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Aqueous mixtures of deep eutectic solvents: Tuning the reaction medium and photocatalyst for highly selective amine oxidation

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DOI: 10.1055/a-2505-6356

Please cite this article as: Kare V, Tiwari S. Aqueous mixtures of deep eutectic solvents: Tuning the reaction medium and photocatalyst for highly selective amine oxidation. Sustainability & Circularity NOW 2024. doi: 10.1055/a-2505-6356

Conflict of Interest: The authors declare that they have no conflict of interest.

This study was supported by MAHAJYOTI, Mahatma Jyotiba Phule Research Fellowship-2022 (MA

Abstract:

Harvesting light as a source of energy for driving chemical processes is an important aspect of tackling the looming energy crisis. The challenge lies in making the process sustainable while retaining the efficiency and selectivity. In this work, deep eutectic solvents and their aqueous mixtures are used to replace acetonitrile as the reaction medium for the photocatalyzed amine oxidation. It is observed that the use of deep eutectic solvents as reaction media leads to > 90 % conversion but presents issues with efficient workup due to high viscosity. The use of water as a cosolvent mitigates the issue. Further modification of the catalyst surface with alizarin enables the use of higher water content (in a 1:1 ratio) and leads to high conversion (>90%) at one-tenth of irradiation intensity. The high yield and selectivity eliminate the need for tedious purification steps to isolate the product. Control experiments indicate cooperative contributions by TiO₂, TEMPO and alizarin as mechanistic factors responsible for the enhanced reactivity.

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Aqueous mixtures of deep eutectic solvents: Tuning the reaction medium and photocatalyst for highly selective amine oxidation




Authors

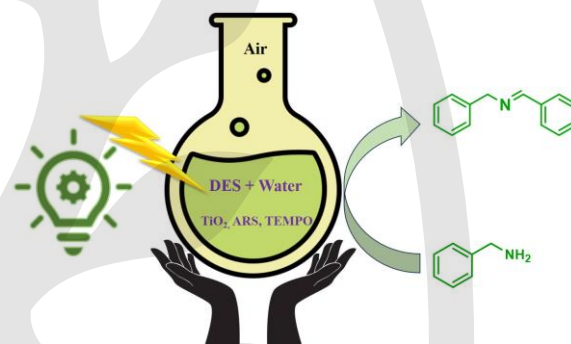
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SIGNIFICANCE

Photocatalyzed oxidative self-coupling of amine to imine in aqueous mixture of deep eutectic solvents is reported to have higher efficiency than conventional solvents. The use of modified reaction media is enabled by incorporating a dye in the catalyst assembly. The reaction required much lower levels of irradiation and the solvent system could be recycled up to 5 times with marginal compromise of the yield. The high selectivity of conversion simplifies the isolation of the product. The plausible mechanism and future scope for scale-up are discussed.



Keywords

Deep eutectic solvent, aqueous mixture, photocatalysis, amine oxidation, heterogenous catalysis

submitted

accepted after revision

accepted manuscript online

published online

Bibliography

Sus. Circ. NOW 2023; x: SCNOW-0000X

DOI [10.1055/XXXXXXX](https://doi.org/10.1055/XXXXXXX)

eISSN 0303-4259

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Georg Thieme Verlag KG, Rüdigerstraße 14, 70469 Stuttgart, Germany

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 Additional material is available at <https://doi.org/10.1055/SCNOW-0000X>.

ABSTRACT

Harvesting light as a source of energy for driving chemical processes is an important aspect of tackling the looming energy crisis. The challenge lies in making the process sustainable while retaining the efficiency and selectivity. In this work, deep eutectic solvents and their aqueous mixtures are used to replace acetonitrile as the reaction medium for the photocatalyzed amine oxidation. It is observed that the use of deep eutectic solvents as reaction media leads to > 90 % conversion but presents issues with efficient workup due to high viscosity. The use of water as a cosolvent mitigates the issue. Further modification of the catalyst surface with alizarin enables the use of higher water content (in a 1:1 ratio) and leads to high conversion (>90%) at one-tenth of irradiation intensity. The high yield and selectivity eliminate the need for tedious purification steps to isolate the product. Control experiments indicate cooperative contributions by TiO₂, TEMPO and alizarin as mechanistic factors responsible for the enhanced reactivity.

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Introduction

Selective oxidation of amines to imines is an important class of synthetic reactions because of the wide applicability of imines as precursors for a range of organic compounds such as nitrogen containing heterocycles (e.g. functionalized piperidines, imidazopyridines and pyrrolidinone derivatives) and alkaloids (e.g. quinolizidines and indolizidines).^{1,2} The emphasis on incorporating environment-friendly strategies for oxidation of amines has led to numerous protocols employing atmospheric oxygen as a oxidizing agent and other “green” measures.^{3,4} The use of TiO₂-based photocatalytic systems for amine oxidation in acetonitrile was first reported in by Lang and coworkers in 2011 and has subsequently been modified for better yields and selectivity.^{5,6} It was demonstrated that the replacement of acetonitrile with water as a reaction medium was possible by employing UV irradiation, with slightly lower conversion.⁷ Subsequent reports focused on the tuning the band gap of the TiO₂ catalyst by sensitizing the surface with organic molecules and incorporating co-catalysts like TEMPO [(2,2,6,6-tetramethylpiperidin-1-yl)oxyl].⁸ For example, Shi et. al. reported excellent yields and selectivity when TEMPO was used in conjunction with TiO₂ coupled with phenol or its derivatives.^{9,10} Li and Lang coupled TEMPO with TiO₂ as a “smart” photocatalyst for selective oxidation of amine to imine.¹¹

