 3 magnification TEM image of sample (Figure 2b) reveals the loading of nanoparticles on the 4 5 CNTs surface and demonstrates that magnetic nanoparticles have been well distributed and anchored on CNTs surface. Dendrimer shells can also be observed clearly with thickness of 6 7 2-5 nm. Figure 2c shows SEM images of prepared samples. Clearly, the CNTs surface has been covered uniformly by magnetic nanoparticles and there is almost no agglomeration. 8 9 Diameter difference between pure and covered CNTs is about 18 nm, indicating that nanoparticles have formed a shell with thickness of about 9 nm around the CNTs. The shell 10 thickness is close to nanoparticles average size (about 10 nm), in agreement with TEM 11 12 results.

13 14





FIGURE 3 Micrograph of MMWCNTs-D-(CH<sub>2</sub>)<sub>4</sub>-SO<sub>3</sub>H nanocomposite: TEM, 50 nm (a),
high magnification TEM, 20 nm (b) and SEM, 100 nm (c)

4

1

The XRD patterns of MMWCNTs -D-(CH<sub>2</sub>)<sub>4</sub>-SO<sub>3</sub>H nanocomposite was shown in Fig. 4. The sharp peaks at  $2\theta = 62.90^{\circ}$ , 57.37°, 53.25°, 43.07, 35.59° and 30.09° are corresponding peaks of (440), (511), (400), (422), (311) and (200) crystal planes, respectively, which are related to the crystalline nature of Fe<sub>3</sub>O<sub>4</sub> nanoparticles [48]. According to obtained XRD pattern and using Debye-Scherrer equation, the crystallite size of Fe<sub>3</sub>O<sub>4</sub> nanoparticles was estimated to be about 12 nm, which is in agreement with the size obtained via TEM and SEM analyses.

11



13 **FIGURE 4** XRD patterns of MMWCNTs-D-(CH<sub>2</sub>)<sub>4</sub>-SO<sub>3</sub>H nanocomposite

14

TGA curves of Fe<sub>3</sub>O<sub>4</sub>, MWCNTs-COOH/Fe<sub>3</sub>O<sub>4</sub>, MMWCNTs-D-NH<sub>2</sub> and MMWCNTs-D-1 (CH<sub>2</sub>)<sub>4</sub>-SO<sub>3</sub>H nanocomposites at the temperature range of 50 to 800 °C shown in Fig. 4. As 2 shown in Figure 4, Fe<sub>3</sub>O<sub>4</sub> nanoparticles showed good thermal stability and had not any 3 apparent weight loss (curve a). In the case of MWCNTs-COOH/Fe<sub>3</sub>O<sub>4</sub> (curve b), 10% weight 4 loss between 100 °C and 300 °C is due to loss of COOH groups on MWCNTs. TGA curve of 5 MMWCNTs-D-NH<sub>2</sub>, as shown in Figure 4c, exhibited an initial ascending behaviour as the 6 consequence of the buoyancy effect of the instrument. Similar ascending trends in TGA 7 curves have also been reported in several studies and explained in that this initial weight gain 8 9 for the sample and platinum pan stems from the differences in heat capacity and thermal conductivity of the purging gas [4]. 10% weight loss between 350 and 500°C is due to the 10 decomposition of the modified PAMAM dendrimer on MMWCNTs-D-NH<sub>2</sub>. TGA curve of 11 MMWCNTs-D-(CH<sub>2</sub>)<sub>4</sub>-SO<sub>3</sub>H shows three distinct steps of weight loss (curve d). The first 12 step (weight loss = ca. 8 wt %) between 100 °C and 300 °C is referred to the elimination of 13 COOH groups. The second step contains 10% weight loss between 350 and 500°C which was 14 assigned to the modified PAMAM dendrimer. The third step indicated a weight loss (ca. 15 15 16 wt %) between 550 and 700°C originated from the decomposition of n-butyl –SO<sub>3</sub>H group. Fig. 4d indicates that MMWCNTs-D-(CH<sub>2</sub>)<sub>4</sub>-SO<sub>3</sub>H is stable to 100 °C (only 5% weight loss 17 in this temperature range). 18



