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Ionic liquid anchored to silica (nano-SB-[PSIM]Cl): a highly efficient nanocatalyst for the solvent-free preparation of 1-thioamidolakyl-2-naphthols

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Abstract

Nano-silica-bonded 3-*n*-propyl-1-sulfonic acid imidazolium chloride (nano-SB-[PSIM]Cl) was applied as a highly efficient, general and heterogeneous catalyst for one pot multi-component reaction of 2-naphthol, arylaldehydes, and thioacetamide leading to 1-thioamidolakyl-2-naphthols. All reactions proceeded with excellent yields in short times under solvent-free conditions. Our protocol was superior than most of the reported methods for the preparation of 1-thioamidolakyl-2-naphthols in terms of some factors included relatively short reaction times, moderate to high yields, and absence of organic solvents.

Keywords: 1-Thioamidoalkyl-2-naphthol; nanocatalyst; nano-silica-bonded 3-*n*-propyl-1-sulfonic acid imidazolium chloride (nano-SB-[PSIM]Cl); ionic liquid; multi-component reaction; solvent-free.

Introduction

The one-pot multi-component reaction of 2-naphthol, arylaldehydes, and thioacetamide is of great interest since it is a practical synthetic protocol toward 1-thioamidoalkyl-2-naphthols. These compounds possess thioamide or *N*-alkyl-thioamide moiety in their structures; that are essential scaffolds with different applications, consisting of: (i) quenching tyrosine and tryptophan fluorescence in a distance-dependent way, and thereby employing to observe the binding of thioamide-bearing peptides to proteins [1], (ii) utilization in chemistry of peptides and in medicinal chemistry [2,3], (iii) showing luminescent action by complexation with palladium [4], and (iv) usage as catalysts for organic reactions [5]. 1-Thioamidoalkyl-2-naphthols are precursors of pharmaceutically important 1,3-amino-alcohols; *e.g.* antipain, antibacterial, hypotensive, secretase inhibitory, and bradycardiac properties [6-9]. Some catalysts have been utilized to perform the reaction of 2-naphthol with arylaldehydes and thioacetamide such as 1,3-dichloro-5,5-dimethylhydantoin [10], $[Et_3N\text{-}SO_3H]Cl$ [11], *p*-toluenesulfonic acid [12], *N*,2-dibromo-6-chloro-3,4-dihydro-2*H*-benzo[*e*][1,2,4]thiadiazine-7-sulfonamide 1,1-dioxide [13], 1,3-dibromo-5,5-dimethylhydantoin [14], trichloro-1,3,5-triazinane-2,4,6-trione [15], $Fe(HSO_4)_3$ [16], 1,3-disulfonic

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acid imidazolium trifluoroacetate [17], and trityl chloride [18]. Nevertheless, many of the reported catalysts for this reaction suffer from one or more problems such as high reaction temperature [10,11,14,15], moderate yield [10,13,15,18], prolonged reaction time [12,14,16], usage of toxic and volatile organic solvents in the reaction [12,16], non-systematic study (only a few number of 1-thioamidoalkyl-2-naphthols have been prepared accompanied with other products) [11], and poor compliance with green chemistry protocols [12,16]. Although the synthesis of 1-thioamidoalkyl-2-naphthols has been barely studied in the literature, development of new catalysts for the preparation of these attractive compounds, without the mentioned drawbacks, is desired.

Application of nanocatalysts to promote organic reactions has various profits, such as bearing large surface-to-volume ratio compared to bulk materials (and thereby increased effectiveness and activity), environmentally-friendly nature, logical chemical and thermal stability, tunability of nano-size, low density, and simple isolation from the reaction media [19-24].

Currently, anchoring ionic liquids (ILs) on solid supports and consequently heterogenizing them have attracted much attention in catalytic organic chemistry, because heterogenized ILs behave like heterogeneous catalysts, and have several advantages, including simple separation form reaction mixture, easy application, eco-friendly nature, excellent stability (chemical and thermal) and aptitude to catalyze a variety of organic reactions [25-27].

