

Tin Pyrophosphate (SnP_2O_7): As a Novel Heterogeneous and Highly Efficient Catalyst for the One Pot-Three Component Synthesis of Tetrahydrobenzo[b]Pyran and Dihydropyran[c]Chromene Derivatives

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Abstract: The tin pyrophosphate (SnP_2O_7) was synthesized from the modification of Mono-Ammonium Phosphate (MAP) by tin chloride (SnCl_2). This solid was used as a heterogeneous catalyst for the one-pot multicomponent synthesis of tetrahydrobenzo[b]pyran and dihydropyrano[3,2-c]chromenes derivatives under green reaction conditions. This synthetic protocol offers several advantages such as short reaction times (8-15 min), high product yields (85-97%), easy work-up procedure, and easy catalyst separation from the reaction mixture. In addition, SnP_2O_7 can be recycled for up to five cycles without a significant loss of catalytic reactivity. The XRD and IR spectra confirm the stability and heterogeneity of SnP_2O_7 in the reaction medium even after its reuse.

KEYWORDS: Tin pyrophosphate; Heterogeneous catalyst; One-pot three-component synthesis; Tetrahydrobenzo [b]pyran; Dihydropyrano[3,2-c]chromene.

INTRODUCTION

Recently, multicomponent reactions (MCRs) have gained considerable attention in combinatorial chemistry. Indeed, they combine more than two reagents in one step to prepare a single product [1-3]. In addition, MCRs increase the simplicity and efficiency of conventional organic transformations [4-6]. This reaction type is commonly applied for the synthesis of poly-functionalized heterocyclic compounds [7-9], which are known as significant structural

units present in many medicinal and biologically active molecules. Nitrogen- and oxygen-containing rings are two of the most important subclasses of these groups of compounds, which are widely found in the skeleton of pharmaceutical and biologically active materials [10-14]. The tetrahydrobenzo [b]pyran and dihydropyrano[c]chromenes were considered among the important heterocyclic compounds that present interesting pharmacological and biological activities [15-19].

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Indeed, they were applied as antibacterial [20], antifungal [20], anti-cancer [21], antioxidant [22], antiviral [23], antimalarial [24], and antidepressant [25]. In addition, tetrahydrobenzo[b]pyran is widely used in the production of fluorescent dyes [26], fluorescent pigments [27, 28], cosmetics [29], and biodegradable agrochemicals and photoactive materials [30]. Due to the importance of tetrahydrobenzo[b]pyran and dihydropyrano[c]chromenes derivatives several methods were developed for their synthesis in the absence and presence of different catalysts [31]. Indeed, in the absence of catalysts, their synthesis showed long reaction times, low yields, and severe reaction conditions [32-35]. These drawbacks have led many researchers to carry out the synthesis of tetrahydrobenzo[b]pyran and dihydropyrano[c]chromenes derivatives in the presence of different homogeneous and heterogeneous catalysts such as L-arginine modified graphene oxide [36], magnetic nanoparticle $\text{Fe}_3\text{O}_4@ \text{Sal}@ \text{Cu}$ [37], nanostructured coumarin-based cobalt complex $[\text{Co}(\text{MCG})(\text{H}_2\text{O})_3]$ [38], WELPSA [39], Nano- SiO_2/DBN [40], HAHS [41], MNP@PEG-ImOH [42], silica-supported DTP/ SiO_2 [43], $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ [44], nano- $\text{CuFe}_2\text{O}_4@ \text{SO}_3\text{H}$ [45], STGP@CA [46], RuD@CA [47], PACMC [48]. These synthesis methods have their benefits, but several of them suffer limitations, such as using expensive and harmful catalysts containing halide and toxic metals, low product yields, long reaction times, complicated purification methods, and tedious work-up procedures. In this context, phosphates have attracted extensive attention as eco-friendly catalysts applied in organic transformations due to their unique properties, such as large surface-to-volume ratio, non-flammability, high potential for recyclability, ease of recovery, and thermal stability [49-51]. As a continuation of the previous works realized by our team of researchers [52-61] based on the development of sustainable and green routes for synthesizing important organic molecules *via* the application of efficient and green phosphate-based catalysts. This paper reports a simple preparation method for SnP_2O_7 from mono-ammonium phosphate (MAP) modification by tin chloride (SnCl_2) [62]. The prepared catalyst SnP_2O_7 has been applied in the synthesis of tetrahydrobenzo[b]pyran and dihydropyrano[c]chromenes from the condensation of various aromatic aldehydes, malononitrile, dimedone, and 4-hydroxycoumarin.

The advantage of this work relies on the simplicity and efficiency of the method used based on the application of a recyclable, non-harmful, and low-cost catalyst.

In addition, this process leads to obtaining derivatives of tetrahydrobenzo[b]pyran and dihydropyrano[c]chromenes with excellent yield in a short reaction time under green reaction conditions. Therefore, this method can contribute to the development of green chemistry.

EXPERIMENTAL SECTION

Materials and instrumentation

The reagents and solvents were purchased from SIGMA ALDRICH. For all reactions, the purity of the tetrahydrobenzo[b]pyrans and dihydropyrano[3,2-c]chromene was monitored by thin-layer chromatography (TLC) using aluminum layers coated with F254 silica gel (Merck) plates. The melting points were recorded on a hot Kofler. In addition, ^1H NMR and ^{13}C NMR spectra were recorded in Bruker spectrometer in the presence of DMSO-d_6 at 300 and 75 MHz, respectively.

Preparation of SnP_2O_7

SnP_2O_7 was prepared by modification of mono-ammonium phosphate (MAP) fertilizer (23,1 g) with tin chloride (SnCl_2) (19 g). SnP_2O_7 was characterized by X Ray Diffraction (XRD), which confirms that the solid is indexed in the cubic system, using the space group Pa-3, with lattice parameters $a=b=c= 7,97 \text{ \AA}$. Furthermore, the energy dispersive X-ray analysis (EDX) and IR of SnP_2O_7 confirm the presence of its constituents such as phosphorus, oxygen, and tin [62].

General Procedure for tetrahydrobenzo[b]pyran derivatives synthesis

A mixture of malononitrile (1 mmol, 0.66 mg), aromatic aldehyde (1 mmol, 1.06 mg), and dimedone (1 mmol, 1.40 mg) in the presence of SnP_2O_7 catalyst (2.1 mol%, 6 mg) was dissolved in ethanol (3 mL) at reflux. TLC was used to check the progress and completion of the reaction (EtOAc/ *n*-hexane, 1:1). After completion of the reaction, the mixture was cooled at room temperature. Then, dichloromethane (5 mL) was added to the mixture to separate the catalyst by simple filtration; the filtrate was evaporated until the precipitates were formed. The product was purified by recrystallization with ethanol to obtain the tetrahydrobenzo[b]pyran derivatives. The catalyst may be reactivated later by washing with ethanol to remove the products on its surface and then dried before reusing.

