Facile Synthesis of Secondary Amines through One-Pot Reductive Amination of Aromatic Aldehydes in [Et₃NH][HSO₄] using Sodium Borohydride as a Reducing Agent: A Mechanistic Investigation through the Computational Method

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Abstract: The reductive amination of aromatic aldehydes and aromatic amines, performed in the Brønsted acidic ionic liquid [Et₃NH][HSO₄], using sodium borohydride as a reducing agent is reported. In this protocol, the ionic liquid plays a crucial role in efficiently converting aromatic aldehydes to amines in excellent yields, without the formation of side products. In the presence of [Et₃NH][HSO₄], the imine was generated *in situ* from the reaction between the aromatic aldehydes and aromatic amines, and underwent smooth reduction with sodium borohydride. This one-pot synthesis is practically simple and sustainable. The catalyst [Et₃NH][HSO₄] also has a demonstrably wide applicability, in that it can be used with a variety of aromatic aldehydes and aromatic amines substituted by various electron-withdrawing and electron-donating groups. The role of IL [Et₃NH][HSO₄] in catalytic reductive amination is validated with the help of density functional theory (DFT)–based computational studies.

Introduction

The principles of green chemistry advocate using environmentally benign catalysts, as environment-friendly and promising alternatives, or avoiding the use of hazardous solvents in organic transformations.[1–5] Therefore, researchers have invested a great deal of time and effort in performing clean, atom-economical, and environmentally safe organic transformations.[6–9] Secondary amine derivatives are important components of several biologically active natural products,[10] pharmaceuticals,[11] and fine chemicals.[12–14] Therefore, they are widely applied in the synthesis of drugs,[15] herbicides,[16] bactericides,[17] rubber accelerators,[18] corrosion inhibitors, surface-active agents, etc. Reductive amination[19–26] of carbonyl compounds has been identified as the most effective and versatile method to synthesize secondary amines, surpassing several other methods such as Gabriel synthesis,[27–28] reduction of nitrogen-containing compounds,[29–32] and alkylation of ammonia and amines.[33–34] Several catalyst systems and reducing reagents have been explored in reductive amination, following direct[35–42] as well as indirect procedures.[43–44] However, most of them suffered from one or more drawbacks, such as harsh reaction conditions, use of expensive and flammable reagents, complex and toxic metal catalyst systems, poor yields in spite of high conversion of aldehydes in some cases, low chemical selectivity, generation of toxic byproducts, and so on.[45–51] Recently, Brønsted acidic ionic liquids (BAILs) have emerged as promising catalysts and green solvents, being used in several chemical and biochemical transformations, as they possess specific properties such as low or negligible volatility, remarkable solubility, facile structural tunability, and good catalytic activity.[52] Imidazolium cation–based ionic liquids (ILs) have been employed as solvent media, with or without another solvent (H₂O or CH₃OH), as catalysts, or both, in direct or indirect amination methods for the synthesis of secondary amines and exhibited excellent catalytic performance. Nagaiah *et al.*[53] reported the use of an ionic liquid ([BMIm][BF₄])/water system as solvent media. Prasad *et al.*[54] reported the use of 1-methyl imidazolium tetrafluoroborate ([HMIm][BF₄]) in the dual role of solvent and catalyst for efficiently converting aldehydes and ketones to amines in excellent yields without the formation of side products through a one-pot reductive amination method using sodium borohydride. However, not only are these reactions lengthy, the use of Im-based BAILs as catalyst/media is also considerably expensive and thus unsuitable for industrial purposes. Improper disposal after utilization also causes environmental pollution. Recently, Heydari *et al.* reported the use of a biodegradable and non-toxic ammonium deep eutectic solvent based on choline chloride and urea as catalysts and sodium borohydride as a reducing agent in the reductive amination method of secondary amine synthesis.[55–57] Given the importance of secondary amines in medicinal chemistry as well as in modern organic synthesis, the development of an efficient, green, and economical catalyst system is still a necessity for the reductive amination reaction of carbonyl compounds with primary amines.

In this work, we report the facile synthesis of secondary amines by the reductive amination of aromatic aldehydes in an inexpensive Et₃N-cation–based BAIL (which plays the dual role of an easily recyclable catalyst and a green solvent), using NaBH₄ as a reducing agent under neat conditions. The IL was prepared simply by heating a mixture of H₂SO₄ and Et₃N in a molar ratio of 1:1 at room temperature until a clear liquid formed.[58–62] We also performed a detailed DFT study of its mechanism to account for the role of IL in the given reductive amination reaction. To the best of our knowledge, to date, there has been no computational study of the mechanism of reductive amination of aromatic aldehydes and aromatic amines catalyzed by an IL.

Results and Discussion

In the beginning, as a control experiment, the reductive amination of benzaldehyde with aniline was performed in MeOH solvent with only sodium borohydride as a reducing agent under the given reaction conditions: benzaldehyde (0.94 mmol), aniline (0.94 mmol), MeOH (2.4 mmol), and sodium borohydride (1.82 mmol) at 60°C. Even after prolonged heating, only a low yield (57%) of N-benzyl aniline was obtained (**Table 1**, Entry 1). When the same reaction was performed in IL **1a** (2 equiv.) using sodium borohydride as a reducing agent under neat conditions at the m.p. of IL **1a**, i.e. 90°C, the corresponding amine derivative was formed in excellent yield (~96 %) under neat conditions (**Table 1**, Entry 2).