1 **FIGURE 5** TGA curves of  $Fe_3O_4$  (a), MMWCNTs (b), MWCNTs-D-NH<sub>2</sub> (c) and 2 MMWCNTs-D-(CH<sub>2</sub>)<sub>4</sub>-SO<sub>3</sub>H (d)

3

# 4 **3.2.** Catalytic activity studies

5 To study of the catalytic activity of MMWCNTs-D- $(CH_2)_4$ -SO<sub>3</sub>H nanocomposite, various 6 benzaldehyde (1 mmol) was reacted with malononitrile (2 mmol) and 1,3-dicarbonyl 7 compounds (1 mmol) in the presence of nanocomposite (0.04 g) as catalyst in reflux 8 conditions to produce tetrahydrobenzo[b] pyran derivatives (Scheme 1).

To define the optimal condition of reaction, the reaction of synthesis of 2-amino-7,7-9 dimethyl-5-oxo-4-phenyl-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (as model) was 10 carried out in polar (CH<sub>3</sub>CN, MeOH, H<sub>2</sub>O) and nonpolar (CH<sub>2</sub>Cl<sub>2</sub>, CCl<sub>4</sub>) solvents in the 11 12 presence of various amount of catalyst (0.03, 0.04 and 0.05 g) and at different temperatures (25, 50, 60, 70°C and reflux) (Table 1). Comparison of different solvents revealed that the 13 14 least time and the best efficiencies were obtained in the presence of ethanol (Table 1, entry 1). Then different amounts of catalysts were investigated in ethanol solvent (Table 1, entry 8 15 16 and 9). By increasing the reaction temperature an increasing trend was observed in the efficiencies. Finally the best result was obtained with 0.04 g of catalyst at reflux in the 17 presence of ethanol solvent (Table 1, entry 1). To investigate the effectiveness of the 18 presented catalytic system the model reaction was performed in the absence of catalyst and in 19 the presence of several nanocatalysts such as Fe<sub>3</sub>O<sub>4</sub>, MWCNTs-COOH, MMWCNTs-COOH 20 and MMWCNTs-D-NH<sub>2</sub> (Table 1, entry 14-19). The obtained values of time and yield 21 (presented in Table 1) showed that the nanomagnetic MMWCNTs-D-(CH<sub>2</sub>)<sub>4</sub>-SO<sub>3</sub>H has the 22 best catalytic efficiency by comparison with the other nanocatalysts. 23





