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Silica-bonded *n*-propyltriethylene-tetramine as a recyclable solid base catalyst for the synthesis of 2-amino-5-oxo-5,6,7,8-tetrahydro-4*H*-chromenes

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ABSTRACT

Silica-bonded *n*-propyltriethylene-tetramine (SBNPTT) was found as an efficient solid base for the synthesis of 2-amino-5-oxo-5,6,7,8-tetrahydro-4*H*-chromenes. Chromene derivatives were obtained *via* the three-component condensation reaction of aromatic aldehydes, malononitrile, and dimedone at 80 ^{o}C under solvent-free conditions. The heterogeneous solid base showed much the same efficiency when used in consecutive reaction runs.

Keywords*: Silica-bonded n-propyltriethylene-tetramine, Chromenes, Solid bases, Catalyst, Synthesis.*

1. Introduction

The important advantages of solid acids and bases such as operational simplicity, environmental compatibility, non-toxicity, reusability, low cost, and ease of isolation recommend them as suitable catalytic systems in organic synthesis. In fact, simplified recovery and reusability are critical advantages of heterogeneous catalytic systems, which could lead to novel environmentally benign chemical procedures for academia and industry [1-6]. Metal colloids, mineral clays and supported reagents on silica gel, alumina and other solid supports are various types of heterogeneous and reusable catalytic systems, which have been designed and used in organic synthesis. Among them, silica-supported catalysts have attracted more attention because they are inexpensive, easy to prepare, and insoluble in most of organic solvents, which makes them being recycled from various reactions.

Recently, we prepared a series of silica functionalized *n*-propylamines such as silica-bonded *n*-propyltriethylene tetramine (SBNPTT), silica-bonded *n*-propyldiethylene triamine (SBNPDT), and silica-bonded *n*-propyl piperazine (SBNPP) and used them as a catalyst for the synthesis of heterocyclic compounds (Fig. 1) [6-9].

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2-Amino-4*H*-pyran derivatives represent an important class of compounds. They are often used in cosmetics and pigments, and utilized as potentially biodegradable agrochemicals [10,11]. Polyfunctionalized 4H-pyrans also constitute a structural unit of many natural products [12,13] and biologically interesting compounds which possess various pharmacological activities [14], such as antiallergic [10], antitumor [15], and antibacterial [16-18]. 4*H*-Pyran derivatives are also potential calcium channel antagonists [19] which are structurally similar to biologically active 1,4-dihydropyridines.

The conventional synthesis of 2-amino-5-oxo-5,6,7,8-tetrahydro-4*H*-chromenes involves the condensation of dimedone with aromatic aldehyde and malononitrile under refluxing in acetic acid [20] or the bi-component condensation of dimedone with α-cyanocinnamonitriles in the presence of ethanolic piperidine [21]. Other effective methods include the use of microwave [22], ultrasonic irradiation [23] or hexadecyltrimethyl ammonium bromide (HMTAB) [24], triethylbenzyl ammonium chloride (TEBA) [25], KF-alumina [26], rare earth perfluorooctanoate ($RE(PFO)_3$) [27], (S)-proline [28], tetrabutyl-ammonium fluoride (TBAF) [29], SB-DABCO [30], and well-ordered mesoporous silica nanoparticles [31] as catalyst in one-pot reaction. However, most of these