Nowadays, carrying out organic reactions by eco-friendly techniques is of great importance. Multi-component reactions (MCRs) are a useful kind of these techniques which have been extensively utilized for the synthesis of complex molecules. In MCRs, three or more reactants are reacted in one-pot to provide the final product without isolation of intermediates. This technique has several benefits with respect to common multi-step methods, including high atom economy, flexibility, high yield, short reaction time, low energy consumption, reducing usage of organic solvents and diminishing side-products and waste [28-32]. Solvent-free technique as an environmentally friendly condition widely used in organic synthesis offers several advantages compared with conventional solution conditions, such as higher yield and selectivity, easier workup and purification of products, shorter reaction time, and saving time as well as energy [33-35].

In continuation of our investigation on developing recyclable nanomaterials [25], we have recently developed nano-SB-[PSIM]Cl as a recyclable catalyst for the one-pot synthesis of α-carbamatoalkyl-β-naphtols [25] under mild reaction conditions. Encouraged by these efforts and aiming to show the efficiency and generality of nano-SB-[PSIM]Cl, we have utilized this catalyst for the multi-component preparation of 1-thioamidoalkyl-2-naphthols in the absence of solvent. Moreover, simultaneous integration of effective techniques, including nanocatalysis, multi-component reactions and the use of solvent-free conditions in an individual methodology to synthesize useful compounds is significant and attractive.

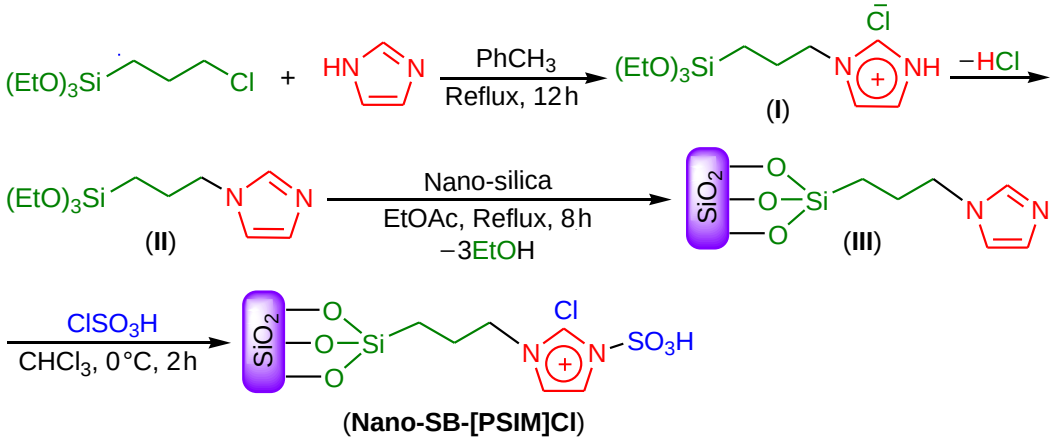
Experimental

All starting materials and solvents were obtained from Merck, Fluka or Acros Chemical Companies. The known compounds were identified by comparing their melting

points/spectroscopic data with those reported in the literature. Monitoring progress of the reactions was achieved by thin layer chromatography (TLC). The melting points were recorded on a Büchi B-545 apparatus in open capillary tubes. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a Bruker Avance DPX, FT-NMR spectrometer.

Procedure for the synthesis of nano-SB-[PSIM]Cl

A mixture of imidazole (0.34 g, 5 mmol), (3-chloropropyl)triethoxysilane (1.125 g, 5 mmol) and toluene (15 mL) in a 50 mL round-bottomed flask connected to a reflux condenser, was stirred for 12 h under reflux conditions. The obtained white precipitate was filtered, washed with toluene (2×5 mL), and dried to give intermediate **II** (Scheme 1). In the next step, the obtained intermediate **II** was reacted with nano-silica (0.30 g, 5 mmol) in refluxed ethyl acetate (15 mL) for 8 h. The formed precipitate was separated by centrifuging and decanting, washed by ethyl acetate (2×5 mL), and dried to afford intermediate **III**. Subsequently, a solution of chlorosulfonic acid (5 mmol) in chloroform (10 mL) was added dropwise to intermediate **III** at 0 °C (ice-water bath), and stirred for 2 hours at this temperature. The solvent was removed by centrifuging and decanting, and the residue was triturated with chloroform (3×10 mL), and dried under powerful vacuum at 90 °C to give nano-SB-[PSIM]Cl as a white precipitate (Scheme 1) [25].



