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REGULAR ARTICLE

Sulfated polyborate as an eco-compatible solid acid catalyst for efficient and facile solvent-free synthesis of polyhydroquinolines

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Abstract. An environmentally viable, green and efficient protocol for the synthesis of polyhydroquinolines using sulfated polyborate catalyst have been developed by Hantzsch four-component condensation between aromatic aldehydes, dimedone, ammonium acetate and ethylacetoacetate or ethylcyanoacetate at 100 °C under solvent-free condition. The sulfated polyborate catalyst is characterized by FT-IR, XRD, SEM and EDAX techniques. The noticeable features of this methodology are mild Brønsted acidic nature of the catalyst, good to excellent product yields (85–94%), short reaction time (18–30 min), solvent-free condition, operational simplicity and applicability to a wide range of substrates (29 examples).

Keywords. Sulfated polyborate; polyhydroquinolines; Hantzsch condensation; solvent-free; solid acid catalyst.

1. Introduction

The solid acid catalyst plays an important role to develop economically and environmentally sustainable processes.[1] Boric acid is a readily available inexpensive mild catalyst used in a variety of organic transformations.[2] It is known that above 100 °C it undergoes polymerization and liberates water molecule which may hamper the rate of reactions.[3] This led to the development of sulfated polyborate with enhanced catalytic activity.[4] Over the past years, the sulfated polyborate has emerged as a potential solid acid catalyst used in several MCRs with excellent yields, short reaction time and operational simplicity.[5–7] The interesting feature of this catalyst is, it possesses Lewis acidic property due to polymeric borate backbone and Brønsted acidic nature due to support of -SO_3H group which makes it more applicable.

Polyhydroquinolines (PHQs) are privileged scaffolds due to the presence of 1,4-dihydropyridine (DHP) moiety which is a core part of calcium channel functioning as well as hypertension preventive drugs *viz*., nimodipine, lacidipine, felodipine, amlodipine, nicardipine, nifedipine, etc.[8] The polyhydroquinolines show diverse biological functions such as antimalarial, bronchodilatory, vasodilator, antidiabetic and antiasthematic activities.[9] In 1881, synthesis of substituted 1,4-dihydropyridines was first reported by Arthur Hantzsch and further Safak's group synthesized 1,4-DHP-annulated novel heterocycle known as polyhydroquinoline (Figure 1).[10]

The straightforward synthesis of polyhydroquinoline involves one-pot four-component condensation reaction between aromatic aldehydes, dimedone, ammonium acetate and ethylacetoacetate or ethylcyanoacetate using a variety of catalytic systems. Among them synthesis of polyhydroquinolines using ethylacetoacetate involves spinel $FeAl_2O_4$,[11] Cu(II)-DCC-CMK-3,[12] AFGO nanosheets,[13] TEDETA@BNPs,[14] MCM-41@serine@Cu(II),[15] ascorbic acid,[16] $Fe_3O_4@SiO_2/ZnCl_2$,[17] SBA-15@Glycine-M,[18] PMOICSPrSO_3H,[19] KH_2PO_4,[20] [PyridineSO_3H]Cl,[21] CdS nanowires,[22] Fe_3O_4/SiO_2-OSO_3H,[23] ZnO[DABCO(C_2COOH$)_2]^{2+}$[Br$]_2$,[24] nano $VTiO_2$,[25] $H_5BW_{12}O_{40}$[26] and nicotinic acid.[27] The condensation reaction using ethylcyanoacetate utilizes

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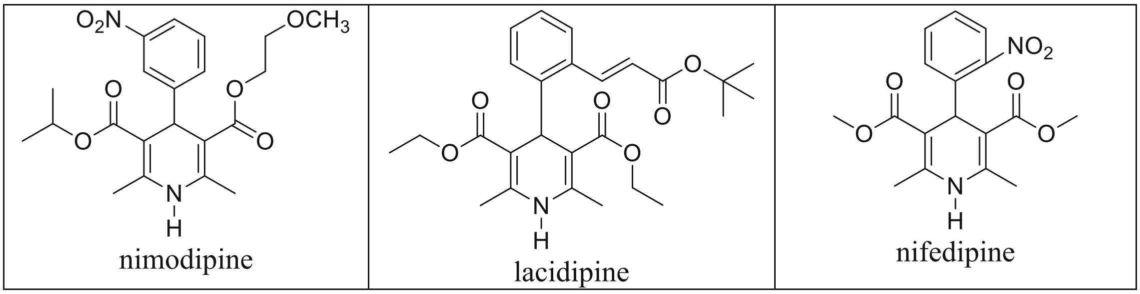


Figrue 1. Some bioactive molecules containing 1,4-dihydropyridine nucleus.

