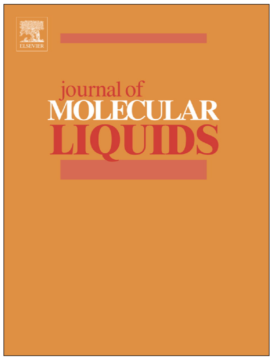

Multicomponent domino reactions in deep eutectic solvent: An efficient strategy to synthesize multisubstituted cyclohexa-1,3-dienamines

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Multicomponent domino reactions in deep eutectic solvent: an efficient strategy to synthesize multisubstituted cyclohexa-1,3-dienamines

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Abstract:

The multicomponent domino reactions of ketones, aldehydes and malononitrile in a deep eutectic solvent (DES) were developed. Urea-choline chloride based DES is effective dual solvents/organocatalysts and affording a series of multisubstituted cyclohexa-1,3-dienamines in good to excellent yields under mild conditions. The DES could be easily recycled several times without appreciable loss of activity. The present protocol offers advantages in terms of environmental sustainability and efficient utilization of natural resources, operational simplicity and short reaction times.

Keywords: multicomponent domino reactions, deep eutectic solvent, multisubstituted cyclohexa-1,3-dienamines, green chemistry

1. Introduction

Recently, a new generation of green solvents, namely deep eutectic solvents (DESs) had emerged an environmentally-benign media alternative to hazardous organic solvents in a variety of applications [1-4]. In fact, DESs are liquid systems formed from an eutectic mixture, and due to the similar common properties of ionic liquids (ILs) serve as a low-cost alternative to ILs [5-9]. DESs can be prepared in a pure state by the combination of hydrogen bond donors and hydrogen bond acceptors by simply mixing of cheaper and biodegradable components [10-14]. DES have some advantages, such as negligible vapor pressure (reduced air pollution), non-flammability (process safety), simple reaction workup, biodegradability and renewability. All the factors discussed above, have made DESs as a hot topic and many researchers recently have focused on their syntheses and properties and particularly their applications in organic synthesis, polymer chemistry, analytical chemistry and biomass valorization [15-21].

Heterocyclic motifs such as multisubstituted cyclohexa-1,3-dienamines and their derivatives represent diverse biological and pharmacological activities and well distributed in naturally-occurring compounds as well as a key synthetic intermediate [22-26]. Because of their immense pharmacological and commercial importance, considerable studies of the synthesis of substituted cyclohexa-1,3-dienamines and their derivatives have been reported [27,28]. While these studies have led to remarkable improvements in the yields of reaction, these processes are usually time and energy-consuming and involve using various volatile organic solvents, unavailable reactants or catalysts. In view of the toxicological effects of any organic solvent to the environment as well as human developing more environmentally friendly method for *N*-heterocyclic construction via multicomponent domino reactions is a challenging but important task on the field of green chemistry [29-34]. The best of our knowledge, this is the first example of no other added catalysts domino reaction in DES for regioselective synthesis of multisubstituted cyclohexa-1,3-dienamines [35-39].

2. Experimental section

2.1. Materials and instrumentation

2.2All chemicals and solvents were obtained from commercially available sources and used. All products were confirmed by ^{1}HNMR, FT-IR spectroscopy and mass spectrometry. ^{1}H NMR spectra were recorded on 500 or 300 MHz ^{1}HNMR, ^{13}C NMR 125.7 and 75 MHz NMR spectrometer using DMSO- d_6 as a solvent and chemical shifts have been expressed in (ppm) 40 downfield from TMS. Melting points were recorded on Buchi 535 melting point apparatus and are uncorrected. FT-IR spectra were determined on a Bruker Vector-22 infrared spectrometer using KBr disks.

2.2. **Deep eutectic solvent preparation**: Choline chloride based DES were prepared by heating with stirring up to 60 °C for 40-100 min of the corresponding individual components (Table 1) until a clear solution was obtained. The obtained deep eutectic solvent was used without any further purification.

General Procedure: In a typical procedure, ketone (0.5 mmol), aromatic aldehyde (0.5 mmol), malononitrile (1.0 mmol) was added to the dried test tube containg DES (0.5 mL).The resulting mixture was stirred at 50 ºC for the required time monitored (that as the reaction mixture becomes more viscous or solids when is completed) and then cooled to room temperature. Water was added and the residue collected by filtration. The resulting solid was washed with water and recrystallized from ethanol or ethyl acetate and diethyl ether to afford the pure products.