			(min)	(%)
1	MMWCNTs-D-(CH <sub>2</sub> ) <sub>4</sub> -SO <sub>3</sub> H (0.04, 0.34 mol %)	EtOH/reflux	15	93
2	MMWCNTs-D-(CH <sub>2</sub> ) <sub>4</sub> -SO <sub>3</sub> H (0.04, 0.34 mol %)	CH <sub>3</sub> CN/ reflux	15	75
3	MMWCNTs-D-(CH <sub>2</sub> ) <sub>4</sub> -SO <sub>3</sub> H (0.04, 0.34 mol %)	CH <sub>3</sub> OH/ reflux	15	88
4	MMWCNTs-D-(CH <sub>2</sub> ) <sub>4</sub> -SO <sub>3</sub> H (0.04, 0.34 mol %)	H <sub>2</sub> O/ reflux	15	55
5	MMWCNTs-D-(CH <sub>2</sub> ) <sub>4</sub> -SO <sub>3</sub> H (0.04, 0.34 mol %)	CH <sub>2</sub> Cl <sub>2</sub> / reflux	30	45
6	MMWCNTs-D-(CH <sub>2</sub> ) <sub>4</sub> -SO <sub>3</sub> H (0.04, 0.34 mol %)	CCl <sub>4</sub> / reflux	30	40
7	MMWCNTs-D-(CH <sub>2</sub> ) <sub>4</sub> -SO <sub>3</sub> H (0.04, 0.34 mol %)	Solvent-free/80°C	20	80
8	MMWCNTs-D-(CH <sub>2</sub> ) <sub>4</sub> -SO <sub>3</sub> H (0.03, 0.25 mol %)	EtOH/reflux	20	86
9	MMWCNTs-D-(CH <sub>2</sub> ) <sub>4</sub> -SO <sub>3</sub> H (0.05, 0.40 mol %)	EtOH/reflux	15	92
10	MMWCNTs-D-(CH <sub>2</sub> ) <sub>4</sub> -SO <sub>3</sub> H (0.04, 0.34 mol %)	EtOH/25 °C	60	42
11	MMWCNTs-D-(CH <sub>2</sub> ) <sub>4</sub> -SO <sub>3</sub> H (0.04, 0.34 mol %)	EtOH/50 °C	30	65
12	MMWCNTs-D-(CH <sub>2</sub> ) <sub>4</sub> -SO <sub>3</sub> H (0.04, 0.34 mol %)	EtOH/60 °C	30	70
13	MMWCNTs-D-(CH <sub>2</sub> ) <sub>4</sub> -SO <sub>3</sub> H (0.04, 0.34 mol %)	EtOH/70 °C	30	84
14	Blank	EtOH/reflux	60	trace
15	Fe <sub>3</sub> O <sub>4</sub> (0.04)	EtOH/reflux	60	40
16	Fe <sub>3</sub> O <sub>4</sub> (0.04)	EtOH/reflux	15	trace
17	MWCNTs-COOH (0.04)	EtOH/reflux	30	51
18	MMWCNTs-COOH (0.04)	EtOH/reflux	25	54
19	MMWCNTs-D-NH $_2$ (0.04)	EtOH/reflux	15	70

<sup>a</sup> 1 mmol benzaldehyde (106 mg), 2 mmol malononitrile (132 mg) and 1 mmol 5,5-dimethylcyclohexane-1,3dione (140.2 mg).
<sup>b</sup> Isolated yield

4

5 To specify the extent of the reaction we react various aromatic aldehydes with 1,3-dicarbonyl 6 compounds and malononitriles to produce various tetrahydrobenzo[b] pyrans under refluxing 7 EtOH (Table 2, entry 1-18). According to the results it was found that electron-withdrawing 8 groups (such as nitrile, nitro and halides) on aldehyde especially on the meta and para 9 position provide better results (Table 2, entry 2- 8).

**TABLE 2** Preparation of tetrahydrobenzo[b] pyrans and Dihydro-1H-Indeno[1,2-b] pyridines

Entry	Product	Time	Yield	Mp (°C)	
		(min)	(%)	Found	Reported
1	Me Me Me	15	93	228-231	225–227 [24]
2		12	94	207-209	211–213 [26]
3	Me NO <sub>2</sub> NO <sub>2</sub> CN Me O NH <sub>2</sub>	12	98	177-180	177–178 [24]
4		12	98	224-227	224–226 [26]
5	Mé V NH <sub>2</sub> F CN Me O NH <sub>2</sub>	12	92	189-192	190-191 [42]











To determine the utility scope of our catalyst in organic reactions we also designed the 2 synthesis reaction of dihydro-1H-Indeno [1,2-b] pyridines using various aldehydes, 1,3-3 indandione, ethyl acetoacetate and ammonium acetate in the presence of MMWCNTs-D-4 5 (CH<sub>2</sub>)<sub>4</sub>-SO<sub>3</sub>H nanocomposite as catalyst at 120 °C (Scheme 1). We tried again to use different kinds of aldehydes containing electron-withdrawing and electron donating groups (Table 2, 6 entry 19-29). Again it was found that aldehydes containing electron withdrawing groups led 7 to a higher percentage of the product. Also the results showed that the reaction efficiency 8 with the aldehyde containing a group in the ortho position was slightly less than aldehyde 9 10 containing the same group in the para position; this can be attributed to steric hindrance.