Table 1. Optimization of catalytic performance of various BAILs in the reductive amination reaction

| Entry	IL used	Amount of IL used	Organic Solvent	Time (min)	Temperature (°C)	Isolated Yield (%)
1.	-	-	MeOH	600	60	57
2.	1a	2 equiv.	Neat	60	90	96
3.	1b	2 equiv.	Neat	60	98	95
4.	1c	2 equiv.	Neat	60	95	90
5.	1d	2 equiv.	Neat	60	95	90
6.	1e	2 equiv.	Neat	60	95	85
7.	1f	2 equiv.	Neat	60	95	80

[a] Reaction conditions (for entries 2–7): aldehyde (0.94 mmol), amine (0.94 mmol), ionic liquid (1.82 mmol) and sodium borohydride (1.82 mmol) at their m.p. for 1 h. [b] Yield is calculated based on the isolated product.
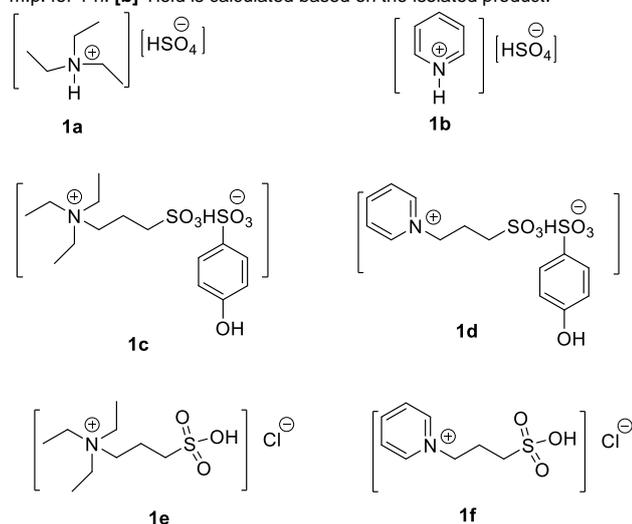
Figure 1. Representing the structures of BAILs, **1a-1f**
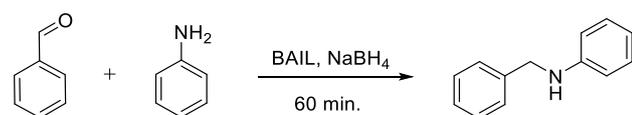
**Scheme 1.** Schematic representation of reductive amination in different BAILs

In order to choose a BAIL that would be best suited as a catalyst for the reductive amination of benzaldehyde with aniline, we compared the catalytic efficiency of **1a** with other BAILs (**1b–1f**, shown in **Figure 1**). The reactions were performed with benzaldehyde (1 equiv.), aniline (1 equiv.), IL (2 equiv.), and sodium borohydride (2 equiv.) at their respective melting points under neat conditions (**Scheme 1**). The results are summarized in **Table 1** (Entries 2–7). IL **1a** gives the best result when compared with other ILs used in the study.

Further, the high-performing catalyst (**1a**) was utilized to optimize the reaction conditions of reductive amination. At first, we studied the effect of temperature on the yield of benzyl aniline. It was observed that increasing the temperature from 60°C to 100°C resulted in a sharp increase in the yield of the secondary amine (up to 96%) (**Figure 2**). It suggests that the IL melted completely at 90°C and acted as an excellent medium to dissolve $NaBH_4$.
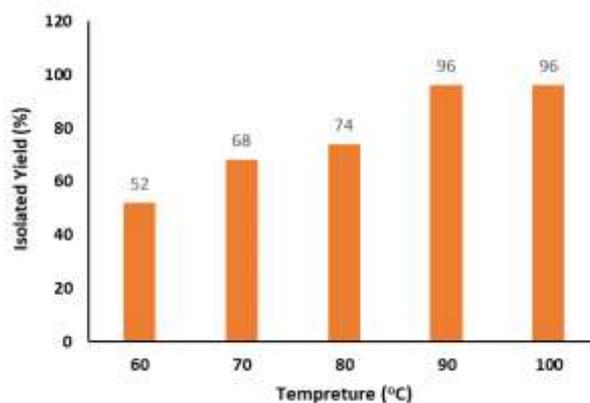

Figure 2. Temperature effect study on reductiveamination reaction of benzaldehyde with aniline in presence of catalyst [Et_3NH][HSO_4] (**1a**). Reaction conditions: benzaldehyde (0.94 mmol), aniline (0.94 mmol), IL **1a** (1.82 mmol), and sodium borohydride (1.82 mmol), at different temperatures for 60 minutes. Yields are based on the isolated product.

