Karaj branch

Journal of Applied Chemical Research
jacr.kiau.ac.ir

Journal of Applied Chemical Research, 12, 2, 53-63 (2018)

One-pot Synthesis of Pyrano[2,3-d]Pyrimidines using Nano-cellulose-$SbCl_5$ as a Highly Efficient and Bio-based Catalyst

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(Received 25 Jun. 2017; Final version received 27 Sep. 2017)

Abstract

The reaction of nano-cellulose and antimony pentachloride in dichloromethane gave nano-cellulose-$SbCl_5$. Also nano-cellulose-$SbCl_5$ has been characterized by energy dispersive X-ray spectroscopy (EDX), scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FT-IR).Nano-cellulose-$SbCl_5$has been applied as a nano-catalyst for synthesis of pyrano [2,3-*d*] pyrimidines from the simple one-pot reaction between aryl aldehydes, barbituric acid or thiobarbituric acid and malononitril. Cleanliness, simple methodology, short time, and excellent yields of products are some advantages of this method.

Keywords: *Nano-cellulose, Antimony pentachloride, Bio-based catalyst, Pyrano [2,3-d] pyrimidines.*

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Introduction

Pyrano[2,3-d]pyrimidine structures are of considerable interest as they possess a wide range of biological properties such as antitumor[1], antimalarial [2], antiallergic, anti-cancer, and potassium channel activators [3]. Multicomponent reactions (MCRs) have enormous benefit with their high yields of products, ease of execution in the aim of analysis of combinatorial chemistry[4,5]. MCRs have gained significant interest from modern medicinal and combinatorial chemists [6].In recent years; there has been growing interest in finding inexpensive and effective solid acid nano-catalyst such as nanocrystallinenano-sawdust-BF_3 [7], nano-$TiCl_4$-SiO_2 [8–10] nano-$SnCl_4$-SiO_2 [11, 12] nano ZnO catalyst [13] and nano-silica sulfuric acid [14–20]. Numerous attempts have recently been made to achieve the synthesis of pyrano [2,3,d] pyrimidine derivatives through the use of protocols including triethylamine, potassium carbonate, pyridine, phosphorus pentoxide (P_2O_5), Phosphorus pentasulfide (P_2S_5)piperidine and Zn[(L) proline]$_2$, nano-basic silica, basic ionic liquid, $(NH_4)_2HPO_4$, Sulfonic acid nanoporous silica (SBA-Pr-SO_3H), ultrasonic and Microwave Irradiation. Yet despite their undeniable significance the inefficiency of such protocols such as unfavorable yields, formation of side product, long reaction time, high temperatures, harsh reaction conditions, expensive and toxic or metallic catalysts has inspired further attempts to achieve a more efficient protocol[21-33]. Nowadays, Support materials include cellulose, synthetic polymers, and silica gel, and sample-immobilization methods include adsorption and covalent binding have been used in different fields [34-36]. In this study, the nano-cellulose has been used as adsorbent for the preparation of Nano-cellulose-$SbCl_5$ whose average size is small and is well distributed. The presence of functional groups on the surface of cellulose-$SbCl_5$resulted in a dramatic increase in the surface polarity and acidity, and as a result raised the catalytic efficiency of the Nano-cellulose-$SbCl_5$.Cellulose is a potentially biodegradable material that can also be used as an efficient support for bonding several functional groups to produce clean and impressive biopolymer-based catalysts. Cotton is a natural, cheap, and readily available source of cellulose [37, 38]. Therefore, one of these catalysts is nano-cellulose-$SbCl_5$which has received significant interest such as being non-toxic, readily available, inexpensive and highly reactive for affording the corresponding products in excellent yields. So in this work nano-cellulose-$SbCl_5$ has been used as an efficient and convenient catalyst for the synthesis of pyrano [2,3-*d*] pyrimidines. The catalyst can be regenerated at the end of the reaction and can be used 3 times without losing its activity.

Experimental

Materials and Instrumentation

Nano-cellulose was prepared by the method reported previously by our research group [37]. All other chemicals for this work were purchased from Fluka chemical companies and used without any additional purification. Melting points were measured by the capillary tube method with an Electrothermal 9100 apparatus. IR spectra were recorded on a Shimadzu IR-470 spectrometer. ^{1}H NMR spectra were recorded on a Bruker Spectrospin Advance 400 spectrometer using TMS as an internal standard. Elemental analyses were recorded using a Thermo Finnigan Flash EA–1112. The morphologies of the nanoparticles were observed using FESEM of a Mira3 TESCAN microscope with an accelerating voltage of 15 kV. The EDX analysis was done using a SAMx analyzer.

