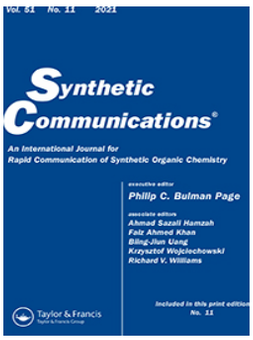

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Dual solvent-catalyst role of deep eutectic solvents in Hantzsch dihydropyridine synthesis

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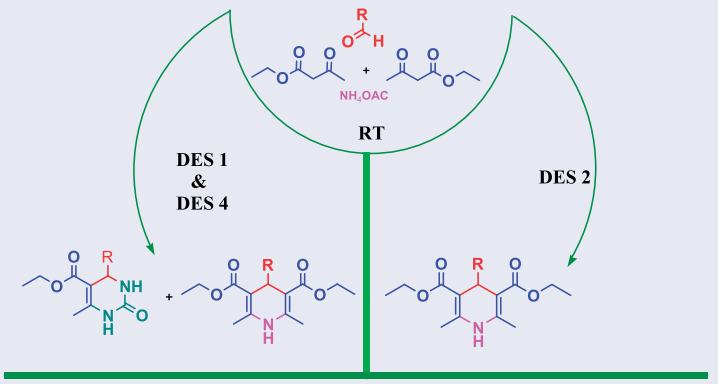
ABSTRACT

Deep eutectic solvents are a class of new generation green solvents formed from two or more components, which furnish a new homogeneous liquid phase with lower melting point than the individual components. Here, for the first time, dual role of DES as catalyst and reaction medium was studied for the synthesis of symmetric dihydropyridine derivatives from aldehyde, ethyl acetoacetate and ammonium acetate. The present article reports the suitability of six DESs for Hantzsch dihydropyridine synthesis at room temperature. Among this, DES 2 ($ZrOCl_2.8H_2O$ and ethylene glycol at 1:2 ratio) was found to be the catalyst of choice with excellent recyclability. The role of DES in the present protocol was to activate the reactants through strong hydrogen bonding interaction and provide suitable medium for the reaction. The major advantages of DESs for the titled reaction are the easy preparation, low cost, non-volatility, biodegradability, simple catalytic process, excellent conversion and the reusability.

GRAPHICAL ABSTRACT



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KEYWORDS
Deep eutectic solvents; dihydropyridine derivatives; Hantzsch pyridine synthesis; multicomponent reaction

Introduction

Recently, most of the fields in chemistry have focused on sustainable methods; these include ILs, deep eutectic solvents and their alternatives.[1] The physicochemical properties of DESs can be tuned by changing the constituents used and also can have a significant

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Supplemental data for this article can be accessed on the publisher's website

influence on the way these interact with other molecules.[2] DESs are found to be most efficient in terms of its preparation method, recycling process, biodegradability, toxicity, cost effectiveness etc. Deep eutectic solvents (DESs) are a new family of green solvents, based on a hydrogen bond donor (HBD) and a hydrogen bond acceptor (HBA) which together have a melting point low enough to be used as solvents.[3–6] Some of them show glass transition temperature instead of melting point and are referred to as low transition temperature mixtures (LTTMs).[7] DESs have some special properties like wide liquid range, non-flammability and non-volatility, safe to operate (because they are generally formed from solids and inflammable liquids and avoid the risk of explosion) which makes them applicable in diverse fields.[8,9] A prosperous increase was observed in the research based on deep eutectic solvents in many fields such as polymerization,[10] metal processing application (like metal electrodeposition, metal electropolishing, metal extraction and the processing of metal oxides),[11] biomass processing,[12] catalysis,[13]ionothermal synthesis,[14] gas adsorption,[15] nanotechnology,[16] biotransformation etc.[17] Deep eutectic solvents are widely applied as sustainable media as well as catalysts in organic synthesis. Some recent advances in organic reactions using DESs include DABCO-derived quaternary ammonium salts for the preparation of terpyridines,[18] synthesis of substituted pyridopyrimidines in low transition temperature mixture (LTTM),[19] synthesis of benzimidazoles in deep eutectic solvents,[20] synthesis of polymers etc.[21] They are also used in different organic transformations like cyclization reactions, oxidation reactions, reducing reactions, addition reactions, multicomponent reactions, replacement reactions and condensation reactions.[22]

