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PAPER

Enhanced reduction of C–N multiple bonds using sodium borohydride and an amorphous nickel catalyst†

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Amorphous nickel powder (Ni^0) was utilised as a catalyst under mild, aqueous, basic conditions for enhancing the sodium borohydride-mediated reduction of C–N multiple bonds such as oximes, imines, hydrazones and nitriles to produce the corresponding amines in good to excellent yields.

Introduction

Nanosized catalysts can efficiently improve heterogeneous catalyst-based reactions in organic synthesis. Certain metal and metal oxide nanocatalysts have been shown to offer great opportunities for a wide range of applications in organic synthesis, including Au, Ag, Fe, Cu, Pt, Pd and Ni.[1] In particular, nickel-based, nanosized catalysts have been used for the Hantzsch condensation,[2a] chemo-selective oxidative coupling of thiols,[2b] reduction of aldehydes and ketones,[2c] hydrogenation of olefins[2d] and as supports for hydrogen adsorption.[2e] Amorphous metals, which are different from nanometals, but are regarded as similar to nanometals, have received considerable attention in terms of their surface chemical phenomena, properties of the valence electrons, surface structure and composition, and as potential heterogeneous catalysts.[3] Recently, with the development[4] of technology for the preparation of amorphous materials, various amorphous alloys (especially nickel) have been successfully prepared and employed in hydrogen storage[5a] and catalytic reactions, including electrolysis,[5b] hydrogenation,[5c] hydrogenolysis,[5d] oxidation,[5e] isomerization[5f] *etc.*

The transformation of compounds bearing C–N multiple bonds, such as nitriles, oximes, imines and hydrazones to the corresponding amines represents one of the most widely used and valuable functional group transformations in organic synthesis.[6] For the reduction of C–N multiple bonds, existing reported methods include catalytic hydrogenation, $LiAlH_4$ and $NaBH_4$. However, these methods are often limited to reducing only some of these C–N multiple bond compounds because they are not general methods and have some obvious disadvantages, [7] such as: (1) catalytic hydrogenation reduction of C–N multiple bonds often gives a mixture of primary, secondary and tertiary amines; (2) $LiAlH_4$ lacks selectivity, is highly water sensitive and can lead to low yields due to the formation of colloidal materials upon work-up; (3) $NaBH_4$ is often inefficient at reducing many C–N multiple bonds unless a Lewis acid[8] such as LiCl,[9] $TiCl_4$,[10] $TiCl_3$[11] or $ZrCl_4$[12] is also used. Hence, the development of mild, more selective, general and practical methods for the reduction of C–N multiple bonds to amino groups are highly desirable. Our interest was, therefore, to seek a versatile and general method for this transformation using a suitable transition metal as a heterogeneous catalyst to enhance the reducing power of $NaBH_4$, and in this paper, we report such a novel procedure.

Results and discussion

Although Ni-based amorphous alloys have been studied widely, the use of amorphous nickel powder (Ni^0) as a heterogeneous catalyst has not been reported in the organic synthesis literature. Herein, an environmentally friendly, highly efficient and chemoselective method for the reduction of C–N multiple bonds is revealed. The method is executed by the combination of amorphous nickel powder (Ni^0) with sodium borohydride in a basic methanolic aqueous solution to reduce compounds bearing C–N multiple bonds to the corresponding amines in high yields. This system has the advantages of versatility and practicality, a simple work-up process, easy recycling of the catalyst and it can be applied for the reduction of many different C–N multiple bonds.

During the attempted synthesis of 2-acetylamino-3-(2-quinolinyl)-propionic acid **2b** from the corresponding ethyl 3-(2-quinolinyl)-2-hydroxyimino propionate **1**, it was found that **1** could be reduced with Zn/AcOH–Ac_2O to the corresponding *N*-acetate **2a** in 78% yield.[13] However, it could not be reduced to the free amine **2b** using either $NaBH_4$–$TiCl_3$, $NaBH_4$–$TiCl_4$ or $NaBH_4$–$NiCl_2$. In order to solve this problem, we discovered that the combination of 10% amorphous nickel (Ni^0) with sodium borohydride was an effective method to obtain the desired product **2b** in 88% yield when carried out in a basic methanolic aqueous solution under ambient conditions (Scheme 1).

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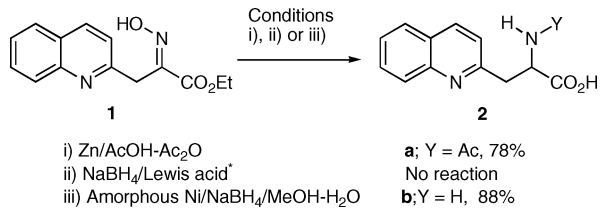
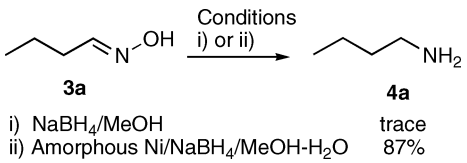


Scheme 1 First example of an amorphous Ni(⁰)-based borohydride reduction of an oxime ether.

Further investigation into this reaction revealed the utility of the method, for example, *n*-butyraldehyde oxime **3a**, which fails to provide *n*-butylamine in presence of sodium borohydride alone, when combined with amorphous nickel (Ni⁰), gave the desired amine **4a** in 87% yield (Scheme 2). Hence, further examination of the reduction of other oximes **1** (Table 1) with a range of different functional groups including α-hydroxyimino carboxylates, aldoximes and ketoximes *etc.*, using this new system, was carried out. As shown in Table 1, oximes with different groups, including electron-withdrawing or electron-donating groups, such as alkyl, carboxyl, carboxylic ester, aryl, substituted-aryl, or heteroaryl groups, could be reduced to the corresponding amines with equal facility.