systems such as MCM-41,[28] Pd-Schiff-Base@Fe_3O_4 MNPs,[29] ZnO-nanoparticle,[30] FSM-16-SO_3H nanoparticles,[31] microwave irradiation,[32] ClO_4^-/Zr-MCM-41,[33] nano ionic liquid 1-methylimidazolium trinitromethanide,[34] Pd(0) nanoparticles,[35] Fe_3O_4@FSM-16-SO_3H[36] and Fe_3O_4@B-MCM-41.[37]

Despite the merits of reported methods, they may also suffer from one or more shortcomings like harsh conditions, expensive catalyst/reagents, tedious workup, use of toxic catalyst/reagents, limited scope, lengthy reaction time and poor product yields. Hence, there is a need for a general, efficient, feasible and environment-friendly protocol for the synthesis of polyhydroquinolines. With this view and in continuation to our research work[38–42] herein, we wish to explore a catalytic application of sulfated polyborate for efficient and facile one-pot four-component Hantzsch condensation between differently substituted aromatic aldehydes, dimedone, ethylacetoacetate/ethylcyanoacetate and ammonium acetate at 100 °C under the solvent-free condition to give polyhydroquinolines with excellent yields in a short time.

2. Experimental

2.1 *General information*

The solvents and reagents used in this work were of AR grade and used without further purification. Fourier transform infrared (FT-IR) spectrum was recorded on Perkin-Elmer, 400 FT-IR spectrometer. The X-ray diffraction pattern was obtained on Panalyticals X Pert Pro, X-Ray Diffractometer. The SEM images were obtained from JSM6100, Jeol Scanning Electron Microscope. The ^1H NMR spectrum was recorded on Bruker Avance 500MHz NMR spectrometer. Mass spectrum was recorded on Waters Q-ToF Micromass spectrometer. The TLC (silica G60 F254 plates, Merck) was used to monitor the progress of the reaction. The melting points were recorded in an open capillary tube and are uncorrected.

2.2 *Preparation of sulfated polyborate acid catalyst*

The readily available and inexpensive boric acid and chlorosulfonic acid were used for the preparation of sulfated polyborate following the literature reported method.[4] The catalyst obtained was solid and crystalline in nature. It was characterized by FT-IR, XRD, SEM and EDAX techniques.

2.3 *General procedure for the synthesis of substituted polyhydroquinolines*

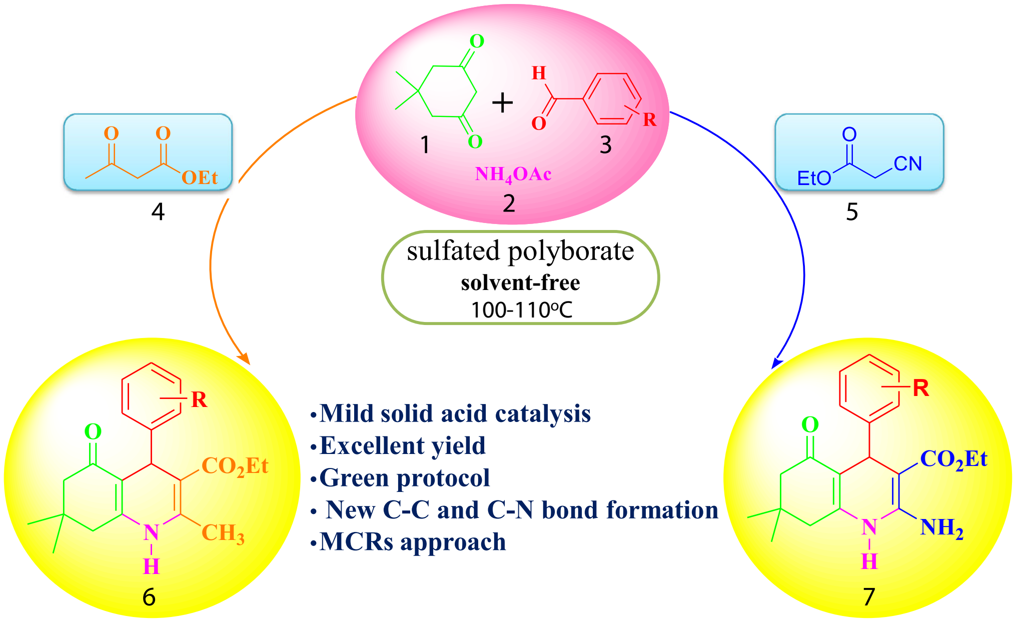
A round bottom flask equipped with water condenser was charged with a mixture of substituted aromatic aldehydes (**1**, 1 mmol), dimedone (**2**, 1 mmol), ammonium acetate (**3**, 1.5 mmol) and ethyl acetoacetate (**4**, 1 mmol) or ethylcyanoacetate (**5**, 1 mmol). To this, 80 mg of sulfated polyborate catalyst was added and the resulting reaction mixture was magnetically stirred in oil-bath at 100–110 °C under solvent-free conditions till completion of the reaction (Table 3). The progress of the reaction was monitored by TLC using ethyl acetate: n-hexane (3:7) as an eluent. The hot ethanol was added to the reaction mixture and filtered to remove insoluble material. The solid appeared in filtrate was filtered to furnish polyhydroquinolines (**6a-p** and **7a-m**). The physical and spectral data of synthesized compounds were compared with the data reported in the literature which supports the formation of polyhydroquinolines (Scheme 1).

