SUPPLEMENTARY INFORMATIONS

Heterogeneous Nickel-supported catalyst: a circular approach to amines synthesis via azides and nitro compounds reduction

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1. General remarks

All chemicals were purchased and used without additional purification unless specified otherwise. Gas-liquid chromatography (GLC) analyses were performed using an Agilent 6850 equipped with a capillary column DB-5MS (30 m, 0.22 mm, 0.25 µm), a Flame Ionization Detector (FID) and Helium as the gas carrier. Gas chromatography with electron impact mass spectrometry (GC-EIMS) analyses were carried out using a Hewlett-Packard HP 6890N Network GC system/5975 Mass Selective Detector equipped with an electron impact ionizer at 70 eV.

Thin layer chromatography analyses were performed with silica gel on aluminium plates (silica gel 60 F254, Fluka). Column chromatography purification was performed with silica gel (230–400 mesh) neutralized with triethylamine, eluting with petroleum ether (PE)/ethyl acetate (EtOAc).

^{1}H-NMR, ^{13}C-NMR and ^{19}F-NMR spectra were recorded at 400, 100.6 and 376 MHz respectively, on a Bruker DRX ADVANCE 400 MHz, using a $CDCl_3$ (99.8 atom% D) or DMSO-*d*6 as the deuterated solvent. Chemical shifts are reported in ppm (δ), coupling constants (J) in Hertz and multiplicity are reported as follows: s = singlet, bs = broad singlet, d = doublet, t = triplet, m = multiplet. Metal loading and leaching were measured using MP-AES 4210 instrument.

Powder X-ray diffraction (PXRD) patterns are obtained by Cu-Kα radiation (λ = 1.5406 A) collected on Rigaku SmartLab-SE X. Angle range: 5-80°, rate: 10°/min. Transmission electron microscopy (TEM) analyses were performed on a JEM-F2100 operating at 200 kV. Field-emission scanning electron microscope was performed on an FEI Sirion 200 operating at 20 kV with spot size 5.0, WD 6mm.

Compounds **1a-h** were prepared by following known procedures.[1-3]

Compounds **1i** and **1j** were prepared as described in literature.[4-5]

2. General procedures

2.1 General procedure for the PiNe support preparation

The PiNe support was prepared following a previously reported procedure.[6-7]

2.2 General procedure for the 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, added at 0°C to the support, and left under stirring. After 1.5 hours, the catalyst was filtered, washed sequentially with ethanol, water, and acetone, and then dried under vacuum at 80°C for 1 hour. The Ni (5.1 wt%; 0.87 mmol/g) and B (0.43 wt%; 0.4 mmol/g) loadings, measured by MP-AES analysis, confirmed the presence of Ni_2B nanoparticles

2.3 General procedure for the azido and nitro compounds reduction

In a 4 mL screw capped vial equipped with a magnetic stirrer, 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 x 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**).

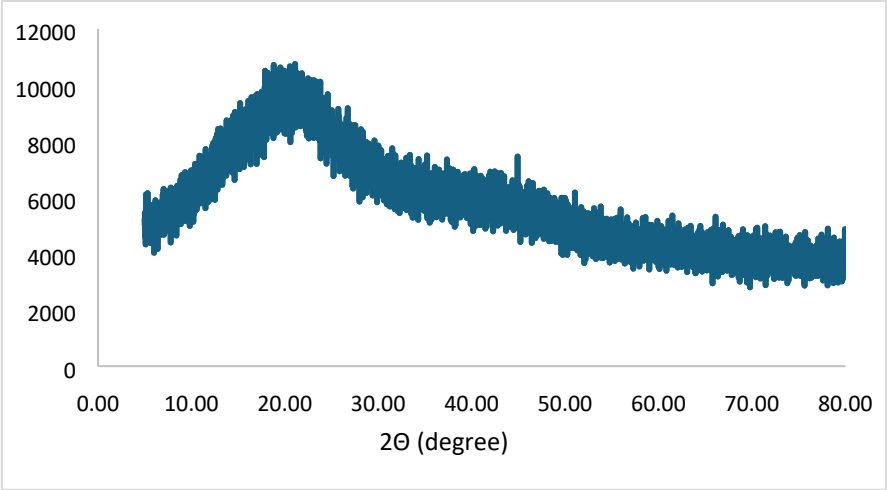


Figure SI-1 PXRD of Ni(B)/PiNe

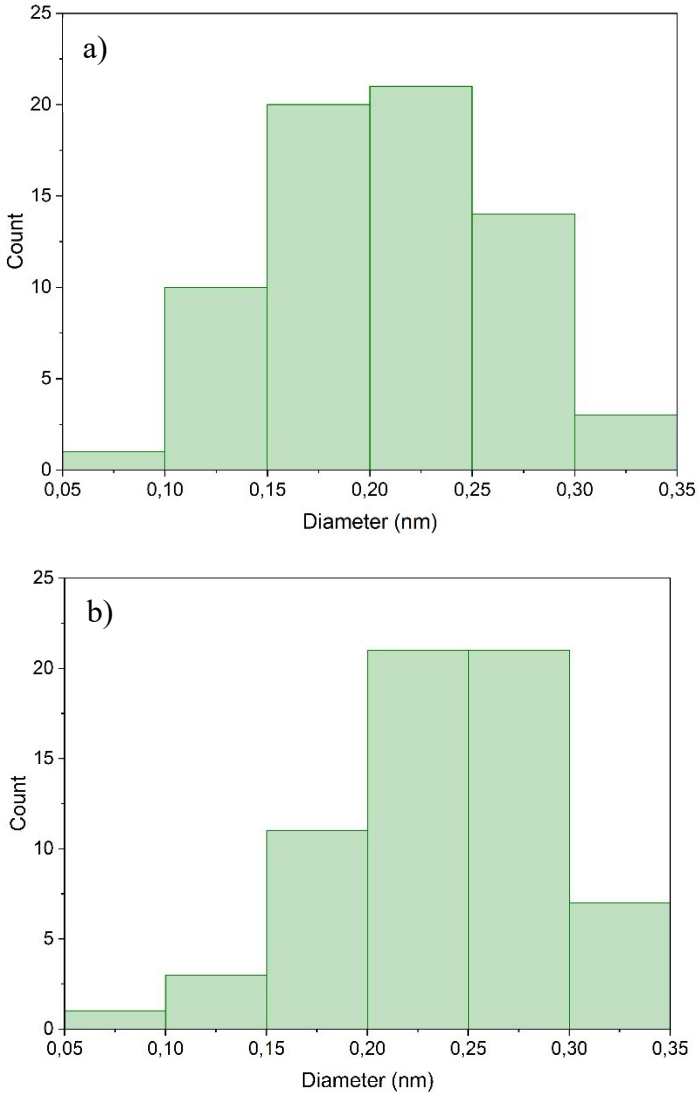


Figure SI-2 Size distribution of metal nanoparticles. a) fresh catalyst; b) catalyst after 5 runs