General Procedure for dihydropyrano[c]chromene derivatives synthesis

A molar ratio mixture of aromatic aldehyde (1 mmol, 1.06 mg), malononitrile (1 mmol, 0.66 mg), and 4-hydroxycoumarin (1 mmol, 1.62 mg) in the presence of SnP_2O_7 (1.7%, 5 mg) as catalyst was reacted in EtOH (3 mL) at reflux. The completion of the reaction was monitored by thin-layer chromatography. After consuming the starting material, the catalyst was separated by filtration, and EtOH was added. Finally, recrystallization with EtOH was applied to afford the pure products. The products obtained were characterized by comparing their melting points and their ^1H and ^{13}C NMR spectroscopic data with those reported in the literature, which show a good agreement.

Spectral data of tetrahydrobenzo[b]pyran and 3,4-dihydropyrano[c]chromene derivatives

2-amino-3-cyano-7,7-dimethyl-5-oxo-4-(4-chlorophenyl)-5,6,7,8-tetrahydrobenzo[b]pyran 4a:

^1H NMR (300 MHz, DMSO-d_6 , δ , ppm): 7.35 (d, 2H, Ar-H), 7.16 (d, 2H, Ar-H), 7.07 (s, 2H, NH_2), 4.20 (s, 1H, CH), 2.54 (s, 2H, CH_2), 2.27 (d, 1H, CH_2), 2.11 (d, 1H, CH_2), 1.04 (s, 3H, CH_3), 0.95 (s, 3H, CH_3). ^{13}C NMR (75 MHz, DMSO-d_6): δ 196.15, 162.39, 158.41, 143.51, 132.01, 129.59, 128.23, 119.21, 113.71, 112.30, 59.13, 50.41, 35.06, 32.24, 28.92, 27.18.

2-amino-3-cyano-7,7-dimethyl-5-oxo-4-phenyl-5,6,7,8-tetrahydrobenzo[b]pyran 4b:

^1H NMR (300 MHz, DMSO-d_6 , δ , ppm): 7.28-6.97 (m, 7H, Ar-H et NH_2), 4.18 (s, 1H, CH), 2.49 (s, 2H, CH_2), 2.22 (d, 1H, CH_2), 2.09 (d, 1H, CH_2), 1.04 (s, 3H, CH_3), 0.96 (s, 3H, CH_3). ^{13}C NMR (75 MHz, DMSO-d_6): δ 196.10, 162.42, 158.45, 143.37, 128.26, 127.10, 126.52, 120.24, 113.18, 58.57, 50.47, 35.41, 32.26, 28.87, 27.15.

2-amino-3-cyano-7,7-dimethyl-5-oxo-4-(4-methylphenyl)-5,6,7,8-tetrahydrobenzo[b]pyran 4c:

^1H NMR (300 MHz, DMSO-d_6 , δ , ppm): 7.10-6.99 (m, 6H, Ar-H et NH_2), 4.12 (s, 1H, CH), 2.51 (s, 2H, CH_2), 2.26 (d, 1H, CH_2), 2.24 (s, 3H, CH_3), 2.08 (d, 1H, CH_2), 1.04 (s, 3H, CH_3), 0.95 (s, 3H, CH_3). ^{13}C NMR (75 MHz, DMSO-d_6): 196.14, 162.77, 158.89, 142.30, 136.06, 129.24, 127.49, 120.11, 113.35, 58.83, 50.51, 35.48, 32.20, 28.94, 27.19, 21.06.

2-amino-3-cyano-7,7-dimethyl-5-oxo-4-(4-methoxyphenyl)-5,6,7,8-tetrahydrobenzo[b]pyran 4d:

^1H NMR (300 MHz, DMSO-d_6 , δ , ppm): 7.06-6.80 (m, 4H, Ar-H), 6.93 (s, 2H, NH_2), 4.12 (s, 1H, CH), 3.72 (s, 3H, OCH_3), 2.56 (d, 1H, CH_2), 2.42 (d, 1H, CH_2), 2.30 (d, 1H, CH_2), 2.07 (d, 1H, CH_2), 1.02 (s, 3H, CH_3), 0.94 (s, 3H, CH_3). ^{13}C NMR (75 MHz, DMSO-d_6): δ 195.66, 162.10, 160.42, 158.38, 157.86, 136.81, 133.31, 128.16, 119.81, 113.62, 112.96, 58.51, 54.97, 49.95, 34.73, 31.72, 28.35, 26.74.

2-amino-3-cyano-7,7-dimethyl-5-oxo-4-(4-nitrophenyl)-5,6,7,8-tetrahydrobenzo[b]pyran 4e:

^1H NMR (300 MHz, DMSO-d_6 , δ , ppm): 8.17 (d, 2H, Ar-H), 7.44 (d, 2H, Ar-H), 7.22 (s, 2H, NH_2), 4.37 (s, 1H, CH), 2.54 (s, 2H, CH_2), 2.26 (d, 1H, CH_2), 2.11 (d, 1H, CH_2), 1.04 (s, 3H, CH_3), 0.96 (s, 3H, CH_3). ^{13}C NMR (75 MHz, DMSO-d_6): δ 196.21, 163.59, 159.03, 152.79, 146.71, 129.10, 124.17, 119.84, 112.17, 57.38, 50.30, 36.10, 32.31, 28.40, 27.39.

2-amino-3-cyano-7,7-dimethyl-5-oxo-4-(4-methylamino phenyl)-5,6,7,8 tetrahydrobenzo[b]pyran 4f:

^1H NMR (300 MHz, DMSO-d_6 , δ , ppm): 6.97-6.61 (m, 6H, Ar-H et NH_2), 4.04 (s, 1H, CH), 2.83 (s, 6H, $\text{N}(\text{CH}_3)_2$), 2.50 (s, 2H, CH_2), 2.24 (d, 1H, CH_2), 2.07 (d, 1H, CH_2), 1.03 (s, 3H, CH_3), 0.95 (s, 3H, CH_3). ^{13}C NMR (75 MHz, DMSO-d_6): δ 196.15, 162.32, 158.80, 149.68, 133.01, 128.20, 120.46, 113.72, 112.29, 59.34, 50.51, 40.22, 39.37, 35.05, 32.24, 28.98, 27.19.

2-amino-3-cyano-7,7-dimethyl-5-oxo-4-(3,4,5-trimethoxy phenyl)-5,6,7,8-tetrahydrobenzo[b]pyran 4g:

^1H NMR (300 MHz, DMSO-d_6 , δ , ppm): 7.01 (s, 2H, Ar-H), 6.38 (s, 2H, NH_2), 4.14 (s, 1H, CH), 3.72 (s, 9H, 3OCH_3), 2.53 (s, 2H, CH_2), 2.29 (d, 1H, CH_2), 2.14 (d, 1H, CH_2), 1.05 (s, 3H, CH_3), 1.02 (s, 3H, CH_3). ^{13}C NMR (75 MHz, DMSO-d_6): δ 196.24, 163.28, 158.81, 153.21, 140.98, 136.51, 120.22, 112.78, 104.54, 60.37, 58.74, 56.22, 50.43, 36.07, 32.21, 28.87, 27.86.