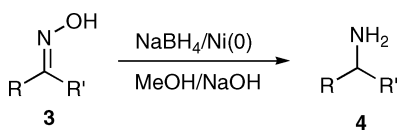


Scheme 2 Amorphous Ni(⁰)-borohydride-based reduction of *n*-butyloxime to the corresponding primary amine.

Hence, both aldoximes and ketoximes (Table 1, Entries 1–5) gave approximately 90% yields of products, and whether conjugated to a phenyl group or not, had no significant effect on the outcome of the reaction. Furthermore, phenyl-substituents such as fluorine, chlorine, bromine and methoxyl groups were readily tolerated (Table 1, Entries 7–8, 10–13) with no dehalogenation[14] detected. Usefully, conjugated carboxylic acids and esters were also inert to these reduction conditions (Table 1, Entries 6–15) with yields of these two series of compounds also around the 80–90% range, although the latter were hydrolysed to corresponding carboxylic acids due to the basic aqueous reaction conditions used (Table 1, Entries 9–15). The bulky 2-naphthalenylmethyl group was also tolerated without problem under these conditions, leading to the corresponding amino compound in 86% yield (Table 1, Entry 15). Similarly, ethyl 3-(4-pyridinyl)-2-hydroxyimino propionate gave the corresponding 2-amino-3-(4-pyridinyl) propionic acid in 84% yield (Table 1, Entry 14), which demonstrates that this method represents a new, selective method for the reduction of oximes, and which could be potentially applied to commercial syntheses of non-proteinogenic amino acid derivatives.

Since imines and hydrazones have similar structures to oximes, these two series of compounds were also selected as substrates to investigate their potential for reduction under the same conditions (see Table 2). Table 2 demonstrates that the reductions occurred smoothly for most imines, including both ketimines and aldimines **5**, providing the corresponding amines **6** in good to high yields, although the yield depended on the stereoelectronic effects of substitutents *R* and *R′*. For example, diphenylmethanimine **5f** gave 69% yield (Table 2, Entry 6), *i.e.* lower than many other examples outlined in Table 2. These results show that this method provides a useful synthetic process for accessing a range of amines through a reductive-amination approach of the corresponding carbonyl compounds. The reduction products obtained from hydrazone

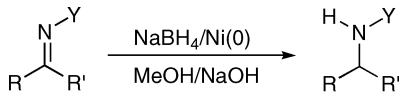
Table 1 Borohydride reduction of oximes using amorphous nickel powder (Ni⁰) as catalyst



No	Substrate **3**		Product **4**		Yield[a] (%)
	R	*R′*	*R*	*R′*	
1	**a** Et	H	**a** Et	H	87
2	**b** Ph	H	**b** Ph	H	91
3	**c** n-Pr	H	**c** n-Pr	H	90
4	**d** Cyclohexanyl		**d** Cyclohexanyl		92
5	**e** Ph	Me	**e** Ph	Me	96
6	**f** Ph	COOH	**f** Ph	COOH	88
7	**g** 4-ClPh	COOH	**g** 4-ClPh	COOH	90
8	**h** 4-FPh	COOH	**h** 4-FPh	COOH	89
9	**i** Bn	COOEt	**i** Bn	COOH	83
10	**j** 4-FBn	COOEt	**j** 4-FBn	COOH	91
11	**k** 4-ClBn	COOEt	**k** 4-ClBn	COOH	90
12	**l** 4-BrBn	COOEt	**l** 4-BrBn	COOH	86
13	**m** 4-MeOBn	COOEt	**m** 4-MeOBn	COOH	92
14	**n** 4-PyCH$_2$	COOEt	**n** 4-PyCH$_2$	COOH	84
15	**o** 2-NaphthylCH$_2$	COOEt	**o** 2-NaphthylCH$_2$	COOH	86

[a] Isolated yields obtained using the general procedure.

Table 2 Borohydride reduction of imines and hydrazones using amorphous nickel powder (Ni^0) as catalyst



5 **6**

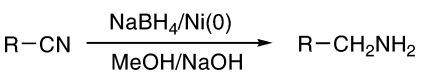
	Substrate **5**			Product **6**			
No	*R*	*R′*	Y	*R*	*R′*	Y	Yield (%)[a]
1	**a** Me	Me	Cyclohexyl	**a** Me	Me	Cyclohexyl	82
2	**b** Ph	H	*n*-Bu	**b** Ph	H	*n*-Bu	86
3	**c** Me	H	Bn	**c** Me	H	Bn	87
4	**d** Ph	H	Ph	**d** Ph	H	Ph	80
5	**e** Ph	H	Bn	**e** Ph	H	Bn	89
6	**f** Ph	Ph	Me	**f** Ph	Ph	Me	69
7	**g** Ph	H	PhNH	**g** Ph	H	PhNH	68
8	**h** Ph	Me	PhNH	**h** Ph	Me	H	72[b]
				h′ = $PhNH_2$			65[b]

[a] Typical reactions conditions as for the oximes[§] but at 40 °C. [b] The reaction was run at 60 °C for 3 h.

derivatives also depended on the reaction conditions used. Most hydrazones could be transformed to the corresponding hydrazines. For example, benzaldehyde phenylhydrazone, Table 2, Entry 7, could be selectively reduced to 1-benzyl-2-phenylhydrazine, at 40 °C for 45 min in 68% yield. However, if the reaction is carried out above 55 °C for 1 h, it is clear that acetophenone phenylhydrazone can be reduced completely with concommitant cleavage of the N–N linkage and is transformed into the two separate amines, *i.e.* 1-phenylethylamine and aniline (Table 2, Entry 8). As longer reaction times are used, this complete reduction outcome and N–N bond cleavage becomes the main result.