Here too the conditions were optimized at first. The optimization results for the reaction of synthesis of ethyl 5-oxo-4-phenyl-4,5-dihydro-1H-indeno[1,2-b]pyridine-3-carboxylate (as model reaction) are shown in Table 3. Among different catalyst values and different temperature and solvent conditions the best results were achieved in the presence of 0.06 g of catalyst at 120 °C under solvent-free conditions (Table 3, entry 1).

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TABLE 3 Optimization of Reaction Conditions for synthesis of dihydro-1H-indeno[1,2-b] 1

2 pyridines<sup>a</sup>



Entry	Amount of Catalyst (g, mol%)	Conditions	Time (min)	Yield <sup>b</sup> (%)
1	MMWCNTs-D-(CH <sub>2</sub> ) <sub>4</sub> -SO <sub>3</sub> H (0.06, 0.5 mol %)	Solvent-free/120 °C	20	92
2	MMWCNTs-D-(CH <sub>2</sub> ) <sub>4</sub> -SO <sub>3</sub> H (0.06, 0.5 mol %)	EtOH/reflux	60	48
3	MMWCNTs-D-(CH <sub>2</sub> ) <sub>4</sub> -SO <sub>3</sub> H (0.06, 0.5 mol %)	Toluene/reflux	60	30
4	MMWCNTs-D-(CH <sub>2</sub> ) <sub>4</sub> -SO <sub>3</sub> H (0.06, 0.5 mol %)	water/reflux	60	35
5	MMWCNTs-D-(CH <sub>2</sub> ) <sub>4</sub> -SO <sub>3</sub> H (0.06, 0.5 mol %)	Dichloromethane/reflux	60	25
6	MMWCNTs-D-(CH <sub>2</sub> ) <sub>4</sub> -SO <sub>3</sub> H (0.06, 0.5 mol %)	Acetonitrile/reflux	60	39
7	MMWCNTs-D-(CH <sub>2</sub> ) <sub>4</sub> -SO <sub>3</sub> H (0.04, 0.34 mol %)	Solvent-free/120 °C	20	72
8	MMWCNTs-D-(CH <sub>2</sub> ) <sub>4</sub> -SO <sub>3</sub> H (0.08, 0.7 mol %)	Solvent-free/120 °C	20	92
9	MMWCNTs-D-(CH <sub>2</sub> ) <sub>4</sub> -SO <sub>3</sub> H (0.06, 0.5 mol %)	Solvent-free/110 °C	20	86
10	MMWCNTs-D-(CH <sub>2</sub> ) <sub>4</sub> -SO <sub>3</sub> H (0.06, 0.5 mol %)	Solvent-free/130 °C	20	91
11	Blank	Solvent-free/120 °C	60	trace
12	Fe <sub>3</sub> O <sub>4</sub> (0.06)	Solvent-free/120 °C	60	30
13	MWCNTs-COOH (0.06)	Solvent-free/120 °C	35	52
14	MMWCNTs-COOH (0.06)	Solvent-free/120 °C	25	63
15	MMWCNTs-D-NH <sub>2</sub> (0.06)	Solvent-free/120 °C	25	68

5 <sup>a</sup> 1 mmol benzaldehyde (106 mg), 1 mmol 1,3-indandione (146.14 mg), 1 mmol ethyl acetoacetate (130.14 mg) 6 7 and 3 mmol ammonium acetate (231.3 mg)

<sup>b</sup> Isolated yield

1 Hot filtration test was carried out to make sure no leaching of catalyst during the course of reactions. For this purpose synthesis of 2-amino-7,7-dimethyl-5-oxo-4-phenyl-5,6,7,8-2 tetrahydro-4H-chromene-3-carbonitrile (as model reaction) was carried out under the 3 optimized condition for 7 min. At this stage, the catalyst was separated from the reaction 4 mixture by use of an external magnetic field (1.4 T field strength). Then, the reaction 5 proceeded for another 8 min under same condition. No increase in the amount of the product 6 7 was observed, which suggests that the leaching of glutathione is low and the prepared catalyst is stable. This result was confirmed by recyclability investigations of the catalyst. 8

