J IRAN CHEM SOC
DOI 10.1007/s13738-017-1186-x

ORIGINAL PAPER

Sulfated polyborate-catalyzed *N*-formylation of amines: a rapid, green and efficient protocol

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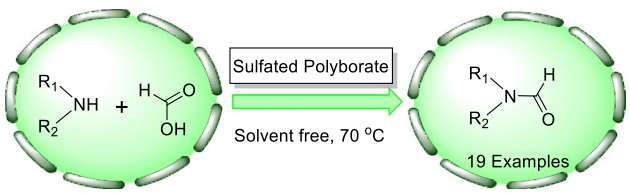
Received: 18 April 2017 / Accepted: 17 August 2017

Abstract A rapid, green and efficient method for *N*-formylation reaction of various amines with formic acid in the presence of sulfated polyborate catalyst under solvent-free conditions has been described. The catalyst has the advantage of mild Bronsted as well as Lewis acid character. The catalyst is recyclable with no significant loss in catalytic activity. The present protocol is advantageous due to its solvent-free condition, short reaction time, high yields, easy workup and ability to tolerate a variety of functional groups.

Graphical Abstract



Keywords Sulfated polyborate · *N*-formylation · Amines · Recyclable catalyst

Electronic supplementary material The online version of this article (doi:10.1007/s13738-017-1186-x) contains supplementary material, which is available to authorized users.

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Introduction

The synthesis of *N*-bonded compounds has received considerable attention in synthetic organic chemistry during the past few years. Formylation of amines is an important reaction in organic and medicinal chemistry [1]. Formamide is an important functionality due to its presence in the pharmaceutically valuable molecules, viz. fluoroquinolones [2], 1,2-dihydroquinolines [3] and substituted aryl imidazoles [4]. These being Lewis bases promote organic transformations such as hydrosilylation and allylation of carbonyl compounds [5, 6]. Moreover, formamides are commonly used reagents in Vilsmeier–Haack formylation [7, 8] and formylation is an important *N*-protecting strategy in peptide synthesis [9]. There are many important drugs molecules having *N*-formyl group in their scaffold such as formoterol, a long-acting β_2 agonist [10]; iguratimod, an anti-arthritis agent [11]; benfotiamine; acefurtiamine; fursultiamine; thiamine diphosphate precursors; and vintiamol [12] (Fig. 1).

Till date, numbers of the literature procedures are available for *N*-formylation of amines. Some reports include various formylating reagents such as chloral [13], formic acid–DCC [14], formic acid–EDCI [15], formic acid–CDMT [16], formic acid esters [17], acetic-formic anhydrides [18], ammonium formate [19], sodium formate [20] and formic acid in polyethylene glycol [21]. Recently, formylation of amines also reported with H_2 and CO_2 gas which require special equipment to carry out the reaction in gaseous phase [22, 23]. Several catalysts were also used which include KF-alumina [24], Amberlite IR 120 [25], ZnO [26], nano-CeO_2 [27], nano-MgO [28], HEU zeolite [29], natrolite zeolite [30], Indium metal [31], sulfated titania [32], sulfated tungstate [33], silica supported perchloric acid [34], sulfonic acid supported on hydroxyapatite-encapsulated-γ-Fe_2O_3 [35], heteropolyanion-based ionic liquids [36],

Published online: 23 August 2017

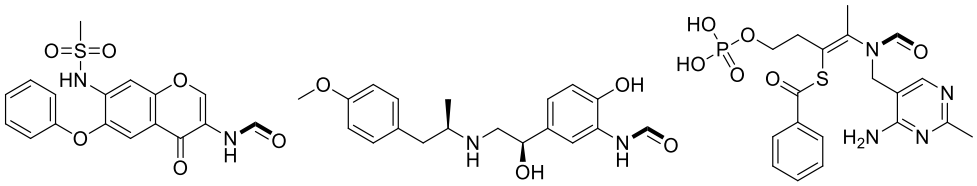


Fig. 1 Pharmaceutically active formamide molecules

heteropolyanion-based sulfated ionic liquid [37], nano-rod-shaped basic Al_2O_3 [38], nano-sulfated TiO_2 [39], phosphotungstic acid supported on silica-coated $CoFe_2O_4$ nanoparticles [40], Na^+-MMT-[prim]HSO_4 [41], silica sulfuric acid [42], sulfonated rice husk ash [43] and melamine trisulfonic acid [44].

However, many of the *N*-formylation methods suffer from various disadvantages such as the use of expensive and toxic formylating reagents/catalysts, difficult accessibility to reagents, long reaction time, thermal instability and non-selectivity. Thus, the development of a safe, mild, efficient, environmentally benign, chemo-selective and high yielding rapid reaction procedure using cost-effective and recyclable catalyst would be valuable.

