

Preparation of pyridinium-based ionic liquid and application as a green catalyst for the synthetic route of 4*H*-1-benzopyran-5(6*H*)-ones

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Abstract:

1-(4-sulfobutyl)pyridinium chlorozincate ionic liquid was synthesised in high yield (89%) through a simple route and characterised using FT-IR, NMR, and HRMS spectroscopy. The one-pot reaction was employed for the condensation reaction of benzaldehydes, 5,5-dimethyl-1,3-cyclohexanedione, and dicyanomethane, utilising the prepared ionic liquid catalyst. The optimal conditions for the reaction were achieved with a catalyst loading of 10 mol%, a solvent mixture of water and ethanol (1:1, v/v), maintained at 100°C for 180 minutes. A broad spectrum of benzopyran-5(6*H*)-one derivatives was prepared, yielding moderate to good results. The notable features of this procedure include readily available substrates, short reaction times, the use of environmentally friendly solvents, and the elimination of the need for chromatography in the isolation of products. A new acidic pyridinium-based ionic liquid was successfully synthesised and used as a catalyst in the synthetic process of 2-amino-3-cyano-4-phenyl-7,7-dimethyl-7,8-dihydro-4*H*-1-benzopyran-5(6*H*)-ones. These reactions involved a condensation reaction of aromatic benzaldehydes, 5,5-dimethyl-1,3-cyclohexanedione, and dicyanomethane in a solvent mixture of ethanol and water, resulting in the desired products in moderate to good yields. The procedure is efficient and eco-friendly, and the products can be easily obtained by recrystallisation. Thus, this protocol offers an alternative to existing methods.

Keywords: Brønsted-Lewis acidic ionic liquid, green catalyst, multicomponent reaction, 1-(4-sulfobutyl)pyridinium chlorozincate, 4*H*-1-benzopyran-5(6*H*)-one.

Classification numbers: 2.2, 2.3

1. Introduction

After being discovered and initially published by Paul Walden in 1914, numerous reports have explored the properties and applications of ionic liquids in various fields. Nowadays, ionic liquids are recognised as environmentally friendly solvents and catalysts in organic synthesis [1]. In comparison to traditional volatile organic solvents, ionic liquids offer increased safety during synthetic procedures due to their low vapour pressure and recyclability [2]. The solubility of ionic liquids can be tailored by designing specific ions. In many instances, ionic liquids have proven to be efficient catalysts in various reactions [3, 4]. A notable feature of ionic liquids is their ease of preparation, with the availability of various active sites, such as basic properties (-OH, -NH₂...), Brønsted or Lewis acidic properties

(-SO₃H, -COOH, or Al_xCl_y, Zn_xCl_y...). Particularly, a novel type of acidic ionic liquid containing both Lewis and Brønsted acidic groups in its structure has garnered significant attention. These task-specific ionic liquids are considered environmentally friendly and hold potential in many catalytic processes that require the presence of both Brønsted and Lewis acidic sites [5].

Currently, the one-pot multicomponent reaction carried out under green conditions has become a popular and sustainable trend in organic synthesis. One-pot three-component reactions, referred to as convergent chemical approaches, are rapid and efficient methods in organic synthesis due to their high levels of atom efficiency [6, 7]. The advantages of multicomponent reactions include cost-effectiveness, high selectivity, good yields, and time savings [8, 9]. Moreover, multicomponent

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reactions have garnered attention from chemists for their ability to minimize steps and reduce waste in experiments. The three-component transformation is the preferred choice and is applied across a wide range of organic reactions, such as the synthesis of polyhydroquinoline [10], dihydropyrimidinones [11], 1-(α -aminoalkyl)-2-naphthols [12], and 1,3-thiazole derivatives [13], as well as pyranopyrazole and pyranopyrimidine derivatives [14]. Additionally, pseudo-six-components have been employed in the synthesis of tetrahydrodipyrzopolpyridines [15].

Pyran is a six-membered heterocyclic compound containing oxygen, and it serves as a valuable building block in many organic compounds. Chromene, also known as benzopyran, is a crucial subgroup in these heterocyclic derivatives and is categorised into chroman, 2*H*-chromene, and 4*H*-chromene, which are commonly observed frameworks in numerous complex natural products [16]. Benzopyrans are described as fundamental structural units found in polyphenols and are explored in alkaloids, tocopherols, flavonoids, and anthocyanins [17]. Due to their significant biological and pharmacological activities, including antibacterial, antitumor, antiallergic, antibiotic, anticancer, antitubercular, antimicrobial, anti-coagulant, antibiotic, and hypolipidemic properties [18-23], benzopyrans have found extensive use in the pharmaceutical industry. Given the attractive bioactivity of benzopyrans, various synthetic protocols for pyrans have been published [24]. The most widely adopted method for preparing benzopyrans involves a three-component reaction of 5,5-dimethyl-1,3-cyclohexanedione, an aldehyde, and dicyanomethane, which undergoes Knoevenagel condensation and Michael addition reactions [24]. A wide range of homogeneous catalysts have been investigated for this reaction, including boric acid [25], ammonium acetate [26], potassium phosphate [27], MgO [28], K_2CO_3 [29], $CeCl_3 \cdot H_2O$ [30], $Mg(ClO_4)_2$ [31], DBU [32], triethylamine [33], iodine [34], and methane sulfonic acid [35]. However, a drawback of these methods is the difficulty of separating the catalysts from the reaction mixture. To address these issues, heterogeneous or solid catalysts, such as amino-functionalized silica gel [36], SiO_2 -Pr-SO₃H [37], NMPs-PhSO₃H [38], CeO_2 [39], CuO-CeO₂ nanocomposite [40], CeO_2 -Al₂O₃ nanocomposite [41], $Ni_{0.5}Zn_{0.5}Fe_2O_4@HA$ -PRS [42], and $CeMg_xZr_{1-x}O_2$ [43], have been prepared and applied in this reaction. Nevertheless, other limitations include the use of volatile organic solvents and the high cost of these catalysts.