To optimize the reaction, we also examined the effect of reaction time on the formation of benzyl aniline. We observed that upon increasing reaction time from 10 to 60 minutes, the yield improved up to 96% (**Figure 3**). Since the viscosity of ILs is greater than that of ordinary organic liquids, higher temperature and longer reaction time are needed for reaching conversion equilibrium.[63] Therefore, there was an improvement in the yield of amines when both temperature and reaction times were increased. After one-and-a-half hours of reaction time, no further increase in the yield of the product was observed (**Figure 3**). Thus, we decided to maintain the reaction time of one hour as the optimized condition.
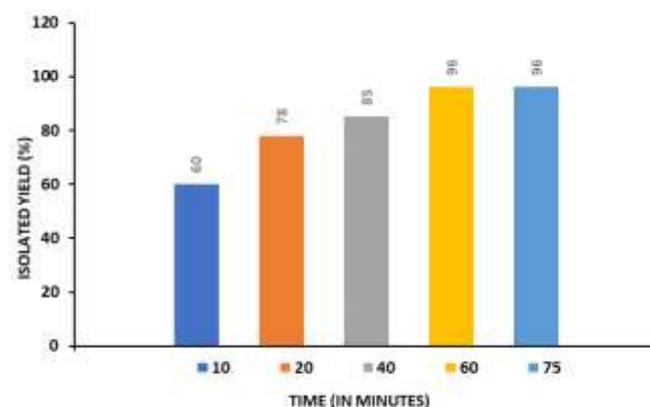
Figure 3. Time effect study on reductive amination of benzaldehyde with aniline in presence of catalyst [Et_3NH][HSO_4] (**1a**). Reaction conditions: benzaldehyde (0.94 mmol), aniline (0.94 mmol), IL **1a** (1.82 mmol), and sodium borohydride (1.82 mmol), 90°C at various reaction times of 10, 20, 40, 60, and 75 minutes. Yields of benzyl aniline are based on the isolated product.

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Using optimized reaction conditions, we further explored the substrate scope of catalyst **1a** for the reductive amination reaction. Initially, benzaldehyde was treated with a variety of anilines, bearing both electron-donating and electron-withdrawing functional groups such as Me, OH, OMe, Br, Cl, and NO_2. We observed the reaction to be smooth, with excellent yields of the corresponding products (**Table 2**; **3a–3f**). Reactions involving benzaldehydes substituted with electron-donating as well as electron-withdrawing functional groups also provided good-to-excellent yields with aniline (**Table 2**, **3g**, **3m**, **3r**, **3t**, **3u**, **3x**, and **3y**). Subsequently, reactions between benzaldehydes and anilines, both substituted with various functional groups, also proceeded efficiently (**Table 2**, **3h–3l**, **3n–3q**, **3s**, **3z**, and **4a**). Polysubstituted benzaldehydes also provided good yields with anilines (**Table 2**, **3v** and **3w**). In all cases, 0.94 mmol aromatic aldehyde, 0.94 mmol aromatic amine, 1.82 mmol **1a**, and 1.82 mmol $NaBH_4$ were treated at 90°C for one hour. Even when the reaction was extended to 1-naphthaldehyde and biomass-derived furfural, the result was a good yield of the corresponding secondary amines **4b** and **4c**, respectively.

Table 2. Reductive amination between a variety of substituted aromatic aldehydes and amines using [Et₃NH][HSO₄] (**1a**) as catalyst under optimized reaction conditions.
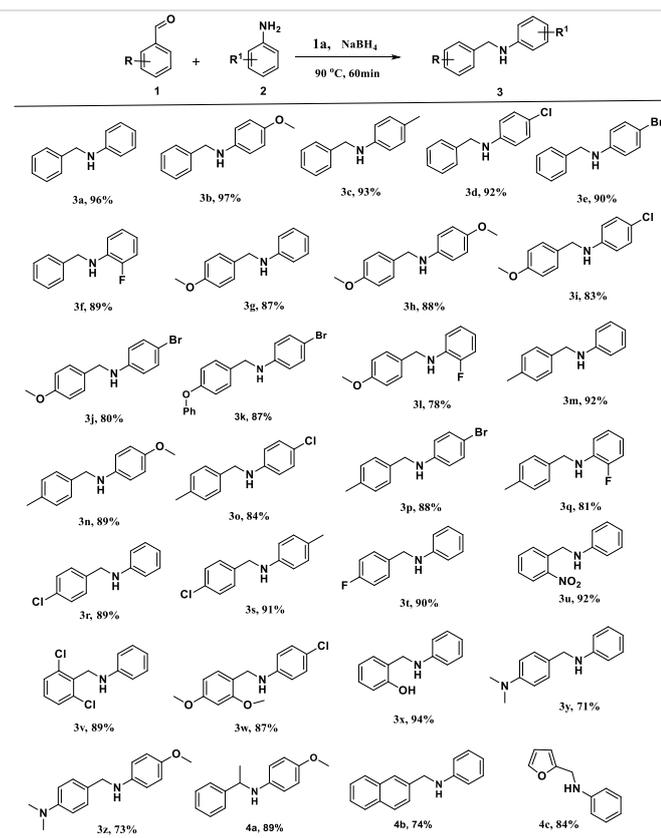
[a] Reaction conditions: 0.94 mmol un/substituted benzaldehyde, 0.94 mmol respective aniline, 1.82 mmol **1a**, and 1.82 mmol $NaBH_4$, at 90°C for 1 hour. **[b]** Yields of the amine derivatives are based on the isolated product.