3. Results and Discussion

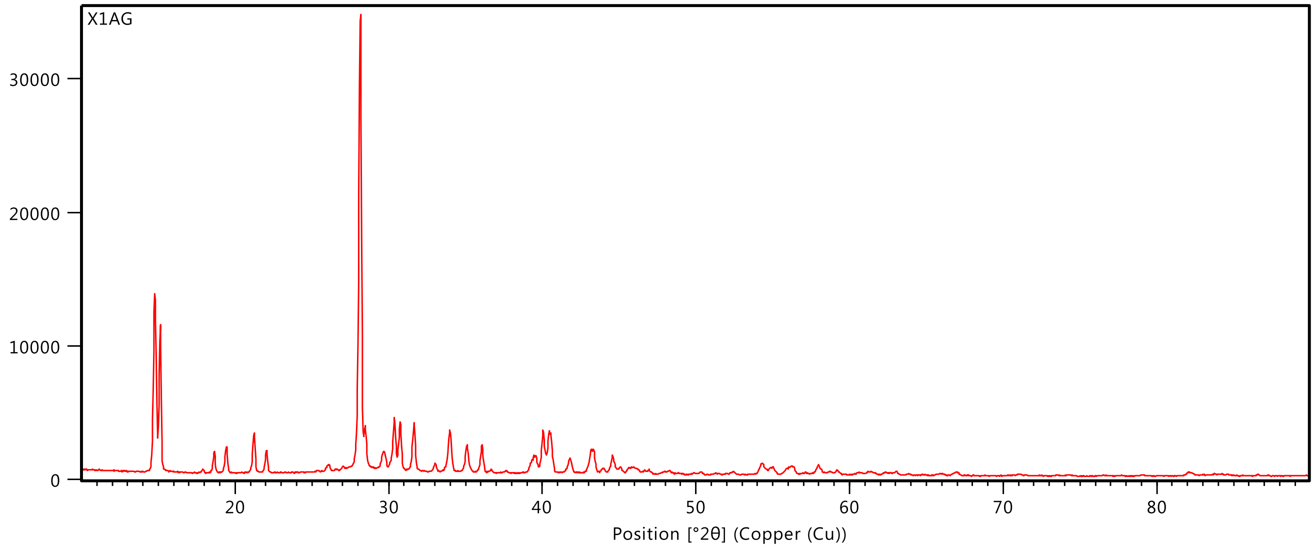
3.1 *Characterization of aluminized polyborate*

The catalyst was synthesized by the following procedure reported in the literature.[4] After preparation of sulfated polyborate its formation was confirmed by FT-IR, XRD, SEM and EDAX techniques.

3.1a *FT-IR analysis*: The FT-IR spectra show characteristic broad band between 3100-3600 cm^{-1} is due to O-H stretching of -SO_3H and B-O-H groups.



Scheme 1. Synthesis of polyhydroquinolines using aldehydes (1 mmol), dimedone (1 mmol), ethylacetoacetate or ethylcyanoacetate (1 mmol) and ammonium acetate (1.5 mmol) catalysed by sulfated polyborate.



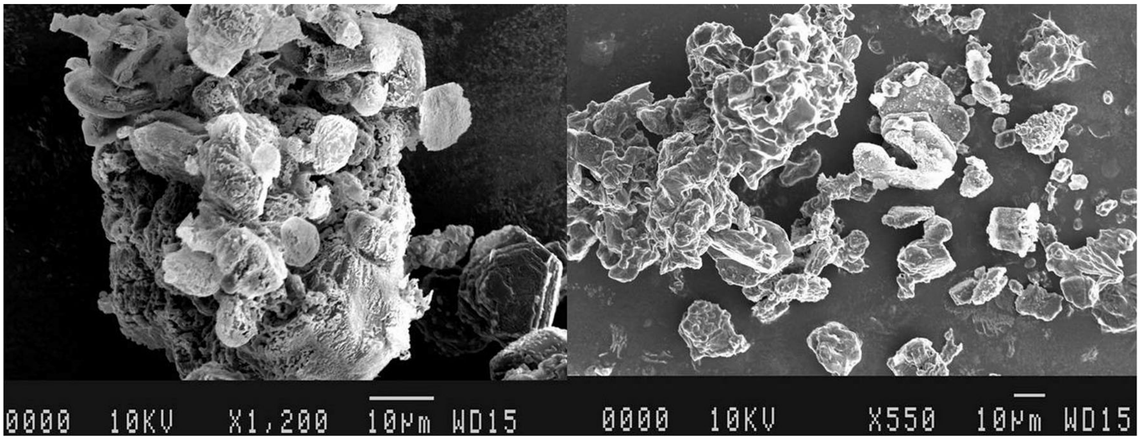
Figrue 2. XRD pattern of sulfated polyborate.

