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A heterogeneous nickel-supported catalyst: a circular approach to amine synthesis *via* azide and nitro compound reduction

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The development of sustainable catalytic methods is a crucial tool for advancing green chemistry and reducing its associated environmental impact. In this study, we present an eco-friendly approach for reducing azido and nitro compounds to their corresponding amines using a heterogeneous nickel-based catalyst supported on sulfonated biochar derived from pine needle (PiNe) valorisation. The system developed, in combination with the use of $NaBH_4$ as a safer reducing agent in water, enables efficient transformations under mild reaction conditions, yielding excellent results. The process also incorporates a green work-up procedure that employs bio-based, non-toxic solvents, such as 2-MeTHF, to aid in product isolation and catalyst recovery, thereby significantly reducing waste generation. Moreover, recycling studies demonstrate that Ni(B)/PiNe retains its catalytic efficiency for over five consecutive cycles. This work highlights the potential of biomass-derived materials in sustainable catalysis, demonstrating that green alternatives can be as effective as traditional methods while providing a protocol that aligns with the growing demand for environmentally friendly chemistry.

Sustainability spotlight

Decarbonizing the chemical industry is a critical step toward reducing global warming emissions and mitigating climate change (SDG 3 and 9). In this context, the development of alternative catalytic systems, such as those designed from the valorisation and upcycling of residual biomass, like the one herein developed for amine synthesis, offers a valuable alternative. This approach helps reduce our dependence on non-renewable resources, lowers energy consumption, and offers cost savings (SDG 12 and 13). Furthermore, the process, which uses smaller quantities of safer, bio-derived solvents, promotes a more sustainable chemistry by redifining waste as a valuable resource. Instead, it becomes a valuable resource that can be further exploited.

Introduction

Amines, particularly if aromatic, are fundamental commodities utilised in several strategic sectors, including agrochemicals, dyes and pigment manufacturing, fine chemical production, and, most notably, pharmaceuticals.[1] They are extensively used as essential intermediates in the synthesis of drugs and antioxidants or the manufacturing of optoelectronic devices, such as dye-sensitized solar cells (DSSCs).[2]

Amines can be synthesized through a variety of well-established methods. Metal-catalysed C–N bond-forming reactions, popularised by Buchwald and Hartwig, have recently enabled the efficient synthesis of structurally complex amines with broad functional group tolerance.[3] Nevertheless, more traditional approaches, such as the reduction of nitro compounds, particularly in industrial settings, remain highly relevant and are of great utility. To put this into perspective, over 90% of aniline, primarily used in the production of isocyanates for polyurethane manufacturing, is produced *via* the reduction of nitrobenzene. In the United States alone, its production reached 1.63 million metric tons in 2019, with global annual sales approaching $10 billion.[4] Alternatively, reduction of imines,[5] nitriles[6] and azides may be considered. The latter are interesting since they can also be used as a protecting group in the synthesis of aminoglycosides with antibacterial effects.[7] As extrapolated from the significant market demand, hydrogenative processes to afford amines are industrially preferred, regardless of that utilization of high H_2 pressure over noble, expensive, and environmentally impactful metals, such as palladium, is generally a drawback. In this context, the use of alternative hydrogen sources, such as liquid organic hydrogen carriers (LOHCs)[8–10] like isopropanol or glycerol,[11] or solid carriers such as sodium borohydride ($NaBH_4$), combined with the development of new catalytic systems,[12] offers a promising route to improve both the sustainability and

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safety of amine synthesis. Moreover, rational catalyst design is central to decarbonizing the chemical industry, as reducing activation barriers enables lower energy consumption. This is especially critical, given that energy use accounts for approximately 75% of greenhouse gas emissions, according to the European Union.[13]

In this regard, the primary objective of the present work is to demonstrate the efficiency of a new heterogeneous, recoverable carbon-based nickel catalyst derived from pine needle valorisation, which is capable of reducing a wide range of azides and nitro compounds.

Over the past few decades, biomass valorization has emerged as a highly viable strategy to reduce dependence on fossil fuels and petroleum-derived raw materials, enabling the development of a wide array of value-added products. In particular, residual biomass, which would otherwise be landfilled or incinerated for energy, can be converted into valuable materials such as fillers,[14] monomers,[15] and bulk chemicals that serve as precursors to fine chemicals.[16]
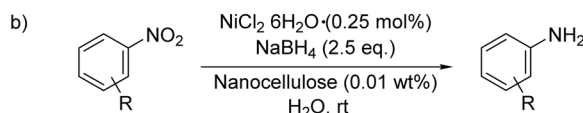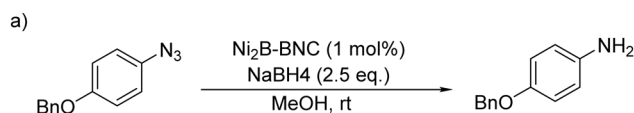
A key step in implementing the principles of a circular economy is the upcycling of urban and agricultural waste into functional materials, including catalysts or supports for metal catalysts. A representative case is the valorization of pine needles, a widely available waste product in Mediterranean coastal regions. Their chemical pretreatment enables the formation of acidic carbonaceous materials, which have shown utility as acid catalysts for alkyl levulinate production[17] and as supports for cross-coupling catalysts[18,19] or nickel-based systems.[20] However, the applicability of such materials has not yet been evaluated under reductive/hydrogenation conditions.