2-amino-3-cyano-7,7-dimethyl-5-oxo-4-(4-bromophenyl)-5,6,7,8-tetrahydrobenzo[b]pyrane 4h:

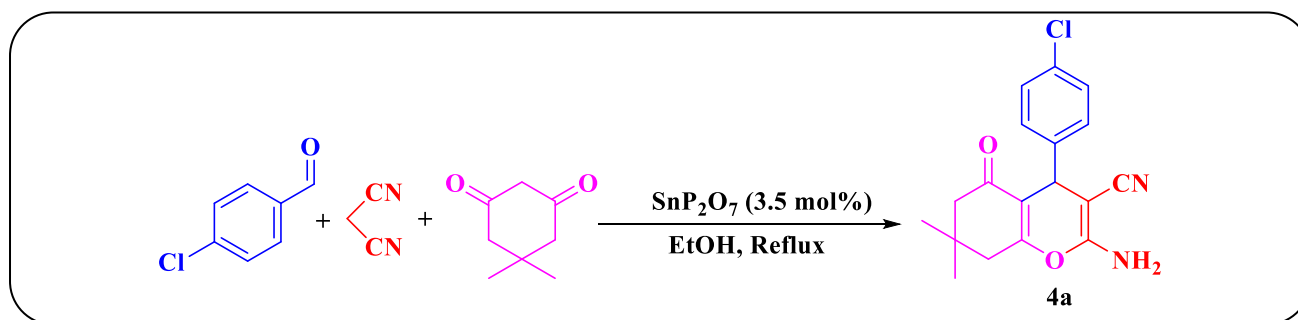
^1H NMR (300 MHz, DMSO-d_6 , δ , ppm): 7.08-7.41 (m, 4H, Ar-H), 7.05 (s, 2H, NH_2), 4.18 (s, 1H, CH), 2.51 (d, 1H, CH_2), 2.41 (d, 1H, CH_2), 2.23 (d, 1H, CH_2), 2.08 (d, 1H, CH_2), 1.02 (s, 3H, CH_3), 0.94 (s, 3H, CH_3). ^{13}C NMR (75

Table 1: Catalytic test on the model reaction^a

Entry	Catalyst	Time (min)	Yield (%) ^b
1	–	120	Trace
2	SnP ₂ O ₇	10	90
3	SnCl ₂	120	30
4	MAP	40	87

^a Reaction conditions: 4-chlorobenzaldehyde (1 mmol), malononitrile (1 mmol), dimedone (1 mmol), catalyst (3.5 mol%), EtOH (3 mL), reflux.

^b Isolated yields.



MHz, DMSO-*d*₆): δ 195.67, 162.60, 158.41, 144.12, 131.17, 129.45, 119.57, 119.53, 112.20, 57.66, 49.90, 35.14, 31.76, 28.27, 26.82.

2-Amino-4-(4-chlorophenyl)-4,5-dihydro-5-oxopyrano[3,2-c]chromene-3-carbonitrile 6a:

¹H NMR (300 MHz, DMSO-*d*₆, delta, ppm): 7.92 (1H, d, Ar-H), 7.71 (1H, t, Ar-H), 7.48 (1H, t, Ar-H), 7.43 (1H, d, Ar-H), 7.40 (2H, s, NH₂), 7.37-7.30 (4H, m, Ar-H), 4.50 (1H, s, CH). ¹³C NMR (75 MHz, DMSO-*d*₆): δ 159.94, 158.54, 154.05, 152.69, 142.73, 133.39, 132.25, 130.05, 129.14, 125.06, 123, 119.40, 116.97, 113.43, 104.04, 58.31.

2-Amino-4-phenyl-4,5-dihydro-5-oxopyrano[3,2-c]chromene-3-carbonitrile 6b:

¹H NMR (300 MHz, DMSO-*d*₆, delta, ppm): 7.91 (1H, d, Ar-H), 7.70 (1H, t, Ar-H), 7.49 (1H, t, Ar-H), 7.45 (1H, d, Ar-H), 7.42 (2H, s, NH₂), 7.35-7.24 (5H, m, Ar-H), 4.45 (1H, s, CH). ¹³C NMR (75 MHz, DMSO-*d*₆): δ 160, 158.46, 153.89, 152.61, 143.80, 133.38, 128.99, 128.10, 127.59, 125.13, 122.94, 119.70, 117.03, 113.43, 104.48, 58.48.

2-Amino-4-p-tolyl-4,5-dihydro-5-oxopyrano[3,2-c]chromene-3-carbonitrile 6c:

¹H NMR (300 MHz, DMSO-*d*₆, delta, ppm): 7.91 (1H, d, Ar-H), 7.72 (1H, t, Ar-H), 7.50-7.42 (2H, m, Ar-H), 7.38 (2H, s, NH₂), 7.17-7.10 (4H, m, Ar-H), 4.40 (1H, s, CH),

2.26 (3H, s, CH₃). ¹³C NMR (75 MHz, DMSO-*d*₆): δ 159.97, 158.41, 153.72, 152.57, 140.87, 136.75, 133.32, 129.53, 127.99, 125.10, 122.91, 119.72, 117, 113.43, 104.61, 58.60, 21.09.

2-Amino-4-(4-nitrophenyl)-4,5-dihydro-5-oxopyrano[3,2-c]chromene-3-carbonitrile 6d:

¹H NMR (300 MHz, DMSO-*d*₆, delta, ppm): 8.17 (1H, d, Ar-H), 7.91 (1H, d, Ar-H), 7.77 (1H, t, Ar-H), 7.74 (1H, t, Ar-H), 7.57 (2H, s, NH₂), 7.55-7.46 (4H, m, Ar-H), 4.68 (1H, s, CH). ¹³C NMR (75 MHz, DMSO-*d*₆): δ 160.05, 158.52, 154.43, 152.75, 151.23, 147.09, 133.66, 129.65, 125.23, 124.20, 123.06, 119.35, 117.11, 113.38, 103.28, 57.24.

2-Amino-4-(4-dimethylaminophenyl)-4,5-dihydro-5-oxopyrano[3,2-c]chromene-3-carbonitrile 6e:

¹H NMR (300 MHz, DMSO-*d*₆, delta, ppm): 7.83 (1H, d, Ar-H), 7.72 (1H, t, ArH), 7.50-7.42 (2H, m, Ar-H), 7.19 (2H, s, NH₂), 7.08-6.65 (4H, m, Ar-H), 4.33 (1H, s, CH), 2.86 (6H, s, N (CH₃)₂). ¹³C NMR (75 MHz, DMSO-*d*₆): δ 159.97, 158.44, 154.88, 152.54, 134.04, 131.41, 128.63, 125.05, 122.89, 119.73, 116.96, 113.56, 105.22, 59.27.