In the present article, the catalytic activity of six deep eutectic solvents (DES 1- DES 6) are reported for the synthesis of symmetric 1,4-dihydropyridine derivatives based on the physicochemical properties and the nature of the constituents used. To the best of our knowledge, there are no previous reports on the DES catalyzed synthesis of 1,4-dihydropyridine derivatives using aldehyde, ethyl acetoacetate and ammonium acetate (symmetric Hantzsch pyridine synthesis). In 2013, Suhas Pednekar *et al* reported the synthesis of polyhydroquinolines (via asymmetric Hantzsch pyridine synthesis) using aldehyde, dimedone, ethyl acetoacetate and ammonium acetate in the presence of ChCl/urea (1:2) deep eutectic system at 60 °C.[23] L. Wang *et al.* in 2014 reported the same reaction, but with a different composition of DES (ChCl/urea at 1:1 ratio) at 80 °C.[24]

Due to the unprecedented biological and chemical activities of dihydropyridine scaffolds, they have revolutionized pharmaceutical research in recent times. They constitute a well explored scaffold which binds to multiple receptors and are the main fulcrum of many drugs that have been manufactured and used all over the world.[25] Several 1,4 DHP derivatives were used for the treatment of hypertension, coronary diseases; some of them are nifedipine, amlodipine, felodipine, Isradipine, Nisoldipine, Nimodipine, Nicardipine etc. (Fig. 1).[26,27] They act as calcium channel modulators and used for the treatment of hypertension, as well as precursor to agrochemicals and pharmaceuticals.[28] 1,4-Dihydropyridine skeleton is also present in many vasodilator, bronchodilator, antidiabetic, antitumour, antiatheroschlerotic, geroprotective, and hepatoprotective agents.[29]

Different methods are available for the synthesis of DHP derivatives in the literature; these include the use of catalysts such as BTPPC,[30] Cobalt Nanoparticles,[31] Fe_3O_4@chitosan,[32] melamine trisulfonic acid (MTSA),[33] ILOS@Fe/

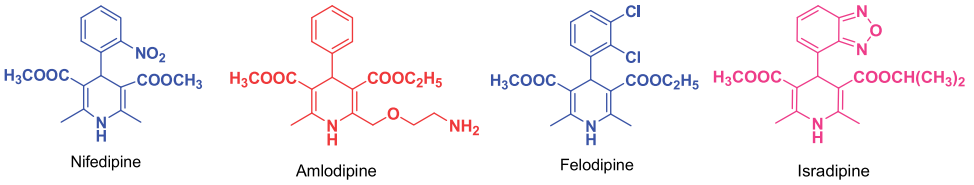


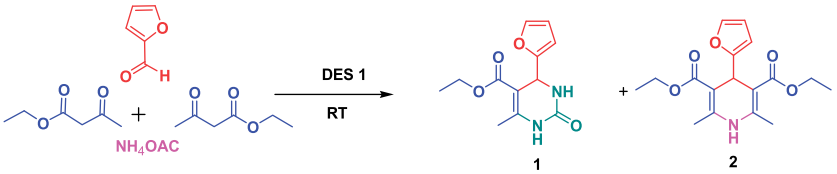
Figure 1. Selective examples for clinically important 1,4-dihydropyridine derivatives.

TSPP,[34] Zr-SBA-16,[35] cadmium metal-organic framework,[36] Ti-SBA-15@IL-BF_4,[37] TiO_2 NPs,[38] silica-coated Fe_3O_4 nanoparticles,[39] $MgAl_2$ hydrotalcites (HT),[40] $CoFe_2O_4$@SiO_2-NH_2-Co^{II} etc.[41] Many of the aforementioned protocols suffer from major or minor limitations, such as use of expensive and toxic catalyst, tedious reaction setup, require prolonged reaction times, side product formation, presence of volatile solvents etc. The search for new green and efficient procedures under mild conditions is still actively continued. This article focuses on the replacement of conventional methods using renewable deep eutectic solvent in symmetric Hantzsch dihydropyridine synthesis.