Palladium, nickel, copper, iron, and cobalt have been widely investigated as active species for the catalytic reduction of nitro and azido compounds,[21–23] using molecular hydrogen, liquid organic hydrogen carriers (LOHCs), and solid hydrogen sources. Over the years, considerable efforts have been made to reduce the environmental impact associated with the production and use of these metals, particularly through their immobilization on solid supports, which facilitates catalyst recovery and reuse. However, the preparation and processing of such supports, including graphene,[24] active nanofibers,[25] and polymeric matrices,[26] often involve environmentally harmful and energy-wasteful procedures.

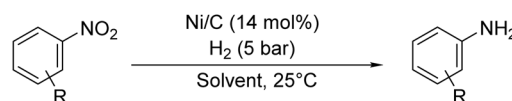The only known literature precedents reporting biomass-derived catalyst supports for this type of transformation were published by Proietti *et al.*[27] and Tang *et al.*[28] (Scheme 1).

The former developed an *in situ*-generated heterogeneous catalyst based on bacterial nanocrystalline cellulose, which proved efficient for the reduction of nitro compounds. However, its application to azide reduction was limited to a single example: the synthesis of 4-(benzyloxy)aniline. The latter employed a nickel-based catalytic system derived from medical absorbent cotton, which was effective for the hydrogen-mediated reduction of nitro-containing molecules only. We now aim to demonstrate the effectiveness of a novel, heterogeneous, and recyclable carbon-supported nickel catalyst derived from pine needles, capable of reducing a broad range of azides and nitro compounds using the safer $NaBH_4$ as a reducing
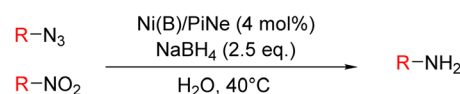

Scheme 1 Carbonaceous Ni-based catalyst for reduction of nitro and azido compounds.

agent in water. To further highlight the significance of this work, it is worth noting that it represents one of the first examples of a nickel boride-supported catalyst. Upon anchoring Ni onto the support, subsequent reduction with $NaBH_4$ leads to the formation of Ni_2B, which acts as the catalytically active species. This Ni_2B phase then promotes amine formation by facilitating the degradation of $NaBH_4$.[29]

Experimental

PiNe support preparation

The PiNe support was prepared following a previously reported procedure.[17]

Ni(B)/PiNe preparation

In a 50 mL two-neck round-bottom flask, 400 mg of the PiNe support was suspended in 20 mL of ethanol and sonicated for 1 hour. Subsequently, a suspension of 79.8 mg of $NiCl_2 \cdot 6H_2O$ was added under sonication, and the resulting mixture was further sonicated for another hour. Next, 118 mg of $NaBH_4$ was suspended in 5 mL of ethanol and added at 0 °C to the support, where it was left under stirring. After 1.5 hours, the catalyst was filtered, washed sequentially with ethanol, water, and acetone, and then dried under a vacuum at 80 °C for 1 hour. The Ni (5.1 wt%; 0.87 mmol g^{-1}) and B (0.43 wt%; 0.4 mmol g^{-1}) loadings, measured by MP-AES analysis, confirmed the presence of Ni_2B nanoparticles.

General procedure for the reduction of azido and nitro compounds

In a 4 mL screw-capped vial equipped with a magnetic stirrer, the azido (**1**) or nitro compound (**3**) (0.25 mmol), H_2O (0.5 M, 0.5 mL), Ni(B)/PiNe (4 mol% calculated on Ni loading, 11.5 mg) and $NaBH_4$ (2.5 eq., 23.65 mg) were consecutively added, and the resulting mixture was left under stirring at 40 °C. After 2 h, the reaction mixture was left to cool to room temperature, diluted with 2-MeTHF (2 × 1 mL) and centrifuged (6500 rpm, 10′, 5 °C) to recover the reaction crude. Ni(B)/PiNe was subsequently washed with additional H_2O (0.5 mL; 6500 rpm, 10′, 5 °C) and dried at 110 °C under vacuum overnight. The combined organic layer, once separated from the aqueous phase, was distilled and recovered (89%) to afford the desired product. If necessary, the concentrated crude was purified by column chromatography (using PE/EtOAc as the eluent) to obtain the final product (**2**).