The broad band between 1400-1650 cm^{-1} includes peaks due to O–H bending of –SO$_3$H group and B-O stretching. The peaks at 1192 cm^{-1}, 1057 cm^{-1}, 1000 cm^{-1} and 546 cm^{-1} corresponds to O=S=O asymmetric stretching, O=S=O symmetric stretching, S=O stretching and O–B–O stretching of catalyst, respectively (Supplementary Information).[43, 44]

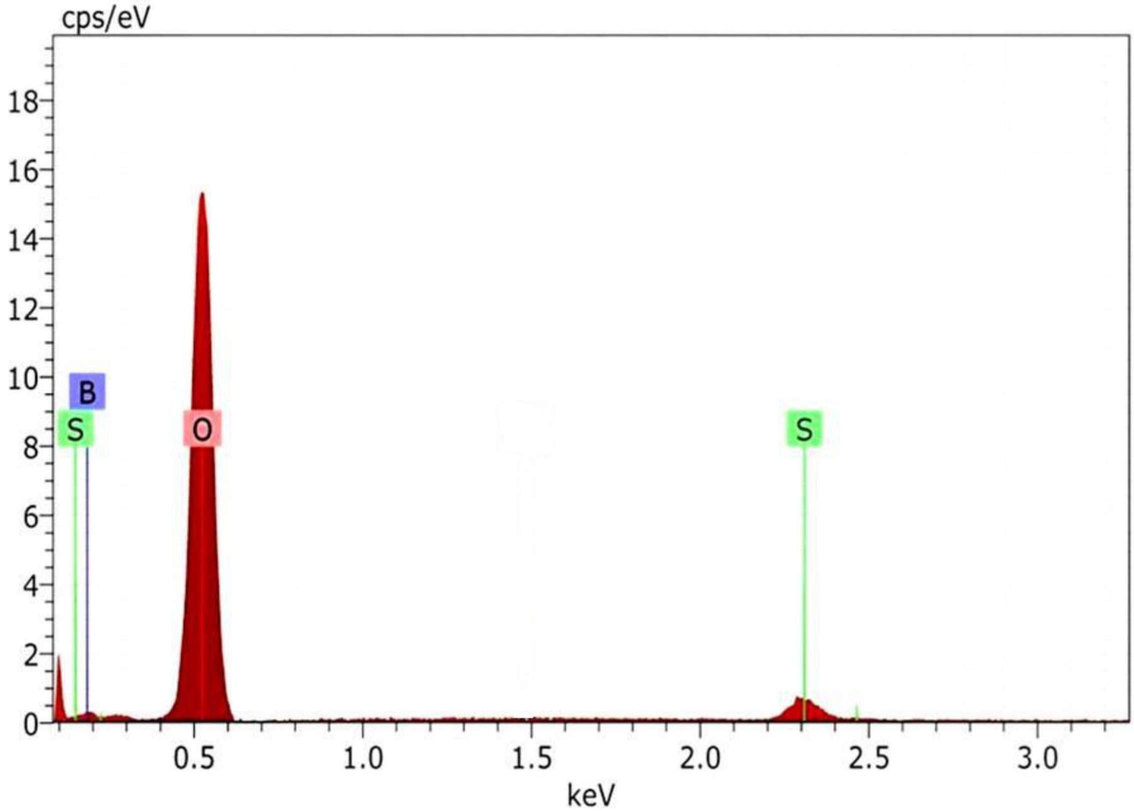
3.1b *XRD analysis*: The formation of sulfated polyborate was confirmed by its powder X-ray diffraction pattern which shows a significant peak at $2\theta = 28.11°$ is due to B–O bonds in the crystalline structure of the catalyst (Figure 2).[45]

3.1c *SEM analysis*: The SEM image shows that catalyst is crystalline in nature with particles of different shapes and sizes (Figure 3).