9 We compared the gained results for the catalytic activity of MMWCNTs-D- $(CH_2)_4$ -SO<sub>3</sub>H 10 with the reported results for other catalysts especially heterogeneous acid catalysts (e.g., 11 zeolites) in the synthesis of dihydro-1H-Indeno[1,2-b] pyridines and tetrahydrobenzo[b] 12 pyrans to show the efficiency of our synthesized catalyst (Table 4). For a more obvious 13 quantitative comparison, the turnover frequency (TOF) of all catalysts were measured. TOF 14 is one of the criteria for selecting a catalyst that the higher the TOF value, the better the 15 catalyst. The TOF was obtained from the following equation:

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$$TOF = \frac{\frac{yield \%}{time (h)}}{amount of catalyst (mol\%)}$$

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Comparison of the TOFs in Table 4 showed that our synthetic catalyst is one of the bestcatalysts for selective reactions.

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**TABLE 4** Comparison of MMWCNTs-D- $(CH_2)_4$ -SO<sub>3</sub>H with some reported catalysts in the

23 synthesis of tetrahydrobenzo[b]pyrans and dihydro-1H-indeno[1,2-b]pyridines

Compound	Conditions	Time	Yield	TOF	Ref.
		(min)	(%)	(h <sup>-1</sup> )	
	NH <sub>4</sub> H <sub>2</sub> PO <sub>4</sub> /Al <sub>2</sub> O <sub>3</sub> (0.03	15	86	_a	[42]
	g)/EtOH/reflux				
	[PVPH]HSO <sub>4</sub> (3.5 mol%)	10	96	165	[26]
	/H <sub>2</sub> O:EtOH (7:3), 80°C				
	[DABCO-PDO][CH <sub>3</sub> COO](1	15	95	38	[24]

Journal Pre-proofs						
Me Me NH <sub>2</sub>	0 mol%)/H <sub>2</sub> O, 80°C					
	NH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> OH (10 mol%)/	15	97	39	[23]	
	H <sub>2</sub> O, rt					
	[Ch][OH] (10	120	96	4.8	[27]	
	mol%)/H <sub>2</sub> O/reflux					
	MGO-D-NH-(CH <sub>2</sub> ) <sub>4</sub> -SO <sub>3</sub> H	5	95	9495	[4]	
	(0.12 mol%)/H2O-EtOH					
	(4:1), rt					
	Ru immobilized in zeolite	35	85	6	[28]	
	beta (25 mol%)/EtOH/reflux					
	ZnO-beta zeolite (0.1	35	95	_a	[29]	
	g)/EtOH/reflux					
	Hydroxy sodalite zeolite (0.5	180	96	_ <sup>a</sup>	[30]	
	g)/solvent-free/rt					
	Zeolite Y (0.14	30	64	_a	[31]	
	g)/EtOH/reflux					
	MMWCNTs-D-(CH <sub>2</sub> ) <sub>4</sub> -SO <sub>3</sub> H	15	93	1094	this	
	(0.34 mol%)/EtOH/reflux				work	
OMe	L-proline (10	60	95	9.5	[32]	
° C	mol%)/water/reflux					
OEt	Yb(OTf) <sub>3</sub> (5 mol%) /EtOH/us,	45	92	25	[34]	
<->	rt					
	HNPBS (2.5 mol%)/solvent-	10	93	223	[46]	
	free/rt					
	MMWCNTs-D-(CH <sub>2</sub> ) <sub>4</sub> -SO <sub>3</sub> H	15	95	760	this	
	(0.5 mol%)/solvent-free/120				work	
	°C					