Results and discussion

Our investigation began with preparing the catalyst support. As reported in a previous study, the pine needles were first chemically manipulated to remove proteins, waxes, and oils. Subsequently, the biobased, carbonaceous material derived from pine needles was obtained through an acidic treatment with sulfuric acid.[30]

Once the support was obtained, it was further treated to immobilize onto its surface Ni nanoparticles (NPs) to obtain the desired heterogeneous catalyst. As reported in the Experimental section, the sulphonated material was first dissolved in ethanol, sonicated, and then a suspension of $NiCl_2 \cdot 6H_2O$ was added, followed by a reduction step using $NaBH_4$. The MP-AES analysis confirmed the immobilization of Ni NPs, highlighting a content of 5.1 wt%, equivalent to 0.87 mmol g^{-1}. To further investigate the nature of the catalyst, and given that the reduction of a Ni salt precursor with $NaBH_4$ is well-documented to yield Ni_2B,[31] we delved into the catalyst nature to assess the presence of boron. Indeed, subsequent MP-AES analysis confirmed boron incorporation, revealing 0.43 wt% (0.4 mmol per gram of catalyst). Given the stoichiometric ratio between Ni and B on the catalyst, which is approximately 2 : 1, this confirms that we successfully generated a nickel boride-supported catalyst. To certify the successful nanoparticles formation and anchoring on the support, SEM and TEM analyses were carried out (Fig. 1), revealing their low dimension (see Fig. SI-2 for further details). This observation was further validated by PXRD analysis, which indicated only the amorphous nature of the bio-derived PiNe support (see Fig. SI-1).

The presence of this metal salt is functional for our purposes, since metal borides such as Ni_2B, are the catalytic species that actually catalyse the controlled decomposition of solid hydrogen carriers as for example $NaBH_4$ or $LiAlH_4$ to generate hydride or molecular hydrogen useful for reductive transformations such as the reduction of azido or nitro compounds into amines.[32,33]

After the catalyst was successfully prepared, its catalytic efficiency was evaluated in the reference reduction of
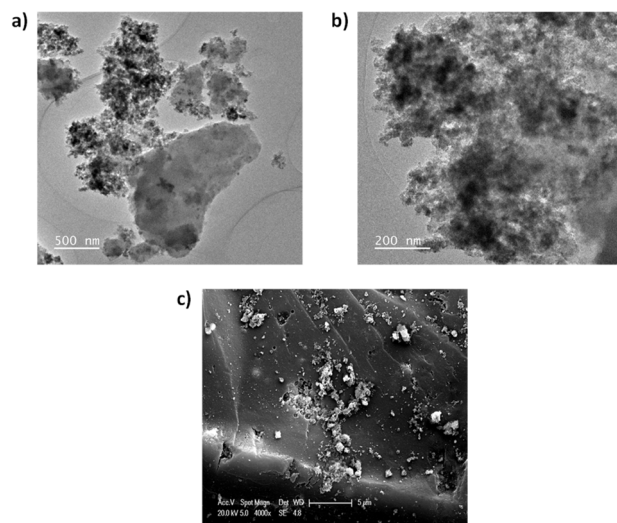

Fig. 1 Microscopic characterization of Ni(B)/PiNe. (a) TEM image (500 nm); (b) TEM image (200 nm); (c) SEM image (5 μm).

azidobenzene (**1a**) to aniline (**2a**), using $NaBH_4$ as a safe and cost-effective reducing agent in water. The decision to carry out the transformation in water stems from the fact that it is well known that reduction reactions are more controllable and selective in aqueous solutions compared to using polar protic solvents like methanol. In the latter case, the degradation of $NaBH_4$ into hydrogen is more pronounced, leading to a significantly faster reaction that can, in contrast, promote the formation of undesired by-products, thereby reducing the reaction's selectivity.[34]

Initially, the reaction optimization was conducted at room temperature for 1 h, using 1 mol% of catalyst in 0.15 M H_2O as the reaction medium. As specified in Table 1, entry 1, under these conditions just traces of the product were detected after GLC analysis; considering the importance of the contact among a heterogeneous catalyst and reagents, water volume was diminished to a reagent concentration of 0.5 M. Under these conditions, the conversion increased to 33%, reaching a further 51% when the temperature was increased to 40 °C.

Despite this, the conversion was not yet satisfactory, and so, both the amount of catalyst and $NaBH_4$ was increased (2 mol% and 2.5 eq., respectively), resulting in a conversion of 93% (entry 5).