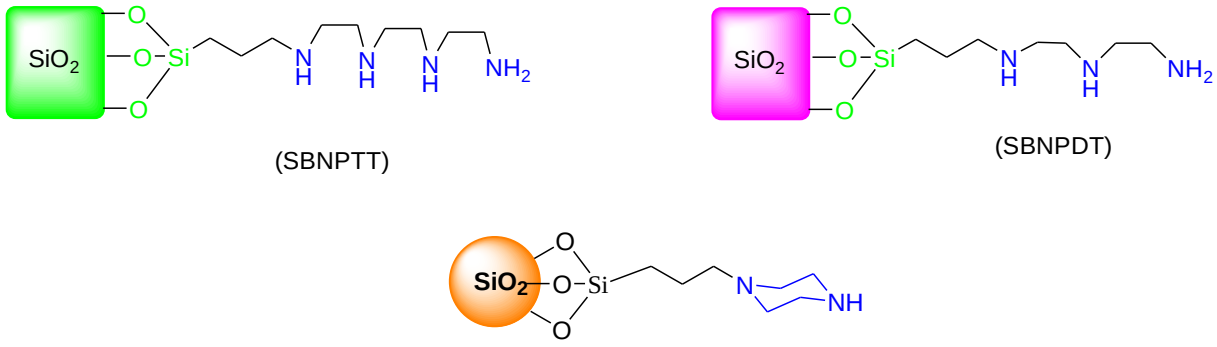


Fig. 1. The proposed structure for SBNPTT, SBNPDT, and SBNPP.

methods suffer from some drawbacks such as low yields, long reaction times, harsh reaction conditions, tedious work-up procedures and application of expensive catalysts.

2. Experimental

2.1. General

Chemicals were purchased from Fluka, Merck and Aldrich Chemical Companies. All the products were characterized by comparison of their IR, ^{1}H NMR and ^{13}C NMR spectroscopic data and their melting points with the reported values [26-31]. Reaction progress was followed by TLC using silica gel SILG/UV 254 plates. Silica functionalized n-propylamines were prepared according to our previous reported procedures [6-9].

2.2. General procedure for the synthesis of 2-amino-5-oxo-5,6,7,8-tetrahydro-4H-chromenes

To a mixture of aromatic aldehyde (1 mmol), malonitrile (1 mmol), and dimedone (1 mmol) under solvent-free conditions, catalyst silica functionalized n-propylamine [SBNPTT, SBNPDT, or SBNPP (0.1 g)] was added and the mixture was heated at 80 ^{o}C for appropriate time. After completion of the reaction, as indicated by TLC, ethanol (10 mL) was added and the reaction mixture was filtered. The remaining was washed with warm ethanol (3 × 5 mL) in order to separate heterogeneous catalyst. After cooling, the crude products were precipitated. The crude products were purified by recrystallization from ethanol (95%). The recovered catalyst was dried and reused for subsequent runs.

Selected spectral data

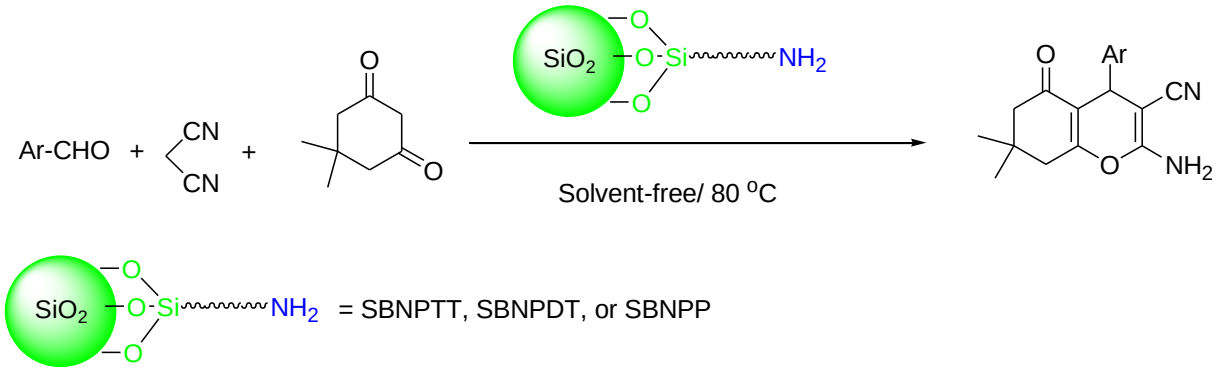
2-Amino-7,7-dimethyl-5-oxo-4-phenyl-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (**1a**): m.p. 224-226˚C, (Lit. [26]: m.p. 226-228˚C). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 1.07 (s, 3H), 1.14 (s, 3H), 2.22 (d, 1H, *J*= 16.4 Hz), 2.28 (d, 1H, *J*= 16.4 Hz), 2.45-2.53 (m, 2H), 4.43 (s, 1H), 4.54 (s, 2H, NH_2), 7.20-7.33 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 27.7, 28.9, 32.2, 35.5, 40.7, 50.7, 114.1, 118.6, 127.2, 127.6, 128.6, 143.6, 157.4, 161.5, 195.8.

