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A retrospective 9-years overview of sulfated polyborate as a robust catalyst for organic transformations

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Sulfated polyborate (SPB) is a homogeneous catalyst that showcases dual acidic properties of Brønsted and Lewis acid. The SPB catalyst is boron-centered, which makes it more sustainable as it inherits non-metallic and non-hazardous traits. SPB, a green and adaptable metal-free catalyst, is prepared from readily available boric acid, offering economic and environmental benefits. It is highly tolerable to functional groups due to its simple, facile, eco-friendly, and hassle-free isolation procedure, which establishes it as a versatile, promising, and flexible catalyst compared to metal-based catalysts. The general overview of SPB preparation is followed by its manifold applications in Betti-base synthesis, Kabachnik–Field reaction, Ritter reaction, Biginelli reaction, Kindler reaction, and various other organic transformations. The catalyst interacts with the reactant species to enhance the reaction rates. It follows a common reaction mechanism to frame products, specifically Knoevenagel condensation, followed by the Michael addition pathway. This review presents the preparation and characterization of SPB, followed by its various catalytic applications in organic synthesis over the past 9 years.

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1. Introduction

Catalysis has significantly influenced advancements in modern society, affecting numerous industries,¹ with more than half of the chemical reactions that require a catalyst.² Catalysts are broadly classified into two classes, namely homogeneous and

heterogeneous. When homogeneous catalysts are compared with heterogeneous ones, they evolve with enhanced performance and reaction optimization.³ Traditionally, these catalysts were developed due to their chemoselectivity and activity under mild reaction conditions.⁴ Along with further advancements, where renewable and reusable materials have owned the dimensions, polymer-supported organic catalysts have fascinated many chemists' minds in the synthetic, industrial, and philosophical fields.⁵ From the synthesis of peptides and oligosaccharides (polymers) to organic molecules, polymers

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have emerged as a benefaction in the reaction arrangement and product isolation.⁶ Though a lot of research has been done on the catalysts, including metals and non-metals with their wide applications, they carry several drawbacks too. One of such elements is boron, which forms covalent bonds in its crystalline form.⁷ In its crystalline form, boric acid (BA) is an important compound, having significant physical properties. It is a white powder/crystal and soluble in water (Table 1 and Fig. 1). Boron-centered catalyst offers a compatible and affordable metal-free protocol⁸ along with disclosing unique properties⁹ and plays a significant role in chemistry,¹⁰ material science, and in nanostructured materials too. It also serves as an aid in biomedical fields,¹¹ in ophthalmic products,¹² hygiene products for women^{13,14} [Fig. 2] as well as in the mineralization of osteoblasts.¹⁵



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Table 1 Some properties of boric acid

Property	Explanation
Appearance	White crystalline solid (powder)
Bond length of BA	B–O bond = 136 ppm; O–H bond = 97 ppm (ref. 16)
Shape of borate	Tetrahedral [Fig. 1]
Structure of BA	Planar configuration; three oxygen atoms surround boron atom
Polymerization	Above 0.02 M; confirmed experimentally ^{17–19}
Sensitivity	Sensitive to temperature, ionic strength, and concentration
Acidity	Weak Lewis acid
pK_a value and variations	pK_a value ranging between 8.92–9.24 and varies due to changes in concentration

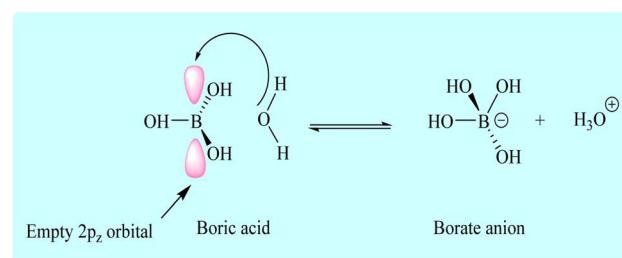


Fig. 1 Structure of boric acid and borate anion.¹²

Many works of the literature revealed that BA works as a catalyst for several organic transformations at temperatures exceeding 100 °C.^{20,21} It has Brønsted acid properties, which play a pivotal role in catalyzing reactions as an active species.²² BA dehydrates at 200 °C to generate polyboric Lewis acid.



Shikha Agarwal

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BORIC ACID POWDER BENEFITS

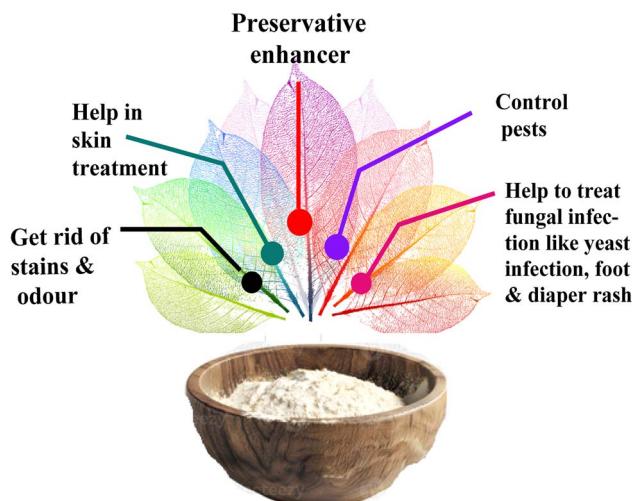


Fig. 2 Medicinal benefits of boric acid.

Sulfonation of polyboric acid (PBA) enhances its acidity and results in the synthesis of sulfated polyborate (SPB).

In the field of chemistry, SPB has been applied to the solvent-free synthesis of trisubstituted methane, reductive amination of ketones and aldehydes, Kabachnik–Field reactions, Biginelli reactions, transamidation of carboxamides with amines, synthesis of (un) symmetrical urea and benzimidazolones, functionalized imidazoles, solvent-free synthesis of polyhydroquinolines, synthesis of Betti-base, and various other transformations. The C–C bond formation is the most performed and always insightful organic reaction in the synthetic

chemistry,²³ and the SPB catalyst has made great accomplishments in organic synthesis.

In the literature survey, it was found that SPB has been highlighted since 2016 and proven adaptable and encouraging material in the catalyst field. It was first synthesized and characterized in 2016.²⁴ It displays several properties such as good solubility in organic solvents and a low UV cut-off to serve as a mobile phase buffer for reverse-phase liquid chromatography.²⁵ On examining its performance in various organic transformations, it has been found as an eco-friendly, reusable, and functional group-tolerant catalyst.^{26,27} Sequencing its high number of publications since 2016, an updated review detailing its catalytic applications is indeed required (Fig. 3). Reflecting on this desire, this review entails its detailed synthesis and catalytic applications in the scientific world.

2. Preparation and characterisation of SPB

The preparation of SPB requires polymerisation of BA followed by its sulfonation. BA was heated at 200 °C for 4 h for polymerisation and was then introduced to sulfonation using chlorosulfonic acid²⁴ (Fig. 4).

The synthesized SPB has been well characterized by FT-IR spectrum, powder XRD, and SEM morphology (Fig. 5). Fig. 5(A) represents FTIR spectrum of SPB, exhibiting 3446 and 1629 cm^{-1} bands of absorption for –OH stretching and bending of SO_3H groups²⁴ respectively. To confirm the presence of B–O bond in the crystalline structure, powder XRD of SPB displayed 2θ peak at 28.1° as shown in Fig. 5(B).³⁰ The SEM image in Fig. 5(C) indicates diversity in dimensions for the surface morphology of SPB, ranging between 4–10 μm .²⁴

3. Applications of SPB in organic synthesis

3.1 Ritter reaction

Indalkar *et al.*²⁹ synthesized *N*-*tert*-butyl/*N*-trityl protected amides using SPB (10 wt%), a catalyst that offers advantages in terms of reusability, non-hygroscopic properties, and environmental friendliness. The reaction proceeded *via* condensation of equimolar nitrile and *tert*-butanol or trityl alcohol at 100 °C without using solvent (Scheme 1). The protocol yielded 17 derivatives within 1–3 h and displayed 81–96% yield. However, product purification entails either recrystallization from ethanol or column chromatography. This pathway proved futile for nitriles with primary and secondary alcohols and exhibited comparatively lower yields with nitriles bearing electron-withdrawing substituents. Additionally, SPB was reused five times with 90–95% yields.

3.2 Kabachnik–Field reaction

Khatri and his co-workers³⁰ explored SPB as an eco-benign catalyst for the synthesis of α -amino phosphonates *via* the Kabachnik–Field reaction. The multi-component transformation involved various aldehydes, amines/anilines, diethyl

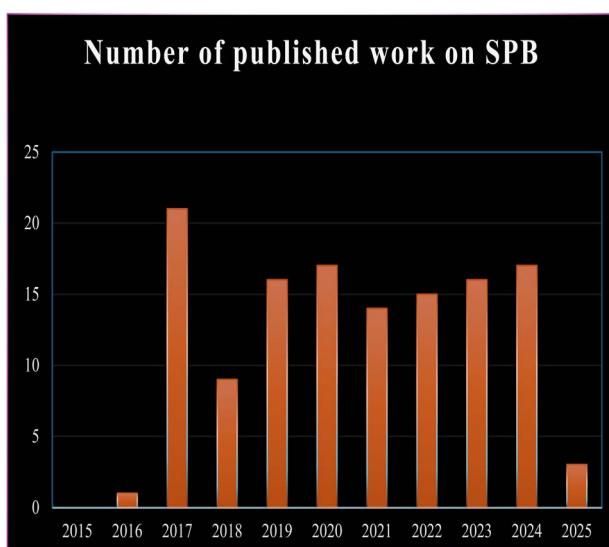


Fig. 3 Number of published works on SPB according to Google Scholar. [2016–2025 (accessed 31-March, 2025)] Keywords used for the literature survey include sulfated polyborate as a catalyst.



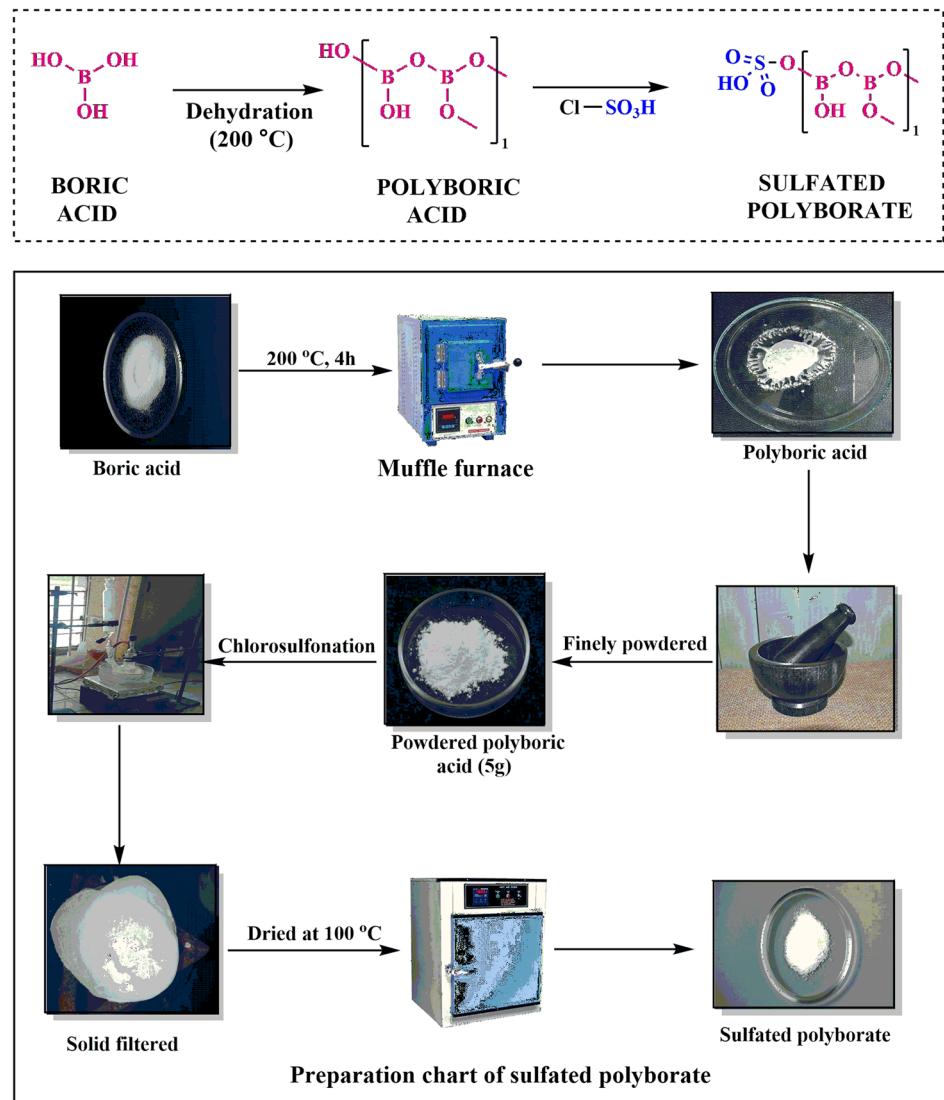


Fig. 4 General preparation method of SPB.