To explore the scope and limitations of this method further, nitrile substrates were also examined as shown in Table 3. Both conjugated and non-conjugated nitriles **7** give the corresponding reduction products **8** in 85–93%. In the case of hexane dinitrile **7c**, the dosage of amorphous nickel powder (Ni^0) used was 15% (Table 3, Entry 3) with two equivalents borohydride being employed, giving the desired 1,6-hexamethylenediamine **8c** in 90% yield. Overall, the results in Table 3 show that this process is facile and convenient for the conversion of any nitrile to corresponding amine.

Table 3 Borohydride reduction of nitriles using amorphous nickel powder (Ni^0) as catalyst



7 **8**

	Substrate **7**	Substrate **8**	
No	*R*	*R*	Yield[a] (%)
1	**a** Et	**a** Et	89
2	**b** *n*-Pr	**b** *n*-Pr	93
3	**c** $NC(CH_2)_4CN$	**c** $NC(CH_2)_4CN$	90
4	**d** Bn	**d** Bn	89
5	**e** 4-MeBn	**e** 4-MeBn	92
6	**f** 4-FPh	**f** 4-FPh	88
7	**g** 4-FBn	**g** 4-FBn	93

[a] Typical reaction conditions as for the oximes.[§]

It is also important to note that the methanol used as solvent can be replaced with other alcohols, such as ethanol, *iso*-propanol and *tert*-butanol, however, this led to longer reaction times and decreased yields. To determine the appropriate amount of the amorphous nickel catalyst required, we selected substrates **3j** from Table 1, **5e** from Table 2 and **7f** in Table 3 as model substrates to check the optimal nickel loading. This showed that between 9–12 mol% was ideal, and after the reaction, the catalyst was easily filtered from reaction mixture and could be re-used up to 5 times without loss of activity.

The mechanism of amorphous Ni-catalyzed reduction is not clear at present. However, it is clear that this type of amorphous Ni does not behave like RANEY® Ni in catalytic hydrogenation reactions. Fig. 1 and 2 are SEMs of amorphous Ni before and after use in reduction reactions.

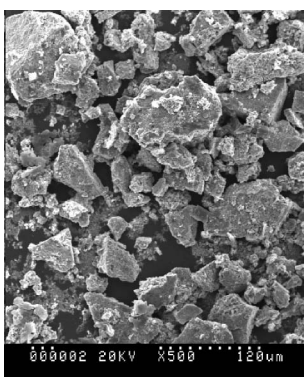


Fig. 1 SEM of amorphous nickel.

Fig. 1 and 2 show that the morphology of the amorphous Ni has changed, from a angular morphology to a more aggregated mixed state. In contrast, Fig. 3 and 4 show the amorphous Ni state using the reduction reaction conditions in the absence and presence of substrate. These also show differences in the Ni state after the reaction and after exposure to the substrates. These SEMs demonstrate that the reaction conditions do not cause the morhphology changes, but that exposure to the substrates does

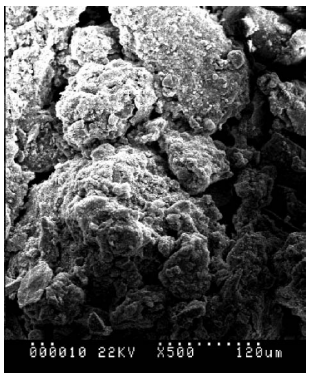


Fig. 2 SEM of nickel after reaction.

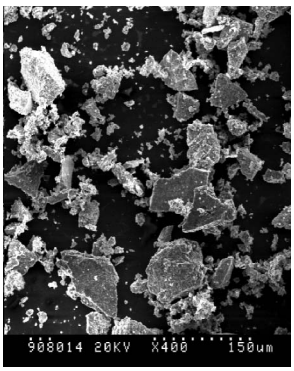


Fig. 3 SEM of amorphousnickel after blank test.

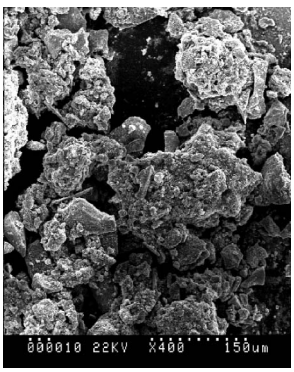


Fig. 4 SEM of nickel after reaction.

have an effect and the Ni state changes as a consequence. The exact mechanism by which the amorphous Ni takes part in these reduction processes, however, is not clear.

Summary and conclusions

In conclusion, this new method of sodium borohydride with amorphous nickel (Ni^0) under basic aqueous methanolic solution offers a useful approach for the reduction of C–N multiple bonds. It is an excellent alternative to the many other methods available, especially because it has been successfully applied to the reduction of oximes, imines, hydrazones and nitriles. In addition, many functional groups, such as methoxy, halides and carboxylate groups are compatible, as are heterocyclic compounds. This method can be easily scaled-up and has the potential be used for the synthesis of amines on a kilogram scale. Thus, using amorphous nickel as a heterogeneous catalyst is expected to contribute to the development of more environmentally-benign reaction methods, being simple, easy to work-up, and with products that are easily isolated in good to excellent yields.

