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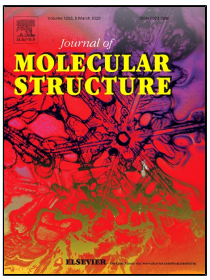

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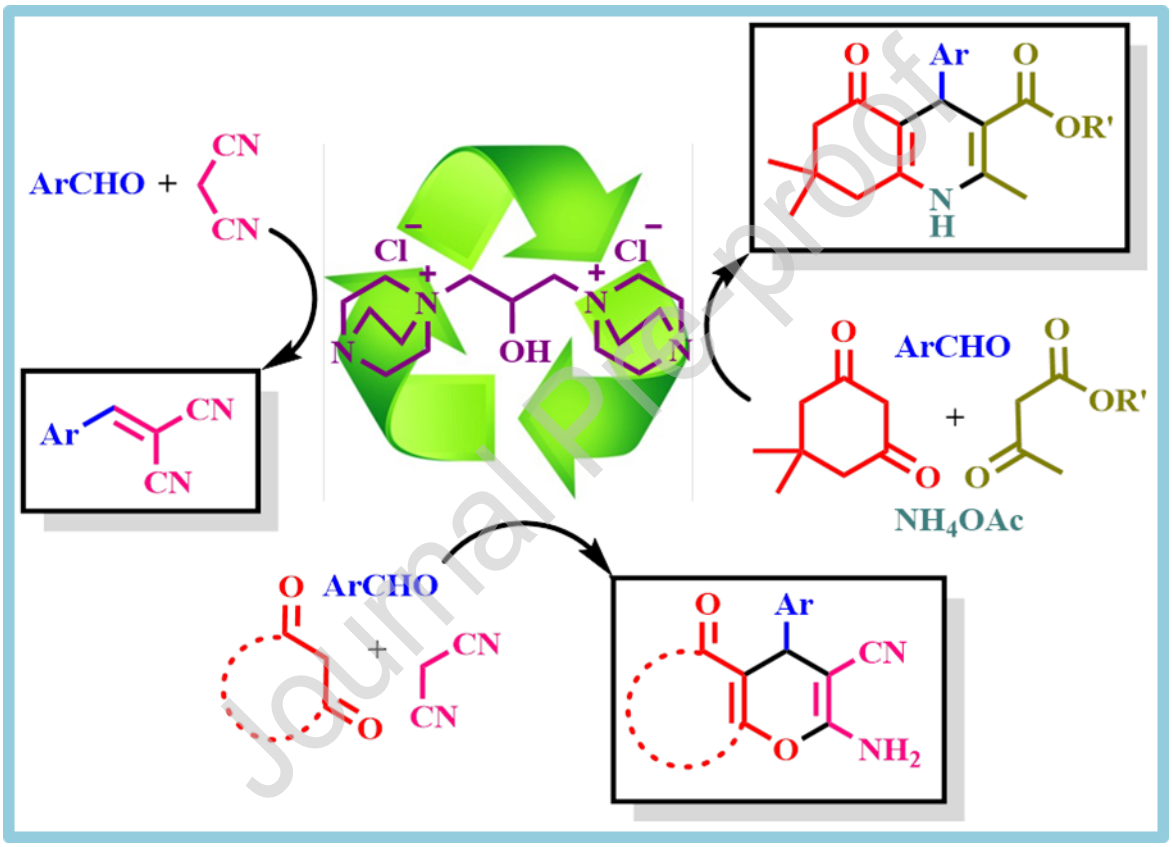

Introduction of an efficient DABCO-based bis-dicationic ionic salt catalyst for the synthesis of arylidenemalononitrile, pyran and polyhydroquinoline derivatives

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Abstract—An affordable DABCO-based bis-dicationic ionic salt ($[(DABCO)_2C_3H_5OH]\cdot 2Cl$) was utilized for the synthesis of arylidenemalononitrile, tetrahydrobenzo[*b*]pyran, pyrano[2,3-*d*]-pyrimidinone (thione), dihydropyrano[3,2-*c*]chromene, and polyhydroquinoline derivatives. The significant features of the presented method are ease of preparation and handling of the catalyst, high catalytic activity, short reaction times, no column chromatographic separation and simple work-up procedure. Also, the catalyst can be recovered easily and reused for several cycles in the studied reactions.

Keywords: DABCO, Dicationic ionic salt, Knoevenagel condensation, Multi-component reactions, pyran derivatives, polyhydroquinolines.

1. Introduction

One of the most rapidly growing areas of chemistry research is the design and development of green and economical catalytic systems. Nowadays, ionic liquids (ILs) are accepted as appropriate green catalysts/solvents in organic synthesis. This is due to their distinctive properties such as negligible vapor pressure, thermal and chemical stability, ease of handling, environmental friendly nature, and ability to dissolve many organic and inorganic substances [1, 2]. Dicationic ionic liquids (DILs) are attractive new members of ILs. These compounds contain two cationic head groups, linked by a rigid or flexible alkyl chain(s) in different lengths. Aside from the basic properties of traditional monocationic ILs, DILs have more active sites, higher selectivity, and higher thermal stability. Because of their unique properties, these compounds have been used as electrolytes, lubricants, and stationary phase in gas chromatography [3, 4].

1,4-Diazabicyclo[2.2.2]octane (DABCO) is a small cage-like tertiary amine that is used as an easily available, inexpensive and non-toxic catalyst for miscellaneous organic reactions [5, 6]. In recent years, dicationic ionic liquids based on DABCO have been synthesized and utilized as efficacious catalysts, potent antimicrobial and antibacterial agents [7-10].

The Knoevenagel condensation is one of the most important organic reactions for C=C bond formation. The reaction occurs through nucleophilic attack of a compound containing active methylene group to an aldehyde followed by dehydration [11]. This method is appropriate for the preparation of various substituted electrophilic alkenes which can be utilized as versatile intermediates for many

other types of reactions. Moreover, Knoevenagel adducts themselves exhibit a range of significant biological properties including anti-oxidant, anti-inflammatory, and anti-cancer activities [12].

4*H*-Pyrans and pyran-annulated heterocyclic scaffolds have been attracted the great attention due to their diverse useful biological and pharmacological activities such as anti-cancer [13, 14], anti-HIV [15], anti-diabetic [16], antimicrobial [17], antiviral and antileishmanial properties [18]. They are also used as cognition-enhancing drugs for the treatment of neurodegenerative disease, including Parkinson's disease, Schizophrenia, Alzheimer's disease, Huntington's disease and Down's syndrome [19]. Apart from their pharmaceutical importance, pyran derivatives like 2-amino-4*H*-pyrans exhibit significant photochemical activities [20]. They also utilized in pigments and cosmetics applications [21]. Some of 2-amino-3-cyano-4*H*-pyran derivatives which display strong pharmacological activities are shown in figure 1.

Polyhydroquinoline (PHQ) derivatives are another important class of heterocyclic compounds that possess a variety of remarkable pharmacological and biological properties. The derivatives of these heterocycles are known to exhibit antitumor, antitubercular, antibacterial, and antimalarial activities [22, 23]. Also, these compounds are well known as Ca^{2+} channel blockers for treatment of cardiovascular diseases [24].

