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Zn_2SnO_4 nanostructure as an efficient catalyst for the preparation of pyrano[3,2-c]chromene and pyrano[4,3-b]pyran derivatives under ultrasonic irradiation conditions

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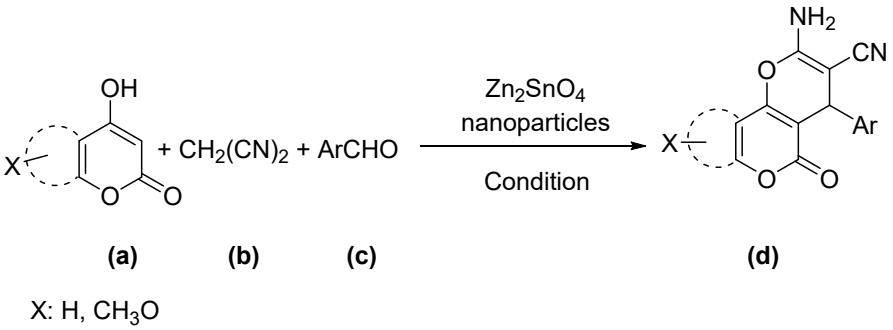
HIGHLIGHTS

- Zn_2SnO_4 nanoparticles were prepared by a sol-gel method and characterized.
- Pyrano[3,2-c]chromenes and pyrano[4,3-b]pyran derivatives were synthesized under ultrasonic irradiation conditions using Zn_2SnO_4 nanoparticles as catalyst.
- The heterogeneous recoverable catalyst, and mild reaction conditions are the advantages of this method.

GRAPHICAL ABSTRACT



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ABSTRACT

We plan to study the synthesis of Zn_2SnO_4 nanoparticles via a sol-gel method and evaluate their catalytic activity in the three-component reaction including active enolates, active methylene, and aldehydes leading to the formation of the pyran derivatives. Functionalized pyrano[3,2-c]chromenes and pyrano[4,3-b]pyran derivatives were synthesized via a one-pot, a three-component reaction under ultrasonic irradiation conditions in good to excellent yields. The catalyst was characterized by XRD, FESEM and TEM analyses.

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1. Introduction

Multi-component reactions (MCRs) are an attractive and favored area of study for many chemists and currently hold a special place in organic chemistry and medicine. In general, reactions in which more than two primary materials are present and produce products that contain most of the atoms that make up the raw material in its structure are known as multi-component reactions. Hence, the study of new multi-dimensional reactions and the attempt to exploit known multi-component reactions is an attractive topic for many organic chemists. However, due to the obvious application of these reactions in biological processes, the use of MCRs in the pharmaceutical field, both industrial and academic, has received a large amount of attention. An example of the use of MCR in pharmaceuticals is the synthesis of a family of pyran containing compounds. Compounds with a pyran nucleus play a key role in the synthesis of different drugs. Such compounds have many biological properties and medicinal uses and are found in many important natural products. Due to the widespread use of these compounds, a great deal of interest has emerged for the synthesis of other derivatives with more appropriate methods such as multicomponent reactions and their biological effects. The MCR method provides the synthesis of pyran containing compounds using processes with fewer steps [1-10].

Among the different methods used for the preparation of compounds with pyran cores, multicomponent reactions of active enolates, active methylenes, and aldehydes are some of the simplest and most practical synthetic methods for the preparation of these compounds. This reaction requires the use of acid and base catalysts, and published sources have reported the use of catalysts such as thiourea dioxide [11], MgO nanopowders [12], $ZnAl_2O_4$-Bi_2O_3 composite nanopowder [13], MgO nanoplates [14], ZnO nanoparticles [15], CuO nanostructures [16], Bi_2O_3 nanoparticles [17], Silica-bonded N-propylpiperazine sodium n-propionate [18], DBU [19], nanostructured diphosphate $Na_2CaP_2O_7$ [20] and piperidine [21].