Further increasing the amount of $NaBH_4$ to 5 eq. while doubling the reaction time to 2 h (entry 6 and 7) did not lead to significant changes in the conversion rate. Considering this, it was decided to maintain the amount of the reductant unaltered (2.5 eq.) and, at the same time, increase the catalyst amount to 4 mol%.

In this case, after 1 h, we observed an excellent 96% conversion, which was further optimized to almost complete conversion into **2a** after 2 h (entry 9).

It is essential to note that, from a sustainability perspective, using a high amount of $NaBH_4$ leads to excessive waste production. In contrast, increasing the amount of the

Table 1 Optimization of the reaction conditions for the reduction of azidobenzene (**1a**) to aniline (**2a**)[a]

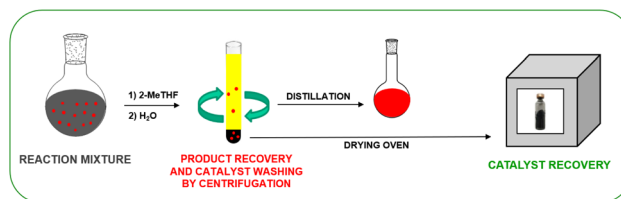| Entry	H_2O [M]	Ni(B)/PiNe (mol%)	NaBH$_4$ (eq.)	T (°C)	t (h)	C (%)[b]
1	[0.15]	1	1	rt	1	Traces
2	[0.5]	1	1	rt	1	33
3	[0.5]	1	1	40	1	51
4	[0.5]	1	2.5	40	1	70
5	[0.5]	2	2.5	40	1	93
6	[0.5]	2	5	40	1	92
7	[0.5]	2	5	40	2	95
8	[0.5]	4	2.5	40	1	96
9	[0.5]	4	2.5	40	2	>99.5
10	[0.5]	—	2.5	40	2	Traces
11	[0.5]	—	5	40	2	Traces
12	[0.5]	PiNe	2.5	40	2	10

[a] Reaction conditions: **1a** (0.25 mmol); catalyst amount calculated on Ni loading (0.87 mmol g^{-1}). [b] Determined by GLC analysis.

heterogeneous catalyst, which is easily recoverable, ensures a lower environmental impact.

Control tests were also conducted under non-catalysed conditions or in the presence of the neat sulphonated support (entries 10, 11, and 12), which showed low or negligible conversion. These results underscore both the importance of the catalytic system, which effectively enhances the degradation of NaBH$_4$ in an aqueous environment,[35] and the fundamental role of –SO$_3$H moieties on the support surface that effectively tune the catalytic efficiency of the metal NPs, stabilizing them.

Once the optimal reaction conditions were defined, catalyst recycling was investigated to validate the experimental procedure. From a technical perspective, several approaches were tested to optimise the recovery process. The general strategy involved centrifuging the reaction mixture (6500 rpm, 10 min, 5 °C) with 2 × 1 mL of extraction solvents and 0.5 mL of water to recover the crude reaction mixture while simultaneously washing the catalyst. After separating the organic phase from the aqueous layer, it was concentrated under reduced pressure to isolate the desired product. Meanwhile, the recovered catalyst was dried under vacuum at 110 °C overnight for reuse in the next reaction cycle.
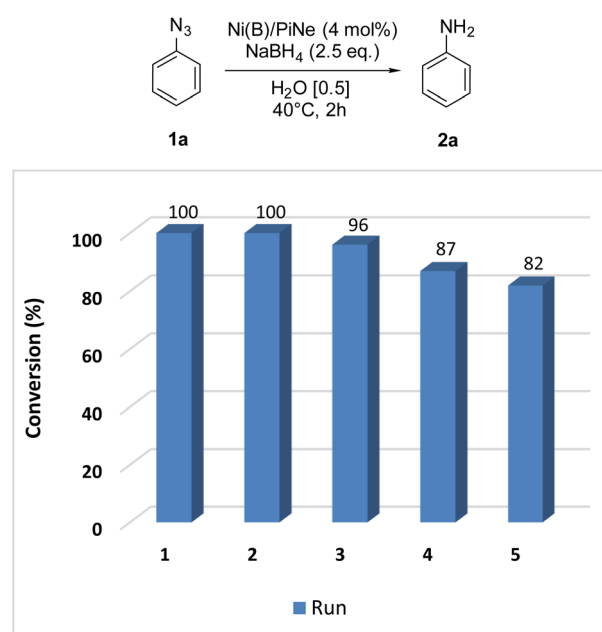
Initially, ethyl acetate was tested as the extraction solvent. However, we observed a significant decrease in conversion during the second run, which we attribute to the precipitation of inorganic salts onto the catalyst surface, potentially poisoning it. Consequently, we shifted to ethanol, which did not cause a decrease in reactivity during the second run. However, a reduced yield of the isolated product was noted. Based on our experience, this was likely due to ethanol's relatively low vapor pressure, which is similar to that of the product, potentially causing some product loss during the evaporation step.
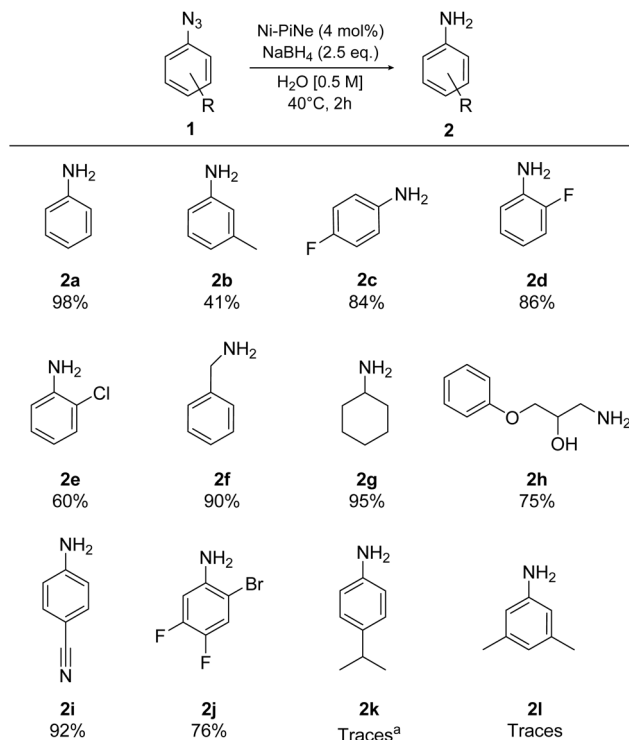

