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PAPER

Sulfated polyborate: a new and eco-friendly catalyst for one-pot multi-component synthesis of 3,4-dihydropyrimidin-2(1*H*)-ones/ thiones via Biginelli reaction

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This report describes an efficient method for the synthesis of three-component Biginelli reaction of various aldehydes, β-ketoesters/β-diketone and urea/thiourea catalyzed by sulfated polyborate with high yields under a solvent free condition at 100 °C. The catalyst has been prepared and used as a Bronsted as well as Lewis acid catalyst for the reaction. The catalyst was prepared by dehydration of boric acid followed by sulfonation and characterized by different analytical techniques. The key advantages of the present method are high yields, short reaction time, solvent free condition, easy workup, recyclability of catalyst and ability to tolerate a variety of functional groups which gives economical as well as ecological rewards.

Introduction

More than a century ago Italian chemist Pietro Biginelli has reported the synthesis of 3,4-dihydropyrimidin-2(1*H*)-ones (DHPM). However, in last few years, its attractiveness and demand have grown in the field of catalysis. Much effort has covered for new synthetic methodologies, due to their pharmacological properties such as anti-viral, anti-tumour, anti-bacterial, anti-inflammatory, anti-hypertensive and most importantly, as calcium channel modulators.[1-4] Monastrol is a 3,4-dihydropyrimidin-2(1*H*)-thione, which blocks mitosis by specifically inhibiting the motor activity of the mitotic kinesis Eg5 and it is a lead molecule for the development of new anticancer drugs. In addition, (R)-SQ32926 acts as an antihypertensive agent with potent oral activity, whereas promising anticancer activity is also reported with Mon-97 (Fig. 1).[5]

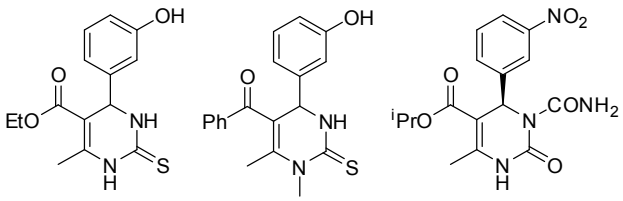

Fig. 1 Pharmacologically active 3,4-dihydropyrimidin-2(1H)-ones/thiones

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The most simple and straightforward reaction reported by Biginelli involves the one-pot three component condensation of an aldehyde, ethyl acetoacetate, and urea.[6,7] However, this procedure suffered from shortcomings such as the harsh reaction conditions, long reaction time and frequently low yields. This has rekindled development of new methodologies for the Biginelli reaction, which involves the use of a number of Bronsted and Lewis acid catalysts such as sulfated silica tungstic acid,[8] SiO_2-polyphosphoric acid (SiO_2-PPA),[9] $Al(HSO_4)_3$,[10] Al_2O_3-$MeSO_3H$,[11] polyvinyl sulfonic acid,[12] sulfated tungstate,[13] Wells-Dawson hetero-poly acid,[14] boric acid,[15] silica-HBF_4,[16] H_2SO_4-Al_2O_3,[17] Al_2O_3-SO_3H,[18] *p*-toluene sulfonic acid,[19] sulfated zirconia,[20] cellulose sulfuric acid,[21] silica sulfuric acid,[22] PPF-SO_3H,[23] montmorillonite KSF,[24] H_2SO_4-silica,[25] $SnCl_2.2H_2O$,[26] graphite,[27] $Bi(NO_3)_3$,[28] *L*-proline,[29] molybdenum(VI) dichloride dioxide,[30] 1-methyl-3-(3-tri methoxysilylpropyl) imidazolium hydrogen sulfate immobilized on magnetic Fe_3O_4 nanoparticles,[31] organosilane sulfonated graphene oxide nanocatalyst,[32] ZnO nanoparticles,[33] phosphomolybdic acid immobilized on imidazole functionalized Fe_3O_4-SiO_2 core-shell nanosphere[34] and so on. 3,4-dihydropyrimidin-2(1*H*)-ones/thiones have also been synthesized under microwave and ultrasound irradiations using different catalysts.[35-38] However, some of the newer literature methods suffer from drawbacks of unsatisfactory yields, longer reaction time, extractive product isolation procedures with toxic organic solvents, use of expensive, metal-based, toxic/corrosive catalysts, which limits their use due to environmental issues.