Results and discussion

Recently, six DESs (formed from $ZrOCl_2.8H_2O$/$CeCl_3.7H_2O$ with urea, ethylene glycol & glycerol) were reported and their activities were compared in Kabachnik-Fields reaction for the synthesis of α-aminophosphonates.[42–44] This manuscript reports the exploration of the applicability of DESs as catalyst for the synthesis of 1,4-dihydropyridine derivatives via Hantzsch reaction. A reaction was performed by stirring benzaldehyde (1 mmol), ethyl acetoacetate (2 mmol) and ammonium acetate (1.5 mmol) at room temperature under solvent free and catalyst free condition. Only traces of the product (with impurity) were obtained after 6 h. Later, the same reaction was repeated using DES 1, excellent yield with high purity was obtained within 30 min at room temperature and this indicated the necessity of a catalyst in the reaction. Reaction was repeated using some other aldehydes like 4-chlorobenzaldehyde, 4- bromobenzaldehyde and furfural. In the presence of DES 1, a mixture of dihydropyridine (1) and dihydropyrimidinone (2) was observed with some aldehydes like furfural as shown in Scheme 1. The GC profile and mass spectra of the corresponding dihydropyridine (1) and dihydropyrimidinones (2) are given in Figure 2.

The formation of dihydropyrimidinones (Biginelli product with m/z = 250) is due to the presence of urea in DES 1(mixture of $ZrOCl_2.8H_2O$ and urea at 1: 5 ratio), which will act as a coupling agent as well as catalyst in the reaction (over all, a triple role of DES 1 was observed here, as catalyst, reaction medium and reagent). Separate experiments were conducted using the remaining five DESs (DES 2-DES 6) in the same reaction using furfural (1 mmol), ethyl acetoacetate (2 mmol) and ammonium acetate (1.5 mmol) at RT. Similar to DES 1, a mixture of dihydropyridine and dihydropyrimidinone was observed using DES 4 ($CeCl_3.7H_2O$- Urea at 1: 5 ratio) due to the multiple action of DES as catalyst as well as reagent. Higher yield was observed using DES 2 and low yield (with impurity) were observed for DES 3, DES 5 and DES 6. Even though, DES 2 is not acidic in the conventional sense (pH = 6.99) compared to DES 5 (pH = 4.44) and DES 6 (pH = 4.27), its activity may be due to the strong ability to activate the reactants through hydrogen bonding interaction. In addition to this, the lower viscosity of



Scheme 1. Hantzsch pyridine synthesis in DES 1.

DES 2 may also favor the reaction as it is one of the most important physical properties of a solvent.[42–43] Both these effects contributed to the better activity of DES 2. $CeCl_3.7H_2O$ based deep eutectic solvents (DES 4- DES 6) were found to be less reactive for the synthesis of dihydropyridine derivatives compared to $ZrOCl_2.8H_2O$ based DESs (DES 1- DES 3). The observations are given in Table 1.

DES 1 and DES 4 may create problems in future studies, especially during the studies based on substrate scope by forming mixture of products (dihydropyridine and dihydropyrimidinone) and recycling. So DES 1 and DES 4 were eliminated from further catalytic activity studies. Single product with higher yield was observed using DES 2 (formed from $ZrOCl_2.8H_2O$ and ethylene glycol at 1:2 ratio) and was selected for future optimization studies. In order to find out the optimum catalyst (DES 2) needed for Hantzsch pyridine synthesis, experiments were conducted under different catalytic conditions (0.2–0.8 mmol of DES 2) using benzaldehyde, ethyl acetoacetate and ammonium acetate as model substrates for about 30 min (Table 2) at room temperature. An excellent yield was obtained using 0.6 mmol of DES 2 (95%, Table 2, Entry 6) and after that there was no considerable change in the product yields (Table 2, Entry 7 and 8). The use of DES 2 at 0.6 mmol was found to be the optimum amount of catalyst (Table 2, Entry 6) needed for the synthesis of 1,4-dihydropyridine derivatives from benzaldehyde (1 mmol), ethyl acetoacetate (2 mmol) and ammonium acetate (1.5 mmol) at room temperature.

Using this optimum catalytic condition, the efficacy and versatility of DES 2 was monitored by repeating the experiment using different varieties of aldehydes and the results are summarized in Table 3. A variety of aromatic aldehydes were smoothly converted in to corresponding dihydropyridine derivatives with excellent efficiency (Table 3, Entry 1–10). Here at first, the reaction was performed using benzaldehyde by doing TLC analysis in each 5 min. The reaction was completed within 10−30 min with an yield above 90% (Table 3). The process was repeated using different substituted benzaldehydes with ethyl acetoacetate and ammonium acetate and the reaction was monitored by TLC. Excellent yields were obtained for both electron donating and electron withdrawing substituents (Table 3, Entry 1–5). Disubstituted aromatic aldehyde (veratraldehyde) was also converted to the corresponding dihydropyridine derivative with excellent efficiency (Table 3, Entry 6). Further, the activity was checked using heteroaromatic aldehydes like furfural and thiophene aldehyde, efficient conversion was observed with DES 2 (Table 3, Entry 7 & 8). Appreciable yield was obtained for aldehyde with bulky substrate (1-Naphthaldehyde) with high purity (Table 3, Entry 9). An outstanding yield was observed for cinnamaldehyde without any side product formation (Table 3, Entry 10).