Recently, ionic liquids have emerged as potential catalysts for this transformation due to their high efficiency and recyclability. 1-Butyl-3-methylimidazolium hydroxide was employed as an efficient homogeneous catalyst in the synthesis of substituted 2-amino-2-chromenes by K. Gong, et al. (2008) [44]. This condensation reaction involving malononitrile, aldehydes, and naphthols was conducted in aqueous media. M.N. Elinson, et al. (2015) [24] reported a three-component reaction of benzaldehydes, 5,5-dimethyl-1,3-cyclohexanedione, and dicyanomethane using 1-butyl-4-methylimidazolium tetrafluoroborate as the catalyst. Subsequently, A.R.M. Zare, et al. (2014) [45] synthesised tetrahydrobenzo[*b*]-pyrans through Knoevenagel-Michael cyclocondensation, employing (1-carboxymethyl-3-methylimidazolium bromide ionic liquid as an efficient catalyst under solvent-free conditions. Another acidic ionic liquid catalyst utilised in the preparation of 2-amino-4*H*-chromene derivatives was $Li(OHCH_2CH_2NH_2)(CF_3OAC)$. E.A. Gilandeh, et al. (2014) [46] demonstrated that this ionic liquid efficiently catalysed the cyclisation of aldehydes, malononitrile, and various enol compounds. A green synthetic route for 2-amino-4*H*-chromene using a basic ionic liquid in water was reported by V.P. Pagore, et al. (2015) [47]. The condensation reactions occurred in the presence of 1-ethyl-3-methylimidazolium hydroxide under microwave irradiation, resulting in high yields [47]. 2-(2-Hydroxyethoxy)ethan ammonium formate ionic liquid was described as an ammonium-type basic catalyst for synthesising various derivatives of chromenes with excellent yields [48]. To enhance the recycling capability of the catalyst, *N*-propyl-imidazolium hydrogen sulfate was grafted onto the surface of silica by K. Niknam, et al. (2013) [49]. The synthesis of 3,4-dihydropyrano[*c*]-chromenes was effectively carried out under solvent-free conditions. Similarly, a newly supported ionic liquid (HAP-Pd-[BMIM][OH]) was found to be an efficient heterogeneous catalyst in the multicomponent cyclocondensation of 2-amino-4*H*-chromenes by P. Sharma, et al. (2016) [50]. In this study, a new environmentally friendly synthetic method for benzopyran compounds was developed through the condensation of three substrates, namely benzaldehydes, 5,5-dimethyl-1,3-cyclohexanedione, and dicyanomethane, in the presence of an ionic liquid containing Brønsted-Lewis acidic sites as a catalyst.

2. Materials and methods

2.1. Chemicals

All reactants were purchased from Merck. Organic solvents were purchased from Xilong. Deuterated solvents for NMR experiments, including CDCl_3 , CD_3OD , $(\text{CD}_3)_2\text{SO}$ and $(\text{CD}_3)_2\text{CO}$, were purchased from Cambridge Isotope Laboratories (Andover, MA).

2.2. Methods

The melting point was determined using a Buchi B-545 melting point apparatus. Fourier-transform infrared (FT-IR) spectra were recorded with a Bruker E400 FT-IR spectrometer. Nuclear magnetic resonance (^1H and ^{13}C NMR) experiments were conducted on a Bruker Advance 500 MHz NMR spectrometer. Mass spectrometry (MS) was performed in negative ionization mode using an Agilent 1200 series HPLC coupled to a Bruker micrOTOF-QII EIS mass spectrometer detector.

Synthesis of 1-(4-sulfobutyl)pyridinium chlorozincate (IL3): A mixture of pyridine (10.0 mmol, 790 mg) and 1,4-butane sultone (10.0 mmol, 1360 mg) was initially combined and heated to 40°C . After 6 h, the resulting white solid was washed with Et_2O and dried at 80°C for 30 min to yield an intermediate zwitterion. Next, the intermediate 4-(pyridinium-1-yl)butane-1-sulfonate (10.0 mmol, 2150 mg) was reacted with hydrochloric acid (10.0 mmol, 365 mg) at 80°C for 15 min to produce 1-(4-sulfobutyl)pyridinium chloride (IL0). Finally, 1-(4-sulfobutyl)pyridinium chloride (10.0 mmol, 2514 mg) and zinc chloride (10.0 mmol, 1363 mg) were added to a round-bottom flask containing 20 ml of toluene and refluxed for 10 h. The resulting acidic ionic liquid was decontaminated with Et_2O and dried under reduced pressure for 60 min. The 1-(4-sulfobutyl)pyridinium chlorozincate ionic liquid (IL3) was characterised by FT-IR, ^1H and ^{13}C NMR, and HRMS. Similarly, 1-(4-sulfobutyl)pyridinium chlorotinate (IL1) and 1-(4-sulfobutyl)pyridinium chlorocopperate (IL2) were also prepared by mixing 1-(4-sulfobutyl)pyridinium chloride with tin chloride and copper chloride, respectively.

Synthetic procedure of 2-amino-3-cyano-4-phenyl-7,7-dimethyl-7,8-dihydro-4H-1-benzopyran-5(6H)-one: 5,5-Dimethyl-1,3-cyclohexanedione (1.0 mmol, 140 mg), benzaldehyde (1.0 mmol, 106 mg) and dicyanomethane (1.0 mmol, 66 mg) were added into round-bottom flask containing a solvent mixture (4 ml) of ethanol and water (1:1, v/v). Next, the ionic liquid catalyst (10 mol%, 35.4

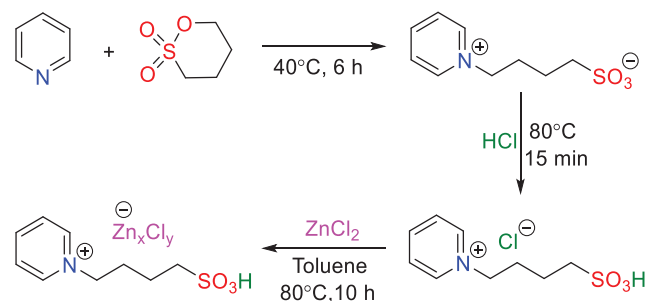
mg) was added dropwise to the mixture. The reaction was carried out by heating at 100°C for 180 min, and its progress was monitored using thin-layer chromatography. After the completion of the reaction, the crude product was collected by filtration and recrystallized in ethanol. The melting point was measured, and the R_f value was calculated based on thin-layer chromatography. The product was characterized using ^1H and ^{13}C NMR spectroscopy.

