FULL PAPER

Mn(III)-pentadentate Schiff base complex supported on multiwalled carbon nanotubes as a green, mild and heterogeneous catalyst for the synthesis of tetrahydrobenzo[*b*]pyrans via tandem Knoevenagel-Michael cyclocondensation reaction

Jamshid Rakhtshah | Sadegh Salehzadeh | Mohammad Ali Zolfigol | Saeed Baghery

Faculty of Chemistry, Bu-Ali Sina University, Hamedan 6517838683, Iran

Correspondence

Sadegh Salehzadeh, Faculty of Chemistry, Bu-Ali Sina University, Hamedan 6517838683, Iran. Email: saleh@basu.ac.ir; ssalehzadeh@gmail.com Mn(III)-pentadentate Schiff base complex supported on multi-walled carbon nanotubes as a recyclable and reusable, green and nano-heterogeneous catalyst was designed and fully characterized using infrared spectroscopy, X-ray diffraction, scanning electron microscopy, energy-dispersive X-ray spectroscopy, inductively coupled plasma mass spectrometry, elemental analysis and thermogravimetric analysis. A facile, eco-friendly, mild and green procedure was developed for the one-pot three-component synthesis of tetrahydrobenzo[*b*]pyrans via tandem Knoevenagel–Michael cyclocondensation reactions between aromatic aldehydes, 1,3-diones and malononitrile using a catalytic amount of Mn(III)-pentadentate Schiff base complex supported on MWCNTs as an efficient recyclable heterogeneous catalyst under solvent-free conditions at room temperature. This process has the advantages of easy availability, stability, recyclability and eco-friendliness of the catalyst, short reaction times, high to excellent yields and simple work-up procedure.

KEYWORDS

azo-azomethine, manganese(III) complex, solvent-free, supported complex, tetrahydrobenzo[*b*]pyrans

1 | INTRODUCTION

Multi-component reactions (MCRs) are those in which three or more substrates react together to provide products in one pot under appropriate reaction conditions. MCRs suggest the benefit of ease and synthetic efficacy over conventional chemical reactions. MCRs have the further benefits of synthetic convergence, selectivity and atom-economy.^[1–3]

As a novel type of nanomaterial, carbon nanotubes (CNTs) have attracted much attention during the past two decades.^[4,5] Multi-walled CNTs (MWCNTs) are composed of a series of concentric single-walled CNTs with an intertube distance of 0.34 nm.^[6,7] Since CNTs are insoluble in most solvents, these materials can be used as catalyst supports.^[8–21] A good approach that has opened up a large number of research opportunities and potential applications

MWCNTs is chemical functionalization. in The functionalization of CNTs may expand the range of their potential applications.^[22] Metal complexation has been a recent choice for functionalization of CNTs and fabrication of CNTs/inorganic hybrid materials. Although a few examples have been demonstrated for complexation,^[23] this field has not been fully investigated. A general procedure for surface functionalization is to affect the reaction of surface hydroxyl groups with organosilane coupling reagents, such as tri(alkoxy)organosilanes or trichloroorganosilanes. The nature of the linker can also influence the enantioselectivity, stability and performance of a supported catalyst.^[24]

To the best of our knowledge, homogeneous catalysts of transition metals are often more difficult to prepare and expensive to purchase. Also, some industrial problems such as deposition on reactor walls and difficulty in recovery and separation of catalysts from reaction products are associated with homogeneous catalysts. One way to overcome these disadvantages is the immobilization of homogeneous catalysts on solid supports.^[20] Tetrahydrobenzo[b]pyran derivatives have lately been the subject of much consideration as a significant class of heterocycles having useful biological and pharmacological activities, such as anticancer, anticoagulant, diuretic and anti-anaphylactic activities.[25-30] Correspondingly, they have a broad range of application as cognitive enhancers, for the therapy of neurodegenerative illnesses, including Alzheimer's disease, Down's syndrome, Parkinson's disease and AIDS-associated dementia, as well as for the therapy of schizophrenia.^[31] Recently, many procedures have been described for the synthesis of 4*H*-benzo[b] pyran derivatives via one-pot three-component tandem Knoevenagel-Michael cyclocondensation involving the use of several media or catalysts such as ionic liquids,^[32-35] $Fe_{3}O_{4}@SiO_{2}@TiO_{2}$,^[36] SO₄²⁻@MCM-41,^[37] KF-alumina,^[38] Fe₃O₄@MWCNTs,^[39] tetrabutylammonium bromide^[40] and Zn(Phen)₂Cl₂.^[41]

Different approaches have been used for immobilization of complexes on CNTs to prepare heterogeneous catalysts.^[15–22] Among the synthesized catalysts are a few examples of Schiff base complexes. Baleizao and co-workers have reported efficient cyanosilylation of aldehydes catalysed by vanadyl salen complexes covalently anchored to singlewalled CNTs.^[16] Also, Salavati-Niasari *et al.* have synthesized a novel hybrid material composed of MWCNTs and cobalt(II) salen complex and investigated its catalytic activity in liquid-phase epoxidation of cyclohexene by air.^[42]

Increasing demand for eco-friendly, green and mild methods using heterogeneous recyclable and reusable catalysts encouraged us to improve a safe alternative process for the synthesis of tetrahydrobenzo[b]pyrans via tandem Knoevenagel-Michael cyclocondensation reactions in the presence of a recyclable and reusable heterogeneous catalyst under solvent-free conditions at room temperature. With this aim and following our studies on design and synthesis of Schiff base complexes,^[43,44] complex supported on MWCNTs^[45] and pyran derivatives,^[46,47] in the work reported here we decided to immobilize Mn(III)-pentadentate Schiff base complex on the surface of MWCNTs using (3-chloropropyl)trimethoxysilane as a Si linker and spacer. The designed MWCNT@Si-H2azosaldien system could be a novel and simple approach for loading metals in a variety of coordination modes (Scheme 1).