The $ZrOCl_2.8H_2O$/ethylene glycol DES employed played the dual role of catalyst and solvent, no additional organic solvent was required in the reaction. All the

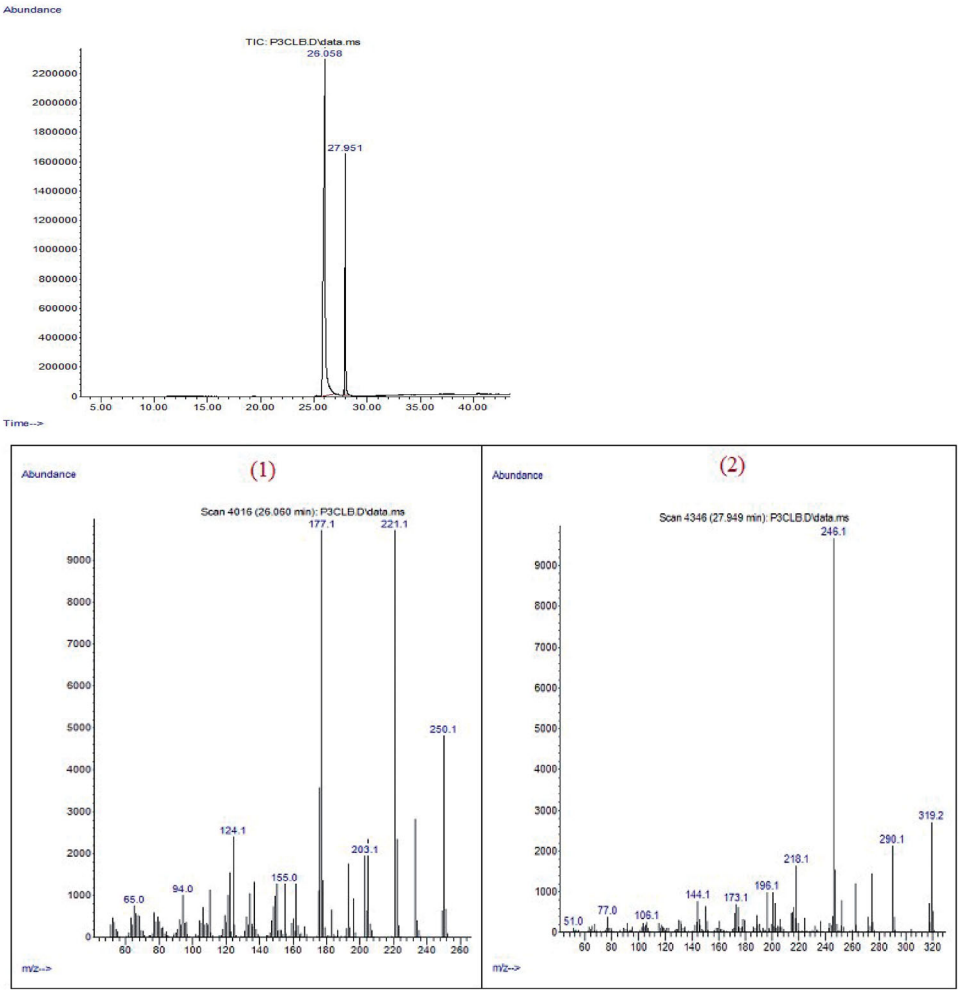


Figure 2. GC profile and mass spectra of the corresponding dihydropyrimidinone with m/z = 250 (1) and dihydropyridine with m/z = 319 (2).

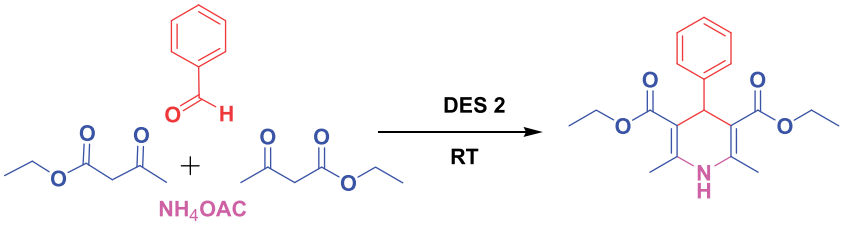
Table 1. Hantzsch pyridine synthesis using six DESs.