Regarding notable properties of pyran and polyhydroquinoline derivatives and importance of the Knoevenagel condensation, their reactions have been investigated in the presence of different types of catalysts including, sodium carbonate [25], Fe_3O_4 MNPs–guanidine [26], silica-*L*-proline [27], sulfonated carbon/silica composites [28], Fe_3O_4@SiO_2@Ni-Zn-Fe LDH [12], 1,1,3,3-tetramethylguanidium lactate [29], MP(DNP) [30], Fe_3O_4@SiO_2@CuO–Fe_2O_3 [31], Na_2S/Al_2O_3 [32], KF-Clinoptilolite [33], $[C_4(MIm)_2]\cdot 2HSO_4$ [34] HAP–Cs_2CO_3 [35], and Fe_3O_4–cysteamine hydrochloride [36] for the promotion of the Knoevenagel condensation, $ZnFe_2O_4$ nanopowder [37], SO_4^{2-}/MCM-41[38], Fe_2O_3@SiO_2@VB_1 [39], (*S*)-proline [40], Urea [41], Fe_3O_4@SiO_2/DABCO [42], NH_4VO_3 [21], Nano ZnO [43], diammonium hydrogen phosphate [40], 2,2,2-trifluoroethanol [44], *p*-dodecylbenzenesulfonic acid [45], Nano-sawdust-OSO_3H [46], *N*-methylimidazole [47], Urea:ChCl [48], DABCO [49], Al-HMS-20 [50], $CaHPO_4$ [51], $[H_2\text{-pip}][H_2PO_4]_2$ [52], Fe_3O_4@MCM-41@Zr-piperazine-MNPs [53], Fe_3O_4@SiO_2@$(CH_2)_3$-Urea-SO_3H/HCl [54], Nano-titania Sulfuric Acid and $B(OH)_3$ [55] for the synthesis of pyran derivatives, ED/MIL-101(Cr) [56], *L*-Proline [57], P_2O_5/AL_2O_3 [58], NS-$[C_4(DABCO\text{-}SO_3H)_2]\cdot 4Cl$ [23], $BiBr_3$ [59], ChCl/urea [60], [*β*CD/Im]$(OTs)_2$-Silica [61], ceric ammonium nitrate (CAN) [62], tetraethylammonium 2-(carbamoyl) benzoate [63], La^{3+}/4A [22], FSM-16-SO_3H [64], and Glycine [65] for the synthesis of polyhydroquinoline derivatives.

Despite undeniable advantages of these methods, most of them suffer from some disadvantages like long reaction times, need to excess amounts of reagents or catalysts, generation of a waste containing metals and transition metals, difficulties in the preparation of the catalyst, and tedious work-up procedure. Therefore, further efforts are needed to introduce more efficient and cleaner procedures for the synthesis of the above mentioned important target molecules.

2. Experimental

2.1. Materials

Chemicals were purchased form Merck (Munich) and Aldrich (Mumbai) Chemical Companies and utilized without any further purification. Products were characterized by comparison of their physical constants such as melting point, FT-IR and/or NMR spectra with those of the authentic samples or those reported in the literature. Yields refer to the isolated products. Thin layer chromatography (TLC) was used for determination of the purity of substrates, products and reaction monitoring over silica-gel polygram SILG/UV 254 plates.

2.2. Characterization techniques

Melting points were determined by electro-thermal IA9100 melting point apparatus in capillary tubes. The starting temperature of the approximate melting range was input *via* the keyboard and the melting point range was observed visually. FT-IR spectra were recorded on a Perkin-Elmer Spectrum BX series and KBr pellets were used for solid samples. The ^{1}H NMR and ^{13}C NMR spectra were acquired by a Bruker Ultrashield 400 MHz instrument using deuterated solvents and TMS as an internal standard. Mass spectra were obtained with an Agilent Technologies 5975C spectrometer *via* a mass selective detector (MSD) operating at an ionization potential of 70 eV.

2.3. Preparation of 1,1'-(2-hydroxypropane-1,3-diyl)bis(1,4-diazabicyclo[2.2.2]octan-1-ium) chloride {[(DABCO)$_2$C$_3$H$_5$OH]·2Cl}

1, 3-Dichloro-2-propanol (0.464 mL, 5.0 mmol) was added to a mixture of DABCO (1.121 g, 10.0 mmol) in dry CH_3CN (50 mL) and stirred for 24 h under reflux conditions. After completion of the reaction the solvent was removed under vacuum, and the obtained solid was washed with diethyl ether. After drying, [(DABCO)$_2$C$_3$H$_5$OH]·2Cl was obtained as a white solid in 98 % yield. Spectral data for [(DABCO)$_2$C$_3$H$_5$OH]·2Cl: ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 3.04 (t, J=7.6 Hz, 12 H), 3.40-3.43 (m, 4 H), 3.44-3.51 (m, 6 H), 3.56-3.63 (m, 6H), 5.03 (sep, 1H), 7.05 (d, J=8 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) 44.6, 52.7, 54.0, 66.0. FT-IR (KBr, cm^{-1}) υ_{max}: 3419, 2962, 2895. MS: m/e=353(M^{+}).

2.4. General procedure for the Knoevenagel condensation of aldehydes and malononitrile

In a 15 mL round-bottomed flask, a mixture of aromatic aldehyde (1 mmol), malononitrile (1.1 mmol) and [(DABCO)$_2$C$_3$H$_5$OH]·2Cl (10 mg, 2.8 mol%) in water (3 mL) was stirred magnetically at 85 ^{o}C while the reaction progress was monitored by TLC (*n*-hexane-EtOAc (7:3)). After completion of the reaction, the mixture was cooled to room temperature and filtered off. The solid product was recrystallized from ethanol to afford the pure product.

2.5. General procedure for the synthesis of pyran derivatives

In a 15 mL round-bottomed flask, a mixture of aromatic aldehyde (1 mmol), molononitrile (1.1 mmol), the requested C–H activated acidic compound (1 mmol), and $[(DABCO)_2C_3H_5OH]\cdot 2Cl$ (10 mg, 2.8 mol%) in water (3 mL) stirred magnetically under reflux conditions. The progress of the reaction was monitored by TLC (*n*-hexane-EtOAc (8:2)). After completion of the reaction, the mixture was diluted with water (3 mL) and the solid product was decanted. Recrystallization from ethanol afforded the pure product in high yields.

2.6. General procedure for the synthesis of polyhydroquinoline derivatives

In a 10 mL round-bottomed flask a mixture of aromatic aldehyde (1 mmol), dimedone or 1,3-cyclohexanedione (1 mmol), ethyl acetoacetate or methyl acetoacetate (1 mmol), ammonium acetate (2 mmol) and $[(DABCO)_2C_3H_5OH]\cdot 2Cl$ (30 mg, 8.5 mol%) was stirred and heated in an oil-bath at 120 ^oC for an appropriate period of time. After completion of the reaction (Monitored by TLC), water was added to separate the catalyst and the crude product was separated and recrystallized from EtOH to afford the requested product.

2.7. Spectroscopic data of the selected previously introduced and new compounds

2-amino-4-(2-chlorophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4*H*-chromene-3-carbonitrile (Table 3, entry 3, **2c**): ^{1}H NMR (500 MHz, DMSO-d_6): δ (ppm) 0.98 (s, 3H), 1.07 (s, 3H), 2.09 (d, *J*=8.0 Hz, 1H), 2.27 (d, *J*=8.0 Hz, 1H), 2.53(s, 2H), 4.70 (s, 1H), 7.03 (s, 2H), 7.16-7.22 (m, 2H), 7.26-7.29 (m, 1H), 7.36-7.38 (m, 1H); ^{13}C NMR (125 MHz, DMSO-d_6): δ (ppm) 196.0, 163.6, 159.1, 119.7, 112.2, 57.3, 50.4, 40.5, 39.4, 32.3, 28.8, 27.3, 142.0, 130.4, 129.9, 128.6. FT-IR (KBr, cm^{-1}): 3469, 2962, 2196, 1600. White solid, m.p.= 213-215 °C.

Ethyl 4-(4-chlorophenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (Table 4, entry 2, **5b**): ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 0.948 (s, 3H, CH_3), 1.086 (s, 3H, CH_3), 1.219 (t, *J*=7.2 Hz, 3H, CH_3), 2.143-2.345 (m, 4H, CH_2), 2.386 (s, 3H), 4.08 (q, *J* = 7.2 Hz, 2H), 5.047 (s, 1H, CH), 6.5 (br, 1H, NH), 7.18 (d, *J*= 8.3 Hz, 2H, ArH), 7.28 (d, *J* = 8.2 Hz, 2H, ArH). FT-IR (KBr, cm^{-1}): 3284, 3212, 3075, 2948, 1698, 1611, 1481, 1377, 1227, 1079, 828. White solid, m.p.= 236-238 °C.