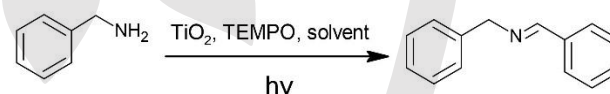
These improved synthetic protocols are mired by the fact that acetonitrile remains the most widely used solvent for the photocatalytic oxidation till date, despite rising concerns about its potential hazard under various reaction conditions.¹² It must be noted that numerous studies reported the successful use of water or other green solvents for amine oxidation in thermal conditions.¹³ Reports about the use of green solvents for photocatalytic oxidation of amines have been relatively limited. For example, Zhao and coworkers have reported excellent selectivity for photocatalyzed oxidative coupling of amines to imines in aqueous medium using bismuth oxybromide photocatalyst.¹⁴ The scarcity of research related to incorporation of “green” reaction media in photo-oxidative coupling of amines is even more surprising given the fact that solvents like water, ionic liquids and deep eutectic solvents have been widely used for other photocatalyzed processes.^{13,15,16} In particular, deep eutectic solvents (DES) have shown exceptional promise in terms of ease of handling, cost-effectiveness and solvating ability.^{17,18} DES comprise of eutectic mixtures of Lewis or Bronsted acid / base with a variety of cations / anions. Their use as reaction media is known to improve the reactivity and selectivity for a wide range of organic processes.^{19,20}

Our research focuses on the use of green solvents as reaction media and investigating the underlying mechanistic principles.^{21,22} In the present work, we report our attempts towards tuning the reaction medium for the photocatalytic aerobic oxidation of amines to imines to ensure an efficient and circular synthetic process. Our results show that aqueous solutions of DES yield the most optimum reaction condition. Coupling the catalyst/co-catalyst system with

aqueous DES allowed the use of a light source with lower intensity and was amenable to recycling protocols. The scaled up synthetic protocol is also reported without compromising the efficacy of the process.

Results and Discussion

Self-coupling reaction of benzylamine to imine was chosen as the model reaction for all the experiments (Scheme 1). Initial experiments used TiO₂ as the photocatalyst and TEMPO as co-catalyst in various reaction media (Table 1). After 2h exposure to a blue light irradiation (Hg lamp, ~450 nm, 30 W) with ethaline (1:2 choline chloride + ethylene glycol) as the reaction medium, excellent results were obtained with reline (1:2 choline chloride + urea) and glyceline (1:2 choline chloride + glycerol) – both yielding ~ 99% of imine in 2 h of irradiation (entry 1 and 2). With ethaline (1:2 mixture of choline chloride and ethylene glycol), 70% of the benzyl amine was converted to imine product (entry 3). Interestingly, the yield was only 23 % after 2 h of irradiation when pure acetonitrile was used as the solvent under identical conditions (entry 4). Higher yields reported in literature (69% conversion) when acetonitrile was used as a reaction medium but the difference could arise from the different luminous efficiency of the LED light source employed in the literature and the scale of the reaction (entry 6). It must be noted that our protocol leads to better conversions with higher selectivity at much lower irradiation intensity. The use of water led to better conversion (52%) as compared to acetonitrile under the present conditions. Previous studies of amine oxidation have also reported ~51% conversion when water was used as the medium⁵ – albeit under very different reaction conditions. The previous study in water was carried out in the absence of TEMPO and required much higher irradiation (100 W, 9 h).



Scheme 1

Table 1: Photocatalyzed oxidation of amine to imine with (TiO₂ + TEMPO) catalyst and irradiation by 30 W blue light (~450 nm) for 2 h^[a]

Entry	Solvent	% conversion ^[b]
1	Reline	99
2	Glyceline	~99
3	Ethaline	70
4	Acetonitrile	23
5	Water	52
6	Acetonitrile	42 ^[c]

[a] 250 mg TiO₂, 11.7 mg TEMPO, 0.168 mL benzylamine (1.5 mmol) in 5 mL solvent

[b] GC analysis with anisole as internal standard

[c] Reference ¹¹: Reaction conditions: benzylamine (0.3 mmol), TiO₂ (50 mg), TEMPO (0.003 mmol), CH₃CN (1 ml), 460 nm

blue LED
irradiation (3W× 4), air (1 atm), 50 min

A plausible mechanism for the cooperative catalysis by TiO_2 + TEMPO in acetonitrile was proposed by Li and Lang.¹¹ Accordingly, the adsorbed benzylamine acts as a surface ligand on TiO_2 and is oxidized to a radical cation, which is restored by TEMPO to generate the TEMPO^+ species. It is the TEMPO^+ which converts benzylamine to imine in a two-step process while getting reduced to TEMPOH. The TEMPO is regenerated by O_2 to complete the catalytic cycle. It was important to control if the same catalytic pathway was valid even when DES were used as reaction media. Control experiments were performed to confirm the mechanistic details and are summarized in Table 2. The decrease in yield on purging the reaction medium with N_2 confirms the role of O_2 as the oxidant. The decrease in yield in the presence of *p*-benzoquinone indicates the role of superoxide radical ($\text{O}_2^{\cdot -}$) as the reactive species (which is quenched by *p*-benzoquinone). It is also important to note that both TiO_2 and TEMPO work in tandem to catalyze the reaction and the absence of either one will lead to a compromised yield. The overall mechanism that can be inferred from these studies is consistent with the previously reported mechanism in molecular solvents.¹¹ This pathway is completely different from the one followed in the absence of TEMPO. The existence of two independent alternative pathways is justified by the fact that the oxidation still proceeds, albeit with lower yields, in the absence of TEMPO or TiO_2 (entry 4 and 5). The use of DES as reaction media do not seem to alter the reaction pathway and their role is limited to influencing the yield of imine formation.

Table 2: Control experiments for the photocatalytic oxidative coupling of amine to imine in reline.^[a]

Entry	Control condition	% conversion ^[b]
1	N_2 atm	41
2	AgNO_3 ^[c]	21 ^[e]
3	Benzoquinone ^[d]	20 ^[e]
4	No TEMPO	24
5	No TiO_2	35

[a] 250 mg TiO_2 , 11.7 mg TEMPO, 0.168 mL benzylamine (1.5 mmol) in 5 mL solvent, irradiation by 30 W blue light (~450 nm) for 2 h

[b] GC analysis with anisole as internal standard

[c] 50 mg (0.3 mmol) of silver nitrate added

[d] 22 mg (0.2 mmol) of benzoquinone added

[e] No further increase with time

We explored the possibility of standardizing the work-up and recyclability of the reaction. The use of reline as a reaction medium gave comparable yield for up to 5 or more cycles, with only a marginal loss in the conversion (Figure 1). Centrifugation of the crude reaction mixture (which caused the titania catalyst to settle down) was followed by extraction of the organic product with ethyl acetate. The

near-stoichiometric conversion precluded the need for purification process and the crude product has reasonably good purity, as confirmed by NMR analysis of the crude product (Fig S4 and S5 of Supporting Information). The reline + TiO_2 mixture could be charged with TEMPO and fresh reactant for the next cycle. It can be seen that there was a marginal loss in reactivity even up to the fifth cycle. The only drawback of the protocol was the high viscosity of reline which necessitated the use of EtOAc for the extraction. This in turn hindered the benefits of recycling the reaction media – since every cycle of work-up would mean incremental emission of VOCs.