The reusability of IL **1a** for the reductive amination reaction was also tested using benzaldehyde and aniline under optimal conditions. For this, IL **1a** was at first separated from sodium borohydride residue by dissolving it in acetonitrile, and reused as

such after removing the water content. We are pleased to report that the same batch of catalyst **1a** could be used at least five times with only a slight reduction in the yield of benzyl aniline, as shown in Figure 4. This slight reduction may be attributed to the loss of IL during the work-up after each cycle.
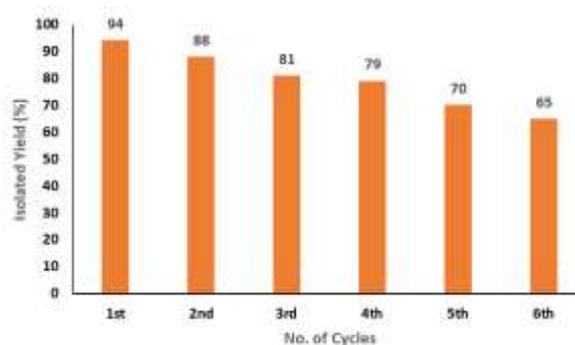

Figure 4. Recyclability test of ionic liquid for reductive amination reaction. Reaction conditions: Aldehyde (0.94mmol), amine (0.94mmol), and sodium borohydride (1.82mmol), at 90 °C for 60 min. Yields of benzyl aniline are based on the isolated product.

Mechanistic investigation through DFT-based computational studies

DFT-based computational calculations were performed to investigate the possible mechanism of the reductive amination reaction of benzaldehyde with aniline, promoted by IL. We first investigated the reaction pathway in the absence of IL. DFT results indicated that activation energy for the reaction was rather high, ~45 kcal mol⁻¹ (R → TS, **FS 65** in SI), which explains the slow and low conversion in the absence of IL and supports the experimental result mentioned in **Table 1** (entry 1). Next, we studied the effect of IL on the energy profile of the reaction. As part of our investigation, a computational model **A**, comprising the IL [Et₃NH⁺][HSO₄⁻], benzaldehyde, and aniline was constructed to perform DFT computations as shown in **Figure 5**.
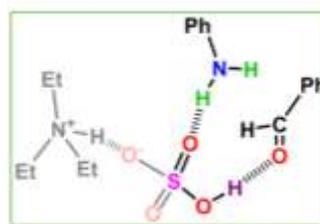

Figure 5. Schematic representation of computational model **A**.

Figures 6 and **7** show the calculated energy profile for the reductive amination assisted by IL, and the corresponding optimized structures, respectively. The reaction mechanism studies were initiated using computational model **A** in which IL interacts with benzaldehyde and phenylamine through noncovalent interaction (hydrogen bonding), which is evident from the distance between the O atom of HSO₄⁻ and the H atom attached to the N atom of aniline (1.73 Å), and the distance between the H atom of HSO₄⁻ and the O atom of benzaldehyde (1.54 Å). The first step, i.e., conversion of the intermediate model

A to **B** through a transition state **AB** (**A**→**TS$_{AB}$**→**B**) involves an attack of N of phenylamine on the electrophilic carbon of benzaldehyde with the simultaneous intramolecular transfer of the two protons; one from aniline to the O of HSO$_4^-$ ion and the other from HSO$_4^-$ to the carbonyl O of benzaldehyde that leads to the formation of a new sigma C–N bond (**Figure 7**). In **A**→**TS$_{AB}$**→**B** conversion, the C–N bond distance changes from 2.66 Å to 1.54 Å which suggests the formation of a new σ C–N bond in the carbinolamine intermediate **B**. The activation energy barrier associated with the **A**→**TS$_{AB}$**→**B** step was calculated to be 6.3 kcal mol^{-1} (**Figure 6**). In the second step, we expected that **B** would undergo proton transfer from N to O of OH, leading to the elimination of the H$_2$O molecule to yield imine. Instead, what we observed was proton shuttling through abstraction of the proton attached to the N atom by O of carbinolamine, with simultaneous proton transfer from OH to O of HSO$_4^-$ and from HSO$_4^-$ to N of carbinolamine in the consequent conversion step (**B**→**TS$_{BC}$**→**C**) (**Figure 7**). This step results in a change in the position of H of HSO$_4^-$ in intermediate **C** with an activation energy barrier of 31 kcal mol^{-1}. In the next step **C**→**TS$_{CD}$**→**D**, an umbrella inversion occurs at the N atom attached to the phenyl group, which orients the H atom attached to N in the direction of O of HSO$_4^-$ via transition state **TS$_{CD}$** resulting in a new conformer **D**. The activation energy barrier for this nitrogen inversion is 7.3 kcal mol^{-1}. In the upcoming step **D**→**TS$_{DE}$**→**E**, **D** easily undergoes a σ(C–O) bond fission with the concurrent transfer of a proton from N to O of HSO$_4^-$ resulting in the formation of an imine π(N–C) bond via transition state **TS$_{DE}$**. Concomitantly, oxygen(O) of OH abstracts a proton from HSO$_4^-$ to form a water molecule. The formation of imine is apparent from the shortening of the N–C bond from 1.44 Å in **D** to 1.35 Å in **TS$_{DE}$** and finally 1.30 Å in **E**. The activation barrier computed for **D**→**TS$_{DE}$**→**E** conversion is 7.1 kcal mol^{-1}. The water molecule coordinated in **E** gets eliminated easily to