Even though these reported strategies are effective, the exploration of a heterogeneous catalysis, which is an active strategy, is still in demand. Herein, we wish to report an efficient and facile procedure for the easy access of functionalized novel pyrano[3,2-c]chromenes and pyrano[4,3-b]pyran derivatives via a one-pot, a three-component reaction using Zn_2SnO_4 nanoparticles as an efficient catalyst (Scheme 1).

2. Experimental

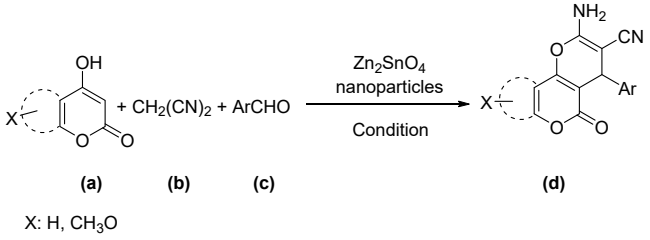
All reagents were purchased from Merck and Aldrich Co. and were used without further purification. All yields refer to isolated products after purification. The powder X-ray diffraction patterns were measured with D_8, Advance, Bruker, axs, and a diffractometer using Cu-K_α irradiation. FE-SEM was taken by a Hitachi S-4160 photograph to examine the shape of the sample. The NMR spectra were recorded on a Bruker Avance DPX 400 MHz instrument. The spectra were measured in DMSO-d_6 relative to TMS (0.00 ppm). Elemental analysis was performed on a Heraeus CHN-O-Rapid analyzer. FE-SEM coupled with EDAX was taken by a Hitachi S-4160 photograph to examine the shape and metallic composition of the samples.

2.1. Preparation of Zn_2SnO_4 nanoparticles

In a 250 mL beaker, zinc chloride (20 mmol) and tin (II) chloride (20 mmol) were dissolved in 100 ml of ethanol (solution A). In a separate beaker, ammonia solution (37%; 30 mL) was dissolved in water (50 mL) (solution B). Solution (B) was slowly added dropwise to solution (A) under vigorous magnetic stirring. The mixture was continuously stirred for another 60 min. The resulting precipitate was filtered, washed with water several times, then dried in an oven, and finally calcined at 500 °C for 3h.

2.2. Typical procedure for the preparation of pyrano[3,2-c]chromene and pyrano[4,3-b]pyrans

A mixture of 1 mmol of (a), (b), and (c) (from Scheme 1), and Zn_2SnO_4 nanoparticles (0.025 g) was refluxed in ethanol (20 mL) under ultrasonic irridiation at 80 °C.



Scheme 1. Synthesis of pyrano[3,2-c]chromene and pyrano[4,3-b] pyran derivatives using Zn_2SnO_4 nanoparticles

After the completion of the reaction (TLC monitoring, EtOAc: hexane 10/90 v/v), the solid formed in the reaction mixture was dissolved in hot ethanol, filtered, and recrystallized from ethanol to afford the desired products.

Spectral data:

2- Amino-8, 9, 10- trimethoxy-5- oxo-4- phenyl- 4H, 5H- pyrano[3,2-c]chromene-3- carbonitrile **(16d)**: ^{1}H NMR (400 MHz, DMSO-d_6): δ 3.76 (s, 3H, OCH_3), 3.85 (s, 3H, OCH_3), 3.92 (s, 3H, OCH_3), 4.53 (s, 1H, CH), 5.63 (s, 1H), 7.25-7.32 (m, 5H), 7.49 (s, 2H, NH_2) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ 56.3, 57.9, 59.7, 62.3, 99.6, 100.1, 102.8, 112.2, 118.2, 127.6, 128.4, 128.7, 140.3, 145.2, 146.5, 154.1, 157.2, 158.9, 159.3, 161.2 ppm; Elemental analysis for $C_{22}H_{18}N_2O_6$: found C, 65.11; H, 4.51; N, 6.83%; calculated C, 65.02; H, 4.46; N, 6.89%.

