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Synthesis and characterization of bis-thiazolidinone derivatives by using novel dibutyl benzimidazolium tetrafluoroborate based task specific ionic liquid

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Abstract
This present work exhibits synthesis of Dibutyl Benzimidazolium tetrafluoroborate [DBBim]BF_4^- Based Task Specific Ionic Liquid (TSIL). [DBBim]BF_4^- used as a catalyst for quickly synthesis of Bis-thiazolidinone derivatives via reaction of Aromatic aldehydes, para-phenylene diamine, and Thioglycolic acid. Dibutyl Benzimidazolium tetraflouroborate task specific ionic liquid has demonstrated noticeably higher activity compared to those containing other anion and other catalyst in the literature in less time. This TSIL serves as a catalyst and solvent during the synthesis of Bis-thiazolidinone derivatives, providing a moderate to good yield. Bis-Thiazolidinone derivative synthesis takes 20 minutes when TSIL utilized for the reaction. The ionic liquid was easily extracted from the reaction medium and reused for the subsequent run without any loss of its catalytic activity. The Characterization of these synthesized compounds was done by spectral analysis Like IR, ^{1}H-NMR, ^{13}C-NMR. Mass Spectra.

Keywords: Aromatic Aldehydes, *p*-Phenylene diamine, Ionic Liquids. Thioglycolic acid, Bis-Thiazolidinones

1. Introduction
Eco-friendly synthetic route is a key challenge in the present for achieving the advancement of heterocyclic Chemistry compounds are form one of the most important classes of organic molecules because due to their wide occurrence in natural products and their extensive applications in pharmaceuticals, agrochemicals, and functional materials. Among the various heterocyclic systems, sulphur- and nitrogen-containing five-membered rings have attracted considerable attention because of their diverse chemical reactivity and broad spectrum of biological activities. In this context, thiazolidin-4-ones (Commonly referred to as thiazolidinone) occupy a prominent position in medicinal and synthetic chemistry. The thiazolidinone scaffold is often regarded as a privileged structure because as minor structural modifications around the core ring can lead to significant variations in biological activity [1-5].

Thiazolidinones are characterized by a five-membered heterocyclic ring containing one sulphur atom, one nitrogen atom, and a carbonyl group at the 4-position. This unique structural arrangement provides a favourable electronic distribution and conformational flexibility, enabling effective interactions with a wide range of biological targets. Consequently, thiazolidinone derivatives have been reported to exhibit numerous pharmacological properties such as antibacterial, antifungal, antitubercular, antiviral, anti-inflammatory, analgesic, anticonvulsant, antidiabetic, anticancer, antiproliferative, and antioxidant activities [6-13]. In addition, several thiazolidinone-based molecules have demonstrated enzyme inhibitory activity, including cyclooxygenase inhibition, calcium channel blocking, and modulation of specific receptors, highlighting their importance in drug discovery programs [14-16]. Owing to their biological significance, substantial efforts have been devoted to the development of efficient synthetic routes for thiazolidinone derivatives. Conventionally, thiazolidinone are synthesized via cyclocondensation reactions involving an amines and aldehydes or ketones and mercapto acetic acids, i.e. Thioglycolic acid. These reactions are often carried out as three-component or multicomponent reactions (MCRs), which are attractive because they allow the construction of complex heterocycles in a single

step with good atom economy [17-19]. Alternative synthetic strategies include reactions of isothiocyanates with amines, followed by cyclization, microwave-assisted synthesis, solvent-free protocols, and catalyst-mediated approaches [20-22]. However, many of these traditional methods suffer from limitations such as long reaction times, harsh conditions, and the use of toxic or volatile organic solvents, moderate yields, and difficulties in catalyst recovery.