3. Results and discussion

As a part of our continued interest for eco-friendly solvents in organic synthesis, we recently succeeded in developing the deep eutectic solvent as a green media in chemical reactions [40-43]. In this paper, we would like to report a green and efficient multicomponent domino reaction of ketones, aldehydes and malononitrile in urea-choline chloride based DESs. DES catalyzed one-flask tandem Knoevenagel-

Michael-cyclocondensation reactions to the construction of multisubstituted cyclohexa-1,3-dienamines in good to excellent yield.

A series of choline chloride-based deep eutectic solvents were prepared in the simplest manner according to the reported procedure [25] and were used without further purification.

After preparation of DES, in order to optimize the reaction condition, benzaldehyde, (0.5 mmol), cyclohexanone (0.5 mmol) and malononitrile (1.0 mmol) was chosen as a model reaction to evaluate several choline chloride based DESs under various conditions (Table 1). Stirring the reaction mixture in ChCl-urea as the solvent at room temperature gives fair conversion and yield (Table 1, entry 1). To improve the reaction conditions, various critical parameters were examined. Further studies found that the best results in terms of conversions and times were obtained by heating the reaction mixture in 50 °C in various DES. One possible reason for this is that the lowering of the viscosity thanks to the increase of the temperature. When performed in 50 °C, the reaction is complete in 40 min and a satisfactory conversion was achieved and the yield could be increased to as high as 95 % for ChCl–urea. To our great delight, a significant improvement was observed when the ChCl and glycerol DES was used (Table 1, entry 2). A ChCl and metal halides based DESs (Table 1, entries 3-6) resulted in good conversion, but unsatisfactory yield. The natural carboxylic acids as well as PTSA based DESs, was the least efficient reaction medium among the DES studied and did not achieve full conversion. Due to the high acidic properties of these DESs, side reactions were observed (Table 1, entries 7-10).

Table 1

Screening the ten DESs revealed that ChCl-urea emerges as the best catalyst for the synthesis of multisubstituted cyclohexa-1,3-dienamines under mild conditions. Furthermore, ChCl-urea based DES has low price, an operationally simple and efficient workup. With the optimal conditions in hand, we turned our attention toward the scope and tolerance of the multicomponent domino reactions of various aldehydes, clohexanone and malononitrile at 50 °C in DES. As summarized in Table 2, a wide range of aromatic aldehydes can be employed in construction of multisubstituted cyclohexa-1,3-dienamines compounds with biological and chemical properties. A broad range of aromatic aldehydes bearing diverse functional groups including halogen, methyl, methoxy, and ester proceeded smoothly and a series of multisubstituted cyclohexa-1,3-dienamines were afforded in good to excellent yields (73–95%). Generally, substituents on the *para* positions of aryl groups slightly influenced the yields of reaction. For example, aryl aldehydes bearing both electron-withdrawing and electron-donating groups gave the desired products in excellent yields. Marginally, good yields were achieved for *ortho*-substituted arylaldehydes due to the steric factors. To further explore the potential of this protocol for domino reaction for the construction of highly functionalized heterocyclic synthesis, we investigated one-pot reactions involving various ketones partner. The reactions employing tetrahydro-4H-pyran-4-one with aromatic aldehydes and malononitrile, proceeded smoothly and a variety of the desired products were obtained in good yields (Table 2).

Table 2

The present protocol is potentially useful in organic synthesis in industrial applications due to the advantage of environmental sustainability and efficient utilization of natural resources. For this propose, the model reaction was performed on a relatively large scale (5 mmol), the reaction to give good yields (92 %) of **4a** with simple work-up, which shows its potential for scale-up applications.

The recyclability of DES was important, which helps address both economical and environmental view points in industrial scale. To demonstrate this issue, the recyclability of the DES was examined for compound **4a** between benzaldehyde (5 mmol), clohexanone (5 mmol) and malononitrile (10 mmol) under the optimized conditions (Table 1, entry 1). It is worthwhile to mention that the DES was recycled up to four times without any significant loss and diminution in its amount and efficacy. After completion of reaction, water was added slowly to the reaction mixture and a precipitate was formed. DES is completely recovered by using the water phase containing DES from solid products. The DES solvent easily was recycled by evaporating of water under vacuum (reduced pressure) and washed with ethyl acetate and used for the next run (Figure 1).