2- Amino-8, 9, 10- trimethoxy-5- oxo-4- (p-tolyl)-4H,5H- pyrano[3,2-c]chromene-3- carbonitrile **(17d)**: ^{1}H NMR (400 MHz, DMSO-d_6): δ 2.26 (s, 3H, CH_3), 3.75 (s, 3H, OCH_3), 3.85 (s, 3H, OCH_3), 3.91 (s, 3H, OCH_3), 4.51 (s, 1H, CH), 5.64 (s, 1H), 7.02 (d, J = 8.1 Hz, 2H), 7.26 (d, J = 8.1 Hz, 2H), 7.48 (s, 2H, NH_2) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ 21.09, 56.3, 57.9, 59.7, 62.1, 99.8, 100.0, 103.1, 112.4, 118.0, 124.6, 127.8, 128.3, 133.1, 145.1, 146.5, 154.0, 157.3, 158.7, 159.2, 161.3 ppm; Elemental analysis for $C_{23}H_{20}N_2O_6$: found C, 65.64; H, 4.73; N, 6.58%; calculated C, 65.71; H, 4.80; N, 6.66%.

2- Amino-4-(4- chlorophenyl)-8, 9, 10- trimethoxy-5-oxo- 4H,5H- pyrano[3,2-c]chromene-3- carbonitrile **(18d)**: ^{1}H NMR (400 MHz, DMSO-d_6) δ 3.76 (s, 3H, OCH_3), 3.85 (s, 3H, OCH_3), 3.92 (s, 3H, OCH_3), 4.57 (s, 1H, CH), 5.63 (s, 1H), 7.25 (d, J = 8.1 Hz, 2H), 7.43 (d, J = 8.1 Hz, 2H), 7.56 (s, 2H, NH_2) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ 56.4, 58.1, 60.2, 62.5, 100.1, 102.9, 112.7, 118.6, 128.2, 130.6, 134.4, 140.3, 145.2, 146.3, 146.7, 154.2, 157.2, 159.0, 159.2, 161.1 ppm; Elemental analysis for $C_{22}H_{17}ClN_2O_6$: found C, 59.89; H, 3.86; N, 6.27%; calculated C, 59.94; H, 3.89; N, 6.35%.

2- Amino-4-(4- bromophenyl)-8, 9, 10- trimethoxy-5-oxo- 4H,5H- pyrano[3,2-c]chromene-3- carbonitrile **(19d)**: ^{1}H NMR (400 MHz, DMSO-d_6): δ 3.76 (s, 3H, OCH_3), 3.84 (s, 3H, OCH_3), 3.92 (s, 3H, OCH_3), 4.55 (s, 1H, CH), 5.63 (s, 1H), 7.23 (d, J = 8.0 Hz, 2H), 7.41 (d, J = 8.0 Hz, 2H), 7.46 (s, 2H, NH_2) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ 56.4, 57.9, 60.1, 62.4, 100.0, 103.2, 112.5, 118.7, 127.8, 130.6, 134.4, 140.2, 142.3, 145.1, 146.7, 154.1, 157.0, 159.0, 159.2, 161.1 ppm; Elemental analysis for $C_{22}H_{17}BrN_2O_6$: found C, 54.39; H, 3.49; N, 5.70%; calculated C, 54.45; H, 3.53; N, 5.77%.

2- Amino-8, 9, 10- trimethoxy-4-(4- nitrophenyl)-5-oxo- 4H,5H- pyrano[3,2-c]chromene-3- carbonitrile **(20d)**: ^{1}H NMR (400 MHz, DMSO-d_6): δ 3.76 (s, 3H, OCH_3), 3.86 (s, 3H, OCH_3), 3.93 (s, 3H, OCH_3), 4.73 (s, 1H, CH), 5.61 (s, 1H), 7.47 (s, 2H, NH_2), 7.53 (d, J = 8.2 Hz, 2H), 8.213 (d, J = 8.2 Hz, 2H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ 56.4, 58.1, 62.6, 64.5, 100.1, 103.1, 114.7, 118.9, 120.2, 128.8, 131.6, 136.4, 140.3, 145.2, 148.3, 154.2, 157.2, 159.0, 159.2, 161.1 ppm; Elemental analysis for $C_{22}H_{17}N_3O_8$: found C, 58.48; H, 3.74; N, 9.26%; calculated C, 58.54; H, 3.80; N, 9.31%.