Experimental

General experimental

^{1}H NMR and ^{13}C NMR were recorded on a Bruker Avance II 500 spectrometer in $CDCl_3$ unless stated otherwise, using tetramethylsilane as an internal reference, operated at 500.13 for ^{1}H and 125.67 MHz for ^{13}C, and J values are given in Hz. HR-EI-MS data were measured with a Micromass Autospec-Ultima ETOF spectrometer. The surface morphology and the diffusion of Ni^0 was observed by scanning electronic microscopy (SEM) performed on a LEO 1530VP instrument. Flash chromatography was performed with silica gel or neutral aluminum oxide (200–300 mesh) using petroleum ether (PE) and ethyl acetate (Et) mixtures as eluent unless stated otherwise. Reactions were monitored by thin layer chromatography (TLC) on silica gel plate (GF_{254}). Organic extracts were washed with brine, dried over anhydrous sodium sulfate and concentrated under reduced pressure on a rotary evaporator. Amorphous nickel was provided by Sinopec Corp's Research Institute in Shijiazhaung, China.

Starting materials

Hydroxyimino compounds **3a–3e** (Table 1, Entry 1–5) were prepared from the reaction of the corresponding aldehydes and ketones with hydroxyamino hydrochloride.[15] α-Hydroxyimino compounds **3f–3o** (Table 1, Entry 6–15) were prepared by the nitrosation reaction of the corresponding substituted malonate with ethyl nitrite.[13] Imine compounds **5a–5f** and **5g–5h** were prepared by the reaction of corresponding aldehydes and ketones with corresponding amines or phenylhydrazine respectively.[16] Nitrile compounds **7a–7g** (Table 3, Entry 1–7) were commercially available and directly used without further purification. All reagents and solvents were commercially available and used without further purification unless stated otherwise. All synthetic compounds are known, were characterized by their NMR spectra and compared with the reported literature.

General procedure of reduction of hydroxyimino derivatives

To stirred mixture of amorphous nickel (10 mmol%) and solution of substrate (25 mmol) dissolved in methanol or ethanol (20 mL) an aqueous solution of sodium hydroxide (50 mL, 5.0 M), methanol or ethanol (15 mL) and sodium borohydride (3.0 g, 79 mmol) was added dropwise at 20–30 °C for 2–4 h. The reaction was then kept at room temperature another 3 h, and monitored by TLC. The mixture was filtered and the solution was neutralized to pH 9 (for the reduction of **3a–3e**) or pH 4–4.5 (for the reduction of **3f–3o**) with 5 M aqueous HCl. The aqueous phase was extracted with ethyl acetate and the organic phase was washed with brine. The combined organic phase was dried over anhydrous Na_2SO_4, and the solvent was removed under vacuum to obtain the crude product. The crude product for **4f–4o** could be collected by filtering

as a solid product was formed by adjusting pH to the isoelectric point.

n-Propylamine 4a

Product **4a** (CAS registry No: 107-10-8) was obtained according to the general procedures at 87% yield after purification by fractional distillation, b.p. 46.5–47 °C (literature data: 46–47 °C).[17] ^{1}H NMR ($CDCl_3$, 500 MHz): δ 2.66 (t, J = 7.0, 2H), 1.50–1.44 (m, 4H), 0.92 (t, J = 7.5, 3H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 44.0, 26.8, 11.2.

Benzylamine 4b

Product **4b** (CAS registry No: 100-46-9) was obtained according to the general procedures at 91% yield after purification by reduced pressure distillation, b.p. 180–181.5 °C (literature data: 180–183 °C/755 Torr).[18] ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.37–7.19 (m, 5H), 3.82 (s, 2H), 1.48 (br, s, 2H).

1-Butylamine 4c

Product **4c** (CAS registry No:109-73-9) was obtained according to the general procedures at 90% yield after purification by fractional distillation, b.p. 75–77 °C (literature data: 75–78 °C).[19] ^{1}H NMR ($CDCl_3$, 500 MHz): δ 2.68 (t, J = 7.0 Hz, 2H, NCH_2), 1.44–1.40 (m, 2H, CH_2), 1.37–1.33 (m, 2H, CH_2), 1.23 (br, s, 2H, NH_2), 0.92 (t, J = 7.0 Hz, 3H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 41.7, 35.8, 19.8, 13.7.

Cyclohexylamine 4d

Product **4d** (CAS registry No:108-91-8) was obtained according to the general procedures at 92% yield after purification by fractional distillation, bp 132–134 °C (literature data: 132–133 °C).[20] ^{1}H NMR ($CDCl_3$, 500 MHz): δ 2.64–2.59 (m, 1H, NCH), 1.83–1.80 (m, 2H), 1.80–1.69 (m, 2H), 1.62–1.58 (m, 1H), 1.39 (br, s, 2H, NH_2), 1.31–1.22 (m, 2H), 1.16–1.13 (m, 1H), 1.13–0.98 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 50.1, 36.6(2), 25.4, 24.9(2).

1-Phenylethylamine 4e

Product **4e** (CAS registry No: 618-36-0) was obtained according to the general procedure at 96% yield after purification by reduced pressure fractional distillation, b.p. 68.5–69.5 °C/1.33 kPa (literature data: 184–186 °C).[21] ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.34–7.30 (m, 4H, ArH), 7.24–7.20 (m, 1H, ArH), 4.09 (q, J = 6.5 Hz, 1H, NCH), 1.49 (br, s, 2H, NH_2), 1.37 (d, J = 6.5 Hz, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 147.9, 128.5(2), 126.8, 125.7(2), 51.4, 25.7.