Ethyl 4-(4-methoxyphenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (Table 4, entry 6, **5f**): ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 0.952 (s, 3H, CH_3), 1.073 (s, 3H, CH_3), 1.236 (t, 3H, *J*=7.4 Hz, CH_3), 2.178-2.269 (m, 4H), 2.362 (s, 3H), 3.744 (s, 3H), 4.085 (q, 2H, *J*=7.4 Hz, OCH_2), 5.17 (s, 1H, CH), 6.742-6.764 (d, 2H, *J*=8.8 Hz, ArH), 7.23 (d, 2H, *J*=8.8 Hz, ArH), 7.292 (s, 1H, NH). FT-IR (KBr, cm^{-1}): 3278, 3201, 3077, 2959, 1702, 1604, 1498, 1379, 1272, 1223, 1108, 1071, 1030, 841, 760. Pale yellow solid, m.p = 255-257 °C.

Ethyl 2,7,7-trimethyl-4-(4-nitrophenyl)-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (Table 4, entry 11, **5k**): ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 0.920 (s, 3H, CH_3), 1.092 (s, 3H, CH_3), 1.199 (t, 3H, *J*=7.3 Hz, CH_3), 2.15 (dd, 2H, CH_2), 2.26 (dd, 2H,

CH_2), 2.402 (s, 6H, CH_3), 4.07 (q, 2H, *J*=7.4 Hz, OCH_2), 5.178 (s, 1H, CH), 6.718 (s, 1H, NH), 7.51 (d, 2H, *J*=9.4 Hz, ArH), 8.09 (d, 2H, *J*=9.4 Hz, ArH). FT-IR (KBr, cm^{-1}): 3293, 3215, 3082, 2958, 1699, 1619, 1528, 1487, 1379, 1221, 1068, 698. Pale yellow solid, m.p = 228-232 °C.

Ethyl 2-methyl-5-oxo-4-(o-tolyl)-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (Table 4, entry 13, **5m**, **new compound**): ^{1}H NMR (500 MHz, DMSO-d_6): δ (ppm) 1.09 (t, *J*=7 Hz, 3H), 1.64-1.73 (m, 1H), 1.85-1.89 (m, 1 H), 2.10-2.23 (m, 2H), 2.31 (s, 3H), 2.43-2.51 (m, 2H), 2.64 (s, 3H), 3.93-4.01 (m, 2H), 4.99 (s, 1H), 6.91-6.96 (m, 2H), 7.02 (t, *J*=7.5 Hz, 1H), 7.13 (d, *J*=7.5 Hz, 1H), 9.07 (s, 1H). ^{13}C NMR (125 MHz, DMSO-d_6): δ (ppm) 13.5, 17.8, 18.8, 20.1, 25.7, 31.8, 36.2, 58.4, 104.6, 112.2, 124.9, 125.5, 128.1, 128.5, 134.3, 143.7, 147.4, 150.4, 166.5, 194.1. FT-IR (KBr, cm^{-1}): 3307, 2983, 2958, 1695, 1607. Lemon solid, m.p: 234–236 °C.

3. Results and Discussion

In recent years, preparation, characterization and use of ionic liquid catalysts in organic reactions have been an important part of our ongoing research program. In this regard, a number of mono- and dicationic ionic liquids based on DABCO have been synthesized and their catalytic activities have been studied by our research group [10, 66, 67]. In continuation of these studies, we found that $[(DABCO)_2C_3H_5OH]\cdot 2Cl$ is prepared and used as an intermediate for the preparation of a new catalyst which is formulated as $[(DABCO)_2C_3H_5OH]\cdot 2BF_4$. Our further investigations clarified that $[(DABCO)_2C_3H_5OH]\cdot 2Cl$ is also able to act as an efficient catalyst in organic transformations by itself, which was not attended by the previous research group [8]. So, in this article in addition to full characterization of this reagent, we wish to report its efficiency in the promotion of some multi-component reactions leading to the synthesis of some very important organic compounds.

3.1. Characterization of the catalyst

After preparation of the $[(DABCO)_2C_3H_5OH]\cdot 2Cl$ (Scheme 1), various techniques were used for the characterization of this compound.

The amount of chloride in $[(DABCO)_2C_3H_5OH]\cdot 2Cl$ was determined by potentiometric titration method. For this purpose, 0.1 g of the prepared ionic salt was solved in water and the obtained solution was titrated with 0.1 M $AgNO_3$. As shown in Figure 2, the change happened at 4.7 mL of consumed $AgNO_3$. On the basis of this study it can be concluded that $[(DABCO)_2C_3H_5OH]\cdot 2Cl$ has 2 equivalents of chloride ion per one mol of this reagent.

The FT-IR spectra of DABCO, 1,3-dichloro-2-propanol and $[(DABCO)_2C_3H_5OH]\cdot 2Cl$ are presented in Figure 3. The IR spectrum of DABCO exhibits a variety of stretching and bending vibrations which were eliminated or reduced in the spectrum of the prepared ionic salt, probably due to the limitation of vibrations in the rings. In the case of $[(DABCO)_2C_3H_5OH]\cdot 2Cl$, the broad absorption

bond centered at 3419 cm^{-1} is related to the presence of the hydroxyl group. The absorption bands at 2962 and 2895 cm^{-1} can be attributed to the asymmetric and symmetric stretching vibrations of C–H bonds.

In the mass spectrum of $[(DABCO)_2C_3H_5OH]\cdot 2Cl$, as shown in Figure 4, the molecular ion peak (M+) appeared at m/e = 353 is equal to the molecular weight of the catalyst. Also, other peaks related to the other fragmentations can be seen in this spectrum.

^1H NMR and ^{13}C NMR spectra of $[(DABCO)_2C_3H_5OH]\cdot 2Cl$ are presented in Figures 5 and 6. The ^1H NMR spectrum of $[(DABCO)_2C_3H_5OH]\cdot 2Cl$ as a symmetric dicationic ionic salt displayed a triplet peak at 3.04 ppm for H_a, a multiplet peak at 3.44–3.51 ppm for H_b, a multiplet peak at 3.40–3.43 ppm for H_c, a septet peak at 5.03 ppm related to the proton attached to tertiary carbon containing hydroxyl group (H_d), and a doblet peak for H_e (OH). Also the ^{13}C NMR of $[(DABCO)_2C_3H_5OH]\cdot 2Cl$ properly showed four types of carbons.

3.2. Catalytic activity

The catalytic study commenced with the optimization of the two-component Knoevenagel condensation of 4-chlorobenzaldehyde (1 mmol) and malononitrile (1.1 mmol) as a model reaction (Table 1, entries 1-13). In this reaction, the presence of the catalyst is necessary. Preliminary trials revealed that the reaction did not proceed under solvent-free conditions and only a trace amount of the desired product was obtained. Then, we tried to find the best solvent for the reaction. For this purpose, the reaction was tested in green solvents, such as water and EtOH. No significant product was observed when the mixture of the reaction was refluxed in EtOH. In contrast, when the reaction was carried out in water, the yield improved drastically and the desired product was formed in good yield. The best result was achieved when the reaction was performed in water using 2.8 mol% of $[(DABCO)_2C_3H_5OH]\cdot 2Cl$ at 85 ^oC (Table 1, entry 12) (Scheme 2). Any further increase in the catalyst amounts or temperature did not improve the reaction time or yield. In order to study the generality of this catalytic system, a variety of aromatic aldehydes containing electron-donating or electron-withdrawing groups in *ortho*, *meta* and *para* positions of the aromatic ring were used to obtain various arylidenemalononitriles. The results are depicted in Table 2. According to this table, all reactions proceeded smoothly producing the products in excellent yields (89−95 %) within 8−19 min of the reaction time and no significant difference for the substituent effect was observed. Also, the isolated products were extremely pure and there was no need for further purification or even recrystallization.