Figure 1

Although the detailed mechanism and the role of DES in the present work have not been confirmed yet, the possible mechanism is proposed in a manner similar to that described in the IL catalyzed reactions is suggested by Lohar *et al*. [38]. We supposed that the DES had two functions: (1) to activate carbonyl groups of aldehyde and ketone through hydrogen binding to start the nucleophilic addition of malononitrile; (2) to provide a nucleophilic urea via capturing a proton of malononitrile to form corresponding carbanions. Activation of both the starting ketones and the aldehyde by hydrogen bonding increases the electrophilicity of the aldehyde and cyclohexanone and assists the formation of separate Knoevenagel condensations aldehyde and cyclohexanone with malononitrile (Scheme 1). The resulting Knoevenagel condensation products undergo the concerted stereospecific [4 + 2] Diels-Alder reaction and gave the final desired product **(4a).**

Scheme 1

4. Conclusion

In summary, the present work describes DES-catalyzed multicomponent reactions for the easy access of a wide range of multisubstituted cyclohexa-1,3-dienamines. The significant advantages of these methodologies are high yields, the wide scope of substrates, easy preparation and lower cost of the DES, simple work-up procedures, with good to high isolated yields.

Acknowledgements

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References

[1] A.P. Abbott, G. Capper, D.L. Davies, R.K. Rasheed, V. Tambyrajah, Novel solvent properties of choline chloride / urea mixtures. Chem. Commun. (2003) 70–71.

[2] Y. Cui, C. Li, J. Yin, S. Li, Y. Jia, M. Bao, Design, synthesis and properties of acidic deep eutectic solvents based on choline chloride, J. Mol. Liq. 236 (2017) 338-343

[3] Q. Zhang, K. De Oliveira Vigier, S. Royer, F. Jérôme, Deep eutectic solvents: syntheses, properties and applications, Chem. Soc. Rev. 41 (2012) 7108-7145.

[4] B.L. Gadilohar, G.S. Shankarling, Choline based ionic liquids and their applications in organic transformation, J. Mol. Liq. 227 (2017) 234-261.

[5] R. Germani, M. Orlandini, M. Tiecco, T. Del Giacco, Novel low viscous, green and amphiphilic N-oxides/phenylacetic acid based Deep Eutectic Solvents J. Mol. Liq. 240 (2017) 233-239.

[6] Z. Maugeri, W. Leitner, P. Domínguez De María, Practical separation of alcohol-ester mixtures using Deep-Eutectic-Solvents, Tetrahedron Lett. 53 (2012) 6968–6971.

[7] V. De Santi, F. Cardellini, L. Brinchi, R. Germani, Novel Brønsted acidic deep eutectic solvent as reaction media for esterification of carboxylic acid with alcohols, Tetrahedron Lett. 53 (2012) 5151–5155.

[8] A. Hayyan, F.S. Mjalli, M.A. Hashim, M. Hayyan, I.M. AlNashef, S.M. Al-Zahrani, M.A. Al-Saadi, Ethanesulfonic acid-based esterification of industrial acidic crude palm oil for biodiesel production, Bioresour. Technol. 102 (2011) 9564–9570.

[9] A. Hayyan, F.S. Mjalli, I.M. Alnashef, T. Al-Wahaibi, Y.M. Al-Wahaibi, M.A. Hashim, Fruit sugar-based deep eutectic solvents and their physical properties, Thermochim. Acta. 541 (2012) 70–75.

[10] M. Zhang, P. Liu, Y.-H. Liu, Z.-R. Shang, H.-C. Hu, Z.-H. Zhang, Magnetically separable graphene oxide anchored sulfonic acid: a novel, high efficient and recyclable catalyst for one-pot synthesis of 3,6-di(pyridin-3-yl)-1H-pyrazolo[3,4-b]pyridine-5-carbonitriles in deep eutectic solvent under microwave irradiation., RSC Adv. (2016) 106160-106170.