General procedure for catalyst recycle test: A mixture of 5,5-dimethyl-1,3-cyclohexanedione (1.0 mmol, 140 mg), benzaldehyde (1.0 mmol, 106 mg), and dicyanomethane (1.0 mmol, 66 mg) was blended in a solvent mixture of ethanol and water (1:1, v/v). The IL3 catalyst (10 mol%, 35.4 mg) was added to the reactor, and the reaction mixture was refluxed at 100°C for 180 min. After cooling to room temperature, 10 ml of water was introduced into the reactor. Following 5 min of stirring, vacuum filtration was used to remove the solvents. The solid was purified to obtain the product, while the liquid solution containing the ionic liquid was dried at 110°C for 6 h to remove water and organic solvent. Finally, the ionic liquid was washed with 10 ml of diethyl ether and dried at 110°C for 1 h. The purified ionic liquid was reused for the next cycles.

3. Results and discussion

3.1. Synthesis and characterization of acidic ionic liquid

1-(4-sulfobutyl)pyridinium chlorozincate (IL3) was prepared through a three-step procedure (Scheme 1). Initially, the nucleophilic substitution reaction between pyridine and 1,4-butane sultone was conducted at 40°C for 6 h. The resulting solid, 4-(pyridinium-1-yl)butane-1-sulfonate zwitterion, was then protonated using hydrochloric acid. In the final step, 1-(4-sulfobutyl)pyridinium chloride was reacted with zinc chloride salt to yield the desired ionic liquid, with a yield of 89%.



Scheme 1. Synthetic procedure of 1-(4-sulfobutyl)pyridinium chlorozincate.

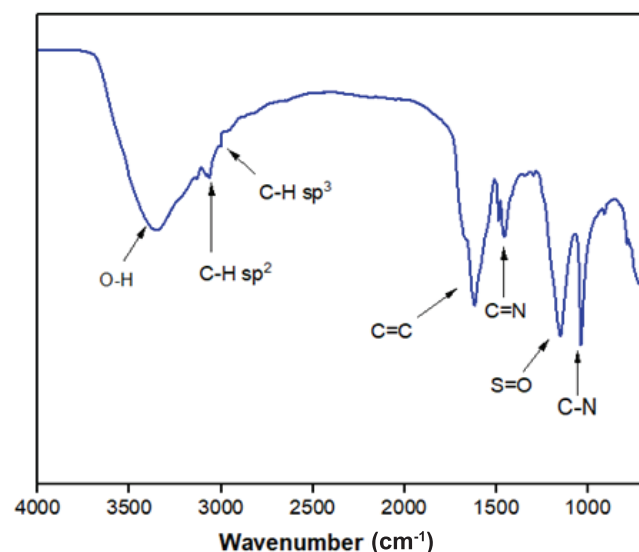


Fig. 1. FT-IR of 1-(4-sulfobutyl)pyridinium chlorozincate.

The structure of the acidic ionic liquid was analysed using Fourier-transform infrared spectroscopy (FT-IR), nuclear magnetic resonance spectroscopy (NMR), and high-resolution mass spectrometry (HRMS). In the FT-IR spectrum (Fig. 1), the ionic liquid exhibited a broad stretching absorption band for the O-H bond at 3340 cm^{-1} and a characteristic stretching absorption of the S=O bond in the SO_3H group at 1145 cm^{-1} . Pyridine displayed characteristic absorptions at 3056 and 1610 cm^{-1} corresponding to the H-C sp^2 and C=C bonds. Furthermore, the presence of methylene was confirmed by the peak at 2982 cm^{-1} , representing H-C sp^3 stretching absorption. Absorption bands at 1456 and 1037 cm^{-1} were attributed to the C=N and C-N bonds.

The ^1H NMR spectrum (Fig. 2) revealed characteristic absorptions of pyridine, including peaks at 9.04 (d, $J=5.0$