A literature search revealed that boric acid catalyzes many important organic transformations at a temperature above 100 °C.[39] Boric acid dehydrates above 100°C and converts to its polymeric forms, which presumably is the active species

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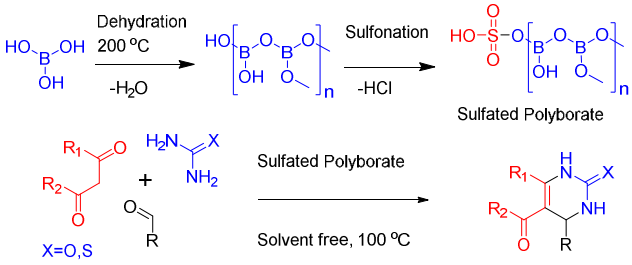

Scheme 1 Schematic representation of sulfated polyborate catalyzed synthesis of 3,4-dihydropyrimidin-2(1H)-ones/thiones

catalyzing the reaction.[39,40] Dehydrative polymerization of boric acid liberates of water molecules which may hamper the progress of the reaction.

This inspired us to develop a polymeric boric acid catalyst with mild Bronsted acidity. To accomplish this boric acid was dehydrated at 200 °C to convert it into its polymeric Lewis acid form and then sulfonated to introduce the mild Bronsted acid character. Boron being an electron deficient element and electron withdrawing effect of adjacent sulfate enhances its Lewis acidity; hence it has both Lewis as well as Bronsted acid characters (Scheme 1).

The development of novel synthetic procedures with an objective of green chemistry and green technology, the use of recyclable catalysts for organic synthesis to maximize catalyst efficiency and minimize waste production been currently in demand. To achieve these objectives, herein this report describes sulfated polyborate as an efficient and eco-friendly catalyst for the 3,4-dihydropyrimidin-2(1*H*)-ones/thiones synthesis under a solvent free condition with high yields and non-extractive product isolation. The catalyst was prepared from boric acid which is a readily available, non-toxic, and inexpensive starting material. To the best of our knowledge, this is the first report on the use of sulfated polyborate for the synthesis of 3,4-dihydropyrimidin-2(1*H*)-ones/thiones (Scheme 1). This catalyst is environmentally benign due to its mild acidity and non-toxic nature.

Experimental

Materials and methods

Melting points of all the compounds were recorded by AnalabThermoCal melting point apparatus in open capillary tube and are uncorrected. The FTIR spectra (KBr) were recorded on Shimadzu FTIRAffinity-1 Fourier Transform Infrared spectrophotometer. ^{1}H NMR spectra were recorded on MR400 Agilent Technology NMR spectrometer using tetramethylsilane (TMS) as an internal standard and DMSO-d_6/$CDCl_3$ as a solvent. X-ray diffractograms (XRD) were recorded on Rigakuminiflex X-ray Diffractometer. The SEM-EDAX characterization was performed on a JEOL JSM-638DLA scanning electron microscope equipped with energy dispersive X-ray spectrometer. The potentiometric analysis was performed on Elico LI 120 pH meter. The chirality has been ascertained on JASCO P-2000 polarimeter. Chemicals and solvents used were of LR grade and purchased from SD fine, AvraSynthesis and Spectrochem and used without purification. The purity determination of the starting materials and the reaction monitoring was accomplished by thin-layer chromatography (TLC) on Merck silica gel G F_{254} plates. All the products are known compounds and were characterized by melting points in comparison with the literature values, FTIR and ^{1}H NMR spectroscopy for structural identification.

Results and discussion

Preparation and characterization of the catalyst

Boric acid was heated in a petri dish at 200 °C for 4h to convert it to the polyboric acid; resultant glassy solid was ground into fine powder. Polyboric acid powder (5 g) was suspended in chloroform (20 ml) in 250 ml round bottom flask, chlorosulfonic acid (4.23 ml) was added drop wise over 30 minutes at room temperature. The mixture was stirred for 120 minutes at the same temperature. The reaction was quenched by adding ethanol (10 ml). Residual HCl gas was eliminated by nitrogen flush, the solid was filtered and washed several times with chloroform. Finally solid sulfated polyborate was dried at 100 °C in hot air oven till constant weight.

The catalyst was characterized by techniques such as potentiometric analysis, Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), scanning electron microscopy (SEM) energy dispersive X-ray spectroscopy (EDAX).

