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Advancing green chemistry: a surfactant-enabled approach for nitro reduction in aqueous medium

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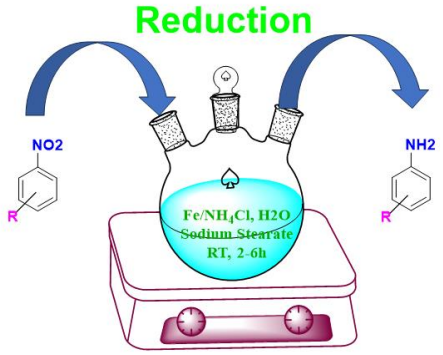
Abstract

We present a sustainable and highly efficient protocol for the selective reduction of nitro compounds to amines, employing a water-based Fe/NH_4Cl system enhanced by surfactant assistance. Utilizing sodium stearate, a readily available, soap-derived surfactant, markedly boosts catalytic performance, delivering excellent yields under mild, organic solvent free conditions. This green methodology provides a cost-effective, scalable, and environmentally benign alternative to traditional reduction techniques. The findings highlight the transformative potential of surfactant-stabilized micellar catalysis in promoting eco-friendly and industrially viable organic syntheses.



Here R: -H, Electron-donating group (EDG), Electron withdrawing group (EWG) or Heterocyclic group

Keywords: Green chemistry, surfactant-assisted catalysis, nitro reduction, sodium stearate, aqueous-phase reaction, eco-friendly catalysis

Introduction

The selective hydrogenation of functionalized nitro compounds to their corresponding amines is a fundamental transformation in organic synthesis, given the critical role of functionalized amines as key intermediates and precursors in the production of a wide range of industrially significant compounds. [1] These include dyes, pigments, agrochemicals, polymers, herbicides and pharmaceuticals. [2] Traditional methods for achieving this transformation often rely on the use of various reducing agents in combination with transition metal-based catalysts. [3] However, the widespread application of such methodologies is hindered by the high cost associated with the use of stoichiometric amounts of these reducing agents. [4] Additionally, concerns regarding safety and handling arise due to the hazardous and potentially unstable nature of these reagents. [5-6]

In this context, catalytic hydrogenation has emerged as a highly attractive alternative due to its cost-effectiveness and suitability for large-scale industrial applications. [7] Nevertheless, achieving high selectivity in the hydrogenation of functionalized nitro compounds to their desired amine products remains a persistent challenge in this field. [8-9] Commonly employed catalysts for this purpose include Raney nickel, palladium, and platinum, often modified with specific additives to enhance their performance. [10-12] Despite their widespread use and demonstrated efficiency, these catalysts exhibit several notable drawbacks. [13] Key limitations include moisture sensitivity, pyrophoricity, poor selectivity towards the desired amine product, and operational constraints necessitating specialized reactor systems due to the high temperatures and pressures required for the reaction. [14] Additionally, the high cost of noble metal catalysts and prolonged reaction times further limit their practical utility. [15]

Moreover, Pd- and Pt-based catalytic systems suffer from additional disadvantages, including susceptibility to deactivation by trace impurities present in the reaction medium and the leaching of metal species, which compromises catalyst stability and recyclability. [16] In recent years, efforts to address these challenges have led to the development of alternative catalytic systems. [17] Notably, Corma et al. and Xia-Bing Lou et al. have independently reported the successful application of heterogeneous gold-based catalysts capable of achieving selective hydrogenation of nitro compounds in the presence of diverse functional groups. [18] Beyond noble metal catalysts, other emerging catalytic systems have also demonstrated promising results. These include heterogenized cobalt oxide catalysts, [19] active copper nanoparticles generated in situ, [20] as well as recyclable copper (II) and cobalt (II) phthalocyanine-based catalysts. [21-22] These novel approaches offer enhanced chemo- and regioselectivity for the reduction of aromatic nitro compounds while addressing some of the limitations associated with traditional catalytic systems. [23]

The development of novel green methodologies remains a central focus of our research program, with the overarching objective of advancing sustainable and environmentally benign catalytic processes. [24-26] This approach utilizes a soap- and detergent-based surfactant, specifically sodium stearate, in combination with a mild and inexpensive reducing agent, sodium borohydride, in an aqueous phase as a key component of the catalytic system.

Given the significance of nitro to amine reduction in modern synthetic chemistry and the growing emphasis on green chemistry, the use of water as a solvent has become increasingly desirable. To facilitate such environmentally benign transformations, surfactant chemistry has gained importance. While surfactants such as Coolade, [27] TPGS-750M [28-30] and PTS [31] have demonstrated excellent reaction efficiency and selectivity, their high cost and limited commercial availability present challenges for widespread adoption.

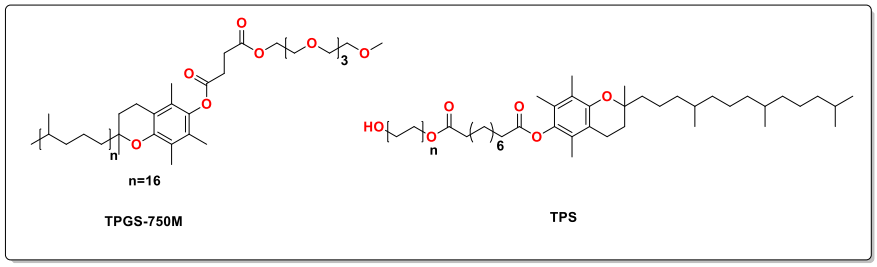


Figure-1: Chemical structure of the designer surfactants TPGS-750M and TPS

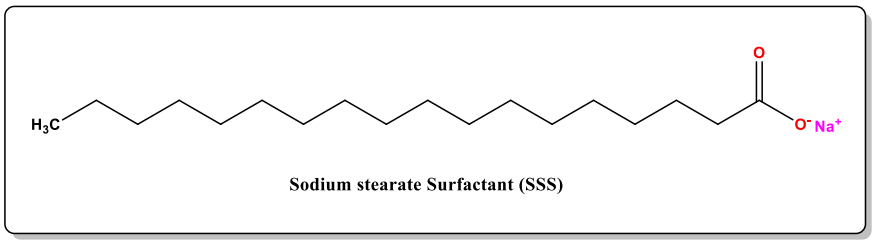


Figure-2: Chemical structure of the surfactant SSS

To address this limitation, we introduce sodium stearate surfactant (SSS) with iron powder in water as a novel and cost-effective alternative for synthetic chemistry. Despite being a widely available and inexpensive component in soaps and detergents, sodium stearate has not been previously explored for catalytic applications. In this study, we successfully employed SSS in this reduction, achieving outstanding results in terms of conversion, selectivity, and yield. Sodium stearate, a white solid and the sodium salt of octadecanoic acid, possesses a unique amphiphilic nature due to its hydrophobic 17-membered aliphatic chain and hydrophilic carboxylate head. This property enables the formation of micelles, which are crucial for facilitating the reduction in aqueous media. The micellar catalysis with SSS offers multiple advantages, including: high yields across a broad reaction scale (mg to kg), mild reaction conditions (room temperature to 40 °C), efficient catalyst loading (palladium or copper in ppm levels), minimal use of organic solvents, recyclability of catalytic agents and surfactants, reduced carbon footprint and environmentally sustainable processes. By integrating SSS into synthetic methodologies, we provide a practical, scalable, and eco-friendly alternative to conventional organic solvent-based reduction. This study establishes a strong foundation for further exploration of low-cost, sustainable surfactant systems in catalysis and green chemistry. Reductions using sodium borohydride with surfactants can stabilize reactive intermediates, aid in electron transfer, and modulate the redox environment, leading to selective reduction.