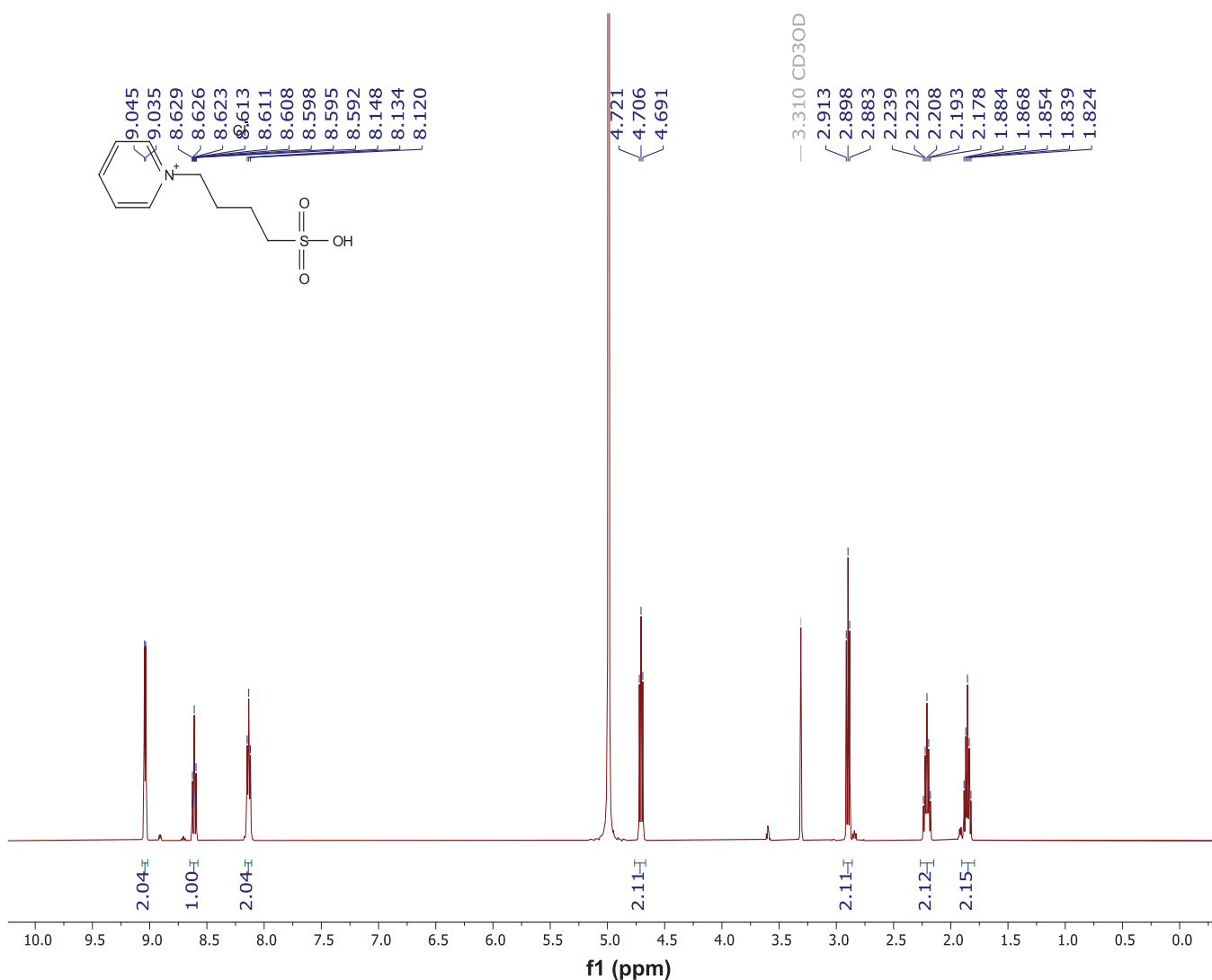


Fig. 2. ^1H NMR of 1-(4-sulfobutyl)pyridinium chlorozincate.

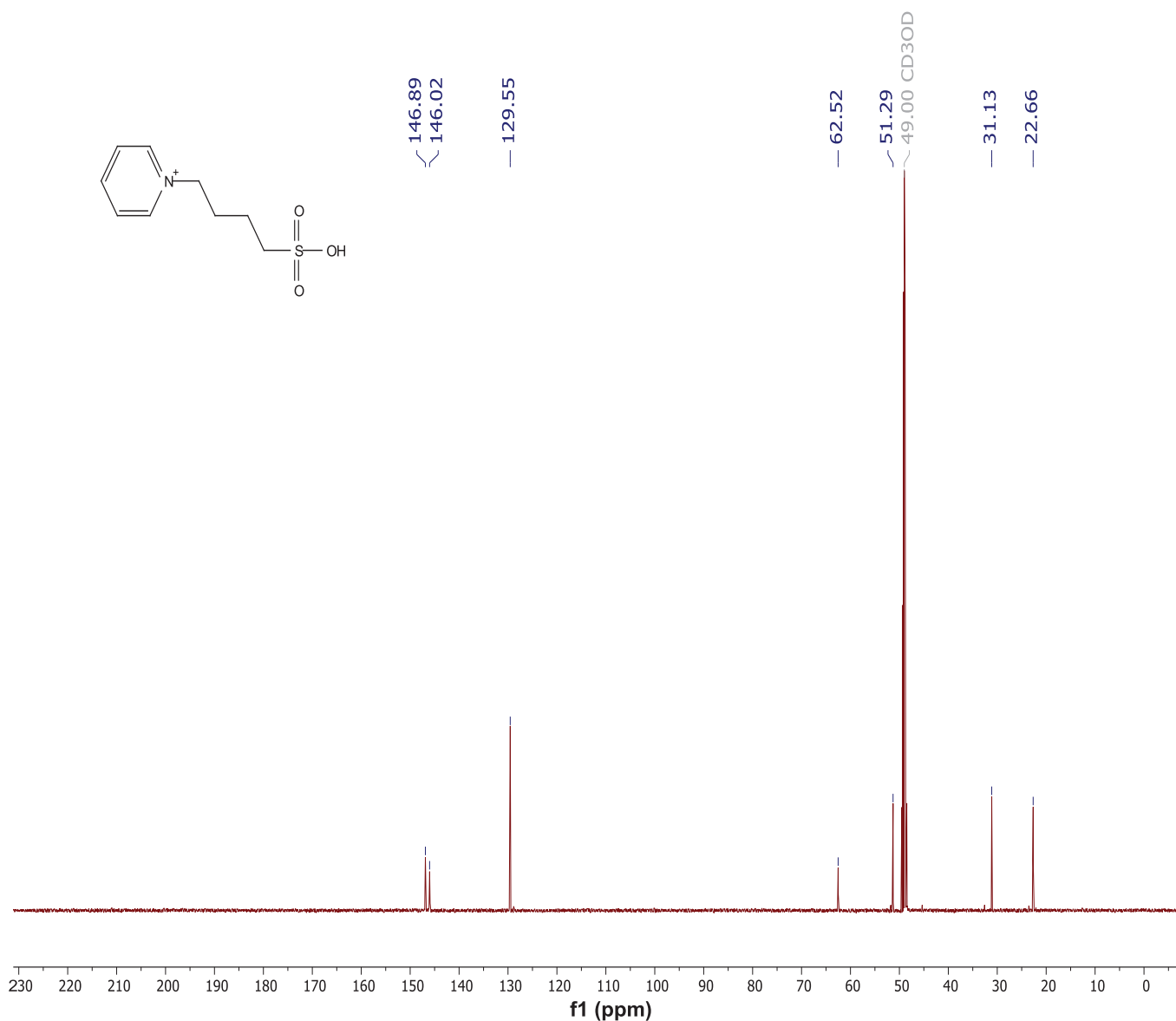


Fig. 3. ¹³C NMR of 1-(4-sulfobutyl)pyridinium chlorozincate.

Hz, 2H), 8.61 (tt, $J=8.0$, 1.5 Hz, 1H), and 8.13 (t, $J=7.0$ Hz, 2H). A triplet signal corresponding to protons in the -CH₂-N- group was observed at 4.71 (t, $J=7.5$ Hz, 2H). The chemical shift of the protons in the -CH₂-SO₂- group was observed at 2.89 (t, $J=7.5$ Hz, 2H). Additionally, two quintets corresponding to other methylene groups were detected at 2.21 (qui, $J=8.0$ Hz, 2H) and 1.85 (qui, $J=8.0$ Hz, 2H).

The data from the ¹³C NMR spectrum supported the above findings (Fig. 3). Indeed, the signals of carbon atoms within the pyridine ring were observed at 146.89, 146.02

and 129.55 ppm. Carbon atoms linked to heteroatoms, including nitrogen and sulphur, were characterized by signals at 62.5 and 51.29 ppm. The singlets at 31.13 and 22.66 ppm corresponded to the carbon atoms in the methylene groups.

In addition, the mass spectrum of the ionic liquid corresponded to the molecular cation at m/z 216.0398 (C₉H₁₄NO₃S⁺) and the peak at m/z 169.0444 in the HRMS was attributed to the ZnCl₃⁻ anion (Fig. 4). Consequently, the above data confirms the successful synthesis of 1-(4-sulfobutyl)pyridinium chlorozincate.