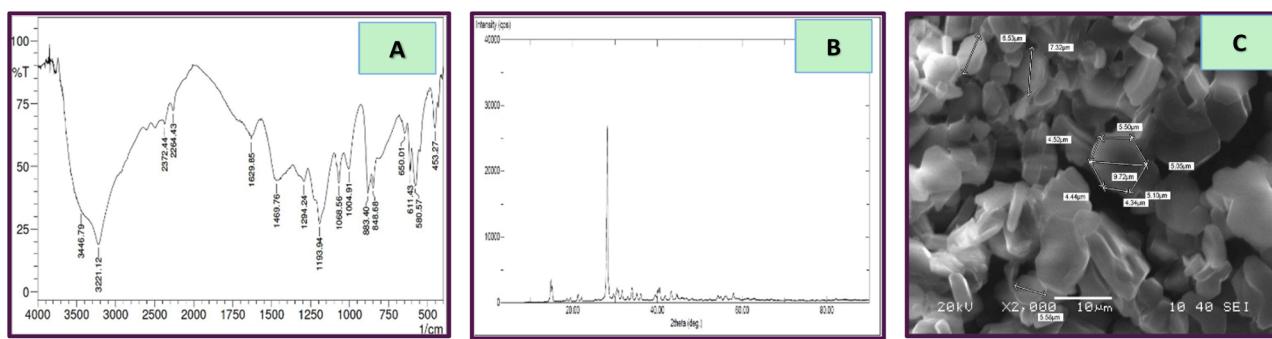
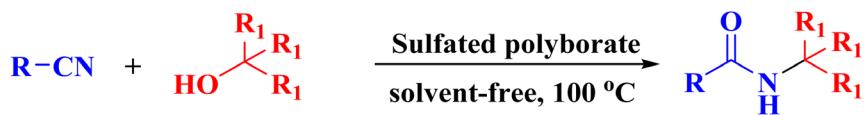
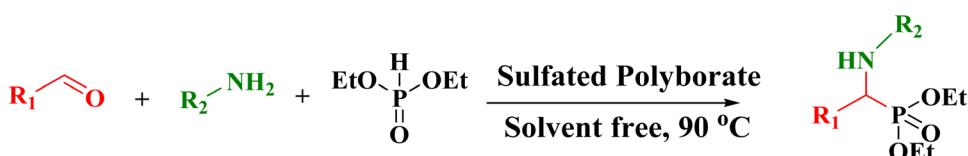


Fig. 5 (A) FT-IR, (B) XRD, and (C) SEM studies of SPB catalyst.^{24,28}

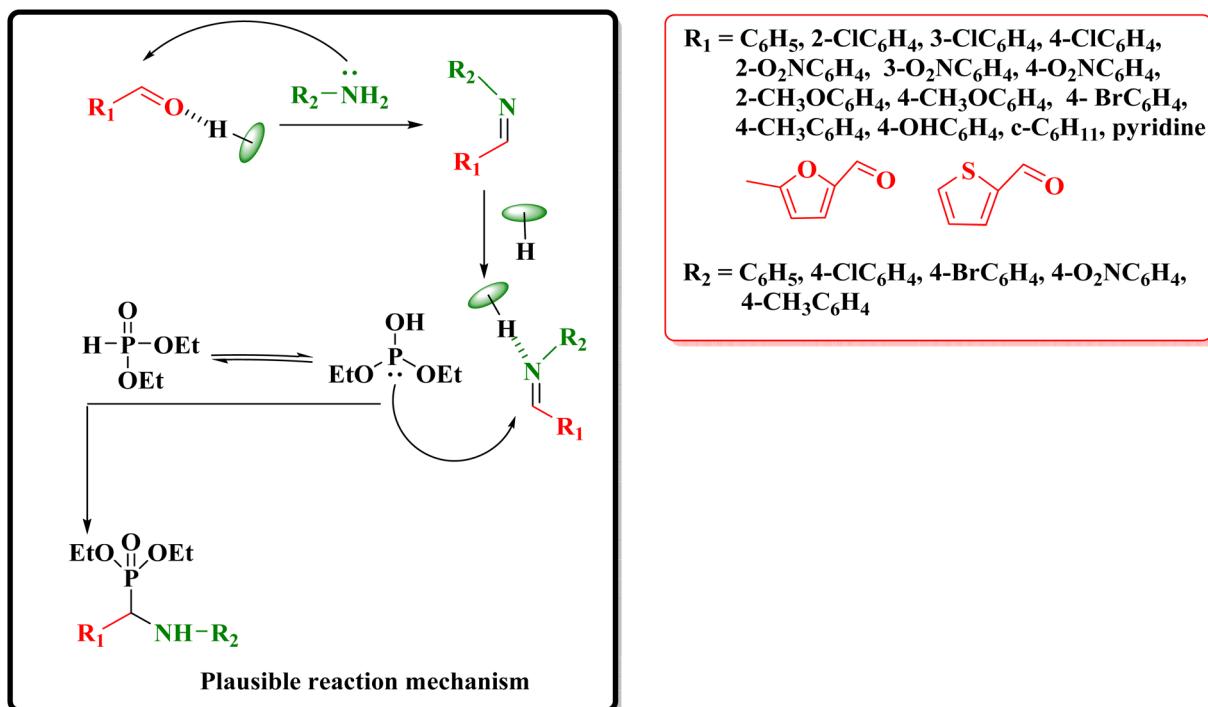


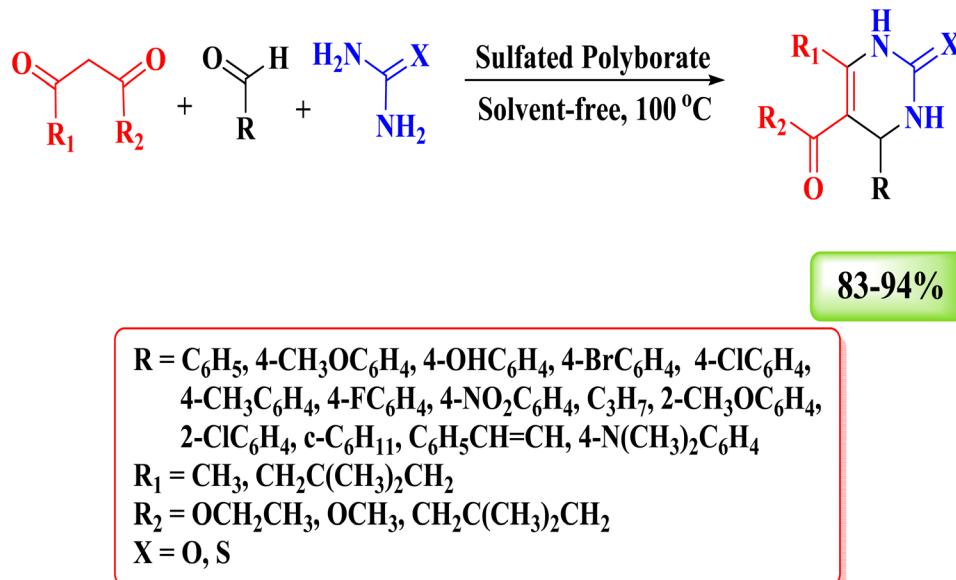
81-96%

$R_1 = \text{CH}_3, \text{C}_6\text{H}_5$
 $R = \text{C}_6\text{H}_5, 2\text{-ClC}_6\text{H}_4, 3\text{-ClC}_6\text{H}_4, 4\text{-ClC}_6\text{H}_4, 4\text{-BrC}_6\text{H}_4,$
 $4\text{-CH}_3\text{C}_6\text{H}_4, 4\text{-O}_2\text{NC}_6\text{H}_4, 4\text{-CH}_3\text{COC}_6\text{H}_4, \text{CH}_3$
 $n\text{-C}_4\text{H}_9, 3\text{-OHC}_6\text{H}_4, 4\text{-OHC}_6\text{H}_4, \text{C}_6\text{H}_5\text{CH}_2, 4\text{-CH}_3\text{OC}_6\text{H}_4$

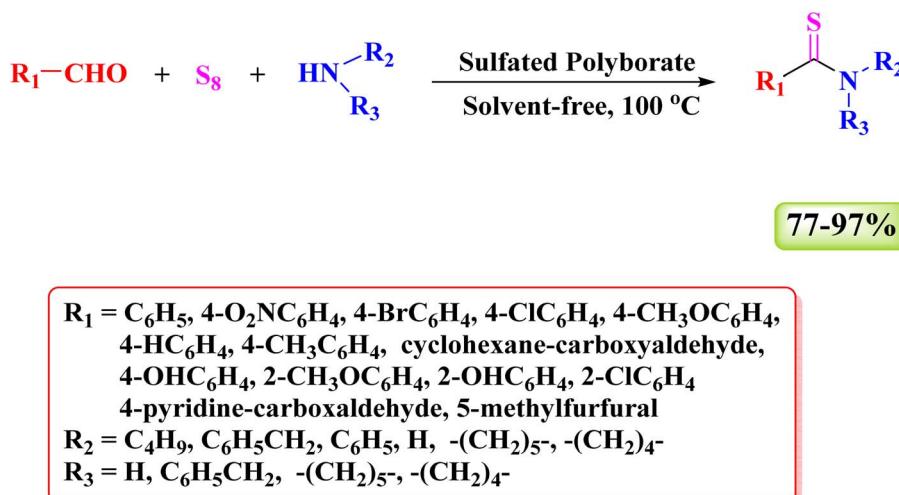
Scheme 1 Synthesis of *N*-tert-butyl/*N*-trityl protected amides using 10 wt% SPB.

93-98%

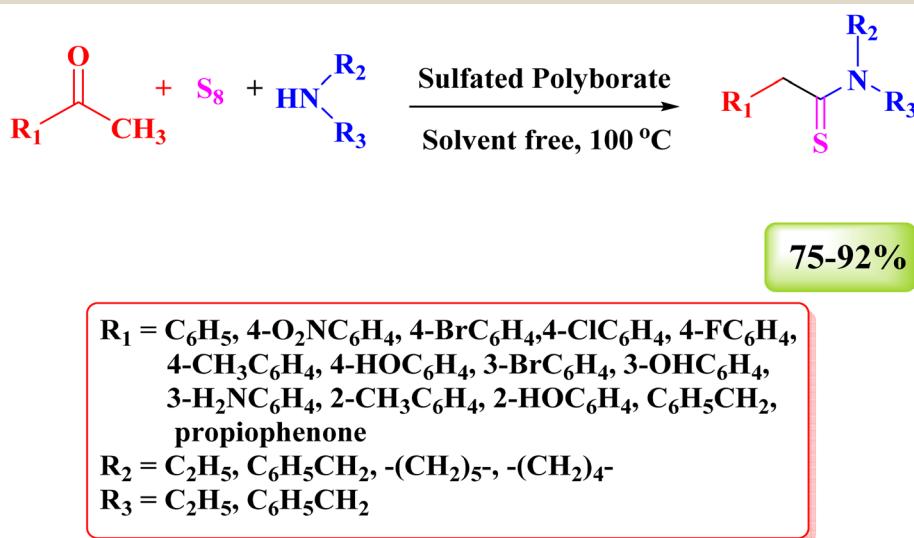
Scheme 2 Synthesis of α -amino phosphonates using 5 wt% SPB.



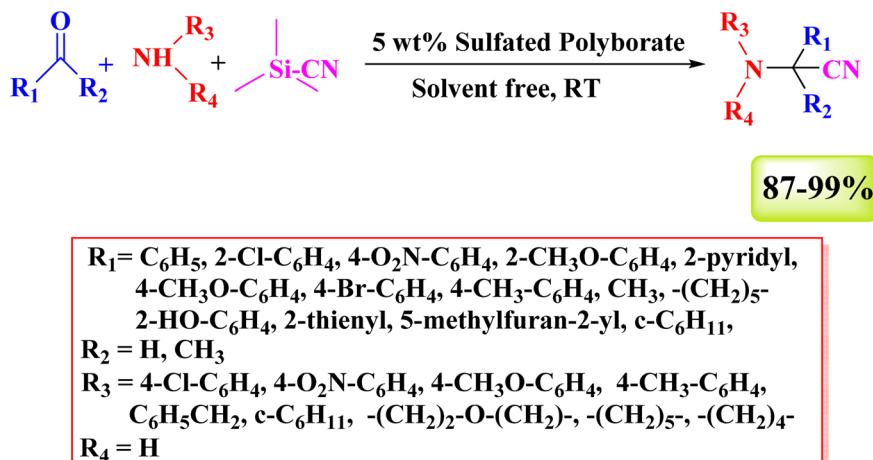
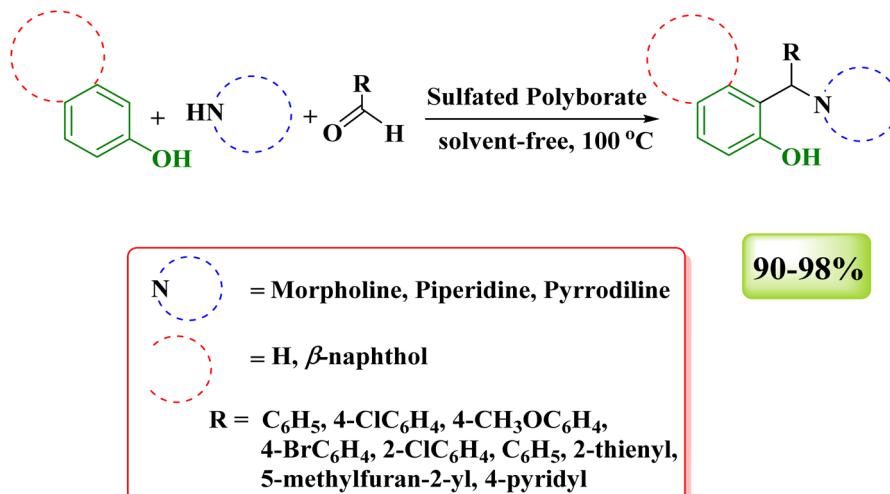
Scheme 3 Synthesis of 3,4-dihydropyrimidin-2(H)-ones/thiones using 5 wt% SPB.



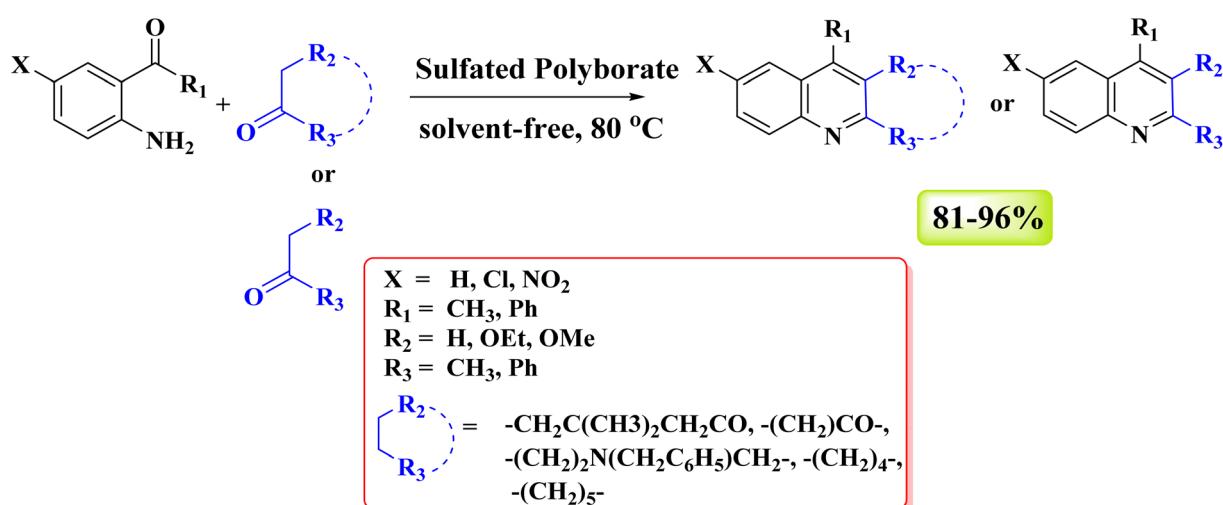
Scheme 4 Synthesis of thioamide using 10 wt% SPB.