Phenylglycine 4f

Product **4f** (CAS registry No: 2835-06-5) was obtained according to the general procedures at 88% yield after purification by recrystallisation in H_2O (2 M NaOH/2 M HCl), m.p. 296 °C (dec.) (literature data: 294–297 °C (dec.)).[22] ^{1}H NMR (D_2O, 500 MHz): δ (ppm) 7.43–7.39 (m, 4H, ArH), 7.39–7.36 (m, 1H, ArH), 4.36 (s, 1H, CH); ^{13}C NMR (D_2O, 125 MHz) δ 181.1, 142.2, 128.9(2), 127.5, 126.9(2), 60.6.

4-Chlorophenylglycine 4g

Product **4g** (CAS registry No: 6212-33-5) was obtained according to the general procedures at 90% yield after purification by recrystallisation in H_2O (2 M NaOH/2 M HCl), m.p. 243–247 °C (dec.). ^{1}H NMR (D_2O, 500 MHz): δ 7.02–7.00 (d, J = 8.5 Hz, 2H, ArH), 6.76–6.75 (d, J = 8.0 Hz, 2H, ArH), 3.77 (s, 1H, CH); ^{13}C NMR (D_2O, 125 MHz) δ 180.5, 141.0, 132.2, 128.5(2), 128.3(2), 59.8; HRMS (m/z): 208.0115 $[M+Na]^+$ (calcd for $C_8H_8ClNO_2$, 185.0244).

4-Fluorophenylglycine 4h

Product **4h** (CAS registry No: 7292-73-1) was obtained according to the general procedures at 89% yield after purification by recrystallization in H_2O (2 M NaOH/2 M HCl), m.p. 281.5–283.5 °C (dec.). ^{1}H NMR (DMSO, 500 MHz): δ 7.45–7.42 (dd, J = 8.5 Hz, J = 5.5 Hz, 2H, ArH), 7.18 (t, J = 8.5 Hz, 2H, ArH), 4.24 (s, 1H, CH), 2.64 (t, J = 1.5 Hz, 2H, NH_2); ^{13}C NMR (DMSO, 125 MHz) δ 180.9, 162.8, 160.9, 138.2, 128.6, 128.5, 115.4, 115.3, 59.8; HRMS (m/z): 192.0421 $[M+Na]^+$ (calcd for $C_8H_8FNO_2$, 169.0539).

Phenylalanine 4i

Product **4i** (CAS registry No:150-30-1) was obtained according to the general procedures at 83% yield after purification by recrystallisation in H_2O, m.p. 268 °C (dec.) (literature data: 271–274 °C (dec.)).[23] ^{1}H NMR (D_2O, 500 MHz): δ 7.45–7.43 (d, J = 7.5 Hz, 2H, ArH), 7.42–7.38 (m, 1H, ArH), 7.34–7.32 (d, J = 7.5 Hz, 2H, ArH), 4.01–3.98 (m, 1H, NCH), 3.31–3.28 (dd, J = 14.5 Hz, J = 5.0 Hz, 1H, CHH), 3.15–3.11 (dd, J = 14.5 Hz, J = 5.0 Hz, 1H, CHH); ^{13}C NMR (D_2O, 125 MHz) δ 173.9, 135.1, 129.4(2), 129.1(2), 127.7, 56.1, 36.4.

4-Fluorophenylalanine 4j

Product **4j** (CAS registry No: 51-65-0) was obtained according to the general procedures at 91% yield after purification by recrystallization in H_2O, m.p. 251–253.5 °C (dec.) (literature data: 252–255 °C(dec.)).[24] ^{1}H NMR (D_2O, 500 MHz): δ 7.27–7.24 (dd, J = 8.5 Hz, J = 6.0 Hz, 2H, ArH), 7.09 (t, J = 9.0 Hz, 2H, ArH), 3.48 (t, J = 6.5 Hz, 1H, NCH), 2.97–2.93 (dd, J = 13.5 Hz, J = 5.5 Hz, 1H, CHH), 2.86–2.82 (dd, J = 13.5 Hz, J = 7.0 Hz, 1H, CHH); ^{13}C NMR (D_2O, 125 MHz) δ 182.1, (162.5, 160.6), (134.1, 134.0), (131.0, 130.9), (115.2, 115.1), 57.5, 39.9.

4-Chlorophenylalanine 4k

Product **4k** (CAS registry No: 7424-00-2) was obtained according to the general procedures at 90% yield after purification by recrystallization in H_2O, m.p. 216–219 °C (dec.). ^{1}H NMR (D_2O, 500 MHz): δ (ppm) 7.37 (d, J = 8.0 Hz, 2H, ArH), 7.23 (d, J = 8.5 Hz, 2H, ArH), 3.49–3.47 (dd, J = 7.0 Hz, J = 6.0 Hz, 1H, NCH), 2.98–2.94 (dd, J = 13.5 Hz, J = 5.5 Hz, 1H, CHH), 2.86–2.82 (dd, J = 13.8 Hz, J = 7.0 Hz, 1H, CHH);^{13}C NMR (D_2O, 125 MHz) δ 182.2, 137.0, 131.7, 130.9(2), 128.4(2), 57.4, 40.3; HRMS (m/z): 222.0286 $[M+Na]^+$ (calcd for $C_9H_{10}ClNO_2$, 199.0400).