3.1d *EDAX analysis*: The energy dispersive spectrum shows the presence of oxygen/sulfur/boron



Figrue 3. SEM image of sulfated polyborate.



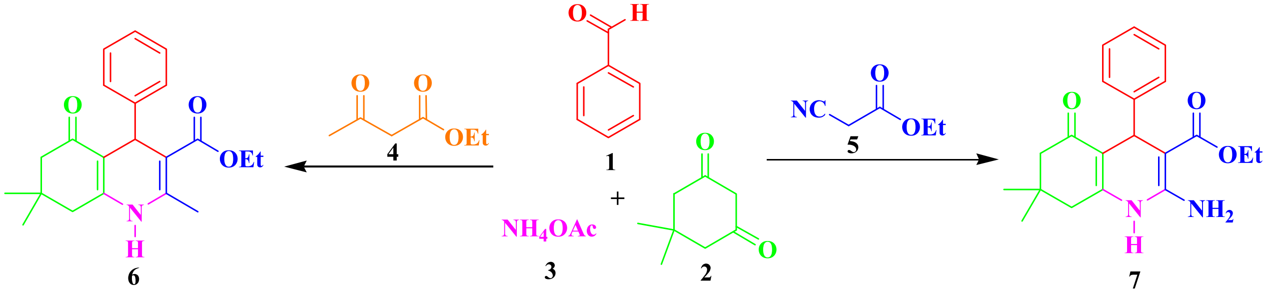
Figrue 4. EDAX analysis of sulfated polyborate.

with a ratio of 81.82: 2.47: 15.58 wt % over different areas which indicate the formation of sulfated polyborate (Figure 4).

3.2 *Study of catalytic activity of sulfated polyborate in the synthesis of polyhydroquinolines*

Inspired by catalytic applications of sulfated polyborate reported in the literature[4–7] we explored its catalytic utility in the multicomponent synthesis of polyhydroquinolines. In order to set the best reaction conditions, we choose a model reaction of benzaldehyde (**1a**, 1 mmol), dimedone (**2**, 1 mmol), ammonium acetate (**3**, 1.5 mmol) and ethylacetoacetate (**5**, 1 mmol) or ethylcyanoacetate (**6**, 1 mmol). We first performed a series of trial experiments to optimize the influence of different solvents and temperature for the synthesis of polyhydroquinolines (**6a/7a**) with 80 mg of fixed amount of sulfated polyborate catalyst. The

Table 1. Optimization of solvent and temperature for the synthesis of polyhydroquinolines[a].



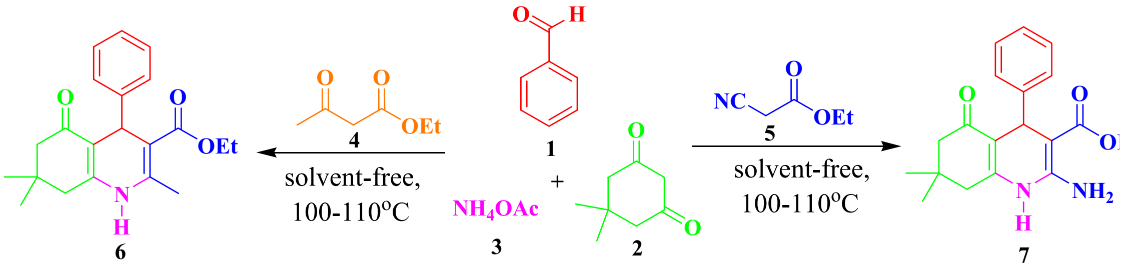
Entry	Solvent	Temperature (°C)	Time (min)	Yield[b] (%)	Yield[c] (%)
1	H_2O	r.t.	60	–	–
2	EtOH	r.t.	60	–	–
3	H_2O:EtOH	r.t.	60	–	–
4	H_2O	reflux	60	37	41
5	EtOH	reflux	60	85	79
6	CH_3CN	reflux	60	60	56
7	THF	reflux	60	45	47
8	DMF	80 °C	60	52	51
9	solvent-free	r.t.	60	45	41
10	solvent-free	80 °C	30	85	80
11	**solvent-free**	**100 °C**	**20**	**93**	**92**
12	solvent-free	110 °C	20	92	92

[a] Reaction conditions: benzaldehyde (1 mmol), dimedone (1 mmol), ammonium acetate (1.5 mmol) and ethylacetoacetate or ethylcyanoacetate (1 mmol) using sulfated polyborate catalyst (80 mg).

[b] Isolated yield of **6a**.

[c] Isolated yield of **7a**.

Table 2. Optimization of the amount of catalyst.