2 | RESULTS AND DISCUSSION

The reactions leading to the nanomaterial of Mn(III)– pentadentate Schiff base complex supported on MWCNTs are summarized in Scheme 2. This synthesis was carried out as described in Section 2.



SCHEME 1 Synthesis of tetrahydrobenzo[*b*]pyrans using Mn(III)– pentadentate Schiff base complex supported on MWCNTs

2.1 | Characterization of Mn(III)-pentadentate schiff base complex supported on MWCNTs as heterogeneous catalyst

The surface structure of the materials was confirmed using Fourier transform infrared (FT-IR) spectroscopy. Figure 1 shows the FT-IR spectra obtained for HOOC@MWCNTs, Cpm@MWCNTs, MWCNTs@Si-H₂azosaldien and Mn(III)-pentadentate Schiff base complex@MWCNTs. The FT-IR spectrum of HOOC@MWCNTs (Figure 1a) shows a strong band at 1709.14 cm⁻¹ and a weaker band at 1228.58 cm⁻¹ attributed to C=O and C-OH groups in oxidized MWCNTs, respectively, as well as a broad band at about 3440-3480 cm⁻¹ assigned to O-H stretching vibrations which are not observed in the spectrum of pristine MWCNTs. As can be seen in Figure 1(b), in the FT-IR spectrum of Cpm@MWCNTs there is a broad band at about



SCHEME 2 Sequence of stages in preparation of Mn(III)-pentadentate Schiff base complex supported on MWCNTs



FIGURE 1 FT-IR spectra of (a) HOOC@MWCNTs, (b) Cpm@MWCNTs, (c) MWCNTs@Si-H₂azosaldien and (d) Mn(III)-pentadentate Schiff base complex@MWCNTs

1000–1100 cm^{-1} assigned to Si–O stretching vibrations which is not present in the spectra of pristine MWCNTs and/or HOOC@MWCNTs. The presence of anchored propyl chain is confirmed from C-H stretching vibrations appearing at about 2927 cm^{-1} . The above bands suggest that during the anchoring of CPTMS, a condensation reaction occurs between the OH surface groups of the oxidized MWCNTs and methoxy groups of CPTMS to form the stable covalent Si-O-C linkage, leading to the attachment of chloropropyl groups on the surface of MWCNTs. The most informative spectroscopic data to support the covalent anchoring of the [Mn(H₂azosaliden)] complex on the modified MWCNTs were obtained from a comparison of the set of FT-IR data corresponding to Cpm@MWCNTs, MWCNTs-Si-H₂azosaldien and Mn(III)-pentadentate Schiff base complex@MWCNTs. The appearance of azomethine peak at 1642 cm^{-1} in Figure 1(c) suggests binding of the Schiff base to the MWCNTs through a covalent bond. This sharp band in the spectrum of Mn(III)-pentadentate Schiff base complex@MWCNTs (Figure 1d) shifts to a lower wavenumber, and appears at 1622 cm⁻¹, which indicates the involvement of the azomethine nitrogen in coordination. It should be noted that in the FT-IR spectra of neat Schiff base H₂azosaliden and its neat metal complex the vibrational stretching frequency of C=N bond appears at 1647 and 1622 cm^{-1} , respectively (Figs 110S and 111S). Thus the attachment of H₂azosaliden and/or its Mn(III) complex to the MWCNTs has a small effect on stretching frequency of imine bond.

Figure 2 shows the X-ray diffraction (XRD) patterns of MWCNTs and Mn(III)–pentadentate Schiff base complex supported on MWCNTs. The XRD pattern of MWCNTs bearing the Mn(III) complex is similar to that of MWCNTs. This indicates that the crystallinity and morphology of MWCNTs are preserved during the grafting process. The XRD pattern

of MWCNTs is similar to that of highly oriented pyrolytic graphite.^[42] The MWCNT pattern shows typical peaks of (002), (110) and (400) at $2\theta = 26^{\circ}$, 43° and 53° , respectively. Indeed, the crystalline structure of the matrix is only slightly affected due to the reaction of the MWCNTs with acid.

The structural and morphology study of the nanomaterial was conducted using field emission scanning electron microscopy (SEM). A representative image of immobilized complex supported on MWCNTs is shown in Figure 3. From the SEM micrograph it can be concluded that there is a difference between the nanotube structure for pristine MWCNTs^[48] and immobilized complex supported on MWCNTs. The smooth surface of pristine MWCNTs has been altered to a rough surface after the immobilization process, which can be associated with the complex moieties attached to the nanotube surface. From the SEM micrograph of immobilized complex supported on MWCNTs, it can be seen that there is no structural damage to the MWCNTs. This is probably due to the mild conditions of aqueous acid solution used for MWCNT functionalization.[49]

The functionalization process of the MWCNTs with the Schiff base and the formation of its complex were also confirmed by the presence of C, O, N, Cl, Si and the



FIGURE 2 XRD patterns of (a) MWCNTs and (b) Mn(III)–pentadentate Schiff base complex@MWCNTs

4 of 10 WILEY-Organometallic Chemistry



FIGURE 3 SEM image of Mn(III)-pentadentate Schiff base complex@MWCNTs

corresponding Mn signals in the energy-dispersive X-ray spectroscopy (EDX) pattern of the nanocatalyst. The presence of the manganese is confirmed by inductively coupled plasma (ICP) analysis as well as the EDX results as can be clearly seen in Figure 4.