Accurately weighed catalyst (0.1g) was dissolved in a mixture of water and glycerine (2:1) and titrated against standard 0.1N NaOH solution. The concentration of H^+ was found as 1 mmol/g at first equivalence point which indicates the presence of SO_3H group and the total concentration of H^+ were found as 19.5 mmol/g at second equivalence point due to H^+ of associated B-O-H and SO_3H groups. First equivalence point was absent in boric acid as well as its polymeric form prior to sulfonation (Fig. 2).

FTIR spectrum of the catalyst was recorded to ascertain incorporation of the sulfonic acid group in polyboric acid. Sulfated polyborate exhibited characteristic absorption bands at 3446 and 1629 cm^{-1} that could be assigned to the -OH stretching and bending of the SO_3H groups, which can be regarded as ''Bronsted active sites'' of the catalyst. The band at 3221 cm^{-1} corresponds to O-H stretching of B-O-H and at 1469 cm^{-1} for B-O stretching. Bands at 1294 cm^{-1} for O=S=O asym. stretching, 1068 cm^{-1} for sym. stretching, 1004 cm^{-1} for S=O stretching of the SO_3H group. Band at 580 cm^{-1} represents O-B-O stretching of catalyst (Fig. 3).[41,42]

Powder XRD pattern of sulfated polyborate shown significant peaks positioned at 2θ = 28.1° which confirms the presence of B–O bonds in the crystalline structure of the catalyst (Fig. 4).[43]

The surface morphology of sulfated polyborate catalyst in the SEM image clearly indicated that the catalyst is crystalline with various shapes and sizes in the range of 4-10 µm (Fig. 5).

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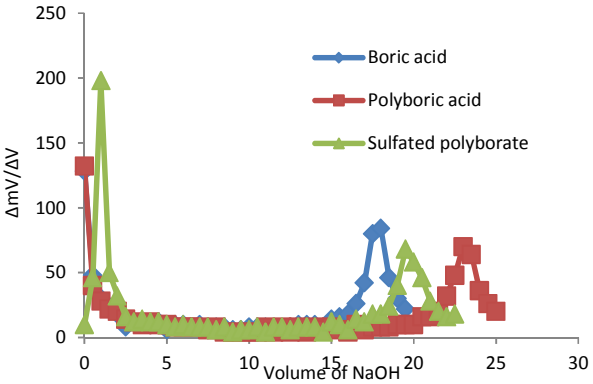

Fig. 2 Potentiometric titration curves of boric acid, polyboric acid and sulfated polyborate catalyst