Scheme 5 Synthesis of thioacetamide using 10 wt% of SPB.

Scheme 6 Synthesis of α -aminonitriles using 5 wt% SPB.

Scheme 7 Synthesis of Betti base using 10 wt% of SPB.



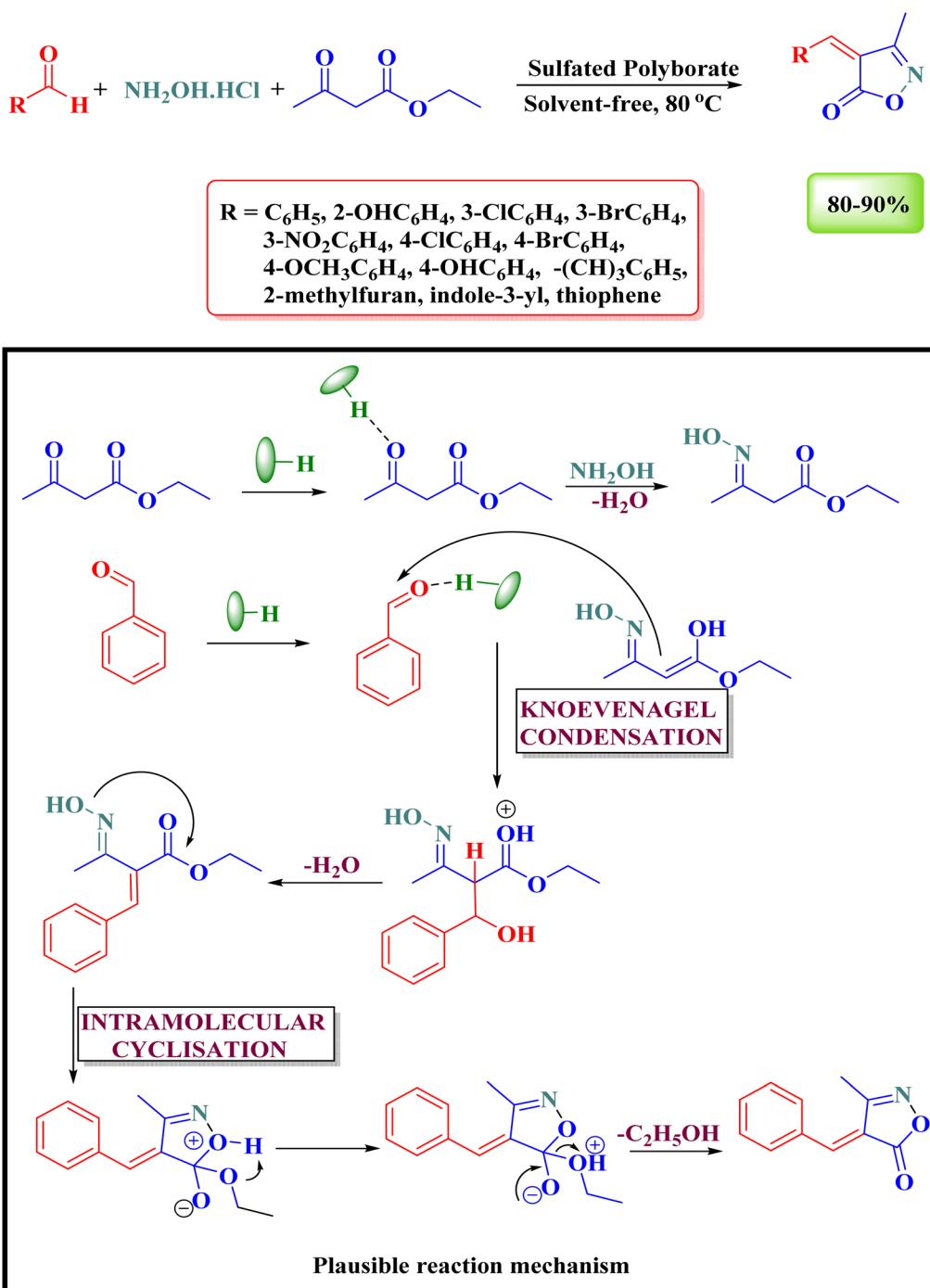
Scheme 8 Synthesis of 2-methyl-4-phenylquinoline-3-carboxylate using 15 wt% of SPB.



phosphite, and 5 wt% SPB at 90 °C to afford the desired product within the timeframe of 5–10 min under solvent-free conditions, with product yield ranging from 93–98% (Scheme 2). The SPB-activated $\text{C}=\text{O}$ group of aldehyde was followed by a nucleophilic attack of anilines/amines that resulted in an imine intermediate, which subsequently underwent phosphite attack on SPB-activated imine, resulting in α -amino phosphonates. Moreover, the catalyst demonstrated recyclability up to four runs with 90% efficacy.

3.3 Biginelli reaction

Khatri and his colleagues²⁴ reported SPB as a superior catalyst for the straightforward, one-pot condensation of β -diketoester/ β -ketoester (2 mmol), various aldehydes (2 mmol), and urea/thiourea (2.4 mmol) to yield 3,4-dihydropyrimidin-2(H)-ones/thiones *via* Biginelli reaction. This methodology fabricated the product swiftly (20–45 min) with excellent yields (83–94%) in solvent-free conditions (Scheme 3). The product was obtained using 5 wt% SPB at 100 °C. Furthermore, the reported method



Scheme 9 Synthesis of 3-methyl-4-(hetero)arylmethyleneisoxazole-5(4H)-ones using 10 wt% SPB.



furnished 22 derivatives, disclosing a wide variety of substrate scopes with different functional groups. Also, the SPB was utilized five times without any appreciable loss in its performance.

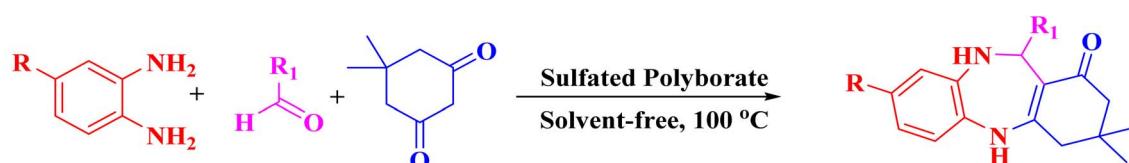
3.4 Kindler multicomponent condensation reactions

For thioamide synthesis, Kindler multicomponent condensation reactions of aldehydes, amines, and sulfur are highly viable due to their high atom economy. Although some evolutions in the reaction to enhance its reaction performance have been reported, still there was a need for some improvement in the catalyst protocol. Therefore, to enhance the efficacy of thioamide synthesis, SPB was chosen as a rapid, hustle-free, and environment-benign catalyst by Khatri and his co-authors.²⁶ The reaction involved aldehydes (2 mmol), amines (2.4 mmol), and sulfur (2.4 mmol) in the presence of SPB (10 wt%) (Scheme 4).

The reaction mixture was stirred at 100 °C for 0.5–6 h without solvent. The resulting product derivatives (21 compounds) exhibited 77–97% yields. Additionally, the catalyst masked reusability over four runs without significant loss of efficiency (>85%).

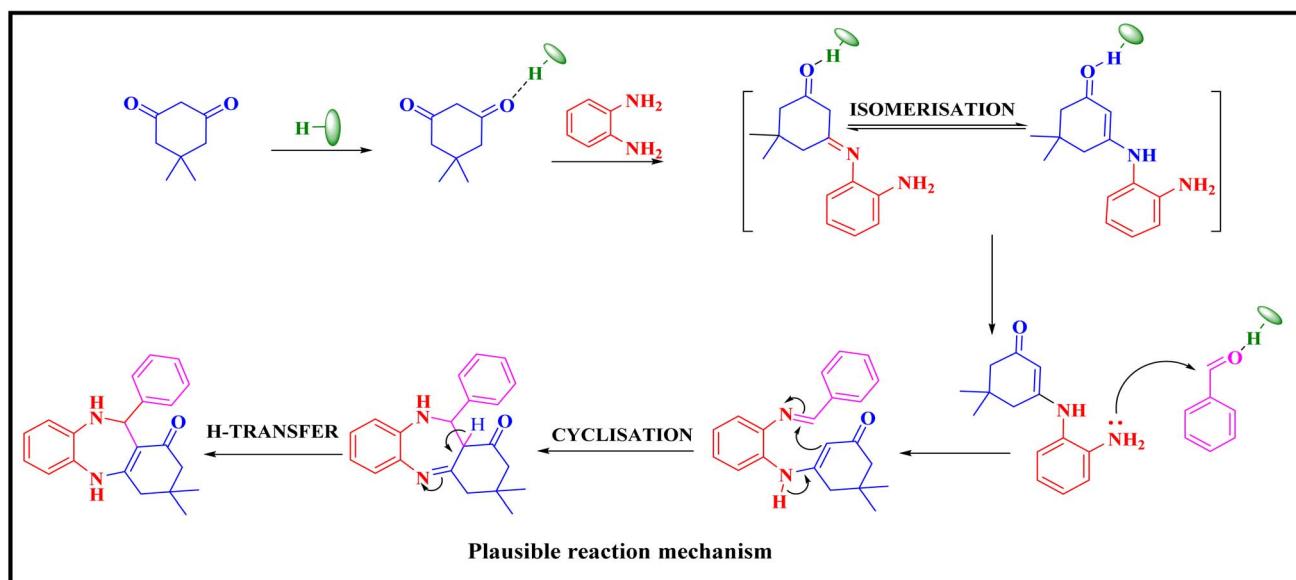
3.5 Willgerodt-Kindler reaction

A highly efficient thioacetamide synthesis has been reported *via* Willgerodt-Kindler reaction by Rekunge and his colleagues³¹ utilizing a variety of ketones (2 mmol), secondary amines (2.4 mmol), and sulfur (2.4 mmol) under the influence of SPB (10 wt%) at 100 °C (Scheme 5). The authors optimized solvent-free conditions as a reliable platform for the reaction. The reaction yielded 18 product derivatives within 30–60 min, showcasing 75–92% yield. Among other variants of secondary amines, pyrrolidine accelerated the reaction, and in the case of



83-98%

R = NO₂, Cl, CH₃, H
R = 4-CH₃C₆H₄, 4-CH₃OC₆H₄, 2-OHC₆H₄, 4-OHC₆H₄, C₆H₅CH₃, 2-thienyl, 5-methyl furan-2-yl, 2-pyridyl, c-C₆H₁₁, n-C₃H₇, C₆H₅, 2-ClC₆H₄, 3-ClC₆H₄, 4-ClC₆H₄, 4-BrC₆H₄, 2-O₂NC₆H₄, 3-O₂NC₆H₄, 4-O₂NC₆H₄



Scheme 10 Synthesis of 4-substituted 1,5-benzodiazepines using 10 wt% SPB.

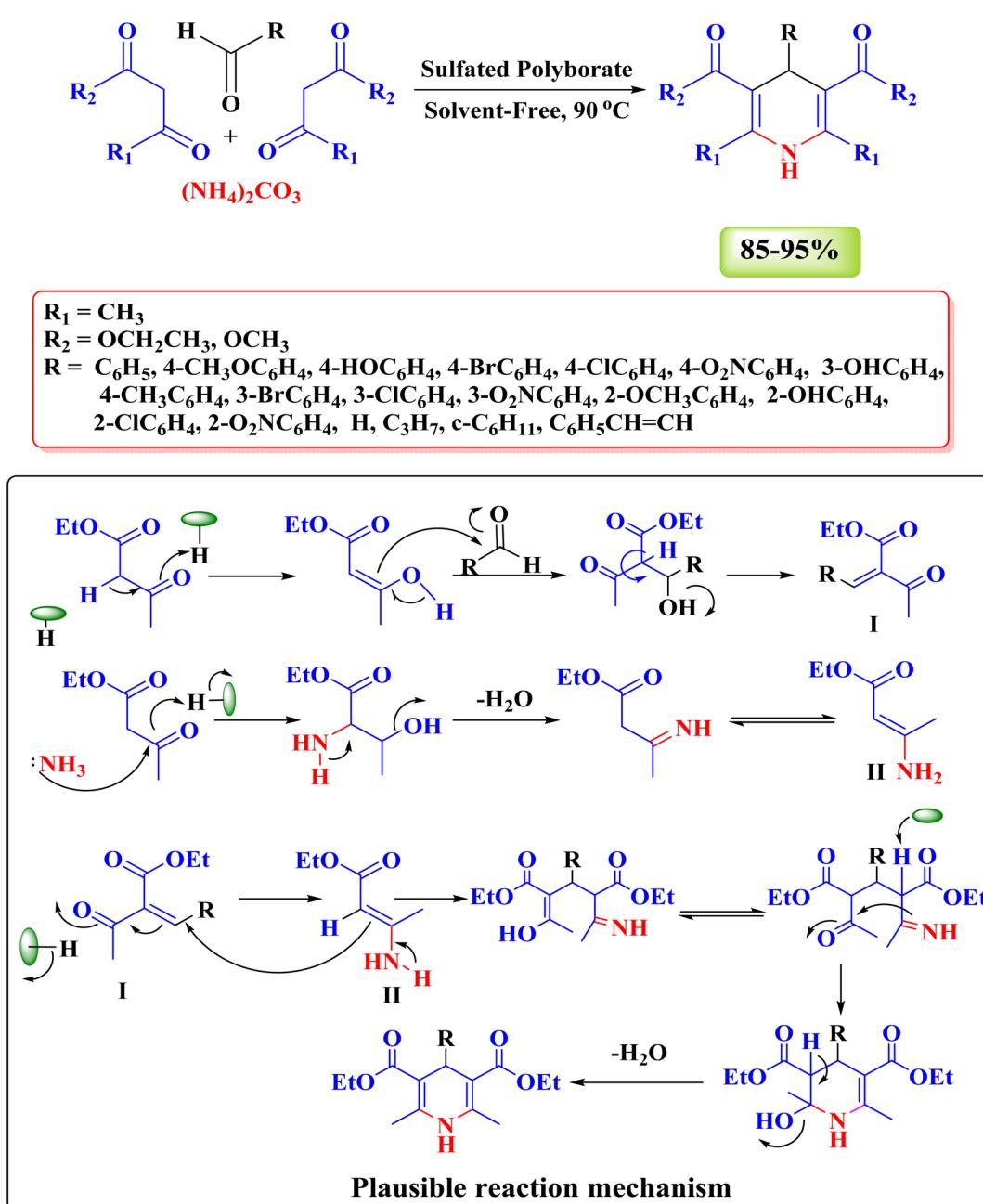


ketones, *para*-substituted compounds demonstrated a more noticeable effect than *ortho* substituents. Furthermore, SPB demonstrated its reusability with 86% catalytic efficiency for five runs.