[11] H.C. Hu, Y.H. Liu, B.L. Li, Z.S Cui, Z.H. Zhang, deep eutectic solvent based on choline chloride and malonic acid as an efficient and reusable catalytic system for one-pot synthesis of functionalized pyrroles. RSC Adv. 5 (2015) 7720–7728.

[12] A. Hayyan, M.A. Hashim, M. Hayyan, F.S. Mjalli, I.M. Alnashef, A new processing route for cleaner production of biodiesel fuel using a choline chloride based deep eutectic solvent, J. Clean. Prod. 65 (2014) 246–251.

[13] P. Liu, J.W. Hao, L.P. Mo, Z.H. Zhang, Recent advances in the application of deep eutectic solvents as sustainable media as well as catalysts in organic reactions. RSC Adv. 5 (2015) 48675-48704.

[14] A.P. Abbott, R.C. Harris, K.S. Ryder, C. D’Agostino, L.F. Gladden, M.D. Mantle, Glycerol eutectics as sustainable solvent systems, Green Chem. 13 (2011) 82–90.

[15] H.C. Hu, Y.H. Liu, B.L. Li, Z.S. Cui, Z.H. Zhang, Deep eutectic solvent based on choline chloride and malonic acid as an efficient and reusable catalytic system for one-pot synthesis of functionalized pyrroles, RSC Adv. 5 (2015) 7720–7728.

[16] J. Lu, X.T. Li, E.Q. Ma, L.P. Mo, Z.H. Zhang, Superparamagnetic $CuFeO_2$ Nanoparticles in Deep Eutectic Solvent: an Efficient and Recyclable Catalytic System for the Synthesis of Imidazo[1,2-a]pyridines. ChemCatChem, 6 (2014) 2854-2859.

[17] P. Liu, J. Hao, Z. Zhang, A General, Effcient and Green Procedure for Synthesis of Dihydropyrimidine-5-carboxamides in Low Melting Betaine Hydrochloride/Urea Mixture. Chin. J. Chem. 34 (2016) 637-645

[18] M. Zhang, Y.H. Liu, Z.R. Shang, H.C. Hu, Z.H. Zhang, Supported molybdenum on graphene oxide/Fe_3O_4: An efficient, magnetically separable catalyst for one-pot construction of spiro-oxindole dihydropyridines in deep eutectic solvent under microwave irradiation, Catal. Commun. 88 (2017) 39–44.

[19] A.P. Abbott, G. Frisch, H. Garrett, J. Hartley, Ionic liquids form ideal solutions, Chem. Commun. 47 (2011) 11876-11878.

[20] S.B. Phadtare, K.J. Jarag, G.S. Shankarling, Greener protocol for one pot synthesis of coumarin styryl dyes, Dye. Pigment. 97 (2013) 105–112.

[21] B.S. Singh, H.R. Lobo, D. V. Pinjari, K.J. Jarag, A.B. Pandit, G.S. Shankarling, Comparative material study and synthesis of 4-(4-nitrophenyl)oxazol-2-amine via sonochemical and thermal method, Ultrason. Sonochem. 20 (2013) 633–639.

[22] D. Enders, M.R.M. Hüttl, C. Grondal, G. Raabe, Control of four stereocentres in a triple cascade organocatalytic reaction, Nature. 441 (2006) 861–863.

[23] A. Padwa, Domino reactions of rhodium(ii) carbenoids for alkaloid synthesis, Chem. Soc. Rev. 38 (2009) 3072.

[24] B. V. Pipaliya, A.K. Chakraborti, Cross-Dehydrogenative Coupling of Heterocyclic Scaffolds with Unfunctionalized Aroyl Surrogates by Palladium(II) Catalyzed C(sp2)-H Aroylation through Organocatalytic Dioxygen Activation, J. Org. Chem. 82 (2017) 3767–3780.

[25] C. Selvam, S.M. Jachak, R. Thilagavathi, A.K. Chakraborti, Design, synthesis, biological evaluation and molecular docking of curcumin analogues as antioxidant, cyclooxygenase inhibitory and anti-inflammatory agents, Bioorganic Med. Chem. Lett. 15 (2005) 1793–1797.

[26] A.A.M. Abdel-Aziz, H.I. El-Subbagh, T. Kunieda, Lewis acid-promoted transformation of 2-alkoxypyridines into 2-aminopyridines and their antibacterial activity. Part 2: Remarkably facile C-N bond formation, Bioorganic Med. Chem. 13 (2005) 4929–4935.