Results and Discussion

Despite advances in catalytic hydrogenation, effective heterogeneous systems for selective and greener nitro compound reduction remain limited due to challenges in selectivity, scalability, and functional-group compatibility. There is a critical need for efficient, environmentally sustainable catalytic systems that can selectively reduce nitro groups in the presence of other reducible functionalities such as ketones, aldehydes, alkenes, and alkynes. A system with high functional-group tolerance would enhance reaction precision, reduce protecting group use, and streamline complex molecule synthesis by minimizing steps and improving overall

efficiency. Consequently, research focuses on developing robust, selective, and reusable catalysts aligned with green chemistry principles.

Our proposed methodology offers key advantages like cost-effectiveness, sustainability, and scalability for nitro-to-amine reductions. Using sodium stearate as a surfactant improves reactant dispersion in water, enhancing efficiency while avoiding hazardous solvents. Combined with Fe/NH_4Cl as a mild reducing agent, this system enables selective reduction under mild conditions without excessive catalyst loading. This approach addresses issues such as harsh conditions, costly catalysts, and waste, making it a significant advancement in sustainable synthesis.

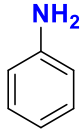
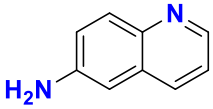
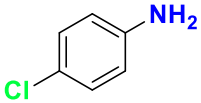
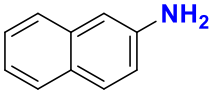
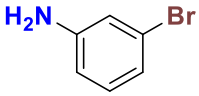
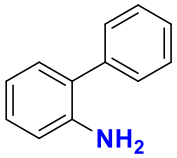
To optimize conditions, we used nitrobenzene as a model substrate. A reaction with 1.0 eq of nitrobenzene, 2% SSS (10 vol), Fe powder (5.0 eq), and NH_4Cl (1.2 eq) in water at room temperature for 2 h yielded 95% of the amine [General procedure-1]. Using TPGS-750M [4] under similar conditions yielded 94% [General procedure-2], while Pd-C in methanol under 1 atm H_2 for 2 h gave 83% [General procedure-3]. This strategy enabled efficient reduction of various substituted heteroaryl and aliphatic nitro compounds to corresponding amines in moderate to high yields.

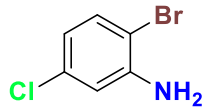
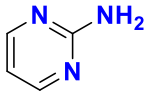
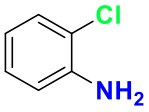
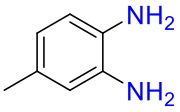
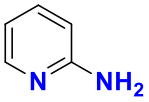
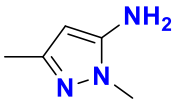
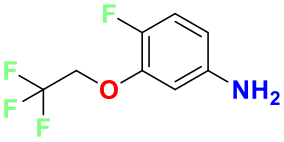
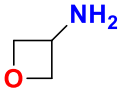
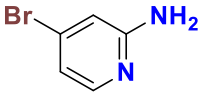
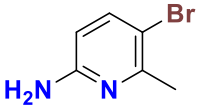
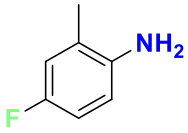
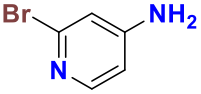
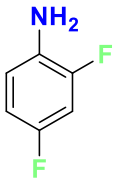
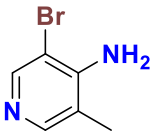
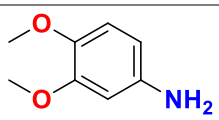
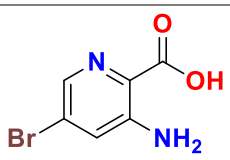
Table 1. Reaction condition comparison of existing methods with its advantages and disadvantages

Substract Product (A1)

Reducing agent	Solvent	Time	Yield	Advantages	Disadvantages
SSS and Fe/NH_4Cl	Water	2-6 h	95%	Cheap metal and Surfactant, Mild, aqueous, High yield	Requires filtration
SSS and Zn/NH_4Cl	Water	2-6 h	93%	Costly metal, More hazardous than Fe, Mild, aqueous, High yield	Requires filtration
TPGS-750M [44] Zn/NH_4Cl	Water	2 h	94%	Eco-friendly, Aqueous, High yield	Very Expensive, Requires filtration
Pd-C/H_2 [45]	Methanol	2 h	83%	Mild, Selective	Requires transition metal catalyst filtration, Pyrophoric nature
Fe/HCl [46]	Ethanol	3 h	87%	Cheap	Acidic conditions, need organic solvent

In the case of the isolated compounds, we observed that the overall reaction outcomes were satisfactory, with consistent isolated yields. A detailed comparison of the yields obtained using TPGS-750M and catalytic hydrogenation (H_2, Pd-C) revealed distinct trends based on the nature of the starting materials. Notably, simple aromatic amines such as compounds **A1**, **A15**, and **A16**, which were synthesized from their corresponding nitro precursors, exhibited comparable isolated yields when subjected to both TPGS-750M and H_2, Pd-C reactions. This suggests that both systems are effective for such substrates without significant variation in efficiency. In contrast, heterocyclic compounds such as **A6**, **A14**, **A17**, and **A19** afforded moderate isolated yields. However, these yields were still comparable between the TPGS-750M and H_2, Pd-C reaction systems, indicating that the presence of heterocyclic moieties does not significantly diminish the catalytic performance under either set of reaction conditions. Interestingly, halogen-containing compounds such as **A2**, **A3**, **A4**, and **A5** produced comparable yields when reacted under TPGS-750M-catalyzed conditions. However, when subjected to catalytic hydrogenation with H_2, Pd-C, the major product was identified as the corresponding des-halogenated compound, resulting in the formation of **A1**. A similar dehalogenation pathway was observed in the case of pyridine-containing compounds **A7** and **A8**, which underwent reductive dehalogenation to yield **A6** as the primary product. Moreover, des-halogenation was also the predominant outcome for compounds **A21** to **A26** under H_2, Pd-C conditions, leading to the formation of the corresponding des-halogenated derivatives. The des-halogenated products were successfully isolated and thoroughly characterized using spectroscopic techniques, which confirmed their structural identity and the completion of the dehalogenation process. These findings highlight the divergent reactivity of aromatic and heterocyclic substrates under different catalytic systems and underscore the impact of substrate electronic properties on the outcome of the reaction. The consistent yields observed with TPGS-750M further reinforce its potential as an efficient and sustainable alternative to conventional catalytic methods (Table -2).