3.6 Streaker's α -aminonitriles synthesis

S. Indalkar *et al.*³² proposed an efficient scheme for one-pot synthesis of Streaker's α -aminonitriles synthesis using SPB as a convenient and non-toxic catalyst. The protocol followed a complete green pathway for the synthesis of the desired product in terms of a solvent-free platform at RT. The Streaker

reaction, a multi-component organic transformation, involves ketones/aldehydes (1 mmol), amines/secondary anilines (1 mmol), and trimethylsilyl cyanide (TMSCN) (1 mmol) under the influence of 5 wt% SPB (Scheme 6). This method furnished 25 derivatives within 2–30 minutes exhibiting 87–99% product yield. SPB demonstrated recyclability up to five runs with >90% efficiency. However, the protocol proved to be unsuccessful when applied to aliphatic aldehydes with straight chains and underwent retarded reaction times when aldehydes were replaced with ketones, due to steric hindrance.



Scheme 11 Synthesis of 1,4-dihydropyridines using 5 wt% SPB.



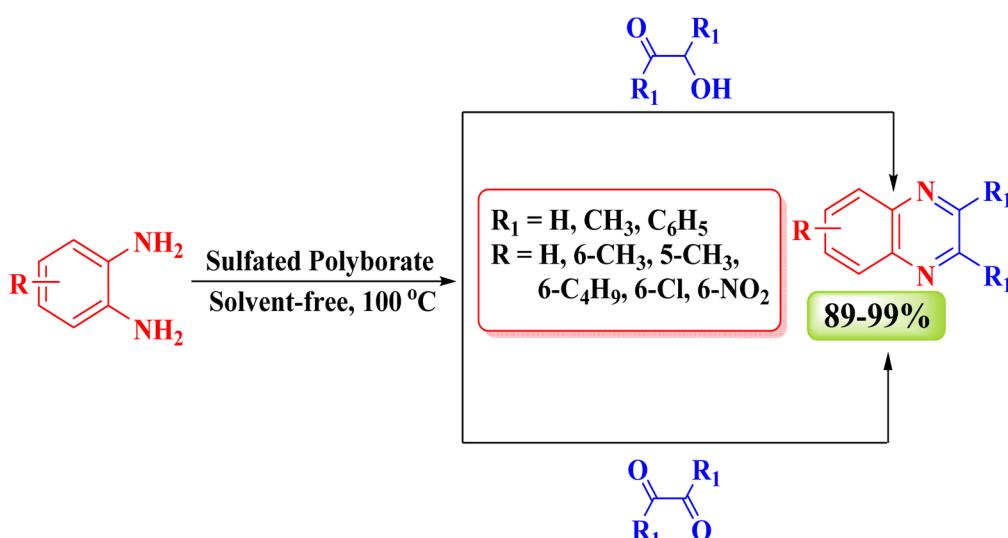
3.7 Betti base synthesis

Patil *et al.*³³ investigated the Betti base synthesizing pathway utilizing SPB (10 wt%). The organic transformation involved phenols (1 mmol), aldehydes (1 mmol), and amines (1.2 mmol) at 100 °C without using solvent (Scheme 7). The products were obtained with 90–98% yields within 10–45 min without side products. Furthermore, the authors reported 85% efficiency on recyclability up to five runs. Additionally, accelerated reaction times were seen with β -naphthol but were found ineffective with aliphatic aldehydes. However, when morpholine, piperidine, and pyrrolidine were

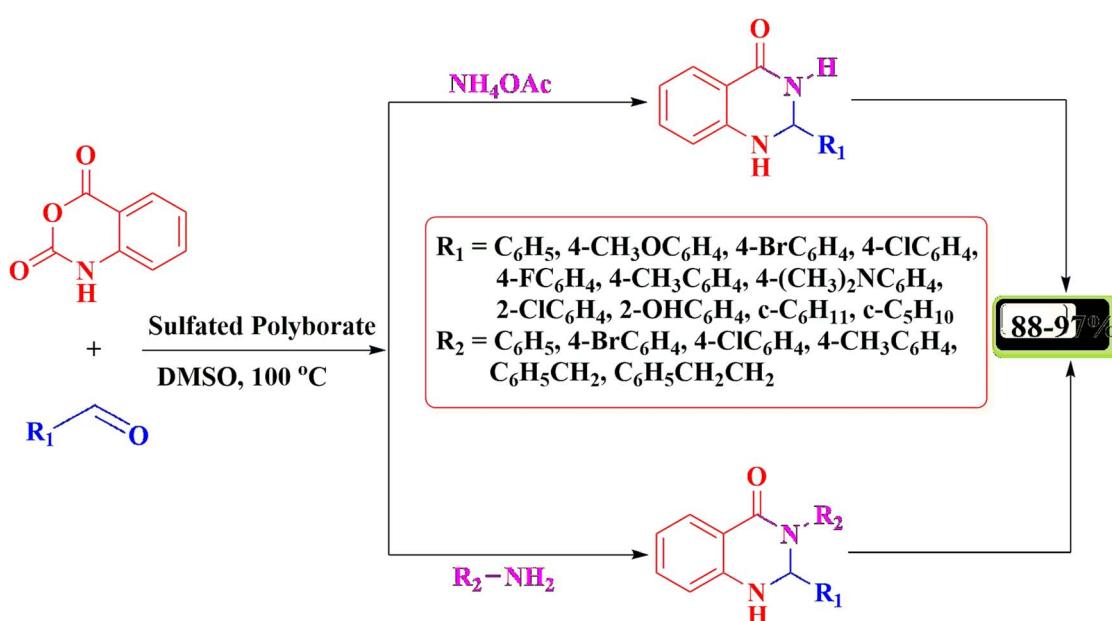
condensed with aliphatic amines, morpholine increased the reaction time.

3.8 Friedlander annulation

Mali *et al.*³⁴ noted the specified role of SPB in the Friedlander annulation for synthesizing 2-methyl-4-phenylquinoline-3-carboxylate. The uncatalyzed procedure resulted in a non-Friedlander product. The model reaction consisted of 2-aminobenzophenone and ethyl acetoacetate at a ratio of 1 : 1.2. The reaction was accelerated by optimizing solvent-free conditions, instead of using a toxic solvent, at an 80 °C, charged up with

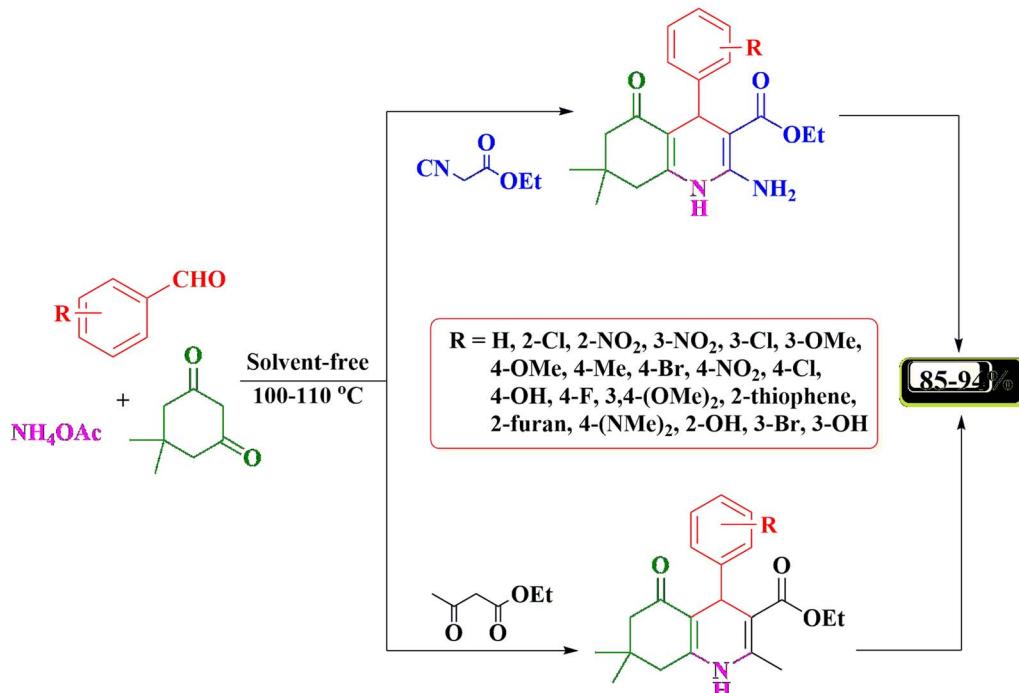


Scheme 12 Synthesis of quinoxaline using 10 wt% SPB.

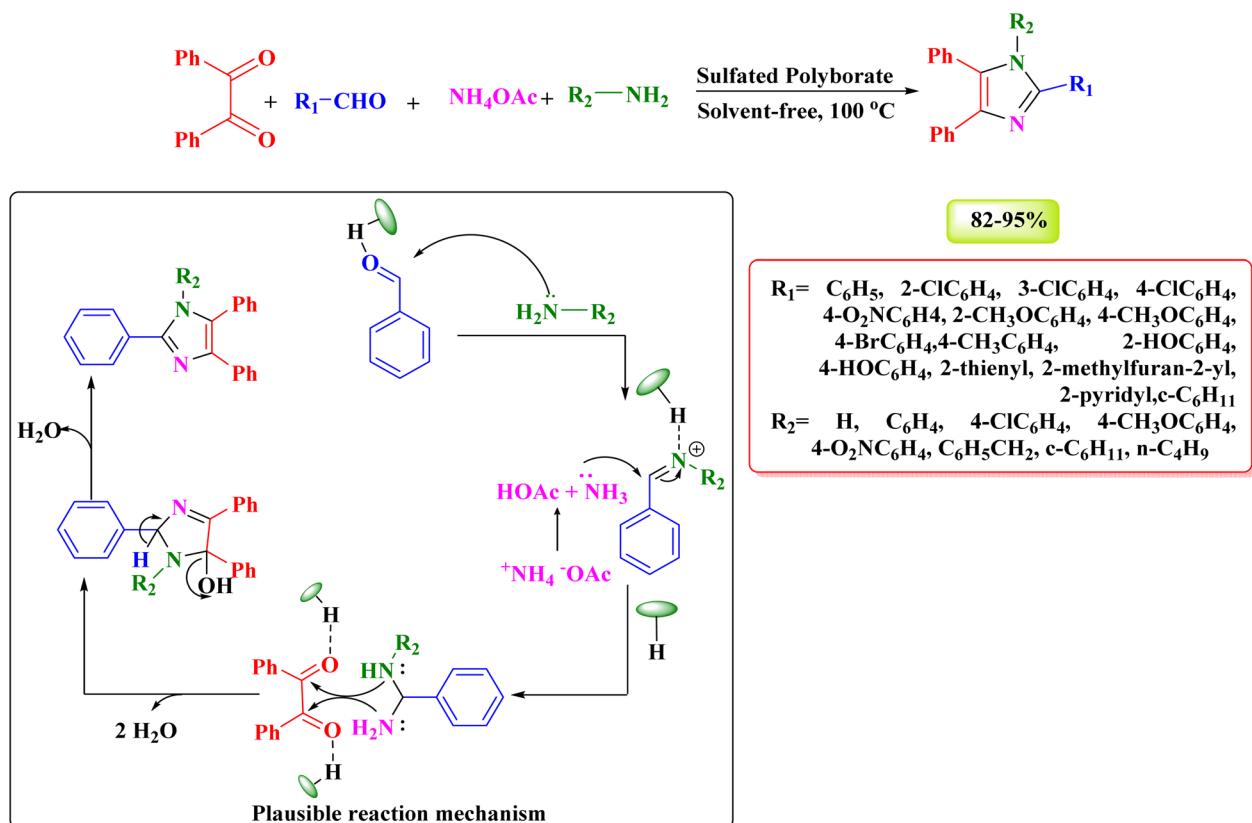


Scheme 13 Synthesis of 2,3-dihydroquinazolin-4(1H)-ones using 10 wt% SPB.





Scheme 14 Synthesis of polyhydroquinolines using 80 mg SPB.



Scheme 15 Synthesis of 2,4,5-tri and 1,2,4,5-tetrasubstituted imidazoles using 10 wt% SPB.

15 wt% SPB (Scheme 8). The reported method unveils a broad range of substrates (26 derivatives) and results in yields of 81–96% within the timeframe of 10–35 min. The protocol was selectively applied to the Friedlander reaction without interrupting the formation of non-Friedlander products. Additionally, SPB disclosed 87% catalytic efficacy in the fourth run, making it an efficient catalyst.