In recent years, the growing emphasis on sustainable and environmentally benign chemical processes has led to the adoption of green chemistry principles in organic synthesis. One of the key objectives of green chemistry is to be replacement of hazardous solvents and reagents with safer alternatives while improving reaction efficiency and minimizing waste generation [23]. In this regard, non-traditional reaction media such as water, supercritical fluids, solvent-free systems, and ionic liquids have emerged as promising tools for green synthesis [24-26]. Among these, ionic liquids (ILs) have gained particular attention as versatile and tunable reaction media. Ionic liquids are salts composed entirely of ions that remain in liquid form at or near room temperature. They possess unique physicochemical properties such as negligible vapor pressure, high thermal stability, non-flammability, and excellent solvating ability for a wide range of organic and inorganic compounds [27-29]. An important advantage of ionic liquids is lies in their structural tunability; by appropriate selection of cations and anions, their polarity, acidity, hydrophobicity, and coordinating ability can be tailored for specific applications [30, 31]. As a result, ionic liquids have been successfully employed as green solvents and catalysts in numerous organic transformations, including condensation reactions, cyclizations, multicomponent reactions, and heterocycle synthesis [32-34]. In addition to beyond their role as alternative solvents, ionic liquids have evolved into functional materials capable of actively participating in chemical reactions. This has led to the development of task-specific ionic liquids (TSILs), which are designed by incorporating functional groups into another ionic framework to impart catalytic activity or selectivity [35-36]. Task-specific ionic liquids can act simultaneously as solvents and catalysts, thereby simplifying the reaction protocols and reducing the need for additional reagents. Bronsted acids and Lewis acidic TSILs, in particular have proven to be highly effective in promoting a variety of organic transformations, including esterification, acetalization, and multicomponent heterocycle synthesis [37-39].

The combination of ionic liquids and multicomponent reactions is especially attractive from a green chemistry perspective. Multicomponent reactions inherently align with sustainable chemistry principles by enabling the formation of complex molecules from simple starting materials in a single operational step, with high atom economy and reduced waste [40-41]. Several studies have demonstrated that ionic liquids and TSILs can significantly enhance the efficiency of multicomponent reactions by accelerating the reaction rates, improving product yields, and allowing easy recovery and reuse of the catalytic system.[42, 43] In the context of thiazolidinone synthesis, Ionic liquids mediated methodologies have emerged as efficient and environmentally friendly alternatives to conventional solvent-based approaches. Early reports have described the use of Imidazolium-based ionic liquids such as 1-butyl-3-methylimidazolium salts as reaction media for the one-pot synthesis of thiazolidinone derivatives, resulting in reduced reaction times and improved yields [44-46]. The unique solvation properties of ionic liquids, along with their ability to stabilize reaction intermediates, play a crucial role in facilitating the cyclization process [47].

More recently, research efforts have focused on the design and application of task-specific ionic liquids tailored for thiazolidinone synthesis. Among these, Bronsted acidic TSILs have shown remarkable catalytic efficiency because due to their ability to activate carbonyl compounds and promote nucleophilic addition through hydrogen bonding and protonation effects. [48-51] Urazolium-based ionic liquids, in particular, have attracted attention as novel dicationic Bronsted acidic catalysts that are easy to prepare, thermally stable, and reusable. Such systems have been successfully employed in the multicomponent synthesis of thiazolidinone derivatives under mild or solvent-free conditions, offering significant advantages in terms of sustainability and operational simplicity [52-53]. In addition to synthetic efficiency, the biological evaluation of thiazolidinone derivatives synthesized using ionic liquid-based protocols has been widely reported. Many of these compounds exhibit promising antibacterial and antifungal activities against both Gram-positive and Gram-negative microorganisms as well as notable anticancer and anti-inflammatory properties [54-57]. The use of green and recyclable catalytic systems does not compromise the biological potential of the synthesized molecules; rather, it provides an environmentally responsible route to biologically active heterocycles suitable for further pharmaceutical development. Although ionic liquids are often regarded as green solvents, concerns related to their toxicity and environmental persistence have been raised for certain classes of ionic liquids. Consequently, the rational design of task-specific ionic liquids with improved biodegradability and lower toxicity has become an important research focus. [58-61] In this context, the development and application of functionalized ionic liquids that combine catalytic efficiency with reduced environmental impacts are of considerable significance. Considering the medicinal importance of thiazolidinone derivatives and the growing demand for sustainable synthetic methodologies, the synthesis of thiazolidinone using task-specific ionic liquids represents a timely and relevant research area. Such approaches integrate the advantages of multicomponent reactions, green solvents, and recyclable catalysts, to provide efficient access to pharmaceutically relevant heterocycles. Furthermore, systematic characterization and biological evaluation of these compounds can provide valuable insights into structure-activity relationships and support their potential application in drug discovery.

The present study is therefore directed toward the synthesis and characterization of bis- thiazolidinone derivatives using task-specific ionic liquids, with particular emphasis on reaction efficiency, catalyst reusability. This study frame works aim to demonstrate that task-specific ionic liquids serve as powerful and sustainable tools for the green synthesis of biologically active thiazolidinone, thereby contributing to the advancement of environmentally benign practices in medicinal and synthetic organic chemistry.