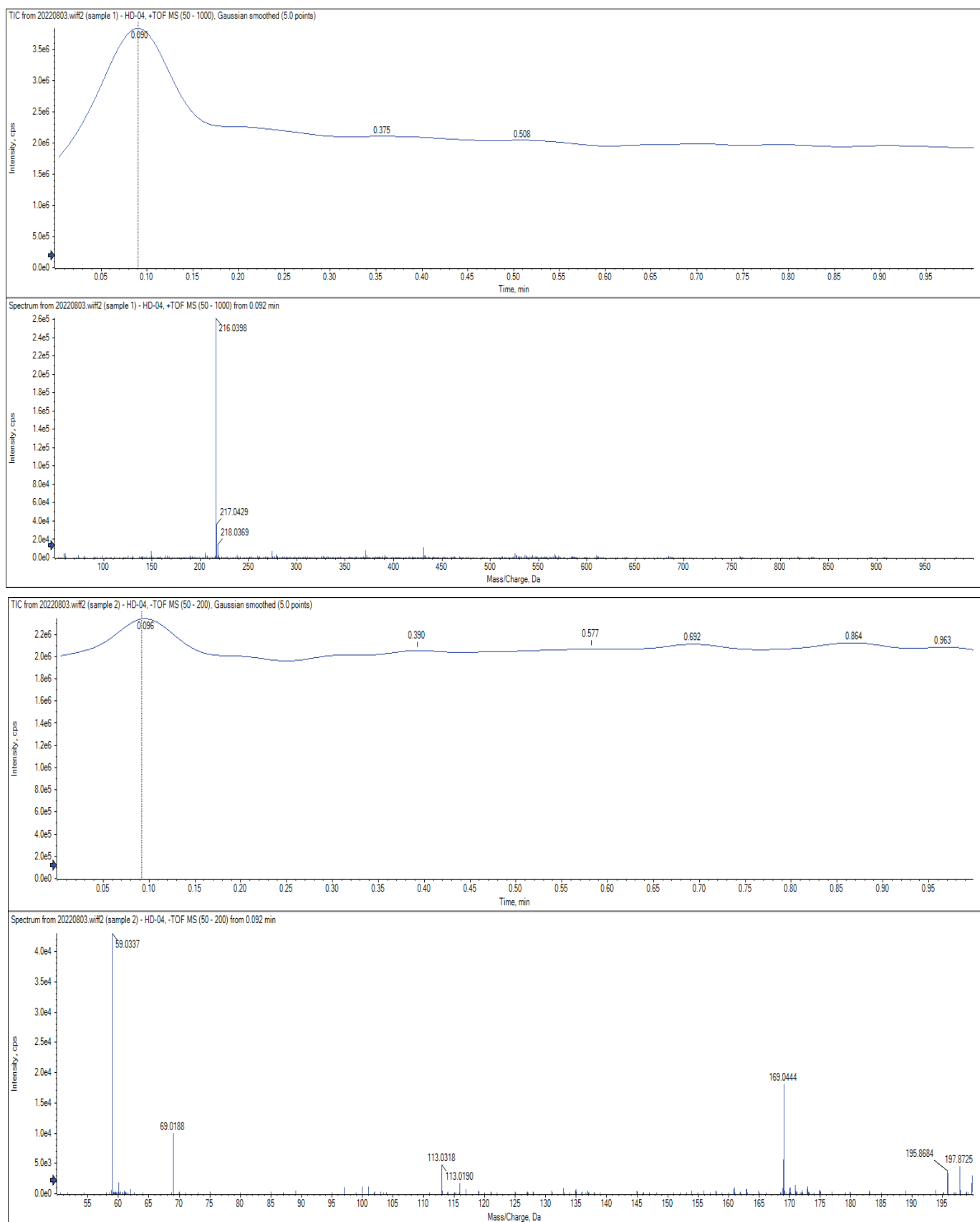


Fig. 4. HR-MS of 1-(4-sulfobutyl)pyridinium chlorozincate.

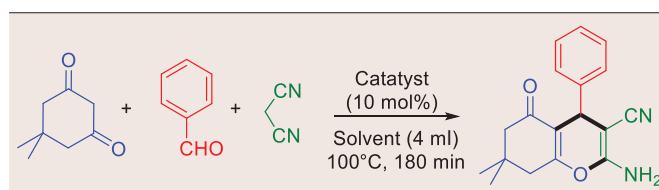
3.2. Reaction condition optimisation for the synthesis of 4H-1-benzopyran-5(6H)-one

The optimal conditions for the catalytic condensation of benzaldehydes, 5,5-dimethyl-1,3-cyclohexanedione, and dicyanomethane were investigated. When 1-(4-sulfobutyl)pyridinium chloride (IL0) was initially employed as the catalyst in this reaction, it provided the target product (**4a**) with a yield of 35% (Table 1, entry 2). To compare the catalytic activity of various ionic liquids (IL1, IL2, and IL3) with different anions, cyclization reactions were conducted in the presence of these three ionic liquid catalysts. The results demonstrated that the ionic liquid containing the chlorozincate anion was more effective than those containing the chlorotriate and chlorocopperate anions (Table 1, entries 3, 4, and 5). Furthermore, the catalytic activity of IL3 was higher than that of zinc chloride salt (Table 1, entries 1 and 5). This can be attributed to the involvement of both the sulfonic acid group and the chlorozincate anion in the structure of IL3 in this catalytic cyclocondensation.

Subsequently, various types of solvents were applied in this reaction (Table 1, entries 4-9). Polar solvents, including ethanol and methanol, yielded low yields of the target product in this three-component reaction. Notably, water provided a good yield for this reaction (Table 1, entry 6). To further enhance the reaction yield, we performed this reaction by mixing water and an organic solvent. The mixture of water and ethanol (1:1, v/v) as the reaction solvent offered a satisfactory yield of 69% for the target product (**4a**) (Table 1, entry 4). Moreover, this solvent mixture was selected for subsequent experiments due to its non-toxic properties.

The effect of temperature was investigated in this reaction, and the results are presented in Fig. 5. The reaction yield increased rapidly from 24 to 69% as the temperature was raised from 30 to 100°C. However, a 60% yield of the desired product was achieved at 120°C. Subsequently, we also examined the effect of reaction time at the same temperature. From Fig. 6, it can be observed that the reaction yield slightly increased from 53 to 69% when the reaction time was extended to 180

Table 1. Effect of catalyst and solvent^[a].



