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Iron–water mediated chemoselective reduction of nitroarenes in a ball mill: a highly efficient and sustainable approach

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Highly selective and efficient reduction of nitroarenes has been achieved using iron powder and water under mechanochemical conditions. A wide spectrum of reducible functionalities remained inert under these sustainable and green reaction conditions. During the reaction, Fe powder partially converted into valuable Fe_3O_4 nanoparticles.

Aromatic amines play a crucial role as building blocks in the synthesis of various pharmaceuticals, agrochemicals, dyes, polymers, and other biologically important compounds.[1] In addition they serve as precursors for synthetically significant intermediates like imines, azo compounds, amides, diazonium salts and isocyanates.[2] In general, synthesis of aniline derivatives is achieved by reduction of nitro arenes. Precious metal (Pd/Pt/Ni)-catalysed hydrogenation using hydrogen gas as a reductant is a widely used process for nitro reduction.[3] However, achieving the selective reduction of the nitro group in the presence of other reducible functionalities within a molecule poses a significant challenge. In addition, the traditional method for reducing the nitro group is complex, as it often proceeds in stages and can result in the formation of side products such as hydroxylamine, hydrazine, and azoarene at intermediate stages.[4] The limited availability and high cost of these precious metals challenge synthetic chemists to explore more economical, sustainable, and cleaner reaction conditions.[5] Therefore, several methods involving inexpensive catalysts such as iron, copper, zinc, cobalt, and other metals have been developed.[6] In particular, attention has been focused on exploring inexpensive and eco-friendly Fe metal. Use of iron powder along with a proton donor like $NH_4Cl/HCl/CH_3CO_2H$[7] is well known. Moreover, $Fe(acac)_3$- and Fe_2O_3-based catalysts,[8] iron-phenanthroline supported on carbon[9] and an $Fe–CaCl_2$ system[10] for nitro reduction have also been reported. However, co-reductants[8b,9,11] are required with these iron catalysts for efficient reduction and in some cases harsh conditions[7a] are required. An efficient metal-catalysed reduction using water as a green source of hydrogen is desirable, but it is one of the most challenging transformations in chemistry.[12] Several groups have reported $Fe–H_2O$-mediated direct reduction of the nitro group, but these methods have limitations, including a high reaction temperature,[13] long reaction time[14] and the use of pre-synthesized expensive iron nanoparticles (NPs),[15] that impose additional challenges.

Here we describe the development of a new mechanochemical (MC) methodology for nitro reduction using iron powder and water as a source of H_2.

Our approach is inspired by the established understanding that H_2 can be generated under MC conditions using Fe and water in redox conditions.[16] The continuous MC impact within the system brings iron powder (∼200 mesh, 99%) into the comminution region, where it reacts faster with H_2O and results in the evolution of hydrogen gas and the formation of Fe_3O_4 NPs. Our aim was to harness this phenomenon by employing easily available Fe powder and water in a ball-mill system to produce H_2 *in situ*, enabling selective reduction of nitro arenes, without affecting the other delicate functional groups present in the molecule.

Mechanochemistry[17] refers to chemical reactions induced by mechanical forces, such as milling, grinding, or other types of mechanical agitation. This science has emerged as a sustainable alternative to solution chemistry and was listed as one of the "10 chemical innovations that will change our world" by IUPAC in 2019.[18] Mechanochemistry offers minimal solvent use, which reduces waste generation, but due to its unique reaction environments it also accelerates reaction rates,[19] is easy to setup, is highly efficient,[20] provides unique reaction conditons[21] and can unlock new routes towards the synthesis of various compounds that are not attainable by conventional synthesis.[22] With our keen interest[19b] in exploring novel, green and sustainable chemistry, we have studied the use of