2. Experimental

2.1. Materials

All the chemicals and solvents are available commercially, 1-bromobutane, were obtained from sigma Aldrich (India), Sodium hydride (60%) Tetrahydrofuran, (Specially dried) toluene (Specially dried), sodium tetrafluoro borate, diethyl ether, chloroform, Aldehydes, Para phenylene diamine and Thioglycolic acid all chemical were purchase from S.D fine Chemicals and Co. Ltd. All the chemical were used as received unless it is specified all the glassware are special washed and dried under suitable temperature in Oven at 100 ºC to 150 ºC. TLC of the synthesized compound was taken on TLC Silica gel 60 F254 aluminum coated sheet.

FT-IR Spectra of the synthesized compounds were obtained by using Fourier Transform Infrared Spectrophotometer (Shimadzu, IR Affinity-1 Japan) in the wave range 400-4000 cm^{-1} in the transmittance mode using KBr pellets. NMR Spectra of synthesized ionic liquids and products were recorded in DMSO-d_6 on a Brucker Spectrometer operating at 400 MHz and chemical shifts are given in ppm downfield from TMS (∂=0.00). Mass spectra of all catalyst were recorded on a Water USA, XEVO-G2-XS-QTOF.

2.2. Characterization

The Ionic liquid catalyst and All synthesized Bis-thiazolidinone derivatives were characterized using analytical techniques as IR, ^{1}H NMR and ^{13}C NMR spectroscopy. Also the melting points were measured for all synthesized derivatives.

2.3. Method

2.3. Preparation of Ionic Liquid

2.3.1. Synthesis of 1- butyl -1 H-benzo[d]imidazole (2)

The synthesis of N-butyl Benzimidazole was carried out according to our previous work [62]. 4.0 g (100 mmol) Sodium hydride was taken in 250 mL clean and dry two neck Round bottom flask. In this 50 mL n-hexane was added and stirred for 30 minutes then decanted the n-hexane in order to remove mineral oil present in 40% Sodium hydride. Further 50 mL Tetrahydrofuran (THF) was added in washed sodium hydride and then added the Benzimidazole 11.8 g (100 mmol) (Benzimidazole in THF) drop wise under stirring condition at room temperature for 1 hour. Finally, 1-Butyl bromide 13.7g (100 mmol) was added at 60ºC and stirred it for next 48 hours (Scheme-1). The reaction mixture was filtered to remove sodium bromide precipitate and filtrate was kept under Rotary evaporator for removing the THF solvent. Crude butyl Benzimidazole liquid was dissolved in Chloroform and washed it with distilled water (3 x 25 mL) in separating funnel. Finally, dried the chloroform layer on anhydrous sodium sulphate and removed chloroform under rotary evaporator and then high vacuum. The light brown liquid was obtained. Yield: 95%.

2.3.2. Synthesis of 1, 3-dibutyl-1H-benzo[d]imidazole-3-ium Bromide [DBBim]Br^- (3a)

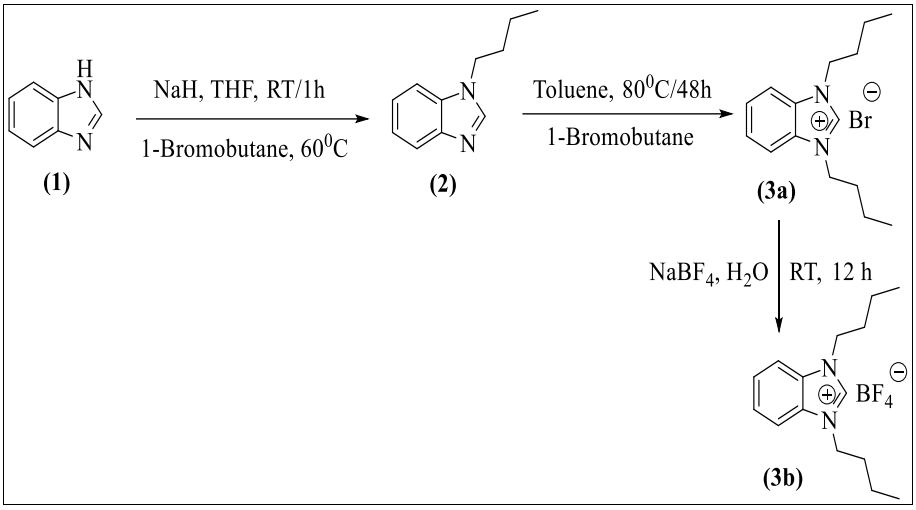
The synthesis of [DBBim]Br^- was carried out according to Muskawar P.N *et al*. [61] Butyl Benzimidazole (11.63g, 66 mmol) and 1- butyl bromide (9 ml, 66mmol) was taken in 100 mL Round bottom flask and 50 mL Toluene was added (Scheme-1). The reaction mixture was stirred at 80ºC temperature for next 48 hours. After completion of reaction solvent toluene was decanted and sticky solid was washed with ethyl acetate (3 x 15 mL) and finally with diethyl ether (2 x 10 mL) and then dried it under high vacuum, the white solid powdered was obtained.