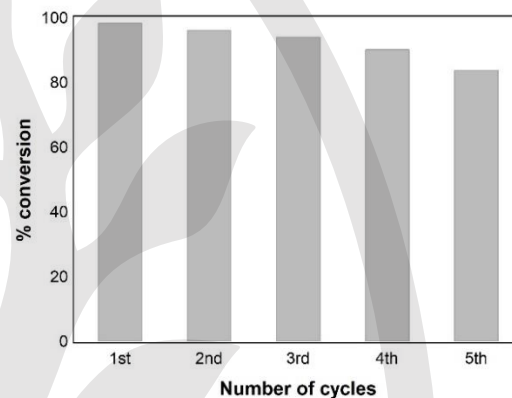


Figure 1: Percent conversion of amine with successive recycling of reline and TiO_2 medium

This led us to explore the use of co-solvent with DES as reaction media and prompted the use of water as a co-solvent in the DES reaction mixture. Previous reports have indicated that presence of water in DES may augment the reactivity and selectivity of biochemical processes.²³ On the other hand, the presence of water is bound to disrupt the HBD – HBA interaction in DES since water can itself act as a HBA / HBD. Varying amounts of water were added to the DES solvents and the % conversion was measured under conditions identical to those used for pure DES. It was observed that the effect of water was non-linear, the reasons for which may be difficult to delineate (Table 3). While adding a small amount of water in reline led to marginal change in the yield, increasing the water content beyond 50% v/v led to a sharp decrease in the conversion (entry 1, 3 and 5). The effect of water also depends on the identity of the DES component – the maximal effect on % conversion being observed in mixtures with ethaline and glyceline (entry 9 and 13). It must be noted that presence of water had a kinetic effect and slowed down the reaction but did not alter the overall yield – all mixtures yield stoichiometric conversion after 24 h (entry 2, 4, 6, 10 and 14). The chief advantage of using 1:1 v/v mixture of DES and water was that the reaction medium was now easier for work-up and recycling primarily due to lower viscosity and hydrophobic nature of the substrate.

The observations showed that presence of water at the TiO_2 interface compromised the yield by possibly influencing the interaction between the semiconductor photocatalyst, co-catalyst and substrate. One of the possibilities is that water molecules increase the local acidity of the TiO_2 interface.²⁴ This in turn may lead to acid-promoted disproportionation of

TEMPO to TEMPOL which cannot be regenerated and hence, the net activity of TEMPO is limited.²⁵ Since the amount of “free” TEMPO (active form of the co-catalyst) is reduced in the presence of water, the reaction rate is expected to slow down (Figure 2). One strategy to counter the detrimental effect of water would be to limit or prevent the access of water molecules on the interface of the TiO₂ catalyst. In the current system, benzylamine is proposed to assemble on the interface and contribute to the photoactivation process. In order to overcome this hurdle, it was necessary to add a hydrophobic component which would shield the catalyst interface from the aqueous environment without affecting the light harvesting pathway adversely.

The presence of alizarin S (ARS) was intended to achieve the same effect with the additional benefits of augmenting the light-harvesting efficiency of the system. In previous reports, ARS-TiO₂ systems have been used for amine oxidation with encouraging results.²⁶ The reported amount of catalyst required was lower than that required in experiments without ARS. For the present report, yields for the benzylamine oxidation carried out using (TiO₂ +ARS + TEMPO) photocatalyst in aqueous DES mixtures is shown in Table 4. It can be seen that the addition of ARS has the desired effect and is instrumental in improving the rate of conversion. The conditions yield complete conversion in approximately 2 h or less for all the DES mixtures.

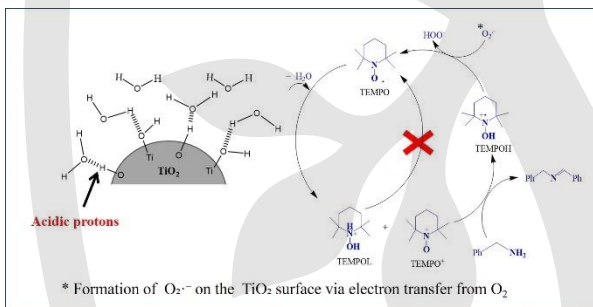


Figure 2: Possible mechanism for effect of aqueous media on visible light-mediated selective aerobic oxidation of amine

Table 3: Effect of composition of the reaction medium (DES + water) on the reactivity in photocatalyzed oxidation of benzylamine^[a]

Entry	Solvent	Composition of solvent (% v/v of DES)	% conversion ^[b]
1	Reline + water	95	90
2			99 ^[c]
3		90	95
4			99 ^[c]
5		50	55
6		50	91 ^[c]
7	Ethaline + water	95	77
8		90	73
9		50	70
10		50	99 ^[c]
11	Glyceline + water	95	91
12		90	92

13	50	60
14	50	99 ^[c]

[a] 250 mg TiO₂, 11.7 mg TEMPO, 0.168 mL benzylamine in 5 mL solvent, irradiation by 30 W blue light (~450 nm) for 2 h
 [b] GC analysis with anisole as internal standard
 [c] % conversion after 24 h