2- Amino-7- methyl-5- oxo-4- phenyl-4H,5H- pyrano [4,3-b]pyran-3- carbonitrile **(21d)**: ^{1}H NMR (400 MHz, DMSO-d_6): δ 2.26 (s, 3H, CH_3), 4.43 (s, 1H, CH), 4.49 (s, 2H, NH_2), 5.93 (s, 1H), 7.11-7.25 (m, 5H) ppm; Elemental analysis for $C_{16}H_{12}N_2O_3$: found C, 68.45; H, 4.21; N, 9.93%; calculated C, 68.56; H, 4.32; N, 9.99%.

2-Amino- 7-methyl- 4- (4-nitrophenyl) -5 -oxo -4,5-dihydropyrano [4,3-b] pyran-3-carbonitrile **(31d)**: ^{1}H NMR (400 MHz, DMSO-d_6): δ 2.27 (s, 3H, CH_3), 4.52 (s, 1H, CH), 4.76 (s, 2H, NH_2), 5.95 (s, 1H), 7.52 (d, J = 8.2 Hz, 2H), 8.19 (d, J = 8.2 Hz, 2H) ppm; Elemental analysis for $C_{16}H_{11}N_3O_5$: found C, 59.00; H, 3.36; N, 12.88%; calculated C, 59.08; H, 3.41; N, 12.92%.

3. Results and discussions

Figs. 1 to 3 show the XRD pattern, FE-SEM and TEM images of Zn_2SnO_4 nanoparticles calcined at 500°C. The XRD pattern states that Zn_2SnO_4 nanoparticles are crystallized in the cubic phase with the characteristic peaks of 17.7, 29.1, 34.2, 35.9, 41.6, 45.6, 55.1, 60.4, and 86.2 [2θ°]. Using Sherrer's formula (Eq. (1)), the mean grain size was determined to be 71nm.

$$D = 0.9\,\lambda/\beta\,\cos\theta \quad (1)$$

where λ is the wavelength of radiation with the value of 1.5406 Å, β is the full width at half maximum (FWHM), and θ is the Bragg's angle. The pure and impurity-free Zn_2SnO_4 single phase has a lattice parameter of a=b=c= 8.64 Å related to their cubic phase.

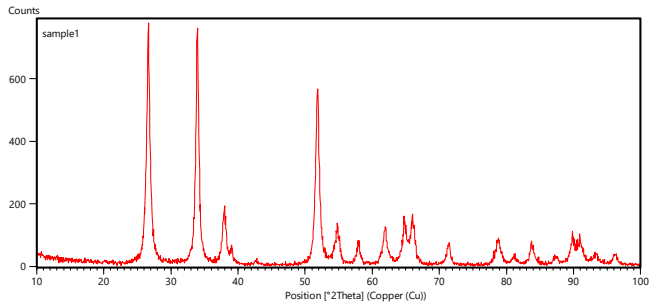


Fig. 1. XRD pattern of Zn_2SnO_4 nanoparticles.

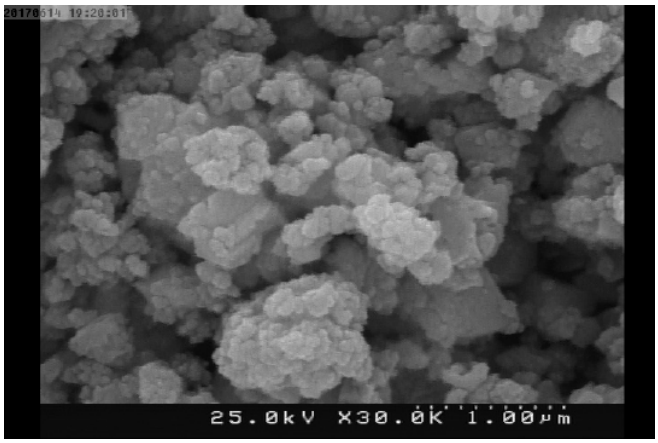


Fig. 2. FE-SEM image of Zn_2SnO_4 nanoparticles.

