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Deep Eutectic Solvent/Lipase: Two Environmentally Benign and Recyclable Media for Efficient Synthesis of *N*-Aryl Amines

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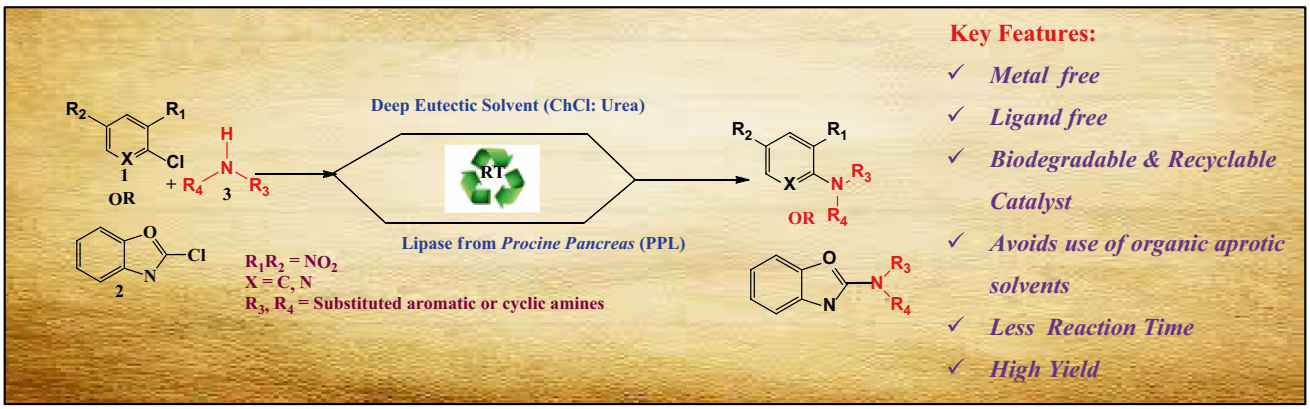
Abstract Deep eutectic solvent (DES)/lipase catalyzed efficient synthesis of *N*-aryl amines from electron deficient aryl chlorides and amines at ambient temperature is reported. Its significant features include excellent yields of products, use of biodegradable, non-toxic and recyclable catalysts, thereby avoiding toxic metal catalyst/solvents making these protocols environmentally benign.

Graphical Abstract



Keywords *N*-Arylation · Deep eutectic solvent (DES) · Lipase enzyme · Choline chloride (ChCl) · Aromatic nucleophilic substitution (S_NAr)

1 Introduction

N-Arylation is a significant transformation in organic chemistry and the resulting arylated products have been used extensively in pharmaceutical and agrochemical industries [1]. The different approaches for *N*-arylation reaction include aromatic nucleophilic substitution (S_NAr) [2] of amines with aryl halides or via metal catalyzed reactions [3, 4]. The spectacular contributions of Buchwald and Ullmann [5, 6] to *N*-arylation reactions using metal as catalyst

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has generated huge interest in this area of research. Despite these significant achievements these coupling reactions suffer from serious drawbacks: (1) use of expensive and toxic metal catalysts and ligands, (2) tedious work up procedure, (4) utilization of aprotic solvents and (5) non recyclability of catalysts. One of the most promising solutions to this problem is by using a simplified metal free approach. Literature reports reveal undue utilization of metal catalysts in reactions involving activated halides which could be avoided [7–13].

Lately, considerable improvements in metal free synthesis have been reported by microwave heating [14–17], ionic liquids [18, 19], aprotic solvents [20–23] at high temperature [24] and pressure [25]. Although interesting, these above methodologies remained linked to cyclic amines, and were not applicable for aromatic amines. Milder conditions (toluene, KO^{t}Bu, 135 °C) were successfully applied by Beller et al. nevertheless they required longer reaction times (36 h) to achieve high yields [26]. In continuation of our endeavors, we have tried to overcome these limitations and wish to report metal and ligand-free C–N cross coupling reaction catalyzed by efficient and recyclable biocatalyst lipase as well as DES.