2-Amino-4-(4-bromphenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (**1b**): m.p. 201-203˚C, (Lit. [27]: m.p. 201-203˚C). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 1.25 (s, 3H), 1.27 (s, 3H), 2.19-2.29 (m, 2H), 2.47 (s, 2H), 4.40 (s, 1H), 4.63 (s, 2H), 7.14 (d, 2H, *J*= 8.0 Hz), 7.44 (d, 2H, *J*= 8.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 27.7, 28.9, 32.2, 35.2, 40.7, 50.6, 118.4, 121.0, 129.4, 131.7, 135.7, 142.9, 195.9.

2-Amino-4-(4-fluorophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (**1c**): m.p. 198-200˚C, (Lit. [29]: m.p. 210-211˚C). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 1.05 (s, 3H), 1.14 (s, 3H), 2.22 (d, 1H, *J*= 16.4 Hz), 2.28 (d, 1H, *J*= 16.4 Hz), 2.47 (s, 2H), 4.42 (s, 1H), 4.58 (s, 2H), 6.98-7.02 (m, 2H), 7.22-7.29 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 27.7, 28.9, 32.2, 34.9, 40.7, 50.7, 114.0, 115.4, 115.6, 118.5, 129.2, 129.3, 139.0, 157.5, 160.7, 161.5, 195.9.

2-Amino-4-(2,4-dichlorophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (**1d**): m.p. 114-116˚C, (Lit. [27]: m.p. 115-117˚C). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 1.07 (s, 3H), 1.13 (s, 3H), 2.19 (d, 1H, *J*= 16.4 Hz), 2.26 (d, 1H, *J*= 16.4 Hz), 2.43-2.51 (m, 2H), 4.81 (s, 3H), 7.15-7.22 (m, 2H), 7.36 (d, 1H, *J*= 1.6 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 27.7, 28.9, 32.1, 33.6, 40.6, 50.5, 112.3, 118.4, 127.4, 130.0, 131.5, 133.5, 134.0, 138.5, 158.0, 162.6, 195.9.

2-Amino-4-(4-cyanophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (**1e**): m.p. 208-210˚C, (Lit. [31]: m.p. 209-211˚C). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 1.03 (s, 3H), 1.13 (s, 3H), 2.19-2.29 (m, 2H), 2.40-2.48 (m, 2H), 4.47 (s, 1H), 4.64 (s, 2H), 7.38-7.48 (m, 2H), 7.58-7.64 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 27.6, 28.9, 32.2, 36.3, 50.5, 58.3, 110.3, 112.7, 118.8, 119.5, 128.6, 132.3, 149.8, 159.0, 162.8, 195.8.



Scheme 1. Condensation of aldehydes, malononitrile, and dimedone catalyzed by SBNPTT, SBNPDT, or SBNPP

2-Amino-4-(3-cyanophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (**1f**): m.p. 170-172˚C. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 1.05 (s, 3H), 1.14 (s, 3H), 2.22 (d, 1H, *J*= 16.4 Hz), 2.28 (d, 1H, *J*= 16.4 Hz), 2.45-2.55 (m, 2H), 4.47 (s, 1H), 4.75 (s, 2H) 7.41-7.45 (m, 1H), 7.52-7.59 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 27.8, 28.8, 32.3, 35.5, 40.7, 50.7, 112.7, 113.2, 118.2, 118.9, 129.4, 130.9, 131.2, 144.8, 157.8, 162.1, 195.8. Elemental analysis: for $C_{19}H_{17}N_3O_2$: C, 71.46; H, 5.37; N, 13.16; Found: C, 71.20; H, 5.47; N, 12.96.