Entry	Catalyst	Solvent	Isolated yield (%)
1	ZnCl ₂	H ₂ O:EtOH (1:1)	42
2	IL0	H ₂ O:EtOH (1:1)	35
3	IL1	H ₂ O:EtOH (1:1)	10
4	IL2	H ₂ O:EtOH (1:1)	11
5	IL3	H ₂ O:EtOH (1:1)	69
6	IL3	H ₂ O:EtOH (1:2)	51
7	IL3	H ₂ O	47
8	IL3	EtOH	6
9	IL3	MeOH	4
10	IL3	Solvent-free	15

^[a]: 5,5-dimethyl-1,3-cyclohexanedione (0.5 mmol), benzaldehyde (0.5 mmol), dicyanomethane (0.5 mmol), catalyst (10 mol%), solvent (4 ml), 100°C, 180 min.

minutes. Further prolonging the reaction time led to slight decreases in the reaction yield. Consequently, the optimal reaction time of 180 minutes was chosen for this cyclisation.

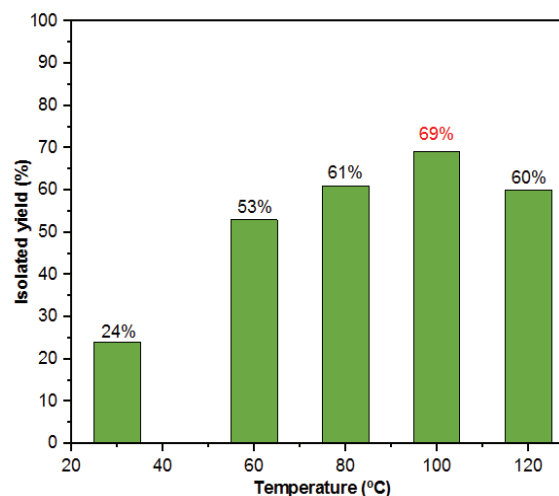


Fig. 5. Temperature screening.

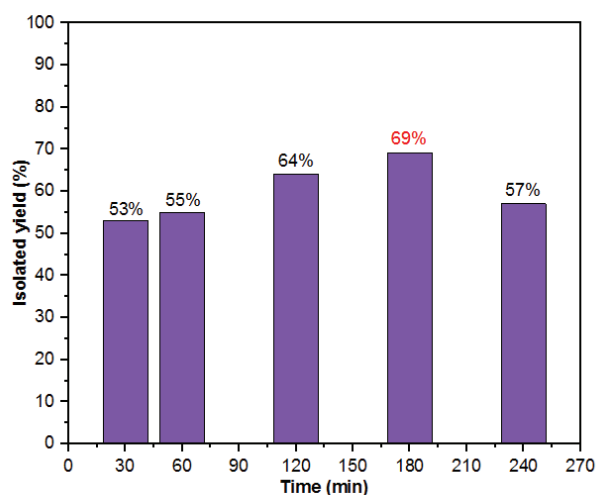


Fig. 6. Reaction time investigation.

The use of 5 mol% of 1-(4-sulfobutyl)pyridin-1-ium chlorozincate resulted in the production of 2-amino-3-cyano-4-phenyl-7,7-dimethyl-7,8-dihydro-4*H*-1-benzopyran-5(6*H*)-one with a relatively low yield (48%). However, increasing the catalyst amount to 10 mol% led to a significant improvement in the reaction yield, reaching up to 69%. It should be noted that the results indicated a pronounced negative effect when 20 mol% and 30 mol% of the catalyst were employed under the same conditions (Fig. 7). Consequently, 10 mol% was determined to be the optimal amount of catalyst for this method. Notably, one-pot three-component reactions in organic synthesis often result in by-product formation, but fortunately, only the major product was obtained under the optimal conditions.

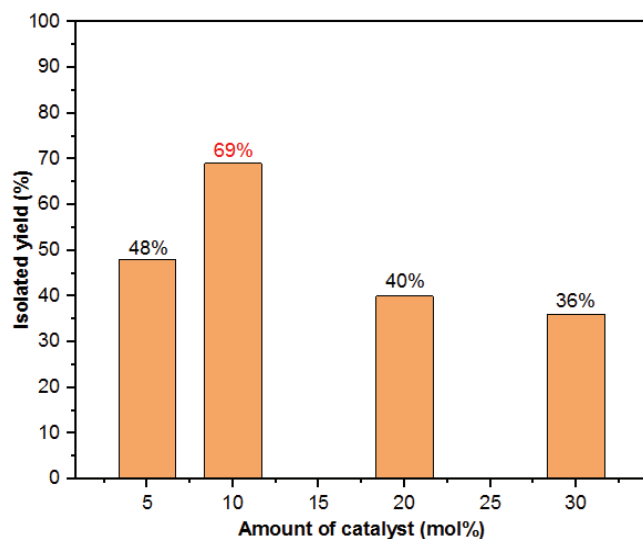
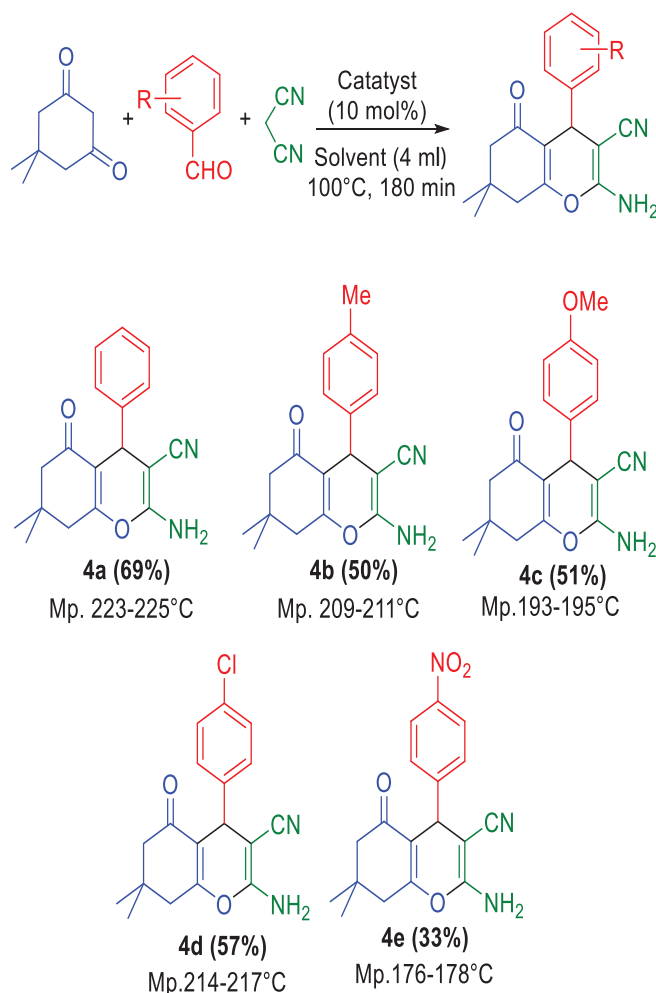


Fig. 7. Amount of catalyst screening.