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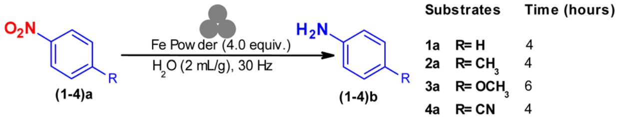
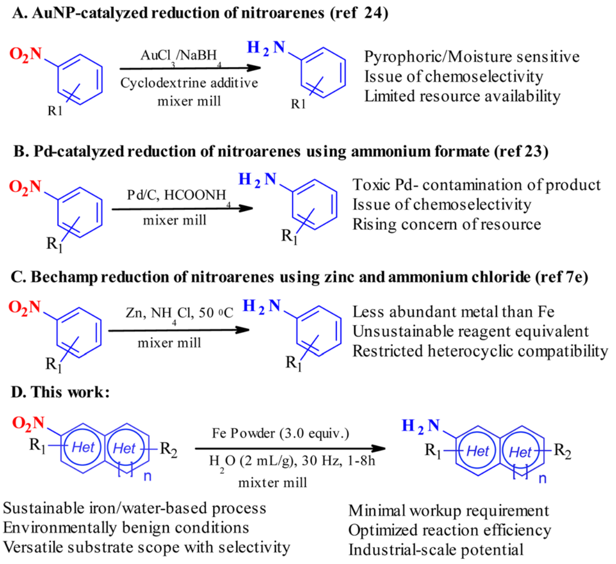
mechanochemistry for the reduction of nitro arenes. Thus far only three reports of nitro reduction in a ball-mill system have been reported. Portada *et al.* reported the use of a Pd/C catalyst with ammonium formate to generate H_2 for nitro reduction.[23] This method suffers from the disadvantage of using precious Pd metal (Scheme 1A) and the formation of hazardous byproducts (CO_2 and NH_3). In another report, Menuel *et al.*[24] used a cyclodextrin-stabilized gold NPs (AuNPs) catalyst with sodium borohydride to achieve nitro reduction; however, the use of hazardous $NaBH_4$, limited substrate scope, use of expensive gold catalysts and its pre-synthesis limit this method (Scheme 1B). Kubota *et al.*[7e] reported the solvent-free Bechamp reduction using Zn/NH_4Cl, enabling rapid conversion of nitroarenes to aromatic amines, but this method requires external heating and excess reagents for efficient reduction (Scheme 1C). Sawama *et al.* reported a non-selective reduction using only water as a source of hydrogen in a planetary mill.[25] Harsh conditions, non-selective reduction, and the requirement for specific metal constituents for the SS planetary mixture make this method unsuitable for nitro reduction.

In this report, we have explored the use of a cheap iron powder in water as a source of hydrogen for a selective and efficient nitro reduction process. Notably, the developed protocol worked with various substrates having both electron-donating and electron-withdrawing groups, sensitive protecting groups (*O*-allyl, *O*-benzyl, *N*-benzyl), halogens, reducible functional groups (ester, aldehyde, amide), and heterocycles, affording a highly efficient, versatile, and economical alternative for nitro reductions under ambient conditions.



Scheme 2 Reduction of nitroarenes using 4.0 equiv. of Fe powder.


A. AuNP-catalyzed reduction of nitroarenes (ref 24)

B. Pd-catalyzed reduction of nitroarenes using ammonium formate (ref 23)

C. Bechamp reduction of nitroarenes using zinc and ammonium chloride (ref 7e)

D. This work:

Scheme 1 Mechanochemical protocols for reduction of nitroarenes to anilines.

In our study, we initially selected substrates **(1–4)a** and subjected them to mechanochemical conditions using 4.0 equivalents of iron powder and 2 mL g^{-1} of water (relative to nitroarenes) as the grinding auxiliary (Scheme 2). The reaction was carried out in a 5 mL stainless steel (SS) jar using one 10 mm SS ball at a frequency of 30 Hz. To ensure that the reaction proceeded undisturbed, we conducted monitoring at 2-hour intervals. Our observations revealed that reduction was successfully achieved within 4–6 hours for all substrates, resulting in complete conversion into **(1–4)b**. To optimize the reaction conditions, substrate **4a** was selected as a model compound for screening various mechanochemical parameters (Table 1).