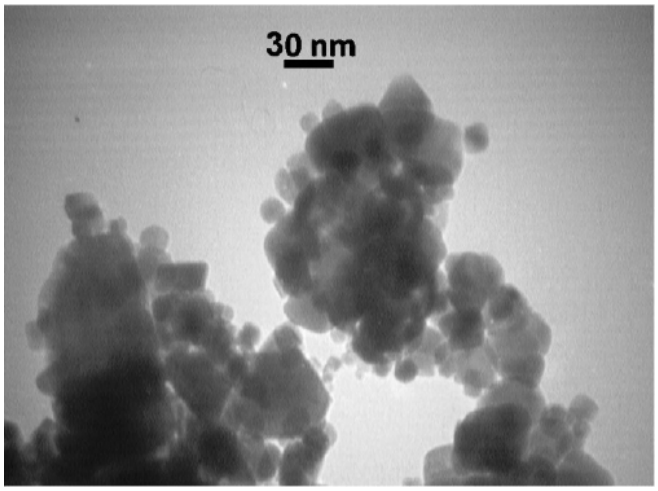


Fig. 3. TEM image of Zn_2SnO_4 nanoparticles

The FE-SEM and TEM images were used to perform the surface morphology and particle size distribution analysis and indicated that the amorphous particles of nanocomposite are relatively spherical in shape with an approximate size less than 100 nm (Figs. 2 and 3).

The particle size distribution of Zn_2SnO_4 nanoparticles was determined by the dynamic light scattering (DLS) technique and the results are shown in Fig. 4. Before analysis, the sample was dispersed in ethanol (1 g in 25 mL) and sonicated for 30 min. The mean particle size of the Zn_2SnO_4 nanoparticles was approximately 80 nm.

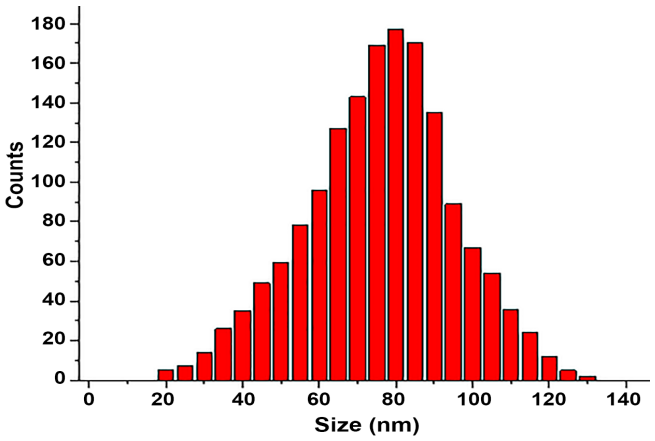


Fig. 4. The particle size distribution curve of Zn_2SnO_4 nanoparticles.

This study investigates the use of Zn_2SnO_4 nanoparticles on the catalytic multi-component reaction of 4- hydroxy-6- methyl-2*H*- pyran-2- one / 4- hydroxy-2*H*-chromen-2-one, aldehydes, and malononitrile results to the pyrano[3,2-c]chromene and pyrano[4,3-b] pyran derivatives.

To achieve the optimal conditions with higher yields and shorter reaction time, the condensation reaction of 4-hydroxy-2*H*-chromen-2-one (1 mmol), malononitrile (1 mmol) and benzaldehyde (1 mmol) was chosen as a model of reaction in both solvent-free and in the presence of different solvents, under ultrasonic irrdiation, different temperatures, and catalyst dosage. The results are summarized in Table 1. According to

Table 1. Optimization of the reaction conditions.