Compound I. D	Structure	Yield with different condition	Compound I. D	Structure	Yield with different condition
A1		SSS: 95% TPGS-750M: 95% H_2, Pd-C: 91%	**A14**		SSS: 78% TPGS-750M: 75% H_2, Pd-C: 60%
A2		SSS: 93% TPGS-750M: 90% H_2, Pd-C: 20% and 70% I*	**A15**		SSS: 93% TPGS-750M: 92% H_2, Pd-C: 85%
A3		SSS: 90% TPGS-750M: 85% H_2, Pd-C: 30% and 63% I*	**A16**		SSS: 91% TPGS-750M: 92% H_2, Pd-C: 80%

A4		**SSS: 91%** **TPGS-750M: 89%** **H_2, Pd-C: 15%** **and 75%I***	**A17**		**SSS: 70%** **TPGS-750M: 65%** **H_2, Pd-C: 35%**
A5		**SSS: 96%** **TPGS-750M: 96%** **H_2, Pd-C: 22%** **and 22% I***	**A18**		**SSS: 96%** **TPGS-750M: 93%** **H_2, Pd-C: 87%**
A6		**SSS: 80%** **TPGS-750M: 75%** **H_2, Pd-C: 69%**	**A19**		**SSS: 74%** **TPGS-750M: 71%** **H_2, Pd-C: 20%**
A7		**SSS: 75%** **TPGS-750M: 19%** **H_2, Pd-C: 19%** **and 55% I***	**A20**		**SSS: 69%** **TPGS-750M: 69%** **H_2, Pd-C: 40%**
A8		**SSS: 78%** **TPGS-750M: 74%** **H_2, Pd-C: 12%** **and 65% I***	**A21**		**SSS: 84%** **TPGS-750M: 86%** **H_2, Pd-C: 32% and 58%I***
A9		**SSS: 95%** **TPGS-750M: 96%** **H_2, Pd-C: 86%**	**A22**		**SSS: 85%** **TPGS-750M: 83%** **H_2, Pd-C: 25% and 60% I***
A10		**SSS: 92%** **TPGS-750M: 90%** **H_2, Pd-C: 89%**	**A23**		**SSS: 95%** **TPGS-750M: 83%** **H_2, Pd-C: 22% and 55% I***
A11		**SSS:95%** **TPGS-750M: 94%** **H_2, Pd-C: 83%**	**A24**		**SSS: 75%** **TPGS-750M: 73%** **H_2, Pd-C: 25% and 60% I***

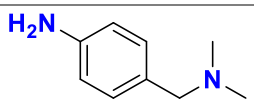
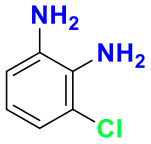
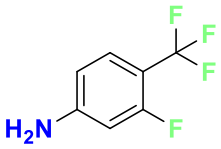
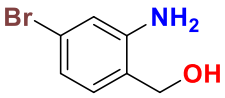
A12		**SSS: 78%** **TPGS-750M: 75%** **H_2, Pd-C: 70%**	**A25**		**SSS: 90%** **TPGS-750M: 88%** **H_2, Pd-C: 12% and 81% I***
A13		**SSS: 87%** **TPGS-750M: 83%** **H_2, Pd-C: 78%**	**A26**		**SSS: 75%** **TPGS-750M: 75%** **H_2, Pd-C: 15% and 89% I***

Table 2. List of Nitro to amine product with yield in different condition, Here I*= Halogenated byproduct

Comparative analysis between **TPGS-750M** [4] and sodium stearate **(SSS)** revealed that both surfactants exhibited similar catalytic efficiency across a range of substrates. The isolated yields obtained with SSS were largely in agreement with those obtained using TPGS-750M, indicating that both micellar systems provide comparable microenvironments that facilitate effective catalytic activity. However, in the case of halogen-containing compounds, SSS showed a slightly higher tendency toward dehalogenation under catalytic hydrogenation conditions, which may be attributed to subtle difference in the surfactant's micellar structure and the stabilization of reactive intermediates. These findings highlight the effectiveness of both TPGS-750M and SSS as micellar catalytic systems, with comparable performance across a range of aromatic and heterocyclic substrates. The consistent yields observed with TPGS-750M and SSS reinforce their potential as efficient and sustainable alternatives to conventional catalytic methods, aligning with the principles of green chemistry.

The use of **iron (Fe)** metal instead of **zinc (Zn)** for the reduction of the nitro compounds to amines offers several significant advantages, particularly from environmental, economic, and operational perspectives. Iron is commonly employed in acidic conditions, typically in the presence of hydrochloric acid (HCl), to facilitate the stepwise reduction of nitro groups ($–NO_2$) to the corresponding amines ($–NH_2$), proceeding through intermediates such as nitroso and hydroxylamine derivatives. This method, often referred to as Fe/HCl reduction, is a well-established and effective approach in both laboratory and industrial settings. One of the primary benefits of using Fe over Zn lies in its cost-effectiveness. Iron is considerably cheaper and more abundantly available than zinc, making it highly attractive for large-scale applications. From an environmental standpoint, iron is a greener alternative, as it generates less hazardous waste. The by-products of Fe-mediated reduction, such as ferric salts (e.g., $FeCl_3$), are generally less toxic and easier to handle or dispose of compared to the zinc salts formed in Zn-mediated reactions, which can contribute to heavy metal pollution and require more stringent waste management protocols. Additionally, iron sludge formed during the reaction is magnetic and can be more easily separated from the reaction mixture, simplifying work-up and purification. In contrast, zinc sludge tends to be gelatinous and more challenging to filter. Furthermore, iron tends to operate under milder conditions, which can offer better functional group compatibility, especially for substrates containing acid-sensitive moieties. On the other hand, zinc can be overly reactive and may lead to undesired side reactions or degradation of sensitive functional groups. From a sustainability perspective, iron is one of the most earth-abundant elements, and its mining and usage have a lower environmental footprint than zinc. Overall, choosing Fe over Zn for the reduction of nitro groups to amines aligns well with the principles of green chemistry, offering a safer, more economical, and environmentally friendly route without compromising on reaction efficiency.

The reduction of a nitro group to an amine using Fe/NH_4Cl in a surfactant medium follows the same fundamental electron-transfer mechanism as in traditional aqueous or alcoholic media, but surfactants introduce micellar catalysis—which enhances rate, selectivity, and solubility of hydrophobic substrates in water.

Importance of nitro to amine reduction reaction

Selective reduction: Depending on the reaction conditions, selective reduction can be achieved, avoiding over-reduction to hydroxylamine or other side products. [34]

Applications in the Pharmaceutical Industry: **Drug Synthesis:** Many pharmaceutical drugs contain amine functional groups, which are crucial for their biological activity. For example: Paracetamol (Acetaminophen): Synthesized from nitrobenzene reduction. Lidocaine: A local anesthetic that requires amine intermediates. Chloramphenicol: An antibiotic synthesized using nitro reduction. [35]

Heterocyclic and API (Active Pharmaceutical Ingredient) synthesis. Amines are key components in the synthesis of heterocyclic compounds like pyrroles, indoles, and quinolines, which form the core structure of many drugs (e.g., anti-cancer and anti-inflammatory drugs). Many Active Pharmaceutical Ingredients (APIs) involve amine-functionalized molecules, which are synthesized using nitro reduction. [36]

Green chemistry and catalysis. The pharmaceutical industry seeks green and sustainable methods for nitro reduction, avoiding toxic reagents like tin chloride ($SnCl_2$) or iron. Catalytic hydrogenation (H_2/Pd, Raney Nickel, or PtO_2) and metal-mediated reductions (Zn/HCl, Fe/AcOH, Cu/H_2) are preferred for high efficiency and selectivity. The nitro-to-amine reduction is indispensable in organic synthesis and drug development, providing a route to key amine intermediates used in the manufacture of pharmaceuticals, dyes, and advanced materials. The choice of reduction method depends on factors like efficiency, cost, environmental impact, and selectivity, making it a continually evolving area in green chemistry and industrial processes. [37]