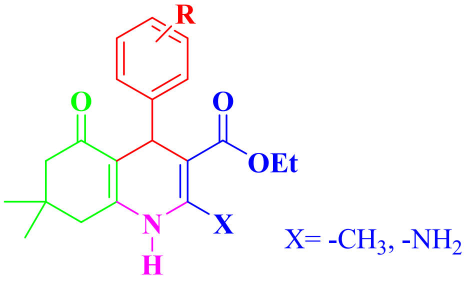
Entry	Catalyst amount (mg)	Time (min)	Yield[b] (%)	Yield[c] (%)
1	none	30	trace	trace
2	20	30	48	40
3	40	30	70	66
4	60	25	82	83
5	**80**	**20**	**93**	**92**
6	100	20	91	90

[a] Reaction conditions: **1** (1 mmol), **2** (1 mmol), **4** or **5** (1 mmol) and **3** (1.5 mmol) at 100–110 °C under solvent-free condition.

[b] Isolated yield of **6a.**

[c] Isolated yield of **7a.**

Table 3. Synthesis of polyhydroquinoline derivatives.[a]



Entry	Substituents ('R')	'X'	Product	Time (min)	Yield[b] (%)	M. P. (^{o}C)		Ref.
						Observed	Reported	
1	–H	$–CH_3$	**6a**	20	93	217–219	218–220	[14]
2	2-Cl	$–CH_3$	**6b**	28	85	206–207	207–209	[22]
3	$2-NO_2$	$–CH_3$	**6c**	23	89	206–208	206–207	[12]
4	$3-NO_2$	$–CH_3$	**6d**	25	92	183–184	182–184	[21]
5	3-Cl	$–CH_3$	**6e**	27	90	204–206	205–207	[21]
6	3-OMe	$–CH_3$	**6f**	30	88	199–201	199–201	[21]
7	4-OMe	$–CH_3$	**6g**	25	92	258–260	257–260	[22]
8	4-Me	$–CH_3$	**6h**	26	91	260–262	259–262	[22]
9	4-Br	$–CH_3$	**6i**	20	90	254–256	256–257	[22]
10	$4-NO_2$	$–CH_3$	**6j**	18	94	240–242	240–242	[22]
11	4-Cl	$–CH_3$	**6k**	20	93	244–246	244–246	[22]
12	4-OH	$–CH_3$	**6l**	30	86	231–233	232–234	[22]
13	4-F	$–CH_3$	**6m**	24	91	186–187	184–186	[14]
14	$3,4\ (OMe)_2$	$–CH_3$	**6n**	30	87	196–197	196–198	[15]
15	2-Thiophene	$–CH_3$	**6o**	26	89	240–241	240–241	[22]
16	2-Furan	$–CH_3$	**6p**	28	85	247–249	248–250	[22]
17	–H	$–NH_2$	**7a**	20	92	158–160	158–161	[33]
18	2-Cl	$–NH_2$	**7b**	25	90	180–182	182–183	[33]
19	2-OH	$–NH_2$	**7c**	28	85	113–114	114–116	[37]
20	3-OMe	$–NH_2$	**7d**	30	88	157–159	155–158	[33]
21	$3-NO_2$	$–NH_2$	**7e**	20	90	182–183	183–184	[36]
22	3-Br	$–NH_2$	**7f**	20	89	136–137	135–136	[36]
23	3-OH	$–NH_2$	**7g**	25	91	166–167	165–168	[36]
24	4-Me	$–NH_2$	**7h**	20	92	158–162	158–161	[33]
25	4-F	$–NH_2$	**7i**	20	91	156–157	155–158	[36]
26	$4-NO_2$	$–NH_2$	**7j**	19	93	188–190	189–190	[33]
27	4-OMe	$–NH_2$	**7k**	20	92	134–136	134–136	[33]
28	4-Cl	$–NH_2$	**7l**	20	93	161–162	160–162	[33]
29	$4-(NMe)_2$	$–NH_2$	**7m**	25	86	122–125	123–124	[36]

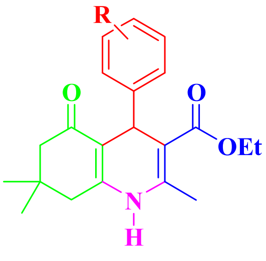
[a] Synthesized under optimized conditions.

[b] Isolated yield.

model reaction was performed in solvents like H_2O, EtOH, H_2O:EtOH (1:1), DMF, THF and CH_3CN as well as a solvent-free condition at different temperature (Table 1). From these experiments, a reaction under the solvent-free condition at 100–110 °C is found to be the most suitable for the synthesis of polyhydroquinolines (**6a**/**7a**) with excellent yields in a short time.