Entry	DES	Mole ratio	Abbreviation	pH	Viscosity (η)/ (mPa.s)	Catalytic activity
1	Zr: U	1:5	DES 1	2.20	52.40	Mixture of products
2	Zr: EG	1:2	DES 2	6.93	149.50	Higher yield and purity
3	Zr: Gly	1:2	DES 3	6.97	532.73	Lower yield
4	Ce: U	1:5	DES 4	4.71	195.39	Mixture of products
5	Ce: EG	1:2	DES 5	4.44	290.40	Lower yield
6	Ce: Gly	1:2	DES 6	4.27	868.73	Lower yield

Reaction conditions: furfural (1 mmol), ethyl acetoacetate (2 mmol) and ammonium acetate (1.5 mmol), RT.

dihydropyridine derivatives were obtained with high purity and the catalyst was removed from the reaction mixture by simply washing with, since DES was highly soluble in water. The products were characterized by using TLC, melting point measurements, GCMS and ^{1}H & ^{13}C NMR spectra.

Table 2. Optimization of catalyst for Hantzsch pyridine synthesis.



Entry	Amount of DES 2 (g)	Amount of DES 2 (mmol)	Time (min)	Yield (%)
1	–	–	30	Trace
2	0.009	0.2	30	60
3	0.013	0.3	30	75
4	0.019	0.4	30	80
5	0.022	0.5	30	82
6	0.026	0.6	30	95
7	0.031	0.7	30	96
8	0.035	0.8	30	96

Reaction conditions: benzaldehyde (1 mmol), ethyl acetoacetate (2 mmol) and ammonium acetate (1.5 mmol), RT.

Mechanism of the reaction

A possible mechanism for DES 2 catalyzed Hantzsch dihydropyridine synthesis was proposed in Scheme 2. The main role of DES here was to activate the reactants and intermediates through strong hydrogen bonding interactions.

Here, a hydrogen bonded activated complex was formed by the interaction of DES with the carbonyl group of aldehyde, which was followed by the formation of Knoevenagel adduct (intermediate 1) by the nucleophilic attack of one equivalent of ethyl acetoacetate to this activated complex. Or another ethyl acetoacetate was activated by DES followed by the ester enamine formation (intermediate 2) by the nucleophilic attack of ammonia (formed from ammonium acetate) on the carbonyl of ethyl acetoacetate. Finally in the presence of DES, cyclocondensation of both Knoevenagel adduct (intermediate 1) and ester enamine (intermediate 2) took place via Michael type addition yielding the DHP derivative.

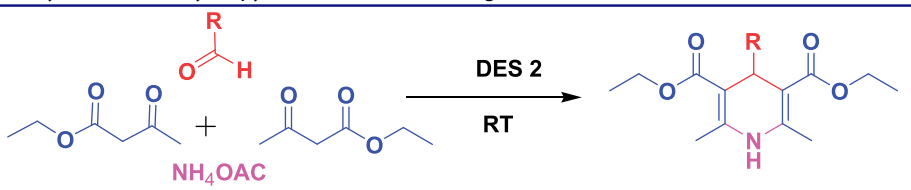
Reusability of DES

It is very important to recover and reuse the catalyst in the aspect of green chemistry and here the reusability of deep eutectic solvent was checked. Highly water soluble deep eutectic solvents are separated by washing the product with water. The catalyst can be reused up to five times for the synthesis of dihydropyridine derivatives without remarkable loss in its activity. The details of the reusability study are given in Table 4 (using benzaldehyde, ethyl acetoacetate, ammonium acetate as model substrates).

Comparison with previous reports

A detailed comparative study of the present catalyst was performed with some prior reports using benzaldehyde, ethyl acetoacetate and ammonium acetate as model

Table 3. Synthesis of dihydropyridine derivatives using DES 2.