Synthesis of nano-cellulose-$SbCl_5$

To a stirred mixture of nano-cellulose (1 g) and diethyl ether (15 ml), Antimony pentachloride (1 ml) was added dropwise at 0 °C during 15 min. The reaction mixture was filtered, washed well with diethyl ether and dried at room temperature.

General procedure for the preparation of pyrano[2,3-d]pyrimidines

In a typical experiment, a round-bottomed flask fitted with magnetic stirring bar was charged with EtOH (5 mL), nano-cellulose-$SbCl_5$ (0.03 g), barbituric acid or thiobarbituric acid (1 mmol), malononitrile (1 mmol) and aryl aldehyde (1 mmol). The flask was stirred and refluxed for 5-10 min. After the completion of the reaction, the mixture was filtered to remove the catalyst. After the evaporation of the solvent, the crude product was re-crystallized from hot ethanol to obtain the pure compound.

*7-Amino-5-(4-nitrophenyl)-2,4-dioxo-2,3,4,5-tetrahydro-1H-pyrano[2,3-d]pyrimidine-6-carbonitrile (**4a**)*

White powder; IR (KBr, cm^{-1}): 3312 (NH_2), 3160 (NH), 2200 (CN), 1736 (C=O),); ^{1}H NMR (400 MHz, DMSO) δ: 10.92 (s, 1H, NH), 10.80 (s, 1H, NH), 7.94 (d, J = 7.1 Hz, 2H, Ar-H), 7.45 (d, J = 7.1 Hz, 2H, Ar-H), 6.82 (s, 2H, NH_2), 4.80 (s, 1H, CH) ppm; Anal. calcd. for $C_{14}H_9N_5O_5$: C, 51.38; H, 2.77; N, 21.40. Found: C, 51.42; H, 2.79; N, 21.47.

7-Amino-5-(3-nitrophenyl)-2,4-dioxo-2,3,4,5-tetrahydro-1H-pyrano[2,3-d]pyrimidine-6-carbonitrile (***4b***)

White powder; IR (KBr, cm^{-1}): 3316 (NH_2), 3300, 3245 (NH), 2210 (CN), 1600 (C=O; ^{1}H NMR (400 MHz, DMSO) δ: 10.88 (s, 1H, NH), 10.76 (s, 1H, NH), 8.40 (s, 1H, Ar-H), 8.22 (d,

J = 7.3 Hz, 2H, Ar-H), 6.80 (s, 2H, NH_2), 3.96 (s, 1H, CH) ppm; Anal. calcd. for $C_{14}H_9N_5O_5$: C, 51.38; H, 2.77; N, 21.40. Found: C, 51.41; H, 2.79; N, 21.48.

7-amino-2,4-dioxo-5-phenyl-1,3,4,5-tetrahydro-2H-pyrano[2,3-d]pyrimidine-6-carbonitrile (***4c***)
Yellow powder; IR (KBr, cm^{-1}): 3378 (NH_2), 3301, 3216 (NH), 2130 (CN), 1694 (C=O); ^1H NMR (400 MHz, DMSO) δ: 10.91 (s, 1H, NH), 10.80 (s, 1H, NH), 7.41 (t, *J*=7.3Hz, 2H, Ar-H), 7.18-7.06 (m, 3H, Ar-H), 6.82 (s, 2H, NH_2), 4.32 (s, 1H, CH) ppm; Anal. calcd. for $C_{14}H_{10}N_4O_3$: C, 59.57; H, 3.57; N, 19.85. Found: C, 59.52; H, 3.66; N, 19.79.

7-Amino-5-(3-chlorophenyl)-4-oxo-2-thioxo-1,3,4,5-tetrahydro-2H-pyrano[2,3-d]pyrimidine-6-carbonitrile (***4d***)
White powder; IR (KBr, cm^{-1}): 3380 (NH_2), 3222 (NH), 2210 (CN), 1702 (C=O); Anal. calcd. for $C_{14}H_9ClN_4O_2S$: C, 50.53; H, 2.73; N, 16.84. Found: C, 50.64; H, 2.77; N, 16.92.