Initial investigation of the reaction parameters focused on optimizing the Fe powder equivalents. Interestingly, there was not much difference in conversion using 4.0 and 3.0 equivalents of Fe powder (Table 1, entries 1 and 2). However, using 2.0 equivalents of Fe powder (entry 3) resulted in slow and incomplete conversion. Therefore, we fixed 3.0 equivalents of iron as the optimum amount for the reaction. To investigate the influence of the SS jar composition on the reduction process, we performed the reaction in the absence of iron (entry 5). However, no product formation was observed, indicating that iron is necessary for the transformation. No conversion using 0.1 equivalent of Fe (entry 4) ruled out the possibility of a catalytic effect from Fe. Water amount optimization (entries 6 and 7) revealed that 1 mL g^{-1} resulted in incomplete reduction and led to the mixture drying, while 2 and 3 mL g^{-1} yielded similar conversion rates. Therefore, 2 mL g^{-1} of water was selected as optimal, serving both to generate hydrogen for the reduction process and facilitate grinding. Although the jar was sealed, it was not hermetically closed, resulting in some hydrogen loss. The effect of different solvents was systematically investigated. Anhydrous organic solvents, including ethanol (entry 8) and acetonitrile (entry 9), proved ineffective in initiating the reaction, while adding water to these organic solvents (entries 10 and 11) maintained reaction efficiency, but the reaction rate was slower compared to water alone. These observations suggest that water is essential for the reaction, which is further confirmed by performing the reaction in deuterated water (entry 12). The formation of deuterated aniline was confirmed by ^{1}H-NMR analysis of the reaction mixture (SI, Fig. S15). Initial mechanochemical frequency optimization revealed complete conversion at 25 Hz within 4 hours (entry 13), demonstrating effective energy transfer. Decreasing the frequency to 20 Hz (entry 14) resulted in incomplete conversion, indicating insufficient mechanical energy input. Consequently, 30 Hz was established as the optimal frequency for maximum milling efficiency. Investigation of milling parameters showed that reducing the ball size (entry 15) diminished the reduction efficiency, leading to slower conversion rates. Similarly, utilizing two smaller balls (entry 16) failed to achieve complete conversion. The influence of jar volume was evaluated by conducting the reaction in

Table 1 Optimization study of nitroarenes reduction under mechanochemical conditions

Entry	Scale (g)	Solvent	Volume (mL g^{-1})	Type of jar	Fe (equiv.)	Jar size (mL)	Ball size (mm)	Frequency (Hz)	Time (hours)	% Conversion by GC-MS (yield)
1	0.2	Water	2	SS	4.0	5	10	30	4	100
2	0.2	Water	2	SS	3.0	5	10	30	4	100 (96%)
3	0.2	Water	2	SS	2.0	5	10	30	6	85
4	0.2	Water	2	SS	0.1	5	10	30	6	NR
5	0.2	Water	2	SS	None	5	10	30	6	NR
6	0.2	Water	1	SS	3.0	5	10	30	6	92
7	0.2	Water	3	SS	3.0	5	10	30	4	100
8	0.2	Ethanol	2	SS	3.0	5	10	30	2	ND
9	0.2	ACN	2	SS	3.0	5	10	30	2	ND
10	0.2	EtOH + water (1 : 1)	2	SS	3.0	5	10	30	4	88
11	0.2	ACN + water (1 : 1)	2	SS	3.0	5	10	30	4	72
12	0.2	D_2O	2	SS	3.0	5	10	30	4	100
13	0.2	Water	2	SS	3.0	5	10	25	4	100
14	0.2	Water	2	SS	3.0	5	10	20	4	89
15	0.2	Water	2	SS	3.0	5	5	30	4	87
16	0.2	Water	2	SS	3.0	5	5 × 2	30	4	89
17	0.2	Water	2	SS	3.0	10	10	30	4	100
18	0.2	Water	2	SS	3.0	10	10 × 2	30	4	82
19	0.2	Water	2	Zirconia	3.0	10	10	30	4	85
20	0.2	Water	2	Teflon	3.0	10	10	30	4	68
21	2.0	Water	2	SS	3.0	25	10	30	6	100 (94%)