Scheme 2 Work-up and catalyst recycling procedure.

Therefore, the need for a solvent with low water solubility and a significantly higher vapor pressure than the final product became apparent. For this reason, 2-MeTHF was chosen. It not only provided high conversions (with limited solubility in water preventing salt precipitation on the catalyst surface) but also improved isolated product yields in subsequent runs.

Additionally, 2-methyltetrahydrofuran contributes to the sustainability of the procedure, as it can be derived from the valorisation of lignocellulosic biomass,[36] as discussed earlier. With the optimized work-up procedure in place (Scheme 2), a catalyst recycling study was conducted, demonstrating the easy recoverability of the catalyst over five consecutive reaction cycles with negligible loss of activity (Scheme 3). This outcome strongly supports the efficiency of the developed catalytic system (see the SI for further details about TON and TOF calculations).

To test the applicability of the developed optimal synthetic methodology and to investigate how substrates with different substituents could influence the process reactivity, a substrate scope study was conducted involving different azides and nitro compounds.

Scheme 3 Catalyst recycle study in the reference reduction of **1a** into **2a**. Reaction conditions: **1a** (0.25 mmol); catalyst amount calculated on Ni loading (0.87 mmol g^{-1}); conversion determined by GLC analysis.

Scheme 4 Substrate scope of the reduction of different azides (**1**) to amines (**2**). Reaction conditions: **1** (0.25 mmol); catalyst amount calculated on Ni loading (0.87 mmol g^{-1}). [a]Negligible conversion observed also using 8 mol% of the catalyst.
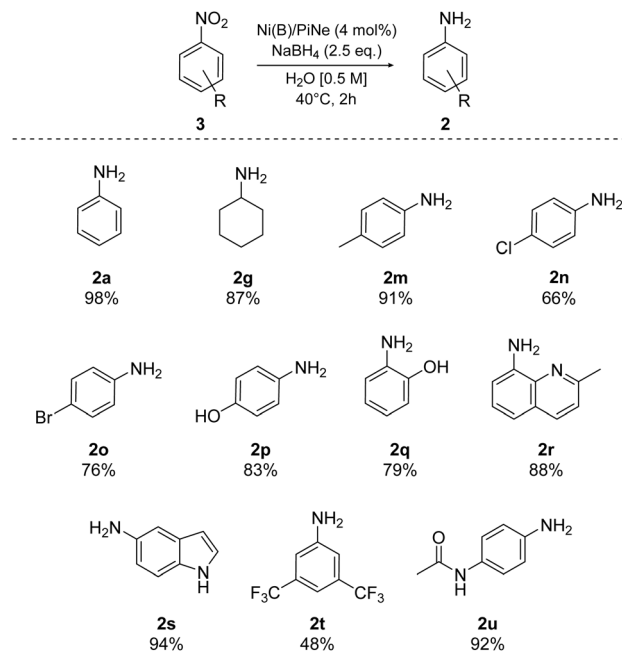
Working with azides (**1**), good to excellent yields were obtained, ranging from 41% to 98%.