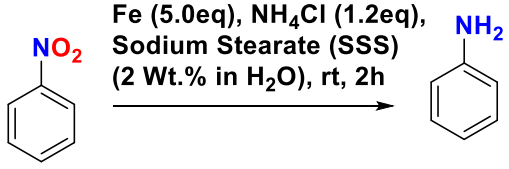
Conclusions

This study establishes the sodium stearate surfactant (SSS) as a cost-effective and sustainable alternative for micellar catalysis in the reduction of nitro compounds to amines. Unlike expensive conventional surfactants, SSS enables high-yielding, scalable, and environmentally friendly transformations in aqueous media under mild conditions. Its amphiphilic nature facilitates stable micelle formation, enhancing catalytic efficiency by increasing substrate solubility and reactant localization. This approach not only optimizes reaction performance, but also minimizes solvent consumption, catalyst loading, and waste generation contributing to a more sustainable process. Furthermore, the SSS-based methodology aligns with the principles of green chemistry by promoting water as a solvent, reducing hazardous reagents, and improving atom economy. Its practicality and scalability position it as a viable solution for industrial applications were cost and environmental considerations are paramount. By demonstrating the efficacy of SSS in micellar catalysis, this study broadens the scope of surfactant-assisted catalysis in sustainable chemical synthesis, including pharmaceuticals, agrochemicals, and fine chemicals. These findings underscore the potential of leveraging inexpensive and readily available surfactants to drive greener and more efficient chemical processes, advancing the development of eco-friendly and economically viable alternatives in modern organic synthesis.

Experimental Section

General. All chemicals, reagents, and surfactants sodium stearate were obtained commercially and used as received, without further purification. Surfactant solutions were prepared using condensed, demineralized water. Reaction products were purified using either flash chromatography (Combi Flash system) or conventional glass column chromatography with silica gel of various mesh sizes (60–120, 100–200, and 350–400). Elution typically employed mixtures of n-hexane and ethyl acetate, or methanol and dichloromethane (DCM), depending on compound polarity. The structural identity of compounds was confirmed using spectroscopic techniques. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Ascend™ 400 MHz NMR spectrometer, with samples dissolved in standard deuterated solvents such as DMSO-d_6, MeOD-d_4, or $CDCl_3$. Tetramethylsilane (TMS) was used as an internal standard when applicable. Chemical shifts (δ) are reported in parts per million (ppm), and multiplicities are indicated as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), or br (broad). High-resolution mass spectrometry (HRMS), the acquisition parameters were set as follows: the ion source type used was ESI with a nebulizer pressure of 0.3 bar. The ion polarity was set to positive, and the dry heater temperature was maintained at 200 °C. The capillary voltage was set at 3000 V, with the capillary active. A dry gas flow rate of 4.0 L/min was maintained. The scan began at 50 m/z and ended at 600 m/z. The end plate offset was set to 500 V, and the charging voltage was 2000 V. The divert valve was directed to waste, and the scan end temperature was 0 °C. M.P. were determined in open capillary tubes using either a Bucki M.P. apparatus or an Avi Scientific Blue Digital device. All values reported are uncorrected. Thin-layer chromatography (TLC) was used for monitoring reaction progress, employing silica gel 60 F_{254} plates (Merck). Eluents included combinations of hexane with ethyl acetate or dichloromethane with methanol. Visualization of TLC spots was achieved under UV light or by staining with reagents such as potassium permanganate ($KMnO_4$), phosphomolybdic acid (PMA), or ninhydrin. Key reagents, solvents, and starting materials were sourced from suppliers including BLD Pharma (Hyderabad), Spectrochem (Pune), Combi-Blocks Ltd. (Delhi), and Merck (Mumbai). Flash chromatography was performed using a Combi Flash system equipped with a programmable injector, capable of flow rates from 1 to 200 mL/min and a maximum pressure of 200 psi.

Scale-up reaction for nitro to amine reduction



A1

Exact Mass: 123.03
50.0 g/ 1.0eq/ 406mmol

Exact Mass: 93.06
36.0 g, 480 mmol, 95%

In a 1.0 L round-bottom flask fitted with a magnetic stir bar, nitrobenzene (50.0 g, 406 mmol, 1 eq) and ammonium chloride (26.06 g, 487.2 mmol, 1.2 eq) were combined. Subsequently, 500 mL of a 2 wt. % aqueous SSS solution (500 mL) was added, rinsing down the inner walls of the flask to ensure complete transfer. The mixture was stirred for about 10 minute to achieve homogeneity and allow partial dissolution of the nitroarene. Finely powdered iron (111.65 g, 2030 mmol, 5 eq) was then added in a single portion. The resulting mixture was stirred at room temperature, and the progress of the reaction was monitored via thin-layer chromatography (TLC). The reaction was deemed complete upon the full consumption of the nitrobenzene and disappearance of any intermediates such as nitroso or hydroxylamine species, typically observed within 2 hours. The mixture was

then passed through celite bed to remove residual solids and eluted using a minimal amount of ethyl acetate (500 mL). Alternatively, the reaction mixture was extracted three times with small portions (500 mL each) of ethyl acetate, and the combined organic layers were dried over anhydrous sodium sulphate. The solvent was removed under reduced pressure to offered aniline (**A1**) as a brown liquid (36.0 g, 480 mmol, 95%) without additional purification.

General procedure for the reduction of nitro compounds in SSS. In a 50 mL round-bottom vial fitted with a magnetic stir bar, nitroarene (0.5 mmol, 1 eq) and ammonium chloride (0.6 mmol, 1.2 eq) were combined. Subsequently, 1.0 mL of a 2 wt. % aqueous SSS solution was added, rinsing down the inner walls of the vial to ensure complete transfer. The mixture was stirred for about one minute to achieve homogeneity and allow partial dissolution of the nitroarene. Finely powdered iron (2.5 mmol, 5 eq) was then added in a single portion. The resulting mixture was stirred at room temperature, and the progress of the reaction was monitored via thin-layer chromatography (TLC). The reaction was deemed complete upon the full consumption of the nitroarene and disappearance of any intermediates such as nitroso or hydroxylamine species, typically observed within 2 to 6 hours. The mixture was then passed through a short (approximately 1 cm) through celite bed to remove residual solids and moisture, and eluted using a minimal amount of ethyl acetate. Alternatively, the reaction mixture was extracted three times with small portions of ethyl acetate or diethyl ether, and the combined organic layers were dried over anhydrous sodium sulphate. The solvent was removed under reduced pressure, and the crude product was analyzed by electrospray ionization mass spectrometry (ESI-MS), nuclear magnetic resonance (NMR), and carbon-13 NMR (CMR) without additional purification unless specified otherwise.

General procedure for the reduction of nitro compounds in TPGS-750M. In a 50 mL round-bottom vial fitted with a magnetic stir bar, nitroarene (0.5 mmol,) and ammonium chloride (0.6 mmol, 1.2 eq) were combined. Subsequently, 1.0 mL of a 2 wt. % aqueous TPGS-750M solution was added, rinsing down the inner walls of the vial to ensure complete transfer. The mixture was stirred for about one minute to achieve homogeneity and allow partial dissolution of the nitroarene. Finely powdered Zinc (2.5 mmol, 5 eq) was then added in a single portion. The resulting mixture was stirred at room temperature, and the progress of the reaction was monitored via thin-layer chromatography (TLC). The reaction was deemed complete upon the full consumption of the nitroarene and disappearance of any intermediates such as nitroso or hydroxylamine species, typically observed within 2 to 6 hours. The mixture was then passed through a short (approximately 1 cm) through celite bed to remove residual solids and moisture, and eluted using a minimal amount of ethyl acetate. Alternatively, the reaction mixture was extracted three times with small portions of ethyl acetate or diethyl ether, and the combined organic layers were dried over anhydrous sodium sulphate. The solvent was removed under reduced pressure, and the crude product was analyzed by electrospray ionization mass spectrometry (ESI-MS), nuclear magnetic resonance (NMR), and carbon-13 NMR (CMR) without additional purification unless specified otherwise.