In the next step, the efficiency of $[(DABCO)_2C_3H_5OH]\cdot 2Cl$ in the promotion of the one pot three-component synthesis of pyran derivatives *via* the tandem Knoevenagel-Michael reaction was investigated. For this purpose and to obtain the optimum reaction conditions, we first conducted a series of trial reactions with 4-chlorobenzaldehyde (1 mmol), malononitrile (1.1 mmol), and dimedone (5,5-dimethyl-1,3-cyclohexanedione) (1 mmol) under a variety of conditions (Table 1, entries 14-18). As shown in Table 1 (entry 17), the best result was obtained in refluxing water using 2.8 mol% of $[(DABCO)_2C_3H_5OH]\cdot 2Cl$. Higher amounts of the

catalyst gave no further improvement. To demonstrate the scope and generality of this protocol, different types of aromatic aldehydes and other C−H activated acidic compounds such as 4-hydroxycoumarin and (thio) barbituric acids were reacted with malononitrile using identical reaction conditions to obtain tetrahydrobenzo[*b*]pyran, pyrano[2,3-*d*]-pyrimidinone (thiones), and dihydropyrano[3,2-*c*]chromene derivatives, respectively (Scheme 3, Table 3). As indicated in Table 3, all of them reacted smoothly during acceptable reaction times. Furthermore, pyridine-4-carbaldehyde was used as a heterocyclic aldehyde under the same conditions, and the related dihydropyrano[3,2-*c*]chromene derivative was successfully obtained in high yields (Table 3, entry 24).

Encouraged by these results, we decided to use this catalyst to promote the synthesis of polyhydroquinoline derivatives. These compounds can be synthesized according to Hantzsch condensation using aromatic aldehydes, 1,3-cyclohexanedione derivatives, *β*-ketoesters, and ammonium acetate *via* one-pot four-components reaction. Initially, in order to determine the optimized reaction conditions, we checked the reaction of 4-chlorobenzaldehyde (1 mmol), dimedone (1 mmol), ethyl acetoacetate (1 mmol) and various amount of ammonium acetate as a model system in the absence and/or presence of $[(DABCO)_2C_3H_5OH]\cdot 2Cl$ in green solvents (H_2O, EtOH) and also under solvent-free conditions at various temperatures. A summary of the obtained results is listed in (Table 1, entries 19-28). The results showed when the reaction was carried out in the absence of the catalyst, only a trace amount of the desired product was formed and the reaction progress is highly affected by catalyst loading and temperature. Also, when the reaction was carried out in the absence of solvent, high yield during a short reaction time was achieved. Finally, the best result was obtained using 2 mmol of ammonium acetate and 8.5 mol% of $[(DABCO)_2C_3H_5OH]\cdot 2Cl$ under solvent-free conditions at 120 ^oC (Table 1, entry 27). Subsequently, to reveal the generality of this method, different derivatives of polyhydroquinolines were prepared and the results were summarized in Table 4.

The results of experiments on the synthesis of pyrans and polyhydroquinoline derivatives exhibits that $[(DABCO)_2C_3H_5OH]\cdot 2Cl$ can be an efficient ionic salt catalyst for the multi-component reactions.

It should be mentioned that although the conversion yields in all of the above-mentioned reactions were 100 %, a small amounts of the products wasted through the work-up procedure and therefore the percentage yields are less than the conversion yields. Also, using aliphatic aldehydes in these reactions led to a mixture of products, showing that this procedure is not suitable for these substrates.

The possibility of the recycling of $[(DABCO)_2C_3H_5OH]\cdot 2Cl$ was also studied at modified conditions in the synthesis of **1b**, **2b**, **5b**. For this purpose, after completion of the reactions (Monitored by TLC), water was added into the reaction mixtures in order to separate the catalyst ($[(DABCO)_2C_3H_5OH]\cdot 2Cl$ is soluble in water). Afterwards the reaction mixtures were filtered off and the filtrates were evaporated under vacuum at 70 ^oC. The obtained white precipitates were washed with diethyl ether and reused again for the same reaction. The obtained results are demonstrated in Figure 7.

Plausible mechanisms for the mentioned reactions are depicted in Scheme 5. As can be seen, $[(DABCO)_2C_3H_5OH]\cdot 2Cl$ as a bi-functional donor–acceptor reagent, simultaneously can activate the carbonyl group of aldehyde and the methylene groups of malononitrile or *β*-dicarbonyl. Then, the activated aldehyde is attacked by the activated malononitrile or *β*-dicarbonyl through a Knoevenagel condensation reaction to generate arylidenemalononitriles (intermediate **a**) or the intermediate **b**. For the synthesis of pyran derivatives, the Michael addition of the catalyst-activated enol **c** and the intermediate **a** generates the intermediate **d**. Finally, intramolecular cyclization of the intermediate **d** affords the desired pyran derivatives. For the synthesis of polyhydroquinolines, conjugate addition of the enamine (**e**) with the intermediate b leads to the formation of polyhydroquinolines followed by cyclization. It was essential that the catalytic ability of $[(DABCO)_2C_3H_5OH]\cdot 2Cl$ compare with previous methods to clarify the merit of the catalyst. Thus, the obtained results in the synthesis of 2-(4-chlorobenzylidene)malononitrile **1b**, 2-amino-4-(4-chlorophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4*H*chromene-3-carbonitrile **2b**, and ethyl 2,7,7-trimethyl-4-(4-cholorophenyl)-5oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate **5b** were compared to the various types of catalysts especially some of the DABCO-based ionic liquids (Table 5). As shown in Table 5, $[DABCO)_2C_3H_5OH]\cdot 2Cl$ can be proposed as a useful catalyst in terms of the amount of the catalyst, reaction times and yields.

4. Conclusion

In this study, $[(DABCO)_2C_3H_5OH]\cdot 2Cl$ was prepared as an efficient, affordable, and green ionic salt catalyst by a simple nucleophilic reaction for the one-pot synthesis of a diverse set of arylidenemalononitrile, pyran and polyhydroquinoline derivatives. The green conditions, easy catalyst preparation, use of a commercially available and inexpensive reagents, simple separation and recovery of the catalyst from the reaction mixture, easy work-up procedure needing no special separation methods and absence of organic solvents, short reaction times, high purity and high yields of the products are the considerable advantages of this protocol.

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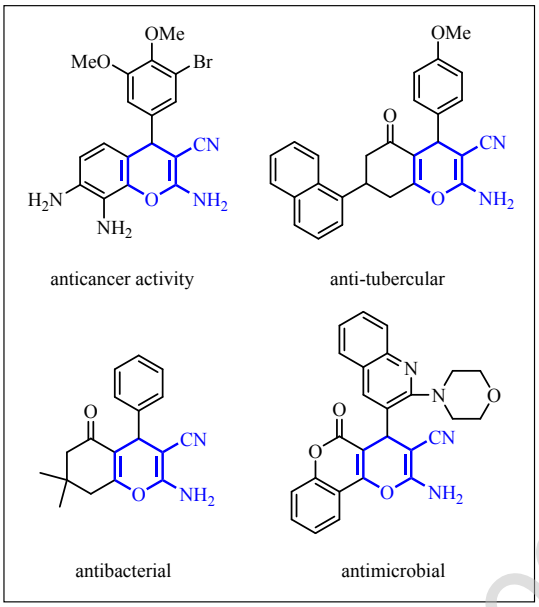


Fig. 1. Some examples of 2-amino-3-cyano-4*H*-pyran derivatives with pharmacological activities**.**