2-Amino-7,7-dimethyl-5-oxo-4-m-tolyl-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (**1g**): m.p. 198-200 ˚C. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 0.97 (s, 3H), 1.13 (s, 3H), 2.16 (s, 3H), 2.25 (d, 1H, *J*= 16.0 Hz), 2.32 (d, 1H, *J*= 16.0 Hz), 2.58 (s, 2H), 4.31 (s, 1H), 6.76 (s, 2H, NH_2), 7.17 (d, 1H, *J*= 7.6 Hz), 7.34 (s, 1H), 7.39 (d, 1H, *J*= 7.2 Hz), 7.73-7.80 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 20.3, 27.3, 28.9, 32.3, 36.1, 50.5, 58.8, 113.3, 120.2, 126.8, 128.8, 133.0, 145.3, 158.9, 162.9, 196.2. Elemental analysis: for $C_{19}H_{20}N_2O_2$: C, 74.00; H, 6.54; N, 9.08; Found: C, 73.73; H, 6.65; N, 8.92.

2-Amino-4-(4-isopropyl-phenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (**1h**): m.p. 198-200 ˚C. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 0.99 (s, 3H), 1.11-1.15 (s, 9H), 2.26 (d, 1H, *J*= 16.0 Hz), 2.31 (d, 1H, *J*= 16.0 Hz), 2.53-2.62 (m, 2H), 2.72-2.80 (m, 1H), 4.23 (s, 1H), 6.98 (s, 2H, NH_2), 7.01 (d, 2H, *J*= 8.0 Hz), 7.24 (d, 2H, *J*= 8.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 22.8, 23.5, 26.3, 28.3, 31.9, 35.1, 50.2, 58.4, 113.1, 120.1, 126.2, 126.8, 143.0, 146.3, 158.9, 162.4, 195.7. Elemental analysis: for $C_{21}H_{24}N_2O_2$: C, 74.97; H, 7.19; N, 8.33; Found: C, 74.71; H, 7.30; N, 8.07.

2-Amino-7,7-dimethyl-5-oxo-4-(3,4,5-trimethoxy-phenyl)-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (**1i**): m.p. 171-173˚C. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 1.10 (s, 3H), 1.14 (s, 3H), 2.25-2.32 (m, 2H), 2.44-2.54 (m, 2H), 3.81 (s, 3H), 3.84 (s, 6H), 4.35 (s, 1H), 4.54 (s, 2H), 6.43 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 27.3, 29.2, 32.1, 35.8, 40.7, 50.6, 56.1, 60.7, 62.8, 104.5, 113.7, 118.9, 136.9, 139.2, 153.2, 157.7, 161.9, 196.1. Elemental analysis: for $C_{21}H_{24}N_2O_5$: C, 65.61; H, 6.29; N, 7.29; Found: C, 65.36; H, 6.39; N, 7.02.

2-Amino-4-(4-dimethylamino-phenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (**1j**): m.p. 201-203˚C, (Lit. [27]: m.p. 202-204˚C). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 1.05 (s, 3H), 1.10 (s, 3H), 2.19-2.27 (m, 2H), 2.42-2.48 (m, 2H), 2.91 (s, 6H), 4.33 (s, 1H), 4.44 (s, 2H), 6.64 (d, 2H, *J*= 8.0 Hz), 7.08 (d, 2H, *J*= 8.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$ & DMSO-d_6): δ (ppm) 27.5, 29.0, 32.1, 34.9, 50.7, 60.4, 112.5, 114.1, 120.2, 128.2, 132.5, 149.4, 158.5, 161.7, 195.9.