With this optimized condition, our next aim was to find the role and amount of sulfated polyborate catalyst towards the synthesis of polyhydroquinolines (**6a**/**7a**). The model reaction was performed with different amount of catalyst and results obtained are summarized in Table 2. The outcome of this study indicates that reaction does not occur in absence of the catalyst. The increase in the amount of catalyst in order of 20 mg, 40 mg, 60 mg and 80 mg increases the yield of the product and decreases the time required for conversion into the product. Further increase in the amount of catalyst has no significant effect on the

Table 4. The comparison of obtained results with literature reported methods for the synthesis of polyhydroquinolines.



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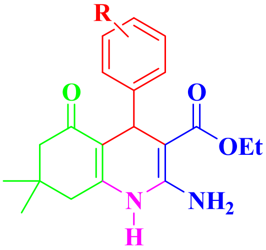
Entry	Catalyst and solvent	Catalyst amount	Temp. (°C)	Time (min)	Yield (%)	Ref.
1	spinel $FeAl_2O_4$, EtOH	40 mg	80 °C	30–80	96	[11]
2	Cu(II)-DCC-CMK-3, solvent-free	30 mg	80 °C	20–90	98	[12]
3	AFGO nanosheets, EtOH	25 mg	r.t.	120–240	87–91	[13]
4	MCM-41@serine@Cu(II), EtOH	5 mg	80 °C	170–215	96	[15]
5	Ascorbic acid, solvent-free	5% mol	80 °C	90–300	70–99	[16]
6	Fe_3O_4@SiO_2/$ZnCl_2$, solvent-free	5 mg	110 °C	30	92	[17]
7	SBA-15@Glycine-M, EtOH	80 mg	60 °C	110–220	92	[18]
8	Sulfated polyborate, solvent-free	80 mg	100 °C	20	93	Present work



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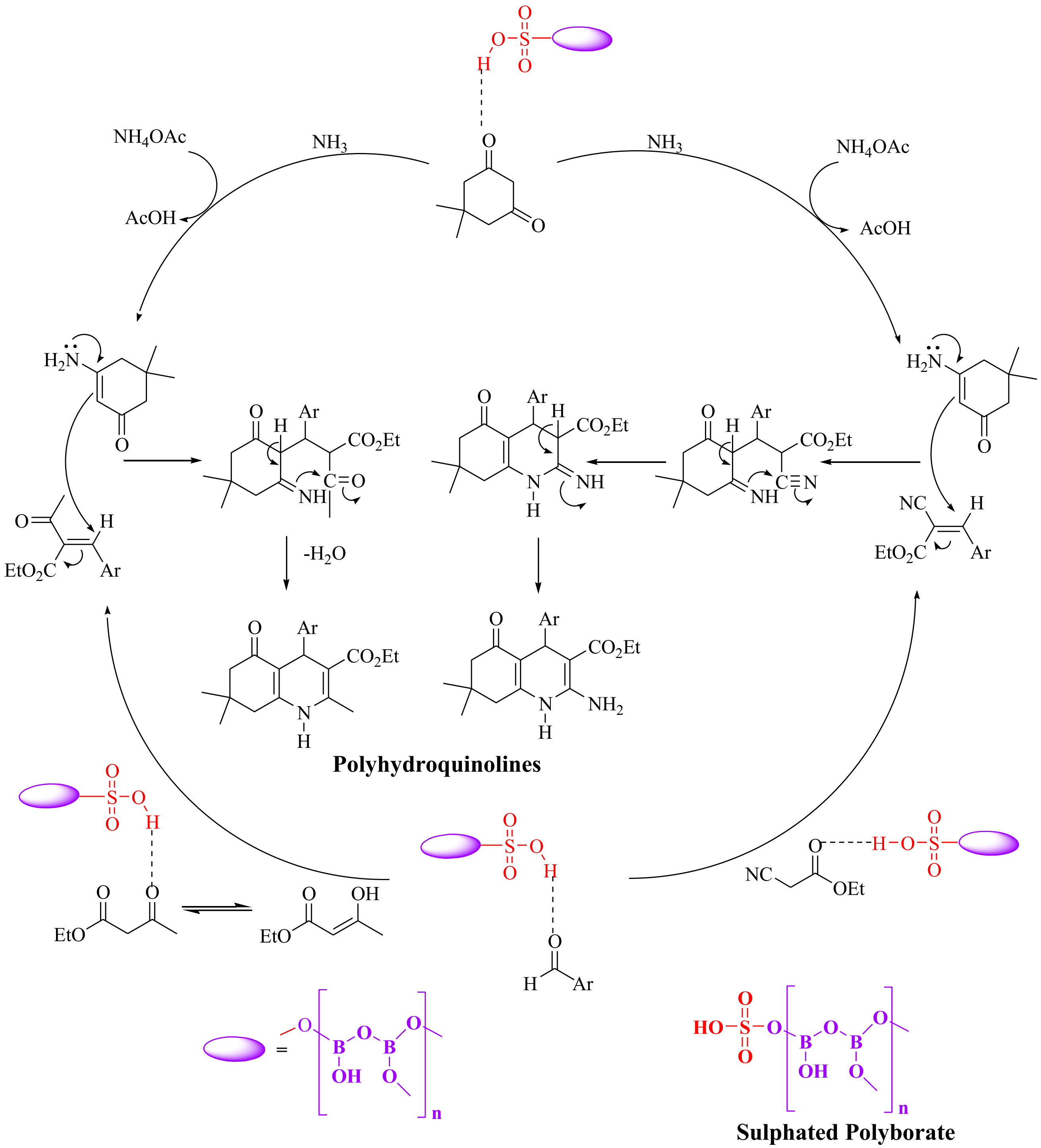
Entry	Catalyst and solvent	Catalyst amount	Temp. (°C)	Time (min)	Yield (%)	Ref.
1	MCM-41-OBF_2, EtOH	50 mg	reflux	15–110	75–95	[28]
2	Pd-Schiff-Base@Fe_3O_4 MNPs, solvent-free	3 mg	70 °C	15	99	[29]
3	ZnO-NPs, solvent-free	10 mol%	r.t.	20–25	91	[30]
4	FSM-16-SO_3H NPs, EtOH	40 mg	reflux	5–60	80–94	[31]
5	MWI/EtOH	–	MWI	5–7	89–92	[32]
6	ClO4^{-}/Zr-MCM-41, EtOH	10 mg	reflux	10–60	80–94	[33]
7	Fe_3O_4@FSM-16-SO_3H, EtOH	40 mg	reflux	10–50	85–96	[36]
8	Fe_3O_4@B-MCM-41, EtOH	50 mg	reflux	15–130	75–90	[37]
9	Sulfated polyborate, solvent-free	80 mg	100 °C	20	92	Present work