[27] D.N. Kommi, P.S. Jadhavar, D. Kumar, A.K. Chakraborti, "All-water" one-pot diverse synthesis of 1,2-disubstituted benzimidazoles: hydrogen bond driven "synergistic electrophile–nucleophile dual activation" by water, Green Chem. 15 (2013) 798.

[28] D. Kumar, D.N. Kommi, N. Bollineni, A.R. Patel, A.K. Chakraborti, Catalytic procedures for multicomponent synthesis of imidazoles: selectivity control during the competitive formation of tri- and tetrasubstituted imidazoles. Green Chem. 14 (2012) 2038-2049.

[29] S. Bhagat, A.K. Chakraborti, Zirconium(IV) Compounds As Efficient Catalysts for Synthesis of α-Aminophosphonates. J. Org. Chem. 73 (2008) 6029-6032.

[30] S. Bhagat, A.K. Chakraborti, An Extremely Efficient Three-Component Reaction of Aldehydes/Ketones, Amines, and Phosphites (Kabachnik−Fields Reaction) for the Synthesis of α-Aminophosphonates Catalyzed by Magnesium Perchlorate. J. Org. Chem. 72 (2007) 1263-1270.

[31] P.E. Thompson, V. Manganiello, E. Degerman, Re-discovering PDE3 inhibitors-new opportunities for a long neglected target., Curr. Top. Med. Chem. 7 (2007) 421–436.

[32] S.L. Cui, X.F. Lin, Y.G. Wang, Parallel synthesis of strongly fluorescent polysubstituted 2,6-dicyanoanilines via microwave-promoted multicomponent reaction, J. Org. Chem. 70 (2005) 2866–2869.

[33] N. Parikh, S.R. Roy, K. Seth, A. Kumar, A.K. Chakraborti, ‘On-Water’ Multicomponent Reaction for the Diastereoselective Synthesis of Functionalized Tetrahydropyridines and Mechanistic Insight. Synthesis 48 (2016) 547-556.

[34] D. Kumar, M. Sonawane, B. Pujala, V.K. Jain, S. Bhagat, A.K. Chakraborti, Supported protic acid-catalyzed synthesis of 2,3-disubstituted thiazolidin-4-ones: enhancement of the catalytic potential of protic acid by adsorption on solid supports. Green Chem. 15 (2013) 2872-2884.

[35] M.N. Khan, S. Pal, S. Karamthulla, L.H. Choudhury, Imidazole as organocatalyst for multicomponent reactions: diversity oriented synthesis of functionalized hetero- and carbocycles using in situ-generated benzylidenemalononitrile derivatives, RSC Adv. 4 (2014) 3750–3759.

[36] M.M. Mojtahedi, L. Pourabdi, M.S. Abaee, H. Jami, M. Dini, M.R. Halvagar, Facile one-pot synthesis of novel ortho-aminocarbonitriles and dicyanoanilines fused to heterocycles via pseudo four-component reactions, Tetrahedron. 72 (2016) 1699–1705.

[37] J. Wang, Q. Li, C. Qi, Y. Liu, Z. Ge, R. Li, Primary 1,2-diamine catalysis III: An unexpected domino reaction for the synthesis of multisubstituted cyclohexa-1,3-dienamines, Org. Biomol. Chem. 8 (2010) 4240–4242.

[38] T. Lohar, A. Kumbhar, M. Barge, R. Salunkhe, DABCO functionalized dicationic ionic liquid (DDIL): A novel green benchmark in multicomponent synthesis of heterocyclic scaffolds under sustainable reaction conditions, J. Mol. Liq. 224 (2016) 1102–1108.