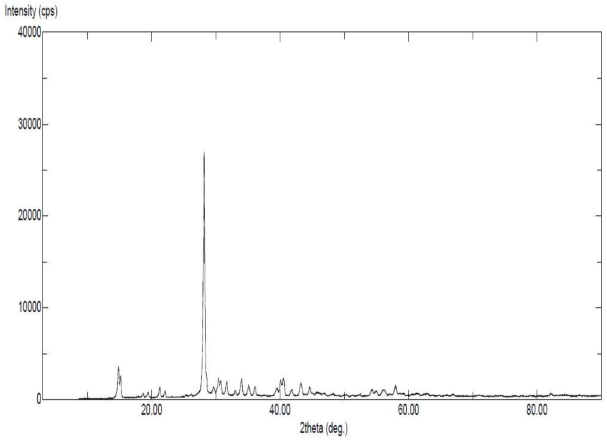

Fig. 4 XRD pattern of the catalyst

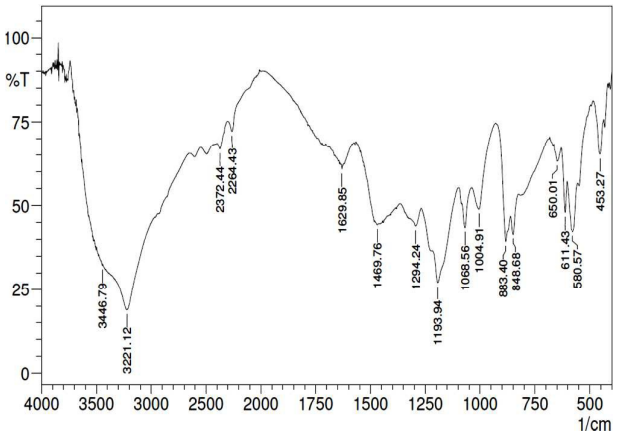

Fig. 3 FTIR spectrum of the catalyst

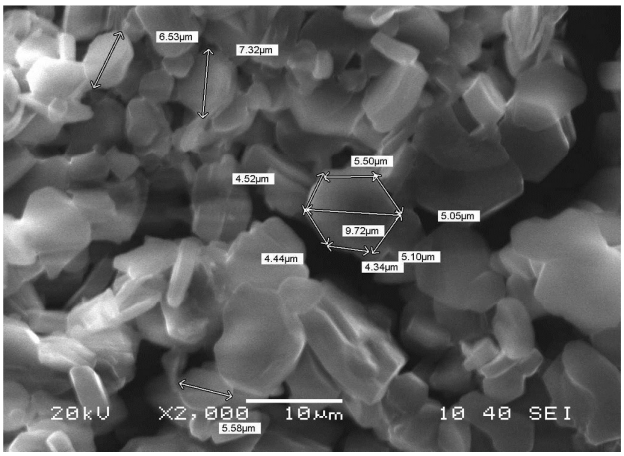

Fig.5 SEM image of the catalyst

The average elemental distribution mapping of the catalyst by EDAX showed boron: oxygen: sulfur signal ratio of 30.32: 68.73: 0.96 wt % over different areas.

Application of sulfated polyborate in Biginelli reaction

We structured our study to investigate the suitability of sulfated polyborate as a catalyst for Biginelli reaction at different reaction conditions. For the preliminary experiment benzaldehyde (2 mmol), a representative substrate, ethyl acetoacetate (2 mmol) and urea (2.4 mmol) were used to afford Ethyl 6-methyl-2-oxo-4-phenyl-1,2,3,4-tetrahydropyrimidine-5-carboxylate. (Table 1 and 2) The product has a chiral center and the present method produces racemate which is confirmed by polarimetry.

Effect of the catalyst loading on time and yields of the reaction was assessed (Table 1, entries 1-6). The reaction does not proceed in the absence of a catalyst at room temperature (Table1, entry 1) while proceeds at 100 °C with low product yield (Table 1, entry 2). An increase of the catalyst loading increased the product yield with a reduction in reaction time (Table 1, entries 3-6). The catalyst loading beyond 5 wt % was not advantageous (Table 1, entries 5 and 6), hence 5 wt % catalyst loading was chosen for further study.

Temperature played an important role in the synthesis of 3,4-dihydropyrimidin-2(1*H*)-ones (Table 1, entry 7 and 8). The temperature effect was examined at ambient, 70 °C and 100 °C under the solvent free condition with sulfated polyborate as a catalyst. The reaction does not proceed at room temperature while proceeds with low product yield at 70 °C. Further increasing temperature to 100 °C resulted in increased product yield in shorter reaction time (Table 1, entries 5). Therefore, this was the optimum temperature for performing the reaction.

The effect of various solvents on time and yield of the reaction was ascertained (Table 2, entries 1-7). None of the solvents has the advantage of time and yield over solvent free condition. Hence, the solvent free condition was regarded as best for the cost and environmental acceptability.

In all the experiments the products were isolated by aqueous quenching followed by filtration and washing the solids with water.

The reusability of the catalyst in the model reaction under

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Table 1 Effect of catalyst loading for the Biginelli reaction

Entry	Catalyst (wt %)	Temperature (°C)	Time (min)	Yield[a] (%)
1	-	rt	360	NR*
2	-	100	120	28
3	1	100	60	81
4	2.5	100	30	89
5	**5**	**100**	**20**	**94**
6	10	100	20	94
7	5	rt	60	NR[a]
8	5	70	60	76

[a]Isolated Yield

*NR= No Reaction

Table 2 The effect of various solvents for the Biginelli reaction

Entry	Solvent	Temperature (°C)	Time (min)	Yield[a] (%)
1	**Solvent free**	**100**	**20**	**94**
2	Ethanol	reflux	60	69
3	Acetonitrile	reflux	60	62
4	Tetrahydrofuran	reflux	60	58
5	Water	reflux	60	Traces
6	Toluene	reflux	60	60
7	DMF	100	60	62

[a]Isolated Yield

solvent free condition at 100 °C was evaluated. In this study, after completion of each reaction cycle, water was added and the product was filtered off. The filtrate was evaporated under vacuum rotary evaporator to recover catalyst. Recovered catalyst was recycled for four times with no significant loss in catalytic activity (Fig. 6).