The nitrogen and hydrogen contents of Mn(III)– pentadentate Schiff base complex@MWCNTs were determined using CHN elemental analysis, which shows values of 2.28 and 4.16%, respectively. The Mn content of the immobilized complex supported on MWCNTs was also measured using ICP analysis, the value for which is about 0.82 mmol g⁻¹.

Thermogravimetric analysis (TGA) was used to characterize the Mn(III)-pentadentate Schiff base complex supported on MWCNTs. These studies were made in the temperature range 50–950 °C in air. The decomposition behaviour of the raw MWCNTS (Figure 5a) and grafted complex (Figure 5b) has been compared in order to understand the effect of the support. The free complex shows a



FIGURE 4 EDX diagram of Mn(III)-pentadentate Schiff base complex@MWCNTs

weight loss within the temperature range 240–275 °C.^[49] However, for the corresponding supported complex, weight losses of 0.47, 0.63, 3.18, 8.42, 18.76 and 43.93% appear at 147, 243, 340, 438, 532 and 629 °C, respectively, and of 68.79% at 725 °C.

2.2 | Application of Mn(III)–pentadentate schiff base complex supported on MWCNTs as heterogeneous catalyst

After the synthesis of Mn(III)-pentadentate Schiff base complex supported on MWCNTs as a green heterogeneous catalyst, in order to optimize the reaction conditions we considered the efficacy of the catalyst in the synthesis of tetrahydrobenzo[b]pyrans via tandem Knoevenagel-Michael cyclocondensationreactions(Scheme1).Forthisaim,asamodel reaction, the condensation reaction of 1-naphthaldehyde, dimedone and malononitrile was studied using various amounts of the catalyst at room temperature to 100 °C under solvent-free conditions (Table 1). As evident from Table 1, the best results are achieved when the reaction is conducted using 0.002 g of nanocatalyst at room temperature (Table 1, entry 5). In the absence of catalyst a low yield of the product is obtained after 30 min (Table 1, entries 1 and 2). Increasing the reaction temperature and catalyst loading does not increase the rate of the reaction (Table 1, entries 6-12).

We also investigated the effects of solvent. As a model reaction, the reaction of 1-naphthaldehyde, dimedone and malononitrile catalysed using 0.002 g of Mn(III)–pentadentate Schiff base complex supported on MWCNTs as a green heterogeneous catalyst in various solvents was conducted. The results are summarized in Table 2. It is evident that solvent-free reaction conditions are obviously the best choice for this reaction.

Encouraged by the important results and with the aim of investigating the scope of this original procedure, numerous tetrahydrobenzo[b]pyrans were synthesized from tandem Knoevenagel-Michael cyclocondensation reactions of aromatic aldehydes, 1,3-diones and malononitrile using a catalytic amount of Mn(III)-pentadentate Schiff base complex supported on MWCNTs as a green recyclable heterogeneous catalyst under solvent-free conditions at room temperature. The results are summarized in Table 3. The effect of substituents on the aromatic ring shows estimated strong effects in terms of yields under these reaction conditions. All aromatic aldehydes including those with electronreleasing substituents and electron-withdrawing substituents on their aromatic ring give the linked products in high to excellent yields in short reaction times. The reaction times of aromatic aldehydes having electron-withdrawing groups are rather faster than those having electron-donating groups. Additionally, the reaction under the same conditions in the presence of dimedone goes faster than in the presence of 1,3-cyclohexanedione.



FIGURE 5 TGA comparative analysis curves of (a) MWCNTs and (b) Mn(III)–Schiff base complex@MWCNTs

A suggested mechanism is shown in Scheme 3. Initially, malononitrile (3) reacts with carbonyl group of aldehyde 1 which is activated via the Mn(III)–pentadentate Schiff base complex supported on MWCNTs as a heterogeneous catalyst to give arylidene malononitrile (5) after eliminating one molecule of water. 1,3-Dione (2) converts to enol form (6) after tautomerization and attacks arylidene malononitrile 5 as Michael acceptor to provide intermediate 7. Finally, cyclocondensation of intermediate 7 produces intermediate 8 which is converted to preferred product 4.^[36]

Moreover, the recyclability of the Mn(III)–pentadentate Schiff base complex supported on MWCNTs catalyst was established using the condensation of 1-naphthaldehyde, dimedone and malononitrile. At the end of the reaction, ethyl acetate was added to the reaction mixture and heated to extract product and remaining starting materials. This solution was washed with water to separate the catalyst from other materials (the product is soluble in hot ethyl acetate and nanocatalyst is insoluble). The aqueous layer was decanted, separated and used for alternative reaction after removal of water. It is found that the catalytic activity of the catalyst remains within the limits of experimental error for six continuous runs (Figure 6). The general methods to check the presence or absence of leached soluble Mn in the reaction solution are a hot filtration test or elemental analysis of the recovered catalyst. The heterogeneity of the nanocatalyst in solvent-free condition and at room temperature is obvious and in such condition the hot filtration is useful. Analysis using ICP-AES of manganese in the product after isolation of catalyst shows no loss of metal during the catalytic reaction, indicating that no metal leaching occurs. Also, the XRD pattern of the catalyst after six cycles shows that the structure of the catalyst is maintained during the reaction.