Lipases are enzymes of considerable industrial importance and catalyze many important reactions [27–30]. Besides enzymatic catalysis greener methods such as DES has fascinated significant attention due to their unique properties. DES includes simple eutectics made from combination of quaternary ammonium salts like choline chloride with either hydrogen bond donors like urea, glycerol or lewis acids with 100% atom economy. Relative to conventional ILs, DES has significant advantages such as being non-toxic, insensitive towards moisture, recyclable, cost-effective and bio-degradable [31–38].

In our previous work [39], we have reported *N*-alkylation of aromatic primary amines catalyzed by bio-catalyst as well as DES. This work is an extension of previous work, wherein we report an efficient, metal and ligand free strategy for synthesis of *N*-aryl amines using lipase or DES as catalyst (Scheme 1).

2 Experimental Methods

2.1 General Information

Lipase from Porcine pancreas (PPL), *Candida antarctica* (CALB) and *Mucor javanicus* (MJL) was purchased from Aldrich. FT-IR spectrums were recorded on Jasco FT-IR ATR-PRO/4100 spectrophotometer. ^{1}H NMR spectrums were recorded on Jeol 400-MHz NMR spectrophotometer and mass spectral data were obtained with Shimadzu-LCMS with ESI probes. Common reagent grade chemicals were procured from M/s S.D. Fine Chemical Ltd. India and were used without further purification.

2.2 Preparation of DES

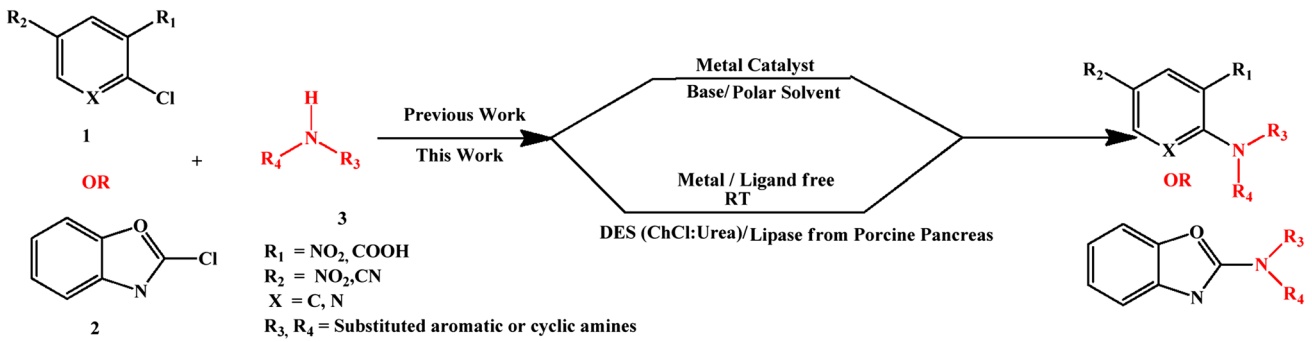
The DES was prepared by combining ChCl with urea according to the procedure reported in the literature [40].

2.3 General Procedure for DES Catalyzed *N*-Arylation of Amines with Aryl Halides

To a solution of amine (1.2 mmol) dissolved in 20% DES, aryl halide (1 mmol) was added at room temperature and stirred for appropriate time. The progress of the reaction was monitored by TLC. After completion of the reaction cold water was added to the reaction mixture. The precipitated solid was filtered off, and recrystallized using ethanol.

2.4 General Procedure for Lipase Catalyzed *N*-Arylation of Amines with Aryl Halides

To a solution of amine (1.2 mmol) and ethanol (1 ml) containing lipase catalyst (15% by weight of amine), aryl halide (1 mmol) was added. The reaction mixture was stirred



Scheme 1 Comparative representation of previous and present work

for appropriate time at room temperature. The progress of the reaction was monitored by TLC. After completion of the reaction, the catalyst was filtered through filter paper and washed with ethanol. The filtrate was evaporated on a rotary evaporator and recrystallized using ethanol to afford pure product.