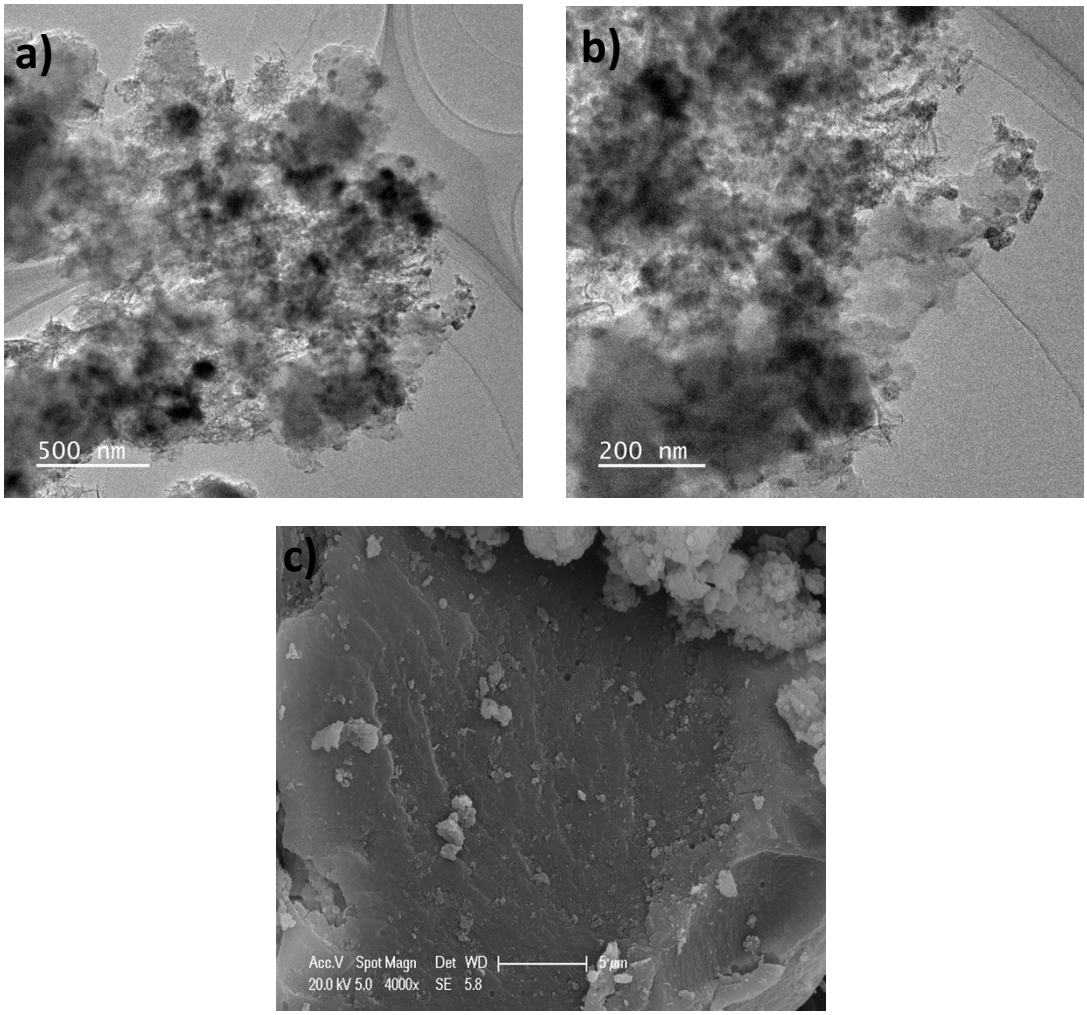


Figure SI-3 Images of recovered Ni(B)/PiNe. a) TEM image of recycled Ni(B)/PiNe (500 nm); b) TEM images of recycled Ni(B)/PiNe (200 nm); c) SEM of recycled Ni(B)/PiNe (5 µm)

3. Catalyst activity and E-factors calculations

Table SI-1 TON and TOF calculations

Ref.	**TON**	**TON**	**TOF (h^{-1})[c]**	**TOF (h^{-1})[c]**
Synth., 2022, **54**, 133–146.[a]	6.9	34.3	1.1	1.1
This work[b]	25	116.3	12.5	11.6

[a]Calculated considering the experimental procedures published and a catalyst loading of 7.15 mmol/g; [b]Calculated considering the experimental procedure herein developed and a catalyst loading of 0.87 mmol/g; [c] Calculated on five consecutive runs

Table SI-2 Leaching experiments[a]

Run	Leaching (ppm)
1	16.7
2	18.2
3	28.4
4	45

[a]Leaching values have been calculated up to the 4th run because of the sensitive conversion drop starting from the 5th.

Table SI-3 E-factor calculations.[a]

Ref.	E-Factor
Synth., 2022, **54**, 133–146.	71.47 mg (azidobenzene) + 3164 (methanol) + 0.71 mg ($NiCl_2 \cdot 6H_2O$) + 56.75 ($NaBH_4$) + 3000 mg (H_2O) + 8100 mg (ethyl acetate) – 45 mg (aniline) / 45 mg (anliline) = **318.84**
React. Chem. Eng., 2020, **5**, 58–65.	123.11 mg (nitrobenzene) + 10000 mg (H_2O) + 20 mg (Ni/C) + 0.0121 (H_2) + 1170 (dichloromethane) + 5000 mg (H_2O) + 3945 mg (ethanol) – 20 mg (Ni/C) – 93.13 mg (aniline) / 93.13 mg (aniline) = **332.27**
This work (calculated on **1a** reduction)	29.78 mg (nitrobenzene) + 500 mg (H_2O) + 11.5 mg (Ni(B)/PiNe) + 23.65 mg ($NaBH_4$) + 1708 mg (2-methyltetrahydrofuran) + 500 mg (H_2O) – 11.5 mg (Ni(B)/PiNe) – 1520 mg (recovered 2-methyltetrahydrofuran) – 22.8 mg (aniline) / 22.8 mg (aniline) = **53.44**
This work (calculated on **3a** reduction)	30.78 mg (nitrobenzene) + 500 mg (H_2O) + 11.5 mg (Ni(B)/PiNe) + 23.65 mg ($NaBH_4$) + 1708 mg (2-methyltetrahydrofuran) + 500 mg (H_2O) – 11.5 mg (Ni(B)/PiNe) – 1520 mg (recovered 2-methyltetrahydrofuran) – 22.8 mg (aniline) / 22.8 mg (aniline) = **53.49**

[a]Given the data gaps in the reviewed literature's experimental procedures, the amount of solvent used for extractions and washing has been estimated based on our experimental expertise.

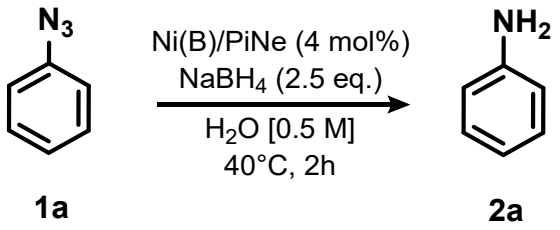
References

1. L. Luciani, E. Goff, D. Lanari, S. Santoro and L. Vaccaro, *Green Chem.*, 2018, **20**, 183–187.
2. S. Dey and P. Ghosh, *ACS Omega*, 2023, **8**, 11039–11064.
3. S. K. Kang, J. Du Ha, H. G. Cheon, J. K. Choi, C. S. Hong and E. K. Yum, *Bull. Korean Chem. Soc.*, 2003, **24**, 1381–1384.
4. N. A. Dangroo, J. Singh, A. A. Dar, N. Gupta, P. K. Chinthakindi, A. Kaul, M. A. Khuroo and P. L. Sangwan, *Eur. J. Med. Chem.*, 2016, **120**, 160–169.