5 of 10

2.3 | Comparison of catalytic activity of Mn(III)pentadentate schiff base complex@MWCNTs with that of known catalysts

To compare the applicability and efficiency of Mn(III)– pentadentate Schiff base complex@MWCNTs with that of other reported catalysts in the synthesis of tetrahydrobenzo[*b*] pyrans, we evaluated the catalytic activity of this catalysts in 6 of 10 | WILEY-Organometallic Chemistry

TABLE 1 Optimization of reaction conditions for condensation between 1-naphthaldehyde, dimedone and malononitrile catalysed by Mn(III)–pentadentate Schiff base complex@MWCNTs under solvent-free conditions^a

CHO R' R' N N Mn(III)-pentadentate Schiff base complex supported on MVCNTs as a nano catalyst (?) Solvent-free, Temperature (?) R' R' N N N N					
Entry	Catalyst loading (g)	Reaction temperature (°) ^c	Reaction time (min)	Yield (%) ^b	
1	Catalyst-free	r.t.	30	31	
2	Catalyst-free	100	30	35	
3	0.001	r.t.	30	75	
4	0.001	100	30	75	
5	0.002	r.t.	4	97	
6	0.002	50	4	97	
7	0.002	75	4	97	
8	0.002	100	4	97	
9	0.005	r.t.	4	97	
10	0.005	100	4	97	
11	0.01	r.t.	4	97	
12	0.01	100	4	97	

^aReaction conditions: 1-naphthaldehyde (1 mmol), dimedone (1 mmol), malononitrile (1 mmol).

^bIsolated yield.

^cThis is the temperature of oil bath and not inside the reaction medium.

the condensation reaction of dimedone and malononitrile with 4-chlorobenzaldehyde (Table 4). As is evident, the catalytic activity of both discrete manganese(III) Schiff base complex and MWCNTs@COOH is very good. Therefore the excellent catalytic activity and high efficiency of Mn(III)–pentadentate Schiff base complex @MWCNTs is quite expected.

3 | EXPERIMENTAL

3.1 | Materials

All of the reagents and solvents involved in synthesis were of analytical grade and used as received without further purification. Azo-coupled aldehyde (5-(4-

chlorophenylazosalicylaldehyde)) was prepared as described previously.^[69] MWCNTs of purity >85%, length of 1–10 mm and outer diameter of 5–20 nm were purchased from Kermanshah Petrochemical Industries Company.

3.2 | Instrumentation

Reaction progress and purity determination of the compounds were checked by TLC using silica gel SIL G/UV 254 plates. The ¹H NMR (400.13 MHz) and ¹³C NMR (100.62 MHz) spectra were recorded with a Bruker spectrometer (δ in ppm). Melting points are uncorrected and were recorded with a Buchi B-545 apparatus in open capillary tubes. FT-IR spectra were recorded with a Jasco 300 FT-IR

TABLE 2 Solvent effect in the synthesis of tetrahydrobenzo[b]pyrans catalysed by 0.002 g of Mn(III)-pentadentate Schiff base complex@MWCNTs^a

CHO R' + N N N N N N N N N N N N N N N N N N					
Entry	Solvent	Time (min)	Yield (%) ^b		
1	Solvent-free	4	97		
2	H ₂ O	60	45		
3	C ₂ H ₅ OH	10	96		
4	CH ₃ CN	15	96		
5	CH ₃ CO ₂ Et	30	70		
6	CH ₂ Cl ₂	30	60		
7	Toluene	60	55		
8	Benzene	60	50		

^aReaction conditions: 1-naphthaldehyde (1 mmol), dimedone (1 mmol), malononitrile (1 mmol).

^bIsolated yield.

TABLE 3 Synthesis of tetrahydrobenzo[b]pyrans via tandem Knoevenagel–Michael cyclocondensation reactions in presence of Mn(III)–pentadentate Schiff base complex @MWCNTs^a

	$ \begin{array}{c} $	Mn(III)-pentadent supported on MW ((Solvi	ate Schiff base complex CNTs as a nano catalyst 0.002 g) ent-free, r.t. R' R' 4	⊨N NH2	
Entry	Aldehyde	R'	Time (min)	Yield (%) ^b	M.p. (°C)
1	4-Nitrobenzaldehyde	Me	3	98	164–166 ^[37]
2	4-Nitrobenzaldehyde	Н	5	96	254–256 ^c
3	4-Chlorobenzaldehyde	Me	5	96	231-233 ^[37]
4	4-Chlorobenzaldehyde	Н	7	95	267–269°
5	Naphthalene-1-carbaldehyde	Me	4	97	230-232 ^[50]
6	Naphthalene-1-carbaldehyde	Н	6	96	176–178 ^c
7	α- Methylcinnamaldehyde	Me	10	94	207–209 ^c
8	α - Methylcinnamaldehyde	Н	12	93	251–253 ^c
9	Naphthalene-2-carbaldehyde	Me	5	96	284-286 ^[51]
10	Naphthalene-2-carbaldehyde	Н	7	95	273–275 ^c
11	4-Hydroxybenzaldehyde	Me	10	95	245-247 ^[52]
12	4-Hydroxybenzaldehyde	Н	12	94	257–259 ^c
13	Biphenyl-4-carbaldehyde	Me	5	96	275-277 ^[51]
14	Biphenyl-4-carbaldehyde	Н	7	95	225–227 ^c
15	3-Nitrobenzaldehyde	Me	5	96	224-226 ^[52]
16	3-Nitrobenzaldehyde	Н	7	95	247–249 ^c
17	4-Methoxybenzaldehyde	Me	8	95	216-218 ^[37]
18	4-Methoxybenzaldehyde	Н	10	94	204–206 ^c
19	2,5-Dimethoxybenzaldehyde	Me	10	95	203–205 ^c
20	2,5-Dimethoxybenzaldehyde	Н	12	94	249–251 ^c