Yield: 94%, White Solid, ^{1}H NMR (400 MHz, DMSO-d_6/TMS): δ = 9.94 (s, 1H), 8.11-8.13 (q, J = 3.12 Hz, 2H), 7.68-7-71 (q, J = 3.07 Hz, 2H), 4.49-4.53 (t, J = 7.21 Hz, 3H), 1.86-1.94 (q, J = 7.31 Hz, 4H), 1.30-1.39 (m, J = 7.54 Hz. 4H), 0.91-0.94 (t, J = 7.33 Hz, 6H). ^{13}C-NMR (100 MHz, DMSO-d_6) δ = 142.56, 131.60, 127.00, 126.15, 114.22, 113.56, 46.90, 31.19, 31.00, 19.56, 13.87. FT-IR (KBr, v/cm^{-1}): 3468, 3416, 3113, 3032, 2949, 2176, 1567, 1459, 1213, 1130, 1031, 553. HR-MS (TOP MS US+): [$C_{15}H_{23}N_2Br$] calculated mass [M-Br] (231.19) found (231.1944).

2.3.3. Synthesis of 1,3-dibutyl-1H-benzo[d]imidazole-3-ium) tetrafluoro borate [DBBim]BF_4^- (3b)

The synthesis Dibutyl Benzimidazolium Tetrafluoroborate [DBBim]BF_4^- was carried out according to Muskawar P.N *et al*. [61] (Scheme-1). 1,3-dibutyl-1H-benzo[d]imidazole-3-ium Bromide was dissolve in minimum quantity of Deionized water and Equimolar amount of sodium tetrafluoroborate (Dissolve in deionized water) added drop wise at room temperature and stirred at room temperature for next 12 hours. After the completion of the reaction Dibutyl Benzimidazolium Tetrafluoroborate Ionic Liquid was precipitated out. Precipitate [DBBim]BF_4^- IL was filtered and washed the using diethyl ether (3 x 10 mL) times and finally dried under high vacuum, the white Solid was obtained.

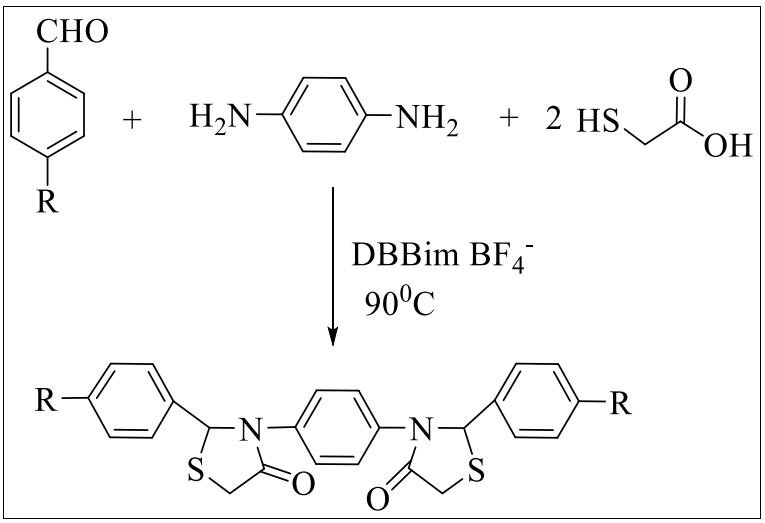
Yield: 92%, White Solid, ^{1}H NMR (400MHz. DMSO-d_6/TMS): δ = 9.835 (s, 1H), 8.09 - 8.13 (m, J = 3.11 Hz, 2H), 7.68-7.72 (m, J = 3.11 Hz, 2H), 4.48-4.52 (t, J = 7.20 Hz, 4H), 1.68-1.94 (qt, J = 7.39 Hz, 4H), 1.32-1.39 (qt, J = 7.61 Hz, 4H), 0.91-0.95 (t, J = 7.40 Hz, 6H). ^{13}C NMR (100MHz. DMSO-d_6/TMS) δ = 142.54, 131.60, 127.00, 114.18, 46.90, 31.00, 19.55, 19.38, 13.83. FT-IR (KBr, v/cm^{-1}): 3466, 3036, 2951, 2266, 1570, 1460, 1215, 1086. HR-MS (TOP MS US+): [$C_{15}H_{23}BF_4N_2$] calculated mass [M-BF_4] (231.19) found (231.1932).