2-Amino-4-(4-bromophenyl)-4,5-dihydro-5-oxopyrano[3,2-c]chromene-3-carbonitrile 6f:

¹H NMR (300 MHz, DMSO-*d*₆, delta, ppm): 7.93(1H, d, ArH), 7.73 (1H, t, Ar-H), 7.68 (1H, t, Ar-H), 7.52-7.48 (3H,

Table 2: Solvent effect study on the model reaction^a

Entry	Solvent	Yield (%) ^b
1	EtOH	90
2	MeOH	86
3	Dioxane	60
4	Acetonitrile	83
5	Dichloromethane	75
6	EtOH/water	82
7	Solvent-free	Trace

^a Reaction conditions: 4-chlorobenzaldehyde (1 mmol), malononitrile (1 mmol), dimedone (1 mmol), SnP₂O₇ (3.5 mol%), solvent (3 mL), reflux.

^b Isolated yields.

Table 3: Study of the influence of the catalyst amount in the model reaction^a

Entry	SnP ₂ O ₇ (mol %)	Yield (%) ^b
1	0.4	85
2	0.7	89
3	1.1	90
4	1.4	93
5	1.7	94
6	2.1	97
7	2.5	97
8	2.7	95
9	3.1	92
10	3.5	90

^a Reaction conditions: 4-chlorobenzaldehyde (1 mmol), malononitrile (1 mmol), dimedone (1 mmol), SnP₂O₇ (x mol%), EtOH (3 mL), reflux.

^b Isolated yields.

m, Ar-H), 7.45(2H, s, NH₂), 7.26 (2H, d, Ar-H), 4.48 (1H, s, CH). ¹³C NMR (75 MHz, DMSO-d₆): δ 159.95, 158.53, 154.07, 152.70, 143.17, 133.43, 131.82, 130.42, 125.09, 123.02, 120.70, 119.39, 117, 113.43, 103.97, 58.22.

ReSULTS AND DISCUSSION

Application of SnP₂O₇ catalyst in tetrahydrobenzo [b]pyran derivatives synthesis

The SnP₂O₇, was used as a heterogeneous catalyst for tetrahydrobenzo[b]pyran derivatives synthesis. The reaction performed by the condensation of 4-chlorobenzaldehyde, malononitrile, and dimedone in ethanol at reflux was chosen as the model reaction (Scheme 1).

In order to show the catalytic efficiency of SnP₂O₇ prepared from MAP and SnCl₂, the reaction was carried out in the absence of the catalyst and in the presence of SnCl₂, MAP, and SnP₂O₇. Product yields and reaction times are listed in Table 1.

The comparison of the product yield and reaction time (Table 1) proves that in the absence of the catalyst the synthesis of product 4a is kinetically very slow. The reaction gave only product traces even after 120 min, whereas the presence of catalysts decreased the reaction time and increased the product yield. The results obtained in the presence of SnP₂O₇ as a catalyst show a significant time saving compared to MAP or SnCl₂. Indeed, the desired product was formed rapidly after only 10 minutes with a good yield (90%), which confirms the efficiency of SnP₂O₇ in this synthesis.

The effect of the solvent was studied by performing the model reaction in the presence of 3.5 mol% of SnP₂O₇ in various solvents at reflux. The obtained results are collated in Table 2.

The results (Table 2) show that the model reaction realized in the absence of the solvent led only to traces of product 4a, while, the low yield of the product was obtained in the presence of apolar solvents dioxane, and dichloromethane. In the case of the reaction carried out in the presence of polar solvents such as methanol, acetonitrile, and a mixture of ethanol-water, good yields were obtained. The reaction was carried out more easily in ethanol, which allows the separation of charges, thus facilitating the formation of product 4a with an excellent yield. Therefore, ethanol is the most suitable solvent for the synthesis of product 4a.

In order to determine the optimal reaction conditions, the effect of the amount of catalyst was also studied by varying the mass of SnP₂O₇ between 0.4 and 3.5 mol%. The results are summarized in Table 3.

The results (Table 3) show that good yields were obtained when 2.1 mol% of SnP₂O₇ was used. However, it is remarkable that the yield decreases for higher catalyst amounts, which can be explained by the dispersion of the reagents at the catalyst's surface. From these results, we can conclude that this synthesis method takes into consideration the principles of green chemistry. therefore, it can minimize the risk accompanied by the use of a large amount of catalysts.

The generalization of the reaction was studied under

Table 4: Generalization of tetrahydrobenzo[b]pyran synthesis^a

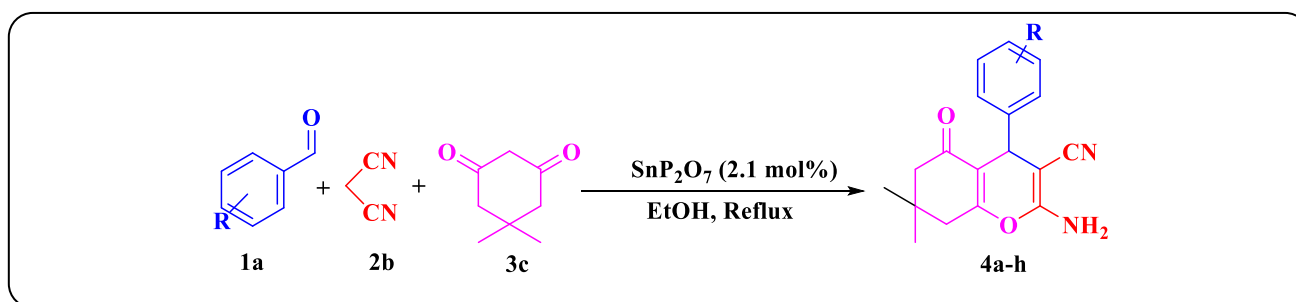
Entry	R	Time (min)	Yield (%) ^b	TON ^c	TOF (min^{-1}) ^d	mp (°C) Found	mp (°C) Reported
4a	4-Cl	10	97	47530	4753	216-218	216-218 [63]
4b	H	10	96	47040	4704	234-236	234-236 [63]
4c	4-CH ₃	10	93	45570	4557	220-222	220-222 [64]
4d	4-OCH ₃	10	87	42630	4263	202-204	202-204 [63]
4e	4-NO ₂	10	91	44590	4459	180-182	179-182 [63]
4f	4-N(CH ₃) ₂	15	90	44100	2940	210-212	210-211 [63]
4g	3,4,5-OCH ₃	20	85	41650	2082.5	246-248	247-249 [65]
4h	4-Br	15	88	43120	2874.6	213-215	213-215 [64]

^a Reaction conditions: aromatic aldehyde (1 mmol), malononitrile (1 mmol), dimedone (1 mmol), SnP_2O_7 (2.1 mol%), EtOH (3 mL), reflux.

^b Isolated yields.

^c TON (turnover number) = moles of desired product formed/moles of catalyst.

^d TOF (turnover frequency) = turnover number (TON)/hours.

**Scheme 2: Synthesis of tetrahydrobenzo[b]pyran derivatives**

the determined optimal conditions. For this, various aromatic aldehydes were used (Scheme 2). Table 4 collects the results obtained for each aldehyde derivative.