4-Bromophenylalanine 4l

Product **4l** (CAS registry No: 14091-15-7) was obtained according to the general procedures at 86% yield after purification by recrystallization in H_2O, m.p. 260.5–262 °C (dec.) (literature data: 258 °C (dec.)).[25] ^{1}H NMR (D_2O, 500 MHz): δ 7.52 (d, J = 8.5 Hz, 2H, ArH), 7.18 (d, J = 8.5 Hz, 2H, ArH), 3.49–3.47 (dd, J = 7.0 Hz, J = 5.5 Hz, 1H, NCH), 2.96–2.92 (dd, J = 13.5 Hz, J = 6.0 Hz, 1H, CHH), 2.84–2.80 (dd, J = 13.5 Hz, J = 7.5 Hz, 1H, CHH); ^{13}C NMR (D_2O, 125 MHz) δ 182.1, 137.6, 131.4(2), 131.(2), 119.8, 57.4, 40.4; HRMS (m/z): 265.9785, 267.9762 $[M+Na]^+$ (calcd for $C_9H_{10}BrNO_2$, 242.9895, 244.9874).

4-Methoxyphenylalanine 4m

Product **4m** (CAS registry No: 7635-29-2) was obtained according to the general procedures at 92% yield after purification by recrystallization in H_2O, m.p. 236–238 °C (dec.) (literature data: 237–241 °C (dec.)).[26] ^{1}H NMR (D_2O, 500 MHz): δ 7.22 (d, J = 8.5 Hz, 2H, ArH), 6.97 (d, J = 8.5 Hz, 2H, ArH), 3.83 (s, 3H, OCH_3), 3.48–3.45 (dd, J = 7.0 Hz, J = 5.5 Hz, 1H, CHH), 2.95–2.91 (dd, J = 13.5 Hz, J = 5.5 Hz, 1H, CHH); ^{13}C NMR (D_2O, 125 MHz) δ 182.5, 157.5, 131.0, 130.6(2), 114.1(2), 57.5, 55.5, 40.0; HRMS (m/z): 218.0778 $[M+Na]^+$ (cald for $C_{10}H_{13}NO_3$, 195.0895).

4-Pyridinylalanine 4n

Product **4n** (CAS registry No: 1956-21-4) was obtained according to the general procedures at 84% yield after purification by recrystallization in H_2O, m.p. 251.5–253 °C (dec.). ^{1}H NMR (D_2O, 500 MHz): δ 8.43 (d, J = 6.0 Hz, 2H, ArH), 7.32 (d, J = 6.0 Hz, 2H, ArH), 3.57–3.54 (dd, J = 7.5 Hz, J = 6.0 Hz, 1H, NCH), 3.03–2.99 (dd, J = 13.5 Hz, J = 6.0 Hz, 1H, CHH), 2.91–2.87 (dd, J = 13.3 Hz, J = 6.0 Hz, 1H, CHH); ^{13}C NMR (D_2O, 125 MHz) δ 180.1, 148.6(2), 125.2(2), 56.6, 39.6. HRMS (m/z): 189.0628 $[M+Na]^+$ (calcd for $C_8H_{10}N_2O_2$, 166.0742).

2-Naphthylalanine 4o

Product **4o** (CAS registry No: 14108-60-2) was obtained according to the general procedures at 86% yield after purification by recrystallization in H_2O and EtOH (13 : 3), m.p. 240.5–243 °C. ^{1}H NMR (D_2O, 500 MHz): δ 7.83–7.79 (m, 3H, ArH), 7.66 (s, 1H, ArH), 7.45–7.42 (m, 2H, ArH), 7.34(d, J = 9.0 Hz, 1H, ArH), 3.50 (t, J = 5.5 Hz, 1H, NCH), 3.08–3.05 (dd, J = 7.5 Hz, J = 5.5 Hz, 1H, CHH), 2.93–2.88 (dd, J = 7.5 Hz, J = 6.0 Hz, 1H, CHH); ^{13}C NMR (D_2O, 125 MHz) δ 182.0, 166.1, 136.0, 133.2, 132.0, 128.0, 127.9, 127.6, 127.5, 126.4, 125.8, 57.3, 40.8; HRMS (m/z): 216.1014 $[M+H]^+$ (cald for $C_{13}H_{13}NO_2$, 215.0946).

General procedures of reduction of imines and hydrazones

To stirred mixture of amorphous nickel (9–11 mmol%) and solution of substrate (25 mmol) dissolved in methanol (20 mL) an aqueous solution of sodium hydroxide (50 mL, 5.0 M), methanol (15 mL) and sodium borohydride (3.0 g, 79 mmol) was added dropwise at 20–40 °C for 2–4 h. Then, the reaction was kept at 30–60 °C for another 0.5–3 h, and monitored by TLC. The mixture was filtered and the solution was neutralized to pH 9–10 with 2 M aqueous HCl. The aqueous phase was extracted with ethyl acetate and the organic phase was washed with brine. The combined organic phase was dried over anhydrous Na_2SO_4, and the solvent was removed under vacuum to obtain the crude product. All purified products gave satisfactory physical and spectroscopic analyses by comparison with the reported literature.

***N*-Isopropylcyclohexylamine 6a**

Product **6a** (CAS registry No: 1595-42-2) was obtained according to the general procedures at 82% yield after purification by reduced pressure distillation, b.p. 53–55 °C/1.33 kPa (literature data: 60–65 °C/12 Torr).[27] ^{1}H NMR ($CDCl_3$, 500 MHz): δ 2.99–2.94 (m, 1H), 2.52–2.47 (m, 1H), 1.89–1.86 (m, 2H), 1.74–1.70 (m, 2H), 1.63–1.59 (m, 2H), 1.28–1.13 (m, 3H), 1.05 (d, J = 4.0 Hz, 3H), 1.03 (d, J = 6.5 Hz, 3H), 1.03–1.00 (m, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 53.3, 44.5, 34.1(2), 26.1, 25.1(2), 23.3(2).