Scheme 1: Synthesis of 1,3-dibutyl-1H-benzo[d]imidazole-3-ium) tetrafluoro borate

2.4. General Procedure for Synthesis of Thiazolidinone Derivatives

In a clean and dry two naked 50 mL RB flask *p*-Phenylene diamine (1 mmol) with substituted aldehyde (2 mmol) and Thioglycolic acid of (2 mmol) in 1:2:2 ratio was taken and then added [DBBim]BF_4^- (3b) (2 g) of ionic liquid. Further, the reaction mixture in RB flask was bubbled with nitrogen gas and attached with the nitrogen balloon to maintained moisture free reaction and stirred the reaction mixture at 90ºC for require time. Progress of the reaction was monitored by checking Thin Layer Chromatography. After completion, reaction mixture was cooled down to room temperature then the crude product was extracted in ethyl acetate (15 mL) and separated catalyst i.e. [DBBim]BF_4^- was washed with ethyl acetate (3 x 5 mL), decanted and dried in oven at 60ºC. Finally, Thiazolidinone derivative was isolated by removing ethyl acetate using rotary evaporator and solid product was purified by recrystallization in Methanol or some compounds were purified by column chromatography. The melting points and spectroscopic data of these thiazolidinone derivatives are in good concurrence with the literature.



3. Result and Discussion

3.1 Catalytic studies

In the present work, we report new based ionic liquid catalyst and solvent. Their operation is safe, simple and fast synthesis of thiazolidinone derivatives by using *p*-Phenylenediamine, substituted aromatic aldehyde and thioglycolic acid in 1:2:2 equimolar amount. We have examined catalytic activity of [DBBim]BF_4^- catalyst/solvent towards Thiazolidinone synthesis under solvent free condition with different aromatic aldehyde. In order to optimize reaction condition, the model reaction of *p*-nitro Benzaldehyde, *p*-phenylene diamine and Thioglycolic acid was carried out with [DBBim]BF_4^- ionic liquid. The catalytic activities were evaluated under different condition by varying the parameters such as amount of catalyst, reaction temperature and time (Table 1).

Table 1: Optimization of synthesis of Bis-Thiazolidinone Derivatives synthesis.

Entry	Catalyst	Amount of Ionic Liquid (g)	T (°C)	Time	Yield (%)[b]
1	[DBBim]BF_4^-	0	80	6 h	NR[b]
2	[DBBim]BF_4^-	0	80	24 h	NR[b]
3	[DBBim]BF_4^-	10 mole%	80	24 h	37
4	[DBBim]BF_4^-	0.5	80	24 h	65
5	[DBBim]BF_4^-	1.0	80	24 h	69
6	[DBBim]BF_4^-	1.5	80	4 h	81
7	[DBBim]BF_4^-	2.0	80	25 min	90
8	[DBBim]BF_4^-	2.0	80	3 h	67
9	[DBBim]BF_4^-	2.0	RT	24 h	Trace
10	[DBBim]BF_4^-	2.0	40	24 h	13
11	[DBBim]BF_4^-	2.0	50	24 h	27
12	[DBBim]BF_4^-	2.0	60	24 h	56
13	[DBBim]BF_4^-	2.0	70	24 h	63
14	[DBBim]BF_4^-	2.0	80	10 h	84
15	[DBBim]BF_4^-	2.0	90	20 min	96
16	[DBBim]BF_4^-	2.0	90	12 h	98
17	[DBBim]BF_4^-	2.0	90	8 h	97
18	[DBBim]BF_4^-	2.0	90	4 h	97
19	[DBBim]BF_4^-	2.0	90	1 h	96

Reaction conditions: *p*-nitro benzaldehyde (2.0 mmol), *para*-phenylene diamine (1.0 mmol), and thioglycolic acid (2.0 mmol). [b] Isolated yields.