Table 4 shows that compounds 4a-h were obtained with good to excellent yields (85-97%) in short reaction times (10-20 min) and high values of TON and TOF were obtained by using a variety of aromatic aldehydes possessing different substituents. Indeed, the aromatic aldehydes with electron-donating groups (4-CH₃, 4-N(CH₃)₂, 4-OCH₃, 3,4,5-OCH₃) give desired products with good yields (Table 4, entries 4c, 4d, 4f, 4j). When the aromatic aldehyde having an electron-withdrawing group (4-NO₂) is used, the reaction gives the product 4e with a yield of 91%. For the aldehyde having a halogen functionality (4-Cl, 4-Br), it is shown that the product was obtained with a yield of 97% after 10 min of reaction and 88% in 15 min as a time of reaction respectively.

The role of tin diphosphate (SnP_2O_7) in the synthesis

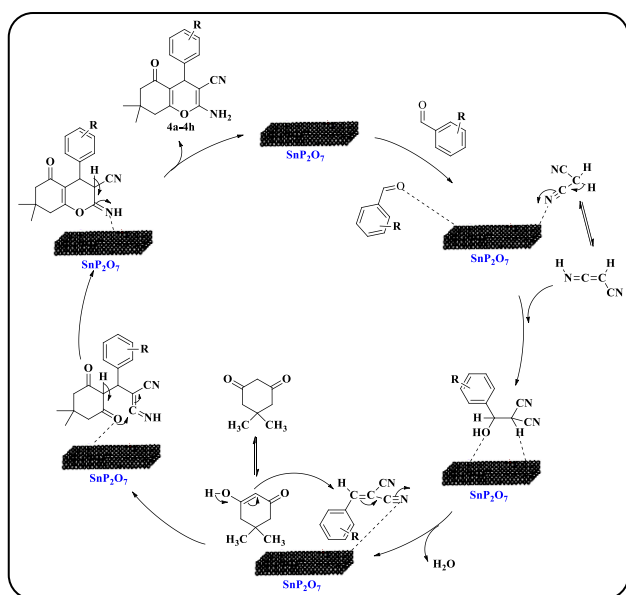
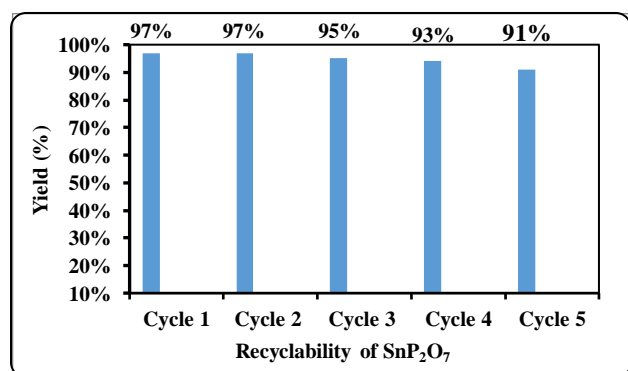
of tetrahydrobenzo[b]pyran derivatives can be explained by a mechanism involving the condensation of aromatic aldehyde, malononitrile, and dimedone where SnP_2O_7 acts as a bifunctional catalyst due to its acidic and basic sites, $\text{P}_2\text{O}_7^{4-}$, PO_4^{3-} and Sn^{2+} [66,67]. We suggest that the condensation reaction occurs at acidic and basic sites of the SnP_2O_7 catalyst. The plausible mechanism for this reaction was described in Scheme 3.

First, SnP_2O_7 activates the carbonyl group of the aromatic aldehydes by the acidic sites, followed by a nucleophilic attack of malononitrile and dimedone and then cyclization to give the products (4a-h).

To confirm the long durability of SnP_2O_7 , a study of its reuse was realized. After the first reaction was performed under optimal conditions, the catalyst was recovered by simple filtration, washed with dichloromethane, dried in the oven, and reused in the same reaction. The results are shown in Fig. 1.

Table 5: Comparison between some catalysts described in the literature and SnP₂O₇ catalyst

Entry	Catalyst	Conditions	Yield (%)	Ref
1	γ -CD	5 mol%, chlorure de choline, 60°C, 28 min	94	[68]
2	TMDPS	0.05 mmol, sans solvant, t.a, 30 min	96	[69]
3	Zn(L-proline) ₂	20 mol%, EtOH, reflux, 3h	89	[70]
4	FSM-16/AEPC-SO ₃ H	6 mol%, EtOH/H ₂ O, 80°C, 30 min	89	[71]
5	MMWCNTs-D-(CH ₂) ₄ -SO ₃ H	5 mg, EtOH, reflux, 12 min	93	[72]
6	[H ₂ -DABCO] [H ₂ PO ₄] ₂	5 mg, EtOH/H ₂ O, reflux, 15 min	95	[73]
8	SnP ₂ O ₇	2.1 mol%, EtOH, reflux, 10 min	96	Present work

Scheme 3: Proposed mechanism for tetrahydrobenzo[b]pyran synthesis using SnP₂O₇ as a catalystFig. 1: Recyclability of SnP₂O₇ in the synthesis of product 4a

The results obtained (Fig. 1) show that the yield of product **4a** remains practically unchanged even after five subsequent reuses, which confirms the long-term stability of SnP₂O₇.

Many methods were developed for carrying out the tetrahydrobenzo[b]pyran reaction. The efficiency of our catalyst was compared with those of other catalysts cited in the literature. Table 5 presents the reaction conditions, the yields, and the reaction time for each catalyst.

The comparison of the catalytic activity of SnP₂O₇ with other catalysts reported in the literature confirms its efficiency. Indeed, the application of SnP₂O₇ allows obtaining the desired product with excellent yield in a short reaction time. Therefore, this simple, efficient, and ecological method can be considered an improvement of other procedures described previously.

Application of SnP₂O₇ catalyst in 3,4-dihydropyrano[c]chromene derivatives synthesis

The catalytic activity of SnP₂O₇ was also evaluated on the 3,4-dihydropyrano[c]chromenes derivatives synthesis (Scheme 4). 4-chlorobenzaldehyde, malononitrile, and 4-hydroxycoumarin were chosen as the model reaction to optimize the reaction conditions (Table 6).