As reported in Scheme 4, the reduction reaction provided the best results in the presence of aromatic substrates presenting electron-withdrawing substituents. In other words, it has been shown that strongly activated aromatic rings reduce the reactivity of the azido group reduction. Conversely, the reaction proceeds better when deactivating or weakly activating substituents are present.

For example, substrates like 1-azido-4-isopropylbenzene (**1k**) and 1-azido-3,5-dimethylbenzene (**1l**), which have a strongly activated aromatic ring, gave negligible yields toward the desired products **2k** and **2l**, even though the catalyst was doubled.

By applying the optimal reaction conditions identified earlier, we broadened the applicability of our method further exploring the efficiency of the Ni(B)-PiNe catalyst in reducing several nitro-substituted compounds (**3**) to their corresponding amines (**2**) (Scheme 5), achieving yields ranging from good to excellent (48% to 91%).

Worth mentioning is the case of the reduction of 4-nitroacetanilide (**3k**) into 4-aminoacetanilide (**2u**), a plausible key intermediate in the production of paracetamol. Beyond the yield, which was consistent with previously reported data, the most notable finding is that the designed catalytic species exhibited remarkable chemoselectivity toward the nitro group, leaving the amide moiety unaffected. This behavior is particularly important in multistep synthesis, as it enables a mild and straightforward reduction step without compromising other functionalities.

In line with the results obtained for azides (**1**), our observations confirmed the same trends, showing that electron-donating groups impede the reduction to amines.
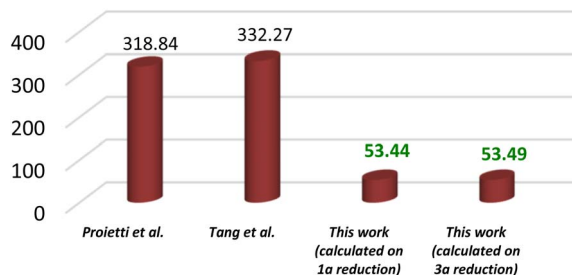
This behaviour is also confirmed in the study by Fountoulaki *et al.*,[37] which investigates the reduction of nitro compounds to anilines by NaBH$_4$ using a supported gold nanoparticle catalyst.

This experimental evidence led us to hypothesize a reaction mechanism for the reduction under investigation based exclusively on the experimental data obtained in the study described. The proposed hypothesis suggests that the catalytic species, nickel-boride supported on sulfonated biochar, acts both as a "hydride generator" and "carrier", facilitating the transfer of NaBH$_4$ derived hydrides to nitro or azido groups and allowing their reduction to amines. This mechanism could validate why substrates bearing electron-withdrawing substituents are more susceptible than those presenting electron-donor groups. Indeed, the electron-withdrawing functionalities reduce the electron density on the azido or nitro group, making them more electrophilic and, thus, more vulnerable to nucleophilic attack by the hydride provided by NaBH$_4$. Considering the latter, it is therefore believed that the reduction occurs through a catalysed hydride transfer rather than through the generation of H$_2$ from the catalysed degradation of NaBH$_4$ in water.

Environmental evaluation

To provide further insight into the methodology investigated, an environmental assessment was conducted. Firstly, the kg of waste produced for each kg of product obtained was evaluated through the *E*-factor calculation (see Table SI-3). As can be

Scheme 5 Substrate scope of the reduction of different nitro compounds (**3**) to amines (**2**). Reaction conditions: **3** (0.25 mmol); catalyst amount calculated on Ni loading (0.87 mmol g^{-1}).

Scheme 6 *E*-factor comparison.

observed in Scheme 6, the process outlined and optimised here was around six times less impactful than similar literature processes considered for comparison.

The primary reason for this process being green is the reduced use of solvents and their recovery during the evaporation process required for product isolation. Indeed, it is well known that solvents, representing the major constituents of waste associated with a chemical process,[38] deeply impact the overall sustainability and they play a pivotal role in the instauration of more sustainable chemical processes.[39]

Minimizing solvent use and enhancing their recovery significantly reduce waste, thereby improving the overall environmental benignity of the procedure.

Despite the solvent amount, another aspect that needs to be considered is related to their nature. In fact, bio-renewables are intrinsically less problematic for the environment than oil-derived ones. For this purpose, Ω values of the solvents used in this work and in literature comparisons were calculated to consider the environmental footprint using Andraos algorithms (Table 2).[40]

Seven categories have been considered for the environmental evaluation: Ozone Depletion Potential (ODP), Smog Formation Potential (SFP), Global Warming Potential (GWP), Inhalation Toxicity Potential (INHTP), Ingestion Toxicity Potential (INGTP), Bioaccumulation Potential (BAP), and Abiotic Resource Depletion Potential (ARDP).