5. Z. S. Cheruvallath, S. L. Gwaltney, M. Sabat, M. Tang, J. Feng, H. Wang, J. Miura, P. Guntupalli, A. Jennings, D. Hosfield, B. Lee and Y. Wu, *Bioorganic Med. Chem. Lett.*, 2013, **23**, 2166–2171.
6. F. Campana, F. Valentini, A. Marrocchi, L. Vaccaro, D. Chimica, B. Biotecnologie, P. Via, D. Ingegneria and P. Via, 2023, **40**, 1989–1998.
7. F. Valentini, E. Cerza, F. Campana, A. Marrocchi and L. Vaccaro, *Bioresour. Technol.*, 2023, **390**, 129847.

4. Characterization data and ^{1}H, ^{13}C, ^{19}F NMR spectra

Chem. Name	**Aniline (2a)**
Lit. Ref.	*Synth.*, 2022, **54**, 133–146.



METHOD:

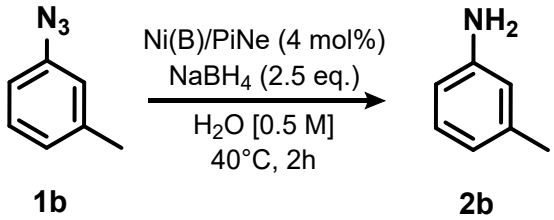
In a 4 mL screw capped vial equipped with a magnetic stirrer, azidobenzene (**1a**) (0.25 mmol, 29.78 mg), H_2O (0.5 M, 0.5 mL), Ni(B)/PiNe (4 mol%, 11.5 mg) and $NaBH_4$ (2.5 eq., 23.65 mg) were consecutively added, and the resulting mixture was left under stirring at 40°C. After 2 h, the reaction mixture was left to cool to room temperature, diluted with 2-MeTHF (2 x 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 overnight under vacuum. The combined organic layers, once separated from the aqueous phase, were concentrated under reduced pressure to afford the title **2a** as a pale yellow oil, 98% (22.8 mg).

Mol Formula	C_6H_7N			**m.p.**	oil
^{1}H NMR	**δ value**	**No. H**	**Mult.**	**j value/Hz**	
400 MHz	7.21	2	*t*	7.87	
$CDCl_3$	6.81	1	*t*	7.18	
	6.72	2	*d*	3.81	
	3.66	2	*s*		

^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 146.6; 129.4; 118.6; 115.2.

GC-EIMS (m/z, %): 94.1 (M+1, 14.1); 93.1 (M^+, 100); 92.1 (M-1, 22.2); 66.1 (60.8); 65.1 (29.9).

Chem. Name	3-Methylaniline (2b)
Lit. Ref.	*ACS Appl. Nano Mater.,* 2024, **7**, 16669−16678



1b **2b**

METHOD:

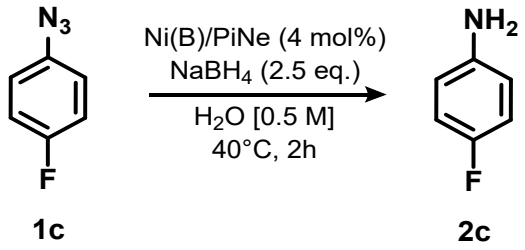
In a 4 mL screw capped vial equipped with a magnetic stirrer, 1-azido-3-methylbenzene (**1b**) (0.25 mmol, 33.29 mg), H_2O (0.5 M, 0.5 mL), Ni(B)/PiNe (4 mol%, 11.5 mg) and $NaBH_4$ (2.5 eq., 23.65 mg) were consecutively added, and the resulting mixture was left under stirring at 40°C. After 2 h, the reaction mixture was left to cool to room temperature, diluted with 2-MeTHF (2 x 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 overnight under vacuum. The combined organic layers, once separated from the aqueous phase, were concentrated under reduced pressure and the crude oil was purified by flash chromatography over silica gel (PE/EtOAc 9:1) to afford the title compound **2b** as a pale yellow oil, 41% (11 mg).

Mol Formula	C_7H_9N			**m.p.**	oil
^{1}H NMR	**δ value**	**No. H**	**Mult.**	**j value/Hz**	
400 MHz	7.08	1	*t*	7.67	
$CDCl_3$	6.62	1	*d*	3.44	
	6.57-6.50	2	*m*		
	3.61	2	*bs*		
	2.30	3	*s*		

^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 146.5; 139.2; 129.2; 119.5; 116.0; 112.3; 21.5.

GC-EIMS (m/z, %): 107.1 (M^+, 95.4); 106.1 (M-1, 100); 79.1 (18.2); 77.0 (21.1).

Chem. Name	4-Fluoroaniline (2c)
Lit. Ref.	*Green Chem.,*2017,**19**,4268–427



1c **2c**

METHOD:

In a 4 mL screw capped vial equipped with a magnetic stirrer, 1-azido-4-fluorobenzene (**1c**) (0.25 mmol, 34.28 mg), H_2O (0.5 M, 0.5 mL), Ni(B)/PiNe (4 mol%, 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 x 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 overnight under vacuum. The combined organic layers, once separated from the aqueous phase, were concentrated under reduced pressure to afford the title **2c** as a clear colorless oil, 84% (23.3 mg).

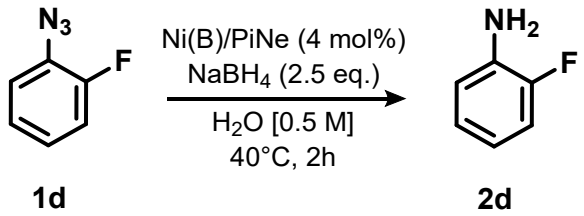
Mol Formula	C_6H_6FN			**m.p.**	oil
^{1}H NMR	**δ value**	**No. H**	**Mult.**	**j value/Hz**	
400 MHz	6.90-6.82	2	*m*		
$CDCl_3$	6.67-6.57	2	*m*		
	3.53	2	*bs*		

^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 157.6; 155.3; 142.4; 116; 116.0; 115.8; 115.6.

^{19}F NMR (376 MHz, $CDCl_3$) δ: -126.9.

GC-EIMS (m/z, %): 111.1 (M^+, 100); 84.0 (40.2); 83.0 (25.7).