In comparison with literature reported catalysts used for Biginelli reaction of benzaldehyde, ethyl acetoacetate, and urea; the present method has an advantage in many cases with respect to reaction condition, workup procedure, time and yields (Table 3).

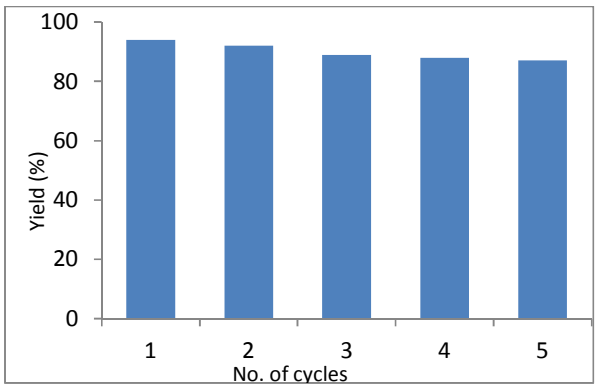

Fig. 6 Reusability of the catalyst

Table 3 Efficiency of sulfated polyborate **in** comparison with literature reported catalysts for the Biginelli reaction

Entry	Catalyst	Reaction Condition	Time	Yield (%)	Ref.
1	Sulfated polyborate	Solvent free/100 °C	20 min	94	This work
2	Sulfated silica tungsten acid	Solvent free/70 °C	15 min	94	8
3	SiO_2-PPA	Acetonitrile/reflux	30 min	85	9
4	$Al(HSO_4)_3$	Solvent free/120 °C	35 min	79	10
5	Al_2O_3-$MeSO_3H$	Ethanol/60 °C	1h	98	11
6	PSA	Water/90 °C	1h	94	12
7	Sulfated tungstate	Solvent free/80 °C	1h	92	13
8	Wells-Dawson heteropoly acid	Solvent free/80 °C	1.5h	83	14
9	Boric acid	Glacial acetic acid/ 100 °C	2h	97	15
10	Silica-HBF_4	Ethanol/rt	2h	94	16
11	H_2SO_4-Al_2O_3	Hexane/reflux	2h	95	17
12	Al_2O_3-SO_3H	Solvent free/120 °C	2.1h	88	18
13	*p*-TSA	Ethanol/reflux	2.5h	91	19
14	Sulfated zirconia	Solvent free/80 °C	4h	94	20
15	Cellulose sulfuric acid	Water/100 °C	5h	80	21
16	Silica sulfuric acid	Ethanol/reflux	6h	91	22
17	PPF-SO_3H	Ethanol/reflux	8h	81	23
18	Montmorilionite KSF	Solvent free/130 °C	48h	82	24

To investigate the substrate scope, optimized reaction condition was applied to substituted aromatic/aliphatic/α,β-unsaturated aldehydes, β-ketoesters/β-diketone and urea/thiourea variants.[49] All the substrate variants reacted well and afforded higher yields of the corresponding 3,4-dihydropyrimidin-2(1*H*)-ones/thiones within short reaction time (Table 4). Several electron releasing or electron withdrawing substituents at *ortho* and *para* positions of aromatic aldehydes have been examined. The nature of substitution has no significant effect on reaction time and yields. However, for 4-*N*,*N*-dimethyl, and 2-methoxy substrates, the reaction time was longer with similar product yield presumably due to electron releasing effects (Table 4, entry 9, 10).

3,4-dihydropyrimidin-2(1*H)*-thiones were also synthesized using thiourea instead of urea under optimized reaction conditions. Reaction with thiourea took little longer reaction time with similar product yields (Table 4, entry 12-16).