^aReaction conditions: aldehyde (1 mmol), dimedone (1 mmol), malononitrile (1 mmol), solvent-free conditions at room temperature.

^bIsolated yield.

^cNew derivatives.

spectrometer using compressed KBr discs. Mass spectra of new compounds were obtained with an Agilent Technologies 5975C VL MSD spectrometer. Thermal analyses were performed with a PerkinElmer TG/DTA 6300 instrument. Nanostructure observations were conducted using SEM. XRD patterns were collected using a Bruker D8 ADVANCE diffractometer. The samples were scanned at a rate of 0.05° min⁻¹ from $2\theta = 10^{\circ}$ to 90°.



SCHEME 3 Proposed mechanism for the synthesis of tetrahydrobenzo[*b*] pyrans via tandem Knoevenagel–Michael cyclocondensation reactions catalysed by Mn(III)–pentadentate Schiff base complex@MWCNTs

3.3 | Mn(III)–pentadentate schiff base complex immobilized on MWCNTs: preparation and purification

onlied

ganometallic emistry 7 of 10

3.3.1 | MWCNT functionalization and purification

Following careful purification, MWCNTs (2 g) were oxidized in a mixture of concentrated sulfuric and nitric acids (3:1, 98 and 70%, respectively) by ultrasonication for 24 h to obtain oxidized MWCNTs (MWCNT@COOH).^[42] In order



FIGURE 6 Reusability of Mn(III)-pentadentate Schiff base complex supported on MWCNTs as a heterogeneous catalyst in 4 min

TABLE 4 Comparison of various catalysts in the synthesis of tetrahydrobenzo[b]pyrans with our catalyst

Entry	Catalyst	Solvent	Temp. (°C)	Time (min)	Yield (%)	Ref.
1	p-Dodecylbenzenesulfonic acid (0.4 mmol)	H ₂ O/reflux	_	240	69	[53]
2	SO ₄ ²⁻ @MCM-41 (25 mg)	EtOH/reflux		60	80	[37]
3	KF-Al ₂ O ₃ (250 mg)	DMF/reflux		180	81	[54]
4	Phenylboronic acid (5 mol%)	EtOH/H ₂ O/reflux		30	84	[55]
5	Red Sea sand (0.5 g)	EtOH/reflux		280	85	[56]
6	Molecular iodine (10 mmol%)	DMSO	120	210	88	[57]
7	Ni(NO ₃) ₂ ·6H ₂ O (10 mol%)	H ₂ O/reflux	_	20	88	[58]
8	$NH_4H_2PO_4-Al_2O_3 (0.03 g)$	Solvent free	80	30	88	[59]
9	Sodium selenite (0.1 g)	EtOH/H ₂ O/reflux		180	90	[60]
10	NaBr (42 mg)	Solvent free	70	10	90	[61]
11	β-Cyclodextrin-glycerin	H ₂ O	35	30	90	[50]
12	KF-alumina (0.2 mmol)	EtOH/reflux	—	120	92	[38]
13	Acetic acid@ionic liquid	Solvent free	110	10	93	[51]
14	Nano-TiO ₂ /H ₁₄ [NaP ₅ W ₃₀ O ₁₁₀] (25 mg)	EtOH	40	15	94	[62]
15	$Ce_1Mg_xZr_{1-x}O_2 (0.2 g)$	EtOH/reflux	—	35	94	[63]
16	$Zn(Phen)_2Cl_2 (2 mol\%)$	H ₂ O	r.t.	5	94	[41]
17	Nano-titania sulfuric acid 10 mg	EtOH	40	15	94	[46]
18	Tetrabutylammonium bromide (10 mol%)	H ₂ O/reflux	—	35	94	[52]
19	$NH_4Al(SO_4)_2 \cdot 12H_2O$ (0.2 g)	EtOH/reflux	—	120	94	[64]
20	Tetrabutylammonium bromide (10 mol%)	EtOH/reflux	—	30	95	[40]
21	Nano-Fe ₃ O ₄ @SiO ₂ @TiO ₂ (0.01 g)	Solvent free	100	10	96	[36]
22	CaCl ₂ (20 mol%)	EtOH	r.t.	8	96	[65]
23	KF/Al ₂ O ₃ (145 mg)	EtOH	r.t.	30	96	[66]
24	$Fe_3O_4@SiO_2$ -Imid-PMA ⁿ (0.015 g)	H ₂ O	r.t.	5	97	[67]
25	La _{0.7} Sr _{0.3} MnO ₃ (5 mol%)	EtOH	r.t.	9	97	[68]
26	Fe ₃ O ₄ NPs/MWCNTs/ (5 mg)	EtOH /reflux	—	8	97	[39]
27	MnCl ₂ (0.002 g)	Solvent free	r.t.	40	63	
28	Mn(III)-pentadente Schiff base complex (0.002 g)	Solvent free	r.t.	7	90	—
29	MWCNTs-COOH (0.002 g)	Solvent free	r.t.	20	81	_
30	$Mn(III)\mbox{-}pentadentate \ Schiff \ base \ complex @MWCNTs \ (0.002 \ g)$	Solvent free	r.t.	5	96	—