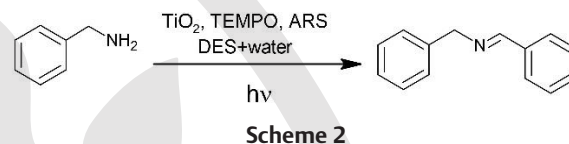


Table 4: Effect of composition of the reaction medium (DES + water) on the reactivity in photocatalyzed oxidation of benzylamine^[a]

Entry	Solvent	Composition of solvent (% v/v of DES)	% conversion ^[b]
1	Reline + water	95	98
2		90	99
3		50	99
4		50	89 ^[c]
5	Ethaline + water	95	96
6		90	96
7		50	96
8		50	86 ^[c]
9	Glyceline + water	95	94
10		90	94
11		50	96
12		50	92 ^[c]
13	Acetonitrile	--	39

[a] 125 mg TiO₂, 1.14 mg of ARS dye, 3.12 mg TEMPO, 0.109 mL benzylamine in 5 mL solvent, irradiation by 30 W blue light (~450 nm) for 2 h
 [b] GC analysis with anisole as internal standard
 [c] irradiation by 3 W blue light (~450 nm) for 8 h

Given the excellent conversion efficiency for all the solvent systems studied, we explored the possibility of reducing the energy consumption of the reaction by reducing the power of the irradiation source. The 30 W light source was replaced by a 3 W lamp with the same wavelength. The results show that although the reaction takes longer to reach completion, the conversion is almost stoichiometric after 8 h (entry 4, 8 and 12). It may be noted that when acetonitrile was used as the solvent with the (TiO₂ +ARS + TEMPO) photocatalyst, the yield was 39%, in comparison to the 23% reported without ARS (Table 1). The addition of ARS ensures comparable yields but in lower time and with exposure to low intensity light source. For example, it is possible to obtain comparable yields after 24 h photocatalyzed oxidation in the absence of ARS and using 30 W irradiation source (entry , 10 and 14 of Table 3). But the

energy cost of the 2 h exposure to a 3 W source (24 W-h) is lower than the ~ 24 h exposure to a 30 W light source (720 W-h, Table 3). More importantly, photocatalysts enabling the use of low intensity light sources are a step towards harnessing ambient sunlight and should be considered as the first choice. Clearly, the dye sensitization of the TiO₂ catalyst is more effective in aqueous DES media than organic solvents.

The origin of this enhanced reactivity is the adsorption of the ARS dye on the catalyst surface and improve its photosensitivity. The presence of water in the reaction medium will thus attenuate the process by increased adsorption of the hydrophobic dye. This is evident from the fact that faster conversion is seen in reaction systems with higher proportion of water. It may also be possible that ARS may initiate an alternative catalytic pathway, independent of the one facilitated by TEMPO. Detailed kinetic and mechanistic studies would be necessary to confirm the detailed reaction process. In order to confirm that the effect of ARS is in alignment with our hypothesis, we studied the adsorption of ARS on the surface of TiO₂. Briefly, a mixture was ARS and TiO₂ was allowed to equilibrate in the 1:1 v/v DES+water system. The supernatant solution was then analyzed using UV-visible spectroscopy to determine the amount of dye adsorbed.

Our results show that 26 µg of ARS was adsorbed per gram of catalyst in a 1:1 mixture of ethaline + water. The amount was slightly higher in the glyceline + water solvent system (30 µg /g of TiO₂). This is comparable to the dye adsorbed when pure water was used for comparison (32 µg /g of TiO₂). It must be noted that the least amount of dye was adsorbed when reline + water solvent mixture was used – the amount being only 6.5µg /g of TiO₂ and this could be due to the “salting-in” effect of urea in aqueous solutions. Further discussions about the mechanism would require mechanistic studies which are currently underway.

Conclusions

Substitution of organic solvent with aqueous mixture of DES along with use of dye-TiO₂-TEMPO catalyst complex results in substantial improvement of the yield for amine oxidation. Stoichiometric conversion (~99 %) is obtained using a TiO₂+TEMPO+ARS catalyst system with 1:1 water + reline solution in ~ 2 h. Using 3W irradiation also leads to similar yields, but requires longer exposure time (8 h). The use of (1:1 DES +water) as reaction media allows for better work-up conditions and lower energy requirement. Future efforts would include detailed mechanistic studies and substrate scope for the current protocol. The present work successfully demonstrates that (DES + water) can be promising alternative to conventional reaction media – providing the means to improve the yields without compromising with the environmental aspects.

Experimental Section

Materials

>99% purity anatase TiO₂, alizarin red dye and TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy) were used as obtained. The purity of benzylamine was confirmed using GC-MS (>98%). High purity choline chloride, urea, ethylene glycol and glycerol were purchased and used without any purification for preparation of DES. HPLC grade water was used to make water fractions and LR grade organic solvents were used for work-up and purification, if required.

Preparation of DES

All three DES used in the present work were prepared by mixing 1:2 mol ratio of choline chloride with hydrogen bond donors in round bottom flask. The mixture was stirred at 80°C till colourless homogeneous liquid formed. The resulting DES was dried in a vacuum oven at 60°C for 8 h and stored in desiccator till required. The three DES (reline, ethaline and glyceline) were characterized by using FT-IR (see Fig S1 to S3 of Supplementary Information).

General procedure for amine oxidation

250 mg of anatase TiO₂, 11.7 mg TEMPO and 0.168 mL benzylamine (1.5 mmol) were added in a round bottom flask containing 5 ml solvent media.¹¹ The reaction mixture was sonicated for 5 min and then stirred under dark for 30 min to allow equilibration. The reaction was initiated by irradiating with blue light (~450 nm, 3W or 30W) and stirred at 1500 rpm. The progress of the reaction was monitored using TLC (5% EtOAc in *n*-hexane). Ethyl acetate and water (if not already present) were added to the reaction mixture for work-up. The pure product was isolated as a yellow viscous liquid and characterized using NMR and GC-MS (Figure S4 and S5 of Supplementary Information).

For the dye-sensitized experiments, 1.14 mg of ARS dye was added to 125 mg of anatase TiO₂, 3.12 mg TEMPO and 0.109 mL benzylamine (1.0 mmol) in 5 mL of reaction medium.²⁶ The reaction conditions and work-up procedures were same as above.