3. Results and Discussion

In line with of our studies towards the development of new routes to the synthesis of highly-substituted heterocycles and using solid base catalysts [5-7], herein we wish to report a valid and an efficient procedure for the synthesis of 2-amino-5-oxo-5,6,7,8-tetrahydro-4*H*-chromenes *via* three-component conden-sation of aldehydes, malononitrile, and dimedone in the presence of silica functionalized *n*-propylamine derivatives as solid base catalysts (Scheme 1).

To study the effect of catalyst loading on the condensation reaction of aldehydes, malononitrile, and dimedone to the corresponding 2-amino-5-oxo-5,6,7,8-tetrahydro-4*H*-chromenes, the reaction of benzaldehyde and malononitrile with dimedone was chosen as a model reaction (Table 1). The results show clearly that silica functionalized *n*-propylamine derivatives are effective catalysts for this condensation and the optimal amount of SBNPTT was 0.1 g per 1 mmol of aldehyde at 80 °C under solvent-free conditions (Table 1, entry 4). This condensation was carried out with the lower amounts of SBNPTT 0.05 g and 0.07 g and the corresponding product was obtained in 65% and 85% yield (Table 1, entries 2,3). Also, this three-component

Table 1. Investigation of the effect of catalyst on the reaction of benzaldehyde, malononitrile and dimedone.[a]

Entry	Catalyst	Catalyst loading (g)	Time (min)	Yield (%)[b]
1	SBNPTT	0.03	30	55
2	SBNPTT	0.05	30	65
3	SBNPTT	0.07	30	85
4	SBNPTT	0.1	15	93
5	SBNPTT	0.15	15	93
6	SBNPDT	0.05	55	75
7	SBNPDT	0.07	30	94
8	SBNPDT	0.1	30	94
9	SBNPP	0.07	45	85
10	SBNPP	0.1	30	92
11	SBNPP	0.15	30	91

[a]Reaction conditions: benzaldehyde (1 mmol), malononitrile (1 mmol), dimedone (1 mmol), at 80 ^{o}C under solvent-free conditions.
[b]Isolated Yield.

condensation was accomplished in the presence of SBNPDT (0.07 g per 1 mmol of aldehyde) under solvent-free conditions at 80 ^{o}C after 30 min in 94% yield (Table 1, entry 7). The model reaction was reacted in the presence of SBNPP (0.1 g per 1 mmol of aldehyde) under optimized conditions and gave corresponding product after 30 min in 92% yield (Table 1, entry 10).

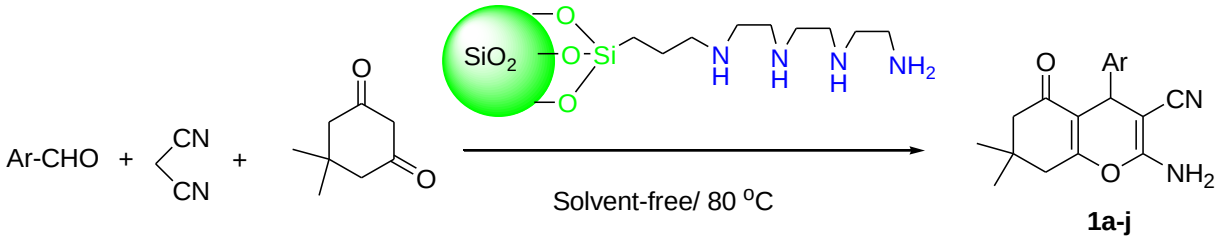
In addition, the effect of solvents (ethanol, water, acetonitrile, dichloromethane, and ethyl acetoacetate) and temperature was investigated on the model reaction using SBNPTT (0.1 g) as catalyst. As shown in Table 2, the condensation reaction of benzaldehyde, malononitrile, and dimedone in the presence of SBNPTT as catalyst in ethanol gave the corresponding product after 50 min in 90% yield (Table 2, entry 1), but the best result was obtained under solvent-free conditions at 80 ^{o}C (Table 2, entry 8). The other solvents gave the corresponding product in longer reaction times and lower yields.