In search of convenient, green and practical catalytic methods for the current interest in organic synthesis and commercial process, recently we have introduced a sulfated polyborate catalyst and evaluated its effectiveness for catalyzing various organic transformations [45–55]. Its easy preparation, mild acidity, reusability and eco-friendliness have inspired us to find out its potential to catalyze other useful reactions. Therefore, in the extension of our previous studies, in this paper, we explored a rapid, green and efficient *N*-formylation protocol under solvent-free conditions using sulfated polyborate, which has many advantages over reported methods such as safe, environmentally benign and economic formylating agents and catalyst; however, recyclability of the catalyst, mild reaction conditions, shorter reaction time, high yields, easy of workup procedure and chemoselectivity are the key features of this procedure.

Experimental

The FTIR spectra were recorded on Shimadzu FTIRAffinity-1 Fourier transform infrared spectrophotometer. Melting points of all the compounds were recorded by Analab ThermoCal melting point apparatus in open capillary tube and are uncorrected. ^{1}H NMR spectra were recorded on MR400 Agilent Technology NMR spectrometer using $CDCl_3$ or DMSO-d_6 as a solvent with tetramethylsilane internal standard. Solvents and chemicals used were of LR grade, which were purchased from Avra Synthesis, Spectrochem and SD fine chemicals and used without purification. The purity determination of the starting materials and reaction monitoring was performed by thin-layer chromatography (TLC) on Merck silica gel G F_{254} plates. All the products are known compounds and were identified by ^{1}H NMR spectroscopy.

Preparation of sulfated polyborate

The sulfated polyborate catalyst was prepared as per procedure reported in the literature [45].

General procedure for *N*-formylation

To a mixture of amine (2.0 mmol) and formic acid (2.4 mmol), sulfated polyborate (7.5 wt%) was added and the reaction mixture was stirred at 70 °C. During the reaction, the mixture turns into homogenous liquid. The progress of the reaction was observed by TLC. After completion of the reaction, the mixture was cooled to room temperature and poured into water (5 mL). The solid was filtered off or in few cases extracted with ethyl acetate (10 mL). The products were isolated by evaporation of solvent in pure form or recrystallized from ethyl acetate and petroleum ether. The products obtained were known compounds and identified by their melting point and ^{1}H NMR spectroscopy, and the analytical data were compared with the literature values.

Procedure for the recyclability study

The reusability of the catalyst in the model reaction of 4-chloroaniline and formic acid (98%) under solvent-free conditions at 70 °C was evaluated. After completion of each reaction cycle, water was added and the product was filtered off. The catalyst being soluble in water, the filtrate was evaporated in vacuum rotary evaporator to recover the catalyst quantitatively. The recovered catalyst was recycled for four times with no significant loss in a catalytic activity.

Representative spectral data

N-Phenylformamide **(3a)** (Table 3, *entry* 1) White solid; m.p. 46–48 °C (lit. 46–47 °C); ^{1}H NMR (400 MHz, $CDCl_3$) the product was a mixture of two rotamers (ratio 1:1) δ 8.68 (d, J = 11.4 Hz, 1H), 8.36 (s, 1H), 8.29 (br s, 1H), 7.53 (d, J = 7.8 Hz, 2H), 7.47 (br s, 1H), 7.37–7.30 (m, 4H), 7.20–7.07 (m, 4H).

N-(2-Methylphenyl)formamide **(3b)** (Table 3, *entry* 2) White solid; m.p. 60–61 °C (lit. 60–62 °C); ^{1}H NMR (500 MHz, $CDCl_3$) the product was a mixture of two rotamers (ratio 1:0.5) δ 8.53 (d, J = 11.4 Hz, 1H), 8.45 (s, 0.5H), 7.67 (br s, 1H), 7.36–6.94 (m, 7H), 2.29 (s, 4.5H).

N-(4-Methylphenyl)formamide **(3c)** (Table 3, *entry* 3) White solid; m.p. 50–54 °C (lit. 50–54 °C); ^{1}H NMR (400 MHz, $CDCl_3$) the product was a mixture of two rotamers (ratio 1:1) δ 8.62 (d, J = 11.5 Hz, 1H), 8.35 (s, 1H), 7.96 (br s, 1H), 7.42 (d, J = 8.3 Hz, 2H), 7.26–7.13 (m, 5H), 6.98 (d, J = 8.2 Hz, 2H), 2.34 (s, 6H).

N-(2-Hydroxyphenyl)formamide **(3d)** (Table 3, *entry* 4) White solid; m.p. 128–129 °C (lit. 129–131 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (s, 1H), 8.13 (s, 1H), 7.57 (br s, 1H), 7.20–7.13 (m, 2H), 7.02 (d, J = 8.0 Hz, 1H), 6.90 (t, J = 7.5 Hz, 1H).