7-Amino-5-(2-chlorophenyl)-2,4-dioxo-1,3,4,5-tetrahydro-2H-pyrano[2,3-d]pyrimidine-6-carbonitrile (***4e***)
White powder; IR (KBr, cm^{-1}): 3320, 3101(NH_2), 2202 (CN), 1700, 1651 (C=O; ^1H NMR (400 MHz, DMSO) δ: 10.97 (s, 1H, NH), 10.02 (s, 1H, NH), 7.21-7.37(m, 4H, Ar-H), 7.02 (s, 2H, NH), 4.71 (s, 1H, CH) ppm; Anal. calcd. for $C_{14}H_9ClN_4O_3$: C, 53.10; H, 2.86; N, 17.69. Found: C, 53.00; H, 3.09; N, 17.77.

*7-Amino-5-(3,4-dimethoxyphenyl)-2,4-dioxo-1,3,4,5-tetrahydro-2H-pyrano[2,3-d]pyrimidine-6-carbonitrile (**4f**)*
Yellow powder; IR (KBr, cm^{-1}): 3201 (NH_2), 2223 (CN), 1734 (C=O), 1662 (C=O); ^1H NMR (400 MHz, DMSO) δ: 10.86 (s, 1H, NH), 10.73 (s, 1H, NH), 6.84-6.81 (m, 5H, Ar-H & NH_2), 4.31 (s, 1H, CH), 3.84 (s, 3H, OCH_3), 3.76 (s, 3H, OCH_3) ppm; Anal. calcd. for $C_{16}H_{14}N_4O_5$: C, 56.14; H, 4.12; N, 16.37. Found: C, 56.16; H, 4.17; N, 16.40.

*7-Amino-5-(2-methoxyphenyl)-2,4-dioxo-1,3,4,5-tetrahydro-2H-pyrano[2,3-d]pyrimidine-6-carbonitrile (**4g**)*
Yellow powder; IR (KBr, cm^{-1}): 3380 (NH_2), 3202, 3137 (NH), 2262(CN), 1761 (C=O); ^1H NMR (400 MHz, DMSO) δ: 10.81 (s, 1H, NH), 10.73 (s, 1H, NH), 7.42 (d, *J* = 4.6 Hz, 1H, Ar-H), 7.15-7.12 (m, 4H, Ar-H & NH_2), 4.16 (s, 1H, CH), 3.75 (s, 3H, OCH_3) ppm; Anal. calcd. for $C_{15}H_{12}N_4O_4$: C, 57.69; H, 3.87; N, 17.94. Found: C, 57.53; H, 3.90; N, 17.99.

*7-Amino-5-(4-methoxyphenyl)-2,4-dioxo-1,3,4,5-tetrahydro-2H-pyrano[2,3-d]pyrimidine-6-carbonitrile (**4h**)*

Yellow powder; IR (KBr, cm^{-1}): 3319 (NH_2), 3285, 3131 (NH), 2218(CN), 1736 (C=O), 1670 (C=O); ^1H NMR (400 MHz, DMSO) δ: 10.92 (s, 1H, NH), 10.82 (s, 1H, NH), 7.11 (d, J = 7.5 Hz, 2H, Ar-H), 6.89-6.85 (m, 4H, Ar-H & NH_2), 4.17 (s, 1H, CH), 3.80 (s, 3H, OCH_3) ppm; Anal. calcd. for $C_{15}H_{12}N_4O_4$: C, 57.69; H, 3.87; N, 17.94. Found: C, 57.70; H, 3.91; N, 17.96.

*7-Amino-2,4-dioxo-5-(4-methylphenyl)-2,3,4,5-tetrahydro-1H-pyrano[2,3-d]pyrimidine-6-carbonitrile (**4i**)*

Yellow powder; IR (KBr, cm^{-1}): 3310 (NH), 2221(CN), 1741(C=O), 1656(C=O); ^1H NMR (400 MHz, $CDCl_3$) δ: 10.72 (s, 1H, NH), 10.61 (s, 1H, NH), 7.82 (s, 1H, Ar-H), 7.79 (s, 1H, Ar-H), 7.71 (s, 2H), 7.36 (d, J =8.0 Hz, 2H, , Ar-H), 7.30 (d, J = 8.0 Hz, 2H, Ar-H), 7.21 (s, 1H, Ar-H), 3.09 (s, 3H, CH_3) ppm; Anal. calcd. for $C_{15}H_{12}N_4O_3$: C, 60.81; H, 4.08; N, 18.91. Found: C, 60.90; H, 4.11; N, 18.98.