Chem. Name	2-Fluoroaniline (2d)
	Dalton Trans., 2016, **45**, 7421-7426



1d **2d**

METHOD:

In a 4 mL screw capped vial equipped with a magnetic stirrer, 1-azido-2-fluorobenzene (**1d**) (0.25 mmol, 34.28 mg), H_2O (0.5 M, 0.5 mL), Ni(B)/PiNe (4 mol%, 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 x 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 overnight under vacuum. The combined organic layers, once separated from the aqueous phase, were concentrated under reduced pressure to afford the title **2d** as a pale yellow oil, 86% (24 mg).

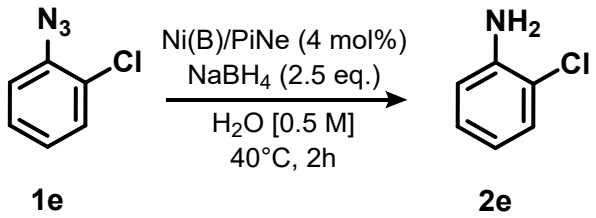
Mol Formula	C_6H_6FN			**m.p.**	oil
^{1}H NMR	**δ value**	**No. H**	**Mult.**	**j value/Hz**	
400 MHz	7.04-6.90	2	*m*		
$CDCl_3$	6.82-6.75	1	*m*		
	6.74-6.66	1	*m*		
	3.71	2	*bs*		

^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 153.0; 150.6; 134.6; 134.5; 124.5; 118.7; 117.0; 115.3; 115.2.

^{19}F NMR (376 MHz, $CDCl_3$) δ: -135.4.

GC-EIMS (m/z, %): 112.0 (M+1, 11.1); 111.1 (M^+, 100); 93.1 (34.9); 91.0 (16.9); 84.0 (33.0); 83.0 (27.3); 66.0 (14.9); 65.0 (12.9); 64.0 (19.6); 63.0 (10.1); 57.0 (10.7).

Chem. Name	2-Chloroaniline (2e)
	RSC Adv., 2013, **3**, 1050-1054



1e **2e**

METHOD:

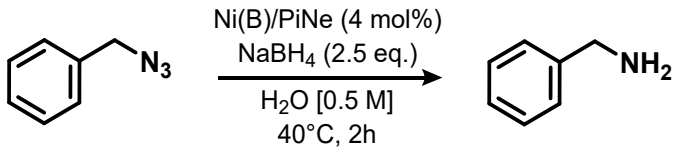
In a 4 mL screw capped vial equipped with a magnetic stirrer, 1-azido-2-chlorobenzene (**1e**) (0.25 mmol, 38.39 mg), H_2O (0.5 M, 0.5 mL), Ni(B)/PiNe (4 mol%, 11.5 mg) and $NaBH_4$ (2.5 eq., 23.65 mg) were consecutively added, and the resulting mixture was left under stirring at 40°C. After 2 h, the reaction mixture was left to cool to room temperature, diluted with 2-MeTHF (2 x 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 overnight under vacuum. The combined organic layers, once separated from the aqueous phase, were concentrated under reduced pressure and the crude oil was purified by flash chromatography over silica gel (PE/EtOAc 9:1) to afford the title compound **2e** as a pale yellow oil, 60% (19.14 mg).

Mol Formula	C_6H_6ClN			**m.p.**	oil
^{1}H NMR	**δ value**	**No. H**	**Mult.**	**j value/Hz**	
400 MHz	7.33-7.26	1	*m*		
$CDCl_3$	7.15-7.10	1	*m*		
	6.83-6.77	1	*m*		
	6.76-6.70	1	*m*		
	4.07	2	*bs*		

^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 143.0; 129.5; 127.7; 119.3; 119.1; 116.0.

GC-EIMS (m/z, %): 129.0 (M+2, 33.8); 127.0 (M^+, 100); 92.0 (20.5); 91.0 (9.7); 65.0 (27.5); 64.0 (13.8); 63.1 (13.3).

Chem. Name	Benzylamine (2f)
Lit. Ref.	*ChemistrySelect*, 2023, **8**, e202204642



1f **2f**

METHOD:

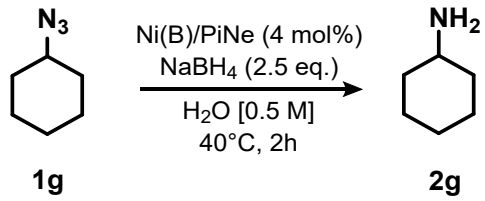
In a 4 mL screw capped vial equipped with a magnetic stirrer, benzylazide (**1f**) (0.25 mmol, 33.29 mg), H_2O (0.5 M, 0.5 mL), Ni(B)/PiNe (4 mol%, 11.5 mg) and $NaBH_4$ (2.5 eq., 23.65 mg) were consecutively added, and the resulting mixture was left under stirring at 40°C. After 2 h, the reaction mixture was left to cool to room temperature, diluted with 2-MeTHF (2 x 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 overnight under vacuum. The combined organic layers, once separated from the aqueous phase, were concentrated under reduced pressure to afford the title **2f** as a pale yellow oil, 90% (24.1 mg).

Mol Formula	C_7H_9N			**m.p.**	oil
^{1}H NMR	**δ value**	**No. H**	**Mult.**	**j value/Hz**	
400 MHz	7.37-7.21	5	*m*		
$CDCl_3$	3.85	2	*s*		
	1.44	2	*s*		

^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 143.5; 128.6; 127.1; 126.8; 46.6.

GC-EIMS (m/z, %): 107.1 (M+, 61.6); 106.1 (M-1, 100); 91.1 (14.2); 79.1 (41.2); 78.1 (13.3); 77.1 (23.7); 51.1 (10.7).

Chem. Name	Cyclohexylamine (2g)
Lit. Ref.	*ChemCatChem*., 2021, **13**, 2583 – 259



1g **2g**

METHOD:

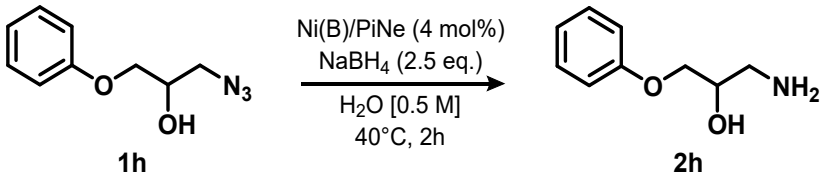
In a 4 mL screw capped vial equipped with a magnetic stirrer, azidocyclohexane (**1g**) (0.25 mmol, 31.30 mg), H_2O (0.5 M, 0.5 mL), Ni(B)/PiNe (4 mol%, 11.5 mg) and $NaBH_4$ (2.5 eq., 23.65 mg) were consecutively added, and the resulting mixture was left under stirring at 40°C. After 2 h, the reaction mixture was left to cool to room temperature, diluted with 2-MeTHF (2 x 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 overnight under vacuum. The combined organic layers, once separated from the aqueous phase, were concentrated under reduced pressure to afford the title **2g** as a pale yellow oil, 95% (23.6 mg).

Mol Formula	$C_6H_{13}N$			**m.p.**	oil
^{1}H NMR	**δ value**	**No. H**	**Mult.**	**j value/Hz**	
400 MHz	2.61-2.50	1	*m*		
$CDCl_3$	1.18-1.70	2	*m*		
	1.70-1.59	2	*m*		
	1.58-1.48	1	*m*		
	1.27-0.90	7	*m*		

^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 143.0; 129.5; 127.7; 119.3; 119.1; 116.0.