form the secondary amine along with regeneration of the catalyst ([Et$_3$NH$^+$][HSO$_4^-$]). After the elimination of water from **E**, the reducing agent NaBH$_4$ reacts with **E** to form an adduct **F**, which readily transfers H from HSO$_4^-$ to N of imine to form intermediate **G**. The Mulliken atomic charge analysis of intermediates **F** and **G** shows that the charges on O of HSO$_4^-$ increase from -0.453 to -0.498 and +0.355 to +0.414 on Na from intermediate **F** to **G**, respectively. The increase in charges favors the formation of intermediate **G** via a barrier-free transition state due to favorable electrostatic interaction. The subsequent conversion step, **G**→**TS$_{GH}$**→**H**, proceeds via transition state **TS$_{GH}$** through the hydride transfer from NaBH$_4$ to the imine carbon, which is evident from the increase of the B–H bond distance in NaBH$_4$ from 1.26 Å to 1.44 Å, resulting in the generation of intermediate **H** in which boron and carbon atoms are bridged by a H atom. The final step **H**→**I** involves B–H bond dissociation to afford the secondary amine, **I**, which is ~20.5 kcal mol^{-1} more stable in comparison to **G**. In the entire reaction profile diagram, **I** is the most stable species, so the formation of **I** is the main driving force of the reaction. It is clear from the computational analysis as discussed above that the hydrogen sulfate anion of [Et$_3$NH][HSO$_4$] plays an essential catalytic role in the promotion of the reaction under study. This result is further supported by the experiment in which reductive amination was performed in the presence of a catalytic amount of IL [Et$_3$NH][HSO$_4$] **1a** (10 mol%) in the MeOH solvent using sodium borohydride as a reducing agent under the given reaction conditions: benzaldehyde (0.94 mmol), aniline (0.94 mmol), IL **1a** (10 mol%), MeOH (2.4 mmol), and sodium borohydride (1.82 mmol) at room temperature. The reaction was completed within five minutes and the yield of N-benzyl aniline obtained was 98%. The same result was obtained with IL [C$_5$H$_5$NH][HSO$_4$] **1b** too.
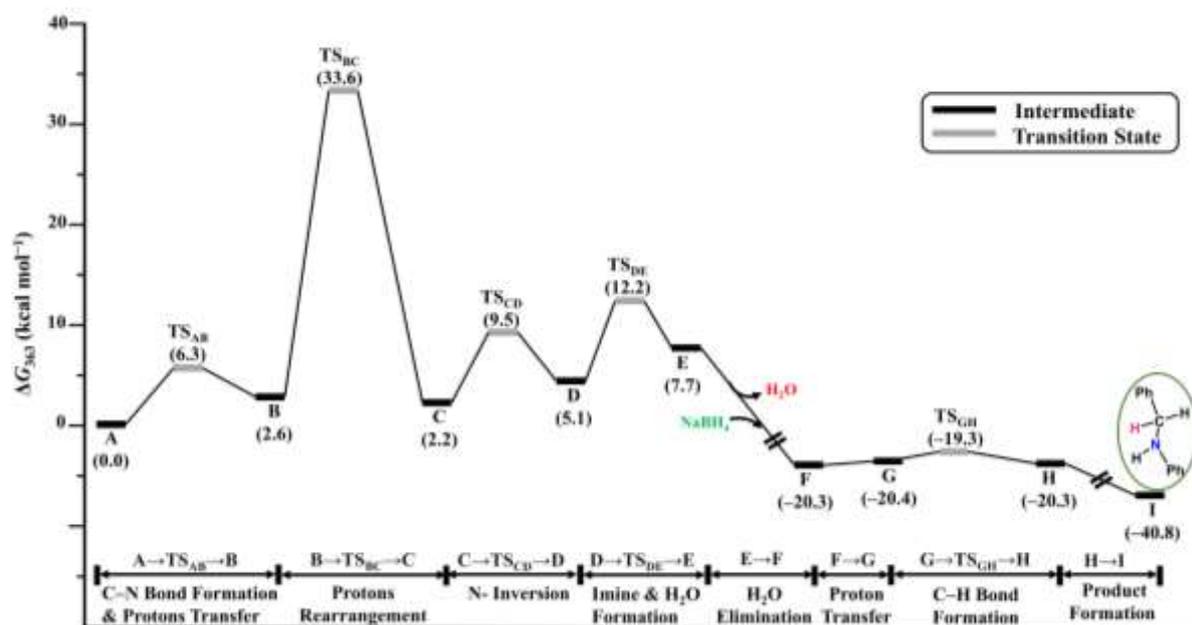