***N*-*n*-Butylbenzylamine 6b**

Product **6b** (CAS registry No: 2403-22-7) was obtained according to the general procedures at 86% yield after purification by reduced pressure distillation, b.p. 105–107 °C/1.33 kPa (literature data: 122–125 °C/12 Torr).[28] ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.33–7.32 (d, J = 4.5 Hz, 4H, ArH), 7.26–7.24 (m, 1H, ArH), 3.79 (s, 2H, NCH_2), 2.63 (t, J = 7.5 Hz, 2H, CH_2), 1.60 (br, s, 1H, NH), 1.53–1.47 (m, 2H, CH2), 1.37–1.33 (m, 2H), 0.91 (t, J = 7.5 Hz, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 140.6, 128.4(2), 128.1(2), 126.9, 54.1, 49.2, 32.3, 20.5, 14.1.

***N*-Ethylbenzylamine 6c**

Product **6c** (CAS registry No: 14321-27-8) was obtained according to the general procedures at 87% yield after purification by reduced pressure distillation, b.p. 75–77 °C/1.33 kPa (literature data: 82–85 °C/11 Torr) [29] ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.32–7.31 (t, J = 4.5 Hz, 4H, ArH), 7.26–7.23 (m, 1H), 3.79 (s, 2H, CH_2), 2.70–2.67 (q, J = 7.0 Hz, 2H), 1.62 (br, s, 1H), 1.14 (t, J = 7.0, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 140.5, 128.4(2), 128.2(2), 126.9, 53.9, 43.6, 15.3.

***N*-Benzylphenylamine 6d**

Product **6d** (CAS registry No: 103-32-2) was obtained according to the general procedures at 80% yield after purification by flash chromatography with neutral aluminum oxide (7/1 PE/Et as eluent). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.36–7.32 (m, 4H, ArH), 7.28–7.23 (m, 1H, ArH), 7.18–7.15 (m, 2H, ArH), 6.71 (t, J = 7.5 Hz, 1H, ArH), 6.63 (d, J = 7.5 Hz, 2H, ArH), 4.32 (s, 2H, CH_2), 4.04 (br, s, 1H, NH); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 148.3, 139.6, 129.3(2), 128.7(2), 127.6(2), 127.3, 117.7, 113.0(2), 48.4; HRMS (m/z): 184.1120 $[M+H]^+$ (cald for $C_{13}H_{13}N$, 183.1048).

Dibenzylamine 6e

Product **6e** (CAS registry No: 103-49-1) was obtained according to the general procedures at 89% yield after purification by flash chromatography with neutral aluminum oxide (6/1 PE/Et as eluent). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.35–7.31 (m, 8H, ArH), 7.27–7.24 (m, 2H, ArH), 3.82 (s, 4H, 2CH2), 1.59 (br, s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 140.6, 128.6(4), 128.4(4), 127.1(2), 53.4(2); HRMS (m/z): 198.1269 $[M+H]^+$ (cald for $C_{14}H_{15}N$, 197.1204).

N-Methyldiphenylmethylamine 6f

Product **6f** (CAS registry No: 14683-47-7) was obtained according to the general procedures at 69% yield after purification by flash chromatography with neutral aluminum oxide (8/1 PE/Et as eluent). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.37 (d, J = 8.0, 4H, ArH), 7.27 (t, J = 7.5, 4H, ArH), 7.20–7.17 (m, 2H), 4.67 (s, 1H), 2.39 (s, 3H), 1.59 (br, s, 1H, NH); ^{13}C NMR (125 MHz, CDCl3) δ 144.0, 128.5(4), 127.3(4), 127.04(2), 69.6, 35.2; HRMS (m/z): 198.1271 $[M+H]^+$ (cald for $C_{14}H_{15}N$, 197.1204).

1-Benzyl-2-phenylhydrazine 6g

Product **6g** (CAS registry No: 15806-20-9) was obtained according to the general procedures at 68% yield after purification by flash chromatography with neutral aluminum oxide (8/1 PE/Et as eluent). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.80–7.78 (m, 2H, ArH), 7.52–7.49 (m, 1H, ArH), 7.45–7.42 (m, 2H, ArH), 7.36 (d, J = 4.5 Hz, 4H), 7.32–7.29 (m, 1H), 6.39 (br, s, 1H, NH), 4.65 (d, J = 6.0 Hz, 2H, CH2), 1.59 (s, 1H, NH); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 167.5, 138.4, 134.4, 131.5, 128.7(2), 128.6(2), 127.9, 127.5, 127.1(2), 44.0; HRMS (m/z): 199.1223 $[M+H]^+$ (calcd for $C_{13}H_{14}N_2$, 198.1157).