Entry	Catalyst (g)	Condition (under ultrasonic irradiation)	Yield (%)[a]
1	0.025	Solvent-free; 100 °C	-
2	-	EtOH; Reflux	-
3	0.025	EtOH; Reflux	93
4	0.025	CH_2Cl_2; Reflux	-
5	0.025	*n*-Hexane; Reflux	-
6	0.025	EtOAc; Reflux	-
7	0.025	H_2O; Reflux	-
8	-	EtOH; Reflux	-
9	0.05	EtOH; Reflux	90
10	0.01	EtOH; Reflux	82
11	0.075	EtOH; Reflux	89
12	0.1	EtOH; Reflux	90

[a] Isolated yields; based on the synthesis of 2-amino-5-oxo-4-phenyl-4*H*,5*H*-pyrano[3,2-c]chromene-3-carbonitrile, reaction time: 3h.

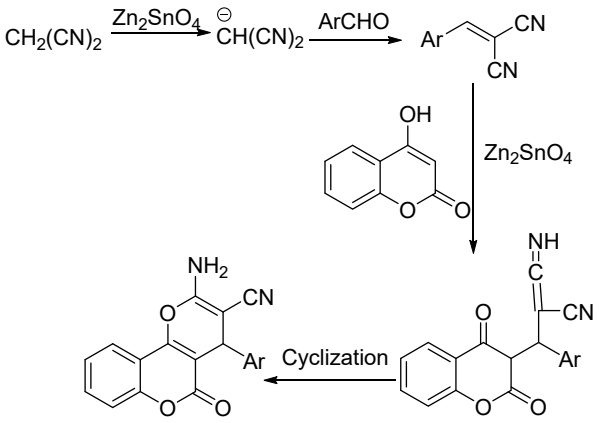
Table 1, 0.025 g of Zn_2SnO_4 nanoparticles as a catalyst and ethanol was selected as the optimum conditions.

Based on the optimal results obtained, various derivatives of the pyrano[3,2-c]chromene derivatives (**1d-15d**) were prepared, and the results are summarized in Table 2. The aldehydes with electron-withdrawing or halogen groups as well as hetero-aromatic aldehydes will participate in the reaction in less time than those containing electron-donating groups. In general, the electronic nature of the substituents had little influence on the product yields, but it did have considerable influence on the reaction times. Aromatic aldehydes substituted at para and meta positions with halogen atoms and electron-withdrawing groups (e.g. NO_2, Cl, Br) show more reactivity compared to those of electron-donating groups (e.g. CH_3, OCH_3). *Ortho*-substituted aldehydes showed longer reaction times than their *para*-counterparts. Furfural was also able to achieve high yield in a reasonably short time. In summary, all of the reactions took place in high to excellent yields.

Next, 4- hydroxy-2*H*- chromen-2- one was replaced with 4- hydroxy-5,6,7- trimethyl-2*H*- chromen-2- one and 4- hydroxy-6- methyl-2*H*- pyran-2-one as starting materials to synthesis a variety of pyrano[3,2-c] chromene and pyrano[4,3-b]pyran derivatives (**16d-31d**). Aryl aldehydes bearing electron-donating and electron-withdrawing groups successfully furnished the desired products **(16d-31d)** in good to excellent yields. However, substrates with electron withdrawing groups were more reactive than those of electron-donating groups.

The reaction mechanism consists of two stages. The first stage is knoevenagel condensation and the second stage gives the desired product. At first, the acidic hydrogen of malononitrile is taken by the basic factors of Zn_2SnO_4 and the resulting anion reacted with an aldehyde. At this stage, after the removal of a water molecule, 2-arylidenemalononitrile intermediate is formed. This process is known as the knoevenagel condensation reaction. In the next step, the desired product is obtained by the nucleophilic attack of 4-hydroxy-2*H*-chromen-2-one to the 2-arylidenemalononitrile intermediate followed by a cyclization reaction (Scheme 2).

Finally, the catalyst was recovered from the reaction medium and used for new reactions. Recycled catalyst shows a high potential in the catalytic process (Fig.5).