GC-EIMS (m/z, %): 99.1 (M^+, 13.7); 70.1 (10.4); 56.1 (100); 43.1 (35.3); 28.1 (10.7).

Chem. Name	1-Amino-3-phenoxy-2-propanol (2h)
Lit. Ref.	*GreenChem.*, 2023, **25**, 720–727



1h **2h**

METHOD:

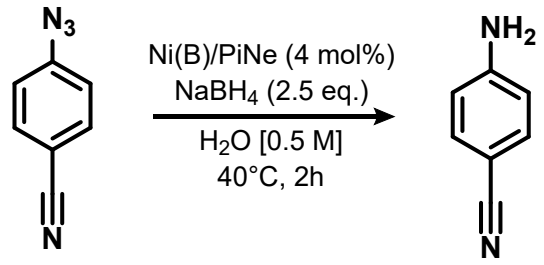
In a 4 mL screw capped vial equipped with a magnetic stirrer, 1-azido-3-phenoxy-2-propanol (**1h**) (0.25 mmol, 48.30 mg), H_2O (0.5 M, 0.5 mL), Ni(B)/PiNe (4 mol%, 11.5 mg) and $NaBH_4$ (2.5 eq., 23.65 mg) were consecutively added, and the resulting mixture was left under stirring at 40°C. After 2 h, the reaction mixture was left to cool to room temperature, diluted with 2-MeTHF (2 x 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 overnight under vacuum. The combined organic layers, once separated from the aqueous phase, were concentrated under reduced pressure and the crude oil was purified by flash chromatography over silica gel (PE/EtOAc 9:1) to afford the title compound **2h** as a white solid, 75% (31.4 mg).

Mol Formula	$C_9H_{13}NO_2$			**m.p.**	90-92°C
	δ value	**No. H**	**Mult.**	**j value/Hz**	
^{1}H NMR	7.28	2	*t*	7.90	
400 MHz	6.97-6.88	3	*m*		
DMSO-*d*6	3.98-3.90	1	*m*		
	3.89-3.81	1	*m*		
	3.77-3.67	1	*m*		
	3.23-3.02	2	*bs*		
	2.75-2.54	2	*m*		
	2.53-2.46	1	*s*		

^{13}C NMR (100.6 MHz, DMSO-*d*6) δ: 159.2; 130.0; 120.9; 115.0; 70.9; 70.6; 45.3.

GC-EIMS (m/z, %): 167.1 (M+, <10); 149.1 (13.9); 123.1 (40.8); 94.1 (100); 77.1 (27.6); 66.1 (10.8); 65.1 (13.2); 60.1 (17.8); 56.1 (16.6); 51.1 (11.5).

Chem. Name	4-Aminobenzonitrile (2i)
	Chem. Commun., **2009,** 3035-3037



1i **2i**

METHOD:

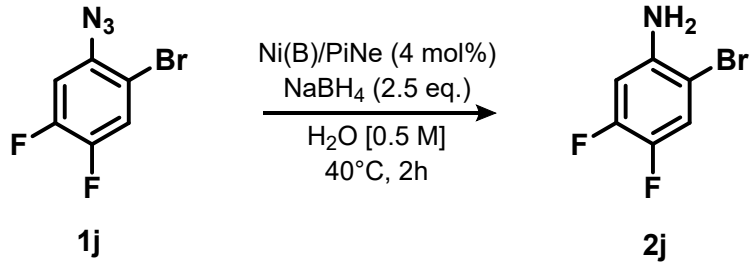
In a 4 mL screw capped vial equipped with a magnetic stirrer, 4-azidobenzonitrile (**1i**) (0.25 mmol, 36.1 mg), H_2O (0.5 M, 0.5 mL), Ni(B)/PiNe (4 mol%, 11.5 mg) and $NaBH_4$ (2.5 eq., 23.6 mg) were consecutively added, and the resulting mixture was left under stirring at 40°C. After 2 h, the reaction mixture was left to cool to room temperature, diluted with 2-MeTHF (2 x 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 overnight under vacuum. The combined organic layers, once separated from the aqueous phase, were concentrated under reduced pressure to afford the title compound **2i** as a pale-yellow solid, 92% (27.2 mg).

Mol Formula		$C_7H_6N_2$		**m.p.**	82-84 °C
^{1}H NMR 400 MHz $CDCl_3$	**δ value**	**No. H**	**Mult.**	**j value/Hz**	
	7.38-7.40	2	d	8	
	6.63-6.65	2	d	8	
	4.20	2	s		

^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 150.6, 133.9, 120.3, 114.5, 100.1

GC-EIMS (m/z, %): 118 (M+ 100); 91 (27)

Chem. Name	1-Amino-2-bromo-4,5-difluorobenzene (2j)
Lit. Ref.	-



1j **2j**

METHOD:

In a 4 mL screw capped vial equipped with a magnetic stirrer, 1-azido-2-bromo-4,5-difluorobenzene (**1j**) (0.25 mmol, 58.5mg), H_2O (0.5 M, 0.5 mL), Ni(B)/PiNe (4 mol%, 11.5 mg) and $NaBH_4$ (2.5 eq., 23.6 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 x 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 overnight under vacuum. The combined organic layers, once separated from the aqueous phase, were concentrated under reduced pressure and the crude oil was purified by flash chromatography over silica gel (PE/EtOAc 9:1) to afford the title compound (**2j**) as a transparent solid, 76% (39.5 mg).

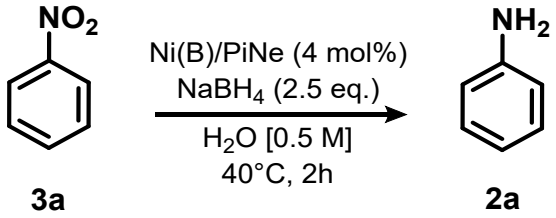
Mol Formula		$C_7H_6N_2$		**m.p.**	82-84 °C
^{1}H NMR 400 MHz $CDCl_3$	**δ value**	**No. H**	**Mult.**	**j value/Hz**	
	7.26-7.30	1	m		
	6.59-6.64	1	m		
	4.04	2	s		

^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 151.5-151.4, 149.1-149.0, 144.4-144.3, 142.0-141.9, 141.1-144.0, 121.0-120.7, 104.0-103.7, 102.0-101.9

^{19}F NMR (376 MHz, $CDCl_3$) δ: -137.5, -149.3

GC-EIMS (m/z, %): 209 (M+ 100); 207 (M+ 100); 128 (52); 127 (17); 101 (68); 100 (18)

Chem. Name	Aniline (2a)
Lit. Ref.	*Synth.*, 2022, **54**, 133–146.