General procedure for the reduction of nitro compounds in H_2/Pd-C. The aromatic nitro compound (1.0 mmol) was dissolved in methanol in a hydrogenation flask. To this solution, 10 mol% of 10% palladium on carbon (Pd/C) catalyst was added under an inert atmosphere (e.g., nitrogen). The reaction mixture was stirred at room temperature under a hydrogen atmosphere 1 atm for 2 hours, or until complete consumption of the nitro compound was confirmed by thin-layer chromatography (TLC), Upon completion, the catalyst was removed by

filtration through a Celite pad and washed thoroughly with methanol. The filtrate was concentrated under reduced pressure, and the crude product was purified by recrystallization or column chromatography using an appropriate solvent system to afford the corresponding aromatic amine.

Aniline (A1). Bp 183 °C, ^{1}H NMR (400 MHz, DMSO-d6) δ 7.01 (t, *J* 8.4 Hz, 2H, ArH), 6.59 – 6.53 (d, *J* 8.4 Hz, 2H, ArH), 6.49 (t, *J* 7.3, 1H, ArH), 4.99 (s, 2H, -NH2), ^{1}H NMR (400 MHz, D2O in DMSO-d6) δ 7.01 (dd, *J* 8.5, 7.3 Hz, 2H, ArH), 6.56 (dt, *J* 7.6, 1.2 Hz, 2H, ArH), 6.50 (tt, *J* 7.3, 1.2 Hz, 1H, ArH), ^{13}C NMR (100 MHz, DMSO-d6) δ 148.64, 128.85, 115.67, 113.90, HRMS: *m/z* calculated for C6H7N: 93.1290; [M+Na] + found: 116.1515, Rf=0.5, TLC System Hexane: EtOAc, 2:8, Physical Appearance: Brown liquid (95% yield).

4-Chloroaniline (A2). Mp 70°C**,** ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.00 (d, *J* 8.8 Hz, 2H, ArH), 6.54 (d, *J* 8.8 Hz, 2H, ArH), 5.22 (s, 2H, -NH_2),^{1}H NMR (400 MHz, D_2O in DMSO-d_6) δ 7.00 (d, *J* 8.8 Hz, 2H, ArH), 6.54 (d, *J* 8.8 Hz, 2H, ArH), ^{13}C NMR (100 MHz, DMSO-d_6) δ 148.16, 128.96, 119.18, 115.64, HRMS: *m/z* calculated for C_6H_6ClN: 127.5710 and 129.5710; $[M]^+$ & $[M+H]^{+2}$ found: 127.5912, 129.5912, Rf=0.4, TLC System Hexane: EtOAc, 2:8, Physical Appearance: Pale yellow solid (93% yield).

3-Bromoaniline (A3). Bp 252 °C, ^{1}H NMR (400 MHz, DMSO-d6) δ 6.94 (t, *J* 8.0 Hz, 1H, ArH), 6.74 (t, *J* 2.0 Hz, 1H, ArH), 6.61 (ddd, *J* 7.8, 2.0, 0.9 Hz, 1H, ArH), 6.53 (ddd, *J* 8.1, 2.2, 0.9 Hz, 1H, ArH), 5.37 (s, 2H, -NH_2), ^{1}H NMR (400 MHz, D_2O in DMSO-d_6) δ 6.94 (t, *J* 8.0 Hz, 1H, ArH), 6.74 (t, *J* 2.1 Hz, 1H, ArH), 6.62 (ddd, *J* 7.9, 2.0, 0.9 Hz, 1H, ArH), 6.3 (ddd, *J* 8.1, 2.2, 0.9 Hz, 1H, ArH), ^{13}C NMR (100 MHz, DMSO-d6) δ 151.04,131.13, 122.55, 118.25, 116.34, 113.16, HRMS: *m/z* calculated for C_6H_6BrN: 172.0250; $[M]^+$ & $[M+H]^{+2}$ found: 172.0247 & 174.049, Rf=0.5, TLC System Hexane: EtOAc, 2:8, Physical Appearance: Pale yellow liquid (90% yield).

2-Bromo-5-chloroaniline (A4). Bp 128 °C**,** ^{1}H NMR (400 MHz, DMSO-d6) δ 7.33 (dd, *J* 8.4, 1.2 Hz, 1H, ArH), 6.81 (d, *J* 2.5 Hz, 1H, ArH), 6.48 (ddd, *J* 8.4, 2.6, 1.2 Hz, 1H, ArH), 5.61 (s, 2H, -NH_2), ^{1}H NMR (400 MHz, D_2O in DMSO-d_6): δ 7.32 (dd, *J* 8.5, 2.6 Hz, 1H, ArH), 6.81 (d, *J* 2.5 Hz, 1H, ArH), 6.48 (dd, *J* 8.5, 2.6 Hz, 1H, ArH), ^{13}C NMR (100 MHz, DMSO-d6) δ 147.68, 133.86, 133.14, 117.090, 106.00, HRMS*: m/z* calculated for C_6H_5BrClN:206.4670; $[M]^+$ & $[M+H]^{+2+}$ found: 206.4665, 208.4662 & 210.4665, Rf=0.4, TLC System Hexane: EtOAc, 1:9, Physical Appearance: Brown solid (91% yield).

2-Chloroaniline (A5). Bp 209 °C**,** ^{1}H NMR (400 MHz, DMSO-d_6)δ 7.17 (dd, *J* 7.9, 1.5 Hz, 1H, ArH), 7.01 (ddd, *J* 8.6, 7.2, 1.5 Hz, 1H, ArH), 6.79 (dd, *J* 8.0, 1.6 Hz, 1H, ArH), 6.53 (ddd, *J* 8.0, 7.3, 1.6 Hz, 1H, ArH), 5.30 (s, 2H, -NH_2), ^{1}H NMR (400 MHz, D_2O in DMSO-d_6): δ 7.17 (dd, *J* 7.9, 1.5 Hz, 1H, ArH), 7.01 (ddd, *J* 8.1, 7.2, 1.5 Hz, 1H, ArH), 6.79 (dd, *J* 8.1, 1.6 Hz, 1H, ArH), 6.54 (ddd, *J* 8.0, 7.2, 1.6 Hz, 1H, ArH), ^{13}C NMR (100 MHz, DMSO-d_6) δ 144.67, 128.96, 127.65, 117.04, 116.77, 115.41, HRMS: *m/z* calculated for C_6H_6ClN: 127.5710; [M^+], $[M+H]^{+2}$ found: 127.5912, 129.5912, Rf=0.5, TLC System Hex ne: EtOAc, 3:7, Physical Appearance: Pale yellow liquid (96% yield).

Pyridin-2-amine (A6). Mp 57 °C**,** ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.88 (ddd, *J* 5.0, 2.1, 1.0 Hz, 1H, ArH), 7.33 (ddt, *J* 8.4, 7.0, 1.6 Hz, 1H, ArH), 6.67 – 6.24 (m, 2H, ArH), 5.85 (s, 2H, -NH_2),^{1}H NMR (400 MHz, D_2O in DMSO-d_6): δ 7.93 – 7.80 (m, 1H, ArH), 7.34 (ddt, *J* 8.3, 4.6, 1.6 Hz, 1H, ArH), 6.58 – 6.28 (m, 2H, ArH), ^{13}C NMR (100 MHz, DMSO-d_6) δ 160.24, 148.17, 137.38, 112.26, 108.42 HRMS*: m/z* calculated for $C_5H_6N_2$: 94.1117; [M+ Na] $^+$ found: 117.0179, Rf=0.5, TLC System DCM: MeOH, 9:1, Physical Appearance: Pale yellow solid (80% yield).