Scheme 2. Proposed mechanism for the synthesis of pyrano[3,2-c] chromenes.

4. Conclusions

The use of heterogeneous catalysts in chemical reactions is growing day by day due to their high performance and the possibility of recycling as well as the goals of green chemistry. Thus, in this study, a three-component preparation of pyrano[3,2-c] chromene and pyrano[4,3-b]pyran derivatives in mild conditions and the presence of Zn_2SnO_4 nanoparticles as a heterogeneous catalyst were examined. Various derivatives of aldehydes were used and products were synthesized in high yields. The advantages of this method is the use of a heterogeneous recoverable catalyst and the reaction being carried out under mild conditions.

Acknowledgments

We are thankful to the Najafabad Branch, Islamic Azad University research council for partial support of this research.

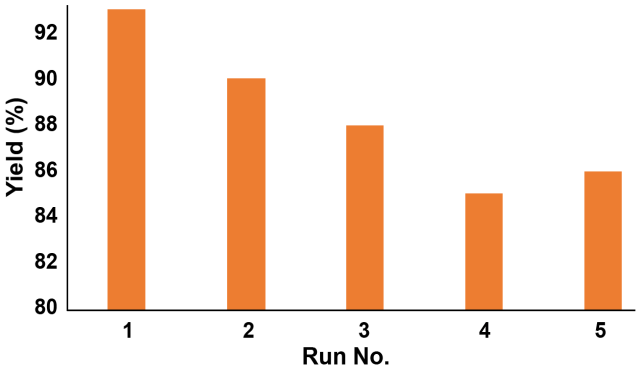
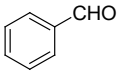
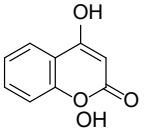
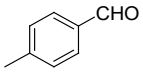
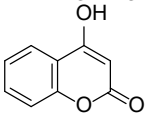
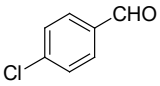
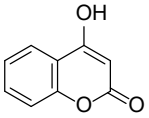
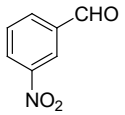
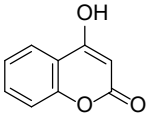
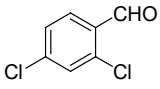
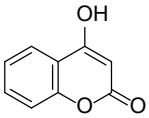
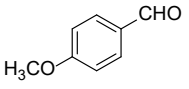
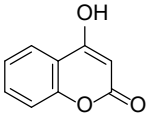
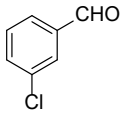
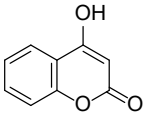
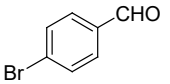
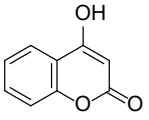
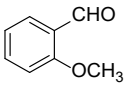
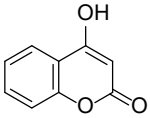
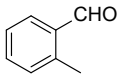
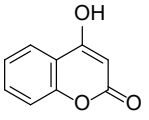
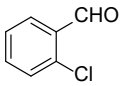
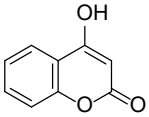
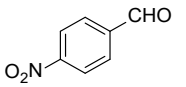
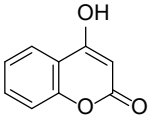
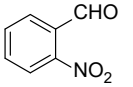
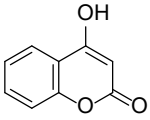
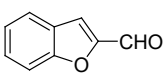
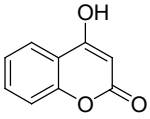
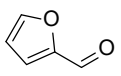
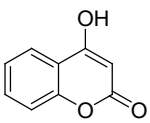