3.9 Miscellaneous reactions

3.9.1 Synthesis of 3-methyl-4-(hetero)arylmethyleneisaox-

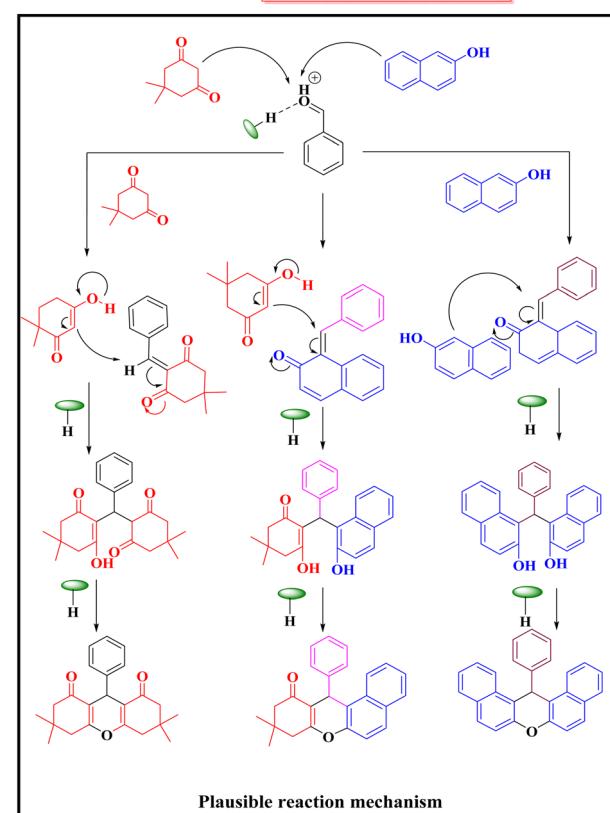
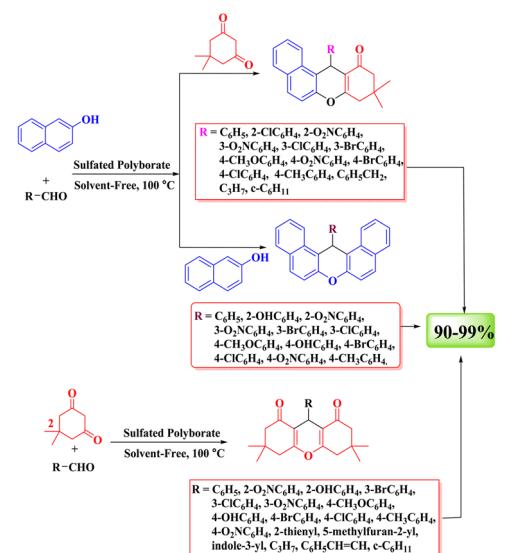
azole-5(4H)-ones. Patil *et al.*³⁵ established a remarkable methodology for the preparation of 3-methyl-4-(hetero) arylmethyleneisaoxazole-5(4H)-ones employing SPB as a catalyst. The organic transformation included condensation of equimolar aromatic/heterocyclic aldehyde, ethyl acetoacetate (EAA), and hydroxylamine hydrochloride in the solvent-free environment at 80 °C. The reaction reached completion in 15–30 min with high yields (80–90%), on loading of 10 wt% of SPB (Scheme 9). However, the optimized transformation was ineffective for aliphatic and alicyclic aldehydes. The SPB activated the >C=O group of aldehyde as well as interacted with ethyl acetoacetate to activate the carbonyl group. Moreover, the catalyst holds the efficiency for four runs without appreciable loss in its activity.

3.9.2 Synthesis of 4-substituted 1,5-benzodiazepines

3.3.2 **Synthesis of 4-substituted 1,5-benzodiazepines**
 Indalkar *et al.*³⁶ examined SPB (10 wt%) as a promising, environmentally friendly, reusable, and effective catalyst for the formation of 4-substituted 1,5-benzodiazepines. The initial reaction involved equimolar amounts of aldehyde, *o*-phenylenediamine, and dimedone (Scheme 10). SPB protonated one of the oxygens of the >C=O group of dimedone and afterward underwent Michael addition with *o*-phenylenediamine, followed by enamine formation. It further reacted with aromatic aldehyde to yield diimine, followed by Knoevenagel cyclization to fabricate 4-substituted 1,5-benzodiazepines (21 derivatives) within 10–15 minutes with 83–98% yield under solvent-less conditions at 100 °C. Furthermore, the SPB demonstrated reusability for up to five cycles with 91% catalytic efficiency.

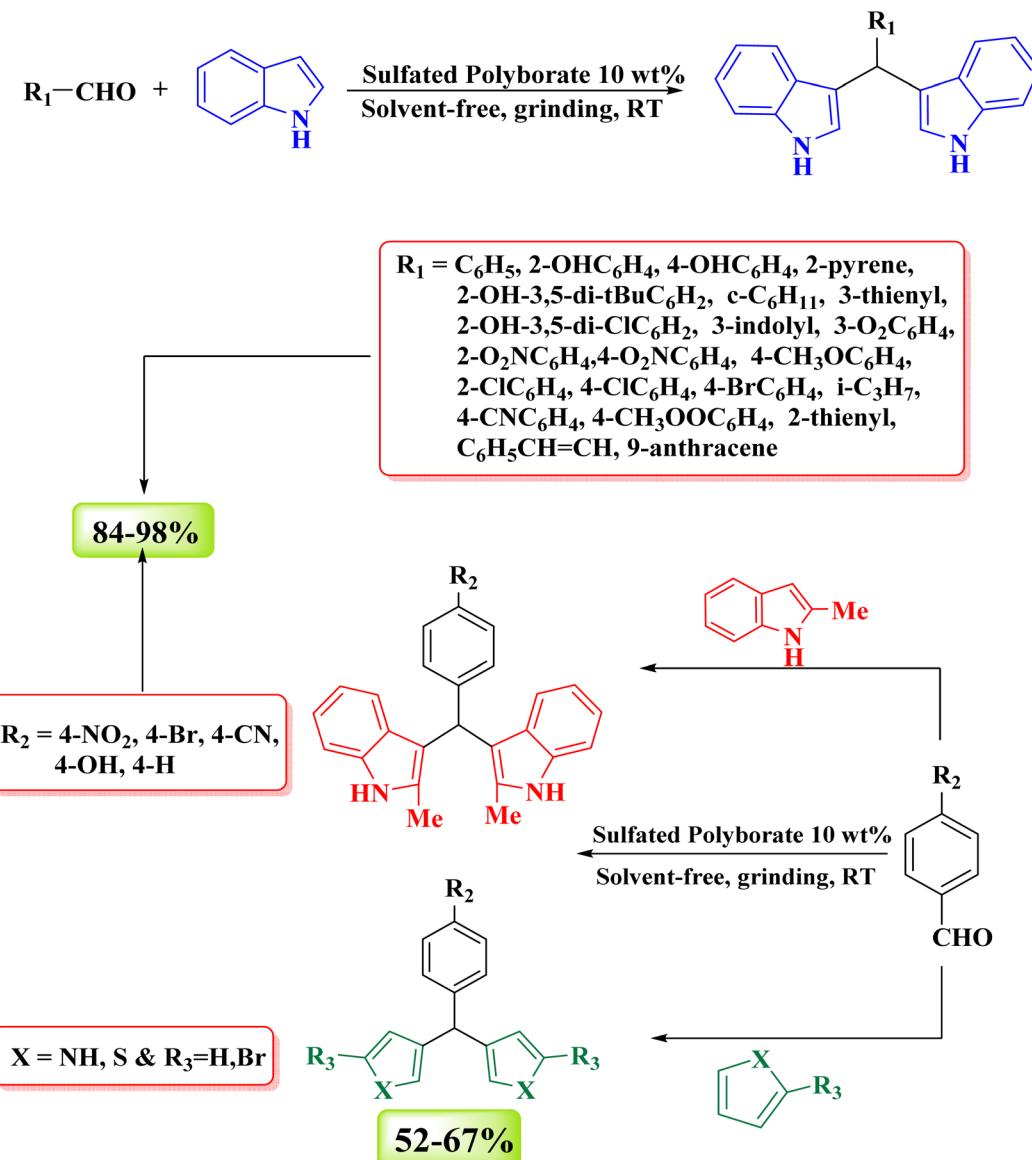
3.9.3 Synthesis of 1,4-dihydropyridines. Rekunge and his

39.3.3 **Synthesis of 1,4-dihydropyridines.** Rekunge and his lab mates³⁷ investigated SPB (5 wt%) as a feasible catalyst for 1,4-dihydropyridines synthesis, attaining shorter reaction times (15–40 minutes) and high yields (85–95%). The reaction was directed at 90 °C using various benzaldehyde (2 mmol), EAA (4 mmol), and ammonium carbonate ($(\text{NH}_4)_2\text{CO}_3$) (1.2 mmol) without using solvent (Scheme 11). The researchers examined $(\text{NH}_4)_2\text{CO}_3$, ammonium acetate ($\text{CH}_3\text{COONH}_4$), ammonium bicarbonate (NH_4HCO_3), and ammonium chloride (NH_4Cl) as nitrogen sources in the model reaction. $(\text{NH}_4)_2\text{CO}_3$ yielded peak results with 95% yield in 15 min; hence, it was selected as the preferred reagent. SPB facilitated Knoevenagel product formation from β -ketoester and aliphatic or aromatic aldehydes, followed by β -aminoester formation, Michael addition of unsaturated carbonyl



Scheme 16 Synthesis of symmetrical and unsymmetrical xanthenes using 10 wt% SPB

compounds with enamine, proton transfer, and cyclization. Furthermore, the protocol was applied to aliphatic and α,β -unsaturated aldehydes, and ethyl/methyl ester variants of β -ketoesters. However, 2-OMe and 2-OH substituents demanded extended reaction times. Furthermore, the SPB catalyst was used for up to five cycles with >80% efficiency.



Scheme 17 Synthesis of tri-substituted methane using 10 wt% SPB.

3.9.4 Synthesis of quinoxalines. Indalkar *et al.*³⁸ identified SPB as a suitable and replaceable catalyst in comparison to high-cost/corrosive reagents, strong oxidants, and harmful organic solvents for quinoxaline synthesis. The reaction involved *o*-phenylenediamine (OPD) derivatives and α -hydroxy ketones/1,2-diketones (1 : 1) catalyzed by SPB (10 wt%) at 100 °C without using any solvent (Scheme 12). The product was isolated within 3–30 minutes with 89–99% yield. The catalyst was successfully reused for five runs with 90% catalytic efficiency. However, the protocol loaded column chromatography for product purification, which was one of the constraints, along with lower yield and prolonged reaction time observed with *o*-phenylenediamine bearing electron-withdrawing substituents and benzoin under optimized reaction conditions.

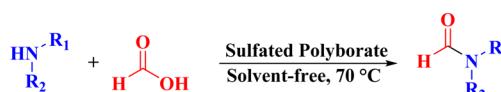
3.9.5 Synthesis of 2,3-dihydroquinazolin-4(1*H*)-ones. Khatri and colleagues³⁹ recognized SPB as a superior catalyst in terms of convenience, environmental sustainability, ease of isolation, and approachability for synthesizing 2,3-dihydroquinazolin-4(1*H*)-ones. The reaction required CH₃COONH₄ (2.4 mmol)/amines (2 mmol), isatoic anhydride (2 mmol), and aldehydes (2 mmol) in DMSO solution under the influence of SPB (10 wt%) at 100 °C (Scheme 13). This method afforded 17 product derivatives within 15–20 min and represented good to excellent yields (88–97%). The recovered SPB exhibited 90% catalytic efficiency for up to five cycles.

3.9.6 Synthesis of polyhydroquinolines. Aute and colleagues⁴⁰ examined SPB as a facile and eco-compatible catalyst for solvent-free one-pot multicomponent synthesis of



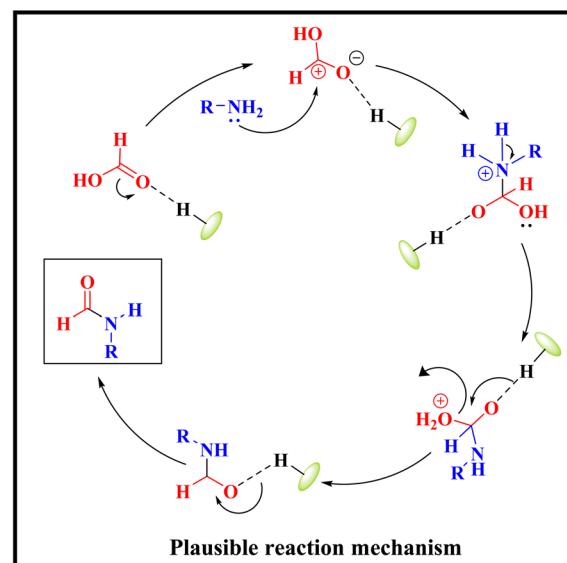
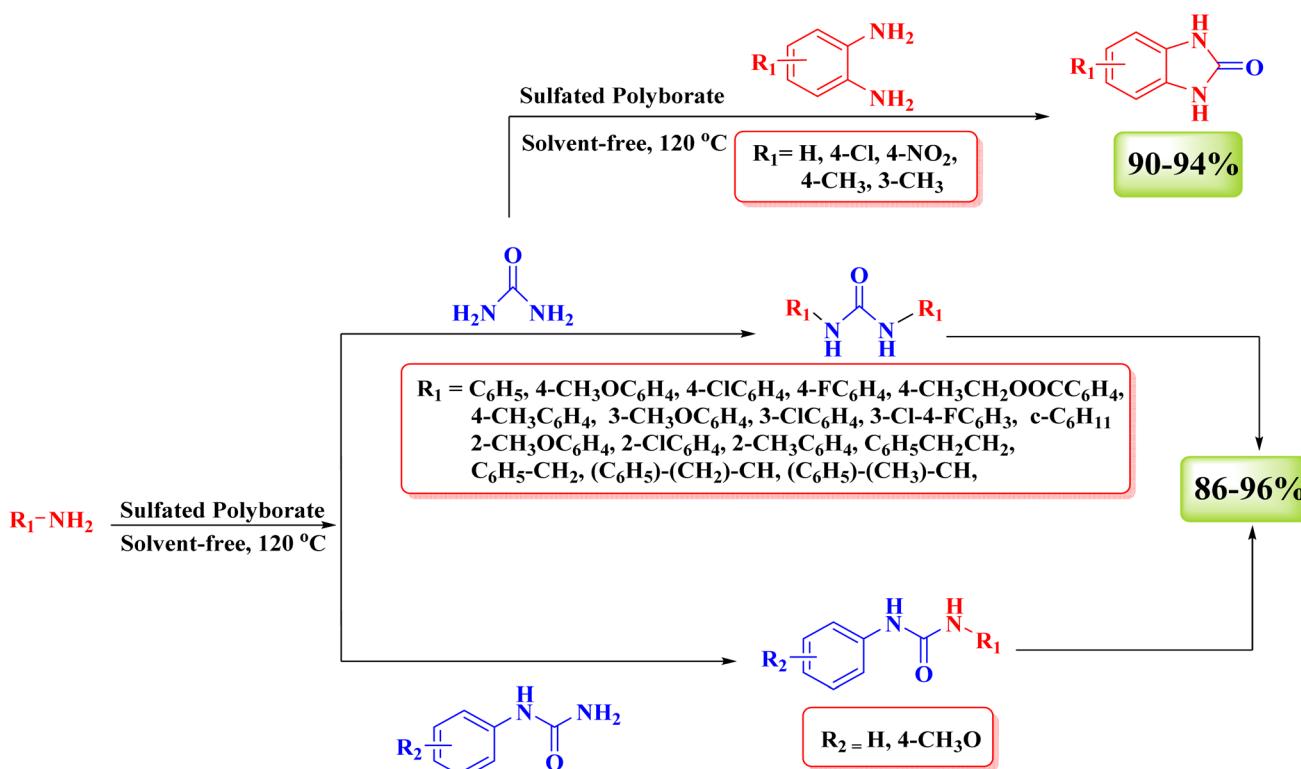
polyhydroquinolines. The reaction involved a mixture of aromatic aldehydes (1 mmol), dimedone (1 mmol), $\text{CH}_3\text{COONH}_4$ (1.5 mmol), and EAA/ethyl cyanoacetate (1 mmol) at 100–110 °C for 18–30 min, yielded 85–94% of the desired product (Scheme 14). SPB activated the carbonyl group of aldehydes, ethyl cyanoacetate, and dimedone for the formation of enamine, followed by Knoevenagel condensation of aromatic aldehydes with ethyl cyanoacetate to form an intermediate. This intermediate subsequently engaged in Michael's addition with enamine, followed by cyclization and dehydration. The reported method synthesized 29 derivatives using 80 mg SPB, decoding the substrate scope. The optimized reaction was successfully applicable to heteroaromatic aldehydes. However, the reusability of SPB in the protocol remains undetermined which was unsatisfactory.