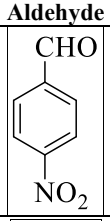
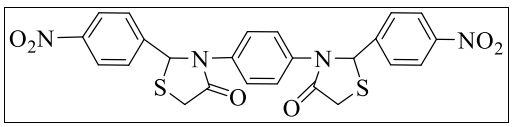
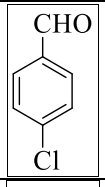
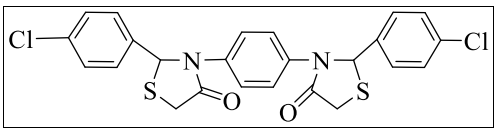
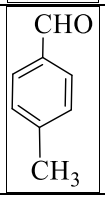
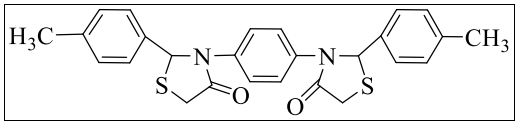
After optimizing the amount] of [DBBim]BF_4^- ionic liquid, we investigated the effect of temperature on the model reaction involving p-Nitrobenzaldehyde, *p*-Phenylene diamine, and Thioglycolic acid. Initially, the reaction was conducted at ambient temperature, resulting in only trace amounts of the product even after 24 hours (Table 1, entry 9). This low yield may be attributed to the poor solubility of the starting materials in the ionic liquid. To improve substrate solubilization, we increased the reaction temperature from 40 ºC to 70 ºC (Table 1, Entries 10-13), observing a gradual increase in the yield of thiazolidinone from 13 to 63% over 24 hours. Stirring the reaction mixture at 80 ºC yielded a moderate result of 84% in 10 hours (Table 1, entry 14). The maximum yield of 95% was achieved at 90 ºC within 20 minutes (Table 1, entry 15), establishing this temperature as optimal for catalytic studies.

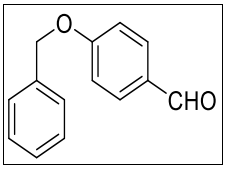
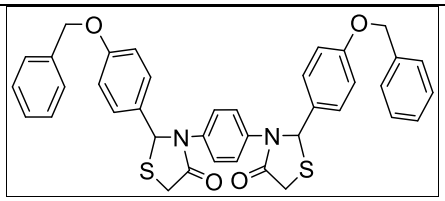
Since maximum activity for the model reaction of thiazolidinone synthesis was achieved using 2 g of ionic liquid at 90 ºC, our final protocol aimed to optimize the reaction time. We successfully reduced the reaction time from 12 hours to 20 minutes. However, no appreciable changes in the yield of the product were observed with increased reaction time (Table 1, entries 15-19).

To broaden the scope of our developed protocol, we have carried out the reactions using *p*-phenylenediamine, thioglycolic acid, and various aromatic aldehydes containing electron-withdrawing and electron-donating groups in equimolar ratios (1:2:2) with [DBBim]BF_4^- ionic liquid (Table 2). It was observed that electron-withdrawing groups on the aromatic aldehyde (Table 2, entries 1 and 2) promoted higher yields compared to electron-donating groups.

Further, to assess the effectiveness of [DBBim]BF_4^- ionic liquid, we used 4-methylbenzaldehyde and 4-(benzyloxy) benzaldehyde for thiazolidinone synthesis. The yield of the desired product was comparatively lower due to the donating nature of the methyl group and the carbonyl group of 4-(benzyloxy) benzaldehyde.

Table 2. Synthesis of Bis -Thiazolidinone Derivatives from various aromatic aldehyde.

Entry	Aldehyde	Product	Time (min)	Yield[b] (%)
1		 (4a)	20	98
2		 (4b)	25	97
3		 (4c)	24	94

4		 (4d)	30	94

[a]Reaction conditions: Benzaldehydes (2.0 mmol), *p*-phenylene diamine (1.0 mmol), and Thioglycolic acid (2.0 mmol), $[DBBim]BF_4^-$, 90 ^{0}C.