Scheme 1. The preaparation of nano-SB-[PSIM]Cl

General method for the synthesis of 1-thioamidoalkyl-2-naphthols

To a mixture of 2-naphthol (0.144 g, 1 mmol), arylaldehyde (1 mmol) and thioacetamide (1.6 mmol, 0.120 g) in a test tube, was added nano-SB-[PSIM]Cl (0.032 g), and the resulting mixture was vigorously stirred at 100 °C by a small rod; monitoring the reaction progress was achieved by TLC. After completing the reaction, the mixture was cooled to room temperature, ethyl acetate (5 mL) was added to it, stirred and refluxed for 1 min, followed by centrifugation and decanting to separate the insoluble nanocatalyst (this action was achieved for three times). The crude reaction mixture collected after decanting the supernatant solutions was evaporated, and the solid residue was recrystallized from ethanol (95%) to give the pure product.

Selected spectral data of the synthesized products

Compound c

^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 2.04 (s, 3H, CH_3), 7.20-7.26 (m, 2H, methine hydrogen and H_{Ar}), 7.31 (t, J = 7.2 Hz, 1H, H_{Ar}), 7.44 (t, J = 7.7 Hz, 1H, H_{Ar}), 7.55-7.62 (m, 2H, H_{Ar}), 7.82-7.91 (m, 3H, H_{Ar}), 8.04-8.08 (m, 2H, H_{Ar}), 8.65 (d, J = 8.0 Hz, 1H, NH), 9.90 (s, 1H, OH); ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) 22.6, 47.6, 117.8, 118.5, 120.4, 121.2, 122.6, 122.8, 126.8, 128.4, 128.7, 129.6, 129.9, 132.2, 132.9, 145.4, 147.7, 153.4, 169.7.

Compound f

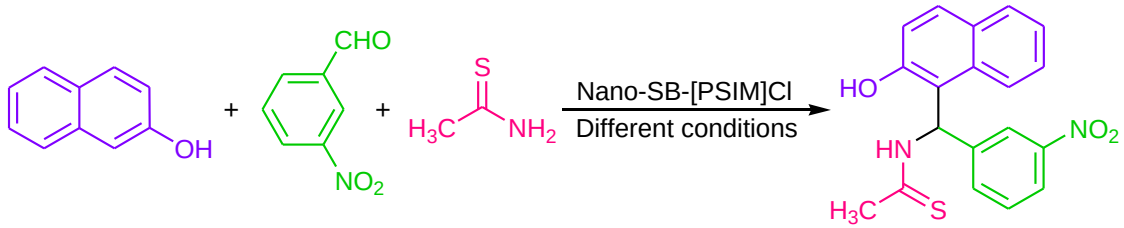
^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 1.85 (s, 3H, CH_3), 6.93 (d, J = 7.8 Hz, 1H, methine hydrogen), 7.04 (d, J = 8.8 Hz, 1H, H_{Ar}), 7.18 (t, J = 7.4 Hz, 1H, H_{Ar}), 7.32-7.34 (m, 2H, H_{Ar}), 7.39 (d, J = 2.2 Hz, 1H, H_{Ar}), 7.51 (d, J = 8.5 Hz, 1H, H_{Ar}), 7.66 (d, J = 8.8 Hz, 1H, H_{Ar}), 7.71 (d, J = 7.8 Hz, 1H, H_{Ar}), 7.89 (d, J = 7.0 Hz, 1H, H_{Ar}), 8.59 (d, J = 7.8 Hz, 1H, NH), 9.74 (s, 1H, OH); ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) 30.0, 47.9, 116.9, 119.2, 123.0, 123.2, 127.0, 127.1, 128.9, 129.1, 129.3, 130.3, 131.9, 132.2, 133.4, 133.5, 140.0, 154.3, 169.4.