*7-Amino-5-(4-bromophenyl)-2,4-dioxo-2,3,4,5-tetrahydro-1H-pyrano[2,3-d]pyrimidine-6-carbonitrile (**4j**)*

White powder; IR (KBr, cm^{-1}): 3363 (NH_2), 3191 (NH), 2216 (CN), 1681 (C=O); ^1H NMR (400 MHz, DMSO) δ: 10.88 (s, 1H, NH), 10.71 (s, 1H, NH), 7.76 (d, J = 7.1 Hz, 2H, Ar-H), 7.31 (d, J = 7.1 Hz, 2H, Ar-H), 6.85 (s, 2H, NH_2), 3.92 (s, 1H, CH) ppm; Anal. calcd. for $C_{14}H_9BrN_4O_3$: C, 46.56; H, 2.51; N, 15.51. Found: C, 46.61; H, 2.57; N, 15.63.

Reaction condition in the synthesis pyrano[2,3-d]pyrimidines

This reaction was considered as a model reaction. Several dry solvents such as, CH_2Cl_2, EtOH, CH_3CN, H_2O and DMF were tested as media (Table 1). It was noticed that the best yield was found with ethanol (Table 1, Entry 2). In order to determine the optimum quantity of nano-cellulose-$SbCl_5$, the reaction of barbituric acid or thiobarbituric acid, malononitrile and aryl aldehyde was carried out under reflux in ethanol using different quantities of nano-cellulose-$SbCl_5$. As shown in Table 1, 0.03 g of nano-cellulose-$SbCl_5$ gives an excellent yield in 10 min. Also we have found in the absence of the catalyst (Table 1, Entry 8), in the presence of nano-cellulose (Table 1, Entry 9) and antimony pentachloride (Table 1, Entry 10) the product formation was unsuccessful.

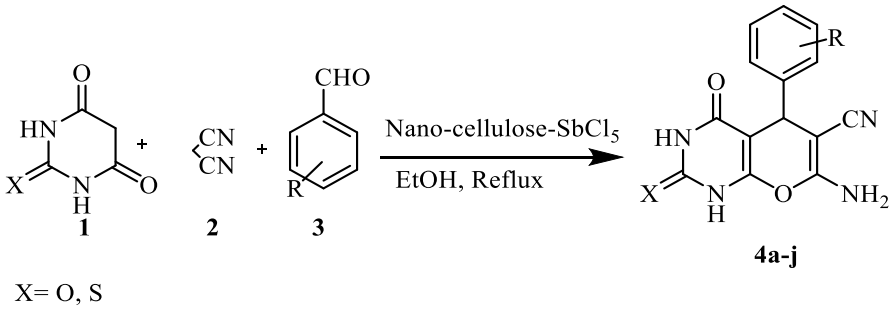
Table 1. Optimization of the reaction conditions for synthesis of 4a[a].

Entry	Catalyst (amount)	Solvent/condition	Time (min)	Yield%
1	nano-cellulose-$SbCl_5$(0.03g)	CH_2Cl_2/reflux	10	Trace
2	nano-cellulose-$SbCl_5$(0.03g)	EtOH/reflux	10	95
3	nano-cellulose-$SbCl_5$(0.03g)	CH_3CN/reflux	10	Trace
4	nano-cellulose-$SbCl_5$(0.03g)	H_2O/reflux	10	75
5	nano-cellulose-$SbCl_5$(0.03g)	DMF/reflux	10	33
6	nano-cellulose-$SbCl_5$(0.02g)	EtOH/reflux	10	81
7	nano-cellulose-$SbCl_5$(0.04g)	EtOH/reflux	10	92
8	no catalyst	EtOH/reflux	10	Trace
9	nano-cellulose(0.03g)	EtOH/reflux	10	Trace
10	$SbCl_5$(0.03g)	EtOH/reflux	10	Trace

[a]Isolated yield

Results and discussion

In this study, nano-cellulose andnano-cellulose-$SbCl_5$ were prepared and characterized. The catalytic activity of nano-cellulose-$SbCl_5$ was investigated for the synthesis of pyrano[2,3-*d*] pyrimidines derivatives (4a-j) by condensation of barbituric acid or thiobarbituric acid 1, malononitrile 2 andaryl aldehyde 3 (Scheme 1, Table 2). Morphology and structural of the nano-cellulose andnano-cellulose-$SbCl_5$ were observed by SEM images as shown in Figures 1 and 2 respectively. The results of EDX analyses of the nano-cellulose and nano-cellulose-$SbCl_5$are given in Table 3, Figures 3 and 4 respectively.



Scheme1. Synthesis of pyrano[2,3-*d*] pyrimidines.