The proposed reaction pathway mechanism for the preparation of Bis -thiazolidinone in the presence of a novel $[DBBim]BF_4^-$ ionic liquid is shown in Scheme 2. In this, we introduce a novel and simple Benzimidazolium-based ionic liquid having a tetrafluoroborate anion. This simple ionic liquid has a reacting site, i.e., Benzimidazolium N-CH-N hydrogen, which forms a non-covalent interaction (hydrogen bonding) with carbonyl group oxygen, which makes carbonyl carbon electron deficient, and hence hydrogen bonding makes the carbonyl group of aldehyde more susceptible to *p*-phenylene diamine nucleophilic addition. According to the researchers P. Pinate *et al.* [62] at the initial step of the catalytic pathway, $[DBBim]BF_4^-$ facilitated the condensation of *p*-Phenylene diamine with substituted aldehyde for the generation of Schiff base. Then, imine reacts with Thioglycolic acid to generate the carbon-sulphur bond, followed by intermolecular cyclization, which gives the targeted product after the release of water molecules.

3.2 Recyclability

The recyclability of the solvent/catalyst $[DBBim]BF_4^-$ was investigated in the model reactions of p-nitrobenzaldehyde, p-Phenylene diamine, and thioglycolic acid. After every run, thiazolidinone was diluted with ethyl acetate, and the $[DBBim]BF_4^-$ was obtained by solvent decantation. Any leftover traces of the non-ionic compounds were removed by washing with ethyl acetate and diethyl ether. After being vacuum-dried for three hours at 60 °C, the $[DBBim]BF_4^-$ was used for the next run of the model reaction. Our catalyst is recyclable, as shown by Fig. 1, where $[DBBim]BF_4$ has shown good catalytic activity across seven runs without a noticeable drop in yield.

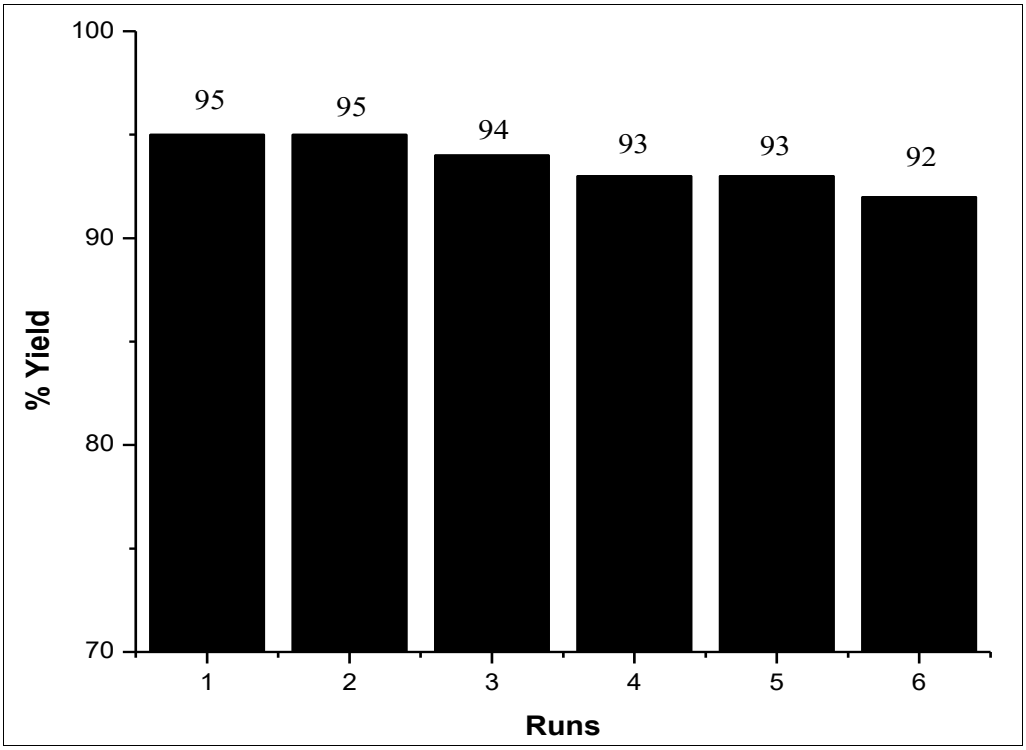


Fig 1: Recyclability of $[DBBim]BF_4$ in Bis Thiazolidinone synthesis

3, 3-(1, 4-phenylene) bis (2-(4-nitrophenyl) thiazolidin-4-one. (4a)