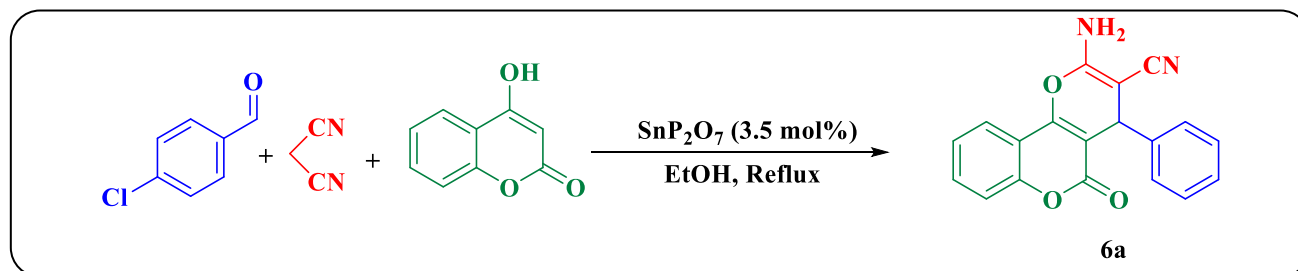
According to the obtained results, it is shown that the reaction performed in the absence of a catalyst produced only traces of **6a**, even after 120 min (Table 6, entry 1). When the MAP was added as a catalyst, the yield of product **6a** was about 84 % in only 30 min (Table 6, entry 2). In the case of the use of SnCl₂ as a catalyst, the reaction allows obtaining only 41 % yield of the product **6a** even after 120 min of reaction (Table 6, entry 3). However, when the reaction was performed in the presence of 3.5 mol% of SnP₂O₇, the reagents were consumed quickly (8 min), providing a high yield of product **6a** (87 %, Table 2, entry 4). For this, SnP₂O₇ was considered the suitable catalyst for this reaction.

Table 6: The effect of solvent nature and catalyst amount on time and yield of 3,4-dihydropyrano[c]chromenes derivatives synthesis^a

Entry	Amount of catalyst (mol%)	Solvent (3 mL)	Temperature (°C)	Time (min)	Yield(%) ^b
1	-	EtOH	Reflux	120	Trace
2	MAP (3.5)	EtOH	Reflux	30	84
3	SnCl_2 (3.5)	EtOH	Reflux	120	41
4	SnP_2O_7 (3.5)	EtOH	Reflux	8	87
5	SnP_2O_7 (3.5)	MeOH	Reflux	8	83
6	SnP_2O_7 (3.5)	Dioxane	Reflux	8	65
7	SnP_2O_7 (3.5)	CH_3CN	Reflux	8	78
8	SnP_2O_7 (3.5)	Dichloromethane	Reflux	8	70
9	SnP_2O_7 (3.5)	EtOH/water	Reflux	8	88
10	SnP_2O_7 (3.5)	Solvent-free	Reflux	8	Trace
11	SnP_2O_7 (3.1)	EtOH	Reflux	8	88
12	SnP_2O_7 (2.5)	EtOH	Reflux	8	91
13	SnP_2O_7 (2.1)	EtOH	Reflux	8	93
14	SnP_2O_7 (1.7)	EtOH	Reflux	8	95
15	SnP_2O_7 (1.4)	EtOH	Reflux	8	92
16	SnP_2O_7 (0.7)	EtOH	Reflux	8	89

^a Reaction conditions: 4-chlorobenzaldehyde (1 mmol), malononitrile (1 mmol), 4-hydroxycoumarin (1 mmol), SnP_2O_7 (x mol%), solvent (3 mL), reflux.

^b Isolated yields.

**Scheme 4: Synthesis of 3,4-dihydropyrano[c]chromenes derivatives**

The optimal solvent for the reaction was determined by using different solvents (3 mL), such as polar protic solvents (EtOH, MeOH), polar aprotic solvents (CH_3CN), nonpolar (dioxane, dichloromethane). The reaction was also realized without solvent in the presence of 3.5 mol% of SnP_2O_7 at reflux. Table 6 shows that the reaction carried out in polar aprotic solvents gives the desired product **6a** with moderate yields (Table 6, entry 8). However, the reaction realized in nonpolar solvents (Table 6, entries 6, 8) leads to a low yield of product **6a**. Therefore, the optimal solvent for this synthesis is ethanol (Table 6, entry 4).

The optimal amount of catalyst was also determined. For this, the model reaction was performed in the presence of different amounts of SnP_2O_7 . From the obtained results (Table 6), it is shown that the yields depend on the amount

of catalyst; the best yield of the reaction is 95%, corresponding to the optimal amount of SnP_2O_7 (1.7 mol%) (Table 6, entry 14). A large catalyst amount leads to a decrease in yields, which can be explained by the dispersion of the reagents on the catalyst surface.

The optimal reaction conditions were applied in the synthesis of a large series of product derivatives of 3,4-dihydropyrano[c]chromenes by using different groups of aromatic aldehydes (Scheme 5). The results are shown in Table 7.

The results show that the synthesized product was obtained by excellent yield in a short reaction time with high calculated values of TON and TOF whatever the aldehyde nature (donor/acceptor) used. Indeed, the substituting group of aldehyde does not significantly affect the obtained results. Therefore, one can deduce that

Table 7: Generalization of 3,4-dihydropyrano[c]chromenes derivatives synthesis ^a

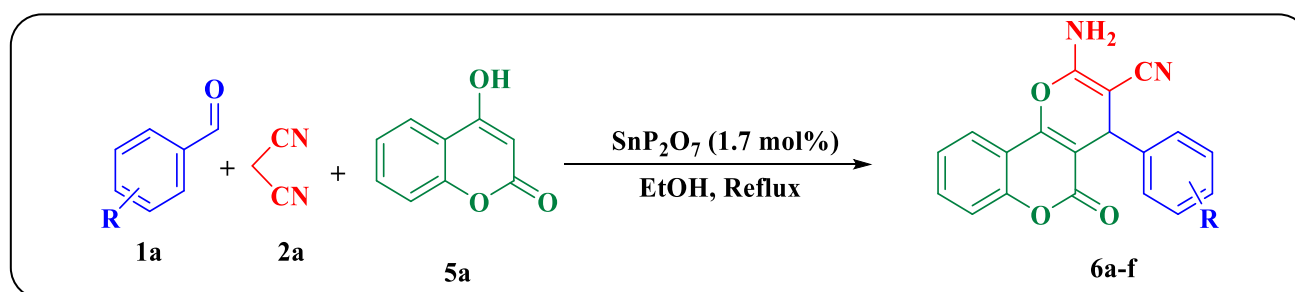
Entry	R	Time (min)	Yield (%) ^b	TON ^c	TOF (min ⁻¹) ^d	mp (°C) Found	mp (°C) Reported
6a	4-Cl	8	95	55860	6982.5	258-260	258-260 [74]
6b	H	8	95	55860	6982.5	256-258	256-258 [75]
6c	4-CH ₃	8	94	55272	6909	251-253	250-252 [74]
6d	4-NO ₂	10	93	54684	5468.4	258-260	258-260 [75]
6e	4-N(CH ₃) ₂	10	91	53508	5350.8	>260	266-268 [74]
6f	4-Br	8	90	52920	6615	247-249	247-249 [75]

^a Reaction conditions: aromatic aldehyde (1 mmol), malononitrile (1 mmol), 4-hydroxycoumarin (1 mmol), SnP₂O₇ (1.7 mol%), EtOH (3 mL), reflux.

^b Isolated yields.

^c TON (turnover number) = moles of desired product formed/moles of catalyst.