Based on the aforementioned optimal conditions, we investigated the reactions involving five aromatic aldehydes with dimedone and dicyanomethane (Scheme 2). In general, aldehydes containing electron-donating groups such as *p*-Me and *p*-MeO proved to be viable substrates under the current reaction conditions, yielding the corresponding products (**4b** and **4c**) in moderate to good yields. Aromatic aldehydes containing chlorine on their aromatic ring were also successfully employed in the reaction, for instance, *p*-Cl derivatives (**4d**) were obtained in moderate yields. Aldehydes containing *p*-NO₂ groups provided the target products (**4e**) with a yield of 33%. The structures of all derivatives were confirmed through NMR methods, and the data from the ¹H and ¹³C NMR spectra are presented in Table 2.



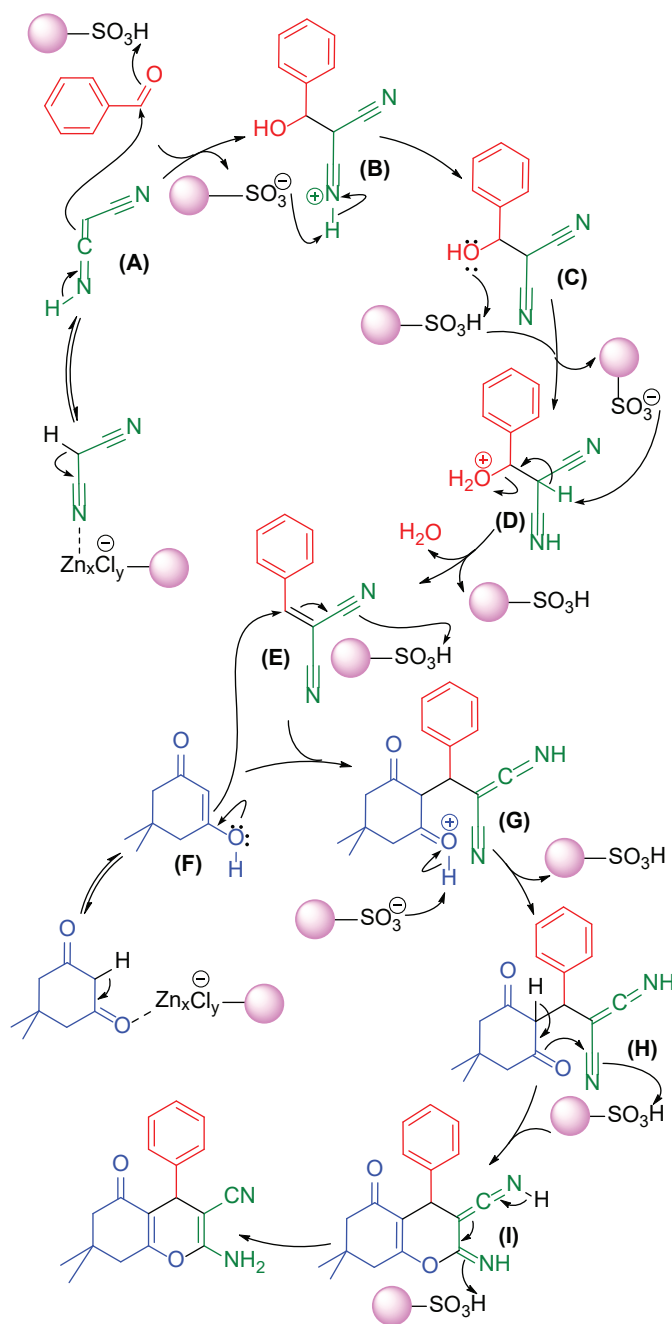
Scheme 2. Scope of reaction.

Table 2. Nuclear magnetic resonance data of benzopyran-5(6H)-ones.

Compounds	¹ H NMR (500 MHz, (CD ₃) ₂ SO) δ _H (ppm)	¹³ C NMR (125 MHz, (CD ₃) ₂ SO) δ _C (ppm)
4a	7.29 (t, <i>J</i> =7.5 Hz, 2H), 7.20 (d, <i>J</i> =7.5 Hz, 1H), 7.17-7.13 (m, 2H), 6.98 (s, 2H), 4.18 (s, 1H), 2.54-2.51 (m, 2H), 2.26 (d, <i>J</i> =16.0 Hz, 1H), 2.11 (d, <i>J</i> =16.0 Hz, 1H), 1.05 (s, 3H), 0.96 (s, 3H).	196.1, 163.0, 159.0, 145.2, 128.8, 127.6, 127.0, 120.2, 113.2, 58.9, 50.5, 36.1, 32.3, 28.9, 27.3
4b	7.09 (d, <i>J</i> =7.5 Hz, 2H), 7.02 (d, <i>J</i> =8.0 Hz, 2H), 6.96 (s, 2H), 4.13 (s, 1H), 2.51 (dd, <i>J</i> =4.0, 2.0 Hz, 2H), 2.24 (d, <i>J</i> =9.5 Hz, 4H), 2.10 (d, <i>J</i> =15.5 Hz, 1H), 1.04 (s, 3H), 0.96 (s, 3H).	196.1, 162.8, 159.0, 142.3, 136.1, 129.3, 127.6, 120.2, 113.4, 59.0, 50.5, 35.7, 32.3, 28.9, 27.3, 21.1.
4c	7.06 (d, <i>J</i> =9.0 Hz, 2H), 6.95 (s, 2H), 6.84 (d, <i>J</i> =9.0 Hz, 2H), 4.12 (s, 1H), 3.72 (s, 3H), 2.51-2.50 (m, 2H), 2.25 (dd, <i>J</i> =16.0, 5.5 Hz, 1H), 2.12-2.07 (m, 1H), 1.04 (s, 3H), 0.95 (s, 3H).	196.1, 162.6, 158.9, 158.4, 137.3, 128.7, 120.3, 114.2, 113.5, 59.1, 55.5, 50.5, 35.2, 32.3, 28.9, 27.3.
4d	7.34 (d, <i>J</i> =8.5 Hz, 2H), 7.17 (d, <i>J</i> =8.5 Hz, 2H), 7.05 (s, 2H), 4.19 (d, <i>J</i> =1.0 Hz, 1H), 2.51-2.50 (m, 2H), 2.25 (d, <i>J</i> =16.0 Hz, 1H), 2.10 (d, <i>J</i> =16.0 Hz, 1H), 1.03 (s, 3H), 0.95 (s, 3H).	195.7, 162.6, 158.5, 143.7, 131.1, 129.1, 128.3, 119.5, 112.3, 57.8, 49.9, 35.1, 31.8, 28.3, 26.9.
4e	8.18 (d, <i>J</i> =8.5 Hz, 2H), 7.45 (d, <i>J</i> =9.0 Hz, 2H), 7.17 (s, 2H), 4.37 (s, 1H), 2.56-2.53 (m, 2H), 2.27 (d, <i>J</i> =16.0 Hz, 1H), 2.12 (d, <i>J</i> =16.0 Hz, 1H), 1.06-1.04 (m, 3H), 0.97 (s, 3H).	195.7, 163.1, 158.6, 152.3, 146.3, 128.6, 123.7, 119.3, 111.7, 57.0, 49.9, 35.7, 31.8, 28.2, 26.9.