Compound i

^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 1.98 (s, 3H, CH_3), 3.68 (s, 3H, OCH_3), 6.82 (d, J = 8.6 Hz, 2H, H_{Ar}), 7.09 (d, J = 8.4 Hz, 3H, methine hydrogen and H_{Ar}), 7.23-7.27 (m, 2H, H_{Ar}), 7.36 (s, 1H, H_{Ar}), 7.75-7.81 (m, 2H, H_{Ar}), 7.87 (s, 1H, H_{Ar}), 8.45 (d, J = 8.3 Hz, 1H, NH), 10.00 (s, 1H, OH); ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) 23.2, 47.9, 55.4, 113.9, 119.0, 119.5, 122.8, 123.8, 126.7, 127.7, 129.0, 129.6, 132.8, 134.9, 153.5, 158.2, 169.6.

Results and discussion

At first, a set of reactions were screened in order to optimize the reaction conditions; for this purpose, the condensation of 2-naphthol (1 mmol), 3-nitrobenzaldehyde (1 mmol) and thioacetamide (1.6 mmol) was selected as a model reaction (Scheme 2), and effect of the catalyst amount, temperature and solvent on the reaction was studied; the results are summarized in Table 1. The reasonable results were obtained in the presence of 0.032 g of nano-SB-[PSIM]Cl at 100 ºC in solvent-free conditions (Table 1, Eentry 3). Increasing the catalyst amount (up to 0.036 g) and the temperature (up to 105 ºC) slightly decreased the reaction time; nevertheless, 0.032 g and 100 ºC were chosen as the optimal catalyst amount and temperature, respectively; because these conditions were more logical, and one of the important aim of this work was performing the reaction using fewer amount of the catalyst in lower temperature. The model reaction was also tested using 1.4 mmol of thioacetamide in which the product was obtained in 91% after 30 min.



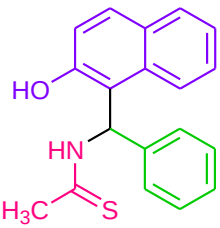
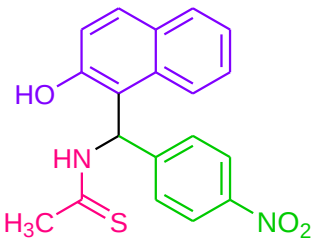
Scheme 2. The model reaction

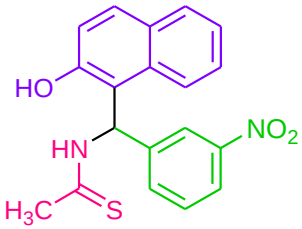
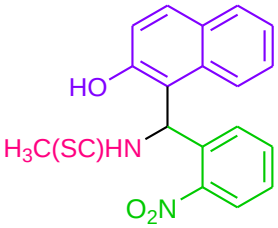
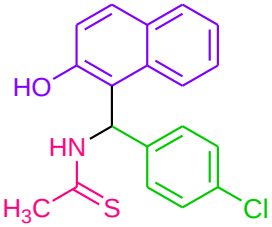
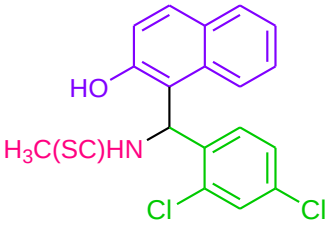
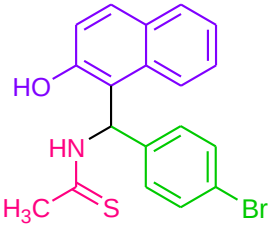
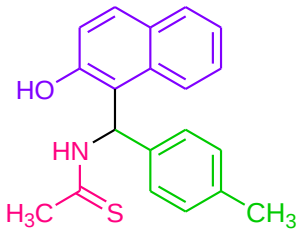
Table 1. The reaction of 2-naphthol (1 mmol), 3-nitrobenzaldehyde (1 mmol) and thioacetamide (1.6 mmol)