2.5 Selected Spectral Data

*2.5.1 4- (4-Nitrophenyl) Morpholine **(3a)***

Yellow solid, mp 148 °C (lit mp 148–150 °C); IR (neat, cm^{-1}): 1602, 1511, 1490, 1331, 1243, 1119, 1109, 1052, 927, 825, ^1H NMR ($CDCl_3$, 400 MHz): 3.37 (t, J = 4.8 Hz, 4H), 3.83 (t, J = 4.8 Hz, 4H), 8.12–8.16 (m, 2H), 6.81–6.85 (m, 2H); m/z (EI) 209 ($M^{++}1$); $C_{10}H_{12}N_2O_3$ calculated m/z: 208.21.

*2.5.2 1-(4-Nitrophenyl)-piperidine **(3b)***

Yellow solid, mp 159 °C (lit mp 158–160 °C); IR (neat, cm^{-1}): 2942, 1508, 1450, 1311, 1248, 1200, 1109, ^1H NMR ($CDCl_3$, 400 MHz): 8.06 (d, J = 9.3 Hz, 2H), 6.77(d, J = 9.3 Hz, 2H),3. 43 (s, 4H), 1.68 (s, 6 H);m/z (EI) 207 ($M^{++}1$); $C_{11}H_{14}N_2O_2$ calculated m/z: 206.11.

*2.5.3 1-(4-Nitrophenyl)-4-phenylpiperazine **(3c)***

Yellow solid, mp 175 °C (lit mp 174–176 °C); IR (neat, cm^{-1}):1328 ,1590, 2831, 830, ^1H NMR ($CDCl_3$, 400 MHz): 8.16 (m, 2H), 7.31 (m, 2H), 6.94 (m, 5H), 3.59 (m,4H), 3.36 (m, 4H); m/z (EI) 284 ($M^{++}1$); $C_{16}H_{17}N_3O_2$ calculated m/z: 283.33.

*2.5.4 4-(2, 4-Dinitrophenyl) Morpholine **(3d)***

Bright yellow needles, mp 117–118 °C (lit mp 116–117 °C); IR (neat, cm^{-1}): 3113, 1607, 1587, 1533, 1507, 1340; ^1H NMR ($CDCl_3$, 400 MHz): 8.70 (d, J = 2.8 Hz,1H),8.27 (dd, J = 9.2 Hz, 2.8 Hz,1H), 7.10 (d, J = 9.2 Hz, 1H), 3.87 (t, J = 4.6 Hz), 3.27 (t, J = 4.6 Hz); m/z(EI) 254 ($M^{++}1$); $C_{10}H_{11}N_3O_5$ calculated m/z: 253.07.

*2.5.5 1-(2, 4-Dinitrophenyl) piperidine **(3e)***

Yellow solid, mp 92 °C (lit mp 91–92 °C); IR(neat, cm^{-1}); 3100,1600,1585,1535,1360,1500; ^1H NMR ($CDCl_3$, 400 MHz):δ 8.68 (d, J = 2.0 Hz, 1H), 8.20 (dd, J = 9.4, 2.4 Hz, 1H), 7.09 (d, J = 9.2 Hz, 1H), 3.26 (d, J = 5.6 Hz, 4H), 1.74 (d, J = 7.2 Hz, 6H); m/z (EI) 252 ($M^{++}1$); $C_{11}H_{13}N_3O_4$ calculated m/z: 251.24

*2.5.6 4-Dinitro-N-phenylaniline **(3 f)***

Orange-red solid, mp 156 °C (lit mp 156–157 °C); IR (neat, cm^{-1}): 3319, 1518, 1495,1336; ^1H NMR ($CDCl_3$, 400 MHz): 9.98 (s, 1H, NH), 9.17 (d, J = 2.0 Hz, 1-H), 8.16 (dd, J = 9.2 Hz, 2.4 Hz, 1H), 7.30–7.53 (m, 5H), 7.15 (d, J = 9.6 Hz, 1H); m/z (EI) 260 ($M^{++}1$); $C_{12}H_9N_3O_4$ calculated m/z: 259.22.