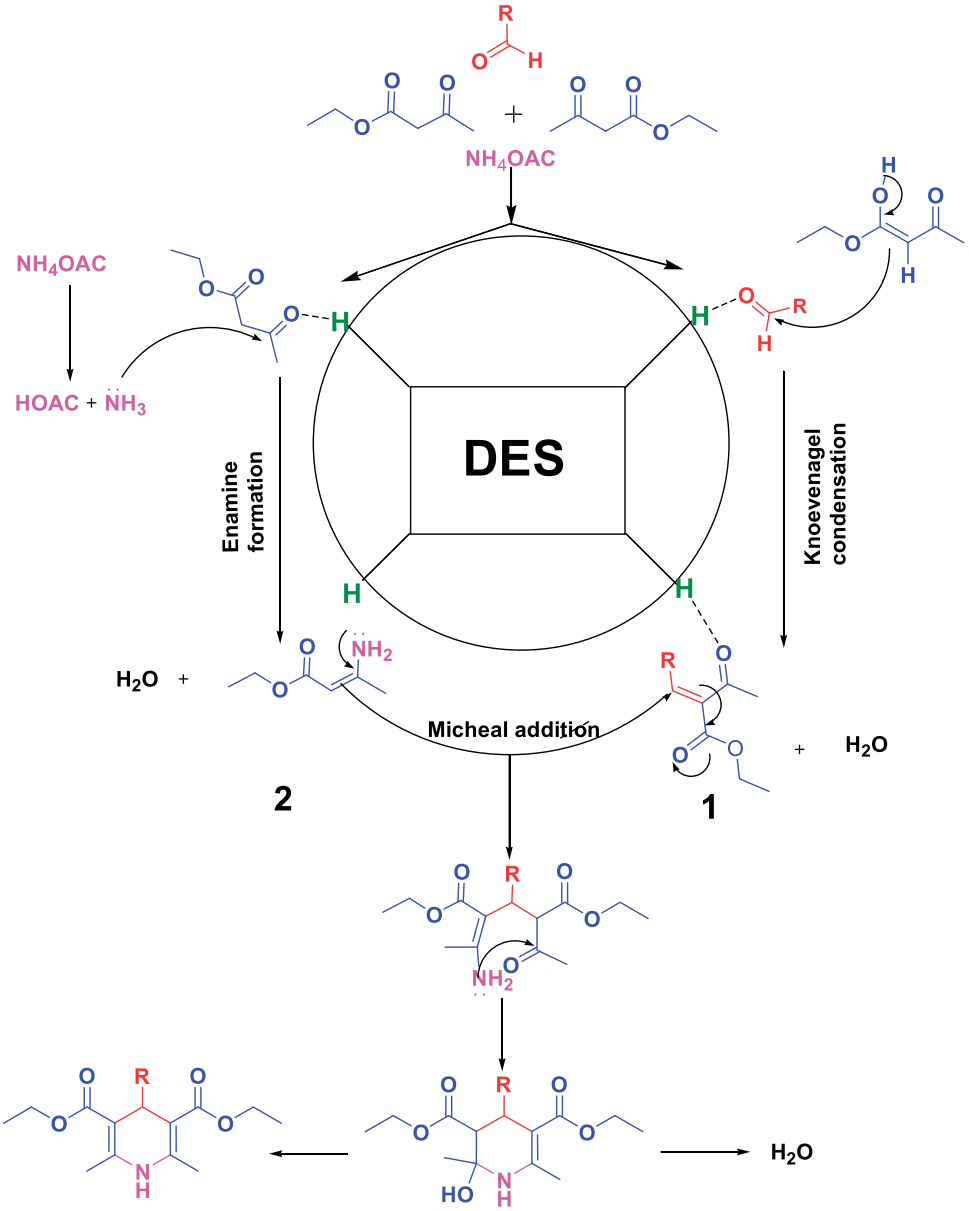
Entry	R	Time (min)	Yield (%)
1	C_6H_5	20	95
2	4-Cl-C_6H_4	15	96
3	4-Br-C_6H_4	15	90
4	4-MeO-C_6H_4	15	95
5	4- NO_2- C_6H_4	15	95
6	3,4,-$(OMe)_2$-C_6H_3	25	97
7	1-Furyl	25	92
8	1-Thienyl	10	96
9	1-Naphthyl	30	95
10	Cinnamyl	10	98

Reaction conditions: benzaldehyde (1 mmol), ethyl acetoacetate (2 mmol) ammonium acetate (1.5 mmol) and DES 2 (0.6 mmol), RT.

substrates, the results are presented in Table 5. To the best of our knowledge, there was no previous report for the synthesis of symmetric 1,4-dihydropyridine derivatives from aldehyde, ethyl acetoacetate and ammonium acetate in the presence of deep eutectic solvents. In 2013, S.S. Mansoor *et al.* reported the synthesis of 1,4-DHPs using melamine trisulfonic acid (MTSA), but it required prolonged reaction time (4 h) and temperature. In addition to this, tedious work up process was required for the synthesis of MTSA (Table 5, Entry 1).