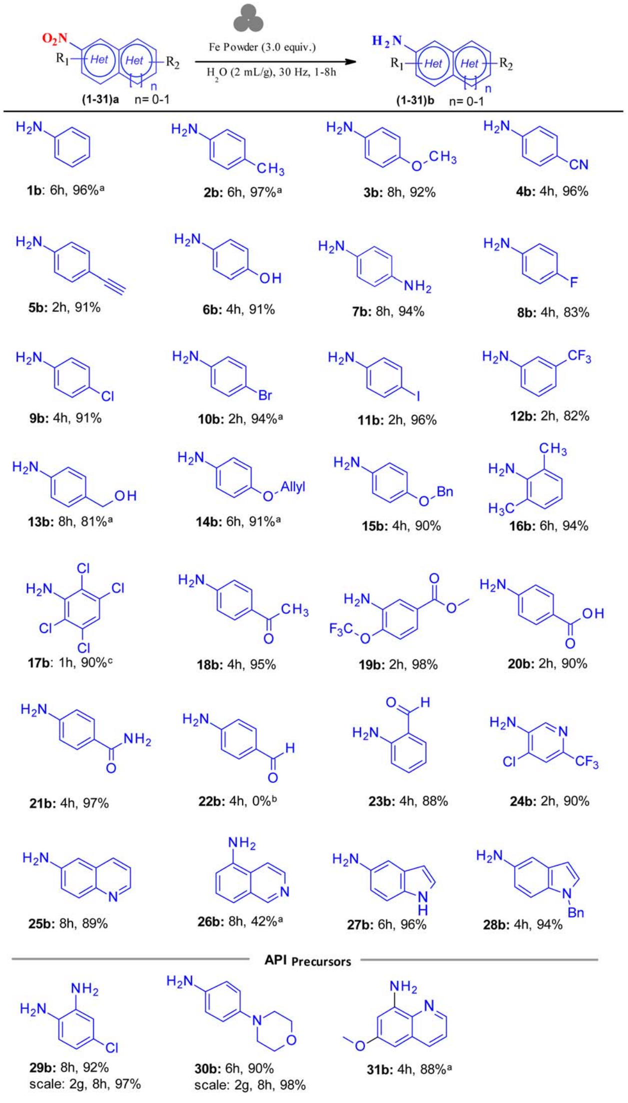
a 10 mL vessel (entry 17). GC-MS analysis demonstrated comparable reduction efficiency regardless of jar size.

However, introducing an additional ball to the same jar (entry 18) adversely affected reaction efficiency, resulting in incomplete conversion after 4 hours. This observation can be attributed to increased space occupancy, which diminishes their impact efficiency, resulting in slower reaction kinetics. Examination of the milling jar composition (entries 19 and 20) revealed that the reduction of **4a** proceeded in both zirconia (ZrO_2) and Teflon-coated jars, albeit at slower rates compared to stainless steel vessels. This is likely due to the limited collision impact[26] in the zirconia and Teflon-coated vessels, resulting in reduced efficiency. To test the applicability of the optimized protocol for scale-up, we carried out the reaction of **4a** at 2-grams scale in a 25 mL SS jar using one 10 mm SS ball (entry 21). The reaction was completed within 6 hours and afforded a 94% isolated yield.

A wide range of substrates were screened under the optimized condition and the results are summarized in Table 2. The reduction was uniform irrespective of the physical state of the nitro compound. All substrates provided good to excellent isolated yields, except compounds **13b** and **26b**, which exhibited slower conversion and required extended milling times for completion.

The reaction exhibited broad substrate scope, accommodating both electron-rich (**2b**, **3b**, **6b**, and **7b**) and electron-deficient nitroarenes (**4b** and **5b**). Notably, electron-deficient nitroarenes demonstrated enhanced reaction kinetics compared to their electron-rich counterparts, suggesting an electronic effect on the reaction rate. The methodology demonstrated excellent chemoselectivity in several aspects. Halogen-substituted (**8–11b**, **17b**, **24b** and **29b**) and trifluoromethyl-substituted (**12b** and **24b**) substrates underwent transformation without any dehalogenated product, highlighting the selective reduction while preserving the halogen substituents. Sensitive groups like triple bonds (**5b**), *O*-allyl (**14b**), *O*-benzyl (**15b**) and *N*-benzyl (**28b**) remain well tolerated under these conditions. The reaction was conducted in sterically hindered **16b** to evaluate the impact of steric hindrance on the reduction, and it took 6 hours for the reaction to reach completion, which is significantly longer compared to the complete reduction of the other hindered compound tetrachloro nitrobenzene (**17b**) within 1 hour, suggesting that the reduction process is primarily influenced by electronic factors rather than steric effects. Substrates (**24b**) containing pyridine rings bearing chloro and trifluoromethyl substituents as well as fused heterocyclic systems including quinoline (**25b**), isoquinoline (**26b**), indole (**27b**), and *N*-benzyl-protected indole (**28b**) underwent selective nitro reduction while maintaining the structural integrity of these important heterocyclic motifs. Importantly, easily reducible groups like ketone (**18b**), ester (**19b**), carboxylic acid (**20b**) and amide (**21b**) remain unaffected, demonstrating the protocol's ability to selectively reduce nitro groups in the presence of these functional groups. Investigation of aldehyde-containing substrates 4-nitrobenzaldehyde (**22a**)