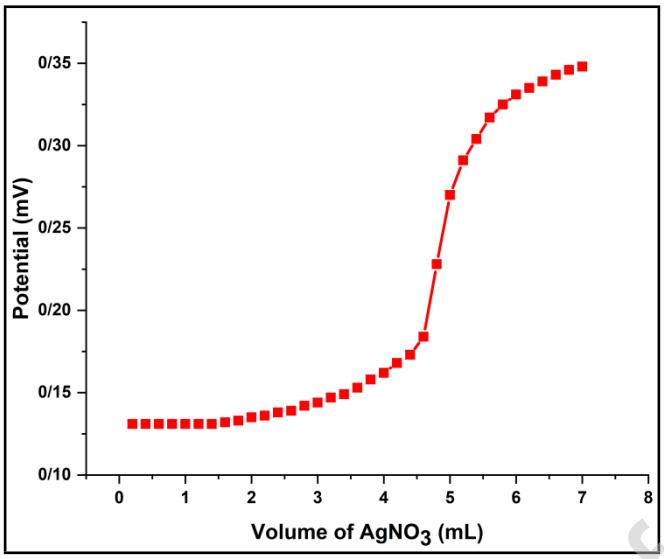


Fig. 2. Potentiometric titration curve of $[(DABCO)_2C_3H_5OH].2Cl$.

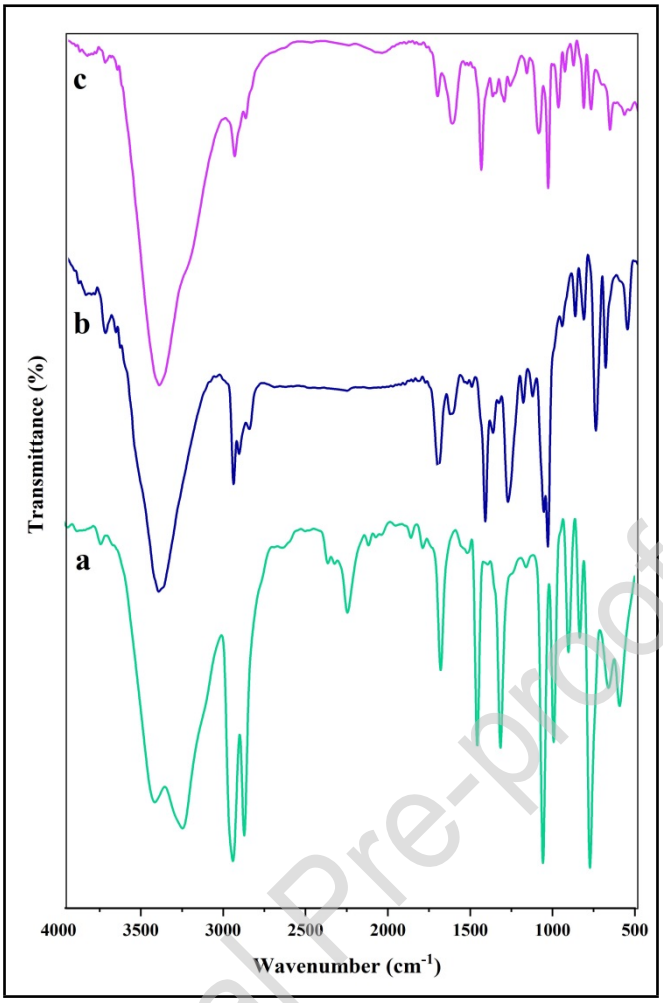


Fig. 3. FT-IR spectra of DABCO (a), 1, 3-dichloro-2-propanol (b) and $[(DABCO)_2C_3H_5OH]\cdot 2Cl$ (c).

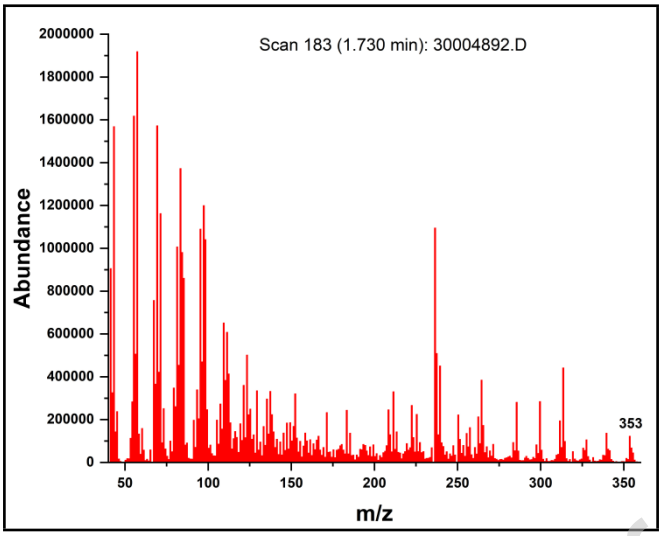


Fig. 4. The mass spectrum of $[(DABCO)_2C_3H_5OH]\cdot 2Cl$.

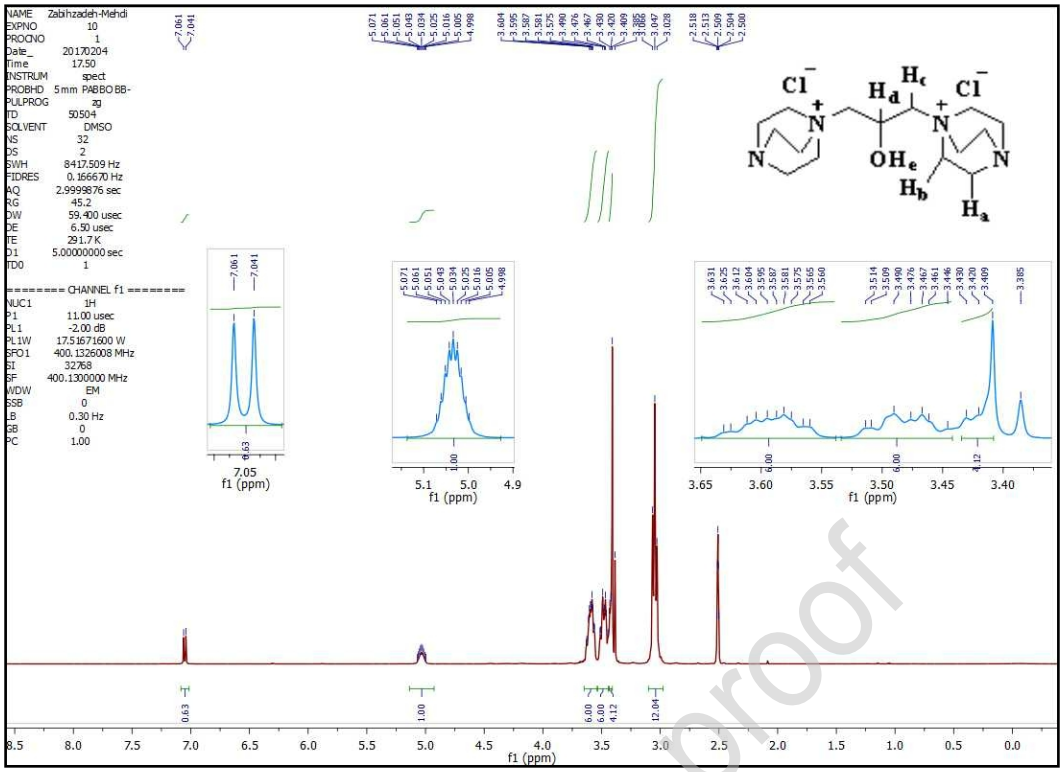


Fig. 5. The ^{1}H NMR spectrum of $[(DABCO)_2C_3H_5OH]\cdot 2Cl$.