All reactions were carried out in a custom-made photoreactor, constructed as per previous literature.²⁷ The performance of photoreactor was confirmed by checking the reproducibility of the previous reports.

GC Analysis

GC analysis was conducted on Young Lin Autochro-3000 (6500 GC system) equipped with Elite 1701 column (15 m × 0.53 mm × 1 µm) and FID using N₂ as a carrier gas, with slight modifications to the reported method.¹¹ For analysis of the imine product, the injector temperature was maintained at 250 °C and detector temperature was 280 °C. The column temperature was programmed as: 80 °C (hold 2 min) raised up to 280°C (at a rate of 40 °C min⁻¹ and finally hold 2 min). Anisole was used as the internal standard to determine the % conversion and yield.

Adsorption studies

0.125 g of TiO₂ and 1.14 mg ARS dye (3.33 × 10⁻³ mmol) were added in 5 ml solvent and allowed to equilibrate. The solution

was centrifuged at 35000 rpm for 10 min to separate the adsorbent from the solution. The supernatant solution was analyzed using a Shimadzu UV-1800 UV-Visible spectrophotometer to determine the concentration of the dye. The amount of ARS dye adsorbed on the TiO₂ was determined using the following formula:

$$q = \frac{(C_0 - C_f)}{m} V$$

where q is the amount of ARS dye adsorbed on anatase TiO₂ (mg g⁻¹), C_0 is the initial strength of the ARS dye (mg L⁻¹), C_f is the dye strength after adsorption (mg L⁻¹), V is the volume of the ARS dye (L), and m is the mass of the adsorbent (g).

Funding Information

Mahatma Jyotiba Phule Research & Training Institute (MAHAJYOTI) – Mahatma Jyotiba Phule Research Fellowship-2022 (MAHAJYOTI/2022/Ph.D. Fellow/1002)

Acknowledgment

VK acknowledges MAHAJYOTI for the Research Fellowship.

Primary Data

NO

Conflict of Interest

The authors declare no conflict of interest.

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Supplementary Information

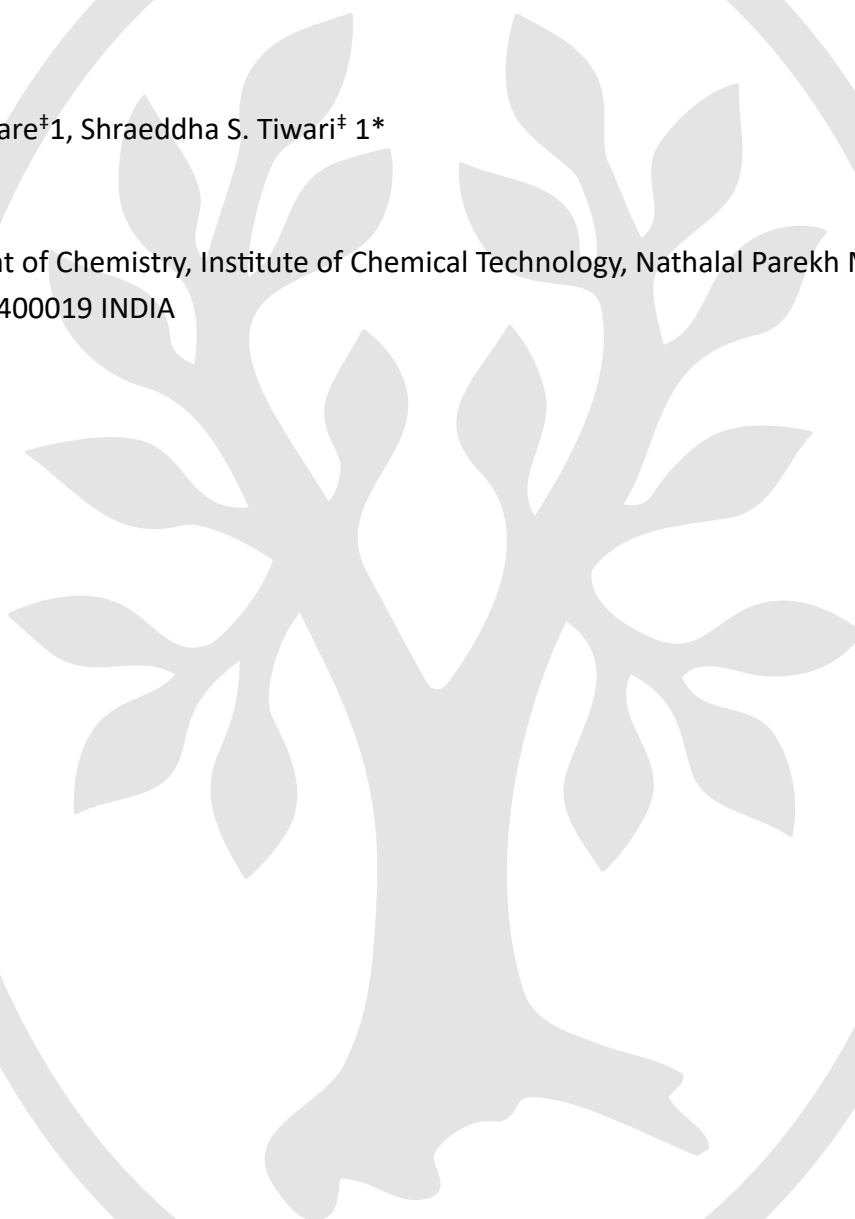
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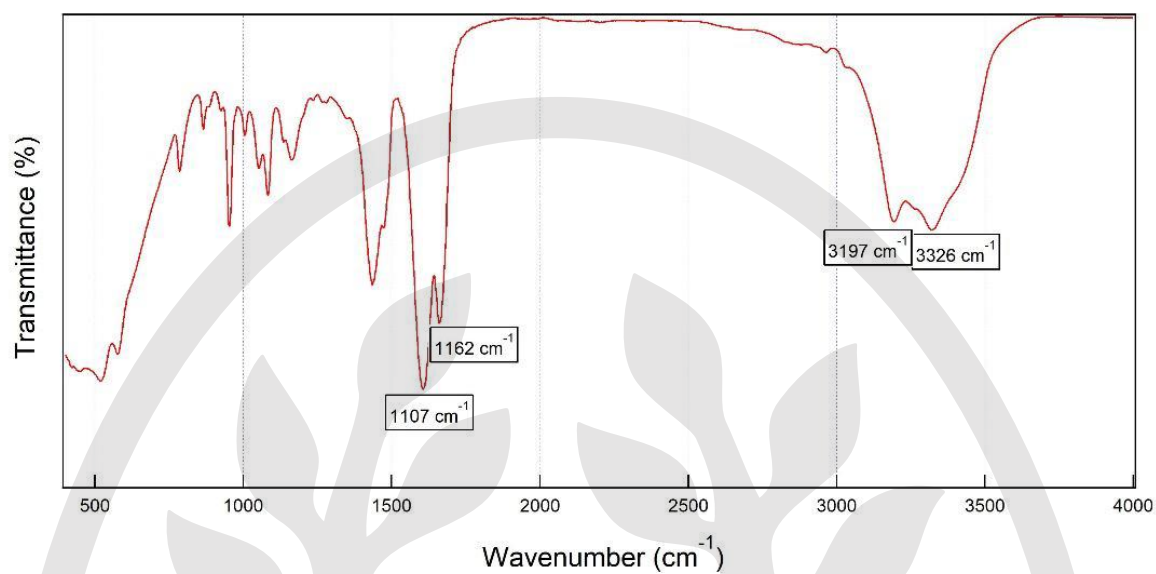