Table 2. Synthesis of pyrano[2,3-*d*]pyrimidines using nano-cellulose-$SbCl_5$.

Entry	Product	R	X	Yield %	M.P. (°C)	
					Found	Reported
1	4a	4-$NO_2C_6H_4$	O	97	236-240	238-239 [23]
2	4b	3-$NO_2C_6H_4$	O	90	263-265	262-263 [24]
3	4c	C_6H_5	O	92	221-224	224-225 [24]
4	4d	3-ClC_6H_4	S	94	233-236	234-237 [25]
5	4e	2-ClC_6H_4	O	88	212-217	213-215 [23]
6	4f	3,4-$(MeO)_2$ C_6H_3	O	86	304-305	303-306 [4]
7	4g	2-MeO C_6H_4	O	90	231-233	230 [26]
8	4h	4-$MeOC_6H_4$	O	93	288-290	290-293[4]
9	4i	4-$CH_3C_6H_4$	O	87	226-228	226-227 [27]
10	4j	4-BrC_6H_4	O	91	236-238	235-236 [27]

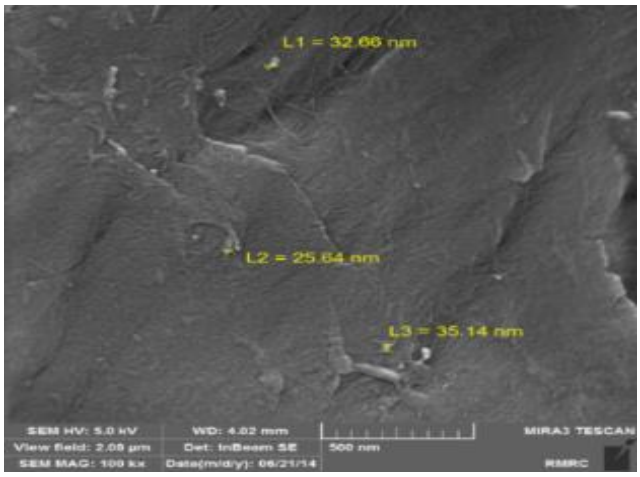


Figure 1. SEM image of nano-cellulose.

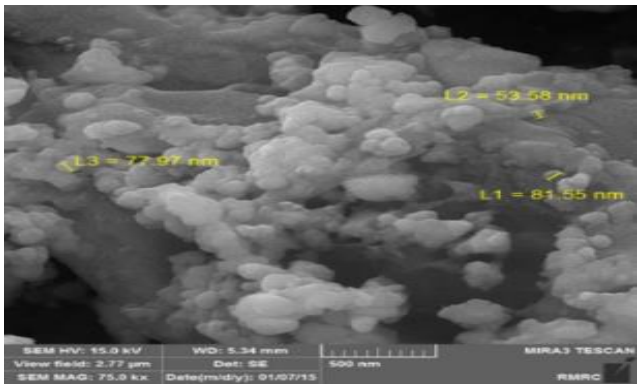


Figure 2. SEM image of nano-cellulose-$SbCl_5$.

Table 3. Chemical analysis of nano-Cellulose and nano-cellulose-$SbCl_5$.

Element	Nano-cellulose (W%)	Nano-cellulose-$SbCl_5$ (W%)
C	69.20	53.57
O	22.80	28.53
Cl	-	3.25
Sb	-	14.65

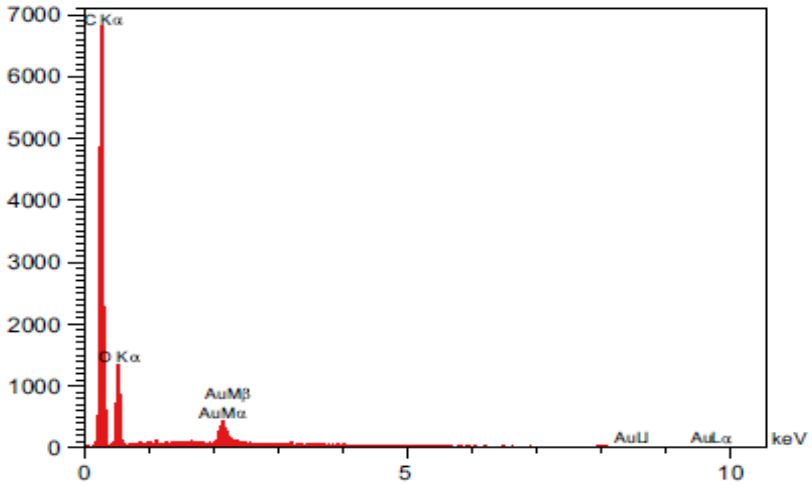


Figure 3. EDX of nano-cellulose.