3.3. The possible mechanism

Based on our work and previous literature [26, 51, 52], the mechanistic steps of this condensation are illustrated in Scheme 3. Both the -SO₃H group and the Zn_xCl_y⁻ anion in the structure of the IL3 catalyst, known as Brønsted



Scheme 3. The possible mechanism.

and Lewis acidic sites, respectively, play similar roles in each step of the reaction mechanism.

The first step involves a nucleophilic addition reaction between benzaldehyde and dicyanomethane, known as Knoevenagel condensation. Under the acidic catalyst conditions, dicyanomethane undergoes tautomerization to form 3-iminoacrylonitrile (A). The π electron in C=C of (A) nucleophilically attacks the electrophilic carbon of benzaldehyde, facilitated by the acidic ionic liquid,

resulting in intermediate (B). After the removal of a proton from the nitrogen atom, 2-(hydroxy(phenyl)methyl) dicyanomethane (C) is formed, followed by protonation to provide intermediate (D). Subsequently, the elimination of water from (D) yields 2-benzylidenedicyanomethane (E). Finally, 5,5-dimethylcyclohexane-1,3-dione tautomerizes to 3-hydroxy-5,5-dimethylcyclohex-2-en-1-one (F).

The second step involves a Michael addition reaction between an electron-poor alkene and 1,3-diketone *via* 1,4-addition. In this step, intermediate (E) is attacked by the π electron from the nucleophilic double bond of (F) with the assistance of an acidic catalyst, leading to intermediate (G). After the formation of 2-((4,4-dimethyl-2,6-dioxocyclohexyl)(phenyl)methyl)-3-iminoacrylonitrile (H) through proton removal, intramolecular cyclization of intermediate (H) occurs through nucleophilic incursion between the C=O group and the nitrile group, resulting in 2-imino-3-(iminomethylene)-7,7-dimethyl-4-phenyl-2,3,4,6,7,8-hexahydro-5*H*-chromen-5-one (I). Finally, the target products are obtained through the isomerization of intermediate (I) with the support of an acidic catalyst.

3.4. Recycling of 1-(4-sulfobutyl)pyridinium chlorosincate

At the conclusion of this study, we investigated the recyclability of 1-(4-sulfobutyl)pyridinium chlorosincate. Under the optimized conditions, recycling experiments were conducted using a three-component reaction of

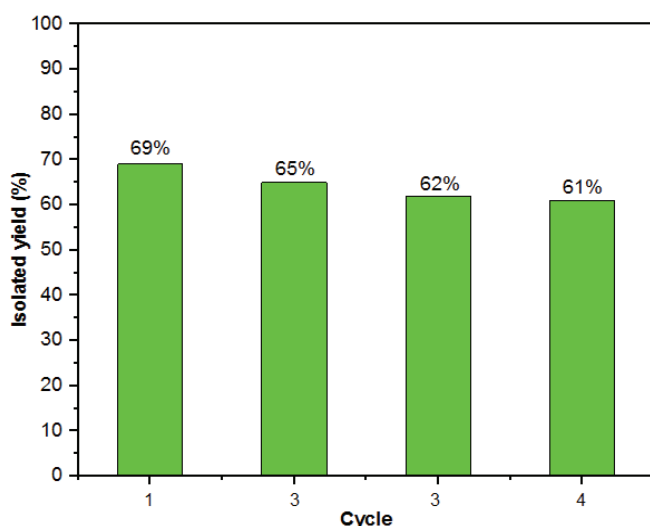


Fig. 8. Recycling of 1-(4-sulfobutyl)pyridinium chlorosincate.

benzaldehyde, dimedone, and dicyanomethane. After filtering and recrystallizing the crude product, the catalyst was easily separated through filtration and dried at 80°C. As seen in Fig. 8, there was a slight decrease in yield after each cycle (approximately 1-4% for each cycle). This decrease can be attributed to the loss of catalyst after each recycling. However, the ionic liquid catalyst retained its catalytic activity even after four cycles. Notably, the reaction yield reached 61% after the fourth-time reuse of IL3 catalyst, which is less than 8% lower than the reaction yield using fresh IL3 catalyst. This result demonstrates that IL3 is a green catalyst suitable for industrial applications.

4. Conclusions

In conclusion, a new acidic pyridinium-based ionic liquid was successfully synthesized and used as a catalyst in the synthetic process of 2-amino-3-cyano-4-phenyl-7,7-dimethyl-7,8-dihydro-4*H*-1-benzopyran-5(6*H*)-ones. These reactions involved a condensation reaction of aromatic benzaldehydes, 5,5-dimethyl-1,3-cyclohexanedione, and dicyanomethane in a solvent mixture of ethanol and water, resulting in the desired products in moderate to good yields. The procedure is efficient and eco-friendly, and the products can be easily obtained by recrystallization. Thus, this protocol offers an alternative to existing methods.

CRediT author statement

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COMPETING INTERESTS

The authors declare that there is no conflict of interest regarding the publication of this article.

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