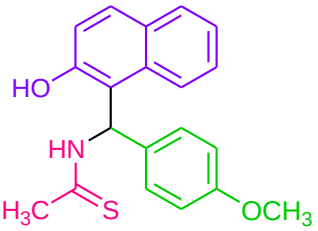
Entry	The catayst amount (g)	Solvent	Temp. (ºC)	Time (min)	Yield (%)
1	-	-	100	60	35
2	0.028	-	100	30	92
3	0.032	-	100	30	98
4	0.036	-	100	23	98
5	0.032	-	90	60	95
6	0.032	-	105	25	98
7	0.032	EtOAc	Reflux	90	46
8	0.032	EtOH	Reflux	90	54
9	0.032	MeCN	Reflux	90	51
10	0.032	DMF	100	90	63

In order to recognize effectuality and scope of nano-SB-[PSIM]Cl for the production of 1-thioamidoalkyl-2-naphthol, after acquiring the optimized reaction conditions, the one-pot multi-component reaction of 2-naphthol, diverse arylaldehydes and thioacetamide was examined. The relevant results are presented in Table 2. As it can be observed in this Table, both electron-deficient and electron-reach aromatic aldehydes effectively underwent the reaction, and furnished the related 1-thioamidoalkyl-2-naphthols with excellent yields in short times. Moreover, in the case of the arylaldehydes bearing substituents on ortho position, the reaction times were increased (Table 2, compounds **d** and **f**). Methoxy substituent also enhanced the reaction time (Table 2, compound **i**). Considering the results, the nanostructured material based on ionic liquid anchored to silica was a highly effectual and general nanocatalyst for the transformation.

Table 1. Nano-SB-[PSIM]Cl-catalyzed the preparation of 1-thioamidoalkyl-2-naphthols in solvent-free conditions at 100 ºC

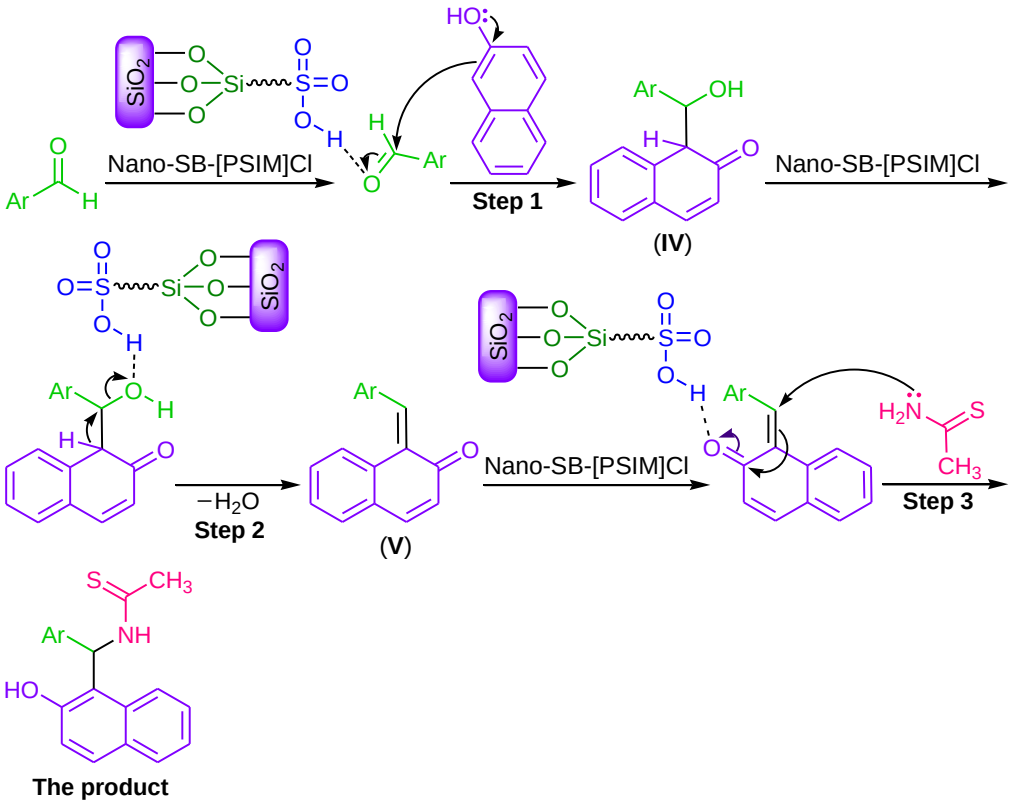
Compd. no.	Product	Time (min)	Yield (%)[a]	M.p. (ºC) [Lit.]
a		30	98[b]	193-195 (190-193) [11]
b		30	98[b]	243-245 (243-245) [16]