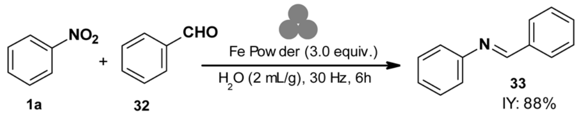
Table 2 Selective reduction of nitroarenes by Fe powder and water in a ball-mill system



[a] Purified by column chromatography using ethyl acetate and cyclohexane as the eluent. [b] Polymerized. [c] Reaction repeated to monitor at 1 h.

and 2-nitrobenzaldehyde (**23a**) under the optimized conditions revealed distinct reactivity patterns.

While **23a** underwent selective reduction to yield the corresponding amine **23b** with 88% yield, substrate **22a** exhibited a more complex reaction pathway. Following initial nitro reduction, the nascent amine underwent spontaneous intermolecular self-condensation[27] with the aldehyde moiety, generating polymeric material *via* imine linkages. IR spectroscopic analysis confirmed the formation of the polymer, evidenced by the disappearance of the carbonyl stretching band at 1662 cm^{-1} and the emergence of a characteristic imine (C═N) absorption at 1624 cm^{-1} (SI, Fig. S3).



Scheme 3 Synthesis of Schiff base in mechanochemical conditions.

The scope of this methodology was demonstrated through a tandem reaction of benzaldehyde (**32**) and nitrobenzene (**1a**) (Scheme 3), affording Schiff base **33** in 88% yield. This result further supported the proposed polymerization pathway of substrate **22a**. Schiff bases are versatile intermediates widely used in pharmaceutical development, coordination chemistry, and catalytic systems.

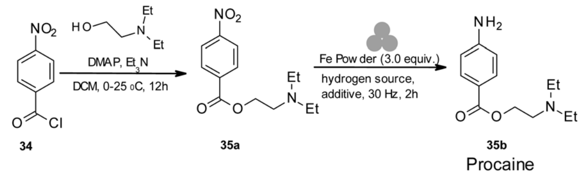
The synthetic utility of this methodology was demonstrated through the synthesis of procaine (**35b**), a widely used local anaesthetic for dental procedures and nerve blocks (Table 3). The key intermediate 4-nitrobenzoyl-2-(diethylamino)ethyl ester (**35a**) was readily accessed *via* the reaction of **20a** with 2-(diethylamino) ethanol following literature procedures.[28]

Initial reduction of **35a** under the optimized mechanochemical conditions afforded procaine in 23% yield (Table 3, entry 1), with significant ester hydrolysis observed due to the basicity of the compound. To suppress this side reaction and improve the yield, acidic additives were investigated (entries 2 and 4). The addition of acetic acid or (+)-10-camphorsulfonic acid (CSA) significantly improved the yields to 95% and 85%, respectively (entries 3 and 5). The optimized conditions were successfully scaled up using a 25 mL stainless-steel jar, delivering procaine in 94% yield at gram scale (entry 6). Additionally, we synthesized three key pharmaceutical intermediates (Table 2): 4-chlorobenzene-1,2-diamine (**29b**, tizanidine precursor), 4-morpholinoaniline (**30b**, intermediate for momelotinib and rivaroxaban), and 6-methoxy-8-nitro-quinoline (**31b**, primaquine precursor). Gram-scale syntheses of **29b** and **30b** demonstrate the scalability and pharmaceutical relevance of our MC approach.