to increase the reactivity and/or population of OH surface groups, the material was further treated with sodium borohydride methanol carboxyl in and groups were reduced CH_2OH groups. The obtained to MWCNT@OH (2 g) was suspended in xylene (100 ml) and then 3-chloropropyltrimethoxysilane (CPTMS) (2 ml) was added under dry nitrogen atmosphere. The mixture was refluxed for 24 h and the resultant solid (CpmMWCNTs) was separated and washed with methanol to remove the unreacted residue of silylating reagent and then dried at 80 °C.

A solution of diethylenetriamine (1 mmol) in absolute EtOH (20 ml) was added to a stirring solution of azo-coupled aldehyde (5-(4-chlorophenylazosalicylaldehyde); 2 mmol) in absolute EtOH (60 ml) during a period of 15 min at 50 °C. The solution was then heated for 4 h at 80 °C with stirring. The mixture was filtered and the obtained solid was washed with hot ethanol (three times) and then with

diethyl ether. The resulting product was dried in air (yield: 81%).^[42]

3.3.3 + Synthesis of MWCNTs@Si-H_2azosaldien and its Mn(III) complex

Triethylamine was added to a dry ethanol solution (60 ml) of H_2 azosaldien and then 1 g of CpmMWCNTs was added to the solution and the reaction mixture was refluxed at 60 °C under ultrasonic irradiation in nitrogen atmosphere for 20 h to produce MWCNTs@Si-H_2azosaldienin. Then, an excess amount of metal salt (MnCl₂) was added to a mixture of MWCNTs@Si-H_2azosaldien (1 g) in methanol (100 ml) containing a few drops of triethylamine and the resulting mixture was refluxed and irradiated with ultrasound for 3 h. The resulting precipitate was filtered and washed several times with hot water and ethanol until the solution became colourless. The obtained product, immobilized Mn(III)-pentadentate Schiff base complex supported on MWCNTs (*ca* 1 g), was dried and stored in a vacuum desiccator.

3.4 | General procedure for synthesis of tetrahydrobenzo[*b*]pyran derivatives

To a mixture of aromatic aldehyde (1 mmol), 1,3-dione (1 mmol) and malononitrile (1 mmol) in a round-bottom flask was added Mn(III)-pentadentate Schiff base complex supported on MWCNTs as a heterogeneous catalyst (0.002 g), and the resulting mixture was stirred magnetically under solvent-free conditions at room temperature. After completion of the reaction, as checked via TLC (*n*-hexane–ethyl acetate, 5:2), ethyl acetate (10 ml) was added to the reaction mixture, stirred and refluxed for 3 min, and then was washed with water (10 ml) and decanted to separate catalyst from other materials (the reaction mixture was soluble in hot ethyl acetate and nanocatalyst was insoluble). The solvent of organic layer was evaporated and the crude product was purified by recrystallization from ethanol. In this study, the nano-heterogeneous catalyst was recycled and reused six times without sifnificant loss of its catalytic activity (spectral data analysis for compounds are in the supporting information).

4 | CONCLUSIONS

In summary, a green, mild and eco-friendly Mn(III)pentadentate Schiff base complex supported on MWCNTs as a recyclable heterogeneous catalyst was synthesized, studied and characterized using FT-IR spectroscopy, XRD, SEM, EDX, ICP analysis, elemental analysis (CHN) and TGA. The synthesized Mn(III) Schiff base complex immobilized on MWCNTs was shown to have excellent catalytic activity in the synthesis of tetrahydrobenzo[b]pyrans via tandem Knoevenagel–Michael cyclocondensation reactions between aromatic aldehydes, 1,3-diones and malononitrile under solvent-free conditions at room temperature. Of the 20 synthesized derivatives of tetrahydrobenzo[b]pyrans, 12 are new compounds. The various main advantages of this protocol are reasonably clean reaction profile, high yield, short reaction time, low cost and recyclability of the green nano-heterogeneous catalyst, and simplicity of product isolation.

ACKNOWLEDGEMENT

We are grateful to Bu-Ali Sina University for financial support.

REFERENCES

- J. Zhu, H. Bienayme (Eds), Multicomponent Reactions in the Total Synthesis of Natural Products, Wiley-VCH, Weinheim 2005.
- [2] N. M. Evdokimov, A. S. Kireev, A. A. Yakovenko, M. Y. Antipin, I. V. Magedov, A. Kornienko, J. Org. Chem. 2007, 72, 3443.
- [3] H. Bienayme, C. Hulme, G. Oddon, P. Schmitt, Chem. A Eur. J. 2000, 6, 3321.
- [4] D. Tasis, N. Tagmatarchis, A. Bianco, M. Prato, Chem. Rev. 2006, 106, 1105.
- [5] N. Karousis, N. Tagmatarchis, Chem. Rev. 2010, 110, 5366.