This protocol was extendable to aliphatic aldehydes (Table 4,

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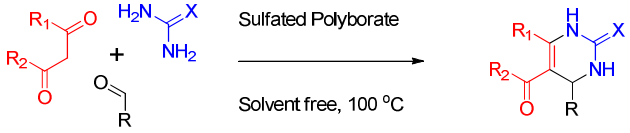

Table 4 Sulfated polyborate catalyzed Biginelli reaction under solvent free condition

Entry	Aldehydes (R)	β-Ketoesters		X	Time (min)	Yield[a](%)	M.P. °C	
		R1	R2				Obs.	Lit.
1	C_6H_5	CH_3	OCH_2CH_3	O	20	94	204-205	205-206[34]
2	4-CH_3O-C_6H_4	CH_3	OCH_2CH_3	O	20	91	199-200	200-201[34]
3	4-HO-C_6H_4	CH_3	OCH_2CH_3	O	30	86	232-234	234-235[21]
4	4-Br-C_6H_4	CH_3	OCH_2CH_3	O	20	89	211-212	213-214[34]
5	4-Cl-C_6H_4	CH_3	OCH_2CH_3	O	20	91	214-215	215-216[34]
6	4-CH_3-C_6H_4	CH_3	OCH_2CH_3	O	20	86	199-200	203-204[34]
7	4-NO_2-C_6H_4	CH_3	OCH_2CH_3	O	20	89	210-211	209-210[34]
8	4-F-C_6H_4	CH_3	OCH_2CH_3	O	20	88	184-185	182-184[22]
9	4-$N(CH_3)_2$-C_6H_4	CH_3	OCH_2CH_3	O	45	90	232-233	230-232[32]
10	2-CH_3O-C_6H_4	CH_3	OCH_2CH_3	O	30	90	259-260	262-263[34]
11	2-Cl-C_6H_4	CH_3	OCH_2CH_3	O	20	90	214-215	215-216[34]
12	H-C_6H_4	CH_3	OCH_2CH_3	S	30	92	207-208	208-210[34]
13	4-CH_3O-C_6H_4	CH_3	OCH_2CH_3	S	45	90	155-156	152-153[34]
14	4-Cl-C_6H_4	CH_3	OCH_2CH_3	S	30	91	181-182	179-180[34]
15	2-CH_3O-C_6H_4	CH_3	OCH_2CH_3	S	45	87	188-189	189-190[44]
16	2-Cl-C_6H_4	CH_3	OCH_2CH_3	S	45	88	216-217	218-220[21]
17	C_3H_7	CH_3	OCH_2CH_3	O	30	83	154-155	155-156[45]
18	*c*-C_3H_5	CH_3	OCH_2CH_3	O	20	92	189-190	NA*
19	*c*-C_6H_{11}	CH_3	OCH_2CH_3	O	20	91	230-231	232-234[46]
20	C_6H_5CH=CH	CH_3	OCH_2CH_3	O	45	85	221-223	223-224[34]
21	C_6H_5	CH_3	OCH_3	O	20	94	212-213	216-218[47]
22	C_6H_5	R_1,R_2=$CH_2C(CH_3)_2CH_2$		O	30	90	176-177	168-170[48]

[a]Isolated Yield

*NA= Not Available in literature

entry 17-19) and cinnamaldehyde (Table 4, entry 20). On The other hand, variations in β-ketoesters and a β-diketone were also adaptable (Table 4, entry 21-22).

This protocol tolerates a variety of substituents on aromatic aldehydes and extendable to aliphatic/α,β-unsaturated aldehydes along with the thiourea and ethyl acetoacetate variants as β-ketoesters/β-diketone of Biginelli reaction under optimized conditions.

Conclusions

In conclusion, the present procedure is an efficient and eco-friendly protocol for the synthesis of 3,4-dihydropyrimidin-2(1*H*)-ones/thiones through one-pot reaction of various aldehydes, β-ketoesters/β-diketone and urea/thiourea under optimal conditions. Mild reaction conditions, shorter reaction time, higher yield, ease of workup and recyclability of the catalyst are the key features of this procedure. Moreover, this method also has the ability to tolerate a wide variety of substituents.

Acknowledgements

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49. *General procedure for 3,4-dihydropyrimidin-2(1H)-ones/thiones:* A mixture of β-ketoester/β-diketone (2 mmol), aldehyde (2 mmol), urea or thiourea (2.4mmol) and sulfated polyborate (5 wt %) was heated at 100 °C. The reaction was monitored by thin layer chromatography. After completion of the reaction, the mixture was cooled to room temperature and quenched by water; solid precipitated was filtered at vacuum pump, washed with water (3 X 5 mL), dried under vacuum and recrystallized from ethanol to afford the pure products.

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Graphical abstract:

Rapid, high yielding, solvent free reaction with easy workup procedure using recyclable catalyst with no loss in catalytic activity.