N-(2-Methoxyphenyl)formamide **(3e)** (Table 3, *entry* 5) White solid; m.p. 79–80 °C (lit. 80–81 °C); ^{1}H NMR (400 MHz, $CDCl_3$) the product was a mixture of two rotamers (ratio 1:2) δ 8.73 (d, J = 11.6 Hz, 1H), 8.45 (s, 2H), 8.35 (d, J = 8.0 Hz, 2H), 7.79 (br s, 2H), 7.67 (br s, 1H), 7.19 (d, J = 7.8 Hz, 1H), 7.14–7.08 (m, 3H), 7.04–6.87 (m, 6H), 3.88 (s, 9H).

N-(4-Methoxyphenyl)formamide **(3f)** (Table 3, *entry* 6) White solid; m.p. 77–78 °C (lit. 78–80 °C); ^{1}H NMR (400 MHz, $CDCl_3$, the product was a mixture of two rotamers (ratio 1:1) δ 8.49 (d, J = 11.5 Hz, 1H), 8.30 (s, 1H), 8.02 (br s, 1H), 7.43 (d, J = 8.9 Hz, 2H), 7.35 (br s, 1H), 7.02 (d, J = 8.8 Hz, 2H), 6.89–6.84 (m, 4H), 3.78 (s, 6H).

N-(2-Chlorophenyl)formamide **(3g)** (Table 3, *entry* 7) White solid; m.p. 80–81 °C (lit. 81–82 °C); ^{1}H NMR (400 MHz, $CDCl_3$) the product was a mixture of two rotamers (ratio 1:2) δ 8.71 (d, J = 11.2 Hz, 1H), 8.49 (s, 2H), 8.40 (d, J = 8.3 Hz, 2H), 7.67 (br s, 3H), 7.43–7.37 (m, 3H), 7.29–7.25 (m, 4H), 7.17–7.02 (m, 3H).

N-(4-Chlorophenyl)formamide **(3h)** (Table 3, *entry* 8) White solid; m.p. 99–100 °C (lit. 99–101 °C); ^{1}H NMR (400 MHz, $CDCl_3$) the product was a mixture of two rotamers (ratio 1:1) δ 8.63 (d, J = 11.3 Hz, 1H), 8.35 (s, 1H), 8.29 (br s, 1H), 7.48 (d, J = 8.4 Hz, 2H), 7.40 (br s, 1H), 7.32 - 7.26 (m, 4H), 7.02 (d, J = 8.3 Hz, 2H).

N-(4-Bromophenyl)formamide **(3i)** (Table 3, *entry* 9) White solid; m.p. 112–114 °C (lit. 115–119 °C); ^{1}H NMR (400 MHz, $CDCl_3$) the product was a mixture of two rotamers (ratio 1:1) δ 8.66 (d, J = 11.3 Hz, 1H), 8.39 (s, 1H), 7.93 (br s, 1H), 7.52–7.42 (m, 7H), 6.98 (d, J = 8.1 Hz, 2H).

N-(4-Fluorophenyl)formamide **(3j)** (Table 3, *entry* 10) White solid; m.p. 63–64 °C (lit. 63–65 °C); ^{1}H NMR (500 MHz, $CDCl_3$) the product was a mixture of two rotamers (ratio 1:1) δ 8.56 (d, J = 11.4 Hz, 1H), 8.34 (s, 1H), 8.08 (br s, 1H), 7.52–7.48 (m, 2H), 7.37 (br s, 1H), 7.08–6.99 (m, 6H).

N-(2-Methoxycabonylphenyl)formamide **(3k)** (Table 3, *entry* 11) White solid; m.p. 49–50 °C (lit. 49–50 °C); ^{1}H NMR (400 MHz, $CDCl_3$) the product was a mixture of two rotamers (ratio 2.5:1) δ 10.99 (br s, 2.5H), 8.94 (br s, 1H), 8.69 (d, J = 8.4 Hz, 2.5H), 8.51 (s, 2.5H), 8.05–8.01 (m, 3.5H), 7.84 (d, J = 8.1 Hz, 1H), 7.55 (t, J = 7.9 Hz, 2.5H), 7.37 (d, J = 8.4 Hz, 1H), 7.12 (t, J = 7.6 Hz, 2.5H), 6.66–6.61 (m, 2H), 3.92 (s, 7.5H), 3.86 (s, 3H).