- [6] R. Saito, M. S. Dresselhaus, G. Dresselhaus, *Physical Properties of Carbon Nanotubes*, World Scientific, Singapore 1998, 1.
- [7] P. G. Collins, P. Avouris, Sci. Am. 2000, 283, 62.
- [8] X. Zhang, J. Zhang, R. Wang, Z. Liu, Carbon 2004, 42, 1455.
- [9] R. S. Ruoff, D. C. Lorents, Carbon 1995, 33, 925.
- [10] J. Garcia, H. T. Gomes, P. Serp, P. Kalck, J. L. Figueiredo, J. L. Faria, *Catal. Today* 2005, *102*, 101.
- [11] P. Serp, M. Corrias, P. Kalck, Appl. Catal. A 2003, 253, 337.
- [12] L. R. Radovic, F. Rodríguez-Reinoso, Chemistry and Physics of Carbon, Marcel Dekker, New York 1997, 243.
- [13] J. Chen, M. Wang, B. Liu, Z. Fan, K. Cui, Y. Kuang, J. Phys. Chem. B 2006, 110, 11775.
- [14] S. Domínguez-Domínguez, A. Berenguer-Murcia, B. K. Pradhan, A. Linares-Solano, D. Cazorla-Amorós, J. Phys. Chem. C 2008, 112, 3827.
- [15] C. Baleizao, B. Gigante, H. García, A. Corma, Tetrahedron 2004, 60, 10461.
- [16] C. Baleizao, B. Gigante, H. García, A. Corma, J. Catal. 2004, 221, 77.
- [17] M. Moghadam, I. Mohammadpoor-Baltork, S. Tangestaninejad, V. Mirkhani, H. Kargar, N. Zeini-Isfahani, *Polyhedron* 2009, 28, 3816.
- [18] S. Tangestaninejad, M. Moghadam, V. Mirkhani, I. Mohammadpoor-Baltork, M. S. Saeedi, *Appl. Catal. A* 2010, 381, 233.
- [19] M. Moghadam, S. Tangestaninejad, V. Mirkhani, I. Mohammadpoor-Baltork, A. Mirjafari, N. S. Mirbagheri, *Mol. Catal. A* 2010, 329, 44.
- [20] M. Moghadam, S. Tangestaninejad, V. Mirkhani, I. Mohammadpoor-Baltork, N. S. Mirbagheri, J. Organometal. Chem. 2010, 695, 2014.
- [21] M. Moghadam, S. Tangestaninejad, V. Mirkhani, I. Mohammadpoor-Baltork, N. S. Mirbagheri, *Appl. Organometal. Chem.* 2010, 74, 708.
- [22] M. Masteri-Farahani, S. Abednatanzi, Inorg. Chem. Commun. 2013, 37, 39.
- [23] D. Shi, J. Lian, W. Wang, G. Liu, P. He, Z. Dong, L. M. Wang, R. C. Ewing, *Adv. Mater.* 2006, 18, 189.
- [24] C. Baleizao, H. Garcia, Chem. Rev. 2006, 106, 3987.
- [25] W. O. Foye, Prinicipi di Chemico Farmaceutica, Piccin, Padova, Italy 1991.
- [26] G. R. Green, J. M. Evans, A. K. Vong, in *Comprehensive Heterocyclic Chemistry II*, (Eds: A. R. Katritzky, C. W. Ress, E. F. V. Scriven) Vol. 5, Pergamon Press, Oxford **1995**, 469.
- [27] Y. L. Zhang, B. Z. Chen, K. Q. Zheng, M. L. Xu, X. H. Lei, *Chin. Acta Pharm. Sin.* **1982**, *17*, 17; *Chem. Abstr.* 1982, *96*, 135383e.
- [28] L. Bonsignore, G. Loy, D. Secci, A. Calignano, Eur. J. Med. Chem. 1993, 28, 517.
- [29] L. L. Andreani, E. Lapi, Bull. Chim. Farm. 1960, 99, 583.
- [30] E. C. Witte, P. Neubert, A. Roesch, Ger. Offen DE 3427985, 1986; Chem. Abstr. 1986, 104, 224915 f.
- [31] C. S. Konkoy, D. B. Fick, S. X. Cai, N. C. Lan, J. F. W. Keana, PCT Int. Appl. WO 0075123, 2000; *Chem. Abstr.* 2001, *134*, 29313a.
- [32] D. Fang, H. B. Zhang, Z. L. Liu, J. Heterocycl. Chem. 2010, 47, 63.
- [33] L. Chen, Y. Q. Li, X. J. Huang, W. J. Zheng, Heteroatom Chem. 2009, 20, 91.
- [34] A. Shaabani, S. Samadi, Z. Badri, A. Rahmati, Catal. Lett. 2005, 104, 39.
- [35] H. R. Shaterian, M. Arman, F. Rigi, J. Mol. Liq. 2011, 158, 145.
- [36] A. Khazaei, F. Gholami, V. Khakyzadeh, A. R. Moosavi-Zare, J. Afsar, *RSC Adv.* 2015, 5, 14305.
- [37] M. Abdollahi-Alibeik, F. Nezampour, React. Kinet. Mech. Cat. 2013, 108, 213.
- [38] A. Hasaninejad, N. Jafarpour, M. Mohammadnejad, E. J. Chem. 2012, 9, 2000.
- [39] A. F. Shojaei, K. Tabatabaeian, F. Shirini, S. Z. Hejazi, RSC Adv. 2014, 4, 9509.
- [40] S. Gurumurthi, V. Sundari, R. Valliappan, E. J. Chem. 2009, 6, S466.
- [41] E. Mosaddegh, A. Hassankhani, G. Mansouri, E. J. Chem. 2011, 8, 529.
- [42] M. Salavati-Niasari, E. Esmaeili, H. Seyghalkar, M. Bazarganipour, *Inorg. Chim. Acta* 2011, 375, 11.
- [43] S. Salehzadeh, M. D. Ward, H. Adams, Inorg. Chem. Commun. 2009, 12, 433.