Figure 6. DFT-computed free energy profile of IL catalyzed the reductive amination reaction of aromatic aldehyde and aromatic amine using NaBH$_4$ as the reducing agent. Gibbs free energies ΔG$_{363}$ [kcal mol^{-1}] are relative to A, calculated at BP86-D3/def2-TZVP//BP86-D3/def2-SVP level of DFT. (Computational details of A→I conversion is available in SI).
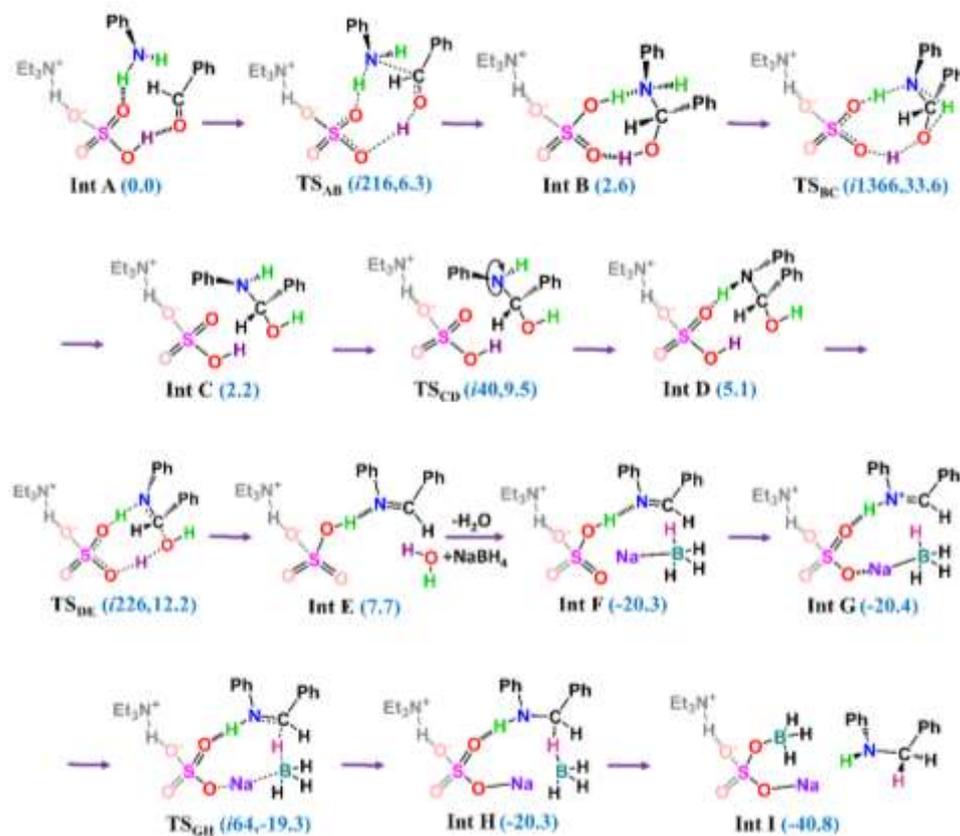
Figure 7. Optimized structures of intermediates and transition states involved in the reaction mechanism of **A**→**I** conversion. In case of transition states, the first number in the parentheses is the imaginary frequency, whereas the second number represents the Gibbs free energy change relative to A.

Conclusion

The present study shows the valuable application of IL [Et$_3$NH][HSO$_4$] in the production of secondary amines which are highly important in medicinal chemistry as well as in modern organic synthesis. In this study, IL [Et$_3$NH][HSO$_4$] is introduced as an efficient catalyst and reaction medium for the one-pot reductive amination of aromatic aldehydes with sodium borohydride at ambient temperature. Low cost and easy recycling/reusability of the ionic liquid, neat reaction conditions, use of the non-toxic and environmentally benign reducing agent sodium borohydride, and simple experimental/product isolation procedures make this method sustainable and practical. Another important aspect of this protocol are broad substrate scope, wide functional group tolerance, and short reaction time. This study also sets out the mechanistic investigation of the reductive amination reaction with DFT computational studies, revealing the essential catalytic role of [Et$_3$NH][HSO$_4$] in the promotion of the reaction under study.

Supporting information summary

Synthesis procedure and characterization data of ILs **1a**–**1e**, general procedure for catalytic reductive amination reactions and characterization data of catalytic reaction products (**3a**–**3z** and **4a**–**4c**), and Figures and Tables containing atomic coordinates, calculated energies without and with zero-point energy correction (in au), and free energies (in au, at 313.15 K) for all the stationary structures reported in this paper are given in the electronic supporting information. This material is available free of charge via the Internet at http://www.wiley.com.

References

[1] M. Vafaeezadeh, H. Alinezhad, *J. Mol. Liq.* **2016**, *218*, 95–105.
[2] S. Kotha, P. Khedkar, *Chem. Rev.* **2012**, *112*, 1650-1680.
[3] C. J. Li, B. M. Trost, *PNAS* **2008**, *105*, 13197-13202.
[4] M.-O. Simona, C.-J. Li, *Chem. Soc. Rev.* **2012**, *41*, 1415-1427.
[5] C. Jadhav, A. Nipate, A. Chate, C. Gill, *ACS Omega* **2021**, *6*, 18215–18225.
[6] R. L. Vekariya *J. Mol. Liq.* **2016**, *11*, 123.
[7] A. S. Amarasekara, *Chem. Rev.,* **2016**, *116*, 6133−6183.