*2.5.7 4-Fluoro-N-(2,4-dinitro phenyl) benzamine **(3 g)***

Yellow solid, mp 186 °C (lit mp 186–188 °C); IR (neat, cm^{-1}): 3315, 1515, 1490, 1330; ^1H NMR ($CDCl_3$, 400 MHz): 9.88 (s, 1H, NH), 9.18 (d, J = 3.2 Hz, 1H), 8.2 (dd, J = 7.2 Hz, 3.2 Hz, 1H), 7.18–7.32 (m, 4-H), 7.02 (d, J = 7.4 Hz, 2H); m/z (EI) 278 ($M^{++}1$); $C_{12}H_8FN_3O_4$ calculated m/z: 277.21.

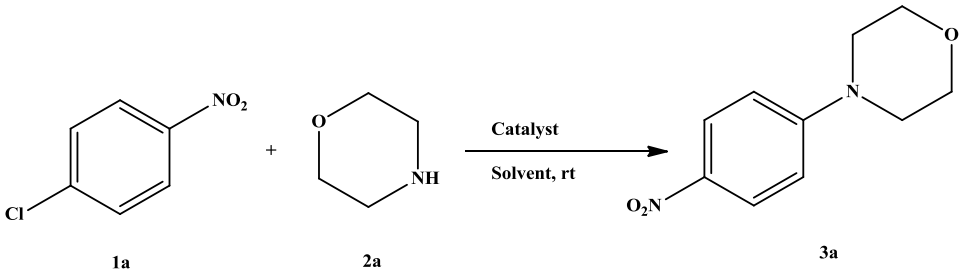
*2.5.8 N-(3-Methoxy phenyl)-2,4-dinitrobenzenamine **(3h)***

Orange-red solid, mp 138 °C (lit mp 137–138 °C); IR (neat, cm^{-1}): 3312,1521,1499,1337,1303; ^1H NMR ($CDCl_3$, 400 MHz): 9.87 (s, 1H, NH), 9.17 (d, J = 2.6 Hz, 1H), 8.15 (dd, J = 2.4 Hz, 9.6 Hz, 1H), 7.34 (t, J = 7.6 Hz, 7.6 Hz, 2H), 7.04–7.12 (m, 4H), 3.86 (s, 1H); m/z (EI) 290 ($M^{++}1$); $C_{13}H_{11}N_3O_5$ calculated m/z: 289.24.

3 Results and Discussions

Our initial studies focused on the reaction between 1-chloro-4-nitrobenzene (**1a**) and morpholine (**2a**) with the aim of identifying reaction conditions. Initially, 10% ChCl: urea DES proved to an efficient catalyst which resulted in product with 80% yield respectively (Table 1, entry 4). To confirm the role of ChCl: urea DES, the reaction was conducted in the sole presence of ChCl or urea for prolonged time which resulted in poor results (entries 1–3).These results clearly showed the fundamental function of ChCl and urea in catalyzing the reaction. The reason being ChCl and urea increase the reactivity of the aryl halide by hydrogen bonding and act as a benign media to drive the process.

Table 1 Optimization of reaction parameters



1a 2a 3a

Entry no	Catalyst	Catalyst loading	Solvent	Time (min)	Yield (%)[b]
1	ChCl		Water	60	55
2	ChCl		Ethanol	60	50
3	Urea		Ethanol	60	20
4	DES (ChCl: urea)	10%	–	20	80
5	DES (ChCl: urea)	15%	–	20	82
6	**DES (ChCl: urea)**	**20%**	**–**	**20**	**88**
7	DES (ChCl: urea)	30%	–	20	88
8	DES (ChCl: urea)	20%	Ethanol	60	65
9	DES (ChCl: urea)	20%	Methanol	60	55
10	DES (ChCl: urea)	20%	DCM	60	50
11	DES (ChCl: urea)	20%	THF	60	60
12	DES (ChCl: urea)	20%	1,4-Dioxane	60	58
13	DES (ChCl: urea)	20%	Acetonitrile	60	62
14	Blank (no enzyme)	–	Ethanol	80	NR
15	αAmylase from *Aspergillus oryzae*	15%	Ethanol	80	6
16	Protease from *Bacillus subtilus*	15%	Ethanol	80	50
17	Lipase from porcine pancreas (PPL)	15%	Ethanol	30	82
18	Lipase from *Candida antarctica* (CALB)	15%	Ethanol	80	60
19	Lipase from *Mucor javanicus* (MJL)	15%	Ethanol	80	50
20[a]	Lipase from porcine pancreas	15%	Ethanol	80	Trace
21	Bovine serum albumin	15%	Ethanol	80	Trace
22	Lipase	5%	Ethanol	30	70
23	Lipase	10%	Ethanol	30	75
24	**Lipase**	**15%**	**Ethanol**	**30**	**82**
25	Lipase	20%	Ethanol	30	82
26	Lipase	15%	Methanol	30	75
27	Lipase	15%	DCM	30	60
28	Lipase	15%	THF	30	78
29	Lipase	15%	1,4-Dioxane	30	65
30	Lipase	15%	Acetonitrile	30	62