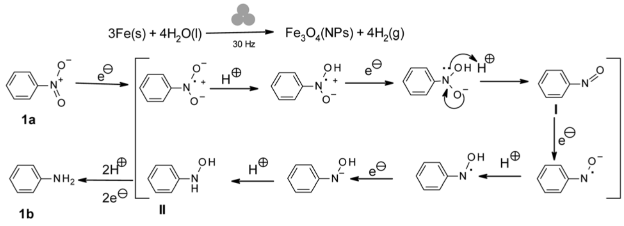
This solvent-free protocol not only provides an efficient route to this important pharmaceutical but also represents a more sustainable alternative to conventional solution-based methods, aligning with green chemistry principles.

Based on our experimental observations, literature reports[29] and mechanistic studies, we propose that the reduction (Scheme 4) proceeds through a radical-mediated pathway involving both direct electron transfer from iron and *in situ*-generated hydrogen. This hypothesis is strongly supported by the complete inhibition of the reaction in the presence of TEMPO ((2,2,6,6-tetramethylpiperidin-1-yl)oxyl), a well-known radical scavenger, indicating the crucial role of radical intermediates in the reduction process. Mechanochemical activation creates fresh iron surfaces that react with water to generate active Fe–H species and Fe^{2+} ions, along with *in situ* H_2 production. The reduction is likely to progress through sequential steps involving nitroso (–N═O) and hydroxylamine (–NHOH) intermediates, although these intermediates were not detected during the reaction, suggesting rapid conversion

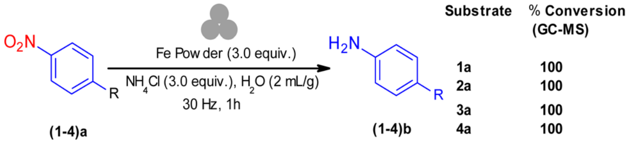
Table 3 Optimization of mechanochemical reduction conditions for the conversion of **35a** to procaine: effect of acidic additives and scale-up studies



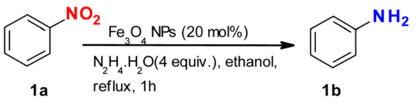
Entry	Scale (g)	Hydrogen source	Additive	Procaine yield
1	0.2	Water	No	23%
2	0.2	CSA	No	0%
3	0.2	Water	CSA	85%
4	0.2	CH_3COOH	No	0%
5	0.2	Water	CH_3COOH	95%
6	1.0	Water	CH_3COOH	94%



Scheme 4 Proposed mechanism of the reduction pathway for conversion of nitrobenzene to aniline using Fe and water.



Scheme 5 Reaction using ammonium chloride.



Scheme 6 Reduction of nitrobenzene using Fe_3O_4 NPs.

under mechanochemical conditions, which is advantageous for obtaining pure amines without intermediate impurities.

The enhanced reaction rates observed with electron-deficient nitroarenes further support this mechanism. During the reduction process, iron undergoes partial oxidation to form Fe_3O_4 nanoparticles, as confirmed by scanning transmission electron microscope (STEM) imaging (Fig. 1) and powder X-ray diffraction (PXRD) analyses (SI, Fig. S4).

In most cases, pure products were obtained simply by diluting the reaction mixture with ethyl acetate followed by filtration of the Fe_3O_4 particles or by magnetic separation (SI, Fig. S2) and decanting the solvent, unless otherwise specified in Table 2. The effect of ammonium chloride as another hydrogen source along with water was also studied using a similar procedure with **(1–4)a**, and surprisingly the reaction was completed within 1 hour (Scheme 5). The fast conversion was probably due to the presence of dual sources for hydrogen.

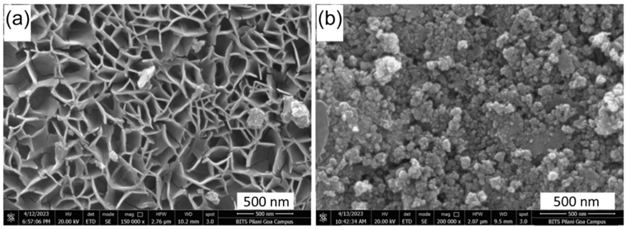


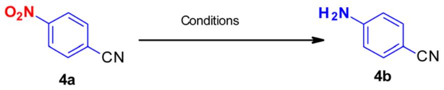
Fig. 1 STEM image of commercial Fe powder (a) before reaction and (b) after the reaction of **4a** in a ball-mill.