N-(4-Ethoxycabonylphenyl)formamide **(3l)** (Table 3, *entry* 12) White solid; m.p. 110–111 °C (lit. 110 °C); ^{1}H NMR (400 MHz, $CDCl_3$) the product was a mixture of two rotamers (ratio 1:1) δ 8.82 (d, J = 11.3 Hz, 1H), 8.43 (s, 1H), 8.06 - 8.01 (m, 4H), 7.87 (br s, 1H), 7.61 (d, J = 8.0 Hz, 2H), 7.48 (br s, 1H), 7.09 (d, J = 8.5 Hz, 2H), 4.36 (m, 4H), 1.38 (t, J = 7.0 Hz, 6H).

N,N-Diphenylformamide **(3m)** (Table 3, *entry* 13) White solid; m.p. 68–69 °C (lit. 67–71 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (s, 1H), 7.43–7.38 (m, 4H), 7.32–7.26 (m, 4H), 7.17 (d, J = 8.1 Hz, 2H).

N-Cyclohexylformamide **(3n)** (Table 3, *entry* 14) Light yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) the product was a mixture of two rotamers (ratio 0.30:1) δ 8.43 (s, 0.3H), 8.35 (s, 1H), 6.28 (br s, 2H), 3.87–3.79 (m, 1H), 3.30 - 3.26 (m, 0.3H), 2.01–1.60 (m, 7H), 1.39–1.14 (m, 6H).

N-Benzylformamide **(3o)** (Table 3, *entry* 15) White solid; m.p. 60–61 °C (lit. 60–62 °C); ^{1}H NMR (400 MHz, $CDCl_3$) the product was a mixture of two rotamers (ratio 1:0.25) δ 8.26 (s, 1H), 8.18 (d, J = 12.2 Hz, 0.25H), 7.35 - 7.24 (m, 6.25H), 5.97 (br s, 1.25H), 4.48 (d, J = 5.7 Hz, 2H), 4.41 (d, J = 6.4 Hz, 0.5H).

N,N-Diethylformamide **(3p)** (Table 3, *entry* 16) Light yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (s, 1H), 3.16–3.04 (m, 4H), 0.98–0.88 (m, 6H).

N,N-Dibenzylformamide **(3q)** (Table 3, *entry* 17) Light yellow solid; m.p. 50–51 °C (lit. 51–52 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (s, 1H), 7.39–7.29 (m, 6H), 7.26–7.16 (m, 4H), 4.42 (s, 2H), 4.27 (s, 2H).

N-Formylmorpholine **(3r)** (Table 3, *entry* 18) Light yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (s, 1H), 3.71 (t, J = 3.7 Hz, 2H), 3.67 (t, J = 3.7 Hz, 2H), 3.58 (t, J = 3.6 Hz, 2H), 3.41 (t, J = 3.4 Hz, 2H).

N-Formylimidazole **(3s)** (Table 3, *entry* 19) Light yellow liquid; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.14 (s, 1H), 7.75 (s, 1H), 7.04 (s, 2H).

Results and discussion

The reaction screening was begun to investigate the efficiency of sulfated polyborate to catalyze *N*-formylation reaction at different reaction conditions. Preliminary experiments were performed using 4-chloroaniline, a representative substrate and formic acid (Scheme 1). The results are summarized in Table 1.

The significance of catalyst loading on yields and time of the reaction was assessed. In the absence of a catalyst, the reaction proceeded at 70 °C and took longer reaction time with a lower yield (Table 1, entry 1) compared to the presence of catalyst. The catalyst loading was increased from 1 to 10 wt%, which showed increased product yield with shorter reaction time (Table 1, entries 2–5). The catalyst loading beyond 7.5 wt% did not show a significant advantage on product yields and the reaction time (Table 1, entries 4 and 5). Hence, a 7.5 wt% catalyst loading significantly reduced the reaction time and found optimum to perform the further studies.

The temperature effect on *N*-formylation reaction was assessed (Table 1, entries 4, 6 and 7). The reaction was performed at ambient, 55 and 70 °C under solvent-free condition using a sulfated polyborate catalyst. The reaction at room temperature took longer reaction time with a lower yield (Table 1, entry 6), but at increased temperature to 70 °C afforded high product yield in shorter reaction time (Table 1, entry 4). Therefore, 70 °C was chosen as optimum temperature to perform further reactions.

The solvent effect on product yields and reaction time was ascertained with different solvents (Table 1, entries 8–13). All the solvent assessed took longer reaction time with low product yield compared to the solvent-free condition. Hence, the solvent-free condition was chosen for its cost and environmental benefits.

N-formylation reaction was reported with various Lewis as well as Bronsted catalysts. Herein, the catalyst containing sulfonic acid is compared with the present study which indicates that sulfated polyborate catalyst showed an advantage in many cases with respect to reaction time and product yields, reaction conditions and workup procedure (Table 2, entries 1–9).