^d TOF (turnover frequency) = turnover number (TON) /hours.



the catalyst presents an interesting catalytic activity in 3,4-dihydropyrano[c] chromene derivatives synthesis.

The suggested mechanism for 3,4-dihydropyrano[c] chromenes derivatives synthesis in the presence of SnP₂O₇ as catalyst was given in Scheme 6.

The activation of the C-H bond of malononitrile leads to the attack of the activated carbonyl group of the aldehyde to give gem-dicyanoethylene III. This undergoes a nucleophilic attack of 4-hydroxycoumarin and leads to intermediate IV. The latter undergoes intramolecular cyclization and tautomerization to provide the 3,4-dihydropyrano[c]chromene derivatives.

The ability of the catalyst to be reused without significant loss of its catalytic activity was evaluated. The model reaction was performed under optimal conditions. SnP₂O₇ was washed with ethanol, dried at 100°C, and reused several times (Fig. 2).

According to Fig. 2, it can be seen that the yield of product **6a** remains unchanged (91 to 95%) during the catalyst reuse. Therefore, no loss of catalytic activity was observed even after five reuses.

In order to confirm the stability of the catalyst after its reuse, XRD and FT-IR analyses were carried out to compare the structure of the catalyst before and after reuse.

The FT-IR spectra (Fig. 3) clearly show no change in the IR bands of the catalyst before and after five catalytic cycles. Indeed, the structure of the recovered catalyst is identical to that of the catalyst before its reuse (fresh).

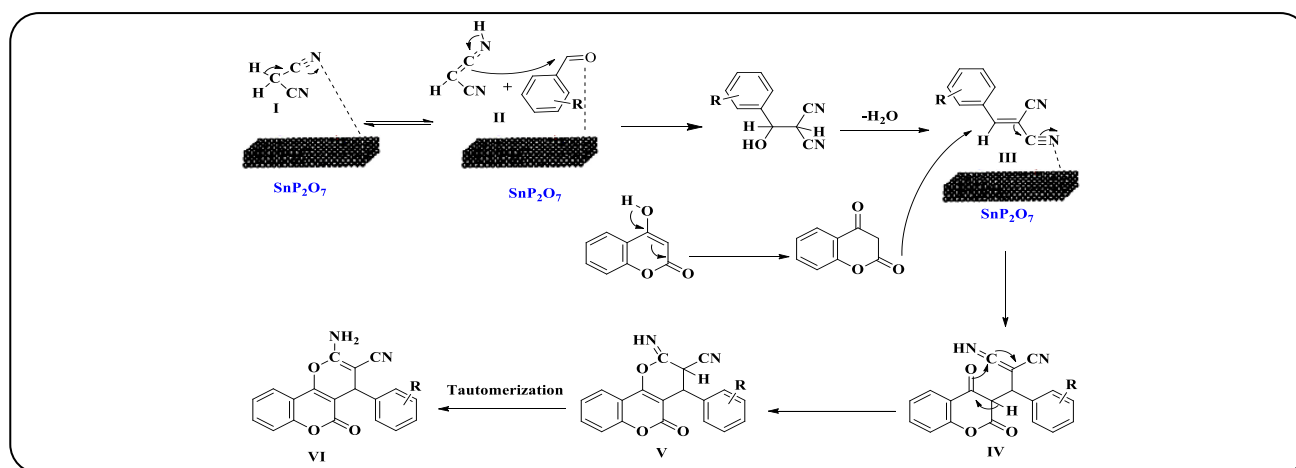
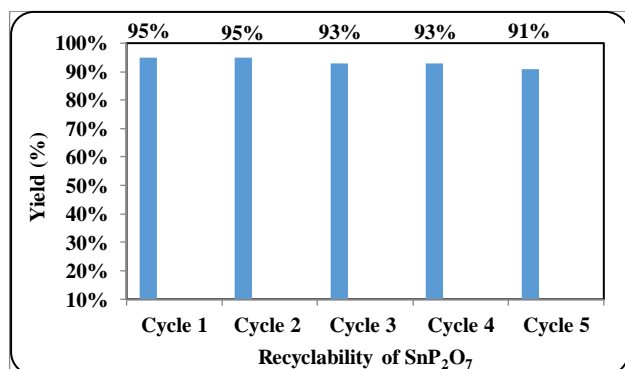
The structure of SnP₂O₇ remained unchanged before and after its reuse, as shown in the FT-IR spectra and X-ray diffraction patterns (Fig. 3). This study confirmed that the structure of the catalyst didn't undergo any modification even after five reuses, which confirms the stability of SnP₂O₇ in the reaction medium.

To investigate the morphology of the catalyst, the SEM experiment was performed (Fig. 4).

The scanning electron microscopy images of the SnP₂O₇ catalyst were taken at different resolutions and show that it consists of a set of small grains (Fig. 2). These have a certain surface heterogeneity and a high porosity which can act positively on the adsorption of the precursor.

Table 8: Comparison of catalytic performance of SnP_2O_7 with that of other catalysts reported in the literature

Entry	Catalyst	Conditions	Yield (%) ^b	Ref
1	$\text{Fe}_3\text{O}_4@ \text{SiO}_2$ -guanidine-PAA	50 mg, H_2O , 70°C , 30 min	96	[76]
2	Ni(II)-Schiff base/SBA-15	5mg, H_2O , 70°C , 10-15 min	90-97	[77]
3	Ni@Imine- Li^+ -MMT	10 mg, solvent-free, 100°C , 14 min	95	[78]
4	Si-Mg-FA	3 mol%, EtOH : H_2O , reflux, 60 min	90	[79]
5	$\text{CoFe}_2\text{O}_4@ \text{FA}$ -Er	40 mg, solvent-free, 80°C , 26 min	93	[80]
6	SnP_2O_7	1.7 mol%, EtOH, reflux, 8 min	95	Present work

**Scheme 6: The suggested mechanism for one-pot synthesis of 3,4-dihydropyrano[c]chromenes derivatives****Fig. 2: Recyclability of SnP_2O_7 applied in model reaction**

To determine the elements present in the prepared sample, the analysis of its surface composition was carried out by the Energy Dispersion X-ray (EDX) analysis (Fig. 5).

The Energy Dispersive X-ray (EDX) analysis of SnP_2O_7 shows the presence of the elements constituent SnP_2O_7 such as phosphorus, oxygen, and tin.

The efficiency of SnP_2O_7 was compared with that of other catalysts reported in the literature applied in 3,4-dihydropyrano[c]chromenes derivatives synthesis;

the results are collected in Table 8.

From Table 8, it can be deduced that the SnP_2O_7 catalyst presents an interesting catalytic activity; it allows to obtain 3,4-dihydropyrano[c]chromenes derivatives with excellent yields in short reaction times compared to $\text{Fe}_3\text{O}_4@ \text{SiO}_2$ -guanidine-PAA, Ni(II)-Schiffbase/SBA-15, Ni@Imine- Li^+ -MMT, Si-Mg-FA, and $\text{CoFe}_2\text{O}_4@ \text{FA}$ -Er catalysts.