Figure S1: IR spectrum of reline

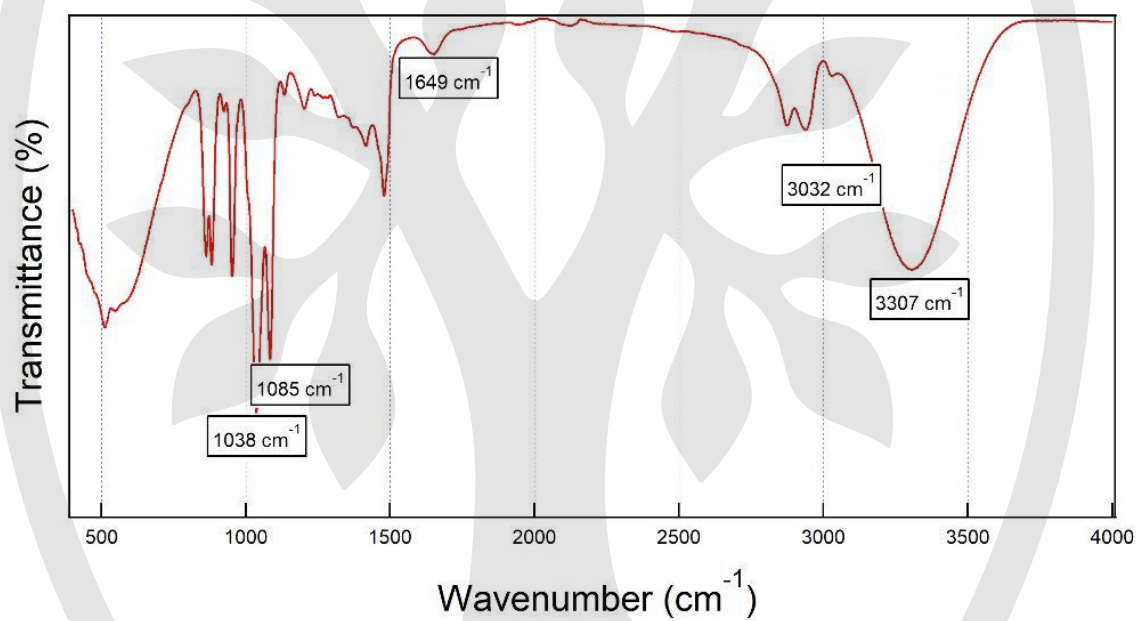


Figure S2: IR spectrum of ethaline

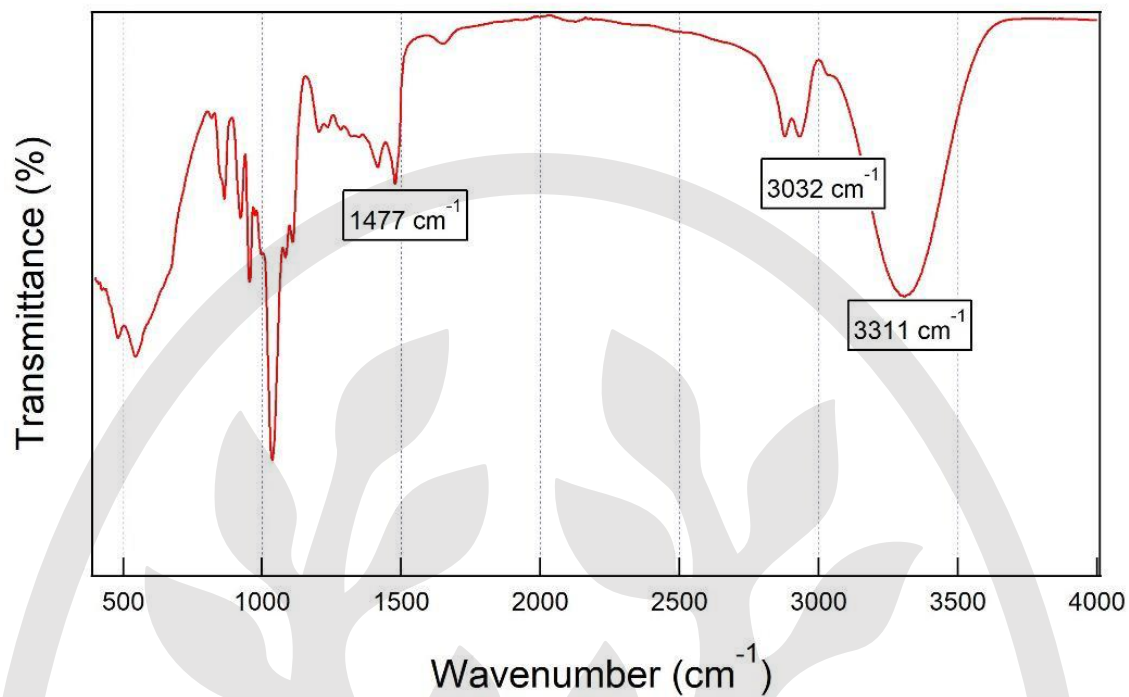
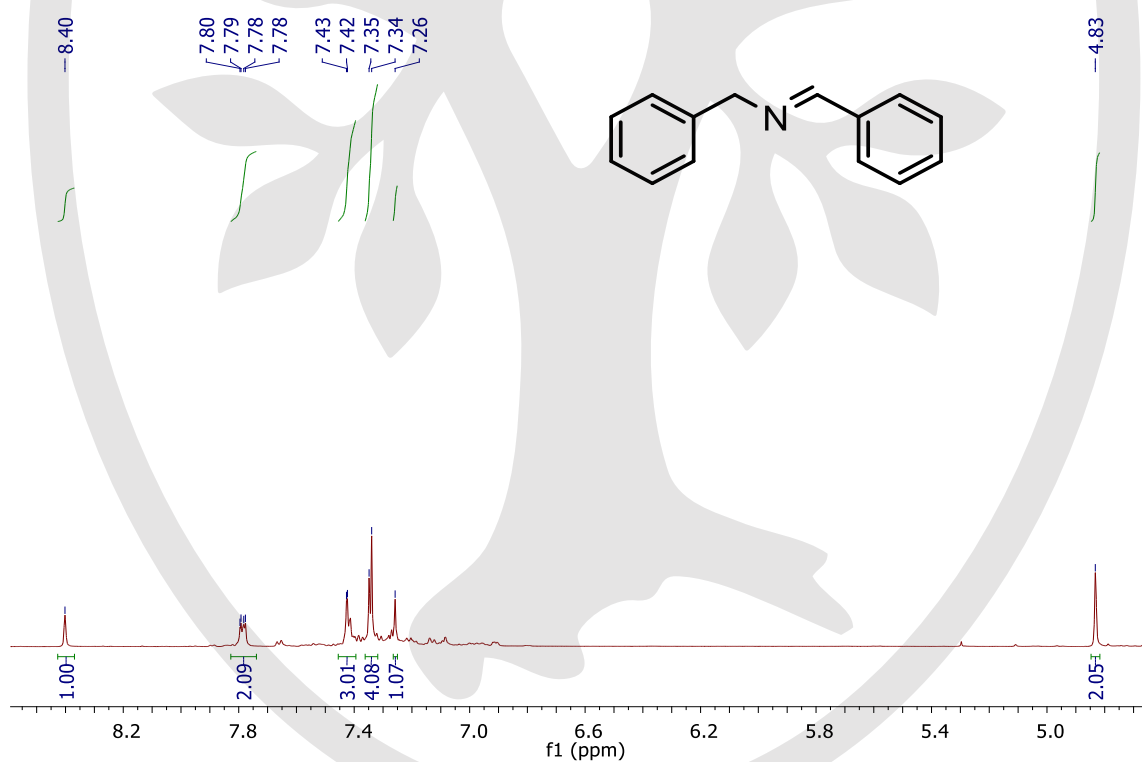


Figure S3: IR spectrum of glyciline

Figure S4: ¹H NMR of the imine product (500 MHz, CDCl₃); δ= 4.83 (d, 2H), 7.26-7.29 (m, 1H), 7.37-7.35 (m, 4H), 7.40-7.43 (m, 3H), 7.78-7.80 (m, 2H), 8.42 (t, 1H)

-162.14

-139.45

-136.27

-130.92

-128.75

-128.64

-128.43

-128.12

-127.15

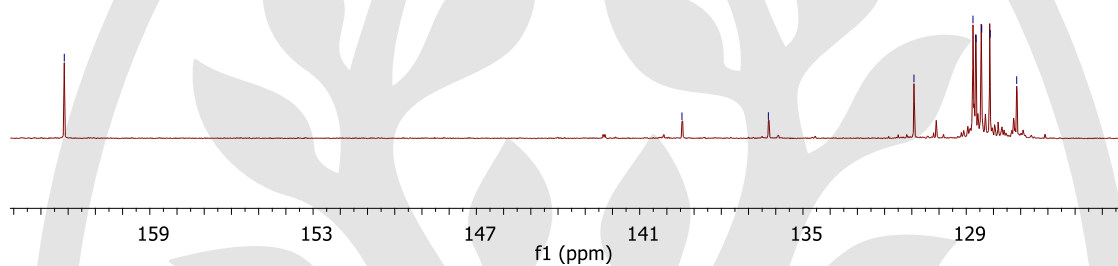


Figure S5: ^{13}C NMR (101 MHz, CDCl_3): δ 65.1, 127.1, 128.1, 128.4, 128.6, 128.7, 130.9, 136.2, 139.4, 162.2