The conditions highlighted in bold signify optimum reaction conditions for the reaction

Reaction conditions: **1a** (1 mmol), **2a** (1.2 mmol), room temperature 32 ± 2 °C

[a]Lipase from Porcine pancreas predenatured with urea at 100 °C for 24 h

[b]Isolated yields

Encouraged by the above results, the catalyst loading studies (entries 4–7) reveal 20% ChCl: urea DES was most effective resulting in the desired product with 88% yield within 20 min (entry 6). Further increasing the amount of catalyst showed no improvement in the yield (entry 7).Having identified ChCl: urea as a suitable catalyst, a brief solvent screen was conducted (entries 8–13). No substantial improvement in the product yield was observed with the other tested solvents. Therefore, solvent-free conditions using 20% ChCl: urea DES proved to be an efficient catalytic system. On the other hand, optimization study was further extended by using different biocatalysts (entries 14–19). A control experiment was conducted without any biocatalyst which displayed no catalytic activity (entry 14). Initially 15% (w/w) of lipase enzyme from porcine pancreas (PPL) in ethanolic medium resulted in effective results (entry 17). We carried the optimization study using different lipase strains from *Candida antarctica* (**CALB**) and *Mucor javanicus* (**MJL**) which exhibited the ability to catalyze the reaction, but they were found to be ineffective (entries 18–19).When the reaction was incubated with denatured PPL or bovine serum albumin respectively, the reaction rate was almost comparable to that of the control reaction (entries 20–21). These results suggest lipase from porcine pancreas (**PPL**) as an efficient catalyst responsible for this reaction. Catalytic loading studies reveal 15% (w/w) of lipase enzyme as an effective catalyst (entries 22–25). Solvent study suggests lipase in ethanolic medium as a best solvent compared to other solvents (entries 26–30). Having developed an effective protocol for C–N bond formation with ChCl: urea or lipase as catalyst, we thought to evaluate the scope and generality of this reaction by coupling various amines and activated aryl halides.

With a defined catalytic system, we applied our protocol towards amination of various activated aryl halides with a range of aromatic and cyclic amines yielding the corresponding *N*-aryl amines as summarized in Table 2. Coupling of **1a** with various cyclic amines (Table 2, entries 1–3) under optimized conditions resulted in good yields (80–88%) at room temperature conditions in shorter time (15–30 min) as compared to previously reported methods which require use of metal catalyst [9–14] at high temperature (80–110 °C) with (2–40 h) for completion. To expand the scope of this protocol further, electron deficient aryl chlorides were coupled with cyclic and aromatic amines to give the corresponding *N*-arylated products in good yields. It was observed that increase in presence of electron-withdrawing nitro functionality in the aryl chloride moiety significantly increased the yield as well as the rate of reaction, on the other hand, no restrictions were observed for the amine reaction partner.