Table 2. Investigation the effect of solvent on the reaction of benzaldehyde, malononitrile and dimedone using SBNPTT as catalyst.[a]

Entry	Solvent	Conditions	Time (min)	Yield (%)[b]
1	Ethanol	Reflux	50	90
2	Water	Reflux	90	72
3	Acetonitrile	Reflux	120	55
4	Dichloromethane	Reflux	120	23
5	Ethyl acetoacetate	Reflux	120	58
6	Solvent-free	40 ^{o}C	100	45
7	Solvent-free	60 ^{o}C	50	78
8	Solvent-free	80 ^{o}C	15	93
9	Solvent-free	100 ^{o}C	15	91

[a]Reaction conditions: benzaldehyde (1 mmol), malononitrile (1 mmol), dimedone (1 mmol), and 0.1 g of SBNPTT in different solvents at reflux conditions.
[b]Isolated Yield.

Table 3. Synthesis of 2-amino-5-oxo-5,6,7,8-tetrahydro-4H-chromene derivatives in the presence of SBNPTT as catalyst.[a]



Entry	Ar	Product	Time (min)	Yield (%)[b]
1	C_6H_5-	**1a**	15	93
2	4-BrC_6H_4-	**1b**	10	91
3	4-FC_6H_4-	**1c**	12	91
4	2,4-$(Cl)_2C_6H_3$-	**1d**	20	85
5	4-(CN)C_6H_4-	**1e**	10	85
6	3-(CN)C_6H_4-	**1f**	12	87
7	3-MeC_6H_4-	**1g**	50	85
8	4- iso-PrC_6H_4-	**1h**	50	84
9	3,4,5-$(CH_3O)_3C_6H_2$-	**1i**	50	75
10	4-$(Me)_2$N-C_6H_4-	**1j**	50	82

[a]Reaction conditions: dimedone (1 mmol), malononitrile (1 mmol), aldehyde (1 mmol), SBNPTT (0.1 g), solvent-free conditions, 80 °C.
[b]Isolated yield.

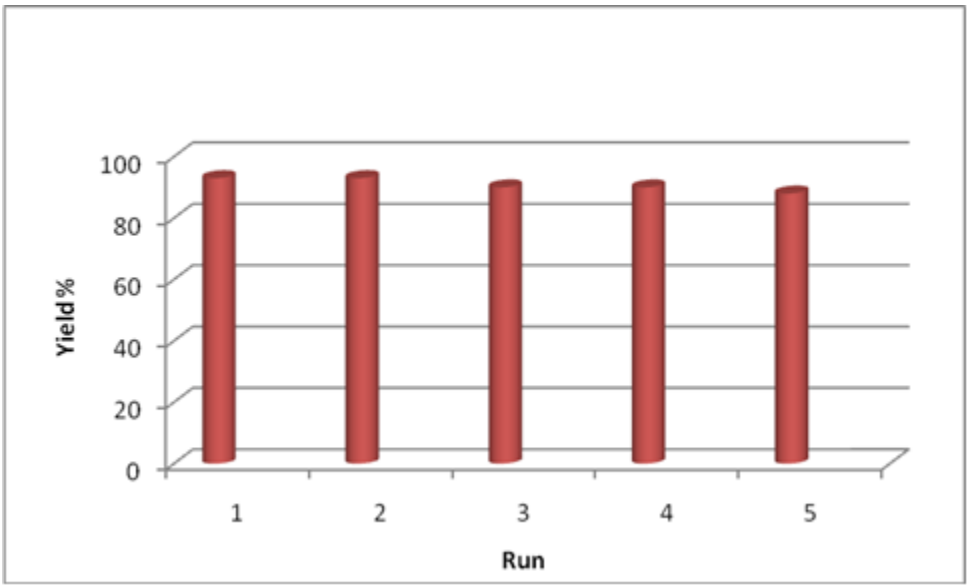


Fig. 2. Recyclability of solid bases SBNPTT (0.1 g) in the reaction of benzaldehyde (1 mmol) and malononitrile (1 mmol) with dimedone (1 mmol) under solvent-free conditions at 80 °C. Time = 15 min.