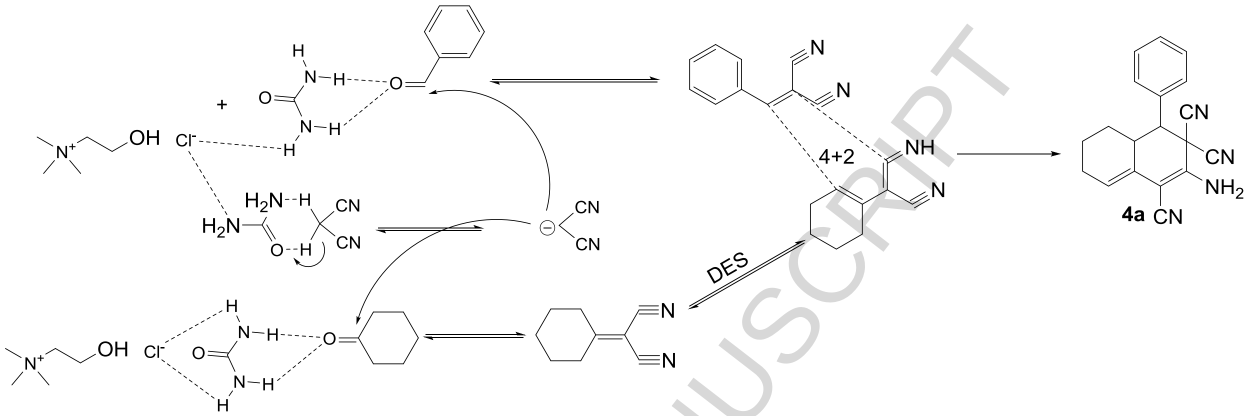
[39] L.Z. Zhang, Y. Wan, X.X. Zhang, H. Cui, H. Zou, Q.J. Zhou, H. Wu, Noncovalent catalysis of glucose-containing imidazolium salt in solvent-free one-pot synthesis of Ortho-aminocarbonitriles, Tetrahedron Lett. 56 (2015) 4934–4937.

[40] N. Azizi, S. Dezfooli, M. Mahmoudi Hashemi, Greener synthesis of spirooxindole in deep eutectic solvent. J. Mol. Liq. 194 (2014) 62-67.

[41] N. Azizi, M.R. Saidi, $LiClO_4$.$3H_2O$ promoted highly regioselective ring-opening of epoxides with thiols under neutral conditions. Catal. Commun. 7 (2006) 224-227.

[42] N. Azizi, E. Batebi, Highly efficient deep eutectic solvent catalyzed ring opening of epoxides, Catal. Sci. Technol. 2 (2012) 2445.

[43] N. Azizi, M.R. Saidi, Phosphorus, Lithium perchlorate diethyl ether solution: A highly efficient media for the abramov reaction. Sulfur Silicon Relat. Elem. 178 (2003) 1255-1259.



Scheme 1. A supposed mechanism

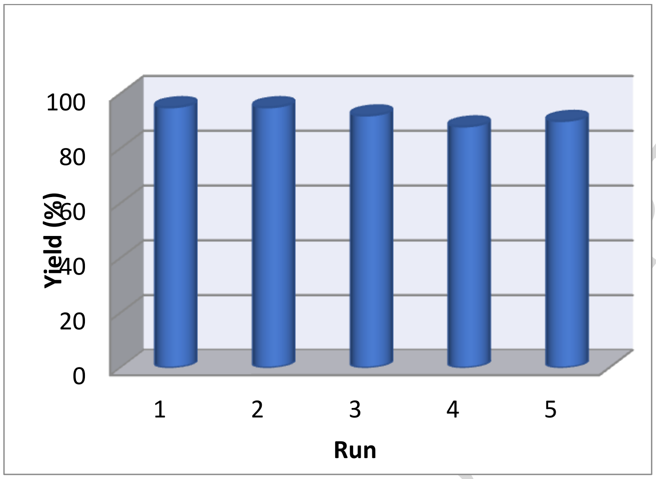
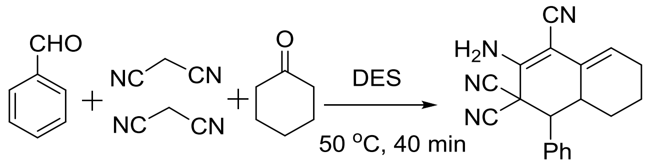


Figure 1. Recyclability experiments of DES in the model reaction

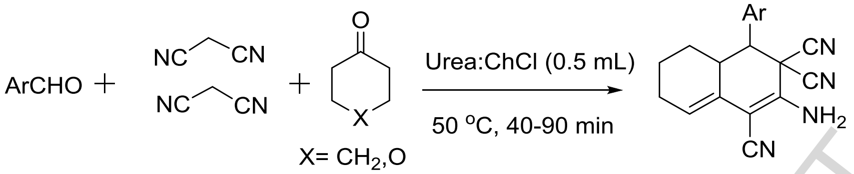
Table 1. Investigation of deep eutectic solvents in model reaction