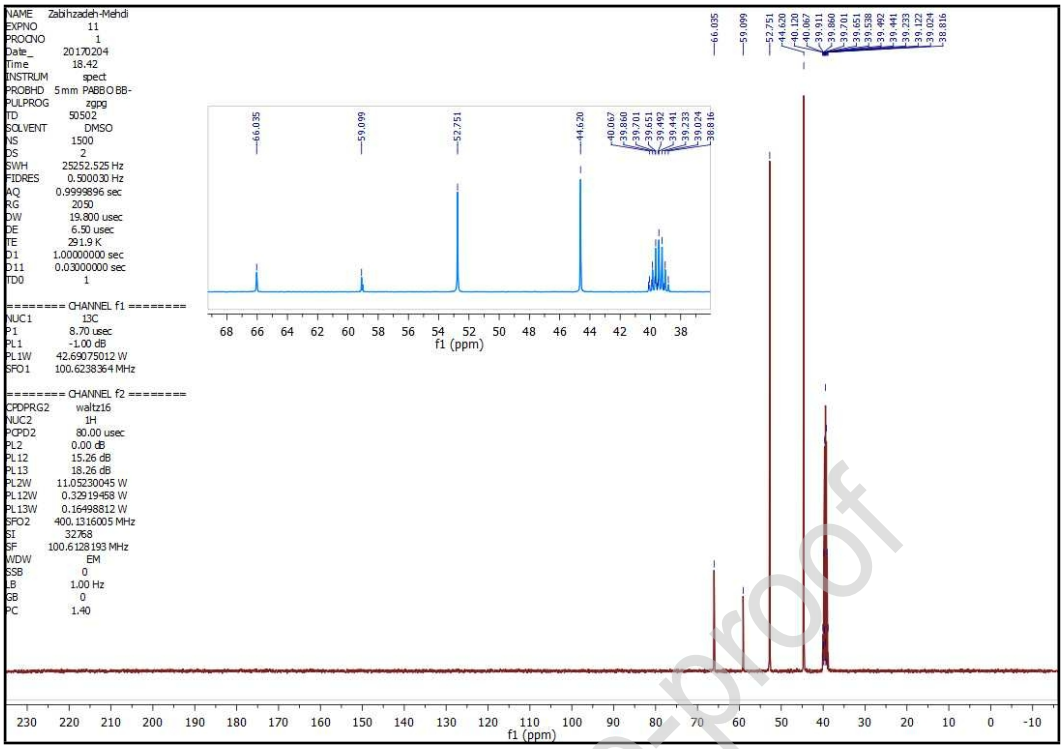


Fig. 6. The ^{13}C NMR spectrum of $[(DABCO)_2C_3H_5OH]\cdot 2Cl$.

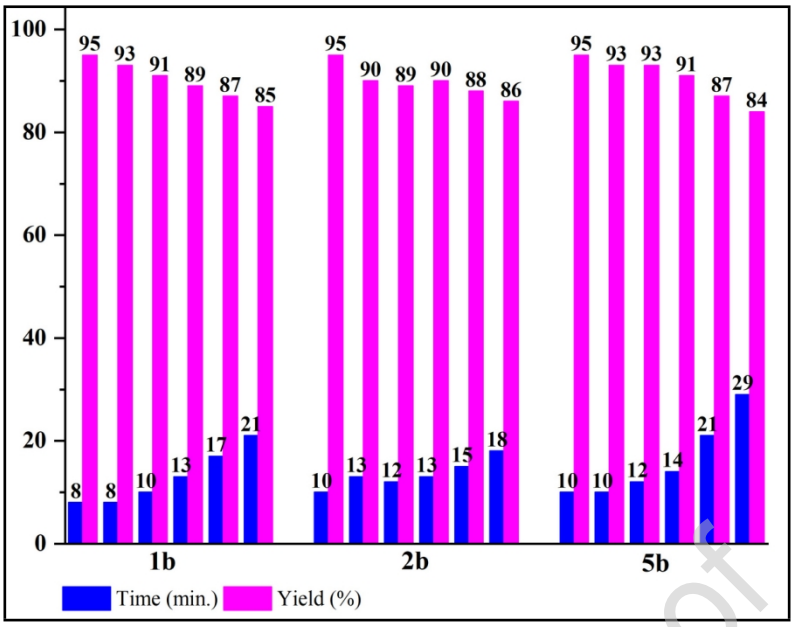
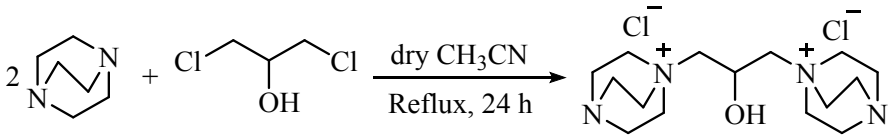
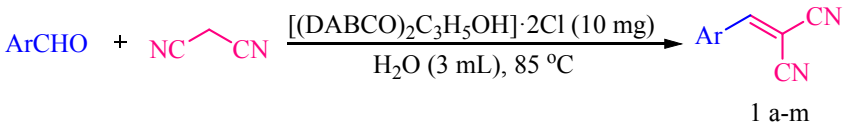


Fig. 7. Reusability of $[(DABCO)_2C_3H_5OH]\cdot 2Cl$ in the synthesis of 1b, 2b and 5b.

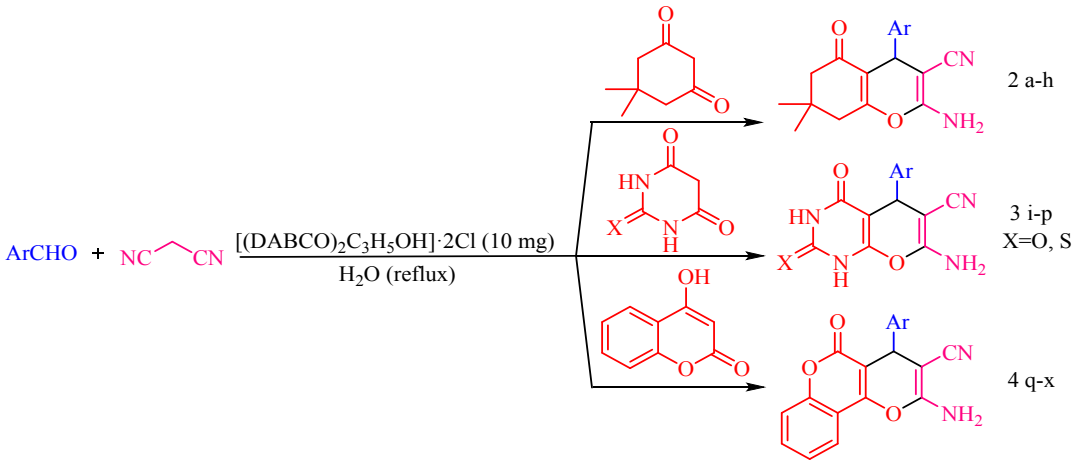


Scheme 1. Preparation of $[(DABCO)_2C_3H_5OH]\cdot 2Cl$.