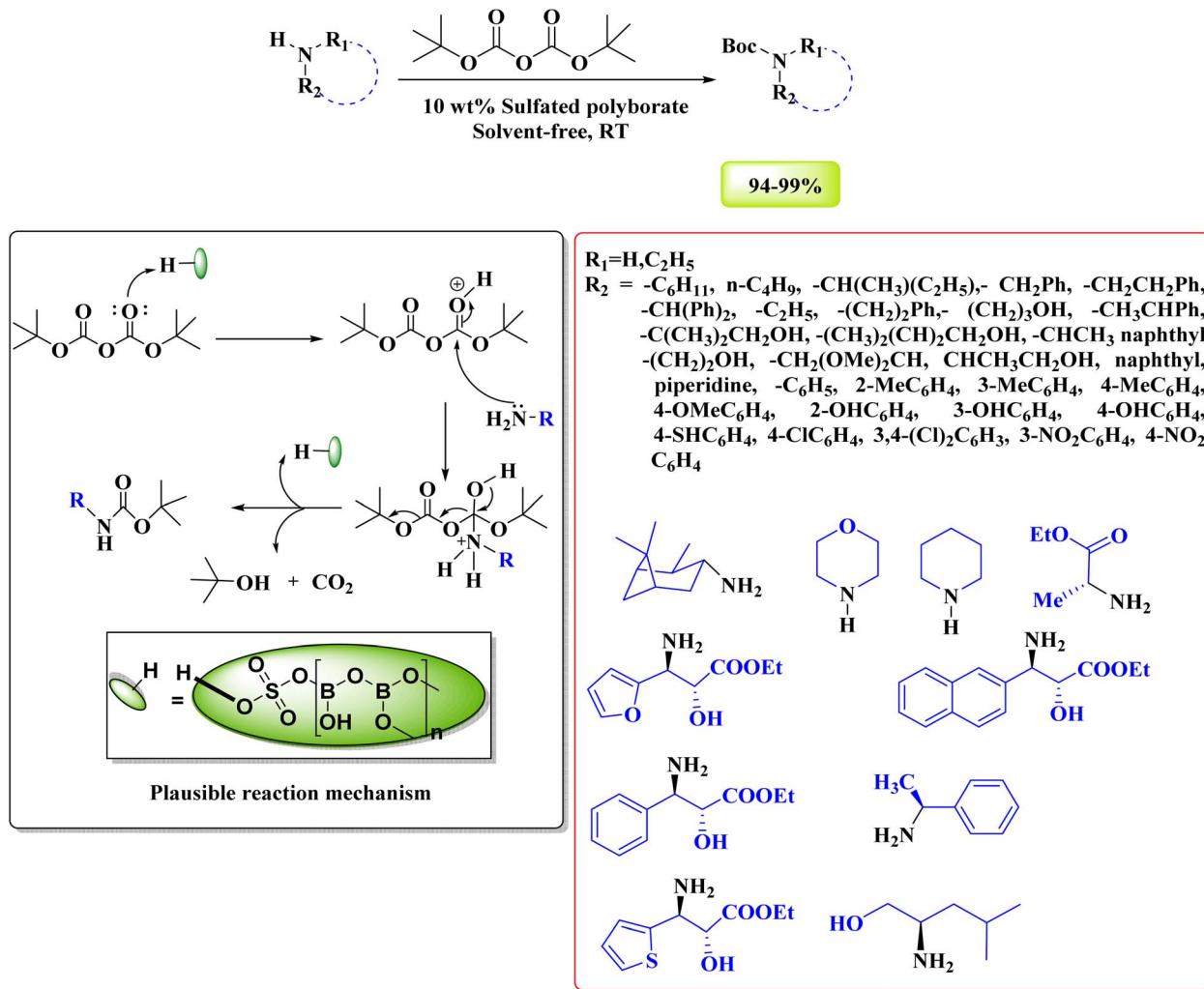
3.9.7 Synthesis of 2,4,5-tri and 1,2,4,5-tetrasubstituted imidazoles. Indalkar *et al.*⁴¹ identified an effortless and efficient, solvent-free method for the one-pot synthesis of multi-substituted imidazoles, especially for 2,4,5-tri and 1,2,4,5-tetrasubstituted imidazoles, catalyzed by SPB at 100 °C (Scheme 15). The organic transformation utilized 1 mmol of benzil, 1 mmol of aldehydes, and 2 mmol of $\text{CH}_3\text{COONH}_4$ in 10 wt% SPB to yield 2,3,4-triphenyl-1*H*-imidazole. The endpoint of the reaction was achieved within a timeframe of 8–20 min with high yields of 86–98%. An equimolar mixture of benzil, benzaldehyde, $\text{CH}_3\text{COONH}_4$, and amines required 10–25 minutes in the same optimized route to synthesize 1,2,4,5-tetra-substituted imidazole with an 82–95% yield. The catalyst not only triggered carbonyl activation but also interacted with the



86–98%

$\text{R}_1 = \text{C}_6\text{H}_5, 2\text{-CH}_3\text{C}_6\text{H}_4, 4\text{-CH}_3\text{C}_6\text{H}_4, 2\text{-OHC}_6\text{H}_4, 4\text{-CH}_3\text{OC}_6\text{H}_4, 2\text{-ClC}_6\text{H}_4, 4\text{-BrC}_6\text{H}_4, 2\text{-CH}_3\text{OC}_6\text{H}_4, 4\text{-ClC}_6\text{H}_4, 4\text{-FC}_6\text{H}_4, \text{c-C}_6\text{H}_{11}, \text{C}_6\text{H}_5\text{CH}_2, 2\text{-CH}_3\text{OCOC}_6\text{H}_4, 4\text{-C}_2\text{H}_5\text{OCOC}_6\text{H}_4, \text{C}_6\text{H}_5\text{C}_2\text{H}_5, \text{morpholine}, \text{imidazole}, \text{C}_6\text{H}_5\text{OH}, \text{C}_6\text{H}_5\text{CH}_2\text{OH}$
 $\text{R}_2 = \text{H}, \text{C}_6\text{H}_5, \text{C}_2\text{H}_5, \text{C}_6\text{H}_5\text{CH}_2$

Scheme 19 *N*-Formylation of amines using 7.5 wt% SPB.Scheme 18 Synthesis of 1,3-disubstituted urea and 1*H*-benzimidazol-2(3*H*)-ones using 10 wt% SPB.



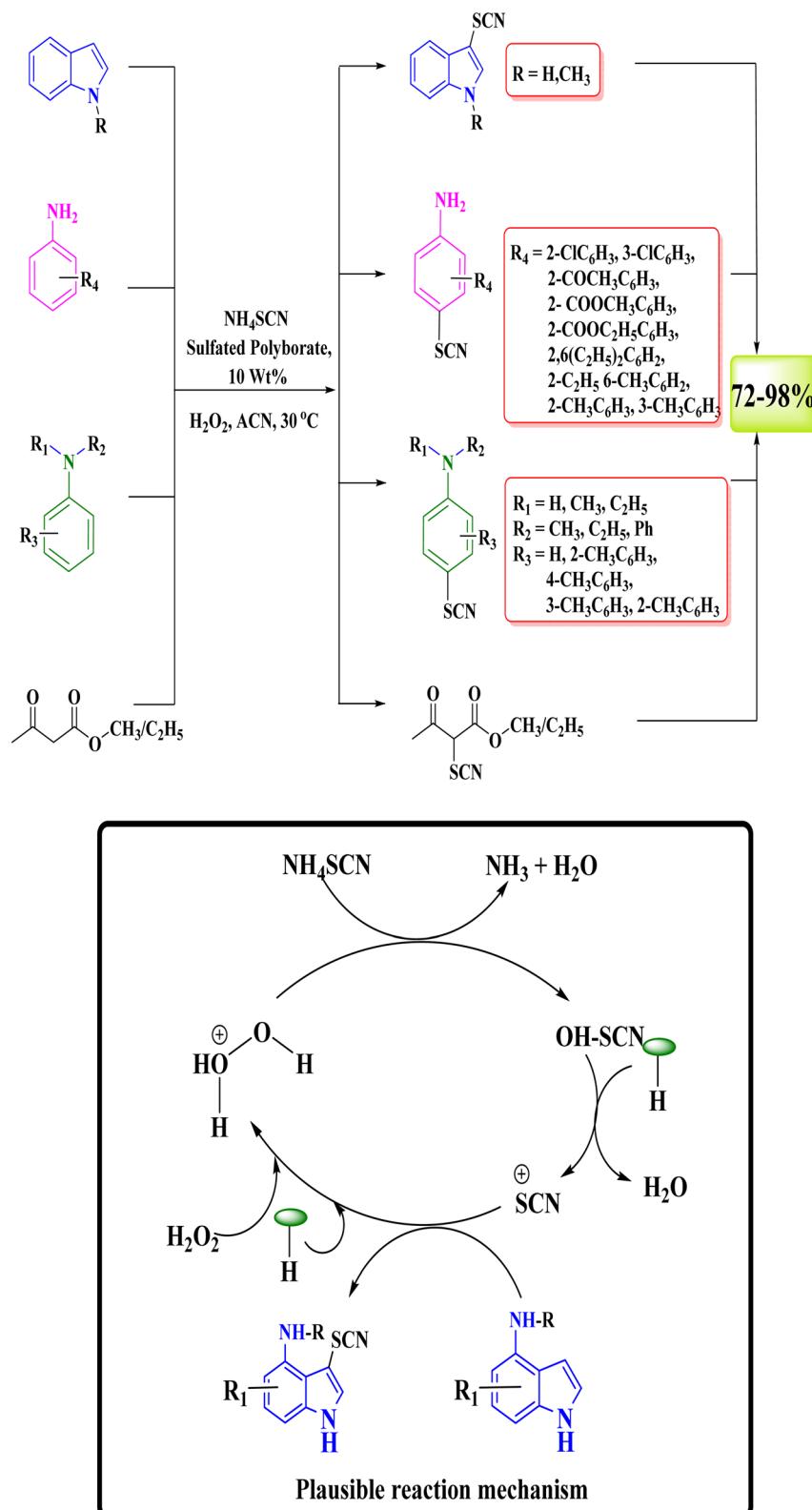
Scheme 20 Protection of amines using 10 wt% SPB.

intermediate species. SPB also facilitated diamine intermediate formation, which then underwent a nucleophilic reaction with ammonia (*in situ*), which resulted in another intermediate that underwent aromatization to yield tri- and tetra-substituted imidazoles. Additionally, following four cycles, SPB achieved 92% catalytic yield.

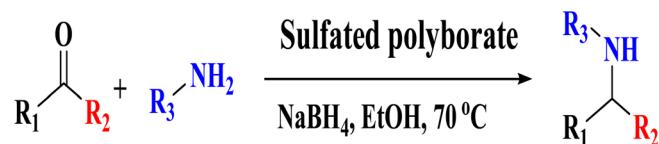
3.9.8 Synthesis of symmetrical and unsymmetrical xanthenes. Patil and co-authors have discussed an eco-benign, cost-effective, SPB (10 wt%) catalysed, solvent-free approach⁴² to synthesize xanthene derivatives. To furnish symmetrical (1,8-dioxo-octahydro and 14-phenyl-14H-dibenzo xanthene) and unsymmetrical xanthenes (tetrahydrobenzo xanthene-11-ones), mixture of aldehyde (1 mmol) and dimedone/β-naphthol (2 mmol) were stirred for 3–8 min at 100 °C with 94–99% product yield, and similarly equimolar mixture of aldehydes, β-naphthol and dimedone required 6–10 min accompanied by 90–99% product yield respectively (Scheme 16). The protocol signified extension to aliphatic/alicyclic/aromatic/hetero-aromatic

aldehydes and reusability of SPB up to four runs with good performance. The mechanism began with aldehyde activation by SPB followed by a nucleophilic attack of β-naphthol/dimedone following Knoevenagel condensation. Then, it underwent addition with another mole of β-naphthol/dimedone, subsequently generating the adduct, which further underwent intramolecular cyclization for the desired outcome. Moreover, the catalyst showed recyclability for five runs without notable loss in efficacy (>80%).