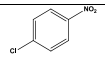
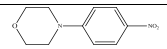
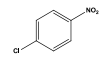
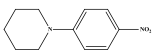
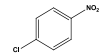
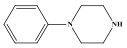
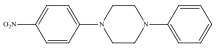
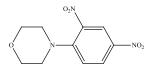
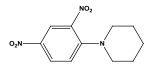
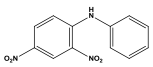
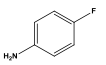
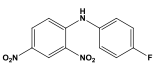
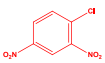
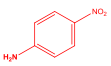
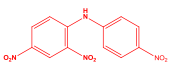
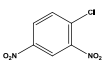
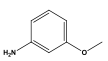
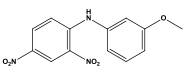
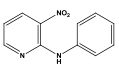
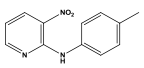
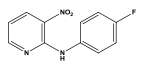
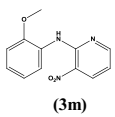
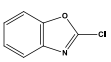
In further experiments, we investigated the importance of the electron-withdrawing functionalities in aryl halides. Chlorobenzene lacking nitro functionality failed to react with cyclic amines using our protocol, indicating that an electron withdrawing nitro functionality was essential for the reaction to proceed according to our protocol. The reaction was extended to heterocyclic aryl chlorides such as **1c** and **1d** which proceeded with excellent yields in short time.

To elaborate the scope of the catalyst, aromatic amines with different electron donating and electro withdrawing substituents were investigated. In case of electron donating aromatic amine with electron donating substituents such as 4-methyl aniline (entry 11) the reaction was faster as compared to electron withdrawing counterparts such as 4-fluoro aniline (entry 12). *N*-Arylation of amines developed here using the cheaper chloroarenes is more attractive than the one using the expensive bromo- and iodoarenes in terms of economic feasibility. The scope of our methodology was further extended by reacting aryl halides with diverse electron withdrawing functionalities like nitrile resulting in moderate yields (50–55%) of desired *N*-arylated products at room temperature. The yield of these substrates were found to be enhanced (78%) as the reaction temperature is increased to 80 °C (entry 15). Intrigued by the above-described results, we further investigated both these protocols for the synthesis of *N*-substituted 5-nitro anthranilic acid derivatives (entry 16) which is a simple alternative to palladium catalyzed Buchwald–Hartwig or copper catalyzed Ullman–Goldberg reactions. Generally these reactions suffer from drawbacks [41], the present methodology eliminates these drawbacks, the carboxylic acid groups are not required to be protected, and this procedure does not require inert conditions. It can easily be scaled to multigram quantities for formation of some valuable intermediates in synthesis of some pharmacologically active compounds.