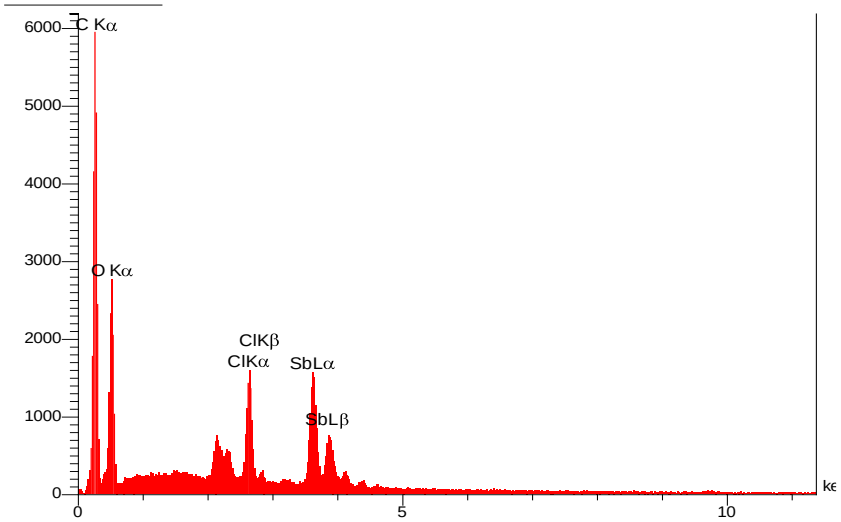


Figure 4. EDX of nano-cellulose-$SbCl_5$.

The FT-IR spectrum of the nano-cellulose (reported previously by our research group [37]) exhibited a broad peak for an OH absorption band at 3352 cm^{-1}. The peaks at 1155 and 1053 cm^{-1} represented C–O stretching vibration of the glucose unit. The FT-IR spectrum of nano-cellulose-

$SbCl_5$ appeared in addition to the stretching vibrations of C–O–Sb at 667 cm^{-1}, indicating that antimony chloride is supported on nano-cellulose.

The synthesis of pyrano[2,3-*d*]pyrimidines by nano-cellulose-$SbCl_5$ was compared with other catalysts reported in literature[6 and 21–39] (Table 3).Synthesis of pyrano[2,3-*d*]pyrimidine catalyzed by nano-cellulose-$SbCl_5$offers production of the corresponding products in shorter time and milder condition is done, while other methods require more amount of catalyst and longer reaction time for synthesis of pyrano[2,3-*d*]pyrimidines.

Table 4. Comparison of preparation of pyrano[2,3-*d*]pyrimidines catalyzed by nano-cellulose-$SbCl_5$ and various catalyst.

Entry	Catalyst	Solvent	Condition	Time	Yield %	Ref.
1	Dibutylamine	EtOH	Reflux/ r.t.	43–129min	83–94	[6]
2	DAHP[a]	EtOH	r.t.	120 h	71–81	[28]
3	l-proline	EtOH	r.t.	30–150 min	68–88	[29]
4	$H_{14}[NaP_5W_{30}O_{110}]$	EtOH	Reflux	30–60 min	85–90	[30]
5	Nano-cellulose-$SbCl_5$	EtOH	Reflux	5-10min	86-97	This work

[a] *3-Deoxy-d-arabino-heptulosonate-7-phosphate*

Recycling of the Catalyst

After the completion of the reaction, the mixture was filtered to remove the catalyst. The catalyst was washed well with diethyl ether and dried at room temperature for 8 h. The reusability of nano-cellulose-$SbCl_5$ was tested by repeating the model study in the presence of nano-cellulose-$SbCl_5$under optimized conditions. The results of these experiments showed that nano-cellulose-$SbCl_5$can be regenerated at the end of the reaction and can be used 4 times without losing too much activity (Table 5).

Table 5. Recoverability of nano-cellulose-$SbCl_5$.

Yield (%)			
First	Second	Third	Fourth
95	92	86	80

Conclusion

We have demonstrated a rapid and an efficient synthetic route for nano-cellulose-$SbCl_5$ catalyzed one-pot three component synthesis of pyrano [2,3-*d*] pyrimidines in ethanol as solvent. This method was compared with other catalysts reported in literature; indicating cleanliness, simple methodology and short time are some advantages of this method.

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