METHOD:

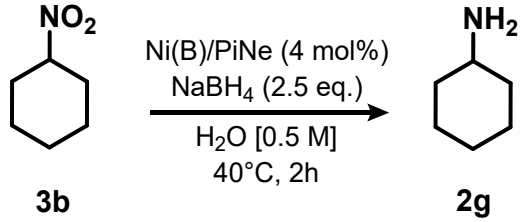
In a 4 mL screw capped vial equipped with a magnetic stirrer, nitrobenzene (**3a**) (0.25 mmol, 30.78 mg), H_2O (0.5 M, 0.5 mL), Ni(B)/PiNe (4 mol%, 11.5 mg) and $NaBH_4$ (2.5 eq., 23.65 mg) were consecutively added, and the resulting mixture was left under stirring at 40°C. After 2 h, the reaction mixture was left to cool to room temperature, diluted with 2-MeTHF (2 x 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 overnight under vacuum. The combined organic layers, once separated from the aqueous phase, were concentrated under reduced pressure to afford the title **2a** as a pale yellow oil, 98% (22.8 mg).

Mol Formula	C_6H_7N			**m.p.**	oil
^{1}H NMR	**δ value**	**No. H**	**Mult.**	**j value/Hz**	
400 MHz	7.20	2	*t*	7.60	
$CDCl_3$	6.80	1	*t*	7.44	
	6.71	2	*d*	3.36	

^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 146.5; 129.4; 118.6; 115.2.

GC-EIMS (m/z, %): 94.1 (M+1, 14.1); 93.1 (M^+, 100); 92.1 (M-1, 22.2); 66.1 (60.8); 65.1 (29.9).

Chem. Name	Cyclohexylamine (2g)
Lit. Ref.	*ChemCatChem.,* 2021, **13**, 2583 – 259



3b **2g**

METHOD:

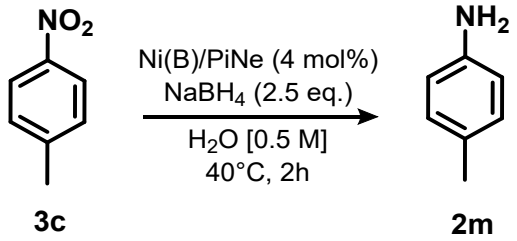
In a 4 mL screw capped vial equipped with a magnetic stirrer, nitrocyclohexane (**3b**) (0.25 mmol, 32.3 mg), H_2O (0.5 M, 0.5 mL), Ni(B)/PiNe (4 mol%, 11.5 mg) and $NaBH_4$ (2.5 eq., 23.65 mg) were consecutively added, and the resulting mixture was left under stirring at 40°C. After 2 h, the reaction mixture was left to cool to room temperature, diluted with 2-MeTHF (2 x 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 overnight under vacuum. The combined organic layers, once separated from the aqueous phase, were concentrated under reduced pressure to afford the title compound 2**g** as a pale yellow oil, 87% (21.6 mg).

Mol Formula	$C_6H_{13}N$			**m.p.**	oil
^{1}H NMR	**δ value**	**No. H**	**Mult.**	**j value/Hz**	
400 MHz	2.62-2.51	1	*m*		
$CDCl_3$	1.81-1.71	2	*m*		
	1.70-1.61	2	*m*		
	1.58-1.50	1	*m*		
	1.28-1.13	4	*m*		
	1.12-0.92	3	*m*		

^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 50.5; 36.9; 25.7; 25.2.

GC-EIMS (m/z, %): 99.1 (M^+, 13.7); 70.1 (10.4); 56.1 (100); 43.1 (35.3); 28.1 (10.7).

Chem. Name	4-Methylaniline (2m)
Lit. Ref.	*ACS Appl. Nano Mater.,* 2024, **7**, 16669−16678



3c **2m**

METHOD:

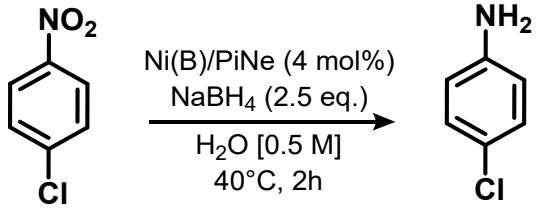
In a 4 mL screw capped vial equipped with a magnetic stirrer, 4-nitrotoluene (**3c**) (0.25 mmol, 34.28 mg), H_2O (0.5 M, 0.5 mL), Ni(B)/PiNe (4 mol%, 11.5 mg) and $NaBH_4$ (2.5 eq., 23.65 mg) were consecutively added, and the resulting mixture was left under stirring at 40°C. After 2 h, the reaction mixture was left to cool to room temperature, diluted with 2-MeTHF (2 x 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 overnight under vacuum. The combined organic layers, once separated from the aqueous phase, were concentrated under reduced pressure to afford the title compound **2m** as a pale yellow oil, 91% (24.4 mg).

Mol Formula	C_7H_9N			**m.p.**	oil
^{1}H NMR	**δ value**	**No. H**	**Mult.**	**j value/Hz**	
400 MHz	7.00	2	*d*	4.07	
$CDCl_3$	6.64	2	*d*	4.21	
	3.55	2	*bs*		
	2.28	3	*s*		

^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 143.9; 129.7; 127.9; 115.4; 20.51.

GC-EIMS (m/z, %): 107.1 (M^+, 71.2); 106.1 (M-1, 100); 79.1 (11.2); 77.0 (18.2).

Chem. Name	4-Chloroaniline (2n)
Lit. Ref.	*Green Chem.,*2017,**19**,4268–427



3d **2n**

METHOD:

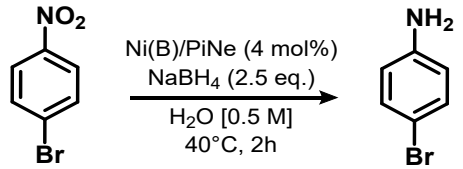
In a 4 mL screw capped vial equipped with a magnetic stirrer, 1-chloro-4-nitrobenzene (**3d**) (0.25 mmol, 39.4 mg), H_2O (0.5 M, 0.5 mL), Ni(B)/PiNe (4 mol%, 11.5 mg) and $NaBH_4$ (2.5 eq., 23.65 mg) were consecutively added, and the resulting mixture was left under stirring at 40°C. After 2 h, the reaction mixture was left to cool to room temperature, diluted with 2-MeTHF (2 x 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 overnight under vacuum. The combined organic layers, once separated from the aqueous phase, were concentrated under reduced pressure and the crude oil was purified by flash chromatography over silica gel (PE/EtOAc 9:1) to afford the title compound **2n** as a white solid, 66% (21.1 mg).

Mol Formula	C_6H_6NCl			**m.p.**	72.5°C
^{1}H NMR	**δ value**	**No. H**	**Mult.**	**j value/Hz**	
400 MHz	7.10	2	*d*	4.22	
$CDCl_3$	6.60	2	*d*	4.35	
	3.65	2	*bs*		

^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 145.0; 129.1; 123.1; 116.3.

GC-EIMS (m/z, %): 129 (M+2, 59.9); 128.1 (M+1, 15.8); 127.1 (M^+, 100); 100.0 (22.6); 99.0 (12.5), 92.1 (33.4); 91.1 (11.3); 65.1 (46.2); 64.1 (13.1); 63.2 (19.2).