1-Phenylethanamine 6h and phenylamine h′

Product **6h** (CAS registry No: 618-36-0) and **h′** (CAS registry No: 62-53-3) were obtained at 75 and 65% yields, respectively, according to the general procedure at 60 °C for 3 h after purification by flash chromatography with neutral aluminum oxide (8/1 PE/Et as eluent), **6h**: b.p. 68.5–69.5 °C/1.33 kPa (literature data: 184–186 °C),[21] which is the same with compound **4e**; **h′**: b.p. 62–65 °C/1.33 kPa (literature data: 183–184 °C).[30]

General procedures for the reduction of nitriles

To stirred mixture of amorphous nickel (10–15 mmol%) and solution of substrate (25 mmol) dissolved in methanol (20 mL) an aqueous solution of sodium hydroxide (50 mL, 5.0 M), methanol (15–25 mL) and sodium borohydride (3.0 g, 79 mmol) was added dropwise at 30–40 °C for 4 h. Then, the reaction was kept at 30–60 °C for another 3–5 h, and monitored by TLC. The mixture was filtered and the solution was neutralized to pH 9–10 with 2 M aqueous HCl. The aqueous phase was extracted with ethyl acetate and the organic phase was washed with brine. Combined organic phase was dried over anhydrous Na_2SO_4, and the solvent was removed under vacuum to obtain crude product. All purified products gave satisfactory physical and spectroscopic analyses by comparison with the reported literature.

n-Propylamine 8a

Product **8a** (CAS registry No: 107-10-8) was obtained according to the general procedures at 89% yield after purification by fractional distillation, b.p. 46–47.5 °C (literature data: 46–47 °C),[17] ^{1}H NMR ($CDCl_3$, 500 MHz): δ 2.66 (t, J = 7.0 Hz, 2H), 1.50–1.44 (m, 4H), 0.92 (t, J = 7.5 Hz, 3H, CH_3); ^{13}C NMR ($CDCl_3$,125 MHz) δ 44.0, 26.8, 11.2.

n-Butylamine 8b

Product **8b** (CAS registry No: 109-73-9) was obtained according to the general procedure in 93% after purification by fractional distillation, b.p. 75–76.5 °C (literature data: 75–78 °C).[19] ^{1}H NMR ($CDCl_3$, 500 MHz): δ 2.68 (t, J = 7.0 Hz, 2H, NCH_2), 1.44–1.40 (m, 2H, CH_2), 1.37–1.33 (m, 2H, CH2), 1.23 (br, s, 2H, NH_2), 0.92 (t, J = 7.0 Hz, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 41.7, 35.8, 19.8, 13.7.

1,6-Hexenediamine 8c

Product **8c** (CAS registry No: 124-09-4) was obtained according to the general procedures at 90% yield after purification by flash chromatography with neutral aluminum oxide (6/1 PE/Et as eluent), m.p. 41–42.5 °C (literature data: 41–42 °C).[31] ^{1}H NMR ($CDCl_3$, 500 MHz): δ 2.68 (t, J = 7.0 Hz, 4H), 1.48–1.42 (m, 4H), 1.37–1.30 (m, 4H), 1.26 (br, s, 4H, NH2); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 41.9 (2), 33.6 (2), 26.6 (2).

2-Phenylethanamine 8d

Product **8d** (CAS registry No: 64-04-0) was obtained according to the general procedures at 89% yield after purification by reduced pressure distillation, b.p. 82–85 °C/1.33 kPa (literature data: 104 °C/34 Torr).[32] ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.31–7.26 (m, 2H, ArH), 7.22–7.19 (m, 3H, ArH), 2.96 (t, J = 7.0 Hz, 2H, CH_2), 2.74 (t, J = 7.0 Hz, 2H, CH_2), 1.28 (br, s, 2H, NH_2); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 139.9, 128.8(2), 128.4(2), 126.1, 43.6, 40.1.

(4-Methylphenyl)-2-ethylamine 8e

Product **8e** (CAS registry No: 3261-62-9) was obtained according to the general procedures at 92% yield after purification by flash chromatography with neutral aluminum oxide (7/1 PE/Et as eluent). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.12–7.07 (m, 4H, ArH), 2.94 (t, J = 7.0 Hz, 2H, CH_2), 2.70 (t, J = 6.5 Hz, 2H, CH_2), 2.32 (s, 3H, CH_3), 1.32 (br, s, 2H, NH_2); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 136.8, 135.5, 129.2(2), 128.7(2), 43.7, 39.7, 21.0; HRMS (m/z): 136.1109 $[M+H]^+$ (calcd for $C_9H_{13}N$, 135.1048).

4-Fluorobenzylamine 8f

The product **8f** (CAS registry No: 140-75-0) was obtained according to the general procedure in 88% after purification by recrystallization (ethanol/hexanes), m.p. 173–175.5 °C (literature data: 176.5–178.5 °C).[33] ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) 7.27–4.25 (m, 2H), 7.02–6.98 (m, 2H), 3.82 (s, 2H), 1.49 (br, s, 2H, NH_2); ^{13}C NMR ($CDCl_3$, 125 MHz) δ (162.7,160.8), 139.0, (128.7, 128.6), (115.3, 115.1), 45.7.

2-(4-Fluorophenyl)ethylamine 8g

Product **8g** (CAS registry No: 1583-88-6) was obtained according to the general procedures at 93% yield after purification by reduced pressure distillation, b.p. 93–95 °C/1.33 kPa (literature data: 99–100 °C/24 Torr).[34] ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.16–7.14 (q, J = 8.0 Hz, J = 5.5 Hz, 2H), 6.98 (t, J = 8.5 Hz, 2H), 2.94 (t, J = 7.0 Hz, 2H), 2.72 (t, J = 7.0 Hz, 2H), 1.24 (br, s, 2H, NH_2); ^{13}C NMR ($CDCl_3$, 125 MHz) δ (162.4,160.5), 135.5, (130.2, 130.1),

(115.2, 115.1), 43.6, 39.2; HRMS (*m*/*z*): 140.0858 $[M+H]^+$ (calcd for $C_8H_{10}FN$, 139.0797).

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