- <sup>a</sup>The amount mol% of catalyst was not available in the paper.
- 2

- Our proposed mechanism for one-pot synthesis of tetrahydrobenzo[b] pyrans and dihydro 1H-indeno[1,2-b] pyridines in the presence of MMWCNTs-D-(CH<sub>2</sub>)<sub>4</sub>-SO<sub>3</sub>H nanocomposite
- 5 as catalyst were given in Scheme 4. In both reactions it can be suggested that in the first step

- the Knoevenagel condensation reaction was performed between benzaldehyde and
   malononitrile (or diketone in second reaction) activated with catalyst.
- 3



SCHEME 4 Proposed mechanisms for one-pot synthesis of tetrahydrobenzo[b] pyrans and
 dihydro-1H-Indeno[1,2-b] pyridines

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In accordance with the reaction mechanism (Scheme 4), activation of the carbonyl group by 8 acidic protons produced from MMWCNTs-D- $(CH_2)_4$ -SO<sub>3</sub>H is the major driver of the reaction 9 progress. Based on the comparison of the carbonyl group activated by MMWCNTs-D-10 (CH<sub>2</sub>)<sub>4</sub>-SO<sub>3</sub>H and MMWCNTs-D-NH<sub>2</sub> (Fig. 6) it is found that the reaction is more likely to 11 progress through the formation of intermediate A (entry 1 vs. entry 19 in Table 1 and entry 1 12 vs. entry 15 in Table 3), which may be explained by more steric hindrance of basic groups in 13 14 MMWCNTs-D-NH<sub>2</sub> than acid groups in MMWCNTs-D-(CH<sub>2</sub>)<sub>4</sub>-SO<sub>3</sub>H, because amino group is part of a bulk dendrimer, while sulphonic group is sufficiently distant from the bulk 15

dendrimer due to the presence of  $-(CH_2)_4$ . Resende Filho et al. [49] also achieved similar results for Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-nN catalyst when the distance (n) between the terminal amino group and the nanoparticle surface was increased.

- 4  $MMWCNTs-D-(CH_2)_4-SO3H$   $\downarrow H^+ \qquad \oplus \downarrow H$   $\downarrow H^- \qquad \downarrow H^- \qquad$
- 8 Also, in other experimental method, to determine the catalytic performance differences of NH<sub>2</sub> terminated CNTs and SO<sub>3</sub>H terminated CNTs, we performed the tetrahydrobenzo [b] 9 10 pyran reactions in Table 2 in the presence of MMWCNTs-D-NH<sub>2</sub> as catalyst. The experiments were repeated three times and the average of yields were reported (Table 5). As 11 can be seen in the Table 5, the yields in the presence of NH<sub>2</sub> terminated CNTs were between 12 13 22-32% lower than those in the presence of SO<sub>3</sub>H terminated CNTs. This significant difference is a confirmation of the correct choice of MMWCNTs-D-(CH<sub>2</sub>)<sub>4</sub>-SO<sub>3</sub>H as the 14 15 catalyst.
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TABLE 5 Comparison one-pot synthesis of tetrahydrobenzo[b] pyrans with MMWCNTs-D (CH<sub>2</sub>)<sub>4</sub>-SO<sub>3</sub>H and MMWCNTs-D-NH<sub>2</sub>









<sup>a</sup>The average of yields after three times.

Since the reusability of catalyst is of great importance in the industry, the reusability of MMWCNTs-D-(CH<sub>2</sub>)<sub>4</sub>-SO<sub>3</sub>H nanocomposite was studied in the reaction of synthesis of ethyl 5-oxo-4-phenyl-4,5-dihydro-1H-indeno[1,2-b]pyridine-3-carboxylate and 2-amino-7,7dimethyl-5-oxo-4-phenyl-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile as model reactions (Fig. 7). The catalyst was separated using an external magnet and then dried at 70 °C for 4 h. It was then reused in the same reaction for five successive runs.