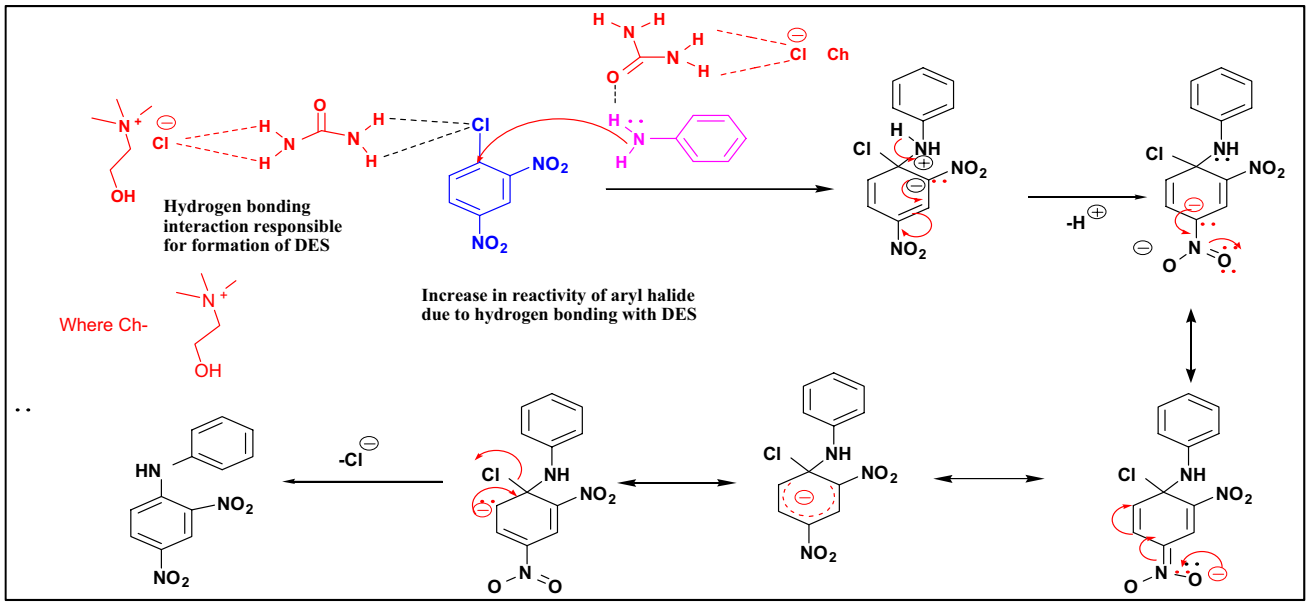
3.1 Plausible Mechanistic Pathway

Based on the present experimental observations and literature reports [42–44], the proposed mechanism is depicted in Schemes 2 and 3. The enhanced reactivity of aryl halides bearing an electron-withdrawing group and no reactivity for electron-donating counterparts suggests that the reactions occur via S_NAr addition–elimination mechanism. According to this mechanism in DES catalyzed reactions, the hydrogen bonding interactions are responsible for facilitating the attack of aryl amine resulting in the product formation. Lipase catalysts increase the nucleophilicity of aromatic amine by abstracting proton through Asp–His dyad, thereby favoring product formation.

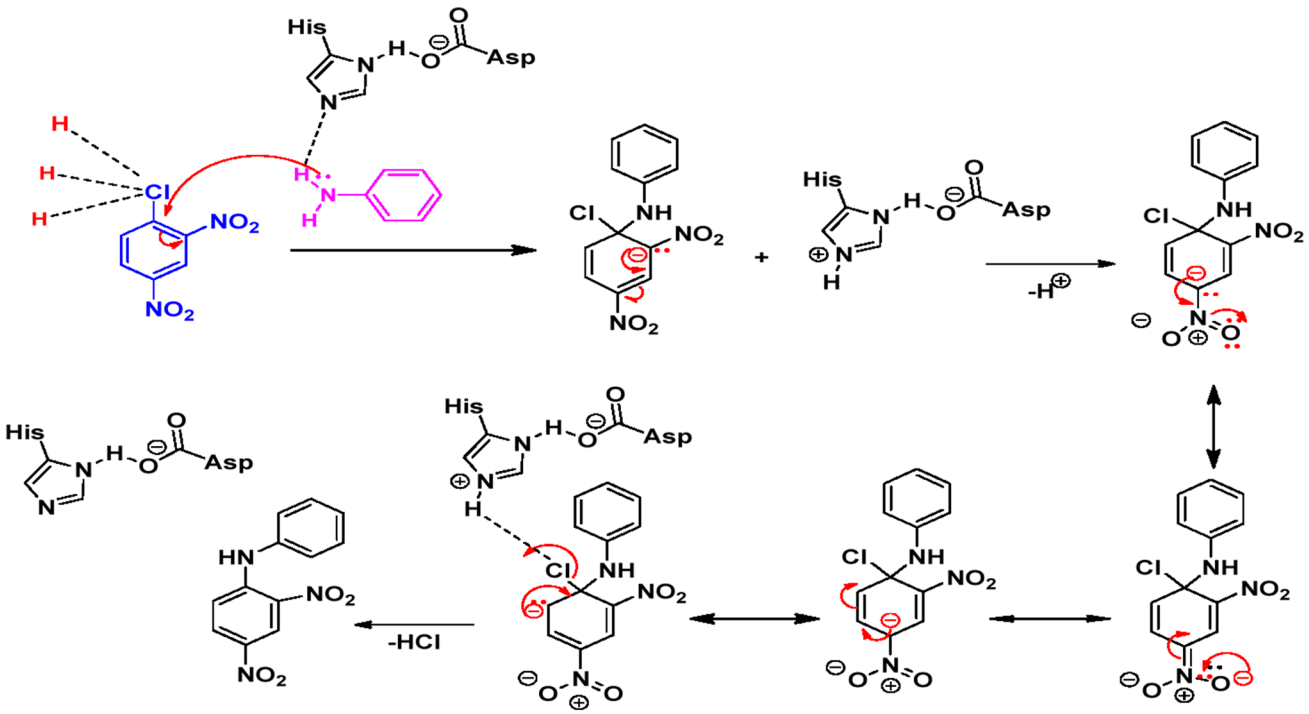
Table 2 *N*-Arylation of amines with aryl halides at room temperature