4-Chloropyridin-2-amine (A7). Bp 226 °C**,** ^{1}H NMR (400 MHz, DMSO-d_6) δ 6.90 (dd, *J* 11.4, 8.7 Hz, 1H, ArH), 6.40 (dd, *J* 7.4, 2.6 Hz, 1H, ArH), 6.19 (dt, *J* 8.8, 3.1 Hz, 1H, ArH), 5.04 (s, 2H, -NH_2), 4.68 (q, *J* 8.9 Hz, 2H, -CH_2), ^{1}H NMR (400 MHz, D_2O in DMSO-d_6) δ 6.89 (dd*, J* 11.4, 8.7 Hz, 1H, ArH), 6.40 (dd, *J* 7.4, 2.6 Hz, 1H, ArH), 6.20 (dd, *J* 7.1, 4.1 Hz, 1H, ArH), 4.64 (q, *J* 8.8 Hz, 2H, -CH_2), ^{13}C NMR (100 MHz, DMSO-d_6) δ 146.29-146.28, 145.46-143.10,

128.47-120.18, 116.88-116.70, 107.73-107.67, 66.42-66.08, HRMS: *m/z* calculated for C_8H_7F4NO: 209.1436; $[M+H]^+$ found: 210.1433, Rf=0.5, TLC System Hexane: EtOAc, 2:8, Physical Appearance: Black liquid (75% yield).

4-Bromopyridin-2-amine (A8). Mp 145 °C**,** ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.78 (d, *J* 5.3 Hz, 1H), 6.75 – 6.56 (m, 2H), 6.24 (s, 2H), ^{1}H NMR (400 MHz, D_2O in DMSO-d_6) δ 7.76 (dd, *J* 5.0, 1H), 6.76 – 6.56 (m, 2H) **,** ^{13}C NMR (100 MHz, DMSO-d_6) δ 161.21, 149.56, 132.47, 114.93, 110.49, HRMS*: m/z* calculated for C_5H_5BrN: 173.0130; $[M^+]$, $[M+H]^{+2}$ found: 173.029, 175.0126, Rf=0.5, TLC System DCM: MeOH, 1:9, Physical Appearance: Brown solid (78% yield).

4-Fluoro-2-methylaniline (A9). Bp 92 °C**,** ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.30 (s, 2H, -NH_2), 7.50 (dd, *J* 8.7, 5.2 Hz, 1H, ArH), 7.22 (dd, *J* 9.5, 3.0 Hz, 1H, ArH), 7.13 (td, *J* 8.5, 3.0 Hz, 1H, ArH), 2.36 (s, 3H, -CH_3), ^{1}H NMR (400 MHz, D_2O in DMSO-d_6): δ 7.45 (dd, *J* 8.7, 5.2 Hz, 1H, ArH), 7.23 (dd, *J* 9.5, 2.9 Hz, 1H, ArH), 7.14 (td, J 8.5, 2.9 Hz, 1H, ArH), 2.34 (s, 3H, -CH_3), ^{13}C NMR (100 MHz, DMSO-d_6) δ 162.68-160.26, 135.63-135.54, 127.52-127.50, 125.73-125.64, 118.43-118.20, 114.12-113.90, 17.67, HRMS*: m/z* calculated for C_7H_8FN: 125.1464; $[M+H]^+$ found: 126.1464, Rf=0.6, TLC System Hexane: EtOAc, 2:8, Physical Appearance: Pale yellow liquid (95% yield).

2,4-Difluoroaniline (A10). Bp 170 °C**,** ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.07 – 6.95 (m, 1H, ArH), 6.75 (m, 2H, ArH), 4.97 (s, 2H, -NH_2), ^{1}H NMR (400 MHz, D_2O in DMSO-d_6): δ 6.98 (m, 1H, ArH), 6.75 (m, 2H, ArH), 13C NMR (400MHz, DMSO-d_6) δ 154.63-152.20, 151.41-148.91, 133.55-133.39, 116.58-116.43, 111.34-111.10, 104.05-103.56, HRMS*: m/z* calculated for $C_8H_5F_2N$: 129.1098; $[M+H]^+$ found: 130.1101, Rf=0.4, TLC System Hexane: EtOAc, 2:8, Physical Appearance: Pale yellow liquid (92% yield).

3,4-Dimethoxyaniline (A11). Mp 87 °C**,** ^{1}H NMR (400 MHz, DMSO-d_6) δ 6.63 (d, J 8.4 Hz, 1H, ArH), 6.26 (d, *J* 2.6 Hz, 1H, ArH), 6.05 (dd, *J* 8.4, 2.5 Hz, 1H, ArH), 4.65 (s, 2H, -NH_2), 3.66 (s, 3H, -CH_3), 3.60 (s, 3H, -CH_3). ^{1}H NMR (400 MHz, D_2O in DMSO-d_6): δ 6.63 (d, *J* 8.4 Hz, 1H, ArH), 6.26 (d, *J* 2.5 Hz, 1H, ArH), 6.06 (dd, *J* 8.4, 2.5 Hz, 1H, ArH), 3.65 (s, 3H, -CH_3), 3.58 (s, 3H, -CH_3), ^{13}C NMR (100 MHz, DMSO-d_6) δ 150.27, 143.88, 140.45, 115.08, 100.35, 57.13, 55.55, HRMS: *m/z* calculated for $C_8H_{11}NO_2$: 153.1810; $[M+H]^+$ found: 154.1809, Rf=0.5, TLC System Hexane: EtOAc, 2:8, Physical Appearance: Reddish brown solid (95% yield).

4-((Dimethylamino)methyl) aniline (A12). Bp 235 °C, ^{1}H NMR (400 MHz, DMSO-d_6)δ 6.90 (d*, J* 8.3 Hz, 2H, ArH), 6.50 (d, *J* 8.3 Hz, 2H, ArH), 4.93 (s, 2H, -NH_2), 3.17 (s, 2H, -CH_2), 2.08 (s, 6H, $(-CH_3)_2$), ^{1}H NMR (400 MHz, D_2O in DMSO-d_6) δ 6.90 (d, *J* 8.3 Hz, 2H, ArH), 6.50 (d, *J* 8.3 Hz, 2H, ArH), 3.17 (s, 2H, -CH_2), 2.07 (s, 6H, $(-CH_3)_2$), ^{13}C NMR (100 MHz, DMSO-d_6) δ 147.92, 130.03, 126.27, 114.08, 63.76, 45.25, HRMS: m/z calculated for $C_9H_{14}N_2$: 150.2250; $[M+H]^+$ found: 151.2248, Rf=0.5, TLC System DCM: MeOH, 1:9, Physical Appearance: Brown liquid (78% yield).