Table 2 Environmental assessment of the solvents used in the reduction of azido and nitro compounds

	Ω	$\sum\Omega$
Proietti *et al.*		
H$_2$O	1.41	18.28
Ethyl acetate	3.74	
Methanol	13.13	
Tang *et al.*		
H$_2$O	1.41	16.36
Dichloromethane	6.17	
Ethanol	8.79	
This work		
H$_2$O	1.41	5.52
2-Methyltetrahydrofuran	4.12	

As shown above, the solvent adopted in this work proved to be the best choice in terms of environmental impact and benignity for human health. The main reason behind these results is undoubtedly the high INGTP observed for methanol and ethanol, which are used as purification and reaction solvents in the literature references.

Conclusions

In the present study, we report the preparation of a heterogeneous catalyst derived from the valorisation of pine needles, containing nickel-boride nanoparticles, which was successfully prepared and employed for reductive processes. The developed method enabled the selective reduction of a range of azido and nitro compounds to their corresponding amines, using NaBH$_4$ as the reducing agent in water under mild conditions, thereby minimising both energy and material consumption.

Additionally, an innovative purification method was established, utilising 2-MeTHF as a green extraction solvent. This approach not only allowed efficient catalyst recovery but also simplified the work-up procedure. The study further demonstrated the high activity and stability of the Ni(B)/PiNe catalyst, which remained effective over five consecutive reaction cycles without significant loss of performance.

The results revealed that both nitro and azido groups underwent excellent reductions when electron-withdrawing or weakly activating substituents were present. At the same time, reactions were hindered in the presence of strongly activating aromatic rings. Based on these experimental findings, a reaction mechanism was proposed, suggesting that nickel-boride acts as both a "hydride generator" and "carrier," facilitating the transfer of hydride from NaBH$_4$ to the nitro or azido group of the substrate, thus enabling its reduction.

Author contributions

The manuscript was written through the contributions of all authors. All authors have given approval to the final version of the manuscript. F. C.: investigation, methodology, data analysis, and manuscript preparation–review; F. B.: investigation, methodology, data analysis and manuscript review; F. V.: investigation, methodology and manuscript review; D. G.: investigation, methodology, data analysis and manuscript review; D. M.: investigation, methodology, data analysis and manuscript review; L. V.: conceptualization, project administration and manuscript review/editing.

Conflicts of interest

There are no conflicts to declare.

Data availability

The data supporting this article have been included as part of the supplementary information (SI). Supplementary information: general procedures, *E*-factor calculations, full characterization of both the catalyst and the synthesized compounds,

copies of ^{1}H, ^{13}C and ^{19}F NMR spectra. See DOI: **https://doi.org/10.1039/d5su00323g**.