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9 **FIGURE 7** Recyclability of MMWCNTs-D-(CH<sub>2</sub>)<sub>4</sub>-SO<sub>3</sub>H nanocomposite

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To confirm that  $Fe_3O_4$  is stable and no convert to  $Fe_2O_3$  after each runs of recyclability we compared the XRD of fresh and reused MMWCNTs-D-(CH<sub>2</sub>)<sub>4</sub>-SO<sub>3</sub>H after three and five runs with XRD of standard  $Fe_2O_3$  and  $Fe_3O_4$  (Fig. 8). The results shows XRD of fresh MMWCNTs-D-(CH<sub>2</sub>)<sub>4</sub>-SO<sub>3</sub>H is similar to XRD of standard  $Fe_3O_4$  and also there is almost no change after third performance run compared to peaks of standard  $Fe_3O_4$  in terms of position

and intensity of peaks. In the case of XRD of reused MMWCNTs-D- $(CH_2)_4$ -SO<sub>3</sub>H after five runs a small amount of mismatch in peak intensity was observed compared to peaks of standard Fe<sub>3</sub>O<sub>4</sub>.





1 SO<sub>3</sub>H nanocomposite (c), MMWCNTs-D-(CH<sub>2</sub>)<sub>4</sub>-SO<sub>3</sub>H nanocomposite after three runs of 2 recyclability (d) and MMWCNTs-D-(CH<sub>2</sub>)<sub>4</sub>-SO<sub>3</sub>H nanocomposite after five runs of 3 recyclability (e)

4

Also we used the method of active-site titration as a standard method for evaluation of the 5 catalytic active sites of the synthesized MMWCNTs-D-(CH<sub>2</sub>)<sub>4</sub>-SO<sub>3</sub>H. For this purpose 6 adequate amount of fresh catalyst (200 mg) was mixed and stirred with 30 ml solution of 7 NaCl (2 M) for 12 h at ambient temperature. Calculated pH was determined to be about 2.4 8 which is equivalent to 0.085 mmol  $g^{-1}$  of -SO<sub>3</sub>H functional groups in the structure of the 9 proposed catalyst. Furthermore, the active sites for the catalyst after fifth performance run 10 11 was appraised and the results shows pH of active site is about of 2.7 that proves the catalyst is recyclable at experimental conditions. 12

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# 14 CONCLUSION

In conclusion, we have presented a novel, green and highly effective heterogeneous reusable nanocatalyst based on magnetic multi-walled carbon nanotubes which functionalized with polyamidoamine (PAMAM) dendrimers for the one-pot multi-component synthesis of tetrahydrobenzo[b] pyrans and dihydro-1H-indeno[1,2-b] pyridines. This methodology suggests several potential advantages including short reaction times, easy work up, low waste, excellent yields, easy for separation.

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# **Graphical Abstract:** 1 toluene 100° C/ 48h .OH o o NH(CH<sub>2</sub>)<sub>4</sub>SO<sub>3</sub>H 2 3

# **1** Graphical Abstract:

- 2 One-Pot Synthesis of Dihydro-1H-Indeno[1,2-b] Pyridines and Tetrahydrobenzo[b]
- Pyran Derivatives using a New and Efficient Nanocomposite Catalyst Based on
   *N*-Butylsulfonate-Functionalized MMWCNTS-D-NH<sub>2</sub>
- Fatemeh Adibian,<sup>1</sup> Ali Reza Pourali,<sup>\*1</sup> Behrooz Maleki,<sup>\*2</sup> Mehdi Baghayeri,<sup>2</sup> Amirhassan
   Amiri<sup>2</sup>
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For the first time, MMWCNTs-D-SO<sub>3</sub>H nanocomposite was synthesized by
functionalization of magnetic MWCNTs with a modified PAMAM dendrimer and then with
1,4-butanesultone.

• High catalytic ability of nanocomposite as well as recycling of catalyst.

# • One-pot synthesis of dihydro-1H-Indeno[1,2-b] pyridines and tetrahydrobenzo[b] pyrans

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