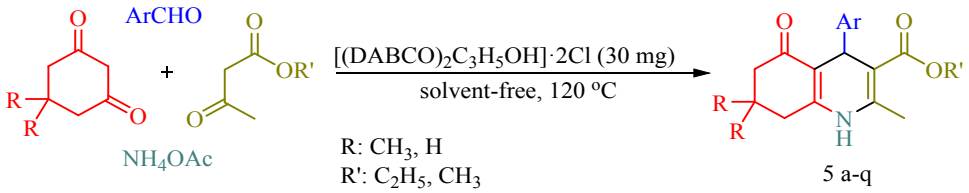


1 a-m

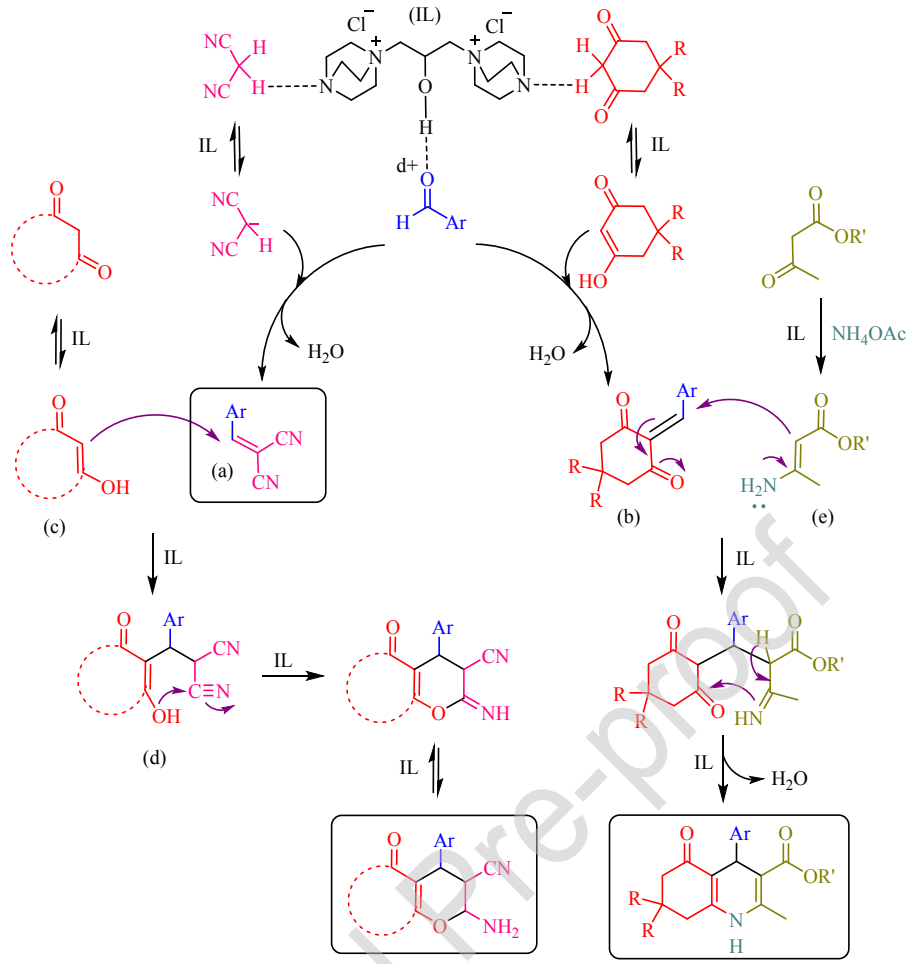
Scheme 2. Synthesis of arylidenemalononitriles by $[(DABCO)_2C_3H_5OH]\cdot 2Cl$.



Scheme 3. One-pot three-component reaction of different aldehydes, malononitrile and 1,3-dicarbonyl derivatives, catalyzed by $[(DABCO)_2C_3H_5OH]\cdot 2Cl$ in water.



Scheme 4. $[(DABCO)_2C_3H_5OH]\cdot 2Cl$ catalyzed the synthesis of polyhydroquinoline derivatives.



Scheme 5. The plausible mechanisms of the studied reactions in the presence of $[(DABCO)_2C_3H_5OH]\cdot 2Cl$.

Table 1. Optimization of the amounts of the catalyst, temperature and solvent for the synthesis of arylidenemalononitrile (entries 1-13), tetrahydrobenzo[*b*]pyran (entries 14-18) and polyhydroquinoline (entries 19-28) derivative of 4-chlorobenzaldehyde

Entry	Catalyst (mg)	Solvent	Temp. (°C)	Time (min)	Yield (%)
1	-	Solvent-free	100 °C	90	Trace
2	10	Solvent-free	100 °C	90	Trace
3	20	Solvent-free	100 °C	90	Trace
4	50	Solvent-free	100 °C	90	Trace
5	10	C_2H_5OH	r.t.	90	Trace
6	10	C_2H_5OH	Reflux	90	Trace
7	50	C_2H_5OH	Reflux	90	Trace
8	10	H_2O	r.t.	120	Not completed
9	10	H_2O	50 °C	55	100(82)[a]
10	10	H_2O	Reflux	10	100(91)[a]
11	10	H_2O	70 °C	50	100(93)[a]
12	10	H_2O	85 °C	8	100(95)[a]
13	20	H_2O	85 °C	11	100(90)[a]
14	10	Solvent-free	100 °C	60	Trace
15	10	C_2H_5OH	Reflux	60	100(85)[a]
16	10	H_2O	50 °C	30	100(75)[a]
17	10	H_2O	Reflux	10	100(95)[a]
18	20	H_2O	Reflux	15	100(95)[a]
19	-	Solvent-free	100 °C	120	Trace
20	-	C_2H_5OH	Reflux	90	Trace
21	-	H_2O	Reflux	90	Trace
22	10	H_2O	Reflux	120	Not completed
23	20	H_2O	Reflux	120	Not completed
24	10	C_2H_5OH	Reflux	120	Not completed
25	10	Solvent-free	100 °C	50	100(84)[a]
26	30	Solvent-free	100 °C	55	100(87)[a]
27	30	Solvent-free	120 °C	10	100(95)[a]
28	-	Solvent-free	120 °C	60	Trace

[a]Isolated yields

Table 2. The Knoevenagel reaction of aromatic aldehydes and malononitrile in the presence of $[(DABCO)_2C_3H_5OH]\cdot 2Cl$ in water medium

Entry	Aldehyde	Pro.	Time (min)	Yield (%)[a]	Mp (°C)	[Ref.]
1	C_6H_5-	1a	8	91	82-84	[12]
2	4-ClC_6H_4-	1b	8	95	161-163	[68]
3	2-ClC_6H_4-	1c	11	91	94-96	[36]
4	4-BrC_6H_4-	1d	10	94	162-164	[26]
5	4-OHC_6H_4-	1e	11	93	187-189	[68]
6	4-OH-3-$CH_3OC_6H_3$-	1f	15	91	133-135	[27]
7	4-$CH_3OC_6H_4$-	1g	13	91	113-115	[26]
8	4-$CH_3C_6H_4$-	1h	11	90	138-140	[32]
9	2-$CH_3C_6H_4$-	1i	13	91	100-102	[36]
10	4-$NO_2C_6H_4$-	1j	13	90	161-163	[28]
11	3-$NO_2C_6H_4$-	1k	17	89	102-104	[12]
12	2-$NO_2C_6H_4$-	1l	19	89	140-142	[36]
13	Terephthalaldehyde	1m	17	92	268-270	[31]

[a]The yields are related to the isolated products

Table 3. Synthesis of pyran derivatives (tetrahydrobenzo[*b*]pyran (2a-h), Pyrano[2,3-*d*]-pyrimidinone(thione) (3i-p), and dihydropyrano[3,2-*c*]chromene (4q-x)) using 2.8 mol% of $[(DABCO)_2C_3H_5OH]\cdot 2Cl$ in refluxing water