Chem. Name	4-Bromoaniline (2o)
Lit. Ref.	*Green Chem.,*2017,**19**,4268–427



3e **2o**

METHOD:

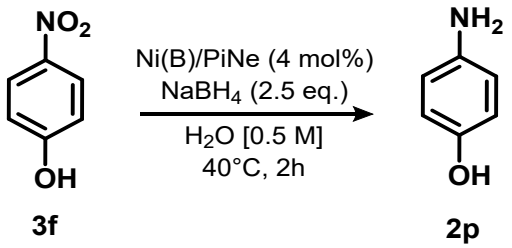
In a 4 mL screw capped vial equipped with a magnetic stirrer, 1-bromo-4-nitrobenzene (**3e**) (0.25 mmol, 50.5 mg), H_2O (0.5 M, 0.5 mL), Ni(B)/PiNe (4 mol%, 11.5 mg) and $NaBH_4$ (2.5 eq., 23.65 mg) were consecutively added, and the resulting mixture was left under stirring at 40°C. After 2 h, the reaction mixture was left to cool to room temperature, diluted with 2-MeTHF (2 x 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 overnight under vacuum. The combined organic layers, once separated from the aqueous phase, were concentred under reduced pressure to afford the title compound **2o** as a white solid, 76% (32.7 mg).

Mol Formula	C_6H_6NBr			**m.p.**	62°C
^{1}H NMR	**δ value**	**No. H**	**Mult.**	**j value/Hz**	
400 MHz	7.27	2	*d*	4.21	
$CDCl_3$	6.58	2	*d*	4.35	
	3.70	2	*bs*		

^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 145.6; 132.1; 116.8; 110.1.

GC-EIMS (m/z, %): 172.9 (M+1, 80.7); 171.9 (M^+, <10); 170.9 (M-1, 83.6); 92.1 (61.8); 91 (11.4); 66.0 (11.8); 65.0 (100); 64.0 (15.6); 63.0 (29.3); 62.0 (12.9); 52.0 (12.3).

Chem. Name	4-Aminophenol (2p)
Lit. Ref.	*ACS Appl. Nano Mater.,* 2024, **7**, 16669−16678



3f **2p**

METHOD:

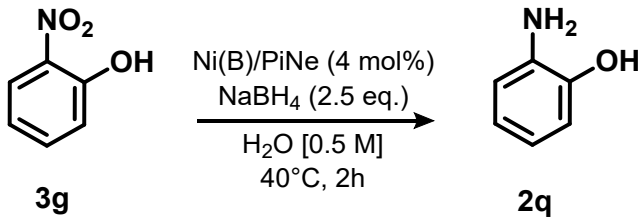
In a 4 mL screw capped vial equipped with a magnetic stirrer, 1-chloro-4-nitrobenzene (**3f**) (0.25 mmol, 34.8 mg), H_2O (0.5 M, 0.5 mL), Ni(B)/PiNe (4 mol%, 11.5 mg) and $NaBH_4$ (2.5 eq., 23.65 mg) were consecutively added, and the resulting mixture was left under stirring at 40°C. After 2 h, the reaction mixture was left to cool to room temperature, diluted with 2-MeTHF (2 x 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 overnight under vacuum. The combined organic layers, once separated from the aqueous phase, were concentred under reduced pressure and the crude oil was purified by flash chromatography over silica gel (PE/EtOAc 8:2) to afford the title compound **2p** as a white solid, 83% (22.6 mg).

Mol Formula	C_6H_7NO			**m.p.**	187.5°C
^{1}H NMR	**δ value**	**No. H**	**Mult.**	**j value/Hz**	
400 MHz	8.35	1	*s*		
DMSO-*d*6	6.52-6.41	4	*m*		
	4.36	2	*s*		

^{13}C NMR (100.6 MHz, DMSO-*d*6) δ: 148.7; 141.1; 113.0; 115.7.

GC-EIMS (m/z, %): 109.1 (M^+, 100); 108.0 (M-1, 16.3); 81.1 (18.1); 80.1 (66.3); 54.1 (11.9); 53.0 (21.5); 52.0 (14.0).

Chem. Name	**2-Aminophenol (2q)**
Lit. Ref.	*ACS Appl. Nano Mater.,* 2024, **7**, 16669−16678



3g **2q**

METHOD:

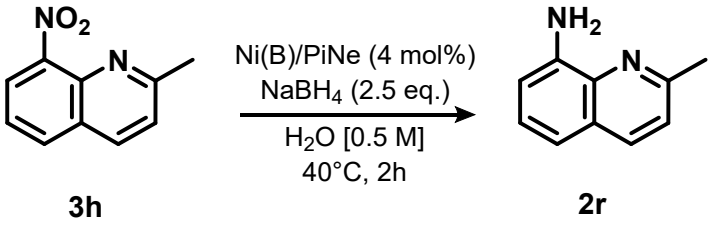
In a 4 mL screw capped vial equipped with a magnetic stirrer, 2-nitrophenol (**3g**) (0.25 mmol, 34.8 mg), H_2O (0.5 M, 0.5 mL), Ni(B)/PiNe (4 mol%, 11.5 mg) and $NaBH_4$ (2.5 eq., 23.65 mg) were consecutively added, and the resulting mixture was left under stirring at 40°C. After 2 h, the reaction mixture was left to cool to room temperature, diluted with 2-MeTHF (2 x 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 overnight under vacuum. The combined organic layers, once separated from the aqueous phase, were concentrated under reduced pressure and the crude oil was purified by flash chromatography over silica gel (PE/EtOAc 8:2) to afford the title compound **2q** as a white solid, 79% (21.6 mg).

Mol Formula	C_6H_7NO			**m.p.**	174°C
^{1}H NMR	**δ value**	**No. H**	**Mult.**	**j value/Hz**	
400 MHz	8.92	1	*bs*		
DMSO-*d*6	6.73-6.35	4	*m*		
	4.46	2	*bs*		

^{13}C NMR (100.6 MHz, DMSO-*d*6) δ: 144.5; 137.0; 120.0; 116.9; 114.9; 114.8.

GC-EIMS (m/z, %): 109.1 (M^+, 100); 108.1 (M-1, 14.0); 81.1 (10.2); 80.1 (67.1); 53.1 (16.3); 52.0 (10.9).

Chem. Name	2-Methylquinolin-8-amine (2r)
Lit. Ref.	-



3h **2r**

METHOD:

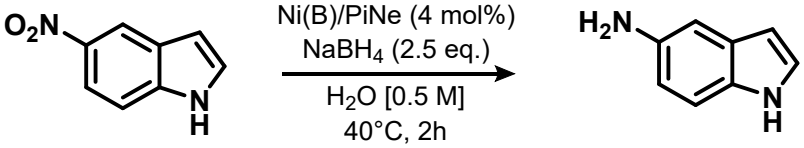
In a 4 mL screw capped vial equipped with a magnetic stirrer, 2-methyl-8-nitroquinoline (**3h**) (0.25 mmol, 47.05 mg), H_2O (0.5 M, 0.5 mL), Ni(B)/PiNe (4 mol%, 11.5 mg) and $NaBH_4$ (2.5 eq., 23.65 mg) were consecutively added, and the resulting mixture was left under stirring at 40°C. After 2 h, the reaction mixture was left to cool to room temperature, diluted with 2-MeTHF (2 x 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 overnight under vacuum. The combined organic layers, once separated from the aqueous phase, were concentrated under reduced pressure and the crude oil was purified by flash chromatography over silica gel (PE/EtOAc 9:1) to afford the title compound **2r** as a white solid, 88% (34.8 mg).