To study the substrate scope, optimized reaction conditions were applied to various amines. All the amine substrates reacted well and afforded higher yields of the corresponding formamides in shorter reaction time (Table 3, entries 1–19). Various electron withdrawing and electron donating substituents at *ortho* and *para* position of aromatic amines have been examined. The nature of substitutions on aromatic amines has no significant effect on the reaction time and yields. However, in the case of 2-methoxycarbonyl and 4-ethoxycarbonyl anilines, the reaction time was longer with similar product yields apparently due to electron withdrawing effect of the substituents (Table 3, entries 11 and 12).

This protocol tolerated a variety of substituents on primary aromatic amines and also extendable to primary aliphatic, secondary aromatic, aliphatic and heterocyclic

Scheme 1 *N*-formylation of 4-chloroaniline

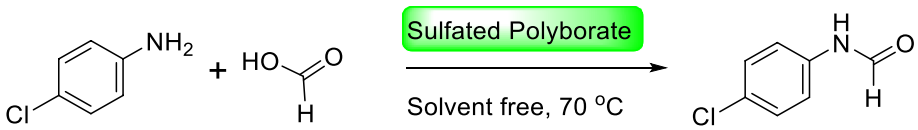


Table 1 Optimization study for the catalyst loading, temperature and solvent effects

Entry	Catalyst (wt%)	Solvent	Temperature (°C)	Time (min)	Yield[a] (%)
1.	0	Solvent free	70	120	48
2.	2.5	Solvent free	70	30	93
3.	5.0	Solvent free	70	30	95
4.	7.5	Solvent free	70	10	98
5.	10.0	Solvent free	70	10	98
6.	7.5	Solvent free	rt	60	88
7.	7.5	Solvent free	50	30	96
8.	7.5	EtOH	Reflux	60	63
9.	7.5	MeCN	70	60	41
10.	7.5	THF	Reflux	60	44
11.	7.5	Water	70	60	36
12.	7.5	Toluene	70	60	53
13.	7.5	DMF	70	60	56

[a] Isolated yield

Table 2 Comparison of efficiency of sulfated polyborate with the literature reported catalysts for the *N*-formylation of 4-chloroaniline by formic acid

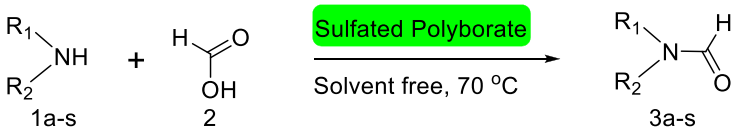
Entry	Catalyst	Condition	Time (min)	Yield[a] (%)	Refs.
1.	Sulfated polyborate	Solvent free/70 °C	10	98	This work[b]
2.	Sulfated tungstate	Solvent free/70 °C	10	98	[33][c]
3.	Sulfonated rice husk ash	Solvent free/60 °C	10	96	[43][c]
4.	Na^+-MMT-[pmim]HSO_4	Solvent free/60 °C	20	95	[41][c]
5.	[γ-Fe_2O_3@HAp-SO_3H]	Solvent free/rt	20	97	[35][c]
6.	Silica sulfuric acid	Solvent free/60 °C	26	90	[42][c]
7.	Nano-sulfated titania	Solvent free/rt	40	90	[39][c]
8.	Melamine trisulfonic acid	Solvent free/60 °C	60	93	[44][c]
9.	Sulfated titania	MeCN/rt	360	98	[32][c]

[a] Isolated yield

[b] Aqueous workup

[c] Extractive workup procedure

Table 3 *N*-formylation of various amines using sulfated polyborate catalyst



Entry	Amine substrates		Products	Time (min)	Yield[a] (%)	Melting point (°C)	
	R_1	R_2				Obs.	Lit.
1.	C_6H_5	H	3a	10	98	46–48	46–47 [35]
2.	2-CH_3–C_6H_4	H	3b	15	95	60–61	60–62 [56]
3.	4-CH_3–C_6H_4	H	3c	15	97[b]	50–51	50–54 [35]
4.	2-HO–C_6H_4	H	3d	15	95	128–129	129–131 [35]
5.	2-CH_3O–C_6H_4	H	3e	20	94	79–80	80–81 [57]
6.	4-CH_3O–C_6H_4	H	3f	15	96	77–78	78–80 [35]
7.	2-Cl–C_6H_4	H	3g	15	96	80–81	81–82 [58]
8.	4-Cl–C_6H_4	H	3h	10	98	99–100	99–101 [56]
9.	4-Br–C_6H_4	H	3i	15	97	112–114	115–119 [56]
10.	4-F–C_6H_4	H	3j	15	96	63–64	63–65 [59]
11.	2-CH_3OCO–C_6H_4	H	3k	30	92[b]	49–50	49–50 [36]
12.	4-C_2H_5OCO–C_6H_4	H	3l	30	94	110–111	110 [60]
13.	C_6H_5	C_6H_5	3m	45	89	68–69	67–71 [35]
14.	*c*-C_6H_{11}	H	3n	20	98[b]	Liq	–
15.	$C_6H_5CH_2$	H	3o	30	97	60–61	60–62 [35]
16.	C_2H_5	C_2H_5	3p	20	86[b]	Liq.	–
17.	$C_6H_5CH_2$	$C_6H_5CH_2$	3q	30	97	50–51	51–52 [61]
18.	Morpholine		3r	30	97[b]	Liq	–
19.	Imidazole		3s	15	96[b]	Liq	–
Phenol/alcohol substrates							
20.	C_6H_5OH	–	–	60	NR[c]	–	–
21.	$C_6H_5CH_2OH$	–	–	60	NR[c]	–	–