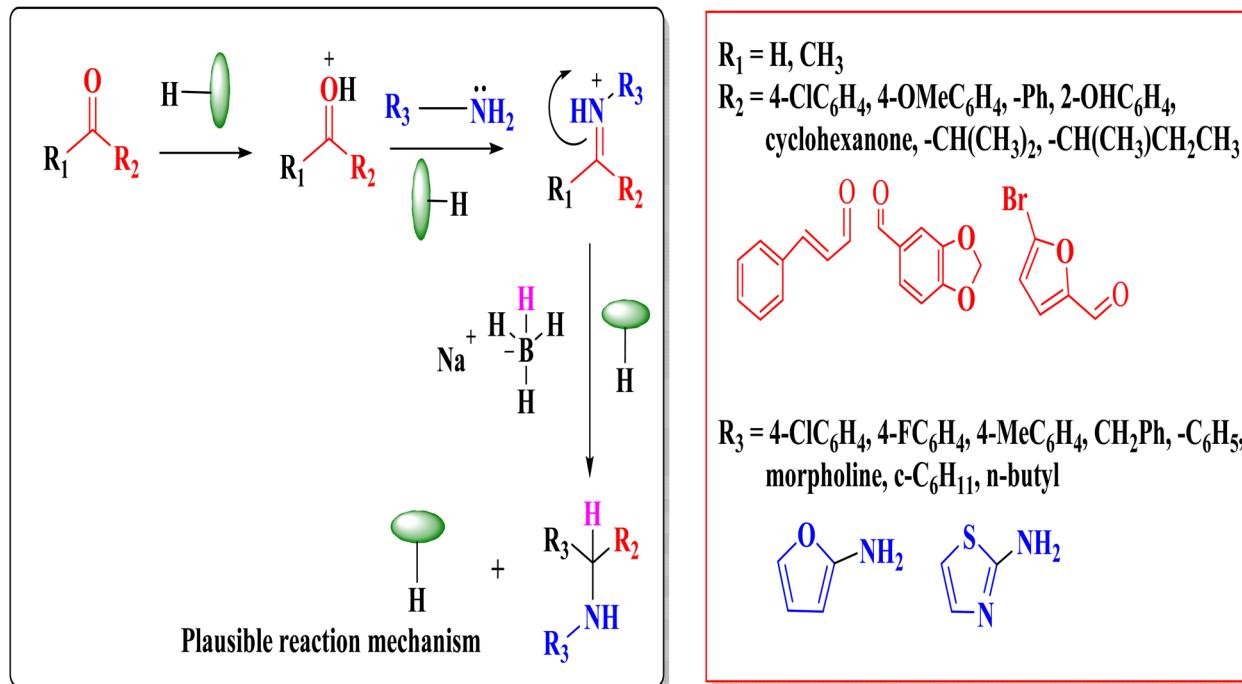
3.9.9 Synthesis of tri-substituted methanes. Jejurkar *et al.*⁴³ fabricated a solvent-free grinding technique which offered hazardous waste-free route for the preparation of tri-substituted methane catalysed by SPB (10 wt%) at RT. The protocol achieved a wide substrate scope including aldehydes and indoles/thiophene/pyrrole in a ratio of 1 : 2 in terms of concentration (Scheme 17). The methodology withstands polyaromatic and hetero-aromatic aldehyde and furnished the products within the timeframe of 3–8 min accompanied by



Scheme 21 Thiocyanation of activated arenes using 10 wt% SPB.



75-99%



Scheme 22 Reductive amination of ketones and aldehydes using 5 wt% SPB.

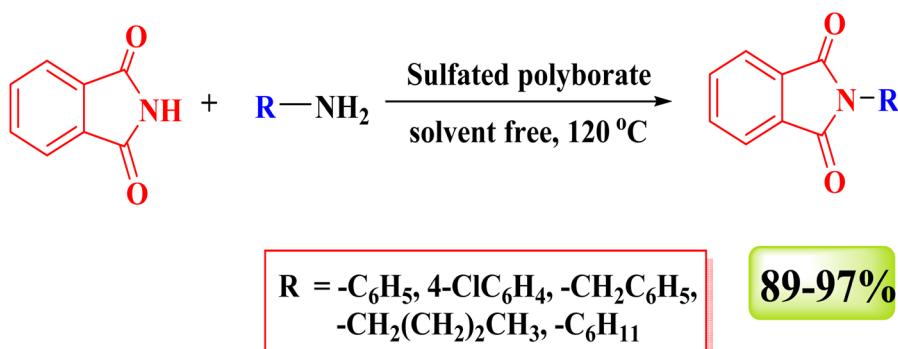
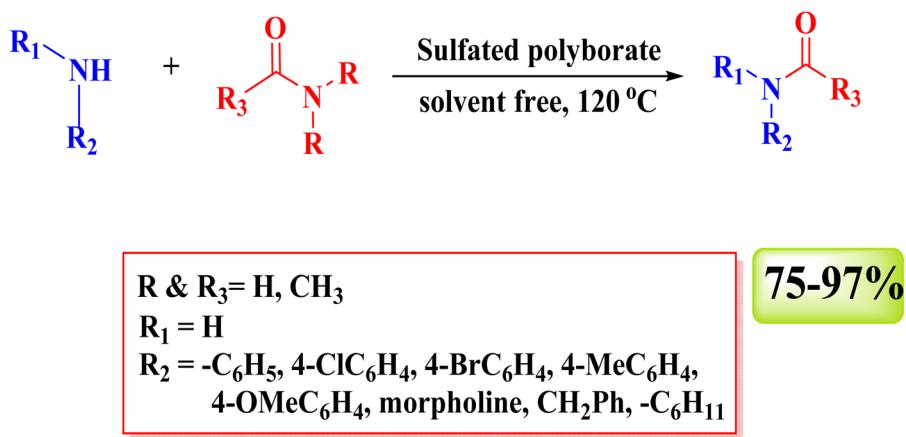
excellent yields (84–98%) in the case of indoles, whereas it took extended reaction time for thiophenes and pyrroles (8–17 min) with average yield 52–67%. The reusability test of SPB signifies 93% catalytic efficacy over four runs. Overall, the protocol had a good score on an economical scale making it a green and approachable synthesis.

3.9.10 Synthesis of (un) symmetrical urea and benzimidazolone. Rekunge *et al.*²⁷ demonstrated a phosgene-free, organic solvent-free pathway for synthesizing (un) symmetrical urea and benzimidazolones at 120 °C under the influence of superior Brønsted as well as Lewis acid-focused SPB. The model reaction for synthesizing symmetrical 1,3-disubstituted urea comprised amine/aniline (4 mmol), urea (2.4 mmol), and 10 wt% of SPB at 120 °C (Scheme 18). The expected outcome revealed within 0.75–2 h with 86–96% yield. The protocol successfully derived 21 derivatives. Anilines bearing electron-donating substituents at *para* positions exhibited a high reaction rate. SPB also catalyzed 1*H*-benzimidazol-2(3*H*)-ones under the same reaction condition with OPDA (2 mmol) and

urea (2.4 mmol) within 1.5–2.5 h in excellent yields (90–94%). The researchers also reused the catalyst four times with good outcomes.

3.9.11 *N*-Formylation of amines. Khatri *et al.*⁴⁴ analyzed SPB as an inexpensive, affordable, and rapid catalyst highlighting Brønsted and Lewis acid properties for *N*-formylation of amines within 10–45 minutes, yielding 86–98%. Formylation occurred in a solvent-free medium in the presence of various amines (2 mmol), formic acid (2.4 mmol) at 70 °C, and SPB (7.5 wt%) (Scheme 19), which enhanced the electrophilic property of formic acid by protonation of the oxygen atom of the $\text{C}=\text{O}$ group for nucleophilic attack of amine and subsequent dehydration. The protocol exhibited extended reaction time for secondary aromatic, primary, and secondary aliphatic amines, 2-methoxycarbonyl, and 4-ethoxycarbonyl anilines but proved unsuccessful with phenol and benzyl alcohol. The authors utilized the SPB for five cycles with 90% efficiency.





Scheme 23 Transamidation of carboxamides and phthalamides using 10 wt% SPB.

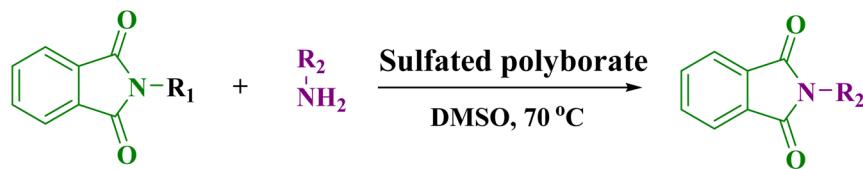
3.9.12 Protection of amines. Pise *et al.*⁴⁵ demonstrated a practicable and straightforward protection method for amines *via* eco-benign methodology under ultrasonic irradiation. The protocol chemoselectively introduced *N*-*tert*-butyloxycarbonylation as a protecting group of amines under the influence of 10 wt% SPB, which proved to be more convenient than other methodologies. The scheme begins with an ultrasound-assisted reaction of equimolar cyclohexyl amine/anilines with di-*tert*-butyl-dicarbonate in the solvent-free environment at RT (Scheme 20). The SPB enhances the electrophilicity of the oxygen atom of the carbonyl group of Boc₂O, making it more facile for nucleophilic attack. Hence, protection was done within 2–15 min with 94–99% yield. Furthermore, the methodology disclosed a broad range of substrate scope. However, the nitro-anilines took extended reaction time (20–35 min) along with 60 °C with comparatively low yields (85–89%). The catalyst was reused successfully even after five iterations without appreciable loss in efficacy.

3.9.13 Thiocyanation of activated arenes. Patil *et al.*⁴⁶ developed a simple and risk-free method for the electrophilic thiocyanation of activated arenes *viz.* anilines, *N*-substituted anilines, indoles, and β -ketoesters by SPB (10 wt%) and H₂O₂ (30%, 3 mmol) as an oxidizer. The model reaction for the protocol comprises arenes (1 mmol), and ammonium

thiocyanate (3 mmol) in acetonitrile at 30 °C (Scheme 21). The methodology furnished 20 derivatives in 3–10 min with 72–98% in which diphenylamine exhibited an average yield of 72% yield. The reported method utilized SPB for up to four cycles with good catalytic efficacy.

3.9.14 Reductive amination of ketones and aldehydes. P. Ganwir and his colleagues⁴⁷ found SPB as a dual catalyst for a hustle-free, quick, efficient, and eco-friendly protocol for the reductive amination of ketones and aldehydes (1 mmol), amines (1 mmol), using NaBH₄ (2 mmol) utilizing SPB (5 wt%) in ethanol at 70 °C (Scheme 22). The technique reduced the carbonyl group within 4–60 min and revealed 75–99% yields with 21 derivatives. SPB triggered the mechanism by protonating the oxygen of the carbonyl group, followed by a nucleophilic attack of the amine, resulting in imine formation. Additionally, the catalyst also charged up borohydride for nucleophilic attack and protonated imine, statutory for the desired product. However, the reaction had a wide substrate scope, but when benzaldehyde was reduced with morpholine in the presence of NaBH₄, the resulting product isolation required column chromatography, and alicyclic, aliphatic, and acetophenones took an extended reaction time (35–60 min).