Entry	Ar	Pro.	Time (min)	Yield (%)[a]	Mp (°C)	[Ref]
1	C_6H_5-	2a	30	90	225-228	[53]
2	4-ClC_6H_4-	2b	10	95	208-210	[68]
3	2-ClC_6H_4-	2c	15	93	213-215	[69]
4	4-$NO_2C_6H_4$-	2d	15	89	176-179	[70]
5	3-$NO_2C_6H_4$-	2e	15	87	202-205	[53]
6	2-$NO_2C_6H_4$-	2f	15	90	213-217	[70]
7	4-$CH_3OC_6H_4$-	2g	30	87	200-204	[70]
8	4-HOC_6H_4-	2h	25	85	210-214	[8]
[b]9	C_6H_5-	3i	30	86	224-225	[71]
[b]10	4-ClC_6H_4-	3j	15	93	237-240	[52]
[b]11	4-FC_6H_4-	3k	10	87	260-264	[52]
[b]12	4-$NO_2C_6H_4$-	3l	15	83	236-237	[53]
[b]13	3-$NO_2C_6H_4$-	3m	20	85	266-268	[52]
[b]14	4-$CH_3OC_6H_4$-	3n	30	88	266-270	[46]
[c]15	4-ClC_6H_4-	3o	30	80	>300	[70]
[c]16	4-$NO_2C_6H_4$-	3p	35	80	234-235	[53]
17	C_6H_5-	4q	20	95	252-254	[19]
18	4-ClC_6H_4-	4r	60	98	259-261	[72]
19	3-ClC_6H_4-	4s	30	95	240-242	[72]
20	4-$NO_2C_6H_4$-	4t	60	95	257-258	[45]
21	3-$NO_2C_6H_4$-	4u	60	93	250-252	[73]
22	4-$CH_3OC_6H_4$-	4v	20	95	219-220	[19]
23	3-$CH_3OC_6H_4$-	4w	30	96	242-244	[73]
24	Pyridine-4-carbaldehyde	4x	30	95	249-251	[73]

[a] The yields are related to the isolated products [b]X=O [c]X=S

Table 4. Synthesis of various polyhydroquinolines in the presence of $[(DABCO)_2C_3H_5OH]\cdot 2Cl$

Entry	Ar	R	R'	Product	Time (min)	Yield (%)a	Mp(°C)	Ref.
1	C_6H_5-	CH_3	C_2H_5	5a	14	92	222-224	[23]
2	4-ClC_6H_4-	CH_3	C_2H_5	5b	10	95	236-238	[74]
3	4-BrC_6H_4-	CH_3	C_2H_5	5c	15	93	252-254	[23]
4	4-OHC_6H_4-	CH_3	C_2H_5	5d	15	90	232-235	[57]
5	4-OH-3-$CH_3OC_6H_3$-	CH_3	C_2H_5	5e	12	95	227-230	[63]
6	4-$CH_3OC_6H_4$-	CH_3	C_2H_5	5f	14	93	255-257	[74]
7	3-$CH_3OC_6H_4$-	CH_3	C_2H_5	5g	10	93	200-203	[23]
8	3,4,5-$(CH_3O)_3C_6H_2$-	CH_3	C_2H_5	5h	12	90	192-194	[57]
9	4-$(CH_3)_2NC_6H_4$-	CH_3	C_2H_5	5i	8	95	229-231	[57]
10	2-$CH_3C_6H_4$-	CH_3	C_2H_5	5j	21	87	210-212	[75]
11	4-$NO_2C_6H_4$-	CH_3	C_2H_5	5k	37	90	228-232	[76]
12	4-OH-3-$CH_3OC_6H_3$-	H	C_2H_5	5l	11	90	228-230	[63]
13	2-$CH_3C_6H_4$-	H	C_2H_5	5m	21	87	234-236	New
14	3-$NO_2C_6H_4$-	H	C_2H_5	5n	35	85	206-208	[77]
15	4-ClC_6H_4-	CH_3	CH_3	5o	14	94	257-259	[78]
16	4-ClC_6H_4-	H	CH_3	5p	17	91	198-200	[78]
17	Terephthalaldehyde	CH_3	C_2H_5	5q	12	93	>300	[76]

[a] The yields are related to the isolated products.

Table 5. Comparison of the activity of $[(DABCO)_2C_3H_5OH]$•2Cl with previously reported catalysts in the synthesis of 2-(4-Chlorobenzylidene)malononitrile 1b (entries 1-8), 2-amino-4-(4-chlorophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4*H*chromene-3-carbonitrile 2b (entries 9-17), and ethyl 2,7,7-trimethyl-4-(4-cholorophenyl)-5oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate 5b (entries 18-26).

Entry	Catalyst	Amount	Conditions	Time (min.)	Yield (%)[a]	Ref.
1	SiO_2/NH_4OAc	200 mg	CH_2Cl_2/60 °C	390	90	[79]
2	Na_2S/Al_2O_3	20 mol% on 500mg	CH_2Cl_2/reflux	30	90	[32]
3	Silica-*L*-prolin	100 mg	CH_3CN/80 °C	540	95	[27]
4	Fe_3O_4 MNPs–Guanidine	5 mg	PEG/H_2O/r.t.	150	96	[26]
5	CSC-Star-Glu-IL2	200 mg	H_2O/r.t.	180	88	[28]
6	KF-CP	160 mg	C_2H_5OH /40 °C/ultrasound	20	95	[33]
7	$Fe_3O_4@SiO_2@CuO–Fe_2O_3$ MNPs	30 mg	H_2O/reflux	7	91	[31]
8	$[(DABCO)_2C_3H_5OH]\cdot2Cl$	10 mg (2.8 mol%)	H_2O /85 °C	8	95	This work
9	SO_4^{2-}/MCM-41	25 mg	C_2H_5OH /reflux	60	80	[38]
10	Urea	10 mol%	C_2H_5OH:H_2O (1:1)/r.t.	180	87	[41]
11	$Fe_3O_4@SiO_2$/DABCO	50 mg	H_2O /80 °C	25	90	[42]
12	Urea:ChCl	2 mL	80 °C	60	92	[48]
13	DABCO	10 mol%	H_2O/reflux	120	94	[49]
14	$[H_2\text{-DABCO}][H_2PO_4]_2$	50 mg	C_2H_5OH:H_2O (2:1)/reflux	15	95	[70]
15	Fe_3O_4@MCM-41@Zr-piperazine-MNPs	30 mg	C_2H_5OH:H_2O (7:3)/ 75 °C	10	90	[53]
16	2,2,2-trifluoroethanol	2 mL	reflux	300	95	[44]
17	DABCO	20 mol%	H_2O/r.t.	150	68	[8]
18	$[(DABCO)_2C_3H_5OH]\cdot2Cl$	10 mg (2.8 mol%)	H_2O/reflux	10	95	This work
19	$[C_4(DABCO\text{-}SO_3H)_2]\cdot4Cl$	10 mg	Solvent-free/100 °C	18	92	[23]
20	ED/MIL-101(Cr)	500 mg	C_2H_5OH/80 °C	120	90	[56]
21	*L*-Proline	10 mol%	C_2H_5OH /reflux	360	87	[57]
22	$BiBr_3$	2 mol%	CH_3CH_2OH/r.t.	150	93	[59]
23	FSM-16-SO_3H	40 mg	C_2H_5OH /reflux	20	88	[64]
24	La^{3+}/4A	100 mg	C_2H_5OH /reflux	240	96	[22]
25	SBA-15@AMPD-Co	8 mg	Solvent-free/100 °C	35	97	[80]
26	MBM-450	50 mg	C_2H_5OH /reflux	40	92	[74]
27	$[(DABCO)_2C_3H_5OH]\cdot2Cl$	30 mg (8.5 mol%)	Solvent-free/120 °C	10	95	This work

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Credit

This article introduces $[(DABCO)_2C_3H_5OH]\cdot 2Cl$ as an efficient, affordable, and green ionic liquid catalyst in the promotion of the synthesis of arylidenemalononitrile, pyran and polyhydroquinoline derivatives.

It should be emphasized that the submission is original, not under consideration for publication elsewhere and that all authors are aware of the submission and agree to its publication.

Highlights

- $[(DABCO)_2C_3H_5OH]\cdot 2Cl$ is prepared and introduced as an inexpensive and eco-friendly dicationic ionic liquid catalyst.
- Introduction of a simple method for the preparation of arylidenemalononitrile, pyran and polyhydroquinoline derivatives.
- Easy separation and recyclability of the catalyst.