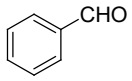
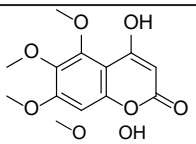
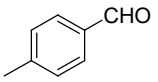
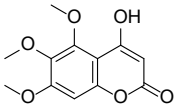
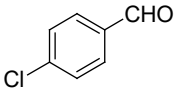
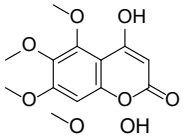
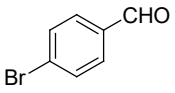
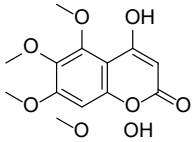
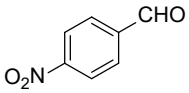
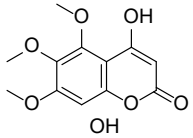
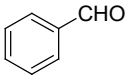
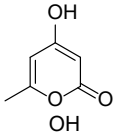
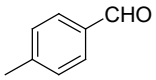
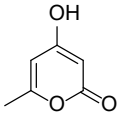
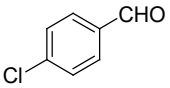
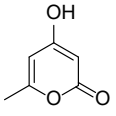
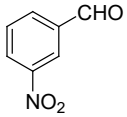
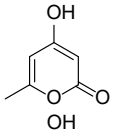
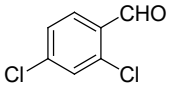
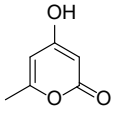
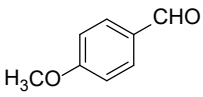
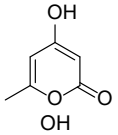
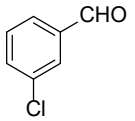
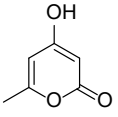
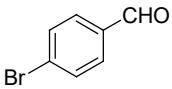
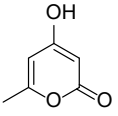
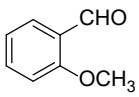
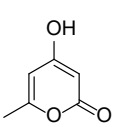
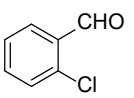
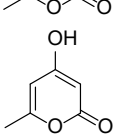
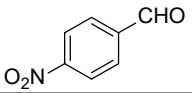
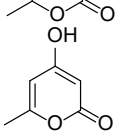
Fig. 5. Reusability of Zn_2SnO_4 nanoparticles.

Table 2. Preparation of of pyrano[3,2-c]chromene and pyrano[4,3-b]pyran derivatives using Zn_2SnO_4 nanoparticles.

Entry	Aldehyde	A	Time (h) / Yield (%)*	M.p. (°C) [Lit. m.p.][Ref.]
1d			3/93	257-259 [255-257][14]
2d			3.5/88	256-258 [255-257][14]
3d			2.5/92	261-263 [259-261][14]
4d			2/90	259-261 [262–264][14]
5d			3/82	259-261 [260-262][14]
6d			3.5/79	248-250 [248-250][14]
7d			2.5/90	246-248 [244-246][18]
8d			2.5/86	251-253 [249–251][14]
9d			4/71	237-239 [234–236][22]
10d			4/73	262-264 [259–261][22]
11d			3.3/79	275-277 [274-276][14]
12d			2.5/89	262-264 [261-263][14]
13d			3/77	260-262 [258-260][18]
14d			4/86	280-282 [279-281][15]
15d			5/79	253-255 [251-253][14]

* Isolated yield.

Table 2. Continued.

Entry	Aldehyde	A	Time (h) / Yield (%)*	M.p. (°C) [Lit. m.p.][Ref.]
16d			4/90	287-289 [New product]
17d			5/92	284-286 [New product]
18d			3.5/90	295-297 [New product]
19d			3.5/87	>300 [New product]
20d			3.5/89	>300 [New product]
21d			2.5/83	236-238 [236-238][21]
22d			3.5/85	229-231 [226-228][23]
23d			2.5/89	219-221 [219-221][23]
24d			2.5/90	238-240 [234-236][21]
25d			3/84	232-234 [230-231][24]
26d			3.5/82	210-212 [205-207][23]
27d			2.5/83	258-260 [255-256][24]
28d			2.5/87	222-224 [219-221][23]
29d			4/77	239-241 [242-244][23]
30d			3/72	257-259 [258-260][23]
31d			2.5/90	219-221 [216-218][21]

* Isolated yield.

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