CONCLUSIONS

A simple and ecologically methodology for tetrahydrobenzo[b]pyrane and dihydropyrano[3,2-c]chromene derivatives synthesis via one-pot, three-component condensation in the presence of SnP_2O_7 as a heterogeneous catalyst was described. Indeed, the catalyst shows interesting catalytic activity due to the presence of acidic and basic sites. Moreover, the reactions were carried out in a short time and allowed to obtain the products in good to excellent yields. The advantages of these methods are the simplicity of the procedure, mild reaction conditions, atom economy, eco-friendly profile of reactions, recyclability of the catalyst, and easy isolation of products.

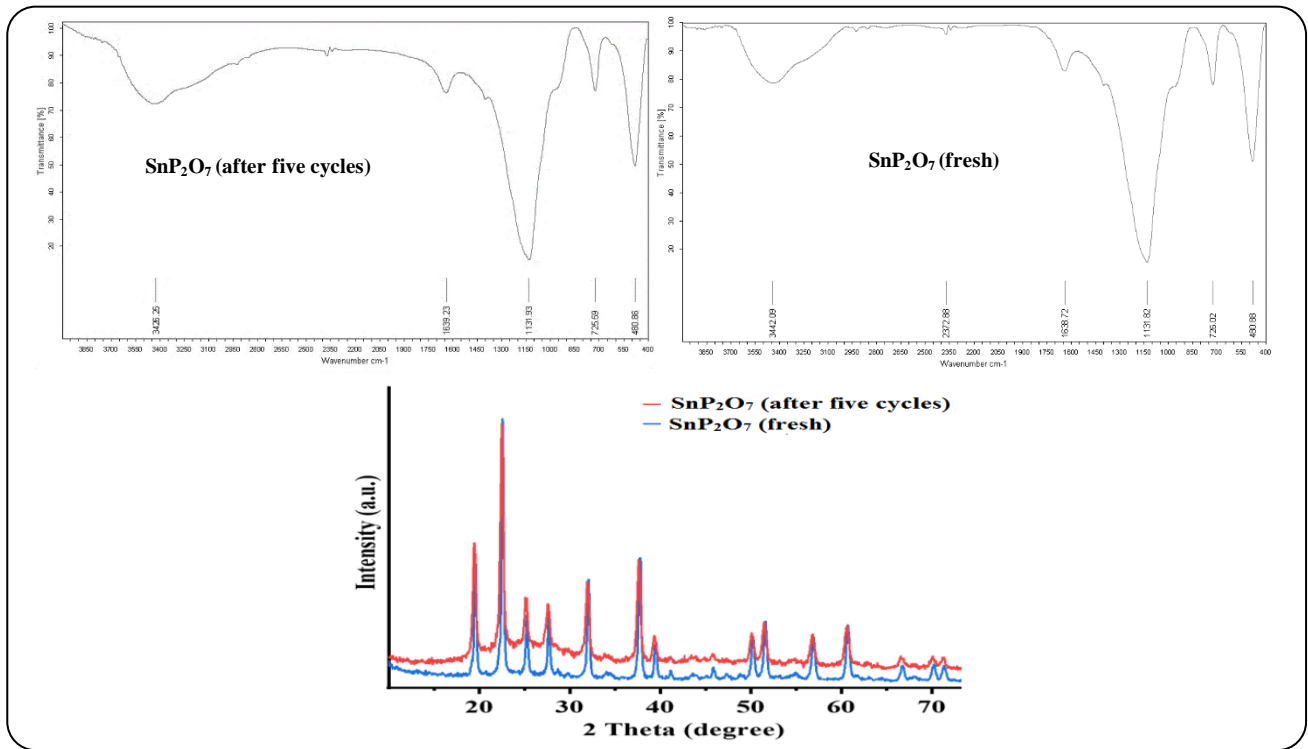


Fig. 3: XRD and FT-IR analysis of SnP₂O₇ fresh and after five cycle of reuse

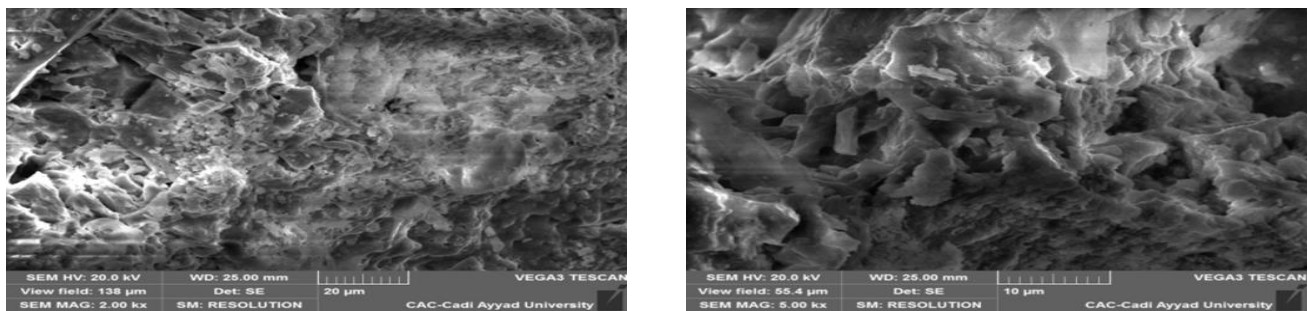


Fig. 4: SEM of SnP₂O₇ catalyst

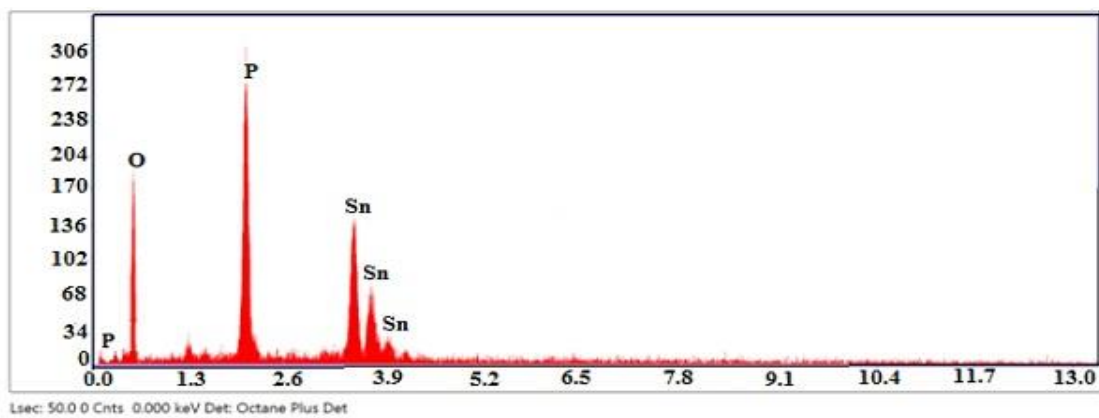


Fig. 5: EDX analysis of the constituent chemical elements of SnP₂O₇

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