c		30	98[b]	238-240 (234-236) [14]
d		60	95	227-229 (229-231) [12]
e		30	98[b]	240-241 (240-242) [14]
f		40	96	223-225 (219-221) [13]
g		30	96	231-233 (230-232) [14]
h		30	98[b]	217-219 (220-222) [14]

i		60	92	182-184 (181-182) [13]

[a]Isolated yield
[b]This reaction was progressed completely when monitored by TLC.

A plausible mechanism based on the literature [10,13,17] is illustrated in Scheme 2. The acidic group of nano-SB-[PSIM]Cl (i.e. SO_3H) promotes the reaction as following: (i) activating the carbonyl group of aldehyde to accept nucleophilic attack of 2-naphthol to give intermediate **IV** (step 1), (ii) assistance to remove a H_2O molecule from **IV** (step 2), and (iii) activation of the carbonyl group of intermediate **V** to facilitate Michael-type addition of thioacetamide to provide 1-thioamidoalkyl-2-naphthols (step 3).



Scheme 2. The proposed mechanism for the production of 1-thioamidoalkyl-2-naphthols

In another study, the advantages of our catalyst was compared with the reported catalysts; for this purpose, the results and the reaction conditions for the production of 1-thioamidoalkyl-2-naphthol **a** in the presence of these catalysts are illustrated in Table 3. Nano-SB-[PSIM]Cl is superior than all catalysts in term of the reaction yield. Moreover, it is better in some cases in term of the reaction time (Entries 2, 4, 6, 8 and 9), and in some other cases in terms of reaction time (Entries 2, 3, 6 and 7). Our reaction media is also superior to Entries 4 and 8.

Table 3. Comparing the superiorities of nano-SB-[PSIM]Cl with the reported catalysts for the synthesis of **a**

Entry	Catalyst	Conditions	Time (min)	Yield (%)	Ref.
1	Nano-SB-[PSIM]Cl	Solvent-free, 100 °C	30	98	-
2	1,3-Dichloro-5,5-dimethylhydantoin	Solvent-free, 120 °C	35	73	[10]
3	$[Et_3N\text{-}SO_3H]Cl$	Solvent-free, 110 °C	30	88	[11]
4	*p*-Toluenesulfonic acid	1,2-Dichloroethane, Reflux	60	95	[12]
5	DCDBTSD[a]	Solvent-free, 80 °C	25	80	[13]
6	1,3-Dibromo-5,5-dimethylhydantoin	Solvent-free, 130 °C	200	93	[14]
7	Trichloro-1,3,5-triazinane-2,4,6-trione	Solvent-free, 120 °C	25	80	[15]
8	$Fe(HSO_4)_3$	1,2-Dichloroethane, 60 °C	390	88	[16]
9	1,3-Disulfonic acidimidazolium trifluoroacetate	Solvent-free, 60 °C	35	96	[17]
10	Trityl chloride	Solvent-free, 70 °C	12	78	[18]

[a] *N*,2-dibromo-6-chloro-3,4-dihydro-2*H*-benzo[*e*][1,2,4]thiadiazine-7-sulfonamide 1,1-dioxide

Conclusion

In summary, we have developed a nanocatalyst for the synthesis of 1-thioamidoalkyl-2-naphthols. The merits of our method consists of generality, high effectuality, excellent yields, short reaction times, simplicity, cleaner reaction profile, application of nanotechnology, low costs, performing the reactions in the absence of solvent, simple synthesis of the catalyst and good agreement with green chemistry protocols.

Acknowledgements

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