[8]   Y. Zhang, N. Wang, Z. B. Xie, L. H. Zhou, X. Q. Yu, *J. Mol. Catal. B Enzym.* **2014**, *110*, 100–110.

[9]   V. I. Parvulescu, C. Hardacre, *Chem. Rev.* **2007,** *107*, 2615-2665.

[10] M. Cicek, N. Gurbuz, N. Ozdemir, I. Ozdemir, E. Ispir, *New J. Chem.* **2021**, *45*, 11075.

[11] A. Singh, A. Maji, M. Joshi, A. R. Choudhury, K. Ghosh, *Dalton Trans.* **2021**, *50*, 8567.

[12] E. Vitaku, D. T. Smith, J. T. Njardarson, *J. Med. Chem.* **2014**, *57,* 10257−10274.

[13] S. Kobayashi, H. Ishitani, *Chem. Rev.* **1999**, *99*, 1069−1094.

[14] W. Li, M. Huang, J. Liu, Y. L. Huang, X. B. Lan, Z. Ye, C. Zhao, Y. Liu, Z. Ke, *ACS Catal.* **2021**, *11*, 10377−10382.

[15] T. C. Nugent, M. E. Shazly, *Adv. Synth. Catal.* **2010**, *352*, 753−819.

[16] X. Zhua, X. Zhoua, W. Zhanga, *J. Chem. Res.* **2015**, *39*, 390-393.

[17] J. J. Brunet, D. Neibecker, F. Niedervorn, *J. Mol. Catal.* **1989**, *49*, 235-259.

[18] D. Zareyeea, B. Karimia, *Tetrahedron Lett.* **2007**, *48*, 1277–1280.

[19] C. Wang, A. Pettman, J. Basca, J. Xiao, *Angew. Chem. Int. Ed.* **2010**, *49*, 7548-7552.

[20] V. Fasano, M. J. Ingleson, *Chem. Eur. J.,***2017**, *23*, 2217–2224.

[21] S. Liang, P. Monsen, G. B. Hammond, B. Xu, *Org. Chem. Front.* **2016**, *3*, 505–509.

[22] D. Talwar, N. Poyatos Salguero, C. M. Robertson, J. Xiao, *Chem. Eur. J.* **2014**, *20*, 245–252.

[23] V. Fasano, J. E. Radcliffe, M. J. Ingleson, *ACS Catal.* **2016**, *6*, 1793–1798.

[24] E. Dorko, M. Szabo, B. Kotai, I. Papai, A. Domjan, T. Soos, *Angew. Chem. Int. Ed.* **2017**, *56*, 9512–9516; *Angew. Chem.* **2017**, *129*, 9640.

[25] E. Kim, S. Park, S. Chang, *Chem. Eur. J.* **2018**, *24*, 5765–5769.

[26] H. Alinezhad, H. Yavari, F. Salehian, *Curr. Org. Chem.* **2015**, *19*, 1021-1049.

[27] S. H. Chung, T. J. Lin, Q. Y. Hu, C. H. Tsai, P. S. Pan, *Molecules* **2013**, *18*, 12346-12367.

[28] A. K. Yadav, L. D. S. Yadav, *RSC Adv.* **2014**, *4*, 34764–34767.

[29] D. B. Bagal, B. M. Bhanage, *Adv. Synth. Catal.* **2015**, *357*, 883-900.

[30] S. Gomez, J. A. Peters, T. Maschmeyer. *Adv. Synth. Catal.* **2002**, *344*, 1037-1057.

[31] L. Jiang, P. Zhou, Z. Zhang, S. Jin, Q. Chi, *Ind. Eng. Chem. Res.* **2017**, *56*, 12556–12565.

[32] L. Hu, X. Cao, D. Ge, H. Hong, Z. Guo, L. Chen, X. Sun, J. Tang, J. Zheng, J. Lu, H. Gu, *Chem. Eur. J.* **2011**, *17*, 14283-14287.

[33] T. Yan, B. L. Feringa, K. Barta, *Nat. Commun.* **2014**, *5*, 5602, 1-7.

[34] F. Qi, L. Hu, S. Lu, X. Cao, H. Gu, *Chem. Commun.* **2012**, *48*, 9631-9633.

[35] K. N. Gusak, Z. V. Ignatovich, E. V. Koroleva, *Russ. Chem. Rev.* **2015**, *84*, 288–309.

[36] E. W. Baxter, A. B. Reitz, *Org. React.* **2002**, *59*, 1–57.

[37] R. P. Tripathi, S. S. Verçma, J. Pandey, V. K. Tiwari, *Curr. Org. Chem.* **2008**, *12*, 1093–1115.

[38] K. Matos, S. Pichlmair, E. R. Burkhardt, *Chim. Oggi.* **2007**, *25*, 17–20.