Notes and references

1 M. Orlandi, D. Brenna, R. Harms, S. Jost and M. Benaglia, *Org. Process Res. Dev.*, 2018, **22**, 430–445.
2 Z. Li, S. Kelkar, L. Raycraft, M. Garedew, J. E. Jackson, D. J. Miller and C. M. Saffron, *Green Chem.*, 2014, **16**, 844–852.
3 R. Dorel, C. P. Grugel and A. M. Haydl, *Angew. Chem., Int. Ed.*, 2019, **58**, 17118–17129.
4 M. Yaghmaei, A. E. Lanterna and J. C. Scaiano, *iScience*, 2021, **24**, 103472.
5 R. Ma, L.-N. He, Q.-W. Song, Y.-B. Zhou and K.-X. Liu, *RSC Adv.*, 2014, **4**, 11867–11871.
6 J. A. Garduño and J. J. García, *ACS Catal.*, 2020, **10**, 8012–8022.
7 P. T. Nyffeler, C. H. Liang, K. M. Koeller and C. H. Wong, *J. Am. Chem. Soc.*, 2002, **124**, 10773–10778.
8 P. Holakooei, F. Valentini and L. Vaccaro, *ACS Sustain. Chem. Eng.*, 2025, **13**, 527–534.
9 F. Valentini, A. Marrocchi and L. Vaccaro, *Adv. Energy Mater.*, 2022, **12**, 2103362.
10 F. Ferlin, F. Valentini, A. Marrocchi and L. Vaccaro, *ACS Sustain. Chem. Eng.*, 2021, **9**, 9604–9624.
11 P. Holakooei, F. Valentini, F. Campana and L. Vaccaro, *Mol. Catal.*, 2024, **563**, 114235.
12 B. Y. Kara, B. Kilbaş and H. Göksu, *New J. Chem.*, 2016, **40**, 9550–9555.
13 https://commission.europa.eu/strategy-and-policy/priorities-2019-2024/european-green-deal/energy-and-green-deal_e, accessed March 2025.
14 Z. Tabassum, M. Girdhar, A. Anand, N. Kumari, B. Sood, T. Malik, A. Kumar and A. Mohan, *Mater. Adv.*, 2025, **6**, 527–546.
15 F. Campana, G. Brufani, F. Mauriello, R. Luque and L. Vaccaro, *Green Synth. Catal.*, 2024, **6**, 217–238.
16 W. Deng, Y. Feng, J. Fu, H. Guo, Y. Guo, B. Han, Z. Jiang, L. Kong, C. Li, H. Liu, P. T. T. Nguyen, P. Ren, F. Wang, S. Wang, Y. Wang, Y. Wang, S. S. Wong, K. Yan, N. Yan, X. Yang, Y. Zhang, Z. Zhang, X. Zeng and H. Zhou, *Green Energy Environ.*, 2023, **8**, 10–114.
17 F. Campana, F. Valentini, A. Marrocchi and L. Vaccaro, *Biofuel Res. J.*, 2023, **40**, 1989–1998.
18 F. Valentini, B. Di Erasmo, M. Ciani, S. Chen, Y. Gu and L. Vaccaro, *Green Chem.*, 2024, **26**, 4871–4879.
19 F. Ferlin, F. Valentini, D. Sciosci, M. Calamante, E. Petricci and L. Vaccaro, *ACS Sustain. Chem. Eng.*, 2021, **9**, 12196–12204.
20 F. Valentini, S. Chen, G. Brufani, Y. Gu and L. Vaccaro, *ChemSusChem*, 2025, **18**, e202402011.
21 D. Formenti, F. Ferretti, F. K. Scharnagl and M. Beller, *Chem. Rev.*, 2019, **119**(4), 2611–2680.
22 B. Y. Kara, B. Kilbaş and H. Göksu, *New J. Chem.*, 2016, **40**, 9550–9555.
23 F. Fringuelli, F. Pizzo and L. Vaccaro, *Synthesis*, 2000, 646–650.
24 D. Formenti, C. Topf, K. Junge, F. Ragaini and M. Beller, *Catal. Sci. Technol.*, 2016, **6**, 4473–4477.
25 O. Beswick, A. Parastaev, I. Yuranov, T. LaGrange, P. J. Dyson and L. Kiwi-Minsker, *Catal. Today*, 2017, **279**, 29–35.
26 M. Ben Said, T. Baramov, T. Herrmann, M. Gottfried, J. Hassfeld and S. Roggan, *Org. Process Res. Dev.*, 2017, **21**, 705–714.
27 G. Proietti, K. J. Prathap, X. Ye, R. T. Olsson and P. Dinér, *Synth.*, 2022, **54**, 133–146.
28 Q. Tang, Z. Yuan, S. Jin, K. Yao, H. Yang, Q. Chi and B. Liu, *React. Chem. Eng.*, 2020, **5**, 58–65.
29 A. Nose and T. Kudo, *Chem. Pharm. Bull.*, 1988, **36**, 1529.
30 F. Valentini, F. Ferlin, S. Lilli, A. Marrocchi, L. Ping, Y. Gu and L. Vaccaro, *Green Chem.*, 2021, **23**, 5887–5895.
31 D. Hua, Y. Hanxi, A. Xinping and C. Chuansin, *Int. J. Hydrogen Energy*, 2003, **28**, 1095–1100.
32 B. Ganem and J. O. Osby, *Chem. Rev.*, 1986, **86**, 763–780.
33 D. Amantini, F. Fringuelli, F. Pizzo and L. Vaccaro, *Org. Prep. Proced. Int.*, 2002, **34**, 109–147.
34 J. March, *Advanced Organic Chemistry*, Wiley-Interscience, New York, 4th edn, 1992.
35 A. Kytsya, V. Berezovets, Yu. Verbovytskyy, L. Bazylyak, V. Kordan, I. Zavaliy and V. A. Yartys, *J. Alloys Compd.*, 2022, **908**, 164484.
36 R. Bijoy, P. Agarwala, L. Roy and B. N. Thorat, *Org. Process Res. Dev.*, 2022, **26**, 480–492.
37 S. Fountoulaki, V. Daikopoulou, P. L. Gkizis, I. Tamiolakis, G. S. Armatas and I. N. Lykakis, *ACS Catal.*, 2014, **4**, 3504–3511.
38 S. Trastulli Colangeli, F. Campana, F. Ferlin and L. Vaccaro, *Green Chem.*, 2024, **27**, 633–641.
39 G. Quaglia, F. Campana, L. Latterini and L. Vaccaro, *ACS Sustain. Chem. Eng.*, 2022, **10**, 9123–9130.
40 J. Andraos, *Org. Process Res. Dev.*, 2012, **16**, 1482–1506.