Entry no.	Aryl halide	Amine	Product	DES[a] Yield (%)[d] t (min)	Lipase[b] Yield (%)[d] t (min)
1	 (1a)		 (2a)	88 (20)	82 (30)
2	 (1a)		 (2b)	85 (15)	82 (30)
3	 (1a)		 (3c)	80 (15)	80 (25)
4	 (1b)		 (3d)	98 (8)	96 (10)
5	 (1b)		 (3e)	96 (5)	95 (5)
6	 (1b)		 (3f)	95 (10)	92 (10)
7	 (1b)		 (3g)	85 (15)	80 (20)
8	 (1b)		 (3h)	82 (25)	80 (25)
9	 (1b)		 (3i)	90 (15)	88 (18)
10	 (1c)		 (3j)	95 (30)	90 (40)
11	 (1c)		 (3k)	92 (15)	86 (20)
12	 (1c)		 (3l)	82 (30)	78 (45)
13	 (1c)		 (3m)	90 (10)	88 (10)
14	 (1d)		(3n)	90 (25)	82 (30)
15[c]	(1e)		(3o)	85(200)	78(320)
16[c]	(1f)		(3p)	85 (180)	76 (360)

[a]Reaction conditions: Aryl halide (1 mmol), amine (1.2 mmol), DES catalyst (20% v/v), temp. 30 ± 2 °C. [b]Aryl halide (1 mmol), amine (1.2 mmol), lipase catalyst (15% by weight of amine), 2 ml ethanol, temp 30 ± 2 °C.[c]Reaction performed at 80 °C for DES and 50 °C for lipase catalyzed reaction [d]Isolated yields



Scheme 2 Proposed mechanism for synthesis of *N*-aryl amines using DES as catalyst



Scheme 3 Proposed mechanism for synthesis of *N*-aryl amines using Lipase as biocatalyst

Table 3 Recyclability studies

No of cycles					
Catalyst	Fresh	First	Second	Third	Fourth
DES (% yield)	88	87	86	86	84
Lipase(% yield)	82	82	80	77	75

3.2 Recyclability Study

To test the industrial applicability of our protocol, recycling of DES and lipase catalysts studied up to four runs considering *N*-arylation of **1a** (10 mmol) with **2a** (10 mmol) in DES under the above conditions. In view of the need for

environmental benign methodologies, the recovery and reuse of the catalyst is essential.

In DES catalyzed reaction, the reaction mass was filtered to obtain crude solid product where the DES catalyst is recovered by removing water under vacuum from the filtrate. The work-up, thus, did not involve any volatile organic solvent and is completely eco-friendly in nature. It could be observed that DES could be recycled up to four successive cycles, with slight decrease in the catalytic activity after the fourth cycle (Table 3) without significant loss in activity.

Recycling experiments of lipase catalyst were performed by direct filtration of reaction mass. The lipase catalyst as well as ethanol were recovered and successfully reused. The recycled lipase enzyme was used up to four runs with decrease in yield from the third cycle (Table 3). This reduction in yield might be due to inactivation of enzyme as the cycles are increased. To our delight the recyclability of both the catalysts were appreciable when the reaction was performed on multigram scales.

4 Conclusions

In summary, we have demonstrated a simple, metal and ligand free strategy for facile synthesis of *N*-aryl amines using deep eutectic solvent or lipase as a catalyst. The proposed reaction proceeds under mild conditions resulting in products with quantitative yields ranging from 76 to 98%. Moreover, this method offers several advantages including use of biodegradable and recyclable deep eutectic solvent or lipase as biocatalyst, offers experimental simplicity, and does not require an inert atmosphere and anhydrous solvents, which is lacking in existing procedures. Exploitation of this reaction media for other organic synthesis is currently under way in our laboratory.

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