[a] Isolated yield

[b] Extractive workup

[c] No reaction

amines. On the other hand, secondary aromatic, primary and secondary aliphatic amines took longer reaction time than primary aromatic amines (Table 3, entries 13–18). Result obtained from *N*-formylation of imidazole is comparable to aromatic amines (Table 3, entry 19).

The chemoselectivity of the catalyst for *O*-formylation versus *N*-formylation was ascertained using a substrate bearing both OH and NH_2 groups, which resulted in *N*-formylation selectively (Table 3, entry 4), while formylation of phenol and benzyl alcohol was unsuccessful (Table 3, entries 20 and 21) (Fig. 2).

The reusability of the catalyst in the model reaction of 4-chloroaniline and formic acid (98%) under solvent-free conditions at 70 °C was evaluated. The recovered catalyst was recycled for four times with no significant loss in a catalytic activity (Fig. 3).

A plausible mechanism for the *N*-formylation reaction is depicted in Fig. 4. First step is the activation of carbonyl of formic acid by the coordination with the catalyst. Thus, the electrophilic character of formic acid may increase and could be much more active for the nucleophilic attack of amine [36]. The protonation and subsequent dehydration produce formamide and regenerate the catalyst.

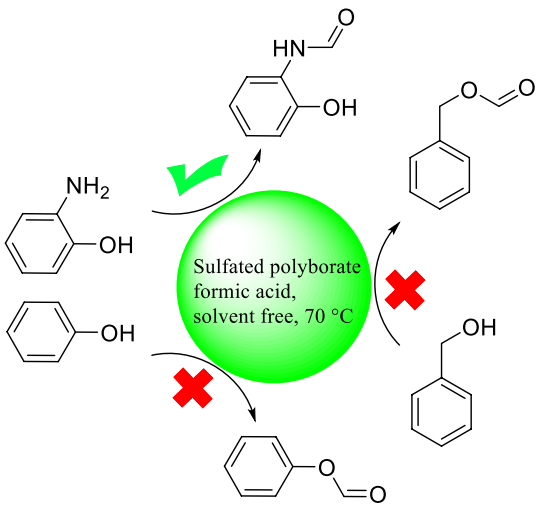


Fig. 2 Chemo-selectivity for formylation

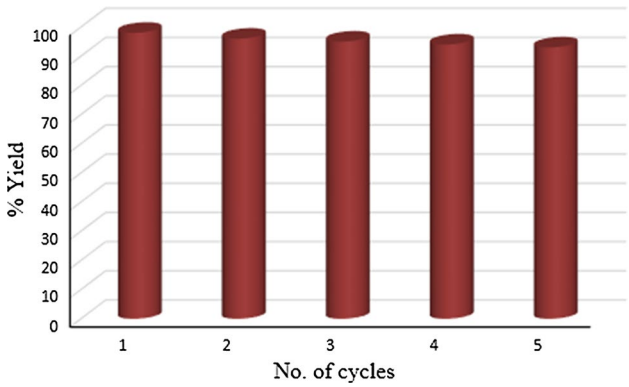


Fig. 3 Reusability of the catalyst

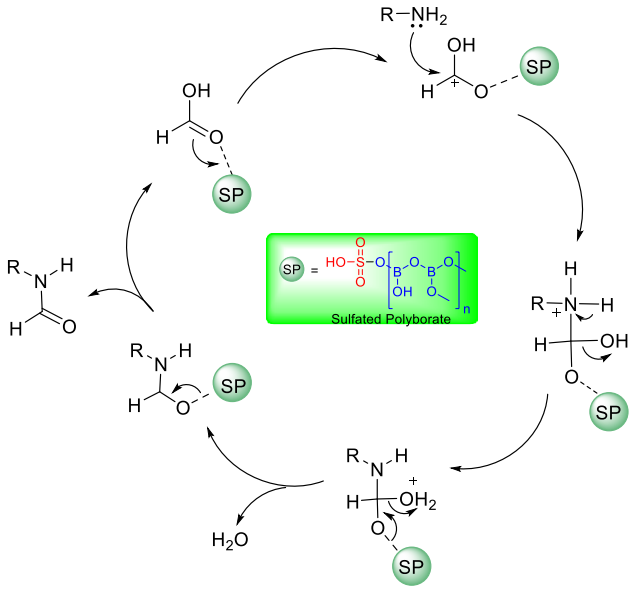


Fig. 4 Plausible mechanism of sulfated polyborate-catalyzed *N*-formylation

Conclusion

In conclusion, the present procedure is a rapid, green, efficient and eco-friendly protocol for *N*-formylation of various primary and secondary aromatic, aliphatic, heterocyclic amines under optimized conditions. Mild reaction conditions, shorter reaction time, high yields, easy of workup procedure, chemoselectivity and recyclability of the catalyst, are the key features of this procedure. Moreover, present method tolerates a wide variety of substituents. This protocol gives enhanced product purity and promises economical as well as ecological rewards.

Acknowledgements The authors are grateful to University Grants Commission (UGC), India, for their financial support.

References

1. A.C. Shekhar, A.R. Kumar, G. Sathaiah, V.L. Paul, M. Sridhar, P.S. Rao, Tetrahedron Lett. **50**, 7099 (2009)
2. A. Jackson, O. Meth-Cohn, J. Chem. Soc. Chem. Commun. **13**, 1319 (1995)