10 of 10 WILEY-Organometallic Chemistry

- [44] S. Salehzadeh, R. Golbedaghi, I. S. Tidmarsh, N. K. Al-Rasbi, H. Adams, M. D. Ward, *Polyhedron* 2008, 27, 3549.
- [45] J. Rakhtshah, S. Salehzadeh, Appl. Organometal. Chem. 2016, DOI: 10.1002/aoc.3560
- [46] D. Azarifar, S. M. Khatami, M. A. Zolfigol, R. Nejat-Yami, J. Iran. Chem. Soc. 2014, 11, 1223.
- [47] A. Khazaei, M. A. Zolfigol, F. Karimitabar, I. Nikokarb, A. R. Moosavi-Zare, RSC Adv. 2015, 5, 71402.
- [48] S. Mallakpour, A. Zadehnazari, Synth. Met. 2013, 169, 1.
- [49] M. Mirzaeian, A. M. Rashidi, M. Zare, R. Ghabezi, R. Lotfi, J. Nat. Gas Sci. Eng. 2014, 18, 439.
- [50] S. R. Kamatmobi, A. H. Mane, S. M. Arde, R. S. Salunkhe, Int. J. Pharm. Chem. Biol. Sci. 2014, 4, 1012.
- [51] A. R. Moosavi-Zare, M. A. Zolfigol, O. Khaledian, V. Khakyzadeh, M. Darestani Farahani, H. G. Kruger, New J. Chem. 2014, 38, 2342.
- [52] A. Mobinikhaledi, M. A. Bodaghi-Fard, Acta Chim. Slov. 2010, 57, 931.
- [53] E. Sheikhhosseini, D. Ghazanfari, V. Nezamabadi, Iran. J. Catal. 2013, 3, 197.
- [54] X. S. Wang, D. Q. Shi, S. J. Tu, C. S. Yao, Synth. Commun. 2003, 33, 119.
- [55] S. Nemouchi, R. Boulcina, B. Carboni, A. Debache, C. R. Chimie 2012, 15, 394.
- [56] N. M. A. El-Rahman, R. M. Borik, World Appl. Sci. J. 2014, 31, 1.
- [57] R. S. Bhosale, C. V. Magar, K. S. Solanke, S. B. Mane, S. S. Choudhary, R. P. Pawar, *Synth. Commun.* **2007**, *37*, 4353.
- [58] B. Boumoud, A. A. Yahiaoui, T. Boumoud, A. Debache, J. Chem. Pharm. Res. 2012, 4, 795.
- [59] B. Maleki, S. S. Ashrafi, RSC Adv. 2014, 4, 42873.
- [60] R. Hekmatshoar, S. Majedi, K. Bakhtiari, Catal. Commun. 2008, 9, 307.
- [61] I. Devi, P. J. Bhuyan, Tetrahedron Lett. 2004, 45, 8625.

- [62] D. Azarifar, S. M. Khatami, R. Nejat-Yami, J. Chem. Sci. 2014, 126, 95.
- [63] S. Rathod, B. Arbad, M. Lande, Chinese J. Catal. 2010, 31, 631.
- [64] A. A. Mohammadi, M. R. Asghariganjeh, A. Hadadzahmatkesh, Arabian J. Chem. 2013, DOI: 10.1016/j.arabjc.2013.07.055
- [65] H. R. Safaei, M. Shekouhy, A. Shirinfeshan, S. Rahmanpur, *Mol. Divers.* 2012, 16, 669.
- [66] J. T. Li, W. Z. Xu, L. C. Yang, T. S. Li, Synth. Commun. 2004, 34, 4565.
- [67] M. Esmaeilpour, J. Javidi, F. Dehghani, F. Nowroozi-Dodeji, RSC Adv. 2015, 5, 26625.
- [68] A. Azarifar, R. Nejat-Yami, M. A. Kobaisi, D. Azarifar, J. Iran. Chem. Soc. 2013, 10, 439.
- [69] K. Nejati, Z. Rezvani, M. Seyedahmadian, Dyes Pigments 2009, 83, 304.

SUPPORTING INFORMATION

Additional Supporting Information may be found online in the supporting information tab for this article.

How to cite this article: Rakhtshah J, Salehzadeh S, Zolfigol MA, Baghery S. Mn(III)–pentadentate Schiff base complex supported on multi-walled carbon nanotubes as a green, mild and heterogeneous catalyst for the synthesis of tetrahydrobenzo[*b*]pyrans via tandem Knoevenagel–Michael cyclocondensation reaction, *Appl Organometal Chem.* 2017;e3690. doi: 10.1002/ aoc.3690