Yield: 99%, Yellow solid; m.p 145ºC; ^{1}H-NMR (400MHz. DMSO-d_6/ TMS): δ = 8.146-8.075 (d, J = 1.44 Hz, 4H), 7.693 -7.612 (d, 4H), 7.324, 6.648 (d, 2H), 4.062-3.357 (dd, 4H) 3 2.50 (d,1H). ^{13}C-NMR (100MHz. DMSO-d_6/TMS) δ = 170.96,170. 90, 148.12.148.08, 147.71, 135.67, 28.49, 128.46, 125.83, 125.73, 124.38, 62.43, 62.30, 40.60, 40.39, 40.18, 39.97, 39.76, 39.55, 39.35, 32.91. FT-IR (KBr, v/cm^{-1}): 3921, 3344, 3083, 2933, 2623, 2529, 2358, 2312, 2202, 2277, 1919, 1683, 1615, 1520, 1351, 1312, 1263, 1118, 1029, 841, 719, 505.

3,3-(1,4-phenylene)bis(2-(4-Chlorophenyl)thiazolidin-4-one. (4b)

Yield: 97%, Yellow solid; m.p 160 ºC; ^{1}H-NMR (400MHz. DMSO-d_6/ TMS): δ = 7.104 -7.259 (d, 4H), 5.977 - 5.989 (d, 2H), 3.780-3.925 (dd, 2H) ^{13}C-NMR (100MHz. DMSO-d_6/TMS) δ = 170.83, 170.79, 137.85, 137.75, 135.71, 134.85, 129.26, 128.06, 125.40, 77.29, 77.03. 76.78, 64.60,

33.27, 33.22. FT-IR (KBr, v/cm^{-1}): 3885, 3308, 3066, 2926, 2614, 2357, 2298, 2312, 2163, 1899, 1682, 1516, 1350, 1249, 1179, 1109, 1020, 949, 897, 833, 841, 764, 570,

3,3-(1,4-phenylene)bis(2-(p-tolyl) thiazolidin-4-one. (4c)
Yield: 97%, Yellow solid; m.p 153ºC; ^{1}H-NMR (400MHz. DMSO-d_6/ TMS): δ = 7.258 (d, 2H), 7.053 -7.126 (d, 4H), 5.955 - 5.979 (d, 1H), 3.748 - 3.939 (dd, 2H) 2.293 - 2.300 (d, 3H). ^{13}C-NMR (100MHz. DMSO-d_6/TMS) δ = 171.60, 139.46, 135.83, 129.82, 127.18, 77.25, 77.24, 77.03, 76.78, 63.68, 32.67, 21.24. FT-IR (KBr, v/cm^{-1}): 3873, 3807, 3343, 3195, 3067, 2927, 2624, 2552, 2307, 2143, 2059, 1893, 1686, 1603, 1515, 1410, 1254, 1166, 1047, 905, 818, 710, 655, 481.

3,3'-(1,4-phenylene)bis(2-(4-(benzyloxy)phenyl)thiazolidin-4-one) (4d)
Yield: 94%, Yellow solid; m.p 120ºC; ^{1}H-NMR (400MHz. DMSO-d_6/ TMS): δ = 7.400 (d, 2H), 7.313 -7.366 (d, 4H) 6.836 - 7.256 (m, 4H),6.780 - 6.796 (q, 1H), 5.927 - 5.929 (q, 1H), 4.997-5.002 (d, 2H), 3.734 - 3.922 d, 2H) ^{13}C-NMR (100MHz. DMSO-d_6/TMS) δ = 171.07, 159.28, 141.35, 136.56, 135.83, 130.82,128.66, 128.11, 127.51, 127.49, 125,17, 125,07,118.80, 115.20, 112.76, 112.71, 77.25, 77.02, 70.03, 76.78,70.09, 65.15, 33.13. FT-IR (KBr, v/cm^{-1}): 3433, 3027, 2927, 1686, 1512, 1373, 1334, 1298, 1277, 1246, 1216, 1179, 1128, 1019, 899, 826, 780, 747, 569, 512.

4. Conclusion
In contrast to previous research, the [DBBim]BF_4^- ionic liquid was created simply and affordably. It both solubilizes the substrate molecule and facilitates the reaction. Using a novel and straightforward [DBBim]BF_4^- ionic liquid, an effective and simple approach for the synthesis of thiazolidinone derivatives from a variety of aromatic aldehydes, *p*-phenylene diamine, and Thioglycolic acid has been devised in this work. Numerous special advantages come with this protocol, including high conversion rates, ease of use, cost effectiveness, and solvent-free operation. Solvents and hazardous chemicals are not used in this process. Consequently, it makes a major contribution to the field of green chemistry.

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