3. K. Kawashima, M. Sisido, K. Ichimura, Chem. Lett. **24**, 491 (1995)
4. B.C. Chen, M.S. Bednarz, R. Zhao, J.E. Sundeen, P. Chen, Z. Shen, A.P. Skoumbourdis, J.C. Barrish, Tetrahedron Lett. **41**, 5453 (2000)
5. S. Kobayashi, M. Yasuda, I. Hachiya, Chem. Lett. **25**, 407 (1996)
6. S. Kobayashi, K. Nishio, J. Org. Chem. **59**, 6620 (1994)
7. I.M. Downie, M.J. Earle, H. Heaney, K.F. Shuhaibar, Tetrahedron **49**, 4015 (1993)
8. M. Viji, R. Nagarajan, J. Chem. Sci. **126**, 1075 (2014)
9. J. Martinez, J. Laur, Synthesis (Stuttg) **1982**, 979 (1982)
10. G.P. Anderson, Life Sci. **52**, 2145 (1993)
11. K. Tanaka, Rheumatol. Rep. **1**, 11 (2009)
12. M.-L. Volvert, S. Seyen, M. Piette, B. Evrard, M. Gangolf, J.-C. Plumier, L. Bettendorff, BMC Pharmacol. **8**, 10 (2008)
13. F.F. Blicke, C.-J. Lu, J. Am. Chem. Soc. **74**, 3933 (1952)
14. M. Waki, J. Meienhofer, J. Org. Chem. **42**, 2019 (1977)
15. F.M.F. Chen, N.L. Benoiton, Synthesis (Stuttg) **1979**, 709 (1979)
16. L. De Luca, G. Giacomelli, A. Porcheddu, M. Salaris, Synlett **2004**, 2570 (2004)
17. W. Duczek, J. Deutsch, S. Vieth, H.-J. Niclas, Synthesis (Stuttg) **1996**, 37 (1996)
18. P. Strazzolini, A.G. Giumanini, S. Cauci, Tetrahedron **46**, 1081 (1990)
19. P.G. Reddy, G.D.K. Kumar, S. Baskaran, Tetrahedron Lett. **41**, 9149 (2000)
20. G. Brahmachari, S. Laskar, Tetrahedron Lett. **51**, 2319 (2010)
21. B. Das, M. Krishnaiah, P. Balasubramanyam, B. Veeranjaneyulu, D.N. Kumar, Tetrahedron Lett. **49**, 2225 (2008)
22. L. Zhang, Z. Han, X. Zhao, Z. Wang, K. Ding, Angew. Chem. Int. Ed. Engl. **54**, 6186 (2015)
23. P. Daw, S. Chakraborty, G. Leitus, Y. Diskin-Posner, Y. Ben-David, D. Milstein, ACS Catal. **8**, 2500 (2017)
24. M. Mihara, Y. Ishino, S. Minakata, M. Komatsu, Synthesis (Stuttg) **2003**, 2317 (2003)
25. M. Bhojegowd, M. Reddy, A. Nizam, M.A. Pasha, Chin. J. Catal. **31**, 518 (2010)
26. M.H. Sarvari, H. Sharghi, J. Org. Chem. **71**, 6652 (2006)
27. S.M. Sajadi, M. Maham, A. Rezaei, Lett. Org. Chem. **11**, 49 (2014)
28. M.B.M. Reddy, S. Ashoka, G.T. Chandrappa, M.A. Pasha, Catal. Lett. **138**, 82 (2010)
29. S. Bahari, B. Mohammadi-Aghdam, S.M. Sajadi, F. Zeidali, Bull. Korean Chem. Soc. **33**, 2251 (2012)
30. D. Habibi, M. Nasrollahzadeh, H. Sahebekhtiari, J. Mol. Catal. A: Chem. **378**, 148 (2013)
31. J.-G. Kim, D. Jang, Synlett **2010**, 1231 (2010)
32. B. Krishnakumar, M. Swaminathan, J. Mol. Catal. A Chem. **334**, 98 (2011)