Table 4. Comparison of the result of condensation reaction between benzaldehyde, malononitrile, and dimedone in the presence of different catalysts.

Entry	Catalyst	Catalyst loading (g, or mol%)	Solvent/ Temp.	Time (min)	Yield (%)[a]	Ref.
1	HTMAB	10 mol%	H_2O /90 ^oC	180	91	[24]
2	$Yb(PFO)_3$	5 mol%	EtOH/60 ^oC	300	90	[27]
3	(S)-Proline	5 mol%	H_2O/ rt	30	82	[28]
4	TBAF	10 mol%	H_2O/Reflux	30	97	[29]
5	SB-DABCO	6 mol%	EtOH/ rt	35	96	[30]
6	MSNs	0.01 g	EtOH/60 ^oC	15	94	[31]
7	SBNPTT	0.1 g	Solvent-free/80 ^oC	15	93	This work

[a]Isolated yield.

The synthesis of 2-amino-5-oxo-5,6,7,8-tetrahydro-4*H*-chromenes was achieved by the three-component condensation of an aromatic aldehyde, malononitrile, and dimedone in the presence of SBNPTT (0.1 g) under solvent-free conditions at 80 ^oC (Table 3).

Thereafter, a series of different 2-amino-5-oxo-5,6,7,8-tetrahydro-4*H*-chromene derivatives were prepared successfully from different aromatic aldehydes bearing electron-withdrawing and electron donating groups, dimedone and malononitrile under optimized condition. Electron-withdrawing groups such as 4-cyano and 3-cyano-benzaldehyde reacted under optimized conditions into corresponding **1e** and **1f** in 90% and 91% yield respectively (Table 3, entries 5 and 6). Electron-donating groups such as 3-methyl, 4-iso-propyl, 3,4,5-trimethoxy and 4-*N*,*N*-dimethylamino-benzaldehyde treated with malononitrile and dimedone under optimized conditions, gave corresponding products **1g**, **1h**, **1i**, and **1j** in high yields (Table 3, entries 7-10). The results clearly indicate that reactions can tolerate a wide range of differently substituted aromatic aldehydes.

In addition, the possibility of recycling the catalyst was examined using the reaction of malononitrle, benzaldehyde, and dimedone under the optimized conditions. Upon completion, the reaction mixture was washed with warm ethanol (3 × 30 mL). The recovered catalyst was dried and reused for subsequent runs. The recycled catalyst could be reused fourth times without any additional treatment. No observation of any appreciable loss in the catalytic activity of SBNPTT was observed (Fig. 2).

Finally, a comparative study of SBNPTT with other recently reported catalysts for condensation of benzaldehyde, malononitrile, and dimedone as a model compound was made which revealed that SBNPTT is an equally efficient and reusable catalyst (Table 4).

A plausible mechanism in the presence of a base according to our previous report [5] and Khurana et al. [32] was drawn in Scheme 2. The α-cyanocinnamonitrile formed initially by Knoevenagel condensation in the presence of solid base undergoes subsequent reactions with dimedone in the presence of solid base to give the desired product.

4. Conclusion

In conclusion, we have shown that silica-bonded *n*-propyltriethylene-tetramine (SBNPTT), which can be prepared from commercially available and cheap starting materials, catalyzed efficiently the synthesis of 2-amino-5-oxo-5,6,7,8-tetrahydro-4*H*-chromenes. The mild reaction conditions and simplicity of the procedure and reusability of catalyst are the advantages of this method.