Symmetric dihydropyridines were synthesized using lewis acidic Zr-SBA-16 by R. Maheswari *et al.* in 2015. Here also the catalyst preparation required more steps and time. DHPs were synthesized in the presence of solvents and temperature, also there was no discussion about the recycling studies (Table 5, Entry 2). Similarly, Cd metal-organic framework was used as a catalyst for the synthesis of dihydropyridine in 2017 (Table 5, Entry 3). Here the synthesis of the catalyst was more difficult and involved step by step process. This included (1) preparation of N,N′-(oxybis(4,1-phenylene))-bis(1-(pyridin-4-yl)methanimine) (OPP), (2) synthesis of {[$Cd_3(BDC)_3(OPP)(DMF)_2$]. 2DMA}n (TMU-33) and (3) synthesis of TMU-33 nanostructures and was the main difficulty related with this metal organic framework. Titanium incorporated mesoporous material supported ionic liquid, titanium dioxide nanoparticles, and $MgAl_2$ hydrotalcites (HT) were also used for the synthesis of Hantzsch esters with excellent yield and recyclability (Table 5, Entry 4-6). But all these methods required difficult preparation process and the use of organic solvents. A magnetically heterogeneous $CoFe_2O_4$@SiO_2-NH_2-Co^{II} nanoparticle was reported by Allahresani *et al.* in 2020 (Table 5, Entry 7). Here also, the synthesis part was very hard, required five synthesis steps. This included (1) synthesis of $CoFe_2O_4$ nanoparticles, (2) synthesis of $CoFe_2O_4$@SiO_2, (3) synthesis of NH_2-Pr (4) synthesis of NH_2-Pr-Co^{II} and (5) synthesis of $CoFe_2O_4$@SiO_2-NH_2-Co^{II}.

The comparison highlights the urgency to introduce a sustainable catalyst for the easy preparation dihydropyridine derivatives through Hantzsch reaction. Here, DES 2



Scheme 2. Probable mechanism for Hantzsch pyridine synthesis using DES 2.

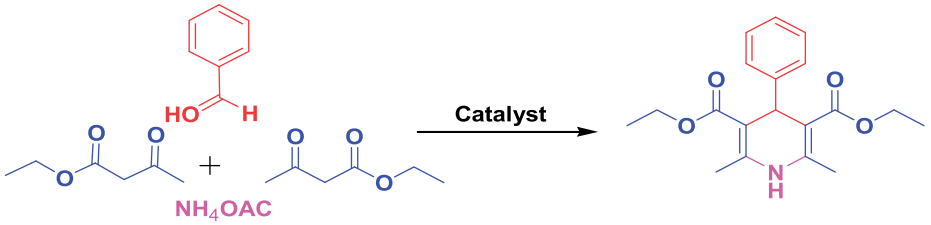
(formed from $ZrOCl_2.8H_2O$ and ethylene glycol at 1:2 ratio) was used as a catalyst for the synthesis of dihydropyridine derivatives using different aldehydes containing both electron donating and withdrawing substituents. The main advantages of the present protocol were the easy method of preparation (formed by simple mixing of the constituents with gentle heating, the clear and colorless homogeneous mixture was formed with hundred percentage atom economy), relatively low cost, low toxicity, biodegradability, eco-friendly, dual role (acts as catalyst as well as reaction medium and no additional

Table 4. Recyclability of the DES 2.

No. of runs	Yield (%)
1	95
2	91
3	90
4	88
5	85

Reaction conditions: benzaldehyde (1 mmol), ethyl acetoacetate (2 mmol) ammonium acetate (1.5 mmol), RT.

Table 5. Comparison of DES 2 with some prior reports.



Entry	Catalyst	Reaction condition	Yield (%)	Reusability	Ref.
1	MTSA	4h/60 °C	86	4 Runs	33
2	Zr-SBA-16	3h/80 °C/Ethanol	77	–	35
3	Cd metal-organic framework	RT/2 h/Ethanol	97	4 Runs	36
4	Ti-SBA-15@IL-BF_4	2h/80 °C/Ethanol	94	5 Runs	37
5	TiO_2 NPs	2 h/80 °C/Ethanol	92	6 Runs	38
6	$MgAl_2$ hydrotalcites (HT)	6.5 h/RT/Acetonitrile	61	–	40
7	$CoFe_2O_4$@SiO_2-NH_2-Co^{II}	2.5h/Reflux/Ethanol	85	6 Runs	41
8	DES 2	20 min/RT	95	5 Runs	Present work

Reaction conditions: benzaldehyde, ethyl acetoacetate, ammonium acetate.

organic solvent was required) and recyclability. These attributes make deep eutectic solvents more dominant over other previously reported catalysts for the synthesis of symmetric Hantzsch Dihydropyridine Synthesis.