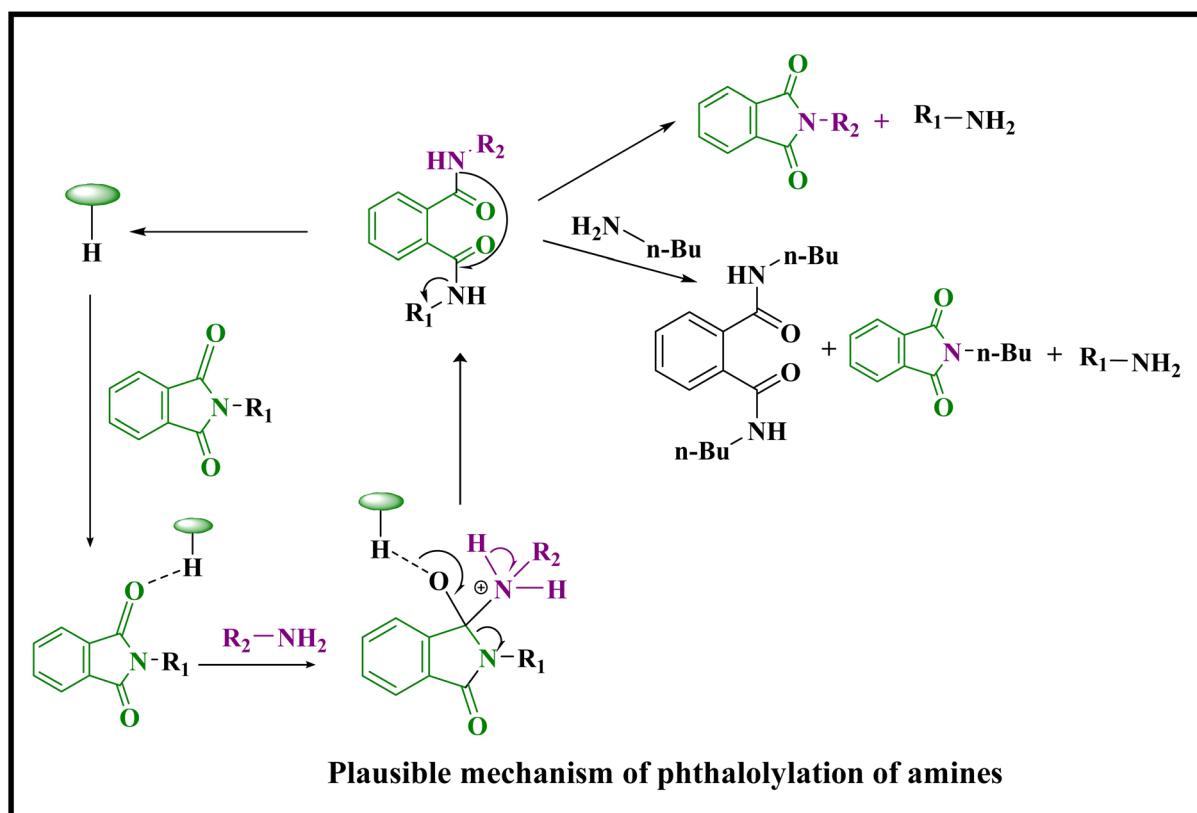




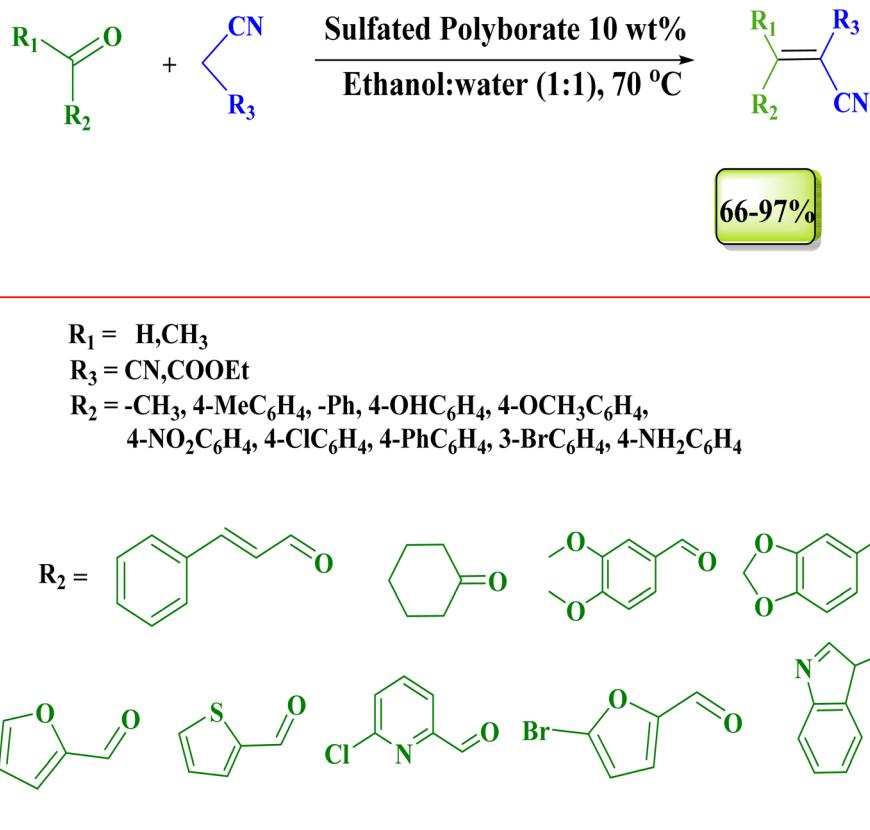
88-99%

$R_1 = H, -OH, -OMe$

$R_2 = 4-OCH_3C_6H_4, C_6H_5, C_6H_5NH, C_6H_5CONH,$
 $C_6H_{11}, CH_3(CH_2)_3, C_6H_5CH_2, C_6H_5(CH_2)_2$



Scheme 24 Phthaloylation of amines, hydrazines, and hydrazides using 10 wt% SPB.



Scheme 25 Knoevenagel condensation using 10 wt% SPB

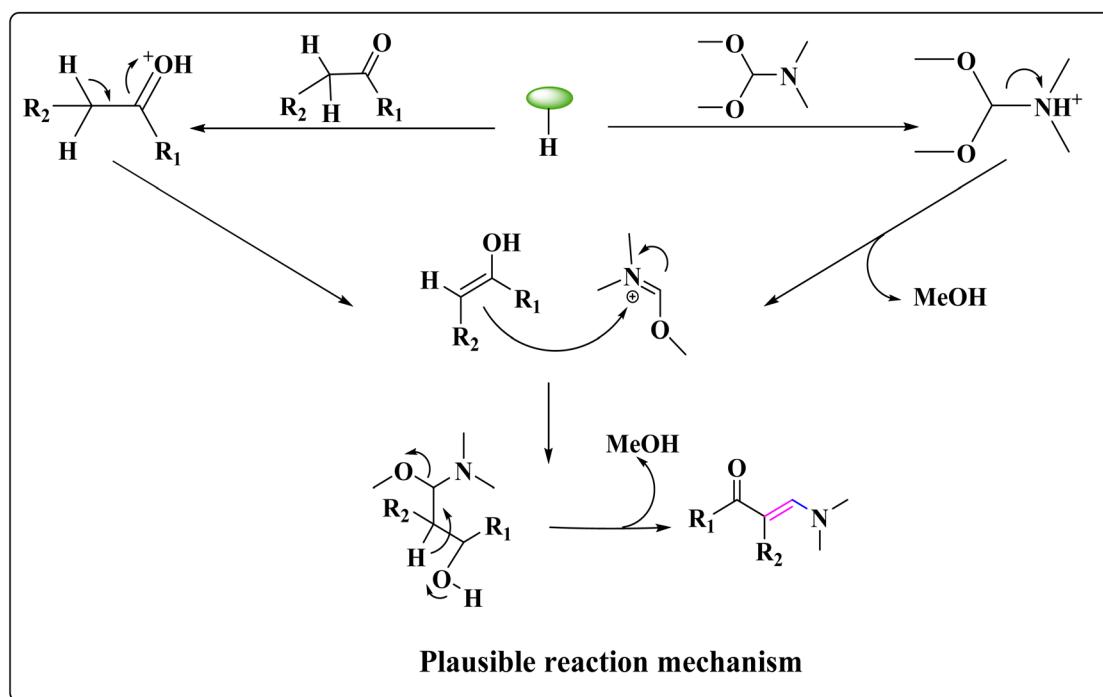
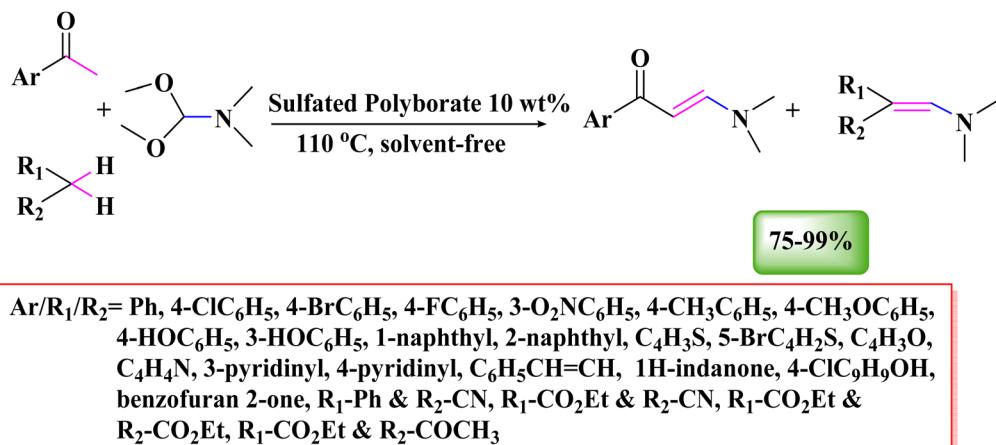
3.9.15 Transamidation of carboxamides and phthalamides with amines. Mali and his coworkers⁴⁸ employed transamidation of carboxamides and phthalamides with amines, implementing SPB. The transformation required aniline (1 mmol), amide (1.2 mmol), and SPB (10 wt%) in the solvent-free medium at 120 °C (Scheme 23). The methodology furnished 18 product derivatives within a timeframe of 1–8 h, highlighting yields of 75–97%. The recyclability test of SPB showed no notable loss even after four iterations, achieving an 89% yield.

3.9.16 Phthaloylation of amines, hydrazines, and hydrazides. The research outlines the role of SPB in phthaloylation of amines, hydrazines, and hydrazides *via* *N*-substituted phthalimides. Ganwir *et al.*⁴⁹ examined the catalyst (10 wt%) as promoter of the reaction and facilitated quick phthaloylation. The transamidation required phthalimide (1.4 mmol) and phenyl hydrazine/amine/hydrazide (1 mmol) in DMSO solvent at 70 °C (Scheme 24). The approach fabricated a broad range of substrates within the timeframe of 15–45 min and exhibited 88–99% yield. SPB interacted with phthalimide's carbonyl followed by a nucleophilic attack of hydrazine/amines/hydrazide to form an intermediate which subsequently underwent proton exchange to generate another intermediate and finally, the amide broke down to release ammonia, methoxyamine, or hydroxylamine. However, the protocol reused the catalyst three times with good yields but concise when carried out with *n*-

butylamine and *N*-hydroxyphthalamide/*N*-methoxyphthalamide, it resulted in a mixture of products with low yields (28–72%) and necessitated column chromatography for separation.

3.9.17 Knoevenagel condensation. Ganwir *et al.*⁵⁰ for the first time developed Knoevenagel condensation *via* SPB by using it as a Brønsted acid. The reported method proved to be more compatible with traditional methods. The reaction accommodates various aldehydes/ketones, active methylene substrates; ethyl cyanoacetate/malononitrile (1:1) in the presence of EtOH:H₂O (1:1) and 10 wt% SPB at 70 °C (Scheme 25). The products were obtained within 5–60 min with satisfactory yields of 66–97%. However, when furfural reacted with ethyl cyanoacetate only an acceptable yield of 68% with extended reaction time was noticed. Also, the reusability of SPB remains undetermined.

3.9.18 Synthesis of enaminones and enamine of methyl ketones and active methylene compounds. Bandivadekar and coworkers⁵¹ analyzed that SPB facilitated the synthesis of enaminones and enamine of methyl ketones and active methylene compounds. The reaction was performed with ketone/active methylene and DMF-DMA in 1:3 molar ratios at 110 °C in a solvent-free environment in 10 wt% SPB (Scheme 26). Though data were limited on catalyst-induced activation of carbonyl and active methylene functionalities with DMF-DMA;



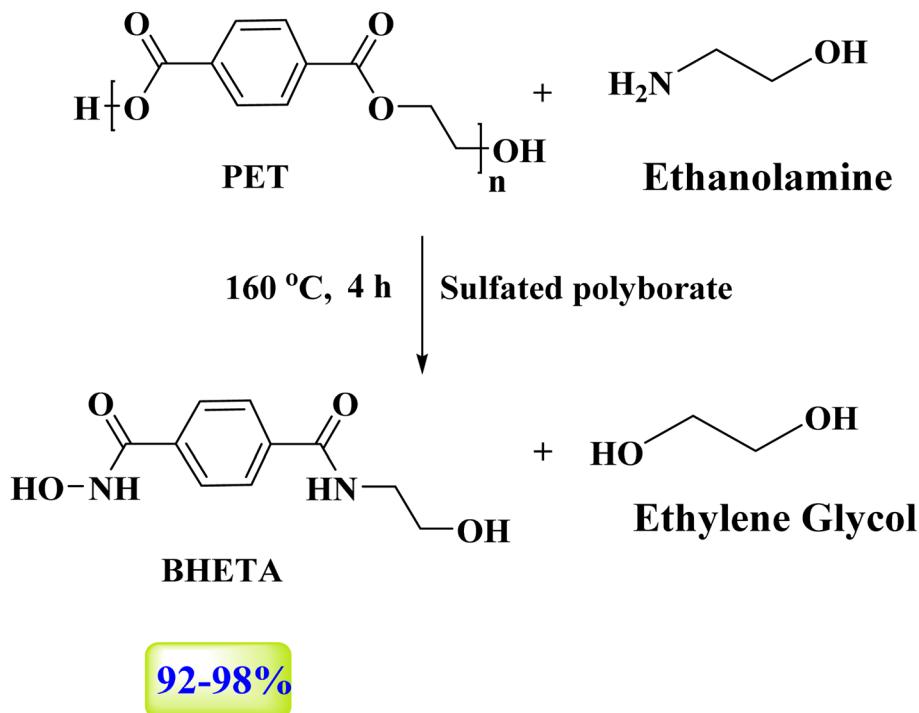
Scheme 26 Synthesis of enaminones and enamine using 10 wt% of SPB.

however, the fabricated methodology revealed a wide scope of substrates within 10 minutes to 4.5 h, accommodating an average to excellent yield of 75–99%. The SPB activated the $\text{C}=\text{O}$ group of ketone *via* protonation, which led to enol formation and simultaneously protonated DMF-DMA, which released the methoxy group and formed an iminium ion. Thereafter, enol attacked the iminium ion, followed by methanol elimination, leading to enaminone formation. However, the protocol does not define the reusability of SPB.

3.9.19 Aminolytic depolymerization of waste polyethylene terephthalate (PET). A wide range of crystalline terephthalamides has been generalized by aminolytic

depolymerization of waste polyethylene terephthalate (PET) utilizing SPB as a more compatible catalyst over metal catalyst by Singh *et al.*⁵² The proposed approach encountered an extraordinary yield for PET was confirmed with SPB rather than conventional methodology. The aminolysis involved PET (waste): ethanolamine in molar concentrations of 1 : 4 within a range of 140 °C–160 °C for 4 h and SPB as 1 wt% of PET under a nitrogen atmosphere (Scheme 27). The fragmentation yielded bis (2-hydroxyethyl) terephthalamide (BHETA) with 92–98% yield and ethylene glycol as depolymerized products. The BHETA was further utilized for resin formation and as a Hot Melt Adhesive (HMA) as it contains amide and hydroxyl groups.





Scheme 27 Aminolytic depolymerization of waste polyethylene terephthalate (PET) using SPB.

4 Conclusion

In conclusion, SPB underscores the role of a catalyst in achieving high reaction rates within short timeframes. A thorough examination of literature on the synthesis, characterization, and catalytic applications in organic transformations revealed that SPB catalyst interacts with reactive species and accelerates the reaction rate while maintaining tolerance to a broad range of functional groups. SPB has demonstrated itself as a promising green and industrial catalyst that embodies dual Brønsted and Lewis acid characteristics. Moreover, the catalyst recovery and ease of workup procedures adhere to the more efficient protocol. Further research into its thermal, long-term stability, and recyclability could strengthen its viability in industrial practices for large-scale applications. Further incorporation of the SPB catalyst into industrial processes can offer remarkable environmental and economic benefits.

Abbreviations

PBA	Polyboric acid
PET	Polyethylene terephthalate
BHETA	Bis(2-hydroxyethyl)terephthalamide
HMA	Hot melt adhesive
Boc ₂ O	Di- <i>tert</i> -butyldicarbonate
OPDA	<i>o</i> -Phenyl diamine
DMSO	Dimethyl sulfoxide
H ₂ O ₂	Hydrogen peroxide

H ₂ O	Water
EtOH	Ethanol
DMF	Dimethyl formamide
DMA	Dimethyl acetamide
H ₂ SO ₄	Sulfuric acid
HNO ₃	Nitric acid
TMSCN	Trimethylsilyl cyanide

Data availability

No primary research results, software or code have been included and no new data were generated or analysed as part of this review.

Conflicts of interest

The authors confirmed that this article has no conflict of interest.

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