To validate both the formation and catalytic activity of the mechanochemically synthesized Fe_3O_4 NPs, we conducted a model reduction reaction using nitrobenzene (**1a**) as the substrate. After completion of the reaction, the generated F_3O_4 NPs were collected with an external magnet and the solution was decanted (SI, Fig. S2). The recovered NPs were washed with ethanol and used for the successful conversion to aniline (**1b**), achieved using hydrazine hydrate as the co-reductant under the reported conditions[8b] (Scheme 6), confirming the catalytic competency of the generated nanoparticles.

To assess the environmental impact and sustainability of our mechanochemical approach, we calculated and compared the *E*-factors and Eco-score between our method and previously reported solution-based conditions[15] (Table 4). The *E*-factor and Eco-score, metrics quantifying environmental impact of chemical processes, revealed striking differences.[30] Our mechanochemical reduction of **4a** demonstrated superior environmental performance with an *E*-factor of 4.33 and an Eco-score of 94 (entry 1), while the conventional solution-based method[15a] using sodium borohydride, ferrous sulfate, and citric acid for iron nanoparticle generation showed a significantly higher *E*-factor of 965.74 and a lower Eco-score of 74 (entry 2). This dramatic difference primarily stems from our method's elimination of bulk solvents and excess reagents.

These results demonstrate that our mechanochemical approach offers significantly improved environmental sustainability compared to traditional solution-based methods, representing a step forward in developing greener synthetic protocols for the chemical industry. Due to the known impact sensitivity of nitro compounds,[31] a safety analysis was conducted before initiating the ball-mill reaction. Our organization recently conducted a study[32] on the safety of ball mill reactions, which concluded that a desktop safety screening of all the substrates should be performed prior to milling the reaction mixture. This screening involved evaluating three parameters: (1) the number of carbons per phosphoric group, where a count exceeding six indicates the unlikelihood of explosiveness; (2) the oxygen balance, between 200(−ve) to 40(+ve) indicating a potential

Table 4 Comparison of *E*-factors and Eco-scores[a]



Entry	Condition	*E*-Factors	Eco-scores
1	Fe-powder, H_2O (2 mL g^{-1}), ball mill 30 Hz, 4 h	4.33	94
2	(i) Fe-NPs {sodium borohydride (5 mmol), [$FeSO_4 \cdot 7H_2O$] (834.3 mmol) and citric acid (0.25 mmol) water (100 mL)} (ii) Water (5 mL), 25 °C, 3 h	965.74	74

[a] For details of *E*-factor and Eco-score calculations, see the SI, Fig. S3–S5.

safety issue; and (3) the nitrogen content, where a total nitrogen content of less than 10% by weight for organic materials suggests the unlikelihood of explosiveness. If all three parameters suggest that a material is explosive, it should be further analysed using differential scanning calorimetry (DSC) prior to milling.

During the desktop screening (SI, Table S1), it was found that only substrate **1a** exhibited a red flag against all three parameters. Consequently, the DSC of **1a** was recorded (SI, Fig. S5), revealing an exothermic reaction at 430 °C, confirming its safety for ball milling. As for the scale-up of substrate **4a**, which raised concerns in two parameters, DSC analysis was performed and indicated an exotherm at 418 °C (SI, Fig. S6), ensuring its safety under milling conditions at a higher scale. It is important to note that for our study, we used only 200 mg of substrate, and therefore safety is not a concern during ball milling at this scale.

Conclusion

In conclusion, we have developed a green, sustainable, cost-effective, and gram-scale MC protocol for the selective reduction of aromatic nitro compounds to amines using a cheap reducing agent involving Fe powder without any pre-activation and water under ball-mill conditions. Additionally, under these conditions, the Fe powder partially converts into Fe_3O_4 NPs, which adds further value as a potential material for different organic transformations.[33] The simple setup, use of inexpensive and nonhazardous Fe powder and water, without using organic solvents, affords efficient and chemoselective reduction over a wide range of functional groups, making this method a useful and preferred choice for nitro reduction.

Conflicts of interest

There are no conflicts to declare.

Data availability

The data supporting this article have been included as part of the SI. See DOI: https://doi.org/10.1039/d5mr00055f.

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