[39] M. Zhang, H. Yang, Y. Zhang, C. Zhu, W. Li, Y. Cheng, H. Hua, *Chem. Commun.* **2011**, *47*, 6605-6607.

[40] M. M. Aghayan, M. M. Tavana, M. Rahimifard, R. Boukherroub, *Appl. Organometal. Chem.* **2014**, *28*, 113-115.

[41] A. Cabrera, P. Sharma, F. J. P. Flores, L. Velasco, J. L. Arias, L. R. Perez, *Catal. Sci. Technol.* **2014**, *4*, 2626-2630.

[42] P. Mattei, G. Moine, K. Pntener, R. Schmid, *Org. Process Res. Dev.* **2011**, *15*, 353-359.

[43] S. S. Ekbote, S. T. Gadge, B. M. Bhanage, *Catalysts* **2014**, *4*, 289-298.

[44] R. Zhanga, S. Liuc, K. J. Edgara, *Carbohydrate Polymers* **2017**, *171*, 1–8.

[45] F. I. McGonagle, D. S. MacMillan, J. Murray, H. F. Sneddon, C. Jamieson, A. J. B. Watson, *Green Chem.* **2013**, *15*, 1159–1165.

[46] B. T. Cho, S. K. Kang, *Tetrahedron* **2005**, *61*, 5725.

[47] A. F. Abdel-Magid, K. G. Carson, B. D. Harris, C. A. Maryanoff, R. D. Shah, *J. Org. Chem.* **1996**, *61*, 3849.

[48] D. Imao, S. Fujihara, T. Yamamoto, T. Ohta, Y. Ito, *Tetrahedron* **2005**, *61*, 6988.

[49] D. Menche, J. Hassfeld, G. Menche, A. Ritter, S. Rudolph, *Org. Lett.* **2006**, *8*, 741. 5.

[50] T. Ito, K. Nagata, A. Kurihara, M. Miyazaki, A. Ohsawa, *Tetrahedron Lett.*, **2002**, *43*, 3105.

[51] V. Ravi, E. Ramu, P. V. Kumar, A. S. Rao, *Chin. J. Chem.* **2006**, *24*, 807.

[52] P. N. Reddy, P. Padmaja, B. V. S. Reddy, G. Rambabua, *RSC Adv.* **2015**, *5*, 51035.

[53] K. Nagaiah, V. N. Kumar, R. S. Rao, B. V. S. Reddy, A. V. Narsaiah, and J. S. Yadav, *Synth. Commun.* **2006**, *36*, 3345–3352.

[54] P. S. Reddy, S. Kanjilal, S. Sunitha, R. B. N. Prasad, *Tetrahedron Lett.* **2007**, *48*, 8807–8810.

[55] A. Heydari, S. Khaksar, J. Akbari, M. Esfandyari, M. Pourayoubi, M. Tajbakhsh, *Tetrahedron Lett.* **2007**, *48*, 1135.

[56] A. Heydari, S. Khaksar, M. Esfandyari, M. Tajbakhsh, *Tetrahedron* **2007**, *63*, 3363.

[57] A. Heydari, A. Arefi, M. Esfandyari, *J. Mol. Catal. A: Chem.* **2007**, *274*, 169.

[58] Z. N. Siddiqui, K. Khan, *ACS Sustainable Chem. Eng.* **2014**, *2*, 1187−1194.

[59] X. Tong, W. Zhu, M. Zhu, Q. Wu, F. Cao, W. Yan, A. B. Yaroslavtsev, *Russ. J. Electrochem.* **2013,**1023-1935.

[60] Y. Bian, J. Zhang, S. Zhang, C. Liu, D. Zhao, *ACS Sustainable Chem. Eng.* **2019**, *7*, 17220−17226.

[61] D. Fang, X. L. Zhou, Z. W. Ye, and Z. L. Liu, *Ind. Eng. Chem. Res.* **2006**, *45*, 7982-7984.

[62] S. Liu, Z. Wang, K. Li, L. Li and S. Yu, *J. Renewable Sustainable Energy*, **2013**, *5*, 023111.

[63] T. Jiang, Y. Chang, G. Zhao, B. Han, and G. Yang, *Synth. Commun* **2004***, 34*, 225-230.

[64] F. Neese, The ORCA program system, Wiley Interdiscip. *Rev: Comput. Mol. Sci.* **2012**, *2*, 73–78.

[65] J. P. Perdew, Density-functional approximation for the correlation energy of the inhomogeneous electron gas, *Phys. Rev. B: Condens. Matter Mater. Phys.* **1986**, *33*, 8822–8824.

[66] A. D. Becke, Density-functional exchange-energy approximation with correct asymptotic behaviour, *Phys. Rev. A* **1988**, *38*, 3098-3100.

[67] S. Grimme, S. Ehrlich and L. Goerigk, Effect of the damping function in dispersion corrected density functional theory, *J. Comput. Chem.* **2011**, *32*, 1456–1465.

[68] F. Weigend, R. Ahlrichs, Balanced basis sets of split valences, triple zeta valence and quadruple zeta valence quality for H to Rn: Design and assessment of accuracy, *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297–3305