33. S.P. Pathare, R.V. Sawant, K.G. Akamanchi, Tetrahedron Lett. **53**, 3259 (2012)
34. M.I. Ansari, M.K. Hussain, N. Yadav, P.K. Gupta, K. Hajela, Tetrahedron Lett. **53**, 2063 (2012)
35. L. Ma'mani, M. Sheykhan, A. Heydari, M. Faraji, Y. Yamini, Appl. Catal. A Gen. **377**, 64 (2010)
36. Z. Chen, R. Fu, W. Chai, H. Zheng, L. Sun, Q. Lu, R. Yuan, Tetrahedron **70**, 2237 (2014)
37. S.P. Satasia, P.N. Kalaria, D.K. Raval, J. Mol. Catal. A Chem. **391**, 41 (2014)
38. V.K. Das, R.R. Devi, P.K. Raul, A.J. Thakur, Green Chem. **14**, 847 (2012)
39. M. Hosseini-Sarvari, E. Safary, A. Jarrahpour, R. Heiran, Comptes Rendus Chim. **15**, 980 (2012)
40. M. Kooti, E. Nasiri, J. Mol. Catal. A Chem. **406**, 168 (2015)
41. F. Shirini, M. Mazloumi, M. Seddighi, Res. Chem. Intermed. **42**, 1759 (2016)
42. D. Habibi, P. Rahmani, Z. Akbaripanah, J. Chem. **2013**, 1 (2012)
43. M. Seddighi, F. Shirini, M. Mamaghani, J. Iran. Chem. Soc. **12**, 433 (2015)
44. X.J. Yang, Y. Sen, Zhang. Res. Chem. Intermed. **39**, 2843 (2013)
45. C.K. Khatri, D.S. Rekunge, G.U. Chaturbhuj, New J. Chem. **40**, 10412 (2016)
46. C.K. Khatri, V.B. Satalkar, G.U. Chaturbhuj, Tetrahedron Lett. **58**, 694 (2017)
47. K.S. Indalkar, C.K. Khatri, G.U. Chaturbhuj, J. Chem. Sci. **129**, 141 (2017)
48. D.S. Rekunge, C.K. Khatri, G.U. Chaturbhuj, Tetrahedron Lett. **58**, 1240 (2017)
49. K.S. Indalkar, C.K. Khatri, G.U. Chaturbhuj, J. Chem. Sci. **129**, 415 (2017)
50. C.K. Khatri, A.S. Mali, G.U. Chaturbhuj, Monatsh. Chem. **148**, 1463 (2017)
51. C.K. Khatri, M.S. Patil, G.U. Chaturbhuj, J. Iran. Chem. Soc. **14**, 1683 (2017)
52. K.S. Indalkar, C.K. Khatri, G.U. Chaturbhuj, Tetrahedron Lett. **58**, 2144 (2017)
53. M.S. Patil, A.V. Palav, C.K. Khatri, G.U. Chaturbhuj, Tetrahedron Lett. **58**, 2859 (2017)
54. M.S. Patil, C. Mudaliar, G.U. Chaturbhuj, Tetrahedron Lett. **58**, 3256 (2017)
55. D.S. Rekunge, C.K. Khatri, G.U. Chaturbhuj, Monatsh. Chem. (2017). doi:10.1007/s00706-017-2013-x
56. M. Hong, G. Xiao, J. Fluor. Chem. **146**, 11 (2013)
57. G.W. Gribble, F.P. Bousquet, Tetrahedron **27**, 3785 (1971)
58. Z. Wang, M. Lu, RSC Adv. **4**, 1234 (2014)
59. K.B. Muchowska, C. Adam, I.K. Mati, S.L. Cockroft, J. Am. Chem. Soc. **135**, 9976 (2013)
60. G. Kobayashi, T. Saito, Y. Kitano, Synthesis (Stuttg) **2011**, 3225 (2011)
61. D. Habibi, H. Sahebekhtiari, M. Nasrollahzadeh, A. Taghipour, Lett. Org. Chem. **10**, 209 (2013)