Acknowledgment

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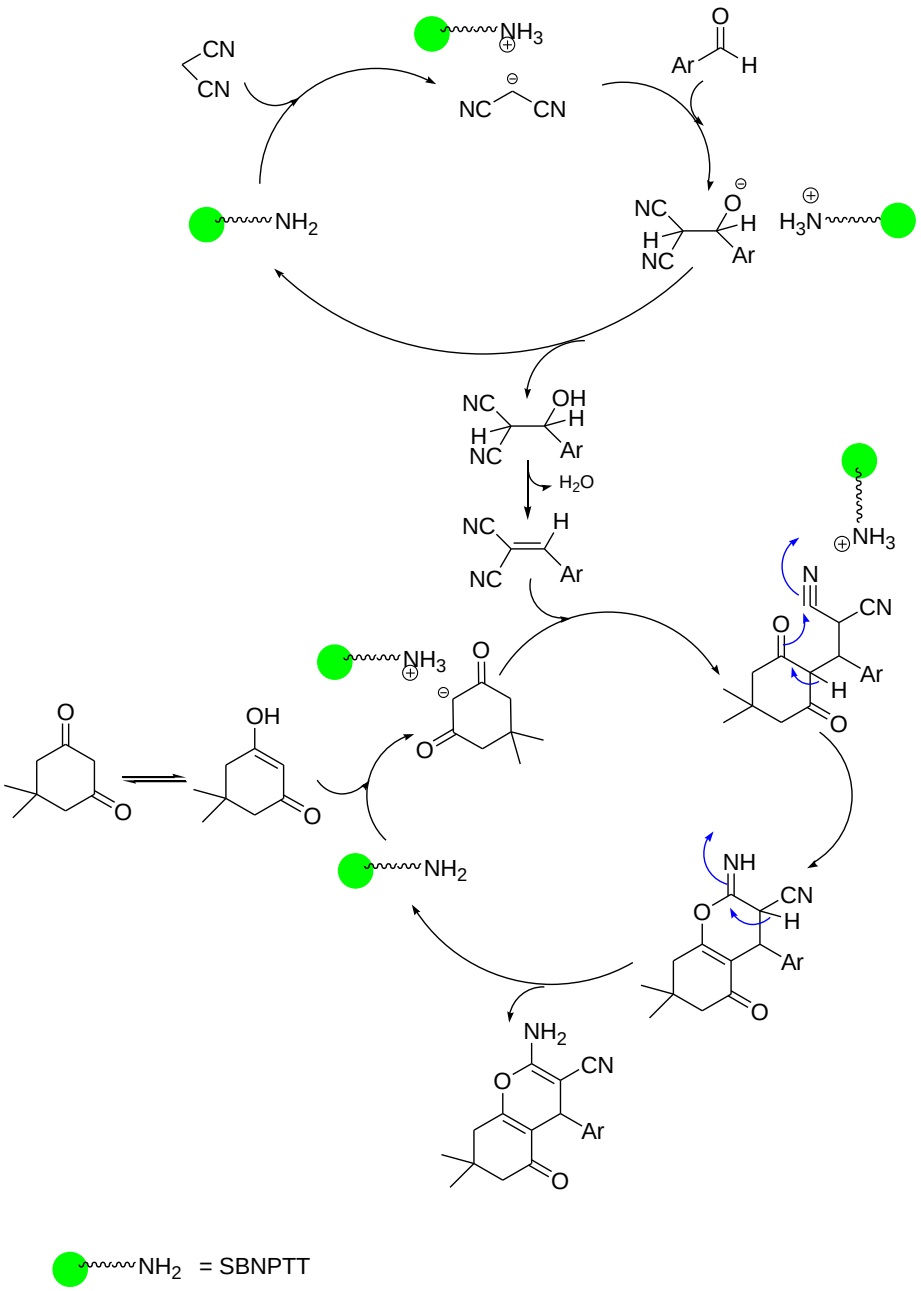

Scheme 2. A plausible mechanism for synthesis of pyran derivatives.

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