Conclusion

Dual solvent-catalyst activity of six deep eutectic solvents (combination of $ZrOCl_2.8H_2O/CeCl_3.7H_2O$ with urea, ethylene glycol and glycerol) were compared and a sustainable solvent-free procedure for the multicomponent synthesis of symmetric dihydropyridine derivatives was developed at room temperature. Among the six DES (DES 1- DES 6), mixture of both dihydropyridine and dihydropyrimidinones (Biginelli product) were observed while using DES 1 and DES 4 ($ZrOCl_2.8H_2O/CeCl_3.7H_2O$ with urea at 1:5 ratio). This was due to the presence of urea in the DES mixture, which acted as a coupling agent as well as a constituent of the catalyst in the reaction and was removed from further studies. DES 2 (combination of $ZrOCl_2.8H_2O$/ethylene glycol at 1:2 ratio) was established as the premier solvent- catalyst system with excellent recyclability. This may be due to the lower viscosity and stronger hydrogen bonding ability compared to the remaining deep eutectic solvents. Substrate scope was checked by

repeating the experiment using different aldehydes like monosubstituted and disubstituted aromatic aldehydes, heteroaromatic aldehydes, unsaturated aldehydes etc. Excellent conversion was observed for all the aldehydes with high purity. The catalyst was recovered from the mixture by washing with water and was reused up to 5 catalytic cycles without much loss in its activity. A detailed comparative study was performed with some previous reports and the dominance of the described catalyst over others included simple method of preparation of DES without any additional purification step, dual activity as catalyst and medium (no need of additional organic solvent), high and fast catalytic activity, low cost, non volatility, simple reaction condition (reaction performed at room temperature without more experimental setup). In addition to this, the catalyst could be reused up to five runs without any remarkable loss in its activity and all these make the procedure attractive.

Experimental section

Preparation of DES

By heating (at 40–60 °C for 10–15 min) a mixture of metal chloride hydrate ($ZrOCl_2.8H_2O$/$CeCl_3.7H_2O$) and hydrogen bond donors (urea, ethylene glycol and glycerol) at different molar ratios, clear, colorless, homogeneous liquids were formed. After cooling, the mixtures could be used for further studies without any purification process.[42,43] Full experimental details with recycling process of deep eutectic solvents are given in the supplementary information.

General procedure for the synthesis of diethyl 2,6-dimethyl-4-phenyl-1,4-dihydropyridine-3,5-dicarboxylate in DES

A mixture of benzaldehyde (1 mmol), ethyl acetoacetate (2 mmol), ammonium acetate (1.5 mmol) and DES (0.2–0.8 mmol) was stirred in an RB flask at room temperature for the time as indicated in Table 3. Completion of the reaction was observed using TLC with hexane- ethyl acetate (1:1) mixture as developing solvent. After completion of the reaction, the mixture was washed with distilled water and filtered and analyzed using TLC, melting point measurements, GCMS and ^1H & ^{13}C NMR spectra. General procedure for Hantzsch dihydropyridine synthesis, structure of synthesized products, melting point, NMR data, GC MS and ^1H & ^{13}C NMR spectra of the compounds can be found in the Supplementary Content section of this article's Web page.

Spectroscopic data of diethyl 2,6-dimethyl-4-phenyl-1,4-dihydropyridine-3,5 dicarboxylate (P1)

White solid (95%); Melting point 157–159 °C; GC-MS (M^+): 329; ^1H NMR (500 MHz, DMSO- d_6) δ ppm: 1.19 (t, 6H), 2.33 (s, 6H), 4.08 (q, 4H), 4.96 (s, 1H), 5.97 (s, 1H, NH), 7.16–7.33 (m, 5H). ^{13}C NMR (125 MHz, DMSO-d_6) δ ppm: 14.0, 19.4, 39.6, 59.5, 104.0, 121.8, 129.0, 131.0, 144.4, 146.5, 166.8.

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