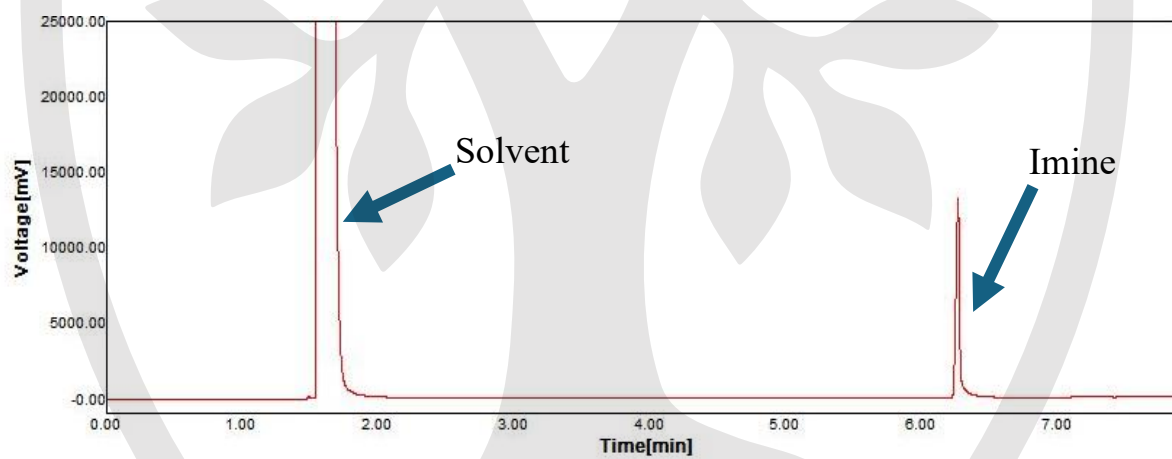


Figure S6: GC chromatogram of the imine product

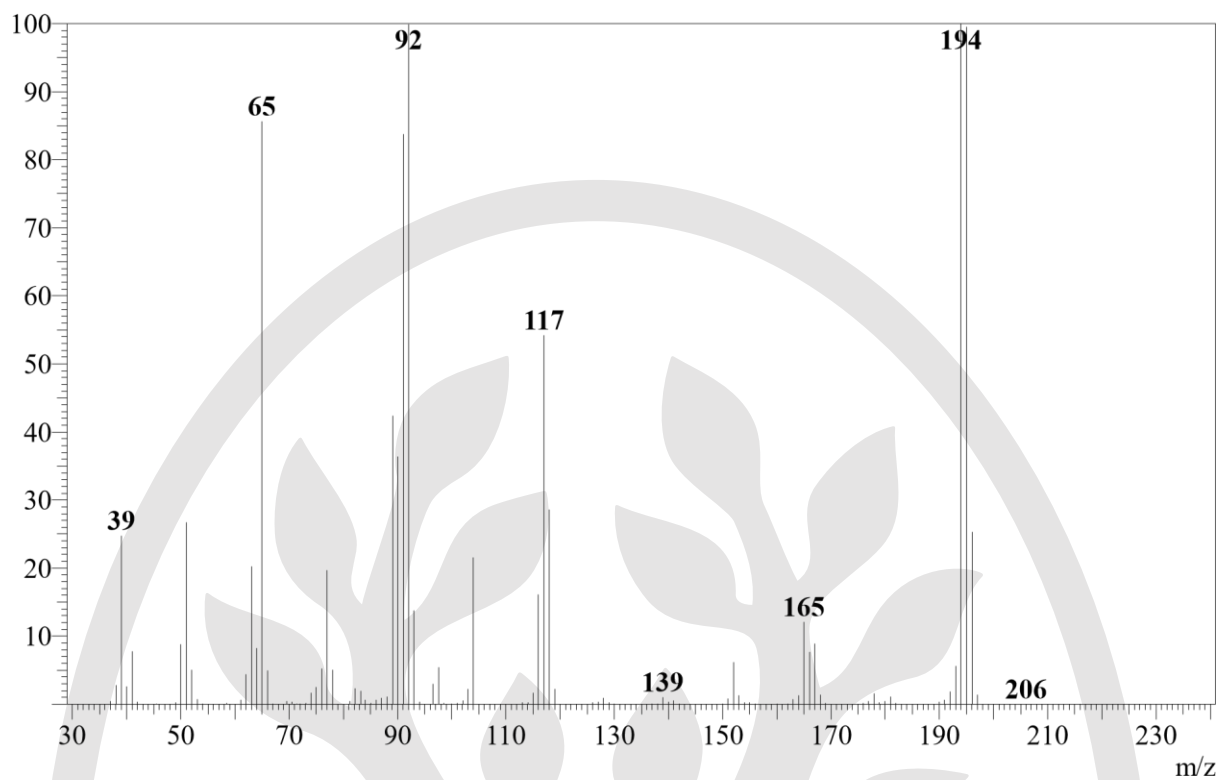


Figure S7: GC-MS analysis of the imine product

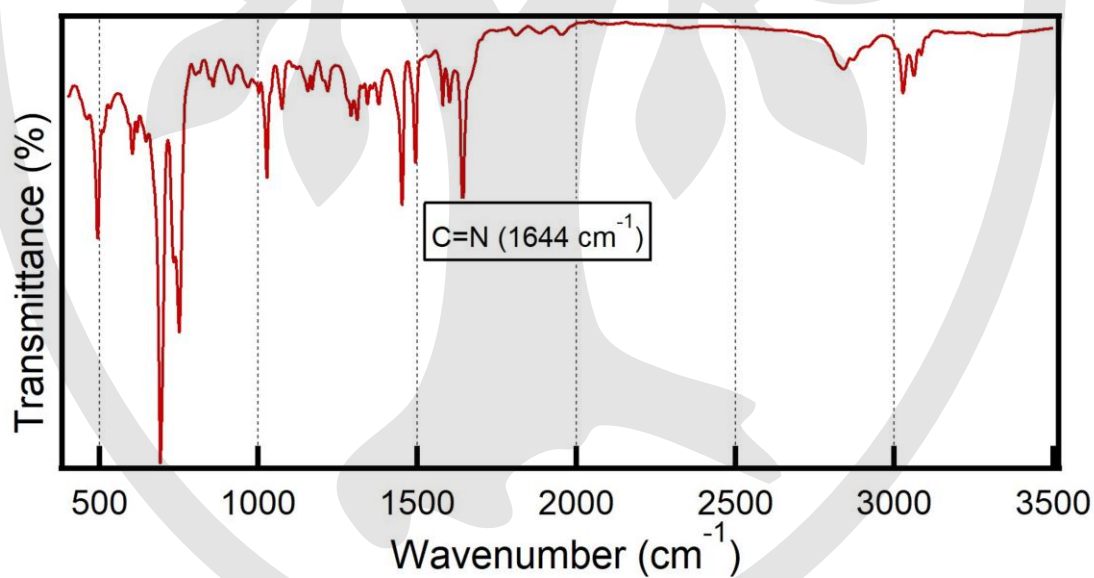


Figure S8: IR spectrum of imine