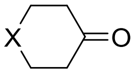
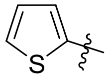
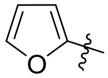
Entry	DES	Yields (%)[a,c]
1	Choline chloride:urea (2:1) 0.5 mL	95 (25)[b]
2	Choline chloride:glycerol (2:1) 0.5 mL	84
3	Choline chloride:$SnCl_2$ (2:1) 2 drop	78
4	Choline chloride:$ZnCl_2$ (2:1) 2 drop	82
5	Choline chloride:$ZnCl_2$:$SnCl_2$ (2:1) 2 drop	76
6	Choline chloride:$LaCl_3$ (2:1) 2 drop	58
7	Choline chloride:PTSA (2:1) 0.5 mL	42
8	Choline chloride:malonic acid (1:1) 0.5 mL	40
9	Choline chloride:tartaric acid (1:1) 0.5 mL	35
10	Choline chloride:oxalic acid (1:1) 0.5 mL	40
11	Choline chloride (0.1 g)	62
12	Glycerol (0.1 mL)	74
13	$SnCl_2$ (10 mg)	25
14	$ZnCl_2$ (10 mg)	70
15	$LaCl_3$ (10 mg)	38

[a] isolated yields. [b] reaction in rt. [c] Reaction condition: benzaldehyde, (0.5 mmol), cyclohexanone (0.5 mmol) and malononitrile (1.0 mmol) at 50 °C in DES (0.5 mL).

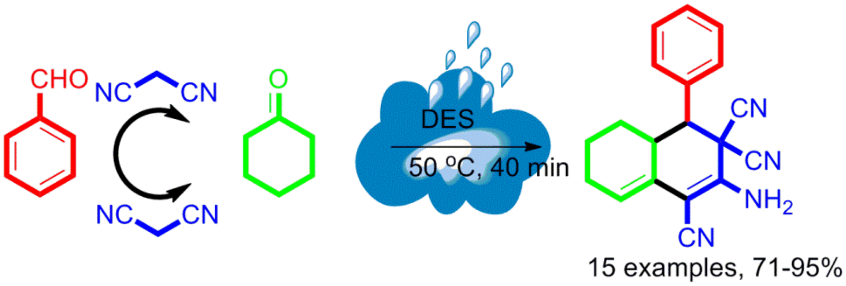
Table 2. Synthesis of various multisubstituted cyclohexa-1,3-dienamines under optimum conditions



1 2 3 4

Entry	Ar (Aldehyde)		Product **(4a-4o)**	Time (min.)	Yields (%)[a,b]	Ref.
1	C_6H_5	CH_2	4a	40	95	37
2	$4\text{-}ClC_6H_4$	CH_2	4b	50	86	38
3	$4\text{-}MeC_6H_4$	CH_2	4c	45	92	38
4	$4\text{-}BrC_6H_4$	CH_2	4d	50	80	38
5	$3\text{-}OMeC_6H_4$	CH_2	4e	50	78	39
6	$3\text{-}BrC_6H_4$	CH_2	4f	60	90	37
7	$2\text{-}BrC_6H_4$	CH_2	4g	60	74	38
8	$4\text{-}OMeC_6H_4$	CH_2	4h	80	78	39
9	$3\text{-}NO_2C_6H_4$	CH_2	4i	60	74	38
10	$2,4\text{-}Cl_2C_6H_3$	CH_2	4j	70	72	38
11	$3,4\text{-}(OMe)_2C_6H_3$	CH_2	4k	80	78	39
12		CH_2	4l	90	64	36
13		CH_2	4m	90	68	36
14	4-Me-Ph	O	4n	80	74	36
15	Ph	O	4o	80	72	36

[a] Isolated yields. [b] The reaction mixture becomes more viscous or solids when is completed



Graphical abstract

Huighlights

►greener strategy under operational simplicity was reported.

► Good to excellent yields of the products..

► This approach eliminates the use of hazardous organic solvents and toxic catalysts.

► Biorenewable and recyclable solvent.