Mol Formula	$C_{10}H_{10}N_2$			**m.p.**	56-58°C
	δ value	**No. H**	**Mult.**	**j value/Hz**	
^{1}H NMR	7.95	1	*d*	4.39	
400 MHz	7.29-7.22	2	*m*		
$CDCl_3$	7.14-7.08	1	*m*		
	6.93-6.88	1	*m*		
	4.96	2	*bs*		
	2.71	3	*s*		

^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 156.2; 143.4; 137.9; 136.1; 126.9; 126.3; 122.2; 115.9; 110.1; 25.3.

GC-EIMS (m/z, %): 159.1 (M+1, 25.0); 158.1 (M^+, 100); 157.1 (M-1, 37.4); 131.1 (38.4); 130.1 (34.5); 129.1 (10.3); 103.1 (10.0); 79.0 (10.6).

Chem. Name	5-Aminoindole (2s)
	Synthetic Communications, 2012, **42**, 213–222



3i **2s**

METHOD:

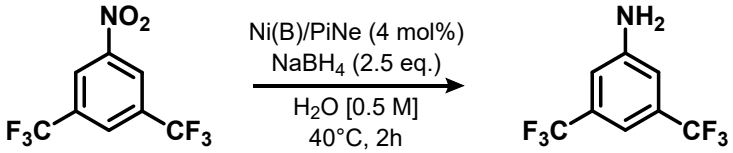
In a 4 mL screw capped vial equipped with a magnetic stirrer, 5-Nitroindole (**3i**) (0.25 mmol, 40.5 mg), H_2O (0.5 M, 0.5 mL), Ni(B)/PiNe (4 mol%, 11.5 mg) and $NaBH_4$ (2.5 eq., 23.6 mg) were consecutively added, and the resulting mixture was left under stirring at 40°C. After 2 h, the reaction mixture was left to cool to room temperature, diluted with 2-MeTHF (2 x 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 overnight under vacuum. The combined organic layers, once separated from the aqueous phase, were concentrated under reduced pressure to afford the title compound **2s** as a brown solid, 94% (31.1 mg).

Mol Formula		$C_8H_8N_2$		**m.p.**	131-135 °C
^{1}H NMR	**δ value**	**No. H**	**Mult.**	**j value/Hz**	
400 MHz	7.97	1	s		
$CDCl_3$	7.12-7.20	2	m		
	6.96	1	s		
	6.67-6.69	1	m		
	6.38	1	s		
	3.51	2	s		

^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 139.7, 130.8, 128.9, 124.8, 113.1, 111.6, 105.7, 101.7

GC-EIMS (m/z, %): 133 (44);132 (M+ 100); 131 (100); 105 (54); 104 (100); 78 (29); 77 (34); 66 (25); 52 (18); 51 (19);

Chem. Name	3,5-Bis(trifluoromethyl)aniline (2t)
Lit. Ref.	-



3j 2t

METHOD:

In a 4 mL screw capped vial equipped with a magnetic stirrer, 3,5-Bis(trifluoromethyl)nitrobenzene (**3j**) (0.25 mmol, 64.8 mg), H_2O (0.5 M, 0.5 mL), Ni(B)/PiNe (4 mol%, 11.5 mg) and $NaBH_4$ (2.5 eq., 23.6 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 x 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 overnight under vacuum. The combined organic layers, once separated from the aqueous phase, were concentrated under reduced pressure and the crude oil was purified by flash chromatography over silica gel (PE/EtOAc, 9:1) to afford the title compound **2t** as a transparent liquid, 48% (27.5 mg).

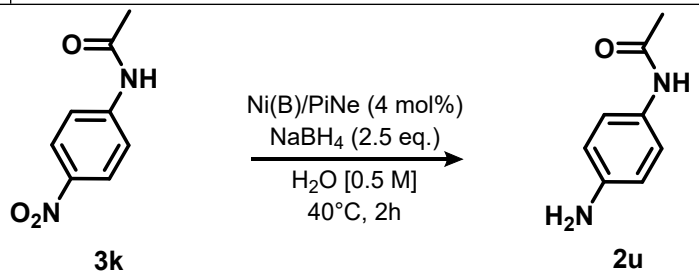
Mol Formula		$C_8H_5F_6N$		**m.p.**	liquid
^{1}H NMR	**δ value**	**No. H**	**Mult.**	**j value/Hz**	
400 MHz	7.22	1	s		
$CDCl_3$	7.03	2	s		
	4.04	2	s		

^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 147.6, 133.2-132.2, 127.7-119.6, 114.3, 111.8-111.5

^{19}F NMR (376 MHz, $CDCl_3$) δ: -63.4

GC-EIMS (m/z, %): 230 (69); 229 (M+ 100); 213 (15); 211 (30); 210 (100); 209 (39); 208 (41); 190 (21); 188 (44); 183 (21); 182 (100); 181 (31); 179 (62); 170 (21);163 (83); 160 (97); 159 (23); 143 (17); 140 (60); 139 (27); 133 (28); 132 (79); 120 (24); 114 (20); 113 (49); 88 (16); 83 (17); 75 (30); 69 (64); 63 (39); 62 (17)

Chem. Name	4-Aminoacetanilide (2u)
Lit. Ref.	*Advanced Synthesis & Catalysis*, 2009, **351**, 1189–1193.



3k **2u**

METHOD:

In a 4 mL screw capped vial equipped with a magnetic stirrer, 4-nitroacetanilide (**3k**) (0.25 mmol, 45.0 mg), H_2O (0.5 M, 0.5 mL), Ni(B)/PiNe (4 mol%, 11.5 mg) and $NaBH_4$ (2.5 eq., 23.6 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 x 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 overnight under vacuum. The combined organic layers, once separated from the aqueous phase, were concentrated under reduced pressure and the crude oil was purified by flash chromatography over silica gel (PE/EtOAc, 9:1) to afford the title compound **2u** as a pale yellow solid, 92% (34.5 mg).

Mol Formula		$C_8H_{10}N_2O$		**m.p.**	164°C
^{1} H NMR	**δ value**	**No. H**	**Mult.**	**j value/Hz**	
400 MHz DMSO-*d*^{6}	7.22	2	d	4	
	6.68	2	d	4	
	4.86	2	s		
	2.06	3	s		

^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 171.3, 145.6, 130.7, 123.2, 116.7, 23.5

GC-EIMS (m/z, %): 150 (M^+, 8); 135 (M–15, 28); 134 (M–16, 6); 120 (M–30, 10); 109 (40); 93 (100); 77 (32); 65 (18); 51 (10)