yield and rate of reaction. From all these investigations, we report that optimal results were obtained with 80 mg of sulfated polyborate catalyst under the solvent-free condition at 100–110 °C for the synthesis of polyhydroquinolines (**6a/7a**).

To explore the generality, effectiveness, versatility and scope of the present protocol, we carried out reactions between dimedone, ammonium acetate, ethylacetoacetate or ethylcyanoacetate with aromatic aldehydes having –OMe, –Me, –Cl, –Br, –F, $–NO_2$ at the ortho, meta or para positions under the optimized conditions (Table 3). It is worth noting that all reactions with aldehydes having electron-donating as well electron-withdrawing groups occurred with no side reaction with good to excellent yields (85–94%) within a short time (18–30 min). This method is also suitable for heteroaromatic aldehydes such as furan-2-carbaldehyde (**6o**)



Scheme 2. Plausible mechanism for the synthesis of polyhydroquinolines.

and thiophene-2-carbladehyde (**6p**). The aldehydes having ortho substituents also give products with good yields (**6b**, **6c**, **7b**, **7c**).

To see the merits of the present protocol, we compared results obtained with literature reported methods for the synthesis of polyhydroquinolines (**6**/**7**). The data summarized (Table 4) indicates that sulfated polyborate shows excellent catalytic efficacy for the synthesis of **6** and **7** under environmentally benign conditions.

3.3 *Plausible mechanism*

A reaction mechanism was proposed for the four-component synthesis of polyhydroquinolines as depicted in Scheme 2. The electrophilicity of carbonyl group of aldehyde, dimedone and ethylacetoacetate or ethylcyanoacetate is activated due to the acidic nature of sulfated polyborate catalyst. In presence of a catalyst, the dimedone reacts with ammonia to give enamine. The subsequent Knoevenagel condensation of aromatic aldehydes with ethylacetoacetate or ethylcyanoacetate gives intermediate. The enamine and the intermediate undergo Michael addition followed by sequential cyclization and dehydration reaction gives polyhydroquinolines (**6/7**).

4. Conclusions

This study reports an application of sulfated polyborate as a mild solid acid catalyst in a cost-effective, efficient and facile protocol for the synthesis of polyhydroquinolines using aromatic aldehydes, dimedone, ammonium acetate and ethylacetoacetate or ethylcyanoacetate at 100-110 °C under solvent-free condition. The key features of this protocol are, use of inexpensive and non-toxic sulfated polyborate catalyst, eco-sustainable and green approach, short reaction times, good to excellent product yields, synthetic simplicity, safe and clean reaction profile and simple purification of the product.

Supplementary Information (SI)

Spectral data is available at www.ias.ac.in/chemsci.

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