3-Fluoro-4-(trifluoromethyl) aniline (A13). Bp 208 °C**,** ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.29 (td, *J* 8.5, 2.8 Hz, 1H, ArH), 6.48 – 6.39 (m, 2H, ArH), 6.16 (s, 2H, -NH_2), ^{1}H NMR (400 MHz, D_2O in DMSO-d_6) δ 7.28 (td, *J* 8.5, 2.8 Hz, 1H, ArH), 6.55 – 6.25 (m, 2H, ArH), ^{13}C NMR (100 MHz, DMSO-d_6) δ162.19-159.72, 155.29-155.17, 128.30-128.08, 125.62-120.27, 109.35, 103.10-102.00, 100.38-100.15, HRMS: *m/z* calculated for $C_7H_5F_4N$: 178.1176; $[M+H]^+$ found: 180.1178, Rf=0.5, TLC System Hexane: EtOAc, 2:8, Physical Appearance: Colorless liquid (87% yield).

Quinolin-6-amine (A14). Mp 118 °C**,** ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.48 (dd, *J* 4.2, 1.7 Hz, 1H, ArH), 7.93 (dt, J 8.3, 1.3 Hz, 1H, ArH), 7.71 (d, *J* 9.0 Hz, 1H, ArH), 7.27 (dd, *J* 8.3, 4.2 Hz, 1H, ArH), 7.17 (dd, *J* 9.0, 2.5 Hz, 1H, ArH), 6.80 (d, *J* 2.5 Hz, 1H), 5.61 (s,2H, -NH_2), ^{1}H NMR (400 MHz, D_2O in DMSO-d_6) δ 8.47 (dd, *J* 4.2, 1.7 Hz, 1H), 7.93 (dt, *J* 8.5, 1.2 Hz, 1H), 7.71 (d, *J* 8.9 Hz, 1H), 7.28 (dd, *J* 8.3, 4.2 Hz, 1H), 7.18 (dd, *J* 8.9, 2.5 Hz, 1H), 6.81 (d, *J* 2.5 Hz, 1H), ^{13}C NMR (100 MHz, DMSO-d_6) δ 147.50, 145.52, 142.50, 133.32, 130.30,122.10, 121.68, 105.23, HRMS:

m/z calculated for $C_9H_8N_2$:144.1770; $[M+H]^+$ found: 145.7768, Rf=0.5, TLC System DCM:MeOH, 1:9, Physical Appearance: Yellow solid (78% yield).

Naphthalen-2-amine (15). Mp 112°C**,** ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.68 – 7.61 (m, 2H, ArH), 7.49 (dd, *J* 8.3, 1.1 Hz, 1H, ArH), 7.27 (dt, *J* 8.1, 6.7, 1.3 Hz, 1H, ArH), 7.08 (dt, *J* 8.0, 6.7, 1.2 Hz, 1H, ArH), 6.94 (dd, *J* 8.7, 2.2 Hz, 1H), 6.81 (d, *J* 2.3 Hz, 1H), 5.36 (s, 2H, -NH_2), ^{1}H NMR (400 MHz, D_2O in DMSO-d_6) δ 7.60 (dd, *J* 15.4, 8.4 Hz, 2H, ArH), 7.49 (d, *J* 8.2 Hz, 1H, ArH), 7.27 (ddd, *J* 8.2, 6.8, 1.3 Hz, 1H, ArH), 7.09 (ddd, J 8.1, 6.8, 1.2 Hz, 1H, ArH), 6.94 (dd, *J* 8.7, 2.3 Hz, 1H, ArH), 6.82 (d, *J* 2.3 Hz,1H, ArH), ^{13}C NMR (100 MHz, DMSO-d_6) δ 146.62, 135.01, 128.46, 127.45, 126.34, 125.82, 125.01, 120.83, 118.39, 105.83, HRMS: *m/z* calculated for $C_{15}H_{14}O$:211.28; $[M+H]^+$ found: 211.33, Rf=0.5, TLC System Hexane: EtOAc, 2:8, Physical Appearance: Red solid (93% yield).

[1,1'-Biphenyl]-2-amine (16). Mp 45-50°C, ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.47 – 7.38 (m, 4H, ArH), 7.33 (ddt, *J* 6.9, 5.7, 1.9 Hz, 1H, ArH), 7.04 (ddd, J 9.6, 6.2, 1.7 Hz, 1H, ArH), 6.98 (dd, *J* 7.5, 1.7 Hz, 1H, ArH), 6.76 (dd, *J* 8.1, 1 , 1H, ArH 6.63 (td, *J* 7.4, 1.3Hz,1H, ArH), 4.75 (s, 2H), -NH_2), ^{1}H NMR (400 MHz, D_2O in DMSO-d_6) δ 7.48 – 7.36 (m, 4H. ArH), 7.32 (td, *J* 7.0, 1.8 Hz, 1H, ArH), 7.04 (td, *J* 7.7, 1.7 Hz, 1H, ArH), 6.97 (dd, J 7.6, 1.7 Hz, 1H, ArH), 6.75 (d, *J* 8.0 Hz, 1H, ArH), 6.64 (td, *J* 7.3, 1.3 Hz, 1H, ArH), ^{13}C NMR (100 MHz, DMSO-d_6) δ 149.91, 139.67, 130.00, 1282, 128.62, 128.16, 126.74, 125.76, 116.75, 115.23, HRMS*: m/z* calculated for $C_{12}H_{11}N$: 169.2270; $[M+H]^+$ found: 170.2267, Rf=0.5, TLC System Hexane: EtOAc, 2:8, Physical Appearance: colorless solid (91% yield).

Pyrimidin-2-amine (17). Mp 125 °C, ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.21 (d, *J* 4.8 Hz, 2H, ArH), 6.57 (s, 2H, -NH_2), 6.54 (t, *J* 4.8 Hz, 1H, ArH), ^{1}H NMR (400 MHz, D_2O in DMSO-d_6) δ 8.21 (d, *J* 4.8 Hz, 2H, ArH), 6.56 (t, *J* 4.8 Hz, 1H, -NH_2), 6.49 (s, 1H, ArH), ^{13}C NMR (100 MHz, DMSO-d_6) δ 164.06, 158.47, 110.56, HRMS: *m/z* calculated for C_4H_5N: 95.1050; $[M+ Na]^+$ found: 118.0051, Rf=0.5, TLC System Hexane: EtOAc, 2:8, Physical Appearance: Pale yellow solid (70% yield).

1-Phenylethan-1-amine (18). Bp 123 °C**,** ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.78 (d, J 5.3 Hz, 1H, ArH), 6.75 – 6.56 (m, 2H, ArH), 6.24 (s, 2H, -NH_2), ^{1}H NMR (400 MHz, D_2O in DMSO-d_6) δ 7.76 (dd, *J* 5.0, 1H, ArH), 6.76 – 6.56 (m, 2H, ArH), ^{13}C NMR (100 MHz DMSO-d_6) δ 135.22, 132.51, 125.83, 117.83, 115.54, 114.93, 20.67, HRMS: *m/z* calculated for $C_7H_{10}N2$: 122.1710; $[M+H]^+$ found: 122.1710, Rf=0.5, TLC System Hexane: EtOAc, 2:8, Physical Appearance: Brown liquid (96% yield).

1,3-Dimethyl-1*H*-pyrazol-5-amine (19). Mp 66 °C, ^{1}H NMR (400 MHz, DMSO-d_6) δ 5.06 (s, 1H, ArH), 5.02 (s, 2H, -NH_2), 3.40 (s, 3H, -NCH_3), 1.94 (s, 3H, -CH_3), ^{1}H NMR (400 MHz, D_2O in DMSO-d_6) δ 5.08 (s, 1H, ArH), 3.39 (s, 3H, -NCH_3), 1.93 (s, 3H, -CH_3). ^{13}C NMR (100 MHz DMSO-d_6) δ 147.20, 144.90, 87.78, 33.56, 13.68, HRMS: *m/z* calculated for C_5H_9N: 111.1480; $[M+H]^+$ found: 112.1477, Rf=0.5, TLC System Hexane: EtOAc, 2:8, Physical Appearance: pale orange solid (74% yield).

Oxetan-3-amine (20). Bp 99 °C**,** ^{1}H NMR (400 MHz DMSO-d_6) δ 4.66 – 4.55 (t, J 6.4 Hz, 1H, ArH), 4.23 (t, J 6.4 Hz, 1H, ArH), 3.96 (m, 1H, ArH), 2.27 (s, 2H, -NH_2), ^{1}H NMR (400 MHz, D_2O in DMSO-d_6) δ 4.63 – 4.54 (m, 2H, ArH), 4.24 (t, J 6.5 Hz, 2H, ArH), 3.93 (p, J 7.0 Hz, 1H, ArH), ^{13}C NMR (100 MHz DMSO-d_6) δ 82.00, 48.07, HRMS: *m/z* calculated for C_3H_7NO: 95.995; $[M+Na]^+$ found: 95.9948, Rf=0.5, TLC System Hexane: EtOAc, 2:8, Physical Appearance: Yellow liquid (69% yield).

5-Bromo-6-methylpyridin-2-amine (21). Mp 101 °C, ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.45 (d, J 8.6 Hz, 1H, ArH), 6.23 (d, J 8.6 Hz, 1H, ArH), 6.06 (s, 2H, -NH_2), 2.32 (s, 3H, -CH_3), ^{1}H NMR (400 MHz, D_2O in DMSO-d_6) δ 7.46 (d, *J* 8.7 Hz, 1H, ArH), 6.28 – 6.18 (m, 1H, ArH), 2.32 (s, 3H, CH_3), ^{13}C NMR (100 MHz, DMSO-d_6) δ 158.36, 153.58, 140.36, 107.58, 105.18, 24.03, HRMS: *m/z* calculated for $C_6H7BrN2$: 187.0400; $[M]^+$ & $[M+H]^{+2}$found: 187.0396, 189.0395, Rf=0.5, TLC System Hexane: EtOAc, 2:8, Physical Appearance: Yellow solid (84% yield).

6-Methylpyridin-2-amine (A21I*). Analytical data in accordance with literature. [38]**2-Bromopyridin-4-amine (22):** mp 143 °C, ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.73 (d, *J* 5.7 Hz, 1H, ArH), 6.62 (d, *J* 2.1 Hz, 1H, ArH), 6.51 – 6.43 (m, 1H, ArH), 6.37 (s, 2H, -NH2), ^{13}C NMR (100 MHz, DMSO-d_6) δ 156.54, 149.46, 142.04, 110.59, 108.84, HRMS: *m/z* calculated for C_5H_5BrN2: 173.0130; [M] $^{+}$ & [M+H] $^{+2}$ found: 173.0132, 175.0135, Rf=0.5, TLC System Hexane: EtOAc, 2:8, Physical Appearance: Yellow solid (85% yield).

Pyridin-4-amine (A22I*). Analytical data in accordance with literature. [39]

3-Bromo-5-methylpyridin-4-amine (23). Mp 115 °C, ^{1}H NMR (400 MHz, $CDCl_3$-d_3) δ 8.12 (s, 1H, ArH), 7.87 (s, 1H, ArH), 5.98 (s, 2H, -NH_2), 2.08 (s, 3H, -CH_3). ^{13}C NMR (100 MHz, DMSO-d_6) δ 149.88, 149.15, 148.61, 118.45, 105.78, 15.29, HRMS*: m/z* calculated for $C_6H_7BrN_2$: 187.0400; [M] $^{+}$ & [M+H] $^{+2}$ found: 187.0397, 189.395, Rf=0.5, TLC System Hexane: EtOAc, 2:8, Physical Appearance: light brown solid (95% yield).

3-Methylpyridin-4-amine (A23I*). Analytical data in accordance with literature.[40]

3-Amino-5-bromopicolinic acid (24). Mp 100 °C, ^{1}HNMR (400 MHz, DMSO-d_6) δ 7.88 (d, *J* 2.1 Hz, 1H), 7.47 (d, *J* 2.0 Hz, 1H), 6.93 (s, 2H), ^{1}H NMR (400 MHz, D_2O in DMSO-d_6) δ 7.87 (d, *J* 2.1 Hz, 1H), 7.46 (d, *J* 2.0 Hz, 1H), ^{13}C NMR (100 MHz, DMSO-d6) δ 168.68, 148.90, 136.76, 126.19, 125.98, 124.66, , HRMS: *m/z* calculated for $C_6H_5BrN_2O_2$: 217.0220; [M] $^{+}$ & [M+H] $^{+2}$ found: 217.0217, 219.0219, Physical Appearance: White Solid (75% yield).

3-Aminopicolinic acid (A24I*). Analytical data in accordance with literature. [42]

3-Chlorobenzene-1,2-diamine (A25). Mp 125 °C**,** ^{1}H NMR (400 MHz, DMSO-d_6) δ 6.54 – 6.43 (m, 2H, ArH), 6.38 (td, *J* 7.8, 2.7 Hz, 1H, ArH), 4.81 (s, 2H, -NH_2), 4.61 (s, 2H, -NH_2), ^{1}H NMR (400 MHz, D_2O in DMSO-d_6) δ 5.53-6.50 (m, 2H), 6.49 (ddt, *J* 13.1, 7.8, 1.8 Hz, 1H), ^{13}C NMR (100 MHz, DMSO-d_6) δ 136.38, 130.98, 117.68, 117.39, 116.93, 112.61, HRMS: *m/z* calculated for $C_6H_7ClN_2$: 142.5860; [M] $^{+}$ & [M+H] $^{+2}$ found: 142.5858, 144.5859, Rf=0.5, TLC System Hexane: EtOAc, 2:8, Physical Appearance: Black solid (90% yield).

Benzene-1,2-diamine (A25I*). Analytical data in accordance with literature.[15]

(2-Amino-4-bromophenyl) methanol (26). ^{1}H NMR (400 MHz, DMSO-d_6) δ 6.99 (d, *J* 8.0 Hz, 1H, ArH), 6.78 (d, *J* 2.1 Hz, 1H, ArH), 6.64 (dd, J 7.9, 2.1 Hz, 1H, ArH), 5.19 (s, 2H, -NH_2), 5.06 (t, *J* 3.6 Hz, 1H, -OH), 4.32 (s, 2H- -CH_2), ^{1}H NMR (400 MHz, D_2O in DMSO-d_6) δ 6.98 (d, *J* 8.0 Hz, 1H, ArH), 6.78 (d, J 2.1 Hz, 1H, ArH), 6.65 (dd, *J* 8.0, 2.1 Hz, 1H, ArH), 4.30 (s, 2H, -CH_2), ^{13}C NMR (100 MHz, DMSO-d_6) δ 148.45, 129.70, 125.09, 120.80, 118.36, 116.76, 60.77, HRMS: *m/z* calculated for C_7H_8BrNO: 202.0510; [M] $^{+}$ & [M+H] $^{+2}$found: 202.0508, 202.0509, Rf=0.5, TLC System DCM: MeOH, 1:9, Physical Appearance: brown liquid (75% yield).

(2-Aminophenyl) methanol (A26I*). Analytical data in accordance with literature. [42]

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